A COMBINED THEORETICAL AND EXPERIMENTAL STUDY OF THE HX+CN→X+HCN (X = F, Cl, Br) REACTION; THE CN-HX ENTRANCE CHANNEL COMPLEX

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Weak van der Waals forces, which exist in the entrance and exit channels of chemical reactions, can have a dramatic effect on the ensuing reaction dynamics despite being much weaker than the forces at the transition state. Heavy—light-heavy complexes, such as X-HY (where X & Y = CN, F, Cl, Br, ...), are prototypical systems to study these effects. Here we present *ab initio* calculations on HF+CN at the CASSCF/MRCI level which have yielded quantitative information on the topology of the entrance channel region of the potential energy surface. The ground electronic state of the complex, as well as states correlating with CN in its excited $A^2\Pi$ and $B^2\Sigma^+$ electronic states have been investigated. These calculations are used as a guide in our experimental work, where we have attempted to observe the CN-HF complex formed in a free-jet expansion. The experimental results are based on laser induced fluorescence of the CN chromophore.