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VIBRATIONAL AUTOIONIZATION IN NH_3 AND ITS ISOTOPOMERS IN THE 10-12 eV PHOTON ENERGY RANGE.

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In the frame of the dissociative ionization work on NH_3 , the contribution of autoionization was shown to play an important role[1] .However autoionization in this molecule has scarcely been investigated.

This phenomenon was first examined in the 10-12 eV photon energy range for NH_3 and its isotopomers NH_2D, NHD_2 and ND_3. The abovemen-tioned energy range lying below the lowest appearance energy for fragmentation of NH_3 in the NH_2^+ +H channel, photoionization mass spectrometry is a suitable method for this investigation. Synchrotron radiation provided by the electron storage ring BESSY (Berlin) has been used as a light source dispersed by a 1m NIM-monochromator. A quadrupole filter is used for mass analysis.

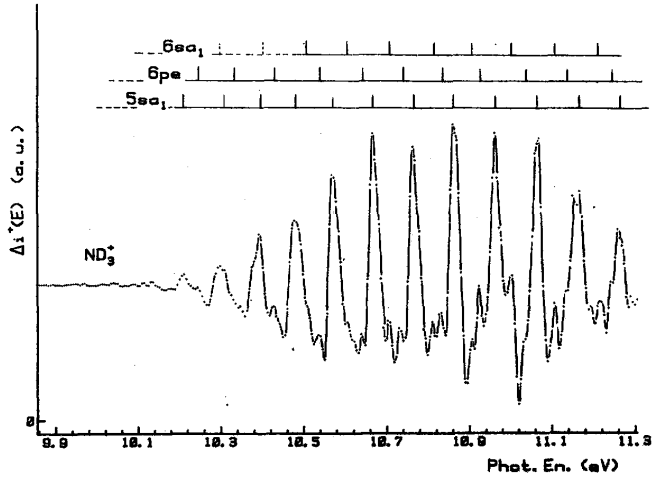
The photoionization efficiency curves of the four molecular ions were recorded. An abundant and fairly well resolved structure is observed. The photoion yield curves show drastic differences in shape and intensity distribution.

By proper filtering and by numerical differentiation of the photoion yield curves, simulated photoelectron spectra are obtained. Onsets, corresponding to the adiabatic ionization energies, are measured at 10.072 ± 0.010 eV for NH_3, NH_2D and NHD_2 and at 10.083 ± 0.010 eV for ND_3 . Wavenumbers and anharmonicities could be deduced and compared to photoelectron spectroscopic data when available[2,3]

By subtracting the filtered photoion yield curve from the original photoionization efficiency curve, the autoionization structure could be enhanced. A typical example is shown in figure 1 in the case of ND_3^+. The same procedure has been applied to NH_3, NH_2D^+ and NHD_2^+

All autoionization features could be classified into long vibrational progressions belonging to nsa_1 and npe (n=5,6,7) Rydberg series converging to the NH_3^+ ($X\ ^2A_1$) state. The relative intensity of each series markedly varies with the isotopic substitution. In the case of NH_3 the results are in good agreement with those obtained by EELS [4].

FIG.1 :*Autoionization spectrum of ND_3^+ .*



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These Rydberg states autoionize vibrationally. A close correlation is observed between the parity of the vibrational transition Δv and the intensity of the corresponding autoionization process. Although both even and odd Δv transitions are observed, to odd Δv values correspond the strongest intensities. This observation can be understood by applying symmetry considerations to vibrational autoionization theory [5] .

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