

RESONANT AUTOIONIZATION IN VINYLCHLORIDE BETWEEN 10 AND 12 eV.

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In the framework of our research programme on the ionization and dissociation dynamics of halogenoethylenes, we have investigated the autoionization processes taking place in vinylchloride (C_2H_3Cl) above the lowest ionization threshold (9.99 eV) using the synchrotron radiation at BESSY on the 3m-NIM-I beamline.

The following techniques have been used: Threshold Photoelectron Spectroscopy (TPES), Constant Ionic State (CIS) spectroscopy and absorption spectroscopy. The tandem hemispherical electron analyzer used has been described previously [1]. Due to the large second order contribution of the monochromator, which is especially noticeable, for vinylchloride, in the 10-12 eV region we are interested in, we have used either a MgF₂ filter (cut-off energy = -10.8 eV) or a LiF filter (cut-off energy = ~11.8 eV).

The TPES spectrum is shown in Figure 1a in the 10-25 eV photon energy range (without filter). The 10-12 eV region is enlarged in Figure 1b, which shows data obtained with a LiF filter. By comparing these data with the high resolution HeI photoelectron spectrum, one notices the appearance of a rich autoionization structure between 10.5 eV and the onset of the second electronic band. The absorption spectrum as well as the constant ionic state data, displayed together in Figure 2, show clearly the good correlation between the available experimental data. Furthermore, the correspondance between the peaks observed in TPES, CIS and absorption shows how important resonant ionization is for this molecule.

The analysis of the autoionization structure shows three principal series of Rydberg states converging to the first excited ionic state, $\tilde{A}^2 A'$. This state corresponds to the removal of one electron from the Cl lone pair and has an adiabatic ionization energy of 11.64 eV. Two vibrational frequencies can be deduced from the photoelectron spectroscopic data: 1130 cm⁻¹ (CH₂ deformation) and 560 cm⁻¹ (CCl stretch). The vibrational frequencies extracted from the autoionization data in the absorption spectra are very similar (1150 ± 150 cm⁻¹ and 600 ± 150 cm⁻¹).

The three most intense Rydberg series can be assigned the following characters: ns (quantum defect = 1.07), np (quantum defect = 0.59) and nd (quantum defect = -0.12). These quantum defects are similar to those observed for the Rydberg series converging to the ground electronic state of the ion. The TPES data show that decay channels corresponding to resonant autoionization are favoured. This behaviour could be related to the large geometry differences between the ground and the first excited electronic states of the ion, which could lead to non negligible Franck-Condon factors even for excited vibrational states.

¹ Chercheur qualifié du Fonds National de la Recherche Scientifique (Belgium)

This research project has been supported by the EC (Contract CHGE-CT93-0027).

Figure 1. a. TPES spectrum of C_2H_3Cl in the 10-25 eV photon energy range (without filter),
b. TPES spectrum of C_2H_3Cl in the photon energy range of the $\tilde{\chi}^2 A''$ ionic state with a LiF filter. The beginning of the $\tilde{A}^2 A'$ band also shows up.

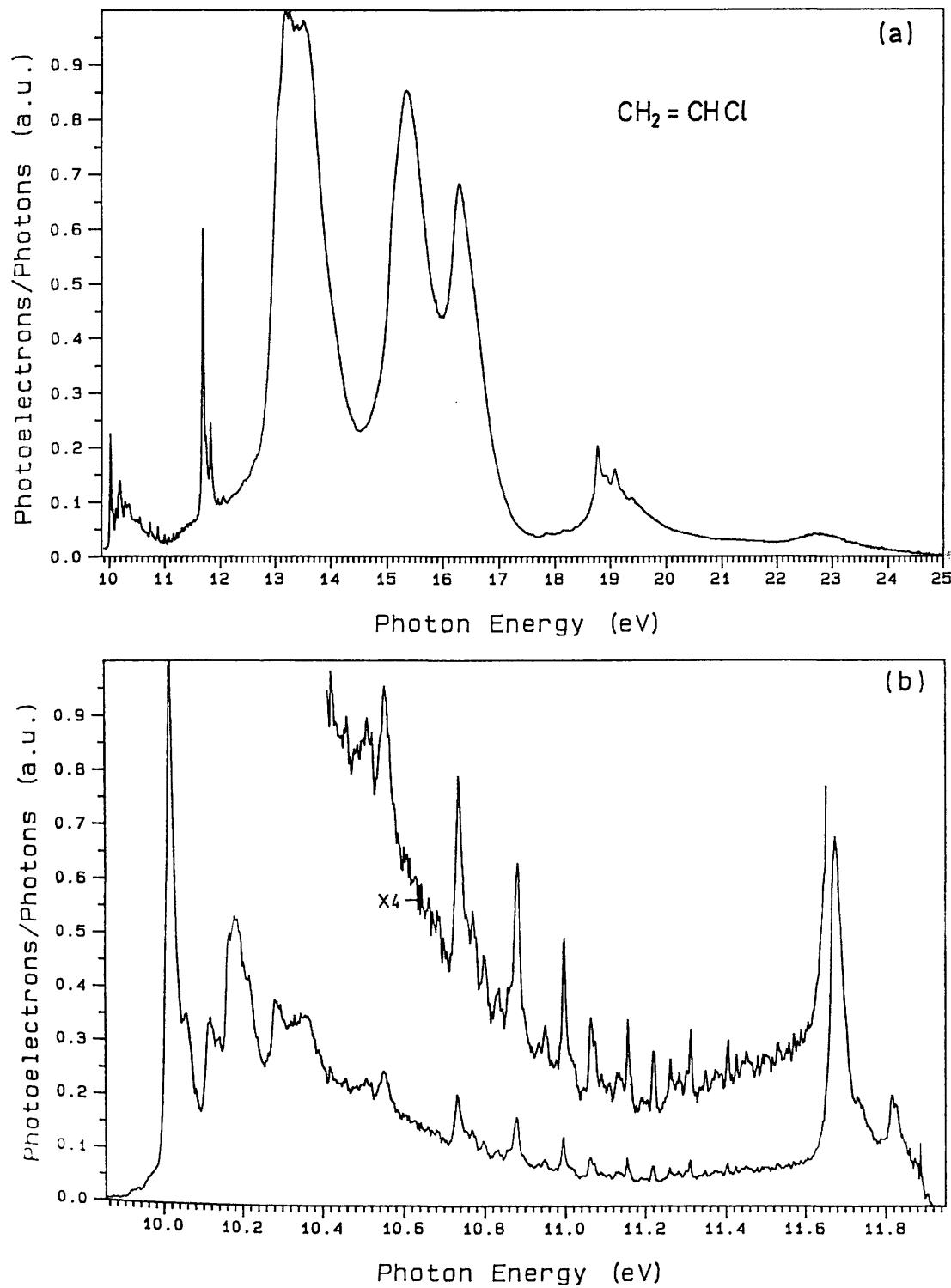
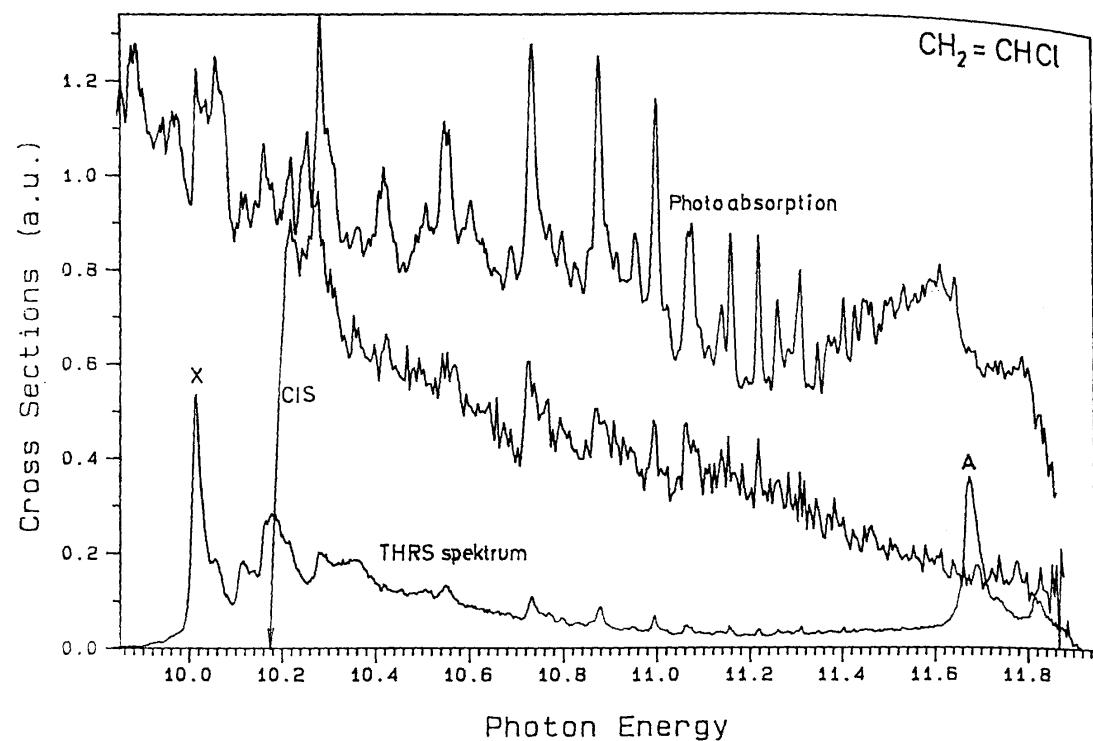


Figure 2 Absorption spectrum of C_2H_3Cl with LiF filter. For comparison, a CIS curve is also displayed on the same energy scale.



References

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