

## OBSERVATION OF COMPETING PATHWAYS IN THE RELAXATION OF ICl\* IN A He SUPERSONIC EXPANSION

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Collision-induced relaxation of ICl\* and differing caging mechanisms of electronically excited ICl\* within He · · ICl\* complexes are investigated using laser-induced fluorescence and two-laser, pump-probe spectroscopy. It is found that collisions of He atoms with molecules prepared in the short-lived ICl( $B^3\Pi_{0+}, v'=3$ ) rotor states occurs on timescales sufficient for vibrational relaxation down to the long-lived ICl( $B, v'=2$ ) rotor states. It is also shown that when linear He · · ICl( $X^1\Sigma_{0+}, v''=0$ ) complexes are promoted to the continuum of states correlating with the repulsive, inner wall of the ICl( $A^3\Pi_1$ ) potential, the dissociating ICl( $A$ ) molecule undergoes kinematic one-atom caging, ejecting the weakly bound He atom, and re-stabilizing the molecule in high lying vibrational levels within the  $A$  electronic state with very little rotational excitation. Features associated with transitions of the linear He · ·  $I^{35}\text{Cl}(X, v''=0)$  complex to intermolecular states associated with the ICl( $B$ ) diabat that are coupled with those in the ICl( $B'$ ) adiabat formed by an avoided curve crossing are also observed in laser-induced fluorescence spectra. The ICl\* molecules within the excited state complex undergoes a non-adiabatic one-atom caging mechanism forming  $I^{35}\text{Cl}(B, v')$  products with little rotational excitation.