

The elementary reactions of energy selected 1,1-Difluoroethene Ions

F. Güthe, K.-M. Weitzel and H. Baumgärtel

Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, Berlin, Germany

B. Leyh and R. Locht

Département de Chimie Générale et de Chimie Physique, Université de Liège, Liège, Belgium

We have investigated the unimolecular reactions of energy selected 1,1-Difluoroethene (1,1-DFE) ions by means of the threshold photoelectron photoion coincidence technique (TPEPICO) in a reflecting ion time of flight mass spectrometer (Reflectron). A typical Reflectron time of flight (RETOF) spectrum is shown in fig. 1. The fragment ions observed agree with those reported earlier in the literature [1,2]. The dominant reaction channels correspond to the loss of HF, F, CF and CH_2F . Note that the latter two reactions must involve an isomerization step.

The breakdown curves of 1,1-DFE including the four most intense fragment ions are shown in fig. 2. The energetically lowest reaction channel is the HF loss, but the F loss occurs only slightly higher in energy. The other two important fragment ions are the CF^+ ion and the CH_2F^+ ion. All other fragment ions observed (sc. fig. 1) have been included in the calculation of the fractional abundance.

It is interesting to note that the energetically lowest reaction channel exhibits a pronounced metastability. The energetically next higher reaction, i.e. the F loss, seems to be fast right from the threshold. In the future our RETOF spectra, where fragmentation events taking place in the first field free drift region are distinguished from spontaneous fragmentation events will enable us to derive the $k(E)$ curves for the HF loss reaction.

An expanded view of the region of F and HF loss from the TPEPICO-RETOF spectra are shown in fig. 3. These data reveal information on the kinetic energy released (KER) in the respective bond fission processes. Most strikingly a very high non thermal KER is observed for the HF loss at 14.949 eV (fig. 3A) and a thermal KER for the F loss. The high KER in the HF loss has also been observed in a mass analyzed ion kinetic energy (MIKES) experiment [3]. This is the situation expected for a concerted elimination reaction (HF loss) and a simple bond fission (F loss). However, at 19.612 eV the opposite situation is observed, i.e. an almost thermal KER for the HF loss and a high non thermal KER for the F loss. In the latter case this may hint at a direct bond cleavage from a repulsive excited electronic state. A better understanding of the relevant potential energy surfaces is needed in order to explain this reversal of the KER. We are currently simulating the RETOF spectra directly based on complete kinetic energy release distribution (KERD) functions.

Fig. 1 TPEPICO-RETOF spectrum of 1,1-DFE at 19.612 eV. All fragment ions observed are marked by arrows. Note that all parent ions dissociate at this excitation energy.

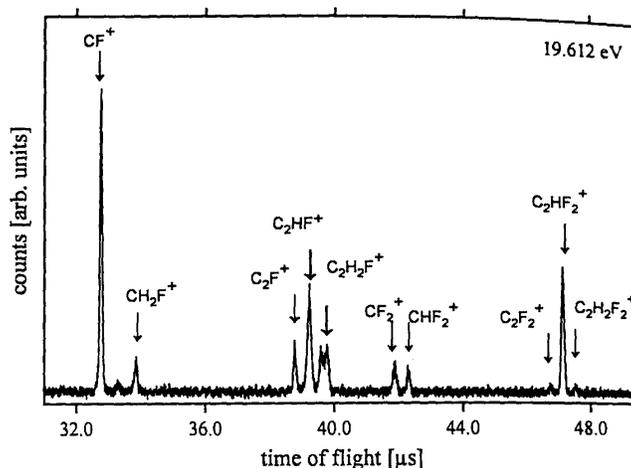


Fig. 2 TPEPICO breakdown curves of 1,1-DFE. Note that only the parent ion and the four most intense fragment ions are displayed.

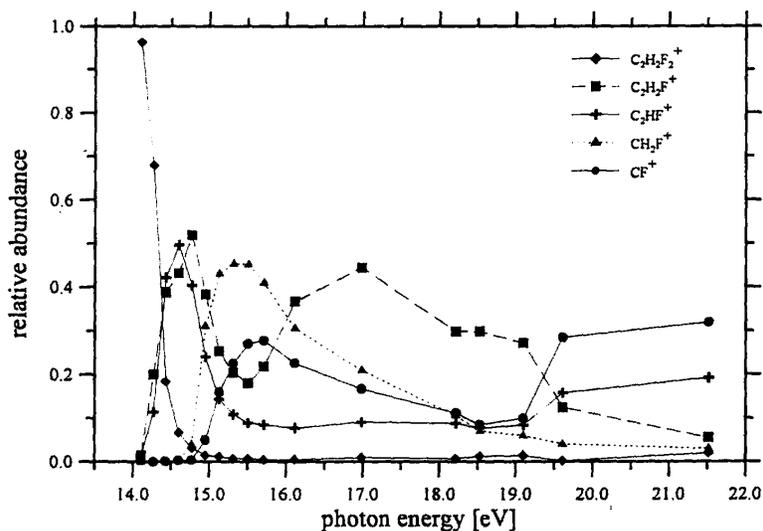
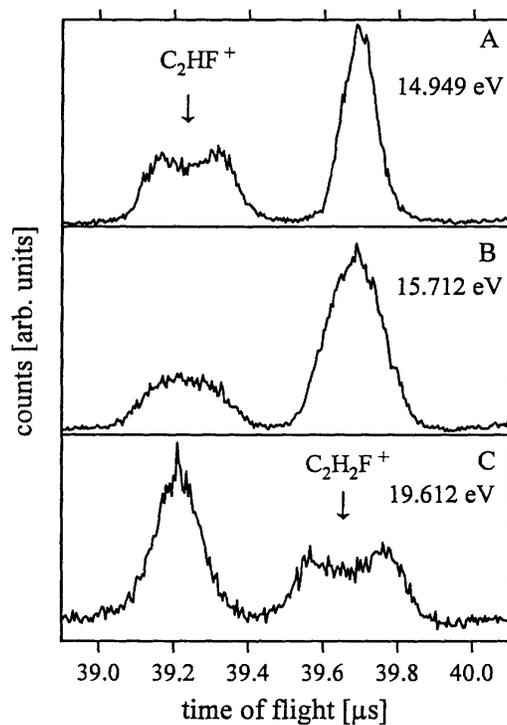


Fig. 3 TPEPICO-RETOF spectra of 1,1-DFE in the region of the C_2HF^+ ion (HF loss) and the $C_2H_2F^+$ ion (F loss).



Acknowledgement

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References

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