Femtosecond Photon Echoes from Molecules in Solution

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Two-pulse photon echoes were observed in organic dye molecules in solution using 6-fs optical pulses. The results show an initial rapid dephasing of the echo due to level multiplicity followed by quantum beats. The temporal decay of the quantum beats is characterized by a T_2 of about 60 fs.

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Recent hole-burning experiments performed with large molecules in solution[1] suggest that it might be possible to observe photon echoes in these systems. The photon-echo technique has proven useful in a variety[2-4] of systems to study processes which influence the dephasing of an induced polarization. The use of coherent optical transients to study such processes in molecules has been frustrated by the very fast dephasing rates in such systems. Recent advances in short-pulse techniques have led to the generation of optical pulses as short as 6 fs.[5] With this increased time resolution we have recently observed two-pulse photon echoes from bulk GaAs and directly measured the rate of polarization dephasing.[6] We report here the observation of femtosecond photon echoes and quantum beats from organic dye molecules in solution.

Several attempts have been made to observe coherent transient processes in organic dyes, using techniques in both the time domain[7-10] and the frequency domain.[1,11,12] In the experiments reported here we observe photon echoes using a two-pulse sequence. Two pulses, one having wave vector $\mathbf{k}_1$ and the other wave vector $\mathbf{k}_2$, generate an echo in the momentum-matched direction $2\mathbf{k}_2-\mathbf{k}_1$.[2] The echo is then separated spatially from the exciting pulses. The energy of the generated echo is measured as a function of the relative time delay between the exciting pulses.

The primary utility of a photon echo is to measure the polarization dephasing time, T_2. For a two-level system which is purely inhomogeneously broadened the echo energy will decay exponentially with the relative time delay τ between the two pulses as

$$E(\tau) \propto \exp(-\tau/T_{\text{echo}}) , \tag{1}$$

where $T_{\text{echo}} = T_2/4$. For the case of a homogeneously broadened transition the radiated signal at $2\mathbf{k}_2-\mathbf{k}_1$, corresponding to the polarization free decay, will relax as $\exp(-2t/T_2)$.[8] These relations show that an optical pulse shorter than $T_2/4$ must be used to time resolve the echo decay.

The experiment was performed using compressed pulses phase corrected to third order in a manner described previously.[5] The duration of the pulses was measured to be in the range 6 to 10 fs using the second-harmonic up-conversion technique. The pulse repetition rate was 8 kHz and the pulse energy was about 1 nJ. The energy of the pulse was much less than that needed for a π pulse so the echoes observed in the experiments described here are in the small-signal perturbation limit. The pulses were split in two in a modified Michelson interferometer configuration to form the two excitation pulses. The two pulses were focused with a 5-cm focal-length lens into a flowing stream of ethylene glycol containing the molecule under study. One pulse was delayed with respect to the other using a stepper-motor-controlled delay.

The signal was detected in the $2\mathbf{k}_2-\mathbf{k}_1$ direction with a lens spatial filter to reject stray light. The selected signal was then directed into a photomultiplier. The detection electronics consisted of a boxcar integrator followed by a phase lock detector. The signal was recorded as a function of relative time delay τ between the pulses.

The measured echo for the oxazine dye, nile blue, is plotted in Fig. 1(a) and that for the triphenylmethane dye, malachite green, is plotted in Fig. 1(b). Note that an initial rapid decay within a time constant of roughly 4 fs is observed followed by oscillations in time indicating the presence of quantum beats.[13,14] In Fig. 1(b) beats in the echo are observed beyond 100 fs as shown in the expanded inset. For nile blue the period of the oscillation is measured to be about 18 fs while for malachite green it is roughly 22 fs. This indicates that a component of the echo is coming from transitions involving a pair of vibronic levels in the excited state with level spacings of 1850 and 1515 cm^{-1}, respectively.

To understand these data we need to consider the photon echo from a system of vibronic levels. Each vibronic level in the ground electronic state is coupled to a manifold of vibronic levels in the excited electronic state via Franck-Condon overlap. For the purposes of our discus-

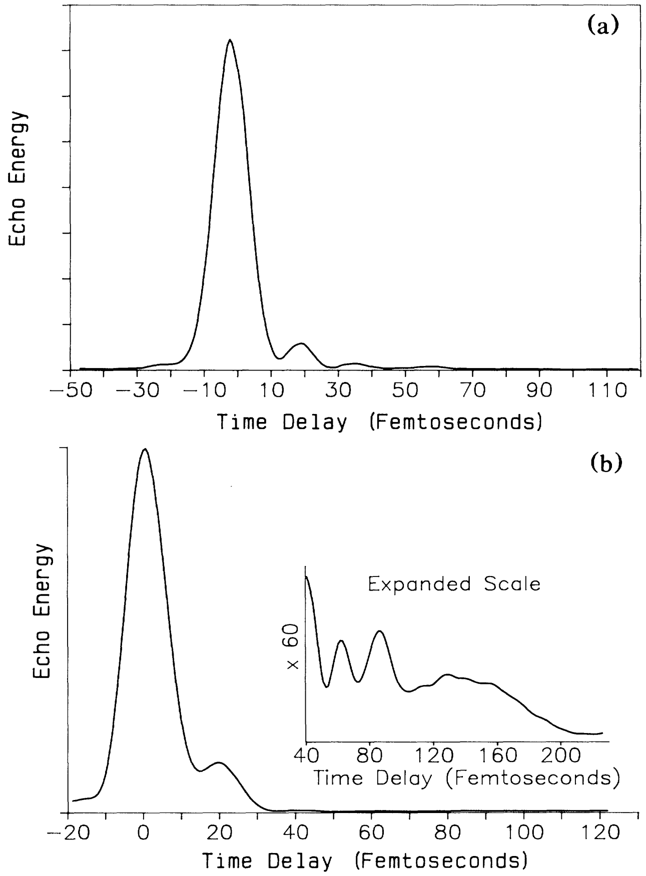

FIG. 1. (a) Echo energy in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ as a function of the relative time delay between the two excitation pulses, for the dye nile blue in ethylene glycol. (b) Echo energy in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ as a function of the relative time delay between the two excitation pulses, for the dye malachite green in ethylene glycol.

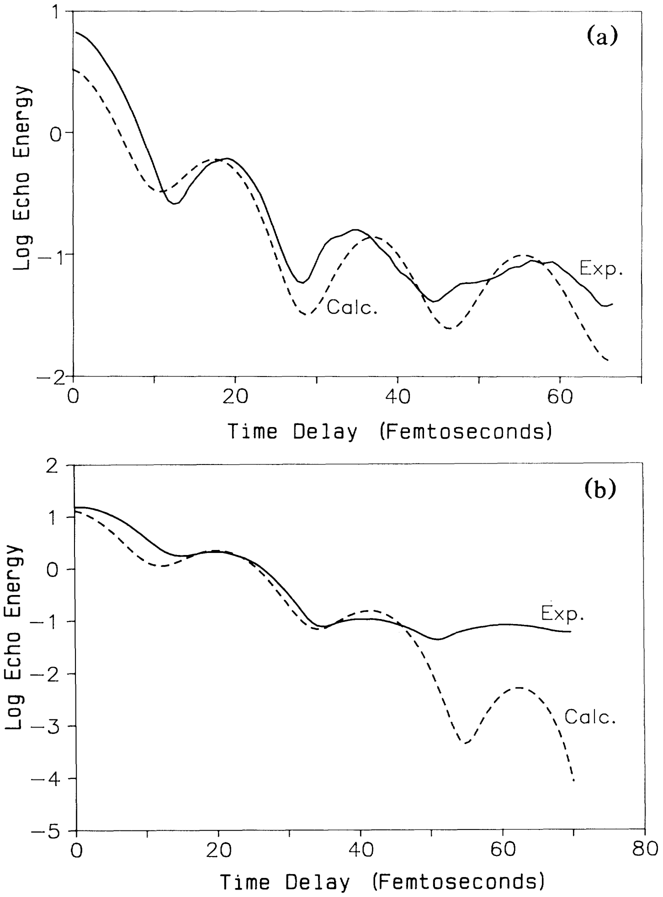

FIG. 2. (a) Experimental (solid line) and calculated (dashed line) logarithm of the echo energy for the dye nile blue in ethylene glycol. The parameters used for the calculated curve are two modes with frequencies 555 and 1850 cm^{-1} with the squares of the transition dipole moments from the ground state to the 0 level of the excited state and the two vibronically excited states in the ratio 1:0.15:0.2 and T_2 equal to 65 fs. (b) Experimental (solid line) and calculated (dashed line) logarithm of the echo energy for the dye malachite green in ethylene glycol. The parameters used for the calculated curve are two modes with frequencies 247 and 1515 cm^{-1} with the squares of the transition dipole moments from the ground state to the 0 level of the excited state and the two vibronically excited states in the ratio 1:0.6:0.3 and T_2 equal to 60 fs.

sion let us assume δ-function-in-time excitation pulses, strong inhomogeneous broadening, and only one electronic polarization dephasing time T_2. The echo energy as a function of relative time delay between the two pulses of the echo sequence can then be calculated to be

$$E(\tau) \propto \left[\sum_{i,j} \mu_{1i}^2 \mu_{1j}^2 \cos(\omega_{ji}\tau)\right]^2 \exp(-4\tau/T_2)\,, \tag{2}$$

where the ground state is labeled 1 and the excited states i and j. Here ω_{ji} is the (angular) frequency difference between the excited states and μ_{1i} is the transition dipole moment between the ground state and level i. For a simple system with just a few levels the cosine term in the above expression predicts quantum beats which decay with a time constant $T_2/4$. For a system with a large number of modes approaching a continuum the term in square brackets becomes proportional to the Fourier transform of the absorption spectrum with a bandwidth $\Delta\omega$. Expression (2) then becomes $\exp(-\Delta\omega\tau) \times \exp(-4\tau/T_2)$. This expression represents the polarization dephasing of the entire manifold of levels. As a consequence it is a polarization free decay and contains no information about the dephasing of the coherent polarization.[15] For molecules discussed in these experiments the absorption is dominated by a few modes having a large oscillator strength often referred to as system modes. We can approximate the echo decay by using Eq. (2) with a sum over just the system modes.

In Fig. 2 we have plotted the logarithm of the echo energy (solid lines), for nile blue and malachite green, as a function of the relative time delay between the two exciting pulses. The dashed lines were calculated using Eq. (2) assuming two dominant system modes. The parameters used in the calculation are shown in the caption of Fig. 2. The result is a reasonable fit to the data for T_2 equal to 65 fs (in the case of nile blue) and T_2 equal to 60 fs (for malachite green). These system modes have all been observed in recent pump-probe experiments done with these same dyes.[16] The values of T_2 are also close to those reported in recent hole-burning experiments.[1] The agreement between the observed and calculated echo decays is quite reasonable. We can also reconstruct the essential features of the absorption spectra of the dye molecules using the parameters determined above and inhomogeneous broadening characterized by $T_2/T_2^* \approx 10$.

In conclusion, this experiment is the first report of a femtosecond coherent transient in a large molecule in solution in a time domain shorter than the polarization dephasing time. The measurements described here are possible only with the large spectral bandwidth and ultrashort time duration of coherent optical pulses of less than 10 fs. The observed oscillations in the photon echo signal are the first observation of polarization quantum beats in these systems. Rosker, Wise, and Tang[17] and Chesnoy and Mokhtari[18] have applied the term "quantum beats" to oscillations in the transient absorption spectrum which have a different physical origin[16] than the beats observed in the experiment described here.

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