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Hyperfine components of rovibrational dipole transitions in HT and DT

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ABSTRACT

We report a list of positions and intensities of 331 892 hyperfine components of all 18 585 rovibrational dipole transitions in the HT and DT isotopologues of molecular hydrogen. Apart from the study of hyperfine structure, we investigate the intensities of all rovibrational dipole transitions in the two isotopologues, which were not known prior to this work. The results presented here are crucial for a reliable interpretation of accurate measurements of rovibrational transition frequencies in the tritium-bearing isotopologues of hydrogen, which are useful for tests of quantum electrodynamics for molecules and searches for new physics beyond the Standard Model.

1. Introduction

Rovibrational structures of tritium-bearing isotopologues of molecular hydrogen are of particular importance for the spectroscopic community. Accurate experimental data for the three tritium-bearing isotopologues broadens the perspective of recent studies of rovibrational transitions in H_2 [1–3], D_2 [4–8] and HD [9–14]. Such an abundance of experimental results has stimulated a detailed theoretical analysis of the hydrogen molecule. Since the tritiated species are significantly heavier than the three most-common isotopologues of hydrogen (H_2, HD and D_2), they are less susceptible to the mass-dependent contributions to the molecular binding energies, such as the adiabatic and nonadiabatic corrections to the Born-Oppenheimer energies. Three recent papers [15–17] on the Coherent Anti-Stokes Raman Spectroscopy (CARS) of T_2, DT and HT constitute a perfect example of validation of theoretical results on accurate spectra of the tritium-bearing isotopologues. In Ref. [15] the Raman spectra of T_2 were used to test the nonrelativistic calculations from Ref. [18] and to extract the relativistic and QED corrections to the rovibrational energy levels. In a joint theoretical and experimental study from Ref. [16], the recently developed nonadiabatic perturbation theory (NAPT) [18–22], as well as the relativistic and QED corrections, were validated on the spectra of DT, leading to an excellent agreement with the experimental values. Finally, in Ref. [17], the authors refined the data for T_2 and DT and measured several lines of HT. We also note that the tritiated species can be used in searches for physics beyond the Standard Model [23–25], i.e. by putting constraints on a certain form of the hypothetical fifth force parametrized by the Yukawa potential, which appear to be tighter than that of H_2 [16].

In general, the experimental studies of tritium-bearing isotopologues are hindered by the instability of tritium, as it undergoes a β-decay into ^{3}He. As pointed out in Ref. [15], a use of tritium in experimental setups is restricted to minute amounts, which rules out the possibility of molecular beam studies and might lead to material degradation. Rovibrational structures of the HT and DT molecules were studied in only a few experiments. Dieke et al. recorded emission spectra of the two heteronuclear tritium-bearing isotopologues of hydrogen [26,27]. Rovibrational structures of HT and DT were also investigated by means of Raman spectroscopy. Edwards et al. [28] reported observed pure rotational and rovibrational transitions from the first overtone in HT and DT. Veirs et al. [29], in a study of Raman spectra of the six isotopologues of hydrogen, analyzed the Q lines from the fundamental band in HT and DT. A study of the first, third and fourth overtones in HT was performed by Chuang and Zare [30] using optoacoustic spectroscopy. Finally, the two aforementioned CARS studies of the fundamental band in DT [16] and HT [17] were reported recently. The last two papers focused on several lines from the Q branch and provided an accurate test of NAPT, reaching accuracies of 12, 16 and 20 MHz for the Q lines in T_2, HT and DT, respectively.

Accurate experimental measurements of the frequencies of rovibrational transitions require knowledge about the underlying (yet

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unresolved) hyperfine structure [31–36]. Recently, we have analyzed hyperfine interactions in the three tritium-bearing isotopologues and reported a set of coupling constants for the nuclear spin-rotation interaction, nuclear spin-nuclear spin dipole coupling and, in the case of DT, for the interaction between the quadrupole moment of the deuteron with molecular field gradient [35]. These three leading hyperfine interactions result in splittings of rovibrational levels, which are of an order of hundreds of kHz. We have also calculated intensities of all possible quadrupole transitions in T_2, HT and DT, as well as the intensities of the respective hyperfine components.

Following our previous studies of hyperfine structure in molecular hydrogen [33–35], here, we investigate the rovibrational dipole transitions from the *P* and *R* branches in the HT and DT isotopologues. Our study results in a comprehensive list of all 331 892 hyperfine components of 18 585 rovibrational transitions in the two heteronuclear tritium-bearing isotopologues of hydrogen. Moreover, we provide the intensities of rovibrational dipole transitions in HT and DT, which, to our knowledge, were neither calculated nor measured previously. The theory behind the calculations is briefly recalled in Sections 2 and 3 and we provide two examples of the calculated dipole transitions for the two molecules in Section 4.

2. Hyperfine interactions in HT and DT

Hyperfine interactions in HT and DT involve the nuclear spin-rotation interaction, the nuclear spin-spin dipole coupling and, in the case of the DT molecule, the interaction of the electric quadrupole moment with the molecular electric field gradient (EFG). In Ref. [35], we reported hyperfine coupling constants, which determine the strength of these interactions, for all bound states of the three tritium-bearing isotopologues of hydrogen, in their ground electronic Σ^+ (or Σ_g^+, in the case of T_2) states. It was pointed out recently [36], that the slight discrepancies between the hyperfine coupling constants calculated in our previous papers [33–35] and other theoretical results [32,36] might originate from the Born-Oppenheimer (BO) potential used in our calculations. Indeed, we used the potential of Schwenke [37] to obtain the rovibrational wavefunctions of the isotopologues of hydrogen instead of the state-of-the-art potential of Pachucki [38]. However, the choice of the potential energy curve influences only the rovibrational wavefunctions which are used to calculate the hyperfine coupling constants for a given rovibrational state (see, for example Eq. (7) in Ref. [35]). The error introduced by the choice of a different potential is of an order of tens of Hz, as it can be deduced from the comparison of the nuclear spin-spin dipole constants reported in Refs. [33,34] with those given in Table 1 in Ref. [36]. Therefore, for the sake of consistency, we use the data reported by us in the previous paper [35].

Matrix elements of the effective hyperfine Hamiltonian for the HT and DT molecules were determined using a coupling scheme which is suitable for the heteronuclear molecules. The rotational angular momentum of the molecule, $\mathbf{N}$, was coupled with one of the nuclear spins, $\mathbf{I}_1$, to form the intermediate angular momentum, $\mathbf{F}_1$, which was in turn coupled with the nuclear spin of the other nucleus, $\mathbf{I}_2$. The resulting total angular momentum and its projection on the space-fixed *z*-axis were denoted by $\mathbf{F}$ and m_F, respectively. The coupled basis vector is denoted as $|\nu;((NI_1)F_1I_2)Fm_\mathrm{F}\rangle$, where ν is the vibrational quantum number. We recall that for the HT molecule $I_1=I_\mathrm{T}$ and $I_2=I_\mathrm{H}$, and for the DT molecule $I_1=I_\mathrm{D}$ and $I_2=I_\mathrm{T}$.

As it was discussed in Ref. [35], the hyperfine Hamiltonian is block diagonal with respect to the total angular momentum. Energy levels of the hyperfine levels were determined by diagonalization of the *F*-labelled blocks, each of them of $(2I_1+1)(2I_2+1)\times(2I_1+1)(2I_2+1)$ size. The eigenvectors of the hyperfine Hamiltonian are denoted as $|\nu;NFm_\mathrm{F}(\pm)\rangle$, where the $\pm$ labels denote the eigenstates for given *N* and *F*, which are of higher (+) or lower (−) energy. The relation between the eigenbasis and the coupled basis is given by:

$$|\nu;NFm_\mathrm{F}(\pm)\rangle = \sum_{F_1=|F-I_2|}^{F+I_2}\sum_{N'=|F_1-I_1|}^{F_1+I_1} a_{N'F_1}^{\nu NF(\pm)}\,|\nu;((N'I_1)F_1I_2)Fm_\mathrm{F}\rangle\,, \tag{1}$$

where $a_{N'F_1}^{\nu NF(\pm)}$ denote the mixing coefficients.[1] Let us remind that the off-diagonal matrix elements, which couple different rotational states, are from 9 to 11 orders of magnitude smaller than the diagonal terms. Therefore, the mixing coefficients which couple $N'\neq N$, are negligibly small.

3. Intensities of hyperfine components of rovibrational dipole transitions

Line intensity of the dipole transition between two degenerate states (initial and final) is given [39–41] as:

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

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

$$P_\mathrm{fi}(T) = w_\mathrm{i}(2N_\mathrm{i}+1)\frac{\left(e^{-E_\mathrm{i}/k_\mathrm{B}T}-e^{-E_\mathrm{f}/k_\mathrm{B}T}\right)}{Q(T)}, \tag{3}$$

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

$$Q(T) = \sum_\mathrm{k} w_\mathrm{k}(2N_\mathrm{k}+1)e^{-E_\mathrm{k}/k_\mathrm{B}T}. \tag{4}$$

w_k is the degeneracy factor of each rovibrational level due to nuclear spin statistics and equals 4 and 6 for HT and DT, respectively. E_k is the energy of the kth rovibrational state, k_B is the Boltzmann constant and T is the temperature.

Matrix elements of the dipole moment operator, d_fi, which couple the initial and final rovibrational states, are given by:

$$d_\mathrm{fi} = \int \mathrm{d}R\,\chi_f^*(R)d(R)\chi_i(R). \tag{5}$$

We used the dipole moment function reported by Pachucki and Komasa for the HD molecule [42], rescaled with the mass-dependent factor:

$$d(R) = \left(\frac{m_1-m_2}{m_1m_2}\right)\left(\frac{m_\mathrm{H}m_\mathrm{D}}{m_\mathrm{H}-m_\mathrm{D}}\right)d^\mathrm{HD}(R), \tag{6}$$

where $d^\mathrm{HD}(R)$ denotes the dipole moment function reported in Ref. [42] and m_X is the mass of the nucleus of a particular isotope (X = H, D or T). Following the notation from Section 2, we set $m_1=m_\mathrm{T}$ and $m_2=m_\mathrm{H}$ for the HT molecule, and $m_1=m_\mathrm{D}$ and $m_2=m_\mathrm{T}$ for the DT molecule.

Line intensity of each hyperfine component of a rovibrational dipole transition is given as [31,33]:

$$S_\mathrm{fi}^\mathrm{HF} = \frac{2\pi^2}{3hc\epsilon_0}\nu_0\frac{1}{w_i(2N_i+1)}P_\mathrm{fi}(T)\left|d_\mathrm{fi}^\mathrm{HF}\right|^2, \tag{7}$$

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[1] We note that in our previous papers [33–35] we did not denote the mixing coefficients with the vibrational quantum number.

Table 1
Example of the calculated positions and intensities of the hyperfine transitions. The full list is provided in Supplementary Material [45]. Frequencies of the rovibrational transition are calculated with H2Spectre code of Czachorowski et al. [46] and Komasa et al. [22]. Please note that for the rovibrational transition d corresponds to d_{fi} from Eq. (2), while for the hyperfine components d denotes $d_{\mathrm{fi}}^{\mathrm{HF}}$ from Eq. (7).

Band	Line	Hyperfine transition $\vert N'F'(\pm)\rangle \leftarrow \vert NF(\pm)\rangle$	Frequency (MHz)	d (10^{-4} D)	Intensity (cm/molecule)	Intensity at 296 K (cm/molecule)
2-0	$P(2)$		158417160.5(9.3)	0.0452	1.796×10^{-26}	5.034×10^{-27}
(DT)		$\vert 1\,3/2-\rangle \leftarrow \vert 2\,1/2\rangle$	−0.22606	0.0083	5.050×10^{-29}	1.415×10^{-29}
		$\vert 1\,3/2-\rangle \leftarrow \vert 2\,3/2+\rangle$	−0.21116	0.0291	6.194×10^{-28}	1.736×10^{-28}
		$\vert 1\,5/2\rangle \leftarrow \vert 2\,3/2+\rangle$	−0.19570	0.0097	6.885×10^{-29}	1.930×10^{-29}
		$\vert 1\,1/2-\rangle \leftarrow \vert 2\,1/2\rangle$	−0.17431	0.0250	4.583×10^{-28}	1.285×10^{-28}
		$\vert 1\,1/2-\rangle \leftarrow \vert 2\,3/2+\rangle$	−0.15942	0.0061	2.679×10^{-29}	7.511×10^{-30}
		$\vert 1\,3/2-\rangle \leftarrow \vert 2\,5/2+\rangle$	−0.15728	0.0078	4.416×10^{-29}	1.238×10^{-29}
		$\vert 1\,5/2\rangle \leftarrow \vert 2\,5/2+\rangle$	−0.14182	0.0323	7.649×10^{-28}	2.144×10^{-28}
		$\vert 1\,3/2-\rangle \leftarrow \vert 2\,3/2-\rangle$	−0.13805	0.0016	1.888×10^{-30}	5.292×10^{-31}
		$\vert 1\,5/2\rangle \leftarrow \vert 2\,3/2-\rangle$	−0.12259	0.0083	5.088×10^{-29}	1.426×10^{-29}
		$\vert 1\,1/2-\rangle \leftarrow \vert 2\,3/2-\rangle$	−0.08630	0.0454	1.510×10^{-27}	4.234×10^{-28}
		$\vert 1\,3/2+\rangle \leftarrow \vert 2\,1/2\rangle$	−0.07205	0.0143	1.491×10^{-28}	4.178×10^{-29}
		$\vert 1\,3/2+\rangle \leftarrow \vert 2\,3/2+\rangle$	−0.05716	0.0197	2.846×10^{-28}	7.978×10^{-29}
		$\vert 1\,3/2+\rangle \leftarrow \vert 2\,5/2+\rangle$	−0.00328	0.0616	2.783×10^{-27}	7.800×10^{-28}
		$\vert 1\,1/2+\rangle \leftarrow \vert 2\,1/2\rangle$	0.00768	0.0271	5.394×10^{-28}	1.512×10^{-28}
		$\vert 1\,3/2+\rangle \leftarrow \vert 2\,3/2-\rangle$	0.01595	0.0324	7.703×10^{-28}	2.159×10^{-28}
		$\vert 1\,1/2+\rangle \leftarrow \vert 2\,3/2+\rangle$	0.02257	0.0436	1.395×10^{-27}	3.910×10^{-28}
		$\vert 1\,5/2\rangle \leftarrow \vert 2\,7/2\rangle$	0.05580	0.0808	4.789×10^{-27}	1.342×10^{-27}
		$\vert 1\,3/2-\rangle \leftarrow \vert 2\,5/2-\rangle$	0.05617	0.0668	3.275×10^{-27}	9.180×10^{-28}
		$\vert 1\,5/2\rangle \leftarrow \vert 2\,5/2-\rangle$	0.07163	0.0207	3.126×10^{-28}	8.762×10^{-29}
		$\vert 1\,1/2+\rangle \leftarrow \vert 2\,3/2-\rangle$	0.09569	0.0091	6.114×10^{-29}	1.714×10^{-29}
		$\vert 1\,3/2+\rangle \leftarrow \vert 2\,5/2-\rangle$	0.21018	0.0024	4.247×10^{-30}	1.190×10^{-30}
2-0	$R(1)$		205380036.1(33.0)	0.2676	1.361×10^{-24}	5.002×10^{-25}
(HT)		$\vert 2\,1\rangle \leftarrow \vert 1\,0\rangle$	−0.09442	0.2185	1.134×10^{-25}	4.169×10^{-26}
		$\vert 2\,2-\rangle \leftarrow \vert 1\,1+\rangle$	−0.06910	0.0173	7.090×10^{-28}	2.606×10^{-28}
		$\vert 2\,3\rangle \leftarrow \vert 1\,2\rangle$	−0.06265	0.4477	4.764×10^{-25}	1.751×10^{-25}
		$\vert 2\,2-\rangle \leftarrow \vert 1\,2\rangle$	−0.02089	0.1885	8.443×10^{-26}	3.103×10^{-26}
		$\vert 2\,2+\rangle \leftarrow \vert 1\,1+\rangle$	0.00035	0.3779	3.394×10^{-25}	1.247×10^{-25}
		$\vert 2\,2-\rangle \leftarrow \vert 1\,1-\rangle$	0.00674	0.3277	2.551×10^{-25}	9.377×10^{-26}
		$\vert 2\,2+\rangle \leftarrow \vert 1\,2\rangle$	0.04857	0.0164	6.400×10^{-28}	2.352×10^{-28}
		$\vert 2\,2+\rangle \leftarrow \vert 1\,1-\rangle$	0.07620	0.0105	2.611×10^{-28}	9.594×10^{-29}
		$\vert 2\,1\rangle \leftarrow \vert 1\,1+\rangle$	0.37213	0.0090	1.920×10^{-28}	7.057×10^{-29}
		$\vert 2\,1\rangle \leftarrow \vert 1\,2\rangle$	0.42035	0.0489	5.671×10^{-27}	2.084×10^{-27}
		$\vert 2\,1\rangle \leftarrow \vert 1\,1-\rangle$	0.44798	0.1890	8.488×10^{-26}	3.120×10^{-26}

where $d_{\mathrm{fi}}^{\mathrm{HF}}$ is the reduced matrix element of the dipole moment tensor:

$$\begin{aligned}\left|d_{\mathrm{fi}}^{\mathrm{HF}}\right|^2 &= \left|\langle \nu_f; N_f F_f(\pm) \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i; N_i F_i(\pm)\rangle\right|^2 \\ &= \Big| \textstyle\sum_{F_{1_f}=|F_f-I_2|}^{F_f+I_2} \sum_{N'_f=|F_{1_f}-I_1|}^{F_{1_f}+I_1} \sum_{F_{1_i}=|F_i-I_2|}^{F_i+I_2} \sum_{N'_i=|F_{1_i}-I_1|}^{F_{1_i}+I_1} \\ &\quad a_{N'_f F_{1_f}}^{\nu_f N_f F_f(\pm)} a_{N'_i F_{1_i}}^{\nu_i N_i F_i(\pm)} \\ &\quad \times \langle \nu_f; ((N'_f I_1) F_{1_f} I_2) F_f \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i; ((N'_i I_1) F_{1_i} I_2) F_i \rangle \Big|^2 .\end{aligned} \tag{8}$$

Here, we use a common representation of a dipole moment operator as a spherical tensor of rank 1, $\mathrm{T}^{(1)}(\mathbf{d})$ [31,33]. Matrix elements of this spherical tensor in the coupled basis are evaluated using spherical tensor algebra [43,44]:

$$\begin{aligned}&\langle \nu_f; ((N_f I_1) F_{1_f} I_2) F_f \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i; ((N_i I_1) F_{1_i} I_2) F_i \rangle \\ &\quad = (-1)^{F_i+I_2+F_{1_f}+F_{1_i}+I_1+N_f} \sqrt{(2F_i+1)(2F_f+1)} \\ &\quad\quad \times \sqrt{(2F_{1_i}+1)(2F_{1_f}+1)} \begin{Bmatrix} I_2 & F_i & F_{1_i} \\ 1 & F_{1_f} & F_f \end{Bmatrix} \\ &\quad\quad \times \begin{Bmatrix} I_1 & F_{1_i} & N_i \\ 1 & N_f & F_{1_f} \end{Bmatrix} \langle \nu_f N_f \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i N_i \rangle .\end{aligned} \tag{9}$$

The $\langle \nu_f N_f \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i N_i \rangle$ is further reduced to (in a $^1\Sigma$ state):

$$\begin{aligned}&\langle \nu_f N_f \| \mathrm{T}^{(1)}(\mathbf{d}) \| \nu_i N_i \rangle \\ &\quad = (-1)^{N_f} \sqrt{(2N_f+1)(2N_i+1)} \begin{pmatrix} N_f & 1 & N_i \\ 0 & 0 & 0 \end{pmatrix} d_{\mathrm{fi}} .\end{aligned} \tag{10}$$

4. Example of the complete dataset record

We calculate the positions and intensities of the hyperfine components of all dipole transitions in the ground $^1\Sigma$ electronic state of the HT and DT molecules. Our calculations result in 331 892 hyperfine components of 18 585 dipole lines from the R and P branches. The complete dataset can be found in Supplementary Material [45].

The accuracy of the calculated transition frequencies is determined by the accuracy of the hyperfine coupling constants reported in Ref. [35]. As mentioned in our previous papers [33–35], the dominant contribution to the uncertainty of the hyperfine coupling constants originates from the quantum chemical calculations of the nuclear spin-rotation constant, which is of an order of 300 Hz. In principle, one should also consider the influence of the neglected nonadiabatic effects, which are expected to be of the order of the ratio of the electron mass to the reduced nuclear mass [32]. However, this uncertainty is significantly smaller than the one originating from the calculations of the spin-rotation coupling constant. Therefore, we claim the uncertainty of the transition frequencies to be of an order of about 0.3 kHz. The accuracy of the transition moments and line intensities is determined by the accuracy of the dipole moment function reported in Ref. [20], which, according to the authors, should be of a relative order of 10^{-3}.

Table 1 presents an example of the calculated parameters for the two lines from the first overtone (2-0) band, for the DT and HT molecules. The central frequency of the rovibrational transition is taken from the H2Spectre code [22,46]. In the case of the DT molecule, we present the 2-0 $P(2)$ line, which consists of 21 hyperfine components, that are spread over a range of over 400 kHz. We note that each $\nu_f - \nu_i P(1)$ and $R(0)$ line in DT consist of 9 hyperfine components, each $P(2)$ and $R(1)$ line involve 21 hyperfine components, while all the remaining rovibrational lines involve 22 components. In the case of the HT molecule, we present the 2-0 $R(1)$ line, which consists of 11 hyperfine components, that are spread over a range of over 500 kHz. Contrary to DT, this particular number of hyperfine components is characteristic for every $\nu_f - \nu_i$ P and R line, except for the $R(0)$ and $P(1)$ transitions, which involve 6 components.

5. Conclusion

We provide a comprehensive list of positions and intensities of the 331 892 hyperfine components of 18 585 rovibrational dipole transitions from the P and R branches of HT and DT. Moreover, we have calculated the intensities of all rovibrational dipole transitions in these two isotopologues, which were not analyzed before. The results presented here can serve as reference data for future accurate measurements of transition frequencies in tritium-bearing molecules, which are 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.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2021.107662.

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