Accurate absolute frequency measurement of the S(2) transition in the fundamental band of H 2 near 2.03 μm

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Key words

Frequency metrology; H_2; hydrogen; CRDS; frequency comb

Abstract

Series of spectra of the quadrupolar electric S(2) transition of H_2 in the 1-0 band near 4917 cm^{-1} has been recorded at seven pressure values between 2 and 100 Torr. Comb-referenced cavity ring down spectroscopy technique (CR-CRDS) was used for the recordings of this very weak transition. The accuracy of the spectra frequency axis is achieved by linking the CRDS setup to an optical frequency comb referenced to a GPS-referenced 10 MHz rubidium clock. Applying a multi-spectrum fit procedure to the seven averaged spectra with a quadratic Speed Dependence Nelkin-Ghatak profile, the transition frequency is determined (ν_0= 147 408 142 357 kHz) with an uncertainty of 150 kHz (~1×10^{-9} in relative). This represents the smallest uncertainty achieved so far for a transition in the fundamental band of H_2. The experimental frequency reported in this work is 1.53 MHz higher than the best-to-date theoretical value. This difference represents 1.5 times the 1σ-uncertainty (about 1 MHz) on the calculated frequency. The measurements also allow for the determination of the absolute intensity value of the S(2) line which shows an agreement with the *ab initio* value at the per mil level. In addition, the cross section of the collision induced absorption (CIA) underlying the S(2) line is accurately retrieved from the quadratic pressure dependence of the baseline level of the recorded spectra.

1. Introduction

Di-hydrogen and its isotopologues being the simplest neutral molecular systems, their rovibrational energy levels in the electronic ground state can be accurately determined by theoretical calculations [1]. To achieve a high degree of accuracy, these calculations include corrections to the Born-Oppenheimer approximation, as well as high order quantum electrodynamics (QED) corrections and finite nuclear size effects. Comparison of the theoretical values with accurate experimental measurements provides a strong test of the QED theory which fully describes the molecular systems and puts a higher limit on the coupling strength of a potential 5^{th} force [2,3]. Because H_2 and D_2 are homonuclear molecules, their ro-vibrational absorption spectrum consists only in very weak electric-quadrupole transitions. This results in a real experimental challenge to measure the absolute frequency of such weak transitions with accuracy competing with that reported for the theoretical value. As an example, the strongest transition in the 1-0 fundamental band of H_2 has a line intensity of 3.2×10^{-26} cm molecule^{-1} at 296 K [4] and the minimal required uncertainty should be below 1 MHz. Thanks to the presence of a weak electric dipole moment, HD isotopologue possesses transitions which are stronger than the H_2 and D_2 quadrupolar transitions, making it a better choice for metrological frequency determination. Nevertheless, to check potential (vibrational, isotopologue) dependence of the *ab initio* calculations, it is important to have at disposal the largest number of accurate experimental frequency measurements as possible for the different isotopologues, vibrational bands and transitions. Up to now, such measurements are relatively scarce (5,6 and references herein). Most of them were obtained by Doppler limited spectroscopy. Saturation spectroscopy has been applied to HD transitions but with the drawback of an hyperfine structure limiting the final accuracy on the line centre determination [7,8,9,10,11]. Very recently, Cozijn and co-workers achieved the feat of saturating the S(0) transition in the 2-0 band of H_2 with the NICE-OHMS technique and a H_2 gas sample at 72 K [12] and reported a transition frequency uncertainty of 8 kHz, in agreement with the frequency measured with a 60 kHz uncertainty in Doppler regime by comb-referenced cavity ring down spectroscopy (CR-CRDS) [5]. This latter work, also including the frequency determination of five other transitions in the 2-0 band, evidenced a systematic underestimation of about 2.58 MHz of the most recent calculated H_2 frequencies, about twice their claimed uncertainties. Apart these six transition frequencies measured with a sub-MHz uncertainty in the 2-0 band, only the Q(1) transition in the 1-0 band has been measured with such a level of accuracy [6]. The Q(1) 1-0 transition frequency near 4155 cm^{-1} was very recently reported with an uncertainty of 310 kHz using stimulated Raman scattering metrology [6]. The measured value was found 0.84 MHz larger than predicted by theory. In order to extend the measurements in the 1-0 fundamental band, we consider here the S(2) transition (ν_0= 4917.006312 cm^{-1} [4]; S= 4.577×10^{-27} cm/molecule [13]). The S(2) transition frequency is presently derived from series of spectra recorded

with a CRDS spectrometer referenced to an optical frequency comb (OFC). The setup and the acquisition procedure are detailed in the next section, followed by a description of the adopted multi-spectrum fit procedure (Section 3) and the budget error (Section 4). Retrieved absolute frequency and line shape parameters are then discussed and compared to previous works before concluding remarks (Section 5).

2. Setup and acquisition procedure

2.1. Experimental setup

The comb-referenced cavity ring down spectrometer used in this work is identical to the one described in [14]. Briefly, it consists in an extended cavity diode laser (ECDL) which is coupled into a temperature stabilized high finesse cavity (TS-HFC) [15,16]. The cavity is made of two high reflectivity mirrors (with a reflection coefficient R>99.99% over the 1950-2250 nm range) separated by 45.5 cm. Periodic resonances between the laser light and a cavity mode are achieved by applying a voltage triangular ramp on the PZT tube on which the output cavity mirror is installed. At each resonance, ring-down (RD) events are detected by a photodiode after switching off the injection of photons with an acousto-optic modulator (AOM). The ring down time at frequency ν, $\tau(\nu)$, is derived from a fit of the RD event with a purely decreasing exponential function. The extinction coefficient, $\alpha(\nu)$, is thus retrieved using Eq. (1):

$$\alpha(\nu) = \frac{n}{c\tau(\nu)} - \frac{1-R(\nu)}{L_{cav}} \quad (1)$$

Where c is the speed of light, n is the refractive index of the absorbing gas, $R(\nu)$ is the reflectivity of the mirrors and L_{cav} is the cavity length. Typical RD times of the evacuated cell are τ ~ 51 µs at 4917 cm^{-1}.

The rest of the ECDL light is mixed with the output of an OFC to obtain a beat note (BN) signal detected with a fast photodiode. After acquisition of the signal, the beat note frequency, f_{BN}, is derived allowing retrieving the absolute frequency associated to the RD event from Eq. (2):

$$\nu = nf_{rep} + f_{CEO} + f_{BN} - f_{AOM} \quad (2)$$

Where the repetition rate, f_{rep}= 250 MHz, and the carrier-envelop offset, f_{CEO}=-20 MHz, of the OFC are referenced to a 10 MHz rubidium frequency standard phase-locked to a GPS timing receiver. The sinusoidal wave of frequency f_{AOM}=94.15 MHz applied to the AOM is generated with a direct digital synthesizer (DDS) also referenced to the 10 MHz frequency standard as well as the fast BN acquisition board. Note that the minus sign for f_{AOM} is due to the fact that the beam of order -1 is used. The tooth number, n, is determined with a commercial wavelength meter (HighFinesse WS7-60 IR-II). At the end, an absolute frequency known with an uncertainty of ~200 kHz is associated to each RD event.

2.2. Acquisition procedure

Spectra are recorded step-by-step over a 0.3 cm^{-1} interval around the H_2 line with a typical spectral sampling of 5×10^{-3} cm^{-1}. The laser tuning is achieved by changing the voltage applied to the piezoelectric transducer (PZT) inside the ECDL. At each spectral step, the frequency of the laser source is smoothly stabilized thanks to the measured BN frequency and 200 RD events are acquired. About 20 minutes are necessary to record one spectrum in these conditions. A home-made software is then used to average the RD times and associated absolute frequencies, for each spectral step. A flow of high purity H_2 is established in the TS-HFC (Alphagaz 2 from Air Liquide; 99.9999% of purity) to limit the water vapour volume mixing ratio (**Table 1**). Indeed, the 8_{35}-9_{54} transition of the $\nu_2+\nu_3$ band of $H_2{}^{16}O$ (ν_0= 4916.9468 cm^{-1}; S= 8.097×10^{-25} cm/molecule) [4] is slightly interfering with the studied H_2 line. The pressure inside the cell is measured either by a heated absolute capacitance manometer (Model AA02A Baratron from MKS; 1000 mbar full scale; accuracy better than 0.12% of the reading) or an absolute capacitance manometer (Model AA01A Baratron from MKS; 10 mbar full scale; accuracy better than 0.25% of the reading) (**Table 1**). The pressure is regulated with an electro-valve (2871 series from Burkert; 0.3 mm orifice dia.) and a homemade PID software. Series of single spectra recorded for 7 pressure values ranging from 2 Torr to 100 Torr are displayed in **Figure 1**. The temperature measured with an accuracy of 0.04 K was maintained at an almost constant value of 297.43(3) K. Note that on **Figure 1**, we clearly observe that the baseline level of the spectra increases with the pressure (or density) squared due to the underlying collision induced absorption (CIA). The corresponding CIA cross-section will be derived below using the baseline determined during the fit of the S(2) line profile.

Table 1. *Experimental conditions for the different series of spectra of the S(2) 2-0 line of H_2.*

P_{tot} (Torr)	**2**	**5**	**10**	**20**	**50**	**75**	**100**
# spectra	61	30	55	18	17	57	22
QF [a]	342	515	1350	1604	2599	3419	4067
RMS (cm^{-1})	2.0×10^{-11}	3.3×10^{-11}	2.5×10^{-11}	4.2×10^{-11}	6.6×10^{-11}	7.8×10^{-11}	8.9×10^{-11}
VMR_{H2O} [b] **(ppm)**	325.4	129.4	130.8	71.8	54.2	51.4	21.7
Pressure gauge [c]	Gauge #1	Gauge #1	Gauge #2	Gauge #2	Gauge #2	Gauge #2	Gauge #2
Temp. (K)	297.42	297.41	297.41	297.46	297.46	297.40	297.42

Notes

[a] QF (Quality factor) correspond to the ratio of the absorption at the peak to the RMS of the residuals obtained with a qSDNG profile.,

[b] VMR: volume mixing ratio

[c] Gauge #1: 10 mbar full scale; Gauge #2: 1000 mbar full scale.

All the spectra recorded for the same pressure value (between 17 and 61 – see **Table 1**) were merged together and averaged by bins. More precisely, over each equally spaced bin of 0.002 cm^{-1} a

mean value is calculated for the frequency and the loss rate, $1/c\tau$. As a result, seven averaged spectra are obtained for the multi-spectrum fit procedure described below.

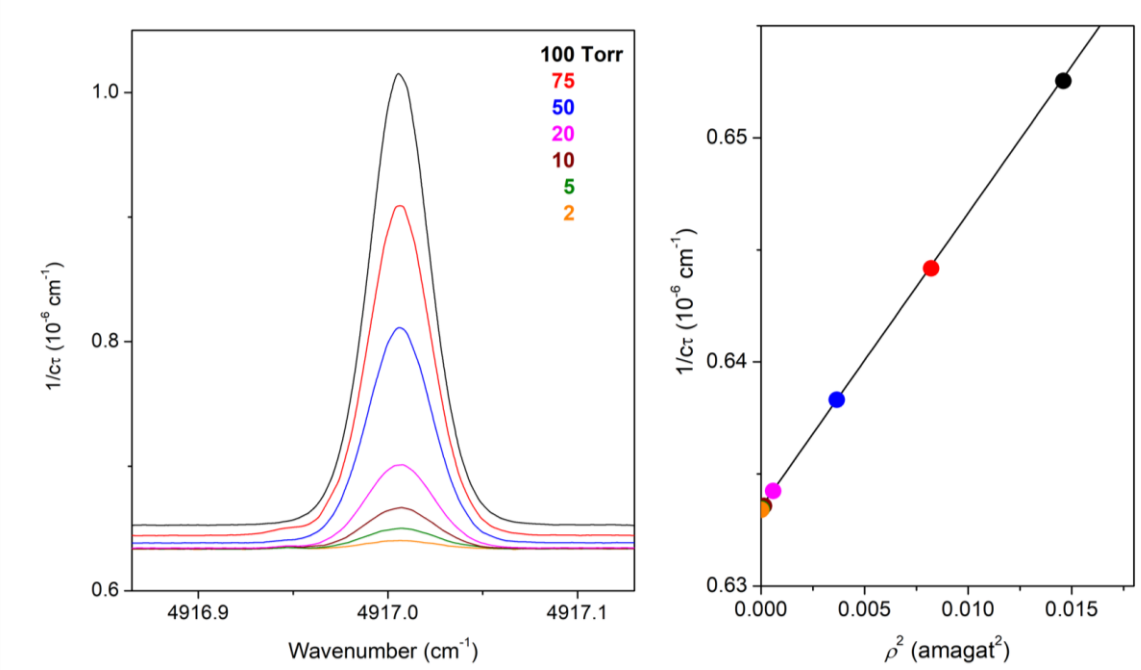

Figure 1. *Overview of the CRDS spectra recorded for the S(2) transition at the different pressures (left panel). Note the increase of the spectrum baseline with the squared density, ρ^2, due to collisional induced absorption (CIA) of H_2 measured at 4916.860 cm^{-1} (right panel).*

3. Multispectrum fit procedure

The frequency of the S(2) transition, ν_0, is determined from a multi-spectrum fit procedure using the *Multi-spectrum Analysis Tool for Spectroscopy (MATS)* fitting program developed at NIST [17]. This procedure is applied to the seven averaged spectra corresponding to the seven pressure values between 2 and 100 Torr. Two different line profiles have been tested:

(i) A quadratic speed-dependent Nelkin-Ghatak (qSDNG) profile [18] which takes into account the Doppler effect, the collision-induced velocity changes (or Dicke narrowing), quantified by the velocity changing collision rate, ν_{VC}, the collisional broadening and shift and their quadratic speed-dependence. In this profile, the parameter, η, describing the correlation between velocity and internal-states changes in the Hartmann Tran (HT) profile is fixed to zero.

(ii) A β-qSDNG profile [19,20] for which the Dicke narrowing is treated with an approximation of the billiard ball model [21] including the mass ratio of colliding molecules and the relative importance of speed- and direction-changing collision. This latter profile is supposed to better model molecular systems with large Dicke narrowing such as H_2 and its isotopologues [19].

The qSDNG profile is characterized by the transition frequency at zero pressure, ν_0, the line-broadening and pressure-shift coefficients (γ_0 and δ_0, respectively), the Dicke narrowing parameter (ν_{VC}/P_{tot}), the speed dependence of the pressure-broadening (γ_2) and of the pressure-shift (δ_2), (all in $cm^{-1}atm^{-1}$). In the β-qSDNG profile, ν_{VC} is replaced by $\beta(\chi)\nu_{VC}$ where β is a correction depending of $\chi = \nu_{VC}/\Gamma_D$. Γ_D is the Doppler width which is fixed to its value calculated at the measured temperature. During the fitting procedure, the mole fraction of H_2 is fixed to 1 while the integrated intensity of the S(2) transition is fitted independently for each pressure together with a linear baseline. As already mentioned, it is necessary to consider the interfering water vapour absorption lines in the fit and especially the 8_{35}-9_{54} transition of $H_2{}^{16}O$ at ν_0= 4916.9468 cm^{-1} with a line intensity S= 8.097×10^{-25} cm/molecule [4], the other water interfering lines being at least two orders of magnitude weaker. For that, the water vapour volume mixing ratio is also fitted (**Table 1**) as well as the position, pressure-broadening and pressure-shift coefficients of the strongest water transition.

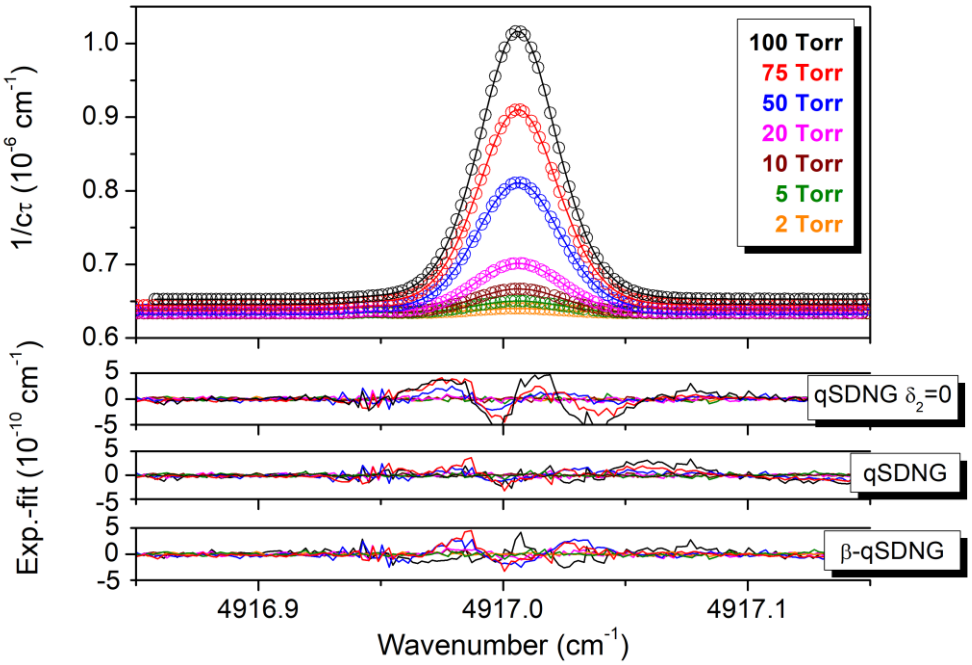

Figure 2.
Upper panel: CRDS spectra of the S(2) transition of H_2 in the 1-0 band recorded at seven pressure values.
Lower panels: Corresponding (exp.-fit) residuals obtained after the multi-spectrum fit procedure using the qSDNG and β-qSDNG profiles.

The results of the multi-spectrum fit procedure obtained with the different profiles are illustrated on **Figure 2** and the retrieved parameters are reported in **Table 2**. Residuals exceeding the noise level are observed if the speed-dependence of the pressure-shift is not considered, δ_2= 0, when using a qSDNG profile. Improved residuals, but still above the noise level for the four highest pressures, are obtained both for the qSDNG and β-qSDNG profiles with δ_2 fitted. Contrary to what could be expected, the latter profile shows no real improvement of the residuals compared to the qSDNG profile: residuals are slightly better at 100 Torr but larger at 50 and 20 Torr and equivalent for

the other pressures. This leads to quality factors between 4067 for the 100 Torr spectrum and 342 for the 2 Torr spectrum (**Table 1**) with the qSDNG profile.

Table 2. *Line shape parameters of the S(2) transition obtained from the multi-spectrum treatment of the CRDS spectra recorded at seven pressure values using the ß-qSDNG, qSDNG profiles. The uncertainties given within parenthesis in the unit of the last quoted digit correspond to the (1σ) statistical values provided by the fit. The ab initio absolute frequency value given for the S(2) transition by the H2spectre software [22]. The ab initio line shape parameters and measured absolute frequency provided in [6] for the Q(1)(1-0) transition are also listed for comparison.*

	ν_0 cm^{-1}	γ_0 10^{-4} cm^{-1} atm^{-1}	δ_0 10^{-3} cm^{-1} atm^{-1}	ν_{VC}/P_{tot} 10^{-2} cm^{-1} atm^{-1}	γ_2 10^{-4} cm^{-1} atm^{-1}	δ_2 10^{-3} cm^{-1} atm^{-1}
Ab initio	4917.006312(33)					
TW β-qSDNG	4917.0063643(41)	11.8(7)	-1.05(4)	1.87(2)	1.25(7)	1.82(11)
qSDNGP	4917.0063637(32)	10.6(6)	-1.04(3)	1.24(1)	1.03(11)	1.76(13)
qSDNGP (δ_2= 0)	4917.0063651(56)	10.3(9)	-1.56(5)	1.25(2)	0.96(16)	0
Recommended value	**4917.006363(5)**[a]					
Ref. [6]	4155.253790(10)	6.4(6)	-1.17(12)	4.31(21)	1.06(10)	2.30(22)

Note

[a] *The recommended value is corrected from the recoil and second-order Doppler shifts. The uncertainty includes all the uncertainty sources discussed in the budget error section.*

In addition, the CIA can be extracted from the baselines obtained with the multi-spectrum fit procedure. For this purpose, the loss rate, 1/cτ, corresponding to the baseline value for the 4916.860 cm^{-1} wavenumber, is plotted *versus* the squared density in $amagat^2$ (**Figure 1**, right panel) and then fitted with a linear function. The retrieved slope ($1.310(4)\times10^{-6}$ $cm^{-1}amagat^{-2}$) at 4916.86 cm^{-1} and 297.43 K is very close (0.7%) to the (calculated) value of 1.319×10^{-6} $cm^{-1}amagat^{-2}$ reported in the HITRAN2020 database [4] at 4917.00 cm^{-1} and 300 K.

4. Budget error

More important than the fit residuals, is the statistical uncertainty on the retrieved ν_0 value for the different profiles and the dependence of ν_0 to the choice of profile. As can be seen from **Table 2**, the retrieved ν_0 value varies by no more than 6×10^{-7} cm^{-1} (18 kHz) between the β-qSDNG and qSDNG profiles, largely within the statistical uncertainty given by the fit (between 100 and 170 kHz according to the profile). The limited impact of the choice of the profile on ν_0 has already been discussed in the study of the (2-0) transitions of Ref. [5]. In addition, we see in **Table 2** (as in [5]) that the δ_2 value has a very limited impact on the retrieved ν_0 value.

In Ref. [23], it was shown that the uncertainty on the frequency due to the optical frequency comb, the Doppler shift induced by the moving speed of the output mirror of the optical cavity and the AC/DC Stark shifts are well below the kHz level.

As mentioned in [24], the *off-diagonal elements relat(ing) to the numerical correlation between floated parameters in the fit, (...) are not used in calculation of the standard error* leading to possible underestimation of the «real error». To estimate if this is the case here, we first simulated 100 sets of seven spectra with different random noise and then calculated the standard deviation of the retrieved ν_0 frequency from the multi-spectrum fit procedure. In the typical noise conditions of our recordings (10 kHz on the *x*-axis and 5×10^{-11} cm^{-1} on the *y*-axis), we found that the uncertainty given by the fit for ν_0 (and for δ_0 and δ_2 too) is representative of the « real error ».

We also evaluated the impact on ν_0 of the uncertainty given by the fit procedure for δ_0 and δ_2 which are the two parameters which are significantly correlated with ν_0. The fit procedure was run twice: the first one with δ_0 or δ_2 fixed to their fitted values and the second time by fixing them to their fitted values increased by the fit uncertainty. We obtained a variation of 3.0×10^{-6} cm^{-1} (≈90 kHz) on ν_0 for δ_0 and of 1.8×10^{-6} cm^{-1} (≈48 kHz) for δ_2. Note that in the *MATS* program, $a_s = \delta_0/\delta_2$ is the parameter which is fitted instead of δ_2 directly.

We proceeded in the same way to evaluate the impact of an error on the position, pressure-broadening and pressure-shift coefficients of the interfering water transition. The fit uncertainty on ν_{0_H2O}, $\gamma_{0\text{-}H2O}$ and δ_{0_H2O} propagates to an uncertainty of 3.3×10^{-7} cm^{-1}, 2.3×10^{-7} cm^{-1} and 7.4×10^{-7} cm^{-1} on ν_0, respectively. The retrieved values for ν_{0_H2O}, $\gamma_{0\text{-}H2O}$ and δ_{0_H2O} are 4916.94687(8) cm^{-1}, 0.0591(11) cm^{-1} atm^{-1} and -0.0074(11) cm^{-1} atm^{-1}, respectively. The position value is very close to the value included in the HITRAN2020 database (with a difference of 7×10^{-5} cm^{-1}). The pressure broadening and the pressure-shift coefficients of the considered H_2O line by H_2 are in agreement within the error bars with the values calculated in Refs. [25,26] using the Modified Complex Robert-Bonamy (MCRB) formalism (0.0695(139) cm^{-1} atm^{-1} and -0.0082(5) cm^{-1} atm^{-1}, respectively).

It is also necessary to mention that the R(17)e transition of $^{12}C^{18}O^{16}O$ in the 20012-00001 band (ν_0=4916.969519 cm^{-1}; S=2.431×10^{-24} cm/molecule)[4] is a potential interfering line. To evaluate its potential impact on ν_0 we looked for possible traces of CO_2 in the sounded gas by recording spectra of the stronger P(60) $^{12}C^{16}O_2$ line (ν_0=4918.07704 cm^{-1}; S=7.37×10^{-24} cm/molecule) of the 20012-00001 band. No absorption due to this line was observed in our spectra giving an upper limit of 0.25 ppm for the CO_2 mixing ratio in our sample. Neglecting the potential presence of 0.25 ppm of CO_2 in our cell (at all pressure values) leads to a bias of 1.7×10^{-6} cm^{-1}.

The fitted value of ν_0 needs to be corrected from the recoil shift [27], leading to a reduction of the frequency by -23.9 kHz in our case, and the second-order Doppler shift [28] corresponding to an almost negligible shift of +1 kHz. The recommended absolute wavenumber of the S(2) transition is reported in **Table 2** with a final uncertainty of 5×10^{-6} cm^{-1} (*i.e.* 150 kHz) corresponding to the quadrature sum of all the different contributions described above.

As can be observed on **Figure 2**, residuals are not at the noise level for the highest pressures, showing some limitations of the qSDNGP model. To overcome these limitations and evaluate the impact of the highest-pressure spectra, we removed the 100, 75 and 50 Torr averaged spectra from the multi-fit procedure keeping only the 2, 5, 10 and 20 Torr spectra for the fit. The retrieved ν_0 values in both cases are very close to each other: a difference of 1×10^{-6} cm^{-1} with a qSDNG profile and 2.4×10^{-6} cm^{-1} with a β-qSDNG profile were observed, largely within the uncertainty of 1×10^{-5} cm^{-1} provided by the fit of the four lowest pressure spectra. In other words, including the highest pressure spectra allows improving the fit uncertainty but does not impact the retrieved ν_0 value.

5. Discussion and concluding remarks

When comparing the *ab initio* values reported in [6] for the Q(1) transition in the 1-0 band of H_2 with the fitted line profile parameters obtained for a β-qSDNG profile (**Table 2**), we notice that δ_0, γ_2 and δ_2 parameters are close but the ν_{VC}/P_{tot} *ab initio* value is two times larger than our fitted value. This large difference could be due to the fact that a slightly different profile, including an imaginary part for ν_{VC}, is used in [6]. Finally, the γ_0 *ab initio* value is about two times smaller than our retrieved value. This could come from the fact that these two transitions do not involve the same *J* values. As observed in [20,29] a *J*-dependence exists for γ_0. Indeed, the γ_0 value retrieved for the Q(1) transition is clearly smaller than those reported for other Q transitions measured by Raman spectroscopy in Ref. [29].

Even though it was not the initial goal of this work, it is interesting to mention that the integrated intensity of the S(2) transition at 296 K, retrieved from the spectra recorded at the different pressures, show values between 4.567×10^{-27} and 4.579×10^{-27} cm/molecule (if we except the 10 Torr spectrum for which the pressure value measured with the 1000 mbar gauge leads to a clear outlier with a value of 4.594×10^{-27} cm/molecule). The mean value of $4.572(2)\times10^{-27}$ cm/molecule confirms the *ab initio* intensity value included in the HITRAN database (4.577×10^{-27} cm/molecule) at the per mil level.

In summary, in this work, series of spectra obtained using a highly sensitive CRDS spectrometer linked to an optical frequency comb referenced to a rubidium atomic clock phase-locked to a GPS timing receiver have allowed to determine the frequency of the S(2) transition (ν_0= 147 408 142 357 kHz) with a final uncertainty of 150 kHz. Note that, to the best of our knowledge (see review included in Ref. [30], the detection of the considered S(2) 1-0 was not reported since the early works by Fink *et al.* [31] and Bragg *et al.* [32] using a grating spectrograph (1.4 km absorption path length) and a Fourier transform spectrometer (path length of 434 m and pressure values between 0.8 and 2.8 atm), respectively. With its 150 kHz final uncertainty, the reported transition frequency is the most accurate determination reported so far in the fundamental band of H_2, improving by more than two

orders of magnitude the accuracy of these previous determinations. This is also two times smaller than the best uncertainty achieved in the fundamental band of H_2 (for the Q(1) transition which is 4.5 times stronger [6]).

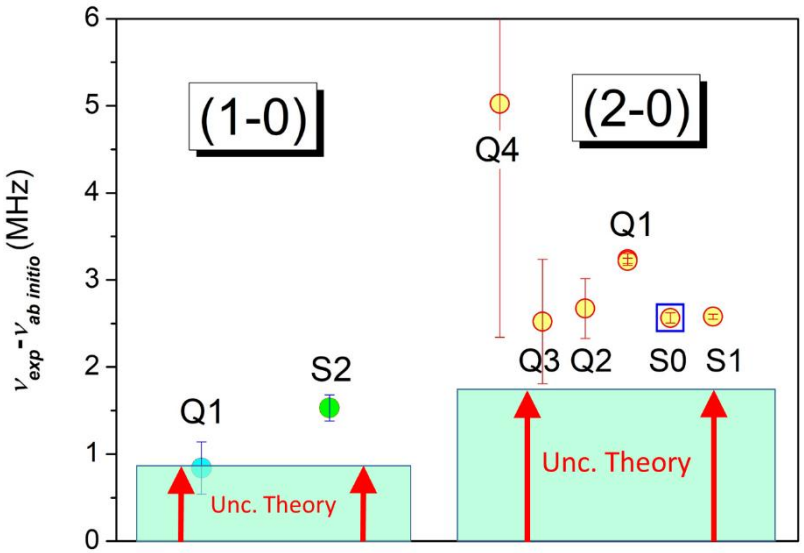

Figure 3. *Differences between experiment and theory for the H_2 transition frequencies of the 1-0 and 2-0 bands referenced to an absolute frequency standard. The theoretical values [1] were obtained from the H2spectre software [22]. The red arrows represent the typical uncertainty on the calculated values. The experimental values in the 1-0 band are from Lamperti et al. [6] and this work (Q(1) and S(2), respectively) and from Fleurbaey et al. [5] for the 2-0 band (yellow dots), the Lamb dip measurement of the S(0) 2-0 frequency is also indicated (blue open square) [12].*

The measured value of the S(2) transition frequency is 51×10^{-6} cm^{-1} (i.e. 1.53 MHz) higher than the *ab initio* value given by the H2spectre software V7.4 [22]. This difference is 1.5 times larger than the 1 σ-uncertainty reported in [22] and confirms the fact that *ab initio* values are systematically smaller than experimental ones for H_2 and its isotopologues [5,6,11]. This tendency is illustrated in **Figure 3** which compares the H_2 transition frequencies of the 1-0 and 2-0 bands referenced to an absolute frequency standard to the best *ab initio* values [22]. Note that a smaller difference of 0.84 MHz (equivalent to the *ab initio* error bar) was found by Lamperti and co-workers [6] for the Q(1) transition belonging to the same 1-0 band of H_2 and given with a 310 kHz uncertainty.

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