FAR-INFRARED SPECTROSCOPY

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1. Introduction

This review concerns spectroscopy in the frequency range which lies above that of the microwave region, but below that accessible by prism spectrometers, that is, from about 10 cm.$^{-1}$ to 200 cm.$^{-1}$. Although the spectral region denoted by "far-infrared" is an artificial one in the sense that it has arisen from the limitations of experimental technique rather than as a result of any fundamental characteristics, it is of particular interest because its potentialities have been as yet relatively little exploited. The increasing interest that this region has recently attracted, probably largely owing to improved techniques, has made it an appropriate subject for review. Most of the applications of far-infrared spectroscopy are not different in kind from those of the neighbouring regions of the spectrum, particularly the ordinary infrared. However, certain features become increasingly pronounced in the far-infrared region, and these have been given more attention in this account. The distinction between chemical and physical applications is rather arbitrary, and with time the physical applications usually pass into the hands of chemists. For this reason, a number of applications which are at present mainly physical, *e.g.*, cyclotron resonance, are included in the review.

A large part of the far-infrared frequency range is also accessible by Raman spectroscopy, but this does not mean that either technique is redundant. As is well known, although the energy levels concerned are the same in both cases, the selection rules governing transitions between these levels are different. Even when no symmetry considerations are involved, so that in principle all transitions are allowed in both the infrared and Raman spectra, the intensity of a band in the infrared is quite unrelated to that in the Raman spectrum, and it is often possible to record strong bands in the infrared that are weak or undetectable in the Raman spectrum. A further distinction of principle is that polarisation studies in the infrared region require the alignment of the molecules, *e.g.*, in crystals, but with Raman spectroscopy this is unnecessary. There are also distinctions on experimental grounds. A resolution of a few tenths of a cm.$^{-1}$ is quite easily achieved in the far-infrared region, this being much better than can usually be obtained in Raman work. Far-infrared spectroscopy can also be applied with ease to all forms of material—gas, liquid, solution, plastic, crystal, or mull—while low-frequency Raman work on gases or solids is distinctly difficult. Fluorescence, absorption in the visible region, and photolysis can also be troublesome in Raman work, but do not interfere in far-infrared spectroscopy. As a consequence of such considerations, many new applications in the field of low-frequency spectroscopy are introduced by the use of infrared techniques.

Two limitations should be added to complete this comparison. Firstly, analytical use of far-infrared spectroscopy, at least quantitatively, is premature. Secondly, water and certainly some other hydroxylic solvents, such as glycerol, are quite opaque in some parts of the far-infrared region.

A fairly complete survey of the relevant literature, covering the period up to July 1962, has been made. This task was made much easier by the publication by Palik of an exhaustive bibliography of the subject up to the beginning of 1960.[1] As the subject is developing quite rapidly, no very strenuous effort was made to add "stop-press" results, but occasionally a few papers which appeared after July 1962 have been included.

Excellent reviews of several branches of infrared spectroscopy have appeared in the last few years and readers will be particularly interested in one of these which deals with the far-infrared region.[2]

2. Technique

(a) Sources.—The major experimental difficulty in far-infrared spectroscopy is that there are no suitable sources. The peak of the radiation intensity of a black body is at a frequency $\nu(\text{cm.}^{-1}) = 3{\cdot}45T$ (°K). Thus a black-body source with peak intensity at 100 cm.$^{-1}$ would be at 29°K, and at this temperature the maximum intensity, proportional to T^5, would be negligible. The only practical possibility is to use a source at a much higher temperature (usually *ca.* 1300°K) which gives greater intensity in the far-infrared region, at the expense of even more greatly increased intensity in the high-frequency range. The removal of the higher-frequency radiation, which would appear in the higher orders diffracted from a grating, is a severe filtering problem. For example, with a black-body source at 1300°K, the power reaching the detector in the sixth order will be 161 times that in the first order when working near the blaze of an ideal echelette grating.[3] At present, the source giving the best relative far-infrared/infrared output appears to be the fused-quartz mercury lamp. This is better than a globar below 150 cm.$^{-1}$ [4] or 100 cm.$^{-1}$ [5] (depending on the temperature of operation?). The radiation is mostly emitted by the envelope above 35 cm.$^{-1}$ and by the arc at lower frequencies.[6] It seems probable that, as a source of far-infrared radiation, the mercury lamp, which has not been designed for this purpose, could be greatly improved.

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[1] Palik, *J. Opt. Soc. Amer.*, 1960, **50**, 1329.

[2] Wilkinson, Inglis, and Smart, "Spectroscopy," Institute of Petroleum, London, 1962, p. 157.

[3] Oetjen, Haynie, Ward, Hansler, Schauwecker, and Bell, *J. Opt., Soc. Amer.*, 1952, **42**, 559.

[4] Plyler, Yates, and Gebbie, *J. Opt. Soc. Amer.*, 1962, **52**, 859.

[5] Perkin-Elmer Corporation, technical brochure.

[6] Genzel and Eckhardt, *Z. Physik*, 1954, **139**, 578.

(b) Monochromator and Detector.—For conditions obtaining in the far-infrared region, where resolution is governed by source energy and detector sensitivity, the design factors have been discussed by Strong.[7] It is desirable to minimise the ratio focal length/slit height.[8] The most suitable monochromator layouts have proved to be the Ebert (Fig. 1) or Czerny–Turner types which have become almost standard. Spherical aberration is minimised by the use of slits which are curved and can therefore be large. Further advantages are that the mirror is spherical and the system compact, thus facilitating evacuation. Until a few years ago, it was necessary to rule ones own far-infrared grating, and wire gratings have even been used in the past.[9] Recently, however, high-quality replica echelette gratings have become available from Messrs. Bausch and Lomb. The production of replica gratings for the far-infrared region is also under development at the National Physical Laboratory, Teddington (Light Division).

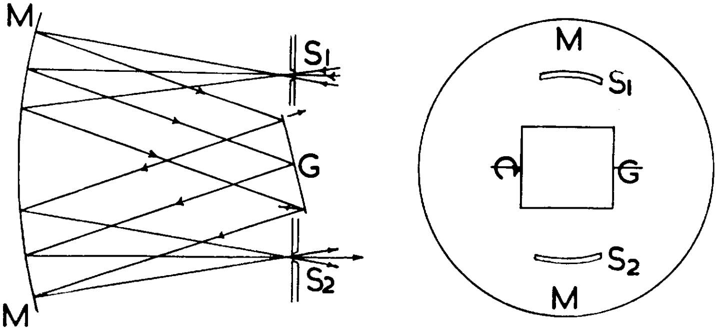

FIG. 1. *Plan and end-view of Ebert monochromator;* S_1 *and* S_2 *are slits,* G *is the grating, and* M *is the mirror.*

Golay pneumatic detectors[10] are used most frequently. These are compact and may be placed in a vacuum, and have the further advantage that the direction, focusing, and frequency of the radiation entering the window (*ca.* 3 mm. × 3 mm.) is not critical. A major optical problem is that of condensing the slit image on to the detector. Condensation has been effected by combinations of various devices; beam slicers,[8] axial[8] and off-axis[3] mirror systems, and light guides[11] have been found useful. The problem has been eased by the development of Golay detectors with larger, slit-shaped windows.[12] The noise in the detector can be greatly reduced by using detectors cooled to low temperatures, and for the lowest frequencies a superconducting bolometer has been recommended.[11]

[7] Strong, *J. Opt. Soc. Amer.*, 1949, **39**, 320.

[8] Robinson, *J. Opt. Soc. Amer.*, 1959, **49**, 966.

[9] Barnes, *Rev. Sci. Instr.*, 1934, **5**, 237.

[10] Golay, *J. Opt. Soc. Amer.*, 1951, **41**, 468.

[11] Bloon, Dean, Jones, Martin, Mawer, and Perry, *Proc. Roy. Soc.*, 1961, *A*, **260**, 510.

[12] Golay detectors are manufactured by Messrs. Eppley Laboratories Inc., Newport, R.I. (U.S.A.) and by Unicam Limited, Cambridge (U.K.).

A rough vacuum of 10^{-2} mm. throughout the instrument is sufficient to remove the water-vapour lines almost completely. Flushing with "dry" gas is never very satisfactory.

(c) **Filters.**—There is still a wide variation in the choice of filters, and combinations of two or three of those listed in the Table are usually used.

Filters.

Type	Material	Ref.
Transmission	Black polythene (polythene with added graphite)	13
	Polythene and powdered crystal*	14
	Crystal quartz	11
Christiansen†		15, 16
Reflection	Single reststrahlen‡	17
	Two reststrahlen with "crossed" polarisation§	18
	Roughened Al plate	11
	Scatter grating	19
Transmission chopper‖	Crystal opaque in far-infrared region, clear at higher frequencies	20

* Performance improves with finer powder size. Absorption by particles appears to be more important than Christiansen effect. † Far-infrared performance reported is not very encouraging. ‡ Performance improves on cooling and is sensitive to polarisation. § About 2-fold improvement over two uncrossed reststrahlen. ‖The subject of choppers based on selective reflection does not seem to have been explored.

As the filtering performance depends on a wide variety of factors, *e.g.*, thickness, surface polish, and polarisation, the reader is referred to the references for these details. It should be appreciated that, in the higher part of the frequency range, the water-vapour spectrum is a poor test of filtering, as the intensities of higher-frequency water bands are too low; chloroform, with strong bands at 260 and 364 cm.$^{-1}$, provides a more critical test of the presence of the second order. Data obtained by using only a series of filters without a grating monochromator have, in the past, often proved unreliable.

(d) **Calibration.**—The water-vapour spectrum provides a very suitable and convenient means of calibration.[21] Accurate rotational energy levels of water have been tabulated[22] and these may be used as the basis of the calibration.[23]

The spectrometers recently constructed by Genzel and Eckhardt,[6]

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[13] Plyler and Blaine, *J. Res. Nat. Bur. Stand.*, 1960, *C*, **64**, 55.
[14] Yoshinaga, *J. Opt. Soc. Amer.*, 1962, **52**, 17.
[15] Hadni, *J. Phys. Radium*, 1954, **15**, 375.
[16] Barnes and Bonner, *Phys. Rev.*, 1936, **49**, 732.
[17] Yoshinaga, *J. Opt. Soc. Amer.*, 1962, **52**, 14.
[18] Mitsuishi, Yamada, Fujita, and Yoshinaga, *J. Opt. Soc. Amer.*, 1960, **50**, 433.
[19] White, *J. Opt. Soc. Amer.*, 1947, **37**, 713.
[20] Lord and McGubbin, *J. Opt. Soc. Amer.*, 1957, **47**, 689.
[21] Yaroslavskii and Stanevich, *Optika i Spektroskopiya*, 1958, **5**, 384.
[22] Benedict, Claassen, and Shaw, *J. Res. Nat. Bur. Stand.*, 1952, **49**, 91.
[23] Blaine, Plyler, and Benedict, *J. Res Nat. Bur. Stand.*, 9162, *A*, **66**, 223.

Yoshinaga *et al.*,[24] and Yaroslavskii *et al.*[25] demonstrate the excellent performance which can now be achieved by utilising the methods described here.

(e) **Other Methods.**—The most notable alternative method that has been developed to obtain far-infrared spectra is that of interferometry. A lamellar grating[26] or a thin film[27] divides the beam from the source into two parts which reach the detector by paths of different length. The signal received, $F(x)$, is related to the spectrum of the source, $E(\nu)$, by:

$$F(x) = \int_{0}^{\infty} E(\nu)\cos 2\pi\nu x \, \mathrm{d}\nu$$

where x is the path difference. $E(\nu)$ is obtained from $F(x)$ by use of a computer. The resolution, which is determined by the maximum path difference, is comparable with that achieved in grating spectrometers. A number of spectra have been obtained by this method,[28,29] which has the advantage of covering a wide frequency range (*e.g.*, 20—400 cm.$^{-1}$) continuously. A notable application has been the observation of the emission spectrum of ammonia.[29] It is difficult, however, to assess from the literature how the performance and reliability compares with that of grating spectrometers. A commercial far-infrared interferometer has been recently marketed.[30]

(f) **Sample Handling.**—Ordinary low-density polythene has no strong bands in the far-infrared region and is the most widely used window material. Contamination can be avoided by always using new windows. When rigidity is important, crystal-quartz windows can be used (below *ca.*150 cm.$^{-1}$). Interference effects, arising from reflection at window surfaces, can be marked and are minimised by using as "background" for comparision a run with a smaller amount of the same sample.

Gases, liquids, and plastics present little difficulty. Solids can be examined in Nujol mulls, or embedded in polythene. Although in itself Nujol or polythene is not troublesome, there may be Christiansen filter effects. The spectra are, of course, those of the entire lattice, and unless there is particular interest in the solid state, alternative methods are to be recommended. Many solvents are fairly clear below 200 cm.$^{-1}$, *e.g.*, benzene, n-hexane, carbon tetrachloride, chloroform, and carbon disul-

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[24] Yoshinaga, Fujita, Minami, Mitsuishi, Oetjen, and Yamada, *J. Opt. Soc. Amer.*, 1958, **48**, 315.

[25] Yaroslavskii, Zheludov, and Stanevich, *Optika i Spektroskopiya*, 1956, **1**, 507.

[26] Strong and Vanasse, *J. Opt. Soc. Amer.*, 1960, **50**, 113.

[27] Gebbie, *J. Phys. Radium*, 1958, **19**, 230.

[28] Genzel, *J. Mol. Spectroscopy*, 1960, **4**, 241; Loewenstein, *J. Opt. Soc. Amer.*, 1960, **50**, 1163; 1961, **51**, 108.

[29] Gebbie, unpublished results.

[30] Messrs. Grubb-Parsons, Walkergate, Newcastle-on-Tyne (U.K.).

phide.[31] Solvents with high dielectric constant, useful for ionic species, are acetonitrile and *N*-methylformamide, but water has poor transmission. The "matrix isolation" method,[32] in which the species to be examined is trapped as a dilute solid solution in an inert-gas matrix at low temperature, appears to be particularly promising for use with far-infrared spectroscopy. Internal rotation in the formic acid monomer has been studied in this way.[33] It is experimentally easier to examine single crystals by reflection than by transmission. The reflection data can then be converted to obtain the transmission spectra,[34] but there is less margin for error if the latter are observed directly. Polarisation can be studied using a polariser consisting of a pile of polythene films which gives 75% transmission and a 97% polarised beam.[18] It should be remembered that dispersion by the grating alone appreciably polarises the beam in grating monochromators.

(g) **New Developments.**—The technique of far-infrared spectroscopy would be revolutionised by the availability of either a tunable monochromatic radiation source or of a tunable selective detector. Prototypes of both devices have been described in the *New Scientist* in the past year.[35] The source produces radiation by shooting an electron beam over a charged metallic grating and is tuned by varying the beam velocity. The detector, a cooled InSb semiconductor in a strong magnetic field, is based on the cyclotron-resonance principle (q.v.). The radiation frequency to which the device is sensitive is determined by the strength of the magnetic field.

Both devices are in the development stage and are, at present, probably more difficult to operate than a "conventional" far-infrared spectrometer.

3. General Effects

In this section some general effects are described with particular reference to their relevance at low frequencies.

(a) **The Boltzmann Factor.**—The ratio of the numbers of molecules in two levels, of energy ϵ_1 and ϵ_2, is given by the Boltzmann expression

$$\frac{n_2}{n_1} = \frac{w_2}{w_1} e^{-(\epsilon_2-\epsilon_1)/kT}$$

where w_1 and w_2 are the degeneracies of the levels. For a vibration, $w_1 = w_2$ and $n_2/n_1 = e^{-(h\nu/kT)}$, where ν is the frequency, so that at room temperature $h\nu/kT = 1$ when $\nu = 209$ cm.$^{-1}$, and $h\nu/kT = 0{\cdot}478$ when $\nu = 100$ cm.$^{-1}$. Consequently, for low frequencies the numbers of molecules in upper vibrational levels are far from negligible. "Hot bands"—transitions originating from these levels—will be of appreciable intensity, and as low-

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[31] Stanevich and Yaroslavskii, *Optika i Spektroskopiya*, 1961, **11**, 31.

[32] Pimental, *J. Chem. Phys.*, 1956, **25**, 224; 1958, **29**, 1405.

[33] Pitzer, *J. Chem. Phys.*, 1959, **30**, 1076.

[34] Wilkinson, Price, and Bradbury, *Spectrochim. Acta*, 1959, **14**, 284.

[35] *New Scientist*, p. 68 (July 12, 1962) *ibid.*, p. 442 (November 22, 1962).

frequency vibrations are often markedly anharmonic, the bands may be displaced appreciably (as much as 88 cm.$^{-1}$ in hydrazine[36]) from the position of the ground-state band. The hot bands may be separately resolved[36] or may fuse into the contour of the ground-state band.[37] Difference bands which involve a decrease in the energy of a low-frequency vibration will be strong by the same token.

(b) Sum Rules.—The vibration frequencies, ν_i, of isotopic molecules obey a series of rules relating to the sums over the frequencies:

$$\sum_i \lambda_i, \quad \sum_{i,j} \lambda_i \lambda_j, \quad \sum_{i,j,k} \lambda_i \lambda_j \lambda_k, \text{ etc.}$$

where $\lambda_i = 4\pi^2\nu_i^2$.[38] For the application of these rules, *all* the vibration frequencies (corrected for anharmonicity) of the molecules must be known. The sums are rather insensitive to the values of the low frequencies, and it is more important to correct for the anharmonicity of the dominating high frequencies. The Teller–Redlich product-rule,[39] relating to $\Pi_i\lambda_i$, is the most sensitive to the low frequencies, but is still dominated by the higher frequencies. These rules are thus of little use for checking the assignment of low frequencies, although when the molecules possess symmetry the rules may be more helpful if applied to each vibrational symmetry species separately.

(c) Thermodynamic Functions.—The contributions of a normal vibration frequency to the free energy, F, and heat content, E, of a molecule in the ideal-gas state are given by:

$$(F - E_0)/T = \boldsymbol{R}\ln(1 - e^{-x})$$

$$(E - E_0)/T = \boldsymbol{R}xe^{-x}/(1 - e^{-x}) \quad (x = \boldsymbol{h}\nu/\boldsymbol{k}T)$$

The entropy, S, is given by $S = (E - F)/T$. To calculate thermodynamic functions for the molecule, contributions summed over all the normal vibrations are added to the rotational and translational contributions. Low frequencies give rise to the largest vibrational contributions at room temperature, and the effect is marked. For example, from tables,[40] one finds

$T = 300°\text{K}$	$(E - E_0)/T$	$-(F - E_0)/T$
$\nu = 100$ cm.$^{-1}$	1·5484	1·9180
$\nu = 1000$ cm.$^{-1}$	0·0796	0·0164

so that the assignment of the medium and high frequencies is of very little

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[36] Yamaguchi, Ichishima, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1959, **31**, 843.

[37] Danti and Wood, *J. Chem. Phys.*, 1959, **30**, 582.

[38] Heicklen, *J. Chem. Phys.*, 1962, **36**, 721; Sverdlov, *Optika i Spektroskopiya*, 1960, **8**, 17.

[39] Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, New York, 1945, p. 231.

[40] Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand, New York, 1942, 3rd edn., vol. 1, appendix, 1.

importance compared to that of the low frequency modes in computing thermodynamic values. The above expressions relate to a harmonic oscillator; anharmonicity changes the vibrational energy levels, and consequently the contributions. Anharmonicity is particularly large in a torsional-type vibration, and the contributions to the thermodynamic functions have been tabulated in the form of corrections to the free internal rotor contribution.[41]

4. Applications

The applications of far-infrared spectroscopy will now be discussed, commencing with the spectra of isolated molecules, *i.e.*, those in the gaseous state, and dealing first with rotation and then with vibration. Whenever the motion is primarily intramolecular, the spectra will also be included in this section. Subsequent sections will deal with specific phenomena that arise in the liquid and crystalline states as a result of the intermolecular interactions present in these phases.

(a) **Pure Rotation.**—Molecules containing only a single non-hydrogen atom have small moments of inertia, and so the rotation spectrum lies largely in the far-infrared rather than the microwave region. Such molecules will be dealt with first.

Pure rotation spectra usually consist of a number of quite sharply defined "lines", and so display the performance of far-infrared spectrometers to best advantage. Notable technical advances thus demonstrated were the detailed water-vapour spectrum recorded down to 74 cm.$^{-1}$ by Randall *et al.*[42] in 1937 and, more recently, observation of the water-vapour line at 5·6 cm.$^{-1}$ by Yaroslavskii and Stanevich.[43]

The pure rotation spectrum of atmospheric water is often an unwelcome imprint superimposed on far-infrared spectra, and not surprisingly was the first rotation spectrum investigated in detail.[42] The three moments of inertia of H_2O are all unequal, and as a result the spectrum is complex. Using moments of inertia obtained from vibration–rotation spectra, some of the lines which arise from the lower rotational energy levels were identified from their position and intensity. A semi-empirical correction for centrifugal distortion, based on the lower energy levels, was extended to the higher levels, where the correction may be 20%, and a most satisfactory account of the entire spectrum was obtained. Soon afterwards, D_2O was similarly treated.[44] The H_2O rotational spectrum has since been extended to lower and higher frequencies[43] and the energy levels have been tabulated.[22] Centrifugal-distortion theory has also been more fully de-

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[41] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

[42] Randall, Dennison, Ginsburg, and Weber, *Phys. Rev.*, 1937, **52**, 160.

[43] Yaroslavskii and Stanevich, *Optika i Spektroskopiya*, 1959, **6**, 799; **7**, 621.

[44] Fuson, Randall, and Dennison, *Phys. Rev.*, 1939, **56**, 982.

developed.[45] H_2S[46] and H_2Se[47] have been treated in a similar manner, the three moments of inertia obtained from a best fit agreeing with the more accurate microwave values.[48]

The pure rotation spectra of the chlorides, bromides, and iodides of hydrogen and deuterium have been recorded[49] and the equilibrium bond lengths are found to agree with the more accurate values obtainable from vibration–rotation spectra.[50] Good agreement with the calculated centrifugal-distortion correction is also found.[49b] The rotation spectrum of ammonia was investigated as early as 1929,[51] and later in more detail[52] together with those of NH_2D,[53] NHD_2,[53] ND_3,[54] PH_3,[55] PH_2D,[56] PHD_2,[56] PD_3,[55] AsH_3,[55] and AsD_3.[55] The dimensions obtained from the rotational constants agree, within experimental accuracy, with the microwave values.

The splitting of the NH_3 lines due to inversion, predicted from the vibration spectrum by Dennison,[52d] was observed by Wright and Randall in 1933.[52a] The potential energy for the symmetrical bending has a double minimum (Fig. 2). Quantum-mechanical tunnelling splits the zero (and higher) vibrational energy levels into two. The rotational levels of the ground vibrational state are similarly split,[57] the wave functions of these levels being either symmetric (+) or antisymmetric (—) to reflection in the HHH plane. As the selection rule in the rotation spectrum is $+ \rightleftharpoons -$, the pure rotation lines show twice the splitting of the zero vibrational level ($2\Delta E \simeq 1{\cdot}38$ cm.$^{-1}$).[52c] It is found from the microwave spectrum[58] that the splitting is not constant but depends somewhat on the rotational quantum numbers J and K, and this effect is noticeable in the higher-frequency rotation bands.[49b,59]

The low-frequency rotation lines of molecules containing two or more heavy atoms lie in the microwave region, but the higher-frequency lines, lying in the far-infrared region, have been observed in HCN,[60] CO,[61]

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[45] Polo, *Canad. J. Phys.*, 1957, **35**, 880.

[46] Genzel, *Z. Physik*, 1956, **144**, 311.

[47] Palik and Oetjen, *J. Mol. Spectroscopy*, 1957, **1**, 223.

[48] Bird and Townes, *Phys. Rev.*, 1954, **94**, 1203; Veselago, *Izvest. Akad. Nauk, S.S.S.R.*, Ser. Fiz., 1958, **22**, 1150.

[49] (*a*) Palik, *J. Chem. Phys.*, 1955, **23**, 217; Czerny, *Z. Physik*, 1925, **34**, 227; McCubbin, *J. Chem. Phys.*, 1952, **20**, 668; (*b*) Hansler and Oetjen, *J. Chem. Phys.*, 1953, **21**, 1340.

[50] Mills, Thompson, and Williams, *Proc. Roy. Soc.*, 1953, *A*, 218, 29; Pickworth and Thompson, *Proc. Roy. Soc.*, 1953, *A*, **218**, 37; Keller and Nielsen, *J. Chem. Phys.*, 1954, **22**, 294.

[51] Badger and Cartwright, *Phys. Rev.*, 1929, **33**, 692.

[52] (*a*) Wright and Randall, *Phys. Rev.*, 1933, **44**, 391; (*b*) Foley and Randall, *ibid.*, 1941, **59**, 171; (*c*) Genzel, *Z. Physik*, 1956, **144**, 311; (*d*) Dennison and Hardy, *Phys, Rev.*, 1932, **39**, 938.

[53] Palik and Bell, *J. Chem. Phys.*, 1957, **26**, 1093.

[54] Stroup, Oetjen, and Bell, *J. Chem. Phys.*, 1953, **21**, 2072.

[55] Stroup, Oetjen, and Bell, *J. Opt. Soc. Amer.*, 1953, **43**, 1096.

[56] Stroup and Oetjen, *J. Chem. Phys.*, 1953, **21**, 2092.

[57] Ref. 39, p. 222.

[58] Good, *Phys. Rev.*, 1946, **70**, 213.

[59] Hadni, *Spectrochim. Acta*, 1956, **11**, 632.

[60] Genzel and Eckhardt, *Z. Physik*, 1954, **139**, 592; Williams, *J. Opt. Soc. Amer.*, 1960, **50**, 1159.

[61] Palik and Rao, *J. Chem. Phys.*, 1956, **25**, 1174.

NO,[61] N_2O,[61] MeCN,[62] MeC≡CH,[62] HCF_3,[62] Me_3N,[62] MeF,[63] MeCl,[63] MeBr,[63] and MeI.[63] All these molecules are symmetrical tops, but the resolution is insufficient to display all the expected features.[64] The almost symmetrical tops NO_2,[65] O_3,[66] and SO_2[66] give spectra composed of well-spaced Q branches ($\Delta J = 0$). The MeOH rotation spectrum shows the effects of torsion about the C–O bond, and a very thorough treatment[67] gives a torsion barrier of 1·07 kcal., and also shows that the barrier potential is a cosine to ± 1%. In all cases the spectra are in accord with the available microwave data which give more accurate values of molecular parameters. Interest in infrared pure rotation spectra therefore lies largely in centrifugal-distortion effects which increase more than linearly with J and possibly in Coriolis coupling and pressure-broadening effects.

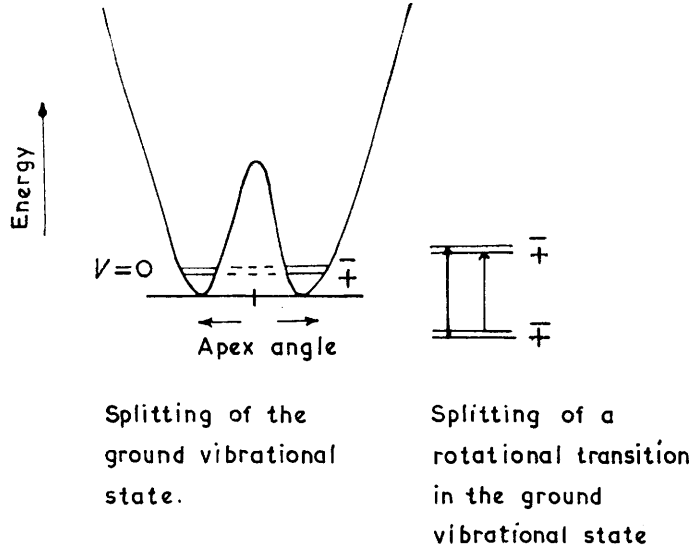

FIG. 2. *Inversion splitting of the rotational energy levels of* NH_3.

(b) Intramolecular Vibrations.—The fundamental vibration frequency of a harmonic oscillator is equal to $1/2\pi\sqrt{k/\mu}$ where k, the force constant, is the restoring force per unit displacement, and μ is the effective mass. Most bond-stretching valence force constants lie in the range from about 2×10^5 to 1×10^6 dyne cm.$^{-1}$, so that only bonds linking very heavy atoms give rise to stretching frequencies below 200 cm.$^{-1}$. The I_2 stretching frequency, normally inactive in the infrared region, can be activated by the

[62] Robinson and McQuarrie, *J. Chem. Phys.*, 1960, **32**, 556.
[63] Palik and Rao, *J. Chem. Phys.*, 1957, **26**, 1401.
[64] Ref. 39, p. 400.
[65] Bird, Danti, and Lord, *Spectrochim. Acta*, 1958, **12**, 247.
[66] Danti and Lord, *J. Chem. Phys.*, 1959, **30**, 1310.
[67] Burkhard and Dennison, *J. Mol. Spectroscopy*, 1959, **3**, 299.

environment in solution, and has been observed[68] at 174 cm.$^{-1}$ in pyridine solution.

Bending valence force constants are usually about one-tenth the magnitude of stretching force constants, and consequently the bending frequencies of a molecular skeleton of heavy atoms often lie in the far-infrared region. An interesting early attempt to observe such molecular vibration bands in the infrared region was that of Strong and Woo[69] in 1932. Gaseous samples of $CHCl_3$ and of $CH_3{\cdot}CHO$ were examined, but the results were rather inconclusive as the monochromatic radiation was obtained by filtering alone. More recently, the bending frequencies of many halogen compounds have been observed in the 100—200 cm.$^{-1}$ range,[70] and often complete assignments of the vibrational fundamentals have been made. Particularly satisfactory accounts of CI_4[71] and of some Group V trihalides[72] have been given. Many of the bending frequencies of co-ordination compounds will lie in the far-infrared region and, although at present few have been reported, this will almost certainly become a major application. $Fe(CO)_5$ has a strong band at 105 cm.$^{-1}$,[73] and iron, cobalt, and nickel acetylacetonates have a strong band at about 100 cm.$^{-1}$.[74] The low-frequency vibrations of polyatomic ions have so far been little investigated, possibly owing to the difficulty of finding satisfactory ionising solvents for use in the far-infrared region, although both acetonitrile[75] and *N*-methylformamide are useful. Spectra of solutions of the ions ICl_2^-, ICl_4^-, $BrCl_2^-$, and Br_3^- have been recorded from 170 cm.$^{-1}$ upwards,[75] and show some marked differences from the spectra in nujol mulls.

An unusual vibration spectrum is found in trimethylene oxide. In the frequency range where the ring-puckering mode is expected, the vapour shows a series of sharp bands with maxima at 89·8, 118·3, 128·9, 147·6, 154·9, and 161·8 cm.$^{-1}$ and of steadily decreasing intensity.[76] These have been interpreted as arising from the unusual nature of the ring-puckering vibration.[77] The puckering of the trimethylene oxide ring (see Fig. 3) can be represented by the co-ordinate z, the distance of the O atom from the C–C–C plane. The microwave spectrum[77] indicates that the potential energy is slightly *higher* when the oxygen is in the plane of the ring than when displaced on either side, and this potential function accounts rather well for the observed spectrum, the individual bands arising from transitions between successive vibrational levels.

[68] Plyler and Mullikan, *J. Amer. Chem. Soc.*, 1959, **81**, 823.

[69] Strong and Woo, *Phys. Rev.*, 1932, **42**, 267.

[70] Miller and Carlson, *Spectrochim Acta*, 1960, **16**, 6; Miller and Baer, *ibid.*, 1961, **17**, 112; Wilmhurst, *J. Mol. Spectroscopy*, 1960 **5**, 343.

[71] Stammreich, Tavares, and Bassi, *Spectrochim, Acta*, 1961, **17**, 661.

[72] Davis and Oetjen, *J. Mol. Spectroscopy*, 1958, **2**, 253.

[73] McDowell and Jones, *J. Chem. Phys.*, 1962, **36**, 3321.

[74] Gillard, Silver, and Wood, *Spectrochim. Acta*, in the press.

[75] Person, Anderson, Fordemwalt, Stammreich, and Forneris, *J. Chem. Phys.*, 1961, **35**, 908.

[76] Danti, Lafferty, and Lord, *J. Chem. Phys.*, 1960, **33**, 294.

[77] Chan, Zinn, and Gwinn, *J. Chem. Phys.*, 1960, **33**, 295.

Change in vibrational level	0→1	1→2	2→3	3→4
Calculated change in energy (cm.$^{-1}$)	70·1	118	126·6	138·7
Change in vibrational level	4→5	5→6	6→7	
Calculated change in energy (cm.$^{-1}$)	147·0	154·7	161·2	

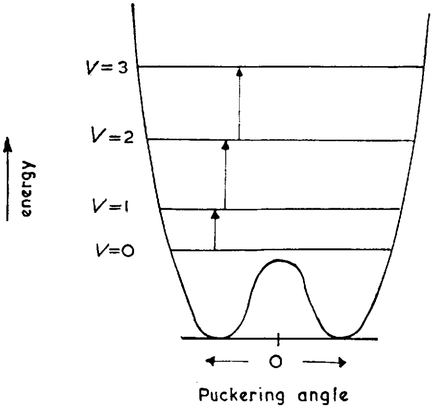

FIG. 3. *The puckering potential energy and vibrational transitions of trimethylene oxide.*

As the walls of the potential well rise more steeply than those of a harmonic oscillator, the higher levels are more widely separated than the lower ones—an unusual occurrence.

(i) *Torsional vibrations.* Vibrational modes arising from torsion about double bonds usually occur at frequencies above 200 cm.$^{-1}$ and are not included in this review. The potential-energy barriers to rotation about single bonds are usually below about 5 kcal.[78] and the resulting torsional vibrations lie in the far-infrared region. In many cases, the torsional vibration is the only low-frequency mode, and the identification is simple.[79] In other cases, comparison with related compounds is required,[80] but this presents no essential difficulty. Experimentally, the centre of the torsional band can usually be fixed to within 1 or 2 cm.$^{-1}$,[81] although further uncertainty can arise in some cases because absorption from hot bands may not coincide with the ground-state band. The barriers calculated from torsional-vibration frequencies are probably accurate, depending on the case, to within 1—5%, but this could undoubtedly be greatly improved by trapping the molecules in an inert-gas matrix at low temperature. The present accuracy is much lower than that of the microwave method of Wilson,[78] but as the infrared method is at its best when applied to compounds in which the torsional axis unites heavy groups, and the microwave

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[78] Wilson, *Adv. Chem. Phys.*, 2, 367.

[79] Dodd, Roberts, and Woodward, *J.*, 1957, 2783.

[80] Silver and Wood, *Trans. Faraday Soc.*, 1963, **59**, 588.

[81] (*a*) Fateley and Miller, *Spectrochim. Acta*, 1961, **17**, 857; 1962, **18**, 977; (*b*) Danti and Wood, *J. Chem. Phys.*, 1959, **30**, 582.

method is less suitable for such molecules, the methods are in this sense complementary. A third method which has been used to obtain barriers, by thermodynamic comparisons,[82] involves several assumptions which are difficult to verify, and has sometimes led to erroneous values of barrier heights (compare refs. 78 and 82). As the determination of torsional barriers is at present one of the more important applications of far-infrared spectroscopy, some further remarks are appropriate.

The separation of the vibration of a molecule into independent normal vibrations is dependent on the atomic displacements being small.[83a] In torsion, the atomic displacements are large, but it is still useful to consider the torsion as a normal vibration; this is facilitated because the torsion interacts only weakly with the other molecular vibrations (in a few cases, this is in part a consequence of symmetry, *e.g.*, in ethane). If there are two or more torsional motions of the same frequency in a molecule, these interact to produce normal vibrations which are linear combinations of the individual torsions. Thus in dimethyl ether, in one normal vibration the two methyl groups rotate in the same sense [normal co-ordinate $\frac{1}{2}(\alpha_1 + \alpha_2)$, symmetry A_2], and in the other the two methyl groups rotate in the opposite sense [co-ordinate $\frac{1}{2}(\alpha_1 - \alpha_2)$, symmetry B_2], α_1 and α_2 being the angular displacements of the individual methyl groups. A more detailed discussion of the interaction has recently been given.[83b] To the extent that the torsion is a normal vibration, the selection rules governing the infrared activity follow in the usual way, and these also apply to overtones and hot bands. The rotational fine structure can also, when the barrier is fairly high, be decided in exactly the same manner as for any other normal vibration though in only a few cases so far has this structure been resolved, *e.g.*, in H_2O_2[84] and N_2H_4.[36]

So far nothing has been said about the splitting of vibrational levels by quantum-mechanical tunnelling through the barrier. The splitting is greatest with light torsional groups, with low barriers, and for the levels nearest the top of the barrier, and in suitable cases can be quite large. Thus in acetaldehyde,[85] the $V = 1$ vibrational level is split by *ca.* 2·9 cm.$^{-1}$ and the $V = 2$ level by *ca.* 17·6 cm.$^{-1}$.

The torsional motion is coupled with the overall rotation of the molecule about the torsional axis. Nielsen[86] and Koehler and Dennison[87] have shown that in molecules where the torsion axis coincides with a symmetry axis (*e.g.*, $CH_3{\cdot}CCl_3$), this coupling can be taken into account by choosing axes which are not fixed in either top, but which conserve overall angular momentum (inertial-axes method). The effect of the coupling is entirely

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[83] Taylor and Glasstone, "Treatise on Physical Chemistry," D. van Nostrand, New York, 1942, Vol. 1, Chap. 4.

[83] (*a*) Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955; (*b*) Moller and Andreson, *J. Chem. Phys.*, 1962, **37**, 1800.

[84] Chin and Giguere, *J. Chem. Phys.*, 1961, **34**, 690.

[85] Kilb, Lin, and Wilson, *J. Chem. Phys.*, 1957, **26**, 1695.

[86] Nielsen, *Phys. Rev.*, 1932, **40**, 445.

[87] Koehler and Dennison, *Phys. Rev.*, 1940, **57**, 1006.

removed from the overall rotational spectrum and is accounted for in the splitting of the torsional levels. The torsion is, of course, inactive in molecules such as $CH_3{\cdot}CCl_3$, but the method has been very successfully applied by Koehler and Dennison[87] to the less symmetrical case of MeOH, where the torsion is active and strong. They showed that the correction which must be introduced to take account of the asymmetry of the OH group is small.

The inertial-axes method may be applied whatever the reduced moments of the two tops and so is suitable for most molecules which have torsional vibrations which are strong in the infrared region. When the symmetrical top is much lighter than the frame to which it is attached, *e.g.*, in $MeCH_2Cl$, and the overall rotational energy is low, useful approximation methods can be used.[88] These have been extensively developed for the interpretation of microwave spectra, and have been reviewed from this viewpoint.[89]

(ii) *Torsional isomers.* When rotation about the torsional barrier produces more than one form* of the molecule, the distinct forms, called torsional isomers, can be regarded as separate molecular species in kinetic equilibrium, provided the potential barriers separating the isomers are high. Each isomer gives its own spectrum, and far-infrared spectra are particularly suitable for supporting and extending the conclusions which have, in the main, been reached from Raman spectroscopy.[90] With low barriers, treatment as separate isomers is unsuitable and methods similar to that of Koehler and Dennison[87] must be used.

(iii) *Intensity of torsional bands.* The integrated intensity, I, of an infrared absorption band is given by [83]

$$I = \int_{\text{band}} K(\nu)\,\mathrm{d}\nu = N\pi/3c\sum_{i=x,y,z}\left(\int \psi_u{}^* \mu_i \psi_l d\tau\right)^2$$

where ψ_u and ψ_l refer, respectively, to the upper and lower state involved in the transition. When the dipole-moment component, μ_i, is expanded as a power series in the normal co-ordinates Q_j, *i.e.*,

$$\mu_i = (\mu_i)_0 + (\partial\mu_i/\partial Q_j)_0 Q_j + \ldots,$$

the largest contribution to the integral comes from the second term. Noting that the change in dipole moment is, in effect, with respect to inertial axes in the molecule, it is evident that this term is small for the torsional motion of a methyl group attached to a heavier group with an off-axis dipole moment. One might say that the light group does not wag the polar group very much. The weakness of the torsional mode in compounds such as

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* A form is distinct if it cannot be obtained from any other form by *overall* rotation of the molecule.

[88] Herschbach, *J. Chem. Phys.*, 1959, **31**, 91.

[89] Lin and Swalen, *Rev. Mod. Phys.*, 1959, **31**, 842.

[90] Sheppard, *J. Chem. Phys.*, 1949, **17**, 83.

EtCl, $CH_3{\cdot}CHO$, or Me_2O is probably the primary reason for the difficulty in the experimental observation of these modes. When the polar group is light, as in MeOH[87] or $MeNH_2$,[91] or the non-polar group is heavy, as in $CF_3{\cdot}CH_2F$,[81b] $CCl_3{\cdot}CHO$,[80] or PhCHO,[92] the torsion band is much stronger, and in the latter compounds quite narrow. PhCHO has the added advantage that the phenyl anchor group itself introduces no far-infrared fundamentals and, in addition, the influence of substituents on the torsional barrier can be studied.

(iv) *Origin of torsional barriers.* A satisfactory account of the origin of torsional barriers has proved unexpectedly difficult, but it should be borne in mind that the quantitative prediction of other force constants by valence theory is also far from satisfactory. The reader is referred to an excellent discussion of the torsional problem which has recently been given.[78] The additional data obtained from far-infrared spectra should help in forming a satisfactory theory.

(v) *Complexes.* The direct stretching frequency of the link joining two molecules in a complex will lie in the far-infrared region if the complex is sufficiently strong, and this vibration has recently been observed in the trimethylamine–iodine complex.[93] This method provides much more direct information about the complex than does the usual method of following changes in the internal vibration frequencies of the individual components.

(c) **Liquids.**—Only specific effects in liquids will be mentioned; vibrational spectra of substances examined in the liquid state as a matter of convenience alone are included in Section (**b**).

As would be expected from the strong hydrogen bonding, liquid water shows none of the rotational bands of water in the gas phase. In a most interesting series of early studies, Cartwright examined the absorption and reflection spectra of liquid water and aqueous electrolytes from 100 cm.$^{-1}$ upwards.[94] A band at *ca.* 160 cm.$^{-1}$ was also present in aqueous dioxan and in ice, the decrease of the frequency in D_2O, by $\sqrt{18/20}$, indicating that this is a translational mode. The next higher band, at *ca.* 550 cm.$^{-1}$, decreases in frequency in D_2O by $1/\sqrt{2}$, and is therefore associated with rocking. However, the intensities of these two bands in the Raman spectrum of water are not as would be expected from this interpretation. In spite of the primitive apparatus used by Cartwright, the presence of both the bands in water (H_2O only) has been subsequently confirmed,[95] but otherwise this topic has received little further attention.

Even in unsaturated solution in benzene, in which water is present as a monomer, the intense H_2O rotational lines are undetectable. HCl in

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[91] Lord, U.S. Department of Commerce Off. Tech. Service, P.B. Report, 1960, pp. 161, 738.

[92] Silver and Wood, *Trans. Faraday Soc.*, in the press.

[93] Yada, *J. Mol. Spectroscopy*, 1962, **9**, 461.

[94] Cartwright, *Phys. Rev.*, 1936, **49**, 470; *J. Chem. Phys.*, 1937, **5**, 776.

[95] Kislovskii, *Optika i Spektroskopiya*, 1959, **7**, 201.

benzene also gives no rotational lines.*[96] However, these results may be indicative of specific solute–solvent interactions, and it is notable that water is much more soluble in benzene than in n-hexane.

Interaction of the liquid environment with vibrations is usually much less than with rotations. An interesting intermediate is torsion. In $CH_3{\cdot}CHO$, the gas-phase frequency is unchanged in the liquid,[81] but in H_2O_2 the torsion frequency is reported to increase from 314 $cm.^{-1}$, in the vapour, to 635 $cm.^{-1}$ in the liquid.[84] Hydrogen bonding must play am important rôle, but the nature of the "torsional mode" in liquid H_2O_2 is not clear, and data obtained from D_2O_2 would be interesting.

Solvent effects on low-frequency vibrations may, in general, be expected to follow along the same lines as with higher frequencies; these effects have been summarised recently.[97] As the frequency shift, caused by a solvent is not directly dependent on the shifted frequency, the solvent shifts may appear more pronounced in the far-infrared region since the proportionate change is larger.

(d) Crystalline Solids.—(i) *General.* A crystal with only a single atom in the unit cell can sustain a continuous band of low-frequency vibrations from zero frequency to an upper limit (the acoustical band).[98] With n atoms per unit cell (based on the translational symmetry[99]) there are, in addition, $(3n - 3)$ higher-frequency "optical" bands; thus in NaCl, $n = 2$, and there is a single (three-fold degenerate) optical band. The absorption spectra of many crystals show $(3n - 3)$ lines rather than bands; the band reduces to a single frequency if the only component of an optical band that interacts with radiation is that in which all the corresponding atoms in any two unit cells move in phase. This conclusion was reached semi-empirically by Bhagavantam and Venkatarayudu[100] (from Raman data), but justification attempted on symmetry grounds alone was inconclusive. Vedder and Hornig have shown that the whole of a band is allowed in principle, but that the intensity falls off rapidly for component modes in which the corresponding atoms are not in phase.[99] This also holds true in the far-infrared region. There are several excellent reviews on crystal spectra.[34,99]

(ii) *Molecular crystals* If the unit cell contains q p-atomic molecules, the total of $(3pq - 3)$ crystal modes is composed of $(3p - 6)$ internal molecular modes each repeated q-fold, *i.e.*, $q(3p - 6)$, $3q$ lattice-rocking modes, and $(3q - 3)$ lattice translational modes. The lattice modes lie in the far-

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* It follows that though one often notices the absence of the water rotational lines from spectra of samples and solvents, this does not prove them to be dry. The water lines that appear in many reported far-infrared spectra are probably caused by gas-phase water vapour only.

[96] Silver and Wood, *Spectrochim. Acta*, in press.

[97] Hallam, "Spectroscopy," Institute of Petroleum, London, 1962, p. 245.

[98] Wannier, "Elements of Solid State Physics," Cambridge University Press, 1959.

[99] Vedder and Hornig, *Adv. Spectroscopy*, **2**, p. 189.

[100] Bhagavantam and Venkatarayudu, "Theory of Groups and its Application to Physical Problems," Andhra University Press, Waltair, 1951.

infrared region, and, as in the Raman spectrum, the rocking modes are expected to be more intense than the translational ones. The selection rules for all ($3pq - 3$) modes are derivable from the unit-cell symmetry, as is also the polarisation. Alternatively, the selection rules for the ($3p - 6$) internal molecular modes can be obtained from the local site symmetry of a molecule. The potential field at the site can remove internal degeneracy, and shift internal frequencies—the "static field effect". The vibrations of the q molecules within the unit cell can couple together ("correlation field splitting"), producing in principle a further q-fold splitting. It can be shown that the number of frequencies active in both infrared and Raman spectra, calculated from the local symmetry, including all non-equivalent molecules, is equal to the number derived on the unit-cell basis; however, the site method is inadequate for polarisation values, and for the selection rules for overtone and combination modes.[99] The internal vibrations can couple with lattice modes of the appropriate symmetry; normally this effect is small, but will be more important sith the low-frequency internal modes. Crystals containing polyatomic ions can be dealt with along very similar lines.[100]

Perhaps owing to experimental difficulties, there have been surprisingly few far-infrared studies of molecular crystals, in contrast to the substantial amount of Raman work. Various metal borates were examined in 1937,[101] and more recently crystalline HCl and HBr,[102] methyl halides,[103] benzoic acid,[104] and benzene, naphthalene, and anthracene[105] have been studied. It is not possible to resolve fine structure; the interpretation, which is not always satisfactory, would probably be aided by extension of the frequency range and the addition of polarisation data which are usually absent. Many lattice modes have been predicted to account for combination bands at higher frequencies but have not been checked by measurement of the far-infrared spectrum. In this way, the libration of OH^- in brucite, $Mg(OH)_2$, and portlandite, $Ca(OH)_2$, has been predicted at 400 cm.$^{-1}$ and 350 cm.$^{-1}$,[106] respectively, but an attempt to observe the latter directly was unsuccessful.[107] Bands in KH_2PO_4 and $KHAsO_4$ at 120—150 cm.$^{-1}$ have been interpreted as arising from tunnelling of the H atom of the OH^- ion in a double potential minimum.[108]

(iii) *Monatomic ions.* The single optical band in sodium chloride-type lattices has been very intensively studied by both transmission and reflection techniques.[109] Classical theory predicts a band of perfect reflectivity in the

[101] Parodi, *Compt. rend.*, 1937, **204**, 1111.
[102] Gebbie, *Phil. Mag.*, 1962, **7**, 1243.
[103] Lafferty and Robinson, *J. Chem. Phys.*, 1962, **36**, 83.
[104] Maier, *Spectrochim. Acta*, 1962, **18**, 709.
[105] Cruikshank, *Rev. Mod. Phys.*, 1958, **30**, 163.
[106] Hexter, *J. Opt. Soc. Amer.*, 1958, **48**, 770.
[107] Busing and Morgan, *J. Chem. Phys.*, 1958, **28**, 998.
[108] Hadzi, *J. Chem. Phys.*, 1961, **34**, 1445.
[109] Hass, *Phys. Rev.*, 1960, **119**, 633; Jones, Martin, Mawer, and Perry, *Proc. Roy. Soc.*, 1961, *A*, **261**, 10.

neighbourhood of an absorption frequency;[110] this is the "reststrahlen" reflection. Anharmonic terms in the potential energy—mechanical damping—decrease the maximum reflectivity and broaden the peak.[99] Secondary peaks, observed on the high-frequency side, have been ascribed to polarisation of the ions displaced by a vibration,[111] and this has been suggested as the origin of the weak absorption bands in diamond at 2000 cm.$^{-1}$ and germanium at 350 cm.$^{-1}$; as these crystals are non-ionic, they would otherwise have no infrared-active lattice vibration.

The increase in the coulomb force shifts the reststrahlen maximum to higher frequencies in crystals of polyvalent ions, *e.g.*, ZnO[112] at 414 cm.$^{-1}$ and ZnS[2] at 286 cm.$^{-1}$. The frequency in ZnS is lower than would be predicted by comparison with ZnO if the forces were entirely electrostatic, and reflects the increasing covalent character in ZnS. The interpretation of the lattice spectra of less-simple ionic crystals is usually incomplete, but the infrared and Raman spectra of tetragonal TeO_2, which has four TeO_2 units per unit cell, has been satisfactorily accounted for on the unit-cell symmetry.[113] Crystals intermediate between the ionic and covalent archetypes have so far received little attention.

(e) **Semiconductors.**—Absorption by semiconductors in the infrared region has been reviewed by Fan.[114]

The low-frequency limit of the intrinsic absorption due to electron excitation across the energy gap usually lies in the near-infrared region. Lower-frequency absorption can arise from:

(i) Lattice modes. These are recognised by their insensitivity to impurity concentration. The strong band in InSb at 192 cm.$^{-1}$ is a lattice fundamental;[115] the low-frequency bands in selenium are ascribed to lattice combination modes.[116]

(ii) Transitions localised at impurities or lattice defects. Electronic transitions to a localised excited state have been observed in the far-infrared region in boron-doped silicon.[117] It is also possible for the bound electron (or hole) to be excited by radiation to non-localised states, this being the basis of a far-infrared detector currently under development.[35] Excitation may also occur thermally, and to avoid this the sample must be cooled.

(iii) Free carriers. The resulting absorption shows a smooth increase with wavelength. The absorption below 100 cm.$^{-1}$ in *n*-InSb has been ascribed to free electrons.[115]

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[110] Born and Huang, "Dynamical Theory of Crystal Lattices," Oxford University Press, 1954.

[111] Lax and Burstein, *Phys. Rev.*, 1955, **97**, 39; Szigeti, *Proc. Roy. Soc.*, 1960, *A*, **258**, 377.

[112] Collins and Kleinmann, *J. Phys. and Chem. Solids*, 1959, **11**, 190.

[113] Cheremisinov and Zlomanov, *Optika i Spektroskopiya*, 1962, **12**, 112.

[114] Fan, *Reports Progr. Phys.*, 1956, **19**, 107.

[115] Spitzer and Fan, *Phys. Rev.*, 1955, **99**, 1893.

[116] Caldwell and Fan, *Phys. Rev.*, 1959, **114**, 664.

[117] Hrostowski and Kaiser, *J. Phys. and Chem. Solids*, 1958, **4**, 148.

(f) Cyclotron Resonance.—Free charge carriers in a magnetic field, of strength H, can absorb electromagnetic radiation at the cyclotron resonance frequency, $\omega_c = \epsilon H/m^*C$; m^*, the effective mass of the charge carrier (an electron or electron hole), depends on H and is usually less than the electronic mass. A general review has recently been given.[118] In semiconductors, ω_c lies in the far-infrared region for fields in the range 20—100 kilogauss. So far, most observations have been made at a few fixed frequencies, by using the reststrahlen filtering method, while H was varied. InSb has been the most extensively used material.[119] InAs, InP,[120] and GaAs[121] have also shown far-infrared cyclotron resonance absorption. The absorption band is broad at room temperature, but when the width is due to the interaction of the charge carrier with lattice vibrations it can be reduced by cooling. Cyclotron resonance in InSb forms the basis of another type of far-infrared detector at present being developed.[35]

(g) Superconductors.—The transmission of tin or lead films, cooled below the critical superconducting temperature, T_c, has been measured over the range 10—100 cm.$^{-1}$ by Glover and Tinkham.[122] From the transmission data, with the help of the Kramers–Kronig relation,[34] the real and imaginary components of the electrical conductivity have been inferred as a function of frequency, and imply that energy is absorbed in the superconductor by excitation of electrons across an energy gap of 3—4kT_c.

The energy gap in seven bulk superconducting metals has been measured from the position of the absorption edge,[123] and found to be close to the value of 3·5 kT_c predicted by the theory of Bardeen.[124]

It should be added that these experiments, which involve very low temperatures as well as extreme far-infrared frequencies, constitute an outstanding technical achievement.

(h) Magnetic Materials.—A recent development is the investigation of magnetic materials at low temperatures by means of their far-infrared spectra. Antiferromagnetic FeF_2[125] and ytterbium iron garnet[126] have been examined.

(i) Polymers.—The infrared spectra of crystalline polymers can be interpreted on the unit-cell basis,[127] and this can be justified by the arguments used by Vedder and Hornig.[99] In an infinite crystal, modes in which the atoms in adjoining cells are not in phase are inactive on the unit-cell basis. However, when the chain length is finite, vibrations with $(n + \frac{1}{2})$

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[118] Lax and Mavroides, *Solid State Physics*, 1960, **11**, 261.

[119] Boyle and Brailsford, *Phys. Rev.*, 1957, **107**, 903; Palik, Picus, Teitler, and Wallis, *ibid.*, 1961, **122**, 475.

[120] Palik and Wallis, *Phys. Rev.*, 1961, **123**, 131.

[121] Palik, Stevenson, and Wallis, *Phys. Rev.*, 1961, **124**, 701.

[122] Glover and Tinkham, *Phys. Rev.*, 1957, **108**, 243.

[123] Richards and Tinkham, *Phys. Rev.*, 1960, **119**, 575.

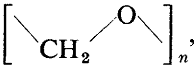
[124] Bardeen, *Phys. Rev.*, 1957, **108**, 1175.

[125] Tinkham, *Phys. Rev.*, 1961, **123**, 425.

[126] Siever and Tinkham, *Phys. Rev.*, 1961, **124**, 321.

wavelengths in the chain are infrared-active, although weak.[127b] In this way the polymer spectra link up with those of long-chain molecules.

In practice, the site group is usually a sufficient basis for dealing with the fundamentals, but not with overtones, combinations, and polarisation. Transmission spectra of polyethylene, polytetrafluoroethylene, and polychlorotrifluoroethylene, down to 100 cm.$^{-1}$, have been satisfactorily interpreted on the site-group symmetry.[128]

There is particular interest in the barriers to torsional rotation of the polymer chain, which play an important part in determining the mechanical and thermodynamic properties. The infrared activity of the torsional modes depends on the unit cell in the polymer in question. In polyoxymethylene,  $\left[\diagdown \mathrm{CH_2} \diagup \mathrm{O} \diagdown\right]_n$, a torsional-type vibration at 235 cm.$^{-1}$ gives a barrier of 3·6 kcal./mole.[129] Barriers which are unobtainable directly can be transferred from "prototype" compounds, though the exact reliability of this has not yet been tested. Torsion is not a fundamental vibration of polyethylene or polytetrafluoroethylene on the site group $-[CX_2]_2-$ basis, nor is any other low-frequency chain skeletal motion. The spectra of these compounds are correspondingly fairly clear below 200 cm.$^{-1}$ and this makes them useful as window materials.

In finite paraffin chains, the torsional modes can be active, though weak, and Szigeti has suggested that the intensity may be greatly enhanced, without appreciable change of frequency, by replacement of a CH_2 by a polar (*e.g.*, C=O) group.[130].

[127] (*a*) Tobin, *J. Chem. Phys.*, 1955, **23**, 891; (*b*) Liang, *J. Mol. Spectroscopy*, 1957, **1**, 61.

[128] Liang, Krimm, and Sutherland, *J. Chem. Phys.*, 1956, **25**, 543, *et seq.*

[129] Yoshinaga, *Bull. Chem. Soc. Japan*, 1962, **35**, 1429.

[130] Szigeti, *Proc. Roy. Soc.*, 1961, *A*, **264**, 198.