VIBRATIONAL DYNAMICS OF THE ACETYLENIC C-H STRETCH OVERTONE OF TERMINAL ACETYLENES IN GAS AND DILUTE SOLUTION STUDIED BY ULTRAFAST TRANSIENT ABSORPTION SPECTROSCOPY

PAM L. CRUM, HYUN S. YOO, and B.H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, Va 22904*.

We have recently studied the vibrational dynamics of the first overtone (v = 2) of the acetylenic C-H stretch in a series of terminal acetylenes in both gas and dilute (0.05M) CCl_4 solution. Using ultrafast transient absorption infrared spectroscopy, we have measured the intramolecular vibrational-energy redistribution (IVR) rate of room-temperature gas phase molecules and the total relaxation rate of these molecules in dilute solution. The v = 2 state population for gas phase molecules is directly pumped with the v = 2-0 transition frequency (~6550 cm^{-1}). Population of the v = 2 state in dilute solution samples is pumped by either this direct method, or by a sequential pumping method. In this sequential pump scheme, two regenerative amplifiers, one picosecond and one femtosecond, are time-synchronized and used to pump three independently tunable OPAs. Using the two picosecond OPAs, the v = 1-0 acetylenic C-H stretch is excited, immediately followed by excitation of the v = 2-1 transition. The third OPA is used as a femtosecond probe in the experiment. We have found that the sequential pumping scheme for dilute solutions gives the same results as the direct pumping scheme, but with higher sensitivity. In both schemes, the relaxation rates are obtained by directly monitoring through the v = 3-2 transition frequency. Gas phase terminal acetylene measurements give the molecule-dependent intramolecular vibrational-energy redistribution (IVR) rate, while measurements in dilute solution provide the total relaxation rate to which both purely intramolecular and solvent-assisted processes contribute. In the acetylenic C-H stretch overtone, as in the case of the fundamental, the total relaxation rate in solution is simply the sum of intramolecular vibrational-energy redistribution (IVR) and the solvent-induced vibrational energy relaxation (VER). The same gas-phase IVR rate is found in solution and the VER rate is constant for all terminal acetylenes studied (~$(30ps)^{-1}$). This VER rate is faster than the value observed for the fundamental measurements.