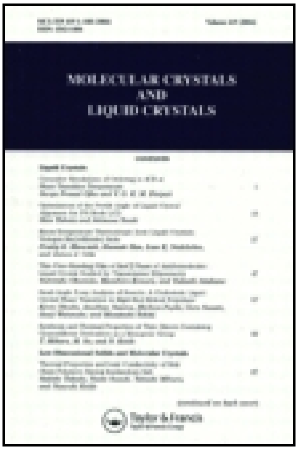

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TRANSIENT HOLE BURNING IN LIQUIDS

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Abstract The connections between electronic line broadening processes in solids and liquids have been explored with transient hole burning measurements. Homogeneous and inhomogeneous broadening in solids correspond to phonon-induced and structural components of relaxation in the liquid. These ideas lead to a quantitatively accurate viscoelastic model of electronic state solvation in liquids in which changes in molecular size upon excitation are responsible for the coupling to the surrounding medium. Mode-coupling theory accurately represents the decay shapes and temperature dependence of the structural relaxation.

INTRODUCTION

When an impurity molecule, i.e a solute, is placed in condensed phase matrix, its electronic states are strongly perturbed. Studies dating back to the 1950's have revealed the major mechanisms involved when the matrix is a low temperature crystal.[1] However, in the case of a liquid matrix, many basic features are being seen only now. The dynamics in liquids are both complex and very rapid and have been difficult to study until recently. Building on the more familiar permanent hole burning technique used in solids, we have developed the ultrafast transient hole burning (THB) experiment to tackle this problem. Using THB, we have traced the connection between standard concepts of solid-state spectroscopy, such as phonon sidebands and inhomogeneous broadening, and liquid-state spectroscopy.

Any study of line broadening must deal with two intertwined effects: describing the dynamics of the matrix, and determining the mechanism through which the solute electronic states couple to the matrix. The dynamics of the matrix consist of many different types of motion with a wide range of characteristic time scales. The coupling mechanism determines which of these time scales affects the solute.

After a brief introduction of transient hole burning, we will discuss the connection between liquid and solid dynamics. The next section presents a model for the coupling of the solute to the solvent, which is the analog of electron-phonon coupling in solids. Finally, we return to the dynamics of liquids and compare transient hole burning results to recent mode-coupling theories, which attempt to address the dynamics leading to the liquid-glass transition.

TRANSIENT HOLE BURNING

At any instant, the solute molecules in a solution experience a variety of local environments. A distribution of transition energies and broadening of the absorption line result. In the ideal transient hole burning experiment, a pulse of light shorter than the dynamics of the solvent excites only those molecules which are resonant at that instant. A subsequent, rapid transmission measurement will see a narrow "hole" in the absorption spectrum. In addition, it will see a narrow replica of the fluorescence spectrum due to stimulated emission from the excited-state molecules. As the time between creating and reading the hole increases, movement of the solvent molecules randomizes the solute transition energies, causing the hole in both the ground and excited states to broaden. In the excited state, the solvent distribution will also shift to a new mean position, in which the solvent is equilibrated to the excited state properties of the solute. The result is a Stokes shift, i.e. a separation of the 0-0 transitions observed in the ground-state hole and the excited-state emission.

Both of these effects, hole broadening and Stokes shifting are measured as a function of delay time to monitor the dynamics of the solvent perturbations. Figure 1 shows typical hole burning spectrum. A detailed model of the absorption and emission vibronic structure is broadened and shifted to match the observed spectrum. The current experiments have a time resolution of 1.5 ps. However, because the broadening and Stokes shift are zero in the absence of any solvent motion, the amount of relaxation which has occurred within the time resolution is known. Other experimental methods give only relative amounts of relaxation,[2] complicating the interpretation.

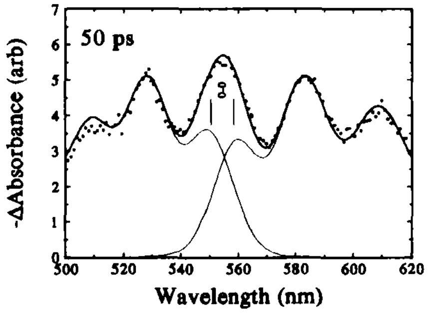

FIGURE 1 A typical transient hole burning spectrum (dots) and model fit (heavy curve). The light curves are the absorption bleach (right) and stimulated emission (left) components of the model. Both the broadening of the components and the separation of the 0-0 lines (Stokes shift) indicate the amount of solvent relaxation which has occurred within the delay time of the measurement.

LIQUID DYNAMICS I - PHONON-LIKE VS STRUCTURAL MOTION

In low-viscosity, room-temperature liquids, most of the solvent relaxation is complete within a picosecond. However, as the temperature is reduced, two distinct components to the relaxation become evident. One component remains subpicosecond as the temperature is lowered. The other component slows dramatically.[3-7]

We have attributed the fast component of the relaxation to the liquid-phase analog of phonon sidebands in solid-state spectroscopy. To confirm this idea, we have measured the phonon-induced linewidth of dimethyl-*s*-tetrazine in glassy *n*-butylbenzene by permanent hole burning.[5,6] The linewidths fit simple solid-state theory, which predicts a $T^{1/2}$ temperature dependence (Fig. 2A). When this line is extrapolated into the liquid phase, it correctly predicts the amount broadening due to the fast component of solvent relaxation, as indicated by the hole width seen at 1.5 ps. Similar results have been seen in other systems.[3,4,7] Despite the liquid's high mobility, it is possible to define an instantaneous structure within it. At short times, the dynamics consist only of phonon-like vibrations about this structure.

After this fast phonon-induced relaxation, the hole spectra undergo further relaxation until they match the full widths and shifts of the equilibrium absorption and fluorescence spectra. We attribute this slower relaxation to reorganization of the instantaneous solvent structure. Figure 2B shows that this structural relaxation time is proportional to the solvent viscosity in the nonpolar solvent *n*-butylbenzene.[6] This result contrast with results in polar solvents, where structural relaxation is found to be proportional to the dielectric relaxation time. This differing results indicate that a

FIGURE 2 Results for dimethyl-s-tetrazine in *n*-butylbenzene.

A. Phonon-induced linewidths in the glass measured by permanent hole burning (+) are fit to a $T^{1/2}$ temperature dependence (line). The extrapolation into the liquid phase agrees well with the fast component seen by transient hole burning in the liquid (∗, taken at 1.5 ps).

B. The time constant of the structural relaxation component compared to the solvent viscosity for.

different coupling mechanism is important in nonpolar as opposed to polar solvents. In either case, the structural relaxation time diverges at the glass transition. The structural component of the liquid linewidth becomes static inhomogeneous broadening in the solid.

A SOLUTE-SOLVENT INTERACTION MODEL

Previous models of solvent-solute electronic state interaction have been based on the interaction of the fixed charges on the solute and solvent, most prominently the permanent dipole moments.[2] These models cannot plausibly be applied to nonpolar solvent and solutes, nor do they predict the proportionality between viscosity and structural relaxation in *n*-butylbenzene.

We have proposed that the coupling in nonpolar systems arises primarily from the size difference between the ground and excited states.[8] As a simple, specific model, we have taken a viscoelastic continuum to represent the solvent and a cavity to represent the solute. Upon excitation, the radial force on the cavity boundary from the solute changes. The solvent responds on two time scales. First, an elastic wave propagates outward allowing partial expansion of the cavity and leaving shear strain in the solvent. This process is the phonon-induced relaxation seen in the experiments. On a slower time scale determined by the viscosity of the solvent, the shear strain dissipates, allowing the final reequilibration of the cavity size.

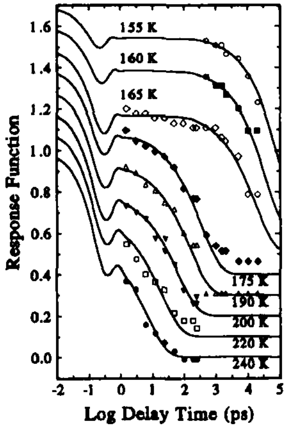

FIGURE 3 A comparison of transient hole burning data (points) to a viscoelastic model (curves). Each successive temperature has been shifted vertically by 0.1 for clarity. The subpicosecond component is due to phonon-induced relaxation Although experimental points in the subpicosecond region are not available, the model does predict the amount of relaxation seen in the first data points. The temperature dependence of the slower structural relaxation component agrees with the measured viscosity.

Figure 3 shows calculations from this model compared to experimental data from DMST in *n*-butylbenzene. The phonon-induced component is subpicosecond and largely temperature-independent as found by the experiment. The second component is slow at low temperatures, speeds up as the solvent viscosity decreases, and merges with the phonon-component at sufficiently a high temperature and low viscosity. Recent experiments on *s*-tetrazine in propylene carbonate have shown that this model also gives good agreement in a mixed system with a nonpolar solute and a polar solvent.[7]

LIQUID DYNAMICS II - COMPARISON TO MODE-COUPLING THEORY

In recent years, mode-coupling theories (MCT) have been developed which show promise for quantitatively explaining the dynamics of supercooled liquids.[9,10] Although many of the parameters of the theory will vary with the experiment used to measure the dynamics, two of them should be independent of experiment: the crossover temperature T_c, and the exponent parameter λ. An detailed set of light scattering results on propylene carbonate has recently been analyzed with MCT.[11] We have analyzed THB measurements on *s*-tetrazine in propylene carbonate, first to see if MCT can be successfully applied to solvation, and secondly to determine if the parameters determined by transient hole burning match those determined by light scattering.[12]

Relaxation in supercooled liquids is usually nonexponential. It has often been

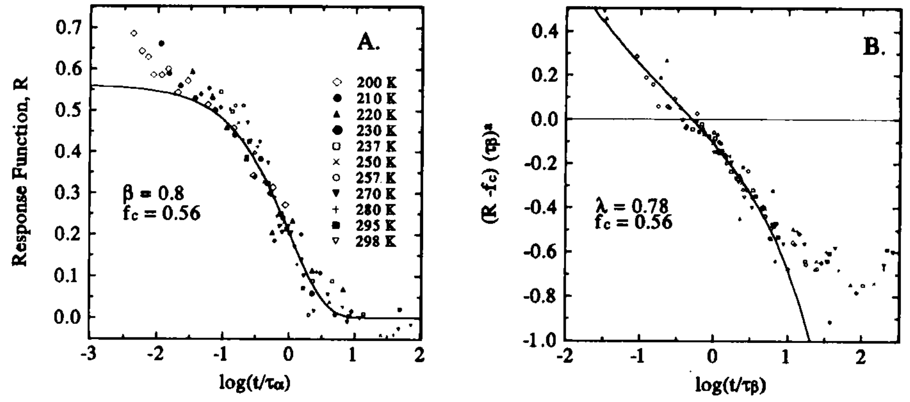

FIGURE 4 Transient hole burning of *s*-tetrazine in propylene carbonate.

A. The response function for each temperature has been shifted by τ_a. The curve is a stretched exponential representing the common α-relaxation. Deviations at short times and low temperatures are due to β-relaxation.

B. The response function for each temperature has been scaled by τ_β to test β-scaling. The curve is the mode-coupling β-relaxation function for $\lambda = 0.78$. Deviations at long times and high temperatures are due to α-relaxation.

hypothesized that the shape of the relaxation is invariant as the average relaxation time changes, but careful measurements show that this hypothesis often fails. Mode-coupling theory concludes that the decay should be divided into two overlapping time regions: an early β-relaxation and the main α-relaxation. Although the α-relaxation shape does not change, the β-relaxation shape obeys a more complicated scaling relationship.

The structural relaxation functions in propylene carbonate measured by THB clearly change shape as the temperature is lowered. However, the later stage of relaxation does have a constant shape, as shown in Fig. 4A. This shape is modeled as a stretched exponential. The early portions of the relaxation functions, which contain the deviations from stretched exponential behavior, are well described by the scaling laws predicted by MCT for the β-relaxation region (Fig. 4B). We conclude that α- and β-relaxation regions exist in propylene carbonate solvation dynamics and that MCT accurately describes the temperature dependence of the shape of the relaxation function.

The fitting of the relaxation function shapes yields two characteristic times for each function, τ_α and τ_β, and the exponent parameter λ. According to MCT, τ_α and τ_β should have power law temperature dependencies diverging at the same crossover temperature T_c. The power-law exponents, γ and a, are calculated from λ. Figure 5 tests these predictions. The times should fall on straight lines converging on a single value of T_c. Over most of the temperature range a good fit to the MCT predictions is found. The deviations seen at high temperature may signal a breakdown of the theory, or increased experimental error in measuring short decays.

Mode-coupling theory not only works well to describe the results from transient hole burning, but also describes light scattering with the same parameters. In fitting the THB results, the value of λ found by light scattering experiments is used.[11] The

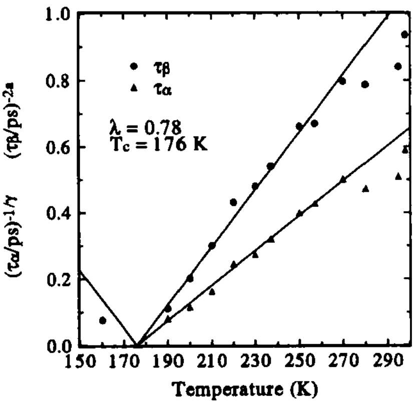

FIGURE 5 The characteristic times of the α- and β-relaxations follow the power laws predicted by MCT. The exponents are determined independently from light scattering experiments.[11]

crossover temperature is determined independently in the THB analysis, but the THB value of $T_c = 176$ K is close to the value of $T_c = 179$ K found in light scattering. The agreement of these parameters from fitting MCT to two distinctly different experiments is compelling evidence in favor of MCT.

SUMMARY

Transient hole burning is revealing new aspects of both the dynamics of liquids and the means by which electronic states couple to those dynamics. As the temperature is lowered, the dynamics split into two components: phonon-induced and structural. These components evolve into the phonon-sidebands and inhomogeneous broadening seen in solid-state spectra. A model based on coupling from a size difference in the electronic states predicts both the relative sizes of the phonon-induced and structural components and the temperature dependence of the structural relaxation times. Mode-coupling theory is successful in accounting for the nonexponential shape of the structural relaxation function and in relating the dynamics seen by transient hole burning with those seen by light scattering.

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