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# Calculation of Raman intensities for the ring-puckering vibrations of cyclopentene and 2,5-dihydrofuran

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Raman intensities are calculated for the ring-puckering vibrations of cyclopentene and 2,5-dihydrofuran using an anisotropic atom-point dipole interaction model to calculate the elements of the molecular polarizability tensor. Large second-order terms are calculated for both molecules in the expansions of the molecular polarizability tensor elements in the ring-puckering coordinate  $[(\partial^2 \alpha_{\mu\nu} / \partial Z^2)_0 | \gg 0]$ . These terms result in intense calculated  $\Delta v = 2$  overtone transitions, in agreement with experimental observations. The calculations predict that the  $\Delta v = 2$  transitions of cyclopentene are one to two orders of magnitude more intense than the  $\Delta v = 1$  fundamentals, while the two sets of transitions are comparable in intensity in 2,5-dihydrofuran. Although the shape of the band contours precludes observation of the  $\Delta v = 1$  transitions for either molecule, the calculations suggest that the fundamental transitions of cyclopentene would not be observable even if the band shape were amenable to observation.

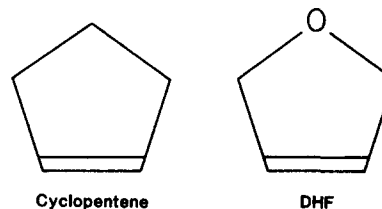
## I. INTRODUCTION

We recently reported the calculation of molecular polarizability expansions and Raman intensities for the large-amplitude, low-frequency puckering vibrations of several small ring molecules (cyclobutane,<sup>1(a)</sup> trimethylene oxide,<sup>1(a)</sup> trimethyleneimine,<sup>1(b)</sup> and 2,5-dihydropyrrole<sup>1(b)</sup>). Our calculations predict large second-order (electrically anharmonic) terms in the expansions of the molecular polarizability tensor elements in the ring-puckering coordinate  $[(\partial^2 \alpha_{\mu\nu} / \partial Z^2)_0 | \gg 0]$ . The large electrical anharmonicity results in intense calculated  $\Delta v = 2$  overtones for the ring-puckering vibrations, in agreement with experimental observations.<sup>2-13</sup> The calculations also accurately predict the relative intensities of the  $\Delta v = 1$  and  $\Delta v = 2$  progressions for the two nitrogen substituted ring molecules.<sup>1(b)</sup> These two are the only molecules for which both overtone and fundamental ring-puckering transitions have been observed in the Raman spectrum.<sup>10</sup> The  $\Delta v = 1$  transitions are not Raman allowed for cyclobutane which has effective  $D_{4h}$  symmetry.<sup>3,4</sup> The  $\Delta v = 1$  transitions are Raman allowed for trimethylene oxide and other ring molecules which have effective  $C_{2v}$  symmetry; however, these transitions are not observed for any of the molecules with this effective symmetry.<sup>5-7,10,12,13</sup> The apparent weakness of the non-totally symmetric  $\Delta v = 1$  transitions is in part due to the fact that they derive intensity from the anisotropic components of the molecular polarizability tensor and therefore exhibit broad band contours and weak Q branches. The totally symmetric  $\Delta v = 2$  transitions, on the other hand, derive intensity from the isotropic components of the polarizability tensor and thus exhibit sharp, well defined Q branches.<sup>3</sup> The two nitrogen-substituted rings, for which both the overtones and fundamentals are observed, have effective  $C_s$  symmetry, and both types of transitions are totally symmetric, exhibiting sharp Q branches.<sup>10</sup>

The absence of  $\Delta v = 1$  ring-puckering transitions from the Raman spectra of molecules with effective  $C_{2v}$  symmetry precludes the direct comparison of the intensities of the overtone and fundamental transitions. It is not known whether the  $\Delta v = 1$  transitions of certain molecules might be intrinsically much weaker than the  $\Delta v = 2$

transitions and unobservable regardless of the sharpness of the band contour. The relative intensities of the overtone and fundamental progressions vary considerably between the molecules for which we have calculated Raman intensities.<sup>1</sup> Only the  $\Delta v = 2$  transitions are expected to be observed in cyclobutane since the  $\Delta v = 1$  transitions are forbidden by symmetry.<sup>3,4</sup> The observed overtone and fundamental transitions are of comparable intensity in 2,5-dihydropyrrole, while the fundamentals are one to two orders of magnitude more intense than the overtones in trimethyleneimine.<sup>10</sup> Our calculations predict that the  $\Delta v = 1$  transitions of trimethylene oxide are at most an order of magnitude greater in intensity (although they are not observed) than the  $\Delta v = 2$  transitions.<sup>1(a)</sup>

In this paper we report the calculation of molecular polarizability expansions and Raman intensities for the ring-puckering vibrations of two five-membered rings, cyclopentene and 2,5-dihydrofuran (DHF). Both molecules have effective  $C_{2v}$  symmetry and only the  $\Delta v = 2$  transitions are observed in the Raman spectra.<sup>6</sup> We find that the calculated relative intensities of the  $\Delta v = 1$  and  $\Delta v = 2$  transitions of these two cycloalkenes are similar to those



of the analogous saturated four-membered rings, cyclobutane and trimethylene oxide, i. e.,  $I(\Delta v = 2) \gg I(\Delta v = 1)$  for cyclopentene, as is the case for cyclobutane [where  $I(\Delta v = 1) = 0$ ], and  $I(\Delta v = 1) \geq I(\Delta v = 2)$  for DHF, as is the case for trimethylene oxide.

## II. THEORETICAL SECTION

### A. Anisotropic atom-point dipole interaction model of the molecular polarizability

The expansions of the elements of the molecular polarizability tensor as a function of the ring-puckering

coordinate were calculated using the anisotropic atom-point dipole interaction (AAPDI) model developed by Birge.<sup>14</sup> A complete description of the model is given in Ref. 14 and the details of its application to ring-puckering motions are given in Ref. 1(a). We briefly outline below parametrization of the model for cyclopentene and DHF.

The mean polarizabilities of cyclopentene and DHF required to parametrize the AAPDI model were determined using the Lorentz-Lorenz equation<sup>15</sup>

$$\bar{\alpha}(\text{\AA}^3) = 0.39642 [M/d] [(n^2 - 1)/(n^2 + 2)], \quad (1)$$

where  $d$  is the density (g/ml),  $M$  is the molecular weight, and  $n$  is the refractive index. The molecular weights and ambient-temperature refractive indices and densities were taken from Ref. 16:

cyclopentene ( $n_D = 1.4225$ ,  $d = 0.7720$  g/ml,  $M = 68.13$ ),

DHF ( $n_D = 1.4262$ ,  $d = 0.9265$  g/ml,  $M = 70.10$ ).

Application of Eq. (1) yields

$$\bar{\alpha}(\text{cyclopentene}) = 8.90 \text{ \AA}^3,$$

$$\bar{\alpha}(\text{DHF}) = 7.69 \text{ \AA}^3.$$

The atomic polarizabilities of the carbon and hydrogen atoms were assigned based on our previous studies (Refs. 1 and 14). The calculated polarizability of cyclopentene ( $8.77 \text{ \AA}^3$ ) is in satisfactory agreement with the experimental value ( $8.90 \text{ \AA}^3$ ). However, the use of an atomic polarizability of  $0.465 \text{ \AA}^3$  (Refs. 1 and 14) for the oxygen atom in DHF yielded a much lower calculated polarizability ( $6.57 \text{ \AA}^3$ ) than experimentally observed ( $7.69 \text{ \AA}^3$ ). We therefore reoptimized the oxygen  $\alpha_A$  value to match the calculated molecular polarizability to the experimental value. The final parametrization is presented in Table I.

TABLE I. Atomic parameters used in the anisotropic atom point dipole interaction calculations on DHF and cyclopentane.<sup>a</sup>

Atom (type)	$\bar{\alpha}_A$ ( $\text{\AA}^3$ ) <sup>b</sup>	$\xi_A$ °	$g_{AA}$ (eV) <sup>d</sup>
H	0.135	0.430	12.848
C ( $sp^3$ )	0.878	0.347	10.333
C ( $sp^2$ )	0.928 <sup>c</sup>	0.196	10.333
O	0.541 <sup>f</sup>	0.184	13.907

<sup>a</sup>Optimized for experimental molecular polarizabilities based on sodium D line (5893 Å) refractive index data (see Ref. 16).

<sup>b</sup>Average atomic polarizabilities used to determine the mean molecular polarizabilities using the isotropic atom approximation ( $\xi_A$ 's = 0). These values are then used as initial guesses for the AAPDI calculation [see Refs. 1(a) and 14].

<sup>c</sup>Atomic anisotropy constants taken from Table I of Ref. 14 assuming transferability for similar atomic environments.

<sup>d</sup>One-center valence state electron repulsion integrals taken from Table I of Ref. 14.

<sup>e</sup>Optimized for ethylenic carbon atoms in 2,5-dihydropyrrole [see Ref. 1(b)].

<sup>f</sup>Optimized for oxygen atom in DHF (see Sec. IIA).

TABLE II. Observed and calculated Raman intensities for the ring-puckering transitions of DHF.

Transition	Frequency (cm <sup>-1</sup> ) <sup>a</sup>	Relative intensity	
		Observed <sup>a</sup>	Calculated
$\Delta v = 2$			
0-2	216.5	0.77	0.67
1-3	243.5	(1.0)	(1.0)
2-4	262.4	1.3	0.98
3-5	277.5	0.85	0.78
4-6	290.5	0.54	0.55
5-7	301.2	0.31	0.35
$\Delta v = 1$			
0-1	99.9	...	5.3
1-2	116.2	...	5.3
2-3	126.8	...	3.9
3-4	135.2	...	2.4
4-5	142.1	...	1.4
5-6	148.1	...	0.77
6-7	153.6	...	0.39

<sup>a</sup>The frequencies and observed intensities of the  $\Delta v = 2$  transitions were taken from Ref. 6. The intensities were estimated from the peak heights in Fig. 2 of this reference. This method of determining intensities may result in errors, particularly for weak or overlapping bands. The frequencies of the  $\Delta v = 1$  transitions were taken from the far-infrared data reported in Ref. 28.

Two complete sets of calculations were carried out on DHF to determine the degree to which our calculated Raman intensities were sensitive to changes in the oxygen  $\alpha_A$  value. These calculations differed only in the choice of  $\alpha_O$  ( $0.465$  or  $0.541 \text{ \AA}^3$ ). The only significant difference (albeit small) was in the intensity calculated for the  $\Delta v = 2$  relative to the  $\Delta v = 1$  progression. The calculation using  $\alpha_O = 0.541$  predicts  $\Delta v = 1$  transitions  $\sim 1.5$  times more intense relative to the  $\Delta v = 2$  transitions than those calculated using  $\alpha_O = 0.465$ . However, no significant differences in relative intensities were calculated within the  $\Delta v = 1$  or  $\Delta v = 2$  sets. For example, the calculation using  $\alpha_O = 0.465$  predicts the following relative intensities for the  $\Delta v = 2$  progression: 0.67(0-2), 1.0(1-3) (by definition), 0.98(2-4), 0.79(3-5), 0.36(5-7). These values are virtually identical to those obtained using  $\alpha_O = 0.541$  (Table II). Accordingly, the calculation of relative Raman intensities appears to be quite insensitive to atomic  $\alpha_A$  parametrization within a given  $\Delta v = n$  manifold. A similar lack of sensitivity to changes in  $\xi_A$ , the atomic anisotropy constant, was previously reported.<sup>1(b)</sup> We conclude that the results of this theoretical investigation are not critically dependent upon parametrization. Consequently, our procedures can probably be applied with confidence to molecules for which data on the molecular polarizability are unavailable, provided atomic polarizabilities for similar atom types are available (Refs. 1 and 14).

## B. Origin of the Raman intensity

The intensity of a Stokes-Raman transition is given by the following expression<sup>17</sup>:

$$I_{\nu''\nu'} = N(\bar{\nu}_0 - \bar{\nu})^4 \frac{\exp(-h\bar{\nu}c/kT)}{Q} \left[ \frac{45\bar{\alpha}_{\nu''\nu'}^2 + 7\gamma_{\nu''\nu'}^2}{45} \right], \quad (2)$$

where  $\nu''$  and  $\nu'$  are the initial and final vibrational states,  $N$  is a constant,  $\bar{\nu}_0$  and  $\bar{\nu}$  are the frequencies of the incident radiation and the vibrational mode,  $Q$  is the partition function, and  $\bar{\alpha}$  and  $\gamma^2$  are the invariants of the molecular polarizability tensor, defined by

$$\bar{\alpha} = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (3)$$

$$\gamma^2 = (1/2)[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)]. \quad (4)$$

The standard expansion of the elements of the polarizability tensor in a Taylor series in the vibrational coordinate  $Z$  results in the following expression for any element  $\alpha_{\mu\nu}(\mu, \nu = x, y, z)$ :

$$\alpha_{\mu\nu} = \alpha_{\mu\nu}^0 + (\partial\alpha_{\mu\nu}/\partial Z)_0 Z + (1/2)(\partial^2\alpha_{\mu\nu}/\partial Z^2)_0 Z^2 + \dots \quad (5)$$

The corresponding matrix elements for the transition  $\nu' \rightarrow \nu''$  are

$$[\alpha_{\mu\nu}]_{\nu''\nu'} = (\partial\alpha_{\mu\nu}/\partial Z)_0 \langle \nu'' | Z | \nu' \rangle + (1/2)(\partial^2\alpha_{\mu\nu}/\partial Z^2)_0 \langle \nu'' | Z^2 | \nu' \rangle + \dots \quad (6)$$

The potential function for the puckering motion determines the contributions of the various polarizability expansion terms to the Raman intensities. The  $\Delta\nu = 2$  overtones of molecules with effective  $C_{2v}$  symmetry can only gain intensity from the second- (or higher even-) order terms in Eq. (6). This is because the eigenfunctions for the quartic-quadratic potential function governing the ring-puckering motion are either symmetric or antisymmetric with respect to inversion through the plane of the ring.<sup>18,19</sup> Thus, the matrix elements of the first- (and higher odd-) order terms vanish between states of the same parity. Similarly, the  $\Delta\nu = 1$  transitions cannot obtain intensity from the even-order terms in the expansions, because matrix elements of these terms vanish between states of different parity.

### III. CALCULATION OF THE POLARIZABILITY EXPANSIONS AND RAMAN INTENSITIES FOR THE RING-PUCKERING TRANSITIONS OF CYCLOPENTENE AND DHF

The expansions of the elements of the polarizability tensor in terms of the ring-puckering coordinate were obtained by calculating the polarizability (see Sec. IIA) for conformations of the ring ranging from  $Z = 0$  (planar) to  $Z = 0.20 \text{ \AA}$  in steps of  $0.02 \text{ \AA}$  and then fitting the calculated values of the  $\alpha_{\mu\nu}$  to power series expanded about  $Z = 0$  using a nonlinear least squares procedure. The atomic Cartesian coordinates used in the polarizability calculations were obtained from the geometrical parameters of the molecule in the various conformations. The reference coordinate system in which the atomic displacements for the ring-puckering motion were evaluated is the principal inertial axis system of the planar ring. The  $z$  axis for both cyclopentene and DHF is defined as being coincident with the inertial axis which is perpendicular to the plane of the ring. The  $x$  and  $y$  axes were chosen such that the  $x$  axis is coincident with the

inertial axis which bisects the carbon-carbon double bond.

The model used for the ring-puckering motions of cyclopentene and DHF is one in which all bond lengths remain constant and no independent motions of the hydrogen atoms occur as the ring puckers. There is evidence that the methylene groups on four-membered molecules rock and wag several degrees as the ring deviates from planarity.<sup>20-25</sup> The occurrence of hydrogen motion during the puckering of five-membered rings containing one double bond is less well characterized. It appears, though, that the methylene groups on five-membered rings undergo considerably less motion ( $\frac{1}{2}$  to  $\frac{1}{3}$  as much) as the ring puckers than do these groups on four-membered rings.<sup>26</sup> Consequently, we calculated the Raman intensities for cyclopentene and DHF assuming a rigid geometry. The geometrical parameters for the two molecules were taken from Ref. 26.

The Raman intensities for the ring-puckering transitions were determined using the calculated expansions of the  $\alpha_{\mu\nu}$  and Eqs. (2)-(4). The vibrational transition moments were evaluated for the various eigenfunctions of the appropriate quartic-quadratic oscillator which were obtained by diagonalizing the Hamiltonian  $[H = (P_z^2/2\mu) + aZ^4 + bZ^2]$  in a  $40 \times 40$  harmonic oscillator basis set. The values of  $\mu$ ,  $a$ , and  $b$  were obtained for cyclopentene and DHF from Refs. 27 and 28, respectively.

The following polarizability expansions were obtained for cyclopentene:

$$\begin{aligned} \alpha_{xx} &= 9.28 - 36.4Z^2 + 261Z^4 + \dots, \\ \alpha_{yy} &= 11.0 - 25.5Z^2 - 32.7Z^4 + \dots, \\ \alpha_{zz} &= 6.04 + 3.73Z^2 - 115Z^4 + \dots, \\ \alpha_{xx} &= 0.765Z + 4.19Z^3 + \dots, \end{aligned} \quad (7)$$

and for DHF

$$\begin{aligned} \alpha_{xx} &= 7.72 - 28.6Z^2 + 160Z^4 + \dots, \\ \alpha_{yy} &= 9.95 - 34.8Z^2 - 1.51Z^4 + \dots, \\ \alpha_{zz} &= 5.44 - 13.5Z^2 + 54.2Z^4 + \dots, \\ \alpha_{xx} &= 5.01Z - 75.2Z^3 + \dots, \end{aligned} \quad (8)$$

where the units of  $\alpha_{\mu\nu}$  and  $Z$  are  $\text{\AA}^3$  and  $\text{\AA}$ , respectively, and the numerical coefficients have units which maintain consistency between the left- and right-hand sides of the equations. Higher order terms occur in the expansions, but these are negligible compared to those listed. The  $\alpha_{xy}$  and  $\alpha_{yz}$  elements of the polarizability tensor are zero by symmetry. The occurrence of a nonzero  $\alpha_{xx}$  term (rather than  $\alpha_{yy}$ ) reflects the (arbitrary) designation of the bisector of the carbon-carbon double bond as the  $x$  axis.

The relative Raman intensities calculated for the ring-puckering transitions of cyclopentene and DHF using Eqs. (7) and (8) are listed along with the observed intensities in Table III and II, respectively. The Raman spectra simulated using the calculated intensities for the  $\Delta\nu = 2$  transitions are compared with the observed spectra in Figs. 1 and 2. The calculated relative in-

TABLE III. Observed and calculated Raman intensities for the ring-puckering transitions of cyclopentene.

Transition	Frequency (cm <sup>-1</sup> ) <sup>a</sup>	Relative intensity	
		Observed <sup>a</sup>	Calculated
$\Delta v = 2$			
0-2	128.4	0.59	0.87
1-3	151.8	(1.0)	(1.0)
2-4	108.8	0.88	0.79
3-5	160.5	0.94	0.79
4-6	168.8	0.76	0.58
5-7	191.5	0.65	0.47
6-8	207.1	0.41	0.34
7-9	221.8	0.22	0.23
8-10 <sup>b</sup>	234.8	~0.27	0.15[0.39] <sup>b</sup>
$\Delta v = 4$			
0-4 <sup>b</sup>	234.8	~0.27	0.24[0.39] <sup>b</sup>
$\Delta v = 1$			
1-2	127.1	...	0.024
2-3	25.2	...	0.087
3-4	83.1	...	0.052
4-5	76.6	...	0.049
5-6	92.0	...	0.039
6-7	99.8	...	0.028
7-8	107.5	...	0.019
8-9	113.3	...	0.012
9-10	119.4	...	0.008

<sup>a</sup>The frequencies and observed intensities of the  $\Delta v = 2$  and  $\Delta v = 4$  transitions were taken from Ref. 6. The intensities were estimated from the peak heights in Fig. 1 of this reference. This method of determining intensities may result in errors, particularly for weak or overlapping bands. The frequencies of the  $\Delta v = 1$  transitions were taken from the far-infrared data reported in Ref. 27.

<sup>b</sup>The 8-10 and 0-4 transitions are reported to occur at the same frequency in Ref. 6. The bracketed intensity represents the sum of the two transition intensities.

tensities of the members of the  $\Delta v = 2$  progression are in excellent agreement with those observed for both molecules.<sup>6</sup> The calculations predict that the relative intensities of the  $\Delta v = 1$  and  $\Delta v = 2$  transitions are quite different for cyclopentene and DHF. The fundamental transitions are calculated to be between one and two orders of magnitude *weaker* than the overtones for cyclopentene. On the other hand, the fundamentals are calculated to be approximately five times *more intense* than the overtones for DHF. The  $\Delta v = 1$  transitions of cyclopentene are calculated to be sufficiently weak compared to the  $\Delta v = 2$  transitions that they probably would not be observable, even if the bands were to have sharp Q branches.

A direct analogy can be drawn between the results of our calculations on cyclopentene and DHF and the results for cyclobutane and trimethylene oxide. The  $\Delta v = 1$  transitions of cyclobutane are rigorously forbidden. This "forbiddenness" appears to be "carried over" to cyclopentene. Our calculations predict that the  $\Delta v = 1$

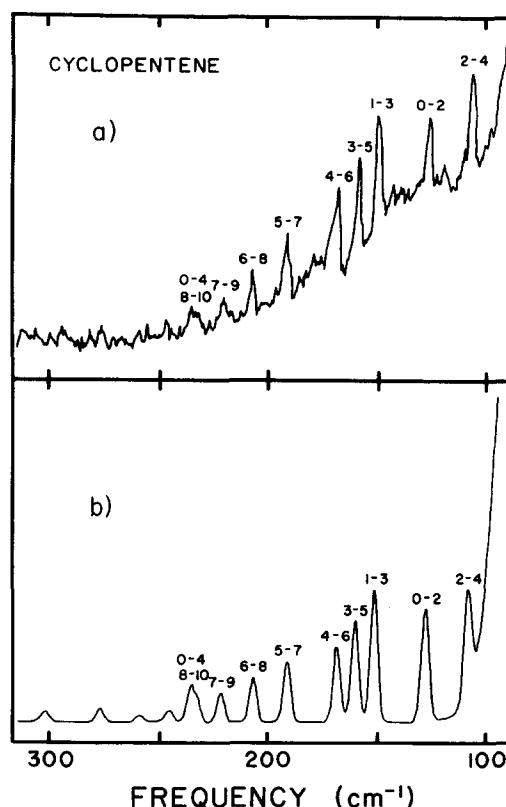


FIG. 1. (a) Observed (Ref. 6, reproduced by permission) and (b) calculated low-frequency gas-phase Raman spectra of cyclopentene. The spectrum was simulated using the polarizability expansions given in Eq. (7). Gaussian band shapes were used for the Raman bands and the incipient Rayleigh line.

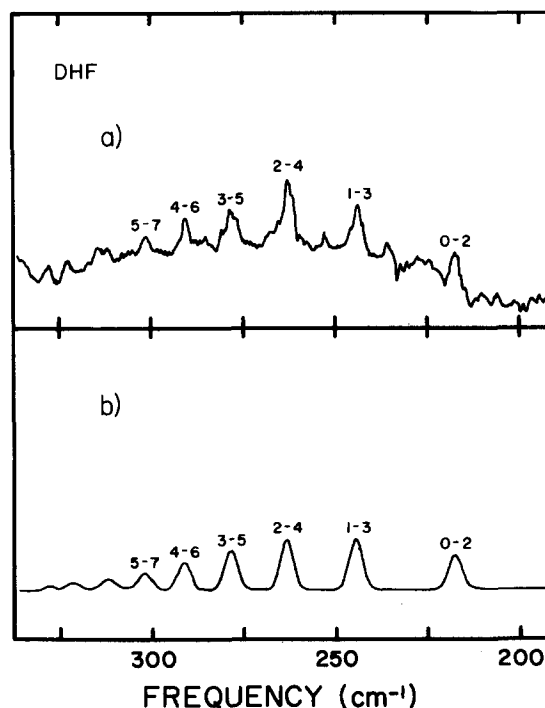


FIG. 2. (a) Observed (Ref. 6, reproduced by permission) and (b) calculated low-frequency gas-phase Raman spectra of DHF. The spectrum was simulated using the polarizability expansions given in Eq. (8). Gaussian band shapes were used for the Raman bands.

transitions of DHF are less than an order of magnitude more intense than the  $\Delta\nu=2$  transitions. The two progressions in trimethylene oxide<sup>1(a)</sup> have nearly the same calculated relative intensities.

#### IV. CONCLUSIONS

The Raman intensities calculated for the ring-puckering transitions of cyclopentene and DHF are consistent with our calculations for other small ring molecules.<sup>1</sup> The large amplitude of the ring-puckering motion results in large electrically anharmonic terms in the expansions of the molecular polarizability tensor elements in the ring-puckering coordinate. These terms result in intense  $\Delta\nu=2$  overtone transitions. The prediction that the  $\Delta\nu=1$  transitions of cyclopentene are much weaker than the  $\Delta\nu=2$  transition is, however, the only example for which the fundamentals are calculated to be substantially weaker than the overtones (presuming both are allowed and neglecting band shape differences). The calculations of Raman intensities for cyclopentene and DHF, taken together with those for the other four ring molecules, provide a more comprehensive picture of the nature of the changes which occur in the molecular polarizability tensor for the large-amplitude motion.

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