Theory of rovibrational line intensities in allowed and collision-induced absorption spectra of linear molecules

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A theoretical approach is developed for the Herman-Wallis factors describing the variation of the line intensities caused by rovibrational interaction in a linear molecule. In the case of ν_2 and ν_3 fundamentals and the $\nu_1 + \nu_3/2\nu_2 + \nu_3$ resonance combination band in a CO_2 molecule, our theory is capable of generating reliable numerical estimates for the linear Herman-Wallis coefficients without recourse to complicated algebra. On the assumption of nearly free rotating monomers, an analog of the Herman-Wallis factors is introduced for the dipole-forbidden $\nu_2 + \nu_3$ band, which manifests itself in CO_2 collision-induced absorption (CIA). The rovibrational perturbation is appropriate to explain a pronounced crossflow of intensity among rovibrational branches in a virtually rotationally unresolved CIA envelope.

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I. INTRODUCTION

The interaction between rotational and vibrational degrees of freedom is known to affect notably the intensities of absorption lines of molecules. Although the theoretical aspects of this problem were largely formulated over the past hundred years, it is still open for profound examination. In particular, examination of the effect of rovibrational interaction on the observed band shapes for collision-induced absorption (CIA) spectra is lacking. In this paper we suggest a modified theory of the Herman-Wallis factor for the fundamental and combination transitions in a CO_2 molecule. We extend the theory to the electric-dipole-forbidden $\nu_2 + \nu_3$ CIA band, whose unconventional band shape has remained enigmatic for a long time. Whereas other CO_2 CIA bands have a nearly perfect slightly asymmetric bell-shaped form, the $\nu_2 + \nu_3$ band looks almost like a triangle-shaped band, the maximum of which is shifted by more than 10 cm^{-1} from its nominal band origin [1]. It is noteworthy that no trace of true CO_2 dimer structure is discernible in the absorption profile of this band, a fact that contrasts with reliable observation of dimeric structures in several other CO_2 CIA bands [2,3]. Baranov was the first to remark [1] that the maximum of the absorption profile miraculously coincides with the position of the maximum of the then hypothetical R branch. The latter was long believed forbidden in CIA [4]. A recent paper by the present authors [5] showed that the selection rules for the CO_2 $\nu_2 + \nu_3$ band must be reconsidered so that the manifestations of R and P branches are allowed. Nevertheless, the observations [1] require the intensity of the R branch to be significantly greater than that of the P branch, thus contradicting conventional Hönl-London weights of the relevant subbands (Fig. 1).

In what follows we substantiate that the rovibrational interaction is capable of strongly modifying the profile of the CIA band in question. We emphasize from the beginning that our consideration of the CIA profile is based on a simplified assumption of a nearly free rotation of CO_2 monomers in the course of their intermolecular interaction. This assumption is not entirely valid because a notable portion of the CO_2 molecules at ambient temperature is tightly bound together. It seems reasonable to suggest that individual monomers of which a true dimer is formed are unable to rotate freely. According to [6], nearly 90% of CO_2 molecules near room temperature are in the form of either free or quasibound species. For this reason, at least as far as the overall spectral profile at not too low temperature is concerned, the contribution from nearly free rotating molecules can be considered to dominate in the absorption.

The basic theory of rotation-vibration interaction in molecules began to be developed by, e.g., Fowler [7], Dunham [8], and Adel and Dennison [9–11]. Later, this topic was the concern of many investigators, of which a spectacular advance in the theory was due to Herman and Wallis [12] and Watson [13]. Comprehensive details concerning intensity calculations in rovibrational spectra of diatomics can be found, e.g., in [14]. The theory of rovibrational molecular spectra is conventionally constructed based on a first-approximation assumption of virtually independent rotational and vibrational movement of nuclei. The interaction between rotational and vibrational degrees of freedom is then taken into account as a perturbation. Several mechanisms can be considered to cause this perturbation. The product of the moment of inertia and the angular speed of rotation is an integral of the motion. As the moment of inertia is modulated slightly by the vibrational displacement of the nuclei, one can expect variations in the angular speed to occur. The impact of this effect on the intensities of absorption lines in linear molecules was first considered by Gallup [15]. Also centrifugal distortion results in a slight change of molecular geometry that affects the intramolecular potential that governs the vibrational movements of the nuclei. The Coriolis effect modifies the force field of the rotating

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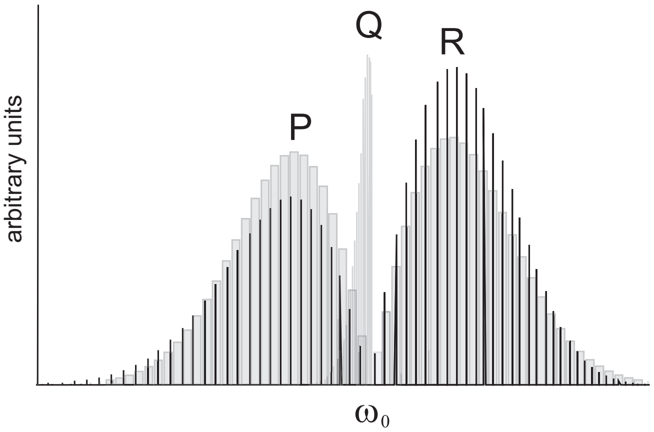

FIG. 1. Illustrative sketch showing the qualitative effect of the Herman-Wallis correction on rovibrational line intensities of P and R branches. The underlying intensity distribution (the histogram in gray) is drawn according to respective Hönl-London weights, whereas measurable intensities are shown by black solid sticks.

frame in which lengthwise displacements of atoms occur. The relevant theory for linear molecules was first suggested by Jacobi and Jaffe [16].

Our consideration below is based largely on an original perturbative technique elaborated previously by Kazakov [17–20]. This technique was applied [18–22] in the analysis of the Herman-Wallis factors for diatomic hydrogen halides. We show how the initial theory of rovibrational effects in diatomic molecules must be modified to describe the electric-dipole-permitted or -forbidden spectra of a linear polyatomic molecule.

II. ANSATZ

The solution of a rovibrational problem is sought conventionally on the assumption that the rotational quantum numbers play the role of parameters in the vibrational Hamiltonian; such parametric quantum numbers in the Schrödinger equation can be called extraneous quantum numbers. Assuming that the vibrational wave functions are functions of extraneous quantum numbers, the matrix elements should contain vibrational wave functions with different rotational quantum numbers, thus giving rise to a significant computational complication. This effect can be overcome by undertaking lengthy computations involving perturbation theory. Otherwise, a solution is obtainable with the so-called theorem of extraneous quantum numbers suggested in [19].

Let Schrödinger's equation of a molecular system have the form

$$[H_{\rm vib} + \rho u(J)]|nJ) = E_{nJ}|nJ). \tag{1}$$

Here $H_{\rm vib}$ is a vibrational Hamiltonian, n is a set of vibrational quantum numbers, ρ is some function of vibrational coordinates, and u is some function of extraneous quantum number J. Hereafter, a vector designated with either a closing or opening round bracket is used to characterize a perturbed but otherwise exact rovibrational state

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

or vibrational state

$$\Psi^{\rm vib}(n) = |n).$$

In contrast, the unperturbed vector, i.e., the harmonic state vector, is defined with the respective angular bracket $|n\rangle$.

We consider the matrix elements of some function f of vibrational coordinates. We know already the matrix elements, which are diagonal with respect to the extraneous quantum number J and we seek the relevant nondiagonal matrix elements. The theorem of extraneous quantum numbers [19,20] offers an opportunity to proceed as shown below. We formally expand $(nJ|f|n'J')$ with respect to $\Delta u = u' - u$:

$$\begin{aligned}(nJ|f|n'J') &= (nJ|f\exp\left(\Delta u\frac{\partial}{\partial u}\right)|n'J)\\ &= (nJ|f|n'J) + (nJ|f\frac{\partial}{\partial u}|n'J)\Delta u\\ &\quad + (nJ|f\frac{\partial^2}{\partial u^2}|n'J)\frac{\Delta u^2}{2} + \cdots .\end{aligned} \tag{2}$$

The first equality in (2) stems from an intuitive suggestion to introduce the yet undefined shift operator $\exp(\Delta u\frac{\partial}{\partial u})$, as if u were a continuous variable. The action of the shift operator is suggested to result in a transition from J' to J. As shown below, this formal operation is supported by a definition of the action of the partial derivative on the wave function.

To define the action of the derivative $\frac{\partial}{\partial u}$ on the $|nJ)$ vector we differentiate Eq. (1) with respect to u. We obtain then

$$\begin{aligned}\rho\frac{\partial}{\partial u}|nJ) + (H + \rho u)\frac{\partial}{\partial u}|nJ)\\ = \frac{\partial E_{nJ}}{\partial u}|nJ) + E_{nJ}\frac{\partial}{\partial u}|nJ).\end{aligned}$$

Representing

$$\frac{\partial}{\partial u}|nJ) = \sum_{m\neq n} O_{mn}|mJ),$$

we arrive at

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

After some algebra we obtain

$$\frac{\partial E_{nJ}}{\partial u} = (nJ|\rho|nJ)$$

and

$$O_{mn} = \frac{(nJ|\rho|mJ)}{E_{nJ} - E_{mJ}}.$$

The latter formula justifies an expansion of the matrix element with respect to Δu in (2) and allows us to enunciate the theorem of extraneous quantum numbers in this closed form:

$$\begin{aligned}(nJ|f|n'J') &= (nJ|f\exp\left(\Delta u\frac{\partial}{\partial u}\right)|n'J),\\ \frac{\partial}{\partial u}|nJ) &= \sum_{m\neq n}\frac{(nJ|\rho|mJ)}{E_{nJ} - E_{mJ}}|mJ).\end{aligned} \tag{3}$$

As an example we write the first-order correction

$$|n,1\rangle = \frac{\partial}{\partial u}|nJ)\bigg|_{J=0} = \sum_{m\neq n}\frac{\langle n|\rho|m\rangle}{E_n - E_m}|m\rangle, \tag{4}$$

which appears in a general expansion

$$|nJ) = |n,0\rangle + |n,1\rangle\Delta u + \cdots .$$

Regarding the rovibrational line intensities, we assume that J is the rotational quantum number so that $u = J(J+1)/2$. The problem of the rovibrational interaction in the spectra of diatomic molecules is reduced to a determination of the set of coefficients $c_{nn'}, d_{nn'}, \ldots$ in an expansion of the matrix element of the dipole μ in powers of Δu:

$$(nJ|\mu|n'J') = (n|\mu|n')\left(1 + c_{nn'}\Delta u + d_{nn'}\frac{\Delta u^2}{2} + \cdots\right). \tag{5}$$

Here

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

The coefficients just introduced are related to those used in the theory of effective operators [13] according to

$$c_{nn'} = A_1, \quad d_{nn'} = 2A_2.$$

In the case of the P branch $\Delta u = -J$, whereas for the R branch $\Delta u = J+1$. Setting $\rho = \hbar^2 I^{-1}$, in which I is the moment of inertia, and applying the theorem of extraneous quantum numbers (3), we obtain

$$c_{nn'} = \frac{1}{(n|\mu|n')}\sum_{m\neq n'}(n|\mu|m)\frac{(m|\rho|n')}{E_{n'} - E_m}. \tag{6}$$

In what follows we disregard centrifugal distortion because it has a minor effect on the rovibrational line intensities. As a result, we ignore the J dependence, if any, of the harmonic frequencies or parameters of mechanical anharmonicity. Our approach, which is based on the use of the theorem of extraneous quantum numbers [20], differs substantially from that conventionally used in the literature. The Herman-Wallis coefficients are generally expressed in terms of an expansion containing the dipole derivatives. The present consideration permits the Herman-Wallis factors to be expressed via the ratio of matrix elements $(n|\mu|m)/(n|\mu|n')$ with $m \neq n'$. As a result, the derivation of the sought coefficients becomes routine because all that we need is to have retained the pertinent nonvanishing terms in the sum (6).

Raising (5) to the second power, we can establish how the coefficients $c_{nn'}, d_{nn'}, \ldots$ relate to the well-known coefficients $C_{nn'}, D_{nn'}, \ldots$ of the canonical Herman-Wallis series

$$|(nJ|\mu|n'J')|^2 = (n|\mu|n')^2(1 + C_{nn'}\Delta u + D_{nn'}\Delta u^2 + \cdots). \tag{7}$$

For instance,

$$C_{nn'} = 2c_{nn'}$$

and

$$D_{nn'} = c_{nn'}^2 + d_{nn'}.$$

III. ALLOWED BANDS OF A POLYATOMIC LINEAR MOLECULE

In the case of polyatomic molecules, the Herman-Wallis expansion must be performed separately for each component of a dipolar moment. We represent the Schrödinger equation for a CO_2 molecule in the form

$$\left(H_{\rm vib} + H_{\rm rot}^0\right)\Psi(nJ) = E_{nJ}\Psi(nJ), \tag{8}$$

in which n means a set of quantum numbers n_1, n_{2x}, n_{2y}, and n_3. Without external perturbation, the rotational Hamiltonian $H_{\rm rot}^0$ is represented as

$$H_{\rm rot}^0 = \frac{\hbar^2 J(J+1)}{2I}.$$

The corresponding rotational wave functions are those of the rigid rotor [5,23,24]

$$\Psi^{\rm rot}(J,K,M) = \sqrt{\frac{2J+1}{4\pi}}D_{M,K}^{(J)*}(\phi,\theta,0). \tag{9}$$

The vibrational Hamiltonian is

$$H_{\rm vib} = H_{\rm vib}^0 + \Delta H_{\rm anh}^{\rm free},$$

in which

$$H_{\rm vib}^0 = \frac{\hbar\omega_1}{2}\left(p_1^2 + q_1^2\right) + \frac{\hbar\omega_{2x}}{2}\left(p_{2x}^2 + q_{2x}^2\right) + \frac{\hbar\omega_{2y}}{2}\left(p_{2y}^2 + q_{2y}^2\right) + \frac{\hbar\omega_3}{2}\left(p_3^2 + q_3^2\right) \tag{10}$$

represents a harmonic Hamiltonian. For each normal mode dimensionless quantities q_s and p_s designate the coordinate and conjugate momentum. Here ω_s is a harmonic frequency. Throughout this paper we use ω and ν to denote the angular frequency and wave numbers, respectively. The subscripts $s = 1$ and $s = 3$ label symmetric and antisymmetric stretching vibrations, respectively, whereas $s = 2$ relates to the bending vibration labeled supplementarily by x and y subscripts in agreement with the respective Cartesian axes of the body-fixed (BF) frame. Here and in the following the axes for the BF reference frame are shown with lowercase letters, whereas these values referring to a laboratory-fixed (LF) frame are shown with respective capital letters. The z axis of the BF frame coincides with the C_∞ symmetry axis of the CO_2 molecule.

In a harmonic representation, the vibrational wave function $\Psi^{\rm vib}(n)$ is factorized as a product $|n_1\rangle|n_{2x}\rangle|n_{2y}\rangle|n_3\rangle$ of four one-dimensional oscillator vectors, whereas in the general case

$$\Psi^{\rm vib}(n) = |n_1, n_{2x}, n_{2y}, n_3). \tag{11}$$

We recall that in an isolated CO_2 molecule the bending vibration is doubly degenerate, but under the action of an intermolecular perturbation the degeneracy of the bending mode is lifted [5,25,26]. For the sake of generality, we leave purposely in (10) the distinction between ω_{2x} and ω_{2y}. Our work focuses in particular on consideration of the rovibrational intensity effects in a collision-induced $\nu_2 + \nu_3$ absorption band in interacting CO_2 molecules, so retaining a distinction between ω_{2x} and ω_{2y} is justified. Before proceeding to the CIA case, we demonstrate how our suggested approach works in the case of permitted fundamental and combination absorption bands of an isolated CO_2 molecule.

We introduce the pertinent laboratory-fixed component of the dipole moment as

$$\mu^{\mathrm{LF}} = \Phi_x\mu_x + \Phi_y\mu_y + \Phi_z\mu_z, \tag{12}$$

in which Φ_j is the direction cosine of the Eckart BF j axis and

$$\mu_j = \sum_s \frac{\partial \mu_j}{\partial q_s} q_s + \frac{1}{2}\sum_{sr} \frac{\partial^2 \mu_j}{\partial q_s \partial q_r} q_s q_r + \cdots \tag{13}$$

is the BF component of the dipole, with $j = x, y, z$. We recall that a linear molecule like CO_2 having $D_{\infty h}$ symmetry lacks a permanent dipolar moment.

A. The ν_3 band

1. *Herman-Wallis factor determined by variation of the moment of inertia*

We begin from an evaluation of the first coefficient $c_{nn'}$ for an allowed ν_3 rovibrational transition in a CO_2 molecule. In this case we involve only the z projection of a dipolar moment in a BF frame, μ_z. According to (6), we obtain, for the first coefficient in the series (5),

$$c_{\nu_3} = \sum_{m\neq 0001} \frac{(0000|\mu_z|m)}{(0000|\mu_z|0001)} \frac{(m|\rho|0001)}{E_{0001} - E_m}. \tag{14}$$

Quantum numbers in (14) correspond to the notation in (11). We retain only the most significant terms in (14) containing, with respect to m states, $|1001\rangle$, $|0201\rangle$, and $|0021\rangle$. All other terms such as, e.g., $|1000\rangle$, $|0100\rangle$, $|0010\rangle$, $|0101\rangle$, and $|2000\rangle$ vanish because of the symmetry requirements. The wave functions that we retain are easily seen to be mixed by Fermi resonance. We consequently introduce these normalized states

$$|F_\pm\rangle = \frac{|1001\rangle}{\sqrt{2}} \pm \frac{|0201\rangle + |0021\rangle}{2} \tag{15}$$

that correspond to the Fermi energies [27] E_+ and E_-, respectively. As in a first approximation

$$\langle 0201|\rho|0001\rangle = 0,$$

$$\langle 0021|\rho|0001\rangle = 0,$$

$$\langle 1001|\rho|0001\rangle = \frac{\partial \rho}{\partial q_1}\langle 1|q_1|0\rangle,$$

and

$$E_{0001} - E_+ \approx E_{0001} - E_- \approx -\hbar\omega_1;$$

then

$$c_{\nu_3} = -\frac{(0000|\mu_z|F_+) + (0000|\mu_z|F_-)}{2\hbar\omega_1(0000|\mu_z|0001)} \frac{\partial \rho}{\partial q_1}. \tag{16}$$

Here we take into account only the linear term in the expression of the moment of inertia as a function of the normal coordinate q_1, that is [10],

$$I = I_0(1 + \lambda_1 q_1)^2,$$

in which

$$I_0 = \frac{M_{\mathrm{O}}}{2} r_{\mathrm{OO}}^2, \quad \lambda_1 = \frac{1}{r_{\mathrm{OO}}}\sqrt{\frac{2\hbar}{M_{\mathrm{O}}\omega_1}} = \sqrt{\frac{2B_e}{\nu_1}},$$

with

$$B_e = \frac{\hbar^2}{2I_0}.$$

The λ_1 value just introduced has the meaning of a dimensionless vibrational amplitude.

In a CO_2 molecule $B_e = 0.3916\ \mathrm{cm}^{-1}$, the harmonic frequency $\nu_1 = 1353.714\ \mathrm{cm}^{-1}$ [28], the mass of atomic oxygen is $M_{\mathrm{O}} = 16$ a.u., and the separation between oxygen atoms is $r_{\mathrm{OO}} = 2r_{\mathrm{CO}} = 2.32$ Å. As a result we have

$$\frac{1}{\hbar\omega_1}\frac{\partial \rho}{\partial q_1} = -2\lambda_1^3 = -2.8 \times 10^{-5}.$$

The matrix elements of least order vanish from the numerator of (14), so the coefficient c_{ν_3} is proportional to the matrix element of a combination band. For this reason the absolute value of c_{ν_3} becomes small. Assuming values $(0000|\mu_z|0001) = 0.473$ D, $(0000|\mu_z|F_+) = 3.38 \times 10^{-2}$ D, and $(0000|\mu_z|F_-) = -2.74 \times 10^{-2}$ D from [28], we achieve the estimated value that we seek: $c_{\nu_3} = -1.88 \times 10^{-7}$. This value disagrees strongly with what was derived experimentally [29]: $c_{\nu_3} = -1.432(82) \times 10^{-4}$. In the next section we show that the Coriolis effect largely determines the first Herman-Wallis correction in this case.

The Coriolis contribution to the ν_3 rotational energy was first estimated by Nielsen [30]. The theory of the Herman-Wallis correction terms in linear molecules was developed in various publications, e.g., [13,16,28,31–33]. In the seminal paper by Watson [13] the effect of a Coriolis interaction in linear molecules was thoroughly considered; taking the Coriolis terms into account was shown to be crucial to achieve agreement between the calculated and observed Herman-Wallis factors for the fundamental bands.

2. *Coriolis effect on the Herman-Wallis factor in the ν_3 band*

To examine how the Coriolis effect impacts rovibrational line intensities we represent the Schrödinger equation in the form

$$\left(H_{\mathrm{vib}} + H_{\mathrm{rot}}^0 + T_{\mathrm{cor}}\right)\Psi_{\mathrm{cor}}(nJ) = E_{nJ}\Psi_{\mathrm{cor}}(nJ), \tag{17}$$

in which kinetic-energy term T_{cor} relevant to Coriolis interaction consists of contributions that relate to the doubly degenerate bending coordinate

$$T_{\mathrm{cor}} = T_{\mathrm{cor}}^x + T_{\mathrm{cor}}^y. \tag{18}$$

Here [23]

$$T_{\mathrm{cor}}^x = -\frac{\hbar}{I_0\sqrt{\omega_2\omega_3}}(\omega_2 q_3 p_{2y} - \omega_3 q_{2y} p_3)J_x \tag{19}$$

and

$$T_{\mathrm{cor}}^y = \frac{\hbar}{I_0\sqrt{\omega_2\omega_3}}(\omega_2 q_3 p_{2x} - \omega_3 q_{2x} p_3)J_y. \tag{20}$$

The Coriolis coupling parameter ζ is set to $+1$ in (19) and -1 in (20) because we are dealing with the case of a symmetric triatomic molecule [13]. In this section we consider an isolated monomer only, so we assume $\omega_{2x} = \omega_{2y} = \omega_2$. Besides opposite signs, expressions (19) and (20) differ only by the interchange of x and y coordinates. We hence consider below only one term T_{cor}^y in detail.

According to the above relations, kinetic energy is parametrized with components of angular momentum; the theorem of extraneous quantum numbers is hence applicable. In this case we apply the theorem as if it were valid not only for the quantum numbers but also for the operators themselves. For the wave function we have

$$\Psi_{\rm cor}(nJ) = |nJ\rangle + J_y|nJ, 1\rangle + \cdots .$$

This relation must be understood as that quantity J_y is by no means a c number in the Dirac notation. Instead, it acts directly on $|nJ, 1\rangle$ to obtain a correction due to a vibration-rotation interaction. Applying the theorem (3) to the operator J_y, we replace u by J_y and ρ by $\frac{\hbar}{I_0\sqrt{\omega_2\omega_3}}(\omega_2 q_3 p_{2x} - \omega_3 q_{2x} p_3)$. As a result, in the first order with respect to J_y we obtain, in agreement with (4),

$$\begin{aligned}|nJ, 1\rangle &= \left.\frac{\partial\Psi_{\rm cor}(nJ)}{\partial J_y}\right|_{J_y=0}\\ &= \frac{\hbar}{I_0\sqrt{\omega_2\omega_3}}\sum_{m\neq n}\frac{\langle m|(\omega_2 q_3 p_{2x} - \omega_3 q_{2x} p_3)|n\rangle}{E_n - E_m}|mJ\rangle\\ &= \Psi^{\rm rot}(J, K, M)|n, 1\rangle, \qquad (21)\end{aligned}$$

in which $\Psi^{\rm rot}$ is the wave function of a rigid rotor (9); the first-order correction to the harmonic vibrational wave function becomes

$$\begin{aligned}|n, 1\rangle = {}&[\sqrt{(n_{2x}+1)(n_3+1)}|n_1, n_{2x}+1, n_{2y}, n_3+1\rangle\\ &+ \sqrt{n_{2x}n_3}|n_1, n_{2x}-1, n_{2y}, n_3-1\rangle]\\ &\times \frac{i}{2I_0\sqrt{\omega_2\omega_3}}\left(\frac{\omega_3-\omega_2}{\omega_2+\omega_3}\right)\\ &+ [\sqrt{(n_{2x}+1)n_3}|n_1, n_{2x}+1, n_{2y}, n_3-1\rangle\\ &+ \sqrt{n_{2x}(n_3+1)}|n_1, n_{2x}-1, n_{2y}, n_3+1\rangle]\\ &\times \frac{i}{2I_0\sqrt{\omega_2\omega_3}}\left(\frac{\omega_2+\omega_3}{\omega_3-\omega_2}\right). \qquad (22)\end{aligned}$$

Thus, restricting to the first order, we obtain

$$\Psi_{\rm cor}(nJ) = |nJ\rangle + J_y\Psi^{\rm rot}|n, 1\rangle, \qquad (23)$$

and the corresponding matrix element of a component of dipolar moment (12) is

$$\begin{aligned}&\langle\Psi_{\rm cor}(nJ)|\mu^{\rm LF}|\Psi_{\rm cor}(n'J')\rangle\\ &\quad = \langle nJ|\mu^{\rm LF}|n'J'\rangle + \left\langle\Psi_i^{\rm rot}\middle|\mathfrak{m}\middle|\Psi_f^{\rm rot}\right\rangle + \cdots , \qquad (24)\end{aligned}$$

in which

$$\langle nJ|\mu^{\rm LF}|n'J'\rangle = \left\langle\Psi_i^{\rm rot}\middle|\langle n|\mu^{\rm LF}|n'\rangle\middle|\Psi_f^{\rm rot}\right\rangle \qquad (25)$$

is the matrix element for the transition moment with no vibration-rotation coupling,

$$\mathfrak{m} = \langle n, 1|J_y\Phi_x\mu_x|n'\rangle + \langle n|\mu_x\Phi_x J_y|n', 1\rangle \qquad (26)$$

is the operator that corresponds to the effective dipolar-moment operator in Watson's theory [13], and

$$\Psi_i^{\rm rot} = \Psi^{\rm rot}(J, K, M), \qquad \Psi_f^{\rm rot} = \Psi^{\rm rot}(J', K', M').$$

Setting

$$J_y\Phi_x = \tfrac{1}{2}\{J_y, \Phi_x\} + \tfrac{1}{2}[J_y, \Phi_x]$$

and

$$\Phi_x J_y = \tfrac{1}{2}\{J_y, \Phi_x\} - \tfrac{1}{2}[J_y, \Phi_x],$$

in which the anticommutator and commutator are denoted by $\{\ldots, \ldots\}$ and $[\ldots, \ldots]$, respectively, we obtain

$$\mathfrak{m} = \frac{\{J_y, \Phi_x\}}{2}(\langle n, 1|\mu_x|n'\rangle + \langle n|\mu_x|n', 1\rangle). \qquad (27)$$

Only the terms containing anticommutators are retained in expression (27) as only these terms in (26) depend on the rotational operator J_y. The commutators are expressible via the BF direction cosines, for instance, $[J_y, \Phi_x] = i\hbar\Phi_z$. The commutator terms hence are disregarded while calculating the first Herman-Wallis correction factors; the relevant part of the dipole-moment operator has a purely vibrational nature.

For band ν_3 we have $n_3' = 1$, whereas $n_1 = n_{2x} = n_{2y} = n_3 = n_1' = n_{2x}' = n_{2y}' = 0$. Using (22), we find

$$\mathfrak{m} = \frac{i}{I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2 - \omega_2^2}\langle 0000|\mu_x|0100\rangle\{J_y, \Phi_x\}. \qquad (28)$$

We proceed to find the $\mathfrak{m}^\star$ component following the transformations with $T_{\rm cor}^x$ (19) analogous to what has been done with $T_{\rm cor}^y$ (20). Equation (23) transforms thus into

$$\Psi_{\rm cor}(nJ) = |nJ\rangle + J_y\Psi^{\rm rot}|n, 1\rangle - J_x\Psi^{\rm rot}|n, 1\rangle^\star. \qquad (29)$$

Here the starred vector $|n, 1\rangle^\star$ is determined according to (22), in which x is replaced with y. The corresponding complete matrix element becomes of form

$$\begin{aligned}\langle\Psi_{\rm cor}(nJ)|\mu^{\rm LF}|\Psi_{\rm cor}(n'J')\rangle &= \langle nJ|\mu^{\rm LF}|n'J'\rangle\\ &\quad + \left\langle\Psi_i^{\rm rot}\middle|(\mathfrak{m} + \mathfrak{m}^\star)\middle|\Psi_f^{\rm rot}\right\rangle + \cdots , \qquad (30)\end{aligned}$$

in which

$$\mathfrak{m}^\star = -\frac{i}{I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2 - \omega_2^2}\langle 0000|\mu_y|0010\rangle\{J_x, \Phi_y\}. \qquad (31)$$

Noting that

$$\langle 0000|\mu_x|0100\rangle = \langle 0000|\mu_y|0010\rangle,$$

$$i\hbar(\{J_y, \Phi_x\} - \{J_x, \Phi_y\}) = \left[\Phi_z, J_x^2 + J_y^2\right],$$

and $K = K'$, the element $\langle\Psi_i^{\rm rot}|(\mathfrak{m} + \mathfrak{m}^\star)|\Psi_f^{\rm rot}\rangle$ is equal to $\frac{2\hbar}{I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\langle 0000|\mu_x|0100\rangle\mathfrak{F}_z\Delta u$, in which

$$\mathfrak{F}_z = \left\langle\Psi_i^{\rm rot}\middle|\Phi_z\middle|\Psi_f^{\rm rot}\right\rangle.$$

Summation of $|\mathfrak{F}_z|^2$ with respect to M and M' yields a Hönl-London factor that is accurate within a constant factor [24]. As $\frac{\hbar^2}{2I_0} = B_e$ and

$$\langle nJ|\mu^{\rm LF}|n'J'\rangle = \langle 0000|\mu_z|0001\rangle\mathfrak{F}_z,$$

we find eventually

$$\begin{aligned}&\langle\Psi_{\rm cor}(nJ)|\mu^{\rm LF}|\Psi_{\rm cor}(n'J')\rangle\\ &\quad = \langle 0000|\mu_z|0001\rangle\mathfrak{F}_z(1 + c_{\nu_3}\Delta u), \qquad (32)\end{aligned}$$

in which

$$c_{\nu_3} = \frac{4B_e}{\hbar}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\frac{\langle 0000|\mu_x|0100\rangle}{\langle 0000|\mu_z|0001\rangle} \tag{33}$$

or

$$c_{\nu_3} = 4B_e\frac{\sqrt{\nu_2\nu_3}}{\nu_3^2-\nu_2^2}\frac{\mu_2'}{\mu_3'}, \tag{34}$$

in which μ_2' and μ_3' are the dipole derivatives with respect to normal coordinates q_2 and q_3. The formula (34) is identical to what Watson obtained [13]. To estimate numerically this coefficient we insert the following values from [13]: $\nu_1 = 1353.714\ \text{cm}^{-1}$, $\nu_2 = 672.743\ \text{cm}^{-1}$, $\nu_3 = 2396.445\ \text{cm}^{-1}$, $\mu_2' = -0.169$ D, and $\mu_3' = 0.473$ D. After substitution of these values into (34) we obtain $c_{\nu_3} = -1.34 \times 10^{-4}$, i.e., the value reported previously in [13]. This value agrees satisfactorily with the experimental value

$$-1.432(82) \times 10^{-4}$$

obtained in [29].

B. The ν_2 band

For the ν_2 band we might have either $n_{2x}' = 1$ or $n_{2y}' = 1$, whereas $n_1 = n_{2x} = n_{2y} = n_3 = n_1' = n_3' = 0$. In general, the wave function of a degenerate bending mode is a mixture of two wave functions relevant to individual vibrations in the xz and yz planes. We consider first the case $n_{2x}' = 1$. Using the formulas (12) and (22), we obtain

$$\begin{aligned}\langle\Psi_{\text{cor}}(nJ)|\mu^{\text{LF}}|\Psi_{\text{cor}}(n'J')\rangle \\ = \langle nJ|\mu^{\text{LF}}|n'J'\rangle + \big\langle\Psi_i^{\text{rot}}\big|\mathfrak{m}^{(x)}\big|\Psi_f^{\text{rot}}\big\rangle + \cdots ,\end{aligned} \tag{35}$$

in which

$$\begin{aligned}\mathfrak{m}^{(x)} &= \frac{i}{I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\langle 0000|\mu_z|0001\rangle\{J_y,\Phi_z\} \\ &= \frac{i\mu_3'}{\sqrt{2}I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\{J_y,\Phi_z\}.\end{aligned} \tag{36}$$

We find analogously the pertinent effective dipole matrix element for the case $n_{2y}' = 1$:

$$\mathfrak{m}^{(y)} = -\frac{i\mu_3'}{\sqrt{2}I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\{J_x,\Phi_z\}. \tag{37}$$

To consider a general case we proceed as follows, introducing a new operator

$$\mathfrak{m}^{(xy)} = \frac{i\mu_3'}{I_0}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}(\{q_{2x}J_y,\Phi_z\} - \{q_{2y}J_x,\Phi_z\}) \tag{38}$$

that yields exact expressions for both (36) and (37), required for the calculation of vibrational matrix elements $\langle 0000|\cdots|0100\rangle$ and $\langle 0000|\cdots|0010\rangle$, respectively. As

$$\begin{aligned}i\hbar(\{q_{2x}J_y,\Phi_z\} - \{q_{2y}J_x,\Phi_z\}) \\ = -\big[q_{2x}\Phi_x + q_{2y}\Phi_y, J_x^2 + J_y^2\big]\end{aligned} \tag{39}$$

and

$$\begin{aligned}\big\langle\Psi_i^{\text{rot}}\big|\big[q_{2x}\Phi_x + q_{2y}\Phi_y, J_x^2 + J_y^2\big]\big|\Psi_f^{\text{rot}}\big\rangle \\ = \big\langle\Psi_i^{\text{rot}}\big|(q_{2x}\Phi_x + q_{2y}\Phi_y)\big|\Psi_f^{\text{rot}}\big\rangle \\ \times [J'(J'+1) - K'^2 - J(J+1) + K^2],\end{aligned} \tag{40}$$

then

$$\begin{aligned}\big\langle\Psi_i^{\text{rot}}\big|\mathfrak{m}^{(xy)}\big|\Psi_f^{\text{rot}}\big\rangle = -\frac{2\mu_3'}{I_0}\frac{\hbar\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\Delta u \\ \times\big\langle\Psi_i^{\text{rot}}\big|(q_{2x}\Phi_x + q_{2y}\Phi_y)\big|\Psi_f^{\text{rot}}\big\rangle + \cdots ,\end{aligned} \tag{41}$$

in which we write explicitly only the term that contributes to the first Herman-Wallis coefficient. To return to (35), in which the corresponding vibrational matrix element is suggested to be calculated, we must find the matrix element from $\langle\Psi_i^{\text{rot}}|\mathfrak{m}^{(xy)}|\Psi_f^{\text{rot}}\rangle$ between the vibrational ground state $|n\rangle = |0000\rangle$ and excited state $|\mathfrak{n}'\rangle$ involved in the degenerate bending vibration. Here we use the denotation $\mathfrak{n}'$ to emphasize that the excited state relates to a combination of n_{2x}' and n_{2y}' with phases that we do not define concretely. We rewrite (35) as

$$\begin{aligned}\langle\Psi_{\text{cor}}(nJ)|\mu^{\text{LF}}|\Psi_{\text{cor}}(\mathfrak{n}'J')\rangle \\ = \langle nJ|\mu^{\text{LF}}|\mathfrak{n}'J'\rangle + \langle n|\big\langle\Psi_i^{\text{rot}}\big|\mathfrak{m}^{(xy)}\big|\Psi_f^{\text{rot}}\big\rangle|\mathfrak{n}'\rangle + \cdots ,\end{aligned} \tag{42}$$

in which for a perpendicular band μ^{LF} is reduced to $\Phi_x\mu_x + \Phi_y\mu_y$ or, in a harmonic approximation, $\mu_2'(q_{2x}\Phi_x + q_{2y}\Phi_y)$. Combining (41), (42), and the quantity $\mu_2'\langle n|\langle\Psi_i^{\text{rot}}|(q_{2x}\Phi_x + q_{2y}\Phi_y)|\Psi_f^{\text{rot}}\rangle|\mathfrak{n}'\rangle$, which is equal to $\langle nJ|\mu^{\text{LF}}|\mathfrak{n}'J'\rangle$, we obtain

$$\begin{aligned}\langle\Psi_{\text{cor}}(nJ)|\mu^{\text{LF}}|\Psi_{\text{cor}}(\mathfrak{n}'J')\rangle \\ = \langle nJ|\mu^{\text{LF}}|\mathfrak{n}'J'\rangle(1 + c_{\nu_2}\Delta u),\end{aligned} \tag{43}$$

in which

$$c_{\nu_2} = -\frac{4B_e}{\hbar}\frac{\sqrt{\omega_2\omega_3}}{\omega_3^2-\omega_2^2}\frac{\mu_3'}{\mu_2'}. \tag{44}$$

Hence

$$c_{\nu_2} = -4B_e\frac{\sqrt{\nu_2\nu_3}}{\nu_3^2-\nu_2^2}\frac{\mu_3'}{\mu_2'}. \tag{45}$$

Substituting here the set of molecular parameters reported at the end of the preceding section, we obtain the numerical value $c_{\nu_2} = 10.4 \times 10^{-4}$. This value agrees satisfactorily with the values $c_{\nu_2} = 10.52 \times 10^{-4}$ and 9.64×10^{-4}, cited in [13,34], respectively. A comparison of (34) and (45) shows that the latter is obtainable from the former (or vice versa) by simply interchanging subscripts 3 ↔ 2.

C. The $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ bands

The linear term in the Herman-Wallis expansion largely dominates over the quadratic and higher-order terms in the case of fundamental transitions considered in the previous sections. The bands associated with vibration-rotation resonances were shown by Watson [35] to have a significantly more important contribution from the quadratic $d_{nn'}\Delta u^2/2$ part. The dominance of the quadratic term is evident from an analysis of experimental data reported by Johns [29]. In this section, despite the importance of quadratic factors, we restrict ourselves to examine only linear terms in the Herman-Wallis expansion for the Fermi-coupled bands $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$. The reasons for this restriction are that we intend to expand somewhat the presentation of our theoretical approach and that this example is instructive for further consideration of the vibration-rotation intensity effect in the combination CIA band.

Combination bands $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ originate from the two states ν_1 and $2\nu_2$ coupled by Fermi resonance. The relevant wave functions mixed by Fermi resonance are denoted by $|F_+)$ and $|F_-)$ to emphasize that, in contrast to (15), these functions remain operative even beyond a harmonic approximation. The matrix elements for both transitions are expandable up to the first Herman-Wallis correction in the form

$$(0000, J|\mu_i|F_\pm, J') = (0000|\mu_i|F_\pm)(1 + c^i_{F_\pm}\Delta u). \tag{46}$$

The dipolar moment μ^{LF} (12) has three components in the LF frame. For a linear molecule we must consequently distinguish between a parallel absorption band, which is associated with component μ_z, and a perpendicular band, which relates to components μ_x and μ_y. We consider first the perpendicular band issued from dipole projection μ_x. We have

$$\begin{aligned} c^x_{F_\pm} &= \sum_{m\neq F_\pm} \frac{(0000|\mu_x|m)}{(0000|\mu_x|F_\pm)} \frac{(m|\rho|F_\pm)}{E_\pm - E_m} \\ &= \frac{(0000|\mu_x|0100)}{(0000|\mu_x|F_\pm)} \frac{(0100|\rho|F_\pm)}{\hbar(\omega_2+\omega_3)}. \end{aligned} \tag{47}$$

Because

$$(0100|\rho|F_\pm) \approx \frac{\langle 0100|\rho|0201\rangle}{\sqrt{2}},$$

the inverse moment of inertia ρ fails to comprise simultaneously both q_{2x} and q_3. In the harmonic approximation $(0100|\rho|F_\pm) = 0$ and $c^x_{F_\pm} = 0$.

To evaluate the influence of the vibration-rotational interaction on dipole matrix elements, it suffices to consider only the parallel contribution. Equation (6) enables us to derive directly the expressions for both Herman-Wallis coefficients

$$\begin{aligned} c^z_{F_\pm} &= \sum_{m\neq F_\pm} \frac{(0000|\mu_z|m)}{(0000|\mu_z|F_\pm)} \frac{(m|\rho|F_\pm)}{E_\pm - E_m} \\ &= \frac{(0000|\mu_z|0001)}{(0000|\mu_z|F_\pm)} \frac{1}{2\hbar\omega_1} \frac{\partial\rho}{\partial q_1} \\ &= -\frac{(0000|\mu_z|0001)}{(0000|\mu_z|F_\pm)} \lambda_1^3, \end{aligned} \tag{48}$$

in which

$$(0001|\rho|F_\pm) \approx \frac{\langle 0001|\rho|1001\rangle}{\sqrt{2}};$$

λ_1 has the meaning of vibrational amplitude and has thus a positive value. The qualitative effect of the rovibrational correction depends on the signs of the matrix elements in the numerator and denominator of (48). Provided the signs of both matrix elements are the same, the correction causes line intensities within the P branch to increase and those within the R branch to decrease.

To evaluate the coefficients in question we apply the values λ_1^3 and $(0000|\mu_z|0001)$ cited in the preceding section and borrow the denominator of (48) from [29], i.e., $(0000|\mu_z|F_\pm)^2 = 0.001\,084$ D^2 or $0.000\,722$ D^2, for two values of matrix elements, respectively. We hence evaluate the absolute values $c_{F_\pm} = 2.46 \times 10^{-4}$ and 2.01×10^{-4}. These values must be compared with experimental data from [29] (see also [36]): $c_{F_\pm} = 1.02(14) \times 10^{-4}$ and $0.37(18) \times 10^{-4}$. Although both sets of values appear to be somewhat overestimated in our calculations compared to experiment, we bear in mind that our estimate is made in a first approximation only. We thus suggest that the correspondence between both calculated and experimental coefficients is almost as satisfactory for the considered combination bands as it is for the fundamental bands.

IV. COLLISION-INDUCED CO$_2$ $\nu_2 + \nu_3$ BAND

To interpret the phenomenon of rovibrational interaction in the CIA spectrum of a linear molecule it suffices to examine only one component of the induced dipolar moment in the laboratory-fixed frame of reference. Choosing for this purpose the Z component, in terms of spherical tensor operators for which $\mu_Z^{\mathrm{LF}} = \mu_0^{\mathrm{LF}}$ we have [24]

$$\mu_0^{\mathrm{LF}} = \sum_{\Omega'=0,\pm1} D^{(1)*}_{0,\Omega'}(\phi,\theta,0)\mu^{\mathrm{BF}}_{\Omega'}. \tag{49}$$

The corresponding BF components, represented through Cartesian BF μ^{ind} projections labeled with x, y, and z, are

$$\mu_0^{\mathrm{BF}} = \mu_z^{\mathrm{ind}}, \quad \mu_{\pm1}^{\mathrm{BF}} = \frac{1}{\sqrt{2}}\left(\mp\mu_x^{\mathrm{ind}} - i\mu_y^{\mathrm{ind}}\right).$$

The z axis of the BF frame coincides with the symmetry axis C_∞ of a CO$_2$ molecule.

Note that in this section we choose to consider the CIA rovibrational intensities expressed via the effective dipole moment components (see [5] for details) in order to maintain consistency with the theory of allowed transitions as developed in the precedent sections. In reality, the vector of the permanent dipole transforms according to the irreducible $D^{(1)}$ representation, whereas the induced dipole components transform in agreement with their genesis from molecular polarizability, which is the second-rank tensor. As a result, the rotationally invariant component of the polarizability has to transform in agreement with the fully symmetrical $D^{(0)}$ representation, whereas other components have to follow the $D^{(2)}$ representation. The above-mentioned distinction affects somewhat the Hönl-London rotational factors [5], although it is irrelevant to rovibrational Herman-Wallis factors, which are considered in the present paper.

Using the rotational wave functions (9), we readily calculate the rotational matrix elements

$$\begin{aligned} &\langle\Psi^{\mathrm{rot}}(J,K,M)|D^{(1)*}_{0,\Omega'}|\Psi^{\mathrm{rot}}(J',K',M')\rangle \\ &\quad = (-1)^{M-K}\sqrt{(2J+1)(2J'+1)} \\ &\quad\quad \times \begin{pmatrix} J' & 1 & J \\ M' & 0 & -M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \Omega' & -K \end{pmatrix}. \end{aligned} \tag{50}$$

In general, two possibilities must be considered, which correspond to $\Delta K = K' - K$ equal either ±1 or 0; we hence have either perpendicular or parallel bands, respectively. Both parallel and perpendicular subbands are capable of manifesting themselves in the combination transition. In this respect the CIA band $\nu_2 + \nu_3$ differs substantially from the allowed fundamental bands considered above, for which ν_2 is a perpendicular band and ν_3 is a parallel band.

Another distinction from the case of an allowed bands arises because the intensity of a CIA band is entirely determined by the perturbation caused by an intermolecular interaction. The observed CIA intensity is hence a result of the statistical average over a broad ensemble of pair states, no part of which in general warrants neglect. We must consequently bear in mind that the respective CIA matrix elements are no longer considered in terms of static molecular parameters characteristic of an isolated molecule; these values instead vary as a function of coordinates describing the instantaneous spatial positions of the interacting molecules. In what follows, we assume that the matrix elements for CIA, as well as all other values which vanish in the absence of an intermolecular perturbation, are effective parameters that arise from a statistical averaging over all available pair states.

A. Perpendicular contribution

We first consider a perpendicular contribution with its respective selection rule $\Delta K = \pm 1$. In this case we calculate the vibrational matrix element from either μ_{+1}^{ind} or μ_{-1}^{ind}, which is parametrically affected by a rotational movement. As both μ_{+1}^{ind} and μ_{-1}^{ind} include μ_x^{ind} and μ_y^{ind}, one might consider the general expression

$$\begin{aligned}(nJ|\mu_i^{\mathrm{ind}}|n'J') \\ = (n|\mu_i^{\mathrm{ind}}|n')\left(1 + c_{nn'}^i \Delta u + d_{nn'}^i \frac{\Delta u^2}{2} + \cdots\right),\end{aligned} \tag{51}$$

which is a natural extension of a Herman-Wallis series to induced-absorption spectra. In this exotic case the analogs of the Herman-Wallis coefficients are readily obtained with the theorem of extraneous quantum numbers (3)

$$c_{nn'}^i = \frac{1}{(n|\mu_i^{\mathrm{ind}}|n')} \sum_{m \neq n'} (n|\mu_i^{\mathrm{ind}}|m) \frac{(m|\rho|n')}{E_{n'} - E_m} \tag{52}$$

and

$$d_{nn'}^i = \frac{(nJ|\mu_i^{\mathrm{ind}} \frac{\partial^2}{\partial u^2}|n'J)}{(n|\mu_i^{\mathrm{ind}}|n')}. \tag{53}$$

Higher-order terms can be obtained in a similar way, although such an extension is superfluous for the sake of the present work.

We consider the first $c_{nn'}^i$ coefficient in (51) in detail taking the CO$_2$ CIA band $\nu_2 + \nu_3$ as an example. We restrict ourselves to consider only the x component of the bending vibration involved in this combination band. In this case the matrix elements for either μ_{+1}^{ind} or μ_{-1}^{ind} reduce obviously to the matrix element for μ_x^{ind}. We have

$$c_{\nu_2+\nu_3}^x = \frac{(0000|\mu_x|0100)}{(0000|\mu_x^{\mathrm{ind}}|0101)} \frac{(0100|\rho|0101)}{E_{0101} - E_{0100}}. \tag{54}$$

Here $(0000|\mu_x^{\mathrm{ind}}|0101)$ is the matrix element for an induced dipole transition and $(0000|\mu_x|0100)$ is the matrix element for a ν_2 allowed transition. The matrix element of ρ, $(0100|\rho|0101)$, vanishes unless a molecule is subject to an intermolecular perturbation. In a harmonic representation it suffices to restrict the function ρ to

$$\rho = \frac{\partial \rho}{\partial q_1} q_1 = -4 B_e \lambda_1 q_1.$$

An external perturbation breaks the initial symmetry of an isolated linear molecule so that harmonic frequencies of a perturbed molecule slightly alter; a harmonic vibrational potential can thus be written as $\frac{\hbar\omega_1'}{2} q_1'^2 + \frac{\hbar\omega_{2x}'}{2} q_{2x}'^2 + \frac{\hbar\omega_{2y}'}{2} q_{2y}'^2 + \frac{\hbar\omega_3'}{2} q_3'^2$. The new vibrational coordinates are related to the initial variables through the linear combinations with the pertinent expansion coefficients $b_{s',s}$:

$$q_{s'}' = b_{s',1} q_1 + b_{s',2x} q_{2x} + b_{s',2y} q_{2y} + b_{s',3} q_3.$$

For the potential energy expressed in the initial, i.e., unperturbed, coordinates we hence have $\frac{\hbar\omega_1}{2} q_1^2 + \frac{\hbar\omega_{2x}}{2} q_{2x}^2 + \frac{\hbar\omega_{2y}}{2} q_{2y}^2 + \frac{\hbar\omega_3}{2} q_3^2 + \Delta H_{\mathrm{anh}}^{\mathrm{ind}}$, in which

$$\Delta H_{\mathrm{anh}}^{\mathrm{ind}} = a_{12} q_1 q_{2x} + a_{13} q_1 q_3 + a_{23} q_{2x} q_3 + \cdots . \tag{55}$$

We focus on only the x component of the bending vibration for the perpendicular subband and on the z component for the parallel subband. We consequently consider only this part $a_{12} q_1 q_{2x} + a_{13} q_1 q_3$ of $\Delta H_{\mathrm{anh}}^{\mathrm{ind}}$, because the former and the latter make $(0001|\rho|0101)$ and $(0100|\rho|0101)$ not vanish. To find a first-order correction to a vibrational wave function we apply the perturbation theory in its formalism of polynomials of quantum numbers, which is described in detail in [17,20,22]. As a result we have

$$\begin{aligned}|n_1, n_{2x}, n_{2y}, n_3) = {} & |n_1, n_{2x}, n_{2y}, n_3\rangle + \frac{a_{12}}{2\hbar}\left(\frac{\sqrt{n_1 n_{2x}}}{\omega_1 + \omega_{2x}} |n_1 - 1, n_{2x} - 1, n_{2y}, n_3\rangle + \frac{\sqrt{(n_1+1) n_{2x}}}{-\omega_1 + \omega_{2x}} |n_1 + 1, n_{2x} - 1, n_{2y}, n_3\rangle \right. \\ & \left. + \frac{\sqrt{n_1 (n_{2x}+1)}}{\omega_1 - \omega_{2x}} |n_1 - 1, n_{2x} + 1, n_{2y}, n_3\rangle + \frac{\sqrt{(n_1+1)(n_{2x}+1)}}{-\omega_1 - \omega_{2x}} |n_1 + 1, n_{2x} + 1, n_{2y}, n_3\rangle \right) \\ & + \frac{a_{13}}{2\hbar}\left(\frac{\sqrt{n_1 n_3}}{\omega_1 + \omega_3} |n_1 - 1, n_{2x}, n_{2y}, n_3 - 1\rangle + \frac{\sqrt{(n_1+1) n_3}}{-\omega_1 + \omega_3} |n_1 + 1, n_{2x}, n_{2y}, n_3 - 1\rangle \right. \\ & \left. + \frac{\sqrt{n_1 (n_3+1)}}{\omega_1 - \omega_3} |n_1 - 1, n_{2x}, n_{2y}, n_3 + 1\rangle + \frac{\sqrt{(n_1+1)(n_3+1)}}{-\omega_1 - \omega_3} |n_1 + 1, n_{2x}, n_{2y}, n_3 + 1\rangle \right).\end{aligned} \tag{56}$$

Consequently,

$$(0100|\rho|0101) = \frac{\omega_1 a_{13}}{\sqrt{2}\hbar\left(\omega_3^2 - \omega_1^2\right)}$$

and

$$c^x_{\nu_2+\nu_3} = -2\sqrt{2}\frac{a_{13}B_e\omega_1\lambda_1}{\hbar^2\omega_3\left(\omega_3^2 - \omega_1^2\right)}\frac{(0000|\mu_x|0100)}{(0000|\mu_x^{\mathrm{ind}}|0101)} \tag{57}$$

or

$$c^x_{\nu_2+\nu_3} = -2\sqrt{2}\frac{a_{13}B_e\nu_1\lambda_1}{\nu_3\left(\nu_3^2 - \nu_1^2\right)}\frac{(0000|\mu_x|0100)}{(0000|\mu_x^{\mathrm{ind}}|0101)}. \tag{58}$$

In the latter expression the quantities a_{13}, B_e, ν_1, and ν_3 are in cm^{-1}.

The pronounced skewness between P and R branches is obviously expected because the matrix element for a weakly induced transition in the denominator of (58) is significantly less than that of a dipole-allowed transition in the respective numerator. We pay attention, however, to the smallness of the a_{13} mixed derivative, which is strictly equal to zero in the absence of an external perturbation.

B. Parallel contribution

For the parallel contribution $\Delta K = 0$. We take into account the z component of the dipole moment to find the matrix element

$$(nJ|\mu_z^{\mathrm{ind}}|n'J') = (n|\mu_z^{\mathrm{ind}}|n')\left(1 + c^z_{nn'}\Delta u\right), \tag{59}$$

with

$$c^z_{\nu_2+\nu_3} = \frac{(0000|\mu_z|0001)}{(0000|\mu_z^{\mathrm{ind}}|0101)}\frac{(0001|\rho|0101)}{E_{0101} - E_{0001}}. \tag{60}$$

Here, only the term $a_{12}q_1q_{2x}$ in $\Delta H^{\mathrm{ind}}_{\mathrm{anh}}$ makes $(0001|\rho|0101)$ not vanish. Applying (56), we obtain

$$(0001|\rho|0101) = -\frac{\omega_1 a_{12}}{\sqrt{2}\hbar\left(\omega_1^2 - \omega_{2x}^2\right)}.$$

As a result,

$$c^z_{\nu_2+\nu_3} = 2\sqrt{2}\frac{a_{12}B_e\omega_1\lambda_1}{\hbar^2\omega_{2x}\left(\omega_1^2 - \omega_{2x}^2\right)}\frac{(0000|\mu_z|0001)}{(0000|\mu_z^{\mathrm{ind}}|0101)} \tag{61}$$

or

$$c^z_{\nu_2+\nu_3} = 2\sqrt{2}\frac{a_{12}B_e\nu_1\lambda_1}{\nu_{2x}\left(\nu_1^2 - \nu_{2x}^2\right)}\frac{(0000|\mu_z|0001)}{(0000|\mu_z^{\mathrm{ind}}|0101)}, \tag{62}$$

in which a_{12}, B_e, ν_1, and ν_{2x} are expressed in cm^{-1}. Here again we emphasize the opportunity of an important distortion between the line intensities within P and R branches, which is likely to exceed significantly the effect of conventional Hönl-London factors. Also, analogously to the case of perpendicular transitions, the smallness of the a_{12} derivative is able to mitigate somewhat the effect of the enhanced ratio of allowed and induced matrix elements.

V. DISCUSSION

In this work we consider how the rovibrational interaction in linear molecules affects the distribution of the intensities of absorption lines within P and R rotational branches. These line intensities are known to be determined primarily by the respective selection rules and thermal populations of initial and final states of a rovibrational transition. In a first approximation the distribution of intensity is governed by the Hönl-London factors that are functions of the quantum numbers for angular momentum and its projection. Herman and Wallis [12] first suggested that taking into account the rovibrational interaction, which modifies the intensity distribution, can be implemented on multiplying the vibrational transition matrix element by a factor which can be cast into a series against increasing powers of Δu. Only the first two terms in this series suffice conventionally to achieve desirable agreement with the measured data. The effect of the correction of the unperturbed intensity distribution is thus determined by the magnitude of the first two coefficients in the Herman-Wallis expansion.

We have reformulated the existing theory to calculate the Herman-Wallis factors through the so-called theorem of extraneous quantum numbers [19]. The advantage of this approach consists in making the calculations significantly easier, to such an extent that the derivation of the Herman-Wallis factors becomes routine.

In the first part of our work we focused on the calculation of the Herman-Wallis factors for allowed absorption bands in a CO_2 molecule. The opportunity has arisen to apply the theorem of extraneous quantum numbers to operators instead of quantum numbers themselves. The theorem was initially developed in [18–20,22] to calculate vibrational matrix elements parametrized by a rotational quantum number (called at that time extraneous). In the present work we showed that the theorem is valid also provided that vibrational matrix elements are parametrized with an operator. In the case we considered, the angular momentum, which is involved in a Coriolis interaction, plays the role of such an operator. As a result, we obtained the first Herman-Wallis coefficients arising from Coriolis interaction. The contribution from the modulation of the moment of inertia by the vibrational movement is shown to have an almost negligible effect on the Herman-Wallis coefficients. Our obtained expressions coincide with those derived earlier by Watson [13]. The corresponding factors agree satisfactorily with observations.

In the second part of this work we extended our theory to the case of a collision-induced absorption band. We remark that the effect of rovibrational interaction on the line intensities was considered in a number of publications (see, e.g., [14]) dedicated to analysis of the diatomic Raman spectra, for which the rotational selection rules are similar to the CIA case. However, this effect was never investigated in much detail and relevant analytic theory is worth improving. An extension of our theory to CIA might seem somewhat ill-grounded because the CIA spectra, beyond minor exclusions, do not demonstrate the traces of individual rovibrational lines. The envelope of a CIA rovibrational band is known to be roughly decomposable into individual rotational branches, in agreement with convention for the CIA selection rule $\Delta J = 0, \pm 2$. Baranov [1] first suggested that the band $\nu_2 + \nu_3$ of CO_2 has a pronounced contribution from the lines obeying $\Delta J = \pm 1$ selection rules, thus forming P and R branches. This *ad hoc* idea was supported theoretically in [5] by presupposing a virtually free rotation of CO_2 molecules interacting with each other. Although this assumption obviously is not entirely justified, we adopted it in terms of a reasonable hypothesis, which is valid at least in the vicinity of room temperature. We have introduced a series (51) which is an analog of a conventional Herman-Wallis expansion. We suggested further that the vibrational wave functions are affected by the rotational movement via a variation of the moment of inertia of a CO_2 molecule. As a result, we concluded that the first coefficient of Herman-Wallis type for the CIA band $\nu_2 + \nu_3$ is proportional to the ratio of two rovibrational transition matrix elements as it occurs for allowed transitions. In this case, however, we have a weak matrix element of the CIA transition in the denominator, whereas the matrix element for an allowed transition appears in the numerator. As a result, we expect a pronounced distortion of the line intensities in the *P* and *R* branches. We emphasize, however, that the final effect is mitigated by small force constants a_{13} and a_{12} in (58) and (62).

In contrast to induction in diatomic molecules, the effect of an externally applied perturbation might have multifarious consequences in the case of polyatomic molecules. Besides the direct effect that gives rise to an induced dipole, there is a somewhat indirect effect, which stems from the violation of the initial molecular symmetry. For a linear molecule of symmetry $D_{\infty h}$ an expansion of the potential energy and induced dipole against normal coordinates has some zero elements because the respective terms fail to satisfy symmetry requirements [9–11]. The application of an arbitrarily oriented external field might eliminate this restriction, as shown, e.g., in [5]. The matrix element for μ_x^{ind} can be expressed in the form

$$(0000|\mu_x^{\mathrm{ind}}|0101) = \frac{\partial \mu_x^{\mathrm{ind}}}{\partial q_{2x}} \frac{a_{223}\omega_{2x}}{\hbar\omega_3(\omega_3 + 2\omega_{2x})} + \frac{1}{2}\frac{\partial^2 \mu_x^{\mathrm{ind}}}{\partial q_{2x}\partial q_3}. \tag{63}$$

The terms on the right-hand side of Eq. (63) contain the parameters a_{223} and $\frac{\partial^2 \mu_x^{\mathrm{ind}}}{\partial q_{2x}\partial q_3}$ that arise because of the broken symmetry of a CO_2 molecule and vary as functions of an external perturbation. The analogous formula for μ_z^{ind} becomes

$$(0000|\mu_z^{\mathrm{ind}}|0101) = \frac{\partial \mu_z^{\mathrm{ind}}}{\partial q_3} \frac{a_{233}\omega_3}{\hbar\omega_{2x}(\omega_{2x} + 2\omega_3)} + \frac{1}{2}\frac{\partial^2 \mu_z^{\mathrm{ind}}}{\partial q_{2x}\partial q_3}. \tag{64}$$

The greater the strength of an applied external field is, the more important these newly induced terms become. At zero perturbation these terms vanish.

Both harmonic force coefficients a_{12} and a_{13} and anharmonic coefficients, such as a_{223}, a_{233}, $\frac{\partial^2 \mu_x^{\mathrm{ind}}}{\partial q_{2x}\partial q_3}$, and $\frac{\partial^2 \mu_z^{\mathrm{ind}}}{\partial q_{2x}\partial q_3}$, are ensemble-averaged values; they vanish completely in an isolated CO_2 molecule, i.e., in the case when an intermolecular or other external perturbation is absent. In the case of CIA we state intuitively that the magnitude of these parameters is related to the gaseous density. Moreover, we speculate that the density dependence of the "indirect" force coefficients and dipole derivatives are the same, so the factor $c_{\nu_2+\nu_3}$ is independent of the gas density. This effect means that the analog of the Herman-Wallis factor we introduced can be regarded as a true molecular characteristic which does not depend on the strength of an external perturbation. Regarding (58) and (62), we speculate further on the possible signs of factors $c^x_{\nu_2+\nu_3}$ and $c^z_{\nu_2+\nu_3}$. Because the sign of the matrix element for the ν_1 allowed transition is known to be positive, we have several options, which can be verified by comparison with an as yet tentative representation of the CIA band shape from [1]. From the simulation performed in [1], the lines in the *R* branch seem to gain significant intensity, whereas the lines in the *P* branch lose intensity in comparison to that prescribed by Hönl-London factors only. If so, we state that the effective force coefficient a_{12} has the same sign as the matrix element $(0000|\mu_z^{\mathrm{ind}}|0101)$, whereas the force coefficient a_{13} has an opposite sign with respect to $(0000|\mu_x^{\mathrm{ind}}|0101)$.

VI. CONCLUSION

A theoretical approach was developed to calculate the Herman-Wallis factors for rovibrational spectra of symmetrical linear molecules. This approach relies largely on the use of the theorem of extraneous quantum numbers [19]. Taking allowed bands ν_3 and ν_2 and resonances $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ as examples, we demonstrated the validity of our approach. The first Herman-Wallis factor was shown to be largely due to a Coriolis interaction in the case of a fundamental transition. In contrast, for a combination band the variation of inertia moment determines the Herman-Wallis linear factors. Using a simplifying assumption of free rotation of CO_2, we considered the impact of rovibrational interaction on the shape of the collision-induced absorption band $\nu_2 + \nu_3$. After introducing an analog of the Herman-Wallis expansion, we found expressions for the effective $c_{\nu_2+\nu_3}$ coefficients for both parallel and perpendicular constituents of the induced *P* and *R* branches. The possibility for these branches to manifest themselves in CIA spectra was initially suggested *ad hoc* by Baranov [1] and then proved theoretically in [5]. Regarding the $c_{\nu_2+\nu_3}$ CIA profile as simulated [1], we speculated about the relative signs of the effective force coefficients and transition matrix elements, which are involved in collision-induced absorption.

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