DYNAMICS OF LINEAR AND T-SHAPED ArI_2 DISSOCIATION UPON B←X EXCITATION: A DISPERSED INTRACAVITY LASER-INDUCED FLUORESCENCE STUDY

AMY E. STEVENS MILLER, CHENG-CHI CHUANG, KELLY J. HIGGINS, HENRY FU and WILLIAM KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*.

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.