

EXPERIMENTAL INVESTIGATION OF THE DISSOCIATION MECHANISMS OF $\text{He} \cdots \text{ICl}(B, v')$ VAN DER WAALS COMPLEXES

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Two-laser, pump-probe spectroscopy experiments reveal different dissociation pathways for $\text{He} \cdots \text{ICl}(B, v')$ intermolecular levels. Weakly bound $\text{He} \cdots \text{I}^{35}\text{Cl}(B, v'=3)$ complexes that are prepared with different quanta of intermolecular vibrational excitation are observed to undergo vibrational predissociation to yield predominantly $\text{I}^{35}\text{Cl}(B, v'=2)$ products. The $\text{I}^{35}\text{Cl}(B, v'=2)$ rotational product state distributions formed following the excitation of different intermolecular vibrational levels and rotational states are all bimodal. Less rotational excitation is found in the products when preparing $\text{He} \cdots \text{ICl}(B, v')$ bending levels that preferentially sample the linear He–I–Cl and anti-linear I–Cl–He orientations than when preparing the lowest intermolecular vibrational energy level, which has a preferred T-shaped geometry. Additionally, linear $\text{He} \cdots \text{I}^{35}\text{Cl}(B, v'=2)$ complexes undergo a direct dissociation mechanism when prepared above the $\text{He} + \text{I}^{35}\text{Cl}(B, v'=2)$ dissociation limit. The $\text{I}^{35}\text{Cl}(B, v'=2)$ products are formed with significantly less rotational excitation via this mechanism. Dynamical effects believed to be associated with tunneling through the centrifugal barrier are observed and result in highly non-statistical rotational distributions.