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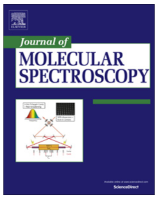

The HD spectrum near 2.3 μm by CRDS-VECSEL: Electric quadrupole transition and collision-induced absorption

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ABSTRACT

The HD absorption spectrum is investigated near 2.3 μm with the help of a newly developed Cavity Ring Down Spectrometer (CRDS) using a VECSEL (Vertical External Cavity Surface Emitting Laser) as light source. The HD CRDS spectra were recorded for a series of ten pressure values in the range 50–650 Torr. The sensitivity of the recordings – noise equivalent absorption of the spectra on the order of $\alpha_{min} \approx 5 \times 10^{-10}$ cm^{-1} – has allowed for the first detection of the $S(3)$ quadrupole electric transition of the HD fundamental band, at 4359.940 cm^{-1}. The line center determined with an uncertainty of 0.002 cm^{-1} agrees with the most recent theoretical calculations. The retrieved value of the line intensity (2.5×10^{-27} cm/molecule at 296 K) agrees within 12% with the *ab initio* values included in the HITRAN spectroscopic database. We take the opportunity of this contribution to provide an exhaustive review of seventy-three HD absorption lines previously detected up to 20,000 cm^{-1}.

From the pressure dependence of the baseline of the CRDS spectra, the binary absorption coefficient of the HD collision induced absorption band is determined to be $1.17(4) \times 10^{-6}$ cm^{-1}amagat^{-2} at 4360 cm^{-1}.

1. Introduction

For about a century, the hydrogen molecule and its isotopologues have provided challenges both for theoretical calculations and high sensitivity absorption techniques (see Refs. [1–3] for some pioneering works and the review included in Ref. [4] for H_2 transitions). As a result of significant progress of theory (e.g. Refs. [5–8]) and experiment (e.g. Refs. [4,9–15]), this interest has been recently renewed and concerns different aspects including transition frequencies and line strengths [4,9–15], line profile [16,17] and collision induced absorption [18–20]. The present accuracy of theoretical calculations of the hydrogen energy levels including non-adiabatic, relativistic and quantum electrodynamical effects (e.g. Ref. [8]) and the sub-MHz accuracy on line centers allowed by combining laser techniques and frequency standards [11] or auto-referenced frequency combs [15] have given rise to a challenging competition and prospects to search for physics beyond the Standard Model as was recently discussed in Ref. [21].

Experimentally, the main difficulty is related to the weakness of the absorption lines to be detected. The absorption spectrum of molecular hydrogen and deuterium, H_2 and D_2, consists of vibrational bands of very weak electric quadrupole (E2) transitions. As a result of the large values of the vibrational frequency (about 4160 and 2993 cm^{-1}, respectively) and of the rotational constant (about 60 and 30 cm^{-1}, respectively), the H_2 and D_2 spectra are extremely sparse. For instance, less than fifty H_2 absorption lines have been reported so far in the literature, up to the fourth overtone band near 19,000 cm^{-1} [4,13,14].

Contrary to the symmetric isotopologues, the deuterated species, HD, possesses a (weak) permanent dipole moment resulting from non adiabatic effects due to the difference of masses of the proton and the deuteron. The existence of weak electric dipole (E1) transitions in HD was predicted by Wick in 1935 [1]. Thus the HD absorption spectrum exhibits electric dipole rovibrational

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transitions in addition to the even weaker electric quadrupole (E2) transitions. The electric dipole transitions form *P* and *R* branches corresponding to $\Delta J = -1$ and +1, respectively while the electric quadrupole transitions form *O*, *Q* and *S* branches corresponding to $\Delta J = -2$, 0 and +2, respectively. Fig. 1 shows an overview of the calculated stick spectrum of HD [6,8,22] in the 0–20,000 cm^{-1} range covering the rotational spectrum, the fundamental and vibrational overtone bands up to 6–0. Note that in the 1–0 fundamental band, the E2 transitions are typically two orders of magnitude weaker than E1 transitions.

The present Special Issue of the Journal of Molecular Spectroscopy dedicated to Spectroscopic Databases provides an opportunity for an exhaustive review of the HD absorption lines reported in the literature, presented in Table 1. On the overview spectrum of Fig. 1, the transitions detected so far are highlighted.

In 1950, Herzberg reported the first detection of HD transitions in the photographic infrared. Herzberg used path lengths up to 1 km to detect a few transitions of the (V'–V'') = (3–0) and (4–0) bands [2]. Since then, a number of experimental works have been devoted to the detection and measurement of HD transitions [3,23–38]. Table 1 presents the seventy-three transitions reported so far by using a variety of experimental techniques, from the pure rotational spectrum to the (6–0) vibrational band near 520 nm. Twenty-seven of them were reported by Durie and Herzberg using pressure × pathlength products up to 360 atm × m [3]. A major contribution is due to the group of McKellar et al. who reported a total of 39 transitions in the 70s and early 80s [23–26]. These observations were obtained with a multiple pass cell associated with a grating spectrograph [24–26] or a Fourier Transform Spectrometer [23]. Accurate line positions and line intensities were used to derive the spectroscopic parameters and the electric dipole moments relative to the V' = 1–6 upper vibrational levels [26]. A few transitions of the 5–0 and 6–0 overtone bands were detected by photoacoustic spectroscopy in the visible [30,36,37].

In the rotational region, let us mention the accurate determination of the pure rotational transition frequencies reported by Ulivi et al. by far infrared FTS [27] and the *R*(0) line center reported by Drouin et al. with a 10^{-8} relative accuracy [28] providing an interesting challenge for *ab initio* calculations.

The traditional detection scheme based on a long path multiple pass cell associated with grating spectrographs or Fourier Transform Spectrometers (FTS) gives access to lines with minimum intensity values in the 10^{-27}–10^{-26} cm/molecule range. As a result, prior to our recent CRDS investigation of the 2–0 band [38], the only E2 absorption lines of HD reported in the literature were the *S*(0)–*S*(2) transitions of the fundamental band studied by Rich et al. in 1982 [23]. These authors reported line centers from FTS spectra recorded with an absorption path of 48 m. To the best of our knowledge, the only E2 intensity measurement performed with long path techniques was reported by McKellar [25] for the *S*(0) line (intensity of about 1×10^{-26} cm/molecule at 296 K), by using a pressure of about 6 atm of HD and a low temperature (77 K) to make the molecules concentrated in their lowest rotational levels.

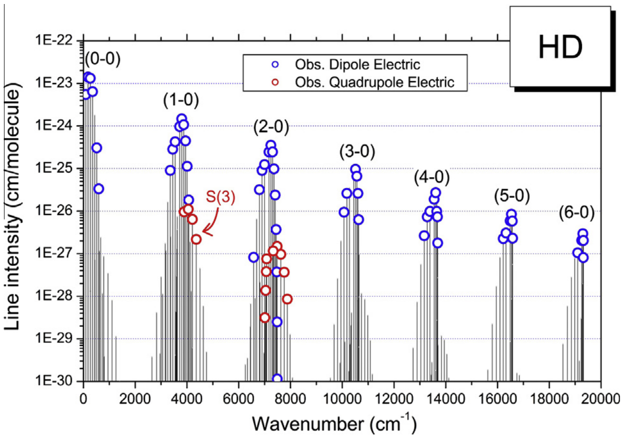

Fig. 1. Overview of the spectrum of (pure) HD between 0 and 20,000 cm^{-1} as provided by the HITRAN database [22]. The line positions and line intensities are calculated values from Refs. [6,8]. The electric dipole and electric quadrupole transitions which were previously detected by absorption spectroscopy [3,23–38] are highlighted with blue and red circles, respectively. The newly detected *S*(3) transition is indicated.

Modern laser spectroscopic techniques like Cavity Ring Down Spectroscopy (CRDS) provide a much higher sensitivity and require a small gas quantity (typical CRDS cells have a volume of 100 cm^3). Our CRDS investigation of the first overtone band of HD between 6900 and 7900 cm^{-1} [38] allowed for accurate measurements of nine E2 and eleven E1 transitions, including the weakest HD line detected so far, the *R*(8) 2–0 line with intensity of 1.04×10^{-30} cm/molecule at 296 K [38] (see Fig. 1). The noise equivalent absorption of the spectra was on the order of $\alpha_{\min} \approx 5 \times 10^{-11}\ \text{cm}^{-1}$ i.e. about three orders of magnitude better than FTS sensitivity. Other laser detections of HD transitions include the above mentioned photoacoustic studies of high overtone transitions and the *P*(5) 2–0 line reported by Lin et al. using frequency-modulated difference spectroscopy [29].

Compared to the telecom frequency range where the CRDS technique allows achieving record performances [39], the development of cavity enhanced laser techniques in the 2.3 μm range corresponding to HD fundamental band, is more challenging because laser sources are less powerful and generally non-fibered, detectors are less sensitive and the optical elements adapted for this spectral region are less efficient. In the present work, we report the first detection of *S*(3) 1–0 quadrupole transition of HD spectrum near 2.3 μm by using a newly developed cavity ring down spectrometer (CRDS) with a Vertical External Cavity Surface Emitting Laser (VECSEL) light source.

During, the recordings performed at different pressures up to 650 Torr, we noted that the baseline level of the CRDS spectra was increasing rapidly with the pressure as a result of the 1–0 collision induced absorption band of HD. After the description of the experimental set up (Section 2), we will present the line parameters retrieval of the *S*(3) 1–0 line and the derivation of the collision induced absorption from the pressure dependence of the spectra baseline (Section 3).

2. Experiment details

The CRD spectroscopy technique [39–41] allows to determine the extinction coefficient, $\alpha(\nu)$ (in cm^{-1}), at a wavenumber ν, as the increase of the loss rate, $\frac{1}{c\tau}$, of the CRDS cell when the cell is filled with the gas under study:

$$\alpha(\nu) = \frac{n}{c\tau(\nu)} - \frac{1}{c\tau_0(\nu)}, \qquad (1)$$

where τ and τ_0 are the ring-down times with gas in the cell and with evacuated cell, respectively, c is the speed of light and n is the refractive index considered as equal to 1 in the following.

In this work, a single frequency tunable VECSEL device [42,43] developed by Innoptics was used as a light source near 2.3 μm. A VECSEL is an extended cavity diode laser formed by a 1/2 VCSEL semiconductor structure including the amplification medium and a Bragg mirror, and an external output mirror mounted on a piezoelectric transducer (PZT). The structure was optically pumped with a commercial multimode diode emitting at 975 nm and temperature stabilized thanks to a Peltier thermoelectric cooler. Typical