VIBRATIONAL ENERGY RELAXATION DYNAMICS OF ACETYLENIC COMPOUNDS IN ROOM TEMPERATURE GAS-PHASE

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Vibrational energy relaxation rates of the acetylenic C-H stretch fundamental are measured for a series of molecules in room temperature gas-phase. Vibrational lifetimes are measured by directly monitoring the excited state population using time-dependent absorption spectroscopy of the anharmonically shifted v=1 - v=2 transition following picosecond infrared excitation. Molecule-dependent IVR rates are observed. The IVR rates in the room-temperature sample are significantly faster than IVR rates measured in the molecular beam. However, the same trends are observed in both measurements. Also, bi-exponential decay of the vibrational energy is observed for the molecules with fast IVR rates in room temperature gas-phase. The fast component of the bi-exponential decay is attributed to the strong coupling between the acetylenic C-H stretch and near-resonant combination bands involving the overtone of the acetylenic C-H bend. This assignment is supported by measurements that directly monitor the acetylenic C-H bend overtone population following the initial excitation of the acetylenic C-H stretch. The rise time of the acetylenic C-H bend overtone signal matches the fast time component of the acetylenic C-H stretch decay. The slow component of the relaxation rate corresponds to statistical vibrational energy redistribution to the full set of near-resonant vibrational states. The statistical nature of the second step in the IVR process is quantified by measuring the acetylenic C-H stretch absorption spectrum at variable times following the initial excitation. The steady state spectrum of the hot molecule that is produced by the IVR process is compared to predictions based on the structure of the vibrational bath and known vibrational anharmonicities of the acetylenic C-H stretch.