Journal of Quantitative Spectroscopy & Radiative Transfer 253 (2020) 107171

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Positions and intensities of hyperfine components of all rovibrational dipole lines in the HD molecule

Hubert Jóźwiak[a,*], Hubert Cybulski[b], Piotr Wcisło[a]

[a] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, Toruń 87-100, Poland
[b] Institute of Physics, Kazimierz Wielki University, ul. Powstańców Wielkopolskich 2, Bydgoszcz 85-090, Poland

ARTICLE INFO

Article history:
Received 19 May 2020
Revised 9 June 2020
Accepted 10 June 2020
Available online 11 June 2020

Keywords:
Hydrogen molecule
Hyperfine structure
Dipole transitions

ABSTRACT

We report results of a theoretical analysis of hyperfine interactions in the HD molecule. We present the calculated coupling constants: spin-rotation, spin-spin and electric quadrupole coupling constants for all bound states of HD in its ground electronic $^1\Sigma$ state. We provide a list of positions and intensities of 108 320 hyperfine components of 5 129 dipole transitions from the P and R branches. The positions and intensities of the hyperfine components are necessary for a proper interpretation of accurate measurements of rovibrational transition frequencies in HD which are used for tests of quantum electrodynamics of molecules and searches for new physics beyond the Standard Model.

1. Introduction

Molecular hydrogen and its isotopologues constitute perfect benchmark systems for performing ultra-accurate tests of various theoretical models. Nowadays, theoreticians are able to employ the state-of-the-art computational methods to determine the rovibrational structure of the ground electronic state of H_2, reaching remarkable accuracy of the calculated transition frequencies [1,2] at the level of 2×10^{-5} cm^{-1}. Owing to the success of the nonadiabatic perturbation theory (NAPT) [3–5], as well as the inclusion of relativistic effects and QED corrections [1,6], current accuracy of theoretical results opens a possibility for searches for the physics beyond Standard Model [7], such as new forces [8] or extra dimensions [9].

On the other hand, the experimental studies of the H_2 rovibrational transitions are hindered by the lack of strong dipole couplings between the levels. Due to the symmetry of the ground electronic state of the hydrogen molecule, dipole transitions are either forbidden (in the case of H_2 and D_2) or weak (in the case of HD). Nevertheless, recent studies of quadrupole lines in D_2 [10–12] and dipole lines in HD [13–17] resulted in the sub-MHz accuracy of the determined transition frequencies, reaching, in the case of the 1-0 R(0) line studied by Fast and Meek [16], a relative accuracy of 1.2×10^{-12}. Such remarkable experimental results impose a need for a detailed analysis of the components of the unresolved hyperfine structure of each rovibrational transition. Moreover, the disagreement between the three experimental results of Tao et al. [14], Cozijn et al. [13] and Fasci et al. [15], who investigated the R(1) line from the first overtone in HD, is attributed to the presence of 21 hyperfine components and 68 cross-over resonances, analyzed by Diouf et al. [18]. Recently Dupré [19] reported hyperfine coupling constants for three vibrational levels ($\nu = 0, 1, 2$, $N = 1$) and studied hyperfine components of the P(1) and R(1) lines from the first overtone in HD at room temperature. For these reasons, it is desirable to obtain a comprehensive list of positions and intensities of hyperfine components of rovibrational resonances in molecular hydrogen isotopologues.

In this paper, we report a complete line list of hyperfine transitions between all 400 bound states of the HD molecule. We cover all possible dipole transitions, i.e. all rovibrational transitions from the P and R branches, which results in 108 320 hyperfine components of 5 129 dipole transitions. In order to properly reproduce line positions and intensities, we prepare a list of rovibrationally-averaged values of hyperfine coupling constants, i.e. spin-spin, spin-rotational and quadrupole coupling constants, for all bound states of HD. Positions and intensities of hyperfine components are necessary for a proper interpretation [17,18] of accurate measurements of rovibrational transition energies in HD which are used for tests of quantum electrodynamics of molecules [2] and searches for new physics beyond the Standard Model [7–9].

* Corresponding author.
E-mail addresses: hubert.jozwiak@stud.umk.pl (H. Jóźwiak), piotr.wcislo@umk.pl (P. Wcisło).

https://doi.org/10.1016/j.jqsrt.2020.107171

The paper is organised as follows: Section 2 provides a brief description of the hyperfine terms in the effective Hamiltonian of the HD molecule. The discussion is supplemented with an analysis of the rovibrationally-averaged coupling constants, reported in Section 3. Section 4 contains details about the diagonalization of the hyperfine Hamiltonian. Section 5 provides a description of the calculated rovibrational and hyperfine line intensities, while the example of the data provided in Supplementary Materials is given in Section 7. In Section 8 we give a brief conclusion of our results.

2. Hyperfine interactions

In the following analysis, we consider the effective hyperfine (HF) Hamiltonian for HD molecule in its ground electronic ($^1\Sigma$) state, which consists of four terms [19–21]:

$$\mathcal{H}_{\mathrm{HF}} = \mathcal{H}_{\mathrm{nsr_H}} + \mathcal{H}_{\mathrm{nsr_D}} + \mathcal{H}_{\mathrm{dip}} + \mathcal{H}_{\mathrm{quad}}. \tag{1}$$

The first two terms correspond to the nuclear spin-rotation coupling of proton and deuteron, respectively. $\mathcal{H}_{\mathrm{dip}}$ denotes the dipolar interaction between the two nuclear spins and $\mathcal{H}_{\mathrm{quad}}$ represents the interaction of the electric quadrupole moment of deuteron with the electric field gradient (EFG) produced by the proton and electrons. We remind the reader that the proton, as a nuclei with spin angular momentum $I_{\mathrm{H}} = \frac{1}{2}$, does not have an electric quadrupole moment. Here, we neglect the electron-coupled spin-spin interaction [21–25], which is, at least for the ground vibrational state of HD, almost three orders of magnitude smaller than the interactions contained in Eq. (1).

We choose a basis set appropriate for calculations of the matrix elements of the Hamiltonian from Eq. (1). Since we do not consider external magnetic field in this analysis, it is convenient to use a coupled basis formed of three angular momenta: the nuclear spin of the proton, $\mathbf{I}_{\mathrm{H}}$, the nuclear spin of the deuteron, $\mathbf{I}_{\mathrm{D}}$, and the rotational angular momentum, $\mathbf{N}$. As it was pointed out by Dupré [19], none of the three possible coupling schemes leads to a diagonal hyperfine structure Hamiltonian. Following Ref. [19], we first couple the rotational angular momentum $\mathbf{N}$ to deuteron's nuclear spin $\mathbf{I}_{\mathrm{D}}$ to form the intermediate angular momentum $\mathbf{F}_1$, which is then coupled to the nuclear spin of the proton, $\mathbf{I}_{\mathrm{H}}$ to form the total angular momentum, $\mathbf{F}$. We denote the state vector as $|\nu; NI_{\mathrm{D}}F_1I_{\mathrm{H}}Fm_{\mathrm{F}}\rangle$, where ν and m_{F} are the vibrational quantum number and the projection of the total angular momentum on the laboratory-fixed frame, respectively. Here, we confine ourselves to the analysis of the ground electronic $^1\Sigma$ state and we neglect any coupling between vibrational states.

2.1. Nuclear spin-rotation coupling

Nuclear spin-rotation coupling originates from the interaction of each nuclear magnetic moment with the magnetic field resulting from the overall rotation of the molecule. This phenomenon was firstly observed in $^1\Sigma$ molecules by Kellogg *et al.* [26,27], and analyzed theoretically by many authors [28–39]. In general case, the strength of this interaction is determined by the nuclear-spin coupling tensor [21,39]. However, for a diatomic molecule in a $^1\Sigma$ state, the coupling tensor reduces to a simple scalar value, which consists of the sum of the nuclear and electronic contributions to the molecule's magnetic field, averaged over the rovibrational wavefunction of the molecule. This part of the Hamiltonian can be written in the following manner:

$$\mathcal{H}_{\mathrm{nsr_H}} = c_{\mathrm{H}}\mathbf{I}_{\mathrm{H}} \cdot \mathbf{N} \tag{2}$$

and

$$\mathcal{H}_{\mathrm{nsr_D}} = c_{\mathrm{D}}\mathbf{I}_{\mathrm{D}} \cdot \mathbf{N}, \tag{3}$$

where c_{H} and c_{D} denote the spin-rotation coupling constant of the proton and deuteron, respectively (see Section 3).

Matrix elements of the spin-rotation interaction can be evaluated using spherical tensor operators [19,21,40], if one represents $\mathbf{I}_{\mathrm{H}}$, $\mathbf{I}_{\mathrm{D}}$ and $\mathbf{N}$ as spherical tensors of rank 1. The deuteron spin-rotation interaction part is diagonal in the chosen basis:

$$\begin{aligned}&\langle \nu; N'I'_{\mathrm{D}}F'_1I'_{\mathrm{H}}F'm'_{\mathrm{F}}|\mathcal{H}_{\mathrm{nsr_D}}|\nu; NI_{\mathrm{D}}F_1I_{\mathrm{H}}Fm_{\mathrm{F}}\rangle\\ &= \delta_{NN'}\delta_{I_{\mathrm{D}}I'_{\mathrm{D}}}\delta_{F_1F'_1}\delta_{I_{\mathrm{H}}I'_{\mathrm{H}}}\delta_{FF'}\delta_{m_{\mathrm{F}}m'_{\mathrm{F}}}\\ &\times \tfrac{c_{\mathrm{D}}}{2}\left(F_1(F_1+1) - I_{\mathrm{D}}(I_{\mathrm{D}}+1) - N(N+1)\right),\end{aligned} \tag{4}$$

while the proton spin-rotation interaction is not:

$$\begin{aligned}&\langle \nu; N'I'_{\mathrm{D}}F'_1I'_{\mathrm{H}}F'm'_{\mathrm{F}}|\mathcal{H}_{\mathrm{nsr_H}}|\nu; NI_{\mathrm{D}}F_1I_{\mathrm{H}}Fm_{\mathrm{F}}\rangle\\ &= \delta_{NN'}\delta_{I_{\mathrm{D}}I'_{\mathrm{D}}}\delta_{I_{\mathrm{H}}I'_{\mathrm{H}}}\delta_{FF'}\delta_{m_{\mathrm{F}}m'_{\mathrm{F}}}\\ &\times(-1)^{F+I_{\mathrm{H}}+I_{\mathrm{D}}+N'+2F_1+1}c_{\mathrm{H}}\sqrt{(2F_1+1)(2F'_1+1)}\\ &\times\sqrt{N(N+1)(2N+1)I_{\mathrm{H}}(I_{\mathrm{H}}+1)(2I_{\mathrm{H}}+1)}\\ &\times\begin{Bmatrix}F & I_{\mathrm{H}} & F'_1\\ 1 & F_1 & I_{\mathrm{H}}\end{Bmatrix}\begin{Bmatrix}I_{\mathrm{D}} & N & F'_1\\ 1 & F_1 & N\end{Bmatrix},\end{aligned} \tag{5}$$

which mixes states with different F_1 quantum numbers.

2.2. Spin-spin dipole interactions

The next term in the Hamiltonian from Eq. (1) corresponds to the magnetic dipole interaction between the nuclear magnetic moments of proton and deuteron. It can be written as

$$\mathcal{H}_{\mathrm{dip}} = g_{\mathrm{H}}g_{\mathrm{D}}\mu_{\mathrm{N}}^2\tfrac{\mu_0}{4\pi}\left[\tfrac{\mathbf{I}_{\mathrm{H}}\cdot\mathbf{I}_{\mathrm{D}}}{R^3} - \tfrac{3(\mathbf{I}_{\mathrm{H}}\cdot\mathbf{R})(\mathbf{I}_{\mathrm{D}}\cdot\mathbf{R})}{R^5}\right], \tag{6}$$

where g_{H} and g_{D} are the nuclear g factors of the proton and deuteron, respectively, μ_{N} is the nuclear magneton, μ_0 is the vacuum permeability and R is the internuclear distance.

One can again represent the nuclear angular momenta $\mathbf{I}_{\mathrm{H}}$ and $\mathbf{I}_{\mathrm{D}}$ as spherical tensors of rank 1 and couple the latter with the rank-2 tensor $\mathrm{T}^{(2)}(\mathbf{C})$, describing the spherical harmonics Y_{2q} associated with the transformation of the rovibronic wavefunction from the laboratory-fixed to the molecule-fixed frame of reference [19], to form the rank-1 tensor $\mathrm{T}^{(1)}(\mathbf{I_D}, \mathbf{C})$. The final form of the $\mathcal{H}_{\mathrm{dip}}$ term in the spherical tensorial representation is given as [19]:

$$\mathcal{H}_{\mathrm{dip}} = g_{\mathrm{H}}g_{\mathrm{D}}\mu_{\mathrm{N}}^2\tfrac{\mu_0}{4\pi}\sqrt{10}\mathrm{T}^{(1)}(\mathbf{I}_{\mathrm{H}})\cdot\mathrm{T}^{(1)}(\mathbf{I}_{\mathrm{D}}, \mathbf{C}), \tag{7}$$

and the matrix elements in the coupled basis are found to be:

$$\begin{aligned}&\langle \nu; N'I'_{\mathrm{D}}F'_1I'_{\mathrm{H}}F'm'_{\mathrm{F}}|\mathcal{H}_{\mathrm{dip}}|\nu; NI_{\mathrm{D}}F_1I_{\mathrm{H}}Fm_{\mathrm{F}}\rangle\\ &= \delta_{I_{\mathrm{D}}I'_{\mathrm{D}}}\delta_{I_{\mathrm{H}}I'_{\mathrm{H}}}\delta_{FF'}\delta_{m_{\mathrm{F}}m'_{\mathrm{F}}}(-1)^{F_1+I_{\mathrm{H}}+F+N'}c_{\mathrm{dip}}\\ &\times\sqrt{3(2F_1+1)(2F'_1+1)(2N+1)(2N'+1)}\\ &\times\sqrt{I_{\mathrm{H}}(I_{\mathrm{H}}+1)(2I_{\mathrm{H}}+1)I_{\mathrm{D}}(I_{\mathrm{D}}+1)(2I_{\mathrm{D}}+1)}\\ &\times\begin{pmatrix}N' & 2 & N\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}F & I'_{\mathrm{H}} & F'_1\\ 1 & F_1 & I_{\mathrm{H}}\end{Bmatrix}\begin{Bmatrix}I_{\mathrm{D}} & I_{\mathrm{D}} & 1\\ N & N' & 2\\ F_1 & F'_1 & 1\end{Bmatrix},\end{aligned} \tag{8}$$

where we introduced the coupling constant:

$$c_{\mathrm{dip}} = g_{\mathrm{H}}g_{\mathrm{D}}\mu_{\mathrm{N}}^2\frac{\mu_0}{4\pi}\langle \nu N|\frac{1}{R^3}|\nu N\rangle, \tag{9}$$

which can be easily evaluated using fundamental constants and numerical determination of the integral. Contrary to the previous terms, the spin-spin interaction mixes different rotational states, introducing a coupling between the N and $N' = N \pm 2$ states. However, as pointed out by Dupré [19], the corresponding matrix elements barely contribute to the coupling, since their values are significantly smaller than the energy differences between the rotational levels. Nevertheless, these matrix elements are included in our analysis.

2.3. Electric quadrupole interaction

The last term in the Hamiltonian from Eq. (1) corresponds to the quadrupole interaction. Deuteron, as a nucleus with spin angular momentum $I_{\mathrm{D}} = 1$, has an electric quadrupole moment, which

Table 1
Vibrationally-averaged nuclear spin-rotation coupling constants of the proton, c_H (in kHz), for all bound states (except for $v, N = 0$) of HD.

$v\backslash N$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	85.84	85.09	83.98	82.54	80.79	78.77	76.50	74.03	71.38	68.61	65.73	62.79	59.82	56.84
1	84.63	83.87	82.75	81.30	79.53	77.49	75.20	72.71	70.06	67.27	64.39	61.44	58.47	55.49
2	83.09	82.32	81.20	79.74	77.96	75.91	73.62	71.12	68.46	65.67	62.79	59.85	56.89	53.92
3	81.22	80.46	79.33	77.87	76.09	74.04	71.75	69.25	66.60	63.82	60.95	58.02	55.08	52.13
4	79.03	78.27	77.15	75.68	73.91	71.87	69.58	67.10	64.46	61.70	58.85	55.95	53.02	50.10
5	76.51	75.75	74.63	73.18	71.42	69.38	67.12	64.66	62.04	59.30	56.48	53.61	50.71	47.83
6	73.65	72.89	71.78	70.34	68.59	66.58	64.33	61.90	59.31	56.60	53.81	50.98	48.12	45.27
7	70.41	69.66	68.56	67.13	65.41	63.42	61.20	58.80	56.24	53.57	50.82	48.03	45.21	42.40
8	66.76	66.03	64.94	63.54	61.84	59.88	57.69	55.32	52.80	50.18	47.47	44.72	41.94	39.17
9	62.67	61.95	60.88	59.50	57.82	55.89	53.75	51.42	48.94	46.35	43.69	40.98	38.24	35.51
10	58.06	57.35	56.31	54.95	53.31	51.41	49.30	47.01	44.58	42.03	39.41	36.73	34.03	31.31
11	52.87	52.17	51.14	49.81	48.20	46.34	44.27	42.01	39.62	37.11	34.51	31.85	29.16	26.44
12	46.97	46.29	45.28	43.97	42.39	40.56	38.52	36.30	33.92	31.43	28.84	26.16	23.43	20.62
13	40.24	39.57	38.58	37.29	35.72	33.91	31.89	29.67	27.29	24.77	22.12	19.33	16.39	
14	32.48	31.81	30.83	29.55	27.99	26.17	24.12	21.85	19.38	16.69	13.74			
15	23.45	22.78	21.78	20.47	18.85	16.95	14.75	12.20						
16	12.83	12.11	11.02	9.54	7.61									
17	0.77													

$v\backslash N$	15	16	17	18	19	20	21	22	23	24	25	26	27	28
0	53.87	50.94	48.07	45.27	42.54	39.91	37.37	34.94	32.61	30.39	28.27	26.26	24.35	22.54
1	52.53	49.61	46.75	43.95	41.25	38.63	36.11	33.70	31.39	29.19	27.09	25.09	23.20	21.41
2	50.97	48.07	45.23	42.46	39.77	37.18	34.69	32.29	30.01	27.82	25.75	23.77	21.89	20.11
3	49.20	46.33	43.51	40.77	38.11	35.54	33.07	30.71	28.44	26.28	24.22	22.26	20.40	18.62
4	47.21	44.36	41.57	38.86	36.23	33.70	31.26	28.91	26.67	24.53	22.48	20.53	18.67	16.89
5	44.96	42.15	39.40	36.72	34.12	31.62	29.20	26.88	24.66	22.53	20.49	18.53	16.65	14.83
6	42.45	39.67	36.95	34.31	31.74	29.26	26.87	24.56	22.34	20.21	18.15	16.15	14.20	
7	39.62	36.88	34.20	31.58	29.04	26.57	24.19	21.88	19.64	17.46	15.33			
8	36.42	33.72	31.06	28.46	25.93	23.46	21.06	18.70	16.38					
9	32.79	30.10	27.46	24.86	22.30	19.79	17.29							
10	28.61	25.92	23.24	20.59	17.93	15.23								
11	23.70	20.94	18.15	15.27										
12	17.73	14.69												

$v\backslash N$	29	30	31	32	33	34	35	36
0	20.83	19.22	17.69	16.25	14.89	13.61	12.40	11.25
1	19.71	18.11	16.59	15.15	13.79	12.50	11.27	
2	18.42	16.82	15.30	13.86	12.48			
3	16.93	15.33	13.79	12.32				
4	15.18	13.54						

interacts with the electric field gradient at the position of the nucleus. This term can be represented using spherical tensorial algebra as:

$$\mathcal{H}_{\text{quad}} = -e\mathrm{T}^{(2)}(\mathbf{Q}) \cdot \mathrm{T}^{(2)}(\nabla\mathbf{E}), \tag{10}$$

where both the quadrupole moment, $\mathbf{Q}$, and the electric field gradient, $\nabla\mathbf{E}$, are given as the rank-2 spherical tensors (see Chapter 8.4 of Ref. [21] for more details).

Matrix elements of the quadrupole interaction are found to be:

$$\begin{aligned}&\langle v; N'I'_{\mathrm{D}}F'_1I'_{\mathrm{H}}F'm'_{\mathrm{F}}|\mathcal{H}_{\text{quad}}|v; NI_{\mathrm{D}}F_1I_{\mathrm{H}}Fm_{\mathrm{F}}\rangle\\ &= \delta_{I_{\mathrm{H}}I'_{\mathrm{H}}}\delta_{I_{\mathrm{D}}I'_{\mathrm{D}}}\delta_{F_1F'_1}\delta_{FF'}\delta_{m_{\mathrm{F}}m'_{\mathrm{F}}}(-1)^{N+I'_{\mathrm{D}}+F'_1+N'}\frac{c_{\mathrm{Q}}}{4}\\ &\times\sqrt{(2N+1)(2N'+1)}\begin{pmatrix}N' & 2 & N\\ 0 & 0 & 0\end{pmatrix}\\ &\times\begin{pmatrix}I_{\mathrm{D}} & 2 & I_{\mathrm{D}}\\ -I_{\mathrm{D}} & 0 & I_{\mathrm{D}}\end{pmatrix}^{-1}\begin{Bmatrix}F_1 & N' & I_{\mathrm{D}}\\ 2 & I'_{\mathrm{D}} & N\end{Bmatrix},\end{aligned} \tag{11}$$

where the quadrupole coupling constant:

$$c_{\mathrm{Q}} = eQ_{\mathrm{D}}q_0, \tag{12}$$

involves the electric quadrupole moment, Q_{D}, defined as the expectation value of the Q_{33} element of the traceless and symmetric nuclear quadrupole moment tensor Q_{ij}, in the spin-stretched state:

$$Q_{\mathrm{D}} = \langle I, m_I = I|Q_{33}|I, m_I = I\rangle\,, \tag{13}$$

and the rovibrationaly-averaged EFG at the nucleus, q_0, which is the expectation value of the V_{33} component of EFG, V_{ij}, in the given rovibrational state. Similarly to the spin-spin interaction, the quadrupole coupling weakly contributes to the mixing of the N and $N' = N \pm 2$ states.

3. Hyperfine coupling constants

The need for accurate determination of the hyperfine constants, including their internuclear distance dependence, was already recognized in the 1950s [34,41]. In order to properly reproduce the hyperfine structure, in particular for highly-excited rovibrational states, one has to determine the dependence of the coupling constants on the internuclear distance, R, and calculate the expectation values of the coupling constants in a given rovibrational state. In this section, we present the obtained coupling constants for all bound states of HD. Please note that Tables 1–4 do not include the $v, N = 0$ levels, since none of the analyzed hyperfine terms from Eq. (1) affect the ground rotational levels. Actually, it is the neglected electron coupled spin-spin interaction that causes a small hyperfine splitting of the $v, N = 0$ states (see Eq. (16) of Ref. [19]).

In the following analysis, we made use of the rovibrational wavefunctions of the HD molecule, $\chi_{v,N}(R) = \langle R|vN\rangle$, obtained from numerical solution of the Schrödinger equation for the isolated molecule within the Born-Oppenheimer approximation. The numerical calculations were performed on the intramolecular potential of Schwenke [42], using finite basis representation version of the discrete variable representation method (DVR-FBR), and resulted in the wavefunctions of all 400 bound states of HD. The

Table 2
Vibrationally-averaged nuclear spin-rotation coupling constants of the deuteron, c_D (in kHz), for all bound states (except for $\nu, N = 0$) of HD.

$\nu\backslash N$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	13.18	13.06	12.89	12.67	12.40	12.09	11.74	11.36	10.96	10.53	10.09	9.64	9.18	8.73
1	12.99	12.87	12.70	12.48	12.21	11.90	11.54	11.16	10.75	10.33	9.88	9.43	8.98	8.52
2	12.75	12.64	12.46	12.24	11.97	11.65	11.30	10.92	10.51	10.08	9.64	9.19	8.73	8.28
3	12.47	12.35	12.18	11.95	11.68	11.37	11.01	10.63	10.22	9.80	9.36	8.91	8.45	8.00
4	12.13	12.02	11.84	11.62	11.35	11.03	10.68	10.30	9.90	9.47	9.03	8.59	8.14	7.69
5	11.75	11.63	11.46	11.23	10.96	10.65	10.30	9.92	9.52	9.10	8.67	8.23	7.78	7.34
6	11.31	11.19	11.02	10.80	10.53	10.22	9.88	9.50	9.10	8.69	8.26	7.83	7.39	6.95
7	10.81	10.69	10.52	10.31	10.04	9.74	9.40	9.03	8.63	8.22	7.80	7.37	6.94	6.51
8	10.25	10.14	9.97	9.75	9.49	9.19	8.86	8.49	8.11	7.70	7.29	6.86	6.44	6.01
9	9.62	9.51	9.35	9.13	8.88	8.58	8.25	7.89	7.51	7.12	6.71	6.29	5.87	5.45
10	8.91	8.80	8.64	8.43	8.18	7.89	7.57	7.22	6.84	6.45	6.05	5.64	5.22	4.81
11	8.12	8.01	7.85	7.65	7.40	7.11	6.80	6.45	6.08	5.70	5.30	4.89	4.48	4.06
12	7.21	7.11	6.95	6.75	6.51	6.23	5.91	5.57	5.21	4.82	4.43	4.02	3.60	3.17
13	6.18	6.07	5.92	5.72	5.48	5.21	4.89	4.55	4.19	3.80	3.39	2.97	2.52	
14	4.99	4.88	4.73	4.54	4.30	4.02	3.70	3.35	2.97	2.56	2.11			
15	3.60	3.50	3.34	3.14	2.89	2.60	2.26	1.87						
16	1.97	1.86	1.69	1.46	1.17									
17	0.12													

$\nu\backslash N$	15	16	17	18	19	20	21	22	23	24	25	26	27	28
0	8.27	7.82	7.38	6.95	6.53	6.13	5.74	5.36	5.01	4.66	4.34	4.03	3.74	3.46
1	8.06	7.62	7.18	6.75	6.33	5.93	5.54	5.17	4.82	4.48	4.16	3.85	3.56	3.29
2	7.82	7.38	6.94	6.52	6.11	5.71	5.32	4.96	4.61	4.27	3.95	3.65	3.36	3.09
3	7.55	7.11	6.68	6.26	5.85	5.46	5.08	4.71	4.37	4.03	3.72	3.42	3.13	2.86
4	7.25	6.81	6.38	5.97	5.56	5.17	4.80	4.44	4.09	3.77	3.45	3.15	2.87	2.59
5	6.90	6.47	6.05	5.64	5.24	4.85	4.48	4.13	3.79	3.46	3.14	2.84	2.56	2.28
6	6.52	6.09	5.67	5.27	4.87	4.49	4.12	3.77	3.43	3.10	2.79	2.48	2.18	
7	6.08	5.66	5.25	4.85	4.46	4.08	3.71	3.36	3.01	2.68	2.35			
8	5.59	5.18	4.77	4.37	3.98	3.60	3.23	2.87	2.52					
9	5.03	4.62	4.22	3.82	3.42	3.04	2.65							
10	4.39	3.98	3.57	3.16	2.75	2.34								
11	3.64	3.21	2.79	2.34										
12	2.72	2.26												

$\nu\backslash N$	29	30	31	32	33	34	35	36
0	3.20	2.95	2.72	2.49	2.29	2.09	1.90	1.73
1	3.03	2.78	2.55	2.33	2.12	1.92	1.73	
2	2.83	2.58	2.35	2.13	1.92			
3	2.60	2.35	2.12	1.89				
4	2.33	2.08						

accuracy of the calculations was estimated by comparing the obtained dissociation energies with those reported in Ref. [2]. Overall, the average value of the relative differences is approximately 0.16% and is mostly attributed to the weakly bound states with large values of ν.

3.1. Nuclear spin-rotation coupling constant

Nuclear spin-rotation constants were calculated at the coupled cluster with single and double (CCSD) excitation level using gauge-including atomic orbitals (GIAOs). For two-electron hydrogen molecule and its isotopologues the CCSD method is equivalent to a full configuration-interaction (FCI) treatment. The uncontracted cc-pV6Z basis set [43,44] was used. The calculations were performed for the interatomic R distances in the 0.30–4.00 Å range with steps of 0.01 Å (for distances larger than 4.00 Å the values of the nuclear spin-rotation constants drop to zero). The numerical results of the R-dependent coupling constants are provided in Supplementary Materials [45]. All the calculations have been performed with the CFOUR quantum-chemical package [46] (version 2.1). In Tables 1 and 2 we collected the rovibrationally-averaged values of the spin-rotation constants for proton and deuteron, respectively.

3.1.1. Spin-spin dipole interaction

The coupling constant which determines the strength of the spin-spin interaction, Eq. (9), were obtained using DVR-wavefunctions $\chi_{\nu N}$ and the fundamental constants which were taken from CODATA [47]. Table 3 contains the results for all bound states of the HD molecule.

3.2. Electric quadrupole interaction

The analysis of the quadrupole coupling constant, Eq. (12), is based on the data provided by Pavanello et al. [48]. The authors performed calculations of the EFG at the nucleus in the H_2 molecule, within the Born-Oppenheimer approximation. 53 values of EFG, determined for different internuclear distances, were vibrationally averaged over the wavefunctions of isolated D_2 and HD molecules, obtained from the potential energy curve of Kołos and Wolniewicz [49]. Finally, the authors used the averaged values of q_0 and the quadrupole coupling constant reported by Ramsey from measurements performed for $\nu = 0, N = 1$ level of HD [20] and $\nu = 0, N = 1$ and $\nu = 0, N = 2$ levels of D_2 [24], to determine the electric quadrupole moment of the deuteron. On the other hand, Dupré [19] calculated the averaged value of the EFG independently and obtained the set of quadrupole coupling constants for first three vibrational states.

Here, we have performed rovibrational average of the EFG values reported in Ref. [48] and, using the experimental value of Quinn et al. [20] reported for the $\nu = 0, N = 1$ state of HD ($c_Q = 224.54(6)$ kHz), we determined the value of Q_D:

$$Q_D = 0.28591(8)\ \text{fm}^2, \tag{14}$$

Table 3
Spin-spin dipole coupling constants, c_{dip} (in kHz), for all bound states (except for $\nu, N = 0$) of HD.

$\nu\backslash N$	1	2	3	4	5	6	7	8	9	10	11	12
0	44.396	44.089	43.636	43.043	42.322	41.484	40.541	39.508	38.397	37.223	36.000	34.739
1	43.029	42.723	42.272	41.684	40.967	40.135	39.200	38.176	37.077	35.916	34.708	33.464
2	41.605	41.302	40.855	40.271	39.561	38.737	37.811	36.798	35.712	34.566	33.374	32.149
3	40.121	39.821	39.377	38.799	38.097	37.282	36.368	35.368	34.297	33.167	31.993	30.787
4	38.569	38.272	37.834	37.263	36.570	35.765	34.863	33.878	32.822	31.710	30.555	29.368
5	36.942	36.649	36.216	35.653	34.969	34.176	33.288	32.317	31.278	30.184	29.048	27.882
6	35.227	34.938	34.512	33.957	33.283	32.503	31.628	30.674	29.652	28.576	27.460	26.314
7	33.409	33.125	32.706	32.160	31.497	30.729	29.870	28.931	27.926	26.869	25.771	24.644
8	31.471	31.192	30.780	30.243	29.591	28.836	27.991	27.067	26.079	25.039	23.958	22.848
9	29.389	29.114	28.708	28.180	27.540	26.797	25.965	25.056	24.083	23.058	21.991	20.893
10	27.130	26.860	26.461	25.941	25.310	24.579	23.759	22.862	21.900	20.885	19.827	18.735
11	24.657	24.390	23.997	23.484	22.861	22.138	21.326	20.437	19.481	18.468	17.409	16.309
12	21.916	21.652	21.262	20.754	20.135	19.415	18.605	17.715	16.754	15.730	14.650	13.518
13	18.837	18.574	18.184	17.675	17.054	16.328	15.508	14.600	13.611	12.546	11.404	10.178
14	15.326	15.059	14.663	14.142	13.504	12.754	11.896	10.934	9.865	8.677	7.335	
15	11.246	10.965	10.547	9.993	9.305	8.481	7.510	6.364				
16	6.392	6.072	5.585	4.917	4.022							
17	0.505											

$\nu\backslash N$	13	14	15	16	17	18	19	20	21	22	23	24
0	33.453	32.153	30.848	29.547	28.257	26.985	25.737	24.515	23.324	22.167	21.045	19.960
1	32.196	30.916	29.632	28.353	27.087	25.838	24.613	23.416	22.249	21.114	20.015	18.951
2	30.901	29.641	28.380	27.123	25.880	24.655	23.453	22.279	21.134	20.021	18.942	17.898
3	29.559	28.321	27.082	25.848	24.627	23.425	22.246	21.093	19.969	18.876	17.815	16.786
4	28.162	26.946	25.728	24.517	23.318	22.137	20.978	19.845	18.739	17.662	16.615	15.597
5	26.697	25.502	24.305	23.115	21.937	20.775	19.634	18.517	17.424	16.358	15.318	14.303
6	25.148	23.973	22.797	21.625	20.465	19.319	18.191	17.084	15.999	14.934	13.891	12.865
7	23.497	22.340	21.180	20.024	18.876	17.740	16.619	15.513	14.422	13.345	12.277	11.213
8	21.717	20.574	19.426	18.279	17.136	16.000	14.872	13.750	12.633	11.513	10.378	
9	19.772	18.637	17.493	16.344	15.192	14.038	12.880	11.710	10.518			
10	17.616	16.477	15.321	14.150	12.964	11.755	10.512	9.209				
11	15.175	14.010	12.813	11.579	10.295	8.930						
12	12.334	11.093	9.780	8.357								
13	8.849											

$\nu\backslash N$	25	26	27	28	29	30	31	32	33	34	35	36
0	18.912	17.901	16.929	15.993	15.093	14.229	13.399	12.601	11.835	11.097	10.386	9.700
1	17.923	16.932	15.977	15.057	14.171	13.318	12.496	11.704	10.938	10.197	9.477	
2	16.888	15.912	14.971	14.062	13.184	12.336	11.514	10.717	9.939			
3	15.790	14.826	13.892	12.987	12.109	11.254	10.418	9.595				
4	14.608	13.648	12.712	11.799	10.904	10.021						
5	13.312	12.342	11.387	10.443								
6	11.852	10.847	9.837									
7	10.140											

where the uncertainty, following Ref. [48], is propagated from the experimental standard uncertainty (this estimation does not include the contribution from the EFG calculations). In Table 4 we show results of the quadrupole coupling constant for all bound states of HD molecule.

3.2.1. Comparison with previous results

Table 5 presents a comparison of our vibrationally-averaged coupling constants with the available literature data.

In the case of the nuclear spin-rotation constants (c_H and c_D), the error emerging from basis-set truncation, neglect of the relativistic effects, contributions beyond the Born-Oppenheimer approximation, and inaccuracies in the used potential curve was previously estimated to be 0.5 kHz [19]. In this work, for the vibrationally-averaged geometry ($\langle R\rangle = 0.7666393$ Å [50,51]), the differences between the spin-rotation constants in the complete-basis limit (CBS) and calculated with the uncontracted cc-pV6Z basis are - 0.063 kHz for c_H and - 0.010 kHz and c_D. The CBS values were evaluated with the two-parameter formula proposed by Helgaker et al. [52]:

$$c(X) = c_{CBS} + bX^{-3} \tag{15}$$

where c_{CBS} and b are fitted parameters and X is the cardinal number of a cc-pVXZ basis set.

For the remaining errors we can use the estimate of 200 Hz previously quoted in Refs. [53,54], which gives the total uncertainty of the spin-rotation constants at the level of ca. 300 Hz. Nevertheless, we obtain significantly better agreement with the experimental data [20] than the previous theoretical investigation [19].

The uncertainties of the spin-spin dipole constants, c_{dip}, are determined by the accuracy of the rovibrational wavefunctions used, which was estimated at the beginning of Section 3. Our results for the $(\nu = 0, N = 1)$ state agree with the experimental value [20].

In the case of the quadrupole constant, c_Q, the uncertainty of our results depends on the accuracy of EFG reported by Pavanello et al. [48], which was estimated to be of five to six decimal digits, the quality of the of the rovibrational wavefunctions and the uncertainty of the measurments reported by Quinn et al. [20] (0.06 kHz).

We assume that the hyperfine constants reported by Dupré correspond not to $\nu, N = 1$, but to $\nu, N = 0$ states. Actually, having observed the slight disagreement between his results and experimental data, Dupré phenomenologically adjusted his values for $\nu = 1$ and 2, and effectively obtained values that are much closer to the ones reported here.

Table 4
Quadrupole coupling constants, c_Q (in kHz), for all bound states of HD. Please note that the value for $\nu = 0$, $N = 1$ correspond to the experimental value of Ref. [20].

$\nu\backslash N$	1	2	3	4	5	6	7	8	9	10	11
0	224.540	222.080	218.452	213.729	208.002	201.377	193.969	185.903	177.302	168.291	158.987
1	223.018	220.538	216.883	212.128	206.365	199.705	192.266	184.174	175.556	166.537	157.238
2	220.415	217.927	214.261	209.493	203.721	197.055	189.615	181.531	172.930	163.939	154.679
3	216.762	214.276	210.614	205.854	200.095	193.448	186.037	177.990	169.437	160.505	151.315
4	212.059	209.584	205.939	201.205	195.479	188.876	181.519	173.538	165.063	156.222	147.134
5	206.305	203.850	200.236	195.544	189.873	183.336	176.058	168.169	159.798	151.072	142.111
6	199.460	197.033	193.462	188.827	183.228	176.778	169.602	161.829	153.588	145.005	136.197
7	191.471	189.080	185.564	181.001	175.491	169.148	162.094	154.459	146.369	137.949	129.316
8	182.247	179.900	176.448	171.971	166.567	160.349	153.437	145.960	138.042	129.805	121.364
9	171.667	169.370	165.993	161.613	156.329	150.250	143.498	136.195	128.466	120.429	112.194
10	159.564	157.323	154.029	149.757	144.604	138.678	132.097	124.980	117.450	109.619	101.597
11	145.712	143.532	140.326	136.171	131.157	125.392	118.988	112.063	104.732	97.104	89.282
12	129.815	127.697	124.583	120.546	115.675	110.070	103.840	97.096	89.947	82.492	74.824
13	111.482	109.425	106.400	102.475	97.734	92.271	86.186	79.581	72.550	65.174	57.518
14	90.192	88.185	85.231	81.389	76.737	71.355	65.327	58.728	51.612	43.990	35.770
15	65.244	63.256	60.318	56.478	51.787	46.289	39.997	32.835			
16	35.754	33.676	30.558	26.362	20.913						
17	27.094										

$\nu\backslash N$	12	13	14	15	16	17	18	19	20	21	22
0	149.504	139.943	130.397	120.948	111.666	102.612	93.834	85.373	77.259	69.516	62.159
1	147.770	138.237	128.731	119.333	110.113	101.129	92.430	84.054	76.030	68.381	61.121
2	145.263	135.792	126.359	117.043	107.914	99.027	90.432	82.163	74.251	66.716	59.571
3	141.979	132.600	123.268	114.062	105.050	96.289	87.822	79.687	71.910	64.511	57.501
4	137.911	128.654	119.452	110.384	101.514	92.898	84.579	76.594	68.968	61.719	54.859
5	133.025	123.913	114.866	105.957	97.252	88.804	80.655	72.838	65.378	58.291	51.591
6	127.273	118.332	109.460	100.731	92.208	83.942	75.975	68.338	61.054	54.138	47.600
7	120.575	111.824	103.146	94.614	86.287	78.215	70.438	62.984	55.875	49.122	42.733
8	112.824	104.277	95.806	87.479	79.355	71.479	63.886	56.604	49.647	43.024	36.732
9	103.865	95.530	87.268	79.144	71.212	63.514	56.078	48.923	42.050	35.448	
10	93.478	85.350	77.283	69.339	61.561	53.981	46.611	39.439	32.412		
11	81.354	73.399	65.477	57.633	49.890	42.239	34.612				
12	67.018	59.131	51.194	43.195	35.038						
13	49.613	41.430									

$\nu\backslash N$	23	24	25	26	27	28	29	30	31	32	33
0	55.199	48.639	42.481	36.721	31.352	26.367	21.754	17.502	13.599	10.031	6.787
1	54.258	47.798	41.738	36.076	30.805	25.917	21.401	17.246	13.440	9.970	6.825
2	52.826	46.483	40.541	34.995	29.839	25.064	20.658	16.612	12.915	9.555	6.523
3	50.888	44.676	38.862	33.443	28.412	23.760	19.477	15.552	11.973	8.731	
4	48.395	42.328	36.655	31.372	26.472	21.946	17.784	13.976			
5	45.281	39.363	33.834	28.687	23.913	19.501					
6	41.443	35.667	30.265	25.228	20.540						
7	36.706	31.034	25.700								
8	30.753										

$\nu\backslash N$	34	35	36
0	3.852	1.215	-1.135
1	3.993	1.463	

Table 5
Comparison of the coupling constants calculated in this work with the experimental [20] and previous theoretical [19] data.

(ν, N)	c_H (kHz)	c_D (kHz)	c_{dip} (kHz)	c_Q (kHz)	
	85.84	13.18	44.396	224.540	This work
(0,1)	86.2832	13.2450	44.5792	226.6493	Ref. [19]
	85.600(18)	13.122(11)	44.403(30)	224.540(60)	Ref. [20]
(1,1)	84.63	12.99	43.029	223.018	This work
	85.0775	13.0599	43.2106	225.0968	Ref. [19]
(2,1)	83.09	12.75	41.605	220.415	This work
	83.5670	12.8289	41.7974	222.5516	Ref. [19]

4. Determination of the energy levels

The hyperfine energy levels were determined by numerical diagonalization of each $(2I_D+1)(2I_H+1) \times (2I_D+1)(2I_H+1)$ Hamiltonian matrix in the coupled basis, corresponding to each total angular momentum F. The eigenvectors of the hyperfine matrix are referred to as $|\nu; NFm_F(\pm)\rangle$. Following Ref. [19], we retain the rotational quantum number in the description of the eigenstates, since, due to a very weak coupling between rotational levels which differ by $\Delta N = \pm 2$, it remains a good quantum number. Moreover, similar to Diouf et al., [17], we introduce the $(\pm)$ labels to distinguish between the eigenstates of the same N and F level, which are characterized by higher $(+)$ or lower $(-)$ energy. We note that this convention differs from the one used by Dupré, who uses the $(+)$ label for the states corresponding to $N = F_1$, and the $(-)$ label otherwise, and from the description of Fast and Meek [16], who label each eigenstate with quantum numbers N, F_1, F, which correspond to the basis vector with the largest contribution to each eigenstate.

For the sake of argument, we introduce the relation between the coupled basis vectors and the eigenvectors, namely:

$$|\nu; NFm_F(\pm)\rangle = \sum_{F_1=F-\frac{1}{2}}^{F+\frac{1}{2}} \sum_{N'=F_1-1}^{F_1+1} a_{N'F_1}^{NF(\pm)} |\nu; N' I_D F_1 I_H F m_F\rangle , \quad (16)$$

Table 6
Example of the calculated positions and intensities of the hyperfine transitions, which are provided in Supplementary Materials [45]. Frequencies of the rovibrational transition are calculated with H2Spectre code of Czachorowski et al. [59] and Komasa et al. [2]. Please note that for the rovibrational transition d corresponds to d_{fi} from Eq. (17), while for the hyperfine components d denotes $d_{\mathrm{fi}}^{\mathrm{HF}}$ from Eq. (21). Intensity (in the sixth column) corresponds to the temperature-independent line intensity, $S_{\mathrm{fi}}/P_{\mathrm{fi}}(T)$ (see Section 5).

Band	Line	Hyperfine transition $\lvert N'F'\pm\rangle \leftarrow \lvert NF\pm\rangle$	Frequency (MHz)	d (10^{-4} D)	Intensity (cm/molecule)	Intensity at 296 K (cm/molecule)
2-0	P(1)		209784240.0(5.7)	0.18057	3.1657×10^{-25}	1.2362×10^{-25}
		$\lvert 0\,1/2\rangle \leftarrow \lvert 1\,1/2+\rangle$	-0.18763	0.08693	1.2228×10^{-26}	4.7751×10^{-27}
		$\lvert 0\,3/2\rangle \leftarrow \lvert 1\,1/2+\rangle$	-0.18763	0.11908	2.2946×10^{-26}	8.9602×10^{-27}
		$\lvert 0\,1/2\rangle \leftarrow \lvert 1\,3/2+\rangle$	-0.05429	0.07613	9.3777×10^{-27}	3.6619×10^{-27}
		$\lvert 0\,3/2\rangle \leftarrow \lvert 1\,3/2+\rangle$	-0.05429	0.19411	6.0971×10^{-26}	2.3809×10^{-26}
		$\lvert 0\,1/2\rangle \leftarrow \lvert 1\,3/2-\rangle$	0.00198	0.19411	6.0971×10^{-26}	2.3809×10^{-26}
		$\lvert 0\,3/2\rangle \leftarrow \lvert 1\,3/2-\rangle$	0.00198	0.07613	9.3777×10^{-27}	3.6619×10^{-27}
		$\lvert 0\,3/2\rangle \leftarrow \lvert 1\,5/2\rangle$	0.05844	0.25537	1.0552×10^{-25}	4.1206×10^{-26}
		$\lvert 0\,1/2\rangle \leftarrow \lvert 1\,1/2-\rangle$	0.11692	0.11908	2.2946×10^{-26}	8.9602×10^{-27}
		$\lvert 0\,3/2\rangle \leftarrow \lvert 1\,1/2-\rangle$	0.11692	0.08693	1.2228×10^{-26}	4.7751×10^{-27}
2-0	R(1)		217105179.9(5.7)	0.21224	9.0552×10^{-25}	3.5348×10^{-25}
		$\lvert 2\,3/2-\rangle \leftarrow \lvert 1\,1/2+\rangle$	-0.29920	0.04340	3.1542×10^{-27}	1.2317×10^{-27}
		$\lvert 2\,3/2-\rangle \leftarrow \lvert 1\,3/2+\rangle$	-0.16586	0.06724	7.5702×10^{-27}	2.9561×10^{-27}
		$\lvert 2\,3/2-\rangle \leftarrow \lvert 1\,3/2-\rangle$	-0.10960	0.12459	2.5995×10^{-26}	1.0151×10^{-26}
		$\lvert 2\,5/2-\rangle \leftarrow \lvert 1\,3/2+\rangle$	-0.08282	0.07228	8.7489×10^{-27}	3.4164×10^{-27}
		$\lvert 2\,3/2-\rangle \leftarrow \lvert 1\,5/2\rangle$	-0.05314	0.03309	1.8340×10^{-27}	7.1617×10^{-28}
		$\lvert 2\,7/2\rangle \leftarrow \lvert 1\,5/2\rangle$	-0.05292	0.37967	2.4139×10^{-25}	9.4262×10^{-26}
		$\lvert 2\,1/2\rangle \leftarrow \lvert 1\,1/2+\rangle$	-0.03941	0.13997	3.2806×10^{-26}	1.2811×10^{-26}
		$\lvert 2\,5/2-\rangle \leftarrow \lvert 1\,3/2-\rangle$	-0.02655	0.29921	1.4493×10^{-25}	5.8546×10^{-26}
		$\lvert 2\,3/2-\rangle \leftarrow \lvert 1\,1/2-\rangle$	0.00534	0.22147	8.2142×10^{-26}	3.2076×10^{-26}
		$\lvert 2\,5/2+\rangle \leftarrow \lvert 1\,3/2+\rangle$	0.01218	0.27345	1.2522×10^{-25}	4.8898×10^{-26}
		$\lvert 2\,3/2+\rangle \leftarrow \lvert 1\,1/2+\rangle$	0.01566	0.19644	6.4619×10^{-26}	2.5233×10^{-26}
		$\lvert 2\,5/2-\rangle \leftarrow \lvert 1\,5/2\rangle$	0.02991	0.11557	2.2367×10^{-26}	8.7341×10^{-27}
		$\lvert 2\,5/2+\rangle \leftarrow \lvert 1\,3/2-\rangle$	0.06845	0.11940	2.3876×10^{-26}	9.3233×10^{-27}
		$\lvert 2\,1/2\rangle \leftarrow \lvert 1\,3/2+\rangle$	0.09393	0.07215	8.7172×10^{-27}	3.4040×10^{-27}
		$\lvert 2\,5/2+\rangle \leftarrow \lvert 1\,5/2\rangle$	0.12491	0.13812	3.1946×10^{-26}	1.2475×10^{-26}
		$\lvert 2\,3/2+\rangle \leftarrow \lvert 1\,3/2+\rangle$	0.14900	0.17434	5.0901×10^{-26}	1.9877×10^{-26}
		$\lvert 2\,1/2\rangle \leftarrow \lvert 1\,3/2-\rangle$	0.15020	0.02830	1.3408×10^{-27}	5.2356×10^{-28}
		$\lvert 2\,3/2+\rangle \leftarrow \lvert 1\,3/2-\rangle$	0.20527	0.00347	2.0209×10^{-29}	7.8913×10^{-30}
		$\lvert 2\,3/2+\rangle \leftarrow \lvert 1\,5/2\rangle$	0.26173	0.05008	4.2008×10^{-27}	1.6404×10^{-27}
		$\lvert 2\,1/2\rangle \leftarrow \lvert 1\,1/2-\rangle$	0.26514	0.10218	1.7483×10^{-26}	6.8271×10^{-27}
		$\lvert 2\,3/2+\rangle \leftarrow \lvert 1\,1/2-\rangle$	0.32021	0.02387	9.5430×10^{-28}	3.7265×10^{-28}

where $a_{NF_1}^{NF(\pm)}$ denote the mixing coefficients, obtained from the diagonalization of the Hamiltonian from Eq. (1) and we used the fact that $I_{\mathrm{D}}=1$ and $I_{\mathrm{H}}=\frac{1}{2}$.

5. Line intensities

The goal of this section is to provide a complete list of intensities of the hyperfine components of all dipole lines in the HD molecule. We remind the reader that the intensity of the dipole transition between two degenerate states (initial and final) is given [55–57] as:

$$S_{\mathrm{fi}}=\frac{2\pi^2}{3hc\epsilon_0}\nu_0\frac{m}{2N_i+1}P_{\mathrm{fi}}(T)|d_{\mathrm{fi}}|^2, \tag{17}$$

where the transition frequency and the electric dipole moment are denoted by ν_0 and d_{fi}, respectively, and $m=N_i+1$ for the R(N_i) transition and N_i for the P(N_i) transition. h, c and ϵ_0 are the Planck's constant, the speed of light in vacuum and vacuum permittivity, respectively. The temperature-dependent part, $P_{\mathrm{fi}}(T)$ is given as

$$P_{\mathrm{fi}}(T)=w_i(2N_i+1)\frac{\left(e^{-E_i/k_{\mathrm{B}}T}-e^{-E_f/k_{\mathrm{B}}T}\right)}{Q(T)}, \tag{18}$$

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

$$Q(T)=\sum_k w_k(2N_k+1)e^{-E_k/k_{\mathrm{B}}T}. \tag{19}$$

w_k denotes the degeneracy factor due to nuclear spin statistics and is equal to $(2I_{\mathrm{H}}+1)\times(2I_{\mathrm{D}}+1)=6$ for all rovibrational states. E_k corresponds to the energy of the k-th rovibrational state, k_{B} denotes the Boltzmann constant and T is the temperature.

Apart from the line intensity defined in Eq. (17), we provide the temperature-independent line intensity, $S_{\mathrm{fi}}/P_{\mathrm{fi}}(T)$ (see Table 6). This parameter corresponds to the case in which the entire population of HD molecules occupies the i-th rovibrational state. One can use the temperature-independent values to calculate line intensities at any T.

As the intensity of the transition is determined by the dipole moment d_{fi}, we calculated this parameter for all considered resonances, using data reported by Pachucki and Komasa [58]. The authors provided dipole moment curves, $d(R)$, in the ground electronic state of the HD molecule for a wide range of internuclear distances. Using the previously described rovibrational wavefunctions, we performed numerical calculations of the transition moments:

$$d_{\mathrm{fi}}=\int dR\chi_f^*(R)d(R)\chi_i(R). \tag{20}$$

for all possible dipole transitions $f\leftarrow i$. Our results agree well with the values reported in Ref. [58].

6. Line intensities of hyperfine transitions

Similarly to Eq. (17), one can calculate the intensity of the hyperfine components of each rovibrational line:

$$S_{\mathrm{fi}}^{\mathrm{HF}}=\frac{2\pi^2}{3hc\epsilon_0}\nu_0\frac{1}{w_i(2N_i+1)}P_{\mathrm{fi}}(T)\left|d_{\mathrm{fi}}^{\mathrm{HF}}\right|^2, \tag{21}$$

where $d_{\mathrm{fi}}^{\mathrm{HF}}$ is the reduced matrix element of the dipole moment tensor (see Appendix B of Ref. [19]):

$$\begin{aligned}\left|d_{\mathrm{fi}}^{\mathrm{HF}}\right|^2 &= \left|\langle \nu_f; N_f F_f m_{\mathrm{F}_f}(\pm)\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu; N_i F_i m_{\mathrm{F}_i}(\pm)\rangle\right|^2 \\ &= \Bigg|\sum_{F_{1_f}=F_f-\frac{1}{2}}^{F_f+\frac{1}{2}}\sum_{N_f'=F_{1_f}-1}^{F_{1_f}+1}\sum_{F_{1_i}=F_i-\frac{1}{2}}^{F_i+\frac{1}{2}}\sum_{N_i'=F_{1_i}-1}^{F_{1_i}+1} a_{N_f' F_{1_f}}^{N_f F_f(\pm)} a_{N_i' F_{1_i}}^{N_i F_i(\pm)} \\ &\times \langle \nu_f; N_f' I_{\mathrm{D}} F_{1_f} I_{\mathrm{H}} F_f m_{\mathrm{F}_f}\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu_i; N_i' I_{\mathrm{D}} F_{1_i} I_{\mathrm{H}} F_i m_{\mathrm{F}_i}\rangle\Bigg|^2\end{aligned} \tag{22}$$

and the last term is evaluated using spherical tensor algebra [21]:

$$\begin{aligned}&\langle \nu_f; N_f I_{\mathrm{D}} F_{1_f} I_{\mathrm{H}} F_f m_{\mathrm{F}_f}\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu; N_i I_{\mathrm{D}} F_{1_i} I_{\mathrm{H}} F_i m_{\mathrm{F}_i}\rangle \\ &= (-1)^{F_i+I_{\mathrm{H}}+F_{1_f}+F_{1_i}+I_{\mathrm{D}}+N_f}\sqrt{(2F_i+1)(2F_f+1)} \\ &\times\sqrt{(2F_{1_i}+1)(2F_{1_f}+1)}\begin{Bmatrix} I_{\mathrm{H}} & F_i & F_{1_i} \\ 1 & F_{1_f} & F_f\end{Bmatrix} \\ &\times\begin{Bmatrix} I_{\mathrm{D}} & F_{1_i} & N_i \\ 1 & N_f & F_{1_f}\end{Bmatrix}\langle \nu_f N_f\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu_i N_i\rangle\,.\end{aligned} \tag{23}$$

Finally, the $\langle \nu_f N_f\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu_i N_i\rangle$ is related to the transition moment defined in Eq. (20) in the following way (in a $^1\Sigma$ state)

$$\begin{aligned}&\langle \nu_f N_f\|\mathrm{T}^{(1)}(\mathbf{d})\|\nu_i N_i\rangle \\ &= (-1)^{N_f}\sqrt{(2N_f+1)(2N_i+1)}\begin{pmatrix} N_f & 1 & N_i \\ 0 & 0 & 0\end{pmatrix} d_{\mathrm{fi}}.\end{aligned} \tag{24}$$

As it was pointed out in Ref. [19], the algebraic factor that multiples d_{fi} in Eq. (24) corresponds to m which appears in Eq. (17) but is absent in Eq. (21).

7. Example of the complete dataset record

The data gathered from the discussion above allows us to calculate the positions and intensities of the hyperfine components of all dipole transitions between the bound states of the HD molecule in its $^1\Sigma$ electronic state. Our calculations result in total 108 320 hyperfine components of 5 129 dipole lines from the R and P branches. The complete dataset can be found in Supplementary Materials [45].

Table 6 presents an example of the calculated parameters for R(1) and P(1) lines from the first overtone band, which were recently investigated both experimentally [13–15,17] and theoretically [18,19]. The central frequency of the rovibrational transition is taken from the H2Spectre code [2,59], while the dipole moment d is calculated as described in Section 5. We report line intensities at the reference temperature of 296 K (following the convention adopted in the HITRAN database [60]), as well as the temperature-independent line intensities, $S_{\mathrm{fi}}/P_{\mathrm{fi}}$, from which one can calculate the spectral line intensity at any T. In the case of hyperfine components of each line, we denote each transition using $N'F'(\pm)' \leftarrow NF(\pm)$ labels.

8. Conclusion

We provided a list of the hyperfine coupling constants, i.e. spin-rotation, spin-spin and quadrupole coupling constants, for all bound states of the HD molecule. Rovibrational averages of the hyperfine coupling constants were performed using wavefunctions of the HD molecule calculated within the Born-Oppenheimer approximation. In the presented analysis, we considered the leading hyperfine interactions and we disregarded the electron coupled spin-spin interaction, which is, almost three orders of magnitude smaller than the hyperfine couplings considered here. The results agree well with the experimental data from Ref. [20]. Our calculations of the hyperfine splittings of all 400 rovibrational states of the HD molecule in the $^1\Sigma$ state led to the complete list of positions and intensities of the 108 320 hyperfine components of 5 129 possible dipole transitions. The intensities, positions, as well as the coupling constants, can be found in Supplementary Materials [45]. The results will be useful as a reference data for a proper interpretation of accurate measurements of rovibrational HD lines, which are used for testing the quantum electrodynamics for molecules and searching for new physics beyond the Standard Model.

Note added after reviewer's suggestion

It was pointed out that recently Komasa et al. [61] analyzed leading hyperfine interactions in the HD molecule. The authors provided coupling constants for several low lying states and calculated 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. Moreover, the authors published a publicly available code, which calculates hyperfine splittings for a given rovibrational level.

In the case of the spin-rotation constants, our results differ slightly from the values reported in Ref. [61]. For the ground vibrational level, c_{H} values calculated by Komasa et al. lie within our estimated uncertainty (300 Hz). The differences increase with ν, but decrease with N, and the largest one is at the level of 3σ (σ is the standard uncertainty). The same trend is observed for the c_{D} constant, but the differences do not exceed 225 Hz (for a majority of rovibrational levels, the differences are much smaller). We attribute this discrepancy to different methods of determining the spin-coupling curves and to differences in the wavefunctions used to rovibrationally average the coupling constants (the authors of Ref. [61] obtained rovibrational wavefunctions from the Born-Oppenheimer potential of Pachucki [62]). Our spin-spin dipole constants are in perfect agreement with those calculated by Komasa et al.; the largest discrepancy is at the level of 30 Hz (we note that the authors used a different notation for the spin-spin dipole constant, $d_1 = 2c_{\mathrm{dip}}/5$). In the case of the quadrupole coupling constant, the authors in Ref. [61] performed the calculations of the EFG using explicitly correlated Gaussian (ECG) basis functions and obtained good agreement with the data reported by Pavanello et al. [48] except for the shortest internuclear distances. In contrast to this work, the authors determined the electric quadrupole moment of the deuteron using the experimental value for the $N = 1$ state in D_2. This led to a slightly different value of $Q = 0.2856(2)$ fm^2, which differs from our result by 1.5σ. Nevertheless, our values of the quadrupole coupling constants lie within the estimated uncertainties reported in Ref. [61]. Due to the observed slight differences between the values of the coupling constants, we note a similar discrepancy of the determined positions of the hyperfine components of the three analyzed transitions.

To sum up, the agreement between our results and the data reported by Komasa et al. is, on average, 400 Hz, which is more than 30 times less than the accuracy of the most accurate measurement of the rovibrational line frequency in HD [16].

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 [16].

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. 2018/31/B/ST2/00720. Calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl), grant no. 294.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at 10.1016/j.jqsrt.2020.107171

References

[1] Czachorowski P, Puchalski M, Komasa J, Pachucki K. Nonadiabatic relativistic correction in H_2, D_2, and HD. Phys Rev A 2018;98:052506. doi:10.1103/PhysRevA.98.052506.
[2] Komasa J, Puchalski M, Czachorowski P, Łach G, Pachucki K. Rovibrational energy levels of the hydrogen molecule through nonadiabatic perturbation theory. Phys Rev A 2019;100:032519. doi:10.1103/PhysRevA.100.032519.
[3] Pachucki K, Komasa J. Nonadiabatic corrections to the wave function and energy. J Chem Phys 2008;129(3):034102. doi:10.1063/1.2952517.
[4] Pachucki K, Komasa J. Nonadiabatic corrections to rovibrational levels of H_2. J Chem Phys 2009;130(16):164113. doi:10.1063/1.3114680.
[5] Pachucki K, Komasa J. Leading order nonadiabatic corrections to rovibrational levels of H_2, D_2, and T_2. J Chem Phys 2015;143(3):034111. doi:10.1063/1.4927079.
[6] Pachucki K, Komasa J. Nonadiabatic rotational states of the hydrogen molecule. Phys Chem Chem Phys 2018;20:247–55. doi:10.1039/C7CP06516G.
[7] Ubachs W, Koelemeij J, Eikema K, Salumbides E. Physics beyond the standard model from hydrogen spectroscopy. J Mol Spectrosc 2016;320:1–12. doi:10.1016/j.jms.2015.12.003.
[8] Salumbides EJ, Koelemeij JCJ, Komasa J, Pachucki K, Eikema KSE, Ubachs W. Bounds on fifth forces from precision measurements on molecules. Phys Rev D 2013;87:112008. doi:10.1103/PhysRevD.87.112008.
[9] Salumbides EJ, Schellekens AN, Gato-Rivera B, Ubachs W. Constraints on extra dimensions from precision molecular spectroscopy. New J Phys 2015;17(3):033015. doi:10.1088/1367-2630/17/3/033015.
[10] Wcisło P, Thibault F, Zaborowski M, Wójtewicz S, Cygan A, Kowzan G, et al. Accurate deuterium spectroscopy for fundamental studies. J Quant Spectrosc Radiat Transf 2018;213:41–51. doi:10.1016/j.jqsrt.2018.04.011.
[11] Zaborowski M, Słowiński M, Stankiewicz K, Thibault F, Cygan A, Jóźwiak H, et al. Ultrahigh finesse cavity-enhanced spectroscopy for accurate tests of quantum electrodynamics for molecules. Opt Lett 2020;45(7):1603–6. doi:10.1364/OL.389268.
[12] Wójtewicz S, Gotti R, Gatti D, Lamperti M, Laporta P, Jóźwiak H, et al. Accurate deuterium spectroscopy and comparison with ab initio calculations. Phys Rev A 2020;101:052504. doi:10.1103/PhysRevA.101.052504.
[13] Cozijn FMJ, Dupré P, Salumbides EJ, Eikema KSE, Ubachs W. Sub-doppler frequency metrology in HD for tests of fundamental physics. Phys Rev Lett 2018;120:153002. doi:10.1103/PhysRevLett.120.153002.
[14] Tao L-G, Liu A-W, Pachucki K, Komasa J, Sun YR, Wang J, et al. Toward a determination of the proton-electron mass ratio from the lamb-dip measurement of HD. Phys Rev Lett 2018;120:153001. doi:10.1103/PhysRevLett.120.153001.
[15] Fasci E, Castrillo A, Dinesan H, Gravina S, Moretti L, Gianfrani L. Precision spectroscopy of HD at 1.38μm. Phys Rev A 2018;98:022516. doi:10.1103/PhysRevA.98.022516.
[16] Fast A., Meek S.A.. Sub-ppb measurement of a fundamental band rovibrational transition in HD. 2020. arXiv:2002.09333.
[17] Diouf ML, Cozijn FMJ, Lai K-F, Salumbides EJ, Ubachs W. Lamb-peak spectrum of the HD (2-0) P(1) line. Phys Rev Res 2020;2:023209. doi:10.1103/PhysRevResearch.2.023209.
[18] Diouf ML, Cozijn FMJ, Darquié B, Salumbides EJ, Ubachs W. Lamb-dips and lamb-peaks in the saturation spectrum of HD. Opt Lett 2019;44(19):4733–6. doi:10.1364/OL.44.004733.
[19] Dupré P. Hyperfine transitions in the first overtone mode of hydrogen deuteride. Phys Rev A 2020;101:022504. doi:10.1103/PhysRevA.101.022504.
[20] Quinn WE, Baker JM, LaTourrette JT, Ramsey NF. Radio-frequency spectra of hydrogen deuteride in strong magnetic fields. Phys Rev 1958;112:1929–40. doi:10.1103/PhysRev.112.1929.
[21] Brown JM, Carrington A. Rotational spectroscopy of diatomic molecules. Cambridge Molecular Science. Cambridge University Press; 2003. doi:10.1017/CBO9780511814808.
[22] Carr HY, Purcell EM. Interaction between nuclear spins in HD gas. Phys Rev 1952;88:415–16. doi:10.1103/PhysRev.88.415.2.
[23] Ramsey NF, Purcell EM. Interactions between nuclear spins in molecules. Phys Rev 1952;85:143–4. doi:10.1103/PhysRev.85.143.
[24] Code RF, Ramsey NF. Molecular-beam magnetic resonance studies of HD and D_2. Phys Rev A 1971;4:1945–59. doi:10.1103/PhysRevA.4.1945.
[25] Puchalski M, Komasa J, Pachucki K. Nuclear spin-spin coupling in HD, HT, and DT. Phys Rev Lett 2018;120:083001. doi:10.1103/PhysRevLett.120.083001.
[26] Kellogg JMB, Rabi II, Ramsey NF, Zacharias JR. The magnetic moments of the proton and the deuteron. The radiofrequency spectrum of H_2 in various magnetic fields. Phys Rev 1939;56:728–43. doi:10.1103/PhysRev.56.728.
[27] Kellogg JMB, Rabi II, Ramsey NF, Zacharias JR. An electrical quadrupole moment of the deuteron the radiofrequency spectra of HD and D_2 molecules in a magnetic field. Phys Rev 1940;57:677–95. doi:10.1103/PhysRev.57.677.
[28] Wick GC. On the magnetic field of a rotating molecule. Phys Rev 1948;73:51–7. doi:10.1103/PhysRev.73.51.
[29] Ramsey NF. The rotational magnetic moments of H_2, D_2, and HD molecules. the rotational radiofrequency spectra of H_2, D_2, and D in magnetic fields. Phys Rev 1940;58:226–36. doi:10.1103/PhysRev.58.226.
[30] Foley HM. Second-order magnetic perturbations in nuclear quadrupole spectra and the "pseudo-quadrupole" effect in diatomic molecules. Phys Rev 1947;72:504–5. doi:10.1103/PhysRev.72.504.
[31] Ramsey NF. Magnetic shielding of nuclei in molecules. Phys Rev 1950;78:699–703. doi:10.1103/PhysRev.78.699.
[32] Ramsey NF. Theory of molecular hydrogen and deuterium in magnetic fields. Phys Rev 1952;85:60–5. doi:10.1103/PhysRev.85.60.
[33] Ramsey NF. Chemical effects in nuclear magnetic resonance and in diamagnetic susceptibility. Phys Rev 1952;86:243–6. doi:10.1103/PhysRev.86.243.
[34] Ramsey NF. Vibrational and centrifugal effects on nuclear interactions and rotational moments in molecules. Phys Rev 1952;87:1075–9. doi:10.1103/PhysRev.87.1075.
[35] Frosch RA, Foley HM. Magnetic hyperfine structure in diatomic molecules. Phys Rev 1952;88:1337–49. doi:10.1103/PhysRev.88.1337.
[36] Ramsey NF. Spin interactions of accelerated nuclei in molecules. Phys Rev 1953;90:232–3. doi:10.1103/PhysRev.90.232.
[37] White RL. Magnetic hyperfine structure due to rotation in $^1\Sigma$ molecules. Rev Mod Phys 1955;27:276–88. doi:10.1103/RevModPhys.27.276.
[38] Reid RV, Chu AH-M. Spin-rotation interaction and magnetic shielding in $^1\Sigma$ molecules. Phys Rev A 1974;9:609–13. doi:10.1103/PhysRevA.9.609.
[39] Flygare WH. Spin rotation interaction and magnetic shielding in molecules. J Chem Phys 1964;41(3):793–800. doi:10.1063/1.1725962.
[40] Fano U, Racah G. Irreducible Tensorial Sets. Cambridge Molecular Science. Academic Press Inc; 1959.
[41] Barnes RG, Bray PJ, Ramsey NF. Variations of hydrogen rotational magnetic moments with rotational quantum number and with isotopic mass. Phys Rev 1954;94:893–902. doi:10.1103/PhysRev.94.893.
[42] Schwenke DW. Calculations of rate constants for the three body recombination of H_2 in the presence of H_2. J Chem Phys 1988;89(4):2076–91. doi:10.1063/1.455104.
[43] Woon DE, Dunning TH Jr.. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. J Chem Phys 1994;100:2975. doi:10.1063/1.466439.
[44] Peterson KA, Woon DE, Dunning Jr TH. Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H+H_2 \rightarrow H_2+H$ reaction. J Chem Phys 1994;100(10):7410. doi:10.1063/1.466884.
[45] Jóźwiak H., Cybulski H., Wcisło P.. Supplementary material for hyperfine line positions, intensities and coupling constants.
[46] CFOUR, coupled-cluster techniques for computational chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
[47] 2018 codata recommended values. 2018. https://physics.nist.gov/cuu/Constants.
[48] Pavanello M, Tung W-C, Adamowicz L. Determination of deuteron quadrupole moment from calculations of the electric field gradient in D_2 and HD. Phys Rev A 2010;81:042526. doi:10.1103/PhysRevA.81.042526.
[49] Kołos W, Szalewicz K, Monkhorst HJ. New Born-Oppenheimer potential energy curve and vibrational energies for the electronic ground state of the hydrogen molecule. J Chem Phys 1986;84(6):3278–83. doi:10.1063/1.450258.
[50] Le Roy RJ, Hutson JM. Improved potential energy surfaces for the interaction of H_2 with Ar, Kr, and Xe 1987;86:837. doi:10.1063/1.452284.
[51] Jankowski P, Szalewicz K. A new ab initio interaction energy surface and high-resolution spectra of the H_2-CO van der Waals complex. J Chem Phys 2005;123:104301. doi:10.1063/1.2008216.
[52] Helgaker T, Klopper W, Koch H, Noga J. Basis-set convergence of correlated calculations on water. J Chem Phys 1997;106:9639. doi:10.1063/1.473863.
[53] Sundholm D, Gauss J. Isotope and temperature effects on nuclear magnetic shieldings and spin-rotation constants calculated at the coupled-cluster level. Mol Phys 1997;92:1007. doi:10.1080/002689797169628.
[54] Gauss J, Sundholm D. Coupled-cluster calculations of spin-rotation constants. Mol Phys 1997;91:449. doi:10.1080/002689797171346.
[55] Bunker P.R., *Molecular Symmetry and Spectroscopy*, Academic Press, New York; 1979. ISBN 978-0-12-141350-7, https://doi.org/10.1016/B978-0-12-141350-7.50002-1.

[56] Rich N, Johns J, McKellar A. Frequency and intensity measurements in the fundamental infrared band of HD. J Mol Spectrosc 1982;95(2):432–8. doi:10.1016/0022-2852(82)90141-2.
[57] Kassi S, Campargue A. Electric quadrupole and dipole transitions of the first overtone band of HD by CRDS between 1.45 and 1.33μm. J Mol Spectrosc 2011;267(1):36–42. doi:10.1016/j.jms.2011.02.001.
[58] Pachucki K, Komasa J. Electric dipole rovibrational transitions in the HD molecule. Phys Rev A 2008;78:052503. doi:10.1103/PhysRevA.78.052503.
[59] H2SPECTRE ver. 7.0. Fortran source code, 2019; P. Czachorowski, Ph.D. thesis, University of Warsaw, Poland, 2019.https://www.fuw.edu.pl/~krp/codes.html; http://qcg.home.amu.edu.pl/qcg/public_html/H2Spectre.html.
[60] Gordon I, Rothman L, Hill C, Kochanov R, Tan Y, Bernath P, et al. The HITRAN2016 molecular spectroscopic database. J Quant Spectrosc Radiat Transfer 2017;203:3–69. doi:10.1016/j.jqsrt.2017.06.038.
[61] Komasa J., Puchalski M., Pachucki K.. Hyperfine structure in the HD molecule. 2020. arXiv:https://arxiv.org/abs/2005.02702.
[62] Pachucki K. Born-Oppenheimer potential for H_2. Phys Rev A 2010;82:032509. doi:10.1103/PhysRevA.82.032509.