Femtosecond Relaxation Dynamics of Large Molecules

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The ultrafast relaxation in solution of two large organic molecules, malachite green and nile blue 690, has been investigated with the equal-pulse correlation technique. In addition to previously known picosecond processes, we have observed fast initial exponential decays (less than 100 fs) and damped sinusoidal oscillation over intermediate time delays. We believe that the latter behavior, the first such decay observed on a femtosecond time scale for any material, represents quantum beats.

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The initial relaxation of photoexcited large molecules, which occurs on a subpicosecond time scale, has been the subject of considerable current interest. Recent developments in experimental apparatus have significantly improved both the amplitude and time resolution relative to earlier experiments. Because of the absence of intermolecular collisions on the subpicosecond time scale, the ultrafast relaxation properties of isolated molecules can be effectively studied in condensed-phase experiments. We have employed the equal-pulse correlation technique to observe a saturation effect in the transmission of short pulses through a thin jet of organic dye in solution. The results reveal details of the relaxation dynamics which have not been observed before and which are considerably more complex than was previously thought to be the case. In particular, we believe that we have observed quantum beats in molecules for the first time on a femtosecond time scale. Quantum beats have been previously observed in the fluorescence decay of large molecules[1]; however, the beat period in our experiment is 3 orders of magnitude shorter.

We have studied the ultrafast relaxation of the triphenyl methane dye malachite green, which is dominated by a strong internal-conversion mechanism. Data from transmission correlation experiments performed on this dye exhibit a rapid oscillatory decay following photoexcitation as well as a previously identified process with a decay time of 5 ps. Measurements of the relaxation of nile blue 690 clearly reveal a fast component with a decay time of 80 fs as well as a slower process which has been observed by other workers. Although these results are not entirely understood, a possible mechanism for the observed features will be presented.

A number of factors have enhanced our capability to observe and analyze ultrafast processes. The temporal resolution of this experiment (Fig. 1) can be attributed to the use of a modified colliding-pulse mode-locked laser as a source. This produces nearly transform-limited pulses as short as 40 fs with very clean profiles.[2] The emission is peaked at 630 nm (1.97 eV) and the pulse repetition frequency is 10^8 Hz. A multiple-prism arrangement external to the laser cavity permits the control of frequency chirp and compensates for dispersion in other optical elements. The prisms were adjusted to ensure that the experiments were performed with pulses of zero net chirp. We have verified that, for an unfocused beam, transmission through the dye jet does not affect the pulse autocorrelation. A piezoelectric transducer (Physik Instrumente, model P-285) controls delay in our interferometer and for this experiment the entire range of delay values was scanned at 10 Hz. We detected the difference between transmitted and incident power for increased sensitivity, and simple averaging of this signal was found to provide outstanding noise reduction. The excellent signal-to-noise ratio in the wings of measured transmission correlation peaks makes it pos-

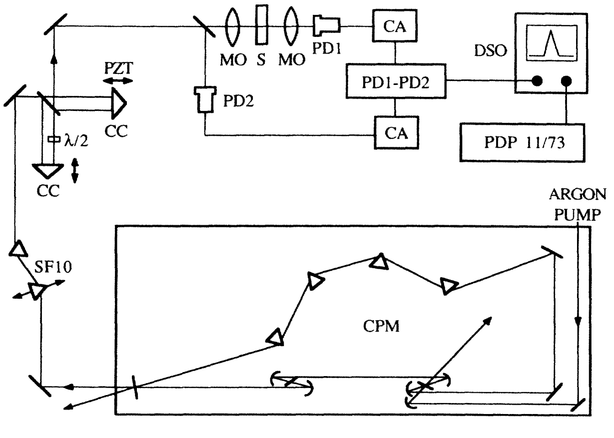

FIG. 1. Schematic of the experiment. Key: CPM, colliding-pulse mode-locked ring dye laser; SF10, SF10 glass dispersive prisms; CC, corner cube; λ/2, $\frac{1}{2}$ wave plate; MO, microscope objective; S, sample; PD1, PD2, photodiodes; PZT, piezoelectric transducer; CA, current amplifier; DSO, digital storage oscilloscope.

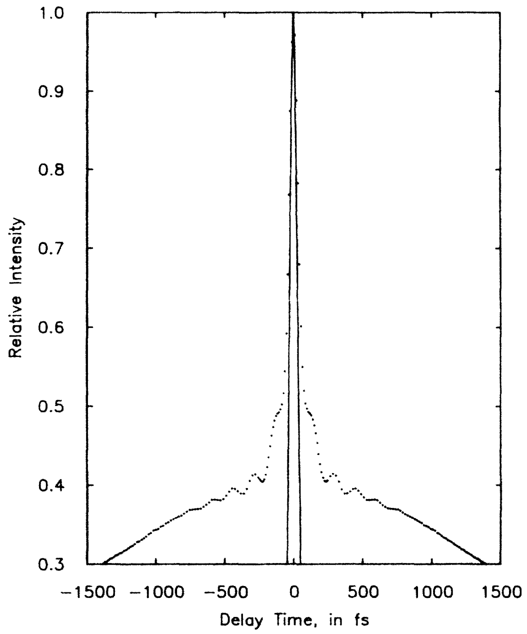

FIG. 2. Malachite green transmission correlation. The solid line is the pulse autocorrelation.

sible to deduce relaxation times from portions of the data which are beyond the coherence length of the source and thus largely unaffected by any coherence artifact. Furthermore, we employ a least-squares linear prediction algorithm[3] to extract the amplitudes and time constants of any exponentials present in the data. No manipulation of the data is required before it is submitted to the linear-prediction routine.

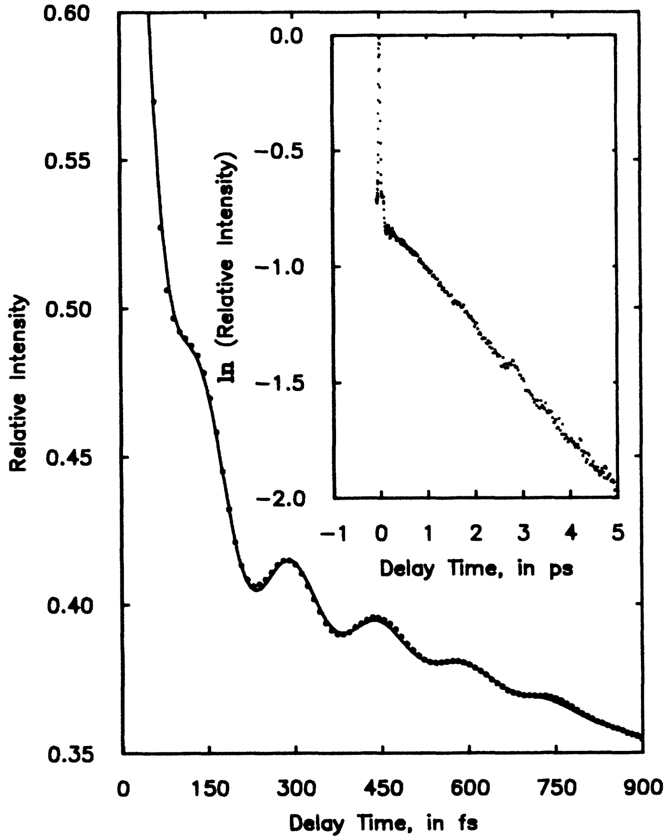

FIG. 3. The data of Fig. 2 expanded (symbols). The solid line is a relaxation which includes the 60-fs decay and a sinusoid which is damped with a time constant of 190 fs, as well as the picosecond-time-scale process. Inset: Long-time behavior (semilogarithmic scale) of the decay. Note that for delays beyond 1.5 ps the data agree well with the 4.8-ps time constant obtained from linear prediction.

A typical experimental scan for malachite green in ethylene glycol is shown in Fig. 2. For this data the sample was a 30-μm jet of dye dissolved in ethylene glycol to a concentration of 2×10^{-3} M. The average power incident on the sample was 1.5 mW per arm of the interferometer and the beams were orthogonally polarized to minimize the coherent contribution to the signal. The initial decay is markedly oscillatory, with a period of 150 fs. The linear-prediction method finds three components to this relaxation: exponential decays with time constants of 60 fs and 4.8 ps, and a sinusoid which is exponentially damped with a time constant of 190 fs. The relative amplitudes of these terms are 1, 1, and 0.05, respectively; the fit to the data is shown in Fig. 3. The data is an average of 10^4 scans and we have ruled out the possibility that some experimental artifact is the source of the observed oscillations. Nearly identical results are obtained when the jet thickness is increased to 100 μm, when the power incident on the sample is decreased by up to a factor of 3, and for parallel and perpendicular polarizations. The period of the decay is also independent of pulse duration, to the extent that this can be varied while still resolving the oscillatory features. Finally, we have performed similar experiments with a different solvent. A mixture of glycerol and distilled water with a viscosity of 2.4 cP produced similar results for the ultrafast decay and a decreased value of the picosecond time constant, as expected. The measurement of essentially identical relaxation processes in distinct solutions practically eliminates the possibility that nonlinear processes in the solvent may contribute to the observed signal.

A similar experimental trace for nile blue, taken with the two beams polarized parallel to each other, is shown in Fig. 4. (Identical results are obtained with perpendicularly polarized input beams.) This trace displays very obvious and repeatable nonexponential behavior. Preliminary data, which had a substantially lower signal-to-noise ratio, was fitted well by two exponentials with time constants of 80 and 520 fs. The 80-fs decay is still quite apparent in the latest data and the 520-fs decay is similar to the result of a recent

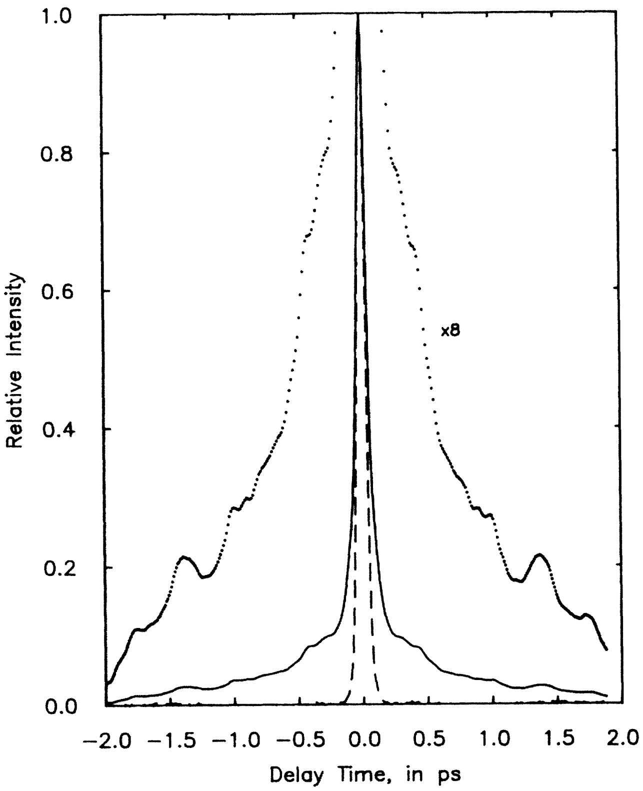

FIG. 4. Nile blue transmission correlation. The dashed line is the pulse autocorrelation, shown for reference. The raw data are also shown on an expanded scale (multiplied by 8), revealing the complex decay structure.

pump-probe study of nile blue.[4] However, this fit entirely overlooks the structure evident in Fig. 4. This unexpected detail suggests extremely complex decay mechanisms after photoexcitation for nile blue.

While the experimental results are unambiguous, the interpretation of the observed relaxation processes is not completely clear. The shortest relaxation time in both cases (60 fs for malachite green and 80 fs for nile blue) may well correspond to a dephasing time for the light-induced coherence between the ground and excited electronic states of the molecules. It should be mentioned that a previous equal-pulse correlation study of nile blue produced data which are consistent with the presence of a fast ($<$ 100 fs) relaxation component of small amplitude.[5] Because of the use of much broader pulses and the relatively poor signal-to-noise ratio of those results, however, the authors did not attach significance to portions of the data near the signal baseline.

The damped oscillatory relaxation clearly seen in the decay of malachite green is puzzling. It is tempting to explain the observed relaxation in terms of a model for quantum beats between two molecular eigenstates of an isolated large molecule. Although the large dye molecules that we study are in liquid solvents, they may be considered isolated on a femtosecond time scale since the collision time with solvent molecules should be on the order of picoseconds. According to this model, only a selected subset of excited states can participate in the initial excitation process. Within this subset there are, say, two states $|a\rangle$ and $|b\rangle$ which are coupled. This leads to two molecular eigenstates,

$$|1\rangle = \alpha|a\rangle + \beta|b\rangle, \quad |2\rangle = \beta|a\rangle - \alpha|b\rangle,$$

with an energy separation of $h\nu_{12}$. As an extreme example, if state $|a\rangle$ is optically allowed from the ground electronic state but state $|b\rangle$ is not allowed, the femtosecond laser pulse excites only state $|a\rangle$, provided that the coherence width of the pulse is greater than ν_{12} and spans the split states $|1\rangle$ and $|2\rangle$, which would be the case in our experiment. Following excitation to $|a\rangle$ at $t=0$, energy will transfer alternately from $|a\rangle$ to $|b\rangle$ and back, with a damping constant Γ. This type of oscillation will occur even if $|b\rangle$ is optically allowed as long as the corresponding optical coupling to the ground state is different from that of $|a\rangle$. In our experiment, the problem is of course much more complicated than this simple two-mode picture. As discussed by Bloembergen and Zewail,[6] in any particular many-mode case the observation of this type of coherent oscillation will depend very much on (1) whether selectivity in mode coupling is clear enough, and (2) the degree of irreversible relaxation between the subset states and the large number of "bath" modes to which this subset is weakly coupled in such a large system. It is conceivable that the conditions for observing such coherent oscillations happen to be favorable in the case of femtosecond optical excitation of malachite green. The intermediate relaxation region observed in the case of nile blue may have the same physical origin, although more complex in this case.

Previous observations of quantum beats were made for fluorescence after picosecond excitation in the vapor phase of the large molecule anthracene.[1] This coherence was also found to be related to coupling of molecular states within the vibrational manifold. Our experimental results are distinguished from these not only by the vastly higher beat frequency (6.7 THz, as compared to 11 GHz), but also because the ultrafast time scale allows examination of these molecular levels in the condensed phase.

We note that each dye exhibits a range of times for which the relaxation appears to be neither a simple exponential nor a damped sinusoid. In the case of malachite green, this is manifested by a slight deviation between the fit and the data for delays around 1 ps. According to Weiner and Ippen, the final long (500-fs) relaxation time in nile blue is only weakly solvent dependent and probably corresponds to intramolecular population relaxation.[4] The picosecond recovery time of malachite green depends strongly on solvent viscosity (as observed previously[7]) and is probably an intermolecular population relaxation time.

In conclusion, we have observed the initial relaxation of photoexcited organic dyes with unprecedented resolution. These measurements clearly indicate the presence of complex processes which are extremely fast and substantiate the results of previous work for the slower decays. We believe that we have observed quantum beats in large molecules on a femtosecond time scale for the first time.

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