A COMPREHENSIVE 4 POTENTIAL ENERGY CURVE ANALYSIS OF UV PHOTODISSOCIATION DATA FOR HI AND DI

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A comprehensive unified analysis of all available total absorption cross section and branching ratio data for the UV photodissociation of HI and DI has yielded a quantitative empirical determination of the repulsive potential energy curves for the four electronic states giving rise to these spectra. Different types of potential functions and transition moment functions are considered, and their influence on the resulting fit is explored. Since the available data only involve initial-state $X\,^1\Sigma^+$ state HI and DI in the ground ($v'' = 0$) vibrational level, the distance-dependence of the transition moment functions could not be determined from our empirical analysis. A better fit is obtained when the model potential for the $B\,^3\Pi_0^+$ state dissociating to $\mathrm{I}^* + \mathrm{I}$ has a shallow minimum near 2.7 Å, as predicted by theory,[a] rather than a purely repulsive shape. An examination of the effect of the unresolved discrete transitions into the high-energy $b\,^3\Pi_2$ and $^3\Pi_1$ states on the observed continuum spectra in the higher-energy B–band region facilitated our delineation of the effect of the $T\,^3\Sigma_1^+$ state on the main A–band portion of the UV photodissociation spectrum. Within the experimental uncertainties, all of the available data are fully explained by an analysis which neglects non-adiabatic coupling among the various final states. This analysis was performed using program BCONT.[b]

[a] A.B. Alekseyev, H.-P. Liebermann, D.B. Kokh and R.J. Buenker, *J. Chem. Phys.* **113**, 6174 (2000).

[b] R.J. Le Roy and G.T. Kraemer, *BCONT-2.0*, University of Waterloo Chemical Physics Research Report CP-650 (2001); also available from http://leroy.uwaterloo.ca.