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Measurement of vibrational energy redistribution rates in molecular clusters by time-resolved stimulated emission pumping

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In this note, we report the first time-resolved stimulated emission pumping (TRSEP) measurement of vibrational energy redistribution (IVR) in a van der Waals cluster. There are a few TRSEP measurements on bare molecule systems showing the various regimes of IVR (coherent and dissipative) and showing the interesting phenomenon of quantum beats.[1] The details of the TRSEP technique are described by Smith and McDonald.[1] Also, Felker and co-workers have recently measured rotational constants by the related technique of rotational coherence fluorescence depletion spectroscopy.[2] Briefly, the TRSEP technique involves initially populating a specific vibronic state of a molecule or cluster with a laser pulse, typically in the S_1 electronic manifold. Population is then removed from a specific excited vibronic state (usually the one just produced) by stimulating emission from that state with a second laser pulse. The second pulse results in a decrease in the total S_1 population. This depletion of excited state population is then measured as a decrease in the total observed fluorescence signal. Wavelength and time resolution in TRSEP experiments are both provided by the lasers.

We have undertaken these studies in the interest of making systematic measurements of IVR rates for several cluster vibrational states to determine the effect of vibrational energy and density of vibrational states on the rates of IVR in cluster systems. Several measurements of vibrational redistribution and vibrational predissociation (VP) in clusters have been made using time-correlated single photon counting (TCSPC).[3,4] These studies have provided a great deal of information on IVR and VP times in clusters; however, the two independent rate constants (k_{IVR} and k_{VP}) are frequently difficult to separate because often one or the other will dominate the dynamics for a particular cluster. Because of the temporal resolution limits of TCSPC, the kinetics of very short-lived states are often difficult to measure using that technique. Additionally, fluorescence techniques have an inherent sensitivity problem: very short-lived states emit very few photons. In particular, our measurements on aniline $(N_2)_1$ and $(CH_4)_1$ clusters indicate the need for better temporal resolution and sensitivity for these systems. We expect that other systems, which have high densities of van der Waals vibrations, will also exhibit fast IVR rates and thus require better temporal resolution. TRSEP studies provide a direct measurement of the dynamics of the probed state even if it does not live long enough to emit strongly.

The laser system used in this study is the same system used in this laboratory for time-described previously.[5] A cw, mode locked, Nd:YAG laser synchronously pumps two dye lasers and seeds a 10 Hz regenerative amplifier. The output of the regenerative amplifier pumps two four-cell dye amplifier trains. The amplified dye beams are frequency doubled to provide the excitation and probe beams. Total fluorescence (without wavelength resolution) is collected and directed into a photomultiplier. Because this is a pump–probe type experiment, the time resolution of the system is limited by the cross correlation of the two amplified dye laser pulses. The temporal resolution of this system full width at half maximum (fwhm) of the instrument response function varies from about 10 ps to about 40 ps, depending upon the extent of saturation in the amplifiers. This system is similar to the laser system used by McDonald's group[1] except that the repetition rate is lower and pulse energy higher for our lasers.

We have measured the TRSEP signal for aniline $(N_2)_1$ clusters excited by a laser tuned to the $\overline{1_0^1}$ transition. The

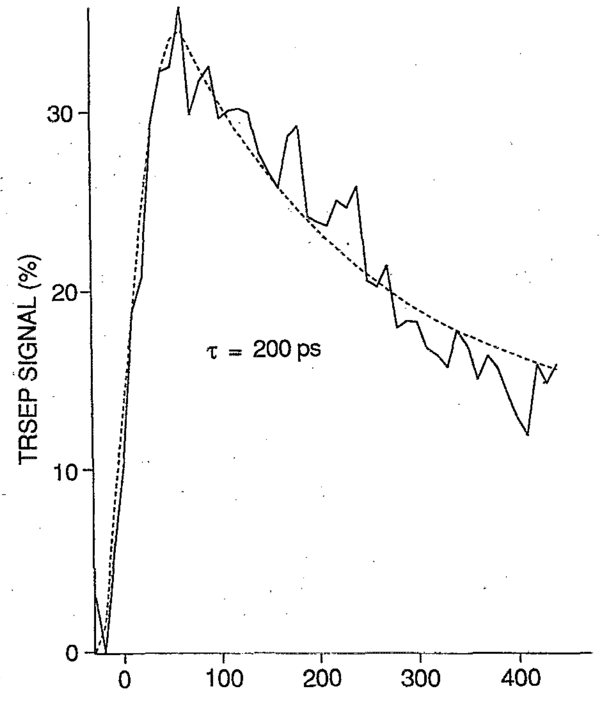

FIG. 1. TRSEP signal for the aniline $(N_2)_1$ clusters. Excitation laser is turned to the $\overline{1_0^1}$ transition, and the probe laser is tuned to the $\overline{1_0^1 6a_1^0}$ transition. This plot shows the extent to which the probe pulse diminishes the total fluorescence. The time axis is the difference between the arrival times of the pump and probe pulses. The maximum diminution of the fluorescence is about 30%. The smooth curve is generated using the results of a nonlinear fitting routine. The fast component time constant is 200±50 ps.

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dump laser is tuned to the $\overline{1_0^1 6a_1^0}$ transition so that it probes the dynamics of the $\overline{1^1}$ state. The results of this experiment are shown in Fig. 1. The nonlinear least squares fit curve is an exponential decay with a 200±50 ps time constant. This fitted τ_{IVR} is in agreement with the 360±100 ps which we obtained in the TCSPC experiments.[4(b)] A long-time component is also observed under the $\overline{1^1}$ state signal. This contribution has a lifetime which is longer than 4 ns and its contribution to the signal is determined by a longer time scan. The origin of this contribution is probably hot monomer background, or possibly higher order clusters, the aniline dimer, etc. This background intensity is not due to states populated by the IVR process as the same signal is observed if the excitation laser is tuned away from the aniline $(N_2)_1$ cluster $\overline{1_0^1}$ transition. We have attempted to eliminate unwanted contributions to the signal by dispersing the emission and observing only those features which arise from $\overline{1_0^1}$ excitation of the cluster; however, signal levels are sufficient to allow emission dispersion only for the case of monomer excitation. Clusters are present at much lower concentration and signals become too small to be viable for this experiment.

Our attempts to measure the IVR rates of other clusters and vibrational states have, in some cases, been thwarted by the same interferences observed for the aniline $(N_2)_1$ clusters $\overline{1^1}$ state. For example, aniline $(N_2)_1$ $\overline{15^2}$ and $\overline{1^2}$ show large spectral interferences presumably from weak monomer transitions. The interferences become more important as the intensity of the excited transition decreases and as the lifetime of the probed state approaches the instrumental resolution (ca. 10 ps).

We are continuing these experiments using analogous ionization-detected mass-resolved techniques in an attempt to remove the effects of spectral contamination apparent in the fluoresence signals. This approach is similar to the ionization detected methods introduced for rotational coherence spectroscopy experiments.[6]

We are presently beginning experiments to attempt a systematic measurement of IVR rates in the ground electronic state of clusters using time-resolved, ionization-detected, stimulated Raman spectroscopy (TR IDSRS). IDSRS was introduced by Esherick and Owyoung[7] and TR IDSRS entails varying the delay of the excitation and ionization lasers with respect to the Raman pumping lasers. Previous studies of ground electronic state IVR indicate that ground state IVR times are much longer than excited state IVR times;[8–10] we are therefore interested in making a systematic comparison of the IVR rates in both S_0 and S_1 electronic state of the aniline clusters.

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