The Threshold Photoelectron Spectrum of NH_3 in the 10-31 eV Photon Energy Range.

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Pursuing our work devoted to the investigation of the autoionization and its possible consequences on the dissociative ionization, the photoionization efficiency of NH_3^+ has been investigated in the appearance energy region of NH_2^+. Weak structures were observed above 15.75 eV photon energy. Below this energy an extended analysis of the autoionization of NH_3 has already been reported (see previous contribution). Beside photoionization mass spectrometry, the threshold photoelectron spectroscopy is a sensitive technique to investigate autoionization.

Synchrotron radiation is dispersed by a 3m NIM monochromator and threshold photoelectrons are analyzed with an electrostatic tandem photoelectron spectrometer described earlier /1/. A FWHM of about 25 meV is measured on $Ar(^2P_{3/2})$.

The threshold photoelectron spectrum of NH_3 has been recorded between 125-40 nm (9.9-30.9 eV) and shows three bands corresponding roughly to the $\tilde{X}^2A_1$, $\tilde{A}^2E$ and $\tilde{B}^2A_1$ states of NH_3^+.

With respect to the He(I)-photoelectron spectum two major differences are observed:

(i). in the energy range of the $\tilde{X}^2A_1$ state a long progression of complex structured peaks is observed and displayed in fig.1. The spacing between the maxima varies from 123 meV to 136 meV instead of about 110 meV measured in the He(I) PES of NH_3 for the vibrational progression of the NH_3^+ ($\tilde{X}^2A_1$) state. On the other hand vibrational spacings of about 130 meV characterise the Rydberg series converging to this state. The structures are assigned to autoionizing states of NH_3 already observed by photoionization (see foregoing contribution).

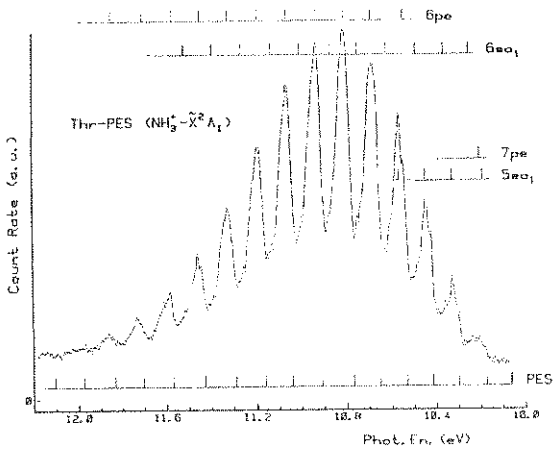

Fig.1 Th-PES of NH_3 in the 10-12 eV photon energy range.

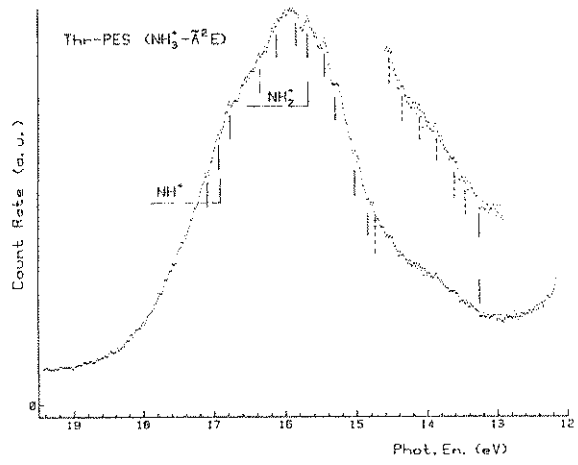

Fig.2 Th-PES of NH_3 in the 12-19 eV photon energy range.

(ii). in the energy range between 12-14.7 eV the threshold photoelectron spectrum shows a "new" broad and fairly intense shoulder starting at 13.26 eV (see fig. 2). In the He(I)-photoelectron spectrum no ionization cross section is measured in the corresponding energy region. This "new" band has to be assigned to the population of high-lying vibrational levels of the NH_3^+ ($\tilde{X}^2A_1$) state.

This observation could be related to the existence, in the EELS of NH_3, of a weak band extending from 13.3-14.6 eV /2/. However, it is followed by a broad band starting at 14.7 eV and spreading up to 18 eV. These bands look essentially structureless.

Up from the adiabatic ionization energy of the NH_3^+ ($\tilde{A}^2E$) state the threshold photoelectron signal increases. Within experimental error, the position of the stuctures observed in this work agree with those observed in the He(I)-photoelectron spectrum /3/.

References.

/1/. G.Hagenow, K.Hottmann, H.Baumgärtel, Chem.Phys.Letters 164(1989)395.

/2/. M.Furlan, Ph.D.Thesis, Université de Liège, (1989).

/3/. J.W.Rabalais, L.Karlsson, L.O.Werme, T.Bergmark, K.Siegbahn, J.Chem.Phys. 58(1973)3370.