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PHOTOIONIZATION OF NH_3 AND ITS ISOTOPOMERS BETWEEN 10 AND 12 eV

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The autoionization in NH_3 has scarcely been studied. This phenomenon has therefore been investigated first in the 10-12 eV photon energy range by photoionization mass spectrometry using synchrotron radiation (BESSY, Berlin) for NH_3, NH_2D, NHD_2 and ND_3.

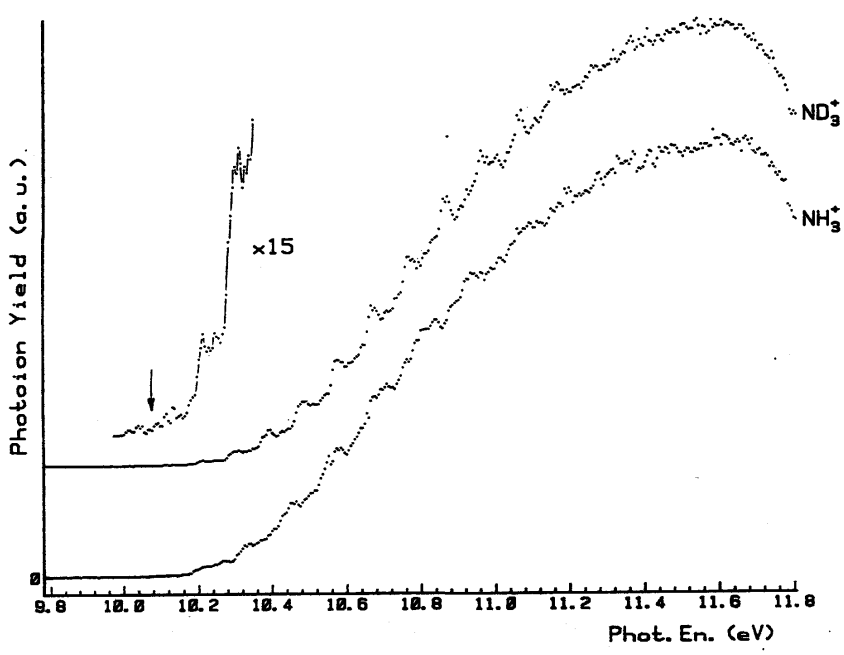
Fig. 1 shows typical photoion yield curves of NH_3^+ and ND_3^+ exhibiting an abundant autoionization structure for which the shape and intensity seem to depend strongly on isotopic substitution.

By FFT-filtering and numerical differentiation of the photoion yield curves, simulated photoelectron spectra are obtained. Ionization energies, wave numbers and anharmonicities have been measured for the four isotopic species.

By subtracting the filtered photoion yield curve from the original photoionization efficiency curve, the autoionization spectra are obtained. All features fit in Rydberg series corresponding to nsa_1, npe (n=5, 6, 7) ← $3a_1$ transitions characterized by long vibrational progressions. These Rydberg states autoionize vibrationally to NH_3^+ X^2A_1 with $|\Delta v| \leq 9$.

From this detailed analysis of the photoion yield curves, an adiabatic ionization energy of 10.073 eV ± 0.010 eV is determined for NH_3, NH_2D and NHD_2 and 10.083 ± 0.010 eV for ND_3. The intensities of the autoionization features show strong correlation with the parity of Δv. This is interpreted by applying group theory considerations to vibrational autoionization theory [1].

Fig. 1. *Photoionization efficiency curves of NH_3^+ and ND_3^+. Arrows locate the adiabatic ionization energy.*



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