

PHOTOIONIZATION DYNAMICS OF MONO- AND DIFLUOROETHYLENES

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Halogenated ethylenes are important compounds in many areas of chemistry. The physical and chemical properties of these neutral compounds have already been the subject of thorough investigations. They are also ideal compounds for the study of the dynamics of molecular ions and cluster ions by mass spectrometry and photoelectron spectroscopy and for the analysis of the influence of the substituent polarizability on their decay channels.

The results presented here represent the first part of a work which aims at studying in detail the ionization and dissociation dynamics of mono- and disubstituted ethylenes. The present report will focus on the ionization dynamics above the first ionization threshold of vinylfluoride and 1,1-difluoroethylene (10,36 eV and 10,29 eV, respectively) studied using synchrotron radiation at BESSY on the 3m-NIM-I beamline.

Three experimental techniques have been used: Threshold Photoelectron Spectroscopy (TPES), Constant Ionic State (CIS) spectroscopy and absorption spectroscopy. The photoelectron spectroscopy experiments have been performed using a tandem hemispherical electron analyzer, described in detail in an earlier publication [1], coupled with the 3 meter normal incidence monochromator.

Figure 1 shows the TPES spectrum of both vinylfluoride (C₂H₃F) and vinylidene fluoride (F₂CCH₂) in the 10-28 eV photon energy domain. Compared to the HeI (21.21 eV) fixed-wavelength photoelectron spectrum, the TPES data show (i) a much larger relative cross section for the excited electronic states with respect to the ground state and (ii) a cross section enhancement for a photon energy between 11.5 and 13 eV, i.e. just below the threshold of the \tilde{A} state. These observations are valid for both compounds.

Although a thorough analysis of the experimental data has still to be performed, the most intense observed features can be assigned to autoionizing neutral states converging to the ionic states which correspond to the second and the third bands in the photoelectron spectrum. In the F₂CCH₂ case, these bands can be assigned to the \tilde{A}^2B_2 and \tilde{B}^2A_1 ionic states (vertical ionization energy = 14.85 eV) and to the \tilde{C}^2B_2 and \tilde{D}^2A_2 ionic states (vertical ionization energy = 15.75 eV). Figure 2 shows the absorption spectrum of F₂CCH₂ as well as the CIS spectra for a few vibrational states of the electronic ionic ground state, \tilde{X}^2B_1 . The most prominent structures can be assigned to the ns Rydberg series converging to the four above-mentioned states as well as to a np or nd series converging to the \tilde{C}^2B_2 and the \tilde{D}^2A_2 states. It is interesting to mention the good correlation between the absorption spectrum and the CIS data for the first vibrational levels of the \tilde{X}^2B_1 ionic state. A CIS curve at a higher vibrational energy (which corresponds to an ionization energy of 13 eV) is also displayed in Figure 2. It shows a very different behaviour, with a rapid initial decrease followed by a broad structure at higher energy (hν = 16-19 eV).

Acknowledgments

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References

- [1] K. Hottmann, H.W. Jochims and H. Baumgärtel, BESSY Jahresbericht (1987), p. 398

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Figure 1. TPES spectrum of C_2H_3F (a) and $1,1-C_2H_2F_2$ (b) in the 10-28 eV range.

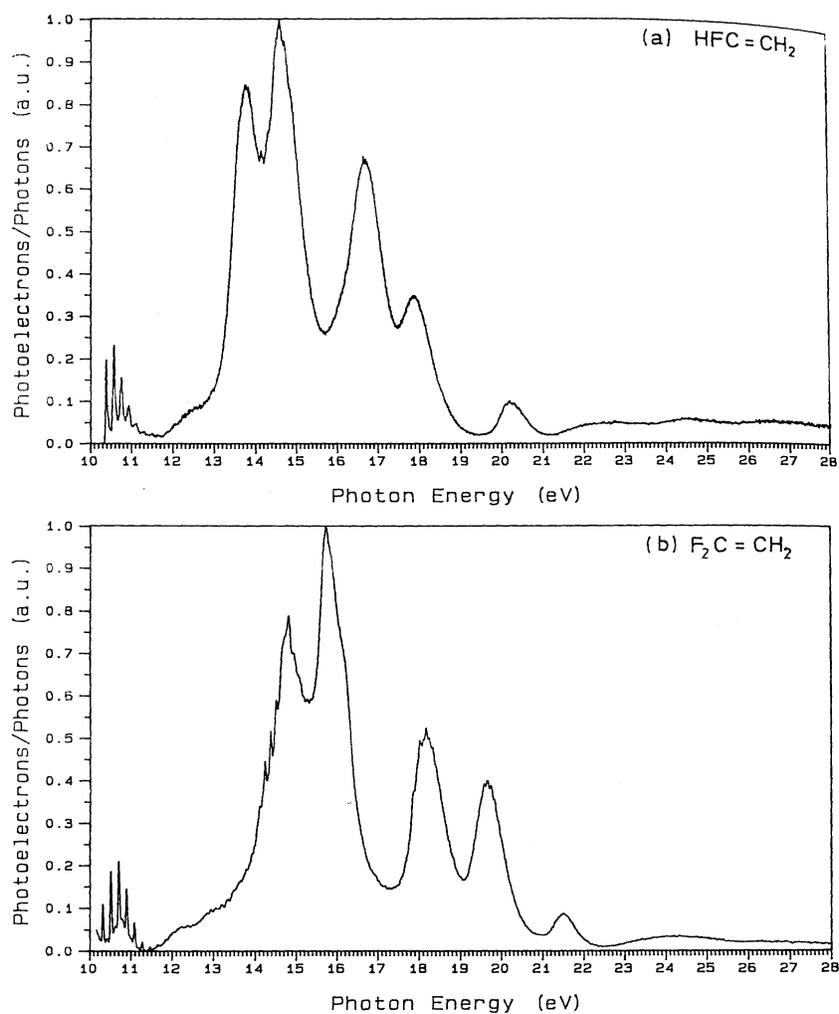


Figure 2. Absorption spectrum of $1,1-C_2H_2F_2$ displayed with CIS curves for the $v = 0, 1, 2$ and 3 levels of the main vibrational progression ($C=C$ stretch) of the $\tilde{X}^2 B_1$ ionic state. A CIS curve corresponding to an ionization energy of 13.0 eV is also shown.

