DYNAMICS OF LINEAR AND T-SHAPED ArI$_2$ DISSOCIATION UPON B←X EXCITATION: A DISPERSED INTRACAVITY LASER-INDUCED FLUORESCENCE STUDY

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We have recorded the dispersed fluorescence spectra of the linear and the previously well-studied T-shaped isomeric ArI$_2$ complexes following B←X excitation. The dispersed fluorescence features originate from the free I$_2$ B→X emission and reveal the I$_2$ product vibrational state distribution. The vibrational distribution of photofragment I$_2$(B) produced from dissociation of the T-shaped isomer shows a sharp Poisson distribution, beginning with $\Delta v' = -3$, which is nearly independent of excitation energy. The vibrational distribution of I$_2$(B) from the linear isomer is quite different. For excitation energies greater than that corresponding to I$_2$ (B,v'=22), the product distribution is quite similar to that observed for excitation above the dissociation energy of the B state, i.e., it shows a broad, nearly gaussian distribution of I$_2$(B) vibrational states, well below the excitation energy. For excitation energies below that, the distribution becomes increasingly like the Poisson distribution observed for the T-shaped isomer. Bond dissociation energies for linear and T-shaped isomers are determined for the spectra. The dissociation time scale for the two isomers differs by about 3 orders of magnitude. To model the product state distribution of the linear isomer and therefore gain further insight into the Ar-I$_2$ interaction potential, a simple trajectory calculation based upon the classical dynamics of a compressed oscillator (I—I) ejecting a freely attached particle (Ar) is in progress. Results from the calculation are in good accord with the experiment.