

Transverse Optical to Longitudinal Optical Splitting and Dipole Moment Derivatives from Infrared Spectra of Thin Films of Molecular Solids

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For a number of molecular solids as thin films, longitudinal optical (LO) and transverse optical (TO) frequencies have been observed for molecular vibrations absorbing in the mid-infrared spectral region. From the LO–TO splitting, dipole moment derivatives have been calculated from equations previously derived for molecules on sites of tetrahedral or greater symmetry. For spherical top molecules these calculated derivatives are compared with values calculated from intensities reported in the literature. The agreement is remarkably good considering that most of the intensity data was determined for the gas phase and most of the solids have the molecules on sites of symmetry lower than tetrahedral. This offers a useful technique for determining dipole moment derivatives and infrared absorption intensities for gas-phase species as well as molecular and ionic solids.

Introduction

For a crystalline molecular solid, an infrared-active internal vibration has TO (transverse optical) and LO (longitudinal optical) modes generally absorbing at different frequencies. As pointed out by Kittel,¹ for a given normal vibration the LO frequency, ν_{LO} , is greater than the TO frequency, ν_{TO} , because the local electric field causes polarization of the surrounding atoms in the opposite direction for the LO mode but in the same direction for the TO mode. This polarization gives increased resistance for the LO mode but assistance for the TO mode. As discussed by Decius and Hexter² and by Turrell³ the quantity $(\nu_{LO}^2 - \nu_{TO}^2)^{1/2}$ is proportional to the dipole moment derivative for that normal vibration. The expression is relatively simple for molecules on sites of T_d or greater symmetry in cubic crystals but becomes more complex as the site symmetry is lowered. For molecules on sites of lower than tetrahedral symmetry each infrared-active molecular vibration may have more than one transverse and more than one longitudinal mode. However, for molecules that are isotropic (spherical tops) when isolated, even though they suffer some loss of symmetry in the crystal lattice, it seems that the lower site symmetry should not be critical and that one might obtain useful dipole moment derivative calculations from observation of the average LO–TO splittings for molecular solids of lower than cubic symmetry. We have observed such splittings for a number of molecular solids and wish to compare the results with intensity measurements already in the literature.

It was shown by Berreman⁴ that, for a thin film of a cubic crystal, for radiation at nonnormal incidence, absorption can occur at a transverse optical mode frequency for radiation having an electric field component parallel to the film surface and at a longitudinal optical mode frequency for radiation having an electric field component perpendicular to the film surface. The film thickness must be significantly smaller than the wavelength of the LO and TO frequencies. Indeed he presented as an example the transmittance spectrum for s-polarized and p-polarized radiation through a LiF film 0.20 μm thick, with the radiation incident at 30° to the plane of the film. The s-polarized radiation has its electric vector parallel to the film surface while the p-polarized radiation has its electric vector in the plane defined by the incident beam direction and a normal to the surface. We have used this technique with infrared spectroscopy to observe the LO–TO splitting for a number of molecular solids. The results

are used to calculate dipole moment derivatives which are compared to those derived from intensity measurements reported in the literature. In the course of these studies we have observed some rather remarkable isotope and other impurity effects which we shall discuss in a later article.

We note that there have been other observations of LO modes appearing in the infrared spectra of solids at nonnormal incidence: for example, for CO,^{5,6} for CO₂,⁷ and for SiF₄.^{8,9} These will be discussed below along with our observations.

Theory

As pointed out by Vedder and Hornig,^{10a} as well as Haas and Hornig,^{10b} Turrell,³ and Decius,¹¹ for molecules on sites of T_d or greater symmetry

$$\nu_{LO}^2 - \nu_{TO}^2 = (N/\pi c^2)[(n_\infty^2 + 2)/3n_\infty]^2(\partial\mu/\partial Q)^2 \quad (1)$$

$$\nu_0^2 = \nu_{TO}^2 + (N/9\pi c^2)(n_\infty^2 + 2)(\partial\mu/\partial Q)^2 \quad (2)$$

In these expressions n_∞ is the refractive index at high frequency, which is also the square root of the dielectric constant at high frequency, $(\epsilon_\infty)^{1/2}$. N is the number of molecules/cm³, and ν_0 is the frequency of the oscillator in cm⁻¹ "expected in the absence of the long-range, electrostatic coupling".¹¹ The quantity $\partial\mu/\partial Q$ is the derivative of the dipole moment with respect to the normal coordinate for ν_0 ($0 \rightarrow 1$). The subscripts LO and TO are for longitudinal and transverse optical modes.

The units of $\partial\mu/\partial Q$ are cm^{3/2} s⁻¹ which equals esu g^{-1/2}. Much of the data in the literature are given in these units; however, it is now more appropriate to use SI units which for $\partial\mu/\partial Q$ are e u^{-1/2} where e is the magnitude of the charge on an electron (4.803 $\times 10^{-10}$ esu or 1.6022 $\times 10^{-19}$ C) and u is the atomic mass unit (1.66054 $\times 10^{-27}$ kg). Therefore, to convert the units of $\partial\mu/\partial Q$ from esu g^{-1/2} to e u^{-1/2} in eqs 1 and 2 we must multiply the coefficient of $(\partial\mu/\partial Q)^2$ by $(4.803 \times 10^{-10})^2 \times (1.66054 \times 10^{-24})^{-1} = 1.3892 \times 10^5$. Including this factor in eq 1 we find

$$\partial\mu/\partial Q = (1.4274 \times 10^8 / N^{1/2})[3n_\infty / (n_\infty^2 + 2)](\nu_{LO}^2 - \nu_{TO}^2)^{1/2} \quad (3)$$

The quantities n_∞ and ϵ_∞ are not known for many crystals; however, for a number of ionic diatomic crystals Kittel (ref 1, p

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190) reports ϵ_∞ ranging from 1.5 to 5.4 (or $n_\infty = 1.2$ –2.3). For molecular crystals we believe that n_∞ should be significantly less than 2.3. It is reported as about 1.5 for liquid CCl_4 .¹² We note that if we limit n_∞ to the range 1.0–2.5 the quantity $3n_\infty/(n_\infty^2 + 2)$ varies from 1.0 by less than 6%. Therefore, for cubic crystals we feel secure in reducing eq 3 to

$$\partial\mu/\partial Q = (1.4274 \times 10^8 / N^{1/2})(\nu_{\text{LO}}^2 - \nu_{\text{TO}}^2)^{1/2} \quad (4)$$

in which the units are cm^{-1} for ν , molecules/ cm^3 for N , and $e \text{ u}^{-1/2}$ for $\partial\mu/\partial Q$.

Thus observation of ν_{LO} and ν_{TO} for molecules on sites of tetrahedral or greater symmetry should lead to reasonably accurate values of $\partial\mu/\partial Q$ if the approximate density is known. The error introduced by assuming $3n_\infty/(n_\infty^2 + 2) = 1.0$ is less than 6%. It seems that for noncubic crystals the polarization forces for normally isotropic molecules will not be greatly altered and thus eq 4 may give a fairly good value for $\partial\mu/\partial Q$. Part of this report is aimed at testing this hypothesis, using weighted averages where more than one peak is observed for ν_{LO} and/or more than one peak is observed for ν_{TO} .

Intensity Relations

Some intensity data are available from various sources, which will be referenced when used. The units vary in published reports; however, Pugh and Rao¹³ give conversions among the various units. For a given sample one observes the integrated absorbance, $B = (\text{cm}^{-1}) \ln [I_0/I]$, for a given concentration, c , and path length, d . A common measurement of intensity is B/cd which has units of cm^2/mol when c is in mol/cm^3 and d is in cm . However, this leads to rather large numbers and the preferred units are km/mol , leading to

$$S = (B/cd) \times 10^{-5} \text{ km/mol} \quad (5)$$

with c in mol/cm^3 and d in cm . The ordinate of integrated absorbance, $\ln [I_0/I]$, has no units but one must keep in mind that natural logarithms are generally used and that otherwise a correction multiplier must be applied. If instead c is in atmospheres the observed intensity is often reported as

$$S' = 4.064S \text{ cm}^{-2} \text{ atm}^{-1} \quad \text{at } 300 \text{ K} \quad (6)$$

The units of eq 6 are those reported by Pugh and Rao¹³ in the most thorough list of intensities found in the literature.

Intensity relations have been discussed rather extensively in the literature.^{14,15} From these articles and the work of Brown and Person¹⁶ and that of Fox and Person¹⁷ we find

$$\partial\mu/\partial Q_s = (S/g_s)^{1/2} [(3c^2 \times 10^5) / \pi N_a^2 e^2]^{1/2} (\omega_s/\nu_s)^{1/2} \quad (7)$$

In eq 7, $e = 4.803 \times 10^{-10}$ esu, N_a is 6.0222×10^{23} molecules/mol, c is the velocity of light, g_s is the degeneracy of mode s , S is the intensity in km/mol , and $\partial\mu/\partial Q_s$ is in units of $e \text{ u}^{-1/2}$. We note that the harmonic frequency, ω_s , is generally only slightly greater than the observed fundamental, ν_s , except perhaps for hydrogen stretching frequencies. Thus, the ratio $(\omega_s/\nu_s)^{1/2}$ can be well approximated by 1.0. Making the indicated numerical substitutions in eq 7 we find

$$\partial\mu/\partial Q_s = 0.03203(S/g_s)^{1/2} \quad (8)$$

As above, S is the intensity in km/mol , g_s is the degeneracy of mode s , and $\partial\mu/\partial Q_s$ is in units of $e \text{ u}^{-1/2}$.

We have chosen to calculate $\partial\mu/\partial Q_s$ from intensities reported in the literature for comparison of $\partial\mu/\partial Q_s$ calculated from $\nu_{\text{LO}}^2 - \nu_{\text{TO}}^2$ as an indication of the usefulness of eq 4 for both cubic and noncubic crystals.

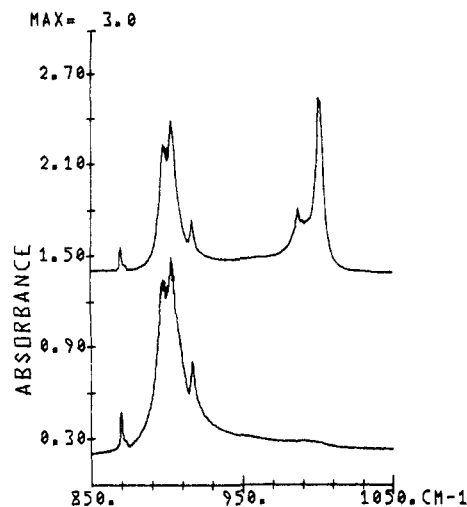


Figure 1. The ν_3 mode of SF_6 at 70 K for a thin film deposited at 70 K. Thickness is about $0.3 \mu\text{m}$. Substrate is at 25° to incident beam through rotation about vertical axis. Upper curve with polarizer horizontal, p polarization. Lower curve, s polarization.

Experimental Section

Thin films of several molecular solids were prepared by deposition from the vapor phase onto a cold CsI window mounted in a Displex refrigerator. The amount deposited varied from 0.1 to 0.2 Torr L which we estimate gave a thickness of 0.2 – $0.4 \mu\text{m}$ (based on intensity measurements) which, for mid-infrared absorption, should satisfy the Berreman equations.⁴ The film was rotated about the vertical axis so that the incident beam was at 30° (sometimes 45°) to the plane of the film. A germanium "double diamond" polarizer (purchased from Harrick Scientific Corp. Ossining, NY) was inserted in the beam to distinguish between vibrational modes parallel to the film substrate (TO) and those normal to the film substrate (LO). The spectra were observed with a Fourier transform spectrometer (Bomen DA3-002 or Nicolet 7600) using a KBr beam splitter and wide-band MCT detector. The resolution was generally 0.5 or 1.0 cm^{-1} .

The frequency measurements are accurate to 0.1 cm^{-1} . An error of $+\delta$ for ν_{LO} and $-\delta$ for ν_{TO} leads to an error of $[100\delta/(\nu_{\text{LO}} - \nu_{\text{TO}})]\%$ or 0.1% if $\delta = 0.1 \text{ cm}^{-1}$, and the frequency difference is 100 cm^{-1} . This error is negligible compared to the 6% uncertainty in the refractive index expression of eq 1. However, the TO modes show some splitting and taking a weighted average will no doubt introduce some further uncertainty. Furthermore, alteration of eq 1 and 2 for sites of lower symmetry than tetrahedral³ leads to further uncertainty but, as we have stated above, testing the agreement with experimental intensity measurements is a major goal of this report.

Results

LO–TO Splitting for SF_6 . In Figure 1 we show the absorption spectra at 70 K for the ν_3 mode of SF_6 in a thin film about $0.3 \mu\text{m}$ thick, deposited at 70 K. The substrate of CsI was at 25° to the incident beam. The isotopic concentration is that of natural abundance (95.0% ^{32}S and 4.2% ^{34}S). The lower curve is for s-polarized incident radiation (polarized parallel to the plane of the film), while the upper curve is for p-polarized radiation. The high-frequency peak at 1002.1 cm^{-1} and its satellite at 987.6 cm^{-1} are obviously polarized completely perpendicular to the film plane and are thus due to LO modes. The lower frequency absorptions are all parallel to the plane and thus arise from TO modes. Figure 2 shows the spectra of the ν_4 mode in the same sample. We see the high-frequency LO mode at 618.5 cm^{-1} and TO modes at 610.5 , 607.8 , and 606.6 cm^{-1} .

The crystal structure of SF_6 below 94 K was determined by Raynerd et al.¹⁸ to be hexagonal ($P3m1 [D_{3d}^3]$) with three

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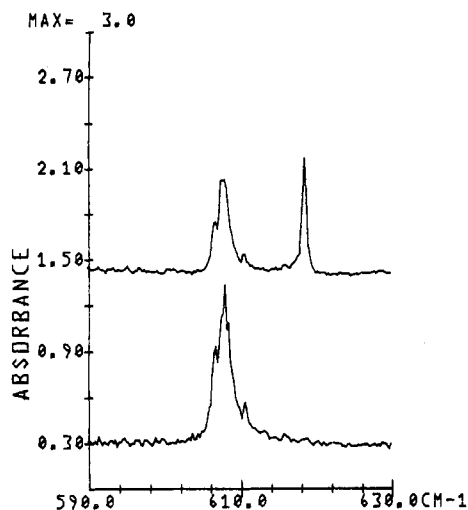


Figure 2. The ν_4 mode of SF_6 at 70 K for a thin film deposited at 70 K. Thickness is about $0.3 \mu\text{m}$. Substrate is at 25° to incident beam through rotation about vertical axis. Upper curve with polarizer horizontal, p polarization. Lower curve, s polarization.

molecules per unit cell between 50 and 94 K. At lower temperatures ($T < 50 \pm 5$ K) the structure distorts slightly to a lower symmetry (probably monoclinic with $Z = 6$). NMR¹⁹ and Raman²⁰ studies indicate that there are two distinct sites in the SF_6 lattice. Thus, there may be more than one infrared-active TO mode and more than one infrared-active LO mode for solid SF_6 . However, of the LO absorptions we believe the weak peak at 987.6 cm^{-1} arises because of the presence of 4.2% ^{34}S impurity in the sample—we are unable to obtain pure $^{32}\text{SF}_6$. This will be discussed further in a later article on the effect of impurities on the LO and TO modes. We believe the true infrared-active LO frequency for pure $^{32}\text{SF}_6$ is then slightly above 1002 cm^{-1} . The TO frequency we take as 903.0 cm^{-1} , which is a weighted average of the strong peaks at 899.7 , 903.8 , and 917.3 cm^{-1} . The weak peak at 870.2 cm^{-1} arises from the combination mode $\nu_5(\text{F}_{2g}) + \nu_6(\text{F}_{2u})$. Thus for calculations of $\partial\mu/\partial Q_3$ from eq 3 we use $\nu_{\text{TO}} = 903.0 \text{ cm}^{-1}$ and $\nu_{\text{LO}} = 1002.1 \text{ cm}^{-1}$. Similarly for ν_4 we use $\nu_{\text{TO}} = 607.5 \text{ cm}^{-1}$ and $\nu_{\text{LO}} = 618.5 \text{ cm}^{-1}$.

From the crystal structure¹⁸ the quantity N to be used in eq 3 is 1.12×10^{22} molecules/ cm^3 . From the above TO and LO frequencies we then calculate from eq 4 that

$$\partial\mu/\partial Q_3 = 0.588 \text{ e u}^{-1/2} \quad \partial\mu/\partial Q_4 = 0.157 \text{ e u}^{-1/2}$$

Person²¹ gives preferred intensities for the gas phase of SF_6 , as $S = 1075$ and 75 km/mol for ν_3 and ν_4 , respectively. From these values we calculate

$$\partial\mu/\partial Q_3 = 0.606 \text{ e u}^{-1/2} \quad \partial\mu/\partial Q_4 = 0.160 \text{ e u}^{-1/2}$$

This agreement is quite good, indicating that even for this noncubic crystal lattice eq 3 is appropriate and can be used to estimate peak intensities. We note that Dows and Wieder²² reported intensity measurements for solid SF_6 and found an S value of 1040 km/mol for ν_3 and 122 km/mol for ν_4 . From these values and eq 8 we find

$$\partial\mu/\partial Q_3 = 0.596 \text{ e u}^{-1/2} \quad \partial\mu/\partial Q_4 = 0.204 \text{ e u}^{-1/2}$$

Our own observations are that the ratio S_4/S_3 is indeed greater for thin solid films than for the gas but not as great as found by Dows and Wieder.²² The observed absorption bands in these solids have extensive wings which lead to uncertainty in the baseline for area measurements and possible error in the estimated intensities. It is also possible that these thin films are uneven, leading to the "hole" effect discussed by Davies et al.,²³ which would lead to

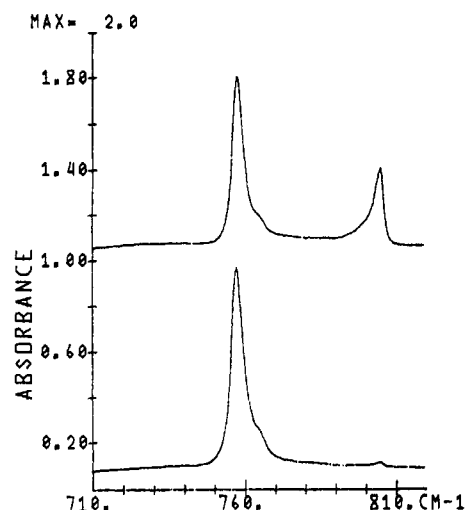


Figure 3. The ν_3 mode of SF_6 at 70 K for a thin film deposited at 70 K. Thickness is about $0.2 \mu\text{m}$. Substrate is at 45° to incident beam. Upper curve, p polarization. Lower curve, s polarization.

weaker bands appearing relatively stronger. In any case our results suggest that the gas-phase intensity for ν_4 agrees somewhat better than that reported for the solid when compared with calculations from LO-TO splitting using eq 3. The errors in intensity measurements are believed²⁴ to be better than $\pm 10\%$ for ν_3 which would lead to a possible $\pm 5\%$ error in $\partial\mu/\partial Q_3$ and somewhat less²¹ for ν_4 . Thus the agreement is well within experimental error for all but the ν_4 intensity for the solid.

At this point we also investigate the usefulness of eq 2. In fact this equation, combined with eq 1, can give a useful expression from which it may be possible to estimate the refractive index at high frequency, n_∞ .

$$[n_\infty^2/(n_\infty^2 + 2)] = (\nu_0^2)/(\nu_{\text{LO}}^2 - \nu_{\text{TO}}^2) \quad (9)$$

which by rearrangement gives

$$n_\infty = [2(\nu_0^2 - \nu_{\text{TO}}^2)/(\nu_{\text{LO}}^2 - \nu_0^2)]^{1/2} \quad (10)$$

If we take the eigenfrequency, ν_0 , as that of the isolated molecule (gas-phase values of 947.5 and 615 cm^{-1} for ν_3 and ν_4 , respectively), we calculate from eq 10 that $n_\infty = 1.24$ from ν_3 and 2.06 from ν_4 . These numbers are not unreasonable; however, they are obviously not in agreement with each other. Actually the ν_0 values used should be those of the SF_6 molecule surrounded by other SF_6 molecules without the long-range electrostatic coupling which leads to the LO-TO splitting. The closest we have to this situation is for dilute SF_6 in thin films of SeF_6 for which we find 611.5 and 938.0 cm^{-1} for ν_4 and ν_3 , respectively, of SF_6 . Using these values for ν_0 in eq 2 we calculate $n_\infty = 1.03$ from ν_3 and 1.08 from ν_4 . These values are essentially in agreement; however, they are certainly too low. Equation 10 is for molecules on sites of tetrahedral or higher symmetry. From the more general equations given by Turrell,³ we can modify eq 10 to

$$n_\infty = [(1/\beta) - 1]^{1/2} [(\nu_0^2 - \nu_{\text{TO}}^2)/(\nu_{\text{TO}}^2)/(\nu_{\text{LO}}^2 - \nu_0^2)]^{1/2} \quad (11)$$

For molecules on sites of tetrahedral or higher symmetry $\beta = 1/3$, giving eq 10. For lower symmetry sites β , which is a constant modifying the polarization field,³ can vary from $1/3$. For SF_6 the crystal structure¹⁸ indicates that there are molecules on two different sites, of D_{3d} and C_{3v} symmetry. Therefore, we can expect β to be different than $1/3$. If we assume a reasonable value of 1.3 for n_∞ we find that $\beta = 1/4.3$. We are not sure how β should change with site symmetry; however, it is clear that eq 10 is unsatisfactory for sites of lower than tetrahedral symmetry.

LO-TO Splitting for SeF_6 . Figure 3 presents the polarized spectra of the ν_3 mode for a thin film of SeF_6 . One LO mode is observed at 805.7 cm^{-1} and a TO mode at 757.0 cm^{-1} with a weak

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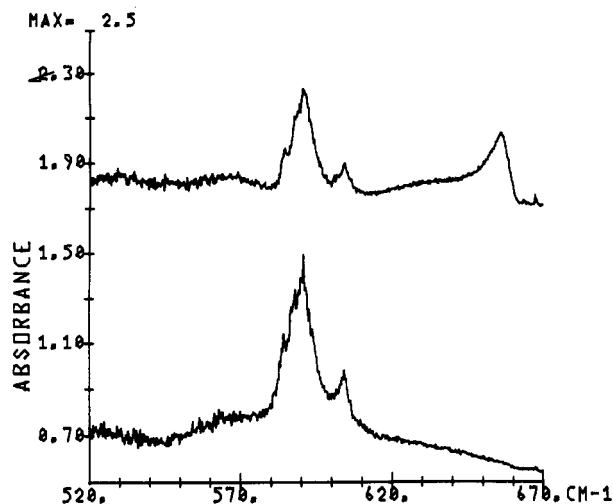


Figure 4. The ν_3 mode of UF_6 at 150 K for a thin film about $0.2 \mu\text{m}$ thick deposited at 150 K. Upper curve, p polarization. Lower curve, s polarization. Substrate at 40° to incident beam.

shoulder at about 764 cm^{-1} . We note that the ratio of LO to TO intensity is less than for SF_6 in Figure 1, primarily because the angle of incidence of the spectrometer beam to the film plane is greater. The structure of solid SeF_6 is not known to us; however, we expect it to be similar to that of SF_6 except for the slightly larger molecular size. We then calculate the value of N in eq 3 as 1.02×10^{22} molecules/ cm^3 compared to 1.12×10^{22} molecules/ cm^3 for SF_6 . Then from eq 3 and the above LO and TO frequencies we calculate $\partial\mu/\partial Q_3 = 0.349 \text{ e u}^{-1/2}$.

Intensities for SeF_6 have not been reported in the literature; however, we can estimate the values from the intensity in our thin films and from relative intensities in krypton matrices containing known amounts of SF_6 and SeF_6 . Thus, from the mixed matrix we find that the intensity/mole for ν_3 of SeF_6 is about 1/3 that of ν_3 of SF_6 , or 347 km/mol . We find essential agreement with this from the intensity in the lower spectrum in Figure 3 for which we believe the film thickness is about $0.25 \mu\text{m}$. From this value for S , using eq 8 we calculate $\partial\mu/\partial Q_3 = 0.344 \text{ e u}^{-1/2}$, in excellent agreement with the value of 0.349 calculated from the LO–TO splitting.

We estimate a value of ν_0 as 772 cm^{-1} which we have observed for 5% SeF_6 in a matrix of SF_6 . From eq 11 if we assume $\beta = 1/4.26$ as we found for SF_6 we calculate $n_\infty = 1.2$ which may be a bit low.

LO–TO Splitting for UF_6 . The polarized spectrum for the ν_3 mode of UF_6 is shown in Figure 4. We find the LO mode at 656.2 cm^{-1} while the TO mode appears at 590.7 cm^{-1} with satellites at 584.5 and 604.2 cm^{-1} . The weighted average for the TO mode is 592 cm^{-1} . The crystal structure has been determined²⁵ to be orthorhombic ($Pnma$), with a density of 0.866×10^{22} molecules/ cm^3 . Using 656 and 592 cm^{-1} for the LO and TO modes, respectively, we then find, from eq 3, $\partial\mu/\partial Q_3 = 0.434 \text{ e u}^{-1/2}$. The most recent intensity measurement for ν_3 in the gas phase is given as $750 \pm 15 \text{ km/mol}$ by Person et al.²⁶ From eq 8 we then calculate $\partial\mu/\partial Q_3 = 0.506 \pm 0.005 \text{ e u}^{-1/2}$. Thus the intensity measurement gives a derivative about 16% higher than obtained from the LO–TO splitting. This is more than our estimate of $\pm 10\%$ error from use of eq 3. We note that the uncertainty in the intensity measurement²⁶ may be a bit optimistic especially considering the difficulty of handling UF_6 and the lower values reported earlier.^{17,27}

For ν_3 $617\text{--}619 \text{ cm}^{-1}$ was observed²⁸ in dilute matrices of UF_6 in rare gas solids. If we use 618 cm^{-1} for ν_0 of the solid, from

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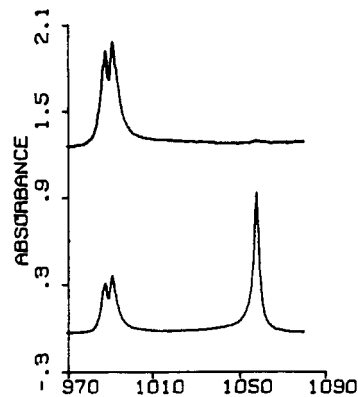


Figure 5. The ν_3 mode of SiF_4 at 70 K for a thin film about $0.2 \mu\text{m}$ thick deposited at 70 K. Upper curve, s polarization. Lower curve, p polarization. Substrate at 25° to incident beam.

eq 11 we find $n_\infty[\beta/(1-\beta)]^{1/2} = 0.80$ compared to 0.72 for SF_6 , suggesting larger n_∞ or larger β for UF_6 .

LO–TO Splitting for SiF_4 . There have been numerous investigations of SiF_4 Raman and infrared spectra. Bessette et al.⁸ from Raman spectra have reported in the ν_3 region a longitudinal mode at 1057.3 cm^{-1} and a transverse doublet at $991.3, 987.8 \text{ cm}^{-1}$. They also report for the ν_4 mode an LO frequency at 407.5 cm^{-1} and a TO doublet at $373.3, 370.6 \text{ cm}^{-1}$. Schettino⁹ has observed these frequencies also. From the polarized infrared spectra, as shown in Figure 5, we observe only the ν_3 region and find $\nu_{\text{LO}} = 1057.8 \text{ cm}^{-1}$ and $\nu_{\text{TO}} = 991.1, 987.8 \text{ cm}^{-1}$ in excellent agreement with the Raman results of Bessette.⁸ From these frequencies, using eq 3, we calculate $\partial\mu/\partial Q_3 = 0.475 \text{ e u}^{-1/2}$ and $\partial\mu/\partial Q_4 = 0.211 \text{ e u}^{-1/2}$. Intensities for SiF_4 vapor were reported by Schatz and Hornig.²⁴ From their results we calculate $\partial\mu/\partial Q_3 = 0.449 \text{ e u}^{-1/2}$ and $\partial\mu/\partial Q_4 = 0.197 \text{ e u}^{-1/2}$. The agreement is quite satisfactory.

The crystal structure of SiF_4 was determined as cubic with one molecule per primitive cell.²⁹ As pointed out by Bessette et al.⁸ and by Schettino⁹ the doublet structure for the TO mode is not consistent with a cubic structure with one molecule per primitive cell and it was suggested⁸ that the structure may be in error and should be redetermined. We are not aware of any redetermination of the structure since 1954.²⁹ However, we believe another possible explanation should be considered; namely, the TO doublet structure may arise from the presence of isotopic impurities in Si of natural isotopic abundance (92.2% ^{28}Si , 4.7% ^{29}Si , and 3.1% ^{30}Si) leading to loss of translational symmetry. The result can be infrared activity of modes for which the wave vector $\mathbf{k} \neq 0$ as well as the appearance of local impurity modes. This will be discussed further in an article on the effect of impurities and defects.

Since the molecules are on sites of T_d symmetry eq 10 should apply. Dilute SiF_4 in SeF_6 shows a peak at 1026 cm^{-1} which we assign to ν_0 . This, along with ν_{TO} and ν_{LO} , in eq 10, yields a value of 1.35 for n_∞ , using eq 10 we calculate $\nu_0 = 389 \text{ cm}^{-1}$ for the ν_4 mode, somewhat lower than the gas-phase value of 391 cm^{-1} , as expected.

Bernstein and Meredith³⁰ have observed Raman spectra of large single crystals of SiF_4 and find no "observable changes" in the spectra at various scattering angles between 0° and 90° . They cite this as evidence that the LO–TO splitting model⁸ is incorrect and propose that the two modes arise from factor group splitting, implying that the reported crystal structure is incorrect and SiF_4 has a multimolecular unit cell. This splitting of 68 cm^{-1} is extremely large for factor group splitting; furthermore, our infrared studies, showing peaks at exactly the same frequency as the Raman peaks³⁰ and strong polarization for the LO peak, confirm the LO–TO splitting explanation.⁸

LO–TO Splitting for CF_4 . The crystal structure of CF_4 is reported³¹ as monoclinic, space group $P2_1/c$ (C_{2h}^5), with four

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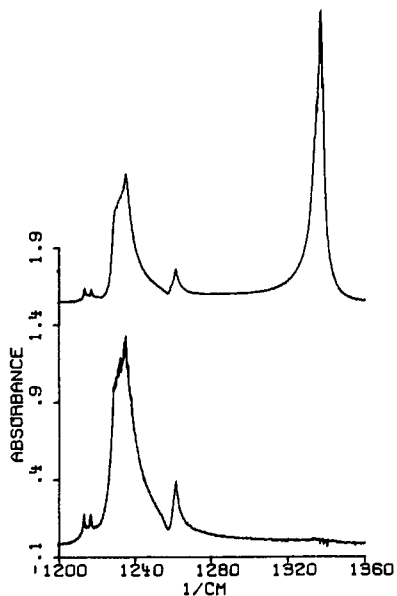


Figure 6. The ν_3 mode of CF_4 at 10 K for a thin film about $0.1 \mu\text{m}$ thick deposited at 30 K. Upper curve, p polarization. Lower curve, s polarization. Substrate at 25° to incident beam.

molecules per unit cell. From the results of ref 4 and far-infrared spectra the structure was reinterpreted³² as belonging to space group $C2/c$. The number of molecules/ cm^3 is 1.505×10^{22} compared to 1.263×10^{22} for SiF_4 . These numbers are about in the inverse ratio of the molecular volume as expected for similar packing. However, since the symmetry is lower, we may expect more complex spectra.

The polarized spectra in the ν_3 region for a thin film of CF_4 are shown in Figure 6. The TO portion from 1200 to 1270 cm^{-1} is similar to that reported by Fournier et al.³³ The weighted average is 1235 cm^{-1} . We observe an LO mode at 1337 cm^{-1} . For ν_4 we observe a TO doublet at ($629.2, 629.8 \text{ cm}^{-1}$) and an LO peak at 631.7 cm^{-1} . From these sets of values we calculate from eq 4

$$\partial\mu/\partial Q_3 = 0.596 e u^{-1/2}; \quad \partial\mu/\partial Q_4 = 0.061 e u^{-1/2}$$

Averages of several intensity measurements are reported by Person²¹ with standard deviations as $S_3 = 1080 \pm 177 \text{ km/mol}$ and $S_4 = 11.7 \pm 2.2 \text{ km/mol}$. From these values and eq 8 we find

$$\partial\mu/\partial Q_3 = 0.608 \pm 0.052 e u^{-1/2}$$

$$\partial\mu/\partial Q_4 = 0.063 \pm 0.006 e u^{-1/2}$$

The agreement is excellent.

LO-TO Splitting for CCl_4 . The crystal structure of CCl_4 has been determined to be monoclinic³⁴ with space group $C2/c$ with 32 molecules per unit cell. From the density of 1.94 there are 0.76×10^{22} molecules/ cm^3 . From Figure 7 we see there are two TO absorptions, at 759 and 781 cm^{-1} . These two peaks arise from ν_3 and the combination $\nu_1 + \nu_4$ in Fermi resonance with ν_3 (see ref 35). Analysis of the Fermi resonance puts the unperturbed ν_{TO} at 767 cm^{-1} . The LO mode is seen at 799.8 cm^{-1} . From eq 3 we then calculate $0.370 e u^{-1/2}$ for $\partial\mu/\partial Q_3$. Intensity studies over the years give quite varied results for CCl_4 vapor¹³ leading to $\partial\mu/\partial Q_3$ ranging from 0.303 to $0.376 e u^{-1/2}$. However, intensity measurements³⁶ in the solid state give $\partial\mu/\partial Q_3 = 0.376 e u^{-1/2}$ and

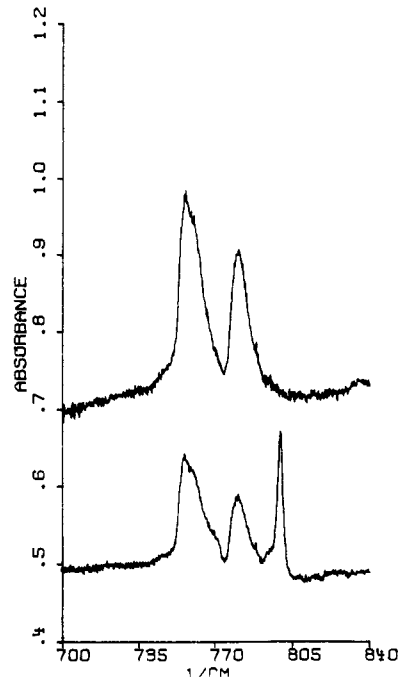


Figure 7. The ($\nu_3, \nu_1 + \nu_4$) Fermi doublet of CCl_4 at 110 K for a thin film about $0.1 \mu\text{m}$ thick deposited at 110 K. Upper curve, s polarization. Lower curve, p polarization. Substrate at 30° to incident beam.

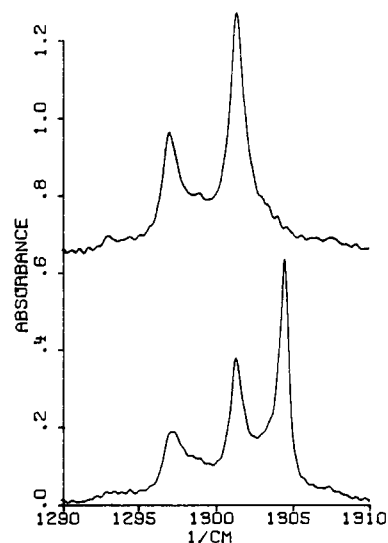


Figure 8. The ν_4 mode of CH_4 at 10 K for a thin film about $0.3 \mu\text{m}$ thick deposited at 25 K. Upper curve, s polarization. Lower curve, p polarization. Substrate at 25° to incident beam.

$\partial\mu/\partial Q_4 = 0.016 e u^{-1/2}$. The value of 0.370 calculated from the LO-TO splitting of ν_3 is quite satisfactory.

We might expect to see a Fermi resonance doublet for the LO mode. However, since $\partial\mu/\partial Q_4$ is so small, the LO-TO splitting for ν_4 will be less than 1 cm^{-1} . Analysis of the Fermi resonance predicts a very weak LO component for the combination ($\nu_1 + \nu_4$) at about 769 cm^{-1} . Indeed we do see a weak LO polarized component at about 770 cm^{-1} .

LO-TO Splitting for CH_4 and CD_4 . At temperatures below 22 K CH_4 and CD_4 have different structures³⁷—an fcc and partially ordered phase for CH_4 and a tetragonal, orientationally ordered phase for CD_4 . In Figure 8 we show the polarized spectra for the ν_4 mode of CH_4 . Our TO spectrum is in essential agreement with the early study of Savitsky and Hornig;³⁸ however, Maselli et al.³⁷ report four strong peaks for phase II of CD_4

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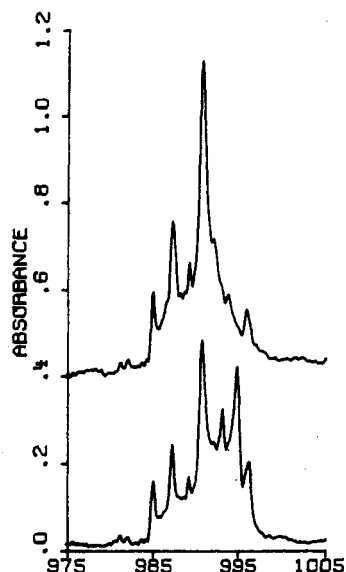


Figure 9. The ν_4 mode of CD_4 at 10 K for a thin film about $0.3 \mu\text{m}$ thick deposited at 25 K. Upper curve, s polarization. Lower curve, p polarization. Substrate at 25° to incident beam.

contrary to Savitsky and Hornig.³⁸ We believe the structure for phase II of CH_4 is not yet understood; however, for our purpose it is appropriate to use a weighted average of 1300.0 cm^{-1} for ν_{TO} and the observed value 1304.4 cm^{-1} for ν_{LO} leading to a calculated value of $\partial\mu/\partial Q_4 = 0.107 \text{ e u}^{-1/2}$. From reported intensities^{13,17} we calculate values ranging from 0.098 to $0.113 \text{ e u}^{-1/2}$, bracketing the value calculated from LO-TO splitting.

The absorption for the ν_3 mode consists of a rather broad peak; polarization shows only a high-frequency shoulder for the LO mode. We estimate $\nu_{\text{TO}} = 3008.7 \text{ cm}^{-1}$ and $\nu_{\text{LO}} = 3011.3 \text{ cm}^{-1}$ leading to a calculated value of $\partial\mu/\partial Q_3 = 0.126 \text{ e u}^{-1/2}$. From intensities^{13,17} we calculate values from 0.099 to $0.161 \text{ e u}^{-1/2}$.

For CD_4 we studied the polarized spectra for only the lowest temperature phase, phase III, which does not exist for CH_4 . In Figure 9 we show the spectrum for ν_4 . The complexity apparently arises from the fact that there are 32 molecules per unit cell and several distinct sites.³⁷ Our TO spectrum (Figure 9) resembles that of Maselli et al.³⁷ We see two definite LO peaks but it is not clear how to match them up with the TO peaks. We choose the most intense LO and TO as one set (994.8 and 990.6 cm^{-1}) leading to a calculated $\partial\mu/\partial Q_4 = 0.091 \text{ e u}^{-1/2}$. From the reported intensity¹⁷ we calculate $\partial\mu/\partial Q_4 = 0.083 \text{ e u}^{-1/2}$. For ν_3 we observe an LO peak at 2252.5 cm^{-1} and a TO peak at 2250.8 cm^{-1} leading to a calculated value $\partial\mu/\partial Q_3 = 0.089 \text{ e u}^{-1/2}$ to be compared with $0.099 \text{ e u}^{-1/2}$ as calculated from intensities.¹⁷

LO-TO Splitting for CO, CO₂, and N₂O. We also report results on the nonisotropic linear molecules CO, CO₂, and N₂O which form crystals of cubic space groups but for which the molecules reside on sites of C_3 or C_3 symmetry.

Zumofen⁶ has discussed LO-TO splitting for solid CO based on spectra reported by Dubost.⁵ He has calculated the expected splitting from intensity data including a correction factor for short-range interactions in the solid state. We have observed polarized spectra of thin films of CO at 10 K and find frequencies of $\nu_{\text{LO}} = 2143.0$ and $\nu_{\text{TO}} = 2138.5 \text{ cm}^{-1}$, similar to those reported by Dubost.⁵ The crystal structure of CO at low temperature is cubic (space group P_{213}) with four molecules per unit cell and 2.23×10^{22} molecules/cm³. The molecules lie on C_3 sites. From the LO-TO splitting we calculate $\partial\mu/\partial Q = 0.140 \text{ e u}^{-1/2}$ in rather poor agreement with the value of 0.228 we calculate from the most recent intensity measurement for the vapor, listed in ref 12.

We have not studied the spectrum of CO₂; however, we wish to note that Parker and Eggers⁷ have reported TO and LO modes from the infrared spectrum of thin films of CO₂ observed at nonnormal incidence. They find for ν_3 , TO and LO modes at 2344

TABLE I: Comparison of Dipole Moment Derivatives (in $\text{e u}^{-1/2}$) Calculated from LO-TO Splitting and from Measured Intensities

molecule	mode	$\partial\mu/\partial Q_i$ (LO-TO) ^a	$\partial\mu/\partial Q_i$ (intensity) ^b	
			gas phase	solid
SF ₆	ν_3	0.588	0.606 (30) ²¹	0.60 (3) ²²
	ν_4	0.157	0.160 (5) ²¹	0.20 (1) ²²
SeF ₆	ν_3	0.349		0.34 ^c
UF ₆	ν_3	0.434	0.506 (5) ²⁶	
SiF ₄	ν_3	0.475	0.449 (23) ²⁴	
	ν_4	0.211	0.197 (10) ²⁴	
CF ₄	ν_3	0.596	0.608 (52) ²¹	
	ν_4	0.061	0.063 (6) ²¹	
CCl ₄	ν_3	0.370	0.34 (4) ¹³	0.38 (3) ³⁶
CH ₄	ν_3	0.126	0.13 (3) ¹³	
	ν_4	0.107	0.106 (8) ¹³	
CD ₄	ν_3	0.089	0.099 (1) ¹⁷	
	ν_4	0.091	0.083 (1) ¹⁷	
CO	ν	0.140	0.228 ¹³	
CO ₂	ν_2	0.158	0.17 ³⁹	0.17 (1) ³⁹
	ν_3	0.402	0.81 ³⁹	0.55 (4) ³⁹
N ₂ O	ν_1	0.121	0.25 ³⁹	0.20 (2) ³⁹
	ν_3	0.292	0.58 ³⁹	0.48 (4) ³⁹
¹⁵ N ₂ ¹⁸ O	ν_1	0.118		
	ν_3	0.276		

^a We estimate the uncertainty in $\partial\mu/\partial Q_i$ calculated from eq 4 to be less than 10% based on the uncertainty in n_s and experimental error. The sign of $\partial\mu/\partial Q_i$ is undetermined. ^b After most values of $\partial\mu/\partial Q_i$, uncertainties are given in parentheses as units (\pm) of the last digit reported. These are based where possible on the uncertainty reported in the reference. For CCl₄ gas and CH₄ they are based on the variation in range of values given. Numerical superscripts give references for intensity data from which $\partial\mu/\partial Q_i$ is derived. ^c Derived from our results for matrices and for thin films of pure SeF₆, see text.

and 2383 cm^{-1} and for ν_2 , a TO doublet at 654.5 and 659.0 cm^{-1} and an LO mode at 678.3 cm^{-1} . Yamada and Person³⁹ measured intensities for CO₂ in the vapor and solid phases. Their results give $\partial\mu/\partial Q_3 = 0.807 \text{ e u}^{-1/2}$ for the vapor and $0.553 \text{ e u}^{-1/2}$ for the solid and $\partial\mu/\partial Q_2 = 0.167 \text{ e u}^{-1/2}$ for the vapor and $0.173 \text{ e u}^{-1/2}$ for the solid. From these values, using the relation of our eq 1, Parker and Eggers⁷ were able to fit the observed LO-TO splitting for ν_2 quite well using a weighted average of 657 cm^{-1} for the TO mode. However, the calculated splitting was much larger than observed for ν_3 .

The crystal structure of CO₂ is cubic (space group $Pa3$) and the molecules are centered on sites of C_{3i} symmetry. From the observed LO-TO splitting, using a weighted average of 657 cm^{-1} for the TO mode of ν_2 , we calculate $\partial\mu/\partial Q_3 = 0.402 \text{ e u}^{-1/2}$ and $\partial\mu/\partial Q_2 = 0.158 \text{ e u}^{-1/2}$. From these calculations and those of Parker and Eggers⁷ it is apparent that ν_2 fits the treatment but ν_3 does not.

We have also observed spectra for thin films of ¹⁴N₂¹⁶O and of ¹⁵N₂¹⁸O to evaluate the LO-TO splittings. The crystal structure is similar to that of CO₂ with a slightly larger unit cell. For ν_3 , LO, TO doublets are observed at 2258.1, 2237.2 for the 14, 16 isotope and 2180.4, 2160.4 for the 15, 18 isotope. For ν_1 the LO, TO doublets are 1299.2, 1293.0 for the 14, 16 isotopic species and 1239.2, 1233.0 for the 15, 18 isotopic species. From these values we calculate $\partial\mu/\partial Q_3 = 0.292$ and $0.276 \text{ e u}^{-1/2}$ and $\partial\mu/\partial Q_1 = 0.121$ and $0.118 \text{ e u}^{-1/2}$ for the 14, 16 and 15, 18 isotopic species, respectively. Yamada and Person³⁹ reported 0.475 and $0.204 \text{ e u}^{-1/2}$ for $\partial\mu/\partial Q_3$ and $\partial\mu/\partial Q_1$, respectively, for ¹⁴N₂¹⁶O in the solid state. Here again, for both of these stretching vibrations the LO-TO splitting is much less than predicted by eq 1. The decrease in dipole moment derivative for the 15, 18 isotopic species from that of the 14, 16 isotopic species is probably quite accurate as it depends primarily on accurately determined frequencies. Thus the possible error of 0.1 cm^{-1} in frequency difference measurement leads to a change of less than $0.002 \text{ e u}^{-1/2}$ for calculated values of $\partial\mu/\partial Q_3$ and $\partial\mu/\partial Q_1$. This accuracy is much greater than one can hope to obtain from intensity measurements.

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We note that, for CO, CO₂, and N₂O, though the crystals are cubic, the free molecules are not isotropic so the polarization forces from stretching modes are not aligned with transition moments for the same mode of neighboring molecules. This is not true for the doubly degenerate bending modes. These observations may explain the agreement of LO-TO splitting and intensity for ν_2 of CO₂ but lack of agreement for the stretching modes of these linear molecules, for which the intensity yields values of $\partial\mu/\partial Q_i$, 50-60% greater than calculated from the LO-TO splitting.

The results of the above comparisons of values of $\partial\mu/\partial Q_i$, calculated from LO-TO splittings using eq 3 with those calculated from intensities (eq 8 or 9) are listed in Table I.

Summary

We have observed LO-TO splittings for a number of molecular solids using polarized infrared spectra of thin films deposited from the vapor phase. From the theory for molecules on sites of T_d or higher symmetry in cubic lattices we have calculated dipole moment derivatives for the observed molecular vibrations and compared them with values calculated from integrated intensities reported in the literature. Even though for most of the molecules

treated the site symmetry is lower than T_d , and for most the crystal symmetry is not cubic, the agreement is quite good for dipole moment derivatives calculated by the two methods for molecules which are spherical tops in the isolated state, especially considering that most of the intensities were measured in the gas phase. For the few solid-state intensities we have found in the literature the only significant difference is for ν_4 of SF₆ for which the gas-phase intensity agrees better with the LO-TO splitting.

For stretching modes of the linear molecules CO, CO₂, and N₂O the LO-TO splitting is 20-30% less than predicted from intensities. Thus, without further study, it appears that for nondegenerate modes the LO-TO splitting will yield low values for the dipole moment derivative and intensities.

The technique should be useful for calculating dipole moment derivatives, and thus also intensities, for mid-infrared-active vibrations of molecular and ionic solids for which it is possible to form films thinner than 1 μm or so. For longer wavelength modes one could use somewhat thicker films.

Registry No. SF₆, 2551-62-4; SeF₆, 7783-79-1; UF₆, 7783-81-5; SiF₄, 7783-61-1; CF₄, 75-73-0; CCl₄, 56-23-5; CH₄, 74-82-8; CD₄, 558-20-3; CO, 630-08-0; CO₂, 124-38-9; N₂O, 10024-97-2; ¹⁵N₂¹⁸O, 20259-33-0.

Matrix Infrared and Raman Spectra of the Inequivalent Submolecules in the Ammonia Dimer

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Vibrational modes in the N-H stretching region have been assigned to each submolecule in (NH₃)₂ on the basis of comparison of infrared and Raman spectra and the spectra of (NH₃)(N(CH₃)₃) dimers. The submolecules are clearly different with one perturbed more strongly than the other and one exhibiting stronger Fermi resonance interaction between its internal ν_1 and $2\nu_4$ modes. The small vibrational perturbations show that the interaction is weaker than that normally associated with classical hydrogen bonding.

Introduction

Ammonia dimer has become a maverick for hydrogen-bonded complexes. Although the more strongly bound dimers (HF)₂ and (H₂O)₂ exhibit nearly linear hydrogen bonds,^{1,2} (NH₃)₂ involves a cyclic intermolecular association with inequivalent ammonia submolecules.^{3,4} Extensive theoretical studies of ammonia dimer have been performed,⁵⁻⁹ and cyclic structures are energetically

competitive with linear hydrogen-bonded molecules.^{8,9} Recent electrically based molecular mechanics for clusters calculations also reveal a dimer structure with inequivalent NH₃ subunits.¹⁰ Infrared spectra of ammonia dimers have been studied in solid matrices (hereafter referred to as I)¹¹ and in the gas phase.^{12,13} Several very recent observations, the infrared photodissociation¹⁴⁻¹⁶ and CARS spectra of gaseous ammonia clusters,¹⁷ vibrational analysis and Fermi resonance assignment of ammonia monomer

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