

FEMTOSECOND DEPHASING STUDIES OF DYE MOLECULES IN A POLYMER HOST

S. DE SILVESTRI¹, A.M. WEINER², J.G. FUJIMOTO and E.P. IPPEN

*Department of Electrical Engineering and Computer Science and Research Laboratory of Electronics,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

Received 10 September 1984

A femtosecond three-pulse scattering technique is used to observe dephasing of the lowest electronic transition of cresyl violet in poly-methyl methacrylate. The transition from inhomogeneous to homogeneous broadening is studied as temperature is increased from 15 to 290 K.

1. Introduction

The optical dephasing properties of molecular impurities in low-temperature amorphous solids have been extensively studied in recent years as a means of probing the host environment. Non-linear optical frequency domain techniques, such as fluorescence line narrowing [1], photochemical [2,3] and non-photochemical [4,5] hole burning, resonant Rayleigh scattering [6] and polarization spectroscopy [7], have been used to measure the homogeneous linewidth within the inhomogeneously broadened lines of such materials. There exist in addition a variety of time-domain techniques with potential for application in this area [8–11]. We have recently developed a transient three-pulse scattering scheme which seems particularly advantageous for femtosecond dephasing studies [12,13]. Our method provides sub-pulsewidth resolution, clear distinction between homogeneous and inhomogeneous broadening and sensitivity to spectral cross-relaxation effects.

In this Letter we report the application of three-pulse scattering to investigate dephasing of cresyl violet in poly-methyl methacrylate (PMMA) on a femtosecond time scale. At low temperatures the effects of inhomogeneous broadening are clearly evident

and demonstrate the validity of our technique. As the temperature is increased, a transition from inhomogeneous to homogeneous broadening is observed, apparently due to smearing of the individual dye molecule vibrational structure. Additional time-resolved experiments indicate that spectral cross-relaxation does not play a major role in this transition.

2. Theoretical

The interaction geometry for three-pulse scattering is illustrated in fig. 1. The method relies on an optically induced grating formed by the interference of pulses 1 and 2. When the two pulses are separated temporally, a grating can still be formed provided that the dephasing time T_2 is sufficiently long. By measuring the grating amplitude as a function of the delay between pulses 1 and 2, one can measure the dephasing time. This is accomplished using pulse 3 as a delayed probe to scatter off the grating into background-free directions $\vec{k}_4 = \vec{k}_3 + (\vec{k}_1 - \vec{k}_2)$ and $\vec{k}_5 = \vec{k}_3 - (\vec{k}_1 - \vec{k}_2)$.

We have analyzed three-pulse scattering in an optically thin medium, using a third-order density matrix perturbation expansion [14]. For pulses much shorter than the inverse absorption width, the scattered energy U from a two-level system has the following behavior. For a homogeneously broadened system, scattering in the two directions is always symmetric with regard to the delay τ between pulses 1 and 2:

¹ Permanent address: Centro di Elettronica Quantistica e Strumentazione Elettronica del CNR, Istituto di Fisica del Politecnico, Milan, Italy.

² Permanent address: Bell Communications Research, Holmdel, New Jersey 07733, USA.

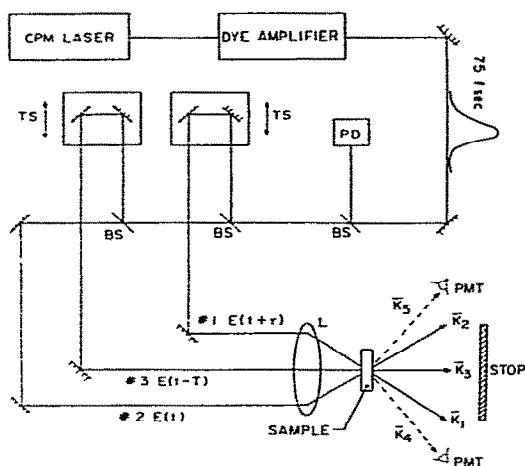


Fig. 1. Schematic of the experimental apparatus. PD = reference photodiode, TS = translation stage, BS = beam splitter, PMT = photomultiplier, L = lens.

$$U_{\vec{k}_4}^- = U_{\vec{k}_5}^- \propto \exp(-2|\tau|/T_2), \quad (1)$$

where T_2 is the transverse relaxation time and τ is positive when pulse 1 precedes pulse 2. For an inhomogeneously broadened system, scattering is no longer symmetric. In the limit $T_2^* \ll T_2$ (where T_2^* is the inverse inhomogeneous width [15]), we obtain for $\tau \geq 0$:

$$U_{\vec{k}_4}^- = 0, \quad U_{\vec{k}_5}^- \propto \exp(-4\tau/T_2), \quad (2a)$$

and for $\tau \leq 0$:

$$U_{\vec{k}_4}^- \propto \exp(4\tau/T_2), \quad U_{\vec{k}_5}^- = 0. \quad (2b)$$

The asymmetry of the inhomogeneous case provides a simple criterion for differentiating between the two types of line broadening. Note that our three-pulse scattering theory includes as a special case the weak-field limit of the stimulated photon echo [9].

For pulses much longer than T_2 , the expression for the scattered energy is simply the envelope of the electric-field autocorrelation squared for both homogeneous and inhomogeneous broadening:

$$U_{\vec{k}_4}^- = U_{\vec{k}_5}^- \approx \left| \int dt E(t) E^*(t + \tau) \right|^2. \quad (3)$$

This property was used previously to measure the coherence properties of mode-locked pulses [16]. Because the electric-field autocorrelation function is readily

measured [12], the $T_2 = 0$ limit can be determined experimentally. Therefore, fast dephasing times can be resolved by looking for small differences between the scattering data and the measured instantaneous response. Furthermore, because the $T_2 = 0$ response depends not on the pulsewidth but on the pulse coherence, resolution well below the pulsewidth can be achieved using spectrally broadened pulses.

A brief discussion is in order to explain how asymmetric scattering curves arise. A more complete derivation will be published elsewhere [17]. For an inhomogeneously broadened system, pulses 1 and 2 create a series of population gratings, spatially shifted with respect to each other because of the different subgroup frequencies. The arrival of pulse 3 at time T generates for each grating a third-order polarization, whose initial phase is determined by the spatial shift of the grating and which oscillates at the appropriate resonant frequency. At time $T + |\tau|$, all the polarization components interfere constructively to form a phased array for radiation in direction \vec{k}_4 for $\tau < 0$ or in direction \vec{k}_5 for $\tau > 0$. Thus, for a fixed value of τ , scattering occurs preferentially in a single direction.

In the presence of spectral cross-relaxation, the scattering behavior is sensitive to the delay T of pulse 3. For delays longer than the characteristic spectral diffusion time ($T \gg T_3$), rephasing is no longer possible because the various gratings are no longer distinct. In this case the scattering is a symmetric function of τ (characteristic of homogeneous broadening); however, the width of the scattering curve reflects the inverse absorption width rather than the actual dephasing time T_2 . Thus, the three-pulse scattering technique can yield information about spectral cross-relaxation as well as dephasing. This is accomplished by repeating the experiment for various settings of T and looking for a transition from asymmetric to symmetric scattering curves. The ability to investigate spectral diffusion using our transient three-pulse technique constitutes an advantage over recently proposed techniques which use incoherent light [18,19].

3. Experimental

All of the results described in this Letter were obtained with thin samples of cresyl violet dissolved in polymer host. Poly-methyl methacrylate, selected in

molecular weight, and cresyl violet were obtained respectively from Polysciences Inc. and from Exciton Chemical Co. Samples were prepared by first dissolving PMMA powder in cyclohexanone. Crystals of cresyl violet were then added to the polymer solution and the mixture was stirred. Undissolved material was removed by filtering. Portions of the final solution were then poured onto 2" square glass plates and allowed to dry into thin ($\approx 50 \mu\text{m}$) films. Film sections were selected for optical density and high optical quality. The optical density of the resulting films was measured by a spectrophotometer and was roughly 0.3 at the excitation wavelength 620 nm (25 nm to the red of the $S_0 \rightarrow S_1$ absorption peak of the cresyl violet). The samples were mounted on a cold finger in an evacuated flow-type helium cryostat covering the temperature range between 15 and 300 K with a precision of about 0.1 K.

The experimental system for the present study is shown in fig. 1. The laser source consists of a colliding pulse mode-locked (CPM) ring dye laser [20] and a four-stage dye amplifier [21]. The ring laser uses rhodamine 6G dye pumped by a cw Ar^+ laser and is passively mode-locked with a thin jet of DODCI saturable absorber. The laser produces transform-limited pulses of 70 fs duration at 620 nm. The dye amplifier system consists of four gain stages isolated by saturable absorber jets and pumped by a Nd:YAG laser at a repetition rate of 10 Hz. The total amplifier gain of $\approx 10^7$ results in 75 fs output pulses with energies of 250 μJ (following grating pair compensation). In the experiments reported here, the amplifier output was attenuated and divided to produce three equal pulses of approximately 50 nJ each. Relative delays between the pulses were varied by computer-controlled mechanical stages with 1 μm resolution. For the experiment, a non-coplanar configuration (not shown in fig. 1) was chosen to achieve better spatial separation of the two scattered beams from the incident beams. The pulses were focused into the sample with a spot size of $\approx 100 \mu\text{m}$ using a 30 cm focal length lens. The beams have parallel polarization and cross at a 3° angle. After the sample the light was collimated using a second lens and the input beams were blocked. To emphasize any possible asymmetry in the scattering curves, we measured the energy of both scattered beams (using a 1P28A photomultiplier). The photomultiplier signal was digitized and stored by a computer. In order to improve the

signal-to-noise ratio, the pulse energy was monitored using a reference photodiode, and data corresponding to pulse energies outside of a selected window were rejected.

4. Results and discussion

As a preliminary experiment, we measured the grating lifetime by scanning the delay T of pulse 3 with the delay τ between pulses 1 and 2 set to zero [22]. The result for the cresyl violet/PMMA sample is shown in fig. 2 for a sample temperature of 15 K. The scattering is zero when pulse 3 arrives before pulses 1 and 2; this demonstrates that no persistent grating develops and provides evidence that in our experiment the grating is dominated by depletion of dye molecules from the ground state and that long-lived photochemical and non-photochemical hole-burning mechanisms are not important. For large T the scattering approaches a constant level (for our 2 ps delay range) that decays on a nanosecond time scale. The large peak near $T = 0$ is an artifact which occurs when all three beams interact coherently. The tail of the $T = 0$ peak is evidence of intraband excited state relaxation of the dye molecule occurring on a time scale of several hundred femtoseconds. Similar rapid intraband relaxation has also recently been observed for other

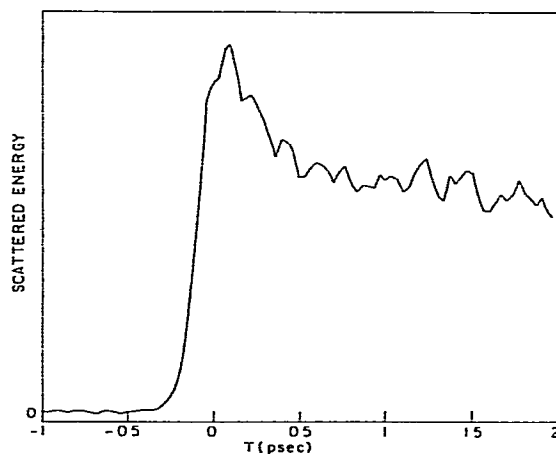


Fig. 2. Scattered energy for cresyl violet in PMMA at 15 K as a function of the delay T of pulse 3. Pulses 1 and 2 are set at zero relative delay.

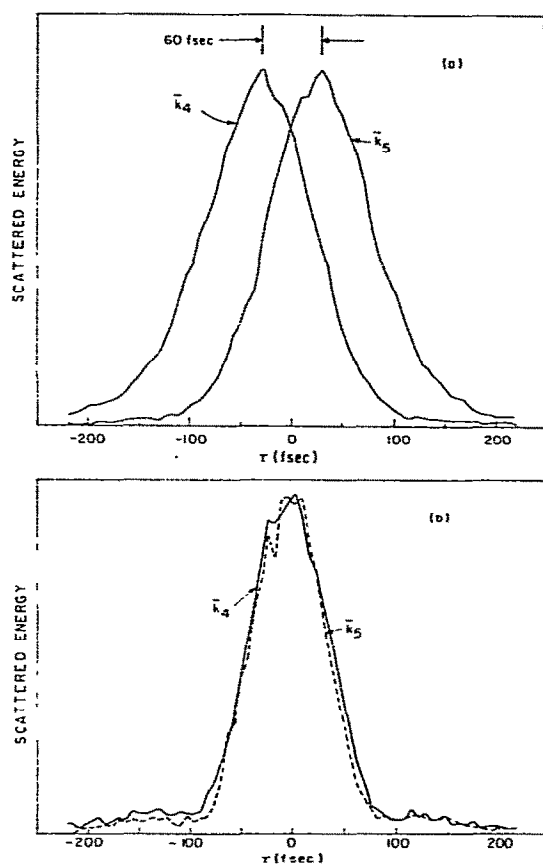


Fig. 3. Scattered energy for cresyl violet in PMMA as a function of delay τ between pulses 1 and 2. The temperatures are: (a) 15 K, (b) 290 K. The delay of pulse 3 was set to 1.3 ps.

dye molecules in liquid solution at room temperature [23].

Scattering curves taken at a temperature of 15 K are shown in fig. 3a for both scattering directions. The delay of the third pulse was set to 1.3 ps. The asymmetry of the curves, illustrated by the 60 fs peak shift, shows that inhomogeneous broadening is present. With increasing temperature the asymmetry and peak shift decrease, as illustrated in table 1. The peak shift is no longer evident in the room temperature data of fig. 3b; at this temperature homogeneous broadening apparently dominates.

To check for spectral cross-relaxation, we repeated the dephasing measurements with the delay of the third pulse varying between 200 fs and 200 ps. The

Table 1
Peak shift between the two scattered beams as a function of temperature for cresyl violet in poly-methyl methacrylate

| Temperature (K) | Peak shift (fs) |
|-----------------|-----------------|
| 15 | 60 ± 3 |
| 35 | 44 |
| 100 | 33 |
| 195 | 16 |
| 290 | — |

observed peak shifts of 60 fs at 15 K and 33 fs at 100 K were found to be independent of the third pulse delay. Thus, spectral diffusion is not evident in this time scale and temperature range.

Despite the clearly resolved peak shifts in our low-temperature scattering data, we do not observe a pronounced tail indicative of a long T_2 . On the basis of calculations assuming a simple two-level model [17], this would indicate dephasing on a one hundred femto-second time scale. However, low-temperature non-photochemical hole-burning measurements on cresyl violet in polyvinyl alcohol polymer [4] indicate that the dephasing time should be on the order of one or two picoseconds.

We explain our results by noting that the presence of a multilevel rather than a two-level structure can lead to an apparent dephasing that is faster than that due to one line individually. Unlike inhomogeneous dephasing, beating between several lines of a single molecule leads to irreversible dephasing in a time related to the inverse excitation bandwidth; this tends to suppress the tail in our time-domain data. Based on the hole-burning spectrum [4], we infer that for our laser bandwidth several lines are indeed excited. Because the lines of a single cresyl violet molecule are well resolved at low temperature inhomogeneous broadening still contributes to the dephasing and a peak shift is detected. As the temperature is increased the individual lines broaden and eventually overlap; the molecule behaves like a homogeneously broadened two-level system with a linewidth equal to the total absorption width. This explanation applies to the room temperature data shown in fig. 3b as well as to the room temperature data recently reported for dye molecules in solution [12].

In summary, we have used a recently developed three-pulse scattering technique to study dephasing

of dye molecules in a polymer host. At low temperatures the temporal effects of inhomogeneous broadening have been observed with femtosecond time resolution. As the temperature is increased, a transition from inhomogeneous to homogeneous broadening is observed. Our experiments indicate that spectral cross-relaxation does not play a major role; rather, the transition occurs in a manner consistent with smearing of the vibrational structure of individual dye molecules.

Acknowledgement

We would like to acknowledge valuable discussions with Professor Keith Nelson. This research was supported in part by a grant from the Joint Services Electronics Program under contract DAAG 29-83-K-003. AMW was a Fannie and John Hertz Foundation Graduate Fellow. SDS is a NATO Science Fellow.

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