DIRECT OBSERVATION OF INTRAMOLECULAR ENERGY TRANSFER BY SELECTIVE PICOSECOND LASER EXCITATION OF A SINGLE CHROMOPHORE IN JET-COOLED MOLECULES

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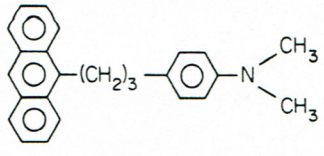
Here we report on the direct observation of time-resolved formation of a product of intramolecular energy transfer in isolated, jet-cooled $A^*-CH_2-CH_2-CH_2-B$. The anthracene chromophore (A) was excited by picosecond pulses, and the transfer of energy was probed at various excess energies by observing the emission arising from the exciplex formed between B (dimethyl aniline) and A^*. The threshold is at 3 kcal/mole.

Energy redistribution and its dependence on total energy in isolated large molecules is of great current interest. The methods applied to such studies [1] have varied from fluorescence quenching and lifetime measurements in bulbs to the dispersion of fluorescence in jets. The approach we have taken has been to time-resolve (picosecond) the emission of molecules cooled by supersonic jet expansion [2]. Although coherence and "threshold" effects have been observed in different systems [2], it has not yet been possible to find a molecule in which the intramolecular decay of an optically-prepared state could be linked to the build-up in population of a known final state.

In this note, we report the first observation of time-resolved formation of a product of intramolecular energy transfer in a jet-cooled molecule having different excess energies. The molecule studied (DMA)



has been examined extensively in solution by the Columbia group [3] and others [4]. Details of the synthesis of DMA will be given in ref. [5]. The DMA used was recrystallized from ethanol and had a melting point of 101.5–102.5°C. Upon excitation of the anthracene chromophore in the near-UV, DMA can decay radiatively in two ways: the chromophore can promptly emit, or emission can arise from a charge-transfer (CT) state, which involves the anthracene and aniline moieties. The CT emission is characterized by a rise time that matches the decay time of the prompt, anthracene-like emission. Evidently, the excited anthracene moiety can encounter the aniline moiety and from the CT complex only after a finite time has elapsed during which geometrical changes involving the propyl chain have occurred. The methods of supersonic jet spectroscopy allow one to study this reaction free from solvent interactions and as a function of well-defined molecular energy. The results presented here reveal a marked energy dependence to the CT formation rate and help to clarify the effect of solvent interactions on this rate. Because vibrational energy flow must be intimately associated with CT formation, the results also indicate that the rate can be used as a probe to study intramolecular vibrational energy redistribution.

The experimental apparatus has been described

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previously [2]. DMA at ≈200°C was expanded through a 150 μm pinhole together with 30 psi helium. The frequency-doubled output ($\Delta\bar{\nu} \approx 10$ cm^{-1}; $\Delta t \approx 15$ ps) of a synchronously-pumped dye laser, cavity-dumped at 4 MHz was used as excitation source. Fluorescence was collected through a monochromator and transients were obtained by using a fast photomultiplier. Excitation spectra were obtained by frequency doubling the output of a N_2 laser/dye laser combination.

Fig. 1a displays the jet-cooled dispersed fluorescence spectrum corresponding to excitation 1400 cm^{-1} above 26674 cm^{-1} (0,0 of anthracene-like state). The spectrum exhibits anthracene-like emission [2,5] ‡ as well as a broad tail to the red which

‡ At zero-excess energy, the emission spectrum is very sharp (anthracene-like) and shows the usual progressions of the totally-symmetric modes (no exciplex emission was observed). At higher resolution, the 0,0 region displays low-frequency bands most probably due to the propyl chain. The relevance of these bands to the dynamics will be addressed later [5].

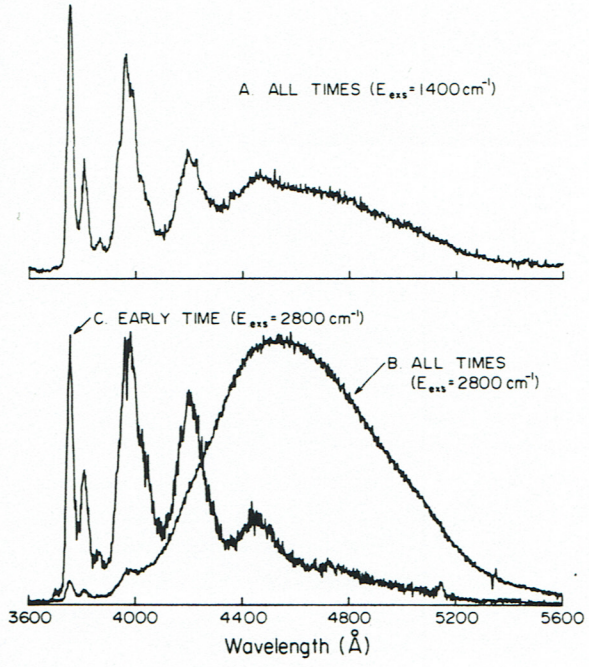

Fig. 1. Frequency-dispersed jet-cooled fluorescence spectra of DMA. Monochromator resolution (R) = 16 Å, laser–nozzle distance (χ) = 4 mm. Spectrum (c) represents the emission occurring within the first 1.5 ns. A full description of the procedure involved in obtaining (c) will be given in ref. [5].

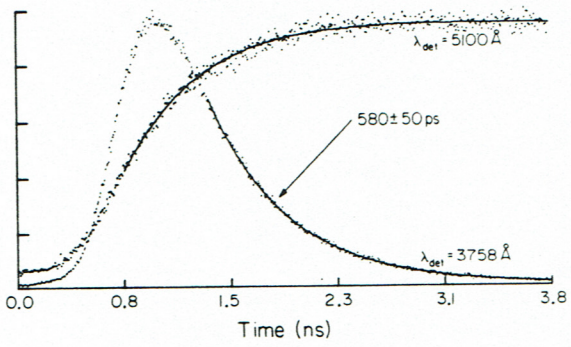

Fig. 2. Time-resolved spectra at two detection wavelengths (λ_{det}) for excitation corresponding to $E_{exs} \approx 2800$ cm^{-1} R = 50 Å, χ = 4 mm.

arises from the CT complex ‡. The anthracene-like emission (e.g. λ_{det} = 3758 Å) appears promptly in time and decays with an exponential time constant of 2.7 ns. The CT emission is much longer-lived and exhibits a rise time that matches the 2.7 ns lifetime.

Excitation corresponding to E_{exs} = 2800 cm^{-1} results in a spectrum (fig. 1b) dominated by CT emission. The fluorescence decay behavior (fig. 2) parallels that at E_{exs} = 1400 cm^{-1} except that the characteristic decay (rise) time becomes appreciably shorter. To emphasize the decay and build-up of fluorescence in different regions of the spectrum, an ear-early-time (gated) spectrum for E_{exs} = 2800 cm^{-1} is presented in fig. 1c.

The spectra of figs. 1a and 1b clearly indicate that increasing the amount of energy deposited in the anthracene chromophore results in an enhanced rate for CT formation that parallels the decrease in lifetime of the anthracene-like emission. Data at other values of E_{exs} also bear this out (e.g. at E_{exs} = 800 cm^{-1} almost no CT emission is observed, and at no excess energy was *only* anthracene-like emission seen). Given an efficient decay channel leading to CT formation, it is not surprising that the lifetime behavior, as a function of E_{exs}, of the anthracene-like emission does not parallel that of bare anthracene [2], for which a limiting value of 5.6 ns prevails, even at E_{exs} = 4200 cm^{-1}.

‡ The red-shifted (CT complex) emission in the jet is similar to that observed in solution [3,4,6].

It is useful to consider two processes when examining the rate of CT formation in the isolated molecule. First, energy must redistribute from anthracene-like vibrations to vibrations involving the propyl linkage. Second, the vibrationally energetic propyl chain must then undergo geometrical changes such that the anthracene and aniline moieties can interact. Given that the rates of both processes should increase with increasing E_{exs}, the change in the observed decay or build-up times (from ≈10 ns to ≈400 ps at 3500 cm^{-1}) is not surprising. In fact, from a plot of the rates versus E_{exs}, we found a threshold at ≈3 kcal/mole which is close to a C–C barrier height. The ability to determine CT *formation* rates as a function of vibrational mode-specific excitation may allow one to probe the timescale and specificity of redistribution processes [5].

Finally, the study of isolated DMA molecules allows the possibility of elucidating solvent effects. Using an assumed set of vibrational frequencies for DMA along with our jet lifetime data, we have calculated the decay of the anthracene-like emission for a thermal distribution of DMA at 298 K. The calculated lifetime (≈600 ps) is somewhat shorter than actually observed in cyclohexane solution (1.4 ns) [3]. It appears, therefore, that the geometrical changes needed for CT formation are hindered by solvent interaction. The relation of our jet results to Weller's [6] pioneering findings in solutions is still under investigation.

In conclusion, by using picosecond selective excitation of the anthracene chromophore in jet-cooled DMA we have observed population decay and build-up in an isolated molecule. We expect that these studies will be very helpful in understanding intramolecular energy redistribution. A full account of this work and work on other related molecules will be published elsewhere.

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