Abstract

We report results of a theoretical investigation of hyperfine interactions in two homonuclear isotopologues of the hydrogen molecule: \( \text{H}_2 \) and \( \text{D}_2 \). We present a set of hyperfine coupling constants: spin-rotation, spin-spin dipole, and, in the case of the \( \text{D}_2 \) molecule, electric quadrupole coupling constants for all bound states of the two isotopologues in their ground electronic \( X^1\Sigma_g^+ \) state. We provide a list of positions and intensities of 220 997 hyperfine components of 16 079 rovibrational quadrupole transitions of the \( \text{O}, \text{Q} \) and \( \text{S} \) branches. The positions and intensities of the hyperfine components are necessary for a reliable interpretation of accurate measurements of rovibrational transition frequencies in \( \text{H}_2 \) and \( \text{D}_2 \), which are used for tests of the quantum electrodynamics of molecules and searches for new physics beyond the Standard Model.

Keywords: hydrogen molecule, hyperfine structure, quadrupole transitions

1. Introduction

Theoretical studies of the rovibrational structure of the ground electronic state in molecular hydrogen achieve remarkable accuracy in the determined dissociation energy \( \text{D}(\text{H}_2) \) and rovibrational energy levels \( \text{D}(\text{H}_2) \) \( \Sigma \). The progress in the theoretical investigations is enhanced by recent experiments, which aim at the sub-MHz accuracy of both the dissociation energy \( \text{D}(\text{H}_2) \) \( \Sigma \) and the rovibrational transition frequencies in the ground electronic state \( \Sigma \). Comparison between theoretical calculations and accurate measurements can be used as a test for the quantum electrodynamics for molecules \( \Sigma \). Determination of the proton-charge radius \( \Sigma \), determination of the electronic transitions achieved the accuracy of 4.5 MHz \( \Sigma \), comparison of the hyperfine structure origi- nating from the interactions involving nuclear spins and (in the case of deuteron-bearing isotopologues) electric quadrupole moment of the nuclei.

As dipole transitions in the homonuclear isotopologues of hydrogen molecule (\( \text{H}_2 \), \( \text{D}_2 \) and \( \text{T}_2 \)) are forbidden, the experimental studies are limited to quadrupole transitions, which are much weaker than dipole transitions in the HD molecule \( \Sigma \). The quadrupole transitions in \( \text{H}_2 \) and \( \text{D}_2 \) have never been saturated and the most accurate experiments were performed using Doppler-limited cavity-enhanced techniques. Nevertheless, the best measurements for the \( \text{D}_2 \) molecule, performed for the S(2) line from the first overtone, reached the accuracies of 500 kHz \( \Sigma \), 400 kHz \( \Sigma \) and even 161 kHz \( \Sigma \). The first overtone in \( \text{D}_2 \) was also recently studied by Wójtewicz et al. \( \Sigma \), who reported 870 and 999 kHz combined uncertainties for the positions of the S(3) and S(4) lines, respectively. Monde- lain et al. \( \Sigma \) estimated the uncertainty of the frequencies of the S(0) and Q(1)-Q(4) \( \text{D}_2 \) transitions between 0.3 and 1.83 MHz. In the case of the \( \text{H}_2 \) molecule, the most accurate measurements that probed rovibrational levels directly, reached the accuracy of 6.6 MHz \( \Sigma \), while measurements based on subtraction of the energies of two electronic transitions achieved the accuracy of 4.5 MHz \( \Sigma \) for \( \nu = 0, N = 0 \) and \( \nu = 1, N = 0 \) states and 1.5 MHz \( \Sigma \) for the \( \nu = 0, N = 0 \) and \( \nu = 0, N = 1 \) states.

Such accurate measurements of rovibrational transitions require including in the spectral analysis the hyperfine structure originating from the interactions involving nuclear spins and (in the case of deuteron-bearing isotopologues) electric quadrupole moment of the nuclei. The disagreement between recent measurements of rovibrational dipole transitions in the HD molecule \( \Sigma \) has been attributed to the underlying hyperfine structure of rovibrational states, which were recently studied by Dionf et al. \( \Sigma \). Theoretical studies of the hyperfine components of rovibrational dipole lines in HD were reported \( \Sigma \), but no such a study concerning quadrupole transitions in \( \text{H}_2 \) or \( \text{D}_2 \) was performed.

Here, we provide a comprehensive list of all 220 997 hyperfine components of 16 079 rovibrational quadrupole transitions in \( \text{H}_2 \) and \( \text{D}_2 \). We report the list of rovibrationally-averaged hyperfine coupling constants, i.e. spin-rotation, spin-spin dipole, and, in the case of \( \text{D}_2 \) molecule, electric quadrupole constant, for all bound states.
of both molecules.

The paper is organized as follows: Section 2 provides a discussion of the components of the hyperfine Hamiltonian for both molecules. In Sec. 3, we discuss the hyperfine coupling constants, which are calculated for all bound states of H$_2$ and D$_2$, and in Sec. 4 we discuss the hyperfine splittings of the rovibrational levels. Sections 5 and 6 give descriptions of the line intensities of the rovibrational and hyperfine transitions. In Sec. 7, we present examples of calculated positions and intensities for two quadrupole lines in H$_2$ and D$_2$. In Sec. 8 we conclude our results.

2. Hyperfine interactions

In this section, we provide an analysis of the hyperfine (HF) structure Hamiltonian, $\mathcal{H}_{HF}$, of the H$_2$ and D$_2$ molecules. In the case of the H$_2$ molecule, the hyperfine structure of rovibrational levels originates from the interactions involving nuclear spin of the proton ($I_H = \frac{1}{2}$). As the H$_2$ molecule consists of two protons, two nuclear spins couple and the total nuclear spin, $I$, might be either 0, for para-H$_2$, or 1, for ortho-H$_2$. Due to the symmetry relations imposed on fermions, para-H$_2$ and ortho-H$_2$ exhibit rotational structures which involve either even or odd rotational quantum numbers, $N$, only. The rovibrational transitions in para-H$_2$ do not exhibit any hyperfine structure, due to the fact that $I$ equals 0. Hence, we confine the analysis to ortho-H$_2$ and we consider the nuclear spin-rotation and spin-spin dipole coupling terms in the hyperfine Hamiltonian.

On the other hand, since the deuteron is a particle of spin $I_D = 1$, the D$_2$ molecule obeys the symmetry relations for bosons. The coupling of the two nuclear spins leads to three possible values of the total spin, $I = 0, 1$ and 2. para-D$_2$ corresponds to the $I = 0$ and 2 cases, and their rotational structure consists of states described with odd rotational quantum numbers, while the rotational structure of ortho-D$_2$ ($I = 1$) involves only even rotational states, $N$. As the nuclear spin of the deuteron is greater than $\frac{1}{2}$, the interaction of the electric quadrupole moment with the molecular electric field gradient (EFG) must be taken into account, on top of the spin-rotation and spin-spin dipole coupling.

In both cases, we use a coupled basis to calculate matrix elements of the hyperfine Hamiltonian. The coupled basis is formed from coupling of two nuclear spins $I_N$ ($X = H$ or D) to form the total nuclear spin $I$, which is further coupled to the rotational angular momentum $N$, to form the total angular momentum, $F$. The state vector in this representation is given as $|\nu; NIFm_F\rangle$, where $\nu$ and $m_F$ are the vibrational quantum number and the projection of the total angular momentum on the laboratory-fixed frame, respectively. We restrict the analysis to the ground electronic $X^1\Sigma^+_g$ state and we neglect any coupling between vibrational states.

2.1. H$_2$ molecule

We consider the effective hyperfine Hamiltonian, $\mathcal{H}_{HF}$, which consists of two terms [11, 12]:

$$\mathcal{H}_{HF}^{I\mu} = \mathcal{H}_{\text{nsr}} + \mathcal{H}_{\text{dip}}.$$  \hspace{1cm} (1)

The former term, $\mathcal{H}_{\text{nsr}}$, corresponds to the nuclear spin-rotation coupling, while the latter, $\mathcal{H}_{\text{dip}}$, denotes the dipolar interaction between the two nuclear spins.

The nuclear spin-rotation coupling originates from the interaction of a nuclear magnetic moment with the magnetic field resulting from the overall rotation of the molecule. As we consider the diatomic molecule, the strength of the coupling is given by a simple scalar value, namely the spin-rotation constant [12, 10], 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 is given as:

$$\mathcal{H}_{\text{nsr}} = c_{\text{nsr}} \mathbf{I} \cdot \mathbf{N},$$  \hspace{1cm} (2)

where $c_{\text{nsr}}$ denotes the nuclear spin-rotation coupling constant of the H$_2$ molecule.

The matrix elements of the spin-rotation interaction can be evaluated using the spherical tensorial algebra of Fano and Racah [12, 17]. The total nuclear spin, $\mathbf{I}$, and the rotational angular momentum, $\mathbf{N}$, can be represented as rank-1 spherical tensors. This part of the Hamiltonian is diagonal and the evaluation of the matrix elements is straightforward:

$$\langle \nu; N'IF'm_{F'}|\mathcal{H}_{\text{nsr}}|\nu; NIFm_F \rangle = \delta_{NN'}\delta_{I'I}\delta_{F'F}\delta_{m_Fm_{F'}} \times \frac{c_{\text{nsr}}}{2} \left( F(F + 1) - I(I + 1) - N(N + 1) \right).$$  \hspace{1cm} (3)

The second term in the Hamiltonian from Eq. (1) corresponds to the magnetic dipole interaction between the nuclear magnetic moments of the protons. It is given as:

$$\mathcal{H}_{\text{dip}} = \frac{g_I^2 \mu_N^2}{4\pi} \left( I_1 \cdot I_2 \cdot \frac{R^3}{R^6} - \frac{3(\mathbf{I}_1 \cdot \mathbf{R})(\mathbf{I}_2 \cdot \mathbf{R})}{R^6} \right),$$  \hspace{1cm} (4)

where $g_I$ is the $g$ factor of the nucleus (here: proton), $\mu_N$ is the nuclear magneton, $\mu_0$ is the vacuum permeability, and $R$ is the internuclear distance.

In order to employ the spherical tensorial algebra, we represent the nuclear angular momenta $\mathbf{I}_1$ and $\mathbf{I}_2$ as spherical tensors of rank 1 and couple them to form the rank-2 tensor $T^{(2)}(\mathbf{I}_1, \mathbf{I}_2)$. The resulting spherical tensor is coupled with $T^{(2)}(\hat{C})$, the rank-2 tensor describing the spherical harmonics $Y_{2q}$ associated with the transformation of the rovibrionic wavefunction from the laboratory-fixed to the molecule-fixed frame of reference. The final form of the spin-spin dipole interaction Hamiltonian, $\mathcal{H}_{\text{dip}}$, is given as [42]:

\[ \text{[Details of the equation are omitted for brevity.]} \]
respectively. In the case of the D molecule, the effective Hamiltonian involves three terms: 

\[ H_{\text{dip}} = \frac{g}{2} \mu_N^2 \frac{\mu_0}{4\pi} \sqrt{6} \Gamma(2)(C) \cdot T(2)(I_1, I_2), \]  

and the matrix elements in the coupled basis are:

\[
\langle \nu; N'I'F' | H_{\text{dip}} | \nu; NIFm_F \rangle = \delta_{F,F'} \delta_{m_{F'},m_F} (-1)^{N + I + F + N'} \sqrt{30 \text{dip}} \\
\times \sqrt{(2I + 1)(2I' + 1)(2N + 1)(2N' + 1)} \\
\times \sqrt{I_1(I_1 + 1)(2I_1 + 1)(I_2 + 1)(2I_2 + 1)} \\
\times \left( \begin{array}{c} N' \\ 2 \\ N \end{array} \right) \left( \begin{array}{c} I \\ N \\ F \end{array} \right) \left\{ \begin{array}{ccc} I_1 & I_1 & 1 \\ I_2 & I_2 & 1 \end{array} \right\},
\]

where we introduced the coupling constant:

\[ c_{\text{dip}} = g \mu_N^2 \frac{\mu_0}{4\pi} (\nu N) \frac{1}{R^3} (\nu N), \]  

which involves the expectation value of the \( 1/R^3 \) term in given rovibrational state. The quantity in parenthesis is the Wigner 3-j symbol and the quantities in the small and large curly brackets are the Wigner 6-j and 9-j symbols, respectively. In the case of the \textit{ortho}-H\(_2\) molecule (\( I_1 = I_2 = \frac{1}{2} \) and \( I' = 1 \)) Eq. (6) reduces to

\[
\langle \nu; N'I(=1)F'm_F' | H_{\text{dip}} | \nu; N(=1)Fm_F \rangle = -\delta_{F,F'} \delta_{m_{F'},m_F} (-1)^{N + F + N'} \sqrt{15} \frac{1}{2} c_{\text{dip}} \\
\times \sqrt{(2N + 1)(2N' + 1)} \left( \begin{array}{c} N' \\ 0 \\ N \end{array} \right) \left( \begin{array}{c} I \\ N \\ F \end{array} \right) \left\{ \begin{array}{ccc} I_1 & I_1 & 1 \\ I_2 & I_2 & 1 \end{array} \right\},
\]

2.2. \textit{D}\(_2\) molecule

In the case of the \textit{D}\(_2\) molecule, the effective Hamiltonian involves three terms:

\[ H_{\text{D}_2}^{\text{HF}} = H_{\text{anr}} + H_{\text{dip}} + H_{\text{quad}}. \]  

The first two terms as well as the corresponding matrix elements are essentially the same as in the previous section (with the exception of the \( g \)-factor and coupling constants). Note that in the case of \textit{para}-\textit{D}\(_2\), a possible coupling between the \( I = 0 \) and \( I = \pm 2 \) states may arise.

Apart from the spin-rotation and spin-spin dipole coupling, one has to take into account the interaction of the electric quadrupole moment of the deuterium nuclei with the molecular electric field gradient. This term can be represented using the spherical tensorial algebra as:

\[ H_{\text{quad}} = -e \sum_k T^{(2)}(Q_k) \cdot T^{(2)}(\nabla E_k), \]  

where the sum runs over the two deuterium nuclei, labeled with \( k \). The quadrupole moment as well as EFG are represented as spherical tensors of rank 2 (see Chapter 8.4 of Ref. [42] for more details). Matrix elements of the quadrupole interaction are given as:

\[
\langle \nu; N'I'F'm_{F}' | H_{\text{quad}} | \nu; NIFm_F \rangle = \delta_{F,F'} \delta_{m_{F'},m_F} (-1)^{N + I' + F + I + I'} \sqrt{2(N + 1)(2N' + 1)} \\
\times \sqrt{(2I + 1)(2I' + 1)} \left( \begin{array}{c} N' \\ 0 \\ N \end{array} \right) \left( \begin{array}{c} I' \\ N' \\ F \end{array} \right) \left\{ \begin{array}{ccc} I_1 & I_1 & 1 \\ I_2 & I_2 & 1 \end{array} \right\},
\]

where the quadrupole coupling constant:

\[ c_{\text{Q}} = eQ_{\text{D}_2}q_{0k}, \]  

involves the electric quadrupole moment of the \( k \)-th nucleus, \( Q_{\text{D}_2} \), 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:

\[ Q_{\text{D}_2} = \langle I_k, m_{I_k}(= I_k)|Q_{33}|I_k, m_{I_k}(= I_k) \rangle, \]  

and the rovibrationally-averaged EFG at the position of the \( k \)-th nucleus, \( q_{0k} \), which is the expectation value of the \( V_{33} \) component of EFG tensor, \( V_{ij} \), in a given rovibrational state. In the case of a homonuclear molecule such as \( \text{D}_2 \), where \( I_1 = I_2 \), Eq. (11) simplifies to:

\[
\langle \nu; N'I'F'm_{F}' | H_{\text{quad}} | \nu; NIFm_F \rangle = \delta_{F,F'} \delta_{m_{F'},m_F} (-1)^{N + I' + F + I} \left( \begin{array}{c} N' \\ 0 \\ N \end{array} \right) \left( \begin{array}{c} I' \\ N' \\ F \end{array} \right) \left\{ \begin{array}{ccc} I_1 & I_1 & 1 \\ I_2 & I_2 & 1 \end{array} \right\},
\]

Similarly to the spin-spin interaction, the quadrupole coupling mixes the \( N \) and \( N' = N \pm 2 \) states as well as (in the case of \textit{ortho}-\textit{D}\(_2\)) the \( I \) and \( I' = I \pm 2 \) states.

3. Hyperfine coupling constants

Following our previous work [39], we determine the dependence of the coupling constants on the internuclear distance, \( R \), and we calculate their expectation values in a given rovibrational state. Due to very large datasets for both molecules, the coupling constants are given in the Supplementary Materials [38]. Similarly as we did in the case of the HD molecule [39], we do not include the \( N = 0 \) levels, since none of the analyzed hyperfine terms from Eqs. (11) and (12) affect the ground rotational levels.
The rovibrational wavefunctions of the H$_2$ and D$_2$ molecules, $\chi_{\nu,N}(R) = (R|\nu N)$, are numerical solutions of the Schrödinger equation for the isolated molecules within the Born-Oppenheimer approximation. We made use of the potential energy curve of Schwenke [44] and solved the Schrödinger equations using the discrete variable representation (DVR) method. We obtained 146 and 596 wavefunctions for the ortho-H$_2$ and D$_2$ molecules, respectively. Our set of wavefunctions does not include a very weakly bound state $\nu = 21, N = 1$ in D$_2$. The corresponding dissociation energy of this state is 0.0491 cm$^{-1}$, according to Ref. [50], or 0.04119(2) cm$^{-1}$ as calculated with the H2Spectre code of Czachorowski et al. [51] and Komasa et al. [12]. According to Ref. [50], this state does not exist in the Born-Oppenheimer approximation and the potential energy curve of Schwenke [44]. The accuracy of the calculations was estimated by comparing the obtained dissociation energies with those calculated with the H2Spectre code [11, 12]. The average value of the relative differences is approximately 0.32% for H$_2$ and 0.06% for D$_2$ and is mostly attributed to weakly bound states with large values of $\nu$.

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) and the uncontracted cc-pV6Z basis set [52, 53] as described in Ref. [39]. 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 [48]. All the calculations have been performed with the CFOUR quantum-chemical package [54] (version 2.1).

3.2. Spin-spin dipole interaction

The spin-spin dipole coupling constants, Eq. (17), were obtained using DVR-wavefunctions $\chi_{\nu,N}$ and the fundamental constants taken from CODATA [55].

3.3. Electric quadrupole interaction

Following the approach from Ref. [39], we employed the Born-Oppenheimer EFG reported by Pavanello et al. [56]. First, we calculated the expectation value of the $R$-dependent EFG in the $\nu = 0, N = 1$ state of D$_2$, using the experimental quadrupole coupling constant reported by Code and Ramsey [41] ($c_Q = 225.044(24)$ kHz), and determined the value of the electric quadrupole moment, $Q_D$:

$$Q_D = 0.2859(2) \text{fm}^2$$ (15)

where the uncertainty, following Refs. [39] and [56], is propagated from the experimental standard uncertainty. We note that this value is in perfect agreement with the one reported by us in the previous work [39], based on the coupling constant for the HD molecule ($Q_D = 0.28591(8) \text{fm}^2$).

3.4. Comparison with previous results

Table I presents a comparison of our vibrationally-averaged coupling constants with the available literature data. Most of the experimental studies of H$_2$ and D$_2$, which employed molecular beam magnetic resonance method, were focused on the $\nu = 0, N = 1$ state. Values of the hyperfine coupling constants were first extracted from the radiofrequency spectra in strong magnetic field by Kellogg et al. [61, 62] and were later refined by Kolsky et al. [63, 64] in the weak field regime. Those values were used by Ramsey [13] in the theoretical analysis of the hyperfine structure of the first rotational state in both hydrogen and deuterium molecules. Up to this date, the most accurate values of the hyperfine coupling constant in this state of H$_2$ come from the paper of Harrick et al. [58] and we compare our results with this dataset. Hyperfine coupling constants for two more ($\nu = 0, N = 3$ and $\nu = 0, N = 5$) rotational states in H$_2$ were extracted by Verberne et al. [59] from experiments involving the molecular beam magnetic resonance technique in the low-field regime. In the case of the D$_2$ molecule, the most accurate experimental data were reported by Code and Ramsey [41], who refined the data for the $\nu = 0, N = 1$ state and performed additional measurements for the $\nu = 0, N = 2$ rotational level.

In the case of theoretical investigations of the hyperfine coupling constants in H$_2$ and D$_2$, we compare our results with the spin-rotation constants published by Gauss et al. [57], who reported values of $c_{nsr}$ for a wide range of rovibrational levels in both the H$_2$ and D$_2$ molecules.

Theoretical values of the spin-spin dipole coupling constant were reported for the $\nu = 0, N = 1$ (Code et al. [11]), $\nu = 0, N = 3$ and $\nu = 0, N = 5$ (Verberne et al. [59]) levels in H$_2$ and for the $\nu = 0, N = 1$ and $\nu = 0, N = 2$ states in D$_2$ (Code et al. [41]).

The experimental value of the quadrupole coupling constant was mostly used as a reference value in theoretical determination of the deuteron's quadrupole moment from the calculations of EFG [55, 56, 64] and, thus, no theoretical predictions of $c_Q$ are available.

Following our previous work [39], we estimate the uncertainty of the nuclear-spin rotation constants at 300 Hz. Our results agree very well with the experimental data for both H$_2$ and D$_2$. We note that for the $N = 3$ and $N = 5$ levels in H$_2$, the values of $c_{nsr}$ reported here lie within the experimental error bars. In the case of the spin-spin dipole constants, the uncertainty is determined by the quality of the rovibrational wavefunctions, which was estimated at the beginning of this section. In all considered cases, our values are in perfect agreement with the experimental results. In the case of the quadrupole coupling constants,
the comparison concerns only the $\nu = 0, N = 2$ state, and our result lies within the experimental error bars.

4. Determination of the energy levels

Since neither the hyperfine Hamiltonian of $H_2$, Eq. (1), nor the hyperfine Hamiltonian of $D_2$, Eq. (2), are diagonal in the coupled representation, $|\nu; NIFm_F\rangle$, the hyperfine energy levels should be determined by their diagonalization. Owing to the fact that none of the components of Eqs. (1) and (2) mix different $F$ and $F'$ (and $m_F$ and $m'_{F}$) states, one can diagonalize each $F$-labelled submatrix independently. In the case of ortho-$H_2$ and para-$D_2$, each submatrix is of the $3 \times 3$ size, where the columns (or rows) correspond to $N = F - 1$, $N = F$ or $N = F + 1$ coupled basis vectors. Due to the fact that ortho-$H_2$ and para-$D_2$ involve only odd rotational levels, the submatrices are of $1 \times 1$ ($N = F$) or $2 \times 2$ ($N = F - 1$ and $N = F + 1$) dimensions for odd ($F = 0$) and even values of $F$, respectively. In the latter case, the off-diagonal matrix elements, which couple $N = F - 1$ and $N = F + 1$ states, are from 9 to 11 orders of magnitude smaller than diagonal terms. Thus, in the case of ortho-$H_2$ and para-$D_2$, $N$ can be treated as a good quantum number and we retain the coupled basis vectors labeling for the hyperfine energy levels.

In the case of para-$D_2$ ($I = 0$ or 2), the submatrices are of $6 \times 6$ size. Due to the fact that para-$D_2$ involves only even rotational quantum numbers, the dimensions of submatrices are reduced to $2 \times 2$ and $4 \times 4$, for even and odd $F$ values, respectively. The hyperfine energy levels were determined by numerical diagonalization of each submatrix. The eigenvectors of the hyperfine matrix are referred to as $|\nu; NIFm_F(\pm)\rangle$. Due to a very weak coupling between rotational levels which differ by $\Delta N = \pm 2$, $N$ remains a good quantum number. Following the work of Code and Ramsey [41], we introduce the $(\pm)$ labels to distinguish between the eigenstates which originate from the mixing of $I = 0$ and $I = 2$ states and correspond to higher (+) or lower (−) energy.

In the subsequent discussion, we shall employ the following relation between the coupled basis vectors and the eigenvectors:

$$|\nu; NIFm_F(\pm)\rangle = \sum_{I=0,2}^{F+1} \sum_{N'=F-I}^{F+I} a^{NF(\pm)}_{N'F} |\nu; N'IFm_{F}\rangle,$$

where $a^{NF(\pm)}_{N'F}$ denote the mixing coefficients, obtained from the diagonalization of the Hamiltonian of ortho-$D_2$.

5. Line intensities

In this section we provide a complete list of intensities of the hyperfine components of all quadrupole lines in both the $H_2$ and $D_2$ molecules. The intensity of the quadrupole transition between two degenerate states (initial and final), in the SI units, is given by [32, 55, 67]:

$$S_\mathrm{li} = \frac{2\pi^4}{15hc^2\epsilon_0} \nu_0^3 C_N P_6(T) |Q_6|^2,$$

where the transition frequency and the electric quadrupole transition moment are denoted by $\nu_0$ and $Q_6$, respectively. $h$, $c$ and $\epsilon_0$ are the Planck’s constant, the speed of light in vacuum and the vacuum permittivity, respectively. $C_N$, is an algebraic coefficient, which depends on the considered rovibrational branch:

1. O branch ($N_f = N_i - 2$):

$$C_{N_i} = \frac{3N_i(N_i - 1)}{2(2N_i + 1)(2N_i + 3)},$$
2. Q branch \((N_f = N_i)\):

\[
C_{N_i} = \frac{N_i(N_i + 1)}{2(2N_i - 1)(2N_i + 3)},
\]

(19)

3. S branch \((N_f = N_i + 2)\):

\[
C_{N_i} = \frac{3(N_i + 1)(N_i + 2)}{2(2N_i + 1)(2N_i + 3)}.
\]

(20)

The temperature-dependent part, \(P_h(T)\), is given as

\[
P_h(T) = w_i(2N_i + 1) \frac{e^{-E_i/k_BT} - e^{-E_f/k_BT}}{Q(T)},
\]

(21)

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

\[
Q(T) = \sum_k w_k(2N_k + 1)e^{-E_k/k_BT}.
\]

(22)

\(w_k\) denotes the degeneracy factor due to nuclear spin statistics. In the case of the \(\text{H}_2\) molecule, \(w_k\) corresponds to 1 or 3, for even and odd rotational levels, respectively. In the case of \(\text{D}_2\), \(w_k\) equals 3 or 6, for odd and even rotational quantum numbers, respectively. \(E_k\) corresponds to the energy of the \(k\)-th rovibrational state, \(k_B\) denotes the Boltzmann constant and \(T\) is the temperature.

Following our previous work [33], apart from the line intensity defined in Eq. (17), we provide the temperature-independent line intensity, \(S_n/P_h(T)\). This parameter corresponds to the case in which the entire population of a given molecule occupies the \(i\)-th rovibrational state. This parameter can be used to determine line intensities at any \(T\).

Line intensity is determined by the quadrupole transition moment, \(Q_h\), which is obtained as:

\[
Q_h = \int dR \langle \chi_{i}(R) \rangle Q(R) \chi_i(R).
\]

(23)

\(Q(R)\) is the quadrupole moment function, defined as:

\[
Q(R) = \frac{R^2}{2} - \frac{1}{2} \langle \phi \rangle \sum_i 3z_i^2 - r_i^2 \langle \phi \rangle,
\]

(24)

where \(z_i\) and \(r_i\) refer to the coordinates of the \(i\)-th electron and \(|\phi\rangle\) denotes the electronic wavefunction, which is parametrically dependent on the internuclear coordinate, \(R\).

Electric quadrupole moment for the \(\text{H}_2\) molecule was calculated at the CCSD level with the uncontracted double-augmented-six-\(\zeta\) quality (d-aug-cc-pV6Z) basis set [52]. The calculations were performed for the interatomic \(r_{\text{HH}}\) distances in the 0.30–10.60 Å range with steps of 0.01 Å. The numerical results of the \(R\)-dependent quadrupole moment are provided in Supplementary Materials [48].

The calculations have been performed with the CFOUR [54] program (version 2.1).

To estimate the convergence of the calculated values of the quadrupole moment, we have evaluated the complete-basis (CBS) limit values with the two-parameter formula proposed by Helgaker et al. [68]:

\[
c(X) = c_{\text{CBS}} + bX^{-3}
\]

(25)

where \(c_{\text{CBS}}\) and \(b\) are fitted parameters and \(X\) is the cardinal number of an aug-cc-pVXZ basis set. For the vibrationally-averaged geometry \((\langle r_{\text{HH}}\rangle = 0.7666393\ \text{Å} [69, 70])\), the difference between the quadrupole moment in the CBS limit and calculated with the uncontracted d-aug-cc-pV6Z basis is less than \(7 \cdot 10^{-4}\) a.u.

Quadrupole transition moments, \(Q_h\), were evaluated for all the considered rovibrational transitions, using previously described rovibrational wavefunctions. Our results are in excellent agreement (the largest relative difference is at the level of 0.1\%) with values reported by Campargue et al. [52] and Kassi et al. [33] for \(\text{H}_2\) and \(\text{D}_2\) molecules, respectively.

6. Line intensities of hyperfine transitions

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

\[
S_{n,H} = \frac{2\pi^4}{15\hbar c^2} \frac{1}{v_0^3} \frac{1}{w_i(2N_i + 1)} \frac{P_h(T)}{\langle \psi_n^{\text{HF}} \rangle^2},
\]

(26)

where \(\langle \psi_n^{\text{HF}} \rangle\) is the reduced matrix element of the rank-2 quadrupole moment tensor, which, for ortho-\(\text{H}_2\) and para-\(\text{D}_2\) is simply:

\[
S_{n,h}^{\text{HF}} = |\langle \nu_f; N_fI_fF_f m_F, N_iI_iF_i m_F | T^{(2)}(Q) \rangle|^2
\]

(27)

while for ortho-\(\text{D}_2\) corresponds to:

\[
S_{n,h}^{\text{HF}} = |\langle \nu_f; N_fI_fF_f m_F(\pm) | T^{(2)}(Q) \rangle|^2
\]

\[
= \sum_{I_f=0,2} \sum_{N_f=I_f} \sum_{N_i=I_i} \sum_{F_f=I_f} \sum_{F_i=I_i} \sum_{m_F(m_F)} \sum_{m_F(m_F)} \langle \nu_f; N_fI_fF_f m_F, N_iI_iF_i m_F \rangle^2.
\]

(28)

The last term is evaluated using the spherical tensor algebra \(T^{(2)}(Q)\) is a spherical tensor of rank-2, which acts only one part of a coupled scheme, causing a possible change of rotational quantum number, \(N\). The reduced matrix element is evaluated as (see Chapter 5.5.4. of Ref. [42]):

\[
\langle \nu_f; N_fI_fF_f m_F, N_iI_iF_i m_F \rangle = \delta_{l_f l_i} \delta_{F_f + F_i} (2F_f + 1)(2F_i + 1)
\]

\[
\times \left\{ N_f N_i 2 \right\} \langle \nu_f N_f T^{(2)}(Q) \rangle |\nu_i N_i \rangle.
\]

(29)
Table 2: Example of the calculated positions and intensities of the hyperfine components of the quadrupole transitions in the H$_2$ molecule, which are provided in Supplementary Materials $^{[48]}$. Frequencies of the rovibrational transition are calculated with the H2Spectre code of Czchorowski et al. $^{[53]}$ and Komasa et al. $^{[12]}$. Note that for the rovibrational transition, Q corresponds to $\mathcal{Q}_R$ from Eq. (17), while for the hyperfine components, Q denotes $\mathcal{Q}_h^R$ from Eq. (28). Intensity (in the sixth column) corresponds to the temperature-independent line intensity, $S_R/\rho_R(T)$ (see Sec. [5]).

| Band | Line | Hyperfine transition $\left[N'F'\right] \leftarrow \left[NF\right]$ | Frequency (MHz) | Q (a.u.) | Intensity (cm/molecule) | Intensity at 296 K (cm/molecule) |
|------|------|-------------------------------------------------|----------------|----------|------------------------|-------------------------------|
| 1-0  | Q(1) | 124571373.8(6.9) | 0.08782 | 3.29002703x10$^{-27}$ | 2.17091465x10$^{-27}$ |
|      |      | $[12] \leftrightarrow [10]$ | -0.60998 | 0.05554 | 3.65558559x10$^{-27}$ | 2.41112739x10$^{-27}$ |
|      |      | $[12] \leftrightarrow [11]$ | -0.05448 | 0.08332 | 8.22506758x10$^{-27}$ | 5.42503662x10$^{-27}$ |
|      |      | $[12] \leftrightarrow [12]$ | 0.00091 | 0.07348 | 6.39727479x10$^{-27}$ | 4.21947293x10$^{-27}$ |
|      |      | $[11] \leftrightarrow [11]$ | 0.00323 | 0.04810 | 2.74168919x10$^{-27}$ | 1.80834554x10$^{-27}$ |
|      |      | $[11] \leftrightarrow [12]$ | 0.05862 | 0.08332 | 8.22506758x10$^{-27}$ | 5.42503662x10$^{-27}$ |
|      |      | $[10] \leftrightarrow [12]$ | 0.58765 | 0.05554 | 3.65558559x10$^{-27}$ | 2.41112739x10$^{-27}$ |

Table 3: Example of the calculated positions and intensities of the hyperfine components of the quadrupole transitions in the D$_2$ molecule, which are provided in Supplementary Materials $^{[58]}$. Frequencies of the rovibrational transition are calculated with the H2Spectre code of Czchorowski et al. $^{[53]}$ and Komasa et al. $^{[12]}$. Note that for the rovibrational transition, Q corresponds to $\mathcal{Q}_R$ from Eq. (17), while for the hyperfine components, Q denotes $\mathcal{Q}_h^R$ from Eq. (28). Intensity (in the sixth column) corresponds to the temperature-independent line intensity, $S_R/\rho_R(T)$ (see Sec. [5]).

| Band | Line | Hyperfine transition $\left[N'F'\right] \leftarrow \left[NF\right]$ | Frequency (MHz) | Q (a.u.) | Intensity (cm/molecule) | Intensity at 296 K (cm/molecule) |
|------|------|-------------------------------------------------|----------------|----------|------------------------|-------------------------------|
| 2-0  | S(2) | 187104298.7(4.5) | 0.00818 | 1.24370481x10$^{-27}$ | 4.78449686x10$^{-28}$ |
|      |      | $[44] \leftrightarrow [22+]$ | -0.17198 | 0.00225 | 6.09118228x10$^{-30}$ | 2.34326042x10$^{-30}$ |
|      |      | $[44] \leftrightarrow [23]$ | -0.11172 | 0.00462 | 2.57010972x10$^{-29}$ | 9.88713868x10$^{-30}$ |
|      |      | $[42] \leftrightarrow [22+]$ | -0.10029 | 0.00297 | 1.06198190x10$^{-29}$ | 4.08541421x10$^{-30}$ |
|      |      | $[43] \leftrightarrow [22+]$ | -0.06451 | 0.00621 | 4.64617102x10$^{-29}$ | 1.78736872x10$^{-29}$ |
|      |      | $[42] \leftrightarrow [23]$ | -0.04003 | 0.00111 | 1.48060096x10$^{-30}$ | 5.69882959x10$^{-31}$ |
|      |      | $[46] \leftrightarrow [24]$ | -0.03829 | 0.01577 | 2.99410416x10$^{-28}$ | 1.15182332x10$^{-28}$ |
|      |      | $[45] \leftrightarrow [23]$ | -0.02974 | 0.01256 | 1.90014057x10$^{-28}$ | 7.30964797x10$^{-29}$ |
|      |      | $[43] \leftrightarrow [23]$ | -0.00426 | 0.00379 | 1.72736779x10$^{-29}$ | 6.64513452x10$^{-30}$ |
|      |      | $[44] \leftrightarrow [22+]$ | 0.00444 | 0.01094 | 1.44111423x10$^{-28}$ | 5.54392525x10$^{-30}$ |
|      |      | $[44] \leftrightarrow [24]$ | 0.00738 | 0.00158 | 3.00404235x10$^{-30}$ | 1.15639504x10$^{-30}$ |
|      |      | $[44] \leftrightarrow [22+]$ | 0.01333 | 0.00197 | 1.72487831x10$^{-28}$ | 6.63557566x10$^{-30}$ |
|      |      | $[42] \leftrightarrow [21]$ | 0.02126 | 0.00677 | 5.52757692x10$^{-29}$ | 2.12644305x10$^{-29}$ |
|      |      | $[43] \leftrightarrow [21]$ | 0.05703 | 0.00757 | 6.90947119x10$^{-29}$ | 2.65805381x10$^{-29}$ |
|      |      | $[42] \leftrightarrow [20]$ | 0.06154 | 0.00587 | 4.15468269x10$^{-29}$ | 1.59483220x10$^{-29}$ |
|      |      | $[44] \leftrightarrow [23]$ | 0.06469 | 0.00680 | 5.57319556x10$^{-29}$ | 2.14399241x10$^{-29}$ |
|      |      | $[42] \leftrightarrow [24]$ | 0.07907 | 0.00014 | 2.35016026x10$^{-32}$ | 9.04099395x10$^{-33}$ |
|      |      | $[42] \leftrightarrow [22+]$ | 0.08502 | 0.00229 | 6.30133434x10$^{-30}$ | 2.42410532x10$^{-32}$ |
|      |      | $[45] \leftrightarrow [24]$ | 0.08937 | 0.00725 | 6.33368180x10$^{-29}$ | 2.43654932x10$^{-29}$ |
|      |      | $[43] \leftrightarrow [24]$ | 0.11484 | 0.00083 | 8.22556089x10$^{-31}$ | 3.16434977x10$^{-31}$ |
|      |      | $[43] \leftrightarrow [22+]$ | 0.12079 | 0.00478 | 2.75683378x10$^{-29}$ | 1.06054608x10$^{-29}$ |
|      |      | $[44] \leftrightarrow [24]$ | 0.18379 | 0.00233 | 6.51424689x10$^{-30}$ | 2.50596515x10$^{-30}$ |
|      |      | $[44] \leftrightarrow [22+]$ | 0.18974 | 0.00088 | 9.26631702x10$^{-31}$ | 3.56472568x10$^{-31}$ |
Problem statement, background, methods, results, conclusions.

8. Conclusion

We have reported a list of the hyperfine coupling constants, i.e. the spin-rotation, spin-spin and, in case of the D_2 molecule, quadrupole coupling constants, for all bound states of the H_2 and D_2 isotopologues. Our results agree very well with the experimental data of Harrick et al. [55] and Code et al. [51] and Verberne et al. [23]. Our calculations of the hyperfine splittings of all bound states of the two isotopologues resulted in a comprehensive list of the positions and intensities of the 220 997 hyperfine components of the 16 079 rovibrational quadrupole transitions. The intensities, positions, as well as the coupling constants and the quadrupole transition moment function, can be found in Supplementary Materials [48]. The results presented here are useful as a reference data for a proper interpretation of accurate measurements of rovibrational quadrupole lines in H_2 and D_2, which are used for testing the quantum electrodynamics for molecules and searching for new physics beyond the Standard Model.

Acknowledgements

The research is financed from the budgetary funds on science projected for 2019–2023 as a research project under the “Diamantowy Grant” program. P.W. is supported by the National Science Centre in Poland, Project No. 2019/35/B/ST2/01118. Calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl), Grant No. 294.

References

[1] M. Puchalski, J. Komasa, P. Czachorowski, K. Pachucki, Complete αβm corrections to the Ground State of H_2, Phys. Rev. Lett. 117 (2016) 263002. doi:10.1103/PhysRevLett.117.263002

[2] M. Puchalski, J. Komasa, K. Pachucki, Relativistic corrections for the ground electronic state of molecular hydrogen, Phys. Rev. A 95 (2017) 052506. doi:10.1103/PhysRevA.95.052506

[3] M. Puchalski, J. Komasa, A. Spyszkiwicz, J. Komasa, K. Pachucki, Nonadiabatic relativistic correction to the dissociation energy of H_2, D_2, and HD, Phys. Rev. Lett. 121 (2018) 073001. doi:10.1103/PhysRevLett.121.073001

[4] M. Puchalski, J. Komasa, P. Czachorowski, K. Pachucki, Nonadiabatic QED correction to the dissociation energy of the hydrogen molecule, Phys. Rev. Lett. 122 (2019) 103003. doi:10.1103/PhysRevLett.122.103003

[5] M. Puchalski, J. Komasa, A. Spyszkiwicz, K. Pachucki, Dissociation energy of molecular hydrogen isotopologues, Phys. Rev. A 100 (2019) 020503. doi:10.1103/PhysRevA.100.020503

[6] K. Pachucki, J. Komasa, Accurate adiabatic correction in the hydrogen molecule, J. Chem. Phys. 141 (22) (2014) 224103. doi:10.1063/1.4892981

[7] K. Pachucki, J. Komasa, Leading order nonadiabatic corrections to rovibrational levels of H_2, D_2, and T_2, J. Chem. Phys. 143 (3) (2015) 034111. doi:10.1063/1.4927079

[8] K. Pachucki, J. Komasa, Schrödinger equation solved for the hydrogen molecule with unprecedented accuracy, J. Chem. Phys. 144 (16) (2016) 164306. doi:10.1063/1.4948309
K. Pachucki, J. Komasa, Nonadiabatic rotational states of the hydrogen molecule, Phys. Chem. Chem. Phys. 20 (2018) 247–255. doi:10.1039/C7CP06516G

K. Pachucki, J. Komasa, Nonadiabatic energy levels of HD, Phys. Chem. Chem. Phys. 20 (2018) 26297–26302. doi:10.1039/C8CP05493B

P. Czachorowski, M. Puchalski, J. Komasa, K. Pachucki, Nonadiabatic relativistic correction in H2, D2, and HD, Phys. Rev. A 98 (2018) 052506. doi:10.1103/PhysRevA.98.052506

J. Komasa, M. Puchalski, P. Czachorowski, G. Lach, K. Pachucki, Rotational energy levels of the hydrogen molecule through nonadiabatic perturbation theory, Phys. Rev. A 100 (2019) 032519. doi:10.1103/PhysRevA.100.032519

R. K. Altmann, L. S. Dreissen, E. J. Salumbides, W. Ubachs, K. S. E. Eikema, Deep-ultraviolet frequency metrology of H2 for tests of molecular quantum theory, Phys. Rev. Lett. 120 (2018) 043204. doi:10.1103/PhysRevLett.120.043204

N. Hösch, M. Beyer, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, C. Jungen, F. Merkt, Benchmarking theory with an improved measurement of the ionization and dissociation energies of H2, Phys. Rev. Lett. 122 (2019) 103002. doi:10.1103/PhysRevLett.122.103002

E. D. Dickerson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki, W. Ubachs, Fundamental vibration of molecular hydrogen, Phys. Rev. Lett. 110 (2013) 193601. doi:10.1103/PhysRevLett.110.193601

D. Mondelain, S. Kassi, T. Sala, D. Romanini, D. Gatti, A. Campargue, Sub-MHz accuracy measurement of the S(2) 20 transition frequency of D2 by Comb-Assisted Cavity Ring Down spectroscopy, J. Mol. Spectrosc. 326 (2016) 5–8. doi:10.1016/j.jms.2016.02.008

F. M. J. Cozijn, P. Dupré, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, Sub-Doppler frequency metrology in HD for tests of fundamental physics, Phys. Rev. Lett. 120 (2018) 153002. doi:10.1103/PhysRevLett.120.153002

L.-G. Tao, A.-W. Liu, K. Pachucki, J. Komasa, Y. R. Sun, J. Wang, S.-M. Hu, Toward a determination of the proton-electron mass ratio from the lamb-dip measurement of HD, Phys. Rev. Lett. 120 (2018) 153001. doi:10.1103/PhysRevLett.120.153001

E. Fasci, A. Castrillo, H. Dinesan, S. Gravina, L. Moretti, L. Gi- M. Zaborowski, M. S/suppress lowi´ nski, K. Stankiewicz, F. Thibault, M. Beyer, N. H¨ olsch, J. Huelles, C.-F. Cheng, E. J. Salumbides, S. W´ ojtewicz, R. Gotti, D. Gatti, M. Lamperti, P. La- P. Wcis/suppress lo, F. Thibault, M. Zaborowski, S. W´ ojtewicz, G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. Pachucki, W. Ubachs, Bounds on fifth forces from precision measurements on molecules, Phys. Rev. D 87 (2013) 112008. doi:10.1103/PhysRevD.87.112008

E. J. Salumbides, A. N. Shellekens, B. Gato-Rivera, W. Ubachs, Constraints on extra dimensions from precision molecular spectroscopy, New J. Phys. 17 (3) (2015) 033015. doi:10.1088/1367-2630/17/3/033015

S. Kassi, A. Campargue, Electric quadrupole and dipole transitions of the first 001 rovibrational band of HD by CRDS between 1.45 and 1.35µm, J. Mol. Spectrosc. 267 (1) (2011) 36–42. doi:10.1016/j.jms.2011.02.001

S. Kassi, A. Campargue, K. Pachucki, J. Komasa, The absorption spectrum of D2: Ultrasonic cavity ring down spectroscopy of the (20) band near 1.7 µm and accurate ab initio line list up to 35 000 cm−1, Phys. Chem. Chem. Phys. 14 (2012) 802–815. doi:10.1039/C2CP41031C

I. Gordon, L. Rothman, C. Hill, R. Kochanov, Y. Tan, P. Bernath, M. Birk, V. Boudon, A. Campargue, K. Chance, B. Drouin, J.-M. Flaud, R. Gamache, J. Hodges, D. Jacquemart, M. Perevalov, A. Perrin, K. Shin, M.-A. Smith, J. Ten- nysen, G. Toon, H. Tran, V. Tyuterev, A. Barbe, A. Császár, V. Devi, T. Furtenbacher, J. Harrison, J.-M. Hartmann, A. Joly, T. Johnson, T. Karman, I. Kleiner, A. Kyuberis, J. Loos, O. Lyulin, S. Massie, S. Mikhailenko, N. Moazzen-Ahmadi, H. Miller, O. Naumenko, A. Nikitin, O. Polyansky, M. Roy, M. Rotger, S. Starikova, K. Sung, E. Starikova, S. Tashkun, J. V. Auwera, G. Wagner, J. Wilzewski, P. Wcisło, S. Yu, E. Zak, The HITRAN2016 molecular spectroscopic database, J. Quant. Spectrosc. Radiat. Transfer 203 (2017) 3–69. doi:10.1016/j.jqsrt.2017.06.038

P. Wcisło, I. E. Gordon, C.-F. Cheng, S.-M. Hu, R. Ciuryło, Collision-induced line-shape effects limiting the accuracy in doppler- limited spectroscopy of HD, Phys. Rev. A 93 (2016) 022501. doi:10.1103/PhysRevA.93.022501

M. Niu, E. Salumbides, G. Dickenson, K. Eikema, W. Ubachs, Precision spectroscopy of the X1Σ+/X1Σ–, v=0–1 (J=0–2) rovibrational splittings in HD2, H2, and D2, J. Mol. Spectrosc. 300 (2014) 44–54, spectroscopic Tests of Fundamental Physics. doi:10.1016/j.jms.2014.03.011

M. L. Diouf, F. M. J. Cozijn, K. Darque, E. J. Salumbides, W. Ubachs, Lamb-dips and lamb-peaks in the saturation spectrum of HD, Opt. Lett. 44 (19) (2019) 4733–4736. doi:10.1364/OL.44.004733

P. Dupré, Hyperfine transitions in the first overtone mode of hydrogen deuteride, Phys. Rev. A 101 (2020) 022504. doi:10.1103/PhysRevA.101.022504

H. Jóźwik, H. Cybulski, P. Wcisło, Positions and intensities of hyperfine components of all rovibrational dipole lines in the HD molecule, J. Quant. Spectrosc. Radiat. Transfer, accepted.

J. Komasa, M. Puchalski, K. Pachucki, Hyperfine structure in the HD molecule (2020). doi:10.20520/9
[41] R. F. Code, N. F. Ramsey, Molecular-beam magnetic resonance studies of HD and D2, Phys. Rev. A 4 (1971) 1945–1959. doi:10.1103/PhysRevA.4.1945

[42] J. M. Brown, A. Carrington, Rotational Spectroscopy of Diatomic Molecules, Cambridge University Press, 2001. doi:10.1017/CBO9780511814808

[43] N. F. Ramsey, Theory of molecular hydrogen and deuterium in magnetic fields, Phys. Rev. 85 (1952) 60–65. doi:10.1103/PhysRev.85.60

[44] R. L. White, Magnetic hyperfine structure due to rotation in 1Σ molecules, Rev. Mod. Phys. 27 (1955) 276–288. doi:10.1103/RevModPhys.27.276

[45] R. V. Reid, A. H.-M. Chu, Spin-rotation interaction and magnetic shielding in 1Σ molecules, Phys. Rev. A 9 (1974) 609–613. doi:10.1103/PhysRevA.9.609

[46] W. H. Flygare, Spin rotation interaction and magnetic shielding in molecules, J. Chem. Phys. 41 (3) (1964) 793–800. arXiv:https://doi.org/10.1063/1.1725962

[47] U. Fano, G. Racah, Irreducible tensorial sets, Cambridge Molec-...