

# Interpretation of the Microwave and Far Infra-red absorption of some Dipolar Liquids in Terms of Librational and Relaxational Motion

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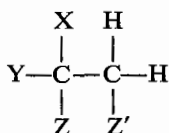
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The microwave and far infra-red spectra of 1,2-dibromo-1,1-dichloroethane; 1,2-dibromo-2-methylpropane; 1-iodo-2-methylpropane; and 1-iodo-3-methylbutane obtained recently by Moisan are discussed in terms of two models of librational and relaxational modes of absorption in dipolar liquids. An acceptable fit to the observed data is obtained on the assumption of a hexagonal symmetry for the planar disposition of the potential wells. The barrier heights to libration suggested by this phenomenological approach are, as expected, greater than results for molecules of enhanced symmetry which form rotator phases.

The models for librational and relaxation absorption by dipolar molecules in the far infra-red ( $2\text{--}200\text{ cm}^{-1}$ ) and microwave region developed by Brot<sup>1, 2</sup> and by Wyllie,<sup>3</sup> and applied to rotator phase molecules by Haffmans and Larkin<sup>4a</sup> and to a liquid crystal molecule by Evans *et al.*<sup>4b</sup> are here applied to some molecules of lower symmetry in the liquid phase. To these molecules can be assigned the general formula given in table 1, where X, Y, Z and Z' are simple substituents such as Cl, Br, CH<sub>3</sub>, I and H. These liquids have been studied in the microwave and far infra-red regions by Moisan,<sup>5</sup> and all experimental data in this paper are from this source. The four molecules to which the models are applied here are listed in table 1.

TABLE 1.—STRUCTURE OF THE MOLECULES STUDIED



X = Y = Cl, Z = Z' = Br	1,2-dibromo-1,1-dichloroethane
X = Y = CH <sub>3</sub> , Z = Z' = Br	1,2-dibromo-2-methylpropane
X = Y = CH <sub>3</sub> , Z = H, Z' = I	1-iodo-2-methylpropane
X = Y = H, Z = -CH(CH <sub>3</sub> ) <sub>2</sub> , Z' = I	1-iodo-3-methylbutane

The purpose of this application is to investigate the extent to which simple models account for the absorptions in the microwave (Debye cooperative relaxation) and the far infra-red (Poley absorption) regions for dipolar molecules of lower symmetry than the rotator phase forming pseudo-spherical molecules with which the models were developed.

Some details<sup>4</sup> of the mathematics of the two models have been published. The parameters of both models shown in table 2 are of the same notative form as those in

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TABLE 2.—BROT AND WYLLIE PARAMETERS OBTAINED AT 295 K

liquid	$\bar{\nu}$ max(obs.)/ cm <sup>-1</sup>	$\bar{\nu}$ max(calc.)/ cm <sup>-1</sup>	$\tau_D$ /ps	$\tau_r$ /ps	barrier height, $V$ kJ mol <sup>-1</sup>	$\xi$ /rad	$10^{10} J$ / g cm <sup>2</sup>	$\alpha$ (calc.)/ $\alpha$ (obs.)	$\tau_f$ /ps	well narrowing factor	Polo Wilson factor
1,2-dibromo-1,1-dichloroethane (Brot model)	30	30	26.5	49	9.9	0.52	1500 ± 500 ref. (5)	0.44	0.9	0.85	0.715
1,2-dibromo-1,1-dichloroethane (Wyllie model)	30	30	26.5	49	10.3	0.52	1500 ± 500 ref. (5)	0.44	—	0.85	0.715
1,2-dibromo-2-methylpropane (Brot model)	40	40	~20	64	11.9	0.52	1200 ± 400 ref. (5)	0.45	0.5	0.76	0.742
1,2-dibromo-2-methylpropane (Wyllie model)	40	40	~20	55	11.6	0.52	1200 ± 400 ref. (5)	0.42	—	0.76	0.742
1-iodo-2-methylpropane (Brot model)	35	35	14.5	34.0	9.8	0.52	800 ± 200 ref. (5)	0.43	0.6	1.00	—
1-iodo-2-methylpropane (Wyllie model)	35	35	14.5	30.0	9.8	0.52	800 ± 200 ref. (5)	0.42	—	1.00	—
1-iodo-3-methylbutane (Brot model)	45	45	29	59	10.7	0.52	1200 ± 100 ref. (5)	0.21	0.8	0.65	0.751
1-iodo-3-methylbutane (Wyllie model)	45	45	29	58	10.8	0.52	1200 ± 100 ref. (5)	0.21	—	0.65	0.751

ref. (4) and include parameters such as the barrier height to libration ( $V$ ), and the time of residence in a well ( $\tau_r$ ) which are suggested by the phenomenological curve fitting procedure used here. The barrier heights  $V$  may be compared with those obtained for the rotator phase molecules and the degree of success in the curve fitting may be judged from the agreement between the experimentally observed and the predicted parameters, such as the frequency of maximum absorption in the far infra-red ( $\bar{\nu}_{\max}$  (in  $\text{cm}^{-1}$ )) and the Debye relaxation time  $\tau_D$  (which is of the order  $\tau_r$ ).

Sometimes, a better fit to the experimental data can be obtained with narrower wells and broader barriers than those predicted by the very simple arbitrary  $U(\theta) = f(\sin^2 \theta)$  form of the wells which was assumed initially. The broadening of barriers between wells is achieved in practice by including a well narrowing factor (table 2) by which the half angular aperture  $^4$  ( $\xi$ ) is multiplied. This factor has a large effect on  $\tau_r$  because of the exponential dependence on the barrier height  $V$ .

The quality of fit achieved with the Larkin modification of the Wyllie model is further judged by the agreement between the observed and calculated  $\bar{\nu}_{\max}$ ; and  $\tau_D$  which in this model is related to the damping coefficient  $^4$   $\zeta$ .

Since the "lattice structure" of the present liquids is not known, an estimate of the aperture angle  $\xi$  is made from a reasonable value of  $Z$ , the number of nearest neighbours that a molecule is likely to have, albeit temporarily, in the liquid. In this work,  $Z$  has been fixed arbitrarily at eight, which gives an upper limit estimate  $^4$  of  $30^\circ$  for  $\xi$ . Trial values of the barrier height  $V$ , and the damping coefficient  $\zeta$  were then used in the calculations, these values being then adjusted to give the best agreement with experimental data.

Using two models derived from very different sources provides a valuable check on the physical significance of the results obtained, and the acceptable magnitude and the agreement in the barrier height  $V$ , for instance, obtained from each model instils confidence that these are meaningful parameters obtained by comparison of experimental and theoretical absorption profiles. The small values of  $V$  obtained here (compared with, for example, the results of the calculations of Rae and Mason  $^6$  on repulsive energies between molecules in the crystal lattice of benzene, where the rotation of an individual molecule is strongly hindered by the proximity of its neighbours) are a reflection of the smaller intermolecular forces in a liquid, and also of the *relative* translational movement of liquid state molecules, which is absent in the solid.

## RESULTS AND DISCUSSION

The experimental data and the best fits obtained from the two models are illustrated in fig. 1, and the values of the parameters discussed above are presented in table 2.

The theoretical curves are all normalised to the observed absorption maximum, and the calculated integrated intensities across the whole band (microwave and far infra-red) are less than the experimentally observed values by the factors  $\alpha(\text{calc.})/\alpha(\text{obs.})$  shown in table 2. A more realistic model would include a distribution of well shapes and depths, and this, together with the limiting uncertainties in the values of the moments of inertia used in the calculation, should be borne in mind when discussing this disagreement. Since Brot's original correlation function obeys Gordon's sum rule  $^{10}$  when Fourier transformed, then the experimental excess could plausibly be due to mechanisms of absorption other than those of the permanent dipole.

Despite the fact that the parameters  $\tau_r$  and  $\zeta$  are usually selected as a compromise to give the best fitting over the complete frequency spectrum (microwave and f.i.r.), the agreement between experiment and theory is good in the microwave region. In

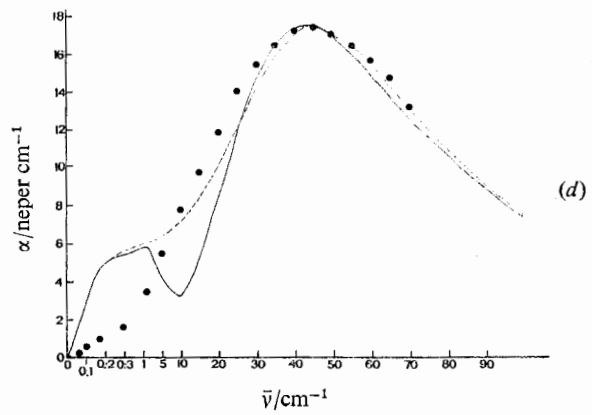
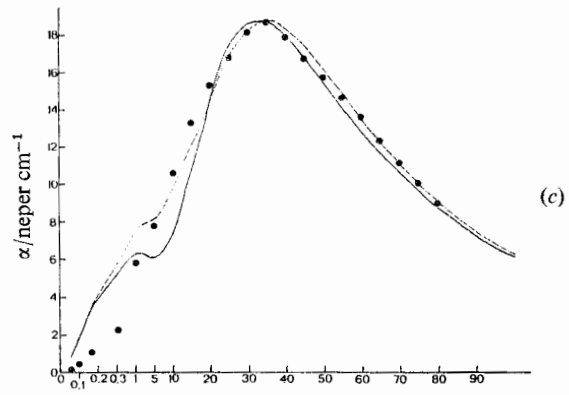
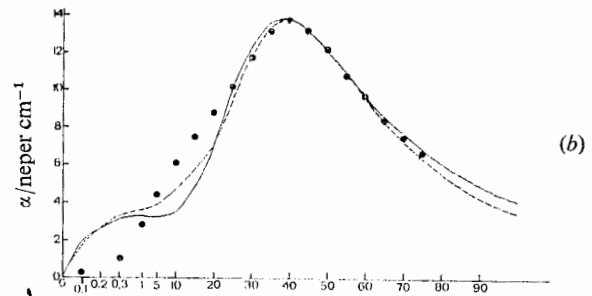
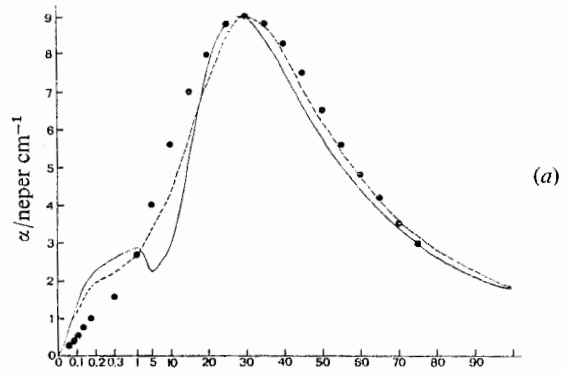


fig. 1 the normalisation makes the calculated microwave  $\alpha$  values look too large, whereas it is the far infra-red  $\alpha(\bar{\nu})$  calculated values which are too low.

However, it is also possible that an induced dipole moment (which causes non dipolar liquids<sup>8, 9</sup> to absorb in the f.i.r. region with a dispersion amplitude  $(\epsilon_\infty - n_{ir}^2)$  may be responsible for some absorption over and above that due to libration of the permanent dipole in the region  $\epsilon_\infty - n_{ir}^2$  combined with the latter dipole's cooperative relaxation with the amplitude  $\epsilon_0 - \epsilon_\infty$ . The amplitude  $\epsilon_\infty - n_{ir}^2$  (with which the region 5-150  $\text{cm}^{-1}$  is associated) is small compared to  $\epsilon_0 - \epsilon_\infty$ , but is emphasised in a plot of  $\alpha(\bar{\nu})$  against  $\bar{\nu}$  because of the Maxwell relation:  $\alpha(\bar{\nu}) = 2\pi\epsilon''(\bar{\nu})\bar{\nu}/n(\bar{\nu})$ . From Gordon's sum rules,<sup>10</sup> which apply to the total anticipated rotational modes (Debye and higher frequency absorptions) of a molecule, (strictly in the gaseous state), then the total integrated intensity  $\int_{\text{band}} \alpha(\bar{\nu}) d\bar{\nu}$  is proportional to the square of the permanent dipole ( $\mu_{\text{gas}}$ ), so that the anticipated total integrated intensities of both models are related to  $\mu_{\text{gas}}$  by:

$$\left( \int_{\text{band}} \alpha(\bar{\nu}) d\bar{\nu} \right)_{\text{theoretical}} = \frac{\pi}{3c^2} \left( \frac{1}{I_x} + \frac{1}{I_y} \right) \mu_{\text{gas}}^2 \quad (1)$$

Using the experimental value of the left hand side of (1) (which is nearly equal to the normalised value of the models) would yield a dipole moment  $\mu_{\text{eff}}^2$  which would give an idea of the magnitude of the induced dipole when all the excess absorption is attributed to this cause. On this simple assumption,  $\mu_{\text{eff}}/\mu_{\text{gas}} = (\alpha(\text{obs.})/\alpha(\text{calc.}))^{1/2}$  and  $\mu_{\text{eff}}/\mu_{\text{gas}}$  can be estimated from table 2. Doubtless this ratio is too big because of other causes for the excess (for example, the Polo/Wilson correction for the internal field (table 2) would reduce the experimental absorption appreciably) but demonstrates that the seemingly large intensity discrepancy can be explained by an acceptable value of an induced dipole.

Powles *et al.*<sup>7</sup> have suggested that group substitution in "spherical" molecules involving increased dipole moment and/or decreased symmetry would result in increased potential barrier heights, which suggestion is borne out by comparison of the barrier heights for molecules studied here with those<sup>4</sup> for the pseudo-spherical rotator phase molecules. Therefore, insofar as the two models yield results in agreement with such a predicted trend, it may be suggested that they give a valid, if simplified, description of the complex dynamics of the liquid state. It is envisaged that asymmetry in an individual molecule would result in a greater distribution of barrier heights, resulting from the greater asymmetry of the transient "cage" in the liquid. Therefore it must be emphasized that the values of  $V$  presented in table 2 should be regarded as statistical means of the distribution envisaged in reality due to the difference in structure of each potential well.

Calculations carried out with a coordination number of greater than eight gave the result for  $\tau$ , (the time of residence in a potential well) of orders of magnitude greater than the observed  $\tau_D$ . To improve the models, incorporation of a statistical distribution of barrier heights and shapes; and of the number of nearest neighbours would be a desirable, if complicated modification.

FIG. 1.—● Some experimental data taken from ref. (5) for the microwave and far infra-red absorptions of (a) 1,2-dibromo-1,1-dichloroethane, (b) 1,2-dibromo-2-methylpropane, (c) 1-iodo-2-methylpropane and (d) 1-iodo-3-methylbutane at 295 K. —, Theoretical curve predicted by the Brot model with the parameters shown in table 2. This curve is normalised to the maximum of the experimental values. ---, Theoretical curve predicted by the Wyllie model with the parameters shown in table 2. This curve is normalised to the maximum of the experimental values.

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