INTRAMOLECULAR VIBRATIONAL DYNAMICS UNDER HIGH PRESSURE CONDITIONS: COLLISIONS AND INTRAMOLECULAR VIBRATIONAL COHERENCE

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For large molecules, the population of a coherently prepared vibrational excited state will decay through intramolecular vibrational energy redistribution (IVR). From a frequency-domain perspective, these intramolecular dynamics are caused by extensive local perturbations to the excited state. When the molecule is excited with a short-pulse infrared laser, several eigenstates are simultaneously excited creating the nonstationary normal-mode state. The IVR population dynamics come from the dephasing dynamics of the excited molecular eigenstates. Using two-color picosecond transient absorption spectroscopy we have previously shown that the IVR rate of the acetylenic C-H stretch first excited state in the isolated molecule is relatively unaffected by the solvent. However, the solution phase dynamics differ from the isolated molecule dynamics in one important way: relaxation appears to be more complete in solution. We have attributed this effect to decoherence caused by interaction with the solvent. To test this model, we have studied the IVR dynamics of a series of terminal acetylenes in variable pressures of argon (up to 100 atm). The evolution of the time-domain spectrum as the pressure is increased is found to be consistent with decoherence models. Two molecules have particularly interesting behavior. The short time dynamics of acetylene and methylbutenyne are dominated by a simple two-level interaction. The fate of this intramolecular coherence as the pressure of an inert gas increases is examined using femtosecond infrared spectroscopy. For acetylene, the intramolecular vibrational coherence is maintained for times longer than 50 ps with about 100 atm of argon or helium present. This time scale is significantly longer than the mean collision time.