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Raman intensities of overtones and combination bands of C_2H_2, C_2HD, and C_2D_2 [a)]

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Measurements of absolute gas phase vibrational Raman scattering cross sections of binary overtone and combination bands of C_2H_2, C_2HD, and C_2D_2 are reported. Calculated values for these cross sections, which take into account the contribution of the anharmonic force field and the electro-optical anharmonicity, are also presented. Within limitations due to approximations in the theory and uncertainties in the parameters, the comparison between the experimental cross sections and the calculated ones is quite encouraging.

I. INTRODUCTION

In a previous paper,[1] the theory of Raman intensities of binary overtones and combination and difference bands has been formulated in the anharmonic approximation up to the cubic terms. There, the various harmonic and anharmonic contributions to the Raman tensors are analyzed, and the expressions for the absolute differential Raman scattering cross sections $(\partial\sigma/\partial\Omega)$ of binary transitions are presented as a function of the invariants of the Raman tensors. The application of this theory is limited by lack of information for the molecular polarizability and its dependence on normal coordinates. Equilibrium polarizability tensors are known with acceptable accuracy for only a few small polyatomic molecules. First derivatives with respect to normal coordinates are known in a few cases, but second derivatives have so far not been measured. These quantities are difficult to estimate with reasonable accuracy on the basis of quantum-mechanical calculations, although significant improvements are occurring in this field.[2,3] Alternatively, a parametric description known as the bond polarizability model may be used.[4,5] In earlier papers,[1,5-7] the methodology for the calculation of first and second derivatives of the molecular polarizability tensor with respect to a given set of coordinates using this model has been presented.

In the present paper, these theoretical developments[1,5-7] are applied to a practical case: acetylene and its two deuterated isotopic derivatives. These molecules were chosen not only for theoretical reasons, but also because of their particularly simple vibrational spectra. The Raman intensities of binary overtones and combinations for these molecules are, on average, two orders of magnitude weaker than those of fundamental transitions, but, even so, many such bands are intense enough for their cross section to be measured in the gas phase with acceptable accuracy for the present purpose. In addition, the vibrational characteristics of acetylene have been thoroughly investigated. Its har-

monic force field is known with a great degree of confidence on the basis of *ab initio* calculations,[8] frequency analysis,[9,10] and a Raman intensity analysis.[11] The anharmonic force field, which is also necessary for the present task, has been reported by different authors.[9,10,12] The Raman cross sections of the fundamental transitions have recently been measured and analyzed in detail[13]; the Raman tensors for these transitions and the bond polarizability parameters of C–H and C≡C bonds are thus well established. In addition, the high-resolution Raman spectrum of some of these transitions in acetylene was measured in a recent study and analyzed to give vibrational anharmonicity constants.[14]

II. EXPERIMENTAL

The differential Raman scattering cross sections $(\partial\sigma/\partial\Omega)$ of several overtones and combination bands of the molecules C_2H_2, C_2HD, and C_2D_2 in the region below 4500 cm^{-1} have been measured using the fundamental bands[13] as absolute internal standards.

The instrumental apparatus included on 0.85 m Czerny–Turner double monochromator with 1800 ℓ/mm holographic gratings in an additive mounting, controlled by a computer based data acquisition system. A Brewster angle fused silica cell was used, in connection with a 90° multipass device[15] and $f/4$ collection optics. The sample pressure was nearly 800 Torr, and the laser output power approximately 5 W at 514.5 nm. No convergence corrections were applied.

Series of spectra were recorded using the scattering geometries $X[YY]Z$ and $X[YX]Z$ from which the two independent cross sections:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{\text{isotropic}} = \left(\frac{\partial\sigma}{\partial\Omega}\right)^{X[YY]Z} - \frac{4}{3}\left(\frac{\partial\sigma}{\partial\Omega}\right)^{X[YX]Z} \tag{1}$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{\text{anisotropic}} = \frac{7}{3}\left(\frac{\partial\sigma}{\partial\Omega}\right)^{X[YX]Z} \tag{2}$$

TABLE I. Observed and calculated isotropic and anisotropic components of the absolute differential Raman scattering cross sections of C_2H_2, C_2HD, and C_2D_2 in the gas phase.[a]

	Mode	Symmetry	ω	ν	$(\partial\sigma/\partial\Omega)$ Experimental Isotropic	Experimental Anisotropic	Calc. anharmonic Isotropic	Calc. anharmonic Anisotropic
C_2H_2	Q_1	Σ_g^+	3495	3373	4.65(90)	3.42(70)		
	Q_2	Σ_g^+	2008	1974	29.0 (29)	4.65(60)		
	Q_4	Π_g	624	613		5.13(170)		
	$2Q_2$	Σ_g^+		3933	≤ 0.04	b	c	c
	$2Q_4$	$\Sigma_g^+ + \Delta_g$		1230	0.39(6)	0.12(3)	≤ 0.42	≤ 0.14
	$2Q_5$	$\Sigma_g^+ + \Delta_g$		1449	0.025(5)	0.03(4)	≤ 0.08	≤ 0.11
	$Q_1 + Q_4$	Π_g		3969		0.30(8)[d]		0.40(8)
	$Q_3 + Q_5$	Π_g		4002		0.13(6)[d]		0.34(7)
	$Q_2 + Q_4$	Π_g		~2590		≤ 0.1		0.0020(4)
C_2HD	Q_1	Σ^+	3460	3336	2.49(50)	1.92(40)		
	Q_2	Σ^+	1884	1845	29.8(45)	5.21(100)		
	Q_3	Σ^+	2656	2584	0.17(3)	0.22(3)		
	Q_4	Π	528	519		9.51(200)		
	Q_5	Π	693	679		1.02(30)		
	$2Q_2$	Σ^+		3700	0.0055(30)	≤ 0.003	c	c
	$2Q_4$	$\Sigma^+ + \Delta$		1034	0.10(6)	0.013(4)	≤ 0.16	≤ 0.14
	$2Q_5$	$\Sigma^+ + \Delta$		1342	0.010(3)	0.008(6)	≤ 0.038	≤ 0.10
	$2Q_4 + Q_5$	$\Sigma^+ + \Delta$		1200	0.21(3)	0.019(6)	0.13(2)	0.011(3)
	$Q_2 + Q_3$	Σ^+		4416	0.0055(30)	≤ 0.003	c	c
	$Q_1 + Q_4$	Π		3855		≤ 0.10		0.033(6)
	$Q_1 + Q_5$	Π		3997		0.41(10)		0.34(7)
	$Q_2 + Q_4$	Π		2370		≤ 0.04		0.013(3)
	$Q_2 + Q_5$	Π		2529		e		0.000(1)
	$Q_3 + Q_4$	Π		3088		0.16(6)		0.23(5)
	$Q_3 + Q_5$	Π		~3260		e		0.023(5)
C_2D_2	Q_1	Σ_g^+	2782	2705	0.025(10)	1.06(20)		
	Q_2	Σ_g^+	1793	1765	30.9(50)	6.0(7)		
	Q_4	Π_g	528	511		13.3(23)		
	$2Q_2$	Σ_g^+		3522	0.014	≤ 0.04	c	c
	$2Q_4$	$\Sigma_g^+ + \Delta_g$		1028	0.17(4) }	0.23(3)	≤ 0.19	≤ 0.08
	$2Q_5$	$\Sigma_g^+ + \Delta_g$		1074	0.030(7) }		≤ 0.033	≤ 0.09
	$Q_1 + Q_4$	Π_g		3203		0.12(3)		0.26(5)
	$Q_3 + Q_5$	Π_g		2972		0.17(5)		0.26(5)
	$Q_2 + Q_4$	Π_g		~2280		≤ 0.04		0.015(3)

[a]Experimental conditions: $T \simeq 300$ K, $\lambda_0 = 514.5$ nm. Units: Cross section, $(\partial\sigma/\partial\Omega)$, in 10^{-31} cm² sr⁻¹. Harmonic wave number ω_{10} in cm⁻¹. Observed wave number ν in cm⁻¹. Uncertainties are given in units of the last significant figure. $\leq$ denotes calculated upper limits (see text). Omitted cross sections vanish by symmetry.
[b]Not observed.
[c]Cross section depends on electro-optical bond anharmonicities (see the text).
[d]Ratio $Q_1 + Q_4 / Q_3 + Q_5$ obtained from Ref. 16.
[e]Not resolved from nearby fundamental.

were generated. The experimental results are listed in Table I in terms of these observables. Note that

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{\text{isotropic}} + \left(\frac{\partial\sigma}{\partial\Omega}\right)^{\text{anisotropic}} = \left(\frac{\partial\sigma}{\partial\Omega}\right)^{X[YY]Z} + \left(\frac{\partial\sigma}{\partial\Omega}\right)^{X[YX]Z} , \quad (3)$$

is the overall Raman scattering cross section, observable when no analyzer is used.

III. THEORY

Expressions for the absolute differential Raman scattering cross sections of binary overtones and combination bands have recently been reported as a function of molecular parameters.[1] These expressions are formally different depending on the type of transition (overtone or combination) and the degeneracy of the vibrational mode(s) involved. The different cases for acetylene and its deuterated derivatives, with a listing of the symmetry allowed transitions involved, are as follows.

(a) *First overtone of nondegenerate fundamentals* ($2Q_1$, $2Q_2$, and $2Q_3$ of C_2H_2, C_2HD, and C_2D_2).

From Eq. (14) of Ref. 1,

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_l}^{isotropic} = \tfrac{1}{2}D_{ll}(\omega_0, T) \cdot 45\bar{\alpha}^2(\alpha_{ll}'') , \qquad (4)$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_l}^{anisotropic} = \tfrac{1}{2}D_{ll}(\omega_0, T) \cdot 7\gamma^2(\alpha_{ll}'') , \qquad (5)$$

for $l = 1$, 2, or 3.

(b) *First overtone of double degenerate fundamentals* ($2Q_4$ and $2Q_5$ of C_2H_2, C_2HD, and C_2D_2).

On the basis of symmetry arguments, it may be demonstrated that Eq. (15) of Ref. 1 can be simplified in the case of linear molecules of type ABBA or ABBA*, (A*, isotope of A), as follows:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_l}^{isotropic} = D_{ll}(\omega_0, T) \cdot 45\bar{\alpha}^2(\alpha_{la,la}'') , \qquad (6)$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{2\nu_l}^{anisotropic} = D_{ll}(\omega_0, T) \cdot 7[\gamma^2(\alpha_{la,la}'') + \gamma^2(\alpha_{la,lb}'')] , \qquad (7)$$

for $l = 4$ or 5, and a and b are the two components of the degenerate pair.

(c) *Combination bands of nondegenerate fundamentals and of nondegenerate with degenerate fundamentals* ($Q_1 + Q_2$, $Q_1 + Q_4$, $Q_2 + Q_4$, and $Q_3 + Q_5$ of C_2H_2 and C_2D_2, and all binary combinations of C_2HD except $Q_4 + Q_5$).

From Eq. (18) of Ref. 1,

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_l+\nu_{l'}}^{isotropic} = D_{ll'}(\omega_0, T) \cdot g_{l'} \, 45\bar{\alpha}^2(\alpha_{ll'}'') , \qquad (8)$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_l+\nu_{l'}}^{anisotropic} = D_{ll'}(\omega_0, T) \cdot g_{l'} \, 7\gamma^2(\alpha_{ll'}'') , \qquad (9)$$

where $l' \neq l$, and the degeneracy factor $g_{l'}$ is 1 for combinations of nondegenerate fundamentals and 2 for combinations of a nondegenerate with a doubly degenerate fundamental.

(d) *Combination bands of doubly degenerate fundamentals* ($Q_4 + Q_5$ of C_2HD).

For linear molecules of the type ABBA*, Eq. (20) of

Ref. 1 can be simplified to give

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_4+\nu_5}^{isotropic} = 2D_{45}(\omega_0, T) \cdot 45\bar{\alpha}^2(\alpha_{4a,5a}'') , \qquad (10)$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\nu_4+\nu_5}^{anisotropic} = 2D_{45}(\omega_0, T) \cdot 7[\gamma^2(\alpha_{4a,5a}'') + \gamma^2(\alpha_{4a,4b}'')] , \qquad (11)$$

where a and b are the two components of each degenerate pair.

In these expressions, the coefficient $D_{ll'}$ is given by

$$D_{ll'}(\omega_0, T)$$
$$= \frac{(2\pi)^4(\omega_0 - \omega_l - \omega_{l'})^4 b_l^2 b_{l'}^2}{45[1 - \exp(-h\omega_l c/kT)][1 - \exp(-h\omega_{l'} c/kT)]} , \qquad (12)$$

where ω_0 is the wave number of the exciting radiation, ω_l is the harmonic wave number of the fundamental mode Q_l and $b_l = (h/8\pi^2 c\omega_l)^{1/2}$ is its zero-point vibrational amplitude, and h, c, k, and T have their usual meaning. The quantities $3\bar{\alpha}(\alpha_{ll'}'')$ and $\gamma^2(\alpha_{ll'}'')$ are the invariants (trace and anisotropy) of the second derivative of the molecular polarizability tensor with respect to the normal coordinates Q_l and $Q_{l'}$.[1] This anharmonic second-order Raman tensor is, for binary overtones ($l = l'$),

$$\left(\frac{\partial^2\alpha}{\partial Q_l^2}\right)_{anh} = \left(\frac{\partial^2\alpha}{\partial Q_l^2}\right)_{har} + \frac{1}{3\sqrt{2}\,b_l}\frac{\phi^{lll}}{\omega_l}\left(\frac{\partial\alpha}{\partial Q_l}\right)_{har}$$
$$+ \sum_{m\neq l}\frac{b_m}{\sqrt{2}\,b_l^2}\frac{\phi^{llm}\omega_m}{(4\omega_l^2 - \omega_m^2)}\left(\frac{\partial\alpha}{\partial Q_m}\right)_{har} , \qquad (13)$$

while for binary combination bands ($Q_l \neq Q_{l'}$),

$$\left(\frac{\partial^2\alpha}{\partial Q_l \partial Q_{l'}}\right)_{anh} = \left(\frac{\partial^2\alpha}{\partial Q_l \partial Q_{l'}}\right)_{har} + \frac{1}{\sqrt{2}\,b_{l'}}\frac{\phi^{lll'}\,\omega_l}{\omega_{l'}(2\omega_l + \omega_{l'})}$$
$$\times \left(\frac{\partial\alpha}{\partial Q_l}\right)_{har} + \frac{1}{\sqrt{2}\,b_l}\frac{\phi^{l'l'l}\,\omega_{l'}}{\omega_l(2\omega_{l'} + \omega_l)}\left(\frac{\partial\alpha}{\partial Q_{l'}}\right)_{har}$$
$$+ \sum_{m\neq l,l'}\frac{b_m}{\sqrt{2}\,b_l b_{l'}}\frac{\phi^{ll'm}\,\omega_m}{[(\omega_l + \omega_{l'})^2 - \omega_m^2]}\left(\frac{\partial\alpha}{\partial Q_m}\right)_{har} . \qquad (14)$$

Here, $(\partial\alpha/\partial Q_l)_{har}$ are the harmonic Raman tensors for the fundamental transitions, which have been reported recently for acetylene.[13] The ϕ^{rst} are cubic force constants in the dimensionless normal coordinate representation,[17] given in Table II. Finally, $(\partial^2\alpha/\partial Q_l \partial Q_{l'})_{har}$ are the harmonic second-order Raman tensors, which may be calculated[6,7] by using

$$\left(\frac{\partial^2\alpha}{\partial Q_l \partial Q_{l'}}\right)_{har} = \sum_p\left(\frac{\partial\alpha}{\partial S_p}\right)\mathcal{L}_p^{ll'} + \sum_p\left(\frac{\partial^2\alpha}{\partial S_p^2}\right)\mathcal{L}_p^l \mathcal{L}_p^{l'}$$
$$+ \sum_{p\neq q}\left(\frac{\partial^2\alpha}{\partial S_p \partial S_q}\right)\mathcal{L}_p^l \mathcal{L}_q^{l'} . \qquad (15)$$

Here $\mathcal{L}_p^{ll'}$ and $\mathcal{L}_p^l$ are elements of the $\mathcal{L}$ normal coordinate tensor defined in Ref. 17. These elements depend only on the L matrix of harmonic vibrational eigenvectors, which are well determined for the molecules C_2H_2, C_2HD, and C_2D_2[8-11]; for the present case, we have calculated the $\mathcal{L}$ tensors using the harmonic force field of Ref. 10. (We also repeated the calculation using the force field of Ref. 9; those results did not agree as well with experiment as those presented here.)

TABLE II. Anharmonic cubic force constants ϕ^{rst} (in cm^{-1}) for isotopic species of acetylene.[a]

r	s	t	C_2H_2	C_2HD	C_2D_2
1	1	1	−1133.7	−1788.2	−316.6
1	1	2	−359.6	−266.2	−503.2
1	1	3		−301.6	
1	2	2	135.8	73.0	65.8
1	2	3		67.5	
1	3	3	−1344.7	−22.5	−754.3
1	4a	4a	682.6	−80.4	196.3
1	4a	5a		198.6	
1	5a	5a	755.2	1167.5	427.8
2	2	2	−540.3	−438.2	−375.5
2	2	3		−31.7	
2	3	3	−289.3	−548.6	−415.8
2	4a	4a	125.6	273.9	205.8
2	4a	5a		−54.0	
2	5a	5a	147.1	85.7	223.4
3	3	3		801.4	
3	4a	4a		−519.6	
3	4a	5a	967.2	211.6	548.1
3	5a	5a		218.9	

[a]From Ref. 10, transformed to the dimensionless normal coordinate representation. Omitted entries vanish by symmetry. For coordinates belonging to two-dimensional representations, the force constant $\phi^{r,ab,tb}$ equals the value $\phi^{r,aa,ta}$ given here.

$(\partial\alpha/\partial S_p)$ and $(\partial^2\alpha/\partial S_p \partial S_q)$ in Eq. (15) are the derivatives of the molecular polarizability with respect to the set of curvilinear symmetry coordinates of Ref. 13. Again, the quantities $(\partial\alpha/\partial S_p)$ are available from our previous paper[13]; thus, in order to predict the measured cross sections, it is necessary to estimate the derivatives $(\partial^2\alpha/\partial S_p \partial S_q)$.

IV. THE CALCULATED RAMAN TENSORS AND SCATTERING CROSS SECTIONS

The derivatives $(\partial^2\alpha/\partial S_p \partial S_q)$ may be calculated from bond polarizability parameters using the approach described earlier.[6,7] Assuming a cylindrical equilibrium bond polarizability,

$$\alpha_{bond} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \gamma \end{pmatrix} , \qquad (16)$$

for each one of the C–H (C–D) and C≡C bonds, and assuming that

$$\alpha'_{bond} = \left(\frac{\partial\alpha_{bond}}{\partial r}\right) = \begin{pmatrix} \alpha' & 0 & 0 \\ 0 & \alpha' & 0 \\ 0 & 0 & \gamma' \end{pmatrix}$$

and (17)

$$\alpha''_{bond} = \left(\frac{\partial^2\alpha_{bond}}{\partial r^2}\right) = \begin{pmatrix} \alpha'' & 0 & 0 \\ 0 & \alpha'' & 0 \\ 0 & 0 & \gamma'' \end{pmatrix}$$

are its first and second derivatives with respect to the stretching of the bond, the parameters that account for

the isotropic component of the Raman scattering cross section of overtones and combinations bands are $(2\alpha' + \gamma')_{C-H}$, $(2\alpha' + \gamma')_{C=C}$, $(2\alpha'' + \gamma'')_{C-H}$, and $(2\alpha'' + \gamma'')_{C=C}$, while the anisotropic component depends on $(\gamma - \alpha)_{C-H}$, $(\gamma - \alpha)_{C=C}$, $(\gamma' - \alpha')_{C-H}$, $(\gamma' - \alpha')_{C=C}$, $(\gamma'' - \alpha'')_{C-H}$, and $(\gamma'' - \alpha'')_{C=C}$.

In generating expressions for the second-order Raman tensors in terms of the bond polarizability parameters, it was found that overtones and combination tones involving the bending modes, Q_4 and Q_5, are independent of the electro-optical bond polarizability parameters, α''_{bond} and γ''_{bond}. From the set of bond parameters $(\gamma - \alpha)$, $(\gamma' - \alpha')$, and $(2\alpha' + \gamma')$ obtained in the previous study,[13] Table III, the $(\partial^2\alpha/\partial S_p\partial S_q)$ and $(\partial^2\alpha/\partial Q_i\partial Q_{i'})_{har}$ tensors of these transitions were calculated, and are given in Table IV. It should be noted that the second derivatives $(\partial^2\alpha/\partial S_p\partial S_q)$ have isotopic invariance properties similar to those for the first derivatives $(\partial\alpha/\partial S_p)$. In particular, when neither of the symmetry coordinates (S_p, S_q) belong to the same irreducible representation as any of the three infinitesimal rotations of the whole molecule, the corresponding second derivative remains invariant with respect to isotopic substitution. In the present case, this occurs, for instance, for the (3, 5a) and (3, 5b) components, as demonstrated in Table V.

In quantum chemistry calculations of molecular polarizabilities, the derivatives $(\partial^2\alpha/\partial S_p\partial S_q)$ would be perhaps the most suitable to compare with the present results, since they represent variations of the polarizability with respect to changes in molecular geometry which are unambiguously defined by the symmetry coordinates. Comparison of the quantities $(\partial^2\alpha/\partial Q_i\partial Q_{i'})_{har}$ and $(\partial^2\alpha/\partial Q_i\partial Q_i)_{anh}$ would be complicated by the dependence on the anharmonic force field used in their calculation.

Using Eqs. (13) and (14) for the second-order transition involving bending modes, the anharmonic Raman tensors were calculated from the harmonic tensors $(\partial^2\alpha/\partial Q_i\partial Q_{i'})_{har}$ of Table IV, the anharmonic force constants ϕ^{rst} of Table II, and the Raman tensors $(\partial\alpha/\partial Q_i)$ reported in Ref. 13. The anharmonic cross sections, calculated using Eqs. (4)–(11), are given in Table I.

These results were obtained using bond polarizability parameters having all the same sign, as shown in Table III. In fact, the isotopic cross sections are independent of the relative sign of $(2\alpha' + \gamma')_{CH}$ and $(2\alpha' + \gamma')_{CC}$. For anisotropic scattering, two solutions were obtained, depending on the relative sign of $(\gamma - \alpha)$ and $(\gamma' - \alpha')$ for each bond. These solutions differ appreciably only for overtones and combination tones of bending modes only, where the agreement with the experimental results is clearly better when these two quantities have the same sign.

TABLE III. C–H and C≡C bond polarizability parameters for acetylene.[a]

	$\gamma - \alpha$ (Å³)	α' (Å²)	γ' (Å²)
C–H	0.025	0.482	2.345
C≡C	1.740	2.507	5.481

[a]Reference 13.

TABLE IV. Calculated second derivatives of the molecular polarizability tensor of acetylenes.[a]

(p,q), (l,l')	Matrix component	C_2H_2 $(\partial^2\alpha/\partial S_p\partial S_q)$	$(\partial^2\alpha/\partial Q_l\partial Q_{l'})_{har}$	C_2HD $(\partial^2\alpha/\partial S_p\partial S_q)$	$(\partial^2\alpha/\partial Q_l\partial Q_{l'})_{har}$	C_2D_2 $(\partial^2\alpha/\partial S_p\partial S_q)$	$(\partial^2\alpha/\partial Q_l\partial Q_{l'})_{har}$
(1,4a)	$xz=zx$	-1.40268	-1.205	-1.28785	-0.295	-1.19888	-0.692
(1,5a)	$xz=zx$			-0.17381	-1.179		
(2,4a)	$xz=zx$	0.52507	-0.067	0.65457	-0.151	0.75494	-0.153
(2,5a)	$xz=zx$			-0.19601	-0.001		
(3,4a)	$xz=zx$			0.00001	0.661		
(3,5a)	$xz=zx$	-1.86833	-1.257	-1.86833	-0.266	-1.86833	-0.708
(4a,4a)	xx	0.10364	0.446	0.18698	0.332	0.23991	0.390
	yy	0	0.332	0	0.223	0	0.245
	zz	-0.13064	1.289	-0.18698	0.754	-0.23991	0.733
(4a,4b)	$xy=yx$	0.06532	0.057	0.09349	0.054	0.11995	0.073
(4a,5a)	xx			-0.04773	0.093		
	yy			0	0.048		
	zz			0.04773	0.091		
(4a,5b)	$xy=yx$			-0.02386	0.022		
(5a,5a)	xx	0.04001	0.316	0.05542	0.335	0.04001	0.171
	yy	0	0.293	0	0.294	0	0.158
	zz	-0.04011	1.411	-0.05542	1.349	-0.04001	0.761
(5a,5b)	$xy=yx$	0.02000	0.012	0.02771	0.021	0.02000	0.006

[a] $(\partial^2\alpha/\partial S_p\partial S_q)$, in Å, with respect to the symmetry coordinates of Ref. 13. $(\partial^2\alpha/\partial Q_l\partial Q_{l'})$, in 10^{16} cm g^{-1}, with respect to normal coordinates from the harmonic force field of Ref. 10. Only symmetry allowed elements are listed. If the indices a and b of coordinates belonging to two dimensional representations are interchanged, the tensor element indices x and y must be interchanged.

In these calculations, rough error estimates were made using the following considerations. Uncertainties in ϕ^{rst} were derived from the reported uncertainties in f^{ijk},[10] assuming the errors in f^{lm} to be negligible. Uncertainties of 10% in $(\partial\alpha/\partial Q_l)_{har}$ were used, which is an upper limit.[13] Similarly, estimated errors of $\sim 10\%$ in $(\partial^2\alpha/\partial Q_l\partial Q_{l'})_{har}$ were made, assuming negligible contributions from the $\mathcal{L}$ tensor elements, and 10% and 7% uncertainties for $(\partial^2\alpha/\partial S_p\partial S_q)$ and $(\partial\alpha/\partial S_p)$, respectively. On this basis, the limits of uncertainty for the calculated cross sections in Table I were determined.

For those transitions whose Raman tensors depend on the electro-optical bond anharmonicities, α''_{CH}, γ''_{CH}, α''_{CC}, and γ''_{CC}, it is not possible to make numerical cross section estimates since no information is available even as to the order of magnitude of these bond parameters. It turns out that the relations between the Raman tensors and the electro-optical bond anharmonicities are very simple for the case of acetylene: $(\partial^2\alpha/\partial S_p^2)=\alpha''_{CH}$, $p=1$ and 3, and $(\partial^2\alpha/\partial S_2^2)=\alpha''_{CC}$ are the only Raman ten-

sors which depend on these quantities. The resulting expressions for $(\partial^2\alpha/\partial Q_l\partial Q_{l'})$ are given in Table V.

V. DISCUSSION

Various contributions to the tensors presented here can be considered as forms of anharmonicity. Some of these are obvious, but others are part of the mathematical formalism, and are not so evident. In the present context, one may distinguish three anharmonic effects and evaluate their relative importance.

A. Geometrical anharmonicity

As a result of the nonlinear transformation between curvilinear symmetry coordinates and rectilinear normal coordinates, the harmonic Raman tensors [Eq. (15)] include a term $(\partial\alpha/\partial S_p)\cdot\mathcal{L}_p''$ which may be considered as a geometrical anharmonic correction. This term is a consequence of the $\mathcal{L}$ tensor formalism[17] and is expected to have an appreciable contribution to the har-

TABLE V. Coefficients in the expression for the elements of the second derivative of the molecular polarizability tensor $(\partial^2\alpha/\partial Q_l\partial Q_{l'})_{har}$ as a function of the electro-optic bond polarizabilities.

(l,l')	C_2H_2 a_{CH}	a_{CC}	C_2HD a_{CH}	a_{CC}	C_2D_2 a_{CH}	a_{CC}
(1,1)	0.6303	0.0188	0.6354	0.0113	0.2908	0.0527
(2,2)	0.0175	0.0816	0.0507	0.0582	0.0584	0.0477
(3,3)	0.6477		0.3109	0.0309	0.3492	
(1,2)	0.1051	-0.0392	0.0687	-0.0256	0.1303	-0.0501
(1,3)			0.0495	-0.0187		
(2,3)			-0.1098	0.0424		

[a] Determined for the normal modes of the harmonic force field of Ref. 10. The xx and yy elements are given by $a_{CH}\,\alpha''_{CH}+a_{CC}\,\alpha''_{CC}$ while the zz component is given by $a_{CH}\,\gamma''_{CH}+a_{CC}\,\gamma''_{CC}$. The second derivatives are in units of 10^{16} cm g^{-1} for electro-optical bond anharmonicities in Å.

TABLE VI. Contributions to the calculated isotropic component of selected second-order Raman tensors for acetylene, and comparison with experimental values (units of 10^{16} cm g^{-1}).

Molecule	CH Upper levels		Harmonic tensor $\bar{\alpha}''_{har}$			Anharmonic corrections			Anharmonic tensor $\bar{\alpha}''_{anh}$	
			CH stretch term	C≡C stretch term	Total	Q_1 term	Q_2 term	Q_3 term	Calculated	Observed (absolute value)
C_2H_2	4a	4a	0.575	0.114	0.689	−0.239	−0.229	0	0.221 ± 0.105	0.320 ± 0.040
	5a	5a	0.674	0	0.674	−0.339	−0.441	0	−0.106 ± 0.079	0.106 ± 0.010
C_2D_2	4a	4a	0.292	0.164	0.456	−0.004	−0.330	0	0.122 ± 0.050	0.162 ± 0.020
	5a	5a	0.363	0	0.363	−0.010	−0.393	0	−0.040 ± 0.042	0.078 ± 0.010
C_2HD	4a	4a	0.318	0.119	0.437	0.017	−0.400	0.035	0.089 ± 0.078	0.131 ± 0.013
	5a	5a	0.636	0.024	0.659	−0.351	−0.246	−0.023	0.039 ± 0.069	0.055 ± 0.008
	4a	5a	0.025	0.053	0.0774	−0.0435	−0.1068	−0.0176	0.123 ± 0.008	0.158 ± 0.010

monic Raman tensor when one or both of the normal coordinates involved have an appreciable bending character. For acetylene, the isotropic parts of the overtones and combination tones of the pure bending modes, Q_4 and Q_5, provide a good example. In this case, Eq. (15) reduces to

$$(\partial^2\bar{\alpha}/\partial Q_l\partial Q_{l'})_{har} = (\partial\bar{\alpha}/\partial S_1)\mathcal{L}_1^{l''} + (\partial\bar{\alpha}/\partial S_2)\mathcal{L}_2^{l''} , \quad (18)$$

where l and l' designate one of the doubly degenerate modes. Thus, the isotropic part of the harmonic Raman tensor for these transitions originates only from geometrical anharmonicity; i.e., the stretching of the C–H (S_1) and C≡C (S_2) bonds caused by the large amplitude of the bending vibrations.[17] The contributions of these terms to the harmonic tensor are given separately in Table VI. It is seen that the geometrical anharmonicity contribution is considerably larger for the C–H bond than the C≡C bond. This is not surprising, since the C–H bonds undergo large amplitude oscillations in the bending modes.

B. Quantum mechanical anharmonicity

The vibrational potential energy of a molecule is in general an anharmonic function including cubic, quartic, and higher-order terms in addition to the harmonic quadratic term. Thus, the vibrational wave function is only approximately given by a single harmonic oscillator function, and is more properly expressed as a linear combination of such functions. Such considerations give rise to Eqs. (13) and (14) where the anharmonic second-order Raman tensor is obtained from the harmonic second-order Raman tensor by adding an anharmonic correction in the form of a linear combination of terms involving the products of the anharmonic cubic force constant with the harmonic first-order Raman tensor.[1]

Examination of Eq. (13) shows that such anharmonic corrections can have a significant effect for an overtone $2\nu_l$, especially if a Raman active fundamental Q_m occurs having a harmonic wave number $\omega_m \simeq 2\omega_l$. From Eq. (14), similar effects are expected for a combination band $\nu_l + \nu_{l'}$, when $\omega_m \simeq \omega_l + \omega_{l'}$.

In the case of acetylene, these conditions on the wave numbers are not especially well fulfilled; however, this effect is strong enough to be observed, again for the case of the isotropic components of the overtones and combination tones of the pure bending modes. For the

isotropic components of the overtones of Q_4 and Q_5, Eq. (13) is given explicitly as

$$(\partial^2\bar{\alpha}/\partial Q_{la}^2)_{anh} = (\partial^2\bar{\alpha}/\partial Q_{la}^2)_{har}$$
$$+ \frac{1}{\sqrt{2}b_i^2}\sum_i \frac{b_i\phi^{i,la,la}\omega_i}{(4\omega_i^2 - \omega_i^2)}(\partial\bar{\alpha}/\partial Q_i)_{har} , \quad (19)$$

where i designates the totally symmetric modes (Q_1, Q_2, and, for C_2HD, Q_3) and $3(\partial\bar{\alpha}/\partial Q_i)_{har}$ is the trace of the first-order Raman tensor $(\partial\alpha/\partial Q_i)$. A similar expression may be obtained from Eq. (14) for the overtone $\nu_4 + \nu_5$, which is Raman active only for C_2HD.

The contribution from the anharmonic correction for each of the modes is given separately in Table VI. It is seen that the quantum-mechanical anharmonic contribution is of similar magnitude but of opposite sign to the contribution of geometrical anharmonicity which, in this case, completely makes up the harmonic tensor. For these cases, a similar behavior is observed for the anisotropy of the anharmonic Raman tensor. It is impossible to tell at present whether this is in fact a general relationship.

Since the anharmonic corrections are in the opposite sense to the harmonic tensor contributions, the relative uncertainty of the resulting anharmonic $\bar{\alpha}''_{anh}$ is very large. For this reason, we have chosen to express the corresponding calculated cross sections in Table I as upper limits, estimated from the upper limit of the calculated anharmonic tensor. However, it can be seen from Tables VI and I that the agreement between the observed and calculated tensors and cross sections for the bands considered is quite reasonable, indicating the importance of the anharmonic correction in these cases. For the other transitions considered in this work, it turns out that the contributions of the anharmonic correction are much smaller, and the calculated cross sections for those cases as given in Table I are essentially completely due to the harmonic tensors.

C. Electro-optical anharmonicity

In usual formulations of the bond polarizability theory it is assumed that the bond polarizability is a linear function of internuclear distance. The justification of this assumption lies in the fact that no behavior of Raman intensities of fundamental transitions has been observed which can be ascribed to such nonlinearity. However, it has been shown here that for overtones and

combinations bands, it is possible for the anharmonic Raman tensor to include a significant contribution from such nonlinearity. In the present approach, this contribution is described by the electro-optical bond anharmonicity α''_{bond} in Eq. (17). For acetylene, it is seen from Table IV that such contributions may be of importance in the overtones or combination bands of stretching modes. Unfortunately, in the present study, intensity data has been obtained for only four of the bands which depend on these parameters; these data are not sufficient to deduce values for the electro-optical C–H and C≡C bond anharmonicities. From consideration of the isotropic cross sections of these bands, we are only able to estimate rough limits:

$$0 \leqslant (2\alpha'' + \gamma'')_{CH} + (2\alpha'' + \gamma'')_{CC} \leqslant 20 \text{ Å} . \qquad (20)$$

VI. CONCLUSIONS

For the interpretation of the Raman intensities of fundamental vibrational transitions, the harmonic approximation has yielded satisfactory results, except in cases of strong resonant interactions. In the present paper, however, it has been demonstrated that a substantial improvement in the accuracy of calculated second derivatives of molecular polarizability with respect to normal coordinates is achieved if anharmonic contributions depending on the cubic force field are included. However, significant discrepancies, which are believed to be real, still remain between the calculated and experimental results. These may be attributed to the use of cubic force constants which were derived from a force field which included quartic contributions,[10] and to the neglect of higher-order resonant interactions which derive from a second contact transformation of the polarizability, not included in the present formulation.[1]

The present results demonstrate the utility of bond polarizability parameters to predict quantities such as the anharmonic Raman tensors, $(\partial^2\alpha/\partial Q_i \partial Q_{i'})_{anh}$, which,

at present, cannot be determined with confidence by other means, such as *ab initio* calculation. In this regard, it must be emphasized that the bond polarizabilities used here were those determined in the analysis of the fundamental modes of acetylene,[13] and were not varied to fit the present results.

It is tempting to speculate as to the utility of deriving anharmonic molecular constants using vibrational intensity data of second order transitions. It appears that useful results could be obtained if the accuracy of the experimental data were improved by at least one order of magnitude; in that event, the theoretical approach should be extended to the second contact transformation, in order to improve the accuracy of the results.

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