# $\begin{array}{l} \mbox{High Resolution Laser and} \\ \mbox{Synchrotron Spectroscopic} \\ \mbox{Studies on } \mathbf{H}_2 \mbox{ and } \mathbf{CO} \end{array}$



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#### VRIJE UNIVERSITEIT

### High Resolution Laser and Synchrotron Spectroscopic Studies on H<sub>2</sub> and CO

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for friends and family

You have to believe in yourself. That's the secret of success. Charles Chaplin This thesis was reviewed by the members of the reviewing committee:

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## CHAPTER **L**

### Introduction and Summary

Spectroscopy can be argued to start with Sir Isaac Newton in his optics experiments describing the rainbow of colors that combine to form white light. Since then, spectroscopy has played and continues to play a significant role in astronomy, physics and chemistry. From such spectroscopic investigations we understand the structure of atoms and molecules. The transition frequencies, line intensities, and natural linewidths provide us with information on the energy levels, transition probabilities, lifetimes of excited states, and so on. However, how much information can be obtained from the spectrum depends essentially on the attainable spectral or temporal resolution that can be achieved. Over the course of history spectroscopic studies were performed at progressively higher resolution. In this thesis, two different high-resolution spectroscopic methods, laser-based Doppler-free spectroscopy and synchrotron-based Fourier-transform absorption spectroscopy are employed. They were used to investigate the  $EF \, {}^{1}\Sigma_{g}^{+} - X \, {}^{1}\Sigma_{g}^{+}$  system of the H<sub>2</sub> molecule and the  $A^{1}\Pi - X^{1}\Sigma^{+}$  system of the CO molecule.

High-resolution spectroscopy is widely used in astrochemistry. There are nearly 180 different molecules identified thus far in the interstellar medium or circumstellar shells via their spectra. These spectra reveal properties of distant stars and galaxies, such as their chemical composition, temperature, density, mass, distance, luminosity, and relative motion. In order to extract information from those spectra, high-resolution laboratory spectra are required. Molecular hydrogen and carbon monoxide are the first and second most abundant molecules in outer space, respectively. They are very important to astronomers and physicists as tracers to investigate our universe.

The present research project was funded by NWO and its subsections CW (Chemical Sciences) and EW (covering Mathematics, Astronomy and Computer Science) via its program "Dutch Astrochemistry Network". The focus was on gas phase molecules, in particular the two most abundant molecules in the Universe, molecular hydrogen and carbon monoxide. The studies were performed in connection to observational studies, performed through optical

astronomy, by the Atomic, Molecular and Laser Physics group at VU University, addressing the use of H<sub>2</sub> and CO molecules for probing possible variations of the proton-electron mass ratio ( $\mu$ ) on a cosmological time scale. Observation of H<sub>2</sub> at high redshift, as well as in white dwarf stars, has been covered in a number of studies by the research group, see Ref. [1, 2, 3, 4, 5, 6]. Since it was realized that also the  $A^1\Pi - X^1\Sigma^+$  electronic system of CO could be used for probing varying constants in the early Universe [7], and that CO has now been detected towards the sight line of a number of quasars, the target of spectroscopic activities has shifted to probing this molecule at the highest possible resolution and accuracy. The present study, with a number of high-precision studies of CO  $A^1\Pi - X^1\Sigma^+$  bands, provides the database to search for varying constants based on CO and from a combination of H<sub>2</sub> and CO.

In 1766, Henry Cavendish produced hydrogen gas from the reaction between different acids and metals [8]. The molecule was later named hydrogen in 1783 by Antoine Lavoisier [9]. In the last century, studies of ever improving experimental accuracy are confronted with ever improving theoretical calculations for the  $H_2$  molecule. It is a benchmark molecule for testing Quantum Electro-Dynamics (QED), a theory which can be considered as a perturbative theory of electromagnetism including effects of the quantum vacuum. The success of this theory started in 1947 by Hans Bethe [10], when it explained the Lamb shift in the hydrogen atom as measured by Lamb and Retherford [11]. At present, QED has been tested to extreme precision by comparing values for the electron q-factor [12, 13] and also for the Lamb shift measurements in atomic hydrogen [14, 15]. Tests of QED were recently extended to the neutral  $H_2$  molecule, which is the first molecule to include two electrons, and hence electron correlation effects. Up until 2010, Wolniewicz [16, 17] produced the most accurate full *ab initio* calculations of the H<sub>2</sub>  $X^1\Sigma_q^+$  ground electronic state, including an estimated QED-correction term, achieving accuracies at the  $10^{-2}$  cm<sup>-1</sup> level. The measurement of the dissociation energies of H<sub>2</sub>, HD and  $D_2$  by the Zürich-Amsterdam collaboration [18, 19, 20] were used to test the newly developed framework for calculating the most recent *ab initio* calculations including relativistic and QED terms [21, 22]. These test were extended to the series of rotational energy levels in the  $H_2$  ground state [23] and to the vibrational ground tone of the molecule [24]. The excellent agreement between the experimental results and theoretical values does not only test QED theory, but also can be interpreted as giving upper bounds for the range of new interactions beyond the Standard Model (SM) of physics. In order to extend the research to highly-excited vibrational states in molecular hydrogen, we will combine accurate transition frequencies on the  $EF^{1}\Sigma_{q}^{+} - X^{1}\Sigma_{q}^{+}$  band, determined from two-photon Doppler-free laser spectra, with previous accurate measurements [25, 26] to obtain vibrational splitting frequencies.

The CO molecule was identified as a compound containing carbon and oxygen

by the Scottish chemist William Cumberland Cruikshank in 1800 [27, 28]. It is also found in the atmospheres of stars and some planets, as well as in comets and in the interstellar medium. Recently a number of high-redshift observations were reported on the  $A^{1}\Pi - X^{1}\Sigma^{+}$  system of CO, making this system a good probe to search for the possible variations of fundamental constants on cosmological timescale alongside  $H_2$ . In the SM, the fundamental constants like the dimensionless proton-to-electron mass ratio and the fine structure constant  $\alpha$  assume the role of free parameters in the theory, and the value of these constants can only be determined by experiment. In order to probe putative variations of the constants, molecular transition frequencies in laboratories on earth will be compared with those in quasar absorption systems. This requires the accurate measurement of transition frequencies and calculation of sensitivity coefficients. In this thesis, we focus on obtaining accurate transition frequencies for the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  system, against the background of probing such variations of the proton-to-electron mass ratio  $\mu$  on a cosmological timescale. While  $H_2$  is generally the molecule of choice, there are benefits for searching variation of  $\mu$  using the CO  $A^1\Pi - X^1\Sigma^+$  system in that the transitions of  $A^{1}\Pi - X^{1}\Sigma^{+}$  system lie outside the Lyman forest, so that high-quality spectra can be obtained. Moreover the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  transitions can be combined with H<sub>2</sub> transitions in the same cloud to find a possible variation of  $\mu$ , providing opportunities to assess systematic effects (that might mimic the effect of  $\mu$ -variation). The CO  $A^1\Pi$  system is of importance from a pure molecular physics perspective, in that it exhibits a celebrated case of perturbations between multiple singlet and triplet states. These phenomena have been amply studied over decades [29], but the present high-resolution studies described in this thesis provide improved and comprehensive information.

Both variations of the fundamental constants of nature as well as deviations for QED-theory may probe new interactions beyond the Standard model of physics. The SM theory concerns the electromagnetic interaction, the weak interaction and the strong interaction, where the electromagnetic interaction is many order of magnitudes stronger than other SM interactions, at least at the typical Ångström-range internuclear distances in molecules, while gravity is definitely much weaker at all length scales. So the excellent agreement between experimental results and the theory values does not only test the QED theory, but also provides upper bounds for the possible existence of new interactions beyond the Standard Model (SM) of physics.

#### Outline

In this thesis, laser based Doppler-free high-resolution spectroscopy experiments as well as vacuum ultraviolet Fourier-transform spectroscopy studies (performed at the DESIRS beamline at the Soleil synchrotron) are described. The experiments deal with spectra of molecular hydrogen and carbon monoxide. The subjects of the chapters of this thesis are outlined below.

In Chapter 2, investigation of the  $X^1\Sigma_g^+$ ,  $v = 0 \rightarrow 1$  (J = 0 - 2) rovibrational splittings in H<sub>2</sub>, HD and D<sub>2</sub> for testing quantum electrodynamics effect in molecules is presented. The energies of the splittings are determined at an absolute accuracy of  $2 \times 10^{-4}$  cm<sup>-1</sup>. This work on rotational quantum states J = 1, 2 extends the results reported in Ref. [24] on J = 0. Using a narrowband Titanium:Sapphire pulsed laser system, transition frequencies in  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0, 1) band have been determined. Combined with a previous accurate measurement on EF, v = 0 level energies, the fundamental ground tone vibrational splittings are obtained. The excellent agreement between the experimental results and the calculations provides a stringent test on the application of quantum electrodynamics in molecules, and can be used to provide bounds to new interactions beyond SM.

Chapter 3 extends the H<sub>2</sub> results in Chapter 2 to highly excited vibrational quantum states. The v = 12, J = 0 - 3 rovibrational levels of H<sub>2</sub> ground electronic state are accurately determined by two-photon Doppler-free spectroscopy at an accuracy of  $3.5 \times 10^{-3}$  cm<sup>-1</sup>. The highly vibrational excited H<sub>2</sub> molecules are produced by photodissociation of H<sub>2</sub>S. A comparison between the experimental results with the best *ab initio* calculations shows excellent agreement.

In Chapter 4, the  $A^1\Pi - X^1\Sigma^+$  band system of carbon monoxide is a new probe to search for possible variations of the proton-electron mass ratio on cosmological time scales is described. Using VUV Fourier-transform absorption spectroscopy, transition frequencies of the  $A^1\Pi - X^1\Sigma^+$  (v,0) bands for v =0-9 have been determined at an accuracy of  $\Delta\lambda/\lambda = 1.5 \times 10^{-7}$ , providing a comprehensive and accurate zero-redshift data set. Two-photon Doppler-free laser spectroscopy has been applied for the (0,0) and (1,0) bands, achieving a  $3 \times 10^{-8}$  accuracy level. Accurate sensitivity coefficients  $K_{\mu}$  for a varying  $\mu$ have been calculated for the CO  $A^1\Pi - X^1\Sigma^+$  bands.

In Chapter 5, an analysis of the perturbation effect in the CO  $A^1\Pi - X^1\Sigma^+$  (0,0) and (1,0) bands is obtained. The data base of CO  $A^1\Pi - X^1\Sigma^+$  (0,0) and (1,0) bands is obtained by two different high-resolution spectroscopic methods, a vacuum ultraviolet Fourier-transform spectrometer and a two-photon Doppler-free laser spectroscopy, with an accuracy of 0.01-0.02 cm<sup>-1</sup> and 0.002 cm<sup>-1</sup>, respectively. The combined data were used to perform an improved analysis of the perturbations by a large number of perturbing states.

Chapter 6 reports on high-precision two-photon Doppler-free frequency measurements of the CO  $A^1\Pi - X^1\Sigma^+$  fourth-positive system for (2, 0), (3, 0) and (4, 0) bands. Due to advanced techniques of two-color 2+1' resonance-enhanced multi-photon ionization, Sagnac interferometry, frequency-chirp analysis on the pulsed laser, and correction for the AC-Stark shifts, the absolute transition frequencies on the three bands (for J < 6) have been determined at an accuracy of  $1.6 \times 10^{-3}$  cm<sup>-1</sup>. These accurate transition frequencies serve as calibration reference lines for synchrotron spectra in the next chapter.

In Chapter 7, the laser-based transition frequencies of Chapter 6 are used to calibrate and analyze the CO  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands measured with the VUV-Fourier-transform spectra. Details of the perturbations in the excited states and interactions with multiple states of singlet and triplet character are presented.

Chapter 8 presents vacuum-ultraviolet photoabsorption spectra of  $N_2$  and CO recorded at 900 K using a heated free-flowing gas cell in the Fourier-transform spectrometer end station of the DESIRS beamline at the SOLEIL synchrotron. Using such a cell enabled the recording of spectral lines with high rotational quantum numbers. This allowed for the extension of the perturbation analysis that can be accessed for room temperature absorption setups.

## CHAPTER 2

## Precision spectroscopy of the $X^{1}\Sigma_{g}^{+}, v = 0 \rightarrow 1$ (J = 0 - 2) rovibrational splittings in H<sub>2</sub>, HD and D<sub>2</sub>

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Accurate experimental values for the vibrational ground tone or fundamental vibrational energy splitting of  $H_2$ , HD, and  $D_2$  are presented. Absolute accuracies of  $2 \times 10^{-4}$  cm<sup>-1</sup> are obtained from Doppler-free laser spectroscopy applied in a collisionless environment. The vibrational splitting frequencies are derived from the combination difference between separate electronic excitations from the  $X^{1}\Sigma_{a}^{+}, v = 0, J \text{ and } v = 1, J \text{ vibrational states to a common } EF^{1}\Sigma_{a}^{+}, v = 0, J$ state. The present work on rotational quantum states J = 1, 2 extends the results reported by Dickenson et al. on J = 0 [Phys. Rev. Lett. 110 (2013) 193601]. The experimental procedures leading to this high accuracy are discussed in detail. A comparison is made with full ab initio calculations encompassing Born-Oppenheimer energies, adiabatic and non-adiabatic corrections, as well as relativistic corrections and QED-contributions. The present agreement between the experimental results and the calculations provides a stringent test on the application of quantum electrodynamics in molecules. Furthermore, the combined experimental-theoretical uncertainty can be interpreted to provide bounds to new interactions beyond the Standard Model of Physics or fifth forces between hadrons.

#### 2.1 Introduction

The first modern explanation of the chemical bond between two neutral hydrogen atoms was put forth in 1927 by Heitler and London [30], and is one of the earliest applications of quantum theory, specifically that of Schrödinger's wave mechanics formulation in 1926 [31]. Heitler and London showed that by accounting for Pauli's exclusion principle [32] in combining atomic hydrogen wavefunctions to construct molecular wavefunctions, the existence of a bound molecular state is explained. Despite their calculated binding energy being off by some 30% from the contemporary experimental value, their pioneering quantum mechanical calculation for the stability of molecular hydrogen ushered the era of quantum chemistry. It is interesting to note that the Born-Oppenheimer approximation [33] was also proposed in 1927, and this approach of separating electronic and nuclear motions has largely shaped molecular theory since. The next breakthrough in *ab initio* potential calculations for H<sub>2</sub> was achieved by James and Coolidge in 1933 in their treatment of the  $(X^1\Sigma_{\sigma}^+)$ ground state [34]. Using two-electron wave functions with explicitly correlated electrons, an approach introduced by Hylleraas for the helium atom [35], they transcended the concept of electrons being in individual states as used in the Hartree-Fock method. The James-Coolidge solution relied on the variational method to determine the correct nonlinear parameters in combining the wave functions. With a set of only 13 of these wave functions, taken as a truncated basis to represent the total Hilbert space of infinite dimension, they improved the minimum energy in the Born-Oppenheimer potential of the  $X^{1}\Sigma_{g}^{+}$  state to  $38\,300 \text{ cm}^{-1}$ . This was a substantial improvement of about  $5\,500 \text{ cm}^{-1}$  with respect to the best theoretical values available at the time. Over the years improvements on the accuracy has been obtained [16, 36, 37, 38, 39, 40], and important methodical reviews can be found in Refs. [41, 42, 43, 44, 45]. The achievement of the initial studies of James and Coolidge [34] can best be appreciated considering that further improvement in the calculated potential has been only 222  $\rm cm^{-1}$  since then, obtained by Wolniewicz in 1995 with essentially the same method but with a basis of 883 wave functions [17]. At present, the Born-Oppenheimer potential energy can be evaluated to accuracies better than 15 digits using more than 22,000 basis functions [46], made possible by developments in numerical procedures and improvements in computing power. The precision of the calculated Born-Oppenheimer energy may be considered exact for the purpose of comparisons with experiment. Corrections beyond the Born-Oppenheimer approximation need to be evaluated to improve upon the accuracy of the *ab initio* values. In addition to adiabatic and nonadiabatic effects comprising the non-relativistic Born-Oppenheimer corrections, it is also necessary to account for accurate relativistic and radiative or quantum electro-



**Figure 2.1** – (Color online) Graphical representation of the level energy contributions (in  $cm^{-1}$ ) as corrections to the Born-Oppenheimer approximation level energy, with respect to the dissociation limit, of the  $X^{1}\Sigma_{g}^{+}$ , v = 0, J = 0state for  $H_{2}$ , HD and  $D_{2}$ . BO: Born-Oppenheimer energy; ad: adiabatic; nad: nonadiabatic; rel: relativistic; QED: radiative corrections.

dynamic (QED) corrections. Until up to 2010, the work of Wolniewicz [17] that included estimates of radiative corrections, had constituted the state-of-the-art for calculations of level energies in the  $X^1\Sigma_g^+$  ground state of molecular hydrogen. This led to a calculated energy of the actual ground state (or equivalently the dissociation limit) to an accuracy 0.01 cm<sup>-1</sup>. The recent work of Pachucki, Komasa and co-workers has achieved breakthroughs in the evaluation of nonadiabatic effects [47, 48] as well as relativistic and radiative corrections [49, 50], resulting in accurate level energies of  $X^1\Sigma_g^+$  rovibrational levels [21, 22, 51]. In Fig. 2.1 the different contributions to the level energy of the lowest quantum state ( $X^1\Sigma_g^+, v = 0, J = 0$ ) with respect to the dissociation energy of molecular hydrogen are represented graphically to give an impression of the scale of the corrections.

Theoretical and experimental efforts on the determination of ground state level

energies in molecular hydrogen mutually stimulated improvements on both fronts as soon as more accurate values were obtained. As an illustration, consider the dissociation energy of the  $X^1 \Sigma_g^+$  ground state, a benchmark quantity for the comparison of experiment and theory. The experimental determination of the dissociation energy by Witmer [52] in 1926 already gave results within 3% of the modern value, an order of magnitude better than the Heitler-London calculations as mentioned. The James-Coolidge calculations in 1933 [34] resulted in a dissociation energy that is within  $10^{-4}$  of the present value, matched later by the experimental determination by Beutler in 1935 [53] that was also accurate to within  $10^{-4}$ . This lively dynamics continued through the 1960s-1970s, between the experimental efforts of Herzberg and co-workers [54, 55, 56] and theoretical efforts by Kolos and co-workers [36, 39]. In the middle of the 1990s, the theoretical result of Wolniewicz [17] for the dissociation energy was expressed in 8 significant digits, although the uncertainty was not explicitly mentioned. Eyler and co-workers determined the dissociation limit to an accuracy of  $0.01 \text{ cm}^{-1}$  [57] in 2004, improving upon their previous result [58] using the same method. The most accurate experimental dissociation energy for  $H_2$ was obtained in 2009 by Liu *et al.* [18], and later extended to  $D_2$  [20] and HD [19]. Remarkably, accurate theoretical values for  $H_2$  and  $D_2$  dissociation energies [21] as well as HD [51] were presented a short time thereafter.

Ab initio theory can also be tested through a comparison with the experimental determinations of level splittings in the rovibrational manifold of the ground state. Herzberg first predicted, in 1938, that it should be possible to record rovibrational transitions in the ground state manifold [59], and later discovered the quadrupole spectrum in 1949 by photographing a total of eight lines in the (2,0) and (3,0) bands [60]. Subsequently the quadrupole spectrum including the fundamental (1,0) band was investigated by several other groups, for example by Rank and co-workers [61, 62]. The measurements by Bragg *et al.* [63]greatly improved the accuracy of the spectroscopy of the quadrupole bands and was until recent years considered as the most accurate work on the direct measurement of the vibrational splittings. Laser-based direct excitation of the weaker (4,0) and (5,0) overtone quadrupole bands was performed in the visible domain [64]. Later investigations using cavity-ring down spectroscopy on the  $H_2$  (3,0) overtone band were carried out by Robie *et al.* [65] using a pulsed source and Hu et al. [66, 67] using a cw source. Campargue and co-workers have recently performed high-resolution determinations of the (2,0) overtone bands of  $H_2$  [68] and  $D_2$  [69] using quantum cascade lasers. Maddaloni *et* al. [70] performed precision measurements using cavity-ring down techniques for the fundamental band of  $D_2$ .

The quadrupole excitations in the ground electronic state described above have very low transition probabilities. The ground state energy splittings can be determined indirectly from appropriate combinations of dipole-allowed transitions

between ground state and excited electronic states. For example, the strongest molecular hydrogen transitions in Lyman  $(B^1\Sigma_u^+ - X)$  and Werner  $(C^1\Pi_u - X)$ bands have been used to derive ground state rovibrational constants. Using this approach, Stanke et al. [71] derived accurate ground state molecular constants based largely on the experimental data of Dabrowski [72] but also including quadrupolar transitions. The natural linewidths of transitions in the Lyman and Werner bands ultimately limit the accuracy that can be achieved [73, 74]. In contrast, the rovibrational levels of the lowest-lying excited singlet gerade state  $EF^1\Sigma_a^+$  of molecular hydrogen have longer natural lifetimes, even up to 150 ns [75], since one-photon transitions to the ground state are forbidden. The gerade states can be accessed from the ground state through two-photon spectroscopies, which also allow for more accurate level energy determinations. This first excited singlet gerade state in molecular hydrogen, the  $EF^{1}\Sigma_{g}^{+}$  state, shown to correspond to a double-well potential [76], has been investigated thoroughly over the years. Eyler and coworkers performed a number of laser spectroscopic studies of increasing accuracy [57, 77, 78, 79, 80]. A determination of frequencies of Q-branch transitions in the lowest  $EF^{1}\Sigma_{q}^{+} - X^{1}\Sigma_{q}^{+}$  (0,0) band was performed with improved accuracy by Hannemann et al. [26]. The lowest rotational levels in the  $EF^{1}\Sigma_{g}^{+}$  state derived from the latter study were used as anchor lines, to which a large number of levels in the excited state manifold, obtained from high-resolution Fourier-transform studies, were connected to the ground state [25, 81]. Accurate values for level energies of the high rotational states up to J = 16 in the  $E^{1}\Sigma_{g}^{+}, v = 0$  electronic state were obtained in Ref. [23] using UV two-photon spectroscopy.

In this paper, we present accurate experimental and theoretical values for the fundamental vibrational splitting of H<sub>2</sub>, D<sub>2</sub> and HD. This extends a recent report [24] on the *rotationless* ground tone frequencies of hydrogen and its isotopomers, now also including values for J = 1 and 2 levels. The experimental determination of the fundamental vibrational splitting is based on combination differences of the transition frequencies between the  $X^1\Sigma_g^+$  and  $EF^1\Sigma_g^+$  states, measured by two-photon Doppler-free spectroscopy.

#### 2.2 Experiment

In this study, high-precision UV two-photon spectroscopy is performed on vibrationally excited molecular hydrogen to determine the transition frequencies of the Q(0), Q(1) and Q(2) lines in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,1)$  band for all three isotopomers H<sub>2</sub>, HD and D<sub>2</sub>. In combination with the previous determination by Hannemann *et al.* [26] for the three Q-branch lines in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,0)$  band, accurate values of the fundamental ground tone splittings are obtained for J = 0, 1 and 2 rotational levels. The excitation



**Figure 2.2** – (Color online) Potential energy diagram of molecular hydrogen, showing the relevant electronic states accessed in the present spectroscopic investigation. The indirect determination of the fundamental vibrational splitting  $E_{01}$  relies on the measurement of Q-line transitions the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) band obtained in the present study and on the measurement of the Q-lines in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,0) band, obtained in Ref. [26]. The excitation channels are indicated by (1) and (0), respectively. An auxiliary laser beam of 355-nm radiation was used in the REMPI detection scheme. The squared moduli of the vibrational wavefunctions are indicated in the inset.

scheme of the present and previous measurements is drawn in Fig. 2.2, with the potential energy curves of the relevant electronic states depicted, and the probed two-photon transitions indicated. The experimental setup is schematically shown in Fig. 2.3, with blocks representing the narrowband laser source, the frequency calibration setup and the molecular beam machine in which the Doppler-free spectroscopy is performed.



Figure 2.3 – (Color online) A schematic layout of the experimental setup, with the laser system, the frequency calibration setup and the molecular beam apparatus with the counter-propagating laser beams in a Sagnac configuration for Doppler-free two-photon spectroscopy. B.S.: beam splitter; Sk.: skimmer. See text for further details.

#### Narrowband laser source

A schematic representation of the laser system is shown as part of Fig. 2.3. The Ti:Sa pulsed laser system is based on an injection-seeded oscillator-amplifier scheme. A continuous wave (cw) Ti:Sa laser serves as the injection-seed for the pulse generation, and is also used to lock the length of the oscillator cavity by a Hänsch-Couillaud scheme. The oscillator cavity is pumped with  $\sim 8$  mJ of 5-ns pulses of the 532-nm (second-harmonic) output from an injection-seeded Nd:YAG laser operating at 10-Hz repetition rate. The resulting pulse from the oscillator cavity is further amplified in a 9-pass bowtie Ti:Sa amplifier pumped with  $\sim 200$  mJ of the same Nd:YAG pump laser. Typical output pulse energies of the amplifier are approximately 45 mJ at the fundamental wavelength of 844 nm. The pulse duration of the fundamental IR pulses is  $\sim 20$  ns corresponding to a Fourier-limited bandwidth of  $\sim 22$  MHz. An extensive

description of the laser system and its operation can be found in Ref. [82], while its performance in the measurements on the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,0) band were described in Ref. [26]. A 1-mm diameter pinhole is used as a spatial filter for the output of the Ti:Sa oscillator-amplifier system before the subsequent harmonic conversion. Spatial filtering selects a smaller portion of the beam thereby reducing frequency chirp effects across the beam profile, which is crucial in subsequent frequency calibrations. The spatially-filtered pulsed output is frequency up-converted in two successive frequency-doubling stages (using  $\beta$ -Barium Borate (BBO) crystals) to yield fourth-harmonic UV radiation, with approximately 350  $\mu$ J pulse energies at 211 nm.

#### Two-photon Doppler-free REMPI

Two-photon Doppler-free techniques were combined with resonantly enhanced multi-photon ionization (REMPI) in the spectroscopic experiment. In an isotropic gas sample, two-photon absorption from two counter-propagating laser beams results in the cancellation of first-order Doppler shifts. However, the application in a molecular beam with a defined unidirectional trajectory, results in residual first-order Doppler shifts if there is a misalignment between the counter-propagating laser beams. To improve the laser beam alignment, an interferometric scheme is implemented [83]. The UV probe beam is split in two arms of equal intensity and arranged as part of a Sagnac interferometer, as depicted in Fig. 2.3, with the interference fringes indicating the degree of alignment. Narrow bandwidth UV radiation at 211 nm was used to probe the two-photon transitions in  $H_2$ , while HD and  $D_2$  measurements required 209 and 207 nm, respectively. A 355-nm laser pulse is used to further ionize the molecules excited in the  $EF^{1}\Sigma_{g}^{+}$ , with the ionization laser delayed by 30 ns with respect to the probe laser. The  $H_2^+$  molecular ions are accelerated by electrostatic lenses and then traverse a field-free time-of-flight (TOF) region. The ions impinge upon a multi-channel plate (MCP) detector attached to a phosphor screen, with the resulting fluorescence collected onto a photomultiplier tube (PMT), for signal registration.

#### **Discharge** excitation

The preparation of vibrationally excited molecules in  $X^1\Sigma_g^+ v = 1, J$  is achieved through electron bombardment of the molecular beam in a discharge source similar to that employed in Ref. [84]. The discharge source is a ceramic pinhole nozzle with metallic electrodes (depicted in the top left corner of Fig. 2.3), attached to a pulsed solenoid valve (General Valve Series 9) operated at 10-Hz. The molecular beam pulse is discharged by applying a high voltage pulse to the cathode, with the discharge electrons moving upstream against the molecular beam trajectory. The anode is kept at the same potential as the valve orifice to avoid disturbing the valve operation. Sufficient population of vibrationally excited molecules was achieved at a voltage of approximately -750 V applied to the cathode. To reduce ions produced in the same discharge from reaching the detection zone, a pair of deflection plates was installed near the end of the discharge nozzle. The vibrationally excited molecular hydrogen passes through a skimmer (2-mm diameter) before entering the interaction zone where the UV spectroscopy takes place.

#### **Frequency** calibration

The fundamental frequency  $f_{\rm IR}$  is calibrated by referencing part of the light from the Ti:Sa cw-seed laser to a (Menlo Systems M-comb femtosecond fiber) frequency comb acting as an optical frequency ruler. The carrier-envelope phase offset frequency  $f_0$  and repetition frequency  $f_{rep}$  of the frequency comb are locked to a local Rubidium-clock that is referenced to the global positioning system. A heterodyne beat note  $f_b$  is made between the cw-Ti:Sa laser and the frequency comb modes on an avalanche photodiode, which is counted electronically. In practice, a number of frequency comb modes participate in the heterodyne process contributing to background noise. Thus, the frequency comb spectrum is dispersed with a grating and subsequent spatial filtering of the unwanted modes is implemented to increase the signal-to-noise ratio in the  $f_b$  measurement. The optical frequency of the UV laser system  $f_{\rm UV}$  can be expressed as

$$f_{\rm UV} = 4 \times f_{\rm IR} = 4 \times (nf_{rep} + f_0 + f_b + f_{ch}),$$

where the prefactor of 4 accounts for the harmonic order, and n is mode number of the frequency comb component used. The cw-pulse frequency offset  $f_{ch}$ of the Ti:Sa system due to frequency chirp will be discussed below. The mode number determination follows from a coarse calibration of the laser using a Burleigh wavemeter accurate to ~30 MHz, which is sufficient for an unambiguous mode assignment since  $f_{rep} \sim 250$  MHz. The sign of the respective frequency contributions to  $f_{\rm IR}$  may be positive or negative but can be easily determined in practice.

#### Ti:Sa cw-pulse frequency offset

In the frequency calibration procedure, the Ti:Sa cw-seed optical frequency  $f_{\rm IR}$  is determined, while the output of the oscillator-amplifier Ti:Sa *pulsed* laser system is actually used in the spectroscopy, after frequency upconversion to the 4<sup>th</sup> harmonic. Any frequency offset  $f_{ch}$  between the Ti:Sa cw-seed frequency and pulsed output frequency needs to be determined, where it is possible that the optical frequency is time-dependent within the laser pulse.

The pulse generated in the Ti:Sa oscillator is subject to cavity-mode pulling effects, as a result of an optically-induced change in refractive index of the Ti:Sa crystal due to the intense 532-nm pump pulse, contributing to a frequency offset. The actual cavity resonance in the presence of the pump pulse is then frequency-shifted with respect to the locking point of the unpumped cavity. The frequency shift can be separated into contributions from a thermal change of the refractive index  $\Delta n_{\rm th}$  and an effect from the population inversion  $\Delta n_{\rm inv}$  in the Ti:Sa crystal [82]. The total effective frequency offset, typically tens of MHz in the fundamental  $f_{\rm IR}$ , can be compensated by controlling the lock setpoint of the Ti:Sa oscillator, e.g. locking at the side of the fringe in the Hänsch-Couillaud scheme.

A related phenomenon is spatial frequency chirp where the pulsed optical frequency varies across the transverse beam profile of the laser beam. This effect occurs in the amplification stage, because subsequent passes sample a different area within the pump beam profile that has a Gaussian intensity distribution. The spatial frequency difference from either edges of the beam profile was found to be a few MHz with respect to  $f_{\rm IR}$ . To minimize such a spatial frequency offset, a 1-mm pinhole after the Ti:Sa amplifier acts as a spatial filter while still providing sufficient energy for the frequency upconversion process.

The cw-pulse offset frequency  $f_{ch}$  is measured by heterodyning the amplified pulsed output of the Ti:Sa system with part of the cw-seed that is shifted by 250 MHz using an acousto-optic modulator (AOM). The resulting beat signal from a fast photo-detector is recorded with an oscilloscope for further frequency chirp analysis [85, 86]. A single-shot frequency chirp analysis is performed for every Ti:Sa pulse in order to account for the frequency offset  $f_{ch}$ during each measurement point. A more detailed description of the frequency chirp measurements and analysis for the Ti:Sa pulsed laser system is given in Refs. [26, 82].

#### Assessment of systematic effects

A spectral recording of the  $D_2 EF^1\Sigma_g^+ - X^1\Sigma_g^+(0,1) Q(1)$  two-photon transition is shown in Fig. 2.4. The full-width half-maximum of the spectral lines is ~ 60 MHz and is well-approximated by a Gaussian profile, limited by the instrumental linewidth of the UV laser source, and accounting for the twophoton excitation. As a test of robustness, the obtained line positions were also checked when imposing different background levels. The uncertainty contribution is then estimated to be better than 500 kHz for most scans of good signal-to-noise ratio. For more noisy spectra, the line fitting uncertainty contribution is difficult to separate from statistical scatter, thus it is subsumed into the statistics entry. Several measurements of a specific transition taken over



**Figure 2.4** – (Color online) Recording of the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,1) Q(1)$  twophoton transition in  $D_{2}$ . A Gaussian profile (blue line) fitted to the averaged datapoints (in red) is shown.

several days, demonstrate reproducibility of within  $\sim 2$  MHz in the transition frequency.

#### ac-Stark effect

An important systematic effect is the ac-Stark frequency shift induced by the power density of the probe radiation. The use of a separate ionization laser, delayed with respect to the probe, allows for sufficient detection efficiency even at a reduced probe beam intensity, thereby minimizing the ac-Stark shift. The ac-Stark measurements are performed in two different beam configurations, referred to as (I) and (II). For most of the measurements, the UV beam is collimated with a beam diameter of 0.5 mm, using a combination of concave mirrors, that also serves to reduce beam astigmatism. This configuration (I) is typical for low UV power density. An additional benefit of configuration (I) is



**Figure 2.5** – (Color online) Assessment of the ac-Stark effect for the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) Q(0) transition in D<sub>2</sub> plotted against the 207-nm probe power density in the interaction zone. Blue datapoints were collected using focused probe beams (Conf. II), while red datapoints were taken with collimated probe beams (Conf. I) as also shown in the inset.

that it reduces residual first-order Doppler shifts compared to the case when using counter-propagating beams with curved wavefronts [80]. Using (I), a 355-nm laser pulse, delayed by 30 ns relative to the probe beam, was employed in order to ionize molecular hydrogen in the  $EF^{1}\Sigma_{g}^{+}$  state. To aid in the ac-Stark shift assessment and to improve the extrapolation to the field-free case, a second configuration is implemented, referred to as (II). In this configuration, a lens with 1-m focal length is placed before the beam splitter in Fig. 2.3, thus reducing the beam diameter to ~ 80  $\mu$ m in the interaction region so that the power density is increased by a factor ~ 40 with respect to that of (I). The intensity of the spectroscopy UV beam in (II) is sufficient to induce ionization, so that a separate ionization laser is not required.

Measurements are performed for different probe beam intensities in both configurations and the results are illustrated in Fig. 2.5. The measurements for higher power densities (II) are shown in the full graph, while the measurements at low power density (I) are enlarged in the inset. The field-free transition frequency at zero intensity is obtained from a weighted linear fit of the combined measurement results of (I) and (II). The horizontal axis represents the relative power density and is derived from a measurement of the probe beam intensity and a measurement of the beam diameter at the interaction region. It is worth noting that for the energy range between 30 and 300  $\mu$ J in (I), the ac-Stark frequency shifts are within statistical scatter. The estimated error from the ac-Stark effect is deduced from the error of the intercept determined in the weighted linear fit, with the extrapolated field-free frequency estimated to be accurate to ~ 0.4 MHz. This extrapolation procedure was performed for every transition measured.

#### dc-Stark effect

The dc-Stark effect is avoided by pulsing the voltages of the ion extraction plates so that the transitions are probed under dc field-free conditions. However, no measurable change in the transition frequencies was observed when the extraction fields were operated in either pulsed- or dc-mode, and we therefore estimate a contribution of  $\leq 0.1$  MHz on the systematic uncertainty due to the dc Stark effect.

#### Laser beam alignment

The residual first-order Doppler shifts estimated from the Sagnac interferometer alignment of the counter-propagating probe beams were experimentally verified by purposely misaligning the probe beams, where the resulting shifts were found to be below statistical scatter. Further tests were also performed by using mixed samples of molecular hydrogen and krypton to reduce the speed of H<sub>2</sub>. More finely-tuned molecular beam velocities were obtained by varying the delay between the timing of the valve opening and the trigger of the laser pulse, by means of which molecules in the leading, middle and trailing parts of the gas pulse are probed. Fig. 2.6 shows the frequency measurements of the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) Q(1) line for the six different H<sub>2</sub> beam velocities thus obtained. No effect above the statistical uncertainty is observed.

#### **Pressure shifts**

To assess possible pressure shifts, we use the pressure shift coefficient for Rydberg states from Ref. [55] of 5.7(5) cm<sup>-1</sup>/amagat as an upper limit, noting that for the pure ground electronic state, quadrupole transition shifts are in the order of  $\sim 3 \times 10^{-3}$  cm<sup>-1</sup>/amagat, see e.g. [68]. From local gas densities used in the experiment, an upper limit for the pressure shift of 0.06 MHz is estimated.



**Figure 2.6** – (Color online) Transition frequency of the  $H_2$  Q(1) line measured at different molecular beam rms speed, obtained from different concentrations of  $H_2$ -Kr mixtures, and time delay settings between valve opening and laser trigger.

#### Uncertainty estimates

Table 2.1 summarizes the uncertainty contributions in MHz from different error sources in the determination of the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,1)$  transitions. Systematic corrections were applied separately for each spectral recording, for example for the frequency chirp and ac-Stark shift. The statistics entries denote the statistical  $1\sigma$  standard deviations of all the measurements after the contributions of various systematic effects have been corrected for. The uncertainties in the determination of the line positions are not indicated as they are already included in the statistical entry, where the averaging is weighted by uncertainty in the line fitting for each recorded spectrum. The data collection for each line covered a period of different days, where the different transitions were remeasured throughout the whole measurement period to confirm the reproducibility of the results.

	Contribution	Species	Unc.
(i)	ac-Stark <sup>a</sup>		< 0.4
(ii)	dc-Stark		< 0.1
(iii)	frequency chirp <sup>a</sup>		2.0
(iv)	frequency calibration		0.1
$(\mathbf{v})$	residual 1st-order Doppler	$H_2$	0.5
		HD	0.3
		$D_2$	0.3
(vi)	2nd-order Doppler	-	< 0.1
(vii)	pressure shift		< 0.1
(viii)	statistics	$H_2$	$1.5^{\mathrm{b}}$
		ΗĎ	$1.6^{\circ}$
		$D_2$	$1.9^{d}$
Total	Uncertainty <sup>e</sup>	$H_2$	2.6
	v	HĎ	2.6
		$D_{2}$	2.8

**Table 2.1** – Estimated systematic and statistical uncertainty contributions for the frequency calibrations of the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) transitions in  $H_{2}$ , HD and  $D_{2}$ . The uncertainty values (Unc.) are given in MHz.

<sup>a</sup> ac-Stark and chirp offsets are corrected for and not indicated in the table.

 $^{\rm b}$  Standard deviation based on 63 measurements.

<sup>c</sup> Standard deviation based on 69 measurements.

<sup>d</sup> Standard deviation based on 64 measurements.

<sup>e</sup> Quadrature sum of errors.

#### 2.3 Results

Q-branch transition frequencies in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) band are listed in Table 2.2 for H<sub>2</sub>, HD, D<sub>2</sub>. The Q(1) and Q(2) transitions for each isotopomer extend the rotationless transitions reported by Dickenson *et al.* [24]. Also listed in Table 2.2 are the corresponding transition frequencies in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$ (0,0) band taken from Hannemann *et al.* [26]. The improved uncertainties for the present  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) transitions are primarily due to the reduction in the spatial frequency chirp of the Ti:Sa laser system output by spatial filtering. The data on the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) band presented here

**Table 2.2** – Transition frequencies for Q-lines in the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,1) band in H<sub>2</sub>, HD and D<sub>2</sub>. Data for the  $EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}$  (0,0) band from Ref. [26]. All values in  $cm^{-1}$ .

	Q(0)	Q(1)	Q(2)			
	$EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,1)$					
$H_2$ HD	$\begin{array}{c} 95003.62055(10)\\ 95669.18610(10) \end{array}$	$\begin{array}{c} 94954.47739(10) \\ 95631.61343(10) \end{array}$	94 856.717 48 (10)			
$D_2$	96467.83202(10)	96442.20932(10)	96 391.100 00 (10)			
$EF^{1}\Sigma_{g}^{+} - X^{1}\Sigma_{g}^{+}(0,0)$						
$H_2$ HD	$\frac{99164.78691(11)}{99301.34662(20)}$	$\frac{99109.73139(18)}{99259.91793(20)}$	99 000.183 01 (11)			
$D_2$	99 461.449 08 (11)	99 433.716 38 (11)	99378.39352(11)			

are in agreement with results of Eyler *et al.* [77], with the present results representing a 100-fold improvement over the previous measurement.

Ab initio values for the vibrational energy splittings in the  $X^1\Sigma_g^+$  electronic ground state were presented in Refs. [21, 22] for H<sub>2</sub> and D<sub>2</sub> while the rovibrational level energies of the HD ground state were given in Ref. [51]. These stateof-art calculations are based on Nonadiabatic Perturbation Theory (NAPT) [47, 48] to obtain the nonrelativistic energy contributions, while the nonrelativistic quantum electrodynamics (NRQED) formalism [49, 87, 88] is used to pertubatively obtain the relativistic and QED energy terms. More accurate theoretical values for the rotationless transitions of  $H_2$ , HD and  $D_2$  were presented in Ref. [24]. The theoretical vibrational energy splittings are summarized in Table 2.3, where the various energy contributions are separately listed, including the estimated uncertainties where available. The most accurate values are for the rotationless transitions from Ref. [24] with accuracies of better than  $1 \times 10^{-4}$  cm<sup>-1</sup>. For the J = 1, 2 transitions of H<sub>2</sub> and D<sub>2</sub>, accurate values were obtained from the supplementary material of Komasa et al. [22], however, only the accuracy of the total level energies was indicated. The obtained fundamental vibrational transition energies are estimated to be accurate to  $1 \times 10^{-3}$  cm<sup>-1</sup>. For the  $J = 1 \rightarrow 1$  HD transition, level energies from Pachucki and Komasa [51] were used, however, the energy contributions were not separately indicated. The estimated theoretical uncertainty for the more accurate rotationless transition energies stems from the better uncertainty of the nonadiabatic corrections. This estimate is aided by available theoretical results for the rotationless vibrational splittings from Adamowic and co-workers [71, 89, 90], using an independent theoretical methodology based on a variational procedure to obtain the nonadiabatic wave functions. Similar calculations for transitions involving  $J \neq 0$ , however, are not available. Since Komasa, Pachucki and coworkers obtain transition energies using the same method for the rotationless case as for all J quantum numbers, the original uncertainty estimates indicated in Refs. [21, 22, 51] are likely to be overestimated.

**Table 2.3** – Ab initio values for the fundamental vibrational energy splittings  $(v = 0 \rightarrow 1)$  of the  $X^1\Sigma_g^+$  ground state for the three isotopomers  $H_2$ , HD and  $D_2$ . The different columns indicate the transitions labeled by the rotational quantum numbers of the states involved. All values are in  $cm^{-1}$  with 1 $\sigma$  uncertainties given in between parentheses (). For the rotationless transitions, values without indicated uncertainties have negligible contributions, limited by numerical precision. For the relativistic and QED effects,  $\mathcal{R}$  denotes the Rydberg constant and the order in  $\alpha$  is indicated for each correction. The higher-order term HQED also includes estimates of the next order corrections. For the  $J = 1 \rightarrow 1$  and  $J = 2 \rightarrow 2$  values the combinations are taken from Refs. [21, 22, 51] where binding energies are listed separately for each (v, J) level; here the uncertainties are taken in quadrature from both independent values. For the  $J = 0 \rightarrow 0$  values a cancellation of uncertainties is assumed as discussed in Ref. [24].

H <sub>2</sub>	$J=0\to 0$	$J=1\to 1$	$J = 2 \rightarrow 2$	
Born-Oppenheimer	4163.40350	4157.4837	4145.6805	
Adiabatic	-1.40284	-1.3963	-1.3832	
Nonadiabatic	-0.83649	-0.8354	-0.8335	
Nonrel subtotal $(\alpha^0 \mathcal{R})$	4161.16416(1)	4155.2520	4143.4638	
Relativistic $(\alpha^2 \mathcal{R})$	0.02341(3)	0.0232	0.0227	
QED $(\alpha^3 \mathcal{R})$	-0.02129(2)	-0.0212	-0.0211	
HQED $(\alpha^4 \mathcal{R})$	-0.00016(8)	-0.0002	-0.0002	
$\operatorname{Rel} + \operatorname{QED} \operatorname{subtotal}$	0.00196(9)	0.0018	0.0014	
Theory total	4161.16612(9)	4155.2538(9)	4143.4653(9)	
HD	$J=0\to 0$	$J=1\to 1$		
Born-Oppenheimer	3633.71956	_		
Adiabatic	-0.93259	_		
continued on next page				

HD	$J = 0 \rightarrow 0$	$J = 1 \rightarrow 1$	•
Nonadiabatic	-0.62872	_	
Nonrel subtotal ( $\alpha^0 \mathcal{R}$ )	3632.15826(1)	—	
Relativistic $(\alpha^2 \mathcal{R})$	0.02093(2)	_	
QED $(\alpha^3 \mathcal{R})$	-0.01863(2)	_	
HQED $(\alpha^4 \mathcal{R})$	-0.00014(7)	—	
$\operatorname{Rel} + \operatorname{QED} \operatorname{subtotal}$	0.00216(8)	_	
Theory total	3632.16041(8)	3628.3044(10)	
D <sub>2</sub>	$J = 0 \rightarrow 0$	$J = 1 \rightarrow 1$	$J=2\rightarrow 2$
Born-Oppenheimer	2994.44084	2992.3295	2988.1133
Adiabatic	-0.52150	-0.5204	-0.5180
Nonadiabatic	-0.30447	-0.3043	-0.3040
Nonrel subtotal ( $\alpha^0 \mathcal{R}$ )	2993.61487(1)	2991.5048	2987.2913
Relativistic $(\alpha^2 \mathcal{R})$	0.01771(2)	0.0176	0.0175
QED $(\alpha^3 \mathcal{R})$	-0.01539(2)	-0.0154	-0.0153
HQED $(\alpha^4 \mathcal{R})$	-0.00012(6)	-0.0001	-0.0001
Rel + QED subtotal	0.002 20 (7)	0.0021	0.0021
Theory total	2993.61708(7)	2991.5070(2)	2987.2934(2)

Ground state  $X^1\Sigma_g^+$  energy splittings are obtained from the combination differences of the  $EF^1\Sigma_g^+ - X^1\Sigma_g^+$  transition energies and are listed in Table 2.4. The indicated uncertainty of the fundamental vibrational energy splittings is the quadrature sum of the uncertainties in the particular  $EF^1\Sigma_g^+ - X^1\Sigma_g^+$ transition energies used. The difference between the experimental and theoretical results  $\Delta E$  is also listed in Table 2.4, along with the combined uncertainty  $\delta E = \sqrt{\delta E_{\exp}^2 + \delta E_{\text{the}}^2}$ , from the experimental  $\delta E_{\exp}$  and theoretical  $\delta E_{\text{the}}$  uncertainties. The accuracy of present experimental values for the vibrational transitions is predominantly limited by the  $EF^1\Sigma_g^+ - X^1\Sigma_g^+$  (0,0) results from Hannemann *et al.* [26]. For the rotationless transitions the theoretical values are more accurate than the experimental ones. However, for transitions involving J = 1, 2 the experimental results are 5 times more accurate. For the transitions listed, the difference  $\Delta E$  is statistically consistent with null within the combined uncertainty  $\delta E$ . (The 1.5 $\sigma$  deviation for the H<sub>2</sub>  $J = 0 \rightarrow 1$ comparison is compatible with expectations from statistics.) The overall com-

**Table 2.4** – Fundamental vibrational energy splittings ( $v = 0 \rightarrow 1$ ) in  $H_2$ , HD and  $D_2$ . The third column is the difference between the experimental and theoretical values,  $\Delta E = E_{exp} - E_{the}$ , while  $\delta E$  represents the combined experimental and theoretical uncertainty. All values in  $cm^{-1}$ .

	Experiment	Theory	$\Delta E$	$\delta E$		
	$J = 0 \rightarrow 0$					
$H_2$	4161.16636(15)	4161.16612(9)	0.00024	0.00017		
HD	3632.16052(22)	3632.16041(8)	0.00011	0.00023		
$D_2$	2993.61706(15)	2993.61708(7)	-0.00002	0.00017		
		$J=1\to 1$				
$H_2$	4155.25400(21)	4155.2538(9)	0.0002	0.0009		
HD	3628.30450(22)	3628.3044(10)	0.0001	0.0010		
$D_2$	2991.50706(15)	2991.5070(2)	0.0001	0.0003		
$J = 2 \rightarrow 2$						
$H_2$	4143.46553(15)	4143.4653(9)	0.0002	0.0009		
$D_2$	2 987.293 52 (15)	2 987.293 4 (2)	0.0001	0.0003		

parison demonstrates excellent agreement between the present experimental and theoretical values.

#### 2.4 Comparison to previous studies

Various methods have been employed in direct excitations of ground state rovibrational transitions that include among others quadrupole absorption studies, Raman spectroscopy and electric-field induced dipole spectroscopy. Since the first measurements of the quadrupole spectra of  $H_2$  overtone bands by Herzberg [60] using long-path classical absorption techniques, refinements have been applied through the years, e.g. by using more accurate echelle spectrometers by Rank and co-workers [61, 62, 93]. The improvements continued in the study of Bragg *et al.* [63] who employed Fourier-Transform (FT) spectroscopy techniques. Since the first measurements of Rasetti [94] and the early investigations of Stoicheff [95], the Raman spectrum has also been measured with ever increasing accuracies. From the first demonstrations by Crawford and Dagg [96] of the electric field induced dipole excitation, parallel improvements in accuracy have also been achieved by later investigators. The weak transitions



**Figure 2.7** – (Color online) Comparison of the present experimental results ( $\circ$ ) for the H<sub>2</sub> ground state fundamental band Q-branch transitions to previous studies representing the most accurate values from a particular method: from long-path absorption reported by Bragg et al. [63] ( $\bullet$ ); from Raman spectroscopy by Rahn and Rosasco [91] ( $\bullet$ ); from spectroscopy of electric field induced transitions by Buijs [92] ( $\bullet$ ). The results on empirical fitting of the global H<sub>2</sub> database by Stanke et al. [71] ( $\Delta$ ) are also included, along with the present theoretical results ( $\Box$ ).

probed necessitated high pressures that led to collisional shifts and broadening effects first investigated by May *et al.* [97, 98]. Numerous other investigations on the  $H_2$  fundamental band at varying accuracies for the transition energies include Refs. [91, 99, 100, 101].

The comparison of the present experimental results to selected previous determinations is shown graphically in Fig. 2.7 for H<sub>2</sub>. Only those investigations with the highest claimed accuracy for a particular method are included in the figure. The results of Bragg and co-workers [63] stood as the most accurate for decades, making use of Fourier Transform spectroscopy with long-path absorption samples. For the Q(1) transition, however, the result from Bragg *et al.* differs from the present result by several standard deviations. In that study, the collision-induced dipole spectrum adds a broad background signal for the (1,0) band (e.g. Fig. 2 in Ref. [63]) that could affect the determination of the line positions. The most accurate electric field induced spectrum was recorded by Buijs [92] who also employed Fourier Transform spectroscopy. For Raman spectroscopy, the most accurate measurements were performed by Rahn and Rosasco [91], using a pulsed laser source based on difference-frequency mixing. The results of Rahn and Rosasco [91] and that of Buijs [92] are in fair agreement


**Figure 2.8** – (Color online) Comparison of the present experimental results ( $\odot$ ) for the HD ground state fundamental band Q-branch transitions to previous studies representing the most accurate values from a particular method: from long-path absorption reported by Rich et al. [102] ( $\bullet$ ); from Raman spectroscopy by Veirs and Rosenblatt [100] ( $\bullet$ ); from spectroscopy of electric field induced transitions by Brannon et al. [103] ( $\bullet$ ). The results on empirical fitting of the global HD database by Stanke et al. [89] ( $\triangle$ ) are also included, along with the present theoretical results ( $\Box$ ). Note that for this energy scale the error bars for the present experimental and theoretical results are not resolved and thus overlap.

with the present results. The latter comparison suggests that electric-field induced frequency shifts are less severe than pressure-induced systematic shifts, even after pressure-shift corrections.

Durie and Herzberg [104] recorded the weak dipole absorption spectrum of the (1,0), (2,0), (3,0) and (4,0) bands in the ground state of HD. Stoicheff [95] performed Raman spectroscopy on the fundamental band of HD, while Brannon *et al.* [103] measured electric-field induced transitions in the same band. McKellar and co-workers [102, 105, 106] carried out several long-path absorption investigations covering the fundamental and overtone bands up to (6,0) band of the HD ground state. In these investigations, the pressure shifts on the transition energies were systemically studied as was the case in Ref. [107]. The Raman study of Veirs and Rosenblatt [100] also included the HD fundamental band, as well as the fundamental band for most other molecular hydrogen isotopologues. Fig. 2.8 is a graphical representation of the comparison of the present experimental results for the HD fundamental band to selected previous determinations. Rich *et al.* [102] reported the most accurate results with Fourier



**Figure 2.9** – (Color online) Comparison of the present experimental results ( $\odot$ ) for the  $D_2$  ground state fundamental band Q-branch transitions to previous studies representing the most accurate values from a particular method: from long-path absorption reported by Jennings et al. [109] ( $\bullet$ ); from Raman spectroscopy by Looi et al. [99] ( $\bullet$ ); from spectroscopy of electric field induced transitions by Brannon et al. [103] ( $\bullet$ ). The results on empirical fitting of the global  $D_2$  database by Bubin et al. [90] ( $\Delta$ ) are also included, along with the present theoretical results ( $\Box$ ). Note that for this energy scale the error bars for the present experimental and theoretical results are not resolved and thus overlap.

Transform spectroscopy on long-path absorption samples. The most accurate electric field induced spectrum was that of Brannon *et al.* [103] while Raman spectra for HD were obtained by Veirs and Rosenblatt [100].

The fundamental band of  $D_2$  was also included in the Raman spectroscopic investigations of Stoicheff [95]. Later, Looi *et al.* [99] improved upon the Raman spectroscopy, and in addition investigated pressure dependent energy shifts. Electric field induced transitions of  $D_2$  were also measured by Brannon *et al.* [103] with pressure shift corrections. McKellar and Oka [108] used a difference-frequency laser system to investigate the fundamental vibrational band of  $D_2$  in a long-path cell. Jennings *et al.* [109] performed accurate longpath absorption measurements using FT spectroscopy. A comparison of the  $D_2$ fundamental band transitions is plotted in Fig. 2.9. The older results from longpath absorption and electric-field induced spectra coincide with the present results. The results from the Raman investigations deviate considerably from the other studies including the present, suggesting systematic errors in Ref. [99]. An indirect approach through empirical fitting of Dunham coefficients have been carried out by Stanke *et al.* [71] for H<sub>2</sub>. Experimental data included in the fit came from Dabrowski [72] for Lyman and Werner band transitions, but also most ground state studies mentioned above [62, 92, 95, 100, 103, 109]. Similar global fitting analyses based on the Dunham relation was also performed by the same group for HD [89] and D<sub>2</sub> [90] resulting in similar uncertainties as in the case of H<sub>2</sub>. Remarkable accuracy was achieved for these global fits, despite considerable deviations of results from individual experiments used.

The excitation of molecular hydrogen in a collisionless environment in the present study is distinct from previous studies, where the low excitation probability required the use of dense gas samples with pressures of a few bars for detection. The recorded lines had Doppler-widths on the order of GHz and the collisional perturbation gives rise to pressure shifts amounting to 100 MHz [69]. These issues are effectively absent in the present study using molecular beam conditions. As a case in point, it is interesting to look at the claimed uncertainty of Maddaloni *et al.* [70], who deployed a high-resolution laser source based on difference-frequency-generation referenced to the Cs-clock primary standard using an optical frequency comb synthesizer. Nevertheless, a comparison with theory gives differences of 0.0015(3) and -0.0010(3) cm<sup>-1</sup> for S(0) and S(1) in Ref. [70], respectively, as pointed out in Ref. [22]. The excellent agreement of the present experimental results with the same *ab initio* calculations suggests that the systematic uncertainties in Ref. [70] might be underestimated.

#### 2.5 Testing QED and fifth forces

As can be seen in Table 2.4, the *ab initio* values of the rotationless ground tone energies are the most accurate for all isotopomers. For these energy splittings, the relativistic and QED terms exhibit the dominant uncertainty contribution to the theoretical value while the nonrelativistic energy hardly contributes to the uncertainy. By subtracting the theoretical nonrelativistic energy term from the experimental value, one obtains a hybrid experimental-theoretical determination of the relativistic and QED contribution of 0.00220(17) cm<sup>-1</sup> for H<sub>2</sub>. Comparing the latter value to the *ab initio* values represents a test of relativistic and QED calculations in molecules on the order of ~ 1%. Applying similar arguments for the dissociation limit of the ground electronic state of molecular hydrogen, and using the experimental results of Ref. [18] and theoretical values from Ref. [21], relativistic and QED calculations in molecules are verified on the order of ~ 0.1%.

The excellent agreement between theory and experiment discussed above, can be exploited to constrain effects beyond the Standard Model of Physics. Since molecular (and atomic) structure is dominated by the electromagnetic interaction, with the effects of the strong-, weak- and gravitational forces many orders of magnitudes weaker (at least for light systems as hydrogen, where weak force effects are not yet detectable), any discrepancy between measurements and theory points to new physics.

New interactions or modifications beyond the Standard Model are expected as it does not provide explanations for several phenomena, e.g. Dark Matter [110] and Dark Energy [111]. The possibility that these hypothetical new interactions or fifth forces have subtle effects in atomic or molecular structure is a complementary approach to the searches and tests in particle physics or astronomy.

Energy resonances in calculable few-body systems provide an ideal search ground. Simple systems to search for extra interactions between lepton and hadrons would be atomic hydrogen or the helium ion [112, 113], while extra hadron-hadron interactions can be probed in molecular hydrogen and molecular hydrogen ions. We express a general fifth force in terms of a Yukawa potential  $V_5(R)$  as a function of the distance R between hadrons, or the internuclear distance in molecular hydrogen:

$$V_5(R) = \alpha_5 N_1 N_2 \frac{\exp\left(-R/\lambda\right)}{R} \hbar c = \alpha_5 N_1 N_2 Y_\lambda(R), \qquad (2.1)$$

where  $\alpha_5$  is an interaction strength, and  $\lambda$  is the characteristic range of the interaction. We assume that the long-range effect (as opposed to the short range of the strong force) scales with the number of nucleons of each nucleus,  $N_1$  and  $N_2$  respectively, and we treat protons and neutrons equally. The potential  $V_5(R)$  can be considered as a perturbation on the energies of quantum states, leading to a differential energy shift  $\langle \Delta V_{5,\lambda} \rangle$  on energy level differences between states (v', J') and (v'', J''):

$$\begin{aligned} \langle \Delta V_{5,\lambda} \rangle &= \alpha_5 N_1 N_2 \left[ \langle \Psi_{v',J'}(R) \, | \, Y(r,\lambda) \, | \, \Psi_{v',J'}(R) \rangle \right. \\ &- \langle \Psi_{v'',J''}(R) \, | \, Y(r,\lambda) \, | \, \Psi_{v'',J''}(R) \rangle \\ &= \alpha_5 N_1 N_2 \Delta Y_\lambda \end{aligned}$$

where  $\Psi_{v,J}(R)$  are the wave functions representing the probability of finding the nuclei at a certain separation R within the molecule. Using accurate wave functions from Ref. [21, 22], the quantity  $\Delta Y_{\lambda}$  has been evaluated taking  $\lambda$  as a parameter in Ref. [114].  $\Delta Y_{\lambda}$  can be considered as the inherent sensitivity coefficient for a specific transition, which becomes larger as the wavefunctions of the two levels involved are more different (e.g. wavefunctions in Fig. 2.2). Thus transitions with greater  $\Delta v$  have a larger  $\langle \Delta V_{5,\lambda} \rangle$  energy shift. The largest inherent sensitivity is expected for the dissociation energy  $D_0$  since the shift is  $\langle \Delta V_{5,\lambda} \rangle = -\alpha_5 N_1 N_2 \langle \Psi_{v=0}(R) | Y(r,\lambda) | \Psi_{v=0}(R) \rangle$ . For a particular



**Figure 2.10** – (Color online) Derived bounds for the interaction strength  $\alpha_5$  of possible fifth forces relative to the fine structure constant (left vertical axis) or the gravitational force (right axis), for different interaction length range  $\lambda$  obtained from the fundamental vibration of molecular hydrogen. Similar bounds from the D<sub>2</sub> dissociation energy D<sub>0</sub> as well as rovibrational transitions in HD<sup>+</sup> are also indicated. The yellow area indicates excluded regions based mainly on constraints obtained from HD<sup>+</sup>.

transition,  $\Delta Y_{\lambda}$  is greatest for H<sub>2</sub> and least for D<sub>2</sub> since the spatial extent of the wavefunctions between any two levels, with corresponding set of quantum numbers, are more similar for D<sub>2</sub> than in H<sub>2</sub>. However, the effect of nucleon numbers, N<sub>1</sub> and N<sub>2</sub>, more than compensates for the lower  $\Delta Y_{\lambda}$  in the heavier isotopomers, so that the expected energy shift  $\langle \Delta V_{5,\lambda} \rangle$  is actually greatest for D<sub>2</sub> and least for H<sub>2</sub> for a particular transition.

An upper bound for the interaction strength  $\alpha_5$  can be be obtained from the combined experimental-theoretical uncertainty  $\delta E$  for a particular transition by the relation  $\alpha_5 < \delta E/(N_1 N_2 \Delta Y_\lambda)$ . Fig. 2.10 shows the constraint for the interaction strength  $\alpha_5$ , for certain range  $\lambda$  of the interaction, obtained from the rotationless fundamental vibrational transitions in H<sub>2</sub>, HD and D<sub>2</sub>, with the shaded area indicating the excluded region. The fifth-force interaction

strength is given in terms of the strengths of the electromagnetic force,  $\alpha$ , and the gravitational force,  $\alpha_G$ . More stringent bounds in the same length scale are discussed in Ref. [114] based on spectroscopic determinations on the dissociation energy  $D_0$  of molecular hydrogen [18, 19, 20] as well as rovibrational transitions in HD<sup>+</sup> [115, 116, 117]. Similar constraints have been extended to shorter interaction length at sub-Angstrom scales in Ref. [118] based on level splittings in exotic molecules. The interaction length scale  $\lambda$  can be associated with the mass  $m_5$  of a fifth-force carrier particle as indicated in the upper horizontal axis in Fig. 2.10. This boson mass range is complementary to the mass sensitivity range in particle accelerators on the high end, and the low-mass sensitivity in gravitational test experiments on the other extreme.

From the present measurements on level splittings of the fundamental ground tones in the hydrogen molecule and its isotopomers, a constraint on the strength of a possible fifth force between hadrons is determined to be  $|\alpha_5/\alpha| < 2 \times 10^{-8}$  for a force range of 1 Å.

#### 2.6 Conclusion

The fundamental vibrational energy splitting of  $H_2$ , HD, and  $D_2$  were determined to absolute accuracies of  $2 \times 10^{-4}$  cm<sup>-1</sup>, or a relative accuracy of a few parts in  $10^{-8}$ . The vibrational splitting frequencies are derived from the combination difference between separate electronic excitations from the  $X^{1}\Sigma_{q}^{+}, v = 0, J$  and v = 1, J vibrational states to a common  $EF^{1}\Sigma_{q}^{+}, v = 0, J$ state. Doppler-free laser spectroscopic investigation applied in a collisionless molecular beam environment leads to high accuracy, where pressure effects are negligible in contrast to studies based on gas cells. The excellent agreement between the experimental results and the calculations provides a stringent test on the application of quantum electrodynamics in molecules, and can be used to provide bounds to new interactions. Upper bounds derived from molecular hydrogen indicate that the interaction strength of possible fifth forces must be at least 8 orders of magnitude weaker than the electromagnetic strength, for a fifth-force interaction range in the order of typical internuclear distances of  $\sim 1$ A. This brings molecular spectroscopy studies again to the forefront of physics, reminiscent of the early days of quantum mechanics.

#### 2.7 Acknowledgments

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# CHAPTER 3

### Test of quantum chemistry in vibrationally-hot hydrogen molecules

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Precision measurements are performed on highly excited vibrational quantum states of molecular hydrogen. The v = 12, J = 0 - 3 rovibrational levels of  $H_2(X^1\Sigma_g^+)$ , lying only 2000 cm<sup>-1</sup> below the first dissociation limit, were populated by photodissociation of  $H_2S$  and their level energies were accurately determined by two-photon Doppler-free spectroscopy. A comparison between the experimental results on v = 12 level energies with the best ab initio calculations shows good agreement, where the present experimental accuracy of  $3.5 \times 10^{-3}$  cm<sup>-1</sup> is more precise than theory, hence providing a gateway to further test theoretical advances in this benchmark quantum system.

#### 3.1 Introduction

Quantum chemistry started as a pioneering application of quantum mechanics, when Heitler and London explained in 1927 the existence of an attractive bonding state between the two hydrogen atoms to form the ground state of molecular hydrogen [30]. Since then, H<sub>2</sub> has been a canonical test system, where innovations in *ab initio* theory, most notably by Kolos and Wolniewicz [17, 36] and experimental measurement techniques, most notably by Herzberg and coworkers [54, 55, 119] have mutually stimulated each other as a driving force toward the highest accuracies [120]. Similar highly-accurate comparisons between theory and experiments are also actively pursued in molecular hydrogen ions  $H_2^+$  and  $HD^+$ , where accuracies achieved in calculations are better, owing to their simpler three-body configuration [115, 116, 121]. This simplicity on the other hand, makes the one-electron ion system to be atypical of molecules as it does not feature electron correlations, which form an essential ingredient in the quantum chemistry of molecules and condensed matter systems for which treatment of H<sub>2</sub> serves as a benchmark.

In recent years, great progress has been made in the quantum chemical calculations of the energy level structure of the H<sub>2</sub>  $X^{1}\Sigma_{g}^{+}$  ground electronic state. For example, the most recent calculation of the chemical bonding energy or dissociation limit  $D_{0}$  of the ground electronic state has an accuracy at the  $10^{-3}$ cm<sup>-1</sup> level, while nearly equally accurate binding energies were calculated for the entire manifold of rovibrational states [21, 22]. To achieve these accuracies, the Born-Oppenheimer (BO) potential energy data points were calculated to  $10^{-9}$  cm<sup>-1</sup> accuracy [46] resulting in BO-level energies of  $10^{-5}$  cm<sup>-1</sup> accuracy. Calculations of adiabatic corrections to the BO energy [122] yield accuracies of  $10^{-6}$  cm<sup>-1</sup>, while non-adiabatic energy corrections were determined at uncertainties at the ~  $10^{-4}$  cm<sup>-1</sup> level [47]. At such level of precision the relativistic and radiative or quantum electrodynamic (QED) effects, amounting to several 0.1 cm<sup>-1</sup>, need to be accurately accounted for, as was accomplished in the novel approach by Komasa *et al.* [22].

Direct purely vibrational transitions in the ground electronic state of  $H_2$  are extremely weak due to their quadrupole nature. They were predicted [59] and subsequently observed by Herzberg [60]. The studies of Bragg *et al.* [63]. using a Fourier-Transform spectrometer combined with high-pressure absorption cells exhibiting effective path lengths of 400 m, enabled the measurement of the fundamental and overtone vibrational splittings up to the (4-0) band. This was further extended to the (5-0) band in laser-based studies [64] using multipass cells with effective absorption paths of 20 m. Recent laser-based measurements have improved the experimental accuracies for the fundamental (1-0) vibrational splitting using molecular beams [24, 123] reaching uncertainties of



**Figure 3.1** – (Color online) Schematic of the measurement setup showing the various lasers used in the photolysis of  $H_2S$  (292 nm), for performing the EF-X spectroscopy step in vibrationally-hot  $H_2$  (291 - 293 nm), and for inducing the ionization step (202 nm). The probe laser is split and interferometrically aligned in counter-propagating fashion to obtain Doppler-free two-photon excitation. Resonantly produced  $H^+$ -ions are detected after a time-of-flight (TOF) region for resolving the ion masses.

 $1 \times 10^{-4}$  cm<sup>-1</sup>. Sensitive cavity-ring down laser spectroscopy was applied to the (2-0) overtone band [69] at uncertainties of  $1 \times 10^{-3}$  cm<sup>-1</sup>, as well as on the (3-0) overtone band achieving ~  $10^{-5} - 10^{-4}$  cm<sup>-1</sup> uncertainty levels [66, 124]. It is unlikely that the direct quadrupole excitations can be extended up to the highest vibrational quanta, since for example the (12-0) transition in H<sub>2</sub> is some six orders of magnitudes weaker than the fundamental (1-0) band [69]. Thus far, the H<sub>2</sub> level energies obtained from the calculational framework of Pachucki and coworkers [21, 22] are in excellent agreement with the experimental determination of the dissociation energy [18], the fundamental vibrational splitting [24], the (2-0) and (3-0) overtone band transitions [69, 66, 124], as well the level energies of the rotational series of the lowest vibrational state [23]. These highly-accurate measurements test the quantum chemical calculations of the low vibrational quantum numbers v = 0 - 3.

The present experiment seeks to test the calculations of H<sub>2</sub> binding energies for vibrational levels v = 6 - 12, where theoretical calculations [22] exhibit the largest uncertainties. We follow up on the experimental findings of Steadman and Baer [125], who first produced highly vibrationally excited hydrogen (H<sub>2</sub>\*) from the photolysis of H<sub>2</sub>S. Besides the main photo-dissociation product channel yielding SH molecules, there exists an energetically allowed channel producing H<sub>2</sub>\* under non-equilibrium conditions, upon absorption of two UV photons in the H<sub>2</sub>S molecule. They performed a single-color excitation experiment, in which the UV-pulses caused two-photon dissociation, two-photon excitation in the H<sub>2</sub> EF - X(v', v'') band, and multi-photon ionization/dissociation producing H<sup>+</sup> ions. These sequential processes may involve some 6 or 7 UV photons near 290 nm depending on the excitation pathway.

In our present study, for which a setup is displayed in Fig. 3.1, we disentangle the laser excitation processes using up to three different tunable UV-laser systems to perform a controlled study aiming at spectroscopic accuracy. In all cases, a powerful UV-laser pulse, obtained from a frequency doubled pulseddye laser and set at 292 nm, is used for optimal photolysis of H<sub>2</sub>S and efficient production of H<sub>2</sub>\*. The other laser pulses are time-delayed in steps of ~ 10 ns with respect to the photolysis laser to avoid temporal overlap, and therewith circumvent broadening of the lines. Signal is obtained by monitoring hydrogen ions, produced in the interaction region, accelerated by ion lenses and propagating over a time-of-flight (TOF) mass separation region onto a multichannel plate detection system, where the mass-resolved signal is recorded. In virtually all cases the H<sup>+</sup> signal is most prominent, although on some lines also H<sub>2</sub><sup>+</sup> signal is detected.

As a first step of our investigation the output of a second frequency-doubled dye laser was spatially overlapped in the interaction region with the photolysis laser. A scan over the two-photon excitation region  $68\,200 - 68\,800$  cm<sup>-1</sup> region is displayed in Fig. 3.2. The lines in this low-resolution spectrum exhibit broadening due to the laser linewidth, Doppler and ac-Stark effects, in the order of several cm<sup>-1</sup>, but are narrower than in the one-color study of Steadman and Baer [125]. At the high intensities used the ac-Stark effects also causes appreciable shifts to the transition frequencies, but the accuracy is sufficient for a tentative identification of the transitions.

#### **3.2** Experiment

In the overview spectrum the two-photon lines in the (3,12), (2,11) and (1,10) bands of the F - X system were identified. Note that the numbering of vibrational levels in the EF double well system can be done separately for the inner



**Figure 3.2** – (Color online) a) An overview spectrum of  $H_2$  showing lines assigned to F - X(1, 10), F - X(2, 11), and F - X(3, 12) bands. Detection is in the  $H^+$  channel. The most intense line, marked by an asterisk (\*) and exhibiting off-scale intensity, is unassigned. b) Potential energy curves of  $EF^1\Sigma_g^+$  and  $X^1\Sigma_g^+$  electronic states, including two-photon transitions in the F - X system probing high vibrational levels.

E and outer F well or jointly for both wells; EF(5) then corresponds to F(3). These spectra and the much narrower lines measured in the Doppler-free spectra (see below) revealed many misassignments in the proposed assignments of Steadman and Baer [125], although the generic finding of H<sub>2</sub>\* is confirmed. In particular the assignment of transitions to the E inner potential well could not be confirmed, and we conclude that it is doubtful that any E - X transitions were detected in their study [125]. However, assignments of most transitions to the F outer well states are confirmed presently. Based on Franck-Condon arguments the vibrationally-excited levels in the  $X^1\Sigma_g^+$  ground state can be most easily excited to the outer well F-levels. The potential energy diagram of Fig. 3.2(b) illustrates that the high vibrational ground state levels v = 10 - 12 have favorable Franck-Condon overlap with levels in the outer F well. In our recordings a number of lines remain unidentified, in particular the strongest resonance observed, which is marked with (\*) in Fig. 3.2. These problems with



**Figure 3.3** – (Color online) (a) Measurements of the Q(1) two-photon Doppler-free transition in the F - X(3, 12) band. (b) Plot of the peak positions at different intensities; the intercept at zero intensity (evaluated for both linear and quadratic fits), yields the (ac-Stark-free) transition frequency.

assignments may be due to the fact that high(er) J-levels in the EF state, in particular in the outer F well, are not known to sufficient precision to establish positive identifications.

#### 3.3 Result and Discussion

We choose the rotational series of Q transitions, *i.e.*  $\Delta J = 0$ , in the F-X(3, 12) band as the main focus for a precision study in H<sub>2</sub> with the aim of testing the recent quantum theoretical *ab initio* calculations [22]. For the precision frequency measurements the beam of a UV laser, obtained from a narrowband injection-seeded traveling-wave pulsed dye amplifier (PDA), is split in two equal parts and interferometrically aligned in counter-propagating fashion, to perform two-photon Doppler-free spectroscopy. Most of the H<sup>+</sup>-signal is produced by the

combination of the photolysis and spectroscopy lasers. In cases where the highest spectroscopic accuracy is desired, the power of the PDA was tuned down, and a third UV laser beam at 202 nm (frequency-tripled dye laser) is used to assist ionization from the F(3) state. To avoid broadening effects induced by this ionization laser, the pulse timing is again delayed by 10 ns with respect to the spectroscopy laser. In the expectation that possibly auto-ionizing resonances could help to increase signal the third laser beam was scanned over the window 202-206 nm, but no such resonances were found.

The two-photon Q-branch lines in the F - X(3, 12) band were recorded under the improved high-resolution spectroscopic conditions using the narrowband PDA laser system with a bandwidth of < 100 MHz. The PDA system has been described recently, including the development and characterization of a novel frequency-chirp analysis procedure to identify possible offsets between the continuous-wave seed frequency and the pulsed output of the PDA. This allows for accuracies of 0.001 cm<sup>-1</sup> to be achieved [126]. In Fig. 3.3 a recording of the two-photon Q(1) transition in the F - X(3, 12) band is displayed, measured at different intensities of the spectroscopy laser.

For absolute frequency calibration of the cw-seed laser, hyperfine-resolved saturation spectra of  $I_2$  are simultaneously recorded, using a split-off portion of the cw-seed radiation, and compared with the  $I_2$  database [127]. At the same time, transmission peaks from a stabilized etalon with a free spectral range (FSR) of 150.01 (1) MHz provide a relative frequency calibration, assisting to bridge the distance between  $H_2$  and  $I_2$  resonances [126]. The contribution to the error budget for the  $H_2$  transition frequencies from the laser scan nonlinearity, etalon calibration, and the  $I_2$  calibration are estimated to be as small as 2 MHz. The chirp-induced frequency offset between cw-seed laser and the pulsed output of the PDA system is determined and corrected for in the final frequency, yielding typical values of 11 (3) MHz. Note that final corrections must be multiplied by a factor of 4, to account for harmonic up-conversion and two-photon excitation.

The major source of line broadening and uncertainty of the transition frequencies is the ac-Stark effect. Since the transitions are weak and the population density of H<sub>2</sub><sup>\*</sup> is low, it was necessary to use relatively high probe laser intensities, causing substantial ac-Stark broadening. With a laser bandwidth of ~ 100 MHz, the UV two-photon line-shapes are expected on the order of ~ 200 MHz, but even at the lowest laser intensities of the combined counter-propagating beams the effective line widths were ~ 1 GHz. Fig. 3.3 displays recordings of the Q(1) two-photon transition at different intensities in the interaction zone. At the lower intensities used the resonance frequency is determined from a Gaussian fit to the recorded spectrum, while at the highest intensities the resulting asymmetric lines shapes were fitted to skewed Gaussian functions of the form  $f_{SG} = (\exp x^2/2)/(\sqrt{2\pi}) \cdot [1 + \operatorname{erf}(x/\sqrt{2})]$ . The resulting peak positions are

**Table 3.1** – Measured two-photon transition frequencies in the F - X(3, 12) band, equivalent to the EF - X(5, 12) band.

Line	Frequency
Q(0)	68476.0459(35)
Q(1)	68446.2834(35)
Q(2)	68387.6623(35)
Q(3)	68302.0250(35)
S(1)	68505.518(7)

plotted against the relative UV intensity as shown in Fig. 3.3(b). To account for the increased widths and skew, the peak position uncertainty in the high intensity scans are larger. In view of the long extrapolation to zero intensity fits were made for a linear and a quadratic fit. Results from these approaches were averaged and the uncertainties were conservatively estimated to cover the values when differing. In Table 3.1 the thus determined two-photon transition frequencies for the Q(0)-Q(3) lines in the F - X(3, 12) band are listed with accuracies of typically 100 MHz or 0.0035 cm<sup>-1</sup> deriving fully from this ac-Stark analysis.

In order to make a comparison with the quantum chemical *ab initio* calculations these values for the accurate transition frequencies must be translated into values of level energies in H<sub>2</sub>  $X^{1}\Sigma_{q}^{+}(v=12, J)$ . This can be accomplished by subtracting transition energies from the accurate level energies of the upper F(3) states from Bailly *et al.* [25], which were determined via combined laserbased and Fourier-transform emission experiments yielding values accurate to within 0.001 cm<sup>-1</sup> for J < 3. So this transformation does not add to the uncertainty of  $H_2^*$  level energies, which are listed in Table 3.2 as experimental values  $(E_{\text{exp}})$  for v = 12. This procedure of combining differences between F(3) level energies [25] and X(12) level energies [22] provides a final and unambiguous assignment of the observed lines. The measurement of a weaker transition S(1)at in the same F - X(3, 12) band ( $\Delta J = 2$  for S transitions) allows for an additional consistency check of the line identification. The combination difference between S(1) and Q(3) transitions delivers a level splitting between J = 1 - 3in X(12) amounting to 203.494 cm<sup>-1</sup>, in agreement, at 0.008 (8) cm<sup>-1</sup>, from the *ab initio* values [22]. In addition, the combination difference between S(1)and Q(1) lines is in reasonable agreement with the splitting between J = 1 - 3in F(3) within 0.010 (8) cm<sup>-1</sup>.

In Table 3.2 a final comparison is made between experimentally determined level energies  $(E_{exp})$  and results from the quantum chemical calculations  $(E_{the})$  by Komasa *et al.* [22]. For three of the four levels determined the difference

**Table 3.2** – Level energies  $(E_{exp})$  of ro-vibrational states  $X^1\Sigma_g^+$  (v = 12, J = 0-3), experimentally determined from the measured F - X(3, 12) two-photon Q-transitions and the accurate F(3) levels from Bailly et al. [25]. Also indicated are the theory values  $(E_{the})$  of Komasa et al. [22], and the difference  $\Delta E_{exp-the}$  between the experimental and theoretical values. The uncertainties in the differences represent the combined uncertainties from experiment and theory taken in quadrature.

$J^{\prime\prime}$	$E_{\rm exp}$	$E_{\rm the}$	$\Delta E_{\rm exp-the}$
0	34302.1823(35)	34302.1741(47)	0.008(6)
1	34343.8531(35)	34343.8483(46)	0.005(6)
2	34426.2216(35)	34426.2179(46)	0.004(6)
3	34547.3362(35)	34547.3332(45)	0.003(6)



**Figure 3.4** – (Color online) Plot of corrections to the ab initio Born-Oppenheimer energies of the  $H_2 X^1 \Sigma_g^+$  ground electronic state [22] as a function of vibrational quantum number v (in all cases J = 0). Adiabatic (ad), nonadiabatic (nad), and relativistic and radiative (rel+QED) corrections are plotted with reference to the scale on the left. The total uncertainty of the calculations (unc) is plotted with reference to the scale on the right.

between the experimental and theoretical values,  $\Delta E_{\rm exp-the}$ , is smaller than their combined uncertainties, while the J'' = 0 level deviated by  $1.3\sigma$ . This allows for the main conclusion of the present study that good agreement is established between experiment and the quantum chemical calculations for v = 12 levels in the electronic ground state in H<sub>2</sub>. This is the highest vibrational level subjected to a precision test below 0.01 cm<sup>-1</sup> for the H<sub>2</sub> molecule.

#### 3.4 Conclusion

In Fig. 3.4 the contributing energy corrections to the accurate BO-energies [46] are plotted as a function of v, as well as the final uncertainties in the theoretical binding energies [22]. It shows that the calculations are least accurate for the range v = 6 - 12. The present test on v = 12 covers this weakest spot in the calculations. Specifically the non-adiabatic contributions to the relativistic and QED energies (the so-called recoil corrections), as well as higher order non-adiabatic,  $\alpha^4$ -QED contributions, and the leading term in  $\alpha^5$ -QED, are mainly held responsible for possible deviations with theory [22]. The presently determined experimental binding energies, being slightly more accurate than theory, may serve to stimulate calculations of such terms.

As an outlook from the experimental perspective, efforts are underway to determine level energies for states up to the highest possible (v = 14) vibrational quantum states in H<sub>2</sub>. At least an order of magnitude improvement is foreseen in the experimental determination of the v = 10 - 14, J level energies, which should be achievable with an improved detection sensitivity, whereby the limiting factor of uncertainty, the ac-Stark broadening, can be suppressed.

Note added during review. After submission of this manuscript a paper reporting recalculation of the non-adiabatic interaction was published [128] improving their accuracy to the  $10^{-7}$  cm<sup>-1</sup> level. It was not specified in how far the newly calculated non-adiabatic wave functions affect the uncertainties of the QED and relativistic corrections.

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## $_{\rm CHAPTER} 4$

### The CO A-X System for Constraining Cosmological Drift of the Proton-Electron Mass Ratio

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The  $A^1\Pi - X^1\Sigma^+$  band system of carbon monoxide, which has been detected in six highly redshifted galaxies (z = 1.6-2.7), is identified as a novel probe method to search for possible variations of the proton-electron mass ratio ( $\mu$ ) on cosmological time scales. Laboratory wavelengths of the spectral lines of the A-X (v,0) bands for v = 0-9 have been determined at an accuracy of  $\Delta\lambda/\lambda = 1.5 \times 10^{-7}$ through VUV Fourier-transform absorption spectroscopy, providing a comprehensive and accurate zero-redshift data set. For the (0,0) and (1,0) bands, two-photon Doppler-free laser spectroscopy has been applied at the  $3 \times 10^{-8}$ accuracy level, verifying the absorption data. Sensitivity coefficients  $K_{\mu}$  for a varying  $\mu$  have been calculated for the CO A-X bands so that an operational method results to search for  $\mu$ -variation.

#### 4.1 Introduction

The search for a variation of the dimensionless proton-to-electron mass ratio  $\mu = m_p/m_e$  on cosmological time scales can be performed by comparing molecular absorption lines in highly redshifted galaxies with the same lines measured in the laboratory. Through detection of H<sub>2</sub> and HD lines in absorbing galaxies upper limits on  $\mu$ -variation have been deduced, resulting in a  $\Delta \mu/\mu < 1 \times 10^{-5}$  constraint at redshifts z = 2 - 3.5, corresponding to look-back times of 10-12 billion years towards the origin of the Universe [129, 130]. For a reliable comparison, a database of accurately calibrated laboratory wavelengths must be available and this has been accomplished through laser spectroscopic investigations of the Lyman and Werner band absorption systems in H<sub>2</sub> [73, 81] and HD [131]. Further, to make such a comparison operational, sensitivity coefficients  $K_{\mu}$  must be calculated for all lines in the spectrum; these  $K_{\mu}$  represent the wavelength shift induced on a line by a varying  $\mu$ . Such calculations have been carried out for the H<sub>2</sub> molecule using different methods [132, 133, 134] as well as for the HD isotopomer [135].

Through radio astronomical observations of the NH<sub>3</sub> molecule even tighter constraints at the  $\Delta \mu/\mu < 1 \times 10^{-6}$  level could be deduced, because the transitions in the NH<sub>3</sub> molecule exhibit much larger  $K_{\mu}$  coefficients. However, this ammonia method has only been applied in the two systems where NH<sub>3</sub> is detected (B0218+365 [136, 137] and PKS1830-211 [138]) at redshifts z < 1, or look-back times of 6-7 billion years. In addition the methanol molecule was identified as a molecule with radio-frequency transitions exhibiting very large sensitivity coefficients due to the internally hindered rotation mode in the molecule [139, 140, 141]. Such methanol lines were observed in the single object PKS1830-211 [142, 143] and a constraint of  $\Delta \mu/\mu < 1 \times 10^{-7}$  was derived [144]. Thus far the radio astronomical observations have been limited to z < 1.

Because the number of useful H<sub>2</sub> high redshift absorber systems is less than ten, additional methods are explored for constraining  $\mu$  variation at redshifts z > 1. Recently a number of high-redshift observations were reported on the A<sup>1</sup>\Pi - X<sup>1</sup>\Sigma<sup>+</sup> vacuum ultraviolet absorption system of carbon monoxide, first in Q1439+113 at  $z_{abs} = 2.42$  [145], then in Q1604+220 at z = 1.64 [146], in Q1237+064 at z = 2.69 [147], and finally in three additional systems: Q0857+18 at z = 1.73, Q1047+205 at z = 1.77, and Q1705+354 at z =2.04 [148]. While these observations, all performed with the ESO Very Large Telescope, were mainly used to measure the local cosmic background temperature, we propose to use the high-resolution spectral observations of CO A-X to search for  $\Delta \mu/\mu$  at these redshifts. We note that, in addition, spectra of the CO A-X system as observed toward  $\gamma$ -ray bursts could be used for the same purpose, although the only system with these spectral features detected so far (GRB060807) was observed at a too limited spectral resolution [149]. The restframe wavelengths of the CO A-X bands are in the wavelength range 130 - 154 nm, hence longward of Lyman- $\alpha$ , so that the CO spectral features in typical quasar spectra will fall outside the region of the Lyman- $\alpha$ -forest (provided that the emission redshift of the quasar  $z_{em}$  is not too far from the redshift  $z_{abs}$  of the intervening galaxy exhibiting the molecular absorption). The occurrence of the Lyman-forest lines is a major obstacle in the search for  $\mu$  variation via H<sub>2</sub> lines [129, 130].

The present study provides the ingredients to make the CO A-X system operational for detecting  $\mu$  variation from quasar absorption spectra. In order to extract bounds on  $\Delta \mu/\mu$  at the competitive level of  $< 10^{-5}$ , a laboratory wavelength data set at an accuracy of  $\Delta\lambda/\lambda = 3 \times 10^{-7}$  is required. The  $A^{1}\Pi$  -  $X^{1}\Sigma^{+}$  absorption system has been investigated over decades, with an important comprehensive study by Field et al. [29, 150], resulting in the most accurate data by Le Floch and coworkers [151, 152, 153, 154]; the data were compiled for astronomical use by Morton and Noreau [155]. The accuracy of those data was however limited to 0.06 cm<sup>-1</sup> or  $\Delta \lambda / \lambda = 1 \times 10^{-6}$ . This is insufficient for an accurate constraint on  $\Delta \mu/\mu$ , since the laboratory values would make up an essential part of the error budget. Moreover Drabbels etal. [156] had performed an intricate multistep excitation study to derive level energies of four (e)-parity levels of  $A^{1}\Pi, v = 0, J = 1 - 4$  at an accuracy of  $0.002 \text{ cm}^{-1}$ ; these results were found to deviate by  $-0.04 \text{ cm}^{-1}$  from the classical data [151, 152, 153, 154, 155]. This has led us to perform two independent studies, a one-photon absorption study employing synchrotron radiation and a two-photon Doppler-free laser-based excitation study, to match the accuracy requirement on the wavelengths for the relevant (v = 0, 0) bands of the CO A-X system. In addition, a calculation of  $K_{\mu}$  sensitivity coefficients for the spectral lines in the CO A-X system was performed.

#### 4.2 Fourier transform spectroscopy

The unique vacuum-ultraviolet (VUV) Fourier-transform spectrometer (FTS) of the VUV DESIRS beamline [157] at the SOLEIL synchrotron, which is based on wavefront division interferometry [158], was employed to record high-resolution absorption spectra of CO in the range 130 – 154 nm. The setup was optimized for obtaining spectra at the highest resolution: a molecular slit jet was used to reduce the Doppler width, and the FTS was set to its lowest linewidth of 0.075 cm<sup>-1</sup>, corresponding to a resolving power of about 900 000. In Fig. 4.1 an overview spectrum and a detail spectrum are presented, showing sharp lines in the  $A^1\Pi$ – $X^1\Sigma^+$  (0,0) band at a linewidth of



**Figure 4.1** – (Color online) Recording of the jet absorption spectrum of  ${}^{12}C^{16}O$  with the Fourier-transform vacuum ultraviolet spectrometer at the SOLEIL synchrotron. (a) Overview spectra; (b) Detail spectrum of the A-X (0,0) band. The line indicated by an (\*) is a Xe absorption line used for absolute calibration.

 $0.09 \text{ cm}^{-1}$ . Wavelength calibration of the FTS spectrum is derived from the scan-controlling He-Ne laser [158] and further optimized for the absolute scale referenced to a Xenon line at 68 045.156 (3) cm<sup>-1</sup> [159], which is based on accurate relative measurements [160] and the measurement of a VUV anchor line [161]. Based on these calibration procedures the uncertainty in the line positions of most CO resonances is estimated to be within 0.01 cm<sup>-1</sup>, corresponding to  $\Delta\lambda/\lambda = 1.5 \times 10^{-7}$ . Resulting transition frequencies for the CO A-X (v, 0) bands are listed in Table 4.1. When comparing the results from this high-resolution VUV-FTS study with the classical spectral data [151, 152, 153, 154, 155] we find an offset of -0.03 cm<sup>-1</sup> between the data sets. These offsets are found to be in agreement with those of Drabbels *et al.* [156] for the four levels studied.

**Table 4.1** – Calibrated one-photon transition frequencies (in vacuum  $cm^{-1}$ ) in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  (v,0) bands. Lines indicated with (\*) are derived from the Doppler-free two-photon laser excitation study of the (0,0) and (1,0) bands and ground state level energies [162]. The other lines are derived from the VUV-FTS study.

J''	R	Q	Р	R	Q	Р
		(0,0)			(1,0)	
0	$64747.983(2)^*$			$66236.228(2)^*$		
1	64750.504 (2)*	$64744.140(2)^*$		66238.502 (2)*	$66232.384(2)^*$	
2	64752.359 (2)*	64742.828 (2)*	$64736.448(2)^*$	66240.016 (2)*	66230.813 (2)*	$66224.694(2)^*$
3	64753.54(1)	64740.863 (2)*	64731.279 (2)*	66240.798 (2)*	66228.482 (2)*	66219.278 (2)*
4	64754.01(1)	64738.233 (2)*	64725.446 (2)*	66240.85(1)	66225.422 (2)*	66213.103 (2)*
5	64753.73(1)	64734.934 (2)*	64718.92(1)	66240.25(1)	66221.654 (2)*	66206.198 (2)*
		(2,0)			(3,0)	
0	67678.89(1)			69091.62(1)		
1	67681.27(1)	67675.04(1)		69093.90(1)	69087.78(1)	
2	67682.93(1)	67673.59(1)	67667.35(1)	69095.42(1)	69086.23(1)	69080.09(1)
3	67683.85(1)	67671.39(1)	67662.05(1)	69096.17(1)	69083.90(1)	69074.70(1)
4	67684.06(1)	67668.47(1)	67656.01(1)	69096.12(1)	69080.79(1)	69068.52(1)
5	67683.51(1)	67664.82(1)	67649.25(1)	69095.31(1)	69076.90(1)	69061.57(1)
		(4,0)			(5,0)	
0	70469.92(1)			71811.97(1)		
1	70472.07(1)	70466.10(1)		71814.05(1)	71808.12(1)	
2	70473.41(1)	70464.43(1)	70458.45(1)	71815.28(1)	71806.38(1)	71800.42(1)
3	70473.85(1)	70461.92(1)	70452.84(1)	71815.64(1)	71803.76(1)	71794.84(1)
4	70473.49(1)	70458.56(1)	70446.46(1)	71815.16(1)	71800.29(1)	71788.39(1)

continued on next page

J''	R	Q	Р	R	Q	Р
5	70472.34(1)	70454.35(1)	70439.25(1)	71813.78(1)	71795.94(1)	71781.08(1)
		(6,0)			(7,0)	
0	73119.52(1)			74394.47(1)		
1	73121.52(1)	73115.67(1)		74396.38(1)	74390.62(1)	
2	73122.57(1)	73113.83(1)	73108.00(1)	74397.33(1)	74388.68(1)	74382.95(1)
3	73122.67(1)	73111.04(1)	73102.29(1)	74397.30(1)	74385.79(1)	74377.16(1)
4	73121.83(1)	73107.29(1)	73095.65(1)	74396.33(1)	74381.92(1)	74370.40(1)
5	73119.97(1)	73102.60(1)	73088.08(1)	74394.38(1)	74377.10(1)	74362.71(1)
		(8,0)			(9,0)	
0	75634.35(1)			76840.23(2)		
1	75636.15(1)	75630.52(1)		76841.92(2)	76836.43(2)	
2	75636.94(1)	75628.46(1)	75622.80(1)	76842.60(2)	76834.26(2)	76828.72(2)
3	75636.73(1)	75625.42(1)	75616.92(1)	76842.16(2)	76831.03(2)	76822.77(2)
4	75635.46(1)	75621.33(1)	75610.03(1)	76840.71(2)	76826.78(2)	76815.61(2)
5	75633.20(1)	75616.24(1)	75602.12(1)	76838.14(2)	76821.50(2)	76807.63(2)



**Figure 4.2** – (Color online) Recording of part of the two-photon laser excitation spectrum of the  $A^1\Pi - X^1\Sigma^+$  (0,0) band of CO. The etalon markers and the  $I_2$  hyperfine line (\*) recorded in the fundamental are used for frequency calibration.

#### 4.3 UV laser spectroscopy

In addition two-photon excitation studies on the CO  $A^1\Pi - X^1\Sigma^+$  system were performed employing a pulsed dye amplifier (PDA) laser, injection seeded by the output of a continuous-wave ring dye laser, delivering narrowband output at ~ 300 nm [163]. Simultaneous recording of I<sub>2</sub> hyperfine lines [127, 164] and transmission peaks from a stabilized etalon using the fundamental wavelength provides frequency calibration. The excitation was performed in a counter-propagating beam geometry to suppress Doppler effects [26]. In a 2+1' resonance-enhance multiphoton ionization (REMPI) scheme a second laser at 207 nm is employed for ionizing the A<sup>1</sup>\Pi excited-state population; this laser is pulse delayed by ~ 10 ns with respect to the first laser pulse to avoid ac-Stark

Source	Uncertainty (MHz)
Line-fitting	2
Residual Doppler	< 1
$I_2$ calibration	2
etalon nonlinearity	2
AC-Stark shift	20
DC-Stark shift	< 1
PDA chirp	60
Statistical	30
Total	70

**Table 4.2** – Estimated uncertainties (in MHz) for the transition frequencies measured with the PDA laser system.

effects by the ionizing laser pulse. Delayed pulsed-electric-field ion extraction is also employed to minimize dc-Stark effects. Figure 4.2 shows a recording of an excitation spectrum of part of the A-X (0,0) band. Due to availability and wavelength tunability of the ring dye laser, the laser studies were performed on the A-X (1,0) and (0,0) bands.

The error budget in Table 4.2 lists the estimate of uncertainty contributions from various sources. The ac-Stark shift corrections were obtained from intensity-dependent measurements and extrapolating the transition frequencies to zero intensity levels. The accuracy of the obtained transition frequencies from the laser measurements is limited by the frequency chirp in the PDA laser. Based on previous characterization of the chirp of our PDA system [163], we estimate a 60 MHz contribution from the chirp for this study since a lower-order frequency upconversion of the laser was used. Furthermore, the measurements were performed at lower PDA-pump energies compared to Ref. [163], which also reduce the chirp effect. We estimate the uncertainty of the line frequencies from the PDA investigation to be 70 MHz or  $0.002 \text{ cm}^{-1}$ .

In view of parity selection rules, in the two-photon laser experiment opposite parity  $\Lambda$ -doublet components in the  $A^1\Pi$  state are excited when compared to the one-photon absorption experiment. Accurate values for the  $\Lambda$ -doublet splittings in the  $A^1\Pi$  state can be deduced from measurements in the S, Q, R and P branches (the O branch was not recorded), and from the accurately known ground state level energies [162]. Based on this analysis, the laser data were converted to transition frequencies for one-photon A-X bands at an accuracy of 0.002 cm<sup>-1</sup>, and listed in Table 4.1.

The results from the laser-based study serve a two-fold purpose. First, they provide a reliable database for comparison with quasar data at the level of  $\Delta\lambda/\lambda = 3 \times 10^{-8}$  for the A-X (0,0) and (1,0) bands. Second, a comparison between the present laser data and the VUV-FTS data show agreement between both data sets at a statistical uncertainty within 0.01 cm<sup>-1</sup>. Hence, we conclude that the calibration procedures on the VUV-FTS spectra yield transition frequencies within the estimated uncertainty of 0.01 cm<sup>-1</sup>. This provides a database of CO A-X lines for bands (v = 2 - 8) at  $\Delta\lambda/\lambda = 1.5 \times 10^{-7}$  accuracy. A slightly worse uncertainty estimate of 0.02 cm<sup>-1</sup> is quoted for the (9,0) band, which has a lower signal-to-noise ration (SNR) compared to the other bands due to its smaller transition strength.

#### 4.4 Sensitivity coefficients

For extracting a possible variation of the proton-to-electron mass ratio  $\mu$  a set of highly redshifted wavelengths  $\lambda_z^i$  is compared with a set of rest-frame wavelengths  $\lambda_0^i$  via [134]:

$$\frac{\lambda_{z}^{i}}{\lambda_{0}^{i}} = (1 + z_{abs})(1 + K_{\mu}^{i}\frac{\Delta\mu}{\mu})$$
(4.1)

where  $z_{abs}$  is the redshift of the intervening galaxy absorbing CO and  $K^i_{\mu}$  the sensitivity coefficient for each line to a variation of  $\mu$ :

$$K^{i}_{\mu} = \frac{d\ln\lambda^{i}}{d\ln\mu} = -\frac{\mu}{E^{i}_{e} - E^{i}_{q}} (\frac{dE^{i}_{e}}{d\mu} - \frac{dE^{i}_{g}}{d\mu})$$
(4.2)

with  $E_e^i$  and  $E_g^i$  the excited- and ground-state energies connecting an optical transition in the molecule. It is noted that the definition of Eq. (4.2) yieleds  $K_{\mu}$  coefficients of opposite sign with respect to other studies, where the definition  $\Delta\nu/\nu = K_{\mu}\Delta\mu/\mu$  is used (see e.g. Ref. [139, 141]). The specific definition of Eq. (4.2) is consistent with its use in Eq. (4.1). The relative variation of the proton-electron mass ratio is defined as  $\Delta\mu \equiv \mu_z - \mu_0$ , meaning that a positive value for  $\Delta\mu/\mu$  indicates a larger value of  $\mu$  in the cosmological past.

Rovibrational level energies E(v, J) can be expressed in terms of a Dunham expansion

$$E(v,J) = \sum_{k,l} Y_{k,l} \left( v + \frac{1}{2} \right)^k [J(J+1) - \Lambda^2]^l$$
(4.3)

with  $Y_{k,l}$  the Dunham coefficients, known to sufficient accuracy for the  $X^1\Sigma^+$ state [165] and for the  $A^1\Pi$  state [166].  $\Lambda$  represents the electronic angular momentum,  $\Lambda = 0$  for  $X^1\Sigma^+$  and  $\Lambda = 1$  for  $A^1\Pi$ . The advantage of the Dunham representation of molecular states is that the coefficients scale as  $Y_{k,l} \propto \mu_{red}^{-l-k/2}$ , with  $\mu_{red}$  the reduced mass of the molecule. In studies focusing on  $\mu$ -variation it is assumed that all atomic masses scale as the proton, *i.e* protons and neutrons treated equally, hence  $\mu_{red}$  can be replaced by  $\mu$  in this analysis [134, 167]. Thus the derivatives for the level energies can be analytically taken with

$$\frac{dY_{k,l}}{d\mu} \approx -\frac{Y_{k,l}}{\mu} \left( l + \frac{k}{2} \right) \tag{4.4}$$

Substitution in Eqs. (4.3) and (4.2) then straightforwardly yields the sensitivity coefficients  $K_{\mu}$  for the A-X lines of CO.

Interactions of the A<sup>1</sup>II state with triplet states in the CO molecule perturb the level structure [29, 150]. The level shifts play an important role in the comparative analysis of quasar data to extract  $\mu$  variation, but these are implicitly included in the experimental determination of spectral line positions, *i.e.* in the values of Table 4.1. However, in the calculation of  $K_{\mu}$  coefficients the admixtures of perturbing character into the wave function composition in A<sup>1</sup>II states should also be accounted for. In Refs. [134, 167] a model is proposed to calculate the  $K_{\mu}$  coefficients in the case of non-adiabatic mixing between B<sup>1</sup> $\Sigma_{u}^{+}$  and C<sup>1</sup> $\Pi_{u}$  levels in H<sub>2</sub>. This model can be adopted for CO and in good approximation one may derive coefficients

$$K_{\mu} = \alpha_{pure} K_{pure} + \sum \alpha_{pert} K_{pert}$$
(4.5)

where  $K_{pure}$  refers to  $K_{\mu}$  coefficients for transitions of the state in consideration and  $K_{pert}$  refer to those of the perturber states, while  $\alpha$  refers to the admixture in the wave function composition (given in Ref. [155]).

Perturbation-corrected  $K_{\mu}$  coefficients were calculated using Dunham representations for the perturbing d<sup>3</sup> $\Delta$  state from Ref. [168], and e<sup>3</sup> $\Sigma^-$ , I<sup>1</sup> $\Sigma^-$ , a'<sup>3</sup> $\Sigma^+$ states from Ref. [169], (we have collected the Dunham coefficients in the Supplementary material [170]). The second-order mass-dependent effect (adiabatic correction) is estimated to be at the 5 × 10<sup>-5</sup> level and has been neglected.

It follows from Eq. (4.5) that the correction to the  $K_{\mu}$  coefficients depends on both the amount of admixture of the perturbing state in the wave function, as well as on the value of the  $K_{\mu}$  coefficients for the pure perturber state. The most pronounced perturbation occurs between  $A^{1}\Pi$  (v = 1) and  $d^{3}\Delta$  (v = 5), with the highest triplet admixture of 17% for the J' = 1 state. In addition, the perturber  $K_{\mu}$  value is more than four times that of the pure A state value, resulting in a correction of 55% to the  $K_{\mu}$  value compared to the case when the perturbation is not included. The  $A^{1}\Pi$  (v = 0) state is only very slightly perturbed by the  $d^{3}\Delta$  (v = 3, 4) states with 0.13% wave function admixture. However, the perturber  $K_{\mu}$  is 10 times larger than that of the pure A state value, resulting in 1.5% correction for  $K_{\mu}$ . The  $A^{1}\Pi$  (v = 4) rotational states can have  $K_{\mu}$ -corrections up to 5%, while the  $A^{1}\Pi$  (v = 6, J = 8) rotational st

**Table 4.3** –  $K_{\mu}$  sensitivity coefficients for  ${}^{12}C^{16}O A^{1}\Pi - X^{1}\Sigma^{+} (v' - v'')$  bands. The uncertainty is estimated to be better than 1%.

J''	R	Q	Р	R	Q	Р	R	Q	Р
		(0-0)			(1-0)			(2-0)	
0	-0.00232			0.01312			0.01850		
1	-0.00227	-0.00237		0.01280	0.01306		0.01853	0.01844	
2	-0.00223	-0.00238	-0.00249	0.01235	0.01269	0.01294	0.01855	0.01842	0.01833
3	-0.00219	-0.00239	-0.00257	0.01183	0.01218	0.01251	0.01856	0.01838	0.01825
4	-0.00216	-0.00240	-0.00264	0.01129	0.01160	0.01195	0.01856	0.01834	0.01816
5	-0.00212	-0.00239	-0.00273	0.01077	0.01100	0.01132	0.01854	0.01828	0.01806
6	-0.00207	-0.00234	-0.00281	0.01029	0.01042	0.01066	0.01847	0.01821	0.01795
7	-0.00199	-0.00219	-0.00289	0.00989	0.00989	0.01002	0.01847	0.01813	0.01782
8	-0.00185	-0.00168	-0.00296	0.00954	0.00943	0.00943	0.01843	0.01804	0.01763
		(3-0)			(4-0)			(5-0)	
0	0.02756			0.03784			0.04329		
1	0.02759	0.02750		0.03783	0.03697		0.04331	0.04324	
2	0.02761	0.02748	0.02740	0.03771	0.03680	0.03695	0.04332	0.04321	0.04314
3	0.02761	0.02744	0.02732	0.03749	0.03659	0.03685	0.04332	0.04317	0.04306
4	0.02761	0.02739	0.02723	0.03720	0.03636	0.03667	0.04331	0.04312	0.04297
5	0.02759	0.02734	0.02712	0.03690	0.03614	0.03643	0.04328	0.04305	0.04286
6	0.02756	0.02726	0.02701	0.03661	0.03594	0.03614	0.04324	0.04297	0.04274
7	0.02751	0.02718	0.02688	0.03636	0.03575	0.03583	0.04318	0.04288	0.04261
8	0.02746	0.02708	0.02675	0.03614	0.03556	0.03552	0.04311	0.04277	0.04247

continued on next page

J''	R	Q	Р	R	Q	Р	R	Q	Р
		(6-0)			(7-0)			(8-0)	
0	0.05039			0.05612			0.06162		
1	0.05044	0.05034		0.05614	0.05607		0.06163	0.06157	
2	0.05051	0.05034	0.05024	0.05615	0.05605	0.05598	0.06169	0.06154	0.06147
3	0.05061	0.05034	0.05019	0.05614	0.05600	0.05590	0.06162	0.06149	0.06139
4	0.05066	0.05037	0.05016	0.05611	0.05594	0.05581	0.06159	0.06143	0.06136
5	0.05124	0.05048	0.05016	0.05607	0.05587	0.05570	0.06154	0.06135	0.06119
6	0.05481	0.05097	0.05011	0.05602	0.05578	0.05558	0.06148	0.06120	0.06106
7	0.05435	0.05452	0.05059	0.05595	0.05568	0.05544	0.06135	0.06109	0.06092
8	0.05202	0.05381	0.05407	0.05587	0.05556	0.05529	0.06132	0.06103	0.06077
		(9-0)			(10-0)				
0	0.06646	· · ·		0.07078	· · ·				
1	0.06647	0.06641		0.07079	0.07074				
2	0.06647	0.06638	0.06632	0.07079	0.07070	0.07064			
3	0.06646	0.06633	0.06624	0.07077	0.07065	0.07057			
4	0.06642	0.06627	0.06615	0.07073	0.07059	0.07047			
5	0.06638	0.06619	0.06604	0.07068	0.07051	0.07036			
6	0.06631	0.06610	0.06591	0.07061	0.07041	0.07023			
7	0.06623	0.06599	0.06577	0.07053	0.07029	0.07009			
8	0.06614	0.06586	0.06561	0.07042	0.07016	0.06993			



**Figure 4.3** – (Color online) Calculated  $K_{\mu}$  coefficients for the spectral lines in the A-X system of CO. The spread in  $K_{\mu}$  values, shown enlarged in the insets for the (1,0) and (4,0) bands, illustrate the effect of perturber states.

ate correction is almost 10%. The rest of the bands have  $K_{\mu}$ -corrections that are less than 1%. The  $K_{\mu}$  coefficients are represented graphically in Fig. 4.3, where the scatter in the (v = 1, 4 and 6) bands show the effect of perturbations. The resulting  $K_{\mu}$  coefficients are listed in Table 4.3. The accuracies in these  $K_{\mu}$ coefficients are estimated to be better than 1%, with the dominant uncertainty contributions from the perturbations (non-adiabatic corrections), which depend on the quantum numbers v', J' of the upper state.

#### 4.5 Discussions

 $K_{\mu}$  coefficients for CO A-X are thus found in the range of values -0.002 to +0.066, giving a spread equal to that of the Lyman and Werner bands of H<sub>2</sub>. This makes the A-X system of CO a good search ground for putting constraints on a possible variation of  $\mu$ , in particular, at look-back times of 9.5-11.5 billion years where these features have been detected so far [145, 146, 147, 148]. A set of zero-rest frame wavelengths of A-X (v = 0-9, 0) bands has

been measured with most transitions at an accuracy of  $\Delta \lambda / \lambda = 1.5 \times 10^{-7}$ . and for the (0,0) and (1,0) bands, even as accurate as  $3 \times 10^{-8}$ . The combined data sets of rest-frame wavelengths and sensitivity coefficients are the basis for a  $\mu$ -variation analysis on CO spectra from high-redshift galaxies, where the analysis will be solely constrained by the quality of the astronomical data. So far six high redshift galaxies have been observed with characteristic CO A-X features. The best example is that of a CO spectrum observed at z =2.69 with a column density of  $\log N(CO) = 14.17 \text{ cm}^{-2}$  in the sight-line of the Q1237+064 quasar system, showing a signal-to-noise ratio of 10-40 (over the wavelength range) and resolution  $R \sim 50\,000$  after 8 hrs observation at the ESO Very Large Telescope [147]. Extended observations with attached Th-Ar calibration of the astronomical exposures (not available yet for the discovery spectrum of Ref. [147]) would result in a competitive result on  $\Delta \mu/\mu$  from the CO spectra, *i.e.* an estimated constraint at  $\Delta \mu/\mu < 10^{-5}$ . The objects where CO is detected exhibit large column densities of H<sub>2</sub> and HD molecules, since extragalactic abundance ratios are generally  $N(H_2)/N(CO) > 10^4$  and  $N(\text{HD})/N(\text{CO}) \sim 1$ . Hence, future comprehensive  $\mu$  constraining analyses can be performed from the features of all three molecules contained in the same quasar spectrum. In view of the increased number of spectral lines, the wider wavelength coverage, and the CO lines lying outside the Lyman- $\alpha$  forest, wellcalibrated (Th-Ar attached) and good signal-to-noise observations (SNR 40) should lead to constraints at  $\Delta \mu/\mu < 3 \times 10^{-6}$ . The system Q1237+064 would be the first target of choice.

#### 4.6 Conclusion

We have identified the  $A^1\Pi - X^1\Sigma^+$  band system of carbon monoxide, a probe system to search for possible variations of the proton-electron mass ratio ( $\mu$ ) on cosmological time scales. Laboratory wavelengths of the spectral lines of the A-X (v,0) bands for v = 0 - 9 have been determined at an accuracy of  $\Delta\lambda/\lambda = 1.5 \times 10^{-7}$  through VUV Fourier-transform absorption spectroscopy, providing a comprehensive and accurate zero-redshift data set. Two-photon Doppler-free laser spectroscopy has been applied for the (0,0) and (1,0) bands, achieving  $3 \times 10^{-8}$  accuracy level. Accurate sensitivity coefficients  $K_{\mu}$  for a varying  $\mu$  have been calculated for the CO A-X bands, where the effect of perturbations has been accounted for. It is expected that future  $\mu$  constraining analyses that include H<sub>2</sub> and HD and CO transitions from the same absorber should result in a more accurate and robust constraint for  $\Delta\mu/\mu$ .

### 4.7 Acknowledgement

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## Chapter 5

## High resolution spectroscopy and perturbation analysis of the CO $A^{1}\Pi - X^{1}\Sigma^{+}$ (0,0) and (1,0) bands

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The two lowest-v' (0,0) and (1,0) bands of the  $A^1\Pi - X^1\Sigma^+$  system of  ${}^{12}C^{16}O$ have been investigated by two high resolution spectroscopic methods. A vacuum ultraviolet Fourier-transform spectrometer, illuminated by synchrotron radiation, was applied to record a jet-cooled spectrum and a room temperature static gas spectrum, resulting in absolute accuracies of  $0.01-0.02 \text{ cm}^{-1}$ . In addition two-photon Doppler-free laser spectroscopy has been applied to a limited number of rotational lines, resulting in an accuracy of  $0.002 \text{ cm}^{-1}$ . The data were used to perform an improved analysis of the perturbations in the  $A^1\Pi$ , v = 0 and v = 1 levels by vibrational levels in the  $D^1\Delta$ ,  $I^1\Sigma^-$ ,  $e^3\Sigma^-$ ,  $d^3\Delta$ , and  $a'^3\Sigma^+$ states.

#### 5.1 Introduction

The  $A^1\Pi - X^1\Sigma^+$  band absorption system of carbon monoxide has been known since its first observation as band heads in 1888 by Deslandres, who labeled it as the fourth positive system [171]. Simmons *et al.* recorded and analyzed rotationally resolved spectra of the  $A^1\Pi - X^1\Sigma^+$  (v', 0) bands in absorption up to v' = 23 [166]. The  $A^1\Pi$  state was also investigated via the Ångstrom bands  $(B^{1}\Sigma^{+} - A^{1}\Pi \text{ system})$ , initially by Birge [172], later by Kepa and Rytel [173], and thereafter with very high accuracy by Fourier-transform (FT) spectroscopy by Le Floch and Amiot [174]. In addition, information is extracted from the Herzberg bands  $(C^1\Sigma^+ - A^1\Pi \text{ system})$  [175] and the  $E^1\Pi - A^1\Pi \text{ system}$  [176]. A comprehensive study of the perturbations in the  $A^1\Pi$  state was performed by Field et al. [150], based on the knowledge available in 1972. For analyzing the perturbations in the  $A^1\Pi$  state the spectroscopic investigations of the perturbing states, observed in forbidden systems, are of relevance. Herzberg and Hugo observed the  $a'^{3}\Sigma^{+} - X^{1}\Sigma^{+}$  and  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  systems [177], while Herzberg *et al.* observed the  $d^3\Delta - X^1\Sigma^+$  system [168], Simmons and Tilford the  $D^1\Delta - X^1\Sigma^+$  system [178] and Herzberg *et al.* the  $I^1\Sigma^- - X^1\Sigma^+$ system [179].

Spectroscopic absorption and emission data of improved resolution were obtained by Le Floch and coworkers for some  $A^1\Pi - X^1\Sigma^+$  bands, as well as the perturbing intercombination bands, at an absolute accuracy of 0.06 cm<sup>-1</sup>. In particular a very detailed perturbation analysis of the  $A^1\Pi$ , v = 0 state was performed for rotational states up to J = 75 [151] and for the specific rotationelectronic interaction between the  $A^1\Pi$  and  $D^1\Delta$  states [180]. Details of an analysis of the  $A^1\Pi$ , v = 1 state, as performed by Le Floch [152], can be found in the compilation of classical data by Morton and Noreau [155]. Notwithstanding the high accuracy of the data obtained from the classical studies, Drabbels *et al.* found small deviations for level energies of four (*e*)-parity levels of  $A^1\Pi$ , v = 0, J = 1-4 from a laser excitation study [156] performed at an accuracy of 0.002 cm<sup>-1</sup>; values for these levels were found to deviate by -0.037 cm<sup>-1</sup> from the classical data [151].

For targeted studies using the  $A^1\Pi - X^1\Sigma^+$  bands of carbon monoxide to probe possible variations of the proton-to-electron mass ratio  $\mu = m_p/m_e$  on cosmological time scales, an absolute accuracy of 0.01 cm<sup>-1</sup> is required [134]. Therefore our team set out to remeasure the  $A^1\Pi - X^1\Sigma^+$  spectra at high resolution and accuracy, and part of the data have been published recently in the context of searching for  $\mu$ -variation [7]. Here we report a more extensive data set for the  $A^1\Pi - X^1\Sigma^+$  (0,0) and (1,0) bands, as obtained from (i) a vacuum ultraviolet (VUV) FT study in both molecular jet and static gas configurations, and (ii) a Doppler-free two-photon laser excitation study. By including highly accurate spectroscopic information on the  $X^1\Sigma^+$  ground state of  ${}^{12}C^{16}O$  obtained from infrared [165] and far-infrared studies [162] an improved analysis of the perturbations in the  $A^1\Pi$ , v = 0 and v = 1 states is presented.

#### 5.2 Experimental

Two independent high-resolution spectroscopic studies of the  $A^1\Pi - X^1\Sigma^+$ (0,0) and (1,0) bands were performed. The experimental methods have been described in Ref. [7], and are only introduced briefly here.

#### **VUV-FT** spectroscopy

The VUV-FT spectrometer installed at the end of the SOLEIL DESIRS (Dichroisme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron) beamline synchrotron was used for recording direct absorption spectra, hence the transitions probed follow one-photon selection rules. For a detailed description of this instrument we refer to Refs. [158, 181]. Of importance are the conditions and configurations under which the gas-phase absorption was monitored: a windowless cell-configuration and a free-jet configuration. A windowless Tshaped cell-configuration of 10 cm length was employed to record a spectrum from quasi-static CO gas. A free-jet configuration was used to measure the narrow lines characteristic of a jet-cooled beam, delivering spectra at a rotational temperature of 12 K, and with reduced Doppler width. Typical VUV-FTS spectra obtained from both configurations are shown in Fig. 5.1

In order to achieve optimum resolution in both configurations, each measurement was recorded by taking 1978 kilo-samples of data throughout the moving arm travel distance of ~ 40 mm. This setting produces an instrumental resolution of 0.075 cm<sup>-1</sup> or resolving power of 900 000. When the travel distance of the moving arm is known [158, 181], the wavelength of the FT spectrometer is intrinsically calibrated. Verification and further fine-tuning of the absolute calibration is obtained from on-line recording of a xenon line, which is produced in the gas filter employed for filtering the harmonics generated in the undulator section of the beam line. The calibration line is the Xe resonance at 68 045.156 (3) cm<sup>-1</sup> [159], which is based on accurate relative measurements [160] and the measurement of a VUV anchor line [161].

#### Two-photon laser study

Two-photon Doppler-free excitation studies on the CO  $A^1\Pi - X^1\Sigma^+$  system were performed with the pulsed-dye-amplifier (PDA) laser system at Amsterdam, which has been used in several studies and described in previous publications (e.g. Ref. [163]). It consists of a three-stage narrowband tunable



**Figure 5.1** – (Color online) Spectra recorded with the vacuum ultraviolet Fourier-transform setup at the SOLEIL synchrotron. On the left the room temperature static gas absorption spectra are displayed, and on the right the jet absorption spectra. In the top row are overview spectra, in the middle panels a zoom-in on the (1,0) band, and the lower panels are detailed views of the spectra that demonstrate the linewidths. Note the narrow linewidth for the lowest J-levels in the jet spectra, and the increased linewidth for the higher J-levels, due to contributing absorption by background static gas.

PDA, seeded by the output of a cw ring dye laser (Spectra Physics 380 D), and pumped by a Nd:YAG laser, delivering nearly FT limited laser pulses of 5 ns duration. For absolute frequency calibration of the seed laser  $I_2$  saturated absorption spectra were recorded for reference [127, 164], while transmission peaks of a length-stabilized etalon (of free spectral range 148.96 MHz) was em-


**Figure 5.2** – (Color online) Experimental configuration employed for the 2+1' REMPI laser measurements. In the top part the CW ring dye laser, and the calibration facilities are shown. In the lower right part the pulsed dye amplifier (PDA) setup is depicted. The lower left part shows the interaction zone of the molecular beam with the two ultraviolet laser beams, and the Sagnac interferometric geometry for the frequency-doubled output of the injection-seeded PDA. The acronyms BBO, KDP and KD\*P refer to crystals used for non-linear upconversion of laser radiation.

ployed for interpolation and for linearization of the scan. The pulsed output of the PDA system was frequency doubled in a KDP crystal, and the tunable UV pulses were employed in the two-photon experiment.

Two-photon laser excitation is performed after splitting the UV-laser beam in two parts, each one perpendicularly crossing a pulsed and skimmed molecular beam, arranged from opposite sides as illustrated in Fig. 5.2. Exact counterpropagation is achieved by aligning the beams as part of a Sagnac interferometer [83] to avoid residual Doppler-shifts. Considering the compromise between the signal-to-noise ratio and AC-Stark effects, each FT limited UV-laser beam



**Figure 5.3** – (Color online) Assessment of the AC-Stark effect on the twophoton S(0) and R(2) lines in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) band of CO. The true value of the transition frequency is determined from extrapolation to zero intensity.

is loosely focused with a 1-m lens. Another deep UV beam of 207 nm, generated by frequency tripling the 621 nm output of a pulsed dye laser system (Spectra-Physics PDL3), is employed for ionizing the  $A^1\Pi$  excited state population in a 2+1' resonance enhanced multi-photon ionization (REMPI) scheme. It is noted that one photon at 207 nm suffices to ionize a molecule excited into the  $A^1\Pi$  state. In order to avoid AC-Stark effects from the ionization laser, its pulse timing is delayed by 10 ns with respect to the excitation laser. CO<sup>+</sup>ions, produced upon REMPI, are accelerated in a time-of-flight tube toward a multichannel plate (MCP) detector.

Sources of uncertainty in the absolute frequency calibration in the laser experiment were investigated. The statistical uncertainty associated with remeasurement of the lines is found to be  $0.001 \text{ cm}^{-1}$ . The dominant source of systematic uncertainty is the effect of frequency chirp in the PDA [163], amounting to  $0.002 \text{ cm}^{-1}$  in the presently used two-photon excitation mode; this estimate is deduced from quantitative investigations of this phenomenon [86]. A second source is in the AC-Stark effect, which is studied in detail. Measurements of the transition frequency as a function of power density are shown

for the example of the S(0) and R(2) lines in the  $A^1\Pi - X^1\Sigma^+$  (0,0) band in Fig. 5.3. The S(0) transition frequency plotted in Fig. 5.3 is offset by 64754 cm<sup>-1</sup>, while that for R(2) is offset by 64752 cm<sup>-1</sup>. It is noted that in view of experimental limitations the power density can only be given on a relative scale in Fig. 5.3. The AC-Stark measurements were used for extrapolation to zero power density, yielding the true transition frequencies. The fitting uncertainty of the extrapolated AC-Stark value is 0.0007 cm<sup>-1</sup>. The possible Doppler-shift in a two-photon experiment on a molecular beam is minimized by employing the Sagnac interferometric scheme to ascertain that laser beams are counter-propagating [83]. The other sources of uncertainty such as linefitting, I<sub>2</sub> calibration, etalon nonlinearity and DC-Stark shift make very small contributions. The overall uncertainty in the strongest laser lines with good signal-to-noise ratio is estimated to be 0.002 cm<sup>-1</sup>.

#### 5.3 Results

#### VUV-FT data

VUV-FT spectra for the  $A^1\Pi - X^1\Sigma^+$  (0,0) and (1,0) bands of CO are recorded in a molecular jet expansion and in a room temperature static gas cell. Overview spectra for both configurations are shown in Fig. 5.1. It is noted that in the jet-cooled spectrum, the spectral contributions from background gas give rise to broadened pedestals to the narrow lines. From the Boltzmann distribution a rotational temperature of  $320 \pm 20$  K and a linewidth of 0.16 cm<sup>-1</sup> are deduced for the static cell configuration. For the jet-configuration a bi-modal temperature distribution is found, as a consequence of some room temperature background gas residing in the VUV beam path. The rotational temperature of the jet component is  $12 \pm 1$  K, while for the room temperature pedestal a rotational temperature of  $340 \pm 60$  K is derived. The linewidth of the jet part of the spectral lines is 0.09 cm<sup>-1</sup>, while the pedestal exhibits a width of 0.16 cm<sup>-1</sup>.

Some 118 transitions of CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands, measured with the VUV-FTS, are presented in Table 5.1. In addition 23 absorption lines of excitations to perturber states are listed in Table 5.2 and Table 5.3. The subscripts *e* and *f* in Tables 5.1–5.3 indicate the electronic symmetry of the upper state to emphasize that the FTS and two-photon laser transitions (see Table 5.5 and detailed descriptions below) obey different selection rules and thus access different upper states for a given lower state. The superscripts *Q* and *O* in Table 5.2 denote the  $e^{3}\Sigma^{-}$  total angular momentum excluding spin, according to the notation in Ref. [155]. Accurate line positions in these tables are obtained by fitting the FTS data with a model that correctly describes the

**Table 5.1** – Calibrated one-photon transition frequencies (in vacuum  $cm^{-1}$ ) in the  ${}^{12}C^{16}O A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands from the VUV-FTS study. Lines marked with b were blended, and with w were weak in the spectrum. The estimated uncertainty is 0.01  $cm^{-1}(1\sigma)$  except for the weak or blended lines.

J	$\mathbf{R}_{e}(J)$	$Q_f(J)$	$P_e(J)$	$\mathbf{R}_{e}(J)$	$Q_f(J)$	$\mathbf{P}_{e}(J)$
		(0,0)			(1,0)	
0	64747.97			66236.22		
1	$64750.50^{b}$	64744.13		66238.49	66232.38	
2	64752.35	$64742.83^{b}$	64736.44	66240.01	66230.80	66224.69
3	64753.54	64740.86	64731.25	$66240.79^{b}$	66228.48	66219.27
4	64754.01	64738.23	64725.44	$66240.85^{b}$	66225.41	66213.09
5	64753.73	64734.93	$64718.92^{b}$	66240.25	66221.64	$66206.20^{b}$
6	64752.62	64730.95	64711.72	66238.99	66217.19	66198.58
7	$64750.33^{b}$	64726.26	64703.77	66237.06	66212.08	$66190.29^{b}$
8	64745.87	64720.84	64694.96	66234.47	$66206.30^{b}$	$66181.35^{b}$
9	64752.11	64714.60	64684.97	66231.24	66199.89	66171.72
10	64747.30	64707.40	64672.84	66227.35	66192.81	66161.47
11	$64742.66^{b}$	64698.87	64671.40	66222.81	66185.09	66150.55
12	64737.56	64688.26	64658.92	66217.60	66176.71	66138.99
13	64731.83	64693.70	64646.61	66211.73	66167.67	66126.77
14	64725.02	64682.70	64633.88	66205.18	66157.96	66113.91
15	64716.31	64671.99	$64620.44^{w}$	66197.96	66147.59	66100.36
16	$64717.69^w$	64661.11	$64606.02^w$	$66190.03^{b}$	66136.54	66086.16
17	64708.31	64649.80		$66181.47^{b}$	66124.81	$66071.28^{b}$
18	64699.22	64638.02		66172.23	66112.41	$66055.77^{b}$
19		64625.66		66162.28	66099.33	$66039.54^{w}$
20		$64612.68^{w}$		$66151.64^{w}$	66085.57	$66022.67^{w}$
21		$64599.05^{w}$			$66071.07^{b}$	
22					$66055.94^{wb}$	
23					66039.81 <sup>w</sup>	

**Table 5.2** – Transition frequencies (in vacuum  $cm^{-1}$ ) in the  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$ (1,0) band of <sup>12</sup> C<sup>16</sup> O obtained in the VUV-FT experiment.

J	${}^{Q}\mathbf{R}_{e}(J)$	$^{Q}\mathbf{Q}_{f}(J)$	$^{O}\mathbf{P}_{e}(J)$
		(1,0)	
8	64758.42	64755.88	
9			64701.24
10			64685.42
11		$64718.75^{b}$	
12		64705.73	
13		64674.65	

**Table 5.3** – Transition frequencies (in vacuum  $cm^{-1}$ ) in the  $d^3\Delta - X^1\Sigma^+$ (5,0) band of  ${}^{12}C^{16}O$  obtained in the VUV-FT experiment. In the  $d^3\Delta - X^1\Sigma^+$ system only the F<sub>3</sub> components are observed, corresponding to transitions to the  ${}^{3}\Delta_{1}$  spin-orbit component.

J	$\mathbf{R}_{e}(J)$	$\mathrm{Q}_f(J)$	$\mathbf{P}_{e}(J)$
		$(5,0) F_3$	
0	$66210.20^{w}$		
2		66204.06	
3	66211.29	66200.58	
4	$66209.16^{w}$	66195.89	
5	$66205.78^{w}$		
6	$66201.09^{w}$	66182.70	$66166.90^w$
7		66174.17	$66155.80^{w}$
8		$66164.35^{w}$	$66143.42^{w}$
9		$66153.06^{w}$	
10		$66140.53^{w}$	

**Table 5.4** – Two-photon transition frequencies  $\nu$  (in vacuum cm<sup>-1</sup>) in the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands and in transitions to perturbing states as obtained from the Doppler-free laser measurements.

J	$S_e(J)$	$\mathbf{R}_f(J)$	$Q_e(J)$	$P_f(J)$	J	$S_e(J)$	$\mathbf{R}_f(J)$	$Q_e(J)$	$P_f(J)$
		$A^1\Pi - X$	$\Sigma^{+}(0,0)$				$A^1\Pi - X$	$\Sigma^{+}(1,0)$	
0	64754.347				0	66242.347			
1	64760.049	64750.518	64744.138		1	66247.707	66238.503	66232.383	
<b>2</b>		64752.398	64742.815	64736.45	0.2	66252.333	66240.017	66230.813	66224.694
3		64753.612	64740.825		3		66240.800	66228.481	
4		64754.156			4		66240.876	66225.419	
5		64754.017			5		66240.267		
<b>6</b>		64753.176			6		66238.994		
7		64751.591			7			66212.085	
8		64749.190			9		66231.249		
9		64745.822			13		66211.731		
10		64741.128			17	66241.303			
11		64734.360			19	66228.352			
12		64743.640					$d^3\Delta - X$	$^{1}\Sigma^{+}(5,0)$	
13		64736.459			1		66211.750		
		$e^{3}\Sigma^{-} - \lambda$	$X^{1}\Sigma^{+}(1,0)$		<b>2</b>		66212.117		
10		64761.036			3	66224.547	66211.268		
11		64751.832			4	66225.005			
					5	66224.151			



**Figure 5.4** – (Color online) Two-photon excitation spectrum of close lying R(1) and R(6) lines in the  $A^1\Pi - X^1\Sigma^+$  (1,0) band of  ${}^{12}C^{16}O$  recorded simultaneously with an  $I_2$  saturated absorption spectrum for absolute reference [127] and the transmission markers of a HeNe-stabilized etalon for relative calibration. The  $I_2$  hyperfine component indicated with an asterisk (\*) was used for absolute reference. The scale on top represents the frequency of the cw-seed laser, the one at the bottom the two-photon excitation energy.

recorded convolved profiles. The accuracy of these transitions is 0.02 cm<sup>-1</sup>. A few weak (denoted by w) and blended (b) lines have larger error of 0.04 cm<sup>-1</sup>. As will be discussed below, the transition frequencies of low-J lines in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  bands are accurate at the 0.01 cm<sup>-1</sup> level.

The data obtained by the FTS methods are analysed for internal consistency. Combination differences between P(J) and R(J-2) lines in the VUV-FT spectra, probing a common excited state J' = J - 1, were calculated and compared to the very accurate far-infrared data [162] yielding a standard deviation of  $0.013 \text{ cm}^{-1}$ . Apart from some outlier points, associated with very weak or blended lines, this analysis demonstrates that the relative accuracies of the low-J values in the FT-spectra are  $0.01 \text{ cm}^{-1}$ .

#### Two-photon laser data

In the two-photon Doppler-free excitation studies spectral lines in the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands were investigated. A typical example of a spectrum, covering the R(1) and R(6) lines in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) band, is shown in Fig. 5.4. Transition frequencies were obtained by producing a linearized absolute scale for the two-photon energy from the simultaneously recorded  $I_2$  and etalon spectra at the fundamental frequency provided by the cw seed-laser, and then fitting the CO resonances on that scale, after multiplying by four. Results (including AC-Stark correction) at an accuracy of 0.002  $\rm cm^{-1}$  are presented in Table 5.4. In the laser experiments some transitions to  $e^{3}\Sigma^{-}$  and  $d^{3}\Delta$  perturbing states were also observed. It is noted that the frequencies in the VUV-FT one-photon spectra and the two-photon laser spectra are different, e.q. the R(1) line observed by both methods probes a different A-doublet component in the excited  ${}^{1}\Pi$  state, and therefore exhibits a different transition frequency. Further, in two-photon excitation the R(0) transition is forbidden [182]. Ground state combination differences were also calculated and compared to accurate far-infrared data, resulting in a standard deviation of only  $0.002 \text{ cm}^{-1}$  and thus proving consistency within the laser data set.

#### Level energies

Using the accurately known level energies in the ground state [162], both the one-photon transition frequencies and the two-photon transition frequencies are converted to level energies, listed in Table 5.5, in order to make a detailed comparison of accuracies. The FTS data are benchmarked against the laser data in Fig. 5.5. This demonstrates that there is an average offset between the two data sets of 0.005 cm<sup>-1</sup>, which is attributed to an offset in the VUV-FT data, well within the estimated uncertainty. The deviations have a  $(1-\sigma)$  spread of 0.01 cm<sup>-1</sup>, showing that the VUV-FT data can be considered reliable within this uncertainty limit.

In a comparison of the present  $A^{1}\Pi v = 0$  level energies from laser data with that of Ref. [151], we obtain an average difference of 0.043 cm<sup>-1</sup> with a standard deviation 0.017 cm<sup>-1</sup>. The latter value is consistent with the statistical uncertainty claimed in Ref. [151]. The discrepancy could be attributed to the accuracy of the absolute reference standard used in that study [183]. A similar comparison of the  $A^{1}\Pi v = 1$  level energies of the present laser data with those in Ref. [152] yield a difference of 0.022(8) cm<sup>-1</sup>. The comparison of the level

**Table 5.5** – Level energies (in vacuum  $cm^{-1}$ ) of  $A^{1}\Pi$  and perturbing states calculated from the combined data sets form the two experiments. Levels indicated with (\*) are derived from the more accurate Doppler-free two-photon laser excitation study. The other levels are derived from the VUV-FTS study. Where possible values are obtained after averaging over transitions frequencies in different branches. e and f denote the electronic symmetry of the state.

J'	e	f	e	f	$F_{1e}$	$F_{2f}$	$F_{3e}$	$F_{3f}$
	$A^{1}\Pi$	v = 0	$A^{1}\Pi$	v = 1	$e^{3}\Sigma$	$\Sigma^{-}, v = 1$	$d^{3}\Delta$ ,	v = 5
1	64747.983*	64747.985*	66236.228*	66236.229*			66210.20	
2	64754.349*	64754.363*	66242.348*	66242.348*				66215.595 *
3	64763.894*	64763.933*	66251.551 *	66251.552 *				66223.652 *
4	64776.60	64776.681*	66263.868 *	66263.870  *			66234.36	66234.338 *
5	64792.46	64792.605*	66279.32	66279.324*			66247.617 *	
6	64811.41	64811.687*	66297.93	66297.937*			$66263.453  {}^{*}$	66263.44
7	64833.35	64833.911*	$66319.728  {}^{*}$	66319.730  *			66281.822*	66281.81
8	64857.95	64859.233*	66344.70	66344.69	64874.22	64894.27		66302.74
9	64884.26	64887.580*	66372.87	66372.87	64896.82			66326.04
10	64925.08	64918.800*	66404.21	66404.227*				66351.93
11	64958.69	64952.532*	66438.76	66438.76		64972.440*		
12	64996.32	64988.027*	66476.47	66476.47		65005.499*		
13	65037.34	65043.406*	66517.37	66517.36		65024.35		
14	65081.53	65086.157*	66561.42	66561.429*				
15	65128.48	65133.05	66608.64	66608.64				
16	65177.37	65183.59	66659.01	66659.01				
17	65240.16	65237.52	66712.53	66712.53				
18	65296.03	65294.81	66769.20	66769.20				
19	65356.01	65355.34	66829.024*	66829.00				
20		65419.06	66891.96	66891.95				
21		65485.96	66958.030*	66957.98				
22				67027.17				
23				67099.18				



**Figure 5.5** – (Color online) Comparison of level energies as obtained from the Doppler-free two-photon laser experiments  $(E_{PDA})$  and those from the VUV-FT data  $(E_{FTS})$ .

energies from Le Floch *et al.* [151, 152] is shown graphically in Fig. 5.6. The average discrepancy with the Le Floch data is different for the v = 0 and v = 1 bands, precluding the possibility of applying a global correction to all previous measurements of the other bands, *e.g.* those listed in Ref. [155]. In the following section, we discuss a deperturbation analysis which also included the high-J  $A^1\Pi$  level energies from [151, 152], which were corrected for by taking into account the average discrepancy in the comparison for each band.

The present laser spectroscopic data can be compared to the results of the laser measurements performed by Drabbels *et al.* [156], probing the  $B^1\Sigma^+ - A^1\Pi$ (0,0) band. The results of a previous investigation from the same group [184] of the  $B^1\Sigma^+ - X^1\Sigma^+$  system are then used to derive the  $A^1\Pi$  level energies. A comparison of the transitions derived for the  $A^1\Pi - X^1\Sigma^+$  system from Ref. [156, 184] and the present laser data set yields an average difference of 0.0035 cm<sup>-1</sup> with a standard deviation of 0.013 cm<sup>-1</sup>. We note that excluding the  $B^1\Sigma^+ - A^1\Pi$  P(2) transition of Table 1 in Ref. [156] reduces the standard



**Figure 5.6** – (Color online) Comparison of level energies obtained in the present laser study with those of Le Floch [151, 152] and Drabbels [156]. The solid line indicates the average deviation for each band, the dashed (v = 0) and dash-dotted (v = 1) lines indicate 1- $\sigma$ .

deviation of the comparison to 0.0034 cm<sup>-1</sup> and the average difference is - 0.0017 cm<sup>-1</sup>. The  $A^1\Pi$  level energies listed in Table 2 of Ref. [156] are slightly different than a derivation from the combination of the  $B^1\Sigma^+ - X^1\Sigma^+$  (from Ref. [184]) and  $B^1\Sigma^+ - A^1\Pi$  (from Ref. [156]) spectroscopic investigations. Using these listed  $A^1\Pi$  level energies of Drabbels *et al.* [156], a comparison with the present laser data yield an average difference of 0.007(4) cm<sup>-1</sup> (the datapoints are included in Fig. 5.6). Although we do not find exact agreement with Drabbels *et al.* [156], nevertheless the overall shift in  $A^1\Pi$ , v = 0 levels with respect to those of Le Floch *et al.* [151] is confirmed.

#### 5.4 Perturbation analysis

**Table 5.6** – Effective Hamiltonian and matrix elements for a perturbation analysis of the rotational level structure of the  $A^1\Pi$  state (i = 0, 1) and its perturbing states. For the  $A^1\Pi$  diagonal element, the + and - signs refer to the e- and f-symmetry states, respectively.

	$A^1\Pi(v=i)$	$D^1\Delta(v=0,1,2)$	$I^1\Sigma^-(v=1,2,3)$	$e^3\Sigma^-(v=1,2,3)$	$a'^3 \Sigma^+(v=9,10,11)$	$d^3\Delta(v=4,5,6)$
$A^{1}\Pi$	$T_v + (B \pm \frac{q}{2})\widehat{N}^2$	$\xi_i(\mathbf{D}_v) \times$	$\xi_i(\mathbf{I}_v) \times$	$\eta_i(\mathbf{e}_v)\widehat{L}\cdot\widehat{S}$	$\eta_i(\mathbf{a}'_v)\widehat{L}\cdot\widehat{S}$	$\eta_i(\mathbf{d}_v)\widehat{L}\cdot\widehat{S}$
$D^1\Delta$	$-DN^{4} + HN^{6}$	$(N_+L + NL_+)$ $T_v + B\widehat{N}^2$	$(N_{+}L_{-} + N_{-}L_{+})$ 0	0	0	0
$I^1\Sigma^-$		$-DN^4 + HN^6$	$T_v + B\hat{N}^2$	0	0	0
$e^{3}\Sigma^{-}$			$-D\widehat{N}^4 + H\widehat{N}^6$	$T_v + B\hat{N}^2$	0	0
				$-D\widehat{N}^4 + H\widehat{N}^6 + \frac{2}{2}\lambda(3\widehat{S}_z^2 - \widehat{S}^2)$		
$a'^3\Sigma^+$				0	$T_v + B\widehat{N}^2  - D\widehat{N}^4 + H\widehat{N}^6$	0
					$+\frac{2}{3}\lambda(3\widehat{S}_z^2 \cdot \widehat{S}^2) \\ +\gamma(\widehat{N} \cdot \widehat{S})$	
$d^{3}\Delta$					1 /(1 ~ ~)	$T_v + B\widehat{N}^2 \\ - D\widehat{N}^4 + H\widehat{N}^6$
						$\frac{-DN}{+1} + \frac{2}{3}\lambda(3\widehat{S}_z^2 - \widehat{S}^2)$
						$+\gamma(N\cdot S) +A\widehat{L}_z\widehat{S}_z$
						$ + \frac{1}{2} A_D \lambda (N^2 L_z S_z + \widehat{L}_z \widehat{S}_z \widehat{N}^2) $

Previous studies [150, 151, 155, 180, 185] have shown that the  $A^{1}\Pi$  state of CO is perturbed by  $D^1\Delta$ ,  $I^1\Sigma^-$ ,  $e^3\Sigma^-$ ,  $d^3\Delta$ , and  $a'^3\Sigma^+$  states. In the analysis, we have adopted an effective Hamiltonian model with matrix elements given in Table 5.6. For the  $A^1\Pi$  state the subscript *i* refers to vibrational quantum numbers v = 0 and 1, the e and f electronic symmetry components of the  $A^{1}\Pi$ state are treated separately, and the + and - signs pertaining to Lambda doubling in the diagonal element refer to the e and f symmetry states, respectively. While the  $D^1\Delta$  and  $d^3\Delta$  states have nearly degenerate e and f components, the  $I^1\Sigma^-$  state exhibits only f components, two fine structure levels of the  $e^{3}\Sigma^{-}$  state have e character and one has f, and for the  $a'^{3}\Sigma^{+}$  state there are two f and one e levels. The interactions between the  $A^1\Pi$  state and the  $D^1\Delta$ and  $I^{1}\Sigma^{-}$  states are due to L-uncoupling and thus produce heterogeneous interactions with J-dependent matrix elements, while interaction with the triplet states is due to spin-orbit interaction represented by J-independent matrix elements [150]. Note that the matrix is symmetric, the lower left non-diagonal elements (not shown) are equivalent to those of the corresponding upper right elements. An approximation is made by neglecting the mutual interactions between the perturbing states, therefore the corresponding matrix elements are set to zero.

In the present study highly accurate level energies of  $A^1\Pi$ , low-J levels are determined (up to J = 21 for v = 0 and to J = 23 for v = 1, respectively), while in previous investigations the rotational manifold could be followed to much higher J-values. For  $A^1\Pi$ , v = 0 values up to J = 75 were listed [151], while for  $A^1\Pi$ , v = 1 extensive measurements were performed, and a listing of up to J = 70 is available in a Thesis study [152]. Representations in terms of molecular constants are given in the open literature [155, 168, 169, 180].

In the perturbation analysis, a least-squares fitting procedure using the Pgopher software [186] was applied to the experimental data. It turned out to be necessary to include literature data from Le Floch and co-workers [151, 152] to constrain fitting of the parameters pertaining particularly to the perturber states that cross the  $A^1\Pi$  rotational manifolds at high-J values. Also included in the global fitting are level energies for the J = 22 - 75 states for the  $A^{1}\Pi$ v = 0 state from Ref. [151] and level energies from J = 24 - 70 states for the  $A^{1}\Pi v = 1$  state from Ref. [152]. For the  $A^{1}\Pi v = 0$  state, the perturbing states as in the previous work of Le Floch *et al.* [151] are comprised in the fit, namely the  $D^1\Delta v = 0$  and 1, the  $I^1\Sigma^- v = 1$  and 2, the  $e^3\Sigma^- v = 1, 2$ and 3, the  $d^3\Delta v = 4$  and 5, and the  $a'^3\Sigma^+ v = 9$  states. While for the  $A^1\Pi$ v = 1 state, we also include the perturbing states as indicated in Fig. 1 of Ref. [185], which are the  $D^1\Delta v = 1$  and 2, the  $I^1\Sigma^- v = 2$  and 3, the  $e^3\Sigma^$ v = 3, the  $d^3\Delta v = 5$  and 6, and the  $a'^3\Sigma^+ v = 10$  and 11 states. We have also included transitions from the ground state  $X^1\Sigma^+$  to the perturber states  $e^{3}\Sigma^{-} v = 1$  and 2;  $d^{3}\Delta v = 4, 5, 6; a'^{3}\Sigma^{+} v = 9$  and 10;  $I^{1}\Sigma^{-} v = 1$  and 3



**Figure 5.7** – (Color online) Fitting residuals from the current perturbation model used. Data points from the FTS and the laser study state are represented by circles in (a), data from literature are represented by open squares. The residuals for transitions of the present laser study only are shown on a reduced scale in (b).

obtained from Refs. [151, 152, 155, 168]. Each datapoint from the literature was weighted according to the claimed accuracy. Relative weights of 1.0, 0.2, 0.04, 0.04, and 0.01 are assigned to the present laser spectroscopy data, the present FTS data, the data from Le Floch [151, 152], the data from Morton and Noreau [155], and the data from Herzberg *et al.* [168], respectively. The parameters were initialized using the centrifugal distortion constants D and H, as well as the overall  $\Lambda$ -doubling constant q values of Ref. [151] for  $A^1\Pi$ v = 0, and using the D constant for  $A^1\Pi v = 1$  from Ref. [150]. The  $\Lambda$ -doublet splitting is highly influenced by the local perturbations as has been pointed out in Ref. [151]. We note that the q-parameter could have been set to zero while still retaining the capacity of the model to reproduce the experimental values to a similar accuracy. Presumably this is because the parameters associated with the perturbation already encode the information of  $\Lambda$ -doubling



**Figure 5.8** – (Color online) Simulated spectrum (lower trace) with FTS spectrum (upper) for  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) band of CO.

itself. (We note that some hint of a systematic trend in the fitting residues could be observed at high-J levels, however, these are within the measurement uncertainty.) Nevertheless, we retained the q-parameter in the model where the initial parameter values were set to the value in Ref. [151].

The residuals of the combined fit, including literature data and all possible perturbing states, are plotted in Fig. 5.7. The contribution to the rms residual value of laser spectroscopy data is  $0.002 \text{ cm}^{-1}$  and the contribution of FTS data is  $0.014 \text{ cm}^{-1}$ . The rms residual value of the combined data set including the less accurate literature data yields  $0.09 \text{ cm}^{-1}$ , demonstrating that the fitting model satisfactorily reproduces the comprehensive experimental data set. In total, some 787 transitions were used in the global fitting procedure, of which 141 transitions are from the present spectroscopic measurements. Inspection of the correlation matrix indicates a satisfactorily low correlation between the



**Figure 5.9** – (Color online) Simulated spectrum (lower trace) with FTS spectrum (upper) for  $A^1\Pi - X^1\Sigma^+$  (1,0) band of CO.

39 fitted model parameters. We note that judiciously fixing parameters which pertain to molecular constants of perturber states with minimal effect further reduces the correlations between the fitted parameters.

The final set of fitted parameters are summarized in Table 5.7. For the  $A^{1}\Pi$  v = 0 state, the perturbers with significant effect include the  $e^{3}\Sigma^{-}v = 1, 2$  and  $3, d^{3}\Delta v = 4$  and  $5, I^{1}\Sigma^{-}v = 1$  and  $2, D^{1}\Delta v = 0$  and 1 and  $a'^{3}\Sigma^{+}v = 9$  states. For the  $A^{1}\Pi v = 1$  state the perturbers are the  $D^{1}\Delta v = 1$ , the  $e^{3}\Sigma^{-}v = 3$ , the  $d^{3}\Delta v = 5$  and  $6, I^{1}\Sigma^{-}v = 2$  and 3, and the  $a'^{3}\Sigma^{+}v = 10$  and 11 states. We note that the molecular constants with an uncertainty indicated within parenthesis () are fitted parameters. The other constants without indicated uncertainty value are taken from literature and fixed during the fitting. It was necessary to fix these parameters to reduce the correlation between parameters. The improvements in the present study mostly affect the molecular constants  $T_{v}$  and B for the  $A^{1}\Pi v = 0$  and 1 and  $e^{3}\Sigma^{-}v = 1$  states, and for the  $T_{v}, B$ 

and A constants for the  $d^3\Delta v = 5$  state, owing to the more accurate dataset for the low-J transitions in the present study. We note that our molecular constants, e.g.  $T_v$  and B, are defined differently in Field [150] and Le Floch et al. [151] as listed in Table 4.2 of Ref. [187]. The definition that we adopt in the present study is convenient in terms of extracting parameters directly from the fit of the experimental data. In this study the level energy is expressed as a polynomial series in x = J(J+1), and thus combine effects from molecular parameters of other interacting states. Although an explicit relation between the different definitions can be derived from the effective elements of the Hamiltonian in Ref. [187], not all values of isolated molecular parameters were available, and thus a direct comparison was not possible. In addition, the spin-orbit interaction parameters  $(\eta_i)$  in our definition are larger by a factor  $\sqrt{3}$  than in Ref. [150, 151]. We note that when the values of parameters are taken from literature (both for fixed parameters and for initialization of fitted parameters), we have carried out the appropriate conversion by taking into account the definitions of Ref. [187]. The improved constants for  $e^{3}\Sigma^{-}$  and  $d^3\Delta$  in the present analysis stem from the few transitions recorded at much improved absolute accuracy in the present measurements. For the perturber states that affect the low-J rotational states the  $A^1\Pi v = 0$  and 1 levels, accurate interaction parameters are obtained from the present deperturbation analysis. The current set of molecular constants gives an accurate description of the structure of  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands, that improves upon previous analyses. The values of matrix elements for other perturbations occurring at higher J-values are determined but should be treated with some caution. Their purpose is to describe the structure of  $A^1\Pi$ , v = 0 and v = 1 at the highest level of accuracy; they do not represent physical information at the highest accuracy levels on the perturbation crossings at higher J-values, which were not observed in the present spectroscopic study.

Simulated spectra using the parameters in Table 5.7 are shown with the FTS spectra in Fig. 5.8 for the  $A^1\Pi - X^1\Sigma^+$  (0,0) band and in Fig. 5.9 for the  $A^1\Pi - X^1\Sigma^+$  (1,0) band. The positions of the observed transitions belonging to the perturbing  $e^3\Sigma^- v = 1$  level and  $d^3\Delta v = 5$  level are also indicated in the figures. It should be noted that in addition to  $A^1\Pi - X^1\Sigma^+$  transitions, the  $d^3\Delta - X^1\Sigma^+ v = 5$  transitions have been recently observed in quasar absorption spectra [147].

**Table 5.7** – Compilation of the molecular constants for the  $A^1\Pi v = 0$  and v = 1 states of  ${}^{12}C^{16}O$  and all perturbing states following from the present analysis. In cases where an uncertainty is specified in () brackets the value was determined from the fit; in cases where this is not specified a value was taken from literature. All values in vacuum  $cm^{-1}$ .

Singlet states	$A^1\Pi(v=0)$	$A^1\Pi(v=1)$	
T	$64746\ 762\ (4)$	66228 801 (3)	
B	1.604069(8)	1.58126(1)	
$a (\times 10^5)$	3.1 (6)	-2.6(5)	
$D(\times 10^{6})$	7.348 (8)	7.41(1)	
$H(\times 10^{12})$	-9 (2)	-22(2)	
Triplet states	$e^3 \Sigma^- (v=1)$	$e^3 \Sigma^- (v=2)$	$e^3\Sigma^-(v=3)$
$T_{v}$	64801.136(4)	$65877.55^{\rm a}$	$66934.08^{\rm a}$
$\ddot{B}$	1.25708(3)	1.23909(2)	$1.22273^{\rm a}$
$\lambda$	$0.517^{\mathrm{a}}$	$0.568^{\mathrm{a}}$	$0.778^{\rm a}$
$D(\times 10^{6})$	$6.77^{\mathrm{a}}$	$6.75^{\mathrm{a}}$	$6.72^{\rm a}$
$H(\times 10^{12})$	$-2^{a}$	-2 <sup>a</sup>	-2 <sup>a</sup>
$\eta_0$	15.104(2)	-17.47(9)	21.6(5)
$\eta_1$			3.0(2)
Triplet states	$d^3\Delta(v=4)$	$d^3\Delta(v=5)$	$d^3\Delta(v=6)$
$T_v$	65102.12 (1)	66173.07(1)	$67225.80^{\rm b}$
$\ddot{B}$	1.23327(1)	1.21628(4)	1.19941(3)
A	-16.465 (6)	-16.674 (6)	-16.909 <sup>b</sup>
$\lambda$	$0.993^{\mathrm{a}}$	$1.2^{\mathrm{a}}$	$1.2^{\mathrm{b}}$
$\gamma ~(\times 10^3)$	$-8.54^{\rm a}$	-8 <sup>a</sup>	-8 <sup>b</sup>
$D(\times 10^{6})$	$6.47^{\mathrm{a}}$	$6.47^{\mathrm{a}}$	$6.44^{b}$
$H(\times 10^{12})$	$-0.8^{a}$	$-0.8^{a}$	-0.8 <sup>c</sup>
$A_{D}(\times 10^{4})$	-1 <sup>a</sup>	-1 <sup>a</sup>	-1 <sup>c</sup>
$\eta_0$	-21.69(2)	17.8(2)	
$\eta_1$		-16.916(5)	18.6(1)
Triplet states	$a'^3\Sigma^+(v=9)$	$a'^3\Sigma^+(v=10)$	$a'^3\Sigma^+(v=11)$
$T_v$	$65492.66^{\rm a}$	$66520.44^{\rm b}$	$67529.59^{\rm b}$
В	1 1019498	1.16640(9)	1.14921 <sup>b</sup>
	1.101042	1.10010 (0)	11110-1
$\lambda$	$-1.153^{a}$	-1.146 <sup>b</sup>	-1.153 <sup>b</sup>
$\lambda \ \gamma \ ( imes 10^3)$	$-1.151342^{\circ}$ $-1.153^{\circ}$ $0.72^{\circ}$	$-1.146^{\mathrm{b}}$ $-0.72^{\mathrm{b}}$	$-1.153^{b}$ $4.47^{b}$

continued on next page

Triplet states	$a'^3\Sigma^+(v=9)$	$a'^3\Sigma^+(v=10)$	$a'^3\Sigma^+(v=11)$
$D(\times 10^{6})$	$6.27^{\mathrm{a}}$	$6.26^{\mathrm{b}}$	$6.26^{\rm b}$
$H(\times 10^{12})$	$-0.4^{a}$	$-0.4^{d}$	$-0.4^{d}$
$\eta_0$	$2.421^{\rm a}$		
$\eta_1$		4.9(1)	3.6(3)
Singlet states	$D^1 \Delta(v=0)$	$D^1\Delta(v=1)$	
$T_v$	$65421.95^{\rm a}$	$66464.59^{\rm a}$	
B	$1.251^{a}$	$1.233^{a}$	
$D \; (\times 10^6)$	$7^{\mathrm{a}}$	$7^{\mathrm{a}}$	
$H(\times 10^{12})$	-0.3 <sup>a</sup>	-0.3 <sup>a</sup>	
$\xi_0$	$0.030^{\mathrm{a}}$	$0.040^{a}$	
$\xi_1$		0.073(4)	
Singlet states	$I^1 \Sigma^- (v=1)$	$I^1\Sigma^-(v=2)$	$I^1\Sigma^-(v=3)$
$T_v$	$65617.26^{\rm a}$	$66667.13^{\rm a}$	$67696.60^{\rm e}$
B	1.24332(4)	1.2254(1)	1.20759(4)
$D~(\times 10^6)$	$6.87^{\mathrm{a}}$	$6.89^{\mathrm{a}}$	$6.89^{\mathrm{f}}$
$H \; (\times 10^{12})$	$3^{\mathrm{a}}$	$3^{\mathrm{a}}$	$3^{\rm f}$
$\xi_0$	-0.076(1)	0.085~(3)	
$\xi_1$		0.079(2)	0.043~(2)

<sup>a</sup> Data from Ref. [151] and converted, see text.

<sup>b</sup> Data from Ref. [187] and converted, see text.

<sup>c</sup> Constant fixed to that of  $d^{3}\Delta$ , v = 5 as first-order approximation.

<sup>d</sup> Constant fixed to that of  $a'^3\Sigma^+$ , v = 9 as first-order approximation. <sup>e</sup> Data from Ref. [169].

<sup>f</sup> Constant fixed to that of  $I^1\Sigma^-$ , v = 2 as first-order approximation.

#### 5.5 Conclusion

We have obtained high resolution spectra of the two lowest-v' (0,0) and (1,0) bands of the  $A^1\Pi - X^1\Sigma^+$  system of  ${}^{12}C^{16}O$ , using two different advanced spectroscopic methods achieving high accuracy on absolute transition frequencies. The combined data were used to perform an improved analysis of the perturbations by a large number of states, in particular of the  $e^3\Sigma^- - X^1\Sigma^+$  (1,0) and  $d^3\Delta - X^1\Sigma^+$  (5,0) bands, crossing at low values of J. The present analysis is of importance to astronomical observations, where CO is often observed in cold environments with population of J < 20 quantum states.

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# CHAPTER 6

# High-precision laser spectroscopy of the CO $A^{1}\Pi - X^{1}\Sigma^{+}(2,0)$ , (3,0) and (4,0) bands

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High-precision two-photon Doppler-free frequency measurements have been performed on the CO  $A^1\Pi - X^1\Sigma^+$  fourth-positive system (2,0), (3,0), and (4,0) bands. Absolute frequencies of forty-three transitions, for rotational quantum numbers up to J = 5, have been determined at an accuracy of  $1.6 \times 10^{-3}$  cm<sup>-1</sup>, using advanced techniques of two-color 2+1' resonance-enhanced multi-photon ionization, Sagnac interferometry, frequency-chirp analysis on the laser pulses, and correction for AC-Stark shifts. The accurate transition frequencies of the CO  $A^1\Pi - X^1\Sigma^+$  system are of relevance for comparison with astronomical data in the search for possible drifts of fundamental constants in the early universe. The present accuracies in laboratory wavelengths of  $\Delta\lambda/\lambda = 2 \times 10^{-8}$ may be considered exact for the purpose of such comparisons.

#### 6.1 Introduction

The carbon monoxide molecule is one of the most thoroughly studied molecules in spectroscopy, from the microwave and infrared to the optical and vacuum ultraviolet parts of the electromagnetic spectrum. This second most abundant molecule in the Universe plays an important role in the chemical dynamics of the interstellar medium, as well as in Earth-based combustion, atmospheric, and plasma science. The  $A^{1}\Pi - X^{1}\Sigma^{+}$  system of CO, known as the fourth positive system, connects the electronic ground state of the molecule to its first excited state of singlet character, and it signifies the onset of strong dipoleallowed absorption features in the vacuum ultraviolet range. The spectroscopy of the  $A^{1}\Pi - X^{1}\Sigma^{+}$  bands has, since the first pioneering study by Deslandres in 1888 [171], been investigated by many authors (notably [166, 174]) culminating in a detailed analysis of the  $A^{1}\Pi$  state and the many perturbing states by Field *et al.* [29].

The present precision-frequency investigation of the (2,0), (3,0) and (4,0) bands of the  $A^{1}\Pi - X^{1}\Sigma^{+}$  system, by two-photon Doppler-free laser spectroscopy, is part of a program to apply the vacuum ultraviolet absorption lines of CO in a search for a variation of the proton-electron mass ratio at high redshift [7]. For this purpose the low-J transitions in the CO absorption bands should be calibrated at an accuracy better than  $\Delta\lambda/\lambda < 10^{-7}$ , and the perturbations with other electronic states should be analyzed as accurately as possible, to obtain reliable line intensities. Highly accurate transition frequencies of lines in  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0,0) and (1,0) bands were reported [7], as well as a detailed analysis of perturbations in the  $A^1\Pi$ , v = 0 and v = 1 levels [188]. Previously, the  $A^{1}\Pi - X^{1}\Sigma^{+}(2,0)$ , (3,0) and (4,0) bands have been investigated, at an accuracy of  $0.06 \text{ cm}^{-1}$ , by Lefloch, although the results were only partially published [152] in semi-open literature. In their compilation of CO-data for use in astronomy Morton and Noreau [155] have included these data of Le Floch. Here the laser-based methods of Ref. [7], providing improved accuracy, are extended to the (2,0), (3,0) and (4,0) bands.

#### 6.2 Experiment

In this study, a narrowband pulsed-dye-amplifier (PDA) laser system is used in a two-photon Doppler-free excitation scheme for a high-resolution spectroscopic investigation of the CO  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands. The measurement setup is schematically shown in Fig. 6.1. The PDA-laser system employed has been described previously [86] as well as its application to highresolution studies in CO [7, 163]. The narrowband PDA system is built as a three-stage traveling-wave amplifier, seeded by a Coherent-899 continuous wave



Figure 6.1 – (Color online) A schematic layout of the experimental setup, with the laser system, the frequency calibration setup and the molecular beam apparatus with the counter-propagating laser beams in a Sagnac configuration for Doppler-free two-photon spectroscopy. B.S.: beam splitter; Sk.: skimmer; MCP: microchannel plate; PMT: photomultiplier tube; TOF: time of fight. See text for further details.

(cw) ring dye laser, and pumped by a pulsed Nd:YAG laser; it delivers nearly Fourier-Transform limited laser pulses of 5 ns duration. The repetition rate of the pulsed laser is 10 Hz. For the present investigation, the cw ring-dye laser was routinely operated in the range 560-590 nm, while running on Rhodamine-6G, but in the PDA system two different dyes were used to cover the three different bands: Rhodamine-B (580 – 590 nm) for the  $A^1\Pi - X^1\Sigma^+$  (2,0) and (3,0) bands, and Rhodamine-6G (560 – 580 nm) covering the  $A^1\Pi - X^1\Sigma^+$  (4,0) band.

The output of the PDA laser passes through a KDP (Potassium Dihydrogen Phosphate) crystal for frequency doubling. Thereupon the laser beam is split in two on a beamsplitter and aligned in the geometry of a Sagnac interferometer to produce exactly counter-propagating beams for avoiding residual Doppler-shifts [83]. To systematically assess AC-Stark effects, different focus-

ing conditions are employed. An auxiliary laser beam at 220 nm is implemented for ionization of the  $A^1\Pi$  excited state population. By this means the 2+1' resonance-enhanced multi-photon ionization (REMPI) scheme efficiently produces signal. In order to reduce AC-Stark effects by the ionization laser, its pulse timing is delayed by 10 ns with respect to the narrowband spectroscopy laser.

The CO molecular beam is produced by a pulsed solenoid valve (General Valve, Series 9) in a source chamber, before entering an interaction chamber via a skimmer (1.5 mm diameter). The collimated CO molecular beam is interrogated by the laser beams under collision-free conditions. CO ions produced in the 2+1' REMPI process are accelerated via pulsed extraction voltages applied after the laser pulses, to avoid DC-Stark effects. The ions are subsequently mass selected in a time-of-flight tube before detection on a multichannel plate (MCP).

For calibrating the frequency of the transitions on an absolute scale, saturated  $I_2$  absorption spectroscopy is used, resolving hyperfine components, which are known to 1 MHz accuracy [189]. For frequency interpolation between CO and  $I_2$  resonances the transmission peaks of an etalon length stabilized to a He-Ne laser (with FSR = 150.01±0.01 MHz), were recorded simultaneously.

An important improvement over the previous laser-based study investigating the  $A^1\Pi - X^1\Sigma^+$  (0,0) and (1,0) bands [7], is that a frequency chirp-analysis setup has been implemented, following methods presented in Refs. [85, 86], thus achieving higher precision. In the present setup an acousto-optic modulator (AOM - Gooch & Housego) shifts the frequency of the cw laser by 595 MHz. The beatnote of this shifted cw laser frequency and the pulsed output of the PDA is detected by a fast photodiode, after the wave fronts are spatially overlapped by propagating through a single-mode fiber. The beat-note signal is then detected on a fast oscilloscope (Tektronix TDS7404) with 1 GHz analog bandwidth and 4 Gs/s sampling. The instantaneous frequency over the duration of the pulse is then determined as well as the frequency chirp over the pulse duration. The resulting frequency determinations of the CO resonances are finally corrected for this chirp effect.

#### 6.3 Results and Discussion

In the present study two-photon resonances in the  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands of CO are measured by two-photon laser spectroscopy. As an example, Fig. 6.2 shows a typical recording of the S(0) line in the  $A^1\Pi - X^1\Sigma^+$  (4,0) band, plotted with simultaneous recordings of etalon markers, the saturated iodine spectrum for absolute calibration, and results of the on-line chirp analyses for each of the data points. The full width at half maximum



**Figure 6.2** – (Color online) Typical recording of the S(0) transition in the CO  $A^1\Pi - X^1\Sigma^+(4,0)$  band, as measured via two-photon laser excitation, plotted as the (black) solid line. The (blue) dashed line and the (blue) full line represent etalon markers and the saturated iodine spectrum used for interpolation and calibration. The (\*) indicates the a4 (7,7) hyperfine component of the B-X (25,3) R(69) iodine line, which was used for the calibration. The (red) circles represent the on-line measured values for the chirp-induced frequency offset at the transition frequency.

(FWHM) of the CO transitions are around 200 MHz, limited by the bandwidth of the PDA laser.

Values for the transition frequencies were obtained from the calibration procedure, with corrections for the chirp and AC-Stark analysis, and multiplying by a factor of four for frequency-doubling and two-photon excitation. Resulting two-photon transition frequencies are listed in Table 6.1. In total, 43 lines in the  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands have been measured with an absolute accuracy of 0.0016 cm<sup>-1</sup>, corresponding to 50 MHz, or a relative accuracy of  $\Delta\lambda/\lambda = 2 \times 10^{-8}$ . In view of the fact that excitation takes place in a molecular beam, only transitions originating in low rotational quantum states (J < 6) could be observed. Lines are denoted with the usual O(J) to S(J)

Line	(2,0)	(3,0)	(4,0)
S(0)	67685.126	69097.776	70475.924
S(1)	67690.629	69103.134	70481.077
S(2)	67695.397	69107.716	70485.399
S(3)	67699.437	69111.519	
S(4)	67702.744	69114.546	
R(1)	67681.278	69093.930	70472.126
R(2)	67682.932	69095.443	70473.460
R(3)	67683.852	69096.179	70473.954
R(4)	67684.038	69096.137	
R(5)		69095.318	
Q(1)	67675.051	69087.795	70466.088
Q(2)	67673.592	69086.240	70464.388
Q(3)	67671.404	69083.910	70461.854
P(2)	67667.360	69080.104	70458.417
P(3)		69074.706	70452.902
P(4)		69068.531	
O(3)	67655.826	69068.571	70446.863

**Table 6.1** – Two-photon transition frequencies in the CO  $A^1\Pi$  -  $X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands as obtained in the present study. Values in  $cm^{-1}$ .

branches for transitions with  $\Delta J = -2$  to +2. It is noted that the two-photon R(0) transition is forbidden [182].

The contributions to the overall uncertainty in the measurement accuracy are determined by statistical effects, AC-stark shifts, residual Doppler shift, and a chirped-induced frequency offset. In the following the two major sources of uncertainty will be discussed one by one. The contribution by the Doppler shift and the etalon non-linearity have been discussed previously [7].

#### AC-Stark effect

AC-Stark frequency shifts can be induced by the power density of the probe laser radiation. In order to reduce a possible AC-Stark shift, a separate ionization laser was used, which was delayed by 10 ns to avoid time overlap with the spectroscopy step. The shift induced by the spectroscopy laser can be analyzed and corrected for by performing an extrapolation to zero power density. Figure 6.3 shows the AC-Stark power extrapolation for the two-photon S(0)lines in the  $A^1\Pi - X^1\Sigma^+$  (3,0) and (4,0) bands of CO.

From a detailed analysis it follows that the two-photon lines in the (2,0), (3,0) and (4,0) bands exhibit different slopes in the AC-stark plots. For lines in the (2,0) and (4,0) bands, the AC-Stark shift appears to be smaller than the



**Figure 6.3** – (Color online) Assessment of the AC-Stark effect on the twophoton S(0) lines in the  $A^1\Pi - X^1\Sigma^+$  (4,0) and (3,0) bands of CO. The (red) circles refer to transition S(0) in the (4,0) band, and the (black) squares to transition S(0) in the (3,0) band. The solid lines represent linear fits for extrapolation to zero intensity.

statistical error, as shown in the example of Fig. 6.3. However, for the lines in the (3,0) band the AC-Stark effect is found to be much larger as exemplified for the S(0) transition. Such differences in slopes were also observed in the case of (0,0) and (1,0) bands [188]. All the measured transitions in the (3,0) band were independently extrapolated to zero power, and corrected for the AC-Stark shift. The AC-Stark effects are a measure for the polarizability of the quantum states involved, and the differences between bands indicate that the  $A^1\Pi$ , v = 3 levels have a strong polarizability. Further analysis of this phenomenon is beyond the scope of the present paper.

#### Frequency chirp in the PDA

In the frequency calibration procedure, the absolute frequency of the cw dye laser is determined from the saturated  $I_2$  absorption spectra providing reference points known to 1 MHz accuracy [189]. Since the CO spectra were recorded



**Figure 6.4** – (Color online) Deduced offset between cw and PDA laser frequency as a result of chirp over a 300 s time interval with PDA laser parked on the Q(2) line in the CO  $A^1\Pi - X^1\Sigma^+$  (4,0) band. The (red) solid line indicates the averaged offset value of 37 MHz at the two-photon transition. The (red) dashed lines indicate the  $(\pm \sigma)$  standard deviation.

with the UV-upconverted pulsed output of the PDA this requires an assessment of the frequency offset between the pulsed output of the pulsed dye amplifier (PDA) and the cw laser seeding the PDA, which is referred to as chirp. The physical mechanisms of frequency chirp in dye amplifiers, associated with timedependent index of refraction and time-dependent gain phenomena, have been well documented [85, 190].

The cw-pulse offset frequency is measured by heterodyning the amplified pulsed output of the PDA system with part of the cw-seed that is shifted by 595 MHz using an AOM, as shown in Fig. 6.1. The resulting beat signal measured on a fast photo-detector is recorded with a 4 Gs/s sampling oscilloscope for further analysis. All laser beams are combined and propagated through single-mode optical fibers in order to overlap wave fronts and stabilize the alignment of the chirp measurement. We follow procedures of chirp signal analysis involving frequency filtering and Fourier-transformation as described in Refs. [26, 85, 86].

Source	MHz	$\mathrm{cm}^{-1}$
PDA chirp	30	0.001
AC-Stark shift	20	0.0007
Line-fitting	2	0.00007
$I_2$ calibration	2	0.00007
Etalon nonlinearity	2	0.00007
DC-Stark shift	< 1	0.00003
Residual Doppler	< 1	0.00003
Statistical	30	0.001
Total	47	0.0016

**Table 6.2** – Estimated contributions to the uncertainty in the two-photon transition frequencies for the  $A^{1}\Pi - X^{1}\Sigma^{+}$  bands of CO.

Figure 6.4 shows a chirp-offset measurement recorded at the frequency of the Q(2) line in the CO  $A^1\Pi - X^1\Sigma^+$  (4,0) band. The chirp-induced shift is measured over a duration of 300 s at 1 point/s with 10 times average. The average value of the offset is 37 MHz at the two-photon transition frequency, with a standard deviation of 10 MHz. The oscillatory structure in Fig. 6.4 is found to be due to a changing polarization during transmission of the cw laser in the fiber. The reduction in beat intensity then leads to an inaccurate determination of the frequency. Such averaged cw-PDA offset was measured during recordings of the different transitions in CO  $A^1\Pi - X^1\Sigma^+$  (4,0) band, results of which are shown in Fig. 6.5. These measurements demonstrate that the chirp-induced offset values do not change over the small frequency ranges of CO resonance lines in a single band, so that averaged values are used for correcting the final transition frequencies.

The frequency chirp is known to vary over the spatial wave front of the laser beam [26]. This phenomenon was also systematically investigated and a maximum variation in the chirp-offset of 24 MHz was found, which is included as a statistical uncertainty for the chirp-offset in the error budget.

#### Uncertainty estimates and consistency

The error budget for the CO transition frequencies is summarized in Table 6.2. The systematic corrections, associated with chirp and AC-Stark effect are applied to each transition. All transitions are recorded more than once, and on different days to confirm reproducibility of the results. The entry for the statistical uncertainty ( $1\sigma$  standard deviation) is derived from a weighted average over individual scans, and including the fitting uncertainty. The overall uncer-



**Figure 6.5** – (Color online) The chirp shift for different transitions in the  $A^{1}\Pi - X^{1}\Sigma^{+}(4,0)$  band of CO. The (black) solid line is the averaged chirp shift in the frequency range of the  $A^{1}\Pi - X^{1}\Sigma^{+}(4,0)$  band. The dashed lines represent the  $(\pm\sigma)$  standard deviation for the offsets.

tainty in the absolute frequencies for the present data set of Table 6.1 results from taking individual errors in quadrature yielding  $0.0016 \text{ cm}^{-1}$ .

The consistency of the error budget can be tested by calculating ground state combination differences from the experimental data. Combination differences between S(J) and Q(J+2), R(J) and P(J+2), and Q(J) and O(J+2) can be calculated and compared to the very accurately known ground state splittings from micro-wave and far-infrared rotational spectroscopy on the ground state of CO [162], yielding the difference  $\Delta E_V$ . Such a comparison is graphically presented in Fig. 6.6, where the transitions used in the comparison are labeled. The comparison yields very good agreement within a standard deviation of only 0.0008 cm<sup>-1</sup>. This is even smaller than the estimated measurement uncertainty and hence proves the internal consistency of the calibrations performed on the individual lines in the data set.



**Figure 6.6** – (Color online) The combination differences in CO  $A^{1}\Pi - X^{1}\Sigma^{+}$ (2,0), (3,0) and (4,0) bands, calculated and compared with the directly measured ground state splitting by Varberg and Evenson [162], represented as  $\Delta E_{V}$ . The solid line is the averaged value  $\Delta E_{V}$  over all measured combination differences. The dashed lines indicate the  $(\pm \sigma)$  standard deviation for the comparison.

#### 6.4 Conclusion

High-precision frequency measurements of 43 rotational lines in CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0), (3,0) and (4,0) bands (for J < 6) have been performed in the collisionless environment of a molecular beam with an absolute accuracy of better than  $2 \times 10^{-3}$  cm<sup>-1</sup>, or a relative accuracy of  $2 \times 10^{-8}$ . The accuracy is an improvement over a previous analysis of the (0,0) and (1,0) bands, accurate to  $3 \times 10^{-8}$  [7, 188], made possible by the chirp detection treatment. The uncertainty is mainly determined by statistics, and by remaining effects of chirp on the laser pulses as well as an AC-Stark induced shift. The accuracy obtained in this study represents a 10-fold improvement over our previous study [7]. After converting the accurate information on the level energies to one-photon

vacuum ultraviolet transition frequencies these values can serve as calibration reference lines for synchrotron spectra [126], as well as implemented in comparisons with astrophysical spectra of high-redshift objects to derive a constraint on a possible variation of the proton-electron mass ratio on a cosmological time scale [7].

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## CHAPTER

### Spectroscopy and perturbation analysis of the CO $A^{1}\Pi - X^{1}\Sigma^{+}$ (2,0), (3,0) and (4,0) bands

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The (2,0) (3,0) and (4,0) bands of the  $A^1\Pi - X^1\Sigma^+$  system of  ${}^{12}C^{16}O$  have been re-investigated by high-resolution vacuum ultraviolet absorption spectroscopy. A VUV Fourier-transform spectrometer, illuminated by synchrotron radiation, was applied to record a jet-cooled spectrum, a room temperature static gas spectrum and a high temperature (900 K) quasi-static gas spectrum, resulting in absolute accuracies of 0.01-0.02 cm<sup>-1</sup> for the rotational line frequencies. Precise laser-based data were included in the analysis allowing for a highly accurate determination of band origins. Rotational levels up to J = 52 were observed. The data were used to perform an improved analysis of the perturbations in the  $A^1\Pi$ , v = 2, v = 3, and v = 4 levels by vibrational levels of the  $D^1\Delta$ ,  $I^1\Sigma^-$ ,  $e^3\Sigma^-$ ,  $d^3\Delta$ , and  $a'^3\Sigma^+$  states.

#### 7.1 Introduction

The spectroscopy of the carbon monoxide molecule remains of central interest to a variety of subfields in science. In particular the  $A^1\Pi - X^1\Sigma^+$  system, investigated by a number of authors over decades [150, 166, 172, 173, 174, 175, 187], is often used as a probe for detecting CO. New and recent examples of its application are the proposal to search for a varying proton-electron mass ratio on cosmological time scales [7], and to probe the local cosmic microwave background temperature as a function of redshift [148]. For these applications the analysis of the  $A^1\Pi - X^1\Sigma^+$  system is warranted at the highest accuracy. At the same time the  $A^1\Pi$  state of CO is known as a celebrated example of perturbations, which makes its study interesting from a pure molecular physics perspective. A first comprehensive perturbation analysis was performed by Field *et al.* [150, 187].

After having performed an improved perturbation analysis for the  $A^1\Pi - X^1\Sigma^+$ (0,0) and (1,0) bands [188] we here extend the updated perturbation analysis to the  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands by using the high resolution vacuum ultraviolet (VUV) Fourier-transform (FT) spectroscopy setup at the DESIRS beamline at the Soleil synchrotron. For the purpose of achieving an absolute wavelength calibration of the rotational lines, a subset of lines was first probed with laser-based Doppler-free two-photon spectroscopy [126]. For the present study the VUV-FT instrument was used in three different modes of operation: gas-jet spectroscopy, room-temperature static gas absorption, and absorption at 900 K, for which a special setup was designed [191]. The combination of these measurements allows for a highly accurate analysis of the spectrum of the three bands, probing rotational states as high as J = 52, providing information on perturbing states interacting at the high rotational quantum numbers. The aim of using these different configurations will be discussed in the next section.

#### 7.2 Experimental Details

The vacuum ultraviolet (VUV) Fourier-transform (FT) spectrometer at the DESIRS beamline of the SOLEIL synchrotron is a unique tool for recording high-resolution absorption spectra in the range 4 - 30 eV [158, 181]. For the present investigation, the instrument was used in three configurations, each being a compromise between obtaining narrow linewidths and high wavelength accuracy, or probing as many rotational levels as possible. The free-jet configuration is used to record the narrowest transitions. First, in the jet-expansion, the perpendicular directionality of the molecular beam gives rise to a much reduced Doppler width, yielding an observed width of 0.09 cm<sup>-1</sup> in combi-



**Figure 7.1** – (Color online) Overview spectra of the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  system including (2,0), (3,0) and (4,0) bands recorded with the vacuum ultraviolet Fourier-transform spectrometer at the SOLEIL synchrotron under three different experimental conditions; (a) free molecular jet expansion; (b) room temperature quasi-static gas cell; (c) a free-flowing gas cell heated to 900 K. The asterisk (\*) indicates the Xe atomic resonance line used in for calibration of the FTS instrument.

nation with the instrument settings of the FT-spectrometer. Under the jet conditions the rotational temperature is reduced to 12 K and only rotational levels J = 0 - 5 are probed at this high resolution.

Second, FT-spectra are recorded under quasi-static room-temperature conditions with the use of a windowless cell. In this configuration the linewidth obtained is 0.16 cm<sup>-1</sup> [188], while rotational lines up to  $J \sim 20$  are observed. In a third configuration, a windowless gas cell was heated up to 900 K, in order to record the highest rotational quantum states. The linewidth under these conditions, at full width of half maximum (FWHM), was 0.39 cm<sup>-1</sup> [191]. The



**Figure 7.2** – (Color online) A zoom-in spectrum recorded with a windowless gas cell heated to 900 K showing absorption lines in the  $A^1\Pi - X^1\Sigma^+$  (2,0) band as well as perturber lines belonging to the  $e^3\Sigma^-$  (4,0) band.
latter spectra were recorded at relatively high column densities, which is around a factor of 100 higher compared to the sample used with the unheated cell. It is used to probe rotational states with the highest J quantum number, in which case the low-J transitions are saturated. In all the FT-experiments, CO gas was used at a purity of 99.997% from Air Liquide, presumably composed of the regular terrestrial  ${}^{12}C/{}^{13}C$  and  ${}^{16}O/{}^{17}O/{}^{18}O$  isotopic abundances.

Figure 7.1 shows characteristic overview VUV-FT spectra recorded under the three measurement conditions, covering the range of the  $A^{1}\Pi - X^{1}\Sigma^{+}(v', 0)$  bands for v' = 0 to v' = 6. The high temperature spectrum also shows hot bands, i.e.  $A^{1}\Pi - X^{1}\Sigma^{+}$  (v' = 1 - 7, 1), originating from the  $X^{1}\Sigma^{+}$ , v'' = 1 state. The (2, 1), (3, 1), and (4, 1) hot bands are expected to be weak due to small Franck-Condon factors [192]. A zoom-in part of the high temperature spectrum is presented in Fig. 7.2, showing transitions in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0) band and some perturber lines belonging to the  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  (4,0) band. The unlabeled weak lines belong to excitation of other perturber states, mentioned below.

In order to obtain the most accurate transition frequencies, different settings on the FT-instrument are used in combination with the various measurement configurations. The free-jet and room temperature spectra are both recorded by taking 1978 kilo-samples of data over the 0 to 40 mm optical path difference within the interferometer, yielding an instrumental resolution of 0.075 cm<sup>-1</sup>, corresponding to the ultimate resolving power of the instrument. For the hot cell spectra, because of the increased Doppler broadening of about 0.28 cm<sup>-1</sup>, constraints on the instrumental resolution are relaxed to 0.27 cm<sup>-1</sup> by taking 1024 kilo-samples of interferometric data to save recording time, which permits more averaging, thus increasing the signal-to-noise ratio. The absolute calibration for all the FT spectra is obtained from on-line recording of a xenon line at 68 045.156 (3) cm<sup>-1</sup> [159].

#### 7.3 Results

Collectively, more than 450 absorption lines are observed in the region from 66 400 to 70 500 cm<sup>-1</sup>, including rotational levels up to J = 52 for the main  $A^{1}\Pi - X^{1}\Sigma^{+}$  bands, as well as a large number of transitions belonging to perturber states. In Table 7.1, transition frequencies in the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0), (3,0) and (4,0) bands are listed. The absorption lines associated with excitation of the perturber states are presented in Table 7.2. In these tables, the subscripts e and f denote the electronic symmetry of the upper state. The superscripts Q, S, R, O and P in Table 7.2, indicate the change in total angular momentum excluding spin for transitions to perturber states [155]. The uncertainties of transition frequencies are  $0.02 \text{ cm}^{-1}$  for most of the transitions, except the weak or blended ones. To verify the accuracy of the FT data, we

**Table 7.1** – Transition frequencies (in vacuum  $cm^{-1}$ ) in the  ${}^{12}C^{16}O A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0), (3,0), and (4,0) bands obtained in the present VUV-FT experiment and absolutely calibrated with respect to the laser data [126]. J" is the rotational quantum number in the ground state. The subscripts e and f indicate the electronic symmetry of the upper state. The superscripts b and w indicate blended and weak transitions, respectively.

	(2,0)				(3,0)			(4,0)		
J''	$\mathbf{R}_e(J'')$	$\mathbf{Q}_f(J'')$	$\mathbf{P}_e(J'')$	$\mathbf{R}_e(J'')$	$\mathbf{Q}_f(J'')$	$\mathbf{P}_e(J'')$	$\mathbf{R}_e(J'')$	$\mathbf{Q}_f(J'')$	$\mathbf{P}_e(J'')$	
0	67678.89			69091.63			70469.93			
1	67681.28	67675.05		69093.91	69087.79		70472.08	70466.11		
2	67682.94	67673.59	67667.35	69095.43	69086.24	69080.10	70473.41	70464.44	70458.45	
3	67683.86	67671.40	67662.06	$69096.18^{b}$	69083.91	69074.71	70473.86	70461.93	70452.85	
4	67684.06	67668.48	67656.02	$69096.13^{b}$	69080.80	69068.53	$70473.50^{b}$	70458.57	70446.47	
5	67683.51	$67664.83^{b}$	67649.25	$69095.32^{b}$	69076.91	69061.58	70472.35	$70454.36^{b}$	70439.26	
6	67682.25	67660.41	67641.77	69093.72	69072.25	69053.85	70470.37	70449.38	70431.23	
7	67680.25	67655.09	67633.55	69091.35	69066.81	69045.35	70467.58	70443.55	70422.38	
8	67677.53	67649.64	67624.60	69088.20	$69060.61^{b}$	69036.07	70463.96	70436.90	70412.72	
9	67674.06	67643.01	67614.92	69084.27	69053.61	69026.02	70459.53	70429.43	$70402.26^{b}$	
10	67669.87	67635.69	67604.51	69079.56	69045.84	69015.19	$70454.30^{b}$	70421.15	70390.95	
11	$67664.92^{b}$	67627.65	67593.38	69074.07	69037.29	69003.58	70448.21	70412.06	70378.84	
12	67659.27	67618.88	67581.50	69067.80	69027.97	68991.20	70441.31	$70402.18^{b}$	70365.92	
13	67652.87	67609.38	67568.90	$69060.76^{b}$	69017.87	68978.04	70433.59	70391.41	70352.18	
14	67645.74	67599.14	67555.57	69052.92	69006.99	68964.12	70425.05	70379.85	70337.61	
15	67637.86	67588.18	67541.51	69044.32	68995.33	68949.40	70415.67	70367.48	70322.23	
16	67629.24	67576.49	67526.73	69034.92	68982.90	68933.92	70405.47	70354.27	70306.04	
17	67619.89	67564.05	67511.19	69024.77	68969.67	68917.65	70394.44	70340.24	70289.00	
18	67609.78	67550.87	67494.92	69013.78	68955.70	68900.60	70382.59	70325.39	70271.16	

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		(2,0)			(3,0)			(4,0)	
J''	$\mathbf{R}_e(J'')$	$\mathbf{Q}_f(J'')$	$\mathbf{P}_e(J'')$	$\mathbf{R}_e(J'')$	$Q_f(J'')$	$\mathbf{P}_e(J'')$	$\mathrm{R}_e(J'')$	$\mathbf{Q}_f(J'')$	$\mathbf{P}_e(J'')$
19	$67598.95^{b}$	67536.94	67477.92	69002.03	68940.89	68882.80	70369.88	70309.72	70252.48
20	67587.33	67522.30	67460.19	68989.48	68925.33	68864.21	70356.37	70293.21	70233.00
21	67574.92	67506.89	67441.70	68976.22	68908.97	68844.79	70342.03	70275.86	70212.65
22	67561.70	67490.78	67422.46	68962.08	68891.89	68824.64	70326.84	70257.68	70191.52
23	67547.46	67473.82	67402.45	68947.17	68873.96	68803.75	70310.78	70239.24	70169.54
24	67530.58	67456.15	67381.62	68931.46	68855.22	68781.99	70293.93	70218.90	70146.73
25	67520.28	67437.66	67359.77	68915.02	68835.70	68759.48	70276.21	70198.21	70123.10
26	67503.39	67418.29	67335.29	68897.69	68815.44	68736.18	70257.68	70176.71	70098.63
27	67486.31	67397.77	67317.41	68879.56	68794.20	68712.16	$70238.31^{b}$	70154.37	70073.34
28	67468.58	67374.63	67292.93	68860.55	68770.99	68687.22	70218.03	70131.19	70047.21
29	67450.03	67361.31	67268.28	68840.30	68750.33	68661.52	70196.95	70107.17	70020.24
30	67430.37	67337.38	67242.97	68822.27	68726.69	68634.95	70175.00	70082.31	69992.43
31	67417.14	67314.00	67216.87	68800.01	68702.36	68607.14	70152.17	70056.60	69963.79
32	67392.61	67290.19	67189.66	68777.81	68677.19	68581.56	70128.35	70030.04	69934.29
33	67370.68	67265.74	67168.90	68754.92	68651.02	68551.76	70106.17	70002.63	69903.92
34	67348.30	67240.58	67136.83	68731.22	68625.59	68522.08	70079.26	69974.35	69872.57
35	67325.89	67214.61	67107.38	68706.74	68597.80	68491.62	70052.93	69945.17	69842.87
36	67301.93	67188.51	67077.50	68681.45	68569.49	68460.41	70025.84	69914.90	69808.45
37	67277.26	67160.83	67047.57	68655.36	68540.43	68428.42	69997.89	69888.36	69774.62
38	67256.49	67132.43	67016.12	68628.46	68510.57	68395.65	69969.03	69853.81	69740.03
39	67227.31	67107.93	66983.97	68600.75	68479.90	68362.08	69938.72	69821.03	69704.61
40	67200.28	67075.00	66955.71	68572.22	68448.23	68327.76	69909.59	69787.59	69668.29
41	67172.06	67044.14	66919.10	68542.87	68416.52	68292.54	69878.01	69753.32	$69630.43^{b}$
42	67145.95	67012.83	66884.61	68512.68	68383.32	$68256.55^{b}$	69845.70	69718.20	69593.95
43	67115.28	66982.80	66848.98	68481.65	68349.41	68219.80	69812.54	69682.03	69554.93
				continued	d on next p	age			

7.3. Results

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		(2,0)			(3,0)			(4,0)	
J''	$\mathrm{R}_e(J'')$	$\mathrm{Q}_f(J'')$	$\mathrm{P}_e(J'')$	$\mathrm{R}_e(J'')$	$\mathrm{Q}_f(J'')$	$\mathbf{P}_e(J'')$	$\mathrm{R}_e(J'')$	$\mathrm{Q}_f(J'')$	$\mathbf{P}_e(J'')$
44	67087.12	66949.46	66815.45	68449.64	68314.71	68182.17	69778.25	$69646.17^{b}$	69515.21
45	67056.40	66915.88	66777.38	68415.42	68279.13	68143.74	69747.15	$69607.90^{b}$	69474.61
46	67023.71	66881.55	66741.82	68384.81	68242.75	$68104.34^{b}$	69708.67	69569.50	$69432.95^{w}$
47	66993.21	66703.75	66703.75	68350.09	68205.49	$68062.70^{w}$		69530.04	69394.53
48	66960.40	66811.29			$68167.17^{b}$	$68024.82^{w}$		69489.51	$69348.60^{b}$
49	66926.80	66774.68	$66625.81^{w}$		$68126.16^{w}$		69596.13	69449.25	$69304.46^{w}$
50	66892.44	66737.33						69407.01	
51	$66857.29^{w}$	66699.10						$69364.03^{w}$	
52	$66821.38^{w}$								

**Table 7.2** – Transition frequencies (in vacuum  $cm^{-1}$ ) for excitation of the various perturber states obtained in the present VUV-FT measurements, recalibrated from the laser data. The quantum number in brackets J" represents the total angular momentum of the ground state. The left-superscripts Q, S, R, O and P denote the total angular momentum excluding spin of the perturber states, according to the notation in Ref. [155]. The subscripts e and f indicate the electronic symmetry of the upper state. The superscripts b and w indicate blended and weak transitions, respectively.

$d^3\Delta - d^3\Delta$	$X^{1}\Sigma^{+}$ (7,0)	$e^3\Sigma^ \lambda$	$\Sigma^{1}\Sigma^{+}$ (4,0)	$I^1\Sigma^ \lambda$	$\Sigma^{1}\Sigma^{+}$ (3,0)
${}^{R}Q_{f}(42)$	$67028.66^{w}$	$^{O}P_{e}(26)$	67346.78	$^{Q}\mathbf{Q}_{f}(6)$	$67666.78^{w}$
$^{R}\mathbf{Q}_{f}(43)$	66964.86	$^{O}\mathrm{P}_{e}(27)$	67298.26	$^{Q}\mathrm{Q}_{f}(7)$	67656.98
${}^{P}\mathrm{P}_{e}(40)$	66947.61	$^{Q}\mathbf{R}_{e}(23)$	$67574.05^{w}$	$^{Q}\mathrm{Q}_{f}(8)$	$67645.13^{b}$
$^{R}\mathbf{R}_{e}(38)$	67248.35	${}^{Q}\mathbf{R}_{e}(24)$	67542.09	$^{Q}\mathbf{Q}_{f}(9)$	$67632.32^{w}$
${}^{Q}\mathbf{Q}_{f}(39)$	67099.82	$^{Q}\mathbf{R}_{e}(25)$	67501.14		
		${}^{Q}\mathbf{Q}_{f}(27)$	67429.16	$I^1\Sigma^ X$	$\Sigma^{1}\Sigma^{+}$ (6,0)
$d^3\Delta - d$	$X^{1}\Sigma^{+}$ (8,0)	$^{Q}\mathrm{Q}_{f}(28)$	67391.50	$^{Q}\mathbf{Q}_{f}(23)$	$70237.93^{b}$
${}^{S}\mathbf{R}_{e}(25)$	$68912.94^{w}$	${}^{Q}\mathbf{Q}_{f}(29)$	67341.85	• • •	
$^{R}Q_{f}(26)$	68813.41	$^{Q}\mathbf{Q}_{f}(30)$	67300.60	$a^{\prime 3}\Sigma^+ - \lambda$	$X^{1}\Sigma^{+}$ (13,0)
		$^{Q}\mathbf{Q}_{f}(32)$	$67210.86^{w}$	${}^{P}\mathrm{P}_{e}(31)$	68624.61
$d^3\Delta - \lambda$	$K^{1}\Sigma^{+}$ (10,0)	$^{Q}\mathrm{P}_{e}(32)$	67212.33	${}^{P}\mathrm{P}_{e}(32)$	68568.47
${}^{Q}Q_{f}(45)$	$69607.35^{b}$	$^{Q}\mathrm{P}_{e}(33)$	67158.32	${}^{R}\mathbf{R}_{e}(29)$	68857.80
		$^{Q}\mathrm{P}_{e}(34)$	67113.40	${}^{R}\mathbf{R}_{e}(30)$	68809.19
$D^1\Delta - $	$X^{1}\Sigma^{+}$ (3,0)	$^{S}\mathbf{R}_{e}(31)$	67406.56	$^{R}Q_{f}(33)$	68664.38
${}^{P}{\rm P}_{e}(48)$	66666.80	$^{S}\mathbf{R}_{e}(32)$	67369.20	$^{R}Q_{f}(34)$	68610.50
$^{R}\mathbf{R}_{e}(46)$	67026.86				
		$e^3\Sigma^ X$	$\Sigma^{1}\Sigma^{+}$ (7,0)	$a^{\prime 3}\Sigma^+ - Z$	$X^{1}\Sigma^{+}$ (15,0)
		${}^{O}\mathrm{P}_{e}(35)$	69836.03	${}^{P}\mathrm{P}_{e}(47)$	$69386.27^{w}$
		$^{Q}\mathbf{R}_{e}(33)$	70099.33	${}^{R}\mathbf{R}_{e}(45)$	69738.97
		${}^{Q}\mathbf{Q}_{f}(36)$	$69941.07^{w}$		
		$^{Q}\mathrm{Q}_{f}(37)$	69879.81		
		$^{S}\mathbf{R}_{e}(39)$	$69948.44^{w}$		

compare combination differences between P(J) and R(J-2) transitions in the FT data with the very accurate far-infrared data [162]. The comparison yields good agreement with a standard deviation of 0.015 cm<sup>-1</sup>, smaller than the estimated FT uncertainty.

In view of parity selection rules, the measured transition frequencies in the present one-photon absorption experiment cannot be compared directly with values obtained in the two-photon laser experiment for the same bands [126]. However, based on accurately known ground-state level energies [18] and the

**Table 7.3** – Level energies (in vacuum  $cm^{-1}$ ) of  $A^{1}\Pi v = 2, 3, 4$  states. The energies indicated with \* are the level energies from the laser data [188]. The FT data include energy corrections deduced from the comparison with laser data.

	v	= 2	v	= 3	v	= 4
J'	e	f	e	f	e	f
1	67678.895*	67678.895*	69091.640*	69091.639*	70469.933*	70469.951*
2	67685.127*	67685.123*	69097.775*	69097.775*	70475.924*	70475.971*
3	67694.474*	67694.467*	69106.979*	69106.979*	70484.923*	70484.995*
4	67706.932*	67706.922*	69119.251*	69119.249*	70496.934*	70497.023*
5	67722.506*	67722.486*	69134.588*	69134.585*	70511.96	70512.03
6	67741.192*	67741.14	69152.994*	$69152.988  {}^{*}$	70530.02	70530.12
7	67762.99	67762.73	69174.46	69174.46	70551.11	70551.19
8	67787.90	67788.03	69198.99	69199.00	70575.23	70575.29
9	67815.92	67815.99	69226.59	69226.59	70602.35	70602.41
10	67847.04	67847.09	69257.25	69257.24	70632.51	70632.56
11	67881.27	67881.31	69290.97	69290.96	70665.69	70665.72
12	67918.59	67918.65	69327.74	69327.74	70701.88	70701.94
13	67959.04	67959.07	69367.57	69367.57	70741.07	70741.11
14	68002.56	68002.61	69410.46	69410.45	70783.29	70783.32
15	68049.20	68049.24	69456.39	69456.39	70828.51	70828.53
16	68098.91	68098.96	69505.37	69505.37	70876.72	70876.75
17	68151.71	68151.77	69557.39	69557.40	70927.95	70927.96
18	68207.60	68207.66	69612.48	69612.49	70982.16	70982.18
19	68266.57	68266.62	69670.58	69670.57	71039.38	71039.40
20	68328.62	68328.68	69731.70	69731.71	71099.56	71099.59
21	68393.70	68393.80	69795.87	69795.87	71162.75	71162.76
22	68461.82	68462.01	69863.12	69863.12	71228.92	71228.92
23	68532.93	68533.19	69933.31	69933.33	71298.06	71298.61
24	68606.83	68607.46	70006.54	70006.54	71370.16	71370.21
25	68681.89	68684.72	70082.78	70082.76	71445.24	71445.27
26	68767.34	68764.89	70162.09	70162.04	71523.27	71523.31
27	68849.99	68847.71	70244.28	70244.14	71604.27	71604.30
28	68936.25	68931.69	70329.49	70328.05	71688.23	71688.25
29	69025.64	69029.28	70417.61	70418.30	71775.09	71775.14
30	69118.00	69120.04	70508.27	70509.35	71864.92	71864.97
31	69213.03	69215.13	70604.93	70603.49	71957.66	71957.73
32	69318.27	69313.57	70701.14	70700.56	72053.30	72053.41
33	69415.98	69415.12	70801.21	70800.40	72151.72	72152.01
34	69520.06	69519.73	70904.30	70904.74	72255.55	72253.50
35	69627.46	69627.29	71010.37	71010.48	72358.41	72357.85

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	v :	= 2	v	= 3	v	= 4
J'	e	f	e	f	e	f
36	69738.57	69738.47	71119.41	71119.45	72465.61	72464.86
37	69851.89	69851.82	71231.41	71231.42	72575.80	72579.35
38	69968.25	69968.19	71346.35	71346.34	72688.88	72689.57
39	70092.23	70092.20	71464.24	71464.17	72804.79	72805.30
40	70211.58	70211.51	71585.02	71584.74	72922.94	72924.10
41	70336.78	70336.61	71708.72	71708.99	73046.10	73045.79
42	70464.53	70464.99	71835.35	71835.47	73170.48	73170.35
43	70598.10	70598.35	71964.83	71964.96	73297.86	73297.58
44	70730.83	70732.11	72097.20	72097.37	73428.08	73428.82
45	70869.77	70869.34	72232.29	72232.59	73560.90	73561.36
46	71009.87	71009.51	72368.85	72370.71	73700.64	73697.45
47	71151.67	71009.89	72512.79	72511.62	73836.61	73836.18
48	71299.35	71299.30	72656.23	72655.17	73978.00	73977.51
49	71448.40	71448.22	69863.12	72799.70		74122.79
50	71600.33	71600.07	69933.31		74269.66	74269.75
51	71755.19	71754.70				74419.63
52	71912.89					
53	72073.49					

derived excited state  $\Lambda$ -doublet splittings, a verification of absolute level energies derived from the VUV-FT experiment can be compared with the more accurate data from the laser experiment, yielding the differences shown in Fig. 7.3. The average offsets between the two data sets are different for different bands, on the order of  $0.01 \text{ cm}^{-1}$ . These small discrepancies are attributed to an offset in the FT data that is well within its estimated uncertainty. The standard deviation of  $\sim 0.005 \text{ cm}^{-1}$ , demonstrates that the relative uncertainty of the FT data is much smaller than the estimated absolute uncertainty. The energy offsets with respect to the more accurate laser spectroscopy data were used to correct the level energies of the  $A^1\Pi v = 2, 3, 4$  levels by 0.005, 0.011 and 0.009 cm<sup>-1</sup>, respectively. The corrected level energies are listed in Table 7.3, where the values derived from laser data are used for J = 1 - 6. The level energies of perturber states are also corrected by the calibration shift and shown in Table 7.4. In a similar way the corrections for the level energies, have also been applied to the transition energies listed in Tables 7.1 and 7.2.

#### 7.4 Perturbation analysis

The CO  $A^1\Pi - X^1\Sigma^+$  system is heavily perturbed by many other electronically excited states. The  $A^1\Pi$  (v = 2) levels are perturbed by levels of the  $e^3\Sigma^-$ 

J'	$d^{3}$	$\Delta(v=7)$	J'	$e^{3}\Sigma$	$\Sigma^{-}(v=4)$	J'	$I^{1}\Sigma$	$\Sigma^{-}(v=3)$
42	F3f	70480.81	24	F1e	68633.43	6	F1f	67747.52
43	F3f	70580.41	25	F1e	68693.40	7	F1f	67764.63
39	F2e	70084.11	26	F1e	68748.20	8	F1f	67783.52
39	F2f	70084.09	27	F2f	68879.09	9	F1f	67805.30
			28	F2f	68948.57			
	$d^3 \Delta$	$\Delta(v=8)$	29	F2f	69009.82		$I^1\Sigma$	$C^{-}(v=6)$
26	F3e	70160.00	30	F2f	69083.27	23	F1f	71297.30
26	F3f	70160.01	32	F2f	69234.24			
			31	F3e	69235.70		$a^{\prime 3}\Sigma$	$E^+(v=13)$
	$d^{3}$	$\Delta(v = 10)$	32	F3e	69307.70	30	F2e	70525.76
45	F2f	73560.81	33	F3e	69392.57	31	F2e	70591.85
						33	F3f	70813.76
	$D^1$	$\Delta(v=3)$		$e^{3}\Sigma$	$C^{-}(v = 7)$	34	F3f	70889.65
47	F1e	71154.81	34	F1e	72248.71			
			36	F2f	72491.03		$a'^3\Sigma$	$E^+(v = 15)$
			37	F2f	72570.80	46	F2e	73692.42
			40	F3e	72932.71			

**Table 7.4** – Level energies (in vacuum  $cm^{-1}$ ) of perturber states for  $A^{1}\Pi$ v = 2, 3, 4 states, with applied energy corrections obtained from the laser data.

 $(v = 4), d^3\Delta$   $(v = 7), a'^3\Sigma^+$   $(v = 11, 12), D^1\Delta$  (v = 3) and  $I^1\Sigma^-$  (v = 3, 4)states; the  $A^1\Pi$  (v = 3) levels are perturbed by  $e^3\Sigma^ (v = 5, 6), d^3\Delta$  (v = 8), $a'^3\Sigma^+$  (v = 13), and  $I^1\Sigma^-$  (v = 5) states; the  $A^1\Pi$  (v = 4) levels are perturbed by  $e^3\Sigma^ (v = 7), d^3\Delta$   $(v = 9, 10), a'^3\Sigma^+$  (v = 14, 15), and  $I^1\Sigma^-$  (v = 6)states. Figure 7.4 plots level energies as function of J(J + 1) for vibrational progressions of the  $A^1\Pi$  and perturber states relevant to this study, showing the crossing points where local perturbations may occur. The labels denote electronic state and vibrational quantum number. As will be discussed below, observable effects from some perturber states which do not cross with the  $A^1\Pi$ state are manifest in the analysis, e.g.  $a'^3\Sigma^+$  (v = 16).

We model each observed  $A^1\Pi - X^1\Sigma^+$  band and interacting levels with a local deperturbation analysis, in a similar style to what was done by Niu. *et.* al. [188]. In this study, we use accurate transition energies obtained from FT spectroscopy for levels up to J'' = 52 of the  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands, as well as transitions attributed to perturber states. The more accurate low-J transition frequencies from the laser-based experiments [126] are preferentially used. In order to perform a more comprehensive perturbation analysis, we also use results from previous investigations. For the perturber state transitions, we used the low-J data from Ref. [168] for  $d^3\Delta - X^1\Sigma^+$ 



**Figure 7.3** – (Color online) The difference between  $A^1\Pi$  level energies derived from the laser and FTS datasets for low J levels. The energy differences are applied as corrections to FTS-derived level energies and transition frequencies reported here.

(7,0), (8,0) and (10,0); for  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  (4,0) and (5,0) data from Ref. [155]; for  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  (6,0) and (7,0) data from Ref. [169]. Since these older spectroscopic investigations are less accurate, we used relative weights that reflect the respective accuracies. A relative weight of 10 is assigned to data from Niu [126], 1 to the present FT data, 0.5-0.25 to weak and blended lines in the present FT data, 0.2 to data from Morton and Noreau [155], and 0.1 to data from Herzberg *et al.* [168] and Simmons and Tilford [169].

We performed a perturbation analysis on CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0), (3,0) and (4,0) bands using the Pgopher software [186], where the same effective Hamiltonian model as Ref. [188] was used, retaining their symbols for the various molecular constants (see Table 6 of Ref. [188]). The unweighted residuals of the fits are dominated by the uncertainties in the literature data. The mean weighted residuals of the fits on the transition energies of the  $A^{1}\Pi - X^{1}\Sigma^{+}$ (2,0), (3,0) and (4,0) bands, including relevant literature data are 0.016 cm<sup>-1</sup>, 0.014 cm<sup>-1</sup> and 0.021 cm<sup>-1</sup>, respectively. In total, 235, 218, and 213 transitions are used to fit 22, 17, and 20 molecular fit parameters for the  $A^{1}\Pi$  (v = 2, 3, and 4) states, respectively. The interaction parameters between  $A^{1}\Pi$  states



**Figure 7.4** – (Color online) Perturbation diagram. Level energies as function of J(J+1) for  $A^1\Pi$  and perturber states. The labels denote the electronic state and vibrational quantum number, e.g. a'16 is shorthand for  $a'^3\Sigma^+$  (v = 16).

and perturbing states are denoted by  $\eta_i$  for triplet perturbers and  $\xi_i$  for singlet perturbers, where the i = 2, 3, 4 indices correspond to the  $A^1\Pi$  (v = 2, v = 3 and v = 4) levels.

In addition to the  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands, we also improve the molecular constants for those perturber states for which a sufficient number of transitions are observed in the present FT experiment. These extra lines are listed in Table 7.2 and, in general, occur at the level crossings of  $A^1\Pi$  (v) rotational series with those of perturber states.

The final set of deperturbed molecular constants obtained from the fits are summarized in Table 7.5. Molecular constants with an uncertainty indicated in parentheses () are fitted (free) parameters. The others are taken from previous deperturbation models, indicated accordingly in the footnote, and used as fixed parameters during the fitting procedures. Note that we include all possible perturber states, even those that have no crossings with  $A^1\Pi$  states (e.g.  $d^3\Delta$ (v = 9) and  $a'^3\Sigma^+$  (v = 11) states), to have a consistent model that facilitates comparisons with previous investigations, such as Ref. [187].

As expected from the extensive coverage of transition energies in the  $A^{1}\Pi - X^{1}\Sigma^{+}$  bands, we obtain accurate molecular constants for the  $A^{1}\Pi$  states. This is also the case for the molecular constants of the  $e^{3}\Sigma^{-}(v = 4, 7)$ ,  $d^{3}\Delta(v = 7)$ ,  $a'^{3}\Sigma^{+}(v = 13)$ , and  $I^{1}\Sigma^{-}(v = 3)$  states as would be expected by inspection of Table 7.2.

The band origin  $T_v$  for  $A^1\Pi$  (v = 3) obtained in the analysis has a larger uncertainty compared to v = 2 and 4, which is attributed to uncertainty regarding its perturbation by the  $e^3\Sigma^-$  (v = 5) state. The rotational progression of  $e^3\Sigma^-$  (v = 5) does not actually cross with  $A^1\Pi$  (v = 3) and no extra perturber transitions are observed. Hence, less accurate literature values for transition energies in the  $e^3\Sigma^- - X^1\Sigma^+$  (5,0) band [155] were included. The effect of this interaction is a global energy shift of  $A^1\Pi$  (v = 3), which ultimately translates to a larger uncertainty of  $T_v$  in  $A^1\Pi$  (v = 3).

From Fig. 7.4, the  $D^1\Delta$  (v = 4, 5, 6) states are expected to cross the  $A^1\Pi$  vibrational states, however, no extra lines are obtained in this work, due to the small interaction parameters involved. Thus the inclusion of these states does not lead to any significant improvements in the quality of the fit. The addition of the  $I^1\Sigma^-$  (v = 7) state, where the crossing is predicted to occur at J = 55 and outside the data range, also does not improve the fitting. Therefore these states are excluded in the final model reported.

The  $A^1\Pi$  (v = 4) state is perturbed by  $d^3\Delta$  (v = 10) at J = 45 and  $a'^3\Sigma^+$ (v = 15) at J = 46, but these perturber lines are only observed weakly and their assignment is tentative. The assigned transition P(46), Q(45) and R(44) in  $A^1\Pi - X^1\Sigma^+$  (4,0) band are off in the resulting fit by 0.5 cm<sup>-1</sup>. Hence, in the final fitting, the relative weights for these lines was set at 0.01.

inglet states	$A^1\Pi(v=2)$	$A^1\Pi(v=3)$	$A^1\Pi(v=4)$		
v	67675.9408(6)	69088.368 (18)	70465.956 (7)		
3	1.55829(1)	1.53503(4)	1.51171(2)		
$\times 10^{6}$	-7 (4)	-4 (3)	-10 (4)		
$0 \times 10^{6}$	7.55(1)	7.68(3)	7.91(2)		
$H \times 10^{11}$	-2.7 (3)	-2.2 (8)	-0.3 (6)		
riplet states	$e^3\Sigma^-(v=4)$	$e^3\Sigma^-(v=5)$	$e^3\Sigma^-(v=6)$	$e^3\Sigma^-(v=7)$	
v	67969.82 (2)	68987.42 (2)	69986.25 (4)	70965.16 (2)	
3	1.20441(5)	$1.1877^{a}$	1.16990(6)	1.15289(6)	
L Contraction of the second seco	$0.69^{-a}$	0.63 <sup>a</sup>	$0.64^{a}$	$0.76^{\rm a}$	
$0 \times 10^{6}$	6.35(4)	$6.664 \ ^{\rm a}$	$6.637 \ ^{\rm a}$	6.22(4)	
$H \times 10^{12}$	-2 <sup>b</sup>	-2 <sup>b</sup>	-2 <sup>b</sup>	-2 <sup>b</sup>	
2	12.93(1)				
3		9.4(3)	11.37(5)		
4				7.36(3)	
Triplet states	$d^3\Delta(v=7)$	$d^3\Delta(v=8)$	$d^3\Delta(v=9)$	$d^3\Delta(v=10)$	
v	68257.71 (4)	69270.92(1)	70266.034 $^{\rm a}$	71242.54(6)	
3	1.18277(9)	1.16629(3)	$1.15010^{\ a}$	1.13312(3)	
1	-16.82(3)	-17.16(2)	-17.34 <sup>a</sup>	-17.28(4)	
L Contraction of the second seco	1.15 <sup>a</sup>	1.2 <sup>a</sup>	1.31 <sup>a</sup>	1.58 <sup>a</sup>	
$\times 10^3$	-9 <sup>a</sup>	-8 <sup>a</sup>	-10 <sup>a</sup>	-8 <sup>a</sup>	
$0 \times 10^{6}$	6.44(4)	6.41 <sup>a</sup>	$6.40^{\ a}$	6.53(2)	
$I \times 10^{12}$	-0.8 <sup>c</sup>	-0.8 <sup>c</sup>	-0.8 <sup>c</sup>	-0.8 <sup>c</sup>	
$A_D \times 10^4$	-1 <sup>a</sup>	-1 <sup>a</sup>	-1 <sup>a</sup>	-1 <sup>a</sup>	
2	10.74(2)				
3		0.79(7)			

**Table 7.5** – Compilation of the molecular constants for the  $A^1\Pi$ , v = 2, v = 3, and v = 4 states of  ${}^{12}C^{16}O$  and all perturbing states following from the present analysis. All values in vacuum  $cm^{-1}$ .  $1\sigma$  uncertainties given in parentheses in units of the least significant digit.

continued on next page

# PERTURBATION ANALYSIS OF CO A-X (2,0), (3,0) and (4,0) bands

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 $7.00^{a}$ -1.6(2)

Triplet states	$a'^3\Sigma^+(v=11)$	$a'^3\Sigma^+(v=12)$	$a'^3\Sigma^+(v=13)$	$a'^3\Sigma^+(v=14)$	$a'^3\Sigma^+(v=15)$
$T_v$	$67529.52 \ {\rm d}$	$68519.7 \ {\rm d}$	69491.43(6)	$70443.55 \ d$	71377.83(2)
B	1.14921 <sup>a</sup>	1.1338 <sup>d</sup>	1.11772(5)	$1.1051 \ ^{\rm a}$	1.08596 <sup>a</sup>
$\lambda$	-1.103 <sup>a</sup>	-1.103 <sup>e</sup>	-1.151 <sup>a</sup>	-1.14 <sup>a</sup>	-1.07 <sup>a</sup>
$\gamma \  imes 10^3$	4.47 <sup>a</sup>	0 a	0 a	0 a	0 a
$D \times 10^6$	$6.255^{\ a}$	$6.251^{\ a}$	$6.254^{\rm a}$	6.263 <sup>a</sup>	6.284 <sup>a</sup>
$H \times 10^{12}$	-0.4 <sup>f</sup>	-0.4 <sup>f</sup>	-0.4 <sup>f</sup>	-0.4 <sup>f</sup>	-0.4 <sup>f</sup>
$\eta_2$	$6.81^{\ a}$	5.82(3)			
$\eta_3$			7.06(2)		
$\eta_4$				8.24(4)	-6.93(5)
Singlet states	$D^1\Delta(v=3)$				
$T_v$	68504.34(2)				
B	1.19 <sup>g</sup>				
$D \times 10^6$	7 h				
$H \times 10^{12}$	-0.3 <sup>h</sup>				
$\xi_2$	0.0331(3)				
Singlet states	$I^1 \Sigma^- (v=3)$	$I^1 \Sigma^- (v = 4)$	$I^1 \Sigma^- (v = 5)$	$I^1 \Sigma^- (v = 6)$	
$T_{v}$	67696.79(3)	68706.08 <sup>d</sup>	69692.39 <sup>d</sup>	70661.38 (3)	
B	1.2069(4)	$1.1915 \ ^{\rm d}$	$1.1748 \ ^{\rm d}$	$1.1568^{\circ}d$	
$D \times 10^6$	$6.89^{i}$	$6.89^{-1}$	$6.89^{-1}$	$6.89^{-1}$	
$H \times 10^{12}$	$3^{i}$	$3^{i}$	3 <sup>i</sup>	3 <sup>i</sup>	
$\xi_2$	0.062(1)	0.079(2)			
$\tilde{\xi}_3$			0.0338(6)		
$\xi_4$				0.0193(7)	

<sup>a</sup> Data from Ref. [187] and converted.

<sup>b</sup> Constant fixed to that of  $e^{3}\Sigma^{-}$ , v = 3 [151] as first-order approximation. <sup>c</sup> Constant fixed to that of  $d^{3}\Delta$ , v = 5 [151] as first-order approximation.

<sup>d</sup> Data from Ref. [169].

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<sup>e</sup> Constant fixed to that of  $a'^{3}\Sigma^{+}$ , v = 11 as first-order approximation. <sup>f</sup> Constant fixed to that of  $a'^{3}\Sigma^{+}$ , v = 9 [151] as first-order approximation. <sup>g</sup> Extrapolated from  $D^{1}\Delta$ , v = 1 and v = 2 [151].

<sup>h</sup> Constant fixed to that of  $D^1\Delta$ , v = 1 [151] as first-order approximation. <sup>i</sup> Constant fixed to that of  $I^1\Sigma^-$ , v = 2 [151] as first-order approximation.

The  $d^3\Delta$  (v = 9) and  $a'^3\Sigma^+$  (v = 11) states perturb the  $A^1\Pi$  (v = 4) and (v = 2) states, but without crossing them. Then the interaction parameters are strongly correlated with the  $T_v$  parameters for the  $A^1\Pi$  states. Hence, the interaction parameter for these two perturbations were fixed using the values from the original analysis of Field [187].

#### 7.5 Discussion and Conclusion

High-precision frequency measurements of more than 450 rotational lines in CO  $A^1\Pi - X^1\Sigma^+$  (2,0), (3,0) and (4,0) bands (for J up to 52) have been performed. Three different configurations are used in the experiment to obtain the accurate transition frequencies for levels extending to high-J. The accuracy of absolute transition frequencies is 0.01-0.02 cm<sup>-1</sup>. The present data, including recent laser data [126] as well as literature values are used to perform a successful global analysis of the perturbations by other electronic states.

In comparison to the original perturbation analysis by Field [187], the present investigation finds more local perturbation crossings, like those involving  $e^{3}\Sigma^{-}$  $(v=6), d^{3}\Delta (v=10), a'^{3}\Sigma^{+} (v=12, 15), I^{1}\Sigma^{-} (v=4, 5)$ . These crossings are found at high rotational quantum number, which could be observed in our high temperature and saturated spectrum. Molecular constants  $T_v$  represent the deperturbed level energy separations between ground state  $X^{1}\Sigma^{+}$  (v = 0, J = 0)and excited state (v, J = 0), and can be compared with the deperturbed G(v)of Field [150, 187]. This yields good agreement at the 0.1 cm<sup>-1</sup> level. Note that  $T_v$  should not be compared directly with E(v) in Field [150, 187], since E(v) is defined as the deperturbed level energy of the lowest existing rotational level in the particular excited state, which for the  $A^1\Pi$  state is J = 1. Overall the extended data set and the improved accuracy of the level energies yields the derivation of molecular constants at a higher accuracy than in the previous analysis. Values for the B constants are found to be the same within  $\sim 10^{-4} \text{ cm}^{-1}$ . The interaction parameters  $\eta$  are similar to those derived previously [187]; here a different definition of interaction matrix elements should be considered, with the present numbers divided by a factor  $\sqrt{3}$  [186].

The accurate transition frequencies in  $A^1\Pi$  and perturber states will be useful in the analysis of the astronomical spectra in order to determine a value for the cosmic microwave background temperature at high redshift [147]. The results presented here are also relevant to studies that probe for a possible variation of the proton-to-electron mass ratio ( $\mu$ ) using CO [7]. Work is in progress in the analysis of CO  $A^1\Pi - X^1\Sigma^+$  spectra toward the quasar J1237+064 combined with H<sub>2</sub> analysis in the same absorption system at redshift z = 2.69 [1]. This work provides more accurate laboratory wavelengths for the comparisons, and in addition the present perturbation analysis will be useful in improving the calculation of sensitivity coefficients for  $\mu$ -variation.

#### 7.6 Acknowledgements

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## CHAPTER 8

# VUV-synchrotron absorption studies of $N_2$ and CO at 900 K

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Photoabsorption spectra of  $N_2$  and CO were recorded at 900 K, using the vacuumultraviolet Fourier-transform spectrometer at the DESIRS beamline of synchrotron SOLEIL. These high-temperature and high-resolution measurements allow for precise determination of line wavelengths, oscillator strengths, and predissociative line broadening of highly-excited rotational states with J up to about 50, and also vibrational hot bands. In CO, the perturbations of the  $A^{1}\Pi X^{1}\Sigma^{+}$  vibrational bands (0,0) and (1,0) were studied, as well as the transitions to perturbing optically-forbidden states  $e^{3}\Sigma^{-}$ ,  $d^{3}\Delta$ ,  $D^{1}\Delta$  and  $a'^{3}\Sigma^{+}$ . In  $N_2$ , we observed line shifts and broadening in several  $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}$  bands due to unobserved forbidden states of  ${}^{3}\Pi_{u}$  symmetry. The observed state interactions are deperturbed and, for  $N_2$ , used to validate a coupled-channels model of the interacting electronic states. These data are appropriate for use in astrophysical or (exo-)planetary atmospheric applications where high temperatures are important and in future spectroscopic models of these molecules.

#### 8.1 Introduction

The technique of Fourier-transform spectroscopy is typically applied to the infrared and optical wavelength domains. The interferometric principle requires a beam-splitter for which no materials exist in the far vacuum ultraviolet (VUV) part of the electromagnetic spectrum. At the DESIRS beamline of the SOLEIL synchrotron [157] this problem was solved by developing a VUV Fourier-transform spectrometer (FTS) based on beam-splitting by wave-front division, thus enabling high-resolution spectroscopy at wavelengths in the range 40-200 nm [158, 181]. In recent years, this unique instrument has been used to perform high resolution spectroscopic studies on a number of small molecules in the gas phase that exhibit strongly-structured multi-line spectra, such as  $H_2$  [193], HD [135],  $N_2$  [194], and CO [188]; as well as for molecules with more continuum-like spectra, such as  $CO_2$  [195]. These studies amply demonstrate the broadband advantage of the Fourier-transform technique by revealing many hundreds of absorption lines in a single-scan window of some 5 nm, determined by the bandwidth of the beam line undulator source. Alternatively, the setup was used to determine photo-absorption cross sections [196] and predissociation linewidths (and hence rates) of excited states of small molecules [194, 197].

The FTS-VUV setup has been used for gas-phase absorption spectroscopy under varied measurement conditions. Most studies have been performed in a quasi-static gas environment where the gas sample effusively flows through a narrow capillary-shaped absorption cell, with the absorption path aligned with the VUV beam emanating from the undulator. This cell was not equipped with windows, to permit passage of the VUV beam through the sample gas into the FTS-VUV instrument for spectroscopic analysis. For this geometry, differential pumping maintains an ultrahigh vacuum in the FTS and DESIRS beam line. The column density of absorbing gas is limited by the pumping conditions and vacuum requirements of the beam line. In any case, there is a pressure gradient over the cell length falling off toward both ends, complicating any absolute column density calibration. In further studies dedicated to cross-section measurements, a movable gas cell was used of  $\sim 19\,\mathrm{mm}$  length and sealed by either  $MgF_2$  or LiF wedged windows. This allowed for somewhat-higher pressures and controlled gas column densities [198]. Studies using this cell are limited in wavelength range to  $\lambda > 105$  nm [199] by the short-wavelength opacity of the windows. In some experiments requiring the simplification of congested spectra, a molecular jet expansion was employed as well as cooling of the quasi-static gas cell with liquid-nitrogen or liquid-helium. A comparison between these techniques was performed in a study of the  $D_2$  spectrum [200] which also demonstrated improved spectral resolution and accuracy through reduction of the Doppler width under these conditions.

For the present study a heated cell is implemented, allowing for the recording of spectra at temperatures of ~ 1000 K. The high-resolution FTS allows for the measurement and analysis of severely congested spectra at these elevated temperatures. Such spectra bear significance for the modeling of astrophysical shock-wave regions [201], or other high-temperature astrophysical regions where the spectroscopy of small molecules is key to understanding the phenomena, such as e.g., in the photospheres of white dwarfs [4]. Another goal of performing spectroscopy of hot samples is to follow rotational progressions to high J-quantum numbers, where perturbations due to non-Born-Oppenheimer effects are abundantly present. Some pertinent perturbation features specifically occurring at high rotational quantum numbers will be shown here in VUV-absorption spectra of CO and N<sub>2</sub> recorded at 900 K.

#### 8.2 Experimental

The VUV Fourier-Transform spectrometer at the DESIRS beamline is a permanent end station dedicated to high-resolution photoabsorption studies in the range 4 – 30 eV [157]. The instrument has been described in detail previously [158, 181]. In short, the spectrometer is based on wave-front division interferometry using reflective surfaces, thus allowing the extension of the FTS technique into the far VUV spectral range. The undulator white beam is used as the background, feeding the FTS branch and permits the recording of a spectral bandwidth  $\Delta E/E = 7\%$ , corresponding to 5 nm, on each scan. The typical integration time for a single scan is less than 30 minutes to obtain a signal-to-noise ratio for the background continuum level of ~ 400.

The windowless absorption cell is a 40 cm long T-shaped tube with a rectangular cross section, installed under vacuum inside the multi-purpose gas sample chamber of the FTS branch (Fig. 8.1). The cross section of the tube (7.5  $\times$ 4.5 mm) is adapted to the astigmatic shape and dimensions of the undulator source in this section of the beam line. An Inconel heating element (thermocoax) is wrapped around the tube sitting in a groove designed to maximise the contact surface between the heating wire and the cell, and ensuring the gas flowing in the tube is uniformly heated. Two semi-cylindrical shells are pressed around the cell in order to improve the thermal contact during the heating operation. An extra stainless steel box is also installed to shield radiation originating from the cell. Inconel allows for heating the cell up to 1000 K, although, the present measurements were done at a maximum temperature of 900 K. The cell is mounted on a copper base plate that can be cooled by water circulation, although during the experiments the setup was operated without the cooling system. The temperature of the base-mount was carefully monitored within the covered range of temperature (for the cell) and never went



**Figure 8.1** – (a) Cross-section drawing of the gas sample chamber mounted in the FTS-branch of the DESIRS beam line at SOLEIL. The high temperature windowless cell is located in the center of the chamber and is separated from the ultra-high vacuum of the beamline by two stages of differential pumping. (b) The inset shows details of the cell and the shielding where half of the cylindrical shell has been removed for clarity. The heating element is wrapped around the cylindrical cell inside a groove in order to increase surface contact with the cell. The gas is flowing through a  $7.5 \times 4.5$  mm tube into the heated cell. The copper base can be cooled down with a thermalized water circulation system.

beyond a maximum of 200°C with no visible consequence or damage. A thermocouple is connected at one end of the cell to obtain an indication of the gas temperature. The quasi-static gas density inside the heated cell was monitored from outside the vacuum by a 1 mbar range capacitive gauge. The gas column density was adjusted by a needle valve in order to have a constant continuous flow through the cell during the photoabsorption measurements. The effective column density along the absorption path inside the cell varied from  $4 \times 10^{14}$  to  $1.2 \times 10^{17}$  cm<sup>-2</sup> and was adjusted according to the cross sections of the recorded bands.

In the present study, the FTS-VUV was set to provide an instrumental linewidth of  $0.27 \,\mathrm{cm}^{-1}$ . The Doppler broadening corresponds to  $0.28 \,\mathrm{cm}^{-1}$  at a frequency of  $65\,000\,\mathrm{cm}^{-1}$ , temperature of 900 K, and molecular mass of 28 amu. After convolution with the instrument width, a spectral linewidth of  $0.39 \text{ cm}^{-1}$ is anticipated for unsaturated and non-predissociation-broadened N<sub>2</sub> and CO lines. The FTS spectra are intrinsically wavelength calibrated by monitoring the movement of the travel arm in the interferometer which is controlled by a HeNe-laser [158, 181]. Additional and improved calibration can be derived from co-recording special calibration lines, e.g. resonance lines of noble gases [159, 161]. In the present case of the CO spectra the very accurate lasercalibration data of the low-J rotational lines in the A - X bands, accurate to  $\Delta\lambda/\lambda = 3 \times 10^{-8}$ , were used [7]. For the present high-temperature measurements with larger Doppler-broadening the FTS was not used in its very highest resolution mode and the spectral accuracy typically reached is estimated at  $0.02 \text{ cm}^{-1}$ . The accuracy is somewhat lower for weaker and blended lines.

#### 8.3 Absorption spectra of $N_2$

Five N<sub>2</sub> vibrational bands were analysed appearing in our spectrum between 100 400 and 108 500 cm<sup>-1</sup> (99.6 and 92.2 nm). These bands are spectroscopically denoted  $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(v', v''=0)$  for  $v'=0, 1, 2, and 10, and <math>c'_{4}{}^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{g}^{+}(v'=0, v''=1)$  (where v' and v'' are upper- and lower-state vibrational quantum numbers, respectively; and hereafter we neglect electronic-state term symbols); and have been previously observed in room-temperature or expansion-cooled synchrotron- or laser-based experiments [202, 203, 204, 205, 206, 207]. Part of our photoabsorption spectrum showing three of these bands is plotted in Fig. 8.2. Apart from the three lowest vibrational bands in the  $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}$  the (10,0) band was chosen for analysis since this band was known to have rapidly varying predissociation linewidths [207] that could now be monitored to higher-J values. A listing of the deduced term values for the e and f components of the observed b(v') levels is given in Table 8.1.



**Figure 8.2** – (Color online) Photoabsorption spectrum showing the bands b - X(2,0),  $c'_4 - X(0,1)$ , and part of b - X(1,0); and further absorption lines arising from  $H_2$  contamination (5 lines), high-J' lines of b - X(3,0) (14 lines), and of unknown origin (21 lines). These extra lines are indicated by circles. The lower trace indicates the residual error after subtracting a model spectrum.

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The analysis of DESIRS FTS spectra of molecular nitrogen has been discussed previously [194]. This involves simulating each observed absorption line with a Voigt profile defined by a Gaussian Doppler width, Lorentzian natural line width, transition wavenumber, and integrated cross section. A summed cross section is then transformed into an absorption spectrum by the Beer-Lambert law and convolved with a sinc function simulating the instrumental resolution of the FTS. All parameters defining the model absorption spectrum are then optimised to best agree with the experimental scan.

In many cases a more useful measurement of the strength of a line than the integrated cross section is a derived band f-value, calculated by factoring the ground-state rotational thermal population as well as rotation-dependent Hönl-London linestrength factors. Band f-values are only weakly dependent on upper-state J' for unperturbed bands.

The main difficulties encountered while analysing the hot-cell N<sub>2</sub> spectrum were the significant contamination from highly-excited rotational structure of nearby bands and obtaining a correct calibration of the temperature in the cell. Groups of lines from the same vibrational band were sometimes analysed while assuming correlated wavenumbers, widths and strengths to facilitate the analysis of blended spectral regions. That is, P(J'' - 1) and R(J'' + 1) transitions are connected to a common excited state so the difference in their transition wavenumbers was fixed to known ground-state energy levels [208] and a common linewidth assumed. A weak J'-dependence (or J'-independence) was also assumed for some linewidths or f-values.

Lines with natural widths below about  $0.05 \,\mathrm{cm}^{-1}$  full-width half-maximum (FWHM) are not reliably measured in our experiment due to concurrent instrument and Doppler broadening by 0.27 and about  $0.4 \,\mathrm{cm}^{-1}$  FWHM, respectively. No linewidths are then measurable from our spectrum for transitions to the weakly-predissociated  $c'_4(0)$  level [209].

We compare our measured f-values and linewidths with those calculated from an existing model of N<sub>2</sub> photoabsorption and dissociation, including photoabsorbing  ${}^{1}\Pi_{u}$  and  ${}^{1}\Sigma_{u}^{+}$  excited states and spin-forbidden but dissociative  ${}^{3}\Pi_{u}$ states [194, 210, 211, 212, 213]. This model solves a coupled-Schrödinger equation (CSE) for the nuclear motion of the excited molecule, where the necessary potential-energy curves and state interactions have been optimised with respect to a large body of room-temperature experimental data. This model has been successfully employed previously in applications of atmospheric [214] and astronomical photochemistry [201, 215], including temperatures as high as 1000 K. Here, we seek to validate the extrapolation of the CSE model to high temperature by comparison to our new measurements.

**Table 8.1** – Experimental upper term values<sup>a</sup> for observed lines in  $N_2$  indexed by excited state angular-momentum, J'.

b	(0)	b(	(1)	b(	(2)	b(10)
J' <i>e</i> -parity	f-parity	e-parity	f-parity	e-parity	f-parity	e/f-parity <sup>b</sup>
1 100 819.84(2)	100 819.91(4)	101 454.460(5)	101 454.455(8)	102154.82(1)	102154.79(3)	108 374.115(7)
2 100 825.54(3)	100 825.61(1)	101 460.090(7)	101 460.097(3)	102160.33(1)	102160.359(7)	108 378.968(4)
3 100 834.25(1)	100 834.27(2)	101468.560(2)	101 468.541(4)	102168.691(5)	102168.658(9)	108 386.239(4)
4 100 845.85(2)	100 845.821(9)	101 479.798(4)	101 479.803(3)	102 179.754(8)	102 179.731(8)	108 395.955(4)
5 100 860.303(7	) 100 860.32(1)	101 493.874(2)	101 493.877(3)	102193.637(4)	102193.70(1)	108 408.050(2)
6 100 877.67(1)	100 877.660(8)	101510.764(3)	101 510.75(1)	102210.295(7)	102210.267(6)	108 422.591(3)
7 100 897.887(6	) 100 897.895(9)	101 530.443(2)	101 530.456(4)	102 229.655(4)	102 229.675(8)	108 439.530(2)
8 100 921.01(1)	100 920.987(7)	101 552.946(2)	101 552.940(3)	102251.874(9)	102251.846(8)	108 458.875(2)
9 100 946.968(6	) 100 946.96(1)	101 578.238(2)	101578.24(1)	102276.746(6)	102 276.770(9)	108 480.618(2)
10100975.83(1)	100 975.815(7)	101 606.338(3)	101 606.348(6)	102 304.416(6)	102 304.426(7)	108504.758(2)
11 101 007.503(6	) 101 007.52(3)	101 637.230(2)	101 637.230(3)	102334.845(3)	102 334.856(7)	108 531.283(2)
12101042.036(9	) 101 042.04(1)	101 670.911(2)	101 670.912(3)	102368.018(4)	102368.018(7)	108 560.191(2)
13 101 079.458(7	) 101 079.44(1)	101 707.379(2)	101 707.378(3)	102403.933(3)	102 403.926(8)	108591.479(2)
14 101 119.70(1)	101 119.690(8)	101746.629(2)	101 746.626(3)	102442.572(3)	102 442.635(8)	108625.157(2)
15101162.74(1)	101162.74(1)	101788.652(2)	101788.654(3)	102483.948(2)	102 483.965(6)	108 661.209(2)
16101208.58(2)	101 208.600(9)	101833.455(2)	101833.456(3)	102528.044(3)	102528.086(5)	108699.644(2)
17 101 257.250(9	) 101 257.29(2)	101 881.006(2)	101 881.013(3)	102574.875(2)	102574.887(4)	108740.459(3)
18 101 308.77(2)	101308.71(1)	101 931.329(3)	101931.332(3)	102624.387(3)	102624.415(4)	108783.684(5)
19101362.95(1)	101362.91(3)	101984.400(2)	101984.400(4)	102676.610(2)	102676.647(4)	$108829.02(1)^c$
20101419.98(3)	101419.92(1)	102040.210(3)	102040.215(3)	102731.545(3)	102731.574(3)	108876.398(7)
21101479.69(2)	101479.66(4)	102098.767(2)	102098.764(5)	102789.153(2)	102789.168(4)	108926.565(6)
22101542.27(6)	101542.13(3)	102160.044(4)	102160.042(3)	102849.447(2)	102849.489(3)	108979.148(5)
23101607.38(2)	101607.27(6)	102224.043(3)	102224.045(6)	102912.413(2)	102912.457(4)	109034.005(5)
24 –	101675.24(3)	102290.766(6)	102290.761(4)	102978.050(3)	102978.097(3)	109091.321(4)
25101745.90(5)	101745.66(7)	102360.177(4)	102360.171(8)	103046.349(2)	103046.384(4)	109150.906(5)
26 –	101819.01(6)	102432.300(8)	102432.275(6)	103117.309(4)	103117.327(3)	109212.899(4)
27101895.03(5)	-	102507.081(5)	102507.08(1)	103190.873(2)	103190.911(5)	109277.088(7)
28 –	101973.59(9)	102584.52(1)	102 584.532(8)	103267.083(4)	103267.124(4)	109 343.734(9)
29 –	-	102664.686(8)	102664.67(2)	103345.914(3)	103345.956(6)	109412.79(1)
30 –	102138.44(6)	102747.45(4)	102747.45(1)	103 427.360(6)	103 427.403(5)	109484.23(4)
31 –	-	102832.91(1)	102832.83(3)	103511.408(4)	103511.446(8)	-
32 –	-	-	102920.94(2)	103598.05(1)	103598.083(6)	-
33 –	-	103011.62(3)	-	103687.265(6)	103687.32(1)	-
34 –	-	-	-	103779.06(1)	103779.09(2)	-
35 –	-	-	-	103873.41(1)	103873.46(2)	-
36 –	-	-	103299.14(5)	103970.27(3)	103970.33(2)	-
37 –	-	-	-	104069.79(4)	104069.80(5)	-
38 –	-	-	-	-	104171.73(4)	-
39 –	-	-	-	-	104276.17(9)	-
40 -	_	_	_	_	104383.05(5)	_

<sup>*a*</sup>With units of cm<sup>-1</sup> and parenthetical  $1\sigma$  fitting uncertainties in terms of the leastsignificant digit. The estimated absolute calibration uncertainty is  $0.04 \text{ cm}^{-1}$ .

 $<sup>^</sup>b\mathrm{No}$  splitting of e- and f- parity levels was observed (apart from for J'=18) and these were assumed identical.

 $<sup>^</sup>c\mathrm{A}$  splitting of e- and f- parity levels was observed, with term values 108 829.02(1) and 108 828.82(3) cm^{-1}, respectively.



**Figure 8.3** – (Color online) Band f-values of all transitions observed in our experiment as a function of excited-state angular-momentum quantum number, J', and with  $1\sigma$  random fitting uncertainties (circles with error bars). A 10% systematic error also applies and some f-values were analysed assuming J'-independent ranges (horizontal error bars). Also shown are previously-measured f-values [206, 207] (crosses), and calculated by the CSE model (solid black curves).



**Figure 8.4** – (Color online) Band f-values of all  $c'_4 - X(0,1)$  transitions observed in our experiment as a function of excited-state angular-momentum quantum number, J', and with  $1\sigma$  random fitting uncertainties (circles with error bars). A 10% systematic error also applies and some f-values were analysed assuming J'-independent ranges (horizontal error bars). Also shown are alternative experimental f-values assuming an 800K ground state excitation (dashed lines, open circles) and reference values calculated from a combination of CSE and experimental data (solid curve).

#### Temperature calibration

The f-values of b - X(v', 0) transitions were used to calibrate the ground-state rotational temperature and N<sub>2</sub> column density in the hot cell by comparison with previously-measured absolutely-calibrated f-values for v' = 0, 1, 2, and 10 [206, 207]. The resultant values are  $(6.35 \pm 0.64) \times 10^{15}$  cm<sup>-2</sup> and 901 \pm 26 K, respectively. The reference data were recorded at room temperature, included rotational levels as high as J = 23, and themselves have an absolute column density uncertainty of 10% which is also the dominant systematic uncertainty of our f-values. The final agreement between the present measurements and the reference data, shown in Fig. 8.3, is very good despite the factor-of-5 difference in ground state populations, for example, at J' = 20, and provides evidence for the validity of the temperature calibration.

The  $c'_4 - X(0,1)$  band appears quite weakly in our spectrum and was analysed

in order to estimate the vibrational temperature in the hot cell. For this, constant band f-values were assumed over small ranges of most P(J'') and R(J'')lines as indicated piecewise in Fig. 8.4. Simulated  $c'_4 - X(0,1)$  f-values are also shown, with magnitude calculated from the ratio of  $c'_4 - X(0,0)$  and  $c'_4 - X(0,1)$ f-values deduced by electron-excited fluorescence [216],  $f_{(0,0)}/f_{(0,1)} = 6.3 \pm 0.4$ , and an absolute  $c'_4 - X(0,0)$  absorption f-value measurement [206]. The stated uncertainties of the two experimental values used in this comparison are 6% [216] and 10% [206], respectively, although the latter should be neglected because our experimental column-density is calibrated to the same reference. We used the CSE model to simulate the significant rotational dependence of  $c'_4 - X(0, 1)$  f-values and assumed a 900 K distribution of ground-state rovibrational levels. This simulation then correctly reproduced the observed splitting of P- and R-branch f-values for  $c'_4 - X(0, 1)$  transitions with increasing J'. This splitting is also known to occur for the  $c'_4 - X(0,0)$  fundamental band [206] and is the result of a rotational-perturbation of  $c'_4(v'=0)$  by nearby  ${}^1\Pi_u$  levels [194]. Additionally,  $c'_4 - X(0, 1)$  transitions to J' = 11, 12, and 13 levels are significantly weakened relative to their neighbours due to a well-known localised perturbation by the crossing rotational term series of  $b'^{1}\Sigma_{n}^{+}(v'=1)$  [203].

The newly-measured  $c'_4 - X(0, 1)$  *f*-values are somewhat smaller than the simulated values and an alternative model adopting an 800 K distribution of groundstate levels leads to the better agreement indicated in Fig. 8.4. This may indicate incomplete thermalisation of the N<sub>2</sub> in our experiment leading to a lesser degree of vibrational excitation than rotational. A similar result is found in Sec. 8.4 for the CO rotational and vibrational temperatures.

As a final check on the temperature of our sample of N<sub>2</sub>, the Doppler broadening in our experiment was measured by reference to lower-J' levels of the b-X(1,0)absorption band, whose predissociation broadening is known to be below our resolution limit [204, 210]. We find a kinetic temperature from this of about 930 K, with an uncertainty estimated to be significantly greater than for our deduced rotational temperature.

#### Results

Transition wavenumbers for all observed b-X(v',0) bands were reduced to term values using accurate N<sub>2</sub> ground-state molecular constants [208]. Term values for these bands have been deduced previously for rotational levels with J' as high as 36 and with about  $0.1 \text{ cm}^{-1}$  uncertainty. Our term values are listed in Table 8.1 and have statistical uncertainties of around  $0.01 \text{ cm}^{-1}$ . The absolute calibration of our experiment was made by comparison of argon resonance lines appearing in our spectra with the NIST database and has an estimated uncertainty of  $0.04 \text{ cm}^{-1}$ . Our deduced band f-values are plotted in Fig. 8.3. The decrease of b - X(v', 0)f-value with J' continues to the highest-excitation lines that we observe and is in excellent agreement with values predicted by the CSE model. This decrease is effectively due to a decreasing Franck-Condon overlap of b(v') and X(0)vibrational wave functions with increasing centrifugal distortion.

Measured natural linewidths and comparable values from previous photoabsorption and resonantly-enhanced photoionisation experiments [202, 205, 206] are shown in Fig. 8.5. The widths of b(0), b(1), and b(2) averaged over their  $J \leq 5$  levels have been previously deduced from laser-based lifetime or linewidth measurements [202, 204, 205]. The rotationally-resolved J-dependent broadening of b(2) and b(10) levels have been measured in synchrotron-based experiments [206, 207], and an increasing b(1) predissociation width with J' has also been experimentally deduced [217, 218]. Our newly-measured widths show good agreement with all reference data but with generally reduced scatter. Two interesting new pieces of information are discussed below.

First, the decreasing b(2) widths are now shown to pass through a minimum at  $J \simeq 28$ . This complex behaviour is well-reproduced by the CSE model which includes a mechanism for predissociative line broadening by including unbound electronic states amongst its coupled channels [210, 211]. The critical interactions in this case are the spin-orbit coupling of b(2) with vibrationallybound levels of the  $C^{3}\Pi_{u}$  state and their subsequent electronic interaction with the unbound continuum of the  $C'^{3}\Pi_{u}$  state. The dominant perturber of b(2) is the C(8) level which lies only  $100 \text{ cm}^{-1}$  lower in energy and has been previously identified in a photoabsorption spectrum [219] and found to have a linewidth of  $18 \text{ cm}^{-1}$  for J' less than about 10, despite the nominally spinforbidden nature of this transition. All other bound  ${}^{3}\Pi_{u}$  states are too remote in energy to contribute significantly to the predissociation of b(2) [212] and the observed J'-dependence of its widths must then closely scale with the broader widths of C(8).

Second, there is a sharp peak in the linewidths of b(10) shown in Fig. 8.5. Increasing widths beginning around J' = 15 were known from a poorer signalto-noise-ratio room-temperature spectrum [207], but are now better resolved and to higher-J'. There is also a perturbation of b(10) rotational energy levels near J' = 19, as shown in Fig. 8.6 as a  $0.8 \text{ cm}^{-1}$  deflection of its reduced term values. The localised perturbation of b(10) energies and widths indicates a level crossing with a predissociation-broadened level of  ${}^{3}\Pi_{u}$  symmetry, as is known to occur elsewhere in the N<sub>2</sub> spectrum [219].

One candidate for the role of b(10) perturber is the v' = 16 level of the  $C^{3}\Pi_{u}$  state, which has been observed for  $J' \leq 10$  [219] and has a band origin only  $80 \text{ cm}^{-1}$  below that of b(10). However, a rotational constant calculated from the observed C(16) levels,  $1.153 \text{ cm}^{-1}$  [212], is too low to cross the b(10) term series where the observed perturbation peaks at  $J \simeq 18$ . Alternatively, the



**Figure 8.5** – (Color online) Natural linewidths of e- and f-parity excited-state levels accessed in our experiment as a function of their angular-momentum quantum number, J', and with  $1\sigma$  random fitting uncertainties (circles with error bars). Some linewidths were analysed assuming J'-independent ranges (horizontal error bars). Also shown are previously-measured linewidths [202, 204, 205, 206, 207] (yellow lines and crosses), and linewidths calculated by the CSE model (solid black curves) and a two-level local interaction model (dashed black curve).



**Figure 8.6** – Experimental f-parity term values of b(10) reduced by the subtraction of a cubic polynomial of best fit in terms of J'(J'+1) (circles). Also shown are reduced term values from the  $b(10)/{}^{3}\Pi_{u}$  interaction model (curve).

v = 2 level of the  $G^{3}\Pi_{u}$  state has been observed [220] to lie nearby,  $340 \text{ cm}^{-1}$  below b(10), and undoubtedly has a larger rotational constant more characteristic of N<sub>2</sub> Rydberg levels, about  $1.9 \text{ cm}^{-1}$ . A crossing between G(2) and b(10) is then conceivable. The observed widths of C(16) for  $J' \leq 10$  are less than  $0.5 \text{ cm}^{-1}$  FWHM, whereas G(2) is predicted to be much broader, about  $90 \text{ cm}^{-1}$  FWHM, by the CSE model of Lewis *et al.* [212].

To analyse the width and term value perturbation of b(10) further we defined a two-level model of b(10) interacting by the spin-orbit operator with a  ${}^{3}\Pi_{u}$ level (including all triplet sublevels) and optimised its various parameters to match our experimental data. This was done in an identical fashion to similar deperturbations of N<sub>2</sub>  ${}^{3}\Pi_{u}/{}^{1}\Pi_{u}$  interactions by Lewis *et al.* [219]. Comparisons of experimental widths and reduced term values with this model are shown in Figs. 8.5 and 8.6 and find overall good agreement when adopting a  ${}^{3}\Pi_{u}$  state with a term origin of approximately 108 150 cm<sup>-1</sup>, a rotational constant of 1.6 cm<sup>-1</sup>, and a spin-orbit splitting of 30 cm<sup>-1</sup> (where the sign of the latter is unconstrained). Two further model parameters are the strength of the b(10)and  ${}^{3}\Pi_{u}$  levels. Good agreement could only be found when assuming



**Figure 8.7** – (Color online) Overview spectrum of the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  system including (0,0), (1,0), and (2,0) bands, and some hot bands. The top panel shows the spectrum which is measured at room temperature (300 K). In the bottom panel is the hot spectrum (900 K). The sharp absorption line in the upper spectrum at 68045.156 cm<sup>-1</sup> is a xenon resonance line.

the latter increases linearly in term of J'(J'+1) from  $20 \text{ cm}^{-1}$  at J' = 18, to  $60 \text{ cm}^{-1}$  at J' = 29. All of these deduced values are intermediate between those known or predicted for C(16) and G(2), [212, 219, 220], indicating that the perturber of b(10) is an electronic admixture of the  $C^3\Pi_u$  and  $G^3\Pi_u$  states. Indeed, the coupled-channels model of Lewis *et al.* [212] predicts this, as well as a further significant admixture of the  $F^3\Pi_u$  Rydberg state into the nominal C(16) and G(2) levels.

### 8.4 Absorption spectra of CO $A^{1}\Pi - X^{1}\Sigma^{+}$ (0,0) and (1,0) bands

The novel hot cell configuration was employed for the further investigation of the  $A^1\Pi - X^1\Sigma^+$  system of CO for the lowest vibrational bands in the excited state. Figure 8.7 shows an overview spectrum of some bands recorded at 300

**Table 8.2** – Observed high-J transition frequencies (in vacuum  $cm^{-1}$ ) of the CO  $A^{1}\Pi - X^{1}\Sigma^{+}(0,0)$  and (1,0) bands obtained with the hot cell. Lower-J transitions are listed in Ref. [188]. The estimated uncertainty (1 $\sigma$ ) is 0.02 cm<sup>-1</sup> except for weak or blended lines.

	$A^1$	$\Pi - X^1 \Sigma^+ ($	0,0)		$A^1$ ]	$\Pi - X^1 \Sigma^+ ($	1,0)
$J^{\prime\prime}$	$\mathrm{R}(J)$	$\mathbf{Q}(J)$	P(J)	$J^{\prime\prime}$	$\mathrm{R}(J)$	$\mathbf{Q}(J)$	P(J)
17			64589.64	21	66140.33		66005.05
18			64583.37	22	66128.24		65986.78
19	64689.77		64566.32	23	66115.44		65967.83
20	64679.86		64549.58	24	66101.66	66023.95	65948.17
21	64669.38		64532.53	25	66091.32	66006.31	65927.76
22	64658.26	64584.85	64515.00	26	66074.03	65989.04	65906.37
23	64646.44	64570.02	64496.90	27	66058.34	65970.28	65888.43
24	64634.07	64554.44	64478.17	28	66042.09	65950.94	65863.57
25	64620.76	64538.20	64458.80	29	66025.18	65929.54	65840.31
26	64604.44	64521.15	64438.67	30	66007.60	65910.53	65816.49
27	64593.32	64501.07	64417.88	31	65989.33	65889.04	65792.02
28	64577.54	64486.13	64393.98	32	65970.28	65866.89	65766.89
29	64559.78	64466.58	64375.28	33	65950.64	65843.98	65741.06
30	64551.43	64445.05	64351.94	34	65930.24	65819.92	65714.55
31	64531.64	64432.91	64326.63	35	65909.14	65798.34	65687.33
32	64512.56	64409.35	64310.71	36	65887.33	65772.41	65659.43
33	64490.76	64386.49	64283.40	37	65864.79	65746.65	65630.83
34	64481.53	64360.95	64256.77	38	65841.53	65720.29	65601.52
35	64459.85	64347.94	64227.48	39	65817.50	65693.27	65571.51
36	64438.85	64322.50	64210.71	40	65793.18	65665.55	65540.79
37		64297.87	64181.54	41	65767.61	65637.11	65509.30
38	64396.16	64272.94	64153.19	42	65741.50	65607.95	65477.54
39	64373.87	64248.16	64124.55	43	65714.55	65577.99	65444.54
40	64350.93	64221.59	64095.36	44	65686.94	65548.84	65410.97
41	64327.65	64194.95	64065.55	45	65658.53	65516.48	65376.69
42	64303.14	64167.66	64035.39	46	65628.96	65484.32	65341.67
43	64278.62	64139.56	64004.55	47	65600.90	65451.21	65305.83
44	64253.03	64111.24	63972.67	48	65569.47	65418.96	65268.92
45	64226.85	64081.88	63940.64	49	65537.24	65383.97	
46	64199.92	64052.09	63907.71	50		65348.14	
47	64172.37			51		65318.08	
48		63989.48		52		65277.96	
51		63892.98		53	65402.39		



**Figure 8.8** – (Color online) The spectrum of the CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  system in the range 63 700 – 64 900 cm<sup>-1</sup> measured using the hot cell in combination with the FTS-VUV. Rotational lines in the A - X (0,0) and (1,1) bands are assigned by the sticks. Transitions to the  $e^{3}\Sigma^{-}$  perturber state are also assigned. The slope on the background continuum is due to the spectral profile of the undulator emission.

K and 900 K. With the higher gas temperature, the rotational envelope of each band includes higher J-quantum numbers and hot bands appear that originate from  $X^1\Sigma^+(v''=1)$ . Figure 8.8 displays a more detailed spectrum of the (0,0) and (1,1) bands of the  $A^1\Pi - X^1\Sigma^+$  system of CO. Note that the strongest transitions in Figs. 8.7 and 8.8 are saturated. A number of spectra were recorded at various gas densities so that transition frequencies for all lines could be analysed in unsaturated recordings. The observed high-J transition frequencies in the  $A^1\Pi - X^1\Sigma^+(0,0)$  and (1,0) bands are collected in Table 8.2. While in a previous room temperature study of the same bands their rotational progression could be followed up to J = 21 and J = 23, respectively [188], the present spectrum reveals lines up to J = 51 and J = 53for the two bands. Accurate transition frequencies for low-J transitions were already given in Ref. [188].

In the observed region, between  $63500-67500 \text{ cm}^{-1}$ , many lines were observed that excite perturber states of the  $A^{1}\Pi$  (v = 0) and (v = 1) levels, and are examined in the present study. Lines pertaining to the  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  (1,0) band, clearly visible in Fig. 8.8, are listed in Table 8.3. Data for the  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}$  (1,0) band had previously been reported by Simmons and Tilford [169] and, at higher accuracy and also up to J = 22, by Lefloch *et al.* [151]. On average the data are offset by 0.04 cm<sup>-1</sup> with respect to present values, which is within the error margins claimed in Ref. [151]. Term values of the  $e^{3}\Sigma^{-}$ (v = 1) level can also be obtained via measurement of lines in the  $B^{1}\Sigma^{+} - e^{3}\Sigma^{-}$ system, with observations of the (0,1) band [221] at accuracies in the range 0.001 - 0.02 cm<sup>-1</sup> combined with the measurements of the  $B^{1}\Sigma^{+} - X^{1}\Sigma^{+}(0,0)$ band, accurate at 0.003 cm<sup>-1</sup> [222]. In comparison with the present data set the overall offset on the term values is within 0.015 cm<sup>-1</sup>, which is well within the quoted uncertainties.

Observed lines associated with the  $d^3\Delta - X^1\Sigma^+$  system are listed in Table 8.4 for the (4,0) band, observed for rotational angular momenta of J = 26 - 36, and in Table 8.5 for the (5,0) band, with observation of J = 0 - 17. In an investigation by Herzberg *et al.* [168] rotational levels up to J = 22 were observed in both bands at low accuracy. The observations in the  $d^3\Delta - X^1\Sigma^+(4,0)$  band were superseded by those of Lefloch *et al.* [151] at higher accuracy. Comparison with the latter and the present data set yields agreement within 0.04 cm<sup>-1</sup>, hence within the quoted error margin of 0.06 cm<sup>-1</sup> in Ref. [151].

The  $d^3\Delta - X^1\Sigma^+(5,0)$  band had been investigated by VUV laser-induced fluorescence measurements [223]. Accurate data on this band were also reported from classical spectroscopic studies by Lefloch [152]; for this set the agreement with the present data is within 0.02 cm<sup>-1</sup>. The  $d^3\Delta$  (v = 5) levels were also observed in emission in the  $B^1\Sigma^+ - d^3\Delta(0,5)$  band [221]. In the present study the  $F_1$  and  $F_2$  fine structure components in the  $d^3\Delta$  state were observed, while in the study of Choe *et al.* [221] the  $F_3$  components were seen as a result of

**Table 8.3** – Observed transition frequencies (in vacuum  $cm^{-1}$ ) of the CO  $e^{3}\Sigma^{-} - X^{1}\Sigma^{+}(1,0)$  band obtained with the hot cell. The estimated uncertainty  $(1\sigma)$  is 0.02  $cm^{-1}$  except for weak or blended lines.

	F	71	$F_2$	F	3
J''	${}^Q\mathbf{R}(J)$	$^{O}\mathbf{P}(J)$	$^{Q}\mathbf{Q}(J)$	${}^{S}\mathrm{R}(J)$	$^{Q}\mathrm{P}(J)$
2			64798.89		
3	64794.01		64794.98		
4			64789.71	64788.84	
5		64759.37	64783.15	64782.45	
6	64811.33		64775.34	64774.92	64746.55
7	64807.10	64764.30	64766.22	64766.60	64732.49
8	64801.53		64755.89	64758.41	64717.25
9		64741.55	64744.31	64794.65	64701.25
10	64726.00		64731.92	64786.42	64685.41
11		64656.88	64718.79	64776.94	64713.88
12	64696.16	64637.39	64705.72		64698.09
13	64679.05	64615.71	64674.65	64754.31	64680.93
14		64592.43	64658.00		64662.50
15		64567.68	64639.20	64728.76	64642.97
16			64618.52	64703.94	64622.54
17			64596.30	64688.01	64602.10
18			64572.61		64569.64
19			64547.41		64545.95
20					64520.00
21			64493.11		64492.39
22					64463.22

different intensity borrowing, In addition two lines in the  $d^3\Delta - X^1\Sigma^+(5,1)$ band were observed and listed in Table 8.6.

Additional lines observed were assigned to the  $D^1\Delta - X^1\Sigma^+(1,0)$  band, the  $I^1\Sigma^- - X^1\Sigma^+(2,0)$  band, and the  $a'^3\Sigma^+ - X^1\Sigma^+(9,0)$  band, and listed in Table 8.6. Some of these transitions probing perturber states were observed previously by Lefloch *et al.* [151, 152], although not all, and at a lower accuracy of 0.06 cm<sup>-1</sup>. Herzberg *et al.* observed states up to J = 22 in the  $I^1\Sigma^- - X^1\Sigma^+(2,0)$  band [179]. Despite the fact that information on the intermediate J-levels is missing, an unambiguous assignment of the transitions originating in J = 34 - 35 could nevertheless be made based on the perturbation patterns. The same holds for the newly observed lines in the  $D^1\Delta - X^1\Sigma^+(1,0)$  band, for which rotational lines up to J = 17 were observed in the past [178], and for

**Table 8.4** – Observed transition frequencies (in vacuum  $cm^{-1}$ ) of the CO  $d^3\Delta - X^1\Sigma^+(4,0)$  band obtained with the hot cell. The estimated uncertainty  $(1\sigma)$  is 0.02  $cm^{-1}$  except for weak or blended lines.

		$F_1$			$F_2$		$F_3$
$J^{\prime\prime}$	$\mathrm{R}(J)$	$\mathrm{Q}(J)$	$\mathrm{P}(J)$	$\mathrm{R}(J)$	$\mathrm{Q}(J)$	$\mathrm{P}(J)$	$\mathrm{Q}(J)$
26	64610.70	64544.08					
27		64507.33					
28			64400.24				
29				64579.94	64504.55		
30				64532.81	64465.22	64389.87	
31				64495.05	64414.40	64346.77	
32					64372.81	64292.14	64464.02
33				64510.13	64421.74		
34				64458.06	64380.33		
35					64324.46	64246.83	
36						64187.21	

**Table 8.5** – Observed transition frequencies (in vacuum  $cm^{-1}$ ) of the CO  $d^3\Delta - X^1\Sigma^+(5,0)$  band obtained with the hot cell. The estimated uncertainty  $(1\sigma)$  is 0.02  $cm^{-1}$  except for weak or blended lines.

		$F_1$			$F_2$	
$J^{\prime\prime}$	$\mathbf{R}(J)$	$\mathrm{Q}(J)$	$\mathbf{P}(J)$	$\mathrm{R}(J)$	$\mathrm{Q}(J)$	$\mathrm{P}(J)$
0				66210.18		
1				66211.77		
2	66176.59			66212.17	66204.04	66198.61
3	66174.74			66211.19	66200.58	
4	66171.62		66149.75	66209.16	66195.87	66185.22
5			66140.16		66189.94	
6	66160.90	66143.98		66201.11	66182.70	66166.87
7			66116.88	66195.03	66174.17	66155.80
8				66187.68	66164.30	66143.38
9				66178.92	66153.03	66129.72
10		66095.82		66168.86	66140.42	66114.67
11			66053.23	66157.25	66126.61	66098.22
12				66144.58	66111.32	66080.43
13				66130.29	66094.65	66061.40
14				66114.67	66076.58	66040.93
15				66097.74	66057.17	66019.02
16					66036.44	65995.79
17					66014.27	65971.17
**Table 8.6** – Observed transition frequencies (in vacuum  $cm^{-1}$ ) of other CO electronic-vibrational bands obtained with the hot cell. The estimated uncertainty  $(1\sigma)$  is 0.02  $cm^{-1}$  except for weak or blended lines.

$D^1 \Delta - X^1 \Sigma^+(1,0)$	$a'^{3}\Sigma^{+} - X^{1}\Sigma^{+}(9,0)$ $^{P}Q1(39)  64245.88$
${}^{P}P(26) = 65916.49$ ${}^{P}P(27) = 65875.99$ ${}^{Q}Q(24) = 66050.52$ ${}^{Q}Q(25) = 66016.10$ ${}^{Q}Q(26) = 65979.36$	$ \begin{array}{c} d^{3}\Delta - X^{1}\Sigma^{+}(5,1) \\ {}^{R}\text{Q31}(3) & 64057.44 \\ {}^{R}\text{Q31}(4) & 64052.92 \end{array} $
${}^{R}R(25) = 66078.85$ ${}^{R}R(27) = 66011.16$	$I^{1}\Sigma^{-} - X^{1}\Sigma^{+}(2,0)$ ${}^{Q}Q(34)  65837.46$ ${}^{Q}Q(35)  65785.95$

which new lines originating from J = 24 - 26 are found.

A reiteration of a previous deperturbation analysis for the  $A^{1}\Pi$  (v = 0) and (v = 1) states [188] is performed including the additional data points for high-J levels. A comprehensive fit was performed based on the diagonalisation of a series of matrices containing J-dependent deperturbed energy levels and interaction energies of multiple states. The entire set of experimental  $A^{1}\Pi - X^{1}\Sigma^{+}(0,0)$  and (1,0) lines were reproduced and all lines exciting perturber states. The form of these perturbation matrices is kept the same as that defined in Table 6 of Ref. [188], keeping the same labels for the parameters. For the  $A^1\Pi$  states, the  $T_v$  and B parameters are fixed to the previous work [188], because these parameters are predominantly determined by the low-J transition frequencies. Most of the molecular constants resulting from this procedure did not undergo a significant change except for the values pertaining to the states  $D^1 \Delta(v=1)$  and  $d^3 \Delta(v=4)$ . These values are listed in Table 8.7. The main difference for the  $d^3\Delta$  state entails the inclusion of a quartic centrifugal distortion D and a spin-spin coupling constant,  $\lambda$ . Values for the  $D^1\Delta$  state were previously kept constant but are now optimized in the present fit.

The rotational temperature  $T_{rot} = 927 \pm 20$  K is determined by fitting the transition intensities of transitions with different *J*-quantum numbers, assuming a Boltzmann distribution of ground state populations. This fitting considers **Table 8.7** – The updated molecular constants for the  $A^1\Pi$  (v = 0) and (v = 1) states of  ${}^{12}C^{16}O$  and the perturber states  $d^3\Delta$  (v = 4) and  $D^1\Delta$  (v = 1) following from the perturbation analysis. In cases where an uncertainty is specified in () parentheses the value was determined from the fit; in cases where this is not specified a value was taken from literature. For the  $A^1\Pi$  states, the  $T_v$  and B parameters are fixed to the previous work [188], because these parameters are predominantly determined by the low-J transition frequencies. All values in vacuum cm<sup>-1</sup>.

$A^1 \Pi(v=0) \qquad \qquad A$		$A^{1}\Pi$	$^{1}\Pi(v=1)$	
$T_v$	64746.762	$T_v$	66228.801	
B	1.604069	B	1.58126	
$q \; (\times 10^5)$	1.4(4)	$q \; (\times 10^5)$	-2.5(4)	
$D(\times 10^{6})$	7.352(5)	$D(\times 10^{6})$	7.438(4)	
$H(\times 10^{12})$	-8 (2)	$H(\times 10^{12})$	-15 (1)	
$d^3\Delta(v=4)$		$D^1 \Delta(v=1)$		
$T_v$	65101.90(3)	$T_v$	66462.11 (9)	
B	1.23381 (8)	B	1.2373(3)	
A	-16.52(1)			
$\lambda$	1.15(3)			
$\gamma \ (\times 10^3)$	-8.54			
$D(\times 10^{6})$	6.80(6)	$D \; (\times 10^6)$	8.8(4)	
$H(\times 10^{12})$	-0.8	$H(\times 10^{12})$	-0.3	
$A_D (\times 10^4)$	-1			
$\eta_0$	-21.72(1)	$\xi_0$	0.040	
$\eta_1$		$\xi_1$	0.077(1)	

perturber states borrowing intensity from the  $A^1\Pi$ - $X^1\Sigma^+$  transitions. The vibrational temperature,  $T_{vib} \sim 845$  K, is calculated by comparing the intensities of the strong  $A^1\Pi - X^1\Sigma^+(1,0)$  band and the weak (1,1) hot band. For this analysis pressure saturation effects must be considered that prevent a direct comparison of intensities of these two vibrational bands with very different cross sections. Instead, spectra recorded at different column densities are used, also involving a comparison with the  $A^1\Pi - X^1\Sigma^+(0,0)$  band of intermediate strength. Further, Franck-Condon factors of the (1,0) and (1,1) vibrational transitions must be considered, which are taken from Ref. [192]. The kinetic temperature, associated with Doppler broadening, is determined at  $T_{kin} \sim 900$  K.

### 8.5 Conclusion

Vacuum-ultraviolet photoabsorption spectra of  $N_2$  and CO were recorded at 930 K using a heated free-flowing gas cell and the Fourier-transform spectrometer end station of the DESIRS beamline at the SOLEIL synchrotron. This novel setup allowed for the measurement of rotational transitions with angular-momentum quantum numbers, J', as high as 51 and also from the first excited ground state vibrational level, which is well beyond the limit of room-temperature experiments. The high-resolution spectrometer permitted quantification of rotationally-resolved transition energies, f-values, and predissociation broadening for many vibrational bands.

In CO, we deduce new high-J' level energies for the upper states of the  $A^{1}\Pi - X^{1}\Sigma^{+}(v', v'' = 0)$  bands with v' = 0 and 1, as well as observe new forbidden transitions to levels of the  $e^{3}\Sigma^{-}$ ,  $d^{3}\Delta$ ,  $D^{1}\Delta$  and  $a'^{3}\Sigma^{+}$  states. The forbidden transitions appear due to intensity-borrowing from the A - X bands and the new data permitted an improved estimate of molecular parameters describing the forbidden levels and their perturbing interactions.

We measure new level energies, f-values, and predissociation linewidths of the N<sub>2</sub> bands  $b^{1}\Pi_{u} - X^{1}\Sigma_{u}^{+}(v',v''=0)$  for v'=0,1,2, and 10. These verify the high-J' predictions of a CSE model which was constructed with respect to room-temperature experimental data. This validates the use of photodissociation cross sections calculated from this model in atmospheric or astrophysical applications at high temperatures. No forbidden levels are observed for the case of N<sub>2</sub>. Instead, the J'-dependent widths of b(v') provide new indirect information on an interacting dissociative manifold of <sup>3</sup>\Pi levels. The analysis of perturbed b(10) level energies and linewidths permitted the characterisation of its level crossing with a <sup>3</sup> $\Pi_{u}$  level of mixed electronic character.

There is some indication that for both target molecules the rotational and vibrational temperatures are not identical, 930 and 800–845 K, respectively. The incomplete equilibration of vibrational and rotational excitation will not affect our conclusions regarding the perturbation of high J' levels but introduces uncertainty into any determination of hot-band absolute f-values.

The present measurements of high-temperature cross sections and line lists have a direct application to the study of astrophysical environments and planetary atmospheres. It also provides detailed extra information on the underlying electronic states of the molecules and their non-Born-Oppenheimer interactions. This information, when incorporated with the larger experimental record, is necessary for constraining predictive models of the photoabsorbing and dissociating excited states; and will allow for improvements to the N<sub>2</sub> CSE model, and similar theoretical developments for the case of CO.

## 8.6 Acknowledgment

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# Bibliography

- M. Daprà, J. Bagdonaite, M. T. Murphy and W. Ubachs. "Constraint on a varying proton-to-electron mass ratio from molecular hydrogen absorption toward quasar SDSS J123714.60+064759.5". Mon. Not. Roy. Astron. Soc., vol. 454, p. 489, 2015.
- [2] J. Bagdonaite, W. Ubachs, M. T. Murphy and J. B. Whitmore. "Constraint on a varying proton-electron mass ratio 1.5 billion years after the big bang". *Phys. Rev. Lett.*, vol. 114, p. 071301, 2015.
- [3] E. J. Salumbides, J. Bagdonaite, H. Abgrall, E. Roueff and W. Ubachs. "H<sub>2</sub> Lyman and Werner band lines and their sensitivity for a variation of the protonelectron mass ratio in the gravitational potential of white dwarfs". Mon. Not. Roy. Astron. Soc., vol. 450, p. 1237, 2015.
- [4] J. Bagdonaite, E. J. Salumbides, S. P. Preval, M. A. Barstow, J. D. Barrow, M. T. Murphy and W. Ubachs. "Limits on a gravitational field dependence of the proton-electron mass ratio from H<sub>2</sub> in white dwarf stars". *Phys. Rev. Lett.*, vol. 113, p. 123002, 2014.
- [5] J. Bagdonaite, W. Ubachs, M. T. Murphy and J. B. Whitmore. "Analysis of molecular hydrogen absorption toward QSO B0642-5038 for a varying proton-to-electron mass ratio". Astrophys. J., vol. 782, p. 10, 2014.
- [6] J. Bagdonaite, M. T. Murphy, L. Kaper and W. Ubachs. "Constraint on a variation of the proton-to-electron mass ratio from H<sub>2</sub> absorption towards quasar Q2348-011". Mon. Not. Roy. Astron. Soc., vol. 421, p. 419, 2012.
- [7] E. J. Salumbides, M. L. Niu, J. Bagdonaite, N. de Oliveira, D. Joyeux, L. Nahon and W. Ubachs. "The CO A-X system for constraining cosmological drift of the proton-electron mass ratio". *Phys. Rev. A*, vol. 86, p. 022510, 2012.
- [8] H. Cavendish. "Three papers, containing experiments on factitious air, by the Hon. Henry Cavendish, F. R. S." *Philosophical Transactions (1683-1775)*, vol. 56, p. 141, 1766.

- [9] A. Stwertka. A Guide to the Elements, p. 16. Oxford University Press, 1996.
- [10] H. A. Bethe. "The electromagnetic shift of energy levels". Phys. Rev., vol. 72, p. 339, 1947.
- [11] W. E. Lamb and R. C. Retherford. "Fine structure of the hydrogen atom by a microwave method". *Phys. Rev.*, vol. 72, p. 241, 1947.
- [12] D. Hanneke, S. Fogwell and G. Gabrielse. "New measurement of the electron magnetic moment and the fine structure constant". *Phys. Rev. Lett.*, vol. 100, p. 120801, 2008.
- [13] R. Bouchendira, P. Cladé, S. Guellati-Khélifa, F. Nez and F. Biraben. "New determination of the fine structure constant and test of the quantum electrodynamics". *Phys. Rev. Lett.*, vol. 106, p. 080801, 2011.
- [14] C. G. Parthey, A. Matveev, J. Alnis, B. Bernhardt, A. Beyer, R. Holzwarth, A. Maistrou, R. Pohl, K. Predehl, T. Udem, T. Wilken, N. Kolachevsky, M. Abgrall, D. Rovera, C. Salomon, P. Laurent and T. W. Hänsch. "Improved measurement of the hydrogen 1S – 2S transition frequency". *Phys. Rev. Lett.*, vol. 107, p. 203001, 2011.
- [15] C. Schwob, L. Jozefowski, B. de Beauvoir, L. Hilico, F. Nez, L. Julien, F. Biraben, O. Acef, J.-J. Zondy and A. Clairon. "Optical frequency measurement of the 2S - 12D transitions in hydrogen and deuterium: Rydberg constant and lamb shift determinations". *Phys. Rev. Lett.*, vol. 82, p. 4960, 1999.
- [16] L. Wolniewicz. "Relativistic energies of the ground state of the hydrogen molecule". J. Chem. Phys., vol. 99, p. 1851, 1993.
- [17] L. Wolniewicz. "Nonadiabatic energies of the ground state of the hydrogen molecule". J. Chem. Phys., vol. 103, p. 1792, 1995.
- [18] J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs and F. Merkt. "Determination of the ionization and dissociation energies of the hydrogen molecule". J. Chem. Phys., vol. 130, p. 174306, 2009.
- [19] D. Sprecher, J. Liu, C. Jungen, W. Ubachs and F. Merkt. "Communication: The ionization and dissociation energies of HD". J. Chem. Phys., vol. 133, p. 111102, 2010.

- [20] J. Liu, D. Sprecher, C. Jungen, W. Ubachs and F. Merkt. "Determination of the ionization and dissociation energies of the deuterium molecule D<sub>2</sub>". *J. Chem. Phys.*, vol. 132, p. 154301, 2010.
- [21] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki and B. Jeziorski. "Theoretical determination of the dissociation energy of molecular hydrogen". J. Chem. Theory Comput., vol. 5, pp. 3039, 2009.
- [22] J. Komasa, K. Piszczatowski, G. Lach, M. Przybytek, B. Jeziorski and K. Pachucki. "Quantum electrodynamics effects in rovibrational spectra of molecular hydrogen". J. Chem. Theory Comput., vol. 7, p. 3105, 2011.
- [23] E. J. Salumbides, G. D. Dickenson, T. I. Ivanov and W. Ubachs. "QED effects in molecules: Test on rotational quantum states of H<sub>2</sub>". *Phys. Rev. Lett.*, vol. 107, p. 043005, 2011.
- [24] G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki and W. Ubachs. "Fundamental vibration of molecular hydrogen". *Phys. Rev. Lett.*, vol. 110, p. 193601, 2013.
- [25] D. Bailly, E. Salumbides, M. Vervloet and W. Ubachs. "Accurate level energies in the  $EF^{1}\Sigma_{u}^{+}, GK^{1}\Sigma_{g}^{+}, H^{1}\Sigma_{g}^{+}, B^{1}\Sigma_{u}^{+}, C^{1}\Pi_{u}, B'^{1}\Sigma_{u}^{+}, D^{1}\Pi_{u}, I^{1}\Pi_{g}, J^{1}\Delta_{g}$  states of H<sub>2</sub>". *Mol. Phys.*, vol. 108, p. 827, 2010.
- [26] S. Hannemann, E. J. Salumbides, S. Witte, R. T. Zinkstok, E. J. van Duijn, K. S. E. Eikema and W. Ubachs. "Frequency metrology on the  $EF^{1}\Sigma_{g}^{+} X^{1}\Sigma_{g}^{+}$  (0,0) transition in H<sub>2</sub>, HD, and D<sub>2</sub>". *Phys. Rev. A*, vol. 74, p. 062514, 2006.
- [27] W. Cruickshank. "Some observations on different hydrocarbonates and combinations of carbone with oxygen, etc. in reply to some of Dr. Priestley's late objections to the new system of chemistry". Journal of Natural Philosophy, Chemistry and the Arts, vol. 5, p. 1, 1801.
- [28] W. Cruickshank. "Some additional observations on hydrocarbonates, and the gaseous oxide of carbon". Journal of Natural Philosophy, Chemistry and the Arts, vol. 5, p. 201, 1801.
- [29] R. W. Field, S. G. Tilford, R. A. Howard and J. D. Simmons. "Fine structure and perturbation analysis of the a<sup>3</sup>Π state of CO". J. Mol. Spectr., vol. 44, p. 347, 1972.
- [30] W. Heitler and F. London. "Wechselwirkung neutraler atome und homöopolare bindung nach der quantenmechanik". Z. Phys., vol. 44, p. 455, 1927.

- [31] E. Schrodinger. "An undulatory theory of the mechanics of atoms and molecules". *Phys. Rev.*, vol. 28, p. 1049, 1926.
- [32] W. Pauli. "On the connection of the arrangement of electron groups in atoms with the complex structure of spectra". Z. Phys., vol. 31, p. 765, 1925.
- [33] M. Born and R. Oppenheimer. "Quantum theory of molecules". Ann. Phys., vol. 389, p. 457, 1927.
- [34] H. M. James and A. S. Coolidge. "The ground state of the hydrogen molecule". J. Chem. Phys., vol. 1, p. 825, 1933.
- [35] E. A. Hylleraas. "Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium". Z. Phys., vol. 54, p. 347, 1929.
- [36] W. Kołos and L. Wolniewicz. "Improved theoretical ground-state energy of the hydrogen molecule". J. Chem. Phys., vol. 49, p. 404, 1968.
- [37] H. M. James and A. S. Coolidge. "On the ground state of lithium". Phys. Rev., vol. 49, p. 688, 1936.
- [38] W. Kołos and L. Wolniewicz. "Accurate adiabatic treatment of the ground state of the hydrogen molecule". J. Chem. Phys., vol. 41, p. 3663, 1964.
- [39] W. Kołos and L. Wolniewicz. "Potential energy curves for the  $X^1\Sigma_g^+$ ,  $b^3\Sigma_u^+$ , and  $C^1\Pi_u$  states of the hydrogen molecule". J. Chem. Phys., vol. 43, p. 2429, 1965.
- [40] W. Kołos and L. Wolniewicz. "Potential-energy curve for B<sup>1</sup>Σ<sup>+</sup><sub>u</sub> state of hydrogen molecule". J. Chem. Phys., vol. 45, p. 509, 1966.
- [41] W. Kołos and C. C. J. Roothaan. "Correlated orbitals for the ground state of the hydrogen molecule". *Rev. Mod. Phys.*, vol. 32, p. 205, 1960.
- [42] W. Kołos and L. Wolniewicz. "Nonadiabatic theory for diatomic molecules and its application to hydrogen molecule". *Rev. Mod. Phys.*, vol. 35, p. 473, 1963.
- [43] W. Kołos. "Adiabatic approximation and its accuracy". Adv. Quantum Chem., vol. 5, p. 99, 1970.
- [44] D. M. Bishop and L. M. Cheung. "Accurate one- and two-electron diatomic molecular calculations". Adv. Quantum Chem., vol. 12, p. 1, 1980.

- [45] J. Rychlewski. "Explicitly correlated functions in molecular quantum chemistry". Adv. Quantum Chem., vol. 31, p. 173, 1998.
- [46] K. Pachucki. "Born-oppenheimer potential for H<sub>2</sub>". *Phys. Rev. A*, vol. 82, p. 032509, 2010.
- [47] K. Pachucki and J. Komasa. "Nonadiabatic corrections to rovibrational levels of H<sub>2</sub>". J. Chem. Phys., vol. 130, p. 164113, 2009.
- [48] K. Pachucki and J. Komasa. "Nonadiabatic corrections to the wave function and energy". J. Chem. Phys., vol. 129, p. 034102, 2008.
- [49] K. Pachucki. "Higher-order effective Hamiltonian for light atomic systems". Phys. Rev. A, vol. 71, p. 012503, 2005.
- [50] K. Pachucki. "Electrodynamics of a compound system with relativistic corrections". *Phys. Rev. A*, vol. 76, p. 022106, 2007.
- [51] K. Pachucki and J. Komasa. "Rovibrational levels of HD". Phys. Chem. Chem. Phys., vol. 12, p. 9188, 2010.
- [52] E. E. Witmer. "Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum". *Phys. Rev.*, vol. 28, p. 1223, 1926.
- [53] I. Siehe and H. Beutler. "Die Dissoziationswärme des Wasserstoffmoleküls H<sub>2</sub>, aus der Rotationabhängigkeit des Beginns des ultravioletten Kontinuums bestimmt (im folgenden als Teil I zitiert)". Z. Phys. Chem. (B), vol. 29, p. 315, 1935.
- [54] G. Herzberg. "The dissociation energy of the hydrogen molecule". J. Mol. Spectrosc., vol. 33, p. 147, 1970.
- [55] G. Herzberg and C. Jungen. "Rydberg series and ionization potential of the H<sub>2</sub> molecule". J. Mol. Spectrosc., vol. 41, p. 425, 1972.
- [56] G. Herzberg. "Dissociation energy and ionization potential of molecular hydrogen". *Phys. Rev. Lett.*, vol. 23, p. 1081, 1969.
- [57] Y. P. Zhang, C. H. Cheng, J. T. Kim, J. Stanojevic and E. E. Eyler. "Dissociation energies of molecular hydrogen and the hydrogen molecular ion". *Phys. Rev. Lett.*, vol. 92, p. 203003, 2004.
- [58] E. E. Eyler and N. Melikechi. "Near-threshold continuum structure and the dissociation energies of H<sub>2</sub>, HD, and D<sub>2</sub>". *Phys. Rev. A*, vol. 48, p. R18, 1993.

- [59] G. Herzberg. "On the possibility of detecting molecular hydrogen and nitrogen in planetary and stellar atmospheres by their rotation-vibration spectra". Astrophys. J., vol. 87, p. 428, 1938.
- [60] G. Herzberg. "Quadrupole rotation-vibration spectrum of the hydrogen molecule". *Nature*, vol. 163, p. 170, 1949.
- [61] U. Fink, T. Wiggins and D. Rank. "Frequency and intensity measurements on the quadrupole spectrum of molecular hydrogen". J. Mol. Spectrosc., vol. 18, p. 384, 1965.
- [62] J. Foltz, D. Rank and T. Wiggins. "Determinations of some hydrogen molecular constants". J. Mol. Spectrosc., vol. 21, p. 203, 1966.
- [63] S. L. Bragg, W. H. Smith and J. W. Brault. "Line positions and strengths in the H<sub>2</sub> quadrupole spectrum". Astrophys. J., vol. 263, p. 999, 1982.
- [64] D. Ferguson, K. Rao, M. Mickelson and L. Larson. "An experimental study of the 4-0 and 5-0 quadrupole vibration rotation bands of H<sub>2</sub> in the visible". J. Mol. Spectrosc., vol. 160, p. 315, 1993.
- [65] D. C. Robie and J. T. Hodges. "Line positions and line strengths for the  $3 \leftarrow 0$  electric quadrupole band of H<sub>2</sub>  ${}^{1}\Sigma_{g}^{+}$ ". J. Chem. Phys., vol. 124, p. 024307, 2006.
- [66] C.-F. Cheng, Y. R. Sun, H. Pan, J. Wang, A.-W. Liu, A. Campargue and S.-M. Hu. "Electric-quadrupole transition of H<sub>2</sub> determined to 10<sup>-9</sup> precision". *Phys. Rev. A*, vol. 85, p. 024501, 2012.
- [67] S.-M. Hu, H. Pan, C.-F. Cheng, Y. R. Sun, X.-F. Li, J. Wang, A. Campargue and A.-W. Liu. "The  $v = 3 \leftarrow 0$  S(0)-S(3) electric quadrupole transitions of H<sub>2</sub> near 0.8  $\mu$ m". Astrophys. J., vol. 749, p. 76, 2012.
- [68] S. Kassi, A. Campargue, K. Pachucki and J. Komasa. "The absorption spectrum of D<sub>2</sub>: Ultrasensitive cavity ring down spectroscopy of the (2-0) band near 1.7  $\mu$ m and accurate ab initio line list up to 24 000 cm<sup>-1</sup>". J. Chem. Phys., vol. 136, p. 184309, 2012.
- [69] A. Campargue, S. Kassi, K. Pachucki and J. Komasa. "The absorption spectrum of H<sub>2</sub>: CRDS measurements of the (2 0) band, review of the literature data and accurate ab initio line list up to 35 000 cm<sup>-1</sup>". *Phys. Chem. Chem. Phys.*, vol. 14, p. 802, 2012.
- [70] P. Maddaloni, P. Malara, E. De Tommasi, M. De Rosa, I. Ricciardi, G. Gagliardi, F. Tamassia, G. Di Lonardo and P. De Natale. "Absolute

measurement of the S(0) and S(1) lines in the electric quadrupole fundamental band of D<sub>2</sub> around 3  $\mu$ m". J. Chem. Phys., vol. 133, p. 154317, 2010.

- [71] M. Stanke, D. Kedziera, S. Bubin, M. Molski and L. Adamowicz. "Orbit-orbit relativistic corrections to the pure vibrational non-Born-Oppenheimer energies of H<sub>2</sub>". J. Chem. Phys., vol. 128, p. 114313, 2008.
- [72] I. Dabrowski. "The Lyman and Werner bands of H<sub>2</sub>". Can. J. Phys., vol. 62, p. 1639, 1984.
- [73] J. Philip, J. Sprengers, T. Pielage, C. de Lange, W. Ubachs and E. Reinhold. "Highly accurate transition frequencies in the H<sub>2</sub> Lyman and Werner absorption bands". *Can. J. Chem.*, vol. 82, p. 713, 2004.
- [74] W. Ubachs and E. Reinhold. "Highly accurate H<sub>2</sub> Lyman and Werner band laboratory measurements and an improved constraint on a cosmological variation of the proton-to-electron mass ratio". *Phys. Rev. Lett.*, vol. 92, p. 101302, 2004.
- [75] D. W. Chandler and L. R. Thorne. "Measured radiative lifetimes for  $H_2$  and HD in the E,F  ${}^{1}\Sigma_{g}^{+}$  electronic state". J. Chem. Phys., vol. 85, p. 1733, 1986.
- [76] E. R. Davidson. "First excited  ${}^{1}\Sigma_{g}^{+}$  state of H<sub>2</sub>. A double-minimum problem". J. Chem. Phys., vol. 33, p. 1577, 1960.
- [77] E. E. Eyler, J. Gilligan, E. F. McCormack, A. Nussenzweig and E. Pollack. "Precise two-photon spectroscopy of E←X intervals in H<sub>2</sub>". *Phys. Rev. A*, vol. 36, p. 3486, 1987.
- [78] J. M. Gilligan and E. E. Eyler. "Precise determinations of ionization potentials and EF-state energy levels of H<sub>2</sub>, HD, and D<sub>2</sub>". *Phys. Rev. A*, vol. 46, p. 3676, 1992.
- [79] D. Shiner, J. M. Gilligan, B. M. Cook and W. Lichten. "H<sub>2</sub>, D<sub>2</sub>, and HD ionization potentials by accurate calibration of several iodine lines". *Phys. Rev. A*, vol. 47, p. 4042, 1993.
- [80] A. Yiannopoulou, N. Melikechi, S. Gangopadhyay, J. C. Meiners, C. H. Cheng and E. E. Eyler. "Determinations of  $\text{EF}^1\Sigma g^+ X^1\Sigma_g^+$  transition frequencies in H<sub>2</sub>, D<sub>2</sub>, and HD". *Phys. Rev. A*, vol. 73, p. 022506, 2006.
- [81] E. J. Salumbides, D. Bailly, A. Khramov, A. L. Wolf, K. S. E. Eikema, M. Vervloet and W. Ubachs. "Improved laboratory values of the H<sub>2</sub> Lyman and Werner lines for constraining time variation of the protonto-electron mass ratio". *Phys. Rev. Lett.*, vol. 101, p. 223001, 2008.

- [82] S. Hannemann, E.-J. van Duijn and W. Ubachs. "A narrow-band injection-seeded pulsed titanium:sapphire oscillator-amplifier system with on-line chirp analysis for high-resolution spectroscopy". *Rev. Sci. Instrum.*, vol. 78, p. 103102, 2007.
- [83] S. Hannemann, E. J. Salumbides and W. Ubachs. "Reducing the firstorder Doppler shift in a Sagnac interferometer". Opt. Lett., vol. 32, p. 1381, 2007.
- [84] D. Zhao, N. Wehres, H. Linnartz and W. Ubachs. "Electronic spectra and molecular geometry of the non-linear carbon chain C<sub>9</sub>H<sub>3</sub>". *Chem. Phys. Lett.*, vol. 501, p. 232, 2011.
- [85] M. S. Fee, K. Danzmann and S. Chu. "Optical heterodyne measurement of pulsed lasers: Toward high-precision pulsed spectroscopy". *Phys. Rev.* A, vol. 45, p. 4911, 1992.
- [86] K. S. E. Eikema, W. Ubachs, W. Vassen and W. Hogervorst. "Lamb shift measurement in the 1<sup>1</sup>S ground state of helium". *Phys. Rev. A*, vol. 55, p. 1866, 1997.
- [87] W. Caswell and G. Lepage. "Effective lagrangians for bound state problems in QED, QCD, and other field theories". *Phys. Lett. B*, vol. 167, p. 437, 1986.
- [88] K. Pachucki. " $\alpha^4 \mathcal{R}$  corrections to singlet states of helium". *Phys. Rev.* A, vol. 74, p. 022512, 2006.
- [89] M. Stanke, S. Bubin, M. Molski and L. Adamowicz. "Non-Born-Oppenheimer calculations of the lowest vibrational energy of HD including relativistic corrections". *Phys. Rev. A*, vol. 79, p. 032507, 2009.
- [90] S. Bubin, M. Stanke, M. Molski and L. Adamowicz. "Accurate non-Born-Oppenheimer calculations of the lowest vibrational energies of and with including relativistic corrections". *Chem. Phys. Lett.*, vol. 494, p. 21, 2010.
- [91] L. Rahn and G. Rosasco. "Measurement of the density shift of the H<sub>2</sub> Q(0-5) transitions from 295 to 1000 K". *Phys. Rev. A*, vol. 41, p. 3698, 1990.
- [92] H. Buijs and G. Bush. "Static field induced spectrum of hydrogen". Can. J. Phys., vol. 49, p. 2366, 1971.

146

- [93] D. Rank, B. Rao, P. Sitaram, A. Slomba and T. Wiggins. "Quadrupole and induced dipole spectrum of molecular hydrogen". J. Opt. Soc. Am., vol. 52, p. 1004, 1962.
- [94] F. Rasetti. "Incoherent scattered radiation in diatomic molecules". Phys. Rev., vol. 34, p. 367, 1929.
- B. P. Stoicheff. "High resolution Raman spectroscopy of gases IX. H<sub>2</sub>, HD and D<sub>2</sub>". Can. J. Phys., vol. 35, p. 730, 1957.
- [96] M. F. Crawford and I. R. Dagg. "Infrared absorption induced by static electric fields". *Phys. Rev.*, vol. 91, p. 1569, 1953.
- [97] A. D. May, V. Degen, J. C. Stryland and H. L. Welsh. "The Raman effect in gaseous hydrogen at high pressures". *Can. J. Phys.*, vol. 39, p. 1769, 1961.
- [98] A. D. May, G. Varghese, J. C. Stryland and H. L. Welsh. "Vibrational frequency perturbations in the Raman spectrum of compressed gaseous hydrogen". *Can. J. Phys.*, vol. 42, p. 1058, 1964.
- [99] E. Looi, J. Stryland and H. Welsh. "Pressure shifts in the vibrational Raman spectra of hydrogen and deuterium, 315-85 K". Can. J. Phys., vol. 56, p. 1102, 1978.
- [100] D. Veirs and G. Rosenblatt. "Raman line positions in molecular hydrogen: H<sub>2</sub>, HD, HT, D<sub>2</sub>, DT, and T<sub>2</sub>". J. Mol. Spectrosc., vol. 121, p. 401, 1987.
- [101] G. J. Germann and J. J. Valentini. "Accurate measurement of vibrational transition energies for a wide range of v, j states using CARS spectroscopy of chemical reaction products: spectroscopy of hydrogen from the hydrogen-atom + hydrogen iodide reaction". J. Phys. Chem., vol. 92, p. 3792, 1988.
- [102] N. Rich, J. Johns and A. McKellar. "Frequency and intensity measurements in the fundamental infrared band of HD". J. Mol. Spectrosc., vol. 95, p. 432, 1982.
- [103] P. Brannon, C. Church and C. Peters. "Electric field induced spectra of molecular hydrogen, deuterium and deuterium hydride". J. Mol. Spectrosc., vol. 27, p. 44, 1968.
- [104] R. A. Durie and G. Herzberg. "Forbidden transitions in diatomic molecules: V. the rotation-vibration spectrum of the hydrogen-deuteride (HD) molecule". Can. J. Phys., vol. 38, p. 806, 1960.

- [105] A. R. W. McKellar. "Intensities and the fano line shape in the infrared spectrum of HD". Can. J. Phys., vol. 51, p. 389, 1973.
- [106] A. R. W. McKellar, W. Goetz and D. A. Ramsay. "The rotation-vibration spectrum of HD - Wavelength and intensity measurements of the 3-0, 4-0, 5-0, and 6-0 electric dipole bands". Astrophys. J., vol. 207, p. 663, 1976.
- [107] S. Nazemi, A. Javan and A. S. Pine. "Collisional effects on the rovibrational transitions of the HD fundamental band". J. Chem. Phys., vol. 78, p. 4797, 1983.
- [108] A. R. W. McKellar and T. Oka. "A study of the electric quadrupole fundamental band of D<sub>2</sub> using an infrared difference frequency laser system". *Can. J. Phys.*, vol. 56, p. 1315, 1978.
- [109] D. E. Jennings, A. Weber and J. W. Brault. "Raman spectroscopy of gases with a Fourier transform spectrometer: the spectrum of D<sub>2</sub>". Appl. Optics., vol. 25, p. 284, 1986.
- [110] G. Bertone, D. Hooper and J. Silk. "Particle dark matter: evidence, candidates and constraints". *Phys. Rep.*, vol. 405, p. 279, 2005.
- [111] P. J. E. Peebles and B. Ratra. "The cosmological constant and dark energy". *Rev. Mod. Phys.*, vol. 75, p. 559, 2003.
- [112] S. G. Karshenboim. "Constraints on a long-range spin-independent interaction from precision atomic physics". *Phys. Rev. D*, vol. 82, p. 073003, 2010.
- [113] W. Ubachs, W. Vassen, E. J. Salumbides and K. S. E. Eikema. "Precision metrology on the hydrogen atom in search for new physics". Ann. Phys. (Berlin), vol. 525, p. A113, 2013.
- [114] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema and W. Ubachs. "Bounds on fifth forces from precision measurements on molecules". *Phys. Rev. D*, vol. 87, p. 112008, 2013.
- [115] J. C. J. Koelemeij, B. Roth, A. Wicht, I. Ernsting and S. Schiller. "Vibrational spectroscopy of HD<sup>+</sup> with 2-ppb accuracy". *Phys. Rev. Lett.*, vol. 98, p. 173002, 2007.
- [116] U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting and S. Schiller. "Manipulation of individual hyperfine states in cold trapped molecular ions and application to HD<sup>+</sup> frequency metrology". *Phys. Rev. Lett.*, vol. 108, p. 183003, 2012.

- [117] J. Koelemeij, D. Noom, D. de Jong, M. Haddad and W. Ubachs. "Observation of the v' = 8 ← v = 0 vibrational overtone in cold trapped HD<sup>+</sup>". Appl. Phys. B, vol. 107, p. 1075, 2012.
- [118] E. Salumbides, W. Ubachs and V. Korobov. "Bounds on fifth forces at the sub-Å length scale". J. Mol. Spectrosc., vol. 300, p. 65, 2014.
- [119] G. Herzberg and L. L. Howe. "The Lyman bands of molecular hydrogen". Can. J. Phys., vol. 37, p. 636, 1959.
- [120] D. Sprecher, C. Jungen, W. Ubachs and F. Merkt. "Towards measuring the ionisation and dissociation energies of molecular hydrogen with sub-MHz accuracy". *Faraday Discuss.*, vol. 150, p. 51, 2011.
- [121] V. I. Korobov, L. Hilico and J.-P. Karr. "Theoretical transition frequencies beyond 0.1 ppb accuracy in H<sub>2</sub><sup>+</sup>, HD<sup>+</sup>, and antiprotonic helium". *Phys. Rev. A*, vol. 89, p. 032511, 2014.
- [122] K. Pachucki and J. Komasa. "Accurate adiabatic correction in the hydrogen molecule". J. Chem. Phys., vol. 141, p. 224103, 2014.
- [123] M. Niu, E. Salumbides, G. Dickenson, K. Eikema and W. Ubachs. "Precision spectroscopy of the  $X^1\Sigma_g^+ \ v = 0 \rightarrow 1(J = 0 - 2)$  rovibrational splittings in H<sub>2</sub>, HD and D<sub>2</sub>". J. Mol. Spectrosc., vol. 300, p. 44, 2014.
- [124] Y. Tan, J. Wang, C.-F. Cheng, X.-Q. Zhao, A.-W. Liu and S.-M. Hu. "Cavity ring-down spectroscopy of the electric quadrupole transitions of H<sub>2</sub> in the 784–852 nm region". J. Mol. Spectrosc., vol. 300, p. 60, 2014.
- [125] J. Steadman and T. Baer. "The production and characterization by resonance enhanced multiphoton ionization of  $H_2$  (v=10-14) from photodissociation of  $H_2S$ ". J. Chem. Phys., vol. 91, p. 6113, 1989.
- [126] M. L. Niu, F. Ramirez, E. J. Salumbides and W. Ubachs. "High-precision laser spectroscopy of the CO  $A^1\Pi$   $X^1\Sigma^+$  (2,0), (3,0), and (4,0) bands". *J. Chem. Phys.*, vol. 142, p. 044302, 2015.
- [127] S. Xu, R. van Dierendonck, W. Hogervorst and W. Ubachs. "A dense grid of reference iodine lines for optical frequency calibration in the range 595-655 nm". J. Mol. Spectr., vol. 201, p. 256, 2000.
- [128] K. Pachucki and J. Komasa. "Leading order nonadiabatic corrections to rovibrational levels of H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub>". J. Chem. Phys., vol. 143, p. 034111, 2015.

- [129] A. L. Malec, R. Buning, M. T. Murphy, N. Milutinovic, S. L. Ellison, J. X. Prochaska, L. Kaper, J. Tumlinson, R. F. Carswell and W. Ubachs. "Keck telescope constraint on cosmological variation of the proton-toelectron mass ratio". Mon. Not. R. Astron. Soc., vol. 403, p. 1541, 2010.
- [130] F. van Weerdenburg, M. T. Murphy, A. L. Malec, L. Kaper and W. Ubachs. "First constraint on cosmological variation of the proton-toelectron mass ratio from two independent telescopes". *Phys. Rev. Lett.*, vol. 106, p. 180802, 2011.
- [131] T. I. Ivanov, M. Roudjane, M. O. Vieitez, C. A. de Lange, W.-U. L. Tchang-Brillet and W. Ubachs. "HD as a probe for detecting mass variation on a cosmological time scale". *Phys. Rev. Lett.*, vol. 100, 093007, 2008.
- [132] D. A. Varshalovich and S. A. Levshakov. "On a time dependence of physical constants". *JETP Lett.*, vol. 58, p. 237, 1993.
- [133] V. Meshkov, A. Stolyarov, A. Ivanchik and D. Varshalovich. "Ab initio nonadiabatic calculation of the sensitivity coefficients for the  $X^1\Sigma^+ \rightarrow B^1\Sigma^+_u$ ;  $C^1\Pi_u$  lines of  $H_2$  to the proton-to-electron mass ratio". *JETP Lett.*, vol. 83, p. 303, 2006.
- [134] W. Ubachs, R. Buning, K. S. E. Eikema and E. Reinhold. "On a possible variation of the proton-to-electron mass ratio: H<sub>2</sub> spectra in the line of sight of high-redshift quasars and in the laboratory". J. Mol. Spectr., vol. 241, p. 155, 2007.
- [135] T. Ivanov, G. Dickenson, M. Roudjane, N. de Oliveira, D. Joyeux, L. Nahon, W. Ü. L. Tchang-Brillet and W. Ubachs. "Fourier transform spectroscopy of HD in the extreme ultraviolet below 115 000 cm<sup>-1</sup>". Mol. Phys., vol. 108, p. 771, 2010.
- [136] M. T. Murphy, V. V. Flambaum, S. Muller and C. Henkel. "Strong limit on a variable proton-to-electron mass ratio from molecules in the distant universe". *Science*, vol. 320, p. 1611, 2008.
- [137] N. Kanekar. "Constraining changes in the proton-electron mass ratio with inversion and rotational lines". Astrophys. J. Lett., vol. 728, p. L12, 2011.
- [138] C. Henkel, K. M. Menten, M. T. Murphy, N. Jethava, V. V. Flambaum, J. A. Braatz, S. Muller, J. Ott and R. Q. Mao. "The density, the cosmic microwave background, and the proton-to-electron mass ratio in a cloud at redshift 0.9". Astron. Astrophys., vol. 500, p. 725, 2009.

- [139] P. Jansen, L.-H. Xu, I. Kleiner, W. Ubachs and H. L. Bethlem. "Methanol as a sensitive probe for spatial and temporal variations of the proton-toelectron mass ratio". *Phys. Rev. Lett.*, vol. 106, 100801, 2011.
- [140] S. A. Levshakov, M. G. Kozlov and D. Reimers. "Methanol as a tracer of fundamental constants". Astrophys. J., vol. 738, p. 26, 2011.
- [141] P. Jansen, I. Kleiner, L.-H. Xu, W. Ubachs and H. L. Bethlem. "Sensitivity of transitions in internal rotor molecules to a possible variation of the proton-to-electron mass ratio". *Phys. Rev. A*, vol. 84, p. 062505, 2011.
- [142] S. Muller, A. Beelen, M. Guélin, S. Aalto, J. H. Black, F. Combes, S. J. Curran, P. Theule and S. N. Longmore. "Molecules at z = 0.89". Astron. Astrophys., vol. 535, p. A103, 2011.
- [143] S. P. Ellingsen, M. A. Voronkov, S. L. Breen and J. E. J. Lovell. "First cosmological constraints on the proton-to-electron mass ratio from observations of rotational transitions of methanol". *Astrophys. J. Lett.*, vol. 747, p. L7, 2012.
- [144] J. Bagdonaite, P. Jansen, C. Henkel, H. L. Bethlem, K. M. Menten and W. Ubachs. "A stringent limit on a drifting proton-to-electron mass ratio from alcohol in the early universe". *Science*, vol. 339, p. 46, 2013.
- [145] R. Srianand, P. Noterdaeme, C. Ledoux and P. Petitjean. "First detection of CO in a high-redshift damped Lyman-α system". Astron. Astrophys., vol. 482, p. L39, 2008.
- [146] P. Noterdaeme, C. Ledoux, R. Srianand, P. Petitjean and S. López. "Diffuse molecular gas at high redshift". Astron. Astrophys., vol. 503, p. 765, 2009.
- [147] P. Noterdaeme, P. Petitjean, C. Ledoux, S. López, R. Srianand and S. D. Vergani. "A translucent interstellar cloud at z=2.69". Astron. Astrophys., vol. 523, p. A80, 2010.
- [148] P. Noterdaeme, P. Petitjean, R. Srianand, C. Ledoux and S. López. "The evolution of the cosmic microwave background temperature". Astron. Astrophys., vol. 526, p. L7, 2011.
- [149] J. X. Prochaska, Y. Sheffer, D. A. Perley, J. S. Bloom, L. A. Lopez, M. Dessauges-Zavadsky, H.-W. Chen, A. V. Filippenko, M. Ganeshalingam, W. Li, A. A. Miller and D. Starr. "The first positive detection of molecular gas in a GRB host galaxy". *Astrophys. J. Lett.*, vol. 691, p. L27, 2009.

- [150] R. W. Field, B. G. Wicke, J. D. Simmons and S. G. Tilford. "Analysis of perturbations in the CO". J. Mol. Spectr., vol. 44, p. 383, 1972.
- [151] A. C. Le Floch, F. Launay, J. Rostas, R. W. Field, C. M. Brown and K. Yoshino. "Reinvestigation of the CO A<sup>1</sup>Π state and its perturbations: The v = 0 level". J. Mol. Spectr., vol. 121, p. 337, 1987.
- [152] A. C. Le Floch. Ph.D. thesis, Univ. Paris-Sud, 1989.
- [153] A. C. Le Floch. "Accurate energy levels for the  $C^1\Sigma^+(v=0)$  and  $E^1\Pi(v=0)$  states of  ${}^{12}C^{16}O$ ". J. Mol. Spectr., vol. 155, p. 177, 1992.
- [154] C. Kittrell, A. C. Le Floch and B. A. Garetz. "Analysis of the two-photon D<sup>1</sup>Δ - X<sup>1</sup>Σ<sup>+</sup> transition in carbon monoxide. 2. perturbations in the (8-0) band". J. Phys. Chem., vol. 97, p. 2221, 1993.
- [155] D. C. Morton and L. Noreau. "A compilation of electronic-transitions in the CO molecule and the interpretation of some puzzling interstellar absorption features". Astrophys. J. Suppl. S., vol. 95, p. 301, 1994.
- [156] M. Drabbels, J. J. ter Meulen and W. L. Meerts. "High resolution pulsedcw double-resonance spectroscopy on the  $B^1\Sigma^+(v'=0) \leftarrow A^1\Pi(v''=0)$ system of CO". *Chem. Phys. Lett.*, vol. 267, p. 127, 1997.
- [157] L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde and F. Polack. "DESIRS: a state-of-the-art VUV beamline featuring high resolution and variable polarization for spectroscopy and dichroism at SOLEIL". J. Synchrotron Radiat., vol. 19, p. 508, 2012.
- [158] N. de Oliveira, M. Roudjane, D. Joyeux, D. Phalippou, J.-C. Rodier and L. Nahon. "High-resolution broad-bandwidth Fourier-transform absorption spectroscopy in the VUV range down to 40 nm". *Nat. Photonics*, vol. 5, p. 149, 2011.
- [159] E. B. Saloman. "Energy levels and observed spectral lines of xenon, Xe I through Xe LIV". J. Phys. Chem. Ref. Data, vol. 33, p. 765, 2004.
- [160] C. J. Humphreys and E. Paul. "Interferometric wavelength determinations in the first spectrum of <sup>136</sup>Xe". J. Opt. Soc. Am., vol. 60, p. 1302, 1970.
- [161] F. Brandi, I. Velchev, W. Hogervorst and W. Ubachs. "Vacuumultraviolet spectroscopy of Xe". Phys. Rev. A, vol. 64, p. 032505, 2001.

- [162] T. D. Varberg and K. M. Evenson. "Accurate far-infrared rotational frequencies of carbon-monoxide". Astrophys. J., vol. 385, p. 763, 1992.
- [163] W. Ubachs, K. S. E. Eikema, W. Hogervorst and P. C. Cacciani. "Narrowband tunable extreme-ultraviolet laser source for lifetime measurements and precision spectroscopy". J. Opt. Soc. Am. B, vol. 14, p. 2469, 1997.
- [164] We used this program, kindly provided to us by Dr. H. Knöckel (Leibniz University, Hannover). See also B. Bodermann, H. Knöckel and E. Tiemann, Eur. Phys. J. D, vol. 19, p. 31, 2002. IodineSpec.
- [165] G. Guelachvili, D. de Villeneuve, R. Farrenq, W. Urban and J. Verges. "Dunham coefficients for seven isotopic species of CO". J. Mol. Spectrosc., vol. 98, p. 64, 1983.
- [166] J. D. Simmons, A. M. Bass and S. G. Tilford. "Fourth positive system of carbon monoxide observed in absorption at high resolution in vacuum ultraviolet region". Astrophys. J., vol. 155, p. 345, 1969.
- [167] E. Reinhold, R. Buning, U. Hollenstein, A. Ivanchik, P. Petitjean and W. Ubachs. "Indication of a cosmological variation of the proton-electron mass ratio based on laboratory measurement and reanalysis of H<sub>2</sub> spectra". *Phys. Rev. Lett.*, vol. 96, p. 151101, 2006.
- [168] G. Herzberg, T. J. Hugo, S. G. Tilford and J. D. Simmons. "Rotational analysis of the forbidden  $d^3\Delta_i \leftarrow X^1\Sigma^+$  absorption bands of carbon monoxide". *Can. J. Phys.*, vol. 48, p. 3004, 1970.
- [169] J. Simmons and S. Tilford. "New absorption bands and isotopic studies of known transitions in CO". J. Res. NBS A. Phys. Ch., vol. 75A, p. 455, 1971.
- [170] See Supplementary Material at http://link.aps.org/supplemental/10.1103 /PhysRevA.86.022510 for further details.
- [171] H. Deslandres. "Spectre de bandes ultra-violet des composés hydrogénés et oxygénés du carbone". Cr. Hebd. Acad. Sci., vol. 106, p. 842, 1888.
- [172] R. T. Birge. "The band spectra of carbon monoxide". *Phys. Rev.*, vol. 28, p. 1157, 1926.
- [173] R. Kepa and M. Rytel. "A compilation of electronic-transitions in the CO molecule". Acta Phys. Pol. A, vol. 37, p. 585, 1970.
- [174] A. C. Le Floch and C. Amiot. "Fourier transform spectroscopy of the CO Ångström bands". Chem. Phys., vol. 97, p. 379, 1985.

- [175] G. Herzberg. "Über die Bandenspektren von CO". Z. Phys., vol. 52, p. 815, 1929.
- [177] G. Herzberg and T. J. Hugo. "Forbidden transitions in diatomic molecules: IV. the  $a'^{3}\Sigma^{+} \leftarrow X^{1}\Sigma^{+}$  and  $e^{3}\Sigma^{-} \leftarrow X^{1}\Sigma^{+}$  absorption bands of carbon monoxide". *Can. J. Phys.*, vol. 33, p. 757, 1955.
- [178] J. D. Simmons and S. G. Tilford. "Fourth positive system of carbon monoxide observed in absorption at high resolution in vacuum ultraviolet region". J. Chem. Phys., vol. 45, p. 2965, 1966.
- [179] G. Herzberg, J. D. Simmons, A. M. Bass and S. G. Tilford. "The forbidden I<sup>1</sup>Σ<sup>-</sup>-X<sup>1</sup>Σ<sup>+</sup> absorption bands of carbon monoxide". *Can. J. Phys.*, vol. 44, p. 3039, 1966.
- [180] A. C. Le Floch, J. Rostas and J. Schamps. "The  $A^{1}\Pi$ -D<sup>1</sup> $\Delta$  rotationelectronic interaction in CO". *Mol. Phys.*, vol. 63, p. 677, 1988.
- [181] N. de Oliveira, D. Joyeux, D. Phalippou, J. C. Rodier, F. Polack, M. Vervloet and L. Nahon. "A Fourier transform spectrometer without a beam splitter for the vacuum ultraviolet range: From the optical design to the first UV spectrum". *Rev. Scient. Instr.*, vol. 80, p. 043101, 2009.
- [182] K. D. Bonin and T. J. Mcllrath. "Two-photon electric-dipole selection rules". J. Opt. Soc. Am. B, vol. 1, p. 52, 1984.
- [183] A. C. Le Floch. "Private communication". Discussion of CO A-X (1,0) band., 2000.
- [184] M. Drabbels, W. L. Meerts and J. J. ter Meulen. "Determination of electric dipole moments and transition probabilities of low-lying singlet states of CO". J. Chem. Phys., vol. 99, p. 2352, 1993.
- [185] B. A. Garetz, C. Kittrell and A. L. Floch. "Analysis of the two-photon  $D^1\Delta$   $X^1\Sigma^+$  transition in CO: Perturbations in the (10-0) band". J. Chem. Phys., vol. 94, p. 843, 1991.
- [186] C. M. Western. "Pgopher, a program for simulating rotational structure, University of Bristol". http://pgopher.chm.bris.ac.uk.
- [187] R. W. Field. Ph.D. thesis, Harvard University, 1971.
- 154

- [188] M. L. Niu, E. J. Salumbides, D. Zhao, N. de Oliveira, D. Joyeux, L. Nahon, R. W. Field and W. Ubachs. "High resolution spectroscopy and perturbation analysis of the CO  $A^{1}\Pi X^{1}\Sigma^{+}$  (0,0) and (1,0) bands". *Mol. Phys.*, vol. 111, p. 2163, 2013.
- [189] I. Velchev, R. van Dierendonck, W. Hogervorst and W. Ubachs. "A dense grid of reference iodine lines for optical frequency calibration in the range 571-596 nm". J. Mol. Spectrosc., vol. 187, p. 21, 1998.
- [190] N. Melikechi, S. Gangopadhyay and E. E. Eyler. "Phase dynamics in nanosecond pulsed dye laser amplification". J. Opt. Soc. Am. B, vol. 11, p. 2402, 1994.
- [191] M. Niu, A. Heays, S. Jones, E. J. Salumbides, E. van Dishoeck, N. D. Oliveira, L. Nahon and W. Ubachs. "VUV-synchrotron absorption studies of N<sub>2</sub> and CO at 900 K". J. Mol. Spectrosc., vol. 315, p. 137, 2015.
- [192] L. W. Beegle, J. M. Ajello, G. K. James, D. Dziczek and M. Alvarez. "High resolution emission spectroscopy of the A<sup>1</sup>Π - X<sup>1</sup>Σ<sup>+</sup> fourth positive band system of CO excited by electron impact". Astron. Astrophys., vol. 347, p. 375, 1999.
- [193] G. D. Dickenson, N. Nortje, C. Steenkamp, E. Rohwer and A. Du Plessis. "Accurate laboratory wavelengths of the  $e^{3}\Sigma^{-}(\nu'=5) - X^{1}\Sigma^{+}(\nu''=0)$ band of <sup>12</sup>C<sup>16</sup>O". Astrophys. J. Lett., vol. 714, pp. L268, 2010.
- [194] A. N. Heays, G. D. Dickenson, E. J. Salumbides, N. de Oliveira, D. Joyeux, L. Nahon, B. R. Lewis and W. Ubachs. "High-resolution Fourier-transform extreme ultraviolet photoabsorption spectroscopy of <sup>14</sup>N<sup>15</sup>N". J. Chem. Phys., vol. 135, p. 244301, 2011.
- [195] L. Archer, G. Stark, P. Smith, J. Lyons, N. de Oliveira, L. Nahon, D. Joyeux and D. Blackie. "Room temperature photoabsorption cross section measurements of CO<sub>2</sub> between 91,000 and 115,000 cm<sup>-1</sup>". J. Quant. Spectrosc. Rad. Transfer, vol. 117, p. 88, 2013.
- [196] G. Stark, A. N. Heays, J. R. Lyons, P. L. Smith, M. Eidelsberg, S. R. Federman, J. L. Lemaire, L. Gavilan, N. de Oliveira, D. Joyeux and L. Nahon. "High-resolution oscillator strength measurements of the v' = 0,1 bands of the B-X, C-X, and E-X systems in five isotopologues of carbon monoxide". Astrophys. J., vol. 788, p. 67, 2014.
- [197] M. Eidelsberg, J. L. Lemaire, S. R. Federman, G. Stark, A. N. Heays, Y. Sheffer, L. Gavilan, J.-H. Fillion, F. Rostas, J. R. Lyons, P. L. Smith, N. de Oliveira, D. Joyeux, M. Roudjane and L. Nahon. "High-resolution

study of oscillator strengths and predissociation rates for  ${}^{12}C^{16}O$ ". Astron. Astrophys., vol. 543, p. A69, 2012.

- [198] L. Gavilan, J. L. Lemaire, M. Eidelsberg, S. R. Federman, G. Stark, A. N. Heays, J.-H. Fillion, J. R. Lyons and N. de Oliveira. "High-resolution study of <sup>13</sup>C<sup>16</sup>O A-X(v' = 0 9) bands using the VUV-FTS at SOLEII: Revised term values". J. Phys. Chem. A, vol. 117, p. 9644, 2013.
- [199] S. R. Federman, M. Fritts, S. Cheng, K. M. Menningen, D. C. Knauth and K. Fulk. "Oscillator strengths for B-X, C-X, and E-X transitions in carbon monoxide". Astrophys. J. Suppl. S., vol. 134, p. 133, 2001.
- [200] A. de Lange, G. D. Dickenson, E. J. Salumbides, W. Ubachs, N. de Oliveira, D. Joyeux and L. Nahon. "VUV Fourier-transform absorption study of the Lyman and Werner bands in D<sub>2</sub>". J. Chem. Phys., vol. 136, p. 234310, 2012.
- [201] A. N. Heays, R. Visser, R. Gredel, W. Ubachs, B. R. Lewis, S. T. Gibson and E. F. van Dishoeck. "Isotope selective photodissociation of N<sub>2</sub> by the interstellar radiation field and cosmic rays". *Astron. Astrophys.*, vol. 562, p. A61, 2014.
- [202] W. Ubachs, L. Tashiro and R. N. Zare. "Study of the N<sub>2</sub> b<sup>1</sup> $\Pi_u$  state via 1 + 1 multiphoton ionization". *Chem. Phys.*, vol. 130, p. 1, 1989.
- [203] P. F. Levelt and W. Ubachs. "XUV-laser spectroscopy on the  $c'_4 \, {}^1\Sigma_u^+$ , v = 0 and  $c_3 \, {}^1\Pi_u$ , v = 0 Rydberg states of N<sub>2</sub>". Chem. Phys., vol. 163, p. 263, 1992.
- [204] J. P. Sprengers, W. Ubachs, A. Johansson, A. L'Huillier, C.-G. Wahlström, R. Lang, B. R. Lewis and S. T. Gibson. "Lifetime and predissociation yield of <sup>14</sup>N<sub>2</sub>  $b^{1}\Pi_{u}(v = 1)$ ". J. Chem. Phys., vol. 120, p. 8973, 2004.
- [205] J. P. Sprengers, W. Ubachs and K. G. H. Baldwin. "Isotopic variation of experimental lifetimes for the lowest  ${}^{1}\Pi_{u}$  states of N<sub>2</sub>". J. Chem. Phys., vol. 122, p. 144301, 2005.
- [206] G. Stark, K. P. Huber, K. Yoshino, P. L. Smith and K. Ito. "Oscillator strength and linewidth measurements of dipole-allowed transitions in  $^{14}N_2$  between 93.5 and 99.5nm". J. Chem. Phys., vol. 123, p. 214303, 2005.
- [207] G. Stark, B. R. Lewis, A. N. Heays, K. Yoshino, P. L. Smith and K. Ito. "Oscillator strengths and line widths of dipole-allowed transitions in <sup>14</sup>N<sub>2</sub> between 89.7 and 93.5nm". J. Chem. Phys., vol. 128, p. 114302, 2008.

- [208] S. Edwards, J. Roncin, F. Launay and F. Rostas. "The electronic ground state of molecular nitrogen". J. Mol. Spectrosc., vol. 162, p. 257, 1993.
- [209] W. Ubachs, R. Lang, I. Velchev, W.-Ü. Tchang-Brillet, A. Johansson, Z. Li, V. Lokhnygin and C.-G. Wahlström. "Lifetime measurements on the c<sub>4</sub><sup>-1</sup>Σ<sub>u</sub><sup>+</sup>, v=0, 1 and 2 states of molecular nitrogen". *Chemical Physics*, vol. 270, p. 215, 2001.
- [210] B. R. Lewis, S. T. Gibson, W. Zhang, H. Lefebvre-Brion and J.-M. Robbe. "Predissociation mechanism for the lowest  ${}^{1}\Pi_{u}$  states of N<sub>2</sub>". *J. Chem. Phys.*, vol. 122, p. 144302, 2005.
- [211] V. E. Haverd, B. R. Lewis, S. T. Gibson and G. Stark. "Rotational effects in the band oscillator strengths and predissociation linewidths for the lowest  ${}^{1}\Pi_{u} X^{1}\Sigma_{g}^{+}$  transitions of N<sub>2</sub>". J. Chem. Phys., vol. 123, p. 214304, 2005.
- [212] B. R. Lewis, A. N. Heays, S. T. Gibson, H. Lefebvre-Brion and R. Lefebvre. "A coupled-channel model of the  ${}^{3}\Pi_{u}$  states of N<sub>2</sub>: Structure and interactions of the  $3s\sigma_{g}F_{3}$   ${}^{3}\Pi_{u}$  and  $3p\pi_{u}G_{3}$   ${}^{3}\Pi_{u}$  Rydberg states". J. Chem. Phys., vol. 129, p. 164306, 2008.
- [213] A. N. Heays, J. M. Ajello, A. Aguilar, B. R. Lewis and S. T. Gibson. "The high-resolution extreme-ultraviolet spectrum of N<sub>2</sub> by electron impact". *Astrophys. J. Suppl. S.*, vol. 211, p. 28, 2014.
- [214] P. Lavvas, M. Galand, R. Yelle, A. Heays, B. Lewis, G. Lewis and A. Coates. "Energy deposition and primary chemical products in Titan's upper atmosphere". *Icarus*, vol. 213, p. 233, 2011.
- [215] X. Li, A. N. Heays, R. Visser, W. Ubachs, B. R. Lewis, S. T. Gibson and E. F. van Dishoeck. "Photodissociation of interstellar N<sub>2</sub>". Astron. Astrophys., vol. 555, p. A14, 2013.
- [216] X. Liu, D. E. Shemansky, C. P. Malone, P. V. Johnson, J. M. Ajello, I. Kanik, A. N. Heays, B. R. Lewis, S. T. Gibson and G. Stark. "Experimental and coupled-channels investigation of the radiative properties of the N<sub>2</sub> c'<sub>4</sub> <sup>1</sup>Σ<sup>+</sup><sub>u</sub> - X<sup>1</sup>Σ<sup>+</sup><sub>g</sub> band system". J. Geophys. Res. Space, vol. 113, p. A02304, 2008.
- [217] B. R. Lewis, S. T. Gibson, J. P. Sprengers, W. Ubachs, A. Johansson and C. G. Wahlström. "Lifetime and predissociation yield of  ${}^{14}N_2 \ b^1\Pi_u(v = 1)$  revisited: Effects of rotation". *J. Chem. Phys.*, vol. 123, p. 236101, 2005.

- [218] C. Y. R. Wu, D. L. Judge, M.-H. Tsai, Y.-C. Lin, T.-S. Yih, J.-I. Lo, H.-S. Fung, Y.-Y. Lee, B. R. Lewis, A. N. Heays and S. T. Gibson. "Experimental verification of strong rotational dependence of fluorescence and predissociation yield in the  $b^1\Pi_u(v=1)$  level of <sup>14</sup>N<sub>2</sub>". J. Chem. Phys., vol. 136, p. 044301, 2012.
- [219] B. R. Lewis, K. G. H. Baldwin, J. P. Sprengers, W. Ubachs, G. Stark and K. Yoshino. "Optical observation of the C,  $3s\sigma_g F_3$ , and  $3p\pi_u G_3 {}^3\Pi_u$  states of N<sub>2</sub>". J. Chem. Phys., vol. 129, p. 164305, 2008.
- [220] A. B. van der Kamp, P. Cosby and W. J. van der Zande. "Charge-transfer production of predissociated N<sub>2</sub> states. I. The n = 3 Rydberg state region (12.8-14 eV)". Chem. Phys., vol. 184, p. 319, 1994.
- [221] J.-I. Choe, D.-K. Lee, A. L. Floch and S. Kukolich. "Fourier transform spectroscopy of CO intercombination bands". J. Mol. Spectrosc., vol. 136, p. 173, 1989.
- [222] M. Drabbels, J. Heinze, J. J. ter Meulen and W. L. Meerts. "High resolution double-resonance spectroscopy on Rydberg states of CO". J. Chem. Phys., vol. 99, p. 5701, 1993.
- [223] A. D. Plessis, E. G. Rohwer and C. M. Steenkamp. "Investigation of four carbon monoxide isotopomers in natural abundance by laser-induced fluorescence in a supersonic jet". J. Mol. Spectrosc., vol. 243, p. 124, 2007.

## List of Publications

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

- Chapter 2: M.L. Niu, E.J. Salumbides, and W. Ubachs, "Test of quantum chemistry in vibrationally-hot hydrogen molecules," J. Chem. Phys. (Comm), vol. 143, p. 081102, 2015.
- **Chapter 3:** M.L. Niu, E.J. Salumbides, G.D. Dickenson, K.S.E. Eikema, and W. Ubachs, "Precision spectroscopy of the  $X^1\Sigma_g^+$ , v = 0 1 (J = 0 2) rovibrational splittings in H<sub>2</sub>, HD and D<sub>2</sub>," *J. Mol. Spectrosc.*, vol. 300, p. 44, 2014.
- Chapter 4: E.J. Salumbides, M.L. Niu, J. Bagdonaite, N. de Oliveira, D. Joyeux, L. Nahon, and W. Ubachs, "The CO A-X system for constraining cosmological drift of the proton-electron mass ratio," *Phys. Rev. A*, vol. 86, p. 022510, 2012.
- **Chapter 5:** M.L. Niu, E.J. Salumbides, D. Zhao, N. de Oliveira, D. Joyeux, L. Nahon, R.W. Field, and W. Ubachs, "High resolution spectroscopy and perturbation analysis of the CO  $A^1\Pi X^1\Sigma^+$  (0,0) and (1,0) bands," *Mol. Phys.*, vol. 111, p. 2163, 2013.
- **Chapter 6:** M.L. Niu, F. Ramirez, E.J. Salumbides, and W. Ubachs, "Highprecision laser spectroscopy of CO  $A^{1}\Pi - X^{1}\Sigma^{+}$  (2,0), (3,0) and (4,0) bands," *J. Chem. Phys.*, vol 142, p. 044302, 2015.
- **Chapter 7:** M.L. Niu, E.J. Salumbides, A.N. Heays, N. de Oliveira, R.W. Field, and W. Ubachs, "Spectroscopy and perturbation analysis of the CO  $A^{1}\Pi X^{1}\Sigma^{+}$  (2,0), (3,0) and (4,0) bands," *Accepted by Mol. Phys.*, 2015. Doi: 10.1080/00268976.2015.1108472

Chapter 8: M.L. Niu, A.N. Heays, S. Jones, E.J. Salumbides, E.F. van Dishoeck, N. de Oliveira, L. Nahon, and W. Ubachs, "VUV-synchrotron absorption studies of N<sub>2</sub> and CO at 900 K," *J. Mol. Spectrosc.*, vol 315, p. 137, 2015.

### The author also contributed to the following publications:

- i G.D. Dickenson, M.L. Niu, E.J. Salumbides, J. Komasa, K.S.E. Eikema, K. Pachucki, W. Ubachs, "Fundamental Vibration of Molecular Hydrogen," *Phys. Rev. Lett.*, vol. 110, p. 193601, 2013.
- ii G.D. Dickenson, E.J. Salumbides, M. Niu, Ch. Jungen, S.C. Ross and W. Ubachs, "Precision spectroscopy of high rotational states in H<sub>2</sub> investigated by Doppler-free two-photon laser spectroscopy in the  $EF^{1}\Sigma_{g}^{+} X^{1}\Sigma_{g}^{+}$  system," *Phys. Rev. A.*, vol. 86, p. 032502, 2012.

结论

本论文主要利用激光高分辨Doppler-free光谱仪和同步辐射真空紫外傅里叶 光谱仪测量与天文相关分子(一氧化碳和氢气)的高精度振动转动光谱。 测量工作分别在阿姆斯特丹自由大学激光实验室和法国巴黎SOLEIL同步辐 射DESIRS光束站完成。希望将来把这些实验光谱与具有足够精度的天文光谱 进行比较,推测出"质子-电子质量比"这一物理学常量是否在宇宙时间尺度上发 生变化。另外,为宇宙中除公认的四大相互作用——"第五力"的存在范围提供 实验依据,从而进一步为理论物理学家,是否需要打破"标准模型",提出全新 的物理学理论提供实验基础。

第一章:简介,描述了高精度实验光谱技术的背景和其与天文化学的紧密 联系、一氧化碳与氢气的研究现状,以及实验与理论相互促进对物理理论发展 的贡献。

第二章:采用高精度光谱研究氢气,氢化氘和氘气电子基态 $X^{1}\Sigma_{g}^{+}$ 上的  $v = 0 \rightarrow 1(J = 0 - 2)$ 的振转动分裂,检验了量子电动力学理论在分子模拟计 算中的影响。本实验利用窄带宽的Titanium:Sapphire脉冲激光系统测量电子 基态 $X^{1}\Sigma_{g}^{+}$ 到电子激发态 $EF^{1}\Sigma_{g}^{+}$ 的双光子跃迁能量,实验的绝对实验精度达 到 $2 \times 10^{-14}$  cm<sup>-1</sup>。结合之前精确测量的 $EF^{1}\Sigma_{g}^{+}$ 态v = 0振转能级,间接获得 电子基态的振转动能级分裂。实验结果与理论计算结果高度一致,验证了量子 电动力学对分子能级计算的精确矫正,同时推测出了第五力的存在范围。

第三章:在第二章的基础上,我们把实验推广到对氢气电子基态的高振动激发态的测量。我们采用光解离硫化氢分子制备高振动态激发的氢气分子。通过激光高分辨Doppler-free光谱实验方法间接地测量了氢气电子基态v = 12, J = 0 - 3的振转能级,实验精度达到 $3.5 \times 10^{-3}$  cm<sup>-1</sup>。实验结果与理论计算十分吻合,首次验证了在高振动激发态上量子电动力学的精确性。

第四章:通过对一氧化碳 $A^{1}\Pi - X^{1}\Sigma^{+}$ 谱带探测,研究"质子——电子质量比"μ在宇宙空间和时间尺度上的演化。我们采用了两种不同的光谱技术,首先利用真空紫外傅里叶吸收光谱,测量了一氧化碳 $A^{1}\Pi - X^{1}\Sigma^{+}(v,0)$ , v = 0 - 9谱带的振转跃迁频率,相对实验精度达到1.5×10<sup>-7</sup>;然后,利用双光子Doppler-free激光光谱,测量了 $A^{1}\Pi - X^{1}\Sigma^{+}(0,0)$ 和(1,0)谱带的部分振转跃迁频率,相对精度达到3×10<sup>-8</sup>。这些结果为获得质子电子质量比提供了零红移的数据。此外,为了获得μ值可能的变化,我们利用被测光谱的频率精确计算了一氧化碳 $A^{1}\Pi - X^{1}\Sigma^{+}$ 谱带的敏感系数 $K_{\mu}$ 。

第五章:报道了对一氧化碳 $A^1\Pi - X^1\Sigma^+(0,0)$ 和(1,0)谱带的扰动分析。 我们的工作基于绝对精度分别为0.01-0.02 cm<sup>-1</sup>和0.002 cm<sup>-1</sup>的真空紫外傅里 叶吸收光谱和双光子Doppler-free激光光谱实验数据。由于在分析中加入大量

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扰动态的影响,扰动分析结果得到了很大提高,获得了更加精确的一氧化碳电子激发态 $A^1\Pi$ , v = 0.1态的转动常数。

第六章:利用双光子Doppler-free激光光谱测量了一氧化碳电子激发态  $A^{1}\Pi$ 到基态 $X^{1}\Sigma^{+}$ 态(2,0)、(3,0)和(4,0)谱带的振转跃迁频率。实验采用了2+ 1'多光子共振增强电离技术、Sagnac干涉技术、脉冲激光频率偏移测量技术 (frequency-chirp)和交流电场斯塔克效应纠正技术等多种方法大幅提高了测 量精度,使其绝对实验精度达到 $1.6 \times 10^{-3}$  cm<sup>-1</sup>。这些结果为第六章同步辐 射实验数据提供了更加精确的校准。

第七章:基于第五章的激光实验结果,校准了在同步辐射利用真空紫外傅 里叶吸收光谱实验测得的一氧化碳电子激发态 $A^{1}\Pi$ 到基态 $X^{1}\Sigma^{+}(2,0)$ 、(3,0) 和(4,0)谱带的振转跃迁频率。利用这两组实验结果对一氧化碳电子激发 态 $A^{1}\Pi$ 态v = 2,3,4振动态进行解扰动分析,获得了更加详细、准确的一氧 化碳电子激发态 $A^{1}\Pi$ 态与多个单重态、三重态之间相互作用,同时得到了更 加准确的一氧化碳电子激发态 $A^{1}\Pi$ 态(2,0)、(3,0)和(4,0)振动态的分子转动常 数。

第八章:利用法国巴黎SOLEIL同步辐射DESIRS光束线上新安装在傅里 叶变换光谱仪上的样品池,我们测量了在900 K条件下的氮气和一氧化碳的真 空紫外吸收光谱。利用这台仪器可以测量分子高转动态布局的跃迁频率,从而 扩展常温吸收光谱的研究范围,获得更加准确的扰动分析结果。

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