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 $^2A_1$, $^2E$ and $^2A_1$ states of NH$_3^+$.

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

(i). in the energy range of the $^2A_1$ 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$_3^+$ ($^2A_1$) 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).
(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 \( \text{NH}_3^+ \left( \tilde{X}^1 \Delta_1 \right) \) state.

This observation could be related to the existence, in the EELS of \( \text{NH}_3 \), 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 \( \text{NH}_3^+ \left( \tilde{X}^1 \Delta_1 \right) \) state the threshold photoelectron signal increases. Within experimental error, the position of the structures observed in this work agree with those observed in the He(I)-photoelectron spectrum /3/.

References.

