

THE THRESHOLD PHOTOELECTRON, CIS- AND PHOTOABSORPTION SPECTRA OF THE METHYL MONOHALIDES (Cl, Br AND I).

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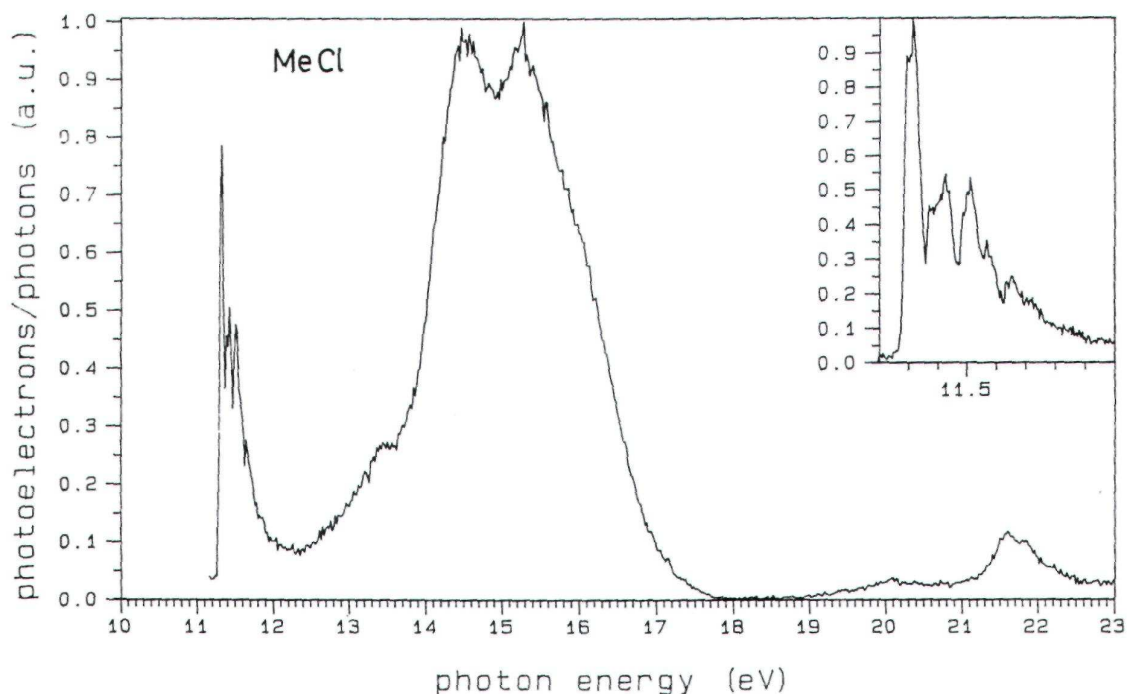
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In several previous papers we reported on the electroionization, photoionization and dissociation of methyl fluoride (CH₃F) [1,2]. Threshold photoelectron spectroscopy and threshold photoelectron-photoion coincidence spectroscopy of this molecule have also been performed [3]. More recently, a surprisal analysis of the translational energy distribution of CH₃⁺ from CH₃F has been reported [4]. Rydberg series lying in the 18-20 eV energy range were shown to play an important role.

The surprisal analysis of the CH₃⁺ kinetic energy distribution from the three other methyl monohalides, i.e. CH₃Cl, CH₃Br and CH₃I tends to show the involvement of Rydberg states lying in the same high energy range. Therefore, a complementary investigation of the photoabsorption spectrum of these compounds at these energies was desirable. The threshold photoelectron spectra (TPES) have also been measured.

Fig. 1: The threshold photoelectron spectrum of methylchloride between 10-22 eV photon energy.



The photoabsorption work was performed on the 1.5m-NIM-2 beamline at the synchrotron radiation facility BESSY. Light is dispersed by a 1.5m-NIM monochromator equipped with a 1200 / mm Pt-grating and its entrance and exit slits were adjusted at 100 μ m [5]. The TPES spectra were recorded on the 3m-NIM-1 line. The 3m-NIM monochromator is equipped with a 2400 / mm Pt-grating and entrance and exit slits were adjusted at

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200 μm . The threshold photoelectrons are selected by a tandem-type electron spectrometer consisting of two 180° electrostatic deflectors [6].

As an example of the data obtained in this work, fig. 1 and 2 show the TPES spectrum of CH_3Cl and CH_3Br , spread over 10-22 eV and 10-23 eV photon energy respectively. A closer examination of the band corresponding to the ground vibronic state, under high resolution conditions, does not reveal considerable differences with the He(I)-PES [7]. Above 12 eV a "diffuse" band is observed and is rather weak in the TPES of CH_3Br whereas it is fairly strong and better resolved (at $\text{IE}_{\text{VERT.}}=13.38$ eV) in the TPES of CH_3Cl .

Fig. 2: The threshold photoelectron spectrum of methylbromide between 10-23 eV photon energy.

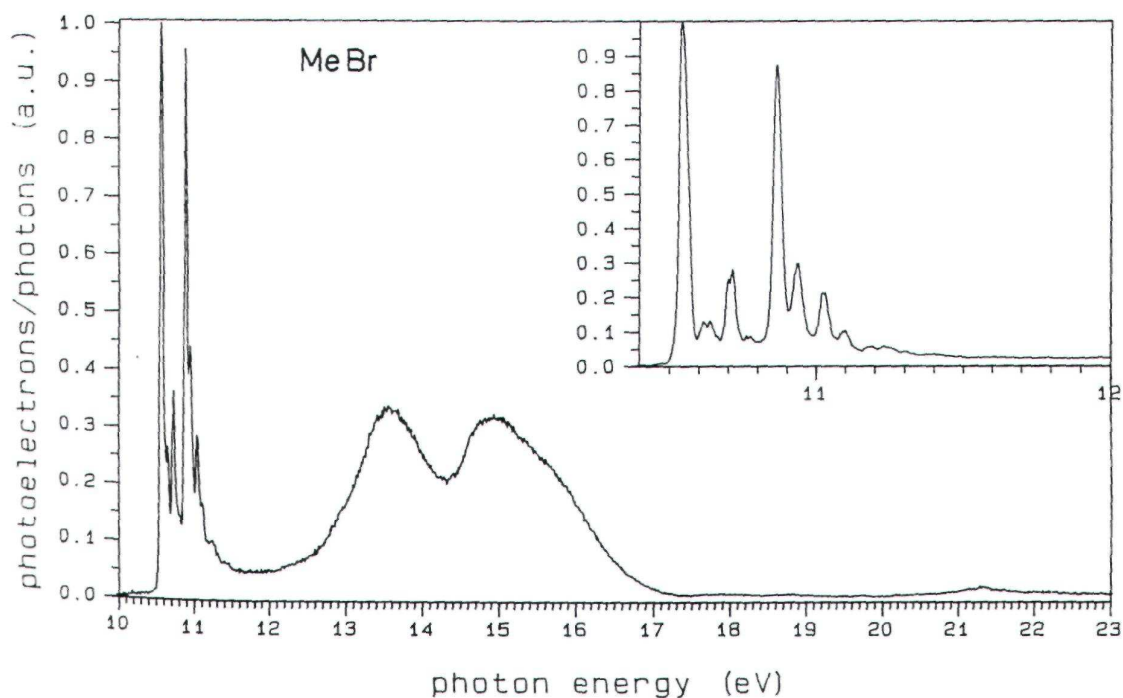
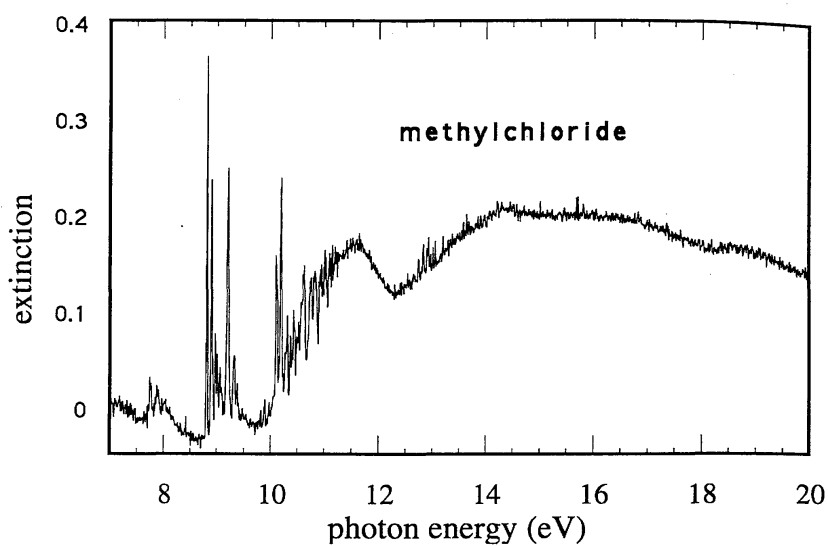


Fig. 3: The photoabsorption spectrum of methylchloride between 7-20 eV photon energy.



The most important difference between the TPES and He(I)-PES spectra is the drastic relative intensity

increase of the bands lying at higher energy, i.e. at vertical ionization energies of 14.45 eV and 15.21 eV in CH_3Cl^+ and at 13.51 eV and 14.95 eV in CH_3Br^+ . In the case of CH_3Cl^+ these bands even dominate the TPES spectrum. At higher photon energies, broad bands are observed at 20.10 eV, 21.56 eV and 21.82 eV in CH_3Cl^+ and at 21.34 eV in CH_3Br^+ . For both molecules the CIS-spectra of the various vibronic states have been measured. The photoabsorption spectra of the above mentioned molecules have been measured. As an example the vacuum UV absorption spectrum of CH_3Cl is displayed in fig.3 between 7-20 eV photon energy.

Acknowledgement.

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