PREDISSOCIATION DYNAMICS OF THE T-SHAPED AND LINEAR ISOMERS OF I_2(B)Ar

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Three-dimensional quantum dynamics models for the predissociation of I_2(B)Ar were examined by Gray and Roncero.[a] Their calculations predicted highly structured rotational population distributions for the I_2(B) products. The distributions were characteristic of dynamics controlled by intramolecular vibrational energy redistribution (IVR). To test this model we have examined final state distributions resulting from predissociation of T-shaped I_2(B)Ar using optical-optical double resonance (OODR) techniques. We observed smooth rotational distributions that are indicative of direct dissociation or IVR occurring with level densities near the statistical limit.

OODR measurements were used to probe the highest vibrational level of I_2(B) populated by predissociation of T-shaped I_2(B)Ar. This is a matter of interest as Stevens Miller *et al.*[b] have suggested that previous measurements[c] may be in error, leading to overestimation of the bond strength for the B and X states of I_2Ar. The previous measurements relied on detection of dispersed fluorescence from I_2(B), and may have been influenced by non-adiabatic decay channels. OODR is a more sensitive technique, potentially capable of detecting the highest energy products prior to non-radiative decay. However, the OODR experiments yield results that are in agreement with the earlier study.[C] The data do not resolve conflicts associated with the relative bond strengths of the T-shaped and linear isomers.[C]

OODR techniques are being used to characterize the predissociation of linear I_2(B)Ar. Initial measurements show that I_2(B) from the linear isomer has less rotational energy than I_2(B) from the T-shaped complex.

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