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Anharmonic Raman intensities of overtone, combination and difference bands^{a)}

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The influence of anharmonicity up to the cubic force constants on the Raman tensors of binary overtone, combination, and difference bands is investigated. Formulas for the absolute differential Raman scattering cross sections of these bands are reported for all possible cases of degeneracy as a function of the invariants of the anharmonic Raman tensors. The evaluation of anharmonic Raman tensors as a function of Hoy, Mills, and Strey's \mathcal{L} tensor, cubic force constants, and bond polarizability parameters is illustrated for the tetrahedral AB₄ molecule.

INTRODUCTION

Harmonic approximation formulas for the absolute differential Raman scattering cross sections of binary overtone, combination, and difference bands have been recently reported.^{1,2} Previous works considering the influence of anharmonicity on the dipole vibrational transition moments³⁻⁶ have shown that, in general, anharmonicity may introduce dramatic perturbations with respect to the values predicted by the harmonic model. Hence, it may also be necessary to take into account anharmonicity in order to go further in the interpretation of the Raman intensities of overtone, combination, and difference bands.

In the present work the anharmonic formulation of the Raman intensities of binary overtone, combination, and difference bands is reported. As an example, detailed expressions for the anharmonic Raman tensors of the tetrahedral AB₄ molecule are given as a function of the cubic force constants and of the polarizability parameters (eop's) of the AB bond.

THEORETICAL BACKGROUND

According to Placzek's theory of the Raman effect,⁷ the absolute differential Raman scattering cross section for a Stokes band related to the transitions between the vibrational levels i and j is given, for a 90° scattering geometry, by the equation

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = (2\pi)^4 (\nu_0 - \nu_{ij})^4 \frac{\sum_{i,j} (|\langle i|\alpha_{yy}|j\rangle|^2 + |\langle i|\alpha_{xy}|j\rangle|^2) \exp(-E_i/kT)}{\sum_v g(v) \exp(-E_v/kT)}, \quad (1)$$

where ν_0 is the wave number of the monochromatic exciting radiation and ν_{ij} the Raman shift of the transitions contributing to the total cross section of the vibrational band; $|i\rangle$ and $|j\rangle$ are the vibrational wave functions of initial and final levels, respectively, E_i the energy of the initial level, and E_v that of the level with vibrational quantum number v ; $g(v)$ stands for the degeneracy, being $g(v) = v + 1$ for doubly degenerate modes and $g(v) = (v + 1)(v + 2)/2$ for the triply degenerate ones. α_{yy} and α_{xy} are elements of the molecular polarizability

in the space-fixed reference frame, and the horizontal bar over the transition moments of Eq. (1) refers to the spatial average of the space-fixed frame with respect to that of the randomly oriented molecule; k and T have the usual meaning.

Equation (1) is subject to the limitations of Placzek's theory⁷ and is only valid for a freely orientable molecule of a sample of noninteracting molecules at thermal equilibrium under the following experimental conditions:

- (i) laser beam direction: X axis of the space-fixed frame (XYZ),
- (ii) laser beam polarization: Y axis,
- (iii) Raman signal direction: Z axis,
- (iv) Raman signal polarization: both components (no analyzer).

In the harmonic approximation, Eq. (1) may be simplified by using the harmonic wave functions $|i_{\text{har}}\rangle$ and $|j_{\text{har}}\rangle$. Hence, the Raman cross sections of binary overtone, combination, and difference bands may be given in terms of molecular properties, namely, the invariants (trace and anisotropy) of the second derivatives of the molecular polarizability with respect to the normal coordinates.^{1,2}

How to properly introduce the vibrational anharmonicity is the question now. In principle, this could be done from the beginning by expanding the actual anharmonic wave functions of Eq. (1) in the harmonic basis set

$$|i_{\text{anh}}\rangle = \sum_k a_{ik} |k_{\text{har}}\rangle, \quad |j_{\text{anh}}\rangle = \sum_k a_{jk} |k_{\text{har}}\rangle. \quad (2)$$

However, the complexity of Eq. (1) soon increases rapidly and its simplification in terms of the molecular polarizability invariants is not evident.

A more elegant procedure arises from the use of an appropriate contact transformation \mathbf{T} of the components α_{yy} and α_{xy} of the molecular polarizability in the same theoretical line earlier developed for the dipole moment operator.³⁻⁶ Accordingly, the vibrational transition moments in Eq. (1) may be expressed as

$$\langle i_{\text{anh}} | (\alpha_{yy}) | j_{\text{anh}} \rangle = \langle i_{\text{har}} | (\alpha_{yy})_{\text{eff}} | j_{\text{har}} \rangle, \quad (3)$$

where

^{a)} Issued as CSIC No. FM90.

$$(\alpha_{yy})_{\text{eff}} = \mathbf{T}(\alpha_{yy})\mathbf{T}^{-1} \quad (4)$$

is the transformed or "effective" yy component of the molecular polarizability operator. In the following, $(\alpha_{yy})_{\text{eff}}$ shall be referred to as the "anharmonic" polarizability. The main advantage of this method is the fact that the anharmonic transition moments are expressed in terms of the harmonic wave functions $|i_{\text{har}}\rangle$ and $|j_{\text{har}}\rangle$ of only the initial and final unperturbed vibrational states.

The anharmonic polarizability tensor has the form

$$\begin{aligned} \alpha_{\text{anh}} = \mathbf{T}\alpha\mathbf{T}^{-1} = & \alpha_0 + \sum_s \left(\frac{\partial \alpha}{\partial q^s} \right)_0 q^s \\ & + \frac{1}{2!} \sum_{ss'} \left(\frac{\partial^2 \alpha}{\partial q^s \partial q^{s'}} \right)_0 q^s q^{s'} + \hbar \sum_{s \leq s'} \sum_m \left(\frac{\partial \alpha}{\partial q^m} \right)_0 [S_{ss'}^m q^s q^{s'} \\ & + S^{ss'm} (1 + \delta_{sm} + \delta_{s'm}) P_s P_{s'}] + \dots, \end{aligned} \quad (5)$$

where q^s are dimensionless normal coordinates and P_s their conjugate momenta. The coefficients $S_{ss'}^m$ and $S^{ss'm}$ have been given by Amat, Goldsmith, and Nielsen⁸ as a function of cubic force constants and harmonic wave numbers. The anharmonic Raman tensors of binary overtone, combination, or difference bands may be deduced from Eq. (5), their general form being

$$\begin{aligned} (\alpha''_{ii'})_{\text{anh}} = & \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_{\text{anh}} = \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_h \\ & + \frac{\hbar(1 + \delta_{ii'})}{\sqrt{2} b_i b_{i'}} \sum_m b_m \left(\frac{\partial \alpha}{\partial Q_m} \right)_h \\ & \times [S_{ii'}^m + \hbar^2 S^{ii'm} (1 + \delta_{im} + \delta_{i'm})] + \dots, \end{aligned} \quad (6)$$

where the (-) option stands for overtones and combination bands, and the (+) for the difference bands. Q are mass-weighted normal coordinates (dimensions of $M^{1/2}L$) and

$$b_i = (\hbar/8\pi^2 \omega_i c)^{1/2} \quad (7)$$

is the zero vibrational amplitude of the normal mode Q_i . Substitution of functions $S_{ii'}^m$ and $S^{ii'm}$ in Eq. (6) yields the explicit form of the Raman tensors whose invariants shall be used in Eqs. (14) to (27) of the present work. These tensors are:

(i) *binary overtones*:

$$\begin{aligned} \left(\frac{\partial^2 \alpha}{\partial Q_i^2} \right)_{\text{anh}} = & \left(\frac{\partial^2 \alpha}{\partial Q_i^2} \right)_h + \frac{1}{3\sqrt{2} b_i} \frac{\phi^{iii}}{\omega_i} \left(\frac{\partial \alpha}{\partial Q_i} \right)_h \\ & + \sum_{m \neq i} \frac{b_m}{\sqrt{2} b_i^2} \frac{\phi^{iim} \omega_m}{(4\omega_i^2 - \omega_m^2)} \left(\frac{\partial \alpha}{\partial Q_m} \right)_h, \end{aligned} \quad (8)$$

(ii) *binary combination bands*:

$$\begin{aligned} \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_{\text{anh}}^c = & \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_h + \frac{1}{\sqrt{2} b_i} \frac{\phi^{iii} \omega_i}{\omega_i (2\omega_i + \omega_{i'})} \left(\frac{\partial \alpha}{\partial Q_i} \right)_h \\ & + \frac{1}{\sqrt{2} b_i} \frac{\phi^{i'i'i} \omega_{i'}}{\omega_i (2\omega_{i'} + \omega_i)} \left(\frac{\partial \alpha}{\partial Q_{i'}} \right)_h \\ & + \sum_{m \neq i, i'} \frac{b_m}{\sqrt{2} b_i b_{i'}} \frac{\phi^{iim} \omega_m}{[(\omega_i + \omega_{i'})^2 - \omega_m^2]} \left(\frac{\partial \alpha}{\partial Q_m} \right)_h, \end{aligned} \quad (9)$$

(iii) *binary difference bands*:

$$\begin{aligned} \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_{\text{anh}}^D = & \left(\frac{\partial^2 \alpha}{\partial Q_i \partial Q_{i'}} \right)_h - \frac{1}{\sqrt{2} b_i} \frac{\phi^{iii} \omega_i}{\omega_i (2\omega_i - \omega_{i'})} \left(\frac{\partial \alpha}{\partial Q_i} \right)_h \\ & - \frac{1}{\sqrt{2} b_i} \frac{\phi^{i'i'i} \omega_{i'}}{\omega_i (2\omega_{i'} - \omega_i)} \left(\frac{\partial \alpha}{\partial Q_{i'}} \right)_h \\ & + \sum_{m \neq i, i'} \frac{b_m}{\sqrt{2} b_i b_{i'}} \frac{\phi^{iim} \omega_m}{[(\omega_i - \omega_{i'})^2 - \omega_m^2]} \left(\frac{\partial \alpha}{\partial Q_m} \right)_h. \end{aligned} \quad (10)$$

Label h in Eqs. (6) and (8)–(10) stands for harmonic Raman tensors. ϕ^{rst} are the cubic force constants in the representation of adimensional normal coordinates. These force constants are defined according to Ref. 9, and are given in units of cm^{-1} . They are related to the quadratic (f^{ij}) and cubic (f^{ijk}) force constants in curvilinear coordinates by

$$\phi^{rst} = 2\sqrt{2} b_r b_s b_t [f^{ijk} L_i^r L_j^s L_k^t + f^{ijl} (L_i^r L_j^s L_l^t + L_i^t L_j^s + L_i^s L_j^t)] \quad (11)$$

with L_i^r , L_i^s , etc. being elements of the \mathfrak{L} tensor of Hoy, Mills, and Strey⁹ in the representation of internal coordinates.

Once the concept of anharmonic polarizability has been introduced, the transition moments $\langle i_{\text{har}} | \alpha_{\text{anh}} | j_{\text{har}} \rangle$ can be calculated for all possible cases of binary overtone, combination, and difference transitions of nondegenerate, doubly and triply degenerate modes. In order to separate the radial and angular parts of the transition moments, doubly degenerate coordinates were defined as

$$\begin{aligned} Q_+ = & (Q_a + iQ_b)/\sqrt{2} = (1/\sqrt{2}) r e^{i\varphi}, \\ Q_- = & (Q_a - iQ_b)/\sqrt{2} = (1/\sqrt{2}) r e^{-i\varphi}, \end{aligned} \quad (12)$$

while the triply degenerate modes were described in terms of spherical harmonics $Y_{l,m}$:

$$\begin{aligned} Q_+ = & (Q_a + iQ_b)/\sqrt{2} = 2i(\pi/3)^{1/2} r Y_{1,1}, \\ Q_- = & (Q_a - iQ_b)/\sqrt{2} = -2i(\pi/3)^{1/2} r Y_{1,-1}, \\ Q_0 = & Q_c = -2i(\pi/3)^{1/2} r Y_{1,0}. \end{aligned} \quad (13)$$

The radial part of the transition moments was evaluated with the aid of the tables for radial matrix elements by Shaffer and Krohn,¹⁰ whereas the transition moments of the spherical harmonics were calculated using its 3- j symbol equivalence.¹¹

The calculation of transition moments of overtones of doubly and triply degenerate modes has been explained in some detail in a previous work.² The method followed here has been essentially the same.

Still, an important problem in connection with the sum over vibrational levels of Eq. (1) is the final temperature dependence of the scattering cross section of binary overtone, combination, and difference bands. Fortunately, Yao and Overend⁴ have given a thorough explanation of the influence of anharmonicity on the temperature dependence of vibrational intensities. At moderate temperatures, binary overtone, combination, and difference bands of fundamentals higher than 200 cm^{-1} have very nearly the same temperature dependence as in the harmonic case. Their conclusions shall be accepted in the present work without further comments.

Finally, it must be emphasized that the contact transformation method is not valid under a condition of strong resonance. In such a case, an exact treatment should be required. However, the frontier between resonance and nonresonance is artificial and quite diffuse since, for instance, functions of the form $(4\omega_i^2 - \omega_m^2)^{-1}$ approach continuously to the resonant value $\omega_m = 2\omega_i$, so that, according to Eqs. (8) to (10), a certain degree of resonance is always present. Establishing clear limits of applicability of the contact transformation method should be the subject of future theoretical work.

The algebraic expansion of the above arguments yields a set of equations for the interpretation of absolute differential Raman scattering cross sections of Stokes transitions, namely, (a) *first overtone of a nondegenerate fundamental* Q_i :

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_i} = \frac{(2\pi)^4}{90} \frac{(\nu_0 - 2\nu_i)^4}{B(\nu_i)^2} b_{il}^4 [45\bar{\alpha}^2(\alpha''_{ii}) + 7\gamma^2(\alpha''_{ii})], \quad (14)$$

with $b_i^2 = h/(8\pi^2\nu_i c)$ the square of the zero vibrational amplitude of the mode Q_i and $\alpha''_{ii} = (\partial^2\alpha/\partial Q_i^2)_{\text{anh}}$; the factor $B(\nu_i)^2 = [1 - \exp(-h\nu_i c/kT)]^2$ describes the temperature dependence of the first overtone; (b) *first overtone of a doubly degenerate fundamental* Q_{pa}, Q_{pb} :

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_p} = \frac{(2\pi)^4}{90} \frac{(\nu_0 - 2\nu_p)^4}{B(\nu_p)^2} b_p^4 2 [45\bar{\alpha}^2(\alpha''_{pa,pa}) + 7\gamma^2(\alpha''_{pa,pa}) + 45\bar{\alpha}^2(\alpha''_{pb,pb}) + 7\gamma^2(\alpha''_{pb,pb})], \quad (15)$$

where

$$\begin{aligned} \alpha''_{pa,pa} &= (\alpha''_{pa,pa} + \alpha''_{pb,pb})/2, \\ \alpha''_{pb,pb} &= (\alpha''_{pa,pa} - \alpha''_{pb,pb} + 2i\alpha''_{pa,pb})/2, \end{aligned} \quad (16)$$

with

$$\alpha''_{pa,pa} = (\partial^2\alpha/\partial Q_{pa}^2)_{\text{anh}}, \quad \alpha''_{pb,pb} = (\partial^2\alpha/\partial Q_{pb}^2)_{\text{anh}},$$

and

$$\alpha''_{pa,pb} = (\partial^2\alpha/\partial Q_{pa}\partial Q_{pb})_{\text{anh}};$$

(c) *first overtone of a triply degenerate fundamental* Q_{ax}, Q_{ay}, Q_{az} :

$$\begin{aligned} \left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_q} &= \frac{(2\pi)^4(\nu_0 - 2\nu_q)^4}{90B(\nu_q)^2} b_q^4 3 [45\bar{\alpha}^2(\alpha''_{qx,qx}) \\ &+ 7\gamma^2(\alpha''_{qx,qx}) + 14\gamma^2(\alpha''_{qx,qy})], \end{aligned} \quad (17)$$

with $\alpha''_{qx,qx} = (\partial^2\alpha/\partial Q_{qx}^2)_{\text{anh}}$ and $\alpha''_{qx,qy} = (\partial^2\alpha/\partial Q_{qx}\partial Q_{qy})_{\text{anh}}$; Eq. (17) is invariant with respect to cyclic substitutions in the set of indices (qx, qy, qz) ; (d) *combination bands of two fundamentals* Q_i, Q_m (at least one of the fundamentals, say Q_m , must be nondegenerate):

$$\begin{aligned} \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_i+\nu_m} &= \frac{(2\pi)^4(\nu_0 - \nu_i - \nu_m)^4}{45B(\nu_i) \cdot B(\nu_m)} \\ &\times b_i^2 b_m^2 g_{il} [45\bar{\alpha}^2(\alpha''_{im})^C + 7\gamma^2(\alpha''_{im})^C], \end{aligned} \quad (18)$$

with $(\alpha''_{im})^C = (\partial^2\alpha/\partial Q_i\partial Q_m)_{\text{anh}}^C$ and $g_i = 1, 2$, or 3 being the degeneracy of the fundamental Q_i ; (e) *difference bands of two fundamentals* Q_i, Q_m (at least one of the fundamentals, say Q_m , must be nondegenerate):

$$\begin{aligned} \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_i-\nu_m} &= \frac{(2\pi)^4(\nu_0 - \nu_i + \nu_m)^4}{45B(\nu_i) \cdot A(\nu_m)} \\ &\times b_i^2 b_m^2 g_{il} [45\bar{\alpha}^2(\alpha''_{im})^D + 7\gamma^2(\alpha''_{im})^D], \end{aligned} \quad (19)$$

with $A(\nu_m) = [\exp(h\nu_m c/kT) - 1]$; as shown in Eqs. (9) and (10), the anharmonic Raman tensors $(\alpha''_{im})^D = (\partial^2\alpha/\partial Q_i\partial Q_m)_{\text{anh}}^D$ of difference bands and $(\alpha''_{im})^C = (\partial^2\alpha/\partial Q_i\partial Q_m)_{\text{anh}}^C$ of combination bands may be different in spite of involving the same fundamentals Q_i and Q_m in both cases; (f) *combination bands of two doubly degenerate fundamentals* Q_{pa}, Q_{pb} and Q_{qa}, Q_{qb} :

$$\begin{aligned} \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_p+\nu_q} &= \frac{(2\pi)^4(\nu_0 - \nu_p - \nu_q)^4}{45B(\nu_p) \cdot B(\nu_q)} b_p^2 b_q^2 2 [45\bar{\alpha}^2(\alpha''_{pa,qa})^C \\ &+ 7\gamma^2(\alpha''_{pa,qa})^C + 45\bar{\alpha}^2(\alpha''_{pb,qb})^C + 7\gamma^2(\alpha''_{pb,qb})^C], \end{aligned} \quad (20)$$

with

$$(\alpha''_{pa,qa})^C = (\alpha''_{pa,qa} + \alpha''_{pb,qb})^C/2, \quad (21)$$

$$(\alpha''_{pb,qb})^C = (\alpha''_{pa,qa} - \alpha''_{pb,qb} + 2i\alpha''_{pa,qb})^C/2;$$

(g) *difference bands of two doubly degenerate fundamentals* Q_{pa}, Q_{pb} and Q_{qa}, Q_{qb} :

TABLE I. Symmetry coordinates for the tetrahedral AB_4 molecule. Geometry: $A(0, 0, 0)$, $B_1(b, -b, b)$, $B_2(-b, b, b)$, $B_3(-b, -b, -b)$, $B_4(b, b, -b)$. $b = r_{AB}/\sqrt{3}$, $a = 1 \text{ \AA}$ as the normalization length.

| Symmetry coordinate | Δr_1 | Δr_2 | Δr_3 | Δr_4 | $\Delta(\alpha\alpha_{12})$ | $\Delta(\alpha\alpha_{34})$ | $\Delta(\alpha\alpha_{13})$ | $\Delta(\alpha\alpha_{23})$ | $\Delta(\alpha\alpha_{24})$ | $\Delta(\alpha\alpha_{14})$ | Normalization factor |
|---------------------|--------------|--------------|--------------|--------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------|
| $S_1(A_1)$ | 1 | 1 | 1 | 1 | | | | | | | 2^{-1} |
| $S_{2a}(E)$ | | | | | 2 | 2 | -1 | -1 | -1 | -1 | $12^{-1/2}$ |
| $S_{2b}(E)$ | | | | | | | 1 | -1 | 1 | -1 | 2^{-1} |
| $S_{3x}(F_2)$ | 1 | -1 | -1 | 1 | | | | | | | 2^{-1} |
| $S_{4x}(F_2)$ | | | | | | | | 1 | | -1 | $2^{-1/2}$ |
| $S_{3y}(F_2)$ | -1 | 1 | -1 | 1 | | | | | | | 2^{-1} |
| $S_{4y}(F_2)$ | | | | | | | 1 | | -1 | | $2^{-1/2}$ |
| $S_{3z}(F_2)$ | 1 | 1 | -1 | -1 | | | | | | | 2^{-1} |
| $S_{4z}(F_2)$ | | | | | -1 | 1 | | | | | $2^{-1/2}$ |

TABLE II. \mathcal{L}_I^{rs} elements of the \mathcal{L} tensor for the tetrahedral AB_4 molecule in the basis set of Table I as a function of the elements of the L matrix of harmonic vibrational eigenvectors.^a Nongiven elements are zero by symmetry. r = bond length; $a = 1 \text{ \AA}$.

| l | r | s | \mathcal{L}_I^{rs} |
|-----|-----|-----|--|
| 2a | 1 | 2a | $-L_{11}L_{22}/2r$ |
| 2b | 1 | 2b | |
| 4x | 1 | 3x | $-L_{11}L_{43}/2r$ |
| 4y | 1 | 3y | |
| 4z | 1 | 3z | |
| 4x | 1 | 4x | $-L_{11}L_{44}/2r$ |
| 4y | 1 | 4y | |
| 4z | 1 | 4z | |
| 1 | 2a | 2a | |
| 1 | 2b | 2b | |
| 2a | 2a | 2a | $-G_{22}/4\sqrt{6}a$ |
| 2b | 2a | 2b | $-\mathcal{L}_{2a}^{2a,2a}$ |
| 3x | 2a | 3x | $rL_{22}L_{43}/4a^2\sqrt{6}$ |
| 3y | 2a | 3y | |
| 3z | 2a | 3z | $-2\mathcal{L}_{3x}^{2a,3x}$ |
| 4x | 2a | 3x | $-L_{22}L_{33}/2r\sqrt{6}$ |
| 4y | 2a | 3y | |
| 4z | 2a | 3z | $-2\mathcal{L}_{4x}^{2a,3x}$ |
| 3x | 2a | 4x | $rL_{22}L_{44}/4a^2\sqrt{6}$ |
| 3y | 2a | 4y | |
| 3z | 2a | 4z | $-2\mathcal{L}_{3x}^{2a,4x}$ |
| 4x | 2a | 4x | $-L_{22}L_{34}/2r\sqrt{6}$ |
| 4y | 2a | 4y | |
| 4z | 2a | 4z | $-2\mathcal{L}_{4x}^{2a,4x}$ |
| 3x | 2b | 3x | $\sqrt{3}\mathcal{L}_{3x}^{2a,3x}$ |
| 3y | 2b | 3y | $-\sqrt{3}\mathcal{L}_{3x}^{2a,3x}$ |
| 4x | 2b | 3x | $\sqrt{3}\mathcal{L}_{4x}^{2a,3x}$ |
| 4y | 2b | 3y | $-\sqrt{3}\mathcal{L}_{4x}^{2a,3x}$ |
| 3x | 2b | 4x | $\sqrt{3}\mathcal{L}_{3x}^{2a,4x}$ |
| 3y | 2b | 4y | $-\sqrt{3}\mathcal{L}_{3x}^{2a,4x}$ |
| 4x | 2b | 4x | $\sqrt{3}\mathcal{L}_{4x}^{2a,4x}$ |
| 4y | 2b | 4y | $-\sqrt{3}\mathcal{L}_{4x}^{2a,4x}$ |
| 1 | 3x | 3x | $rL_{43}L_{43}/4a^2$ |
| 1 | 3y | 3y | |
| 1 | 3z | 3z | |
| 2a | 3x | 3x | $(-3L_{43}/2\sqrt{6})(L_{43}/4a + L_{33}/r)$ |
| 2b | 3x | 3x | $\sqrt{3}\mathcal{L}_{2a}^{3x,3x}$ |
| 2a | 3y | 3y | $\mathcal{L}_{2a}^{3x,3x}$ |
| 2b | 3y | 3y | $-\sqrt{3}\mathcal{L}_{2a}^{3x,3x}$ |
| 2a | 3z | 3z | $-2\mathcal{L}_{2a}^{3x,3x}$ |
| 3z | 3x | 3y | $rL_{43}L_{43}/8a^2$ |
| 3x | 3y | 3z | |
| 3y | 3z | 3x | |
| 4z | 3x | 3y | $(L_{43}/2)(3L_{43}/4a - L_{33}/r)$ |
| 4x | 3y | 3z | |
| 4y | 3z | 3x | |
| 1 | 3x | 4x | $rL_{43}L_{44}/4a^2$ |
| 1 | 3y | 4y | |
| 1 | 3z | 4z | |

TABLE II (Continued)

| l | r | s | \mathcal{L}_I^{rs} |
|-----|-----|-----|---|
| 2a | 3x | 4x | $-(3/4\sqrt{6})[L_{43}L_{44}/2a + (L_{33}L_{44} + L_{43}L_{34})/r]$ |
| 2a | 3y | 4y | |
| 2a | 3z | 4z | $-2\mathcal{L}_{2a}^{3x,4x}$ |
| 2b | 3x | 4x | $\sqrt{3}\mathcal{L}_{2a}^{3x,4x}$ |
| 2b | 3y | 4y | $-\sqrt{3}\mathcal{L}_{2a}^{3x,4x}$ |
| 3z | 3x | 4y | $rL_{43}L_{44}/8a^2$ |
| 3x | 3y | 4z | |
| 3y | 3z | 4x | |
| 3z | 4x | 3y | |
| 3x | 4y | 3z | |
| 3y | 4z | 3x | |
| 4z | 3x | 4y | $3L_{43}L_{44}/8a - (L_{33}L_{44} + L_{43}L_{34})/4r$ |
| 4x | 3y | 4z | |
| 4y | 3z | 4x | |
| 4z | 4x | 3y | |
| 4x | 4y | 3z | |
| 4y | 4z | 3x | |

^aThe elements $\mathcal{L}_I^{4i,4j}$ ($i, j = x, y, z$) are obtained from $\mathcal{L}_I^{3i,3j}$ substituting L_{43} by L_{44} and L_{33} by L_{34} .

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{\nu_p, \nu_q} = \frac{(2\pi)^4 (\nu_0 - \nu_p + \nu_q)^4}{45B(\nu_p) \cdot A(\nu_q)} b_p^2 b_q^2 [45\bar{\alpha}^2(\alpha''_{px, \sigma})^D + 7\gamma^2(\alpha''_{px, \sigma})^D + 45\bar{\alpha}^2(\alpha''_{px, \sigma})^D + 7\gamma^2(\alpha''_{px, \sigma})^D], \quad (22)$$

with $(\alpha''_{ij})^D$ defined as in Eqs. (21); (h) combination bands of two triply degenerate fundamentals Q_{px} , Q_{py} , Q_{pz} and Q_{qx} , Q_{qy} , Q_{qz} :

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{\nu_p, \nu_q} = \frac{(2\pi)^4 (\nu_0 - \nu_p - \nu_q)^4}{45B(\nu_p) \cdot B(\nu_q)} b_p^2 b_q^2 [45\bar{\alpha}^2(\alpha''_{px, \sigma})^C + 7\gamma^2(\alpha''_{px, \sigma})^C + 14\gamma^2(\alpha''_{px, \sigma})^C]; \quad (23)$$

this equation is invariant with respect to cyclic substitutions in the set of indices x, y, z ; (i) difference bands of two triply degenerate fundamentals Q_{px} , Q_{py} , Q_{pz} and Q_{qx} , Q_{qy} , Q_{qz} :

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{\nu_p, \nu_q} = \frac{(2\pi)^4 (\nu_0 - \nu_p + \nu_q)^4}{45B(\nu_p) \cdot A(\nu_q)} b_p^2 b_q^2 [45\bar{\alpha}^2(\alpha''_{px, \sigma})^D + 7\gamma^2(\alpha''_{px, \sigma})^D + 14\gamma^2(\alpha''_{px, \sigma})^D]; \quad (24)$$

(j) combination bands of doubly degenerate fundamental Q_{pa} , Q_{pb} with a triply degenerate fundamental Q_{qa} , Q_{qb} , Q_{qc} :

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{\nu_p, \nu_q} = \frac{(2\pi)^4 (\nu_0 - \nu_p - \nu_q)^4}{45B(\nu_p) \cdot B(\nu_q)} b_p^2 b_q^2 [14\gamma^2(\alpha''_{pa, \sigma})^C + 14\gamma^2(\alpha''_{pa, \sigma})^C + 14\gamma^2(\alpha''_{pa, \sigma})^C], \quad (25)$$

with

$$\begin{aligned} (\alpha''_{pa, \sigma})^C &= (\alpha''_{pa, \sigma} - \alpha''_{pb, \sigma} - i\alpha''_{pa, \sigma} - i\alpha''_{pb, \sigma})^C/2, \\ (\alpha''_{pb, \sigma})^C &= (\alpha''_{pa, \sigma} + \alpha''_{pb, \sigma} + i\alpha''_{pa, \sigma} - i\alpha''_{pb, \sigma})^C/2, \\ (\alpha''_{pc, \sigma})^C &= (\alpha''_{pa, \sigma} - i\alpha''_{pb, \sigma})^C/\sqrt{2}; \end{aligned} \quad (26)$$

(k) difference bands of a doubly degenerate fundamental Q_{pa} , Q_{pb} with a triply degenerate fundamental Q_{qa} , Q_{qb} , Q_{qc} :

TABLE III. First and second derivatives of the molecular polarizability of the tetrahedral molecule AB_4 with respect to the symmetry coordinates of Table I.

$$\begin{aligned} \partial\alpha/\partial S_1 &= [2(2\alpha' + \gamma')/3] \cdot C \\ \partial\alpha/\partial S_{2a} &= [2\sqrt{6}(\gamma - \alpha)/9a] \cdot A \\ \partial\alpha/\partial S_{2b} &= [2\sqrt{6}(\gamma - \alpha)/9a] \cdot B \\ \partial\alpha/\partial S_{3x} &= -[2(\gamma' - \alpha')/3] \cdot D_x \\ \partial\alpha/\partial S_{3y} &= -[2(\gamma' - \alpha')/3] \cdot D_y \\ \partial\alpha/\partial S_{3z} &= -[2(\gamma' - \alpha')/3] \cdot D_z \\ \partial\alpha/\partial S_{4x} &= [2(\gamma - \alpha)/3a] \cdot D_x \\ \partial\alpha/\partial S_{4y} &= [2(\gamma - \alpha)/3a] \cdot D_y \\ \partial\alpha/\partial S_{4z} &= [2(\gamma - \alpha)/3a] \cdot D_z \\ \partial^2\alpha/\partial S_1^2 &= [(2\alpha'' + \gamma'')/3] \cdot C \\ \partial^2\alpha/\partial S_1 \partial S_{2a} &= [\sqrt{6}(\gamma' - \alpha')/9a] \cdot A \\ \partial^2\alpha/\partial S_1 \partial S_{2b} &= [\sqrt{6}(\gamma' - \alpha')/9a] \cdot B \\ \partial^2\alpha/\partial S_1 \partial S_{3x} &= -[(\gamma'' - \alpha'')/3] \cdot D_x \\ \partial^2\alpha/\partial S_1 \partial S_{3y} &= -[(\gamma'' - \alpha'')/3] \cdot D_y \\ \partial^2\alpha/\partial S_1 \partial S_{3z} &= -[(\gamma'' - \alpha'')/3] \cdot D_z \\ \partial^2\alpha/\partial S_1 \partial S_{4x} &= [(\gamma' - \alpha')/3a] \cdot D_x \\ \partial^2\alpha/\partial S_1 \partial S_{4y} &= [(\gamma' - \alpha')/3a] \cdot D_y \\ \partial^2\alpha/\partial S_1 \partial S_{4z} &= [(\gamma' - \alpha')/3a] \cdot D_z \\ \partial^2\alpha/\partial S_{2a}^2 &= -[(\gamma - \alpha)/9a^2] \cdot A \\ \partial^2\alpha/\partial S_{2b}^2 &= -\partial^2\alpha/\partial S_{2a}^2 \\ \partial^2\alpha/\partial S_{2a} \partial S_{2b} &= [(\gamma - \alpha)/9a^2] \cdot B \\ \partial^2\alpha/\partial S_{2a} \partial S_{3x} &= [\sqrt{6}(\gamma' - \alpha')/18a] \cdot D_x \\ \partial^2\alpha/\partial S_{2a} \partial S_{3y} &= [\sqrt{6}(\gamma' - \alpha')/18a] \cdot D_y \\ \partial^2\alpha/\partial S_{2a} \partial S_{3z} &= -2[\sqrt{6}(\gamma' - \alpha')/18a] \cdot D_z \\ \partial^2\alpha/\partial S_{2b} \partial S_{3x} &= \sqrt{3}[\sqrt{6}(\gamma' - \alpha')/18a] \cdot D_x \\ \partial^2\alpha/\partial S_{2b} \partial S_{3y} &= -\sqrt{3}[\sqrt{6}(\gamma' - \alpha')/18a] \cdot D_y \\ \partial^2\alpha/\partial S_{2b} \partial S_{3z} &= 0 \\ \partial^2\alpha/\partial S_{2a} \partial S_{4x} &= [\sqrt{6}(\gamma - \alpha)/36a^2] \cdot D_x \\ \partial^2\alpha/\partial S_{2a} \partial S_{4y} &= [\sqrt{6}(\gamma - \alpha)/36a^2] \cdot D_y \\ \partial^2\alpha/\partial S_{2a} \partial S_{4z} &= -2[\sqrt{6}(\gamma - \alpha)/36a^2] \cdot D_z \\ \partial^2\alpha/\partial S_{2b} \partial S_{4x} &= \sqrt{3}[\sqrt{6}(\gamma - \alpha)/36a^2] \cdot D_x \\ \partial^2\alpha/\partial S_{2b} \partial S_{4y} &= -\sqrt{3}[\sqrt{6}(\gamma - \alpha)/36a^2] \cdot D_y \\ \partial^2\alpha/\partial S_{2b} \partial S_{4z} &= 0 \\ \partial^2\alpha/\partial S_{3x}^2 &= \partial^2\alpha/\partial S_{3y}^2 = \partial^2\alpha/\partial S_{3z}^2 = \partial^2\alpha/\partial S_1^2 \\ \partial^2\alpha/\partial S_{3x} \partial S_{3y} &= [(\gamma'' - \alpha'')/3] \cdot D_x \\ \partial^2\alpha/\partial S_{3x} \partial S_{3z} &= [(\gamma'' - \alpha'')/3] \cdot D_y \\ \partial^2\alpha/\partial S_{3y} \partial S_{3z} &= [(\gamma'' - \alpha'')/3] \cdot D_z \\ \partial^2\alpha/\partial S_{3x} \partial S_{4x} &= [(\gamma' - \alpha')/6a] \cdot (A + \sqrt{3}B) \\ \partial^2\alpha/\partial S_{3y} \partial S_{4y} &= [(\gamma' - \alpha')/6a] \cdot (A - \sqrt{3}B) \\ \partial^2\alpha/\partial S_{3z} \partial S_{4z} &= -2[(\gamma' - \alpha')/6a] \cdot A \\ \partial^2\alpha/\partial S_{3x} \partial S_{4y} &= \partial^2\alpha/\partial S_{3y} \partial S_{4x} = [(\gamma' - \alpha')/6a] \cdot D_x \\ \partial^2\alpha/\partial S_{3y} \partial S_{4z} &= \partial^2\alpha/\partial S_{3z} \partial S_{4y} = [(\gamma' - \alpha')/6a] \cdot D_x \\ \partial^2\alpha/\partial S_{3z} \partial S_{4x} &= \partial^2\alpha/\partial S_{3x} \partial S_{4z} = [(\gamma' - \alpha')/6a] \cdot D_y \\ \partial^2\alpha/\partial S_{4x}^2 &= [(\gamma - \alpha)/12a^2] \cdot (A + \sqrt{3}B) \\ \partial^2\alpha/\partial S_{4y}^2 &= [(\gamma - \alpha)/12a^2] \cdot (A - \sqrt{3}B) \end{aligned}$$

TABLE III (Continued)

$$\begin{aligned} \partial^2\alpha/\partial S_{4z}^2 &= -2[(\gamma - \alpha)/12a^2] \cdot A \\ \partial^2\alpha/\partial S_{4x} \partial S_{4y} &= [7(\gamma - \alpha)/12a^2] \cdot D_x \\ \partial^2\alpha/\partial S_{4x} \partial S_{4z} &= [7(\gamma - \alpha)/12a^2] \cdot D_y \\ \partial^2\alpha/\partial S_{4y} \partial S_{4z} &= [7(\gamma - \alpha)/12a^2] \cdot D_x \\ A &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \quad B = \begin{pmatrix} \sqrt{3} & 0 & 0 \\ 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ D_x &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad D_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad D_z = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

$$\left(\frac{\partial\alpha}{\partial\Omega}\right)_{\nu_p-\nu_q} = \frac{(2\pi)^4(\nu_0 - \nu_p + \nu_q)^4}{45B(\nu_p) \cdot A(\nu_q)} b_p^2 b_q^2 [14\gamma^2(\alpha''_{p',q'})^D + 14\gamma^2(\alpha''_{p',q'})^D + 14\gamma^2(\alpha''_{p',q'})^D], \quad (27)$$

with $(\alpha''_{ij})^D$ defined as in Eqs. (26).

RAMAN TENSORS OF THE TETRAHEDRAL AB_4 MOLECULE

In order to produce the anharmonic Raman tensors according to Eqs. (8) to (10), the harmonic Raman tensors $(\partial\alpha/\partial Q_i)_h$, $(\partial^2\alpha/\partial Q_i^2)_h$, and $(\partial^2\alpha/\partial Q_i \partial Q_j)_h$ must first be generated. For this purpose the introduction of the curvilinear symmetry coordinates of Table I has proved to be useful.

The harmonic Raman tensors expressed in terms of curvilinear symmetry coordinates are

$$\left(\frac{\partial\alpha}{\partial Q_i}\right)_h = \sum_i \mathcal{L}_i^i \left(\frac{\partial\alpha}{\partial S_i}\right) \quad (28)$$

and

$$\begin{aligned} \left(\frac{\partial^2\alpha}{\partial Q_i \partial Q_j}\right)_h &= \sum_i \left(\frac{\partial\alpha}{\partial S_i}\right) \mathcal{L}_i^{ij} + \sum_i \left(\frac{\partial^2\alpha}{\partial S_i^2}\right) \mathcal{L}_i^i \mathcal{L}_i^j \\ &+ \sum_{i \neq m} \left(\frac{\partial^2\alpha}{\partial S_i \partial S_m}\right) \mathcal{L}_i^i \mathcal{L}_m^j, \quad (29) \end{aligned}$$

where \mathcal{L}_i^i , \mathcal{L}_i^{ij} , etc. are elements of the vibrational \mathcal{L} tensor⁹ in the basis set of Table I. Note that the elements $\mathcal{L}_i^i = L_{ii}$ correspond to the well-known \mathbf{L} matrix of vibrational eigenvectors of the harmonic approximation. The elements \mathcal{L}_i^{ij} of the \mathcal{L} tensor are reported in Table II as a function of the elements of the \mathbf{L} matrix.

At this point, two different sources of mechanical anharmonicity may be distinguished. One of them arises from the nonlinear transformation induced by the use of curvilinear coordinates in the description of the normal modes, which are always defined as rectilinear-oscillatory patterns of the atoms. This contribution is apparent in Eq. (11) as a quadratic term (f^{ij}) in the cubic force constant ϕ^{rst} and again in Eq. (29) with the term in \mathcal{L}_i^{ij} . This anharmonicity effect never vanishes, since \mathcal{L}_i^{ij} only depends on the harmonic force constants f^{ij} and on the molecular geometry. Indeed, this contribution is more a mathematical artifact rather

TABLE IV. Harmonic Raman tensors for the AB₄ tetrahedral molecule.

$$\begin{aligned}
(\partial\alpha/\partial Q_1)_h &= 2(2\alpha' + \gamma') L_{11} C/3 \\
(\partial\alpha/\partial Q_{2a})_h &= 2\sqrt{6} (\gamma - \alpha) L_{22} A/9a \\
(\partial\alpha/\partial Q_{2b})_h &= 2\sqrt{6} (\gamma - \alpha) L_{22} B/9a \\
(\partial\alpha/\partial Q_{3i})_h &= [-2L_{3s}(\gamma' - \alpha')/3 + 2L_{4s}(\gamma - \alpha)/3a] \cdot D_i, \\
s &= 3, 4; \quad i = x, y, z \\
(\partial^2\alpha/\partial Q_1^2)_h &= (2\alpha'' + \gamma'') G_{11} C/3 \\
(\partial^2\alpha/\partial Q_1 \partial Q_{2a})_h &= L_{11} L_{22} \sqrt{6} mA/9, \quad m = (\gamma' - \alpha') - (\gamma - \alpha)/r \\
(\partial^2\alpha/\partial Q_1 \partial Q_{2b})_h &= L_{11} L_{22} \sqrt{6} mB/9 \\
(\partial^2\alpha/\partial Q_1 \partial Q_{3i})_h &= L_{11} [L_{4s} m/3a - L_{3s}(\gamma'' - \alpha'')/3] \cdot D_i, \\
s &= 3, 4; \quad i = x, y, z \\
(\partial^2\alpha/\partial Q_{2a}^2)_h &= G_{22} [r(2\alpha' + \gamma') C/9 - (\gamma - \alpha) A/6] \\
(\partial^2\alpha/\partial Q_{2a} \partial Q_{2b})_h &= G_{22} (\gamma - \alpha) B/6 \\
(\partial^2\alpha/\partial Q_{2b}^2)_h &= G_{22} [r(2\alpha' + \gamma') C/9 + (\gamma - \alpha) A/6] \\
(\partial^2\alpha/\partial Q_{2a} \partial Q_{3x})_h &= f_{2s} D_x, \quad (\partial^2\alpha/\partial Q_{2b} \partial Q_{3x})_h = \sqrt{3} f_{2s} D_x \\
(\partial^2\alpha/\partial Q_{2a} \partial Q_{3y})_h &= f_{2s} D_y, \quad (\partial^2\alpha/\partial Q_{2b} \partial Q_{3y})_h = -\sqrt{3} f_{2s} D_y \\
(\partial^2\alpha/\partial Q_{2a} \partial Q_{3z})_h &= -2f_{2s} D_z, \quad (\partial^2\alpha/\partial Q_{2b} \partial Q_{3z})_h = 0, \quad s = 3, 4 \\
f_{2s} &= -m\sqrt{6} L_{22} (rL_{4s}/2a - L_{3s})/18a \\
(\partial^2\alpha/\partial Q_{3x}^2)_h &= p_s C + L_{3s} L_{4s} m(A + \sqrt{3}B)/3a \\
(\partial^2\alpha/\partial Q_{3y}^2)_h &= p_s C + L_{3s} L_{4s} m(A - \sqrt{3}B)/3a \\
(\partial^2\alpha/\partial Q_{3z}^2)_h &= p_s C - 2L_{3s} L_{4s} mA/3a, \quad s = 3, 4 \\
p_s &= L_{4s} L_{4s} r(2\alpha' + \gamma')/6a^2 + L_{3s} L_{3s} (2\alpha'' + \gamma'')/3 \\
(\partial^2\alpha/\partial Q_{3x} \partial Q_{3y})_h &= g_s D_x \\
(\partial^2\alpha/\partial Q_{3y} \partial Q_{3z})_h &= g_s D_x \\
(\partial^2\alpha/\partial Q_{3z} \partial Q_{3x})_h &= g_s D_y, \quad s = 3, 4 \\
g_s &= L_{4s} L_{4s} rm/12a^2 + L_{3s} L_{3s} (\gamma'' - \alpha'')/3 + L_{4s} L_{3s} m/3a, \\
n &= 10(\gamma - \alpha)/r - (\gamma' - \alpha') \\
(\partial^2\alpha/\partial Q_{3x} \partial Q_{4x})_h &= p_{34} C + (L_{33} L_{44} + L_{43} L_{34}) m(A + \sqrt{3}B)/6a \\
(\partial^2\alpha/\partial Q_{3y} \partial Q_{4y})_h &= p_{34} C + (L_{33} L_{44} + L_{43} L_{34}) m(A - \sqrt{3}B)/6a \\
(\partial^2\alpha/\partial Q_{3z} \partial Q_{4z})_h &= p_{34} C - 2(L_{33} L_{44} + L_{43} L_{34}) mA/6a \\
p_{34} &= L_{43} L_{44} r(2\alpha' + \gamma')/6a^2 + L_{33} L_{34} (2\alpha'' + \gamma'')/3 \\
(\partial^2\alpha/\partial Q_{3x} \partial Q_{4y})_h &= q_{34} D_x \\
(\partial^2\alpha/\partial Q_{3y} \partial Q_{4z})_h &= q_{34} D_x \\
(\partial^2\alpha/\partial Q_{3z} \partial Q_{4x})_h &= q_{34} D_y \\
q_{34} &= m(L_{33} L_{44} + L_{43} L_{34})/6a + nrL_{43} L_{44}/12a^2 + (\gamma'' - \alpha'') L_{33} L_{34}/3
\end{aligned}$$

A, B, C, D_i as in Table III; a = 1 Å; r = bond length
G_{ii} = L_{ii} · L_{ii}, i = 1, 2

than a physical reality. Thus, the label *h* in the harmonic Raman tensor $(\partial^2\alpha/\partial Q_i \partial Q_j)_h$ of Eq. (29) can still be justified.

The other source of mechanical anharmonicity is the cubic force constant f^{ijk} in internal coordinates contributing to the cubic force constant ϕ^{rst} in the representation of adimensional normal coordinates [Eq. (11)]. From the physical point of view, f^{ijk} has a simple interpretation, so that the last contribution is closer to the

intuitive concept of mechanical anharmonicity than the former.

The first and second derivatives $(\partial\alpha/\partial S_i)$ and $(\partial^2\alpha/\partial S_i \partial S_m)$, respectively, of the molecular polarizability with respect to the symmetry coordinates [Eqs. (28) and (29)] may be expanded in terms of bond parameters (eop's) according to the methods described elsewhere.^{1,2} The complete set of derivatives necessary to our purpose is given in Table III as a function of the parameters of the polarizability tensor α_{AB} of the bond AB:

$$\alpha_{AB} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \gamma \end{pmatrix}, \quad (30)$$

and its first and second derivatives with respect to the stretching of the bond

$$\frac{\partial\alpha_{AB}}{\partial r_{AB}} = \begin{pmatrix} \alpha' & 0 & 0 \\ 0 & \alpha' & 0 \\ 0 & 0 & \gamma' \end{pmatrix}, \quad \frac{\partial^2\alpha_{AB}}{\partial r_{AB}^2} = \begin{pmatrix} \alpha'' & 0 & 0 \\ 0 & \alpha'' & 0 \\ 0 & 0 & \gamma'' \end{pmatrix}. \quad (31)$$

The derivatives of Table III have been calculated in the so-called "zero order approximation" of the bond polarizability model and do not include bond-interaction parameters.

The anharmonic Raman tensors for binary overtone, combination, and difference bands of the AB₄ molecule are obtained by substitution of Table IV into Eqs. (8)–(10). The symmetry properties of the cubic force constants ϕ^{rst} of the AB₄ tetrahedral molecule are reported in Table V. These properties greatly simplify the final expression of the anharmonic Raman tensors. For instance, the intensity of the overtone $2\nu_2$ of AB₄ molecules is controlled by the tensors

$$\begin{aligned}
\left(\frac{\partial^2\alpha}{\partial Q_{2a}^2}\right)_{\text{anh}} &= \left(\frac{\partial^2\alpha}{\partial Q_{2a}^2}\right)_h + \frac{1}{3\sqrt{2}b_2} \frac{\phi^{222}}{\omega_2} \left(\frac{\partial\alpha}{\partial Q_{2a}}\right)_h + \\
&+ \frac{b_1}{\sqrt{2}b_2^2} \frac{\phi^{122}\omega_1}{(4\omega_2^2 - \omega_1^2)} \left(\frac{\partial\alpha}{\partial Q_1}\right)_h, \quad (32)
\end{aligned}$$

TABLE V. Symmetry properties of the nonzero cubic force constants ϕ^{rst} of the tetrahedral molecule AB₄ in the representation of dimensionless normal coordinates.

| |
|---|
| $\phi^{122} = \phi^{1,2a,2a} = \phi^{1,2b,2b}$ |
| $\phi^{133} = \phi^{1,3x,3x} = \phi^{1,3y,3y} = \phi^{1,3z,3z}$ |
| $\phi^{134} = \phi^{1,3x,4x} = \phi^{1,3y,4y} = \phi^{1,3z,4z}$ |
| $\phi^{144} = \phi^{1,4x,4x} = \phi^{1,4y,4y} = \phi^{1,4z,4z}$ |
| $\phi^{222} = \phi^{2a,2a,2a} = -\phi^{2a,2b,2b}$ |
| $\phi^{233} = \phi^{2a,3x,3x} = \phi^{2a,3y,3y} = -\frac{1}{2}\phi^{2a,3z,3z} = (1/\sqrt{3})\phi^{2b,3x,3x} = -(1/\sqrt{3})\phi^{2b,3y,3y}$ |
| $\phi^{234} = \phi^{2a,3x,4x} = \phi^{2a,3y,4y} = -\frac{1}{2}\phi^{2a,3z,4z} = (1/\sqrt{3})\phi^{2b,3x,4x} = -(1/\sqrt{3})\phi^{2b,3y,4y}$ |
| $\phi^{244} = \phi^{2a,4x,4x} = \phi^{2a,4y,4y} = -\frac{1}{2}\phi^{2a,4z,4z} = (1/\sqrt{3})\phi^{2b,4x,4x} = -(1/\sqrt{3})\phi^{2b,4y,4y}$ |
| $\phi^{334} = \phi^{3x,3y,4z} = \phi^{3x,4y,3z} = \phi^{4x,3y,3z}$ |
| $\phi^{344} = \phi^{3x,4y,4z} = \phi^{4x,3y,4z} = \phi^{4x,4y,3z}$ |
| ϕ^{rst} other than those above given or other than $\phi^{1,1,1}$, $\phi^{3x,3y,3z}$, and $\phi^{4x,4y,4z}$ are zero by symmetry. |

$$\left(\frac{\partial^2 \alpha}{\partial Q_{2b}^2}\right)_{\text{anh}} = \left(\frac{\partial^2 \alpha}{\partial Q_{2b}^2}\right)_h - \frac{1}{3\sqrt{2}b_2} \frac{\phi^{222}}{\omega_2} \left(\frac{\partial \alpha}{\partial Q_{2a}}\right)_h + \frac{b_1}{\sqrt{2}b_2^2} \frac{\phi^{122}\omega_1}{(4\omega_2^2 - \omega_1^2)} \left(\frac{\partial \alpha}{\partial Q_1}\right)_h, \quad (33)$$

$$\left(\frac{\partial^2 \alpha}{\partial Q_{2a} \partial Q_{2b}}\right)_{\text{anh}} = \left(\frac{\partial^2 \alpha}{\partial Q_{2a} \partial Q_{2b}}\right)_h - \frac{1}{3\sqrt{2}b_2} \frac{\phi^{222}}{\omega_2} \left(\frac{\partial \alpha}{\partial Q_{2b}}\right)_h. \quad (34)$$

These tensors shall be substituted into Eqs. (16) to generate $\alpha''_{2^*,2-}$ and $\alpha''_{2-,2-}$, which are necessary for the interpretation of the Raman intensity of the overtone $2\nu_2$ or, alternatively, to derive information about the cubic force constants ϕ^{122} and ϕ^{222} from the experimental intensity and depolarization ratio. From Eqs. (32) and (33) it becomes apparent that the isotropic component of $2\nu_2$ will show an appreciable intensity in tetrahedral molecules with $\omega_1 \sim 2\omega_2$.

FINAL REMARKS

It has been pointed out before⁵ that the nine vibrational modes $Q_1, Q_{2a}, Q_{2b}, Q_{3x}, Q_{3y}, Q_{3z}, Q_{4x}, Q_{4y},$ and Q_{4z} of the tetrahedral AB_4 molecule may be regarded as non-degenerate modes when the basis of the Cartesian symmetry coordinates of Table I is used. Thus, the interpretation of the Raman scattering differential cross sections of binary overtone, combination, and difference bands of the AB_4 molecule can be accomplished as well with only Eqs. (14), (18), and (19) for the nondegenerate cases. In such a case, the different contributions to each band must be separately calculated. For instance, the intensity of $2\nu_3$ should be interpreted as the sum of intensities of the overtones $2\nu_{3x}, 2\nu_{3y},$ and $2\nu_{3z}$ and of the combination bands $\nu_{3x} + \nu_{3y}, \nu_{3y} + \nu_{3z},$ and $\nu_{3z} + \nu_{3x}$. This property of the basis set is an additional test for the consistency of the complete set of Eqs. (14) to (27), describing the absolute differential Raman scattering cross sections of all possible binary overtone, combinations, and difference bands of degenerate fundamentals.

Finally, the potential interest of the present approach

for obtaining cubic force constants ϕ^{rst} from Raman intensity data should still be emphasized. Due to the resonant terms in the anharmonic Raman tensors [Eqs. (8)–(10)], the Raman intensities of several overtone, combination, and difference bands may be strongly dependent on only one cubic force constant. The magnitude of this cubic force constant might be directly estimated from the intensity ratio of the overtone (or combination, or difference band) with respect to the perturbing fundamental. This would be specially true for perturbing fundamentals belonging to the totally symmetric representation, since the isotropic Raman spectrum ($I_{11} - \frac{4}{3}I_1$) yields, in these cases, very neat bands without overlapping problems.

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