Journal of Molecular Spectroscopy 267 (2011) 36–42

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Electric quadrupole and dipole transitions of the first overtone band of HD by CRDS between 1.45 and 1.33 μm

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ARTICLE INFO

Article history:
Available online 17 March 2011

Keywords:
Hydrogen
HD
Electric dipole
Electric quadrupole
Absorption spectroscopy
CRDS

ABSTRACT

The first overtone band of HD has been recorded by CW-Cavity Ring Down Spectroscopy between 6900 and 7900 cm^{-1}. The noise equivalent absorption of the spectra was on the order of $\alpha_{min} \approx 5 \times 10^{-11}$ cm^{-1}. Eleven dipole electric transitions – *P*(1)–*P*(2) and *R*(0)–*R*(8) – and nine quadrupole electric transitions – *Q*(1)–*Q*(4) and *S*(0)–*S*(4) – were accurately measured. The uncertainty on the line positions and the line strengths is on the order of 0.001 cm^{-1} and 2%, respectively. The minimum intensity reported is 1.04×10^{-30} cm/molecule for the *R*(8) line which is the most rotationally excited absorption line of hydrogen reported so far. The dipole and quadrupole transition moments were derived from the measured line strengths. The agreement with the most recent theoretical calculations is found to be within the experimental uncertainty for both line positions and line intensities.

1. Introduction

Contrary to the symmetric isotopologues, H_2 and D_2, 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. Thus the absorption spectrum of HD exhibits weak electric dipole (E1) rovibrational transitions in addition to the even weaker electric quadrupole (E2) transitions which are the only allowed transitions in homonuclear species. Long after the prediction of their existence in 1935 [1], the E1 transitions in HD continue to be of interest. One of the reasons is that hydrogen and its isotopologues are test species for theoretical calculations and that discrepancies have been found between some experimental results and quantum mechanics calculations, in particular for line intensities.

The first detection of E1 transitions of HD was reported in 1950 by Herzberg who used path lengths up to 1 km to detect a few transitions of the (v'–v'') = (3–0) and (4–0) bands in the photographic infrared [2]. Since then, several experimental works have been devoted to the detection and measurement of HD transitions from the pure rotational spectrum to the (6–0) vibrational band near 520 nm [3–16]. A major contribution is due to Robert McKellar et al. who reported position and intensity measurements in a series of contributions published in the 1970s and early 1980s [4–8]. These observations obtained with a multiple pass cell associated with a grating spectrograph or a Fourier Transform Spectrometer were used to derive the spectroscopic parameters and the electric dipole moments of the v = 1–6 upper vibrational levels. The present Special Issue of the Journal of Molecular Spectroscopy dedicated to Robert Mc Kellar and Philip Bunker is an ideal opportunity to present our recent measurements of the first overtone band of HD by high sensitivity CW-Cavity Ring Down Spectroscopy (CRDS) between 6900 and 7900 cm^{-1}.

To the best of our knowledge, the only previous observations concerning this band are due to (i) Durie and Herzberg [3] who measured the positions of seven transitions (*P*(1)–*P*(3) and *R*(0)–*R*(3)), (ii) McKellar [6] who measured the intensities of the *P*(1), *R*(0) and *R*(1) lines and more recently, (iii) Lin et al. [16] who reported the centre of the *P*(5) line with an accuracy better than 0.01 cm^{-1}. The sensitivity provided by the CRDS technique has allowed us to measure accurately not only the *P*(1)–*P*(2) and *R*(0)–*R*(8) electric dipole transitions but also the *Q*(1)–*Q*(4) and *S*(0)–*S*(4) electric quadrupole transitions. Note that only one E2 transition (the *S*(0) line of the fundamental band [6]) was reported for HD prior to our work. Of importance for the comparison of the absolute line intensities with theoretical values is the fact that most of the measurements could be performed at low pressure (10 Torr) which limits the impact of collisional effects on the line profile and then reduced the uncertainty on the derived intensity values (see below).

After the description of the experimental setup (Section 2), we will present the line profile analysis and the line intensities determination (Section 3). Section 4 will be devoted to the derivation of the spectroscopic constants of the v = 0 and 2 vibrational level and to the calculation of the dipole and quadrupole transition moments. Finally, the obtained results will be discussed and compared to very recent theoretical calculations (Section 5).

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doi:10.1016/j.jms.2011.02.001

2. Experiment details

The high sensitivity CW-CRDS absorption spectrum of the first overtone of HD was recorded, line by line, in the 6900–7900 cm^{-1} region, using a highly enriched HD sample from Sigma Aldrich. The stated purity of the sample measured by mass spectrometry was 96.4%.

The fibered distributed feedback (DFB) laser CW-CRDS spectrometer used for the recordings has been described in detail in Refs. [17–19]. Each DFB laser diode has a typical tuning range of about 40 cm^{-1} by temperature tuning from −10 °C to 60 °C. Our set of DFB laser diodes allows for a continuous coverage of the 6900–7920 cm^{-1} region but the spectra were recorded only in a 5 cm^{-1} spectral interval around each predicted line position. The E1 and E2 transitions were searched on the basis of their predicted line centre calculated from the energy levels recently reported in Ref. [20].

The electro-polished stainless steel ring down cell (l = 1.42 m, inner diameter Φ = 11 mm) was fitted by a pair of super-mirrors. A single set of high reflective mirrors was used for all the recordings. The reflectivity of the mirrors in the studied region corresponds to empty cell ring-down times varying from 100 to 300 μs. About 20 ring down events were averaged for each spectral data point; each line together with its surroundings was scanned at a spectral resolution of about 2×10^{-3} cm^{-1} (60 MHz). The achieved noise equivalent absorption α_{min} was in the range of 3×10^{-11} to 10^{-10} cm^{-1} depending on the wavelength. The pressure measured by a capacitance gauge (MKS 10 Torr and 1000 Torr full range with 0.1% stated accuracy) and the ring down cell temperature (T = 294 ± 1 K) measured by a thermo sensor (TSic 501) were monitored during the recordings. The spectra were recorded with pressure values of 10.0 Torr except the $Q(J)$ lines and the $R(8)$ line which were measured at 100 and 737 Torr, respectively. In addition, the pressure dependence of the $P(2)$ and $R(5)$ lines was studied from a series of recordings with pressure values up to 737 Torr.

Each 5 cm^{-1} wide piece of spectrum was calibrated independently on the basis of the wavelength values provided by a Fizeau type wavemeter (WSU-30 Highfinesse, 5 MHz resolution and 20 MHz accuracy). The calibration was further refined by shifting the whole spectrum in order to match reference positions of the water transitions present as an impurity. Water reference line positions were taken from the HITRAN database [21]. The typical uncertainty on the line positions is estimated to be less than 1×10^{-3} cm^{-1} (30 MHz).

The E1 transitions form the P and R branches corresponding to $\Delta J = -1$ and $\Delta J = +1$, respectively while the E2 transitions form the O, Q and S branches corresponding to $\Delta J = -2$, 0 and +2, respectively. In the investigated energy region (6900–7900 cm^{-1}), a total of eleven electric dipole transitions ($P(1)$–$P(2)$ and $R(0)$–$R(8)$) and nine electric quadrupole transitions ($Q(1)$–$Q(4)$ and $S(0)$–$S(4)$) were detected. The observed transitions are listed in Table 1 while Fig. 1 shows an overview of the spectrum. We have included in Table 1, the position values reported in the pioneer work of Durie and Herzberg [3]. To the best of our knowledge, these values are, with the $P(5)$ position of Ref. [16], the only position values available in the literature for this band.

Table 1
Centres, intensities and transition moments of the transitions of HD measured by CRDS between 6900 and 7900 cm^{-1}.

Transition	Position (cm^{-1})	Intensity at 294 K (10^{-26} cm/molecule)	Moment[a]
Electric dipole			
*P*1	6997.6494	12.53	1.815
	6997.666[b]		1.7(2)[c]
*P*2	6901.4014	9.076	1.700
	6901.403[b]		
*R*0	7168.4697	25.55	2.059
	7168.428[b]		1.9(2)[c]
*R*1	7241.8497	35.77	2.131
	7241.818[b]		2.0(2)[c]
*R*2	7306.4839	24.79	2.229
	7306.541[b]		
*R*3	7361.9037	9.788	2.311
	7361.911[b]		
*R*4	7407.7134	2.353	2.385
*R*5	7443.5983	0.3583	2.453
*R*6	7469.3298	0.0357	2.522
*R*7	7484.7654	2.363×10^{-3}	2.579
*R*8	7489.8463	1.044×10^{-4}	2.605
Electric quadrupole			
*Q*1	7079.2422	0.0788	1.314
*Q*2	7064.0077	0.0371	1.281
*Q*3	7041.2418	0.0145	1.348
*Q*4	7011.0492	0.0034	1.385
*S*0	7331.0778	0.1218	1.365
*S*1	7484.3246	0.1512	1.367
*S*2	7627.1438	0.0973	1.378
*S*3	7758.5671	0.0388	1.426
*S*4	7877.7461	8.34×10^{-3}	1.377

[a] For the *P*1–*P*2 and *R*0–*R*7 transitions, the moment is the electric dipole matrix element in 10^{-5} D. For the Q1–Q3 and S0–S4 transitions, the moment is the electric quadrupole matrix element in 10^{-10} D cm.
[b] Ref. [3].
[c] Ref. [6].

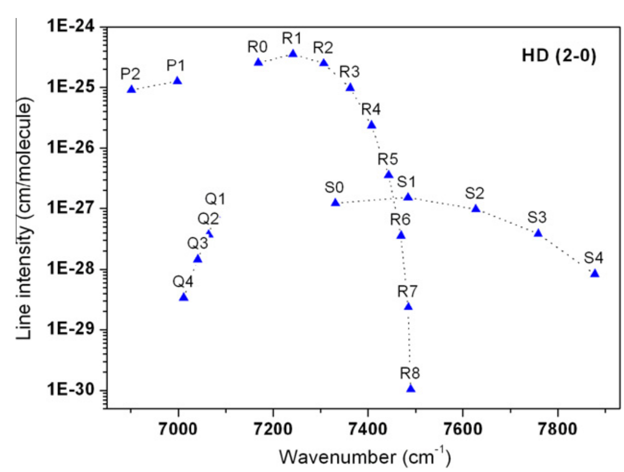

Fig. 1. Overview of the 20 transitions of the first overtone of HD recorded by CRDS between 6900 and 7900 cm^{-1}. The *P* and *R* branches correspond to electric dipole transitions while the *Q* and *S* lines are electric quadrupole transitions. Note that the intensity scale spans over five orders of magnitude.

3. Line profile analysis and intensities derivation

The profiles of hydrogen rovibrational transitions are well known to show a marked Dicke narrowing with increasing pressure values. The width at half maximum of a H_2 line can be reduced by more than a factor of four compared to the Doppler width [22,23]. The detailed modelling of the line shape of hydrogen transition requires the development of sophisticated models and the comparison with high accuracy experimental spectra. Such analyses are out of the scope of the present report but it is nevertheless important to achieve a satisfactory reproduction of the line shape as it has a direct impact on the line intensity values. For instance, the effect of intercollisional interference at moderate pressures (up to 3 atm) has been proposed to explain discrepancies between experimental and theoretical line strengths in H_2 [24,25].

The $R(5)$ line at 7443.5983 cm^{-1} was chosen to study the pressure dependence of its profile. At low pressure, the measured line