DISSOCIATION OF DIFLUOROETHYLENE CATIONS: AN ION-NEUTRAL COMPLEX ALONG THE FLUROETHENYLIDENE$^+$/HF REACTION PATH

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The study of the HF loss dissociation channel in singly charged 1,1- and 1,2-difluoroethylene (C$_2$H$_2$F$_2$)$^+$ cations by collisional activation (this work) or by photoelectron-photoion coincidence spectroscopy (1) has shown a remarkable behaviour of the kinetic energy released on the [C$_2$,H,F]$^+$ fragment: as the internal energy of the C$_2$H$_2$F$_2$ parent ion is increased above a given threshold, the average kinetic energy release (KER) decreases. At low internal energy (MI conditions), a dish-topped peak is observed, due to the inverse activation barrier of the HCCF$^+$/HF channel, which amounts to about 1 eV. A composite signal, with both a low KER and a high KER component, is observed under CAD conditions. Dissociative photoionization experiments coupled with a retarding potential device have also been performed to get complementary KER data in a wide internal energy range (up to 8 eV).

We suggested that this behaviour could be explained by the opening of a competitive reaction channel leading to the fluoroethenylidene isomer of [C$_2$,H,F]$^+$. We show now that this assumption is successfully checked by high-level ab initio calculations.

(i) The fluoroethenylidene cation exists as a minimum on the potential energy surface of the ground $^2$A" electronic state. It is 1.8 eV more energetic than its conventional fluoroacetylene isomer (QCISD/6-311++G(3df,2pd) level).

(ii) The dissociation path leading to the fluoroethenylidene cation from either 1,2-cis- or 1,2-trans- C$_2$H$_2$F$_2$ has been studied at different levels, including the B3LYP/AUG-cc-pVTZ and QCISD/6-311++G(3df,2pd) levels. No reverse activation barrier shows up, a result which is compatible with the small KER observed. Furthermore, an ion-neutral complex is evidenced along the reaction path.

References