VALIDITY OF THE "IVR THRESHOLD" IN THE VIBRATIONAL ENERGY RELAXATION DYNAMICS OF MOLECULES IN SOLUTION AT ROOM TEMPERATURE

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For large polyatomic molecules, the normal-mode vibrations are no longer stationary states of the full molecular Hamiltonian at high energy. In the high-energy regions, the normal-mode states are extensively coupled to the dense set of near-resonant vibrational states comprised of overtones and combination bands of the lower frequency modes. As a result, energy initially deposited in a normal-mode state is redistributed to other vibrational states. This process is called intramolecular vibrational energy redistribution (IVR) and plays a fundamental role in chemical kinetics. Previous molecular-beam, infrared fluorescence studies showed that IVR occurs for the hydride stretch fundamentals once the vibrational state density reaches 10-100 states/cm^{-1}. This "IVR threshold" has been confirmed in recent years by high-resolution, eigenstate-resolved vibrational spectroscopy in molecular beams. Although the threshold state-density is "universal", molecule-specific IVR rates are found. For example, the time scale for IVR in terminal acetylenes measured by high-resolution spectroscopy range from 60 ps - 3000 ps. These rates do not correlate with the total state density, despite the expectation based on Fermi's golden rule. For molecules in solution, new pathways for vibrational energy relaxation exist that come from interaction with the solvent. We present a series of two-color picosecond infrared measurements of the total energy relaxation rate of the acetylenic C-H stretch fundamental in a series of terminal acetylenes. These measurements directly probe the population of the first excited state of the acetylenic C-H by measuring the time-dependent absorption at the anharmonically shifted v=1 - v=2 transition frequency. Molecule-dependent relaxation rates begin to appear at the same IVR threshold previously found in molecular-beam studies. Furthermore, the IVR rates in solution correlate well with the molecular-beam rate determinations, although the rates in solution are about 20 times faster. Using the two-color (double-resonance) measurement we indicate the difficulties in interpreting single-color pump-probe measurements of vibrational relaxation rates when IVR occurs and describe the acetylenic C-H stretch vibrational spectrum of the vibrationally hot molecules created by rapid IVR.