Dielectric and far infrared study of solutions in the glassy state from 100 Hz to 10 THz: Discovery and characterization of the universal γ process

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(Received 18 November 1980; accepted 10 March 1981)

The process of whole molecule libration, or torsional oscillation, of molecular dipoles evolves dynamically in supercooled solutions and glasses on an observable time scale extending from picoseconds to kiloseconds and longer. This can be measured using the dielectric loss spectrum of rigid dipolar solute molecules dissolved in glass-forming solvents such as decalin. The complete spectrum extends from below 100 Hz to THz frequencies, where the short time behavior can be detailed using the far infrared power absorption coefficient. This occurs universally and is characterized here for the first time as the γ process—the high frequency adjunct of the α and β processes discovered by Johari and co-workers. Results are presented over a broad frequency range (kHz to the far infrared, discontinuous) for the halogenated benzenes and for methylene chloride. In C_6H_5F/decalin there is a well defined β process, in C_6H_5Cl/decalin it is much less intense, and in C_6H_5Br/decalin it is either unresolved or vanishingly small. The multidecade loss profile of methylene chloride is reported in various glass-forming solvents. The loss shows three peaks (α, β, γ) in a total range of over 12 decades. Both the α and β processes in various glasses and supercooled solutions are associated with very high activation energies of about 100 kJ/mol. This feature appears to be specific to CH_2Cl_2. The high frequency (γ) part of the loss in the far infrared region may be studied in detail because of the relation between the dielectric loss and the optical power absorption coefficient. In some solvents there is a very large difference between the γ profile in the liquid at ambient temperature and the low temperature glass.

INTRODUCTION

The role of macroscopic (bulk) viscosity in determining the nature of molecular dynamics in the condensed state is revealed most clearly by measurements[1–5] in supercooled and vitreous solutions of small dipolar solute molecules in solvents such as *cis*-decalin, which can be supercooled well below the normal freezing point. The molecular dynamics and interactions in these low temperature states are revealed by broadband dielectric spectroscopy to be different from those in the same environment at room temperature.

This has implications in fields of spectroscopy which provide insights into aspects of molecular dynamics other than dipolar rotational relaxation. These include[6] infrared and Raman band shape analysis (rotovibrational relaxation) incoherent and coherent inelastic scattering of thermal neutrons (rototranslational motions), depolarized light scattering (single particle and collective rotational modes of motion and their interrelation), Brillouin spectroscopy of scattered light and acoustic relaxation (dispersion of thermally propagated sound waves), mechanical visco-elastic relaxation, and others, including the rapidly developing techniques using laser pulses on the time scale of picoseconds to measure directly the equilibration of some property of a molecule initially put out of equilibrium by the laser pulse.

The dynamical evolution from an arbitrary initial $t = 0$ of an ensemble of small dipolar molecules in a low temperature, supercooled environment is enormously slow in comparison with that at room temperatures. Johari *et al.*[1–3] and Williams *et al.*[4,5,7] have shown that at low frequencies in a wide range of solutions the dielectric loss in the supercooled and vitreous environment peaks more than once. There is a secondary relaxation which appears at higher frequencies than the main dielectric loss. Arrhenius plots of the logarithm of the frequency of maximum loss against reciprocal temperature in the region of the latter are nonlinear and the mean activation energy is high compared with that of the higher frequency (β) relaxation, for which these plots are linear. The lower frequency peak is termed the α process. Both α and β peaks appear at very low frequencies (Hz–kHz) compared with the observable loss at room temperature, which for small dipolar solutes appears in the microwave (GHz) region.

However, both these peaks are manifestations of the nature of the dipolar dynamical evolution at elapsed times which are relatively long, i.e., at low frequencies. They are described by the long-time tail of the dipolar correlation function,[8] which is related to the loss spectrum via a Fourier transform. In general, a classical autocorrelation function must be an even function of time, so that as $t \to 0$ the behavior asymptotically approaches $1 - at^2/2 + 0(t^4)$, where a is a thermodynamic equilibrium average. This determines (by Fourier transform) the behavior of the dielectric broadband spectrum as $\epsilon''(\omega)$, where ω is the angular frequency. *The properties of the classical dipole correlation function imply that there will be a further peak in the dielectric loss at* frequencies in the far infrared region (2–250 cm^{-1}). This is because the proper description of far infrared spectra involves memory and inertial effects used in combination. This is not possible with a model whose McClaurin expansion has a term in t^3, because this implies that the mean square torque is not defined properly, being a coefficient of t^4.

In the ultraviscous and vitreous states of matter therefore, the *complete* dielectric loss process consists of a continuous band, *covering many decades of frequency*, which sometimes peaks *three* times (α, β, and γ). The

0021-9606/82/052576-09$02.10

α peak is that which appears at lowest frequencies, the broad β peak lies at intermediate frequencies and the *relatively* sharp far infrared peak, designated as γ, always remains at THz frequencies. In contrast, at about 295 K, the dielectric broadband spectrum consists of the main microwave (GHz) peak, with a barely resolved THz γ shoulder at higher frequencies.

The purpose of this paper is to characterize the dielectric loss process over as much as possible of the range from zero to THz frequencies for dipolar solute molecules in glassy and viscous solvents. In what follows, there will be considerable gaps in the actual coverage we have managed to achieve, e.g., below 10^2 Hz and particularly in the range 10^5–10^{10} Hz. The latter, in particular, needs to be investigated further before the α and β parts of the loss are properly characterized. For example, it is desirable to find the point at which these start to separate, and how they then develop at lower temperatures. The technical problems are most acute in the microwave (wave guide) region. This extends the work of Johari *et al.* and Williams *et al.* to include the γ peak. The implications for the other techniques mentioned above in that *the latter should also be within their frequency range of measurement, and could be characterized by each in turn.* The γ peak (but not the α or β) is also within range of computer simulation methods[10] which are designed to solve the equations of motion of some hundreds of molecules interacting by means of a model potential.

The proposition that only the γ peak is within range of computer simulation is certainly true of "brute force" molecular dynamics calculations but not of Brownian dynamics simulation. Some of this recent work on alkanes is showing remarkable resemblances to experiment and might work on glass systems.[6]

On a still wider basis the existence of peaks in the extreme broadband dielectric spectrum challenges much of the current mathematical thought[11] on molecular dynamical modeling, i.e., on approximating the Liouville equation describing the dynamics of many interacting molecular potentials. This is because a model must be made to describe effectively the complete (zero frequency to THz) dielectric spectrum under all thermodynamic conditions where end-over-end dipole reorientation is still possible. If such a model describes perfectly the spectrum under conditions of low viscosity then it should be developed to see whether it can also produce an (α, β, γ) profile as the viscosity of the environment increases. In this context dielectric and far infrared spectroscopy (or "zero-THz spectroscopy" for convenience) probes the details of molecular dynamical behavior because of the detailed information available, both at very high frequencies [through the optical power absorption coefficient $\alpha(\omega)$] and at very low frequencies, culminating in the static complex permittivity $\epsilon^*(0)$.

The contribution of the far infrared process to the static ϵ^* is measurable, as in the case of liquids, by the difference between ϵ_∞, the high frequency intercept of the Cole–Cole plot, and the square of the refractive index (n_{ir}^2) at about 200 cm^{-1}. The difference $\epsilon_\infty - n_{\mathrm{ir}}^2$ is universally much smaller than the dispersion amplitude ($\epsilon_0 - \epsilon_\infty$), but it is important to realize that this is no indication that the Poley absorption (liquids) or γ process (glasses) is negligible when it comes to molecular dynamics studies. The band *shape* is the overriding criterion.

Dielectric loss spectra of CH_2Cl_2 in glassy solvents have been measured from static to THz frequencies at temperatures from 107 K to ambient. A very high activation energy β process is observed which has characteristics entirely different from those of the halogenobenzene/decalin systems.

EXPERIMENTAL DETAILS

The apparatus needed to cover the dielectric range from static to THz is listed as follows:

(i) Far infrared: 2–250 cm^{-1} (60 GHz to higher frequencies) a Grubb–Parsons/N.P.L. "cube" interferometer with phase modulation and Golay and Rollin detectors. Elliot 4130 Computer, and a Research Machines 380Z microcomputer.

(ii) Microwave: (a) Coaxial wave guide fed by a multiband controller powering two units for sweep frequency measurements (frequency ranges 0.01–4.2 GHz or 4–18 GHz). The units contain varactor type diodes whose characteristic frequencies can be varied with applied voltage so that a given range can be swept continuously. (b) Klystron sources and wave guides for spot frequency measurements at 35–70 GHz (U.C.W., Aberystwyth) and 112, 68, and 35 GHz microwave interferometry at the University of Nancy, Lorraine.

(iii) Low frequency and static permittivities were measured in a cell designed and constructed to produce reproducible capacitance for small (1–5 ml) volumes of sample at room temperature and down to 193 K. Measurements into the kHz–MHz region were made using a "General Radio" inductance bridge.

CELLS FOR MEASUREMENTS IN THE FAR INFRARED

A standard VC-01 variable path length cell was used for measurement of spectra at room temperature. For lower temperatures the liquid was held between TPX (poly 4-methyl pent-1-ene) windows with a polyethylene spacer; the arrangement being supported in a metal clamp below the colder finger of a Dewar vessel. The entire cell is housed in an evacuable sample chamber and temperatures down to about 100 K are reached using $N_2(l)$ coolant in conjunction with an attached heating element. Use of a polyethylene spacer allows a liquid to be injected at room temperature and the hole sealed by heat treatment.

CELLS FOR LOW TEMPERATURE DIELECTRIC MEASUREMENT

Criteria for low temperature/low frequency measurement:

(1) A liquid sample must be held between a pair of electrodes and cooled rapidly into a glassy phase.

(2) Measurements must be made over a range of frequencies at fixed temperatures from about 100 to 150 K so temperature stability must be good.

(3) A sufficiently small cell volume must be used to prevent shattering of the samples upon cooling.

(4) Condensation, especially on electrode terminals, must be avoided.

(5) The insulation material and cell geometry must be such that inherent cell losses are negligible and the ratio of active to support cell capacitance must be large.

(6) Temperature gradients in the sample must be small, and the mean temperature measurable.

The cell was designed and built around the sample holder used for the low temperature far infrared measurements. The problem of sealing with Teflon spacers was overcome by mounting the electrode assembly (active cell) side by side with a (nonactive) reservoir section where the spacer material can be polyethylene. Typically, a 2 K temperature gradient is expected within the measured sample and a similar uncertainty exists in the measurement of its mean temperature. This is in absolute temperature, and not in temperature differences. The cell is described fully elsewhere.[12]

Repeatability and reproducibility were carefully checked against literature results, where available.

MEASUREMENT OF THE GLASS TRANSITION TEMPERATURE (*Tg*)

Standard differential thermal analyzers are not suitable for the low temperatures used in these studies, so apparatus was constructed using a pair of glass tubes containing the two copper–constantan junctions of a thermocouple to monitor temperature differences between the samples in each tube. The tubes, one containing the decalin solution and one standard liquid CCl_4, were frozen in liquid N_2 and then suspended in a Dewar vessel containing a small amount of N_2. The absolute temperature of the decalin system is monitored using a second thermocouple, and potentiometer. At the glass transition which is the point (or range) of temperature over which the ultraviscous solution vitrifies, there is a change in the rate of heat uptake of the decalin system.

ELIMINATION OF SPURIOUS EFFECTS

These can be recognized and controlled by careful monitoring of the capacitance and conductance. They include: (i) conductance proportional to the loss, due to impurity; (ii) insulation losses which decrease with temperature; (iii) separating out of the solute and decalin, crystallization and shattering; (iv) Maxwell/Wagner loss which vanishes at the melting point of the decalin solvent.

The temperature behavior of capacitance and conductance illustrates that decalin solutions may be supercooled but become unstable towards 183 K. To observe the glassy phase the cooling rate must be sufficiently rapid to cool the sample in less than a few minutes through the region from 183 to about 143 K, where it becomes kinetically stable. The behavior of the capacitance in the temperature region from 143 to 113 K appears to indicate considerable rotational freedom, for example, in CH_2Cl_2/decalin solutions.

The methylene chloride systems were less stable than the halobenzene solutions and care was taken to avoid crystallization, which could involve either aggregates to CH_2Cl_2 nucleating in the amorphous matrix or in addition crystallization of the decalin solvent.

DISCUSSION OF RESULTS

Some 23 dipolar solute molecules have been studied[2] in the ultraviscous and vitreous states of various glass forming solvents. In this section we discuss the significance of some of these results (halobenzene and methylene chloride solutes). The existence of a relaxation process at low frequencies must irrespective of its detailed origin be associated with a short-time process which will appear in the far infrared. The α and β features are causally related, i.e., they and the γ peak are manifestations of the same underlying dynamical process and are representable in terms of a single orientational correlation function, which has a natural nonexponential behavior at long and short times.

To exemplify our data, we consider 10% v/v halobenzene/decalin systems. In the following, we present our results in the form of dielectric loss $[\epsilon''(\omega)]$ and infrared power absorption coefficient $[\alpha(\omega)]$ related by

$$\alpha(\omega) = \omega\epsilon''(\omega)/n(\omega)\, c \ , \tag{1}$$

where c is the velocity of light and $n(\omega)$ the frequency-dependent refractive index. The power absorption coefficient is observed naturally by the attenuation of infrared radiation and because of the ω factor in Eq. (1) which provides us with a very detailed "closeup" of the high frequency part of the overall loss curve, i.e., the far infrared spectrum. These are illustrated in decalin glass at 110 K in Fig. 1 and at room temperature (296 K). The glass phase spectra are much more symmetric than those of the liquid solutions due to the proximity of the main microwave (GHz, Debye[13]) loss in the latter.

The peak frequency of the far infrared $\alpha(\omega)$ can be related theoretically to the mean square torque on a solute molecule due to its molecular environment. It is well known[6,8,9] that Debye's description[13] of dielectric loss, using the concept of space-isotropic rotational diffusion, leaves this torque undefined. *The Debye theory produces a plateau in $\alpha(\omega)$ extending to infinite frequencies.* This is related directly to the fact that the orientational correlation function of rotational diffusion takes the form of a single exponential, which behaves incorrectly as $t \to 0$. Rotation diffusion may be described as infinitesimally small changes of orientation taking place infinitely quickly, so that the details of molecular motion at short time are not considered properly because the angular acceleration is infinite.

Viewed on this background the spectra of Fig. 1 give the detail of the short time molecular movements which

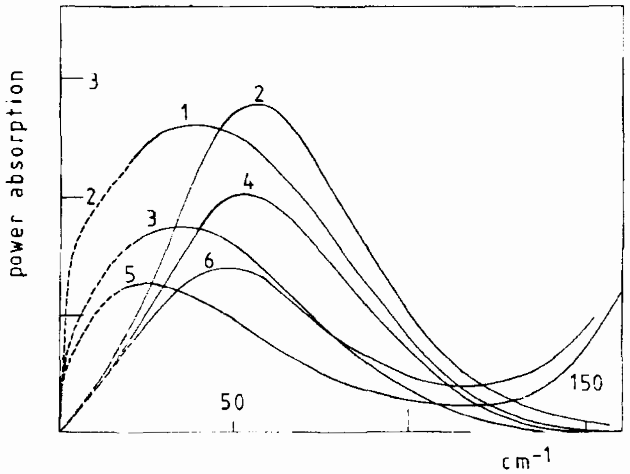

FIG. 1. Power absorption coefficient $\alpha(\bar{\nu})$ (neper cm^{-1}) vs $\bar{\nu}$ (cm^{-1}) for halogenobenzenes in decalin (10% v/v concentration). (1) Fluorobenzene/decalin at 293 K ($\bar{\nu}_{max} = 39$ cm^{-1}, where $\omega = 2\pi\bar{\nu}c$); isotropic liquid solution. (2) At 110 K, $\bar{\nu}_{max} = 57$ cm^{-1}, vitreous solution. (3) Chlorobenzene/decalin at 293 K ($\bar{\nu}_{max} = 34$ cm^{-1}); (4) At 110 K ($\bar{\nu}_{max} = 53$ cm^{-1}). (5) Bromobenzene/decalin at 293 K ($\bar{\nu}_{max} = 23 \pm 3$ cm^{-1}). (6) At 110 K ($\bar{\nu}_{max} = 48$ cm^{-1}).

in supercooled and vitreous media eventually evolve into motions taking place on an immensely slower time scale, observable as (α, β) features in the dielectric loss. The complete dynamical process is governed mathematically by Liouville's equation. It is not enough to approximate this using rotational diffusion.

This point is emphasized by the very large shifts between liquid and glass in the peak frequences ω_{max} of Fig. 1. These are proportionately different for each solute, being 18 cm^{-1} (46% increase) in C_6H_5F solute, 19 cm^{-1} (56%) for C_6H_5Cl, and 20 cm^{-1} (87%) in C_6H_5Br. *This frequency is not defined with rotational diffusion, there is no theoretical peak, only a plateau*, but the *observed* changes reflect environmental effects on molecular dynamics in detail. The integrated cross-sectional absorption intensity [the area of $\alpha(\omega)$] per molecule is smaller in the glass, which indicates a reduced amplitude of molecular torsional oscillation (libration) that counteracts any internal field effects.

By determining the rate of shift of the α and β features to give activation energies, we may reasonably extrapolate to yield the complete dielectric loss spectra of Fig. 2 whose far infrared portion appears as the feature labeled γ. We note that our observation of a β process in C_6H_5F/decalin is novel and of especial interest since it is observable at 10 kHz, 60 K below the glass transition temperature ($Tg = 133$ K). At 148 K, 15 K above Tg, the loss in the kHz range is dominated by the α process of three decades half-width. If the measurement temperature is lowered this moves out of range to lower frequencies while the shoulder of the β loss approaches from higher frequency. At our lowest accessible temperature of 77 K the β process may be dis-

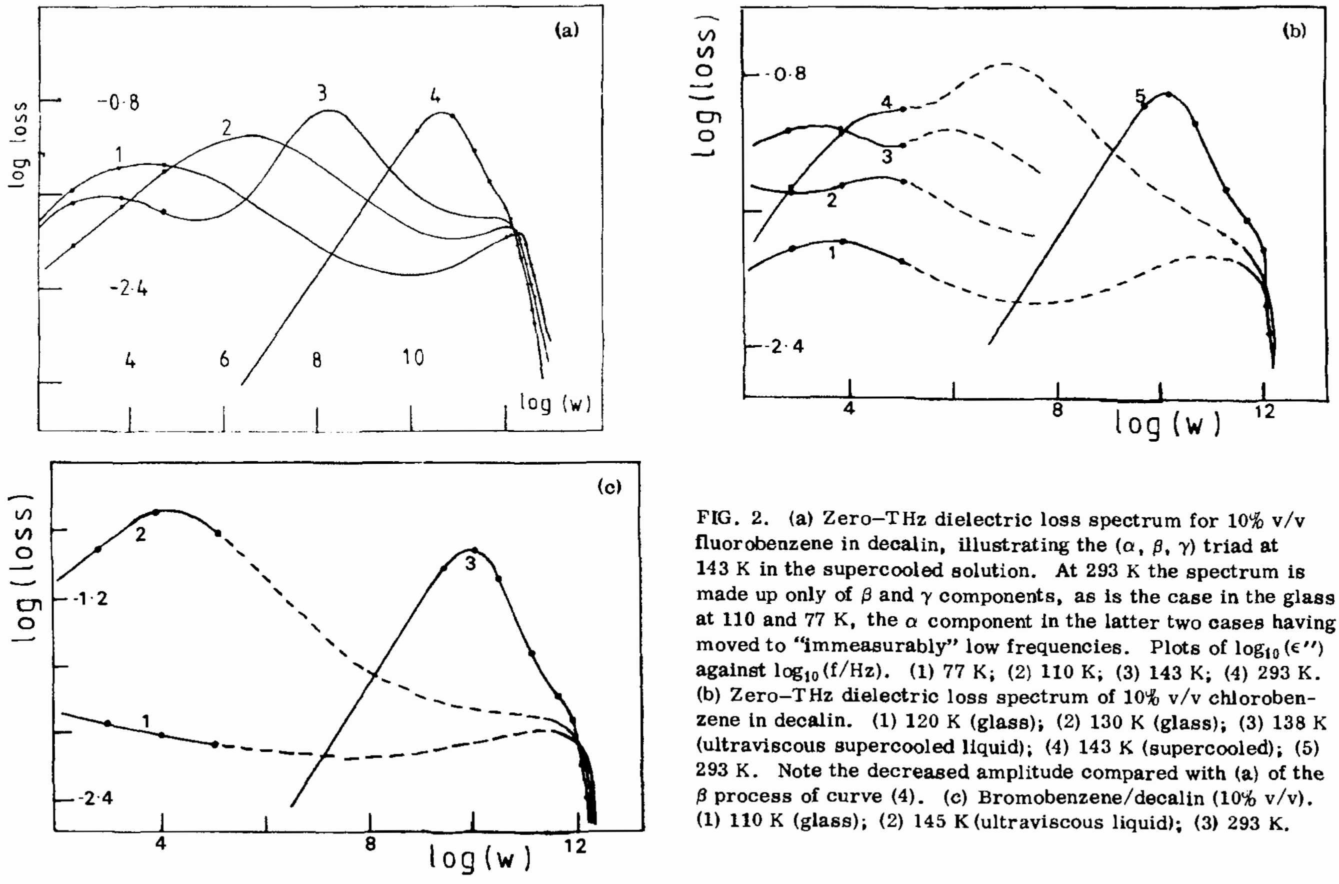

FIG. 2. (a) Zero–THz dielectric loss spectrum for 10% v/v fluorobenzene in decalin, illustrating the (α, β, γ) triad at 143 K in the supercooled solution. At 293 K the spectrum is made up only of β and γ components, as is the case in the glass at 110 and 77 K, the α component in the latter two cases having moved to "immeasurably" low frequencies. Plots of $\log_{10}(\epsilon'')$ against $\log_{10}(f/\text{Hz})$. (1) 77 K; (2) 110 K; (3) 143 K; (4) 293 K. (b) Zero–THz dielectric loss spectrum of 10% v/v chlorobenzene in decalin. (1) 120 K (glass); (2) 130 K (glass); (3) 138 K (ultraviscous supercooled liquid); (4) 143 K (supercooled); (5) 293 K. Note the decreased amplitude compared with (a) of the β process of curve (4). (c) Bromobenzene/decalin (10% v/v). (1) 110 K (glass); (2) 145 K (ultraviscous liquid); (3) 293 K.

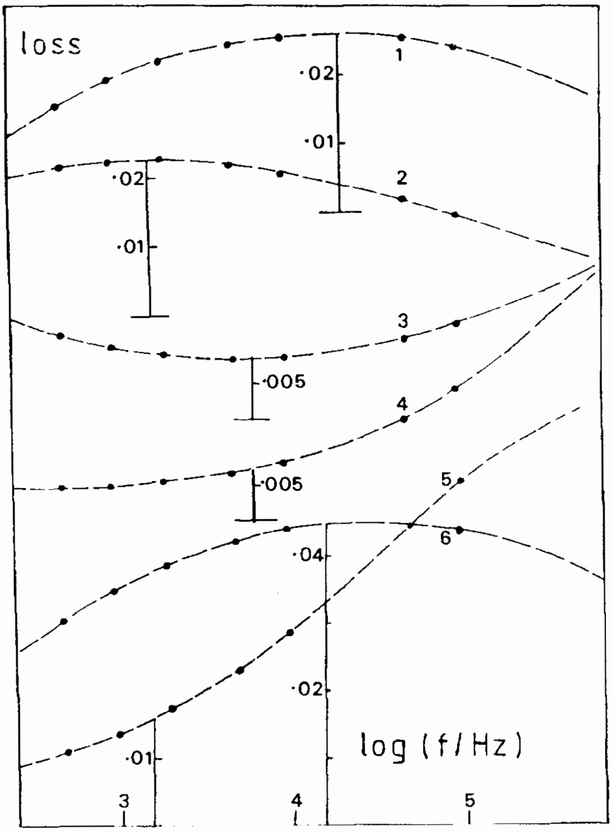

FIG. 3. Isothermal low frequency loss spectra for 10% v/v fluorobenzene in decalin. (1) 148 K; (2) 143 K; (3) 137 K; (4) 127 K; (5) 110 K; (6) 77 K. Glass transition temperature = 133 K. Plots of ϵ'' vs $\log_{10}$ (f/Hz).

tinguished as a band of 4 decades halfwidth.

Figure 2 illustrates how the microwave (or Debye) loss in the room temperature liquid becomes resolved from the γ feature (which shifts with decreasing temperature in the opposite direction), eventually resolving also the α and β features at about 180 K. At this temperature the viscosity of the supercooled liquid solution is a few orders of magnitude higher than in the ambient liquid. At 143 K, where the α process is measurable, we can estimate the β peak to be at 10^8 Hz (by virtue of activation enthalpy). *It is of course desirable to check this estimate with more data measured at low temperatures throughout the technically difficult* MHz–GHz *region*. However, the estimate is based soundly enough on the well-known linearity of the β peak frequency vs temperature plot. Some features of both peaks at 137 K (4 K above *Tg*) may be seen in Fig. 3 and possibly a shoulder of the α process at 127 K (6 K) below *Tg* in the glass). The α loss maximum in the glass must be at extremely low frequencies, as indicated by the Arrhenius plot of Fig. 4. At 110 K (23 K below) the lowest accessible temperature of our far infrared apparatus the β process is estimated to center at 3 MHz, and is losing intensity (ϵ_0 is falling) due to the progressive freezing-in of all large-angled molecular motion. This means that the molecular mean-square torque is larger and that the γ peak shifts to higher frequencies as in Fig. 1. The *whole* process, *from picoseconds to years*, provides us with a new challenge of adequately approximating the Liouville equation in the course of any analytical description. *It is clear that molecular dynamics studies currently restrict the model evaluation to a much too narrow a range of both macroscopic viscosity and of frequency*. There is no description currently available to explain even the gross features of the (α, β, γ) *triad* in terms of the motion of individual molecular dipoles. The fastest computers (e.g., the CRAY) are wholly inadequate to simulate motions over the decades of Fig. 2. It seems a matter of some urgency therefore that a range of experimental techniques should be brought to bear on molecular motion in the vitreous and supercooled states of matter.

To end the discussion on C_6H_5F/decalin we note that the activation energy (ΔE) for the β process, 12 kJ mol^{-1}, is similar to that derived from measurements in the microwave region at around room temperature, while ΔE for the α process is (90 ± 15) kJ mol^{-1}, with no temperature dependence over a limited range of kHz frequencies. The linearly extrapolated intercept of the α and β plots is about 180 K, this being approximately where the two features become resolved in the supercooled liquid.

The zero-THz loss spectra for the C_6H_5Cl/decalin system are shown in Fig. 2(b). At kHz (audio) frequencies the results have been checked with those of Johari and Goldstein,[3] and are very similar. At 143 K the α and β peaks are only just resolved, at a much lower temperature than for C_6H_5F in decalin. The decrease in intensity of the β process as it moves into range from higher frequencies is more than in C_6H_5F/decalin, while ΔE for the α peak is again about seven times that for the β.

Dielectric measurements on C_6H_5Br/decalin reveal in Fig. 2(c) only the single presence of the α peak, whose

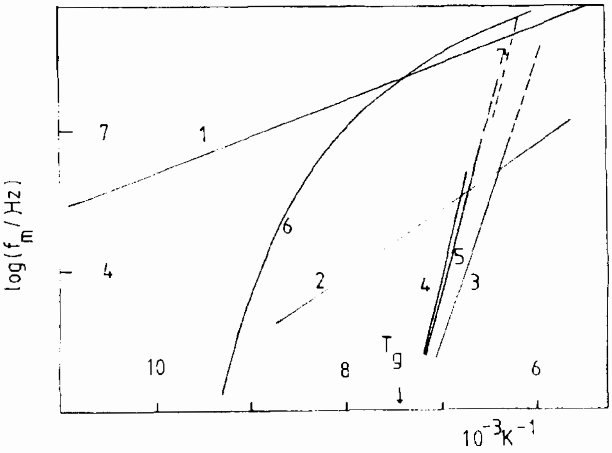

FIG. 4. Activation energy plots (AEP) for 10% v/v solute/decalin systems [plots of $\log(f_{max}/\text{Hz})$ vs 10^{-3} K^{-1}]. (1) Fluorobenzene (β); (2) chlorobenzene (β); (3) fluorobenzene (α); (4) chlorobenzene (α); (5) bromobenzene (α); (6) CH_2Cl_2 (β); (7) CH_2Cl_2 (α).

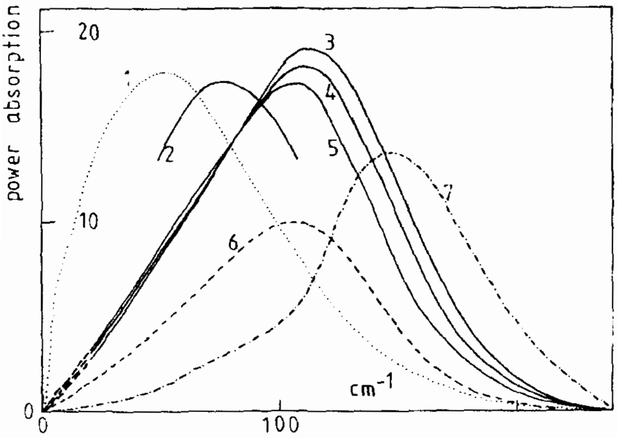

FIG. 5. Far infrared spectra for methylene chloride systems {plot of optical power absorption $[\alpha(\nu)]$ coefficient (neper cm^{-1}) vs wave number ($\bar{\nu}$ in cm^{-1})}. (1) 10% v/v CH_2Cl_2 in decalin at 293 K. (2) At 220 K in the ultraviscous liquid; (3) at 107 K in the glass; (4) at 117 K in the glass; (5) at 127 K in the glass; (6) 5% v/v CH_2Cl_2 in decalin at 110 K; (7) 10% v/v CH_2Cl_2 in a glass solvent made up of 10% pyridine in toluene.

behavior at low frequencies compares well with Johari's measurements. In the glass at 110 K only the wing of this absorption with possibly losses due to impurities and inherent dc conduction are present at low frequencies. There is no discernible β process but the high frequency far infrared γ process is well defined (Fig. 1) indicating torsional oscillation at these frequencies.

To summarize therefore, in C_6H_5F/decalin there is a well-defined β process, in C_6H_5Cl/decalin it is much less intense, and in bromobenzene it is either unresolved or vanishingly small. We therefore form the hypothesis that it exists only for small ratios of solute to solvent size. *This hypothesis may be evaluated by using smaller molecules in decalin.* Such a molecule is methylene chloride, a rigid dipolar, asymmetric top.

The far infrared power absorption coefficient of a rapidly cooled, transparent and presumed monodisperse sample of 10% CH_2Cl_2 in decalin at 107 K is shown in Fig. 5 to peak at $\bar{\nu}_{max} = 114\ cm^{-1}$ compared with its liquid phase value (at 293 K) of 53 cm^{-1}. This 113% increase makes this system ideal for studying the variation of $\bar{\nu}_{max}$ with temperature. Curves for three intermediate temperatures are also shown. The temperature coefficient in the glass is similar to the overall shift from the liquid state, about 3 cm^{-1} per 10 K.

The kHz loss process (β) in the glass is very temperature dependent. In Fig. 6 the peak is observable at 110 K and shifts across the *two decades* of measurement for only a 4 K increase in temperature. By 118 K the glass phase kHz losses are again small, and remain so until at 20 K higher a second loss process becomes apparent. Before this can be characterized, crystallization occurs at 140 K and the losses at this temperature slowly reduce with time. If this temperature is not reached, the loss spectra are reproducible upon cooling and intensities do not vary between samples if they are rapidly cooled. The observed peak at the lowest temperatures was thus interpreted as the β process although in view of the very high apparent activation energy (ΔE) (100 kJ $mol^{-1} \pm 10\%$) its nature is different from those of the halogenobenzene systems discussed already.

The origins of this β process may be investigated further by using different glassy solvents. For this purpose toluene is useful, and also mixtures of pyridine and toluene (10% of the former). A 10% v/v solution of CH_2Cl_2 in toluene/pyridine solvent produces a very large shift in $\bar{\nu}_{max}$ (Fig. 5) of the far infrared, as the temperature is lowered from ambient to 110 K in the glass (53–140 cm^{-1}). The β loss peak, clearly observable in decalin has however disappeared. The rate of shift of $\bar{\nu}_{max}$ has reduced in the glassy state compared with its value in the liquid. The CH_2Cl_2/decalin system produces a linear dependence of $\bar{\nu}_{max}$ on T throughout the accessible range. It appears that in the pyridine/toluene system the rate of shift of $\bar{\nu}_{max}$ has reduced in the glassy state compared with its initial rapid rate in the liquid.

The far infrared behavior is reflected in that of the dielectric process because the CH_2Cl_2/pyridine/toluene system has no β process of measurable intensity, the rotational motion being frozen in as indicated by the nondispersive low values of $\epsilon'(\omega)$ obtained, close to that of the solvent. In other words the activation energy (barrier height) for the process is very high. In decalin, an activation energy of 100 kJ/mol is associated with a prominent β process whose magnitude is about one-third of the total polarization. The C_6H_5F/decalin system has a slight concavity of slope ($d^2\bar{\nu}_{max}/dT^2$) is greater than zero while the curve for C_6H_5Cl/decalin is more linear and that for C_6H_5Br/decalin is of convex slope.

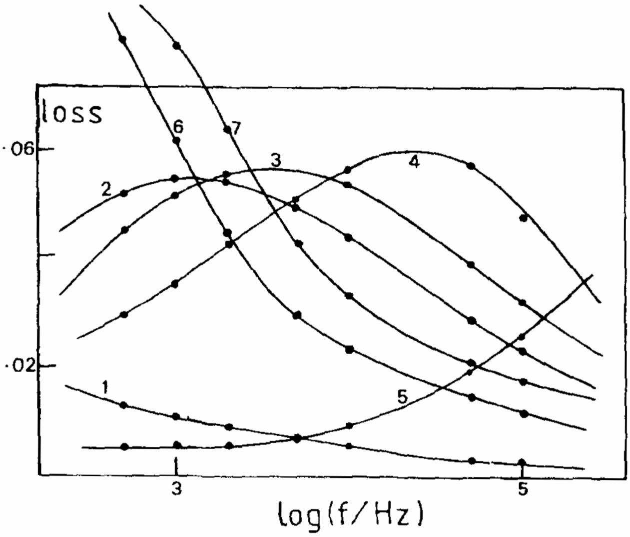

FIG. 6. Low frequency part of the multidecade loss spectrum of 10% CH_2Cl_2 (v/v) in decalin. Plot of dielectric loss (ϵ'') vs log (f/Hz). (1) 106 K (glass); (2) 110 K (glass); (3) 111 K (glass); (4) 113 K (glass); (5) 118 K (glass); (6) 138 K (viscous liquid); (7) 140 K (viscous liquid). Note the very rapid movement of the loss across the scale in the range 110 to 118 K.

The results for several systems can be summarized in terms of the Evans/Reid factor (Tq), or molecular mean square torque[14] which is proportional to $I_r \bar{\nu}^2_{\max}$, where I_r is the reduced moment of inertia of a solute molecule, defined as in the literature.[15,16] *Although several more accurate measurements are required to complete these plots the indication is that for systems where a β process is absent, i.e., of such weak intensity that it is not resolved, the plots reach their maximum values in the supercooled viscous phase above Tg, the glass transition temperature, while for those systems with prominent β peaks*[15] *the curves are generally of overall negative gradients which suffer discontinuities at or below the glass transition range.*

The β loss process in CH_2Cl_2/decalin is classified as such because of its occurrence (at kHz frequencies) at a temperature much lower than the glass transition temperature of the solvent (137 K) and because the presence of a lower frequency region of loss may be discerned at a temperature just above 137 K and prior to crystallization. The activation energy (100 kJ mol^{-1}) for the process is however very high compared with anything reported previously and is comparable with the range of values found by Johari[1-3] for α processes, so that its designation as a β process must be substantiated. In defending this assignment it may be argued that CH_2Cl_2 is a molecule of very different geometry to those studied by Johari *et al.*[1-3] and the high value of the activation enthalpy is not necessarily anomalous. It is, however, remarkable that the β processes of similar solute molecules (such as CH_2Br_2, SCl_2, and $SOCl_2$) which we measured in decalin solvent during the course of this work do not have high activation energies. These solute molecules are only slightly larger than CH_2Cl_2. To confirm the existence of the β peak in CH_2Cl_2 decalin, the solution was monitored for loss and permittivity at a fixed frequency (1 kHz) while rapid cooling from room temperature was effected (about 10 K per min at Tg). Under these conditions measurement of Tg is less accurate and temperature gradients may exist in the sample. However, the permittivity increases from 2.6 at 293 K to 3.3 at about 160 K below which the value decreases and appreciable loss is observed. The loss is again minimal at about 136 K until at lower temperatures the second loss peak appears (as observed under constant temperature conditions). The main loss process is clearly observable in the 130–160 K regions, and not at 110 K.

To characterize this process in more detail a study (see below) of CH_2Cl_2 in more stable decalin/toluene or decalin/cholesteryl oleyl carbonate solvents allows both α and β processes in CH_2Cl_2 to be characterized. The β process appears in the kHz region at the same temperature as for the present system and its activation energy has the same large value.

In view of the possible plasticizing effect of CH_2Cl_2 solute on the fluidity of decalin, the glass transition temperature was measured for 5% and 10% v/v solutions. No appreciable lowering of Tg (less than 10 K) was found so the β process observed at 110 K is a property of the glassy state of this system.

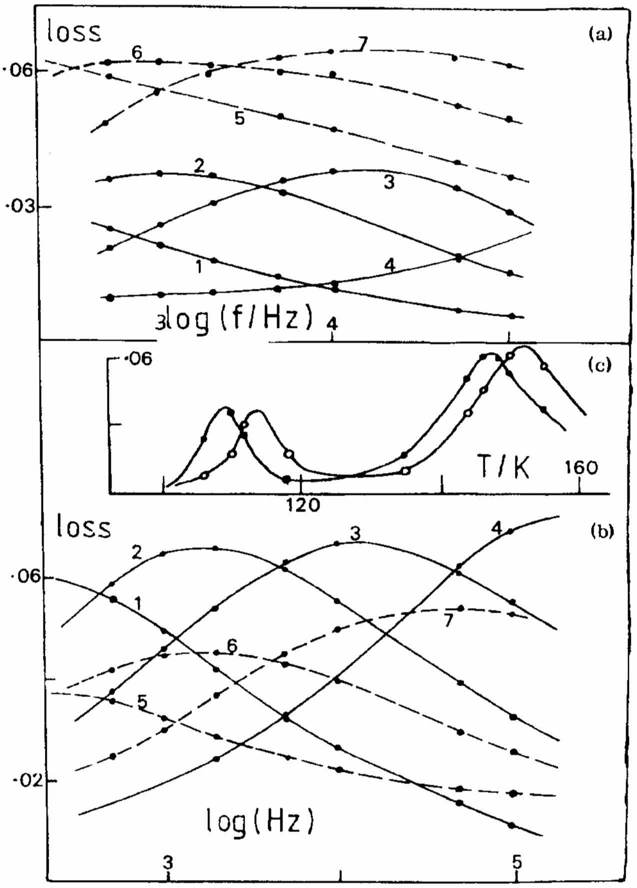

FIG. 7. (a) Dielectric data for 10% v/v CH_2Cl_2 in 1/7 cholesteryl oleyl carbonate/decalin glass forming solvents $\epsilon''(\omega)$ vs log(f/Hz). (1) 106 K (β process); (2) 110 K (β process); (3) 112 K (β process); (4) 116 K (β process); (5) 144 K (α process); (6) 146 K (α process); (7) 150 K (α process). (b) Dielectric data for 10% v/v CH_2Cl_2 in 1/9 toluene/decalin. (1) 115 K (β process); (2) 118 K (β process); (3) 120 K (β process); (4) 123 K (β process); (5) 137 K (α process); (6) 141 K (α process); (7) 144 K (α process). Inset (c) Loss (ϵ'') vs temperature (K) for Fig. 7(a). (1) β process; (2) α process.

The published[16] far infrared spectrum for the 4% v/v CH_2Cl_2/decalin system peaks at 95 cm^{-1} at 114 K which is appreciably lower than the spectrum for a 10% v/v solution. A measurement for a 5% v/v concentration also given in this figure confirms this variation with concentration and thus indicates that "solvent shifts" may occur even in a rigid environment and apparently with greater effect, the shift on dilution from 10% to 5% at 107 K being 10 cm^{-1}, while at room temperature it is only 2 cm^{-1}. A concentration effect was also found in the kHz region as a broadening of the β peak from 3.6 decades of half-width to 4.0 decades, but without any apparent change in activation energy.

To further attempt to verify the hypothesis made for the β process, that it occurs only for favorable solute to solvent geometry and size ratios, the motion of CH_2Cl_2 was studied in several mixed solvents. To create only slight changes from the decalin environment, neopentane- or cyclohexane- (both nondipolar,

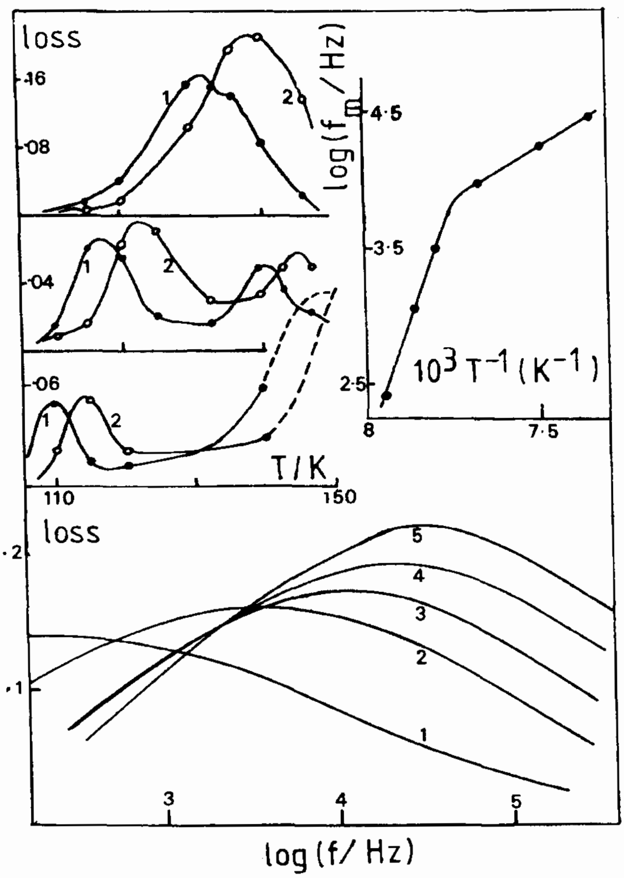

FIG. 8. Dielectric data, for 10% v/v CH_2Cl_2 in toluene/decalin. (a) 3/7 toluene/decalin; (1) 125.5 K; (2) 128 K; (3) 130 K; (4) 133 K; (5) 136 K. (b) Arrhenius plot for the peaks of Fig. 8(a); plot log (f_{peak}/Hz) vs 10^3 T^{-1} (K^{-1}). (c) Comparison of peaks in glasses of increasing toluene content. Loss vs Temp. *Top* (1) 1 kHz; (2) 100 kHz in 3 : 7 toluene/decalin. *Center* (1) 1 kHz; (2) 100 kHz in 1 : 9 toluene/decalin. *Bottom* (1) 1 kHz; (2) 100 kHz in pure decalin.

near-spherical molecules) decalin mixtures were used as solvents. The former gave glassy solutions in all proportions with decalin and the latter at least up to 50% v/v. Despite the differences in glass transition temperature (as low as 120 K for 5% neopentane) the process was still observed at kHz frequencies at about 110 K with the same high activation energy and slightly increased intensity (30%). Again crystallization prevented spectral observation of the α process seen transiently on cooling. However, by combining decalin with the lath-like molecules of cholesteryl oleyl carbonate a more stable system with CH_2Cl_2 may be formed and both α and β processes have been observed. For 10% v/v CH_2Cl_2 in 1–7 cholesteryl oleyl carbonate/decalin, the α peak is observed at 150–146 K. (Figure 7) while almost 40 K lower the β peak is observed with the same activation energy and a lower intensity than for the CH_2Cl_2-decalin system (by 50%). The α process involves relaxation of both CH_2Cl_2 ($\mu = 1.6$ D) and cholesteryl oleyl carbonate ($\mu = 1.14$ D) although the latter appears from pure solution measurement, to contribute less than 20%. For 10% CH_2Cl_2 in 1–3 cholesteryl oleyl carbonate/decalin, the β process disappears and only a more intense α process is observed. A similar behavior occurs for toluene/decalin solvent as shown in Fig. 7. For 10% CH_2Cl_2 in a 1/9 toluene/decalin solvent the system is stable and both α and β peaks may be characterized. Less than 10% of α peak intensity is estimated to be due to toluene so that activation energy of 119 kJ mol^{-1} may be associated with CH_2Cl_2 motion in this solvent and can be compared with values of from 138 to 170 kJ/mol for halobenzene solutes in decalin. The β process has an activation energy of 107 kJ mol^{-1} and is of greater intensity than for this concentration in decalin. In a 2/8 toluene/decalin solvent the β peaks have lost intensity to the α process while in a 3/7 toluene/decalin system the β peak is absent and the α peaks are of variable intensity and over three times the height of those in the 1/9 toluene/decalin system (Fig. 8). One particular feature of the 3/7 toluene/decalin system is that the activation energy plot is nonlinear (Fig. 8). The initial slope implies 28.5 kJ mol^{-1} which increases at 129 K to 120 kJ mol^{-1}. The estimate of *Tg* for this system (by calorimetry) is 127 K, so it appears that at 129 K, the α and β processes separate, the β process being unobserved but presumed to evolve along the line of the lowest slope.

A parallel study has been completed by Moliton[18] for solid solutions of diethyl-ether in *n*-pentane. This revealed kHz dielectric absorptions at low temperatures up to 30 K below the melting point (142 K) whose intensities initially increased linearly with concentration but above 2.5% fell sharply to a negligible level above 4%. The activation energy for each concentration remained at a value of 30.7 kJ mol^{-1}. In the present comparison of CH_2Cl_2 systems, the polarity has been increased by adding toluene or cholesteryl oleyl carbonate to a point where the CH_2Cl_2 absorption has become negligible but without change in ΔE. Moliton's measurements have been repeated for 2% ether concentration to confirm this rotation in the solid phase, and a higher activation energy of 76 kJ mol^{-1} was obtained.

As the activation energy of the CH_2Cl_2 β process does not vary significantly with solvent changes it appears that the solute experiences the same environment in all cases and could be due to a specific association with decalin molecules. This behavior in mixed solvents appears to be specific to CH_2Cl_2 systems as a 10% solution of chlorobenzene in 1 : 1 cholesteryl oleyl carbonate: decalin solution still revealed both α and β processes.

It is clear that further accurate work would help explain the β processes observed. The most common manifestation of the β process is as a high frequency shoulder on the main α process, as exemplified by the 10% chlorobenzene/decalin system. The results for several more solutes have been presented elsewhere.[15] The activation energies for these β shoulders are between 24 and 30 kJ mol^{-1} values which are intermediate between the low ones found for tetrahydrofuran and C_6H_5F and the high value for CH_2Cl_2. Arrhenius plots have been given elsewhere, all the α processes converge to "zero frequency" as *Tg* is approached. A variety of relaxation behavior is exhibited in the decalin glass medium, for various solutes, but none has so high an activation energy as CH_2Cl_2.

An analytical approach to these spectral features has been developed.[19] This is equivalent to assuming a distribution of nonequivalent, time-independent sites (Johari's view[1-3]) and implies that the glassy systems are nonergodic, i.e., the averages over time and over molecules are not equivalent.

Finally, we make a specific comparison of results in three glasses at 107 K. The temperature shift of the γ peak for solutes in pyridine/toluene is greater than for those in the other solvents. If we define a torque increment by $\Delta Tq = Tq\,(107\text{ K})/Tq\,(293\text{ K})$ (where Tq is the product of reduced m of $I(I_r)$ and $\bar{\nu}^2_{\max}$) then ΔTq is large in this glass. (This is true also for other solutes, specifically C_6H_5F (10%); CH_2CN (3%); pyridine (10%); $C_6H_5NO_2$ (5%); C_6H_5CN (3%), all v/v). The low frequency dielectric decrement, defined by $\Delta\epsilon' = (\epsilon_0 - \epsilon')/(\epsilon_0 - \epsilon_\infty)$ is also correspondingly high. The question still remains as to whether it is the greater polarity of the pyridine/toluene medium that prevents rotation in this glass compared to decalin and o-terphenyl, or whether it is the kinematic effects of differing solvent molecular structure. From our results on solvent effects in the far infrared the latter is unlikely.

ACKNOWLEDGMENTS

The S.R.C. is thanked for financial support to both authors and an equipment grant (GR/A/8598.8). Dr. A. H. Price, Dr. G. J. Evans, Dr. G. Williams, Dr. J. Goulon, and Dr. J. L. Rivail are thanked for loan of apparatus and criticisms.

[1] G. P. Johari, J. Chem. Phys. 58, 1766 (1973).

[2] G. P. Johari and C. P. Smyth, J. Chem. Phys. 56, 4411 (1972).

[3] G. P. Johari and M. Goldstein, J. Chem. Phys. 53, 2372 (1970).

[4] G. Williams and P. J. Hains, Chem. Phys. Lett. 10, 585 (1971).

[5] N. G. McCrum, R. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).

[6] M. W. Evans, A. R. Davies, and G. J. Evans, Adv. Chem. Phys. 44, 255 (1980); M. W. Evans, G. J. Evans, W. T. Coffey, and P. Grigolini, *Molecular Dynamics* (Wiley-Interscience, New York, 1982), p. 800.

[7] G. Williams, Chem. Rev. 72, 55 (1972).

[8] M. W. Evans, Adv. Mol. Rel. Int. Proc. 10, 203 (1977) (rev.)

[9] J. S. Rowlinson and M. W. Evans, A. Rep. Chem. Soc. A, p. 5 ff (1975).

[10] D. M. Tildesley and W. B. Streett, Faraday Discuss. No. 66, 27 (1978).

[11] B. J. Berne and R. Pecora, *Dynamical Light Scattering with Applications to Chemistry, Physics and Biology* (Wiley-Interscience, New York, 1976).

[12] C. J. Reid, Ph.D. thesis, University of Wales, 1979.

[13] P. Debye, *Polar Molecules* (Chem. Cat. Co., New York, 1929).

[14] C. J. Reid, R. A. Yadav, G. J. Evans, M. W. Evans, and G. J. Davies, J. Chem. Soc. Faraday Trans. 2 74, 529 (1978).

[15] C. J. Reid and M. W. Evans, J. Chem. Soc. Faraday Trans. 2 75, 1218 (1979).

[16] C. J. Reid, G. J. Evans, and M. W. Evans, Chem. Phys. Lett. 56, 529 (1978).

[17] M. W. Evans, R. F. S. Moutran, and A. H. Price, J. Chem. Soc. Faraday Trans. 2 71, 1854 (1975).

[18] A. Moliton, J. Mol. Struct. 13, 261 (1971).

[19] J. H. Calderwood and W. T. Coffey, Proc. R. Soc. London Ser. A 256, 269 (1977).