# NEW TRENDS IN INFRARED SPECTROSCOPY*

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## INTRODUCTION

ALTHOUGH infrared spectra have been recorded for nearly a hundred years, it is only since about 1925 that the results of such investigations have been of interest to chemists. As soon as the quantum theory of atomic spectra was extended to the interpretation of molecular spectra, it became clear that infrared spectroscopy provided a purely physical method of establishing the structure of simple polyatomic molecules, and in the period between 1920 and 1940 interest was concentrated on the elucidation of the spectra of small molecules, e.g., water, ammonia, methane, methyl halides, etc. Relatively little work was done on the infrared spectra of large polyatomic molecules, because the spectra were observed point by point and the recording of the spectrum occupied many weeks of work with a spectrometer which, if operated to yield high resolving power, was apt to give uncertain results. Moreover, the discovery of the Raman effect in 1928, which allowed the recording of most of the fundamental frequencies of such molecules (in the liquid state) in the time of the order of an hour, made chemists concentrate on Raman spectra rather than infrared spectra in studying large molecules. Indeed, it was the immense amount of work done in the period 1930 — 1940 on Raman spectra which led to the assignment of the majority of the characteristic frequencies of chemical bonds which are now so familiar to us. However, the Raman spectrum does not give all of the characteristic frequencies and if the substance is in the gaseous state, in solid form, (or if it is a colored liquid), the recording of the Raman spectrum presents serious difficulties.

During World War II, there occurred a major revolution in the technique of infrared spectroscopy because of urgent military needs in connection with the analysis of petroleum distillates and various other raw materials of the chemical industry. The time of recording a suitable range of the infrared spectrum of a molecule under low resolving power was reduced from over five hours to a time of the order of fifteen minutes. This meant that the infrared spectrum of a molecule now became easier to record than the Raman spectrum and so interest tended to move from the infrared spectra of small molecules to those of large and complex molecules. Another reason for this change was that the theoretical methods applied to the investigation of the structure of polyatomic molecules by infrared methods are limited in application to small polyatomic molecules containing hydrogen atoms; once the interatomic distances in most of these had been determined, the more intriguing problems were associated either with interaction effects between small molecules or with the larger molecules. The changes just described occurred between the end of the war and about 1950. Since 1950, new trends have begun to appear out of this pattern and it is the purpose of this paper to outline some of the more important of them.

## NEW TRENDS IN INSTRUMENTATION AND TECHNIQUE

(a) Detectors: Detectors of infrared radiation may be divided into two classes, viz., thermodetectors and photo-detectors. In the former, the rise of temperature due to absorption of infrared radiation causes a change in some physical property which is readily measurable (e.g., thermocouple or bolometer); in the latter, the incident quantum interacts directly with the receiver element to cause a change in some physical or chemical property of the receiver (e.g., photo-conductor or photographic plate).

Before 1940, all infrared spectroscopy was done with a thermo-detector, apart from a limited amount of work in the region of wavelengths less than $1\mu$, where photographic plates were used. During the last war, photoconductive detectors based on lead sulphide, lead selenide or lead telluride were successfully developed. Although these have a very limited wavelength range of sensitivity (PbTe goes to about $5.5\mu$), their speed of response is about 100 times faster than any thermodetector and their introduction has led to great advances in resolving

power and speed of recording of spectra in their operative range. There is a continuing trend towards the photoconductive detector, and attempts are continually being made to extend its range to longer wavelengths. Within the past two years, it has been established that indium antimonide in thin layers can be used as a photoconductive detector out to about $8\mu$. Its speed of response is about $10^{-7}$ sec, i.e., much faster than any of the previous photoconductive detectors. Although it does not appear to be as sensitive as any of the detectors of the lead series, it does not require to be cooled and is generally more robust. Silicon and germanium can act as photoconductive detectors out to beyond $30\mu$, but they have to be used at the temperature of liquid helium. Although impracticable at present, these detectors may well have a future for special problems. It also seems that bolometers operated at low temperatures may be a future development. Now that the Peltier probe is coming into use, keeping a detector cool should be much less trouble.

(b) Design of spectrometers: There has been continual progress towards achieving higher resolving power, now that the ultimate sensitivity of the detector no longer limits the performance of an infrared spectrometer. The most successful simple modification of existing designs consists in "multipassing" the grating (or prism). By this means, resolution of lines only a few hundredths of a wave number apart has been achieved in the neighborhood of 2 microns.

There is a trend towards the replacement of a prism spectrometer by a grating spectrometer. This is because it is now possible to produce a grating suitable for infrared work much more cheaply than a prism. This development is due to the work of Dr. Sayce and his colleagues at the National Physical Laboratory, who have successfully developed an original suggestion of Sir Thomas Merton, that it might be feasible to produce a grating by stripping a plastic coating from an accurately cut metal screw, many of the errors of which can be removed by means of a special nut, now known as a "Merton nut". Although the finer gratings commercially produced by this method are as yet inferior to those ruled by a conventional process, they are sufficiently accurate for 90% of the work done in the infrared. A $6 \times 6$ inch grating with 2500 lines to the inch can resolve lines 0.1 $cm^{-1}$ near 6000 $cm^{-1}$. It should be added that the Merton-NPL gratings make it rather easy to record spectra in the far infrared, i.e., out to $150\mu$ (cf. especially the work of Plyler).

There has been a considerable development in micro-spectroscopy in the infrared. By combining a reflecting microscope with an infrared spectrometer it is possible to obtain spectra from little more than $10^{-6}$ gm of material and even from fibers measuring only $650\mu \times 17\mu$.

(c) Interference Spectroscopy: Since this subject has recently been reviewed very fully by Professor Jacquinot, I shall do little more than draw attention to it at this point. The interference method, in which a Fourier transform of the intensity pattern into the required spectrum is made by means of a digital computer, has been particularly successful in the far infrared, where the available energy is very low. Dr. Gebbie of the National Physical Laboratory has built such a spectrometer and it appears likely that this method can be used in the near infrared to achieve higher resolving power than can be obtained by "multipassing" a grating. This problem is now under investigation.. An obvious factor which might limit the wide application of such a method is the fact that a digital computer is required. However, such equipment is becoming standard in any up-to-date research center, and is not likely to prove a serious embarrassment, provided the "programme" is intelligently devised to keep the cost down to a reasonable figure.

Computers are in any case coming into infrared spectroscopy. Their value has been proved in the case of reflection spectra, where the process of converting the reflection spectrum into an absorption spectrum is extremely tedious. Another use is in the analysis of complex mixtures, where a best fit to a whole absorption curve can be achieved, rather than trying to match it at selected maxima.

## STUDY OF MOLECULAR INTERACTIONS

Although some very interesting work is still being done on small molecules, I do not propose to discuss it in this paper, because the most interesting new developments seem to me to lie either in the field of molecular interactions or in the field of polymer molecules. The latter will form the subject of the third section of this paper. Infrared analysis is proving to be an extremely powerful tool in studying molecular interactions, because the weak inter-molecular forces cause changes in the vibration frequencies of the interacting molecules, which are easy to observe. Possibly the best known example of this occurs in hydrogen bonding, which produces a change of the order of 10% in the value of the XH stretching frequency (and also in the intensity and appearance), where

the XH group is hydrogen bonded to a third atom Y. Other examples of molecular interaction which can be observed spectroscopically occur between molecules in the crystalline state, between molecules and surfaces in the adsorbed state, between molecules in gases under high pressure, and between solute and solvent molecules in a solution.

(a) Hydrogen bonding: When a hydrogen bond

H . . . . YZ
X                   is formed either between two molecules

or within one molecule, changes occur in the position and appearance of the three frequencies associated with the XH bond, namely the stretching frequency and the two deformation frequencies, while smaller changes have been detected in the stretching frequency of the YZ bond (and in the two deformation frequencies associated with the YZ bond). In addition, a new low frequency has occasionally been detected, corresponding to the stretching vibration associated with the weak hydrogen bond. An immense literature now exists on this subject and it is neither feasible nor appropriate for me to attempt to review it here. It was the subject of a conference at Ljubljana in August, 1957, and an extensive review has also been published this year by C. G. Cannon. The main unresolved problem is the explanation of the great breadth (and occasional fine structure) which is associated with the XH stretching vibration and the out-of-plane deformation vibration of the XH bond. Undoubtedly, combination of the main frequency with much lower frequencies originating in the weak hydrogen bond must play a part, but the contributions of anharmonicity, Fermi resonance and even pre-dissociation have still to be assessed.

(b) Molecules in crystals: Until recently, most of the infrared studies on molecular interactions were carried out on molecules in the liquid or gaseous state, but more attention is now being directed to molecules in the crystalline state. Here the problem of theoretical interpretation is in some respects more tractable, because the orientation of one molecule with respect to another is usually well known from x-ray analysis (apart from the hydrogen atoms). However, within the past few years, x-ray methods have been refined and improved to such a degree that the positions of the hydrogen atoms are known in a few cases; also, the hydrogen atoms can sometimes be located by using nuclear magnetic resonance or neutron diffraction. Furthermore, by using polarized infrared radiation it is possible in certain cases to place the hydrogen atoms by infrared analysis,

where it would be impossible by x-ray methods (for example, in muscovite and biotite). In the course of such studies, "anomalous" effects were discovered in the spectrum of brucite, which at first appeared to be in conflict with the x-ray results. It has now been shown that these effects are due to the coupling of librational motions of the hydrogen atom with the XH stretching frequency, and the analysis of such effects should yield valuable knowledge on the potential field in which the hydrogen atom moves. There is no other way in which this information can be obtained.

Another method of investigating the forces in an ionic crystal is to substitute for one of the ions a molecular ion and observe the perturbations produced in the vibrations of this molecular ion by the crystalline field. For instance, one can introduce into different alkali halide crystals, ions such as $BH_4^-$, $NCO^-$, $NCS^-$, $OH^-$ in place of some of the halogen ions. The values of the fundamental frequencies of these foreign ions are found to depend in a regular manner on the size of either the alkali or the halide ion. In the case of molecular crystals (e.g., HCl or naphthalene), the substitution of deuterium for hydrogen has been extremely fruitful in elucidating fine structure in many of the bands. For instance it has been shown that in the hydrogen halides, the molecules are arranged in zig-zag hydrogen bonded chains in the low temperature orthorhombic phase.

(c) Other interaction effects: Perhaps the simplest example of an interaction effect in infrared spectroscopy occurs when hydrogen gas is investigated under high pressure. The fundamental frequency, which is normally "forbidden" in such a homonuclear diatomic molecule, becomes active in absorption. This is because under such conditions the molecules become polarized sufficiently long during the collision process to absorb radiation. Such an effect is not unexpected (cf. the breakdown of gaseous selection rules in the condensed state). But when two different gases are used, an unexpected phenomenon was observed, viz., that absorption occurred at a frequency which was the sum of the fundamental frequencies of the two gases. These simultaneous transitions are also associated with the collision process, but now of two dissimilar molecules. The fundamental theory underlying such effects has recently been developed by Van Kranendonk.

It has long been noticed in investigations on the spectra of molecules in solution that the frequency and intensity of the solute bands depend on the nature of the solvent. In recent years a considerable

amount of experimental work has been done on solvent effects in the hope that some systematic rules might emerge connecting the frequency shifts with certain physical properties of the solvent (e.g., dielectric constant). It is not surprising that the conclusion has been reached that the bulk properties of the solvent are not adequate for this purpose. Again, we are dealing with a specific short range interaction between molecules and it will be necessary to develop a satisfactory theory of this interaction. A promising step in this direction has recently been taken by Buckingham.

When a molecule is adsorbed on a surface, that molecule must be distorted to some degree by the forces which bind it to the surface, and this distortion must affect its infrared spectrum. If these interaction effects can be observed, it should be possible to obtain information from them about the nature of adsorption. Such effects can be observed, but the experimental difficulties are obvious and formidable. This field was pioneered in Russia about ten years ago, but in the past four years a considerable amount of work has also been done in the U.S.A. and Britain. As a result, it has been possible to obtain some information about the nature of the forces involved (similar to hydrogen bonding in some cases), about the existence and nature of two different types of adsorption site and about the effective electric field at the surface. In the case of physical adsorption, the observed changes in frequency are relatively small, but in chemisorption the shifts are naturally very much larger. In the latter case it has been possible to show that CO molecules can be attached in linear or in bridged complexes. Since it is extremely difficult to investigate the adsorption process at the molecular level by other physical means, it is to be expected that this will prove to be a very important field of future research in infrared spectroscopy in spite of the experimental difficulties which will have to be overcome.

## STUDY OF HIGH POLYMERS

High polymers form a special class of large molecules in that the repeating unit is frequently quite small and the infrared spectrum of the polymer is almost entirely determined by the fundamental frequencies of the repeating unit. An appreciable fraction of these frequencies is known from studies of appropriate small molecules and the corresponding bands are easily identified in the spectrum of the polymer. Such partial analyses of polymer spectra are usually not of great interest, apart from confirming the structure of the polymer

in those few cases when this cannot be done by chemical means. In analytical work, of course, the presence and nature of impurities can often be established, but structural questions such as the nature and degree of branching or the configuration of the polymer chain remain unanswered. During the last few years, it has been shown that under certain conditions the configuration of the polymer chain can be established by infrared methods, and it is this work which will now be very briefly reviewed.

(a) Synthetic polymers: Let us start with the simplest of all polymers, viz., polyethylene, which consists of repeating $CH_2$ units. If a single chain is in the fully extended form, one may regard it as a one dimensional crystal and the unit cell is found to consist of two $CH_2$ groups. These 6 atoms possess 18 degrees of freedom, of which 4 can be accounted for by the 3 translational motions and the one rotational motion (about the chain axis), leaving 14 to describe the vibrational motions. It can be shown that in the spectrum of this chain only 5 of these 14 can be active in absorption. These are

    (i)   $CH_2$ asymmetric stretching
   (ii)   $CH_2$ symmetric stretching
  (iii)  $CH_2$ bending
  (iv)  $CH_2$ wagging
   (v)  $CH_2$ rocking

However, in practice we are not dealing with an isolated polymer chain but with an assembly of polymer chains. If we assume that the chains are arranged in a regular crystal lattice, selection rules can again be derived. The crystal structure of polyethylene has been established by x-ray analysis; the unit cell in it contains two chains and therefore 12 atoms. One might anticipate that each of the previous 5 fundamentals would become double since we are effectively coupling very weakly two independent vibrating systems. However, only 4 of the previous 5 fundamentals are split, the wagging mode remaining single. Equally interesting is the fact that a single $CH_2$ twisting frequency now becomes active. In addition, two new low frequency lattice modes become active, giving a total of twelve active fundamentals. Thus the spectrum of a single crystal of polyethylene is as accurately predictable as that of a small molecule in the gaseous state. Polyethylene normally contains only a fraction of crystalline material, but this strict selection rule can be verified by examining the spectrum of a single crystal of a long chain paraffin. Having done so, it becomes very illuminating to investigate the spectrum of a specimen of partially crystalline polyethylene in which the crystallites have been

oriented by cold drawing. In the spectrum of the amorphous part of the polymer, the selection rules break down and the "amorphous bands" are thus much more readily identified. If the molecules in the amorphous portion of the polymer are fully extended and oriented to the same degree as the crystallites, one would expect any new bands to be very weak, since the difference between the spectrum of a single chain and that of the whole crystal is not great and is at least well defined. If the amorphous bands are strong, this could indicate that there is probably a good deal of random coiling in the amorphous portion.

This type of analysis is now being supplied to a variety of synthetic polymers. It should prove a most valuable tool in investigating crystallinity in polymers.

(b) Biological polymers: In order to understand certain key biological phenomena, such as the mode of action of genes, protein synthesis, or the production of antibodies, at the molecular level, it will be necessary to establish in detail the molecular configuration of proteins and nucleic acids. The physical method which has been most promising so far is x-ray analysis, but it should be realized that success has not yet been achieved, in that atomic coordinates are still unknown for any globular protein. Infrared analysis has already proved to be a very valuable auxiliary method of attack; it has often given independent confirmation of the main features of a structure and occasionally has given a lead at an early stage of the x-ray investigation by ruling out a model which appeared to fit a preliminary analysis of the diffraction data.

From the preceding section on synthetic polymers it is clear that a precise structure determination by infrared methods would have to be done on a single crystal of a biological polymer. Unfortunately, formidable experimental difficulties are encountered in obtaining satisfactory spectra from single crystals of biological polymers. Consequently, most of the infrared work to date has been on thin sections of fibrous proteins, such as hair, porcupine quill, silk, etc. In this case, the essential problem has been to determine the configuration of the polypeptide chain which forms the backbone of the protein molecule. It is a relatively easy matter to identify the main bands in the protein spectrum and to assign them to vibrations of the CO and NH groups in the peptide link. If the polypeptide chains are fully extended, then the CO and NH bonds should be normal to the fiber axis and should exhibit what is conventionally known as "perpendicular dichoism" (i.e., fiber axis is set parallel to the spectrometer slit). It was found

by Elliott and his co-workers that some fibrous proteins had spectra of this type (e.g., silk), but that in others (e.g., porcupine quill), the dichroism was "parallel." This must mean that in such proteins the polypeptide chain cannot be fully extended. Various ways of folding the chains were at first proposed, but it now seems that the helical configuration proposed by Pauling and Corey is much more likely to be correct. In their $\alpha$-helix, the polypeptide chain winds in a spiral with the CO and NH groups almost parallel to the polymer axis. Internal hydrogen bonds betwen the CO and NH bonds maintain the molecule in the helical configuration.

Since these fibrous proteins are far from being perfectly oriented, the dichroic ratios observed are never very high and it is quite impossible to establish a structure unless the degree of disorientation can be quantitatively estimated. A method of doing this has been recently worked out and applied to a number of proteins, viz., porcupine quill, elephant hair, horse hair, horn, feather quill, silkworm gut, and collagen. For each of these proteins, seven different structures were tested and it was possible to reject all but one or two of the model structures in most cases.

It must be emphasized that this method of attack depends on certain assumptions which may not always be correct. These assumptions are

(1) the direction of change of electric moment (associated with a particular absorption band) bears the same relation to the repeat unit of the polymer as that determined from infrared studies on single crystals of small molecules which contain the repeat unit;

(2) the spatial distribution of the polymer chains has a certain degree of symmetry;

(3) the specimen studied consists of one structural species.

The first assumption is necessary because it is found from work on single crystals of small molecules containing a peptide link that the change of dipole moment in a bond stretching fundamental vibration (e.g., NH or CO) is not exactly along the bond in question, but may make an angle of as much as 20° with it. Thus, the directions of these bonds (and consequently the molecular configuration) cannot be determined unless the corresponding angles are known for a peptide link in a protein. Up to the present, single crystals of only two different molecules have been investigated. The angles in these two crystals did not differ by more than five degrees. However, more work on single crystals of a few other molecules is required in order to estimate accurately the degree of uncer-

tainty arising from this assumption. The second assumption can be shown to be a reasonable one if the sample is prepared in a certain way. At first sight, the third assumption seems reasonable, and is made by the x-ray analysts. The reason for doubting it is that the structure of many of the infrared bands of proteins is complex. Whether this arises from the presence of two different configurations, or is owing to difference in frequency between a para-crystalline and less-ordered arrangements of the polymer molecules cannot easily be determined. In simple synthetic polymers, such as polyethylene, differences in frequency are found between crystalline and amorphous forms of the polymer. Structure can also occur in the absorption band of a single crystal because of interaction between neighboring molecules.

It appeared at one time that infrared analysis might be able to distinguish between various configurations of a protein molecule (specifically between the $\alpha$-helix and the fully extended form of the polypeptide chain) even when the polypeptide chains were not arranged in any ordered pattern. This method depended on a change in the frequency of the CO absorption band in synthetic polypeptides which could be prepared in either of these two forms by precipitation from the appropriate solvent. However, there are so many possible reasons for

a small change in the frequency of an absorption band that the application of any such rule to proteins (even on an empirical basis) leads to serious difficulties and inconsistencies. Until the reasons for these changes are well understood from the study of simpler model compounds, it seems unwise to use them as a guide to protein structure.

In the case of deoxyribonucleic acid (DNA), preliminary x-ray analysis had led to a model (the Crick-Watson model) of this polymer consisting of two spiral chains linked together by hydrogen bonds between the purine and pyrimidine bases. Infrared studies on highly-oriented films of DNA have given independent confirmation of the main features of the Crick-Watson model and led to some modification in the position of the phosphate groups in agreement with the later more precise x-ray analysis. One of the most interesting features of the Crick-Watson model is the proposal that the pairing of the bases is quite specific (i.e., adenine to thymine and guanine to cytosine), since this provides the basis for a possible mechanism for the replication of genes. So far, no proof has been given of this key feature. It provides an excellent example of the kind of challenging problems which are emerging from the application of infrared spectroscopy to biology.