PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY OF HYDROGEN BONDED CLUSTERS AND CHARGE TRANSFER COMPLEXES

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Photofragment translational spectroscopy, using a pulsed-extraction time-of-flight method, has been applied to the study of kinetic energy release (KER) in weakly bound molecular complexes and clusters. The KER for cluster species manifests significant changes relative to the isolated molecule conditions, serving as a sensitive indicator of intermolecular interactions. Studies of neat hydrogen halide clusters, $(HI)_n$, reveal that the I atom fragments experience strong cage effects, in analogy with well known bulk phase phenomena, resulting in a broad, generally isotropic velocity distribution. Under the same conditions, the H atom fragment KER is largely unaltered and cage effects are not as important. However, a second, isotropic H atom velocity distribution is also detected, possibly resulting from trajectories that lead to reactive and near-reactive encounters with neighboring HI solvent species. These results can be compared to the KER of other HI containing molecular complexes. In contrast to these relatively weakly bound systems, we have also investigated KER in charge transfer (CT) complexes where the intermolecular interactions are very strong. Excitation of the CT state in C_6H_6-I_2 complexes leads to the production of two distinct I atom velocity distributions, reflective of the structure of the complex and the dynamics of the photochemical event. The KER of the C_6H_6 and I_2 product fragments was also measured. Wavelength resolved spectra of the C_6H_6 and C_6H_6-I chromophores also illustrate the effects of the CT process, such as the presence of rotational excitation.