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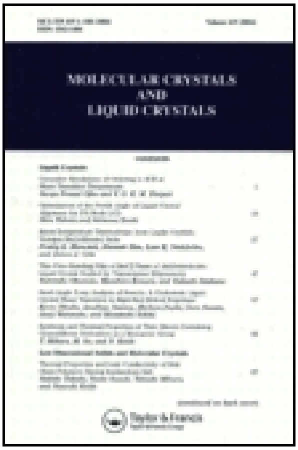

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Solvation in Glassy Materials

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SOLVATION IN GLASSY MATERIALS

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Abstract Time resolved phosphorescence spectroscopy of molecular probes in organic supercooled liquids indicates solvation dynamics active on the ms-s time scale. A detailled analysis of the positive solvatochromism of quinoxaline allows for experimentally quantifying the change in dipole moment upon T_1<-S_0 excitation and the polarity of supercooled liquids. Solvation in macroscopically unpolar solvents indicates the important role of microscopic polarity for rationalizing the local dielectric responses governing the solvation dynamics.

INTRODUCTION

The impact of solvents on the electronic energy levels of a solute molecule is a well known feature as manifested in the Stokes shifts of emission bands relative to gas phase values.[1] Since part of the polarization energy responsible for the spectral shift involves reorientation of permanent solvent dipoles, the energy levels of the probe change gradually. The time scales of these solvation dynamics are linked to the viscosity of the medium and must be of the order of the emission lifetime to be observable. Employing fluorescence dyes gives access to the fs-ns range usable to temporally resolve solvation dynamics in liquids of low viscosity.[2]

Dielectric relaxation data of supercooled liquids clearly indicated the ability of rotational alignment of dipoles in media of high viscosity[3], i.e. just above the glass transition temperature T_G where the dominant molecular motion becomes frozen on the time scale of ≈100s. In analogy, solvation dynamics in such systems are slow but experimentally observable using the emission of long lived triplet probes as recenctly demonstrated[4]. The scope of the present paper is to summarize the results[5] obtained by analysing solvation dynamics for different probe molecules in a variety of organic solvents in a temperature range of approximately $T_G \pm 10K$. The data yields a consistent outline of solvation in supercooled liquids in agreement with theoretical predictions.

EXPERIMENT

Solutions of naphthalene (NA), quinoline (QI) and quinoxaline (QX) at a concentration of $2 \cdot 10^{-4}$ mol/mol in various solvents served as samples. The glass forming solvents covered a T_G range of 90K to 170K and varied in polarity from ≈0 to 0.75 if gauged in terms of E_T^N. In the order of increasing polarity we used 3-methylpentane, 4-methylheptane, triethylamine, 2-methyl-THF, 3-bromopentane, N-methyl-ϵ-caprolactam, n-butanol, 1,3-propanediol and a methanol/ethanol mixture (4v/1v). Probe molecules were excited with the 308nm line of an excimer laser operated at a temporal puls seperation of a least $3 \cdot \tau_{PH}$, τ_{PH} being the phosphorescence lifetime. Emission spectra of the $T_1 \rightarrow S_0$ (0-0) bands were recorded with an optical multichannel analyzer with $2.5 cm^{-1}$ spectral resolution and time windows covering the 500μs to 2s range. Samples were kept in a vacuum sealed cuvette in a $L\text{-}N_2$ cryostat which allowed a thermal stability of ±0.1K at ±0.5K reading accuracy.

RESULTS AND DISCUSSION

The observed $T_1 \rightarrow S_0$ (0-0) emission profiles are characterized by by their mean energy ν and width σ according to a least square Gaussian shape analysis. A typical temperature dependence of ν and σ recorded at a fixed time window is illustrated in Figure 1, also characterizing the notations used below. The increase of the Stokes shift within 0-1ms with temperarture, starting at T_G, indicates the thermally induced dynamics of solvation. In parallel, the width σ increases above T_G and displays a peak of height σ_{tr} at T_S, where T_S denotes the temperature at which $\nu=[\nu(0)+\nu(\infty)]/2$ for the given (arbitrary) time window.

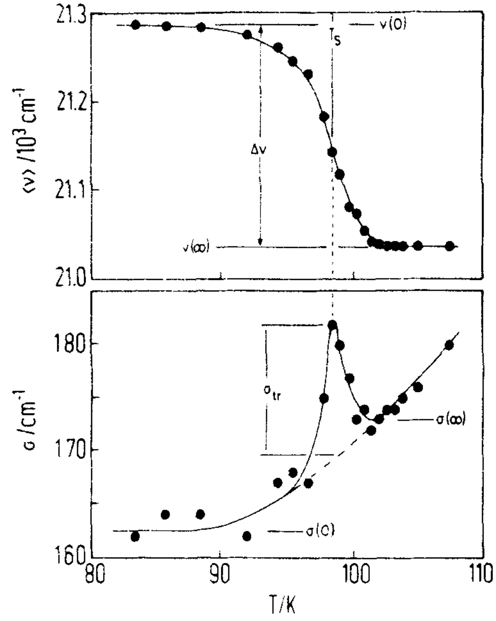

FIGURE 1 Mean emission energy ν and width σ as a function of temperature recorded 1ms after excitation for the sample QX/MTHF (T_G=90K).

Plotting the spectral width $\sigma(0)$ as a function of the total Stokes shift $\Delta\nu$ for all solute-solvent combinations reveals a linear relation of the form $\sigma(0)=0.32\cdot\Delta\nu+84\text{cm}^{-1}$. Approximating the homogeneous contribution σ_{hom} to $\sigma(0)$ by 1cm^{-1} per Kelvin we arrive at $\sigma_{inh}\approx\sigma(0)-0.8\ \text{cm}^{-1}\cdot(T_S/K)$. σ_{inh} obtained in this manner obeys $\sigma_{inh}=0.28\cdot\Delta\nu$, indicating that the inhomogeneous width is governed by the dipolar guest/host coupling as is $\Delta\nu$, rather than reflecting differing degrees of configurational disorder. Noting that σ_{tr}

scales with $\Delta\nu$ ($\sigma_{tr}\approx 0.08\cdot\Delta\nu\approx 30\%\cdot\sigma_{inh}$) while $\sigma(\infty)-\sigma(0)$ does not depend on $\Delta\nu$ shows that the peak of σ at T_S is of inhomogeneous nature and that the constant increase of σ above T_G is a homogeneous contribution, due to the onset of increased molecular mobility above T_G.

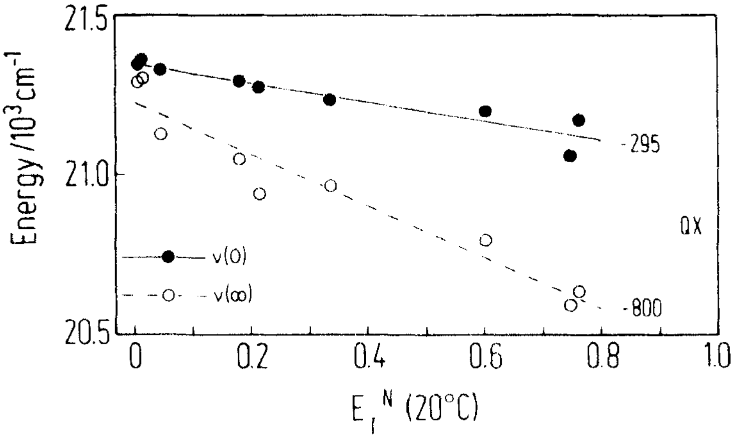

FIGURE 2 Energies $\nu(0)$ and $\nu(\infty)$ plottet versus solvent polarity for the probe QX. The slopes are stated in cm^{-1}.

The solvatochromism of QX is depicted in Figure 2, the corresponding curves for NA and QI are practically horizontal but with a constant offset for $\nu(0)$ and $\nu(\infty)$. The responsible changes in dipole moment $\mu_E-\mu_G$ upon $T_1\text{<-}S_0$ excitation are calculated via the formula[6,7]

$$\nu(0)-\nu(\infty) = \frac{2(\mu_E-\mu_G)^2}{4\pi\epsilon_0 cha^3}\left[\frac{\epsilon_C+2}{3}\right]^2\left[\frac{\epsilon_S-1}{2\epsilon_S+\epsilon_C}-\frac{n^2-1}{2n^2+\epsilon_C}\right] \qquad (1)$$

setting a=3Å and $\epsilon_C=1.75$. The resulting $\mu_E-\mu_G$ values are ≈0 (NA), ≈0 (QI) and 1.6D (QX) in perfect agreement with the theoretical (HF/3) calculations[8] yielding 0.15, 0.01 and 1.31 in the same order. Solvation of probe molecules with $\mu_E\approx\mu_G$ like NA ($\Delta\nu=63\text{cm}^{-1}$) and QI ($\Delta\nu=126\text{cm}^{-1}$) points toward the significance of induced dipole moments by vitue of differing polarizabilities in the ground and excited states.

The observed solvation in 'unpolar' solvents as 4-methylheptane clearly indicates the important role of a microscopic polarity of solvents for local dielectric responses as monitored by the solvation dynamics. Note that Figure 2 suggests a hypothetical unpolar medium at the intercept of the two lines ($E_T^N=-0.22$ and $\nu=21420cm^{-1}$).

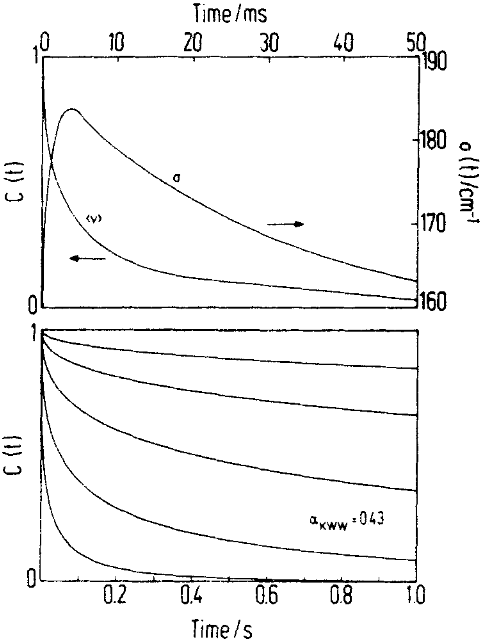

FIGURE 3 Upper: Typical relation between C(t) and the transient broadening of the spectral width σ. Lower: Typical reconstructed C(t) data of QX/MTHF for $91K \leq T \leq 95K$ reflecting highly dispersive relaxation.

The dynamics of the relaxation process are conveniently described by the Stokes shift correlation function $C(t)=[\nu(t)-\nu(\infty)]/[\nu(0)-\nu(\infty)]$. For the samples under study and near T_G we find C(t) curves matched by the KWW decay function $C(t)=\exp[-(t/\tau)^{\alpha}]$ with typical dispersion parameters $\alpha=0.4$. Identical decay behaviour for the probes assures that all data is obtained in the regime of linear responses. The apparent activation energies of mean solvation times τ_S exceed the corresponding values for viscosity or dielectric relaxation by ≈50%. On the other hand, the theoretically predicted relation $\tau_L \leq \tau_S \leq \tau_D$ with τ_D being the dielectric relaxation time and $\tau_L=(\epsilon_\infty/\epsilon_S)\cdot\tau_D$ holds in the cases where dielectric data is available. A similar agreement is found for the dispersion in terms of α accessible by means of the MSA theory[9] basing on dielectric data. The above notions are not compatible with regarding only the continuum aspect of the solvent. In contrast, microscopic details play an important role in the solvation dynamics in supercooled liquids as also true for normal liquids. Distinct behaviours of protic and aprotic solvents are not observed due to the cooperativity of glassy systems obscuring such effects observed in normal liquids.

In summary, experiments on solvation dynamics in supercooled liquids parametric in temperature, solvent polarity and probe molecule serve as a promising tool for delineating relaxational processes in the ms-s regime using spectroscopic techniques. The findings are quantitatively consistent with theories and allow for determining solvent polarities as well as dipole moment changes. In addition, the spectral widths are unambiguously related to the dipolar guest/host coupling.

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