# Saturated Ultra-Precision Spectroscopy of Water and HD with NICE-OHMS



# Meissa L. Diouf

#### VRIJE UNIVERSITEIT

# SATURATED ULTRA-PRECISION SPECTROSCOPY OF WATER AND HD WITH NICE-OHMS

#### ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan de Vrije Universiteit Amsterdam, op gezag van de rector magnificus prof.dr. J.J.G. Geurts, in het openbaar te verdedigen ten overstaan van de promotiecommissie van de Faculteit der Bètawetenschappen op woensdag 6 december 2023 om 9.45 uur in een bijeenkomst van de universiteit, De Boelelaan 1105

door

Meissa Libasse Diouf

geboren te Dakar, Senegal

promotoren:	prof.dr. W.M.G. Ubachs
copromotoren:	prof.dr. K.S.E. Eikema

promotiecommissie:

prof.dr. J.T.M. Kennis prof.dr. F. Merkt dr. F.J.M. Harren dr. B.I. Avci prof.dr. H.V.J. Linnartz

For my aunt Mame Bella and my uncle Pirouz

This work originates as part of the research programme of the Foundation for Fundamental Research on Matter (FOM), and falls as of April 1, 2017 under the responsibility of Netherlands Foundation of Scientific Research Institutes (NWO-I) (NWO-I), which is part of the Dutch Research Council (NWO). Specifically the work is funded through the NWO-program grant: "The mysterious size of the proton".





# Contents

C	Contents		3
1	<b>Intr</b> 1.1 1.2 1.3 1.4	<b>voduction</b> Absorption spectroscopy and the laser         Saturation spectroscopy and broadening effects         NICE-OHMS         Outline of the Thesis	<b>5</b> 6 7 13
Ι	Wa	ter	17
2	<b>Spe</b> <b>app</b> 2.1 2.2 2.3 2.4 2.5 2.6 2.7	ctroscopic-network-assisted precision spectroscopy and its         lication to water         Introduction	<b>19</b> 20 22 31 36 37 37
3	Ultr $H_2^{11}$ 3.1 3.2 3.3 3.4 3.5 3.6	raprecise relative energies in the (200) vibrational band of <sup>6</sup> O Introduction	<b>39</b> 40 41 45 49 52 53
4	Net and kHz	work-based design of near-infrared Lamb-dip experiments the determination of pure rotational energies of $H_2^{18}O$ at accuracy	55

	and	the determination of pure rotational energies of $H_2^{10}O$ at
	kHz	accuracy 53
	4.1	Introduction
	4.2	Methods and Data Treatment
	4.3	Results and Discussion
	4.4	Conclusions and Summary
-	ττ	and a second sec
Э	нур	$\Delta n m m n \Delta - n \alpha n \alpha n \alpha n \alpha n n m - n n m n n \alpha \alpha \alpha n \alpha n m n \alpha n m n m n m$
		erime-resolved hear-initiated spectra of H <sub>2</sub> O 6.
	5.1	Introduction
	5.1 5.2	Introduction
	5.1 5.2 5.3	Introduction

6	Parity-pair-mixing effects in nonlinear spectroscopy of HDO			
	6.1	Introduction		94
	6.2	Methodological details		95
	6.3	Experimental results		99
	6.4	Phenomenological Lamb-dip-profile analysis		102
	6.5	Conclusions		108
7	Sun	nmary and outlook		113
II	Hye	drogen deuteride (HD)	-	117

-	-				
8	Lam	b-dips and Lamb-peaks in the saturation spectrum of HD	119		
	8.1	Introduction	120		
	8.2	Experimental	120		
	8.3	Hyperfine structure	123		
	8.4	Results	124		
	8.5	Conclusion	127		
	8.6	Acknowledgements	127 127		
0	Low	b pool spectrum of the HD $(2.0)$ $P(1)$ line	190		
9		10-peak spectrum of the HD (2-0) $F(1)$ line	120		
	9.1	Introduction	130		
	9.2	Experimental	130		
	9.3	Hyperfine structure	131		
	9.4	Results	132		
	9.5	Conclusion	137		
	9.6	Acknowledgments	137		
10	Rota	ational level spacings in HD from vibrational saturation spec-			
	$\operatorname{tros}$	сору	139		
	10.1	Introduction	140		
	10.2	Experiment and results	141		
	10.3	Discussion and Conclusion	147		
	10.4	Acknowledgments	149		
	G		1 . 1		
11	Sum	imary and outlook	191		
Bi	Bibliography				
Li	List of publications				
Ac	Acknowledgements				

### Chapter 1

### Introduction

#### 1.1. Absorption spectroscopy and the laser

The invention of the laser in 1960 by Theodore H. Maiman [1] was a groundbreaking achievement that laid the foundation for the development of laser-based spectroscopic techniques. The laser has brought the opportunity to generate intense, coherent and monochromatic light beams to perform precise and sensitive spectroscopic measurements, opening up a wide variety of new approaches to spectroscopy.

Spectroscopy, a field dedicated to investigating the interaction of light with matter, benefited greatly from the development of laser technology. Laser spectroscopy allows for detailed analysis of the energy levels and transitions within atoms, molecules, and solids, offering valuable insights into their composition, structure, and dynamic behavior. From the spectroscopy perspective, lasers that exhibit narrow bandwidth and tunability are preferred. Typical examples are the dye laser, the titanium-sapphire laser and diode lasers. The invention of the laser also expanded the techniques of classical spectroscopy, emission and absorption spectroscopy, with all kinds of novel approaches, ranging from laser-induced fluorescence, resonance-enhanced multiphoton ionization, photo-acoustic, and coherent Raman spectroscopy, just to name a few (see Demtröders seminal books [2, 3] for details).

In laser-based absorption spectroscopy, a monochromatic electromagnetic field with wavelength  $\lambda$  is employed to detect and study atoms and molecules. In this study we will restrain ourselves to gas phase species. The technique relies on the Beer-Lambert law which states that the intensity of the electromagnetic field  $I_0$ decreases exponentially as it traverses a gas of absorbance  $\sigma$  and a paths length L:

$$I = I_0 \cdot e^{-\sigma L} \tag{1.1}$$

The classical technique of absorption spectroscopy has greatly advanced through the introduction of lasers. Wavelength and frequency modulation techniques have enormously improved the sensitivity in measuring absorption lines [4]. Also the introduction of optical cavities in conjunction with narrowband lasers has helped to improve detection sensitivity. The invention of cavity ring-down spectroscopy [5], initially as a technique for pulsed lasers, but later also for continuous-wave lasers of narrower bandwidths, found widespread application in spectroscopy, making it possible to measure weak transitions.

A variety of cavity-enhanced laser spectroscopic methods was thereafter developed [6] finding many applications ranging from carbon dating physics [7] to breath analysis [8]. The NICE-OHMS technique, developed by Hall and coworkers [9], and used in the experiments laid down in this Thesis, turned out the most sensitive.

Another novelty that was brought to spectroscopy by the laser is that of optical saturation allowing to measure spectral lines at extremely narrow width. The concept of the Lamb dip was already conceived before the invention of the laser [10]. Finally, the invention of frequency comb lasers by Hänsch [11] and Hall [12] has revolutionized methods of absolute frequency calibration, enabling frequency accuracy reaching kilohertz (kHz) and below.

In the present work the concepts of saturation, intra-cavity absorption, NICE-OHMS and frequency-comb calibration were all employed in the high precision spectroscopic studies of water and hydrogen deuteride (HD).

#### 1.2. Saturation spectroscopy and broadening effects

Spectral lines acquired from absorption spectroscopy are subject to different mechanisms of broadening thus hindering the extraction of the absolute frequency position.

The frequency at which a particle can absorb laser light is shifted with respect to its velocity. This Doppler effect can be represented by:

$$\omega_{abs} = \omega_0 + \vec{k} \cdot \vec{v}, \tag{1.2}$$

where the radial frequency  $\omega_0 = 2\pi f_0$ , the wave vector  $\vec{k} = \frac{2\pi f_0}{c} \cdot \vec{\epsilon}$ , with  $f_0$  the frequency of the laser,  $\vec{\epsilon}$  the direction of propagation of the laser, c the speed of light in vacuum and  $\vec{v}$  the velocity of the particle. Due to the thermal distribution of a gas at a given temperature, this Doppler effect gives rise to broadening of an absorption line taking a Gaussian functional form, which depends on the mass of the particle, the temperature and the frequency of the laser. The width of this Gaussian profile usually spans in the GHz range limiting accuracy in absorption spectroscopy. To mitigate this effect, sub-Doppler techniques like saturation spectroscopy are implemented.

Saturation spectroscopy involves the utilization of two counter-propagating beams. A first intense beam, also known as the pump beam, interacts with particles within a gas cell and induces a change in the population distribution between the two probed levels at a specific velocity v. This phenomenon is referred to as 'hole burning' [13]. Subsequently, when a second beam, or probe beam, interacts with the same velocity class of particles, the reduced population in the ground state results in a decrease in the absorption signal. Due to the condition of resonance and the counter-propagating nature of the beams, their interaction with velocity class of particles is limited to those traveling perpendicularly to the beam, or those with an effective Doppler shift of zero. Consequently, a Lamb-dip is observed precisely at the center of the transition where the Doppler effect is nonexistent.

While Doppler broadening, which is typically the primary source of broadening in spectroscopy, has been mitigated, it is important to consider the presence of other significant broadening mechanisms.

The first and fundamental broadening is the natural linewidth. It arises due to the finite lifetime of the excited state, resulting in an uncertainty in the energy of the state. Due to the Heisenberg uncertainty principle, this leads to broadening proportional to that lifetime  $(\Delta E \cdot \Delta t \ge h/4\pi)$ . Natural broadening leads to a Lorentzian-shaped lineshape. In our case, natural broadening has a minor effect as we will be probing ro-vibrational lines where the states have lifetimes longer than a second (broadening < 1 Hz). In gas-phase environments, collisions between particles contribute to the reduction of excited state lifetimes and can induce dephasing or decoherence of excitation, introducing an additional mechanism for broadening. This phenomenon, known as pressure or collisional broadening, typically manifests as a Lorentzian-shaped profile. It is crucial to minimize pressure in saturation spectroscopy to facilitate the desired exchange of population, as collisions can impede this process.

To be able to saturate spectral lines high intensities are needed, typically for the pump laser. At sufficiently large laser intensities, the optical pumping rate on an absorbing transition becomes larger than the relaxation rates. This leads to a broadening of spectral lines. It should be emphasized that certain transitions demand exceptionally high laser power for saturation.

All lasers possess a finite frequency width, or bandwidth, that contributes to the width of a measured absorption line. Another broadening effect, due to the properties of the laser, is the transit time where the interaction between the finite width of the exciting laser beam and the molecules lead to a broadening as a consequence of the Heisenberg principle. At a given temperature, particles have a certain velocity and thus a limited amount of time spent in the laser beam. Lastly, any frequency modulation or jitters on the laser, also those needed for locking procedures in an experiment, will give rise to additional broadening.

These various phenomena mentioned above exhibit a common characteristic of yielding a Lorentzian lineshape. As a result, the spectral lineshapes observed in Lamb-dip spectroscopy are expected to exhibit a Lorentzian profile.

#### 1.3. NICE-OHMS

The determination of the absolute frequency position of a spectral transition can be hampered by various factors. One such factor is the presence of noise in any physical system, which imposes a threshold limit on detection and limits the overall sensitivity of the system. To address this challenge, researchers have devoted considerable efforts to designing spectroscopic setups that minimize inherent noise, thereby enhancing the sensitivity of detection. Over the years, numerous advancements and innovations in spectroscopic instrumentation have aimed to reduce noise levels and improve the overall performance of spectroscopic systems. Typical examples of these systems use cavities as a core of their spectroscopic techniques. The simplest one is Cavity Enhanced Absorption Spectroscopy (CEAS) where the increased optical path length in a cavity is used to amplify the absorption depth. Then come Cavity Ring-Down Spectroscopy which utilizes the modification of the ring-down time of light in a cavity in the presence of absorbing gas. Lastly, the focus of our thesis, Noise Immuned Cavity Enhanced Absorption Spectroscopy (NICE-OHMS) which is essentially a combination of frequency modulation spectroscopy inside a cavity. For a review of these cavity-enhanced absorption techniques we refer to Ref. [6].

#### Noise

The statistical fluctuation due to the quantum nature of photons arriving on the photodetector give rise to the most fundamental noise effect. The so-called photon shot noise sets the absolute limit of detection of an absorption signal. The shot noise signal can be described by:

$$S_{shot} = \kappa_{det} \sqrt{2e\Delta f P_0},\tag{1.3}$$

where  $\kappa_{det}$  are parameters intrinsic to the detector, e the elementary charge,  $\Delta f$  the electronic bandwidth and  $P_0$  the power of the laser.

The shot noise limit is not achieved in direct absorption spectroscopy because there are additional factors that impose limitations, such as electronic noise and laser excess noise. The laser excess noise, which follows a 1/f frequency dependence, is particularly significant at low frequencies where direct absorption spectroscopy operates.

Noise in the system can be reduced by shifting the detection to higher frequencies (laser 1/f noise), which is achieved by using modulation techniques. There are two types of modulation techniques; frequency modulation spectroscopy (FMS) and wavelength modulation spectroscopy (WMS).

#### Frequency modulation

Frequency modulation was proposed to enhance the sensitivity and selectivity of spectroscopic measurements [4]. In FM, the phase of the laser is modulated at high frequency  $f_m$ , typically in the radio-frequency (MHz) region with an amplitude represented by a modulation index  $\beta$ . The generation of sidebands is derived in the next paragraphs. The complex electric field after modulation is written as:

$$\vec{E}^{FM}(f_c, t) = \frac{E_0}{2} \vec{\epsilon} \cdot e^{i[2\pi f_c t + \beta sin(2\pi f_m t)]},$$
(1.4)

where  $E_0$  is the amplitude and  $\vec{\epsilon}$  the direction of propagation of the electric field and  $f_c$  the frequency of the carrier. This field can be expressed in terms of series of Bessel functions  $J_j(\beta)$ :

$$\vec{E}^{FM}(f_c, t) = \frac{E_0}{2} \vec{\epsilon} \cdot e^{i2\pi f_c t} \cdot \sum_{j=-\infty}^{+\infty} J_j(\beta) e^{i2\pi j f_m t}, \qquad (1.5)$$

At low modulation index (used in the present study), the only significant order present will be the first one (i.e.  $\beta \leq 1$ ). Thus the electric field will be expressed as:

$$\vec{E}^{FM}(f_c, t) = \frac{E_0}{2} \vec{\epsilon} \cdot e^{i2\pi f_c t} \cdot [J_0(\beta) + J_1(\beta)e^{i2\pi f_m t} - J_{-1}(\beta)e^{-i2\pi f_m t}], \quad (1.6)$$

where  $J_{-1}(\beta) = -J_1(\beta)$ . This leads to show that the optical beam will now consist of a carrier and two sidebands generated at  $f_{sb} = f_c \pm f_m$ . Note that the sidebands are out of phase.

Once the carrier traverses a certain amount of absorbing particles  $N_{gas}$ , on resonance with intensity S, the interaction induces a phase shift that can be detected at the modulation frequency. To extract the signal, the transmitted FM signal is demodulated and detected at the frequency  $f_m$ , effectively isolating contributions from terms oscillating at this specific frequency. By incorporating the transmission parameters, which rely on the susceptibility  $\chi$  responsible for both dispersion and absorption signals, the FM signal can be expressed as follows:

$$S^{FM}(\Delta f, \theta_{FM}) = P_0 J_0(\beta) J_1(\beta) \frac{SN_{gas}L}{2} \cdot \left\{ \left[ \chi^{disp}(\Delta f - f_m) - 2\chi^{disp}(\Delta f) + \chi^{disp}(\Delta f + f_m) \right] \cos \theta_{fm} + \chi^{abs}(\Delta f - f_m) - \chi^{abs}(\Delta f + f_m) \right] \sin \theta_{fm} \right\},$$
(1.7)

where  $\theta_{fm}$  is the demodulation phase. These expressions demonstrate that the FM signal is composed of two distinct signals in quadrature, which implies that the dispersion component and absorption component have a phase shift of 90 degrees relative to each other. The dispersion phase consists of three functional terms, while the absorption phase consists of two functional terms. By phase demodulation, typically with a phase-sensitive or lock-in amplifier, either signal phase component can be individually obtained.

#### Cavity

To increase the optical path L for absorption Fabry-Perot cavities can be used. These cavities are built from two reflective mirrors mounted along the same axis. The quantity of light that enters a cavity is determined by two factors: impedance matching, which refers to the reflectivity of the in-coupling mirror, and cavity mode matching, which involves selecting the appropriate in-coupling lens. For the purposes of our discussion, we assume the use of a flawless Gaussian beam that perfectly matches a cavity mode. The cavity is then on resonance when its length is a multiple half integer of the laser wavelength. This leads to the apparition of resonant modes equally spaced by the free spectral range FSR expressed by:

$$FSR = \frac{c}{2L},\tag{1.8}$$

where c is the speed of light in vacuum and L the distance between the mirrors. On the other hand the width of a cavity mode is expressed as:

$$\Delta \nu = \frac{c(1-R)}{2L\pi\sqrt{R}},\tag{1.9}$$

where R is the reflectivity of both mirrors. The term usually used to describe a Fabry-Perot cavity is the Finesse (F) and is expressed as:

$$F = \frac{FSR}{\Delta\nu}.$$
(1.10)

The use of cavities in spectroscopy yields many advantages. Primarily, the high power circulating beams propagating in both directions provide a natural scheme for saturation spectroscopy. In this case, the counter-propagating beams will both act as pump and probe at similarly high intensities.

Secondly, when a laser is coupled to a stable cavity, the properties of the cavity can be transferred to the optical beam thus acting as a low pass filter. Despite these advantages ensuring consistent in-coupling is not a straightforward task, necessitating the implementation of an efficient locking mechanism, particularly when dealing with high finesse etalons.

In the 1980s, Pound, Drever, and Hall [14] developed a technique, known as the Pound-Drever-Hall (PDH) technique, which utilizes frequency modulation to stabilize a laser to a specific cavity mode. To be able to obtain that result, the laser is modulated at a frequency  $f_{PDH}$  smaller than the FSR but larger than the width of a cavity mode. As a pure FM technique, two sidebands are then generated with the carrier. When the modulated electric field hits the in-coupling mirror a FM signal can be produced. If the carrier is perfectly on top of an etalon fringe, the two out of phase sidebands cancel each other. Any deviation in frequency of the carrier from the peak of the mode will give rise to an unbalance with the modulated field which will yield a FM signal. By demodulating at the PDH frequency and optimizing the phase, an error signal can be derived. Typically, one of the mirrors is placed on a piezoelectric module enabling the adjustment of the cavity length. Subsequently, this error signal is employed in a feedback system to stabilize the length of this specific mode by controlling the piezo.

By achieving a highly stabilized distance between the two mirrors comprising the cavity, it becomes feasible to attain kHz-level frequency stability for the laser. When the carrier travels back and forth within the cavity, numerous additional advantages arise from this technique. The foremost advantage, as previously mentioned, is the extension of the optical path length. By utilizing a reflectivity value of R = 0.99998, the interaction length within the cavity can extend over distances of tens of kilometers. With such reflectivity, the cavity finesse reaches approximately 150,000, resulting in a tremendous amplification of light power due to its high quality factor Q. As a result, we can achieve an intra-cavity power of up to 150 W, which is essential for saturating the extremely weak transitions in HD.

#### FM in cavity

To enhance the detection sensitivity needed for these weak signals in HD for instance, an ultra-high sensitive technique called Noised Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) has been implemented. This technique consists of combining a cavity and frequency modulation to detect spectroscopic signals. In NICE-OHMS, the carrier is modulated at the frequency of the FSR of the cavity  $f_{FM} = f_{FSR}$ . The two sidebands are generated at the frequency  $f_{SB} = f_c \pm f_{FSR}$ . It is needed to lock the three resulting waves to the cavity with their respective cavity modes. The carrier is locked with the PDH technique, while the sidebands are locked with a technique quite similar to PDH called DeVoe-Brewer or DVB [15]. The modulated electric field inside the cavity is represented in Fig. 1.1.

The three beams are capable to counter-propagate inside the cavity while maintaining the properties of FM spectroscopy. When the beams encounter a resonance the FM signal described in Eq. (1.7) is produced. Typically,  $f_{FSR} \approx 300$  MHz, and the Full-Width at Half-Maximum (FWHM) of a Doppler broadened transition for molecules are wider than 500 MHz at room temperature. Consequently, the FM



Figure 1.1: Illustration of the in-coupling of a modulated laser at frequency  $\nu_0$  inside a cavity. Here the sidebands generated at  $f_{SB} = \nu_0 \pm \nu_m$  perfectly matches the FSR of the cavity.

signal encompasses all the potential signals that emerge from the interaction of the three electromagnetic waves when scanning across a transition.

For the remainder of this thesis, the focus will be put on the sub-Doppler saturation NICE-OHMS case. Under the presence of three counter-propagating waves, there are nine occasions at which two fields can interact with a certain velocity class of particles and fulfill the condition of resonance. These occasions happen at five distinct frequency detunings from the center of the transition as illustrated in Fig. 1.2. In addition to the typical Lamb-dip observed for molecules with no axial motion (depicted in panels (a) and (e)), other types of saturation dips are shown in panels (b), (c), and (d). In these cases, the arrangement of the three waves relative to the center of the Doppler broadened profile allows for selective interaction with specific velocity classes of molecules, resulting in saturation profiles. For example, in panels (b) and (d), which exhibit mirrored configurations, the carrier wave is detuned exactly by  $f_{FSR}/2$  from the center of the transition. As a result, one of the sidebands can interact with the carrier, selectively interacting with molecules having an effective Doppler shift  $\vec{k} \cdot \vec{v} = f_{FSR}/2$ . This leads to a type of dip known as velocity-selective saturation dip.

In panel (c), where the laser carrier coincides with the resonance, the normal Lamb-dip scenario is present, along with the occurrence of velocity-selective saturation dips. The presence of sidebands interacting with their counterparts can saturate molecules with an effective Doppler shift of  $\vec{k} \cdot \vec{v} = f_{FSR}$ . Since the sideband signals are 180 degrees out of phase compared to the generic Lamb-dip, this can result in complex signals for strong lines (Einstein A coefficient of > 10<sup>-1</sup> s<sup>-1</sup>).

#### **Frequency** calibration

Despite achieving high stability of the laser within a cavity and significantly enhancing detection sensitivity, the need for absolute frequency arises to enable precise and accurate spectroscopy. Although the laser can be locked to a cavity mode, determining the specific mode within the cavity presents a challenge. Furthermore, the length of an etalon, which is often used for frequency reference, is susceptible to temperature variations, resulting in a non-fixed free spectral range and frequency drift. To achieve stability in mode, various options can be explored. The temperature of the cavity can be fixed and controlled to high precision. The disadvantages are that although the FSR is fixed, it is still not known which cavity mode the laser is locked to. The use of a frequency comb (FC) laser as a reference



Figure 1.2: Illustration of the five possible occurrences of velocity-selective saturation in a Gaussian velocity distribution by the three counter-propagating waves present in NICE-OHMS. The five panels correspond to the five possible detunings of the carrier from the resonance where a saturated Lamb-dip profile can be recorded. This figure was based on Ref. [16].

is the elegant solution to ensure stability and kHz accuracy. This is done in our setup.

A frequency comb laser is in fact a mode-locked laser, emitting extremely short pulses of light in the time domain, typically lasting femtoseconds. This short pulse duration allows the laser frequency spectrum to span a wide range of frequencies, extending from ultraviolet to infrared wavelengths in the frequency domain. The key feature of a frequency comb is its ability to generate a series of equally spaced frequencies resembling the teeth of a comb. This regular pattern is achieved through precise control of the laser pulse repetition rate. Lastly, a long term stability is assured by stabilizing the comb to a Cs clock frequency standard (Microsemi CSIII Model 4301B). In our studies, the specific model used is Menlo Systems FC1500-250-WG.

When observing the output of the frequency comb laser, we perceive a comb of frequencies starting from a specific frequency called  $f_0$ , with each frequency spaced apart by the repetition rate  $f_{rep}$ . Next, the frequency comb can be combined or mixed with another laser used for spectroscopic purposes. This combination results in a beatnote frequency, denoted as  $f_{BN}$ , which is the difference in frequency between the spectroscopic laser  $f_{laser}$  and the closest frequency mode of the frequency comb (represented by the mode number N). The relationship between the beat-note frequency, repetition rate, mode number and the spectroscopic laser frequency can be described using the following equation:

$$f_{BN} = f_0 + N \times f_{rep} - f_{laser} \tag{1.11}$$

The value of this beat-note will then always be between 0 and  $\pm f_{rep}$ . Usually the repetition rate of the comb is in the radio domain, in our case ~ 250 MHz. Consequently, it is possible to count accurately this frequency with a frequency counter which can then be used to accurately determine the absolute frequency of the spectroscopy laser. Inversely, it is also possible to use the counted value to tightly lock the length of a cavity. By adding this lock, our apparatus which should now be called "Frequency-comb assisted NICE-OHMS" can reach kHz accuracy. Such methods of frequency-comb assisted cavity-enhanced spectroscopy were explored by other groups in the world, either in Doppler-broadened spectroscopic studies [17, 18] or in saturated absorption studies [19, 20, 21].

#### Wavelength modulation in NICE-OHMS

To enhance sensitivity and further reduce background noise, an additional modulation technique called wavelength modulation (WM) is employed. The main distinction between FM and WM lies in the amplitude of modulation and the frequency magnitude. FM modulation is typically utilized in the radio frequency range, whereas WM modulation is applied in the audio domain (with  $f_{WM} \approx 100$ Hz). In our investigation, this modulation technique is implemented by dithering a mirror, causing all the waves propagating inside the cavity to undergo slight fluctuations. The resulting composite signal is subsequently demodulated at the frequency  $f_{WM}$  with an optimized phase, yielding derivative signals that will be utilized for the remaining part of this study. Different orders of demodulation can be performed, leading to higher-order derivatives. The function that describes the first order of demodulation of these signals will be referred to as  $f_{1f}$  and can be written as:

$$f_{1f}^{abs}(\nu) = \frac{8 A \Gamma^2 (\nu - \nu_0)^2}{\left[\Gamma^2 + 4(\nu - \nu_0)^2\right]^2},$$
  
$$f_{1f}^{disp}(\nu) = \frac{4 A \left[\Gamma^2 - 4(\nu - \nu_0)^2\right]}{\left[\Gamma^2 + 4(\nu - \nu_0)^2\right]^2},$$
(1.12)

where the adjustable parameters are the line position  $\nu_0$ , the line intensity A, and width  $\Gamma$ . The line profiles signatures as determined experimentally on a specific water line, are displayed in Fig. 1.3 where in panels (a), (b), (d) and (e) both dispersion and absorption features are plotted. In the center panel (c), only the dispersion Lamb dip is recorded. It is interesting to note the phase differences between the left, center an right panels.

#### 1.4. Outline of the Thesis

This study focuses on saturation precision spectroscopy with the NICE-OHMS technique on two different types of molecules: water and hydrogen deuteride. The thesis is split in two parts covering the studies of these molecular species.

#### Water spectroscopy

Water, with chemical formula  $H_2O$ , holds significant importance across various scientific domains, making it one of the most extensively investigated molecules. In spectroscopy  $H_2^{16}O$  and its less preponderant isotopologues have become benchmark species and have been studied by its rotational microwave lines and the rovibrational spectrum ranging from the infrared to the blue part of the spectrum.



Figure 1.3: Lamb-dip Measurements of a water  $(H_2^{16}O)$  line of quantum assignment:  $(200)_{624} \leftarrow (000)_{533}$  with our NICE-OHMS apparatus. The transition has been recorded at 218 250 754 918.9 (1.5) kHz. The five different recordings correspond respectively to the five spectral hole burning illustrated in Fig. 1.2. The line profiles exhibited in the panels follow the function described in Eq. 1.12.

Water is constituted of two hydrogen atoms bonded to an oxygen atom resulting in a bent structure at an angle of 104°. This structure leads to water being classified as an asymmetric top. Consequently, this gives rise to rich spectral bands of different order of magnitude. In this study, ro-vibrational transitions will be excited while staying in the same electronic state. Therefore, the electronic structure will be omitted.

The vibrational motions of the system can be classified into three distinct modes, each characterized by specific energetic values. These modes include the symmetric stretching mode ( $\nu_1 = 3657 \text{ cm}^{-1}$ ), the bending mode ( $\nu_2 = 1595 \text{ cm}^{-1}$ ), and the asymmetric stretching mode ( $\nu_3 = 3756 \text{ cm}^{-1}$ ). Upon observing these values, it becomes apparent that the two stretching modes possess similar energies, while the energy of the bending mode is approximately half of theirs. This difference in energy levels leads to the grouping of vibrational branches known as "Polyads," where the polyad number corresponds to the order of excitation based on the minimum quantum of vibration allowed ( $\nu_2$ ). For example Polyad number 2 is a grouping of 3 vibrational bands : (020), (100) and (001).

Asymmetric top molecules, such as water, display intricate rotational characteristics. Due to the lack of clearly defined symmetry axes for the process of quantization, we utilize the two classifications of symmetric tops (oblate and prolate) to facilitate the description of rotational behavior. The primary rotational quantum number is represented by J, while the sub-quantum properties are denoted by  $K_a$ and  $K_c$ , aligning with the principal axes of rotational behavior in symmetric tops. These three quantum numbers follow the constraint:  $K_a + K_c \leq J + 1$  (for J > 0). Consequently, a certain ro-vibrational level in one electronic configuration will be assigned by  $(\nu_1 \nu_2 \nu_3) J_{K_a,K_c}$ .

Lastly, some water isotopologues like the most abundant one  $H_2^{16}O$ , will be characterized as "homonuclear" to draw a comparison with linear molecules like  $H_2$ . This analogy stems from the fact that the hydrogen nucleus has a spin of  $I_p = 1/2$ , while the spin of oxygen-16 is  $I_{1^6O} = 0$ . Consequently, these molecular systems can be further characterized based on their nuclear spin configurations. When the two hydrogen nuclei have their spins aligned in the same direction, the corresponding energy levels are classified as ortho states, characterized by triplet states. Conversely, when the spins of the two hydrogen nuclei are in an antiparallel configuration, the levels are labeled as para states, representing singlet states. Notably, the ortho levels are three times more populated than the para levels due to spin statistics. In the case of water, the ortho/para classification is determined by:  $f = (-1)^{\nu_3 + K_a + K_c}$ ; +1 will correspond to para and -1 to ortho. Finally, the parity of a state is given by  $(-1)^{k_c}$ .

The "homonuclear" isotopologues such as  $H_2^{16}O$  and  $H_2^{18}O$  will be extensively studied in the first part of the thesis. Using a spectroscopic network approach, ro-vibrational transitions are measured to determine the rotational structure of the (000) ground vibrational manifolds of both isotopologues. Additionally, this method has been extended to the (200) excited stated of the most abundant isotopologue.

When substituting oxygen-16 or oxygen-18 in water with oxygen-17, which has a nuclear spin of  $I_{1^7O} = 5/2$ , the hyperfine structure becomes significantly larger, spanning megahertz (MHz) frequencies. As a result, it becomes possible to resolve and study the hyperfine splitting. This phenomenon has been investigated, and examples of hyperfine-resolved spectra in  $H_2^{17}O$  will be presented, along with a comparison to theoretical predictions.

Lastly, in the case of HDO which can be classified as "heteronuclear", an atom of hydrogen is substituted with a deuterium one, the ortho/para symmetry is non existent . This effect leads to observed level perturbations, where previously isolated levels belonging to different symmetry classes begin to interact and influence each other. The resulting consequence of mixing two closely spaced levels with different parity is the emergence of perturbed spectra. Extensive documentation of this effect, along with a phenomenological explanation will be described in the last chapter of Part I.

#### Hydrogen deuteride

Molecular hydrogen is the simplest and most abundant molecule in the universe. It consists of two hydrogen atoms bound together by a covalent bond.  $H_2$  plays a fundamental role in various scientific disciplines and has numerous important applications. For instance, it holds significant importance in astrophysics and cosmology as it is a crucial component of interstellar and intergalactic space.

Molecular hydrogen and its different isotopologues are of great interest to spectroscopy in view of their simplicity. As the smallest molecules, They provides excellent test model for studying the fundamental principles of molecular physics and chemistry such as molecular Quantum Electrodynamics (QED) [22, 23].

In this study, the focus will be on its isotopologue hydrogen deuteride (HD). Due to the small displacement of the center of mass in comparison to the center of charge when the molecule rotates, a very weak permanent dipole moment can be used to probe ro-vibrational transitions. In fact, in 1950 Gerhard Herzberg [24] was the first to record the ro-vibrational absorption spectrum of HD. Different vibrational bands, such as the fundamental and several overtone bands have been observed. In the following years, lot of progress was achieved to improve the accuracy of the many HD line frequencies [25, 26, 27]. We have previously taken the task to record for the first time the saturation spectroscopy of the first overtone band in HD [28]. However, substantial inconsistencies were identified when comparing our results with those obtained through a different experimental approach [29]. Consequently, the objective of this study is to address these discrepancies and enhance the accuracy of previous measurements within the first overtone band of HD.

Given that hydrogen deuteride is a linear molecule comprised of two atoms, its energy quantization follows a straightforward approach. In the framework of the Born Oppenheimer approximation, the motion of the electrons is completely disentangled from that of the nuclei. Moreover, it should be noted that the focus will primarily be on transitions occurring within the ground state  $(X^1\Sigma_g^+)$ . The nuclear motion entails vibration, denoted with v and rotation denoted as J. The studies will be performed in the first overtone band which corresponds to transitions from v = 0 to v = 2 at a wavelength of 1.38  $\mu$ m. As a weak dipole moment exists in HD the selection rules for ro-vibrational lines are:  $\Delta J = \pm 1$ . For  $\Delta J = 1$  the transitions will be labeled "R" and for  $\Delta J = -1$  the transitions will be labeled "P".

In addition to the vibrational and rotational motion of the two atoms, the individual spins of the two nuclei are essential. The proton has a spin of  $I_p = 1/2$  while the deuterium spin noted as  $I_d$  is equal to 1. This leads to a rich hyperfine structure that spans hundreds of kHz. It is important to note that hydrogen deuteride, being a heteronuclear molecule, does not exhibit spin statistics due to the differing spins of its constituent nuclei.

In the first two chapters of part II, observations of the two rovibrational lines starting at J = 1 are reported. On the R(1) line, discrepancies between two experimental studies are highlighted and a model based on the hyperfine structure and the saturation process has been proposed. The model and measurement has then been extended to the P(1) line. The last chapter covers an overview of all the rovibrational that has been measured with our apparatus. We then proceed by extracting the rotational intervals from those measurements.

# Part I

# Water

#### Chapter 2

## Spectroscopic-network-assisted precision spectroscopy and its application to water

#### Abstract

Frequency combs and cavity-enhanced optical techniques have revolutionized molecular spectroscopy: their combination allows recording saturated Doppler-free lines with ultrahigh precision. Network theory, based on the generalized Ritz principle, offers a powerful tool for the intelligent design and validation of such precision-spectroscopy experiments and the subsequent derivation of accurate energy differences. As a proof of concept, 156 carefully-selected near-infrared transitions are detected for  $H_2^{16}O$ , a benchmark system of molecular spectroscopy, at kHz accuracy. These measurements, augmented with 28 extremely-accurate literature lines to ensure overall connectivity, allow the precise determination of the lowest *ortho*- $H_2^{16}O$  energy, now set at 23.794 361 22(25) cm<sup>-1</sup>, and 160 energy levels with similarly high accuracy. Based on the limited number of observed transitions, 1219 calibration-quality lines are obtained in a wide wavenumber interval, which can be used to improve spectroscopic databases and applied to frequency metrology, astrophysics, atmospheric sensing, and combustion chemistry. <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: *Spectroscopic-network-assisted precision spectroscopy and its application to water*, R. Tóbiás, T. Furtenbacher, I. Simkó, A G.Császár, M.L. Diouf, F.M.J. Cozijn, J.M.A. Staa, E.J. Salumbides and W. Ubachs, Nature Comm. **11**, 1708 (2020).

#### 2.1. Introduction

Comprehensive spectroscopic information about small gas-phase molecules is indispensable for the characterization of various natural and artificial environments. To serve the large community of users of spectroscopic data, they have been deposited in a number of validated, annotated, and regularly updated spectroscopic information systems, such as the HITRAN database[30]. Concurrently, the majority of wavenumber entries of line-by-line databases is based on less precise (mainly Doppler-limited) experiments, typically accurate to  $10^{-3}$  cm<sup>-1</sup>. The application of precision-spectroscopy techniques, like Doppler-free cavity-enhanced saturation spectroscopy referenced to optical frequency combs, brings a new perspective to the refinement of massive amounts of transitions, entering the kHz ( $10^{-7}$  cm<sup>-1</sup>) regime[31, 32, 33, 34], and improving the accuracy of many lines and energy levels of molecular databases by orders of magnitude.

Up to now, Doppler-free precision spectroscopy has not been employed systematically to improve the quality of comprehensive spectroscopic databases, as there are experimental constraints on what we call primary line parameters (wavenumbers, Einstein-A coefficients, and intensities) and a single observed line may not have direct significance. For precision spectroscopy to be a useful source of line-byline data, one needs to (a) pay particular attention to the utility of the transitions selected for measurement, and (b) know approximately the primary line parameters in advance, as searching for rovibronic lines under saturation conditions is rather time consuming.

Within the experimental constraints of the primary line parameters, one must measure lines whose detection maximizes the amount of accurate spectroscopic information gained with a minimal experimental expenditure. This goal can be achieved by viewing high-resolution spectroscopy with the generalization of the venerable Ritz combination principle<sup>[35]</sup> (see Fig. 2.1). The Ritz principle is arguably the most important microscopic law in spectroscopy, which establishes the connection between a transition and its lower and upper energy levels (case I/1 of Fig. 2.1). Beyond its traditional, but rather limited uses (cases I–II of Fig. 2.1), the Ritz principle can be extended to an arbitrary number of connected spectral lines. This extension allows the definition of paths (case III of Fig. 2.1) and cycles (case IV of Fig. 2.1). Paths secure the formation of energy differences for any pair of underlying energy levels, while cycles can be used to confirm the accuracy of the associated transitions [36]. To increase the number of accurately known energy differences, one must ensure that transitions having minuscule uncertainties are connected, *i.e.*, their paths (and cycles) are not broken with inaccurate lines. Paths and cycles have been used implicitly by several spectroscopic protocols [37, 38, 39, 40, 41, 42, 43] based on least-squares inversion of transition wavenumbers to rovibronic energy values. Nevertheless, it should be noted that the methods of Refs. [37, 38, 39, 40, 41, 42, 43] do not decompose the input dataset into paths and cycles; thus, they cannot reveal which lines cause the inaccuracy of a particular energy value.

Building the list of target lines, forming accurate paths and cycles, necessitates the use of elements of network theory[44] and the concept of spectroscopic networks[45, 46], the most general extension of the Ritz principle. In spectroscopic



Figure 2.1: Graphical illustration of the spectroscopic utilizations of the Ritz principle. In this figure, nodes and edges are energy levels and (one-photon, dipole-moment-allowed) transitions with given energy values  $(E_i)$  and wavenumbers  $(\sigma_i)$ , respectively. The parity (p: even/odd,  $\bar{p}$ : odd/even) is displayed for each rovibronic state. Cases I [panel (a)] and II [panel (b)]: traditional applications of the Ritz principle, usually called combination differences, where case I/1 corresponds to the definition of the Ritz principle. Generalization of the Ritz principle leads to paths [sequences of connected, unrepeated transitions and energy levels – case III, panel (c)] and cycles [series of connected transitions and energy levels, where every rovibronic state has two neighboring energy levels – case IV, panel (d)]. On a path, one can predict the energy differences of all its pairs of states, applying the Ritz principle in a successive way. If the starting point in case III is the lowest-energy state reachable from the ending point via paths, then  $E_{10} - E_1$  is referred to as the relative energy of the ending point. In the special case when the starting point is the rovibronic ground state of the molecule,  $E_1 = 0$  by definition, and  $E_{10} - E_1$  provides the energy value of the ending point. Based on the  $u(\sigma_i)$  wavenumber uncertainties, the accuracy of the predicted energy differences can also be estimated from the law of uncertainty propagation (assuming uncorrelated measurement errors with zero expected values). Cycles reflect the internal accuracy of their lines: in favorable cases,  $D \leq t_{\rm crit} u(D)$ , where D is the discrepancy (absolute signed sum of the related wavenumbers) of the cycle with its u(D) uncertainty, and  $t_{\rm crit} \approx 2$  [see Supplementary Note 1]. If the states denoted with the same (green or red) color have the same vibronic parent, it can be recognized that, due to the rotational selection rule, the jumps altering the vibronic states produce two separate subsets of levels for the green states (and also for the red ones) with parities p and  $\bar{p}$ . These subsets can be linked only by pure rotational lines with  $\sigma_5$  and  $\sigma_{10}$ .

networks, energy levels are the vertices (nodes) and transitions are the edges (links). Among other advanced computer science approaches applied to high-resolution spectroscopy (*e.g.*, genetic algorithms[47, 48, 49] and machine learning involving artificial neural networks[50]) network theory and its sophisticated polynomial algorithms provide interesting and highly useful tools to exploit all the spectroscopic information coded in the connections of rovibronic lines[46].

An essential property of spectroscopic networks is that the vertex degrees (edge counts of the individual nodes) follow an inverse-power-like (heavy-tailed or quasi scale-free[44]) distribution[45]. This property implies the presence of hubs (high-degree nodes) among the rovibronic energy levels. Decreasing the uncertainties with which we know the energies of hubs by precision-spectroscopy experiments is highly beneficial as hubs are the lower states of a large number of observable lines.

Since water is an important benchmark system of high-resolution molecular spectroscopy (*e.g.*, it is molecule no. 1 in HITRAN[30]), its main isotopologue  $H_2^{16}O$  was subject to detailed investigation in the literature. Over the last 100 years, some 200 000 rovibrational lines have been recorded for  $H_2^{16}O$  (linking nearly 20 000 energy levels[51, 52]) to probe water in the interstellar medium[53], in exoplanets[54], on the Sun[55], and in the Earth's atmosphere,[56]

including its greenhouse effect [57, 58]. The rovibrational states of  $H_2^{16}O$  are separated into two subsets, corresponding to the *ortho* and *para* nuclear-spin isomers. As of today, no *ortho-para* transitions have been observed in water vapor [59], and thus the energy separation of the *ortho* and *para* states is not known precisely. The list of spectral lines of  $H_2^{16}O$  measured at high accuracy  $(10^{-7} \text{ cm}^{-1})$  is short, and derives mainly from microwave and THz experiments [60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70], except lines from two near-infrared Doppler-free laser studies [71, 72].

In this study, noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) measurements are performed for  $H_2^{16}O$ , yielding 156 rovibrational transitions under Doppler-free conditions in the near infrared (above 7000 cm<sup>-1</sup>). The lines are selected via a combined network-theoretical and experimental approach (spectroscopic-network-assisted precision spectroscopy, SNAPS), aided by the availability of experimental[75] and first-principles[76] linelists. The extremely accurate lines observed help to (a) provide an extremely accurate estimate of the lowest *ortho*- $H_2^{16}O$  energy value; (b) improve the accuracy of the energies of numerous hubs, (c) assess the accuracy of the present as well as previous literature results, mostly in the THz region and within the ground vibrational state; (d) construct the largest experimental-quality linelist in the literature with some  $10^{-7}$  cm<sup>-1</sup> uncertainty; and (e) analyze subtle systematic effects, mainly ignored in previous studies, like the pressure dependence of the line frequencies.

#### 2.2. Results and discussion

The main result of this paper is the SNAPS approach, which is a universal, versatile, and flexible algorithm, designed for all measurement techniques and molecules where the rovibrational lines are resolved individually (with their frequencies measured at extreme accuracy). The SNAPS procedure (a) starts with the selection of the most useful set of target transitions allowed by the range of primary line parameters, (b) continues with the measurement of the target lines, (c) supports cycle-based validation[77] of the accuracy of a large number of detected lines, and (d) allows the transfer of the high experimental accuracy to the derived

energy values and predicted line positions. Details are presented in the Methods section. Although the SNAPS protocol strongly relies on network theory, it can be deemed as a black-box-type strategy: its output (the target linelist and the sets of generated paths and cycles) can be understood merely via the extended Ritz principle.

Taking into account the experimental constraints on the primary line parameters and employing 28 lines from the literature[60, 66, 68, 71], 156 rovibrational transitions of  $H_2^{16}O$  have been selected with the SNAPS approach and observed with the NICE-OHMS apparatus. Figs. 2.2–2.3 give an overview of the present and former [(sub-)kHz accuracy] measurements for *ortho*- and *para*- $H_2^{16}O$ , respectively. As obvious from Figs. 2.2–2.3, the previous experiments form several isolated single paths (islands), while the inclusion of the NICE-OHMS lines makes both the *ortho* and the *para* lines connected, thus increasing considerably the overall utility of even those lines taken from the literature.



Figure 2.2: Pictorial representation of all the precision measurements for ortho-H2<sup>16</sup>O. The rovibrational states are labelled with  $(v_1v_2v_3)J_{K_a,K_c}$ , where  $(v_1v_2v_3)$  contains the normal-mode quantum numbers (following the Mulliken convention[73]) and  $J_{K_a,K_c}$  corresponds to the asymmetric-top quantum numbers[74]. The ortho energy levels (characterized with odd  $v_3 + K_a + K_c$  values and denoted with circles) are placed palindromically in increasing (upper half) and decreasing (lower half) energetic order of their vibrational parents and distinguished with different colors for improved transparency. The  $J_{K_a,K_c}$  rotational labels are indicated individually for each rovibrational state, while the  $(v_1v_2v_3)$  vibrational assignments[73] are marked in the leftside color legend. The eight vibrational states of the figure correspond to the P = 0 [(000)], P = 4[(040), (120), (021), (200), (101), and (002)] and P = 5 [(050)] polyads, where  $P = 2v_1 + v_2 + 2v_3$ is the polyad number. Transitions with blue arrows are results of the present NICE-OHMS experiments, while those with grey, orange, purple, and cyan colors are taken from Refs. [60], [66], [68], and [71], respectively. Source data are provided as a Source Data file.



Figure 2.3: Pictorial representation of all the precision measurements for para-H<sub>2</sub><sup>16</sup>O. The para energy levels (characterized with even  $v_3 + K_a + K_c$  values and denoted with squares) are placed palindromically in increasing (upper half) and decreasing (lower half) energetic order of their vibrational parents and distinguished with different colors for improved transparency. The  $J_{K_a,K_c}$  rotational labels[74] are indicated individually for each rovibrational state, while the  $(v_1v_2v_3)$  vibrational assignments[73] are marked in the left-side color legend. Transitions with blue arrows are results of the present NICE-OHMS experiments, while those with orange and cyan colors are taken from Refs. [66] and [71], respectively. Source Data are provided as a Source Data file.

The remaining part of this section is divided into two subsections. First, the important experimental results are presented. Then, it is shown how the transitions detected in a limited wavenumber range can be utilized to gain information for other spectral regions.

## NICE-OHMS precision spectroscopy of $H_2^{16}O$

In the experimental part of this study, we used a NICE-OHMS apparatus[28, 78] (see Methods) to record 156 absorption lines of  $H_2^{16}O$  in saturation. The wavenumber coverage of the measurements is limited, mainly by the highly-reflective cavity mirrors, to 7000–7350 cm<sup>-1</sup>. The accessible window of transition dipole moments, represented by the Einstein-A coefficients, falls in the interval of  $10^{-4}$ – $10^2$  s<sup>-1</sup>. Combined with the population distribution at room temperature, this factor leads to the intensity interval of  $10^{-26}$ – $10^{-20}$  cm molecule<sup>-1</sup>.

All experiments were performed through saturation spectroscopy to obtain Doppler-free transitions, typically resulting in linewidths on the order of 100 kHz (half-width at half maximum). The vast increase in resolution compared to Dopplerbroadened techniques allows to resolve closely spaced transitions, such as the  $(040)8_{8,1/0} \leftarrow (000)7_{7,0/1}$  ortho-para doublet shown in Fig. 2.4a, which would otherwise be unresolvable. By comparing the spectroscopy laser to a frequency comb laser, via a beat-note measurement, the spectra are connected to an absolute



Figure 2.4: Overview of the NICE-OHMS experiments performed for  $H_2^{16}O$ . (a) NICE-OHMS spectrum of the  $(040)8_{8,1/0} \leftarrow (000)7_{7,0/1}$  doublet. The scanning frequency, f, is shifted with the line position of the ortho transition,  $f_{ortho} = 218$  444 703.636 MHz (separated by 1.5 MHz from the para line). As clear from this spectral recording, the ortho line exhibits a three times larger intensity than its para counterpart, which is due to the nuclear-spin degeneracy factors and the nearly equal Einstein-A coefficients of the lines. Note that the assignment of this doublet is interchanged in HITRAN2016[30]. (b) Measured linewidth (half-width at half maximum, HWHM) of the saturated resonance as a function of intracavity intensity for the  $(002)2_{2,1/0} \leftarrow (000)3_{3,0/1}$  ortho-para doublet. The pressure-free wavenumbers of these two lines are determined to be 7286.715 825 626(60) (ortho) and 7285.044 729 204(63) cm<sup>-1</sup> (para). (c) Pressure-shift study of the saturated absorption line centers for some  $H_2^{16}O$  lines with their assignments. The error bars represent one standard deviation. Source data are provided as a Source Data file.

frequency scale of sub-kHz accuracy, providing individual uncertainties of a few kHz for the line centers.

Systematic studies of power-broadening and pressure-shift effects were also undertaken. Some typical results are presented in Fig. 2.4 [panels (b) and (c)]. The line center frequencies were extrapolated to zero pressure to correct them for pressure shifts (see also Methods). An additional small effect of line broadening was found as a result of hyperfine structure in the case of  $ortho-H_2^{16}O$  (see also Fig. 2.4b and the Methods section). Based on a combined treatment of statistical and systematic errors, the resulting transition frequencies were associated with individual uncertainties for each line (see also Methods).

The most precise line  $[(200)1_{0,1} \leftarrow (000)1_{1,0}]$ , reported in a near-infrared study of Kassi *et al.*[71] with 3 kHz accuracy, was used for verification, remeasured with 1.8 kHz uncertainty, and found to agree within the uncertainty limits. Beyond this transition, repeated measurements were performed for another three lines of Ref. [71] (see Figs. 2.2–2.3). In these cases, the NICE-OHMS results proved to be a factor of four more accurate than their previous determinations[71].

In addition to these repeated measurements forming trivial (2-membered) cycles, several longer (mostly 4- and 6-membered) cycles were also built from lines of Figs. 2.2–2.3 to check the self-consistency of the line positions and assignments. These cycles occasionally revealed accidental mistakes made during the determination of line centers from the raw experimental data and proved that some literature lines have much larger uncertainties than indicated in the original publications. Consequently, measuring well-designed cycles is highly recommended to check the correctness and the accuracy of the recorded lines. The discrepancies of all the investigated cycles are a few times  $10^{-7}$  cm<sup>-1</sup>. This suggests an excellent internal consistency of the observed lines.

#### Transfer of measurement accuracy

It is a significant problem how to transfer the high accuracy of the NICE-OHMS measurements to that of derived energy values and wavenumbers in the best possible way. The extended Ritz principle and the SNAPS approach offer a solution here, as well. Building paths out of observed lines ensures that several, explicitly unmeasured energy differences can be calculated with definitive uncertainties (see case III of Fig. 2.1). Such a predicted energy difference (a) relies only on the



Figure 2.5: Application of the generalized Ritz principle to the  $(000)1_{1,1}$  state. Panels (a) and (b) show a path ( $\mathcal{P}$ ) and a cycle ( $\mathcal{C}$ ) involving the  $(000)1_{1,1}$  level, respectively. The  $J_{K_a,K_c}$  rotational labels[74] are indicated for each rovibrational state, while the canonical  $(v_1v_2v_3)$  vibrational assignments[73] are marked in the left-side color legend. Transitions with blue arrows are results of the present NICE-OHMS experiments, while those with orange and green colors are taken from Refs. [66] and [79], respectively. Each line is connected with its wavenumber (in cm<sup>-1</sup>) and the uncertainty of the last few wavenumber digits in parentheses. Successive application of the Ritz principle leads to (a) the best estimate of the (000)1\_{1,1} energy value, 37.137 125 52(23) cm<sup>-1</sup>, derived from  $\mathcal{P}$ , and (b) the discrepancy of  $\mathcal{C}$ , supplied with an uncertainty,  $1.68(58) \times 10^{-6}$  cm<sup>-1</sup> (see cases III–IV of Fig. 2.1). The energies of the internal states [(101)1\_{0,1},(000)2\_{2,0}, (000)3\_{1,3}, and (200)2\_{2,0}] can be similarly obtained from  $\mathcal{P}$ . Accepting the line uncertainties of  $\mathcal{P}$ , the relatively large discrepancy of  $\mathcal{C}$  indicates that the (000)1\_{1,1} energy can be more accurately calculated from  $\mathcal{P}$  than from the direct link of Ref. [79]. Source data are provided as a Source Data file.

experimental wavenumbers and therefore does not suffer from overfitting and other numerical effects, (b) may have an accuracy characteristic of the NICE-OHMS setup, (c) is not restricted to the original experimental wavenumber range, (d) may be exempt from some systematic errors which may cancel each other due to subtractions in its defining equation. As a result, these energy-difference estimates can supersede those obtained from effective Hamiltonian models or direct results of lower-resolution techniques. In what follows, three relevant applications are presented, where the accuracy of the NICE-OHMS technique could be transferred for deduced energy differences.

#### Highly-accurate relative-energy values

Since the high-precision ortho (Fig. 2.2) and para (Fig. 2.3) lines of  $H_2^{16}O$  form connected sets, we are able to derive relative energy values for all the available ortho and para states [(000)1<sub>0,1</sub> and (000)0<sub>0,0</sub> energy levels, respectively]. Thus, one can construct paths starting at (000)1<sub>0,1</sub> or (000)0<sub>0,0</sub> and explore all of the rovibrational states of Figs. 2.2–2.3. A typical path is depicted in Fig. 2.5, which defines the (relative) energy value of the (000)1<sub>1,1</sub> state.

During the SNAPS procedure, one of our principal objectives is to obtain relative energies for the most important hubs of  $H_2^{16}O$  as accurately as possible. Among the 185 hubs (top 1 % of the known  $H_2^{16}O$  energy levels in descending order of their vertex degrees) of the IUPAC- $H_2^{16}O$  database[51], 153 and 32 lie on the (000) and (010) vibrational states with  $J \leq 14$  and  $J \leq 9$ , respectively. As the (000) hubs cover virtually all the (000) energy levels for  $J \leq 8$  [only (000) $8_{8,0}$ is missing from the hub list], we decided to redefine the relative energy values of all the (000) $J_{K_a,K_c}$  states up to J = 8 [apart from (000) $8_{8,0}$  and (000) $8_{8,1}$ , which would have required measuring a few too weak target lines] based on paths of Figs. 2.2–2.3. Nevertheless, in the present NICE-OHMS wavenumber range, we could not find paths connecting the (010) hubs to the (000) $0_{0,0}$  or (000) $1_{0,1}$  states. Thus, no (010) relative energies could be determined during this study.

Beyond hubs, some further representative rovibrational states were also investigated within the vibrational states attainable under the experimental conditions applied. In total, 160 relative energy values have been redetermined with an expected accuracy of some  $10^{-7}$  cm<sup>-1</sup>. Of the underlying rovibrational energy levels, 84, 15, 6, 4, 2, 19, 3, and 27 lie on the (000), (002), (021), (040), (050), (101), (120), and (200) vibrational states, respectively. Despite the fact that the NICE-OHMS measurements performed in the near IR region involve highly excited vibrational parents, the accuracy of the energy levels derived within the ground vibrational state is one or even two orders of magnitude better than those obtained by pure rotational measurements in the THz frequency range[79, 80, 81, 82, 83].



Figure 2.6: Two line-disjoint paths used for the derivation of the lowest  $ortho-{\rm H_2}^{16}{\rm O}$ energy. The  $J_{Ka,Kc}$  rotational labels [74] are indicated individually for each rovibrational state, while the canonical  $(v_1v_2v_3)$  vibrational assignments [73] are marked in the left-side color legend. Transitions of paths #1 and #2 are highlighted with green and blue arrows, respectively, where the ortho and para energy levels are represented with circles and squares, respectively. The starting and ending points of these paths,  $(000)0_{0,0}$  and  $(000)1_{0,1}$ , are highlighted by orange and purple squares, respectively. Common states of paths #1 and #2 are placed in the middle row of the figure. Transitions with darker colored arrows are results of the present study, while the rotational lines with lighter colored connectors are taken from Refs. [60], [66], and [68]. The dashed red lines surrounded by red boxes represent virtual transitions whose wavenumbers correspond to small ortho-para energy splittings  $[2.99(17) \times 10^{-6} \text{ and } 4.26(18) \times 10^{-6} \text{ cm}^{-1} \text{ for } (040)8_{8,0/1} \text{ and}$ (040)77,0/1, respectively] derived from nuclear-motion (GENIUSH) computations[84, 85] (see also Source Data and Supplementary Note 4). Relying on the Ritz principle and the law of uncertainty propagation (see formulas of case III in Fig. 2.1) as well as the wavenumbers and uncertainties of the virtual transitions, paths #1 and #2 give the estimated values of 23.794 361 54(59) and 23.794 361 41(71) cm<sup>-1</sup> for the lowest ortho energy, respectively. For details on the generation and evaluation of these two paths, see Methods. Source data are provided as a Source Data file.

### Lowest *ortho* energy value of $H_2^{16}O$

As emphasized in the Introduction, no transitions connecting *ortho* and *para* states of  $H_2^{16}O$  have been detected. This observational hiatus necessitates the use of indirect protocols to obtain the  $(000)1_{0,1} - (000)0_{0,0}$  energy splitting, that is, the lowest *ortho* energy value of the  $H_2^{16}O$  molecule.

The best previous estimates [94, 91, 92, 93] for the lowest *ortho* energy are accurate to  $10^{-6} - 10^{-5}$  cm<sup>-1</sup>. This means that none of the *ortho*-H<sub>2</sub><sup>16</sup>O energy values can have an absolute uncertainty better than some  $10^{-6}$  cm<sup>-1</sup>, even those involved in the much more accurate NICE-OHMS measurements. To improve the

absolute accuracy of all the *ortho* energies, one needs to determine the lowest *ortho* energy with an uncertainty of a few  $10^{-7}$  cm<sup>-1</sup>.

The traditional way to derive the lowest *ortho* energy involves a fit of an effective Hamiltonian model to the largest number of energy differences within the ground vibrational state. To simplify the fitting procedure, we constructed artificial transitions from the vibration-mode-changing lines of Figs. 2.2–2.3 sharing the same upper states and calculated the underlying (000) energy differences with their uncertainties (see also cases II–III of Fig. 2.1). Building a training set (restricted to  $J \leq 8$ ) from the appropriate artificial lines and pure rotational transitions of Refs. [60], [66], and [68], a weighted least-squares fit was performed with a 14th-order Watson-type Hamiltonian. This high order is required due to the considerable accuracy of the lines included in the training set. To make an external validation for the fitting, we excluded all those lines incident to states (000)1<sub>1,1</sub>, (000)2<sub>0,2</sub>, (000)2<sub>1,1</sub>, and (000)2<sub>2,0</sub> from the training set. The fit with this effective Hamiltonian leads to the lowest *ortho* energy estimate of 23.794 361 22(25) cm<sup>-1</sup>, while perfectly reproducing the energies of (000)1<sub>1,1</sub>, (000)2<sub>0,2</sub>, (000)2<sub>1,1</sub>, and (000)2<sub>2,0</sub> within their



Figure 2.7: Overview of selected determinations of the lowest ortho energy of  $H_2^{16}O$ . On the vertical axis, the publication year is provided for the present and the literature[86, 87, 88, 89, 90, 79, 91, 92, 93] determinations. In Ref. [91], two different estimates ([I] and [II] in this figure) are reported. Data of Toth[90], JPL[92], and Coudert et al.[93], as well as of this work are displayed in the purple inset. Our predictions [paths #1 and #2: paths of Fig. 2.6; EH fit: ground-vibrational-state effective Hamiltonian fit [see the main text and Supplementary Note 2] are repeated in the orange inset for improved transparency. Blue dots are published lowest ortho energy values, while the red ones have been calculated during the present study from the effective Hamiltonian parameters of the original publications. Similarly, blue error bars illustrate originally reported uncertainties, while the red ones are our estimates defined in Supplementary Equation 12 and analyzed in Supplementary Note 5. Source data are provided as a Source Data file.

stated uncertainties. Further details on the effective Hamiltonian modeling are given in Supplementary Note 2.

An independent, network-based way to determine the lowest *ortho* energy is to seek and measure all the shortest possible line-disjoint paths from  $(000)0_{0,0}$ to  $(000)1_{0,1}$ , involving accurate virtual transitions that connect closely spaced  $(v_1v_2v_3)J_{J,0/1}$  ortho-para state pairs with sufficiently high J values (for details, see Methods). This protocol yielded only two such paths (see Fig. 2.6) within the experimental restrictions, upon which two independent determinations [23.794 361 54(59) and 23.794 361 41(71) cm<sup>-1</sup>] are obtained for the lowest ortho energy value. These data are in full accord with our effective Hamiltonian value.

Based on a careful consideration of all the results, the estimate of our effective Hamiltonian model,  $23.794\ 361\ 22(25)\ cm^{-1}$ , is recommended as the new reference value for the lowest *ortho* energy A comparison of the present lowest *ortho* energy determinations with results of previous effective Hamiltonian models[86, 87, 88, 89, 90, 79, 91, 92, 93] is displayed in Fig. 2.7 (for comments, see Supplementary Note 5).

Finally, it must be emphasized that the traversal of the (000) rotational energy levels via up and down jumps involving several vibrational bands (see Fig. 2.6) is a fully novel approach, inspired by the network-theoretical view of high-resolution spectroscopy. Construction of paths with similar complexity would be impossible via conventional spectroscopic tools (combination difference relations or effective Hamiltonian models).

#### High-accuracy predicted linelist

The list of lines predicted from the paths of Figs. 2.2–2.3 may act as frequency standards[96] over a wide range, helping future high-resolution experiments. This is especially true for those 30 pairs of predicted transitions whose separation is less than 0.01 cm<sup>-1</sup>, which cannot easily be resolved via Doppler-broadened measurements. These highly-accurate calculated lines, having two or three orders of magnitude smaller uncertainties than their former determinations, give us the opportunity to validate less accurate measurements and reveal individual and systematic (*e.g.*, pressure-shift) effects in their line positions. Such an examination is mostly important for the THz regime, where the usually applied experimental techniques provide a few times  $10^{-6}$  cm<sup>-1</sup> accuracy for the detected transitions. The complete set of predicted lines is presented in Fig. 2.8. An assessment of the literature data sources corresponding to our predicted lines is provided in Supplementary Note 6 and Supplementary Figure 3.

As illustrated here for  $H_2^{16}O$ , the SNAPS method performs excellently; therefore, this approach is highly recommended to enhance our understanding of the spectroscopy of important molecular species, say those in HITRAN. It is expected that SNAPS, once applied to the majority of molecules of interest (note that the latest HITRAN version[30] contains rovibronic transitions for 49 molecules), will improve significantly the accuracy and utility of spectroscopic databases.



Figure 2.8: High-accuracy linelist of  $H_2^{16}O$  generated from paths of Figs. 2.2–2.3 (see also Supplementary Note 6). In addition to the transition wavenumbers, 296 K absorption intensities[95] are also presented on the vertical axis. The data points in the left lower quadrant correspond to low-intensity, vibration-mode-changing transitions. While the directly measured lines are constrained to the interval 7000–7350 cm<sup>-1</sup>, the predicted transitions resulting from lines of Figs. 2.2–2.3 extend between 0–1005 cm<sup>-1</sup> and 6198–8114 cm<sup>-1</sup>. Source data are provided as a Source Data file.

#### 2.3. Methods

#### Theory

The SNAPS procedure can be divided into four major phases (Fig. 2.9): [I] preparation phase, where the SNAPS input is created, [II] selection phase, where the full set of possible target lines is generated, [III] measurement phase, where the list of target lines is reduced and then detected with a precision-spectroscopy setup, and [IV] evaluation phase, where the final paths and cycles are obtained and assessed. Phases II and IV are based on elements of network theory, while phase III is where the theoretical knowledge is turned into experimental information. The network-theoretical notions and methods utilized here are summarized in Supplementary Note 1 and illustrated in Supplementary Figure 1.

In phase I (preparation), five input units are introduced. In the reference dataset, those (highly accurate) literature lines are placed which one desires to build into paths and cycles. The template dataset comprises transitions with their estimated (experimental or calculated) primary line parameters and wavenumber uncertainties. The experimental constraints (the wavenumber window of  $[\sigma_{\min}, \sigma_{\max}]$ , the intensity interval of  $[S_{\min}, S_{\max}]$ , and the Einstein-A coefficient range of  $[A_{\min}, A_{\max}]$ ) imposed upon the template lines are characteristic of the precision-spectroscopy technique applied. If one opts for the determination of the energy differences of



Figure 2.9: Flowchart of the SNAPS approach. Boxes of this picture are explained in the Theory section.

some state pairs, the list of these pairs (state duals) should be provided. For these state duals, all the available line-disjoint paths will be found. The extracted dataset is initially empty, which will be filled with extracted (newly measured and resolved) lines provided by the experimental method chosen.

As the first stage of phase II (selection), a design network is constructed from (a) all the reference and extracted transitions, and (b) those template lines which
meet the experimental constraints and do not have counterparts with the same assignment in the extracted dataset. Then, shortest-path searches are performed by running Dijkstra's algorithm [44] to explore the structure of the design network. For these searches, the weights of the lines are specified as follows: (a) zero weights are assigned to all the transitions of the reference and extracted dataset (that is, they are forced into the shortest paths to reduce the experimental cost), and (b) weights of the template lines are represented by the squared wavenumber uncertainties. Obviously, this weighting scheme can be arbitrarily modified and adapted to the experimental setup applied. The design network is utilized in two different ways. First, a shortest (core-to-state) path is built for every state from its core with a single execution of the Dijsktra procedure, and the basic cycles of the corresponding shortest-path forest (compact cycles) are determined (core-to-state decomposition). Second, the entire list of line-disjoint shortest (state-to-state) paths are composed for each state dual by successive application of the Dijkstra algorithm (state-tostate decomposition). During the repetition of Dijkstra's procedure, the transitions of the actual state-to-state path are temporarily ignored from the design network in each step (these ignored lines are reinstated right before the next state dual is treated). A core-to-state path from  $(000)0_{0,0}$  to  $(000)1_{1,1}$  and two state-to-state paths for the state dual  $[(000)0_{0,0}, (000)1_{0,1}]$  can be found in Figs. 2.5 and 2.6, respectively.

At the end of this step, the core-to-state paths and the compact cycles (grouped by the components of the design network) are printed into a file and the state-tostate paths are stored in a separate file by state duals. In these files, paths and cycles are indicated either as unexhausted or exhausted, depending on whether they contain any template transitions or not. The set of template lines involved in unexhausted paths and cycles (called the linked target linelist, LTL), is also collected into a third file for each component.

In phase III (measurement), a reduced set is created from the linked target linelist by manually selecting the template transitions of those unexhausted paths and cycles which are of interest to the user. If there is at least one line in the reduced target linelist, it must be detected, resolved, and carefully analyzed via the precision-spectroscopy technique employed. Having completed the high-precision experiments, the extracted lines should be included in the extracted dataset, while the lines declared to be rejected for some reasons (for instance, due to incorrect primary line parameters or measurement difficulties) need to be deleted from the template dataset. Thereafter, phases II and III are repeated with the altered input until the reduced target linelist becomes empty.

Once the iteration involving phases II and III is stopped, a response network is assembled from the reference and the extracted datasets (phase IV – evaluation). The weights of the lines in the response subnetwork are initialized as the squared wavenumber uncertainties. Neglecting those reference transitions of the response subnetwork which are not connected to extracted transitions (*i.e.*, form separate islands), a backbone subnetwork is obtained. For this backbone subnetwork, the same decompositions are performed as for the design network of phase II, complemented with the evaluation of the energy differences and discrepancies concerning the output paths and cycles, respectively (see cases III–IV of Fig. 2.1). The relative energies of the rovibronic states (together with their uncertainties) are calculated from the core-to-state paths of the backbone subnetwork.

At the beginning of our measurement campaign on  $H_2^{16}O$ , the reference dataset consisted of the lines taken from Refs. [60], [66], [68], and [71]. In search for linedisjoint paths from  $(000)0_{0,0}$  to  $(000)1_{0,1}$ , virtual transitions (see the main text), constructed from the energy list of Ref. [95], were also included to connect the *ortho* and *para* states (see also next subsection). For the template dataset, the line positions and their uncertainties were predicted from the empirical energies of the IUPAC database[51] of  $H_2^{16}O$ , while the line intensities and Einstein-*A* coefficients were taken from the first-principles linelist of Ref. [95]. The experimental constraints guiding the SNAPS procedure of this study are as follows: [7000, 7350] cm<sup>-1</sup> for the wavenumbers,  $[10^{-26}, 10^{-20}]$  cm molecule<sup>-1</sup> for the intensities, and  $[10^{-4}, 10^2]$  s<sup>-1</sup> for the Einstein-*A* coefficients. The estimates for the primary line parameters of the template dataset proved to be sufficiently accurate to serve as design parameters for precision measurements performed with the NICE-OHMS setup.

## Linking ortho and para states

The splittings of close-lying  $(v_1v_2v_3)J_{J,0/1}$  states (that is, the wavenumbers of the virtual lines) can be estimated as differences of first-principles energies. For these wavenumbers, the nuclear-motion computations[84, 85] lead to sufficiently high accuracy (see Supplementary Note 3 and Supplementary Figure 2), paving the way for the utilization of virtual lines to provide extremely precise lowest *ortho* energy determinations.

During the execution of the SNAPS procedure (see Methods), we took into account all the possible virtual transitions from Ref. [95], with wavenumbers less than  $10^{-5}$  cm<sup>-1</sup>, and searched for all the (shortest possible) line-disjoint paths defining the lowest *ortho* energy. This search yielded only two feasible line-disjoint paths within the experimental constraints, containing virtual lines with state pairs  $(040)7_{7,0/1}$  and  $(040)8_{8,0/1}$ . The near-infrared lines of these paths (see Fig. 2.6) have been redetermined with the NICE-OHMS setup, while the wavenumbers of the virtual transitions have been benchmarked with variational nuclear-motion computations employing the the GENIUSH[84, 85] program system as well as several vibrational basis sets and potentials. The GENIUSH computations resulted in  $4.26(18) \times 10^{-6}$  cm<sup>-1</sup> and  $2.99(17) \times 10^{-6}$  cm<sup>-1</sup> for the wavenumbers of the  $(040)7_{7,0} \leftarrow (040)7_{7,1}$  and  $(040)8_{8,0} \leftarrow (040)8_{8,1}$  virtual lines, respectively. Further details on the GENIUSH computations, see Supplementary Note 4.

Utilizing the line positions and uncertainties of paths #1 and #2, together with the wavenumbers and the uncertainties of the virtual lines, the values of 23.794 361 54(59) and 23.794 361 41(71) cm<sup>-1</sup> are obtained for the lowest *ortho* energy, respectively. The accuracy of these determinations is dominantly determined by the excessive lengths of the underlying paths, and much less by the uncertainty contribution of the first-principles computations. These lowest *ortho*-energy values are overall of slightly lower accuracy, but in excellent agreement with our effective-Hamiltonian-based estimate.



Figure 2.10: Schematic layout of the NICE-OHMS experimental setup The EOM (electro-optic modulator) is double modulated at both frequencies  $f_{\text{PDH}}$  and  $f_{\text{FSR}}$ , which are 20 MHz and 305 MHz, respectively, where the latter is exactly matched to the cavity free spectral range. OFC represents an optical frequency comb laser. For further details, see text.

#### Experiment

Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS, see Refs. [97], and [98]) is an ultrasensitive and ultrahigh-precision method of cavity-enhanced saturation spectroscopy, combining frequency modulation spectroscopy with cavity-enhancement. In our NICE-OHMS setup, shown schematically in Fig. 2.10 and previously developed for precision metrology of HD[28, 78], we used an optical frequency comb as an external reference for long term stabilization. In order to cancel short-time jitter, the external cavity diode laser is electronically locked via a Pound-Drever-Hall (PDH) scheme to the spectroscopy cavity, which has a finesse of 150 000 and a length of 51 cm. Long-term stabilization of the cavity is achieved by beating the laser to an optical frequency-comb laser disciplined by a caesium atomic clock and is further corrected by comparison with signals from the global positioning system. This advanced methodology gives rise to a frequency scale of sub-kHz accuracy. A double modulation scheme is applied via an electro-optic modulator (EOM) for imposing the 20 MHz and 305 MHz modulations for the PDH-locking and for generating the spectroscopy sidebands respectively, where the spectroscopy sidebands are carefully matched to the cavity free spectral range, used in NICE-OHMS. While NICE-OHMS typically yields dispersive signals, in our detection scheme an additional layer of slow modulation is applied via dithering a piezo activated cavity mirror (at 405 Hz) to yield a derivative of the dispersive signal. Hence, our lines exhibit the shape of a Lamb-dip as displayed in Fig. 2.4a.

The water vapor used for the measurements in this study originates from outgassing from the vacuum chamber walls, where water is the dominant component. Pressure levels are controlled by varying the pump speed to the turbo molecular pump to reach a steady state condition, where the pressure is monitored by a capacitance pressure gauge.

To improve the accuracy with which the line centers are measured, which is as low as 3–5 kHz, the broadening and shifting phenomena affecting the spectral lines detected in saturation in the NICE-OHMS setup were systematically investigated. The effect of the enhanced intracavity power gives rise to power broadening, and during the experiments the intracavity power level was reduced and matched to the Einstein-A coefficient to avoid too strong broadening. The observed linewidths are on the order of 100 kHz.

As an example, the spectrum of the  $(002)3_{3,0/1} \leftarrow (000)2_{2,1/0}$  ortho-para doublet was investigated under various conditions of intracavity saturation power. The values for the half-width at half-maximum (HWHM) are plotted in Fig. 2.4b, clearly showing a power broadening effect. It was verified that power broadening does not lead to shifting of the central line position – no systematic effect was observed beyond the statistical uncertainty. Fig. 2.4b also clearly demonstrates that the ortho line is slightly, but consistently, broader than the para line, which is attributed to the underlying and unresolved hyperfine structure of ortho-H<sub>2</sub><sup>16</sup>O. This effect of hyperfine structure does not lead to discernible asymmetries and a shift of the central line position, and hence does not compromise the accuracy of the determination of the ortho line centers.

A second systematic effect, caused by the influence of collisions and pressure, was also considered. While collisions and increased pressure do produce broadening of the lines, this is not of particular relevance for the present study. However, the collisional shift is a crucial issue because it is a limiting contribution in the measurement accuracy of the line centers. In Fig. 2.4c some typical pressure dependence measurements are displayed for a number of lines. The explicit pressure dependence of the line positions has been determined only for a small fraction of the measured NICE-OHMS lines. In addition, due to the large amount of work required for the determination of the pressure shifts, the remaining transitions have been measured at a low pressure of around 0.1 Pa. Thus, based on the highest pressure shift coefficient value ( $\pm 20$  kHz Pa<sup>-1</sup>), a conservative pressure uncertainty of 2–3 kHz has been adopted for those lines for which no explicit pressure curves were measured.

Note that the relative values of the collisional shifts, and even the signs of the collisional shifts, for the presently determined saturated absorption lines do not agree with the self-collision shifts of the HITRAN database[30] for Dopplerbroadened lines. This deviation may be attributed to the fact that in saturation spectroscopy only a partial velocity class is probed for the molecules, but a detailed analysis falls outside the scope of the present study.

Overall, a number of individual uncertainty factors have been assigned to all observed transitions. First, the statistical uncertainties are calculated by taking different results of the fitting procedures for each single transition, and averaging over its multiple recordings. The pressure effects, mentioned above, have also been included in the line uncertainties. In addition, a conservative power shift uncertainty of 1 kHz has also been considered in the error budget. The final uncertainty of a particular line was estimated as the square root taken from the sum of squared individual uncertainty terms.

### 2.4. Data availability

Data supporting the main findings of this work are available in the Supplementary Information files of this paper. The important experimental and calculated data of this study [list of old and new precision lines; high-accuracy predicted linelist; highly accurate relative rovibrational energies; output of the effective Hamiltonian fit; line disjoint paths between  $(000)0_{0,0}$  and  $(000)1_{0,1}$ ; GENIUSH-based predictions for the wavenumbers of the  $(040)7_{7,0} \leftarrow (040)7_{7,1}$  and  $(040)8_{8,0} \leftarrow (040)8_{8,1}$  virtual lines; comparison of the various lowest *ortho* energy estimates; basic cycles built upon the new and old precision measurements; and comparison of the literature lines with our high-accuracy linelist] are provided as a Source Data file. The data underlying Figs. 2.2, 2.3, 2.5, 2.6, 2.7, and 2.8 can also be found in the Source Data file.

# 2.5. Author contributions

Conducted the experiments and resolved the lines: MLD, FMJC, JMAS, and EJS;

Selected the linelist for the experiments and evaluated the resolved lines: RT;

Planned and created the draft of the figures: TF, RT, and FMJC;

Performed nuclear-motion computations and corrected the figures: IS;

Finalized the figures: FMJC;

Designed and supervised the research: AGC and WU;

All authors discussed the results and wrote the manuscript.

# 2.6. Competing interests

The authors declare no competing interests.

# 2.7. Acknowledgement

This research received funding from LASERLAB-EUROPE (grant no. 654148, European Union's Horizon 2020 research and innovation programme). The work performed in Budapest received support from NKFIH (grant no. K119658), from the grant VEKOP-2.3.2-16-2017-000, and from the ELTE Excellence Program (1783-3/2018/FEKUTSTRAT) of the Hungarian Ministry of Human Capacities (EMMI). WU acknowledges the European Research Council for an ERC Advanced Grant (grant no. 670168). Further support was obtained from a NWO-FOM program (16MYSTP) and from the NWO Dutch Astrochemistry Network. The authors are grateful to Prof. Jonathan Tennyson for providing PES subroutines, as well as to Dr. Patrick Dupré, Dr. Csaba Fábri, and Dr. Tamás Szidarovszky for useful discussions.

# Chapter 3

# Ultraprecise relative energies in the $(2\,0\,0)$ vibrational band of $\mathbf{H_2}^{16}\mathbf{O}$

#### Abstract

The sensitive technique of Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) is employed to detect rovibrational transitions of the main isotopologue of water at wavelengths of about 1.4 mum. This intracavity-saturation approach narrows down the typical Doppler-broadened linewidths of about 600 MHz to the sub-MHz domain. The locking of the spectroscopy laser to a frequency-comb laser and the assessment of collisional and further line broadening effects result in transition frequencies with an absolute uncertainty below 10 kHz. The lines targeted for measurement are selected by the spectroscopic-network-assisted precision spectroscopy (SNAPS) approach. The principal aim is to derive precise and accurate relative energies from a limited set of Doppler-free transitions. The transitions selected for measurement by SNAPS establish cycles within the spectroscopic network of  $H_2^{16}O$ , helping to confirm the internal consistency as well as the accuracy of the precision-spectroscopy measurements. The 71 newly observed lines, combined with further highly accurate literature transitions, allow the determination of the relative energies for all of the 59 rovibrational states up to J = 6 within the  $(v_1 v_2 v_3) = (200)$  vibrational parent of  $H_2^{16}O$ , where J is the overall rotational quantum number and  $v_1$ ,  $v_2$ , and  $v_3$  are quantum numbers associated with the symmetric stretch, bend, and antisymmetric stretch normal modes, respectively. An experimental curiosity of this study is that for strong transitions an apparent signal inversion in the Lamb-dip spectra is observed; a novelty reserved to the NICE-OHMS technique.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: Ultraprecise relative energies in the (200) vibrational band of  $H_2^{16}O$ , M.L. Diouf, R. Tóbiás, T.S. van der Schaaf, F.M.J. Cozijn, E.J. Salumbides, A G.Császár, and W. Ubachs, Mol. Phys. e2050430 (2022).

#### 3.1. Introduction

Water isotopologues, all of them asymmetric-top molecules, have been widely employed as test systems for modeling efforts in high-resolution and precision spectroscopy. The interest in water spectroscopy [99] is due partly to the fact that water spectra are involved in a huge number of important scientific and engineering applications, *e.g.*, combustion, atmospheric sciences, and astronomy, either directly or indirectly (in the latter case the application requires the subtraction of water lines to reveal the lines of interest). Therefore, extensive line lists exist for at least nine water isotopologues [30, 100, 101, 102, 103, 104, 105].

For the main water isotopologue,  $H_2^{16}O$ , the related spectroscopic databases contain some 300 000 experimental rovibrational lines and some 20 000 empirical energy levels. Dr. Jean-Marie Flaud, to whom this paper is dedicated, has made significant contributions [106, 107, 108, 109, 37, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128] to these spectroscopic data collections, providing thousands of measured line positions, line intensities, and collision parameters for a number of water isotopologues. Furthermore, the pioneering work of Flaud *et al.* [37] related to the conversion of measured transitions to empirical energy values provided one of the pillars of the MARVEL (Measured Active Rotational-Vibrational Energy Levels) protocol [40, 43, 52] and turned the attention of the Hungarian co-authors of this study toward the analysis and utilization of spectroscopic networks [45].

The rovibrational energy levels of  $H_2^{16}O$  are separated into two components, corresponding to the ortho and para nuclear-spin isomers. As of today, ortho-para transitions have not been detected for  $H_2^{16}O$  due to their extremely low transition intensities [59]; thus, only relative energies can be determined from the measured lines. The relative energy of an ortho(para) state is defined as the difference between the absolute energy of this state and that of the lowest-energy ortho(para) state. In spectroscopy the absolute energy of the lowest para state  $(v_1 v_2 v_3)J_{K_a,K_c} = (000)0_{0,0}$ , is zero by definition, where  $v_1, v_2$ , and  $v_3$  are the symmetric stretch, bend, and asymmetric stretch normal-mode quantum numbers, respectively, while  $J_{K_a,K_c}$  stands for the asymmetric-top rotational quantum numbers [74]; thus, the relative para energies correspond to absolute energies. The most accurate empirical estimate for the absolute energy of the lowest ortho state,  $(000)1_{0,1}$ , is 23.794.361.22(25) cm<sup>-1</sup> [129], enabling the accurate conversion of the relative ortho energies to absolute ones.

While all the experimental studies of Flaud and co-workers were based on Doppler-broadened spectroscopy, the advent of cavity-enhanced techniques has opened up a new territory, allowing experiments with much improved accuracy outside of the microwave spectral region. Such experiments in the near infrared have already been carried out for  $H_2^{16}O$ ,  $H_2^{17}O$ , and  $H_2^{18}O$  [71, 72, 129, 130, 131]. The combination of ultrasensitive Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) [97, 98] and the spectroscopic-network-assisted precision spectroscopy (SNAPS) procedure [129] has led to the derivation of a considerable number of ultraprecise absolute energies of  $H_2^{16}O$  [129] and  $H_2^{18}O$  [130] in the ground vibrational state.

In this study, 71 ultraprecise rovibrational lines of  $H_2^{16}O$  are reported, observed with the NICE-OHMS technique in the 1.4 mum region. Relying on the newly recorded transitions selected via the SNAPS scheme, as well as those of Refs. [129], [71], and [60, 66, 68], accurate relative energies are deduced with an uncertainty of at most 15 kHz. Altogether 59 ultraprecise relative energies are determined this way within the (200) band, forming a complete set up to J = 6. The newly derived relative energies allow the extension of an ultraprecise predicted line list of  $H_2^{16}O$ [129], benefiting all those who require accurate spectroscopic information for their modeling efforts.

#### 3.2. Methodological details

#### NICE-OHMS

NICE-OHMS [97, 98] is an absorption-based saturation-spectroscopy technique combining frequency modulation with cavity enhancement. A detailed description of our in-house NICE-OHMS spectrometer is given in Ref. [28], while the application of our setup to the study of water lines has been described in detail in Refs. [129] and [130].

The principle behind NICE-OHMS is based on the modulation of a laser, the carrier with frequency  $f_c$ , to generate two opposite-phase sidebands with frequencies  $f_c \pm f_m$  for heterodyne detection, where  $f_m$  is the modulation frequency (see Fig. 3.1a). The in-phase sideband, that with frequency  $f_c + f_m$ , has the same phase as the carrier, while the other one with frequency  $f_c - f_m$ , named out-of-phase sideband, is shifted in its phase by 180° with respect to the carrier. The three fields moving in both directions within the cavity must exactly match the resonant cavity modes, requiring  $f_m = \text{FSR}$ , where FSR is the free spectral range of the cavity (see Fig. 3.1b).

When  $f_c = f$  is set, where f is the central position of a molecular resonance, both counter-propagating carrier fields interact with the molecules flying perpendicularly. This interaction produces a hole burnt in the center of the axial velocity distribution and enables the observation of generic Doppler-free Lamb dips.

In addition to this generic Lamb dip, the two counter-propagating sidebands interact with molecules flying parallel to the beam and carrying a velocity of  $\pm \lambda_c f_m$ , where  $\lambda_c$  is the wavelength of the carrier. Due to the Doppler effect, molecules with these velocities perceive the sideband frequencies at f, leading to additional hole burning [132]. These holes appear in the axial velocity distribution at  $\pm \lambda_c f_m$ , forming two additional identical Lamb dips at  $f_c = f$  (see Fig. 3.1c).

All three Lamb dips are acquired simultaneously at  $f_c = f$ , but the Lamb-dips generated by the sidebands are opposite in sign, as the out-of-phase sideband causes the sign to flip. In most conditions the widths of the Lamb dips are nearly identical, leading only to a slight attenuation of the observed Lamp-dip. However, in the case of strong resonances, the carrier-carrier saturation significantly broadens the Lambdip. This broadening ensures sufficient contrast to observe the sideband-sideband Lamb dip separately, resulting in a notable double-dip profile.

Experimental constraints on the selection of target lines are imposed by the operating ranges of the diode laser, the frequency-comb laser, and the high-reflectivity



Figure 3.1: Interaction among the multiple laser fields inside the cavity. Panel (a) shows the generation of the sidebands through the Electro Optic Modulator (EOM) with a modulation frequency  $f_{\rm m}$ . The EOM generates from an input field at frequency  $f_{\rm c}$ , the carrier, two sideband fields at frequencies  $f_c + f_{\rm m}$  and  $f_c - f_{\rm m}$ . The thick green arrow represents the carrier field, at much higher power than the in-phase (blue) and out-of-phase (red) sidebands. The parameter  $f_{\rm m}$  is set to the free spectral range (FSR), which is 305 MHz. Panel (b) illustrates the three fields coupled into three adjacent cavity modes and separated by the FSR. The matching cavity modes of the carrier, the in-phase sideband, and the out-of-phase sideband are denoted with green, blue, and red spikes, respectively. The two arrows labeled with k show the opposite propagation directions of the three bi-directionally propagating laser fields. Panel (c) exhibits the three distinctive holes burnt into the axial velocity distribution profile, all contributing to the observed lineshape.  $\lambda_c$  is the wavelength of the carrier.

mirror. A further constraint is that the Lamb-dip spectra can be probed most efficiently within a limited range of intensities  $(10^{-26}-10^{-21} \text{ cm molecule}^{-1})$  and Einstein A-coefficients  $(10^{-4}-10^2 \text{ s}^{-1})$ .

# SNAPS

The SNAPS procedure, built upon the theory of spectroscopic networks [45] and the Ritz principle [35], is well documented, see Refs. [129] and [130]. Briefly, during the execution of SNAPS, one should (a) build paths and cycles (see Fig. 2 of Ref. [130]) from highly-accurate 'predetermined' (literature) lines, as well as from target transitions satisfying the experimental constraints; (b) continue with recording the target lines; and (c) evaluate the spectroscopic information coded in the paths and cycles of the new and the predetermined transitions. The paths provide ultraprecise estimates for the energy differences and their uncertainties, while the cycles can be applied to test the internal accuracy of the newly resolved lines.



Figure 3.2: Pictorial representation of the precision lines observed for ortho-H<sub>2</sub><sup>16</sup>O. The rovibrational states are designated with  $(v_1 v_2 v_3) J_{K_a,K_c}$ , whereby  $v_3 + K_a + K_c$  is odd. The rovibrational lines correspond to  $(v'_1 v'_2 v'_3) J'_{K'_a,K'_c} \leftarrow (v''_1 v''_2 v''_3) J'_{K''_a,K''_c}$ , where ' and '' distinguish between the upper and lower states, respectively. Based on the even and odd parity of  $K''_c$ , the near-infrared transitions can be divided into two subnetworks,  $o^+$  and  $o^-$ , respectively, which are drawn separately. The  $J_{K_a,K_c}$  rotational label is written out explicitly for each state in a circle, while the  $(v_1 v_2 v_3)$  vibrational labels [73] are indicated in the left-side color legend. The vibrational states of this figure belong to the P = 0, 4, and 5 polyads, where  $P = 2v_1 + v_2 + 2v_3$  is the polyad number. Transitions with light green arrows are results of the present study, while those with cyan, dark blue, gray, orange, and purple colors are taken from Refs. [129], [71], [60], [66], and [68], respectively. Dashed arrows represent pure rotational lines linking the  $o^+$  and  $o^-$  subnetworks. The complete list of these ultraprecise transitions with their line centers and uncertainties are deposited in the Supplementary Material.



Figure 3.3: Pictorial representation of the precision lines observed for para-H<sub>2</sub><sup>16</sup>O. The specification of the rovibrational states and lines, as well as the formalism applied, is similar to that of Fig. 3.2, with the difference that the para levels, identified with even  $v_3+K_a+K_c$  values, are represented with squares. The NICE-OHMS transitions are organized into subnetworks  $p^+$  and  $p^-$ , where the lines are characterized by even and odd  $K''_c$  values, respectively. The complete list of these ultraprecise transitions with their frequencies and uncertainties are deposited in the Supplementary Material.

Figures 3.2 and 3.3 give an overview of all the ultraprecise lines observed for *ortho-* and *para*-H<sub>2</sub><sup>16</sup>O, respectively. The 'light green' transitions of Figs. 3.2 and 3.3 are detected during this study, while all the other lines have been measured before [129, 71, 60, 66, 68], with a few kHz accuracy.

In Figs. 3.2 and 3.3, two poorly-connected subnetworks can be recognized within the ortho and para components. The  $p^+$ ,  $p^-$ ,  $o^+$ , and  $o^-$  subnetworks correspond to the (p'',q'') = (+1,+1), (-1,+1), (+1,-1), (-1,-1) pairs, respectively, where  $p'' = (-1)^{K''_c}$  and  $q'' = (-1)^{v''_3 + K''_a + K''_c}$ , while  $v''_3$ ,  $K''_a$ , and  $K''_c$  are lower-state quantum numbers. Despite the fact that the para (q'' = +1) component cannot be linked via experimental transitions with the ortho (q'' = -1) component, the  $p^+/p^-$  and  $o^+/o^-$  subnetworks are connected with pure rotational lines [60, 66, 68]. Considering only dipole-allowed, vibrational-state-altering lines, these subnetworks are fully decoupled from each other. Unlike in the case of  $H_2^{18}O$  [130], the four subnetworks of  $H_2^{16}O$  remain disconnected in themselves, but the pure rotational lines make the *ortho* and *para* components entirely connected.

# 3.3. Experimental results

### Lineshapes of NICE-OHMS spectra

For the 71 'light green' transitions shown in Figs. 3.2 and 3.3, accurate line centers have been derived from the Lamb dips recorded during this study. The ultraprecise line positions and their individual uncertainties, representing 68 % confidence level, are given in Table 1.

Table 1: The complete list of the rovibrational transitions of  $H_2^{16}O$  measured during this study, together with associated individual uncertainties.

# Assign	ment Frequ	ency/kHz	# -	Assignment	Frequency/kHz
$1(101)4_{1,3} \leftarrow$	$(0\ 0\ 0)5_{3,2}210\ 10$	$06545991.7\pm7.7$	37(200)4	$4_{2,2} \leftarrow (000)$	$3_{3,1}216467935097.0\pm 4.9$
$2(200)2_{2,1} \leftarrow$	$(0\ 0\ 0)3_{3,0}211\ 17$	$73854736.3\pm7.5$	38(200)6	$\delta_{4,3} \leftarrow (000$	$7_{1,6}216533504194.3\pm5.1$
$3(200)3_{0,3} \leftarrow$	$(0\ 0\ 0)3_{3,0}211\ 29$	$97750216.9\pm5.2$	39(200)2	$2_{1,1} \leftarrow (000)$	$2_{0,2}216543604990.8\pm7.7$
$4(200)6_{1,6} \leftarrow$	$(0\ 0\ 0)6_{2,5}212\ 22$	$28360502.3\pm7.5$	40(200)6	$\beta_{2,5} \leftarrow (000)$	$)5_{3,2}216584789651.7\pm7.7$
$5(200)4_{3,1} \leftarrow$	$(000)4_{4,0}21227$	$75745088.6\pm7.8$	41(200)6	$\beta_{3,3} \leftarrow (000)$	$)5_{4,2}216713868387.2\pm5.3$
$6(200)6_{4,3} \leftarrow$	$(000)7_{3,4}21239$	$92094941.0\pm7.6$	42(200)4	$4_{2,2} \leftarrow (000)$	$)4_{1,3}216759402341.3\pm7.5$
$7(200)5_{3,3} \leftarrow$	$(0\ 0\ 0)6_{2,4}212\ 42$	$29214349.8\pm7.5$	43(200)3	$B_{1,2} \leftarrow (000)$	$3_{0,3}216816255011.5\pm8.0$
$8(200)6_{0,6} \leftarrow$	$(0\ 0\ 0)6_{1,5}212\ 51$	$16880028.2\pm7.5$	44(200)	$5_{2,3} \leftarrow (000)$	$)5_{1,4}216845549472.7\pm7.6$
$9(200)4_{2,3} \leftarrow$	$(0\ 0\ 0)5_{1,4}212\ 5_{4}$	$19726957.8\pm7.5$	45(200)3	$B_{1,2} \leftarrow (000)$	$)2_{2,1}216872016984.5\pm7.7$
$10(200)5_{1,5} \leftarrow$	$(000)5_{2,4}21284$	$43780343.4\pm7.6$	46(200)6	$\delta_{3,3} \leftarrow (000)$	$)6_{2,4}216933944189.3\pm7.5$
$11(200)1_{1,0} \leftarrow$	$(0\ 0\ 0)2_{2,1}213\ 06$	$35280386.0\pm7.6$	47(200)	$5_{4,2} \leftarrow (000)$	$)6_{1,5}217091029773.4\pm13.8$
$12(200)3_{0,3} \leftarrow$	$(0\ 0\ 0)4_{1,4}213\ 11$	$13898650.5\pm7.6$	48(200)	$5_{3,3} \leftarrow (000)$	$6_{0,6}217108282261.0\pm7.5$
$13(200)5_{0,5} \leftarrow$	$(0\ 0\ 0)5_{1,4}213\ 31$	$17003151.8\pm7.6$	49(200)	$4_{3,2} \leftarrow (000)$	$(5_{0,5}217135374647.8\pm7.6)$
$14(200)6_{5,1} \leftarrow$	$(000)7_{4,4}21350$	$04626962.6\pm7.6$	50(200)	$\mathbf{l}_{1,3} \leftarrow (000)$	$4_{0,4}217221204437.3\pm7.5$
$15(200)5_{4,2} \leftarrow$	$(0\ 0\ 0)6_{3,3}213\ 53$	$34197982.8\pm7.5$	51(200)3	$B_{0,3} \leftarrow (000)$	$2_{1,2}217471142188.6\pm 8.0$
$16(200)2_{0,2} \leftarrow$	$(0\ 0\ 0)3_{1,3}213\ 66$	$33124480.5\pm7.6$	52(200)	$l_{1,3} \leftarrow (000)$	$3_{2,2}217693417582.6\pm7.6$
$17(200)6_{0,6} \leftarrow$	$(0\ 0\ 0)5_{3,3}213\ 68$	$34202168.2\pm15.$	553(200)	$l_{4,1} \leftarrow (000)$	$(5_{1,4}217\ 831\ 529\ 702.9\pm 7.8)$
$18(101)4_{1,3} \leftarrow$	$(0\ 0\ 0)4_{3,2}213\ 89$	$92779969.1\pm7.7$	54(200)6	$\delta_{4,2} \leftarrow (000$	$)6_{3,3}217840321863.3\pm7.5$
$19(200)5_{4,1} \leftarrow$	$(000)6_{3,4}21391$	$17346155.8\pm7.5$	55(200)4	$\mathbf{l}_{3,2} \leftarrow (000)$	$)4_{2,3}217884424690.3\pm7.5$
$20(200)6_{6,1} \leftarrow$	$(0\ 0\ 0)7_{5,2}213\ 93$	$30734812.6\pm7.5$	56(200)	$l_{0,4} \leftarrow (000)$	$3_{1,3}218048663367.3\pm7.5$
$21(200)6_{6,0} \leftarrow$	$(0\ 0\ 0)7_{5,3}213\ 93$	$36479008.5\pm7.7$	57(002)6	$\delta_{4,2} \leftarrow (000$	$)6_{5,1}218094331523.0\pm7.5$
$22(200)4_{0,4} \leftarrow$	$(0\ 0\ 0)4_{1,3}214\ 05$	$54871531.4\pm7.6$	58(200)5	$5_{4,1} \leftarrow (000)$	$5_{3,2}218119436295.0\pm7.7$
$23(200)5_{5,1} \leftarrow$	$(0\ 0\ 0)6_{4,2}214\ 32$	$27159420.1\pm16.$	859(200)4	$l_{1,4} \leftarrow (000)$	$3_{0,3}218281318913.5\pm7.9$
$24(200)5_{5,0} \leftarrow$	$(0\ 0\ 0)6_{4,3}214\ 35$	$59556842.4\pm7.5$	60(200)4	$l_{4,1} \leftarrow (000)$	$)4_{3,2}218\ 339\ 397\ 004.6\pm 8.1$
$25(200)4_{1,3} \leftarrow$	$(000)4_{2,2}21441$	$11346495.5\pm7.5$	61(200)6	$b_{2,5} \leftarrow (000)$	$)6_{1,6}218430303230.1\pm7.5$
$26(200)4_{4,1} \leftarrow$	$(000)_{53,2}21453$	$53163026.1\pm7.7$	62(200)	$p_{0,5} \leftarrow (000)$	$)4_{1,4}218551953037.4\pm7.5$
$27(200)2_{1,1} \leftarrow$	$(0\ 0\ 0)2_{2,0}214\ 56$	$52783143.0\pm7.6$	63(200)	$b_{5,1} \leftarrow (000)$	$)6_{4,2}218600010890.1\pm7.9$
$28(200)0_{0,0} \leftarrow$	$(000)1_{1,1}21478$	$33393303.8\pm4.9$	64(200)5	$p_{1,5} \leftarrow (000)$	$)4_{0,4}218664430158.9\pm7.6$
$29(200)2_{0,2} \leftarrow$	$(000)2_{1,1}2150$	$(5223293.4\pm7.5$	65(200)	$p_{5,0} \leftarrow (000)$	$)5_{4,1}218748027171.1 \pm 7.8$
$30(200)5_{2,3} \leftarrow$	$(000)6_{1,6}2154$	$12696377.5\pm7.5$	66(200)	$p_{5,1} \leftarrow (000)$	$)5_{4,2}218754067492.0 \pm 7.5$
$31(200)6_{1,6} \leftarrow$	$(000)5_{2,3}21541$	$18173888.3\pm7.7$	67(200)6	$b_{6,0} \leftarrow (000)$	$)6_{5,1}219063350040.7\pm7.6$
$32(200)5_{1,5} \leftarrow$	$(000)4_{2,2}21583$	$54572224.0 \pm 7.7$	68(200)	$b_{6,1} \leftarrow (000)$	$)6_{5,2}219064282101.9\pm7.6$
$33(200)4_{2,3} \leftarrow$	$(000)3_{3,0}21596$	$58528410.1 \pm 4.9$	69(200)	$p_{2,4} \leftarrow (000)$	$)4_{1,3}219622319934.8 \pm 7.6$
$34(200)4_{1,4} \leftarrow$	$(000)_{32,1}21602$	$21042437.9\pm4.9$	70(200)6	$p_{4,2} \leftarrow (000)$	$7_{1,7}220090855818.2 \pm 8.4$
$35(200)5_{2,4} \leftarrow$	$(000)4_{3,1}21637$	$(4204401.9\pm4.8)$	71(200)	$\mathbf{a}_{3,1} \leftarrow (000)$	$(4_{0,4}220252665298.9\pm7.6)$
$36(200)1_{1,0} \leftarrow$	$(000)1_{0,1}21639$	$96192933.5\pm5.3$			

In Fig. 3.4, characteristic Lamb-dip spectra are shown for four distinct lines probed with our NICE-OHMS spectrometer. For the weaker transitions, see panels (a) and (c), an ordinary single-dip absorption feature can be observed. These Lambdip profiles, which are typical in saturation spectroscopy [133], have a full width at half maximum (FWHM) of ~ 600 kHz. For the stronger transitions, connecting low-J energy levels, see panels (b) and (d), atypical, double-dip Lamb-dip profiles have been observed. The signature of strong saturated lines in NICE-OHMS consists of three independent Lamb-dip contributions when the carrier frequency is tuned to  $f_c = f$ as described in Sec. 3.2. The interference of the three Lamb-dips yields a notable double-dip profile if their widths are significantly different. This is the case for strong water transitions, as the high-power carrier induces much higher power broadening in comparison to the weaker sidebands, allowing the detection of double-dip signals.

During the course of the experimental campaign, the characteristic Lamb-dip reversal was detected for lines with Einstein-A coefficients > 0.1 s<sup>-1</sup>. Figure 3.5a exhibits a number of spectra for the  $(200)0_{0,0} \leftarrow (000)1_{1,1}$  transition, demonstrating the enhancement of Lamb-dip reversion at increasing sideband powers, without any shift in the line center. As Fig. 3.5b shows, the recorded signal can be fitted accurately by using a combination of two opposite sign fitting functions (*i.e.*, first derivatives of dispersive Lorentzians [131]). Note that these double-dip line profiles, presented for the first time, occur exclusively in NICE-OHMS spectra and cannot be observed with other cavity-enhanced methods using only one intracavity laser field.

#### Uncertainty quantification

The uncertainties of the transition frequencies displayed in Table 1 depend on several experimental effects arising mostly from homogeneous broadening mechanisms [133]. In this study, the following decomposition is applied to estimate the uncertainty of a measured frequency,  $\delta$ :

$$\delta = \sqrt{\delta_{\text{stat}}^2 + \delta_{\text{day}}^2 + \delta_{\text{pow}}^2 + \delta_{\text{pres}}^2 + \delta_{\text{instr}}^2}.$$
(3.1)



Figure 3.4: Spectral recordings of four Lamb-dip lines obtained in this study with their rovibrational assignments indicated. On panels (a)–(b) and (c)–(d), para- and ortho- $H_2^{16}O$  transitions are depicted, respectively. Note that the double-dip line profiles, depicted in panels (b) and (d), arise when the underlying transitions have larger Einstein-A coefficients.



Figure 3.5: Spectral recordings of NICE-OHMS signals for the  $(200)0_{0,0} \leftarrow (000)1_{1,1}$ line of  $H_2^{16}O$ . Panel (a) shows the spectral profile at various sideband (SB) powers [see the legend of panel (a)] and at fixed carrier power of 15 W. The dashed marker represents the position of the line center. Panel (b) illustrates the individual components of the double-dip spectra at a sideband power of 122 mW. The orange profile corresponds to the two coincident Lamb-dips, with a FWHM of 0.5 MHz, induced by the sideband fields. The blue profile of ordinary sign, with a FWHM of 2.4 MHz, is generated by the carrier. The combination of the orange and blue profiles leads to the recorded signal, denoted with a green curve.

The statistical uncertainty,  $\delta_{\text{stat}}$ , describes the reproducibility of the NICE-OHMS line positions.  $\delta_{\text{stat}}$  is approximated as the standard deviation of the transition frequencies derived from 3–4 scans. The day-to-day uncertainty,  $\delta_{\text{day}}$ , is related to  $\delta_{\text{stat}}$ , specifying the *long-term* reproducibility of the line centers and the stability of the NICE-OHMS setup. The spectra of some transitions were repeatedly recorded on 2–3 different days, yielding an average deviation of 2.5 kHz for these lines. This average deviation is used as  $\delta_{\text{day}}$  for each line probed. The uncertainty due to power-induced shifts,  $\delta_{\text{pow}}$ , was diminishing, *i.e.*, below 1 kHz, during the experiments. Therefore, a robust estimate of  $\delta_{\text{pow}} = 0.5$  kHz is applied for all transitions.

If the vapor pressure is not negligible in the sample cell, the pressure-shift uncertainty,  $\delta_{\text{pres}}$ , is significant. For lines  $(200)0_{0,0} \leftarrow (000)1_{1,1}$  and  $(200)4_{1,4} \leftarrow (000)3_{2,1}$ , the pressure-shift effects were explicitly considered by recording spectra over a range of pressure values and extrapolating the transition frequencies to zero pressure and fitting a linear model,  $f = Cp + f_{\text{vac}}$ , where f and  $f_{\text{vac}}$  are the transition frequencies at pressure p and in vacuum, respectively, and C denotes the pressure-shift coefficient (slope). The C coefficients determined in this study are +17.3 kHz Pa<sup>-1</sup> [(200)0\_{0,0} \leftarrow (000)1\_{1,1}] and +4.5 kHz Pa<sup>-1</sup> [(200)4\_{1,4} \leftarrow (000)3\_{2,1}]. Since the C values found in this study and in Ref. [129] fall into the range of [-21, +22] kHz Pa<sup>-1</sup>,  $\delta_{\text{pres}} = C_{\text{eff}}p$  is set for each new line, where  $C_{\text{eff}} = 20$ kHz Pa<sup>-1</sup>, and p is the measurement pressure for the particular line. Since the pressure range applied is 0.01–0.2 Pa,  $\delta_{\text{pres}}$  corresponds to 0.2–4 kHz.

The  $\delta_{\text{instr}}$  factor is included in the uncertainty budget to describe the small frequency shifts due to an unbalanced Pound–Drever–Hall 'lock' causing slight

asymmetries in the line profiles leading to fitting errors [134]. For nine selected transitions, this unbalance in the lock was corrected, revealing an average shift of  $\approx 7$  kHz. For these nine lines,  $\delta_{instr} = 4$  kHz was chosen, while for all the other transitions  $\delta_{instr} = 7$  kHz was adopted. For all the lines recorded in the present study, the values of the five uncertainty factors are listed in the Supplementary Material.

As an independent confirmation of the frequency uncertainties and the rovibrational assignments, all but one of the new NICE-OHMS lines were enclosed into cycles of different lengths. The only exception is the  $(200)0_{0,0} \leftarrow (000)1_{1,1}$  line, whose upper state is not attainable from another pure rotational level through dipole-allowed transitions. To accelerate the experimental part of the cycle-based verification, the lines of the intermediate dataset were used to refine the initial positions via the  $\Lambda$ -correction scheme [130]. Furthermore, only two scans were performed instead of the usual four for those lines whose upper states were already determined accurately from other transitions. A subset of cycles, which helped to recognize an accidental mistake during the experiments, is plotted in Fig. 3.6, while a collection of basic cycles [77, 135], whose discrepancy is typically 10 kHz or better for the final dataset, are placed in the Supplementary Material.



Figure 3.6: Typical short cycles formed during the SNAPS analysis. For the definitions of the color codes and the elements of this figure, see the captions to Figs. 3.2 and 3.3. The values on the arrows are transition frequencies in kHz, with the uncertainties of the last few digits given in parentheses. Combining any pairs of the three green lines with the blue transitions, three cycles of length 4, 6, and 8 are obtained. The brown frequency contains an additional error of +113.8 kHz, which was due to a miscalibration made during the measurement campaign. Using this erroneous frequency, the discrepancy [129] of the 6-membered cycle became an unacceptably large value of 119.4(121) kHz. Assuming that the blue transitions are correct, the green transition frequency was measured to decide which of the other two green lines causes the large discrepancy. Using the green frequency, the discrepancies of the 4- and 8-membered cycle suggested that the brown frequency missing from this cycle should be responsible for the significant discrepancies of the other two cycles. After remeasuring the brown frequency, a new line center of 218 664 430 158.9 kHz was obtained. With this new line center, the discrepancies of the 4- and 6-membered cycles have been reduced to fairly small values, 2.3(126) and 5.6(121) kHz, respectively.



Figure 3.7: Path from the  $(200)0_{0,0}$  (para) state to the  $(200)1_{0,1}$  (ortho) state. The color codes and the elements of the figure are explained in the captions to Figs. 3.2 and 3.3, except the red dash-dotted line, which symbolizes the calculated energy difference between the lowest ortho and para states, taken from Ref. [129]. The values on the arrows are transition wavenumbers in cm<sup>-1</sup>, with the uncertainties of the last few digits given in parentheses. Utilizing the Ritz principle in a successive form and exploiting the law of uncertainty propagation (see also Ref. [129]), the  $(200)1_{0,1} - (200)0_{0,0}$  energy difference is estimated to be 23.040 646 42(39) cm<sup>-1</sup>. Note that from the subpaths of this path one can derive absolute energies for all the rovibrational states displayed in the figure.

## 3.4. SNAPS-based results

# Highly accurate relative energies

From the connected sets of the kHz-accuracy ortho and para transitions displayed in Figs. 3.2 and 3.3, ultraprecise relative energies can be determined for the underlying ortho and para states, respectively. The relative energy of a particular ortho/para state is estimated here by constructing a lowest-uncertainty path from  $(000)1_{0,1}/(000)0_{0,0}$  to the desired state and employing the Ritz principle in a successive way [129]. If the ortho and para components are linked with an artificial transition  $(000)1_{0,1} \leftarrow (000)0_{0,0}$ , whose wavenumber is set to 23.79436122(25) cm<sup>-1</sup> [129], then one can also form paths from para states to their ortho siblings.

As an example, a path from  $(200)0_{0,0}$  to  $(200)1_{0,1}$  is presented in Fig. 3.7. This path is capable of providing energy differences for any pair of the underlying states with definitive uncertainties. By taking the subpath from  $(000)0_{0,0}$  to  $(200)0_{0,0}$ , the  $(200)0_{0,0}$  energy, which is actually the VBO of the (200) vibrational parent, can be calculated as 7201.53995061(29) cm<sup>-1</sup>. This datum is nearly 1000 times more accurate than the W2020 estimate of 7201.54000(45) cm<sup>-1</sup> [105].

Based on the lines of Fig. 3.7, the energy difference of the ortho  $(200)1_{0,1}$  and para  $(200)0_{0,0}$  states,  $\epsilon^{(200)}$ , is 23.040 646 42(39) cm<sup>-1</sup>, which is much lower than its counterpart in the ground vibrational state,  $\epsilon^{(000)} = 23.79436122(25)$  cm<sup>-1</sup> [129]. To understand the change  $\Delta \epsilon = \epsilon^{(000)} - \epsilon^{(200)}$ , recall that  $\epsilon^{(v_1 v_2 v_3)}$  is the 'rotational energy' of the  $(v_1 v_2 v_3)1_{0,1}$  level within the normal-mode and rigidrotor approximations. Then,  $\epsilon^{(v_1 v_2 v_3)}$  can be given as the sum of the two smallest effective rotational constants:  $\epsilon^{(v_1 v_2 v_3)} \approx B^{(v_1 v_2 v_3)} + C^{(v_1 v_2 v_3)}$ . In the case of H<sub>2</sub><sup>16</sup>O,  $\begin{array}{l} \Delta\epsilon\approx B^{(0\,0\,0)}-B^{(2\,0\,0)}+C^{(0\,0\,0)}-C^{(2\,0\,0)}\approx 14.51-14.17+9.29-8.95=0.68~{\rm cm}^{-1},\\ {\rm where the effective rotational constants are taken from Ref. [136]. This simple estimates in good agreement with the SNAPS-based determination of 0.75371480(29) <math display="inline">{\rm cm}^{-1}. \end{array}$ 

Relying on the lines of Figs. 3.2 and 3.3, ultraprecise relative energies are derived, via the SNAPS scheme, for 192 energy levels. Of these states, 59 lie on the (200) band and form a complete set up to J = 6. The relative energies of the 59 states, among which 32 have not been investigated in previous Lamb-dip studies [71, 129], are displayed, with individual uncertainties, in Table 2. The complete list of the 192 relative rovibrational energies is given in the Supplementary Material.

Assignment(para)	Rel. Energy $(para)/cm^{-1}$	Assignment(ortho)	Rel. Energy $(ortho)/cm^{-1}$
$(200)0_{0,0}$	7201.53995061(29)	$(200)1_{0,1}$	7200.786235810(61)
$(2\ 0\ 0)1_{1,1}$	7236.80750451(14)	$(200)1_{1,0}$	7218.20003002(18)
$(2\ 0\ 0)2_{0,2}$	7269.31316664(29)	$(200)2_{1,2}$	7253.893683916(53)
$(2\ 0\ 0)2_{1,1}$	7293.20798308(29)	$(200)2_{2,1}$	7 305.625 797 494(71)
$(2\ 0\ 0)2_{2,0}$	7331.62273401(16)	$(200)3_{0,3}$	7309.75850566(24)
$(2\ 0\ 0)3_{1,3}$	7338.25106968(14)	$(200)3_{1,2}$	7345.17909462(27)
$(2\ 0\ 0)3_{2,2}$	7398.40716108(23)	$(200)3_{2,1}$	7381.44363884(15)
$(2\ 0\ 0)3_{3,1}$	7472.95224315(18)	$(200)3_{3,0}$	7449.26681703(12)
$(2\ 0\ 0)4_{0,4}$	7415.59899771(29)	$(200)4_{1,4}$	7394.04836537(27)
$(200)4_{1,3}$	7467.77221388(30)	$(200)4_{2,3}$	7465.55889585(23)
$(200)4_{2,2}$	7505.81243506(33)	$(200)4_{3,2}$	7544.41002417(30)
$(2\ 0\ 0)4_{3,1}$	7568.89086382(30)	$(200)4_{4,1}$	7641.74087077(32)
$(200)4_{4,0}$	7665.57141588(25)	$(200)5_{0,5}$	7491.15247461(33)
$(2\ 0\ 0)5_{1,5}$	7515.91304208(30)	$(200)5_{1,4}$	7563.59182176(19)
$(200)5_{2,4}$	7601.30908677(34)	$(200)5_{2,3}$	7608.85211103(33)
$(2\ 0\ 0)5_{3,3}$	7688.64936255(35)	$(200)5_{3,2}$	7666.63979709(26)
$(2\ 0\ 0)5_{4,2}$	7784.28307110(41)	$(200)5_{4,1}$	7760.69894239(32)
$(2\ 0\ 0)5_{5,1}$	7906.96469276(42)	$(200)5_{5,0}$	7883.19559200(38)
$(200)6_{0,6}$	7631.70585896(41)	$(200)6_{1,6}$	7608.29313870(33)
$(2\ 0\ 0)6_{1,5}$	7725.44885815(25)	$(200)6_{2,5}$	7709.50864049(32)
$(200)6_{2,4}$	7784.02966286(27)	$(200)6_{3,4}$	7797.89506440(28)
$(2\ 0\ 0)6_{3,3}$	7838.91097588(36)	$(200)6_{4,3}$	7903.19993741(32)
$(200)6_{4,2}$	7927.91990288(40)	$(200)6_{5,2}$	8 025.531 218 47(29)
$(2\ 0\ 0)6_{5,1}$	8049.49167620(44)	$(200)6_{6,1}$	8172.00229382(45)
$(200)6_{6,0}$	8195.79946638(41)	$(200)7_{2,5}$	7 933.874 344 22(29)
$(2\ 0\ 0)7_{3,5}$	7985.28524726(37)	$(200)7_{6,1}$	8 338.642 985 56(38)
$(200)7_{6,2}$	8362.40069771(34)	$(200)8_{6,3}$	8 528.914 465 81(40)
$(200)7_{7,1}$	8530.40686109(40)	$(200)9_{3,6}$	8 417.787 730 38(34)
$(200)8_{0,8}$	7917.72240604(29)		
$(2\ 0\ 0)8_{3,5}$	8 216.203 568 96 (39)		
$(200)9_{4,6}$	8 482.466 747 19(37)		

Table 2: Ultraprecise relative energies in the (200) vibrational band of H<sub>2</sub><sup>16</sup>O.<sup>a</sup>

<sup>a</sup> The relative energy is zero for the lowest *ortho* and *para* states. The uncertainties of the last few digits, related to 68 % confidence level, are displayed in parentheses. The boldface entries are results of this study, all the other values are taken from Ref. [129]. For *ortho*-H<sub>2</sub><sup>16</sup>O, the formulas  $E = e + E_0$  and  $u_E = \sqrt{u_e^2 + u_{E_0}^2}$  can be used to derive absolute energies, where  $E_0 = 23.79436122 \text{ cm}^{-1}$  is the absolute energy of the lowest *ortho* state [129] with an uncertainty of  $u_{E_0} = 2.5 \times 10^{-7} \text{ cm}^{-1}$ , and *e* and *E* are the relative and absolute energies of a given state with uncertainties  $u_e$  and  $u_E$ , respectively.

# Ultrahigh-accuracy predicted line list

Utilizing the relative SNAPS energies deduced from the lines of Figs. 3.2 and 3.3, an ultraprecise predicted line list, satisfying one-photon, electric-dipole selection rules, has been compiled (for further details, see Supplementary Note 6 of Ref. [129]). In the line list, the SNAPS wavenumbers, which are typically 100–1000 times more accurate than the previous line positions, are augmented with intensities determined from the Einstein-A coefficients of Ref. [95]. The complete

line list, corresponding to the ranges of 0-1005 and 6200-8110 cm<sup>-1</sup>, is available in the Supplementary Material (see also Fig. 3.8).

Our extended SNAPS-predicted line list contain 1743 transitions, including 524 extra entries in comparison to that of Ref. [129]. Of the 1743 lines, 983 are characterized with an intensity larger than  $1 \times 10^{-26}$  cm molecule<sup>-1</sup>. These 983 entries, out of which 207 are results of the present study, may serve as calibration standards for high-resolution studies (*e.g.*, in atmospheric spectroscopy).

The predicted line list contains 21 closely-spaced ortho-para doublets with intensities of at least  $1 \times 10^{-26}$  cm molecule<sup>-1</sup> for the more intense member of each line pair. The separation of such a doublet is smaller than the Doppler FWHM at room temperature, that is < 0.02 cm<sup>-1</sup> in the 6200–8110 cm<sup>-1</sup> region. Resolving these line pairs in room-temperature Doppler-broadened measurements is difficult, if possible at all.



Figure 3.8: Illustration of the ultrahigh-accuracy predicted line list of  $H_2^{16}O$  assembled during this study. The wavenumbers are estimated from the SNAPS-based relative energies, while the one-photon, dipole-allowed intensities are deduced from the Einstein-A coefficients of Ref. [95]. The green diamonds designate the results of this study, while the blue squares represent estimates of Ref. [129]. Although the direct experimental lines used in the derivation of the relative energies are restricted to the regions 0–20 and 7000–7350 cm<sup>-1</sup>, the predicted transitions extend between 0–1005 and 6200–8110 cm<sup>-1</sup>. The points located in the upper left, lower left, and upper right quadrants correspond to P' - P'' = 0 - 0, 4 - 4, and 4 - 0, transitions, respectively, where P' and P'' are the polyad numbers of the upper and lower states, respectively.

#### 3.5. Conclusions

A saturation spectroscopic technique, the Noise-Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS), is employed to accurately measure rovibrational lines of  $H_2^{16}O$  in the 1.4 mum wavelength region. The observed lines are selected based on the scheme called spectroscopic-network-assisted precision spectroscopy (SNAPS) to form a complete set of ultraprecise relative energies within the  $(v_1 v_2 v_3) = (200)$  band of  $H_2^{16}O$  up to  $J \leq 6$ , where J is the overall rotational quantum number and  $v_1$ ,  $v_2$ , and  $v_3$  are quantum numbers associated with the symmetric stretch, bend, and antisymmetric stretch normal modes, respectively. The typical accuracy achieved for the relative energies is  $3 \times 10^{-7}$  cm<sup>-1</sup>. Since most previous determinations of the (200) relative energies were obtained from Doppler-limited spectroscopy, the present values represent an improvement in accuracy of 2-3 orders of magnitude.

Unlike in our previous studies [129, 130], focusing on the ground vibrational state of  $H_2^{16}O$  and  $H_2^{18}O$ , no fitting of an effective Hamiltonian (EH) was attempted to the ultraprecise relative energies of the (200) band, part of the P = 4 polyad, where  $P = 2v_1 + v_2 + 2v_3$  is the polyad number. As the published EH fits [137, 138, 139] prove, these models of strongly interacting states are unable to reproduce the accuracy of the Doppler-broadened P = 4 dataset, which is a few times  $10^{-3}$  cm<sup>-1</sup>, not even after invoking a large number of parameters. The accuracy issue would be even more pronounced for the ultraprecise measurements of the present study.

A curiosity related to the NICE-OHMS measurements performed is that for relatively strong, low-J transitions an interesting signal inversion in their Lamb-dip spectra was observed. This phenomenon, reported for the first time, can be understood as the interference of strong saturation signals from the carrier frequency, leading to broadening of the generic Lamb dip, and the saturation signals originating from the much weaker sidebands, typically used in NICE-OHMS, one of which is out-of-phase leading to an inverted sign for the signal.

The 71 newly measured lines, forming a carefully designed spectroscopic network with the ultraprecise transitions of previous papers [129, 71, 60, 66, 68], allow a highly accurate determination of the  $(200)1_{0,1}$ – $(200)0_{0,0}$  energy difference, which is 23.040 646 421(39) cm<sup>-1</sup>. A similarly accurate estimate, 7201.539 950 61(29) cm<sup>-1</sup>, is obtained for the vibrational band origin (VBO) of the (200) state, providing the most accurate VBO of of H<sub>2</sub><sup>16</sup>O. In comparison, the best previous estimate for this VBO, that in the W2020 dataset [104], is 7 201.540 00(45) cm<sup>-1</sup>.

The empirical line list based upon the relative energies determined in this and a previous NICE-OHMS [129] study of  $H_2^{16}O$  consists of 1743 transitions. Out of the 1743 transitions, 983 are characterized with electric-dipole-allowed intensities larger than  $1 \times 10^{-26}$  cm molecule<sup>-1</sup>; thus, they are relevant to a number of applications, including atmospheric modeling.

# 3.6. Acknowledgements

The research described has received funding from LASERLAB-EUROPE (Grant No. 654148), a European Union's Horizon 2020 research and innovation programme. The work performed in Budapest received support from NKFIH (grant no. K138233). WU acknowledges the European Research Council for an ERC Advanced Grant (grant no. 670168). Further support was obtained from a NWO-FOM program (16MYSTP) and from the NWO Dutch Astrochemistry Network.

# Chapter 4

# Network-based design of near-infrared Lamb-dip experiments and the determination of pure rotational energies of $H_2^{18}O$ at kHz accuracy

#### Abstract

Taking advantage of the extreme absolute accuracy, sensitivity, and resolution of noise-immunecavity-enhanced optical-heterodyne-molecular spectroscopy (NICE-OHMS), a variant of frequencycomb-assisted Lamb-dip saturation-spectroscopy techniques, the rotational quantum-level structure of both nuclear-spin isomers of  $H_2$ <sup>18</sup>O is established with an average accuracy of 2.5 kHz. Altogether 195 carefully selected rovibrational transitions are probed. The ultrahigh sensitivity of NICE-OHMS permits the observation of lines with room-temperature absorption intensities as low as  $10^{-27}$  cm molecule<sup>-1</sup>, while the superb resolution enables the detection of a doublet with a separation of only 286(17) kHz. While the NICE-OHMS experiments are performed in the near-infrared window of 7000–7350 cm<sup>-1</sup>, the lines observed allow the determination of all the pure rotational energies of  $H_2^{18}O$  corresponding to J values up to 8, where J is the total rotational quantum number. Both network and quantum theory have been employed to facilitate the measurement campaign and the full exploitation of the lines resolved. For example, to minimize the experimental effort, the transitions targeted for observation were selected via the Spectroscopic-Network-Assisted Precision Spectroscopy (SNAPS) scheme, built upon the extended Ritz principle, the theory of spectroscopic networks, and an underlying dataset of quantum chemical origin. To ensure the overall connection of the ultraprecise rovibrational lines for both nuclearspin isomers of  $H_2^{18}O$ , the NICE-OHMS transitions are augmented with six accurate microwave lines, taken from the literature. To produce absolute ortho- $H_2^{18}O$  energies, the lowest ortho energy is determined to be 23.75490461(19) cm<sup>-1</sup>. A reference, benchmark-quality line list of 1546 transitions, deduced from the ultrahigh-accuracy energy values determined in this study, provides calibration standards for future high-resolution spectroscopic experiments between 0-1250and 5900–8380 cm<sup>-1</sup>. <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: Network-based design of near-infrared Lamb-dip experiments and the determination of pure rotational energies of H<sub>2</sub><sup>18</sup>O at kHz accuracy, M.L. Diouf, R. Tóbiás, I. Simkó, F.M.J. Cozijn, E.J. Salumbides, W. Ubachs, A G.Császár, J. Phys. Chem. Ref. Data **50**, 023106 (2021).

#### 4.1. Introduction

Detailed analysis of the spectra of water vapor, the most important greenhouse gas in the atmosphere of the Earth, has been at the center of (ultra)high-resolution molecular spectroscopy for many decades. [99, 140, 141, 51, 75, 142, 104, 105] During this period, ever-improving techniques have been devised to resolve spectral features in diverse environments and determine the line parameters (e.q., positions, intensities, and shapes, as well as cross sections and collisional parameters) with rapidly increasing accuracy and coverage. These spectroscopic results, related mostly to the electronic ground state of water, have been collated into popular spectroscopic databases, such as HITRAN (HIgh-resolution TRANsmission molecular absorption database).[30] HITRAN2016, for example, contains more than 300 000 water lines, nearly 40 000 of which correspond to the second most abundant isotopologue of water,  $H_2^{18}O$ , with a natural terrestrial abundance of 0.2 %. These water datasets find widespread use among scientists and engineers, including modelers of atmospheric chemistry, combustion systems, exoplanets, cool stars, etc. In cases when lines of the main isotopologue are too strong, lines of less-abundant isotopologues are used to trace the chemical environment, e.q., in outer space, while in radio astronomy,  $H_2^{18}O$  transitions are utilized to assess the isotopic ratios of the interstellar medium.[143]

Several microwave, [144, 62, 66] terahertz, [145, 146, 147, 148] as well as far- and mid-infrared [149, 150, 88, 151, 152, 153] studies have been conducted to observe purely rotational transitions of  $H_2^{18}O$ . Naturally, an even larger number of papers have been dedicated to record vibration-changing lines involving high-lying vibrational states, [154, 119, 155, 156, 157, 158, 159, 160] whereby the lower quantum states of the transitions are mostly determined by the pure rotational lines. The experimental results reported in articles dealing with infrared transitions are typically based on linear absorption, producing Doppler-broadened lineshapes with a line-position uncertainty of 3–300 MHz.

A new scientific era arrived when experimental protocols employing optical frequency-comb (OFC) lasers were introduced.[161, 162] The OFC is linked to the spectroscopy laser so as to interrogate the spectra of gas-phase molecules with sub-MHz accuracy.[72, 163, 164] Despite the promise of these new techniques, up to now only two articles[165, 166] dealing with sub-Doppler laser spectroscopy of  $H_2^{18}O$  have been published, reporting 18 lines with 30 kHz accuracy.

OFCs are often coupled with cavity enhancement, [167, 168] this is the case for the noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS). [97, 98, 31, 28, 169] In the previous sub-Doppler studies of  $H_2^{18}O$ mentioned, [165, 166] Lamb dips calibrated with 30 kHz accuracy have been recorded. The narrow line shapes result in an increase of the accuracy of the line-center determination, generally by a factor of a thousand or so, reducing the experimental uncertainty from the MHz to the kHz regime.

Some 10 years ago, after collecting all the experimental lines from the literature, an IUPAC-sponsored effort resulted in lists of observed transitions and empirical energy levels for  $H_2^{18}O.[140, 141]$  These large datasets have recently been updated, significantly extended, and integrated into the W2020 database.[104, 105] The empirical energy values of the original IUPAC dataset served as a basis for the

development of first-principles line lists, [170, 102] with accurate Einstein-A coefficients and line intensities. Together with the line positions derived from W2020 energy levels, the latter data were employed during this study to guide the selection of lines for measurement.

In this study, the NICE-OHMS intracavity absorption method is applied, in combination with OFC-linked laser spectroscopy, to record saturated spectra of the  $H_2^{18}O$  species. The Lamb-dip measurements are conducted in the near infrared in a systematic fashion; the lines chosen for measurement have been selected *via* the Spectroscopic-Network-Assisted Precision Spectroscopy (SNAPS) scheme,[129] with the aim to determine ultraprecise pure rotational energies within the ground vibrational state of  $H_2^{18}O$ . Determining a large number of pure rotational energies is a significant achievement since these quantum states are all hubs in the spectroscopic network (SN) of  $H_2^{18}O$ ;[45, 43, 171, 46] thus, they are the lower states of a huge number of transitions measured in absorption by a number of different experimental techniques. As a useful by-product, energy levels with high-lying vibrational parents are also obtained. Based on the SNAPS energies, a benchmark-quality reference line list is constructed, providing frequency standards for a number of future high-resolution spectroscopic measurements.

# 4.2. Methods and Data Treatment

## NICE-OHMS spectroscopy

A NICE-OHMS apparatus, [28, 129] shown schematically in Fig. 4.1, has been deployed to detect saturated absorption lines of  $H_2^{18}O$  in the near-infrared region. In our setup, an infrared diode laser functioning at 1.4 mum is used along with a high-finesse cavity. This laser is modulated at 305 MHz, equivalent to the free spectral range (FSR) of the cavity, for generating the side-band signals, and at 20 MHz for the cavity-lock via a Pound–Drever–Hall (PDH) stabilization scheme. Thanks to the highly reflective mirrors, the intracavity power can be increased up to 150 W. This high upper power limit enabled the saturation of several rovibrational transitions for  $H_2^{18}O$ , inducing extremely narrow Lamb-dip profiles. In addition, one of the mirrors is dithered at a low frequency of 405 Hz. The spectroscopic signal is treated and demodulated by a powerful lock-in system (Zurich Instruments; HF2LI). A high-stability OFC, disciplined by a cesium atomic clock, is also incorporated in the NICE-OHMS spectrometer to stabilize the infrared laser and to obtain sub-kHz accuracy on the frequency axis.

Due to the long-term stabilization of the cavity and the demodulated signal, NICE-OHMS is a highly sensitive method, while its accuracy is warranted by its lock to the OFC. The Lamb-dip signals exhibit very narrow profiles with widths of 400–800 kHz (full width at half maximum). The linewidth is governed by power and pressure broadening, as well as by the transit time of the molecules across the laser beam.

The individual line centers are somewhat shifted by the laser power and the vapor pressure within the water cell. The vapor pressure is controlled by injecting, using an inlet valve, an enriched  $H_2^{18}O$  sample (Sigma Aldrich; 97% <sup>18</sup>O isotopic purity). To overcome the effect of outgassing from the cavity walls, the absorption cell is directly linked to a vacuum pump removing any excess of  $H_2^{18}O$  molecules.



Figure 4.1: Schematic layout of the NICE-OHMS setup.

Hence, the spectroscopic recordings are performed under slow but steady gas flows, at pressures in the range of 0.03–1.0 Pa, measured by a capacitance pressure gauge. Collisional shifts are also studied experimentally, facilitating an extrapolation to zero pressure.

Limited by the operation range of the diode laser, the reflectivity of the cavity mirrors, and the transmission of some optical elements, our NICE-OHMS setup works in the wavenumber interval of 7000–7350 cm<sup>-1</sup>. By varying the intracavity power, transitions with  $A_{\rm E} = 10^{-4} - 10^2 \,{\rm s}^{-1}$  and  $S = 10^{-27} - 10^{-20} \,{\rm cm}$  molecule<sup>-1</sup> can be resolved in saturation with sufficient signal-to-noise ratio (SNR) and negligible power broadening, where  $A_{\rm E}$  is the Einstein-A coefficient, while S means the line intensity without abundance scaling. These constraints on the three quantities, called primary line parameters in the remainder of this paper, dictate which lines can effectively be probed and included in the SNAPS scheme.

# The SNAPS scheme

The near-infrared transitions of  $H_2^{18}O$  observable with our NICE-OHMS setup were selected *via* the SNAPS procedure [129] to maximize the accurate spectroscopic information that can be extracted from the newly probed lines. While SNAPS was discussed in detail before [129], it is briefly outlined here for readability and completeness.

During the SNAPS design, one should (a) determine paths and cycles (see Fig. 4.2) involving accurate literature transitions as well as target lines in the accessible range of the primary line parameters, (b) proceed with the recording of the targeted transitions selected based on the knowledge of these paths and cycles, and (c) evaluate the paths and cycles of the new and literature transitions to estimate accurate energy differences and their uncertainties as well as to verify the internal accuracy of the experiments. Despite the fact that SNAPS is built upon the use of network theory, it is a black-box-type strategy, and its output requires only the understanding of Fig. 4.2 (for interested readers a concise summary of network theory related to high-resolution spectroscopy is given as Supplementary Note 1 of Ref. [129]).



Figure 4.2: Traditional and generalized connection schemes characterizing spectroscopic measurements. Nodes and edges of the connection schemes (a)-(e) are quantum states with energies  $E_i$  and transitions with wavenumbers  $\sigma_i$ , respectively. Eq. (1a) corresponds to the definition of the Ritz principle. Panels (b) and (c) are connection schemes widely utilized by spectroscopists, usually referred to as combination differences. In an analogous way, extended connections can also be defined, involving not two but more transitions. Panel (d) illustrates a path (a series of connected, unrepeated lines and states), while panel (e) exhibits a cycle (a sequence of linked transitions and energy levels, where each energy level is connected to two neighboring states). The connection schemes mentioned, linear,  $\Lambda$ , and V, are themselves examples of paths. Employing the Ritz principle in a successive fashion, the energy differences between any node pairs of a path can be determined straightforwardly. If the starting point of the path is the lowest-energy level attainable from the ending point through paths, then  $E_8 - E_1$  is defined as the relative energy of the ending point. In the case that the starting point is the rovibrational ground state of the species under study (*i.e.*,  $E_1 = 0$ ),  $E_8 - E_1$  gives an estimate for the absolute energy of the ending point. Knowledge of the  $u(\sigma_i)$  wavenumber uncertainties yields the uncertainty of the  $E_8 - E_1$  difference, expressed from the law of uncertainty propagation (as long as measurement errors are uncorrelated and they have zero expected values). Cycles demonstrate the internal accuracy of their transitions: in favorable cases,  $D \leq t_{\rm crit} u(D)$ , where D is the discrepancy (the absolute signed sum of the observed wavenumbers) of the cycle with its u(D) uncertainty, and  $t_{\rm crit} = 2$  assuring a 95 % confidence level.



Figure 4.3: Graphical representation of all the precision lines recorded for  $para-H_2^{18}O$ . The rovibrational eigenstates are characterized with the ordered sextuple  $(v_1 v_2 v_3) J_{K_q,K_c}$ , where  $(v_1 v_2 v_3)$  is composed of the vibrational normal-mode quantum numbers according to the Mulliken convention, [73] while  $J_{K_a,K_c}$  are the standard asymmetric-top rotational quantum numbers [74] Lines with lower states having even and odd  $K_c$  values, forming two subcomponents  $(p^+ \text{ and } p^-, \text{ respectively})$  are drawn separately. Within the subcomponents, the para energy levels, those with even  $v_3 + K_a + K_c$  values and symbolized with squares, are arranged palindromically in increasing (upper half) and decreasing (lower half) energy order of their vibrational parents and are denoted with distinct colors. The  $J_{K_a,K_c}$  rotational assignment is marked individually for each state, while the  $(v_1 v_2 v_3)$  vibrational quantum numbers[73] are specified in the left-side color legend. The six vibrational bands lie in the P = 0 [(000)] and the P = 4 [(120), (021), (200), (101), and (002)] polyads, where  $P = 2v_1 + v_2 + 2v_3$  is the polyad number. The blue arrows indicate the outcome of the present NICE-OHMS measurements, while those with dashed orange arrows are taken from Ref. [66]. Frequencies of the two literature lines are as follows: 203 407 498(4) kHz  $[(000)3_{1,3} \leftarrow (000)2_{2,0}]$  and 322 465 122(2) kHz  $[(000)5_{1.5} \leftarrow (000)4_{2.2}]$ . The non-starred arrows specify lowest-uncertainty unique paths from  $(000)0_{0,0}$  to all the other energy levels of this figure. Each starred transition defines a cycle with the unique path of non-starred lines between its lower and upper states. Throughout the paper, the rovibrational transitions are designated with  $(v'_1 v'_2 v'_3) J'_{K'_a,K'_c} \leftarrow (v''_1 v''_2 v''_3) J''_{K''_a,K''_c}$ where ' and " refer to the upper and lower states, respectively.



Figure 4.4: Graphical representation of all the precision lines recorded for ortho-H<sub>2</sub><sup>18</sup>O. The arrangement of the energy levels and the lines, as well as the formalism employed, is analogous to that of Fig. 4.3, with the exception that the ortho levels, characterized by odd  $v_3+K_a+K_c$  values, are denoted with circles rather than squares. The NICE-OHMS transitions are concentrated in two subcomponents ( $o^+$  and  $o^-$ , whose lower states are identified with even and odd  $K_c$  values, respectively), which are linked with the following transitions:[66] 253 913 309(7) kHz [(000)10<sub>2</sub>,9  $\leftarrow$  (000)9<sub>3,6</sub>], 390 607 776(4) kHz [(000)4<sub>1,4</sub>  $\leftarrow$  (000)3<sub>2,1</sub>], 489 054 250(4) kHz [(000)4<sub>2,3</sub>  $\leftarrow$  (000)3<sub>3,0</sub>], and 547 676 470(15) kHz [(000)1<sub>1,0</sub>  $\leftarrow$  (000)1<sub>0,1</sub>]. The non-starred lines provide lowest-uncertainty unique paths from (000)1<sub>0,1</sub> to all the other energy levels of this figure. Moreover, every starred arrow forms a cycle with the unique path of non-starred lines between its lower and upper levels.

As to the primary line parameters of the target transitions, (a) the approximate wavenumbers were calculated from the W2020 energies of Ref. [105] with an uncertainty of  $10^{-4} - 10^{-2}$  cm<sup>-1</sup> in the 7000–7350 cm<sup>-1</sup> window, (b) the Einstein-A coefficients,  $A_{\rm E}$ , were adopted from Ref. [102], and (c) the line intensities were calculated according to Eq. (3) of Ref. [95]. Even though the accuracy of the W2020 positions were sufficient to detect the majority of the target transitions, the very weak lines (with  $S < 1 \times 10^{-25}$  cm molecule<sup>-1</sup> or with  $A_{\rm E} < 1 \times 10^{-3}$  s<sup>-1</sup>) required much smaller uncertainties for the initial wavenumbers to avoid extreme scanning times.

A solution found to the refinement of the starting wavenumbers involves building a  $\Lambda$ -shape connection (see Fig. 4.2), whereby one of the lines is easily observable (has a large intensity), while the other is the weak transition. After recording the stronger signal ( $\sigma_1$ ) and employing accurate lower-state energies ( $E_1$  and  $E_3$ , see Fig. 4.2), an improved initial position ( $\sigma_2$ ) can be obtained for the weaker transition via Eq. (2b) of Fig. 4.2. (High-accuracy lower-state energies can be extracted, e.g., from an effective Hamiltonian (EH) fit to the intermediate transition dataset.) Utilizing the (two or three orders of magnitude) more precise  $\sigma_2$  position, the weaker line can be detected within reasonable time limits. This kind of wavenumber adjustment is called here  $\Lambda$ -correction. Typical short cycles and paths formed during the SNAPS analysis of H<sub>2</sub><sup>18</sup>O are depicted in Fig. 4.5, the interested reader should consult this figure to gain further insight into the utility of elements of spectroscopic network theory to high-resolution spectroscopy.

Relying on the SNAPS approach extended with the  $\Lambda$ -correction scheme, and utilizing six accurate pure rotational transitions from the literature,[66] 195 near-infrared lines of H<sub>2</sub><sup>18</sup>O were selected and then detected *via* NICE-OHMS measurements. Graphical representations of these accurate H<sub>2</sub><sup>18</sup>O transitions, old and new, are displayed in Figs. 4.3 and 4.4 for *para-* and *ortho*-H<sub>2</sub><sup>18</sup>O, respectively. All the newly measured lines, with their assignments, are listed in Table 1.

#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz
1	$(200)3_{2,2} \leftarrow (000)4_{3,1}$	$209868445082.8\pm2.6$	97	$(200)9_{6,4} \leftarrow (000)8_{7,1}$	$214741979846.0\pm7.5$
2	$(0\ 2\ 1)7_{5,3} \leftarrow (0\ 0\ 0)8_{3,6}$	$209882452997.8\pm2.2$	97	$(0\ 2\ 1)6_{5,2} \leftarrow (0\ 0\ 0)6_{3,3}$	$215084984856.9\pm1.8$
3	$(200)6_{1,5} \leftarrow (000)7_{2,6}$	$209899496368.1\pm1.7$	101	$(101)1_{0,1} \leftarrow (000)2_{0,2}$	$215313738118.4\pm2.2$
4	$(0\ 0\ 2)7_{1,7} \leftarrow (0\ 0\ 0)8_{2,6}$	$209921492496.8\pm 3.6$	102	$(200)5_{3,2} \leftarrow (000)4_{4,1}$	$215518271848.0\pm2.5$
5	$(200)7_{0,7} \leftarrow (000)8_{1,8}$	$210061488259.7\pm1.9$	103	$(200)4_{2,3} \leftarrow (000)3_{3,0}$	$215540744478.2\pm2.0$
6	$(200)7_{1,7} \leftarrow (000)8_{0,8}$	$210068848907.1\pm2.2$	104	$(200)4_{1,4} \leftarrow (000)3_{2,1}$	$215562753539.0\pm2.4$
7	$(200)3_{1,3} \leftarrow (000)4_{2,2}$	$210077627952.7\pm1.9$	105	$(101)7_{4,3} \leftarrow (000)7_{4,4}$	$215591396440.7\pm2.0$
8	$(200)10_{7,4} \leftarrow (000)11_{6,5}$	$210082791341.3\pm5.2$	106	$(101)3_{1,3} \leftarrow (000)3_{1,2}$	$215607014166.6\pm2.0$
9	$(0\ 2\ 1)8_{3,6} \leftarrow (0\ 0\ 0)8_{1,7}$	$210094473065.9\pm2.1$	107	$(200)9_{5,4} \leftarrow (000)8_{6,3}$	$215780605369.9\pm2.3$
10	$(120)10_{5,6} \leftarrow (000)10_{4,7}$	$210102547824.2\pm 3.9$	108	$(0\ 0\ 2)4_{2,3} \leftarrow (0\ 0\ 0)5_{3,2}$	$215812069399.3\pm2.0$
11	$(120)8_{5,4} \leftarrow (000)8_{4,5}$	$210109231135.4\pm2.9$	109	$(0\ 0\ 2)7_{5,3} \leftarrow (0\ 0\ 0)7_{6,2}$	$216093103792.3\pm2.6$
12	$(0\ 2\ 1)\ 5_{3,2} \leftarrow (0\ 0\ 0)\ 4_{3,1}$	$210208825509.3\pm1.9$	110	$(0\ 0\ 2)7_{5,2} \leftarrow (0\ 0\ 0)7_{6,1}$	$216103706730.5\pm5.9$
13	$(0\ 0\ 2)7_{5,3} \leftarrow (0\ 0\ 0)8_{6,2}$	$210238338294.5\pm2.9$	111	$(101)2_{1,2} \leftarrow (000)2_{1,1}$	$216129993563.2\pm2.2$
14	$(0\ 0\ 2)7_{5,2} \leftarrow (0\ 0\ 0)8_{6,3}$	$210250167306.0\pm2.0$	112	$(0\ 0\ 2)6_{5,2} \leftarrow (0\ 0\ 0)6_{6,1}$	$216168223250.8\pm2.5$
15	$(200)6_{2,5} \leftarrow (000)7_{1,6}$	$210261620255.5\pm2.4$	113	$(0\ 0\ 2)6_{5,1} \leftarrow (0\ 0\ 0)6_{6,0}$	$216170204632.1\pm2.3$
16	$(200)8_{1,8} \leftarrow (000)8_{2,7}$	$210373340020.8\pm 2.0$	114	$(101)5_{2,3} \leftarrow (000)6_{0,6}$	$216199773829.6\pm2.3$
17	$(0\ 2\ 1)6_{5,2} \leftarrow (0\ 0\ 0)7_{3,5}$	$210463636255.0\pm1.9$	115	$(200)3_{1,2} \leftarrow (000)3_{0,3}$	$216346256445.2\pm1.9$
18	$(200)7_{4,4} \leftarrow (000)7_{5,3}$	$210470423741.5\pm2.5$	116	$(200)2_{0,2} \leftarrow (000)1_{1,1}$	$216352817189.0\pm1.8$
19	$(101)2_{1,2} \leftarrow (000)3_{3,1}$	$210514705424.9\pm1.9$	117	$(200)3_{1,2} \leftarrow (000)2_{2,1}$	$216432023528.1\pm1.8$
20	$(200)9_{5,4} \leftarrow (000)10_{4,7}$	$210533593552.4\pm2.6$	118	$(101)2_{2,0} \leftarrow (000)3_{0,3}$	$216433278881.6\pm1.8$
21	$(0\ 0\ 2)6_{1,5} \leftarrow (0\ 0\ 0)7_{4,4}$	$210543831004.2\pm2.1$	119	$(200)1_{1,1} \leftarrow (000)0_{0,0}$	$216472584311.6\pm1.8$
22	$(0\ 2\ 1)\ 87,2 \leftarrow (0\ 0\ 0)\ 87,1$	$210623111969.9\pm2.1$	120	$(120)8_{8,0} \leftarrow (000)8_{7,1}$	$216483694353.7\pm9.0$
23	$(0\ 2\ 1)\ 8_{7,1} \leftarrow (0\ 0\ 0)\ 8_{7,2}$	$210623149726.8\pm2.0$	121	$(120)8_{8,1} \leftarrow (000)8_{7,2}$	$216483717383.2\pm6.7$
$^{24}$	$(200)6_{4,2} \leftarrow (000)6_{5,1}$	$210642347124.0\pm1.9$	122	$(0\ 2\ 1)\ 8_{7,2} \leftarrow (0\ 0\ 0)\ 7_{7,1}$	$216489812790.6\pm3.8$
		Contd on next page			

Table 1: The list of experimental transition frequencies of  ${\rm H_2}^{18}{\rm O}$  measured as part of the present study.<sup>*a*</sup>

rabie i Conta. from prettoas page	Table	1	- C	Contd.	from	previous	page
-----------------------------------	-------	---	-----	--------	------	----------	------

#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz
25	$(200)^{2}_{2}_{1} \leftarrow (000)^{3}_{2}_{2}_{0}$	$2107512782923 \pm 18$	123	$(021)871 \leftarrow (000)770$	2164898256835+24
26	$(200)60.6 \leftarrow (000)71.7$	$2107613614192 \pm 21$	124	$(021)642 \leftarrow (000)522$	$2165807217418\pm 2.2$
27	$(200)4_{1,2} \leftarrow (000)5_{2,4}$	2109730921832+21	125	$(101)_{302} \leftarrow (000)_{220}$	$2166341446526\pm1.8$
28	$(021)6_{2,3} \leftarrow (000)5_{2,4}$	$2109849036963\pm1.9$	126	$(101)00,3 \leftarrow (000)22,0$	$2167578059091 \pm 20$
29	$(002)6z 2 \leftarrow (000)7e 1$	$2110423471867 \pm 34$	127	$(101)92.6 \leftarrow (000)85.2$	$2167993575825 \pm 3.8$
30	$(200)972 \leftarrow (000)1065$	$2110440131612 \pm 49$	128	$(200)221 \leftarrow (000)212$	$2168466091413\pm18$
31	$(002)6_{7,2} \leftarrow (000)7_{2,2}$	$21104401010101.2 \pm 4.0$ $2110445077554 \pm 3.0$	120	$(002)9_{22,1} \leftarrow (000)10_{21,2}$	$21606400000141.0 \pm 1.0$ $2160684067406 \pm 14.5$
30	$(002)05,1 \leftarrow (000)06,2$	$211044507755.4 \pm 3.0$ $2111855511707 \pm 7.7$	120	$(002)37,2 \leftarrow (000)106,5$	$210903490740.0\pm14.0$ $2160827735170\pm2.1$
33	$(101)_{500} \leftarrow (000)_{500}$	$211100001110.1\pm1.1$	131	$(002)6_{1,2} \leftarrow (000)7_{0,1}$	$216902110011.0\pm2.1$
34	$(101)02,3 \leftarrow (000)04,2$	$211412100010.4 \pm 2.0$ $2114746383610 \pm 1.9$	132	$(200)6r_{2,5} \leftarrow (000)72r_{2,5}$	$2177772834039 \pm 21$
35	$(200)31.5 \leftarrow (000)40.8$	$21141400000100 \pm 100000000000000000000000$	133	$(200)8_{0,2} \leftarrow (000)9_{2,3}$	$2171778083917 \pm 55$
36	$(200)8_{1,2} \leftarrow (000)9_{2,3}$	$211401121010.1\pm2.2$ $2115172040841\pm2.2$	134	$(200)(6,3) \leftarrow (000)(3,6)$	217271100000000000000000000000000000000
37	$(200)8_{0,3} \leftarrow (000)9_{5,4}$	$2116017148904 \pm 2.2$	135	$(200)4_{1,3} \leftarrow (000)4_{1,4}$	$217201114072.7 \pm 2.2$ $2172038850321 \pm 1.0$
38	$(021)8_{01} \leftarrow (000)8_{00}$	$211601114600.4 \pm 2.2$ $2116251559658 \pm 126$	136	$(101)542,3 \leftarrow (000)41,4$	$217 230 600 302.1 \pm 1.5$ $217 331 676 827 7 \pm 1.8$
39	$(021)88.0 \leftarrow (000)88.1$	$2116251562515\pm113$	137	$(101)04,2 \leftarrow (000)02,3$ $(002)64,2 \leftarrow (000)65,3$	$2173676771273 \pm 1.8$
40	$(101)6_{24} \leftarrow (000)6_{44}$	$2117578136975 \pm 20$	138	$(200)^{31}_{31}_{32} \leftarrow (000)^{20}_{32}_{32}_{33}$	$2174085128527\pm21$
41	$(200)7_{5,2} \leftarrow (000)8_{4,3}$	$2117722556660 \pm 1.8$	139	$(101)101 \leftarrow (000)20,2$	$217400012002.17 \pm 2.17$ $2174101095676 \pm 1.7$
42	$(021)642 \leftarrow (000)541$	$2117922000000 \pm 1.0$ $2117950071754 \pm 1.8$	140	$(101)10,1 \leftarrow (000)550,0$	$21741010500100 \pm 1.1$ $2174478654431 \pm 21$
43	$(200)4_{2,1} \leftarrow (000)4_{4,0}$	$2118698668125 \pm 20$	141	$(101)9_{0.0} \leftarrow (000)10_{0.0}$	$2175693351810 \pm 253$
40	$(021)522 \leftarrow (000)515$	$2118722753764\pm2.1$	142	$(101)58,2 \leftarrow (000)51 =$	$2176029885568\pm1.8$
45	$(200)_{60,6} \leftarrow (000)_{61,6}$	$2120446628578 \pm 20$	143	$(200)7_{44} \leftarrow (000)7_{25}$	$2176123351097 \pm 1.9$
46	$(200)4_{0.0} \leftarrow (000)5_{1.0}$	$212.041.002.001.0 \pm 2.0$ $212.061.548.824.1 \pm 2.3$	144	$(002)94 = \leftarrow (000)954$	$2176267367446 \pm 22$
47	$(101)7_{44} \leftarrow (000)6_{61}$	$212001040024.1\pm2.0$ $2121292303543\pm2.6$	145	$(101)6_{24,5} \leftarrow (000)6_{25,4}$	2177711125962 + 23
48	$(021)^{3}_{3}_{2}_{2} \leftarrow (000)^{2}_{1}_{1}_{1}$	$2121539030365 \pm 27$	146	$(101)02,4 \leftarrow (000)02,3$	$2178860182638\pm253$
40	$(200)414 \leftarrow (000)20505$	$2121676789481 \pm 21$	147	$(200)7_{\text{E},2} \leftarrow (000)7_{4,4}$	$2179043103165\pm1.8$
50	$(002)6_{4,2} \leftarrow (000)7_{5,2}$	$2122374225974 \pm 2.5$	148	$(200)^{13,3} \leftarrow (000)^{14,4}$	2179467408204 + 18
51	$(101)7_{4,3} \leftarrow (000)6_{6,0}$	$2122547458241\pm61$	149	$(200)2_{2,3} \leftarrow (000)1_{1,0}$	$2179547987340 \pm 22$
52	$(101)3_{12} \leftarrow (000)3_{20}$	$212326561977.8\pm1.8$	150	$(200)964 \leftarrow (000)955$	$217999528718.1\pm3.1$
53	$(200)524 \leftarrow (000)522$	$212345214231.0 \pm 2.0$	151	$(101)4_{12} \leftarrow (000)4_{14}$	$218001743321.6\pm2.4$
54	$(200)82.6 \leftarrow (000)83.5$	$212396174588.1\pm1.8$	152	$(200)652 \leftarrow (000)643$	$218059270648.7\pm1.8$
55	$(021)6_{4,2} \leftarrow (000)7_{0,7}$	$212425021216.0\pm1.9$	153	$(200)1074 \leftarrow (000)1065$	$218150542878.7\pm6.1$
56	$(200)1_{11} \leftarrow (000)2_{20}$	$212431888691.5\pm1.8$	154	$(200)862 \leftarrow (000)853$	$218161537779.0\pm2.4$
57	$(200)7_{6,2} \leftarrow (000)8_{5,3}$	$212457641964.8\pm 4.0$	155	$(200)5_{15} \leftarrow (000)4_{04}$	$218178362696.5\pm1.9$
58	$(0\ 0\ 2)\ 5_{0\ 5} \leftarrow (0\ 0\ 0)\ 6_{3\ 4}$	$212468032491.7\pm1.9$	156	$(200)8_{6,3} \leftarrow (000)8_{5,4}$	$218179986634.9\pm1.9$
59	$(200)7_{6,1} \leftarrow (000)8_{5,4}$	$212483637001.1\pm2.5$	157	$(200)7_{6,1} \leftarrow (000)7_{5,2}$	$218334548220.7\pm2.0$
60	$(002)9_{3,6} \leftarrow (000)10_{4,7}$	$212522812549.7\pm2.0$	158	$(200)7_{6,2} \leftarrow (000)7_{5,3}$	$218340043754.4\pm2.0$
61	$(200)6_{4,2} \leftarrow (000)7_{3,5}$	$212661534864.2\pm5.3$	159	$(200)9_{7,2} \leftarrow (000)9_{6,3}$	$218340933409.3\pm2.8$
62	$(0\ 2\ 1)6_{3,3} \leftarrow (0\ 0\ 0)6_{1,6}$	$212795126999.3\pm2.9$	160	$(200)9_{7,3} \leftarrow (000)9_{6,4}$	$218345299533.4\pm 3.4$
63	$(200)6_{5,2} \leftarrow (000)7_{4,3}$	$212822890978.6\pm 1.9$	161	$(200)3_{2,2} \leftarrow (000)2_{1,1}$	$218439924827.2\pm1.9$
64	$(0\ 2\ 1)6_{5,2} \leftarrow (0\ 0\ 0)5_{5,1}$	$212834466230.7\pm2.4$	162	$(0\ 0\ 2)\ 5_{0,5} \leftarrow (0\ 0\ 0)\ 6_{1,6}$	$218464971503.2\pm2.1$
65	$(101)9_{4,5} \leftarrow (000)10_{2,8}$	$212866421839.1\pm5.7$	163	$(200)6_{0,6} \leftarrow (000)5_{1,5}$	$218519112560.5\pm1.9$
66	$(200)3_{1,3} \leftarrow (000)4_{0,4}$	$212872456178.3\pm2.0$	164	$(0\ 0\ 2)5_{3,3} \leftarrow (0\ 0\ 0)5_{4,2}$	$218573455208.2\pm2.1$
67	$(200)4_{1,4} \leftarrow (000)4_{2,3}$	$212929950045.8\pm2.0$	165	$(1\ 0\ 1)3_{0,3} \leftarrow (0\ 0\ 0)2_{0,2}$	$218578468816.8\pm2.0$
68	$(200)6_{1,5} \leftarrow (000)6_{2,4}$	$213058109278.7\pm1.9$	166	$(0\ 0\ 2)6_{4,3} \leftarrow (0\ 0\ 0)7_{3,4}$	$218582638989.0\pm2.3$
69	$(0\ 0\ 2)5_{4,1} \leftarrow (0\ 0\ 0)6_{5,2}$	$213059106853.4\pm1.8$	167	$(0\ 2\ 1)6_{5,2} \leftarrow (0\ 0\ 0)6_{1,5}$	$218605445288.7\pm2.0$
70	$(0\ 0\ 2)9_{7,3} \leftarrow (0\ 0\ 0)9_{8,2}$	$213163968943.1\pm 6.7$	168	$(0\ 0\ 2)4_{3,2} \leftarrow (0\ 0\ 0)4_{4,1}$	$218657009780.6\pm 4.4$
71	$(0\ 0\ 2)9_{7,2} \leftarrow (0\ 0\ 0)9_{8,1}$	$213164208347.5\pm5.8$	169	$(200)6_{1,5} \leftarrow (000)5_{2,4}$	$218666316036.3\pm2.2$
72	$(200)2_{0,2} \leftarrow (000)3_{1,3}$	$213210411131.7\pm2.2$	170	$(1\ 2\ 0)\ 10_{5,6} \leftarrow (0\ 0\ 0)\ 10_{2,9}$	$218682073260.7\pm4.3$
73	$(101)4_{1,3} \leftarrow (000)4_{3,2}$	$213341078668.5\pm1.9$	171	$(0\ 0\ 2)4_{3,1} \leftarrow (0\ 0\ 0)4_{4,0}$	$218712072101.4\pm4.3$
74	$(200)3_{1,3} \leftarrow (000)3_{2,2}$	$213366458394.9\pm2.2$	172	$(2\ 0\ 0)4_{2,3} \leftarrow (0\ 0\ 0)3_{1,2}$	$218821196666.6\pm 1.9$
75	$(002)8_{7,2} \leftarrow (000)8_{8,1}$	$213391938172.9\pm3.3$	173	$(0\ 2\ 1)7_{5,3} \leftarrow (0\ 0\ 0)7_{1,6}$	$218876570693.2\pm2.2$
76	$(002)8_{7,1} \leftarrow (000)8_{8,0}$	$213391975467.9\pm2.0$	174	$(200)7_{0,7} \leftarrow (000)6_{1,6}$	$218924924113.5\pm2.1$
77	$(0\ 2\ 1)64,2 \leftarrow (0\ 0\ 0)62,5$	$213424139718.3 \pm 1.9$	175	$(200)7_{1,7} \leftarrow (000)6_{0,6}$	$218944686727.2\pm2.2$
78	$(200)2_{1,2} \leftarrow (000)3_{0,3}$	$213607657721.6\pm1.9$	176	$(0\ 2\ 1)8_{3,6} \leftarrow (0\ 0\ 0)7_{1,7}$	$218953589662.3\pm4.2$
79	$(101)9_{8,1} \leftarrow (000)9_{8,2}$	$213764920554.2\pm2.9$	177	$(002)4_{2,3} \leftarrow (000)5_{1,4}$	$219030888618.5\pm2.2$
80	$(101)9_{8,2} \leftarrow (000)9_{8,1}$	$213765046786.3 \pm 10.5$	178	$(200)5_{2,4} \leftarrow (000)4_{1,3}$	$219114318272.8 \pm 1.8$
81	$(002)4_{4,1} \leftarrow (000)5_{5,0}$	$213838639896.6 \pm 4.3$	179	$(101)10_{4,7} \leftarrow (000)10_{2,8}$	$219116362450.6 \pm 2.9$
82	$(002)44,0 \leftarrow (000)55,1$	$213840105039.0\pm 4.3$	180	$(200)8_{0,8} \leftarrow (000)7_{1,7}$	$219303346196.8\pm1.6$
83	$(101)8_{8,0} \leftarrow (000)8_{8,1}$	$213842661994.1 \pm 5.4$	181	$(200)8_{1,8} \leftarrow (000)7_{0,7}$	$219311239691.7 \pm 1.8$
84	$(101)8_{8,1} \leftarrow (000)8_{8,0}$	$213842677140.0\pm 5.5$	182	$(101)5_{4,2} \leftarrow (000)4_{4,1}$	$219364489739.6 \pm 2.2$
00 96	$(101)^{94,5} \leftarrow (000)^{86,2}$	$213012092028.0 \pm 0.2$	103	$(200)62,6 \leftarrow (000)73,5$	$213420014010.7 \pm 2.0$
00 97	$(101)_{30,3} \leftarrow (000)_{40,4}$	$214042412142.1 \pm 2.7$ $2141120245675 \pm 1.0$	104	$(200)04,2 \leftarrow (000)/1,7$	$213 320 042 431.7 \pm 4.9$ 210 706 210 845 0 $\pm$ 1 8
01 88	$(200)31,2 \leftarrow (000)32,1$ $(002)5aa \leftarrow (000)6 \cdot -$	$214 113 924 007.0 \pm 1.9$ $214 147 221 487 0 \pm 2.1$	186	$(101)(4,4 \leftarrow (000)(2,5)$ $(002)9\pi_{2} \leftarrow (000)8$ -	$219700219840.0 \pm 1.8$ $2197759122028 \pm 45$
80	$(101)^{2}_{2}_{2}_{3} \leftarrow (000)^{2}_{4}_{2}_{2}$	$214 147 221 407.9 \pm 2.1$ $214 200 947 005 1 \pm 1.7$	187	$(002)97,3 \leftarrow (000)88,0$	$213770312292.0 \pm 4.0$ 2107761551437 $\pm 4.0$
90	$(120)1074 \leftarrow (000)32,1$	$214260.947.005.1 \pm 1.7$ $214260.053267.7 \pm 4.3$	188	$(101)_{200} \leftarrow (000)_{101}$	$219770100140.7 \pm 4.9$ 2198083946787 $\pm 2.0$
91	$(101)9e_2 \leftarrow (000)9e_3$	$2142853372874 \pm 54$	189	$(101)9_{e_2} \leftarrow (000)10_{e_2}$	2198574984282 + 182
92	$(200)1_{11} \leftarrow (000)2_{00}$	$2143762128560\pm20$	190	$(101)871 \leftarrow (000)777$	$2198639609032\pm 26.3$
93	$(002)9_{45} \leftarrow (000)8_{72}$	$2144469718305 \pm 258$	191	$(101)8_{7,2} \leftarrow (000)7_{7,3}$	$2198642057809 \pm 2.9$
94	$(101)7_{24} \leftarrow (000)6_{51}$	$214581817277.2 \pm 2.3$	192	$(002)6_{15} \leftarrow (000)5_{42}$	$220057792912.1 \pm 2.5$
95	$(101)7_{34} \leftarrow (000)8_{17}$	214600396009.0 + 2.4	193	$(101)955 \leftarrow (000)954$	$214669009738.4\pm 2.0$
96	$(200)2_{0.2} \leftarrow (000)2_{1.1}$	$214612822648.1\pm2.0$		( - , - 3, - (	

<sup>a</sup> The assignments given follow the notation of Fig. 4.3. The uncertainties behind the  $\pm$  signs represent 68 % confidence level. Note that three of the listed transitions were determined to be 214 200 946 980(30) kHz [(101)2<sub>2,0</sub>  $\leftarrow$  (000)3<sub>2,1</sub>], 215 607 014 210(30) kHz [(101)3<sub>1,3</sub>  $\leftarrow$  (000)3<sub>1,2</sub>], and 216 129 993 490(30) kHz [(101)2<sub>1,2</sub>  $\leftarrow$  (000)2<sub>1,1</sub>] by Gianfrani *et al.*, [165] showing deviations of 25, 43, and 73 kHz from the NICE-OHMS frequencies, accurate to about 2 kHz, respectively.

It is important to emphasize that within the two components, corresponding to the two nuclear-spin isomers of H<sub>2</sub><sup>18</sup>O, two poorly-connected subnetworks ('subcomponents') can be seen in Figs. 4.3 and 4.4. The  $p^+$ ,  $p^-$ ,  $o^+$ , and  $o^-$  subcomponents pertain to the (p'',q'') = (+1,+1), (-1,+1), (+1,-1), (-1,-1) pairs, respectively, where  $p'' = (-1)^{K''_c}$  and  $q'' = (-1)^{v''_3+K''_a+K''_c}$ , while  $v''_3$ ,  $K''_a$ , and  $K''_c$  are lower-state quantum numbers (see also the footnote to Fig. 4.3). While the para (q'' = +1) component cannot be linked experimentally with the ortho (q'' = -1) one, the p'' = 1 and p'' = -1 subcomponents  $(p^+/p^- \text{ and } o^+/o^-)$  can be connected with pure rotational lines,[66] though they cannot be linked with



Figure 4.5: Typical short cycles and paths formed during the SNAPS analysis of  $H_2^{18}O$ . The color codes of this figure are explained in Figs. 4.3 and 4.4. Panels (a)/(c) and (b)/(d) exhibit 4- and 6-membered cycles, respectively. Each transition is associated with its frequency, in kHz, and the uncertainty of the last few frequency digits, given in parentheses. Successive application of the Ritz principle [see the formulas of Fig. 4.2(e)] yields the following discrepancies: 0.8(39) [panel (a)], 11.5(69) [panel (b)], 6.4(39) [panel (c)], and 0.5(39) kHz [panel (d)]. All these cycles obey the relation  $D \leq t_{crit}u(D)$  (see also the footnote to Fig. 4.2). The line with bold-faced frequency was first confused with a close-lying  $H_2^{16}O$  transition [(0 2 1)6<sub>1.5</sub>  $\leftarrow$  (0 0 0)5<sub>2.4</sub>], exhibiting a line center of 210 642 354 724.6(50) kHz and leading to an unrealistically large discrepancy of 7600.7(91) kHz. Panels (e) and (f) are example paths for the determination of relative energies of  $H_2^{18}O$ . Repeated utilization of the Ritz principle [see the formulas of Fig. 4.2(d)] provides relative energies of 274.865 192 41(13) cm<sup>-1</sup> [corresponding to 82 40 251 165.0(39) kHz] and 94.788 628 80(19) cm<sup>-1</sup> [that is, 2841 691 601.7(56) kHz] for (000)4<sub>2.3</sub> and (000)2<sub>1.1</sub>, respectively. The energy values of the intermediate states can also be deduced from these paths.

dipole-allowed vibration-altering transitions. One should also realize that these kHz-accuracy rotational lines are fully disconnected in themselves, hindering their independent utilization in the derivation of accurate rovibrational energies

#### Variational nuclear-motion computations

Due to their extremely low intensities ( $S < 10^{-30}$  cm molecule<sup>-1</sup>), no ortho-para transitions of H<sub>2</sub><sup>18</sup>O have been observed (see Ref. [59], dealing with H<sub>2</sub><sup>16</sup>O). Therefore, the energy of the ortho states relative to the para-type rovibrational ground state cannot be derived solely from experiment. A possible way to link the ortho and para components is to find a path, from  $(000)0_{0,0}$  to  $(000)1_{0,1}$ , which comprises highly accurate experimental transitions and a virtual line between nearly degenerate para and ortho levels.[51, 129] Adjacent  $(v_1 v_2 v_3)J_{J,0/1}$  pairs with fairly large J values are the most suitable candidates for the virtual transitions, as their energy differences, here called 0/1 splittings, can be obtained with high accuracy via state-of-the-art variational nuclear-motion computations.[172] These accurate quantum-chemical computations were executed here with the latest version[173] of the fourth-age [172] GENIUSH (GEneral rovibrational code with Numerical, Internal-coordinate, User-Specified Hamiltonians) code.[84, 85]

During the quantum-chemical computations, enlarged vibrational basis sets were utilized, involving multiple potential energy surfaces (PES) of spectroscopic quality. Several outstanding PESs have been reported in the literature for  $H_2^{16}O$ and  $H_2^{18}O$ ,[174, 175, 176, 103] which can be employed to deduce accurate 0/1 splittings. As the computational details are quite similar to those presented in Supplementary Note 4 of Ref. [129], only the most important aspects are emphasized here. Above all, in spite of the fact that absolute energies cannot be determined with an accuracy comparable to (ultra)-high-precision experiments, the 0/1 splittings can have ultrasmall uncertainties. The reason is that energy shifts resulting from deficiencies of the PES are almost fully compensated when differences between rovibrational energies of highly similar, nearby states are formed. In addition, errors arising from the incompleteness of the vibrational basis set are also wiped out this way (the rotational basis is complete). As a consequence, the 0/1 splittings are more or less independent of the PESs and the basis sets used for their computation.

Besides the 0/1 splittings, the energy differences of other close *ortho/para* state pairs, differing only in their  $K_a$  or  $K_c$  numbers, can also be derived with high accuracy. Similarly precise predictions can be given for the relative positions, both their signs and absolute values, of nearby  $(U_1 \leftarrow L_1, U_2 \leftarrow L_2)$  transition doublets, showing roughly 1:3 intensity ratios, where  $U_1/U_2$  and  $L_1/L_2$  are *ortho/para* or *para/ortho* state pairs. These relative positions can be determined from a properly signed sum of the underlying *ortho/para* energy splittings.

#### 4.3. Results and Discussion

#### Ultraprecise NICE-OHMS spectra

Lamb dips of 195 rovibrational transitions, involving six vibrational bands [(000), (120), (021), (200), (101), and (002)] and characterized with  $J \leq 11$ , were recorded. Due to the careful (SNAPS) design of the NICE-OHMS measure-



Figure 4.6: Lamb-dip spectra of four typical  $H_2^{18}O$  transitions recorded with the NICE-OHMS setup. On the left and right panels, *para-* and *ortho-* $H_2^{18}O$  transitions are depicted, respectively. The Lamb dips are plotted along the same (relative) frequency axis and they exhibit varying degree of power broadening. The vertical axis refers to relative absorption strengths for the Lamb dips.

ments, the ultraprecise lines of both *ortho-* and  $para-H_2^{18}O$  are internally connected, allowing the transfer of the observational accuracy to that of the derived relative energies. Typical Lamb-dip spectra of the observed transitions are seen in Fig. 4.6.

As one of the most important experimental results of this work, nine transition doublets separated by less than 300 MHz were observed. The resolution of these closely spaced lines is far from being trivial in Doppler-limited spectroscopy, if feasible at all. Thus, it is not surprising that while these nine doublets were studied, they could not be resolved in Refs. [177, 178, 179, 180], which report a single wavenumber for each of these line pairs. In the NICE-OHMS spectra, the lines of these doublets, with a separation greater than 300 kHz, are well isolated, yielding accurate individual frequencies for the underlying transitions.

It is emphasized that these small doublet separations derived from NICE-OHMS spectra can be reproduced well by quantum-chemical computations having a relative uncertainty of 1–5 %. For example, the separation of  $(101)9_{8,2/1} \leftarrow (000)9_{8,1/2}$  is measured as 126.2321(108) MHz by NICE-OHMS, which agrees well with the quantum-chemical prediction of 128.1(24) MHz, obtained as part of this study (see Sec. 1 and 2). Likewise, the NICE-OHMS separation of the  $(021)8_{8,0/1} \leftarrow (000)8_{8,1/0}$  doublet, 286(17) kHz, exhibits an excellent compliance with its quantum-chemical counterpart, 306(13) kHz.

The last extremely close-lying doublet, with a separation at the border of the resolvability limit (300 kHz), could be still resolved, at least partially, by exploiting some special features of the NICE-OHMS technique: here we relied on 3f-demodulation with the lock-in detector and recording the Lamb-dip features via



Figure 4.7: Recordings of special features in the spectra of  $H_2^{18}O$ . Panel (a) shows the Lamb-dip spectrum of the  $(0\,2\,1)8_{8,0/1} \leftarrow (0\,0\,0)8_{8,1/0}$  doublet measured by the 3f demodulation technique in saturation by the power circulating on the side-band frequency. Panel (b) exhibits the Lamb-dip profile of the weakest ( $S = 1.4 \times 10^{-27}$  cm molecule<sup>-1</sup> and  $A_E = 1.5 \times 10^{-3}$  s<sup>-1</sup>) line probed during the experimental campaign,  $(0\,0\,2)8_{7,1} \leftarrow (0\,0\,0)9_{6,4}$ , averaging over 20 scans.

saturation by the side-band power shifted by one FSR. The spectrum of this doublet is presented in Fig. 4.7(a). The optical methods applied will be discussed in a future publication.

The lines probed during the measurement campaign for para- and ortho-H<sub>2</sub><sup>18</sup>O are presented in Figs. 4.3 and 4.4, respectively. The measurements were designed to cover all the  $(000)J_{K_a,K_c}$  states up to J = 8; thus, these transitions are very different both in their S and  $A_E$  values. Lines incident to low- $K_a$  states were straightforwardly detectable due to their ideal strength ( $A_E = 10^{-3} - 1 \text{ s}^{-1}$  and  $S = 10^{-25} - 10^{-21} \text{ cm molecule}^{-1}$ ), while those linking  $K_a > J/2$  levels were considerably weaker ( $S < 1 \times 10^{-26} \text{ cm molecule}^{-1}$ ), making their experimental study challenging. The improved accuracy of the initial positions achieved via  $\Lambda$ -correction schemes (see Sec. 4.2) reduced significantly the technical difficulties, but observation of the weakest line profile [see Fig. 4.7(b)] still remained complex. It was a complicated task to build suitable paths linking the (000)8<sub>8,0/1</sub> energy levels to the lowest-energy para/ortho states. The first (unsuccessful) and the second (successful) routes to find an experimental realization for these paths is outlined in Fig. 4.8.

Another issue beyond line strength is that transitions located in the close vicinity of a particular target line may disturb its observation. These disturbing lines, corresponding to  $H_2^{18}O$ ,  $H_2^{16}O$ , and even  $HD^{18}O$ , can distort and often conceal the target transition completely. As an empirical rule, candidate lines adjacent to too strong ( $S > 1 \times 10^{-23}$  cm molecule<sup>-1</sup>)  $H_2^{16}O$  lines at a distance smaller than 350 MHz could not be properly resolved due to spectral overlaps. Thus, such candidates were mostly not considered during the SNAPS analysis.



Figure 4.8: Story of the detection of the two weak lines necessary for the determination of the  $(000)8_{8.0/1}$  states. Panels (a) and (b) indicate the two weak transitions (in light blue and brown) selected for measurement and define the parameters of this figure with their origin (NICE-OHMS observation, SNAPS-based estimate, combined SNAPS/EH prediction, or GENIUSH computation). The SNAPS/EH combination means here that the relative SNAPS energy values are converted to absolute energies by including the  $(000)1_{0.1}$  energy deduced from an EH model (see also Sec. 2). The specification of the energy levels is the same as in Figs. 3 and 4. If the  $\sigma_3$  (virtual) line is not considered, then these two panels correspond to  $\Lambda$ -correction schemes. Panel (c) presents two routes for the observation of the two weak lines (where no units are given, the data are in  $cm^{-1}$ ). The left route, represented with red arrows, relies on the energy value of  $(000)8_{8,0}$  state extrapolated from a preliminary EH fit. This route provided a low-quality Lamb-dip profile for the light blue transition around the refined (initial)  $\sigma_2$  value in a range of  $\pm 2$  MHz, shifted by -0.7 MHz. Based on the center of this scattered profile, no signal could be found for the brown line by scanning a region of  $\pm 2$  MHz around the adjusted (initial)  $\sigma_5$  wavenumber. Therefore, the right route, illustrated with green arrows, was tried, where the W2020 energy of  $(000)8_{8,0}$ , having an uncertainty of ~1.5 MHz, was adopted to give a refined  $\sigma_2$  line position. From this empirical energy, a well-behaved Lamb-dip curve [see Fig. 4.7(b)] could be recorded whose position is translated by 3 MHz from the W2020-based prediction for  $\sigma_2$ . The newly probed line is separated by 8 MHz from that resolved on the left route, which must be a ghost transition produced by the optical system of NICE-OHMS. Then, drawing on the NICE-OHMS value of  $\sigma_2$  and the  $\sigma_3$  splitting (see Sec. 2), an accurate estimate could be derived for  $\sigma_5$ , from which a similarly correct line profile was observed for the brown transition with a shift of just 20 kHz. With the aid of the experimental  $\sigma_5$  position, the SNAPS/EH prediction for  $(000)8_{8,1}$  could be derived.
In the cases when the adjacent lines have almost identical S and  $A_{\rm E}$  values, one cannot fully decide which isotopologue is interrogated by the spectroscopy laser. For example, when the  $(200)6_{4,2} \leftarrow (000)6_{5,1}$  transition of  ${\rm H_2}^{18}{\rm O}$  was targeted, its neighboring  ${\rm H_2}^{16}{\rm O}$  line,  $(021)6_{2,5} \leftarrow (000)5_{2,4}$ , separated by just 10 MHz, was accidentally measured (these close-lying lines would be unresolvable under Doppler-broadened conditions, distorting the effective position of the unresolved line pair). A similar "mistake" was made during the planned observation of the  $(200)9_{7,2} \leftarrow (000)9_{6,3}$  transition of  ${\rm H_2}^{18}{\rm O}$ : in this case, the  $(002)4_{3,1} \leftarrow (000)4_{2,2}$ line of HD<sup>18</sup>O, located 39 MHz away from the  ${\rm H_2}^{18}{\rm O}$  line, was probed. These issues were discovered when the discrepancies of the newly formed cycles were analyzed as part of the SNAPS scheme, and the EH fit was performed for the lower-state energy differences of the  $\Lambda$  shapes composed of NICE-OHMS transitions. The sixmembered cycle which helped to reveal the inconsistency in the first example given can be inspected in Fig. 4.5(d).

## Uncertainty quantification

The uncertainties of the line positions listed in Table 1 depend on several experimental factors. In this study, the following decomposition is used to estimate the frequency uncertainty  $(\delta)$ :

$$\delta = \sqrt{\delta_{\text{stat}}^2 + \delta_{\text{day}}^2 + \delta_{\text{cal}}^2 + \delta_{\text{pow}}^2 + \delta_{\text{pres}}^2},$$

where the meaning of the individual terms is explained below.

The statistical uncertainty,  $\delta_{\text{stat}}$ , gauges the reproducibility of the NICE-OHMS frequencies. For transitions with ideal strength,  $\delta_{\text{stat}}$  is approximated as the standard deviation of the line centers obtained from 3–4 scans (requiring about 10 minutes for each scan). For extremely weak ( $S < 10^{-26}$  cm molecule<sup>-1</sup>) lines,  $\delta_{\text{stat}}$  is estimated individually from their data-averaged spectra overlaid by multiple scans (the locking of the diode laser to the OFC laser enabled merging multiple recordings without causing drifts on the frequency scale). Due to the high sensitivity of the NICE-OHMS spectrometer, the very strong ( $A_{\text{E}} > 1 \text{ s}^{-1}$ ) transitions with low J values may be affected by power broadening, inducing somewhat larger  $\delta_{\text{stat}}$  values in certain cases. Similarly, in our pressure range (0.03–1.0 Pa), pressure broadening effected by molecular collisions also leads to a slight increase in  $\delta_{\text{stat}}$ , at least for a few lines.

The day-to-day uncertainty,  $\delta_{day}$ , is connected to  $\delta_{stat}$ , characterizing the *long-term* reproducibility of the line frequencies and the stability of the NICE-OHMS setup. The spectra of some transitions were repeatedly recorded on 2–3 different days, yielding an average deviation of 1.5 kHz for these lines. This average deviation is assigned to  $\delta_{day}$ , as a conservative estimate, for each transition observed with NICE-OHMS.

If a target transition could not be properly detected from the main signal (mostly due to disturbing lines within the scanning range), then this candidate was extracted from a sideband signal, which can be calibrated with an accuracy of only 5–10 kHz. Therefore, an additional calibration uncertainty,  $\delta_{cal}$ , is included in the uncertainty budget, setting  $\delta_{cal} = 5$  kHz or  $\delta_{cal} = 10$  kHz for sideband-based transitions and  $\delta_{cal} = 0$  for the other lines.



Figure 4.9: Pressure shifts of the Lamb-dip centers for a number of selected transitions in  $H_2^{18}O$ . The shifts are related to the line frequencies in vacuum. The rovibrational assignments and the pressure-shift coefficients (slopes, inside the brackets, given in kHz Pa<sup>-1</sup>) are provided for each line in the legend to the figure.

The uncertainty due to laser-power-induced shifts,  $\delta_{\text{pow}}$ , was indiscernible, *i.e.*, below 1 kHz, during the measurements. Thus, a robust estimate of  $\delta_{\text{pow}} = 0.5$  kHz is employed for all transitions. Nonetheless, to suppress power effects, the circulating power in the cavity was lowered in those cases where possible.

As long as the vapor pressure is non-negligible within the water cell (see Fig. 4.1), the pressure-shift uncertainty,  $\delta_{\text{press}}$ , can be significant. For eight lines, the pressureshift effects were explicitly investigated by determining spectra over a range of pressure values (see Fig. 4.9). The frequency (f) of a particular transition for which pressure-dependent experiments were conducted was extrapolated to zero pressure by fitting a linear pressure-shift model,

$$f = Cp + f_{\rm vac},\tag{4.1}$$

where p is the vapor pressure applied,  $f_{\rm vac}$  is the line frequency in vacuum, and C is the pressure-shift coefficient (slope). For those transitions recorded at multiple pressure values,  $\delta_{\rm press} = 0$  is used, except one line,  $(2\,0\,0)9_{5,4} \leftarrow (0\,0\,0)8_{6,3}$ , which is associated with  $\delta_{\rm press} = 1$  kHz due to the higher (0.4 Pa) pressure applied during its observation. As the C values of these transitions were all well within the range of [-20, +15] kHz Pa<sup>-1</sup>,  $\delta_{\rm press} = C_{\rm eff}p$  is assigned to the rest of the lines, where  $C_{\rm eff} = 20$  kHz Pa<sup>-1</sup> is the (unsigned) effective value of C, and p = 0.04 Pa for most transitions. This means that  $\delta_{\rm press}$  is less than 1 kHz for all the lines. Similar to the Lamb dips[129] and Doppler-broadened [181] transitions of H<sub>2</sub><sup>16</sup>O, the experimental C values of the H<sub>2</sub><sup>18</sup>O lines do not exhibit clear trends, at least not for low J values (that is, for  $J \leq 11$  probed in our case), as a function of the rovibrational quantum numbers.

Three lines of the Gianfrani group, [165] claimed to be accurate to 30 kHz, were remeasured with the NICE-OHMS spectrometer, permitting to make a direct comparison between the old and new frequency values (for details, see the footnote to Table 1). This comparison demonstrates that (a) our observations are an order of magnitude more accurate than the values of Ref. [165], and (b) the deviations of the second two lines are outside the uncertainty claimed by the authors of Ref. [165]. The larger differences may be ascribed to the fact that the transitions of Ref. [165] were recorded at a pressure of 10 Pa, which is 250 times higher than that applied during most of our experiments (furthermore, the 15 kHz pressure-shift uncertainty given in Ref. [165] seems to be slightly optimistic in view of our  $C_{\rm eff} = 20$  kHz Pa<sup>-1</sup> value).

As an independent verification of the frequency uncertainties and the line assignments, the NICE-OHMS transitions were closed into cycles of varying lengths. In a few cases, these cycles helped to uncover that certain lines were misassigned or other mistakes were made during the experiments. The discrepancies of the cycles built from the validated transition dataset are typically on the order of 10 kHz or better, corroborating the outstanding internal consistency of the resolved lines. The fact that several transitions take part in multiple cycles further validates the accuracy of the observed lines. A couple of short cycles are drawn in Fig. 4.5 [panels (a)–(d)], while the cycles specified by the starred transitions of Figs. 4.3 and 4.4 are collected in the Supplementary Information. Note that the cycle of Fig. 4.5(a) exhibits a fairly small discrepancy (0.8 kHz) due to its transitions of low  $\delta_{\text{stat}}$  values (well below 1 kHz). Although it may occur that these lines have sub-kHz accuracy, this assumption needs further experimental investigation and verification.

## Ultraprecise relative energy values

Owing to the SNAPS design of the measurements, the ultrahigh-accuracy para (Fig. 4.3) and ortho (Fig. 4.4) lines of  $H_2^{18}O$  form connected sets, allowing the determination of ultrahigh-accuracy relative energies for the involved ortho and para states [of course, relative to  $(000)1_{0,1}$  and  $(000)0_{0,0}$ , respectively]. The relative energy of a rovibrational state is calculated here by assembling a lowest-uncertainty path from  $(000)1_{0,1}$  or  $(000)0_{0,0}$  to the desired energy level and using the Ritz principle in a successive fashion. Two illustrative examples of such paths are given in Fig. 4.5 [see panels (e) and (f)], which specify the relative energies of the  $(000)4_{2,3}$  and  $(000)2_{1,1}$  states with definitive uncertainties (the full list of the utilized paths are placed in the Supplementary Information).

As exemplified in Fig. 4.5(e), the relative energies of the  $p^+$  and  $o^-$  levels are determined by paths consisting only of NICE-OHMS transitions and running within their subcomponents. This means that the underlying energy levels are extremely well determined by the new observations. However, to derive the relative energy values of the  $p^-$  and  $o^+$  states, the related paths should include at least one pure rotational line linking  $p^-$  with  $p^+$  or  $o^+$  with  $o^-$ .

Table 2: SNAPS-based relative energies, in cm<sup>-1</sup>, for states within the (000) vibrational band of  $H_2^{18}O^a$ 

Assignment	Relative Energy/ $\rm cm^{-1}$	Assignment	Relative $Energy/cm^{-1}$
$(000)0_{0,0}$	0.0	$(000)1_{0,1}$	0.0
$(000)1_{1,1}$	36.74865833(18)	$(000)1_{1,0}$	18.26852034(21)
$(000)2_{0,2}$	69.927424779(90)	$(0\ 0\ 0)2_{1,2}$	55.23374622(20)
			Continued on next nage

Continued on next page

		<u></u>	
Assignment	Relative Energy/cm <sup>-1</sup>	Assignment	Relative Energy/cm <sup>-1</sup>
$(000)2_{1,1}$	94.78862880(19)	$(0\ 0\ 0)2_{2,1}$	109.72086272(12)
$(000)2_{2,0}$	134.783097849(85)	$(0\ 0\ 0)3_{0,3}$	112.581744705(90)
$(000)3_{1,3}$	141.56804165(16)	$(0\ 0\ 0)3_{1,2}$	149.12799158(18)
$(000)3_{2,2}$	204.75584857(14)	$(0\ 0\ 0)3_{2,1}$	187.044320962(88)
$(000)3_{3,1}$	282.09447951(21)	$(000)3_{3,0}$	258.55209818(18)
$(000)4_{0,4}$	221.23398882(13)	$(000)4_{1,4}$	200.07359390(16)
$(000)4_{1,3}$	274.80316905(17)	$(000)4_{2,3}$	274.86519241(13)
$(000)4_{2,2}$	314.45942365(13)	$(0\ 0\ 0)4_{3,2}$	355.53663270(19)
$(000)4_{3,1}$	380.70241696(17)	$(000)4_{4,1}$	458.88854282(19)
$(000)4_{4,0}$	482.67252623(17)	$(0\ 0\ 0)\ 5_{0.5}$	300.291 819 37(14)
$(000)5_{1,5}$	325.21570198(15)	$(000)5_{1,4}$	374.60557322(19)
$(000)5_{2,4}$	414.16811769(17)	$(000)5_{2,3}$	421.40364013(17)
$(000)5_{3,3}$	500.59617555(17)	$(000)5_{3,2}$	481.97382527(21)
$(000)5_{4,2}$	604.54410353(19)	$(0\ 0\ 0)5_{4,1}$	581.03789505(16)
$(000)5_{51}$	733.679 238 47(20)	$(000)5_{50}$	709.928 031 39(28)
$(000)6_{0.6}$	444.846 163 06(16)	$(000)6_{1.6}$	421.59127545(24)
$(000)6_{1.5}$	541.18009768(17)	$(000)6_{25}$	526.69588279(16)
$(000)6_{24}$	601.23775897(20)	$(0\ 0\ 0)6_{3\ 4}$	621.62762898(26)
$(000)6_{3,3}$	658,610,017,54(19)	$(000)6_{4,3}$	727.27794342(19)
$(000)6_{4,2}$	752.187.368.14(21)	$(000)6_{\rm F,0}$	856.321.260.19(27)
$(000)6_{\pm,2}$	880,114,466,94(25)	$(000)6_{6,1}$	1009,43903553(24)
$(000)6_{60}$	1033.194.397.48(31)	$(000)7_{0.7}$	560.02288871(16)
$(000)7_{1.7}$	583 986 426 00(17)	(000)71.6	677 939 304 22(26)
$(000)7_{1,7}$	$706\ 597\ 744\ 73(19)$	$(000)7_{0.5}$	$756\ 697\ 871\ 15(21)$
$(000)7_{2,6}$ $(000)7_{2,6}$	812 761 614 04(20)	$(000)7_{2,5}$	815 794 494 78(29)
$(000)7_{4,5}$	921 895 713 09(22)	$(000)7_{4,2}$	$901\ 944\ 768\ 10(21)$
$(000)7_{4,4}$	105000013430(22)	$(000)7_{4,3}$	102744813123(20)
(000)75,3 (000)7	1000.33013433(22) 120416024157(33)	(000)75,2 (000)7-	1027.44010120(29) 118041085667(28)
$(000)7_{6,2}$ $(000)7_{-1}$	1204.10524107(33) 137808613510(42)	$(000)7_{6,1}$	135523128807(03)
$(000)7_{7,1}$	740,012,244,22(10)	$(000)7_{7,0}$	717 949 671 54(96)
$(000)8_{0,8}$	$(40.912\ 244\ 22(19)\ 870\ 404\ 747\ 17(92)$	(000)81,8	717.24307134(20) 85815012028(10)
(000)81,7	019.49414111(23) 080.999.99709(95)	$(000)8_{2,7}$	$077\ 050\ 777\ 24(28)$
$(000)8_{2,6}$	104722854662(23)	$(000)8_{3,6}$	100288115540(24)
$(000)8_{3,5}$	1047.32804002(22) 1196.42002001(22)	$(000)8_{4,5}$	1092.86110049(24) 1092.61259104(21)
(000)84,4	1120.43903921(23)	$(000)8_{5,4}$	1222.01302194(31)
$(000)8_{5,3}$	1247.20593744(27)	$(000)8_{6,3}$	1375.67291485(35)
$(000)8_{6,2}$	1399.46319716(36)	$(000)8_{7,2}$	1550.92253380(92)
$(000)8_{7,1}$	1574.67821030(40)	$(000)8_{8,1}$	1745.04628423(71)
$(000)8_{8,0}$	1768.8011952(12)	$(0\ 0\ 0)9_{3,6}$	1256.04258983(37)
$(000)9_{5,5}$	1466.01807609(29)	$(000)9_{5,4}$	1444.85699315(33)
$(000)9_{6,4}$	1618.89606329(78)	$(0\ 0\ 0)9_{6,3}$	1595.30062769(45)
$(000)9_{8,2}$	1989.3518853(12)	$(000)9_{8,1}$	1965.59708929(71)
$(000)10_{2,8}$	1433.02877436(45)	$(000)10_{2,9}$	1264.51222585(41)
		$(000)10_{4,7}$	1550.69438979(36)
		$(000)10_{6,5}$	1838.69968772(49)
		$(000)11_{6,5}$	2107.81091190(56)

Table 2 – Continued from previous page

<sup>a</sup> The uncertainties of the last few digits are indicated in parentheses and related to the 68 % confidence level. The *ortho* and *para* states are separated within the table and provided with their energy values relative to the  $(0\,0\,0)_{0,0}$  and  $(0\,0\,0)_{1,1}$  energies, respectively. The relative energy values of the vibrationally excited rotational states determined in this study are reported in the Supplementary Information.

While the NICE-OHMS measurements were performed to explore the relative energies of the  $(0\ 0\ 0)J_{K_a,K_c}$  states with  $J \leq 8$ , construction of the underlying paths demanded the inclusion of several higher-J states, up to J = 11. These rotational energy levels, important junction points (hubs) within the entire experimental SN of H<sub>2</sub><sup>18</sup>O,[105] are the lower states of 16 724 lines out of the 26 696 observed transitions with distinct assignment.

The relative energies of Table 2 are highly useful to experimentalists whose desire is to utilize their spectra to derive precise relative upper-state energy values from a bunch of linear schemes [see Fig. 4.5(a)].[72, 182] (Although the uncertainties of the lower-state energies are often neglected during the analysis of these connection schemes,[72, 182] they might affect significantly the accuracy of the upper-state energies deduced.[104, 105]) Taking all the vibrational bands into consideration, altogether 188 energy levels are redetermined with high accuracy, of which 93, 5, 11, 35, 23, and 21 lie on the vibrational parents (000), (120), (021), (200), (101), and (002), respectively. Although the 7000–7350 cm<sup>-1</sup> region includes observable lines with lower states on the (010) bending fundamental, they are not linked to the *ortho* or the *para* ground state by paths. Hence, such target lines were not selected by the SNAPS method for measurement.

The relative energy values of Table 2 have an uncertainty of  $2-4 \times 10^{-7}$  cm<sup>-1</sup> for most states, while those passing through very weak lines [such as  $(0\,0\,0)8_{8,0}$  and  $(0\,0\,0)9_{8,2}$ ] are accurate to  $\sim 1 \times 10^{-6}$  cm<sup>-1</sup>. This accuracy, albeit based on near-infrared transitions visiting highly excited vibrational states, is at least one (but often two) orders of magnitude higher than that[105] achieved *via* the direct traversal of the  $(0\,0\,0)$  pure rotational levels.[148]

### Benchmark-quality reference line list

The pure rotational energies of Table 2 allow the construction of an ultrahighaccuracy transition dataset, called benchmark line list, for both *para-* and *ortho*- $H_2^{18}O$ , obeying one-photon, electric-dipole selection rules (for technical details, see Supplementary Note 6 of Ref. [129]). The intensities of the lines were taken from Ref. [102]. The benchmark line list, extending between 0–1250 and 5900–8380



Figure 4.10: Graphical representation of the high-accuracy benchmark line list of  $H_2^{18}O$ . The wavenumbers are calculated from the SNAPS-based relative energies of Table 2, while the one-photon, electric-dipole-allowed intensities are derived from the Einstein-A coefficients of Ref. [102]. The green squares and the red triangles denote transitions observed in this study and in Ref. [66], respectively, while the blue dots correspond to SNAPS-predicted lines. In spite of the fact that the direct experimental transitions are limited to the ranges 5–15 and 7000–7350 cm<sup>-1</sup>, the predicted lines extend between 0–1250 and 5900–8380 cm<sup>-1</sup>. The points related to the upper left, lower left, and upper right quadrants represent P' - P'' = 0 - 0, 4 - 4, and 4 - 0, transitions, respectively, where P' and P'' denote the polyad numbers of the upper and lower states, respectively.

 $cm^{-1}$ , is available in the Supplementary Information, its graphical overview is in Fig. 4.10.

The benchmark line list contains 1546 transitions, about half of which are below 1250 cm<sup>-1</sup>. The majority of these lines is now known with an accuracy two or even three orders of magnitude higher than before.[145, 146, 147, 148, 149, 150, 88, 151, 152, 153] 557 transitions are characterized by an intensity larger than  $5 \times 10^{-24}$  cm molecule<sup>-1</sup>, corresponding to  $1 \times 10^{-26}$  cm molecule<sup>-1</sup> by taking into account the atmospheric abundance of H<sub>2</sub><sup>18</sup>O. These ultraprecise lines may serve as calibration standards for high-resolution experiments in atmospheric spectroscopy. The benchmark line list also contains 54 (mostly *ortho-para*) doublets, with separations less than 0.01 cm<sup>-1</sup>; among them there are 17 lines characterized with  $S > 5 \times 10^{-24}$  cm molecule<sup>-1</sup> help to assess the former measurements performed in this region [145, 146, 147, 148, 149, 150, 88, 151, 152, 153] and claimed to be accurate to  $10^{-6} - 10^{-4}$  cm<sup>-1</sup>. Pressure-shift effects appear to lower significantly the accuracy of the previously observed lines.



Figure 4.11: Theoretical 0/1 splittings up to J = 10 for various vibrational bands of  $\mathbf{H}_2^{18}\mathbf{O}$ . This figure displays the 0/1 splitting values (see Sec. 1) obtained with the GENIUSH code.[84, 85, 173] The points denoting the 0/1 splittings are related to the left vertical axis, while the bars representing the uncertainties of the 0/1 splittings are plotted on the right vertical axis. For splittings illustrated with dots, the  $K_c = 0$  energy is greater than its  $K_c = 1$  pair, while for those indicated with squares the converse relation is satisfied. The red and yellow points with a green box designate the  $(000)8_{8,0/1}$  and  $(120)8_{8,0/1}$  splittings, respectively, which are contained in the two paths from  $(000)0_{0,0}$  to  $(000)1_{0,1}$  (see Fig. 2.6). These two 0/1 splittings are determined to be  $7.112(59) \times 10^{-6}$  and  $4.63(14) \times 10^{-6}$  cm<sup>-1</sup>, respectively.

## Theoretical 0/1 splittings and relative doublet positions

The two elements of the  $(v_1 v_2 v_3) J_{J,0/1}$  pairs, here called 0/1 splittings, have either *ortho* or *para* character. The 0/1 splittings and the relative doublet positions



Figure 4.12: Theoretical 0/1 splittings up to J = 10 for various vibrational bands of  $H_2^{16}O$ . The points and bars of this figure have the same meaning as in Fig. 4.11.

have been obtained through first-principles computations for a series of rovibrational states up to J = 10, within the ground vibrational state and the vibrational bands of the P = 4 polyad. For an improved comprehension of the characteristics of the 0/1 splittings, nuclear-motion computations were performed both for H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>16</sup>O, with their results depicted in Figs. 4.11 and 4.12, respectively.

The following four PESs have been utilized: CVRQD,[174, 175] including as well as excluding the diagonal Born–Oppenheimer correction (DBOC, the D part of the additively built CVRQD PES), POKAZATEL,[103] and FIS3.[176] The CVRQ(D) and POKAZATEL PESs have been developed for  $H_2^{16}O$ , while the FIS3 PES was designed explicitly for  $H_2^{18}O$ . Each computation with a specific PES was repeated with two large but sufficiently different vibrational bases, resulting in eight distinct computations. Designating a relative doublet position or a 0/1 splitting with v, its uncertainty is given as  $U(v) = 2 \operatorname{SD}(v)$ , where  $\operatorname{SD}(v)$  is the empirical standard deviation of the individual estimates for v taken from the eight computations. As the relevance of the relative doublet positions, whose values are deposited in the Supplementary Information, is explained in Sec. 4.3, only the 0/1 splittings are analyzed here in detail.

Upon the increase of J, the computed 0/1 splittings show a roughly exponential decrease, see Figs. 4.11 and 4.12. Typical splitting values of  $10^{-5}$  cm<sup>-1</sup> (corresponding to 300 kHz) are reached by J = 8 for both water isotopologues. The uncertainties of the theoretical 0/1 splittings have to be well below  $10^{-6}$  cm<sup>-1</sup> for the network-based determination of the lowest *ortho* energy value (see Sec. 2). This accuracy is ensured by most 0/1 splitting values with  $J \ge 8$ .

The 0/1 splittings, as well as their accuracy, depend strongly on the underlying vibrational excitation. The computational inaccuracy principally originates from the PES, with gradually increasing relative uncertainties as J increases. Certain points, such as  $(120)7_{7,0/1}$ , do not follow the trends and/or have very large uncertainties. Furthermore, there are a few cases [namely,  $(021)6_{6,0/1}$ ,  $(021)9_{9,0/1}$ , and  $(101)J_{J,0/1}$  above J = 5 in the case of H<sub>2</sub><sup>18</sup>O, and  $(021)9_{9,0/1}$ ,  $(021)10_{10,0/1}$ , and  $(101)J_{J,0/1}$  above J = 5 for H<sub>2</sub><sup>16</sup>O], where the  $K_c = 1$  states lie higher than their  $K_c = 0$  counterparts. These anomalies are due to pronounced couplings among the vibrational parents.

Comparing Fig. 4.11 with Fig. 4.12, a very similar pattern of 0/1 splittings can be observed for  $H_2^{18}O$  and  $H_2^{16}O$ . The rotational constants and the rotational energies of  $H_2^{18}O$  are smaller than those of  $H_2^{16}O$ , but the 0/1 splittings can be larger for  $H_2^{18}O$  than for  $H_2^{16}O$ . The reason behind this behavior is that these splittings depend on the differences of the rotational constants, not on their absolute values.

## The lowest ortho-H<sub>2</sub><sup>18</sup>O energy

To transfer the accuracy of the relative *ortho* energies determined to their absolute energy values, one needs to know the energy of the lowest *ortho*-H<sub>2</sub><sup>18</sup>O state,  $(000)1_{0,1}$ , with a few times  $10^{-7}$  cm<sup>-1</sup> accuracy. The best literature estimates for the  $(000)1_{0,1}$  energy, 23.754 902(5)[183] and 23.754 906(7) [184] cm<sup>-1</sup>, are an order of magnitude less accurate than this, implying the need for the precise redetermination of this quantity *via* indirect approaches.

Following the traditional spectroscopic protocol to derive the  $(0\ 0\ 0)1_{0,1}$  energy of  $H_2^{18}O$ , an EH model was fitted to a set of energy differences on the ground vibrational state. The fitting dataset was built by joining six pure rotational lines [66] and artificial transitions formed by  $\Lambda$ -shape pairs [see Fig. 4.2(b)] of NICE-OHMS lines. From this dataset, all the lines with pure rotational *para* states with  $J \leq 2$  were excluded. Since these 'external' energy levels are missing from the reduced dataset, their energies serve to validate the fitted EH model below J = 3. The absence of the *para* ground state from the dataset implies that not only the absolute *ortho*, but also the absolute *para* energies are undetermined by the reduced set. This means that one can judge the accuracy of the (lowest) absolute EH energies by analyzing the fitting residuals for the external states.

Using a reduced set of 124 transitions, a weighted least-squares fit was performed, utilizing a 49-parameter (16th-order) Watson-type Hamiltonian.[185, 186, 187, 188] The fitting output including the optimized parameters and the fitting residuals is available in the Supplementary Information. The EH model yields an estimate of 23.754 904 61 cm<sup>-1</sup> for the energy of the  $(0\,0\,0)1_{0,1}$  state and reproduces the SNAPS-based energies of the external states perfectly, *i.e.*, well within their uncertainty limits. Based on this observation, one can expect that the lowest *ortho* energy is similarly accurate; thus, the largest energy uncertainty of the external states,  $1.9 \times 10^{-7}$  cm<sup>-1</sup>, is assigned as an uncertainty to the EH-predicted lowest *ortho* energy. The uncertainty for the  $(0\,0\,0)1_{0,1}$  energy is ten times smaller than that of its former determinations.[183, 184] There is an independent, network-theoretical approach to extract the lowest ortho energy of  $H_2^{18}O$ . This approach is based on the compilation of shortest linedisjoint paths from the para ground state to the ortho one, utilizing 0/1 splittings as virtual lines. Adding all the 0/1 splittings with  $J \leq 10$  to the design transition set, the SNAPS procedure returned only two such paths, both given in Fig. 4.13. These paths lead to two estimates for the  $(000)1_{0,1}$  energy, 23.7549037(11) and 23.7549037(14) cm<sup>-1</sup>. These values deviate by only  $9.1 \times 10^{-7}$  cm<sup>-1</sup> from the EH estimate, which is inside their uncertainty intervals.

Owing to the long paths, going through more than 40 quantum states, and the necessary inclusion of very weak transitions in the feasible paths, with uncertainties larger than  $5 \times 10^{-7}$  cm<sup>-1</sup>, the path-based estimates of the lowest *ortho* energy are slightly less precise than the EH value obtained. Therefore, the EH estimate, 23.754 904 61(19) cm<sup>-1</sup>, is recommended as the new reference value for the lowest *ortho* energy of H<sub>2</sub><sup>18</sup>O.

#### 4.4. Conclusions and Summary

The noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS) technique, [97, 98, 31, 28, 169] facilitating the ultraprecise measurement of large numbers of rovibrational transitions in the near infrared region (in



Figure 4.13: Two line-disjoint paths for the determination of the lowest ortho energy of  $H_2^{18}O$ . The arrangement of the energy levels and the lines, as well as the notation employed are similar to that of Figs. 4.3 and 4.4. Transitions of paths #1 and #2 are highlighted with green and blue arrows, respectively, while the two (light green) dashed lines are reproduced from Ref. [66]. The starting and ending points of these paths,  $(000)0_{0,0}$  and  $(000)1_{0,1}$ , are surrounded by orange and purple squares, respectively. Common states of paths #1 and #2 are positioned in the middle row of this figure. The dotted magenta lines highlighted by red frames illustrate virtual transitions whose wavenumbers are 0/1 splittings (see also the caption to Fig. 4.11). Invoking the Ritz principle and the law of uncertainty propagation [see the equations of Fig. 1(d)] along with the wavenumbers and uncertainties of the virtual lines, paths #1 and #2 give (by chance, numerically identical) estimates 23.754 903 7(11) and 23.754 903 7(14) cm<sup>-1</sup> for the (000)1<sub>0,1</sub> energy, respectively.

the present case 7000–7350 cm<sup>-1</sup>), has been used to accurately determine the entire pure rotational quantum-level structure of the second most abundant water isotopologue, H<sub>2</sub><sup>18</sup>O, up to J = 8, where J is the rotational quantum number. These pure rotational states are often the lower states of experimental transitions in water spectroscopy;[75, 142, 30, 105] thus, their accurate knowledge is important for a large number of applications, including some in analytical chemistry.[167] All the relative energies derived with a relative accuracy of ~ 10<sup>-11</sup> form the basis of a benchmark line list assembled during this study, containing more than 1500 transitions. Since water is omnipresent in our universe, the entries of this line list, supplemented with a similar set of transitions for H<sub>2</sub><sup>16</sup>O,[129] serve as useful references for the calibration of high-resolution spectroscopic measurements, as well as for the evaluation of the accuracy characterizing future spectral recordings in the ranges of 0–1250 and 5900–8380 cm<sup>-1</sup>.

As this study proves, transferring the experimental accuracy from the near infrared to the microwave and mid-infared region is possible by taking advantage of the results of advanced quantum-chemical computations [172] and the design principles of the Spectroscopic-Network-Assisted Precision Spectroscopy (SNAPS) scheme.[129] SNAPS is an intelligent and universally applicable network-theorybased protocol, able to provide connected sets of transitions, forming paths and cycles in the language of network theory, possible targets of ultraprecise observations. Furthermore, SNAPS helps to evaluate the utility of and the possible discrepancies related to newly probed lines. The original SNAPS approach [129] was extended in this study with a novel feature, the so-called  $\Lambda$ -correction scheme, accelerating the detection of extremely weak transitions. SNAPS is a particularly useful tool for ultrahigh-resolution laser spectroscopists trying to survey spectroscopic features of isolated molecules of chemical interest with the highest possible efficiency.

Among the 195 carefully selected near-infrared Lamb-dip lines of  $H_2^{18}O$  recorded during this study, the unparalleled instrumental characteristics (resolution, accuracy, and sensitivity) of the NICE-OHMS setup allowed to resolve transitions which cannot be probed under ordinary (*e.g.*, Doppler-limited) experimental conditions, like *ortho-para* doublets. Sensitivity of the NICE-OHMS technique also means that lines observed also include those of disturbing species, like  $H_2^{16}O$  and  $HD^{18}O$ , present in a tiny fraction of the sample. Notably, the Lamb-dip profiles of the disturbing  $H_2^{16}O$  and  $HD^{18}O$  lines are quite similar to those typical of the  $H_2^{18}O$ transitions, making their confusion rather easy. Nevertheless, the SNAPS cycles constructed during this study and the relatively large deviations from an effective Hamiltonian (EH) model help to reveal if a resolved line is not the one searched for.

Appropriate resolution of extremely weak transitions required technical improvements, allowing dependable averaging of multiple scans. The measurements were also helped by the introduction of the  $\Lambda$ -correction scheme mentioned, providing accurate initial positions and allowing narrow-range frequency scans. In 2020, Wu and co-workers [189] stated that the weakest transition which has ever been measured in saturation is their CO<sub>2</sub> line with  $S = 6 \times 10^{-27}$  cm molecule<sup>-1</sup>. In this study, a four times weaker transition, with an intensity of  $S = 1.4 \times 10^{-27}$  cm molecule<sup>-1</sup>, could be observed with a reasonable accuracy of 25 kHz. These studies pave the way to the detection of even weaker transitions, like those of quadrupole lines. Such quadrupole lines of water have recently been detected in Doppler-broadened spectroscopy,[190, 191] but not in saturation and not with the expected accuracy of NICE-OHMS measurements.

To link the parity-related subcomponents formed by electric-dipole-allowed transitions measured by NICE-OHMS of the nuclear-spin isomers, *para* and *ortho*, of  $H_2^{18}O$ , accurate rotational lines taken from the literature[66] had to be utilized. It would be highly useful to record quadrupole-allowed lines *via* NICE-OHMS to establish ultraprecise connections between the appropriate subcomponents. These experiments would further validate the accuracy of microwave transitions, for example those of Ref. [66]. Since these quadrupole lines have room-temperature intensities on the order of  $10^{-28}$  cm molecule<sup>-1</sup>,[191, 190] their observation demands further technical improvements of our NICE-OHMS spectrometer.

To ensure maximum accuracy, a detailed uncertainty analysis of the line positions was conducted, including the evaluation of the short- and long-term reproducibility of the measurements. By keeping the pressure at a remarkably low level, around 0.04 Pa in most cases, an average experimental accuracy of 2.5 kHz is reached, which is even superior to that of our previous study on  $H_2^{16}O$ .[129] Experiments aimed at establishing the effect of sample pressure on the recorded lines suggest that the transitions of  $H_2^{16}O$  (see Ref. [129]) and  $H_2^{18}O$  behave similarly against pressure variation and that the pressure dependence of certain line centers are significantly higher than claimed in Ref. [166].

To convert the relative energies of this study to absolute energies for  $ortho-H_2^{18}O$ , its lowest energy had to be derived. This was achieved both via an EH fit and by a network-theoretical approach based on paths, involving small but highly accurate quantum-chemically computed ortho-para energy splittings as virtual transitions. As a result of this study, many more accurate rotational energies are available than before. The EH-based estimate for the lowest ortho- $H_2^{18}O$  energy has a smaller uncertainty than those of its previous determinations. The large number of accurate absolute energies provide benchmarks for quantum chemical computations, help to improve the accuracy of thermochemical functions at low temperatures, and are important for modelers, for example of (exo)planetary atmospheres.

The ortho-para doublet separations extracted from quantum-chemical computations can be compared directly with the present ultraprecise NICE-OHMS observations. Due to significant error compensation when differences of the rovibrational energies are formed, this comparison reveals excellent agreement between the computed and the observed separations. Although assigning the lines of the doublets is trivial in the knowledge of the (1 : 3) dip ratios, the predicted doublet separations helped to uncover accidental misassignments and calibration errors. The absolute and relative doublet positions provide benchmarks for those who would like to improve the sensitivity and resolution of their spectrometers.

The transitions detailed in the benchmark line list yielded by this study are now known with an accuracy two to three orders of magnitude higher than before. Thus, it is important to discuss how this knowledge affects entries of existing line-by-line (LBL) databanks, such as HITRAN.[30] Replacement of existing transition records would be particularly beneficial in the case of the 557 lines characterized by roomtemperature absorption intensities larger than  $5 \times 10^{-24}$  cm molecule<sup>-1</sup>, because all of these transitions are highly relevant to atmospheric modeling. While the pressure dependence of certain H<sub>2</sub><sup>18</sup>O lines has been explicitly determined during this study, it is not clear how the pressure-shift coefficients revealed could be utilized to improve the related entries of LBL databases. The pure rotational states, whose relative energies are accurately derived *via* the SNAPS scheme, are among the most important hubs in the entire experimental spectroscopic network of H<sub>2</sub><sup>18</sup>O; they are the lower states of a large number of transitions. Therefore, consideration of these ultraprecise pure rotational energy values may help to eliminate systematic errors during the determination of upper-state energies of LBL datasets.

## Supplementary Material

See the supplementary material for the list of experimental transitions recorded with the NICE-OHMS technique (Table S1), the list of experimental transitions taken from Ref. [66] (Table S2), the predicted line list and the relative rovibrational energies derived during this study (Tables S3 and S4, respectively), the output of the effective Hamiltonian fit (Table S5), two line-disjoint paths for the derivation of the lowest ortho energy of H<sub>2</sub><sup>18</sup>O (Table S6), quantum chemical 0/1 splittings, up to J = 10, for H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O (Table S7), comparison of the quantum chemical doublet separations with their experimental counterparts (Table S8), and basic cycles associated with the shortest-path-based forest of the spectroscopic network built upon by lines of Ref. [66] and this study (Table S9).

## Acknowledgements

The research described received funding from LASERLAB-EUROPE (grant no. 654148, a European Union's Horizon 2020 research and innovation programme). The work performed in Budapest received support from NKFIH (grant no. K119658), from the grant VEKOP-2.3.2-16-2017-000, and from the ELTE Institutional Excellence Program (TKP2020-IKA-05) financed by the Hungarian Ministry of Human Capacities. WU acknowledges the European Research Council for an ERC Advanced Grant (grant no. 670168). Further support was obtained from a NWO-FOM program (16MYSTP) and from the NWO Dutch Astrochemistry Network. **AIP Publishing Data Sharing Policy** 

The data that support the findings of this study are available within the article and its supplementary material.

## Chapter 5 Hyperfine-resolved near-infrared spectra of $H_2^{17}O$



## Abstract

Efforts have recently been taken in the derivation of accurate compilations of rovibrational energies of water, one of the most important reference systems in spectroscopy. Precision is desirable for all water isotopologues, although their investigation is challenged by hyperfine effects in their spectra. Frequency-comb locked NICE-OHMS (Noise-Immune Cavity-Enhanced Optical-Heterodyne Molecular Spectroscopy) allows for achieving high sensitivity, resolution, and accuracy. This technique has been employed to resolve the subtle hyperfine splittings of rovibrational transitions of  $H_2^{17}O$  in the near-infrared region. Simulation and interpretation of the  $H_2^{17}O$  saturation spectra have been supported by coupled-cluster calculations performed with large basis sets and accounting for high-level corrections. Experimental <sup>17</sup>O hyperfine parameters are found in excellent agreement with the corresponding computed values. The need of including small hyperfine effects in the analysis of  $H_2^{17}O$  spectra has been demonstrated together with the ability of the computational strategy employed of providing quantitative predictions of the corresponding parameters. 1

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: *Hyperfine-resolved near-infrared spectra of*  $H_2^{17}O$ , M. Melosso, M.L. Diouf, L. Bizzocchi, M. Harding, F.M.J. Cozijn, C. Puzzarini, W. Ubachs, J. Phys. Chem. A **125**, 7884-7890 (2021).

## 5.1. Introduction

Hyperfine parameters constitute an important source of information on physicochemical molecular properties related to electron densities and electronic structure. The nuclear quadrupole coupling is the strongest hyperfine interaction in closedshell molecules. From the associated constants, information on intramolecular interactions and on the ionic or  $\pi$  character of the bonds involving the quadrupolar nucleus can be retrieved. Nuclear spin-rotation interaction and their corresponding constants provide instead insight into the paramagnetic part of the nuclear magnetic shielding constants, and this was the motivation for investigating the hyperfine structure (HFS) of the rotational spectrum of water isotopologues containing a <sup>17</sup>O [192, 193]. Nuclear quadrupole coupling and spin-rotation interaction give rise to splittings in the rotational and rovibrational transitions (the HFS mentioned above), thus providing an experimental approach to the above-mentioned molecular properties.

However, the hyperfine effects in water tend to be small in view of its closedshell nature in the electronic ground state, thus requiring a very high resolving power to reveal subtle splittings in its spectrum. Indeed, the HFS of the  $H_2^{17}O$ rotational spectrum was resolved only in a few investigations. Besides the work reported in ref. [192], there is only the study by DeLucia and Helminger from the 1970s [194]. Both works concerned the vibrational ground state and were performed via pure rotational spectroscopy in the microwave domain. Instead, to the best of our knowledge, the HFS of the <sup>17</sup>O-containing species has never been resolved in vibrational excited states. Water is a crucial reference spectroscopic system and a comprehensive characterization is essential also for this isotopic species. As in the main isotopologue, the rovibrational states are separated into two subsets: the ortho and para nuclear-spin isomers. Ortho–para conversion represents an open issue, with the energy separation of the ortho and para states requiring to be known precisely. In the case of  $H_2^{17}O$ , an accurate determination of the energy levels cannot avoid the full characterization of its hyperfine structure.

In the past decade, the development of intracavity-based optical techniques allowed high resolution and high sensitivity to be achieved also in vibrational spectroscopy. Different groups have applied such approach to the investigation of vibrational excitation of  $H_2^{17}O$  [195, 196, 31, 179, 197]. A large number of spectral lines was accurately measured in a wide spectral region, thereby leading to the revised and updated W2020 database of rovibrational transitions and energy levels of <sup>17</sup>O-containing water[105]. However, all of these studies were Doppler-limited and no hyperfine effects could be resolved. Recently, the intra-cavity techniques were further developed and combined with high accuracy calibration, thus allowing the exploitation of the Lamb-dip effect in rovibrational spectra [198, 199, 200, 163]. In only one study, such Lamb-dip vibrational spectroscopy was applied to  $H_2^{17}O$ , although the linewidth, due to collisional and time-of-flight broadening, was still too large to resolve the HFS [201].

In the present study, we extend our previous work on the saturation spectroscopy of water [129] to the <sup>17</sup>O-containing species, thereby using the advanced capabilities of a frequency-comb locked NICE-OHMS (Noise-Immune Cavity-Enhanced Optical-Heterodyne Molecular Spectroscopy) setup to resolve, for the first time, the HFS of rovibrational transitions of  $H_2^{17}O$ . NICE-OHMS is a precision-spectroscopy technique which brings a new perspective in the field: having the sensitivity to observe saturation spectra at very low pressures and powers, it allows for the resolution of hyperfine structures in vibrational overtones, while at the same time providing an absolute frequency scale at kHz accuracy. The experimental determination of the hyperfine parameters for the vibrational state involved is supported and guided by state-of-the-art *ab initio* computations.



Figure 5.1: Layout of the experimental setup; for details see text.

Each rovibrational energy level of  $H_2^{17}O$  is uniquely labelled by 7 quantum numbers, that can be classified as vibrational quantum numbers,  $(v_1 v_2 v_3)$ , representing the excitation of the symmetric stretching, bending, and antisymmetric stretching modes, respectively, and the rotational quantum numbers. These are the total angular momentum for the end-over-end rotation J, the pseudo-quantum numbers  $K_a$  and  $K_c$  used in the designation of levels in asymmetric-top rotors, and F the total angular momentum accounting for the coupling of J with the  $^{17}\text{O}$ nuclear spin (I = 5/2). The latter coupling, which is caused by the interactions mentioned above, splits each rotational level into different but closely-spaced sublevels. For ortho- $H_2^{17}O$ , additional splittings are due to the hydrogen spins (only spin-rotation interaction), with the involved interaction being too small to produce measurable effects in the present experiment. The splittings of the energy levels generate the already mentioned HFS of the spectrum. While the HFS due to  $^{17}O$ exhibits several components typically separated by a few hundred kHz, that due to the hydrogen nuclei is expected only to give rise to a small broadening of the Lamb-dips, as already observed in a previous study on  $H_2^{16}O$  [129].

To simulate the HFS of rovibrational transitions, the hyperfine parameters of each vibrational state involved in the transition are required. In particular, relying on the additivity approximation, vibrationally averaged parameters are evaluated as the sum of their equilibrium value and the corresponding vibrational correction, with the former term computed by means of a composite scheme (see Methods). As explained in the Methods section, computations were carried out at the coupledcluster level in conjunction with large basis sets and incorporating, for equilibrium values, up to quadruple excitations. This allows for obtaining results that are converged with respect to the wave function and basis sets for both potential and property values [192, 193]. The DVR-QAK [202] scheme was employed to compute the vibrational corrections (see Methods). The hyperfine parameters under consideration are the oxygen (<sup>17</sup>O) quadrupole coupling constants,  $\chi_{ii}$ , and the spin-rotation constants of both oxygen and hydrogen,  $C_{ij}$  (*i* and *j* denote the principal inertia axes). For all of them, the equilibrium values and their vibrational



Figure 5.2: Modelling results for the 1f and 3f spectra recorded for the  $J_{KaKc} = 1_{11} \leftarrow 0_{00}$  (top panels) and the  $J_{KaKc} = 0_{00} \leftarrow 1_{11}$  (bottom panels) transitions of the (200)  $\leftarrow$  (000) overtone. The black and red lines plot the experimental data and the "best-fit" model, respectively. The stick spectra denote the positions and relative intensities of the hyperfine components (in blue) and crossover resonances (orange). The fit residuals (light green) are shown in the boxes below each panel.

correction terms are collected in the Appendix (Table 3 for the  $\chi_{ii}$  (<sup>17</sup>O)'s, Tables 4 and 5 for the  $C_{ij}$ 's of oxygen and hydrogen, respectively). These parameters have been computed for the (000) vibrational ground state as well as for the (040), (120), (021), (021), (200), (101), and (002) vibrational states. All these levels lie around 7000 cm<sup>-1</sup>, which is the frequency region explored in the present experiment.

As previously anticipated, the measurements were performed in the near-infrared region employing the NICE-OHMS apparatus developed for saturation spectroscopy, and already employed for HD [28] and the main water isotopologue [129]. In the present setup, shown schematically in Fig. 5.1, an infrared diode laser operating at 1.4  $\mu$ m is combined with a high-finesse cavity. The intracavity high power laser enabled the saturation of several rovibrational transitions of H<sub>2</sub><sup>17</sup>O, and thus the exploitation of the Lamb-dip effect with extremely narrow dip profiles. While all relevant experimental details are reported in the Methods section, important to the subsequent discussion is the fact that the frequency demodulation, intrinsic to the NICE-OHMS method, was employed both at 1*f* and 3*f*, the latter providing higher resolution, as evident in Figure 5.2. A high-stability optical frequency-comb, referenced to a Cs atomic clock, is also incorporated in the NICE-OHMS spectrometer to stabilize the infrared laser and to obtain sub-MHz accuracy on the frequency axis.

Among the vibrational states investigated computationally, the (200) state has been chosen in view of the intensity of its transitions. A number of saturation spectra were recorded for the (200)  $\leftarrow$  (000) rovibrational band at 7200 cm<sup>-1</sup>. In Fig. 5.2 two spectra are shown: the  $J_{KaKc} = 1_{11} \leftarrow 0_{00} R$ -transition from



Figure 5.3: Experimental recordings and modelling results for the 3f spectra of the  $J_{KaKc} = 2_{02} \leftarrow 1_{11}$  (top-left),  $J_{KaKc} = 2_{02} \leftarrow 3_{13}$  (top-right),  $J_{KaKc} = 6_{16} \leftarrow 5_{05}$  (bottom-left), and  $J_{KaKc} = 8_{27} \leftarrow 8_{18}$  (bottom-right) transitions of the (200)  $\leftarrow$  (000) overtone. The two top spectra pertain to the para-species, while the two bottom spectra to the ortho-species. The black and red lines plot the experimental data and the "best-fit" model, respectively. The stick spectra (blue bars) show the positions and relative intensities of the hyperfine components.

the ground state para-level and the  $J_{KaKc} = 0_{00} \leftarrow 1_{11}$  *P*-transition probing the lowest para-level in the (200) vibrationally excited state. Both 1*f* and 3*f* recordings are depicted, thereby demonstrating the superior resolution obtainable with the 3*f* demodulation scheme. Figure 5.3 collects four additional Lamb-dip spectra recorded in the high-resolution 3*f* mode, and involving transitions for both para- and ortho-H<sub>2</sub><sup>17</sup>O.

Initially, we simulated the spectra using the experimental hyperfine constants previously determined for the ground state [192] and the *ab initio* values computed in this work for the (200) upper state. Simulations of the Lamb-dip spectra based on these "first guess" values were already able to well reproduce the experimental recordings. Nevertheless, as found in the Lamb-dip investigation of the groundstate rotational spectrum [192], additional features due to crossover resonances were occasionally observed. These are also referred to as "ghost transitions", and are a well known effect in Lamb-dip saturation spectra [133]. They appear in the case of transitions with a common state (either upper or lower) and partially overlapping Doppler profiles. Here, we adopt a phenomenological treatment of such features, whose transition frequencies are given by the arithmetic mean of the frequencies of the two "interacting" transitions.

Once the simulations had been refined by including the observed crossovers, a custom Python3 routine was used to accurately model the spectral line profiles and to retrieve the experimental transition frequencies. This code is an adaptation of the tool used in ref. [203] to model the astrophysical spectra of the amidogen radical isotopologues. To reproduce the recorded spectra, the 1f and 3f profile

functions are computed for each hyperfine component (also including crossovers), they are summed up, and the resulting profile is optimized versus the experimental spectra in a least-squares fashion. The 1f and 3f profile functions are defined as derivatives of the typical dispersive NICE-OHMS signals [16]:

$$P(\nu)_{1f} = \frac{4A\left[\gamma^2 - 4(\nu - \nu_0)^2\right]}{\left[\gamma^2 + 4(\nu - \nu_0)^2\right]^2}$$
$$P(\nu)_{3f} = \frac{3072A\gamma^2(\nu - \nu_0)^2}{\left[\gamma^2 + 4(\nu - \nu_0)^2\right]^4} - \frac{96A}{\left[\gamma^2 + 4(\nu - \nu_0)^2\right]^2}$$

The adjustable parameters are the line position  $\nu_0$ , the line intensity A, and the width of each component  $\gamma$ . If necessary, a cubic polynomial is also fitted to reproduce the spectral background. The final agreement between the modelled and experimental spectra is fairly good, as shown in Figs. 5.2 and 5.3. In these plots, the optimized positions and intensities of the hyperfine components and crossovers are depicted as stick spectra.

From the line profile analysis of the spectra recorded, the "best-fit" frequencies were retrieved as explained above; then, they were assigned to the corresponding transitions in terms of quantum numbers and analyzed using the SPFIT routine of the CALPGM suite [204] and adopting the standard Watson Hamiltonian in the  $I^r$  representation [205]. For blended transitions, the retrieved frequencies were assigned to the intensity-weighted average of the involved components. The analysis of 30 hyperfine frequencies led to the very first determination of the nuclear quadrupole coupling and spin-rotation constants of <sup>17</sup>O for vibrationally-excited  $H_2^{17}O$ . Their values, together with their  $3\sigma$  uncertainties, are collected in Table 1. From this table, a very good agreement between experiment and theory is noted, the computed values lying well within the experimental uncertainty. As already pointed out in ref. [192], the level of theory employed is able to provide quantitative prediction of hyperfine parameters. The same accuracy is therefore expected for all computational data reported in the Appendix. Since the inclusion of the spin-rotation constants of hydrogen has a negligible effect on the simulation of the rovibrational spectra of ortho- $H_2^{17}O$ , such interaction was not considered in the final analysis.

As an additional finding, the absolute frequencies of the unperturbed rovibrational transitions recorded in the present study can be retrieved from the analysis. They can be obtained by subtracting the energy contribution due to the hyperfine interactions from the measured hyperfine components. The results of this analysis are collected in Table 2. The absolute accuracy of these transitions is improved by about two orders of magnitude with respect to the line frequencies listed in the W2020 database[105] for  $H_2^{17}O$ .

To conclude, the present study reports on the first observation of hyperfineresolved rovibrational transitions of the (200)  $\leftarrow$  (000) overtone band of H<sub>2</sub><sup>17</sup>O, recorded in the saturation regime by means of the NICE-OHMS technique. Six transitions, four pertaining to the para-species and two to the ortho-species, were investigated and the nuclear quadrupole coupling and spin-rotations constants of oxygen derived for the (200) vibrational level. A very good agreement, within  $3\sigma$ , is

Parameter	<sup>a</sup> Unit	Exp. <sup>b</sup>	Theory <sup>c</sup>
$\chi_{aa}$	MHz	-8.86(9)	-8.824
$\chi_{bb}$	MHz	-1.86(14)	-1.780
$C_{aa}$	kHz	-48.(16)	-40.89
$C_{bb}$	kHz	-38.(9)	-33.01
$C_{cc}$	kHz	-19.(4)	-21.09
No. data		30	
rms	kHz	10.8	

Table 1:  ${}^{17}$ O hyperfine parameters for  $H_2{}^{17}$ O in the (200) excited vibrational level.

<sup>a</sup> Being the nuclear quadrupole coupling tensor traceless, only two  $\chi$ 's are given.

<sup>b</sup> Values in parenthesis denote  $3\sigma$  uncertainties in unit of the last quoted digit.

<sup>c</sup> Results retrieved from Tables 3 and 4.

found with the corresponding computations. As pointed out in refs. [192, 193] and confirmed in the present study, quantitative predictions of the hyperfine parameters can be provided, which however cannot be obtained routinely. For the first time, the variational DVR-QAK scheme has been extended to compute the vibrational corrections for excited states. Finally, the unperturbed frequencies of the observed rovibrational transitions of  $H_2^{17}O$  were determined at an unprecedented accuracy of 20 kHz, corresponding to a relative uncertainty of  $10^{-11}$ . These figures supersede by far the quality of the data available in the W2020 database for  $H_2^{17}O$ .

Table 2: Absolute transitions frequencies of rovibrational transitions in the (200)  $\leftarrow$  (000) overtone band of H<sub>2</sub><sup>17</sup>O.

Line	Frequency / MHz
$1_{11} \leftarrow 0_{00}$	216 698 971.729(20)
$0_{00} \leftarrow 1_{11}$	214 541 043.881(22)
$2_{02} \leftarrow 1_{11}$	216570396.811(10)
$2_{02} \leftarrow 3_{13}$	213423435.893(10)
$6_{16} \leftarrow 5_{05}$	218793162.770(34)
$8_{27} \leftarrow 8_{18}$	218532715.457(17)

## 5.2. Methods

## **Computational section**

The nuclear quadrupole-coupling and nuclear spin-rotation constants have been computed adopting a similar protocol as in refs. [192, 193]. The so-called equilib-

rium values were evaluated at the semi-experimental equilibrium geometry ( $r(OH) = 0.9575 \text{ Å}, \angle(HOH) = 104.51^{\circ})[206]$  using the coupled-cluster singles and doubles approach augmented by a perturbative treatment of triple excitations (CCSD(T)) [207, 208, 209, 210] in conjunction with the aug-cc-pCV6Z [211, 212] basis set. The CCSD(T) values have been augmented by higher-level corrections. These were evaluated as the difference between coupled-cluster singles, doubles, and triples (CCSDT) [213, 214, 215] and CCSD(T) employing the aug-cc-pCVXZ (X=T, Q) [216, 217, 218] basis sets ( $\Delta T$  term), as well as the difference between coupledcluster singles, doubles, triples, and quadruples (CCSDTQ) [213, 214] and CCSDT employing the aug-cc-pCVXZ (X=D, T) [216, 217, 218] basis sets ( $\Delta Q$  term). In the calculations of spin-rotation tensors, perturbation-dependent basis functions were used to ensure fast basis-set convergence, as described in refs. [219, 220]. Scalar relativistic corrections to the nuclear quadrupole-coupling tensors ( $\Delta REL$ term) have been evaluated using direct perturbation theory (DPT) [221] at the CCSD(T)/aug-cc-pCV6Z level.

As in previous studies focusing on the (000) vibrational ground state [192, 193], the DVR-QAK [202] scheme has been employed to compute the vibrational corrections to equilibrium values. In this approach, the treatment of vibrational effects is based on the variation principle and on the use of the so-called Watson Hamiltonian [186] given in terms of rectilinear dimensionless normal coordinates, and fully accounts for Coriolis interactions and anharmonic effects in the potential. Converged vibrationally averaged property values were determined by evaluating the corresponding expectation values over the vibrational wave function of the corresponding vibrational state, using a multidimensional Gauss-Hermite quadrature. For the actual computations, 11–15 quadrature points per each mode have been used to evaluate the matrix elements over the anharmonic part of the potential and 11–15 harmonic-oscillator basis functions per each mode have been used as a product basis. The vibrational corrections were calculated as the difference between the vibrationally averaged and the equilibrium values, both at the CCSD(T)level in conjunction with the aug-cc-pCVQZ [216, 217, 218] basis set. A value of -25.58(22) mb was used for the <sup>17</sup>O nuclear quadrupole moment [222].

All computations were carried out with all electrons included in the correlation treatment and using the CFOUR program package [223, 224]; for some calculations, the parallel version of CFOUR[225] has been employed. All CCSDT and CCSDTQ results were obtained with the string-based many-body code MRCC [226, 227] interfaced to CFOUR.

## Experimental section

The NICE-OHMS apparatus developed for saturation spectroscopy is described in refs. [28, 129]. In this work, a high-finesse (~ 150 000) cavity has been employed together with an infrared diode laser operating at 1.4  $\mu$ m. This laser is modulated at 305 MHz, equivalent to the free spectral range (FSR) of the cavity, for generating the side-band signals, and at 20 MHz for the cavity-lock via a Pound–Drever– Hall (PDH) stabilization scheme. In addition to the first layer of modulation at 305 MHz, a second layer of modulation is applied through dithering one of the cavity mirrors at a low frequency of 415 Hz. The doubly modulated spectroscopic signal is demodulated by a powerful lock-in system (Zurich Instruments; HF2LI), where the 1st and 3rd harmonic (1f and 3f signals, respectively) of the dither modulation are extracted. A stabilized optical frequency-comb (OFC), referenced to a Cs atomic clock, is employed to stabilize the infrared laser and the optical cavity, and to provide a frequency scale accurate to the 1 kHz level.

For spectral recordings, an enriched  $H_2^{17}O$  sample (Cambridge Isotopes; 20%  $H_2^{17}O$  isotopic purity) has been used. The spectroscopic recordings have been carried out under steady gas flow conditions, at pressures in the range of 0.1–0.3 Pa, measured by a capacitance pressure gauge.

Thanks to the highly reflective mirrors, the intra-cavity power can be increased up to 150 W. However, the intra-cavity power is matched to the oscillator strength in order to operate in the weakly saturating regime, thus avoiding significant power broadening. This results in intra-cavity powers below 1 W. The resulting linewidth of the resolved hyperfine components is mainly limited by the transit time of the molecules across the laser beam, overall yielding a width of ~ 400 kHz (full width at half maximum).

## 5.3. Acknowledgements

The authors thank A. Császár and R. Tóbiás (Eötvös Loránd Universit, Budapest) for helpful discussions and Ningjing Jiang (University of Bologna) for the wonderful TOC figure provided. This research received funding from LASERLAB-EUROPE (Grant No. 654148, European Union's Horizon 2020 research and innovation program, Project LLAMS002654). Further support was obtained from a NWO-FOM program (16MYSTP) and from the NWO Dutch Astrochemistry Network. LB acknowledges support by the Italian Space Agency (ASI; 'Life in Space' project, N. 2019-3-U.0). This research was also supported by the German BMBF through the Helmholtz Association via the PoF program Materials Systems Engineering (MSE).

## 5.4. Appendix

This appendix collects the quantum-chemical results for the hyperfine parameters of  $H_2^{17}O$ : nuclear quadrupole-coupling and spin-rotation constants of  $^{17}O$  and nuclear spin-rotation constants of hydrogens. The three tables list the equilibrium values, the vibrational corrections for each state considered, and the resulting vibrationally corrected values. The methodology is detailed in the Methods section.

Table 3: Equilibrium values, vibrational corrections, and vibrationally corrected values of the oxygen quadrupole coupling tensor (NQCT) (MHz).

	$\chi_{aa}$	$\chi_{bb}$	$\chi_{cc}$
Ec	quilibriu	m values	a
$CCSD(T)^{b}$	-8.809	-1.066	+9.876
$\Delta T^{c}$	-0.012	-0.001	+0.012
$\Delta Q^d$	+0.011	-0.001	-0.010
$\Delta \text{REL}^{\text{e}}$	-0.009	-0.014	+0.023
Sum <sup>f</sup>	-8.819	-1.082	9.901
Vibrationa	correct	ions (DV	R-QAK) <sup>g</sup>
(000)	+0.007	-0.223	+0.216
(040)	-0.067	+0.177	-0.111
(120)	+0.023	-0.353	+0.329
(021)	+0.067	-0.415	+0.348
(200)	-0.005	-0.698	+0.704
(101)	+0.023	-0.735	+0.712
(002)	+0.040	-0.760	+0.719
Vibratio	onally co	orrected v	values <sup>h</sup>
(000)	-8.812	-1.305	+10.117
(040)	-8.886	-0.905	+9.790
(120)	-8.796	-1.435	+10.230
(021)	-8.752	-1.497	+10.249
(200)	-8.824	-1.780	+10.605
(101)	-8.796	-1.817	+10.613
(002)	-8.779	-1.842	+10.620

<sup>a</sup> Computed at the semi-experimental geometry.

<sup>b</sup> Computed employing the aug-cc-pCV6Z basis.

<sup>c</sup> Difference of the NQCT at CCSDT/aug-cc-pCVQZ and CCSD(T)/aug-cc-pCVQZ

levels.

<sup>d</sup> Difference of the NQCT at CCSDTQ/aug-cc-pCVTZ and CCSDT/aug-cc-pCVTZ levels.

<sup>e</sup> Computed via DPT2 at the CCSD(T)/aug-cc-pCV6Z level.

<sup>f</sup> Sum of CCSD(T),  $\Delta T$ ,  $\Delta Q$ , and  $\Delta REL$ .

 $^{\rm g}$  Difference of vibrationally averaged and equilibrium value at the

 $\rm CCSD(T)/aug\text{-}cc\text{-}pCVQZ$  level.

<sup>h</sup> Equilibrium values augmented by the corresponding vibrational corrections.

	$C_{aa}$	$C_{bb}$	$C_{cc}$
Eq	uilibriu	n values	a
$CCSD(T)^{b}$	-22.25	-25.20	-17.48
$\Delta T^{c}$	-0.10	-0.11	-0.06
$\Delta Q^d$	+0.05	+0.08	+0.03
Sum <sup>e</sup>	-22.31	-25.22	-17.50
Vibrational	correcti	ions (DV	R-QAK) <sup>f</sup>
(000)	-6.35	-2.78	-1.02
(040)	-25.86	-2.38	+3.13
(120)	-22.93	-5.53	-0.10
(021)	-20.05	-6.82	-1.24
(200)	-18.58	-7.79	-3.59
(101)	-16.80	-8.73	-4.40
(002)	-14.45	-9.67	-4.96
Vibratio	nally co	rrected v	values <sup>g</sup>
(000)	-28.66	-28.01	-18.52
(040)	-48.16	-27.61	-14.37
(120)	-45.23	-30.75	-17.60
(021)	-42.35	-32.04	-18.74
(200)	-40.89	-33.01	-21.09
(101)	-39.10	-33.96	-21.91
(002)	-36.75	-34.89	-22.46

Table 4: Equilibrium values, vibrational corrections, and vibrationally corrected values of the oxygen spin-rotation tensor (SRT) (kHz).

<sup>a</sup> Computed at the semi-experimental geometry.

<sup>b</sup> Computed employing the aug-cc-pCV6Z basis.

 $^{\rm c}$  Difference of the SRT at CCSDT/aug-cc-pCVTZ and CCSD(T)/aug-cc-pCVTZ levels.

<sup>d</sup> Difference of the SRT at CCSDTQ/aug-cc-pCVDZ and CCSDT/aug-cc-pCVDZ levels. <sup>e</sup> Sum of CCSD(T),  $\Delta$ T, and  $\Delta$ Q

<sup>f</sup> Difference of vibrationally averaged and equilibrium value at the

CCSD(T)/aug-cc-pCVQZ level.

<sup>g</sup> Equilibrium values augmented by the corresponding vibrational corrections.

	$C_{aa}$	$C_{bb}$	$C_{cc}$	$C_{ab}^{a}$	$C_{ba}{}^{\mathrm{a}}$
	Equ	ilibrium	values <sup>b</sup>		
$CCSD(T)^{c}$	-35.45	-31.78	-33.98	-47.81	-21.01
$\Delta T^d$	+0.00	+0.00	-0.01	-0.03	-0.02
$\Delta Q^{e}$	-0.01	+0.00	-0.01	-0.03	+0.00
Sum <sup>f</sup>	-35.47	-31.78	-33.99	-47.87	-21.03
Vibr	ational c	orrectio	ns (DVI	R-QAK)	g
(000)	+1.24	+0.62	+1.51	-1.29	-0.09
(040)	+6.22	+0.43	+3.83	-26.56	+3.13
(120)	+4.24	+0.94	+3.08	-9.84	+1.30
(021)	+4.87	+1.65	+4.54	-9.07	+0.61
(200)	+2.69	+1.53	+2.65	-0.24	-0.32
(101)	+3.01	+2.08	+3.85	-0.05	-0.93
(002)	+3.10	+2.60	+4.88	+0.22	-1.51
V	ibration	ally cor	rected va	$alues^h$	
(000)	-34.23	-31.16	-32.48	-46.16	-21.13
(040)	-29.24	-31.36	-30.16	-74.44	-17.91
(120)	-31.23	-30.85	-30.91	-57.71	-19.73
(021)	-30.60	-30.13	-29.45	-56.94	-20.43
(200)	-32.78	-30.25	-31.34	-48.11	-21.35
(101)	-32.46	-29.70	-30.14	-47.93	-21.97
(002)	-32.37	-29.19	-29.11	-47.66	-22.55

Table 5: Equilibrium values, vibrational corrections, and vibrationally corrected values of the hydrogen spin-rotation tensor (SRT) (kHz).

<sup>a</sup> Please note that for the other hydrogen the  $C_{ab}$  and  $C_{ba}$  terms are inverted in sign. <sup>b</sup> Computed at the semi-experimental geometry.

<sup>c</sup> Computed employing the aug-cc-pCV6Z basis.

<sup>d</sup> Difference of the SRT at CCSDT/aug-cc-pCVTZ and CCSD(T)/aug-cc-pCVTZ levels.

<sup>e</sup> Difference of the SRT at CCSDTQ/aug-cc-pCVDZ and CCSDT/aug-cc-pCVDZ levels. <sup>f</sup> Sum of CCSD(T),  $\Delta$ T, and  $\Delta$ Q

 $^{\rm g}$  Difference of vibrationally averaged and equilibrium value at the CCSD(T)/aug-cc-pCVQZ level.

<sup>h</sup> Equilibrium values augmented by the corresponding vibrational corrections.

## Chapter 6

Parity-pair-mixing effects in nonlinear spectroscopy of HDO



## Abstract

A non-linear spectroscopic study of the HDO molecule is performed in the wavelength range of 1.36–1.42 µm using noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS). More than 100 rovibrational Lamb dips are recorded, with an experimental precision of 2–20 kHz, related to the first overtone of the O–H stretch fundamental of  $HD^{16}O$  and HD<sup>18</sup>O. Significant perturbations, including distortions, shifts, and splittings, have been observed for a number of Lamb dips. These spectral perturbations are traced back to an AC-Stark effect, arising due to the strong laser field applied in *all* saturation-spectroscopy experiments. The AC-Stark effect mixes parity pairs, that is pairs of rovibrational states whose assignment differs solely in the  $K_c$  quantum number, where  $K_c$  is part of the standard  $J_{K_a,K_c}$  asymmetric-top rotational label. Parity-pair mixing seems to be especially large for parity pairs with  $K_a \geq 3$ , whereby their energy splittings become as small as a few MHz, resulting in multi-component asymmetric Lambdip profiles of gradually increasing complexity. These complex profiles often include crossover resonances. This effect is well known in saturation spectroscopy, but has not been reported in combination with parity-pair mixing. Parity-pair mixing is not seen in  $H_2^{16}O$  and  $H_2^{18}O$ , because their parity pairs correspond to ortho and para nuclear-spin isomers, whose interaction is prohibited. Despite the frequency shifts observed for  $HD^{16}O$  and  $HD^{18}O$ , the absolute accuracy of the detected transitions still exceeds that achievable by Doppler-limited techniques.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: *Parity-pair-mixing effects in nonlinear spectroscopy of HDO*, M.L. Diouf, R. Tóbiás, F.M.J. Cozijn, E.J. Salumbides, C. Fábri, C. Puzzarini, A.G. Császár, W. Ubachs, Opt. Express **31**, 24142-24156 (2023)

## 6.1. Introduction

Most studies dealing with gas-phase rovibrational spectroscopy of small molecules utilize direct linear absorption and Fourier-transform spectroscopy [228]. In these measurements, the spectral resolution is severely limited by Doppler broadening. This situation can be improved significantly by employing saturation techniques of nonlinear spectroscopy [133]. The application of saturation techniques has the advantage that the linewidth, typically several hundred MHz under Dopplerbroadened conditions, reduces to the sub-MHz regime. Saturation techniques combined with frequency-comb-based calibration, like noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS, see Refs. [97] and [98]), can reach a spectral uncertainty below 10 kHz [33, 34, 189, 163, 129, 130, 164, 229, 230, 231, 232]. This accuracy represents an improvement over 2–3 orders of magnitude in the determination of line centers.

Based on the successful application of our NICE-OHMS apparatus [28, 233] to study the rovibrational energy-level structure of two permutationally symmetric water isotopologues,  $H_2^{16}O$  [129, 230] and  $H_2^{18}O$  [130], the principal objective of the present paper has been to conduct NICE-OHMS measurements on HD<sup>16</sup>O. This investigation was designed to obtain accurate pure rotational energies for this permutationally nonsymmetric water isotopologue. Nevertheless, there is an important, symmetry-related difference between the spectroscopy of H<sub>2</sub>O and HDO. Since H<sub>2</sub>O isotopologues contain two equivalent H nuclei, these species have two nuclear-spin isomers, called *ortho* and *para*, and the interaction between the *ortho* and *para* states is symmetry forbidden. In contrast, HDO isotopologues have a single nuclear-spin isomer, allowing the interaction of close-lying rovibrational states of opposite parity, which may become mixed under the perturbing influence of external electric fields. The extent of such interactions under conditions of saturation spectroscopy has not been explored so far and thus its magnitude has remained unknown.

Our experimental campaign yielded more than 100 Lamb-dip features, involving states in the first overtone of the O–H stretch fundamental of HD<sup>16</sup>O, with an experimental precision of 2–20 kHz. For transitions whose upper and/or lower states have  $K_a > 3$ , multi-component Lamb-dip profiles have been identified ( $K_a$  is part of the standard  $J_{K_a,K_c}$  asymmetric-top rotational label [74]). Even for single Lamb dips, frequency shifts on the order of 100 kHz were detected through a comparison of the experimental (NICE-OHMS-based) energy splittings with their counterparts derived from an effective Hamiltonian (EH) model [234]. The complex Lamb-dip profiles and the frequency shifts are explained with mixing between nearby parity pairs, that is pairs of opposite-parity rovibrational states differing only in their  $K_c$  values. To prove this interpretation, benchmark experiments have been performed for HD<sup>18</sup>O, H<sub>2</sub><sup>16</sup>O, and H<sub>2</sub><sup>18</sup>O, as well, confirming that for transitions with the same lower and upper states (a) no spectral distortions are discernible in the Lamb-dip profiles of H<sub>2</sub><sup>16</sup>O.

### 6.2. Methodological details

## **NICE-OHMS** measurements

A NICE-OHMS apparatus, shown schematically in Fig. 6.1 and described in Refs. [129] and [28], is used to record selected absorption lines of HD<sup>16</sup>O and other water isotopologues, under saturation conditions. NICE-OHMS is a special form of cavity-enhanced absorption spectroscopy (CEAS, see Ref. [235]), endowed with extreme sensitivity [97, 98, 236, 31]. In our setup, a double modulation scheme is included *via* an electro-optic modulator (EOM) for imposing sideband modulations to the central carrier frequency. A low-frequency modulation at 20 MHz is employed for Pound–Drever–Hall (PDH) locking of the laser to the optical cavity with a finesse of 150 000 and a length of 51 cm. Higher-frequency sidebands, generated at 305 MHz and matched to the free spectral range of the cavity, are used to produce the NICE-OHMS signal [98]. For further noise reduction, a low-frequency (405 Hz) wavelength dither is applied on one of the cavity mirrors. For the demodulation steps and registration of the signal, an advanced high-frequency lock-in detector (Zurich Instruments, HF2LI) is utilized.

The frequency of the external-cavity diode laser (ECDL) is calibrated *via* a fiber link to an in-house metrology station, consisting of a frequency-comb laser, a Cs clock, and a device receiving signals from the global positioning system (GPS). Through this metrology station, long-term stabilization is ensured for the beatnote of the cavity-locked laser by a slow feedback on the cavity piezo for controlled acquisition and frequency scans. This construction allows the achievement of a frequency precision below 1 kHz.

Since the generic signal of NICE-OHMS is dispersive, the additional wavelength dither on the cavity produces a symmetric line shape, resembling the second derivative of a Voigt profile if 1f demodulation is employed. For the present measurement campaign, the relative absorption of the Lamb-dip features is typically on the order of  $10^{-11}$  cm<sup>-1</sup>, while the resonance widths are approximately 400–800 kHz (full width at half maximum, FWHM). In this study, intracavity powers of 5–100 W are utilized. Low powers are typically used to probe strong transitions, for which the Lamb-dips may suffer from power broadening. In a previous study [230], it was observed that strong lines eventually exhibit doubled Lamb-dip features at high power. This phenomenon, specifically associated with the NICE-OHMS detection



Figure 6.1: Schematic layout of the NICE-OHMS setup employed during this study. NICE-OHMS = noise-immune cavity-enhanced optical-heterodyne-molecular spectroscopy, OFC = optical frequency comb, EOM = electro-optic modulator, FSR = free spectral range of the cavity, and PDH = Pound-Drever-Hall locking.

technique, is avoided here to not confuse the new features observed in this study with doubled Lamb dips.

The wavenumber coverage of our NICE-OHMS spectrometer in its current setup is 7000–7350 cm<sup>-1</sup>, limited by the tuning range of the ECDL, the highly-reflective cavity mirrors, as well as the transmission properties of certain electro-optical components. The accessible window of dipole moments, represented by the Einstein-A coefficients, falls in the interval of  $10^{-4}$ – $10^2$  s<sup>-1</sup>. Combined with the population distribution at the measurement temperature (T = 293 K), the allowed range of intensities corresponds to  $10^{-26}$ – $10^{-20}$  cm molecule<sup>-1</sup>.

## Notation

In this study, rovibrational states of water isotopologues are labelled as  $(v_1 v_2 v_3) J_{K_a,K_c}$ , where  $(v_1 v_2 v_3)$  is the vibrational assignment based on the normal-mode picture, while  $J_{K_a,K_c}$  stands for the standard asymmetric-top rotational quantum numbers [74]. The  $v_1$ ,  $v_2$ , and  $v_3$  quantum numbers correspond, respectively, to (a) the symmetric stretch, bend, and antisymmetric stretch normal modes for  $H_2^{16}O$ and  $H_2^{18}O$ , and (b) the O–D stretch, bend, and O–H stretch fundamentals for  $HD^{16}O$  and  $HD^{18}O$ . A rovibrational transition is denoted as  $(v'_1 v'_2 v'_3)J'_{K'_a,K'_c} \leftarrow$  $(v''_1 v''_2 v''_3)J''_{K''_a,K''_c}$ , where ' and " distinguish between the upper and lower states, respectively.

The parity of a  $(v_1 v_2 v_3) J_{K_a,K_c}$  state is even/odd (e/o or +/-) if  $K_c$  is even/odd. As the states  $(v_1 v_2 v_3) J_{K_a,K_c}$  and  $(v_1 v_2 v_3) J_{K_a,K_c}$  with  $|\dot{K}_c - \ddot{K}_c| = 1$  practically differ only in their parity, they form what we call a *parity pair*. This parity pair is denoted as  $(v_1 v_2 v_3) J_{K_a,K_c}/\ddot{K}_c$  if  $\dot{K}_c$  belongs to the higher-energy state. The energy difference of a parity pair is hereinafter called  $K_c$  splitting. Clearly, the parity pairs of H<sub>2</sub>O isotopologues are *ortho-para* nuclear-spin-isomer pairs. If  $U_1/U_2$  and  $L_1/L_2$  are parity pairs, then the transition doublet  $(U_1 \leftarrow L_1, U_2 \leftarrow L_2)$  is named a *parity doublet*. By convention,  $(v'_1 v'_2 v'_3) J'_{K'_a,K'_c/K'_c} \leftarrow (v''_1 v''_2 v''_3) J''_{K''_a,K''_c/K''_c}$  indicates a parity doublet whose higher- and lower-frequency lines are assigned as  $(v'_1 v'_2 v'_3) J'_{K'_a,K'_c} \leftarrow (v''_1 v''_2 v''_3) J''_{K''_a,K''_c}$ , respectively.

### Effective Hamiltonian and variational computations

There are several investigations [237, 238, 239, 240, 241, 141, 234] which have helped to determine the empirical energy-level structure of HD<sup>16</sup>O in its ground vibrational state,  $(v_1 v_2 v_3) = (000)$ . These studies involved more than 600 pure rotational Lamb-dip lines, often with resolved hyperfine structure. Based on these transitions, a global fit was performed in Ref. [234], yielding effective-Hamiltonian (EH) energies for the (000) rotational states with an accuracy of  $10^{-8}$ – $10^{-6}$  cm<sup>-1</sup>.

The empirical energies available for the (002) rotational states are considerably less accurate, they are on the order of  $10^{-3}$  cm<sup>-1</sup>, as typically obtained from Doppler-limited rovibrational spectroscopy [141]. As shown in Refs. [129, 130] and [230], small (< 0.01 cm<sup>-1</sup>) energy differences can be estimated much more accurately than  $10^{-3}$  cm<sup>-1</sup> via first-principles nuclear-motion computations, provided that the underlying energy levels share the same vibrational state and J value. Therefore, such computations have been carried out, up to J = 8, for HD<sup>16</sup>O and



Figure 6.2: Variationally computed  $K_c$  splittings of the HD<sup>16</sup>O molecule up to J = 8. Panels (a) and (b) correspond to the (000) and (002) vibrational states, respectively. The  $K_c$  splittings are plotted, with various colors, for each J value separately and connected with solid lines (the exceptions are the single J = 1 points). The  $K_c$  splittings are given both in cm<sup>-1</sup> (left vertical axes) and in Hz (right vertical axes).

 $\mathrm{HD}^{18}\mathrm{O}$  with the GENIUSH (**GE**neral rovibrational code with **N**umerical, Internalcoordinate, User-Specified Hamiltonians) code [84, 85, 173], using the potential energy surface of Ref. [175] and a sufficiently large vibrational basis set (as usual, the rotational basis is complete).

The computed  $K_c$  splittings of HD<sup>16</sup>O and HD<sup>18</sup>O, as well as the EH-based estimates of Ref. [234], are given fully in Dataset 1 (see datasets in [242]) and partly in Fig. 6.2. As apparent from panels (a) and (b) of Fig. 6.2, the variational  $K_c$  splittings of HD<sup>16</sup>O follow a monotonically decreasing trend as a function of  $K_a$ , for each J value, in the (000) and (002) vibrational states, respectively. It must be noted that the computed  $K_c$  splittings are in a remarkable agreement with their EH-based analogues in the (000) state: their deviations are on the order of 0.1–5 % relative to the actual  $K_c$  splitting values. In absolute terms, the discrepancies are well within 1 MHz when both J and  $K_a$  are larger than 2, showing the high absolute accuracy of the computed  $K_c$  splittings, especially at higher J and  $K_a$ values.



Figure 6.3: Typical symmetric Lamb dips observed for a few transitions of  $HD^{16}O$ . The relative absorption strengths are indicated along the vertical axes. The spectra are plotted in the same detuning interval, showing significant differences in the line widths. The line centers, corresponding to zero detunings and given in kHz, are the following: 218 999 237 631 [panel (a)], 218 996 338 105 [panel (b)], 215 464 997 071 [panel (c)], and 217 318 701 228 [panel (d)].



Figure 6.4: Lamb dips for a well-isolated parity doublet of various water isotopologues.

Note the asymmetric broadening for the HD<sup>16</sup>O and HD<sup>18</sup>O isotopologues, in contrast to the fully symmetric resonances of the  $H_2^{16}O$  and  $H_2^{18}O$  species. The line centers, corresponding to zero detunings and given in kHz, are the following: 213 591 493 210 [panel (a)], 213 600 053 170 [panel (b)], 213 012 275 678 [panel (c)], 213 021 144 460 [panel (d)], 219 363 999 176 [panel (e)], 219 416 311 674 [panel (f)], 218 657 009 781 [panel (g)], and 218 712 072 101 [panel (h)].



Figure 6.5: Multi-component saturation spectra detected for a parity doublet of HDO.

Panels (a) and (b) show the recordings for the  $(002)7_{6,1/2} \leftarrow (000)6_{6,0/1}$  doublet of HD<sup>18</sup>O and HD<sup>16</sup>O, respectively. In both spectra, the two outermost dips represent the main transition centers. The colors of the vertical bars are matched with the rovibrational assignments. Note that these transitions are forbidden in H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O due to *ortho-para* selection rules. Panel (c) exhibits the spectrum observed with the wavelength-modulated CEAS (WM-CEAS) technique. The symbols 1*f* and 2*f* denote the demodulation technique employed in the measurements. The detuning scale is relative to the absolute frequencies: 217 816 033 008 kHz for panel (a) and 218 444 739 748 kHz for panels (b) and (c).

## 6.3. Experimental results

#### Regular and perturbed Lamb-dip profiles

During the present NICE-OHMS study, Lamb dips were measured for more than 100 rovibrational transitions of HD<sup>16</sup>O. A number of spectral lines recorded and analyzed exhibit a typical Lamb-dip profile, similar to the cases of the symmetric water isotopologues  $H_2^{16}O$  [129, 230] and  $H_2^{18}O$  [130]. Figure 6.3 displays four symmetric Lamb dips of different strength for four transitions, exemplifying, at the same time, the remarkable signal-to-noise ratio obtained. In panels (b) and (d) of Fig. 6.3, some additional broadening is clearly visible, which is an evident proof of power broadening.

For transitions with  $\max(K'_a, K''_a) > 3$ , asymmetric Lamb-dip profiles have been found. To improve our understanding about the origin of this asymmetry, Lamb dips of a selected transition doublet, involving the  $(000)4_{4,0/1}$  and  $(002)4_{3,1/2}$ parity pairs, were recorded for four water isotopologues:  $\mathrm{HD}^{16}\mathrm{O}$ ,  $\mathrm{HD}^{18}\mathrm{O}$ ,  $\mathrm{H_2}^{16}\mathrm{O}$ , and  $\mathrm{H_2}^{18}\mathrm{O}$ . The experimental results of Fig. 6.4 show that asymmetry occurs only in the spectra of the two HDO species. This clearly suggests that the spectral distortion is due to the H $\rightarrow$ D substitution and must be related to the different nuclear-spin symmetry of H<sub>2</sub>O and HDO. For higher J and  $K_a$  values, the Lamb-dip profiles become gradually more complex, leading to multi-component spectral structures. Figure 6.5 gives an example for a parity doublet,  $(002)7_{6,1/2} \leftarrow (000)6_{6,0/1}$ , yielding very similar multicomponent features for HD<sup>16</sup>O and HD<sup>18</sup>O. In H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O, this doublet, consisting of strongly forbidden *ortho-para* transitions, is not measured. Since the variationally computed line separations are 6.07 and 6.61 MHz for HD<sup>16</sup>O and HD<sup>18</sup>O, respectively, the resonances at detunings of ±3.0 (HD<sup>16</sup>O) and ±3.3 MHz (HD<sup>18</sup>O) are the main transition centers. Our variational computations also suggest that  $(002)7_{6,2} \leftarrow (000)6_{6,1}$  is the lower-frequency line for both species. While the additional resonances are not analyzed in this extreme case, a semi-quantitative approach will be presented in Sec. 6.4 to explain the substructures of various multicomponent HD<sup>16</sup>O lines observed during this study.

To prove that the multi-component Lamb-dip profiles of HDO are not due to the special features of the NICE-OHMS method (*i.e.*, the frequency sidebands shifted by  $\pm 305$  MHz from the carrier frequency), the saturation spectrum of the HD<sup>16</sup>O parity doublet depicted in Fig. 6.5(b) was also recorded with the wavelength-modulated CEAS (WM-CEAS) technique [235]. To obtain the best resemblance with the dispersive 1*f* NICE-OHMS signal, the WM-CEAS spectrum, resulting from direct absorption, was recorded at 2*f* demodulation. The WM-CEAS technique yielded a similarly complex Lamb-dip profile, see Fig. 6.5(c), albeit at lower signal-to-noise ratio. From this observation, one can conclude that these spectral perturbations can be attributed to the use of saturation spectroscopy in general, and not to the special characteristics of the NICE-OHMS method.

## Assessment of line-center uncertainties

A list of selected HD<sup>16</sup>O transitions, whose frequencies could be extracted unambiguously, are presented in Table 1. The majority of the lines listed correspond to those cases for which single, symmetric Lamb dips were measured. For a few transitions, with frequencies set in bold face in Table 1, significant Lamb-dip asymmetry was observed. It must be stressed that no individual uncertainties are reported in Table 1, see the upcoming paragraphs for a detailed reasoning.

Under ideal circumstances, the uncertainty of the HDO line centers determined during this study should be similar to those obtained in previous studies on  $H_2^{16}O$  [129, 230] and  $H_2^{18}O$  [130]. Beyond the statistical uncertainties (2–5 kHz), there is a minor systematic effect due to frequency calibration (1 kHz). To ascertain the magnitude of pressure shifts, five HD<sup>16</sup>O transitions were studied over a set of pressure values. This analysis yielded an estimate of 4–8 kHz for the pressure-shift uncertainties of the remaining transitions measured at a pressure of 0.1–0.2 Pa. Taking all these uncertainty factors into account, the overall precision of the Lamb-dip centers reported in Table 1 is in the range of 2–20 kHz.

Table 1: A list of selected transitions observed during the present study for  $\mathrm{HD}^{16}\mathrm{O.}^{a}$ 

#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz
	0 0	1		0.00	1 1 1 1 1 1 1 1		0 0	1.
1	$4_{3,2} \leftarrow 5_{4,1}$	211255218752	34	$4_{2,3} \leftarrow 5_{1,4}$	215630896331	67	$1_{0,1} \leftarrow 0_{0,0}$	217824645006
2	$4_{3,1} \leftarrow 5_{4,2}$	211264320484	35	$2_{2,1} \leftarrow 3_{2,2}$	215722128619	68	$2_{0,2} \leftarrow 1_{1,1}$	217836884655
3	$2_{0,2} \leftarrow 3_{3,1}$	211744649702	36	$2_{1,2} \leftarrow 2_{2,1}$	215761267929	69	$2_{1,1} \leftarrow 2_{0,2}$	217896321707
4	$2_{1,2} \leftarrow 3_{3,1}$	212040920563	37	$4_{1,3} \leftarrow 3_{3,0}$	215763215736	70	$4_{1,3} \leftarrow 3_{2,2}$	218091469253
							Conti	inued on next page

[242]).

m 11. 1

			abie	o 1 Continue	a from pretious pag	10		
#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz	#	Assignment	Frequency/kHz
5	$3_{2,2} \leftarrow 4_{3,1}$	212893380771	38	$2_{0,2} \leftarrow 3_{0,3}$	215992511353	71	$2_{1,2} \leftarrow 1_{1,1}$	218133155517
6	$3_{2,1} \leftarrow 4_{3,2}$	212961789398	39	$2_{1,2} \leftarrow 3_{1,3}$	216017150744	72	$1_{1,1} \leftarrow 0_{0,0}$	218192618433
7	$3_{0,3} \leftarrow 3_{3,0}$	213071606762	40	$3_{1,2} \leftarrow 3_{2,1}$	216067168586	73	$2_{0,2} \leftarrow 1_{0,1}$	218265598825
8	$2_{2,1} \leftarrow 3_{3,0}$	213393875116	41	$5_{1,4} \leftarrow 5_{2,3}$	216069120601	74	$5_{2,3} \leftarrow 5_{1,4}$	218267454989
9	$2_{2,0} \leftarrow 3_{3,1}$	213407644235	42	$4_{1,3} \leftarrow 4_{2,2}$	216099435929	75	$2_{1,1} \leftarrow 1_{1,0}$	218306340106
10	$3_{0,3} \leftarrow 4_{2,2}$	213407826955	43	$3_{2,2} \leftarrow 4_{1,3}$	216271857536	76	$3_{0,3} \leftarrow 2_{1,2}$	218315704705
11	$4_{3,2} \leftarrow 4_{4,1}$	213591493161	44	$2_{1,2} \leftarrow 3_{0,3}$	216288782215	77	$5_{1,4} \leftarrow 5_{1,5}$	218411396736
12	$4_{3,1} \leftarrow 4_{4,0}$	213600053221	45	$5_{1,4} \leftarrow 4_{3,1}$	216318468066	78	$5_{1,4} \leftarrow 5_{0,5}$	218528878204
13	$4_{1,3} \leftarrow 4_{3,2}$	213891431851	46	$44,1 \leftarrow 44,0$	216390846543	79	$3_{2,1} \leftarrow 2_{2,0}$	218544467143
14	$4_{1,3} \leftarrow 5_{2,4}$	213946914959	47	$4_{4,0} \leftarrow 4_{4,1}$	216391002295	80	$4_{3,2} \leftarrow 3_{3,1}$	218667138981
15	$5_{1,4} \leftarrow 5_{3,3}$	213980435634	48	$1_{1,1} \leftarrow 2_{1,2}$	216450017996	81	$5_{4,2} \leftarrow 4_{4,1}$	218707043907
16	$3_{1,2} \leftarrow 4_{2,3}$	214269098930	49	$4_{3,2} \leftarrow 5_{2,3}$	216539480025	82	$5_{4,1} \leftarrow 4_{4,0}$	218707875972
17	$4_{3,1} \leftarrow 5_{3,2}$	214437102684	50	$2_{0,2} \leftarrow 2_{1,1}$	216746361259	83	$3_{2,2} \leftarrow 3_{1,3}$	218747922447
18	$4_{3,2} \leftarrow 5_{3,3}$	214450795065	51	$5_{3,3} \leftarrow 5_{3,2}$	216751348607	84	$3_{1,3} \leftarrow 2_{0,2}$	218885916082
19	$1_{0,1} \leftarrow 2_{2,0}$	214548840462	52	$3_{1,3} \leftarrow 3_{1,2}$	216778728414	85	$2_{2,1} \leftarrow 2_{0,2}$	218996338105
20	$4_{2,3} \leftarrow 4_{3,2}$	214723994038	53	$3_{0,3} \leftarrow 2_{2,0}$	216782500605	86	$4_{3,2} \leftarrow 5_{0,5}$	218999237631
21	$3_{2,2} \leftarrow 3_{3,1}$	214771692247	54	$4_{3,1} \leftarrow 4_{3,2}$	216803145429	87	$5_{2,4} \leftarrow 5_{1,5}$	219074884146
22	$4_{2,3} \leftarrow 5_{2,4}$	214779477149	55	$2_{2,1} \leftarrow 3_{1,2}$	216889150425	88	$6_{4,3} \leftarrow 5_{4,2}$	219156438857
23	$3_{2,1} \leftarrow 3_{3,0}$	214833573282	56	$5_{2,4} \leftarrow 4_{3,1}$	216981955478	89	$64,2 \leftarrow 54,1$	219160293903
24	$1_{1,1} \leftarrow 2_{2,0}$	214916813889	57	$3_{1,3} \leftarrow 2_{2,0}$	216994346943	90	$5_{3,3} \leftarrow 5_{2,4}$	219172874489
25	$6_{4,3} \leftarrow 5_{5,0}$	215087471023	58	$2_{1,2} \leftarrow 2_{1,1}$	217042632138	91	$5_{2,4} \leftarrow 4_{2,3}$	219339389708
26	$6_{4,2} \leftarrow 5_{5,1}$	215091816331	59	$3_{2,2} \leftarrow 3_{2,1}$	217048884659	92	$2_{2,1} \leftarrow 1_{1,0}$	219406356492
27	$3_{2,2} \leftarrow 4_{2,3}$	215250815000	60	$2_{2,0} \leftarrow 2_{2,1}$	217127991606	93	$2_{2,0} \leftarrow 1_{1,1}$	219499879187
28	$3_{1,2} \leftarrow 4_{1,3}$	215290141481	61	$3_{2,1} \leftarrow 4_{1,4}$	217132050435	94	$4_{4,0} \leftarrow 4_{3,1}$	219588336492
29	$3_{0,3} \leftarrow 3_{2,2}$	215399860259	62	$3_{2,1} \leftarrow 4_{0,4}$	217318701228	95	$4_{4,1} \leftarrow 4_{3,2}$	219593939070
30	$2_{0,2} \leftarrow 2_{2,1}$	215464997071	63	$5_{2,3} \leftarrow 4_{3,2}$	217360552700	96	$2_{2,0} \leftarrow 1_{0,1}$	219928593355
31	$3_{0,3} \leftarrow 4_{0,4}$	215556734694	64	$5_{2,3} \leftarrow 5_{2,4}$	217416035798	97	$3_{2,1} \leftarrow 2_{1,2}$	220077671240
32	$3_{1,3} \leftarrow 4_{1,4}$	215581930240	65	$3_{1,2} \leftarrow 2_{2,1}$	217510323548	98	$4_{2,3} \leftarrow 3_{1,2}$	220091053247
33	$3_{1,3} \leftarrow 3_{2,2}$	215611706593	66	$3_{1,2} \leftarrow 3_{1,3}$	217766206377		. ,	

a 1. 1.

 $\frac{33 \quad 3_{1,3} \leftarrow 3_{2,2} \quad 215 \, 611 \, 706 \, 593 \quad 66 \quad 3_{1,2} \leftarrow 3_{1,3} \quad 217 \, 766 \, 206 \, 377}{a}$ The vibrational states  $(v'_1 v'_2 v'_3) = (0 \, 0 \, 2)$  and  $(v''_1 v''_2 v''_3) = (0 \, 0 \, 0)$  are not indicated in the rovibrational assignments. The plain frequencies are expected to be accurate to 100 kHz or better. The bold values, corresponding to transitions with significant spectral asymmetry around their Lamb dips, may have larger uncertainties (presumably less than 1 MHz). The lines of this table are given as a text file in Dataset 2 (see datasets in

Table 2: Experimental and effective-Hamiltonian  $K_c$  splittings of HD<sup>16</sup>O up to  $J = 5.^a$ 

Parity pair	$\Delta^{\operatorname{expt}}(K_c)/\operatorname{kHz}$	$\Delta^{\rm EH}(K_c)/\rm kHz$	$\delta/\mathrm{kHz}$	Frequency combination
$1_{1,0/1}$	80578326	80 578 309	17	$F_{68} - F_{30} + F_{65} - F_{40} - F_0 + F_{32} - F_{84} + F_{85} - F_{92}$
$2_{1,1/2}$	241561624	241561638	-13	$F_{97} - F_{61} + F_0 + F_{40} - F_{65} + F_{36} - F_{58}$
$2_{2,0/1}$	10278268	10278233	36	$F_{65} - F_{40} - F_0 + F_{32} - F_{57}$
$3_{1,2/3}$	481779626	481779631	$^{-5}$	$F_{66} - F_{40} - F_0 + F_{32} - F_{52}$
$3_{2,1/2}$	50236344	50236309	34	$F_{33} - F_{32} + F_0$
$3_{3,0/1}$	824754	824 663	91	$F_{21} - F_{27} + F_{16} - F_{40} - F_0 + F_{61} - F_{23}$
$4_{1,3/4}$	797487096	797487146	-50	$F_0 + F_{40} - F_{28}$
$4_{2,2/3}$	143727314	143727265	48	$F_{16} - F_{40} - F_0 + F_{61} - F_{23} + F_{37} - F_{42}$
$4_{3,1/2}$	5702838	5702811	28	$F_6 - F_{61} + F_0 + F_{40} - F_{16} + F_{27} - F_5$
$4_{4,0/1}$	55034	54619	414	$F_{11} - F_{18} + F_{15} - F_{45} + F_5 - F_{27} + F_{16} - F_{40} - F_0 + F_{61} - F_6$
-, -, -				$+F_{54}-F_{12}$
$5_{1,4/5}$	1180323536	1180323570	-34	$F_{87} - F_{91} + F_{16} - F_{40} - F_0 + F_{61} - F_6 + F_{20} - F_{34}$
$5_{2,3/4}$	310533410	310533412	$^{-2}$	$F_{14} - F_{37} + F_{23} - F_{61} + F_0 + F_{40} - F_{16} + F_{27} - F_5 + F_{45} - F_{41}$
$5_{3,2/3}$	22307474	22307476	$^{-1}$	$F_{15} - F_{45} + F_5 - F_{27} + F_{16} - F_{40} - F_0 + F_{61} - F_6 + F_{54} - F_{17}$
$5_{4,1/2}$	486638	486536	103	$F_2 - F_{54} + F_6 - F_{61} + F_0 + F_{40} - F_{16} + F_{27} - F_5 + F_{45} - F_{15}$
, ,				$+F_{18}-F_{1}$
$5_{5,0/1}$	3624	3 2 6 0	363	$F_{26} - F_{89} + F_1 - F_{18} + F_{15} - F_{45} + F_5 - F_{27} + F_{16} - F_{40} - F_0$
				$+F_{61}-F_6+F_{54}-F_2+F_{88}-F_{25}$

<sup>a</sup> The first column contains the  $J_{K_a,J-K_a/J-K_a+1}$  assignment of parity pairs, without indicating their vibrational state, (000). The last column specifies which frequency combinations have been taken to obtain the experimental  $K_c$  splittings,  $\Delta^{\exp t}(K_c)$ . Symbol  $F_i$  (i > 0) corresponds to the frequency of the line listed with serial number i in Table 1, while  $F_0 = 20\,459\,990.5 \pm 0.3$  kHz is the extremely accurate frequency of the (000)32,1  $\leftarrow$  (000)41,4 microwave transition taken from Ref. [241]. The effective-Hamiltonian (EH) splittings,  $\Delta^{\operatorname{EH}}(K_c)$ , are derived from the EH model of Ref. [234]. The fourth column includes the signed  $K_c$ -splitting deviations, defined as  $\delta = \Delta^{\exp t}(K_c) - \Delta^{\operatorname{EH}}(K_c)$ .

As noted in Sec. 6.3, those HDO lines with  $\max(K'_a, K''_a) > 3$  produce distorted spectra even when saturation-spectroscopy techniques other than NICE-OHMS are employed. Thus, the possible frequency shifts due to the asymmetry effects observed cannot be uncovered through a direct comparison with results of independent nonlinear spectroscopic methods. For this reason, an indirect procedure is chosen to provide at least a partial assessment for the accuracy of our NICE-OHMS lines. This approach involves the comparison of the experimental  $K_c$  splittings, related to the ground vibrational state and determined by our NICE-OHMS transition dataset, with their counterparts deduced from the pure rotational EH model of Ref. [234].

Numerical values of the  $K_c$  splittings, together with the frequency combinations employed, are presented in Table 2. Table 2 shows that there are a number of deviations larger than our experimental precision, 2–20 kHz, but all deviations remain smaller than 0.5 MHz. (Note that in our earlier study [129] on H<sub>2</sub><sup>16</sup>O, no systematic deviations were observed during the EH analysis of the pure rotational energy levels.) When plotting the unsigned  $K_c$ -splitting deviations as a function of the EH-based  $K_c$  splittings (see Fig. 6.6), it can be observed that these deviations are the largest where the  $K_c$  splittings are the smallest. Although there is no asymmetry in the Lamb dips used to derive the  $K_c$  splitting of the (000)3<sub>3,0/1</sub> pair, a relatively large deviation (91 kHz) can be seen for  $(J, K_a) = (3, 3)$ . Apparently, the centers of symmetric Lamb dips may also become shifted in our nonlinear spectroscopic experiments. Based on the fourth column of Table 2, the underlying transitions may have uncertainties on the order of 100 kHz for max $(K'_a, K''_a) \leq 3$ and even significantly higher (probably less than 1 MHz) for max $(K'_a, K''_a) > 3$ .

## 6.4. Phenomenological Lamb-dip-profile analysis

As mentioned in Sec. 6.3, during this study significant perturbations have been observed for the Lamb dips of  $HD^{16}O$  and  $HD^{18}O$  lines. For a parity doublet of the two HDO species, see panels (a)–(d) of Fig. 6.4, highly asymmetric Lamb-dip shapes were identified, which are similar to the typical profiles resulting from an (optical) AC-Stark effect [243, 244]. In this section, an attempt is made to find a semi-quantitative explanation for the complex Lamb dips of HDO.



Figure 6.6: Unsigned  $K_c$ -splitting deviations as a function of the individual  $K_c$ -splittings.

The  $K_c$  splittings and the unsigned deviations are taken from the third and fourth columns of Table 2, respectively. The data point pertaining to the  $(000)J_{K_a,J-K_a/J-K_a+1}$  parity pair is labelled as  $(J, K_a)$ . The horizontal green strip at 20 kHz represents the typical experimental reproducibility of the NICE-OHMS lines.



Figure 6.7: Illustration of the extra resonances observed during the present study. The panels of this figure show (a) the transitions produced by parity-pair mixing, (b) the crossover resonances in V (left) and  $\Lambda$  (right) schemes, and (c) the nonuplet formed by the lines of panel (a) and their cross-overs. In the V ( $\Lambda$ ) scheme, the two general (cyan) transitions share a common lower (upper) state. The parity pairs  $U = (U_1, U_2)$  and  $L = (L_1, L_2)$  belong to different vibrational states. The parity of a state is indicated within the ket symbol. The kets  $|l\rangle$  and  $|u\rangle$ of panel (b) stand for arbitrary lower and upper states, respectively.  $\Delta_X(K_c)$  and  $V_X$  are the  $K_c$ splitting and the (halfway) virtual state of  $X = (X_1, X_2)$ , respectively. The arrows in solid blue, dashed gray, and dotted red/green/yellow represent dipole-allowed (a-type), dipole-forbidden (ftype), and cross-over (c-type) lines, respectively. The labels on the arrows designate the resonance frequencies. Although  $L_1$  and  $U_1$  are chosen here to have opposite parity, the reverse case can also be realized (see Supplement 1 Fig. S1). Both cases occurred during this study. The possible frequency orderings of the nine lines are presented in Supplement 1 Table S1. The line frequencies relative to  $c_0$  can be expressed as a combination of the two splitting values (see Supplement 1 [242] Sec. S1).

# General framework: Stark-induced parity-pair mixing and cross-overs

We postulate that the cause of the significant perturbations in the Lamb dips of HDO originate in an interaction (mixing) of parity pairs. Since intramolecular perturbations occur only between quantum states of the same parity, the interaction mechanism of parity pairs must be related to an external cause. Such cause can be found in the intense laser field within the cavity, inducing an AC-Stark effect [245, 246] between the two states of a parity pair. An argument supporting our hypothesis stems from perturbation theory, underpinning that interactions become larger when the interacting states, that is the two states of a parity pair in our case, are in proximity. The fact that spectral perturbations do not occur for  $H_2O$ , where parity pairs correspond to non-interacting *ortho-para* nuclear-spin-isomer pairs, further supports our assumption on parity-pair mixing in HDO.

Figure 6.7(a) displays how extra resonances can occur in the presence of closelying parity pairs. The lines with frequencies  $a_1$  and  $a_2$  are dipole-allowed (atype) transitions, following dipole-selection rules. With the decrease of the  $K_c$ splittings, the AC-Stark mixing of parity pairs becomes more significant and thus makes the dipole-forbidden (parity-preserving, f-type) lines, with frequencies  $f_1 = a_2 - \Delta_U(K_c)$  and  $f_2 = a_1 + \Delta_U(K_c)$  [see Fig. 6.7(a) and Supplement 1 [242] Sec. S1], quantum mechanically allowed in an intensity-borrowing process. Although the ftype transitions coincide with quadrupole lines on the frequency scale, they are are much stronger than generic quadrupole transitions. All the lines of Fig. 6.7(a) can be detected in saturation spectroscopy, based on the excitation of velocity components with  $v_z = 0$ , where  $v_z$  is the molecular velocity along the intra-cavity laser-beam propagation.

As explained in Ref. [3], the saturation conditions can induce additional lines, called cross-over (c-type) resonances, due to probing velocity classes different from those leading to regular Lamb dips. If two transition frequencies are close to each other in a V/ $\Lambda$  scheme [see Fig. 6.7(b)], a c-type resonance appears at the average of the two frequencies. In fact, such a c-type resonance is delivered by the interaction of the counter-propagating carrier beams with Doppler-shifted  $v_z \neq 0$  velocity classes. Therefore, cross-overs are only produced when the Doppler profiles overlap for the two transitions of a V/ $\Lambda$  scheme. As obvious from Fig. 6.7(b), these c-type resonances can be treated as artificial transitions  $V_U \leftarrow l$  and  $u \leftarrow V_L$ , where u/ldenotes an arbitrary upper/lower state and  $V_X$  is a virtual state at halfway between the two states of the  $X = (X_1, X_2)$  pair. Cross-over features were previously observed in (hyper)fine spectra [247, 248, 249] and also in the Stark-perturbed spectrum of neon [250].

In our case, the c-type resonances are connected to parity pairs, as illustrated in Fig. 6.7(c). Considering all possible V and  $\Lambda$  schemes between triplets  $(L_1, V_L, L_2)$  and  $(U_1, V_U, U_2)$ , five distinct cross-overs with frequencies  $c_0$ ,  $c_1$ ,  $c_2$ ,  $C_1$ , and  $C_2$  can be specified. The  $c_0$  line, which pertains to the V scheme of  $(C_1, C_2)$  [and also to the  $\Lambda$  scheme of  $(c_1, c_2)$ ], can be viewed as a higher-order cross-over resonance. In total, the nine near-infrared resonances form a nonuplet, as shown in Fig. 6.7(c).

The intensities of the extra (f- and c-type) lines do not straightforwardly result from Wigner-6J symbols, as is the case for hyperfine transitions. These intensities can be obtained from the numerical solution of the optical Bloch equations by integrating signals over the entire velocity distribution within the Doppler profile, as was shown in a recent study on HD [233]. As a result, the extra lines may acquire positive or negative excess intensity and thus generate Lamb dips or Lamb peaks, respectively [251, 233]. In some cases, the c-type lines may be more intense than the a-type transitions.

## Assignment of complex Lamb-dip spectra of $\mathrm{HD^{16}O}$

Relying on the EH-based and variational  $K_c$  splittings of the (000) and (002) vibrational states, respectively, our semi-quantitative approach is followed in this subsection to understand the relative positions of the observed extra lines at a sub-MHz level of accuracy, but no explanation is provided for the resonance intensities. Below, some typical multi-component Lamb-dip spectra of HD<sup>16</sup>O are documented and analyzed. Furthermore, a complex saturation spectrum is presented around the  $(002)3_{2,1/2} \leftarrow (000)3_{3,0/1}$  doublet (see Supplement 1 Sec. S2), where the atype lines are characterized with well-isolated symmetric Lamb-dip profiles. This spectrum (see Fig. S2) shows two f-type resonances shifted from the a-type lines by  $\pm 824.7$  MHz, corresponding to the  $K_c$  splitting of the  $(000)3_{3,0/1}$  parity pair. **The**  $(002)4_{3,1/2} \leftarrow (000)4_{4,0/1}$  **doublet** 

As discussed in Sec. 6.3, highly asymmetric Lamb-dip profiles have been obtained for the  $(002)4_{3,1/2} \leftarrow (000)4_{4,0/1}$  doublet. By performing a wider scan


Figure 6.8: Saturation spectrum recorded for the  $(002)4_{3,1} \leftarrow (000)4_{4,0}$  transition. Panels (a) to (c) contain the lines corresponding to the energy-level diagram of panel (e) with resonance frequencies  $a_2$ ,  $C_2$ , and  $f_2$ , respectively. Panel (d) plots the peak intensity of the dipole-forbidden  $f_2$  line as a function of the intra-cavity laser power, P. The conventions applied in panel (e) are described in the caption to Fig. 6.7. The MHz values of panel (e) denote the  $K_c$  splittings of the upper and lower parity pairs. The parity of the individual states is indicated in square brackets. The vertical bars of panels (a)–(c) represent the theoretically predicted resonance positions relative to  $a_2$ , whose absolute frequency is 213 600 053 170 kHz.

around these a-type transitions, four additional resonances have been identified. Figure 6.8 shows the saturation signal surrounding the  $(002)4_{3,1} \leftarrow (000)4_{4,0}$ transition, where the extra resonances are blue-shifted by 27.7 MHz [panel (b)] and 54.8 MHz [panel (c)]. These values coincide almost perfectly with the predicted positions of  $f_2$  and  $C_2$  relative to  $a_2$ , 27.3 and 54.6 MHz, respectively. The intensity of the  $f_2$  transition, which is much smaller than that of the  $a_2$  and  $c_2$  lines, is strongly dependent on the intra-cavity circulating power [see panel (d)]. This intensity dependence provides further evidence for parity-pair mixing in HD<sup>16</sup>O. The mirror image of Fig. 6.8(a)-(c), where the two additional resonances are redshifted by 27.7 and 54.8 MHz from the  $(002)4_{3,2} \leftarrow (000)4_{4,1}$  line, is not shown here. Since the  $(002)4_{3,1/2}$  splitting, 8.6 GHz, is considerably larger than the Doppler width in the 7000–7350 cm<sup>-1</sup> region, the cross-overs probing the upper virtual state could not be observed.

The  $(002)4_{4,0/1} \leftarrow (000)5_{5,1/0}$  doublet

Figure 6.9 displays the Lamb-dip spectra of the  $(002)4_{4,0/1} \leftarrow (000)5_{5,1/0}$ doublet for HD<sup>16</sup>O, H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O. This parity doublet, whose energy-level scheme [see Fig. 6.9(g)] is an example for the case reverse to that of Fig. 6.7(c), could not be measured in HD<sup>18</sup>O, because its frequencies are not covered by our laser. For H<sub>2</sub>O, single narrow Lamb dips are observed, once more demonstrating that the perturbative effects only occur in HDO, where the nuclear-spin distinction of H<sub>2</sub>O species is lifted. In the complex Lamb-dip profile of HD<sup>16</sup>O, the f-type transitions,  $f_1$  and  $f_2$ , acquire almost no intensity. On the other hand, two strong c-type lines,  $C_1$  and  $C_2$ , can be found near  $a_1$  and  $a_2$ , respectively. The cross-overs linked with the upper virtual state, which should be in principle measurable, were not studied.

#### The $(002)6_{5,2/1} \leftarrow (000)6_{5,1/2}$ doublet

The first example for a complex Lamb-dip spectrum, where the nonuplet lines introduced in Fig. 6.7(c) could be unambiguously resolved, is shown in Fig. 6.10. In this case, the two  $K_c$  splittings are small enough (<80 MHz) to keep the extra lines within the Doppler profiles of the a-type transitions. The nine resonances, whose relative positions agree reasonably well with their theoretical estimates, are contained in a single spectrum covering a frequency range of ±60 MHz. The presence of the (higher-order)  $c_0$  resonance, which can be considered as a novel spectral feature, could be confirmed by studying the ±10 MHz detuning window at high intracavity power [see Fig. 6.10(b)].

The  $(002)5_{5,0/1} \leftarrow (000)6_{5,1/2}$  doublet

In the previous subsections, Lamb-dip spectra were analyzed whereby the  $K_c$  splitting is smaller for the lower-energy parity pair than for the higher-energy one  $[i.e., \Delta_U(K_c) > \Delta_L(K_c)$  in general terms]. The  $(0\,0\,2)5_{5,0/1} \leftarrow (0\,0\,0)6_{5,1/2}$  doublet of Fig. 6.11 demonstrates the opposite case, with  $\Delta_U(K_c) < \Delta_L(K_c)$ , involving the inversions  $a_1 \leftrightarrow a_2$ ,  $C_1 \leftrightarrow c_2$ , and  $C_2 \leftrightarrow c_1$  in the ordering of the line positions. The a-type transitions of Fig. 6.11, from which the f-type lines are shifted by  $\pm 7.2$ 



Figure 6.9: Lamb dips for a close-lying parity doublet of different water isotopologues. For HD<sup>16</sup>O, a multi-component Lamb-dip profile was detected, while the saturation spectra of H2<sup>16</sup>O and H2<sup>18</sup>O exhibit only a single resonance. The analogous HD<sup>18</sup>O line, which should be very similar to that of HD<sup>16</sup>O, falls outside the 7000–7350 cm<sup>-1</sup> region. The line centers, corresponding to zero detunings and given in kHz, are the following: 209 986 146 435 [panel (a)], 209 986 249 858 [panel (b)], 214 512 580 150 [panel (c)], 214 513 924 110 [panel (d)], 213 838 639 897 [panel (e)], and 213 840 105 039 [panel (f)]. Note the one-to-one correspondence between the vertical bars of the spectra and the arrows of the energy-level diagram of panel (g). The theoretical positions of the individual resonances are relative to  $a_1$  [panel (a)] or  $a_2$  [panel (b)]. For further details on the structure of the energy-level scheme, see the captions to Figs. 6.7 and 6.8.



Figure 6.10: Saturation spectrum involving the  $(002)6_{5,2/1} \leftarrow (000)6_{5,1/2}$  doublet. Panel (a) displays a scan of ±60 MHz around the central crossover,  $c_0 = 215\,836\,700\,683$  kHz, corresponding to zero detuning. The environment of this  $c_0$  line was remeasured at increased intra-cavity power, shown separately in panel (b). Note again the one-to-one correspondence between the vertical bars of the Lamb-dip spectrum [panel (a)] and the lines of the energy-level diagram [panel (c)]. The vertical bars indicate the theoretical positions of the nine lines relative to  $c_0$ . In this figure, as well as in subsequent figures, the scale of the vertical axis is not specified, because this information is not necessary to understand the spectral features observed.

MHz, are characterized with a fairly small separation, 28.2 MHz. The  $f_1$  and  $c_2$  resonances are not plotted, they could not be measured due to an overlapping  $H_2^{16}O$  line.

The  $(002)7_{6,1/2} \leftarrow (000)7_{6,2/1}$  doublet

As emphasized in Sec. 6.3, the saturation spectra of HD<sup>16</sup>O reach a higher degree of complexity with increased J and  $K_a$  values. Figure 6.12 shows an interesting example, with an energy-level scheme similar to that of Fig. 6.10, but with significantly smaller (< 10 MHz)  $K_c$  splittings. In view of the dense structure of this multi-component spectrum, an additional measurement was performed with 3f demodulation of the NICE-OHMS signal, thereby obtaining a higher resolving power [131] as compared to the 1f detection scheme.

Although the strongest resonance is assigned to the  $c_0$  cross-over in the 1f profile, the a-type transitions, separated by 8.6 MHz, are the most intense in the 3f recording. As in the preceding examples, the f-type components are extremely weak (in fact, they are barely detectable in the present case). The four c-type resonances are clearly visible in the 3f spectrum and agree particularly well with the theoretical positions relative to  $c_0$ . The two green cross-overs,  $C_1$  and  $C_2$ , appear as Lamb-dips, while the red lines,  $c_1$  and  $c_2$ , produce Lamb peaks, a typical sign-reversing effect in saturation spectroscopy [251, 3]. In the 3f spectrum, further resonances are also observed, for which no assignment can be given based on our semi-quantitative model.



Figure 6.11: Lamb-dip spectrum detected for the  $(002)5_{5,0/1} \leftarrow (000)6_{5,1/2}$  doublet. Note the one-to-one correspondence between the vertical bars of the spectrum [panel (a)] and the lines of the energy-level diagram [panel (b)]. The vertical bars provide the theoretical positions of the nine lines relative to the  $c_0$  resonance coinciding with the line center at 213065604238 kHz. The detuning region below -13 MHz, which is overlapped with the  $(200)1_{1,0} \leftarrow (000)2_{2,1}$ transition of H<sub>2</sub><sup>16</sup>O, is not presented. Since the  $K_c$  splitting is larger for the lower-energy parity pair, the ordering of the nine resonances is different from that of Fig. 6.10 (in fact, the difference is connected to the  $a_1 \leftrightarrow a_2$ ,  $C_1 \leftrightarrow c_2$ , and  $C_2 \leftrightarrow c_1$  inversions).

#### The $(002)8_{7,1/2} \leftarrow (000)7_{6,2/1}$ and $(002)8_{7,1/2} \leftarrow (000)7_{7,0/1}$ doublets

During the spectral investigations, a large number of Lamb dips were found mimicking a double-spike phenomenon, for which two examples are given in Fig. 6.13. For both examples, the upper states correspond to the  $(0\,0\,2)8_{7,1/2}$  parity pair with a 0.6 MHz splitting. In one case [Fig. 6.13(a)], the lower-state  $K_c$  splitting is 2.3 MHz, while the same splitting reduces to 10 kHz in the other example [Fig. 6.13(b)]. Due to their fairly high intensity, the  $C_1$ ,  $c_0$ , and  $C_2$  cross-overs can be easily recognized in Fig. 6.13(a), but no convincing assignment emerged for the remaining resonances.

As to the other doublet, the minuscule lower-state splitting leads to the coalescence of those lines with the same upper state at the current resolution of our NICE-OHMS spectrometer (200–300 kHz). Therefore, the prominent features of Fig. 6.13(b) can be ascribed to the  $t_1$ ,  $t_2$ , and  $t_3$  triplets defined in Fig. 6.13(d), which are located at detunings of -0.3, 0, and 0.3 MHz, respectively. In those cases when both splittings become smaller 200 kHz, only a single-spike feature, resembling a regular Lamb-dip with some spectral distortions, can be detected with our setup.

#### 6.5. Conclusions

Motivated by our previous studies on  $H_2^{16}O$  [129, 230] and  $H_2^{18}O$  [130], the original aim of this study was the derivation of kHz-accuracy energy levels within the ground vibrational state of HD<sup>16</sup>O, by measuring near-infrared transitions *via* the NICE-OHMS saturation-spectroscopy technique. In principle, saturation spec-



Figure 6.12: Lamb-dip spectrum recorded for the  $(002)7_{6,1/2} \leftarrow (000)7_{6,1/2}$  doublet. Panels (a) and (b) are related to 1f and 3f demodulation signals, respectively. The nine resonances, which appear to be better resolved in the 3f spectrum, are associated with the lines of the energy-level scheme of panel (c). As in Figs. 6.10 and 6.11, the theoretical positions marked with vertical bars are relative to the central resonance,  $c_0 = 215\,196\,861\,851$  kHz. As clear from panels (a) and (b), the Lamb dips of the a-type transitions are somewhat shifted from the theoretical predictions.

troscopy enables the extraction of line frequencies with a few kHz uncertainty, corresponding to a 100–1000 times improvement in comparison to the MHz-level accuracy of Doppler-broadened approaches. Previously, over 50 000 rovibrational lines have been detected for  $\rm HD^{16}O$ , linking some 10 000 of its quantum states in the electronic ground state [141, 252].

In the present study, Lamb dips were recorded for more than 100 rovibrational transitions in the first overtone of the O–H stretch fundamental of HD<sup>16</sup>O, yielding line positions with an experimental reproducibility of 2–20 kHz. For transitions with max( $K'_a, K''_a$ ) > 3, multi-component Lamb-dip profiles with highly varying complexity were observed. Analyzing the experimental (NICE-OHMS-based)  $K_c$  splittings of parity pairs (that is, pairs of opposite-parity energy levels differing only in their  $K_c$  values) in the ground vibrational state, significant deviations were identified from predictions provided by an accurate effective-Hamiltonian (EH) model [234]. Even in view of the frequency shifts revealed, the line centers of symmetric Lamb dips still have an absolute accuracy on the order of 100 kHz, leading to a ten times improvement with respect to the uncertainties of Doppler-limited HD<sup>16</sup>O lines.

The spectral perturbations discovered in the Lamb-dip profiles of HD<sup>16</sup>O transitions can be semi-quantitatively described by assuming that an (optical) AC-Stark effect causes mixing between the states of parity pairs. This assumption was verified by measuring transition doublets with the same assignment for four water isotopologues:  $H_2^{16}O$ ,  $H_2^{18}O$ ,  $HD^{16}O$ , and  $HD^{18}O$ . The comparison of the results obtained for the different species suggests that (a) there is no perturbation in the near-infrared Lamb-dip spectra of  $H_2^{16}O$  and  $H_2^{18}O$ , and (b) the perturbative effects are equally present in  $HD^{16}O$  and  $HD^{18}O$ . The reason behind the dissimilar behavior of  $H_2O$  and HDO is that the parity pairs of  $H_2O$  are *ortho-para* nuclear-spin-isomer pairs, preventing their significant interaction. This means that the distortion effects are related to the reduction of the molecular symmetry under the  $H \rightarrow D$  replacement. Moreover, it is shown that the multi-component spectral features are not caused by the sidebands of the NICE-OHMS technique, but result from saturation spectroscopy as such.

To establish a semi-quantitative model, a general four-state scheme of two parity pairs is presented, explaining the appearance of extra resonances in the saturation spectra of HDO. In this scheme, four infrared lines (two dipole-allowed and two dipole-forbidden) are specified, where parity-pair mixing yields intensity for the two dipole-forbidden transitions, making them quantum mechanically allowed. Furthermore, cross-over resonances, previously observed in non-linear spectroscopy but not in connection to parity-pair mixing of polyatomic molecules, may also occur in the multi-component Lamb-dip profiles of HDO, leading to altogether nine near-infrared resonances in our four-state scheme.

As illustrated for eight transition doublets, the experimental positions of the nine resonances, relative to the central cross-over, agree reasonably well with their theoretical (EH-predicted and/or variationally-computed) counterparts. Thus, the good matches between the experimental and theoretical relative positions confirm the assignments provided for the individual frequency components. The theoretical



Figure 6.13: Typical double-spike Lamb-dip features identified during the present study. Panels (a) and (c) visualize the saturation spectra of the  $(002)8_{7,1/2} \leftarrow (000)7_{7,0/1}$  and  $(002)8_{7,1/2} \leftarrow (000)7_{6,1/2}$  doublets, respectively, together with the associated energy-level schemes in panels (b) and (d), respectively. Owing to the tiny  $K_c$  splitting of the  $(000)7_{7,0/1}$  pair, only the unresolved triplets of lines, sharing the same upper state and denoted with  $t_1$ ,  $t_2$ , and  $t_3$  [see also panel (d)], can be seen in panel (c).

predictions also helped to find the weak forbidden lines for the  $(002)3_{2,1/2} \leftarrow (000)3_{3,0/1}$  transition doublet (see Supplement 1 Sec. S2), whose lines exhibit symmetric saturation spectra, but their frequency shifts are larger than 90 kHz. These weak signals demonstrate that the AC-Stark perturbations occur even in those cases when there is no asymmetry around the Lamb dips of the dipole-allowed transitions.

Although our four-state scheme provides unique assignments for the resonances of complex saturation spectra in HDO, a sophisticate quantum-chemical model is needed for a fully quantitative description of the multi-component Lamb-dip profiles and the frequency shifts observed. This model should consider (a) the usual conditions applied in saturation spectroscopy, (b) the dynamic coupling between lower and upper states by the laser field, (c) the AC-Stark interaction between the two states of parity pairs, and (d) the 2J + 1 Stark-induced "sub-levels" of the rovibrational states [244, 253]. A set of optical Bloch equations, involving the possible sub-levels, might deal with all the coherences, also including cross-over resonances, as shown recently for HD [233] and for general multi-state interaction schemes [254, 255, 256]. Since the cited papers investigate interactions between states with the same parity, their formulas cannot be employed directly for the complex Lamb-dip shapes of HDO, where the AC-Stark effect takes place between the two energy levels of parity pairs.

#### Acknowledgements

The authors thank Prof. Ad van der Avoird (Radboud University Nijmegen) for insightful discussions on the symmetries of quantum states of water isotopologues.

### Chapter 7 Summary and outlook

Our highly sensitive NICE-OHMS apparatus has been used to measure a multitude of lines in the different isotopologues of water. More than five hundred frequencies of line centers have been determined at unprecedented accuracy.

In the first three chapters, these accurately measured rovibrational lines have been used in parallel with a spectroscopic network (SNAPS) approach. The main challenge of these studies was to measure a large amount of lines while keeping their uncertainties at the level of 10 kHz or below. Every single line measured needed to be individually treated with care. The SNAPS procedure involves a selection of 'important' lines for setting up the network. To make sure that no errors arose in the extraction of individual transitions, closing cycles for verification in the network was essential. Thanks to implementation of cycles, experimental mistakes were avoided and corrected. By extending the cycles to accurately measured rotational transitions from literature, we have even found some discrepancies which could be attributed to underestimated uncertainty values in those measurements. This then helped us discard some rotational lines that were needed to include high rotational quantum states in the network.

At high J rovibrational levels "quasi degeneracy" in the ortho-para doublets is approached; for increasingly higher J levels the splitting becomes smaller. By this means the two different subsets of para and ortho levels can be connected. In a spectroscopic experiment these close-lying levels also appear in a doublet of nearby resonances, which is challenging to resolve. For example, as shown in Fig. 2.4, the closest doublet measured in  $H_2^{16}O$  is separated by 1.5 MHz, while for  $H_2^{18}O$  the doublet is only split by 286 kHz, as shown in Fig. 4.7. These doublet spectra cannot be resolved in a Doppler-broadened spectrum. One of the main conclusions of the precision saturated absorption studies was that the gap between ortho and para levels could be accurately determined. By invoking the SNAPS approach with the ab initio calculation of the para-ortho splitting at high J, the absolute splitting between the ground para state and the ground ortho state were retrieved with extreme accuracy. This 'magic number' has been retrieved for two vibrational states, (200) and (000)) in the main isotopologue, and for the ground vibrational (000) of  $H_2^{18}O$ .

By combining the measured accurate rovibrational transition frequencies, with the magic number and with some extremely accurate frequencies of rotational lines as obtained from literature, absolute excitation energies of levels up to J = 8 are determined. In an alternative analysis an effective Hamiltonian was used to fit the data collected for the absolute level energies. For the ground vibrational level of both species  $H_2^{16}O$  and  $H_2^{18}O$ , a  $14^{th}$  order Watsonian function could fit and reproduce all the obtained results with high fidelity. However, for the (200) excited state, the vibrational levels are perturbed by the other vibrational levels in the same polyad number. To be able to extract this perturbation a complete set of measurements of all the nearby vibrational states would need to be performed. In the effective Hamiltonian description the interactions between the various vibrational levels within a polyad should be described at a high accuracy level. This would be a large undertaking and this task is reserved for future investigations. The rotational structure of the (010) lowest bending mode is isolated from such perturbations and the question is whether it can be described without including vibrational interactions. It is also essential to note that the effective Hamiltonian typically describes a Born-Oppenheimer approach without inclusions of non-adiabatic, QED and relativistic effects. It will be a major challenge, both for theory and experiment, to be sensitive for and test these molecular effects.

The investigation of the  $H_2^{17}O$  isotopologue focuses on the hyperfine structure. We showcase in chapter V the resolving power of our NICE-OHMS setup, in particular by making use of the 3f demodulation option. It is for the first time that hyperfine structure is resolved in rovibrational transitions in the water molecule. The extracted hyperfine constants based on the few measured lines, where the hyperfine splitting could be resolved, match very well with their theoretical prediction. A SNAPS approach has been tried on this isotopologue, however it proved too hard to complete. Additionally, only transitions in one band could be very well measured and studied. It remains a challenge for future research to apply the SNAPS method to  $H_2^{17}O$ .

In an attempt to extend the SNAPS approach to the HDO isotopologue, more than 60 rovibrational lines were measured for this species in the NICE-OHMS saturation setup. It was discovered that many closed cycles had large discrepancies and inconsistencies. Consequently, an effective Hamiltonian fit was used in HDO to verify the results. Large deviations, i.e. at the level of several 100 kHz, were found depending on the value of the  $K_c$  splitting. This splitting typically represents the separation between a specific ortho/para doublet in the "homonuclear" species. The doublet splitting tends to become closer in energy for high J and high  $K_a$ quantum numbers. Subsequent detailed studies revealed that the observed spectral lineshapes gradually become more asymmetric mostly when  $J \geq 4$  and  $K_a \geq -1$ 4. Another test within the SNAPS framework was performed for quantum levels limited to  $J \leq 4, K_a \leq 3$ . Even in that case deviations from the EH fit were still observed. It was concluded that some perturbation is at play in HDO under the measurement conditions of high-power saturation. The perturbation effect is attributed to the interaction between  $K_c$  doublet states, which have different parities. In the presence of an electric field, produced by the laser intensity, states of opposite parity couple, as in a Stark effect. As the laser field produces such field we postulate that the origin of the perturbation resides in an AC-Stark effect. At high J and for  $K_c$  splittings smaller than 1 MHz, the individual pairs of spectral lines merge into a complex modulated lineshape.

Interestingly, due to the coupling of opposite parity states, dipole forbidden transitions become visible. The extra lines find their origin in the mixing of opposite parity levels. In addition to these forbidden transitions becoming observable, crossover transitions which are specific to the saturation technique are observed as well. If all the transitions, allowed, forbidden and crossover are added into a single spectrum, the complexities of the lines at high J can be understood. As of yet we could not perform a fully quantitative AC Stark effect calculation to explain all

the different perturbations and observed extra resonances with very accurate shifts and line intensities. Such calculation remains a challenge for future studies.

## Part II

## Hydrogen deuteride (HD)

Chapter 8

## Lamb-dips and Lamb-peaks in the saturation spectrum of HD

#### Abstract

The saturation spectrum of the R(1) transition in the (2-0) band in HD is found to exhibit a composite line shape, involving a Lamb-dip and a Lamb-peak. We propose an explanation for such behavior based on the effects of cross-over resonances in the hyperfine substructure, which is made quantitative in a density-matrix calculation. This resolves an outstanding discrepancy on the rovibrational R(1) transition frequency, which is now determined at 217105181901 (50) kHz and in agreement with current theoretical calculations. <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: Lamb-dips and Lamb-peaks in the saturation spectrum of HD, M.L. Diouf, F.M.J. Cozijn, B. Darquié, E.J. Salumbides, W. Ubachs, Opt. Lett. **44**, 4733 (2019).

#### 8.1. Introduction

Vibrational transitions in the hydrogen deuteride (HD) molecule, associated with the small permanent dipole moment of this hetero-nuclear species, were first detected by Herzberg [24]. Thereafter transition frequencies of a number of lines in the (2-0) overtone band were spectroscopically investigated early on [25, 26], and over the decades at increasing accuracy [27]. A vast number of spectroscopic studies have been performed on the HD vibrational spectra, but all were limited by Doppler broadening. In two recent studies laser precision experiments were performed that, for the first time, saturated the absorption spectrum of the very weak R(1) line at 1.38  $\mu$ m in the (2-0) overtone band in HD and acquired a Dopplerfree resonance, resulting in orders-of-magnitude improved accuracies. In one study the method of noise-immune-cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) was employed [28], while in a second study a Lamb-dip was observed via cavity ring-down spectroscopy [29]. Where in both experiments the spectroscopy laser was locked to a frequency-comb laser for achieving accuracy at  $10^{-10}$  levels, the resulting transition frequencies deviated by 900 kHz, corresponding to  $9\sigma$  discrepancy for the combined uncertainties. In view of the importance of such precision measurements for testing quantum electrodynamics in hydrogen molecular systems [22, 23], for probing fifth forces [257] and extra dimensions [258], we have reinvestigated this R(1) line of HD at improved background suppression and signal-to-noise ratio, and under varying pressure conditions with the aim of finding the cause of this discrepancy.

#### 8.2. Experimental

The frequency-comb locked NICE-OHMS setup described in the previous study [28] is significantly modified on both the signal and frequency acquisition. It now involves a high-speed lock-in amplifier (Zurich Instruments, HF2LI), which allows parallel demodulation to extract all relevant signal components simultaneously as both the down-converted high-frequency modulation ( $f_{FSR}$ ) and low-frequency dither ( $f_{WM}$ ) all fall inside the lock-in amplifier bandwidth (50 MHz). A schematic layout of the experimental setup is displayed in Fig. 8.1.

The spectroscopy laser is directly stabilized onto the high-finesse cavity through a Pound-Drever-Hall (PDH) lock for short term stabilization, while long term stability and accuracy (1 kHz) is obtained by a direct comparison with a Cs-stabilized frequency comb. To remove the effect of the periodic frequency dither ( $f_{WM} = 415$  Hz, 90 kHz peak-to-peak amplitude) in the acquisition, the counter operates at a gate time set to an integer value of the dither period. The measured beatnote value is used in a digital feedback loop to feedback the cavity piezo. The DeVoe-Brewer signal, required to stabilize the modulation frequency onto the cavity Free-Spectral-Range  $f_{FSR} = 305$  MHz, is also retrieved within the lock-in amplifier. It occurs at both frequencies of  $f_{FSR} \pm f_{PDH}$ , which are located at 5 MHz or 45 MHz within the lock-in amplifier due to the down-conversion. To allow retrieval of this error function, it is required that both the internal oscillators of the lock-in amplifier and the PDH frequency generator are all stabilized to an external reference to ensure a fixed phase relationship.



Figure 8.1: Schematic layout of the experimental setup used in the present study. The ECDL laser is modulated twice by the EOM at both the FSR and PDH frequencies, of which the latter is used for short term stabilization onto the high-finesse cavity. Additionally, the laser is wavelength-modulated through a dither on the cavity piezo for derivative detection. A slow lock with the frequency comb is performed for long term stabilization.

Saturated absorption spectra of the HD R(1) line were measured as a function of pressure in the range 0.25 to 10 Pa, recordings of which are displayed in Fig. 8.2. With a cavity finesse of  $\sim 150\,000$ , the circulating power is estimated to be  $\sim 100$  W. The spectra represent the average of 8 scans, each taken at 20 minutes recording time (with 50-kHz frequency steps), yielding more than a five-fold improvement in signal-to-noise ratio with respect to the previous study [28]. It should be noted that the NICE-OHMS technique employed, which is essentially a form of frequency modulation spectroscopy in an optical cavity, yields a dispersive spectral line shape [132, 259, 31, 260]. However, the recordings are performed with an additional slow wavelength modulation at frequency  $f_{WM}$ , which improves the signalto-noise ratio and allows for detecting the extremely weak HD signal in saturation. Hence, after 1f demodulation at  $f_{WM}$ , a derivative of the NICE-OHMS dispersion channel is expected in the form of a symmetric line shape. Indeed, a symmetric saturated absorption line is observed for  $C_2H_2$  (an R(9) line at 271 377 365 327 (5) kHz), recorded under the same NICE-OHMS modulation conditions and displayed in the right panel of Fig. 8.2. The  $C_2H_2$  line reflects the expected line shape, and the characteristic Lamb-dip of saturation spectroscopy.

The measurements performed on the HD R(1) line exhibit a variation in line profiles at different pressures. At low pressures (0.25-1 Pa) the line profile is dominated by a feature with a reversed sign when compared to the  $C_2H_2$  spectrum. These HD-signals at low pressure form Lamb-peaks, that were interpreted in the previous study [28] as the saturated line from which the centre frequency of the R(1) line was derived, at 217 105 181 895(20) kHz.



Figure 8.2: Observed 1*f*-spectra of the HD R(1) transition under conditions of varying pressure are shown in the left panel. For comparison in the right panel, an R(9) acetylene line ( $f_0 = 217\,377\,365\,327$  kHz) recorded at 0.1 Pa with identical settings of modulation and demodulation phases for the HD measurements. The acetylene spectrum reflects the expected 1*f*-derivative of the dispersion profile for a saturated NICE-OHMS Lamb dip. The vertical lines in the left panel indicate the line positions reported in Refs. [28] (Amsterdam), [261] (Hefei), and [262] (Caserta), as well as the theoretical value from Ref. [263]. The shaded areas indicate the uncertainty estimates of the reported line positions.

At the lowest pressures (0.25 Pa), besides the marked enhanced absorption (peak) at low frequencies some reduced absorption at higher frequencies is observable. The reduced absorption feature, or a Lamb-dip, becomes more pronounced as a more intense and gradually broader signal with increasing pressure. With these two features, the resonance resembles a dispersive line shape. This deviation from an expected *symmetric* line shape is the central finding of the present experimental study.

While the Lamb-peak signal at low frequencies corresponds to the feature analyzed in Ref. [28], a broader feature, of the same sign as the  $C_2H_2$  feature is also observed. This feature, having the sign of a Lamb-dip, is located in the range of higher frequencies, where the Lamb-dip of the HD R(1) line was found in the cavity ring-down study, at 217 105 182.79(8) MHz [261]. These observations on pressure-dependent line shapes may form the basis for resolving the discrepancy between the two results previously published [28, 261]. The line position reported in a recent study, a Doppler-limited measurement using frequency-comb assisted cavity ring-down spectroscopy [262], is also indicated in Fig. 8.2. In the following, an analysis of the line shape is presented that should quantitatively support this assumption, although a number of approximations and hypotheses must be made.



Figure 8.3: A stick spectrum representing the 21 hyperfine components (in blue) and the 68 cross-over resonances (in red and green) in the R(1) line of HD. The zero on the *x*-axis represents the location of the hyperfineless rovibrational transition. The line strengths of the cross-over resonances represent the root of the product of hyperfine line intensities of the two connecting transitions.

#### 8.3. Hyperfine structure

Crucial for our proposed interpretation of the line shape is the underlying hyperfine structure of the R(1) transition. The nuclear spins for the deuteron  $I_D = 1$ and the proton  $I_H = 1/2$  give rise to a splitting in 5 hyperfine substates in the J = 1 ground state and into 6 hyperfine substates in the J = 2 excited state. This gives rise to 21 possible hyperfine components within the saturated absorption profile of the R(1) line. The level structure for the v = 0, J = 1 level follows from the analysis of RF-spectra by Ramsey and Lewis [264]. For the v = 2 level hyperfine coupling constants were calculated via *ab initio* theory, and from these the hyperfine level splitting in v = 2, J = 2 were derived and assumed to be accurate within 5% [265]. Relative line intensities of the 21 components were calculated via angular momentum algebra [265]. The calculated hyperfine structure is shown as a stick spectrum in Fig. 8.3. This graph also includes the locations of so-called cross-over resonances that couple non-zero velocity classes in a narrow saturation peak. Between the 5 ground state levels and the 6 excited state levels there exist 32 resonances where two ground state levels are connected to a common upper state ( $\Lambda$ -type cross overs), and 36 resonances that couple two excited levels to a common ground state (V-type cross overs). The occurrence of cross-over resonances is well documented in saturation spectroscopy [247, 249, 251, 266]. They give rise to sign reversals, hence Lamb peaks, depending on the V-type or  $\Lambda$ -type connection of hyperfine levels [267, 268].

To study the general features of the observed HD R(1) line profile, an approximate model was set up using the density matrix formalism that includes the 5 hyperfine sub-levels of the v = 0, J = 1 ground level and the 6 hyperfine sub-levels of the v = 2, J = 2 excited level. The coupled Bloch equations involving populations of excited sub-levels  $\rho_{jj}$  and ground sub-levels  $\rho_{ii}$  and the coherences  $\rho_{ij}$ are:

$$\frac{d}{dt}\rho_{ii} = \sum_{j} \rho_{jj}\gamma_{pop,ij} - \frac{i}{\hbar}\sum_{j} (V_{ji}\rho_{ji} - \rho_{ji}V_{ij}), \qquad (8.1)$$

$$\frac{d}{dt}\rho_{jj} = -\sum_{i}\rho_{jj}\gamma_{pop,ij} - \frac{i}{\hbar}\sum_{i}(V_{ij}\rho_{ij} - \rho_{ij}V_{ji}), \qquad (8.2)$$

$$\frac{d}{dt}\rho_{ij} = -(i\Delta_{ij} + \gamma_{coh,ij})\rho_{ij} + \frac{i}{\hbar}V_{ij}(\rho_{ii} - \rho_{jj}) - \frac{i}{\hbar}\sum_{k\neq j}V_{ik}\rho_{kj}, \qquad (8.3)$$

$$\frac{d}{dt}\rho_{jk} = (i\Delta_{jk} - \gamma_{coh,jk})\rho_{jk} - \frac{i}{\hbar}(V_{ij}\rho_{ji} - \rho_{ki}V_{ki}),$$
(8.4)

with the detuning  $\Delta_{ij} = \omega_L - (\omega_{ij} + \vec{k} \cdot \vec{v})$ , where  $\omega_L$  is the laser frequency,  $\omega_{ij}$  is the transition frequency between states *i* and *j*, and  $\vec{k} \cdot \vec{v}$  is the Doppler shift for the velocity class *v*. The population relaxation rates  $\gamma_{pop,ij}$  connecting *i* and *j* states with allowed dipole transitions and relaxation rates for coherences  $\gamma_{coh,ij}$  effectively describe radiative and non-radiative processes. The coupling  $V_{ij} = \mu_{ij}(E_+ + E_-) + c.c.$  consists of electric field contributions from forward +kand backward -k propagating laser beams with equal intensities. The electronic transition dipole moment as well as relative intensities of the hyperfine transitions are included in  $\mu_{ij}$ . In the calculation, the detuning  $\Delta$  of the applied laser field is scanned over the vicinity of the resonances, with the Doppler shift accounted for both +k and -k beams and for each of the  $n_v$  velocity classes around v = 0. We have neglected the effect of the two laser sidebands at  $f_{FSR} = \pm 305$  MHz (at field strengths of about 1% of the carrier), to simplify the treatment. The occurrence of a recoil doublet [269], with a splitting of 68 kHz for the R(1) line, is ignored as well.

Another complication in explaining the observed spectra lies in the reduction of transit-time broadening. We note here, as was discussed in [28], that the observed linewidth of the HD R(1) line is observed much narrower than expected from transit time broadening for a room-temperature velocity distribution. This was attributed to the mechanism of selection of cold molecules under conditions of very weak saturation, which is a known phenomenon [270, 271, 272]. In the model description no attempt was made to explicitly explain this behavior.

#### 8.4. Results

The coupled Bloch equations were solved by numerical integration using a Python code and associated numerical and scientific libraries. The computation was performed in a cluster computer utilizing 32 nodes with 16 cores. For  $n_v \sim 4400$  velocity classes that cover Doppler shifts in the range of [-1.8, 1.8] MHz around each resonance, a calculation of a spectrum typically takes around 18 hours.

A first calculation was performed that was restricted to the v = 0 velocity fraction (v = 0 along the propagating laser beams). Its result shows a spectrum displaying all hyperfine resonances at the expected positions indicated as proper hyperfine resonances in Fig. 8.3 as Lamb-dips. Subsequently, more elaborate calculations were performed, integrating the spectrum over extended velocity classes. Depending on the parameters invoked for  $\gamma_{coh}$  and  $\gamma_{pop}$ , this treatment produces cross-over resonances with the same sign as a Lamb-dip, but also cross-over features with a reversed-sign. The simulations reveal the effects of velocity selective optical pumping that are observed at particular velocity classes where the cross-over interaction between the counter-propagating beams occur. From a parameter-space analysis it is found that the sign-reversed cross-over peaks occur only under certain values for the input parameters. Clear anti-crossovers are produced only when the population decay  $\gamma_{pop}$  occurs at a faster rate than the Rabi frequency that was estimated at  $V/\hbar = 20$  kHz in the measurements [28].

This suggests that there must be a mechanism transferring population from the excited v = 2 state to the lower v = 0 state in the molecule, a *refilling* mechanism. This rate should be much larger than the radiative lifetime of the upper HD level, being on the order of  $\Gamma \sim 1$  Hz. Hence, in this specific case of a saturated transition with a long upper state lifetime in a molecule, similar to the case of NH<sub>3</sub> [273], the population decay ( $\gamma_{pop}$ ) cannot be induced by spontaneous radiative decay, as in the case of atoms [249, 251, 268].

In order to effectively produce anti-crossovers or Lamb peaks an hypothesis must be invoked as to the refilling mechanism for ground state population. In some examples, that bear some similarity, the main contribution to the rate of population decay  $\gamma_{pop}$  was attributed to optical pumping in a multi-level system, with the transit-time effect as the absorbers traverse the beam playing a role [267, 268]. In a model for saturation in coherent anti-Stokes spectroscopy in H<sub>2</sub> the mechanism of velocity-changing collisions was adopted as a possible transfer mechanism [274]. The decay value in the latter CARS experiment was close to the value of the pressure broadening coefficient of  $\gamma_P = 35$  kHz/Pa for saturated absorption extracted in Ref. [28], while Ref. [262] reports a coefficient of  $\gamma_P = 10$  kHz/Pa for a Dopplerlimited study (without saturation). For the pressure  $P \sim 1$  Pa accessed in the measurements, the collision rate contribution of  $\gamma_P P$  to  $\gamma_{coh,ij}$  is  $\sim 10 - 35$  kHz. Without further speculation on the nature of the mechanism, a range of values for the refilling rate was used in solving the density matrix framework.

Figure 8.4 shows numerical results obtained for conditions that mimic the observations of spectra at different pressures. The line profiles qualitatively agree with experimental observations. In particular the Lamb-peak and dip features correspond to the measurements, although the intensities and widths are not well reproduced. Both the experiments and simulations demonstrate that the Lambpeak persists at the lowest pressures (lowest values of  $\gamma_{coh,ij}$ ), while the Lamb-dip decreases in intensity at the low pressures.

The simulations show that the saturation line profiles of HD R(1) exhibit a composite line shape with a Lamb-peak at low frequency and a broader Lamb-dip occurring at higher frequencies. We postulate this as an explanation for the results obtained in previous studies, where a low-frequency Lamb-peak was analyzed [28].



Figure 8.4: Comparison between observed and modeled spectral line shapes of the **R(1)** line of **HD**; (a) Experimental spectra for 0.25, 0.5, 1.0 and 10 Pa on an absolute frequency scale; (b) Calculated spectra on a relative frequency scale with respect to the hyperfineless point (at 0 MHz) for different values of  $\gamma_{coh}$  and  $\gamma_{pop}$  in units of kHz and the Rabi frequency fixed at 20 kHz.

We assume that the high-frequency component was measured in the cavity ring down study [261], presumably at somewhat higher pressures. We emphasize that a number of approximations were made in the numerical treatment which could affect the intensities and widths, such as the neglect of the recoil doublet, the inclusion of approximate results on the hyperfine structure from calculations, the lack of a quantitative description of the mechanism selecting cold molecules resulting in larger transit times, absence of cavity standing-wave effects, and in particular the lack of understanding of the refilling mechanism.

A comparison can be made between the observed line shapes and the composite profiles from the numerical treatment, i.e. in a fit. Since the numerical analysis is based on the hyperfine components dispersed at well-known frequencies, such a fit results in a value for the hyperfineless HD R(1) rovibrational transition. It is interesting to note that a pressure-induced shift of -10 kHz/Pa for the Lamb peak line position in the simulations (Fig. 8.4) is close to that extracted in the experimental results. By taking into account profiles for various pressures in the simulations, the extrapolated collision-free Lamb peak line center can be related to the hyperfineless transition frequency. Adopting this treatment to the measurements yields a value of 217 105 181 901 kHz for the R(1) transition frequency. In view of the numerous assumptions made and the pressure-dependent line shape we take a conservative estimate for the uncertainty of the hyperfineless transition frequency of some 50 kHz. The analysis shows also that the zero-pressure extrapolation for the Lambpeak, as determined in [28], is rather close to the hyperfine center-of-gravity to within 20 kHz. The present result agrees, within its 50 kHz uncertainty, with our previous determination [28].

#### 8.5. Conclusion

The presently obtained transition frequency may be compared to the theoretical values obtained from advanced molecular QED calculations. While a calculation of early 2018 yielded a value of 217 105 174.8 (1.8) MHz, included in [261], deviating by 7 or 8 MHz from both experimental values, recently a theoretical value was reported at 217 105 180.2 (0.9) MHz [263]. The latter value, that was based on an improved treatment of relativistic corrections in non-adiabatic perturbation theory, is within  $2\sigma$  from the presently obtained experimental value. This allows for the conclusion that agreement is obtained between experiment and theory of infrared transitions in hydrogen at the  $5 \times 10^{-9}$  level, where the present result is of higher accuracy than current state-of-the art calculations. Meanwhile a theoretical framework has been developed that should produce a more accurate value [23], to be confronted with the experimental value. On the experimental side the observation of the R(0) line in the (2-0) band, exhibiting a much simpler hyperfine structure with a near-degenerate ground state [275], could be measured. Unfortunately that line is overlaid by a water resonance prohibiting its measurements in the current setup.

#### 8.6. Acknowledgements

The authors thank J.M.A. Staa (VU) for assisting in the measurements and P. Dupré (Dijon) for making available calculations on the hyperfine structure. The work was supported by the Netherlands Organisation for Scientific Research (NWO) via the program "The mysterious size of the proton". SURFsara (www.surfsara.nl) is acknowledged for the support in using the Lisa Compute Cluster. WU acknowledges the European Research Council for an ERC-Advanced Grant under the European Union's Horizon2020 research and innovation programme (Grant agreement No. 670168).

# Chapter 9 Lamb-peak spectrum of the HD (2-0) P(1) line

#### Abstract

A saturation spectroscopy measurement of the P(1) line of the (2-0) band in HD is performed in a sensitive cavity-enhanced optical setup involving frequency comb calibration. The spectral signature is that of a Lamb-peak, in agreement with a density-matrix model description involving 9 hyperfine components and 16 crossover resonances of  $\Lambda$ -type. Comparison of the experimental spectra with the simulations yields a rovibrational transition frequency at 209,784,242,007 (20) kHz. Agreement is found with a first principles calculation in the framework of non-adiabatic quantum electrodynamics within  $2\sigma$ , where the combined uncertainty is fully determined by theory. <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: Lamb-peak spectrum of the HD (2-0) P(1) line, M.L. Diouf, F.M.J. Cozijn, K.-F. Lai, E.J. Salumbides, W. Ubachs, Phys. Rev. Res **2**, 023209 (2020).

#### 9.1. Introduction

In the recent decade the hydrogen molecule has become a benchmark system for testing quantum electrodynamics (QED) and probing physics beyond the Standard Model [276]. Such tests can be accomplished by comparison between accurate measurements, of e.g. dissociation energies of the H<sub>2</sub> molecule [277, 22, 278], with non-adiabatic calculations of the hydrogen molecule based on a 4-particle variational framework and including relativistic and QED-terms up to  $m\alpha^6$  [279]. Alternatively, tests were performed on splittings between rovibrational levels in the H<sub>2</sub> and D<sub>2</sub> molecules, measured at increasing accuracy [280, 281, 282]. In view of the very small oscillator strengths of the quadrupole transitions probed in these homonuclear species, measurements were performed from Doppler-broadened and collision-broadened spectra limiting the accuracy. The application of sophisticated line-shape models in combination with high signal-to-noise ratio has nevertheless pushed the accuracy to the sub-MHz regime [283, 284].

In case of the heteronuclear HD isotopologue the molecule exhibits a small electric dipole moment [285, 286] giving rise to an electric dipole absorption spectrum which was discovered by Herzberg [24] and investigated over the years under conditions of Doppler broadening, for the vibrational bands [25, 287, 27, 262], as well as for pure rotational transitions [288, 289].

Recently, intracavity absorption techniques were explored in which saturation of the R(1) transition in the (2-0) overtone band was demonstrated [261, 28], delivering a reduction in linewidth of over a thousand compared to the Doppler-broadened lines. While these studies produced highly accurate transition frequencies for the R(1) (2-0) line in HD, a large discrepancy was found between the two studies. A reanalysis at improved signal-to-noise ratio obtained with the NICE-OHMS (Noise-Immune Cavity-Enhanced Optical-Heterodyne Molecular Spectroscopy) technique by the Amsterdam team showed that the line shape appeared as dispersive-like [78]. This phenomenon was explained as a result of underlying hyperfine structure involving a large number of crossover resonances in the saturation spectrum. A simulation of the spectrum was produced via a density-matrix model with optical Bloch equations that well reproduced the dispersive line shape. An extended analysis by the Hefei group, using three different cavity-enhanced techniques, resulted in a similar dispersive line shape [290]. That was however interpreted as a Fano line shape, caused by an interference between the rovibrational R(1) transition and an underlying continuum, reminiscent of the Fano line shape observed by the interference between transitions in the fundamental vibration of HD and broad collisionally-induced continuum resonances [291]. These discrepancies on transition frequencies and diverging explanations for the observed line shapes call for extended measurements, in particular since rovibrational transitions in the heteronuclear HD molecule, allow for extreme precision and constitute an excellent test ground for molecular QED.

#### 9.2. Experimental

The P(1) line at  $1.43 \,\mu\text{m}$  was measured under conditions of saturation at a number of pressures in the range 0.5 Pa to 16 Pa, using the NICE-OHMS setup, details of which were previously documented [28, 78]. Some notable changes were

made for the measurement of P(1). Firstly, the modulation frequency has been doubled to twice the free-spectral-range (FSR) of the cavity at 2 times 305 MHz. This was necessary to avoid absorption from a neighbouring water transition giving rise to a Lamb-dip from the carrier-sideband saturation occurring at half the FSR detuning. Secondly, a dominant source of residual amplitude modulation due to spurious background etaloning was identified and eliminated, which allowed multiple scans to be much more effectively averaged. This averaging for attaining a good signal-to-noise ratio was made possible through the lock of the spectroscopy laser to a frequency comb; averages over up to 60 recordings were taken. Thirdly, a liquid nitrogen cryotrap was installed to continuously pump outgassing water vapor during the measurements, which otherwise gave a significant background drift.

#### 9.3. Hyperfine structure

For an interpretation of the measured spectra of the P(1) line its hyperfine structure must be considered, which is much simpler than that of the R(1) line measured previously [78]. The J = 1 ground level is split into 5 components via the coupling of the J = 1 rotational angular momentum to the nuclear spins  $I_P = 1/2$  for the proton and  $I_D = 1$  for the deuteron, and yields, in energetic order from high to low, F = 1/2(+), F = 3/2(+), F = 3/2(-), F = 5/2, and F = 1/2(-) sub-levels. Here the (+) and (-) refer to the highest and lowest levels with the same F-quantum number. The hyperfine splitting in J = 1 was accurately measured by Ramsey and coworkers [264, 292]. The v = 2, J = 0 excited state is split into two components F = 1/2 and F = 3/2 that are however degenerate within a kHz; we assume the splitting to be approximately similar to that of J = 0in the v = 0 ground state, where it was calculated as 45 Hz [293]. The hyperfine level structure of the P(1) is plotted in Fig. 9.1. Our analysis of the hyperfine structure of this P(1) line is found to be in excellent agreement with that of other recent analyses [294, 295].

The hyperfine structure results in 9 possible transitions connecting ground and excited state. Combination of these ground and excited states gives rise to 16 possible crossovers in the saturation spectrum, which are all of  $\Lambda$ -type due to neardegeneracy of the excited state. These resonances are plotted as a stick spectrum in Fig. 9.2; note that in view of the degeneracy of the F = 1/2 and F = 3/2 upper levels not all individual components are visible. The relative intensities of the direct hyperfine components are calculated via angular momentum algebra [296], where the absolute scale is matched to the measured value of the line intensity of the Doppler-broadened line [27]. Intensities of the crossing hyperfine resonances. Note that these intensities are not used in the density-matrix model discussed below. The hyperfine structure of P(1), as displayed in Fig. 9.2, shows the sharp contrast to the R(1) line where both V-type and  $\Lambda$ -type crossover resonances contribute to the spectrum.

Note that V-type crossovers show as a Lamb-dip, as a common ground state couples to two excited states causing depletion of population, and therewith reduced absorption. However,  $\Lambda$ -type crossover resonances couple two ground states to a common excited state. This may lead to increased population in one ground state, resulting in increased absorption, and hence a Lamb-peak. In the R(1) spec-



Figure 9.1: The hyperfine level structure with the five sub-levels of the v = 0, J = 1 ground state, plotted on a scale corresponding to measurement [264], and the two degenerate levels in the v = 2, J = 0 state

trum of HD, where both V-type and  $\Lambda$ -type crossovers occur, this resulted into an overall dispersive line shape [78]. In a study on an atomic system exhibiting a preponderance of  $\Lambda$ -type crossovers the saturation spectrum was demonstrated to exhibit the shape of a Lamb-peak [268].

#### 9.4. Results

A few typical examples of spectra of the P(1) line of HD in the (2-0) band are shown in Fig. 9.3, where the absolute frequency is accurate to 1 kHz due to the lock of the diode laser to a frequency comb. The observed spectra of the P(1) line display the typical characteristic of a Lamb-peak. For comparison a spectral line of H<sub>2</sub>O is displayed, recorded under the same experimental conditions and settings of the electronics, thus showing a characteristic Lamb-dip and proving the opposite, Lamb-peak, nature of the HD P(1) resonance. It is noted that the NICE-OHMS technique, which is essentially a frequency-modulation spectroscopic technique, results in dispersive signals. The application of an additional slow (415 Hz in the present case) wavelength modulation of the laser is used for heterodyne detection in a lock-in amplifier, therewith improving the signal-to-noise ratio. It produces a first derivative of this dispersive line shape [259] as illustrated by the H<sub>2</sub>O line.

The peak positions of the lines and their widths, as obtained directly from the measurements, are plotted in Fig. 9.4 as a function of pressure over the measurement range of [0.5 - 16] Pa.

The extracted pressure-dependent shift coefficient of -11(1) kHz/Pa for P(1) is consistent with the result for R(1) [28]. This shift coefficient is much larger



Figure 9.2: Stick spectrum displaying hyperfine sub-components (of the 9 only 5 are non-degenerate) and crossover resonances (of the 16 only 10 are non-degenerate) of the P(1) line of HD on a frequency scale, where "0" is the pure rovibrational transition frequency.



Figure 9.3: Recordings of saturation spectra of the P(1) (2 - 0) line in HD at different pressures as indicated. Simulated spectra from the density matrix model with optimized parameters are plotted, after convolution with a Lorentzian function to account for collisional broadening (at 45 kHz/Pa) with a full line (orange). At the right a spectrum of the water line  $(000)3_{30}$  -  $(101)4_{13}$  at 216,803,819,806 kHz is shown, measured under the same conditions, displaying a characteristic Lamb-dip.

than would be expected when using results from Doppler-broadened measurements in [262], and at higher pressures of  $10^4 - 10^6$  Pa in [297] and extrapolating to the Doppler-free and Pa-level conditions in this study. It has recently been observed that the pressure-induced line shifts in water at low pressures [129], using the same setup as in the present study, also do not follow the expected high-pressure trend, with the pressure shift coefficient even changing sign depending on specific transitions. It is also worth noting that a nonlinear dependence is expected at low temperatures due to velocity-changing collisions as shown for D<sub>2</sub> in Ref. [298], which might be of relevance here considering the selection of cold molecules in optical saturation.

From Fig. 9.4, a collisional broadening parameter of 45 kHz/Pa is deduced for the saturated P(1) line. The data point for 0.5 Pa falls somewhat off the linear collision curve because that spectrum was recorded for a cavity dither peakto-peak amplitude of 180 kHz, while for the other lines an amplitude of 90 kHz was used. These results show that the width of the P(1) line is again, similar to the case of the R(1) line [28, 78], narrower than expected from the contributing broadening mechanisms. A number of physical and instrumental effects contribute to the linewidth as observed, all expressed as half-width-half-maximum (HWHM) in the following. Besides the broadening caused by collisions and by amplitude modulation, the cavity-jitter, with the laser locked to the cavity, will contribute for 40 kHz, as was experimentally determined. Intra-cavity saturation spectroscopy gives rise to recoil-doublets [299] separated by 68 kHz. The largest contribution to the line width is expected from the limited time for the molecules to reside in the laser beam, estimated at 400 kHz at room temperature [266]. Finally, the hyperfine structure causes broadening over the span of components, i.e. several hundred kHz.

In view of the fact that the measured linewidth is much smaller than expected from the various contributions, it is assumed that in the saturation experiment the slow molecules, that will undergo less transit-time broadening, are preferentially detected. This is in line with the fact that the actual intracavity power (some 150 W) is much lower than the saturation parameter of the HD resonance (10 kW). Hence, in the present experiment, the saturation spectroscopy acts as a selection mechanism for cold molecules in the sample.

The line shapes as recorded for the various pressures were modeled in terms of a density matrix formalism with coupled Bloch equations as defined previously [78],



Figure 9.4: Transition frequencies and linewidths (HWHM) observed for the P(1) (2-0) line of HD as a function of pressure.

involving populations of excited sub-levels  $\rho_{jj}$  and ground sub-levels  $\rho_{ii}$  and coherences  $\rho_{ij}$ :

$$\frac{d}{dt}\rho_{ii} = \sum_{j} \rho_{jj}\gamma_{pop,ij} - \frac{i}{\hbar}\sum_{j} (V_{ji}\rho_{ji} - \rho_{ji}V_{ij}), \qquad (9.1)$$

$$\frac{d}{dt}\rho_{jj} = -\sum_{i} \rho_{jj}\gamma_{pop,ij} - \frac{i}{\hbar}\sum_{i} (V_{ij}\rho_{ij} - \rho_{ij}V_{ji}), \qquad (9.2)$$

$$\frac{d}{dt}\rho_{ij} = -(i\Delta_{ij} + \gamma_{coh,ij})\rho_{ij} + \frac{i}{\hbar}V_{ij}(\rho_{ii} - \rho_{jj})$$

$$i\sum_{i} V_{ij}(\rho_{ii} - \rho_{jj})$$
(9.3)

$$-\frac{1}{\hbar}\sum_{k\neq j}V_{ik}\rho_{kj},$$

$$\frac{d}{dt}\rho_{jk} = (i\omega_{jk} - \gamma_{coh,jk})\rho_{jk} - \frac{i}{\hbar}(V_{ij}\rho_{ji} - \rho_{ki}V_{ki})$$
(9.4)

with definitions of the Rabi frequency  $V_{ij}/\hbar$ , detuning  $\Delta_{ij} = \omega_L - (\omega_{ij} + \vec{k} \cdot \vec{v})$ , the laser frequency  $\omega_L$ , the transition frequency between *i* and *j* states  $\omega_{ij}$ , and the Doppler shift for the velocity class *v* as  $\vec{k} \cdot \vec{v}$ . Note that the crossover resonances, nor their estimated intensities, are explicitly included in the model; their effect is implicitly imposed when integrating over velocity space. Decisive parameters in the model are the population relaxation rates  $\gamma_{pop,ij}$  connecting *i* and *j* states with allowed dipole transitions and relaxation rates for coherences  $\gamma_{coh,ij}$  effectively describing radiative and non-radiative processes. The refilling of the ground state from collisional decay of the excited states via  $\gamma_{pop,ij}$  can be considered as a twostep process via a thermal bath. The optical Bloch equations are solved in time steps of 1  $\mu$ s for each single detuning frequency, over a span of 4 MHz approached with a step size of 1 kHz. The total integration time is fixed at 3.4 ms in order to reach the steady state solution, which must be obtained to achieve a stable resulting spectrum. The velocity distribution of the particles is divided over 816 velocity classes which are then implemented for each single velocity in the 4000 integration steps.

In the simulations the values of  $\gamma_{pop,ij}$  and  $\gamma_{coh,ij}$  are considered as free parameters and are used as such to find an optimal representation of the observed line shapes. The Rabi frequency  $V/\hbar$  is set at 40 kHz commensurate with the power density in the cavity. The simulation is rather insensitive to the value of  $\gamma_{pop,ij}$ and it finds convergent solutions as long as it is held at > 35 kHz; here we have fixed  $\gamma_{pop,ij} = 55$  kHz. The line shape and the effective width are sensitive to the value of  $\gamma_{coh,ij}$ , which is varied in the calculation to find a matching line shape. In Fig. 9.3 simulated spectra are plotted for an optimized parameter value for  $\gamma_{coh,ij}$ . For the spectrum recorded at 0.5 Pa we find a best match for  $\gamma_{coh,ij} = 95$  kHz, and for the spectra at 1.0 Pa and 4.0 Pa the optimum is at  $\gamma_{coh,ij} = 125$  kHz and  $\gamma_{coh,ij} = 355$  kHz, respectively.

The simulations do not reproduce the line widths beyond 4 Pa ( $\gamma_{coh,ij} > 355$  kHz) although it retains the Lamb-peak structure. We suspect that here another regime is reached that is dominated by collision-induced perturbations on the rovibrational levels, which are not included in the Bloch equation calculations.

After the simulation the result is convolved for the effects of recoil doublet, cavity jitter and wavelength dithering. The resulting simulated spectra are then plotted in Fig. 9.3 to be compared with the experimental spectra.

An important conclusion of the modeling based on this density matrix model is that an overall spectral pattern of a Lamb-peak is found, irrespective of the details and exact values of the  $\gamma$ -parameters invoked. For no realistic set of parameters a sign reversal could be produced. This is in agreement with the expectation (see above) that a saturation spectrum with crossover resonances only of  $\Lambda$ -type should produce a Lamb-peak.

From these optimized simulations, performed for each pressure, a value for the rovibrational (or hyperfine-free) transition frequency is found as shown by the dashed line. This is done by fitting the theoretical line shape to a standard functional form (a first-order derivative of a dispersive Lorentzian [28]), which is subsequently fitted to the observed spectral profile. The resulting hyperfine-less transition frequency deviates somewhat from the center of the Lamb-peaks, on the order of 45 kHz, varying by < 10 kHz for the highest pressures. It was verified that the resulting transition frequency varies only within 10 kHz if the parameter space of  $\gamma_{coh,ij}$  is explored, where the resulting line shape and width form a selection criterion. Similarly the Rabi frequency was varied in the relevant range 35-55 kHz, imposing an additional uncertainty in the simulation of 5 kHz. Extrapolation to zero pressure then yields the final value for the P(1) rovibrational transition. The main sources of uncertainty, related to the simulation (variation of parameter space for  $\gamma_{coh,ij}$ ,  $\gamma_{pop,ij}$  and Rabi frequency  $V/\hbar$ ) and the statistics of line fitting and pressure extrapolation are combined to yield an uncertainty of 20 kHz. As the resulting transition frequency we find 209,784,242,007 (20) kHz.

The result of the present experimental study allows for a comparison with the theoretical result, obtained in the framework of non-adiabatic perturbation theory (NAPT) [263, 300], which is now available as a web-based on-line calculation tool [301]. This NAPT-tool provides binding energies at accuracy of  $3 \times 10^{-4}$  $\rm cm^{-1}$ , or 10 MHz, but in the calculation of transition frequencies a cancellation of uncertainties is accounted for, delivering accuracies of about  $3 \times 10^{-5}$ . Specifically, H2SPECTRE [301] calculates an accuracy of 1.0 MHz for the P(1) line and for the R-branch lines of 1.1 MHz. For the P(1) line a theoretical value of 209,784,240.1(1.0) MHz is produced [301]. Comparison with the experimental value shows that the theoretical value is lower by 1.9 MHz, or by  $2\sigma$ . Also in the previous study on the R(1) line the experimental value was higher by 1.9 MHz, again corresponding to a  $2\sigma$  deviation. For the measurement of the R(2) and R(3) lines no detailed study of the hyperfine structure was performed, but the derived transition frequencies [28] also show an approximate  $+2\sigma$  deviation from the NAPT-results. A similar deviation was found in a recent molecular beam study on HD [302]. It is noted that in all these cases the  $2\sigma$  offset is given in terms of, and is entirely due to the uncertainty in the theoretical value. This consistent deviation by  $+2\sigma$  is indicative of a general and systematic offset of the NAPT-calculations for the rovibrational transitions in the (2-0) band of HD.

#### 9.5. Conclusion

In conclusion we have demonstrated that the line shape as observed for the P(1) line in the (2-0) overtone band of HD can be described in terms of coherences between hyperfine substates. The same density matrix model that previously was developed to explain the observed dispersive-like spectrum of the R(1) line can now describe the shape of a single Lamb-peak for the case of P(1) with a realistic set of population and coherence decay parameters. This line shape analysis provides confidence for the extraction of the hyperfine-free or rovibrational transition frequency, at 209,784,242,007 (20) kHz, which is in agreement with the formalism of non-adiabatic perturbation theory for the hydrogen molecules within  $2\sigma_{\text{theory}}$ .

#### 9.6. Acknowledgments

Financial support from the European Research Council (ERC-Advanced Grant No. 670168) and from the Netherlands Organisation for Scientific Research, via the Program "The Mysterious Size of the Proton" and the "Dutch Astrochemistry Network", is gratefully acknowledged. The authors thank the authors of Ref. [294] for sharing results on the hyperfine structure of HD prior to publication.

#### Chapter 10

## Rotational level spacings in HD from vibrational saturation spectroscopy

#### Abstract

The R(1), R(3) and P(3) ro-vibrational transitions in the (2-0) overtone band of the HD molecule are measured in Doppler-free saturation using the technique of NICE-OHMS spectroscopy. For the P(3) line, hitherto not observed in saturation, we report a frequency of 203 821 936 805 (60) kHz. The dispersive line shapes observed in the three spectra show strong correlations, allowing for extraction of accurate information on rotational level spacings. This leads to level spacings of  $\Delta_{(J=3)-(J=1)} = 13\,283\,245\,098\,(30)$  kHz in the v = 0 ground state, and  $\Delta_{(J=4)-(J=2)} =$ 16 882 368 179 (20) kHz in the v = 2 excited vibration in HD. These results show that experimental values for the rotational spacings are consistently larger than those obtained with advanced ab initio theoretical calculations at  $1.5\sigma$ , where the uncertainty is determined by theory. The same holds for the vibrational transitions where systematic deviations of 1.7- $1.9\sigma$  are consistently found for the five lines accurately measured in the (2-0) band. <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is a reproduction of: *Rotational level spacings in HD from vibrational saturation spectroscopy*, F.M.J. Cozijn, M.L. Diouf, V. Hermann, E.J. Salumbides, M. Schlösser, W. Ubachs, Phys. Rev. A **105**, 062823 (2022).

#### 10.1. Introduction

The spectroscopic investigation of the hydrogen molecule and its isotopologues has played a crucial role in the advancement of quantum mechanics in the molecular domain. The HD isotopologue, observed via its vacuum ultraviolet spectrum immediately after its production and purification [303, 304], undergoes breaking of inversion symmetry, also referred to as q - u symmetry breaking, giving rise to spectroscopic phenomena that are not observed in the homo-nuclear species  $H_2$ and  $D_2$  [305]. One of the special features is the occurrence of a dipole-allowed absorption spectrum in HD in connection the small dipole moment arising from a charge asymmetry in the molecule. Wick was the first to calculate the intensity of this dipole-allowed vibrational spectrum [306] and Herzberg first observed overtone lines combining high-pressure cells with multi-pass absorption [24]. The vibrational spectra of the fundamental [307] and overtone bands [25] were later investigated in more detail and at higher accuracy. In the past decade cavity-enhanced techniques in combination with frequency-comb calibration were employed to investigate the spectrum of the (2-0) band of HD [27]. For a literature compilation of the vibrational spectra of HD we refer to Ref. [308]. The pure rotational spectroscopy of HD, also connected to the dipole moment, was first probed by Trefler and Gush [285], while later more precise spectroscopic measurements were performed [309, 288, 289, 81].

Recently, saturation spectroscopy of R-lines in the (2-0) overtone band was demonstrated [261, 28], to yield linewidths much narrower than in the Dopplerbroadened spectroscopies performed previously. These studies led to accuracies at the 20 kHz level, but the modeling of observed lineshapes appeared to be a limiting factor. In the Amsterdam laboratory subsequent measurements with the NICE-OHMS (Noise-Immune Cavity-Enhanced Optical-Heterodyne Molecular Spectroscopy) technique were carried out and the dispersive-like line shape was interpreted in terms of an Optical Bloch equation (OBE) model including underlying hyperfine structure and crossover resonances in the saturation spectrum [78, 310]. The Hefei group extended their studies on the observation of a dispersive line shape, which was interpreted as a Fano line shape [311]. The uncertainties associated with the observed lineshape remain to be a dominating factor and hinder full exploitation of the extreme resolution of the saturation technique, and the determination of transition frequencies at the highest accuracy. The molecular-beam double-resonance study of the R(0) line of the (1-0) fundamental of HD by Fast and Meek [302] does not suffer from this short-coming, yielding a vibrational splitting in HD at the level of 13 kHz, the most accurate to date. Vibrational splittings in the (1-0) fundamental have also been determined via laser-precision studies in molecular beams and the measurement of combination differences in Doppler-free electronic spectra [312]. The Caserta group applied cavity-enhanced methods for linear absorption spectroscopy of the R(1) line in (2-0). Even though the line is of GHz width an accuracy of 76 kHz is obtained through advanced modeling of the Doppler-broadened line shape [313].

The goals of precision spectroscopy on the hydrogen isotopologues have surpassed the targets of molecular physics. These smallest neutral molecular species have become benchmark systems for probing physics beyond the Standard Model [276],


Figure 10.1: Spectral recordings of the R(1) line in the (2-0) overtone band of HD in saturated absorption employing the NICE-OHMS technique. Pressures as indicated in units of Pa. Recordings are performed using (a) 1f and (b) 2f demodulation. A comparison is made with the recording of a water line, also at (c) 1f and (d) 2f demodulation settings. Note the strong difference in line shape, where the water line represents the generic NICE-OHMS signal shape. The (grey) vertical bar in (a) and (b) represents the transition frequency of the R(1) line of HD as determined in a previous experimental saturation study via modelling of the spectral line shape based on underlying hyperfine structure and including cross-over resonances [78]. The 0.0 value represents a frequency of 217 105 181.901 (0.050) MHz for HD and 217 135 374.644 (0.005) MHz for the H<sub>2</sub>O<sup>16</sup> line.

searching for fifth forces of various nature [257, 314] and for higher dimensions [258]. The searches for new physics depend on the availability of highly accurate ab initio computations of the level structure of the hydrogen molecules. In the past decade the boundaries in this area have been pushed, and currently highly accurate level energies are produced in 4-particle fully variational calculations of the relativistic motion in the molecules, augmented with calculation of quantum-electrodynamic corrections up to level  $m\alpha^6$  [263, 275, 23]. The results of the ab initio calculations are available through the H2SPECTRE on-line program [301].

A comparison between the recent accurately measured vibrational transition frequencies with those computed from the H2SPECTRE code reveals a systematic offset of 1 MHz for the (1-0) band and 2 MHz for the (2-0) band. The deviations extend very much beyond the uncertainties established in the experiments, but remain at the level of  $1.7\sigma$ , when the uncertainty of the calculations is taken into account. In order to investigate the origin of these discrepancies we target measurements, by means of saturation spectroscopy, of combination differences between vibrational lines in the (2-0) band.

#### 10.2. Experiment and results

In the experiment, the NICE-OHMS setup at the Amsterdam laboratory is used to perform saturation spectroscopy of the R(1), R(3) and P(3) lines of HD at wavelengths near  $1.4 \,\mu\text{m}$ . Details of the setup were described in previous papers on the spectroscopy of HD [28, 78, 310] and specific settings of the present experiment are similar. A noteworthy detail is that a new diode-laser and high-reflectivity mirrors are used to reach the P(3) wavelength, while the measurements of the R(1) and R(3) lines are performed with existing components. The essentials remain identical with an intracavity circulating power at the central carrier frequency  $f_c$ of about 150 W, while the sidebands at  $f_c \pm f_m$  are modulated at  $f_m = 404$  MHz delivering circulating powers of 2 W. The diode-laser is locked to the high-finesse cavity (150,000) via Pound-Drever-Hall stabilization, where the cavity is locked to a Cs-clock stabilized frequency-comb laser. This locking sequence leads to a line-narrowing of the diode laser to around 20 kHz at second time scale caused by short term vibration-noise and thermal drift of the cavity. Ultimately, the absolute frequency of the complete measurement data averages down to below kHz precision due to long term measurements of over a few hours. This stability allows for effectively averaging over multiple scans to obtain reasonable signal-to-noise levels. Averages of around 60 scans with a total measurement time of over 10 hours were taken to record a spectrum of the weakest P(3) line.

The generic signals produced in direct NICE-OHMS spectroscopy under saturation exhibit a dispersive lineshape, as a result of the sideband frequency-modulation applied [98, 132]. The application of an additional low-frequency dither modulation to the cavity length (at 415 Hz) and demodulation at 1f by a lock-in amplifier, in principle results in a line shape taking the form of a derivative of a dispersion-like function. Such symmetric line shapes were indeed detected for saturated lines of  $C_2H_2$  [78] and of  $H_2O$  [129] in the same setup. In Fig. 10.1 representative spectra of an HD line, in this case the R(1) line in the (2-0) overtone band, are compared with spectral recordings of a water line. This comparison was performed for both 1f and 2f demodulation of the modulated signal. Details of the applied modulation scheme has been presented earlier for the 1f signal channel [78], but the used lock-in amplifier (Zurich Instruments HF2LI) can be expanded with an additional parallel demodulation channel allowing simultaneous measurements of the 1f and 2f signal channels. This capability has been used in previous work to detect the 1f and 3f demodulation channels simultaneously, which resulted in resolving the hyperfine structure of  $H_2^{17}O$  [131].

These spectra and the comparison between HD and H<sub>2</sub>O resonances as measured in saturation demonstrate two important aspects. Firstly, the line shape of the HD resonance in the 1*f*-recording is asymmetric, unlike the shape of the water resonance that follows the expected pattern for NICE-OHMS signals [129]. Similar asymmetric line shapes are observed for the R(3) and P(3) lines, as presented in Fig. 10.2. This phenomenon of observing unexpected atypical line shapes was discussed in previous papers on the saturation spectroscopy of HD, either using 1*f*demodulation in NICE-OHMS [28, 78], cavity-ring-down spectroscopy [261], or a variety of cavity-enhanced techniques [311]. Secondly, the experimental data show that the 2*f*-demodulation spectra exhibit a better signal-to-noise ratio (SNR) than the 1*f*-demodulated spectra, while the 1*f* spectra display a much better SNR than the direct NICE-OHMS spectra. For these reasons the comparisons and the detailed analyses of rotational line shifts is based on 2*f* demodulated spectra in the following.



Figure 10.2: Recordings of saturated spectra of the R(3) and P(3) (2-0) overtone lines in HD with NICE-OHMS at 2*f*-demodulation for pressures of 1 Pa and 2.5 Pa. The (grey) bars indicate the estimated spin-averaged transition frequencies and their uncertainties of 100 kHz.

In Fig. 10.1 the transition frequency of the R(1) line and its uncertainty are indicated by the (grey) vertical bar. A result for the R(1) transition frequency was initially reported from a NICE-OHMS study only considering the Lamb-dip feature and fitting its line centre; this procedure resulted in a value then considered to be accurate to 20 kHz [28]. However, in a competing study using cavity-ring-down spectroscopy a strongly deviating transition frequency was reported [261]. For this reason a systematic study was performed in which the observed complex line shape, consisting of Lamb-peak and Lamb-dip contributions, was computed via an Optical Bloch Equation (OBE) model from which resulting in a spin-averaged transition frequency of 217 105 181 901 kHz with an uncertainty of 50 kHz [78]. This is the result displayed by the (grey) vertical bar in Fig. 10.1. It shows that the modelled center frequency coincides rather accurately with the Lamb-peak feature in the 1f NICE-OHMS signal channel, and with the zero-crossing in the 2f signal channel.

For the R(3) line an accurate result was reported in a previous study [28], but this was not substantiated with an explicit OBE-model computation. The P(3) line in the (2-0) overtone band has not been reported before from a saturation experiment. Based on the finding that the line shapes of the R(1), R(3) and P(3) lines exhibit similar line shapes (this paper) it is assumed that the central spin-averaged transition frequencies are all in close proximity of the zero-crossing point in the 2f spectral features at the lowest pressures. In view of this assumption the transition frequencies of R(3) and P(3) lines in the observed 2f-spectra are extracted from the zero-pressure extrapolated 2f crossings, displayed in Fig. 10.2, with an uncertainty bar estimated conservatively at 100 kHz. Based on the measurements



Figure 10.3: Level scheme of HD showing how the three lines R(1), R(3) and P(3) correspond to rotational level spacings in the v = 0 ground and v = 2 excited vibrational level.

performed at 1.0 and 2.5 Pa, pressure shifts of -23 kHz/Pa for R(3) and -26 kHz/Pa for P(3) are determined. This leads to values of 220 704 304 963 (100) kHz for R(3) and 203 821 936 786 (100) kHz for P(3).

In Figs. 10.1 and 10.2 it is documented that recorded saturation spectra for the HD resonances deviate from expected and generic line shapes in NICE-OHMS. However, visual inspection indicates that the line shapes of the R(1), R(3) and P(3) lines are very similar. This forms the basis for extracting information on rotational level spacings as illustrated in Fig. 10.3.

In Fig. 10.4 recordings of 2f-demodulated spectra for the three HD lines are compared. For quantifying the similarities auto-correlation functions are computed as well as cross-correlation functions [315] for the pairs R(1)-P(3) and R(3)-P(3). The resulting cross-correlation curves are found to mimic the auto-correlations in a near-perfect fashion, with a peak overlap of 95%. The cross-correlation computations yield values for the frequency differences  $\Delta$  between the line pairs R(1)-P(3) and R(3)-P(3) representing rotational line spacings in the v = 0 and v = 2 levels.

Because the computation of the cross-correlation does not straightforwardly deliver an uncertainty to the values for the line spacing, the 2f modulated spectra for the R(1) and R(3) lines were subjected to a standard cubic spline interpolation [316] to produce a functional form closely representing the data. The cubic spline curves and plotted residuals in Fig. 10.4(e) and (f) show that such cubic splines indeed accurately represent the experimental data for the R(1) and R(3) lines. These resulting functional forms, g(f), were then used to fit the third P(3) line in both cases. Aside from adjustment parameters for the amplitude (A) and zero-level (B) a frequency shift term  $\Delta$  between the R(1)/P(3) and R(3)/P(3) pairs



Figure 10.4: Comparison of the 2f demodulated saturation spectra for three lines in the (2-0) overtone band of HD, all recorded at a pressure of 1 Pa; (a) Comparison for the pair R(1) and P(3); (b) Comparison for the pair R(3) and P(3). Note that the amplitudes for the corresponding spectra are adapted to match each other. (c) Results of auto-correlation and cross-correlation calculations for the R(1)-P(3) pair and (d) for the R(3)-P(3) pair. In panels (e) and (f) fits are made using a cubic spline interpolation for which residuals are computed and plotted (thin grey line). The resulting cubic spline functional form is then fitted to the line shapes of the P(3) lines in (g) and (h). Residuals of the latter are again plotted in grey.



Figure 10.5: Stick spectra of hyperfine components for (a) the R(1) line, (b) the R(3) line; and (c) the P(3) line in the (2-0) overtone band of HD based on the computations of Ref. [317]. These stick spectra were convolved with 1*f*-NICE-OHMS spectral features for each component to yield the curves as plotted.

was included, which results in a general fitting function  $A \cdot g(f + \Delta) + B$ . The latter fits then deliver values for  $\Delta$  as well as an uncertainty:

$$\Delta_{(J=4)-(J=2)}^{v=0} = 13\,283\,245\,098\,(5)\,\text{kHz}$$
  
$$\Delta_{(J=4)-(J=2)}^{v=2} = 16\,882\,368\,179\,(5)\,\text{kHz}$$

in the v = 0 ground and v = 2 excited vibrations in HD. While the results for  $\Delta$  are similar as in the computations of the cross-correlations (deviations as small as 2 kHz and 3 kHz found, respectively), the procedure based on cubic-spline fitting delivers a statistical uncertainty as small as 5 kHz for the spacing between the corresponding line pairs.

Systematic effects should be considered that contribute to the error budget for the frequency spacings between lines. The results presented in Fig. 10.4 pertain to measurements at a pressure of 1 Pa. A similar analysis was performed for data sets obtained at 2.5 Pa leading to values for combination differences  $\Delta$  within 2 kHz. Indeed, the pressure effects on level spacings between rotational lines are expected to be small in view of common-mode cancelation of collisional shifts in the combined transitions.

In the previous study [28] it was established that power broadening does play a role in the saturated NICE-OHMS spectroscopy of HD, but power shifts are constrained to < 1 kHz. Also the frequency calibration reaches kHz accuracy.

The observed composite line shapes, consisting of Lamb-peaks and Lamb-dips, were in our previous studies interpreted as resulting from underlying hyperfine structure and cross-over resonances for which a quantitative model was developed based on optical Bloch equations (OBE) [78]. Such an analysis supported by OBE modeling was developed for the R(1) line. In the derivation of the frequency spacings  $\Delta$  it is assumed that underlying hyperfine structure does not affect the accuracy of this treatment. To assess a possible shift caused by differences in the hyperfine structure of the three lines the underlying hyperfine structure of all three lines is compared, based on the computations of Ref. [317]. In Fig. 10.5 stick spectra of hyperfine components in the spectra of R(1), R(3) and P(3) lines are displayed, convolved with a 1f-demodulated NICE-OHMS function (a 1f derivative of a dispersive line shape) to produce a final width commensurate with the width  $(\Gamma = 400 \text{ kHz FWHM})$  obtained in the auto-correlation functions in Fig. 10.4(c,d). For each of these convoluted functions it is computed in how far the line center deviates from the center-of-gravity of the hyperfine structure, *i.e.* the deviation for the spin-averaged frequency. From these calculations it follows that the center frequencies are shifted from the center-of-gravity of the hyperfine structure by -20 kHz, -10 kHz and +10 kHz for the R(1), R(3) and P(3) lines respectively. These shifts are included as systematic uncertainties in the error budget for the pure rotational line spacings. Hence for the P(3)/R(3) line pair a contribution of 20 kHz, and for the P(3)/R(1) pair a contribution of 30 kHz is included as a systematic uncertainty. These estimates on the uncertainty arising from the underlying hyperfine structure make this contribution the dominant one.

Having established values for the combination differences between the pair P(3)/R(1), including uncertainty, this result can be combined with the accurate result for the transition frequency of the R(1) line based on the OBE-model [78], yielding the transition frequency 203 821 936 805 (60) kHz for the P(3) line, deviating some 19 kHz from the estimate based on the 2f crossing point. Further combining the pair P(3)/R(3) then delivers a transition frequency for the R(3) line, yielding 220 704 304 984 (65) kHz, deviating 21 kHz from the estimates from the 2f crossing point. These frequency separations, obtained via two distinct methods, are in agreement with each other within  $0.3\sigma$ . The values obtained through the combination differences, considered to be most accurate, are included in Table 1.

### 10.3. Discussion and Conclusion

In the present study the vibrational transitions R(1), R(3) and P(3) in the (2-0) overtone band of HD were measured in saturation via the NICE-OHMS technique. These results are compiled in Table 1 including all precision measurements on ro-vibrational and purely rotational transitions hitherto performed. Older data on Doppler-broadened spectroscopy of vibrational overtone transitions [25, 27, 308] are not included. While for the transition frequency of the R(1) line the result based on the systematic study of the line shape, at an accuracy of 50 kHz, was taken [78], results in the present study of R(3) and P(3) are accurate to 65 and 60 kHz, respectively. The experimental results are compared with values obtained via advanced ab initio calculations as in the H2SPECTRE program suite [301]. In this program some level energies and transitions are computed via non-adiabatic perturbation theory (NAPT) [263], while for some specific levels the non-relativistic part is computed via pre-Born-Oppenheimer or 4-particle variational calculations [275, 23]. The theory entries included in Table 1 are partly based on the more accurately

computed values, although some matrix elements and the Bethe-logarithm were computed on a BO-basis [318].

Inspection of the Table shows that for the vibrational transitions there are a large number of entries marked by 'T', where the experimental values are more accurate than the theoretical ones and where the uncertainty is fully determined by theory. Although the deviations are all in the range  $1.6-1.9\sigma$ , or at 10 ppb, it is remarkable that the offsets are so consistently equal and of the same sign. This may be considered as an indication that the ab initio calculations of H2SPECTRE systematically underestimate the vibrational level spacings in HD. Also in the D<sub>2</sub> molecule a recent study yielded a similar underestimate of the theoretical value for the S(0) (1-0) vibrational ground tone frequency by  $1.2\sigma$  [319]. Also in that case, with an experimental accuracy of 17 kHz, the uncertainty was fully determined by theory [300].

Table 1: Comparison between experimental data on purely rotational and ro-vibrational data on transitions frequencies for HD with results of computed results using H2SPECTRE [301]. All frequencies given in MHz. Differences are presented in terms of MHz and in terms of the combined standard deviation ( $\sigma$ ) of experiment and theory. For the entries assigned with 'T' the deviations are entirely determined by the theoretical values from H2SPECTRE.

Band	Line	Exp. (MHz)	Ref.	H2SPECTRE (MHz)	Diff. (MHz)	Diff. $(\sigma)$	
(0-0)							
	R(0)	$2\ 674\ 986.66\ (0.15)$	[288]	$2\ 674\ 986.071\ (0.022)$	0.59(0.15)	3.9	
		$2\ 674\ 986.094\ (0.025)$	[81]	$2\ 674\ 986.071\ (0.022)$	0.023(0.033)	0.7	(T)
	R(1)	$5\ 331\ 560.6\ (4.8)$	[289]	$5\ 331\ 547.053\ (0.045)$	13.5(4.8)	2.8	
	R(2)	7 951 729.9 (5.1)	[289]	7 951 697.887 (0.066)	32(5)	6.4	
	R(3)	$10\ 518\ 306.8\ (3.6)$	[289]	$10\ 518\ 308.641\ (0.087)$	-1.8(3.6)	-0.5	
	R(6)	17 745 695.9 (9.0)	[309]	$17\ 745\ 686.540\ (0.140)$	3.8(6.6)	1.0	
	$S(1)^{a}$	$13\ 283\ 245.098\ (0.030)$	Present	$13\ 283\ 244.944\ (0.110)$	0.15(0.11)	1.4	Т
(1-0)							
	$Q(0)^{a}$	108 889 433.0 (6.6)	[312]	108 889 429.2 (0.5)	3.8(6.6)	0.6	
	R(0)	111 448 815.477 (0.013)	[302]	111 448 814.5 (0.6)	1.0(0.6)	1.6	Т
	$Q(1)^{a}$	108 773 832.4 (6.6)	[312]	108 773 828.4 (0.5)	4.0(6.6)	0.6	
(2-0)							
	P(1)	$209\ 784\ 242.007\ (0.020)$	[310]	$209\ 784\ 240.1\ (1.0)$	1.9(1.1)	1.7	Т
	P(3)	203 821 936.805 (0.060)	$Present^{b}$	203 821 935.0 (1.0)	1.8(1.0)	1.8	Т
	R(1)	217 105 181.901 (0.050)	[78]	217 105 180.0 (1.1)	1.9(1.1)	1.7	Т
		217 105 182.111 (0.240)	[311]	217 105 180.0 (1.1)	2.1(1.1)	1.9	Т
		217 105 181.901 (0.076)	[313]	217 105 180.0 (1.1)	1.9(1.1)	1.7	Т
	R(2)	$219\ 042\ 856.621\ (0.025)$	[28] <sup>c</sup>	219 042 854.7 (1.1)	1.9(1.1)	1.7	Т
	R(3)	220 704 304.951 (0.028)	[28] <sup>c</sup>	220 704 303.0 (1.1)	1.9(1.1)	1.7	Т
		220 704 304.984 (0.065)	Present <sup>b</sup>	220 704 303.0 (1.1)	1.9(1.1)	1.7	Т
(2-2)							
	$S(2)^{a}$	$16\ 882\ 368.179\ (0.020)$	Present	16 882 367.976 (0.140)	0.20(0.14)	1.5	Т

 $^{a}\,$  Derived from a spacing between lines, or a combination difference.

 $b\,$  Results from vibrational transitions in the present study.

<sup>C</sup> Results from fitting center frequency of a Lamb-dip without considering the complex line shape.

For the measurements of pure rotational transitions performed so far there is only a single experimental result claiming the same accuracy as that of theory: a measurement of the R(0) line reported in Ref. [81]. For this result the experimental value is again higher by  $0.7\sigma$  of the combined uncertainties. The present measurements of rotational level spacings, deduced from combination differences of measured transition frequencies, represent equally accurate determinations, with their 20-30 kHz systematic uncertainties. So when comparing the most accurate experimental data with the most advanced ab initio calculations, including relativistic and QED effects [320, 263, 300] the body of experimental data, both vibrational and rotational, are some  $1.5-1.9\sigma$ larger than theory. This might be viewed as an offset scaling with energy. However, that finding cannot be extrapolated to results on dissociation energies of the H<sub>2</sub> molecule, where the most accurate experimental result [278] is found to be in excellent agreement with theory [275, 23]. A recent experimental value for the dissociation energy of the D<sub>2</sub> species [321] was found to be off from theory [23] by 2 MHz, corresponding to  $1.6\sigma$ , but here the uncertainty contributions from experiment and theory were the same. As for the case of the dissociation energy of the HD isotopologue the current experimental value [322] is off from theory [23] by  $2.7\sigma$ . While this might be viewed as another discrepancy for the HD species, where g - u symmetry-breaking plays a role, it should be considered however, that in this case the uncertainty is fully determined by experiment.

Inspection of results from the H2SPECTRE on-line program [301] reveals that the uncertainties for the rotational splittings on the theoretical side fully depend on the uncertainty in the evaluation of the  $E^{(5)}$  leading order QED-term. For the  $\Delta^{v=0}_{(J=3)-(J=1)}$  splitting the uncertainty in  $E^{(5)}$  amounts to 107 kHz, compared to a full uncertainty over all terms of 110 kHz. For  $\Delta_{(J=4)-(J=2)}^{v=2}$  this is 137 kHz out of 140 kHz uncertainty contributed from  $E^{(5)}$ . These uncertainties in the rotational splittings imply already strong cancellation of common-mode contributions, where the uncertainties in the  $E^{(5)}$ -term in the binding energies of HD-levels (v = 0, J = 1and 3) amount to 5.5 MHz [301]. For specific low-lying levels the  $E^{(5)}$  contributions to their binding energy are much more accurate, like for the H<sub>2</sub> (v = 0, J = 0)ground level where  $E^{(5)}$  is accurate to 5 kHz [279], while for HD (v = 0, J = 0)the  $E^{(5)}$ -term is accurate only to 120 kHz [23]. This reflects the higher level of computation pursued for  $H_2$ , an approach that might resolve the presently found discrepancies between experiment and theory for the HD molecule. In this sense the presently determined splittings in HD form a test bench theory for the further development of theory for the hydrogen molecular species.

### 10.4. Acknowledgments

The authors thank IHM van Stokkum (VUA) for fruitful discussions on the data analysis. The research was funded via the Access Program of Laserlab-Europe (Grant Numbers 654148 and 871124), a European Union's Horizon 2020 research and innovation programme. Financial support from the European Research Council (ERC-Advanced Grant No. 670168) and from the Netherlands Organisation for Scientific Research, via the Program "The Mysterious Size of the Proton" is gratefully acknowledged. M. Schlösser wants to thank the Baden-Württemberg Foundation for the generous support of this work within the Elite-Postdoc-Fellowship.

# Chapter 11 Summary and outlook

Our NICE-OHMS setup, designed for highly sensitive measurements, was specifically built to study saturation spectra of HD rovibrational lines. In 2017, two separate research groups (Amsterdam and Hefei) simultaneously measured the saturation signal of this molecule for the first time [28, 29]. Interestingly, the extracted transition frequencies of the R(1) line exhibited significant differences, which posed a puzzle and motivated us to improve our experimental setup.



Figure 11.1: Illustration of the two types of crossover resonances occurring during an excitation by the two counter-propagating waves of similar frequency detuning  $\nu_0$ . At the top, the projected velocity along the laser axis  $\vec{z}$  of the molecule is represented by  $v_z$ . These crossovers appear at the frequency positions matching the difference of energy between (a) the two excited states and (b) the two ground states. Additionally, to match the condition of saturated resonance of the two counter-propagating beams, the effective Doppler shift of the molecule needs to match the following equation:  $k \cdot v_z = \nu_0 = \frac{1}{2}(E_1 + E_2)$  or  $\frac{1}{2}(G_1 + G_2)$ 

Upon further investigation, we discovered that the observed lineshape did not match our initial expectation of a symmetric Lamb-dip. In the first chapter of Part II (also [78]), we presented an improved measurement of the saturated Lamb-dip of R(1), which exhibits a dispersive-like lineshape. We attributed this lineshape to

the rich hyperfine structure of the transition. Our hypothesis was that crossover transitions, virtual transitions between two lines sharing either the same excited state (referred to as "V" type) or the same ground state (referred to as " $\Lambda$ " type), create a peak-like shape in the Lamb-dip profile. The two different mechanisms are illustrated in Fig 11.1. The "V" type is very well known, documented and known to produce normal Lamb-dip profiles. We then postulated that the novelty was in the " $\Lambda$ " type, where the population of one ground state can be moved to another ground state hence enhancing the absorption at this frequency.

To validate this hypothesis, we utilized an optical Bloch equation (OBE) framework, inputting the 21 hyperfine transitions of R(1) along with their splitting and respective strengths. It is worth noting that the crossovers were not explicitly programmed into the OBE but naturally emerged when integrating over the velocities contained in the Doppler broadened profile. Our calculations demonstrated that, for certain relaxation parameters, the experimentally observed lineshapes can be reproduced. Interestingly, the peak of the dispersive-like lineshape closely matches the hyperfineless position of R(1). However, it was emphasized that many approximations were made in the numerical determination, in particular the relatively large values of the relaxation parameter  $\gamma_{pop}$ , which leads to a large uncertainty of 50 kHz in this study.

Building upon these findings, we extended our investigation to another rovibrational HD line, the P(1) line [310]. If our postulate was correct, this line should exhibit a fully peaked lineshape, as it is composed of five ground states connected to two excited states, with only " $\Lambda$ " type crossovers present. As anticipated, the experimental results aligned with our expectations, and the OBE calculations agreed with the observed spectra. Both the experimental and calculated spectra could be superimposed. It is important to mention that approximations on the relaxation parameters remained the same, but we were able to assign a smaller uncertainty to the determination of the P(1) line.

However, it was found out that the agreement between experiment and OBE calculations were proven incomplete when the R(0) line was first recorded under saturation conditions [323]. R(0) exhibits a hyperfine structure inverted in comparison to the P(1). We then expected a normal Lamb-dip as only V-type crossovers should be present. However the measured lineshape exhibits a similar dispersive-like lineshape as R(1) as seen in Fig 11.2.

The similarities in the line profiles for many of the rovibrational transitions in HD led to chapter 10 where different rovibrational lines were superimposed to extract rotational intervals. In addition to measurement of combination differences between R(1), R(3) and P(3) lines [324], combination differences between R(0), R(2) and P(2) [323] were used to extract level splittings between rotational levels in HD.

Although, the OBE used in the HD studies could reproduce the shapes of R(1) and P(1), it has been shown that it was incomplete and the model definitely needs improvements. In our NICE-OHMS studies it was found that a weak transition in CO<sub>2</sub>, measured under saturation conditions, also shows a dispersive-like line shape [323]. From the fact that CO<sub>2</sub> does not exhibit hyperfine structure it must



Figure 11.2: Recordings of the first overtone rovibrational lines in HD of P(1) and R(0). Stick spectra of hyperfine components and two types of crossover components are displayed below the observed spectra. Due to their inverted hyperfine configuration, P(1) exhibits  $\Lambda$ -type crossovers, while R(0) is characterized by V-type crossovers.

be concluded that other mechanisms play a role in producing an asymmetric line shape in such studies.

Simultaneously, the Hefei group put forth a model based on a Fano profile. Initially, it was hypothesized that collisions occurring inside a gas cell could generate a continuum, potentially resulting in a Fano profile [311]. Subsequently, a second hypothesis was proposed, centered around the far-lying electronic B state. It was suggested that the wings of the electronic transition could serve as the continuum necessary for a typical Fano profile. However, this model was also found to be incomplete, requiring further improvements and refinements.

By comparing various experiments conducted on different isotopologues, intriguing observations come to light. In the context of Doppler broadened studies [313, 325], as well as in molecular beam experiments [312, 302], the recorded line profiles do not exhibit any asymmetry. The key difference between these experiments and the ones carried out in Amsterdam and Hefei lies in the utilization of powerful intracavity standing waves for the latter. This distinction led to the proposal of two distinct hypotheses based on the presence of standing waves near weak resonances.

At Hefei the Fano-line shape model was further elaborated by investigating various weak  $CO_2$  lines under saturation in a cavity [326]. Molecules traveling through a standing wave were proposed to undergo periodic excitation and periodic modulation to a far-away lying electronic state occurring simultaneously. The combination of the two effects lead to a perturbation of the probed resonance giving rise to a Fano-like lineshape.

Conversely, in Amsterdam, in a saturation study of a vibrational transition in  $H_2$  we suggest that the dipole force, enhanced by the proximity of resonance, alters the velocity distribution of the Doppler effect, thus distorting the resulting lineshape, especially in the presence of strong standing waves [327]. This hypothesis draws inspiration from the seminal work of Letokhov and Chebotayev [133], where it was proposed that molecules flying along the beam can be trapped or rather slowed down, resulting in a peak observed at the center of the transition. Our observations on the S(0) quadrupole line of  $H_2$  illustrate the effect of a strong standing wave probing an extremely weak line. By varying the intracavity power by two orders of magnitude, the recorded spectra transition from a peak to a dispersive-like lineshape and eventually to a symmetric Lamb-Dip at low intracavity power. From these observations it becomes apparent that the presence of powerful intracavity standing wave are key to contributing to the distortion of the lineshapes of the saturated absorption spectra of HD. Future quantitative investigations, both on the experimental as well as on the theoretical side should provide a more complete understanding of those line shapes. Such better understanding will allow a more accurate determination of quantum level splittings in these systems, and provide an enhanced test of quantum electrodynamics theory in molecules.

## Bibliography

- [1] T. Maiman. Stimulated optical radiation in Ruby. *Nature*, 187:493–494, 1960.
- [2] W. Demtröder. Laser Spectroscopy: Vol. 1 Basic Principles. Springer, Berlin, 2021.
- [3] W. Demtröder. Laser Spectroscopy: Vol. 2 Experimental Techniques. Springer, Berlin, 2021.
- G. C. Bjorklund. Frequency-modulation spectroscopy: a new method for measuring weak absorptions and dispersions. *Optics Letters*, 5:15–17, 1980.
- [5] A. O'Keefe and D. A. G. Deacon. Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources. *Review of Scientific Instruments*, 59:2544–2551, 1988.
- [6] R. D. Van Zee and J. P. Looney. Cavity Enhanced Spectroscopies, Experimental methods in the physical sciences, Vol. 40. Academic Press, 2002.
- [7] I. Galli, S. Bartalini, R. Ballerini, M. Barucci, P. Cancio, M. De Pas, G. Giusfredi, D. Mazzotti, N. Akikusa, and P. De Natale. Spectroscopic detection of radiocarbon dioxide at parts-per-quadrillion sensitivity. *Optica*, 3:385–388, 2016.
- [8] B. Henderson, A. Khodabakhsh, M. Metsälä, I. Ventrillard, F. M. Schmidt, D. Romanini, G. A. D. Ritchie, S. te Lintel Hekkert, R. Briot, T. Risby, N. Marczin, F. J. M. Harren, and S. M. Cristescu. Laser spectroscopy for breath analysis: towards clinical implementation. *Applied Physics B*, 124, 2018.
- [9] J. Ye, L.-S. Ma, and J. L. Hall. Sub-Doppler optical frequency reference at 1.064 μm by means of ultrasensitive cavity-enhanced frequency modulation spectroscopy of a C<sub>2</sub>HD overtone transition. *Optics Letters*, 21:1000–1002, 1996.
- [10] W. E. Lamb Jr. Theory of an optical maser. *Physical Review*, 134:A1429, 1964.
- [11] T. W. Hänsch. Nobel lecture: Passion for precision. Reviews of Modern Physics, 78:1297–1309, 2006.
- [12] J. L. Hall. Nobel lecture: Defining and measuring optical frequencies. *Reviews of Modern Physics*, 78:1279–1295, 2006.
- [13] W. R. Bennett. Hole burning effects in a He-Ne optical maser. *Physical Review*, 126:580–593, 1962.
- [14] R. W. P. Drever, J. L. Hall, F. V. Kowalski, J. Hough, G. M. Ford, A. J. Munley, and H. Ward. Laser phase and frequency stabilization using an optical resonator. *Applied Physics B*, 31:97–105, 1983.
- [15] R. G. DeVoe and R. G. Brewer. Laser-frequency division and stabilization. *Physical Review A*, 30:2827–2829, 1984.
- [16] A. Foltynowicz. Fiber-laser-based Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry. PhD thesis, Umeå University, Umeå, Sweden, 2009.
- [17] J. Domysławska, S. Wójtewicz, Katarzyna Bielska, S. Bilicki, R. Ciuryło, and D. Lisak. Line mixing in the oxygen B band head. *The Journal of Chemical Physics*, 156:084301, 2022.
- [18] H. Fleurbaey, A. O. Koroleva, S. Kassi, and A. Campargue. The high-accuracy spectroscopy of H<sub>2</sub> rovibrational transitions in the (2-0) band near 1.2  $\mu$ m. *Physical Chemistry Chemical Physics*, 25:14749–14756, 2023.

- [19] D. A. Long, G.-W. Truong, J. T. Hodges, and C. E. Miller. Absolute <sup>12</sup>C<sup>16</sup>O<sub>2</sub> transition frequencies at the kHz-level from 1.6 to 7.8 μm. Journal of Quantitative Spectroscopy and Radiative Transfer, 130:112–115, 2013.
- [20] J. Wang, Y. R. Sun, L.-G. Tao, A.-W. Liu, T.-P. Hua, F. Meng, and S.-M. Hu. Comb-locked cavity ring-down saturation spectroscopy. *Review of Scientific Instruments*, 88:043108, 2017.
- [21] E. Fasci, S. Gravina, G. Porzio, A. Castrillo, and L. Gianfrani. Lamb-dip cavity ring-down spectroscopy of acetylene at 1.4 μm. New Journal of Physics, 23:123023, 2021.
- [22] C.-F. Cheng, J. Hussels, M. Niu, H. L. Bethlem, K. S. E. Eikema, E. J. Salumbides, W. Ubachs, M. Beyer, N. Hölsch, J. A. Agner, F. Merkt, L.-G. Tao, S.-M. Hu, and Ch. Jungen. Dissociation energy of the hydrogen molecule at 10<sup>-9</sup> accuracy. *Physical Review Letters*, 121:013001, 2018.
- [23] M. Puchalski, J. Komasa, A. Spyszkiewicz, and K. Pachucki. Dissociation energy of molecular hydrogen isotopologues. *Physical Review A*, 100:020503, 2019.
- [24] G. Herzberg. Rotation-vibration spectrum of the HD molecule. Nature, 166:563, 1950.
- [25] R. A. Durie and G. Herzberg. Forbidden transitions in diatomic molecules: V. The rotation-vibration spectrum of the hydrogen-deuteride (HD) molecule. *Canadian Journal of Physics*, 38:806–818, 1960.
- [26] A. R. W. McKellar. Intensities of dipole and quadrupole rotation-vibration spectra of HD. Canadian Journal of Physics, 52:1144–1151, 1974.
- [27] S. Kassi and A. Campargue. Electric quadrupole and dipole transitions of the first overtone band of HD by CRDS between 1.45 and 1.33 μm. Journal of Molecular Spectroscopy, 267:36–42, 2011.
- [28] F. M. J. Cozijn, P. Dupré, E. J. Salumbides, K. S. E. Eikema, and W. Ubachs. Sub-Doppler frequency metrology in HD for tests of fundamental physics. *Physical Review Letters*, 120:153002, 2018.
- [29] L.-G. Tao, A.-W. Liu, K. Pachucki, J. Komasa, Y. R. Sun, J. Wang, and S.-M. Hu. Toward a determination of the proton-electron mass ratio from the lamb-dip measurement of HD. *Physical Review Letters*, 120:153001, 2018.
- [30] I. E. Gordon, L. S. Rothman, C. Hill, R. V. Kochanov, Y. Tan, P. F. Bernath, M. Birk, V. Boudon, A. Campargue, K. V. Chance, B. J. Drouin, J.-M. Flaud, R. R. Gamache, J. T. Hodges, D. Jacquemart, V. I. Perevalov, A. Perrin, K. P. Shine, M.-A. H. Smith, J. Tennyson, G. C. Toon, H. Tran, V. G. Tyuterev, A. Barbe, A. G. Császár, V. M. Devi, T. Furtenbacher, J. J. Harrison, J.-M. Hartmann, A. Jolly, T. J. Johnson, T. Karman, I. Kleiner, A. A. Kyuberis, J. Loos, O. M. Lyulin, S. T. Massie, S. N. Mikhailenko, N. Moazzen-Ahmadi, H. S. P. Müller, O. V. Naumenko, A. V. Nikitin, O. L. Polyansky, M. Rey, M. Rotger, S. W. Sharpe, K. Sung, E. Starikova, S. A. Tashkun, J. Vander Auwera, G. Wagner, J. Wilzewski, P. Wcisło, S. Yu, and E. J. Zak. The HITRAN 2016 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer, 203:3–69, 2017.
- [31] S. Twagirayezu, M. J. Cich, T. J. Sears, C. P. McRaven, and G. E. Hall. Frequencycomb referenced spectroscopy of ν<sub>4</sub>- and ν<sub>5</sub>-excited hot bands in the 1.5 μm spectrum of C<sub>2</sub>H<sub>2</sub>. Journal of Molecular Spectroscopy, 316:64–71, 2015.
- [32] L. Santamaria, V. Di Sarno, P. De Natale, M. De Rosa, M. Inguscio, S. Mosca, I. Ricciardi, D. Calonico, F. Levi, and P. Maddaloni. Comb-assisted cavity ring-down

spectroscopy of a buffer-gas-cooled molecular beam. *Physical Chemistry Chemical Physics*, 18:16715–16720, 2016.

- [33] D. Gatti, R. Gotti, A. Gambetta, M. Belmonte, G. Galzerano, P. Laporta, and M. Marangoni. Comb-locked Lamb-dip spectrometer. *Scientific Reports*, 6:27183, 2016.
- [34] J. Wang, Y. R. Sun, L. G. Tao, A. W. Liu, T. P. Hua, F. Meng, and S.-M. Hu. Comblocked cavity ring-down saturation spectroscopy. *Review of Scientific Instruments*, 88:043108, 2017.
- [35] W. Ritz. On a new law of series spectra. Astrophysical Journal, 28:237–243, 1908.
- [36] F. Matsushima, N. Tomatsu, T. Nagai, Y. Moriwaki, and K. Takagi. Frequency measurement of pure rotational transitions in the v<sub>2</sub> = 1 state of H<sub>2</sub>O. Journal of Molecular Spectroscopy, 235:190–195, 2006.
- [37] J.-M. Flaud, C. Camy-Peyret, and J. P. Maillard. Higher ro-vibrational levels of H<sub>2</sub>O deduced from high resolution oxygen-hydrogen flame spectra between 2800 – 6200 cm<sup>-1</sup>. *Molecular Physics*, 32:499–521, 1976.
- [38] S. A. Tashkun V. I. Starikov and V. L. G. Tyuterev. Description of vibrationrotation energies of nonrigid triatomic molecules using the generating function method: bending states and second triad of water. *Journal of Molecular Spec*troscopy, 151:130–147, 1992.
- [39] J. K. G. Watson. The use of term-value fits in testing spectroscopic assignments. Journal of Molecular Spectroscopy, 165:283–290, 1994.
- [40] T. Furtenbacher, A. G. Császár, and J. Tennyson. MARVEL: measured active rotational-vibrational energy levels. *Journal of Molecular Spectroscopy*, 245:115– 125, 2007.
- [41] S. N. Mikhailenko, S. A. Tashkun, T. A. Putilova, E. N. Starikova, L. Daumont, A. Jenouvrier, S. Fally, M. Carleer, C. Hermans, and A. C. Vandaele. Critical evaluation of measured rotation-vibration transitions and an experimental dataset of energy levels of HD<sup>18</sup>O. Journal of Quantitative Spectroscopy and Radiative Transfer, 110:597–608, 2009.
- [42] S. A. Tashkun, T. I. Velichko, and S. N. Mikhailenko. Critical evaluation of measured pure-rotation and rotation-vibration line positions and an experimental dataset of energy levels of  ${}^{12}C^{16}O$  in  $X^{1}\Sigma^{+}$  state. Journal of Quantitative Spectroscopy and Radiative Transfer, 111:1106–1116, 2010.
- [43] T. Furtenbacher and A. G. Császár. MARVEL: measured active rotationalvibrational energy levels. II. Algorithmic improvements. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 113:929–935, 2012.
- [44] M. E. J. Newman. Networks. Oxford University Press, Oxford, 2000.
- [45] A. G. Császár and T. Furtenbacher. Spectroscopic networks. Journal of Molecular Spectroscopy, 266:99–103, 2011.
- [46] A. G. Császár, T. Furtenbacher, and P. Árendás. Small molecules big data. Journal of Physical Chemistry A, 120:8949–8969, 2016.
- [47] J. A. Hageman, R. Wehrens, R. de Gelder, W. L. Meerts, and L. M. C. Buydens. Direct determination of molecular constants from rovibronic spectra with genetic algorithms. *Journal of Chemical Physics*, 113:7955–7962, 2000.
- [48] W. L. Meerts, M. Schmitt, and G. C. Groenenboom. New applications of the genetic algorithm for the interpretation of high-resolution spectra. *Canadian Journal of Chemistry*, 82:804–819, 2004.

- [49] N. R. Pillsbury, C. W. Muller, W. L. Meerts, D. F. Plusquellic, and T. S. Zwier. Conformational effects on excitonic interactions in a prototypical H-bonded bichromophore: bis (2-hydroxyphenyl) methane. *Journal of Physical Chemistry A*, 113:5000–5012, 2009.
- [50] D. P. Zaleski and K. Prozument. Automated assignment of rotational spectra using artificial neural networks. *Journal of Chemical Physics*, 149:104106, 2018.
- [51] J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, A. G. Császár, L. Daumont, R. R. Gamache, J. T. Hodges, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, A. C. Vandaele, N. F. Zobov, A. R. Al Derzi, C. Fábri, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, L. Lodi, and I. I. Mizus. IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part III. Energy levels and transition wavenumbers for H<sub>2</sub><sup>16</sup>O. Journal of Quantitative Spectroscopy and Radiative Transfer, 117:29–80, 2013.
- [52] R. Tóbiás, T. Furtenbacher, J. Tennyson, and A. G. Császár. Accurate empirical rovibrational energies and transitions of H<sub>2</sub><sup>16</sup>O. *Physical Chemistry Chemical Physics*, 21:3473–3495, 2019.
- [53] E. F. van Dishoeck, E. Herbst, and D. A. Neufeld. Interstellar water chemistry: from laboratory to observations. *Chemical Reviews*, 113:9043–9085, 2013.
- [54] A. Tsiaras, I. P. Waldmann, G. Tinetti, J. Tennyson, and S. N. Yurchenko. Water vapour in the atmosphere of the habitable-zone eight-Earth-mass planet K2-18b. *Nature Astronomy*, 3:1086–1091, 2019.
- [55] O. L. Polyansky, N. F. Zobov, J. Tennyson, J. A. Lotoski, and P. F. Bernath. Hot bands of water in the ν<sub>2</sub> manifold up to 5ν<sub>2</sub>-4ν<sub>2</sub>. Journal of Molecular Spectroscopy, 184:35-50, 1997.
- [56] R. Lang, A. N. Maurellis, W. J. van der Zande, I. Aben, J. Landgraf, and W. Ubachs. Forward modeling and retrieval of water vapor from the global ozone monitoring experiment: treatment of narrowband absorption spectra. *Journal of Geophysical Research - Atmospheres*, 107:ACH 11–1–ACH 11–23, 2002.
- [57] V. Ramanathan and A. M. Vogelmann. Greenhouse effect, atmospheric solar absorption and the Earth's radiation budget: from the Arrhenius-Langley era to the 1990s. Ambio, 26:38–46, 1997.
- [58] H. Wang and W. Su. Evaluating and understanding top of the atmosphere cloud radiative effects in Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5) Coupled Model Intercomparison Project Phase 5 (CMIP5) models using satellite observations. *Journal of Geophysical Research - Atmospheres*, 118:683–699, 2013.
- [59] A. Miani and J. Tennyson. Can ortho-para transitions for water be observed? Journal of Chemical Physics, 120:2732–2739, 2004.
- [60] S. G. Kukolich. Measurement of the molecular g values in H<sub>2</sub>O and D<sub>2</sub>O and hyperfine structure in H<sub>2</sub>O. Journal of Chemical Physics, 50:3751–3755, 1969.
- [61] C. Huiszoon. A high resolution spectrometer for the shorter millimeter wavelength region. *Review of Scientific Instruments*, 42:477–481, 1971.
- [62] G. Steenbeckeliers and J. Bellet. Spectre micro-onde de molecules H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O et H<sub>2</sub><sup>18</sup>O. Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences Serie B, 273:471–474, 1971.
- [63] A. Bauer, M. Godon, M. Kheddar, and J.M. Hartmann. Temperature and perturber dependences of water vapor line-broadening. Experiments at 183 GHz; calculations

Page 158 of 181

below 1000 GHz. Journal of Quantitative Spectroscopy and Radiative Transfer, 41:49–54, 1989.

- [64] V. N. Markov and A. F. Krupnov. Measurements of the pressure shift of the (110)-(101) water line at 556 GHz produced by mixtures of gases. *Journal of Molecular Spectroscopy*, 172:211–214, 1995.
- [65] G. Y. Golubiatnikov. Shifting and broadening parameters of the water vapor 183-GHz line (313-220) by H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, He, Ne, Ar, and Kr at room temperature. *Journal of Molecular Spectroscopy*, 230:196–198, 2005.
- [66] G. Y. Golubiatnikov, V. N. Markov, A. Guarnieri, and R. Knochel. Hyperfine structure of H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O measured by Lamb-dip technique in the 180–560 GHz frequency range. *Journal of Molecular Spectroscopy*, 240:251–254, 2006.
- [67] M. A. Koshelev, M. Y. Tretyakov, G. Y. Golubiatnikov, V. V. Parshin, V. N. Markov, and I. A. Koval. Broadening and shifting of the 321-, 325- and 380 GHz lines of water vapor by pressure of atmospheric gases. *Journal of Molecular Spectroscopy*, 241:101–108, 2007.
- [68] G. Cazzoli, C. Puzzarini, M. E. Harding, and J. Gauss. The hyperfine structure in the rotational spectrum of water: Lamb-dip technique and quantum-chemical calculations. *Chemical Physics Letters*, 473:21–25, 2009.
- [69] M. A. Koshelev. Collisional broadening and shifting of the 211–202 transition of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, and H<sub>2</sub><sup>18</sup>O by atmosphere gases. Journal of Quantitative Spectroscopy and Radiative Transfer, 112:550–552, 2011.
- [70] M. Y. Tretyakov, M. A. Koshelev, I. N. Vilkov, V. V. Parshin, and E. A. Serov. Resonator spectroscopy of the atmosphere in the 350–500 GHz range. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 114:109–121, 2013.
- [71] S. Kassi, T. Stoltmann, M. Casado, M. Daeron, and A. Campargue. Lamb dip CRDS of highly saturated transitions of water near 1.4  $\mu$ m. Journal of Chemical Physics, 148:054201, 2018.
- [72] J. Chen, T.-P. Hua, L.-G. Tao, Y.R. Sun, A.-W. Liu, and S.-M. Hu. Absolute frequencies of water lines near 790 nm with 10<sup>-11</sup> accuracy. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 205:91–95, 2018.
- [73] R. S. Mulliken. Report on notation for the spectra of polyatomic molecules. Journal of Chemical Physics, 23:1997–2011, 1955.
- [74] H. W. Kroto. Molecular Rotation Spectra. Dover, New York, 1992.
- [75] J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, A. G. Császár, L. Daumont, R. R. Gamache, J. T. Hodges, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, A.C.Vandaele, N. F. Zobov, N. Dénes, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, S.-M.Hu, T. Szidarovszky, and I. A. Vasilenko. IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part IV. Energy levels and transition wavenumbers for D<sub>2</sub><sup>16</sup>O, D<sub>2</sub><sup>17</sup>O, and D<sub>2</sub><sup>18</sup>O. Journal of Quantitative Spectroscopy and Radiative Transfer, 142:93–108, 2014.
- [76] J. Tennyson and S. N. Yurchenko. ExoMol: molecular line lists for exoplanet and other atmospheres. *Monthly Notices of the Royal Astronomical Society*, 425:21–33, 2012.
- [77] R. Tóbiás, T. Furtenbacher, and A. G Császár. Cycle bases to the rescue. Journal of Quantitative Spectroscopy and Radiative Transfer, 203:557–564, 2017.

- [78] M. L. Diouf, F. M. J. Cozijn, B. Darquié, E. J. Salumbides, and W. Ubachs. Lambdips and Lamb-peaks in the saturation spectrum of HD. *Optics Letters*, 44:4733, 2019.
- [79] F. Matsushima, H. Odashima, T. Iwasaki, S. Tsunekawa, and K. Takagi. Frequency measurement of pure rotational transitions of H<sub>2</sub>O from 0.5 to 5 THz. *Journal of Molecular Spectroscopy*, 352:371–378, 1995.
- [80] G. Cazzoli, C. Puzzarini, G. Buffa, and O. Tarrini. Pressure-broadening of water lines in the THz frequency region: improvements and confirmations for spectroscopic databases. Part II. Journal of Quantitative Spectroscopy and Radiative Transfer, 110:609–618, 2009.
- [81] B. J. Drouin, S. Yu, J. C. Pearson, and H. Gupta. Terahertz spectroscopy for space applications: 2.5–2.7 THz spectra of HD, H<sub>2</sub>O and NH<sub>3</sub>. *Journal of Molecular Structure*, 1006:2–12, 2011.
- [82] S. Yu, J. C. Pearson, B. J. Drouin, M.-A. Martin-Drumel, O. Pirali, M. Vervloet, L. H. Coudert, H. S. P. Müller, and S. Brünken. Measurement and analysis of new terahertz and far-infrared spectra of high temperature water. *Journal of Molecular Spectroscopy*, 279:16–25, 2012.
- [83] S. Yu, J. C. Pearson, and B. J. Drouin. Terahertz spectroscopy of water in its second triad. *Journal of Molecular Spectroscopy*, 288:7–10, 2013.
- [84] E. Mátyus, G. Czakó, and A. G. Császár. Toward black-box-type full- and reduceddimensional variational (ro)vibrational computations. *Journal of Chemical Physics*, 130:134112, 2009.
- [85] C. Fábri, E. Mátyus, and A. G. Császár. Rotating full- and reduced-dimensional quantum chemical models of molecules. *Journal of Chemical Physics*, 134:074105, 2011.
- [86] F. C. de Lucia, P. Helminger, R. L. Cook, and W. Gordy. Submillimeter microwave spectrum of H<sub>2</sub><sup>16</sup>O. *Physical Review A*, 5:487–490, 1972.
- [87] J. K. Messer, F. C. de Lucia, and P. Helminger. The pure rotational spectrum of water vapor-a millimeter, submillimeter, and far infrared analysis. *International Journal of Infrared and Millimeter Waves*, 4:505–539, 1983.
- [88] J. W. C. Johns. High-resolution far-infrared (20–350 cm<sup>-1</sup>) spectra of several isotopic species of H<sub>2</sub>O. Journal of the Optical Society of America B, 2:1340–1354, 1985.
- [89] O. I. Baskakov, V. A. Alekseev, E. A. Alekseev, and B. I. Polevoi. New submillimeter rotational lines of water and its isotopes. *Optics and Spectroscopy*, 63:1016–1018, 1987.
- [90] R. A. Toth. v<sub>2</sub> band of H<sub>2</sub><sup>16</sup>O: line strengths and transition frequencies. Journal of the Optical Society of America B, 8:2236–2255, 1991.
- [91] R. Lanquetin, L. H. Coudert, and C. Camy-Peyret. High-lying rotational levels of water: An analysis of the energy levels of the five first vibrational states. *Journal* of Molecular Spectroscopy, 206:83–103, 2001.
- JPL website. https://spec.jpl.nasa.gov//%ftp//pub/catalog/archi ve/c018005.egy. Accessed: 2020-02-26.
- [93] L. H. Coudert, Marie-Aline Martin-Drumel, and Olivier Pirali. Analysis of the high-resolution water spectrum up to the second triad and to J = 30. Journal of Molecular Spectroscopy, 303:36–41, 2014.

Page 160 of 181

- [94] R. A. Toth. Measurements of positions, strengths and self-broadened widths of H<sub>2</sub>O from 2900 to 8000 cm<sup>-1</sup>: line strength analysis of the 2<sup>nd</sup> triad bands. Journal of Quantitative Spectroscopy and Radiative Transfer, 94:51–107, 2005.
- [95] R. J. Barber, J. Tennyson, G. J. Harris, and R. N. Tolchenov. A high-accuracy computed water line list. *Monthly Notices of the Royal Astronomical Society*, 368:1087– 1094, 2006.
- [96] H. Dinesan, E. Fasci, A. Castrillo, and L. Gianfrani. Absolute frequency stabilization of an extended-cavity diode laser by means of noise-immune cavity-enhanced optical heterodyne molecular spectroscopy. *Optics Letters*, 39:2198–2201, 2014.
- [97] L.-S. Ma, Jun Ye, Pierre Dubé, and John L Hall. Ultrasensitive frequencymodulation spectroscopy enhanced by a high-finesse optical cavity: theory and application to overtone transitions of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>HD. Journal of the Optical Society of America B, 16:2255–2268, 1999.
- [98] A. Foltynowicz, F.M. Schmidt, W. Ma, and O. Axner. Noise-immune cavityenhanced optical heterodyne molecular spectroscopy: Current status and future potential. *Applied Physics B*, 92:313–326, 2008.
- [99] P. F. Bernath. The spectroscopy of water vapour: experiment, theory and applications. *Physical Chemistry Chemical Physics*, 4:1501–1509, 2002.
- [100] I. E. Gordon, L. S. Rothman, R. J. Hargreaves, R. Hashemi, E. V. Karlovets, F. M. Skinner, E. K. Conway, C. Hill, R. V. Kochanova, Y. Tana, P. Wcislo, A. A. Finenko, K. Nelson, P. F. Bernath, M. Birk, V. Boudon, A. Campargue, K. V. Chance, A. Coustenis, B. J. Drouin, J.-M. Flaud, R. R. Gamache, J. T. Hodges, D. Jacquemart, E. J. Mlawer, A. V. Nikitin, V. I. Perevalov, M. Rotger, K. P. Shines, J. Tennyson, G. C. Toon, H. Tran, V. G. Tyuterev, E. M. Adkins, A. Baker, A. Barber, E. Canev, A. G. Császár, O. Egorov, A. J. Fleisher, A. Foltynowicz, T. Furtenbacher, J. J. Harrison, J.-M. Hartmann, V.-M. Horneman, X. Huang, T. Karman, J. Karnsa, S. Kassi, I. Kleiner, V. Kofman, F. Kwabia-Tchana, T. J. Lee, D. A. Longo, A. A. Lukashevskaya, O. M. Lyulin, V. Yu. Makhneva, S. T. Massie, M. Melosso, S. N. Mikhailenko, D. Mondelain, H. S. P. Müller, O. V. Naumenko, A. Perrin, O. L. Polyansky, E. Raddaoui, P. L. Rastonah, Z. D. Reed, M. Rey, C. Richard, R. Tóbiás, I. Sadieky, D. W. Schwenke, E. Starikova, K. Sung, F. Tamassia, S. A. Tashkun, J. Vander Auwera, A. A. Vigasina, G. L. Villanueva, B. Vispoel, G. Wagner, and S. N. Yurchenko. The HITRAN2020 molecular spectroscopic database. Journal of Quantitative Spectroscopy and Radiative Transfer, 276:107949, 2021.
- [101] N. Jacquinet-Husson, R. Armante, N. A. Scott, A. Chedin, L. Crepeau, C. Boutammine, A. Bouhdaoui, C. Crevoisier, V. Capelle, C. Boonne, N. Poulet-Crovisier, A. Barbe, D. Chris Benner, V. Boudon, L. R. Brown, J. Buldyreva, A. Campargue, L. H. Coudert, V. M. Devi, M. J. Down, B. J. Drouin, A. Fayt, C. Fittschen, J. M. Flaud, R. R. Gamache, J. J. Harrison, C. Hill, O. Hodnebrog, S. M. Hu, D. Jacquemart, A. Jolly, E. Jimenez, N. N. Lavrentieva, A. W. Liu, L. Lodi, O. M. Lyulin, S. T. Massie, S. Mikhailenko, H. S. P. Mueller, O. V. Naumenko, A. Nikitin, C. J. Nielsen, J. Orphal, V. I. Perevalov, A. Perrin, E. Polovtseva, A. Predoi-Cross, M. Rotger, A. A. Ruth, S. S. Yu, K. Sung, S. A. Tashkun, J. Tennyson, V. I. G. Tyuterev, J. Vander Auwera, B. A. Voronin, and A. Makie. The 2015 edition of the GEISA spectroscopic database. *Journal of Molecular Spectroscopy*, 327:31–72, 2016.
- [102] O. L. Polyansky, A. A. Kyuberis, L. Lodi, J. Tennyson, R. I. Ovsyannikov, and N.F. Zobov. ExoMol molecular line lists XIX: High accuracy computed line lists for

 $H_2^{17}O$  and  $H_2^{18}O$ . Monthly Notices of the Royal Astronomical Society, 466:1363–1371, 2017.

- [103] O. L. Polyansky, A. A. Kyuberis, N. F. Zobov, J. Tennyson, S. N. Yurchenko, and L. Lodi. ExoMol molecular line lists XXX: A complete high-accuracy line list for water. *Monthly Notices of the Royal Astronomical Society*, 480:2597–2608, 2018.
- [104] T. Furtenbacher, R. Tóbiás, J. Tennyson, O. L. Polyansky, and A. G. Császár. W2020: A database of validated rovibrational experimental transitions and empirical energy levels of H<sub>2</sub><sup>16</sup>O. Journal of Physical and Chemical Reference Data, 49:033101, 2020.
- [105] T. Furtenbacher, R. Tóbiás, J. Tennyson, O. L. Polyansky, A. A. Kyuberis, R. I. Ovsyannikov, N. F. Zobov, and A. G. Császár. The W2020 database of validated rovibrational experimental transitions and empirical energy levels of water isotopologues. Part II. H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O with an update to H<sub>2</sub><sup>16</sup>O. Journal of Physical and Chemical Reference Data, 49:043103, 2020.
- [106] J.-M. Flaud, C. Camy-Peyret, and A. Valentin. Spectre infrarouge a haute résolution des bandes  $\nu_1 + \nu_2$  et  $\nu_2 + \nu_3$  de H<sub>2</sub><sup>16</sup>O. Journal de Physique, 33:741–747, 1972.
- [107] C. Camy-Peyret, J.-M. Flaud, G. Guelachvili, and C. Amiot. High resolution Fourier transform spectrum of water between 2930 and 4255 cm<sup>-1</sup>. *Molecular Physics*, 26:825–855, 1973.
- [108] J.-M Flaud and C. Camy-Peyret. The  $2\nu_2$ ,  $\nu_1$  and  $\nu_3$  bands of  $H_2^{-16}O$ . Rotational study of the (000) and (020) states. *Molecular Physics*, 26:811–823, 1973.
- [109] J.-M. Flaud and C. Camy-Peyret. Vibration-rotation intensities in H<sub>2</sub>O-type molecules application to 2ν<sub>2</sub>-band, ν<sub>1</sub>-band and ν<sub>3</sub>-band to H<sub>2</sub><sup>16</sup>O. Journal of Molecular Spectroscopy, 55:278–310, 1975.
- [110] J.-M. Flaud, C. Camy-Peyret, J.-P. Maillard, and G. Guelachvili. The H<sub>2</sub>O spectrum between 4200 and 5000 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 65:219–228, 1977.
- [111] J.-M. Flaud, C. Camy-Peyret, J.-P. Maillard, and G. Guelachvili. H<sub>2</sub><sup>16</sup>O hot bands in the 6-μm region. *Molecular Physics*, 34:413–426, 1977.
- [112] J.-M. Flaud, C. Camy-Peyret, K. N. Rao, D. W. Chen, and Y.-S. Hoh. Spectrum of water vapor between 8050 and 9370 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 75:339–362, 1979.
- [113] C. Camy-Peyret, J.-M Flaud, and J.-P. Maillard. The  $4\nu_2$  band of  $H_2^{16}O$ . Journal de Physique Lettres, 41:23–26, 1980.
- [114] J.-M. Flaud, C. Camy-Peyret, and R. A. Toth. Water Vapour Line Parameters from Microwave to Medium Infrared. Pergamon, Oxford, 1981.
- [115] A. S. Pine, M. J. Coulombe, C. Camy-Peyret, and J-M. Flaud. Atlas of the high-temperature water vapor spectrum in the 3000 to 4000 cm<sup>-1</sup> region. *Journal of Physical and Chemical Reference Data*, 12:413–465, 1983.
- [116] C. Camy-Peyret, J.-M. Flaud, J.-Y. Mandin, J.-P. Chevillard, J. Brault, D. A. Ramsay, M. Vervloet, and J. Chauville. The high-resolution spectrum of water vapor between 16500 and 25250 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 113:208–228, 1985.
- [117] J.-Y. Mandin, J.-P. Chevillard, C. Camy-Peyret, and J.-M. Flaud. Line intensities in the  $\nu_1 + 2\nu_2$ ,  $2\nu_2 + \nu_3$ ,  $2\nu_1$ ,  $\nu_1 + \nu_3$ ,  $2\nu_3$ , and  $\nu_1 + \nu_2 + \nu_3 - \nu_2$  bands of H<sub>2</sub><sup>16</sup>O, between 6300 and 7900 cm<sup>-1</sup>. Journal of Molecular Spectroscopy, 118:96–102, 1986.

- [118] J.-Y. Mandin, J.-P. Chevillard, C. Camy-Peyret, and J.-M. Flaud. The highresolution spectrum of water-vapor between 13 200 and 16 500 cm<sup>-1</sup>. Journal of Molecular Spectroscopy, 116:167–190, 1986.
- [119] J. P. Chevillard, J. Y. Mandin, J.-M. Flaud, and C. Camy-Peyret. H<sub>2</sub><sup>16</sup>O: line positions and intensities between 9500 and 11500 cm<sup>-1</sup>. The (041), (220), (121), (300), (201), (102) and (003) interacting states. *Canadian Journal of Physics*, 65:777–789, 1987.
- [120] J. Y. Mandin, J. P. Chevillard, J.-M. Flaud, and C. Camy-Peyret. H<sub>2</sub><sup>16</sup>O: line positions and intensities between 8000 and 9500 cm<sup>-1</sup>: the second hexad of interacting vibrational states: ((050), (130), (031), (210), (111), (012)). Canadian Journal of Physics, 66:997–1011, 1988.
- [121] J.-P. Chevillard, J.-Y. Mandin, J.-M. Flaud, and C. Camy-Peyret. H<sub>2</sub><sup>16</sup>O Line positions and intensities between 9500 and 11500 cm<sup>-1</sup>. The interacting vibrational states (041), (220), (121), (022), (300), (201), (102), and (003). Canadian Journal of Physics, 67:1065–1084, 1989.
- [122] V. Dana, J. Y. Mandin, C. Camy-Peyret, J.-M. Flaud, and L. S. Rothman. Rotational and vibrational dependences of collisional linewidths in the  $n\nu_2 (n-1)\nu_2$  hot bands of H<sub>2</sub>O from Fourier-transform flame spectra. *Applied Optics*, 31:1179–1184, 1992.
- [123] J. Y. Mandin, V. Dana, C. Camy-Peyret, and J.-M. Flaud. Collisional widths of pure rotational transitions of H<sub>2</sub>O from Fourier-transform flame spectra. *Journal* of Molecular Spectroscopy, 152:179–184, 1992.
- [124] J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. V. Naumenko, T. Petrova, A. Scherbakov, and L. Sinitsa. The high-resolution spectrum of water vapor between 11600 and 12750 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 183:300–309, 1997.
- [125] J.-M. Flaud, C. Camy-Peyret, A. Bykov, O. Naumenko, T. Petrova, A. Scherbakov, and L. Sinitsa. The water vapor linestrengths between 11600 and 12750 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 185:211–221, 1997.
- [126] C. Camy-Peyret, J.-M. Flaud, J.-Y. Mandin, A. Bykov, O. Naumenko, L. Sinitsa, and B. Voronin. Fourier-transform absorption spectrum of the H<sub>2</sub><sup>17</sup>O molecule in the 9711–11335 cm<sup>-1</sup> spectral region: the first decade of resonating states. *Journal* of Quantitative Spectroscopy and Radiative Transfer, 61:795–812, 1999.
- [127] A. Bykov, O. V. Naumenko, L. Sinitsa, B. Voronin, J.-M Flaud, C. Camy-Peyret, and R. A. Lanquetin. High-order resonances in the water molecule. *Journal of Molecular Spectroscopy*, 205:1–8, 2001.
- [128] S. N. Mikhailenko, V. G. Tyuterev, V. I. Starikov, K. K. Albert, B. P. Winnewisser, M. Winnewisser, G. Mellau, C. Camy-Peyret, R. Lanquetin, J.-M. Flaud, and J. W. Brault. Water spectra in the region 4200-6250 cm<sup>-1</sup>: extended analysis of  $\nu_1 + \nu_2$ ,  $\nu_2 + \nu_3$ , and  $3\nu_2$  bands and confirmation of highly excited states from flame spectra and from atmospheric long-path observations. *Journal of Molecular Spectroscopy*, 213:91–121, 2002.
- [129] R. Tóbiás, T. Furtenbacher, I. Simkó, A. G. Császár, M. L. Diouf, F. M. J. Cozijn, J. M. A. Staa, E. J. Salumbides, and W. Ubachs. Spectroscopic-networkassisted precision spectroscopy and its application to water. *Nature Communications*, 11:1708, 2020.
- [130] M. L. Diouf, R. Tóbiás, I. Simkó, F. M. J. Cozijn, E. J. Salumbides, W. Ubachs, and A. G. Császár. Network-Based Design of Near-Infrared Lamb-Dip Experiments and

the Determination of Pure Rotational Energies of  $H_2^{18}O$  at kHz Accuracy. Journal of Physical and Chemical Reference Data, 50:023106, 2021.

- [131] M. Melosso, M. L. Diouf, L. Bizzocchi, M. E. Harding, F. M. J. Cozijn, C. Puzzarini, and W. Ubachs. Hyperfine-resolved near-infrared spectra of H<sub>2</sub><sup>17</sup>O. Journal of Physical Chemistry A, 125:7884–7890, 2021.
- [132] O. Axner, P. Ehlers, A. Foltynowicz, I. Silander, and J. Wang. NICE-OHMS-Frequency Modulation Cavity-Enhanced Spectroscopy-Principles and Performance, chapter 6, pages 211–251. Springer Series in Optical Sciences. Springer, 2014.
- [133] V. S. Letokhov and V. P Chebotayev. Nonlinear Laser Spectroscopy, Springer Series in optical sciences, Vol. 4. Springer Verlag, 1977.
- [134] T.-P. Hua, Y. R. Sun, J. Wang, C.-L. Hu, L.-G. Tao, A.-W. Liu, and S.-M. Hu. Cavity-enhanced saturation spectroscopy of molecules with sub-kHz accuracy. *Chinese Journal of Chemical Physics*, 32:107–112, 2019.
- [135] R. Tóbiás, K. Bérczi, C. Szabó, and A. G Császár. autoECART: automatic energy conservation analysis of rovibronic transitions. *Journal of Quantitative Spectroscopy* and Radiative Transfer, 272:107756, 2021.
- [136] G. Czakó, E. Mátyus, and A. G. Császár. Bridging theory with experiment: a benchmark study of thermally averaged structural and effective spectroscopic parameters of the water molecule. *Journal of Physical Chemistry A*, 113:11665–11678, 2009.
- [137] Y. Y. Kwan. The interacting states of an asymmetric top molecule XY<sub>2</sub> of the group C<sub>2v</sub>. Journal of Molecular Spectroscopy, 71:260–280, 1978.
- [138] V. I. Starikov and S. N. Mikhailenko. Analysis of experimental data for the first hexad {(040), (120), (200), (002), (021), (101)} of H<sub>2</sub>O molecule interacting states. *Journal of Molecular Spectroscopy*, 442:39–53, 1998.
- [139] A. Bykov, O. V. Naumenko, A. P. Shcherbakov, L. Sinitsa, and B. A. Voronin. Identification and simulation of the H<sub>2</sub><sup>16</sup>O absorption spectrum in 5750–7965 cm<sup>-1</sup> region. Atmospheric and Oceanic Optics, 17:940–947, 2004.
- [140] J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, M. R. Carleer, A. G. Császár, R. R. Gamache, J. T. Hodges, A. Jenouvrier, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, R. A. Toth, A. C. Vandaele, N. F. Zobov, L. Daumont, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, S. N. Mikhailenko, and S. V. Shirin. IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part I. Energy levels and transition wavenumbers for H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O. Journal of Quantitative Spectroscopy and Radiative Transfer, 110:573–596, 2009.
- [141] J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, A. G. Császár, L. Daumont, R. R. Gamache, J. T. Hodges, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, R. A. Toth, A. C. Vandaele, N. F. Zobov, S. Fally, A. Z. Fazliev, T. Furtenbacher, I. E. Gordon, S.-M. Hu, S. N. Mikhailenko, and B. A. Voronin. IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part II. Energy levels and transition wavenumbers for HD<sup>16</sup>O, HD<sup>17</sup>O, and HD<sup>18</sup>O. Journal of Quantitative Spectroscopy and Radiative Transfer, 111:2160–2184, 2010.
- [142] J. Tennyson, P. F. Bernath, L. R. Brown, A. Campargue, A. G. Császár, L. Daumont, R. R. Gamache, J. T. Hodges, O. V. Naumenko, O. L. Polyansky, L. S. Rothman, A. C. Vandaele, and N. F. Zobov. A database of water transitions from experiment and theory (IUPAC technical report). *Pure and Applied Chemistry*, 86:71–83, 2014.

- [143] E. González-Alfonso, J. Fischer, J. Graciá-Carpio, E. Sturm, S. Hailey-Dunsheath, D. Lutz, A. Poglitsch, A. Contursi, H. Feuchtgruber, S. Veilleux, H. W. W. Spoon, A. Verma, N. Christopher, R. Davies, A. Sternberg, R. Genzel, and L. Tacconi. Herschel/PACS spectroscopy of NGC 4418 and Arp 220: H<sub>2</sub>O, H<sub>2</sub><sup>18</sup>O, OH, <sup>18</sup>OH, OHCN, and NH<sub>3</sub>. Astronomy and Astrophysics, 541:A4, 2012.
- [144] F. X. Powell and D. R. Johnson. Microwave detection of H<sub>2</sub><sup>18</sup>O. *Physical Review Letters*, 24:637–637, 1970.
- [145] F. C. de Lucia, P. Helminger, R. L. Cook, and W. Gordy. Submillimeter microwave spectrum of H<sub>2</sub><sup>18</sup>O. *Physical Review A*, 6:1324–1326, 1972.
- [146] R. H. Partridge. Far-infrared absorption spectra of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, and H<sub>2</sub><sup>18</sup>O. Journal of Molecular Spectroscopy, 87:429–437, 1981.
- [147] S. P. Belov, I. N. Kozin, O. L. Polyansky, M. Y. Tretyakov, and N. F. Zobov. Rotational spectrum of the H<sub>2</sub><sup>16</sup>O molecule in the (010) excited vibrational state. *Journal of Molecular Spectroscopy*, 126:113–117, 1987.
- [148] F. Matsushima, H. Nagase, T. Nakauchi, H. Odashima, and K. Takagi. Frequency measurement of pure rotational transitions of H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O from 0.5 to 5 THz. *Journal of Molecular Spectroscopy*, 193:217–223, 1999.
- [149] J. Kauppinen, T. Kärkkäinen, and E. Kyrö. High-resolution spectrum of water vapour between 30 and 720 cm<sup>-1</sup>. Journal of Molecular Spectroscopy, 71:15–45, 1978.
- [150] J. Kauppinen and E. Kyrö. High resolution pure rotational spectrum of water vapor enriched by H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O. Journal of Molecular Spectroscopy, 84:405–423, 1980.
- [151] R. A. Toth. Water vapor measurements between 590 and 2582 cm<sup>-1</sup>: line positions and strengths. *Journal of Molecular Spectroscopy*, 190:379–396, 1998.
- [152] S. N. Mikhailenko, V. G. Tyuterev, and G. Mellau. (0 0 0) and (0 1 0) States of  $H_2^{18}O$ : analysis of rotational transitions in hot emission spectrum in the 400–850 cm<sup>-1</sup> region. Journal of Molecular Spectroscopy, 217:195–211, 2003.
- [153] S. N. Mikhailenko, S. Béguier, T. A. Odintsova, M. Y. Tretyakov, O. Pirali, and A. Campargue. The far-infrared spectrum of <sup>18</sup>O enriched water vapour (40–700 cm<sup>-1</sup>). Journal of Quantitative Spectroscopy and Radiative Transfer, 253:107105, 2020.
- [154] G. Guelachvili. Experimental Doppler-limited spectra of the v<sub>2</sub>-bands of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, H<sub>2</sub><sup>18</sup>O, and HDO by Fourier-transform spectroscopy-secondary wavenumber standards between 1066 and 2296 cm<sup>-1</sup>. Journal of the Optical Society of America, 73:137–150, 1983.
- [155] A. Bykov, O. V. Naumenko, T. Petrova, A. Scherbakov, L. Sinitsa, J. Y. Mandin, C. Camy-Peyret, and J.-M. Flaud. The second decade of H<sub>2</sub><sup>18</sup>O: line positions and energy levels. *Journal of Molecular Spectroscopy*, 172:243–253, 1995.
- [156] M. Tanaka, O. V. Naumenko, J. W. Brault, and J. Tennyson. Fourier transform absorption spectra of  $H_2^{18}O$  and  $H_2^{17}O$  in the 3  $\nu$  +  $\delta$  and 4  $\nu$  polyad region. Journal of Molecular Spectroscopy, 234:1–9, 2005.
- [157] A. W. Liu, J. H. Du, K. F. Song, L. Wang, L. Wan, and S.-M. Hu. High-resolution Fourier-transform spectroscopy of <sup>18</sup>O-enriched water molecule in the 1080–7800 cm<sup>-1</sup> region. Journal of Molecular Spectroscopy, 237:149–162, 2006.
- [158] C. Oudot, L. Régalia, S. Mikhailenko, X. Thomas, P. von der Heyden, and D. Décatoire. Fourier transform measurements of  $H_2^{18}O$  and  $HD^{18}O$  in the spectral range

 $1000-2300~{\rm cm}^{-1}.$  Journal of Quantitative Spectroscopy and Radiative Transfer,  $113:859-869,\,2012.$ 

- [159] F. Mazzotti, R. N. Tolchenov, and A. Campargue. High sensitivity ICLAS of H<sub>2</sub><sup>18</sup>O in the region of the second decade (11 520–12 810 cm<sup>-1</sup>). Journal of Molecular Spectroscopy, 243:78–89, 2007.
- [160] O. M. Leshchishina, O. V. Naumenko, and A. Campargue. High sensitivity ICLAS of H<sub>2</sub><sup>18</sup>O between 13 540 and 14 100 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 268:28–36, 2011.
- [161] J. L. Hall. Nobel lecture: defining and measuring optical frequencies. Reviews of Modern Physics, 78:1279–1295, 2006.
- [162] T. W. Hänsch. Nobel lecture: passion for precision. Reviews of Modern Physics, 78:1297–1309, 2006.
- [163] Z. D. Reed, D. A. Long, H. Fleurbaey, and J. T. Hodges. SI-traceable molecular transition frequency measurements at the 10<sup>-12</sup> relative uncertainty level. *Optica*, 7:1209–1220, 2020.
- [164] Z. D. Reed, B. J. Drouin, D. A. Long, and J. T. Hodges. Molecular transition frequencies of  $CO_2$  near 1.6  $\mu$ m with kHz-level uncertainties. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 271:107681, 2021.
- [165] A. Gambetta, E. Fasci, A. Castrillo, M. Marangoni, G. Galzerano, G. Casa, P. Laporta, and L. Gianfrani. Frequency metrology in the near-infrared spectrum of H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O molecules: testing a new inversion method for retrieval of energy levels. New Journal of Physics, 12:103006, 2010.
- [166] G. Galzerano, A. Gambetta, E. Fasci, A. Castrillo, M. Marangoni, P. Laporta, and L. Gianfrani. Absolute frequency measurement of a water-stabilized diode laser at 1.384  $\mu$ m by means of a fiber frequency comb. *Applied Physics B*, 102:725–729, 2011.
- [167] A. Maity, S. Maithani, and M. Pradhan. Cavity ring-down spectroscopy: recent technological advancements, techniques, and applications. *Analytical Chemistry*, 93:388–416, 2021.
- [168] J. C. Visschers, E. Wilson, T. Conneely, A. Mudrov, and L. Bougas. Rapid parameter determination of discrete damped sinusoidal oscillations. *Optics Express*, 29:6863–6878, 2021.
- [169] T. P. Hua, Y. R. Sun, J. Wang, A. W. Liu, and S.-M. Hu. Frequency metrology of molecules in the near-infrared by NICE-OHMS. *Optics Express*, 27:6106–6115, 2019.
- [170] L. Lodi and J. Tennyson. Line lists for H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>17</sup>O based on empirical line positions and *ab initio* intensities. Journal of Quantitative Spectroscopy and Radiative Transfer, 113:850–858, 2012.
- [171] T. Furtenbacher, P. Árendás, G. Mellau, and A. G. Császár. Simple molecules as complex systems. *Scientific Reports*, 4:4654, 2014.
- [172] A. G. Császár, C. Fábri, T. Szidarovszky, E. Mátyus, T. Furtenbacher, and G. Czakó. The fourth age of quantum chemistry: molecules in motion. *Physi*cal Chemistry Chemical Physics, 14:1085–1106, 2012.
- [173] C. Fábri, M. Quack, and A. G. Császár. On the use of nonrigid-molecular symmetry in nuclear-motion computations employing a discrete variable representation: a case study of the bending energy levels of CH<sup>+</sup><sub>5</sub>. Journal of Chemical Physics, 147:134101, 2017.

Page 166 of 181

- [174] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J Knowles. High-accuracy *ab initio* rotation-vibration transitions for water. *Science*, 299:539–542, 2003.
- [175] P. Barletta, S. V. Shirin, N. F. Zobov, O. L. Polyansky, J. Tennyson, E. F. Valeev, and A. G. Császár. CVRQD *ab initio* ground-state adiabatic potential energy surfaces for the water molecule. *Journal of Chemical Physics*, 125:204307, 2006.
- [176] S. V. Shirin, O. L. Polyansky, N. F. Zobov, R. I. Ovsyannikov, A. G. Császár, and J. Tennyson. Spectroscopically determined potential energy surfaces of the H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O isotopologues of water. *Journal of Molecular Spectroscopy*, 236:216–223, 2006.
- [177] A.-W. Liu, O. V. Naumenko, K.-F. Song, B. Voronin, and S.-M. Hu. Fouriertransform absorption spectroscopy of H<sub>2</sub><sup>18</sup>O in the first hexade region. *Journal of Molecular Spectroscopy*, 236:127–133, 2006.
- [178] O. Leshchishina, S. Mikhailenko, D. Mondelain, S. Kassi, and A. Campargue. CRDS of water vapor at 0.1 Torr between 6886 and 7406 cm<sup>-1</sup>. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 113:2155–2166, 2012.
- [179] S. N. Mikhailenko, D. Mondelain, E. V. Karlovets, S. Kassi, and A. Campargue. Comb-assisted cavity ring down spectroscopy of <sup>17</sup>O enriched water between 6667 and 7443 cm<sup>-1</sup>. Journal of Quantitative Spectroscopy and Radiative Transfer, 206:163–171, 2018.
- [180] L. Régalia, X. Thomas, T. Rennesson, and S. Mikhailenko. Line parameters of water vapor enriched by <sup>18</sup>O from 6525 to 8011 cm<sup>-1</sup>. Journal of Quantitative Spectroscopy and Radiative Transfer, 235:257–271, 2019.
- [181] Q. Ma, R. H. Tipping, and N. N. Lavrentieva. Pair identity and smooth variation rules applicable for the spectroscopic parameters of H<sub>2</sub>O transitions involving high-*J* states. *Molecular Physics*, 109:1925–1941, 2011.
- [182] S. N. Mikhailenko, S. Kassi, D. Mondelain, and A. Campargue. Water vapor absorption between 5690 and 8340 cm<sup>-1</sup>: accurate empirical line centers and validation tests of calculated line intensities. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 245:106840, 2020.
- [183] R. A. Toth. Transition frequencies and absolute strengths of H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O in the 6.2-μm region. Journal of the Optical Society of America B, 9:462–482, 1992.
- [184] JPL website. https://spec.jpl.nasa.gov/ftp/pub/catalog/archive/ c020003.egy.
- [185] J. K. G. Watson. Determination of centrifugal distortion coefficients of asymmetrictop molecules. *Journal of Chemical Physics*, 46:1935–1948, 1967.
- [186] J. K. G. Watson. Simplification of the molecular vibration-rotation Hamiltonian. Molecular Physics, 15:479–490, 1968.
- [187] J. K. G. Watson. Determination of centrifugal distortion coefficients of asymmetrictop molecules. II. Dreizler, Drendl, and Rudolph's results. *Journal of Chemical Physics*, 48:181–185, 1968.
- [188] J. K. G. Watson. Determination of centrifugal distortion coefficients of asymmetrictop molecules. III. Sextic coefficients. *Journal of Chemical Physics*, 48:4517–4524, 1968.
- [189] H. Wu, C.-L. Hu, J. Wang, Y. R. Sun, Y. Tan, A.-W. Liu, and S.-M. Hu. A wellisolated vibrational state of CO<sub>2</sub> verified by near-infrared saturated spectroscopy with kHz accuracy. *Physical Chemistry Chemical Physics*, 22:2841–2848, 2020.

- [190] A. Campargue, A. M. Solodov, A. A. Solodov, A. Yachmenev, and S. N. Yurchenko. Detection of electric-quadrupole transitions in water vapour near 5.4 and 2.5 μm. *Physical Chemistry Chemical Physics*, 22:12476–12481, 2020.
- [191] A. Campargue, S. Kassi, A. Yachmenev, A. A. Kyuberis, J. Küpper, and S. N. Yurchenko. Observation of electric-quadrupole infrared transitions in water vapor. *Physical Review Research*, 2:023091, 2020.
- [192] C. Puzzarini, G. Cazzoli, M. E. Harding, J. Vázquez, and J. Gauss. A new experimental absolute nuclear magnetic shielding scale for oxygen based on the rotational hyperfine structure of H<sub>2</sub><sup>17</sup>O. *Journal of Chemical Physics*, 131:234304, 2009.
- [193] C. Puzzarini, G. Cazzoli, M. E. Harding, J. Vázquez, and J. Gauss. The hyperfine structure in the rotational spectra of D<sub>2</sub><sup>17</sup>O and HD<sup>17</sup>O: Confirmation of the absolute nuclear magnetic shielding scale for oxygen. *Journal of Chemical Physics*, 142:124308, 2015.
- [194] F. C. De Lucia and P. Helminger. Microwave spectrum and ground state energy levels of H<sup>17</sup><sub>2</sub>O. Journal of Molecular Spectroscopy, 56:138–145, 1975.
- [195] O. V. Naumenko, M. Sneep, M. Tanaka, S. V. Shirin, W. Ubachs, and J. Tennyson. Cavity ring-down spectroscopy of H<sup>17</sup><sub>2</sub>O in the range 16570–17125 cm<sup>-1</sup>. *Journal of Molecular Spectroscopy*, 237:63–69, 2006.
- [196] D. Mondelain, S. N. Mikhailenko, E. V. Karlovets, S. Béguier, S. Kassi, and A. Campargue. Comb-assisted cavity ring down spectroscopy of <sup>17</sup>O enriched water between 7443 and 7921 cm<sup>-1</sup>. Journal of Quantitative Spectroscopy and Radiative Transfer, 203:206–212, 2017. HITRAN2016 Special Issue.
- [197] A.-W. Liu, G.-L. Liu, X.-Q. Zhao, J. Wang, Y. Tan, and S.-M. Hu. Cavity ringdown spectroscopy of <sup>17</sup>O-enriched water vapor between 12,055 and 12,260 cm<sup>-1</sup>. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 239:106651, 2019.
- [198] J. Burkart, T. Sala, D. Romanini, M. Marangoni, A. Campargue, and S. Kassi. Communication: Saturated CO<sub>2</sub> absorption near 1.6 μm for kilohertz-accuracy transition frequencies. *Journal of Chemical Physics*, 142(19):191103, 2015.
- [199] J. Wang, Y. R. Sun, L.-G. Tao, A.-W. Liu, and S.-M. Hu. Communication: Molecular near-infrared transitions determined with sub-kHz accuracy. *Journal of Chemical Physics*, 147:091103, 2017.
- [200] V. Di Sarno, R. Aiello, M. De Rosa, I. Ricciardi, S. Mosca, G. Notariale, P. De Natale, L. Santamaria, and P. Maddaloni. Lamb-dip spectroscopy of buffer-gascooled molecules. *Optica*, 6:436–441, 2019.
- [201] G. Galzerano, E. Fasci, A. Castrillo, N. Coluccelli, L. Gianfrani, and P. Laporta. Absolute frequency stabilization of an extended-cavity diode laser against Dopplerfree H<sub>2</sub><sup>17</sup>O absorption lines at 1.384 μm. Optics Letters, 34:3107–3109, 2009.
- [202] J. Vázquez, M. E. Harding, J. F. Stanton, and J. Gauss. Vibrational energy levels via finite-basis calculations using a quasi-analytic form of the kinetic energy. *Journal* of Chemical Theory and Computation, 7:1428–1442, 2011.
- [203] M. Melosso, L. Bizzocchi, O. Sipilä, B. M. Giuliano, L. Dore, F. Tamassia, M.-A. Martin-Drumel, O. Pirali, E. Redaelli, and P. Caselli. First detection of NHD and ND<sub>2</sub> in the interstellar medium - amidogen deuteration in iras 16293–2422. *Astronomy and Astrophysics*, 641:A153, 2020.
- [204] H. M. Pickett. The fitting and prediction of vibration-rotation spectra with spin interactions. Journal of Molecular Spectroscopy, 148:371, 1991.

- [205] J. K. G. Watson. Aspects of quartic and sextic centrifugal effects on rotational energy levels. Vibrational spectra and structure, 6:1–89, 1977.
- [206] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton. The accurate determination of molecular equilibrium structures. *Journal of Chemical Physics*, 114:6548–6556, 2001.
- [207] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon. A 5th-order perturbation comparison of electron correlation theories. *Chemical Physics Letters*, 157:479–483, 1989.
- [208] G. E. Scuseria. Analytic evaluation of energy gradients for the singles and doubles coupled cluster method including perturbative triple excitations: Theory and applications to FOOF and Cr<sub>2</sub>. Journal of Chemical Physics, 94:442–447, 1991.
- [209] J. D. Watts, J. Gauss, and R. J. Bartlett. Open-shell analytical energy gradients for triple excitation many-body, coupled-cluster methods: MBPT(4), CCSD+T(CCSD), CCSD(T), and QCISD(T). *Chemical Physics Letters*, 200:1–7, 1992.
- [210] J. Gauss and J. F. Stanton. Perturbative treatment of triple excitations in coupledcluster calculations of nuclear magnetic shielding constants. *Journal of Chemical Physics*, 104:2574–2583, 1996.
- [211] D. E. Woon and T. H. Dunning. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. *Journal of Chemical Physics*, 100:2975–2988, 1994.
- [212] A. K. Wilson, T. van Mourik, and T. H. Dunning. Gaussian basis sets for use in correlated molecular calculations. VI. Sextuple zeta correlation consistent basis sets for boron through neon. *Journal of Molecular Structure: Theochem*, 388:339–349, 1996.
- [213] M. Kállay, J. Gauss, and P. G. Szalay. Analytic first derivatives for general coupled-cluster and configuration interaction models. *Journal of Chemical Physics*, 119:2991–3004, 2003.
- [214] M. Kállay and J. Gauss. Analytic second derivatives for general coupled-cluster and configuration-interaction models. *Journal of Chemical Physics*, 120:6841–6848, 2004.
- [215] J. Gauss. Analytic second derivatives for the full coupled-cluster singles, doubles, and triples model: Nuclear magnetic shielding constants for BH, HF, CO, N<sub>2</sub>, N<sub>2</sub>O, and O<sub>3</sub>. Journal of Chemical Physics, 116:4773–4776, 2002.
- [216] T. H. Dunning. Gaussian basis sets for use in correlated molecular calculations. I. the atoms boron through neon and hydrogen. *Journal of Chemical Physics*, 90:1007–1023, 1989.
- [217] R. A. Kendall, T. H. Dunning, and R. J. Harrison. Electron affinities of the firstrow atoms revisited. systematic basis sets and wave functions. *Journal of Chemical Physics*, 96:6796–6806, 1992.
- [218] D. E. Woon and T. H. Dunning. Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon. *Journal of Chemical Physics*, 103:4572–4585, 1995.
- [219] J. Gauss, K. Ruud, and T. Helgaker. Perturbation-dependent atomic orbitals for the calculation of spin-rotation constants and rotational g tensors. *Journal of Chemical Physics*, 105:2804–2812, 1996.

- [220] J. Gauss and D. Sundholm. Coupled-cluster calculations of spin-rotation constants. Molecular Physics, 91:449–458, 1997.
- [221] S. Stopkowicz and J. Gauss. Relativistic corrections to electrical first-order properties using direct perturbation theory. *Journal of Chemical Physics*, 129:164119, 2008.
- [222] D. Sundholm and J. Olsen. Finite Element Multiconfiguration Hartree-Fock Calculations on Carbon, Oxygen, and Neon: The Nuclear Quadrupole Moments of <sup>11</sup>C, <sup>17</sup>O, and <sup>21</sup>Ne. Journal of Physical Chemistry, 96:627–630, 1992.
- [223] CFOUR, a quantum chemical program package.
- [224] D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T-C. Jagau, P. G. Szalay, J. Gauss, and J. F. Stanton. Coupled-cluster techniques for computational chemistry: The CFOUR program package. *Journal of Chemical Physics*, 152:214108, 2020.
- [225] M. E. Harding, T. Metzroth, J. Gauss, and A. A. Auer. Parallel calculation of CCSD and CCSD(T) analytic first and second derivatives. *Journal of Chemical Theory and Computation*, 4:64–74, 2008.
- [226] MRCC website.
- [227] M. Kállay, P. R. Nagy, D. Mester, Z. Rolik, G. Samu, J. Csontos, J. Csóka, P. B. Szabó, L. Gyevi-Nagy, B. Hégely, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P. D. Mezei, and Á. Ganyecz. The MRCC program system: Accurate quantum chemistry from water to proteins. *Journal of Chemical Physics*, 152:074107, 2020.
- [228] M. Quack and F. Merkt (Eds.). Handbook of high-resolution spectroscopy. Wiley, Chichester, 2011.
- [229] E. Fasci, S. Gravina, G. Porzio, A. Castrillo, and L. Gianfrani. Lamb-dip cavity ring-down spectroscopy of acetylene at 1.4 μm. New Journal of Physics, 23:123023, 2021.
- [230] M. L. Diouf, R. Tóbiás, T. S. van der Schaaf, F. M. J. Cozijn, E. J. Salumbides, A. Császár, and W. Ubachs. Ultraprecise relative energies in the (2 0 0) vibrational band of H<sub>2</sub><sup>16</sup>O. *Molecular Physics*, 120:e2050430, 2022.
- [231] R. Aiello, V. Di Sarno, M. G. D. Santi, M. De Rosa, I. Ricciardi, G. Giusfredi, P. De Natale, L. Santamaria, and P. Maddaloni. Lamb-dip saturated-absorption cavity ring-down rovibrational molecular spectroscopy in the near-infrared. *Photonics Research*, 10:1803–1809, 2022.
- [232] M. Sinhal, A. Johnson, and S. Willitsch. Frequency stabilisation and SI tracing of mid-infrared quantum-cascade lasers for precision molecular spectroscopy. *Molecular Physics*, 0:e2144519, 2022.
- [233] M. L. Diouf, F. M. J. Cozijn, B. Darquié, E. J. Salumbides, and W. Ubachs. Lambdips and Lamb-peaks in the saturation spectrum of HD. *Optics Letters*, 44:4733– 4736, 2019.
- [234] G. Cazzoli, V. Lattanzi, J. L. Alonso, J. Gauss, and C. Puzzarini. The hyperfine structure of the rotational spectrum of HDO and its extension to the THz region: Accurate rest frequencies and spectroscopic parameters for astrophysical observations. Astrophysical Journal, 806:100, 2015.
- [235] D. Romanini, I. Ventrillard, G. Méjean, J. Morville, and E. Kerstel. Introduction to cavity enhanced absorption spectroscopy. In *Cavity-Enhanced Spectroscopy and Sensing*, pages 1–60. Springer, Berlin, 2014.

- [236] H. Dinesan, E. Fasci, A. d'Addio, A. Castrillo, and L. Gianfrani. Characterization of the frequency stability of an optical frequency standard at 1.39  $\mu$ m based upon noise-immune cavity-enhanced optical heterodyne molecular spectroscopy. *Optics Express*, 23:1757–1766, 2015.
- [237] E. B. Treacy and Y. Beers. Hyperfine structure of the rotational spectrum of HDO. Journal of Chemical Physics, 36:1473–1480, 1962.
- [238] P. Thaddeus, L. C. Krisher, and J. H. N. Loubser. Hyperfine structure of the microwave spectrum of HDO, HDS, CH<sub>2</sub>O, and CHDO: beam-maser spectroscopy and asymmetric-top molecules. *Journal of Chemical Physics*, 40:257–273, 1964.
- [239] H. Bluyssen, J. Verhoeven, and A. Dymanus. Hyperfine structure of HDO and D<sub>2</sub>O by beam maser spectroscopy. *Physics Letters A*, 25:214–215, 1967.
- [240] S. G. Kukolich. Beam maser double resonance measurements on HDO. Journal of Chemical Physics, 66:4345–4348, 1977.
- [241] H. A. Fry and S. G. Kukolich. Beam maser measurements of HDO hyperfine structure. *Journal of Chemical Physics*, 76:4387–4391, 1982.
- [242] M. L. Diouf, R. Tóbiás, F. M. J. Cozijn, E. J. Salumbides, C. Fábri, C. Puzzarini, A. G. Császár, and W. Ubachs. Parity-pair-mixing effects in nonlinear spectroscopy of HDO. *Optics Express*, 30:46040–46059, 2022.
- [243] C. E. Otis and P. M. Johnson. The AC-Stark effect in molecular multiphoton ionization spectroscopy. *Chemical Physics Letters*, 83:73–77, 1981.
- [244] W. M. Huo, K. P. Gross, and R. L. McKenzie. Optical stark effect in the two-photon spectrum of NO. *Physical Review Letters*, 54:1012, 1985.
- [245] C. E. Wieman, M. C. Noecker, B. P. Masterson, and J. Cooper. Asymmetric line shapes for weak transitions in strong standing-wave fields. *Physical Review Letters*, 58:1738, 1987.
- [246] J. E. Stalnaker, D. Budker, S. J. Freedman, J. S. Guzman, S. M. Rochester, and V. V. Yashchuk. Dynamic Stark effect and forbidden-transition spectral line shapes. *Physical Review A*, 73:043416, 2006.
- [247] H. J. Foth and F. Spieweck. Hyperfine structure of the R(98), 58-1 line of <sup>127</sup>I<sub>2</sub> at 514.5 nm. *Chemical Physics Letters*, 65:347–352, 1979.
- [248] L. Julien, M. Pinard, and F. Laloë. Hyperfine structure and isotope shift of the 640.2 and 626.6 nm lines of neon. *Journal de Physique Lettres*, 41:479–482, 1980.
- [249] L. A. Bloomfield, H. Gerhardt, T. W. Hänsch, and S. C. Rand. Nonlinear UV-laser spectroscopy of the 2<sup>3</sup>S-5<sup>3</sup>P transition in <sup>3</sup>He and <sup>4</sup>He. Optics Communications, 42:247-250, 1982.
- [250] A. Schabert, R. Keil, and P. E. Toschek. Dynamic stark effect of an optical line observed by cross-saturated absorption. *Applied Physics*, 6:181–184, 1975.
- [251] C. Hertzler and H.-J. Foth. Sub-Doppler polarization spectra of He, N<sub>2</sub> and Ar<sup>+</sup> recorded in discharges. *Chemical Physics Letters*, 166:551–559, 1990.
- [252] A. A. Kyuberis, N. F. Zobov, O. V. Naumenko, B. A. Voronin, O. L. Polyansky, L. Lodi, A. Liu, S.-M. Hu, and J. Tennyson. Room temperature line lists for deuterated water. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 203:175–185, 2017.
- [253] J. S. Bakos. AC Stark effect and multiphoton processes in atoms. *Physics Reports* - *Review Section of Physics Letters*, 31:209–235, 1977.

- [254] S. Mandal and P. N. Ghosh. Line shape and frequency shift of Lamb dip and crossover-resonance dip in closely spaced transitions. *Physical Review A*, 45:4990– 4997, 1992.
- [255] S. Mandal and P. N. Ghosh. Line shape, frequency shift, Rabi splitting, and twophoton resonances in four-level double-resonance spectroscopy with closely spaced intermediate levels. *Physical Review A*, 47:4934, 1993.
- [256] S. Ghosh and S. Mandal. Analytical studies on pump-induced optical resonances in an M-type six-level system. Journal of Physics B: Atomic, Molecular and Optical Physics, 43:245505, 2010.
- [257] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema, and W. Ubachs. Bounds on fifth forces from precision measurements on molecules. *Physical Review D*, 87:112008, 2013.
- [258] E. J. Salumbides, A. N. Schellekens, B. Gato-Rivera, and W. Ubachs. Constraints on extra dimensions from precision molecular spectroscopy. *New Journal of Physics*, 17:033015, 2015.
- [259] A. Foltynowicz, W. Ma, F.M. Schmidt, and O. Axner. Wavelength-modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signal line shapes in the Doppler limit. *Journal of the Optical Society of America B*, 26:1384– 1394, 2009.
- [260] P. Dupré. Sub-Doppler noise-immune cavity-enhanced optical heterodyne molecular spectrometry modeling: from Doppler broadening to cross-sideband resonances. *Journal of the Optical Society of America B*, 32:838–860, 2015.
- [261] L.-G. Tao, T.-P. Hua, Y. R. Sun, J. Wang, A.-W. Liu, and S.-M. Hu. Frequency metrology of the acetylene lines near 789 nm from Lamb-dip measurements. *Journal* of Quantitative Spectroscopy and Radiative Transfer, 210:111–115, 2018.
- [262] E. Fasci, A. Castrillo, H. Dinesan, S. Gravina, L. Moretti, and L. Gianfrani. Precision spectroscopy of HD at 1.38 μm. *Physical Review A*, 98:022516, 2018.
- [263] P. Czachorowski, M. Puchalski, J. Komasa, and K. Pachucki. Nonadiabatic relativistic correction in H<sub>2</sub>, D<sub>2</sub>, and HD. *Physical Review A*, 98:052506, 2018.
- [264] N. F. Ramsey and H. R. Lewis. Theory of hydrogen deuteride in magnetic fields. *Physical Review*, 108:1246–1250, 1957.
- [265] P. Dupré and J. Gauss. Hyperfine structure of HD. Private communication, 2019.
- [266] J. Bordé and C. J. Bordé. Intensities of hyperfine components in saturation spectroscopy. Journal of Molecular Spectroscopy, 78:353 – 378, 1979.
- [267] J. E. Thomas and W. W. Quivers. Transit-time effects in optically pumped coupled three-level systems. *Physical Review A*, 22:2115–2121, 1980.
- [268] O. Schmidt, K. M. Knaak, R. Wynands, and D. Meschede. Cesium saturation spectroscopy revisited: How to reverse peaks and observe narrow resonances. *Applied Physics B*, 59:167 – 178, 1994.
- [269] S. N. Bagayev, V. P. Chebotayev, A. K. Dmitriyev, A. E. Om, Yu. V. Nekrasov, and B. N. Skvortsov. Second-order Doppler-free spectroscopy. *Applied Physics B*, 52(1):63–66, Jan 1991.
- [270] S. N. Bagaev, L. S. Vasilenko, A. K. Dmitriev, M. N. Skvortsov, and V. P. Chebotaev. Narrowing of nonlinear resonances in low-pressure gases. *JETP Letters*, 23:360–363, 1976.

- [271] S. N. Bagaev, A. E. Baklanov, A. S. Dychkov, P. V. Pokasov, and V. P. Chebotaev. Ultrahigh resolution laser spectroscopy with cold particles. *JETP Letters*, 45:471–475, 1987.
- [272] L.-S. Ma, J. Ye, P. Dubé, and J. L. Hall. Ultrasensitive frequency-modulation spectroscopy enhanced by a high-finesse optical cavity: theory and application to overtone transitions of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>HD. *Journal of the Optical Society of America* B, 16:2255–2268, 1999.
- [273] C. Lemarchand, M. Triki, B. Darquié, C. J. Bordé, C. Chardonnet, and C. Daussy. Progress towards an accurate determination of the Boltzmann constant by Doppler spectroscopy. New Journal of Physics, 13:073028, 2011.
- [274] R. P. Lucht and R. L. Farrow. Saturation effects in coherent anti-Stokes Raman scattering spectroscopy of hydrogen. *Journal of the Optical Society of America B*, 6:2313–2325, 1989.
- [275] M. Puchalski, A. Spyszkiewicz, J. Komasa, and K. Pachucki. Nonadiabatic relativistic correction to the dissociation energy of H<sub>2</sub>, D<sub>2</sub>, and HD. *Physical Review Letters*, 121:073001, 2018.
- [276] W. Ubachs, J. C. J. Koelemeij, K. S. E. Eikema, and E. J. Salumbides. Physics beyond the Standard Model from hydrogen spectroscopy. *Journal of Molecular Spectroscopy*, 320:1 – 12, 2016.
- [277] J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt. Determination of the ionization and dissociation energies of the hydrogen molecule. *Journal of Chemical Physics*, 130:174306, 2009.
- [278] N. Hölsch, M. Beyer, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, C. Jungen, and F. Merkt. Benchmarking theory with an improved measurement of the ionization and dissociation energies of H<sub>2</sub>. *Physical Review Letters*, 122:103002, 2019.
- [279] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki. Nonadiabatic QED Correction to the Dissociation Energy of the Hydrogen Molecule. *Physical Review Letters*, 122:103003, 2019.
- [280] C.-F. Cheng, Y. R. Sun, H. Pan, J. Wang, A.-W. Liu, A. Campargue, and S.-M. Hu. Electric-quadrupole transition of H<sub>2</sub> determined to 10<sup>-9</sup> precision. *Physical Review A*, 85:024501, 2012.
- [281] Y. Tan, J. Wang, C.-F. Cheng, X.-Q. Zhao, A.-W. Liu, and S.-M. Hu. Cavity ring-down spectroscopy of the electric quadrupole transitions of in the 784 - 852 nm region. *Journal of Molecular Spectroscopy*, 300:60–64, 2014.
- [282] D. Mondelain, S. Kassi, T. Sala, D. Romanini, D. Gatti, and A. Campargue. Sub-MHz accuracy measurement of the S(2) 2-0 transition frequency of D<sub>2</sub> by combassisted cavity ring down spectroscopy. *Journal of Molecular Spectroscopy*, 326:5 – 8, 2016.
- [283] P. Wcislo, F. Thibault, M. Zaborowski, S. Wójtewicz, A. Cygan, G. Kowzan, P. Maslowski, J. Komasa, M. Puchalski, K. Pachucki, R. Ciurylo, and D. Lisak. Accurate deuterium spectroscopy for fundamental studies. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 213:41–51, 2018.
- [284] M. Zaborowski, M. Słowiński, K. Stankiewicz, F. Thibault, A. Cygan, H. Jóźwiak, G. Kowzan, P. Masłowski, A. Nishiyama, N. Stolarczyk, S. Wójtewicz, R. Ciuryło, D. Lisak, and P. Wcisło. Ultrahigh finesse cavity-enhanced spectroscopy for accurate tests of quantum electrodynamics for molecules. *Optics Letters*, 45:1603–1606, 2020.

- [285] M. Trefler and H. P. Gush. Electric dipole moment of HD. Physical Review Letters, 20:703–705, Apr 1968.
- [286] K. Pachucki and J. Komasa. Electric dipole rovibrational transitions in the HD molecule. *Physical Review A*, 78:052503, 2008.
- [287] T. Lin, C.-C. Chou, D.-J. Lwo, and J.-T. Shy. Absorption spectrum of the P(5) transition of the first overtone band of HD. *Physical Review A*, 61:064502, 2000.
- [288] K. M. Evenson, D. A. Jennings, J. M. Brown, L. R. Zink, K. R. Leopold, and M. D. Vanek. Frequency measurement of the J = 1-0 rotational transition of HD. Astrophysical Journal Letters, 330:L135, 1988.
- [289] L. Ulivi, P. de Natale, and M. Inguscio. Pure rotational spectrum of hydrogen deuteride by far-infrared Fourier transform spectroscopy. Astrophysical Journal Letters, 378:L29, 1991.
- [290] S.-M. Hu. Cavity-enhanced Lamb-dip spectroscopy of HD at 1.39 μm with 10<sup>-10</sup> precision. Conference Proceeding DAMOP, 19-2019:020045, 2019.
- [291] A. R. W. McKellar. Intensities and the Fano line shape in the infrared spectrum of HD. Canadian Journal of Physics, 51:389–397, 1973.
- [292] W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey. Radio-frequency spectra of hydrogen deuteride in strong magnetic fields. *Physical Review*, 112:1929– 1940, 1958.
- [293] M. Puchalski, J. Komasa, and K. Pachucki. Nuclear spin-spin coupling in HD, HT, and DT. *Physical Review Letters*, 120:083001, 2018.
- [294] M. Puchalski, J. Komasa, and K. Pachucki. Hyperfine structure of the first rotational level in H<sub>2</sub>, D<sub>2</sub> and HD molecules and the deuteron quadrupole moment. *Physical Review Letters*, 125:253001, 2020.
- [295] P. Dupré. Hyperfine transitions in the first overtone mode of hydrogen deuteride. *Physical Review A*, 101:022504, 2020.
- [296] Use is made of Pgopher software vs. 10, C. Western, University of Bristol, http://pgopher.chm.bris.ac.uk/, 2019.
- [297] G. J. Rosasco, A. D. May, W. S. Hurst, L. B. Petway, and K. C. Smyth. Broadening and shifting of the Raman Q branch of HD. *Journal of Chemical Physics*, 90:2115– 2124, 1989.
- [298] R. Z. Martínez, D. Bermejo, F. Thibault, and P. Wcisło. Testing the ab initio quantum-scattering calculations for the D<sub>2</sub>-He benchmark system with stimulated Raman spectroscopy. *Journal of Raman Spectroscopy*, 49:1339–1349, 2018.
- [299] S. N. Bagaev, V. P. Chebotaev, A. K. Dimitriyev, A. E. Om, Y. V. Nekrasov, and B. N. Svortsov. Second-order doppler-free spectroscopy. *Applied Physics B*, 52:63, 1991.
- [300] J. Komasa, M. Puchalski, P. Czachorowski, G. Lach, and K. Pachucki. Rovibrational energy levels of the hydrogen molecule through nonadiabatic perturbation theory. *Physical Review A*, 100:032519, 2019.
- [301] H2SPECTRE ver 7.3 Fortran source code, University of Warsaw, Poland, 2019.
- [302] A. Fast and S. A. Meek. Sub-ppb measurement of a fundamental band rovibrational transition in HD. *Physical Review Letters*, 125:023001, 2020.
- [303] C. R. Jeppesen. Bands in the extreme ultraviolet emission spectrum of the H<sup>1</sup>H<sup>2</sup> molecule. *Physical Review*, 45:480–484, 1934.

Page 174 of 181

- [304] H. C. Urey and G. K. Teal. The hydrogen isotope of atomic weight two. Reviews of Modern Physics, 7:34–94, 1935.
- [305] A. de Lange, E. Reinhold, and W. Ubachs. Phenomena of g-u symmetry-breakdown in HD. International Reviews in Physical Chemistry, 21:257–275, 2002.
- [306] G. C. Wick. Oscillation and rotation spectrum of the molecule HD. Atti Reale Accad. Nazionale Lincei, 21:708–714, 1935.
- [307] N.H. Rich, J.W.C. Johns, and A.R.W. McKellar. Frequency and intensity measurements in the fundamental infrared band of HD. *Journal of Molecular Spectroscopy*, 95:432–438, 1982.
- [308] S. Vasilchenko, D. Mondelain, S. Kassi, P. Cermák, B. Chomet, A. Garnache, S. Denet, V. Lecocq, and A. Campargue. The HD spectrum near 2.3 μm by CRDS-VECSEL: Electric quadrupole transition and collision-induced absorption. *Journal* of Molecular Spectroscopy, 326:9–16, 2016.
- [309] P. Essenwanger and H. P. Gush. Rotational spectrum of HD at low pressures. Canadian Journal of Physics, 62:1680–1685, 1984.
- [310] M. L. Diouf, F. M. J. Cozijn, K.-F. Lai, E. J. Salumbides, and W. Ubachs. Lambpeak spectrum of the HD (2-0) P(1) line. *Physical Review Research*, 2:023209, 2020.
- [311] T.-P. Hua, Y. R. Sun, and S.-M. Hu. Dispersion-like lineshape observed in cavityenhanced saturation spectroscopy of HD at 1.4  $\mu$ m. *Optics Letters*, 45:4863–4866, 2020.
- [312] M. L. Niu, E. J. Salumbides, G. D. Dickenson, K. S. E. Eikema, and W. Ubachs. Precision spectroscopy of the X<sup>1</sup>Σ<sup>+</sup><sub>g</sub>, v = 0 → 1 (J = 0 − 2) rovibrational splittings in H<sub>2</sub>, HD and D<sub>2</sub>. Journal of Molecular Spectroscopy, 300:44–54, 2014.
- [313] A. Castrillo, E. Fasci, and L. Gianfrani. Erratum: Doppler-limited precision spectroscopy of HD at 1.4 μm: An improved determination of the R(1) center frequency [Phys. Rev. A 103, 022828 (2021)]. Physical Review A, 103:069902, 2021.
- [314] M. P. Ledbetter, M. V. Romalis, and D. F. Jackson Kimball. Constraints on short-range spin-dependent interactions from scalar spin-spin coupling in deuterated molecular hydrogen. *Physical Review Letters*, 110:040402, 2013.
- [315] L. R. Rabiner and B. Gold. Theory and Application of Digital Signal Processing. Prentice-Hall, 1975.
- [316] C. A. Hall and W. W. Meyer. Optimal error bounds for cubic spline interpolation. *Journal of Approximation Theory*, 16:105–122, 1976.
- [317] H. Jóźwiak, H. Cybulski, and P. Wcisło. Positions and intensities of hyperfine components of all rovibrational dipole lines in the HD molecule. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 253:107171, 2020.
- [318] K. Pachucki. private communication.
- [319] A. Fast and S. A. Meek. Precise measurement of the D<sub>2</sub> S<sub>1</sub>(0) vibrational transition frequency. *Molecular Physics*, 120:e1999520, 2022.
- [320] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki. Complete α<sup>6</sup>m corrections to the ground state of H<sub>2</sub>. *Physical Review Letters*, 117:263002, 2016.
- [321] J. Hussels, N. Hölsch, C.-F. Cheng, E. J. Salumbides, H. L. Bethlem, K. S. E. Eikema, Ch. Jungen, M. Beyer, F. Merkt, and W. Ubachs. Improved ionization and dissociation energies of the deuterium molecule. *Physical Review A*, 105:022820, 2022.

- [322] D. Sprecher, J. Liu, C. Jungen, W. Ubachs, and F. Merkt. Communication: The ionization and dissociation energies of HD. *Journal of Chemical Physics*, 133:111102, 2010.
- [323] F. M. J. Cozijn, M. L. Diouf, and W. Ubachs. Saturation spectroscopy of R(0), R(2) and P(2) lines in the (2-0) band of HD. The European Physical Journal D, 76:220, 2022.
- [324] F. M. J. Cozijn, M. L. Diouf, V. Hermann, E. J. Salumbides, M. Schloesser, and W. Ubachs. Rotational level spacings in hd from vibrational saturation spectroscopy. *Physical Reviews A*, 105:062823, 2022.
- [325] J. Chaillot S. Kassi, C. Lauzin and A. Campargue. The (2-0) R(0) and R(1) transition frequencies of HD determined to a 10<sup>-10</sup> relative accuracy by Doppler spectroscopy at 80 K. *Physical Chemistry Chemical Physics*, 24:23164, 2022.
- [326] Y.-N. Lv, A.-W. Liu, Y. Tan, C.-L. Hu, T.-P. Hua, X.-B. Zou, Y. R. Sun, C.-L. Zou, G.-C. Guo, and S.-M. Hu. Fano-like resonance due to interference with distant transitions. *Physical Review Letters*, 129:163201, 2022.
- [327] Frank M. J. Cozijn, Meissa L. Diouf, and Wim Ubachs. Lamb dip of a quadrupole transition in H<sub>2</sub>. *Physical Review Letters*, 131:073001, 2023.
# List of Publications

### The following publications are reproduced as chapters in this thesis:

### Chapter2

Roland Tóbiás, T. Furtenbacher, Iren Simkó, Attila G. Császár, Meissa L. Diouf, Frank M. J. Cozijn, Joey M. A. Staa, Edcel J. Salumbides, and Wim Ubachs. Spectroscopic-network-assisted precision spectroscopy and its appli- cation to water. Nature Communications, **11**:1708, 2020

#### Chapter3

Meissa L. Diouf, Roland Tóbiás, Tom S. van der Schaaf, Frank M. J. Cozijn, Edcel J. Salumbides, Attila G. Császár, and Wim Ubachs. Ultraprecise relative energies in the  $(2\ 0\ 0)$  vibrational band of  $H_2^{16}O$ . Molecular Physics, 120:e2050430, 2022

### Chapter4

Meissa L. Diouf, Roland Tóbiás, Iren Simkó, Frank M. J. Cozijn, Edcel J. Salumbides, Wim Ubachs, and Attila G. Császár. Network-Based Design of Near-Infrared Lamb-Dip Experiments and the Determination of Pure Rotational Energies of  $H_2^{18}O$  at kHz Accuracy. Journal of Physical and Chemical Reference Data, **50**:023106, 2021

### Chapter5

Mattia Melosso, Meissa L. Diouf, Lucas Bizzocchi, Michael E. Harding, Frank M. J. Cozijn, Christina Puzzarini, and Wim Ubachs. *Hyperfine-resolved near-infrared spectra of*  $H_2^{17}O$ . Journal of Physical Chemistry A, **125**:7884–7890, 2021

#### Chapter6

Meissa L. Diouf, Roland Tóbiás, Frank M. J. Cozijn, Edcel J. Salumbides, Csaba Fábri, Cristina Puzzarini, Attila G. Császár, and Wim Ubachs. *Parity- pair-mixing effects in nonlinear spectroscopy of HDO*. Optics Express, **30**:46040–46059, 2022

#### Chapter8

Meissa L. Diouf, Frank M. J. Cozijn, Benoit Darquié, Edcel J. Salumbides, and Wim Ubachs. *Lamb-dips and Lamb-peaks in the saturation spectrum of HD*. Optics Letters, 44:4733, 2019

#### Chapter9

Meissa L. Diouf, Frank M. J. Cozijn, Kin-Fun Lai, Edcel J. Salumbides, and Wim Ubachs. Lamb-peak spectrum of the HD (2-0) P(1) line. Physical Review Research, 2:023209, 2020

## Chapter10

Frank M. J. Cozijn, Meissa L. Diouf, Valentin Hermann, Edcel J. Salumbides, Magnus Schloesser, and Wim Ubachs. *Rotational level spacings in HD from vibrational saturation spectroscopy*. Physical Reviews A, **105**:062823, 2022

## The author also contributed to the following publications:

Kin-Fun Lai, Valentin Hermann, T. Madhu Trivikram, Meissa L. Diouf, Magnus Schlösser, Wim Ubachs, and Edcel J. Salumbides. *Precision measurement of the fundamental vibrational frequencies of tritium-bearing hydrogen molecules: T2, DT, HT.* Physical Chemistry Chemical Physics, **22**:8973, 2020

Frank M. J. Cozijn, Meissa L. Diouf, and Wim Ubachs. Saturation spectroscopy of R(0), R(2) and P(2) lines in the (2-0) band of HD. The European Physical Journal D, **76**:220, 2022

Frank M. J. Cozijn, Meissa L. Diouf, and Wim Ubachs. Lamb dip of a quadrupole transition in H2. Physical Review Letters, **131**:073001, 2023

## The following papers have been submitted:

Frank M. J. Cozijn, Meissa L. Diouf, Valentin Hermann, Magnus Schlösser, and Wim Ubachs. *Precision measurement of vibrational quanta in Tritium Hydride* (*HT*)

Roland Tóbiás , Meissa L. Diouf, Frank M. J. Cozijn, Wim Ubachs, and Attila G. Császár. All paths lead to hubs: the case of water isotopologues H216O and H218O

# Acknowledgements

The journey throughout a PhD is always a long and arduous path. Without exception, my own experience was not an easy one. And thankfully, there were a lot of people who shouldered me and lifted me up when the difficulties of life were strikingly tough. So obviously, the thesis would not be half of what it currently is without the presence of these exceptional people surrounding me.

I would like to start with Wim Ubachs my supervisor. Without him, there definitely would not be anything to write in this thesis. I sincerely would like to thank him for the leap of faith he took by accepting to take me in and for supervising me during all these years. He is one of the nicest and wisest souls I have ever met and a complete source of inspiration. One of the main lessons I have learned from him is to be patient and know when to stop digging in a location where the output of gold has already been quite depleted. Additionally, he has such strong paternal vibes that working for him was literally the best thing I have personally gone through. Wim, all my heartfelt thanks.

Wim had such a long tenure in academia that he has friends all over the world. This led to many collaborations that helped us perform incredible measurement campaigns. I would thus like to thank Benoit Darquié from Paris for the interesting conversations and insight on the saturation techniques and the emergence of crossovers. For all the water works present in this thesis, we needed the help of our Hungarian friends Roland and Attila. A million thanks for all the theoretical groundwork you have performed to help us collaboratively reach these amazing results. I am really glad to have closely worked with such professional and nice people as you both are. I should also acknowledge Christina from Bologna with whom we had interesting conversations that led to two successful campaigns.

Then I would sincerely want to thank Thérèse Huet who was my professor when I was studying back in Lille. I feel so lucky to have been one of your students and you were by far my favorite lecturer; that is why I became a spectroscopist. It was also Thérèse who who put me in contact with Wim Ubachs and it was the best decision of my life to go to Amsterdam. For that, I have no other words but thank you.

When I first arrived in the lab, I had a lot of gaps to fill. The person who helped me the most was Edcel. In my opinion, he definitely has the best method of teaching. The mixture of patience, cheerfulness, and motivation behind his conversation skills just made coming to the lab one of my biggest pleasures. Every time we talked, we were used to going way over the time we planned. And I never felt tired from that, on the contrary, I always went home happier, more energetic, and more motivated in everything I had decided to undertake in my life. You are truly something special and I feel so blessed to have been supervised by you for the start of my career.

I cannot go through this acknowledgment section without mentioning Frank Cozijn. He has been a mentor, a friend, a moral support, and basically a big brother through my five years living and undergoing my research in the Netherlands. I can sometimes be quite annoying but I only managed to piss him once. This is to show the mental strength of Frank. But in all seriousness, I will directly address this to you. Thank you for helping me through the really tough times, thank you for pushing me when I sometimes lose motivation, thank you for listening to my venting moods, and thank you for your patience and your friendship, you are already and definitely will be the best of dad possible. You just will need to focus sometimes. Thank you for everything.

Throughout my 5 years journey of PhD, I have met different people that I would like to personally show appreciation. Kenneth, my long-time roommate and official "partner". We went through tough times together for sure and I hope that the only things they did were to mold us into more stable human beings. Nevertheless, I wanted to thank you for everything and to honestly tell you that you were and still are a true friend of mine. And lastly, I always admired that work drive of yours, and clearly had a profound impact on how I approach my own pitfalls. I will always cherish our horrible but sometimes extremely delightful time at Bankrashof 87. This leads me to Andy, the one who took care of me and fed me when COVID hit me the most and I could not move from bed. That was extremely nice of him and he always acted like a big brother to me. Thank you, Andy.

Working in the lab also leads to a lot of connections and thoughtful conversations. From the people who were finishing when I first started at Vrije Universiteit, I have learned a lot not only scientifically but also about the world itself. There were brief periods of contact for certain but I would still like to acknowledge you all. And special mention to Cunfeng who spent a lot of evenings during my master's thesis to teach me about optical techniques. Next, I would like to thank the people whom I have the most overlap with and with whom I had time to become friends. Yuri, it was always extremely fun to share our different music tastes. I had an amazing time talking with you when you shared some of your precious knowledge nuggets on cold atom physics. And let's not forget the venting on your magnificent perfectly working UV system that gave you the best of time during your PhD. I would like to thank Charlaine, for being such an amazing person and most of all for having one of the best baking skills !! Let's not forget, Elmer with his amazing humor which always lands perfectly at the best time possible. You always managed to keep your good humor no matter the events. You kept on going with that same drive; truly impressive. Andres, you have shown me how important having a life outside of work was important. I always admired your relaxed and cheerful mood. I would also like to acknowledge Kees, the perpetual nice guy who always annoys me with his approximate Chinese. It is always a treat when we exchange our 'Sup' like two lunatics. But sincerely, you all are incredible people and amazing scientists as well, and I wish you the best in the future. And, all in all, I would like to mention Joel, Marteen, Wander, Vincent, Madhu, Matthieu, Raphael, Ruud and Rodrigo for the incredible and nice chats we have had throughout the years. I should not forget to thank the different PI Rick, Jeroen, Max, Laura and especially Kjeld for his forever enthusiasm and friendly approach which is another source of inspiration for my future career.

During my PhD, I also got to travel and meet other candidates at international conferences. I am truly happy to be able to have met Ioana and that we became

really good friends. Exchanging our eventful journey or sometimes just talking about the things we like is really something I feel thankful for.

Additionally, this work would not be possible without the amazing technical help of Rob. Special thank you for repairing the turbo after I had drowned it with years of continuous water measurements. I would also like to thank Marja and Brigit, the secretaries of our department. They are truthfully two outstanding ladies, always looking to help and give advice. Additionally, I would like to specifically acknowledge and thank Anette Bor from NWO who made dealing with all the administration paperwork extremely easy.

This thesis, or should I say, the journey of the PhD would not have been possible before the support I have had in my personal life. I would thus like to acknowledge the people outside of my work that I have had a great impact on during my PhD. First of all, Bastien one of my best friends, it is so great that we managed to keep our traditions to watch the NBA all-star every year. It is always a treat when we meet or we just play online. And when I go to Lille, I also get to see Betty who has become such an amazing mother to a beautiful baby. It also means a lot when my childhood friend Babacar who is always making sure that I keep representing the color of my people, asks me about what I am doing. I would like to thank Christine who is my biggest fan and always tried to support me. And I also feel so thankful to have met Anna, which made my last period of PhD supposedly hard be extremely dreamy. There are so many people that I have encountered during my life and had an incredible impact on my life and I apologize if I have not named you this section.

I also would not be here without the support of the Cazier family, or my second adoptive family. Every single one of you Francine, Fabrice, Hélène, and Elodie have had a tremendous impact on my life. You have helped me face challenges, grow up, and mature to the person I currently am. That last bit is a strong statement but you all know where I came from. And you were so patient with me and I always feel like I am home when I am in Bierne. For that, I owe you so much that it cannot be quantified.

Lastly, I want to end this acknowledgment section with my family. I feel so lucky to have a family that believed in me and had never one sliver of doubt about my dreams. My father is the most supportive person I have ever met and has always found a way to rekindle lost motivation. My mother, on the other hand, always gives the best advice possible which is extremely helpful as I am quite often in a pinch. Following these two traits characteristics, I would like to thank my elder brothers Tapha and Cheikh who also always supported and helped me out at my lowest point when I was so stressed and I did not know what to do. My aunt Marieme or I should say my second mother who has always been there for us. And last but not least, my lil sister Anta who is just the best. I hope that I will act as a motivational tool to show you that you can be anything. I know that I am not the easiest son nor brother but I am so lucky to have you all in my life. Thank you for everything.

