COLLISION ENERGY TRANSFER IN THE HIGHLY DENSE REGION OF THE S_1 VIBRATIONAL MANIFOLD OF *PARA*-DIFLUOROBENZENE

UROS S. TASIC, and CHARLES S. PARMENTER, *Department of Chemistry, Indiana University, Bloomington IN 47405.*.

Vibrational energy transfer (VET) is studied from a wide range of vibrational levels and state densities of S_1 *para*-difluorobenzene (*p*DFB) in gas phase subject to single collisions with the series of rare gases. The absolute state-to-field collision cross-sections are determined for vibrational regions where states are highly mixed, where enormous state densities constitute a vibrational state quasi-continuum, and dynamics is dominated by fast intramolecular vibrational redistribution. We use these regions as replicas of the vibrational manifold associated with the high energy activation/deactivation problem of thermal unimolecular reactions. While the total cross-sections for the unimolecular problem are commonly assumed to be Lennard-Jones and constant regardless of initial vibrational state identity, state density or energy, our experiments attempt to provide direct evidence on these questions. Even though capabilities of our technique fall way short of really hot molecules (by ˜10 times) in terms of energy, the state densities are well in excess of 10^4 states per cm^{-1} , and thus representative of such hot molecules. Our experiments are designed to tackle the problem of effective size of molecules in high state density regime in terms of VET efficiency, which is one of the key ingredients in evaluating energy transfer rates R(E,E') and a component in treating unimolecular reaction kinetics. The experiments involve preparing *p*DFB in a single vibrational state, exposing fluorescence structure by our chemical timing method via high-pressure electronic quenching with O_2 , and subsequent monitoring of prepared state as it is destroyed in collisions with a rare gas partner into a field of neighboring vibrational states. We shall discuss the trend of the observed absolute VET cross-sections.