

RAMAN EFFECT AND ITS CHEMICAL APPLICATIONS  
Twenty-five Years in Retrospect

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ON 16th March 1928, Prof. C. V. Raman announced in an address in Bangalore the discovery of a new radiation in scattering which has since been termed 'The Raman Effect'.<sup>39</sup> At the conclusion of his address we find the prophetic conclusion, "We are obviously only at the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out". This has been well substantiated

provided us with a large collection of compounds, of which the relative positions of atoms and groups of atoms have been clearly indicated. These have helped in the applications of Raman Effect, while at the same time, the scattering studies have confirmed in a large measure the assignments of structure by the chemist. In this short survey in retrospect, it is not possible to cover the ground of the several thousand papers that have been published, nor is it necessary. There have been numerous monographs on the subject, <sup>a m</sup> each with its distinctive features, but the very nature of the subject makes these serve only as a starting point for further study. We may broadly divide the subject into four divisions: 'Organic Structures'; 'Inorganic Structures'; 'Analytical Applications'; and 'Reaction Mechanisms'.

## § 1. ORGANIC STRUCTURES

Except in the simplest of compounds, the assignment of characteristic frequencies to individual bonds is by no means easy. However, the problem has been simplified, because of the ready availability of a large number of closely related compounds in which changes are confined to parts of the molecule, while one part remains constant. Assignments are then made by essentially empirical rules: that the radicals in question retain their identity and their characteristic frequencies remain constant over a series, without being modified to any appreciable extent by the rest of the molecule. This is probably true of the vibrations of hydrogen along with the valency bond, but, as will be seen later, even this is subject to limitations. In quite a number of instances, the assignments have been made possible by an application of the Teller-Redlich theorem.<sup>30,41,43</sup> Another method, frequently used with success by Daure,<sup>12</sup> Cabannes,<sup>7</sup> Kohlrausch<sup>25</sup> and others, makes use of changes in frequency caused by a progressive increase in the mass of certain atoms while the rest of the molecule remains unchanged. Using these methods bond-stretching frequencies have been assigned to various bonds, some of which are presented in Tables I, II, III and IV.

It will be noticed from Table I that X-H vibrations show systematic variations with the position of the element X in the periodic table. There is the unmistakable drift in the direction of higher frequencies with increasing differences

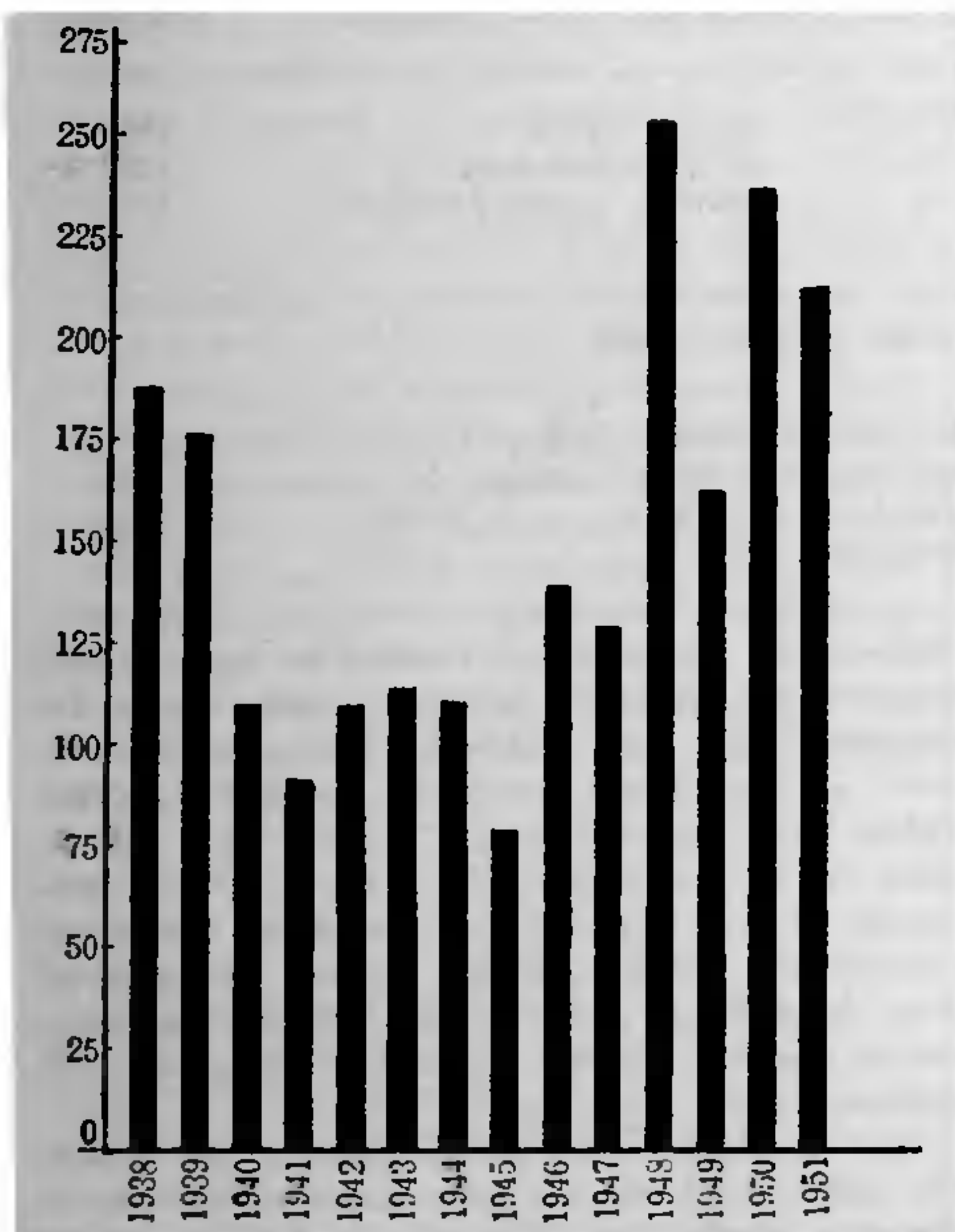


FIG. 1. In the Raman Jubilee Volume of the *Proceedings of the Indian Academy of Sciences* Hibben has analysed the trends in Raman Effect studies upto 1938. The above graph prepared from an analysis of the papers abstracted by *Chemical Abstracts* will be of interest in continuing part of Hibben's analysis. I have to thank Messrs. D. Setu Rao and S. Natarajan for the graph. by the enormous amount of work on the phenomenon published during the last twenty-five years. The classical organic chemist by a combination of intuitive and empirical approach has

TABLE I  
(a) Characteristic frequencies of X-H bonds

Element	..	B	C	N	O	F	Si	P	S	Cl
Raman Line	..	2590	2960-3300	3300-3380	3400-3680	(4140)	2160-90	2400	2680	2800
Force Constant	..	(3.6)	4.97	6.49	8.35	9.62		3.10	4.02	5.13

(b) Characteristic frequencies of X-X bonds

Element	..	C	N	O	Si	P	S
Single bond Frequency	..	900	880	877	435	465	467
Double bond Frequency	..	1640	1442	(1280)			
Triple bond Frequency	..	2050	2328				

TABLE II  
(a) Variations in C-H frequencies

Compound	Frequency	Compound	Frequency	Compound	Frequency
Methane	.. 2918	Ethylene	3019	HCN	3312
Ethane	.. 2913, 2943	Propylene	3012	Acetylene	3287
<i>Iso</i> -Butane	.. 2910, 2936, 2962	Vinyl Chloride	3036	Methyl Acetylene	3305
Nitromethane	.. 2967, 3056				

(b) Change in frequencies of C-C bond

Ethane	.. 990	<i>Iso</i> -Propyl Chloride	1059	Ethyl Chloride	1120, 950
Propane	.. 870, 1050	.. Bromide	1038	<i>t</i> -Butyl ..	1153
<i>n</i> -Butane	.. 979	.. Iodide	1019	.. Bromide	1142
<i>Iso</i> -Butane	.. 794, 964, 1098	.. Mercaptan	1056	.. Iodide	1131

in the electronegativities of the element with reference to hydrogen. Pauling<sup>35</sup> has shown that these differences can be correlated with the degree of ionic character of the bond in question. One can then expect that the hydrogen-fluorine bond is essentially ionic and this is confirmed by the non-observance of a Raman Line even in the most concentrated aqueous solutions of hydrogen fluoride. The changes observed are similar, both for the first and the second short periods but, as may be expected, the values are consistently lower in the latter case. The period relationship is found also when we consider the X-X bond. The individuality of the molecule is clearly demonstrated by the variations noticed in both C-H and C-C bonds and similarly variations in group interactions are exemplified by ethylenic and carbonyl frequencies.

In most correlations of physical properties with structure, it is generally assumed that the contribution of the methylene group or the C-H and C-C bonds remains constant. Careful analysis has, however, revealed that this assumption is not justified (cf. Walsh<sup>44</sup>). Since bond

dissociation energies are related to the characteristic frequencies, a similar position may be expected here also. Table II illustrates the extent of variation involved. Bartholomé and Teller have shown that C-C single bond vibrations lie in the region 809-1143 cm.<sup>-1</sup>,<sup>4</sup> but because of overlapping C-H bending vibrations caused by intramolecular forces, assignment may be difficult. Kellner has indicated a theoretical method for the purpose of assigning C-C frequencies.<sup>23</sup>

The importance of group interactions within the same molecule are even more noticeable in the case of ethylene derivatives and the carbonyl compounds (Tables III and IV).

Isomerism of different types in the case of carbon compounds has been built up and illustrated by several compounds using two simple principles: (i) the valency of carbon is constant having a value of four and with the bonds directed towards the four corners of a tetrahedron, carbon being at the centre; and (ii) free rotation is possible round a single bond but multiple bonds cause greater rigidity. Recent developments in valence theories have



TABLE III  
Characteristic frequencies of ethylene derivatives changes in  $C=C$  frequencies

$CH_2$ CHX X	Frequency	$CH_2$ CX <sub>2</sub>	Frequency	CHX CX <sub>2</sub>	Frequency	CX <sub>2</sub> CX <sub>2</sub>	Frequency
H	1623						
Me	1647		1650		1679		
D			1581				1514
Cl	1608						1571
Br	1598						
CHO	1618	Allene	1480				
CH CH <sub>2</sub>	1634	<i>cis</i> Butane	1669				
CH <sub>2</sub> Cl	1640	<i>trans</i> „	1681				
C <sub>6</sub> H <sub>5</sub>	1601						

TABLE IV  
Carbonyl frequencies

Compound	Frequency	Compound	Frequency	Compound	Frequency
Acetone	.. 1710	Acetophenone	.. 1677	Benzophenone	.. 1663
Formaldehyde	.. 1768	Benzaldehyde	.. 1689	Fluorenone	.. 1718
Acetaldehyde	.. 1715	Acetyl chloride	.. 1798	Oxalic acid	.. 1750
Acetic acid	.. 1666	Benzoic acid	.. 1647		

not materially altered the situation.<sup>11</sup> The thermodynamic properties of ethane and some of its derivatives clearly showed that there is a potential barrier to free rotation and that the methyl groups or substituted methyl groups take up favoured positions. In the case of ethane itself, Raman spectra do not enable one to distinguish between the two alternative forms (Fig. 2)

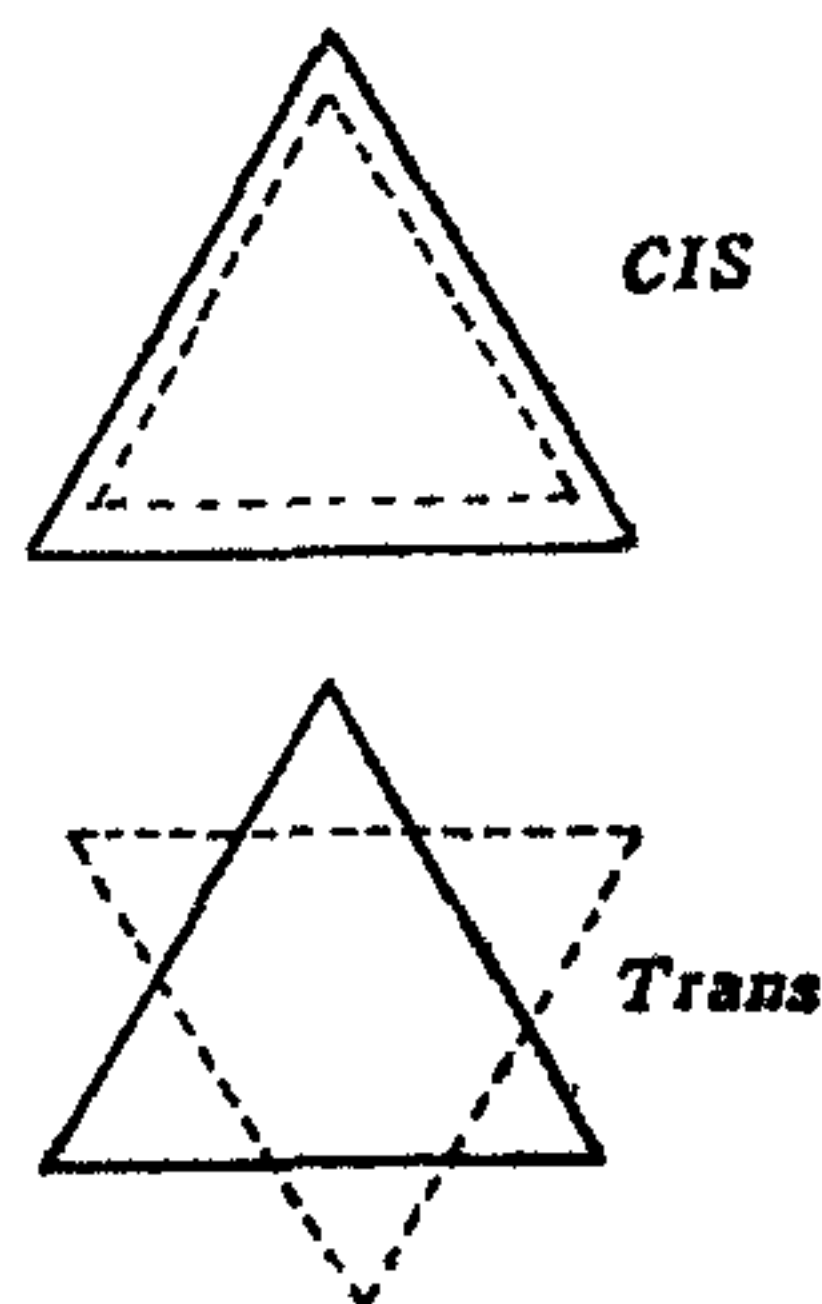


FIG. 2. Alternative (*cis* and *trans*) forms of ethane. but hexadeutero ethane appears to have the transform with  $D_{8d}$  symmetry<sup>10,22,42</sup> The case of substituted ethanes is even more interest-

ing. Taking a number of compounds of the formula  $CH_2X-CH_2Y$  Langseth and Bernstein<sup>28</sup> have shown other possible configurations also (Fig. 3).

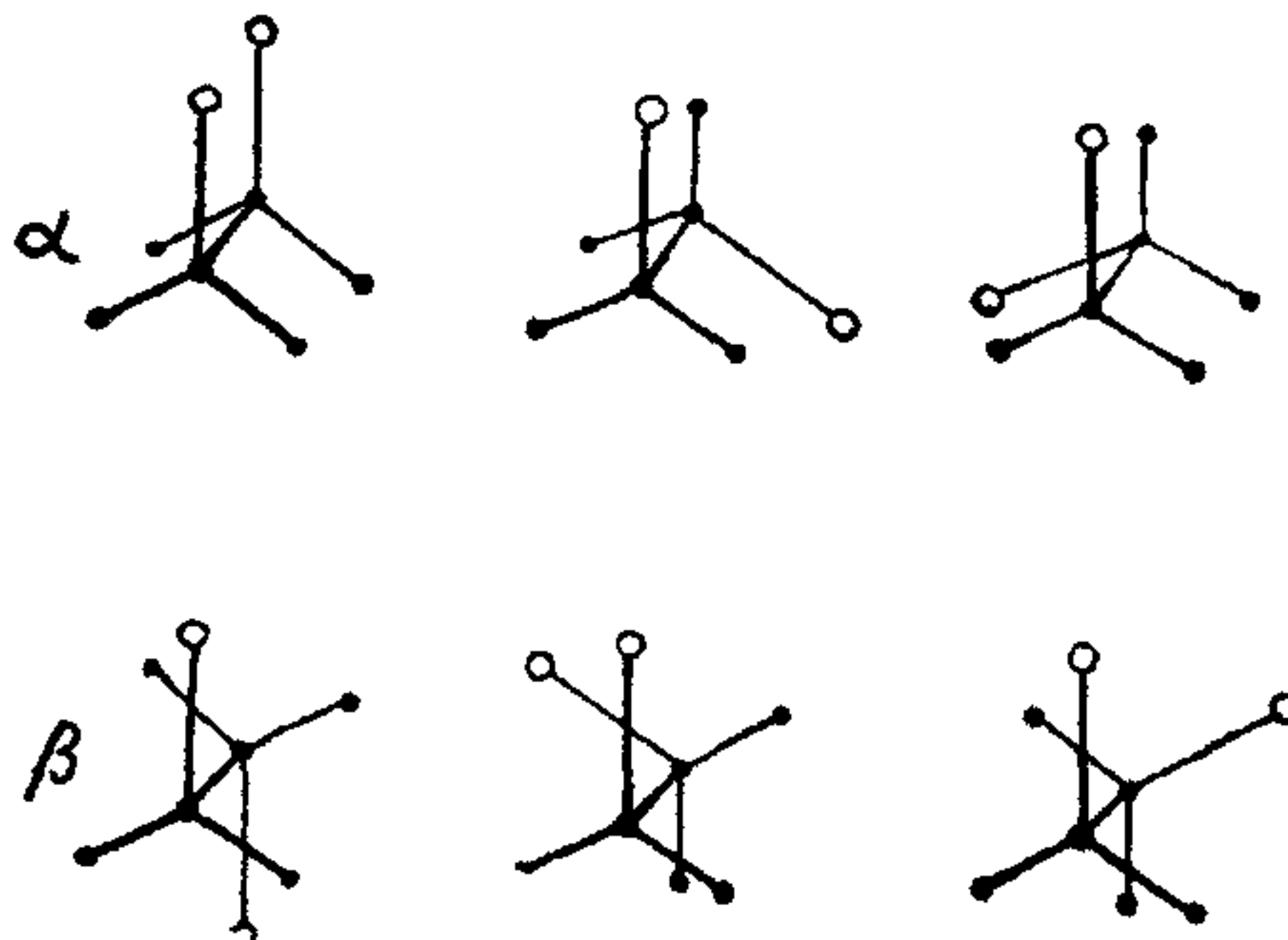


FIG. 3. Possible configurations of the type  $CH_2X-CH_2Y$  Raman spectra studies have thus enabled the detection of the presence of such rotation isomers which are chemically not separate entities if one considers the reactivities alone.

Tautomeric systems have provided us examples of the pitfalls in the use of Raman Spectra data. Kohlrausch,<sup>24</sup> from his study of acetyl acetone concludes that it is necessary to consider the presence of two monoenolic and two

dienolic forms, while Lecomte from his infra-red studies on metal acetylacetonates<sup>29</sup> concludes that there is no hydroxyl group but makes hydrogen part of a six-membered ring system. This is analogous to the approach of the classical chemist to the question of hydrogen bond. One has to expect variations in both hydroxyl and carbonyl frequencies because of group interactions and, in the case of intermolecular hydrogen bonding, it is also necessary to consider the environment which modifies bond polarisabilities. The valuable extensive work of Murti and Seshadri,<sup>34</sup> while providing clear evidence for hydrogen bonding in the systems studied, suffers from this limitation. It is now fairly clear that the hydrogen bond is electrostatic in nature involving an energy change of a higher order than van der Waals forces. While this may cause a preferential orientation of the hydroxyl group, where intramolecular hydrogen bonding is the case, with intermolecular hydrogen bonds, it is difficult to expect the rigidity which is implicit in the structures postulated by these authors.

One of the structural problems that Raman Spectra has helped to solve is that of tetranitromethane. From its reactions, chemists have often favoured the view that one of the nitro groups must be different from the other three. The elucidation of the problem has been the extensive work of Chèdin,<sup>9</sup> and of Mathieu and his associates.<sup>31</sup> The analysis of the Raman lines of nitromethane showed that the two parts of the molecule are not free to rotate with respect to each other about the C-N axis. In the case of tetranitromethane this school of workers have shown that each C-NO<sub>2</sub> group lies in one plane. The complete Raman Spectrum requires a tetrahedral symmetry with all the nitro groups equivalent. The difference in reactivity is obviously similar to the differences in energy required for the rupture of a C-H bond in methane where all the hydrogen atoms are equivalent.

An outstanding triumph of Raman Effect studies concerns the elucidation of the structure of benzene. While the early work of Kohlrausch suggested the two equivalent Kekulé structures, the position was uncertain till the classical investigations of Ingo'd and co-workers on benzene and its partially deuterated derivatives were made.<sup>20</sup> These observations have clearly established the D<sub>6h</sub> symmetry of the molecule.

In dealing with problems of structure, mention should also be made to the contributions to our knowledge of hyperconjugation involving methyl groups. Comparisons of Raman

Spectra have also shown that with alkyl derivatives, primary compounds show a mobile structure while secondary compounds show a greater degree of rigidity which is still greater in the tertiary compounds. The indications may be noticed even in the C-C single bond vibrations indicated by Kellner (*loc. cit.*).

## § 2. INORGANIC STRUCTURES

In spite of the wealth of material, work with inorganic compounds has been comparatively less extensive than with organic ones. The complex nature of the material and the need for the study of a large proportion of these either in the solid state or in solution is partly responsible for this state of affairs. The field, however, has not been neglected. Leaving out the binary compounds of an ionic type, we may consider the developments in a few select instances.

The most exhaustive studies relate to solutions of acids in water, various concentration ranges being generally used. The principal difficulties in the interpretation of the results arise from two causes: considerable changes in the dielectric constant of the solutions have to be expected with large changes in concentration of solute; the hydrogen ion in solution is invariably solvated. Also it is difficult to differentiate between ion-pairs in concentrated solutions and a highly polarised covalent bond that is often postulated in some cases. A limitation in most of the interpretations is the tendency to assume that water remains unaffected by the solute.

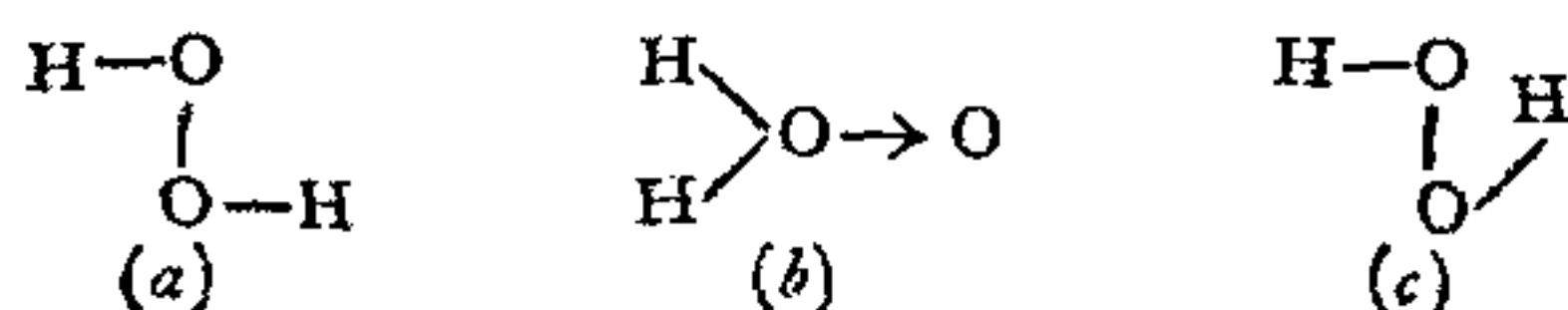
Halides of different groups have been extensively studied. All the halides of the formula XY<sub>3</sub> in the fifth group that have been studied show the expected Raman lines on the basis of a pyramidal structure while in the case of boron trihalides, evidence of the planar structure was obtained by studying isotope shifts. The cases of phosphorus pentachloride and of aluminium chloride are of particular interest. Raman spectral studies of the first compound<sup>33</sup> clearly indicated the presence of PCl<sub>4</sub><sup>+</sup> in the solid which is now known from other physical studies to be essentially PCl<sub>4</sub><sup>+</sup> PCl<sub>6</sub><sup>-</sup>.<sup>10</sup> Anhydrous aluminium chloride which is known to occur normally in the dimeric form has been assigned the D<sub>2h</sub> symmetry by Kohlrausch though the evidence from Raman and infra-red spectra have not been without difficulties.<sup>20</sup>

Among structures that have intrigued both physicists and chemists is that of diborane. Several alternatives have been proposed: (i) the structure proposed by Pauling involving a resonance hybrid with direct bond between



the two boron atoms: (ii) the structure proposed by Bell<sup>5</sup> involving a hydrogen bridge structure; and (iii) a protonated double-bonded structure suggested by Pitzer.<sup>38</sup> While some type of hydrogen bonding is now fairly established, neither Raman Spectra nor infra-red spectra enable any unequivocal decision between the Bell and the Pitzer models.

Hydrogen peroxide has also presented difficulties with the possible structures:



Penney and Sutherland have shown from an analysis of the characteristic frequencies that the puckered dihydroxylic form (c) in which the hydroxy groups are in perpendicular planes, best represents the molecule.<sup>36</sup>

Nitric acid is one of the most thoroughly investigated compound. Earlier work has been no doubt useful as a guide but the nature of the "unionised" form has been uncertain. The exhaustive investigations of Ingold and co-workers<sup>21</sup> on pure nitric acid and in solutions has enabled a complete interpretation of the spectral behaviour in accord with the model of Maxwell and Moseley<sup>32</sup> (Fig. 4).

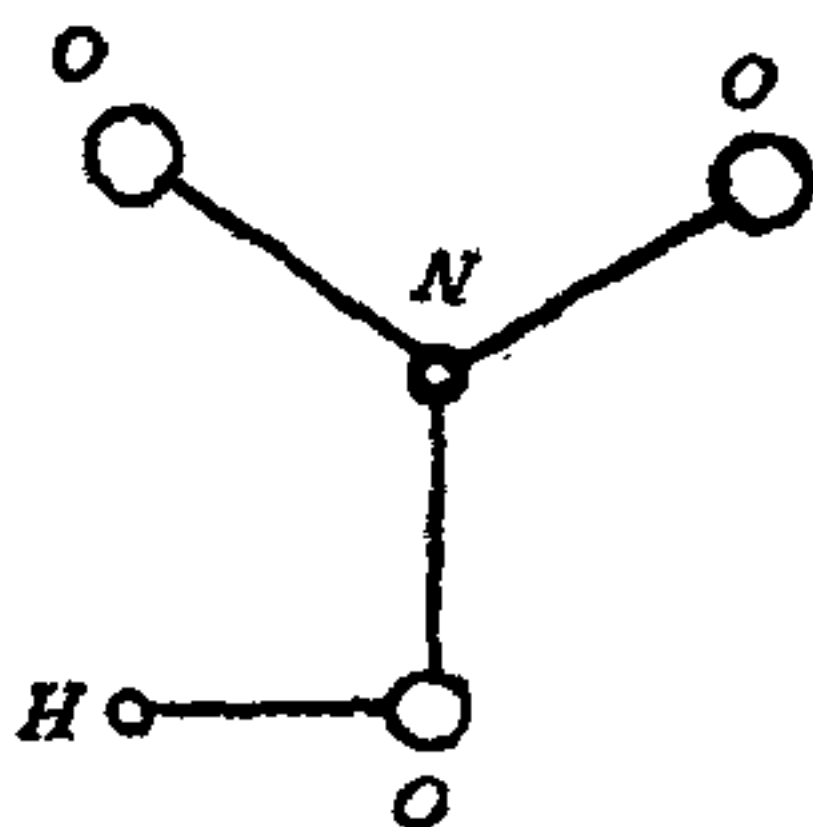


FIG. 4. Structure of Nitric Acid.

It may be mentioned here that Raman Spectra of the monomeric form of cyanic acid and of thiocyanic acid, as also hydrazoic acid, indicate the presence of an N-H bond in all three rather than the isomeric structure with O-H or S-H bond as the case may be.

Raman Spectra studies have also been of use in the study of ions of the type  $XY_3$  and  $XY_4$  besides various complexes.

### § 3. ANALYTICAL APPLICATIONS

The simplicity of technique and the individuality of Raman Spectra have enabled the gradual use of Raman Spectra in the qualitative and quantitative analysis of mixtures of closely related compounds which could not be

handled by the usual chemical means. Other physical methods often involve expensive equipment and, where isomeric hydrocarbons are involved, unsatisfactory in use.

In the present brief survey it is not possible to make any detailed reference to improvements in the techniques. These have been designed to improve the intensity of the scattered radiation, cutting out the background illumination and the development of photoelectric and similar devices for recording as well as detecting Raman line.<sup>18,27</sup> One of the most interesting devices is that of a multiple reflection technique which has made the study of gases more feasible than before.<sup>45</sup>

Quite early in the development of the subject, interesting applications have been noticed in the perfumery industry. The relative amounts of isopropylidene and of isoprenyl isomers in the terpene series, the composition of both natural and synthetic mixtures of the terpene hydrocarbons and similar compounds have been studied extensively in France.

Raman Spectra have been particularly useful for the study of unstable compounds which cannot be frozen out as in the case of nitrogen pentoxide in nitric-sulphuric acid mixtures, nitric-perchloric acid mixtures and similar instances.<sup>8,21</sup> By a measurement of intensities of persistent lines, Goubeau has been able to detect and make a rough estimate of the relative amounts of benzene, toluene and the xylenes<sup>17</sup> while Piaux estimates the amounts of *cis* and *trans* pentenes obtained by the dehydration of pentanol using the specificity of their Raman Spectra.<sup>37</sup> Initial work on aromatic hydrocarbon mixtures dealt with binary mixtures but more recent work has enabled the estimation of as many as eight aromatic compounds with an accuracy of 2%.<sup>40</sup>

The method is particularly handy where the components of a mixture are not affected by intermolecular forces. This is the case with hydrocarbons and both qualitative and quantitative are possible with comparison spectra of the pure hydrocarbons. Fenske and others have prepared a very useful collection of Raman spectrograms for over 350 compounds.<sup>9,15</sup> Recently, a monograph has appeared<sup>1</sup> devoted solely to the analytical applications of the Raman Effect.

### § 4. CHARACTERISTIC FREQUENCY AND CHEMICAL REACTIVITY

While Raman Spectra have not been as useful as ultraviolet absorption or infra-red studies



in the identification of transient molecules, it is nevertheless an important tool in the correlation of reactivity with structural influences.

The concept of mesomerism or resonance has been introduced to account for the behaviour of a variety of compounds<sup>19,35</sup> and Raman Spectra have been helpful in the elucidation of some of these structures. Thus Raman spectral evidence has substantiated the symmetry of the nitro group, the carboxyl, nitrate and carbonate ions and the linear structure of carbon dioxide and carbon disulphide. Both infra-red and Raman Spectra have been used in following the course of polymerisation reactions where the mesomeric structure of a butadiene system is progressively replaced by a system of isolated double bonds. The precision of measurements now possible has enabled a study of the influence of the structure of the initial polyenes on the course of polymerisation. A close correlation between the  $C=C$  double bond frequency and the activation energy of the reaction as well as the relationship between the carbonyl frequency and activation energies for both acid and alkaline hydrolysis of carboxylic esters is noticeable.<sup>2,3</sup> Addition and substitution reactions and the relationship with characteristic vibrations has been the subject of study by Duchesne.<sup>14</sup>

In dealing with reactivity, one has to reckon more with excited structures than with molecules in the ground state and Duchesne has indicated the problem taking the relative rate of addition of hydrogen bromide to ethylene and acetylene as examples.<sup>13</sup> It is interesting to note in this connection that the infra-red studies of Ingold has recently shown that in its excited state, acetylene has a non-linear form. The subject deserves further study.

1. (a) Bhagavantam, S., *Scattering of Light*, Andhra University, Waltair, India, 1940. (b) Daure, P., "Introduction à l'étude de l'effet Raman," *Revue d'optique*, Paris, 1933. (c) Herzberg, G., *Molecular Spectra and Molecular Structure*, 1945, van Nostrand, New York. (d) Hibben, J. H., *Raman Effect and its Applications*, Reinhold, New York, 1939. (e) Kohlrausch, K. W. F., *Der Smekal Raman Effekt*, 1931, 1938, Springer, Berlin. (f) —, *Ramanspektren*, Belcher. (g) Otting, W., *Der Raman-Effekt und seine Analytische Anwendung*, 1952, Springer, Berlin. (h) Placzek, *Rayleigh Streuung und Raman Effect*

1934, *Handbuch der Radiologie*, 6, Part 2. (i) Sutherland, G. B. B. M., *Infra-Red and Raman Spectra*, 1935, Methuen, London. (j) Wu, T. Y., *Vibrational Spectra and Structure of Polyatomic Molecules*, 1939, University of Peking. (k) *Reviews of Modern Physics*, 1943 &c. (l) *Report on the Progress of Physics*, Physical Society, London, 1945 &c. (m) *Annual Reports of Chemical Society*, London, 1934 &c. 2. Anantakrishnan, S. V., *Proc. Ind. Acad. Sci.*, 1948, **27A**, 184. 3. —, *Ibid.*, 1949, **30A**, 23. 4. Bartholome and Teller, E., *Z. Physik. Chem.*, 1932, **19B**, 366. 5. Bell, R. P., and Longuet-Higgins, H. C., *Proc. Roy. Soc.*, 1945, **183A**, 257. 6. Braun, W. G., Sponer, D. F., and Fenske, M. R., *Anal. Chem.*, 1950, **22**, 1074. 7. Cabannes, J., and Rousset, A., *J. Phys. Radium*, 1940, **11**, 155, etc. 8. Chedin, J., *Ann. Chim.*, 1937, ser. xi, **8**, 243. 9. —, *J. Phys. Radium*, 1939, **10**, 445. 10. Clark, D., Powell, H. M., and Wells, A. F., *J. C. S.*, 1942, 642. 11. Coulson, C. A., *Valence*, O.U.P., 1952. 12. Daure, P., *Ann. Phys.*, 1929, **12**, 375; *Ibid.*, 1932, **18**, 285. 13. Duchesne, J., *J. Chem. Phys.*, 1950, **18**, 1120. 14. —, *Bull. Acad. Belg.*, 1952, 5, ser. **38**, 197. 15. Fenske, M. R., et al., *Anal. Chem.*, 1947, **19**, 700. 16. Glockler, G., and Renfrew, W., *J. Chem. Phys.*, 1938, **6**, 170, 409. 17. Goubeau, Z. *Anal. Chem.*, 1936, **105**, 161. 18. Heyl et al., *Anal. Chem.*, 1950, **22**, 154. 19. Ingold, C. K., *J. C. S.*, 1933, 1120. 20. —, et al. *Ibid.*, 1936, 912-987. 21. Ingold and Miller, *Ibid.*, 1950, 2612. 22. Karweil, J., et al., *Z. Physik. Chem.*, 1938, **40B**, 382. 23. Kellner, I., *Trans. Farad. Soc.*, 1945, **41**, 217. 24. Kohlrausch, K. W. F., et al., *Ber.*, 1934, **67**, 976; 1465, &c. 25. Kohlrausch and Wagner, J., *Z. Physik. Chem.*, 1939, **45B**, 93. 26. —, *Ibid.*, 1942, **52B**, 185. 27. Kudrjavseva, V., *Acta Physicochemica URSS.*, 1935, **3**, 613. 28. Langseth and Berastein, *J. Chem. Phys.*, 1940, **8**, 410. 29. Lecomte, *Discussions Farad. Soc.*, 1950, **9**, 125. 30. Lord, R. C. and Teller, E., *J. C. S.*, 1937, 1728. 31. Mathieu, *Ann. Phys.*, 1941, **16**, 5. 32. Maxwell and Moseley, *J. Chem. Phys.*, 1940, **8**, 742. 33. Moureau, Magat M. and Wettröf, *Proc. Int. Acad. Sci.*, 1938, **8A**, 356. 34. Murthi, G. V. L. N., and Seshadri, T. R., *Ibid.*, 1941, **15A**, 154, etc. 35. Bauling, L., *Nature of the Chemical Bond*, 1940, Cornell. 36. Penney, W. G., and Sutherland, G. B. B. M., *Trans. Farad. Soc.*, 1934, **30**, 938. 37. Piaix, L., *Chim. et Ind.*, 1935, **34**, 507. 38. Pitzer, K. S., *J. Chem. Phys.*, 1949, **11**, 1007. 39. Raman, C. V., *Ind. J. Phys.*, 1928, **2**, 387. 40. Rank, D. H., and Weygand, R. V., *J. Opt. Soc. Amer.*, 1946, **36**, 325. 41. Redlich, J., *Phys. Chem.*, 1935, **28B**, 371. 42. Stitt, J., *J. Chem. Phys.*, 1939, **7**, 297. 43. Teller, E., quoted by 20. 44. Walsh, A. W., *Trans. Farad. Soc.*, 1947, **43**, 60. 45. Welsh et al., *J. Opt. Soc. Amer.*, 1951, **4**, 91.