Empirical Relation for the Isothermal Density Derivative of the Optical Dielectric Constant

FOR liquids, the Einstein theory[1] of light scattering, the Gans theory[2] of the Kerr effect and the Leontovitch theory[3] of the Maxwell effect all require knowledge of the isothermal density derivative of the optical dielectric constant, $\rho(\partial n^2/\partial \rho)_T$. Experimental values of this coefficient have been given for only a few liquids. In the past, resource has been made to dielectric equations of state, such as the Lorentz–Lorenz equation, which relate the dielectric constant to the density, in order to calculate this coefficient. Usually, the dielectric constant of a liquid is not a function of density only, however, but depends separately on pressure P and temperature T, so that the coefficients $(\partial n^2/\partial p)_\rho$ and $(\partial n^2/\partial T)_\rho$ are not zero[4]. For example, it has been shown[5] that the use of the Lorentz–Lorenz equation in the Einstein light scattering equation may lead to errors of between 10 and 20 per cent.

Table 1. DENSITY DIFFERENTIALS

$$\rho\left(\frac{n^2}{\partial \rho}\right)_T$$

Liquid	P bar	T° C	λ Å	n	Eykman	Lorentz-Lorenz	This work	Expt.	Ref.
Benzene	1	23	5460	1·503	1·61	1·79	1·62	1·65	5
,,	1	24	5893	1·499	1·60	1·77	1·60	1·58	4
,,	125	24·8	5015	1·514	1·66	1·85	1·67	1·66	6
,,	125	24·8	4678	1·512	1·65	1·84	1·66	1·69	6
,,	370	24·8	5086	1·523	1·70	1·90	1·72	1·74	6
,,	591	34·5	4678	1·545	1·80	2·03	1·83	1·78	6
,,	591	34·5	5016	1·540	1·80	2·02	1·82	1·76	6
,,	137	54·3	6678	1·482	1·52	1·67	1·52	1·53	6
Carbon tetra-chloride	137	24·8	6678	1·461	1·43	1·57	1·43	1·46	6
,,	400	24·8	5876	1·476	1·49	1·64	1·49	1·50	6
,,	591	34·5	4799	1·487	1·54	1·70	1·54	1·53	6
,,	938	34·5	6438	1·487	1·54	1·70	1·54	1·51	6
,,	125	54·3	6678	1·445	1·37	1·48	1·37	1·41	6
,,	125	54·3	4800	1·455	1·41	1·53	1·41	1·46	6
,,	1	23	5460	1·460	1·43	1·56	1·43	1·46	5
n-Hexane	1	25	∞	1·371	1·08	1·14	1·07	1·06	7
,,	2,000	25	∞	1·483	1·34	1·45	1·33	1·33	7
,,	1	0	∞	1·383	1·12	1·19	1·11	1·12	7
,,	2,000	0	∞	1·443	1·36	1·47	1·35	1·35	7
,,	1	-25	∞	1·398	1·18	1·26	1·17	1·17	7
,,	2,000	-25	∞	1·451	1·39	1·51	1·39	1·40	7
,,	1	-50	∞	1·411	1·23	1·32	1·22	1·22	7
,,	1,500	-50	∞	1·450	1·38	1·51	1·38	1·39	7
Toluene	1	23	5460	1·499	1·60	1·77	1·59	1·58	5
Cyclohexane	1	23	5460	1·426	1·29	1·39	1·28	1·29	5
Iso-octane	1	23	5460	1·391	1·15	1·23	1·14	1·15	5
n-Hexane	1	23	5460	1,374	1·09	1·15	1·08	1·08	5
n-Octane	1	23	5460	1·398	1·18	1·27	1·17	1·18	5
n-Decane	1	23	5460	1·413	1·24	1·33	1·23	1·26	5
n-Hexa-dexane	1	23	5460	1·435	1·33	1·43	1·32	1·35	5
Carbon disulphide	1	23	5460	1·634	2·24	2·60	2·32	2·37	5
,,	1	22·6	5893	1·626	2·19	2·53	2·27	2·27	5
Methyl ethyl-ketone	1	23	5460	1·379	1·11	1·17	1·10	1·13	5
Ethyl ether	1	23·4	5893	1·351	1·00	1·05	0·99	0·980	4
Methyl alcohol	1	22·8	5893	1·328	0·92	0·96	0·91	0·898	4

To reduce these errors in the case of liquids for which $\rho(\partial n^2/\partial \rho)_T$ has not been measured, the available experimental data for common organic liquids have been used to provide an empirical relationship between $\rho(\partial n^2/\partial \rho)_T$ and n, both quantities being at the same temperature, pressure and wavelength. This relation is

$$\rho\left(\frac{\partial n^2}{\partial \rho}\right)_T = \frac{1}{30}\,(n^2-1)(23+7n^2)$$

and fits the experimental data to within about ± 1 per cent for most liquids for temperatures between -50° C and $+35^\circ$ C, pressures from 1 to 1,000 bars and over the whole visible spectrum, although sufficient data to test these extremes of range exist for only a few liquids. Static dielectric constant measurements on n-hexane also fit the empirical equation, where the dielectric constant is equated to n^2. The measurements were made in the 100 kHz region, so the measurement wavelength is effectively infinite. The Lorentz–Lorenz equation

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho} = \text{const.}$$

and the Eykman equation

$$\left(\frac{n^2-1}{n+0\cdot4}\right)\frac{1}{\rho} = \text{const.}$$

yield density differentials of

$$\frac{1}{3}\,(n^2-1)(n^2+2) \quad \text{and} \quad \frac{2n(n^2-1)(n+0\cdot4)}{1+n^2+0\cdot8n}$$

respectively, and these are compared with the proposed empirical formula and experimental values in Table 1. It can be seen that the Lorentz–Lorenz equation gives values of $\rho(\partial n^2/\partial \rho)_T$ which are about 8 per cent too high over the whole range, and the Eykman equation is valid only in the region near $n=1\cdot5$, being 3·3 per cent low at $n=1\cdot6$ and 2 per cent high at $n=1\cdot35$. The empirical equation may be integrated to provide a dielectric equation of state at constant temperature, but such an equation of state must necessarily be approximate. It is rather the purpose of this communication to indicate a way of estimating density differentials of the optical dielectric constant to a better accuracy than has hitherto been attained.

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Isotope Shift in Crystal-field Splitting

MARSHALL et al.[1,2] have demonstrated experimentally that the isotope shift in the crystal-field splittings of the magnetic ions doped in some host lattices, δD, is proportional to the mass difference of the isotopic magnetic ions and decreases with temperature. Based on the result that the phonon-induced crystal-field splitting is approximately proportional to the mean square displacement of the atoms[3], I have shown[4] that the isotope shift in the crystal-field splittings of two isotopic magnetic ions is approximately proportional to the difference between the mean square displacements of these two isotopes, $\langle u_0^2\rangle_1$ and $\langle u_0^2\rangle_2$

$$\delta D \propto (\langle u_0^2\rangle_1 - \langle u_0^2\rangle_2) \tag{1}$$

In this communication, I shall try to use this result to explain the temperature dependence of the isotope shifts measured by Marshall et al.[1].

The Einstein model was successfully used by Montgomery to interpret[5] the difference between the lattice constants of ^{6}Li and ^{7}Li. As a result, it could be assumed that the two doped isotopic magnetic ions in a host crystal vibrate with Einstein frequencies ν_1 and ν_2. These frequencies are related to the masses of the isotopic magnetic ions, M_1' and M_2', by the relations $\nu_i = b/(M_i)^{1/2}$, $i=1,2$, where b is the proportionality constant related to the force constant. In this case, the mean square displacement is found to be

$$\langle u_0^2\rangle_i \propto \left[\frac{1}{2} + \frac{1}{\exp\,(h\nu_i/kT)-1}\right]\cdot\,i=1,2 \tag{2}$$