PROBING THE DEPENDENCE OF THE H_2/D_2 + ICl/I_2 ENTRANCE CHANNEL INTERACTIONS ON INTER-MOLECULAR ORIENTATION

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Laser-induced fluorescence and action spectroscopy experiments have identified multiple conformers of the *o*,*p*-$H_2/D_2\cdots ICl$ and *o*,*p*-$H_2/D_2\cdots I_2$ entrance channel complexes. The conformers with the hydrogen molecule localized at the end of the dihalogen are more stable than the conformers with the hydrogen positioned orthogonally to the dihalogen bond axis. Furthermore, complexes containing the H_2/D_2 species with j''=1 are found to be more strongly bound than those with j''=0 for all cases examined. The role of dipole-quadrupole interactions on these systems is elucidated by comparing the binding energy of the *o*-$H_2\cdots ICl(X,v''=0)$ complex with a C_{2v}, prolate top symmetry versus that of the *o*-$H_2\cdots I_2(X,v''=0)$ complex with a similar structure, 186.4(3) cm^{-1} versus 119(2) cm^{-1}. In contrast, the binding energies of the complexes with the hydrogen molecule localized in the T-shaped well are comparable, 82-90 cm^{-1} for *o*-$H_2\cdots ICl(X,v''=0)$ and 91.3-93.3 cm^{-1} for *o*-$H_2\cdots I_2$ $(X,v''=0)$.