PROBING THE DEPENDENCE OF THE $H_2/D_2 + ICI/I_2$ ENTRANCE CHANNEL INTERACTIONS ON INTERMOLECULAR ORIENTATION

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Laser-induced fluorescence and action spectroscopy experiments have identified multiple conformers of the o.p-H₂/D₂···ICl and o.p-H₂/D₂···I₂ 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 H₂/D₂ 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-H₂···ICl(X,v''=0) complex with a C_{2v} , prolate top symmetry versus that of the o-H₂···I₂(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-H₂···ICl(X,v''=0) and 91.3-93.3 cm⁻¹ for o-H₂···I₂(X,v''=0).