DISSOCIATION DYNAMICS OF THE $IBr^-(CO_2)$ VAN DER WAALS CLUSTER: A DIRECT VIEW OF SOLVENT-DRIVEN NON-ADIABATIC TRANSITIONS

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We present the results of several time-resolved pump-probe experiments that explore the photodissociation of a simple dihalide anion, IBr^-, clustered with a single CO_2 solvent molecule. A 100-fs pump laser pulse (λ=800 or 400 nm) initiates the dissociation of IBr^- on either the A'$^2\Pi_{1/2}$ or the higher-lying B$^2\Sigma^+_{1/2}$ state of the anion. A second, time-delayed, tunable 100-fs laser pulse probes the subsequent dynamics by photoelectron spectroscopy.

In the bare anion the A' and B states correlate exclusively to the I^- or the Br^- photoproducts, respectively. However, the addition of a single solvent molecule induces charge switching in a subset of the excited molecules midway through the dissociation, resulting in mixed photoproduct distributions (both I^- and Br^-) from both states.

In the case of dissociation on the A' state (which correlates asymptotically to I^-), the CO_2 solvent molecule produces charge switching to Br^- in about 3% of the products, even though it cannot induce potential curve crossings. Electronic structure calculations and MD simulations point to a subtle mechanism for these non-adiabatic charge hops, involving the effects of the CO_2 bending vibration to bridge the energetic gap of the charge transfer. Conversely, for dissociation on the higher-lying B state (which correlates asymptotically to Br^-), the photoproduct ratio is about 60% Br^-:40% I^-, indicating large amounts of charge switching. In this case it is energetically possible for the CO_2 molecule to cause the B state to cross with the nearby a'$^2\Pi_{1/2}$ state, which correlates with I^-. The charge switching mechanism, which is likely to be more complex than for the A' state, will be discussed in detail.

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