647. Molecular Polarisability. Molar Kerr Constants of Gases

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Molar Kerr constants are recorded for nine gases: SO_2, CO_2, NH_3, CH_3Cl, and five fluorocarbons. Polarisability ellipsoids are derived for the N–H bond in NH_3, and the C–Cl bond in CH_3Cl. Anisotropic polarisabilities of the carbon–fluorine bond in aliphatic environments are determined from the molar Kerr constants of CCl_3F and CHF_3. The C–F bond data are satisfactorily applicable to $CHClF_2$ and CCl_2F_2. The apparent dipole moment and molar Kerr constant of 1,2-dichlorotetrafluoroethane are discussed in relation to internal rotation in this molecule. Apparatus is described for the photoelectric measurement of electric birefringences of gases.

EXPERIMENTAL evidence on the variation of molar Kerr constant (${}_{\mathrm{m}}K$) with state is sparse, relatively few substances having been examined otherwise than as solutes,[1] for which several hundred ${}_{\mathrm{m}}K$'s are now known.[2] Electric birefringences (from which ${}_{\mathrm{m}}K$ can be calculated) have been reported [3-15] for about seventy organic and inorganic gases, but the reliability of some of the data is questionable. Most of these compounds have been investigated only once, and where successive workers have studied the same molecule there has not always been agreement.

Without doubt the situation has been caused by the practical difficulties of measuring double-refractions a thousand times smaller than those encountered with solutions. Leiser [3] and Hansen [4] used an auxiliary liquid-filled Kerr cell to compensate the electric birefringence appearing in the gas-containing Kerr cell. Szivessy [5] replaced the auxiliary cell by a sensitive mica-plate compensation system, a form of which was adopted by Stuart and his collaborators [6-11] for work extending over thirteen years. Both methods involved half-shade matching, which, in our experience, requires visual acuity in the observer, and rapidly induces eye-fatigue.

The authors of refs. 12—15 introduced photoelectric detectors, and assessed the ellipticity in the light transmitted through a crossed polariser–analyser arrangement by observations of intensity. Pressures up to several hundred atmospheres were applied to

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[1] C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261.

[2] R. J. W. Le Fèvre *et al.*, Papers entitled " Molecular Polarisability," *J.*, 1953 to date.

[3] R. Leiser, *Phys. Z.*, 1911, **12**, 955.

[4] D. E. Hansen, Dissertation, Karlsruhe, 1912.

[5] G. Szivessy, *Z. Physik*, 1924, **26**, 323.

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[7] K. L. Wolf, G. Briegleb, and H. A. Stuart, *Z. phys. Chem.*, 1929, **6**b, 163.

[8] H. A. Stuart and H. Volkmann, *Z. phys. Chem.*, 1932, **17**b, 429; *Ann. Physik*, 1933, **18**, 121; *Z. Physik*, 1933, **80**, 107, **83**, 444; *Phys. Z.*, 1934, **35**, 988.

[9] H. A. Stuart and W. Buchheim, *Z. Physik*, 1938, **111**, 36.

[10] E. Kuss and H. A. Stuart, *Phys. Z.*, 1941, **42**, 95.

[11] H. A. Stuart and S. von Schiezl, *Ann. Physik*, 1948, **2**, 321.

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[13] C. W. Bruce, *Phys. Rev.*, 1933, **44**, 682.

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[15] W. M. Breazeale, *Phys. Rev.*, (*a*) 1935, **48**, 237; (*b*) 1935, **49**, 625.

the dielectrics, and the prisms, electrodes, etc., were enclosed in a heavy steel container. The measurements by Kuss and Stuart,[10] although not made photoelectrically, involved pressures above 35 atmospheres. The extrapolation of such data to 1 atmosphere is clearly a possible source of error; another is the inevitable occurrence of strain-birefringences in the cell windows and/or prisms when under such pressures.

We now find that many of the difficulties in the above methods can be avoided by use of a slightly refined version of the simple apparatus for solutions described recently by Le Fèvre and Ritchie.[16]

EXPERIMENTAL

Apparatus.—The arrangement of the optical and electrical components is shown in Figure 1. A worked I-section girder (see plate 1a on p. 2466 of ref. 17), of length *ca.* 8 ft., carries the components S to M, inclusive.

The light source is a 12 v car head-lamp bulb fed from an accumulator; F is an Ilford 605 filter (transmission maximum at 525 mμ); L_1 and L_2 are lenses of 10 cm. focal length; P is a light-chopping disc, powered by a synchronous motor, which gives 500 light pulses per sec. After passing through the polarising prism N_1, a parallel beam of linearly-polarised light, with its electric vector at 45° to the vertical, enters the Kerr cell, K.

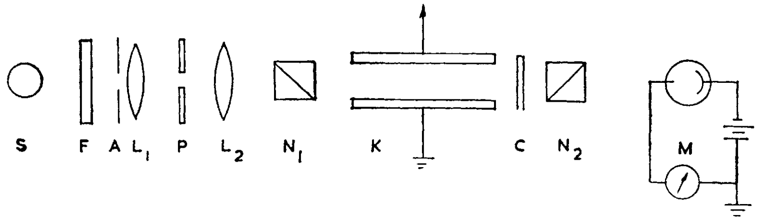

FIGURE 1. Arrangement of optical and electrical components
S = source, F = filter, A = aperture, L_1 and L_2 = lenses, P = chopper, N_1 = polariser, K = Kerr cell, C = compensator, N_2 = analyser, M = photomultiplier

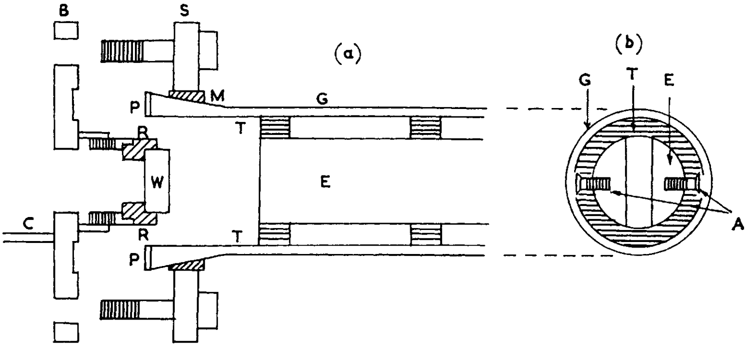

FIGURE 2. Kerr cell for gases: (a) longitudinal section; (b) transverse section
E = electrodes, T = Teflon rings, A = countersunk screws, G = glass jacket, W = window, B = brass end-plate, S = steel collar, M = rubber mounting, R = rubber washer, P = rubber pressure seal, C = copper pressure tubing

Within K, two plane-parallel brass electrodes (length 101·0 cm., width 2·2 cm.) are held apart and insulated from each other by carefully machined Teflon rings (Figure 2b) spaced at

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[16] R. J. W. Le Fèvre and G. L. D. Ritchie, *J.*, 1963, 4933.

[17] C. G. Le Fèvre and R. J. W. Le Fèvre, ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, London, 3rd edn., 1960, vol. 1, p. 2459.

ca. 10 cm. intervals. The interelectrode gap is 0·260 cm. The absence of insulators between the plates permits high field-strengths to be used without breakdown of the gaseous dielectrics.

A heavy Pyrex tube, G (internal diameter 3·8 cm.), with tapered ends encloses the electrode assembly. Optical windows, W (diameter 2 cm., thickness 1 cm.), of strain-free glass are mounted on brass end-plates, B, which are bolted to steel collars, S, behind the tapers (Figure 2a). The window is surrounded by a neatly fitting hard rubber washer, R, which is attached to a threaded brass ring; this unit is screwed into a second brass ring soldered in the centre of the end-plate. In this way, strain-birefringences arising from compression of the brass are eliminated. The three junctions (glass–rubber, rubber–brass, brass–brass) are sealed with Araldite. A compressible rubber ring, P, provides the pressure seal between the end-plate assembly and the ground-glass ends of the jacket.

The cell is evacuated and filled through copper pressure tubing, C, which is sealed through B. Diaphragm-type line valves serve to isolate the cell. Gas pressures between 1 and *ca.* 3 atm. are measured with an open-column mercury manometer.

Fields up to 65 kv cm.$^{-1}$, generated by a 0·5—17 kv 0·1 mA d.c. radiofrequency oscillator unit, are applied to the electrodes by thick tungsten leads sealed through the Pyrex jacket. A Pye electrostatic voltmeter is connected in parallel to the tungsten leads.

The detection system is similar to that described by Le Fèvre and Ritchie.[16] A whole-plate compensator and an RCA-931A photomultiplier are used for measurement of birefringence. The a.c. component of the photomultiplier output is connected to a conventional twin-triode amplifier-detector incorporating a 12AT7 pentode. The high tension voltage for the triodes is stabilised by OC3 and OD3 regulating valves connected in series. A micro-ammeter in the cathode circuit of the second triode registers the amplifier output. In one rotation of the compensator the four settings corresponding to minimum illumination of the photomultiplier can be read to 0·01°.

Materials.—Samples of sulphur dioxide, carbon dioxide, ammonia, and methyl chloride as obtained from cylinders were used without further purification. Gas-chromatographic analyses showed them to be 98—100% pure.

Four gaseous chlorofluorocarbons were provided by Monsanto Chemicals (Aust.) Ltd.: trichlorofluoromethane (CCl_3F), chlorodifluoromethane ($CHClF_2$), dichlorodifluoromethane (CCl_2F_2), and 1,2-dichlorotetrafluoroethane ($C_2Cl_2F_4$). All were highly purified products; analysis of $CHClF_2$ confirmed a purity of at least 99·5%. Fluoroform (CHF_3), obtained from the Matheson Co., U.S.A., had a specified minimum purity of 98%.

Results.—For each gas a series of measurements was made with pressures of 1—3 atm., and voltages of 10—17 kv. The calculation of the electric birefringences is as described by Le Fèvre and Ritchie.[16] The Kerr constants, B, of Table 1 refer to a gas pressure of 1 atm., and a temperature of either 20 or 25°, as indicated. In the cases of SO_2, CO_2, NH_3, and CH_3Cl, the observed gas pressures, P, were expressed as "ideal" pressures, P_i, by making the approximation that $P_i = P(1 + aP/\boldsymbol{R}^2T^2)$, where $\boldsymbol{R}$ and T have their usual meanings, and a is the appropriate van der Waals constant. No such corrections have been made for the five fluorocarbons; except in the case of $C_2Cl_2F_4$, the measured values of B appear to be independent of pressure in the range 1—3 atm. Results for $C_2Cl_2F_4$ were extrapolated to a pressure of 1 atm. Observations at room temperature have been adjusted to 20 or 25° on the rough basis that the B's of non-polar and dipolar gases vary inversely as the square and as the cube of the absolute temperature, respectively.[1]

TABLE 1

Kerr constants of gases

	Temp. (°c)	$10^{10}B$	$10^{12}{}_{m}K$	$10^{12}{}_{m}K$ (lit.)
SO_2	20	−1·77	−16·5	−16·4;[6b] −17·0[5]
CO_2	20	+0·235	+2·2	+2·4;[6b] +2·5;[5] +2·6[14]
NH_3	20	+0·701	+6·5	+6·1;[5] +5·9[15a]
CH_3Cl	20	+7·34	+68·5	+63·6[6b]
CCl_3F	25	−0·178	−1·7	—
CHF_3	25	−0·557	−5·3	—
$CHClF_2$	25	−1·85	−17·6	—
CCl_2F_2	25	+0·143	+1·4	—
$C_2Cl_2F_4$	25	+0·728	+6·9	—

Molar Kerr constants, ${}_{\mathrm{m}}K$, have been computed through the relationship [18]

$${}_{\mathrm{m}}K = 6\lambda nBM/(n^2 + 2)^2(\varepsilon + 2)^2 d,$$

with the assumptions that M/d is a constant for a particular temperature, and that both n and ε for a gas at low pressure may be taken as unity. Literature values for the Kerr constants of SO_2, CO_2, NH_3, and CH_3Cl have been converted into the corresponding molar quantities at 1 atm. and 20° (last column of Table 1). No data have previously been recorded for the electric birefringences of the fluorocarbons. Consideration of the various experimental uncertainties suggests an error of about $\pm 5\%$ in the results of Table 1.

DISCUSSION

Molar Kerr Constants.—Agreement is satisfactory between the various values for the Kerr constants of SO_2, CO_2, NH_3, and CH_3Cl. Several of the previous measurements were made at elevated temperatures and pressures, and uncertainties in extrapolation probably affect the situation. Much more experimental work with gaseous dielectrics is required before the dependence of the Kerr constant on wavelength, temperature, and pressure can be fully understood.

Polarisability Ellipsoids for N–H *and* C–Cl *Bonds.*—The symmetry of the NH_3 and CH_3Cl molecules is such that two of the three principal molecular polarisabilities are equal ($b_1 \neq b_2 = b_3$). These polarisabilities thus can be determined from Kerr effect and refractivity data by use of the equations [1,19]

$$\theta_1 = (2/45kT)({}_{\mathrm{D}}P/{}_{\mathrm{E}}P)(b_1 - b_2)^2 \qquad (1)$$

$$\theta_2 = (2/45k^2T^2)\mu_{\mathrm{r}}^2(b_1 - b_2) \qquad (2)$$

$$\theta_1 + \theta_2 = (9/2\pi N)_{\mathrm{m}}K \qquad (3)$$

$$b_1 + 2b_2 = (9/4\pi N)_{\mathrm{E}}P \qquad (4)$$

where θ_1 and θ_2 are, respectively, the " anisotropy " and " dipole " terms, and b_1 and b_2 are semi-axes of the electro-optical polarisability ellipsoid; ${}_{\mathrm{D}}P$ and ${}_{\mathrm{E}}P$ represent the distortion and electronic polarisations, respectively, and μ_{r} is the molecular dipole moment; other symbols have their usual meanings.

Le Fèvre and Russell [20] have recorded the dipole moment of NH_3(g) as 1·45 D; for CH_3Cl(g), Barclay and Le Fèvre [21] gave $\mu = 1{\cdot}86$ D. Refraction–dispersion measurements by Ramaswamy [22,23] provide electronic polarisations of 5·45 cm.³ and 11·20 cm.³ for NH_3 and CH_3Cl, respectively. Polarisability semi-axes then emerge as in Table 2.

TABLE 2

Molecular polarisability semi-axes * for NH_3 and CH_3Cl

	μ (D)	$10^{12}{}_{\mathrm{m}}K$	${}_{\mathrm{E}}P$ (cm.³)	$10^{35}(\theta_1 + \theta_2)$	$(b_1 + 2b_2)$	b_1	b_2
NH_3	1·45	6·5	5·45	1·546	6·48	2·34	2·07
CH_3Cl	1·86	68·5	11·20	16·289	13·32	5·57	3·87

* Here, and elsewhere, polarisabilities are quoted in 10^{-24} cm.³ units (Å³).

The semi-axes derivable from Szivessy's value of ${}_{\mathrm{m}}K$ for NH_3 ($+6{\cdot}1 \times 10^{-12}$) are the same as those of Table 2; Stuart's value of ${}_{\mathrm{m}}K$ for CH_3Cl ($+63{\cdot}6 \times 10^{-12}$) yields $b_1^{\mathrm{CH_3Cl}} = 5{\cdot}50$ and $b_2^{\mathrm{CH_3Cl}} = 3{\cdot}91$.

In NH_3, the three-fold axis of symmetry makes an angle of 67° 58′ with the N–H bonds; [24] anisotropic bond polarisabilities are thus obtained from the equations

$$b_1^{\mathrm{NH_3}} = 3(b_{\mathrm{L}}^{\mathrm{NH}} \cos^2 67°58' + b_{\mathrm{T}}^{\mathrm{NH}} \sin^2 67°\,58') \qquad (5)$$

$$(b_1 + 2b_2)^{\mathrm{NH_3}} = 3(b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{NH}} \qquad (6)$$

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[18] G. Otterbein, *Phys. Z.*, 1933, **34**, 645; 1934, **35**, 249.

[19] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

[20] R. J. W. Le Fèvre and P. Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.

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[23] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 675.

[24] G. Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 439.

Polarisabilities for the C–Cl bond are derived by use of the equations

$$b_L^{CCl} = b_1^{CH_3Cl} - 3b_i^{CH} \tag{7}$$

$$b_T^{CCl} = b_2^{CH_3Cl} - 3b_i^{CH} \tag{8}$$

where b_i^{CH} is the isotropic polarisability of the carbon–hydrogen bond.[19]

Results are shown in Table 3, together with the corresponding values from dilute-solution measurements.[25,26] For the N–H bond in NH_3, agreement is excellent; the divergence in the results for the C–Cl bond in CH_3Cl arises from the widely different molar Kerr constants obtained from gas and solution measurements, respectively.

TABLE 3

Polarisabilities of C–Cl and N–H bonds from gas and solution measurements

		b_L	$b_T(= b_V)$		b_L	$b_T(= b_V)$
Gas	N–H	0·52	0·82	Solution	0·50	0·83
	C–Cl	3·66	1·96		3·2	2·2

Dipole Moments of Fluorocarbons.—Smyth and McAlpine [27] recorded the dipole moments of CCl_3F, $CHClF_2$, and CCl_2F_2 in the vapour state as 0·45 D, 1·40 D, and 0·51 D, respectively. From microwave-Stark effect studies, Ghosh, Trambarulo, and Gordy [28] found the moment of CHF_3 to be 1·64 D; this is in good agreement with the value of 1·65 D recently obtained by Buckingham and Raab [29] from dielectric virial coefficients. The moment of $C_2Cl_2F_4$, indicated by microwave absorption [30] and dispersion [31] experiments, is 0·56 D.

As the moments of methyl chloride and methyl fluoride differ by only 0·05 D,[32] it is clear that mutual inductive effects among adjacent carbon–halogen bonds are very important in the chlorofluorocarbons. The difference ($\mu^{CF} - \mu^{CCl}$) between the moments of carbon–fluorine and carbon–chlorine bonds in perhalogenated environments can be deduced from the moments of compounds such as $CClF_3$, CCl_3F, C_2ClF_5, and C_2Cl_5F. In each of these cases it follows from the molecular symmetry that $\mu_r = \mu^{CF} - \mu^{CCl}$. Recorded values of μ_r are as follows: $CClF_3$, 0·50 D; [33] CCl_3F, 0·45 D;[27] C_2ClF_5, 0·52 D.[34] It thus appears reasonable to take ($\mu^{CF} - \mu^{CCl}$) as 0·50 D in such environments. The same approximation has been made by Rutner and Bauer [35] in their study of the dipole moments of perchlorofluorobutanes and similar compounds. This result will be used in the discussion of internal rotation in 1,2-dichlorotetrafluoroethane.

Anisotropy of the Carbon–Fluorine Bond.—Le Fèvre and his collaborators used the dilute-solution procedure to obtain the molar Kerr constants of methyl fluoride, fluorobenzene, 1,4-difluorobenzene, and the fluoronaphthalenes.[1] Of these, only methyl fluoride provides a useful estimate of the anisotropy of the C–F bond in an aliphatic environment. Cherry, Hobbs, and Strobel [36] measured the molar Kerr constants of some halogenobenzenes, monohalogenobenzotrifluorides, and benzotrifluoride. In the absence of light-scattering data, C–F bond polarisabilities are not directly accessible from these results. No gas or vapour state measurements of fluorine compounds have been recorded.

For both CCl_3F and CHF_3, two of the three principal molecular polarisabilities are equal ($b_1 \neq b_2 = b_3$). Semi-axes of their polarisability ellipsoids can be determined by use of equations (1)—(4). From atomic refractivities, Smyth and McAlpine [27] calculated

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[25] M. Aroney and R. J. W. Le Fèvre, *J.*, 1958, 3002.

[26] C. G. Le Fèvre and R. J. W. Le Fèvre, *J.*, 1954, 1577.

[27] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, 1933, **1**, 190.

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[32] R. J. W. Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[33] R. C. Johnson, T. L. Weatherley, and Q. Williams, *J. Chem. Phys.*, 1961, **35**, 2261.

[34] A. Di Giacomo and C. P. Smyth, *J. Amer. Chem. Soc.*, 1955, **77**, 774.

[35] E. Rutner and S. H. Bauer, *J. Amer. Chem. Soc.*, 1960, **82**, 298.

[36] L. V. Cherry, M. E. Hobbs, and H. A. Strobel, *J. Phys. Chem.*, 1957, **61**, 465.

$_{\mathrm{E}}P$ for CCl_3F as 20·8 cm.^{3}, whence $(b_1 + 2b_2)^{\mathrm{CCl_3F}} = 24{\cdot}73$. Ramaswamy[37] measured the dispersion of the refractivity of CHF_3; $_{\mathrm{E}}P$ is found to be 6·98 cm.^{3}, so that $(b_1 + 2b_2)^{\mathrm{CHF_3}} =$ 8·30. The derivations of principal molecular polarisabilities for CCl_3F and CHF_3 are summarised in Table 4.

TABLE 4

Molecular polarisability semi-axes for CCl_3F and CHF_3

	μ (D)	$10^{12}{}_{\mathrm{m}}K$	$_{\mathrm{E}}P$ (cm.^{3})	$10^{35}(\theta_1 + \theta_2)$	$(b_1 + 2b_2)$	b_1	b_2
CCl_3F	0·45	−1·7	20·8	−0·404	24·73	7·60	8·57
CHF_3	1·64	−5·3	6·98	−1·260	8·30	2·65	2·83

If the Cl–C–Cl angle θ in CCl_3F is 111·5°,[38] the angle ϕ made by the C–Cl bonds with the b_1 direction follows from the relationship

$$\sin\phi = \sin(\theta/2)/\cos 30°.$$

The longitudinal and transverse polarisabilities of the C–F bond are derived from the equations

$$b_1^{\mathrm{CCl_3F}} = b_{\mathrm{L}}^{\mathrm{CF}} + 3(b_{\mathrm{L}}^{\mathrm{CCl}}\cos^2\phi + b_{\mathrm{T}}^{\mathrm{CCl}}\sin^2\phi) \qquad (9)$$

$$(b_1 + 2b_2)^{\mathrm{CCl_3F}} = 3(b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{CCl}} + (b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{CF}} \qquad (10)$$

In the case of CHF_3, the F–C–F angle has been taken as 108·8°;[38] equations similar to (9) and (10) are used to obtain the semi-axes of the C–F bond.

With the C–Cl bond values obtained from CH_3Cl, anisotropic polarisabilities emerge as in Table 5.

TABLE 5

C–F bond polarisabilities from CCl_3F and CHF_3

	$b_{\mathrm{L}}^{\mathrm{CF}}$	$b_{\mathrm{T}}^{\mathrm{CF}}$	$(b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{CF}}$
CCl_3F	1·26	0·37	2·00
CHF_3	0·83	0·65	2·13

For methyl fluoride, the solution measurements of Le Fèvre and Le Fèvre[26] yield $b_{\mathrm{L}}^{\mathrm{CF}} = 1{\cdot}2_5$ and $b_{\mathrm{T}}^{\mathrm{CF}} = 0{\cdot}4$; these values are almost identical with the results from CCl_3F.

The data of Table 5 suggest that $(b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{CF}}$ is perhaps around $2{\cdot}0_5$, an estimate which would agree with the value of 2·12 which is derivable from $_{\mathrm{E}}P$ for carbon tetrafluoride.[37] Macey[39] measured the refractive indices and specific dispersions of a large number of liquid organic fluorides. His results show that in 1-fluoroalkanes the mean C–F bond refraction, R_{D}, is 1·55 cm.^{3}, whereas in the n-alkyl esters of trifluoroacetic acid (containing the CF_3 group) it is 1·88 cm.^{3}. These data correspond to $(b_{\mathrm{L}} + 2b_{\mathrm{T}})^{\mathrm{CF}}$ values of about 1·8 and 2·1, respectively.

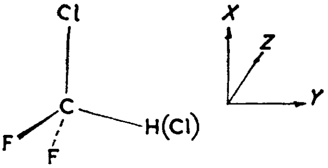

FIGURE 3. Co-ordinate axes for $CHClF_2$ and CCl_2F_2

Anisotropic Polarisabilities of $CHClF_2$ *and* CCl_2F_2.—As a test of the C–F bond polarisabilities derived from CCl_3F and from CHF_3, the observed and calculated molar Kerr constants of $CHClF_2$ and CCl_2F_2 may be compared. To calculate $_{\mathrm{m}}K$ for these two molecules, arbitrary axes X, Y, Z are chosen as in Figure 3; the ClCH group in $CHClF_2$, and the ClCCl group in CCl_2F_2 lie in the XY-plane. The anisotropic polarisabilities of

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[37] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, 1935, **2**A, 630.

[38] L. E. Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11, 1958.

[39] W. A. T. Macey, *J. Phys. Chem.*, 1960, **64**, 254.

each bond, in turn, are resolved along these axes, and the principal molecular polarisabilities are computed by the standard methods.[40] Bond angles as recorded by Sutton [38] have been used. These are: for $CHClF_2$, $\angle$Cl–C–F = 110·5°; for CCl_2F_2, $\angle$Cl–C–Cl = 113° and $\angle$Cl–C–F = 110°. The resultant dipole moment of $CHClF_2$ is assumed to be directed along the H–C bond. In CCl_2F_2 the moment acts along the bisector of the Cl–C–Cl and F–C–F angles. The C–Cl bond polarisabilities used are those derived from methyl chloride.

The principal polarisabilities b_1, b_2, b_3, their direction cosines with the axes X, Y, Z, and the moment components μ_1, μ_2, μ_3 are shown in Table 6, together with the calculated molar Kerr constants. The observed ${}_{\mathrm{m}}K$'s are $-17·6 \times 10^{-12}$ for $CHClF_2$ and $+1·4 \times 10^{-12}$ for CCl_2F_2. As the polarisability of the C–F bond is small, both sets of bond values give calculated ${}_{\mathrm{m}}K$'s in reasonable agreement with experiment.

TABLE 6

Polarisability semi-axes, direction cosines, moment components, and calculated ${}_{\mathrm{m}}K$'s for $CHClF_2$ and CCl_2F_2 *

		Direction cosines with				
		X	Y	Z		
$CHClF_2$ b^{CF} from CCl_3F	b_1 = 5·30	+0·9837	+0·1796	0	μ_1 = +0·235	${}_{\mathrm{m}}K$ = −24·1
	b_2 = 3·68	−0·1796	+0·9837	0	μ_2 = −1·381	
	b_3 = 4·52	0	0	+1	μ_3 = 0	
$CHClF_2$ b^{CF} from CHF_3	b_1 = 5·64	+0·9994	+0·0348	0	μ_1 = +0·433	${}_{\mathrm{m}}K$ = −13·3
	b_2 = 3·98	−0·0348	+0·9994	0	μ_2 = −1·332	
	b_3 = 4·14	0	0	+1	μ_3 = 0	
CCl_2F_2 b^{CF} from CCl_3F	b_1 = 7·03	+0·8535	−0·5210	0	μ_1 = −0·029	${}_{\mathrm{m}}K$ = +0·2
	b_2 = 6·30	+0·5210	+0·8535	0	μ_2 = −0·509	
	b_3 = 5·84	0	0	+1	μ_3 = 0	
CCl_2F_2 b^{CF} from CHF_3	b_1 = 7·58	+0·8365	−0·5479	0	μ_1 = −0·013	${}_{\mathrm{m}}K$ = +1·3
	b_2 = 6·38	+0·5479	+0·8365	0	μ_2 = −0·510	
	b_3 = 5·46	0	0	+1	μ_3 = 0	

* b_1, b_2, b_3 in 10^{-24} cm.^{3} units, moment components in D units, molar Kerr constants in 10^{-12} units.

Rotational Isomerism in 1,2-Dichlorotetrafluoroethane.—Molecular models of this compound show that the $CClF_2$ groups can be rotated about the longitudinal axis of the C–C bond. Raman [41] and infrared [42] spectroscopic data have confirmed the existence of rotational isomers.

From electron-diffraction studies [43,44] it has been concluded that at room temperature gaseous $C_2Cl_2F_4$ is nearly an equimolecular mixture of the *trans-* and *gauche*-forms. Furthermore, it was found [44] that *gauche*-forms could be generated by rotating one $CClF_2$ group approximately 120° from the *trans*-conformation. This situation is analogous to the restricted internal rotation occurring in 1,2-dichloroethane.[45,46]

For $C_2Cl_2F_4$, the observed dipole moment and molar Kerr constant are, respectively, 0·56 D and $+6·9 \times 10^{-12}$.

The resultant moment of the *trans*-isomer (μ_t) is zero; the moment of the *gauche*-isomer (μ_g) acts at right angles to the C–C bond and (assuming tetrahedral bond angles) is given by the expression

$$\mu_g = 2 \cos 20° \cos 30° \, (\mu^{CF} - \mu^{CCl}) \qquad (11)$$

If $(\mu^{CF} - \mu^{CCl})$ is taken as 0·50 D, μ_g is 0·81 D. The apparent dipole moment, μ_a, of

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$C_2Cl_2F_4$ is 0·56 D, so that the composition of the equilibrium mixture can be estimated from the relationship

$$\mu_a^2 = \mu_t^2 x_t + \mu_g^2 x_g \tag{12}$$

where x_t and x_g are the mole fractions of the *trans*- and *gauche*-isomers. Such a treatment suggests an equilibrium mixture containing 48% of the *gauche*-isomer and 52% of the *trans*-isomer at room temperature.

Usually the positions of a *trans–gauche* equilibrium is markedly dependent on temperature. However, microwave absorption studies [30] showed that the total polarisation of $C_2Cl_2F_4$ is a linear function of the reciprocal of the absolute temperature in the range 15—132°. It is thus probable that, for this molecule, the energy separation between *trans*- and *gauche*-isomers is small.

Molar Kerr constants for the *trans*- and *gauche*-isomers of $C_2Cl_2F_4$ can be calculated by the method outlined for $CHClF_2$ and CCl_2F_2. Carbon–fluorine bond polarisabilities from both CCl_3F and CHF_3 have been used, together with the C–Cl values from methyl chloride. Co-ordinate axes are chosen as in Figure 4. Results are shown under the usual headings in Table 7.

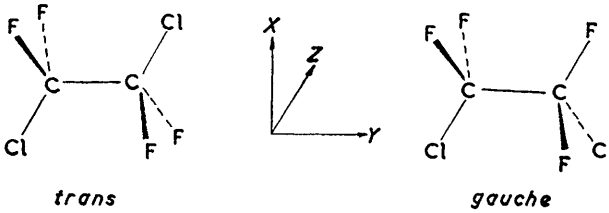

FIGURE 4. Co-ordinate axes for $C_2Cl_2F_4$

TABLE 7

Polarisability semi-axes, direction cosines, moment components, and calculated ${}_mK$'s for $C_2Cl_2F_4$

		Direction cosines with				
		X	Y	Z		
(a) b^{CF} from CCl_3F						
trans	$b_1 = 7·09$	+0·9768	−0·2143	0	$\mu_1 = 0$	${}_mK_t = +2·4$
	$b_2 = 9·57$	+0·2143	+0·9768	0	$\mu_2 = 0$	
	$b_3 = 8·02$	0	0	+1	$\mu_3 = 0$	
gauche	$b_1 = 7·15$	+0·9785	−0·1029	+0·1786	$\mu_1 = 0$	${}_mK_g = +10·9$
	$b_2 = 9·10$	+0·0005	+0·8677	+0·4971	$\mu_2 = -0·809$	
	$b_3 = 8·44$	−0·2061	−0·4864	+0·8491	$\mu_3 = -0·003$	
(b) b^{CF} from CHF_3						
trans	$b_1 = 7·59$	+0·9243	−0·3817	0	$\mu_1 = 0$	${}_mK_t = +4·3$
	$b_2 = 10·36$	+0·3817	+0·9243	0	$\mu_2 = 0$	
	$b_3 = 7·27$	0	0	+1	$\mu_3 = 0$	
gauche	$b_1 = 7·48$	+0·6874	−0·3632	+0·6289	$\mu_1 = 0$	${}_mK_g = +10·7$
	$b_2 = 9·28$	−0·0003	+0·8658	+0·5003	$\mu_2 = -0·810$	
	$b_3 = 8·45$	−0·7262	−0·3441	+0·5951	$\mu_3 = 0$	

By analogy with equation (12), the apparent molar Kerr constant, ${}_mK_a$, of $C_2Cl_2F_4$ may be expressed as

$${}_mK_a = {}_mK_t x_t + {}_mK_g x_g \tag{13}$$

where ${}_mK_t$ and ${}_mK_g$ are the calculated molar Kerr constants of the *trans*- and *gauche*-isomers. The two sets of results in Table 7 are compatible with the observed ${}_mK$ $(+6·9 \times 10^{-12})$ if the mixture contains 53 and 41% of the *gauche*-isomer, respectively. As with $CHClF_2$ and CCl_2F_2, the true C–F bond polarisabilities in $C_2Cl_2F_4$ probably lie between the values derived from CCl_3F and from CHF_3. It therefore seems reasonable to consider $C_2Cl_2F_4$ as a mixture whose composition is the average of the two results quoted, *i.e.*, as 47% of the *gauche*-isomer and 53% of the *trans*-isomer. This result is in excellent agreement with the composition predicted from the apparent dipole moment (48% *gauche*), and with the conclusion from electron-diffraction studies (48 ± 5% *gauche*).[44]

It is of interest to calculate the energy separation, ΔE, between the *gauche*- and *trans*-conformers. If f_g and f_t are the vibrational and rotational partition functions of the *gauche*- and *trans*-forms, then [45]

$$x_g/x_t = 2(f_g/f_t)e^{-\Delta E/RT} \qquad (14)$$

For 1,2-dichloroethane, Mizushima *et al.*[45] found that, at 25°, the ratio $2(f_g/f_t)$ is 1·902. This result provides a reasonable approximation for use in the present case. With $x_g/x_t = 0{\cdot}47/0{\cdot}53$, ΔE emerges as 0·5 kcal. mole^{-1}. The corresponding value for 1,2-dichloroethane is in the range 1·0—1·3 kcal. mole^{-1}.[45]

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