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Breakdown of conventional rovibrational selection rules for field- or collision-induced absorption in symmetric linear molecules

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The objective of this work is to derive approximate rovibrational selection rules for the interaction-induced molecular absorption in dipole-less polyatomic molecules. Taking a combination $\nu_2+\nu_3$ band in the CO_2 molecule as an example, we show that selection rules $\Delta J = \pm 1$ are allowed in collision-induced absorption (CIA) along with conventional selection rules $\Delta J = 0, \pm 2$ characteristic for CIA in homonuclear diatomics. The basis of that condition relates to the combined effect of the anisotropy of an external electric perturbation and the anharmonicity of the vibrations.

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I. INTRODUCTION

Collision-induced absorption (CIA) in symmetric molecules lacking an electric dipole moment arises when a weak intermolecular interaction perturbs the electronic cloud of a molecule in such a way that a slight dipole moment becomes induced (see, e.g., [1]). The first experiments on such interaction-induced infrared absorption in the fundamental bands of pressurized dioxygen and dinitrogen were reported by Crawford *et al.* [2]. The possibility to observe absorption within nominally forbidden absorption bands was discussed, however, much earlier by Condon [3], who suggested a theory of induced molecular absorption in an external static electric field. These theoretical predictions were confirmed then [4] in experiments with compressed hydrogen.

The basic theory of collision-induced absorption (CIA) in diatomic molecules was developed largely by Kranendonk *et al.* in a series of works (see [1,5,6], and references therein). It was established that to a first approximation, the observed induced spectra can be understood in terms of a nearly freely rotating homonuclear diatomic molecule that is polarized in the quadrupole field of the neighboring molecule. This simplified view relies on a reasonable idea of the small anisotropy of potential energy, which is characteristic at least of the most popular prototypical molecules such as dihydrogen, dinitrogen, and dioxygen, mainly considered at that time. Colpa and Ketelaar [7] showed that the selection rules for rovibrational CIA restrict the variation of the total angular momentum quantum number J in a rovibrational transition to values either zero or ±2. The observation of distinct branches O, Q, S in the infrared CIA bands (see, e.g., Fig. 1) apparently supports this conclusion.

Moreover, the appearance of selection rule ±2 for induced absorption instead of ±1 for permitted dipole absorption is easily understandable on a qualitative level. When a diatomic molecule that possesses an electric dipole moment rotates 180°, its dipole vector orients oppositely to the initial direction; a rotation by 360° is required to make the permanent dipole vector coincide with its initial direction. In contrast, a rotation by 180° suffices for an induced dipole in a homonuclear diatomic molecule to return to its initial position. Oscillations of a dipole in the course of molecular rotation are hence twice as frequent in the case of induced absorption as in the case of permitted dipole absorption. Apparently, similar qualitative consideration has to yield valid selection rules in the case of a linear dipole-less molecule as well. In what follows, it is shown, however, that somewhat more elaborated consideration is in fact required in this case. Note that our consideration below is restricted by only one example of the electric dipole forbidden $\nu_2 + \nu_3$ combination band in the CO_2. This band falls in the 3.3 μm spectral range, in which weak magnetic dipole CO_2 absorption lines were recently identified [9] in the spectra taken *in situ* in the atmosphere of Mars. We are focused on how the unconventional shape of this CIA band can be understood starting from a simplified assumption of a linear molecule nearly freely rotating in an external electric field. To our belief, the theory suggested here may be useful in consideration of a much broader variety of problems concerning dipole-forbidden absorption bands which become slightly permitted under the action of a perturbing field.

In contrast to simple diatomic molecules, the intermolecular interaction between carbon dioxide molecules is characterized by a notable anisotropy. Moreover, as dipole-permitted vibrational transitions are allowed for a CO_2 molecule, the manifestations of induced bands can be expected to be at variance with the diatomic case. No clear evidence of any O, Q, S branch was ever reported for the CO_2 collision-induced spectra. Note that distinct fingerprints sitting atop a nearly structureless background, e.g., in the region of the Fermi doublet, definitely belong to truly bound CO_2–CO_2 dimers [10], but no true dimer features were ever observed in the range of combination CIA band $\nu_2 + \nu_3$, in which

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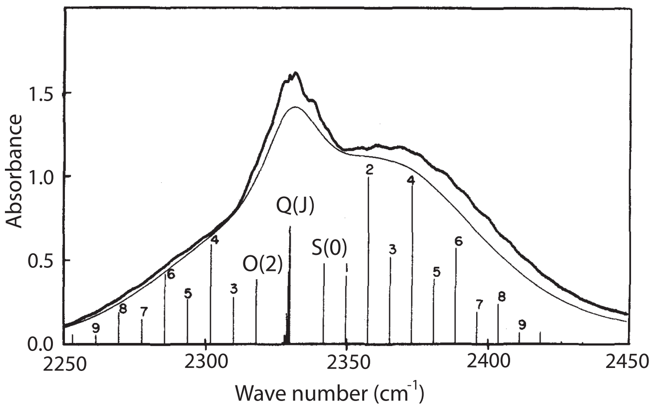

FIG. 1. Example of a pure N_2 infrared spectrum recorded by McKellar [8] at temperature 77 K. The light curve is a simulated collision-induced profile calculated on the basis of a stick spectrum for $O(J)$, $Q(J)$, and $S(J)$ transitions.

the maximum of absorption is notably shifted from the band origin (see Fig. 2). In the most recent study of this CIA band [11], Baranov questioned whether selection rules other than those established for symmetric diatomic molecules are applicable in the case of CO_2. Baranov's idea was based on a pictorial resemblance of the stick structure adjusted so that it can roughly fit the observed band shape of band $\nu_2 + \nu_3$, as shown in Fig. 2.

Our theoretical examination below largely supports the principal idea that Baranov proposed, although we are not in a position to entirely share that explanatory point of view [11].

Before proceeding to details of our theoretical consideration, we clearly state that we treat the problem in question assuming the induced spectrum arises from nearly freely rotating molecules in interaction either with each other pairwise or with an external field. In the real world, any CIA spectra result from an average absorption of molecular or intermolecular states over a broad statistical ensemble, not all of which are characterized by nearly free rotation of the individual monomers. A consistent method to simulate collision-induced spectrum in a gas should be based either on a pure quantum (see, e.g., [12]) or a semiclassical (e.g., [13]) consideration. For this reason, the theory suggested below must be considered to have been developed with a simplified approach that permits one, however, to reveal the important physical details of the induced absorption mechanism.

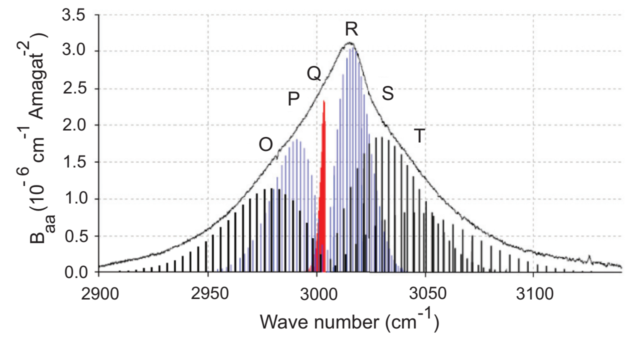

FIG. 2. A solid line shows the binary absorption coefficient B_{aa} for the collision-induced band $\nu_2 + \nu_3$ recorded by Baranov [11] at 295 K. Vertical lines show a calculated stick spectrum of various branches, the intensities of which are intentionally adjusted visually to fit the observed band shape.

II. CONVENTIONAL ROTATIONAL SELECTION RULES FOR PERMITTED DIPOLE AND INDUCED ABSORPTION IN LINEAR MOLECULES

The rotation of a linear molecule is characterized with quantum number J that specifies the total angular momentum $\mathbf{J}$ in the molecule. Quantum numbers K and M can also be introduced, specifying the projections of $\mathbf{J}$ along the molecular axis C_∞ and some laboratory-fixed z axis, respectively. Let us start from an assumption that the rovibrational wave function of a linear molecule can be factorized as the product of rotational and vibrational wave functions $\Psi = \Psi^{\rm rot}\Psi^{\rm vib}$, where $\Psi^{\rm vib}$ can be taken in the form of anharmonically coupled oscillator wave functions. The rotational wave function $\Psi^{\rm rot}$ can be represented following various prerequisites, for instance in the form suggested by Hougen [14], which assumes a specific choice of the reference frame. The choice of the isomorphic Hamiltonian and relevant wave functions [14] means that the vibrational angular momentum is taken into account. The rotational wave function can be represented as [15]

$$\Psi^{\rm rot}_{\rm iso} = \sqrt{\frac{2J+1}{8\pi^2}}\, D^{(J)*}_{M,K+l}(\phi,\theta,\kappa), \qquad (1)$$

where l is the vibrational angular momentum quantum number, $D^{(J)*}_{M,K+l}(\phi,\theta,\kappa)$ denotes a complex conjugate rotational Wigner function, the arguments of which, Euler angles θ, ϕ and κ, determine the orientation of a linear molecule as if it were a nonlinear one. The vibrational wave function $\Psi^{\rm vib}_{\rm iso}$ contains exponential factor $e^{il\epsilon}$, with the angle ϵ introduced in [14], which refers to the ω_2 degenerate bending vibration. As shown in the next section, the choice of the rotational wave function has no effect on the matrix elements that we intend to examine.

A. An illustrative example of permitted transitions

In this section, we consider a somewhat model example of rotational selection rules for a symmetric linear molecule that possesses a permanent electric dipole moment $\boldsymbol{\mu}$. We disregard here the degeneracy of bending vibration as if this mode is frozen or the relevant degeneracy is lifted. We also admit that the total angular momentum $\mathbf{J}$ of a molecule is composed of rotational angular momentum $\mathbf{J}_{\rm rot}$ of the nuclei and electronic orbital momentum $\mathbf{L}$: $\mathbf{J} = \mathbf{J}_{\rm rot} + \mathbf{L}$. Indeed, under the Born-Oppenheimer approximation, the electronic state is capable of significantly affecting the rotational state.

To derive rotational selection rules, we have to take into account the relation

$$\mu^{\rm LF}_{\Omega} = \sum_{\Omega'=0,\pm1} D^{(1)*}_{\Omega,\Omega'}(\phi,\theta,0)\,\mu^{\rm BF}_{\Omega'} \qquad (2)$$

between dipole moment components $\mu^{\rm LF}_{\Omega}$ in the laboratory-fixed (LF) frame of reference and that body fixed (BF) (called also molecule fixed), in which the dipole moment has components

$$\mu_0^{\mathrm{BF}} = \mu_z \quad \text{and} \quad \mu_{\pm 1}^{\mathrm{BF}} = \frac{1}{\sqrt{2}}(\mp\mu_x - i\mu_y),$$

expressed via Cartesian BF coordinates x, y, z of the dipole vector. In (2), $\Omega = 0, \pm 1$. Axis z of the BF frame is assumed to lie along symmetry axis C_∞ of a molecule.

For an isolated linear molecule having moment $I = I_B = I_C$ of inertia, the rotational part of a Hamiltonian has the form

$$H_{\mathrm{rot}} = \frac{(\mathbf{J} - \mathbf{L})^2}{2I},$$

in which $\mathbf{J}$ and $\mathbf{L}$ are the total angular momentum and the electronic orbital momentum, respectively. The wave equation with H_{rot} produces eigenfunctions [15,16]

$$\Psi^{\mathrm{rot}} = |J, K, M\rangle = \sqrt{\frac{2J+1}{4\pi}} D_{M,K}^{(J)*}(\phi, \theta, 0). \tag{3}$$

Rotational matrix elements are expressed as

$$\begin{aligned} &\langle \Psi^{\mathrm{rot}}(J, K, M) | D_{\Omega,\Omega'}^{(1)*} | \Psi^{\mathrm{rot}}(J', K', M') \rangle \\ &= (-1)^{M-K} \sqrt{(2J+1)(2J'+1)} \\ &\times \begin{pmatrix} J' & 1 & J \\ M' & \Omega & -M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ K' & \Omega' & -K \end{pmatrix}. \end{aligned} \tag{4}$$

Note that under assumption $l = 0$, the result of calculation of the matrix elements (4) does not depend on whether the wave functions (3) or

$$\Psi_{\mathrm{iso}}^{\mathrm{rot}} = \sqrt{\frac{2J+1}{8\pi^2}} D_{M,K}^{(J)*}(\phi, \theta, \kappa)$$

are taken in terms of basis rotational wave functions. In fact, the combination of $e^{il\epsilon}$ and $e^{il\kappa}$ results in $e^{il(\epsilon+\kappa)}$, which is appropriate to degenerate vibrations in conventional polar coordinates prior to transition to isomorphic Hamiltonian coordinates introduced by Hougen [14]. This means that we can interpret $\Psi_{\mathrm{iso}}^{\mathrm{vib}} e^{il\kappa}$ in terms of Ψ^{vib}. Provided there is no degeneracy, i.e., the l quantum number is not applicable, the wave functions which relate to the isomorphic Hamiltonian can be factorized as the product of rotational and vibrational ones,

$$\Psi_{\mathrm{iso}} = \Psi_{\mathrm{iso}}^{\mathrm{rot}} \Psi_{\mathrm{iso}}^{\mathrm{vib}} = \sqrt{\frac{2J+1}{8\pi^2}} D_{M,K}^{(J)*}(\phi, \theta, \kappa) \Psi_{\mathrm{iso}}^{\mathrm{vib}}. \tag{5}$$

The use of isomorphic wave functions thus results in the change of the normalizing factor, which, in the case of Ψ_{iso}, is entirely conditioned by introduction of the angle of rotation against the molecular C_∞ axis. The only difference consists in the *ad hoc* chosen $\kappa = 0$ in wave function (3), whereas in [14] the angle κ is introduced in terms of an independent variable, and neither in the Wigner function in (2) nor in the $\Psi_{\mathrm{iso}}^{\mathrm{rot}}(J, K, M)$ can it be assumed zero. This difference does not, however, affect the calculated matrix elements from the Wigner functions. Bearing in mind our intention here to establish approximate selection rules for the J quantum number only, we conclude from Eq. (4) that an absorption line does not vanish if and only if condition

$$J' - J = 0, \pm 1$$

($J \equiv J''$; a transition with $J = J' = 0$ is forbidden) is fulfilled.

B. External field- or interaction-induced transitions

External field $\mathbf{F}$ induces a dipole moment in a previously dipole-less symmetric molecule,

$$(\mu_k^{\mathrm{LF}})^{\mathrm{ind}} = \sum_l \alpha_{kl}^{\mathrm{LF}} F_l, \tag{6}$$

in which $\alpha_{kl}^{\mathrm{LF}}$ are the components of the polarizability matrix. Rotational selection rules can be determined in this case from the relations in [3] bearing in mind that

$$\alpha_{kl}^{\mathrm{LF}} = \sum_{j,r} \Phi_{kj}(0, \phi, \theta) \Phi_{lr}(0, \phi, \theta) \alpha_{jr}^{\mathrm{BF}}, \tag{7}$$

in which $\Phi_{ab}(0, \phi, \theta)$ $(a, b = k, j$ or $l, r)$ is the direction cosine matrix. This formula is also expressible using spherical tensor operators [17],

$$\alpha_{\Omega}^{\mathrm{LF}} = \sum_{\Omega'=0,\pm 1,\pm 2} D_{\Omega,\Omega'}^{(2)*}(\phi, \theta, 0) \alpha_{\Omega'}^{\mathrm{BF}}. \tag{8}$$

These five components of the polarizability tensor are complemented with a sixth component, i.e., the averaged trace,

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{9}$$

which, being a scalar polarizability, is rotationally invariant.

Here again we define rotational matrix elements as

$$\begin{aligned} &\langle \Psi^{\mathrm{rot}}(J, K, M) | D_{\Omega,\Omega'}^{(2)*} | \Psi^{\mathrm{rot}}(J', K', M') \rangle \\ &= (-1)^{M-K} \sqrt{(2J+1)(2J'+1)} \\ &\times \begin{pmatrix} J' & 2 & J \\ M' & \Omega & -M \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ K' & \Omega' & -K \end{pmatrix}. \end{aligned} \tag{10}$$

Noting the normalizing condition

$$\sum_{M,\Omega,M'} \begin{pmatrix} J' & 2 & J \\ M' & \Omega & -M \end{pmatrix}^2 = 1 \tag{11}$$

for the $i \rightarrow f$ transition probability $P(i \rightarrow f)$, we obtain

$$\begin{aligned} &P(i \rightarrow f) \\ \sim &\left| \sum_{\Omega'=0,\pm 1,\pm 2} (-1)^{-K} \begin{pmatrix} J' & 2 & J \\ K' & \Omega' & -K \end{pmatrix} \right. \\ &\left. \times \langle \Psi_i^{\mathrm{vib}} | \alpha_{\Omega'}^{\mathrm{BF}} | \Psi_f^{\mathrm{vib}} \rangle \right|^2. \end{aligned} \tag{12}$$

Here, Ψ_i^{vib}, Ψ_f^{vib} are vibrational wave functions characteristic of the initial and final vibrational states, respectively. Provided that total angular momentum $\mathbf{J}$ is assumed to relate to the rotation of only linearly aligned nuclei in a set, i.e., the electronic contribution is disregarded, it is reasonable to assume a zero value for quantum number K, i.e., $K' = K = 0$. The selection rules are hence determined by the value of

$$\begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix}, \tag{13}$$

which is nonzero provided that $J' - J = 0, \pm 2$. This result is entirely justified under an assumption that the molecular polarizability has only two nonzero components, which are conventionally called trace $\bar{\alpha}$ (9) and anisotropy $\Delta\alpha$ of the polarizability tensor:

$$\Delta\alpha = \frac{1}{2}[2\alpha_{zz} - (\alpha_{xx} + \alpha_{yy})]. \tag{14}$$

To resume this introductory section, we suggest that the effect of induction must be sensitive to whether the symmetry of the electronic cloud alters while the molecule is interacting with the field. Given that the symmetry of the electronic distribution does not coincide with the symmetry of the nuclear arrangement in a molecule, one consequently expects a change in the CIA selection rules.

III. EXTENDED SELECTION RULES FOR $\nu_2 + \nu_3$ COMBINATION TRANSITION IN A LINEAR *XYX* MOLECULE

Considering a molecule in the absence of an external perturbation, the vibrational Hamiltonian H_{vib} is represented as

$$H_{\text{vib}} = H^0_{\text{vib}} + \Delta H^{\text{free}}_{\text{anh}},$$

in which

$$\begin{aligned} H^0_{\text{vib}} = &\frac{\hbar\omega_1}{2}\left(p_1^2 + q_1^2\right) + \frac{\hbar\omega_{2x}}{2}\left(p_{2x}^2 + q_{2x}^2\right) \\ &+ \frac{\hbar\omega_{2y}}{2}\left(p_{2y}^2 + q_{2y}^2\right) + \frac{\hbar\omega_3}{2}\left(p_3^2 + q_3^2\right) \end{aligned} \tag{15}$$

is an unperturbed Hamiltonian, q_s, p_s, and ω_s are coordinates, conjugate momenta, and harmonic frequencies, respectively, for symmetric ($s = 1$), doubly degenerate (labeled supplementary x and y) bending ($s = 2$), and antisymmetric ($s = 3$) vibrational modes. The term $\Delta H^{\text{free}}_{\text{anh}}$ means an anharmonic perturbation operator for a single free CO_2 molecule. Note that we intentionally leave, in (15), the distinction between ω_{2x} and ω_{2y} vibrations, although in an isolated molecule the ω_2 mode is obviously degenerate, so that $\omega_{2x} = \omega_{2y}$. We express the vibrational Hamiltonian in the form (15) because, as soon as a linear molecule is subject to a perturbing external field at an angle, the degeneracy of ω_2 is lifted (see, e.g., [18] for the carbon dioxide dimer as an example). The case of a nondegenerate bending mode is exactly what we intend to deal with below in due course.

In a harmonic approximation, quantum state vector $|n_1, n_{2x}, n_{2y}, n_3\rangle$ is factorized as a product of four vectors of unidimensional oscillators $|n_1\rangle|n_{2x}\rangle|n_{2y}\rangle|n_3\rangle$, in which n_s are vibrational quantum numbers.

A. Vibrational problem in an isolated *XYX* molecule

We proceed to demonstrate that vibrational anharmonicity in a nonrotating *XYX* molecule has no intrinsic effect on the change of rovibrational selection rules for induced transition $\nu_2 + \nu_3$. As we see in the next section, however, the intensity of this transition is largely determined by mechanical and dipolar anharmonic terms issued from expansions of the potential energy and the induced dipole moment against vibrational coordinates.

Consider first the vibrational selection rule for transition $\nu_2 + \nu_3$ in molecule *XYX*. Provided that the sign of vibrational matrix element

$$\left\langle \Psi_i^{\text{vib}} \middle| \boldsymbol{\mu} \middle| \Psi_f^{\text{vib}} \right\rangle \tag{16}$$

does not change upon symmetry operations, the transition is permitted; the matrix element must otherwise be zero—the transition is forbidden. In a harmonic approximation, $\Delta H^{\text{free}}_{\text{anh}} = 0$. The oscillator wave functions are represented in this case with Hermite polynomials in which k is an integer so that the $|2k\rangle$ functions are even and their signs do not alter upon permutation of the end X atoms. In contrast, wave functions $|2k + 1\rangle$ are odd; their signs change upon permutation. For the combination transition $\nu_2 + \nu_3$, we have

$$|n_1, n_{2x}, n_{2y}, n_3\rangle \rightarrow |n_1, n_{2x} + 1, n_{2y}, n_3 + 1\rangle. \tag{17}$$

We conclude that this transition must be forbidden.

Given that the z axis is directed along the symmetry axis of a molecule, one can expand the Cartesian components of the dipole moment with respect to normal coordinates q_s:

$$\begin{aligned} \mu_x &= \mu^x_2 q_{2x} + \mu^x_{12} q_1 q_{2x} + \cdots , \\ \mu_y &= \mu^y_2 q_{2y} + \mu^y_{12} q_1 q_{2y} + \cdots , \\ \mu_z &= \mu^z_3 q_3 + \mu^z_{13} q_1 q_3 + \cdots . \end{aligned} \tag{18}$$

Here, μ^x_{12}, μ^y_{12}, μ^z_{13}, and so forth are anharmonic electro-optical coefficients; the subscripts in (18) mean derivatives with respect to relevant coordinates. Only those terms which satisfy the symmetry condition do not vanish from (18). These terms are different, however, for an isolated molecule and for the same molecule subjected to an external electric field because the symmetry of the electronic cloud is distorted under the perturbation in the field. We shall consider below only those terms in an induced dipole moment which are capable of giving rise to nonzero intensity of rotational transitions within a specific collision-induced absorption band.

As the dipole moment in harmonic approximation is a linear function of q_{2x} and q_3 coordinates [19], its sign must change upon inversion of the sign of the coordinates. As a consequence, the relevant matrix element

$$\langle n_1, n_{2x}, n_{2y}, n_3|\boldsymbol{\mu}|n_1, n_{2x} + 1, n_{2y}, n_3 + 1\rangle$$

vanishes, as otherwise its sign should change upon a symmetry operation.

Taking into account that anharmonicity has no obvious impact on the above conclusion, the first nonzero anharmonic correction to the wave function of an isolated CO_2 molecule is determined by the cubic terms in a vibrational Hamiltonian with respect to coordinates

$$\Delta H^{\text{free}}_{\text{anh}} = a_{111} q_1^3 + a_{122} q_1 \left(q_{2x}^2 + q_{2y}^2\right) + a_{133} q_1 q_3^2, \tag{19}$$

in which $a_{111}, a_{122}, a_{133}$ are mechanical anharmonicity coefficients. Operator $\Delta H^{\text{free}}_{\text{anh}}$ contains only those cubic terms that are shown in (19) as other combinations of vibrational coordinates are prohibited according to the symmetry requirements [20–22]. As a result, in the first-order correction to the harmonic approximation vector $|n_1, n_{2x}, n_{2y}, n_3\rangle$, vectors

$$\begin{aligned} &|n_1 \pm 1, n_{2x}, n_{2y}, n_3\rangle, \\ &|n_1 \pm 1, n_{2x} \pm 2, n_{2y}, n_3\rangle, \\ &|n_1 \pm 1, n_{2x}, n_{2y}, n_3 \pm 2\rangle, \\ &|n_1 \pm 1, n_{2x}, n_{2y} \pm 2, n_3\rangle, \\ &|n_1 \pm 3, n_{2x}, n_{2y}, n_3\rangle \end{aligned}$$

must be added. All combinations of these vectors yield zero matrix elements for the (17) transition. The prohibition of vibrational transition (17) in an isolated *XYX* molecule is thus strict, regardless of whether harmonic or anharmonic vibrations are considered.

B. Polarizability of a molecule in external field

When molecule *XYX* is exposed to an external field, either static, radiative, or produced by a neighboring molecule, the combination transition (17) becomes slightly permitted. Examination of the selection rules for such an induced transition requires a consideration of the rovibrational matrix element in detail, as the vibrational anharmonic effect is tightly entangled with the rotational properties of the polarizability tensor.

Consider an electronic Schrödinger equation written as

$$[T + V(\rho, Q)]|\chi_A\rangle = E_A|\chi_A\rangle. \tag{20}$$

Here, T and V are kinetic and electronic potential-energy operators, ρ and Q are, respectively, the sets of electronic and nuclear coordinates, and $|\chi_A\rangle$ and E_A are electronic eigenvectors and eigenvalues, which are parametrized with nuclear coordinates. An application of external electric field $\mathbf{F}$ causes a change in the molecular energy so that the electronic Hamiltonian becomes $T + V - \mathbf{MF}$, in which $\mathbf{M}(\rho, Q)$ is the molecular dipole moment, which is, in general, a function of both electronic and nuclear coordinates. To obtain a conventional molecular dipole moment $\boldsymbol{\mu}(Q)$, which in the body-fixed frame is a function of only nuclear coordinates, one has to average $\mathbf{M}(\rho, Q)$ over electronic coordinates ρ within a given electronic state. Considering $-\mathbf{MF}$ as a perturbation, we express the first-order energy correction in a diagonal form, $\langle\chi_A|(-\mathbf{MF})|\chi_A\rangle$, which reduces to operator $-\boldsymbol{\mu}\mathbf{F}$ that relates to rovibrational transitions in a field as $\boldsymbol{\mu}(Q) = \langle\chi_A|\mathbf{M}|\chi_A\rangle$. Given that the molecule lacks a permanent electric dipole and that the matrix element for the vibrational transition is zero, the first-order energy correction is zero. As a result, one must consider the second-order perturbation term, in which the induced dipole (6) arises. Here, $\alpha_{kl}^{\mathrm{LF}}$ is given by (7), in which $\alpha_{jr}^{\mathrm{BF}}$ is determined by the Placzek formula for the polarizability tensor [23],

$$\begin{aligned}(\alpha_{jr}^{\mathrm{BF}})_{AB} &= \sum_C \left[\frac{\langle\chi_A|M_j|\chi_C\rangle\langle\chi_C|M_r|\chi_B\rangle}{E_C - E_B + \hbar\omega_0}\right.\\ &+ \left.\frac{\langle\chi_A|M_r|\chi_C\rangle\langle\chi_C|M_j|\chi_B\rangle}{E_C - E_A - \hbar\omega_0}\right].\end{aligned} \tag{21}$$

Here, frequency ω_0, characteristic of an applied external field, must be assumed to be zero provided that a static field is considered, e.g., for the CIA case.

Potential $V(\rho, Q)$ in (20) is a function of electronic and normal vibrational coordinates, which we develop in a series with respect to vibrational coordinates,

$$V(\rho, Q) = V_0 + \sum_s g_s Q_s + \sum_{s\leqslant r} g_{sr} Q_s Q_r + \cdots, \tag{22}$$

in which $V_0 = V_0(\rho)$ and coefficients $g_s, g_{sr}, \ldots$ are functions of only electronic coordinates.

We also represent the electronic energy and wave functions in terms of series over vibrational coordinates,

$$\begin{aligned}E_A &= E_A^0 + \sum_s E_{A(s)}^{(1)} Q_s + \sum_{s\leqslant r} E_{A(sr)}^{(2)} Q_s Q_r + \cdots,\\ |\chi_A\rangle &= |\chi_A^{(0)}\rangle + \sum_s |\chi_{A(s)}^{(1)}\rangle Q_s + \sum_{s\leqslant r} |\chi_{A(sr)}^{(2)}\rangle Q_s Q_r + \cdots.\end{aligned} \tag{23}$$

According to [19,24], the wave equation (20) is expressible in an equivalent form as this system of equations:

$$\begin{aligned}\frac{\partial E_A}{\partial Q_s} &= \langle\chi_A|\frac{\partial V}{\partial Q_s}|\chi_A\rangle,\\ \frac{\partial|\chi_A\rangle}{\partial Q_s} &= \sum_{C\neq A}\frac{\langle\chi_C|\frac{\partial V}{\partial Q_s}|\chi_A\rangle}{E_A - E_C}|\chi_C\rangle.\end{aligned} \tag{24}$$

Having introduced (22) and (23) into (24) and then set all Q_s equal to zero, we obtain the first correction terms $E_{A(s)}^{(1)}$ and $|\chi_{A(s)}^{(1)}\rangle$,

$$\begin{aligned}E_{A(s)}^{(1)} &= \langle\chi_A^{(0)}|g_s|\chi_A^{(0)}\rangle,\\ |\chi_{A(s)}^{(1)}\rangle &= \sum_{C\neq A}\frac{\langle\chi_C^{(0)}|g_s|\chi_A^{(0)}\rangle}{E_A^0 - E_C^0}|\chi_C^{(0)}\rangle.\end{aligned} \tag{25}$$

To find the second-order terms $E_{A(s)}^{(2)}$ and $|\chi_{A(s)}^{(2)}\rangle$, we differentiate the system (24) with respect to Q_r and then set all Q_s equal to zero. After some algebra, we obtain the second-order correction to eigenvalues,

$$\begin{aligned}E_{A(sr)}^{(2)} &= \sum_{C\neq A}\frac{\langle\chi_C^{(0)}|g_s|\chi_A^{(0)}\rangle\langle\chi_C^{(0)}|g_r|\chi_A^{(0)}\rangle}{E_A^0 - E_C^0}\\ &\quad + \sum_{C\neq A}\frac{\langle\chi_A^{(0)}|g_s|\chi_C^{(0)}\rangle\langle\chi_C^{(0)}|g_r|\chi_A^{(0)}\rangle}{E_A^0 - E_C^0}\\ &\quad + \langle\chi_A^{(0)}|g_{sr}|\chi_A^{(0)}\rangle,\end{aligned} \tag{26}$$

and eigenfunctions,

$$\begin{aligned}&|\chi_{A(sr)}^{(2)}\rangle\\ &= \sum_{C\neq A}\sum_{D\neq C}\frac{\langle\chi_D^{(0)}|g_r|\chi_C^{(0)}\rangle\langle\chi_D^{(0)}|g_s|\chi_A^{(0)}\rangle}{(E_A^0 - E_C^0)(E_C^0 - E_D^0)}|\chi_C^{(0)}\rangle\\ &+ \sum_{C\neq A}\sum_{D\neq A}\frac{\langle\chi_C^{(0)}|g_s|\chi_D^{(0)}\rangle\langle\chi_D^{(0)}|g_r|\chi_A^{(0)}\rangle}{(E_A^0 - E_C^0)(E_A^0 - E_D^0)}|\chi_C^{(0)}\rangle\\ &+ \sum_{C\neq A}\sum_{D\neq C}\frac{\langle\chi_C^{(0)}|g_s|\chi_A^{(0)}\rangle\langle\chi_D^{(0)}|g_r|\chi_C^{(0)}\rangle}{(E_A^0 - E_C^0)(E_C^0 - E_D^0)}|\chi_D^{(0)}\rangle\\ &+ \sum_{C\neq A}\frac{\langle\chi_C^{(0)}|g_{sr}|\chi_A^{(0)}\rangle}{E_A^0 - E_C^0}|\chi_C^{(0)}\rangle\\ &- \sum_{C\neq A}\frac{[\langle\chi_A^{(0)}|g_r|\chi_A^{(0)}\rangle - \langle\chi_C^{(0)}|g_r|\chi_C^{(0)}\rangle]}{(E_A^0 - E_C^0)^2}\\ &\times\langle\chi_C^{(0)}|g_s|\chi_A^{(0)}\rangle|\chi_C^{(0)}\rangle.\end{aligned} \tag{27}$$

The wave functions and energies obtained so far are functions of vibrational coordinates, which become inserted into the Placzek formula (21). The resulting expression for the polarizability tensor is not too difficult to derive, although reproduction here is not worthwhile because of its cumbersome extent. We restrict ourselves by showing the development of only one denominator in (21),

$$\frac{1}{E_A - E_B + \hbar\omega_0} = \frac{1}{E_A^0 - E_B^0 + \hbar\omega_0} - \sum_s \frac{E_{A(s)}^{(1)} - E_{B(s)}^{(1)}}{(E_A^0 - E_B^0 + \hbar\omega_0)^2} Q_s + \sum_{s\leqslant r}(\ldots)Q_s Q_r + \cdots. \quad (28)$$

The components of the polarizability tensor thus obtained depend on the vibrational coordinates; the nondiagonal components of the polarizability tensor (21) no longer vanish. This condition means that when a symmetric molecule is subjected to an external field, the distorted symmetry of the electronic cloud is apt to produce nonvanishing parallel or perpendicular components of an induced dipole with respect to symmetry axis z of the linearly arranged nuclei in that molecule.

An external field breaks the symmetry of an electronic cloud surrounding the nuclei in a molecule. In addition to only diagonal components of the polarizability tensor, nondiagonal terms α_{xz} and α_{yz} arise as functions of coordinates q_{2x} and q_3. In terms of a spherical tensor, we hence supplement (9) and (14) with

$$\alpha_{\pm 1} = \mp\alpha_{xz} - i\alpha_{yz}. \quad (29)$$

C. Integrated intensity of the combination $\nu_2 + \nu_3$ band

The integrated intensity of a vibrational transition in an external field is determined by matrix element (16) with $\boldsymbol{\mu} = \boldsymbol{\mu}^{\text{ind}}$ from (6) in the BF system.

Let axis z be aligned with the nuclear arrangement symmetry axis C_∞. As the anisotropy of induction results in a distortion of an initially symmetric charge distribution, new terms arise in the vibrational Hamiltonian H_{vib}:

$$\begin{aligned} \Delta H_{\text{anh}}^{\text{ind}} &= a_{233} q_{2x} q_3^2 + a_{223} q_{2x}^2 q_3 \\ &+ a'_{233} q_{2y} q_3^2 + a'_{223} q_{2y}^2 q_3. \end{aligned} \quad (30)$$

Note that the coefficients $a_{\ldots}$ in expansion (30) originate from the coefficients $g_{\ldots}$ in (22), which are averaged over the electronic state making use of the relationships (24). In (30) and hereafter, we use q_s for the normal coordinates instead of nuclear displacements Q_s, which arise initially in (22) as a natural measure of nuclear movements. Coordinates q_s are known to be such linear combinations of the natural coordinates Q_s, which diagonalize the harmonic part of the vibrational potential energy. Consequently, after the averaging over the electronic state, the potential function developed against normal coordinates has to contain harmonic (quadratic) and higher-order anharmonic (cubic, quartic, etc.) terms. Some of these anharmonic terms are responsible for conventional anharmonic vibrational frequency corrections in an unperturbed CO_2, whereas the supplementary terms shown in (30) are due to violation of the symmetry restrictions caused by external perturbation. As shown below, these new terms are crucial for the formation of the induced band shape.

In subsequent paragraphs, we consider only those terms in (30) that contain coordinates q_{2x}. An off-axial perturbation results in the splitting of the degenerate bending vibration so that the degeneracy of vibration ω_2 is lifted. The induction that breaks the initial symmetry causes ω_{2x} and ω_3 vibrations to become mixed, whereas the ω_{2y} vibration can be disregarded in our consideration below. We also disregard the term $\Delta H_{\text{anh}}^{\text{free}}$ because, as shown in the preceding paragraphs, it does not affect the matrix elements that we are interested in examining. As a result, the anharmonic part of the Hamiltonian (30) is reduced to

$$\Delta H_{\text{anh}}^{\text{ind}} = a_{233} q_{2x} q_3^2 + a_{223} q_{2x}^2 q_3. \quad (31)$$

We also take into account that the electronic cloud is distorted because of the $\nu_2 + \nu_3$ vibration. As a result, the nondiagonal polarizability components (29) appear, which depend simultaneously on the q_{2x} and q_3 coordinates. According to (6) and (8), these components contribute into $\boldsymbol{\mu}^{\text{ind}}$. Consequently, new anharmonic terms appear in the expansion of the induced dipole moment,

$$\begin{aligned} \mu_x^{\text{ind}} &= \frac{\partial \mu_x^{\text{ind}}}{\partial q_{2x}} q_{2x} + \frac{\partial^2 \mu_x^{\text{ind}}}{\partial q_{2x}\partial q_3} q_{2x} q_3 + \cdots, \\ \mu_y^{\text{ind}} &= \frac{\partial \mu_y^{\text{ind}}}{\partial q_{2y}} q_{2y} + \frac{\partial^2 \mu_y^{\text{ind}}}{\partial q_{2y}\partial q_3} q_{2y} q_3 + \cdots, \\ \mu_z^{\text{ind}} &= \frac{\partial \mu_z^{\text{ind}}}{\partial q_3} q_3 + \frac{\partial^2 \mu_z^{\text{ind}}}{\partial q_{2x}\partial q_3} q_{2x} q_3 \\ &+ \frac{\partial^2 \mu_z^{\text{ind}}}{\partial q_{2y}\partial q_3} q_{2y} q_3 + \cdots. \end{aligned} \quad (32)$$

Only those terms that concern an excitation of the bending and asymmetric stretching vibrations are kept in (32). Armed with this knowledge we proceed to calculate the matrix element for the combination transition (17).

Consider first only the former term in (31) that acts as a perturbation on the unperturbed Hamiltonian H_{vib}^0 (15). The first-order correction $|n, 1\rangle$ to harmonic vector $|n\rangle$ defines pertinent wave function $\Psi^{\text{vib}} = |n\rangle + |n, 1\rangle$ and can be readily found using the formalism of so-called quantum number polynomials, described in detail in [19,24–27],

$$\begin{aligned} |n, 1\rangle = \frac{a_{233}}{2\hbar\sqrt{2}} \Bigg[& \frac{\sqrt{n_{2x} n_3 (n_3 - 1)}}{(\omega_{2x} + 2\omega_3)} |n_1, n_{2x} - 1, n_{2y}, n_3 - 2\rangle + \frac{\sqrt{n_{2x}(n_3 + 1)(n_3 + 2)}}{(\omega_{2x} - 2\omega_3)} |n_1, n_{2x} - 1, n_{2y}, n_3 + 2\rangle \\ & + \frac{(2n_3 + 1)\sqrt{n_{2x}}}{\omega_{2x}} |n_1, n_{2x} - 1, n_{2y}, n_3\rangle - \frac{\sqrt{(n_{2x} + 1)(n_3 + 1)(n_3 + 2)}}{(\omega_{2x} + 2\omega_3)} |n_1, n_{2x} + 1, n_{2y}, n_3 + 2\rangle \\ & - \frac{\sqrt{(n_{2x} + 1) n_3 (n_3 - 1)}}{(\omega_{2x} - 2\omega_3)} |n_1, n_{2x} + 1, n_{2y}, n_3 - 2\rangle - \frac{(2n_3 + 1)\sqrt{n_{2x} + 1}}{\omega_{2x}} |n_1, n_{2x} + 1, n_{2y}, n_3\rangle \Bigg]. \end{aligned} \quad (33)$$

In agreement with the algorithm of the perturbation theory described in [19,25], matrix element $\frac{\partial \mu_z^{\text{ind}}}{\partial q_3} q_3$ of the dipole term was calculated using the first-order wave functions, whereas the matrix element from $\frac{\partial^2 \mu_z^{\text{ind}}}{\partial q_{2x} \partial q_3} q_{2x} q_3$ was taken using zero-order wave functions, i.e., harmonic functions. Polynomials $\Pi_{\alpha\beta}^{s_1 s_{2x} s_{2y} s_3}(n, m)$ define the matrix elements taken between wave functions $|n, \alpha\rangle$, $|m, \beta\rangle$ of orders α and β, respectively, as shown below:

$$\langle n, \alpha | q_1^{s_1} q_{2x}^{s_{2x}} q_{2y}^{s_{2y}} q_3^{s_3} | m, \beta \rangle = 2^{\frac{-(s_1 + s_{2x} + s_{2y} + s_3)}{2}} \sqrt{\frac{m_1! m_{2x}! m_{2y}! m_3!}{n_1! n_{2x}! n_{2y}! n_3!}} \Pi_{\alpha\beta}^{s_1 s_{2x} s_{2y} s_3}(n_1, m_1; n_{2x}, m_{2x}; n_{2y}, m_{2y}; n_3, m_3), \tag{34}$$

in which $n_r \leqslant m_r$ is assumed for all subscripts r. Taking into account only the former term in (31), we eventually obtain

$$\begin{aligned} Z(n_1, n_{2x}, n_{2y}, n_3) &= \big\langle \Psi_i^{\text{vib}}(n_1, n_{2x}, n_{2y}, n_3) \big| \mu_z^{\text{ind}} \big| \Psi_f^{\text{vib}}(n_1, n_{2x}+1, n_{2y}, n_3+1) \big\rangle = \frac{\partial \mu_z^{\text{ind}}}{\partial q_3} \sqrt{(n_{2x}+1)(n_3+1)} \\ &\quad \times \big[\Pi_{10}^{0001}(n_1, n_1; n_{2x}, n_{2x}+1; n_{2y}, n_{2y}; n_3, n_3+1) + \Pi_{01}^{0001}(n_1, n_1; n_{2x}, n_{2x}+1; n_{2y}, n_{2y}; n_3, n_3+1) \big] \\ &\quad + \frac{1}{2} \frac{\partial^2 \mu_z^{\text{ind}}}{\partial q_{2x} \partial q_3} \sqrt{(n_{2x}+1)(n_3+1)}\, \Pi_{00}^{0101}(n_1, n_1; n_{2x}, n_{2x}+1; n_{2y}, n_{2y}; n_3, n_3+1) \\ &= \left(\frac{\partial \mu_z^{\text{ind}}}{\partial q_3} \frac{a_{233} \omega_3}{\hbar \omega_{2x}(\omega_{2x} + 2\omega_3)} + \frac{1}{2} \frac{\partial^2 \mu_z^{\text{ind}}}{\partial q_{2x} \partial q_3} \right) \sqrt{(n_{2x}+1)(n_3+1)}. \end{aligned} \tag{35}$$

In a similar way, we consider the latter term in (31) that yields

$$\begin{aligned} X(n_1, n_{2x}, n_{2y}, n_3) &= \big\langle \Psi_i^{\text{vib}}(n_1, n_{2x}, n_{2y}, n_3) \big| \mu_x^{\text{ind}} \big| \Psi_f^{\text{vib}}(n_1, n_{2x}+1, n_{2y}, n_3+1) \big\rangle \\ &= \left[\frac{\partial \mu_x^{\text{ind}}}{\partial q_{2x}} \frac{a_{223} \omega_{2x}}{\hbar \omega_3(\omega_3 + 2\omega_{2x})} + \frac{1}{2} \frac{\partial^2 \mu_x^{\text{ind}}}{\partial q_{2x} \partial q_3} \right] \sqrt{(n_{2x}+1)(n_3+1)}. \end{aligned} \tag{36}$$

The intensity of the combination band (17) that we seek is thus found from the sum of the two matrix elements squared,

$$\begin{aligned} I(i \to f) &\sim \big| \big\langle \Psi_i^{\text{vib}} \big| \boldsymbol{\mu}^{\text{ind}} \big| \Psi_f^{\text{vib}} \big\rangle \big|^2 \\ &= |X(0,0,0,0)|^2 + |Z(0,0,0,0)|^2. \end{aligned} \tag{37}$$

The expressions obtained here for the matrix elements and the intensity of the combination band agree well with what has been derived in previous investigations [22,28] for permitted transitions. Induced dipole $\boldsymbol{\mu}^{\text{ind}}$ is given by

$$(\mu_j^{\text{BF}})^{\text{ind}} = \sum_r \alpha_{jr}^{\text{BF}} F_r^{\text{BF}}.$$

In this formula, F_r^{BF} implies the components of an external field; polarizability tensor α_{jr}^{BF} is defined by (21) in which the energy, wave functions, and matrix elements depend on vibrational coordinates, as explained.

Lifting a prohibition of the combination transition (17) modifies the selection rules. Quantum number K is no longer zero; the rotational wave functions in the form (3) are applicable. For the line strength, we hence must have the same expression as (12). In (12), the terms

$$(-1)^{-K} \begin{pmatrix} J' & 2 & J \\ K' & \pm 1 & -K \end{pmatrix} \big\langle \Psi_i^{\text{vib}} \big| \alpha_{\pm 1}^{\text{BF}} \big| \Psi_f^{\text{vib}} \big\rangle$$

give rise to selection rules $J' - J = 0, \pm 1, \pm 2$ and $K' - K = \pm 1$. As matrix element

$$\big\langle \Psi_i^{\text{vib}} \big| \alpha_{\pm 1}^{\text{BF}} \big| \Psi_f^{\text{vib}} \big\rangle, \tag{38}$$

in which

$$\alpha_{\pm 1}^{\text{BF}} = \cdots + \frac{\partial^2 \alpha_{\pm 1}^{\text{BF}}}{\partial q_{2x} \partial q_3} q_{2x} q_3 + \cdots, \tag{39}$$

was shown above not to vanish, the transitions having $\Delta J = \pm 1$ can occur as well as transitions with the $\Delta J = 0, \pm 2$ characteristic to induced absorption in a symmetric diatomic molecule.

Interestingly, the vibrating molecule in an external field manifests itself as if the induced dipole moment were permanent. Using (4), for the line strength, we obtain

$$\begin{aligned} &S(i \to f) \\ &\sim \Bigg| \sum_{\Omega' = 0, \pm 1} (-1)^{-K} \begin{pmatrix} J' & 1 & J \\ K' & \Omega' & -K \end{pmatrix} \\ &\quad \times \big\langle \Psi_i^{\text{vib}} \big| \mu_{\Omega'}^{\text{ind}} \big| \Psi_f^{\text{vib}} \big\rangle \Bigg|^2, \end{aligned} \tag{40}$$

where the matrix element $\langle \Psi_i^{\text{vib}} | \mu_{\Omega'}^{\text{ind}} | \Psi_f^{\text{vib}} \rangle$ for the $\nu_2 + \nu_3$ combination band was calculated above. This means that induced transitions with $\Delta J = \pm 1$ are permitted and can be perceived in the measured band shapes. Worth noting is that the manifestation of extended selection rules is the more pronounced the more important is the vibrational anharmonicity.

To resume, we can state that once a linear molecule is exposed to an external field directed at an angle with respect to the C_∞ molecular axis, the symmetry of electronic distribution is most likely broken. As a result, supplementary terms may appear in the Hamiltonian, whereas new nondiagonal components of the polarizability tensor give rise to new terms in the dipole moment expansion. Expectedly, the dipole-forbidden $\nu_2 + \nu_3$ rovibrational transition with conventional quasidiatomic rotational selection rules $\Delta J = 0, \pm 2$ becomes slightly permitted. The integrated intensity of this transition is given by (37). Moreover, the rotational structure of this rovibrational band is enriched by transitions with $\Delta J = \pm 1$ as it was initially suggested in [11].

IV. CONCLUSION

We have shown that in symmetric polyatomic molecules, the selection rules for induced absorption proceed beyond $\Delta J = 0, \pm 2$ derived for diatomic molecules. In a linear molecule *XYX,* the induced dipole moment related to polarizability components (29) does not turn into itself upon rotation of a molecule by 180° against its B axis; the reason is that the nonzero polarizability terms arise from the dependence of the electronic wave function on normal coordinates q_{2x} and q_3. Induced dipole moment $\boldsymbol{\mu}^{\text{ind}}$ hence does not transform into itself when angle θ is replaced by $\pi - \theta$. The anisotropy of the induced dipole produced with an externally applied field is intrinsic to the induced absorption within a combination band and makes a molecule behave as if the induced dipole were permanent. As a result, the conventional selection rules appropriate to induced absorption become supplemented with extended selection rules that, presumably, are not restricted to $\Delta J = \pm 1$, but can include other weaker rotational transitions with $\Delta J = \pm 3$, and so forth, provided that higher terms in expansions against the vibrational coordinates are taken into account. As a result, the pictorial guess suggested by [11] receives its theoretical confirmation.

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