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 $\alpha_{\text{min}} \approx 5 \times 10^{-10} \text{ cm}^{-1}$ - 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 ($2.5 \times 10^{-27} \text{ cm/molecule at 296 K}$) 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 20000 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 $1.17(4) \times 10^{-6} \text{ cm}^{-1} \text{ amagat}^{-2}$ 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].

Fig. 1

Overview of the spectrum of (pure) HD between 0 and 20000 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.

Band ($V'-V''$)	Transition	Experimental observation		Theory [6, 8, 22]	
		Meas. Pos.(cm ⁻¹)	Reference observation	Pos. (cm ⁻¹)	Line intensity (cm/molecule)
(0-0)	R(0)	89.22793400(83) 89.227950(5) 89.36	Drouin et al. 2011 [28] Evenson, et al, 1988 [32] Trefler and Gush, 1968 [31]	89.227933(8)	1.918E-24
	R(1)	177.84172(16) 178.21	Ulivi, De Natale, Inguscio, 1991[27] Trefler and Gush, 1968 [31]	177.84127(2)	8.130E-24
	R(2)	265.24116(17) 265.64	Ulivi, De Natale, Inguscio, 1991 [26] Trefler and Gush, 1968 [31]	265.24010(2)	9.562E-24
	R(3)	350.85295(12) 350.852(2)	Ulivi, De Natale, Inguscio, 1991 [26] Essenwanger and Gush, 1984 [33]	350.85302(3)	5.221E-24
	R(5)	514.656(1)	Essenwanger and Gush, 1984 [33]	514.64965(4)	2.801E-25
	R(6)	591.9327(3)	Essenwanger and Gush, 1984 [33]	591.93240(5)	3.139E-26
(1-0)	O(2)	3365.056(50) ^a	Brannon, Church, Peters, 1968 [34]	3365.0912(5)	2.487E-27
	P(3)	3355.361	Rich, Johns and McKellar, 1982 [23]	3355.3700(5)	9.022E-26
	P(2)	3450.463	Rich, Johns and McKellar, 1982 [23]	3450.4631(5)	2.842E-25
		3450.440	Durie and Herzberg, 1960 [3]		
	P(1)	3542.932 3542.934	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	3542.9325(5)	4.254E-25
	Q(4)	3593.910(30) ^a	Brannon, Church, Peters, 1968 [34]	3593.8658(5)	2.992E-28
	Q(3)	3609.093(30) ^a	Brannon, Church, Peters, 1968 [34]	3609.1131(5)	1.325E-27
	Q(2)	3620.616(30) ^a	Brannon, Church, Peters, 1968 [34]	3620.6101(5)	3.702E-27
	Q(1)	3628.278(30) ^a	Brannon, Church, Peters, 1968 [34]	3798.4514(5)	7.410E-27
	Q(0)	3632.165(30) ^a	Brannon, Church, Peters, 1968 [34]	3632.1604(5)	-
	R(0)	3717.532 3717.527	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	3717.5323(5)	9.671E-25
	R(1)	3798.455 3798.471	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	3798.4514(5)	1.473E-24
	R(2)	3874.357 3874.374	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	3874.3532(5)	1.073E-24
	R(3)	3944.720 3944.718	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	3944.7188(5)	4.471E-25
	R(4)	4009.088 4009.096	Rich, Johns and McKellar, 1982 [23] Durie and Herzberg, 1960 [3]	4009.0868(5)	1.134E-25
	R(5)	4067.066	Rich, Johns and McKellar, 1982 [23]	4067.0618(5)	1.817E-26
	S(0)	3887.683 3887.668(30)	Rich, Johns and McKellar, 1982 [23] Brannon, Church, Peters, 1968 [34]	3887.6793(5)	9.620E-27
	S(1)	4052.196 4052.214(30)	Rich, Johns and McKellar, 1982 [23] Brannon, Church, Peters, 1968 [34]	4052.1945(5)	1.104E-26
	S(2)	4209.963 4209.870(30)	Rich, Johns and McKellar, 1982 [23] Brannon, Church, Peters, 1968 [34]	4209.9589(6)	6.420E-27
	S(3)	4359.9402(20)	This work	4359.9398(6)	2.172E-27
(2-0)	P(5)	6576.896(8)	Lin et al. 2000 [29]	6576.901(1)	8.198E-28
	P(3)	6798.787	Durie and Herzberg, 1960 [3]	6798.768(1)	3.183E-26
	P(2)	6901.4014 6901.403	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	6901.401(1)	9.013E-26
	P(1)	6997.6494 6997.666	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	6997.649(1)	1.235E-25
	Q(1)	7079.2422	Kassi and Campargue, 2011 [38]	7079.242(1)	7.552E-28
	Q(2)	7064.0077	Kassi and Campargue, 2011 [38]	7064.008(1)	3.799E-28
	Q(3)	7041.2418	Kassi and Campargue, 2011 [38]	7041.243(1)	1.374E-28
	Q(4)	7011.0492	Kassi and Campargue, 2011 [38]	7011.050(1)	3.144E-29
	R(0)	7168.4697 7168.428	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	7168.470(1)	2.449E-25
	R(1)	7241.8497 7241.818	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	7241.849(1)	3.533E-25
	R(2)	7306.4839 7306.541	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	7306.483(1)	2.456E-25
	R(3)	7361.9037 7361.911	Kassi and Campargue, 2011 [38] Durie and Herzberg, 1960 [3]	7361.903(1)	9.806E-26
	R(4)	7407.7134	Kassi and Campargue, 2011 [38]	7407.713(1)	2.394E-26
	R(5)	7443.5983	Kassi and Campargue, 2011 [38]	7443.598(1)	3.703E-27
	R(6)	7469.3298	Kassi and Campargue, 2011 [38]	7469.329(1)	3.726E-28
	R(7)	7484.7654	Kassi and Campargue, 2011 [38]	7484.763(1)	2.498E-29
	R(8)	7489.8463	Kassi and Campargue, 2011 [38]	7489.846(1)	1.141E-30

	S(0)	7331.0778	Kassi and Campargue, 2011 [38]	7331.077(1)	1.157E-27
	S(1)	7484.3246	Kassi and Campargue, 2011 [38]	7484.324(1)	1.486E-27
	S(2)	7627.1438	Kassi and Campargue, 2011 [38]	7627.143(1)	9.671E-28
	S(3)	7758.5657	Kassi and Campargue, 2011 [38]	7758.566(1)	3.673E-28
	S(4)	7877.7462	Kassi and Campargue, 2011 [38]	7877.747(1)	8.569E-29
(3-0)	P(3)	10068.365	McKellar, Goetz and Ramsay, 1976 [26]	10068.375(1)	9.436E-27
		10068.395	Durie and Herzberg, 1960 [3]		
	P(2)	10178.413	McKellar, Goetz and Ramsay, 1976 [26]	10178.434(1)	2.610E-26
		10178.382	Durie and Herzberg, 1960 [3]		
	P(1)	10278.378	McKellar, Goetz and Ramsay, 1976 [26]	10278.402(1)	3.508E-26
		10278.373	Durie and Herzberg, 1960 [3]		
	R(0)	10445.490	McKellar, Goetz and Ramsay, 1976 [26]	10445.503(1)	6.738E-26
		10445.466	Durie and Herzberg, 1960 [3]		
	R(1)	10511.443	McKellar, Goetz and Ramsay, 1976 [26]	10511.456(1)	9.599E-26
		10511.462	Durie and Herzberg, 1960 [3]		
	R(2)	10564.986	McKellar, Goetz and Ramsay, 1976 [26]	10564.992(1)	6.597E-26
		10564.987	Durie and Herzberg, 1960 [3]		
(4-0)	R(3)	10605.680	McKellar, Goetz and Ramsay, 1976 [26]	10605.688(1)	2.608E-26
		10605.657	Durie and Herzberg, 1960 [3]		
	R(4)	10633.213	McKellar, Goetz and Ramsay, 1976 [26]	10633.210(1)	6.312E-27
	P(3)	13166.588	McKellar, Goetz and Ramsay, 1976 [26]	13166.595(2)	2.651E-27
	P(2)	13283.996	Trauger and Mickelson, 1983 [35]	13284.007(2)	7.333E-27
		13283.993	McKellar, Goetz and Ramsay, 1976 [26]		
		13283.982	Durie and Herzberg, 1960 [3]		
	P(1)	13387.665	Trauger and Mickelson, 1983 [35]	13387.661(2)	9.860E-27
		13387.646	McKellar, Goetz and Ramsay, 1976 [26]		
		13387.652	Durie and Herzberg, 1960 [3]		
	R(0)	13551.069	Trauger and Mickelson, 1983 [35]	13551.077(2)	1.897E-26
		13551.065	McKellar, Goetz and Ramsay, 1976 [26]		
(5-0)		13551.066	Durie and Herzberg, 1960 [3]		
	R(1)	13609.681	Trauger and Mickelson, 1983 [35]	13609.676(2)	2.705E-26
		13609.664	McKellar, Goetz and Ramsay, 1976 [26]		
		13609.650	Durie and Herzberg, 1960 [3]		
	R(2)	13652.216	Trauger and Mickelson, 1983 [35]	13652.218(2)	9.860E-27
		13652.215	McKellar, Goetz and Ramsay, 1976 [26]		
		13652.205	Durie and Herzberg, 1960 [3]		
	R(3)	13678.322	McKellar, Goetz and Ramsay, 1976 [26]	13678.326(2)	7.362E-27
		13678.330	Durie and Herzberg, 1960 [3]		
	R(4)	13687.715	McKellar, Goetz and Ramsay, 1976 [26]	13687.723(2)	1.782E-27
	P(2)	16219.473	McKellar, Goetz and Ramsay, 1976 [26]	16219.479(2)	2.264E-27
	P(1)	16326.791	McKellar, Goetz and Ramsay, 1976 [26]	16326.805(2)	3.055E-27
	R(0)	16486.533	Trauger and Mickelson, 1983 [35]	16486.548(2)	5.916E-27
(6-0)		16486.537	McKellar, Goetz and Ramsay, 1976 [26]		
			Smith and Gelfand, 1980 [50]		
	R(1)	16537.820	Trauger and Mickelson, 1983 [35]	16537.818(2)	8.459E-27
		16537.816	McKellar, Goetz and Ramsay, 1976 [26]		
			Smith and Gelfand, 1980 [50]		
		16537.8368(30)	Dalby and Vigué, 1979 [36]		
	R(2)	16569.404	McKellar, Goetz and Ramsay, 1976 [26]	16569.400(2)	5.834E-27
			Smith and Gelfand, 1980		
	R(3)	16581.008	McKellar, Goetz and Ramsay, 1976 [26]	16580.958(2)	2.314E-27
	P(1)	19095.994	McKellar, Goetz and Ramsay, 1976 [26]	19096.018(3)	1.054E-27
	R(0)	19252.044	McKellar, Goetz and Ramsay, 1976 [26]	19252.075(3)	2.055E-27
	R(1)	19295.975	Trauger and Mickelson, 1983 [35]	19295.984(3)	2.947E-27
(6-0)		19295.961	McKellar, Goetz and Ramsay, 1976 [26]		
	R(2)	19316.541	McKellar, Goetz and Ramsay, 1976 [26]	19316.557(3)	2.038E-27
	R(3)	19313.507	McKellar, Goetz and Ramsay, 1976 [26]	19313.495(3)	8.103E-28

Table 1.

Review of the observations of HD absorption lines available in the literature. The corresponding calculated values of the line centers and line intensities as obtained from Refs. [6, 8, 22] are given. Part of the experimental line positions are not corrected from their pressure shift.

Notes

The list is limited to transitions detected by absorption spectroscopy.

^a Observation from electric field induced spectra [34] (not plotted on Fig. 1).

Experimentally, the main difficulty is related to the weakness of the absorption lines to be detected. The absorption spectrum of molecular hydrogen and deuterium, H₂ and D₂, 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 H₂ and D₂ spectra are extremely sparse. For instance, less than fifty H₂ absorption lines have been reported so far in the literature, up to the fourth overtone band near 19000 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 E1 transitions in HD was predicted by Wick in 1935 [1]. Thus the HD absorption spectrum exhibits weak electric dipole (E1) rovibrational 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 0-20000 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, 23-37]. **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 R.A. McKellar et al. who reported a total of 39 transitions in the 70's and early 80's [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) give 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.

Modern laser spectroscopic techniques like CRDS provide a much higher sensitivity and require a small gas quantity (typical CRDS cells have a volume of 100 cm³). 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 $\alpha_{\min} \approx 5 \times 10^{-11}$ 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 μ m 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 μ m by

using a newly developed cavity ring down spectrometer (CRDS) with a VECSEL (Vertical External Cavity Surface Emitting Laser) 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:

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

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 (Vertical External Cavity Surface Emitting Laser) [42, 43] developed by Innoptics was used as a light source near $2.3\mu\text{m}$. 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 output power of the VECSEL was 3 mW for temperature of the structure regulated from -4°C to 12°C . A mode hop free tuning range of about 11 cm^{-1} was achieved *via* cavity length modulation for PZT voltage of 30V, maintaining constant both the temperature of the structure and the pump current (typically 380 mA here). Overall, a total tuning range from 4295 to 4380 cm^{-1} could be covered with the VECSEL at disposal. In the present experiment, the recordings were performed at 2°C and limited to a spectral region of about 3 cm^{-1} around the predicted position of the $S(3)$ 1-0 line of HD at 4359.94 cm^{-1} [6].

The VECSEL beam is collimated by an antireflection coated lens followed by an optical isolator to avoid perturbation by backscattered light. The light emitted by the VECSEL is then

injected into an acousto-optic modulator (AOM Model ACM-1002AA1 from IntraAction Corp.) which interrupts the beam injection at resonance with cavity. As a consequence of the distortion of the Gaussian beam profile by the AOM, the beam is coupled into a single mode fluoride fiber (from Thorlabs) for spatial filtering before injection into the CRDS cell. Resonances between the laser light and a longitudinal mode of the CRDS cavity are achieved by changing the cavity length over one Free Spectral Range (FSR) thanks to the rear mirror of the cavity mounted on a PZT. Ring-down times are measured with an InGaAs PIN photodiode. At the considered wavelength, the 1.4 meter long CRDS cavity has a finesse of about 78000 leading to ring-down times of about 105 μ s for the evacuated cavity.

The CRDS cell was filled with HD at room temperature. The pressure measured by a capacitive transducer (model ATM.1ST from STS; 1000 mbar full range; accuracy of $\pm 0.1\%$ of the full range) and the cell temperature ($T = 297.5 \pm 0.5$ K) measured by a thermo sensor (TSic 501) were monitored during the recordings. A total of 10 spectra were recorded with typical spectral step of 0.002 cm^{-1} , for different pressures ranging between 50 and 650 Torr. About 35 ring-down events were averaged for each spectral point leading to a minimum detectable absorption coefficient, $\alpha_{min} \approx 5 \times 10^{-10} \text{ cm}^{-1}$.

The HD sample (from Sigma-Aldrich) has a 99.3% chemical purity and 98.5% isotopic purity. As shown below, in spite of its low relative concentration (< 30 ppm), methane absorption spectrum was detected leading to partial overlapping with the HD line under study.

The frequency calibration of the spectra was achieved by deflecting about 10% of the light emitted by the VECSEL to a double reference channel composed of a Fabry-Pérot étalon and of a 10 cm reference cell filled with CH_4 at atmospheric pressure. The fringes of the Fabry-Pérot signal (0.05 cm^{-1} FSR) were used as a ruler to correct the non-linearity of the PZT scanning. The maximum error related to this linearization of the frequency axis was determined to be $\pm 1 \times 10^{-3} \text{ cm}^{-1}$. After linearization of the frequency axis, a rough absolute spectral calibration was performed using the spectrum of the methane reference cell. The calibration was then refined by using CH_4 impurity lines present in the CRDS spectrum and CH_4 position values from the HITRAN database [22]. The HITRAN CH_4 reference lines are given with a wavenumber uncertainty below 0.001 cm^{-1} (error codes 4 or better). In order to minimize the uncertainty related to the unknown pressure shifts of the CH_4 and HD line centers, the $S(3)$ HD line center was determined from the recording at 100 Torr. At this pressure, pressure shifts are expected to be smaller than $2 \times 10^{-4} \text{ cm}^{-1}$ [44]. The fitted center of the HD line was provided by the fit procedure with 1σ standard deviation equal to $2.4 \times 10^{-4} \text{ cm}^{-1}$. As a result, the uncertainty budget on our wavenumber scale leads to an overall error bar

of about 0.002 cm^{-1} , mainly dominated by errors related to the linearization of the frequency axis and by the uncertainty on the methane line positions used as reference lines. The resulting value of the HD $S(3) 1-0$ position at null pressure is determined to be $4359.9402(20) \text{ cm}^{-1}$.

Fig. 2 shows a sample of the recorded spectra at 100, 200, 450 and 600 Torr. The HD line is detected superimposed to a dense background of lines due to methane. It is interesting to note that, the relative height of the HD and nearby methane lines vary markedly with pressure. The HD peak maximum increases much quicker than the CH_4 peak maxima. This is due to a strong Dicke narrowing of the HD line with increasing pressure values [38, 45]. Contrary to methane lines, the width of the HD line is decreasing with pressure up to 650 Torr.

Fig. 2.

Pressure dependence of the cavity loss rates, $\frac{1}{c\tau}$, in the region of the $S(3) 1-0$ line of HD for different pressures varying from 0 Torr (empty cell) to 600 Torr of HD.

Another interesting observation from **Fig. 2** is a strong increase of the spectra baseline level with pressure. This increase which largely exceeds the cumulative effect of methane

lines broadened by pressure is interpreted as due to the collision induced absorption (CIA) band of HD.

The retrievals of the $S(3)$ 1-0 HD line intensity and of the CIA require to account satisfactorily for the methane contribution at different pressures by using a multiline fitting program. The treatment of the spectra is presented in the next Section.

3. RESULTS

3.1 The $S(3)$ 1-0 line

Fig. 3.

Comparison of the CRDS spectrum of HD at 650 Torr with a spectrum fit in the vicinity of the $S(3)$ 1-0 line. All the lines belong to CH_4 except the HD and CH_3D lines which are indicated. A Voigt profile was used for the fit of CH_4 and HD lines (see Text).

Upper panel: Experimental (red solid line) and fitted (dashed line with grey under the curve) spectra.

Lower panel: Residuals between the experimental spectra and the simulation.

The background absorption due to methane present in our sample was an important drawback for the spectra analysis which limited the accuracy of the retrieved spectral parameters. According to the HITRAN database [22], the investigated spectral range includes CH_4 lines with intensities larger than 10^{-21} cm/molecule *i.e.* six orders of magnitude larger than the intensity of the HD line under study. On the basis of spectral fits and HITRAN line

intensities, the relative concentration of CH_4 in our sample was estimated to range between 14 to 23 ppm, depending on the spectrum. In addition, the different spectra show strong CH_3D lines as a result of considerable deuterium, most probably resulting from the HD synthesis: the CH_3D relative concentration was found to be mostly identical in the different spectra at a value of 28.5 ppm i.e. larger than the CH_4 concentration.

Fig. 4.

Line profile simulations of the CRDS spectrum of HD in the region of the $S(3)$ 1-0 line of HD. Note that the baseline is corrected from the collisional induced absorption contribution.

Upper panels: Experimental spectra at 100 and 600 Torr,

Lower panels: Corresponding residuals between the experimental spectra and the simulations using a Nelkin-Ghatak profile for the HD line and a Voigt profile for the superimposed methane lines (see Text).

Even if the overall agreement was good, the comparison of the CRDS spectra to spectra simulations based on HITRAN positions and scaled CH_4 and CH_3D intensities revealed significant deviations which may be attributed to some inaccuracies in the HITRAN methane line list and/or possible contribution of additional impurities (the certificate analysis of our HD sample indicates that the total amount of CH_4 and C_2H_6 should be less than 30 ppm). In those circumstances, we decided to perform our own fit of the background contribution to the recorded CRDS spectra by using an interactive least squares multi-line fitting program assuming a Voigt profile [46] (<http://sourceforge.net/projects/fityk/> version v 1.1.1). The Half Width at Half Maximum (HWHM) of the Gaussian component was fixed to the theoretical value of the Doppler width of the considered molecule or isotopologue. **Fig. 3** illustrates the quality of the spectrum reproduction at 100 and 600 Torr. In the simulation displayed in **Fig.**

3, the HD line was also fitted using a Voigt-type line shape. While methane lines are very well reproduced with the Voigt profile, the W shape residual corresponding to the HD line is a typical signature of the Dicke narrowing effect.

As illustrated in **Fig. 4**, much reduced residuals are obtained using a Nelkin-Ghatak line profile for the HD line. For each pressure value, the line center (ν_0), integrated line absorption coefficient, A_{ν_0} (cm^{-2}), and the corresponding local baseline (assumed to be constant over the fitted spectral interval) were provided by a homemade multi-line fit.

As mentioned above, our line center value at zero pressure was determined to be $4359.9402(20) \text{ cm}^{-1}$ in excellent agreement with its *ab initio* value [6] - $4359.940(1) \text{ cm}^{-1}$ - but the accuracy of our determination (about 0.002 cm^{-1}) did not allow reducing the error bar or estimating the pressure shift.

Fig. 5 shows the pressure dependence of the integrated line absorption coefficient. The line intensity, S_{ν_0} ($\text{cm}/\text{molecule}$), was derived from the fitted value of the proportionality factor:

$$S_{\nu_0}(T) = A_{\nu_0}(T) / N \quad (2)$$

where ν is the wavenumber in cm^{-1} , and N is the HD concentration in $\text{molecule}/\text{cm}^3$ obtained from the measured pressure and temperature values: $N = 0.978P/kT$ (0.978 is the stated HD relative concentration of our sample).

Fig. 5.

Variation of the integrated absorption coefficient of the $S(3) 1-0$ line *versus* the HD pressure. The line intensity was derived from the fitted slope (black solid line).

We obtain an intensity at 297.5 K of $2.54(6) \times 10^{-27}$ cm/molecule leading to a value of $2.52(6) \times 10^{-27}$ cm/molecule at the 296 K HITRAN reference temperature. The error bar of about 3% corresponds to the fit error and does not include systematic errors (see below). The HITRAN intensity value - 2.166×10^{-27} cm/molecule - is given with a 10-20% error bar which is consistent with our value. In fact the most recent theoretical calculations by Komasa and Pachucki [8] can provide electric dipole and electric quadrupole moments with a much higher accuracy (<1%), probably out of reach by experiment. The quality of these *ab initio* intensity (and position) values was validated by recent state-of-the-art experimental studies of H₂ [11], HD [38] and D₂ [15] transitions of both E1 and E2 types. Unfortunately, Komasa and Pachucki did not publish a separate electric quadrupole moment function for HD. Thus, the HITRAN intensities of E2 transitions were calculated using the electric quadrupole moment of H₂ [47]. As a result of possible error related to the Born Oppenheimer breakdown, a conservative uncertainty value between 10% and 20% was attached to the HITRAN E2 intensities of HD. In fact, the comparison to HITRAN values of the E2 HD intensities measured by CRDS in the first overtone band [38] (see **Fig. 1**) indicates that HITRAN error bars are overestimated. This comparison leads to an intensity ratio of 1.031(38) for nine E2 lines, what is a remarkable result considering that the considered E2 transitions include line intensities spanning five orders of magnitude down to 3×10^{-29} cm/molecule. In summary, our intensity measurement of the *S*(3) 1-0 line of HD is consistent with HITRAN value. Considering the line overlapping with methane impurity lines, the 12% difference between the two values can be considered as a satisfactory result. The main part of this deviation is believed to have an experimental origin related to nearby CH₄ lines not fully accounted by the multi-line fit or to underlying weak lines due to methane or other impurities not included in the fit.

At the final stage of the analysis, Komasa and Pachucki provided us with their complete HD line list. The agreement with HITRAN intensity values was found excellent (better than 0.1%) both for E1 and E2 transitions. Consequently, the approximation used for the calculation of HITRAN intensities of E2 transitions has no impact on the obtained values and HITRAN error bars are believed to be largely overestimated.

3.2 The HD collision induced absorption near 4360 cm^{-1}

Fig. 6

Retrievals of the HD CIA at 4360 cm^{-1} from CRDS-VECSEL spectra at 200 and 600 Torr.

The loss rate, $(\frac{1}{c\tau})$, of the CRDS cell (red solid line) is superimposed to the spectrum simulation of methane lines broadened by HD (black line with grey under the curve). The HD CIA is obtained by difference between the baseline of the spectrum simulation and the loss rate of the evacuated cell.

The broad collision induced absorption (CIA) bands of molecular hydrogen have attracted interest for a long time. Considerable experimental efforts were undertaken to measure the H_2 bands in a large range of pressure and temperature conditions relevant for planetary atmospheres and “cool” stellar objects [19, 48-51]. Due to the weakness of the CIAs, most of the literature measurements were performed with very high gas densities ranging between a few tens and more than 100 atm. As shown by our recent measurements of the H_2 CIA in the region of the first overtone band near 8075 cm^{-1} [14], the CRDS technique provides sufficient sensitivity and base line stability to derive the hydrogen CIA with pressure values limited to 1 atm. This is an important advantage to make negligible three-body collision effects which may have a significant contribution at higher pressure. In the case of HD, to the best of our knowledge, no study was dedicated to the CIA measurements. The only result we could find in the literature is the CIA spectrum between 3300 and 4000 cm^{-1} displayed in Fig. 1 of Ref. [20] dedicated to the study of interference effects between the allowed HD dipole transition moments and the dipoles induced during collisions.

In a CRDS experiment, the CIA is expected to show up as an increase of the baseline level of the spectra when the cell is filled by the gas. In the present case, as illustrated by **Fig. 2**, part of the increase of the baseline level is due to the contribution of the methane lines which are pressure broadened by HD. This contribution has to be estimated from a spectra fit and subtracted to get the CIA value. Note that losses due to Rayleigh scattering are negligible at the considered wavelength.

We chose a spectral interval showing weak methane absorption near 4360.4 cm^{-1} in order to minimize the uncertainty on the methane contribution. The multi-line fit of the methane lines located in the considered spectral interval provided the local baseline corresponding to the sum of the loss rate at zero pressure, the CIA and a weak contribution of the wings of the strong methane lines located outside the fitted spectral interval (see **Fig. 6**). The latter, estimated from a spectrum simulation was found to be small (4% of the CIA at most) and subtracted. In this way, the CIA could be derived at different pressures. The resulting pressure dependence presented in **Fig. 7** is approximately quadratic. The fit of the CIA values *versus* P^2 leads to an absorption coefficient normalized by the gas density squared equal to of $1.17(4)\times 10^{-6}\text{ cm}^{-1}\text{ amagat}^{-2}$. For comparison, we estimated this normalized coefficient from the absorption coefficients at 35 amagat of Fig. 1 of Ref. [20]: the CIA frequency dependence displayed in the $3300\text{--}4000\text{ cm}^{-1}$ interval corresponds at maximum to value of about $2.6\times 10^{-6}\text{ cm}^{-1}\text{ amagat}^{-2}$ near 3650 cm^{-1} decreasing down to $1.6\times 10^{-6}\text{ cm}^{-1}\text{ amagat}^{-2}$ at 4000 cm^{-1} ; which is consistent with our value of $1.17(4)\times 10^{-6}\text{ cm}^{-1}\text{ amagat}^{-2}$ at 4360 cm^{-1} .

In the case of H_2 , *ab initio* calculations have made possible to account for the measured CIA bands of H_2 with remarkable precision [18,19]. For instance, an agreement within 10% was obtained between the *ab initio* and CRDS values in the 2-0 H_2 band near 8075 cm^{-1} . Unfortunately, similar calculations were not reported so far for HD, probably because of the lack of astrophysics interest. Nevertheless, the H→D substitution may provide valuable tests for the theoretical models used for H_2 .

Fig. 7

Pressure dependence of the HD CIA at 4360.4 cm^{-1} for pressure values up to 650 Torr.

4. CONCLUDING REMARKS

In this contribution, we have presented the first spectroscopic application of a VECSEL (Vertical External Cavity Surface Emitting Laser) for Cavity Ring Down Spectroscopy (CRDS) near $2.3 \text{ }\mu\text{m}$. As an illustration of the capabilities of the CRDS-VECSEL set up, the first detection of the $S(3)$ quadrupole electric transition of the fundamental band of HD is reported. The HD line parameters were retrieved from spectra simulations including a dense background of lines due to CH_4 and CH_3D present in the sample with concentration on the order of 30 ppm. Our line center value was found in good agreement ($0.4 \times 10^{-4} \text{ cm}^{-1}$ or 12 MHz) with the more accurate *ab initio* value $4359.9398(6) \text{ cm}^{-1}$ [6]. Our intensity value is overestimated by 12% compared to the *ab initio* value provided in the HITRAN database. This agreement can be estimated satisfactory considering the overlapping with methane absorption lines.

The mechanical stability of the CRDS set up allowed us deriving the CIA absorption coefficient from the increase of the spectra baseline from its value at zero pressure, after subtraction of the methane contribution. The pressure dependence of the CIA was found to be

quadratic and the absorption coefficient at 4360.4 cm^{-1} normalized by the gas density squared was estimated to be $1.17(4)\times 10^{-6}\text{ cm}^{-1}\text{ amagat}$

The developed CRDS-VECSEL set up gives access to the important $2.3\text{ }\mu\text{m}$ transparency window of major interest for various atmospheric applications. An important advantage of VECSEL light sources is their wide tunability allowing for a spectral coverage significantly wider than that provided by commercial DFB diode lasers. For instance, the VECSEL at disposal allowed for a continuous coverage of the $4295\text{-}4380\text{ cm}^{-1}$ spectral interval. In the near future, we are planning to use the high sensitivity provided by the CRDS-VECSEL technique for wide range investigations of the major atmospheric species in particular water, carbon dioxide and their isotopologues.

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