Probing Intermolecular Interactions with Picosecond Photon Echo Experiments

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I. Introduction

Because a tremendous amount of chemistry occurs in condensed phases, a detailed understanding of intermolecular interactions and dynamics on a microscopic level is very important. A molecule in a medium, whether it is a liquid, a glass, a membrane, or a crystal, feels a constantly changing array of intermolecular interactions. Heat is molecular motions: changing molecular positions and orientations. Since intermolecular interactions are distance- and angle-dependent, any condensed-phase system confronts us with a complex, time-dependent problem. Application of picosecond nonlinear spectroscopic experiments to condensed-phase systems is providing detailed new probes of fundamental condensed matter phenomena.

In this paper we will briefly discuss two problems: the nature of the electronic states of interacting solute molecules and the coupling of electronic states of a solute molecule to the mechanical degrees of freedom of the medium. These examples will illustrate the unique nature of the information that can be obtained from fast nonlinear experiments. In the picosecond photon echo experiments presented below, the samples are mixed molecular crystals or organic molecules in organic glasses. Molecular crystals have a long history as prototype molecular systems. Problems of electronic and vibronic spectroscopy, spin–orbit coupling, and intersystem crossing, to name a few, have received detailed study in molecular crystal systems. A mixed crystal contains guest molecules (solute) in a host crystal. The mixed crystal is a solid solution in which the guest molecules are randomly distributed spatially, but unlike a liquid solution, there is orientational order.

In contrast to a crystal, organic molecules in an organic glass do not experience environments which have orientational order. Molecules in a glass, as in liquid solution, have a wide distribution of environments which are associated with the structures of the solvent shells around each molecule. Unlike a crystal, the glass environments are not fixed, even at very low temperature (1.5 K).[1] In organic glasses, a particular local mechanical configuration is separated from other configurations by small potential barriers. Tunneling and thermal activation result in constantly changing environments around a solute molecule. This is somewhat akin to a liquid solution, except the time scale on which the environments change is orders of magnitude faster than in a liquid.

In a crystal, heat manifests itself as vibrations of the lattice, i.e., acoustic and optical phonons.[2] Acoustic phonons derive from molecular translations in the gas phase, whereas optical phonons derive from molecular rotations. The restoring forces present in the densely packed crystal couple the motions of the individual molecules. This coupling transforms the gas-phase translations and rotations into collective vibrational motions of the solid, the phonons. Thermal population of many different phonon modes produces an environment about a solute molecule which is constantly and rapidly fluctuating about some equilibrium lattice configuration. In a glass, similar fluctuations occur, but in addition, the local configuration can actually change.

If a sample is optically excited at the S_0 to S_1 transition frequency of a dilute solute (no solute–solute interactions) at very low temperature (phonon-induced fluctuations and configuration changes frozen out), then the only dynamics will be relaxation of the molecular

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electronic excited state to the ground state. This relaxation will result in a finite homogeneous line width in accord with the uncertainty relation $\Delta E \Delta t \geq \hbar/2$.[3] If the concentration of the solute is increased while remaining at low temperature, intermolecular interactions among the solute molecules should lead to the creation of a band of delocalized states.[4] The electronic excitation is no longer associated with a single molecule but rather with a state of the "impurity band", which has a complex structure of energy levels and transition probabilities. In principle, the onset of delocalization and the creation of an impurity band will be manifested in a broadening and change in shape of the homogeneous absorption line. On the other hand, if the concentration is kept low, but the temperature is raised, the phonon-induced fluctuations in a crystal or the phonon-induced fluctuations and configuration changes in a glass will lead to fluctuations in the solute molecule's energy and thereby cause broadening of the homogeneous absorption line.[5] If both the concentration and temperature are increased above the low-concentration, low-temperature limits, an additional line broadening mechanism, phonon-induced scattering between the delocalized states, can occur.[6,7]

The above discussion indicates that information about both solute electronic intermolecular interactions and solute–solvent interactions can be obtained from the solute homogeneous absorption line in mixed crystals or glasses. The problem is that a homogeneous absorption line is not usually observed in either crystals or glasses.[8] Different solute molecules have different static local environments, which give rise to a spread in absorption frequencies broader than the homogeneous line width. In crystals, lattice strains, defects, and vacancies result in inhomogeneous S_0 to S_1 absorption spectra which are typically 1–2 cm^{-1} wide.[9] In glasses the wide distribution of solvent shell structures results in inhomogeneous absorption spectra which are typically several hundred wavenumbers wide.[10] Therefore, absorption experiments yield line widths and shapes that are related to the distribution of local environments and not to solute intermolecular interactions or dynamics.

II. Picosecond Photon Echo Experiments

The Nature of the Experiment. The picosecond photon echo experiment is a time domain nonlinear experiment which can effectively extract the homogeneous line shape even when the inhomogeneous line width is thousands of times wider than the homogeneous width. The echo technique was originally developed as the spin echo in magnetic resonance in

1950.[11] In 1964, Kurnit, Abella, and Hartmann showed that this phenomenon could be extended to the optical regime as the photon echo.[12] Since then, photon echoes have been used extensively to study many gaseous and crystalline systems.[13] It is a two-pulse sequence. The first high-power pulse, tuned to the transition frequency, puts the solute molecules into superposition states which are mixtures of the ground and excited state. Each superposition has a microscopic electric dipole associated with it. This dipole oscillates at the molecular transition frequency. Immediately after the first pulse all of the microscopic dipoles in the sample oscillate in phase. Because there is an inhomogeneous distribution of molecular transition frequencies, the individual dipoles oscillate with some distribution of frequencies. Thus, the initial phase relationship is very rapidly lost. This is referred to as the optical free induction decay. After a time τ, a second high-powered pulse traveling along a path making an angle θ with that of the first pulse passes through the sample. This second pulse changes the phase factors of each molecular superposition state in a manner that initiates a rephasing process. Exactly at time τ after the second pulse, the sample emits a third coherent pulse of light along a unique path which makes an angle 2θ with the direction of the first pulse.

Two pulses enter the sample, but three pulses leave the sample. The third pulse is the photon echo. It is generated when the ensemble of microscopic dipoles are rephased at time 2τ. The phased array of microscopic dipoles behaves as a macroscopic oscillating dipole, and light is emitted. Free induction decay again destroys the phase relationships, so only a short pulse of light is generated. The rephasing at 2τ has removed the effects of the inhomogeneous broadening. However, fluctuations due to phonons, which contribute to the homogeneous line width, cause the oscillation frequencies to fluctuate. Thus, at time 2τ there is not perfect rephasing. As τ is increased, the fluctuations have a greater effect and the size of the echo is reduced. A measurement of the echo intensity vs. τ, the delay time between the pulses, is called an echo decay curve. In many instances, the Fourier transform of the echo decay is the homogeneous line shape.[14,15] For example, in the experiments described below, all the decays are exponential. Therefore, the homogeneous line is a Lorentzian with a width determined by the exponential decay constant. The echo makes the homogeneous line shape an experimental observable. In fact, the echo measures directly the decay of the system's off-diagonal density matrix elements and is the most fundamental observable.

To get a physical feel for how the echo experiment reveals the homogeneous fluctuations in spite of a broad inhomogeneous spread, consider the following footrace. Initially, all the runners are lined up at the starting line.

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At $t = 0$ the starting gun (analogous to the first laser pulse) is fired and the runners take off down the track. After running for some time, the faster runners have pulled out in front and the slower runners are somewhat behind. The runners are no longer in a line because of the inhomogeneity in their speeds. At time τ, the gun is again fired (analogous to the second laser pulse) and everyone turns around and runs back toward the starting line. If each runner maintains a constant speed out and back, then all the runners will cross the starting line exactly in line again. When the second gun was fired, the faster runners were farther away from the starting line than the slower runners, but since they run faster, the differences in distances is exactly made up for by the differences in speeds. At the starting line the group is rephased; the inhomogeneity in speeds has been nullified. If the runners do not run at exactly constant speeds, but each runner has some fluctuation in speed about his average (homogeneous fluctuations), then the runners will not all cross the starting line exactly in a line; there will not be perfect rephasing. A snapshot of the group as it crosses the starting line will reveal the small fluctuations in the runners' speeds, in spite of the large inhomogeneous distribution of speeds. In the same manner, the photon echo experiment reveals the fluctuations in the transition frequency in spite of the large inhomogeneous distribution of transition energies. In this paper, two current applications of the photon echo will be discussed which provide new insights into dynamics and interactions in condensed matter systems.

Experimental Apparatus. To obtain optical pulses with the high repetition rate and good shot-to-shot reproducibility required for these nonlinear experiments, a new type of amplified picosecond laser system was employed (see Figure 1).[16] A CW mode-locked Nd: YAG laser is used as the pump laser. The output consists of a stable ($\pm 2\%$) continuous stream of ~ 55-ps, 1064-nm pulses separated by 12.4 ns. The average mode-locked power can be as high as 12 W TEM$_{00}$, but typically only 6 W is required. The pulses are frequency-doubled to 532 nm and then synchronously pump a dye laser. The 70-mW output of the dye laser consists of 1.75-ps pulses with a bandwidth of 3.5 Å, near the transform limit.

The ~ 1-nJ dye laser pulses are amplified with the frequency-doubled output of a CW-pumped, Q-switched, and mode-locked Nd:YAG laser at a 600-Hz repetition rate. The amplifying pulses are synchronized to the dye laser pulses by mode-locking both Nd:YAG lasers with the same crystal oscillator. (Hence, the cavity lengths of both lasers must be matched.) The amplified pulse is isolated from the unamplified pulses by using a Pockels cell to give a >10^6 ratio of the single amplified pulse to the background pulses. The final output is a single tunable pulse of 2–10 μJ at a 600-Hz repetition rate. For the experiments described below on pentacene and resorufin, which absorb in the yellow-orange part of the spectrum, the laser is tuned to the transition frequency of interest. For the experiments on tetracene, which absorbs at 493 nm, a single 1.06-μm pulse from the mode-locked and Q-switched laser is quadrupled to 266 nm and the dye laser fre-
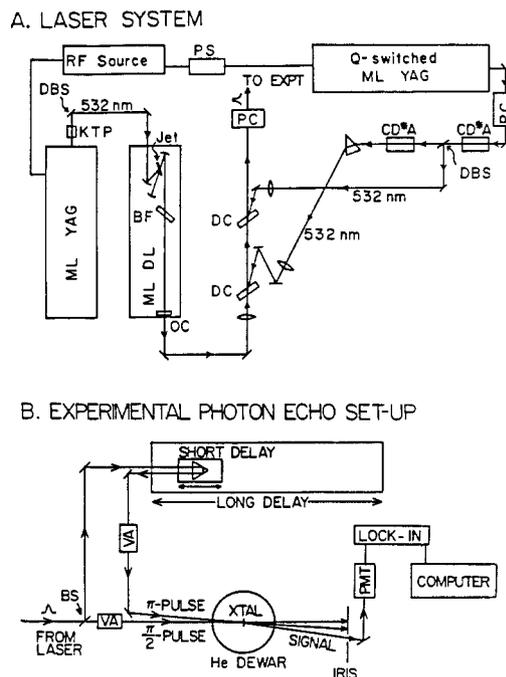

Figure 1. (A) Amplified CW mode-locked dye laser system: PS, phase shifter; PC, Pockels cell; DBS, dichroic beam splitter; DC, Brewster angle flowing dye cell; BF, birefringent filter; OC, output coupler. A CW mode-locked Nd:YAG laser synchronously pumps a mode-locked dye laser. The dye laser pulses are amplified with a Q-switched, mode-locked Nd:YAG laser. See experimental section for details. (B) Experimental photon echo setup: BS, beam splitter; VA, variable attenuator which consists of a polarizer–half-wave plate–polarizer sequence. The single amplified dye laser pulse is split into two excitation pulses. The π pulse is directed into a corner cube mounted on a motorized micrometer driven translation stage. This allows up to 330-ps delay of the π pulse relative to the $\pi/2$ pulse. The translation stage sits on top of a motor-driven carriage on a precision optical rail, which allows up to 9-ns delay of the π pulse, without optical realignment.

quency is mixed (subtracted) with the 266-nm pulse. This gives tunable blue-green light without requiring a picosecond blue-green dye laser.

The single, amplified dye pulse is split into two pulses, called the π and $\pi/2$ pulses (see Figure 1). The π pulse is delayed relative to the $\pi/2$ pulse by using a double motorized delay line. A corner cube sits on top of a motorized micrometer driven translation stage which provides 330-ps delay. The motorized micrometer translation stage itself sits on top of a carriage on a precision optical rail which is motor-driven to provide a 9-ns delay. This double delay line allows measurement of both very fast and slower decays without any optical realignment. The $\pi/2$ and π pulses are crossed at a small angle in the sample. The echo signal propagates in a unique direction, and it is spatially isolated from the excitation pulses. The photon echo signal is detected by a cooled photomultiplier tube and a lock-in amplifier.

III. Delocalization of Electronic Excitations among Interacting Solute Molecules

The nature of the optically excited states of interacting molecules or atoms in solids has been a subject of great interest for many decades.[17] For pure crystals,

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it is well established that the eigenstates are collective, delocalized excitations of the crystal.[17] In the other limit, an extremely low concentration impurity has localized eigenstates whose properties are in part determined by nonresonant interactions with the environment provided by the host crystal.[5,18,19] Between these two limits, when impurity intermolecular interactions are not negligible, the question of the proper description of the electronic eigenstates remains open.

In an idealized system in which the randomly distributed guest molecules (impurities) have identical site energies (no inhomogeneity) and in which there are not thermal fluctuations (absolute zero temperature), even small intermolecular interactions among the guest molecules should result in delocalization. However in real crystals, site energies are not identical. The static inhomogeneity in guest site energies breaks the perfect degeneracy among the interacting molecules and inhibits delocalization. In addition, at any finite temperature, fluctuations in molecular positions and orientations result in fluctuations in both site energies and the magnitudes of the intermolecular interactions.[7] Delocalization depends on a complex interplay between the strengths of the intermolecular interactions, which tend to delocalize an excitation, and the static and dynamic variations in site energies and intermolecular interactions, which tend to localize an excitation.

In these experiments, we examined the concentration dependence of photon echo decays from crystals of pentacene in *p*-terphenyl.[16] The inhomogeneous broadening of the S_0 to S_1 absorption line led a number of groups to consider theoretically the influence of delocalization on the photon echo decay. Warren and Zewail obtained the general form of the dephasing time given in eq 1.[20] Subsequent treatments developed by Loring et al.[21] and Root and Skinner[22] provided more details of the dephasing processes. For the physical situation manifested in the experiments, these two groups obtained identical results using two distinct theoretical approaches. They determined that the short-time behavior of the photon echo goes as $1 - Ct$, where C is a constant. This is the short-time expansion of an exponential and leads to an expression for T_2, the homogeneous dephasing time arising from delocalization

$$T_2^{-1} = 5.07\mu^2 f/a^3\hbar \qquad (1)$$

where μ is the transition dipole moment, f is the fraction of occupied sites, and a^3 is the unit cell volume.

Figure 2 displays typical data.[16] The curves are for crystals of three different concentrations ($a = 1.0 \times 10^{-5}$ mol/mol, $b = 2.9 \times 10^{-5}$ mol/mol, $c = 8.8 \times 10^{-5}$ mol/mol). The decay of the photon echo signal, $I_E(\tau)$, is related to the homogeneous dephasing time by

$$I_E(\tau) = I_E^0 e^{-4\tau/T_2} \qquad (2)$$

where τ is the separation between the pulses. At very low concentration and temperature, $T_2 = 2t_f$, where t_f is the excited-state lifetime. For pentacene in *p*-terphenyl at low concentration ($\sim 10^{-7}$ mol/mol), $T_2 = 44$
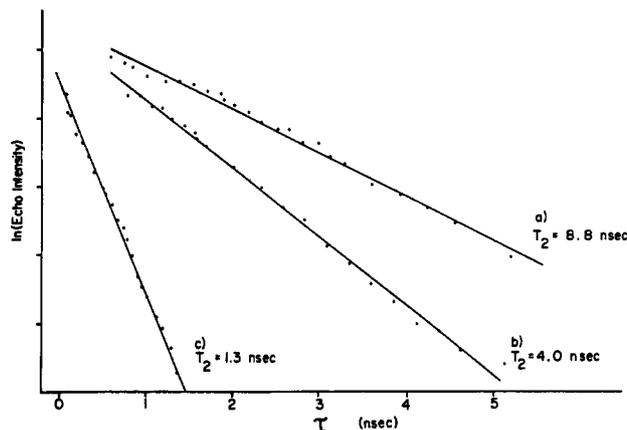
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Figure 2. Photon echo decays for crystals with various concentrations. T_2 is 4 times the echo decay constant (see eq 2). The concentrations and theoretically predicted T_2s are given in the text. The data demonstrate the concentration-dependent delocalization of the electronic excited states.

ns $= 2t_f$.[23] The data displayed in Figure 2 clearly demonstrate the effect of concentration on T_2. Taking into account the approximations that went into the derivation of eq 1 and the extraordinary difficulty of these measurements, the results are in excellent agreement with theoretical predictions. From eq 1, the T_2s calculated *without adjustable parameters* for the three crystals are $a = 6.3$ ns, $b = 2.2$ ns, and $c = 0.7$ ns. These should be compared to the experimental T_2s given in Figure 2.

The data in Figure 2 represent the first demonstration of the onset of delocalization of electronic excited states among solute molecules as the concentration is increased from the low-concentration limit. Physically, the system should be thought of in terms of states delocalized over clusters. The random spatial distribution of solute molecules results in some molecules having nearby neighbors and others being more isolated. As the concentration is increased, the electronic wave functions delocalize over an increasingly large number of molecules because the increasingly large intermolecular interactions overwhelm the molecular site energy fluctuations. At the very low temperature of these experiments, thermally induced fluctuations are frozen out and substantial delocalization occurs even when only 1 molecule in 10^5 is a solute.

The next question to address is how temperature affects delocalized excited states. Temperature-dependent experiments on the impurity bands discussed above are in progress. However, we already examined the effect of temperature on delocalized states of nearest-neighbor molecular dimers.[7,24] Figure 3a displays echo decay data from a tetracene dimer in a *p*-terphenyl host crystal at 2.61 K.[24] The interaction between two tetracene molecules, which are nearest neighbors in the lattice, is so large that the delocalized dimer states produce well-resolved peaks in the optical spectrum of the crystal. By tuning the laser into a delocalized dimer state, we can directly examine dephasing of a single delocalized state. This is in contrast to the impurity band situation in which there are many

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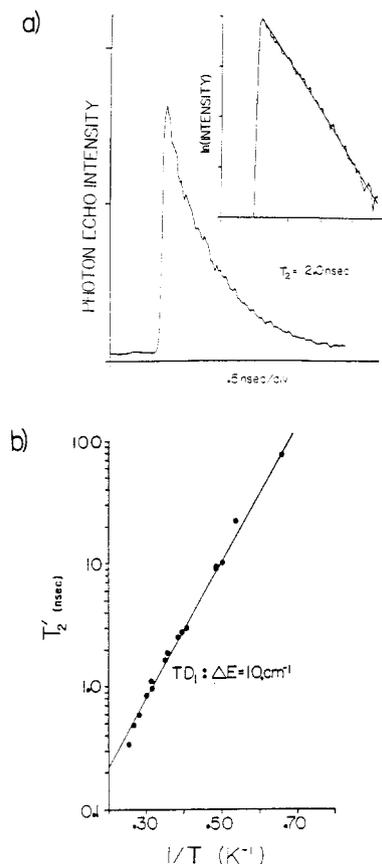
a)

b)

Figure 3. (a) Photon echo decay for the TD_1 tetracene dimer state in p-terphenyl at 2.61 K. The inset is the logarithm of the data showing that the decay is exponential. T_2 is 4 times the echo decay constant (see eq 2). (b) Temperature dependence of T_2' (the dephasing time with the excited-state lifetime contribution removed) of tetracene dimer state TD_1 in p-terphenyl. The solid line is the best fit to the data, giving an exponential activation energy, $\Delta E = 10$ cm^{-1}.

closely spaced levels which are all simultaneously affected by the laser.

Figure 3b displays the temperature dependence of the homogeneous dephasing of a tetracene dimer state.[24] The data show that the homogeneous dephasing arises from an exponentially activated process with an activation energy of 10 cm^{-1}. Note the dramatic temperature dependence. The dephasing rate increases by ∼300 between 1.4 and 3.4 K.

By detailed experimental studies of several distinct tetracene dimer absorption lines, tetracene monomers, pentacene dimers, and monomers also in p-terphenyl host crystals[24] and an exhaustive theoretical study of delocalized dimer state dephasing mechanisms,[7] we have been able to unambiguously determine the mechanism for dimer dephasing in this type of system. For example, if the dephasing was due to direct coupling of the delocalized state to the crystal's acoustic phonons, then a T^7 temperature dependence would be observed. The mechanism in the tetracene and pentacene dimers involves the excitation of a librational motion of the dimer molecules.[7,24] Coupling to the acoustic phonon heat bath excites a librational (rocking) motion of the dimer molecules, and this rocking motion causes the dephasing. The activation energy obtained from the temperature dependence is the energy of the librational mode. The prefactor of the exponential

describing the temperature dependence is the librational mode's lifetime. The tetracene dimer temperature dependence (for the data displayed in Figures 3) has a prefactor of 11 ps. This librational lifetime is typical of all the dimers and monomers studied to date.[13b,24]

Temperature-dependent studies of the dephasing of the impurity bands states will allow us to determine whether librational activation is also important in many level systems. The high density of closely spaced levels could make phonon-induced scattering among the levels the dominant dephasing mechanism.

IV. Optical Dephasing of a Solute in a Glass

As discussed in the Introduction, glasses have additional degrees of freedom not found in crystals. The local configuration of the glass is constantly changing, even at liquid helium temperatures. There has been considerable interest in understanding how the glass dynamics affect a solute molecule.[10] Heat capacity measurements on glasses reveal a very high density of low-frequency modes. The heat capacity has been explained in terms of a simplified model which considers the configurational degrees of freedom as two-level systems (TLS).[25] A particular mechanical degree of freedom is taken to have two states (two energy levels). There are a large number of TLS with a range of level splittings and potential barriers between the levels. As the temperature is raised from absolute zero, there are phonon-induced transitions between the levels. A transition represents a change in the mechanical configuration of the system. Because a solute molecule is sensitive to the structure of the solvent shell surrounding it, transitions in the TLS will perturb the solute and provide a mechanism for temperature-dependent dephasing in addition to the phonon mechanisms possible in crystals.

Two-pulse photon echo experiments have been used to measure optical dephasing in an inorganic glass system,[26] but until recently the only information related to the temperature dependence of the optical dephasing of an electronic transition of a solute molecule in an organic glass has come from hole-burning experiments.[10] In a hole-burning experiment a narrow-band dye laser is tuned to a position in the solute's inhomogeneous absorption line. In many glasses (and some crystals[27]) there is a small probability that optical absorption will trigger a mechanical rearrangement of the environment, causing the absorbing molecules (those resonant with the narrow-band dye laser frequency) to shift their absorption to a new frequency. This reduces the absorption in the vicinity of the laser frequency. The region of reduced absorption appears as a dip in the absorption spectrum. This dip is referred to as the hole. It is generally assumed that the hole width, when measured free of broadening artifacts, is directly related to the homogeneous T_2.[28] The hole width is just $2/\pi T_2$.

Hole-burning experiments are tricky because the hole width increases with laser intensity and irradiation time.

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It is believed that the true hole width is only obtained in the limit of zero power and zero burn time. In addition, since the actual mechanism producing the hole is generally unknown, the relationship between the temperature-dependent hole width and the homogeneous dephasing time is not clear. A wide variety of hole-burning experiments in organic glasses have given $T^{-1.3}$ or $T^{-1.4}$ temperature dependences for what is believed to be the homogeneous T_2'.[29] (T_2' is the echo decay time constant with the excited-state lifetime removed.) There has been no satisfactory explanation of this temperature dependence based on a single mechanism for the glass dynamics.

Recently, we have conducted a detailed picosecond photon echo study of resorufin in an ethanol glass.[30] This system was studied with hole burning and gave a $T^{-1.3}$ dependence.[29] We used photon echo experiments because there is the well-defined relationship between the echo observable and the homogeneous T_2. Great care was taken to be sure that the results were independent of the manner of preparation of the glass and other experimental details.

The results of the echo experiments were immediately surprising and intriguing. First, at all temperatures studied, the homogeneous T_2s directly measured by the echo experiments were considerably *longer* than those measured by hole burning. For example, at 1.5 K the echo gave 1.90 ns for T_2' while the hole-burning experiment gave 0.40 ns. This means that the echo was still giving strong signals for times which the hole-burning experiment indicates there should be no signal. This suggests that the holes are broadened by factors besides T_2.

Figure 4 shows three plots of T_2' obtained from the echo experiments.[30] Figure 4a is a log–log plot. The points are the data, and the solid line i is a $T^{-1.3}$ temperature dependence. The solid line ii shows dephasing times inferred from hole-burning measurements.[29] The T_2's measured by photon echoes do not appear to be described by $T^{-1.3}$ or T^x, where x is any constant.

As discussed in section III, it has been shown in a number of cases that optical dephasing of chromophores in molecular crystals is caused by phonon excitation of librational modes of the chromophore, which gives rise to an Arrhenius temperature dependence. It is possible that a chromophore in a glass is dephased by librational modes in addition to the TLS characteristic of the glass. This idea was originally put forward by Jackson and Silbey[31] and more recently by Silbey and Bässler.[32] From existing theories, they assume the TLS contribution has a linear temperature dependence, so that the overall dephasing rate is

$$1/T_2' = aT + be^{-\Delta E/kT} \qquad (3)$$

where ΔE is the librational frequency and $1/b$ is related to the librational lifetime. Figure 4b shows a plot of log T_2' vs. $1/T$ (as in Figure 3b). The solid line through the data is the best fit to eq 3, with the parameters $a = 3.8 \times 10^{-4}$ ps^{-1} K^{-1}, $1/b = 4.8$ ps, and $\Delta E = 19.4$ cm^{-1}.

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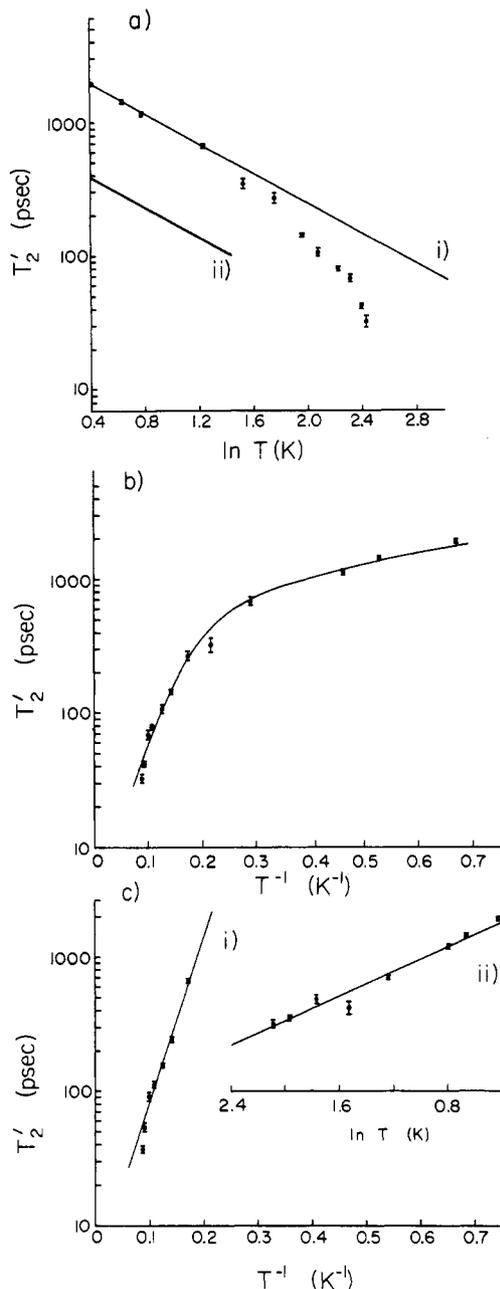(32) Jankowiak, R.; Bässler, H.; Silbey, R. *Chem. Phys. Lett.* **1986**, *125*, 139.

Figure 4. Temperature-dependent dephasing (lifetime contribution removed) of resorufin in an ethanol glass. (a) A log–log plot. The solid line i shows a $T_2' \propto T^{-1.3}$ temperature dependence fit to low temperature points. The solid line ii shows dephasing times implied by hole-burning measurements (ref 29). The data are not well represented by T^x, where x is a constant. (b) An Arrhenius plot, i.e., ln T_2' vs. $1/T$. The curve is the best fit to eq 3. (c) The dephasing data are decomposed into (i) the librational contribution, $T_2' = 4.8$ ps$\cdot e^{19.4 \text{ cm}^{-1}/kT}$, and (ii) the intrinsic glass dynamics contribution, $T_2' = 2625$ ps K T^{-1}. Note different temperature axis for (ii). See text for discussion of mechanisms.

These values are consistent with those measured for librations of chromophores in molecular crystals.[13b,24] In Figure 4c, the individual contributions to the dephasing from the TLS dynamics and the libration of the chromophore are shown. These curves were obtained by subtracting the TLS component from the high-temperature data (i) and the librational component from the low-temperature data (ii). At low temperature, the dependence is linear in T plus a small contribution from the exponential. At higher temper-

ature, a librational dephasing mechanism, identical with that found in crystals, dominates. The apparent $T^{-1.3}$ dependence is really a combination of the two mechanisms at low temperature.

Many more questions remain to be answered. Why is the hole width not directly related to T_2? What is the detailed microscopic mechanism for the T dependence? Is the behavior seen here common to all organic glasses? What can we learn about the dynamical structure of glasses from studies of a variety of glasses and solutes? The application of photon echo experiments to glass systems frees us from the uncertainties of the hole-burning experiments and will provide a detailed picture of the dynamical interactions of a solute molecule in a glass.

V. Concluding Remarks

The ability of temperature-dependent picosecond photon echo experiments to extract information on condensed-phase systems has been illustrated for two specific areas. Picosecond photon echo experiments are used to probe excitation delocalization in systems in which there are interacting solute molecules and to study organic glass systems in which time-dependent solvent configuration changes of the glass are coupled to the solute molecules. However, the photon echo is only one example of a wide class of ultrafast nonlinear experiments which can obtain information of fundamental importance on a variety of systems. The application of picosecond nonlinear experiments to problems of chemical interest has just begun. We are at a stage that is similar to the situation in magnetic resonance which existed in the early 1950s. The methods, the equipment, the theory, and the applications are evolving very rapidly. Over the next several decades, picosecond nonlinear experiments will dramatically expand our understanding of molecular systems.