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Calculation of Raman intensities for the ring-puckering vibrations of 2,5-dihydropyrrole and trimethyleneimine. Electrical versus mechanical anharmonicity in asymmetric potential wells

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Raman intensities are calculated for the ring-puckering transitions of 2,5-dihydropyrrole (DHP) and trimethyleneimine (TMI) using an anisotropic atom-point dipole interaction model to evaluate the elements of the molecular polarizability tensor. The calculated relative intensities for the members of the $\Delta v = 1$ and $\Delta v = 2$ ring-puckering progressions for DHP are in good agreement with those observed. The calculations predict that the observed $\Delta v = 2$ overtones of DHP occur *not* because of the first-order allowedness expected for these transitions in the asymmetric double-minimum potential well which governs the ring-puckering motion, but rather because of unusually large second-order terms in the expansions of the polarizability tensor elements in the puckering coordinate $[(\partial^2 \alpha_{\mu\nu} / \partial Z^2)_0] \gg 0$. Raman intensities are calculated for the ring-puckering transitions of TMI using the two different potential functions which have been proposed for the puckering motion. It is found that the intensities calculated for the slightly asymmetric double-minimum potential $V(Z) = (0.922\,05 \times 10^6)Z^4 - (0.379\,44 \times 10^5)Z^2 + (0.159\,13 \times 10^5)Z^3$ proposed by Carreira and Lord [J. Chem. Phys. **51**, 2735 (1969)] cannot be reconciled with experiment. On the other hand, the intensities calculated for the highly asymmetric single-minimum potential $V(Z) = (0.7553 \times 10^5)Z^2 - (0.4336 \times 10^6)Z^3 + (0.7035 \times 10^6)Z^4$ proposed by Robiette *et al.* [Mol. Phys. **42**, 1519 (1981)] are in excellent agreement with experiment. Our calculations confirm that the three most intense ring-puckering transitions observed in the Raman (and far-infrared) spectrum of TMI are the lowest members of a $\Delta v = 1$ rather than a $\Delta v = 2$ progression. The calculations further indicate that high-order electrical terms in the polarizability expansions contribute significantly to the Raman intensities of both the $\Delta v = 1$ and $\Delta v = 2$ ring-puckering progressions. Neglect of the electrically anharmonic terms in the intensity calculation for the single-minimum well results in a significant disparity between calculation and experiment.

I. INTRODUCTION

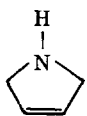
Gas-phase Raman spectroscopic investigations of the large-amplitude, low-frequency puckering vibrations of four-membered rings and five-membered rings containing one double bond have revealed unusual intensities for the members of the $\Delta v = 2$ overtone progression relative to those of the $\Delta v = 1$ fundamental progression.¹⁻¹⁴ In molecules with effective D_{4h} or C_{2v} symmetry, the puckering motion is governed by a symmetric potential function of the form $V(Z) = aZ^4 \pm bZ^2$, where Z is the ring-puckering coordinate.² Only the totally symmetric $\Delta v = 2$ ring-puckering transitions are Raman allowed in D_{4h} symmetry. Both the $\Delta v = 1$ (B_1 symmetry) and $\Delta v = 2$ (A_1 symmetry) ring-puckering transitions are Raman allowed in C_{2v} symmetry; however, only the $\Delta v = 2$ overtones are observed.^{7,8,10,12-14} The weakness of the fundamental transitions relative to the overtones in the Raman spectra of molecules with effective C_{2v} symmetry has been attributed to two effects: (i) the $\Delta v = 1$ transitions derive intensity from anisotropic components of the molecular polarizability tensor and therefore exhibit broad band contours and weak Q -branches, whereas the $\Delta v = 2$ transitions derive intensity from the isotropic components of the tensor and thus exhibit sharp, well defined Q -branches¹⁵; (ii) the large amplitude of the ring-puckering motion results in unusually large second-order (electrically anharmonic) terms in the expansions of the molecular polarizability tensor elements in the ring-puckering coordinate, $[(\partial^2 \alpha_{\mu\nu} / \partial Z^2)_0] \gg 0$, which enhances the in-

tensities of the $\Delta v = 2$ relative to the $\Delta v = 1$ transitions.³

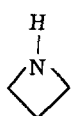
We recently reported¹⁶ calculations of molecular polarizability expansions and Raman intensities for the puckering vibrations of two four-membered ring molecules, cyclobutane (D_{4h} effective symmetry) and trimethylene oxide (C_{2v} effective symmetry). Raman intensities had not been previously calculated for the ring-puckering transitions of any of the molecules which have been studied spectroscopically. Our calculations predict unusually large second-order polarizability expansion terms for the puckering motions of both cyclobutane and trimethylene oxide. These terms result in intense calculated $\Delta v = 2$ overtones for both molecules, which is in agreement with the spectroscopic observations. The calculations also predict that, for trimethylene oxide, in which both $\Delta v = 1$ and $\Delta v = 2$ transitions are Raman allowed, the overtone intensities are comparable to those of the fundamentals. This estimate, when taken together with the expected differences in the band shapes for the two types of transitions, readily accounts for the pre-dominance of the overtone transitions in the Raman spectrum.

The absence of $\Delta v = 1$ ring-puckering transitions from the Raman spectra of molecules with effective C_{2v} symmetry, of course, precludes the direct comparison of the calculated and observed intensities of the overtone and fundamental vibrational progressions. The direct assessment of the importance of high-order terms in the polarizability expansions for the ring-puckering motion

requires the examination of molecules in which both $\Delta v = 1$ and $\Delta v = 2$ transitions are observed. Fundamental transitions are observed in the Raman spectra of mono-substituted cyclobutanes^{9,12} and four- and five-membered nitrogen heterocycles.¹⁰ The equilibrium axial and equatorial conformations of these molecules have different energies and the ring-puckering motion is governed by an asymmetric potential function^{17,18} of the form $V(Z) = aZ^4 + bZ^2 + cZ^3$. The asymmetric ring molecules have effective C_s symmetry and both the $\Delta v = 1$ and $\Delta v = 2$ puckering transitions are totally symmetric (A' symmetry), exhibiting sharp Q-branches. In the monosubstituted cyclobutanes, the $\Delta v = 2$ transitions are obscured by other Raman active modes, and it is not possible to compare the intensities of the $\Delta v = 1$ and $\Delta v = 2$ progressions.^{9,12} The only molecules for which both the fundamental and overtone transitions have been observed thus far are the nitrogen heterocycles 2,5-dihydropyrrole (DHP) and trimethyleneimine (TMI).¹⁰



2,5-Dihydropyrrole (DHP)



Trimethyleneimine (TMI)

In this paper we report the calculation of Raman intensities for the ring-puckering transitions of DHP and TMI. The comparison of the relative intensities of the $\Delta v = 1$ and $\Delta v = 2$ transitions of these molecules calculated both with and without the inclusion of electrical anharmonicity offers an opportunity to directly evaluate the relative importance of electrical and mechanical anharmonicity in determining the Raman intensities for the puckering vibrations. The comparison of the electrical and mechanical effects in DHP and TMI is especially interesting for several reasons. The far-infrared spectra of these molecules have been interpreted by Carreira and Lord to predict that the barrier heights and energy differences between the axial and equatorial conformations of both rings are relatively small, resulting in asymmetric double-minimum potential wells for the puckering motions.¹⁷ The vibrational selection rules for the asymmetric double-minimum potential are much more complex than those for a low-barrier symmetric double-minimum well or asymmetric single-minimum well. If only the *first-order terms* in the expansion of the polarizability (dipole moment) are significant, the Raman (infrared) intensities for the symmetric double-minimum and asymmetric single-minimum wells go in the order³: $I(\Delta v = 1) > I(\Delta v = 3)$; $I(\Delta v = 2) = 0$ and $I(\Delta v = 1) > I(\Delta v = 2) > I(\Delta v = 3)$, respectively. The intensities for the asymmetric double-minimum well are as follows¹⁹: $I(\Delta v = 1) > I(\Delta v = 2) > I(\Delta v = 3)$ above the barrier; $I(\Delta v = 2) \geq I(\Delta v = 1) > I(\Delta v = 3)$ near the top of the barrier; $I(\Delta v = 2) \gg I(\Delta v = 1) \geq I(\Delta v = 3)$ well below the barrier but to a level above the higher of the two minima. Transitions occurring in the well of the lower minimum and between levels lying well below the higher minimum follow the same intensity pattern as those above the barrier. These selection rules for the asymmetric double-minimum well indicate that $\Delta v = 2$ overtones can obtain significant intensity from mechanical anharmonicity alone. The occurrence of large second-order terms in

the polarizability expansions, as are predicted by our calculations for the ring-puckering motions of DHP and TMI, further adds to the complexity of the Raman intensity pattern.

Recently, Robiette *et al.*²⁰ have offered an alternative assignment to that of Carreira and Lord¹⁷ for the far-infrared spectrum of TMI. The latter workers assigned the three most intense far-infrared bands observed at 207, 184, and 148 cm^{-1} to the $\Delta v = 2$ overtones originating from the $v = 0, 1$, and 2 levels in a slightly asymmetric double-minimum potential well (Fig. 1). On the other hand, the former workers showed that the three intense bands can be assigned equally well to the lowest $\Delta v = 1$ transitions in a highly asymmetric single-minimum potential well (Fig. 1). Transitions which originate from levels with $v \geq 4$ have identical assignments in the two different potential wells. The analogues of the three intense infrared bands are observed in the gas-phase Raman spectrum of TMI.¹⁰ In addition, a number of bands which can be unambiguously assigned to $\Delta v = 1$ or $\Delta v = 2$ transitions are observed in the Raman spectrum. These transitions occur from levels with $v \geq 4$. Most of the observed high-lying $\Delta v = 1$ Raman transitions have analogues in the far-infrared spectrum. On the other hand, no counterparts to the high-lying $\Delta v = 2$ Raman transitions are observed in the infrared. This is indicative of the importance of electrical anharmonicity in determining the Raman intensities.

The contribution of electrical anharmonicity to the Raman intensities of the ring-puckering transitions of TMI suggests that Raman intensity calculations can aid in determining which of the two proposed potential functions for the puckering motion is correct. We have calculated the Raman intensities for the ring-puckering transitions for both the asymmetric double-minimum and asymmetric single-minimum potential wells. We find that the calculated Raman intensities for the highly asymmetric single-minimum well are in better agreement with the observed intensities. This result is consistent with recent *ab initio* calculations on TMI which predict a single puckered equilibrium conformation with the N-H hydrogen in an equatorial position.²¹

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 recently developed by Birge.²² A complete description of the model is given in Ref. 22 and the details of its application to ring-puckering motions are given in Ref. 16. We briefly outline below parametrization of the model for DHP and TMI.

The mean polarizabilities of DHP and TMI required to parameterize the AAPDI model were determined using the Lorentz-Lorenz equation,²³

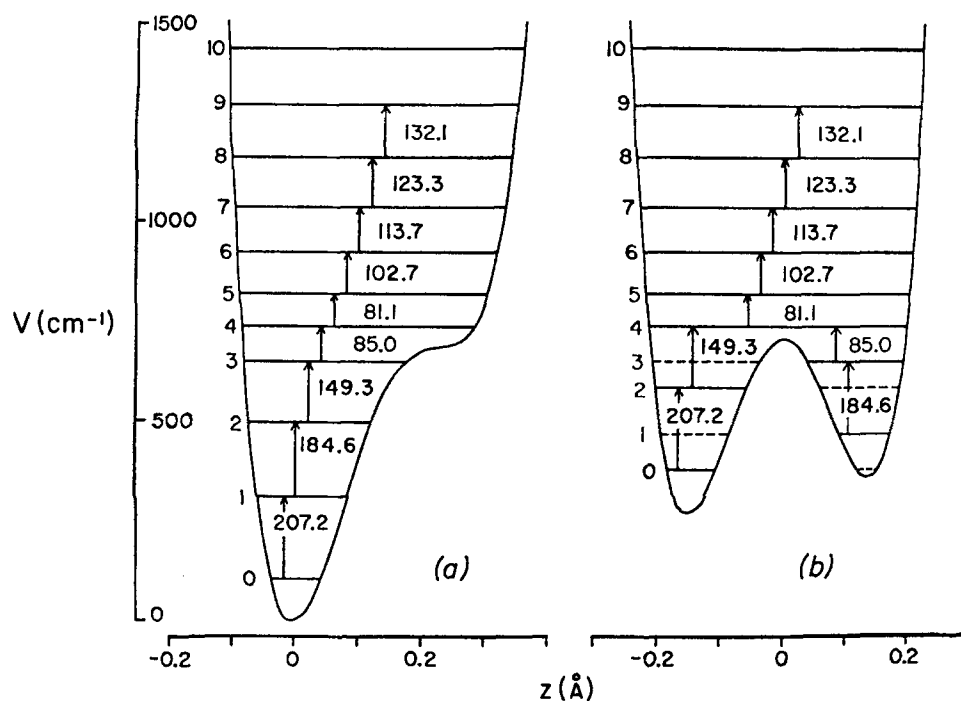


FIG. 1. Two potential wells which have been proposed for the ring-puckering vibration of TMI (Ref. 20, reproduced by permission). The transitions originating from the $v=0, 1$ and 2 levels are members of the $\Delta v=1$ series in the single-minimum well (a) [$V(Z) = (0.7553 \times 10^5)Z^2 - (0.4336 \times 10^6)Z^3 + (0.7035 \times 10^6)Z^4$] proposed in Ref. 20 and members of the $\Delta v=2$ series in the double-minimum well (b) [$V(Z) = (0.92205 \times 10^6)Z^4 - (0.37944 \times 10^5)Z^2 + (0.15913 \times 10^5)Z^3$] proposed in Ref. 17 (see text).

$$\bar{\alpha}(\text{\AA}^3) = \frac{(3 \times 10^{24})M}{4N_A \pi d} \left[\frac{n^2 - 1}{n^2 + 2} \right] = 0.39642 \left[\frac{M}{d} \right] \left[\frac{n^2 - 1}{n^2 + 2} \right], \quad (1)$$

where d is the density (g/ml), M is the molecular weight, N_A is Avogadro's number, and n is the refractive index. The molecular weights and ambient-temperature refractive indices and densities were taken from Ref. 24:

DHP ($n_D = 1.4664$, $d = 0.9097 \text{ g/ml}$, $M = 69.11$),

TMI ($n_D = 1.4287$, $d = 0.8436 \text{ g/ml}$, $M = 57.09$).

Application of Eq. (1) yields:

$$\bar{\alpha}(\text{DHP}) = 8.35 \text{ \AA}^3,$$

$$\bar{\alpha}(\text{TMI}) = 6.91 \text{ \AA}^3.$$

These values were used to optimize the atomic polarizabilities ($\bar{\alpha}_A$) of the nitrogen atom in TMI and the ethylenic carbon atoms in DHP. The results are tabulated in Table I. There are no data available on the components of the molecular polarizabilities of DHP and TMI and therefore, it was not possible to optimize the atomic anisotropy constants (ξ_A) for these two molecules. Fortunately, sufficient data are available for these constants from previous calculations (Ref. 22) to permit reasonable assignments. We tested the validity of our parameterization by carrying out calculations using various ξ_A values for the carbon and nitrogen atoms and found that the calculated relative intensities of the Raman transitions (reported in Sec. III) are changed by 10% or less by modest changes ($\pm 40\%$) in the atomic anisotropy constants. This observation gives us confidence that the salient theoretical predictions are not an artifact of fortuitous parametrization.

B. Origin of the Raman intensity

The intensity of a Stokes Raman transition is given by the following expression²⁵:

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

TABLE I. Atomic parameters used in the anisotropic atom-point dipole interaction calculations on DHP and TMI.^a

Atom (type)	$\bar{\alpha}_A$ (\AA^3) ^b	ξ_A ^c	g_{AA} (eV) ^d
H	0.135	0.430	12.848
C (sp^3)	0.878	0.347	10.333
C (sp^2)	0.928 ^e	0.196	10.333
N	0.678 ^f	0.198	11.308

^aOptimized for experimental molecular polarizabilities based on sodium D line (5893 \AA) refractive index data (see Ref. 22).

^bAverage 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. 16 and 22).

^cAtomic anisotropy constants taken from Table I of Ref. 22 assuming transferability for similar atomic environments.

^dOne-center valence state electron repulsion integrals taken from Table I of Ref. 22.

^eOptimized for ethylenic carbon atoms in DHP.

^fOptimized for nitrogen atom in TMI and assumed to be identical for nitrogen atom in DHP.

where v'' and v' 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 γ^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 $\alpha_{\mu\nu}(\mu, \nu = x, y, z)$:

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

The corresponding matrix elements for the transition $v' \leftarrow v''$ are

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

Normally, the first term in Eq. (6) is much larger than any of the higher-order terms when the transition is first-order allowed. The result is the appearance of $\Delta v = 1$ transitions in the Raman spectrum. When the vibrational motion is anharmonic, overtone transitions can also obtain intensity from the first term in Eq. (6). The contribution of mechanical anharmonicity is generally the major source of intensity for overtone transitions. Second- and higher-order terms can also contribute to overtone intensities, and for the large amplitude ring-puckering motions these terms can become much larger than the first-order terms.¹⁶

The potential function for the puckering motion determines the contributions of the various polarizability expansion terms to the Raman intensities. The $\Delta v = 2$ 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 are either symmetric or antisymmetric with respect to inversion through the plane of the ring.^{26,27} Thus, the matrix elements of the first- (and higher odd-) order terms vanish between states of the same parity. Similarly, the $\Delta v = 1$ transitions cannot obtain intensity from the even-order terms in the expansions, because matrix elements of these terms vanish between states of different parity. The addition of a cubic term to the potential function removes the inversion symmetry of the eigenfunctions. Consequently, there are no symmetry restrictions on the contributions of the various expansion terms to the Raman intensities for the ring-puckering transitions in molecules with effective C_s symmetry. This leads to the prediction of a complex intensity pattern for the $\Delta v = 1$ and $\Delta v = 2$ progressions of DHP and TMI.

III. CALCULATION OF THE POLARIZABILITY EXPANSIONS AND RAMAN INTENSITIES FOR THE RING-PUCKERING TRANSITIONS OF DHP AND TMI

The expansions of the elements of the polarizability tensor in terms of the ring-puckering coordinate for the asymmetric double-minimum well were obtained by calculating the polarizability (see Sec. II A) for conformations of the ring ranging from $Z = 0$ (planar) to $Z = \pm 0.20$ Å in steps of 0.02 Å 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 DHP and TMI is defined as being coincident with the inertial axis which is approximately 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 lies in the plane containing the nitrogen atom and β -carbon atom (TMI) or bisecting the carbon-carbon double bond (DHP). The z axis is not perpendicular to the ring plane and the x axis is not coincident with the nitrogen atom in the planar rings because of the slight asymmetry introduced by the N-H hydrogen.

When the puckering motion is governed by an asymmetric single-minimum potential well, as is predicted for TMI by Robiette *et al.*,²⁰ it is not possible to determine the equilibrium dihedral angle from the potential function.¹⁸ *Ab initio* calculations place the equilibrium dihedral angle of TMI at $\sim 14^\circ$ ($Z \sim -0.07$ Å) and indicate that the equatorial conformer is the lowest in energy.²¹ Electron diffraction studies suggest that the equilibrium dihedral angle is much larger $\sim 33^\circ$ ($Z \sim -0.15$ Å).²⁸ It is appropriate to expand the $\alpha_{\mu\nu}$ about the equilibrium puckered conformation for the asymmetric single-minimum well and redefine this conformation to have a $Z = 0$.^{18,20} Since the equilibrium conformation of TMI is not known with certainty, we calculated polarizability expansions and Raman intensities for a number of different equilibrium conformations with dihedral angles ranging between 14° and 33° . The expansions of the $\alpha_{\mu\nu}$ were determined in the same manner as described above for the double-minimum potential wells. The reference coordinate system is the principal inertial axis system of the puckered ring at equilibrium. The results of these calculations are discussed in Sec. III B.

The model used for the ring-puckering motions of DHP and TMI 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 small ring molecules rock and wag several degrees as the ring deviates from planarity.^{21,29-34} We have examined the effects of these types of hydrogen motions on the calculated Raman intensities of the ring-puckering transitions in our previous study of cyclobutane and trimethylene oxide.¹⁶ While hydrogen motions do effect the calculated relative

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

Transition	Frequency (cm ⁻¹) ^a	Relative intensity		
		Observed ^a	Calculation I ^b	Calculation II ^c
$\Delta v = 2$				
0-2 ^d	117.8	1.7	1.1 [1.4] ^d	0.053 [0.37] ^d
1-3	155.7	(1.0)	(1.0)	<0.01
2-4	184.1	1.0	1.0	<0.01
3-5	208.1	0.88	0.86	<0.01
4-6	227.3	0.63	0.65	<0.01
5-7	241.9	0.50	0.45	<0.01
$\Delta v = 1$				
0-1	46.7 ^e	...	1.6	0.81
1-2	71.3 ^e	...	0.84	0.93
2-3	84.9 ^e	...	0.86	0.87
3-4	98.3	1.3	0.61	0.68
4-5	107.9	1.1	0.41	0.48
5-6 ^d	117.8	1.7	0.26 [1.4] ^d	0.32 [0.37] ^d
6-7	123.4	~0.3	0.16	0.20
7-8	129.0	~0.3	0.091	0.12
8-9	137.5	~0.3	0.031	0.068

^aThe observed frequencies and intensities were taken from Ref. 10. The intensities were estimated from the peak heights in Fig. 1 of this reference. This method of determining the intensities may result in errors, particularly for weak or overlapping bands.

^bCalculated using the complete polarizability expansions given in Eq. (7).

^cCalculated neglecting electrical anharmonicity by including only the first-order terms in the polarizability expansions in Eq. (7).

^dThese transitions occur at the same frequency. The bracketed intensity represents the sum of the two transition intensities.

^eThese bands are not observed in the Raman spectrum because of their proximity to the Rayleigh line. The observed frequencies are those reported for the infrared bands in Ref. 17.

intensities of the $\Delta v = 1$ and $\Delta v = 2$ progressions, the effects are relatively small (a factor of two or less), which does not change the qualitative prediction that electrically anharmonic terms in the expansions of the $\alpha_{\mu\nu}$ are large for the puckering motion. Consequently, we calculated the Raman intensities for DHP and TMI assuming a rigid geometry.

The initial conformation for which the expansions of the $\alpha_{\mu\nu}$ are evaluated is either a puckered equilibrium conformation (TMI) or the hypothetical planar form of the ring (TMI and DHP). The various conformers of TMI were assumed to have the same bond lengths and bond angles as those given in Ref. 21 for the puckered equilibrium conformation. The planar form of DHP was assumed to have a C-N-C bond angle identical to the C-O-C bond angle given for 2,5-dihydrofuran in Ref. 34. A standard length was assumed for the C-N bond³⁵ and the remaining bond lengths were taken to be the same as those of 2,5-dihydrofuran. The location of the N-H hydrogen in DHP with respect to the plane defined by the C-N-C atoms was taken to be the same as that in TMI.²¹ It should be noted that the calculated Raman intensities for the ring-puckering transitions are not particularly sensitive to those changes in the geometry of the puckered equilibrium or hypothetical planar forms of the ring which result in plausible structures for these conformations.¹⁶

The Raman intensities for the ring-puckering transi-

tions 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–cubic oscillator which were obtained by diagonalizing the Hamiltonian, $\mathcal{H} = (P_z^2/2\mu) + aZ^4 + bZ^2 + cZ^3$, in a 40×40 harmonic oscillator basis set. The values of μ , a , b , and c for the asymmetric double-minimum potential wells were obtained for DHP and TMI from Ref. 17. The values of the constants for the asymmetric single-minimum potential well predicted for TMI were obtained from Ref. 20.

A. Calculated Raman intensities for DHP

The polarizability expansions obtained for DHP are as follows:

$$\begin{aligned}
 \alpha_{xx} &= 8.81 + 1.52Z - 44.5Z^2 - 73.9Z^3 + 449Z^4 + \dots, \\
 \alpha_{yy} &= 11.0 - 2.14Z - 20.1Z^2 + 45.4Z^3 - 95.1Z^4 + \dots, \\
 \alpha_{zz} &= 5.63 + 1.39Z + 2.38Z^2 + 18.7Z^3 - 204Z^4 + \dots, \\
 \alpha_{xz} &= 0.202 + 0.740Z - 5.72Z^2 + 20.0Z^3 + 224Z^4 + \dots,
 \end{aligned} \tag{7}$$

where the units of $\alpha_{\mu\nu}$ and Z are Å³ and Å, respectively, and the numerical coefficients have units which maintain consistency between the left- and right-hand sides of the equation. Higher-order terms occur in the expansions, but these are negligible compared to those

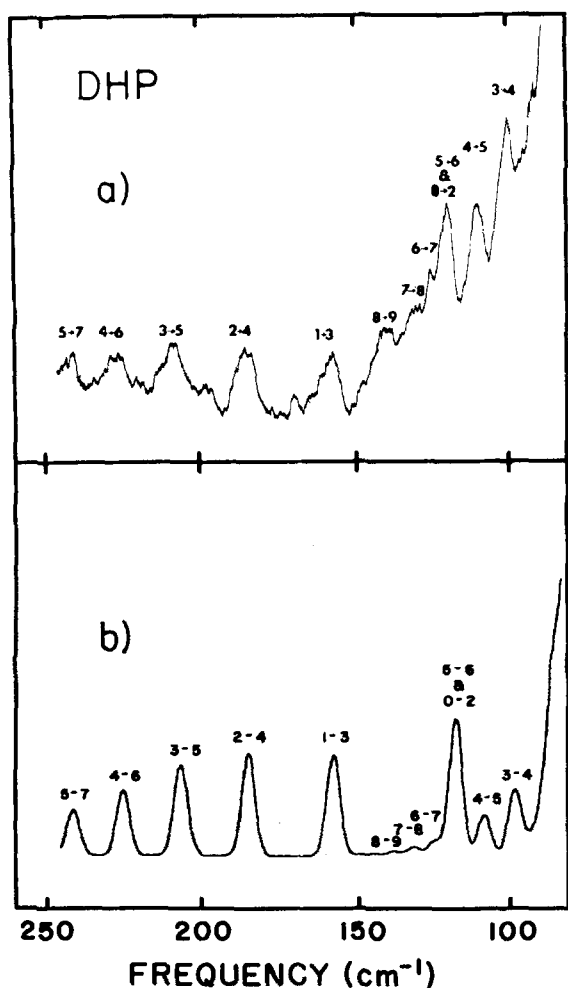


FIG. 2. (a) Observed (Ref. 10, reproduced by permission) and (b) calculated low-frequency gas-phase Raman spectra of DHP. The spectrum was simulated using the complete polarizability expansions given in Eq. (7). Gaussian bandshapes were used for the Raman bands and the incipient Rayleigh line.

listed. The α_{xy} and α_{yz} elements of the polarizability tensor are zero by symmetry. The occurrence of a nonzero α_{xx} term (rather than α_{yz}) reflects the (arbitrary) location of the nitrogen atom in the xz plane.

The relative Raman intensities calculated for the ring-puckering transitions of DHP using Eq. (7) are listed in Table II along with the observed intensities. The Raman spectrum simulated using the calculated intensities is compared to the observed spectrum in Fig. 2. The calculated relative intensities of the members of the $\Delta v=2$ progression are in excellent agreement with those observed. It is difficult to accurately measure the intensities of the $\Delta v=1$ transitions because of the steeply sloping background of the incipient Rayleigh line [see Fig. 2(a)]. Nonetheless, the calculated relative intensities of the members of the $\Delta v=1$ progressions are in reasonable agreement with those observed. The calculation does appear to slightly underestimate the intensity of the $\Delta v=1$ relative to the $\Delta v=2$ series. However, the observed intensities reported in Table II are the measured peak heights rather than peak areas. No attempt was made in the simulation of the Raman spectrum [Fig. 2(b)] to take into account

the differences in linewidth of the overtone and fundamental transitions [Fig. 2(a)]. The consideration of the relative linewidths would bring the calculated relative intensities of the two different progressions into better agreement with experiment.

The energy difference between the axial and equatorial conformation of DHP is relatively small ($\sim 50 \text{ cm}^{-1}$), so an exceptionally strong $\Delta v=2$ selection rule is not in effect as a result of the asymmetry of the potential.¹⁷ Nonetheless, $\Delta v=2$ overtones are prevalent in the Raman spectrum and are comparable in intensity to the $\Delta v=1$ fundamentals.¹⁰ This can be contrasted with the far-infrared spectrum of the molecule which is dominated by the $\Delta v=1$ progression.¹⁷ Several $\Delta v=2$ transitions are observed in the far-infrared spectrum, but, with the exception of the 0-2 transition, these are very weak. Only the 0-2 transition is expected to become strongly allowed because of mechanical effects, since the asymmetry of the potential well is slight. Our calculations predict that the intensities of the $\Delta v=2$ Raman transitions are primarily derived from the second-order terms in the expansions of the $\alpha_{\mu\nu}$. This is dramatically illustrated by calculating the intensities using only the first-order terms from Eq. (7). The intensities calculated using these terms are compared in Table II to those determined using the complete polarizability expansions. The use of only the first-order terms results in predicted intensities for the members of the $\Delta v=2$ progression several orders of magnitude less than those of the $\Delta v=1$ series (with the exception of the 0-2 transition). Thus, the mechanical anharmonicity in the ring-puckering motion of DHP is a minor contributor to the intensity of the $\Delta v=2$ Raman overtones compared to the electrical anharmonicity.

B. Calculated Raman intensities for TMI

The polarizability expansions obtained for TMI about a puckered equilibrium conformation with a dihedral angle of $\sim 33^\circ$ are as follows:

$$\begin{aligned}\alpha_{xx} &= 7.65 + 0.493Z - 1.06Z^2 - 13.9Z^3 - 110Z^4 + \dots, \\ \alpha_{yy} &= 7.48 - 0.287Z - 0.647Z^2 - 34.0Z^3 + 287Z^4 + \dots, \\ \alpha_{zz} &= 5.59 - 5.61Z + 25.5Z^2 - 21.8Z^3 - 148Z^4 + \dots, \\ \alpha_{xx} &= 0.272 + 0.647Z + 1.31Z^2 + 2.17Z^3 - 25.9Z^4 + \dots.\end{aligned}\quad (8)$$

The expansions about the planar form of the ring are given by

$$\begin{aligned}\alpha_{xx} &= 7.63 - 0.960Z - 6.36Z^2 + 11.8Z^3 + 114Z^4 + \dots, \\ \alpha_{yy} &= 7.40 - 1.11Z - 4.72Z^2 + 3.55Z^3 + 46.8Z^4 + \dots, \\ \alpha_{zz} &= 5.34 + 2.43Z + 27.2Z^2 - 22.0Z^3 - 132Z^4 + \dots, \\ \alpha_{xx} &= 0.395 + 0.860Z - 1.33Z^2 - 11.7Z^3 + 15.5Z^4 + \dots.\end{aligned}\quad (9)$$

Higher-order terms occur in the expansions but these are negligible compared to those listed. The relative Raman intensities calculated for the ring-puckering transitions of TMI for the single-minimum potential well using Eq. (8) and for the double-minimum well using Eq. (9) are listed in Table III along with the observed intensities. The Raman spectra simulated using the

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

Observed ^a		Calculated			
		Single-minimum well ^b		Double-minimum well ^c	
Frequency (cm ⁻¹)	Intensity	Transition	Intensity	Transition	Intensity
207.1	(1.0)	0-1	(1.0)	0-2	(1.0)
184.2	0.64	1-2 ^d	0.56[0.68] ^d	1-3 ^d	1.4 [1.8] ^d
148.6	0.23	2-3	0.19	2-4	0.43
85.0 ^e	...	3-4	0.081	3-4	0.48
81.1 ^e	...	4-5	0.29	4-5	0.15
102.7 ^e	...	5-6	0.25	5-6	0.25
113.8 ^f	~0.04	6-7	0.18	6-7	0.14
121.8 ^f	~0.04	7-8	0.10	7-8	0.085
133.9 ^f	~0.04	8-9	0.051	8-9	0.048
233.6 ^g	~0.06	2-4	0.080	2-5	0.17
166.1	0.10	3-5	0.081	3-5	0.77
184.2	0.64	4-6 ^d	0.12[0.68] ^d	4-6 ^d	0.42[1.8] ^d
216.9	~0.04	5-7	0.13	5-7	0.39
236.6	~0.04	6-8	0.095	6-8	0.26
255.8	~0.03	7-9	0.059	7-9	0.17

^aThe observed frequencies and intensities were taken from Ref. 10. The intensities were estimated from the peak heights in Fig. 3 of this reference. This method of determining the intensities may result in errors, particularly for weak or overlapping bands.

^bThese assignments are based on the asymmetric single-minimum potential function from Ref. 20. The intensities were calculated using this potential function and the polarizability expansions given in Eq. (8).

^cThese assignments are based on the asymmetric double-minimum potential function from Ref. 17. The intensities were calculated using this potential function and the polarizability expansions given in Eq. (9).

^dThese transitions occur at the same frequency. The bracketed intensity represents the sum of the two transition intensities.

^eThese bands are not observed in the Raman spectrum because of their proximity to the Rayleigh line. The observed frequencies are those reported for the infrared bands in Ref. 20.

^fThese bands are extremely weak and have been only tentatively identified as members of the $\Delta v = 1$ progression.

^gThe band observed at this frequency in the Raman spectrum is attributed in Ref. 10 to an impurity.

calculated intensities are compared to the observed spectrum in Fig. 3.

The relative intensities of the three strong Raman bands at 207, 184, and 148 cm⁻¹ calculated for the asymmetric single-minimum potential are in much better agreement with the observed intensities than are those calculated for the asymmetric double-minimum well. The single-well potential results in a calculated progression in which the intensity monotonically decreases as the frequency decreases, which is in agreement with the observed intensity progression. On the other hand, the 184 cm⁻¹ band is predicted to be the strongest for the double well. Thus, our calculations support the assignment of the 207, 184, and 148 cm⁻¹ Raman (and infrared) bands as the 0-1, 1-2, and 2-3 transitions²⁰ rather than the 0-2, 1-3 and 2-4 transitions.¹⁷

A progression which monotonically decreases in intensity is calculated for the three strongest Raman bands in the single-minimum well for any value of the equilibrium dihedral angle between 14° and 33°. However, the polarizability expansions obtained for the smaller values of the angle result in calculated intensities for the $\Delta v = 1$ transitions originating in levels with $v \geq 4$ which are

much larger than those observed. The intensities of the high-lying transitions steadily decrease as the equilibrium angle approaches the value predicted by the electron diffraction studies (~33°).²⁸ The intensities for the high-lying $\Delta v = 1$ transitions calculated at this value of the equilibrium angle are in good agreement with those observed, as are the calculated intensities of the high-lying $\Delta v = 2$ overtones (see Table III). Our calculations also suggest an assignment for the band observed in the Raman spectrum at 233 cm⁻¹ [see Fig. 3(a)]. This band, which partially obscures the 6-8 transition, has been previously attributed to an impurity.¹⁰ The calculations indicate that the 233 cm⁻¹ band could be the 2-4 transition in the single-minimum well [see Fig. 3(b)]. Note also that the 2-5 transition is predicted to occur at this frequency in the double-minimum well [see Fig. 3(c)].

The relative contribution of electrical and mechanical anharmonicity to the ring-puckering transitions observed in the Raman spectrum of TMI can be determined by calculating the intensities using only the first-order terms in Eq. (8). The intensities calculated for the single-minimum well using these terms are compared in Table IV to those obtained using the complete polarizability

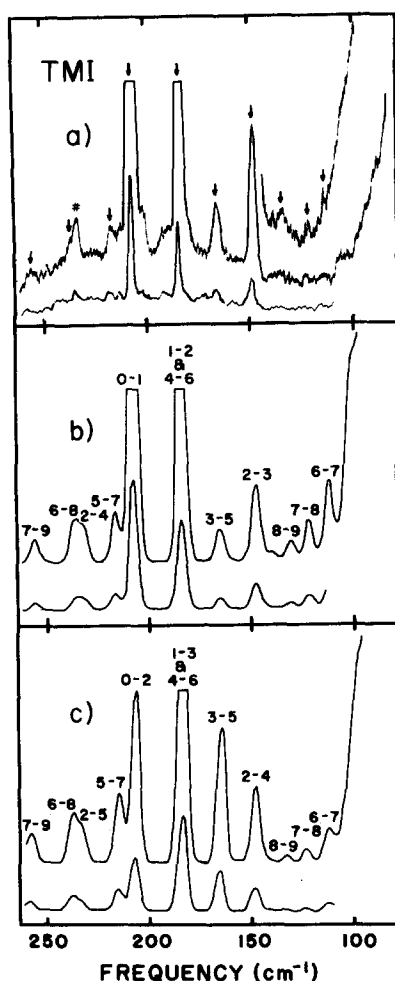


FIG. 3. (a) Observed (Ref. 10, reproduced by permission) and (b), (c) calculated low-frequency gas-phase Raman spectra of TMI. The simulated spectrum in (b) is that predicted for the asymmetric single-minimum potential well from Ref. 20 using the complete polarizability expansions given in Eq. (8). The simulated spectrum in (c) is that predicted for the asymmetric double-minimum potential well from Ref. 17 using the complete polarizability expansions given in Eq. (9). Gaussian band shapes were used for the Raman bands and the incipient Rayleigh line. The arrows in the observed spectrum in (a) label the bands which were assigned in Ref. 10 on the basis of the transitions predicted for the double-minimum well (see b). The band label by the symbol # in the spectrum was attributed in Ref. 10 to an impurity. The calculations suggest that it is the 2 → 4 (2 → 5) transition in the single-minimum (double-minimum) well (see text).

expansions. This calculation predicts that both the $\Delta v = 1$ and $\Delta v = 2$ transitions are significantly influenced by the high-order electrical terms. The neglect of these terms results in calculated relative intensities for the 0 → 1, 1 → 2 and 2 → 3 transitions which are in substantially worse agreement with experiment than those predicted using the complete expansions. The accurate prediction of the contribution of the electrically anharmonic terms to the Raman intensities by our calculation is gratifying and supports the utility of the AAPDI model for determining molecular polarizabilities. The contribution of the high-order electrical terms to the intensities of the $\Delta v = 1$ transitions is not surprising

though (given that these terms are indeed large) in view of the extreme asymmetry of the potential well.

It should be noted in closing that the relative Raman intensities calculated for the double-minimum potential well neglecting electrical anharmonicity are actually in better agreement with experiment than those calculated using the complete polarizability expansions of Eq. (9). However, these calculated intensities still cannot be reconciled with experiment. The improved agreement between the observed and calculated intensities which occurs for the double-minimum well upon neglect of electrical anharmonicity coupled with the diminished quality of the fit obtained for the single-minimum well would, however, render the unambiguous choice between the two potential functions more difficult. Thus, the assessment of the contribution of the electrically anharmonic terms to the Raman intensities for the ring-puckering transitions is important for obtaining a cor-

TABLE IV. Comparison of electrical and mechanical effects on the Raman intensities for the ring-puckering transitions of TMI.

Transition ^a	Relative intensity		
	Observed ^b	Calculation I ^c	Calculation II ^d
$\Delta v = 1$			
0-1	(1.0)	(1.0)	1.3
1-2 ^e	0.64	0.56[0.68] ^e	0.98 [1.0] ^e
2-3	0.23	0.19	0.63
3-4 ^f	...	0.081	0.48
4-5 ^f	...	0.29	0.48
5-6 ^f	...	0.25	0.39
6-7 ^g	~ 0.04	0.18	0.26
7-8 ^g	~ 0.04	0.10	0.16
8-9 ^g	~ 0.04	0.051	0.086
$\Delta v = 2$			
2-4 ^h	~ 0.06	0.080	0.064
3-5	0.10	0.081	0.12
4-6 ^e	0.64	0.12[0.68] ^e	0.018 [1.0] ^e
5-7	~ 0.04	0.13	< 0.01
6-8	~ 0.04	0.095	< 0.01
7-9	~ 0.03	0.059	< 0.01

^aThese assignments are based on the asymmetric single-minimum potential function from Ref. 20.

^bThe observed frequencies and intensities were taken from Ref. 10. The intensities were estimated from the peak heights in Fig. 3 of this reference. This method of determining the intensities may result in errors, particularly for weak or overlapping bands.

^cCalculated using the complete polarizability expansions given in Eq. (8).

^dCalculated neglecting electrical anharmonicity by including only the first-order terms in the polarizability expansions given in Eq. (8).

^eThese transitions occur at the same frequency. The bracketed intensity represents the sum of the two transition intensities.

^fThese bands are not observed in the Raman spectrum because of their proximity to the Rayleigh line.

^gThese bands are extremely weak and have been only tentatively identified as members of the $\Delta v = 1$ progression.

^hThe band observed at this frequency in the Raman spectrum is attributed in Ref. 10 to an impurity.

rect assignment of the spectrum and determining the potential function.

IV. SUMMARY AND CONCLUSIONS

The polarizability expansions calculated for the ring-puckering motions of DHP and TMI result in calculated relative intensities for the various $\Delta v = 1$ and $\Delta v = 2$ Raman transitions which are in good agreement with those observed. Large second-order terms are obtained in the expansions for both molecules. The contribution of the electrically anharmonic terms to the Raman intensities of the ring-puckering transitions of TMI allows an unambiguous choice to be made between the two different potential functions which have been proposed or the puckering motion. Our calculations indicate that the asymmetric single-minimum potential well proposed by Robiette *et al.*,²⁰ yields Raman intensities in much better agreement with experiment than does the asymmetric double-minimum well proposed by Carreira and Lord.¹⁷

The calculation of large second-order polarizability expansion coefficients for the ring-puckering motions of DHP and TMI is in agreement with our previous study¹⁶ of cyclobutane and trimethylene oxide. The calculations for the four ring molecules indicate that high-order electrical terms are much more significant in the expansions of the molecular polarizability than in those of the dipole moment. First-order expansion terms for the dipole moment are generally sufficient to reproduce the observed far-infrared intensities, whereas the initial terms in the expansion of the polarizability are insufficient to account for the Raman intensities.

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¹Comprehensive reviews of gas-phase far-infrared and Raman studies of the puckering motion of small ring molecules can be found in Refs. 2 and 3, respectively.

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