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The evolution of molecular dynamics from picoseconds to years

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Abstract—The dielectric relaxation of dipolar solutes in vitreous and viscous decalin is composed of at least two loss peaks. There is an universal γ process appearing at THz frequencies and equivalent to the Poley absorption in liquids, and a low frequency process sometimes resolved into α and β components. The complete spectrum covers twelve frequency decades or more.

The process of whole molecule vibration, or torsional oscillation, of molecular dipoles evolves dynamically in ultra-viscous and vitreous environments 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 sub-hertzian frequencies to THz frequencies (far i.r.), where the short-time molecular dynamics can be detailed using the power absorption coefficient. This occurs universally and can be characterized as a γ loss-process, the high frequency adjunct of the α and β processes discovered by Johari and Williams and their coworkers[1–6]. The complete (α, β, γ) profile stretches over many decades of frequency and provides the molecular dynamicist with the challenge of simulating or describing it mathematically. Debye-type rotational diffusion, for example, results in a loss curve which peaks only once with a half-width of 1.12 decades[7–11].

This has widespread implications in fields of spectroscopy[7–10] which give insights into aspects of molecular dynamics other than dipolar rotational relaxation. These include i.r. and Raman bandshapes analysis (roto-vibrational 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 viscoelastic relaxation and others.

Johari *et al.* [1–3] and Williams *et al.* [4–6] has shown that at low frequencies in a wide range of solutions the dielectric loss in the ultra-viscous and vitreous environments peaks more than once. There is a secondary relaxation which appears at higher frequencies than the main dielectric loss. Arrhenius plots of the frequency of maximum loss against 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 apppear 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 [7–9].

However, both peaks are reflections 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, which is related to the spectrum via a Fourier transform. *The properties of the classical, orientation (dipole) auto-correlation function* [7–10] *imply that there will be a further peak in the dielectric loss at frequencies in the far i.r. region* (2–250 cm^{-1}).

The (α, β, γ) triad can be characterized over the whole range from zero to THz frequencies for dipolar solute molecule in glassy and viscous solvents. This extends the work of Johari and Williams *et al.* to include the γ peak. The implications for the other techniques mentioned above is 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 β or α) is also within range of computer simulation methods which are designed to solve the equations of motion of some hundreds of molecules interacting by means of a model potential.

On a still wider basis the existence of three peaks in the extreme broad-band dielectric spectrum challenges much of the current thought on molecular dynamical modelling [7–10, 12–14]. 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 discarded if it cannot also produce an (α, β, γ) profile as the viscosity of the environment increases. In this context we believe that dielectric and far i.r. spectroscopy (or "zero-THz spectroscopy" for convenience) is an incisive probe into 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 $\epsilon^*(0)$.

We have studied [12–14] some 23 dipolar solute molecules in ultra-viscous and vitreous states of various glass forming solvents. To exemplify our data we consider 10% v/v halogenobenzene/decalin systems, and CH_2Cl_2/decalin systems. In Figs. 1 and 2 we show results in the form of dielectric loss $[\epsilon''(\omega)]$ and i.r. power absorption coefficient $[\alpha(\omega)]$ related by

$$\alpha(\omega) = \omega\epsilon''(\omega)/[n(\omega)c] \qquad (1)$$

where c is the velocity of light and $n(\omega)$ the frequency dependent refractive index. The power absorption coefficient is observed naturally by attenuation of i.r. radiation, and because of the ω factor in equation (1) provides us with a detailed "close-up" of the high frequency part of the overall loss curve—i.e. the far i.r. spectrum. These are illustrated in CH_2Cl_2/decalin glass and halogenomethane/decalin glass. These spectra detailed the short-time molecular movements which in ultra-viscous and vitreous media eventually evolve into motions taking place on an immensely slower time scale, observable as (α, β) features in the dielectric loss. This point is emphasized by the very large shifts between liquid and glass in the peak frequencies of the far i.r. (γ) process. These are proportionately different for each solute, and are particularly large for CH_2Cl_2 in various glassy mixtures (Fig. 1). Note that for models such as classical rotational diffusion, the far i.r. peak is not even defined as such. The theory produces an unrealistic plateau absorption due in effect to neglect of all memory and inertial effects [7–10].

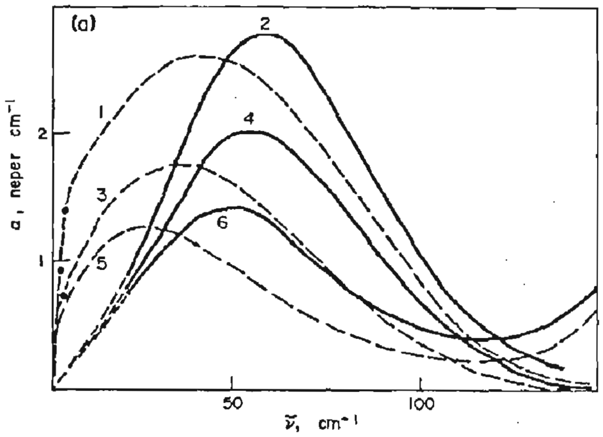

Fig. 1(a). Power absorption coefficient $\alpha(\bar{\nu})$ (neper cm^{-1}) vs $\bar{\nu}$(cm^{-1}) for halogenobenzenes in decalin (10% v/v concentration). (1) Fluorobenzene/decalin at 293 K ($\lambda_{max} = 39$ cm^{-1}, where $\omega = 2\pi\bar{\nu}c$); isotropic liquid solution; (2) at 110 K, $\bar{\nu}_{max} = 57$ cm^{-1}, vitrous 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}).

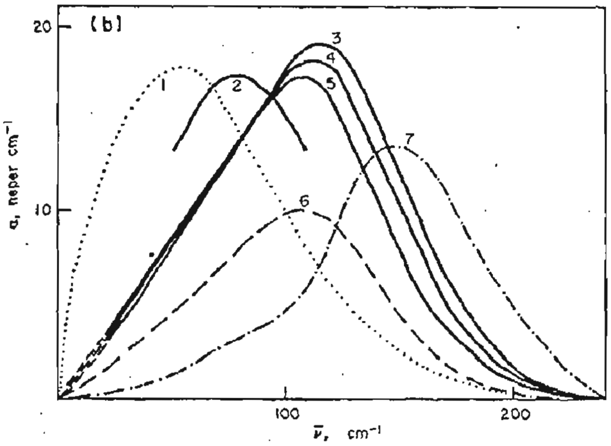

Fig. 1(b). Far i.r. spectra for methylene chloride systems [plot of optical power absorption $[\alpha(\bar{\nu})]$ coefficient (neper cm^{-1}) vs wavenumber ($\bar{\nu}$ in cm^{-1})]. (1) 10% v/v CH_2Cl_2 in decalin at 293 K; (2) at 220 K in the ultra-viscous liquid; (3) at 107 K in the glass; (4) at 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.

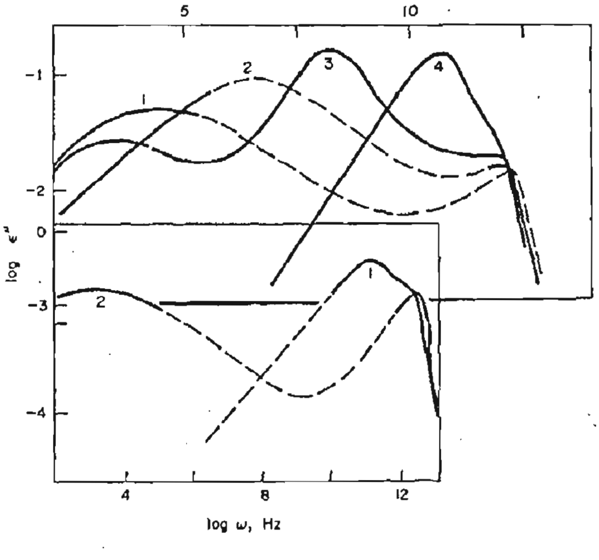

Fig. 2. *Top.* Zero-THz dielectric loss spectrum for 10% v/v fluorobenzene in decalin, illustrating the (α, β, γ) triad at 143 K in the supercooled solution. At 293 K the spectrum is made up only of β and γ components, as is the case in the glass at 110 and 77 K, the α component in the latter two cases 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. *Bottom.* CH_2Cl_2/decalin (10% v/v). (1) 293 K; (2) 110 K (Glass, illustrating the β process peak at low frequencies, the α peak is off scale at sub-hertzian frequencies). Log/log plots.

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 i.r. portion appears as the highest frequency feature labelled γ. The complete loss curve (α, β, γ), 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 dynamicists are currently restricting their model evaluations to a much too narrow a range of both macroscopic viscosity and of frequency.

The kHz α process and THz γ process in CH_2Cl_2/decalin are both dramatically temperature dependent, but in *opposite* senses, the latter shifts to higher frequencies (Fig. 1) and the former to lower on supercooling and vitrification. The β process of CH_2Cl_2 is unique in that it is associated with a very high activation energy comparable with that of its own α process and the α processes of other small dipolar solutes. We have fully characterized the (α, β, γ) triad in CH_2Cl_2 using different solvent glasses and this work is reported elsewhere[14].

We speculate on the physical origins of the α, β and γ loss processes as follows:

(1) The far i.r. frequency range is that in which the fast torsional oscillations of the molecular dipole cause absorption. In the limit of free rotation the orientational spectrum is the quantized set of $\Delta J = 1$ transitions where j is the rotational quantum number.

(2) In liquids the presence of frequent collisions and a mean square torque causes the peak frequency of the $\Delta J = 1$ envelope to move to high frequencies essentially because energy is dissipated and regenerated during each collision process. This shift is continued as the viscosity of the liquid increases and during the vitrification process. In the glassy condition, although the lower temperature means less energetic collisions, the hindrance (or potential well) to torsion [7–10] is very high and fast angular reorientation through large arcs almost impossible.

(3) As time evolves from an arbitrary initial $t = 0$ the lack of long range ordering in the ultraviscous and vitreous solutions implies that, very slowly, a molecule of dipolar solute is able to reorient through the complete arc of solid angle available. The orientational autocorrelation function decays gradually to zero. The details of this dynamical process appears at long times as the (α, β) loss, theories for which are available in the technical literature [1–6]. These theories are incomplete.

It is overwhelmingly important to realize the enormous sweep of timescale involved in the complete evolution from γ frequencies to those of the β and ultimately α processes. This lies at the heart of the dynamical problem.

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