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COMMUNICATIONS

Negative ion photoelectron spectroscopy of the negative cluster ion $\text{H}^-(\text{NH}_3)_1$

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We have recorded the negative ion photoelectron spectrum of the gas phase, negative cluster ion $\text{H}^-(\text{NH}_3)_1$. Several spectroscopic studies of negative cluster ions have been reported previously.¹⁻³ Here, we report the first photodetachment study of a negative cluster ion by negative ion photoelectron spectroscopy. In this technique a mass-selected negative ion beam is crossed with a fixed-frequency laser beam, and the resulting photodetached electrons are subjected to energy analysis.⁴ Our apparatus employs a Wien velocity filter for mass selection, an argon ion laser operated intracavity in the ion-photon interaction region, and a magnetically shielded, hemispherical electron energy analyzer. In this work negative cluster ions were generated with a nozzle-ion source similar to that developed by Haberland *et al.*⁵ This source involves the injection of electrons from a biased hot filament into an expanding supersonic jet. A typical mass spectrum showing $\text{H}^-(\text{NH}_3)_1$ as well as other negative cluster ions is shown in Fig. 1.

Kleingeld *et al.*⁶ have reported the formation of stable NH_4^- ions in the gas phase using Fourier transform ion cyclotron resonance spectrometry. On the basis of deuterium labeling experiments, they concluded that NH_4^- is best described as a H^- ion solvated by NH_3 , i.e., as $\text{H}^-(\text{NH}_3)_1$. Calculations performed by Kalcher *et al.*,⁷ Squires,⁸ and Kos *et al.*⁹ all agree that the hydride ion in the NH_4^- ion-dipole complex is bound at a relatively long distance to only one of ammonia's hydrogens and that $\text{H}^-(\text{NH}_3)_1$ is more stable than $\text{NH}_2^-(\text{H}_2)_1$.

The tetrahedral configuration of the ground electronic state of the ammonium radical is thought to possess a barrier to dissociation.¹⁰⁻¹⁷ Our experiment, however, accesses neutral NH_4 in the configuration of its negative ion. It seems likely that the portion of the potential surface corresponding to this NH_4 configuration possesses even more dissociative character than that of the tetrahedral form, and that we are accessing a relatively gently sloping portion of the potential not far above the energy of the dissociation asymptote.

Our negative ion photoelectron spectrum of $\text{H}^-(\text{NH}_3)_1$, recorded with 2.540 eV photons, is presented in Fig. 2. This

spectrum is dominated by a large peak centered at 1.430 ± 0.019 eV with a smaller peak centered at 0.997 ± 0.031 eV. Our spectrum of $\text{D}^-(\text{ND}_3)_1$ shows the larger peak at essentially the same electron energy with the smaller feature shifted to a slightly higher electron energy. The observed bands are ~ 140 meV wide (FWHM), considerably broader than the 30 meV instrumental resolution.

Our interpretation of this spectrum is that the main peak contains the origin of the photodetachment transition, and that the smaller peak is due primarily to the excitation of a stretching mode in the NH_3 solvent during photodetachment. The main peak is due to the photodetachment of the solvated hydride ion "chromophore" within $\text{H}^-(\text{NH}_3)_1$. For this reason, it resembles the photoelectron spectrum of free

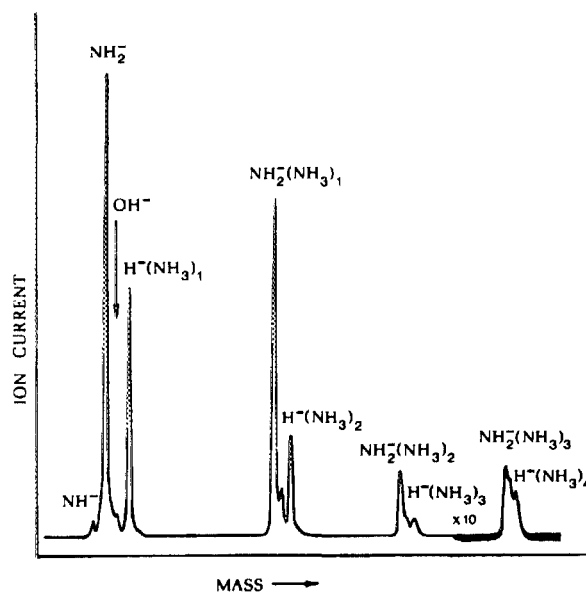


FIG. 1. A typical mass spectrum showing the negative ions generated by our nozzle-ion source with 3 atm of ammonia behind a water cooled ~ 25 μm diam glass nozzle. While not shown here, substantial currents of H^- were also detected. A homologous series of the negative cluster ions $\text{NH}_2^-(\text{H}_2)_n$ was not observed.

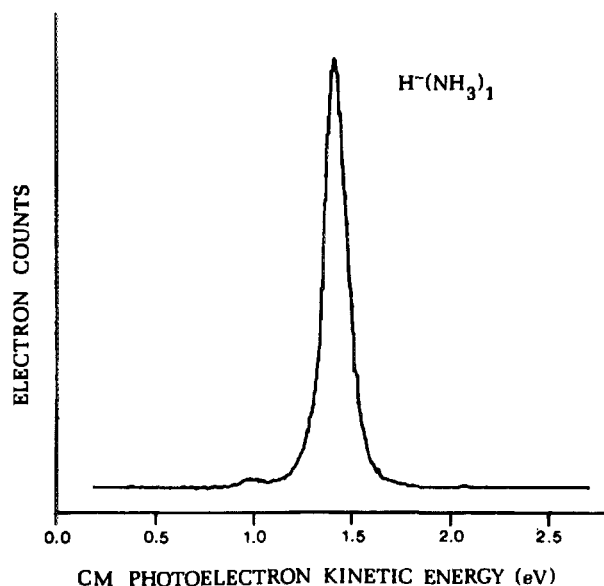


FIG. 2. The negative ion photoelectron spectrum of $\text{H}^-(\text{NH}_3)_1$ presented in terms of center-of-mass (c.m.) electron kinetic energies. This spectrum was recorded over ~ 45 min with 5×10^{-10} A of $\text{H}^-(\text{NH}_3)_1$ and ~ 60 circulating watts of 4880 Å laser power.

H^- (a single peak) except for being *shifted* to lower electron kinetic energy due to the stabilizing effect of solvation. Since we are probably accessing the neutral NH_4 potential surface near its dissociation asymptote, the magnitude of this shift corresponds to an upper limit to the dissociation energy of $\text{H}^-(\text{NH}_3)_1$ into $\text{H}^- + \text{NH}_3$ (also the solvation energy). Its value, which is equal to the difference between the vertical detachment energy of $\text{H}^-(\text{NH}_3)_1$ and the electron affinity of the H atom (0.754 eV) is 0.36 eV. Rosmus,⁷ Squires,⁸ and Schleyer⁹ have calculated the dissociation energy of $\text{H}^-(\text{NH}_3)_1$ to be 0.36 eV [not including the zero point energy (ZPE) correction which is thought to be ≤ 0.12 eV], 0.23 eV (the likely thermochemical solvation enthalpy), and 0.35 eV (includes ZPE corrections), respectively. The agreement between our results and these three calculations supports our interpretation of the main peak.

The main peak in the spectrum is separated from the smaller one by $3490 \pm 130 \text{ cm}^{-1}$ which is close to the symmetric stretching frequency of ammonia (3506 cm^{-1}).¹⁸ Our assignment of the smaller peak to an ammonia stretching excitation is also supported by the $\text{D}^-(\text{ND}_3)_1$ spectrum where the peak separation is close to the symmetric stretch-

ing frequency of ND_3 . The small Franck-Condon factor observed in this study suggests that the ammonia solvent is only slightly distorted by complexation with H^- .

The observed broadening may have contributions from (a) excited weak-bond vibrations in the cluster ion, (b) low-frequency modes in the neutral complex, and/or (c) access to a repulsive portion of the neutral's potential surface. Contributions from the latter mechanism are expected to be relatively small owing to the likelihood that the NH_4 potential surface is fairly flat in the region where it is sampled. The broadening is probably due primarily to high vibrational state densities. Lifetime broadening due to vibrational predissociation of the nascent neutral complex (lifetimes $\geq 10^{-12}$ s) would be too small to be observed in this experiment.

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