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COMMUNICATIONS

Picosecond IVR dynamics of *p*-difluorobenzene and *p*-fluorotoluene in a molecular beam: Comparison with chemical timing data^{a)}

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Experimental techniques which probe the dynamics of intramolecular vibrational energy redistribution (IVR) in the time domain are of two kinds: direct picosecond time-resolved detection of spectra from isolated molecules in beams¹ and chemical timing by collisional quenching of molecules in a bulb.² This latter technique has been applied to the study of IVR of room temperature paradifluorobenzene (pDFB)³ and parafluorotoluene (pFT).⁴ Model analysis of the chemical timing results provided IVR parameters for the two molecules. For pDPB there have also been some time-resolved studies at room temperature.⁵⁻⁷ For room temperature vapors, Parmenter has pointed out that the high rotational and torsional⁸ excitation is an important factor in the dynamics. Rotations can play a role in IVR⁹ and it is important to address the following questions: What is the nature of IVR dynamics in the isolated, cold molecule and how does it compare with the results of chemical timing?

We present in this Communication preliminary time-resolved fluorescence measurements of supersonically cooled samples of pDFB and pFT. These measurements indicate that IVR in both cold molecules up to ~ 1600 cm^{-1} of excess vibrational energy is substantially less than that reported for the same vibrational excitations in the room temperature chemical timing studies.

The experimental apparatus employed has been described elsewhere.^{1,10} For these experiments, however, because of the spectral region of these molecules the total time response of the excitation/detection system was limited to several hundred picoseconds. (Typically 300 ps with a microchannel plate detector, or 550 ps with a high-gain photomultiplier with enhanced UV sensitivity.) The laser excitation bandwidth was approximately 5 cm^{-1} .

Figure 1 displays time-resolved fluorescence decays measured for 5_0^2 ($S_1 + 1636$ cm^{-1}) excitation of pDFB at two different detection energies, along with the corresponding measured instrument response and convoluted single exponential fits. The dispersed fluorescence in the beam is virtually background free at this energy.¹¹ The detected band at -1350 cm^{-1} is especially clean, lying as it does well to the

blue of the pDFB 0_0^0 transition. As clearly seen, these measurements show no hint of deviation from single exponential decay. Room temperature chemical timing experiments at this excitation energy have predicted biexponential evolution of structured emission with a 290 ps fast component.^{3(a)} Numerical simulations have shown that with our system response a decay of the predicted form can be readily distin-

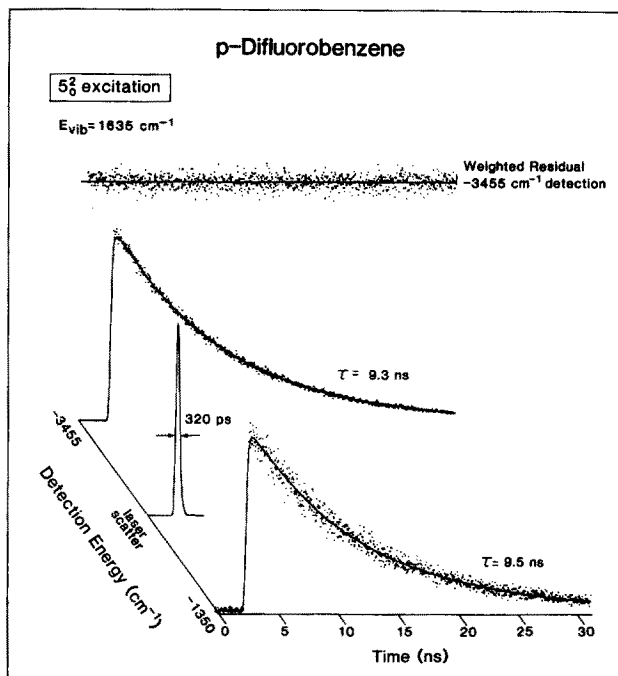


FIG. 1. Time-resolved fluorescence for 5_0^2 excitation of jet-cooled pDFB. The sample was held in a room temperature reservoir and expanded through a 60 μ diameter nozzle under 3.7 atm of helium backing pressure. Laser excitation occurred 2 mm from the nozzle. The shift of detection energy from the excitation is indicated. The detection bandwidth was 160 cm^{-1} for the upper and 220 cm^{-1} for the lower decay. The detected laser scatter served as the instrument response for convoluted fits. These are shown and the extracted lifetimes are given. The plotted residual is the difference between the data and the fit, normalized to the square root of the data value.

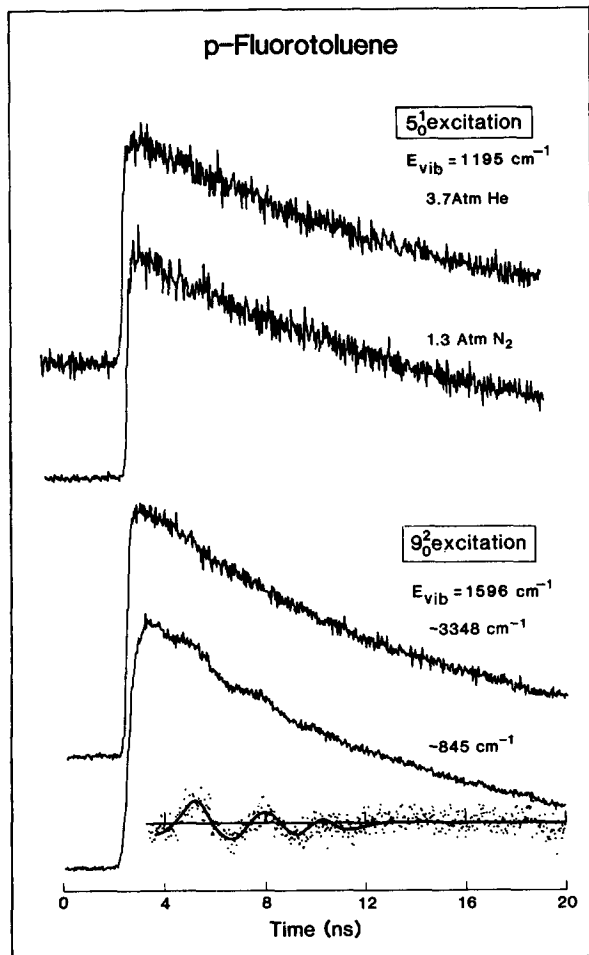


FIG. 2. Time-resolved fluorescence of jet-cooled pFT. The sample was heated to 50 °C and expanded as pDFB, except for the different backing gas and pressure indicated for the second decay. Detection was centered 4100 cm^{-1} from the excitation for the 5_0^1 decays and is given in the figure for the 9_0^2 decays. The detection bandwidths are 90 cm^{-1} for the second decay and $\sim 200 \text{ cm}^{-1}$ for the others. The bottom decay was detected with a temporal response of $\sim 550 \text{ ps}$ FWHM. The solid line through the residual is drawn only for visual enhancement of the beats. Decays measured with similar time resolution exciting 5_0^1 and detecting 845 cm^{-1} from the excitation showed no beats. In all cases, faster beats and/or greater modulation depth might be observed with better time resolution.

guished from a single exponential, even at the signal to noise of the -1350 cm^{-1} decay in Fig. 1.

Figure 2 displays a selection of time-resolved measurements for 5_0^1 ($S_1 + 1195 \text{ cm}^{-1}$) and 9_0^2 ($S_1 + 1596 \text{ cm}^{-1}$) excitation of pFT.¹² The dispersed fluorescence at 5_0^1 is dominated by sharp structure with a featureless background of congested emission appearing to the red of the pFT 0_0^0 transition (at 2712 Å). For 9_0^2 excitation, the congested background becomes the dominant component of emission to the red of 2712 Å. Detection for the top two decays shown is centered on structured emission in the red region of the 5_0^1 spectrum, at two different molecular beam expansion conditions. The third decay was recorded for 9_0^2 excitation and detection at the maximum of fluorescence intensity, where structured and broad emission are not resolved. These fit well to single exponentials convoluted with the appropriate instrument response ($\sim 300 \text{ ps}$ FWHM).

Of greatest significance, however, is the obvious quan-

tum beat pattern present in the fourth decay of Fig 2. The appearance of a regular modulation on the fluorescence is indicative of restricted IVR dynamics,¹ i.e., IVR among at most a few closely spaced coupled levels. Given that this situation prevails at 1596 cm^{-1} , it is not surprising that no deviation from single exponential behavior was discernible at lower energies, where the sparser level structure is even less favorable to IVR. We note also that the substantial increase in sample temperature achieved by low pressure nitrogen expansion does not alter the apparent absence of redistribution at 5_0^1 .

Though chemical timing measurements for pFT have indicated IVR times of 15 ps or less at the energies in question, it has already been recognized, solely on the basis of dispersed fluorescence that such rates do not characterize the jet-cooled molecule.⁴ The large difference in bulb and beam measurements may be due to the involvement of torsions/rotations⁸ and the purity of the initial state excited.^{14,15}

In conclusion, our results indicate that the IVR in pDFB and pFT in the molecular beam is substantially less than found at room temperature via chemical timing analysis. Time-resolved experiments at room temperature are now in planning to compare with beam results and address the role of rotations and dephasing.¹⁶

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¹²The pFT mode labeling in this work follows that of Parmenter (Ref. 4). In Varsanyi notation (Ref. 13) the modes 5 and 9 are labeled 13 and 1, respectively.

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