Sub-MHz accuracy measurement of the S(2) 2–0 transition frequency of D_2 by Comb-Assisted Cavity Ring Down spectroscopy

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ABSTRACT

The line position of the very weak S(2) transition of deuterium in the 2–0 band has been measured with a Comb-Assisted Cavity Ring Down spectrometer. The high sensitivity spectra were recorded at 5 and 10 mbar with a Noise Equivalent Absorption, α_{min}, of 8×10^{-11} cm^{-1}. The line positions at 5 and 10 mbar were measured with sub-MHz accuracy (460 and 260 kHz, respectively). After correction of the line pressure-shift, the frequency at zero pressure of the S(2) transition of the first overtone band was determined to be 187104 299.51 ± 0.50 MHz. This value agrees within 1.7 MHz with the frequency obtained from the best available *ab initio* calculations and corresponds to only 15% of the claimed theoretical uncertainty.

1. Introduction

Highly sophisticated *ab initio* calculations predicting all the rovibrational energy levels and transition moments of H_2, HD and D_2 are now available [1–3]. These calculations, including relativistic and Quantum Electro Dynamic (QED) corrections, lead to predictions of the transition frequencies with accuracies from a few 10^{-5} cm^{-1} for pure rotational transitions to 10^{-3} cm^{-1} for electronic transitions around 23000 cm^{-1}.

In the case of the H_2 [4,5] and HD [6] isotopologues, we have recently reported a systematic CRDS investigation of the transitions of the first overtone band (2–0) with line positions determined with a typical uncertainty of 10^{-3} cm^{-1} (30 MHz). The error bar on the corresponding theoretical values is of the same order of magnitude and experimental and computed values were found to agree within their combined error bars [4–6]. A similar agreement was reported for the S(3) electric-quadrupole transition of the 3–0 overtone of H_2 at ~12424 cm^{-1} which was determined with a 1.6 MHz accuracy [7] using a CRDS spectrometer, a temperature-stabilized Fabry-Perot interferometer and a Rb refer-ence line. The authors of Ref. [7] noted that the difference between their value and the theoretical calculations (9.6 MHz) was one order of magnitude smaller than the claimed uncertainty of the calculations (75 MHz). As a sake of completeness, let us mention that the same experimental approach was used to determine eight line positions of the same 3–0 H_2 band between 11737 and 12755 cm^{-1} with uncertainties ranging from 9 to 231 MHz, depending on the line strength [8].

In the case of D_2, several studies reviewed in [9] have reported line positions of the very weak electric quadrupole transitions using different spectroscopic techniques [10–21]. From all these measurements, very few transition frequencies are determined with sufficient accuracy to test the best theoretical predictions. Maddaloni et al. [12] measured the S(0) and S(1) transitions for the 1–0 fundamental band near 3200 cm^{-1} with an accuracy of 6 MHz with a Cavity Ring Down (CRD) spectrometer based on a difference-frequency-generation source related to the Cs-clock pri-mary standard *via* an optical frequency comb synthesizer. Gupta et al. [21] reported the S(2) 2–0 position near 6241 cm^{-1} with a 3 MHz uncertainty using an off-axis integrated cavity output spectrometer (ICOS) and a reference cell. Finally, we performed an extensive CRDS study of the Q(2), Q(1), S(0)–S(8) 2–0 transitions by very high sensitivity CW-CRDS between 5850 and 6720 cm^{-1} but the accuracy of the reported line positions was at the 30 MHz level [9].

In the present work, the frequency of the S(2) 2–0 line position is reported with a sub-MHz accuracy by using a CRD spectrometer coupled to a self-referenced frequency comb. The intensity of this very weak line has been measured to be 4.78×10^{-28} cm/molecule [9].

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2. Experimental set-up

The CRD spectrometer used here is detailed in Refs. [22–24]. A fibered DFB laser diode is coupled to a 1.40-m long high finesse optical cavity (with mirrors reflectivity better than 99.999%). The CRDS cell was filled with high purity D_2 from Isotec (99.97% of D atoms; chemical purity of 99.999%) at 5 and 10 mbar. The cell temperature and pressure were monitored during the spectrum acquisition by temperature sensors (TSic 501, IST-AG, ±0.1 °C accuracy) fixed on the cell surface and a capacitance gauge (model 626B from MKS Instruments; 10 mbar, 0.25% accuracy of reading), respectively. The spectra were recorded at temperatures remaining within 296.9 ± 0.1 K.

The absorption coefficient, derived from the ring-down time, is recorded as a function of the frequency by changing continuously the laser temperature. Noise Equivalent Absorption coefficients at the 8×10^{-11} cm^{-1} level are achieved without averaging of the ring-down events.

Fig. 1 shows a typical example of a spectrum of the S(2) 2–0 line recorded over a 0.25 cm^{-1} (7.5 GHz) interval (600 points) within 1 min. Overall, 118 and 116 of such spectra were recorded at 5 and 10 mbar, respectively.

The data acquisition is similar to that used in [25] for the measurements of CO (3–0) transitions frequencies with sub-MHz accuracy. The laser diode frequency is accurately determined through the beat note between a fraction of the DFB laser beam and the nearest mode of an Er-based 100-MHz self referenced comb (FFS model from Toptica). The repetition and carrier-envelop offset frequencies of the comb are referred to a 10 MHz rubidium frequency standard with a relative instability of 10^{-12} in one second. The uncertainty of the DFB laser frequency is limited by the determination of the beat note frequency measured with an uncertainty of about ±400 kHz mainly coming from the jitter of the DFB source during the beat note measurement. According to the fact that the S(2) line is typically described here by ~200 spectral points, within its full width, the resulting contribution to the uncertainty on the line center determination is expected to be about $\sqrt{200} \approx 15$ times better (~26 kHz). In such conditions the main contribution to the line position error derives from the ordinate axis, i.e. from the shot to shot fluctuations of the ring downs.

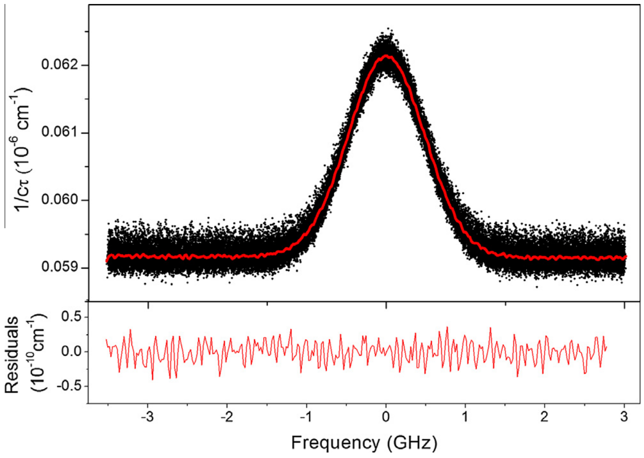

Fig. 1. Superposition of all the CRDS spectra (black dots) recorded at 10 mbar for the S(2) transition of the first overtone band of D_2. The red line is an average of the raw data over 20 MHz large bins. The residuals, with a noise level of 1.5×10^{-11} cm^{-1}, correspond to the difference between the averaged data and the Gaussian fit (not shown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We have verified that only a very small systematic bias (<20 kHz) affects the frequency axis of our comb-calibrated CRDS spectra by measuring the positions of C_2H_2 lines and comparing them against literature data reported with kHz accuracy [26]. Consequently, the line center determined from a fit of the line profile can be considered as an absolute value.

3. Results and discussion

Each recorded spectrum is fitted with a Voigt profile providing the transition frequency (Fig. 1). For this fit, the Gaussian component was fixed to the value calculated from the temperature measured during the spectrum recording (i.e. 296.9 K) and a linear base line was adopted.

For the 5 mbar and 10 mbar series of spectra, the averaged positions are found to be 187 104 299.50 ± 0.46 MHz and 187 104 298.90 ± 0.26 MHz, respectively. The uncertainty given here corresponds to the standard deviation of the mean center given by the fit.

Other error sources related to the fit may contribute to the uncertainty budget.

Negligible change of the fitted frequency is observed when the Lorentzian part is fixed to zero or introduced in the fitting procedure. The impact of the base line fit was investigated by varying the amplitude and the center of the fitted spectral region. We observed that for an extension above 4.5 GHz, the average value of the fitted positions becomes essentially insensitive to the adopted extension and center. A 40 kHz uncertainty (1σ) was determined for the averaged line center coming from the base line uncertainty.

Due to a small frequency shift of the recorded spectral range with time, in some of the 10 mbar spectra, it was possible to detect a signature from the very close R(8) transition of the 3–0 band of $^{13}C^{16}O$, which was present as an impurity inside the cavity. The position of this line was measured at 187 099 538.98 MHz with an accuracy of 500 kHz [25]. Several tests including or not this CO line in the fit indicated that it contributes to the global error by no more than 20 kHz.

Weak interfering lines may also affect the D_2 transition frequency. Using the HITRAN2012 database [27], we have checked that the absorption due to the impurity species of our D_2 sample is below the noise level. In addition, we could not detect a signifi-cant drift of the measured frequencies with time (during 2.5 h) which could be caused by interfering lines resulting from desorption of molecules adsorbed on the wall of the CRD cell.

Finally, the impact of the line profile was considered. The experimental line shapes are satisfactorily reproduced with a Gaussian profile down to the noise level (Fig. 1). As our spectra were recorded at low pressure, the Dicke narrowing and speed dependence effects, which are known to affect the D_2 line profiles at higher pressures [21, 28], are believed to have a negligible impact on the retrieved line positions.

In summary, the total uncertainty on the 5 and 10 mbar positions is largely dominated by the fit uncertainty (0.46 and 0.26 MHz, respectively).

In spite of the low pressure of our recordings, the self pressure shift must be taken into account to derive the zero pressure line center to be compared to the *ab initio* value. The self-pressure shift coefficient was determined to be $-1.536 \pm 0.028 \times 10^{-3}$ cm^{-1} atm^{-1} and $-2.5 \pm 0.5 \times 10^{-3}$ cm^{-1} atm^{-1} by Gupta et al. [21] and Kassi et al. [9], respectively. To correct the 5 mbar and 10 mbar positions of their respective pressure shift, we adopted the error weighted mean value, namely $-1.6\,(2) \times 10^{-3}$ cm^{-1} atm^{-1}. It leads to a correction of −476 ± 65 kHz for the 10 mbar position. It is worth underlining that the uncertainty on the pressure shift

Table 1
Comparison between the frequencies measured in this work and reported in the literature for the S(2) transition of the 2–0 deuterium band.

		Absolute frequency (MHz)
This work	5 mbar	187 104 299.50 ± 0.46
	10 mbar	187 104 298.90 ± 0.26
	Null pressure	187 104 299.51 ± 0.50
Literature	ICOS [21]	187 104 280.4 ± 3
	CRDS [9]	187 104 340.4 ± 30
	ab initio [9]	187 104 301.4 ± 12

Table 2
Comparison of the calculated and measured wavenumbers of the transitions of the 2–0 band of D_2.

Band (v–0)	Transition	Line position		Ref.
		Calc. (cm^{-1}) [9]	Meas. (cm^{-1}) [a]	
(2–0)	Q(2)	5855.5834 (4)	5855.583 (1)	[9]
	Q(1)	5863.9371 (4)	5863.938 (1)	[9]
	S(0)	6034.6505 (4)	6034.650 (1)	[9]
			6034.6498 (10)	[21]
	S(1)	6140.6185 (4)	6140.620 (1)	[9]
			6140.62 (1)	[21]
	S(2)	6241.1277 (4)	6241.129 (1)	[9]
			6241.1270 (1)	[21]
			6241.12764 (2)	This work
	S(3)	6335.7173 (4)	6335.718 (1)	[9]
			6335.7168 (10)	[21]
	S(4)	6423.9668 (4)	6423.968 (1)	[9]
	S(5)	6505.5016 (4)	6505.502 (1) [b]	[9]
	S(6)	6579.9972 (4)	6580.002 (1)	[9]
	S(7)	6647.1828 (4)	6647.186 (3) [c]	[9]
	S(8)	6706.8422 (4)	6706.841 (1) [c]	[9]

[a] Line position at zero pressure limit. This note corrects the footnote *a* of Table 1 of Ref. [9] which mentioned that all positions were given for a 600 Torr pressure while all but S(7) and S(8) positions were given at null pressure.
[b] Highly blended with a water line.
[c] Value at 600 Torr.

coefficient has a limited impact in the present analysis because the CRDS sensitivity allows recordings to be performed at a low pressure. The global uncertainty resulting from the pressure shift correction and from the fit are 492 and 320 kHz for the 5 and 10 mbar determinations of the zero pressure values, respectively. Our final position at zero pressure, obtained as a mean value of these two determinations is 187 104 299.51 ± 0.50 MHz.

Table 1 summarizes the different frequency values in MHz reported up to now in the literature for the S(2) transition. In Table 2 we have gathered our measurement (in cm^{-1}) and the line positions of all 2–0 transitions of D_2 available in the literature. This table includes a correction of the footnote *a* of Table 1 of Ref. [9] which mentioned that all positions were given for a 600 Torr pressure while all but S(7) and S(8) positions were given at null pressure.

The center frequencies and the uncertainties listed in Table 1 are plotted in Fig. 2. Our frequency value is in very good agreement with the *ab initio* value with a difference of +1.75 MHz well below the 12 MHz uncertainty claimed for the calculated value [9]. A difference of +40.75 MHz is observed when comparing our value to that measured by CRDS in [9]. This difference is larger than the claimed (1σ) uncertainty but is compatible with a 2σ uncertainty. This is not the case for the value reported in [21], which deviates by −19.25 MHz and thus largely above the 3 MHz reported error bar. The accuracy given in Ref. [21] is directly related to the uncertainty of the R(18) transition of the 30013← 00001 band of $^{12}CO_2$ used as a reference line. This latter has been recently measured with a 33 kHz uncertainty in [29] and differs by −1.5 MHz from the value adopted in [21]. It is mentioned in [21] that the secondary ICOS absorption cell used for calibration contained 1–75 Torr of pure CO_2. Nevertheless the eventual impact of pressure shift effects on the CO_2 reference line positions is not discussed in Ref. [21]. For the reference CO_2 transition, the self-pressure shift is measured to be equal to −0.00624 (4) cm^{-1} atm^{-1} at 294 K in [30]. Depending of the CO_2 pressure used in [21], not specified, the frequency shift may reach a value of 18.5 MHz at 75 Torr. If we apply this correction for the pressure shift at 75 Torr and a −1.5 MHz correction due to the new absolute position for the CO_2 reference line, the deviation between our value and the resulting value of Ref. [21] is reduced to −2.25 MHz, well within the 3 MHz uncertainty claimed in Ref. [21].

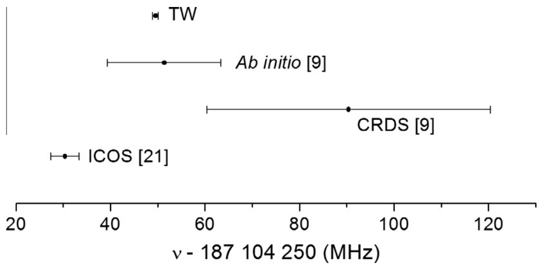

Fig. 2. Comparison of the present results (TW) to experimental and theoretical values reported in the literature for the S(2) 2–0 frequency of D_2, and corresponding error bars.

4. Conclusion

In summary, our measurement of a transition frequency of D_2 with sub-MHz accuracy fully confirms the quality of the theoretical *ab initio* calculations of Ref. [9] with a difference between our measurement and the *ab initio* values seven times smaller than the claimed uncertainty of the calculations (12 MHz).

Finally let us underline the advantage of the high sensitivity of the CRDS technique which allows for low pressure measurements and then for small uncertainties related to the pressure shift correction. In the present experiment, the contribution of about 500 kHz to the error bar on the line center is dominated by the fit error on the line center determination. It represents about 1/1000 of the HWHM Doppler width of the considered D_2 line. This achievement was made possible by averaging more than 100 spec-tra with good signal to noise ratio. This level of accuracy could even be improved using saturated absorption as done in Ref. [31] for stronger transitions of the 30013← 00001 band of CO_2 near 1.6 μm where an accuracy at the kHz level is achieved.

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