EXCEPTIONALLY FAST INITIAL INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN CYCLOPROPYLACETYLENE: STUDY OF THE VIBRATIONAL DYNAMICS OF THE FIRST EXCITED STATE OF THE ACETYLENIC C-H STRETCH OF CYCLOPROPYLACETYLENE IN A COLD MOLECULAR-BEAM, THE ROOM-TEMPERATURE GAS, AND THE DILUTE SOLUTION

GORDON G. BROWN, KEVIN O. DOUGLASS, JAMES E. JOHNS, JOHN C. KESKE, PRADEEP M. NAIR, FRANCES S. REES, HYUN S. YOO, AND BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904*.

The vibrational dynamics of the first excited state of the acetylenic C-H stretch of cyclopropylacetylene (CPA) in both gas- and solution-phase are investigated. FTMW-detected infrared spectroscopy and high-resolution molecular-beam spectroscopy techniques are used to investigate the dynamics of ultracold molecular-beam CPA, while ultrafast time-domain transient absorption spectroscopy is used to study the dynamics of CPA in gas and dilute solution at room-temperature. The newly developed FTMW-detected IR spectrometer provides fast infrared frequency scanning rates (scanning speeds of up to 18 cm^{-1}/hr) as well as high sensitivity to detect weak infrared transitions. With the newly accessible information provided by the FTMW-detected IR spectrum, excellent agreement among the results measured by different techniques is achieved. Both FTMW-detected IR spectroscopy and femtosecond pump-probe spectroscopy show a very fast initial IVR rate of the first excited state of the acetylenic C-H stretch of CPA. When CPA is solvated (0.05M CCl_4 solution), the IVR rate maintains the room-temperature isolated molecule value. The solvent contribution to the total relaxation rate in solution (k_{TOT} = k_{IVR} + k_{VER}) is minor and the main effects of the solvent are attributed to pure dephasing effects that destroy the intramolecular coherence.