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The Photoionization of Ammonia Revisited. The Autoionization in NH_3 and its Three Isotopomers in the 10-12 eV Photon Energy Range.

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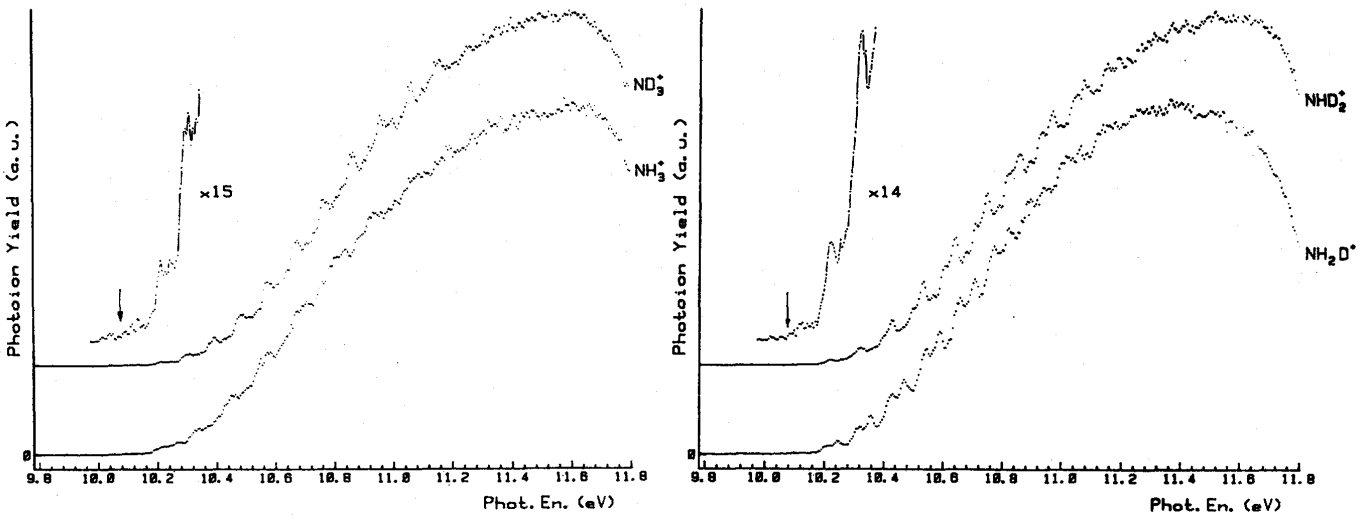
In the frame of the dissociative ionization study of NH_3 the contribution of autoionization was shown to play an important role /1/. However autoionization in this molecule has scarcely been investigated /2/.

This phenomenon was studied first in the 10-12 eV photon energy range for NH_3 and its three isotopomers NH_2D, NHD_2 and ND_3. The abovementioned energy range lying below the lowest appearance energy for fragmentation of NH_3 into $NH_2^+ + H$, the photoionization mass spectrometric method has been used.

FIG.1. *Photoionisation efficiency curves of NH_3^+, ND_3^+, NH_2D^+ and NHD_2^+. Arrows locate the adiabatic ionization energy.*



Typical photoionization efficiency curves of the four molecular ions are displayed in fig.1. An abundant and fairly well resolved autoionization structure is observed. Noteworthy is the drastic isotope effect on the shape and intensity of this structure.

By properly filtering and by numerical differentiation of the photoion yield curves the simulated photoelectron spectra are obtained for the four isotopic species. Ionization energies, wavenumbers and anharmonicities could be measured and compared to photoelectron spectroscopic data when available /3,4/ (see table 1).

By subtracting the filtered photoion yield curve from the original photoionization efficiency curve, the autoionization spectrum is obtained. A typical example is shown in fig.2 in the case of ND_3^+. The same procedure has been applied to NH_3^+, NH_2D^+ and NHD_2^+.

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Unambiguously we are dealing with vibrational autoionization. Long vibrational progressions belonging to different Rydberg series are identified. The relative intensities of each series varies with the isotopic substitution.

In the case of NH_3 the results and their interpretation can be compared with those obtained by electron energy-loss spectroscopy /5/. Very good agreement is found between both experimental data.

FIG.2. *Autoionization spectrum of ND_3. Vertical bars indicate vibrational progressions of the Rydberg states.*

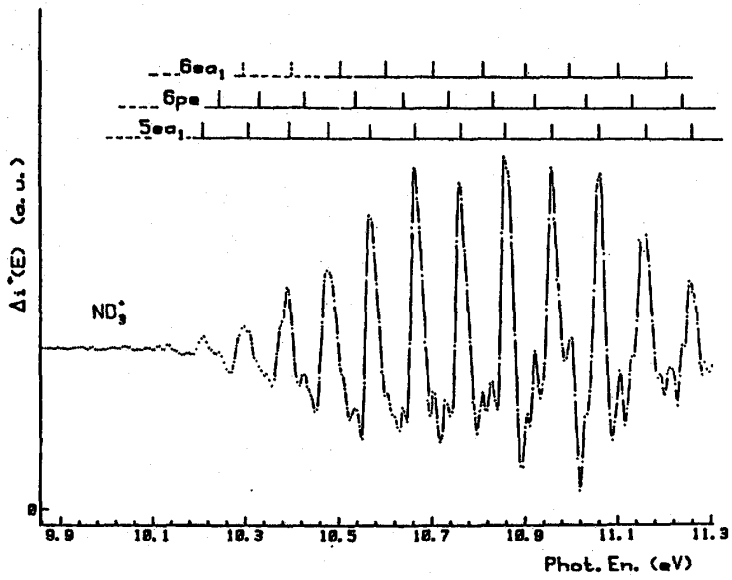

TABLE 1. *Ionization energy (IE), wavenumber (ω_e) and anharmonicity ($\omega_e x_e$) for NH_3^+, NH_2D^+, NHD_2^+ and ND_3^+.*

	IE(eV)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	ω_e^{calc} (cm^{-1})
NH_3^+	10.072	890	-8.0	914
	10.063[a]	904	-8.0	
	10.154[b]	926	-6.6	
NH_2D^+	10.072	848	-7.3	849
NHD_2^+	10.072	780	-6.2	779
ND_3^+	10.083	701	-5.0	701[*]
	10.081[b]	713	-3.9	

(a) Ref.3; (b) Ref.4; (*) used for scaling.

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