

# THE APPLICATION OF INFRA-RED SPECTRA TO CHEMICAL PROBLEMS

## A GENERAL DISCUSSION.

A GENERAL DISCUSSION held by the Faraday Society on 2nd January, 1945, in the Large Lecture Theatre at King's College, University of London, from 10 a.m. to 5 p.m. (By kind permission of the Principal and Delegacy of the College.)

Over 250 members and visitors were present and the Chair was taken throughout by the President (Professor E. K. Rideal). The papers which had been circulated in Advance Proof before the meeting and the Discussion thereon appear in the following pages.

## INTRODUCTION.

BY THE PRESIDENT.

The purpose of our meeting here to-day is to discuss some recent advances in infra-red spectroscopy. We have to deplore the death, after a short illness, of Sir John Fox, the Government Chemist. We had hoped that he, always an enthusiastic worker in this field, would have opened this discussion. Not only do we miss him here to-day, but our Society has suffered a great loss in his death. He was one of our most active and kindly members, willingly taking on burdens which the Society from time to time loaded him with.

It is one of the difficulties inherent in war time that the Secrecy Act intervenes with different degrees of rigour in the various nations. Here in this country much work in the field of infra-red spectroscopy has still to be withheld from publication. Our trans-Atlantic cousins are more fortunate in this respect. We have to thank Drs. Sutherland and Thompson for the trouble they have gone to and the great care they have exercised in separating the secret from the non-secret, permitting here and there a peep behind the scenes.

The successful complete analysis of the vibration rotation spectra of even simple triatomic molecules still proves to be a formidable undertaking. Its extension to higher polyatomic molecules, an important field of enquiry, may however be facilitated by the great technological advances which have been made in recent years, both in resolving power and in mechanisation and speed of recording. The next important development in infra-red analysis consists in the correct assignment of the fundamental frequencies to the specific intra-molecular atomic vibrations. This has been accomplished for a large number of triatomic and several polyatomic molecules. Information derived in this way has proved of service in the evaluation of specific heat and entropy data required for the computation of chemical equilibria for obtaining the axes of symmetry, moments of inertia and bond lengths. The replacement of hydrogen by deuterium in molecules containing hydrogen results in specific vibrations moving to lower frequencies, thus serving to check and confirm the assignments, evaluate more distances and check force fields. Again, these assignments in simple molecules permit us to develop the idea of vibrations localised inside particular groups and thus we can utilise the infra-red analysis for

the identification of particular groups in more complex organic molecules. Since the infra-red vibrational frequencies involve a change in dipole moment in the molecule or group, when we are considering a particular vibration in a compound, slight alterations in the magnitude of the vibrational quantum indicate that the constraints in the intra-molecular oscillations, *i.e.* the force constants, are affected by the proximity of other groups (*e.g.* dipole interaction) or by the mode and position of attachment of the group to the rest of the molecule. Closer analyses of these shifts are required since definite information on the force fields round groups are clearly of the greatest importance in Organic Chemistry.

The possibility of assignment of individual interatomic vibrations and frequencies within a particular group is proving of the greatest importance in the examination of the natural and synthetic polymers. It is well known that the evaluation of the ratio between 1 : 2 and 1 : 4 addition in the synthetic asymmetric vinyl class of polymers presents great experimental difficulties. Exact evaluation of this ratio under different conditions of polymerisation would take us another very definite step forward in the elucidation of the kinetics of the formation of this class of polymers. It is an interesting speculation whether the "link" or kinetic unit of which the macromolecular chains are formed (as postulated from data on viscosity and colligative properties) is revealed in the infra-red spectrum.

Another general field of investigation by means of infra-red analysis which merits detailed attention is the hydrogen bond. Thermochemical and colligative data, *e.g.* the freezing-point depressions have permitted us to get rough approximations to the free energy and heat changes involved in several hydrogen bondings. Even more accurate analysis of the equilibria between bonded and non-bonded species over a wide range in temperature is now possible; the importance of such is not restricted to the simple groups OH, NH and SH, but hydrogen bonding may play an important part in both the structure of the proteins and the remarkably large changes in entropy associated with the phenomenon of inactivation or denaturation.

Finally, one might mention the advances in radar which permit us to examine the infra-red spectrum in the region of a few centimetres. It is hoped that this interesting region may be examined in the near future.