And we, students of science, on our part lose nothing; we shall not be committing any intellectual 'Harakari' if we grant the hypothesis that those great prophets and seers had seen farther in their own way in these matters of religion and morality. As regards their conception of God it is conceivable that they may have felt more intensely the presence of some unique agency, the unity underlying the diversity of phenomena, that men of science are unravelling to-day. They have proclaimed in no uncertain terms that man can aspire to realize 'One' in all. They saw the same face in the myriads of faces animate and inanimate.

And finally, it may be that the great justification of science, the true philosophy, is yet to come. The present-day scientist, the devotee of the external, soul bewildering frills and frescoes of the outer temple may some day find unimaginable peace and harmony by withdrawing in the inner temple of the soul where all is one, heartily subscribing to the truth and

utility of the profound adage, 'Do unto others as you would have them do to you'.

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## THE APPLICATION OF INFRA-RED SPECTRA TO CHEMICAL PROBLEMS\*

APPLICATIONS of spectroscopy in different directions have been the subject of so many conferences on the subject that Professor Mulliken in opening the conference on spectroscopy in 1942 remarked, "Less attention has been given lately to spectroscopy as a pure science ..... It seems to us that the pure science aspects of spectroscopy deserved new emphasis." In the case of infra-red spectroscopy, however, difficulties confronting the investigator have been such that the number of votaries have been relatively small and the report under review represents one of the few conferences that have been specially devoted to this part of the subject. The collection of papers here constitutes a welcome report of the present position of the subject, though it represents essentially the contributions of the British school of workers from Oxford and Cambridge, an isolation presumably due to the difficulties of war time.

As one peruses the different papers, Professor Rideal's introductory remark, "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" constantly occurs to one's mind and it is to be hoped that the Faraday Society will soon have a fuller discussion on the subject.

The report falls naturally into two divisions, the first part dealing with experimental technique and the second with applications to different chemical problems. A brief review by

Drs. Sutherland and Thompson on recent developments and present position of spectrometers, optical systems, calibration, detection and recording of infra-red spectra begins the This is followed by a useful note on sources of radiation and the preparation of absorption cells and another on accurate measurement of cell thickness. The very brief contribution on solvents gives no doubt valuable information but one cannot help commenting on its laconic character. The timesaving device described by Willis and Philpotts for making hand-operated spectrometers automatic and Dr. Conn's Thermocouple Bolometer detector fill an important need and the increased speed for a given sensitivity should remove one of the disadvantages of infra-red and lead to a larger volume of work.

The greater part of the discussion is devoted to the second section referred to earlier. The value of infra-red spectra lies in the principle that except optical isomers, no two molecules can have an identical array of frequencies and the improved techniques have made it speedier. The principal obstacles in the way have been the difficulties in detecting, recording and computing accurately. An introductory note discussing these is followed by examples of typical analyses of closely related organic compounds, usually of common occurrence, and the report presented bears out clearly the advantanges of this tool.

A critical analysis of available experimental evidence leads Dr. Simpson to a new assignment of the fundamental frequencies of the ozone molecule. While due note is taken in making the assignments of the contour relationships, intensities, and probable values of the force constants, both the paper and the discussion thereon point to the necessity of reinvestigation of both electron diffraction and infra-red results. The paucity of the Raman

<sup>\*</sup> Transactions of the Faraday Society, 1945, 41, 171 297. Report of a discussion held on 2nd Januar-1945. Price 15s. (Messrs. Gurney & Jackson, London.)

spectra studies is quite noticeable, the only reported investigation being that of Sutherland and work on this also should lead to more valuable data for a correct assignment of frequencies. Still, the essential features of the structure of the ozone molecule may not be altered. In deciding on the possible contributing structures, however, the magnetic susceptibility value cannot rule out structures II and VI (p. 210), the observed feeble diamagnetism being of the right order of magnitude if these structures are also taken into account.

Of considerable interest to the chemist is information concerning the carbon-carbon bond and the bonds between hydrogen and the elements of the first short period. Bartholomè and Teller have shown that C-C vibrations lie between 809 and 1143 cm,-1 but this region sometimes involves overlapping with the C-H bending vibrations. Using Teller's method for a system of mass points in one plane, Kellner has found a remarkable agreement between his calculated and observed values of frequencies for open chain and alicyclic hydrocarbons as well as for various degrees of branching in the chains. There are, however, a number of instances where the frequencies given as "observed" by Kellner differ from those values reported by other authors and these other values bring out discrepancies. This only shows the limitations of any oversimplified method of approach as is the case here but the approach is none the less useful.

Linnett's evaluation of the force constants leads to a number of interesting results with the C-H bond. Abnormal values are obtained in the case of saturated hydrocarbons of the aliphatic series and their derivatives, whenever a resonance hybrid structure involving ionic structures is possible, as, for example, methyl fluoride and diphenylmethane. special behaviour of the first member of a homologous series is noticeable here too. The change from these saturated aliphatic structures to olefinic or benzenoid structures leads to an increase in the force constant which becomes still higher for the C-H bond in acetylenes. This leads to the surprising result that the strength of the bonds increases as the proportion of s-orbital in the hybrid bond increases. It is well known that the ease of hydrogen replacement by metals increases as one changes from saturated to acetylenic hydrocarbons and both phenomena have apparently the same explanation; that ionic structures with hydrogen positive make appreciable contribution to the hybrid form. As Higgins has pointed out, the same explanation is possible for the higher force constant in nitromethane. The presence of an aldehydic group also alters the force constant appreciably, in this case a decrease which is quite marked.

Using the Douglas Clark relation and the value of the force constants calculated, values of bond lengths have been obtained which agree reasonably well with observed values.

The calculations also bring out the periodicity in the M-H link (M being any element of the III to VII groups). The value of the force constant for the bond between hydrogen and a member of the first short period appears to bear a constant ratio to that of a bond between hydrogen and the corresponding member of the second short period. These generalisations obtained by the use of a drastically simplified potential field has to be treated with some reserve, as other factors also influence the force constant and may not be negligible in all cases. The results are, however, quite useful in correlating approximately the different properties of the bonds in question.

Dr. Sutherland has reported the results of a fresh investigation on the infra-red spectrum of the diamond. "Type II" diamonds are found to exhibit the peculiarity that transmission over the whole range of spectrum investigated was poor with a complete blackout in the region 4.5 to  $5\mu$ . "Type I" diamonds which may all be expected to behave alike, however, show very definite differences as may be noticed from the diagram on p. 290. This difference in behaviour among "Type I" diamonds is noticeable also in ultra-violet absorption. Obviously, a division of diamonds into just two classes is not adequate for a proper classification. While the prominent infra-red absorption bands remain to be explained, the mass of experimental evidence on which Raman has based his theory, makes it a better approximation to truth. As Sutherland suggests, more experimental work in the infra-red is needed and existing discrepancies between theory and experiment have to be accounted for.

The last contribution to the discussion is a brief note by Bell in which by taking a reasonable physical picture of the torsional potential energy, an agreement as good as those with planar vibrations is obtained for the bond torsion.

A group of three papers deal with topics of considerable technical interest. They present a useful account of the technique for the investigation of substances with high molecular weights and indicate means for the standardisation as well as for following the course of polymerisation or vulcanisation of rubber. The report on coal and coal extracts is enough to indicate the usefulness of infra-red spectra in the study of different grades of coal.

The collection of papers in this number lives up to the level aimed at in Discussions of the Faraday Society and should find a place in any library, academic or technological.

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