

Photodissociation of ICN in polar solvents: evidence of long lived rotational excitation in real liquids

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Abstract. The ICN \tilde{A} band photodissociation in polar solvents is studied using ultrafast pump-probe spectroscopy. The transient anisotropy reveals that highly rotationally excited CN photoproducts survive in methanol, ethanol, and water for several picoseconds.

Introduction: Photodissociation dynamics in a liquid environment are of considerable complexity and interest. In liquids, effects such as caging and collisions with surrounding solvent molecules that cause dissipation of electronic, translational, rotational and vibrational energy to the surroundings must be considered in addition to the often complex intrinsic dissociation dynamics manifested in the gas phase. The \tilde{A} band photodissociation of ICN is an excellent candidate to study the effects of the solvent on dissociation. This system has been studied extensively in the gas phase, both experimentally and theoretically. Three electronic states comprise this band and two product channels, $\text{ICN}^* \rightarrow \text{I} + \text{CN}$ and $\text{I}^* + \text{CN}$, are observed [1]. In the $\text{I} + \text{CN}$ channel, the CN is produced highly rotationally excited, $N \sim 50$, also making the system an excellent choice for studies of relaxation of highly rotationally excited molecules in the liquid phase.

Time resolved anisotropy measurements are a powerful tool to study rotational excitation and relaxation after photodissociation in a solvent environment. For example, in recent experiments on the photodissociation of HgI_2 and I_3^- in ethanol, the pump-probe polarization anisotropy results indicate an initial super-thermal rotational distribution of the diatomic fragments after dissociation followed by rapid thermalization. This is evidenced by a very fast Gaussian component in the anisotropy decay with correlation times shorter than a calculated thermal free-rotor time, in addition to the longer, ~ 10 ps, rotational diffusion time constants for HgI and I_2^- [2,3]. In contrast, the experiments in this paper present evidence for surprisingly long-lived rotational excitation and unperturbed free-rotor type motion of the CN product for ~ 100 rotational periods.

Experimental Methods: Pump-probe spectroscopy is used to study the ICN photodissociation dynamics in the polar solvents methanol, ethanol, H_2O and D_2O . An amplified Ti:Sapphire and OPA laser system with appropriate frequency doubling provides tunable UV pump and probe. The ICN \tilde{A} band is excited at two wavelengths, 224 nm and 255 nm. Due to the considerable blue shift of the \tilde{A} band in polar solvents this corresponds to ~ 260 nm (band center) and ~ 300 nm in the gas phase absorption. The reaction dynamics are probed via the CN $\text{B} \leftarrow \text{X}$ transition at 385 nm. Time resolution is optimized with prism pairs in both the

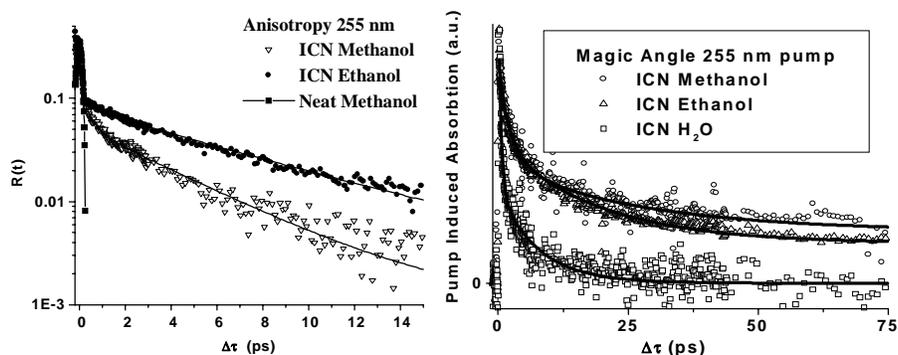


Figure 1 (Left) Transient anisotropy of CN fragment in methanol (lower trace) and ethanol (upper trace) with a 255 nm pump; neat solvent signal vanishes by 0.2 ps; (Right) Isotropic pump-probe signal of ICN in MeOH, EtOH and H₂O at 255 nm.

pump and probe beam paths to compensate for the considerable dispersion in the UV. Experimental time resolution is ~ 140 fs at 255 nm and ~ 180 fs at 225 nm as determined from the FWHM of the solvent coherent response. The sample is a ~ 200 μm free flowing jet of ~ 0.1 M ICN solution. High signal-to-noise pump-probe anisotropy measurements are achieved through the simultaneous detection of the parallel and perpendicular signals. The probe polarization is set 45° relative to the pump polarization and a Wollaston polarizing prism is used after the sample to separate the parallel and perpendicular components of the probe.

Results and Discussion: *Fig. 1(left)* shows the pump-probe anisotropy data for ICN in ethanol and methanol at 255 nm. The early signal is dominated by a strong solvent coherent spike. Thus, it is difficult to separate out the early portion of the anisotropy signal due to ICN. After ~ 200 fs the solvent signal has reached zero and the anisotropy is entirely due to the CN photofragment. These data sets show relaxation on two time scales from an initial anisotropy of 0.1. The short time constant is 400 fs in methanol and 500 fs in ethanol. These are approximately the timescales expected for rotational diffusion of thermalized CN and the characteristic time in ethanol is slightly longer due to the higher viscosity. The longer time constants at 255 nm are 3.7 ps and 6.7 ps in methanol and ethanol respectively. This several picosecond relaxation process is much longer than would be expected for rotational diffusion of a thermalized CN photofragment. We note that CN in room temperature water is believed to drag considerable solvent in its tumbling and has a characteristic reorientation time of 0.8 ps[4]. One possible assignment is this feature is due to long-lived rotationally hot CN fragments. In the gas phase, a large fraction of the CN product is released with the majority of the excess kinetic energy going into rotation, yielding a rotational distribution centered near $N=50$ (~ 0.6 eV). The highly rotationally excited CN requires ~ 1000 gas phase collisions to dissipate the rotational kinetic energy [5].

After photodissociation of a linear or bent triatomic in a collision-free regime, due to conservation of angular momentum, the long time anisotropy is not expected to be zero but 0.1 for parallel pump and probe transition dipoles or -0.05 for perpendicular transition dipoles [6]. The same will hold in a liquid over the period where collisions are ineffective at interrupting the rotational motion. It is thus reasonable to believe the surprisingly long several picosecond anisotropy decay may be attributed to the highly torqued CN photofragments requiring a large number of collisions with the solvent before slowing enough for their orientations to be completely randomized. We are making the analogy with a classical spinning top – it is hard to push the top off its axis of rotation. A similar result holds for water: the long time constant is 3.7 ps. This implies that water is no more effective at interrupting the CN rotations than the alcohols. With a 224 nm pump, we see similar decay times in methanol and ethanol with a lower initial anisotropy of 0.07. Additionally, preliminary data in weakly interacting cyclohexane suggest an order of magnitude longer lived anisotropy for the CN product.

Fig. 1(right) shows the isotropic signals at 255 nm for ICN in three polar solvents at a common pump wavelength. There are two timescales for consumption of the CN photoproduct. The short timescale ranges from 0.55 ps in water to 3 ps in methanol and is assigned to geminate caging recombination. The timescales are similar, but shorter than a previous experiment in chloroform [7]. Our results suggest faster cage recombination and a smaller fraction escaping for solvents with more rigid cages due to hydrogen bonding. The longer time process ranges from 7.7 ps in water to 27 ps in methanol. In previous experiments on chloroform, a second ~ 70 ps time constant was observed and assigned to abstraction of a H or Cl atom from the solvent by the CN [7,8]. We have not yet confirmed that this is the case in these polar solvents. The CN may also escape the cage and undergo a secondary recombination with its geminate partner. A kinetic isotope effect $k_D/k_H \sim 2.2$ is observed for the long time constant in D_2O . Another point of interest is that no CN fragments survive to timescales longer than we can measure (400 ps) in H_2O and D_2O while in ethanol and methanol 20-25% survive. Finally, we note that at 224 nm caging recombination occurs more rapidly; however, the longer time constant remains the same in all solvents.

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