Journal of Quantitative Spectroscopy & Radiative Transfer 272 (2021) 107753

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Hyperfine structure of rovibrational quadrupole transitions in HD

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ARTICLE INFO

Article history:
Received 1 April 2021
Revised 13 May 2021
Accepted 13 May 2021
Available online 21 May 2021

Keywords:
Hydrogen molecule
Hyperfine structure
Hydrogen deuteride

ABSTRACT

We perform a theoretical investigation of hyperfine structure of all rovibrational quadrupole transitions in the ground electronic $^1\Sigma^+$ state of the HD molecule. We determine positions and intensities of 185 631 hyperfine components of 7 251 quadrupole rovibrational transitions from the O, Q and S branches. Moreover, we provide a list of hyperfine splittings of all bound states in the six isotopologues of hydrogen which we considered in previous papers. The results reported here are necessary for a reliable interpretation of accurate experimental studies of rovibrational transition frequencies in the HD isotopologue, which are useful for tests of quantum electrodynamics for molecules and searches for new physics beyond the Standard Model.

1. Introduction

Accurate experimental studies of rovibrational transitions in the ground electronic state of molecular hydrogen provide a stringent test of quantum electrodynamics for neutral molecules [1] and can be used to put constraints on hypothetical beyond-Standard-Model interactions [2,3] or higher dimensions [4]. The presence of a weak dipole moment in the HD isotopologue makes it a suitable candidate for accurate measurements using saturation spectroscopy [5–9], molecular beam spectroscopy [10] or Doppler-limited cavity-enhanced techniques [11–13]. Although the latter require careful treatment of collisional effects, which might affect the determined transition frequency [14], current state-of-the-art cavity-enhanced measurements have already achieved a sub-MHz accuracy for both dipole transitions in HD [12] and quadrupole transitions in D_2 [15–19].

Quadrupole transitions in HD, which are significantly weaker than dipole transitions, have been studied less frequently [11,20–23] (see Ref. [23] for a thorough review of detected absorption lines in HD). The most accurate experimental data was reported by Kassi and Campargue [11], who measured the transitions frequencies of the Q($N = 1$–4) and S($N = 0$–4) lines from the first overtone with an uncertainty at a level of several MHz. As the accuracy of future experiments will most likely surpass the MHz level, the underlying hyperfine structure of rovibrational transitions should be taken into account. As shown recently by Castrillo et al. [13], neglecting the hyperfine splittings in the analysis of Doppler-limited spectra of the 2-0 R(1) line leads to a significant underestimation of the determined transition frequency.

Hyperfine interactions in the HD molecule were recently studied by several authors [24–27]. Dupré [24] reported the hyperfine coupling constants for the first three vibrational levels ($\nu = 0, 1, 2, N = 1$) and studied the hyperfine components of the 2-0 P(1) and R(1) lines in HD. In our previous work [25] on the hyperfine structure of HD, we reported hyperfine coupling constants for all bound states of HD in its ground electronic state. Moreover, we provided a list of positions and intensities of 108 320 hyperfine components of 5 129 dipole transitions from the P and R branches. Komasa et al. [26] calculated coupling constants for several rovibrational states and analyzed the relative intensities of the hyperfine components of the 2-0 P(1) and R(1) transitions and of the R(0) line from the fundamental band. The authors have also provided a publicly available code, which allows the user to calculate hyperfine splittings for a given rovibrational level. Very recently, Puchalski et al. [27] have determined the value of the hyperfine coupling constants for the ($\nu = 0, N = 1$) level, taking into account the nonadiabatic effects, which led to the most accurate determination of the quadrupole moment of the deuteron.

In this work, we extend our previous study [25] and we analyze the hyperfine structure of all rovibrational quadrupole transitions from the O, Q and S branches in the HD molecule. Our calculations result in a list of all 185 631 hyperfine components of 7 251 rovi-

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https://doi.org/10.1016/j.jqsrt.2021.107753

Table 1
Example of the calculated positions and intensities of the hyperfine components of the quadrupole transitions in the HD isotopologue. Frequencies of the rovibrational transitions are calculated with H2Spectre code of Czachorowski et al. [40] and Komasa et al. [1]. Please note that for the rovibrational transition $\mathcal{Q}$ corresponds to $\mathcal{Q}_{\mathrm{fi}}$ from Eq. (2), while for the hyperfine components $\mathcal{Q}$ denotes $\mathcal{Q}_{\mathrm{fi}}^{\mathrm{HF}}$ from Eq. (9). Intensity (in the sixth column) corresponds to the temperature-independent line intensity, $S_{\mathrm{fi}}/P_{\mathrm{fi}}(T)$.

Band	Line	Hyperfine transition $\|N'F'\pm\rangle \leftarrow \|NF\pm\rangle$	Frequency (MHz)	$\mathcal{Q}$ (10^{-2} a.u.)	Intensity (cm/molecule)	Intensity at 296 K (cm/molecule)
2-0	Q(1)		212 230 347.4 (5.7)	0.958	1.935×10^{-27}	7.556×10^{-28}
		$\|1\,5/2\rangle \leftarrow \|1\,1/2+\rangle$	−0.2446	0.656	1.262×10^{-28}	4.929×10^{-29}
		$\|1\,3/2-\rangle \leftarrow \|1\,1/2+\rangle$	−0.1893	0.550	8.858×10^{-29}	3.459×10^{-29}
		$\|1\,1/2-\rangle \leftarrow \|1\,3/2+\rangle$	−0.1683	0.401	4.720×10^{-29}	1.843×10^{-29}
		$\|1\,3/2+\rangle \leftarrow \|1\,1/2+\rangle$	−0.1336	0.025	1.872×10^{-31}	7.310×10^{-32}
		$\|1\,1/2-\rangle \leftarrow \|1\,3/2-\rangle$	−0.1121	0.584	9.987×10^{-29}	3.900×10^{-29}
		$\|1\,5/2\rangle \leftarrow \|1\,3/2+\rangle$	−0.1113	0.895	2.348×10^{-28}	9.168×10^{-29}
		$\|1\,3/2-\rangle \leftarrow \|1\,3/2+\rangle$	−0.0557	0.519	7.887×10^{-29}	3.080×10^{-29}
		$\|1\,1/2-\rangle \leftarrow \|1\,5/2\rangle$	−0.0556	0.482	6.793×10^{-29}	2.653×10^{-29}
		$\|1\,5/2\rangle \leftarrow \|1\,3/2-\rangle$	−0.0550	0.351	3.611×10^{-29}	1.410×10^{-29}
		$\|1\,3/2+\rangle \leftarrow \|1\,3/2+\rangle$	−0.0003	0.486	6.905×10^{-29}	2.696×10^{-29}
		$\|1\,3/2-\rangle \leftarrow \|1\,3/2-\rangle$	0.0003	0.657	1.264×10^{-28}	4.935×10^{-29}
		$\|1\,5/2\rangle \leftarrow \|1\,5/2\rangle$	0.0014	0.785	1.806×10^{-28}	7.052×10^{-29}
		$\|1\,3/2+\rangle \leftarrow \|1\,3/2-\rangle$	0.0556	0.517	7.831×10^{-29}	3.058×10^{-29}
		$\|1\,3/2-\rangle \leftarrow \|1\,5/2\rangle$	0.0568	0.341	3.413×10^{-29}	1.333×10^{-29}
		$\|1\,5/2\rangle \leftarrow \|1\,1/2-\rangle$	0.0599	0.479	6.727×10^{-29}	2.627×10^{-29}
		$\|1\,3/2+\rangle \leftarrow \|1\,5/2\rangle$	0.1125	0.899	2.368×10^{-28}	9.246×10^{-29}
		$\|1\,3/2-\rangle \leftarrow \|1\,1/2-\rangle$	0.1153	0.590	1.020×10^{-28}	3.985×10^{-29}
		$\|1\,1/2+\rangle \leftarrow \|1\,3/2+\rangle$	0.1261	0.018	9.330×10^{-32}	3.643×10^{-32}
		$\|1\,3/2+\rangle \leftarrow \|1\,1/2-\rangle$	0.1709	0.395	4.569×10^{-29}	1.784×10^{-29}
		$\|1\,1/2+\rangle \leftarrow \|1\,3/2-\rangle$	0.1823	0.552	8.934×10^{-29}	3.489×10^{-29}
		$\|1\,1/2+\rangle \leftarrow \|1\,5/2\rangle$	0.2388	0.655	1.256×10^{-28}	4.903×10^{-29}
2-0	S(3)		232 595 960.8 (5.7)	1.025	3.475×10^{-27}	3.675×10^{-28}
		$\|5\,9/2-\rangle \leftarrow \|3\,5/2+\rangle$	−0.4196	0.062	6.429×10^{-31}	6.798×10^{-32}
		$\|5\,9/2-\rangle \leftarrow \|3\,7/2+\rangle$	−0.2661	0.046	3.528×10^{-31}	3.731×10^{-32}
		$\|5\,11/2-\rangle \leftarrow \|3\,7/2+\rangle$	−0.2279	0.062	6.267×10^{-31}	6.627×10^{-32}
		$\|5\,9/2-\rangle \leftarrow \|3\,7/2-\rangle$	−0.1078	0.567	5.313×10^{-29}	5.618×10^{-30}
		$\|5\,13/2\rangle \leftarrow \|3\,9/2\rangle$	−0.0908	2.112	7.372×10^{-28}	7.795×10^{-29}
		$\|5\,11/2-\rangle \leftarrow \|3\,7/2-\rangle$	−0.0696	1.875	5.811×10^{-28}	6.144×10^{-29}
		$\|5\,9/2-\rangle \leftarrow \|3\,5/2-\rangle$	−0.0393	1.688	4.707×10^{-28}	4.977×10^{-29}
		$\|5\,9/2-\rangle \leftarrow \|3\,9/2\rangle$	−0.0069	0.104	1.780×10^{-30}	1.882×10^{-31}
		$\|5\,11/2-\rangle \leftarrow \|3\,9/2\rangle$	0.0313	0.551	5.019×10^{-29}	5.307×10^{-30}
		$\|5\,11/2+\rangle \leftarrow \|3\,7/2+\rangle$	0.0442	1.892	5.915×10^{-28}	6.255×10^{-29}
		$\|5\,7/2\rangle \leftarrow \|3\,5/2+\rangle$	0.0536	0.592	5.789×10^{-29}	6.122×10^{-30}
		$\|5\,9/2+\rangle \leftarrow \|3\,5/2+\rangle$	0.0572	1.628	4.379×10^{-28}	4.631×10^{-29}
		$\|5\,7/2\rangle \leftarrow \|3\,3/2\rangle$	0.0874	1.415	3.310×10^{-28}	3.500×10^{-29}
		$\|5\,11/2+\rangle \leftarrow \|3\,7/2-\rangle$	0.2024	0.196	6.320×10^{-30}	6.683×10^{-31}
		$\|5\,7/2\rangle \leftarrow \|3\,7/2+\rangle$	0.2072	0.145	3.471×10^{-30}	3.670×10^{-31}
		$\|5\,9/2+\rangle \leftarrow \|3\,7/2+\rangle$	0.2108	0.632	6.603×10^{-29}	6.982×10^{-30}
		$\|5\,11/2+\rangle \leftarrow \|3\,9/2\rangle$	0.3034	0.454	3.407×10^{-29}	3.602×10^{-30}
		$\|5\,7/2\rangle \leftarrow \|3\,7/2-\rangle$	0.3655	0.153	3.884×10^{-30}	4.107×10^{-31}
		$\|5\,9/2+\rangle \leftarrow \|3\,7/2-\rangle$	0.3691	0.326	1.757×10^{-29}	1.858×10^{-30}
		$\|5\,7/2\rangle \leftarrow \|3\,5/2-\rangle$	0.4339	0.388	2.485×10^{-29}	2.628×10^{-30}
		$\|5\,9/2+\rangle \leftarrow \|3\,5/2-\rangle$	0.4375	0.076	9.630×10^{-31}	1.018×10^{-31}
		$\|5\,7/2\rangle \leftarrow \|3\,9/2\rangle$	0.4664	0.032	1.672×10^{-31}	1.768×10^{-32}
		$\|5\,9/2+\rangle \leftarrow \|3\,9/2\rangle$	0.4700	0.157	4.071×10^{-30}	4.305×10^{-31}

brational quadrupole transitions. Moreover, we provide a list of hyperfine levels of all bound states in the six isotopologues of hydrogen which we have considered in previous papers. This work concludes the series of papers devoted to the hyperfine interactions and analysis of the structure of electric dipole [25,28] and electric quadrupole [29,30] transitions in the ground electronic state of the six isotopologues of hydrogen. We summarize the theory behind the calculations in Sections 2 and 3 and we provide the examples of the calculated hyperfine structure in Section 4.

2. Hyperfine interactions in HD

Hyperfine splittings of rovibrational states in HD originate from three leading interactions: the nuclear-spin–rotation interaction, the nuclear dipole-dipole coupling, and the interaction of the electric quadrupole moment of the deuteron with the molecular electric field gradient (EFG). Following our previous works [25,28–30], we neglect the electron-coupled spin-spin interaction [24,31–34], which is almost three orders of magnitude smaller than the leading hyperfine interactions considered here. We recall that in Ref. [25] we reported hyperfine coupling constants for all bound states in the ground electronic $^1\Sigma^+$ state of HD. It was pointed out [27] that the discrepancies between the hyperfine coupling constants calculated in our previous papers [25,29] and other theoretical results [26,27] might originate from the fact that we used the Born–Oppenheimer (BO) potential of Schwenke [35] instead of the state-of-the-art potential of Pachucki [36]. We note, however, that the BO potential is used only to obtain the rovibrational wavefunctions that are employed to average the hyperfine coupling curves (see, for example Eq. (9) in Ref. [25]). The error introduced by performing the average over rovibrational wavefunctions can be estimated by comparing the quantities which depend only on such averaging, namely the nuclear dipole-dipole constants (evaluation of this constant does not require quantum-chemical calculations; it is given by a simple formula). A comparison between the values of these constants reported in Ref. [25] with those reported by Komasa et al. (see Tab. IV in Ref. [26]) and Puchalski et al. (see Tab. I in Ref. [27]) indicates that the error is of an order of tens of Hz. Therefore, we attribute the differences between our previous

Table 2
Example of the calculated hyperfine splittings in the three isotopologues of hydrogen. $E_{(\nu,N,F,(\pm))} - E_{(\nu,N)}$ denotes the energy of each hyperfine level with respect to the energy of each rovibrational state. See text for details.

Isotopologue	ν	N	F	$(\pm)$	$E_{(\nu,N,F,(\pm))} - E_{(\nu,N)}$ (MHz)	Mixing coefficients	
						F_1/I	$a^{\nu,N,F(\pm)}_{F_1/I}$
HD	0	1	1/2	−	−0.1169	0	$-9.47737204 \times 10^{-1}$
						1	$3.19052022 \times 10^{-1}$
	0	1	5/2		−0.0584		
	0	1	3/2	−	−0.0020	1	$-7.13360400 \times 10^{-1}$
						2	$7.00797360 \times 10^{-1}$
	0	1	3/2	+	0.0543	1	$7.00797369 \times 10^{-1}$
						2	$7.13360391 \times 10^{-1}$
	0	1	1/2	+	0.1876	0	$3.19052022 \times 10^{-1}$
						1	$9.47737204 \times 10^{-1}$
H_2	0	1	2		−0.0853		
	0	1	1		−0.0299		
	0	1	0		0.5165		
D_2	0	2	2	−	−0.0690	0	$7.92215947 \times 10^{-1}$
						2	$6.10240848 \times 10^{-1}$
	0	2	4		−0.0631		
	0	2	0		−0.0455		
	0	2	1		−0.0052		
	0	2	3		0.0560		
	0	2	2	+	0.1163	0	$6.10240849 \times 10^{-1}$
						2	$-7.92215947 \times 10^{-1}$

results [25] and the results reported in Refs. [26] to the possible differences in the calculated nuclear spin-rotation curve. We note, however, that the discrepancy between the position of hyperfine levels reported in Ref. [25] and Ref. [26] is, on average, 400 Hz, which is within the combined uncertainty of our results (300 Hz) and those reported in Ref. [26] (100 Hz), and is of an order of magnitude smaller than the uncertainty of the most accurate measurement of the rovibrational line frequency in HD [10]. Here, for the sake of consistency, we use the data reported by us in the previous paper [25].

Matrix elements of the effective hyperfine Hamiltonian are determined using coupling scheme which is suitable for the heteronuclear molecules. The rotational angular momentum of the molecule, $\mathbf{N}$, is coupled to the nuclear spin of the deuteron, $\mathbf{I}_{\mathrm{D}}$, to form the intermediate angular momentum, $\mathbf{F}_1$. The intermediate angular momentum is in turn coupled to the nuclear spin angular momentum of the proton, $\mathbf{I}_{\mathrm{H}}$, to form the total angular momentum, $\mathbf{F}$. The coupled basis vector is denoted as $|\nu;((NI_{\mathrm{D}})F_1I_{\mathrm{H}})Fm_{\mathrm{F}}\rangle$, where m_{F} is the projection of the total angular momentum on the space-fixed z-axis.

The hyperfine Hamiltonian does not couple states with different values of the total angular momentum F. Energy levels were obtained from diagonalization of each $(2I_D+1)(2I_H+1) \times (2I_D+1)(2I_H+1) = 6 \times 6$ blocks, and the eigenvectors of the hyperfine Hamiltonian are denoted as $|\nu; NFm_{\mathrm{F}}(\pm)\rangle$. The $\pm$ labels denote the eigenstates for given N and F which are of higher (+) or lower (−) energies. The relation between the eigenbasis and the coupled basis is given by:

$$|\nu; NFm_{\mathrm{F}}(\pm)\rangle = \sum_{F_1=|F-I_{\mathrm{H}}|}^{F+I_{\mathrm{H}}} \sum_{N'=|F_1-I_{\mathrm{D}}|}^{F_1+I_{\mathrm{D}}} a^{\nu NF(\pm)}_{N'F_1} \left|\nu; \left((N'I_{\mathrm{D}})F_1I_{\mathrm{H}}\right)Fm_{\mathrm{F}}\right\rangle, \tag{1}$$

where $a^{\nu NF(\pm)}_{N'F_1}$ denote the mixing coefficients. Since the mixing between different rotational levels is negligibly small, we can disregard the sum over N' and simplify the notation by putting $a^{\nu NF(\pm)}_{N'=NF_1} = a^{\nu NF(\pm)}_{F_1}$.

3. Intensities of hyperfine components of rovibrational quadrupole transitions

The intensity of each quadrupole transition between two degenerate states, in the SI units, is given [37–39] as:

$$S_{\mathrm{fi}} = \frac{2\pi^4}{15hc^3\epsilon_0}\nu_0^3 C_{N_{\mathrm{i}},N_{\mathrm{f}}} P_{\mathrm{fi}}(T)|\mathcal{Q}_{\mathrm{fi}}|^2, \tag{2}$$

where ν_0 is the transition frequency and the electric quadrupole transition moment is denoted by $\mathcal{Q}_{\mathrm{fi}}$. h, c and ϵ_0 are Planck's constant, the speed of light in vacuum and vacuum permittivity, respectively. $C_{N_{\mathrm{i}},N_{\mathrm{f}}}$ is an algebraic coefficient, which depends on the initial and final rotational quantum number:

$$C_{N_{\mathrm{i}},N_{\mathrm{f}}} = (2N_{\mathrm{f}}+1)\begin{pmatrix} N_{\mathrm{f}} & 2 & N_{\mathrm{i}} \\ 0 & 0 & 0 \end{pmatrix}^2. \tag{3}$$

Here, we give the direct formulas for:

1. the O branch ($N_{\mathrm{f}} = N_{\mathrm{i}} - 2$):

$$C_{N_{\mathrm{i}},N_{\mathrm{f}}} = \frac{3N_{\mathrm{i}}(N_{\mathrm{i}}-1)}{2(2N_{\mathrm{i}}-1)(2N_{\mathrm{i}}+1)}, \tag{4}$$

2. the Q branch ($N_{\mathrm{f}} = N_{\mathrm{i}}$):

$$C_{N_{\mathrm{i}},N_{\mathrm{f}}} = \frac{N_{\mathrm{i}}(N_{\mathrm{i}}+1)}{(2N_{\mathrm{i}}-1)(2N_{\mathrm{i}}+3)}, \tag{5}$$

3. the S branch ($N_{\mathrm{f}} = N_{\mathrm{i}} + 2$):

$$C_{N_{\mathrm{i}},N_{\mathrm{f}}} = \frac{3(N_{\mathrm{i}}+1)(N_{\mathrm{i}}+2)}{2(2N_{\mathrm{i}}+1)(2N_{\mathrm{i}}+3)}. \tag{6}$$

The temperature-dependent term, $P_{\mathrm{fi}}(T)$, is given as

$$P_{\mathrm{fi}}(T) = w_{\mathrm{i}}(2N_{\mathrm{i}}+1)\frac{\left(e^{-E_{\mathrm{i}}/k_{\mathrm{B}}T} - e^{-E_{\mathrm{f}}/k_{\mathrm{B}}T}\right)}{Q(T)}, \tag{7}$$

with the partition function, $Q(T)$, defined as:

$$Q(T) = \sum_{\mathrm{k}} w_{\mathrm{k}}(2N_{\mathrm{k}}+1)e^{-E_{\mathrm{k}}/k_{\mathrm{B}}T}. \tag{8}$$

w_{k} is the degeneracy factor due to nuclear spin statistics and equals 6 for each rovibrational state of HD. E_{k} is the energy of the

k-th rovibrational state, k_B denotes the Boltzmann constant and T is the temperature.

Line intensity of each hyperfine component of a rovibrational quadrupole transition is given as [29,30]:

$$S_\mathrm{fi}^\mathrm{HF} = \frac{2\pi^4}{15hc^3\epsilon_0}\nu_0^3\frac{1}{w_\mathrm{i}(2N_\mathrm{i}+1)}P_\mathrm{fi}(T)\left|\mathcal{Q}_\mathrm{fi}^\mathrm{HF}\right|^2, \tag{9}$$

where $\mathcal{Q}_\mathrm{fi}^\mathrm{HF}$ is the reduced matrix element of the quadrupole moment spherical tensor, evaluated using Eq. (1):

$$\begin{aligned}&\left|\mathcal{Q}_\mathrm{fi}^\mathrm{HF}\right|^2 = \left|\langle\nu_\mathrm{f};N_\mathrm{f}F_\mathrm{f}(\pm)_\mathrm{f}\|\mathrm{T}^{(2)}(\mathcal{Q})\|\nu_\mathrm{i};N_\mathrm{i}F_\mathrm{i}(\pm)_\mathrm{i}\rangle\right|^2 = \\ &\Bigg|\sum_{F_{1_\mathrm{f}}=|F_\mathrm{f}-I_\mathrm{H}|}^{F_\mathrm{f}+I_\mathrm{H}}\sum_{N'_\mathrm{f}=|F_{1_\mathrm{f}}-I_\mathrm{D}|}^{F_{1_\mathrm{f}}+I_\mathrm{D}}\sum_{F_{1_\mathrm{i}}=|F_\mathrm{i}-I_\mathrm{H}|}^{F_\mathrm{i}+I_\mathrm{H}}\sum_{N'_\mathrm{i}=|F_{1_\mathrm{i}}-I_\mathrm{D}|}^{F_{1_\mathrm{i}}+I_\mathrm{D}} \\ &a_{N'_\mathrm{f}F_{1_\mathrm{f}}}^{\nu_\mathrm{f}N_\mathrm{f}F_\mathrm{f}(\pm)_\mathrm{f}}a_{N'_\mathrm{i}F_{1_\mathrm{i}}}^{\nu_\mathrm{i}N_\mathrm{i}F_\mathrm{i}(\pm)_\mathrm{i}} \\ &\times\langle\nu_\mathrm{f};\big((N'_\mathrm{f}I_\mathrm{D})F_{1_\mathrm{f}}I_\mathrm{H}\big)F_\mathrm{f}\|\mathrm{T}^{(2)}(\mathcal{Q})\|\nu_\mathrm{i};\big((N'_\mathrm{i}I_\mathrm{D})F_{1_\mathrm{i}}I_\mathrm{H}\big)F_\mathrm{i}\rangle\Bigg|^2.\end{aligned} \tag{10}$$

The latter term can be related to the quadrupole transition moment of the rovibrational transition

$$\mathcal{Q}_\mathrm{fi} = \int \mathrm{d}R\chi_\mathrm{f}^*(R)\mathcal{Q}(R)\chi_\mathrm{i}(R), \tag{11}$$

where $\mathcal{Q}(R)$ is the quadrupole moment function [37–39]:

$$\mathcal{Q}(R) = e\left(\frac{R^2}{2}-\frac{1}{2}\langle\phi|\sum_i 3z_i^2-r_i^2|\phi\rangle\right). \tag{12}$$

Here, z_i and r_i denote the coordinates of the ith electron and $|\phi\rangle$ is the electronic wavefunction, which is parametrically dependent on the internuclear coordinate, R. The relation between Eq. (10) and the quadrupole transition moment is given as:

$$\begin{aligned}&\langle\nu_\mathrm{f};\big((N_\mathrm{f}I_\mathrm{D})F_{1_\mathrm{f}}I_\mathrm{H}\big)F_\mathrm{f}\|\mathrm{T}^{(2)}(\mathcal{Q})\|\nu_\mathrm{i};\big((N_\mathrm{i}I_\mathrm{D})F_{1_\mathrm{i}}I_\mathrm{H}\big)F_\mathrm{i}\rangle \\ = \;&(-1)^{F_\mathrm{i}+I_\mathrm{H}+F_{1_\mathrm{f}}+F_{1_\mathrm{i}}+I_\mathrm{D}+N_\mathrm{f}}\sqrt{(2F_\mathrm{i}+1)(2F_\mathrm{f}+1)} \\ &\times\sqrt{(2F_{1_\mathrm{i}}+1)(2F_{1_\mathrm{f}}+1)}\begin{Bmatrix}I_\mathrm{H} & F_\mathrm{i} & F_{1_\mathrm{i}}\\ 2 & F_{1_\mathrm{f}} & F_\mathrm{f}\end{Bmatrix} \\ &\times\begin{Bmatrix}I_\mathrm{D} & F_{1_\mathrm{i}} & N_\mathrm{i}\\ 2 & N_\mathrm{f} & F_{1_\mathrm{f}}\end{Bmatrix}\langle\nu_\mathrm{f}N_\mathrm{f}\|\mathrm{T}^{(2)}(\mathcal{Q})\|\nu_\mathrm{i}N_\mathrm{i}\rangle\,.\end{aligned} \tag{13}$$

For a $^1\Sigma$ state, the last term in Eq. (13) is given as:

$$\begin{aligned}&\langle\nu_\mathrm{f}N_\mathrm{f}\|\mathrm{T}^{(2)}(\mathcal{Q})\|\nu_\mathrm{i}N_\mathrm{i}\rangle \\ &= (-1)^{N_\mathrm{f}}\sqrt{(2N_\mathrm{f}+1)(2N_\mathrm{i}+1)}\begin{pmatrix}N_\mathrm{f} & 2 & N_\mathrm{i}\\ 0 & 0 & 0\end{pmatrix}\mathcal{Q}_\mathrm{fi}.\end{aligned} \tag{14}$$

In this work, we use the quadrupole transition moment function reported in Ref. [29], to evaluate the quadrupole transition matrix for all quadrupole transitions in the ground state of the HD molecule.

4. Example of the complete dataset record

4.1. Hyperfine components of rovibrational quadrupole transitions

We calculate the positions and intensities of the hyperfine components of all quadrupole transitions in the ground $^1\Sigma^+$ electronic state of the HD isotopologue. Our calculations result in 185 631 hyperfine components of 7 251 transitions from the O, Q and S branches. Following our previous papers [25,28–30] we estimate the uncertainty of the determined transition frequencies to be approximately 0.4 kHz and the uncertainty of the transition moment and line intensity to be of an order of 10^{-3}.

Table 1 presents an example of the calculated parameters for the Q(1) and S(3) lines from the first overtone (2-0) band, which were investigated by Kassi and Campargue [11]. The central frequency of the rovibrational transition is taken from the H2Spectre code [1,40]. The 2-0 Q(1) line consists of 21 hyperfine components spread over a range of almost 500 kHz. The 2-0 S(3) line consists of 23 hyperfine components spread over a range of over 900 kHz.

We note that every $\nu_\mathrm{f}-\nu_\mathrm{i}$ O(2) and S(0) lines in HD consist of 10 hyperfine components, every O(3) and S(1) lines involve 22 hyperfine components, while all the remaining rovibrational lines from these two branches involve 23 components. In the case of the Q branch, the Q(1) and Q(2) lines involve 21 and 33 hyperfine components, respectively, while all the remaining lines involve 34 components.

4.2. List of hyperfine splittings

We also provide a list of hyperfine splittings of all bound states in the six isotopologues of hydrogen which we have considered in the previous papers [25,28–30]. Such a list should be a practical tool for the spectroscopic community and a more convenient way to determine hyperfine splittings of a given state than using the hyperfine coupling constants and diagonalizing the effective Hamiltonian. Example lists of the hyperfine splittings for the chosen states in HD, H_2 and D_2 are given in Table 2. The complete dataset can be found in Supplementary Material [41]. We recall that the uncertainty of the determined energy of each hyperfine level is approximately 300 Hz.

Apart from the energy levels of the hyperfine states, we provide values of the mixing coefficients for the heteronuclear isotopologues and for *ortho*-D_2. The hyperfine states in these isotopologues can be expressed as a linear combination of the coupled basis vectors (Eq. (1)). For example, the $|\nu=0,N=1,F=1/2+\rangle$ state in HD is a linear combination of the coupled basis vectors with $F_1=0$ and $F_1=1$, with mixing coefficients of approximately -0.948 and 0.319, respectively (see the two last columns of the first entry in Table 2). Similarly, the $|\nu=0,N=2,F=2-\rangle$ state in D_2 is a combination of coupled basis vectors (see Eq. (16) in Ref. [29]) with $I=0$ and $I=2$ with mixing coefficients of approximately 0.792 and 0.610, respectively.

5. Conclusion

We provide a comprehensive list of positions and intensities of the 185 631 hyperfine components of 7 251 rovibrational quadrupole transitions from the O, Q and S branches in HD. We also report a list of hyperfine splittings of all bound states in the six isotopologues of hydrogen which we analyzed in our previous papers. The results presented here can serve as a reference data for future accurate measurements of transition frequencies in the HD isotopologue, which could be useful for testing the quantum electrodynamics for molecules and searching for new physics beyond the Standard Model.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hubert Jóźwiak: Conceptualization, Methodology, Software, Investigation, Writing - original draft, Writing - review & editing, Funding acquisition. **Hubert Cybulski:** Software, Investigation, Writing - original draft, Writing - review & editing. **Piotr Wcisło:** Conceptualization, Methodology, Validation, Writing - original draft, Writing - review & editing.

Acknowledgements

The research is financed from the budgetary funds on science projected for 2019–2023 as a research project under the "Diamentowy Grant" program. P.W. is supported by the National Science Centre in Poland, Project no. 2019/35/B/ST2/01118. The research is a part of the program of the National Laboratory FAMO in Toruń, Poland.

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