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$\cdots$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$\cdots$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$\cdots$I^{35}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}Cl(B,v') products with little rotational excitation.