Improved determination of the dissociation energy of H₂, HD and D₂

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VRIJE UNIVERSITEIT

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CHAPTER

Introduction

1.1 The hydrogen molecule and tests of fundamental physics

The hydrogen molecule, consisting of only two protons and two electrons, is the simplest neutral molecule. This simplicity makes it one of the best calculable systems and a principal testbed for comparisons between measurements and *ab initio* calculations. Such high-level calculations of the energy structure of the hydrogen molecule are based on quantum electrodynamics (QED) – the theory of the electromagnetic interaction between light and matter. QED together with the weak and strong nuclear interactions comprise the so-called Standard Model of particle physics, which is currently considered to be our best description of elementary particles and fundamental forces, except gravity. The effects of the weak and strong nuclear interactions on the energy level structure of the hydrogen molecule are small: the impact of the strong nuclear interaction is only significant through nuclear finite-size effects, the impact of the weak interaction is not significant at all [1]. Thus a precision test for the dominant QED interaction is by extension a test for the Standard Model.

Due to the vibrational and rotational degrees of freedom the energy level structure of a simple molecular system like H₂ (and the stable isotopologues HD and D₂) is very rich. It is not only possible to excite the system to higher electronic levels, but also to higher vibrational- and rotational (v,J) levels. Any energy interval ΔE that can be accurately measured and calculated from theory, like the difference in energy between two of these rovibrational levels, can be used to test theory. If the difference between the experimental (ΔE_{exp}) and theoretical (ΔE_{th}) value is smaller than the combined uncertainty in ΔE_{exp} and ΔE_{th} , theory and experiment agree. Such a result would put constraints on physics beyond the Standard Model. If, on the other hand, the difference is larger than the combined uncertainty, there is a discrepancy between theory and experiment. Such a discrepancy would hint at physics beyond the Standard Model, like new forces or extra dimensions [1, 2]. New experimental techniques are in constant development to measure these energy intervals at increasingly higher accuracy [3, 4, 5, 6, 7]. The results discussed in this thesis test theory at the 10^{-9} level of accuracy.

The value of ΔE_{th} does not only depend on the theory, but also on the parameters that go into the theory: the fundamental constants of nature. Besides testing theory, a comparison between ΔE_{exp} and ΔE_{th} can be used to extract precise values for the fundamental constants. The theory can be seen as a function of the fundamental constants

$$\Delta E_{th} = f(\alpha, R_{\infty}, r_p, \mu_p, \dots) \tag{1.1}$$

where α , the fine-structure constant, R_{∞} , the Rydberg constant, r_p , the radius of the proton and μ_p , the proton-to-electron mass ratio are some examples of the input parameters of the theory. This can also be reversed: fundamental constants can be extracted from this function if both ΔE_{th} and ΔE_{exp} are known accurately, for example

$$r_p = f^{-1}(\alpha, R_\infty, \mu_p, \Delta E_{exp}, \dots)$$
(1.2)

Since the determination of a fundamental constant depends on the other involved fundamental constants, the extracted values of the constants are correlated. Multiple energy intervals ΔE need to be measured or the other fundamental constants need to be known from different experiments to constrain this parameter space, as was shown recently by Patra et al. [8]. In recent years the value for r_p obtained from experiments on muonic hydrogen atoms, i.e. hydrogen atoms where the electron is replaced with a muon, were in conflict with those from measurements on ordinary hydrogen atoms [9]. This issue seems to be resolved now [10, 11]. Accurate tests on molecular systems will contribute to more accurate, and better tested, values of the fundamental constants. One of the best calculable energy intervals ΔE of the hydrogen molecule is the binding or dissociation energy (D_0) of the ground state, the lowest amount of energy that is needed to dissociate the molecule from the ground state into two separate atoms in their ground state. This thesis describes the experimental determination of the dissociation energies of H₂ and its isotopologue D₂, with an order of magnitude improved accuracy in comparison to previous experimental values [12, 13], and the first step towards the improved determination of the dissociation energy of HD. In the subsequent sections, I will give a brief overview of previous measurements and calculations of D_0 and an introduction to the experimental setup used in this work. This chapter will finish with an outline of this thesis.

1.2 Historical development of the dissociation energy of the hydrogen molecule

More than a century ago, before the development of quantum mechanics, the first experimental determination of $D_0(H_2)$ was published by Langmuir [14]. Langmuir's experiment involved heating up H₂ gas, and measuring how much energy was needed to dissociate the molecules. In 1926, Witmer was the first to determine D_0 by determining the vibrational splittings in the ground state of H₂ from measurements of the Lyman bands in a discharge cell [15]. In 1927, just after the birth of quantum mechanics, Heitler and London were the first to show that that molecular binding is a direct consequence of quantum mechanics, and published the first theoretical value for the dissociation energy [16].

Theoretical and experimental physicists inspired each other in the next decades to decrease the uncertainty in D_0 , as shown in Fig. 1.1. By using a large vacuum spectrograph to study the far UV absorption edges of H₂, Herzberg determined the second dissociation limit, i.e. the energy where dissociation results with one of the atoms in the n=1 state and the other in the n=2 state [17]. From this energy a significantly improved experimental value for D_0 is derived by subtracting the energy required to excite the atom to the n=2 state. After the invention of the laser, the accuracy of D_0 improved again. Eyler et al. and Zhang et al. studied the second dissociation limit, to determine D_0 , by using laser



Figure 1.1 – History of the uncertainty in the dissociation energy of H_2 . The point indicated with "Cheng2018" is the result of the experiment described in Chapter 2 of this thesis. The yellow bar shows the level of uncertainty needed to determine the proton size with an error smaller than the discrepancy level of the proton size puzzle (see Section 1.1).

double-resonance spectroscopy [18, 19]. All these techniques revolved around getting as close to a dissociation limit as possible. However, since there is no quantum state at the dissociation limit, these methods are fundamentally limited in the accuracy at which D_0 can be determined.

To go around this limit Liu et. al. (for H₂ and D₂) and Sprecher et al. (for HD) were the first to use the so called "thermochemical cycle", shown in Fig. 1.2, determining D_0 from of the ionization energies of the neutral molecule ($E_i(H_2)$), the molecular ion ($E_i(H_2^+)$) and the atom ($E_i(H)$). [12, 13, 20]. According to this thermochemical cycle

$$D_0(\mathbf{H}_2) = E_i(\mathbf{H}_2) + E_i(\mathbf{H}_2^+) - 2 \times E_i(\mathbf{H}).$$
(1.3)

Or alternatively

$$D_0(\mathbf{H}_2) = E_i(\mathbf{H}_2) + D_0(\mathbf{H}_2^+) - E_i(\mathbf{H}).$$
(1.4)

4

For the deuterated isotopologues (a deuteron is a heavier isotope of hydrogen consisting of a proton and a neutron), similar relations holds:

$$D_0(\text{HD}) = E_i(\text{HD}) + E_i(\text{HD}^+) - E_i(\text{H}) - E_i(\text{D}), \qquad (1.5)$$

$$D_0(D_2) = E_i(D_2) + E_i(D_2^+) - 2 \times E_i(D).$$
(1.6)

Liu et al. and Sprecher et al. determined the ionization energy of the neutral molecules by summing three energy intervals: the first from the $X^1\Sigma_g^+$ to the $EF^1\Sigma_g^+$ state (both shown in Fig. 1.2), the second from the $EF^1\Sigma_g^+$ state to a high lying 54p Rydberg series and the third between a Rydberg state and the $X^2\Sigma_g^+$ state in the molecular ion. The first measurements on this kind of Rydberg states to extrapolate the ionization potential was already done by Herzberg and Jungen in 1972 [21]. Unlike the dissociation limit, there is no fundamental limit to how close a state can be to the ionization limit, since Rydberg series are infinite series of states with increasing principal quantum number n, converging to the ionization limit. However, the Rydberg electron interacts with the vibrational and rotational modes of the H_2^+ core. This heavily perturbs the Rydberg states. The method of Multi-channel Quantum Defect Theory (MQDT), by which the ionization limit of a (measured) Rydberg series can be extrapolated, was extended to molecules to account for these perturbations [21, 22].

In this way, the accuracy of the determinations of the ionization energy of the neutral molecules by the Zürich-Amsterdam collaboration were improved to 11 MHz for H₂ and HD, and to 20 MHz for D₂ [12, 13, 20]. From these values the dissociation energies can be determined by combining them with the ionization energies of the atoms and molecular ions. Since the H and D atoms and the H_2^+ , D_2^+ and HD⁺ molecular ions are even simpler systems than the neutral molecules, as they only have a single electron, their ionization energy is better calculable [23, 24, 25]. The theories that can calculate the ionization energies of the single electron system have been tested to the kHz level of accuracy [8, 26, 23]. The ionization energies of the H- and D atoms are experimentally determined with an accuracy of 3 kHz [23, 25]. The ionization energies of the H₂⁺, HD and D₂⁺ molecular ions are known with an accuracy of 18 kHz [24]. Thus the accuracy of the value of the dissociation energies of the neutral molecules are currently determined by the analysis of the neutral molecules are currently determined by the accuracy of the value of the dissociation energies of the neutral molecules are currently determined by



Figure 1.2 – Potential energy diagrams of the $X^1\Sigma_g^+$, $GK^1\Sigma_g^+$ and $EF^1\Sigma_g^+$ states in H_2 and the $X^2\Sigma_g^+$ in H_2^+ . The first three vibrational levels, and the first three rotational levels of the v = 0 level, of the $X^1\Sigma_g^+$ state in H_2 as well as the first vibrational level of the inner well of the $GK^1\Sigma_g^+$ state in H_2 and the first vibrational level of the $X^2\Sigma_g^+$ state in H_2 and the first vibrational level of the of the $X^2\Sigma_g^+$ state in H_2^+ are indicated with a horizontal line. Arrows illustrate how $D_0(H_2)$ can be obtained from $E_i(H)$, $E_i(H_2)$ and $E_i(H_2^+)$.

the accuracy of the experimental value of the ionization energies of the neutral molecules.

Challenged by the new experimental values discussed in the previous paragraph, the theoreticians improved the calculated value of the dissociation energy. First by using an adiabatic approximation with relativistic corrections, later by performing adiabatic calculations on the non-relativistic energy and including non-adiabatic, relativistic and QED corrections [27, 28, 29]. The latest work by Puchalski et al. involves a full four-body calculation for the non-relativistic energy and the relativistic correction, while QED corrections in the 5th and 6th order of α are performed using the Born-Oppenheimer approximation and an estimate of QED corrections in the 7th order of α is included, resulting in an accuracy of below 1 MHz [30].

Not only $D_0(H_2)$ was calculated to high accuracy, but also $D_0(D_2)$ and $D_0(HD)$ were theoretically determined ever since the experimental determination of these values by Herzberg [17]. This provided for separate tests of the theory, since the different terms (adiabatic, nonadiabatic, relativistic etc.) have a different dependence on the mass of the two atoms. The accuracy of both $D_0(D_2)$ and $D_0(HD)$ were improved in a similar fashion as the accuracy of $D_0(H_2)$ shown in Fig. 1.1, since most groups that measured or calculated $D_0(H_2)$ repeated their work in the deuterated isotopologues.

In this thesis the thermochemical cycle exploited by Liu et al. is used to determine a more accurate value of D_0 [12]. The ionization energy is determined using the $GK^1\Sigma_q^+$ state as the intermediate state. As discussed in Sprecher et al., the advantage of measuring a transition from the $GK^1\Sigma_q^+$ state, instead of the $EF^1\Sigma_q^+$ state, to a high-n Rydberg state is that the lower transition frequency reduces the uncertainty due to Doppler broadening [22]. Furthermore, the possibility to populate the $GK^1\Sigma_q^+$ state via the $B^1\Sigma_u^+$ state increases the number of molecules in the intermediate state, thus increasing the signal. The transition from the $GK^1\Sigma_q^+$ state to a high-*n* Rydberg state can be measured, and the Doppler shift can be assessed, by monitoring the signal from two counter-propagating beams originating from a continuous wave (cw) laser referenced by a frequency comb. In order to induce the transition from the $X^1\Sigma_a^+$ state of hydrogen to the $GK^1\Sigma_a^+$ state, two vacuum ultraviolet (VUV) photons at 179 nm are needed, which poses a challenge. In the next section I will describe the laser system used to generate this light.

1.3 Generation of vacuum ultraviolet laser pulses

To generate laser light at a wavelength of 179 nm, required to drive the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition, a special KBe₂BO₃F₂ (KBBF) crystal is used, of which a photograph is displayed in Fig. 1.3. Due to the limited

1. INTRODUCTION



Figure 1.3 – $KBe_2BO_3F_2$ slab in the centre, sandwiched by optical contact with two CaF_2 prisms.

thickness (2 mm) of the KBBF¹ crystal, it is very hard to cut the crystal along the phase-matching (~ 65° at our wavelength) direction [31]. To solve this problem the KBBF is clamped between, and in optical contact with, two CaF₂ prisms [31, 32, 33]. Though the efficiency of the KBBF drops rapidly below 180 nm, previous experiments already achieved wavelengths of less than 160 nm [34]. It is currently the only known non-linear crystal to generate light at these short wavelengths, using either second harmonic generation (SHG) or sum frequency generation (SFG) [35, 36]. It allows us to generate up to 20 μ J of VUV light per pulse using SHG of 358 nm pulses, limited by the damage threshold of the optical contact.

¹We thank Prof. S.M. Hu (University of Science and Technology China, Hefei) and the Chinese Academy of Sciences for making available the KBBF crystal for a collaborative effort to measure the two-photon transitions in molecular hydrogen and its isotopologues.



Figure 1.4 – Locking and scanning schemes of the seed laser to the frequency comb. See text for details.

The 358 nm pulses are generated by the upconversion of 716 nm pulses using a BaB₂O₄ (BBO) crystal. The 716 nm pulses are the output of a chirp-compensated Ti:Sa oscillator-amplifier system which will be described in more detail in Chapter 4. The oscillator-amplifier system is seeded by a continuous wave (cw) Ti:Sa seed laser. Since the gain of the Ti:Sa crystal, which peaks around 800 nm, is only around 50% of the maximum gain at 716 nm, a new low-noise Sprout G diode-pumped solid-state laser was installed, during the course of my PhD, to pump the Ti:Sa crystal with 12.7 W of 532 nm cw laser light. This ensures a stable 600 mW output of the cw Ti:Sa laser at 716 nm.

To stabilise the frequency of the 716 nm laser light the cw Ti:Sa seed laser is locked to an optical frequency comb. The frequency comb is referenced by a Cs-clock, resulting in a long-term stability of 10^{-12} . The short term stability of a few tens of kHz of the seed laser is ensured by a reference cavity. To lock the cw Ti:Sa laser to the frequency comb, a beat-note with a frequency of 50 to 70 MHz between the cw light and one mode of the comb is chosen. To ensure unique identification of the nearest mode of the frequency comb the frequency of the cw 716 nm light is measured using a wavemeter with an accuracy of 10 MHz, which is small with respect to the 250 MHz spacing between the comb modes. The beat-note between the comb and the Ti:Sa laser, detected by a photodiode, is electronically amplified and read out by an rf frequency counter with a 225-MHz bandwidth. The read out of the counter is continuously compared to the desired frequency, and an active feedback loop using a 80 MHz arbitrary waveform generator (AWG) to the reference cavity of the cw Ti:Sa laser counteracts the laser drift. The full locking scheme is displayed in Fig. 1.4.

After the lock to the frequency comb, an acousto-optic modulator (AOM) is implemented in a double pass scheme (shown in Fig. 1.4) to scan the cw laser, and thus the frequency of the VUV laser. The frequency of the AOM (340 to 350 MHz) is controlled by a Direct Digital Synthesizer (DDS) which is linked to a Cs-clock to ensure a sub-kHz level of accuracy. To transfer the frequency stability and calibration of the cw seed laser to the VUV laser pulses a chirp-cancellation scheme is used, as discussed in Chapter 4.

Molecules excited to the $GK^1\Sigma_g^+$ state are selectively ionised with a single photon from a pulsed ionization laser. The ionization probability is enhanced by the exploitation of auto-ionising resonances. This ionization process and the detection of the ions is discussed in Chapter 5.

1.4 Outline of this thesis

This thesis describes the experimental determination of the dissociation energies of H₂ and its isotopologue D₂, with an order of magnitude improved accuracy in comparison to previous experimental values [12, 13]. Furthermore, an accurate measurement of the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition in HD is described, which, once combined with other measurements, will lead to an improved value of the dissociation energy of HD.

Determining D_0 experimentally at high precision is a direct test of calculations in the QED framework and the Standard Model of physics. Once D_0 is measured and calculated at high enough accuracy, it will be possible to constrain physics beyond the Standard Model. If in the future the accuracy in the dissociation energy increases even further, it will be possible to determine constants like r_p and μ_p . From the dissociation energies of the deuterated isotopologues, D₂ and HD, it will then also be possible to determine constants like the deuteron radius (r_d) and the deuteron-to-electron mass ratio (μ_d) .

To reach a sub-MHz level of accuracy, a Doppler-free two photon transition from the $X^1\Sigma_g^+$ state to the $GK^1\Sigma_g^+$ was measured at the Vrije Universiteit Amsterdam. The ionization energy of the $GK^1\Sigma_g^+$ state was determined at ETH Zürich, by measurements of the interval between the $GK^1\Sigma_g^+$ state and high lying Rydberg states that are members of a Rydberg series, and further extrapolation of this series to the ionization limit using MQDT.

In Chapters 2 and 3 accurate values for the dissociation energies of ortho- and para H₂ are presented. Chapter 4 describes the effect of frequency chirp in pulse generation and a scheme to measure and counteract this. In Chapter 5 an accurate value for the dissociation energy of D₂ is presented. The vacuum setup will also be described in more detail in this chapter. In Chapter 6 an accurate measurement of the $GK^1\Sigma_g^+-X^1\Sigma_g^+$ transition in HD is presented. Finally, in Chapter 7 an outlook on directions of future research is discussed.

CHAPTER 2

Dissociation energy of the hydrogen molecule at 10^{-9} accuracy

Abstract

The ionization energy of ortho-H₂ has been determined to be $E_{\rm I}^{\rm o}({\rm H}_2)/(hc) = 124\,357.238\,062(25)~{\rm cm}^{-1}$ from measurements of the GK(1,1)–X(0,1) interval by Doppler-free two-photon spectroscopy using a narrow band 179-nm laser source and the ionization energy of the GK(1,1) state by continuous-wave near-infrared laser spectroscopy. $E_{\rm I}^{\rm o}({\rm H}_2)$ was used to derive the dissociation energy of H₂, $D_0^{N=1}({\rm H}_2)$, at 35 999.582 894(25) cm⁻¹ with a precision that is more than one order of magnitude better than all previous results. The new result challenges calculations of this quantity and represents a benchmark value for future relativistic and QED calculations of molecular energies.

This chapter is based on: Dissociation Energy of the Hydrogen Molecule at 10^{-9} Accuracy, 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, *Phys. Rev. Lett.* **121**, 013001 (2018)

2.1 Introduction

The dissociation energy of the hydrogen molecule $D_0(H_2)$ is a fundamental quantity for testing molecular quantum theory. The pioneering calculations of Heitler and London on H₂ demonstrated that molecular binding is a consequence of quantum mechanics [16]. In almost a century of mutually stimulating activities by experimentalists and theorists, the accuracy of this benchmark value has been improved by seven orders of magnitude [22]. Great progress in the theoretical calculations has been achieved by including relativistic and quantum-electrodynamic (QED) effects [28, 29]. Over the past decade, improved calculations of the Born-Oppenheimer energies [37], adiabatic corrections [38], leadingorder nonadiabatic corrections [39], exact nonadiabatic energies [40, 41], and a further refinement of QED calculations [42] have been reported. The latest efforts, however, led to a deterioration of the agreement between experimental and theoretical results [43].

Direct measurements of dissociation energies in H₂ are complicated by perturbing resonances near the continuum limits and vanishing direct photo-dissociation cross sections at the thresholds [44, 19]. Such difficulties can be overcome by a measurement of the adiabatic ionization energy $E_{\rm I}({\rm H}_2)$ combined with a thermodynamic cycle involving the ionization energy of atomic hydrogen $E_{\rm I}({\rm H})$ and the dissociation energy of the molecular ion $D_0({\rm H}_2^+)$ [21] via

$$D_0(H_2) = E_I(H_2) + D_0(H_2^+) - E_I(H)$$

as illustrated in Fig. 2.1. The dissociation energies $D_0^{N=1}$ and $D_0^{N=0}$ of ortho- and para-H₂ differ by the rotational term value of the X(v = 0, N = 1) level, i.e., 118.486 84(10) cm⁻¹ [45].

The most accurate previous determination of $D_0(\text{H}_2)$, at a relative accuracy of 10^{-8} [12], involved two-photon Doppler-free laser excitation to the EF ${}^{1}\Sigma_{g}^{+}(v=0, N=1)$ intermediate state [46], one-photon ultraviolet excitation from the EF ${}^{1}\Sigma_{g}^{+}(0,1)$ to the 56p1₁ Rydberg state [12], and millimeter wave (MMW) spectroscopy of high-lying Rydberg states [47] allowing for an extrapolation to the ionization energy by Multi-Channel Quantum Defect theory (MQDT) [48]. The initial EF-X step in this scheme has recently been improved by two orders of magnitude



Figure 2.1 – Potential energy diagram of electronic states in molecular hydrogen relevant to this study.

to an accuracy of 73 kHz [49], but an improvement of $D_0(H_2)$ awaits an improved measurement of the EF-*n*p interval.

In the present work, we adopt an alternative excitation scheme to determine $D_0(H_2)$, through the GK ${}^{1}\Sigma_{g}^{+}(1,1)$ intermediate state, which offers the possibility of using continuous wave (cw) infrared laser excitation to high-*n* Rydberg states [50]. Experimental results from two laboratories are combined: the measurement of the Doppler-free two-photon transition GK(1,1) $\leftarrow X(0,1)$ in Amsterdam, and the determination of the interval between GK(1,1) and the 56p1 Rydberg state by near-infrared (NIR) cw-laser spectroscopy in Zürich.

2.2 Experiments

2.2.1 Measurement of the GK(1,1)-X(0,1) interval

In the GK-X experiment, schematically depicted in Fig. 2.2, a narrow bandwidth (~9 MHz) injection-seeded oscillator-amplifier titanium sapphire (Ti:Sa) laser system delivers 50-ns-long pulses at the fundamental wavelength of 716 nm. The amplified pulsed output is frequency upconverted in two doubling stages, with BBO and $KBe_2BO_3F_2$ (KBBF) crystals, leading to the generation of 179-nm radiation to drive the $GK(1,1) \leftarrow X(0,1)$ transition in a two-photon scheme. The vacuumultraviolet (VUV) output power of 20 μ J per pulse is limited by the optical damage threshold of the KBBF crystal [33]. A glass pinhole with a diameter of 0.5 mm is employed to align the reflected beam in a counter-propagating Doppler-free configuration. A separate 633-nm pulsed dye laser is used to ionize the molecules from the GK(1,1) state in a single-photon ionization process. To reduce AC Stark effects, this laser is delayed by 30 ns with respect to the 179-nm pulse. Further increase of the delay is detrimental because the lifetime of the GK(1,1)state is 24(3) ns [51]. The H_2^+ ions are collected and detected by the velocity-map-imaging method [52].

The cw Ti:Sa laser, which has a short-term (one second) frequency stability of a few tens of kHz, is locked to an optical frequency comb, resulting in a long-term relative accuracy better than 10^{-12} . An acousto-optic modulator (AOM) was implemented in a double-pass scheme to



Figure 2.2 – Schematic layout of the GK-X experimental setup, where the pulsed pump laser for the oscillator and amplifier is not shown.

scan the cw laser frequency, the output of which is used as a seed for the oscillator cavity. The frequency offset or chirp, between the pulsed output and cw seed was measured for each pulse [46]. An intra-cavity electro-optic phase modulator (EOM), driven by an arbitrary function generator, is used for active frequency chirp compensation, as shown in Fig. 2.2. In addition, the residual chirp value is recorded and corrected at each frequency scan step. An upper limit of the systematic uncertainty associated with chirp is extracted from the statistical analysis, by repeating the measurements after changing the anti-chirp parameters.

A typical scan is shown in Fig. 2.3(a) with 50-shot averaging for each frequency scan step. The observed two-photon transition linewidth is dominated by the laser bandwidth, with a small contribution of the natural linewidth ($\Gamma = 6.6$ MHz). An imperfect counter-propagating align-

ment may result in a residual first-order Doppler shift. This was quantified by performing velocity-dependent measurements using various mixtures of H₂ and Ne, and extrapolating to a zero-velocity transition frequency, as shown in Fig. 2.3(b). Several measurements were performed using different alignment configurations of the counter-propagating VUV laser beams. After accounting for the second-order Doppler shift, which is 150(30) kHz in pure H₂ with a velocity of 2900(300) m/s, a global fitting procedure is applied, where the zero-velocity intercept is shared for all alignment settings. The extrapolation yields the Doppler-free transition frequency with a systematic uncertainty of 350 kHz, which is the largest contribution to the error budget. The normalized velocity of the H₂ beam in Fig. 2.3 is defined as $v_{\rm norm} = v_{\rm mix}/v_{\rm pure} = \sqrt{m_{\rm H_2}/(n_{\rm H_2} \cdot m_{\rm H_2} + n_{\rm Ne} \cdot m_{\rm Ne})}$, where $n_{\rm H_2}$ and $n_{\rm Ne}$ are the mixture fractions of H₂ and Ne, and $m_{\rm H_2}$ and $m_{\rm Ne}$ are their masses [53].

The AC Stark effect for both the 179-nm and the ionization lasers was studied by performing intensity-dependent measurements. Typically the 179-nm laser power was fixed to 2 μ J per pulse during the residual Doppler-shift determination, while up to 10 μ J was generated to assess the AC Stark effect. A similar procedure is applied for the ionization laser, including the assessment of systematic shifts caused by the temporal overlap between the two laser pulses. The Doppler-extrapolated value was corrected for the AC Stark shifts. Other possible systematic and statistical uncertainties were derived from day-to-day frequency differences (in total 215 measurements) over several days (see Fig. 2.3(c)). The uncertainty budget is given in Table 2.1, and the combined statistical and systematic uncertainty of the GK-X transition is 650 kHz, corresponding to a relative accuracy of 2×10^{-10} .

2.2.2 Ionization energy of the GK(1,1) state

The interval between the GK(1,1) state and the $56p1_1(v^+ = 0, S = 0, F = 0 - 2)$ Rydberg state of ortho-H₂ was measured using the same apparatus, laser setup and calibration procedure as described in detail in a recent article presenting a measurement of the $50f0_3 \leftarrow GK(0,2)$ interval [50]. The measurement was carried out using a pulsed and skimmed supersonic beam of pure H₂ and the procedure involved (i) the compensation of the stray electric fields in three dimensions to better



Figure 2.3 – (a) Recording of a $GK(1,1) \leftarrow X(0,1)$ transition in H_2 (black circles). The red line is a fitted Gaussian curve with the residuals shown below. (b) Assessment of the residual first-order Doppler effect. Each color indicates an individual alignment configuration, where the largest deliberate misalignment is about 0.3 mrad. The blue and magenta points are shifted by 0.02 and -0.02 in velocity axis for clarity. The colored lines show a linear global fit for all alignments, resulting in the Doppler-free value indicated with the open circle. (c) Transition frequency measurements in different days. Each point indicates an average value for one day with its standard deviation. The dash line shows the mean value. The magenta line and the cyan area give the standard deviation of the data and of the mean, respectively, where the former is taken as a conservative statistical uncertainty.

GK(1	$(1) \leftarrow X(0 \ 1)$	5 6 n1	$f \leftarrow GK(1 1)$
3348281	018.58(49) MHz	378809	479.24(30) MHz
rrection	Uncertainty	Correction	Uncertainty
	$<10 \mathrm{ kHz}$		$7 \mathrm{kHz}$
40 kHz	$90 \mathrm{kHz}^{,a}$		$4 \mathrm{kHz}$
90 kHz	$200 ext{ kHz},^{b}$		
	$(<490 \text{ kHz})_{\text{stat}},^{c}$	I	
	$< 10 \mathrm{~kHz}$		$10 \mathrm{kHz}$
	<1 m kHz		$1 \mathrm{kHz}$
	$350 \mathrm{~kHz}$		$(<110 \text{ kHz})_{\text{stat}},^{c}$
	$<\!30~{ m kHz},^d$	+4.1 kHz	$0.5 \mathrm{kHz}$
			200 kHz
	$<100 \mathrm{~kHz}$		100 kHz
		-160 kHz	
	426 kHz		$224 \mathrm{~kHz}$
348281018.	$35(49)_{\rm stat}(43)_{\rm sys}{\rm MHz}$	378809479.0	$08(30)_{\rm stat}(22)_{\rm sys}{ m MHz}$
	GK(1 3348281 rrection 10 kHz 90 kHz - - - - - - - - - - -	$\begin{array}{c c} \mathrm{GK}(1,1)\leftarrow\mathbf{X}(0,1)\\ 3348281018.58(49)\mathrm{MHz}\\ \mathrm{rrection} & \mathrm{Uncertainty}\\ \mathrm{rrection} & & <10\mathrm{kHz}\\ \mathrm{10\mathrm{kHz}} & 90\mathrm{kHz},^{a}\\ \mathrm{90\mathrm{kHz}} & 200\mathrm{kHz},^{b}\\ & & (<490\mathrm{kHz})_{\mathrm{stat}},^{c}\\ & <10\mathrm{kHz}\\ & & <10\mathrm{kHz}\\ \mathrm{350\mathrm{kHz}}\\ \mathrm{-}\\ $	$\begin{array}{c c c} \mathrm{GK}(1,1) \leftarrow \mathrm{X}(0,1) & \mathbf{56p1} \\ 3348281018.58(49)\mathrm{MHz} & 378809 \\ \mathrm{rrection} & \mathrm{Uncertainty} & \mathrm{Correction} \\ & <10\mathrm{kHz} & 90\mathrm{kHz},^a \\ 90\mathrm{kHz} & 90\mathrm{kHz},^b \\ (<490\mathrm{kHz},^b \\ (<490\mathrm{kHz},^b \\ (<490\mathrm{kHz},^{b} \\ <490\mathrm{kHz} \\ 350\mathrm{kHz} \\ <10\mathrm{kHz} \\ 350\mathrm{kHz} \\ <30\mathrm{kHz} \\ <30\mathrm{kHz} \\ - \\ & <100\mathrm{kHz} \\ - \\ & - \\ & <100\mathrm{kHz} \\ - \\ & - \\ $

Table 2.1
Transition.
frequencies
of H_2
and their
uncertainties.

^{*a*} For the ionization laser.

 b For the VUV laser.

 c This systematic uncertainty is already included in the statistical uncertainty of the frequency measurements.

error is included in the residual first-order Doppler shift uncertainty. d The second-order Doppler shift values are subtracted for different velocities in Fig. 2.3(b) and the than 1 mV/cm, which limits possible Stark shifts to below 7 kHz for the 56p1₁ level [54], (ii) shielding external magnetic fields so that the maximal Zeeman shifts are below 10 kHz, (iii) the cancellation of the first-order Doppler shift to better than 110 kHz by performing the excitation with the NIR-laser beam of 792-nm wavelength and its back reflection overlapped to better than 0.05 mrad and averaging the central frequencies of both Doppler components (see Fig. 2.4(a)); repeating the measurements after full alignment of the laser and molecular beams transforms the systematic uncertainty associated with the residual Doppler shift into a statistical uncertainty, (iv) cooling the valve used to generate the supersonic beam to 80 K, thus reducing the mean beam velocity to 1290(20) m/s and leading to a second-order Doppler shift of -4.1(5) kHz, (v) calibrating the excitation frequency with a frequency comb referenced to a 10-MHz Rb oscillator (Stanford Research Systems, FS275).

A typical individual spectrum is displayed in Fig. 2.4(a) as dots with error bars. The figure also depicts a fit of a model line shape consisting of two Doppler components. Each of these is the sum of three hyperfine components (stick spectrum) having the same Lorentzian width, intensities given by their statistical weights of 2F+1, and relative positions corresponding to those measured by millimeter-wave spectroscopy [47, 22]. In the fit, the data points were weighted by taking into account the Poissonian statistics of the ion counts and the background noise as explained in Ref. [50]. The central positions determined from 39 measurements are plotted in Fig. 2.4(b) with their statistical uncertainties. Their weighted mean, indicated by the dashed line, is 378 809 479.24(30) MHz where the statistical uncertainty of 300 kHz corresponds to $\bar{\sigma} = \sigma/\sqrt{N}$, N being the number of independent measurements, which we took to be the number of measurement sets recorded on different days rather than the number of individual measurements (i.e., 6, as indicated by the different symbols in Fig. 2.4(b), rather than 39).

The systematic uncertainties considered in the analysis are summarized in Table 2.1 and sum up to 224 kHz, dominated by the uncertainty resulting from the possible deviations from a statistical intensity distribution of the unresolved hyperfine structure of the $56p1_1 \leftarrow GK(1,1)$ line (Line-shape Model entry in Table 2.1). After subtraction of the photon recoil shift of 160 kHz, our final result for the $56p1_1 \leftarrow GK(1,1)$



Figure 2.4 – (a) Typical spectrum of the $56p1_1 \leftarrow GK(1,1)$ transition of H_2 and its analysis based on a Lorentzian line-shape model and the hyperfine structure of the $56p1_1$ Rydberg state given as red (F = 1), blue (F = 0) and green (F = 2) sticks. The weighted residuals are depicted below the spectrum. (b) Doppler-free frequencies with standard deviations of individual measurements. The magenta line and the cyan area give the standard deviation of the full data set and of the mean, respectively. The symbols label measurements carried out on different days.

interval is shown in Table 2.1. This value is consistent with, but four times more precise than, the value of 378 809 478.7(12) MHz reported in [54].

The experimental values of the $56p1_1 \leftarrow GK(1,1)$ interval in Table 2.1 correspond to the center of gravity (c.g.) of the hyperfine components. The hyperfine splitting of the GK(1,1) state, which has d character, is estimated to be 330 kHz from the known hyperfine structure of high-*n*d Rydberg states [47] and leads to a systematic uncertainty contribution of 100 kHz for the transition center frequency. In addition, the hyperfine splitting of the X(0,1) state, which was observed by Ramsey to be 600 kHz [57], also contributes to the systematic uncertainty for the GK(1,1) \leftarrow X(0,1) measurement. In the center-of-gravity transition frequency determination, a contribution of less than 100 kHz is estimated.

The binding energy of the 56p1₁ Rydberg state with respect to the first rovibronic state X⁺ ($v^+ = 0, N^+ = 1$) of ortho-H₂⁺ was determined via a MQDT-assisted fitting procedure applied to 76 measured np hyperfine components with 54 < n < 64, as described in Ref. [55] and the value is given in Table 2.2.

2.3 Results and Discussion

Combining all contributions, the ionization energy of ortho-H₂, $E_{\rm I}^{\rm o}({\rm H}_2)$, is determined to be 124357.238062(25) cm⁻¹ (see Table 2.2), corresponding to a relative accuracy of 2×10^{-10} . The dissociation energy, $D_0^{N=1}({\rm H}_2)$, is derived from $E_{\rm I}^{\rm o}({\rm H}_2)$ to be 35999.582894(25) cm⁻¹ or 1079240344.3(8) MHz with a relative accuracy of 7×10^{-10} , by using the values of $D_0^{N^+=1}({\rm H}_2^+)$, calculated to an accuracy of 6×10^{-7} cm⁻¹ [24, 56], and $E_{\rm I}({\rm H})$, which is included in CODATA 2014 [56].

A comparison between our new value of $D_0^{N=1}(H_2)$ and the most recent experimental and theoretical results is presented in Fig. 2.5. Our result confirms the validity of the previous experimental result [12] using a different excitation sequence, but improves its accuracy by one order of magnitude. It deviates from the newest theoretical result reported in Ref. [43] by more than three times the uncertainty. Possible reasons for the discrepancy between the experimental and theoretical values of

Energy level interval	Value	Ref.	Comment
(1) $GK(v = 1, N = 1) - X(v = 0, N = 1)$	111686.632836(22)	This work	
(2) $56p1_1(v^+ = 0, S = 0, center) - GK(v = 1, N = 1)$	12635.724114(12)	This work	
$(3)X^+(v^+ = 0, N^+ = 1, \text{center}) - 56p1_1(v^+ = 0, S = 0, \text{center})$	$34.881\ 112(5)$	[55]	
(4) $[H(1s) + H^+] - X^+(v^+ = 0, N^+ = 1, center)$	21321.1165755(6)	[24, 56] L	$\Omega_0^{N^+=1}({ m H}_2^+)$
(5) $[H(1s) + H^+] - [H(1s) + H(1s)]$	109678.77174307(10)) $[56]$	$E_{\rm I}({\rm H})$
(6) $(1)+(2)+(3)$	124357.238062(25)	This work	$E_{ m I}^{ m o}({ m H}_2)$
(7) (1)+(2)+(3)+(4)-(5)	35999.582894(25)	This work	$D_0^{N=1}({ m H}_2)$

Table 2.2 – Energy level intervals and determination of the ionization $E_{\rm I}$ and dissociation energies D_0 of ortho-H₂ (in cm⁻¹).



Figure 2.5 – Comparison between experimental and theoretical values of $D_0^{N=1}$ for ortho- H_2 .

 $D_0({\rm H}_2)$ include the underestimation of nonadiabatic effects in the determination of the relativistic and QED corrections to $D_0({\rm H}_2)$ [43], or a more fundamental problem in the molecular quantum theory. Resolving this puzzle and further improvement of this value to 10-kHz accuracy, for both experiment and theory, will open a new route for determining the proton charge radius [9, 43] with 1% accuracy, or an improved value of the proton-to-electron mass ratio [1, 4].

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CHAPTER 3

Determination of the Interval between the Ground States of Para- and $Ortho-H_2$

Abstract

Nuclear-spin-symmetry conservation makes the observation of transitions between quantum states of ortho- and para-H₂ extremely challenging. Consequently, the energy-level structure of H₂ derived from experiment consists of two disjoint sets of level energies, one for para-H₂ and the other for ortho-H₂. We use a new measurement of the ionization energy of para-H₂ ($E_{\rm I}({\rm H}_2)/(hc) = 124417.491\,098(31)\,{\rm cm}^{-1}$) to determine the energy separation (118.486770(50) cm⁻¹) between the ground states of para- and ortho-H₂ and thus link the energy-level structure of the two nuclear-spin isomers of this fundamental molecule. Comparison with recent theoretical results (M. Puchalski *et al.*, Phys. Rev. Lett. **122**, 103003 (2019)) enables the derivation of an upper bound of 1.5 MHz for a hypothetical global shift of the energy-level structure of ortho-H₂ with respect to that of para-H₂.

This chapter is based on: Determination of the Interval between the Ground States of Para- and Ortho-H₂, M. Beyer, N. Hölsch, J. Hussels, C.-F. Cheng, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, Ch. Jungen and F. Merkt, *Phys. Rev. Lett.* **123**, 163002 (2019)

3.1 Introduction

The conservation of parity and nuclear-spin symmetry represents the basis for selection rules in molecular physics, with applications ranging from reaction dynamics to astrophysics [58, 59, 60, 61, 62, 63]. Hydrogen, in its different molecular and charged forms, e.g., H_2 , H_2^+ , H_3 , H_3^+ , etc., has played a crucial role in the derivation of the current understanding of nuclear-spin symmetry conservation and violation. H_2 , for instance, exists in two distinct nuclear-spin forms, called nuclear-spin isomers, with parallel (I = 1, ortho- H_2) or anti-parallel (I = 0, para- H_2) proton spins. The para isomer can be isolated and stored in large amounts [64].

The restrictions on the total molecular wave function imposed by the Pauli principle allow only even (odd) rotational levels for para (ortho) H_2 and H_2^+ in their electronic ground state X ${}^{1}\Sigma_{q}^+$ and X ${}^{+2}\Sigma_{q}^+$, respectively. Consequently, the spectra of ortho- and para- H_2 and H_2^+ do not have common lines and appear as spectra of completely different molecules. Linking the energy-level structures of both nuclear-spin isomers is thus extremely challenging. A significant mixing of states of ortho and para (and gerade and ungerade) character is predicted to only occur in the highest vibrational states, because the hyperfine interaction of the atomic fragments becomes dominant at large internuclear separations and decouples the two nuclear spins [65, 66, 67, 68]. The $N^+ = 1 \leftarrow N^+ = 0$ ($v^+ = 19$) pure rotational transition in H_2^+ was measured with an accuracy of 1.1 MHz (2σ) by Critchley et al. and represents today the only experimental connection between states of orthoand para- H_2^+ [69]. The frequency of this transition was also determined in first-principles calculations that included quantum-electrodynamics corrections and hyperfine-induced ortho-para mixing [66, 68]. This connection enables one to relate the energy-level structure of ortho- and $para-H_2^+$ through high-level first-principles calculations [24], which have been validated by precision spectroscopy in molecular hydrogen ions |70, 71|.

In this letter, we extend this connection to the entire spectrum of H_2 by determining the ionization energy of para- H_2 following the scheme illustrated in Fig. 3.1. Using our recent results for the ionization energy of ortho- H_2 [72, 73] and the calculated energy difference between the



Figure 3.1 – Schematic diagram illustrating the energy levels and intervals of H_2 and H_2^+ (not to scale) used to determine the energy difference ΔE_{o-p} between the ground state of ortho- and para- H_2 .

ground states of ortho- and para- H_2^+ , we determine a value for the orthopara separation in the electronic and vibrational ground state of H_2 and thus accurately link the energy-level structure of both nuclear-spin isomers of this fundamental molecule for the first time.
3.2 Method

As in our previous work on ortho-H₂ [12, 72, 73], we determine the ionization energy of para-H₂ through the measurement of intervals between rovibrational levels of the X ${}^{1}\Sigma_{g}^{+}$ ground state, the EF and GK ${}^{1}\Sigma_{g}^{+}$ excited states and high-lying Rydberg states, with subsequent extrapolation of the Rydberg series using multichannel quantum-defect theory (MQDT).

A major difficulty that arises when applying this scheme in para- H_2 is the fact that the only p Rydberg series converging to the $v^+ = 0, N^+ = 0$ ground state of H_2^+ , the $np0_1(0)$ series (using the notation $nlN_N^+(v^+)$ [55]) of mixed Σ^+ and Π^+ character, is heavily perturbed by rotational channel interaction with the $np2_1(0)$ series and is additionally affected by predissociation into the continuum of the $3p\sigma B'^{-1}\Sigma_{\mu}^{+}$ state mediated by the D $3p\pi \ ^{1}\Pi_{u}^{+}$ state [74, 75]. In contrast, our previous determinations in ortho-H₂ [12, 54, 72, 73] relied on the excitation of Rydberg states of the $np1_1(0)$ series of Π_n^- character, which is not predissociative. Moreover, there are no p Rydberg series with N = 1 converging on $N^+ > 1$ ionic levels in ortho-H₂, so that rotational channel interactions are strongly suppressed. In this case, perturbations can only occur by interactions with low-n Rydberg states having a vibrationally excited ion core $v^+ \geq 1$ and from weak interactions between p and f series [47]. Consequently, an MQDT extrapolation of the $np1_1(0)$ series to the ionic ground state $(X^+(v^+ = 0, N^+ = 1))$ could be made at an accuracy of better than 150 kHz [47, 55]. These considerations are illustrated in Fig. 3.2, which shows that the calculated effective quantum defect, $\mu = n + \sqrt{-\mathcal{R}/(\epsilon_{\text{bind}}/hc)}$, of the $np1_1(0)$ series (open squares) is indeed nearly constant for the n < 100 Rydberg states used in the extrapolation, and is only significantly perturbed near the ionization threshold by the $7p1_1(1)$ state (\mathcal{R} is the Rydberg constant for H₂ and $\epsilon_{\rm bind}/hc$ the Rydberg electron binding energy).

In contrast, the effective quantum defect of the $np0_1(0)$ series (crosses in Fig. 3.2) reveals very large perturbations with the typical divergences at the positions of the successive members of the $np2_1(0)$ series [76, 21]. The extrapolation of the Rydberg series with kHz accuracy is impossible in this case because of (i) difficulties arising from the treatment of the energy dependence of the quantum defects in the MQDT framework [77] (see also Ref. [78] for a proposed solution to this problem), and (ii) the predissociation of $np0_1(0)$ Rydberg states which can shift the positions of the $n \sim 55 - 75$ members of the series by several MHz according to preliminary studies [79].

To overcome this problem, we choose to determine the ionization energy of para-H₂ through extrapolation of the nonpenetrating $nf0_3(0)$ Rydberg series, which is much less perturbed than the $np0_1(0)$ series. The $l(l + 1)/r^2$ centrifugal barrier in the effective electron-H₂⁺ interaction potential leads to a strong reduction of all nonadiabatic interactions between the electron and the ion core (i.e., predissociation and rovibrational channel interactions). The hydrogen-atom-like nature of the $nf0_3(0)$ series is illustrated in Fig. 3.2, which shows that the quantum defect of this series (full diamonds) is nearly zero and constant over the entire range of binding energies, allowing for a very accurate extrapolation of the ionization energy. Nonpenetrating Rydberg states have been used to derive ionization energies in more complex molecules at lower resolution (e.g., CaF [80] or benzene [81]) and to determine rovibrational intervals of molecular ions [48].

3.3 Experiments

The experiments relied on the same setups and procedures as used in our recent determination of the ionization energy of ortho-H₂, and we refer to Ref. [72] for details. The GK(1,0)-X(0,0) transition, which is two-photon allowed, turned out to be about 100 times weaker than the GK(1,1)-X(0,1) transition of ortho-H₂, insufficient to perform a precision study. This is attributed to the lack of mixing of the N = 0 level with the nearby I ${}^{1}\Pi_{g}$ state [82]. The GK(1,2)-X(0,0) transition, probing N = 2, had sufficient intensity and was subjected to a precision study in Amsterdam.

3.3.1 Measurement of the GK(1,2)-X(0,0) interval

Frequency-comb-referenced Doppler-free two-photon spectroscopy was performed using pulsed narrow-band vacuum-ultraviolet (VUV) laser radiation generated by nonlinear frequency upconversion of light from a chirp-compensated injection-seeded oscillator-amplifier titanium-sapphire



Figure 3.2 – Calculated effective quantum defects of the $np1_1(0)$ (open squares), $np0_1(0)$ (crosses) and $nf0_3(0)$ (full diamonds) Rydberg series. The color code indicates the character of the individual states, blue indicating an unperturbed level of series converging to $N^+ = 0$ and dark red a strongly perturbed Rydberg level with large $N^+ = 2$ character.

(Ti:Sa) laser system in a BBO and a KBBF crystal. The transitions were detected by photoionizing the GK(1,2) level with a separate pulsed dye laser which was delayed in time. The measurements were carried out in three campaigns distinct in time. In the first round, the Ti:Sa laser system was pumped by a seeded Nd:YAG laser. An unseeded Nd:YAG laser was used in the other two rounds, resulting in different settings for the timing and chirp compensation.

The chirp effect on the laser pulses was counteracted by an electrooptic modulator placed inside the Ti:Sa oscillator cavity, and the chirp of the amplified pulses was measured on-line for each pulse and used to correct the frequency. Each campaign had a different setting for

the BBO- and KBBF-crystal angles and a different wavelength for the ionization laser. Therefore, ac-Stark-shifts caused by the VUV and ionization lasers were measured and compensated independently in each round. Comparing the analyses of the ac-Stark effect from the 3 campaigns, the maximal error (470 kHz) was taken as the final uncertainty contribution for both VUV and ionization pulses, thus yielding a conservative estimate of this contribution to the systematic uncertainty. Possible Doppler shifts induced by non-perfectly counter-propagating VUV beams crossing the H_2 molecular beam were analysed as in Ref. [72], by varying the velocity of the molecular beam. But instead of constraining the extrapolation to a global fit, all ac-Stark and second-order Doppler compensated line positions, grouped by velocity, were averaged and a residual Doppler-free value was obtained for every day. These values were averaged (see Fig. 3.3), yielding the Doppler-free transition frequency with an accuracy of 410 kHz. Combining this error (including statistics, residual Doppler effects and chirp phenomena) and the major systematic uncertainties from the ac-Stark and second-order Doppler effects, the final uncertainty of the GK(1,2)-X(0,0) interval, dominated by systematic effects, was determined to be 630 kHz as listed in Table 3.1.

3.3.2 Ionization energy of the GK(1,2) state

The natural linewidth of the transitions to long-lived high-*n* Rydberg states is determined by the lifetime of the rovibrational level of the GK ${}^{1}\Sigma_{g}^{+}$ state used as initial state. We therefore chose the GK(0,2) level rather than the GK(1,2) level to record the positions of the $nf0_{3}(0)$ series because its wavefunction is localized in the K outer well, leading to a threefold increase in lifetime. To combine the results of the GK(1,2)-X(0,0) measurements carried out in Amsterdam and the $nf0_{3}(0)$ -GK(0,2) measurements carried out in Zurich, we use the relative position of the GK(0,2) and GK(1,2) rovibrational levels determined very accurately in Ref. [83] (see Table 3.1).

The intervals between the GK(0,2) state and 14 members of the $nf0_3(0)$ Rydberg series with n values between 40 and 80 were recorded using single-mode continuous-wave near-infrared radiation from a Ti:Sa laser, referenced to a frequency comb, intersecting a pulsed skimmed



Figure 3.3 – Upper panel: Example of a chirp-compensated scan of the GK(1,0)-X(0,0) line, before corrections of Stark and Doppler effects. The best fit is a Gaussian with FWHM of 27 MHz, resulting from the Fourier-transform limited bandwidth of the 25 ns laser pulse and the 30 ns lifetime of the GK-state. Lower panel: Day-by-day residual Doppler extrapolated values of 323 Stark- and second-order-Doppler-compensated line position determinations. The dashed line is the weighted mean of all 16 days. The pink lines indicate the standard deviation (940 kHz) and the blue area the standard error of the mean (410 kHz). This is thus the combined uncertainty of the residual first-order Doppler shift and the statistical error.

supersonic beam of pure H₂ emanating from a cryogenic pulsed valve. Compensating stray electric fields in three dimensions, shielding magnetic fields, and cancelling the first-order Doppler shift enabled the determination of transition frequencies with uncertainties ranging from 33 kHz at n = 50 to 490 kHz at n = 80. We included a scaled systematic uncertainty of $\sigma_{n,dc} = 18 \cdot (n/50)^7$ kHz, based on the value for n = 50, to account for possible dc Stark shifts resulting from stray electric fields. We refer to Ref. [50] for further details concerning the determination of experimental uncertainties.

The binding energy of the GK(0,2) state was determined by MQDTassisted extrapolation of the $nf0_3(0)$ series in a fit where we adjusted the Hund's case (d) effective quantum defect [77]. We found that the adjustment was on the order of 10^{-5} , i.e. within the error limits given in Ref. [47]. Because the $N^+ = 0$ ion core is structureless, most of the observed $nf0_3(0)$ Rydberg states have pure singlet (S = 0) character [48]. The $nf0_3(0)$ levels located in the immediate vicinity of $n'f2_3(0)$ perturbing states represent an exception because they have mixed singlet and triplet character induced by the spin-rotation interaction in the $(v^+ = 0, N^+ = 2)$ ion core. These states were not included in the MQDT fit. The residuals of this fit are depicted in Fig. 3.4. We estimate the uncertainty $\delta\mu$ of the nf quantum defects to be $1.6 \cdot 10^{-5}$, corresponding to an uncertainty of 500 kHz at n = 60, and to an n-dependent uncertainty $\delta\epsilon_{\text{bind}}$ in the binding energy given by

$$\delta \epsilon_{\rm bind}/(hc) \approx \frac{2\mathcal{R}}{n^3} \delta \mu,$$
 (3.1)

illustrated by the blue area in Fig. 3.4. The extrapolated series limit corresponds to the absolute value of the binding energy of the GK(0,2) state and its uncertainty of 700 kHz is given by the dashed horizontal lines in Fig. 3.4. A list of the measured $nf0_3(0)$ -GK(0,2) intervals with corresponding experimental uncertainties and fit residuals is provided in the supplementary material [84].

3.4 Results and Discussion

Table 3.1 summarizes the main experimental results and all intervals needed to determine the ionization energy of para-H₂ $(E_I^{\text{para}}(\text{H}_2))$ =

Energy level interval	Value (cm^{-1})	Uncertainty (kHz)	Reference
(1) $GK(v = 1, N = 2) - X(v = 0, N = 0)$	111827.741986(21)	630	This work
(2) $GK(v = 1, N = 2) - GK(v = 0, N = 2)$	134.0083485(22)	66	[83]
$(3) \ \mathrm{X}^+(v^+=0, N^+=0) - \mathrm{GK}(v=0, N=2)$	12723.757461(23)	700	This work
(4) $E_I^{\text{para}}(\text{H}_2) = (1) - (2) + (3)$	124417.491098(31)	940	This work
(5) $E_I^{\text{ortho}}(\text{H}_2)$	124357.238003(11)	340	[73]
(6) $X^+(v^+ = 0, N^+ = 1, \text{center}) - X^+(v^+ = 0, N^+ = 0)$	$58.233\ 675\ 1(1)^a$	30	[86, 87, 88]
(7) $D_0^{N^+=0}(\mathrm{H}_2^+)$	21379.3502496(6)	18	[24]
(8) $E_I(\mathrm{H})$	109678.77174307(10)	ယ	[23]
(9) $D_0^{N=0}(\mathrm{H}_2) = (4) + (7) - (8)$	36118.069605(31)	940	This work
$(10) D_0^{N=0}({\rm H}_2)$	36118.069632(26)	780	[30]
$(11)\Delta E_{\text{o-p}} = (4) + (6) - (5)$	$118.486\ 770(50)^b$	1500	This work
$(12)\Delta E_{\text{o-p}}$	118.4868127(11)	33	[30]

third column. **Table 3.1** – Overview of energy intervals used in the determination of the ionization and dissociation the uncertainties (one standard deviation) in the last digit. These uncertainties are given in kHz in the energies and the ortho-para separation of H_2 . The values in parentheses in the second column represent

A recent calculation by v. 1. ROTODOV gave the value of 30.2330730374(0) cm 00

splitting). addition to the uncertainties of the para- and ortho- H_2 ionization energies (assuming no anomalous effect on the para-ortho para states of H_2^+ [69] and the theoretical uncertainty of the term values of the highest bound states of H_2^+ , respectively, in ^bThe uncertainty includes contibutions of 550 kHz and 1 MHz for the experimental frequency connecting the ortho and



Figure 3.4 – MQDT fit residuals for the measured nfO_3 Rydberg states. The uncertainty of the binding energies of the GK(0,2) state and of the high-n Rydberg states are indicated by the magenta dashed lines and the blue area, respectively.

124417.491098(31) cm⁻¹), the dissociation energy of para-H₂ ($D_0^{N=0}(H_2) = 36118.069605(31) \text{ cm}^{-1}$), and the interval between the ground states of ortho- and para-H₂ ($\Delta E_{\text{o-p}} = 118.486770(50) \text{ cm}^{-1}$). The uncertainty (1 σ) of $\Delta E_{\text{o-p}}$ includes contributions from the measurement of the $N^+ = 1 \leftarrow N^+ = 0$ ($v^+ = 19$) transition from Ref. [69] (1 $\sigma = 550 \text{ kHz}$) and a conservative estimate of the uncertainty of the relevant calculated H₂⁺ term values [24, 66, 68].

The present results were obtained in what may be referred to as a blind analysis, i.e., the intervals obtained in Amsterdam and Zurich were first determined independently with their respective uncertainties and then added for comparison with theoretical results. In this context, it is worth mentioning that the dissociation energy of ortho-H₂ reported in Ref. [30] was determined from the value of the dissociation energy of para-H₂ obtained from full four-particle nonrelativistic calculations by adding the value of $\Delta E_{\text{o-p}}$ calculated in the realm of nonadiabatic perturbation theory. The present values of the ionization and dissociation energies of para-H₂ thus represent a more stringent test of the theory than the $\Delta E_{\text{o-p}}$ value and the dissociation and ionization energies of ortho-H₂ reported in Ref. [73].

Our value of $\Delta E_{\text{o-p}}$ is compatible with, but more precise than, the value of 118.48684(10) cm⁻¹ determined from the molecular constants derived from a combination of laboratory and astrophysical data on electric-quadrupole transitions of H₂ [45] (which is based on the assumption that the level structure of ortho- and para-H₂ can be described by the same constants).

 $D_0^{N=0}$ (para-H₂) and $\Delta E_{\text{o-p}}$ both agree within the combined error bars with the theoretical values of 36118.069632(26) cm⁻¹ and 118.4868127(11) cm⁻¹, respectively, reported by Puchalski et al. [30]. Given that the first-principles calculations reported in Ref. [30] did not consider an anomalous effect on the ortho-para energy separation [89], the agreement between the experimental and theoretical values of $\Delta E_{\text{o-p}}$ implies an upper bound of $5 \cdot 10^{-5}$ cm⁻¹, given by the combined uncertainty of the experimental and theoretical values, for a hypothetical global shift of the energy-level structure of ortho-H₂ with respect to that of para-H₂. This upper bound is almost three orders of magnitude smaller than the upper bound (780 MHz) one can derive from measurements of the dissociation energies of the EF(0,0) and EF(0,1) states [19].

Measurements of the dissociation energy of H_2 in para- H_2 , as presented in the present work, eliminate the uncertainty related to the unresolved hyperfine structure in the X and GK (or EF) states in ortho- H_2 and thus hold the promise of a further increase in accuracy. The optimal scheme for para- H_2 would make use of a measurement of the X(0,0)-EF(0,0) interval by Ramsey-type spectroscopy, as reported by Altmann *et al.* for the X(0,1)-EF(0,1) interval [49]. The long lifetime of the EF(v = 0) levels would enable the measurement of extremely narrow transitions to high Rydberg states. Unfortunately, transitions from the EF state to *n*f Rydberg states have negligible intensity because the EF state has predominant 2s character. To nevertheless benefit from a highly accurate X-EF Ramsey-type measurement in para- H_2 , we plan to use transitions to long-lived $np0_1$ Rydberg states to relate the EF and GK energies, and to use $nf0_3$ -GK(0,2) transitions to extrapolate to the X⁺(0,0) ionization limit. A similar procedure resulted in a 40 kHz relative determination of the rovibrational levels of the GK and H states [83], indicating significant potential for an even more accurate $D_0^{N=0}$ (para-H₂) value.

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$_{\rm CHAPTER} 4$

A chirp-compensated pulsed Titanium-Sapphire oscillator-amplifier laser for precision spectroscopy

Abstract

Active frequency-chirp control for a narrowband pulsed Titanium-Sapphire laser system is demonstrated using an intra-cavity electrooptic modulator resulting in improved spectral resolution and stability. Beat-note measurements of the output of this pulsed laser to a cw-laser locked to an optical frequency comb yields an Allan deviation of 5×10^{-11} (at 10 s). Correction of residual chirp from a comparison with the 4th harmonic upconverted pulsed output to a molecular H₂ two-photon resonance delivers a value for the uncertainty contribution due to frequency chirp below the 1.5×10^{-10} level.

This chapter is based on: *Chirp-compensated pulsed Titanium-Sapphire laser* system for precision spectroscopy, J. Hussels, C. Cheng, E.J. Salumbides, W. Ubachs, *Opt. Lett.* **45**, 5909 (2020)

4.1 Introduction

Frequency metrology experiments are generally performed with continuouswave lasers, allowing for long term stability and highly accurate readout of the center-frequency of narrow resonances, such as in optical clocks [90, 91]. However, in a variety of applications the use of pulsed lasers in precision experiments is required, for the necessity of power density, for triggered detection, in cases of multi-photon experiments, or at wavelengths in otherwise inaccessible regions. In some fundamental physics experiments lasers with a well-controllable pulse structure are prerequisite, such as in investigations of positronium [92], muonium [93], anti-protonic helium [94], and muonic hydrogen [9]. Moreover, laser pulses are required to reach the domain of the extreme ultraviolet, e.g. for the excitation of the He resonance at 58 nm [95]. Time-dependent gain in the lasers and amplifiers, as well as mode-pulling phenomena inside a laser cavity during build-up of the population inversion give rise to a non Fourier-transform limited pulse and to a time dependence of its central frequency, thus causing overall offsets in the frequency measurements. Such chirp effects have been investigated over the years in traveling-wave pulsed dye amplifiers [96, 97, 98, 99], in optical parametric oscillators [100], in an alexandrite laser [101], as well as in pulsed Titanium-Sapphire (Ti:Sa) lasers [102, 103, 54].

Here we report studies on chirp-reduction, measurement and compensation in nanosecond pulsed Ti:Sa lasers, by extending our passive mode-locking scheme [102] to an active scheme following a method explored by Hori and Dax [103]. Aim is to improve the accuracy limits and operate the Ti:Sa laser far away from the peak of the gain profile at a wavelength of 716 nm. The chosen wavelength allows for comparing the resulting absolute frequency uncertainty of actively chirp-compensated and frequency upconverted pulses to a molecular resonance in H_2 .

4.2 Experimental setup

The optical layout of the Ti:Sa laser system, shown in Fig. 4.1, consists of two main components: an oscillator cavity, in which pulses of about 80 ns duration are generated, and a bowtie multipass traveling-wave



Figure 4.1 – Overview of the setup. For explanation see main text.

amplifier, where the cavity output is further enhanced for subsequent efficient harmonic upconversion. The oscillator is built in the form of a stable ring cavity with a Brewster-cut Ti:Sa crystal inserted as the gain material. A Q-switched Nd:YAG pump laser operating at 10 Hz repetition rate produces pulses of 300 mJ at 532 nm, where the major part is used for the amplifier and a fraction of 10 mJ is split for pumping the oscillator. In the oscillator, the pump pulses are propagated through dichroic cavity mirrors and focused on the crystal from both sides to earn maximum volume utilization. Measurements with both an unseeded and an injection-seeded Nd:YAG laser were performed and no significant differences found.

The output of a continuous-wave (cw) Ti:Sa ring laser (Coherent MBR E-110) at a power of 200 mW is injected into the cavity as a seed. To suppress broadband super-fluorescent pulses produced by the Ti:Sa crystal at wavelengths of higher gain, the reflectivity of the cavity mirrors is designed to be 99.9% at 716 nm and less than 40% for wavelengths longer than 740 nm. The output coupler has a reflectivity of 98% (equivalent cavity finesse of about 300) at the desired wavelength (716 nm). Pulse energies of up to 1 mJ can be generated from the Ti:Sa oscillator and sent to the multi-pass amplifier. After 10 amplification steps through the crystal inside the amplifier, also pumped from both sides, the pulse energies are enhanced to about 40 mJ.

In order to generate controlled and stable pulses, the oscillator cavity is stabilized by locking to the seed light using a Hänsch-Couillaud (HC) locking method [104]. The locking system has a bandwidth of about 10 kHz and the feedback signal is sent to a fast piezoelectric ceramics (PZT) attached to one of the cavity mirrors. The frequency accuracy of the seed light is guaranteed by locking the cw Ti:Sa laser to an optical frequency comb referenced to a Cs atomic clock. The short-term (one second) frequency stability is a few tens of kHz, and the longterm relative accuracy of 10^{-12} is limited by Cs frequency standard. An acousto-optic modulator (AOM) is implemented in a double-pass scheme for reasons of scanning the cw laser frequency for spectroscopic acquisition and for generating a large enough frequency shift (690 MHz) for the chirp measurements.

4.3 Frequency pulling and chirp

When the Ti:Sa crystal inside the cavity is optically pumped, the refractive index of the crystal changes due to population inversion. This results in a fast change in optical path length inside the cavity, and thus the frequency of the generated pulses will undergo cavity mode pulling. During the pulse evolution the excited state population of the Ti:Sa decays, emitting 716 nm light, thus resulting in a continuous, and in first order linear change in the instantaneous frequency during the pulse, *i.e.* chirp. The settings of the Hänsch-Couillaud lock as well as the pump power can be manipulated to affect the pulling and chirp effects in the cavity, as was demonstrated in the 780-860 nm optimum gain region of Ti:Sa [102].

The chirp of the Ti:Sa oscillator-amplifier laser is measured by combining a fraction of the output pulses with cw-laser light, after propagating both beams through a single-mode fiber for spatial mode overlap. Their beat-note as detected on a fast photo detector connected to an 8 GHz bandwidth oscilloscope (sampling rate 40 Gsamples/s and 8 bits vertical) is shown in Fig. 4.2a. The time base of this Agilent infinitum VSA80000A oscilloscope is specified at 1 ppm peak, which for a signal of 690 MHz corresponds to 0.7 kHz. This time-base accuracy was verified in a calibration experiment be measuring a sinusoidal signal at this RF-frequency, and analyzing by the same software routine. The Fouriertransform of the signal, calculated in a computer after data transfer, shows two peaks in the frequency spectrum as plotted in Fig. 4.2b, where the low frequency peak is associated with the pulse envelope. The high frequency peak, associated with the 690 MHz shift in the double pass AOM, contains information on the chirp. Reversing the Fourier transformation separately for the two peaks generates the pulse envelope $\epsilon(t)$ and the phase evolution $\Phi(t)$ of the oscillatory function. A more detailed description of the computational procedures can be found in [102].

The instantaneous frequency offset $f_{\text{offset}}(t)$ at time t is obtained via:

$$f_{\text{offset}}(t) = \frac{1}{2\pi} \frac{d\Phi}{dt} - f_{\text{AOM}}$$
(4.1)

where any offset from 0 is due to the pulling and chirp effects. This $f_{\text{offset}}(t)$ is displayed in Fig. 4.2c for three specific cases (to be discussed below). The average offset is defined by

$$\langle f_{\text{offset}} \rangle = \int f_{\text{offset}}(t)w(t)dt$$
 (4.2)

with the pulse envelope $\epsilon(t)$ taken as a weight factor $w(t) = \epsilon(t)/(\int \epsilon(t)dt)$. The average slope of the chirp profile is defined by

$$\langle f_{\rm slope} \rangle = \int \frac{df_{\rm offset}}{dt}(t)w(t)dt$$
 (4.3)

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Figure 4.2 – a) Beat-note signal of a pulse combined with the unshifted cw light, displaying 69 periods of the beat over 100 ns, at an average of 58 samples/period. b) Fourier-transform of this pulse, showing the two components (see text). c) Dashed curve (red) represents the pulse envelope $\epsilon(t)$; Full curves represent the instantaneous offset without chirp control (blue), for unoptimized chirp control (orange), for optimized chirp control (black).

4.4 An EOM to change the frequency chirp

To manipulate and actively compensate the chirp effects, an Electro-Optic Modulator (EOM), made of a LiTaO₃-crystal, is placed inside the oscillator cavity. The optical end faces of the EOM are coated to obtain a transmission of 99.7% to minimize optical losses. The EOM is coated with a gold layer on the side faces, where the lower side is grounded and the upper side is connected to an electric amplifier, which has a slew rate of 2000 V/ μ s and is driven by an arbitrary waveform generator (AWG). For one pass through the EOM, the acquired phase is:

$$\Phi(t) = -\frac{\pi n_0^3 L}{\lambda d} \left[\left(\frac{n_e}{n_0}\right)^3 \gamma_{33} - \gamma_{13} \right] U(t)$$
(4.4)

where $n_o = 2.175$ and $n_e = 2.180$ are ordinary and extraordinary refractive indices of the EOM of length L = 16 mm and thickness d = 2.7 mm, and $\gamma_{33} = 33 \times 10^{-12}$ m/V and $\gamma_{13} = 8 \times 10^{-12}$ m/V the relevant electro-optical constants. This results in a phase shift of 0.017 radians per Volt per pass. The wavelength is set at $\lambda = 716$ nm and U(t) is the applied voltage.

The total frequency shift is produced by the cumulative effect of multiple cavity-roundtrips, involving mode-pulling of the cavity, chirp in the Ti:Sa crystal, counteracted by the phase effects imposed by the EOM. This bears the advantage that low voltages of 30-35 V are already sufficient to change the instantaneous frequency significantly. The chirp in the Ti:Sa amplifier is relatively small [102], in view of the limited number of passes (10 times), and the fact that the population inversion is produced some 200 ns before arrival of the oscillator pulse. During the amplification process this inversion, and hence the refractive index of the amplifier crystal remain constant, only decaying on the excited state time scale (3μ s). It is noted that all chirp measurements pertain to the combined oscillator-amplifier system.

The EOM is driven by an AWG, programmed to provide a sawtoothlike triangle function, starting with a linear drop of -34 V (after electrical amplification) during the initial 500 ns, followed by an instantaneous return to 0 V. The limited slew rate $(2000V/\mu s)$ of the amplifier delivers an exponentially increasing voltage over the EOM during return, resulting in an effective voltage profile as shown in Fig. 4.3b. This profile, imposed on the EOM, is well-suited to counteract the disturbances of the oscillator cavity. The linear decay in the initial phase affects the average frequency, therewith canceling the mode pulling effect and stabilizing the oscillator. The exponential return in the latter part is exploited to produce a fast voltage change over the EOM, therewith effectively canceling chirp effects. Different functions have been explored, but the fast exponential rise proved to be the most effective.

The timing of the voltage pattern, U(t), with respect to the Ti:Sa pulse, (Δt_{EOM}) , proved to be the most sensitive parameter for the chirp control. Fig. 4.3c and d show $\langle f_{\text{offset}} \rangle$ and $\langle f_{\text{slope}} \rangle$ of the measured chirp profile, using Eqs. (4.2) and (4.3), as a function of the timing of the voltage, where $\Delta t_{EOM} = 0$ corresponds to the situation where the dip in the voltage and the peak of the Ti:Sa pulse overlap.

In order to produce quantitative understanding of the chirp phenomena simulations were performed, resulting in the curves shown in Fig. 4.3c and d. The build-up time shown in Fig. 4.3a and the known round-trip time of 1.3 ns (optical path length of 39 cm) were used to determine the number of passes through the EOM for every point in the Ti:Sa pulse. Hence, steps of 1.3 ns were taken so that every point corresponds to a different number of round-trips. The added phase per pass is calculated with Eq. (4.4), where the input values for the voltage are obtained from the measured profiles in Fig. 4.3b. To determine the accumulated phase of each point over the laser pulse evolution, the added phase per pass is summed over all the passes through the EOM. Consequently, the change in instantaneous frequency over the Ti:Sa pulse can be determined using

$$f_{\rm EOM} = \frac{1}{2\pi} \frac{\Delta \Phi}{\Delta t},\tag{4.5}$$

where $\Delta \Phi$ is the difference in total accumulated phase between two sequential points ($\Delta t = 1.3$ ns). For a certain setting of the delay of the voltage pattern over the EOM, this results in a set of simulated chirp parameters, for offset and slope. However, these simulated chirp profiles are solely due to the EOM, and cannot be directly compared to the measurements, since the measurements also include chirp effects from both the Ti:Sa crystals in oscillator and multi-pass amplifier. For a true comparison the average offset and slope due to the Ti:Sa must be subtracted. These can be obtained from the measurements without antichirp (e.g. at very high EOM-delay). In this way the simulations of the chirp control effects reflect the observed data points for $\langle f_{\text{offset}} \rangle$ and $\langle f_{\text{slope}} \rangle$ as shown as the curves in Fig. 4.3c and d. Importantly, the optimum setting of the EOM voltage pulse, for obtaining $\langle f_{\text{offset}} \rangle \approx 0$ and $\langle f_{\text{slope}} \rangle \approx 0$ is determined, for use in the spectroscopic application.



Figure 4.3 – a) The Nd: YAG pump pulse followed by - a slightly asymmetric - Ti:Sa pulse, at a build-up time of 200 ns. The amplitudes of the two pulses are not to scale with respect to each other. b) Measured voltage evolution over the EOM at different time settings. c) Average slope of the chirp profile, as a function of the delay of the voltage pattern over the EOM. d) Average offset of the chirp profile, as a function of the delay of the voltage pattern over the EOM. The (square) colour coded data points in c) and d) correspond to the voltages settings in b) and the color-coded chirp profiles in Fig. 4.2c). The black squares correspond to the setting of optimized chirp control. The (grey) curves in c) and d) are from simulations using the voltage patterns in b) as input.

4.5 Spectroscopic use

For a laser spectroscopic precision measurement the laser output (at 716 nm) is frequency upconverted in two doubling stages, with BBO and KBBF crystals, leading to the generation of 179 nm radiation to drive the GK-X Q(1) transition of molecular hydrogen in a two-photon scheme. The vacuum-ultraviolet (VUV) output beam of up to 20 μ J per pulse is then intersected with a pulsed molecular hydrogen beam. After in-vacuum retro-reflection 2+1' two-photon enhanced ionization Doppler-free spectroscopy is achieved using counter-propagating VUVbeams in combination with a delayed ionization pulse [72, 105]. After driving the EOM the chirp is detected and analyzed, and thereupon the EOM control parameter (the timing) is manually set for optimal compensation of the chirp phenomena (setting indicated by the black squares in Fig. 4.3c and d). While performing a spectroscopic measurement, the EOM is fixed in this optimal condition, but nevertheless final residual chirp effects are detected for determining pulse-to-pulse variations, and to numerically correct transition frequencies for each pulse. Due to the frequency upconversion in the multiple doubling stages and the two-photon transition scheme, any residual instantaneous frequency offset in the fundamental pulse will be multiplied by 8, thus providing a sensitive test for our chirp control method.

Following the investigation by Hannemann et al. [102], in this experiment we have carefully chosen parameters of HC-lock setting, pump energy, and mirror reflectivities to reduce the cavity-pulling and chirpinduced frequency shifts. While the frequency chirp was previously only passively controlled, the intracavity EOM now allows for the active frequency chirp control. The highest spectral resolution for precision spectroscopy is achieved when using the longest pulse duration at zero frequency chirp, corresponding to a FT-limited spectral bandwidth. At 806 nm very good control of the frequency chirp can be obtained, since near the centre of the Ti:Sa bandwidth changes in the index of refraction are small [102]. However, the precision spectroscopy of H₂ [72, 105] requires the oscillator to work at 716 nm, which is on the edge of the Ti:Sa gain profile, leading to larger frequency pulling and chirp effects, as well as to larger pulse-to-pulse fluctuations. The active chirp compensation with the EOM eliminates cavity frequency pulling, since by counteracting the



Figure 4.4 – a) Allan Deviation of the average frequency offset over 5000 sequential pulses, measured with and without compensation for the pulling and chirp effects. b) Two-photon spectra of H_2 X-GK Q(1) with and without EOM-control and averaging over 50 shots. The residuals show that the spectrum with active chirp compensation is Gaussian, while the passive spectrum is asymmetric.

large refractive index change the cold cavity resonance condition is preserved even in the presence of the pump pulse. This leads to improved temporal stability of the pulses as shown by the Allan deviation of the frequency offset in Fig. 4.4a defined as:

$$\sigma_{\rm AD}(\tau)^2 = \frac{1}{2} < (\langle f_{n+1} \rangle - \langle f_n \rangle)^2 >$$
(4.6)

where $\langle f_n \rangle$ is the nth $\langle f_{\text{offset}} \rangle$ average over time τ . The Allan deviation is a factor of 3-5 lower when the active anti-chirp (black curve) is engaged. It is apparent in Fig. 4.4a, that 10-s averaging is the optimum, with the increase in instability at longer times probably limited by the locking electronics and pump pulse stability. The effect of the frequency chirp compensation on the spectral resolution, which is of main importance in precision spectroscopy, is shown in Fig. 4.4b. Note that the frequency (horizontal) axis in Fig. 4.4b includes a factor of 8 from the frequency upconversion and the two-photon excitation with respect to the fundamental Ti:Sa frequency. The full width at half maximum (FWHM) of the Gaussian fit is reduced from 49.8 MHz without compensation to 25.9 MHz when cancelling the linear frequency chirp (2 MHz/100 ns). Deconvolving for the lifetime of the GK (v = 1, J = 1) state, at 16.9(5) ns [83], we estimate 7.2(4) MHz for the bandwidth of the Ti:Sa laser for chirp compensated pulses. The difference in line centers of the two curves in Fig. 4.4b, is largely due to cw-pulse frequency offset compensation but also includes contributions from ac-Stark effects in the spectroscopic measurements [72, 105].

Figure 4.4a shows that the Allan deviation of the Ti:Sa output minimizes at 20 kHz (at 10 s), corresponding to a relative uncertainty of 5×10^{-11} . This can in principle be considered as an accuracy, since the chirp measurements were performed with respect to a cw-laser locked to Cs-frequency standard with an accuracy of $\sim 10^{-12}$. In addition, we performed stability measurements of the pulsed output referencing against a molecular resonance (H₂, X-GK Q(1) line in two-photon excitation [72]), where each data point was averaged over 50 laser shots (at 10 Hz operation). It is noted that in addition to the active frequency control, the residual chirp was measured for every laser shot for (outof-loop) numerical compensation of the frequency. This assessment of the chirp yields an upper limit to the absolute accuracy of 1.5×10^{-10} . The latter result improves a previous experiment with an intra-cavity EOMs [103] by a factor of five, and the passively compensated Ti:Sa oscillator-amplifier system [102] by a factor of 15.

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CHAPTER 5

Precision measurement of the GK(1,2) - X(0,0) transition in D_2

5.1 Introduction

In Chapters 2 and 3 the experimental values of the dissociation energies of ortho- and para- H_2 were determined and compared to *ab initio* calculations. A logical extension of this is to test theory with the dissociation energy of D_2 . As discussed in Chapter 1, this provides for a different test of theory, as the diverse terms (adiabatic, non-adiabatic, relativistic, etc.) have a distinct dependence on the masses of the two atoms. The latest experimental value of $D_0(D_2)=36748.36286(68) \text{ cm}^{-1}$ [13], determined in 2010, agreed well with the most accurate theoretical value known at that time, $D_0(D_2)=36748.3633(9) \text{ cm}^{-1}$ [29]. In recent years, the calculations from theory were improved and a new theoretical value, with more than an order of magnitude improved accuracy, of $D_0(D_2) = 36748.362342(26) \text{ cm}^{-1}$ was published [106]. Thus the latest experimental value is more than an order of magnitude less accurate than the latest theoretical value. This encouraged us to improve the experimental value as well, allowing a comparison between experiment and theory and test QED (and by extension the Standard Model) on a higher level of accuracy, as discussed in Chapter 1.

In order to improve the experimental value of $D_0(D_2)$, we use the thermochemical cycle (see Eq. (1.6)) that links $E_i(D_2)$ to $D_0(D_2)$. The ionization energy of D_2 is determined by combing a precision measurement on the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition with an accurate value of the ionization energy of the $GK^1\Sigma_g^+$ state.

In H₂, the GK¹ $\Sigma_g^+(1,2)$ - X¹ $\tilde{\Sigma}_g^+(0,0)$ transition turned out to be about a 100 times stronger than the GK¹ $\Sigma_g^+(1,0)$ - X¹ $\Sigma_g^+(0,0)$ transition (see Chapter 3). This is attributed to the strong mixing between GK ¹ Σ_g^+ states with non-zero rotational quantum number N and the nearby I¹ Π_g state [82]. This advantageous mixing of II-character into the GK¹ Σ_g^+ state does not occur for N = 0 states, which is the reason that the Q(0) two-photon transition remains so very weak. In H₂, the II-character of the excited state enhances the transition probability, which is attributed to a wider class of intermediate states contributing to the transition rate [107]. The same is true in D₂, hence we measured the GK¹ $\Sigma_g^+(1,2)$ -X¹ $\Sigma_g^+(0,0)$ transition.

5.2 Experimental setup

The experimental setup used to measure the $GK^1\Sigma^+_a(1,2)$ - $X^1\Sigma^+_a(0,0)$ transition in D_2 is the same as used in our previous work, see Chapters 2, 3 and 4, with the notable exception that a new pulsed valve, built at ETH Zürich,¹ was installed. The operation and characteristics of this pulsed valve are described in research papers by the ETH-team [108, 50]. Both the new valve and the previously used valve exploit the effect of supersonic expansion. In a supersonic expansion a gas at high pressure (3 to 9 bar in our case) is released into vacuum. In this process, the energy in the system is converted into forward velocity, resulting in a decrease of the translational temperature of the gas in the moving frame of the molecular beam [53]. The rotational and vibrational temperatures are also decreased, resulting in our case in hydrogen beams where mainly the ortho- and para-ground states are populated. The new valve provides two advantages with respect to the valve (General Value Series 9) used in the previous studies for H_2 . Firstly, it can be cooled using liquid nitrogen therewith causing a reduced velocity for the molecules in the outflowing beam. By comparing measurements

¹We thank Prof. F. Merkt of the ETH Zürich for making available a copy of the pulsed molecular beam source and the electronic driver system developed in his laboratory.

at different valve temperatures the residual Doppler effect is directly assessed. This method is both more reliable and results in more signal than the method discussed in Chapters 2 and 3. Secondly, due to the fast response and short opening time (20 μ s) of the valve, the velocity of the molecules is determined more accurately.

In Fig. (5.1) a schematic drawing of the molecular beam setup and detection system is shown. The setup consists of two differentially pumped vacuum chambers. A skimmer (Beam dynamics, type II, 8 mm), mounted 14 cm behind the valve, is used to select the most intense and coldest part of the beam. The aperture of the skimmer is relatively large, which increases the amount of molecules in the interaction zone, and allows the use of relatively high pressures (up to 9 bar at room temperature) while avoiding skimmer interference [109].

At a distance 27 cm behind the valve, the molecular beam is crossed with a VUV laser beam that excites the molecules to the $GK^1\Sigma_g^+(1,2)$ state and a second laser beam with a wavelength of 723 to 793 nm to selectively ionise molecules in the $GK^1\Sigma_g^+$ state. The Ti:Sa oscillatoramplifier system used to generate high intensity 714 nm-pulses which are up-converted to the VUV using a BBO and KBBF crystal is described in detail in Chapters 2, 3 and 4.

The two-photon transition to the $GK^1\Sigma_g^+$ -state of D_2 is induced by counter-propagating laser beams. If the two beams are exactly counterpropagating to each other, the recorded transition frequency does not depend on the velocity of the molecules. In general a molecule will have a finite velocity in the transverse direction, hence the frequency of one of the photons will be red-shifted in the reference frame of the molecule, while the other one will be blue-shifted by the same amount. Thus the transition is in first order Doppler-free. In practise there will be a small angle between the two laser beams, resulting a small dependence of the measured frequency on the molecular beam velocity. This residual firstorder Doppler effect is measured by determining the transition frequency at different velocities, as will be discussed in the next section.

To accurately determine the frequency of the $GK^1\Sigma_g^+(1,2) - X^1\Sigma_g^+(0,0)$ transition, the frequency of the VUV laser is stabilised and determined as described in Chapter 1. The chirp is cancelled, and any residual chirp is measured and compensated for shot-by-shot, as described in Chapter 4. A Pulsed Dye Laser (PDL) is used to selectively ionise



Figure 5.1 – Cross section of the vacuum chamber, not to scale. A molecular beam of D_2 originates from a pulsed valve, which can be cooled by liquid nitrogen. After a supersonic expansion the beam is skimmed. In the interaction zone, which is indicated by the coloured circles representing the VUV and ionization beam, the molecules are excited from their ground state to the GK state if the VUV frequency is on resonance. The molecules in the GK state are selectively ionised. The D_2^+ ions are pushed upwards by a pulsed electric field from the repeller and extractor plates. The ions that reach the MCP generate electrons, which fly to the phosphor plate to generate photons. The photons are detected by the PMT. The signal from the PMT is recorded by a 1-GHz-bandwith oscilloscope. The base pressure in the source chamber is below 10^{-7} mbar, the operating pressure is 4×10^{-6} mbar, the pressure in the interaction chamber is below 10^{-6} mbar.

the molecules from the GK-state with a single photon. The D_2^+ ions are extracted using ion optics (a repeller and an extractor plate) as in [52]. The ions are detected using a cascade of a pulsed microchannel plate (MCP), a phosphor plate and a photon multiplier tube (PMT) as shown in Fig. (5.1). The signal from the PMT is recorded and integrated by a 1-GHz-bandwith oscilloscope. The frequency of the VUV laser is changed using the double-pass-AOM, as described in Chapter 1, with steps of 1.6 MHz to scan over the transition. After every step, typically 50 shots are measured at a rate of 10 Hz. The read-out from the oscilloscope as well as the residual chirp of these 50 shots are averaged and result in one data point. Typically, 1-10 ions per shot are detected at spectrum of the $GK^1\Sigma_g^+(1,2) - X^1\Sigma_g^+(0,0)$ transition in D₂ emerges, as shown in Fig. 5.2. Note that the baseline is not at zero due to the Doppler-broadened pedestal and ionization of background gas.

The width of the $GK^1\Sigma_g^+(1,2) - X^1\Sigma_g^+(0,0)$ spectral line (FWHM ~ 30 MHz) is mainly determined by the Fourier-transform limit of the 25 ns VUV pulses and the lifetime (18 ns [110]) of the GK state. The Fourier-transform of the Gaussian time profile of the pulses result in a Gaussian distribution of the frequencies in the bandwidth of the laser (see Chapter 4). The total contribution of the bandwidth from the two photon absorption of the incoming and back-reflected VUV pulse to the linewidth of the spectrum is 29 MHz. The contribution to the linewidth of the lifetime of the GK-state is Lorentzian, and is calculated to be 8.8 MHz. The contribution to the linewidth of the limited transit time of molecules through the interaction zone is Gaussian and is calculated to be 3 MHz. We found that fitting either a Gaussian function or a Voigt function (a convolution of a Gaussian and a Lorentzian function) to the profile resulted in identical linewidths, due to the small Lorentzian contribution to the linewidth. Hence we use Gaussian fits.

The molecules in the GK-state are selectively ionised with a single photon, originating from the ionization laser: a Pulsed Dye Laser (Spectra Physics PDL 2) which is pumped by a Nd:YAG laser. The frequency of the emitted light can be changed by tuning a grating in the oscillator. The intensity of the emitted light depends on the gain curve of the dye. Using either Styryl-7 or Styryl-11 we were able to generate laser light between 723 nm and 793 nm. Most signal is obtained when the



Figure 5.2 – Example of a scan of the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ twophoton transition in D_2 , not compensated for Doppler or AC-Stark effects. Every point is the average of the signal resulting from 50 chirpcompensated shots. The red line is a Gaussian fit of the data, where each data point is (instrumentally) weighted with the reciprocal of the square of the error in the data point. The frequency uncertainty in the data points (~ 100 kHz) is not visible at this scale.

wavelength of the ionization laser is in resonance with a transition to a so-called auto-ionising state. These states are Rydberg states that converge to an excited state in the ion and lie above the lowest ionization energy of the molecule. These states are strongly mixed with the continuum and ionise immediately [111, 112].

Scanning the ionization laser while the VUV laser is on resonance with the GK¹ $\Sigma_g^+(1,2)$ - X¹ $\Sigma_g^+(0,0)$ transition results in the spectra shown in Fig. 5.3. These spectra show multiple auto-ionising resonances corresponding to different Rydberg series converging to different states of the D₂⁺ molecular ion. The lowest Rydberg series converges to the ($v^+=0$, $J^+=0$) ground state of D₂⁺, which corresponds to the lowest ionization energy of D₂. States above this threshold auto-ionise by mixing with the continuum state of the (D₂⁺(0,0) + e⁻) system. The states which are slightly below this threshold are ionised by electric-field ionization. Note that the observed signal strength depends both on the strength of



Figure 5.3 – Auto-ionization spectra (averaged over 50 shots) of the $GK^1\Sigma_g^+(1,2)$ state. The asterisks (*) in (a) and (b) indicate the autoionization resonances used in measurement campaigns 1 and 2 respectively. Coloured diamonds indicate resonances predicted by MQDT calculations. States of different Rydberg series are colour-coded as indicated in the figure. The black (v⁺=0, J⁺=0) series in (b) converges to the red vertical line, which indicates the ionization energy (E_i) of the D₂ molecule. 59

the auto-ionising resonance and the power of the laser, which varies on the order of 20% over the scan. Two measurement campaigns were performed using auto-ionising resonance at high energy $(13740(1) \text{ cm}^{-1})$ and one near the ionization threshold at $12645(1)\text{ cm}^{-1}$, indicated by an asterisk in Fig. 5.3a and b, respectively. In order to suppress the AC-Stark effect of the ionization laser, we usually delay the ionization laser with respect to the VUV laser. This, however, comes at the cost of reduced signal. We found that the AC-Stark effect due to the ionization laser is smaller at ionising resonances near the ionization threshold. So in measurements using the auto-ionization resonance indicated in Fig. 5.3b, the two pulses could be overlapped in time, resulting in increased signal strength.

5.3 Systematic effects

There are four main sources of systematic offsets on the determined frequency of the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ two-photon resonance: (i) frequency chirp is a (time dependent) frequency offset between the pulsed laser used for exciting the transition and the cw laser that is used a seed for this pulsed laser. (ii) AC-Stark effects, the lasers used for exciting the transition and ionising the molecule induce an intensity dependent shift of the relevant energy levels. (iii) Doppler effects, the fact that molecules are moving with respect to the lab frame give rise to first- and second-order Doppler effects. (iv) Hyperfine structure, the nuclear spins of the deuterons give rise to hyperfine splittings that are unresolved in our measurements. These four effects are dealt with at different levels of the measurement procedure, as will be discussed in the next paragraph. Note that the recoil effect does not give a systematic offset, as the momentum of the molecules does not change upon absorbing two photons from counter-propagating laser beams.

A frequency scan of the VUV laser is performed at a certain velocity of the molecules and intensity of the lasers, from which a line centre is determined by fitting a Gaussian, as discussed in the previous section. For every shot during the scan the residual chirp is measured and compensated for, see Chapter 4 for a full description of these procedures. In order to assess the AC-Stark effects the transition frequency is measured as a function of the intensity of the VUV or ionization laser pulses. These measurements are performed on the same day to ensure that the alignment of the VUV laser, and hence the residual first-order Doppler shift, is constant. In order to assess the residual first-order Doppler effect measurements are performed at different velocities by cooling the valve. Transition frequencies, compensated for the AC-Stark shifts and the calculated second-order (relativistic) Doppler shift, are plotted as a function of velocity and extrapolated to zero velocity. Measurements of the AC-Stark effects and the residual first-order Doppler effect are presented and discussed in detail in the next subsections.

Finally, there can be an offset due to the hyperfine structure in both the ground state and the excited state. As D_2 consists of two bosons with nuclear spin I=1, the total nuclear spin of the molecule I=0, 1 or 2. Since I=0 and I=2 both have a symmetric spin wavefunction, and the total wavefunction of the (bosonic) molecule needs to be symmetric, they both couple to states with a symmetric angular momentum wavefunction (J is even). So the J=0 state is coupled to both an I=0 and I=2 nuclear spin. None of the terms in the hyperfine Hamiltonian for D_2 affect the ground rotational level, however, the J=0 levels are weakly coupled with the J=2 levels, which leads to two hyperfine levels, separated by the energy difference of the order of mHz [113], negligibly small compared to our accuracy.

The hyperfine structure in the $\mathrm{GK}^1\Sigma_g^+(1,2)$ state can still be larger due to the non-zero J. We can estimate the magnitude of the splitting in this state by comparing it to the splitting in the $\mathrm{X}^1\Sigma_g^+(0,2)$, which, according to Jóźwiak et al., is more than a factor three smaller than the hyperfine structure in the $\mathrm{X}^1\Sigma_g^+(0,1)$ state of H₂ [113]. Extrapolating this to the $\mathrm{GK}^1\Sigma_g^+(1,2)$ state in D₂, the uncertainty due to the hyperfine structure is estimated to be below 100 kHz, the uncertainty due to the hyperfine structure measured in the $\mathrm{GK}^1\Sigma_g^+(1,1)$ state in H₂ at ETH Zürich (see Chapter 2). In the near future, the hyperfine splittings in the $\mathrm{GK}^1\Sigma_g^+(1,2)$ state of D₂ will be determined at ETH Zürich, which will allow for making a more reliable estimate.

5.3.1 AC-Stark effects

Both the ionization laser and the VUV laser pulses give rise to an AC-Stark effect, that scale with the intensity of the laser. These AC-Stark effects are reduced by measuring the transition at the lowest power of the pulses for which there is still sufficient signal. The AC-Stark effect of the ionization laser is further reduced by introducing a delay between the ionization pulse and the VUV pulse. Ideally, this delay should be long compared to the pulse duration of the VUV laser (25 ns). However, as the lifetime of the $GK^1\Sigma_g^+(v=1)$ state is only 18 ns [110], this would result in an unacceptably large decrease of signal. In the first measurement campaign, where we used an auto-ionising resonance at 13740(1) cm⁻¹, far above the lowest ionization energy, the delay is set at 30 ns. In the second measurement campaign the wavelength of the ionization laser was tuned to 12645(1) cm⁻¹, near the ionization threshold, which resulted in a much smaller AC-Stark effect. Hence, the delay between the ionization laser and the VUV laser could be set to zero.

The remaining AC-Stark effects are compensated by measuring the transition frequency as a function of laser power and extrapolating to zero power. The results of both measurement campaigns for the VUV laser are shown in Fig. 5.4. During a measurement campaign, the alignment of the UV-beam and the orientation of the KBBF-crystal are kept constant at optimal phase-matching angle to keep the efficiency of the KBBF constant. Before each measurement session (which corresponds to one day of measurements) the alignment of the back-reflected VUV beam is reoptimised, which can induce small changes in the residual first-order Doppler effect. The different colours in Fig. 5.4 represent measurements done on different days, resulting in different offsets.

Since the VUV is generated inside the vacuum chamber, the power of the VUV can not be measured directly. To bypass this issue, the change in frequency is plotted versus power of the 357 nm pulse (P_b) squared, which is linear to the VUV power. At optimal conditions, 1 mJ per pulse of UV (357 nm) corresponds to approximately 1 μ J per pulse of VUV (179 nm), which, with a pulse duration of 25 ns FWHM and a beam diameter of 0.5 mm, corresponds to an intensity of 20 kW/cm². The slope of the curves measured on different days are the same within the measurement error. This slope is used to calculate the AC-Stark effect



Figure 5.4 – AC-Stark effect due to the VUV laser pulse in a) measurement campaign 1 and b) measurement campaign 2. Every point represents the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition frequency determined from a single scan of the VUV laser. Every colour represents a different alignment of the back-reflected VUV laser, with a different offset due to the residual Doppler effect. The data points are fitted with a linear function.

at a given laser power, and correct for it. With $P_b=1.5$ mJ (used in both measurement campaigns), the AC-Stark effect of the VUV laser is 260 ± 240 kHz during measurement campaign 1 and 480 ± 240 kHz during measurement campaign 2.

In Fig. 5.5 similar measurements for the AC-Stark effect due the ionization laser are shown. With a pulse duration of 8 ns FWHM and a beam diameter of 6 mm, 1 mJ per pulse of the ionization laser (P_{ion}) corresponds to an intensity of 350 kW/cm². With $P_{ion}=0.08$ mJ per pulse in campaign 1 and $P_{ion}=0.1$ mJ per pulse in campaign 2, the AC-Stark effect of the ionization laser is -75±35 kHz and 78±100 kHz, respectively.



Figure 5.5 – AC-Stark effect due to the ionization laser pulse in a) measurement campaign 1 and b) measurement campaign 2. Every point represents the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition frequency determined from a single scan of the VUV laser. Every colour represents a different alignment of the back-reflected VUV laser, with a different offset due to the residual Doppler effect. The data points are fitted with a linear function.

5.3.2 Doppler effects

As explained in the previous section, the measured transition frequency is not affected by the first-order Doppler shift, provided that the incoming and back-reflected VUV beams are exactly counter-propagating. However, if there is a (small) angle between the two beams a residual first-order Doppler shift arises. To reduce this residual Doppler shift, we make sure that the incoming and reflected VUV pulse both go through a 0.5 mm pinhole at a distance of 80 cm of the mirror, as show in Fig. 5.6. In this way, the angle between the counter-propagating beams is constrained to 0.6 mrad, limiting the residual Doppler shift to 6 MHz. This residual Doppler shift is compensated by measuring the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition frequency as a function of velocity of the molecular beam and extrapolating to zero velocity. The velocity of the molecules was changed by changing the temperature of the pulsed valve and changing the delay time between the trigger that opens the valve and the trigger of the pulsed lasers (t_{trig}) .



Figure 5.6 – Schematic overview of the interaction zone of the D_2 molecular beam with the VUV laser beam as described in the text. A small residual Doppler shift may arise when the angle between the incoming and reflected beam (θ) is non-zero.

Fig. 5.7 shows the observed ion signal as a function of t_{trig} with the frequency of the VUV laser set at the centre of the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition and the ionization laser set at the peak of the auto-ionization resonance at 13740 cm⁻¹. For the measurements shown in Fig. 5.7a the valve was kept at room temperature, while for the measurements shown in Fig. 5.7b the valve was cooled down to 77 K using liquid N₂. As the opening time of the valve is short compared to time it takes for the molecules to fly to the interaction zone, the observed density profiles mainly reflect the velocity distribution of the molecular beam. A detailed study of the valve at ETH Zürich showed that the response time of the valve (t_{resp}) is 30 μ s, independent of the temperature of the valve and backing pressure. Knowing the distance between the valve and the interaction zone (l = 27 cm), we can calculate the mean velocity (v)corresponding to a certain t_{trig} using the following expression:

$$v = \frac{l}{t_{trig} - t_{resp}}.$$
(5.1)

The velocity calculated in this way is given in the top axes of Fig. 5.7. The average velocity of the beam decreases from about 1700 m/s to 850 m/s upon cooling the valve, while the intensity of the molecular beam
increases about a factor of two. As observed, the density profile recorded at room temperature has a near Gaussian profile, while the density profile recorded at low temperature displays a double peak structure which is attributed to collisions at the skimmer [109]. Note that at 77 K the backing pressure was reduced from 9 to 7 bar, in later measurements the backing pressure was reduced even further. In the following, at room temperature the trigger time was set near the peak of the density profile to maximise the signal. For measurements at 77 K, the trigger time was set to be slightly earlier in the beam, to select the, more abundant, faster molecules, which are not affected by skimmer interference.



Figure 5.7 – Observed density of the molecular beam in the interaction zone as a function of the delay time with the value at a temperature of a) 293 K and b) 77 K. In the top axes the delay time is converted to velocity using Eq. 5.1.

Fig. 5.8 shows the extracted transition frequencies as a function of velocity. The different colours in Fig. 5.8 represent measurements performed on different days, with a different alignment of the back-reflected VUV laser beam, resulting in different slopes. Every data point in Fig. 5.8 results from the average of 5 to 10 frequency scans. Before extrapolating the Doppler free value, every scan was compensated for the AC-Stark effects measured in their respective measurement campaign and the relativistic Doppler shift. The relativistic Doppler shift is

given by

$$f_r = \frac{f_s}{\sqrt{1 - \left(\frac{v}{c}\right)^2}},\tag{5.2}$$

where f_r is the frequency of the VUV laser as seen by the D₂ molecules, f_s the measured frequency, v the velocity of the molecules and c the speed of light, resulting in a shift of about 50 kHz at 293 K and 20 kHz at 77 K. The uncertainty due to the relativistic (second-order) Doppler effect (30 kHz) and the uncertainties due to the AC-Stark effects is added to the final uncertainty.



Figure 5.8 – Transition frequency as a function of velocity. Every data point results from the average of five to ten AC-Stark- and second-order Doppler compensated scans. Every line is the linear fit for a different alignment of the reflected VUV beam. Solid lines result from measurement campaign 1, dashed lines from measurement campaign 2. By extrapolating these lines to zero velocity the Doppler free $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_q^+(0,0)$ transition frequency is found.



Figure 5.9 – Final values of the 12 measurements sessions, corrected for the residual first- and second-order Doppler effects, AC-Stark effects and chirp effect, of the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition frequency in D_2 at 12 different alignments of the VUV laser. In black is the first measurement campaign, in blue the second measurement campaign. The dotted line at 3360646104.46 MHz is the average value. The blue bar is the standard error of the mean (0.35 MHz). The red lines indicate the standard deviation (1 MHz).

5.4 Results and Discussion

In this section, the final value for the GK-X transition obtained from all data taken during the measurement campaigns will be presented. Combined with the ionization energy of the GK-state measured at ETH Zürich this results in accurate values for the ionization and dissociation energy of the D_2 molecule. In Fig. 5.9 the extrapolated Doppler- and AC-Stark- free values of the transition frequency are shown for each day that data was taken. Each point in Fig. 5.9 results from the extrapolation of the measurement shown in Fig. 5.8, which are already compensated for the relevant (calculated) second-order Doppler effect and the (measured) AC-Stark effects of the ionization and VUV pulses. The black and blue data points result from measurement campaign 1 and 2, respectively.

The 12 Doppler- and AC-Stark- free data points have a standard deviation of 1 MHz, indicated by the red lines in Fig. 5.9. The average of the 12 data points is 3360646104.46 MHz, with a standard error of the (weighted) mean of 0.35 MHz, indicated by the blue bar. We use the standard error of the mean as the statistical uncertainty in the transition frequency since all systematic effects are compensated for and the extrapolated values are randomly distributed ($\chi_r^2 = 0.94$). This error contains the statistical error as well as the error due to the (measured and compensated for) chirp and residual first-order Doppler effect. Apart from this error, the error in both AC-Stark measurements, the secondorder Doppler calculation and the estimated error due to the hyperfine structure (as discussed in previous section) are accounted for in final error budget given in Table 5.1. This results in a final accuracy of 0.45 MHz.

It is instructive to compare the final error of this measurement with those from our earlier measurement on H_2 in Chapters 2 and 3. The measurement in D_2 is slightly more accurate, mainly due to the improved velocity determination by making use of the cooling capabilities of the pulsed valve.

In order to determine a new value of the ionization energy of the ground state of D₂, our value of the $\mathrm{GK}^1\Sigma_g^+(1,2)$ - $\mathrm{X}^1\Sigma_g^+(0,0)$ transition energy is combined with the ionization energy of the $\mathrm{GK}^1\Sigma_g^+(1,2)$ state measured at ETH Zürich. The ETH-Zürich team determined the energy interval between the $\mathrm{GK}^1\Sigma_g^+(1,2)$ state and the $\mathrm{GK}^1\Sigma_g^+(0,2)$ state by recording the transitions from both these states to a common low-*n* Rydberg state. Subsequently, the intervals between the $\mathrm{GK}^1\Sigma_g^+(0,2)$ state and several $nf0_3(0)$ Rydberg states with *n* between 40 and 70 were measured using frequency-comb calibrated cw radiation. The $\mathrm{GK}^1\Sigma_g^+(0,2)$ was used because it has a longer lifetime (~ 360 ns [110]) than the $\mathrm{GK}^1\Sigma_q^+(1,2)$ state which allows for a more accurate determination of the

Table 5.1 – Error budget of the measurement of the $GK^1\Sigma_g^+(1,2)$ – $X^1\Sigma_g^+(0,0)$ transition in D_2 . The statistical error of 0.35 MHz also contains the uncertainty of the first-order Doppler extrapolation and the chirp measurements. The uncertainty due to the second-order Doppler effect originates from the calculations discussed in the text. The uncertainty due to the measurements of the AC-Stark effects were different in the two measurement campaigns. The largest value of these two uncertainties is adopted. The uncertainty due to the hyperfine structure is extrapolated from the uncertainty due to the hyperfine structure in the $GK^1\Sigma_g^+(1,1)$ in H_2 as discussed in the previous section. The final error in the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_q^+(0,0)$ transition frequency in D_2 is 0.45 MHz.

Measured frequency	$3360646104.46 \ \mathrm{MHz}$
Effect	Uncertainty
Residual 1^{st} order Doppler and Chirp	$(350 \text{ kHz})_{stat}$
2^{nd} order Doppler	$30 \mathrm{~kHz}$
AC-Stark ionization laser	100 kHz
AC-Stark VUV laser	240 kHz
Hyperfine structure	100 kHz
Final frequency	3360646104.46(45) MHz

line centres. The ionization energy of the $GK^1\Sigma_g^+(0,2)$ state in D_2 was then determined by extrapolating the $nf0_3(0)$ Rydberg-series to the ionization limit using multichannel quantum defect theory (MQDT). The procedures of these measurements and MQDT calculations are similar to those performed in H₂, as discussed in Chapter 3 and in the works of Beyer et al. and Hoelsch et al. [50, 83].

The values of the $GK^1\Sigma_g^+(0,2)$ - $GK^1\Sigma_g^+(1,2)$ energy interval and the ionization energy of the $GK^1\Sigma_g^+(0,2)$ state are collected in Table 5.2. By combining these values with our new value of GK-X transition frequency, the ionization energy (E_I) of the D₂ molecule is found to be 124745.393737(21) cm⁻¹. Finally, using Eq. 1.6 and the values for $E_I(D)$ and $E_I(D_2^+)$ from Table 5.2, the dissociation energy (D_0) of the rovibrational ground state of D₂ is determined to be 36748.362280(21) cm⁻¹. This value is consistent with the previously best experimental value, $D_0 = 36748.36286(68)$ cm⁻¹ [13], but 32 times more accurate. The deviation between the latest theoretical value, $D_0 = 36748.362342(26)$ cm⁻¹[106], and our experimental value of D_0 is -0.000062(34) cm⁻¹, which corresponds to a 1.8 σ difference.

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Value (cm^{-1}) Ref.	112099.087712(15) This work	:) 333.038776(9) ETH Zürich	0) $12979.344801(10)$ ETH Zürich + MQDT	124745.393737(21) This work	124745.39407(58) $[13]$	-0.00033(58)	109708.61455294(17)[25]	131420.19764920(75)[24]	36748.362280(21) This work	36748.362342(26) $[106]$	-0.00062(34)
Energy level interval	X(v = 0, N = 0) - GK(v = 1, N = 2)	GK(v = 0, N = 2) - GK(v = 1, N = 2)	$GK(v = 0, N = 2) - X^+(v^+ = 0, N^+ = 0)$	$E_i(\mathrm{D}_2)$	$E_i(\mathrm{D}_2)$	Change of IP	$E_i(D)$	$E_i(\mathrm{D}^+_2)$	$D_0(\overline{\mathrm{D}}_2)$	$D_0(\mathrm{D}_2)$	obs-calc
	(1)	(2)	(3)	(4) = (1) - (2) + (3)	(5)	(4)-(5)	(9)	(2)	$(8) = (4) + (7) - 2 \times (6)$	(6)	(8)-(9)

CHAPTER 6

Precision measurement of the GK(1,2)-X(0,0) transition in HD

6.1 Introduction

In Chapters 2, 3 and 5 the experimental values of the dissociation energies of H_2 and D_2 were determined and compared to *ab initio* calculations. A further extension of this is to test theory with the dissociation energy of HD. As discussed in Chapters 1 and 5, this provides for a different test of theory, as the diverse terms (adiabatic, non-adiabatic, relativistic, etc.) have a distinct dependence on the masses of the two atoms. In contrast to H_2 and D_2 , HD is a hetero-nuclear molecule, which causes the breakdown of g-u symmetry [114]. The currently most accurate experimental value of $D_0(\text{HD}) = 36405.78366(36) \text{ cm}^{-1}$ [20], determined in 2010, agreed well with the most accurate theoretical value calculated independently at the same time, $D_0(\text{HD}) = 36405.7828(10)$ $\rm cm^{-1}$ [115]. However, meanwhile the calculations from theory are improved and a new theoretical value, with a more than order of magnitude improved accuracy, of $D_0(\text{HD}) = 36405.782477(26) \text{ cm}^{-1}$ was published [106], which deviates by 3.3 σ from the experimental value. This discrepancy encouraged us to improve the experimental value as well, allowing a comparison between experiment and theory and test QED (and by extension the Standard Model) on a higher level of accuracy, as discussed in Chapter 1.

In order to improve the experimental value of $D_0(HD)$, we will use the

thermochemical cycle (see Eq. (1.5)), that links $E_i(\text{HD})$ to $D_0(\text{HD})$. In this chapter, the measurement of the $\text{GK}^1\Sigma_g^+(1,2) - \text{X}^1\Sigma_g^+(0,0)$ transition frequency in HD is presented. An experiment to measure the ionization energy of the $\text{GK}^1\Sigma_g^+(1,2)$ state of HD is planned at ETH Zürich, once the result of this experiment is available it will be combined with our measurement to determine an improved value for the ionization energy of the HD molecule $(E_i(\text{HD}))$, and thus the dissociation energy of the HD molecule $(D_0(\text{HD}))$.

The experimental procedure discussed in this chapter is similar to the experimental procedure applied during the second measurement campaign to measure the $GK^1\Sigma_g^+(1,2) - X^1\Sigma_g^+(0,0)$ transition frequency in D_2 , as discussed in Chapter 5. Therefore, I will discuss only the aspects of the experiment that deviate from the experiment on D_2 . For a more detailed explanation of the other features of this measurement the reader is referred to previous chapters.

6.2 Experimental setup

The HD molecular beam expands from the Zürich valve, working under the same conditions as in Chapter 5. The HD gas originates from a bottle which was specified to contain 98% HD. However, during the 3 years it was kept in storage, the HD molecules reacted with each other, resulting in a mixture of 25% H₂, 25% D₂ and 50% HD. This does not affect our measurements, as the ion detection scheme is mass selective.

To perform a Doppler-free two-photon transition from the $X^1\Sigma_g^+(0,0)$ to the $GK^1\Sigma_g^+(1,2)$ state, pulses of 178.8 nm light are generated using our special KBBF crystal, in the same way as described in Chapters 1,2,3 and 5. The frequency of the VUV laser is stabilised and measured as described in Chapters 1 and 4. The molecules in the $GK^1\Sigma_g^+(1,2)$ state are selectively ionised and detected as described in Chapter 5.

In Fig. 6.1, an example of a scan of the VUV frequency is shown, together with a Gaussian fit. The linewidth of the spectrum (FWHM \sim 30 MHz) is mainly determined by the linewidth of the laser.

As in Chapter 5, the signal was enhanced by tuning the wavelength of the ionization laser to an auto-ionization resonance. Scanning the ionization laser while the VUV laser is on resonance with the $GK^1\Sigma_a^+(1,2)$



Figure 6.1 – Example of a scan of the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition in HD, not compensated for Doppler or AC-Stark effects. Every point is the average of the signal resulting from 50 chirp-compensated shots. The red line is a Gaussian fit of the data, where each data point is (instrumentally) weighted with the reciprocal of the square of the error in the data point. The frequency uncertainty in the data points (~ 100 kHz) is not visible at this scale.

- $X^1\Sigma_g^+(0,0)$ transition results in the spectrum shown in Fig. 6.2. By choosing an auto-ionising resonance just above the ionization limit, the AC-Stark effect due to the ionization laser was reduced, so the VUV pulse and ionization pulse are overlapped in time. The auto-ionising resonance used in the measurements (at 12641(1) cm⁻¹) is indicated by an asterisk in Fig. 6.2.

6.3 Systematic effects

There are four main sources of systematic offsets on the determined frequency of the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ two-photon resonance: (i) frequency chirp, (ii) AC-Stark effects, (iii) Doppler effects and (iv) Hyper-



Figure 6.2 – Auto-ionization spectrum (averaged over 50 shots) of the $GK^1\Sigma_g^+(1,2)$ state in HD. The asterisk (*) indicates the auto-ionization resonance used in the measurements. Coloured diamonds indicate resonances predicted by MQDT calculations. States of different Rydberg series are colour-coded as indicated in the figure. The black $(v^+=0, J^+=0)$ series converges to the red vertical line, which indicates the ionization energy (E_i) of the HD molecule.

fine structure. Frequency chirp is cancelled, and any residual chirp is measured and compensated for shot-by-shot, as described in Chapter 4. Measurements of the AC-Stark effects and the residual first-order Doppler effect in HD are presented in the next subsections. In the remainder of this section, I will discuss a possible offset due to the hyperfine structure in both the ground state and the excited state.

Differently from H₂ and D₂, HD is a heteronuclear molecule, hence both symmetric and anti-symmetric nuclear wavefunctions may be combined with both odd and even rotational wavefunctions. The nuclear spin of the H-atom, $I=\frac{1}{2}$, and the nuclear spin of the D-atom, I=1, form a total nuclear spin of $I=\frac{1}{2}$ or $\frac{3}{2}$. These nuclear spin states combine with the J=0 state, resulting in a hyperfine splitting that is measured by Code and Ramsey and calculated by Puchalski et al. to be on the order of 50 Hz [116, 117], which is negligibly small compared to our accuracy.

The hyperfine structure in the $GK^1\Sigma_q^+(1,2)$ state in HD can still be

larger due to the non-zero J. Similarly as in Chapter 5, we will estimate the magnitude of the splitting in this state by comparing it to the splitting in the $X^1\Sigma_g^+(0,2)$ state in HD, which, according to Jóźwiak et al., is smaller than the hyperfine structure in the $X^1\Sigma_g^+(0,1)$ state of H₂ [113]. Extrapolating this to the $GK^1\Sigma_g^+(1,2)$ state in HD, the uncertainty due to the hyperfine structure is estimated to be below 100 kHz, the previously used uncertainty due to the hyperfine structure in the $GK^1\Sigma_g^+(1,1)$ state in H₂ (see Chapter 2). In the near future, the hyperfine splittings in the $GK^1\Sigma_g^+(1,2)$ state of HD will be determined at ETH Zürich, which will allow for making a more reliable estimate.

6.3.1 AC-Stark effects

Both the ionization laser and the VUV laser pulses give rise to an AC-Stark effect, that scale with the intensity of the laser. The reduction and measurement procedure of the AC-Stark effects is the same as used in the experiment on D_2 , as discussed in Chapter 5. In the measurements presented here, the wavelength of the ionization laser was tuned to $12641(1) \text{ cm}^{-1}$, near the ionization threshold. The delay between the ionization laser and the VUV laser was set to zero.

The AC-Stark effects are compensated by measuring the transition frequency as a function of laser power and extrapolating to zero power. The result for the measurement of the AC-Stark effect of the VUV laser is shown in Fig. 6.3. The different colours in Fig. 6.3 represent measurements done on different days, resulting in different offsets due to the Doppler effect. The slope of the curves measured on different days are the same within the measurement error. This slope is used to calculate the AC-Stark shift at a given laser power. At $P_b=1.5$ mJ per pulse, the AC-Stark shift of the VUV laser is 100 ± 160 kHz.

In Fig. 6.4 similar measurements for the AC-Stark effect due the ionization laser are shown. At $P_{ion}=0.1$ mJ per pulse, the AC-Stark effect of the ionization laser is -50 ± 100 kHz. Both results are shown in Table 6.1 and are used to compensate for the AC-Stark effect after a value for transition frequency has been determined.



Figure 6.3 – AC-Stark effect due to the VUV laser pulse. Every point represents the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency determined from a single scan of the VUV laser. Every colour represents a different alignment of the back-reflected VUV laser, with a different offset due to the residual Doppler effect. The data points are fitted with a linear function.

6.3.2 Doppler effects

A residual first-order Doppler shift arises if there is a (small) angle between the the incoming and back-reflected VUV beams. This Doppler shift is measured and compensated, by determining the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency as a function of velocity of the molecular beam and extrapolating to zero velocity, as described in Chapter 5.

The velocity of the molecules was varied by changing the temperature of the pulsed valve and changing the delay time between the trigger that opens the valve and the trigger of the pulsed lasers (t_{trig}) . Fig. 6.5 shows the observed ion signal as a function of t_{trig} with the frequency of the VUV laser set at the centre of the $GK^1\Sigma_g^+(1,2)-X^1\Sigma_g^+(0,0)$ transition and the ionization laser set at the peak of the auto-ionization resonance at 12641 cm⁻¹. For the measurements shown in Fig. 6.5a the valve was kept at room temperature, while for the measurements shown in



Figure 6.4 – AC-Stark effect due to the ionization laser pulse. Every point represents the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency determined from a single scan of the VUV laser. Every colour represents a different alignment of the back-reflected VUV laser, with a different offset due to the residual Doppler effect. The data points are fitted with a linear function.

Fig. 6.5b the valve was cooled down to 77 K using liquid N_2 . The backing pressure was set to 3 bar in these measurements. The velocity, calculated using Eq. 5.1, is given in the top axes of Fig. 6.5.

The average velocity of the beam decreases from about 1850 m/s to 1000 m/s upon cooling the valve, while the intensity of the molecular beam increases by about a factor of two. As observed, the density profile recorded at room temperature has a near Gaussian profile, while the density profile recorded at low temperature displays a similar double peak structure, albeit less pronounced, as observed for measurements in D_2 . As discussed in Chapter 5, the double peak structure is attributed to collisions at the skimmer [109]. In the following, the trigger time was set near the peak of the density profile for measurements at room temperatures, while for measurements at 77 K the trigger time was set to be slightly earlier in the beam to select the faster molecules which are not affected by skimmer interference.



Figure 6.5 – Observed density of the molecular beam in the interaction zone as a function of the delay time with the value at a temperature of a) 293 K and b) 77 K. In the top axes the delay time is converted to velocity using Eq. 5.1.

Fig. 6.6 shows the extracted transition frequencies as a function of velocity. The different colours in Fig. 6.6 represent measurements performed on different days, with a different alignment of the back-reflected VUV laser beam, resulting in different slopes. Every data point in Fig. 6.6 results from the average of 5 to 10 frequency scans. Before extrapolating the Doppler free value, every scan was compensated for the relativistic Doppler shift, which is calculated using Eq. (5.2). This resulted in shifts of 60 kHz at 293 K and 20 kHz at 77 K. To account for the uncertainty of the relativistic (second-order) Doppler effect, 30 kHz was added to the final error budget.

6.4 Results and Discussion

In this section, the final value for the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency in HD will be presented. In Fig. 6.7 the extrapolated Doppler-free values of the transition frequency are shown for each day of measurements. Each point in Fig. 6.7 results from the extrapolation



Figure 6.6 – Transition frequency as a function of velocity. Every data point results from the average of five to ten second-order Doppler compensated scans. Every line is the linear fit for a different alignment of the reflected VUV beam. By extrapolating these lines to zero velocity the Doppler free $GK^1\Sigma_a^+(1,2)-X^1\Sigma_a^+(0,0)$ transition frequency is found.

of the measurements shown in Fig. 6.6, which are already compensated for the relevant (calculated) second-order Doppler effect.

The eight Doppler-free data points have a standard deviation of 1 MHz, indicated by the red lines in Fig. 6.7. The average of the eight Doppler free values is 3355532273.72 MHz, with a standard error of the (weighted) mean of 0.31 MHz, indicated by the blue bar. This value is compensated for the AC-Stark effects, of which the measurements were presented in the previous section, resulting in a value of 3355532273.67 MHz. We use the standard error of the mean as the statistical uncertainty in the transition frequency, which also contains the error due to the (measured and compensated for) chirp and residual first-order Doppler effect. Apart from this error, the error in both AC-Stark measurements, the second-order Doppler calculation and the estimated error due to the hyperfine structure (as discussed in previous section) are accounted for in final error budget given in Table 6.1. This results in a final accuracy of 0.38 MHz. The measurement in HD is slightly more



Figure 6.7 – Final values of the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency in HD for eight measurements sessions, taken at different alignments of the VUV laser, corrected for the residual first and second-order Doppler effects and chirp effect. The dotted line at 3355532273.72 MHz is the average value of the eight data points. The blue bar is the standard error of the mean (0.31 MHz). The red lines indicate the standard deviation (1 MHz).

accurate than that in D_2 , mainly due to the higher transition probability in HD due to a more favourable Franck-Condon factor [110].

Our measurement of the $GK^1\Sigma_g^+(1,2) - X^1\Sigma_g^+(0,0)$ transition frequency will be combined with other measurements and calculations to obtain an improved value for the dissociation energy of the ground state of HD. An experiment is being planned at ETH Zürich to determine the ionization energy of the $GK^1\Sigma_g^+(1,2)$ state, which, combined with our measurement, results in an improved determination of the ionization energy of the ground state $(E_i(\text{HD}))$. The ionization energy of HD will then be combined with the accurate values of the ionization energy of the molecular ion $(E_i(\text{HD}^+) = 131224.6841650(6))$ [24] and the ionization energy of the separate atoms $(E_i(\text{H}) = 109678.77174307(10)$ cm^{-1} [23] and $E_i(\text{D}) = 109708.61455294(17)$ cm⁻¹ [25]) via Eq. (1.5), resulting in the dissociation energy of HD. This dissociation energy will **Table 6.1** – Error budget of the measurement of the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition in HD. The statistical error of 0.31 MHz also contains the uncertainty of the first-order Doppler extrapolation and the chirp measurements. The corrections and uncertainties due to the AC-Stark effects of both laser pulses were measured and compensated for as described in previous section. The uncertainty due to the hyperfine structure is extrapolated from the uncertainty due to the hyperfine structure in the $GK^1\Sigma_g^+(1,1)$ in H₂ as discussed in the previous section. The final error in the $GK^1\Sigma_g^+(1,2)$ - $X^1\Sigma_g^+(0,0)$ transition frequency in HD is 0.38 MHz.

Measured frequency		$3355532273.72 \mathrm{~MHz}$
Effect	Correction	Uncertainty
Residual 1^{st} order Doppler and Chirp		$(310 \text{ kHz})_{stat}$
2^{nd} order Doppler		$30 \mathrm{~kHz}$
AC-Stark ionization laser	$50 \mathrm{~kHz}$	100 kHz
AC-Stark VUV laser	-100 kHz	160 kHz
Hyperfine structure		100 kHz
Final frequency		3355532273.67(38) MHz

be compared with theory to reveal if the observed discrepancy between the latest theoretical and experimental values holds or not [20, 106]. If the discrepancy holds, it may be a hint for physics beyond the Standard Model.

CHAPTER

Outlook

The improved values of $D_0(\text{ortho-H}_2)$, $D_0(\text{para-H}_2)$ and $D_0(D_2)$ presented in Chapters 2, 3 and 5 provide for tests of calculations in the QED framework on the sub-MHz level of accuracy. Once the ionization energy of the $\text{GK}^1\Sigma_g^+$ -state of HD is determined, it can be combined with the result presented in Chapter 6 to determine $D_0(\text{HD})$, which would provide for another test, potentially on the sub-MHz level of accuracy. These comparisons are more than an order of magnitude more accurate compared to previous studies [12, 13, 20]. As discussed in Chapter 1, these tests can either be used to determine the fundamental constants of theory or to put constraints (or point toward) physics beyond the Standard Model.

The results presented in this thesis may be used to constrain the possible existence of extra dimensions and forces on the Ångström scale, as discussed in [2, 118]. The constraint on a hypothetical fifth force calculated by Salumbides et al. [118] is based on the combination of the experimental value of $D_0(D_2)$ of Liu et al. [13] and the theoretical value of Komasa et al. [119], these values have a combined uncertainty of 0.0011 cm⁻¹. The improved experimental determination of $D_0(D_2)$ presented in Chapter 5, in combination with the improved theoretical value from Puchalski et al. [106], reduces the combined uncertainty to 0.000034 cm⁻¹. Due to this reduced combined uncertainty, the strength of a hypothetical fifth-force with an interaction range of 1 Å, as described in [118, 120], must be 10 orders of magnitude weaker than the electromagnetic force. This is complementary to the best constraints

7. Outlook

on fifth-forces at the Ångström scale, which stem from measurements of rovibrational transitions in the HD⁺ molecular ion [8, 26, 120], that constrain the strength of this hypothetical fifth-force to be 11 orders of magnitude weaker than the electromagnetic force. At shorter distances, constraints of hypothetical fifth-forces are more sensitive to accurate tests on D₂ than on HD⁺, since D₂ has a smaller internuclear separation. The combination of measurements in different systems (H₂, D₂, HD and HD⁺, but also H- and D- atoms) give a collection of independent tests of fundamental physics. Increasing the accuracy of all these tests pushes the boundaries of the Standard Model of Physics.

To provide values for some of the fundamental constants, like r_p and μ_p , with a similar accuracy as the most accurate values known now, the value of D_0 needs to be tested on the 10 kHz level of accuracy. To test D_0 at a higher level of accuracy, both the theoretical value and the experimental value need to be further improved. The uncertainty in the experimental value of D_0 is still dominated by the error in the ionization energy of the neutral molecule. To reduce the uncertainty in the extrapolation to the ionization potential need to be improved. In the remainder of this Chapter, I will discuss different options to reduce the uncertainty in our measurements and other possible measurements which could lead to an improved determination of the ionization energy.

The current measurement on the $GK^1\Sigma_g^+ \cdot X^1\Sigma_g^+$ transition is limited by various systematic effects. Reducing the uncertainty would require an improvement in the determination of (i) the hyperfine structure, (ii) the AC-Stark shifts, (iii) residual Doppler shifts and (iv) the residual frequency chirp.

As discussed in Chapter 3, the best determination of the dissociation energy can be performed in para-H₂, since it possesses no hyperfine structure. In comparison to the measurements presented in Chapter 3, the signal can even be increased a factor four by using a bottle of pure para-H₂, instead of a standard mixture of ortho- and para-H₂.

The AC-Stark shifts can be reduced by reducing the power of the ionization and VUV laser pulses, however, this is at the cost of signal quality. The extrapolation of an AC-Stark free value can be improved by increasing the range of powers over which is measured, for both lasers. Especially for the VUV laser this is currently difficult: when the power of the laser is reduced, there is a non-linear decrease in signal due to the two-photon character of the transition. While increasing the power of the UV laser before the KBBF-crystal can be dangerous for the crystal. This would require the development of a KBBF-crystal that can withstand higher peak intensities. Higher precision on the determination of the AC-Stark shift due to the VUV laser might be possible if the power of the VUV can be determined in the vacuum chamber, pulse by pulse. Up to now this has been difficult, since the available photo diodes are very sensitive to the scattering 358-nm light. The AC-Stark effect due to the ionization laser might be reduced further as discussed in Chapter 5: by delaying the ionization laser (at the cost of signal) or by choosing the right auto-ionising resonance. One would need to study which auto-ionising resonance gives rise to the least AC-Stark shift.

The residual Doppler effects can be reduced by cooling down the valve even further, or by mixing the hydrogen gas with another gas like neon while the valve is cooled down. One would still need to perform measurements at two or more velocities to extrapolate to zero velocity. A second option would be to use a Sagnac-interferometer similar to [46]. This will be a challenge due to the short wavelength of the laser and the lack of good optics for light in this wavelength range. A third option is to measure the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition frequency only at one velocity of the molecules, preferably a low velocity. Then, after each measurement, the alignment of the back-reflected VUV laser beam should be randomly changed. Thus the (systematic) Doppler effect can be turned into a statistical measurement. One would still need to account for the second-order Doppler effect.

To reduce the frequency chirp effect it is possible to use a longer and thinner intra-cavity EOM. This improves the control over the phase change per pass through the EOM given by Eq. (4.4). Also, an active feedback loop can be implemented to cancel the chirp effect pulse-bypulse. The chirp can further be reduced by using longer laser pulses [121]. This will also reduce the contribution of the bandwith of the laser to the linewidth of the spectra. To generate longer laser pulses, one could for example switch the Ti:Sa oscillator with an AOM.

Implementing all these improvements could reduce the uncertainty on the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition frequency to 100 kHz. In the near future it will probably be limited by the determination of the VUV AC-Stark shift due to the limited efficiency and robustness of the KBBF-crystal.

Instead of determining the ionization energy by using the $GK^1\Sigma_q^+$ state as an intermediate state, it can be determined via the $\mathrm{EF}^{1}\Sigma_{q}^{+}$ state, as discussed in Chapter 1. A new Ramsey-type experiment on the $\mathrm{EF}^{1}\Sigma_{q}^{+}$ - $\mathrm{X}^{1}\Sigma_{q}^{+}$ transition in ortho-H₂ has already reached an accuracy of 73 kHz [49]. This value has been combined with an accurate determination of the ionization energy of the $\mathrm{EF}^{1}\Sigma_{a}^{+}$ state, to determine the most precise (340 kHz) experimental value of the ionization and dissociation energy of ortho- H_2 [73]. The first step to increase the accuracy even further, would be to measure the $\mathrm{EF}^1\Sigma_g^+$ - $\mathrm{X}^1\Sigma_g^+$ transition in para- H_2 in a similar Ramsey-type experiment. Due to the absence of hyperfine structure, this can potentially be performed with an accuracy of 10 kHz, according to [49]. The second step would be to determine the ionization energy of the $\mathrm{EF}^{1}\Sigma_{a}^{+}$ state in para-H₂. This can either be done in a similar way as in [73], or by linking the $EF^{1}\Sigma_{a}^{+}$ state to the $X^+(0,0)$ ionization limit via the $GK^1\Sigma_q^+$ state, as proposed in Chapter 3.

Finally, one could combine the Ramsey comb method from [49] and the special KBBF from this work to directly determine the $GK^1\Sigma_g^+$ $X^1\Sigma_g^+$ in a Ramsey-type experiment, provided that an in vacuo Sagnacinterferometer can be built. Since the Ramsey comb method is inherently insensitive to AC-Stark shift, the AC-Stark effect due to the VUV laser would not be limiting the accuracy anymore. All other systematic effects can in principle be dealt with in the same way as by Altmann et al. [49]. The only problem would be the short lifetime of the GK state (18 ns compared to 200 ns for the $EF^1\Sigma_g^+$ state), which seriously limits the maximum inter-pulse delay, and thus the accuracy of the measurement.

Bibliography

- Ubachs, W., Koelemeij, J. C. J., Eikema, K. S. E. & Salumbides, E. J. Physics beyond the Standard Model from hydrogen spectroscopy. J. Mol. Spectrosc. 320, 1 – 12 (2016).
- Salumbides, E. J., Schellekens, A. N., Gato-Rivera, B. & Ubachs, W. Constraints on extra dimensions from precision molecular spectroscopy. *New J. Phys.* 17, 033015 (2015).
- Cozijn, F. M. J., Dupré, P., Salumbides, E. J., Eikema, K. S. E. & Ubachs, W. Sub-doppler frequency metrology in HD for tests of fundamental physics. *Phys. Rev. Lett.* **120**, 153002 (2018).
- [4] Tao, L. G. et al. Toward a determination of the proton-electron mass ratio from the Lamb-dip measurement of HD. Phys. Rev. Lett. 120, 153001 (2018).
- [5] Fasci, E. *et al.* Precision spectroscopy of HD at $1.38 \,\mu\text{m}$. *Phys. Rev. A* **98**, 022516 (2018).
- [6] Dickenson, G. D. et al. Fundamental vibration of molecular hydrogen. Phys. Rev. Lett. 110, 193601 (2013).
- [7] Lai, K.-F. et al. Precision measurement of the fundamental vibrational frequencies of tritium-bearing hydrogen molecules: T₂, DT, HT. Phys. Chem. Chem. Phys. 22, 8973–8987 (2020).
- [8] Patra, S. *et al.* Proton-electron mass ratio from laser spectroscopy of HD⁺ at the part-per-trillion level. *Science* **369**, 1238–1241 (2020).
- [9] Pohl, R. et al. The size of the proton. Nature 466, 213–216 (2010).
- [10] Grinin, A. *et al.* Two-photon frequency comb spectroscopy of atomic hydrogen. *Science* **370**, 1061–1066 (2020).

- [11] Ubachs, W. Crisis and catharsis in atomic physics. *Science* **370**, 1033–1033 (2020).
- [12] Liu, J. et al. Determination of the ionization and dissociation energies of the hydrogen molecule. J. Chem Phys. 130, 174306 (2009).
- [13] Liu, J., Sprecher, D., Jungen, C., Ubachs, W. & Merkt, F. Determination of the ionization and dissociation energies of the deuterium molecule (D₂). J. Chem Phys. **132**, 154301 (2010).
- [14] Langmuir, I. The dissociation of hydrogen into atoms.1. J. Am. Chem. Soc. 34, 860–877 (1912).
- [15] Witmer, E. E. Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum. *Phys. Rev.* 28, 1223–1241 (1926).
- [16] Heitler, W. & London, F. Wechselwirkung neutraler Atome und homopolare Bindung nach der Quantenmechanik. Zeitschr. f. Phys. 44, 455–472 (1927).
- [17] Herzberg, G. & Monfils, A. The dissociation energies of the H₂, HD, and D₂ molecules. J. Mol. Spectrosc. 5, 482–498 (1961).
- [18] Eyler, E. E. & Melikechi, N. Near-threshold continuum structure and the dissociation energies of H₂, HD, and D₂. *Phys. Rev. A* 48, R18 (1993).
- [19] Zhang, Y. P., Cheng, C. H., Kim, J. T., Stanojevic, J. & Eyler, E. E. Dissociation energies of molecular hydrogen and the hydrogen molecular ion. *Phys. Rev. Lett.* **92**, 203003 (2004).
- [20] Sprecher, D., Liu, J., Jungen, C., Ubachs, W. & Merkt, F. Communication: The ionization and dissociation energies of HD. J. Chem. Phys. 133, 111102 (2010).
- [21] Herzberg, G. & Jungen, C. Rydberg series and ionization potential of the H₂ molecule. J. Mol. Spectrosc. 41, 425–486 (1972).

- [22] Sprecher, D., Jungen, C., Ubachs, W. & Merkt, F. Towards measuring the ionisation and dissociation energies of molecular hydrogen with sub-MHz accuracy. *Farad. Discuss.* **150**, 51–70 (2011).
- [23] Mohr, P. J., Newell, D. B. & Taylor, B. N. CODATA recommended values of the fundamental physical constants: 2014. J. Phys. Chem. Ref. Data 45, 043102 (2016).
- [24] Korobov, V. I., Hilico, L. & Karr, J.-P. Fundamental transitions and ionization energies of the hydrogen molecular ions with few ppt uncertainty. *Phys. Rev. Lett.* **118**, 233001 (2017).
- [25] Yerokhin, V. A., Pachucki, K. & Patkóš, V. Theory of the Lamb shift in hydrogen and light hydrogen-like ions. Ann. d. Physik 531, 1800324 (2019).
- [26] Alighanbari, S., Giri, G. S., Constantin, F. L., Korobov, V. I. & Schiller, S. Precise test of quantum electrodynamics and determination of fundamental constants with HD⁺ ions. *Nature* 581, 152–158 (2020).
- [27] Kołos, W. & Wolniewicz, L. Accurate adiabatic treatment of the ground state of the hydrogen molecule. J. Chem. Phys. 41, 3663– 3673 (1964).
- [28] Wolniewicz, L. Nonadiabatic energies of the ground state of the hydrogen molecule. J. Chem Phys. 103, 1792–1799 (1995).
- [29] Piszczatowski, K. et al. Theoretical determination of the dissociation energy of molecular hydrogen. J. Chem. Theory Comput. 5, 3039–3048 (2009).
- [30] Puchalski, M., Komasa, J., Czachorowski, P. & Pachucki, K. Nonadiabatic QED correction to the dissociation energy of the hydrogen molecule. *Phys. Rev. Lett.* **122**, 103003 (2019).
- [31] Chen, C., Lin, Z. & Wang, Z. The development of new boratebased UV nonlinear optical crystals. Appl. Phys. B 80, 1–25 (2005).

- [32] Chen, C. T., Kanai, T., Wang, X. Y., Zhu, Y. & Watanabe, S. High-average-power light source below 200 nm from a KBe₂BO₃F₂ prism-coupled device. *Opt. Lett.* **33**, 282–284 (2008).
- [33] Zhang, H. et al. 175 to 210 nm widely tunable deep-ultraviolet light generation based on KBBF crystal. Appl. Phys. B 93, 323– 326 (2008).
- [34] Kanai, T. *et al.* Generation of vacuum-ultraviolet light below 160 nm in a KBBF crystal by the fifth harmonic of a single-mode ti:sapphire laser. *J. Opt. Soc. Am. B* **21**, 370–375 (2004).
- [35] Togashi, T. et al. Generation of vacuum-ultraviolet light by an optically contacted, prism-coupled KBe₂BO₃F₂ crystal. Opt. Lett. 28, 254–256 (2003).
- [36] Li, Y.-J. et al. Experimental and theoretical investigations on high power vacuum-ultraviolet laser at 165 nm by eighth-harmonic generation in KBBF. Optics & Laser Technology 120, 105756 (2019).
- [37] Pachucki, K. Born-Oppenheimer potential for H₂. *Phys. Rev. A* 82, 032509 (2010).
- [38] Pachucki, K. & Komasa, J. Accurate adiabatic correction in the hydrogen molecule. J. Chem. Phys. 141, 224103 (2014).
- [39] Pachucki, K. & Komasa, J. Leading order nonadiabatic corrections to rovibrational levels of H₂, D₂, and T₂. J. Chem. Phys. **143**, 034111 (2015).
- [40] Pachucki, K. & Komasa, J. Schrödinger equation solved for the hydrogen molecule with unprecedented accuracy. J. Chem. Phys. 144, 164306 (2016).
- [41] Simmen, B., Mátyus, E. & Reiher, M. Elimination of the translational kinetic energy contamination in pre-Born-Oppenheimer calculations. *Mol. Phys.* 111, 2086–2092 (2013).

- [42] Puchalski, M., Komasa, J., Czachorowski, P. & Pachucki, K. Complete $\alpha^6 m$ corrections to the ground state of H₂. *Phys. Rev. Lett.* **117**, 263002 (2016).
- [43] Puchalski, M., Komasa, J. & Pachucki, K. Relativistic corrections for the ground electronic state of molecular hydrogen. *Phys. Rev.* A 95, 052506 (2017).
- [44] Herzberg, G. The dissociation energy of the hydrogen molecule. J. Mol. Spectrosc. 33, 147–168 (1970).
- [45] Jennings, D. E., Bragg, S. L. & Brault, J. W. The v = 0 0 spectrum of H₂. Astroph. J. Lett. **282**, L85–L88 (1984).
- [46] Hannemann, S. *et al.* Frequency metrology on the $EF^1\Sigma_g^+ X^1\Sigma_g^+$ (0,0) transition in H₂, HD, and D₂. *Phys. Rev. A* **74**, 062514 (2006).
- [47] Osterwalder, A., Wüest, A., Merkt, F. & Jungen, C. Highresolution millimeter wave spectroscopy and multichannel quantum defect theory of the hyperfine structure in high Rydberg states of molecular hydrogen H₂. J. Chem Phys. **121**, 11810–11838 (2004).
- [48] Haase, C., Beyer, M., Jungen, C. & Merkt, F. The fundamental rotational interval of para-H⁺₂ by MQDT-assisted Rydberg spectroscopy of H₂. J. Chem. Phys. **142**, 064310 (2015).
- [49] Altmann, R. K., Dreissen, L. S., Salumbides, E. J., Ubachs, W. & Eikema, K. S. E. Deep-ultraviolet frequency metrology of H₂ for tests of molecular quantum theory. *Phys. Rev. Lett.* **120**, 043204 (2018).
- [50] Beyer, M. *et al.* Metrology of high-*n* Rydberg states of molecular hydrogen with $\Delta \nu / \nu = 2 \times 10^{-10}$ accuracy. *Phys. Rev. A* **97**, 012501 (2018).
- [51] Astashkevich, S. A. & Lavrov, B. P. Lifetimes of vibro-rotational levels in excited electronic states of diatomic hydrogen isotopologues. J. Phys. Chem. Ref. Data 44, 023105 (2015).

- [52] Eppink, A. T. J. B. & Parker, D. H. Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen. *Rev. Sci. Instrum.* 68, 3477 (1997).
- [53] Scoles, G., Bassi, D., Buck, U. & Lainé, D. Atomic and Molecular Beam Methods (Oxford University Press, 1988).
- [54] Sprecher, D., Beyer, M. & Merkt, F. Precision measurement of the ionisation energy of the 3dσ GK state of H₂. Mol. Phys. **111**, 2100–2107 (2013).
- [55] Sprecher, D., Jungen, C. & Merkt, F. Determination of the binding energies of the *np* Rydberg states of H₂, HD, and D₂ from highresolution spectroscopic data by Multichannel Quantum-Defect Theory. J. Chem Phys. **140**, 104303 (2014).
- [56] Mohr, P. J., Newell, D. B. & Taylor, B. N. Codata recommended values of the fundamental physical constants: 2014. *Rev. Mod. Phys.* 88, 035009 (2016).
- [57] Ramsey, N. F. Theory of molecular hydrogen and deuterium in magnetic fields. *Phys. Rev.* 85, 60–65 (1952).
- [58] Quack, M. Detailed symmetry selection rules for reactive collisions. Mol. Phys. 34, 477 (1977).
- [59] Uy, D., Cordonnier, M. & Oka, T. Observation of ortho-para H⁺₃ selection rules in plasma chemistry. *Phys. Rev. Lett.* **78**, 3844 (1997).
- [60] Quack, M. Handbook of High-resolution Spectroscopy, Editors: F. Merkt and M. Quack, Chapter: Fundamental Symmetries and Symmetry Violations from High-resolution Spectroscopy (John Wiley and Sons, Chichester and New York, 2011).
- [61] Oka, T. Handbook of High-resolution Spectroscopy, Editors: F. Merkt and M. Quack, Chapter: Orders of Magnitude and Symmetry in Molecular Spectroscopy (John Wiley and Sons, Chichester and New York, 2011).

- [62] Longuet-Higgins, H. The symmetry groups of non-rigid molecules. Mol. Phys. 6, 445 (1963).
- [63] Bunker, P. R. & Jensen, P. *Molecular symmetry and spectroscopy* (NRC Research Press, 2006).
- [64] Bonhoeffer, K. F. & Harteck, P. Experimente über para- und orthowasserstoff. *Natürwissenschaften* 17, 182 (1929).
- [65] Ehrenfest, P. & Oppenheimer, J. R. Note on the statistics of nuclei. *Phys. Rev.* 37, 333 (1931).
- [66] Moss, R. E. Electronic g/u symmetry breaking in H⁺₂. Chem. Phys. Lett. 206, 83 (1993).
- [67] Pachucki, K. & Komasa, J. Gerade-ungerade mixing in the hydrogen molecule. *Phys. Rev. A* 83, 042510 (2011).
- [68] Beyer, M. & Merkt, F. Hyperfine-interaction-induced g/u mixing and its implication on the existence of the first excited vibrational level of the $A^{+2}\Sigma_u^+$ state of H_2^+ and on the scattering length of the H + H⁺ collision. J. Chem. Phys. **149**, 214301 (2018).
- [69] Critchley, A. D. J., Hughes, A. N. & McNab, I. R. Direct measurement of a pure rotation transition in H₂⁺. *Phys. Rev. Lett.* 86, 1725 (2001).
- [70] Biesheuvel, J. et al. Probing QED and fundamental constants through laser spectroscopy of vibrational transitions in HD⁺. Nat. Comm. 7, 10385 (2016).
- [71] Alighanbari, S., Hansen, M. G., Korobov, V. I. & Schiller, S. Rotational spectroscopy of cold and trapped molecular ions in the Lamb–Dicke regime. *Nat. Phys.* 14, 555 (2018).
- [72] Cheng, C.-F. et al. Dissociation energy of the hydrogen molecule at 10⁻⁹ accuracy. Phys. Rev. Lett. **121**, 013001 (2018).
- [73] Hölsch, N. et al. Benchmarking theory with an improved measurement of the ionization and dissociation energies of H₂. Phys. Rev. Lett. **122**, 103002 (2019).

- [74] Borrell, P., Guyon, P. M. & Glass-Maujean, M. H₂ and D₂ photon impact predissociation. J. Chem. Phys. 66, 818–827 (1977).
- [75] Mezei, J. Z., Schneider, I. F., Glass-Maujean, M. & Jungen, C. Resonances in photoabsorption: Predissociation line shapes in the $3p\pi$ D¹ Π_u^+ X¹ Σ_g^+ system in H₂. J. Chem. Phys. **141**, 064305 (2014).
- [76] Fano, U. Quantum defect theory of l uncoupling in H₂ as an example of channel-interaction treatment. *Phys. Rev. A* **2**, 353–365 (1970).
- [77] Jungen, C. Handbook of High-resolution Spectroscopy, Editors: F. Merkt and M. Quack, Chapter: Elements of Quantum Defect Theory (John Wiley and Sons, Chichester and New York, 2011).
- [78] Gao, H. & Greene, C. H. Alternative vibrational frame transformation for electron-molecule scattering. *Phys. Rev. A* 42, 6946 (1990).
- [79] Beyer, M., Hölsch, N., Jungen, C. & Merkt, F. (To be published).
- [80] Kay, J. J., Coy, S. L., Wong, B. M., Jungen, C. & Field, R. W. A quantum defect model for the s, p, d, and f Rydberg series of CaF. J. Chem. Phys. 134, 114313 (2011).
- [81] Neuhauser, R. G., Siglow, K. & Neusser, H. J. High n Rydberg spectroscopy of benzene: Dynamics, ionization energy and rotational constants of the cation. J. Chem. Phys. 106, 896 (1997).
- [82] Yu, S. & Dressler, K. Calculation of rovibronic structures in the lowest nine excited ${}^{1}\Sigma_{g}^{+} + {}^{1}\Pi_{g} + {}^{1}\Delta_{g}$ states of H₂, D₂, and T₂. J. Chem Phys. **101**, 7692 (1994).
- [83] Hoelsch, N., Beyer, M. & Merkt, F. Nonadiabatic effects on the positions and lifetimes of the low-lying rovibrational levels of the GK ${}^{1}\Sigma_{g}^{+}$ and H ${}^{1}\Sigma_{g}^{+}$ states of H₂. *Phys. Chem. Chem. Phys.* **20**, 26837–26845 (2018).

- [84] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.163002 for a list of the measured $nfO_3(0)$ -GK(0,2) transition frequencies of H_2 with corresponding experimental uncertainties and fit residuals.
- [85] Korobov, V. I. (private communication).
- [86] Korobov, V. I. Leading-order relativistic and radiative corrections to the rovibrational spectrum of H_2^+ and HD^+ molecular ions. *Phys. Rev. A* **74**, 052506 (2006).
- [87] Korobov, V. I. Bethe logarithm for the hydrogen molecular ion H⁺₂. Phys. Rev. A 73, 024502 (2006).
- [88] Korobov, V. I. Relativistic corrections of $m\alpha^6$ order to the rovibrational spectrum of H_2^+ and HD⁺ molecular ions. *Phys. Rev. A* **77**, 022509 (2008).
- [89] Ledbetter, M. P., Romalis, M. V. & Jackson Kimball, D. F. Constraints on short-range spin-dependent interactions from scalar spin-spin coupling in deuterated molecular hydrogen. *Phys. Rev. Lett.* **110**, 040402 (2013).
- [90] Rosenband, T. et al. Frequency ratio of Al⁺ and Hg⁺ single-ion optical clocks; Metrology at the 17th decimal place. Science **319**, 1808–1812 (2008).
- [91] Bloom, B. J. *et al.* An optical lattice clock with accuracy and stability at the 10^{-18} level. *Nature* **506**, 71–75 (2014).
- [92] Fee, M. S. et al. Sensitive detection of Doppler-free two-photonexcited 2S positronium by spatially separated photoionization. *Phys. Rev. A* 44, R5–R8 (1991).
- [93] Meyer, V. et al. Measurement of the 1s 2s energy interval in muonium. Phys. Rev. Lett. 84, 1136–1139 (2000).
- [94] Hori, M. et al. Two-photon laser spectroscopy of antiprotonic helium and the antiproton-to-electron mass ratio. Nature 475, 484–488 (2011).

- [95] Eikema, K. S. E., Ubachs, W., Vassen, W. & Hogervorst, W. Precision measurements in helium at 58 nm: Ground state Lamb shift and the 1¹S-2¹P transition isotope shifts. *Phys. Rev. Lett.* **76**, 1216 (1996).
- [96] Fee, M. S., Danzmann, K. & Chu, S. Optical heterodyne measurement of pulsed lasers - toward high-precision pulsed spectroscopy. *Phys. Rev. A* 45, 4911–4924 (1992).
- [97] Melikechi, N., Gangopadhyay, S. & Eyler, E. E. Phase dynamics in nanosecond pulsed dye-laser amplification. J. Opt. Soc. Am. A 11, 2402–2411 (1994).
- [98] Reinhard, I., Gabrysch, M., Fischer von Weikersthal, B., Jungmann, K. & Zu Putlitz, G. Measurement and compensation of frequency chirping in pulsed dye laser amplifiers. *Appl. Phys. B* 63, 467–472 (1996).
- [99] Eikema, K. S. E., Ubachs, W., Vassen, W. & Hogervorst, W. Lamb shift measurement in the 1¹S ground state of helium. *Phys. Rev.* A 55, 1866 (1997).
- [100] White, R. T., He, Y., Orr, B. J., Kono, M. & Baldwin, K. G. H. Control of frequency chirp in nanosecond-pulsed laser spectroscopy. 1. Optical-heterodyne chirp analysis techniques. J. Opt. Soc. Am. B 21, 1577–1585 (2004).
- [101] Bakule, P. et al. A chirp-compensated, injection-seeded alexandrite laser. Appl. Phys. B 71, 11–17 (2000).
- [102] Hannemann, S., van Duijn, E.-J. & Ubachs, W. A narrow-band injection-seeded pulsed titanium:sapphire oscillator-amplifier system with on-line chirp analysis for high-resolution spectroscopy. *Rev. Scient. Instrum.* 78, 103102 (2007).
- [103] Hori, M. & Dax, A. Chirp-corrected, nanosecond Ti:sapphire laser with 6 MHz linewidth for spectroscopy of antiprotonic helium. *Opt. Lett.* 34, 1273–1275 (2009).

- [104] Hänsch, T. & Couillaud, B. Laser frequency stabilization by polarization spectroscopy of a reflecting reference cavity. *Opt. Commun.* 35, 441 (1980).
- [105] Beyer, M. et al. Determination of the interval between the ground states of para- and ortho-H₂. Phys. Rev. Lett. **123**, 163002 (2019).
- [106] Puchalski, M., Komasa, J., Spyszkiewicz, A. & Pachucki, K. Dissociation energy of molecular hydrogen isotopologues. *Phys. Rev.* A 100, 020503 (2019).
- [107] Halpern, J., Zacharias, H. & Wallenstein, R. Rotational line strengths in two- and three-photon transitions in diatomic molecules. J. Mol. Spectrosc. 79, 1–30 (1980).
- [108] Allmendinger, P. *et al.* New method to study ion-molecule reactions at low temperatures and application to the $H_2^+ + H_2 \rightarrow H_3^+ + H_3$ reaction. *ChemPhysChem* **17**, 3596–3608 (2016).
- [109] Even, U. The Even-Lavie valve as a source for high intensity supersonic beam. *EPJ Techn. Instrum.* **2**, 17 (2015).
- [110] Fantz, U. & Wünderlich, D. Franck–Condon factors, transition probabilities, and radiative lifetimes for hydrogen molecules and their isotopomeres. At. Data Nucl. Data Tables 92, 853–973 (2006).
- [111] Sommavilla, M., Merkt, F., Mezei, J. Z. & Jungen, C. Absorption, autoionization, and predissociation in molecular hydrogen: Highresolution spectroscopy and multichannel quantum defect theory. J. Chem. Phys. 144, 084303 (2016).
- [112] Trivikram, T. M., Salumbides, E. J., Jungen, C. & Ubachs, W. Excitation of H₂ at large internuclear separation: outer well states and continuum resonances. *Mol. Phys.* **117**, 2961–2971 (2019).
- [113] Jóźwiak, H., Cybulski, H. & Wcisło, P. Hyperfine components of all rovibrational quadrupole transitions in the H₂ and D₂ molecules. J. Quant. Spectrosc. Radiat. Transf. 253, 107186 (2020).
- [114] Lange, A. D., Reinhold, E. & Ubachs, W. Phenomena of g-u symmetry-breakdown in HD. Int. Rev. Phys. Chem. 21, 257–275 (2002).
- [115] Pachucki, K. & Komasa, J. Rovibrational levels of HD. Phys. Chem. Chem. Phys. 12, 9188–9196 (2010).
- [116] Code, R. F. & Ramsey, N. F. Molecular-beam magnetic resonance studies of HD and D₂. *Phys. Rev. A* 4, 1945–1959 (1971).
- [117] Puchalski, M., Komasa, J. & Pachucki, K. Nuclear spin-spin coupling in HD, HT, and DT. Phys. Rev. Lett. 120, 083001 (2018).
- [118] Salumbides, E. J. et al. Bounds on fifth forces from precision measurements on molecules. Phys. Rev. D 87, 112008 (2013).
- [119] Komasa, J. et al. Quantum electrodynamics effects in rovibrational spectra of molecular hydrogen. J. Chem. Theory Comput. 7, 3105–3115 (2011).
- [120] Germann, M. et al. Three-body QED test and fifth-force constraint from vibrations and rotations of HD⁺. Phys. Rev. Research 3, L022028 (2021).
- [121] Hannemann, S. Deep-ultraviolet frequency metrology with a narrowband titanium:sapphir laser. Ph.D. thesis, VU University, Amsterdam (2007).

List of Publications

The chapters in this thesis are based on the following publications:

- Chapter 2: 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 10⁻⁹ Accuracy," *Phys. Rev. Lett.* **121**, 013001, 2018.
- Chapter 3: M. Beyer, N. Hölsch, J. Hussels, C.-F. Cheng, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, Ch. Jungen and F. Merkt, "Determination of the Interval between the Ground States of Para- and Ortho-H₂," *Phys. Rev. Lett.* **123**, 163002, 2019.
- Chapter 4: J. Hussels, C. Cheng, E.J. Salumbides, W. Ubachs, "Chirpcompensated pulsed Titanium-Sapphire laser system for precision spectroscopy," Opt. Lett. 45, 5909, 2020.

The results discussed in **Chapter 5** and **Chapter 6** will be submitted for publication in the near future.

Summary

The hydrogen molecule is the simplest neutral molecule. This simplicity makes it one of the best calculable systems and thus a principal testbed for comparisons between measurements and *ab initio* calculations. These calculations are based on quantum electrodynamics (QED), and by extension the Standard Model.

One of the best calculable properties of H_2 is the dissociation energy (D_0) of the ground state, the lowest amount of energy that is needed to dissociate the molecule from the ground state into two separate atoms in their ground state. The same holds for the deuterated isotopologues, HD and D₂. Over the last century, the uncertainties in the experimental and theoretical values of D_0 have been reduced by eight orders of magnitude. The first part of Chapter 1 describes previous measurements and calculations of D_0 , and how these are used to test fundamental physics.

In this thesis a more accurate value of D_0 is determined from the ionization energies of the neutral molecule, the molecular ion and the atoms. The ionization energy of the neutral molecule is determined by combining measurements on the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition with measurements of the ionization energy of the $GK^1\Sigma_g^+$ state. The ionization energy of the $GK^1\Sigma_g^+$ state is determined by measurements on high lying Rydberg states and extrapolating the Rydberg series to the ionization continuum using Multi-channel Quantum Defect theory.

To generate laser light at a wavelength of 179 nm, required to drive the $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ two-photon transition, a special KBBF crystal is exploited, using second-harmonic generation of 358 nm pulses. The 358 nm pulses are generated by the upconversion of 716 nm pulses using a BBO crystal. The 716 nm pulses are the output of a narrowband Ti:Sa oscillator-amplifier system. The oscillator-amplifier system is seeded by a continuous wave (cw) Ti:Sa seed laser. To stabilise the frequency of the 716 nm laser light the cw Ti:Sa seed laser is locked to an optical frequency comb, which is referenced by a Cs-clock. An acousto-optic modulator (AOM) is implemented to scan the cw laser, and thus the frequency of the VUV laser. Molecules excited to the $GK^1\Sigma_g^+$ state are selectively ionised with a single photon from a pulsed ionization laser. The second part of Chapter 1 describes the used methods and introduces the experimental setup. The first part of Chapter 5 describes the molecular beam, and the ionisation and detection processes.

There are four main sources of systematic offsets on the determined frequency of the $GK^1\Sigma_g^+ \cdot X^1\Sigma_g^+$ two-photon resonance: frequency chirp, AC-Stark effects, Doppler effects and hyperfine structure. Frequency chirp is reduced using an intra-cavity EOM, and any residual chirp is measured shot-by-shot and compensated for. Chapter 4 describes the the effect of frequency chirp in pulse generation and the scheme to measure and counteract it. Systematic offsets due to AC-Stark effects are assessed by measuring the transition at different laser intensities. The first order Doppler effect is reduced by performing the two-photon transition in a counter-propagating configuration. Any systematic offset due to a residual Doppler effect is assessed by measuring the transition at different molecular beam velocities. Possible uncertainties due to hyperfine splittings, not present in para-H₂, are extrapolated from the known hyperfine structure of high-lying Rydberg states.

The $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ transition was measured at sub-MHz accuracy in both spin isomers of H₂ (ortho- and para-H₂) and in D₂ and HD. These four measurements, and all systematic effects involved, are described in Chapter 2, 3, 5 and 6 respectively. The results of these measurements lead to the improved determination of the dissociation energies of para-H₂, ortho-H₂ and D₂, reducing the relative uncertainty to below 10^{-9} , and will lead to an improved determination of the dissociation energy of HD in the near future. Due to these results the strength of a hypothetical fifth-force with an interaction range of 1 Å must be 10 orders of magnitude weaker than the electromagnetic force. Chapter 7 describes the impact of these measurements, and an outlook on further measurements.

Samenvatting

Het waterstofmolecuul is het eenvoudigste neutrale molecuul. Dit maakt het een van de beste systemen om berekeningen aan te doen en dus een belangrijke proefbank om metingen en *ab initio* berekeningen te vergelijken. Deze berekeningen zijn gebaseerd op quantumelektrodynamica (QED), en uiteindelijk op het Standaard Model. Een van de best berekenbare eigenschappen van H₂ is de dissociatie-energie (D_0) van de grondtoestand, de minimale energie die nodig is om het molecuul vanuit de grondtoestand te scheiden in twee afzonderlijke atomen in de grondtoestand. Hetzelfde geldt voor de gedeutereerde isotopen, HD en D₂. De foutenmarges in de experimentele en theoretische waarden van D_0 zijn in de afgelopen eeuw acht ordes van grootte kleiner geworden. Het eerste deel van Hoofdstuk 1 beschrijft eerdere metingen en berkeningen van D_0 , en hoe deze zijn gebruikt voor het testen van fundamentele fysica.

In dit proefschrift wordt de waarde van D_0 nog nauwkeuriger bepaald vanuit de ionisatie-energieën van het neutrale molecuul, het moleculaire ion en het atoom. De ionisatie-energie van het neutrale molecuul wordt bepaald door metingen van de $GK^1\Sigma_g^+-X^1\Sigma_g^+$ overgang te combineren met metingen van de ionisatie-energie van de $GK^1\Sigma_g^+$ toestand. De ionisatie-energie van de $GK^1\Sigma_g^+$ toestand werd bepaald door metingen aan hoogenenergetische Rydberg toestanden en extrapolatie van de Rydberg serie naar het ionisatiecontinuüm met behulp van de Multichannel Quantum Defect theorie.

Om de $GK^1\Sigma_g^+-X^1\Sigma_g^+$ overgang met twee fotonen te induceren is laserlicht met een golflengte van 179 nm nodig. Dit laserlicht word gegenereerd door middel van frequentieverdubbeling van laserlicht met een golflengte van 358 nm, in een speciaal KBBF kristal. De laserpulsen met een golflengte van 358 nm worden gegenereerd door frequentieverdubbeling van laserpulsen van 716 nm in een BBO kristal. De pulsen van 716 nm laserlicht zijn op hun beurt de output van een smalbandig Ti:Sa oscillator-versterker systeem. Het oscillator-versterker systeem wordt gestabiliseerd door een continue Ti:Sa laser. Om de frequentie van het laserlicht van deze stabilisatielaser constant te houden wordt deze gekalibreerd aan een optische frequentiekam, die op zijn beurt wordt gekalibreerd aan een Cesium klok. Door middel van een akoesto-optische modulator (AOM) wordt de frequentie van de continue laser, en daarmee de frequentie van de VUV laser, gescand. Succesvolle excitaties naar de $\mathrm{GK}^1\Sigma_g^+$ toestand worden selectief geioniseerd door een foton van een ionisatielaser. Het tweede deel van Hoofdstuk 1 beschrijft de gebruikte methodes en introduceert de experimentele opstelling. Het eerste deel van Hoofdstuk 5 beschrijft de molecuulbundel, het ionisatieproces, en de detectie van de ionen.

Er zijn vier belangrijke bronnen van systematische verschuivingen in de gemeten frequentie van de $GK^1\Sigma_q^+$ - $X^1\Sigma_q^+$ resonantie: frequentie chirp, AC-Stark effecten, Doppler effecten en hyperfijn structuur. De frequentie chirp wordt verminderd met behulp van een EOM in de optische trilholte. Eventuele resterende chirp wordt per puls gemeten en gecompenseerd. Hoofdstuk 4 beschrijft het effect van frequentie chirp tijdens het genereren van pulsen, en het schema dat gebruikt is om het te meten en tegen te gaan. Verschuivingen als gevolg van AC-Stark effecten worden bepaald door de overgang bij verschillende laserintensiteiten te meten. Verschuivingen door het eerste orde Doppler-effect worden grotendeels opgeheven door de overgang in een configuratie uit te voeren waarbij de twee fotonen uit tegengestelde richting komen. Resterende Doppler-verschuivingen worden bepaald door de overgang te meten bij verschillende snelheden van de moleculaire bundel. Eventuele fouten als gevolg van hyperfijnsplitsingen, die niet aanwezig zijn in para- H_2 , zijn bepaald aan de hand van de bekende hyperfijnstructuur van hogere Rydberg toestanden.

De $GK^1\Sigma_g^+$ - $X^1\Sigma_g^+$ overgang is gemeten met een nauwkeurigheid van minder dan een MHz in beide spin-isomeren van H₂ (ortho- en para-H₂) en in D₂ en HD. Deze vier metingen, en alle relevante systematische effecten, worden respectievelijk beschreven in Hoofdstuk 2, 3, 5 en 6. Deze metingen hebben geleid tot een nauwkeurige bepaling van de dissociatieenergieën van para-H₂, ortho-H₂ en D₂, met een relatieve onzekerheid van minder dan 10⁻⁹, en het zal binnenkort leiden to een nauwkeurige bepaling van de dissociatie-energie van HD. Als gevolg van deze resultaten moet de sterkte van een hypothetische vijfde kracht met een interactiebereik van 1 Å 10 ordes van grootte kleiner zijn dan de elektromagnetische kracht. Hoofdstuk 7 beschrijft de impact van de resultaten, en geeft een vooruitzicht op verdere metingen.

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