FEMTOSECOND VIBRATIONAL RELAXATION OF LARGE ORGANIC MOLECULES

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The intramolecular relaxation time of highly excited states of the vibronic manifold of the first excited singlet state of large organic molecules such as Nile Blue, Rhodamine 640, DODC iodide, Cresyl Violet, and Oxazine 725 in solution is shown to be extremely fast, less than 30 fs. We believe that this is a characteristic time of the relaxation due to anharmonic coupling among the many degrees of freedom of the molecule.

Relaxation of highly excited vibrational states of large organic molecules is a subject of considerable recent interest [1–6]. Experimentally, earlier results [1–3] obtained using picosecond lasers on dye molecules in solutions generally showed the relaxation times to be on the order of a few picoseconds and solvent dependent. Later studies carried out by Shank et al. [4] using subpicosecond lasers showed, however, that relaxations from highly excited molecular vibronic states are less than 0.2 ps and solvent independent. The reasons for these discrepancies have never been clarified, to our knowledge. Current theoretical understanding of these relaxation processes is also limited [2]. It is not clear, for example, by what routes excess energy in the highly excited vibrational states is eventually dissipated in the medium. The relative rates of intramolecular relaxation and relaxation through coupling to the nuclear motion of nearby solvent molecules are not known even roughly.

Recent developments in femtosecond laser techniques have greatly improved the time resolution in measuring ultrafast relaxation processes. Using the equal-pulse correlation technique [7] a time resolution down to ≈20 fs can now be achieved using existing femtosecond lasers. In this letter, we report the results of a study of the relaxation time out of a highly excited band of vibrational states in the vibronic manifold of the first excited electronic state of dye molecules made using this technique. An extremely fast relaxation process, less than 30 fs, is observed.

We believe that this fast process corresponds to the rapid intramolecular redistribution of the initial excess vibrational energy due to anharmonic coupling among the many degrees of freedom of the molecule, and the ps relaxation processes seen earlier in some of these molecules may actually correspond to the subsequent dissipation of the excess vibrational energy into the solvent.

Our measurement is based upon a study of the saturation effect on the transmission characteristics of a thin jet of dye dissolved in ethylene glycol. In the experiment, the sample is excited by two ≈90 fs laser pulses of equal power and orthogonal polarization derived from the same laser but with a variable delay τ between them. The combined flux (photons/s) incident on the sample is then

$$I_{in}(t) = I[f(t) + f(t + \tau)], \tag{1}$$

where $If(t)$ is the flux of a single pulse. The time-averaged combined transmitted power through the jet is measured as a function of τ. A simple model of the saturable absorption process in dye molecules uses a three-level system shown schematically in fig. 1b. Absorption is through the $1 \rightarrow 3$ transition. The extremely fast relaxation time t_{32} is what we wish to determine by this experiment. t_{21} is assumed to be much longer than t_{32}, the laser pulse width, and the maximum delay τ used in the experiment, but less than the 10 ns period of the laser pulse train.

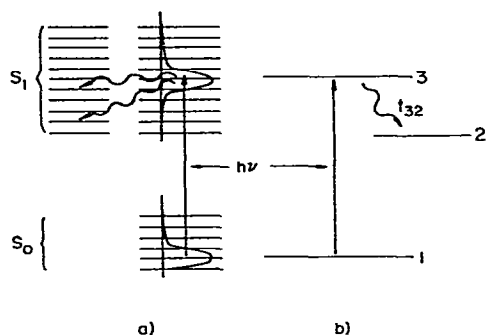The transmitted flux through the absorbing medium

Fig. 1. (a) The ultrafast relaxation process in photoexcited dye molecules. Dye molecules in the ground electronic state, S_0, have a thermal distribution of populated vibrational–rotational levels. Optical absorption promotes this distribution to a band of vibrational states in the first excited electronic state, S_1, from which the initial excess vibrational energy relaxes to the other vibrational levels in S_1. (b) The three-level system used to model this process. A photon absorbed from level 1 to 3 relaxes from level 3 to 2 with a time constant t_{32}. Relaxation from level 2 to 1 is assumed to be much longer than t_{32} and the laser pulse width. Note that if the relaxation process corresponding to t_{32} is strictly intramolecular, with no loss of energy from the molecule, then level 2 represents the group of states which are isoenergetic with level 3, but, unlike, level 3, are not optically connected to level 1. In this case, the decay to level 1 from level 2 could proceed by intermolecular relaxation processes to yet another group of vibrational levels in S_1.

is dependent on the time-varying population difference between the ground and excited states $(N_1 - N_3)$. Because of the rapid decay of the population N_3 out of the photoexcited level, the total transmitted flux of both pulses maximizes when the two pulses overlap within a lifetime t_{32} of each other. That way the transmission of the second pulse benefits from the population N_3 generated from the passage of the first pulse before it has time to decay away. For $\tau \gg (t_{32}$ and laser pulse width), the total transmitted flux of both pulses is reduced and independent of τ because the population N_3 generated from the passage of the first pulse has completely decayed into level 2 by the time the second pulse has arrived. Thus, the combined transmitted flux of both pulses versus τ forms a peak symmetrical about $\tau = 0$, which we call the transmission correlation peak (TCP), and reduces to a constant background value for large τ. It can be shown [8] for an optically thin absorbing material that the TCP is proportional to the convolution of the

pulse autocorrelation and an exponentially decaying factor with decay time t_{32}:

$$TCP(\tau) \propto I^2 \int_{-\infty}^{\infty} C(\tau - x)\exp(-|x|/t_{32})dx, \qquad (2)$$

where

$$C(\tau) = \int_{-\infty}^{\infty} f(t + \tau)f(t)\,dt \qquad (3)$$

is the autocorrelation of the single pulse. Thus, the relaxation time t_{32} manifests itself as an increase in the width of the TCP over the width of the autocorrelation of the laser pulse. It should be emphasized that even if the width of the TCP is not measurably greater than the autocorrelation width, the very appearance of a TCP indicates the presence of a fast relaxation process $3 \to 2$ with a finite t_{32} [7]. Note that excited state absorption from both levels 2 and 3 does not affect the height of the TCP significantly, and therefore is neglected in the model described above.

The experimental arrangement for measuring the TCP is shown in fig. 2. An argon-ion pumped passively mode-locked Rh6G dye ring laser produces a train of pulses at $\lambda = 612$ nm and at a 10^8 Hz repetition rate. The pulse train is divided into two arms of orthogonal polarization and equal power by the half-wave plate and polarizing beam splitter (PBS). After retro-
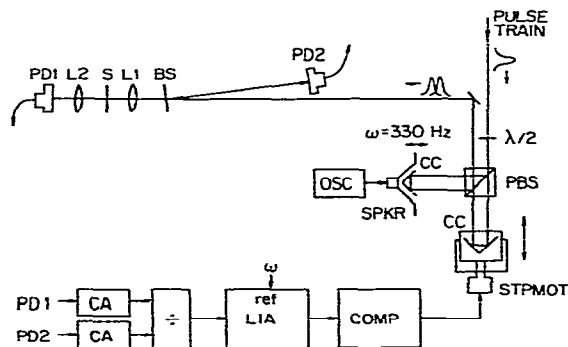

Fig. 2. Experimental apparatus. $\lambda/2$ = half-wave plate; PBS, BS = polarizing and ordinary beam splitter respectively; CC = corner cube retroreflector; STPMOT = stepping motor driven linear translator; SPKR = speaker driven at ω by oscillator OSC; L1, L2 = 40×. 18× microscope objectives respectively; S = sample, a ≈30 μm thick jet of ethylene glycol/dye solution; PD1, PD2 = photodiodes; CA = current amplifiers; ÷ = dividing circuit; LIA = lock-in amplifier; COMP = computer.

reflecting from corner cube prisms, the two arms are recombined collinearly at the PBS. The time delay τ between the two arms is determined by the instantaneous positions of the speaker and the linear translator on which the corner cubes are mounted. The recombined pulse train is focused onto the sample by lens L1, and the transmitted light of both arms is collected by L2 and detected by photodiode PD1. Since the response time of the photodiode is much slower than the repetition rate of the pulse train, the photodiode measures the time-averaged transmitted power of both arms of the recombined pulse train. To reduce fluctuations in the signal due to changes in the laser power, a portion of the pulse train is reflected by a beam splitter onto another photodiode PD2. The two photodiodes are connected to current amplifiers, the outputs of which are divided by a dividing circuit to yield a normalized signal. The resulting signal is digitized and stored by computer for subsequent numerical analysis.

Because the height of the TCP relative to the background value is often very small, sometimes comparable to the noise in the signal, we use a derivative dithering technique to extract the shape of the TCP. In this technique, the speaker corner cube is dithered at a frequency $\omega = 330$ Hz with an excursion equivalent to ± 15 fs (which is $\approx 10\%$ of the full width at half maximum (fwhm) of the TCP). Let the average time delay, determined by the average position of the speaker corner cube and the position of the linearly translated corner cube, be denoted by τ_{ave}. For each value of τ_{ave} set by the linear translator, the lock-in amplifier detects the component of the signal from the dividing circuit at ω. A scan is made, recording the amplitude of the ω component versus τ_{ave}. Since the dither amplitude is small compared to the width of the TCP, the amplitude of the ω component is proportional to the derivative of the TCP with respect to τ for that value of τ_{ave}. After the scan is complete, it is integrated numerically to yield the TCP versus τ.

The autocorrelation of the laser pulse used in the experiment was also taken using the derivative dither method on an apparatus similar to that shown in fig. 2, with an ordinary beam splitter replacing the polarizing one, a 0.5 mm thick KDP crystal in place of the sample, and a photomultiplier tube detecting the generated second harmonic UV replacing PD1. The normalizing photodiode and dividing circuit were

not used in this case. The amount of dither on the speaker, the scanning procedure, and the electronics were otherwise identical to that used in measuring the TCP.

Our primary sample consists of a ≈ 30 μm thick jet of the organic dye Nile Blue 690 dissolved in ethylene glycol at a concentration of 1.8×10^{-3} M. This yields a small signal absorption of the jet of 37%. Ethylene glycol is used as a solvent because it produces a thin, quiet jet. For Nile Blue 690 and the wavelength of our laser pulse, $\lambda = 612$ nm, absorption of a photon excites an electron ≈ 800 cm^{-1} above the bottom of the excited state manifold.

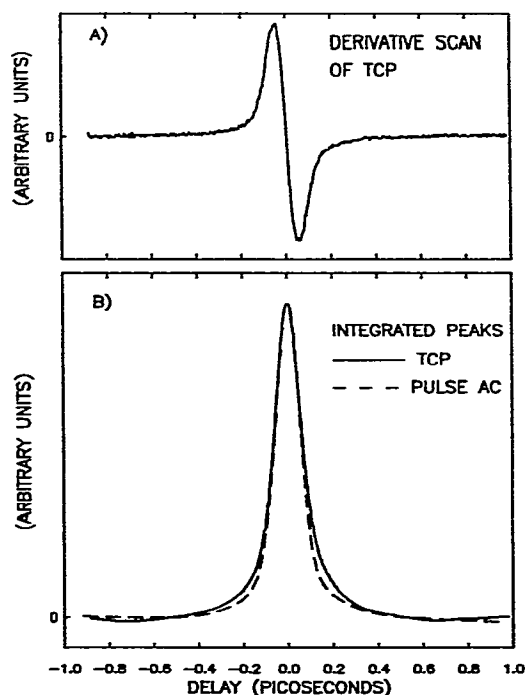In fig. 3 we exhibit a TCP trace of Nile Blue ob-

Fig. 3. (A) The derivative dither trace of the TCP as a function of delay between pulses (in picoseconds) for Nile Blue in ethylene glycol with 5 mW input average power per pulse. The vertical axis is the amplitude of the ω component in the transmitted flux as the delay is dithered at ω. The solid line in (B) is the corresponding integrated curve for the TCP. The vertical axis is the increase in transmitted flux; at this input power the TCP height is $\approx 1\%$ of background transmitted flux. The dashed curve is the autocorrelation of the laser pulse, also taken by the derivative dither technique and normalized to the same height as the TCP.

tained with 5 mW average power incident on the sample per each arm of the interferometer. Fig. 3a is the derivative trace and the solid line in fig. 3b is the corresponding integrated TCP. The dashed line in fig. 3b is the autocorrelation of the laser pulse, taken using the same derivative technique and normalized to the same height as the TCP for comparison. At this input power, the height of the TCP was $\approx 1\%$ of the background value of the transmitted flux. When the input power was reduced, the height of the TCP was found to vary quadratically, in agreement with eq. (2).

The fwhm of the TCP shown in fig. 3b is 145 fs, while that of the autocorrelation is 138 fs. In fact, we took a series of TCP traces and autocorrelations; the average width of the former is 146 ± 2 fs, while that of the latter is 138 ± 3 fs. By eq. (2), the very small increase in width of the TCP over that of the autocorrelation of the laser pulse implies a very small value for t_{32}. However, we must include an additional uncertainty in the width of the autocorrelation, due to the method of its measurement. Because the bandwidth of the doubling crystal is slightly smaller than the potential bandwidth of the doubled laser pulse, the autocorrelation obtained is not truly representative; in fact, the width obtained is a function of the center frequency of the crystal bandwidth [9], and thus the orientation angle of the crystal. Because of this, we estimate that our measurement may slightly overestimate the autocorrelation width, by at most 20 fs, thus putting an upper bound on the difference between measured TCP fwhm and the autocorrelation fwhm of 20 + 8 fs. According to eq. (2) for our TCP width, this yields an upper bound of ≈ 30 fs for the relaxation time out of the photoexcited vibrational states in Nile Blue. The absorption linewidth (≈ 1800 cm^{-1}) places a lower limit of 5.8 fs on this relaxation time.

An order of magnitude estimate of t_{32} can also be made on the basis of the experimentally measured TCP height at a given input flux. Since t_{32} is presumed to be much shorter than the laser pulsewidth, it can be assumed that on a time scale of the variations in $I_{in}(t)$, the photoexcited state population has reached a quasi-steady state; the decay of this population through t_{32} is balanced by the instantaneous absorption of the incident flux $I_{in}(t)$. When the rate equations are solved assuming an optically thin

absorber, the fractional height of the TCP over the background transmitted flux is found to be approximately proportional to the product $t_{32}I$, where I is the time-averaged flux of a single pulse defined by eq. (1). For our measured TCP height of $\approx 1\%$ of the background transmitted flux at an input average power per arm of 5 mW, and using estimated experimental parameters, we find $t_{32} \approx 10$ fs, consistent with the upper and lower bounds discussed earlier.

We can discount the possibility that the measured TCP is a result of some coherent artifact between the laser pulses. First, since the polarizations of the two pulses are orthogonal and the beams are collinear, no induced grating can be formed [10]. Secondly, because the sum of the transmitted power of both beams is measured, not just the power of one beam, the signal is indifferent to any transfer of energy from one beam to another that would be caused by an induced grating. Also, the effects of rotational diffusion are insignificant in our experiment because the rotational diffusion time is much longer than the time scale considered here [10].

Since the dye solution constitutes a dispersive medium, the width of the laser pulse may change while passing through the dye jet. We have calculated the change to be less than 1 fs for a typical dye solution under our experimental conditions. Experimentally, we have measured the autocorrelation width of the laser pulse before and after passing through the jet and found no significant difference in the width. The spectrum of the laser pulse before and after the jet was also measured and found to be the same, implying no change in the coherence length of the laser pulse.

Using the same technique, we studied in a qualitative manner several other dye molecules, including Rhodamine 640, DODC iodide, Cresyl Violet and Oxazine 725 dissolved in ethylene glycol. (All dyes were obtained from Exciton, Inc.) These particular dyes were chosen to allow our 612 nm laser to explore regions of the excited state from near the bottom of the vibrational–rotational manifold (Rh 640, DODCI) to ≈ 1300 cm^{-1} above the bottom (Oxazine). For each of these dyes a TCP with a width comparable to that of the autocorrelation, and a height $\leqslant 1\%$ of the background for input average powers per arm of 5 mW was observed. Thus, all of these dyes exhibit very fast (<30 fs) relaxation out of the photoexcited

states. We studied the dye Cresyl Violet at concentrations of 3×10^{-4}; 6×10^{-4}, and 10^{-3} M, with a range of input powers from 0.25 to 5 mW, and found the TCP width remained unchanged as a function of power and concentration. Similarly for the dyes DODCI and Rh 640, no change in the TCP width was seen as the input power was varied.

Our experiments show, therefore, that in all these cases the relaxation out of the initially excited vibrational band in the vibronic manifold of the first excited electronic state (S_1) has an extremely fast component, less than 30 fs. Earlier studies using picosecond lasers and conventional pump-and-probe techniques could not have seen this fast relaxation process due to the lack of time resolution. Experiments based upon lineshape analyses tend to miss such fast relaxation processes because these fast processes are superimposed on other slower processes, and hence affect mainly the lineshapes of the wings in the spectral domain. We did not, however, see in our experiments any picosecond relaxation processes except in the cases (Cresyl Violet and Malachite Green) where the non-radiative relaxation back to the ground electronic state (S_0) is known to be on the order of a few picoseconds due to strong internal conversion [11]. In all the other cases, we did see the much slower (nanosecond) radiative ground recovery process.

In our experiment we measure how long the molecules stay in the group of states that are optically connected to the ground state; therefore, we cannot distinguish between intramolecular and intermolecular relaxation processes. However, to understand qualitatively our results vis à vis the observed picosecond relaxation processes seen in some of the earlier experiments [1,3], we suggest the following conjectured model of how the initial excess vibrational energy in the highly excited vibrational states eventually dissipates into the solvent medium: Because of the anharmonic coupling to the large number of degrees of freedom of large molecules, the initial energy is first quickly redistributed within the large molecule. There is a characteristic time for this intramolecular relaxation due to anharmonic coupling. It can be less than 30 fs, as in the cases we studied. This intramolecular energy distribution, now shared among many vibrational states of the molecule, "cools" down subsequently to that corresponding to the solvent temperature through collisions with the solvent molecules.

The corresponding collision frequency is known to be on the order of a few picoseconds in liquids. This intermolecular relaxation corresponding to the second stage of "cooling" is what, we believe, was primarily observed in some of the earlier picosecond experiments. We feel that this model is the only interpretation that is consistent with our results and those obtained in earlier experiments.

The 2970 cm^{-1} infrared absorption band of Coumarin 6 in CCl$_4$, studied extensively by Laubereau et al. [1], clearly shows isolated absorption peaks. The linewidth of this peak is ≈ 14 cm^{-1} corresponding to a shortest possible relaxation time of 0.4 ps; the measured population relaxation time reported by them is ≈ 1.3 ps at room temperature. In this case, because the vibrational manifold studied is the ground electronic state, the density of states is much lower than in the excited electronic states. The anharmonic coupling to the other vibrational modes therefore has to be much stronger to produce femtosecond relaxation rates in the ground electronic states. Our suggested model and estimated rates for the relaxation processes clearly apply only to those cases where the corresponding spectrum is broad and relatively smooth, which is the case for the vibrational part of the $S_0 \rightarrow S_1$ Franck–Condon transition of many dye molecules.

The reason we did not see in our experiments the picosecond relaxation corresponding to "cooling" to the solvent temperature is that the pulse energy deposited in the sample is relatively low (5 $\times 10^{-11}$ J). With femtosecond pulse excitation, when the initial excess vibrational energy is spread over many states following the femtosecond intramolecular relaxation process, the number of molecules remaining in the initially photoexcited states is insufficient to cause an observable saturation effect. On the other hand, in the pump-and-probe experiments using picosecond Nd lasers [1,3], the photoexcited volume is much larger, the pulse energy is much higher, and the pulse length long enough compared to the intramolecular relaxation time to populate the probed states sufficiently to see a signal.

References

[1] A. Laubereau and W. Kaiser, Rev. Mod. Phys. 50 (1978) 607;
A. Laubereau, A. Seilmeier and W. Kaiser, Chem. Phys. Letters 36 (1975) 232;
A. Seilmeier, W. Kaiser and A. Laubereau, Opt. Commun. 26 (1978) 441.

[2] P.M. Rentzepis, M.R. Topp, R.P. Jones and J. Jortus, Phys. Rev. Letters 25 (1970) 1742.

[3] D. Ricard and J. Ducuing, J. Chem. Phys. 62 (1975) 3616;
D. Ricard, J. Chem. Phys. 63 (1975) 3841.

[4] C.V. Shank, E. Ippen and O. Teschke, Chem. Phys. Letters 45 (1977) 291.

[5] J.W. Wiesenfeld and E. Ippen, Chem. Phys. Letters 67 (1978) 213.

[6] J.J. Song, J.H. Ree and M.D. Levenson, Phys. Rev. A 17 (1978) 1439.

[7] A.J. Taylor, D.J. Erskine and C.L. Tang, Appl. Phys. Letters (December 1983), to be published.

[8] C.L. Tang and D.J. Erskine, Phys. Rev. Letters 51 (1983) 840.

[9] A.M. Weiner, Intern. J. Quantum Electron. 19 (1983) 1276.

[10] A. von Jena and H.E. Lessing, Appl. Phys. 19 (1979) 131.

[11] D. Magde and M.W. Windsor, Chem. Phys. Letters 24 (1974) 144;
E.P. Ippen, C.V. Shank and A. Bergman, Chem. Phys. Letters 38 (1976) 611.

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S. Runge, The atomic Fues potential applied to a molecular model-potential calculation of the first $^3\Pi_{u,g}$ states of He_2, Chem. Phys. Letters 101 (1983) 167.

There are two errors in the paper: Eq. (6) should read

$$H_{ij} = V_{ij} + \tfrac{1}{2}(E_i + E_j)\varphi_{ij}$$

instead of

$$H_{ij} = V_{ij} + \tfrac{1}{2}(E_i + E_j)_{ij} \ .$$

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