# 142. *Molecular Polarisability. The Apparent Anisotropy of Methane and Other Quasi-spherical Molecules.*

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By the formulæ ordinarily used, containing the terms $b_1 - b_2$, $b_2 - b_3$, and $b_3 - b_1$, tetrahedral molecules such as $CH_4$, $CCl_4$, $CBr_4$, etc., should not exhibit Kerr effects and should show zero depolarisation factors for light scattered by them. Actually, however, small values for both these properties have been observed. Past explanations of this anomaly have been qualitative. An *a priori* quantitative treatment, along the lines of that currently given for atomic polarisation, is here attempted. The expression derived for the molar Kerr constant of a structure $CX_4$ involves link moments, longitudinal and transverse polarisabilities $a$ and $b$ of bonds, stretching and bending force constants, effective charges on atoms, and the derivatives $\mathrm{d}a/\mathrm{d}r$ and $\mathrm{d}b/\mathrm{d}r$ ($r$ being an internuclear distance). The new theory requires that the quantity $(\mathrm{d}a/\mathrm{d}r - \mathrm{d}b/\mathrm{d}r)$ should be a few powers of ten larger than $\mathrm{d}\alpha/\mathrm{d}r$ ($\alpha$ being the mean polarisability). Data are presented showing that the electric double refraction of liquid carbon tetrachloride follows Kerr's law. The ${}_{\infty}({}_mK_2)$ and ${}_{\infty}P_2$ for carbon tetrabromide in carbon tetrachloride are recorded.

LE FÈVRE and LE FÈVRE [1] have adopted the definition (1) as the molar Kerr constant ${}_mK$ of a substance :

$$ {}_mK = 6\lambda nBM/(n^2 + 2)^2 (\varepsilon + 2)^2 d \qquad (1) $$

where $n$ is the refractive index, $M$ the molecular weight, $\varepsilon$ the dielectric constant, and $d$ the density. This property, except for an omitted numerical factor of 9, may be regarded as the difference between the molecular refractions per unit field taken perpendicular and parallel to an applied field $E$. By the theory ordinarily used for electric double refraction, $B$ (and hence ${}_mK$) should be zero for quasi-spherical non-polar regular tetrahedral molecules of the type $CR_4$ (cf. relations and references given by Le Fèvre and Le Fèvre [1,2]); in practice, however, small but definite values of $B$ are observed, *e.g.*, for gaseous methane [3,4] or liquid carbon tetrachloride (see Table 1). A connected phenomenon is that these

[1] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.
[2] *Idem, J.*, 1954, 1577.
[3] Breazeale, *Phys. Rev.*, 1936, **49**, 625.
[4] Kuss and Stuart, *Phys. Z.*, 1941, **42**, 95.

supposedly isotropic substances give depolarisation factors $\rho$ greater than the expected zero (cf. Cabannes [5]).

The problem posed by the apparent anisotropy of such molecules has not received much attention. Cabannes (ref. 5, pp. 133—134) comments on suggestions involving a square-based pyramidal configuration for $CR_4$, and on those depending on deformations during thermal agitation; he finally favours the hypothesis that atoms may have an intrinsic anisotropy measured by a depolarisation factor of 0·005. Bhagavantam [6] thinks that in the cases of silicon tetrachloride and tetrafluoride and carbon tetrachloride " the presence of an appreciable proportion of unsymmetrical isotopic molecules may be responsible for at least part of the observed depolarisation." [The unlikelihood of this is clear from the fact that although the relative abundance of $^{35}Cl$ to $^{37}Cl$ is 75 : 25, that of $^{1}H$ to $^{2}H$ is 5000 : 1; fluorine is 100% $^{19}F$. The high values of $\rho$ listed for silicon tetrachloride and tetrafluoride (ref. 6, p. 54) obviously require verification.] Quantum calculations cited by Beams [7] forecast the existence of a third small and temperature-invariant component of the quantity $B$, additional to the anisotropy and dipole terms provided by the Langevin–Born orientation theory.[8] Stuart [9] mentions the above proposals, together with others, *e.g.*, that in carbon tetrachloride, stannic chloride, etc., " schon bei Zimmertemperatur in ungefähr der Hälfte aller Molecüle angeregt sind, wodurch die Moleküle merklich anisotrop werden können," or that " die Nullpunktsbewegung der Kerne zu einer dauerndén Störung der Symmetrie führen, so dass in jedem Augenblick eine geringe Anisotropie vorhanden wäre," so that, if the nuclear vibrations are slow relative to the frequency of light the molecules will scatter or behave in a Kerr cell as " verwackelte Tetraeder." Von Hippel [10] and Stuart [9] (*op. cit.*) note that anharmonicity of the oscillators responsible for electronic and atomic polarisation can produce a small temperature-insensitive effect, usually negligible except near an absorption line, although Neugebauer (quoted by Stuart ref. 9, p. 454) advances reasons why this " Voigtsches Glied " may be somewhat significant in the particular instance of methane.

FIG. 1.

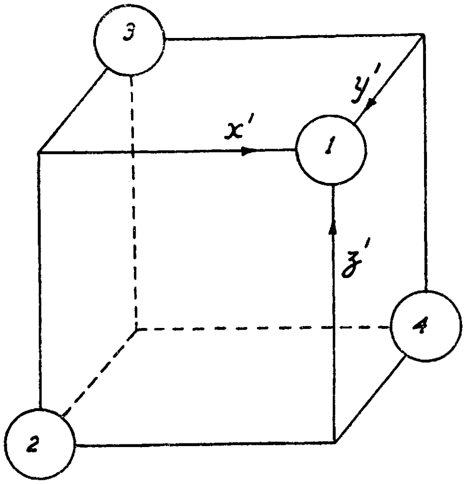
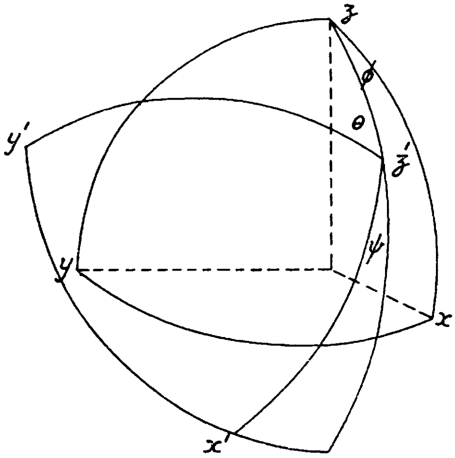


FIG. 2.



While many of the above possibilities may be involved in the small Kerr constants, or depolarisation factors, reported for quasi-spherical molecules, the magnitudes of their

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[5] Cabannes, " La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, 1929, Tables 3, 9, 16, and 17.

[6] Bhagavantam, " Scattering of Light and Raman Effect," Andhra Univ., Waltair, 1940, pp. 53—56.

[7] Beams, *Rev. Modern Phys.*, 1932, **4**, 133.

[8] Van Vleck, " The Theory of Electric and Magnetic Susceptibilities," Oxford Univ. Press, 1932.

[9] Stuart, " Die Struktur des Freien Moleküls, " Springer, Berlin–Göttingen–Heidelberg, 1952, Sections 50, 57, and 62.

[10] Von Hippel, " Dielectrics and Waves," Wiley, New York, 1954, p. 264.

contributions cannot be usefully predicted quantitatively. Accordingly it seemed of interest to explore the results of assuming the types of distortion envisaged previously to explain atomic polarisation.[11, 12]

It is first necessary to compute the average polarisability per molecule along and at right angles to the applied field. In Figs. 1 and 2 let $xyz$ be a space-fixed co-ordinate system whereon a static electric field $E_0$ is incident along the $z$ axis. Let $x'$, $y'$, and $z'$ be the principal axes of a tetrahedral molecule whose orientation with respect to $xyz$ is given by $\theta$, $\phi$, and $\psi$. Consider the $E_{x'}$ component of the field: it distorts the molecule in such a way that the angle between the bond to atoms 1 and 4 decreases by $2\delta$ (where $\delta = \mu \sin\alpha \,.\, E_{x'}/2k_\delta$) and that between the bonds 2 and 3 increases by the same amount (bending and stretching force constants are denoted by $k_\delta$ and $k$ respectively). This distortion of the molecule leads to changes in its principal polarisabilities. Let $a$ and $b$ be the longitudinal and transverse polarisabilities of each of the four bonds and let $(\mathrm{d}a/\mathrm{d}r)$ and $(\mathrm{d}b/\mathrm{d}r)$ be the rates of change of $a$ and $b$ for bond elongation or contraction. Let

$$\Delta_1 = \frac{e\cos\alpha \,.\, E_{x'}}{k}\left(\frac{\mathrm{d}a}{\mathrm{d}r}\right) \quad \text{and} \quad \Delta_2 = \frac{e\cos\alpha \,.\, E_{x'}}{k}\left(\frac{\mathrm{d}b}{\mathrm{d}r}\right)$$

then the altered polarisability $(a_{x'})$ in the $x'$ direction is

$$4a/3 + 8b/3 + 4(a-b)\delta^2/3 + 8(\Delta_1 - \Delta_2)\delta\sin\alpha\cos\alpha = a_0 + 4B_1E_{x'}^2 + 4CE_{x'}^2$$

where $$B_1 = \mu^2\,(a-b)/18k_\delta^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)\ *$$

and $$C = (2\mu e/9kk_\delta)(\mathrm{d}a/\mathrm{d}r - \mathrm{d}b/\mathrm{d}r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The altered polarisability $(\alpha_{y'})$ in the $y'$ direction is

$$4a/3 + 8b/3 - 2(a-b)\delta^2/3 - 4(\Delta_1 - \Delta_2)\delta\sin\alpha\cos\alpha = \alpha_0 - 2B_1E_{x'}^2 - 2CE_{x'}^2$$

and $a_{z'} = a_{y'}$.

The above changes in the polarisabilities are caused by the $E_{x'}$ component of the field. Similar changes will be caused by the $E_{y'}$ and $E_{z'}$ components; taking them into consideration we have:

$$\begin{aligned}
\alpha_{x'} &= \alpha_0 + 4B_1E_{x'}^2 - 2B_1E_{y'}^2 - 2B_1E_{z'}^2 + 4CE_{x'}^2 - 2CE_{y'}^2 - 2CE_{z'}^2\\
\alpha_{y'} &= \alpha_0 + 4B_1E_{y'}^2 - 2B_1E_{x'}^2 - 2B_1E_{z'}^2 + 4CE_{y'}^2 - 2CE_{x'}^2 - 2CE_{z'}^2\\
\alpha_{z'} &= \alpha_0 + 4B_1E_{z'}^2 - 2B_1E_{x'}^2 - 2B_1E_{y'}^2 + 4CE_{z'}^2 - 2CE_{x'}^2 - 2CE_{y'}^2
\end{aligned}$$

To find the average moment induced per molecule per unit field along any of the space-fixed axes $x, y$, and $z$ a random distribution of the molecules may be assumed, as the orientational effect of such small differences in the polarisabilities is negligible:

$$\begin{aligned}
\alpha_z &= \alpha_{x'}\overline{\cos^2 zx'} + \alpha_{y'}\overline{\cos^2 zy'} + \alpha_{z'}\overline{\cos^2 zz'}\\
&= \alpha_0 - 2(B_1 + C)E^2 + 6(B_1 + C)E^2\,[\overline{\cos^4 zx'} + [\overline{\cos^4 zy'} + \overline{\cos^4 zz'}]\\
&= \alpha_0 + 8(B_1 + C)E^2/5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)
\end{aligned}$$

$$\begin{aligned}
\bar{\alpha}_x &= \alpha_{x'}\overline{\cos^2 xx'} + \alpha_{y'}\overline{\cos^2 xy'} + \alpha_{z'}\overline{\cos^2 xz'}\\
&= \alpha_0 - 2(B_1 + C)E^2 + 6(B_1 + C)E^2\,[\overline{\cos^2 zx'\cos^2 xx'}\\
&\qquad + \overline{\cos^2 zy'\cos^2 xy'} + \overline{\cos^2 zz'\cos^2 xz'}]\\
&= \alpha_0 - 4(B_1 + C)E^2/5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)
\end{aligned}$$

* $B_1$ is to be distinguished from $B$, the Kerr constant of a material measured as $(n_p - n_s)/\lambda E^2$, and which, *via* equation (1), gives ${}_mK$.

[11] Coop and Sutton, *J.*, 1938, 1269.

[12] Le Fèvre and Rao, *Austral. J. Chem.*, 1954, **7**, 135; 1955, **8**, 39.

Now, taking the Lorenz–Lorentz relation between refractive index and mean polarisability $(n_0^2 - 1)/(n_0^2 + 2) = 4\pi\nu\alpha/3$ ($\nu$ = number of molecules per c.c.) and differentiating, we have :

$$\frac{\Delta n_0}{n_0} = \frac{(n_0^2 - 1)(n_0^2 + 2)}{6n_0^2}\left[\frac{\Delta\alpha}{\alpha} + \frac{\Delta\nu}{\nu}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Suitable insertions into equation (6) for $\Delta n_0 = n_p - n_0$ or $n_s - n_0$ with corresponding values of $\Delta\alpha$ from (4) and (5) lead to two further equations, which, by subtraction, give (7)

$$\frac{n_p - n_s}{n_0} = \frac{2(n_0^2 - 1)(n_0^2 + 2)(B_1 + C)E^2}{5n_0^2\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By rearrangement of equation (7), introducing the wavelength $\lambda$, substituting $3M(n_0^2 - 1)/4\pi Nd(n_0^2 + 2)$ for $\alpha$, and assuming the effective field to be $E(\varepsilon + 2)/3$, we obtain the Kerr constant, $B$, as

$$B = \frac{n_p - n_s}{\lambda E^2} = \frac{8\pi Nd(n^2 + 2)^2(\varepsilon + 2)^2(B_1 + C)}{135\lambda M n_0} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Equations (9) and (10) then follow from equation (1) :

$$_mK = 16\pi N(B_1 + C)/45 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= 6{\cdot}73 \times 10^{23}\,(B_1 + C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The problem now centres around $B_1$ and $C$, which contain link moments, $\mu$, the longitudinal and transverse polarisabilities $a$ and $b$, of bonds, stretching and bending force constants $k$ and $k_\delta$, effective charges $e$, and the derivatives $\mathrm{d}a/\mathrm{d}r$ and $\mathrm{d}b/\mathrm{d}r$ ($r$ being an internuclear distance). Many of these are, at present, uncertain quantities; especially is this true of link moments [12] and bending force constants.[13]

Values for $\mathrm{d}a/\mathrm{d}r$ and $\mathrm{d}b/\mathrm{d}r$ are unknown, although with a few species attempts to ascertain $\mathrm{d}\alpha/\mathrm{d}r$ (the rate of change of polarisability for the whole molecule with internuclear distance, taken at the equilibrium position) have been made. For methane, Bell,[14] from a consideration of the refractive indices of isotopic compounds, deduces $\mathrm{d}\alpha/\mathrm{d}r$ as $7{\cdot}71 \times 10^{-16}$; Stansbury, Crawford, and Welsh,[15] from Raman–Rayleigh intensity ratios, give it as $4{\cdot}1 \times 10^{-16}$.

It seemed at first possible that $\mathrm{d}\alpha/\mathrm{d}r$ might approach the order of $(\mathrm{d}a/\mathrm{d}r - \mathrm{d}b/\mathrm{d}r)$. However, by taking $7{\cdot}71 \times 10^{-16}$ as $(\mathrm{d}a/\mathrm{d}r - \mathrm{d}b/\mathrm{d}r)$, in conjunction with $\mu = 0{\cdot}31$ D, $e = 0{\cdot}55 \times 10^{-10}$ (from infrared data [12]), $a = 0{\cdot}081 \times 10^{-23}$, $b = 0{\cdot}057 \times 10^{-23}$ (Le Fèvre and Le Fèvre [2]), $k = 5{\cdot}04 \times 10^5$, and $k_\delta = 5{\cdot}51 \times 10^{-12}$ (cf. Herzberg [16]), the molar Kerr constant calculated *via* equation (10) for methane is only $1 \times 10^{-15}$, *i.e.*, some 200—300 times smaller than the values expected from the recorded observations on highly compressed methane by Breazeale [3] or Kuss and Stuart.[4]

For carbon tetrachloride Chien and Bender [17] consider $\mathrm{d}\alpha/\mathrm{d}r$ to be *ca.* $4 \times 10^{-16}$. Noting that this is not far from $a/r + b/r$, and because no estimate of $\mathrm{d}\alpha/\mathrm{d}r$ for carbon tetrabromide is available, we have used $a$ and $b$ as given earlier,[2] together with $r_{\mathrm{CCl}} = 1{\cdot}755$ Å and $r_{\mathrm{CBr}} = 1{\cdot}94$ Å, plus the assumptions that $\mu_{\mathrm{C-Cl}}$ or $\mu_{\mathrm{C-Br}}$ are both *ca.* 1·8 D, that $e = \mu/r$, and that the force constants reported by Heath and Linnett [13b] are applicable, to produce $_mK_{\mathrm{calc.}} = 0{\cdot}053 \times 10^{-12}$ for carbon tetrachloride and $0{\cdot}11 \times 10^{-12}$ for the tetrabromide. As with methane, but to a lesser degree, these are below the observed values.

Either, therefore, our model and argument leading to equations (9) and (10) are incorrect, or it is wrong to expect $(\mathrm{d}a/\mathrm{d}r - \mathrm{d}b/\mathrm{d}r)$ to have the same order of magnitude as $\mathrm{d}\alpha/\mathrm{d}r$. It is conceivable that the latter alternative is the case : consider a total symmetric

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[13] (*a*) Linnett, *Quart. Rev.*, 1947, **1**, 73; (*b*) Heath and Linnett, *Trans. Faraday Soc.*, 1948, **54**, 561.

[14] Bell, *ibid.*, 1942, **38**, 422.

[15] Stansbury, Crawford, and Welsh, *Canad. J. Phys.*, 1953, **31**, 954.

[16] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945.

[17] Chien and Bender, *J. Chem. Phys.*, 1947, **15**, 376.

vibration of, *e.g.*, methane. Let each bond have an extension d$r$. Then, $\alpha$ being the mean polarisability,

$$\alpha + \mathrm{d}\alpha = \frac{4}{3}\left(a + \frac{\mathrm{d}a}{\mathrm{d}r}\,.\,\mathrm{d}r\right) + \frac{8}{3}\left(b + \frac{\mathrm{d}b}{\mathrm{d}r}\,.\,\mathrm{d}r\right)$$

whence, since $(4a + 8b)/3 = \alpha$, $\mathrm{d}\alpha/\mathrm{d}r = \frac{4}{3}\left(\frac{\mathrm{d}a}{\mathrm{d}r} + 2\frac{\mathrm{d}b}{\mathrm{d}r}\right)$. In other words, were $\mathrm{d}b/\mathrm{d}r$ to be nearly $-$ 0·5d$a$/d$r$, admittedly a speculative suggestion, then d$\alpha$/d$r$ might well be a few powers of ten smaller than either d$a$/d$r$ or d$b$/d$r$. It is relevant that, with the force constants and other data cited above, the quantities (d$a$/d$r$ $-$ d$b$/d$r$) need only to be $4{\cdot}2 \times 10^{-13}$, $1{\cdot}5 \times 10^{-14}$, and $7{\cdot}2 \times 10^{-14}$ to give, *via* equation (10), the observed molar Kerr constants respectively for methane, carbon tetrachloride, and carbon tetrabromide (*viz.*, $0{\cdot}395 \times 10^{-12}$, $1{\cdot}14 \times 10^{-12}$, and $7{\cdot}3 \times 10^{-12}$). On such a basis d$a$/d$r$ and d$b$/d$r$ would be, for the C–H link, $2{\cdot}8 \times 10^{-13}$ and $-1{\cdot}4 \times 10^{-13}$, and for the C–Cl link, $1{\cdot}0 \times 10^{-14}$ and $-0{\cdot}5 \times 10^{-14}$. Unfortunately no method is known to us whereby these predictions could be checked by experiment.

*Practical Importance of Equation* (9).—The molar Kerr constant is usually analysed thus:

$$_{m}K = 2\pi N(\theta_1 + \theta_2)/9 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

(cf. refs. 1 and 2 for expansions of $\theta_1$ and $\theta_2$, the anisotropy and dipole terms respectively). Clearly the right-hand side of (9) amounts to an addition to equation (11) (within the parentheses) of $\theta_3 = 8(B_1 + C)/5$. $\theta_3$ differs from $\theta_1$ or $\theta_2$ in being temperature-invariant.

So far as the practical usefulness of the Kerr effect is concerned, $\theta_3$ will only be significant for near-isotropic molecules for which $_{m}K_{\text{obs.}}$ is small and possibly therefore composed relatively considerably of contributions containing $\theta_3$. In such cases molecular ellipsoids computed from $_{m}K_{\text{obs.}}$ would represent the structure as being more anisotropic than it really is.

This type of error may explain why $a$ and $b$ for the carbon–carbon link (cf. ref. 2 for references) have been reported as uniquely (compared with other bonds) dissimilar, $a/b$ ranging with different authors from 20 to 94. Various considerations suggest [18, 19] that the correct $a : b$ ratio is between 2 and 4. The earlier estimates were based essentially on measurements of the Kerr constant of ethane [3] and involved the setting-up of expressions, for the $b_1$ and $b_3$ found, containing $a$ and $b$ for C–C and C–H.

We now note that if from the value of $_{m}K$ for ethane we deduct the amount which could be regarded as approximating to the appropriate $\theta_3$ (*viz.*, subtracting from $_{m}K_{\mathrm{C_2H_6}}$ twice $_{m}K_{\mathrm{CH_4}}$) and calculate from the residue, taken as the " true " $\theta_1$, a new $b_1$ and $b_3$, then $a$ and $b$ for the carbon–carbon bond emerge in the ratio $a : b$ as 3·93 : 1.

Finally it may be remarked that the molecular distortions assumed in this paper may well be part of the mechanism operative in the phenomenon of hyperpolarisability discussed by Coulson, Maccoll, and Sutton.[20]

## EXPERIMENTAL

*Applicability of Kerr's Law to Carbon Tetrachloride.*—A search through the literature disclosed that Kerr's law, stating [21] that the magnitude of the double refraction is proportional to the square of the strength of the electric field applied, has never been tested on a material having tetrahedral quasispherical molecules. Anisotropically polarisable substances, notably carbon disulphide,[22] have, however, received extensive attention, and been found to obey the law accurately so that the omission of, *e.g.*, the readily available carbon tetrachloride arouses the suspicion that its weak electric double refraction may not have the normal dependence on $E^2$. Such a doubt required to be removed at the beginning of the present work.

Apparatus and techniques [1, 2] and carbon tetrachloride [2] as described earlier being used, retardations $\delta$ were observed as listed in Table 1. Constancy is obtained only with the ratio

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[18] Bunn and Daubeny, *Trans. Faraday Soc.*, 1954, **50**, 1173.

[19] Le Fèvre and Le Fèvre, *Chem. and. Ind.*, 1955, 506, 1121.

[20] Coulson, Maccoll, and Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106.

[21] Kerr, *Phil. Mag.*, 1880, **9**, 157; 1882, **13**, 153, 248.

[22] Chaumont, *Ann. Physique*, 1916, **5**, 17; Beams, *Phys. Rev.*, 1931, **37**, 781; Hootman, *ibid.*, 1933, **43**, 749.

TABLE 1. *Electric double refraction of carbon tetrachloride at 25° for light of* $\lambda = 5893$ Å.

| $\delta$ (minutes) | $E$ (kv applied) | $\delta/E$ | $\delta/E^2$ | $10^7B$ | $\delta/E^3$ |
|---|---|---|---|---|---|
| 8·5 | 5 | 1·70 | 0·340 | 0·072 | 0·68 |
| 12 | 6 | 2·00 | 0·333 | 0·071 | $0·55_5$ |
| 16 | 7 | $2·28_5$ | 0·327 | 0·070 | 0·47 |
| 21 | 8 | $2·62_5$ | 0·328 | 0·070 | 0·41 |
| 26·5 | 9 | 2·94 | 0·327 | 0·070 | 0·36 |
| 33 | 10 | 3·30 | 0·330 | 0·070 | 0·33 |
| 40·5 | 11 | 3·68 | $0·334_5$ | 0·071 | 0·30 |
| 47·5 | 12 | 3·96 | 0·330 | 0·070 | $0·27_5$ |

TABLE 2. *Observations on carbon tetrabromide in carbon tetrachloride at* 20°.*

| $10^5w_2$ | $10^7B_{12}$ | $(n_D^t)_{12}$ | $(d_4^t)_{12}$ | $(\varepsilon^t)_{12}$ |
|---|---|---|---|---|
| 0 | 0·072 | 1·4604 | 1·5940 | 2·2360 |
| 1881 | 0·074 | — | — | — |
| 2014 | 0·076 | 1·4621 | 1·6105 | — |
| 3332 | 0·077 | — | — | — |
| 3683 | 0·083 | 1·4637 | 1·6239 | 2·2454 |
| 6303 | 0·085 | 1·4661 | 1·6463 | 2·2525 |
| 6516 | 0·085 | 1·4662 | 1·6475 | 2·2536 |
| 8814 | 0·086 | — | — | — |

Whence $\Sigma(w_2 \,.\, \Delta B)/\Sigma w_2^2 = 0·187$, $\Sigma\Delta n/\Sigma w_2 = 0·089$, $\Sigma\Delta d/\Sigma w_2 = 0·822$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 0·264$.

* For explanations of symbols and methods of calculation used see refs. 1 and 2.

$\delta/E^2$. Use of the dimensions of the plates and their separation gives the " Kerr constants " $B$. The behaviour of carbon tetrachloride is therefore externally orthodox.

*The Molar Kerr Constant of Carbon Tetrabromide.*—From the observations included in Table 2 the following quantities emerge : ${}_{\infty}P_2 = 38·6$ c.c., $\mu =$ *ca.* 0 D., ${}_{\infty}({}_mK_2) = 7·30 \times 10^{-12}$. No previous determination of either the polarisation or the Kerr constant of carbon tetrabromide is on record.

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