

ULTRAFAST OPTICAL DEPHASING IN A LOW-TEMPERATURE ORGANIC GLASS

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The optical dephasing of pentacene in an *o*-terphenyl glass at 1.5 K is examined with picosecond photon echo and fluorescence line narrowing experiments. The homogeneous T_2 is found to be 1–3 ps, in contrast to all previous measurements on glass–chromophore systems in which the homogeneous T_2 are two to three orders of magnitude longer.

1. Introduction

Optical dephasing of chromophores in glasses is characteristically different from the dephasing in crystals, implying that dephasing mechanisms intrinsic to the glassy state are important. In inorganic glasses, fluorescence line narrowing first showed that at low temperature the dephasing time (T_2) can be orders of magnitude faster than in the corresponding crystal [1]. In organic glasses, many early studies of non-photochemical hole burning (NPHB) have found linewidths on the order of 15 GHz at 1.5 K [2]. If these holewidths are taken to be homogeneously broadened, they imply dephasing times of ≈ 20 ps. However, recent studies have suggested that these holes were artificially broadened by excessive laser power [3]. Twenty-five chromophore/glass systems have now been studied by photochemical hole burning or by non-photochemical hole burning taking care to avoid such artifacts [4,5]. The holewidths at 1.5 K are all in the range of 1.5 GHz to 20 MHz, implying longer dephasing times of 200 ps to 30 ns. In addition, a recent two-pulse photon echo study of the dephasing of resorufin in ethanol glass has shown that hole burning experiments do not necessarily measure the homogeneously broadened absorption linewidth, and therefore can only provide a short-time limit to the dephasing time [6]. In the case of resorufin in ethanol, the true dephasing time at 1.5 K is 1.9 ns [6], a factor of four longer than that obtained from the holewidth [5,6]. Thus from this

evidence, it would appear that the dephasing in organic glasses is only moderately fast at 1.5 K.

In this communication, the dephasing time of pentacene in *o*-terphenyl glass is shown to be in the range of 1–3 ps at 1.5 K. This is at least two orders of magnitude faster than in the other glasses which have been carefully examined. In two very similar crystalline systems, pentacene in naphthalene and pentacene in *p*-terphenyl, the dephasing times at this temperature have been found to be limited only by the lifetimes of the excited state, which are 16 ns [7,8] and 22 ns respectively [8,9]. Thus, the very fast dephasing observed in pentacene/*o*-terphenyl glass is due to dynamics characteristic of the glassy state.

Pentacene in *o*-terphenyl is different from previously studied glass systems in that both the chromophore and the glass are completely uncharged and non-polar, virtually eliminating electric field coupling between the chromophore and the glass. The fact that dephasing by the glass can be very fast in the absence of electric field coupling has important implications about the coupling mechanisms in glasses.

2. Experimental

Pentacene and *o*-terphenyl powders were degassed and sealed in a 1 mm spectroscopic cuvette under high vacuum. The mixture was heated to $\approx 150^\circ\text{C}$ and agitated for several minutes to dissolve the pen-

tacene completely. The sample was then immediately plunged into liquid nitrogen to pass through the glass transition (-29°C) [10] quickly enough to prevent pentacene from coming out of solution. The concentration of pentacene in *o*-terphenyl was 3×10^{-4} M (4×10^{-5} mol/mol). The samples did not contain pentacene aggregates, which display a characteristic absorption around 700 nm corresponding to the pure pentacene absorption spectrum [11]. The photon echo experiments were conducted at 591 nm, on the red side of the wide inhomogeneously broadened pentacene absorption spectrum. The peak of the absorption spectrum is at 587 nm, and the inhomogeneously broadened line is 400 cm^{-1} wide.

It was found that the samples did not undergo hole burning. A narrow band (2 MHz) dye laser was used to irradiate the sample with 200 mW/cm^2 for 1 h and no change in transmission could be detected. The lack of hole burning allowed the echo decay to be recorded by simply running the optical delay line to vary the pulse separation without the complications found in samples that do holeburn [6].

Picosecond two-pulse photon echo experiments were conducted using an apparatus which has been described previously [12]. Briefly, the output of a cw acousto-optically mode-locked Nd:YAG laser was

frequency doubled and used to synchronously pump a dye laser. The output of the dye laser was amplified at 700 Hz using a two-stage amplifier pumped by the second harmonic of a single pulse from a cw-pumped, acousto-optically mode-locked and *Q*-switched Nd:YAG laser. The amplified dye pulse was split to make the two-pulse echo excitation sequence. One of the pulses passed down a variable delay line consisting of a corner cube on a precision translation stage driven by a motorized micrometer. The pulses were crossed in the sample at a slight angle, so that the echo signal pulse propagated in a unique direction. After spatial filtering to eliminate scattered light, the echo was detected with a phototube and a lock-in amplifier.

Fig. 1 shows two experimental delay line scans. The first is for pentacene in *o*-terphenyl at 1.5 K, and the second is for cresyl violet in ethanol at room temperature. The second trace is the instrument response function, since the optical dephasing of the room-temperature solution can be taken to be infinitely fast [13]. Detailed comparison of scans such as these, taken within minutes of each other, shows that there is no broadening of the low-temperature curves. This demonstrates that the echo decay is fast compared to the instrument response. Furthermore, when excita-

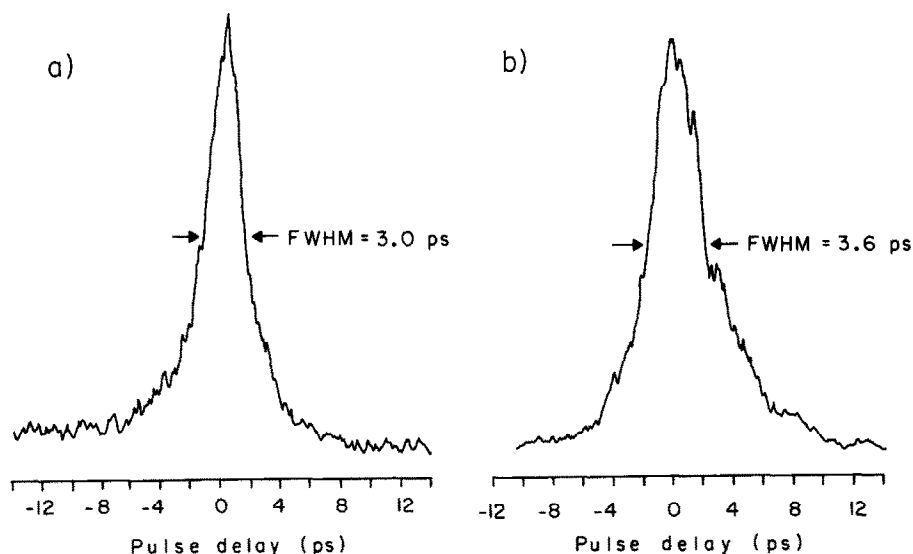


Fig. 1. Photon echo signal versus delay time. (a) Pentacene in *o*-terphenyl glass at 1.5 K. (b) Cresyl violet in ethanol at room temperature. The dephasing at room temperature is much faster than the response time, so curve (b) represents the instrument response function. Curve (a) shows no broadening from the instrument response, indicating a very fast dephasing time.

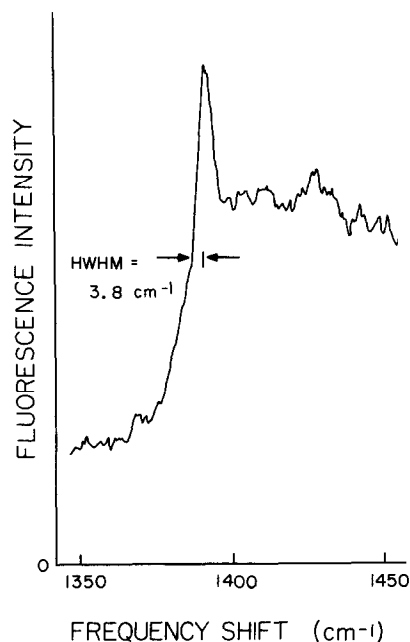


Fig. 2. One vibrational line in the fluorescence line narrowed spectrum of pentacene in *o*-terphenyl glass at 1.5 K. The line is partially obscured on the red side by a broad phonon side band, and therefore the fwhm was obtained by doubling the hwhm. The fluorescence was excited at 590.1 nm. The linewidth of 7.5 cm^{-1} places a lower limit on the dephasing time.

tion pulse 2 is scanned through pulse 1, the echo signal changes from being on the right side of the excitation pulses to the left side. The separation in time of the peaks of the signal in these two directions is an extremely sensitive test for the presence of a decay which is on the order of the instrument response time [13,14]. The peaks of the two signals from pentacene/*o*-terphenyl are coincident to within experimental accuracy, about 0.5 ps. Since the photon echo signal decays four times faster than T_2 , this implies that $T_2 \leq 2\text{ps}$.

To determine a lower limit for T_2 , fluorescence line narrowing was carried out on the same sample. A narrow band (2 MHz) dye laser was used as the excitation source and the resulting fluorescence was dispersed by a monochromator with a resolution of 0.04 nm. As is common in glasses, very broad phonon side bands accompany the sharp vibrational lines. Fig. 2 shows one of the best resolved lines with excitation at 590 nm. An estimate of the linewidth is obtained by doubling the half-width at half-maximum taken

from the blue side of the line. The full width is 7.5 cm^{-1} , which corresponds to a $T_2 \geq 1.4 \text{ ps}$. Other vibrational lines give similar results. Also, excitation at wavelengths varying over the entire inhomogeneous line (565 to 600 nm) resulted in identical linewidths. Because inhomogeneous broadening is only eliminated for the 0-0 line, these higher vibrational lines may not be homogeneously broadened [15]. Thus the linewidth gives only a lower bound on the true T_2 . Combining this result with the photon echo result and allowing for the uncertainty in both procedures, the true T_2 for pentacene/*o*-terphenyl at 1.5 K is between 1 and 3 ps.

3. Discussion

Dephasing occurs because of fluctuations in the electronic transition energy about its mean value. These fluctuations result from a coupling of the electronic transition to some mode or modes in the host which are also fluctuating. In glasses, the important modes are usually called two-level systems, but the actual motion associated with the two-level system and the mechanism which couples it to the electronic transition of a chromophore are poorly understood.

Unlike most of the glass systems which have been studied, pentacene/*o*-terphenyl is non-polar. In light of what is known about coupling between chromophores and glasses, it is surprising that dephasing in a non-polar system is dramatically faster than in more polar systems. Photon echoes in one inorganic [16,17] and three organic [6,18] glasses have found the echo decays to be highly exponential. However, in a glass there is a wide distribution of local environments. If a chromophore interacts with a glass through short-range coupling, the variety of relaxation times of the various environments would be manifest in a variety of chromophore dephasing times. The result would be a highly non-exponential echo decay. In contrast, if the chromophore interacts with the glass through a long-range mechanism, then a statistical sampling of all possible dynamical environments will occur, and an exponential decay will result. A dipole-dipole interaction has the longest range normally encountered and therefore seems the most likely form of interaction. In one model, a dipole-dipole interaction is predicted to be the only

form which will give an exponential echo decay [17]. Theoretical models predicting the temperature dependence of glass dephasing also find that a dipole-dipole interaction gives the closest agreement with the weak temperature dependence ($T_2 \propto T^{-(1-1.3)}$) found in organic glasses [19-21].

There has not been agreement on whether the coupling is due to electric dipoles [20] or "elastic" dipoles [17,19,21,22]. If permanent electric dipoles were important, the dephasing in a non-polar system like pentacene/*o*-terphenyl should be much slower than in polar systems. If "elastic" interactions dominate, the dephasing should be similar to other systems studied, since the mechanical properties of *o*-terphenyl are not expected to be drastically different from other glasses.

At sufficiently high concentrations, impurity transition dipole-impurity transition dipole interactions can shorten dephasing times [23-25]. Electronic delocalization among impurities decreases the dephasing time measured for pentacene in *p*-terphenyl crystals at concentrations similar to that used here [12]. However, quantitative theories of electronic delocalization show that the extremely broad inhomogeneous linewidth of pentacene/*o*-terphenyl glass (300 times broader than the inhomogeneous width in pentacene/*p*-terphenyl crystal) will prevent delocalization effects for concentrations at least two orders of magnitude higher than that used here [24,25]. In addition, delocalization can be enhanced in the crystalline system by local homogeneity [12,24,25] (molecules in a small spatial region have identical transition frequencies), an effect which is unlikely in glasses.

Impurity-impurity interactions can also reduce T_2 by causing incoherent energy transfer. At low temperatures, energy transfer can only occur to resonant or to lower energy sites. If energy transport is important, the lifetime (and hence T_2) will vary with frequency of excitation [26,27] and fluorescence line narrowing will not occur. Significant fluorescence line narrowing is seen for this sample, and the widths of the transitions observed were independent of excitation wavelength. Furthermore, photon-echo decays [6] and fluorescence line narrowing results [28] on chromophores in organic glasses of similar concentrations, but with even larger transition dipole moments, have shown no dependence on excitation

frequency, demonstrating that incoherent energy transfer is not important in this type of system.

The brief discussions presented above suggest that there is a new mechanism responsible for the ultrafast dephasing of pentacene/*o*-terphenyl. One possibility is that *o*-terphenyl has an unusually large number of low-frequency motions in the glass. Most of the glasses in which dephasing has been studied have been polymers or hydrogen-bonding molecules, which have a network structure. This network can restrict the amount of intermolecular motion possible at low temperature. In addition, the substituent rings in *o*-terphenyl can twist easily relative to the central ring, and there can be many low-energy configurations resulting from ring twisting. In pentacene/*p*-terphenyl crystal very slight twists of the phenyl rings result in four distinct absorption sites for pentacene shifted over a range of 200 cm^{-1} [29]. These types of motion could be very localized and have only a short range of coupling to a chromophore.

If pentacene in *o*-terphenyl is a system in which the optical dephasing is dominated by strong local interactions, then the echo decay should be highly non-exponential. Experiments on a faster time scale or at lower temperatures could reveal this behavior. Observation of a non-exponential decay would conclusively demonstrate that a different dephasing mechanism is operative in the pentacene in *o*-terphenyl system than in the previous systems that have been studied. These experiments point out the diversity of phenomena which must be understood if a comprehensive picture of the effects of glass dynamics on the electronic states of a solute molecule is to be obtained.

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