

Potential Constants of Tetrachlorethylene

G. B. B. M. SUTHERLAND and D. M. DENNISON¹ have deduced the relations between the parallel frequencies and the potential constants of the ethylene molecule from a given potential function; the following deals with the extension of these relations to a similar type of molecule, namely, that of tetrachlorethylene.

If from the data on Raman and infra-red spectra² we assume for the frequencies (Sutherland's notations):

$$\nu_1 = 913 \text{ cm.}^{-1}; \quad \nu_2 = 445 \text{ cm.}^{-1}; \quad \nu_3 = 345 \text{ cm.}^{-1}; \\ \nu_4 = 1569 \text{ cm.}^{-1}; \quad \nu_8 = 236 \text{ cm.}^{-1}$$

and substitute these values in equation (a)

$$\nu_1^2 + \nu_3^2 + \frac{M+2m}{M} \frac{\nu_2^2 \nu_4^2 \nu_8^2}{\nu_1^2 \nu_3^2} = \nu_2^2 + \nu_4^2 + \nu_8^2$$

which has been deduced from the potential function, we obtain satisfactory agreement.

However, before computing the potential constants, it is necessary to modify the experimental values of the frequencies in order to satisfy equation (a) exactly. A least square solution gave:

$$\nu_1^* = 913 \text{ cm.}^{-1}; \quad \nu_2^* = 442 \text{ cm.}^{-1}; \quad \nu_3^* = 345 \text{ cm.}^{-1}; \\ \nu_4^* = 1569 \text{ cm.}^{-1}; \quad \nu_8^* = 230 \text{ cm.}^{-1}.$$

The smallness of the change of the experimental frequencies sufficient to verify equation (a) exactly should be noted.

Finally we find:

$$a = 4.59 \times 10^5 \text{ dynes/cm.}; \quad b = 1.89 \times 10^5 \text{ dynes/cm.} \\ c = 6.15 \times 10^5 \text{ dynes/cm.}; \quad d = \pm 1.52 \text{ dynes/cm.}$$

a, b, c, d being the potential constants.

The difference between my value of c (C-C bond) and Sutherland and Dennison's value for ethylene (9.79×10^5 dynes/cm.) is very remarkable. For this reason, I also used the Delfosse potential function³, which is absolutely independent of Sutherland and Dennison's. Furthermore, I used only the three Raman frequencies ν_2, ν_4, ν_8 , which are much more certain than the ν_1 and ν_3 necessary in Sutherland and Dennison's theory. This ought to give more weight to the following results.

We find:

$$F = 6.25 \times 10^5 \text{ dynes/cm.}; \quad \gamma = 2.24 \times 10^5 \text{ dynes/cm.}; \\ f = 1.28 \times 10^5 \text{ dynes/cm.}$$

f and F are respectively proportional to the C-Cl and C-C distances; γ is a force proportional to the angle variation Cl-C-Cl.

The agreement between the two values of the C-C strength bond is very striking. It should be noted that the value γ is greater than f . This is contrary to ordinary chemical conceptions. The difference between the C-C value for ethylene and tetrachlorethylene agrees qualitatively with Badger's formula⁴

$$r_e = (C_{ij}/k_e)^{1/3} + d_{ij},$$

which shows a very definite relation between the force constant k_e for a particular bond and the internuclear distance r_e associated with that bond. Consequently, if the force constant is smaller in C_2Cl_4 than in C_2H_4 , the C-C distance should be larger in C_2Cl_4 than in C_2H_4 . Electronic diffraction and spectroscopic measurements do not invalidate this deduction. L. O. Brockway⁵ gives 1.38 Å. for tetrachlorethylene, W. Scheib and P. Lueg⁶ 1.34 Å. for ethylene. The C-C distance deduced from

Badger's formula is too small. However, Penney and Sutherland⁷ have shown that considerable divergences exist from the formula in other compounds.

If the force constant is real, its variation might be due to the fact that tetrachlorethylene is a combination of molecules showing quite different structures, as for example:



In that case, the C-C value would be a sort of resonance between the double and single bonds.

These considerations do not, however, exclude the possibility that this molecule cannot be treated in the same way as C_2H_4 .

In the preparation of this note, I am especially indebted to Prof. V. Henri for his personal attention, and to Dr. G. B. B. M. Sutherland for correspondence.

JULES DUCHESNE.

Department of Physical Chemistry,
University, Liège.

¹ Sutherland, G. B. B. M., and Dennison, D. M., *Proc. Roy. Soc. A*, **148**, 250 (1935).

² Landolt-Börnstein Tables, 992 and 995; Ta-You-Wu, *Phys. Rev.*, **48**, 465 (1934).

³ Delfosse, J. M., *Ann. Soc. Sci. Brux.*, **55**, 114 (1935).

⁴ Badger, *J. Chem. Phys.*, **3**, 710 (1935).

⁵ Brockway, L. O., *Rev. Mod. Phys.*, **8**, 261 (1936).

⁶ Scheib, W., and Lueg, P., *Z. Phys.*, **81**, 764 (1933).

⁷ Penney, W. G., and Sutherland, G. B. B. M., *Proc. Roy. Soc. A*, **156**, 676 (1936).

Raman Spectra of Oxonium Compounds

THE study of the Raman spectra of oxonium compounds is of interest for the elucidation of the nature of the oxonium bond. Such a study was made by Briegleb and Lauppe¹, who investigated the spectra of mixtures of ethyl ether with hydrogen bromide and stannic chloride. However, their work does not give a clear and unequivocal answer to the question of the nature of such compounds. We have undertaken the study of the oxonium molecule $(CH_3)_2O.HCl$, which is known to exist even in the gaseous state. The equilibrium between methyl ether and hydrogen chloride has been studied in the vapour state with sufficient exactness². It cannot be doubted, therefore, that $(CH_3)_2O.HCl$ exists as an individual molecule. We have obtained for $(CH_3)_2O$ in the liquid state, at 280° K., the following frequencies: 408 (2) (e, k); 921 (6d) (e, k, i); 1095 (1) (k); 1448 (2d) (e, k); 2813 (10) (e, k, q, p); 2868 (3) (e, k, i); 2908 (3) (e, k, q); 2947 (2) (e, k, q); 2988 (6) (e, k, q, p).

These data agree well with the results of Kohlrausch³. We have investigated the spectra of equimolar mixtures of methyl ether, $(CH_3)_2O$, and hydrogen chloride at 280° K. in the liquid state. We obtained the following frequencies: 418 (3) (k); 891 (4d) (e, k); 1081 (1) (k); 1449 (1d) (e, k); 2829 (7) (e, k, q); 2875 (2) (e, k); 2923 (2) (e, k, q, p); 2953 (2d) (e, k, i); 3003 (5d) (e, k, q).

The same mixture was investigated at low temperatures down to 220° K. No shift at all could be observed in comparison with the spectra at 280° K. The comparison of the spectra of $(CH_3)_2O.HCl$ with the spectra of $(CH_3)_2O$ shows the absence of new lines. It may, however, be stated that displacements were noticed in a series of frequencies that were greater than the error of the experiments ($\sim 5 \text{ cm.}^{-1}$). Of the greatest interest is the decrease of the frequency