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Formation of Hypervalent Ammoniated Radicals by Neutralized Ion Beam Techniques

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Abstract: A new series of hypervalent radicals has been generated by neutralizing a fast beam of $NH_4(NH_3)_n^+$ or $CH_3NH_3(NH_3)_n^+$ ions in the electron transfer reactions $NH_4(NH_3)_n^+ + K$ (or Na) $\rightarrow NH_4(NH_3)_n^* + K^+$ (or Na^+) (for $n = 0$–2) and $CH_3NH_3(NH_3)_n^+ + K \rightarrow CH_3NH_3(NH_3)_n^* + K^+$ (for $n = 0$–1). Mass spectra of the reaction products have been obtained by the technique of charge stripping with NO_2 as collisional ionization gas. New results on the stabilities of CH_3NH_3, $CH_3N_2H_6$, N_3H_{10}, and their deuterated forms are presented. The effects of internal excitation on the decomposition pathways of the radicals are discussed. These species constitute a novel class of radicals with ionization energies estimated to be in the range 3 to 4.5 eV.

We have previously described a technique[1] for generating a variety of metastable and hypervalent molecules by neutralizing a fast beam of positively charged ions with an appropriate electron donor. In a recent study[2] we reported observations that the ammonium radical (NH_4), which is slightly unstable thermodynamically, can form stabilized molecular clusters in combination with NH_3. In the present study the technique is extended to investigate the stabilities of other members of this series of hypervalent molecules. Results of the work indicate that these molecules constitute a new class of free radicals with ionization energies in the range 3–4.5 V.

Experimental Section

The apparatus and the experimental procedures were described in detail previously.[2,3] The primary ions were produced by chemical ionization of NH_3 and CH_3NH_2/NH_3 mixtures in a high-pressure ion source. At high pressures cluster ions are produced efficiently by the three-body reactions[4]

$$NH_4^+(NH_3)_n + 2NH_3 \rightarrow NH_4^+(NH_3)_{n+1} + NH_3 \ (n = 0\text{–}2) \quad (1)$$

and

$$CH_3(NH_3)_n^+ + 2NH_3 \rightarrow CH_3(NH_3)_{n+1}^+ + NH_3 \ (n = 1\text{–}2) \quad (2)$$

All of the deuterated ions were produced by the analogous reactions employing deuterated or partially deuterated reagents. The ions were then accelerated through 6 keV mass resolved in a magnetic sector and focussed into a neutralization chamber containing a few mtorr of K or Na metal vapor. The chamber was 0.5 in. thick and has a knife edge entrance slit of 0.025 × 0.200 in. and an exit slit of 0.025 × 0.250 in. The resulting neutral species were permitted to continue undeflected toward the channeltron electron multiplier located 40 cm from the center of the neutralization chamber while the remaining ions were removed from the beam by means of electrostatic deflector plates. After traversing the electrostatic field, a fraction of the neutral beam along the beam axis was re-ionized by charge stripping. For this purpose, a collisional ionization chamber, 4.25 in. long with 0.020 × 0.280 in. entrance and exit slits, was positioned between the detector and the neutralization chamber. This second chamber was pressurized with NO_2 gas at approximately 70 mtorr. The collisionally re-ionized beam ($\sigma \sim 10^{-18}$ cm^2) was deflected electrostatically off axis and detected by translating the detector normal to the beam axis. Since an ion is deflected a distance Δx proportional to the reciprocal of its kinetic energy, a resolved mass spectrum can be obtained from the deflected secondary ion beam. Further, the mass resolution of the apparatus can be increased by floating the collisional ionization chamber at a negative potential to reduce the kinetic energies of the secondary ions by a constant decrement.

It is important to note that as the neutral dissociation fragments have a greater angular dispersion than parent metastable species (which have nearly the width of the primary ion beam), the relative intensity of some species can be affected by the beam alignment through the two chambers.

Table I. Collisionally Ionized Mass Spectra of Neutralized $NH_4(NH_3)_n^+$ (n = 0, 1, 2) and Deuterated Forms[a]

		relative intensity	
neutralized ion	reionized product	target metal K	target metal Na
NH_4^+	NH_4^+	0.0	0.0
	NH_3^+	100	100
	NH_2^+	23	20
	NH^+	8	6
ND_4^+	ND_4^+	600	304
	ND_3^+	100	100
	ND_2^+	29	30
$N_2H_7^+$	$N_2H_7^+$	50	8
	NH_4^+	18	3
	NH_3^+	100	100
	NH_2^+	11	8
$N_2D_7^+$	$N_2D_7^+$	308	62
	ND_4^+	362	157
	ND_3^+	100	100
$N_3H_{10}^+$	$N_3H_{10}^+$	8	0.0
	$N_2H_7^+$	45	4
	NH_4^+	9	0.0
	NH_3^+	100	100
$N_3D_{10}^+$	$N_3D_{10}^+$	14	0.0
	$N_2D_7^+$	124	9
	ND_4^+	105	13
	ND_3^+	100	100

[a] Intensities normalized to NH_3^+(ND_3^+) peaks.

The relative ion intensities reported in this paper were obtained for ion focussing conditions which maximized primary ion beam transmission through the two chambers and hence maximized the intensity of re-ionized peaks arising from metastable species with the mass of the precursor ion. By a slight defocussing of the magnet it was possible to reduce the transmission of the parent neutral but allow scattered neutrals resulting from dissociation to enter the reionization chamber. This procedure is useful in diagnosing breakup of the neutral clusters. Another helpful diagnostic feature is the use of NO_2 as the collisional reionization gas. Collisional ionization of low ionization potential molecules, using NO_2 as the target gas, leads to yields of parent ions which are much higher than those obtained with the usual target gases like He or N_2.[5]

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Table II. Collisionally Ionized Mass Spectra of Neutralized $CH_3NH_3(NH_3)_n^+$ (n = 0, 1) and Deuterated Forms with Metal Target K

neutralized ion	reionized product	rel intensity
$CH_3NH_3^{+}$[a]	$CH_3NH_3^+$	0.0
	$CH_3NH_2^+$	100
	$CH_2NH_2^+$	86
	CH_2NH^+	10
	$CHNH^+$	40
$CH_3ND_2H^{+}$[a]	$CH_3ND_2H^+$	0.0
	$CH_3ND_2^+$	100
	$CH_2ND_2^+$	85
	$CHND^+$	56
$CH_3ND_3^{+}$[a]	$CH_3ND_3^+$	315
	$CH_3ND_2^+$	100
	$CH_2ND_2^+$	75
	$CHND^+$	55
$CD_3ND_3^+$	$CD_3ND_3^+$	118
	$CD_3ND_2^+$	100
	$CD_2ND_2^+$	87
	$CDND^+$	55
	ND_3^+	10
	$ND_2^+ + CD_3^+$	20
$CH_3N_2H_6^+$	$CH_3N_2H_6^+$	28
	$CH_3NH_3^+$	5
	$CH_3NH_2^+$	100
	$CH_2NH_2^+$	111
	$CHNH^+$	65
	NH_4^+	7
	NH_3^+	66
$CD_3N_2D_6^+$	$CD_3N_2D_6^+$	132
	$CD_3ND_3^+$	368
	$CD_3ND_2^+$	100
	$CD_2ND_2^+$	100
	$CDND^+$	60
	ND_4^+	35
	ND_3^+	86

[a] Weak ion signals of NH_3^+, NH_2^+, and CH_3^+ (or deuterated forms) are not listed.

Results

Radicals of the types $NH_4(NH_3)_n$ and $CH_3NH_3(NH_3)_n$ were generated by the electron-transfer reaction

$$NH_4(NH_3)_n^+ + K \text{ (or Na)} \rightarrow NH_4(NH_3)_n^* + K^+ \text{ (or Na}^+\text{)} \quad (n = 0, 1, 2) \qquad (3)$$

and

$$CH_3NH_3(NH_3)_n^+ + K \rightarrow CH_3NH_3(NH_3)_n^* + K^+ \quad (n = 0, 1) \qquad (4)$$

Mass spectra of reionized neutrals from reactions 3 and 4 are displayed on a kinetic energy scale in Figures 1–5 and integrated intensities for each mass peak are listed in Tables I and II.

To interpret the mass spectral data we distinguish between ionization of molecular fragmentation products which are formed in the neutralization chamber from ionization that occurs from hard dissociative collisions of beam molecules with the re-ionization target gas. Resolution of these modes of dissociation is aided by noting variations in mass spectral patterns of products resulting from choice of electron donor in reactions 3 and 4 and the effect on spectral patterns caused by adjustment of the magnetic field. An example of the effect of slight detuning of the magnetic field is illustrated in Figure 6 for the products of the $N_2D_7^+$/K reaction. As the parent ion diminishes with change in magnetic field the $ND_4^+/N_2D_7^+$ increases sharply. This shows that ND_4 is a molecular product formed by dissociation in the neutralization chamber. The same conclusion can be drawn by comparing mass spectra obtained when different electron donors are used in reactions 3 and 4 (Table I).

If the intensity ratio of a pair of ions does not vary significantly by the two test procedures it can be inferred that the ions originate from the same molecular precursor. The NH_4^+ and $CH_3NH_3^+$ ions observed in some spectra can only be due to collisional dissociation since the parent molecules decompose before reaching the collisional ionization chamber.

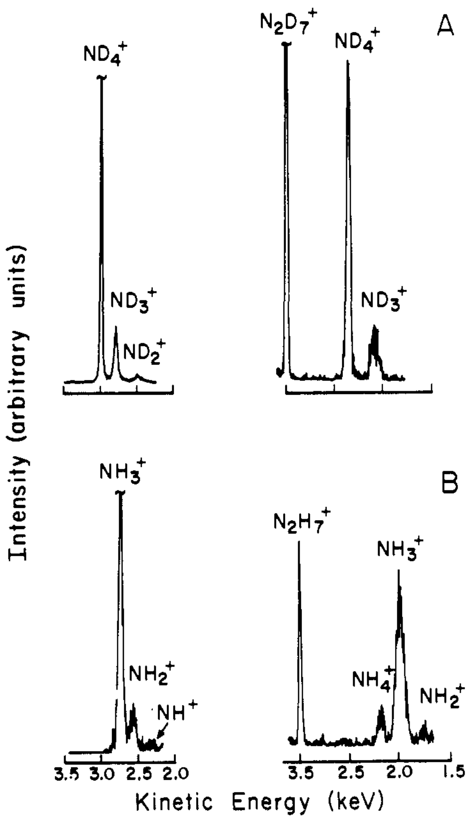


Figure 1. Mass spectra of collisionally ionized neutrals (electron donor = K): (A) ND_4 and N_2D_7; (B) NH_4 and N_2H_7.

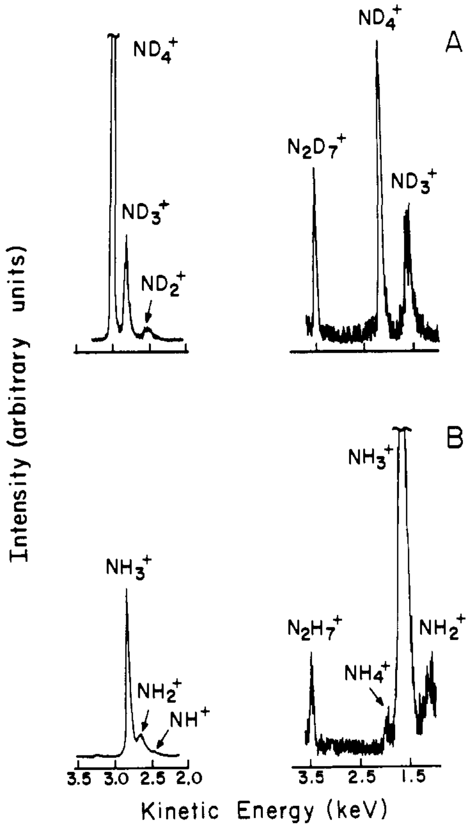


Figure 2. Mass spectra of collisionally ionized neutrals (electron donor = Na): (A) ND_4 and N_2D_7; (B)NH_4 and N_2H_7.

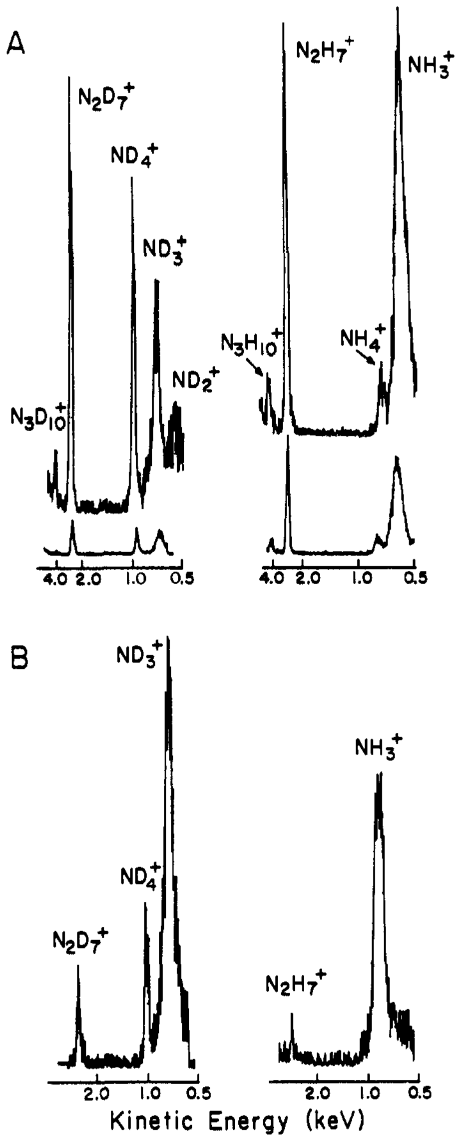


Figure 3. Mass spectra of collisionally ionized N_3D_{10} and N_3H_{10}: (A) electron donor = K; (B) electron donor = Na.

Table III

neutralized ion	major molecular products	ions from collisional dissociation of neutrals
NH_4^+	NH_3	NH_2^+, NH^+
ND_4^+	ND_4, ND_3	ND_2^+, ND^+
$N_2H_7^+$	N_2H_7, NH_3	NH_4^+, NH_2^+, NH^+
$N_2D_7^+$	N_2D_7, ND_4, ND_3	ND_4^+ (minor), ND_2^+, ND^+
$N_3H_{10}^+$	N_3H_{10}, N_2H_7, NH_3	NH_4^+, NH_2^+, NH^+
$N_3D_{10}^+$	N_3D_{10}, N_2D_7, ND_4, ND_3	ND_4^+ (minor), ND_2^+, ND^+
$CH_3NH_3^+$	CH_3NH_2	$CH_2NH_2^+$, CH_2NH^+ (minor), $CHNH^+$
$CH_3ND_3^+$	CH_3ND_3, CH_3ND_2	$CH_2ND_2^+$, $CHND^+$
$CD_3ND_3^+$	CD_3ND_3, CD_3ND_2	$CD_2ND_2^+$, $CDND^+$
$CH_3N_2H_6^+$	$CH_3N_2H_6$, CH_3NH_2, NH_3	$CH_3NH_3^+$, $CH_2NH_2^+$, $CHNH^+$, NH_4^+
$CD_3N_2D_6^+$	$CD_3N_2D_6$, CD_3ND_3, CD_3ND_2, ND_4 (minor), ND_3	$CD_3ND_3^+$ (minor), $CD_2ND_2^+$, $CDND^+$, ND_4^+

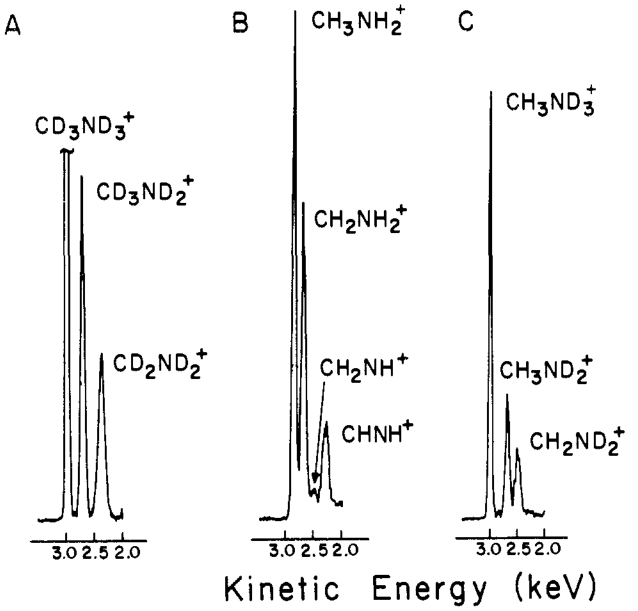


Figure 4. Mass spectra of collisionally ionized neutrals (electron donor = K): (A) CD_3ND_3; (B) CH_3NH_3; (C) CH_3ND_3. The parent $CH_3NH_3^+$ peak would appear at 3.0 keV.

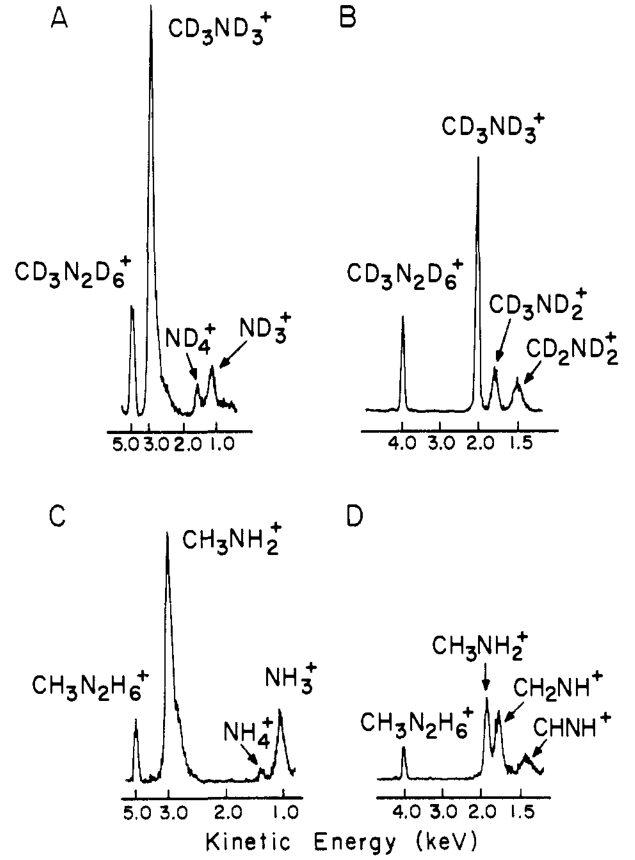


Figure 5. Mass spectra of collisionally ionized neutrals, $CD_3N_2D_6$ and $CH_3N_2H_6$; electron donor = K, B spectrum with increased resolution from A; D spectrum with increased resolution from C.

Results of neutral beam scattering experiments[3] indicated that the *N*-(trideuteriomethyl)ammonium radical was more stable toward dissociation to methylamine than was the totally hydrogenated form. That statement is strikingly demonstrated by the mass spectra in Table II. Parent ions of CH_3ND_3 and CD_3ND_3 are the most intense peaks in the spectra of these molecules, but for CH_3NH_3, the base peak is $CH_3NH_2^+$ and $CH_3NH_3^+$ is not detected. By detuning the magnetic field it was shown that CD_3ND_3 and CD_3ND_2 were the major molecular species formed by neutralization of $CD_3ND_3^+$, confirming results from earlier beam scattering work.[3] With the exceptions of CD_3^+ and ND_3^+ ions other low mass peaks are assigned to collisional fragments from CD_3ND_2. The spectra for methylammonium show that H or D loss is from the NH_3 (or ND_3) group. The fragmentation

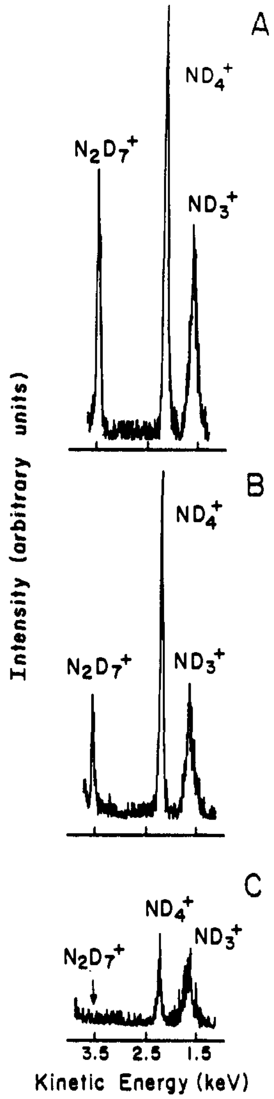


Figure 6. The effect of detuning magnetic field on the mass spectra of neutrals formed by electron transfer from K to $N_2D_7^+$. Field change increase from A → C.

breakdown of the spectra is given in Table III.

Discussion

Considering the very short time scale ($\sim 10^{-15}$ s) for electron transfer to occur in reactions 3 and 4, it is appropriate to treat these processes as vertical transitions.[6] Since the equilibrium structures of the neutral products are likely distorted from those of the precursor ions, vertical electron transfer can leave the neutrals with excess internal energy which can result in molecular breakup. Structures have been calculated theoretically for a number of cluster ions,[7] but at present, detailed information about the structures of the neutrals is not available.

NH_4 and CH_3NH_3 Radicals. Re-ionized parent peaks are not observed in the mass spectra of NH_4 and CH_3NH_3, but these are predominant peaks in the mass spectra of ND_4 and CH_3ND_3 and CD_3ND_3. These results illustrate that the presence of the methyl group does not have a major effect on the stability of the radical. The H–D isotope effect on the stability of the methylammonium radical is further evidence in support of a barrier to dissociation.[3,8] The presence of a single N–H bond in CH_3ND_2H reduces its stability significantly.

For methylammonium radicals the major decomposition pathway is to methylamines. Mass spectral patterns of the collisional dissociation products (Table II) are similar to those observed by electron impact.[9] A second decomposition pathway from CD_3ND_3 leads to $CD_3 + ND_3$. Since these products have nearly equal masses and scatter to large angles, their relative ion intensities underestimate their molecular abundances. The ionization potential of CH_3NH_3 can be derived from the relationship

$$\mathrm{IP}(CH_3NH_3) = \mathrm{IP}(H) - \mathrm{PA}(CH_3NH_2) + \Delta H_6 \qquad (5)$$

where the first two terms on the right are the ionization potential of H and proton affinity of CH_3NH_2 and ΔH_6 is the enthalpy change for the reaction

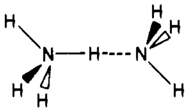
$$CH_3NH_3 \rightarrow CH_3NH_2 + H \qquad (6)$$

The experimental enthalpy change for the process

$$NH_4 \rightarrow NH_3 + H \qquad (7)$$

is about −0.1 eV.[3] Since the H–D isotope effect on reaction 6 indicates that this process is also marginally thermalneutral, we can assume $\Delta H_6 = -0.1 \pm 0.1$ eV to a good level of approximation. This leads in eq 5 to $\mathrm{IP}(CH_3NH_3) = 4.3 \pm 0.1$ eV.[10]

N_2H_7 and $CH_3N_2H_6$ Radicals. Mass spectra of N_2H_7 and $CH_3N_2H_6$ clearly show that these molecules survive transit in our apparatus from the point of neutralization to the point of reionization. It is also evident that clustering with ammonia has a stabilizing effect on NH_4 and CH_3NH_3 radicals most probably through H bonding in structures I and II. This stabilizing effect is also operative for all of the N-deuterated radicals, but the consequence is not as dramatic as it is for the totally hydrogenated species.



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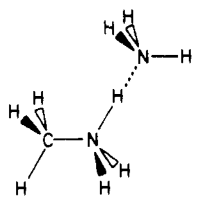

II

The relative importance of the two likely dissociation pathways ($ND_4 + ND_3$ or $2ND_3 + D$) for N_2D_7 can be estimated from the observed mass spectral intensities. Although an earlier similar experiment performed in this laboratory employing N_2 as the collision gas provided no evidence for ND_4 as a dissociation product in this case, it is interesting to reconsider the question in light of the present results. As the NH_4^+ peak observed in the re-ionization mass spectra of N_2H_7 must arise from dissociative re-ionization, its relative intensity can be used to correct for the similar process in the deuterated case. When this is done, the present results imply an N_2D_7/ND_4 neutral beam intensity ratio of about 1.6 near zero scattering angle, assuming the two species have similar ionization efficiencies with NO_2. However, it has already been pointed out that the relative intensities of peaks in collisional ionization mass spectra depend strongly on the nature of the target gas, especially for species of low ionization potential. Thus while it seems clear that some ND_4 is produced as a dissociation product of N_2D_7, the relative importance of this channel, which is probably a sensitive function of internal energy, is difficult to assess.

In the case of $CD_3N_2D_6$, however, the results in Table I indicate that the dissociation products $CD_3ND_3 + ND_3$ are favored over CD_3ND_2 and ND_4. This may well be a consequence of the increased proton affinity of CD_3ND_2 relative to ND_3 which would suggest that the H-bonded deuterium would be more closely associated with the CD_3ND_2 moiety in the ion.

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(10) For this calculation, 13.6 eV was used for ionization potential of H, 214.1 kcal/mol for proton affinity of CH_3NH_2 was chosen from the following: Lias, S. G.; Liebmann, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

The ionization potentials for $R-N_2H_6$ ($R = H, CH_3$) can be estimated from the relationship

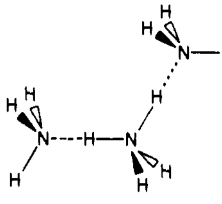
$$IP(R-N_2H_6) = IP(R-NH_3) + \Delta H_{ion} + \Delta H_{diss} \quad (8)$$

where ΔH_{ion} is the enthalpy change for ion clustering ($n = 0$ and 1 in reaction 1 and 2, respectively) and ΔH_{diss} is the enthalpy change for the process

$$R-N_2H_6 \rightarrow R-NH_3 + NH_3 \quad (9)$$

The experimental stabilization energy in $(NH_3)_2$ due to H bonding is about 0.16–0.20 eV.[11,12] However, a recent theoretical calculation by Cao and co-workers[13] gives a value of 0.38 eV for the stabilization energy of structure I. Using the latter value for ΔH_{diss} and clustering energies of -24.8[4] and -21.4[14] kcal/mol for NH_4^+ and $CH_3NH_3^+$, respectively, we obtain $IP(N_2H_7) = 4.0$ eV and $IP(CH_3N_2H_6) = 3.9$ eV with estimated uncertainties of ±0.2 eV.

N_3H_{10} Radical. Re-ionized parent peaks are observed in the mass spectra of N_3H_{10} and N_3D_{10}. Molecular dissociation by loss of one or two ammonias is also observed. The structure of N_3H_{10} is most probably one with two NH_3 units hydrogen bonded to an ammonium radical (structure III). The ionization potential of N_3H_{10} is estimated by combining the sum of the ion clustering energies in reaction 1 for $n = 0$ and 1, the ionization potential of NH_4, and the enthalpy of dissociation for the process



III

$$NH_4(NH_3)_2 \rightarrow NH_4 + 2NH_3 \qquad \Delta H_{diss} \quad (10)$$

The latter quantity is taken as 2(0.38 eV) from the theoretical analysis of Cao and co-workers.[13] This leads to $IP[NH_4(NH_3)_2] = 3.5$ eV with an estimated uncertainty of ±0.2 eV.

Table IV. Estimated Ionization Potential

species	IP, eV	species	IP, eV
NH_4	4.7[a]	CH_3NH_3	4.3 ± 0.1
N_2H_7	4.0 ± 0.2	$CH_3N_2H_6$	3.9 ± 0.2
N_3H_{10}	3.5 ± 0.2		

[a] Value for NH_4 taken from ref 3.

Ion clustering reactions 1 and 2 are quite exothermic, and under our source conditions these ions probably retain a fraction of this energy in their internal modes. We believe this contributes to the differences observed in the breakup patterns (Table I) when different electron donors are used in reaction 3. Since the ionization potential of Na (5.1 eV) is higher than that of K (4.3 eV), resonance electron transfer with Na is likely to access the highly excited ions more efficiently, leading to further instability in the neutral products. For Ground-state reactants electron transfer from K(g) to $N_2H_7^+$ and $CH_3NH_3^+$ is nearly resonant (compare ionization potentials of N_2H_7 and CH_3NH_3 with that of K). A definite trend toward a decrease in ionization potentials for $NH_4(NH_3)_n$ with increase in n is apparent. Scaling of IP values in Table IV predicts the ionization potential for the fully coordinated radical, $NH_4(NH_3)_4$, to fall below 3 eV, a value less than the ionization potential of Cs. This suggests that a solid phase of $NH_4(NH_3)_4$, if it could be isolated, would have interesting electrical properties.

The origin of stability in these ammonium radicals raises interesting questions concerning chemical bonding. A hint to the understanding of the effects is given in the paper by Cao and co-workers. One can visualize NH_4 as a species with a quasi-Na atom electron configuration. Cluster ions are stabilized by ionic interactions between NH_4^+ and the ammonia ligands. Bonding of an electron to the ion core in $NH_4(NH_3)_n^+$ is weakened as n increases and the orbital becomes more delocalized. At the same time a fraction of the ionic bonding between the core and NH_3 units is retained. Further theoretical analyses of these radicals would be of interest.

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Registry No. NH_4, 92075-50-8; NH_3, 7664-41-7; CH_3NH_3, 17000-00-9.

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