

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

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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  $18 \text{ cm}^{-1}/\text{hr}$ ) 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  $\text{CCl}_4$  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.