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Distortion dipole effect in symmetric molecules

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The theory of frame distortion in polyatomic molecules is reconsidered with the aid of a diagonal Herman-Wallis-type concept applied to nominally forbidden pure rotational transitions. Watson's formula for electric dipole forbidden transition moments is obtained using the formalism of extraneous quantum numbers [K. V. Kazakov, *Quantum Theory of Anharmonic Effects in Molecules* (Elsevier, Amsterdam, 2012)]. A similar consideration is permitted to derive the transition moments for magnetic dipole absorption in account of rovibrational interaction. The modified rotational selection rules and some numerical estimates are obtained by taking trial examples of highly symmetric molecules. The distortion electric dipole spectra of methane simulated for various temperatures are compared with the pertinent experimental data. Particular attention is given to trihydrium, for which rovibrational effects in both electric and magnetic dipole spectra are examined. It is shown that, first, the distortion magnetic moment of $H_3{}^+$ is generated solely by electronic motion if the g factor is diagonal, while the nuclear motion manifests itself through the off-diagonal inclusion of g, and, second, the smallness of this magnetic contribution to the line strength is quenched by the strong dependence on the rotational quantum number.

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I. INTRODUCTION

According to conventional theory for a symmetric top molecule, the electric dipole rovibrational transitions are possible obeying the selection rules $\Delta J = 0, \pm 1$ and $\Delta K = 0$, with no change in a nuclear spin and with the wave-function parity changing [1]. These selection rules have to be subject to modification, provided nonrigidity of a molecule is taken into consideration through an accompanying rovibrational interaction. Namely, the so-called distortion dipole effect has been described theoretically [2,3] and then observed in numerous experiments. Due to the effect of frame distortion, the nominally forbidden electric dipole transitions become weakly allowed. Fox [3] showed that the interaction of the methane infrared-active degenerate vibrations ν_3 and ν_4 with molecular rotation yields pure rotational spectra in the ground vibrational and electronic state. Watson [2] generalized substantially the relevant theory by use of the technique of effective operators and predicted the structure of pure rotational spectra for different classes of molecules.

A frame-distortion effect has direct astrophysical applications. It is known that one of the most abundant molecules in the universe, $H_3{}^+$, does not possess a permanent dipole [4]. Due to rovibrational interaction the D_{3h} symmetry of this molecule is lifted, which makes possible the formation of a small dipole moment giving rise to pure rotational transitions, which would otherwise be forbidden. In laboratory-controlled conditions a spontaneous emission is negligible, whereas in the interstellar environment the role of $H_3{}^+$ is important. Laboratory study of the dipole-permitted ν_2 fundamental band [5] stimulated the search for rovibrational transitions of this band in dense interstellar clouds. Eventually, trihydrium was discovered in molecular clouds GL2136 and W33A [6]. Spontaneous emission of $H_3{}^+$, which was detected in the Jupiter ionosphere [7], allowed to identify, in particular, the magnetic equator of Jupiter [8]. The study of $H_3{}^+$ is important for extrasolar atmospheres [9], because this molecule might serve as an effective cooler.

Much less attention is paid to magnetic dipole transitions in comparison to electric dipole transitions. The cooperative motion of electrons and nuclei in a molecule gives birth to slight magnetic moment, which manifests itself in the line shift caused by the Zeeman effect [10–15].

Considering a rotational magnetic moment in the body-fixed frame of reference, we have [13,16]

$$\mathbf{m}_{\mathrm{rot}} = \frac{\mathrm{m_n}}{\hbar}(g_{xx}J_x,\ g_{yy}J_y,\ g_{zz}J_z), \tag{1}$$

in which $\mathrm{m_n} = e\hbar/2m_{\mathrm{p}}c$ denotes the nuclear magneton with m_{p} being the proton mass; the total angular momentum vector $\mathbf{J}$ has Cartesian projections J_x, J_y, and J_z. A nuclear frame is constructed on the principal axes of inertia that are fixed with a molecule. For nonzero components of the rotational tensor $g_{\alpha\alpha} = g^{(\mathrm{n})}_{\alpha\alpha} + g^{(\mathrm{e})}_{\alpha\alpha}$, in which $\alpha = x$, y, or z, it was shown in [12,13,15] that the nuclear contribution is defined as

$$g^{(\mathrm{n})}_{\alpha\alpha} = \frac{m_{\mathrm{p}}}{I^{\alpha\alpha}} \sum_k Z_k\left(r_k^2 - r_{\alpha k}^2\right) \tag{2}$$

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and the electronic contribution is

$$g_{\alpha\alpha}^{(e)} = -\frac{2m_p}{m_e I^{\alpha\alpha}} \sum_{A\neq 0} \frac{|\langle \chi_A | L_\alpha | \chi_0 \rangle|^2}{E_A - E_0}. \tag{3}$$

Here, m_e is the mass of an electron, $I^{\alpha\alpha}$ is the molecular tensor of inertia, and the vector $\mathbf{r}_k = (r_{xk}, r_{yk}, r_{zk})$ is the radius vector for nucleus k; E_A and χ_A represent, respectively, the energy and wave function of unperturbed electronic state A with A equaling zero for the ground state [16]. The nuclear contribution to the gyromagnetic ratio $g_{\alpha\alpha}^{(n)}$ is determined by the number of protons, Z_k, in nuclei and their masses M_k. Typically, $g_{\alpha\alpha}^{(n)} \approx Z_k m_p / M_k$ has an order of magnitude of ~ 0.5. The electronic part is caused by the interaction of total angular momentum $\mathbf{J}$ with electronic angular momentum $\mathbf{L} = (L_x, L_y, L_z)$ [12,16].

Vibrational magnetism arises when excited degenerate vibrations give rise to additional magnetic moment. In contrast to pure rotational magnetism, vibrational magnetism has met relatively small attention in the literature [14,16–19]. For $H_3{}^+$, for instance, both rotational and vibrational contributions to the electronic g factor are small irrespective of possible isomeric structure, D_{3h} or C_{2v}. Provided the nuclear spins are laboratory quantized, rotational magnetism is largely defined by the nuclear g factor (2), which equals $+1$ in this case. The electron and nuclear spins of trihydrium should all be omitted. The former is omitted through the fact that we treat a closed-shell system. The latter is dropped due to the smallness of the interaction between the nuclear spin of the molecule and its orbital motion compared to the differences of rotational energies.

An interesting phenomenon was reported recently [20] while interpreting the spectra taken in the Martian atmosphere on board the ExoMars space vehicle. The series of CO_2 rovibrational transitions obeying $\Delta J = 0, \pm 1$ selection rules was assigned to magnetic dipole transitions in the region of the $\nu_2 + \nu_3$ combination band. This preliminary assignment was confirmed then by observations in laboratory-controlled conditions [21,22]. In contrast to analysis of the g factor appropriate to a pure rotational spectrum, the theory of the rovibrational g factor has to accurately use nonadiabatic effects [16] while calculating the electronic contribution to the magnetic transition moment. Moreover, vibrational magnetism, being a function of nuclei velocities, is obviously determined by joint contributions from the angular momentum of a nonvibrating molecule as well as from the momenta arising in the course of molecular vibrations [23]. A vibrational contribution to the overall magnetic moment in the body-fixed system can be thus represented as

$$\mathbf{m}_{\text{vib}} = (\text{m}_x, \text{m}_y, \text{m}_z) \tag{4}$$

with

$$\text{m}_\gamma = \sum_s \frac{\partial \text{m}_\gamma}{\partial p_s} p_s + \sum_{rs} \frac{\partial^2 \text{m}_\gamma}{\partial q_r \partial p_s} q_r p_s + \cdots, \tag{5}$$

in which the derivatives of m_γ with respect to normal vibrational coordinate q_j and momentum p_s of mode s are obtainable from the concept of atomic tensors [24–27], according to which

$$\text{m}_\gamma = \sum_{\beta k s} \frac{\partial \text{m}_\gamma}{\partial P_{\beta k}} \frac{\partial P_{\beta k}}{\partial p_s} p_s, \tag{6}$$

where $P_{\beta k}$ is the momentum of nucleus k in the Cartesian β direction. The concept of atomic tensors turned out fruitful while interpreting the phenomenon of a circular dichroism in chiral molecules [24–26,28]. Interestingly, generating effects that relate to the body-fixed frame of reference, the pure vibrational magnetic transitions manifest themselves even in harmonic approximation [23,27].

In what follows, we concentrate first on showing how the frame-distortion effect in electric dipole spectra of polyatomic molecules can be considered in the framework of a diagonal Herman-Wallis-type concept. The utility of using the theorem of extraneous quantum numbers [29–32] is demonstrated to calculate, particularly, the distortion electric dipole moment and reproduce the relevant spectra for methane. We focus further on how the rovibrational coupling affects the magnetic dipole moment. The alteration in intensities of magnetic dipole transitions is theoretically described using the theorem [29]. We show that the deformation of the skeleton and distortion of the electronic cloud in trihydrium induce the currents producing the distortion magnetic dipole.

II. BRIEF OUTLOOK OF THE THEORY

To demonstrate the use of our approach in solution of some quantum-mechanical problems relevant to the coupling among vibrational and rotational degrees of freedom in molecules, we assume that the eigenenergies E_{nJ} and eigenstates $|nJ)$ can be found as a solution of the Schrödinger equation,

$$(H_{\text{vib}} + H_{\text{rot}} + \rho u)|nJ) = E_{nJ}|nJ). \tag{7}$$

The theorem of extraneous quantum numbers derived in [29,31,32] can be applied to obtain the vibration-rotational matrix elements of a pertinent transition function f, which is independent of u, through a shift operation:

$$(nJ|f|n'J') = \exp\left(u\frac{\partial}{\partial u}\right)(nJ|f|n'J')|_{u=0} \tag{8}$$

with

$$\frac{\partial}{\partial u}|nJ) = \sum_{m\neq n} \frac{(nJ|\rho|mJ)}{E_{nJ} - E_{mJ}}|mJ). \tag{9}$$

Provided an operator is meant under u and an extraneous quantum number is J, the shift operation with respect to u has to be understood as follows:

$$\exp\left(u\frac{\partial}{\partial u}\right)(nJ|f|n'J')|_{u=0} = \left[\exp\left(u\frac{\partial}{\partial u}\right)(nJ|\right]_{u=0} f \left[\exp\left(u\frac{\partial}{\partial u}\right)|n'J')\right]_{u=0},$$

in which

$$\exp\left(u\frac{\partial}{\partial u}\right)|nJ)|_{u=0} = |nJ)|_{u=0} + u\frac{\partial}{\partial u}|nJ)|_{u=0} + \cdots. \tag{10}$$

Here, a pure vibrational Hamiltonian H_{vib} gives rise to a pure vibrational energy spectrum E_n and accompanying set of vibrational quantum numbers n, and ρ is some function of normal dimensionless coordinates q_s, which are associated with harmonic vibrational frequencies ω_s. The function ρ is assumed to describe the interaction between vibrational and rotational motions. The rotational impact is described by a function u of an extraneous parameter, which can be thought of to be either rotational quantum number J or even body-fixed component J_α of the total angular momentum; $\alpha = x, y$, or z. For both rovibrational state

$$\Psi(nJ) = |nJ\rangle$$

and pure vibrational state

$$\Psi^{\mathrm{vib}}(n) = |n\rangle,$$

an exact perturbed vector is designated with a parenthesis, whereas traditional Dirac notation is applicable for an unperturbed vector. For instance, the harmonic state vector reads as $|n_1, n_2, \ldots, n_s, \ldots\rangle$. All matrix elements and other vectors we also supply with angular brackets. For a pure rotational problem with Hamiltonian H_{rot}, as wave vector $|J, K, M\rangle$, in which K and M represent quantum numbers specifying the projections of the angular momentum vector along the body-fixed and laboratory-fixed frames of reference, we employ a complex conjugate Wigner function [33]

$$\Psi^{\mathrm{rot}}(J, K, M) = \sqrt{\frac{2J+1}{8\pi^2}}D^{(J)*}_{M,K}(\phi, \theta, \chi) \tag{11}$$

with Euler angles ϕ, θ, and χ.

The most popular algorithm to consider vibrational and rotational motion conjointly was suggested by Herman and Wallis [34]. Considering a line strength of a diatomic molecule, they have introduced a vibration-rotational factor into an expansion of the matrix element of a dipole μ in powers of

$$\Delta u = u' - u = \tfrac{1}{2}(J'(J'+1) - J(J+1)).$$

Theoretically, this factor can be found from (8):

$$\begin{aligned}(nJ|\mu|n'J') &= (nJ|\mu\exp\left(\Delta u\frac{\partial}{\partial u}\right)|n'J)\\ &= (n|\mu|n')\left(1 + c_{nn'}\Delta u + d_{nn'}\frac{\Delta u^2}{2} + \cdots\right),\end{aligned}$$

in which the factor coefficients [29–32]

$$c_{nn'} = \frac{1}{(n|\mu|n')}\sum_{m\neq n'}(n|\mu|m)\frac{(m|\rho|n')}{E_{n'} - E_m}, \tag{12}$$

$d_{nn'}, \ldots$ are expressible according to (9), where $\rho = \hbar^2 I^{-1}$ and I is the inertia moment. In a number of papers [35–41], the theory of the Herman-Wallis factor was extended to polyatomic molecules. In [40], theorem (8) was used to obtain the contribution to the Herman-Wallis factor from Coriolis coupling that required consideration of an angular momentum as an extraneous parameter. It is important to note that using theorem (8) allows one to apply in (9) simultaneously either *ab initio* data, or their equilibrium and harmonic analogs, or even experimental values [31].

III. FRAME-DISTORTION EFFECT ACCORDING TO CONCEPT OF EXTRANEOUS PARAMETERS

Let us consider how theorem (8) can be used to characterize the effect of frame distortion on the line intensities. In this case, the role of the extraneous parameter u is performed formally by an operator. According to [2,3], the Schrödinger equation accounting for the frame-distortion effect can be represented in the form

$$\left(H + \frac{1}{2}\sum_{\alpha\beta}\rho_{\alpha\beta}J_\alpha J_\beta\right)\Psi_{\mathrm{fd}}(nJ) = E_{nJ}\Psi_{\mathrm{fd}}(nJ), \tag{13}$$

in which $H = H_{\mathrm{vib}} + H_{\mathrm{rot}}$,

$$\begin{aligned}\rho_{\alpha\beta} &= -\sum_s\sqrt{\frac{\hbar}{\omega_s}}q_s\rho^e_{\alpha\alpha}a_s^{\alpha\beta}\rho^e_{\beta\beta}\\ &= -\sum_s\frac{4B_\alpha B_\beta a_s^{\alpha\beta}q_s}{\hbar^4}\sqrt{\frac{\hbar}{\omega_s}}\end{aligned} \tag{14}$$

is the second term of an expansion of the reciprocal tensor of inertia tensor $I^{\alpha\beta}$ with respect to the normal coordinates [42]

$$(I^{-1})_{\alpha\beta} = (I_e^{-1})_{\alpha\beta} + \rho_{\alpha\beta} + \cdots, \tag{15}$$

I_e is the equilibrium moment of inertia, $a_s^{\alpha\beta}$ are the derivatives of inertia moment (see Appendix A), Ψ_{fd} and E_{nJ} are the wave function and eigenenergy, respectively, and

$$B_\alpha = \frac{\hbar^2}{2I_e^{\alpha\alpha}}. \tag{16}$$

The Hamiltonian in (13) is parametrized with the angular momentum components. Formula (10) enables to express the wave function in this case as

$$\Psi_{\mathrm{fd}}(nJ) = |nJ\rangle + \sum_{\alpha\beta}J_\alpha J_\beta|nJ, 1\rangle + \cdots.$$

The theorem is focused here on the product of operators but not on the quantum numbers. Applying formula (9) to the product of operators $J_\alpha J_\beta$, one must substitute u by $J_\alpha J_\beta$ and ρ by $\frac{1}{2}\rho_{\alpha\beta}$. As a result,

$$\begin{aligned}|nJ, 1\rangle = \left.\frac{\partial\Psi_{\mathrm{fd}}(nJ)}{\partial(J_\alpha J_\beta)}\right|_{J_\alpha J_\beta = 0} &= \frac{1}{2}\sum_{m\neq n}\frac{\langle m|\rho_{\alpha\beta}|n\rangle}{E_n - E_m}|mJ\rangle\\ &= \Psi^{\mathrm{rot}}(J, K, M)|n, 1\rangle,\end{aligned} \tag{17}$$

in which Ψ^{rot} is the wave function of a rigid rotor (11) and

$$\begin{aligned}&|n, 1\rangle\\ &= \sum_s\frac{B_s^{\alpha\beta}}{\hbar\omega_s}(\sqrt{n_s+1}|n_1, \ldots, n_s+1, n_{s+1}, \ldots\rangle\\ &\quad - \sqrt{n_s}|n_1, \ldots, n_s-1, n_{s+1}, \ldots\rangle)\end{aligned} \tag{18}$$

with

$$B_s^{\alpha\beta} = \frac{2B_\alpha B_\beta a_s^{\alpha\beta}}{\hbar^4}\sqrt{\frac{\hbar}{2\omega_s}}. \tag{19}$$

Function (18) can be derived, for instance, in terms of the polynomials of quantum numbers [31,32,43]. In the first order, we hence have

$$\Psi_{\mathrm{fd}}(nJ) = |nJ\rangle + \sum_{\alpha\beta} J_\alpha J_\beta |nJ, 1\rangle. \tag{20}$$

The line intensity of an electric dipole rovibrational transition is defined by the square of the matrix element of a laboratory-fixed component of the dipole moment, for instance, the Z component μ^{LF},

$$\mu^{\mathrm{LF}} = \Phi_x\mu_x + \Phi_y\mu_y + \Phi_z\mu_z, \tag{21}$$

in which Φ_γ is the direction cosine between the laboratory-fixed Z axis and body-fixed γ axis;

$$\mu_\gamma = \mu_\gamma^e + \sum_s \frac{\partial\mu_\gamma}{\partial q_s} q_s + \cdots \tag{22}$$

is the body-fixed γ component of the actual dipole moment with permanent dipole moment μ_γ^e and $\gamma = x, y$, or z. The sought matrix element is

$$\begin{aligned}\langle\Psi_{\mathrm{fd}}(nJ)|\mu^{\mathrm{LF}}|\Psi_{\mathrm{fd}}(n'J')\rangle &= \langle nJ|\mu^{\mathrm{LF}}|n'J'\rangle \\ &\quad + \left\langle\Psi_i^{\mathrm{rot}}\middle|\mathrm{w}_{\mathrm{el}}\middle|\Psi_f^{\mathrm{rot}}\right\rangle + \cdots,\end{aligned} \tag{23}$$

in which the matrix element

$$\langle nJ|\mu^{\mathrm{LF}}|n'J'\rangle = \left\langle\Psi_i^{\mathrm{rot}}\middle|\langle n|\mu^{\mathrm{LF}}|n'\rangle\middle|\Psi_f^{\mathrm{rot}}\right\rangle \tag{24}$$

describes the transition in assumption of the zero rovibrational interaction,

$$\begin{aligned}\mathrm{w}_{\mathrm{el}} &= \sum_{\alpha\beta\gamma} J_\alpha J_\beta \Phi_\gamma \langle n, 1|\mu_\gamma|n'\rangle \\ &\quad + \sum_{\alpha\beta\gamma} \Phi_\gamma J_\alpha J_\beta \langle n|\mu_\gamma|n', 1\rangle,\end{aligned} \tag{25}$$

$$\Psi_i^{\mathrm{rot}} = \Psi^{\mathrm{rot}}(J, K, M) \text{ and } \Psi_f^{\mathrm{rot}} = \Psi^{\mathrm{rot}}(J', K', M').$$

Assuming all the vibrational quantum numbers n_s do not change in the course of a transition, with the aid of (18), we find

$$\langle n, 1|\mu_\gamma|n\rangle = \langle n|\mu_\gamma|n, 1\rangle = \sum_s \frac{\partial\mu_\gamma}{\partial Q_s}\frac{B_\alpha B_\beta}{\hbar^2(\hbar\omega_s)^2} a_s^{\alpha\beta}, \tag{26}$$

hence [2]

$$\langle n|\mu^{\mathrm{LF}}|n\rangle = \sum_\gamma \mu_\gamma^e \Phi_\gamma$$

and

$$\mathrm{w}_{\mathrm{el}} = \frac{1}{2}\sum_\gamma (\mathbb{M}_\gamma\Phi_\gamma + \Phi_\gamma\mathbb{M}_\gamma), \tag{27}$$

in which, restricting to the first order in vibration-rotational coupling,

$$\mathbb{M}_\gamma = \frac{1}{\hbar^2}\sum_{\alpha\beta} \Theta_\gamma^{\alpha\beta} J_\alpha J_\beta \tag{28}$$

and

$$\Theta_\gamma^{\alpha\beta} = 2\sum_s \frac{\partial\mu_\gamma}{\partial Q_s}\frac{B_\alpha B_\beta}{(\hbar\omega_s)^2} a_s^{\alpha\beta} \tag{29}$$

with

$$\frac{\partial\mu_\gamma}{\partial Q_s} = \sqrt{\frac{\omega_s}{\hbar}}\frac{\partial\mu_\gamma}{\partial q_s}.$$

Under a frame distortion, a polyatomic molecule acquires additional electric dipole moment that is expressible by Watson's formula (27). Representing a diagonal Herman-Wallis result, this moment stems from the direct application of theorem (8) to the frame-distortion Hamiltonian, in which the combination $J_\alpha J_\beta$ of angular projections has to be understood under u. To arrive at the rotational selection rules for a molecule of a given symmetry, one must simply define Watson's coefficients $\Theta_\gamma^{\alpha\beta}$ [Eq. (29)] and calculate matrix elements $\langle\Psi_i^{\mathrm{rot}}|\mathrm{w}_{\mathrm{el}}|\Psi_f^{\mathrm{rot}}\rangle$.

The application of theorem (8) allows one to expand the possible use of Watson's formula. As in (9) there arise exact energies and matrix elements, one might strengthen $|nJ, 1\rangle$ [Eq. (17)] by assigning the *ab initio* or experimental values to $\langle m|\rho_{\alpha\beta}|n\rangle$, E_n, and E_m. As a result, we proceed to operate with the transition frequencies and vibrational matrix elements of the reciprocal inertia moment as well as with the dipole-moment matrix elements; the latter appear instead of the dipole derivatives. The theorem [31] enables to control the accuracy of calculation, making Watson's formula more flexible.

A. Tetrahedral molecules

Let us calculate the line intensities of branch R for a molecule like methane. One should find the following sum:

$$S_{J,K}^{J+1,K'} = 3\sum_{M'M} |\langle J+1, K', M'|\mathrm{w}_{\mathrm{el}}|J, K, M\rangle|^2. \tag{30}$$

The result from a permanent dipole moment with components μ_γ^e fails to yield the frame-distortion effect because a molecule of type T_d has no such dipole. The distortion or simply diagonal Herman-Wallis inclusion owes entirely to quantities $\mathbb{M}_\gamma$ for which we have only one independent coupling coefficient,

$$\Theta = \Theta_x^{yz} = \Theta_y^{xz} = \Theta_z^{xy}.$$

To calculate the matrix element entering (30) we proceed to spherical tensor operators $\mathbb{M}_\Omega$, in which $\Omega = 0, \pm 1$, according to the relations

$$\mathbb{M}_0 = \mathbb{M}_z$$

and

$$\mathbb{M}_{\pm 1} = \frac{1}{\sqrt{2}}(\mp\mathbb{M}_x - i\mathbb{M}_y).$$

Hence [44],

$$\begin{aligned}\mathrm{w}_{\mathrm{el}} = \tfrac{1}{2}(&\mathbb{M}_0\Phi_{0,0} + \mathbb{M}_{-1}\Phi_{0,-1} + \mathbb{M}_{+1}\Phi_{0,+1} + \Phi_{0,0}\mathbb{M}_0 \\ &+ \Phi_{0,-1}\mathbb{M}_{-1} + \Phi_{0,+1}\mathbb{M}_{+1}),\end{aligned} \tag{31}$$

in which

$$\Phi_{0,0} = \Phi_z = D_{0,0}^{(1)*}$$

and

$$\Phi_{0,\pm 1} = \frac{1}{\sqrt{2}}(\mp\Phi_x + i\Phi_y) = D_{0,\pm 1}^{(1)*}.$$

Using (28), we rewrite components $\mathbb{M}_\Omega$ as

$$\mathbb{M}_0 = i\Theta(J_+^2 - J_-^2)$$

and

$$\mathbb{M}_{\pm1} = -i\Theta(J_\pm J_0 + J_0 J_\pm)$$

with $J_0 = J_z\hbar^{-1}$ and

$$J_\pm = \frac{1}{\sqrt{2}\hbar}(J_x \mp iJ_y).$$

As we focus on the transition $J \to J+1$, we must involve only the following matrix elements [44]:

$$\langle J, K, M|J_0|J, K, M\rangle = K,$$

$$\langle J, K \pm 1, M|J_\pm|J, K, M\rangle = \sqrt{\frac{(J \mp K)(J \pm K + 1)}{2}}, \tag{32}$$

$$\langle J+1, K, M|\Phi_{0,0}|J, K, M\rangle = \Pi_M^J \sqrt{(J + K + 1)(J - K + 1)} \tag{33}$$

and

$$\begin{aligned}&\langle J+1, K \pm 1, M|\Phi_{0,\pm1}|J, K, M\rangle\\ &\quad = \Pi_M^J \sqrt{\frac{(J \pm K + 1)(J \pm K + 2)}{2}},\end{aligned} \tag{34}$$

in which

$$\Pi_M^J = \frac{1}{J+1}\sqrt{\frac{(J + M + 1)(J - M + 1)}{(2J+1)(2J+3)}}.$$

Introducing the anticommutator $\{\ldots, \ldots\}$, we calculate the nonvanishing matrix elements:

$$\langle J+1, K \pm 2, M|\{\Phi_{0,0}, J_\pm^2\}|J, K, M\rangle = (J \mp K)\Pi_M^J\sqrt{\Lambda_\pm^{JK}} \tag{35}$$

and

$$\begin{aligned}&\langle J+1, K \pm 2, M|\{\Phi_{0,\pm1}, (J_\pm J_0 + J_0 J_\pm)\}|J, K, M\rangle\\ &\quad = 2(K \pm 1)\Pi_M^J\sqrt{\Lambda_\pm^{JK}}\end{aligned} \tag{36}$$

with

$$\Lambda_\pm^{JK} = (J \pm K + 1)(J \pm K + 2)(J \pm K + 3)(J \mp K). \tag{37}$$

For w_{el} [Eq. (31)], we thus have

$$\begin{aligned}&\langle J+1, K \pm 2, M|\mathrm{w}_{\mathrm{el}}|J, K, M\rangle\\ &\quad = \pm\frac{i}{2}\Theta(J - 2 \mp 3K)\Pi_M^J\sqrt{\Lambda_\pm^{JK}}.\end{aligned} \tag{38}$$

Taking into account that

$$\sum_{MM'}\left(\Pi_M^J\right)^2\delta_{MM'} = \frac{1}{3(J+1)}, \tag{39}$$

we find eventually

$$S_{J,K}^{J+1,K\pm2} = \frac{(J - 2 \mp 3K)^2}{4(J+1)}\Theta^2\Lambda_\pm^{JK}. \tag{40}$$

Quantities (40) determine the line strengths of pure rotational transitions $\Delta J = +1$ from the vibronic ground state for the molecules with tetrahedral symmetry. The expressions for transitions $\Delta J = 0$ or $\Delta J = -1$ can be obtained in an analogous manner [2]. Neglecting the nuclear-spin statistical weight, one might calculate the total line strength S_J^{J+1} for the branch R by summation (30) over K and K' with (40) properly taken into account:

$$\begin{aligned}S_J^{J+1} &= \sum_{K'K} S_{J,K}^{J+1,K'}\\ &= \frac{\Theta^2}{4(J+1)}\sum_{K=-J}^{J}((J - 2 - 3K)^2\Lambda_+^{JK}\\ &\quad + (J - 2 + 3K)^2\Lambda_-^{JK}) = \frac{2}{35}\Theta^2\mathrm{j}(J),\end{aligned} \tag{41}$$

in which

$$\mathrm{j}(J) = J(J+2)(2J-1)(2J+1)(2J+3)(2J+5). \tag{42}$$

This result is identical to that reported previously by Watson [2].

Among other molecules, the symmetry of which belongs to point group T_d, methane is of special interest. In what follows, we calculate the distortion dipolar moment of $^{12}\mathrm{CH}_4$ from first principles. The sought dipole is defined according to (29) by only one component Θ_z^{xy}, which we denote as Θ. Such a definition differs from that adopted by Fox [3], the explicit form C_{34} of which relates to Θ:

$$\Theta = -2\sqrt{5}C_{34}.$$

Having applied the sum rule that is derived in Appendix A, we obtain $(a_3^{xy})^2 + (a_4^{xy})^2 = I_e^{zz}$. Coriolis coupling parameters ζ_{23} and ζ_{24} have to satisfy the normalization condition $\zeta_{23}^2 + \zeta_{24}^2 = 1$. Keeping this in mind, one can put [45] $a_3^{xy} = \sqrt{I_e^{zz}}\zeta_{23}$ and $a_4^{xy} = \sqrt{I_e^{zz}}\zeta_{24}$. According to (16) and (29), we arrive eventually at

$$\Theta = \frac{1}{2}\frac{\partial\mu_z}{\partial q_3}\left(\frac{2B_0}{\nu_3}\right)^{\frac{3}{2}}\zeta_{23} + \frac{1}{2}\frac{\partial\mu_z}{\partial q_4}\left(\frac{2B_0}{\nu_4}\right)^{\frac{3}{2}}\zeta_{24}. \tag{43}$$

We can substitute here the rotational constant $B_0 = 5.241046\,\mathrm{cm}^{-1}$ [46] in the ground vibrational state as well as the observed band origin wave numbers $\nu_3 = 3019.2\,\mathrm{cm}^{-1}$ and $\nu_4 = 1310.8\,\mathrm{cm}^{-1}$ [47] for the fundamentals instead of, respectively, the relevant equilibrium and harmonic values. This is justified because we rely on theorem (8), in which the denominators contain exact vibrational energies and the numerators comprise exact matrix elements. In other words, it is justified to use simultaneously either all the observed values or their equilibrium and harmonic analogs. In both cases, the yielded results have to be almost the same. For the derivatives of dipole moment, we adopt their up-to-date values $\partial\mu_z/\partial q_3 = -0.075$ D and $\partial\mu_z/\partial q_4 = 0.076$ D [48]. The pertinent Coriolis parameters are $\zeta_{23} = -0.797$ and $\zeta_{24} = 0.603$ [47]. As a result,

$$\Theta = 2.3 \times 10^{-5}\ \mathrm{D}. \tag{44}$$

This value is in agreement with theoretical estimates 2.6×10^{-5} D [2], 1.8×10^{-5} D [3], and 2.2×10^{-5} D [49]. Ozier

TABLE I. Spectral line positions ΔE_J and their intensities α_{abs} for nominally forbidden rotational transitions of methane from the ground vibronic state at temperature 296 K and density 1.2 amagat.

$J \rightarrow J+1$	ΔE_J (cm^{-1})	α_{abs} (cm^{-2})
9 → 10	104.38	4.47×10^{-5}
10 → 11	114.71	5.66×10^{-5}
11 → 12	125.02	6.36×10^{-5}
12 → 13	135.30	6.43×10^{-5}
13 → 14	145.53	5.92×10^{-5}
14 → 15	155.73	4.95×10^{-5}
15 → 16	165.90	3.81×10^{-5}
16 → 17	176.01	2.73×10^{-5}

confirmed experimentally this value twice: first, in [50] by measuring the Stark shifts using the molecular beam technique, and second, in [51] from the observation of pure rotational methane transitions caused by the ground-state electric dipole moment. Our obtained value (44) is in perfect agreement with the latest experimental data reported in [52], according to which the distortion dipole Θ is equal to 2.4×10^{-5} D.

To demonstrate the efficiency of our theory, we calculate the absolute intensities of absorption,

$$\alpha_{\text{abs}} = \frac{8\pi^3 N_{\text{L}} \eta}{3Zhc} \Delta E_J S_J^{J+1} \left(e^{-\frac{hcE_J}{k_{\text{B}}T}} - e^{-\frac{hcE_{J+1}}{k_{\text{B}}T}} \right). \tag{45}$$

Here, N_{L} is the Loschmidt constant, h is the Planck constant, c is the speed of light in vacuum, k_{B} is the Boltzmann constant, η is the density in amagat, T is the temperature, and Z is a partition function. The latter can be found applying the formula [3]

$$Z = \frac{4}{3}\sqrt{\pi} \left(\frac{k_{\text{B}}T}{B_0 hc} \right)^{\frac{3}{2}} e^{\frac{B_0 hc}{4k_{\text{B}}T}}. \tag{46}$$

The line strength S_J^{J+1} in (45) is given by (41), and the transition energy is

$$\Delta E_J = E_{J+1} - E_J, \tag{47}$$

where $E_J = B_0 J(J+1) - D_0 J^2 (J+1)^2$ is the rotational energy in cm^{-1}; for ^{12}CH$_4$, $D_0 = 1.11 \times 10^{-4}$ cm^{-1} [46]. Let us first consider an example of the spectrum borrowed from [51]. This spectrum has been recorded at room temperature and density $\eta = 1.2$ amagat with an optical path of $\text{L} = 139 \times 10^2$ cm. Eight absorption lines recorded in the spectral range from 100 to 180 cm^{-1} were assigned to the nominally forbidden rotational transitions from $R(9)$ to $R(16)$. Applying (44), we have calculated the transition frequencies (47) and intensities (45) at $T = 296$ K (see Table I).

Figure 1 shows satisfactory agreement of our calculated methane spectrum (red curve) with that measured in [51] (black dots). Note that the original spectrum from [51] is significantly contaminated by unidentified noise. The collision-induced continuous background, which is certainly present, is shown by a dashed line, as calculated here using the FORTRAN suite offered by Borysow [53].

The next example concerns a portion of the methane spectrum in the spectral range from 20 to 100 cm^{-1} at $T = 113.5$ K with $\eta = 2.61$ amagat and $\text{L} = 60 \times 10^2$ cm (see Fig. 2). The calculated line frequencies and intensities are shown in Table II. Our simulated spectra in Figs. 1 and 2 are constructed assuming the Van Vleck–Weisskopf line shape with a manually adjusted width.

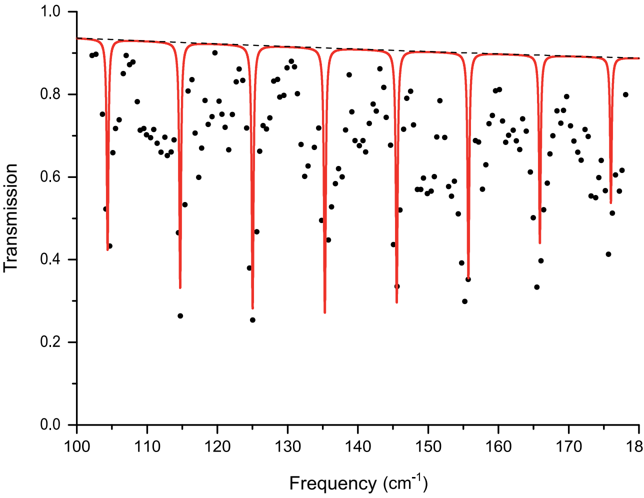

FIG. 1. Simulated pure rotational spectral lines of methane (red curve) obtained at temperature 296 K and density 1.2 amagat. Collision-induced background is indicated by dashed line; black dots show observed transmission [51].

B. D_{3h} and C_{3v} symmetric tops

The perturbation caused by a rotation-vibrational interaction in a direction perpendicular to the C_3 axis breaks down the symmetry of a molecule and gives rise to an electric dipole moment. Such a distortion leads to the principally new rotational selection rules [1,2]. In the case of a D_{3h} molecule, we have [54]

$$a_{ta}^{xx} = -a_{ta}^{yy} = -a_{tb}^{xy}$$

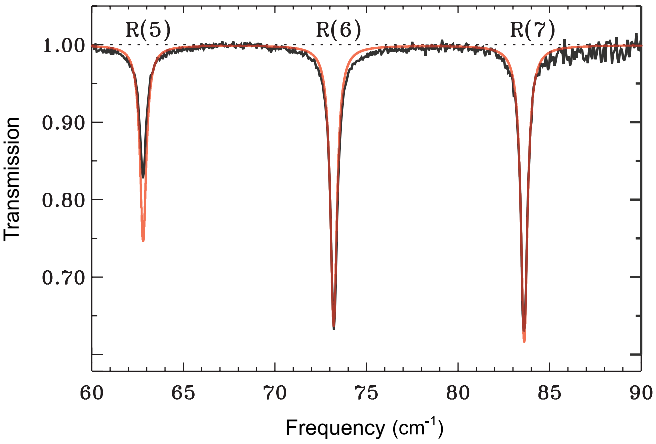

FIG. 2. Calculated distortion electric dipole rotational spectrum of methane (red curve) obtained at temperature 113.5 K and density 2.61 amagat. Observed transmission [52] is shown by the black curve.

TABLE II. Spectral line positions ΔE_J and their intensities α_{abs} for nominally forbidden rotational transitions of methane from the ground vibronic state at temperature 113.5 K and density 2.61 amagat.

$J \to J+1$	ΔE_J (cm^{-1})	α_{abs} (cm^{-2})
$3 \to 4$	41.90	0.25×10^{-5}
$4 \to 5$	52.35	0.92×10^{-5}
$5 \to 6$	62.80	1.98×10^{-5}
$6 \to 7$	73.22	2.99×10^{-5}
$7 \to 8$	83.63	3.22×10^{-5}
$8 \to 9$	94.02	2.83×10^{-5}

with a and b labeling the components of doubly degenerate vibration ν_t; the z axis is along the C_3 axis and the x axis lies in one of the σ_υ vertical planes. Consequently,

$$\theta = \Theta_x^{xx} = -\Theta_x^{yy} = -\Theta_y^{xy},$$

that is, $\mathbb{M}_0 = 0$,

$$\mathbb{M}_{\pm 1} = \frac{1}{\sqrt{2}}(\mp \mathbb{M}_x - i\mathbb{M}_y) = \mp\sqrt{2}\theta J_\pm^2$$

and

$$\begin{aligned} \mathrm{w}_{\text{el}} &= \frac{1}{2}\sum_\gamma (\mathbb{M}_\gamma \Phi_\gamma + \Phi_\gamma \mathbb{M}_\gamma) \\ &= \sqrt{2}\theta(\Phi_{0,-1}J_-^2 - \Phi_{0,+1}J_+^2), \end{aligned} \tag{48}$$

because of

$$\Phi_{0,\pm 1}J_\pm - J_\pm \Phi_{0,\pm 1} = 0. \tag{49}$$

The calculation of the pertinent matrix elements

$$\langle J', K', M'|\mathrm{w}_{\text{el}}|J, K, M\rangle$$

defining the line strength

$$S_{J,K}^{J',K'} = 3\sum_{M'M} |\langle J', K', M'|\mathrm{w}_{\text{el}}|J, K, M\rangle|^2 \tag{50}$$

is obvious. By use of (32), (34), and (39), for the R branch we obtain

$$\begin{aligned} S_{J,K}^{J+1,K\pm 3} &= \frac{\theta^2}{4(J+1)}(J \pm K + 1)(J \pm K + 2)(J \pm K + 3) \\ &\quad \times (J \pm K + 4)(J \mp K - 1)(J \mp K). \end{aligned} \tag{51}$$

As [44]

$$\begin{aligned} &\langle J, K \pm 1, M|\Phi_{0,\pm 1}|J, K, M\rangle \\ &\quad = \frac{\mp M}{J(J+1)}\sqrt{\frac{(J \mp K)(J \pm K + 1)}{2}} \end{aligned} \tag{52}$$

and

$$\begin{aligned} &\langle J - 1, K \pm 1, M|\Phi_{0,\pm 1}|J, K, M\rangle \\ &\quad = -\Pi_M^{J-1}\sqrt{\frac{(J \mp K)(J \mp K - 1)}{2}}, \end{aligned} \tag{53}$$

we readily find [2]

$$\begin{aligned} S_{J,K}^{J,K\pm 3} &= \frac{\theta^2(2J+1)}{4J(J+1)}(J \pm K + 1)(J \pm K + 2) \\ &\quad \times (J \pm K + 3)(J \mp K - 2)(J \mp K - 1)(J \mp K) \end{aligned} \tag{54}$$

and

$$\begin{aligned} S_{J,K}^{J-1,K\pm 3} &= \frac{\theta^2}{4J}(J \pm K + 1)(J \pm K + 2) \\ &\quad \times (J \mp K - 3)(J \mp K - 2)(J \mp K - 1)(J \mp K) \end{aligned} \tag{55}$$

for branches Q and P, respectively.

For a molecule of type $C_{3\upsilon}$, we have the rotational Hamiltonian

$$H_{\text{rot}}^{3\upsilon} = B_x \mathbf{J}^2 \hbar^{-2} + (B_z - B_x)J_0^2 + V$$

with the frame-distortion perturbation

$$V = \frac{\hbar^4 \tau}{\sqrt{2}}(\{J_0, J_-^3\} + \{J_0, J_+^3\}),$$

in which we retain only the term with the quartic centrifugal constant $\tau = \tau_{xxxz}$ (see Appendix B) because only this contribution is responsible for the frame-distortion effect [2]. Applying a convenient perturbation theory to V, one finds

$$\begin{aligned} |J, 1\rangle &= \frac{\hbar^4\tau}{\sqrt{2}}\sum_{K' \neq K}\frac{\langle J, K', M|V|J, K, M\rangle}{E_{JK} - E_{JK'}}|J, K', M\rangle \\ &= \frac{\hbar^4\tau}{3\sqrt{2}(B_x - B_z)}(J_+^3 - J_-^3)|J, K, M\rangle, \end{aligned} \tag{56}$$

in which

$$E_{JK} = B_x J(J+1) + (B_z - B_x)K^2.$$

One should calculate the matrix elements of the permanent dipole moment in the first order in τ with functions (56). As only the z component μ_z^e produces a nonzero result, we have to find the following matrix elements:

$$\langle J', K', M|[\Phi_{0,0}, J_\pm^3]|J, K, M\rangle. \tag{57}$$

Through the commutator relation

$$J_\pm \Phi_{0,0} - \Phi_{0,0}J_\pm = \Phi_{0,\pm 1}$$

and formulas (49), it is legitimate that

$$[\Phi_{0,0}, J_\pm^3] = -3\Phi_{0,\pm 1}J_\pm^2.$$

We hence arrive at the dipole moment (48) with new parameter θ', namely,

$$\theta' = \theta + \frac{\hbar^4 \tau \mu_z^e}{2(B_x - B_z)}. \tag{58}$$

We see that the result for Watson's parameter θ' is here exactly the same as in [2]. For ammonia, using (29) and (B2), formula (58) yields

$$\theta' = 2\sum_{t=3,4} a_t^{xx}\left(\frac{B_0}{\nu_t}\right)^2\left[\frac{\partial \mu_x}{\partial Q_t} - \frac{a_t^{xz}\mu_z^e}{I_e^{zz} - I_e^{xx}}\right], \tag{59}$$

in which t numbers degenerate vibrations; B_0 and ν_t are in cm^{-1}. Distortion dipole (59) permits an estimate [55]

$$\theta' = -1.247 \times 10^{-4}\ \mathrm{D},$$

in which $B_0 = 9.9443\,\mathrm{cm}^{-1}$, $\nu_3 = 3444\,\mathrm{cm}^{-1}$, $\nu_4 = 1627\,\mathrm{cm}^{-1}$, $I_e^{xx} = 1.6957$, and $I_e^{zz} = 2.7215$ in amu Å^2 [56]; $a_3^{xx} = -1.056$, $a_3^{xz} = -0.813$, $a_4^{xx} = 1.242$, and $a_4^{xz} = -0.691$ in amu$^{1/2}$ Å [57]; $\mu_z^e = -1.468$ D, and $\partial\mu_x/\partial Q_3 = 0.186$ and $\partial\mu_x/\partial Q_4 = -0.54$ in D/(amu Å^2)$^{1/2}$ [58,59]. The obtained dipole agrees very well with the value $|\theta'|$=(1.241±0.07)$\times$ 10^{-4} D measured by Ozier and Meerts [60]. The spectra of ammonia in an interstellar environment give clear evidence of the frame-distortion effect [1].

In the case of $H_3{}^+$, the second term in (58) drops out so that this equation transforms to

$$\theta' = \theta = 2\left(\frac{B_0}{\nu_2}\right)^{\frac{3}{2}} \frac{\partial \mu_x}{\partial q_2} = 1.08 \times 10^{-3}\ \mathrm{D}, \tag{60}$$

in which $\partial\mu_x/\partial q_2 = 0.238$ D [61], $B_0 = 43.568\,\mathrm{cm}^{-1}$, and $\nu_2 = 2521.56\,\mathrm{cm}^{-1}$ [5]. The obtained value for the electric-distortion dipole (60) is in good agreement with that reported previously in [1,62], although some elucidations are required according to [63,64]. Being an equilateral triangular formation, trihydrium has no permanent electric dipole and therefore has no allowed rotational spectrum. Nevertheless, the distortion of the molecular frame in the course of rotation gives rise to electric dipole generation, which causes pure rotational transitions. The intensities of these transitions increase substantially with rotational quantum number J. Poor convergence has to be emphasized, however, for the rotational energy expansion in a series against J. In addition, having large amplitudes of vibrations, $H_3{}^+$ fails to fit fully into a concept of a rigid-rotor-harmonic oscillator. Despite this obstacle, the application involving the model of normal coordinates proved to be fruitful [63]. The harmonic frequency of vibration ν_2 equaling 2814 cm^{-1} [61] exceeds significantly its value for the fundamental to yield $\theta = 9.2 \times 10^{-4}$ D; B_e is very close to B_0 [65]. The difference with (60) does not look enormous. It points out that, while using a perturbation approach [31] or a formalism of effective operators [2], one needs to monitor carefully the impact of anharmonicity. The estimation (60) makes possible to conclude that at least for astrophysical applications the effect of frame distortion in $H_3{}^+$ is more pronounced than, e.g., that in NH_3. In $H_3{}^+$, θ' and transition frequency ν are greater than those in ammonia by approximately an order of magnitude. Consequently, the Einstein coefficient of spontaneous emission,

$$A \sim |\Delta E_{JK}|^3 \theta'^2,$$

appears to be significantly greater [1]. As far as direct calculation of the $H_3{}^+$ frame-distortion spectrum and Einstein coefficients are concerned, they were considered in a number of researches, e.g., in [9], following the pioneering investigation by Pan and Oka [62]. Notwithstanding the observation of the $H_3{}^+$ fundamental band ν_2 in [5], the pure rotational transitions borrowing an intensity from the allowed band ν_2 have not yet been detected [1,9].

IV. NOMINALLY FORBIDDEN MAGNETIC TRANSITIONS

Many brilliant investigations have been focused in the past on the problem of molecular magnetism caused by pure vibration-rotational motion of a molecule [10–15, 17–19,24,25,66]. In most cases, it was assumed in these works that electronic shielding has to be taken into consideration along with the nuclear motion. This shielding is able to affect substantially the resulting magnetic moment in such a way that the electronic contribution begins to play a prominent role, correcting the apparent nuclear dominance. The problem of pure rotational magnetism has been considered by Eshbach and Strandberg in their work [12]. According to [12,13,16], the nuclear [Eq. (2)] and electronic [Eq. (3)] contributions to the g factor are in such a relation that they partly compensate each other.

Following the concept developed in [16] let us consider a general electronic-vibrational problem for a molecule obeying the Schrödinger equation,

$$(H^{\mathrm{e}} + T^{\mathrm{n}})\Psi = W\Psi, \tag{61}$$

in which H^{e} is the Hamiltonian of electrons parametrized with nuclear coordinates, W is an energy,

$$T^{\mathrm{n}} = \sum_{\beta k} \frac{P_{\beta k}^2}{2M_k} = \sum_{\beta k} \frac{(-i\hbar)^2}{2M_k} \frac{\partial^2}{\partial r_{\beta k}^2}$$

is the kinetic-energy operator for the nuclei with $r_{\beta k}$ and $P_{\beta k}$ being the Cartesian position and momentum of nucleus k, the greek subscripts relate to Cartesian directions x, y, and z; $k = 1, 2, \dots, N$. According to [16,17,24], to involve correctly the electronic shielding, one must overstep the Born-Oppenheimer approximation characterized by wave function χ_0 and energy $E_0(r)$. Assuming Ψ^{n} be the nuclear state vector and ζ_0 be the nonadiabatic correction, we can substitute the wave function to Eq. (61) in the form $\Psi = \Psi^{\mathrm{n}}(\chi_0 + \zeta_0)$. As a result, we have

$$(H^{\mathrm{e}} + T^{\mathrm{n}} - W)\Psi^{\mathrm{n}}\chi_0 + (H^{\mathrm{e}} + T^{\mathrm{n}} - W)\Psi^{\mathrm{n}}\zeta_0 = 0. \tag{62}$$

Neglecting the nonadiabatic effect for the pure vibrational problem, we have $H^{\mathrm{e}}\chi_0 = E_0(r)\chi_0$ and $(T^{\mathrm{n}} + E_0(r))\Psi^{\mathrm{n}} = W\Psi^{\mathrm{n}}$. Consequently, in the first order,

$$\sum_{\beta k} \frac{1}{M_k}(P_{\beta k}\Psi^{\mathrm{n}})(P_{\beta k}\chi_0) + (H^{\mathrm{e}} - E_0(r))\Psi^{\mathrm{n}}\zeta_0 = 0, \tag{63}$$

because

$$T^{\mathrm{n}}\Psi^{\mathrm{n}}\chi_0 = \sum_{\beta k} \frac{(-\hbar^2)}{M_k} \frac{\partial \Psi^{\mathrm{n}}}{\partial r_{\beta k}} \frac{\partial \chi_0}{\partial r_{\beta k}} + \cdots .$$

Representing the nonadiabatic correction ζ_0 as an expansion of adiabatic vectors χ_A, where A designates an excited electronic state and taking into account that $H^{\mathrm{e}}\chi_A = E_A(r)\chi_A$, we arrive at

$$\zeta_0\Psi^{\mathrm{n}} = -\sum_{\beta k} \frac{(P_{\beta k}\Psi^{\mathrm{n}})}{M_k} \sum_{A\neq 0} \frac{\langle\chi_A|P_{\beta k}|\chi_0\rangle}{E_A - E_0}\chi_A. \tag{64}$$

The electronic magnetic dipole can be written conventionally as

$$\mathbf{m}^{\mathrm{e}} = -\frac{e}{2m_{\mathrm{e}}c}(\langle\chi_0|\mathbf{L}|\chi_0\rangle + [\langle\chi_0|\mathbf{L}|\zeta_0\rangle + \text{c.c.}] + \cdots), \tag{65}$$

in which c.c. denotes a complex conjugate contribution. It is well known that only the imaginary part of function Ψ yields a nonvanishing result [16,17]. As χ_0 is real and ζ_0 is imaginary, then $\langle\chi_0|\mathbf{L}|\chi_0\rangle$ equals zero and

$$\mathrm{m}_\gamma^{\mathrm{e}} = \frac{e}{m_{\mathrm{e}}c}\sum_{\beta k}\sum_{A\neq 0}\frac{\langle\chi_0|L_\gamma|\chi_A\rangle\langle\chi_A|P_{\beta k}|\chi_0\rangle}{E_A - E_0}\frac{P_{\beta k}}{M_k}. \tag{66}$$

As the nuclear contribution is equal to

$$\mathrm{m}_\gamma^{\mathrm{n}} = \frac{e}{2c}\sum_{k\alpha\beta}\frac{Z_k}{M_k}e_{\gamma\alpha\beta}r_{\alpha k}P_{\beta k} \tag{67}$$

and the total magnetic moment comprising both contributions is $\mathbf{m}_{\mathrm{vib}} = \mathbf{m}^{\mathrm{n}} + \mathbf{m}^{\mathrm{e}}$, then [24,25]

$$\frac{\partial \mathrm{m}_\gamma}{\partial P_{\beta k}} = \frac{e}{2M_k c}\left(\sum_\alpha e_{\gamma\alpha\beta}Z_k r_{\alpha k} - \iota_{\gamma\beta}^k\right), \tag{68}$$

in which a vibrational shielding tensor $\iota_{\gamma\beta}^k$ is defined as

$$\iota_{\gamma\beta}^k = -\frac{2}{m_{\mathrm{e}}}\sum_{A\neq 0}\frac{\langle\chi_0|L_\gamma|\chi_A\rangle\langle\chi_A|P_{\beta k}|\chi_0\rangle}{E_A - E_0}; \tag{69}$$

$e_{\gamma\alpha\beta}$ is the Levi-Cività symbol. The pure vibrational effect is thus described by magnetic moment with the components of the form (6). Provided the coefficients before p_s are expressible via q_s, such a definition of a vibrational magnetic moment coincides exactly with conventional concept (5). The electronic shielding occurs only if the pertinent matrix element for $P_{\beta k}$ between the electronic wave functions χ_A and χ_0 fails to equal zero; otherwise the total magnetic moment turns out purely nuclear. In addition, insofar as functions χ_A and energies E_A depend on normal vibrational coordinates, the tensor $\iota_{\gamma\beta}^k$ is a function of nuclear variables as well.

A. Rotational magnetism

The magnetic moment of a rotating molecule is determined according to (1). Because of a frame distortion effect, the slight perturbation of rotational motion may give rise to the appearance of principally new transitions. To elucidate how rovibrational interaction enables nominally forbidden magnetic transitions to be permitted, we calculate the matrix elements of the rotational magnetic moment with the aid of functions (20).

The pertinent projection of a magnetic moment in the laboratory-fixed system can be written as

$$\mathrm{m}^{\mathrm{LF}} = \frac{\mathrm{m}_{\mathrm{n}}}{2\hbar}\sum_\gamma g_{\gamma\gamma}(J_\gamma\Phi_\gamma + \Phi_\gamma J_\gamma). \tag{70}$$

For the matrix elements, as $J_\gamma\Phi_\gamma = \Phi_\gamma J_\gamma$, we have the following expression:

$$\begin{aligned}&\langle\Psi_{\mathrm{fd}}(nJ)|\mathrm{m}^{\mathrm{LF}}|\Psi_{\mathrm{fd}}(n'J')\rangle\\ &\quad= \langle nJ|\mathrm{m}^{\mathrm{LF}}|n'J'\rangle + \left\langle\Psi_i^{\mathrm{rot}}\middle|\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}}\middle|\Psi_f^{\mathrm{rot}}\right\rangle + \cdots,\end{aligned} \tag{71}$$

in which the matrix element

$$\langle nJ|\mathrm{m}^{\mathrm{LF}}|n'J'\rangle = \left\langle\Psi_i^{\mathrm{rot}}\middle|\langle n|\mathrm{m}^{\mathrm{LF}}|n'\rangle\middle|\Psi_f^{\mathrm{rot}}\right\rangle \tag{72}$$

corresponds to the transition in the absence of rovibrational coupling, and

$$\begin{aligned}\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}} &= \frac{\mathrm{m}_{\mathrm{n}}}{\hbar}\sum_{\alpha\beta\gamma}J_\alpha J_\beta J_\gamma\Phi_\gamma\langle n,1|g_{\gamma\gamma}|n'\rangle\\ &\quad+ \frac{\mathrm{m}_{\mathrm{n}}}{\hbar}\sum_{\alpha\beta\gamma}\Phi_\gamma J_\gamma J_\alpha J_\beta\langle n|g_{\gamma\gamma}|n',1\rangle.\end{aligned} \tag{73}$$

The components of factor $g_{\gamma\gamma}$ can be represented as a series expansion with respect to normal coordinates,

$$g_{\gamma\gamma} = g_{\gamma\gamma}^e + \sum_s\frac{\partial g_{\gamma\gamma}}{\partial q_s}q_s + \sum_{sr}\frac{\partial^2 g_{\gamma\gamma}}{\partial q_s\partial q_r}q_s q_r + \cdots, \tag{74}$$

with $g_{\gamma\gamma}^e$ being the equilibrium value of $g_{\gamma\gamma}$. To consider the pure rotational transitions, one has to examine only the terms (73), which are diagonal in vibrational quantum numbers. Retaining linear terms, we have

$$\langle n,1|g_{\gamma\gamma}|n\rangle = \langle n|g_{\gamma\gamma}|n,1\rangle = \sum_s\frac{\partial g_{\gamma\gamma}}{\partial Q_s}\frac{B_\alpha B_\beta a_s^{\alpha\beta}}{\hbar^2(\hbar\omega_s)^2}.$$

Hence,

$$\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}} = \frac{\mathrm{m}_{\mathrm{n}}}{2\hbar}\sum_\gamma(\mathbb{J}_\gamma J_\gamma\Phi_\gamma + \Phi_\gamma J_\gamma\mathbb{J}_\gamma), \tag{75}$$

in which

$$\mathbb{J}_\gamma = \frac{1}{\hbar^2}\sum_{\alpha\beta}\varphi_\gamma^{\alpha\beta}J_\alpha J_\beta \tag{76}$$

with

$$\varphi_\gamma^{\alpha\beta} = 2\sum_s\frac{\partial g_{\gamma\gamma}}{\partial Q_s}\frac{B_\alpha B_\beta}{(\hbar\omega_s)^2}a_s^{\alpha\beta}. \tag{77}$$

The combination of the terms comprising the first series in (74) and the frame-distortion wave functions (20) is thus responsible for the formation of a distortion magnetic dipole (75). This dipole induced by rovibrational interaction gives rise to the pure rotational transitions. The difference from the electrical case lies in the appearance of an extra operator J_γ at the moment function (75) that leads to extra transitions for which the quantum number K may be altered by 4, whereas in the case of moment function (27) K is allowed to change only by 3. The absolute intensity is defined by the first derivative of $g_{\gamma\gamma}$ with respect to Q_s. To evaluate analytically this derivative, we examine the general expression for the g factor that consists of nuclear [Eq. (2)] and electronic [Eq. (3)] contributions. For the nuclear factor, we have a contribution

$$\frac{\partial g_{\gamma\gamma}^{(\mathrm{n})}}{\partial Q_s} = D_1^{(\mathrm{n})} + D_2^{(\mathrm{n})} \tag{78}$$

with

$$D_1^{(\mathrm{n})} = -\frac{a_s^{\gamma\gamma}}{I_e^{\gamma\gamma}}g_{\gamma\gamma}^{(\mathrm{n})}\Big|_e \tag{79}$$

stemming from a moment of inertia and

$$D_2^{(\mathrm{n})} = \frac{2m_{\mathrm{p}}}{I_e^{\gamma\gamma}}e_{\gamma\upsilon\epsilon}e_{\gamma\xi\epsilon}\sum_k\frac{Z_k}{\sqrt{m_k}}r_{\upsilon k}^e l_{\xi k,s} \tag{80}$$

resulting from relation (A2). Both terms in (78) are in such a relation that, provided explicit values of Z_k are taken, these terms virtually compensate each other. In fact, combining (79) with (A2) and (80), we conclude that the nuclear weight in $\partial g_{\gamma\gamma}/\partial Q_s$ is roughly specified by the factors of type $(M_i Z_k - M_k Z_i)$. For instance, examining H_2 or $H_2{}^+$ or $H_3{}^+$, we have $Z_k = 1$; consequently,

$$\frac{\partial g^{(\mathrm{n})}_{\gamma\gamma}}{\partial Q_s} = 0. \tag{81}$$

In other words, a pure hydrogen system is characterized by the fact that nuclear contribution (78) vanishes. For the electronic part, we have

$$\frac{\partial g^{(\mathrm{e})}_{\gamma\gamma}}{\partial Q_s} = D^{(\mathrm{e})}_1 + D^{(\mathrm{e})}_2, \tag{82}$$

in which

$$D^{(\mathrm{e})}_1 = -\frac{a^{\gamma\gamma}_s}{I^{\gamma\gamma}_e} g^{(\mathrm{e})}_{\gamma\gamma}\big|_e. \tag{83}$$

Regarding $D^{(\mathrm{e})}_2$, one should note that this additional contribution, which is highly nonadiabatic by its nature, is caused by variation of the electronic energies E_A and wave functions χ_A as a function of normal vibrational coordinates [16]. Finally, collecting all contributions to $\partial g_{\gamma\gamma}/\partial Q_s$, one might calculate quantity $\varphi^{\alpha\beta}_{\gamma}$ [Eq. (77)], which defines the sought distortion magnetic dipole moment in nuclear magneton units.

In some cases, it may be necessary to involve the off-diagonal components of the g factor. Then an additional magnetic moment [12]

$$\Delta \mathrm{m}^{\mathrm{LF}} = \frac{\mathrm{m_n}}{2\hbar} {\sum_{\gamma\gamma'}}' (g_{\gamma\gamma'} J_{\gamma'} \Phi_\gamma + g^*_{\gamma\gamma'} \Phi_\gamma J_{\gamma'}) \tag{84}$$

should be added to the diagonal one [Eq. (70)]; the prime on the summation symbol denotes that $\gamma \neq \gamma'$. In an analogous manner with (71)–(73), one can derive that the off-diagonal contribution to the frame-distortion effect is defined by the matrix element

$$\langle \Psi^{\mathrm{rot}}_i \big| \Delta \mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}} \big| \Psi^{\mathrm{rot}}_f \rangle.$$

If

$$g_{\gamma\gamma'} = \sum_s \frac{\partial g_{\gamma\gamma'}}{\partial q_s} q_s + \cdots \tag{85}$$

and the vibrational quantum numbers n_s all are not altered in the course of a transition, then

$$\Delta \mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}} = \frac{\mathrm{m_n}}{4\hbar} {\sum_{\gamma\gamma'}}' (J_{\gamma'} \Phi_\gamma \mathbb{J}_{\gamma\gamma'} + \mathbb{J}_{\gamma\gamma'} J_{\gamma'} \Phi_\gamma$$
$$+ \Phi_\gamma J_{\gamma'} \overset{*}{\mathbb{J}}_{\gamma\gamma'} + \overset{*}{\mathbb{J}}_{\gamma\gamma'} \Phi_\gamma J_{\gamma'}), \tag{86}$$

in which

$$\mathbb{J}_{\gamma\gamma'} = \frac{1}{\hbar^2} \sum_{\alpha\beta} \varphi^{\alpha\beta}_{\gamma\gamma'} J_\alpha J_\beta \tag{87}$$

and

$$\overset{*}{\mathbb{J}}_{\gamma\gamma'} = \frac{1}{\hbar^2} \sum_{\alpha\beta} \varphi^{\alpha\beta *}_{\gamma\gamma'} J_\alpha J_\beta \tag{88}$$

with

$$\varphi^{\alpha\beta}_{\gamma\gamma'} = 2 \sum_s \frac{\partial g_{\gamma\gamma'}}{\partial Q_s} \frac{B_\alpha B_\beta}{(\hbar\omega_s)^2} a^{\alpha\beta}_s. \tag{89}$$

Here $\varphi^{\alpha\beta *}_{\gamma\gamma'}$ is defined by (89) provided $g_{\gamma\gamma'}$ is substituted with $g^*_{\gamma\gamma'}$. Summarizing, one might state that molecular vibrations can induce an additional magnetic moment (84) which can generate a nominally forbidden spectrum. To derive the pertinent derivatives $\partial g_{\gamma\gamma'}/\partial Q_s$, in which $g_{\gamma\gamma'} = g^{(\mathrm{n})}_{\gamma\gamma'} + g^{(\mathrm{e})}_{\gamma\gamma'}$ with [12]

$$g^{(\mathrm{n})}_{\gamma\gamma'} = \frac{m_{\mathrm{p}}}{I^{\gamma'\gamma'}} e_{\gamma\sigma\epsilon} e_{\gamma'\xi\epsilon} \sum_k Z_k r_{\sigma k} r_{\xi k} \tag{90}$$

and

$$g^{(\mathrm{e})}_{\gamma\gamma'} = -\frac{2m_{\mathrm{p}}}{m_{\mathrm{e}} I^{\gamma'\gamma'}} \sum_{A\neq 0} \frac{\langle \chi_0 | L_\gamma | \chi_A \rangle \langle \chi_A | L_{\gamma'} | \chi_0 \rangle}{E_A - E_0}, \tag{91}$$

an analysis similar to (78) and (82) is applicable.

Through the symmetry properties that require a magnetic moment to be a pseudovector, the second derivatives of the g factor can happen to be relatively big. Consequently, the terms comprising the second series in (74) can affect the fundamental transitions. Actually, if we disregard the frame-distortion effect and restrict our consideration to harmonic approximation only, the fundamental vibrational matrix elements of type $\langle n_s, n_l | q_s q_l | n_s, n_l + 1 \rangle$ vanish completely. This means, notwithstanding that the overtone or combination transitions can manifest themselves through nonzero matrix elements $\langle n_s, n_l | q_s q_l | n_s + 1, n_l + 1 \rangle$ or $\langle n_l | q_l{}^2 | n_l + 2 \rangle$, the fundamental transitions are forbidden because

$$\langle n | \mathrm{m}^{\mathrm{LF}} | n' \rangle = 0$$

in this case. However, provided the rovibrational interaction is taken into account, the situation drastically changes, so that the nominally forbidden fundamental transitions may become permitted. To demonstrate this, let us apply the correction (18) to calculate $\mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}}$ [Eq. (73)] for the fundamental transition $n_l \rightarrow n_l + 1$. Restricting ourselves by the only first nonvanishing terms from

$$q_l \sum_{s\neq l} \frac{\partial^2 g_{\gamma\gamma}}{\partial q_s \partial q_l} q_s$$

in (74), we obtain

$$G^{\alpha\beta\gamma}_{\mathrm{rot}} = \langle n, 1 | g_{\gamma\gamma} | n' \rangle = \frac{\sqrt{n_l + 1}}{2} \sum_{s\neq l} \frac{\partial^2 g_{\gamma\gamma}}{\partial q_s \partial q_l} \frac{B^{\alpha\beta}_s}{\hbar\omega_s}$$

with $n' = n_1, n_2, \ldots, n_l + 1, \ldots$. Note that

$$\langle n, 1 | g_{\gamma\gamma} | n' \rangle = \langle n | g_{\gamma\gamma} | n', 1 \rangle,$$

whereas element $\langle n, 1 | g_{\gamma\gamma} | n' \rangle$ is not in general identical to $\langle n | g_{\gamma\gamma} | n', 1 \rangle$. Consequently,

$$\mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}} = \frac{\mathrm{m_n}}{\hbar} \sum_{\alpha\beta\gamma} G^{\alpha\beta\gamma}_{\mathrm{rot}} \{ J_\alpha J_\beta, J_\gamma \Phi_\gamma \}. \tag{92}$$

The line strength is defined by $\langle \Psi^{\mathrm{rot}}_i | \mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}} | \Psi^{\mathrm{rot}}_f \rangle$. This presumably small contribution of purely magnetic nature can be expected to be masked by more intense allowed lines.

Nevertheless, it can become perceptible in the far infrared for transitions in which ΔK exceeds 2.

B. Vibrational magnetism

A vibrational magnetic moment owes to a motion of nuclei relative to each other. Along with a pure nuclear skeleton contribution, there exists an electronic one, stemming from the currents in the electronic shell induced by vibrations of nuclei. Involving a nonadiabatic concept [16–18,24,25], one might conclude that electrons from external shells should fail to screen a nuclear core. At the same time, the inner electrons, which follow the nuclei, are apt to shield significantly nuclear charges and cancel thus the nuclear contribution to magnetic moment. The effect of cancellation is included in the components of atomic tensor (68) which define the vibrational magnetic moment (4) in the body-fixed frame of reference. It should be noted that in order to accurately compute the vibrational transition moments, one has to express the magnetic moment in the form of an expansion with respect to both normal coordinates and momenta (5). In this concern, the idea suggested in [67] to have the magnetic moment expanded only with respect to normal coordinates is erroneous. To establish the selection rules affected by the frame distortion, one has to proceed to the laboratory-fixed frame of reference, in which the vibrational magnetic moment is expressed by projection,

$$\mathrm{m}^{\mathrm{LF}} = \sum_{\gamma} \mathrm{m}_{\gamma} \Phi_{\gamma}, \tag{93}$$

and calculate then the nonvanishing matrix elements of m^{LF} employing frame-distortion wave functions (20). As a result,

$$\begin{aligned}&\langle \Psi_{\mathrm{fd}}(nJ)|\mathrm{m}^{\mathrm{LF}}|\Psi_{\mathrm{fd}}(n'J')\rangle \\ &\quad = \langle nJ|\mathrm{m}^{\mathrm{LF}}|n'J'\rangle + \left\langle \Psi_i^{\mathrm{rot}}\middle|\mathrm{w}_{\mathrm{mag}}^{\mathrm{vib}}\middle|\Psi_f^{\mathrm{rot}}\right\rangle + \cdots,\end{aligned} \tag{94}$$

where

$$\begin{aligned}\mathrm{w}_{\mathrm{mag}}^{\mathrm{vib}} = {}& \sum_{\alpha\beta\gamma} J_\alpha J_\beta \Phi_\gamma \langle n, 1|\mathrm{m}_\gamma|n'\rangle \\ &+ \sum_{\alpha\beta\gamma} \Phi_\gamma J_\alpha J_\beta \langle n|\mathrm{m}_\gamma|n', 1\rangle.\end{aligned} \tag{95}$$

The effect analogous to the rotational one [Eq. (75)] in this case is defined by the terms linear in momenta corresponding to the first series members in (5). Having calculated a diagonal vibrational matrix element, we have

$$\mathrm{w}_{\mathrm{mag}}^{\mathrm{vib}} = \sum_{\alpha\beta\gamma} \kappa^{\alpha\beta\gamma} [J_\alpha J_\beta, \Phi_\gamma], \tag{96}$$

where

$$\begin{aligned}\kappa^{\alpha\beta\gamma} &= \langle n, 1|\mathrm{m}_\gamma|n\rangle = -\langle n|\mathrm{m}_\gamma|n, 1\rangle \\ &= i\sqrt{2}\sum_{s} \frac{B_s^{\alpha\beta}}{\hbar\omega_s}\frac{\partial \mathrm{m}_\gamma}{\partial p_s}\left(n_s + \frac{1}{2}\right).\end{aligned} \tag{97}$$

Provided the terms bilinear with respect to q_r and p_s are involved while considering expression (5) for magnetic moment, the fundamental transitions become allowed through a frame-distortion mechanism. Taking into account for simplicity the only contribution

$$q_l \sum_{s\neq l} \frac{\partial^2 \mathrm{m}_\gamma}{\partial q_l \partial p_s} p_s, \tag{98}$$

we readily find for the fundamental transition $n_l \to n_l + 1$ with the aid of (18)

$$\begin{aligned}G_{\mathrm{vib}}^{\alpha\beta\gamma} &= \langle n, 1|\mathrm{m}_\gamma|n'\rangle = -\langle n|\mathrm{m}_\gamma|n', 1\rangle \\ &= i\sqrt{n_l + 1}\sum_{s\neq l} \frac{B_s^{\alpha\beta}}{\hbar\omega_s}\frac{\partial^2 \mathrm{m}_\gamma}{\partial q_l \partial p_s}\left(n_s + \frac{1}{2}\right).\end{aligned} \tag{99}$$

Hence,

$$\mathrm{w}_{\mathrm{mag}}^{\mathrm{vib}} = \sum_{\alpha\beta\gamma} G_{\mathrm{vib}}^{\alpha\beta\gamma} [J_\alpha J_\beta, \Phi_\gamma]. \tag{100}$$

Both (96) and (100) prove that the rotational matrix elements from commutator $[J_\alpha J_\beta, \Phi_\gamma]$ govern the distortion-induced transitions. Because there is no additional angular momentum in (95), it may seem that the rotational structure of a spectrum would resemble that predicted by Watson for electric dipole forbidden spectra [2]. However, this is not quite true, because the anticommutator $\{J_\alpha J_\beta, \Phi_\gamma\}$ appears in (27) instead of a commutator.

C. Application to $H_3{}^+$

The rotational g factor of trihydrium is mainly defined by nuclear contribution (2). The electronic contribution [68] turns out significantly less important due to the absence of low-lying electronic states which could mix with the ground state, contributing to the sum in (3). According to [18], $g_{xx,\mathrm{rot}}^{(\mathrm{e})} = g_{yy,\mathrm{rot}}^{(\mathrm{e})} = -0.0634$ and $g_{zz,\mathrm{rot}}^{(\mathrm{e})} = -0.0198$. Note that, along with the factor g having a rotational nature in $H_3{}^+$, a pure vibrational mechanism of the molecular magnetic moment formation is also possible. The point is that doubly degenerate vibration induces the currents in the electronic shell in such a way that nuclear vibrational magnetic moment becomes partly compensated. For many closed-shell molecules [12,13,17–19], the electronic contribution having a nonadiabatic nature [16,17] dominates entirely over the nuclear-core magnetic moment. This is not the case for $H_3{}^+$, however, by the same reason as it takes place for pure rotational magnetism, i.e., by the lack of low-lying eigenenergy terms.

Because $H_3{}^+$ has D_{3h} symmetry, the distortion effect is defined by only coefficient (19) with $\alpha = \beta = x$ and $s = 2$; that is,

$$B_2^{xx} = \frac{2B_x^2 a_2^{xx}}{\hbar^4}\sqrt{\frac{\hbar}{2\omega_2}}. \tag{101}$$

According to (79), (80), and (83), the first derivative of $g_{\gamma\gamma}$ with respect to Q_s is defined by the corresponding coefficient $a_s^{\gamma\gamma}$. Through the relations for nonzero $a_s^{\gamma\gamma}$ (see Appendix A), we have

$$\frac{\partial g_{xx,\mathrm{rot}}}{\partial Q_{2a}} = -\frac{\partial g_{yy,\mathrm{rot}}}{\partial Q_{2a}} \neq 0$$

and

$$\frac{\partial g_{zz,\mathrm{rot}}}{\partial Q_{2a}} = \frac{\partial g_{xx,\mathrm{rot}}}{\partial Q_{2b}} = \frac{\partial g_{yy,\mathrm{rot}}}{\partial Q_{2b}} = \frac{\partial g_{zz,\mathrm{rot}}}{\partial Q_{2b}} = 0.$$

We consider how the deformation doubly degenerate vibration $Q_2 = (Q_{2a}, Q_{2b})$ affects the sought magnetic moment; the dependence on the fully symmetric vibration Q_1 can be neglected here. The frame-distortion effect is thus determined by this quantity,

$$\varphi = \frac{2B_x^2 a_2^{xx}}{(\hbar\omega_2)^2}\frac{\partial g_{xx,\mathrm{rot}}}{\partial Q_2}, \tag{102}$$

$$\varphi = \varphi_x^{xx} = \varphi_y^{yy} = -\varphi_x^{yy} = -\varphi_y^{xx}.$$

As we have already established in (81), the nuclear contribution (78) to $\partial g_{xx,\mathrm{rot}}/\partial Q_2$ for $H_3{}^+$ is equal to zero exactly. In fact,

$$\frac{\partial g_{\gamma\gamma}^{(\mathrm{n})}}{\partial Q_s} = \frac{\partial}{\partial Q_s}\left(\frac{m_\mathrm{p}}{I^{\gamma\gamma}}\sum_k\left(r_k^2 - r_{\gamma k}^2\right)\right) = \frac{\partial}{\partial Q_s}1 = 0.$$

Because of this, the sought effect is defined by electronic contribution (82) only. We use (16) to estimate φ and, according to (A5), we put $a_2^{xx} = a_{2a}^{xx} = \sqrt{2I_e^{xx}}$. As a result, we have

$$\varphi = -\left(\frac{2B_0}{\nu_2}\right)^2 g_{xx,\mathrm{rot}}^{(\mathrm{e})}. \tag{103}$$

For $H_3{}^+$, we can adopt the following values: $B_0 = 43.568\,\mathrm{cm}^{-1}$ [5], $\nu_2 = 2521.56\,\mathrm{cm}^{-1}$ [5], and $g_{xx,\mathrm{rot}}^{(\mathrm{e})} = -0.0634$ [18]. Note that the rotational constant in the ground vibrational state and observed frequency are chosen here instead of B_e and harmonic frequency. Thus,

$$\varphi = 0.8\times 10^{-4}. \tag{104}$$

Depending on the impact of nonadiabatic effects, which manifest themselves in additional terms containing the derivatives of the electronic energies and wave functions with respect to Q_2, the outcome for φ can vary. It is important to emphasize that the magnetic moment is determined almost entirely by a nuclear contribution, provided rotational magnetism of trihydrium is considered [18,68]. This is not a case for the distortion magnetic dipole, which is produced exclusively by electronic contribution [Eq. (103)]. Inspecting φ, a direct analogy can be pointed out with a distortion dipole electrical effect, for which Pan and Oka [62] found the Watson coefficient in the form (60). In a magnetic case, instead of the derivative of electric dipole μ_x we have the derivative of the g factor with respect to q_2.

The rotational structure of magnetic transitions is governed by matrix elements of (75) for which the operators

$$\mathbb{J}_x = \varphi(J_-^2 + J_+^2) \quad \text{and} \quad \mathbb{J}_y = -\varphi(J_-^2 + J_+^2)$$

represent the distortion dipole. The line strength is given by the expression

$$S_{J,K}^{J',K'} = 3\sum_{M'M}|\langle J', K', M'|\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}}|J, K, M\rangle|^2.$$

The transitions for which $\Delta K = \pm 4$ warrant our scrutiny. We have

$$\begin{aligned}&\langle J', K\pm 4, M|\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}}|J, K, M\rangle\\ &\quad = \mp\varphi\mathrm{m}_\mathrm{n}\langle J', K\pm 4, M|J_\pm^3\Phi_{0,\pm 1}|J, K, M\rangle,\end{aligned} \tag{105}$$

and, consequently,

$$S_{J,K}^{J',K\pm 4} = \frac{(\varphi\mathrm{m}_\mathrm{n})^2}{16}\mathrm{X}_{J,K}^{J',K\pm 4}. \tag{106}$$

Applying (32), (34), and (39), for the R branch we find

$$\begin{aligned}\mathrm{X}_{J,K}^{J+1,K\pm 4} &= (J+1)^{-1}(J\mp K-2)(J\mp K-1)\\ &\quad\times(J\mp K)(J\pm K+1)(J\pm K+2)\\ &\quad\times(J\pm K+3)(J\pm K+4)(J\pm K+5).\end{aligned} \tag{107}$$

In an analogous manner, involving (52) and (53), one might derive that

$$\begin{aligned}\mathrm{X}_{J,K}^{J,K\pm 4} &= (2J+1)J^{-1}(J+1)^{-1}(J\pm K+1)\\ &\quad\times(J\pm K+2)(J\pm K+3)(J\pm K+4)\\ &\quad\times(J\mp K-3)(J\mp K-2)(J\mp K-1)(J\mp K)\end{aligned} \tag{108}$$

and

$$\begin{aligned}\mathrm{X}_{J,K}^{J-1,K\pm 4} &= J^{-1}(J\mp K-4)(J\mp K-3)\\ &\quad\times\ (J\mp K-2)(J\mp K-1)(J\mp K).\\ &\quad\times(J\pm K+1)(J\pm K+2)(J\pm K+3)\end{aligned} \tag{109}$$

for Q and P branches, respectively. We conclude, first, if the rules for the electrical distortion effect of $H_3{}^+$ are $\Delta K = \pm 3$, the transitions with the magnetic mechanism might occur with $\Delta K = \pm 4$. Second, the strong J dependence neutralizes partly the smallness of the distortion magnetic dipole $\varphi\mathrm{m}_\mathrm{n}$. To illustrate the latter, we calculate line strengths $S_{J,K}^{J+1,K+4}$ for $J = 10$ and $J = 20$. Assuming $K = 1$ in (106), for instance, we obtain $S_{10,1}^{11,5} = (10^{-1}\mathrm{m}_\mathrm{n})^2$ and $S_{20,1}^{21,5} = \mathrm{m}_\mathrm{n}^2$. As is not surprising, the distortion magnetic dipole can drive transitions for which the intensities are comparable to those of the conventional magnetic dipole transitions.

The frame-distortion effect for $H_3{}^+$ becomes even more pronounced if we include the off-diagonal g components. We deal here with nuclear terms only, because the electronic contribution (91) vanishes through $\partial g_{\gamma\gamma'}^{(\mathrm{e})}/\partial Q_s = -(a_s^{\gamma'\gamma'}/I_e^{\gamma'\gamma'})g_{\gamma\gamma'}^{(\mathrm{e})}|_e = 0$; for $\gamma \neq \gamma'$, $g_{\gamma\gamma'}^{(\mathrm{e})}|_e = 0$. The nuclear contribution is formed by terms comprising $g_{xy}^{(\mathrm{n})}$ or $g_{yx}^{(\mathrm{n})}$. According to (90),

$$g_{xy}^{(\mathrm{n})} = g_{xy}^{(\mathrm{n})*} = g_{yx}^{(\mathrm{n})} = g_{yx}^{(\mathrm{n})*} = I^{xy}/I_e^{xx}.$$

Only the derivative of $g_{xy}^{(\mathrm{n})}$ with respect to Q_{2b} fails to equal zero; hence

$$\Delta\varphi = \frac{2B_x^2 a_2^{xy}}{(\hbar\omega_2)^2}\frac{\partial g_{xy}^{(\mathrm{n})}}{\partial Q_{2b}} = \left(\frac{2B_0}{\nu_2}\right)^2 = 1.2\times 10^{-3}. \tag{110}$$

$\Delta\varphi = \varphi_{xy}^{xy} = \varphi_{yx}^{xy}$, whereas other $\varphi_{\gamma\gamma'}^{\alpha\beta}$ (89) are equal to zero. The off-diagonal nuclear distortion dipole is defined by

$$\mathbb{J}_{xy} = \mathbb{J}_{yx} = i\Delta\varphi(J_+^2 - J_-^2).$$

According to (86), we have

$$\Delta\mathrm{w}_{\mathrm{mag}}^{\mathrm{rot}} = \frac{\mathrm{m}_\mathrm{n}}{4\hbar}\{\{J_y, \Phi_x\} + \{J_x, \Phi_y\}, \mathbb{J}_{xy}\}.$$

Taking $J_y\Phi_x + J_x\Phi_y = \Phi_x J_y + \Phi_y J_x$ into account, one may readily find that transitions with $\Delta K = \pm 4$ are characterized by

$$\langle J', K \pm 4, M|\Delta \mathrm{w}^{\mathrm{rot}}_{\mathrm{mag}}|J, K, M\rangle = \pm\Delta\varphi \mathrm{m}_{\mathrm{n}}\langle J', K \pm 4, M|J^3_{\pm}\Phi_{0,\pm1}|J, K, M\rangle. \qquad (111)$$

The line strength turns out thus analogous to that of the diagonal electronic one [Eq. (106)]:

$$\Delta S^{J',K\pm4}_{J,K} = \frac{(\Delta\varphi \mathrm{m}_{\mathrm{n}})^2}{16}\mathrm{X}^{J',K\pm4}_{J,K}, \qquad (112)$$

in which relations (107)–(109) determine $\mathrm{X}^{J',K\pm4}_{J,K}$. Two numerical examples $\Delta S^{11,5}_{10,1} = 2(\mathrm{m}_{\mathrm{n}})^2$ and $\Delta S^{21,5}_{20,1} = 2(10 \times \mathrm{m}_{\mathrm{n}})^2$ demonstrate convincingly how significant the frame-distortion effect can be.

Since the components of the g factor behave like the components of the inertia tensor, let us examine whether the totally symmetric vibration Q_1 can affect the transition magnetic moments in principle. Assuming $B_x = B_y$ and $a^{xx}_1 = a^{yy}_1$ [69], one might readily obtain that $\mathbb{J}^{\mathrm{sym}}_{\gamma}$, being the contribution from Q_1 into $\mathbb{J}_{\gamma}$ [Eq. (76)], is equal to

$$\frac{2}{(\hbar\omega_1)^2}\frac{\partial g_{\gamma\gamma,\mathrm{rot}}}{\partial Q_1}\left(B^2_x a^{xx}_1\{J_-, J_+\} + B^2_z a^{zz}_1 J^2_0\right), \qquad (113)$$

in which we imply $\partial g_{xx,\mathrm{rot}}/\partial Q_1 = \partial g_{yy,\mathrm{rot}}/\partial Q_1$. On acting on $|J, K, M\rangle$, the operators $\mathbb{J}^{\mathrm{sym}}_x$, $\mathbb{J}^{\mathrm{sym}}_y$, and $\mathbb{J}^{\mathrm{sym}}_z$ do not change J and K, because they consist only of $\{J_-, J_+\}$ and J^2_0. Consequently, the impact of the symmetric vibration can lead to the small corrections for the conventional magnetic matrix elements, but fails to generate the transitions beyond allowed.

V. DISCUSSION

Highly symmetrical molecules in the universe are often barely detectable by spectroscopic techniques because at least some of the rovibrational transitions are strictly forbidden by selection rules. One way to study such astrophysical molecular systems is to search for the spectral regions in which the collision-induced transitions are capable to manifest themselves. Molecular collisions result in distortion of charge distribution in a molecule, thus giving rise to the appearance of an induced electric dipole [70,71]. This mechanism can be dominant in relatively dense atmospheres of some planets or cold stars, for which the effect of intermolecular interaction is significant. With decreasing gas density, the role of collisions wanes sharply, whereas the relative role of a frame-distortion effect permanently increases. Consequently, in rarefied media, the role of effects induced by molecular collisions becomes negligible, whereas the effects caused by rovibrational interaction in a single molecule persist. Spontaneous transitions offer thus an alternative which can help in the remote detection of monomers, the symmetry of which is broken by a centrifugal force [1]. Even in the ground vibrational state, the nominally forbidden pure rotational spectrum can be detected. One might imagine that vibrations have nothing to do with getting rotational transitions slightly allowed. Oka [1] notes after Watson's pioneering work [2], however, that this effect owes in fact to a vibration-rotational interaction. A frame-distortion effect represents itself as a diagonal result of a Herman-Wallis factor, which enters the expansion of a vibration-rotational matrix element of an electric dipole. In our work, we reproduce the Watson formula for the distortion electric dipole with the aid of the theorem of extraneous quantum numbers [Eq. (8)] [29–31] and expand the possibilities of its use; this theorem can also be called a theorem for shifting matrix elements. Taking spherical and oblate symmetric tops as examples, we showed that the use of the theorem makes it possible to simplify significantly the derivation of the sought matrix elements corresponding to the forbidden transitions.

In a row of molecular species for which a frame-distortion effect can be substantial, the most striking candidate is the methane molecule. Applying the up-to-date spectral parameters, we were able to calculate the distortion electric dipole for ^{12}CH$_4$ and then to simulate the pertinent spectra, which are shown in Figs. 1 and 2. In the line strength (41), the relatively small value of the distortion dipole (44) is quenched by the strong dependence on J [Eq. (42)]. At room temperature, for instance, the most intensive lines are $R(11)$ and $R(12)$; for $J > 12$, the spectral lines deplete quite sharply because of the Boltzmann factor (see Fig. 1).

The present work is focused mainly on consideration of the pure rotational forbidden transitions in molecules having zero permanent dipole. The question can be raised as to whether in the molecules the higher-order anharmonic terms, if any, could give rise to a transition probability comparable to that of a distortion dipole effect. To resolve this problem, we have to compare the strengths of two mechanisms inducing rotational transitions. The first one relates to variation of inertia terms in the course of molecular vibrations, whereas the second one is driven by anharmonic terms in expansions of the potential and electric dipole functions. The contribution of the latter effect can be estimated, for example, by calculating the diagonal vibrational matrix elements within the framework of the formalism of polynomials of quantum numbers [31]. Note that the selection rules, line positions, and relative intensities in this case are significantly at variance with respect to those caused by the frame-distortion mechanism. Moreover, the anharmonic vibration-induced rotational spectrum is allowed, whereas the frame-distortion spectrum is nominally forbidden. As a result, the frame-distortion effect manifests itself most strikingly in the spectral regions free from allowed absorption lines. Pan and Oka [62] calculated the vibration-induced dipole of trihydrium. The sought dipole moment is determined by the cubic anharmonic term in the potential as well as by two first dipole moment derivatives. The obtained value for the induced dipole turned out to be $\sim 10^{-3}$ D. Although the order of the vibrational dipole is similar to that of θ [Eq. (60)], the absorption cross section of the frame-distortion effect is much greater than that of the vibration induced effect. In addition, the vibration-induced transitions are governed by selection rules of a different type, namely, $\Delta K = \pm 1$ and $\Delta l = \mp 2$, in which l is the vibrational angular momentum quantum number. In the course of a transition the l quantum number changes, so that it looks more adequate to call a transition rovibrational rather than pure rotational. As a final note we have to emphasize that the frame-distortion dipole gives rise to the nominally forbidden rotational lines, the intensity of which increases rapidly with growing rotational quantum number. In contrast, the electric dipole induced by anharmonic terms is sufficiently weak irrespective of values J, thus giving rise to rovibrational lines of a negligible intensity.

An increasing interest to explore various effects relevant to weak molecular absorption prompted us to extend the frame-distortion theory to magnetic dipole transitions, which are nominally prohibited. From first glance, the vibration-rotational magnetism does not seem as important as, e.g., the magnetism related to the electron spin effects. In reality, magnetic dipole absorption even in a spinless molecule is rather significant as it was demonstrated recently through observation of the magnetic dipole CO_2 band in the Martian atmosphere [20] and in laboratory-controlled conditions [21,22]. The solid theory [23] proved, first, the dominance of magnetic-dipole absorption over the quadrupole one, and second, the sufficiency of a magnetic dipole value not exceeding one nuclear magneton to produce an observable spectrum. A prospective direction for further investigation could consist in involvement of higher-order terms in expansion (5) to allow to step over the first-order perturbation theory. The higher-order corrections lead to a vibration-induced magnetic dipole, which can contribute the intensity of allowed rovibrational spectral lines. It is important to mention that these lines do not overlap with forbidden pure rotational lines, nor are they characterized by strong J dependence. Thus, the effect of vibration-induced magnetic moment, which has not been studied enough yet, does not compete with the frame-distortion effect.

Developing the theory of distortion dipole in the framework of theorem (8) we arrived at the general expressions for matrix elements of the magnetic dipole, which can be of either pure rotational or vibrational nature. The pure rotational effect comprises four operators changing a rotational state of a molecule [Eq. (73)]; hence, the formally forbidden transitions might occur in the far-infrared region with $\Delta K = \pm 4$, whereas for the electrical case we have $\Delta K = \pm 3$. Particular attention has been given to trihydrium, for which we have computed the magnetic moment caused by vibration-rotational interaction. According to (103), in the approximation of the diagonal g factor, only electronic motion generates the distortion magnetic dipole, whereas the nuclear contribution vanishes entirely. This result gives rise to an interesting conclusion: while the permanent magnetic dipole moment of a rigid trihydrium is largely formed by the motion of nuclei [18,68], the magnetic moment caused by distortion of the molecular frame is conditioned exclusively by electronic contribution. As a measure of the absolute value of the distortion magnetic dipole $\varphi \mathrm{m_n}$ in ${H_3}^+$, we have estimated $\varphi \approx 0.8 \times 10^{-4}$. Provided the off-diagonal components of g are induced, we observe the reverse picture: the nuclear contribution with $\Delta\varphi \approx 1.2 \times 10^{-3}$ prevails over the electronic. The seeming smallness of both $\varphi \mathrm{m_n}$ and $\Delta\varphi \mathrm{m_n}$ is largely compensated by the strong J dependence [Eqs. (106) and (112)].

Such a small value for φ in ${H_3}^+$, first, is likely due to the lack of an estimate for nonadiabatic contribution to the magnetic moment derivative with respect to the normal coordinate. The CO_2 molecule represents a good example in this respect because it has no significant average magnetic moment, but has a substantial moment of $\nu_2 + \nu_3$ magnetic transition. Second, in the sum (3) over electronic states, there are no low-lying terms mixing with the ground state. This is at variance with the case of CH^+, for example, for which there exist low-lying levels and the g factor turns out to be substantial [72,73].

The selection rules for distortion magnetic dipole vibrational effect [Eq. (95)] resemble partly their conventional electric dipole analogs described by Watson in the form of (27). The main distinction is conditioned by the need to expand the magnetic moment function with respect to both normal coordinates and conjugated momenta, while the electrical dipole is a function of coordinates only. Finally, we can speculate that additional absorption of a chiral molecule arising from a frame-distortion contribution [Eq. (95)] might be interesting to explore in upcoming investigations.

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There are no conflicts to declare.

APPENDIX A: SUM RULE FOR THE DERIVATIVES OF INERTIA MOMENT

The derivatives

$$a_s^{\alpha\beta} = \left.\frac{\partial I^{\alpha\beta}}{\partial Q_s}\right|_e = \left(\frac{\hbar}{\omega_s}\right)^{-\frac{1}{2}} \left.\frac{\partial I^{\alpha\beta}}{\partial q_s}\right|_e$$

of inertia-moment tensor

$$I^{\alpha\beta} = e_{\alpha\sigma\epsilon} e_{\beta\xi\epsilon} \sum_i m_i r_{\sigma i} r_{\xi i}$$

for a molecule comprising N atoms with masses m_i are defined as [33,42]

$$a_s^{\alpha\beta} = a_s^{\beta\alpha} = 2 e_{\alpha\upsilon\epsilon} e_{\beta\xi\epsilon} \sum_j \sqrt{m_j} r^e_{\upsilon j} l_{\xi j,s}, \tag{A1}$$

in which according to relation

$$\Delta r_{\alpha i} = r_{\alpha i} - r^e_{\alpha i} = \sum_s \left(\frac{\hbar}{m_i \omega_s}\right)^{\frac{1}{2}} l_{\alpha i,s} q_s \tag{A2}$$

matrix $l_{\alpha i,s}$ sets the transformation between Cartesian displacements $\Delta r_{\alpha i}$ of atoms and dimensionless normal vibrational coordinates q_s; $e_{\alpha\beta\gamma}$ is the antisymmetric unit tensor by Levi-Cività. Latin indices indicating atoms run values from 1 to N. Greek indices correspond to spatial Cartesian coordinates x, y, and z. Following Einstein's rule of summation, whenever a greek index arises twice and only twice, one should understand the summation over this index. Note that the atomic masses are used here, not the masses of nuclei as we have assumed in (2) and (3); the difference fails to be principal.

We must find the sum

$$\sum_s a_s^{\alpha\beta} a_s^{\gamma\pi} = 4 e_{\alpha\upsilon\epsilon} e_{\beta\xi\epsilon} e_{\gamma\upsilon'\epsilon'} e_{\pi\xi'\epsilon'},$$

$$\times \sum_j \sqrt{m_j} r^e_{\upsilon j} \sum_{j'} \sqrt{m_{j'}} r^e_{\upsilon' j'} \sum_s l_{\xi j,s} l_{\xi' j',s}.$$

As [42]

$$\sum_s l_{\xi j,s} l_{\xi' j',s} = \delta_{\xi\xi'}\delta_{jj'} - \delta_{\xi\xi'}\sqrt{m_j m_{j'}}\left(\sum_i m_i\right)^{-1} - e_{\xi\kappa\lambda} e_{\xi'\rho\sigma}\left(I_e^{-1}\right)_{\lambda\sigma}\sqrt{m_j m_{j'}}\, r^e_{\kappa j} r^e_{\rho j'}, \tag{A3}$$

one obtains

$$\sum_s a_s^{\alpha\beta} a_s^{\gamma\pi} = \Sigma_1 + \Sigma_2 + \Sigma_3,$$

where three consecutive contributions Σ_1, Σ_2, and Σ_3 stem from the corresponding moieties in (A3). We compute them separately.

For the first part, taking $e_{\alpha\upsilon\epsilon} e_{\beta\xi\epsilon} = \delta_{\alpha\beta}\delta_{\upsilon\xi} - \delta_{\alpha\xi}\delta_{\upsilon\beta}$ and $e_{\gamma\upsilon'\epsilon'} e_{\pi\xi\epsilon'} = \delta_{\gamma\pi}\delta_{\upsilon'\xi} - \delta_{\gamma\xi}\delta_{\upsilon'\pi}$ into account, we have

$$\Sigma_1 = 4\big(\delta_{\alpha\beta}\delta_{\gamma\pi} K^e_{\upsilon\upsilon} - \delta_{\gamma\pi} K^e_{\alpha\beta} - \delta_{\alpha\beta} K^e_{\gamma\pi} + \delta_{\alpha\gamma} K^e_{\beta\pi}\big),$$

in which

$$K^e_{\upsilon\upsilon'} = \sum_j m_j r^e_{\upsilon j} r^e_{\upsilon' j}.$$

Through the relation

$$\sum_i m_i r^e_{\upsilon i} = 0,$$

the second contribution Σ_2 equals zero. To calculate Σ_3, we involve formulas $e_{\beta\xi\epsilon} e_{\xi\kappa\lambda} = \delta_{\beta\lambda}\delta_{\epsilon\kappa} - \delta_{\beta\kappa}\delta_{\epsilon\lambda}$ and $e_{\pi\xi'\epsilon'} e_{\xi'\rho\sigma} = \delta_{\pi\sigma}\delta_{\epsilon'\rho} - \delta_{\pi\rho}\delta_{\epsilon'\sigma}$; as a result,

$$\Sigma_3 = -4 e_{\alpha\upsilon\lambda} e_{\gamma\upsilon'\sigma} K^e_{\beta\upsilon} K^e_{\pi\upsilon'} \left(I_e^{-1}\right)_{\lambda\sigma}.$$

The sought sum rule for the derivatives of inertia moment is thus

$$\sum_s a_s^{\alpha\beta} a_s^{\gamma\pi} = 4\big(\delta_{\alpha\beta}\delta_{\gamma\pi} K^e_{\upsilon\upsilon} - \delta_{\gamma\pi} K^e_{\alpha\beta} - \delta_{\alpha\beta} K^e_{\gamma\pi} + \delta_{\alpha\gamma} K^e_{\beta\pi}\big) - 4 e_{\alpha\upsilon\lambda} e_{\gamma\upsilon'\sigma} K^e_{\beta\upsilon} K^e_{\pi\upsilon'} \left(I_e^{-1}\right)_{\lambda\sigma}. \tag{A4}$$

We adduce the proof of this rule based on the general scenario proposed in [41], just for completeness. Equation (A4) has been proved in the seminal works [74] and [75], in which it has been presented in parts. Our derived form matches exactly that obtained previously by Watson [42]. For rule (A4), of course, there exist many alternative representations.

Applying this rule to $H_3{}^+$ for which $a_{2a}^{xx} = -a_{2a}^{yy} = -a_{2b}^{xy}$, $a_1^{xy} = 0$, $I_e^{\alpha\beta} = I_e^{\alpha\alpha}\delta_{\alpha\beta}$, and $(I_e^{-1})_{\alpha\beta} = (I_e^{\alpha\alpha})^{-1}\delta_{\alpha\beta}$ [45,54], one might obtain [62]

$$\sum_s \left(a_s^{xy}\right)^2 = I_e^{zz},$$

in which index 1 denotes the totally symmetric vibration ν_1, whereas $2a$ and $2b$ belong to the doubly degenerate vibration ν_2; as $I_e^{zz} = I_e^{xx} + I_e^{yy} = 2I_e^{xx}$, then

$$a_{2a}^{xx} = \sqrt{2I_e^{xx}}. \tag{A5}$$

The nonvanishing derivatives of inertia moment with respect to the normal coordinates can be of course calculated directly using the explicit form of $l_{\alpha i,s}$ [69,76]; putting the mass of hydrogen to be m_{p}, one might readily find that $a_1^{zz} = 2a_1^{xx} = 2a_1^{yy} = 2R_e\sqrt{m_{\mathrm{p}}}$ and $a_{2a}^{xx} = -a_{2a}^{yy} = -a_{2b}^{xy} = R_e\sqrt{m_{\mathrm{p}}}$, in which R_e is the internuclear distance that corresponds to the equilibrium equilateral geometry.

APPENDIX B: QUARTIC CENTRIFUGAL EXPANSION

The parameters $\tau_{\alpha\beta\gamma\delta}$ of centrifugal distortion are introduced according to [77]

$$V = \frac{1}{4}\sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta.$$

These parameters can be found by use of (13) and (20). The diagonal calculation for

$$\frac{1}{2}\sum_{\alpha\beta} \rho_{\alpha\beta} J_\alpha J_\beta$$

in the second order by perturbation theory with (20) yields

$$V = \frac{1}{4}\sum_{\alpha\beta\gamma\delta} (\langle n|\rho_{\alpha\beta}|n, 1\rangle + \langle n, 1|\rho_{\alpha\beta}|n\rangle) J_\alpha J_\beta J_\gamma J_\delta.$$

Taking (14), (18), and (19) into account, we readily obtain [75]

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{I_e^{\alpha\alpha} I_e^{\beta\beta} I_e^{\gamma\gamma} I_e^{\delta\delta}} \sum_s \frac{a_s^{\alpha\beta} a_s^{\gamma\delta}}{2\omega_s^2}. \tag{B1}$$

Applying (B1) to NH_3, for instance, we have

$$\tau = \tau_{xxxz} = -\frac{2\hbar^{-2}}{I_e^{xx} I_e^{zz}} \sum_t \left(\frac{B_x}{\hbar\omega_t}\right)^2 a_t^{xx} a_t^{xz}, \tag{B2}$$

in which, running over degenerate vibrations, $t = 3$ or 4. The parameter τ defines the contribution into the frame-distortion effect that borrows the intensity from the rotational transition [see formula (58)].

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