Optical dephasing of a near infrared dye in PMMA: photon echoes using the superconducting accelerator pumped free electron laser

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A superconducting accelerator pumped free electron laser is used to perform picosecond photon echo experiments on the near infrared dye 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITCI) in poly(methyl methacrylate) (PMMA). The temperature dependence of the optical dephasing is measured from 1.5 to 10 K. At the lowest temperatures a temperature dependence, $T^{-1.4}$, characteristic of two-level system glass dynamics is observed. Above 5 K, the optical dephasing is exponentially activated with an activation energy of 15 cm^{-1}. This is the same activation energy reported for rhodamine B in PMMA, demonstrating that 15 cm^{-1} corresponds to an intrinsic glass mode. These are the first photon echo experiments, and to our knowledge, the first nonlinear optical coherence experiments, performed using a FEL as a source.

1. Introduction

A number of temperature-dependent studies of optical dephasing of organic molecules in organic glasses at low temperatures (<5 K) using both optical hole burning [1–3] and photon echo [4–7] methods have shown an optical dephasing time temperature dependence of $T^{-\alpha}$, where α varies between 1.2 and 1.8, depending on the system. This power law dependence is characteristic of optical dephasing induced by tunneling two-level systems associated with glass dynamics [8,9]. At higher temperatures, several studies have revealed exponentially activated optical dephasing, with the activation energies on the order of 20 cm^{-1} [5,6,10–13].

While the cause of the low temperature dephasing is understood (although not well characterized), the mechanism responsible for the dephasing at the higher temperatures is still open to question. In mixed molecular crystals, exponentially actived temperature-dependent dephasing is seen from the lowest temperatures (≈ 1 K) to the highest temperatures that have been studied (≈ 20 K) [10,14]. The mechanism has been demonstrated to be quadratic coupling of the guest molecule's S_0 and S_1 electronic excited states to a pseudolocal mode of the guest molecule [10,14,15]. The guest molecule can undergo librational and translational motions in its lattice site that are relatively decoupled from the host lattice modes. Weak coupling of the local modes of the guest to the acoustic phonons of the host provides a mechanism for excitation of the guest modes. The mixing with the acoustic phonons makes the guest modes somewhat delocalized, hence they are pseudolocal. Recent studies have shown that the pseudolocal modes are actually mixtures of local librations and translations, as opposed to pure librations [14].

Initially, the exponentially activated dephasing in glasses had been assumed to arise from excitation of pseudolocal modes in a manner analogous to mixed crystals [5]. Jackson and Silbey [16] suggested that exponentially activated behavior could also arise from coupling of the chromophore electronic states to modes of the glass. Recently Elschner et al. [13] performed photon echo studies of rhodamine B (RB) and octadecyl rhodamine B (ODRB) in PMMA glass. They found that the activation energy was identical for the two molecules. ODRB is an 18-carbon alkyl ester of RB. Since ODRB and RB has vastly different masses and moments of inertia, their pseudolocal mode activation energies should be dramat-

ically different. Therefore Elschner et al. proposed that the high temperature dephasing mechanism involved a mode of the PMMA glass rather than a pseudolocal mode of the guest molecules.

In this paper we report a temperature-dependent photon echo study of the optical dephasing of the near infrared (IR) dye, 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITCI) in poly(methyl methacrylate) (PMMA) glass. The experiments were performed in the near IR using the superconducting accelerator pumped free electron laser as the source of tunable picosecond pulses. HITCI has a drastically different structure than RB (see inset in fig. 2b). If pseudolocal modes are responsible for the dephasing, these molecules will certainly have different activation energies. There is another consideration which is more subtle. A recent study has shown that ionic dyes can perturb the local structure of a glass [6,12]. Such a perturbation could lead to a mode of the glass near the dye which is different from any bulk mode of the glass. RB and ODRB are identical except for the alkyl chain. Therefore any perturbation of the glass structure arising from electrostatic interactions will be the same. If, however, RB, ODRB, and HITCI all have the same activation energy, then that energy is associated with a mode of the unperturbed bulk glass.

Another motivation for this paper is to report the first use a free electron laser to perform photon echo experiments, and to our knowledge, any nonlinear optical experiment. Previous uses of FELs have involved various types of absorption studies [17,18] and have not taken advantage of the picosecond pulses which are obtained from some types of FELs, particularly the SCA/FEL [19]. The SCA/FEL can provide picosecond time resolution throughout the near IR, the mid IR and, in the future, the far IR. While the experiments reported here, in principle, could have been performed with a conventional laser, they demonstrate the potential to use the SCA/FEL to perform complex nonlinear as well as linear time-resolved experiments.

2. Experimental procedures

The SCA/FEL is located in a tunnel 30 ft below the High Energy Physics Laboratory (HEPL) at Stanford University. The SCA/FEL produces macropulses at a 10 Hz repetition rate. Each macropulse is several ms long and consists of micropulses which are 3.2 ps Gaussian pulses, ≈ 1 μJ, and separated by the round trip time in the laser cavity of 84.6 ns. The optical beam is delivered to our photon echo laboratory in HEPL by a 80 m long optical transport system which comes up from the tunnel through a hole in the ground.

Fig. 1 shows a schematic of the experimental setup. The beam from the SCA/FEL, operating at 1.55 μm, is brought onto the experimental table by the transport system. The beam is doubled in $LiIO_3$ to the experimental wavelength of 0.776 μm. It is then passed through an acousto-optic modulator (AOM) with a feed back system for intensity stabilization. A pick-off going through a pinhole and quad-detector permitted the beam alignment to be monitored, and rapid realignment of the system if necessary. A second AOM, synchronized to the FEL master oscilla-

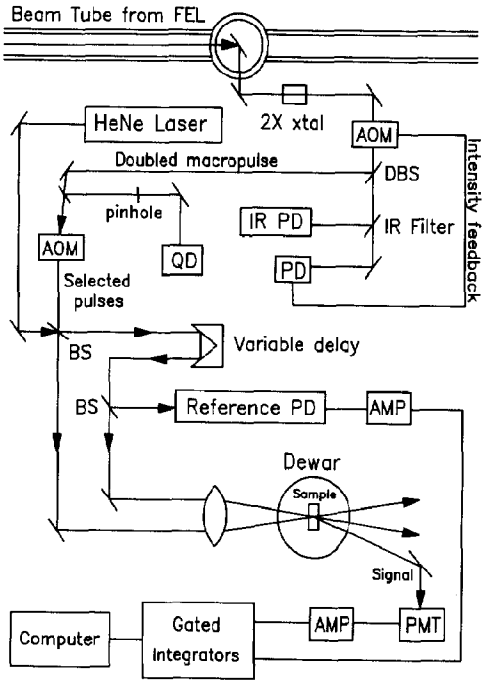

Fig. 1. Schematic of experimental setup. AOM = acousto-optic modulator, DBS = dichroic beamsplitting, QD = quad-detector, BS = beamsplitter, PD = photodiode, PMT = photomultiplier tube, AMP = transient impedance amplifier.

tor frequency, was used to select single pulses from the macropulses. The number of single pulses that can be selected from each macropulse was limited only by the repetition rate of the detection electronics. However, the rate of pulses used was reduced to 5 kHz, the point where the echo decays did not change because of sample heating.

A HeNe alignment beam was made collinear with diffracted beam of single pulses from the second AOM. The pulses were beam split, and one pulse was passed down a computer-controlled stepper motor delay line. The two pulses in the echo sequence were crossed at a small angle in the sample which was held in a liquid helium dewar. Each excitation pulse was ≈ 15 nJ, and the spot size was ≈ 100 μm. At the lowest temperatures (<2.17 K) an immersion dewar was used. At higher temperatures a Janis flow cryostat was employed. The temperature was measured with resistance thermometers in direct contact with the sample. The temperature could be measured with an accuracy of 0.05 K.

Since the excitation pulses were crossed at a small angle ($\approx 1^{\circ}$), the photon echo pulses propagates in a unique direction. The echo was detected using a photomultiplier tube and a gated integrator. A photodiode and a second gated integrator measured the intensity of each selected single pulse. If the pulse amplitude did not fall within a present window, the signal was not averaged in with previous shots. A $\pm 5\%$ window was used. Typically 70% of the shots fell within the window. During some periods of operation, 99% of the shots fell within this window. At each point on the delay line, a large number of shots was averaged. A typical decay curve required three minutes to obtain. The instrument response, measured by liquid N_2 temperature self-diffraction, had a 2.6 ps fwhm.

The dye-doped polymer samples were solvent cast. HITCI was dissolved with PMMA in methylene chloride. Clear films of thickness ≈ 1 mm and optical density ≈ 0.5 were obtained by holding the samples at room temperature under vacuum to remove the solvent. The samples were prepared using the exact same method used to make the RB and ODRB samples studied previously [13], except that the RB and ODRB samples were heated to 60°C to more quickly remove the solvent. Not heating produces films of better optical quality.

The fluorescence lifetime (T_1) of HITCI was measured with a time-correlated single-photon counting system. A sample with OD ≈ 0.1 was used to eliminate effects due to reabsorption.

3. Results and discussion

HITCI/PMMA photon echo decays were measured at 12 temperatures from 1.5 to over 10 K. Fig. 2a shows a decay curve at 1.5 K. The signal to noise ratio is excellent, as good as that achieved using our conventional laser system for molecules which absorb in the visible [5,6,12,13]. Fig. 2b displays a semilog plot of the same data. The echo decay is 284

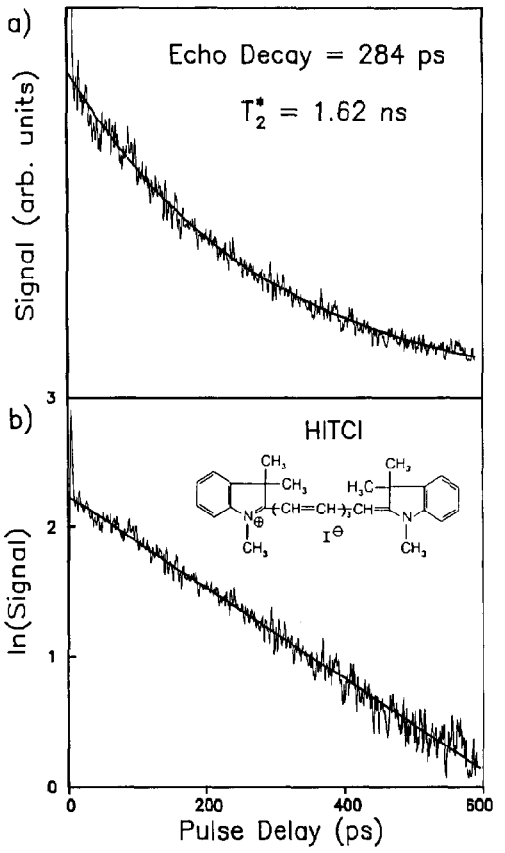

Fig. 2. Photon echo data. (a) Photon echo decay of HITCI at 1.5 K. The solid line through the data is a single exponential fit. (b) Semi-log plot of same decay and fit. The spike at $t=0$ is due to the broad phonon side band. The structure of HITCI is shown in the inset.

ps, and is a single exponential following a very fast transient at $t=0$. The echo decay time is $\frac{1}{4}T_2$, where T_2 is the homogeneous dephasing time [20]. The fast transient arises from the very broad phonon side band [21], while the exponential decay reflects the optical dephasing of the zero-phonon line of interest.

Fig. 3a shows the experimentally determined temperature dependence on a log–log plot. At each temperature the excited state lifetime (1.9 ns) contribution to T_2 has been subtracted from T_2 to yield T_2^*, the pure dephasing time. The data can be fit to a model proposed by Jackson and Silbey [16],

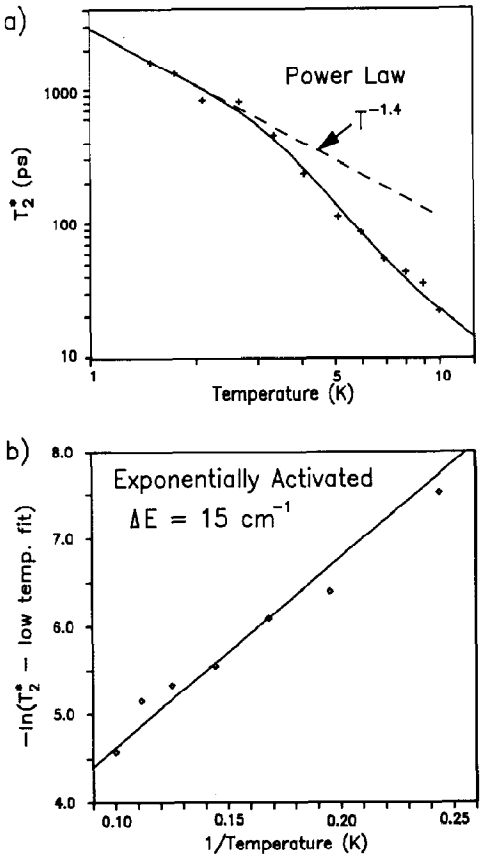

Fig. 3. Temperature dependence of dephasing. (a) Log–log plot of the homogeneous dephasing time. The fit to eq. (1) is shown as the solid line. The low temperature $T^{-1.4}$ power law dependence is shown as a dashed line. (b) Arrhenius plot of the homogeneous dephasing time. The contribution of the low temperature pure dephasing has been subtracted out (eq. (2)). The straight line fit to the data is indicative of an exponentially activated process with an activation energy of 15 cm^{-1}.

$$1/\pi T_2^* = aT^{\alpha} + \{b/[1-\exp(-\Delta E/kT)]\} \times \exp(-\Delta E/kT)\,. \quad (1)$$

This fit is shown as the solid line in fig. 3a with $\alpha = 1.4$ and $\Delta E = 15$ cm^{-1}. At low temperature, the temperature dependence of the pure dephasing time is a power law, $T^{-1.4}$, as can be seen by the dashed line. This power law dependence is consistent with many experiments [1,3,7] and theories of glasses based on the TLS model [2,4–6]. The temperature dependence provides information on the distribution of energy levels associated with the TLS [4,5]. The exponential form of the photon echo decays at low temperatures arises from a dipole–dipole interaction between the dye molecules and the glass TLS [4,5]. A second condition which is necessary to produce an exponential decay is that the TLS fluctuation rate distribution, $P(R) \propto 1/R$ for rates R which contribute on the ≈ 1 ps to ≈ 1 ns timescale of the echo decay [4,5,22] [#1].

At the higher temperatures the data deviates from the low temperature power law behavior (see fig. 3a). Fig. 3b plots the high temperature data with the fit to the low temperature pure dephasing data subtracted out

$$-\ln\{(1/\pi T_2^* - aT^{\alpha})[1-\exp(-\Delta E/kT)]\} = \Delta E/kT - \ln b\,. \quad (2)$$

Fig. 3b is similar to an Arrhenius plot. It is seen that the high temperature data fall on a straight line which is indicative of an exponentially activated process. The activation energy is 15 cm^{-1}.

The data for RB and ODRB were superimposable over the entire range of temperatures studied and also gave an activation energy of 15 cm^{-1} [13]. The experimental error of the HITCI and RB/ODRB measurements are less than 2 cm^{-1}. The agreement between the activation energies of the three molecules, RB, ODRB, and HITCI, in spite of large differences in structures, masses and moments of inertia confirms that a pseudolocal mode is not responsible for the high temperature dephasing. As discussed in section 1, the fact that the HITCI and RB systems yield the same activation energy not only shows that a

[#1] Note that there is an error in a numerical integral in ref. [22]. The value reported as 2.63 should be 3.66.

mode of the host is responsible for the dephasing, but that it is an intrinsic mode the PMMA glass unperturbed by the presence of the ionic dye molecules. The exponentially activated optical dephasing temperature dependence is consistent with a mechanism of quadratic coupling to an optical phonon [13]. In a disordered material, an optical phonon could become a localized host mode and still possess the narrow distribution of energies which is necessary for the observation of the exponentially activated temperature dependence.

4. Concluding remarks

This set of experiments demonstrates that it is possible to do a detailed study using a complex optical set up with the SCA/FEL as the source. Considerably more detail about the experimental method and the problems which were encountered to bring these experiments to fruition will be presented elsewhere [23].

Picosecond pulses of light have made it possible to examine dynamical interatomic and intermolecular interactions on the timescales of fundamental events. Most lasers capable of producing short pulses operate in the visible wavelength range. Lasers which can generate light in the IR are generally fixed frequency devices which produce long duration pulses. Techniques which can produce picosecond pulses in the IR typically produce low peak power and low average power and are limited to the shorter wavelength portion of the IR spectrum. The SCA/FEL has operated from 0.5 to 4.2 μm and is capable of producing picosecond pulses out to 100 μm with megawatts of peak power and tens of watts of average power. Thus the SCA/FEL can contribute to research in broad areas of chemistry, physics, and biology.

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