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Electric quadrupole transitions and collision-induced absorption in the region of the first overtone band of H_2 near 1.25 μm

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ABSTRACT

The $Q(1)$–$Q(4)$ electric quadrupole transitions of the first overtone band of 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 $\alpha_{min} \approx 5 \times 10^{-12}$ cm^{-1}. Line intensities derived from a profile fit accounting for Dicke narrowing effects, range from 1.0×10^{-29} to 2.6×10^{-27} cm/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 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.

1. Introduction

The H_2 absorption spectrum has been the subject of interest for a long time, in particular for applications in planetary science (e.g. [1]) 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 [8]. 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 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^{-9} precision (1.6 MHz or 4.8×10^{-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 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 H_2 being centered at 8087 cm^{-1}, only the $O(J)$ 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 ($\alpha_{min} \approx 5 \times 10^{-12}$ 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

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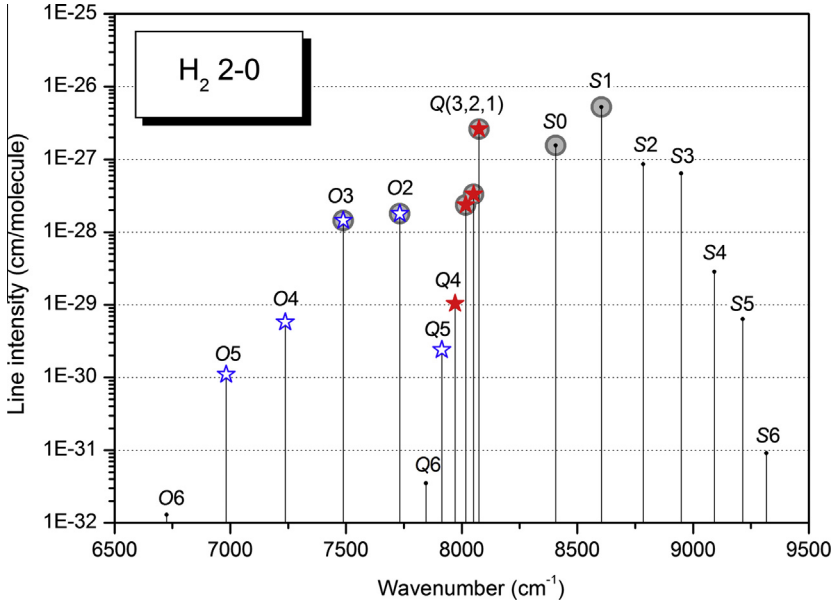

Fig. 1. Overview of the first overtone band of H_2 as predicted by *ab initio* calculations [4,12]. Transitions previously reported in the literature by FTS [8] are highlighted with full grey circles. CRDS observations of Ref. [4] and of this work are marked with open and full stars, respectively.

experimental results available in the literature. Finally, the variation of the base line of the CRDS spectra will be used to derive the contribution of the H_2 collision induced absorption in the vicinity of the $Q(1)$ (2–0) 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 5×10^{-13} cm^{-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 μs 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, $\alpha(\nu)$ (in cm^{-1}) was obtained from the cavity ring down time, τ (in s): $\alpha(\nu) = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$ where c is the light velocity, τ_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 8×10^{-4} cm^{-1}. The noise equivalent absorption evaluated as the *rms* of the baseline fluctuation is $\alpha_{min} \sim 5 \times 10^{-12}$ 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 1×10^{-3} cm^{-1} (30 MHz) the accuracy of the absolute calibration of the wavenumber scale.

The spectrum of the H_2 (2–0) $Q(1)$ 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_{ν_0} (cm/molecule), of a rovibrational transition centred at ν_0 (cm^{-1}), was derived from the integrated absorption coefficient, A_{ν_0} (cm^{-2}/molecule) using the following relation:

$$A_{\nu_0}(T) = \int_{line} \alpha_\nu d\nu = S_{\nu_0}(T)N \qquad (1)$$

where ν 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 3.5×10^{-2} cm^{-1}, HWHM) and the ECDL linewidth contribution (~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