

Zero-THz spectroscopy of rotator phases

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The molecular dynamical evolution from hertzian frequencies to the far infrared (THz) is reported for various kinds of rotator phase environment. The zero to THz frequency spectral profiles are analysed in terms of itinerant libration and developments on this theme. The systems analysed are (i) the plastic rotator phase of *t*-butyl chloride and solid solutions of this solute in tetramethylsilane; (ii) these results are compared with those from a spectral study in the range up to THz frequencies of *t*-butyl chloride in vitreous decalin solvent; (iii) single crystalline pentachloronitrobenzene and a pressed disc thereof. This solid is representative of a class of rotator phases where orientational disorder is gradually frozen in at low temperatures, unlike the plastic rotators; (iv) solid solutions of dipolar solute molecules in non-dipolar rotator phase benzene and tetramethylsilane. This is an attempt at evaluating the electro-dynamics of dipole-dipole interaction.

The data over the complete range of frequency is rationalized in terms of the itinerant libration mean square torque and theoretical evaluations of the observable sub-THz Debye relaxation times. This is the first attempt at modelling the molecular dynamics of the various kinds of rotator phases over the complete range of frequency at which the kinematics and electro-dynamics of the constituent molecules are observable, either as the complex dielectric permittivity or the optical power absorption coefficient. This methodology is named zero-THz spectroscopy. Used properly, it is one of the most incisive methods available for studies of molecular dynamics.

1. INTRODUCTION

The aim of this paper is to investigate by zero-THz spectroscopy [1-3] the electro-dynamics and kinematics of molecules in the rotator phase and rotator phase solid solutions. A rotator phase may be defined as a solid with a low entropy (and enthalpy) of fusion and, if polar, a high static permittivity. The former is an indication that such a solid is disordered (as in the liquid phase), although X-ray observations [4] of well defined but simple lattice symmetries (e.g. face-centred cubic) indicate the disorder to be in respect of molecular orientation rather than of lattice sites. The reverse is usually the case in liquid crystals. The high permittivity ϵ' indicates this disorder to be dynamic. The molecules undergo liquid state rotation but with little translational diffusion. Rotation is observable with dielectric spectroscopy where loss curves (generally broader than Debye) are measurable [5], and also with the use of N.M.R. relaxation [6] and neutron quasi elastic scattering [7]. If a model of activated jumping [8] is accepted (site model) then the activation energy remains almost constant through the phase transition into the liquid. At lower temperatures

there is a transition into the ordered and rigid solid. This is not, however, true of the hexasubstituted benzenes, which exemplify a class of rotator phase where in some cases disorder gradually becomes frozen in; this is not always the case, however. These solids melt at over 600 K, are brittle, and have large activation enthalpies of about 50 kJ mol^{-1} compared with the plastic rotator phases exemplified in this paper by *t*-butyl chloride and tetramethylsilane.

In a detailed paper by Brot and Darmon [9] a semi-stochastic Monte-Carlo simulation of the disordered phases of the hexasubstituted benzenes was carried out to explain the results of sub-THz spectral data. The progressive orientational decorrelation in the well defined system trichlorotrimethylbenzene (TCTMB) and 1,2-dichloro,3,4,5,6-tetramethylbenzene (DCTMB) was investigated as the temperature was increased towards ambient. In these strongly dipolar solids the molecules show a single axis six-fold disorder at higher temperatures. The permittivity decreases on cooling, indicating the development of orientational order, i.e. of significant cross correlation in the complete orientational correlation function. The energy which governs the ordering is essentially electrodynamic and antiferroelectric. Using a Coulomb distribution of charges to represent the intermolecular potential, Brot and Darmon reproduced quite accurately the temperature dependence of the complex permittivity. The rotational freedom remaining to these molecules in the solid state is temperature dependent via higher order thermodynamic transitions, which means there is a progressive evolution of cooperative effects. The system is therefore well adapted for the study of dipole cross-correlations. The orientational freedom is due to the fact that the molecules are sterically very symmetrical. At 300 K each chlorine or methyl group is distributed with equal probability among six substituent sites. However as the temperature is decreased an ordered superstructure sets in gradually and reversibly. The molecular centres and orientation of the aromatic planes remain the same as in the structure at 300 K but the dipoles become antiparallel along the crystal axes *b* and *c* and parallel along *a* (i.e. antiferroelectric). The superstructure appears as domains with non-corresponding families of molecules. There is no fundamental change of structure as appears in plastic crystals where first-order thermodynamic transitions are observable. In the disc-like benzene derivatives the molecules occupy only orientations corresponding to their own steric symmetry, the volume of each substituent group is very nearly the same, and no volume increase with respect to the ordered phase occurs when replacing a chlorine by a methyl and vice versa. Eliminating the volume change eliminates the discontinuity in the cohesive (or attractive) energy associated with a first order thermodynamic transition. The van der Waals forces impose several almost equivalent potential wells (as in sterically symmetric molecules), and as a consequence the electrostatic part of the overall potential energy becomes important and governs the orientational transition processes.

Although molecular symmetry (and the absence of strong intermolecular forces such as hydrogen-bonds) must be a major factor in allowing the existence of rotator phases, no general theory for the prediction of such phases is available. One useful criterion for prediction is based on measurements on solids of known structure to estimate the degree of interlocking of molecules. When this is small the solid (at that temperature) may be a rotator phase, as discussed by Brot and Darmon. In approaching the problem dynamically, we must attempt to model

the rotational behaviour and particularly its short time details. Such detail is clearly observable in the far infrared, and in this paper we are concerned with using these data to supplement the sub-THz dielectric measurements and to form the complete zero-THz profile.

The planar and plastic types of rotator phase are investigated using solid solutions in non-dipolar rotator phases such as that of benzene and tetramethylsilane to vary the effect of dipole-dipole interaction and its associated electro-dynamics. The planar rotator phase is an ideal testing ground for the itinerant librator model of the molecular dynamics [10], and we shall be concerned with rationalizing the spectral data in terms of factors such as volume of rotation and mean square torque which have been shown to be useful in previous studies of a large number of liquid phase systems. Given the mechanism of planar itinerant libration, Reid [11-13] has shown how a large amount of spectral data can be correlated in terms of the effective volume of rotation. Reid's equations are used in this paper with the following solids and solid solutions.

- (i) rotator (plastic) *t*-butyl chloride;
- (ii) solid solutions of *t*-butyl chloride in rotator phase tetramethylsilane;
- (iii) a glassy solution of *t*-butyl chloride in decalin at 110 K;
- (iv) a single crystal of pentachloronitrobenzene;
- (v) 10 per cent *v/v* solid solutions of fluorobenzene, pyridine, tetrahydrofuran, bromobenzene, and dichloromethane in rotator phase benzene (to minimize the effect of dipole-dipole electro-dynamics);
- (vi) a repetition of (v) in plastic phase solid tetramethylsilane.

2. EXPERIMENTAL DETAILS

An N.P.L./Grubb-Parsons Cube interferometer was used in the frequency range $10\text{--}250 \text{ cm}^{-1}$. Considerable manipulative skill was required to optimize ordinate accuracy (power absorption coefficient, $\alpha(\nu)$); this is estimated to within ± 5 per cent. The cell designs are described fully elsewhere [11, 12]. PCNB was measured both as a pressed disc and as a single crystal. Solution spectra in the liquid phase were taken with a R.I.C. VC-01 variable pathlength cell, with poly(4-methyl-pent-1-ene) windows, occasionally replaced by quartz, silica, high density poly(ethylene) and other polymer material in the search for ordinate optimization.

Benzene possesses [6] a rotator phase from its melting point (298 K) to below 77 K. If solid solutions of similarly shaped molecules in benzene could be formed, then we expect and find that these guests would rotate and contribute a dielectric loss at audio frequencies as well as a librational process in the far infrared. *The complete loss process from kHz to THz must be taken in its entirety for model analysis.*

10 per cent *v/v* solutions of dipolar solutes in benzene were cooled rapidly to 110 K in a dielectric cell described fully elsewhere. The dielectric complex permittivity was monitored in the range 0.5 to 100 kHz for a series of higher temperatures with a General Radio bridge. Necessary precautions are listed elsewhere [12, 14].

3. RESULTS AND DISCUSSION

(i) *T-Butyl chloride systems*

Figure 1 (a) represents the spectra for the rotator phase I solid at 240 ± 5 K and the liquid at 293 K; the latter peaks here at 26 cm^{-1} . As in the liquid phase above 273 K, the temperature rate of shift is found to be less than 2 cm^{-1} in 5 K. This rate increases in the region of the transition into the rotator phase or below it. This was reported also by Brot *et al.* [15], who obtained a spectrum at 238 K peaking at about 40 cm^{-1} , while at 200 K (20 K below the transition to rotator phase II) the band had broadened and was centred at about 90 cm^{-1} . Whether these changes occur abruptly or progressively poses a question for further investigation. Transforming the rotator phase bandshape into the time domain gives the rotational velocity correlation function $C_v(t)$ on a normalized time scale shown in figure 1 (b) ($I_r = 1.43 \times 10^{-45} \text{ kg m}^2$, the reduced moment of inertia defined elsewhere [12] by Reid).

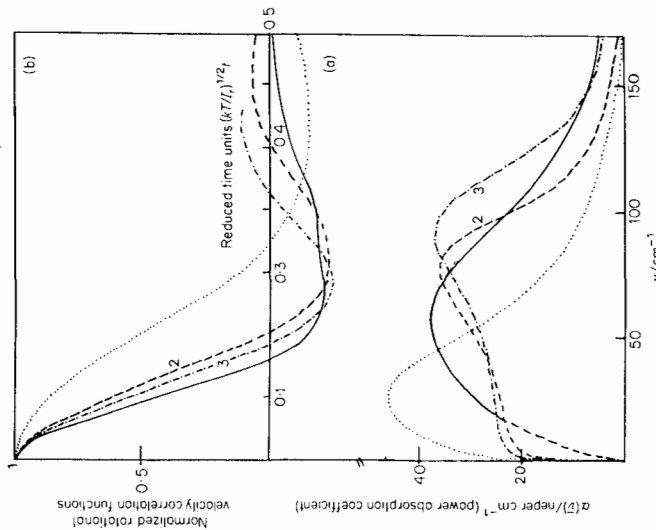


Figure 1. (a), Absorption in the far infrared of liquid *t*-butyl chloride at 293 K; —, —, —, two possible itinerant librator fittings (see text); —, —, —, absorption of *t*-butyl chloride in rotator phase I at 243 K. (b) As for figure (a), rotational velocity correlation functions.

The use of an analytical model for the description of the molecular dynamics in these phases must needs be in the nature of a stop-gap until more accurate methods (such as computer simulation) are more widely available. One such model is that of itinerant libration, as developed by Coffey and coworkers for use

[1–3] in liquids. The model is based on inferences [1] by Frenkel, Poley and Hill and was developed [1–3] by Wiley and Larkin. The central point is that a molecule is engaged by a group of nearest neighbours which undergoes isotropic rotational diffusion as a rigid entity. The mathematics are simplified considerably if the motion of the inner molecule's dipole is constrained to a plane. In this case it is possible to obtain closed forms for both the angular momentum and the orientational auto-correlation functions (and therefore the rotational velocity auto-correlation function).

The model consists of an annulus (the cage) of moment of inertia I_1 , free to rotate about a central axis, concentric with the annulus and constrained to rotate about the same central axis in a disc (the molecule) of moment of inertia I_2 , carrying a dipole μ along one of its diameters. The dipolar position is specified by an angle $\theta(t)$ relative to a fixed axis (the direction of the static electric field E). The equations governing the motion of the system at any time $t > 0$ are

$$I_1 \ddot{\psi}(t) + \xi \dot{\psi}(t) - \gamma [\theta(t) - \psi(t)] = \lambda(t),$$

$$I_2 \ddot{\theta}(t) + \gamma [\theta(t) - \psi(t)] = 0.$$

Here γ is the restoring torque constant, $\xi \dot{\psi}$ is the frictional couple acting on the annulus and $\lambda(t)$ is the noise, represented by a Wiener process. For convenience we define the model parameters $K_0 = \gamma/I_2$; $K_1 = (I_2/I_1)K_0$.

In the pseudo-tetrahedral lattice of *t*-butyl chloride the use of the itinerant librator model is justifiable (as a first approximation) on the grounds that for this compound the existence of discrete orientationally allowed directions has not been demonstrated unambiguously. The total dipolar spectrum of *t*-butyl chloride in its plastic (and liquid) phases has been investigated by Lassier and Brot [25]. These authors report the dielectric relaxation time, which is in agreement with the present measurements, and a model of a jumping librator is sketched, together with the hypotheses on the allowed orientations of the molecules. This model does not, however, allow us to obtain the complete zero-THz spectral profile to a sufficient degree of accuracy, so that a description such as itinerant libration is a prerequisite for further analytical development of the molecular dynamics. Using as a model of the molecular dynamical process the itinerant librator, we have best-fitted the data as in curve (2) of figure 1. The itinerant librator parameters, as defined in the literature, are $K_1 = 307 \text{ ps}^{-2}$; $K_0 = 184 \text{ ps}^{-2}$ and $\gamma = 27.7 \text{ ps}^{-1}$. The adequacy of the fit at short times allows us to take the K_0 value as a measure of the mean square torque present in the system. An alternative time fit represented by curve (3) ($K_0 = 260 \text{ ps}^{-2}$; $K_1 = 415 \text{ ps}^{-2}$; $\gamma = 32 \text{ ps}^{-1}$) is less representative in the spectral domain but indicates the degree of uncertainty in these curve matchings. The parameters for the liquid phase at 293 K should be very similar to those of the decalin solution ($K_0 = 76 \text{ ps}^{-2}$; $K_1 = 194 \text{ ps}^{-2}$; $\gamma = 21.8 \text{ ps}^{-1}$). This indicates that the mean square torque has doubled on going from the liquid phase (293 K) to the rotator phase—phase I (240 K). In addition the ratio $K_0/(2\pi c \bar{\nu}_{\text{max}})^2$ where $\bar{\nu}_{\text{max}}$ is the far infrared peak frequency, has decreased from 3.7 to 2.3. Using the results of an extensive correlation study [11–14] involving the itinerant librator and some fifty solute molecules in both liquid and glassy environments, it is clear that this ratio decrease is a sign that the effect of collision-induced absorption and translation-rotation coupling are both reduced in the rotator phase. This is, of course, expected

a priori, and gives us confidence in the meaningfulness of the itinerant librator as a simple ideal of the molecular dynamics. The itinerant oscillator appears therefore to describe fairly adequately observable features of our zero-THz data. A further test is its ability to forecast the so-called Debye relaxation time [5] $\tau_D = (I_r/kT)\gamma K_0/K_1$, which is calculated to be 7.0 ps (at a slightly higher value for the poorer fit). From Urban *et al.*'s study [8], the experimental relaxation time is about 8.1 ps, which according to Cole's hypothesis [16] for the internal field correction $3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)$ gives, with $\epsilon_0 = 15$ and, $\epsilon_\infty = 2.3$, a microscopic time of 5.8 ps. The prediction is accordingly acceptable and almost lies within the lower limit of temperature uncertainty, ± 5 K. This value may be compared with the prediction $\tau_D = 3.0$ ps from fitting the t-butyl chloride/decalin solution spectrum at 293 K. This value is also relevant to pure t-butyl chloride at this temperature (the spectra are nearly identical [8]), whose experimental microscopic time is 3.6 ps. The comparison indicates that as the Debye relaxation time increases with falling temperature then so does the far infrared absorption peak shift to higher frequency.

A further comparison can be made between the rotator phase dynamics of t-butyl chloride and those in the glassy environment of supercooled and vitreous decalin solvent [14]. Having indicated above how the sub-THz (Debye) and far infrared loss peak are related, it is surprising to find that the far infrared spectrum of the rotator phase peaks at a higher wavenumber (57 cm^{-1}) than does that of the glassy solution (53 cm^{-1}) despite the fact that the latter is associated with a very much larger Debye relaxation time. This may be due to cross-correlation effects in the rotator phase of the pure t-butyl chloride which begin to take effect as dielectric friction as the phase transition is approached, and which are almost absent in the non-dipolar glass.

(ii) *Pentachloronitrobenzene (PCNB)*

A pressed disc specimen was measured [17] to reveal a detailed spectrum of overlapping bands in the 20 cm^{-1} to 200 cm^{-1} range, the lowest frequency band being assigned as the librational component. To support this assignment a solution spectrum in decalin was recorded. The lowest band at 40 cm^{-1} in the solid was unshifted but appreciable shifts of the modes at 90 cm^{-1} and 110 cm^{-1} were observed (to 75 cm^{-1} and 100 cm^{-1} respectively). Without further evidence the comparison of the solid and solution does not unambiguously allow the lowest peak of the former the assignment of librational origin, and it may be a lattice mode or torsion mode. Alternatively the Poley band may correspond to the peak at 90 cm^{-1} in the solid as this is environment dependent. To consider these possibilities a single crystal of PCNB was grown in benzene solution to a size (8 mm disc) sufficient to record its spectrum at room temperature. This spectrum is compared with that of the pressed disc in figure 2. It was recorded with the hexad axis (*c* axis of the rhombohedral lattice) parallel to the optic axis. The relative intensity of the lowest frequency band has increased, as would be expected for in-plane libration, while out-of-plane torsion should become inactive. That the two mid-range peaks are reduced suggests that they are the torsions of NO_2 , the heaviest group, which has its oxygen atom plane at 62° to the ring plane [18]. As neither peak becomes completely inactive we assume that neither corresponds to a purely out-of-plane torsion, although the peak at 110 cm^{-1} is closest to such. Alternatively the out-of-plane torsion may couple to the active

group rotation caused by changes in the C-N bond length. The highest frequency band at 160 cm^{-1} may be associated with chlorine torsion, the contribution found in the single crystal spectrum being the in-plane component. The intense peak found in the sintered sample may therefore be a doublet of chlorine torsions. Finally the lowest frequency peak, attributed to whole molecule libration, is expected at roughly twice the intensity in the single crystal compared with the pressed disc. It is not possible to carry out this comparison accurately because of reflection losses, interstitial effects etc., but also because the librational motions are mainly but not wholly in the plane, so that out-of-plane libration contribution is lost in spectrum 1 of figure 2. In this respect it would be useful to grow a crystal so as to observe the spectrum for the *c* axis perpendicular to the measuring beam.

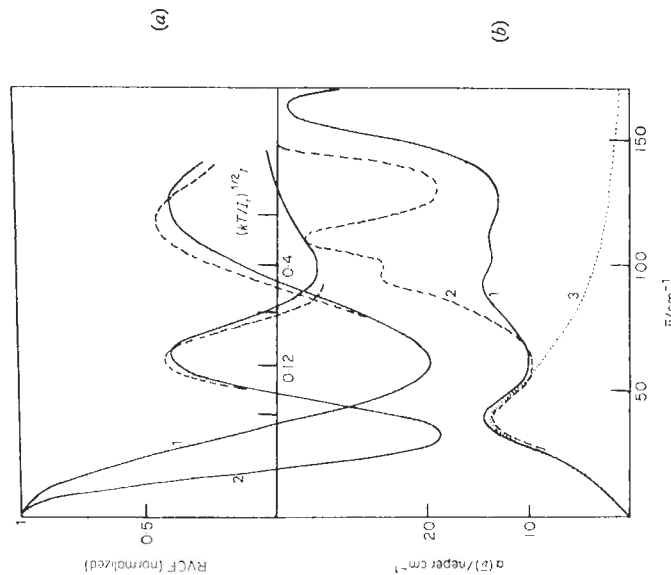


Figure 2. Time and spectral domain data for the rotator phase of PCNB (a) Rotational velocity correlation functions at (1) 300 K; (2) 110 K. —, experimental data; - - - - - , itinerant librator best fit (see text). (b) Far infrared spectra of PCNB at 300 K. (1) Single crystal; (2) pressed disc; (3) modified itinerant librator best fit.

In this system there is evidence [9] that the motion of the instantaneous mean orientation of the librator is not diffusive, but has the form of large angle discrete jumps of finite and well-defined amplitude. This is the case of the rotator, but not plastic, disordered phase of the hexasubstituted benzenes. For example, a methyl group can replace chlorine only by jumps of approximately 60° , not by a

adapted to an in-plane hexagonal symmetry of wells. The use of the itinerant librator for this situation is therefore an approximation.

We may analyse the Poley band in this approximation by fitting the rotational velocity correlation function at the two available temperatures. The fitting of the itinerant librator model to the data are shown in figure 2(a) and the parametric results tabulated below. We take the effective moment of inertia I as $I_0 = 38.6 \times 10^{-45} \text{ kg m}^2$ for this analysis.

Table 1. Fitting the itinerant librator (figure 2).

| Curve | T/K | $(I/kT)^{1/2}/\text{ps}$ | γ/ps^{-1} | K_0/ps^{-2} | K_1/ps^{-2} | τ_D/ps |
|-------|-------|--------------------------|-------------------------|----------------------|----------------------|--------------------|
| 1 | 300 | 3.05 | 11.7 | 67.5 | 41.2 | 178.3 |
| 2 | 100 | 5.3 | 12 | 79.2 | 40.5 | 659 |

The actual mean square torque effective in the system may be determined using [11-14] $\langle \Gamma(0)^2 \rangle = K_0/kT$, or, more manageably, one may quote the model determined root mean square torque which for PCNB is 62.5 kJ mol^{-1} at 300 K and 39 kJ mol^{-1} at 100 K. The torque decreases with cooling despite the contraction of the lattice. Similar behaviour has been reported for supercooled liquid systems [11-14]; a comparison is made in table 2. Only the t-butyl chloride system experiences an increasing torque with decreasing temperature.

Table 2. A comparison of mean square torques.

| System | T/K | $N_A \langle \Gamma(0)^2 \rangle^{1/2} / \text{kJ mol}^{-1}$ | T/K | $N_A \langle \Gamma(0)^2 \rangle^{1/2} / \text{kJ mol}^{-1}$ |
|---|---------|--|---------|--|
| PCNB | 300 (r) | 62.5 | 100 (r) | 39 |
| t-butyl chloride | 293 (l) | 12.6 | 243 (r) | 17.7 |
| t-butyl chloride/decalin | 293 (l) | 12.6 | 110 (g) | 11.0 |
| $\text{CH}_2\text{Cl}_2/\text{decalin}$ | 293 (l) | 8.8 | 110 (g) | 7.6 |
| bromonaphthalene | 293 (l) | 30.0 | 110 (g) | 24.6 |

(r) = rotator phase; (l) = liquid; (g) = glass.

Table 1 lists the calculated Debye relaxation times using the itinerant librator model to fit the far infrared spectrum. In the brittle rotator phase of PCNB these are many orders of magnitude shorter than those actually observed [19] (10^{-3} s at 300 K). In terms of our model analysis the long experimental times are due to highly cooperative large angle jumps. For the liquid systems the itinerant librator is more successful in the sub-THz range because the dipole is assumed theoretically to diffuse at a rate independent of the angular distance from its initial position. This is acceptable when translation is appreciable as in liquids, but in the solid phase the cog-wheel effect is expected *a priori* which is not

responses physically with a model consisting of a simple coupled harmonic oscillator inner and outer concentric annuli. The present version can be force fitted to the extra low frequency dielectric loss curves but this means that the theoretical far infrared part of the overall profile is a pseudo delta function for all allowable combinations and permutations of K_0 , K_1 and γ . Accordingly the latter will have no physical significance.

A more accurate simulatory form may be obtained by including a damping term to account for non-harmonicity in the libration. This introduces, however, a technical weakness [21] in that the Taylor expansion of the angular velocity autocorrelation function has a non-vanishing coefficient of t . If we denote the new damping parameter by γ_1 then the Debye relaxation time in this new representation is given by $\tau_D = (I_0/kT)(\gamma I_0/I_2 + \gamma_1)$. Subsequently the values available to γ_1 are restricted by the need to reproduce both the measured far infrared profile and τ_D . When τ_D is very long γ_1 may be regarded as a variable used to adjust the far infrared bandshape. The best fit parameters for PCNB at room temperature are $\gamma = 1.07 \times 10^{18} \text{ s}^{-1}$; $\gamma_1 = 10 \times 10^{18} \text{ s}^{-1}$; and $K_0 = 51 \times 10^{24} \text{ s}^{-2} = 10 K_1$, which results in the analytical curve (3) shown in figure 2(b) and a Debye-type loss spectrum at audio frequencies centred at the experimental peak position (1.5 kHz), but narrower than the observed width. As $\gamma \gg \gamma_1$ the parameter K_0 should be approximately equivalent to that in the conventional itinerant librator. In fact the latter is larger by about 30 per cent, indicating the extent to which the two theoretical approaches differ.

(iii) Benzene rotator phase and solid solutions

Benzene possesses a reorientation phase to below 77 K. We report that solid solutions of small dipolar solutes in rotator phase benzene behave similarly to 110 K. In fluorobenzene/benzene (10 per cent v/v) the loss peaks at a series of temperatures are 1.3 decades half-width, and so very similar to Debye curves (1-12 decades). These are illustrated in figure 3. The Cole-Cole plot for the system at 147 K is shown in figure 5 and has a distribution parameter of 0.1. In comparison PCNB at 300 K has a distribution parameter of 0.21. This indicates perhaps how the presence of dipole-dipole coupling broadens the loss curve as described theoretically by Evans [22] using a Smoluchowski equation. The magnitude of the process, $\epsilon_0 - \epsilon_\infty = 0.187$, is much lower than that of $\text{C}_6\text{H}_5\text{F}$ in decalin at 293 K, where $\Delta\epsilon = 0.28$, indicating either the presence of further absorptions at higher frequencies, or, more likely, the extent of component separation on freezing. Further studies with various concentrations and cooling rates would be useful in this respect. No losses were found for either pure component.

A linear Arrhenius plot allows the measurement of an unambiguous activation energy for the process of 28.7 kJ mol^{-1} . This is high compared with those typical of the liquid, indicating the cooperative nature of the process in the solid. This allows us to obtain a barrier height (V) to libration. Use of the latter in Brost's formula [23] for the frequency of harmonic libration $\nu_0 = (\pi/2\pi)(V/2I)$ where n , the well multiplicity is taken as 6 and $I = I_c$ gives $\nu_0 = 2 \text{ THz}$ or $\nu_0 = 70 \text{ cm}^{-1}$. The far infrared spectrum for a 20 per cent v/v solution at 110 K is shown (curve 1) in figure 6 and compared with the spectrum (curve 2) obtained

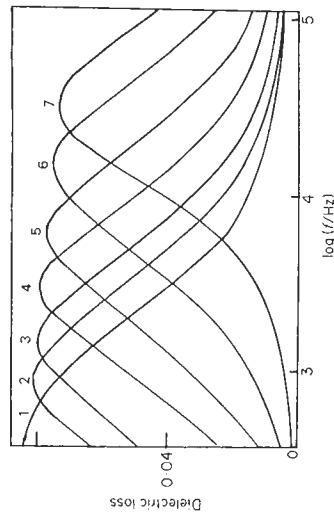


Figure 3. Loss spectra for 10 per cent v/v fluorobenzene in rotator phase benzene (1) 133 K; (2) 136 K; (3) 138 K; (4) 143 K; (5) 147 K; (6) 153 K; (7) 160 K.

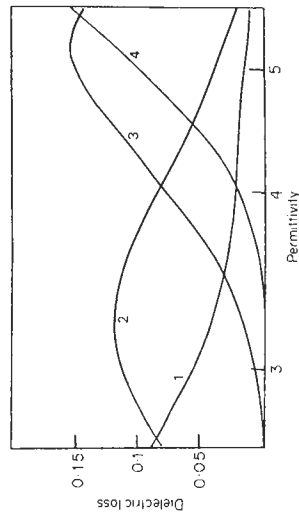


Figure 4. Loss spectra for t-butyl chloride in solid tetramethylsilane (implying a rotator phase for the solvent). (1) 77 K; (2) 88 K; (3) 103 K; (4) 111 K.

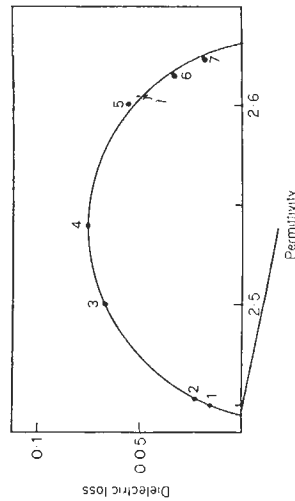


Figure 5. Cole-Cole plot for 10 per cent v/v fluorobenzene in phase benzene at 147 K. (1) 100 kHz; (2) 50 kHz; (3) 10 kHz; (4) 5 kHz; (5) 2 kHz; (6) 1 kHz; (7) 500 Hz.

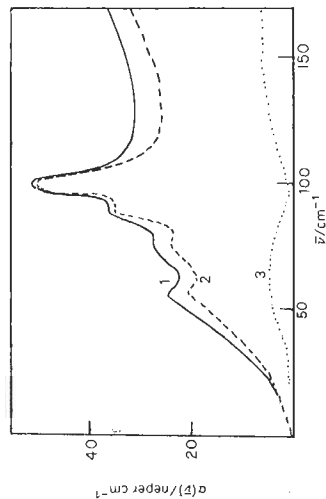


Figure 6. The high frequency part of the data in figure 5. It is important to realize that the data in both figures 5 and 6 together form the complete spectral profile for theoretical analysis. The dynamical evolution in the rotator phase solution covers the complete observable frequency range from Hz to THz. ---, rotator phase benzene solvent (scaled by 0.8), 110 K; —, solution of 20 per cent fluorobenzene in rotator phase benzene, 110 K; ·····, difference.

for pure benzene at this temperature. For clarity the latter is drawn to 8/10th scale so that the fluorobenzene contribution is the difference between curves 1 and 2 and is illustrated in curve 3. We first note the presence of structure on the benzene spectrum which are in excellent agreement with those found previously [24] for a monocrystalline sample at 80 K. In addition there is probably reflection loss in the spectrum of figure 6 due to the microcrystalline nature of the sample and this limits the accuracy of absolute intensities as does the flexible nature of the cell and the necessity of using small path lengths. The C_6H_5F component spectrum obtained as a small difference between large absorptions is not satisfactory, but does appear to indicate a band centred around 65 cm^{-1} . This is presumably librational in origin and thus represents a shift of 25 cm^{-1} from the Poley band present in decalin solution. This in close agreement with the predictions of the model proposed by Brot.

The more polar probe molecules, pyridine and tetrahydrofuran, were also measured at 10 per cent v/v concentrations in rotator phase benzene. Dielectrically their behaviour is similar and activation energies were measured and tabulated below. Only approximate far infrared bands were obtained, which

Table 3. Zero-THz spectra of solid solutions.

| Probe | Temperature range of observation | ϵ''_{max} | $\Delta E/\text{kJ mol}^{-1}$ | $\bar{\nu}_0/\text{cm}^{-1}$ |
|--------------------------|----------------------------------|---------------------------|-------------------------------|------------------------------|
| 10 per cent C_6H_5F | 133 to 160 K | 0.08 | 28.7 | 70 |
| 10 per cent pyridine | 116 to 140 K | 0.15 | 23.0 | — |
| 10 per cent THF | 136 to 170 K | 0.09 | 30.0 | — |
| 10 per cent bromobenzene | No losses | 0.09 | 30.0 | — |
| 10 per cent CH_2Cl_2 | No losses | 0.09 | 30.0 | — |

were similar to those for the C_6H_5F solute. In future it will be necessary to improve absolute intensities by using laser sources (to allow larger path lengths) and single crystals of the solid solutions. Finally, bromobenzene and methylene dichloride were also tried as probes but no dielectric absorption was observed, indicating that significant departures from benzene geometry prevented solute rotation in these rotator phases.

These probe studies have also been used for tetramethylsilane and tetrachloromethane at low temperatures where well defined dielectric processes were observed for dichloromethane and t-butyl chloride (figure 4) probes in the former but no losses were found for the latter for several solutes. This is taken to indicate that tetramethylsilane exists as a rotator phase at these low temperatures, 100 K to 160 K, but tetrachloromethane does not (i.e. its rotator phase range is limited).

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