326. *The Dipole Moments of Furan and Thiophen measured in the Dissolved and in the Gaseous State.*

By B. Harris, R. J. W. Le Fèvre, and E. P. A. Sullivan.

The magnitudes of μ_{gas} and $\mu_{benzene}$ of furan and thiophen are found to agree, qualitatively for furan and quantitatively for thiophen, with equations (1), (2), and (4) listed previously by Buckingham and Le Fèvre (*J.*, 1952, 1932). An analysis of the observed dielectric constants, densities, and refractive indexes of solutions in benzene supports various suggestions made by Guggenheim and by Smith. Consequent changes are indicated in the routine procedures to be used here for obtaining $_\infty P_2$.

OUR recent communications on molecular polarity have discussed, *inter alia* : (*a*) the calculation of the total polarisation of a solute at infinite dilution from a set of dielectric constant, density, and composition data covering a range of concentrations of a given substance in one solvent, and (*b*) the devising of relations whereby " apparent " moments measured in solution may be converted into the " true " values observed for the gaseous state. For (*a*), we refer principally to a paper by Le Fèvre (*Trans. Faraday Soc.*, 1950, **46**, 1) giving our methods of computation and comparing them with those of other groups of workers. On (*b*) we cite particularly Buckingham and Le Fèvre's equations (*J.*, 1952, 1932) based partly on previous work (*J.*, 1950, 276, 283, 290, 295, 556, 1829, 2166, 3370; 1951, 2583; 1952, 1643 1649 1651; *Trans. Faraday Soc.*, 1947, **43**, 374; 1950, **46**, 812; 1951, **47**, 357.

Following Le Fèvre's paper, three others bearing on topic (*a*) have appeared (Smith, *Trans. Faraday Soc.*, 1950, **46**, 394; Everard, Hill, and Sutton, *ibid.*, p. 417; Guggenheim, *ibid.*, 1951, **47**, 573). All accept that the molecular polarisation of a solute at infinite dilution should be computed with quantities actually measured rather than extrapolated from the partial polarisations derived from individual solutions *via* earlier mixture " rules " (such as $P_{12} = P_1 w_1 + P_2 w_2$). Minor differences between the authors concern the modes of concentration dependence to be best assumed for ε_{12} and d_{12} : on one hand, Sutton and his colleagues take *straight-line* relations for ε_{12} or v_{12} (specific volume of solution) versus w_2; on the other, Le Fèvre, Smith, and Guggenheim prefer to regard these as, in general, *curved*, although many sets of data lead to only very slight curvature. Ultimately in either case values of $[(\varepsilon_{12} - \varepsilon_1)/w_2]_{w_2 = 0}$, $[(v_{12} - v_1)/w_2]_{w_2 = 0}$, or $[(d_{12} - d_1)/w_2]_{w_2 = 0}$, etc., are required.* Accordingly, Le Fèvre (*loc. cit.*) wrote $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2 + \alpha' w_2^2)$, so that $[(\varepsilon_{12} - \varepsilon_1)/w_2]_{w_2} = \alpha\varepsilon_1 + \alpha'\varepsilon_1 w_2$. Similar expressions were set up for d_{12}. The quotients on the left-hand sides of these equations should have been therefore—whenever α' was not zero—rectilinear against w_2, so that $\alpha\varepsilon_1$ (or βd_1) could be determined by the method of least squares. Guggenheim (personal communications, and *Trans. Faraday Soc.*, 1951, **47**, 573) has criticised the last step on the ground that minimising $\Sigma[(\varepsilon_{12} - \varepsilon_1 - \alpha\varepsilon_1 w_2 - \alpha'\varepsilon_1 w_2^2)/w_2]^2$ unduly weights the measurements of lower accuracy at higher dilutions. We concur, and in future work intend to fit observations of $\delta\varepsilon = \varepsilon_{12} - \varepsilon_1$ (or $\delta d = d_{12} - d_1$) to formulæ of the type $\delta\varepsilon = \alpha w_2 + b w_2^2$. The constant a will then be $(\alpha\varepsilon_1)_{w_2 = 0}$ or $(\beta d_1)_{w_2 = 0}$, respectively, for the variation of ε_{12} or d_{12} with w_2.

Both Guggenheim (*Trans. Faraday Soc.*, 1949, **45**, 715; *loc. cit.*) and Smith (*loc. cit.*) have described the estimation of orientation polarisations at infinite dilution, $_\infty(_oP_2)$, by methods which do not appear to involve the accurate measurement of densities. Thus, if the limiting values at $w_2 = 0$ of $\delta\varepsilon/w_2$ and $\delta n^2/w_2$ (n being the refractive index) are $\alpha\varepsilon_1$ and γn_1^2, Smith's proposal leads to $_\infty(_oP_2) = 3M_2 v_1[\alpha\varepsilon_1/(\varepsilon_1 + 2)^2 - \gamma n_1^2/(n_1^2 + 2)^2]$. However, this simplification involves an error which can be assessed by subtracting from *e.g.*, Halverstadt and Kumler's equation (*J. Amer. Chem. Soc.*, 1942, **64**, 2988) for $_\infty P_2$ a corresponding equation, *viz.*, $R_2 = M_2[(v_1 + b)(n_1^2 - 1)/(n_1^2 + 2) + 3v_1\gamma n_1^2/(n_1^2 + 2)^2]$, for the molecular refraction, whereupon the full $_\infty(_oP_2)$ is seen to exceed that from Smith's

---

* Subscripts 1 and 2 refer to solvent and solute respectively. This is the reverse of the convention followed by Le Fèvre for many years (cf. *J.*, 1952, 1932). A solution is denoted by the subscript 12.

expression by the extra term $3M_2(v_1 + b)(\varepsilon_1 - n_1{}^2)/(\varepsilon_1 + 2)(n_1{}^2 + 2)$. This is negligible when ε_1 and $n_1{}^2$ are nearly equal and M_2 not too great, but if b {*i.e.*, $[(v_{12} - v_1)/w_2]_{w_2 = 0}$} is large, or $\alpha\varepsilon_1$ of the same order as $\gamma n_1{}^2$, results may be disappointing. Two numerical applications are discussed later.

The primary motive for the present work arose from the matters listed at the outset under (*b*). Buckingham and Le Fèvre (*loc. cit.*) recorded polarity measurements for thirteen compounds, chosen for their range of molecular shapes, to guide the selection of the best relation with which to connect μ_{solution} with μ_{gas}. On the whole the greatest success was achieved with the larger molecules. Published figures for small molecules as vapours and as solutions are sparse; usually only μ_{gas} is available, and μ_{solution} is lacking. With dissolved gases dependable accuracy is difficult to ensure, as experience with carbon suboxide, carbonyl chloride (*J.*, 1935, 1696), methylamine, etc. (*Trans. Faraday Soc.*, 1947, **43**, 374), sulphur dioxide (*J.*, 1950, 276), methyl chloride (*J.*, 1950, 556), ethylene oxide (*J.*, 1950, 3370), keten (*J.*, 1951, 2583), dimethyl ether (*J.*, 1952, 1643), hydrogen sulphide (*J.*, 1952, 1651), etc., has shown. We therefore decided to examine furan and thiophen since both these are ordinarily *liquid* and have had their structures metrically described (cf. Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46). Moreover, their low dipole moments made them suitable for illustrating the points raised under (*a*).

EXPERIMENTAL

Furan, prepared as in *Org. Synth.* (Coll. Vol. I, 1941, p. 274), was dried (Na) and distilled immediately before use; it had b. p. 32°/760 mm. Thiophen, supplied by the Socony-Vacuum Oil Co., U.S.A., was dried (Na) and fractionated; the portion collected had b. p. 84·0°/761·4 mm. The benzene used as solvent was " crystallisable " grade which had been refluxed over aluminium chloride for some hours, washed several times with sulphuric acid followed by water, then dried (Na) and distilled. The product was partially frozen in contact with sodium wire and the fully solid portion remaining after decantation allowed to remelt.

The polarisations of furan and thiophen as gases were measured relatively to carbon dioxide with the apparatus and procedure described in *J.*, 1950, 290. Data are presented in Table 1,

TABLE 1. *Polarisation–temperature relations for furan and thiophen as gases.*

		Pressure range (cm. Hg)		P	P			Pressure range (cm. Hg)		P	P
T, °K	No. of obs.		x/x'	(obs.)	(calc.) *	T, °K	No. of obs.		x/x'	(obs.)	(calc.) †
		Furan						Thiophen			
329	17	16—60	3·987	29·27	29·30	295	9	2—7	4·106	30·14	30·17
340	15	14—52	3·952	29·01	28·98	353	14	14—41	3·982	29·23	29·13
351	10	13—46	3·895	28·59	28·69	373	12	26—49	3·964	29·10	28·85
373	13	13—57	3·849	28·26	28·15	390	16	11—46	3·891	28·56	28·63
390	16	15—47	3·796	27·87	27·78	405	16	12—44	3·883	28·50	28·45
430	14	12—51	3·670	26·94	27·03	411	12	14—51	3·813	27·99	28·38
						431	14	11—48	3·849	28·26	28·17

* From equation : $P = 19\cdot63 + 3180/T$.   † From equation : $P = 23\cdot83 + 1871/T$.

[The calibration equation used for both the above sets was $(\delta C/p)_{\text{CO}_2} = -0\cdot054 + 2307\cdot4/T$.]

the headings of which are self-explanatory except for x/x' which is the *observed* ratio $(\delta C/p)_{p=0}^{\text{gas}}/(\delta C/p)_{p=0}^{\text{CO}_2}$, whence P_{gas} follows as xP_{CO_2}/x'.

Dielectric constants (ε), densities (d), and refractive indices (n_D) for each of the solutes at various concentrations expressed as weight fractions (w) in benzene at 25° are recorded in Table 2. They were determined by standard techniques (cf. *J.*, 1948, 1949; 1949, 333; " Dipole Moments," Methuen, 1948, Chap. II).

Calculation of Results.—The equations of the form $P = A + B/T$ shown in Table 1 were computed by the method of least squares. If $P_{\text{obs.}}$ minus $P_{\text{calc.}}$ is Δ, and n the number of temperatures studied, the standard errors in the A and B terms are given by $\pm s\{[\Sigma(1/T)^2]/D\}^{\frac{1}{2}}$ and $\pm s(n/D)^{\frac{1}{2}}$, respectively, where $s = [(\Sigma\Delta^2)/(n - 2)]^{\frac{1}{2}}$ and $D = n\Sigma(1/T)^2 - [\Sigma(1/T)]^2$ (cf. Youden, *Analyt. Chem.*, 1947, **19**, 946). Inserting appropriate values, we have

for furan : $P = (19\cdot63 \pm 0\cdot47) + (3180 \pm 170)/T$ whence $\mu = 0\cdot72 \pm 0\cdot02_\text{D}$

for thiophen : $P = (23\cdot83 \pm 0\cdot67) + (1871 \pm 249)/T$ whence $\mu = 0\cdot55 \pm 0\cdot04_\text{D}$

The measurements listed in Table 2 have been utilised to test the three extrapolation procedures used here for several years. All are based on the proposals made by Le Fèvre and Vine (*J.*, 1937, 1805) and require estimates of the two " constants " α or β (p. 1622); these may be

TABLE 2.   *Dielectric constants, densities, etc., for furan and thiophen in benzene at 25°.*

Furan

$10^5 w_2$	ε	d	n_D	$10^5 w_2$	ε	d	n_D	$10^5 w_2$	ε	d	n_D
0	2·2725	0·87378	1·4976	4425	2·3003	0·87596	1·4940	7995·5	2·3208	0·87774	—
1709·5	2·2833	0·87469	—	5622·5	2·3077	0·87659	—	8276	—	—	1·4911
3565	2·2948	0·87562	—	5935	2·3090	0·87679	—	8510·5	2·3231	0·87803	—
3702	2·2956	0·87567	—	5935·5	2·3090	0·87678	1·4930	8995	—	—	1·4907
4397·5	2·2990	0·87601	—								

Thiophen

$10^5 w_2$	ε	d	n_D	$10^5 w_2$	ε	d	n_D	$10^5 w_2$	ε	d	n_D
0	2·2725	0·87378	1·4976	2459	—	0·87769	—	5403	—	0·88225	—
634	2·2754	0·87481	—	3088	2·2820	0·87806	1·4980	5874	2·2909	0·88250	—
1318·5	2·2777	0·87587	—	3758	—	0·87970	—	6994	2·2947	0·88452	—
1673	2·2783	0·87685	—	4312	2·2876	—	—	8890	—	—	1·4992
1962	2·2802	—	—	4960	—	—	1·4985				

obtained by averaging expressions (1), (2), (7), and (8), fitting a straight line to the apparent values of $\alpha\varepsilon_1$ or βd_1 at each w_2 [expressions (3), (4), (9), (10)], or assuming that $\delta\varepsilon = \varepsilon_{12} - \varepsilon_1$ and $\delta d = d_{12} - d_1$ are related to w_2 by a power series [expressions (5), (6), (11), (12)]. Thus from Table 2 we derive for furan :

$$\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma(w_2) = 0.613 \qquad (1)$$

$$\Sigma(d_{12} - d_1)/\Sigma(w_2) = 0.0503_5 \qquad (2)$$

$$(\alpha\varepsilon_1)_{w_2} = 0.641_5 - 0.48w_2 \qquad (3)$$

$$(\beta d_1)_{w_2} = 0.0528 - 0.042w_2 \qquad (4)$$

$$\delta\varepsilon = 0.646w_2 - 0.57w_2{}^2 \qquad (5)$$

$$\delta d = 0.0517w_2 - 0.024w_2{}^2 \qquad (6)$$

and for thiophen :

$$\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma(w_2) = 0.336 \qquad (7)$$

$$\Sigma(d_{12} - d_1)/\Sigma(w_2) = 0.154_5 \qquad (8)$$

$$(\alpha\varepsilon_1)_{w_2} = 0.415 - 1.71w_2 \qquad (9)$$

$$(\beta d_1)_{w_2} = 0.166 - 0.231 \qquad (10)$$

$$\delta\varepsilon = 0.373w_2 - 0.86w_2{}^2 \qquad (11)$$

$$\delta d = 0.156w_2 - 0.042_5w_2{}^2 \qquad (12)$$

We have used all the above to calculate $\delta\varepsilon$ and δd and find that the sums, for each equation, of the squares of the differences from the observed values run in descending orders as follow :

$$\text{for furan} \begin{cases} \delta\varepsilon & . \; . \; . \; (1) > (3) = (5) \\ \delta d & . \; . \; . \; (2) > (4) > (6) \end{cases} \qquad \text{for thiophen} \begin{cases} \delta\varepsilon & . \; . \; (7) > (9) > (11) \\ \delta d & . \; . \; (8) \doteqdot (10) > (12) \end{cases}$$

Similar surveys, *e.g.*, on the solutions discussed in *Trans. Faraday Soc.*, 1950, **46**, 1, have shown the same sequences. Accordingly, we propose in future to replace forms such as (3) or (4) by (5) or (6) whenever ε_{12} or d_{12} measurements are clearly seen not to be rectilinear with w_2. This amends the practice recommended in the paper just cited.

In such cases it will be of interest therefore to assess the standard error of the constant α in a regression of the type $\delta Q = aw_2 + bw_2{}^2$. If Δ is the difference between $(\delta Q)_{\text{obs.}}$ and $(\delta Q)_{\text{calc.}}$, the desired standard error is $\pm [(\Sigma\Delta^2)/(\text{degrees of freedom}) \Sigma(w_2 - \bar{w}_2)^2]^{\frac{1}{2}}$.

Thus $\alpha\varepsilon_1$ and βd_1 at $w_2 = 0$ become, from Table 2,

$$\text{for furan :}\quad \alpha\varepsilon_1 = 0.646 \pm 0.008; \quad \beta d_1 = 0.0517 \pm 0.0006$$

$$\text{for thiophen :}\quad \alpha\varepsilon_1 = 0.373 \pm 0.013; \quad \beta d_1 = 0.156 \pm 0.005$$

whence, using $_\infty P_2 = p_1 (1 - \beta) + C\alpha\varepsilon_1$, and multiplying by M_2, we find $_\infty P_2$ to be 30.10 ± 0.12 c.c. for furan or 29.45 ± 0.34 c.c. for thiophen.

Using the distortion polarisations reported above (*viz.*, 19.63 ± 0.47 and 23.83 ± 0.67 c.c., respectively), we obtain the apparent moments in benzene of these solutes as :

$$\text{furan :}\quad \mu = 0.71_5 \pm 0.02 \text{ D} \qquad\qquad \text{thiophen :}\quad \mu = 0.52 \pm 0.05 \text{ D}$$

We now refer to the approximate calculation of orientation polarisations by routes which avoid d_{12} determinations (see p. 1622). Knowledge of $(n_{12}{}^2 - n_1{}^2)/w_2$ for $w_2 = 0$ is required; since usually the refractive index of a solution obeys the equation $n_{12}{}^2 = n_1{}^2(1 + \gamma w_2)$, a mean value of $\gamma n_1{}^2$ can be obtained as $\Sigma(n_{12}{}^2 - n_1{}^2)/\Sigma w_2$. From Table 2 this magnitude is -0.234 for furan and $+0.0514$ for thiophen. As a check on these, R_2 may be computed as $M_2 r_2$ *via*

$$_\infty r_2 = r_1(1 - \beta) + G\gamma n_1{}^2 \qquad\qquad . \; . \; . \; . \; . \; . \; . \; . \; (a)$$

where $G = 3/d_1(n_1{}^2 + 2)^2 = 0.1907$, and $r_1 = 0.3352$ c.c. The molecular refractions thus derived (18·4 and 24·0 c.c.) are close to those (18·4 for α line, 24·3 for D line) listed in Landolt–Börnstein's " Tabellen." If equation (a) is subtracted from Le Fèvre and Vine's equation (b)

$$_\alpha p_2 = p_1 (1 - \beta) + C\alpha\varepsilon_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

the specific orientation polarisation at infinite dilution follows as :

$$_\infty({}_0 p_2) = \frac{3(1 - \beta)(\varepsilon_1 - n_1{}^2)}{d_1(\varepsilon_1 + 2)(n_1{}^2 + 2)} + \frac{3}{d_1}\left[\frac{\alpha\varepsilon_1}{(\varepsilon_1 + 2)^2} - \frac{\gamma n_1{}^2}{(n_1{}^2 + 2)^2}\right] \quad . \quad . \quad . \quad . \quad (c)$$

These terms are equivalent to those quoted on p. 1622, but are more suitable for the insertion of quantities already recorded in this paper. Smith's suggestion (*loc. cit.*) is to omit the left-hand member of (c).

Substitution of the appropriate values of β, $\alpha\varepsilon_1$, etc., shows that (c) is, for furan $_\infty({}_0 p_2) = 0.005 + 0.166$ c.c., and for thiophen $_\infty({}_0 p_2) = 0.005 + 0.060$ c.c.

Smith's proposal therefore neglects terms which are *ca.* 3 or 8% respectively of the apparent orientation polarisations deducible by the normal " refractivity " method. Guggenheim's approximation (*loc. cit.*), that $_\infty({}_0 p_2) = 3(\alpha\varepsilon_1 - \gamma n_1{}^2)/d_1(\varepsilon_1 + 2)^2$, applied to the present examples yields values (0.165_5 and 0.060_5 c.c.) which are close to those by Smith's procedure. However, despite the percentage errors just mentioned, the moments (*viz.*, 0·7 and 0·5 D) estimated *via* these " short-cut " routes compare satisfactorily with the values $0.71_5 \pm 0.02$ and 0.52 ± 0.05 D recorded above.

Discussion

Comparison with Earlier Determinations.—Moments previously reported for furan and thiophen are included in Table 3 (measurements in solution being indicated by the formula of the solvent).

TABLE 3. *Recorded dipole moments of furan and thiophen.*

μ, D	How determined	Reference
Furan		
0·63	C_6H_6	Hunter and Partington, *J.*, 1931, 2062
0·71	C_6H_6	Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230
0·67 $\pm$ 0·02	C_6H_6	Robles, *Rec. Trav. chim.*, 1939, **58**, 111
0·661 $\pm$ 0·006	Stark splitting	Sirvetz, *J. Chem. Phys.*, 1951, **19**, 1609
0·72 $\pm$ 0·02	Gas	Present paper
0·71$_5$ $\pm$ 0·02	C_6H_6	,, ,,
Thiophen		
0·63	Solvent unstated	Hassel and Naeshagen, *Tids. Kjemi Berg.*, 1930, **10**, 31
0·53	C_6H_6	Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, **11**, 729
0·54	C_6H_{14}	
0·58	Gas	Kubo, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 122
0·54 $\pm$ 0·02	C_6H_6	Robles, *loc. cit.*
0·53	C_6H_6	Keswani and Freiser, *J. Amer. Chem. Soc.*, 1949, **71**, 218
0·55 $\pm$ 0·04	Gas	Present paper
0·52 $\pm$ 0·05	C_6H_6	,, ,,

The Ratios $\mu_{\text{solution}}/\mu_{\text{gas}}$.—These are seen to be, from experiment, 0.99 ± 0.06 for furan and $0.94_5 \pm 0.16$ for thiophen ; they will now be compared with predictions by Buckingham and Le Fèvre's equations nos. (1), (2), and (4) (*loc. cit.*).

Necessary data—other than those already quoted in this paper—are the following : From scale drawings, using the dimensions listed by Allen and Sutton (*Acta Cryst.*, 1950, **3**, 46), upon which " Wirkungsradien " are superposed, we derive :

	A	B	C	Exp x^2	ξ
Furan	5·10	6·11	2·90	0·624	0·28
Thiophen	5·82	6·44	3·08	0·555	0·26

The internal field functions ξ are evaluated from A/B and C/B more conveniently by using Osborn's tables of demagnetising factors (cf. *Phys. Review*, 1945, **67**, 351) than by the small diagram originally published by Ross and Sack (*Proc. Phys. Soc.*, 1950, **63**, 893). The refractive indices of the two solutes at 25° (Na light) are 1·4186 and 1·5270, respectively.

Substitution gives $\mu_{C_4H_4}/\mu_{gas}$ by the various equations as follows :

	By eqn. (1)	By eqn. (2)	By eqn. (4)	By expt.
Furan	0·92	0·93	0·93	0·99 ± 0·06
Thiophen	0·94	0·94	0·94	0·94$_5$ ± 0·16

The situation with thiophen is satisfactory; it is less so with furan. However, in both cases all equations give the correct qualitative forecast—that μ_{gas} exceeds $\mu_{C_4H_4}$.

The Ratios μ_{liquid}/μ_{gas}.—The dielectric constant of liquid furan, measured relatively to benzene at 25°, is 2·942, its density is 0·9313 g./c.c., whence $_TP_{liquid} = 28·72$ c.c. and $\mu_{liquid} = 0·67$ D. Buckingham and Le Fèvre's equation (5) requires μ_{liquid}/μ_{gas} to be 0·87, but the value found is 0·93. For thiophen we have $\varepsilon_{25} = 2·705$, $d_4^{25} = 1·0583$, and $_TP_{liquid} = 28·81$ c.c., so $\mu_{liquid} = 0·49$ D and $\mu_{liquid}/\mu_{gas} = 0·89$; equation (5) predicts this ratio as 0·89 also.

Thus from ε, d, and n_D observations on the pure materials we should expect μ_{gas} to be 0·77 and 0·55 D, respectively. Incorrect as is the former figure, it is a better estimate of μ_{gas} than that produced by Onsager's equation (No. 7 in Buckingham and Le Fèvre, *loc. cit.*), which with the data used here leads to 0·42 D for furan and 0·46 D for thiophen.

Atomic Polarisations.—Using the molecular refractions listed by Landolt–Börnstein (" Tabellen, 4th edn., p. 1029) for various wave-lengths, Kubo (*loc. cit.*) calculated R_∞ for thiophen as 22·7 c.c.; from the same source we now obtain 17·9 c.c. for furan. From the P–1/T relations given above, atomic polarisations of furan and thiophen follow as 1·7 ± 0·5 and 1·1 ± 0·7 c.c. (or about 10 and 5% of R_∞), respectively. With diethyl ether and sulphide the magnitudes stand in the same order (*viz.*, *ca.* 2·5 and 1·6 c.c.— figures which are *ca.* 11 and 6% of the corresponding electronic polarisations; cf. Barclay and Le Fèvre, *J.*, 1952, 1643; Kubo, *loc. cit.*).