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Molecular dipole moments in the liquid phase: an assessment introducing the far infra-red dispersion

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Abstract—Apparent dipole moments are calculated using liquid phase microwave and far infra-red absorption data for molecules of different geometry. For the same set of data, it is found that the alternative representations: $\alpha(\bar{\nu})$ vs. $\bar{\nu}$; and $\varepsilon''(\bar{\nu})$ vs. $\bar{\nu}$ yield dipoles μ_z and μ_{ons}, respectively, which differ significantly. The quantities $(\mu_z - \mu_{ons})$ are listed and interpreted in terms of induced dipolar absorption in the range corresponding to $(\varepsilon_\infty - n_{ir}{}^2)$ of the overall dispersion $(\varepsilon_0 - n_{ir}{}^2)$.

INTRODUCTION

RECENT studies have shown that all polar molecules in the liquid or solution phases have an absorption in the far-infrared principally due to the librational-type motions of molecules in their instantaneous local cages [1–6]. This Poley absorption is the high frequency addendum to the Debye microwave dispersion. The latter is regarded as complete at a permittivity ε_∞ which is usually adequately defined by experimental microwave data, and is often equivalent to ε at $\bar{\nu} = 10$ cm^{-1} ($\lambda = 1$ mm). However, the Poley absorption often extends beyond $\bar{\nu} = 100$ cm^{-1}, and the further dispersion it represents $(\varepsilon_\infty - n_{ir}{}^2)$, where n_{ir} is the refractive index at its high frequency termination, must be included if the total dipole is to be measured.

This paper is concerned with the difference in μ values [7] arising from replacement of $(\varepsilon_0 - \varepsilon_\infty)$ by $(\varepsilon_0 - n_{ir}{}^2)$. It also discusses the uncertainties in alternative methods of evaluation, not so much due to numerical aspects as due to the different emphasis they impose and to the inclusion of induced moment contributions in some values. Whilst it has long been realised [8] that condensed phase measurements could directly give only an "effective molecular electric moment," $\mu_{eff} = (\bar{\mu}\mu_0) = (g\mu^2)^{1/2}$, it now seems probable that alternative values of μ_{eff} must be considered.

RESULTS

The dipole moments shown in Table 1 were calculated by two methods which give different emphases to the role of induced dipoles in the total dispersion

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$(\varepsilon_0 - n_{ir}^2)$. The first method is numerical integration of the Kramers Kronig relation:

$$A_2 = \int_{\text{band}} \varepsilon'' \, d(\log_e \tilde{\nu}) = \frac{\pi}{2}(\varepsilon_0 - n_{ir}^2) \quad (1)$$

Table 1. Comparison of dipole moments from microwave and far-infrared data

Liquid	ε_0	n_{ir}^2 (at ν = 100 cm^{-1})	$\varepsilon_\infty - n_{ir}^2$ experimental	ε_∞	$\varepsilon_0 - n_{ir}^2$ (Fig. 1)	$10^{30}\mu_{ons}$ (cm)	10^{20} xA_1/N (cm)*	A_2 (Fig. 1)	$10^{30}\mu_z$ (cm)	$10^{30}x$ $(\mu_z - \mu_{ons})$ (cm)*	$10^{30}x$ μ_{gas} (cm)*
1,1,1-Trichloroethane	7·11 [25]				4·65	6·17	24·1 [25]	7·3	6·34	0·17	5·94
t-Butyl chloride	9·87 [25]				11·5 (29]	7·84	54 [25]	18·1	7·87	0·03	7·10
2,2-Dichloro propane	11·5 [26]			2·3 [26]	9·49	7·74	44·5 [2]	14·9	7·61	−0.10	7·57
2-Chloro-2-nitro-propane	24·0 [26]			3·0 [26]		12·44	100 [2]		12·38	−0·07	
Chloroform	4·806 [27]			2·22 [8]		4·00	15·4 [25]		4·30	0·30	3·37
Chlorobenzene	5·60 [27]	2·22 [27]	0·23	2·55 [27]	3·37	5·00	14·1 [25]	5·30	6·30	1·30	5·64
Bromobenzene	5·39 [28]					4·34	8·6 [25]		6·94	2·54	5·67
Iodobenzene	4·64 [28]					3·60	4·9 [25]		6·90	3·30	5·67
o-Difluorobenzene						8·01	35·8 [30]		9·04	1·03	
o-Dichlorobenzene						7·54	22·3 [30]		8·91	1·37	8·34
o-Dibromobenzene						7·14	16·8 [30]		9·57	2·44	
m-Difluorobenzene						5·27	28·3 [30]		5·94	0·67	5·27
m-Dichlorobenzene						4·97	15·5 [30]		5·84	0·87	5·74
m-Dibromobenzene						5·20	12·2 [30]		6·24	1·03	
Toluene	2·3837 [27]	2·211 [27]	0·056	2·2670 [27]		1·28	9·1		3·17	1·90	1·20
Benzonitrile	25·57 [27]	2·27 [27]	1·48	3·85 [27]	25·2	12·14	107 [25]	39·6	16·34	4·54	13·94
SO_2/cyclohexane						5·37	316 [25]		6·04	0·67	5·44
Bromoethane	9·20 [28]					6·10	43 [25]		7·61	1·50	6·77

* $x = 9n_{i\cdot}/(n_{ir}^2 + 2)^2$. Temperature = 296°K except where stated.

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which weights the lower frequency region of the dispersion ($\varepsilon_0 - \varepsilon_\infty$), and reduces the contribution of the higher frequency region ($\varepsilon_\infty - n_{ir}^2$) to negligible proportions (Fig. 1). A particular theory of the internal field is then assumed, i.e, the Onsager [8] equation from which a value of the dipole, μ_{ons} can be derived. It is interesting to note that eqn. (1) yields a value of the far-i.r. refractive index [9] when ε_0 is known; and with accurate ε'' vs. $\tilde{\nu}$ data, this value of n_{ir} could be compared with the experimental, derived from interferometric techniques [10].

In the five cases where actual numerical integration of (1) was carried out using experimental microwave and far-i.r. data, the $\alpha(\tilde{\nu})$ values of the far-i.r. were transformed into the corresponding $\varepsilon''(\tilde{\nu})$ using, where possible, literature values

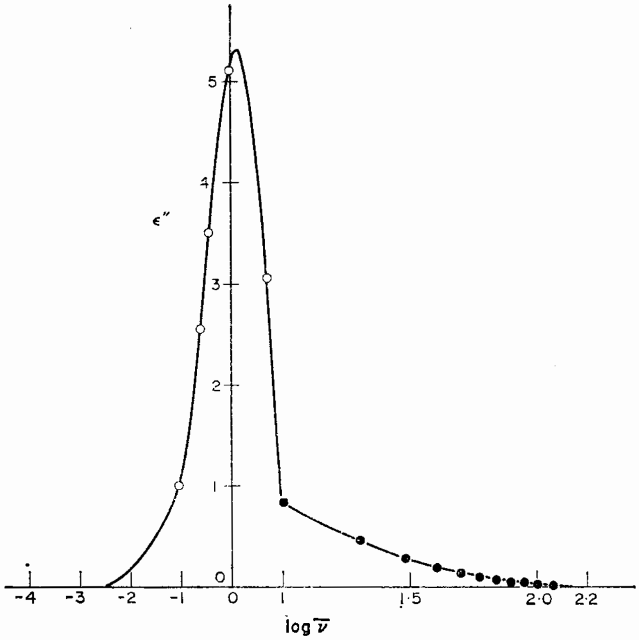

Fig. 1. (a) Loss curve for *t*-butyl chloride at 274°K.
⊙ Microwave points [29].
● Far-infrared points [31].
(b) Loss curve for 1,1,1-trichloroethane at 293°K.
⊙ Microwave points [28].
● Far-infrared points [25].
(c) Loss curve for benzonitrile at 293°K.
⊙ Microwave points [28].
● Far-infrared points [25].
(d) Loss curve for 2,2-dichloropropane at 296°K.
⊙ Microwave points [26].
● Far-infrared points [2].
(e) Loss curve for chlorobenzene at 297°K.
⊙ Microwave data [27, 28].
● Far-infrared data [25, 26].

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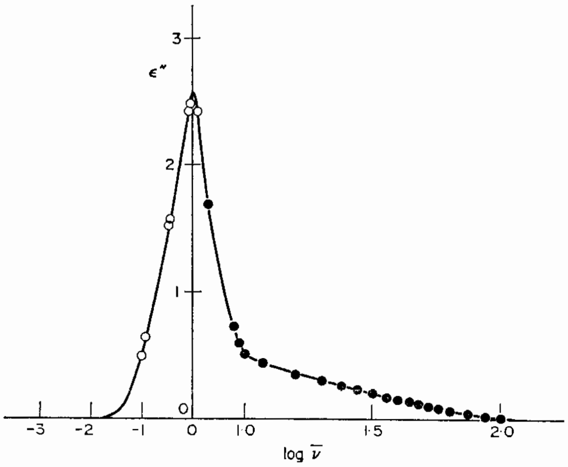
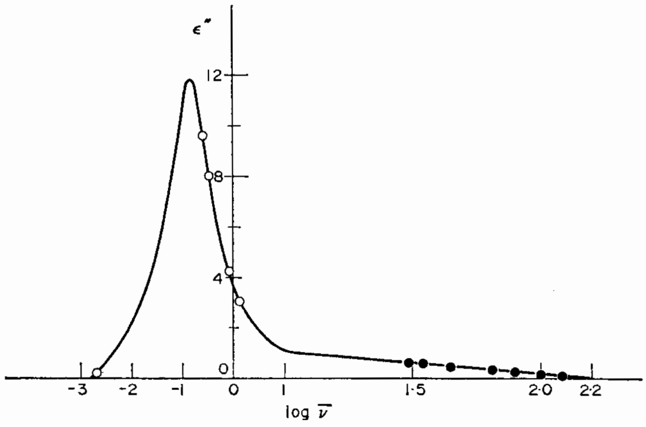
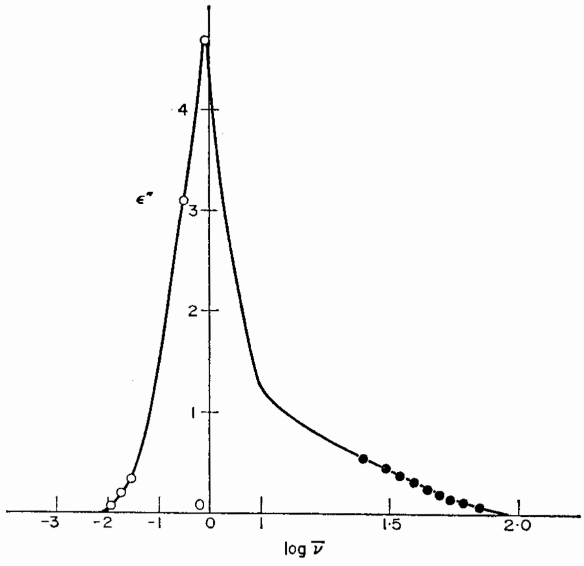

ε″
3
2
1
0
-3
-2
-1
0
1·0
1·5
2·0
log $\bar{\nu}$

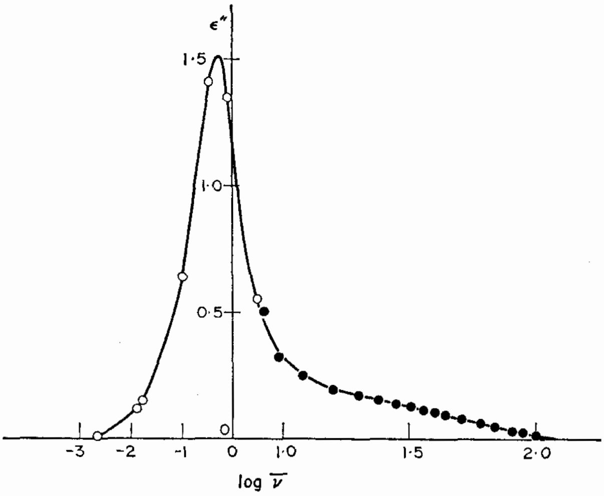
(1b)


ε″
12
8
4
0
-3
-2
-1
0
1
1·5
2·0
2·2
log $\bar{\nu}$

(1c)


4
ε″
3
2
1
0
-3
-2
-1
0
1
1·5
2·0
log $\bar{\nu}$

(1d)



(1e)

of $n(\bar{\nu})$, the refractive index in the 2–200 cm^{-1} region. That this method yields an acceptable dispersion amplitude $(\varepsilon_0 - n_{ir}^2)$ can be checked with the experimentally known ε_0 and n_{ir}^2 for chlorobenzene, for example, to give: $(\varepsilon_0 - n_{ir}^2)$ (Kramers–Kronig) $= 3{\cdot}3(7) \pm 0{\cdot}17$; and $(\varepsilon_0 - n_{ir}^2)$ (exptl.) $= 3{\cdot}38$. The experimental uncertainties ($\pm$ 5%) here and in other parameters of Table 1 are due to those of the numerical integrations in (1), and (2) below. These are derived from actual experimental uncertainties in $\varepsilon''(\bar{\nu})$ and, in particular, $\alpha(\bar{\nu})$.

Secondly, an *effective* dipole moment (μ_z) can be calculated (eqn. (2)) using Gordon's sum rule [11], which applies to the total anticipated rotational modes of a molecule, including both the Debye [12] cooperative process and higher frequency ones [13] which can be detected in the region 2–200 cm^{-1}. The intensity of the far-i.r. band in liquids predicted by using μ_{ons} would be less than that observed [14, 15], since the rule takes no account of the absorption of the induced dipoles. For uncharged free molecules i.e., in gaseous state, the sum rule reduces to:

$$A_1 = \frac{9n_{ir}}{(n_{ir}^2 + 2)^2} \cdot \left(\int_{\text{band}} \frac{\alpha(\bar{\nu})}{N} \, \mathrm{d}\bar{\nu} \right)_{\text{exp}}$$
$$= \frac{\pi}{3_c^2} \cdot \left(\frac{1}{\mathrm{I}_x} + \frac{1}{\mathrm{I}_y} \right) \cdot \mu_z^2 \qquad (2)$$

where I_x and I_y are the moments of inertia mutually perpendicular to μ_z in the molecular frame, N the molecular number density, and the factor $9n_{ir}/(n_{ir}^2 + 2)^2$ is the Polo-Wilson correction [16] for the internal field effects in liquids. The integral is over the total experimental bandwidth (microwave, $(\varepsilon_0 - \varepsilon_\infty)$, and far-i.r. $(\varepsilon_\infty - n_{ir}^2)$ as in eqn. (1).

The differences $(\mu_z - \mu_{ons})$ shown in Table 1 vary markedly with molecules of different geometries. It cannot be suggested that either of these values of μ is of precise physical significance, but they are determined within the limits shown by their respective methods of evaluation. Accordingly, their differences provide measures of interest: (i) they may be taken as an indication of the role of induced dipoles within the region $(\varepsilon_\infty - n_{ir}^2)$; (ii) as an indication of the disparity of using the alternate representations $\varepsilon''(\bar{\nu})$ vs. $\bar{\nu}$ and $\alpha(\bar{\nu})$ vs $\bar{\nu}$ of the total absorption.

DISCUSSION

In Gordon's extension of the Thomas–Reiche–Kuhn sum rules, the evaluation is that for a system of rigid, free molecules; its use for liquids, where intermolecular effects are important, is unsatisfactory, but useful in the absence of a more complete treatment. Thus μ_z from eqn. (2) would be different from the value (μ_{gas}) found using the experimental pure rotational envelope, but the point is that the values found from the relations (1) and (2) for *the same set of liquid data* are different, even after some approximate account of the internal field effect has been taken in each case (i.e., the Onsager field in eqn. (1). and the Polo–Wilson correction in eqn. (2)).

The Onsager model used with (1) is valid only for liquids in which there are no strong local forces, and the derived moment is not quantitatively equivalent to that including absorption by dipoles induced [17–19] in a central molecule by the sometimes [13, 18] highly anisotropic quadrupolar and dipolar fields of neighbouring molecules. This is reflected clearly in the table for benzonitrile, where, even using the amplitude $(\varepsilon_0 - n_{ir}^2)$ in the Onsager equation, the resulting dipole (μ_{ons}) is less than the measured gaseous value, whereas μ_z is greater than both. The low value of μ_{ons} can be explained partly by the fact that $\mu^2/r^3 \approx kT$, i.e., dipole–dipole interaction leading to distinct non-randomisation of molecular dipoles. This (statistical) coupling of dipoles in a general anti-parallel fashion is established very clearly by Piekara's [20] "Nitrobenzene" case, which benzonitrile copies, where an applied high field decouples the dipoles and increases ε_0. However, the large difference between μ_z and the upper limit of μ_{ons}, i.e., μ_{gas}, remains.

The optical parameter $\alpha(\bar{\nu})$ is related to $\varepsilon''(\bar{\nu})$ by:

$$\alpha(\bar{\nu}) = 2\pi\nu\varepsilon''(\bar{\nu})/n(\bar{\nu}) \tag{3}$$

thus the amplitude $(\varepsilon_\infty - n_{ir}^2)$ becomes dominant in the $\alpha(\bar{\nu})$ vs $\bar{\nu}$ spectrum because $\alpha(\bar{\nu}) \propto \varepsilon''(\bar{\nu})\bar{\nu}$. However, if the loss factor $\varepsilon''(\bar{\nu})$ is used alone, the much larger dispersion amplitude of the Debye relaxation, relative to that of the higher frequency process, causes the former to predominate in the $\varepsilon''(\bar{\nu})$ vs $\bar{\nu}$ curves (Fig. 1). The part of the dispersion $(\varepsilon_\infty - n_{ir}^2)$, due to induced dipoles, plays a negligibly small part in the integration of eqn. (1). The eqn. (2), however, *accentuates* this very part of the process, leaving a negligible contribution from the cooperative relaxation process of the permanent dipole. Therefore, the one integral (1) suppresses the induced dipolar absorption intensity, the other accentuates its effect, while both describe the *same* general process of dipolar dispersion in the total range ε_0 to n_{ir}^2.

The evaluation of induced dipoles is well documented [14, 15, 17–19] and a recognisable pattern has emerged that the excess absorption over the Gordon prediction in a given liquid is smaller than in the equivalent compressed gas. An apparently smaller value of the calculated quadrupole moment is found from the liquid state absorptions. This result is interpreted [15, 17, 18] as a "cancellation" of the quadrupolar and dipolar field, of symmetrically arranged nearest neighbours which induce the dipole in a central molecule. However, there always remains [21] an average resultant induced dipole: this arises from the asymmetry of the near neighbour molecular fields leading to their non-cancellation which gives the excess value seen in μ_z of the table. The "rotator phase" molecules–1,1,1-trichloroethane, *t*-butyl chloride, 2,2-dichloropropane, and 2-chloro-2-nitro propane present a specially interesting case [26]. It is well established that in these instances $\varepsilon_\infty \approx n_D^2$, i.e. there is only very small dispersion through the i.r. and the Poley absorption is distinctly weak. The approach to spherical geometry in these cases suggests that they should conform to the Onsager model and give $\mu_{ons} \approx \mu_{gas}$, but this condition will be disturbed by dipole–dipole interactions and also by the induced dipoles which must arise in these cases. As the results for the other molecules show, the more asymmetric the molecule, the greater the difference between μ_z and μ_{ons}. This, of course, could be attributed in part to the dipole–dipole interaction seen in the "nitrobenzene effect" of Piekara; however, in these anisotropic molecules the potential barrier to libration [3, 22–25] within a given energy well becomes distinctly higher, with stronger local dipole-inducing fields

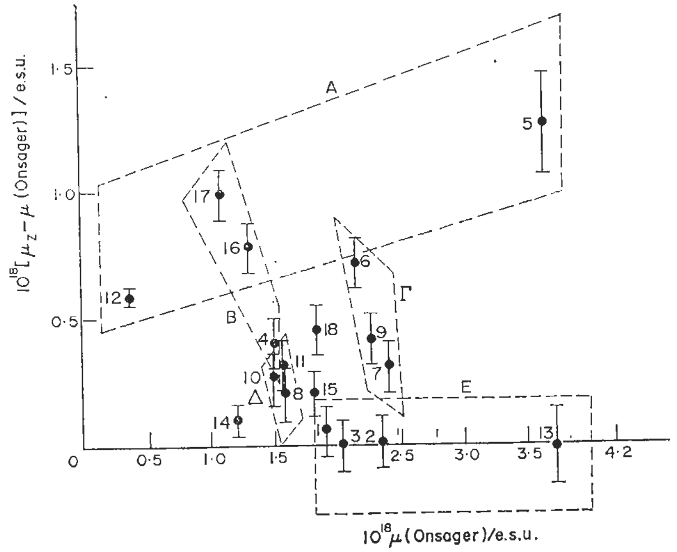


Fig. 2. Graph of $\mu_z - \mu_{onsager}$ vs. $\mu_{onsager}$ for the following moleculares: (1) 1,1,1-trichloroethane; (2) *t*-butyl chloride; (3) 2,2-dichloropropane; (4) chlorobenzene; (5) benzonitrile; (6) σ-dibromobenzene; (7) σ-difluorobenzene; (8) *m*-difluorobenzene; (9) σ-dichlorobenzene; (10) *m*-dichlorobenzene; (11) *m*-dibromobenzene; (12) toluene; (13) 2-chloro, 2-nitropropane; (14) chloroform; (15) SO_2(l) in cyclohexane; (16) bromobenzene; (17) iodobenzene; (18) bromoethane.

A	Some more substituted benzenes.
B	The monochlobenzenes.
Γ	The *o*-dihalobenzenes.
Δ	the *m*-dihalobenzenes.
E	Some rotator-phase forming molecules of pseudo-spherical symmetry.

Accordingly, as the anisotropy and magnitude of these fields increase, so must the Onsager picture become less valid.

Some pattern emerges from a plot of $(\mu_z - \mu_{ons})$ against μ_{ons} (Fig. 2). It can be seen that $(\mu_z - \mu_{ons})$ increases particularly in the monochalogeno- and dihalogeno-benzenes as the subsituents are changed from fluoro- to iodo-; a probable consequence of the increasing dimensions and perhaps quadrupole moments in these anisotropic molecules.

It is perhaps not surprising that no simple relations are shown in Fig. 2, as the discussion above has emphasized that various features contributing to the difference reflect the specific characters of the molecules involved. Thus each case has to be separately analysed. Some blocks of "related" molecules are drawn in the figure.

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