the contribution from transverse polarization, which gives the echo. Time reversal symmetry makes $XX\overline{X}$ equivalent to $\overline{X}XX$. If the Doppler width were much less than the pulse bandwidth, then the sequence $(X\overline{X}X)$ would compensate for flip angle inhomogeneities, and $\tau = \tau' = 0$ would correspond to zero fluorescence. We worked in the opposite limit, however, and theoretical calculations show that shifting the middle pulse then has no effect, as verified experimentally.

In conclusion, we have demonstrated that phase coherent pulse trains can be generated in the optical regime to observe coherent signals. We will list here only a few possible extensions of our technique.[19] Dephasing rates in mixed molecular crystals have been explained[20] by interactions between transition electric dipoles, which can be refocused by well-known NMR line narrowing sequences[3-5] or even simpler dipolar echo sequences.[21] Multiple echo sequences are also useful to reduce the effects of transverse velocity distributions for gaseous samples. Finally, phase coherent pulse trains permit the direct observation of coherences in the rotating frame (i.e., measuring $\langle P_y \rangle$ and not $\langle P_y^2 \rangle$), which can simplify the spectra of multilevel systems.

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Quantum beats and dephasing in isolated large molecules cooled by supersonic jet expansion and excited by picosecond pulses: Anthracene[a)]

Wm. R. Lambert, P. M. Felker, and A. H. Zewail[b)]

Arthur Amos Noyes Laboratory of Chemical Physics,[c)]
California Institute of Technology, Pasadena, California 91125
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Intramolecular relaxation in isolated large molecules is of considerable current interest. The primary questions are: what is the nature of the states which are excited by the light source, and; how does the deposited energy get transferred within the molecule? In this

regard, the possibility of observing coherence effects in the fluorescence decay of large molecules is very important. When large molecules are excited at finite temperatures the existence of many sequence transitions results in spectral broadening and in the masking of

these possible coherence effects. Although recent super-sonic molecular beam spectroscopy[1-3] has been success-ful in circumventing the congestion problem, the large density of excited states may still prevent the observation of such effects.

In this communication we wish to report on the observation of quantum beats and transient spectra of anthracene cooled by a supersonic jet expansion and excited by ~15 ps laser pulses to the singlet manifold.

The supersonic cw-jet was prepared by expanding zone-refined anthracene at a nozzle temperature of 160 C through a 150 μ pinhole with ~50 psi pressure of different carrier gases. The ambient pressure in the expansion chamber was 10^{-4} Torr. The ~15 ps pulses were obtained from a synchronously pumped, cavity-dumped dye laser. The second harmonic was generated using $LiIO_3$ crystals. The fluorescence was collected with $f/1$ optics and dispersed with a monochromator. Spectra were obtained using time-correlated photon counting techniques. The system response was ~150 ps and the coherence width of the laser was ~2 cm^{-1}.

The spectra of anthracene in the gas phase (bulb) and in mixed crystals have previously been characterized.[4,5] The spectra in the gas phase at ~480 K reveal quasisharp lines (15–25 cm^{-1}) and a background that is very broad in nature. Mixed crystal spectra are very complicated due to multiple lattice sites. Our jet spectra (0, 0 excitation) are very sharp with no background features [Fig. 1(a)], and display the well-known vibrations of anthracene (390, 1410 cm^{-1}, etc.). The 0, 0 lifetime is 20 ns and compares with previous work.[6]

Exciting near the 2×1400 cm^{-1} transition and above results in spectral broadening and a red shift similar to that observed in other large molecules.[1,2] The lifetime of the resolved emission for this excitation is 5.7 ns, similar to the lifetime of gaseous anthracene.[7] Very little hot band emission (i.e., resonance fluorescence from the pumped level to the lowest vibrational levels) was seen in our jet spectra at these high excitation energies. On the other hand, at certain medium energies the hot bands are pronounced [see Fig. 1(b)].

Under the same laser and beam conditions, quantum beats were observed on the fluorescence decay for 3439 Å excitation (corresponding to excitation in the region of the anthracene 1380 cm^{-1} fundamental).[5] The most prominent beat pattern was observed [Fig. 2(a)] at 3577.5 Å. Also, at this excitation energy the beats appeared with less modulation depth on the band at 390 cm^{-1} from the excitation energy and on other bands. The observation of beats in large isolated molecules is important and demands careful tests to establish their reproducibility and origin. In this regard, the following observations are pertinent. First, we found that the observation of the beats was very dependent upon the excitation and detection frequencies (see Fig. 2). In addition, the modulation depth was reduced in intensity as the detection bandwidth was increased. Second, there was no change in the beat pattern when the laser pulse repetition rate was reduced from 4.02 MHz to 804 KHz. Third, the modulation depth increased as the nozzle-laser
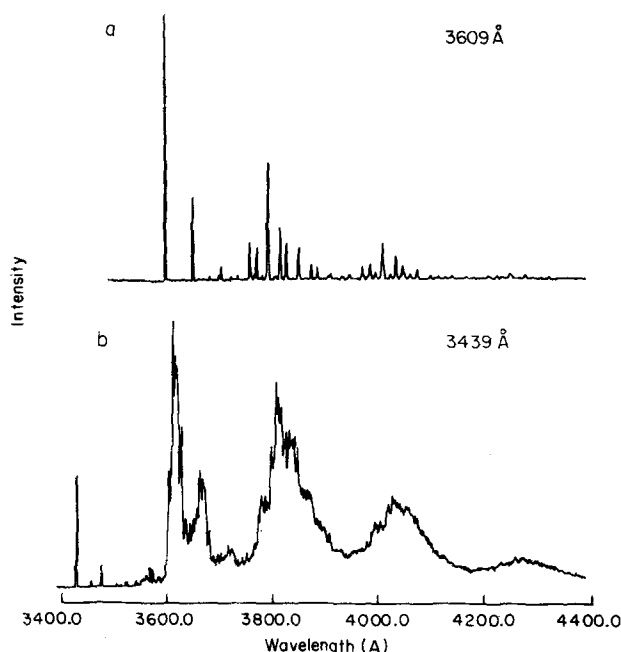

FIG. 1. Frequency-resolved fluorescence spectra for anthracene. The excitation wavelength ($\pm$ 4 Å) is given in the figure and the carrier gas used is nitrogen. The molecular beam conditions were: 40 psi carrier gas, T(nozzle) = 160 °C, p(chamber) = 10^{-4} Torr, and laser to nozzle distance ≃ 5 mm. The monochromator resolution was 2 Å. The first band in the top spectrum is the 0, 0 and the second band is the 390 cm^{-1} mode. The main progression is the 1410 cm^{-1}. Spectrum (b) shows the hot band, the 390 and the 1410 cm^{-1} progression. The prominent beats were seen in the region of the doublet before the 3600 Å main band.

distance was increased from ≃1 to 20 mm and when the back pressure of the carrier gas was increased from 10 to 60 psi. Fourth, the modulation depth depended upon the carrier gas,[8] increasing in the following order: $He < Ne < N_2$. Fifth, no spectral changes were observed with the various carrier gases at the pressures used, indicating the absence of large interactions with the carrier gas. Finally, the beats were observed using zone-refined or nonzone-refined anthracene. Also, the fluorescence spectrum of anthracene-d_{10} correlates with that of h_{10}. These observations lead us to conclude that the beats are due to intramolecular effects arising from the coherent excitation of molecules in the jet, although further work is needed to identify the nature of the states involved.

Upon first consideration, the very high density of molecular states at energies corresponding to S_1 excitation of molecules as large as anthracene might be expected to completely mask any coherence effects in their decay. Corroborating this premise is the fact that beats in fluorescence decays have, until now, only been observed by the McDonald and Schlag groups[9] in smaller molecules with comparatively sparse level structures (the total density of states, including rotational states, is relatively much smaller). Our observation of beats in the fluorescence decay of anthracene indicates that in large molecules there exist energy regions in the level
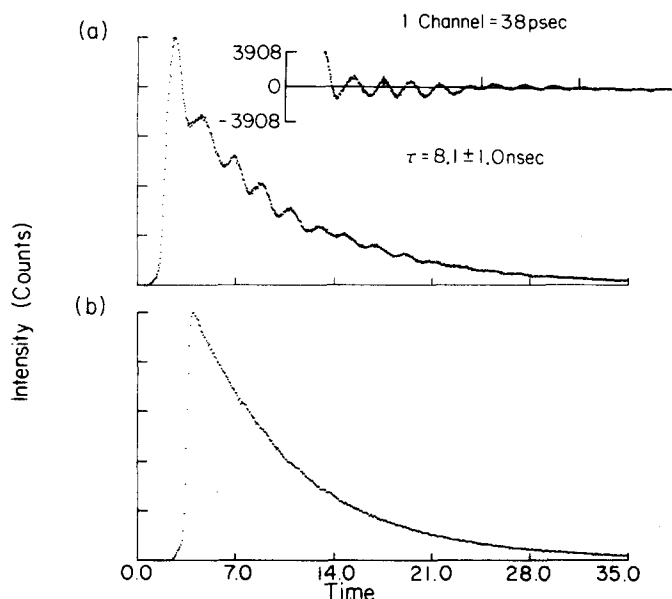
(a)

1 Channel = 38 psec

3908

0

-3908

$\tau = 8.1 \pm 1.0$ nsec

(b)

Intensity (Counts)

0.0   7.0   14.0   21.0   28.0   35.0
Time

FIG. 2. Fluorescence decays of anthracene obtained for the following detection (~5 Å bandwidth), excitation, and molecular beam conditions: (a) λex (excitation wavelength = 3439 Å, λdet (detection wavelength) = 3577.5 Å, x(nozzle/laser distance) ≃ 5 mm, p(nozzle pressure) = 40 psi N_2; (b) λex = 3439 Å, λdet = 3620 Å, x ≃ 5 mm, p = 40 psi N_2. Beats were also absent when λex varied to higher energy at the same λdet. The inset shows the residual obtained upon subtraction of the best exponential fit to the observed decay. We have also obtained these beats, which were observed on a number of emission bands, at 50 psi carrier gas pressure and observed no change.

structure where the effective density of states is small even though the overall density of states reflects the statistical limit. Furthermore, the large rotational density of states[10] does not in fact obscure the coherence effects. If we assume that the beats are due to the coherent preparation of a few levels in the S_1 manifold, then it follows that the dephasing of these states must be slow at these excess energies. In other words, the homogeneous width is less or comparable to the spacing between levels and in that sense we have a nonstatistical case. To know the actual modes involved in the coupling scheme we plan to do the high-resolution excitation spectra and assign bands (if possible).

In conclusion, we have demonstrated the value of combining picosecond excitation and supersonic molecular beam techniques in obtaining new information concerning intramolecular energy and phase dynamics. The observation of quantum beats in such large molecules is important new evidence for understanding intramolecular relaxations.[10,11] We also plan to apply these techniques to other systems where recent important experiments[12] in bulbs have revealed some support for vibrational energy redistribution. A full account of this work will be published later.

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