

## FEMTOSECOND PUMP/PROBE STUDY OF VIBRATIONAL LIFETIMES OF THE FUNDAMENTAL ACETYLENIC C-H STRETCH IN DILUTE SOLUTIONS

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Vibrational lifetimes of the acetylenic C-H stretch for eight molecules in dilute carbon tetrachloride (CCl<sub>4</sub>) solutions have been measured at room temperature using femtosecond infrared pump/probe spectroscopy. The vibrational population relaxation in solution is driven by two factors; intramolecular vibrational energy redistribution (IVR) and collision induced relaxation. The solvent-induced relaxation rate has been determined by measuring the vibrational lifetimes of propyne, propargyl chloride, and propargyl bromide in CCl<sub>4</sub> solutions. High-resolution gas-phase infrared studies of these molecules using an electric-resonance optothermal molecular-beam spectrometer (EROS) show no evidence of IVR. The solvent-induced relaxation rate is approximately  $2 \times 10^{10} \text{ s}^{-1}$  in dilute CCl<sub>4</sub> solutions. The femtosecond pump/probe study shows that lifetimes are independent of the vibrational state densities of molecules, where the state densities range from  $10^0$  to  $10^5$  states/cm<sup>-1</sup> around 3330 cm<sup>-1</sup>, with propyne (HCCCH<sub>3</sub>) being the smallest and trimethylsilylacetylene (HCCSi(CH<sub>3</sub>)<sub>3</sub>) being the largest. The overall trend of the relaxation rates, however, strongly resembles the trend of molecules' IVR rates studied with EROS, which demonstrates the solvent-induced energy relaxation is unvarying for different molecules in the same solvent.