

THE ORIGIN OF THE $\text{Ar} \cdot \cdot \text{I}_2$ $B-X$ CONTINUUM EXCITATION SIGNAL BELOW AND ABOVE THE $\text{I}_2(B)$ DISSOCIATION LIMIT: BOUND-FREE TRANSITIONS OF THE LINEAR COMPLEX

JOSHUA P. DARR, JOHN J. GLENNON, and RICHARD A. LOOMIS, *Department of Chemistry, Washington University, One Brookings Drive, CB 1134, Saint Louis, MO 63130.*

Discrete features associated with transitions of both the T-shaped and linear $\text{Ar} \cdot \cdot \text{I}_2(X, v''=0)$ complexes are observed in laser-induced fluorescence and action spectroscopy experiments performed throughout the $\text{I}_2 B-X$ electronic region. The binding energy of the linear conformer is directly measured to be $250(2) \text{ cm}^{-1}$, 10 to 15 cm^{-1} greater than that of the T-shaped conformer. Continuum signals are observed in the spectra that continue to energies well above the $\text{I}_2(B)$ dissociation limit. Our results indicate that the continuum signals can be attributed to transitions of the linear $\text{Ar} \cdot \cdot \text{I}_2(X, v''=0)$ complex to the inner, repulsive walls of many $\text{Ar} + \text{I}_2(B, v')$ intermolecular potentials. The excited state complexes are thus very short lived and undergo direct dissociation into $\text{Ar} + \text{I}_2(B, v')$ products. There is no evidence for the previously proposed one-atom caging mechanism.