TIME-RESOLVED PHOTOELECTRON IMAGING OF DISSOCIATION DYNAMICS IN GAS-PHASE $IBr(CO_2)_n^-$ CLUSTERS

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Small gas-phase clusters exhibit many of the interesting and complex dynamics found in the more complicated liquid environment. For example, following laser excitation, IBr^- anions clustered with only a few CO_2 molecules undergo photodissociation, excited state trapping, recombination, and charge transfer between the photofragments. These processes are solvent-driven, and their dynamics are very sensitive to the number and orientation of the clustering molecules. In our experiments on small $IBr(CO_2)_n^-$ clusters, time-resolved photoelectron spectroscopy directly probes the electronic wavefunction of the dissociating chromophore, the IBr^- anion, with 100-fs temporal resolution. We cross a mass-selected beam of anion clusters with a pump laser pulse, which initiates the dissociation of the IBr^- chromophore with an excess energy of a few tenths of an eV. A time-delayed probe laser pulse then detaches the excess electron. Our photoelectron spectrometer operates in the velocity-map imaging mode, collecting the electron kinetic energy and angular distributions at the same time. The time-resolved imaging of the evolving electronic wavefunction during the dissociation of the clustered IBr^- anion affords a clear view of its dynamics. We observe the system progressing in several product channels, with their characteristic timescales and spectral signatures. Extending this technique to larger clusters and more complex chromophores promises new dynamical insights into fundamental chemical processes and a test for computational chemistry.

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