

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1984 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Picosecond pump-probe and polarization techniques in supersonic molecular beams: Measurement of ultrafast vibrational-rotational dephasing and coherence^{a)}

N. F. Scherer, J. F. Shepanski, and A. H. Zewail^{b)}

Arthur Amos Noyes Laboratory of Chemical Physics,^{c)} California Institute of Technology, Pasadena, California 91125

(Received 2 April 1984; accepted 8 May 1984)

In the last few years, the time-resolved dynamics of collisionless intramolecular vibrational-energy redistribution (IVR)¹ has been probed² using picosecond excitation and fluorescence detection. By this method new information on IVR, coherence and photochemical changes (e.g., *trans-cis* isomerization) has been obtained.^{2,3} However, in a number of cases the (early time) primary step following picosecond excitation could not be resolved simply because the time resolution was limited to ~ 50 ps.

In this Communication, we wish to report on the direct observation of picosecond transients in supersonic molecular beams. Using pump-probe and polarization techniques we present new data on stilbene and aniline at vibrational and rotational temperatures of < 10 and < 5 K, respectively. In these experiments, the pump laser pulse excites an optically active mode in S_1 and a delayed pulse probes this population as a function of the delay time. To probe the effect of rotations and coherence we polarize the probe parallel or perpendicular with respect to the pump. Our time resolution is typically 1 ps.

The laser system consists of a frequency stabilized mode-locked Ar⁺ laser synchronously pumping a dye laser (containing a two-plate birefringent filter). These pulses (width 3 ps and energy 1 nJ) are amplified in a three stage dye amplifier, which was synchronously pumped at 20 Hz by the second harmonic of a Nd:YAG laser (140 mJ/pulse). The amplified pulses are generally 3 ps in duration and 0.5 mJ in energy.

The pulses are split and sent into the arms of a Michelson interferometer. The second harmonic is generated in one arm while the visible light propagates through the variable delay arm which contains a compensator and polarizer. The beams are combined and focused (1 m lens) onto the supersonic jet, 1.5 cm downstream ($x/D = 75$). Our molecular beam system⁴ has a channeltron electron multiplier to measure the total ion signal produced by the probe (visible) as a function of the delay time. The S/N of our picosecond-beam transients is comparable to nanosecond-type^{5,6} experiments in jets or to ps/fs experiments done in bulbs.^{7,8}

Figure 1 shows the transients obtained for stilbene with zero and different excess energies corresponding to the fundamental mode⁹ (ν_{25} ; $C_e C_e \phi$ bend) and combination bands involving ν_{25} . In Fig. 2 we present the decay of the anisotropy $r(t)$ obtained from \parallel and \perp polarization transients. We made sure that the signal was linear in the pump (UV) intensity so there are no saturation effects. Similar polarization

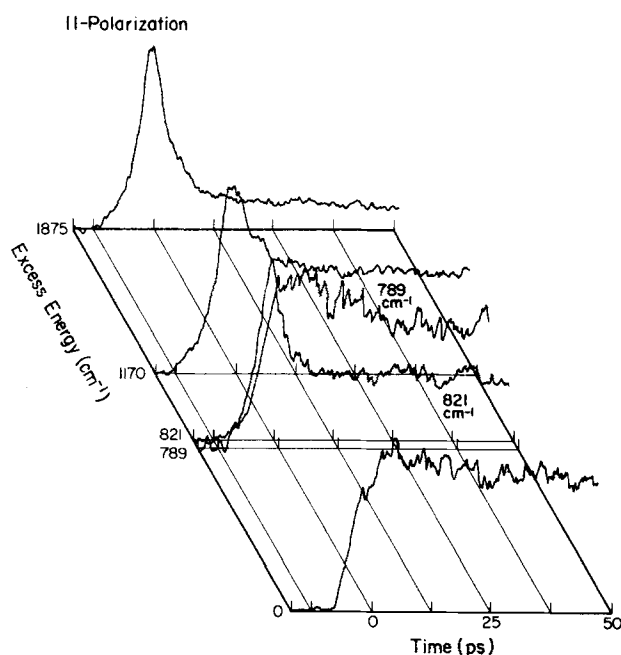


FIG. 1. Picosecond pump-probe transients of stilbene in a supersonic jet expansion. The carrier gas is He (20 to 30 psig), and x/D is 75. The vertical axis refers to the intensity (a.u.) of the total ion signal. The abscissa refers to the delay time between the pump and probe pulses (in ps) while the ordinate refers to the excess vibrational energy (in cm^{-1}). The data presented here are for parallel (\parallel) polarization. The data for \perp polarization (not shown) is reflected in $r(t)$ of Fig. 2. Note the sensitivity of the transient shape to the excess energy. At 200 and 400 cm^{-1} of excess energy we observed results similar to those at zero excess energy. Note that the transients are also normalized for absolute signal levels. By comparison, small signal levels for off-resonance excitation (57 cm^{-1} above 0-0) were observed. This finite signal is attributed to the congested background (see the text) between the modes observed in excitation spectra.

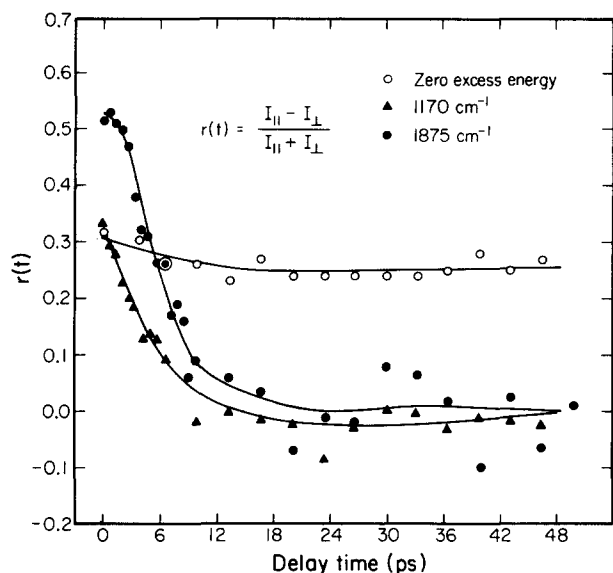


FIG. 2. The polarization anisotropy $r(t)$ as a function of the delay time and excess vibrational energy. Note that for zero excess energy $r(t)$ is essentially flat over the 50 ps time scale, and holds at a value of 0.25. At higher excess energy and long times this $r(t)$ drops to a value of zero within our error.

experiments were performed on aniline and we observed no biexponential behavior at several excess energies.¹⁰

The observed biexponential behavior can be explained using the model of Perry *et al.*⁷ Basically, the pump pulse prepares a "rovibronic packet." Following the coherent preparation, this packet dephases and evolves in time to form a redistributed state distribution. This equilibrated distribution decays (time constant τ_1) by the usual radiative/nonradiative processes. Accordingly, the short-time decay of the biexponential transient gives the dephasing time, while the long-time decay directly measures τ_1 .⁷

The results shown in Figs. 1 and 2 indicate the following: (i) The biexponential behavior is absent for zero (and low) excess energy. At higher excess energies (1200 cm^{-1}), however, the biexponentiality is very pronounced; (ii) there is a very strong polarization effect on the coherent signal, which (unlike liquids) cannot be eliminated by the magic-angle (54.7°) arrangement. This polarization anisotropy, $r(t)$ is very large at early time and goes to zero at long time. Furthermore, $r(t)$ depends on the vibrational mode excited, but does not change with time for zero excess energy; (iii) our beam results are different from those obtained in the bulb in two respects. First, for a given excitation energy the lifetime (τ_1) in the beam is longer, because the bulb τ_1 represents a thermally averaged lifetime where the thermal energy in S_0 is large (2000 cm^{-1}).⁷ Second, $r(t)$ is smaller in bulbs than in the beam.

The picture which emerges from these preliminary experiments is the following. The coherence of modes excited

in large molecules at high excess energy is very polarized. This indicates to us that the pump pulse prepares a well-defined rovibronic packet which is nonstationary and dephases rapidly. For the dephasing to be polarization dependent other symmetry states must be reached by the redistribution process. For this to occur vibrational-rotational coupling (by Coriolis or centrifugal forces) must be invoked. It is possible, although unlikely, that unusual vibronic coupling will access vibrations of a different symmetry, and in this case pure vibrational dephasing is possible. What is not known at this time is the level structure which causes the dephasing; do we excite a discrete set of eigenstates or do we excite discrete structure along with a "continuum" of congested states. The former will give rise to (inhomogeneous) dephasing only on-resonance while the latter will yield fast dephasing even off-resonance. We are currently examining this level structure problem and the off-resonance effect. Finally, we should point out that this picosecond decay of $r(t)$ is due to states in S_1 . It is not due to interelectronic coupling which produces small anisotropies, as shown recently.¹¹

Note added in proof: Very recently we learned of a theoretical treatment¹³ of vibrational-rotational dephasing which is in agreement with our findings here. More accurate comparisons with this theory are underway.

¹This research was supported by grants from the National Science Foundation (DMR-8105034 and CHE-8211356).

²Camille and Henry Dreyfus Foundation Teacher-Scholar.

³Contribution No. 7006.

⁴For a review of the subject see: C. S. Parmenter, *Faraday Discuss. Chem. Soc.* **75**, 7 (1983).

⁵A. H. Zewail, *Faraday Discuss. Chem. Soc.* **75**, 315 (1983).

⁶P. M. Felker and A. H. Zewail, in *NATO Advanced Research Workshop*, edited by K. Eisenthal (Reidel, Dordrecht, 1983); *Phys. Rev. Lett.* **53**, 501 (1984).

⁷J. A. Syage, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.* (to be published).

⁸(a) T. G. Dietz, M. A. Duncan, and R. E. Smalley, *J. Chem. Phys.* **76**, 1227 (1982); (b) C. E. Otis, J. L. Knee, and P. M. Johnson, *J. Phys. Chem.* **87**, 2232 (1983).

⁹(a) P. M. Johnson, *Annu. Rev. Phys. Chem.* **32**, 139 (1981); (b) E. W. Schlag and H. J. Neusser, *Acc. Chem. Res.* **16**, 355 (1983).

¹⁰J. W. Perry, N. F. Scherer, and A. H. Zewail, *Chem. Phys. Lett.* **103**, 1 (1983).

¹¹B. I. Greene and R. C. Farrow, *J. Chem. Phys.* **78**, 3336 (1983).

¹²J. A. Syage, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.* (to be published).

¹³In aniline, according to the dispersed fluorescence (Ref. 12) there is no significant IVR at the excess energies studied. Therefore, we expect the signal to rise with the laser pulse and decay by the lifetime of the state (8 ns). This is consistent with our observation on the picosecond time scale.

¹⁴Y. Matsumoto, L. H. Spangler, and D. W. Pratt in *Proceedings of the International Conference on Photochemistry and Photobiology, Alexandria, Egypt, January 5-10, 1983*, edited by A. H. Zewail (Harwood Academic, Switzerland, 1983), Vol. 1, p. 91.

¹⁵D. A. Chernoff and S. A. Rice, *J. Chem. Phys.* **70**, 2511, (1979).

¹⁶G. Nathanson and G. McClelland, *J. Chem. Phys.* **81**, 629 (1984).