The Scope and Limitations of Infra-red Measurements in Chemistry.

THE TILDEN LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY AT BURLINGTON HOUSE ON JANUARY 20TH, 1944, AND AT THE ROYAL TECHNICAL COLLEGE, GLASGOW, ON FEBRUARY 18TH, 1944.

By H. W. THOMPSON.

THE regulations of the Tilden lectures lay down that they shall deal with progress in some field of pure or applied chemistry. It seemed to me that the time was opportune to present an account of infra-red measurements, since not only have considerable advances been made in their application to many problems in pure chemistry, but also their significance in industrial work is rapidly becoming widely appreciated.[1] It seems probable that infra-red analysis will soon rank highly for routine and research work in organic chemistry, where its usefulness may at least equal that of ultra-violet spectroscopy.

My subject is singularly fitting for another reason. One of the problems studied by Sir William Tilden was the decomposition of terpenes by heat. He found that when turpentine vapour was passed through a heated iron tube, a mixture of gaseous and condensable hydrocarbons was formed, the analysis of which was difficult. His process has been described as the forerunner of the modern methods of cracking petroleum, and it is in just this field that infra-red spectroscopy has been applied so successfully in recent years. Isoprene was also found by Tilden among the decomposition products of terpenes, and without fully realising what had happened, he observed its polymerisation to form a synthetic rubber. In this field of polymeric chemistry, too, infra-red analysis is proving very valuable.

Comparatively few laboratories in this country have carried out work in the infra-red, and I must therefore state at once that in spite of many striking successes, the use of this technique has certain limitations. For these reasons, it seemed to me better to survey the experimental and theoretical principles of the subject, with typical applications, rather than to deal with more advanced applications to some special group of compounds such as hydrocarbons or polymers of high molecular weight, or with other detailed problems of molecular structure. The topics which I shall discuss fall under two headings, first those dealing with molecular structure and the deduction of chemical data, and secondly, problems in qualitative and quantitative analysis.

The infra-red may be said to extend roughly between the wave-lengths 1μ and $10^4\mu$, or 10^{-4} and 1 cm. This corresponds to a range of frequencies from 3×10^{14} to 3×10^{10} per second. Instead of this absolute unit of frequency, the reciprocal wave-length or wave number is commonly used. Thus a wave-length of 1 cm. corresponds to 1 wave per cm., and one of 10^{-4} cm. to 10^4 wave numbers. A very small part of the above spectral range, namely, that from the visible up to about $1{\cdot}2\mu$, can be studied photographically with cyanine-sensitised plates, and by using conventional spectrographs with glass or quartz prisms or finely-ruled diffraction gratings. Between 1μ and 25μ prism spectrometers can be used in which the prism is made of quartz, calcium or lithium fluoride, rock-salt, or potassium halides. The particular characteristics of transmission and dispersive power of these substances make them suitable for different spectral ranges.[2] Unfortunately, natural crystals of rock-salt, fluorite, and sylvine which are of the required size and optical quality are becoming scarce, so the method recently developed in America [3] for producing large blocks of these substances by cooling the molten salts is very valuable. It seems unlikely on theoretical grounds that materials suitable for prisms at wave-lengths beyond 25μ will be discovered, and in this region diffraction gratings have to be used, although these are, of course, used at shorter wave-lengths if higher resolving power is required than can be obtained with a prism spectrometer. The small amount of energy which usually has to be detected makes it desirable to cut the grooves in such gratings so as to obtain favoured angles of reflexion, thereby concentrating the energy in one or two adjacent spectral orders; different "echelette" gratings are then selected for use in particular narrow spectral regions. The manufacture of echelette gratings has hitherto been confined to American laboratories. If these were available from any source in this country, a valuable stimulus would be given to several important fields of research.

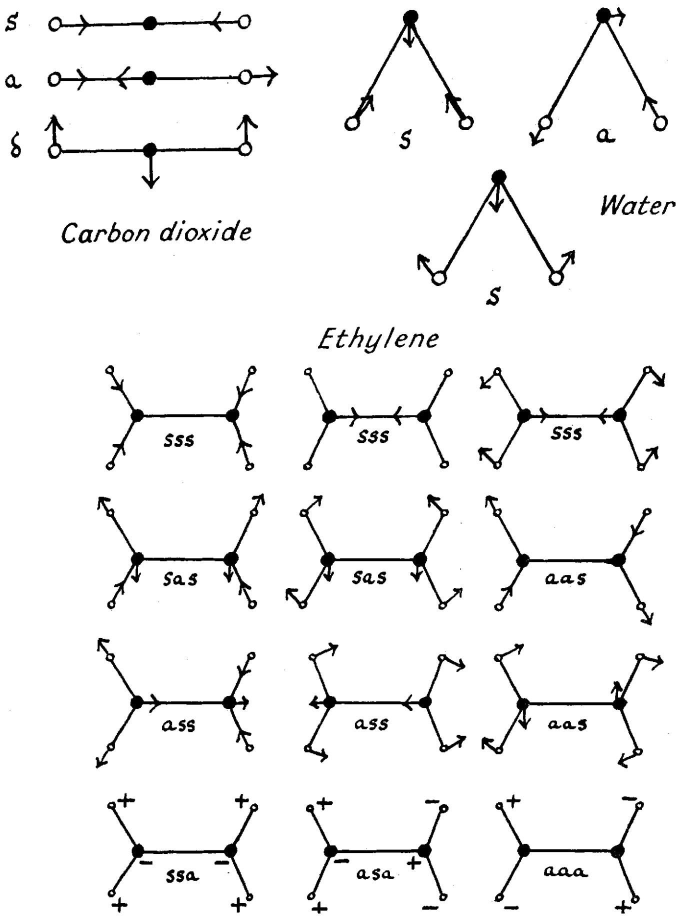
Except in the photographic region around 1μ to which I have just referred, infra-red radiation is usually detected by means of thermoelectric devices. The difficulties of obtaining highly sensitive but stable systems have probably been mainly responsible for the hesitancy with which some workers have entered the field. Very striking advances have now been made, however, in the development of highly sensitive vacuum thermocouples, working with voltage amplifiers of different types. This has led, not only to increased stability of the galvanometric systems, and consequently to increased accuracy, but also to the development of continuously recording automatic infra-red spectrometers which demand no extraordinary manipulative skill. At the present time real progress is being made in this direction, and the study of alternative methods of detection using alternating current bolometers with valve amplifiers may lead to further improvements.

Now, emission spectra in the infra-red have rarely been obtained with sufficient intensity to be measured, and we are nearly always concerned with the absorption spectra, obtained by interposing the substance under investigation between the spectrometer and a source of continuous infra-red emission, such as a Nernst glower or incandescent carborundum rod. In this spectral region energy is absorbed by the molecules as quanta, which cause them to rotate and vibrate. If the molecule, like hydrogen chloride, has a permanent dipole moment, an external field will tend to orient it. A periodically changing electromagnetic field will tend to swing it alternately in opposite directions. Energy can therefore be absorbed to make the molecule rotate.

According to classical theory, a continuous series of energy values will be absorbed, since the molecule will be able to rotate with any frequency. In quantum theory, however, the angular momenta, and therefore the rotational frequencies and values of rotational energy, can only have a series of discrete values, and the frequencies of the radiation absorbed are determined by the quanta of energy according to the well-known relationships of Planck. Diatomic molecules without a permanent dipole moment, such as nitrogen or hydrogen, or spherically symmetrical molecules such as methane, will not absorb rotational quanta.

Similarly, the way in which the dipole moment of a molecule changes during a nuclear vibration will determine whether the particular vibrational quanta are absorbed. If the dipole moment changes during the oscillation, a periodically changing electric field will be set up around the molecule, and its frequency—the same as that of the oscillation—will be absorbed. Here again, homonuclear diatomic molecules will vibrate without the production of a dipole, and will therefore not absorb vibrational quanta. On the other hand, although methane has no permanent dipole moment, it can vibrate in such a way as to produce one, and such a vibration should be absorbed in the infra-red as a fundamental.

FIG. 1.



The quanta of rotational energy, which are determined by the molecular moments of inertia, *i.e.*, by the nuclear masses and internuclear distances, are usually small. The pure rotation spectra therefore lie at low frequencies, that is, at very long wave-lengths, in the region $10^2\mu$ to $10^4\mu$, or 1 to 100 wave numbers. Comparatively little is so far known of these spectra, mainly owing to the technical difficulties in studying this region. With simple diatomic molecules such as the hydrogen halides, the observed spacing of the rotational lines leads to the monent of inertia and hence to the bond length. With polyatomic molecules, the rotational absorption bands are considerably more complicated, and only in a few cases has an analysis been attempted.[4] It may be that developments in the technique of short-wave radio, together with a more accessible supply of coarsely ruled diffraction gratings, will make this an interesting region for future work, particularly for the examination of crystals and solid polymers.

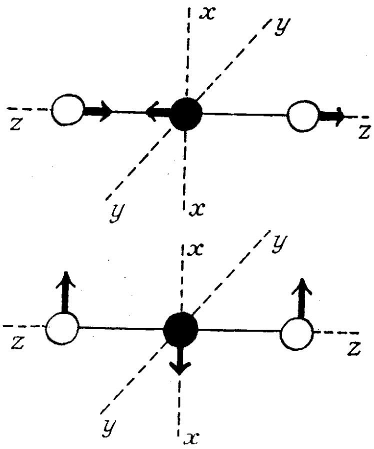
Vibrational quanta, which are determined by the nuclear masses, and the force constants for stretching of bonds and bending of angles, are larger than rotational quanta, the fundamental frequencies varying from about 100 to 4000 cm.$^{-1}$. Accordingly, the fundamentals, lower harmonics, and combination tones are absorbed at shorter wave-lengths, between about 100μ and 1μ. The fact that prism spectrometers cannot be used at wave-lengths longer than 25μ means that vibration frequencies smaller than about 400 cm.$^{-1}$ are not normally measured by infra-red absorption. The absorption of vibrational quanta will usually be accompanied by simultaneous changes in rotational energy. With gases or vapours, these changes give rise to a fine structure of the vibrational absorption bands, measurement of which, as we shall see, has considerable significance. With liquids or solutions, collisions and intermolecular influences lead to the disappearance of the rotational fine structure.

We must now consider the vibrational absorption bands more closely. A rigid molecule of n atoms will have $(3n - 6)$ characteristic normal modes of vibration, in each of which the nuclei are at any instant moving in the same phase. With linear molecules, where there are only two effective axes of rotation, there are $(3n - 5)$ oscillations; on the other hand, if a non-linear molecule can undergo an unrestricted internal rotation about some bond, there will be $(3n - 7)$ vibrations. In simple cases where the molecule has some degree of symmetry, it is possible to specify in a general way the geometrical form of these molecular vibrations. Thus the normal modes of carbon dioxide, water, and ethylene are shown in Fig. 1. The geometrical forms sometimes permit us to speak of "breathing," "rocking," "bending," or "twisting" motions, and in a narrower sense to differentiate between valency vibrations, in which the nuclei move essentially along the valency bonds, and deformations, if the nuclei move essentially at right angles to the bonds. Obviously the sharp distinction between valency vibrations and deformational modes is strictly valid only in the simplest cases, where the restoring forces opposing stretching and bending differ widely in magnitude. For some purposes of discussion, however, the terminology is useful.

Molecular vibrations can often be characterised in two other, more significant ways. If there is molecular symmetry, any given vibration may be either symmetrical or antisymmetrical with respect to the symmetry property. Thus, the " breathing " vibration of carbon dioxide is symmetrical with respect to the centre of symmetry and the other valency vibration is antisymmetrical. In other cases, where two or more elements of symmetry exist, as with ethylene, a given vibration may be symmetrical to all elements, symmetrical to some and antisymmetrical to others, or antisymmetrical to all. Some vibrations have another property : they are degenerate. Thus the deformational mode of carbon dioxide shown in Fig. 1 is not uniquely defined, since the motions could take place either in the plane of the paper or in a plane perpendicular to it. In certain circumstances this directional equivalence may be removed, so that oscillation is two-fold degenerate.

A consideration of the symmetry of these vibrations shows that they differ characteristically in the way in which the molecular dipole moment changes during the oscillation. Some of the vibrations will involve no change in dipole moment, as in the totally symmetrical modes of ethylene; in others, the direction in which the electric moment changes may be either parallel or perpendicular to some axis of molecular symmetry. As I have already explained, the vibrations which involve no change in dipole moment will be absorbed neither as fundamentals nor as overtones in the infra-red, and in general the intensity of a band will be proportional to the square of the position-rate of change of electric moment during the vibration. It frequently happens therefore that overtones or combinations appear in the infra-red spectrum more strongly than some fundamentals, and in assigning the measured absorption frequencies to particular normal modes, mere intensity will be no rigid guide. Sometimes, those vibrations which are not absorbed as fundamentals appear as combinations with other vibrations, the symmetry properties of the combinations making them permissible. Semi-empirical rules may guide us in the allocation of frequencies to normal modes. Some frequencies which persist through a related series of compounds may be allocated to vibrations of particular groups. In general, too, the motions of lighter nuclei will have higher frequencies than those of heavier nuclei, and comparison of two isotopic molecules in this way may be helpful, particularly those containing hydrogen and deuterium. Also, the deformational modes usually have lower frequencies than the stretching vibrations. It is clear, however, that in no case will mere inspection of the infra-red absorption frequencies lead to an unambiguous assignment of the different magnitudes to the normal modes. In some cases, too, when the harmonic of one vibration is roughly equal in magnitude to another fundamental, resonance occurs, and leads to a pair of new frequencies, one lower and one higher than the larger fundamental. This makes the measured frequencies actually misleading.

FIG. 2.



For many purposes, such as the calculation of thermodynamic properties or force constants, a correct assignment of the fundamentals is essential. Other data, in addition to the above, are therefore required. Most important of these is the Raman spectrum, the great value of which arises because the selection rules which determine whether a particular vibration will be allowed in the Raman or the infra-red spectrum are different. In the Raman effect, vibrations are active if they involve a changing molecular polarisability. Each of the totally symmetrical vibrations of ethylene involves such a changing polarisability, and can therefore appear in the Raman spectrum. The selection rules in any particular case will depend upon the symmetry class to which the molecule belongs. Another useful result is that relatively few combinations are observed in the Raman spectrum. Also, Raman frequencies are found to differ in their degree of polarisation, so that measurement of the latter may enable us to allocate the several magnitudes to vibrations in different symmetry classes. Usually, the more symmetrical vibrations give rise to plane-polarised Raman frequencies, and the less symmetrical to depolarised frequencies.

Some frequencies, *e.g.*, the twisting mode of ethylene, are not found as fundamentals in either the Raman or the infra-red spectra. These can sometimes be determined from a consideration of overtones or combinations, from fluorescence data, or from the measured specific heats. In the last case, the measured specific heat is compared with that calculated by statistical mechanics, all the known frequencies being used. If all the frequencies except one are known, the discrepancy found may lead to an estimate of the missing frequency.

There still remains one other very important method for assigning the vibration frequencies, based upon the analysis of the rotational structure of the infra-red absorption bands.[5] In this way, the molecular structure may also be simultaneously established, since the moments of inertia may be obtained. This can be illustrated with reference to the two vibrations of carbon dioxide which are active in infra-red absorption (Fig. 2). In the antisymmetrical valency vibration the vector corresponding to the change in electric moment is parallel to the molecular axis, and in the deformation it is perpendicular. The molecule can rotate about each of the axes *xx* and *yy*. If it vibrates with the " parallel " change of electric moment, and rotates about *xx*, the electric moment vector rotates with the vector of angular momentum. The same is true if the rotation occurs about *yy*. This means that rotational energy changes will always be coupled with the vibrational change, and the "parallel" type bands will consist of two groups of rotation lines, the *P* and the *R* branches, corresponding to decrease or increase in rotational quantum number during absorption. Now, if the molecule vibrates with the change of electric moment perpendicular to the axis of symmetry, rotation about *yy* will again involve coupling of the electric moment vector and angular momentum vector, giving *P* and *R* branches; but if rotation occurs about *xx*, the angular momentum vector will rotate in a plane at right angles to the electric moment vector, and independently of it. This means that the perpendicular-type bands will have, in addition to the *P* and *R* branches, a central *Q* line, really a close branch, corresponding to the absorption of the vibration frequency without simultaneous change of rotational quantum number.

The rotational structure of the absorption bands of a linear molecule will therefore reveal at once whether the particular vibration is parallel or perpendicular in type. Conversely, since no other type of molecule gives absorption bands with a central gap due to the missing *Q* branch, the simple *P–R* branch type of band is immediate proof of a linear structure. The spacing of the lines in the *P* and the *R* branches of both parallel and perpendicular bands is nearly uniform and equal to $\boldsymbol{h}/4\pi^2 I$, so that I can be determined. We may notice in passing that the separation of lines is inversely proportional to I, so that, as the molecule increases in size, the rotation lines become less well separated. Absorption bands of linear molecules such as carbon dioxide, hydrogen cyanide, and acetylene have been analysed in this way.

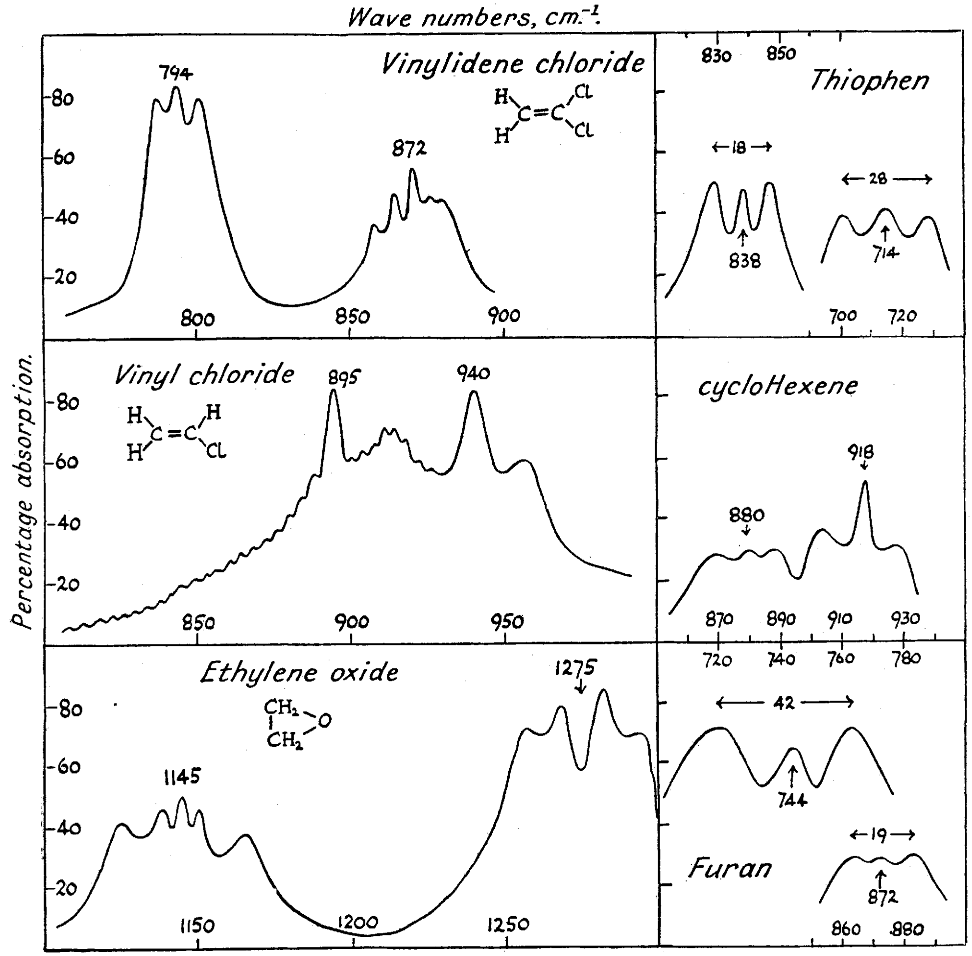
Next in simplicity are the non-linear molecules which have an axis of symmetry, such as ammonia, the methyl halides, or methylacetylene, in which $I_A = I_B \neq I_C$. The energy levels of these so-called symmetrical rotators are given by a more complicated expression than that for linear molecules. The parallel type bands have a *P*, *Q*, *R* type structure like that of the perpendicular type bands of a linear molecule, the spacing of the lines in the *P* and the *R* branches being again very close to $\boldsymbol{h}/4\pi^2 I_A$. The perpendicular-type bands have a different structure. There is first a succession of *Q* branches with roughly uniform spacing $(\boldsymbol{h}/4\pi^2)(1/I_C - 1/I_A)$, I_C being the moment of inertia about the symmetry axis. Each of these *Q* branches has alongside it a *P* and an *R* branch, with spacings $\boldsymbol{h}/4\pi^2 I_A$. The *Q* branches usually stand out above the residual background, but the intensity distribution varies according to the relative values of I_A and I_C. Gerhard and Dennison [6] have shown how the intensities vary for different values of the parameters. Once again, however, we can see that, since the spacing between the *Q* branches in a perpendicular band is in many cases relatively large, I_C being smaller than I_A, inspection reveals whether the bands are parallel or perpendicular in type. If it is possible to measure the spacing between the *Q* branches in a perpendicular-type band, and also the spacing between lines in either a *P* or an *R* branch of a parallel band, the values of I_A and I_C are obtained. In this way highly accurate structural data have been obtained for most molecules which are symmetrical rotators, and for some others which deviate only slightly from this. A number of molecules such as the methyl halides have been measured in the photographic infra-red,[7] where overtone and combination frequencies are taken up. In some of these cases, the identity of the spinning hydrogen nuclei within the methyl group leads to characteristic alternations of intensity in the rotation lines.

The types of rotational structure so far considered relate to molecules which (*a*) are volatile enough to be studied in the vapour state, (*b*) are small enough to have low moments of inertia and hence resolvable structure, and (*c*) have some symmetry. These restrictions are severe, and the majority of molecules with which the chemist has to deal are excluded. Even when (*b*) or (*c*), or both, do not apply, however, it is often possible to get a partial solution. Thus, if there is some symmetry, but the moments of inertia are large, the envelope of the rotational structure, *i.e.*, the band contour, can be studied. This contour, like the rotational structure itself, varies characteristically with the direction in which the electric moment changes with reference to the axis of symmetry. The spacing between maxima in this contour sometimes leads to an approximate value for one moment of inertia. Thus, Gerhard and Dennison [6] have shown that the spacing between the maxima of the *P* and the *R* branches in parallel-type bands is given by $[S(\beta)/\pi]\sqrt{\boldsymbol{k}T/I_A}$, the quantity $S(\beta)$ being nearly unity but slightly dependent upon the relative value of the two moments of inertia. In these cases, the spectral data really only serve to confirm values for moments of inertia which have been determined in other ways, for when the rotational contour is incompletely resolved, the spacing actually found between sub-maxima will depend upon the exact resolving power used. In any case, however, it is usually possible at least to decide from the contour whether the vibration is parallel or perpendicular in type.

If the molecule under consideration is asymmetrical, $(I_A \neq I_B \neq I_C)$, no general expression can be given for the rotational energy levels, and even when the moments of inertia are small, the fine structure of bands is very complex. Few attempts have yet been made to analyse such bands completely, in spite of the fact that many simple molecules like water, hydrogen sulphide, ethylene, and formaldehyde fall in this group. Here again, some progress can be made by the study of band contours, especially if the molecules do not deviate far from being symmetrical rotators. The molecule will have three principal axes of rotation, the greatest, middle, and least axes of inertia. In any vibration the change of electric moment can be regarded as having components parallel to each of these axes. Badger and Zumwalt [8] have computed the rotational energy levels of molecules in which I_A, I_B, and I_C have different values, both absolutely and relatively, and have thus deduced the approximate rotational contours of bands in which the change of electric moment is parallel to each of the three axes. In practice, any actual band will usually be a hybrid, obtained by compounding the *A*, *B*, and *C* type contours in the correct ratios of intensity, depending upon the relative values of the components of the electric moment change in the three directions. Although this might be expected to lead to highly complex contours, as indeed it does in some cases, there are many others in which the results are surprisingly simple. In Fig. 3 examples of rotational contours of vibration bands of vinyl chloride, vinylidene chloride, ethylene oxide, *cyclo*hexene, and thiophen are shown.[9] In all these cases, although the moments of inertia cannot be directly determined from the contour, yet an assumed structure can be confirmed, and the particular vibrations can be assigned to different types by using the contour to establish the direction of change of electric moment.

I must at this stage emphasise that even when all three moments of inertia of a molecule can be determined, the whole structure cannot often be fixed, since there will in nearly all cases be more than three parameters, the bond lengths and angles. In order to fix the structure, some of these parameters will have to be assumed. For instance, methyl chloride has only two unique moments of inertia, but three independent parameters, the methyl group angle and two bond lengths. If the angle is assumed to be tetrahedral, the bond lengths follow.

FIG. 3.

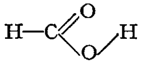


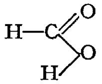
If data are available for a series of molecules, such as the methyl halides, the assumptions made may be substantiated by the self-consistency of the whole series. Another solution may be to use a pair of isotopic molecules. Thus, hydrogen cyanide has only one effective moment of inertia, but two bond lengths. Measurement of the moment of inertia of deuterium cyanide, which has the same bond lengths, will provide a second datum, so that the bond lengths can be deduced.

Another very serious obstacle in the analysis of rotational structure and contours, even with symmetrical molecules, arises from the perturbation of energy levels due to interactions between vibration and rotation. This can be of various types, and results in abnormal spacing of lines, and it unfortunately tends to be specific in different molecules.[10] A particularly interesting interaction of this kind has recently been noticed between two perpendicular vibrations of allene.[11]

Against all these shortcomings, there are, on the other hand, some cases in which an incompletely resolved or analysable rotational structure can still be used to decide between a pair of possible molecular configurations. Thus, hydrogen peroxide has absorption [12] at about 1μ due to an overtone of the O–H stretching frequency. If the molecule had a *cis*-structure, the change in electric moment would be either entirely parallel or entirely perpendicular to the least axis of inertia, the O–O bond. The observed band has in fact a hybrid structure, which excludes the *cis*-configuration. The *trans*-form is excluded by the value found for the molecular dipole moment. An oblique non-planar configuration is therefore indicated, which is entirely consistent with the details of the spectral data. Similarly, the essentially perpendicular type structure of the O–H (stretching) band of formic acid vapour [13] indicates a *cis*-structure (*a*) rather than the *trans*-form (*b*).

(*a*.)





(*b*.)

I must now return to the large majority of molecules which are non-volatile or too big to show rotational contour, and for which the only data derivable spectroscopically may be the vibration frequencies. If all these frequencies are known, it may be possible to calculate some useful thermodynamic properties, using the results of statistical mechanics.[14] Each of the properties in which we are interested, such as specific heat, entropy, or free energy, is an explicit function of the partition function $\Sigma e^{-\varepsilon_i/kT}$, in which the energy levels ε_i are derived from the spectral data. As regards the specific heat, since the contributions from translational and rotational energy terms are constant at most working temperatures, we only have to compute the contribution from vibrational levels $\varepsilon_i = h\nu_i$. It must be noted here that, since the greatest contributions come from the lowest frequencies, these must be known accurately, and these are often the most difficult to determine. It is also essential, when degenerate vibrations are present, to allocate them correctly. There is usually no alternative but to assume harmonic character for the vibrations, but this introduces no large error.

Apart from their intrinsic value, specific heats calculated in this manner have led to other knowledge. For instance, a comparison of the calculated and measured values for some molecules revealed discrepancies which were too large to be explained by either experimental or theoretical error.[15] It was then realised that these could be correlated with the phenomenon of internal rotation in molecules. When the potential-energy barrier resisting an internal rotation is high, the molecule will perform a twisting vibration; if the barrier is small, free rotation will occur. There will obviously be intermediate, complex types of motion, the exact nature of which will depend upon the height of the potential barrier and the function relating this potential energy with the azimuthal angle of rotation. The contribution which this torsional motion makes to the specific heat will therefore depend upon many factors. For our present purpose, the important result is that it has been possible to estimate the potential-energy barriers restricting internal rotation about bonds in a series of molecules, and the results suggest that this may be a useful method for discovering something about the forces in molecules between atoms which are not bonded.

If in addition to the vibration frequencies the moments of inertia of a molecule are known, the entropy and free energy can also be calculated. Equilibrium constants can also sometimes be calculated with high accuracy, and others estimated when they are not easily measurable. For this purpose, however, it is usually essential also to have thermochemical data, such as heats of formation, in order to calculate the change in zero-point energy of the reaction being considered. Clearly, with more complex molecules it may be difficult to fix all the frequencies exactly, and only rough values for the moments of inertia may be available. For other reasons, too, the calculations may become less satisfactory. In particular series of compounds, however, it is known that the frequencies fall into groups, and approximations can often be made, especially if the frequencies are high.

Vibration frequencies can also be used to calculate force constants of bonds, accurate values for which would throw much light on the nature of bonds and the distribution of electrons in molecules. Here we have to assume that the vibrations are harmonic, and we must know the form of the function expressing the change of potential energy with nuclear displacements during the oscillation. Application of the Lagrange equations of motion then leads to a determinantal equation, the determinant being of the same order as the number of normal modes. If there is some molecular symmetry, the determinant can be split up so as to obtain equations of lower order, and this simplification is almost essential if the problem is to be manageable, mathematically, at all. In this way, equations are obtained relating the frequencies with the nuclear masses and force constants.

Force constants for stretching of bonds and bending of angles have thus been calculated for some relatively simple molecules.[16] Chemically, the interesting point is to compare the force constants of the same link in a series of different molecules. In some cases the results clearly show the multiple character of bonds and the existence of resonance hybrids.

There are, unfortunately, fundamental difficulties in the extension of such an analysis. The real problem lies in the choice of the correct potential-energy function, since this determines not only the values of the force constants deduced, but also their physical significance. Thus, with a non-linear molecule ABC, if forces are assumed to act solely between atoms which are joined by a conventional bond, the potential function can be assumed to take the form

$$V = \tfrac{1}{2}k_1\Delta^2{}_{AB} + \tfrac{1}{2}k_2\Delta^2{}_{BC} + \tfrac{1}{2}k\theta\Delta\theta^2$$

This is called simple valency force field. If, on the other hand, we assume that there are forces between all pairs of atoms, whether bonded or not, we should write

$$V = \tfrac{1}{2}k_1\Delta^2{}_{AB} + \tfrac{1}{2}k_2\Delta^2{}_{BC} + \tfrac{1}{2}k_3\Delta^2{}_{AC}$$

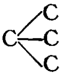
Neither of these functions is completely satisfactory in most cases, in the sense that although a set of values for the constants correctly reproduces some of the frequencies, yet it does not reproduce them all. In order to obtain consistency, "interaction terms" have to be introduced, corresponding to "cross terms" in the mathematical harmonic form. Even then it seems to be necessary in some cases to introduce more arbitrary constants than the total number of normal modes, which makes the solution impossible. The question arises as to how we are to test the suitability of different functions. We might at first think that the most satisfactory one will be that which reproduces correctly the values for all the fundamental frequencies using the minimum number of arbitrary force constants. This does not seem to be entirely true, for although functions have seemed satisfactory in this respect for one molecule, they have failed to give the frequencies of an isotopic molecule so well. The use of the isotopic effect in testing the function is limited, however, since only with hydrogen and deuterium are the changes in frequencies very large.

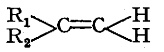
To summarise, it seems that progress will have to be made by considering series of related molecules of gradually increasing complexity, introducing into the simple valency force field as many additional constants as may be necessary. It may then be possible to find which type of interaction terms are the most important, and to formulate general rules which throw light on the intramolecular forces.

I can only briefly mention here the empirical relationships which have been suggested between force constants of links and their length.[17] If force constants could be determined accurately for linkages in polyatomic molecules, these relationships might be very useful for estimating bond lengths where other methods fail. Some useful deductions have already been made in this way, but until more data are available it is difficult to say how valuable the method will be. Another interesting chemical problem to which the infra-red data have been applied is the question of optical isomerism in derivatives of ammonia or phosphine, caused by the motion of the apex atom through the plane of the three attached groups. The President discussed this in detail in his address last year.[18]

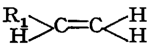
There is one final application to which reference should be made. It will be clear from what I have said that molecular symmetry plays an important rôle in spectroscopic considerations. We have seen that the symmetry class of a molecule determines the selection rules for the appearance of its vibrations in the Raman and the infra-red spectra. If therefore we examine which frequencies appear in the two types of spectra, which in neither, and which in both, it should be possible to allocate the molecule to a particular symmetry class. This has been attempted in two cases, *viz.*, benzene [18] and *cyclo*hexane.[20] In the former case, the occurrence of a centre of symmetry should forbid the occurrence of the same vibration in both Raman and infra-red spectra. In the latter, the rules will differ characteristically according to whether the molecule has a planar, boat-shaped, or chair-shaped structure. In both cases the results are not very convincing, and this probably arises because the Raman data are normally obtained with the liquids; where distortions may cause the selection rules to break down. Comparisons of this sort using Raman data on vapours might be more informative. I should add here that in the infra-red spectrum, too, differences are often found according to whether the vapour or the liquid is used. This is also presumably to be attributed to alterations in the selection rules caused by molecular distortions.

Now, when a molecule vibrates, it does so as a whole. Strictly speaking, it is incorrect to refer to the vibration of an individual link or group. However, certain linkages and groups retain some individuality, and molecules containing them have frequencies which are little changed in the different molecules. This applies particularly to groups such as O–H, S–H, N–H, or C–H, in which the light atom moves against the much heavier residue, the frequency being therefore hardly affected by variations in the mass of this residue. As Fox and Martin [22] have shown too, the C–H stretching vibrations vary characteristically in frequency with the particular type of C–H linkage, such as $-CH_3$, $>CH_2$, $\equiv C-H$, $>C-H$, or $=CH_2$. Some other bonds, such as $C=O$, $C=C$, or $C\equiv N$, have valency vibration frequencies which may be slightly affected by neighbouring groups or electronic influences such as conjugation, but generally remain fairly constant. Groups of this kind can therefore be detected by infra-red absorption, and if proper calibrations are made, estimated quantitatively. Conversely, the absence of such a frequency may be taken to indicate interactions, such as intra- or intermolecular association. By this means the existence of hydrogen bonds has been proved in many systems,[22] and more detailed examination may give quantitative data about their nature.

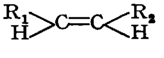
The individuality of linkages tends to disappear when the vibrating nuclei are roughly equal in mass, or the force constants have roughly equal value. In spite of this, however, some nuclear skeletons seem to retain characteristic sets of vibration frequencies in different compounds. For instance, the *tert.*-butyl grouping  shows intense absorption in the region of 8μ in a large number of hydrocarbons,[23] arising from vibrations of the carbon skeleton which are little affected by the residue attached to the butyl group; and this absorption is so characteristic that the group could easily be detected in an unknown sample. In some cases, too, the deformational modes preserve their individuality. For example, there is a deformational mode of the methyl group with absorption at about 7·25μ; this can be used for the detection and determination of methyl groups in polythene.[24] Another interesting case is found with the bending mode of the $>C-H$ structure present in different types of olefin.[24] These can be classified as follows:

(1) 

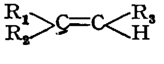
$R_1R_2C=CH_2$

 (2)

$R_1HC=CH_2$

(3) 

$R_1HC=CHR_2$

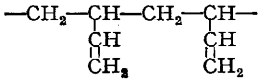
 (4)

$R_1R_2C=CHR_3$

The infra-red spectra of many compounds of each of these three types reveal that all those in class (2), the vinyl derivatives, have two intense bands at 909 and 990 cm.$^{-1}$; those of type (1) have one at about 890 cm.$^{-1}$; and those of type (3) have one at about 965 cm.$^{-1}$. The corresponding vibration for class (4) is not quite so rigidly defined. When it is required to establish the nature of olefins formed in cracked petroleum or hydrocarbon products, the significance of these results becomes obvious. The spectrum of a sample of Buna 85 synthetic rubber was recently measured (Fig. 4), and showed very intense bands corresponding to types (2) and (3), thus indicating that polymerisation had proceeded both by 1 : 4-addition, giving

$$—CH_2—CH{=}CH—CH_2—CH_2—CH{=}CH—CH_2—$$

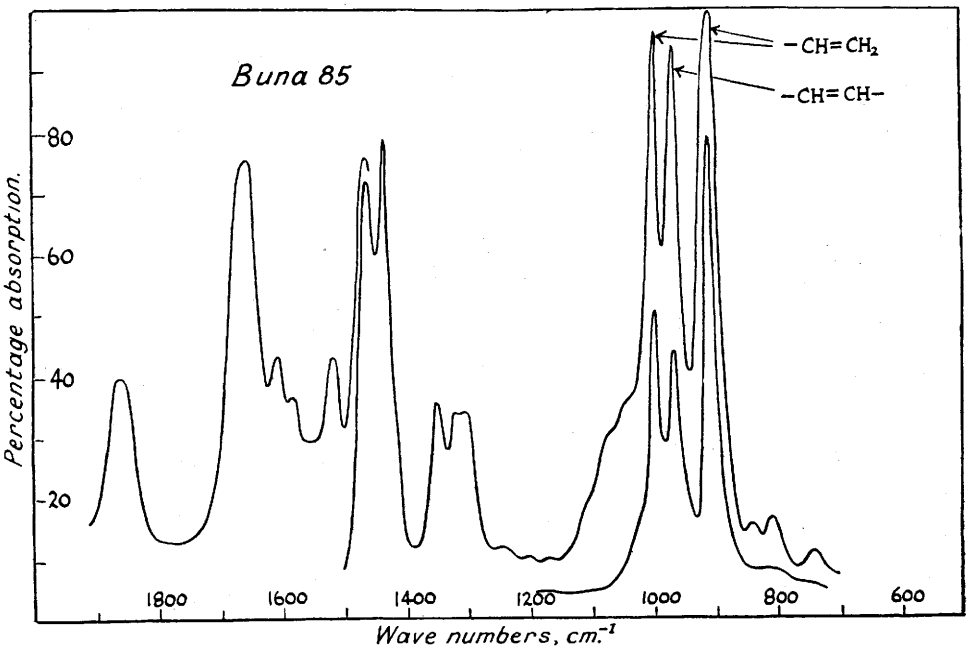
and by 1 : 2 addition, giving



$$—CH_2—\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}{CH}—CH_2—\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}{CH}—$$

From measurements of intensities, it would be possible to determine the extent to which each type of addition proceeds in a given case. More measurements of this kind are needed on selected series of molecules in order to build up reference data. The quantitative estimation of key groups or parts of a nuclear skeleton requires careful measurement of extinction coefficients, and also fundamental work on the validity of the usually accepted absorption laws.

FIG. 4.



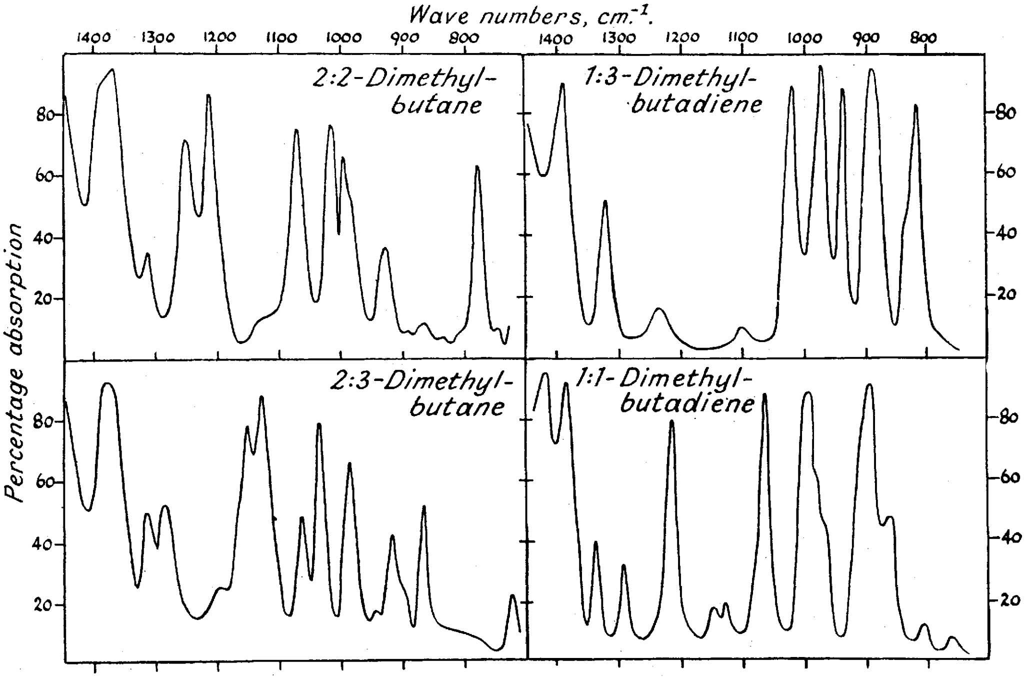
In polymeric chemistry a variety of problems can be explored successfully, such as the determination of head-to-head or head-to-tail condensation, the relative proportions of different components in an interpolymer, or the position and number of particular groups in long-chain systems. Plane-polarised radiation can also be used in studying oriented solid polymers.[24]

I have just emphasised that, in spite of the individualistic behaviour of some goups in a molecule, a normal vibration really involves the entire molecule. The vibration frequencies are determined by the force constants, nuclear masses, and nuclear configuration. It therefore follows that since no two molecules—except a pair of optical isomers—have the same nuclear configuration, no two molecules can have an identical set of normal frequencies. Related molecules will have some frequencies which may be so nearly equal as to be indistinguishable, but there will be other differences. The infra-red spectrum therefore becomes a fingerprint of the molecule, and when two molecules are present together it should always be possible to identify each of them, unless the spectra are very complex. Analysis for whole molecules in this way has now been developed in many cases, of which I can quote only a few. For example, a mixture of *iso*hexanes can be analysed in this manner, and a similar mixture is that of 1 : 3-dimethyl- with 1 : 1-dimethyl-butadiene (Fig. 5); dodecyl thiocyanate and *iso*thiocyanate show differences in the region of 6μ which make estimation of each in the other possible; mixtures of isomers such as the chlorobenzoic acids, or *o*-, *m*-, and *p*-derivatives can usually be analysed. With series of isomers of this type there appear to be some characteristic displacements of bands in passing along the series, and when more compounds have been measured it should be possible to formulate general rules from which the important features of unknown spectra can be predicted. Even the spectra of *cis-trans*-isomers show differences in their vibrational spectra, which must arise from the different forms of interaction between groups in the individual molecules. The characteristic differences in the spectra of a polymer and its associated monomer provide a very easy means for following the rate and course of polymerisation processes.

The sensitivity and accuracy obtainable in such analyses vary from one example to another. The method can be based either upon empirical calibration or upon the assumption of the additivity of optical densities. Obviously the circumstances will be most favourable when there is a wide difference in extinction coefficient at any particular key wave-length between the various compounds present.

Analytical work of this kind can usually be carried out rapidly and with very small amounts of the substances concerned, about 0·5 c.c. of a liquid generally sufficing. Indeed, the intensity of infra-red absorption is sometimes so high that extremely thin layers of liquid, say 0·005 mm., have to be used. When we recall that this thickness has to be measured, say, to 1% in a precision cell made from polished rock-salt plates which deteriorate in damp air, it will be realised that a real experimental problem is involved. Work on precision cells is now in progress. An alternative approach would be to use dilute solutions in suitable non-aqueous solvents. Unfortunately, the solvent will also have its own absorption bands, and although in some spectral regions carbon tetrachloride, chloroform, and carbon disulphide have been used with success, solvents are more often a nuisance. In some cases, solid compounds have to be examined which cannot be got into solution at all. A good example of this class is proteins. The technique for handling such substances is not yet fully developed, but some measurements have been made by spreading the powder on a rock-salt plate and moistening it with Nujol or other liquids to reduce scattering. Another limitation to accurate quantitative analysis at present is the difficulty of measuring absorption intensities accurately. Various technical developments seem likely to remove this difficulty. The accurate measurement of extinction coefficients should then lead to other important information about the nature of different types of bond, since it should become possible to correlate absorption intensities with changes in molecular dipole moment.

FIG. 5·



The diverse applications of which I have spoken illustrate some of the ways in which infra-red measurements have been used in chemistry. In general organic chemistry, other compounds which have been examined [25] include sugars, polycyclic hydrocarbons, celluloses, amino-acids, sterols, vitamins, alkaloids, and hormones. The scope for future investigation is obviously great, though we have seen some limitations. How far the temporary limitations will be permanent must be decided by further work.

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[22] See *Trans. Faraday Soc.*, 1940, **36**, 871.

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