

- Fields R (1972) Fluorine-19 nuclear magnetic resonance spectroscopy. *Annual Reports on NMR Spectroscopy* **5A**: 99–304.
- Fields R (1977) Fluorine-19 nuclear magnetic resonance spectroscopy. *Annual Reports on NMR Spectroscopy* **7**: 1–117.
- Jameson CJ (1987) Fluorine. In: Mason J (ed) *Multinuclear NMR*, pp 305–333, New York: Plenum Press.
- Mooney EF and Winson PH (1967) Fluorine-19 nuclear magnetic resonance spectroscopy. *Annual Reports on NMR Spectroscopy* **1**: 243–311.
- Sohár P (1983) *Nuclear Magnetic Resonance Spectroscopy*, vol II, pp 261–268. Boca Raton, Florida: CRC Press, Inc.
- Wray V (1980) Fluorine-19 nuclear magnetic resonance spectroscopy (1976–1978). *Annual Reports on NMR Spectroscopy* **10B**: 1–507.
- Wray V (1983) Fluorine-19 nuclear magnetic resonance spectroscopy (1976–1978). *Annual Reports on NMR Spectroscopy* **14**: 1–406.

Far-IR Spectroscopy, Applications

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VIBRATIONAL, ROTATIONAL & RAMAN SPECTROSCOPIES
Applications

Introduction and history

The far-infrared spectral region is the range of wavenumbers where one finds many of the large-amplitude anharmonic vibrations. These include both the symmetric and asymmetric internal torsional modes of many small organic and organometallic molecules, ring puckering vibrations of four- and five-membered rings, and the heavy-atom skeletal bending modes. Additionally, this is the spectral region where one finds lattice vibrations from which information is obtained on intermolecular forces that are of considerable interest to both chemists and the physicists.

Historically, this region has been defined from 200 to 10 cm⁻¹, which is the region below the cutoff of CsI, where it can no longer be used as a dispersive material. Initial investigations in this spectral region began before the turn of the twentieth century in Europe, and it has always been more popular in Western Europe and Japan than in the United States. Even before the use of Fourier transform interferometers became common for this spectral region, there were several laboratories in these other countries where the far-infrared spectral region was studied almost exclusively. The first chemical applications of Fourier transform infrared (FT-IR) spectroscopy were made in the far-infrared spectral region because the interferometric instrumentation required to obtain spectra in this region is much simpler than that needed for the mid- or near-infrared regions. The instrumental advantages in the far-infrared spectral region included a lower tolerance for

the mirror drive of a Michelson interferometer, a smaller dynamic range of the interferogram and a longer sampling time, which results in a reduced number of data points.

The far-infrared spectral region initially had its inherent difficulties, such as low-energy sources, poor detectors, lack of suitable optical materials and spectral interference of water vapour. Research workers in this wavenumber area have overcome many of these difficulties and, therefore, spectral investigations in the far-infrared region have become more common. This is particularly true with the commercial availability of Fourier transform spectrometers, which routinely provide spectral data to 30 cm⁻¹ with excellent signal-to-noise ratios. However, because of the absorption of water vapour in this spectral region (see **Figure 1**), it is highly desirable to have a vacuum interferometer bench.

Many of the far-infrared spectral studies for chemical information have emphasized the gas phase. This emphasis should not be interpreted as meaning that far-infrared spectral studies of solids are not important. Physicists have put interferometers to use in the study of the solid state to determine optical constants such as the index of refraction, complex indices, phase angle transmission coefficients and the electronic processes in insulation crystals, as well as the intermolecular vibrations of molecular crystals. These studies have been very important in the development of interpretative theories of solids.

With the increased ability to utilize *ab initio* calculations for predicting relative conformational

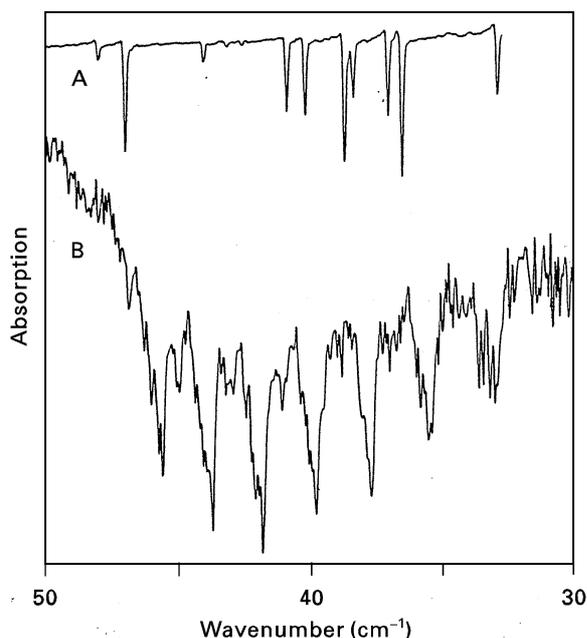


Figure 1 Far-infrared spectra of (A) water vapour and (B) trifluoroacetyl fluoride.

stabilities, barriers to internal rotation, small ring inversions and low-wavenumber vibrations, the theoretical predictions are frequently compared with the experimental results in this spectral region. The use of either an incomplete or an incorrect experimental database in comparisons with theoretical results, may lead to erroneous conclusions with regard to the reliability and accuracy of the theoretical results.

Poor experimental databases with regard to the experimental determination of potential barriers and conformational equilibria arise for three basic reasons. First, there is frequently insufficient structural information in many cases. Numerous potential functions governing internal rotation of asymmetric tops (conformational interchange) have been published without the knowledge of the structures of both conformers, particularly of the high-energy conformer. It is extremely important, for the accurate experimental determination of the energy levels and potential functions, that some reasonable structural information be known about all of the exhibited conformations. Furthermore, in the absence of reliable structures determined from experimental techniques, such as those determined from microwave spectroscopy or analysis of the electron diffraction pattern, the reliability of optimized geometries determined from theory cannot be ascertained.

Secondly, there is frequently a lack of complementary experimental data. Owing to symmetry and the resulting selection rules, both infrared and Raman

spectroscopic results are often needed to identify the high-energy and low-energy conformers. The Raman spectrum of the gas is almost always neglected, and it is not unusual to find vibrational conformational studies for which spectra are not reported for all three phases.

Thirdly, there is often a lack of high-resolution data. The highest possible resolution available should be used to record the low-frequency spectral data. Many torsional bands are extremely sharp and, therefore, transitions may not be observed at the lower resolution. Additionally, insufficient resolution may result in misleading relative intensities of the Q branches from different energy levels.

Low-wavenumber FT-IR spectroscopy is among the most generally applicable methods used in the study of the conformers for certain types of small molecules with few substituents. Infrared spectra can, and variable-temperature experiments may, be investigated in all phases. The gas-phase band contours observed for the infrared spectra, along with Raman depolarization data, provide considerable information on the molecular symmetry of the conformers. The limitation of the vibrational spectroscopic technique is that it is best applied to relatively simple molecules that contain at least one element of symmetry, and one or perhaps no more than two portions of the molecule capable of producing different conformations upon internal rotation.

One of the earlier uses of the far-infrared spectral region was to determine the barrier to internal rotation of symmetric-top rotors. The most frequently studied molecules were those with one threefold internal rotation, and many of those studies were for methyl tops. The first indication that the rotation around single bonds was not free came from thermodynamic data in the mid-1930s. Barriers were calculated from the thermodynamic data by relating the difference in the observed and statistical entropies by tables involving the barrier height and the reciprocal of the partition function for free rotation. Later, barrier values were obtained from investigations of the microwave spectra of small molecules where the observed perturbations on the pure rotational transitions were correlated with the torsional barrier heights by either the splitting or intensity methods. The splitting method is the most exact method since it depends only on the height of the barrier and usually gives barrier values to a few percent. The microwave intensity method is frequently used for the determination of the fundamental frequencies of asymmetric rotors.

One wishes to obtain the fundamental wavenumber for the torsional mode for the gaseous molecule

so that the barrier height in the isolated molecule can be ascertained. However, the dipole moment change associated with the torsional mode may be quite small, and consequently the resulting infrared band intensity may be weak. Therefore, assignments of the torsional modes of molecules in the gas were frequently in error in the initial investigations and the use of isotopic substitution is often necessary to verify the torsional assignments. Also, torsional modes that give rise to B-type infrared band contours may have bands that are very broad and ill-defined because of unresolved excited-state transitions. In favourable cases where the torsional mode gives rise to A-type or C-type band contours with relatively strong Q branches, several excited state transitions may be resolved and not only can the barrier height be obtained but also the detailed shape of the potential well may be ascertained.

When a molecule has a far-infrared spectrum too complicated for quantitative interpretation, estimates of the barrier heights may be obtained by studying the infrared and Raman spectra of the sample in the crystalline state. At liquid-nitrogen temperature, the upper vibrational states are effectively depopulated and only the $1 \leftarrow 0$ torsional transition is observed. The barrier height may be estimated from this single experimental datum, but a detailed analysis of the shape of the potential well is not possible. Additionally, it is sometimes possible to observe the torsional mode in the solid state when it is forbidden for the gaseous molecule. Barriers obtained in the solid state are usually 10–15% higher than those for the gaseous molecules.

Internal rotors

Internal rotors fall into two categories: symmetric and asymmetric tops. For symmetric tops, a rotation about the top-frame bond of $2\pi/n$ (where n is an integer) will bring the top to a position symmetrically equivalent to, or indistinguishable from, the original configuration. Therefore, it is usual to speak of the 'foldness' of the rotor in terms of n . For example, a perfluoromethyl group (CF_3) is a threefold symmetric top (local C_{3v} symmetry), and twofold rotors include $-\text{NO}_2$, $-\text{BF}_2$ and phenyl groups (local C_{2v} symmetry). When a rotation of 360° (i.e. when $n=1$) is the only operation that results in a symmetrically equivalent position for the top, the rotor is known as an asymmetric top. For the case of a symmetric frame, the top with the highest degree of symmetry prevails and, when two tops of different foldness are bonded directly to one another, the resultant foldness is the product of the two individual

tops' foldness. For instance, CH_3BH_2 would be classified as a sixfold internal rotor.

The energy minima and maxima for a symmetrical threefold group (CF_3) are 60° apart. The simplest mathematical function that will reproduce such a potential variation upon rotation is a cosine function. If the problem is assumed to be one-dimensional, the quantum-mechanical energy solutions are readily obtainable. The model employed is a rigid symmetric top (CF_3 group) attached to a rigid frame, which may be completely asymmetric. There are four rotational degrees of freedom, three for overall rotation and one for the hindered rotation of the two groups. The axis of internal rotation is usually assumed to coincide with the unique axis of the symmetric top. Since the top has a threefold symmetry axis, the potential energy hindering rotation may be expressed by a Fourier expansion:

$$V(\phi) = \frac{V_3}{2}(1 - \cos 3\phi) + \frac{V_6}{2}(1 - \cos 6\phi) + \dots$$

where V_3 is the height of the threefold barrier; V_6 the sixfold; and so forth. A positive V_6 makes the minima narrower and the maxima broader, which results in the energy levels near the bottom of the well becoming somewhat more widely separated. A negative V_6 term has the opposite effect. Experimentally it has been found that $0 \leq V_6/V_3 < 0.05$ and $V_6 \gg V_9 \gg$ higher-order terms.

An example of the use of far-infrared spectral data for the determination of the barrier to internal rotation is given by trifluoroacetyl fluoride, CF_3CFO (**Figure 1**). Seven torsional transitions are clearly observed, beginning with the fundamental at 45.65 cm^{-1} and continuing to the $7 \leftarrow 6$ transition at 33.40 cm^{-1} . Utilizing an F number ($h^2/8\pi^2 I_r$ where I_r is the reduced moment of inertia of the top) of 0.5970 cm^{-1} along with the wavenumbers of these seven transitions, the V_3 value is $382 \pm 2 \text{ cm}^{-1}$ and $V_6 = 8 \pm 1 \text{ cm}^{-1}$. The intensity of the $4 \leftarrow 3$ transition and higher excited state transitions are significantly higher than expected on the basis of the Boltzmann factors because of the increased anharmonicity in the higher excited states. The statistical uncertainty is very low for both the V_3 and V_6 terms and the V_6 term is very small. This molecule is too heavy for the barrier to be determined by the microwave splitting method. Molecules with two or three equivalent rotors have also been extensively investigated, but the spectral data are much more complex and frequently there is not sufficient data to obtain values for all of the potential constants. Good barrier determination from far-infrared data requires that the internal

torsional mode is not mixed (potential energy distribution) with other low-wavenumber bending modes.

The asymmetric rotor is the other type of torsional motion frequently studied. These rotors usually lead to two or more stable conformers. One of the major goals of conformational analysis is the calculation of the energy difference between the two conformers and the energy necessary for interconversion. Four types of information are required to characterize an asymmetric potential function: (1) the approximate dihedral (torsional) angle of each conformer, because the number of torsional energy levels is directly related to the number of potential minima; (2) the approximate relative enthalpy difference between the high- and low-energy conformers, since this is one of the constraints defining the potential functions; (3) the change in molecular kinetic energy as a function of torsional angle; and (4) accurate observation of torsional transition frequencies. A typical spectrum for such a rotor is shown in **Figure 2** where the fundamental torsional mode of the *trans* conformer of FCH_2CFO is observed at 118.9 cm^{-1} with the excited torsional modes falling to lower wavenumbers to the $13 \leftarrow 12$ transition at 67.0 cm^{-1} . The fundamental torsional mode for the *cis* conformer is assigned at 52.1 cm^{-1} with five successive excited states falling to lower wavenumber with the last one observed at 43.7 cm^{-1} . These data give the following potential constants: $V_1 = 86 \pm 11$, $V_2 = 946 \pm 33$, $V_3 = 407 \pm 4$, $V_4 = 138 \pm 20$, and $V_6 = -14 \pm 7\text{ cm}^{-1}$ with a *trans* to *cis* barrier of $1297 \pm 26\text{ cm}^{-1}$.

Small ring molecules

Another type of large-amplitude anharmonic vibration is that of the ring puckering modes of small compounds. From the analysis of the frequencies for these ring-bending motions it is possible to obtain the potential surfaces for the interconversion of the different conformers. The equilibrium conformation

of four-membered and unsaturated five-membered rings is determined by two major opposing forces. The first is the ring strain, which tends to keep the ring skeleton planar. Puckering the ring decreases the already strained angles, thereby increasing the angle strain. The second is the torsional forces. The torsional repulsions of adjacent groups are at a maximum for a planar ring since the groups are eclipsed; therefore, bending the ring out of the plane will reduce these repulsive forces. It is the delicate balance between these two large forces that determines the ground-state structure of the molecule.

A single substituent on the cyclobutane ring leads to conformational isomers and introduces asymmetry into the potential function for ring inversion. As the ring inverts, the substituent goes from the axial conformation to the equatorial, or vice versa. These two conformations will of course have different energies and the spectra can be interpreted using a potential function of the form

$$V(x) = ax^4 - bx^2 - cx^3$$

where x is the coordinate of the ring inversion. The cubic term is added to the usual quartic-harmonic potential function because of the asymmetry.

The results for chlorocyclobutane will be used as an example of the utility of far-infrared spectra of the gas for the investigation of ring puckering motions. The far-infrared and Raman spectra of gaseous chlorocyclobutane in the region of the ring puckering fundamental are shown in **Figure 3**. From the far-infrared spectrum, this fundamental is observed as well-defined Q branches occurring at 157.55 , 149.29 , 139.81 , 130.12 and 128.08 cm^{-1} with additional, weaker Q branches at 116.46 , 115.69 , 111.46 and 110.88 cm^{-1} . The first four pronounced Q branches appear to form a reasonable series and are assigned as the first four transitions of the ring puckering mode for the more stable

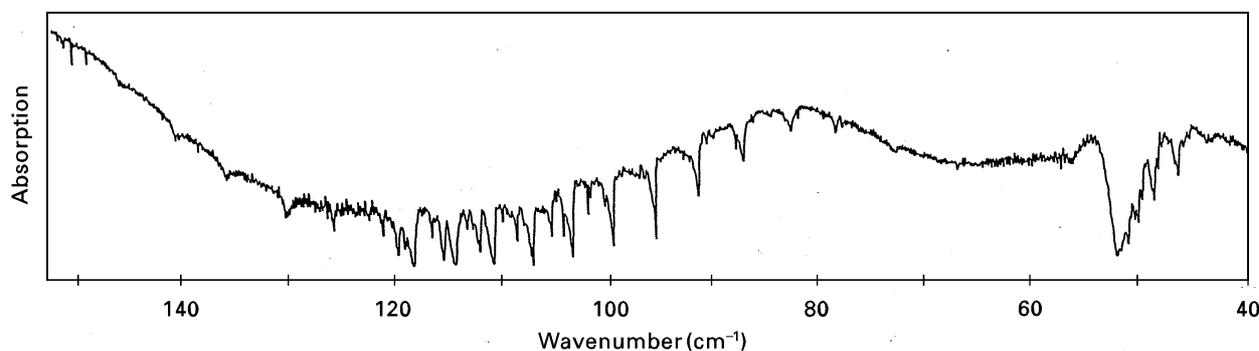


Figure 2 Far-infrared spectrum of fluoroacetyl fluoride, FCH_2CFO .

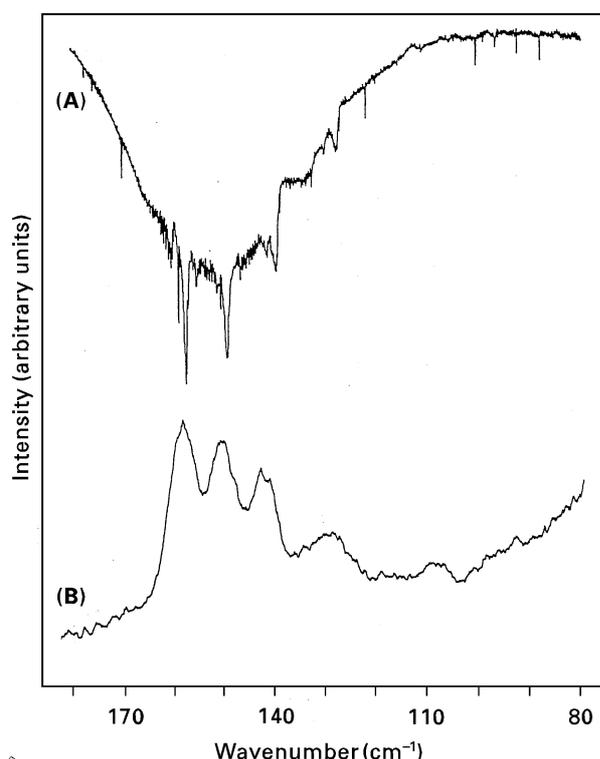


Figure 3 (A) Far-infrared transmission spectrum of chlorocyclopropane; (B) Raman spectrum of gaseous chlorocyclobutane.

equatorial conformer. From the Raman spectrum, the ring puckering fundamental is observed as a weak series of Q branches beginning at $\sim 158\text{ cm}^{-1}$. Although the fundamental for the axial form can be assigned at 128 cm^{-1} in this Raman spectrum, the 128.08 cm^{-1} Q branch observed in the infrared spectrum is far more definitive.

With these assignments, the potential function governing ring inversion can be calculated with the aforementioned function. The function calculated using this assignment is shown in **Figure 4**. This potential is consistent with an energy difference between the equatorial and axial conformers of 449 cm^{-1} ($1.28\text{ kcal mol}^{-1}$) and a barrier to ring inversion of 827 cm^{-1} ($2.36\text{ kcal mol}^{-1}$). Although the uncertainty in the puckering angles determined at the minima is directly related to the uncertainty in the assumed reduced mass (198 amu), as well as the nature of the molecular motion involved, this potential gives puckering angles of 22° for the equatorial form and 17° for the axial conformer. From the *ab initio* calculations utilizing the 6-31G* basis set, the values for these angles are 25.1° and 20.3° , respectively, indicating that the difference in the two angles should be about 5° , which is the value obtained from the potential function.

In five-membered ring molecules, there are two low-frequency out-of-plane ring motions. These are

usually qualitatively described as the ring-twisting (radial mode) and the ring-puckering (pseudorotational mode) motions. Initially, in order to handle the interpretation of the low-frequency far-infrared data, assumptions were made about the forms of these normal vibrations. If the five-membered ring contains an endocyclic double bond, it has usually been assumed that there is no interaction between the 'high'-frequency ring-twisting mode, which falls around 400 cm^{-1} and the 'low'-frequency ring-puckering mode, which is near 100 cm^{-1} . Therefore, the two out-of-plane ring modes are handled as two one-dimensional problems with the anharmonic, low-frequency ring-puckering transitions interpreted in terms of a one-dimensional potential function of the form $V(x) = ax^4 \pm bx^2$. In recent years it has become increasingly clear that while a one-dimensional model of the ring-puckering motion yields reasonably good barrier height values, it does not allow for the interactions with other vibrational modes, which may often be significant.

Some of the most recent advances in the determination of potential surfaces governing ring inversions in four- and five-membered ring molecules have been in the development of two- and three-dimensional models. Such models then allow for the interaction of the ring puckering mode with other vibrational modes. These interactions have been shown to alter the puckering levels in the excited states of interacting motions and, if neglected, can result in poorly calculated barrier heights and misinterpretation of the far-infrared and Raman spectral features arising from the modes involved.

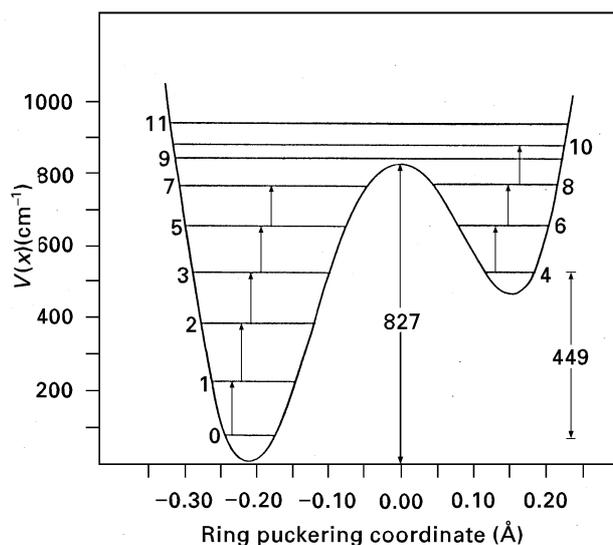


Figure 4 Potential function governing the conformational interchange for axial and equatorial chlorocyclobutane.

Skeletal bending nodes

The third type of low-frequency vibration is heavy-atom skeletal bending modes. Because the vibrations are of very low wavenumbers, there are frequently many excited states populated. Accordingly, the infrared contours in the gas phase can be very complex. In fact, many of these vibrations show a large number of excited states and the band contours are difficult to analyse because of the many vibrational-rotational transitions falling on top of each other. Attention to these types of vibrational modes has been fairly limited.

Gases, liquids and solids

Another type of absorption in the low-wavenumber range is due to the pure rotation of small molecules. The intensity of this type of absorption is frequently 10^4 times that of a low-wavenumber vibration, so very small amounts of HF, HCl, HBr, H₂O (see **Figure 1**) or other similar impurities result in relatively strong absorption from these molecules. This type of far-infrared absorption was studied extensively from the 1930s to the 1960s. The high-resolution infrared data obtained for these molecules made it possible to determine very accurate centrifugal distortional constants.

Only limited studies have been carried out on the far-infrared absorption of molecules in the liquid state, which results in generalized absorption in the region of 30–80 cm⁻¹. However, if the molecule contains hydrogen bonding, a significant amount of information can be obtained for the low-wavenumber vibrations resulting from the absorption of dimers of such molecules. These include the wavenumber for the X··H–Y stretching and bending.

Physicists have primarily carried out the spectroscopic study of solids in the far-infrared spectral region. A major exception to this generalization is the study of the lattice modes of molecular crystals. To account for the lattice (phonon) modes of solids, the Bravais space cell is used by molecular spectroscopists to obtain the irreducible representation for the lattice vibrations. The crystallographic unit cell may be identical with the Bravais cell or it may be larger by a multiple of 2, 3 or 4. The relationship between the Bravais cell and crystallographic cell can be obtained from the Hermann–Mauguin X-ray symbol that is used to designate the crystal symmetry. For all crystal structures designated by a symbol *P* (primitive), the crystallographic unit cell and the Bravais unit cell are identical. Crystal structures designated with capital letters A, B, C or I are double primitive and, therefore, the crystallographic unit

cells contain two Bravais cells. Crystal structures designated with the letters R or F are triply and quadruply primitive, respectively, and the crystallographic unit cells contain three and four Bravais cells, respectively.

The potential energy of a crystal can be considered to be made up of the following terms: $V_{\text{Total}} = \sum_j V_j + \sum_i \sum_j V_{ij} + V_L + V_{Lj}$ where V_j is the potential due to the internal coordinates, V_{ij} is the potential due to the correlation field, V_L is the potential for the external degrees of freedom and V_{Lj} represents the potential due to the interaction of the internal modes with the lattice modes. Three symmetries must be considered when studying the vibrational spectrum of a crystal: the molecular symmetry, the site symmetry, and the factor group symmetry. The factor group is not a point group but it is isomorphous with the space group, which means there is a one-to-one correspondence between the two.

Oxamide (OCNH₂)₂ will be used as an example of the determination of the frequency of lattice modes. This molecule has molecular symmetry *trans* C_{2h} with space group *P1*. Oxamide has one molecule per unit cell so there are three acoustical translations, which are inactive, and three optical librations, which are only Raman active. The three lattice bands are very prominent features in the Raman spectrum and occur at 106, 134, 157 cm⁻¹ (**Figure 5**) with corresponding bands at 100, 137, 156 cm⁻¹ for the deuterated compound. An estimate of the range for the force constant of the librations can be calculated associating the highest torsional wavenumber with the largest moment of inertia and the lowest wavenumber with the smallest moment of inertia. The widest possible range for the force constant is found to be 0.14 to 0.79 mdyne Å⁻¹. These values are relatively large for librational force constants and they reflect a high degree of hydrogen bonding for this compound.

For molecular crystals in which the molecules are nearly spherical there will frequently be a high-temperature crystal phase of which the site symmetry is higher than the molecular symmetry. These crystals are referred to as plastic crystals and they have unusual properties such as very high temperatures of melting and low anisotropic properties similar to those of liquids. The theory of lattice vibrations of orientationally disordered solids has been addressed, and the results indicate that such disorder should lead to a broadening of the vibrational bands and that all modes may be active in both the infrared and Raman spectra. Spectra of this type are referred to as density-of-states spectra, since the bands correspond to the flat points in the dispersion curve.

Ionic crystals are the other type of solid that has been studied extensively in the low-wavenumber

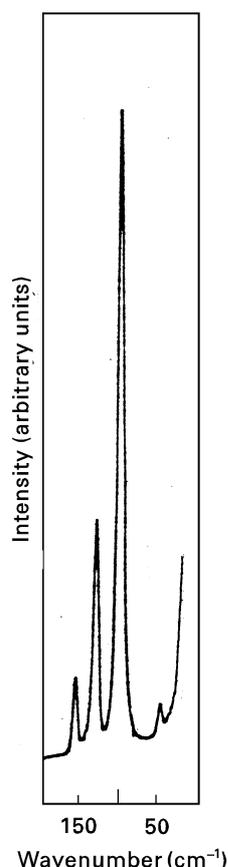


Figure 5 Optical librational modes of oxamide.

spectral range. Of particular interests have been ferroelectrics, where one of the modes can shift from 150 cm^{-1} to nearly zero as the transition temperature is approached.

List of symbols

h = Planck constant; I_r = reduced moment of inertia; $V(x)$ = potential for conformational change; V_n = height of n -fold rotational barrier; $V(\phi)$ = potential

for rotation; x = coordinate of ring inversion; ϕ = rotation angle.

See also: IR Spectrometers; IR Spectroscopy, Theory.

Further reading

- Carreira LA, Lord RC and Malloy TB Jr (1979) In: Eliel EL and Allinger NL (eds) *Topics in Current Chemistry*, Vol 82, pp 1–95. Berlin: Springer-Verlag.
- Chantry GW (1971) *Submillimetre Spectroscopy; A Guide to the Theoretical and Experimental Physics of the Far Infrared*. London: Academic Press.
- Compton DAC (1981) In: Durig JR (ed) *Vibrational Spectra and Structure*, Vol 9, pp 255–404. Amsterdam: Elsevier.
- Durig JR and Cox AW (1978) In: Ferraro JR and Basile LJ (eds) *Fourier Transform Infrared Spectroscopy*, Vol 1, pp 215–274. London: Academic Press.
- Groner P, Sullivan JF and Durig JR (1981) In: Durig JR (ed) *Vibrational Spectra and Structure*, Vol 9, pp 405–487. Amsterdam: Elsevier.
- Hehre WJ, Radom L, Schleyer PVR and Pople JA (1986) *Ab Initio Molecular Orbital Theory*. New York: Wiley.
- Killough PM, Irwin RM and Laane JJ (1982) *Journal of Chemical Physics* **76**: 3890.
- Martin DH (ed) *Spectroscopic Techniques for Far Infrared, Submillimetre and Millimetre Waves*. Amsterdam: North-Holland.
- Mitra SS and Nudelman S (eds), *Far Infrared Properties of Solids*. New York: Plenum Press.
- Möller KD and Rothschild WG (1971) *Far Infrared Spectroscopy*. New York: Wiley-Interscience.
- Palik ED (1960) A far infrared bibliography. *Journal of the Optical Society of America* **50**: 1329.
- Rounds TC and Strauss HL (1978) In: Durig JR (ed) *Vibrational Spectra and Structure*, Vol 7, pp 238–269. Amsterdam: Elsevier.
- Wurrey CJ, Durig JR and Carreira LA (1976) In: Durig JR (ed) *Vibrational Spectra and Structure*, Vol 5, pp 176–220. Amsterdam: Elsevier.