THE ABSOLUTE INTENSITIES OF INFRARED ABSORPTION BANDS

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THE intensity of absorption of infrared radiation by a given system is intimately related to the electronic charge movements during the associated vibrational quantum transition. Molecular deformations must involve bond deformations and are very unlikely to affect any but the valence-shell electrons. Consequently, in principle, absorption intensities could yield not only information on charge distributions in molecules but also information on the manner in which the valence electrons redistribute themselves during molecular deformations. Since chemical reactions, of necessity, involve specific bond deformations, such information could lead to a deeper understanding of reaction mechanisms. The equilibrium charge distributions can lead to a better understanding of the bonding.

During recent years a large number of publications on the theory, measurement, and interpretation of the absolute intensities of infrared absorption bands has appeared in the literature. Many serious difficulties still beset the spectroscopist in the interpretation of the results, but the information gleaned has reached the state where a survey of the gains, the difficulties, and the prospects can be usefully made.

Experimental Techniques.—It has proved to be extremely difficult to make accurate absolute measurements of absorption intensities. The intensities are usually defined as

$$\Gamma_k = 1/cl \int \ln[(\mathrm{I}_0)_\nu/(\mathrm{I})_\nu] \mathrm{d} \ln\nu \qquad (1)$$

where c is the absorbent concentration, l is the path length of the beam through the absorbing material, $(I_0)_\nu$ and (I_ν) are the initial and final intensities of the beam of frequency ν (expressed in cm.$^{-1}$ in all subsequent equations), and the integration is over the complete band. Such a definition follows readily from the usual exponential low of absorption. The experimental difficulties were first made apparent by the early measurements of Bourgin[1] and Bartholomé.[2] Independently they measured the intensity of the vibration–rotation band of hydrogen chloride in the gas phase and obtained results which differed by a factor of four. The major reason for this was that, for finite slit-widths, the beam is not monochromatic and consequently the measured fractional absorption of the sample, $[(T_0\text{-}T)/T_0]_\nu$, at a given frequency setting, ν, generally differs from the true transmission in such a way that the measured absorption value is too low. Bourgin,[3] Bartholomé,[2] Penner and Weber,[4] Wilson and Wells,[5] and others

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[1] D. G. Bourgin, *Phys. Rev.*, 1927, 29, 794; *ibid.*, 1928, **32**, 237.

[2] E. Bartholomé, *Z. phys. Chem.*, 1933, **b23**, 131.

[3] D. G. Bourgin, *Phys. Rev.*, 1928, **31**, 503.

[4] S. S. Penner and D. Weber, *J. Chem. Phys.*, 1951, **19**, 801, 817, 974, *ibid.*, 1953, **21**, 649.

[5] E. B. Wilson and A. J. Wells, *J. Chem. Phys.*, 1946, **14**, 578.

have investigated the conditions under which these two values approach one another and how the true absorption can be evaluated with an instrument of limited resolving power. In the procedure of Wilson and Wells the measured integrated optical density $\int \log_{10} (T_0/T)_\nu \, d \ln \nu$, divided by the concentration, is graphed against the concentration and the plot extrapolated to zero concentration. It was shown that the limiting value of the integral for zero concentration is equal to $\int \log_{10} (I_0/I)_\nu \, d \ln \nu$ if (*a*) the incident intensity, I_0, does not vary over the slit-width, and (*b*) the resolving power is high compared with the variations in the absorption coefficient.

In Bourgin's method $[\int (T_0/T)_\nu \, d\nu]/c$ is graphed against c and the ratio extrapolated, as in the Wilson–Wells technique, to zero concentration. However the curvature of the plot is far greater and the extrapolation consequently less accurate.

Since the aim of absorption intensity measurements is usually to study intramolecular properties, it is necessary to carry out studies on the gaseous phase where intermolecular interactions are reduced to a minimum. Unfortunately, the removal of intramolecular interactions results in sharp vibrational–rotational absorption lines. As a consequence condition (*b*) is difficult to attain. In order that this condition should be satisfied the rotational bands must be collision-broadened by adding a high pressure of a chemically inert, non-absorbing gas, or, for the study of weak absorption bands, by self-broadening at high pressures. The pressure-broadening is considered to be sufficient when an increase of total pressure produces no further change in the molecular extinction coefficient, $\epsilon = 1/cl \log_{10}(I_0/I)_{\text{max}}$. However, even when the individual rotational lines are sufficiently broadened to yield an overall smooth absorption curve, the band contour may still have sufficiently steep gradients to result in low measured values of the absorbance. This is particularly the case with bands having strong sharp Q branches (corresponding to no change in the rotational quantum number, J) such as the out-of-plane deformation bands in aromatic systems. The pressure required to produce broad Q branches may be excessively high, and it is to be noted that in such cases the extrapolation procedure still may not be strictly valid if condition (*b*) has not been fully met. Consequently the use of instruments of high resolving power is really required in such cases.

At very high pressures the molecule is being subjected to excessive collisional perturbations which are often undesirable. Thus it has been shown that absorption by the infrared-inactive a_{1g} mode of methane can be induced in this manner,[6] and many examples are now known of simultaneous transitions in mixed gases at high pressures.[7] In a simultaneous transition, absorption occurs at a frequency $\nu_a \pm \nu_b$, where ν_a and ν_b are transition frequencies for two different molecules and can be for two different

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[6] R. Coulon, B. Oksengorn, J. Robin, and B. Vodar, *J. Phys. Radium*, 1953, **14**, 63.

[7] H. L. Welsh, M. F. Crawford, J. C. F. McDonald, and D. A. Chisholm, *Phys. Rev.*, 1951, **83**, 1264; J. Fahrenfort and J. A. A. Ketelaar, *J. Chem. Phys.*, 1954, **22**, 1631.

chemical species. Such evidence indicates that pressure-broadening must be treated cautiously, especially when dealing with weak bands and easily polarisable molecules.

The sources of error in the Wilson–Wells and Bourgin procedures are so serious that efforts have been made to find alternative techniques. The dispersion of infrared rays has proved to be a very valuable tool in this connection since a vibrating electric moment in a molecule gives a contribution to the refractive index. Molecular vibrations are separable into normal modes each of which makes a contribution to the refractive index, n, of

$$\Delta_i (n - 1) = \frac{N}{6\pi^2 c}\left(\frac{\partial\mu}{\partial Q_i}\right)^2 \Big/ \nu_i^2 - \nu^2, \tag{2}$$

where N is the number of molecules per ml., μ is the molecular dipole moment, Q_i is the ith normal co-ordinate, ν_i is the frequency of the corresponding vibration and ν is that of the incident light (in cm.$^{-1}$). (This formula, known as the Kramers–Heisenberg formula, assumes that the absorption line is infinitely narrow, and has to be modified slightly for finite line widths).

The infrared absorption intensity of a given fundamental band has been shown to be equal to

$$\Gamma_i = \frac{1}{\nu_i}\frac{N\pi}{3c}\left(\frac{\partial\mu}{\partial Q_i}\right)^2. \tag{3}$$

(This formula is derived neglecting rotational quantisation. An exact summation of intensity over the rotational components of a parallel band of a symmetric rotor molecule[8] leads to a correction factor equivalent to multiplying the right-hand side of (3) by

$$1 + \frac{2\ B\,c\ [1 + \exp(-\,h\nu_0/kT)]}{\nu\ [1 - \exp(-\,h\nu_0/kT)]}$$

B, the rotational constant, is equal to $h/8\pi^2 c\ I_B$, where I_B is the moment of inertia perpendicular to the axis of the top, and c is the velocity of light. This factor is unlikely to lead to an error exceeding 5% in $(\partial\mu/\partial Q)^2$, and is usually neglected on the excuse that the experimental uncertainty is generally of the same order of magnitude.)

Thus the vibrational contribution to the refractive index is intimately related to the infrared absorption intensity, and, in fact, these two phenomena are manifestations of the same property. Consequently, absolute infrared absorption intensities can be deduced from dispersion studies. The particular advantage of the dispersion method, as can be seen from equation (2), is that even for infinitely narrow absorption lines the change of the refraction with frequency is quite gradual. A typical refraction spectrum due to the R2–0 bands of H^{35}Cl and H^{37}Cl is shown in Fig. 1,[9]

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[8] B. L. Crawford and H. L. Dinsmore, *J. Chem. Phys.*, 1950, **18**, 1682.

[9] F. Legay, *Rev. Opt.* (*theor. instrum.*), 1958, **37**, 11.

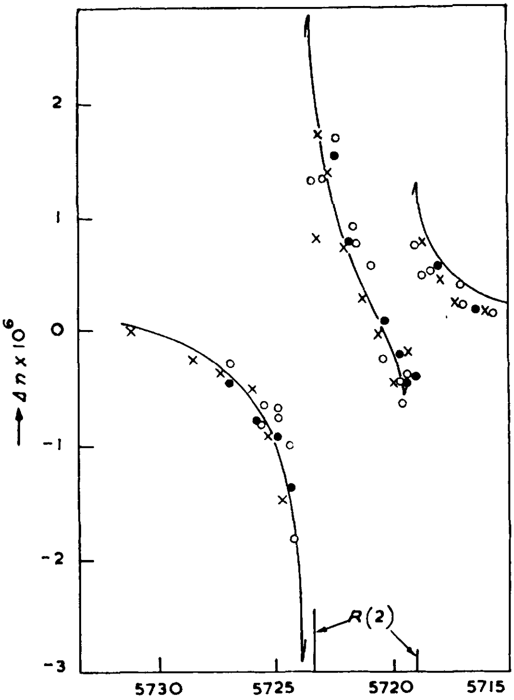

FIG. 1. *The vibration–rotation contribution to the refractive index by the R(2) bands of the 2–0 vibrational transitions of* $H^{35}Cl$ *and* $H^{37}Cl$. *The vertical lines indicated as R(2) represent the relative intensities of the corresponding absorption lines.*

and is compared with the corresponding absorption curve. It can be seen that the distance between opposite branches of the refraction curve is a function of the absorption intensity. The technique is only suitable, at present, for simple molecules with well-separated strong absorption bands. This is a very severe restriction, but fortunately it is for such molecules that the Wilson–Wells procedure is most unsuitable. The results of the dispersion measurements generally compare quite favourably with those of the best absorption measurements and are usually, though by no means always, higher than their Wilson–Wells counterparts. An excellent summary of measurements up to 1960 is given in ref. 10.

Another recent technique capable of giving relatively accurate results is the curve-of-growth method.[11] This involves making measurements at different path-lengths and allows the error due to finite slits to be eliminated if the band shape is known. It can be applied only if the individual rotational lines can be resolved, which seriously restricts its applicability. Where it can be applied, it is usual to assume that the lines can be des-

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[10] J. H. Jaffé, "Advances in Spectroscopy," Interscience, New York, 1961, Vol. 2, p. 263.

[11] S. S. Penner and H. Aroeste, *J. Chem. Phys.*, 1955, **23**, 2244.

cribed by the Lorentzian function. In such cases the technique would be expected to be of superior accuracy to the Wilson–Wells procedure. Consequently there was a great deal of consternation when the intensity of the 670 cm.$^{-1}$ band of carbon dioxide was measured in this way and a result obtained which was 50% higher than previous results.[12] As pointed out by Kaplan and Eggers,[12] this 670 cm.$^{-1}$ band is an extremely difficult band to study as far as the Wilson–Wells procedure is concerned, since: (*a*) it has a great deal of its intensity concentrated in a sharp *Q* branch (half-width, *ca.* 0·35 cm.$^{-1}$); (*b*) to measure it, it is necessary to remove absorption due to atmospheric carbon dioxide; and (*c*) it lies in a range of the spectrum where sodium chloride prisms begin to absorb appreciably and where the dispersion of potassium bromide prisms is low. This means that all the serious problems characteristic of this technique are in force for this case. Crawford and his co-workers[13] have remeasured the intensity by the Wilson–Wells procedure, exercising great care to overcome these problems, and have obtained a result very close to that of the curve-of-growth method (see Table 1). Also they pointed out that calculations made by Kostkowski and Bass[14] on the functional dependence of the errors in measuring intensities of individual rotational lines should be applicable to measurements on sharp *Q* branches. Using Kostkowski and Bass's results and estimating the pressure-broadened line-widths from collision theory, they showed that the pressure-broadening in previous determinations of the intensity (at total pressures of up to 5 atm.) had been inadequate. At the pressures of about 68 atm. that they had employed, the error resulting from slit-widths should be negligible. Also they had failed to observe any induced absorption. These careful measurements indicate that the Wilson–Wells procedure is capable of reasonable accuracy (within 2—3%) if sufficient care is exercised.

TABLE 1. *Measured intensities of* 15μ *band of carbon dioxide.*

Ref.	15	16	17	18	12	13
Method	C-o-G	W–W	W–W	D	C-o-G	W–W
Intensity (10^3cm.^{2}/mole)	7·40	6·28	5·41	6·02	8·07	8·09

C-o-G, curve-of-growth. W–W, Wilson–Wells. D, dispersion.

Interpretation of Results.—The interpretation of the measured intensities in terms of bond properties is best appreciated by considering what can be deduced, with and without assumptions, from the intensity measurements. Equation (3) is derived on the assumption that the dipole moment, μ, can

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[12] L. D. Kaplan and D. F. Eggers, *J. Chem. Phys.*, 1956, **25**, 876.

[13] J. Overend, M. J. Youngquist, E. C. Curtis, and B. Crawford, *J. Chem. Phys.*, 1959, **30**, 532.

[14] H. J. Kostkowski and A. M. Bass, *J. Opt. Soc. Amer.*, 1956, **46**, 1060.

[15] L. D. Kaplan, *J. Chem. Phys.*, 1947, **15**, 809.

[16] A. M. Thorndike, *J. Chem. Phys.*, 1947, **15**, 868.

[17] D. F. Eggers and B. L. Crawford, *J. Chem. Phys.*, 1951, **19**, 1554.

[18] Values reviewed by O. Fuchs, *Z. Physik*, 1927, **46**, 519.

be expanded as a Taylor series in terms of displacements from the equilibrium positions, and all but the first derivatives can be neglected. That is

$$\mu = \mu_0 + \sum_k (\partial\mu/\partial Q_k)_0 \, Q_k + \text{higher terms (negligible).}$$

Q_k represents the molecular distortion in the vibration k (*i.e.*, normal co-ordinate for k). This is the assumption of electrical harmonicity which is true only to a first approximation. The intensity of infrared combination bands ought to be zero in this approximation. This is certainly not so, but the intensities are usually far less than those of fundamentals, unless a combination band gains intensity from a fundamental of the same symmetry, by resonance. This confirms the validity of the assumption. The error involved is certainly much less than the present experimental errors and those, which are to be discussed later, arising from the uncertainty in the normal co-ordinate Q.

If the molecule has any symmetry, the vibrations can be separated into independent groups, each group being characterised by the behaviour of its constituents towards the symmetry elements. This means that the normal co-ordinates, Q_k, separate according to this behaviour. For example, in carbon dioxide there are two non-degenerate vibrations and one doubly degenerate vibration. The linear molecule has three planes of symmetry, mutually perpendicular, and passing through the carbon nucleus. This also implies a centre of symmetry and rotation axes, but a consideration of the symmetry of the vibrations, with respect to the planes, suffices for our present purpose. Each vibration must be symmetric or antisymmetric with respect to a particular plane. If a vibration is symmetric with respect to the XZ and YZ planes (axes defined in Fig. 2), then clearly this cannot involve movements of the nuclei in the Z direction. Consequently, only CO stretching motions belong to the symmetry classes involving these symmetry characteristics. In addition, the CO stretching

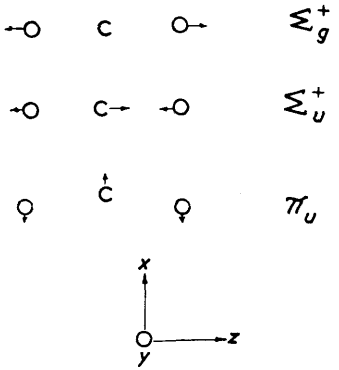

FIG. 2. *The vibrational modes of carbon dioxide, and the definition of the cartesian axes.*

vibrations must be symmetric or antisymmetric with respect to the XY plane. This means that the CO bonds must vibrate either in phase (symmetric stretch) or out of phase (antisymmetric stretch). Similar reasoning shows that the only deformation which can be antisymmetric with respect to either the XZ or the YZ plane is that of the O–C–O angle. Thus in this simple case, the normal co-ordinates are, apart from normalisation factors, $\Delta r_1 + \Delta r_2$, $\Delta r_1 - \Delta r_2$, and $\Delta\alpha$. In general the symmetry of Q_k, and hence of $\partial\mu/\partial Q_k$, is known, but in solving for the dipole gradients from the measured intensities, using equation (3), there are sign ambiguities arising from taking the square root of the intensities. Furthermore, the exact form of the vibrations, Q_k, must be determined before any further interpretation of the gradients is possible. That is, it is necessary to obtain a relationship between the normal co-ordinates, Q, and a set of co-ordinates, such as cartesians, which are defined with respect to the molecular axes. Provided that the potential energy can be expressed as a function of all possible distortions of the molecule, molecular-vibration theory will yield the required relationship as well as the vibration frequencies. In order to know the potential energy it is sufficient to know the force field, *i.e.*,the force constants connecting all atoms in the molecule. Unfortunately, these are known with precision for very few molecules. A simple example is that for the harmonic oscillator, for which the vibrational frequency, ν, is given by

$$\nu = \frac{1}{2\pi}\sqrt{(k/\mu)} \text{ and } V = \tfrac{1}{2}kq^2, \tag{4}$$

where k is the force constant for the distortion, q, and μ is the reduced mass of the system. Such equations describe, to a first approximation, the vibrational motions of a diatomic molecule. Purely theoretical approaches to evaluating the force constants of the system are impossible at present, except for the simplest of molecules. Force constants have been calculated for a number of simple systems such as LiH[19], C–H,[20] CH_4 (C–H stretch),[21] and O_2[22]. Except for diatomic molecules, there are more quadratic force constants than fundamental vibrational frequencies. Thus for the non-linear triatomic system XYX a complete description of the potential energy arising from molecular deformations requires a knowledge of four force constants—those for the X–Y stretch, the XYX deformation, the interaction between the X–Y stretches, and between the stretch and angle motions—whereas there are only three fundamental vibrational frequencies. (The number of vibrational frequencies is $3N - 6$ for a non-linear molecule, or $3N - 5$ for a linear molecule). For molecules with a high degree of symmetry, certain of the fundamental vibrations have the

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[19] A. M. Karo and A. R. Olsen, *J. Chem. Phys.*, 1959, **30**, 1232.

[20] J. Higuchi, *J. Chem. Phys.*, 1954, **22**, 1339.

[21] R. G. Parr and A. F. Saturno, unpublished data; I. M. Mills, *Mol. Phys.*, 1958, **1**, 99, 107.

[22] A. Meckler, *J. Chem. Phys.*, 1953, **21**, 1750.

same frequencies, *i.e.*, they are degenerate. As the number of atoms increases and the molecular symmetry decreases, the situation becomes rapidly more unfavourable. Clearly, additional sources of experimental data are needed in order to deduce the force field.

By means of isotopic substitution, the harmonic vibrational frequencies are altered without affecting the electronic binding. By this expediency, it is possible to obtain further sets of experimental data from which to determine the force constants. At first it would appear that M isotopic substitutions would yield Mx sets of data, where x is the number of fundamental frequencies. In practice, this is not so. There are several reasons for this. First, whilst the molecular vibrational frequencies are properties of the molecule as a whole, it is well known that many bonds vibrate almost independently of the remainder of the molecule. Thus, >X–H stretching modes interact only very weakly with other modes. This clearly means that isotopic substitution of such atoms will not give significant data on the interaction terms which do not involve the X–H stretching motion. Secondly, whilst all the vibrational frequencies may change on isotopic substitution, it may be found that all changes are not independent. Vibrational theory shows that the product of the vibrational frequencies of any symmetry class are related, by the geometry of the molecule and the masses of the atoms, to the product of the equivalent vibrations of an isotopically substituted molecule.[23] Such internal relationships reduce the number of independent equations relating frequencies to force constants. A third limitation arises from the extremely small changes in the majority of the vibrational frequencies which result from isotopic mass changes of atoms other than hydrogen. This insensitivity of the vibrational frequencies to the isotopic masses drastically restricts the usefulness of the observed data. Frequently, all the vibrational frequencies may prove quite insensitive to a particular interaction force constant, thus making the uncertainty in the value of that constant large compared with its actual magnitude. An interesting case of this type has been discussed by Linnett.[24] The two stretching vibrations of HCN belong to the Σ symmetry class and may be considered independently of the angular deformation frequency of the π class. Writing the stretching part of the potential energy as

$$2v = k_1\,(\Delta r_{\mathrm{CH}})^2 + k_2(\Delta r_{\mathrm{CN}})^2 + 2k_{12}\,(\Delta r_{\mathrm{CH}})\,(\Delta r_{\mathrm{CN}}),$$

and using the values of k_1 and k_2 as determined from HCN and DCN, it may be shown that a change in the interaction constant, k_{12}, from 0 to 1 × 10^5 dynes/cm. results in a change in the calculated stretching frequencies of $HC^{14}N$ and $HC^{15}N$ of only 1·7 and 1·1 cm.$^{-1}$, whilst for DCN the corresponding changes are 100 and 74 cm.$^{-1}$. The actual value of k_{12} is near $-0{\cdot}4 \times 10^5$ dynes/cm. Clearly the constant k_{12} contributes little to

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[23] O. Redlich *Z. phys. Chem.*, 1935, **b28**, 371; see also W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson. *J.*, 1936, 971.

[24] J. W. Linnett, *Ann. Reports*, 1952, **49**, 8.

the potential energy of $HC^{14}N$ and $HC^{15}N$, and would be difficult to estimate from the vibrational frequencies of those systems. The reason why the frequencies of DCN are so much more sensitive to k_{12} is that the CD stretching frequency near 2320 cm.$^{-1}$ is much closer to the stretching frequency of the CN group (at 2089 cm.$^{-1}$ in HCN) than is the CH frequency of 3310 cm.$^{-1}$.

If we are to arrive generally at a realistic force field and hence at a good description of the vibrational distortions, we must seek additional sources of information about the force constants. Such information can be obtained, in principle, from the magnitudes of vibration–rotation interactions and centrifugal distortions, from mean-square vibrational amplitudes as determined by electron diffraction, and, in certain circumstances, from absorption intensity studies. According to the Born–Oppenheimer approximation, electronic, vibrational, and rotational motions are independent of one another for non-degenerate vibrational states. For example, the rotational energy levels of a spherical rotor (*e.g.*, CH_4, SF_4) can be written as

$$E_{\mathrm{rot.}}/\boldsymbol{h} = BJ(J+1), \tag{5}$$

where $E_{\mathrm{rot.}}$ is the rotational energy, $\boldsymbol{h}$ is Planck's constant, and B is the moment of inertia about any axis. Hence, since $\Delta J = \pm 1$ for the P and R branches of a vibrational band, we have

$$\Delta E_{\mathrm{rot.}}/\boldsymbol{h} = 2BJ, \tag{6}$$

which is independent of the vibrational and electronic states. In the case of a degenerate vibrational band, the rotational spacings in the R ($\Delta J = +1$) and the P ($\Delta J = -1$) branches are different as a result of vibration–rotation interaction. The rotational spacings are now $2B_\nu(J+\zeta_i)$ and $2B_\nu(J-\zeta_i)$, respectively. ζ_i is the magnitude of the angular momentum arising from the interaction, and may be expressed in terms of the potential constants and the masses. This has been done in algebraic form for many of the more important types of vibration of simple molecules.[25] Clearly, each ζ_i value gives an extra relationship between the force constants and the result of an observation. Unfortunately, Coriolis constants, which is the name given to the vibration–rotation coupling parameters, can only be determined with reasonable precision for small molecules. In a similar manner, the change in rotational spacing with changes in the rotational parameter, J, can be related to the force constants and molecular parameters. This effect of centrifugal distortion has proved of little value, owing to the rather large uncertainties in the observed values.

In principle, it is possible to determine, from the electron-diffraction patterns of gases, the mean-square amplitudes of bond and angle vibrations as well as the bond and angle values themselves.[26] These amplitudes are

[25] G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

[26] J. L. Karle and J. Karle, *J. Chem. Phys.*, 1949, **17**, 1052.

readily evaluated from the force field, and have been used to test assumed fields.[27,28] The precision of the experimental data is again low. Even so, such calculations have served to show inadequacies of assumed fields.

The mathematical difficulties involved in determining the set of force constants which give the most satisfactory fit between observed and calculated frequencies, distortion constants, etc., are very formidable for all but the very simplest of molecules. Electronic computers have been programmed by several groups of research workers to derive optimum sets of force constants.[28–30] Early optimism in obtaining good fields in this way was rapidly dispelled when it was discovered that further mathematical problems were of prime importance. The major problem arises from the fact that the solution of a vibrational problem involving n vibrational frequencies involves the solution of an equation of order n, to which there are generally n solutions. In the computing procedure, a guessed set of constants is used to derive a calculated set of frequencies, distortion constants etc. The difference between the calculated and observed sets are then used to derive an improved set of force constants by a perturbation technique. It was expected that, if a reasonable set of force constants was chosen initially, from previous experience with simpler molecules, then the perturbation would lead to convergence on a unique set of improved constants, which would yield a description of the vibrational distortions close to the truth. In practice it was found that the perturbation problem was often unstable and the perturbed constants diverged to impossible values. This usually arises from the differences between the calculated and observed frequencies being too large for a perturbation treatment, and can sometimes be overcome by taking small fractional improvements, *i.e.*, if f_i is a typical input constant and f_j is its "improved" value, then using $f_i + (f_j - f_i)x$, where $x \leqslant 1$, in the next cycle may remove the divergence of the constants. Occasionally the cause of the divergence is more deep-seated and arises from an unstable situation in the perturbation solution due to a special case of ill-conditioned behaviour.[31] Another frequent occurrence is that the convergence of the force constants terminates at a stage of oscillation. This behaviour has been shown to correspond to a set of complex solutions. Such complex solutions may arise as a result of simplifying assumptions made in the force field to make the problem tractable. It has been shown, however, that the oscillations occur about the real components of the converged set. Finally, and perhaps most disturbing of all, it has been found that in certain cases slightly different initial guesses lead to a different set of converged solutions.[32] Various criteria have been described to test the validity of the final answers, but the uncertainty in the

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[27] D. A. Long and E. A. Seibold, *Trans. Faraday. Soc.*, 1960, **56**, 1105.

[28] D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *J. Chem. Phys.*, 1957, **27**, 43.

[29] J. Overend and J. R. Scherer, *J. Chem. Phys.*, 1960, **32**, 1289.

[30] D. A. Long, R. B. Gravenor, and M. Woodger, *Spectrochim. Acta*, 1963, **19**, 937.

[31] D. A. Long and R. B. Gravenor, *Spectrochim. Acta*, 1963, **19**, 961.

[32] Joan Aldous and I. M. Mills, *Spectrochim. Acta*, 1962, **18**, 1073.

reliability of the distortional co-ordinates remains a major obstacle to progress in the interpretation of absorption intensities.

Once the force field has been deduced and hence the form of the normal co-ordinates determined, or approximated, the next step is to visualise what the resulting $\partial\mu/\partial Q_j$ mean. The molecular dipole gradient will generally be difficult to visualise and to utilise. Since physical chemists almost invariably find life a great deal easier if they can translate molecular properties into comparatively simple, directed, and more-localised properties, the next step is to find a suitable set of assumptions that will yield the desired simplifications. The obvious assumptions are those that will decompose the molecular properties into the sum of a set of bond properties, and are generally chosen as:

(*a*) the stretching of a bond by dr produces a change of dipole moment along the bond of $(\partial\mu/\partial r)\,\mathrm{d}r$;

(*b*) the deformation of a bond through an angle dθ produces a dipole change $(\partial\mu/\partial\theta)\mathrm{d}\theta$ perpendicular to the bond and in the plane of movement;

(*c*) changes in one bond do not result in changes in another bond, except when this is geometrically necessary.

The test of the validity and usefulness of these assumptions is whether any or all of the following criteria are found to hold, and, if not, whether anything positive can be deduced from the discrepancies.

(i) Values of the deduced bond moments and gradients in different molecules are comparable.

(ii) Values of given gradients and moments derived from different symmetry classes of the same molecule are equal.

(iii) The perpendicular gradients to any bond are negligible.

(iv) Values of the bond dipoles derived are comparable with the static dipoles as measured by other methods.

TABLE 2. *Effective bond dipole moments and derivatives for* C–H *bonds.*

Compound	Symmetry Class	Dipole-moment derivative (D/Å)	Effective bond dipole moment (D)	Measurement	Ref.
CH_4	f_2	±0·83	∓0·37	W–W	33
CH_3D, CH_2D_2 CD_3H	a_1,e	−0·61	0·33	W–W	34
C_2H_4, $C_2H_2D_2$ C_2D_4	b_{2u}	±0·26	∓0·42	W–W	35
	b_{3u}	∓0·23	∓0·60		
	b_{1u}	0·67			

[33] I. M. Mills, *Mol. Phys.*, 1958, **1**, 107.

[34] R. E. Hiller and J. W. Straley, *J. Mol. Spectroscopy*, 1960, **5**, 24.

[35] R. C. Golike, I. M. Mills, W. B. Person, and B. L. Crawford, *J. Chem. Phys.*, 1956, **25**, 1266.

TABLE 2.—*continued.*

Compound	Symmetry Class	Dipole-moment derivative	Effective bond dipole moment	Measure-ment	Ref.
C_2H_2	Σ_u^+	0·8		D	36
	Π_u		1·05		
C_2D_2	Σ_u^+	0·78		W–W	37
	Π_u		0·89		
C_2H_2	Σ_u^+	0·87		W–W	37
	Π_u		1·05		
C_2HD	$\left.\begin{matrix}\Sigma^+\\ \Pi\end{matrix}\right\}$	0·79(H)	0·90(H)	W–W	37
		0·78(D)	0·92(D)		
C_2H_6	a_{2u}	$\pm 1·24$	$\mp 0·23$	W–W	40
	e_u	$\pm 0·75$	$\mp 0·26$		
C_6H_6	e_{1u}	$+0·45$	$-0·31$	W–W	38
	a_{2u}		$-0·61$		
CH_3Cl	a_1	$+1·00$	$+0·17$	W–W	39
	e	$+0·24$	$-0·45$		
CH_3Br	a_1	$+0·98$	$+0·27$	W–W	39
	e	$+0·19$	$-0·48$		
CH_3I	a_1	$+0·73$	$+0·42$	W–W	39
	e	$+0·13$	$-0·46$		
NH_3*	a_1	0·61	1·04	W–W	41
	e	0·16	0·52		
PH_3	a_1	1·2		W–W	41
	e	0·8			
SiH_4, SiD_4	f_2	$\pm 1·23$	$\mp 1·58$	W–W	42
	f_2	$\pm 1·44$		W–W	43

W–W, Wilson–Wells method. D, dispersion method.

* Introduction of $\partial\mu_{u.p.}/\partial\alpha$ and assumption of complete bond following leads to: a_1, $\mu_{u.p.} = 0·74$D and $\mu_{NH} = -0·65$D; e, $\mu_{u.p.} = 0·70$D and $\mu_{NH} = -0·68$D.

It can be seen from Tables 2 and 3 that criteria (i), (ii), and, hence, (iv) certainly do not hold, though there is a certain amount of consistency between the gradients and dipoles for similar molecules, and some trends are apparent. The situation is particularly bad for carbon–hydrogen bonds. It is from an analysis of these inconsistencies that a great deal of useful information and knowledge of molecular structure has been gleaned. The first step in such an analysis must be a consideration of the four major reasons for the failure of the model.

[36] R. L. Kelly, R. Rollefson, and B. S. Schurin, *J. Chem. Phys.*, 1951, **19**, 1595.

[37] D. F. Eggers, I. C. Hisatsune, and I. Van Alten, *J. Phys. Chem.*, 1955, **59**, 1124.

[38] H. Spedding and D. H. Whiffen, *Proc. Roy. Soc.*, 1956, *A*, **238**, 245.

[39] A. D. Dickson, I. M. Mills, and B. L. Crawford, *J. Chem. Phys.*, 1957, **27**, 445.

[40] I. M. Nyquist, I. M. Mills, W. B. Person, and B. L. Crawford, *J. Chem. Phys.*, 1957, **26**, 552.

[41] D. C. McKean and P. N. Schatz, *J. Chem. Phys.*, 1956k **24**, 316.

[42] D. F. Ball and D. C. McKean, *Spectrochim, Acta*, 1962, **18**, 1019.

[43] I. W. Levin and W. T. King, *J. Chem. Phys.*, 1962, **37**, 1375.

TABLE 3. *Effective bond dipole moments and derivatives for X–F bonds.*

Compound	Symmetry class	Dipole moment derivative (D/Å)	Effective bond dipole moment (D)	Measurement	Ref.
CF_4	f_2	5·99 or 3·71	1·11 or 2·98	D	44
		4·9 or 3·4	1·1 or 2·4	W–W	45
CH_3F	a_1	4·0		W–W	46
CF_3Br	a_1	+8·1	+2·8	W–W	47
	e	+4·1	+0·5 (ν_5) +1·1 (ν_6)		
C_2F_6	a_{2u}	+3·4	+2·2	W–W	48
	e_u	+3·8	+1·6 +0·7		
C_6F_6	e_{1u}	+5·0	1·6	W–W	49
p-$C_6H_4F_2$ p-$C_6D_4F_2$	b_{1u}	+6·5	1·3	W–W	50
p-$C_6H_2F_4$	b_{1u}	+5·2		W–W	50
BF_3	e'	±4·0 or ∓6·1	±2·6 or ∓0·9	W–W	51
	a_2''		1·7		
NF_3*	a_1	+1·5 to +2·0 or 3·3	+0·9 to +1·2 0 to 0·3	W–W	52
	e	*ca.* +4·7			
SF_6	f_{1u}	3·85	2·65	W–W	53
SiF_4	f_2	3·3 or 7·5	3·3 2·3	W–W	53

D, dispersion method. W–W, Wilson–Wells method.

* Introduction of $\partial\mu_{u.p.}/\partial\alpha$ and assumption of complete bond following for the a_1 class leads to: $\mu_{u.p.} \sim 1·7$ or 1·2D; $\mu_F \sim 1·1$D.

(*a*) In criterion (i) it is implicitly assumed that the charge distribution in the bond XY is always the same and always alters in the same manner. It is common experience that all XY bonds do not have the same chemical reactivity, apart from steric effects, and since chemical reactivity is intimately related to the valence-shell electronic structure of the bonds, this contradicts the above assumption. Furthermore, all XY bonds do not have

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[44] B. Schurin, *J. Chem. Phys.*, 1959, **30**, 1.

[45] P. N. Schatz and D. F. Hornig, *J. Chem. Phys.*, 1953, **21**, 1516.

[46] G. M. Barrow and D. C. McKean, *Proc. Roy. Soc.*, 1952, *A*, **213**, 27.

[47] W. B. Person and S. R. Polo, *Spectrochim. Acta*, 1961, **17**, 101.

[48] I. M. Mills, W. B. Person, J. R. Scherer and B. Crawford, *J. Chem. Phys.*, 1958, **28**, 851.

[49] D. Steele and D. H. Whiffen, *J. Chem. Phys.*, 1958, **29**, 1194.

[50] D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, 1960, **56**, 177.

[51] D. C. McKean, *J. Chem. Phys.*, 1956, **24**, 1002.

[52] P. N. Schatz and I. W. Levin, *J. Chem. Phys.*, 1958, **29**, 475.

[53] P. N. Schatz and D. F. Hornig, *J. Chem. Phys.*, 1953, **21**, 1516.

the same bond length, but this in turn depends on the environment of X and Y. Thus the CH bond decreases in length as the local hybridisation at the carbon atoms takes on less *p* and more *s* character. Thus, this is a further manifestation of the variation of the electronic structure of the bond between two given atoms.

(*b*) The effect of lone-pair electrons on the dipole change during a vibration is ignored. As the molecule vibrates, the hydridisation of the orbitals will generally change and consequently affect the infrared absorption. Burnelle and Coulson[62] have shown, using wave-mechanical

TABLE 4. *Effective bond dipole moments and derivatives for various bonds.*

Compound	Symmetry class	Bond	Dipole-moment derivative (D/Å)	Effective bond dipole moment (*D*)	Measurement	Ref.
C_6H_6	e_{1u}	C–C	0·0		W–W	38
$C^{16}O^{18}O$	Σ	C=O	5·79		W–W	54
CO_2	Σ_u^+	C=O	6·0		W–W	16
	Σ_u^+	C=O	5·85		W–W	17
	Π_u	C=O		1·33	W–W	13
	Π_u	C=O		1·33	C-o-G	12
$(CN)_2$	Σ_u	C≡N	0·585		W–W	55
	Π_u	C≡N		1·2		
$^{12}CN^{13}CN$	Σ	^{12}C≡N	0·595		W–W	56
		^{13}C≡N	0·605			
ClCN	Σ	C≡N	0·3 to 0·7		W–W	57
	Π	C≡N		1·4		
BrCN	Σ	C≡N	0·5 to 0·8	1·3	W–W	58
	Π	C≡N				
CH_3CN	a_1	C≡N			W–W	59
	e			1·3		
HCl	Σ	H–Cl	1·21		W–W	60
HCN }	Σ	C≡N	0·66		W–W	61
DCN }	Π	C≡N		1·8		
SO_2	b_1	S=O	4·17		W–W	33
	a_1	S=O	±2·0 or ±4·3	∓1·3 ±1·2		

W–W, Wilson–Wells method. C-o-G, curve-of-growth method.

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[54] D. F. Eggers and C. B. Arends, *J. Chem. Phys.*, 1957, **27**, 1405.
[55] T. Miyazawa, *J. Chem. Phys.*, 1958, **29**, 421.
[56] J. W. Schultz and D. F. Eggers, *J. Mol. Spectroscopy*, 1958, **2**, 113.
[57] R. W. Hendricks and D. F. Hornig, see ref. 58.
[58] D. F. Hornig and D. C. McKean, *J. Phys. Chem.*, 1955, **59**, 1133.
[59] A. V. Golton, D.Phil. Thesis, Oxford, 1953.
[60] S. S. Penner and D. Weber, *J. Chem. Phys.*, 1953, **21**, 649.
[61] G. E. Hyde and D. F. Hornig, *J. Chem. Phys.*, 1952, **20**, 647.
[62] L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.*, 1957, **53**, 403.

calculations of Ellison and Shull[63] and Higuchi,[64] that the lone-pair contribution to the molecular-dipole change associated with the bending vibrations of H_2O and NH_3 is nearly as large as the contribution resulting from the bond deformations. Thus, for H_2O, $\partial\mu_{\mathrm{L}}/\partial\alpha \sim 1{\cdot}41$D and $\partial\mu_{\mathrm{B}}/\partial\alpha \sim -2{\cdot}13$D, where μ_{L} and μ_{B} are the lone-pair and bonding contributions, respectively, to the molecular dipole. That this must be the case can be seen from the fact that the lone-pair contribution to the molecular dipole is calculated to be 1·69D for H_2O. In the deformed state where the oxygen and hydrogen atoms are collinear, the lone-pair contribution must be zero, by symmetry.

Several of the discrepancies between the effective bond moments given in Tables 2, 3, and 4 can be explained by similar reasoning to the above. Thus in boron trifluoride, which in its equilibrium position is planar, there is a vacant *p* orbital associated with the boron atom and perpendicular to the plane of the molecule. During the symmetrical, out-of-plane, bending vibration, rehybridisation of the B–F bonding electrons at the boron atom results in electron-flow into an orbital on the opposite side of the original atomic plane to the fluorine atoms [see Fig. 3(*a*)]. This makes the fluorine atoms appear to carry less negative charge than they actually do. In the e' class, the F–B–F angular deformation cannot result in electron flow into the vacant p_z orbital. In agreement with this reasoning, the effective BF dipole, as deduced from the a_2'' class, is only 1·7D compared with 2·6D, as deduced from the e' class. In the out-of-plane CH deformation of benzene, a similar effect occurs in the a_{2u} out-of-plane deformation. The p_z orbital is fully occupied in this case, but rehybridisation at the carbon atom takes place in the form of *s* character being introduced in the p_z orbital (Fig. 3(*b*)]. That this must be so, is readily apparent from the fact that when the HCH angles are deformed to 108°, the carbon hybridisation must be sp^3 compared with sp^2 for the planar configuration. The effect

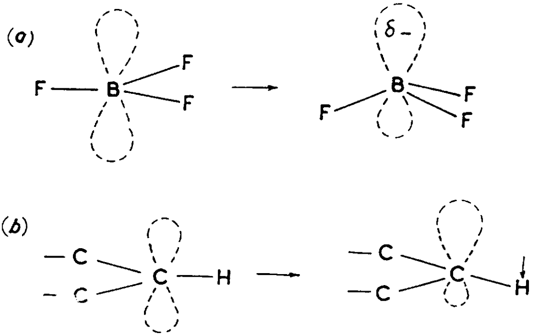

FIG. 3. *Electron rehybridisations in the p_z orbitals during the transitions of symmetry: (a) a''_2 of boron trifluoride; (b) a_{2u} of benzene.*

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[63] F. O. Ellison and H. Shull, *J. Chem. Phys.*, 1953, **23**, 2348.
[64] J. Higuchi, *J. Chem.*, 1956, **24**, 535.

once again is to make the substituent appear less negative. Since the hydrogen atoms in benzene are known to be at the positive end of the CH dipole,[65] the numerical value of the effective dipole should be greater for the a_{2u} class than for the in-plane e_{1u} class. The observed values are 0·61D and 0·31D, respectively. Clearly an adequate theory of infrared intensities must incorporate terms of the nature of $\partial\mu_{p_z}/\partial\alpha$.

Coulson and Stephen[66] have shown that the variations in the deduced effective dipoles in benzene, acetylene, and ethylene are compatible with reasonable degrees of rehybridisation and bond following (see below). However, they were unable to deduce the relative contributions of the two effects.

(*c*) Hybridisation changes can also occur as a bond stretch. If we consider the CH stretching in methane, and assume that in the extreme case we have a CH_3 radical and an H atom, then it can be seen that rehybridisation of the orbitals around the carbon atom must have occurred. The configuration of the CH_3 radical is still uncertain, but it seems probable that it is planar. In this case, the hybridisation at the carbon atom will be sp^2 as compared with sp^3 in CH_4. Though in both the extreme cases *i.e.*, those of the unperturbed CH_4 molecule and of a CH_3 radical and an H atom, there is no total dipole moment, it seems necessary to assume that there is a dipole gradient during the vibrational motion. This gradient can be expected, on the above grounds, to be different from that in, say, the vibrational motion in which the stretching of one CH bond is out of phase with the remaining two (ν_3 of symmetry class f_2).

(*d*) A bond is usually thought of as being directed along the line connecting the bonded atoms. This is frequently a false picture, particularly for vibrationally distorted configurations. Wave-functions are not usually localised in one bond. Indeed, the orthogonality of the wave-functions generally forbids this. By their delocalisation, these wave-functions are not directly related to the usual conception of chemical bonds. Burnelle and Coulson[62] transformed the accurate SCF–LCAO wave-functions for H_2O and NH_3 so that the resulting wave-functions satisfied the following conditions: (*a*) that they were orthogonal; (*b*) that the orbitals associated with identical bonds should be equivalent; and (*c*) that the lone-pair orbitals should contain only orbitals of the central atom. The resulting picture of the molecular orbitals showed that the hybrid orbitals at the central atom are not in general directed along the bond direction. This means that the bonds may be considered to be bent and to have dipole gradients perpendicular to the internuclear axis. The individual contributions to the dipole moment of H_2O are, for an interbond angle of 105°, $\mu_L = 1{\cdot}69$D, $\mu_B = 0{\cdot}20$D, and $\mu_B{}^Y = -0{\cdot}37$D, where μ_L, μ_B, and $\mu_B{}^Y$ are the contributions due to the lone-pair electrons, the

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[65] (*a*) R. P. Bell, H. W. Thomspon, and E. E. Vago, *Proc. Roy. Soc.*, *A*, **192**, 498; (*b*) A. R. H. Cole and H. W. Thompson, *Proc. Roy. Soc.*, 1951, *A*, **208**, 341.

[66] C. A. Coulson and M. J. Stephen, *Trans. Faraday Soc.*, 1957, **53**, 272.

bond electrons in the direction of the internuclear axis, and the bond electrons in a direction perpendicular to the internuclear axis, respectively. If the HOH angle is deformed, the resulting molecular dipole gradient of $-0{\cdot}72$D/radian is derived from the following contributions: $\partial\mu_L/\partial\alpha = 1{\cdot}41$ D/Radian; $\partial\mu_B{}^Z/\partial\alpha = -0{\cdot}20$ D/Radian; and $\partial\mu_B{}^Y/\partial\alpha = 1{\cdot}93$ D/Radian. The transverse moment is very sensitive to the inter-bond angle, and its derivative is the major contributing term to the absorption intensity.

An analysis of the absolute absorption intensities of the infrared bands of 1,2,4,5-tetrafluorobenzene[50] showed that the dipole gradient, $\partial\mu/\partial r_{CF}$, lies along the internuclear axis, within the experimental error. However, the asymmetry of the CF bond in this compound is not very pronounced, and it is not unreasonable to expect the above result.

The Polarity of the Dipole Gradients.—According to equation (3), the absorption intensity is proportional to the square of the dipole gradient. In the preceding section it has been assumed that in solving for the gradient, the sign of the square root of the intensity is known. In fact, the question of these signs introduces what is frequently a serious uncertainty into the interpretations. The seriousness of this problem can be appreciated from the fact that, if there are n fundamental vibrations in a given symmetry class, then there are 2^n possible ways of choosing the sign combinations, leading to 2^n distinct solutions for the bond parameters. Isotopic substitution should leave the dipole gradients unchanged, whilst changing the form of the vibrational modes. The sets of dipole gradients with respect to bond co-ordinates—or with respect to combinations of the co-ordinates in the form of symmetry co-ordinates—will not all be consistent with the observed intensities of the other isotopic system. Generally, there are rarely more than three sets which yield acceptable values for the intensities of the other isotopic system. A choice between sets acceptable by the above criterion is usually made on the basis of lack of credulity of the authors to certain of the derived gradients. When no isotopic data existed, sign choices have often been made on the basis of one set giving bond gradients and dipoles which were in line with values for similar molecules. Clearly this is not an acceptable criterion, especially as the aim has usually been to discover if the gradients and dipoles were indeed comparable for bonds of a given type in similar molecules. Blatant cases of this practice have been excluded from the Tables.

As an example of the above technique, the CN dipole gradient for cyanogen, derived from the infrared-active C$\equiv$N stretching vibration of ^{12}CN^{12}CN, is compared in Table 5 with those derived from the "almost symmetric" CN and CC stretching vibrations of ^{13}CN^{12}CN.[56] Owing to the presence of normal cyanogen in the heavy-isotopic system, the intensity of the antisymmetric mode was not measured. In this case it is very clear that the $\partial\mu/\partial Q$ values must have the same sign.

Occasionally the sign of the square root in equation (3) can be deter-

TABLE 5. *Dipole-moment derivatives for cyanogen* D/Å

Dipole-moment derivative	$(^{12}CN)_2$	Relative signs for $\partial\mu/\partial Q$ values	$^{12}CN^{13}CN$
$\partial\mu/\partial r_{(CN)_1}$	±0·585	same	±0·595
		different	∓0·416
$\partial\mu/\partial r_{(CN)_2}$	∓0·585	same	∓0·607
		different	±0·718
$\partial\mu/\partial r_{(C-C)}$	zero, by symmetry	same	∓0·0003
		different	∓0·107

mined from vibration–rotation interaction studies. Thus Hermann and Wallis[67] were able to show that, for a diatomic molecule, the ratio of intensities of corresponding rotational absorption lines in P and R branches is proportional to $(1 + 4\gamma\theta J)J$, where $\gamma = 2B_e/\nu_e$, $\theta = [\mu_0/(\partial\mu/\partial r)]1/r_e$, and J is the rotational quantum number of the initial state. B_e is the rotational constant for the equilibrium bond length, r_e; μ_0 is the molecular dipole; and $\partial\mu/\partial r$ is the dynamic dipole gradient. If the sign of μ_0 is known then the sign of the dipole gradient can be deduced. In this way they were able to show that $\partial\mu/\partial r$ for HCl has the same sign as μ_0. Clearly, it is also possible to use the above technique to evaluate the ratio of the magnitude of the gradient to the static dipole. Thus $\mu/(\partial\mu/\partial r)r_e$ for LiH has been determined as −1·8 ± 0·3D.[68] Clearly a prerequisite of this technique is the existence of an equilibrium molecular dipole. The Hermann-Wallis theory has been extended to the case of linear polyatomic molecules[69] (group $C_{\infty v}$), but no application to intensity interpretation has yet been made.

Bell, Thompson, and Vago, and Cole and Thompson, have shown[65] that the intensities of the out-of-plane deformations in various alkyl- and halogen-substituted benzenes indicate that the effective CH dipole is of opposite sign to the effective halogen dipole. As it is reasonably certain that the halogen atom is at the negative end, then this implies that the hydrogen atom is at the positive end of the CH dipole in benzenes in the out-of-plane deformations. Since out-of-plane deformations have the effect of making the dipoles appear less positive, the hydrogen atom must also be at the positive pole of the static bond.

Interaction between two vibration–rotation bands can occur if the symmetry of the vibrations and of a principal rotation axis bear a certain simple relationship to one another. Specifically, the Coriolis force on each atom is of magnitude $2m_a v_a w \sin\phi$, where m_a is the mass of the atom, w is the angular velocity of the co-ordinate system with respect to a fixed co-ordinate system, v_a is the velocity of atom "a", and ϕ is the angle between the axis of rotation and the direction of v_a. The force is directed at right-angles to the direction of v_a and to the axis of rotation. If the forces on the

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[67] R. Hermann and R. F. Wallis, *J. Chem. Phys.*, 1955, **23**, 637.

[68] T. C. James, W. G. Norris, and W. Klemperer, *J. Chem. Phys.*, 1960, **32**, 728.

[69] G. A. Gallup, *J. Chem. Phys.*, 1957, **27**, 1338.

atoms constituting the molecule, which arise from a vibration, j, and from rotation about a specific axis, m, have the same symmetry as a second vibration, k, which is not too far removed in frequency from j, then the two vibrations will interact. The effect of this interaction on the vibrational frequencies is to make the P and R rotational band spacings different from one another (apart from the small effect arising from centrifugal distortion). This Coriolis interaction has been mentioned previously in connection with the dependence of the ζ constants on the potential constants. In addition to the frequency effect, the intensities are also altered. In the approximation of no vibration–rotation interaction, the lines in the P and R branches, arising from transitions from the same initial state have equal strengths. The effect of the Coriolis interaction is to increase (or decrease) the R-line intensities of the higher-frequency band, and also the P-line intensities of the lower band, whilst decreasing (or increasing) the intensities of the other $\Delta J = \pm 1$ lines. Which, in fact, occurs, depends on the sing of $\zeta_{jk}{}^{z}\,(\partial\mu/\partial Q_j)^x(\partial\mu/\partial Q_k)^y$, where the j and k subscripts specify the two vibrations. The sign of ζ_{jk} is generally determinable, and hence from the intensity asymmetry of the bands, the relative signs of the two dipole transitions can be deduced.[70] This new technique has considerable promise.

The Effect of Change of State on Intensities.—Recently there has been a renewed interest in the intensities of absorption bands in condensed phases. Until the last two or three years, it was believed that intensity changes arising from intermolecular interactions would be small, except where structural changes took place or where definite bonds were formed between molecules. Examples of these special cases are the crystallisation of *trans*-dichloroethane from a mixture of the *trans*- and *gauche*-forms, and the formation of intermolecular hydrogen bonds in hydroxyl-containing compounds. Considerable theoretical work has been carried out to evaluate the magnitude of the intensity changes in the absence of appreciable intermolecular interactions.[71–75] The basic theory is encompassed in the equation[71,72]

$$\frac{\Gamma_{\text{liq}}}{\Gamma_{\text{gas}}} = \frac{(n^2 + 2)^2}{9n}, \tag{7}$$

which is derived for an oscillating dipole in a spherical cavity in a medium of refractive index n. This equation implies that the intensities ought always to be greater in a condensed phase than in the gaseous phase. Experimental work, until very recently, was restricted to isolated absorption bands—isolated in the sense of a single band of a certain molecule. Equation (7) and its refined forms have met with very limited success.

[70] I. M. Mills, unpublished work.
[71] N. Q. Chako, *J. Chem. Phys.*, 1934, **2**, 644.
[72] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, 1955, **23**, 2376.
[73] J. van Kranendonk, *Physica*, 1957, **23**, 825.
[74] A. D. Buckingham, *Proc. Roy. Soc.*, 1960, *A*, **255**, 32.
[75] L. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

Intensity data now exist for all infrared active bands of benzene[33,76–78] in vapour, liquid, and solid phases. The results are very disturbing. The intensity changes are far greater than can be accounted for by dielectric changes or by the expected magnitudes of intermolecular perturbations. Similar results have been reported for ethylene.[79] The results for benzene are shown in Table 6. These results pose a fascinating theoretical problem on which no headway has been made at the present time, and which is certain to attract considerable attention from theoretical chemists and physicists in the future.

TABLE 6. *Absolute intensities of benzene transitions in various phases* ($10^3 cm^2$/mole).

Band (cm.$^{-1}$)	Γ_g	Γ_l	Γ_s
3060	1·95	1·45	0·65
1480	0·878	1·29	2·56
1036	0·850	1·11	1·69
673	12·95	14·1	13·6

Applications of Absolute Intensity Measurements to Determination of Chemical Structure.—The intensities of some absorption bands characteristic of certain groupings, such as those generally associated with the stretching of —C≡ N, —C = O, —C–H (in hydrocarbons), and —OH bonds, have been correlated in an empirical manner with the structure of the attached group. In many cases it is possible to deduce the number of absorbing centres in an unknown molecule. This aspect of intensity measurement has been thoroughly reviewed by T. L. Brown.[80] It is interesting that such empirical correlations actually do exist. The so-called characteristic group vibrations are rarely confined to one bond, and the mode may change quite drastically for small structure changes without the frequency being much affected. It is likely that the main reason for the success of these empirical correlations is that the groups studied usually have very large dipole gradients associated with their stretching motions so that participation in the vibration by other parts of the molecule is relatively unimportant. Even so, these correlations imply that the stretching gradients of these groups are reasonably constant. Very few detailed studies of molecules involving these groupings have been carried out at present.

As a consequence of the interpretational difficulties of intensity measurements, absorption intensities have been little used in elucidating molecular structure, apart from the empirical approach mentioned above. The following examples show that, in special circumstances, absolute intensity measurements can be used in structure determinations.

[76] D. A. Dows and A. L. Pratt, *Spectrochim. Acta*, 1962, **18**, 433.
[77] I. S. Hisatsune and E. S. Jayadevappa, *J. Chem. Phys.*, 1960, **32**, 565.
[78] J. L. Hollenberg and D. A. Dows, *J. Chem. Phys.*, 1962, **37**, 1300.
[79] G. M. Wieder and D. A. Dows, *J. Chem. Phys.*, 1962, **37**, 2990.
[80] T. L. Brown, *Chem. Rev.*, 1958, **58**, 581.

Until recently, magnesium dicyclopentadienyl was believed to be an ionic salt. However, its solubility in benzene was inconsistent with this belief. An analysis of its vibrational spectrum indicated a marked similarity in its vibrational modes to ferrocene.[81] If it is principally ionic, then the absorption intensity of the antisymmetric ring–metal stretching vibration ought to be well represented by the ionic model Fig. 4, where the rings and the metal atom are represented by point charges. The absolute intensity calculated for this model was approximately seventy times as large as the observed value.[81] This can only be explained on the basis of principally covalent bonding. Magnesium dicyclopentadienyl, or magnacene, is the first established covalently bonded sandwich compound of a non-transition element.

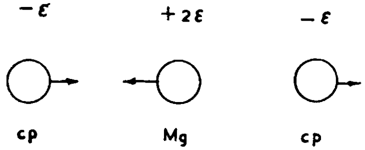

FIG. 4. *An ionic model for the antisymmetric stretching vibration of magnesium dicyclopentadienyl* ($MgCp_2$)

The vibrational stretching frequencies of cyanide bonds are outstanding in their insensitivity to the presence of other groups. Furthermore, there is little coupling between the stretching vibrations of cyanide groups attached to a common atom. Thus, in maleonitrile, only one $C \equiv N$ stretching frequency is observed in the infrared and Raman spectra,[82] and in sulphur dicyanide, the symmetric and antisymmetric modes are at 2184 and 2179 cm.$^{-1}$, respectively, only 5 cm.$^{-1}$ apart.[83] This indicates that the electronic wave-functions are highly localised in the bonds themselves. The stretching gradients for cyanides are all of the same order of magnitude. The only reported absolute intensity measurements on a dicyanide are those on cyanogen.[56] Rather surprisingly, the stretching gradients derived from the symmetric stretching modes of $^{12}CN^{13}CN$ and from the antisymmetric mode of $^{12}CN^{12}CN$ are in excellent agreement. These facts have been used as the basis for a determination of the angle between the cyanide groups in the dicyanamide ion, $N(CN)_2^-$.[84] Assuming that the bond-moment hypothesis holds for this ion, then it is easy to show that the ratio of the intensities of the antisymmetric to the symmetric stretching modes is given by

$$\frac{\Gamma_{as}}{\Gamma_s} = \frac{\sin^2\theta/2}{\cos^2\theta/2},$$

where θ is the inter-bond angle. A fortuitous splitting of the antisymmetric

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[81] E. R. Lippincott, J. Xavier, and D. Steele, *J. Amer. Chem. Soc.*, 1961, **83**, 2262.

[82] F. Halverson and R. J. Francel, *J. Chem. Phys.*, 1948, **17**, 694; K. W. F. Kohlrausch and G. P. Ypsilanti, *Z. phys. Chem.*, 1934, **b29**, 274.

[83] D. A. Long and D. Steele, *Spectrochim. Acta*, 1963, **19**, 1731.

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mode occurs as a result of Fermi resonance. This allowed the relative intensities of the two cyanide bands to be measured with reasonable precision. The value derived for the inter-bond angle was 145°. The original measurements were made in potassium bromide media. According to the dielectric theories of the effects of phase on intensities, the relative intensities should be unaffected by phase changes. However, in view of the previously noted influences on the bands of benzene and ethylene, the measurements have been repeated in aqueous solution.[85] The two results agree well.

Other Aspects and Present Trends.—A certain amount of research has been devoted towards the evaluation of higher-order derivatives of the dipole moment in suitable systems—generally diatomic systems.[86–90] An interesting special case was the interpretation of the intensities of certain combination bands of benzene arising from the out-of-plane motions of the C–H bonds.[91] These bands, which are characteristic of benzene and substituted benzenes, occur in the region 2000—1500 cm.$^{-1}$. It was shown that the intensities of these bands of C_6H_6, C_6D_6, and p-$C_6H_4D_2$ could be interpreted satisfactorily using only one parameter. This parameter, which is the second derivative of the dipole moment with respect to the out-of-plane deformation of the jth bond, $\partial^2\mu/\partial\gamma^2{}_j$, has the value 1·10D.

Several important theorems concerning the vibrational frequencies and intensities of isotopically related systems have been advanced by B. Crawford.[92,93] The most important of these shows that the function $\Sigma\Gamma/\nu_{\rm a}$ is invariant to isotopic substitution when the summation is over all vibrational bands in a given symmetry class. $\Gamma_{\rm a}$ is the absorption intensity of the band centred at a frequency $\nu_{\rm a}$. This theorem, when applicable, provides a very useful test on measured intensities. A typical set of results is shown below for C_2H_6 and C_2D_6[40]

	C_2H_6	C_2D_6
class	2·810 ± 0·024	2·942 ± 0·140 cm.^{3}/mole.
class	0·737 ± 0·008	0·775 ± 0·037 cm.^{3}/mole.

Le Fèvre and Rao,[94,95] Whiffen,[96] and Illinger and Smyth[97] have shown

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that the atomic polarisation of a molecule is related to its infrared absorption by the relationship

$$P_{\mathrm{A}} = \frac{Nc}{3\pi^2}\sum_j \frac{\Gamma_j}{\nu_j}\,.$$

The significance of the atomic polarisation can be understood by considering the effect of an applied oscillating electric field on a molecular gas. The induced and the permanent dipole moments align, as far as permitted by the thermal motions, against the applied field, thus reducing the effective field. The molecular polarisation is defined as the total dipole moment per unit volume, parallel to the field arising from the above contributions. As the field frequency is decreased, the total molecular polarisation decreases in certain frequency ranges. At very high oscillating frequencies, only the electrons are mobile enough to follow the field changes. In the infrared frequency range, the nuclei become able to follow the field, and, finally, at still lower frequencies, the molecular dipoles are able to align with the field (see Fig. 5). Clearly it is reasonable to consider the molecular polarisation as consisting of three parts, the electron and the atomic induced polarisations, and that arising from the permanent dipoles. (P_{E}, P_{A} and P_0).

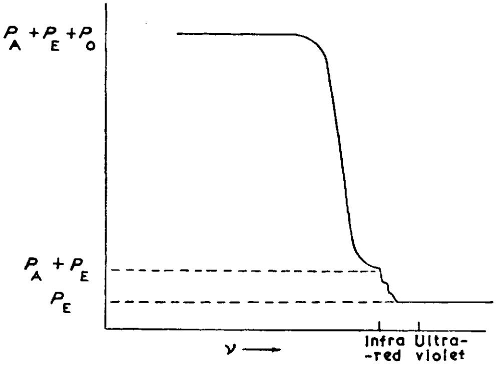

FIG. 5. *The variation of molecular polarisability with frequency.*

Values for the atomic polarisation of non-polar molecules, as determined from refractive-index and dielectric-constant studies (see *e.g.*, ref. 94), agree very well with those deduced from intensity measurements. Some typical results are shown in Table 7.

In the case of polar molecules, the discrepancies are generally much greater, but it is very likely that these discrepancies arise from difficulties in determining the total polarisability at frequencies such that only P_0 is measured.

It is clear from preceding sections that any successful theory of absorption intensities must incorporate terms involving derivatives of the dipole

TABLE 7.

Compound	P_A Infrared studies (cm.^{3})	P_A Dielectric studies (cm.^{3})	Compound	P_A Infrared studies (cm.^{3})	P_A Dielectric studies (cm.^{3})
BF_3	2·19	2·81	C_2H_6	0·12	0·09
CF_4	2·89	2·86	C_6H_6	0·73	0·80
CH_4	0·11	0·08	SiF_4	4·82	5·46
C_2H_2	1·28	1·27	SF_6	5·07	5·20

contribution of lone-pair electrons, rehybridisable orbitals, conjugated systems, etc., with respect to bond deformations. McKean and Schatz[41] and Hornig and McKean[58] have utilised terms involving the lone-pair electrons. Sverdlov[98] has developed a complete second-order bond-moment theory which incorporates terms such as $\partial\mu_i/\partial R_j$, where the i and j subscripts refer to different bonds. In this way, instead of single terms being determinable, only combinations of terms such as $(\partial\mu/\partial\theta_1)_{(1)} - (\partial\mu/\partial\theta_1)_{(4)}$ can be evaluated. An appreciation of these results necessitates a judicious assessment of the relative importance of the additional terms.

Much of the present experimental data cannot be satisfactorily treated, owing to the sensitivity of the modes to uncertainties in the force fields. Further developments in gas-phase intensities must come through the deduction of satisfactory force fields and the use of treatments such as those of Hornig and McKean and of Sverdlov.

It is usually the unexpected results which prove to be the most fascinating and the most rewarding. The changes of intensities with phase changes are certainly the most surprising results during recent years of the field reviewed. It is too early to even surmise the importance of an interpretation, but it must modify the present concepts of condensed phases.

In conclusion, much has been achieved in the interpretation of infrared intensities, but many important problems remain to be solved.

I sincerely thank Dr. I. M. Mills for describing his work on the determination of the sign of dipole gradients from Coriolis interaction studies, prior to its publication.

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