THE T-SHAPED ISOMER OF I_2-Ar DOES NOT EXHIBIT THE ONE-ATOM CAGE EFFECT

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Caged recombination is observed when the binary I_2-Ar complex is excited to energies above the B state dissociation limit. This phenomenon has been the subject of many investigations, and some controversy. Spectra for the complex indicate a T-shaped equilibrium geometry, but this structure appears to be inconsistent with the cage effect. For a T-shaped structure, calculations show that energy transfer from the I-I bond to the I_2-Ar coordinate is not fast enough to cause a significant number of recombination events. To resolve this paradox, Burke and Klemperer[a] propsed that I_2-Ar exists as both linear and T-shaped isomers. The observed caged recombination was ascribed to the linear isomer. Burke and Klemperer also found a diffuse absorption system that was assigned to linear I_2-Ar.

We have investigated the linear isomer hypothesis by a series of fluorescence depletion measurements. These experiments demonstrated that the T-shaped isomer does not exhibit caged recombination. The diffuse absorption detected by Burke and Klemperer was linked to the species that does show recombination.

To test for possible interferences in these measurements, photodissociation of I_2 in a He free-jet expansion was examined. Despite the low collision frequency in the downstream region of the jet, geminate recombination was observed. This result suggests that the cross-section for three-body recombination increases with decreasing temperature. Vibrational relaxation of I_2(B) by He at low temperatures was examined using optical-optical double resonance techniques. The large cross section obtained (63 $Å^2$ for v=40) has implications for previous studies of the product state distributions resulting from I_2-Ar photolysis.

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[a] M. L. Burke and W. Klemperer, *J. Chem. Phys.* 98, 1797 (1993)