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1                                    The (2-0)  $R(0)$  and  $R(1)$  transition frequencies of HD  
2                                    determined to a  $10^{-10}$  relative accuracy by Doppler spectroscopy at 80 K  
3

Samir Kassi <sup>a</sup>, Clément Lauzin <sup>b</sup>, Justin Chaillot <sup>a</sup>, Alain Campargue <sup>a\*</sup>

4                    The Doppler broadened  $R(0)$  and  $R(1)$  lines of the (2-0) vibrational band of HD have been  
5                    measured at liquid nitrogen temperature and at pressures of about 2 Pa, with a comb referenced  
6                    continuous-wave cavity ring-down spectrometer set-up. Transition frequencies of 214905335185 and  
7                    217105181898 kHz were derived from 33 and 83 recordings, with corresponding root mean squared  
8                    deviation of 53 and 33 kHz for the  $R(0)$  and  $R(1)$  transition, respectively. This is the first sub-MHz  
9                    frequency determination of the  $R(0)$  transition frequency and represents a three order of magnitude  
10                    accuracy improvement compared to literature. The  $R(1)$  transition frequency is in very good agreement  
11                    with previous determinations in saturation regime reported with similar accuracy. To achieve such  
12                    accuracy, the transition frequency of a (101)-(000)  $2_{11-3_{12}}$  line of  $H_2^{16}O$  interfering with the  $R(0)$  line  
13                    had to be precisely determined and is reported with a standard error of 100 Hz at 214904329820.80(10)  
14                    kHz (relative uncertainty of  $5 \times 10^{-13}$ ). These measurement sets provide stringent reference values for  
15                    validating future advances in the theoretical description of the hydrogen (and water) molecule.

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## 18 Introduction

19 Due to its relative simplicity, the dihydrogen molecule is of fundamental interest in physics and  
20 chemistry. The HD isotopologue which represents the simplest neutral heteronuclear diatomic molecule  
21 has been at the origin of a fruitful scientific emulation on both theoretical (*e.g.* [1], [2], [3], [4]), and  
22 experimental (*e.g.* [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19]) fronts.

23 Although weak, the rovibrational transitions in HD are about two orders of magnitude stronger  
24 than in H<sub>2</sub>. This is due to the existence of a small electric dipole moment in HD, giving rise to allowed  
25 electric dipole transitions which are strictly forbidden in H<sub>2</sub> (and D<sub>2</sub>), in which only electric quadrupole  
26 transitions remain observable. The electric dipole transitions in HD are thus particularly suitable to  
27 achieve very high accuracy frequency determination using absorption spectroscopy. Since the  
28 pioneering work of Herzberg [5], the weak HD absorption spectrum has been extensively studied using  
29 a variety of experimental techniques (see the review of experimental measurements up to 2016 included  
30 in Table 1 of [14]). Overall, more than seventy transitions were detected from the rotational spectrum  
31 [11] up to the fifth overtone band, (6–0) near 520 nm [8].

32 While the pioneer experimental efforts were motivated by planetary applications, the HD  
33 molecule has become a benchmark system which triggered great efforts to improve quantum physics  
34 calculation accuracy. This includes in particular quantum electrodynamics corrections (QED) of the  
35 energy levels up to the sixth order [20], [3] and hyperfine splitting determination [21], [4], [22].  
36 Interestingly, HD is for now the sole dihydrogen isotopologue for which a disagreement exists on the  
37 dissociation energy between experimental and theoretical values [23], [13], [3]. HD is thus an attractive  
38 molecular candidate to challenge further theoretical predictions and test the amplitude of the QED  
39 corrections.

40 Experimental advances in terms of sensitivity, resolution and accuracy on the frequency  
41 determination of HD rovibrational transitions, ionization potential and dissociations energies provide  
42 stringent validation tests of the most advanced calculations [23], [13].

43 Doppler broadening is a strong limitation factor to achieve sub-MHz precision on line center  
44 determination, even at low temperature. Indeed, the full width at half maximum (FWHM) of the Doppler  
45 limited profile of the (2-0) *R*(0) or *R*(1) HD lines is about 700 MHz at 80 K. Saturation spectroscopy  
46 provides a powerful tool to circumvent Doppler broadening. Recently, accurate measurements of HD  
47 transitions were reported in the sub-Doppler regime using either action spectroscopy schemes [24], [18]  
48 or the power enhancement of a Fabry Perot cavity to observe Doppler free Lamb dip signatures [15],  
49 [25]. In particular, the Hefei [15] and Amsterdam [25] groups retrieved (2-0) *R*(1) transition frequencies  
50 from Lamb dips exhibiting a dispersive-like spectral structure. The initial reported values differed by  
51 900 kHz, a difference significantly larger than the combined error bar of the two measurements. This  
52 discrepancy and the unusual Lamb dip profile were examined in two subsequent studies led by the same  
53 groups [16], [26]. In Hefei, an experimental study was performed with an enhanced signal-to-noise ratio

54 and the use of different spectroscopic techniques confirming the dispersive-like shape, fitted with a Fano  
55 profile [26]. Physical mechanisms at the origin of this Fano-type profile was very recently discussed by  
56 the same group [27]. For the Amsterdam group, the dip was fitted according to Bloch equations  
57 formalism and introducing crossovers transitions [16]. Both groups found line positions in agreement  
58 with each other within the error bars of 50 and 240 kHz for Amsterdam and Hefei, respectively.

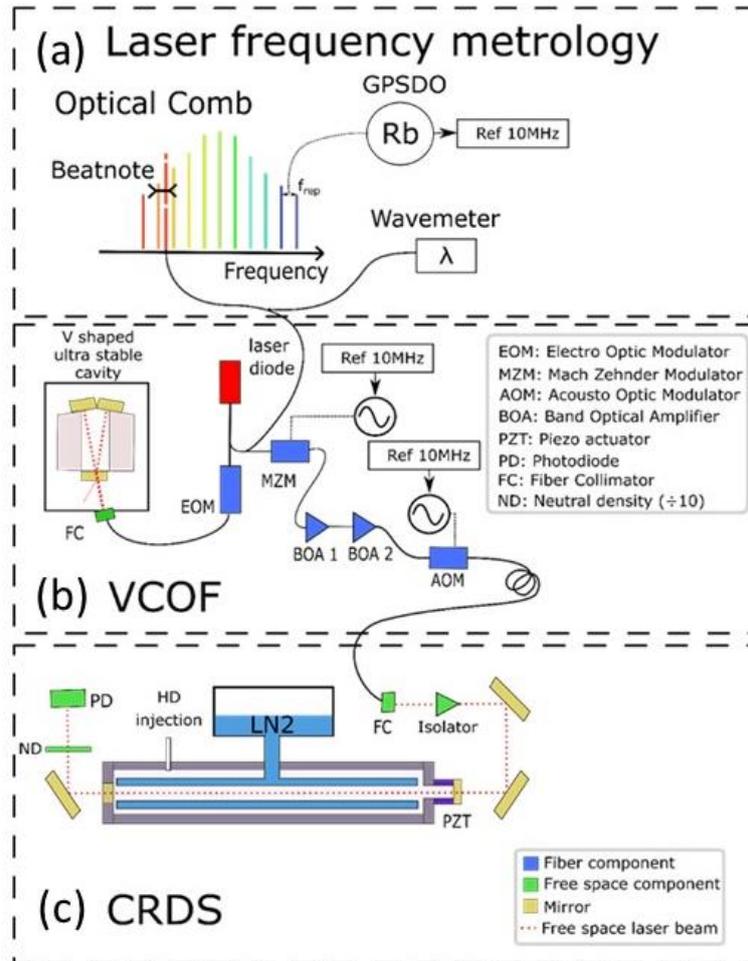
59 Interestingly, the same (2-0)  $R(1)$  transition was measured with similar accuracy in Doppler  
60 regime at room temperature in Caserta [19] providing an error bar of 76 kHz, on the same order as the  
61 one of Doppler free measurements. The line position of the (2-0)  $R(1)$  is now determined within 50 kHz  
62 but the origin of the observed dispersive Lamb-dip profile remains a subject of discussion.

63 In the present work, we report on high accuracy frequency measurements of the  $R(0)$  and  $R(1)$   
64 transitions of the (2-0) vibrational band of HD at liquid nitrogen temperature (about 80 K). The  
65 advantages of cooling are several: (i) the Doppler broadening is reduced by about a factor of two, (ii)  
66 the intensity of the  $R(0)$  transition is increased by a factor of about 3, compared to its 296 K value, the  
67 intensity of the  $R(1)$  transition being mostly unchanged, (iii) spectral interferences with lines due to  
68 impurities, water in particular, are minimized since vapor pressure of most contaminants are drastically  
69 reduced. Note that while the (2-0)  $R(1)$  transition frequency was determined by three groups with an  
70 accuracy better than 100 kHz, the best-to-date frequency determination of the (2-0)  $R(0)$  transition is 30  
71 MHz [12]. The lack of accurate measurements of the  $R(0)$  line is related to the proximity of a  $10^5$  times  
72 more intense water line which precludes room temperature experiments. Our experimental approach for  
73 high accuracy HD measurements at low pressures in a water free environment is described in the next  
74 section. It combines the advantages of (i) a very monochromatic and stable laser source ( $\Delta\nu\sim 100$ Hz,  
75 drift=1Hz/s) developed for cavity ring-down spectroscopy (CRDS) cavity [28], [29], (ii) an absolute  
76 frequency calibration provided by a frequency comb and (iii) a CRDS cell cooled down to liquid  
77 nitrogen temperature. In Section 3, we present the transition frequency determination including a  
78 discussion of the possible impact of the hfs structure on the retrieved line centers and the error budget.  
79 The obtained transition frequencies are discussed in relation with literature results in Section 4, before  
80 the Concluding remarks (Section 5).

## Experiment

81 The spectra were recorded at the Université Grenoble Alpes with a set-up presented in **Fig. 1**. The  
82 figure is structured in three blocks, from top to bottom, those concern (1) the frequency calibration, (2)  
83 the light source and (3) the cavity ring-down spectrometer probing a gas cell working at liquid nitrogen  
84 temperature. The VCOF light source is a DFB laser diode locked through optical feedback to a highly-  
85 stable V-shaped cavity [28], [29], [30]. This source has sub-kHz emission line width, typically 10 mW  
86 output power, and exhibits a maximum frequency drift of 7 Hz/s [30], [31]. Its frequency is first roughly  
87 determined using a wavemeter (Burleigh, 50 MHz resolution) and refined using a self-referenced  
88 frequency comb from Menlo. The repetition rate (250 MHz) and carrier offset frequencies (20 MHz) of

89 the comb are phase locked to a 10 MHz GPS disciplined Rb oscillator (GPS-RbO) with a relative  
 90 frequency stability  $\Delta\nu/\nu=2\times 10^{-12}$  limited by the GPS accuracy. The design of the continuous-wave  
 91 cavity ring-down spectrometer (CW-CRDS) follows mainly the one presented in [28]. The spectrometer  
 92 has been slightly modified by the addition of a pair of optical amplifiers (Thorlabs BOA 1036P, Thorlabs  
 93 BOA 1410P). The very stable laser source is made tunable over 18 GHz range using a single side-band  
 94 generator, the Mach-Zender modulator (MZM) in **Fig. 1**, driven by a frequency synthesizer (SMF 100A,  
 95 Rohde&Schwarz), referenced to the GPS-RbO.



96

97 FIG. 1.

98 Experimental set-up developed in Grenoble. The figure is structured in three blocks, detailing from top to bottom,  
 99 (a) the frequency calibration, (b) the light source and (c) cavity ring-down spectrometer, respectively. GPSDO  
 100 stands for GPS Disciplined Oscillator, VCOF stands for V-shaped Cavity-Based Optical Feedback and LN2 for  
 101 liquid nitrogen. The Acousto-Optic Modulator AOM is driven at 88.5 MHz.

102

103 The gas sample, HD (from ISOTECH with 98 % and 99.3% stated isotopic and chemical purity,  
 104 respectively), was injected through a computer controlled electro-valve and the pressure monitored with  
 105 a 1 Torr gauge (Baratron model 626B). A weak flow was set through a 10 turns needle valve connecting  
 106 the cell to a turbo pump group. The pressure was actively regulated to 2 Pa using a computer based  
 107 Proportional/Integral controller. The design of the cell is very close to the one reported in [32], [33]. It  
 108 is composed of three concentric stainless steel cylinder cell surrounding the gas sample. The external

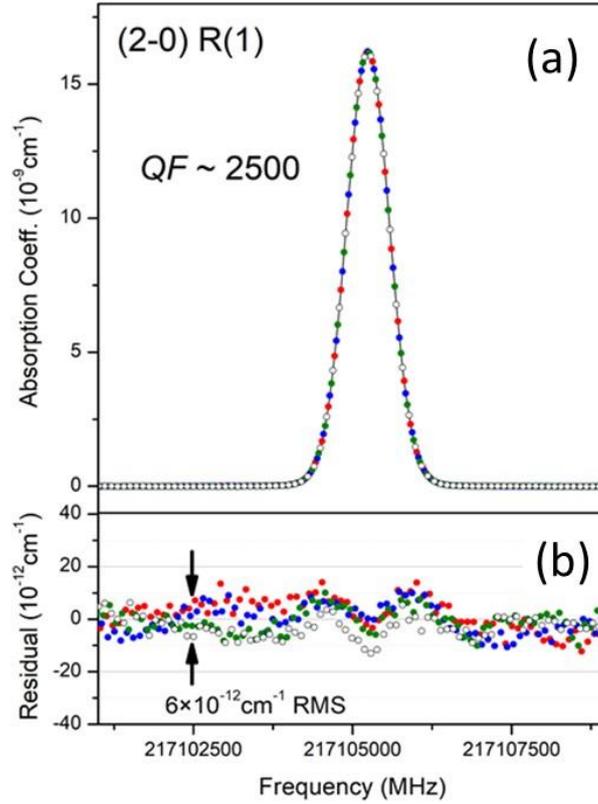
109 stainless-steel cylinder is 1.4 m long, with a diameter of  $d = 63$  mm, while the cryostat is made of the  
110 two inner co-axial tubes ( $d = 1.6$  and  $2$  cm), welded at each end by a hollow disc to form a reservoir. It  
111 is suspended at its center by a jacketed 2 cm diameter tube used to fill the cryostat with liquid nitrogen.  
112 The main difference with [32] is that the mirrors can be further aligned while the cell is put under vacuum  
113 and cooled down. The enhanced conduction of HD compared to CH<sub>4</sub> studied in previous works [32],  
114 [34], [35] forced us to work at very low pressure (2 Pa) to prevent any excessive cooling of the external  
115 part of the cell.

116 During recording, the optical frequency is dynamically adjusted by subtracting an adjustable  
117 microwave frequency between 2 and 20 GHz using the MZM. To speed up the recording, the spectra  
118 are acquired in an interlaced manner with frequency hopping bursts equal to the free spectral range of  
119 the CRD cavity. The cavity modes are thus systematically resonant. To increase the resolution, an  
120 intermediate optical frequency is chosen inducing a procedure of relock of the CRDS cavity modes,  
121 thanks to the PZT mounted mirror. Another burst is then recorded. Thus 4 series of spectra are interlaced  
122 to reach a resolution of 25 MHz with a cavity whose FSR is 100 MHz. A full spectrum, with 10 to 40  
123 RD per spectral point, is recorded within typically 1 minute.

## 124 Results

### 125 *The R(1) line*

126 The  $R(1)$  transition, already accurately measured in [15], [25], [26] and [19] was used to validate  
127 our measurement procedure. Eighty-three fourfold interlaced spectra were recorded at liquid nitrogen  
128 temperature with frequency step of 100 MHz (matching the CRDS cavity free spectral range) leading to  
129 a final 25 MHz step resolution. During each scan, the cell temperature, HD partial pressure and baseline  
130 were slowly evolving, due to thermo-mechanical stress. Before being analyzed by the line fitting routine,  
131 the four interlaced spectra were independently corrected from a linear baseline before being recombined.  
132 This allows for partial compensation of baseline fluctuations related to temperature instability.



133

134 FIG. 2.

135 The (2-0)  $R(1)$  line of HD at liquid nitrogen temperature and a pressure of about 2 Pa.

136 (a) Typical fourfold interlaced spectra measured at liquid nitrogen temperature and at a pressure of 2 Pa. The four  
 137 interlaced spectra are plotted with different colors and provide a 25 MHz step resolution while the cavity free  
 138 spectral range is about 100 MHz. The black trace represents the fit of this line using a Voigt line profile (see text),  
 139 (b) Residuals of the simultaneous fit of the four interlaced spectra. The noise equivalent absorption coefficient,  
 140  $\alpha_{min}$ , evaluated from the baseline fluctuations is about  $6 \times 10^{-12} \text{ cm}^{-1}$  leading to a quality factor of 2500.

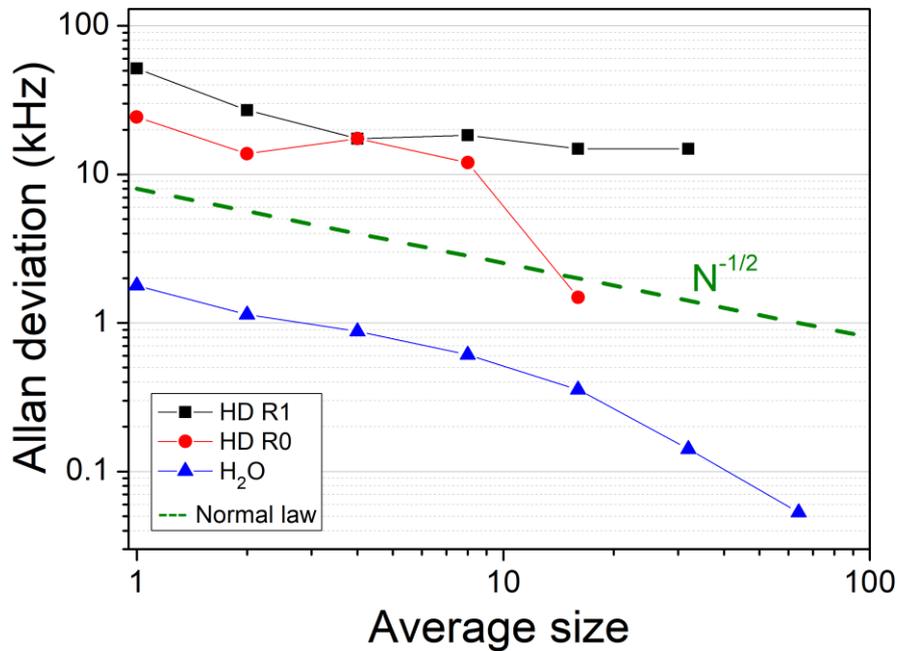
141

142 Each of the eighty-three fourfold interlaced spectra were fitted independently. The line shape was  
 143 chosen as a Voigt profile with the Gaussian width fixed to its 77 K Doppler value (770 MHz FWHM).  
 144 The Lorentzian component width was fixed to 11 MHz to minimize the residuals. This width value has  
 145 been determined by averaging the results of an initial fit for which this parameter was kept free. This  
 146 weak component helps to account for a small temperature gradient existing in the probed gas sample, as  
 147 detailed below for the  $R(0)$  line treatment. The center and area of the HD  $R(1)$  line as well as a quadratic  
 148 baseline were determined by the fit. A typical fourfold spectrum together with the corresponding fit  
 149 residuals are presented on **Fig. 2**. The root mean square (RMS) of the residuals (or noise equivalent  
 150 absorption coefficient) is on the order of  $6 \times 10^{-12} \text{ cm}^{-1}$  which leads to a quality factor of about 2500 (QF  
 151 is defined as the ratio of the absorption coefficient at the peak to the RMS of the residuals).

151

152 The averaged value of the 83 center determinations of the (2-0)  $R(1)$  line is found to be  
 153 217105181934 kHz with a  $1\sigma$  statistical deviation of 53 kHz. The Allan deviation plot of the retrieved  
 154 frequencies, presented in **Fig. 3**, suggests that the accuracy of the averaged line center is below the RMS  
 155 value but higher than the standard error ( $\sigma/\sqrt{N} = 53/\sqrt{83} \approx 6 \text{ kHz}$ ). The Allan deviation trace is going  
 down, below 20 kHz, indicating that the average transition frequency value remains stable beyond this

156 limit. A 20 kHz value seems a conservative estimate of the actual uncertainty on the obtained line center  
 157 value.



158  
 159 FIG. 3.  
 160 Allan deviation plot for the frequency determination of the  $R(1)$ ,  $R(0)$  HD lines and the  $(101)-(000)$   $2_{11-3_{12}}$  line of  
 161  $H_2^{16}O$ . The dataset size is 83, 33 and 247, respectively. The dependence is close to the normal law (in  $1/\sqrt{N}$ , green  
 162 dashed line) for the water line leading to an error bar of about 100 Hz for the Lamb-dip measurement. In the case  
 163 of the  $R(1)$  and,  $R(0)$  line centers, the statistics help to decrease the error bar below a 20 kHz conservative value.

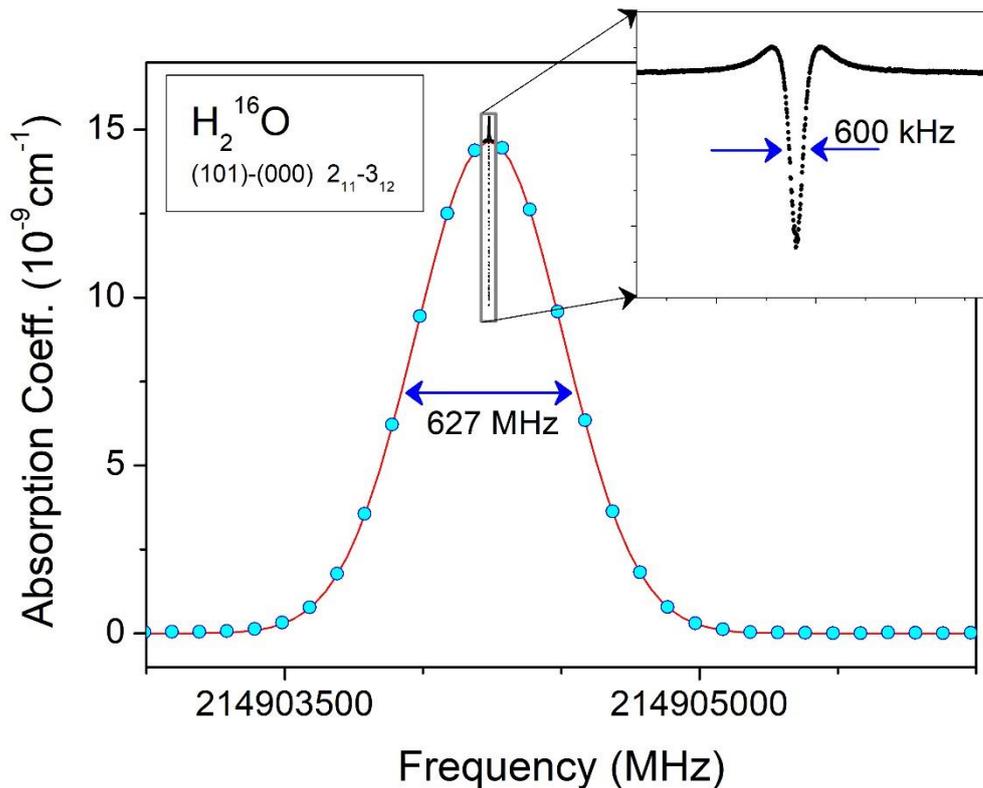
164 *The  $R(0)$  line*

165 For the more intense  $(2-0)$   $R(0)$  line, we recorded a series of 33 spectra. As said above, at 77 K,  
 166 the  $R(0)$  line intensity is increased by a factor of 3 compared to its room temperature value while the  
 167  $R(1)$  line intensity is mostly unchanged. The cryogenic temperature of the cell allowed for a drastic  
 168 reduction of the water contamination which is major issue. The  $(101)-(000)$   $2_{11-3_{12}}$   $H_2^{16}O$  line at  
 169  $7168.4369\text{ cm}^{-1}$  has indeed a  $1.196 \times 10^{-20}$  cm/molecule intensity at room temperature and overlaps the  
 170 profile of the  $R(0)$  HD line at  $7168.4703\text{ cm}^{-1}$  (with a room temperature intensity of  $2.445 \times 10^{-25}$   
 171 cm/molecule) [36].

172 Still, as evidenced in the following analysis of the  $R(0)$  line profile, water traces persist, that we  
 173 attribute to outgasing from the mirrors which are not cooled (see **Fig. 1** and [32], [33]) and remain at a  
 174 temperature close to the room temperature. As shown below, the contribution of the water line to the  
 175 observed absorption remains very weak but is detectable at the achieved sensitivity. In order to  
 176 accurately constrain its position in the fitting of the  $R(0)$  line profile, we determined the center of the  
 177 interfering water line in saturated regime at room temperature, as shown in **Fig. 4**. A series of 247 spectra  
 178 was recorded over 39 hours in order to refine the dip position. The reader is referred to [29] for the  
 179 description of the acquisition of the line profile and Lamb dip spectra with adaptive resolution. Briefly,  
 180 a first low resolution (100 MHz) survey scan was recorded, from which the line center was roughly

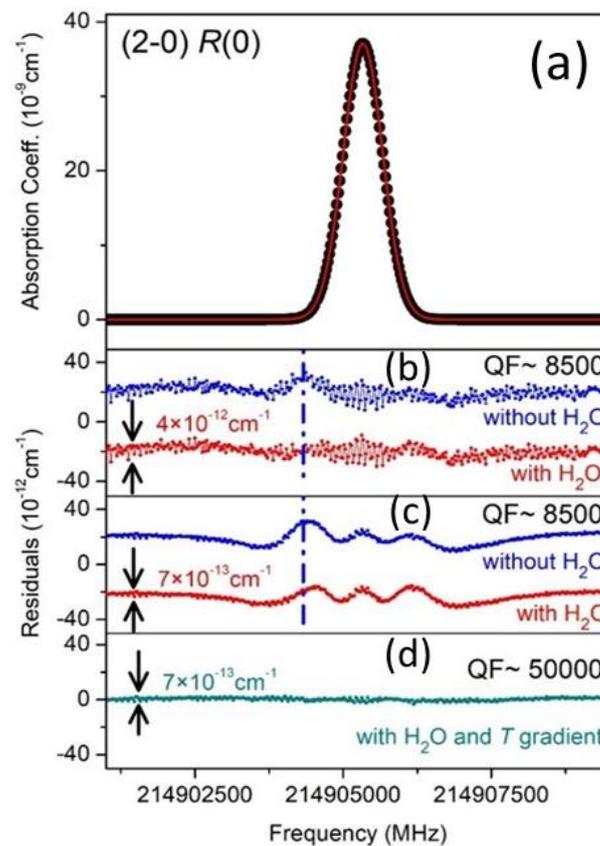
181 determined using a Gaussian profile. This spectrum was immediately supplemented with a high  
 182 resolution (20 kHz) scan around the center as presented in the inset of **Fig. 4**. No effort was made to fit  
 183 the ring-down using an advanced model (see *e.g.* [37]) and a Lorentzian fit was performed to determine  
 184 the center of the Lamb dip. From the 247 determinations, an average center value of  
 185 214904329.8263(15) MHz or 7168.43683327(5)  $\text{cm}^{-1}$  was determined *i.e.* about  $6.6 \times 10^{-4} \text{ cm}^{-1}$  below  
 186 the HITRAN value provided with a  $10^{-3} \text{ cm}^{-1}$  error bar [36].

187 The Allan deviation included in **Fig. 3** indicates that the water line position is determined with  
 188 1.5 kHz accuracy per scan and that the precision is enhanced by the averaging process following the  
 189 normal law in  $1/\sqrt{N}$ , where  $N$  is the number of recordings. The resulting standard error is thus decreased  
 190 by a factor of about 15 ( $\approx\sqrt{243}$ ) compared to the RMS leading to a very small uncertainty value of 0.1  
 191 kHz. This confirms the stability of the frequency detection chain. Note that the room temperature water  
 192 line at  $10^{-3}$  Pa pressure and the 80 K HD line at 2 Pa have similar peak absorption (about  $15 \times 10^{-9} \text{ cm}^{-1}$ )  
 193 and linewidths (627 and 770 MHz FWHM, respectively), but the water dip is remarkably deep ( $5 \times 10^{-9}$   
 194  $\text{cm}^{-1}$ ) and much narrow (600 kHz FWHM). As a result, a gain of an order of magnitude is achieved in  
 195 pointing the line center in saturation regime.



196  
 197 **FIG. 4.**  
 198 Room temperature line profile and Lamb dip of the water line, namely (101)-(000)  $2_{11}-3_{12}$  of  $\text{H}_2^{16}\text{O}$ , interfering  
 199 with the profile of the (2-0)  $R(0)$  line of HD. A first low resolution (100 MHz) survey scan (blue dots) is recorded,  
 200 from which the line center is roughly determined using a Gaussian profile (red line). The spectrum is supplemented  
 201 with a high resolution (20 kHz) scan around the center (see inset). The center of Lamb dip determined is determined  
 202 with a kHz accuracy from a single scan: 214904329.8263(15) MHz.

203 Following the same treatment as described for the  $R(1)$  line, the thirty-three fourfold interlaced  
 204 spectra of the  $R(0)$  line were fitted with a Voigt profile with 77 K Doppler width and an effective  
 205 Lorentzian width of 4 MHz (this value is an averaged value obtained after a first fit session in which the  
 206 Lorentzian width was kept free). In **Fig. 5**, we present one of the 33 fitted spectra with the corresponding  
 207 residuals. The residuals (blue trace) show an asymmetry which is interpreted as due to the above water  
 208 line and may affect the determination of the  $R(0)$  line center. To minimize this effect, a weak water line  
 209 contribution was added in the fit procedure. The center of the water line was fixed at its Lamb dip value  
 210 (dashed vertical line in **Fig. 5**). The profile was taken as a Doppler profile corresponding to a temperature  
 211 of 300K and the amplitude was adjusted. As a result, a symmetric residual is obtained (red trace). The  
 212 fit RMS of a single spectrum is evaluated to  $4 \times 10^{-12} \text{ cm}^{-1}$  leading to a quality factor of about 8500.



213  
 214 **FIG. 5.**  
 215 The (2-0)  $R(0)$  HD line at liquid nitrogen temperature and a pressure of about 2 Pa.  
 216 (a) Averaged spectrum (33 acquisitions, black dots) at a pressure of 2 Pa and corresponding best fit profile (red  
 217 line),  
 218 (b) Residuals obtained from a fit of one of the thirty-three fourfold interlaced spectra, including or not the water  
 219 line (red and blue points, respectively). The water line position is indicated by the vertical blue dashed line,  
 220 (c) Residuals obtained for the averaged spectrum including or not the water line (red and blue points, respectively)-  
 221 see text for details,  
 222 (d) Residuals obtained for a simulation of the  $R(0)$  line as the sum of four different Doppler profiles at 77, 82, 218  
 223 and 275 K centered at the value previously determined and with fitted relative area of 84.6%, 14.3%, 1.1% and  
 224 0.1%, respectively. The water line is included in the fit with its position fixed to its Lamb dip value.

225 Averaging the 33 determinations of the center of the (2-0)  $R(0)$  line leads to a value of  
226 214905335220 kHz with a  $1\sigma$  statistical deviation of 29 kHz. The Allan-variance plot of the line position  
227 series included in **Fig. 3**, confirms the absence of an obvious frequency determination drift over time.  
228 Although the number of recordings is limited, the statistics allows for a gain compared to the RMS  
229 value. In order to be conservative, we adopted the same 20 kHz uncertainty value as for the  $R(0)$  line.

230 To validate our approach and better reveal the water line contribution in the baseline noise, we  
231 averaged together the 33 individual spectra to produce a single spectrum with improved signal-to-noise  
232 ratio. We fitted this spectrum by adjusting exclusively the line area, the line position and widths being  
233 fixed to their above values. The residuals included in **Fig.5** illustrate the gain on the S/N ratio (the trace  
234 thickness is decreased to about  $7\times 10^{-13}$  cm<sup>-1</sup>) and the water line is then clearly visible. It is interesting to  
235 note that the water line is very weak ( $10^{-11}$  cm<sup>-1</sup> peak absorption *e.g.* one order of magnitude stronger  
236 than the noise level) but it shifts the fitted value of the HD line center by about 3 kHz because it slightly  
237 distorts the HD line profile. Let us emphasize that the averaged spectrum only served to confirm the  
238 contribution of the water line and validate the position parameter obtained from the 33 single fit  
239 determinations.

240 A clear symmetric structure remains in the residuals of our best fit (including the water line). We  
241 interpret this structure as a consequence of a temperature gradient due to the mirrors which are kept at  
242 room temperature and in contact with the gas. The effects of this gradient was revealed in spectra of  
243 methane at 80 K recorded with a similar cryogenic cell [38]. The relative population of high rotational  
244 energy levels of methane was found significantly larger than expected from the Boltzmann distribution  
245 at 80 K]. To test this interpretation, the continuous gradient of temperatures was modeled by four zones  
246 of decreasing sizes and increasing temperatures (77, 82, 218 and 275 K). It appears then that the profile  
247 of the HD line can be reproduced at the noise level limit by a sum of four Doppler profiles, corresponding  
248 to 77, 82, 218 and 275 K, with center fixed at the above-determined HD frequency, and a relative weight  
249 to the total area of 84.6, 14.3%, 1.1% and 0.1%, respectively. In this way, the symmetric structure  
250 remaining in the residuals vanishes (see lowest panel of **Fig. 5**) and the quality factor reaches a value of  
251 50000. Even if based on a rough approximation, this result confirms that the linewidth is largely  
252 dominated by temperature rather than collisional effects that would affect the line center. The Lorentzian  
253 component used in the global fit procedure of the individual spectra is only an approximate solution  
254 which has the advantage of preserving the symmetry of the profile.

## 255 Transition frequencies and comparison with literature

### 256 *Transition frequencies and error budget*

257 The line center frequencies of the HD (2-0)  $R(0)$  and  $R(1)$  along with the one of the (101)-(000)  
258  $2_{11-3_{12}}$  H<sub>2</sub>O transition are listed in **Table 1**. After correcting those frequencies by the recoil, the second  
259 order Doppler effect and the pressure shift, we obtain absolute transition frequencies of

260 217105181898(20) and 214905335185(20) kHz for the (2-0)  $R(1)$  and  $R(0)$  HD transitions respectively  
 261 and 214904329820.80(10) kHz for the  $\text{H}_2^{16}\text{O}$  (101)-(000)  $2_{11-3_{12}}$  transition.

262 The  $R(1)$  pressure shift correction was calculated using the pressure-shift coefficient of -  
 263  $0.87 \pm 0.05$  kHz/Pa determined in [19] for the  $R(1)$  transition. It leads to a correction of 1.74(1) kHz for  
 264 our line center measured at 2 Pa. As concerns the  $R(0)$  transition, in absence of literature value, we  
 265 adopted the pressure shift coefficient of the  $R(1)$  transition with a very conservative relative uncertainty  
 266 of 50 % (pressure shifts coefficients measured for  $\text{H}_2$  transitions do not show important rotational  
 267 dependence [38], [39]). The frequency calibration chain is expected to bring no bias.

268 **Table 1**

269 Determination of the zero-pressure frequency and uncertainty ( $\sigma$ ) contributions in kHz for the (2-0)  $R(1)$  and  $R(0)$   
 270 transitions of HD and for the (101)-(000)  $2_{11-3_{12}}$  transition of  $\text{H}_2\text{O}$ .

	HD (2-0) $R(1)$		HD (2-0) $R(0)$		$\text{H}_2^{16}\text{O}$ (101)-(000) $2_{11-3_{12}}$	
Number of recordings	83		33		243	
	Value (kHz)	$\sigma$ (kHz)	Value (kHz)	$\sigma$ (kHz)	Value (kHz)	$\sigma$ (kHz)
Measured line center	217105181934	53/20 <sup>a</sup>	214905335220	29/20 <sup>a</sup>	214904329826.33	1.5/0.1 <sup>a</sup>
Pressure shift <sup>b</sup>	-1.74	0.1	-1.74	0.9	$\approx 0$	$\approx 0$
Quadratic Doppler effect	0.25	0	0.25	0	0.16	
Recoil	-34.62		-33.92		-5.69	
Transition frequency	217105181898	53/20 <sup>a</sup>	214905335185	30/21 <sup>a</sup>	214904329820.80	1.5/0.1 <sup>a</sup>

271  
 272 *Notes*

273 <sup>a</sup> The first value is the RMS of the different determinations. The second value is the reduced value allowed by the  
 274 statistics (see text),

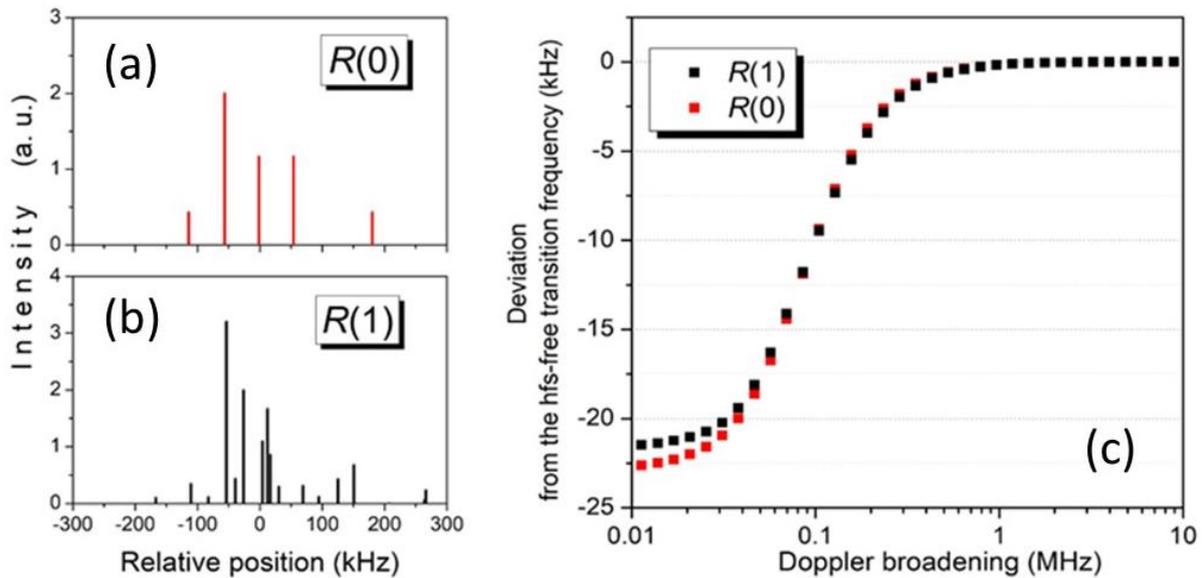
275 <sup>b</sup> The  $R(1)$  pressure shift of  $-0.87(5)$  kHz/Pa was taken from [19] for the  $R(1)$  transition and assumed to be identical  
 276 for the  $R(0)$  transition (see text).

277  
 278 From **Table 1**, it appears that for the three considered lines, the overall uncertainty on the  
 279 transition frequency is largely dominated by the line (or dip) center determination. Due to the low  
 280 pressure of our recordings (2 Pa for HD and  $\sim 10^{-3}$  Pa for  $\text{H}_2\text{O}$ ), the impact of the pressure shift is mostly  
 281 negligible. In **Table 1**, we give for the different transitions the RMS deviation of the different  
 282 determinations together with a (lower) error value resulting of the statistics of the recordings ( $N= 83, 33$   
 283 and 243 recordings for  $R(1)$ ,  $R(0)$  and  $\text{H}_2^{16}\text{O}$ , respectively). In the case of the water line, the Allan  
 284 deviation plot (**Fig. 3**) show that the statistics follows a normal law and the final uncertainty of about  
 285 100 Hz coincides with standard deviation. As discussed above, in the case of the  $R(1)$  and  $R(0)$   
 286 transitions of HD, the  $1/\sqrt{N}$  trend is less obvious and, on the basis of **Fig. 3**, we give a 20 kHz  
 287 uncertainty value as a conservative estimate of the real error bar.

288 Another possible source of error, not mentioned in **Table 1**, is related to the underlying hyperfine  
 289 structure (hfs) of the  $R(1)$  and  $R(0)$  lines. The hfs structure of HD lines has been modeled in the literature  
 290 by *ab initio* calculations [4] and a combination of *ab initio* calculations, an effective Hamiltonian and  
 291 tensorial algebra [21]. The influence of the hfs on the pressure shift value and on the frequency  
 292 determination of the (2-0)  $R(1)$  was discussed in [19]. In the above profile analysis, the effect of the hfs  
 293 was neglected considering it to be barycentric. In order to evaluate quantitatively the error associated to

294 this approximation, we first calculated the hfs of the (2-0)  $R(0)$  and (2-0)  $R(1)$  transitions using the  
 295 parameters provided in [21] and changing the sign of some of them as mentioned in [18]. Other  
 296 spectroscopic parameters were obtained from a global fit including experimental data concerning the  $\nu=$   
 297 0 [11], [40] and  $\nu=2$  [25], [12], [17] states. Eigenvalues and relative intensities were evaluated using  
 298 the PGOPHER software [41]. Simulations were performed by convolving the resulting stick spectra  
 299 (**Fig. 6**) with a Gaussian profile. A series of simulated spectra were obtained by varying the full width  
 300 at half maximum (FWHM) between 10 kHz and 30 MHz. The result of the overall profile was then fitted  
 301 with a single Gaussian whose center, FWHM and area were adjusted. The differences between the line  
 302 center of the Gaussian fit and the hfs-free transition frequency are plotted in **Fig. 6** versus the FWHM  
 303 value used for the convolution. It appears that the apparent line center frequency is systematically  
 304 smaller than the hfs-free transition frequency but the impact is very small for Gaussian widths larger  
 305 than 1 MHz. The two considered HD lines have a Doppler broadening at 77 K of about 770 MHz making  
 306 the impact of the hfs on the line profile totally negligible, as could have been expected from the spectral  
 307 extension of the hfs (on the order of  $\pm 200$  kHz) compared to the Doppler width. Note that the negligible  
 308 impact of the hfs and possible associated cross-overs is an advantage for measurements in Doppler  
 309 regime at low optical power regime.

310



311

312 FIG. 6.

313 Impact of the hyperfine structure on the line center determination.

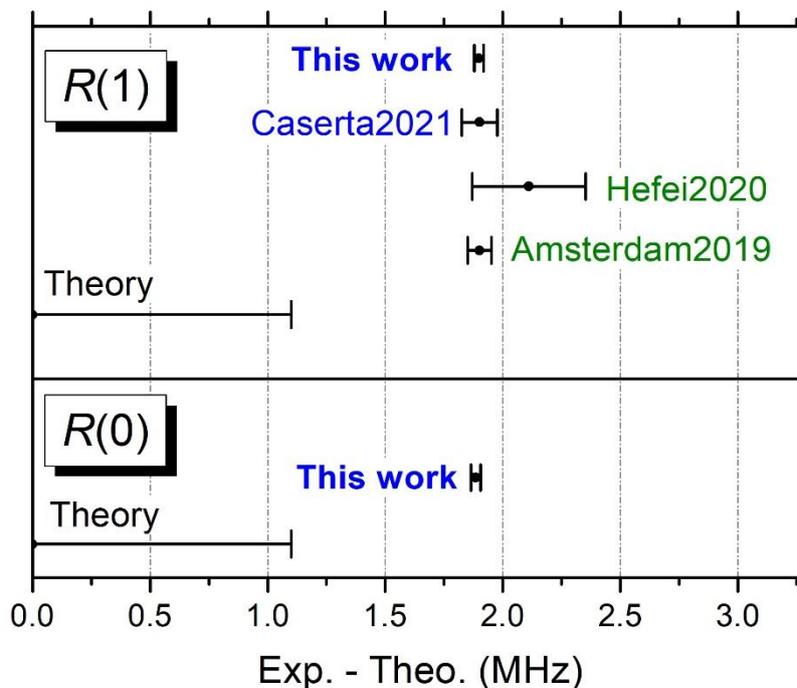
314 (a) (b) Calculated hfs of the (2-0)  $R(0)$  and  $R(1)$  transitions of HD, (c) Deviation of the apparent line center  
 315 from the hfs-free transition frequency as a function of the FWHM of the Gaussian profile used to convolve the hfs  
 316 (see text).

317

#### 317 *Comparison with literature*

318 In **Figure 7** and **Table 2**, our (2-0)  $R(1)$  transition frequency is compared with the most precise  
 319 measurements available to date. As mentioned above, the Hefei [26], and Amsterdam [16] values were

320 obtained in saturation regime while the Caserta value [19] relies on recordings in Doppler regime, as in  
 321 the present work, but at room temperature. The four determinations are consistent. In particular, our  
 322 value is only 3 kHz below the identical values measured in Amsterdam and Caserta, a difference about  
 323 twenty times smaller than the error bars of the Amsterdam and Caserta studies (50 and 76 kHz,  
 324 respectively).



325  
 326 **FIG.7**  
 327 Comparison between the most recent experimental frequencies determination, in MHz, for the  $R(1)$  and  $R(0)$   
 328 transitions of the (2-0) vibrational band of HD. Amsterdam2019 refers to [16], Hefei2020 to [26], Caserta2021 to  
 329 [19]. References related to measurements in Doppler regime or by saturation spectroscopy are indicated in blue  
 330 and green, respectively. The origin of the frequency scale is the frequency evaluated theoretically from the  
 331 H2spectre software detailed in [3] (see **Table 2**).

332  
 333 **Table 2**  
 334 Comparison between the most recent experimental and theoretical frequencies determination, in MHz, for the  $R(0)$   
 335 and  $R(1)$  transitions of the (2-0) vibrational band.

	$R(1)$	$R(0)$
Grenoble 2011 [12]	217 105 192(30)	214 905 315(30)
Amsterdam 2019 [16]	181.901(50)	
Hefei 2020 [26]	182.111(241)	
Caserta 2021 [19]	181.901(76)	
<b>This work</b>	<b>217 105 181.898(20)</b>	<b>214 905 335.185(20)</b>
Theory [3]	180.0(1.1)	333.3(1.1)

336  
 337 The frequency of the (2-0)  $R(0)$  transition is consistent with the previous determination of [12]  
 338 reported with a 30 MHz uncertainty. The uncertainty value is presently reduced by three orders of  
 339 magnitude.

340 We have also included in **Table 2** the transition frequency provided by theory (values were  
 341 computed using the H2spectre software detailed in Ref. [3]). These calculated values were used as

342 frequency origins in **Fig. 7**. For both for the  $R(0)$  and  $R(1)$  transitions, theoretical values are  
343 underestimated by about 1.88 MHz, what represents 1.7 times their claimed error bar (1.1 MHz). A  
344 similar deviation was already reported for the (2-0)  $P(1)$ ,  $R(2)$ ,  $R(3)$  lines measured with sub-MHz  
345 accuracy in Doppler-free regime [25], [17]. The mean deviation is of 1.91 MHz with a standard deviation  
346 of only 25 kHz for the five transitions,  $P(1)$  and  $R(0-3)$ .

## 347 Conclusion

348 The (2-0)  $R(0)$  and  $R(1)$  transition frequencies have been determined in Doppler regime with an  
349 accuracy of 20 kHz (relative accuracy of about  $10^{-10}$ ). This level of accuracy was made possible by  
350 combining a very stable and coherent laser source, an absolute calibration of the frequency scale and the  
351 sensitivity of the CRDS technique, together with a liquid nitrogen cooled cell. The latter permitted to  
352 decrease Doppler transition linewidth and spectra contamination by water lines.

353 Indeed, up to now, the spectral interference with a water line had hampered high accuracy  
354 transition frequency measurements of the  $R(0)$  transition. The accuracy of the reported  $R(0)$  transition  
355 frequency represents a gain by three orders of magnitude compared to literature. The analysis of the  
356  $R(0)$  line profile benefited of the accurate determination of the transition frequency of the (101)-(000)  
357  $2_{11-3_{12}}$  interfering line of  $H_2^{16}O$ , from separate recordings performed in saturation regime. A series of  
358 247 Lamb dips were recorded, each scan providing a 1.5 kHz accuracy on the Lamb dip center  
359 determination. The Allan deviation indicates that the obtained dip centers follow the normal law, the  
360 final precision is enhanced to about 100 Hz. This level of accuracy (relative uncertainty of  $5 \times 10^{-13}$ ) is at  
361 the state-of-the-art for molecular transition frequencies [42], [43], [44].

362 In the case of the  $R(1)$  transition of HD, our accuracy is at the level of the best previous  
363 determinations both in saturation regime and in Doppler regime. Note that the only accurate  
364 determination in Doppler regime was obtained from room temperature spectra recorded with pressures  
365 between 100 and 1500 Pa [19]. The sensitivity of the CRDS set-up used in the present work allowed us  
366 to record spectra at a significantly smaller pressure of 2 Pa which simplified the line profile analysis and  
367 made the self-pressure shift of the line center almost negligible.

368 The obtained results extend the set of accurate transition frequencies in the first overtone band of  
369 HD. The comparison to the most recent theoretical values [3] shows a systematic underestimation of 1.9  
370 MHz of the calculated transition frequencies compared to the five accurate values at disposal,  $P(1)$  and  
371  $R(0-3)$ . This observation provides a challenge for future refinement of the non-adiabatic perturbation  
372 theory or any other theory applied to HD.

## 373 Conflicts of interest

374 There are no conflicts to declare.

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378

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