

THE MAGNETIC ANISOTROPY OF CARBON DISULPHIDE*

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The anisotropies in the molar magnetic susceptibilities of OCS and CO₂ have recently been recorded as -8.4×10^{-6} e.m.u.¹ and -6×10^{-6} e.m.u.^{1,2} respectively. From these data Taft and Dailey¹ predicted that the magnetic anisotropy of CS₂ would be larger than that of OCS. In the present work we have used the Cotton-Mouton effect to obtain an experimental estimate of the magnetic anisotropy of CS₂.

Solutions of carbon disulphide (b.p. 46°) in carbon tetrachloride were prepared and were found to exhibit the following magnetic birefringences at 20° and with sodium light.

| | | | | | | |
|---|------|------|------|------|------|------|
| $10^5 w_2$ | 1177 | 2408 | 2569 | 3168 | 3927 | 4526 |
| $-10^{15} \Delta C$ | 5.9 | 12.2 | 13.2 | 15.7 | 20.0 | 23.8 |
| whence $10^{12} \Sigma \Delta C / \Sigma w_2 = -0.51$ | | | | | | |

The weight fraction of the solute is here denoted by w_2 ; ΔC is the difference between the magnetic birefringences of the solution and the solvent.

The magnetic birefringence of carbon tetrachloride cannot be detected with the present apparatus.³ Techniques used have been described previously.⁴

The molar Cotton-Mouton constant of carbon disulphide as a solute in carbon tetrachloride emerges as -0.73×10^{-15} . Burge and Snellman⁵ have earlier reported a value of -0.8082×10^{-15} in the same solvent but at a wavelength of 5461 Å.

If the anisotropy* ($b_1 - b_3$) in the electro-optical polarizability of CS₂ is known and the magnetic-field dependence of its polarizability⁶ is neglected, the magnetic anisotropy‡ ($k_1 - k_3$) of CS₂ can be calculated using the relationship

$$\infty(mC_2) = (4\pi N/45kT)(b_1 - b_3)(k_1 - k_3) \quad (1)$$

where $\infty(mC_2)$ is the molar Cotton-Mouton constant of CS₂ at infinite dilution in carbon tetrachloride.

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‡ The 1-direction is taken to be that of the molecular axis.

¹ Taft, H., and Dailey, B. P., *J. chem. Phys.*, 1968, **48**, 597.

² Buckingham, A. D., Prichard, W. H., and Whiffen, D. H., *Trans. Faraday Soc.*, 1967, **63**, 1057.

³ Le Fèvre, R. J. W., and Murthy, D. S. N., *Aust. J. Chem.*, 1966, **19**, 179.

⁴ Le Fèvre, R. J. W., Williams, P. H., and Eckert, J. M., *Aust. J. Chem.*, 1965, **18**, 1133.

⁵ Burge, E. J., and Snellman, O., *Phil. Mag.*, 1949, **40**, 1233.

⁶ Buckingham, A. D., and Pople, J. A., *Proc. phys. Soc. B*, 1956, **69**, 1133.

The anisotropy in the optical polarizability of CS_2 as a solute in carbon tetrachloride has been deduced from Kerr effect measurements⁷ as 7.5 \AA^3 . When our experimental Cotton-Mouton constant is considered in equation (1) together with this polarizability anisotropy, the molecular magnetic susceptibility anisotropy of CS_2 emerges as $-2.3 \times 10^{-29} \text{ e.m.u.}$

We conclude that the anisotropy, $K_1 - K_3$, in the molar magnetic susceptibility of CS_2 is $-14 \times 10^{-6} \text{ e.m.u.}$ From this value of the magnetic anisotropy and a mean molar susceptibility⁸ of -42.2×10^{-6} , K_1 and K_3 appear as -51.5×10^{-6} and -37.5×10^{-6} . As predicted,¹ the magnetic anisotropy of CS_2 exceeds those of CO_2 and OCS .

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⁷ Armstrong, R. S., Aroney, M. J., Le Fèvre, R. J. W., and Smith, M. R., *J. chem. Soc.*, 1958, 1474.

⁸ Foex, G., "Constantes sélectionnées, diamagnétisme et paramagnétisme", in "Tables de Constantes et Données Numériques." (Masson: Paris 1957.)