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THE SPECTROSCOPY OF ETHYLENE AND ITS DERIVATIVES. C₂H₄ AND THE THREE C₂H₂FCI ISOMERS. THE CIS- AND THRESHOLD PHOTOELECTRON SPECTRA

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Since several years we proceed with the systematic investigation of the halogenated derivatives of ethylene (C_2H_4). The spectroscopy and/or photoionization mass spectrometry of C_2H_3F and 1,1- $C_2H_2F_2$ [1,2], C_2H_3C1 [3,4], C_2H_3Br [5], the 1,1-, 1,2-cis- and 1,2-trans isomers of $C_2H_2Cl_2$ [6] have been investigated. The aim of this measuring campaign was to investigate ethylene itself and the three C_2H_2FCl isomers. In an earlier work the He(I)-photoelectron spectrum (PES), the photoabsorption spectrum [7] and the dissociative ionization of these molecules by photoionization [8] and electron impact [9] have been investigated.

In the present study, we analyzed the threshold photoelectron spectrum (TPES) of the four compounds as well as their constant ion state (CIS) photoelectron spectra. These experiments were performed on a 3m-NIM monochromator (3m-NIM-l beam line) equipped with a Pt-grating with 2 400 ℓ /mm. The entrance and exit slits of the monochromator were set at 100 μ m. A double focussing electron energy analyzer, operating at constant energy resolution is used for threshold photoelectron detection. The electron energy analyzers pass energy (PE) was adjusted between PE= 1.5-5.0 V depending upon the signal intensity. The corresponding electron energy resolution was about 10-30 meV.

The TPES of C_2H_4 has been recorded between 10-20 eV photon energy. With respect to its He(I)-PES, this spectrum only differs by the important intensity increase and the band profile of the A^2B_{3g} photoelectron band. The origin of these modifications lies in the autoionization contribution of several identified Rydberg states

The TPES of the three C_2H_2FCl isomers have been measured between 9.0-24.0 eV photon energy. The good signal intensity allowed us to use high resolution conditions for both the electron energy and the monochromator (about 10 meV and 1.5 meV at 10 eV photon energy respectively). Fig. 1 shows the TPES of the 1,1- C_2H_2FCl isomer. The most salient feature is observed between the first two bands, exhibiting an extended vibrational structure. This feature is absent in the He(I)-PES of the same compound [7]. This relatively intense band shows a vibrational progression of 17 peaks separated by 62 ± 3 meV or 492 ± 25 cm⁻¹. This progression has been observed in the "F"-band in the photoabsorption spectrum.

Fig. 2 shows the TPES of cis-1,2- C_2H_2FCl . In the 11-12 eV photon energy range a fairly strong band arises in the TPES whereas no ionization cross section is measured in the He(I)-PES [7]. Here again this observation has to be ascribed to Rydberg states autoionization. The strongest band is assigned to the Cl-lone pair orbital ionization. The band shape markedly differs from the same band at about 12 eV in the 1,1-isomer. Owing to the good resolution obtained in this work, at about 13 eV a long vibrational progression is observed with a spacing of 56 ± 9 meV or 448 ± 70 cm⁻¹.

The examination of the CIS spectra of these molecules and their full interpretation as supported by quantum mechanical calculations are in progress.

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FIG. 1: Threshold photoelectron spectrum of $1,1-C_2H_2FCl$.

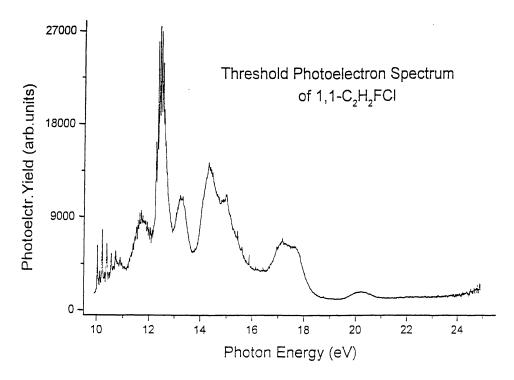
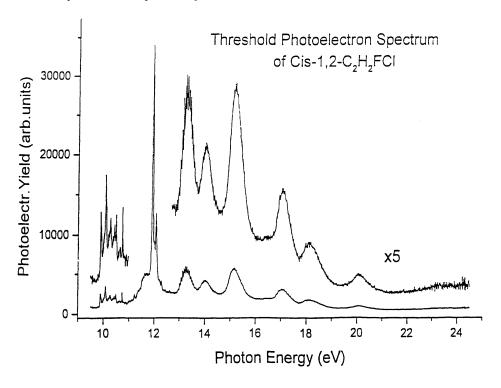


FIG. 2: Threshold photoelectron spectrum of Cis-1,2-C₂H₂FCl.



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