Electric quadrupole transitions and collision-induced absorption in the region of the first overtone band of $\text{H}_2$ near 1.25 $\mu$m

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ABSTRACT

The $Q(1)$–$Q(4)$ electric quadrupole transitions of the first overtone band of $\text{H}_2$ have been recorded for six pressure values up to 640 Torr, by CW-Cavity Ring Down Spectroscopy near 8000 cm$^{-1}$. The noise equivalent absorption of the spectra is on the order of $\gamma_{\text{noise}} \approx 5 \times 10^{-12}$ cm$^{-1}$. Line intensities derived from a profile fit accounting for Dicke narrowing effects, range from $1.0 \times 10^{-20}$ to $2.6 \times 10^{-27}$ cm$^{-1}$/molecule for the $Q(4)$ and $Q(1)$ line, respectively. The claimed absolute uncertainty on the derived line positions and on the line strengths are of the order of 0.001 cm$^{-1}$ and 1%, respectively. The pressure line shifts of the four lines were derived allowing for an accurate determination of the position at zero pressure limit. The obtained positions and intensities agree within the experimental uncertainty with the most recent theoretical calculations including non-adiabatic, relativistic and quantum electrodynamical effects. The present frequency determinations confirm the high accuracy of these calculations. From the pressure dependence of the baseline of the CRDS spectra, the self continuum cross section of the collision induced absorption band of $\text{H}_2$ is determined in the vicinity of the $Q(1)$ line. The derived cross section is found in good agreement with recent theoretical values.

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1. Introduction

The $\text{H}_2$ absorption spectrum has been the subject of interest for a long time, in particular for applications in planetary science (e.g. [11]) and as a test for high level quantum mechanics calculations (e.g. [2–6]). Another strong motivation is the modeling of the line profile which exhibits a marked Dicke narrowing (e.g. [7]).

Most of the available measurements were performed in the 70's and 80's using long base multipass cells. The most extensive study is due to Bragg, Brault and Smith who reported a total of 26 positions and 22 intensity values for transitions of the (1–0), (2–0), (3–0) and (4–0) bands [5]. The spectra were recorded with the Kitt Peak Solar Fourier transform spectrometer with an absorption pathlength of 434 m and pressure values between 0.8 and 2.8 atm. An extreme example of this “heavy” experimental approach is the detection of the (4–0) $S(0)$ and $S(1)$, and the (5–0) $S(1)$ lines with a 5.984 km pathlength achieved with 272 passes in a 22 m-base multi-pass cell and a pressure up to 4 atm [9], after signal averaging over several hours.

Nowadays, cavity enhanced absorption techniques allow investigating the $\text{H}_2$ absorption spectrum at higher sensitivity and higher accuracy together with reduced sample volumes (and hazardous risks): (i) in relation to the present work, let us mention the study of the $Q(1)$ line of the (2–0) band near 8075 cm$^{-1}$ reported by Gupta et al. using Integrated Cavity Output Spectroscopy (ICOS) [10], (ii) the position of the $S(3)$ (3–0) line near 12,560 cm$^{-1}$ was very recently reported with a 10$^{-12}$ precision (1.6 MHz or $4.8 \times 10^{-5}$ cm$^{-1}$) by CW-Cavity Ring Down Spectroscopy (CRDS) combined with an ultra stable Fabry–Perot spectrometer [6], (iii) in recent contributions, we reported the CRDS detection of the (2–0) transitions of $\text{H}_2$ [4], HD [11] and D$_2$ [5] located between 5850 and 7920 cm$^{-1}$ i.e. in the spectral range accessible with the set of about 90 Distributed Feedback (DFB) laser diodes that we have at disposal.

The (2–0) band of $\text{H}_2$ being centered at 8087 cm$^{-1}$, only the $Q(J)$ lines with $J = 2–5$ and the very weak $Q(5)$ line were reported in Ref. [4] (see Fig. 1). In the present work, the use of a newly developed CRDS spectrometer based on a fiber-connected External Cavity Diode Laser (ECDL) allowed us to detect the $Q(J)$ lines with $J = 1–4$ located between 7970 and 8080 cm$^{-1}$. The present contribution is devoted to the analysis of these spectra recorded with an unprecedented sensitivity ($\gamma_{\text{noise}} \approx 5 \times 10^{-12}$ cm$^{-1}$).

After the description of the experimental setup (Section 2), we will present in Section 3 the line profile analysis and the discussion of the derived spectroscopic parameters (line position, line intensity, pressure line shift) in relation with theoretical and...
collision induced absorption in the vicinity of the $Q(1)$ ($2\rightarrow0$) transition.

2. Experiment details

The $Q(1)$–$Q(4)$ electric quadrupole transitions of $H_2$ were searched on the basis of their predicted line center listed in Table 1. The CRDS spectra were recorded using a fiber-connected External Cavity Diode Laser (ECDL: Toptica DL pro, 1200 nm) as light source. The setup is very similar to the CRDS spectrometer based on Distributed Feed Back (DFB) which was used to achieve a record sensitivity of $5 \times 10^{-10}$ molecule$^{-1}$ s$^{-1}$ on Distributed Feed Back (DFB) which was used to achieve a record sensitivity of $5 \times 10^{-10}$ molecule$^{-1}$ s$^{-1}$ for CRDS [14] and the reader is referred to Ref. [14] for a detailed description of the experimental arrangement and of the data acquisition procedure. Briefly, the 1.40 m long CRDS cell is fitted by very high reflectivity mirrors leading to ring down times of about 200 $\mu$s in the considered spectral interval. The CRDS cell was filled with $H_2$ (Fluka 99.999% stated purity) and the spectrum of each line was recorded at six pressure values: 10, 42, 80, 160, 320 and 640 Torr. The pressure and the ring down cell temperature were monitored during the spectrum acquisition. Over the whole measurement period, the temperature varied between 295.88 and 296.22 K. The absorption coefficient, $\alpha(v)$ (in cm$^{-1}$) was obtained from the cavity ring down time, $\tau$ (in s): $\alpha(v) = \frac{1}{\tau} \left( 1 - e^{-\tau/c} \right)$ where $c$ is the light velocity, $\tau_0$ is the ring-down time of the evacuated cavity.

The typical mode-hop free tuning range of this ECDL is about 0.8 cm$^{-1}$. The laser frequency was tuned over a 1.6 cm$^{-1}$ wide region around the line center by changing the grating angle together with the laser current. In general, three consecutive and partially overlapping spectra were recorded to cover the range of interest. About ten ring-down events were averaged for each spectral data point separated by $8 \times 10^{-4}$ cm$^{-1}$. The noise equivalent absorption evaluated as the rms of the baseline fluctuation is $\sigma_{\text{min}} \approx 5 \times 10^{-12}$ cm$^{-1}$. An important advantage of this ECDL compared to DFB diode lasers lies in its smaller linewidth (typically 150 kHz compared to 2 MHz) which insures a better light injection and limits the noise resulting from the conversion of the frequency jitter in intensity fluctuations on the wings of the line profile [15]. Moreover, an optical isolator was introduced before the cavity in order to avoid spurious fringes due to light interferences between the fiber and the cavity.

The wavenumber of the light emitted by the laser diode was measured by a commercial Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 h) that allows the laser frequency to be determined at a typical 100 Hz refresh rate. In order to further refine the absolute calibration, a very low pressure scan was recorded previous to this experiment, showing $H_2O$ lines (present as impurity) for which accurate positions are provided by the HITRAN database [16]. We estimate to $1 \times 10^{-3}$ cm$^{-1}$ (30 MHz) the accuracy of the absolute calibration of the wavenumber scale.

The spectrum of the $H_2$ ($2\rightarrow0$) $Q(1)$ line is displayed on Fig. 2. The strongest $Q(1)$, $Q(2)$ and $Q(3)$ lines were previously measured by Bragg et al. by Fourier Transform Spectroscopy (FTS) [8] while the weakest $Q(4)$ line is newly reported (see Table 1).

3. Line parameter retrieval

The profile of hydrogen rovibrational transitions is affected by a marked Dicke narrowing increasing with the pressure [4–11,17]. The reduction of the line width and the significant position shift of the $Q(1)$ line are illustrated in Fig. 2 where the profiles at 10 and 640 Torr are superimposed. The line intensity, $S_{\nu_0}$ (cm/molecule), of a rovibrational transition centred at $\nu_0$ (cm$^{-1}$), was derived from the integrated absorption coefficient, $A_{\nu_0}$ (cm$^{-2}$/molecule) using the following relation:

$$A_{\nu_0}(T) = \int_{\nu_0} S_{\nu_0}(T) d\nu$$

where $\nu$ is the wavenumber in cm$^{-1}$, $N$ is the $H_2$ concentration in molecule/cm$^3$ obtained from the measured pressure and temperature values: $N = P/kT$.

An interactive multi-line fitting program was used to reproduce the spectrum. In the line profile fitting, the width of the Gaussian component was fixed to its Doppler value (1.04 GHz or $3.5 \times 10^{-2}$ cm$^{-1}$, HWHM) and the ECDL linewidth contribution ($\sim 150$ kHz) was neglected.

The fitting of the $H_2$ line using a Voigt profile leads to a W shape residual, which is a typical signature of Dicke narrowing effects.
A much better line profile reproduction is achieved using a Galatry profile corresponding to a soft collision process. The collision frequency factor, $b$, was found to increase linearly with the pressure. The fitted value of the proportionality factor, $0.0502(8) \text{ cm}^{-1} \text{atm}^{-1}$ (at 296 K), compares satisfactorily with the value $0.0488 \text{ cm}^{-1} \text{atm}^{-1}$ provided by diffusion theory using the relation:

$$b = \frac{k_B T}{2 \pi m c D}$$

where $k_B$ is the Boltzmann constant, $m$ is the molecular mass, $c$ is the speed of light and $D$ the mass-diffusion coefficient in H$_2$ ($D = 1.338 \times 10^{-5} \text{ m}^2/\text{s}$ [18]).

As a consequence of the high sensitivity of the recordings, lines due to water at the ppm level were detected in several H$_2$ spectra. They were taken into account in the line profile fitting (see Fig. 3). Note that a very weak non-symmetric residual is obtained with the Galatry profile indicating that a more sophisticated model as that of Ref. [7] is required to fully reproduce the experimental profile.

In order to increase the accuracy, the line intensities were derived from the proportionality factor between the integrated absorption coefficient and the pressure values (Eq. 1). Fig. 4 shows that the linear dependence is nearly perfect yielding a statistical error bar of less than 1‰ on the derived slope value, even for the very weak Q(4) line.

The stability of the used wavemeter over the duration of a series of recordings at different pressure values (20 MHz accuracy over 10 h) makes possible an accurate determination of the line shifts. Fig. 4 shows that the centre of the four studied lines decreases linearly with the pressure in a very similar way. The derived pressure shift values were used to extrapolate the line centre at the zero pressure limit.

Table 1 summarises the retrieved line parameters (position, intensity, line shift) and compares them to the previous experimental and theoretical results.

### Table 1

<table>
<thead>
<tr>
<th>Transition</th>
<th>Line position</th>
<th>Line intensity</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Calc. (cm$^{-1}$)</td>
<td>Meas. (cm$^{-1}$)</td>
</tr>
<tr>
<td>Q(4)</td>
<td>7971.1001(17)</td>
<td>7971.1006(10)</td>
</tr>
<tr>
<td>Q(3)</td>
<td>8017.1833(17)</td>
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<td>Q(2)</td>
<td>8051.9877(17)</td>
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<tr>
<td>Q(1)</td>
<td>8075.3074(17)</td>
<td>8075.3105</td>
</tr>
</tbody>
</table>

|        | Calc. $(10^{-28} \text{ cm/molecule})$ | Meas. $(10^{-28} \text{ cm/molecule})$ |
| Q(4)   | 0.1042 | 0.10491(11)$^a$ |
| Q(3)   | 2.353 | 2.233(74) |
| Q(2)   | 3.289 | 3.200(37) |
| Q(1)   | 25.980 | 29.0238 |

$^a$ The given error bar (in units of the last quoted digit) is the statistic error obtained from the fit of the integrated absorption coefficient versus the pressure (Fig. 4). The given values do not take into account other error sources such as that related to the choice of the line profile function. We estimate to about 1% the real uncertainty of our intensity values.

Fig. 2. Comparison of the profile of the Q(1) (2–0) line profile at 10 Torr and 640 Torr. For the clarity of the figure, the absorption coefficients have been divided by the pressure values in Torr. Note the pressure shift of the line centre.

Fig. 3. A much better line profile reproduction is achieved using a Galatry profile corresponding to a soft collision process. The collision frequency factor, $b$, was found to increase linearly with the pressure. The fitted value of the proportionality factor, $0.0502(8) \text{ cm}^{-1} \text{atm}^{-1}$ (at 296 K), compares satisfactorily with the value $0.0488 \text{ cm}^{-1} \text{atm}^{-1}$ provided by diffusion theory using the relation:

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Table 1 summarises the retrieved line parameters (position, intensity, line shift) and compares them to the previous experimental and theoretical results.

### 3.1. Line positions

The ab initio values of the line positions of Ref. [4] were obtained by difference of the energy levels computed including the relativistic and quantum electrodynamic corrections as well as the effects of the finite nuclear mass [12]. An error bar of $1.7 \times 10^{-3} \text{ cm}^{-1}$ was attached to the (2–0) Q(4) positions of interest.

Fig. 3. Line profile simulation of the Q(2) (2–0) transition at 320 Torr. Upper panel: CRDS spectrum. Lower panels: Residuals between the experimental and simulated spectra for the Voigt and Galatry profiles. The weak contribution of a H$_2$O line present as an impurity was taken into account in the simulation.


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while we claim for $1.0 \times 10^{-3}$ uncertainty on the experimental values. The CRDS and $ab\ initio$ values collected in Table 1 show an excellent agreement, the experimental values being larger by about $0.4 \times 10^{-3}$ cm$^{-1}$. Compared to previous FTS measurements of the Q(1), Q(2), Q(3) lines [8,13], the obtained agreement is significantly improved. In fact, recent very accurate CRDS measurements of (3–0) line positions [19] seem to indicate that the claimed theoretical uncertainty is overestimated and it is reasonable to believe that theoretical position values have an uncertainty lower than our experimental values. The quality of the full $ab\ initio$ calculations of Ref. [12] was also confirmed by recent highly accurate investigation of the ground tone in H$_3$, HD and D$_2$ determined to an accuracy of $2 \times 10^{-4}$ cm$^{-1}$ [20].

3.2. Line intensities

Theoretical line intensities were derived from quadrupole transition moments calculated using highly accurate adiabatic wave functions [4]. Their claimed uncertainty is better than 0.1%, which is practically out of reach for absolute experimental values. The retrieved CRDS intensities obtained for a pressure series are consistent within much less than 1%: the proportionality factor between the integrated absorption coefficient and the pressure (Fig. 4) are all determined with a relative uncertainty better than 0.1%. Nevertheless, the achieved 1% agreement between CRDS and $ab\ initio$ intensity values was not anticipated. Indeed systematic biases such as that related to the choice of the line profile function used to reproduce the measured profile may lead to errors on the order of 1% increasing with the pressure [11]. In the present work, the high sensitivity of our spectrometer has allowed using relatively low pressure values, which has the advantage to limit the collisional effects whose description require more sophisticated line profile models. This may explain the quality of the achieved intensity agreement.

3.3. Line shifts

Accurate values of the pressure shift coefficients could be derived, improving significantly the rough previous determinations by Bragg et al. [8] The values of $-3.71(8)$, $3.34(21)$, $-3.41(13)$ and $3.2(2) \times 10^{-3}$ cm$^{-1}$/amagat obtained for the Q(1), Q(2), Q(3) and Q(4) lines, respectively, are very close to each other and in very good agreement with the constant value of $-3.8 \times 10^{-3}$ cm$^{-1}$/amagat calculated by Kelley and Bragg using a semi classical approach [17]. We nevertheless note that the difference between the Q(1) shift coefficient derived by ICOS ($-2.8(2) \times 10^{-3}$ cm$^{-1}$/amagat) [10] and our value largely exceed the combined error bars.

4. Collision-induced absorption

As a result of dipole moments induced by molecular interactions, molecular hydrogen shows broad collision induced absorption (CIA) bands, which have attracted widespread interest for a long time. Considerable experimental efforts were undertaken to measure these H$_2$ bands in a large range of pressure and temperature conditions relevant for planetary atmospheres and “cool” stellar objects [21,22]. $ab\ initio$ calculations have made possible to account for the measured CIA bands of H$_2$ with remarkable precision [22–24].

In the range of the second overtone band, the H$_2$ CIA is a superposition of the bands involving single (2–0) excitation of one H$_2$ molecule and double (1–0) excitation of two molecules. At room temperature, the resulting absorption structure extends from 7500 to 10,000 cm$^{-1}$. At low temperature, the large H$_2$ rotational constant enables to “resolve” the CIA rotational structure [21–24].

In the present recordings limited to narrow spectral intervals around the electric quadrupole H$_2$ lines, the CIA is expected to show up as an increase of the baseline level of the spectra. But the measurement of very weak broad band continua is particularly demanding because the baseline of the spectra should not be affected by the pressure change resulting from the injection of hydrogen in the cell. Our recent study of the water continuum using similar CRDS spectrometer in the 1.5 µm atmospheric window [25] has shown that a baseline stability better than $1 \times 10^{-10}$ cm$^{-1}$ is routinely achieved. As illustrated in Fig. 5, this stability is sufficient to measure the H$_2$ CIA in the region of the (2–0) Q(1) line.
electrodynamic and relativistic corrections up to the \( z^2 \) order\,[12]; the differences being smaller than the respective experimental uncertainties (0.001 cm\(^{-1}\) and 1%, respectively). A significant gain on the line position accuracy is then required to provide a test for these high level quantum chemical calculations. Note that the reported uncertainty on the \textit{ab initio} line positions (1.7 \times 10^{-3} \text{ cm}^{-1} \[4\]) is believed to be overestimated\,[19]. The combination of our CRDS spectrometer with a frequency comb is expected to provide the requested performances in a near future.

An interesting result of the present study is the measurement of the H\(_2\) CIA at room temperature and low pressure (<1 atm). The derived cross section was found in agreement with both \textit{ab initio} value and previous experimental determination at much higher pressure. To the best of our knowledge, no measurements of H\(_2\) CIA were previously reported for pressure values below 1 atm.

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References