EXPERIMENTAL DETERMINATION OF GROUND STATE BINDING ENERGIES IN HETERO- AND HOMONUCLEAR RARE GAS-DIHALOGEN COMPLEXES

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A simple Arrhenius model based on the assumptions of a thermodynamic equilibrium between the T-shaped and linear isomers of the He$\cdots$I^{35}Cl(X,v''=0) rare gas-heteronuclear dihalogen complex and of a Boltzmann rotational distribution for each isomer is used to find the relative binding energies of the isomers. The model was tested by comparing the intensities of the T-shaped and linear bands observed in laser-induced fluorescence spectra recorded in the ICl $B-X$, $3-0$ spectral region in varying temperature regions in the expansion. The results reveal that the T-shaped isomer is 3.2(1.0) cm^{-1} higher in energy than the linear isomer. Using two-laser, pump-probe and high-resolution action spectroscopy the linear binding energy was precisely determined to be 21.97(12) cm^{-1}, thereby indicating a T-shaped He$\cdots$I^{35}Cl(X,v''=0) binding energy of 18.8(1.0) cm^{-1}. The approach was then extended to the He$\cdots^{79}$Br$_2$(X,v''=0) rare gas-homonuclear dihalogen complexes. The intensities of the features associated with transitions of the T-shaped and linear isomers observed in the ro-vibronic spectra recorded in the Br$_2$ $B-X$, $11-0$ region are used to monitor changes in the relative populations of the isomers. The T-shaped He$\cdots^{79}$Br$_2$ isomer is found to be only 0.7(2) cm^{-1} higher in energy than the linear isomer. Action spectra reveal that the ground state linear isomer is bound by 17.6(4) cm^{-1}, and thus a binding energy of 16.9(4) cm^{-1} for the T-shaped isomer is determined. The experimental energies agree remarkably well with those obtained using a two-dimensional He + Br$_2$(X,v''=0) *ab initio* potential energy surface,17.4 and 16.6 cm^{-1} for the linear and T-shaped isomers, respectively.