Relative intensities of hyperfine components of rovibrational transitions in molecular hydrogen

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We provide an analytical formula for the relative intensities of hyperfine components of rovibrational transitions in the H_2, T_2, and *para*-D_2 isotopologues of hydrogen. The resulting expression is essentially an algebraic factor independent of vibrational quantum numbers. For other molecular hydrogen isotopologues, we show that it is possible to distinguish a certain class of hyperfine components which hold a similar property. The results presented here can be used as an approximation for rovibrational transitions in other diatomic molecules in a $^1\Sigma$ electronic state with smaller rotational constant.

I. INTRODUCTION

Theoretical interest in hyperfine interactions in diatomic molecules is driven by remarkable precision of the experimental studies of rovibrational resonances [1–4] and increasing number of optically cooled and trapped species [5–7]. Careful analysis of the hyperfine splittings and Zeeman sublevels of ground and electronically excited states is crucial for preparing an efficient cooling cycle. This is due to the fact that hyperfine interactions mix different rotational states which might lead to losses from the optical cycling transition [8,9]. Hyperfine-resolved electronic transitions in molecular iodine are commonly used as frequency reference for the laser stabilization [10,11].

Apart from positions of hyperfine components of molecular resonances, knowledge about hyperfine intensity factors in molecular spectra is equally important. More than 40 years ago, careful analysis of intensity ratios in the spectra of LaO allowed for a determination of a spin-rotation interaction constant [12]. Based on a theory applicable to various Hund's coupling cases by Féménias [13], Merer *et al.* explained an unexpected intensity cancellation effect in hyperfine-resolved electronic transition in NbO [14]. Hyperfine intensity factors were also used in the analysis of two-color saturation spectroscopy of CN [15] and are of significant importance in high-resolution photoelectron spectroscopy [16].

Both positions and intensities of hyperfine components of rovibrational transitions in hydrogen molecular ions and neutral hydrogen isotopologues are crucial in the experimental studies of the rovibrational structure of their ground electronic states [1–4,17–20]. Comparison of the experimentally determined transition frequencies with calculations from first principles [21,22] opens the possibility to test the quantum electrodynamics for molecules [22–25] and to search for the physics beyond the standard model [26], such as extra dimensions [27] or new forces [28].

The need for careful analysis of hyperfine interactions in molecular hydrogen sparked several recent theoretical investigations. Dupré [29] reported hyperfine coupling constants for the first three vibrational levels ($v = 0, 1, 2, N = 1$) and studied hyperfine components of the 2-0 P(1) and R(1) lines in the HD isotopologue. In a series of papers [30–34] we reported hyperfine coupling constants for all bound states in the six isotopologues of hydrogen (H_2, HD, D_2, HT, DT, and T_2) and we provided lists of positions and intensities of hyperfine components of all rovibrational electric dipole and quadrupole transitions within the ground electronic $^1\Sigma$ state. At the same time, Komasa *et al.* [35] calculated coupling constants for several rovibrational states and analyzed the relative intensities of the hyperfine components of the P(1) and R(1) transitions from the first overtone and of the R(0) line from the fundamental band. In another paper [36], the authors determined the value of the hyperfine coupling constants for the $v = 0, N = 1$ level in HD, H_2 and D_2, taking into account the nonadiabatic effects, which led to the most accurate determination of the quadrupole moment of the deuteron. Recently we have studied the hyperfine structure of several low-lying rovibrational levels of the excited double-well $EF^1\Sigma_g^+$ electronic state of H_2 [37].

Here, we analyze the vibrational dependence of the relative intensities of hyperfine components reported in Refs. [30–34]. We show analytically, that for the homonuclear isotopologues of hydrogen (except for the *ortho*-D_2), relative intensities are independent of both the initial and final vibrational quantum numbers. The relative intensity in this case is given by a simple algebraic factor which involves Wigner 6-j symbols. For the remaining isotopologues of molecular hydrogen, we show that it is possible to distinguish a class of hyperfine transitions which also do not depend on the vibrational quantum numbers.

II. RELATIVE INTENSITIES OF HYPERFINE COMPONENTS OF ROVIBRATIONAL TRANSITIONS

We consider hyperfine components of rovibrational transition between the initial (v_i, N_i) and final (v_f, N_f) rovibrational

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states. Here, ν and N denote the vibrational and rotational quantum numbers, respectively. Following Refs. [30–34], we label the initial and final hyperfine states (the eigenstates of the effective hyperfine Hamiltonian) as $|\nu_i; N_i F_i m_{F_i}(\pm)_i\rangle$ and $|\nu_f; N_f F_f m_{F_i}(\pm)_f\rangle$, respectively. The $(\pm)$ label is defined in Sec. II B. The eigenstates $|\nu; N F m_F(\pm)\rangle$ are related to the coupled basis vectors suitable for the homonuclear

$$|\nu; N F m_F(\pm)\rangle = \sum_{I} \sum_{N'=|F-I|}^{F+I} a_{N'I}^{\nu NF(\pm)} |\nu; (N'I)F m_F\rangle, \quad (1)$$

and the heteronuclear isotopologues

$$\begin{aligned} &|\nu; N F m_F(\pm)\rangle \\ &= \sum_{F_1=|F-I_2|}^{F+I_2} \sum_{N'=|F_1-I_1|}^{F_1+I_1} a_{N'F_1}^{\nu NF(\pm)} |\nu; [(N'I_1)F_1 I_2]F m_F\rangle. \end{aligned} \quad (2)$$

We recall that in the former case the two nuclear spin angular momenta are coupled to form the total nuclear spin angular momentum, $\mathbf{I}$, which is coupled to the rotational angular momentum, $\mathbf{N}$, to form the total angular momentum, $\mathbf{F}$. In the heteronuclear case one of the nuclear spin angular momenta, $\mathbf{I}_1$, is coupled to the rotational angular momentum, to form the intermediate angular momentum, $\mathbf{F}_1$. The latter is coupled to the remaining nuclear spin angular momentum, $\mathbf{I}_2$, to form the total angular momentum, $\mathbf{F}$. In both cases m_F denotes the projection of the total angular momentum on the laboratory-fixed frame.

In Eqs. (1) and (2), $a_{N'I}^{\nu NF(\pm)}$ and $a_{N'F_1}^{\nu NF(\pm)}$ denote the mixing coefficients which, in general, depend on the vibrational quantum number. Following Refs. [30–34] we neglect a very weak coupling between different rotational levels (the off-diagonal terms in the effective hyperfine Hamiltonian, which couple N and $N' = N \pm 2$ levels are almost ten orders of magnitude smaller than the energy difference between the two rotational levels) and we simplify the notation:

$$a_{N'I}^{\nu NF(\pm)} = \delta_{NN'} a_{NI}^{\nu NF(\pm)} = \delta_{NN'} a_I^{\nu NF(\pm)}, \quad (3)$$

$$a_{N'F_1}^{\nu NF(\pm)} = \delta_{NN'} a_{NF_1}^{\nu NF(\pm)} = \delta_{NN'} a_{F_1}^{\nu NF(\pm)}. \quad (4)$$

For H_2, *para*-D_2, and T_2, the remaining sum over I is trivial $(a_I^{\nu NF(\pm)} = \delta_{I,1})$ and the coupled basis vectors are the eigenvectors of the effective hyperfine Hamiltonian:

$$|\nu; N F m_F(\pm)\rangle = |\nu; (NI)F m_F\rangle. \quad (5)$$

Relative intensities of hyperfine components of rovibrational transitions of rank n are given by the following formula (see Appendix A for a detailed discussion):

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = \frac{|\langle \nu_f; N_f F_f(\pm)_f \| T^n(\mathbf{M}) \| \nu_i; N_i F_i(\pm)_i \rangle|^2}{w_I f_n(N_i, N_f) |\mathbf{M}_{fi}^n|^2}, \quad (6)$$

where $\mathbf{M}^n$ denotes the molecule-fixed multipole moment of the rovibrational transition and corresponds to the electric dipole moment, $\mathbf{d}$, for $n = 1$ and to the electric quadrupole moment, $\mathcal{Q}$, for $n = 2$. $T^n(\mathbf{M})$ is a spherical tensor of rank n which describes the proper multipole moment. w_I is the nuclear degeneracy factor of the initial rotational state which equals $(2I_1 + 1) \times (2I_2 + 1)$ for the heteronuclear isotopologues and $(2I + 1)$ for the homonuclear species. The

$f_n(N_i, N_f)$ factor depends on the rank of the transition and the considered branch and is associated with the transformation of the multipole moment from the space-fixed frame, where the intensity of the transition is measured to the molecule-fixed frame, where the $\mathbf{M}_{fi}^n$ is defined. For instance, for electric dipole transitions $f_n(N_i, N_f)$ reduces to $N_i + 1$ and to N_i for the transitions from the R ($N_f = N_i + 1$) and P ($N_f = N_i - 1$) branches, respectively (see Appendix A).

A. Homonuclear isotopologues

The homonuclear isotopologues (except for the *ortho*-D_2 molecule) are well described by the set of quantum numbers which is proper for the coupled basis—the rotational quantum number, N, the total nuclear spin quantum number, I, and the total angular momentum quantum number, F [see Eq. (5)]. In this case, Eq. (6) reduces to (see Appendix B for the proof)

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = \frac{(2F_f + 1)(2F_i + 1)}{2I + 1} \begin{Bmatrix} N_i & F_i & I \\ F_f & N_f & n \end{Bmatrix}^2. \quad (7)$$

The quantities on the right-hand side of Eq. (7) do not depend on any vibrational quantum number. Thus, we conclude that for homonuclear isotopologues (except for *ortho*-D_2), the relative intensities of hyperfine components of rovibrational transitions are essentially the same for all vibrational bands. We note that Cook and De Lucia [38] derived a similar formula for the case of electric dipole ($n = 1$) transitions as a first approximation of the relative intensities of hyperfine spectra. The authors neglected possible coupling between different intermediate quantum numbers (here: the total nuclear spin, I), and, hence, they did not consider the vibrational dependence of hyperfine components in Ref. [38].

A formula similar to Eq. (7) was used by Korobov *et al.* [39] as an approximation of the relative intensities of hyperfine components of rovibrational quadrupole transitions ($n = 2$) in H_2^+ [see Eq. (22) therein]. The general formula used by the authors involved the mixing coefficients (see the discussion in Appendix B), which, in zeroth-order perturbation theory could be approximated as Dirac deltas. The difference between Eq. (7) and the formulas used in Ref. [39] stems from the presence of a nonzero electronic spin and a more complex coupling scheme used by the authors. We stress that, contrary to H_2^+, the result presented here is exact for the homonuclear isotopologues of hydrogen molecule (except for the *ortho*-D_2), since the hyperfine coupling between the rotational level is negligibly small [see Eqs. (3) and (4)].

Interestingly, Eq. (7) remains valid for heteronuclear molecules involving only one nuclei with nonzero spin, for which $\mathbf{I}_1 = \mathbf{I}$ and $\mathbf{I}_2 = 0$. For such cases, the coupled basis vectors are the eigenvectors of the effective Hamiltonian, as in Eq. (5). In fact, the same formula (with $n = 1$) was used in the interpretation of the hyperfine-resolved $B^4\Pi$-$X^4\Sigma^-$ electronic transition in NbO [see Eq. (2) in Ref. [14]]. We recall that the spin of the ^{93}Nb nucleus is $I_1 = 9/2$ and that the spin of the most abundant isotope of oxygen, ^{16}O, is $I_2 = 0$. Similarly, the intensity of hyperfine components of the electric dipole ($n = 1$) transitions from the $A^2\Sigma^+$-$X^2\Pi_{3/2}$ band in the ^{32}S ^{1}H molecule were approximated by a factor proportional to Eq. (7) [40] (the spins of the ^{1}H and ^{32}S nuclei are $I_1 = 1/2$ and $I_2 = 0$, respectively). We note that the authors use this

term as a first approximation, due to the fact that hyperfine coupling between different J levels in the SH molecule is non-negligible. We conclude that Eq. (7) describes properly the relative intensities of hyperfine components of molecular transitions whenever the coupled basis from Eq. (5) is the eigenbasis of the effective hyperfine Hamiltonian.

B. Heteronuclear isotopologues and ortho-D_2

For the heteronuclear isotopologues each rovibrational level is split into $(2I_1 + 1) \times (2I_2 + 1)$ hyperfine levels. The exception is the $N = 0$, which is degenerate (provided that one neglects the electron-coupled nuclear spin-spin interaction [41–44]), and the $N = 1$ state for the HD and DT molecules, which has five hyperfine components. The ortho-D_2 isotopologue, which was not considered in Sec. II A, involves $2I + 1$ hyperfine components for each rovibrational level, except for the $N = 0$ level, which is also assumed to be degenerate.

Each hyperfine level is a superposition of the coupled basis vectors [Eqs. (1) and (2)]. However, a more detailed analysis shows that some (one—for the case of the $N = 1$ level in HD and DT; two—for the remaining levels in these two isotopologues and for each rotational state in HT; and four—for each rotational state in ortho-D_2) of the hyperfine states are well described by the coupled basis vectors, $|v; [(NI_1)F_1I_2]Fm_F\rangle$ (or $|v; (NI)Fm_F\rangle$ in the case of ortho-D_2) and the linear combination [Eqs. (1) and (2)] becomes trivial. Other states (two—for all rotational states in HT and ortho-D_2 and four—for all rotational states in HD and DT) are superpositions of two coupled basis vectors [Eqs. (1) and (2)] which correspond to the same (N, F) quantum numbers. In order to distinguish between the nontrivial superposition states, we use the $(\pm)$ labels, which denote the eigenstates with higher $(+)$ and lower $(-)$ energy. Therefore, one can distinguish four classes of possible hyperfine components of rovibrational transitions:

(1) Class 1: transitions between hyperfine states described by coupled basis vectors.

(2) Class 2: transitions from a state described by a coupled basis vector to a hyperfine superposition state.

(3) Class 3: transitions from hyperfine superposition state to a state described by a coupled basis vector.

(4) Class 4: transitions between hyperfine superposition states.

The number of transitions which belong to each class depends on the isotopologue, rank of the transition, and the considered rovibrational branch. Relative intensities of the hyperfine components from the first class of transitions exhibit no dependence on vibrational quantum numbers and are given by Eq. (7) for the case of ortho-D_2 and by (see Appendix B)

$$\frac{S_{fi}^{nHF}}{S_{fi}^{n}} = \frac{(2F_f + 1)(2F_i + 1)(2F_{1_f} + 1)(2F_{1_i} + 1)}{(2I_1 + 1)(2I_2 + 1)}$$
$$\times \begin{Bmatrix} F_{1_i} & F_i & I_2 \\ F_f & F_{1_f} & n \end{Bmatrix}^2 \begin{Bmatrix} N_i & F_{1_i} & I_1 \\ F_{1_f} & N_f & n \end{Bmatrix}^2 \quad (8)$$

for the heteronuclear isotopologues.

Relative intensities of the class-2 transitions do not depend on the initial vibrational quantum number. Similarly, relative intensities of the class-3 transitions do not depend on the final vibrational quantum number (see the central and bottom panel
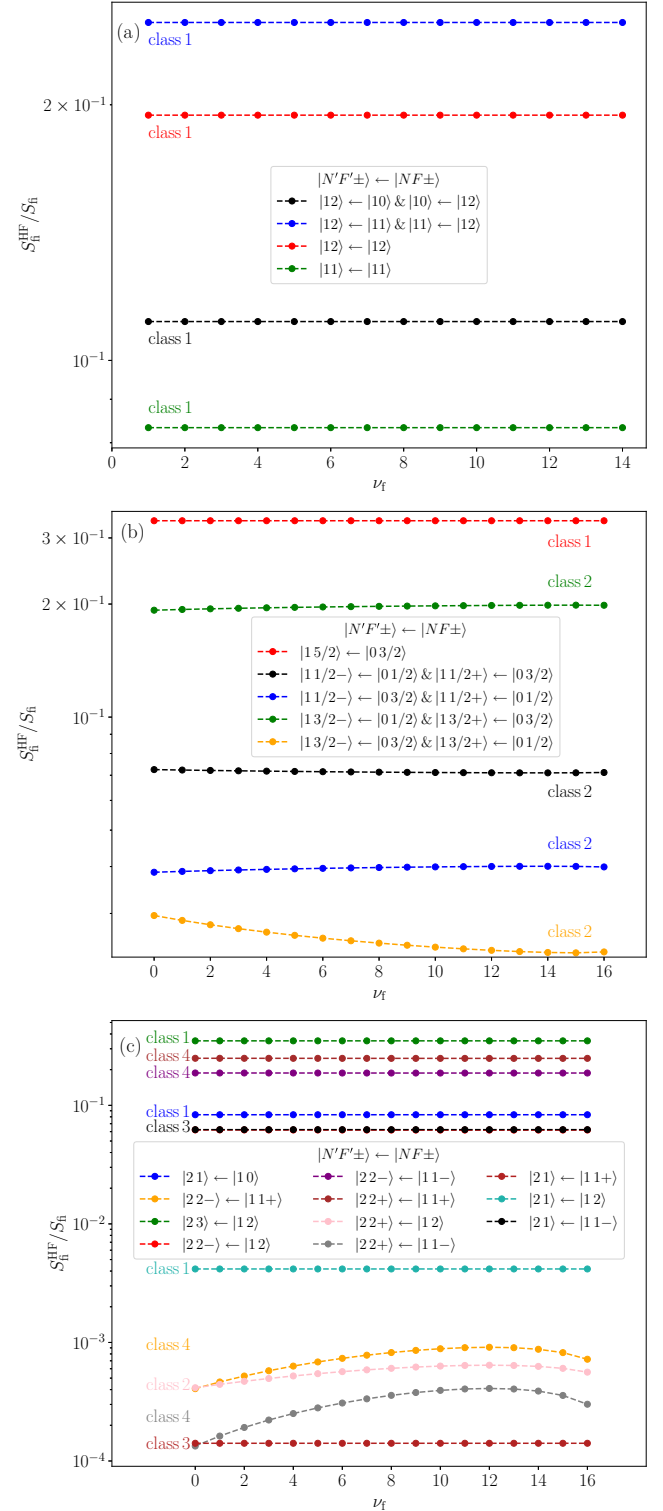

FIG. 1. Relative intensities of the 6 hyperfine components of the ν_f-0 Q(1) transitions in H_2 (top panel), 9 hyperfine components of the ν_f-0 R(0) transitions in HD (central panel), and 11 hyperfine components of the ν_f-0 R(1) transitions in HT (bottom panel).

in Fig. 1 and the discussion in the next section). Relative intensities of hyperfine transitions from the fourth class depend on both the initial and final quantum numbers through

the mixing coefficients, which are related to the hyperfine coupling constants in a nontrivial way.

III. EXAMPLES OF THE CALCULATED RELATIVE INTENSITIES OF HYPERFINE COMPONENTS

An example of the values of relative intensities for different v_f-0 Q(1) lines in H_2 are shown in the top panel in Fig. 1. A quick inspection of Eq. (7) reveals that the six possible components have the relative intensity of 1/4, 7/36, 1/9, and 1/12. We note that the $|12\rangle \leftarrow |10\rangle$ and $|10\rangle \leftarrow |12\rangle$ transitions (as well as $|12\rangle \leftarrow |11\rangle$ and $|11\rangle \leftarrow |12\rangle$ transitions) have the same relative intensities.

We also provide an example for the heteronuclear isotopologues. The dependence of relative intensities of hyperfine components for the v_f-0 R(0) lines in HD is presented in the central panel in Fig. 1. In this particular case, each rovibrational transition involves nine components: one class-1 component of relative intensity 1/3 (the top red line in the central panel in Fig. 1) and eight components of class 2. The relative intensity of class-2 transitions depends on the vibrational quantum number v_f through the mixing coefficients which slightly differ between vibrational bands.

Finally, the bottom panel in Fig. 1 presents relative intensities of 11 hyperfine components of the v_f-0 R(1) lines in HT. The relative intensities of the three class-1 components are 7/20 (the top green line), 1/12 [the blue (dark gray) line], and 1/240 [the light-blue line in the center of Fig. 1(c)]. The R(1) transitions involve two class-2 and two class-3 components, out of which only one (the lower pink line) exhibits a significant dependence on v_f. Out of four class-4 hyperfine components of the R(1) transitions, only the two least intense [the gray and the orange at the bottom of Fig. 1(c)], that involve a change in the $(\pm)$ sign, significantly depend on v_f.

IV. CONCLUSIONS

We provided an analytical formula for the relative intensities of hyperfine transitions in the homonuclear isotopologues of hydrogen (except for the *ortho*-D_2 isotopologue). The formula is independent of both the initial and final vibrational quantum numbers. For the remaining isotopologues we distinguish a class of hyperfine transitions which share a similar property. The analytical formula remains valid for all diatomic molecules for which the coupled basis vectors are the eigenvectors of the effective hyperfine Hamiltonian. In particular, this condition is fulfilled by heteronuclear molecules involving only one nuclei with a nonzero spin. The results presented here are important for the accurate rovibrational spectroscopy of the six isotopologues of hydrogen, which is used for testing the quantum electrodynamics for molecules and searching for new physics beyond the standard model.

ACKNOWLEDGMENTS

APPENDIX A: INTENSITIES OF ROVIBRATIONAL TRANSITIONS AND THEIR HYPERFINE COMPONENTS

In this Appendix we justify the form of Eq. (6). We recall the most common formula for the intensities of rovibrational electric dipole and quadrupole transitions found in the literature [46–49]:

$$S_{fi}^{n=1} = \frac{2\pi^2}{3hc\epsilon_0} v_0 \frac{m}{2N_i + 1} P_{fi}(T)|d_{fi}|^2, \qquad (A1)$$

$$S_{fi}^{n=2} = \frac{2\pi^4}{15hc^3\epsilon_0} v_0^3 C_{N_i} P_{fi}(T)|\mathcal{Q}_{fi}|^2, \qquad (A2)$$

where v_0 is the transition frequency and d_{fi} or $\mathcal{Q}_{fi}$ denotes the matrix elements of the electric dipole and quadrupole moment operator, respectively. h, c, and ϵ_0 are the Planck's constant, the speed of light in vacuum, and vacuum permittivity, respectively. Although this is not relevant for the following discussion, we recall that the temperature-dependent factor, $P_{fi}(T)$, is given as

$$P_{fi}(T) = w_I(2N_i + 1)\frac{(e^{-E_i/k_B T} - e^{-E_f/k_B T})}{Q(T)}, \qquad (A3)$$

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

$$Q(T) = \sum_k w_k(2N_k + 1)e^{-E_k/k_B T}. \qquad (A4)$$

w_k is the degeneracy factor of each rovibrational level due to nuclear spin statistics, E_k is the energy of the kth rovibrational state, k_B is the Boltzmann constant and T is the temperature.

The m factor in Eq. (A1) is simply $N_i + 1$ for the R branch and N_i for the P branch. The C_{N_i} in Eq. (A2) takes the following form for the O branch:

$$C_{N_i} = \frac{3N_i(N_i - 1)}{2(2N_i + 1)(2N_i - 1)}; \qquad (A5)$$

for the Q branch:

$$C_{N_i} = \frac{N_i(N_i + 1)}{(2N_i - 1)(2N_i + 3)}; \qquad (A6)$$

and for the S branch:

$$C_{N_i} = \frac{3(N_i + 1)(N_i + 2)}{2(2N_i + 1)(2N_i + 3)}. \qquad (A7)$$

The m and C_{N_i} factors are directly related to the transformation between the space-fixed frame of reference, where the intensity is measured, and the molecule frame of reference, where the transition moment (dipole or quadrupole) is defined. The formulas for the m and C_{N_i} factors can be justified by the relation between the reduced matrix elements of the spherical tensor of rank n (associated with the transition moment of rank n) with the molecule-fixed transition moment [50]. Let us remind the transformation of a spherical tensor of rank n between the space-fixed (p) and molecule-fixed (q) frame of

reference:

$$T_p^{(n)}(\mathbf{M}) = \sum_{q=-n}^{n} \mathcal{D}_{pq}^{(n)}(\zeta)^* T_q^{(n)}(\mathbf{M}), \tag{A8}$$

where $\mathcal{D}$ is the rotational matrix and ζ denotes the set of angles which describe the transformation from the space-fixed to molecule-fixed frame of reference. For transition moments which couple different rovibrational levels in a given electronic state, the space-fixed reduced matrix elements are transformed as follows [50]:

$$\langle \nu_f; N_f || T^{(n)}(\mathbf{M}) || \nu_i; N_i \rangle$$

$$= \langle \nu_f; N_f \left| \sum_{q=-n}^{n} \mathcal{D}_{\cdot q}^{(n)*} T_q^{(n)}(\mathbf{M}) \right| \nu_i; N_i \rangle$$

$$= (-1)^{N_f} \sqrt{(2N_i+1)(2N_f+1)} \begin{pmatrix} N_f & n & N_i \\ 0 & 0 & 0 \end{pmatrix} \mathbf{M}_{fi}^n, \tag{A9}$$

where the dot in the subscript in the second line of this equation comes from the fact that the reduced matrix element is independent of the space-fixed projection quantum numbers.

Using the tabulated values of the 3-j coefficients for $n=1$ and $n=2$ (see, e.g., Appendix C in Ref. [50]) we obtain the following relations:

$$|\langle \nu_f; N_f || T^{(n=1)}(\mathbf{d}) || \nu_i; N_i \rangle|^2 = m |\mathbf{d}_{fi}|^2, \tag{A10}$$

$$|\langle \nu_f; N_f || T^{(n=2)}(\mathcal{Q}) \ || \nu_i; N_i \rangle|^2 = (2N_i+1) C_{N_i} |\mathcal{Q}_{fi}|^2. \tag{A11}$$

In order to introduce a general formula for the relative intensities that could hold for both the electric dipole and quadrupole interactions, we introduce the factor $f_n(N_i, N_f)$, defined as

$$|\langle \nu_f; N_f || T^{(n)}(\mathbf{M}) || \nu_i; N_i \rangle|^2 = f_n(N_i, N_f) \left| \mathbf{M}_{fi}^n \right|^2. \tag{A12}$$

In the case of hyperfine components of each rovibrational transition, we used in Refs. [30–34] the following formulas:

$$S_{fi}^{HF} = \frac{2\pi^2}{3hc\epsilon_0} \nu_0 \frac{1}{w_I(2N_i+1)} P_{fi}(T) |d_{fi}^{HF}|^2, \tag{A13}$$

$$S_{fi}^{HF} = \frac{2\pi^4}{15hc^3\epsilon_0} \nu_0^3 \frac{1}{w_I(2N_i+1)} P_{fi}(T) |\mathcal{Q}_{fi}^{HF}|^2, \tag{A14}$$

where the matrix elements of the transition moment between hyperfine levels are simply the matrix elements of the relevant spherical tensor operator:

$$d_{fi}^{HF} = \langle \nu_f; N_f F_f(\pm) || T^{(1)}(\mathbf{d}) || \nu_i; N_i F_i(\pm) \rangle, \tag{A15}$$

$$\mathcal{Q}_{fi}^{HF} = \langle \nu_f; N_f F_f(\pm) || T^{(2)}(\mathcal{Q}) || \nu_i; N_i F_i(\pm) \rangle, \tag{A16}$$

which we can write in general form as

$$\mathbf{M}_{fi}^{n\,HF} = \langle \nu_f; N_f F_f(\pm) || T^{(n)}(\mathbf{M}) || \nu_i; N_i F_i(\pm) \rangle. \tag{A17}$$

Once again, n denotes the rank of the spectroscopic transition and equals $n=1$ for electric dipole and $n=2$ for electric quadrupole transitions.

This form allows us to write the relative intensity of hyperfine components of rovibrational transition of rank n, using

Eqs. (A1), (A2), (A12), (A13), and (A14) as

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = \frac{|\langle \nu_f; N_f F_f(\pm)_f || T^n(\mathbf{M}) || \nu_i; N_i F_i(\pm)_i \rangle|^2}{w_I f_n(N_i, N_f) \left| \mathbf{M}_{fi}^n \right|^2}. \tag{A18}$$

APPENDIX B: PROOF OF EQS. (7) AND (8)

1. Homonuclear case

Let us explicitly write Eq. (6) for the homonuclear case:

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = \frac{1}{w_I f_n(N_i, N_f) \left| \mathbf{M}_{fi}^n \right|^2} \left(\sum_{I_f', I_i'} a_{I_f'}^{\nu_f N_f F_f(\pm)_f *} a_{I_i'}^{\nu_i N_i F_i(\pm)_i} \right.$$

$$\times \langle \nu_f; (N_f I_f') F_f || T^{(n)}(\mathbf{M}) || \nu_i; (N_i I_i') F_i \rangle \Big)$$

$$\times \left(\sum_{I_f'', I_i''} a_{I_f''}^{\nu_f N_f F_f(\pm)_f *} a_{I_i''}^{\nu_i N_i F_i(\pm)_i} \right.$$

$$\times \langle \nu_f; (N_f I_f'') F_f || T^{(n)}(\mathbf{M}) || \nu_i; (N_i I_i'') F_i \rangle \Bigg)^*. \tag{B1}$$

The multipole moment operator does not modify either of the nuclear spins. Instead, it acts on the subspace of the eigenvectors of the rotational angular momentum. Making use of the well-known properties of the reduced matrix elements of the spherical tensor operators [50,51]

$$\langle \nu_f; (N_f I_f') F_f || T^{(n)}(\mathbf{M}) || \nu_i; (N_i I_i') F_i \rangle$$

$$= \delta_{I_f' I_i'} (-1)^{F_i + N_f + n + I_f'} \sqrt{(2F_f+1)(2F_i+1)}$$

$$\times \begin{Bmatrix} N_i & F_i & I_f' \\ F_f & N_f & n \end{Bmatrix} \langle \nu_f; N_f || T^{(n)}(\mathbf{M}) || \nu_i; N_i \rangle \tag{B2}$$

we obtain

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = (-1)^{2(F_i + N_f + n)} \frac{(2F_f+1)(2F_i+1)}{w_I f_n(N_i, N_f) \left| \mathbf{M}_{fi}^n \right|^2}$$

$$\times \left(\sum_{I', I''} a_{I'}^{\nu_f N_f F_f(\pm)_f *} a_{I'}^{\nu_i N_i F_i(\pm)_i} a_{I''}^{\nu_f N_f F_f(\pm)_f} a_{I''}^{\nu_i N_i F_i(\pm)_i *} \right.$$

$$\times (-1)^{I'+I''} \begin{Bmatrix} N_i & F_i & I' \\ F_f & N_f & n \end{Bmatrix} \begin{Bmatrix} N_i & F_i & I'' \\ F_f & N_f & n \end{Bmatrix}$$

$$\times |\langle \nu_f; N_f || T^{(n)}(\mathbf{M}) || \nu_i; N_i \rangle|^2 \Bigg). \tag{B3}$$

Note that we simplified the notation by putting $I' = I_i' = I_f'$ and $I'' = I_i'' = I_f''$. In the next step we make use of the definition of the $f_n(N_i, N_f)$ factor [Eq. (A12)] and we recall that F_i, N_f, and n are integers, which allows us to reduce the phase factor. Equation (B3) can now be written as

$$\frac{S_{fi}^{nHF}}{S_{fi}^n} = \frac{(2F_f+1)(2F_i+1)}{w_I} \left(\sum_{I', I''} (-1)^{I'+I''} \right.$$

$$\times a_{I'}^{\nu_f N_f F_f(\pm)_f *} a_{I'}^{\nu_i N_i F_i(\pm)_i} a_{I''}^{\nu_f N_f F_f(\pm)_f} a_{I''}^{\nu_i N_i F_i(\pm)_i *}$$

$$\times \begin{Bmatrix} N_i & F_i & I' \\ F_f & N_f & n \end{Bmatrix} \begin{Bmatrix} N_i & F_i & I'' \\ F_f & N_f & n \end{Bmatrix} \Bigg). \tag{B4}$$

This formula is a generalization of Eqs. (14)–(51) in Ref. [52] to spectral transitions of rank n (the authors considered electric dipole transitions).

For the case of *ortho*-H_2, *para*-D_2, and *ortho*-T_2, there is only one total nuclear spin $I = I' = I'' = 1$ and mixing coefficients become trivial. This allows us to obtain Eq. (7):

$$\frac{S_{\text{fi}}^{n\text{HF}}}{S_{\text{fi}}^{n}} = \frac{(2F_{\text{f}}+1)(2F_{\text{i}}+1)}{(2I+1)} \begin{Bmatrix} N_{\text{i}} & F_{\text{i}} & I \\ F_{\text{f}} & N_{\text{f}} & n \end{Bmatrix}^2. \quad \text{(B5)}$$

For the case of *ortho*-D_2, Eq. (B4) gives a general formula for the relative intensity of each component. For class-1 transitions it is easy to see that Eq. (B5) holds. For transitions of class 2 (or 3) $I_i' = I_i''$ (or $I_f' = I_f''$), the delta function from Eq. (B2) reduces both sums in Eq. (B4) ($I' = I'' = I$) and additionally $a_I^{v_i N_i F_i(\pm)_i} = 1$ (or $a_I^{v_f N_f F_f(\pm)_f} = 1$). The relative intensities are given by [53]

$$\frac{S_{\text{fi}}^{n\text{HF}}}{S_{\text{fi}}^{n}} = \frac{(2F_{\text{f}}+1)(2F_{\text{i}}+1)}{w_I} \times \left| a_I^{v_f N_f F_f(\pm)_f *} \right|^2 \begin{Bmatrix} N_{\text{i}} & F_{\text{i}} & I \\ F_{\text{f}} & N_{\text{f}} & n \end{Bmatrix}^2. \quad \text{(B6)}$$

This proves that transitions from class 2 (or class 3) do not depend on the initial (or final) vibrational quantum number.

A relation similar to Eq. (B4) was used in Ref. [39] in the analysis of the hyperfine components of electric quadrupole transitions in the hydrogen molecular ion [see Eq. (20) therein]. Since the H_2^+ involves a nonzero electronic spin, the analog of Eq. (B4) in Ref. [39] involves different angular momenta. As mentioned in Sec. II A, the authors recover a simplified formula for the relative intensities, Eq. (B5), by approximating the mixing coefficients as Dirac deltas in the zeroth-order perturbation theory.

2. Heteronuclear case

For the heteronuclear isotopologues, Eq. (6) takes the following form:

$$\frac{S_{\text{fi}}^{n\text{HF}}}{S_{\text{fi}}^{n}} = \frac{1}{w_I f_n(N_{\text{i}}, N_{\text{f}}) \left| \mathbf{M}_{\text{fi}}^{n} \right|^2} \left(\sum_{F_{1_{\text{f}}}', F_{1_{\text{i}}}'} a_{F_{1_{\text{f}}}'}^{v_f N_f F_f(\pm)_f *} a_{F_{1_{\text{i}}}'}^{v_i N_i F_i(\pm)_i} \right.$$

$$\times \langle v_{\text{f}}; [(N_{\text{f}}I_1)F_{1_{\text{f}}}' I_2]F_{\text{f}} \| T^{(n)}(\mathbf{M}) \| v_{\text{i}}; [(N_{\text{i}}I_1)F_{1_{\text{i}}}' I_2]F_{\text{i}} \rangle \right)$$

$$\times \left(\sum_{F_{1_{\text{f}}}'', F_{1_{\text{i}}}''} a_{F_{1_{\text{f}}}''}^{v_f N_f F_f(\pm)_f *} a_{F_{1_{\text{i}}}''}^{v_i N_i F_i(\pm)_i} \right.$$

$$\times \langle v_{\text{f}}; [(N_{\text{f}}I_1)F_{1_{\text{f}}}'' I_2]F_{\text{f}} \| T^{(n)}(\mathbf{M}) \| v_{\text{i}}; [(N_{\text{i}}I_1)F_{1_{\text{i}}}'' I_2]F_{\text{i}} \rangle \right)^*. \quad \text{(B7)}$$

Using the same arguments as those that lead from Eq. (B1) to Eq. (B3) we apply Eq. (B2) twice, along with Eq. (A12), which leads to

$$\frac{S_{\text{fi}}^{n\text{HF}}}{S_{\text{fi}}^{n}} = (-1)^{2(N_{\text{f}}+2n+F_{\text{i}}+I_1+I_2)} \frac{(2F_{\text{f}}+1)(2F_{\text{i}}+1)}{w_I}$$

$$\times \left(\sum_{F_{1_{\text{f}}}', F_{1_{\text{i}}}', F_{1_{\text{f}}}'', F_{1_{\text{i}}}''} (-1)^{F_{1_{\text{i}}}' + F_{1_{\text{f}}}' + F_{1_{\text{f}}}'' + F_{1_{\text{f}}}''} \right.$$

$$\times a_{F_{1_{\text{f}}}'}^{v_f N_f F_f(\pm)_f *} a_{F_{1_{\text{i}}}'}^{v_i N_i F_i(\pm)_i} a_{F_{1_{\text{f}}}''}^{v_f N_f F_f(\pm)_f} a_{F_{1_{\text{i}}}''}^{v_i N_i F_i(\pm)_i *}$$

$$\times \sqrt{(2F_{1_{\text{f}}}'+1)(2F_{1_{\text{i}}}'+1)(2F_{1_{\text{f}}}''+1)(2F_{1_{\text{i}}}''+1)}$$

$$\times \begin{Bmatrix} F_{1_{\text{i}}}' & F_{\text{i}} & I_2 \\ F_{\text{f}} & F_{1_{\text{f}}}' & n \end{Bmatrix} \begin{Bmatrix} N_{\text{i}} & F_{1_{\text{i}}}' & I_1 \\ F_{1_{\text{f}}}' & N_{\text{f}} & n \end{Bmatrix}$$

$$\times \left. \begin{Bmatrix} F_{1_{\text{i}}}'' & F_{\text{i}} & I_2 \\ F_{\text{f}} & F_{1_{\text{f}}}'' & n \end{Bmatrix} \begin{Bmatrix} N_{\text{i}} & F_{1_{\text{i}}}'' & I_1 \\ F_{1_{\text{f}}}'' & N_{\text{f}} & n \end{Bmatrix} \right). \quad \text{(B8)}$$

Note that the first phase factor is reduced to 1, since N_{f} and n are always integers, and

(1) if the two nuclear spins are integers (which is apparently not the case for any of the heteronuclear isotopologues of hydrogen), the total quantum number is also an integer, and the exponent is an even integer;

(2) if I_1 is a half-integer and I_2 is an integer, F_{i} is also a half-integer and as a result, the exponent is an even integer;

(3) if I_1 is an integer and I_2 is a half-integer (we chose this scheme for the case of HD [30,34] and DT [32,33]), then F_{i} is also a half-integer; the exponent is an even integer; and

(4) if both nuclear spins are half-integers (as in the case of HT [32,34]), the total quantum number, and the exponent is an even integer.

For class-1 transitions all four mixing coefficients equal one, and there is no need to sum over possible intermediate quantum numbers, since both the initial and final hyperfine states are well described by N, F_1, and F. Setting $F_{1_{\text{i}}}' = F_{1_{\text{i}}}'' = F_{1_{\text{i}}}$ and $F_{1_{\text{f}}}' = F_{1_{\text{f}}}'' = F_{1_{\text{f}}}$ we obtain Eq. (8):

$$\frac{S_{\text{fi}}^{n\text{HF}}}{S_{\text{fi}}^{n}} = \frac{(2F_{\text{f}}+1)(2F_{\text{i}}+1)(2F_{1_{\text{f}}}+1)(2F_{1_{\text{i}}}+1)}{(2I_1+1)(2I_2+1)}$$

$$\times \begin{Bmatrix} F_{1_{\text{i}}} & F_{\text{i}} & I_2 \\ F_{\text{f}} & F_{1_{\text{f}}} & n \end{Bmatrix}^2 \begin{Bmatrix} N_{\text{i}} & F_{1_{\text{i}}} & I_1 \\ F_{1_{\text{f}}} & N_{\text{f}} & n \end{Bmatrix}^2. \quad \text{(B9)}$$

Following the discussion for the *ortho*-D_2, we note that class-2 (or class-3) transitions do not depend on the initial (or final) vibrational quantum numbers since their initial (or final) states are well described by N, F_1, and F and the mixing coefficients simply equal 1. Finally, we note that Eq. (B8) is a generalization of Eqs. (14)–(51) in Ref. [52] to spectral transitions of rank n (the authors considered electric dipole transitions) and a different coupling scheme (the authors discussed the relative intensities in the coupling scheme suitable for homonuclear diatomics).

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