

PHOTOABSORPTION AND PHOTOIONIZATION OF MONO- AND DIFLUOROETHYLENES.

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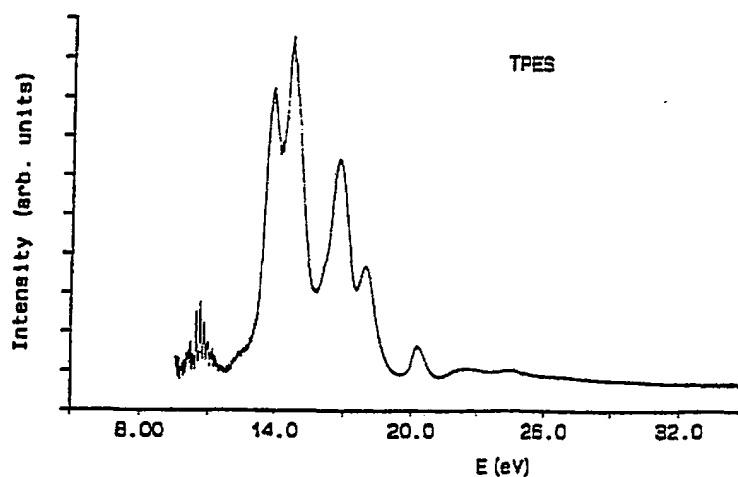
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Halogenated ethylenes are important compounds in many areas of chemistry and physical chemistry. They are ideal compounds to study the influence of the substituent on the dynamics of the molecular ions and on their cluster ions. Experimental data concerning the energetics and photoionization dynamics of these compounds are, however, relatively scarce. The present work focuses on the spectroscopy and photoionization dynamics of vinylfluoride (C₂H₃F) and 1,1-difluoroethylene (C₂H₂F₂) above the first ionization threshold (10.36 eV and 10.29 eV, respectively).

The spectroscopic data were obtained at the BESSY synchrotron facility (Berlin, FRG) using a 3m normal incidence monochromator. Three experimental techniques have been used: Threshold Photoelectron Spectroscopy (TPES), Constant Ionic State Spectroscopy (CIS) and photoabsorption (PA). The photoelectron spectroscopy experiments have been performed using a tandem 180° cylindrical electron analyzer, coupled with the 3m monochromator.

The TPES spectrum of vinylfluoride is shown in fig. 1. Compared to the HeI photoelectron spectrum, this spectrum shows a much larger relative cross section for the excited electronic states relative to the ground state and a cross section enhancement between 11.5 and 13 eV, i.e. just below the threshold for the \tilde{A} state. The behaviour in C₂H₂F₂ is similar.

Fig.1 Threshold photoelectron spectrum of vinylfluoride.



The features observed in the photoabsorption spectrum and in the CIS curves can be assigned to autoionizing neutral states converging to the ionic states which correspond to the second and third bands in the photoelectron spectrum. In the 1,1-C₂H₂F₂ case (C_{2v} symmetry), these composite bands correspond 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 states (vertical ionization energy = 15.75 eV). The comparison between the PA and CIS data is highlighted in fig. 2. The most

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prominent features have been assigned to 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 \tilde{D}^2A_2 states. These autoionizing states decay in all channels corresponding to the main vibrational progression of the X^2B_1 state (CC stretch). A CIS curve corresponding to an ionization energy of about 13 eV, where direct ionization is negligible, displays a very different behaviour, with a rapid initial decrease followed by a broad structure in the 16-19 eV range.

Fig.2 Photoabsorption and Constant Ionic State spectra of vinylidene fluoride (1,1- $C_2H_2F_2$).

