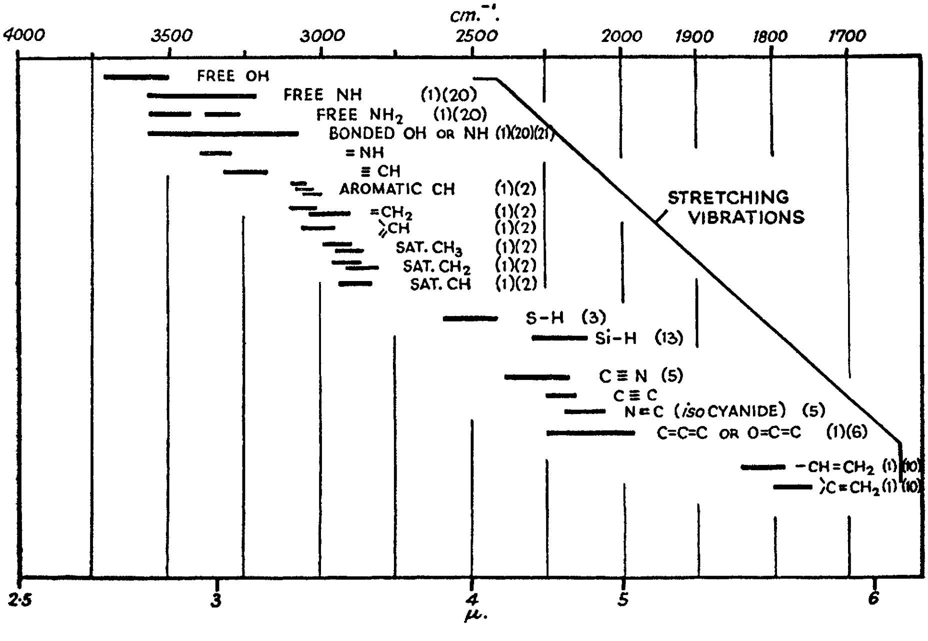
81. *The Correlation of Vibrational Absorption Spectra with Molecular Structure.*

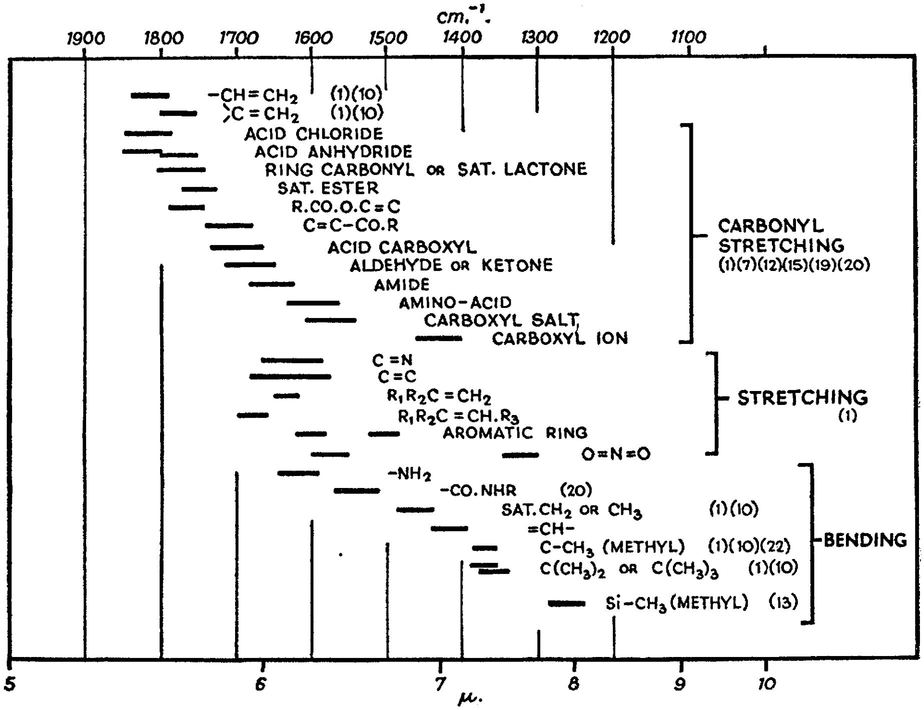
By H. W. Thompson.

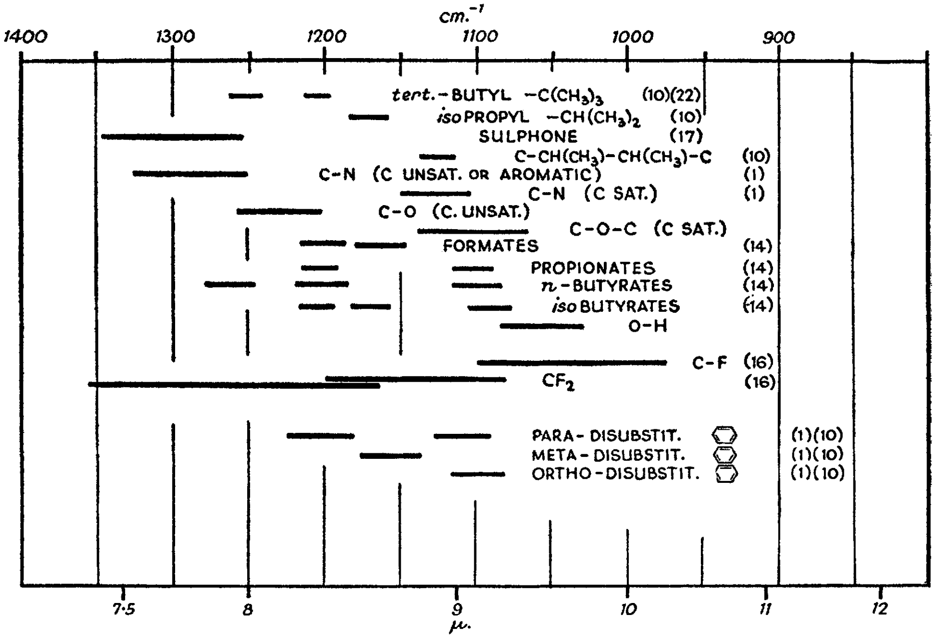
Correlation rules are given relating vibrational spectra to characteristic groupings.

The use of vibrational spectra for structural diagnosis is becoming increasingly important in the study of complex organic substances. The recent rapid developments of experimental technique have made it possible to compare the spectra of many related series of molecules, from which it has been found that certain groups have characteristic vibration frequencies



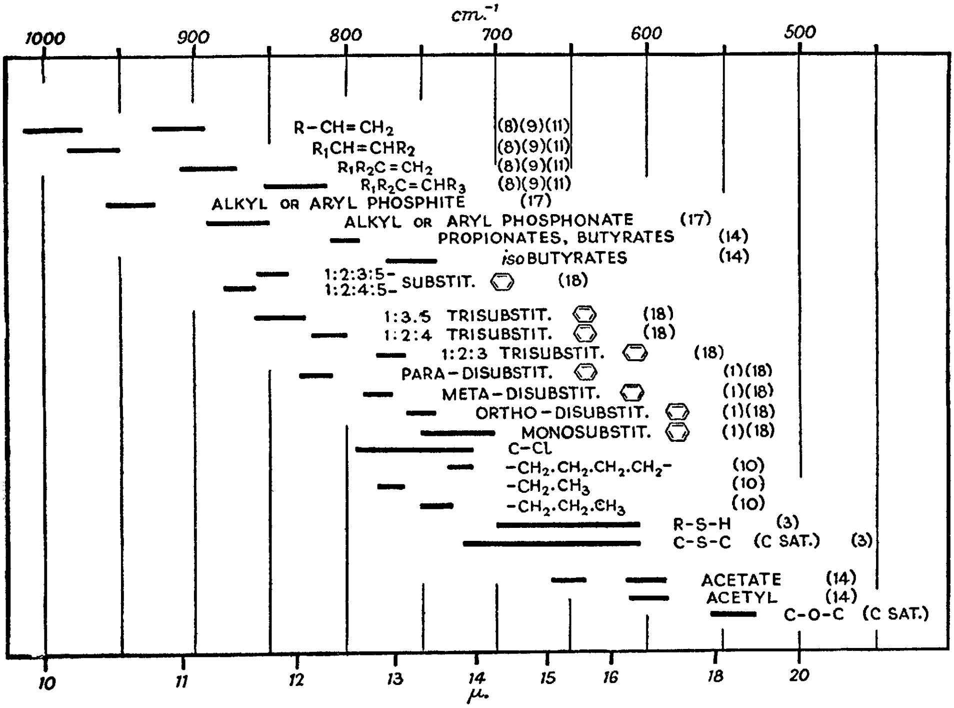
giving rise to marked absorption bands which persist in different compounds. Further, with some linkages or groups such as the carbonyl group, small specific alterations of the joining-





atoms or linkages lead to small but characteristic displacements of the vibration frequencies, and this occasionally provides a further refinement in the diagnosis.

Since it is at present impossible to publish curves for all the substances which have been examined, some correlation rules have been drawn up in the Figures, many of which have been illustrated in recent papers. The charts have been drawn in a manner previously adopted by Barnes, Williams, and Gore, with whom the correlation rules have recently been discussed.



Most of the vibration frequencies given relate to fairly strong absorption bands which can be picked out in the spectrum unless there is accidental overlapping with other bands. Many of the rules given are not infallible, and special electronic effects may lead to abnormalities. The rules should, therefore, be taken as general guidance to be applied with proper caution. In addition, the state of aggregation in which a substance is measured may be of importance. References are given on the charts to some of the papers from which the rules have been drawn. The list is not complete, for some of the correlations are now sufficiently well known to make details superfluous. The rules may be helpful in designing a punched card index of the vibrational spectra of chemical compounds which is under consideration by several laboratories.

References.

1. Barnes, Gore, Liddel, and Williams, "Infra-red Spectroscopy", Reinhold, 1944; *Ind. Eng. Chem.* (*Anal.*), 1943, **15**, 659.
2. Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; 1940, *A*, **175**, 208.
3. Thompson and Trotter, *J.*, 1946, 481.
4. Herzberg, " Infra-red and Raman Spectra ", van Nostrand, 1945.
5. Anderson, Le Fèvre, and Savage, *J.*, 1947, 445; Sheppard and Sutherland, *J.*, 1947, 453.
6. Thompson and Harris, *Trans. Faraday Soc.*, 1944, **40**, 295; Drayton and Thompson, *J.*, in the press; Whiffen and Thompson, *J.*, 1946, 1005.
7. Hartwell, Richards, and Thompson, *J.*, in the press.
8. Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3; *J.*, 1944, 183, 303; *Trans. Faraday Soc.*, 1945, **41**, 246; 1946, **42**, 432.
9. Tuot, Lecomte, and Lorillard, *Compt. rend.*, 1940, **211**, 586.
10. Work on the spectra of hydrocarbons at Oxford and Cambridge, to be published shortly.
11. Brattain and Rasmussen, *J. Chem. Physics*, 1947, **15**, 120, 131, 135.
12. Richards and Thompson, unpublished reports on spectroscopic work on penicillin.
13. Richards and Thompson, *J.*, 1947, 293.
14. Thompson and Torkington, *J.*, 1945, 640.
15. Lecomte, *J. Physique*, 1945, **5**, 1; *J. Phys. Radium*, 1942, **8**, 196.
16. Torkington and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 236; Temple and Thompson, *J.*, in the press.
17. Thompson, unpublished work.

18. Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246; Whiffen and Thompson, *J.*, 1945, 268.
19. Lecomte, papers in *Compt. rend.*, 1941—45 and *Bull. Soc. chim.*, 1942—44.
20. Richards and Thompson, *J.*, in the press.
21. Richards and Thompson, *J.*, in the press.
22. Thompson, The Tilden Lecture, *J.*, 1944, 183.
23. Thompson, Discussion on Macromolecules, *J.*, 1947, 289.
24. Thompson, *Endeavour*, 1945 (Oct.).
25. Thompson, *Ann. Reports*, 1945, **42**, 5.
26. Kohlrausch, " Der Smekal-Raman Effekt ", Springer, 1931; Hibben, " The Raman Effect ", Chem. Catalog Co., 1939.

THE PHYSICAL CHEMISTRY LABORATORY, OXFORD.

[*Received, September* 24*th*, 1947.]