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Accurate deuterium spectroscopy for fundamental studies

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ABSTRACT

We present an accurate measurement of the weak quadrupole S(2) 2-0 line in self-perturbed D_2 and theoretical *ab initio* calculations of both collisional line-shape effects and energy of this rovibrational transition. The spectra were collected at the 247–984 Torr pressure range with a frequency-stabilized cavity ring-down spectrometer linked to an optical frequency comb (OFC) referenced to a primary time standard. Our line-shape modeling employed quantum calculations of molecular scattering (the pressure broadening and shift and their speed dependencies were calculated, while the complex frequency of optical velocity-changing collisions was fitted to experimental spectra). The velocity-changing collisions are handled with the hard-sphere collisional kernel. The experimental and theoretical pressure broadening and shift are consistent within 5% and 27%, respectively (the discrepancy for shift is 8% when referred not to the speed averaged value, which is close to zero, but to the range of variability of the speed-dependent shift). We use our high pressure measurement to determine the energy, ν_0, of the S(2) 2-0 transition. The *ab initio* line-shape calculations allowed us to mitigate the expected collisional systematics reaching the 410 kHz accuracy of ν_0. We report theoretical determination of ν_0 taking into account relativistic and QED corrections up to α^5. Our estimation of the accuracy of the theoretical ν_0 is 1.3 MHz. We observe 3.4σ discrepancy between experimental and theoretical ν_0.

1. Introduction

Molecular hydrogen in its ground electronic state, the simplest neutral chemically bound system, constitutes the most suitable platform for testing quantum electrodynamics (QED) for molecules and for searching for new physics beyond the standard model [1], such as new forces [2] or extra dimensions [3]. However, direct experimental studies on the rovibrational structure of H_2 are difficult to perform because of the absence of strong dipole coupling between the levels. Typical Doppler-free saturation spectroscopy is not applicable to weak quadrupole molecular transitions. Two independent experimental strategies have been advanced to reach the megahertz level of accuracy in the determination of the frequencies of rovibrational lines. The first one [4–8] is based on Doppler-free two-photon spectroscopy of electronic transitions in molecular beams. Two different vibrational levels in the ground electronic state were coupled to the same excited electronic level. This allowed the energy difference between the ($v = 1$, $j = 0$) and ($v = 0$, $j = 0$) ground electronic states to be determined with an accuracy of 2.8 MHz [7]. This approach has great potential for improvements because of recent progress in Ramsey-comb spectroscopic techniques [9]. The second strategy operates in the Doppler-limited regime. It takes advantage of ultra-high finesse cavities to directly measure the weak quadrupole lines and has already achieved the kilohertz level of accuracy [10–12] typical for Doppler-free techniques. However, in the case of molecular hydrogen, the collisional line-shape effects are very pronounced and untypical [13–15]. As a result, the line position does not scale linearly with pressure [16]; this phenomenon usually is not taken into account [17]. To avoid such systematic errors, Mondelain et al. [18] measured the D_2 S(2) 2-0 line at very low pressure, where collisions are negligible, reaching an accuracy of 0.50 MHz.

In this article, we present experimental and theoretical studies on the shape of the D_2 S(2) 2-0 line, which allowed us to bring the previous measurements of the line position into the high-pressure range and reach (despite a twenty times shorter effective optical path) the same sub-megahertz level of accuracy as the Doppler-regime measurements [18]. The spectra were recorded with a frequency-stabilized cavity ring-down spectrometer linked

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Table 1
Line position and line-shape parameters (T = 294.9 K) retrieved from fits to our experimental spectra with different approaches. ν_0 is the unperturbed line position, $\delta\nu_0$ is the deviation of ν_0 from our best determination, Γ_D is the Gaussian half width at half maximum (HWHM), γ_0 and δ_0 are the pressure broadening and shift parameters, γ_{SD} and δ_{SD} are parameters that quantify the strength of the broadening and shift speed dependence (see the text for details), and $\tilde{\nu}^{i}_{opt}$ and $\tilde{\nu}^{i}_{opt}$ are the real and imaginary parts of the frequency of the optical velocity-changing collisions (also called Dicke-narrowing parameter). Rows (a)–(e) present the values of the line-shape parameters retrieved from experimental spectra with different approaches. The corresponding residuals are shown in panels (a)–(e) in Fig. 4. Row (c) shows the parameters retrieved from our ultimate fit. The last three columns define the conditions of the fits. SD denotes the speed dependence of the collisional broadening and shift. The last row shows the theoretical *ab initio* values. The error bars in rows (a) to (e) are 1σ standard uncertainties retrieved from the fits' residuals and the covariance matrix. In particular, the uncertainty of ν_0 in row (c) is the same as the number in the first row of Table 2. The error bars in the last row are our estimations of the 1σ uncertainties of the theoretical calculations (see the text for details). The zero uncertainty means that it is smaller than one at the last reported digit. ν_0, $\delta\nu_0$ and Γ_D are in 10^{-3} cm^{-1}, whereas all the other parameters are in 10^{-3} cm^{-1}/atm.

Line-shape model	ν_0	$\delta\nu_0$	Γ_D	γ_0	δ_0	γ_{SD}	δ_{SD}	$\tilde{\nu}^{r}_{opt}$	$\tilde{\nu}^{i}_{opt}$	Etalons	SD	Fit type
a) VP	6241127.479(29)	−0.176	3.6(1.5)	12.0(3.5)	−1.93(3)	–	–	–	–	no	–	line-by-line
b) HCP	6241127.474(22)	−0.181	19.12(fixed)	1.96(53)	−1.89(3)	–	–	20.2(5)	–	no	–	line-by-line
c) $SD_{ai}BBP$ (ultimate fit)	**6241127.655(4)**	**0.000**	**19.12(fixed)**	**3.57(0)**	**−1.75(0)**	**0.62(fixed)**	**3.41(fixed)**	**30.09(3)**	**−5.76(2)**	**yes**	**fixed**	**multi spect.**
d) $SD_{ai}BBP$ (all param. fitted)	6241127.625(8)	−0.030	19.12(fixed)	4.06(1)	−1.91(1)	−1.27(8)	0.18(7)	34.9(2)	1.0(1)	yes	fitted	multi spect.
e) $SD_{ai}BBP$ (without etalons)	6241127.582(11)	−0.073	19.12(fixed)	3.51(1)	−1.74(1)	0.62(fixed)	3.41(fixed)	29.68(6)	−6.15(5)	no	fixed	multi spect.
f) *Ab initio*	6241127.515(37)	−0.140	19.12(1)	3.38(11)	−1.27(27)	0.62(2)	3.41(15)	30.7(2.3)	–	–	–	–

Table 2
Estimated contributions to the standard uncertainty budget of our experimental determination of the frequency of the S(2) 2-0 transition in D_2, ν_0 = 187 104 300.038 (401) MHz.

Uncertainty source (type)	u(ν_0) / kHz
1) Statistics, 1σ (A)	132
2) Optical frequency comb (A+B)	< 1
3) Line-shape analysis (B)	357
4) Instrumental systematic shift (B)	47
5) Relativistic asymmetry (B)	< 3
6) Pressure gauge nonlinearity (B)	< 1
7) Etalons (B)	59
8) Temperature instability (A+B)	100
Standard combined uncertainty	**401**

to an optical frequency comb (OFC) referenced to a primary time standard. The experiment was carried out at room temperature and pressures varying from 247 to 984 Torr. In contrast to most of the works devoted to the analysis of the shapes of experimental molecular lines, where simple phenomenological models (such as hard- [19,20] or soft-collision [21] models of the velocity-changing collision and quadratic or hypergeometric approximations of the speed dependence) are applied, we employ an approach originating from first principles [14,15,22,23]. We performed fully quantum calculations of molecular scattering to obtain the pressure broadening and shift and their speed dependencies. The complex frequency of optical velocity-changing collisions was fitted to experimental spectra. The velocity-changing collisions are handled with a collisional kernel that originates from the hard-sphere approximation of the potential energy surface [14] (the resulting profile is called speed-dependent billiard-ball profile [24] with *ab initio* speed dependence). Our experimental and theoretical determinations of the pressure broadening are consistent within 5%. The relative discrepancy for the pressure shift is 27%. This value is, however, misleading because for this system the shift is large and strongly depends on absorber speed, but its speed-averaged value is close to zero. Therefore to provide better measure of the relative discrepancy one should refer the difference not to the speed-averaged value but to the range of the shift variability and then the relative discrepancy equals to 8%. The real part of the fitted frequency of the optical velocity-changing collisions is consistent with the frequency of the velocity-changing collisions calculated from kinetic theory. We use our measurement to determine the energy, ν_0, of the S(2) 2-0 transition. The *ab initio* line-shape calculations allowed us to mitigate the expected collisional systematics (the line asymmetry originating from speed dependence of collisional shift) reaching the accuracy of 401 kHz.

We report theoretical determination of ν_0 taking into account relativistic and QED corrections up to α^5. Our estimation of the accuracy of the theoretical ν_0 is 1.3 MHz. We observe 3.4σ discrepancy between experimental and theoretical ν_0. The reason for this discrepancy is not known.

2. *Ab initio* line-shape modeling

2.1. Velocity distribution of an optical coherence at the stationary state

The shapes of molecular lines can be modeled by determining the velocity distribution of an optical coherence associated with the considered transition from the transport-relaxation equation [22,23,25–27]

$$f_m(\vec{v}) = -i(\omega - \omega_0 - \vec{k}\cdot\vec{v})f(\omega,\vec{v}) - \hat{S}f(\omega,\vec{v}), \quad (1)$$

where ω and ω_0 are the angular frequency of the electromagnetic radiation and the unperturbed angular frequency of the molecular