

ROTATION SPECTRA

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WORK on the fine structure in ultra-violet electronic spectra and infra-red vibration spectra has in the past led to a considerable knowledge of rotational energy levels, but only recently has it become convenient to make direct spectroscopic measurements at the longer wave-lengths which correspond to simple changes in the rotational energy alone. This present Review covers this field of pure rotation spectra both for gases and for condensed systems, and also the related subject of inversion spectra.

For gases, the basic principle, namely, that the energy absorbed from the electromagnetic radiation field is used to excite individual molecules to higher energy states, is the same as that for other forms of absorption spectroscopy. The individual quanta of energy are much smaller and can be measured with very great accuracy, so that fine details of molecular behaviour are exposed which are normally lost by comparison with the larger total energy changes involved at shorter wave-lengths. Most of the work on gases has been done in "the microwave region," that is from 5 to 0.5 cm. wave-length. Information is obtained about the accurate moments of inertia, bond distances, isotopic masses, dipole moments, nuclear spins, and quadrupole moments, internal electric fields in molecules, and collision frequencies.

For condensed phases the quantised nature of the rotational energy levels disappears as a result of the strong intermolecular interactions. The knowledge given by the absorption spectrum does not then concern individual molecular properties, apart from dipole moments, but rather intermolecular forces; potential barriers opposing rotation in crystals, the structure of polymeric materials and the pseudo-crystallinity of liquids thus become matters for study.

Experimental Methods

The recent advances have followed from the general technical development consequent on the use of microwave frequencies in military applications both for radar detecting systems and for communication. Variable-frequency, monochromatic Klystron oscillators are the usual source of the radiation and no prism or grating is needed. The use of wave-guide for containing both the radiation and the material under investigation is common, while resonant cavities and other circuit components have their special applications. At longer wave-lengths coaxial cables and Lecher

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wires are used besides resonant circuits with filled condensers; there is also a "thermometer" method in which the energy loss is measured by the resulting rise in temperature of the sample. Those interested in further details must refer elsewhere.¹⁻⁴

Spectral positions are described in various units and it may be noted that 1 cm. is 10,000 μ . and also 10^8 A. and corresponds in frequency to 1 cm.⁻¹ (wave number) or 3×10^{10} cycles/second, that is 30,000 Mc/s.

Gases

Linear Molecules.—For a linear molecule with a moment of inertia, I , the allowed quantised energy states for rotation are given by

$$E_{\text{rot.}} = h^2 J(J + 1)/(8\pi^2 I)$$

where J is the rotational quantum number. Each energy state is $(2J + 1)$ -fold degenerate in the absence of external fields, and the terms with higher powers of $J(J + 1)$ which correct for centrifugal stretching are negligible at low J values. There is a selection rule which requires that interaction with electromagnetic radiation can only lead to a change in the quantum number J by one unit, and so the energy involved in a spectral transition will be the difference in energy between two neighbouring levels, namely,

$$h^2(J + 1)/(4\pi^2 I)$$

where J is now the quantum number in the lower state. Since the energy is related to the absorption frequency ν by $\Delta E = h\nu$, the spectrum of a linear molecule will consist of a set of evenly spaced lines with frequencies in the ratios 1 : 2 : 3 : 4 : . . . corresponding to the J values 0, 1, 2, 3, . . .

Such a series of lines with J values from 4 to 10 was first found by M. Czerny⁵ for hydrogen chloride between 40 and 100 μ . and subsequently⁶ in the other hydrogen halides. Special importance was attached to the initial experiment since the old quantum theory had predicted lines at frequencies given by

$$h(2J + 1)/(8\pi^2 I)$$

which would be in the ratios 1 : 3 : 5 : 7 : . . . ; this prediction could not be reconciled with the experiment, but rather the new quantum theory was confirmed. Recent work has provided more accurate confirmation of the integral ratios between absorption lines. For example, three transi-

TABLE I

Change in J .	1 \rightarrow 2.	3 \rightarrow 4.	4 \rightarrow 5.
Frequency, Mc/s. . .	24,325.92	48,651.7	60,814.1
which is	$2 \times 12,162.96$	$4 \times 12,162.9$	$5 \times 12,162.8$

¹ F. H. Müller, *Ergebn. Exakt. Naturwiss.*, 1938, **17**, 164.

² B. Bleaney, *Rep. Prog. Physics*, 1946—47, **11**, 178.

³ W. Gordy, *Rev. Mod. Physics*, 1948, **20**, 668.

⁴ M. Freymann, R. Freymann, and J. Le Bot, *J. Phys. Radium*, 1948, **9**, 1D.

⁵ *Z. Physik*, 1925, **34**, 227.

⁶ *Ibid.*, 1927, **44**, 235.

tions in carbon oxysulphide^{7, 8} are given in Table I. The very small discrepancies are probably real and are due to centrifugal stretching of the molecule, whose moment of inertia consequently increases with J .

Moments of Inertia and Bond Lengths.—The fact that microwave frequencies can be measured to an absolute accuracy of 0.02 Mc/s. in 25,000 Mc/s., means that the moment of inertia could be determined to the same degree of accuracy, 1 part in 10^6 , were Planck's constant known to this degree of accuracy. The deduced moment will be the mean moment in the ground vibrational state and a correction must be applied to convert this figure into the equilibrium moment, that is, the moment of inertia pertaining to a structure in which the nuclei are clamped in their equilibrium positions. The correction arises partly because, although the mean internuclear distances are unaltered by the zero-point motion of a simple harmonic vibration, the mean of the squares of the distances from the centre of gravity is altered, and it is on this latter quantity that the moment of inertia depends. And secondly, there is a correction of the same order of magnitude for anharmonicity in the vibrations which alters the mean internuclear distances. The total correction, which may be positive or negative and as much as 1%, can be made from measurements of the moments of inertia of the higher vibrational states and extrapolation to zero vibrational energy; this frequently involves the detection of very weak absorption lines and is not generally attempted, so that only ground state moments of inertia are available.

For diatomic molecules the internuclear distance can be directly determined from the moment of inertia and the atomic masses. For linear triatomic molecules there are two bond lengths to be found and so one moment of inertia is insufficient and recourse must be had to isotopic molecules. If then it is assumed that the interatomic distances are the same in the isotopic molecules, the two different moments of inertia lead to two equations in two unknowns, the bond lengths, and these equations are soluble. The equilibrium moments of inertia should be used, for the equilibrium configuration depends on the force field which is justifiably assumed to be unchanged by isotopic substitution. The ground state moments, which are in fact commonly used, are less suitable, for the mean distances will change with zero-point amplitude, and consequently with isotopic substitution. The correction may be important as the computed bond lengths are very sensitive to any change of bond length on isotopic substitution; for instance, a real change of mean bond length of 0.001 Å. on substitution of mass 33 for mass 32 may lead to an error of 0.03 Å. in the value of the computed length. Consequently, unless due allowance is made for the zero-point effects, bond lengths derived from isotopic moments of inertia should not be trusted⁹ to better than 0.01 Å. Apart from this difficulty, errors of 0.005 Å. may be introduced by uncertainty of the exact isotopic masses, and of 0.001 Å. by experimental errors. Carbon oxyselenide,

⁷ T. W. Dakin, W. E. Good, and D. K. Coles, *Physical Rev.*, 1947, **71**, 640.

⁸ R. E. Hillger, M. W. P. Strandberg, T. Wentink, jun., and R. L. Kyhl, *ibid.*, 1947, **72**, 157.

⁹ C. H. Townes, A. N. Holden, and F. R. Merritt, *ibid.*, 1948, **74**, 1113.

to quote but one of several examples,¹⁰ has been investigated¹¹ in this way and found to have C=O 1.159 Å., and C=Se 1.709 Å.

Isotopic Masses.—If the moment of inertia of a third isotopic molecule is available, a knowledge of the two interatomic distances will enable the unknown isotopic mass of the third isotope to be found. Even though ground-state moments of inertia are used, the detailed nature of the calculation is such that the third mass is obtainable with considerable accuracy.¹² For the rare ³⁶S isotope, W. Low and C. H. Townes¹³ find 35.97834 ± 0.0004 m μ . using carbon oxysulphide with only the natural sulphur abundances.

Non-linear Molecules.—Spherically symmetrical molecules, such as carbon tetrachloride, have no permanent dipole moment and cannot have a pure rotation absorption spectrum. For a symmetrical top molecule, such as methyl chloride, in which two of the moments of inertia are equal, $I_A = I_B \neq I_C$, and the dipole moment lies along the symmetry or C axis, the rotational energy levels are given by

$$E_{\text{rot.}} = h^2 J(J+1)/(8\pi^2 I_A) + (1/I_C - 1/I_A) h^2 K^2/(8\pi^2)$$

where K is a second quantum number. For the rotation spectrum the selection rules are $\Delta J = \pm 1$, $\Delta K = 0$, and the absorption frequencies are given by $h(J+1)/(4\pi^2 I_A)$, which is the same expression as for linear molecules with I replaced by I_A . Only this moment of inertia, and not I_C , can be found, and a number of isotopic molecules are required to solve completely for the bond distances and angles. Amongst others,¹⁰ the $J_{1 \rightarrow 2}$ transition of chlorosilane has been observed¹⁴ with each of the isotopes ³⁵Cl and ³⁷Cl and, a Si-H distance of 1.456 Å. being assumed, the Si-Cl distance is 2.035 Å. and the HSiH angle $103^\circ 57'$.

For each value of J , values of K from $-J$ to $+J$ are allowed, but the simple expression for the absorption frequencies shows these not to depend on K . This degeneracy is disturbed by the fact that I_A depends slightly on K as the result of centrifugal stretching.

For molecules without any symmetry in the moments of inertia, asymmetric tops, the rotational energy levels form a complicated set. Consideration of the selection rules and the various permitted transitions leads to an even more complex set of absorption lines, and analysis of the spectrum is difficult. In favourable cases the three moments of inertia can be determined and the structural parameters evaluated with the aid of isotopic substitution. After the introduction of deuterium into ethylene oxide, G. L. Cunningham, A. W. Boyd, and W. D. Gwinn¹⁵ have solved for the distances and find C-O 1.436 Å., C-C 1.47 Å., C-H 1.08 Å., \angle HCH $116^\circ 50'$, and that the C-C bond makes an angle $158^\circ 5'$ with the CH₂ plane. Water

¹⁰ For tables of bond distances and other properties actually determined by microwave measurements, see ref. (3), which is complete to July 1948.

¹¹ M. W. P. Strandberg, T. Wentink, jun., and A. G. Hill, *Physical Rev.*, 1949, **75**, 827.

¹² C. H. Townes, A. N. Holden, and F. R. Merritt, *ibid.*, 1947, **72**, 513.

¹³ *Ibid.*, 1949, **75**, 529.

¹⁴ A. H. Sharbaugh, jun., *ibid.*, 1948, **74**, 1870.

¹⁵ *J. Chem. Physics*, 1949, **17**, 211.

is an important asymmetric top molecule, and lines have been identified^{16, 17} to 18 μ ., while there is one weak line in the microwave region due to the $5_{-1} \rightarrow 6_{-5}$ transition and this has been found both at low pressures¹⁸ and in the atmosphere.¹⁹ *iso*Thiocyanic acid, as made from potassium thiocyanate by liberation with phosphoric acid, is interesting, for lines which correspond to $J_{1 \rightarrow 2}$ in a symmetric-top approximation have been observed²⁰ for $H^{14}N^{12}C^{32}S$, $H^{14}N^{13}C^{32}S$, $D^{14}N^{12}C^{32}S$ and $D^{14}N^{13}C^{32}S$, and the four moments of inertia could not be made to give reasonable values of the bond distances on the assumption that the material was NCSH, whereas the values found for HNCS are H-N 1.2 A., N-C 1.21 A., C-S 1.57 A., and $\angle HNC$ 112°. Absorption lines have also been found in methyl alcohol,²¹⁻²³ but complete interpretation is uncertain; it is an interesting molecule, since internal rotation about the C-O bond is possible and some at least of the lines will involve this degree of freedom.

Excited Vibrational States.—As already stated, there is a change of mean moment of inertia with vibrational quantum number, owing to a change of vibrational amplitude. If then one of the vibration frequencies is sufficiently low to be excited in an appreciable number of molecules at room temperature, absorption due to the vibrationally excited molecules should be detectable near the ground-state absorption lines. The lines of excited molecules can be distinguished by their smaller intensities and by the fact that they are even weaker relative to the ground-state lines at low temperatures where the population of the excited states is less. A quantitative investigation of the change of intensity with temperature¹¹ gave the vibrational frequency of the bending mode of carbon oxyselenide as 474 cm^{-1} , whereas direct measurement subsequently gave 464 cm^{-1} . For most linear triatomic molecules the lowest vibration frequency is that of this degenerate bending mode; when this is excited, each of the rotational energy levels is split into two, as also is each rotational absorption line.²⁴ This phenomenon of *l*-type doubling has been observed,⁹ and in carbon oxysulphide the lines are 25 Mc/s. apart and in agreement with the correct theory.²⁵

Stark Effect.—The $(2J + 1)$ -fold degeneracy of the rotational levels is partly destroyed by an external electric field in the presence of which there are $(J + 1)$ levels for each value of J in linear molecules. These are characterised by a quantum number M which runs from 0 to J while the levels $M \neq 0$ are still doubly degenerate and correspond to levels $+M$ and $-M$. The transitions which are permitted in the absorption spectrum depend on

¹⁶ H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Physical Rev.*, 1937, **52**, 160. ¹⁷ H. Hopf, *Z. Physik*, 1940, **116**, 310.

¹⁸ C. H. Townes and F. R. Merritt, *Physical Rev.*, 1946, **70**, 558.

¹⁹ R. H. Dicke, R. Beringer, R. L. Kyhl, and A. B. Vane, *ibid.*, p. 340.

²⁰ C. I. Beard and B. P. Dailey, *J. Chem. Physics*, 1947, **15**, 762.

²¹ B. P. Dailey, *Physical Rev.*, 1947, **72**, 84.

²² W. D. Herschberger and J. Turkevich, *ibid.*, 1947, **71**, 554.

²³ D. K. Coles, *ibid.*, 1948, **74**, 1194.

²⁴ H. H. Nielsen and W. H. Shaffer, *J. Chem. Physics*, 1943, **11**, 140.

²⁵ H. H. Nielsen, *Physical Rev.*, 1949, **75**, 1961.

the relative orientations of the static electric field and the high-frequency measuring field of the radiation. When these electric fields are parallel the selection rule is $\Delta M = 0$, and when they are perpendicular it is $\Delta M = \pm 1$.

Carbon oxysulphide is one case where the two transitions $J_{1 \rightarrow 2}$, $M_{0 \rightarrow 0}$ and $M_{1 \rightarrow 1}$ have been observed.²⁶ In this case the frequency separation is given theoretically by

$$(3/20 - 1/84)8\pi^2 I \mu^2 E^2 / h^3$$

in which μ is the dipole moment and E is the static field strength; E appears only in a squared term and the Stark effect is of the second order. The frequency separation, which is of the order 6 Mc/s. for a field of 1000 volts/cm., can be measured with considerable accuracy. The greater experimental difficulty is to obtain known uniform static fields inside a wave-guide and the ultimate accuracy of dipole-moment measurements from the Stark effect separation has not been reached. Even so an absolute accuracy of 0.01 D. is obtained, and accuracy in relative moments where the same apparatus is used is considerably higher as the same field strength can be used in the two cases. The advantages of the method are large, for no density determinations and no corrections for atomic polarisations are involved and low pressures, 10^{-3} mm., may be used. Further, the measurement is made on one vibrational state and the change of dipole moment with vibrational energy can be measured; thus values of 0.754 D. for the ground-state dipole moment, and 0.728 D. for a molecule singly excited in the lowest stretching mode, have been reported for carbon oxyselenide.¹¹ Similarly, different isotopic species may be studied even in mixtures, and the change of dipole moment consequent on the change of zero-point amplitude observed; for $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ and $^{16}\text{O}^{13}\text{C}^{32}\text{S}$ the dipole moments are 0.732 and 0.722 D., respectively.²⁷

For asymmetric molecules the Stark effect may be of either the first or the second order and is of great assistance in identifying the lines of a complex spectrum; the dipole moment can still be evaluated. J. K. Bragg and A. H. Sharbaugh²⁸ have found a value of 2.17 D. for formaldehyde, whereas dielectric-constant measurements are severely handicapped by the tendency of formaldehyde to polymerise.

The effect of a high-frequency Stark field has been studied by C. H. Townes and F. R. Merritt²⁹ up to 1.2 Mc/s. For low frequencies the absorption corresponds to the instantaneous value of the field, but as the frequency is increased to the order of magnitude of the collision frequency a complicated pattern is obtained, while at the highest frequency the Stark field reverses many times during the absorption process and the pattern corresponds to the average of the square of the field strength, that is to a static field of the strength of the root mean square of the high-frequency field amplitude.

A Zeeman effect, that is, a shift of absorption frequency with a static

²⁶ T. W. Dakin, W. E. Good, and D. K. Coles, *Physical Rev.*, 1946, **70**, 560.

²⁷ M. W. P. Strandberg, T. Wentink, jun., and R. L. Kyhl, *ibid.*, 1949, **75**, 270.

²⁸ *Ibid.*, p. 1774.

²⁹ *Ibid.*, 1947, **72**, 1266.

magnetic field, has been found in methyl chloride³⁰ but the interaction depends in a complex way on the nuclear spins.

Intensity and Line Shape.—The intensity and shape of an absorption line are best considered together, although they are governed essentially by the dipole moment of the molecule and a collision frequency, respectively. J. H. Van Vleck and V. F. Weisskopf³¹ have shown that the Lorentz formula, satisfactory for visible spectroscopy, requires modification when the actual time of duration of a molecular collision is short compared with the reciprocal of the measuring radiation frequency. Their formula for the power attenuation coefficient may be written

$$8\pi^2\nu \nu_{ij} |\mu_{ij}|^2 n_j F_{ij}/(3kTc)$$

where ν is the measuring frequency, ν_{ij} the resonance frequency for the ij transition, n_j the number of molecules per c.c. in the lower state, $|\mu_{ij}|$ is the matrix element of the dipole moment corresponding to the transition, and F_{ij} is a structure factor, and it has been assumed that $h\nu_{ij} \ll kT$, which is justified in the microwave region. For rotation bands $|\mu_{ij}|$ is the product of a numerical factor depending on J and K and the dipole moment of the molecule, and it can be seen that the intensity depends on the square of this moment. In particular, if the dipole moment is zero, as for homopolar diatomic molecules and for spherical-top molecules, then the intensity is nil and there is no absorption spectrum. The structure factor is given by

$$F_{ij} = \frac{\nu}{\pi\nu_{ij}} \left[\frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + (\Delta\nu)^2} + \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + (\Delta\nu)^2} \right]$$

where $\Delta\nu$ is the collision frequency which is also given by $1/(2\pi\tau)$, where τ is the time between collisions which are effective in terminating the absorption process.

At low pressures where $\Delta\nu \ll \nu_{ij}$ only the first term is important and this is only large when $\nu \simeq \nu_{ij}$, which implies that the absorption consists in a sharp line. Neglecting the second term and the effect of overlapping lines due to other transitions, the shape of any line is given by

$$\Delta\nu/[(\nu_{ij} - \nu)^2 + (\Delta\nu)^2]$$

as is shown in Fig. 1. The curve has a maximum proportional to $1/\Delta\nu$ at $\nu = \nu_{ij}$ and has half its maximum height at $\nu = \nu_{ij} \pm \Delta\nu$, so that the width at half height is $2\Delta\nu$. Thus if collisions are infrequent the line is narrow, and conversely. An increase of collision frequency may be brought about by an increase of gas pressure, and on a simple collision theory there is a direct proportionality. The absorption per unit path length is also proportional to n_j which, too, is directly proportional to the pressure if there is no foreign gas present. Consequently, the maximum absorption will be quite independent of pressure since it depends on the ratio $n_j/\Delta\nu$.

This is confirmed by experiment, though there is an upper limit of pressure, about 50 mm. of mercury, where this independence no longer holds since triple collisions, overlapping of lines, and the second term in the structure factor become important. Also, there must be a lower limit

³⁰ C. K. Jen, *Physical Rev.*, 1948, **74**, 1396.

³¹ *Rev. Mod. Physics*, 1945, **17**, 227.

to this independence, since there can be no absorption when no gas is present: the limit of the pressure-independent absorption is about 10^{-3} mm.

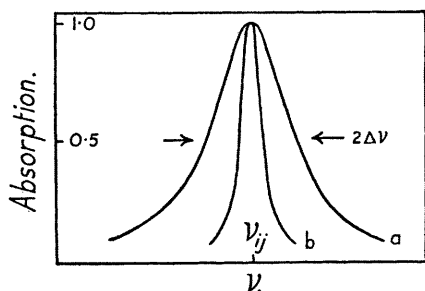


FIG. 1

Gas absorption lines. (Pressure for a four times that for b.)

when processes other than gas collisions contribute materially to the line breadth. Especially important are the Doppler effect and collisions with the walls of the containing vessel. In practice this lower limit can be reached and is required for the resolution of close lines; in one case, two lines of cyanogen chloride only 0.14 Mc/s. or 5×10^{-6} cm.⁻¹ apart have been resolved.³²

Line breadths have been studied³³⁻³⁶ mostly in the ammonia inversion spectrum (see below) where the same formula for the intensity applies. For one particular line, the 3,3 line, the collision frequency $\Delta\nu$ is given by $28P$ Mc/s., where P is the pressure in mm. of Hg. This corresponds to an effective collision diameter of 14 Å. and similar values are found for other lines in the spectrum. This is large compared with the usual model with van der Waals radii, but even at 14 Å. the dipole-dipole interaction energy between the two molecules is of the same order as the energy involved in the transition, and it is hardly surprising that interaction of such strength should be able to terminate the absorption process. The addition of polar foreign gases is found to cause more broadening of an absorption line than an equivalent pressure of a non-polar gas, in which case only the weaker dipole-polarisability interactions are important. Further, if the appropriate value of the transition moment, $|\mu_{ij}|$, is inserted in the absorption expression the maximum absorption is known in terms of the collision frequency. Comparison with experiment³³ gave good agreement for ammonia, and in other cases it may be possible to reverse the procedure and find dipole moments from the intensity of the absorption lines.

It has been found experimentally³⁷⁻³⁹ that lines decrease in peak intensity, and thereby increase in width, if a large amount of measuring power is used at low gas pressures. Under such conditions so much power is absorbed by the gas that the molecules which have been excited by the radiation cannot return to the initial state by means of collisions sufficiently rapidly to maintain the population of this state at its thermal equilibrium value. There is then a maximum capacity of the gas for

³² C. H. Townes, A. N. Holden, J. Bardeen, and F. R. Merritt, *Physical Rev.*, 1947, **71**, 644. ³³ B. Bleaney and R. P. Penrose, *Proc. Roy. Soc.*, 1947, *A*, **189**, 358.

³⁴ *Idem*, *Proc. Physical Soc.*, 1947, **59**, 418.

³⁵ *Idem*, *ibid.*, 1948, **60**, 540.

³⁶ C. H. Townes, *Physical Rev.*, 1946, **70**, 665.

³⁷ B. Bleaney and R. P. Penrose, *Proc. Physical Soc.*, 1948, **60**, 83.

³⁸ T. A. Pond and W. F. Cannon, *Physical Rev.*, 1947, **72**, 1121.

³⁹ R. L. Carter and W. V. Smith, *ibid.*, 1948, **73**, 1053.

absorbing power at the given frequency and this maximum is controlled by the rate of attainment of thermal equilibrium; the absorption coefficient or proportion of the power absorbed will therefore tend to zero as the power of the measuring radiation is increased. From detailed considerations^{37, 40} the frequency of collisions which are effective in maintaining thermal equilibrium can be obtained from the results, and when the saturation is apportioned⁴¹ properly over the individual unresolved Zeeman components of the line, this frequency is found to be exactly the same as that of collisions which interrupt the absorption process as measured from the half width at low powers.

Temperature is one of the quantities involved in the intensity formula both explicitly and through n_j and $\Delta\nu$. The exact effect of a change of temperature will depend on the values of the relevant quantities, but a reduction of temperature normally enhances the strength of a line in the microwave region and a fourfold increase for a reduction to -70° from room temperature is general. Also for any one system the lines at higher frequencies will be stronger by virtue of the explicit $\nu\nu_j$ factors in the intensity expression and of an increase of n_j , the population factor, which reaches a maximum at intermediate J values.

Nuclear Quadrupole Coupling.—The considerations of the absorption frequencies already outlined fail to account for all the observed lines in most cases. Thus in the region from 23,860 to 23,910 Mc/s. which covers the $J_{1\rightarrow 2}$ transition of $^{35}\text{ClCN}$ there are five lines³² none of which can be attributed to $^{37}\text{ClCN}$ or to vibrationally excited states, the lines due to which are known outside this range. Under higher resolution still, two of the lines in the region 23,883—23,887 Mc/s. are resolved into eight clear lines some of which have further shoulders. The origin of this hyperfine structure lies in the coupling of the nuclear spins to the molecular rotation through their electrical quadrupole moments: in the above example the major splitting is due to the Cl nucleus and the finest structure to the lines is due to the weaker N interaction.

To make the nature of the interaction plainer it must be realised that an atomic nucleus, or more precisely its distribution of positive charge, is not necessarily spherical in shape⁴² except when the nuclear spin is zero or one-half. The spin axis must be a completely symmetrical rotational axis, but it remains pos-

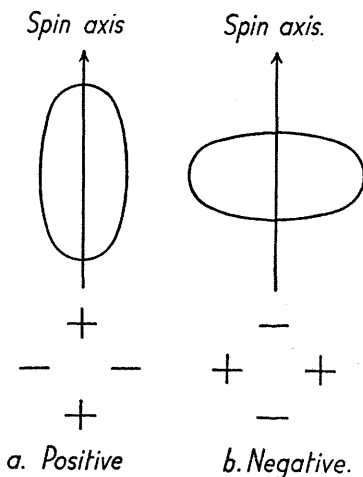


FIG. 2

Nuclear quadrupole moments.

⁴⁰ R. Karplus and J. Schwinger, *Physical Rev.*, 1948, **73**, 1020.

⁴¹ R. Karplus, *ibid.*, p. 1120.

⁴² S. Fluegge, "Nuclear Physics Tables," by J. Mattauch, Interscience, p. 38.

sible for the ellipsoid of positive charge representing the nucleus to be either prolate, as in Fig. 2*a*, or oblate, as in Fig. 2*b*. Either distribution can be regarded as the sum of a spherical distribution and a quadrupole distribution which is indicated in terms of + and - signs in the lower part of Fig. 2. The size of the quadrupole may be numerically the same in the two cases which may be distinguished by the addition of a sign: by convention, the prolate type of nucleus (Fig. 2*a*) is taken to have a positive quadrupole moment.

If an electrical quadrupole is placed in an inhomogeneous electric field it has a potential energy which varies with its orientation in a manner similar to that in which a dipole has a potential energy varying with its orientation in a uniform electric field. For a nucleus in a molecule the possible directions of its spin relative to the axis of rotation of the whole molecule are limited by quantum conditions. In each of the allowed orientations the nucleus may have a different potential energy owing to interaction of the quadrupole moment with the electric field of the molecule and there will be a series of energy states. The pattern of these states depends on the values of the nuclear spin and of the molecular rotational quantum numbers, while the energy scale factor is determined by the nuclear quadrupole moment and the degree of inhomogeneity of the field. For linear molecules the relative energies depend on $Q\partial^2V/\partial z^2$, where Q is the quadrupole moment and V is the electric potential at the position of the nucleus, so that $\partial^2V/\partial z^2$ is the divergence of the field along the molecular axis z . The product $Q\partial^2V/\partial z^2$ may be either positive or negative and is effectively independent of the rotational quantum number. Provided the theoretical values of the energy levels are known, it remains only to investigate the selection rules, which are likewise governed by quantum conditions, in order to predict the absorption spectrum.

The mathematical details^{43, 44} of the theory are somewhat lengthy, but good agreement between theory and experiment has been obtained even in cases where more than one nucleus has a quadrupole moment^{32, 45} and in asymmetric molecules.⁴⁶ The parameter $Q\partial^2V/\partial z^2$ must be chosen in sign and magnitude to fit the observed results, but the number of lines to be expected, their relative frequency separations, and their relative intensities are determined by the nature of the change of rotational quantum number and the values of the relevant nuclear spins. In some cases if the spins are not known they may be found from the absorption spectrum; for instance, the spin of ¹⁰B has been shown to be 3 and of ¹¹B to be 3/2 from the microwave spectrum of borine carbonyl.⁴⁷

The energy parameter, $Q\partial^2V/\partial z^2$ which is found from the experiments does not lead to the quadrupole moment itself unless the field divergence is known, although for isotopic molecules the field is unchanged and the ratio of the two quadrupole moments can be obtained. The field diver-

⁴³ J. Bardeen and C. H. Townes, *Physical Rev.*, 1948, **73**, 97. ⁴⁴ *Idem, ibid.*, p. 627.

⁴⁵ A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, *ibid.*, p. 633.

⁴⁶ J. H. Goldstein and J. K. Bragg, *ibid.*, 1949, **75**, 1453.

⁴⁷ W. Gordy, H. Ring, and A. B. Burg, *ibid.*, 1948, **74**, 1191.

gence can be calculated from a satisfactory molecular wave function, but the hydrogen molecule⁴⁸ is one of the few cases in which even moderate accuracy is possible. C. H. Townes⁴⁹ has suggested a rough approximation in cases where the atom in question is bonded to the rest of the molecule by a pure *p*-type orbital, and in these cases it is thought to be accurate to 20%. Alternatively, if the quadrupole moment can be accurately determined in other ways, such as by atomic-beam techniques, an accurate value of the field divergence can be obtained from the spectrum which may lead to interesting conclusions about the electronic structure of the molecule.

Inversion Spectra

For any non-planar molecule there are always two possible configurations which correspond to the dextro- and lævo-rotatory forms when these exist, and in other cases to the corresponding configurations which would differ in a similar way if identical nuclei could be distinguished. Together they may be considered either as separate molecular species each with their own, identical set of energy levels, or as one species in which there is an extra double degeneracy of each energy level. Quantum theory prefers the latter view with a duplicity of levels whenever the two equivalent structures can be converted into each other by crossing a finite potential-energy barrier. The two energy levels of a pair have slightly different energies if the potential barrier is finite and it is transition from one of these levels to the other which is the transition involved in the inversion spectrum. It is not possible to correlate the energy levels with the dextro- and lævo-forms or their equivalents. Heisenberg's uncertainty principle shows that the two questions "In which energy state is the molecule?" and "Is it in the dextro- or the lævo-form?" cannot receive simultaneous answers, for the energy state can only be found if the molecule is observed for a time longer than the reciprocal of the inversion frequency, which frequency corresponds to the energy difference, whereas the two structures are only defined over shorter times since they transform themselves into each other with this frequency by means of the tunnel effect.

If the asymmetry resides in a four-covalent atom, as in tartaric acid, interconversion is only possible by the rupture of a chemical bond, and the potential barrier opposing racemisation is very high and the inversion frequency correspondingly low, probably a matter of reciprocal centuries. But when no bond rupture is required the barrier may be lower, as in pyramidal molecules such as NH_3 , where interconversion is achieved when the nitrogen atom passes through the plane of the hydrogen atoms, and for NH_3 the inversion frequency lies at 23,000 Mc/s. or 0.8 cm.^{-1} in the ground state.

The NH_3 inversion fundamental is the only one already observed, all others being predicted at lower frequencies. It was first found by C. E. Cleeton and N. H. Williams⁵⁰ in 1934 and has recently been reinvestigated by many workers^{33, 36, 51} who use the high resolving power available with

⁴⁸ A. Nordsiek, *Physical Rev.*, 1940, **58**, 310.

⁴⁹ *Ibid.*, 1947, **71**, 909.

⁵⁰ *Ibid.*, 1934, **45**, 234.

⁵¹ W. E. Good, *ibid.*, 1946, **70**, 213.

modern microwave techniques. It is now found that the band can be resolved into a large series of fine structure lines which correspond to the various rotational energy levels of the molecule, except those with $K = 0$ which are inactive. The dependence of the exact inversion frequency on the rotational level arises from the distortion of the molecule by centrifugal forces and the consequent alteration of the height of the potential energy barrier to which the inversion frequency is very sensitive. The detailed pattern agrees very well with the theoretical predictions of D. M. Dennison and G. E. Uhlenbeck⁵² and others.⁵³⁻⁵⁵ The lines have been very accurately measured⁵⁶⁻⁵⁸ and are useful as secondary frequency standards. The frequency of the 3,3 line has been used⁵⁹ to control the rate of an electric clock to an accuracy of 1 in 10⁷.

Further, ¹⁴N has a spin of 1 and a quadrupole moment and there is a consequent hyperfine structure^{51, 60, 61} to many of the fine structure lines, while the absence of this fine structure with ¹⁵NH₃ confirms that the spin of ¹⁵N is 1/2. A perturbation to the hyperfine structure arises⁶² from the energy of the nuclear magnetic moment in the magnetic field due to the rotation of the whole molecule; the corrections under this head are only of the order of 30 Kc/s. or 10⁻⁶ cm.⁻¹, which indicates the fineness of detail obtainable. Stark and Zeeman effects have also been observed.^{63, 64}

For other molecules in general the inversion frequency may be taken as zero, and reference to the intensity formula above shows that as $\nu_{ij} \rightarrow 0$

$$\nu_{ij} F_{ij} \rightarrow \frac{2}{\pi} \left(\frac{\nu \Delta\nu}{\nu^2 + (\Delta\nu)^2} \right)$$

Half the molecules are in the lower state and $|\mu_{ij}|^2 = \mu^2/3$ and a factor c/ν is introduced to give the attenuation per wave-length which is then

$$\frac{8\pi^2 n \mu^2}{9kT} \left(\frac{\nu \Delta\nu}{\nu^2 + (\Delta\nu)^2} \right)$$

where n is the number of molecules/c.c. The last parentheses contain the frequency-dependent factor which is a very broad peak with a maximum when $\nu = \Delta\nu$, that is, when the measuring frequency equals the collision frequency. This will be at about 1 cm.⁻¹ for most gases at atmospheric pressure. Experimental verification of this formula is difficult, since there

⁵² *Physical Rev.*, 1932, **41**, 313.

⁵³ H. Sheng, E. F. Barker, and D. M. Dennison, *ibid.*, 1941, **60**, 786.

⁵⁴ L. N. Hadley and D. M. Dennison, *ibid.*, 1946, **70**, 780.

⁵⁵ H. H. Nielsen and D. M. Dennison, *ibid.*, 1947, **72**, 1101.

⁵⁶ W. E. Good and D. K. Coles, *ibid.*, 1947, **71**, 383.

⁵⁷ M. W. P. Strandberg, R. L. Kyhl, T. Wentink, jun., and R. E. Hillger, *ibid.*, p. 326.

⁵⁸ *Idem*, *ibid.*, p. 639.

⁵⁹ *Chem. Eng. News*, 1949, **27**, 162.

⁶⁰ B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, *Physical Rev.*, 1946, **70**, 984.

⁶¹ J. W. Simmons and W. Gordy, *ibid.*, 1948, **73**, 713.

⁶² R. S. Henderson, *ibid.*, 1948, **74**, 107.

⁶³ D. K. Coles and W. E. Good, *ibid.*, 1946, **70**, 979.

⁶⁴ C. K. Jen, *ibid.*, 1948, **74**, 1396.

is an implied assumption that the rotational transitions do not contribute to the absorption at these frequencies and pressures, which is not justified except for the lightest gases. However, much of the microwave absorption of polar gases⁶⁵ at atmospheric pressure must be formally attributed to the inversion spectrum, while for ammonia under several atmospheres pressure⁶⁶ the inversion frequency falls effectively to zero but yet the inversion spectrum is still distinct from the rotation spectrum.

Oxygen.—Since the oxygen molecule has no electric dipole moment, the simple rotational absorption is absent. However, the ground state is a triplet state with two unpaired electrons, the three levels corresponding to the different orientations of the parallel electron spins, and consequently of the magnetic dipole moment, with respect to the axis of the molecule. Transitions between the three levels can be induced by a high-frequency magnetic field and so there is a series of absorption lines⁶⁷ which lies near 2 cm.^{-1} , *i.e.*, 5 mm. The different lines are due to different rotational states, but only partial resolution⁶⁸⁻⁷⁰ has so far been possible.

Condensed Systems

Debye Formula.—For some purposes liquids may be considered as the limit of gases at high pressures and it is interesting to see how the absorption of liquids can be obtained as a limiting case from the formula of Van Vleck and Weisskopf quoted above. The detailed quantum levels of rotational energy are lost in the liquid state and so all $\nu_{ij} \rightarrow 0$. This condition is similar to that postulated for the inversion spectrum of heavy molecules except that the rotational levels are also involved and in all cases, $|\mu_{ij}|^2 = \mu^2$, and the rotation and inversion spectra are no longer to be differentiated. The corresponding attenuation per wave-length is

$$\frac{8\pi^2 n \mu^2}{3kT} \left(\frac{\nu \Delta\nu}{\nu^2 + (\Delta\nu)^2} \right)$$

which is just three times that due to the inversion spectra alone. These are not the most common symbols for describing the absorption of liquids, and the frequency may be replaced by the angular frequency ω , which is $2\pi\nu$, the collision frequency by the time of relaxation, τ , which is $1/(2\pi \Delta\nu)$, and the attenuation coefficient per wave-length by the imaginary part of the dielectric constant, ϵ'' , which introduces a factor $1/(2\pi)$; with these substitutions the formula is

$$\epsilon'' = \frac{4\pi n \mu^2}{3kT} \left(\frac{\omega\tau}{1 + \omega^2\tau^2} \right)$$

This differs slightly from that first obtained by P. Debye^{71, 72} for the dielectric loss of liquids, since it has been tacitly assumed that the real

⁶⁵ J. E. Walter and W. D. Hershberger, *J. Appl. Physics*, 1946, **17**, 814.

⁶⁶ B. Bleaney and J. H. N. Loubser, *Nature*, 1948, **161**, 522.

⁶⁷ J. H. Van Vleck, *Physical Rev.*, 1947, **71**, 413.

⁶⁸ R. Beringer, *ibid.*, 1946, **70**, 53. ⁶⁹ H. R. L. Lamont, *ibid.*, 1948, **74**, 353.

⁷⁰ M. W. P. Strandberg, C. Y. Meng, and J. G. Ingersoll, *ibid.*, 1949, **75**, 1524.

⁷¹ "Polar Molecules", 1929, Chemical Catalogue Co.

⁷² P. Debye and H. Sack, Marx's "Handbuch der Radiologie", 1934, VI, Part 2, 69.

part of the dielectric constant is unity, an assumption entirely justified for gases at low pressures but not for condensed systems. The equivalent Debye formula which takes this into account is ⁷³

$$\epsilon'' = \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)4\pi n\mu^2}{27kT} \left(\frac{\omega\tau}{1 + \omega^2\tau^2} \right)$$

where ϵ_0 is the dielectric constant at zero frequency and ϵ_∞ that at a frequency high compared to the absorption range: the previous case is the special case when $\epsilon_0 \doteq \epsilon_\infty = 1$ and the formula relates to the Clausius-Mosotti form of the internal field. By virtue of the relationship between the dipole moment and the dielectric constants an alternative form is

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2)$$

Further, the absorption is necessarily related to the dispersion, that is, the change of dielectric constant with frequency, and the formula which corresponds is

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + \omega^2\tau^2)$$

and these two formulæ may be considered as the constituent parts of the complex equation

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau)$$

This formula, which applies to all condensed systems, can be obtained in a variety of ways,^{71, 74-76} each of which throws into relief a different aspect of the parameter τ . Although effects due to the molecular moment of inertia are usually negligible, the more exact formula is ^{77, 78}

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau)(1 + i\omega\tau')$$

where $\tau' = I/(2kT\tau)$.

In the above forms of the loss equations it has been assumed that only one relaxation mechanism, and so one relaxation time, is operative; for simple systems this is often true, but if it is not, the several contributing terms must be summed so that

$$\epsilon = \epsilon_\infty + \sum_r K_r/(1 + i\omega\tau_r)$$

where K_r describes the amount of the dispersion associated with the relaxation time τ_r . If the dielectric constant is of this form, there is an identity ⁷⁹

$$\int_0^\infty (\epsilon''/\omega)d\omega = \pi(\epsilon_0 - \epsilon_\infty)/2$$

which relates the area under an ϵ'' - $\ln \omega$ curve to the total dispersion $(\epsilon_0 - \epsilon)_\infty$. This last equation may be a useful check on the accuracy of any loss measurements, and it can also be made to show if a sufficient

⁷³ Compare the introduction of a similar factor in ultra-violet absorption intensities: N. Q. Chako, *J. Chem. Physics*, 1934, **2**, 644.

⁷⁴ W. A. Yager, *Physics*, 1936, **7**, 434.

⁷⁵ W. Kauzmann, *Rev. Mod. Physics*, 1942, **14**, 12.

⁷⁶ R. E. Powell and H. Eyring, "Advances in Colloid Science", 1942, Interscience, Vol. I, 213.

⁷⁷ V. A. Dmitriev and S. B. Gurevich, *J. Exp. Theor. Physics U.S.S.R.*, 1946, **16**, 937.

⁷⁸ J. G. Powles, *Trans. Faraday Soc.*, 1948, **44**, 802, 844.

⁷⁹ G. M. L. Sommerman, *J. Franklin Inst.*, 1935, **219**, 433.

part of the frequency range has been covered to obtain all the rotational absorption region. In some cases this area may be more accurately known than the total dispersion and may be used to calculate this quantity and therefrom dipole moments. This method for obtaining moments has the advantage that no determinations of the electronic and atomic polarisation are required. The value 0.19 D. for the dipole moment of *p*-cymene⁸⁰ is considered as good⁸¹ as the static dielectric constant value.

Determination of Relaxation Times.—In principle, if there is only one relaxation time it can be obtained from the measurement of ϵ' or ϵ'' at a single frequency, as it is the only unknown in the equations for these quantities if ϵ_0 and ϵ_∞ are known: when using ϵ'' there may be ambiguity arising from the two solutions of the quadratic equation for τ , but this may be resolved if the sign of $d\epsilon''/d\omega$ is known. At low frequencies, which were all that were available to many early investigators, ϵ' is not very sensitive to the relaxation time, but ϵ'' or the loss is directly proportional to it. There is no way of deciding from low-frequency measurements if one relaxation time is sufficient to describe the loss or whether a distribution is required, in which case the mean time, $\sum_r K_r \tau_r / \sum_r K_r$, is obtained.

When the whole dispersion region can be covered it is possible to compare the experimental curve with the theoretical and determine the distribution of relaxation times. Fig. 3 shows the variation of ϵ' and ϵ'' with frequency for material with a single relaxation time; the curves are drawn to a logarithmic frequency scale which makes the loss curve symmetrical about the frequency at which $\omega\tau = 1$. The same curves are obtained if ϵ' and ϵ'' are plotted against $\ln \tau$ for a fixed measuring frequency; this is effectively obtained by measuring ϵ' and ϵ'' as a function of temperature, since $\ln \tau$ is often proportional to the temperature, although some distortion is introduced from the variation of the dispersion ($\epsilon_0 - \epsilon_\infty$) with temperature. Providing these curves are sharp, that is τ varies rapidly with T , it is fair to assume that the maximum of the curve is given by $\omega\tau = 1$, and many relaxation times have been obtained in this way since it is easier experimentally to change the temperature than to cover a wide frequency range. From the height of such curves some idea of the distribution of relaxation times may be obtained, since if there is but one relaxation time the maximum of ϵ'' should be $(\epsilon_0 - \epsilon_\infty)/2$.

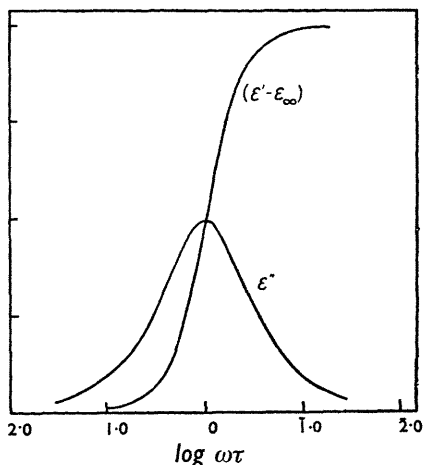


FIG. 3
($\epsilon' - \epsilon_\infty$) and ϵ'' plotted against $\log \omega\tau$.

⁸⁰ D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, 1946, **42**, A, 122.

⁸¹ R. J. W. Le Fèvre, *ibid.*, p. 162.

Several types of distribution for τ , when there is more than one relaxation time, have been proposed, including a Gaussian, but in his discussion Kauzmann⁷⁵ has shown that they all predict very similar absorption curves and no one form is to be preferred on experimental or theoretical grounds. In some systems two or more dispersion regions are observed.^{82, 83}

Molecular Relaxation Times.—The dielectric relaxation times as introduced above describe the decay of induced electric polarisation and must be related to molecular behaviour if knowledge of intermolecular forces is to be obtained. An axis fixed in a body such as a rigid molecule subject to frictional forces and to the fluctuations of Brownian motion, has a relaxation time which describes the average rate of randomisation of the axis after the removal of an aligning mechanism. Quantitatively, the amount of alignment or randomisation is measured by the length of the projection of the axis in question on the external direction. In particular, if the internal axis coincides with a molecular dipole moment and if the projection of the dipole moment is a measure of the electric polarisation, then the relaxation time of the axis, which may be called the molecular relaxation time, and the relaxation time of the dielectric polarisation are the same.

This is not true with the Clausius-Mosotti assumption for the internal field, according to which the polarisation is not so simply related to the alignment of dipoles, and in this case the molecular relaxation time is smaller by a factor $(\epsilon_\infty + 2)/(\epsilon_0 + 2)$. For nitrobenzene this factor is 1/8, and for dilute solutions when $\epsilon_0 \approx \epsilon_\infty$ it is 1 and so the two times are the same. L. Onsager's dielectric theory,⁸⁴ in which the Clausius-Mosotti internal field is abandoned, requires the molecular and dielectric relaxation times to be the same even for strongly polar liquids. Other modifications^{85, 86} have been proposed and it is uncertain⁸⁷ which theory is to be preferred, although experimentally the Onsager theory accounts closely for the values of the dielectric constants of polar liquids.⁸⁸ Consequently, it seems better to accept the experimental values of the dielectric relaxation times and discuss them as if they were molecular relaxation times in all cases. For dilute solutions there is no error, and in polar liquids the difference can scarcely be greater than a factor of ten.

Even the above discussion is somewhat simplified, since a molecule with a most general frictional ellipsoid may have three relaxation times⁸⁹ corresponding to relaxation of the three principal frictional axes, and, unless the dipole moment lies along one of them, the three times are involved in the dielectric loss. In many cases, especially for symmetrical rigid molecules, the dipole moment coincides with one axis and so only one relaxation rate is active: even when this is not strictly true it is nearly so, or else

⁸² A. Schallamach, *Trans. Faraday Soc.*, 1946, **42**, A, 180.

⁸³ P. Girard and P. Abadie, *Compt. rend.*, 1943, **216**, 44.

⁸⁴ *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

⁸⁵ P. Debye and W. Ramm, *Ann. Physik*, 1937, **28**, 28.

⁸⁶ R. H. Cole, *J. Chem. Physics*, 1938, **6**, 385.

⁸⁷ See discussion in *Trans. Faraday Soc.*, 1946, **42**, A, 3—40.

⁸⁸ C. J. F. Böttcher, *Physica*, 1939, **6**, 59.

⁸⁹ F. Perrin, *J. Phys. Radium*, 1934, **5**, 497.

the three times are almost equal, and no rigid molecule has yet been shown to have two or three distinguishable relaxation times on this account.

A large range of relaxation times are possible according to the nature of the material and the temperature, and Table II gives a representative selection.¹⁰⁷ The columns show, respectively, the material, the temperature,

TABLE II

Material.	Temp.	τ , secs.	$\nu_{\max.}$	$\lambda_{\max.}$	Ref.
Polyvinyl acetate	60°	3×10^{-3}	60 c/s.	5000 km.	90
Polymethyl acrylate	25	3×10^{-3}	60 c/s.	5000 km.	91
Ice	- 45	2×10^{-3}	80 c/s.	4000 km.	92
	- 20	1.9×10^{-4}	1 Kc/s.	300 km.	92
Pentachlorotoluene	- 5	4×10^{-6}	40 Kc/s.	7 km.	93
	- 42	1.6×10^{-4}	1 Kc/s.	300 km.	94
(crystal)	10	1.6×10^{-6}	100 Kc/s.	3 km.	94
Cetyl palmitate in para-	- 40	1.6×10^{-4}	1 Kc/s.	300 km.	110
ffin wax	20	5×10^{-8}	3 Mc/s.	100 m.	95
Glycerol	0	8×10^{-9}	20 Mc/s.	15 m.	96
„ (10,000 atm.)	0	6×10^{-7}	250 Kc/s.	1200 m.	97
Octyl alcohol	20	1.6×10^{-9}	100 Mc/s.	3 m.	98
Ethyl alcohol	20	1.4×10^{-10}	1000 Mc/s.	31 cm.	99
Acetic acid in dioxan	20	3×10^{-11}	5500 Mc/s.	6 cm.	100
Nitrobenzene	20	5×10^{-11}	3000 Mc/s.	9 cm.	83
Nitrobenzene in benzene	20	1.2×10^{-11}	14,000 Mc/s.	2.2 cm.	101, 102, 103
Water	75	3.2×10^{-12}	49,000 Mc/s.	6.1 mm.	104
	20	9.6×10^{-12}	17,000 Mc/s.	1.8 cm.	104
5.0M-NaCl solution	21	7.4×10^{-12}	21,000 Mc/s.	1.4 cm.	105
Heavy water (D ₂ O)	20	1.2×10^{-11}	13,000 Mc/s.	2.3 cm.	104
Toluene	- 80	4×10^{-11}	4000 Mc/s.	7 cm.	80
	20	7×10^{-12}	23,000 Mc/s.	1.3 cm.	80
Chloroform	25	7×10^{-12}	22,000 Mc/s.	1.3 cm.	106
Chloroform in <i>n</i> -heptane	25	3×10^{-12}	50,000 Mc/s.	6 mm.	80

⁹⁰ D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1941, **63**, 2832.

⁹¹ *Idem, ibid.*, 1942, **64**, 2389.

⁹² E. J. Murphy, *Trans. Electrochem. Soc.*, 1934, **65**, 133.

⁹³ J. Lamb, *Trans. Faraday Soc.*, 1946, **42**, A, 238.

⁹⁴ A. H. White, B. S. Biggs, and S. O. Morgan, *J. Amer. Chem. Soc.*, 1940, **62**, 16.

⁹⁵ W. Jackson, *Proc. Roy. Soc.*, 1935, A, **150**, 197.

⁹⁶ S. Mizushima, *Physikal. Z.*, 1927, **28**, 418.

⁹⁷ W. E. Danforth, jun., *Physical Rev.*, 1931, **38**, 1224.

⁹⁸ P. Girard and P. Abadie, *Compt. rend.*, 1942, **215**, 84.

⁹⁹ H. C. Bolton, *Proc. Physical Soc.*, 1948, **61**, 294.

¹⁰⁰ G. Potapenko and D. Wheeler, jun., *Rev. Mod. Physics*, 1948, **20**, 143.

¹⁰¹ W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, 1946, **42**, A, 101.

¹⁰² D. H. Whiffen and H. W. Thompson, *ibid.*, p. 114.

¹⁰³ F. J. Cripwell and G. B. B. M. Sutherland, *ibid.*, p. 149.

¹⁰⁴ C. H. Collie, J. B. Hasted, and D. M. Ritson, *Proc. Physical Soc.*, 1948, **60**, 145.

¹⁰⁵ J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Physics*, 1948, **16**, 1.

¹⁰⁶ W. P. Connor and C. P. Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 382.

¹⁰⁷ For fuller bibliographies see refs. 1, 75, 76, 108, 109.

¹⁰⁸ W. Ziegler, *Physikal. Z.*, 1934, **35**, 476.

¹⁰⁹ S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," 1941, McGraw-Hill.

¹¹⁰ R. W. Sillars, *Proc. Roy. Soc.*, 1938, A, **169**, 66.

the dielectric relaxation time the mean value being taken if there is a distribution, the frequency of the maximum in ϵ'' , the corresponding wave-length, and the reference.

Amorphous Solids.—Some of the longest relaxation times are found with various amorphous solids and constructional materials such as wood, paper, ebonite, etc. Very often there is a series of relaxation times and the interpretation is complicated by the existence of ionic conductivity and Maxwell-Wagner dispersion as well as dispersion due to rotating dipoles.

More definite information is to be obtained from measurements on a series of esters, such as cetyl palmitate, dissolved in paraffin wax.^{95, 110} Such solutions show sharp maxima in the absorption if the loss is plotted against temperature at a fixed frequency, indicating a rapid change of relaxation time with temperature. The solvent wax is non-polar and so it can have no loss at any frequency. The heights of the maxima show that the spread of relaxation times is small and that as regards the molecular picture it is possible to ignore such a narrow distribution and discuss the relaxation time as if all the solute molecules behaved identically. The characteristics of this system, namely, a narrow distribution of relaxation times and a large temperature coefficient, are also shown by solid chlorinated diphenyls^{111, 112} and supercooled *isobutyl* bromide in a glassy state.¹¹³

The inverse of the relaxation time may be considered as the average rate of rotation of the dipoles, and the rate of rotation in its turn may be treated as a unimolecular reaction rate, and reaction-rate equations applied.¹¹⁴ Consider a chain molecule such as cetyl palmitate with a polar group for which the resolved part of the dipole moment perpendicular to the chain length is large. The solvent wax has a quasi-crystalline packing of chains and it must be supposed that the long cetyl palmitate molecule can replace one of the wax chains to give effectively a mixed crystal. The dipole moment may point in one of two equally good directions controlled by the packing of the hydrocarbon chains, but intermediate positions are unfavourable since in them the quasi-crystalline structure is disturbed. If an electric field is applied, one of the two positions of the dipole moment will be favoured by the field and molecules from the less favoured position will tend to rotate into the other position so that the induced electric polarisation is established. To reach the new position the molecule must pass through the intermediate most unfavourable state of higher energy. To surmount this potential energy barrier, of height E , the molecule will require this amount of thermal energy; energy derived from the electric field does not enter this part of the discussion since the measuring field is always weak. The chance of any molecule having this amount of thermal energy is $\exp. (-E/RT)$. So the rate of rotation, which is proportional to the probability of a molecule reaching the top of the barrier, will have an exponential dependency on the height of the barrier and the absolute

¹¹¹ W. Jackson, *Proc. Roy. Soc.*, 1935, *A*, **153**, 158.

¹¹² A. H. White and S. O. Morgan, *J. Franklin Inst.*, 1933, **216**, 635.

¹¹³ W. O. Baker and C. P. Smyth, *J. Chem. Physics*, 1939, **7**, 574.

¹¹⁴ F. C. Frank, *Trans. Faraday Soc.*, 1936, **32**, 1634.

temperature. Indeed, a linear relation between $\ln \tau$ and $1/T$ is found, and the barrier height is of the order of 15—30 kcal./mole for the esters dissolved in paraffin wax.

The neighbouring molecules to that concerned in rotation will probably be displaced in the activated state and some of the thermal energy will be distributed among these neighbours and what is effectively a local melting occurs. An increased reaction rate results, for the probability of the energy E being distributed in several degrees of freedom is greater than its probability of appearing in one. The approach of the statistical theory of reaction rates^{76, 109} is slightly different and this requires

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta F^*/RT} = \frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R}$$

where ΔF^* is the increase of free energy of activation, and ΔH^* is the increase of heat content of activation corresponding essentially to E , while the fact that several molecules must be disordered in the activated state requires there to be a large increase of entropy on activation and thus a large positive value of ΔS^* . Both aspects of the theory require a rate faster than the height of the barrier would indicate, and indeed, the figures require⁷⁶ about half a dozen molecules to be involved in the rotation process.

Crystals.—For most crystals the energy barrier preventing molecular rotation is very high, no rotation occurs, and the static and high-frequency dielectric constants are the same, showing that no dispersion or absorption exists. In a few crystals rotation of polar molecules is possible and in these cases high static dielectric constants are found which have the same values as for the molten liquid apart from differences arising from the change of density. Studies of the change of dielectric constant with temperature at low frequencies often show that the rotation remains facile until some low-temperature transition point below which rotation is impossible, as is indicated by the low dielectric constant. Examples of this behaviour are hydrogen sulphide and the hydrogen halides.¹¹⁵ It is necessary to use high frequencies to find dielectric loss and values of the relaxation time above the transition temperature but this has been done with camphor and some of its derivatives^{116, 117} and with a series of methylchlorobenzenes.⁹⁴ Interpretation as in the last section applies and the energy barriers are about 10 kcal./mole, and the entropies of activation are small, indicating that the neighbours of the molecule which rotates are scarcely disturbed.

Ice shows only a small change of static dielectric constant on formation from water at 0°, but at high frequencies and lower temperatures absorption and dispersion are observed.^{92, 93, 118} It is not known if the alignment of dipoles by an electric field is brought about in ice by molecular rotation or by proton jumping, that is by movement of a proton to a second potential minimum in the hydrogen bond.

¹¹⁵ C. P. Smyth and C. S. Hitchcock, *J. Amer. Chem. Soc.*, 1933, **55**, 1830.

¹¹⁶ W. A. Yager and S. O. Morgan, *ibid.*, 1935, **57**, 2071.

¹¹⁷ A. H. White and W. S. Bishop, *ibid.*, 1940, **62**, 8.

¹¹⁸ C. P. Smyth and C. S. Hitchcock, *ibid.*, 1932, **54**, 4631.

Polymers.—Since various polymers are useful dielectric materials for condensers, cables, and other electrical equipment, a large number have been examined, among which polythene and polyfluoroethylene stand out as having specially low loss at all frequencies. In general, there is a spread of relaxation times arising from the inhomogeneity of the material on a microscopic scale, while the area under the loss curve gives the total amount of polar substance present. W. G. Oakes and R. B. Richards¹¹⁹ have used this area to distinguish between one $-\text{CCl}_2-$ group and two $-\text{CHCl}-$ groups in the chain of chlorinated polythene and have shown how the relative amounts of these two types depend on the conditions of chlorination. R. M. Fuoss and others, in a series of papers¹²⁰ on the electrical properties of solids, have measured a number of polymers. Among their conclusions are the facts that plasticisers reduce the relaxation times considerably,¹²¹ that the mean relaxation time for polyvinyl chloride¹²² and polyvinyl acetate⁹⁰ is proportional in each case to the degree of polymerisation, and that the loss peaks of polyvinyl acetate are sharp, which indicates a narrow distribution of relaxation times.

Liquids.—There is no very sharp division between liquids and some amorphous solids and there is a wide range of relaxation times down to 3×10^{-12} sec. as indicated in Table II.

However, there is difficulty in choosing a satisfactory molecular model as a basis for the interpretation of the results. The application of a rate equation, such as any of those used for solids, to mobile liquids is dangerous for in the derivation of such equations is the assumption⁷⁵ that the exponential term is large and that the energy barrier is what chiefly controls the rate. Further, the Eyring expression¹⁰⁹

$$(kT/h)e^{-\Delta F^*R/T}$$

is the rate of crossing the energy barrier, while $1/\tau$, to which it is equated, is the rate of randomisation; these two are only equal if the angular position of a molecule after passing the barrier is independent of its initial position before activation. The assumption that this is so is more easily justified for high barriers than for small ones.

In contrast to the assumptions which presume an appreciable energy barrier to exist, experimental results leave doubt as to whether there is any potential barrier to be crossed for the most mobile liquids. The relaxation times for solutions of polar molecules in *n*-heptane⁸⁰ all show an activation energy E defined by $\tau = A \exp. (E/RT)$ of 1.8 kcal./mole which is obtained from the slope of a $\ln \tau - 1/T$ graph. Arising out of the factor kT/h which contributes to the slope, E must be reduced by an amount RT to give ΔH^* of the Eyring expression which means $\Delta H^* = 1.2$ kcal./mole for the heptane solutions. It is this quantity which should indicate the height of the potential barrier opposing rotation and it is indeed small. But further, it

¹¹⁹ *Trans. Faraday Soc.*, 1946, **42**, A, 197.

¹²⁰ For Part XV see D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1945, **67**, 1566, and thence the earlier papers.

¹²¹ D. J. Mead, R. L. Tichenor, and R. M. Fuoss, *ibid.*, 1942, **64**, 283.

¹²² R. M. Fuoss, *ibid.*, 1941, **63**, 2401.

is assumed that the barrier height is invariant with temperature and this is a condition which is more likely to be fulfilled at constant volume, which implies constant intermolecular distance, than at constant pressure which was the condition for the experiments. On any mechanism relaxation times will almost certainly increase with pressure, as is observed for glycerol,⁹⁷ and so it must be expected that at constant volume the temperature coefficient of the relaxation time will be even smaller and in fact correspond to practically zero as the value of the height of the potential barrier. Further, it is difficult to reconcile such small temperature coefficients with the existence of patches of crystalline order in the liquid state unless these patches are destroyed and re-formed in a time which is short compared to the relaxation time of a molecule in the crystalline lattice; under these conditions the molecules would be able to rotate when the crystallite is destroyed and need never cross the potential barrier. The same small value, about 1.2 kcal./mole or less, of any presumed energy barrier is found for the pure liquids toluene and *o*-xylene,⁸⁰ and in the latter case persists unchanged right down to the freezing point.

The opposite extreme from considering relaxation as a discrete jump or series of jumps, is the consideration of a molecule as a sphere rotating in a viscous medium. Debye's⁷¹ derivation of a relaxation time requires it to be given by $\tau = \zeta/(2kT)$ where ζ is a frictional constant. For macroscopic spheres of radius a in a liquid with a viscosity coefficient η , $\zeta = 8\pi\eta a^3$, whence $\tau = 4\pi\eta a^3/(kT)$, and Debye suggested that the introduction of some reasonable molecular dimension for the radius of the molecule and the macroscopic coefficient of viscosity should give the right order of magnitude for the time of relaxation. As an order of magnitude calculation this is often satisfactory, but attempts to force the expression into an exact calculation have led either to the introduction of a microscopic viscosity coefficient defined so that the formula shall be exact, or else to the conclusion that the molecular radius differs widely with solvent and differs somewhat with temperature. An example is nitrobenzene¹ whose apparent radius varies from 0.31 A. in Shell oil to 1.88 A. in hexane as calculated from the macroscopic viscosity coefficients. But despite this impossibility of correlating the macroscopic viscosity and the relaxation time directly, the two processes must depend on similar intermolecular shear forces and some parallelism is to be expected. A gross increase of viscosity is accompanied by an increase of the relaxation time which is relatively small. For instance, benzophenone,¹⁰¹ which has a relaxation time of 1.6×10^{-11} sec. in benzene, has a mean time of 30×10^{-11} sec. in a paraffin whose viscosity is 300 times greater. The parallel nature may often be found in the temperature coefficients for the two processes as in toluene⁸⁰ where the activation energies are 1.9 and 2.0 kcal./mole for relaxation and viscous flow, respectively. Alcohols, too, have the same activation energy, about 6 kcal./mole, for the two processes and the relation between relaxation time and viscosity seems to be closer with alcohols¹²³ than with other liquids: both the relaxation time and the viscosity are abnormally great

¹²³ R. Goldammer, *Physikal. Z.*, 1932, **33**, 361.

since the intermolecular forces are high as the result of hydrogen-bond formation.

This same close correlation appears to hold for water, and Collie, Ritson, and Hasted¹⁰⁴ have found that the relaxation time and the ratio of the viscosity to the absolute temperature are closely proportional both for water and for heavy water; the derived radius with the Debye expression is 1.38 Å. Extension of the measurements to salt solutions¹⁰⁵ shows that the effect of dissolved ions is to reduce the dielectric constant as a result of the removal of the water molecules in the solvation shell of the ions from the orientation process, and also to reduce the relaxation time of the remainder of the water. The latter effect may be due to the increased ease of destruction of small crystalline patches as a consequence of the disturbance due to the ion impurity; if then relaxation occurs only when the molecule is outside the crystallite, it is facilitated.

Schallamach⁸² has observed the loss in some mixtures of polar compounds and finds that, even though the relaxation times of the two components are very different, yet the mixture usually shows but one region of absorption lying in frequency between the absorption of the two components separately. If one of the components is associated and the other non-associated there is a greater tendency for two separate regions to be observed, as exemplified by *n*-propyl alcohol and *iso*amyl bromide, in contrast to the one region as shown by *n*-propyl alcohol and glycerol mixtures.

From this review of the knowledge of rotation spectra it can be seen that the work with gases rests on a firm quantum-theoretical basis and that it remains to measure the properties of further simple molecules with as many isotopic species and as great an accuracy as possible. The results of special interest to chemists will be accurate bond distances, accurate dipole moments, and possibly electric field gradients at nuclear positions. The interpretation of the spectra of asymmetric top molecules is often possible and further work should lead to conclusions concerning molecules in which some internal rotation is present. For condensed systems the relaxation process of molecules in the solid state can be described in terms of energy barriers, but for liquids an adequate molecular picture seems to be lacking.