CYCLOPROPYLACETYLENE STUDIED IN COLD FREE JET EXPANSION, ROOM TEMPERATURE GAS, AND DILUTE SOLUTION: TIER MODEL IVR

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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 in a free jet expansion 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. Good agreement among the results measured by different techniques was reported previously and improved time-domain results have recently provided excellent agreement as well as new dynamic information. Both FTMW-detected IR spectroscopy and femtosecond pump-probe spectroscopy show a very fast (~0.6 ps) initial IVR rate of the first excited state of the acetylenic C-H stretch and oscillations on the timescales of 5 ps and 20 ps, which is evidence of partial population return into the first excited state of the 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.