Vibrationally state-selected reactions of ammonia ions. II. $NH_3^+(\nu)+CH_4$

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The effects of vibrational excitation of the ammonia ν_2 inversion mode on the reaction of NH_3^+ ($\widetilde{X}$,$v = 0$ to 9) with methane have been measured in a tandem quadrupole mass spectrometer over the center-of-mass collision energy range 1.5 to 10 eV. The hydrogen abstraction channel is enhanced by nearly a factor of 2 at nine quanta of vibrational energy relative to the $v = 0$ level of the ion. Added vibration in the ammonia ion umbrella-bending mode facilitates the transition to the NH_4^+ product ion geometry. Protonated methylamine is formed at lower kinetic energies by attack of the ion at the methane carbon center, but with increasing vibrational excitation of the ammonia ion, the protonated methylamine decomposes by 1,2-elimination of molecular hydrogen and by C–N bond scission.

INTRODUCTION

Previous studies of ion–molecule reactions in the NH_3^+ + CH_4 system have been limited to the ion cyclotron resonance studies by Huntress and co-workers[1,2] and the drift tube study by Adams, Smith, and Paulson.[3] The dominant product ion observed in these two studies was NH_4^+ formed by the abstraction of one of the hydrogen atoms from the neutral methane molecule by the ammonia ion. The rate constant for this reaction at thermal kinetic energies was determined to be $\approx 4\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Deuterium labeling of the methane indicated that no isotopic scrambling occurs in the reaction and that it proceeds by simple H and (D atom) transfer.[2]

In contrast to the NH_3^+ + CH_4 system, the related reaction system of CH_4^+ + NH_3 has been studied quite extensively by numerous workers and with various experimental techniques.[3–9] The proton transfer reaction ($k = 6.6\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}), hydrogen atom abstraction rection ($k = 3\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}), charge transfer reaction ($k = 6.9\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}), and condensation reactions of CH_4^+, CH_3^+, and CH_2^+ ($k \leqslant 1\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) have been investigated.[2] Of particular interest in the methane ion–ammonia system has been the condensation reactions of CH_4^+ and CH_3^+ with NH_3 resulting in the formation of species such as CH_3–NH_3^+, CH_3–NH_2^+, and CH_2=NH_2^+. Deuterium substitution studies of the methane ion or the ammonia neutral indicate that no scrambling of the hydrogen atoms between the methyl and amine centers occurs in the condensation complexes.[2] The vicinal 1,2-elimination of H_2 across the C–N bond and geminal 1,1-elimination of H_2 from the amine group in these ions have been observed to occur at kinetic energies above 3 eV.[7]

The energetics of the NH_3^+ (v) + CH_4 system for various reaction channels are given in Fig. 1. The final energies of the product channels are based on the thermodynamic heats of formation compiled in Table I. Both the hydrogen atom abstraction channel and the CH_3–NH_3^+ condensation channel are exothermic with respect to the reactant channel. The proton transfer and charge transfer channels are endothermic and are accessible at higher reaction energies. No studies of this system have been performed at energies above thermal and the role of the NH_3^+ ion vibrational quantum states in these reactions has not been previously investigated.

EXPERIMENTAL

The experimental apparatus and techniques have been discussed in detail in a previous publication and will only be summarized here.[10] Resonance enhanced 2 + 1 multiphoton ionization via the $NH_3(\widetilde{C}')$ state is used to selectively produce pulsed beams of ammonia ions with a specific number of quanta of vibrational energy in the ν_2 umbrella bending mode. Each vibrational quanta is $\approx$120 meV (950 cm^{-1}). The NH_3^+ (v) ion vibrational level from $v = 0$ to 9 can be state selected to better than 80%–95% purity.

Ions are produced in sufficient numbers to permit reac-

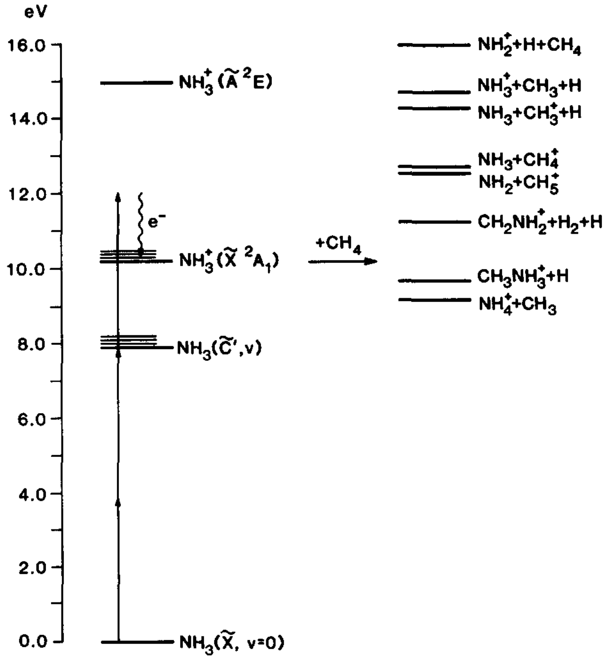

FIG. 1. Energy level diagram for the product ion channels in the NH_3^+ (v) + CH_4 reaction system.

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TABLE I. Thermodynamic data for the $NH_3^+ + CH_4$ reaction system.

M	$\Delta H_f^\circ(M)$	$\Delta H_f^\circ(M^+)$	IP
H	2.239[a]	15.837	13.598
H_2	0.000	15.426	15.426
NH_2	1.70	13.10	11.40
CH_3	1.44	11.27	9.84
NH_3	−0.478	9.70	10.18
CH_4	−0.775	11.92	12.70
NH_4	⋯	6.42[b]	⋯
CH_5	⋯	9.42[c]	⋯
NH_3CH_3	⋯	6.24[d]	⋯
NH_2CH_2	⋯	7.72[d]	⋯

All units are eV. Values are from Rosenstock (Ref. 11), unless otherwise noted.

[a] Reference 12.
[b] Based on a proton affinity of 206 kcal/mol (Ref. 13).
[c] Reference 14.
[d] Reference 15.

tion studies to be carried out in a tandem quadrupole mass spectrometer. The first quadrupole is used to eliminate any mass contamination in the primary ion beam arising from photofragmentation or from isotopes in the sample gas. The ions are then injected into the static gas reaction cell with variable kinetic energy which ranges from 1.5 to 10 eV in the center-of-mass (c.o.m.) reference frame. The static gas is maintained at a pressure of 1.0 mTorr and the reaction occurs under field-free conditions. Ionic reaction products scattered into the second quadrupole are mass analyzed and detected with a multichannel plate electron multiplier array with ion counting electronics. Both the dependence of the product ion signals on the primary ion vibrational quantum state and the primary ion kinetic energy can be observed. Due to the variation of the ion collection efficiency and quadrupole transmission with product ion scattering angle and kinetic energy, we are only able to report relative cross sections for the reactions.

The ammonia (Matheson 99.99%) is seeded 1:10 in helium (Matheson 99.995%) in the supersonic expansion. Methane (Matheson U.H.P. 99.97%) is used in the static gas reaction cell without further purification. All collision energies are given in the center of mass reference frame and have an uncertainty of 0.25 eV. The energy spread in the ion beam is 0.5 eV determined using a retarding field analyzer between the reaction cell and the detection quadrupole. Count rates are typically 0.1 to 5 counts per laser shot and the data is averaged over 1000 laser shots per point.

RESULTS AND DISCUSSION

The mass spectrum observed in the present tandem quadrupole study of the NH_3^+ $(v = 0) + CH_4$ reaction at an intermediate center-of-mass collision energy of 7.5 eV is shown in Fig. 2(a). Two strong peaks appear at masses 15 and 18 near the unreacted $NH_3^+(v)$ primary ion peak at mass 17. In addition, two weaker peaks at higher mass are found at masses 30 and 32. The NH_4^+ $(m/e = 18)$ product ion is formed by the direct abstraction of a hydrogen atom from the neutral methane molecule:

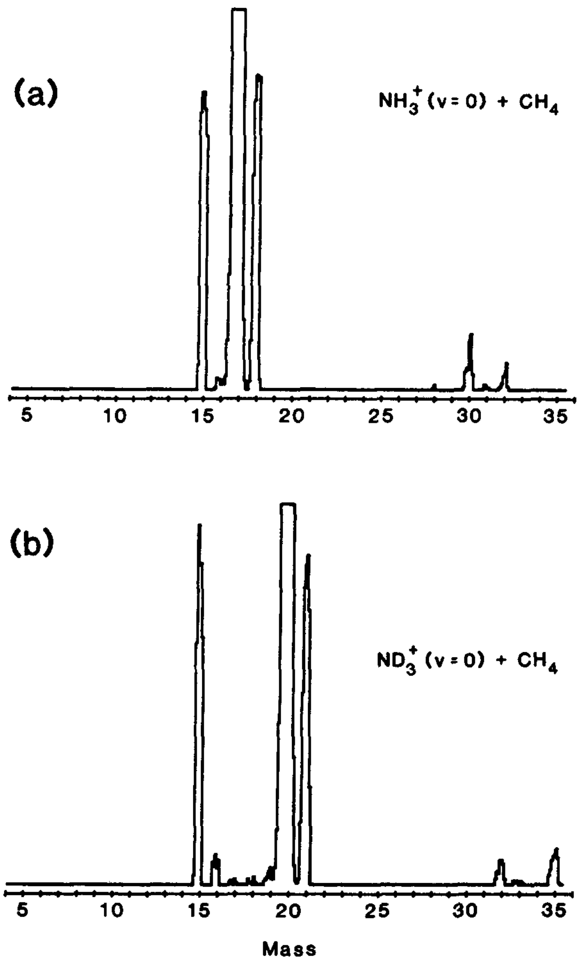


FIG. 2. Product ion mass spectra: (a) NH_3^+ $(v = 0) + CH_4$, and (b) ND_3^+ $(v = 0) + CH_4$. The collision energy for both spectra is 7.5 eV in the center of mass and the CH_4 pressure is 1 mTorr in the scattering cell.

$$NH_3^+ (v=0) + CH_4 \rightarrow NH_4^+ + CH_3, \quad \Delta H = -1.06 \text{ eV}. \tag{1}$$

The formation of the higher mass products at masses 30 and 32 result from the condensation reaction between the NH_3^+ $(m/e = 17)$ and the CH_4 $(m/e = 16)$. The formation of CH_3–NH_3^+ $(m/e = 32)$ is promoted by the loss of a neutral H atom from the CH_4 which stabilizes the complex by carrying off the excess reaction energy as translational motion:

$$NH_3^+ (v=0) + CH_4 \rightarrow CH_3\text{–}NH_3^+ + H, \quad \Delta H = -0.45 \text{ eV}. \tag{2}$$

The CH_3–NH_3^+ species can be thought of as the protonated form of methylamine in which the H^+ is associated with the amine group. The simplest picture for the condensation reaction is that the hydrogen atom is displaced from the CH_4 as the C–N bond is formed either through a direct knockout mechanism or via a nucleophilic substitution mechanism. Ejection of the H atom from the methane and not from the ammonia ion is supported by deuterium labeling studies of the reaction ND_3^+ $(v = 0) + CH_4$. As shown in Fig. 2(b), there is no evidence of isotope exchange during the formation of the CH_3–ND_3^+ $(m/e = 35)$ which would have resulted in species such as $CH_3\text{–}NHD_2^+$ or $CH_4\text{–}ND_2^+$ ($m/e = 34$) if the D atom had been lost from the ammonia ion instead. The protonated tetracoordinate nitrogen of the amine is energetically more stable than the pentacoordinate carbon species produced if the hydrogen atom is lost instead from the ammonia ion, followed by subsequent rearrangement. The charge density from CNDO/2 calculations is shared 0.28 on the $-CH_3$ group and 0.72 on the $-NH_3$ group.[16]

The dependence of the product mass peaks on the ion kinetic energy is shown in Fig. 3. The NH_4^+ ion signal is fairly constant over the entire collision energy range examined. The behavior of the mass 32 peak indicates that $CH_3\text{–}NH_3^+$ is formed predominantly at lower kinetic energies, peaking at 4 eV. Above 4 eV, the $CH_3\text{–}NH_3^+$ signal begins to give way to product ion masses appearing at mass 30 and mass 15. Such an observation indicates that these product ions are appearing directly in competition with the $CH_3\text{–}NH_3^+$, or indirectly through a two-step process at the expense of the $CH_3\text{–}NH_3^+$. At these higher kinetic energies, some of the excess $NH_3^+ (v) + CH_4$ collision energy is channeled into internal excitation of the $CH_3\text{–}NH_3^+$ complex. The $CH_3\text{–}NH_3^+$ can decompose by 1,2-elimination of molecular hydrogen to give $CH_2{=}NH_2^+$ ($m/e = 30$):

$$CH_3\text{–}NH_3^+ \rightarrow CH_2{=}NH_2^+ + H_2, \quad \Delta H = 1.48\ \text{eV} \qquad (3)$$

and scission of the C–N bond to form CH_3^+ ($m/e = 15$):

$$\begin{array}{lll} & & CH_3^+ + NH_3, \quad \Delta H = 4.55\ \text{eV} \qquad (4a)\\ & \nearrow & \\ CH_3\text{–}NH_3^+ & & \\ & \searrow & \\ & & CH_3 + NH_3^+, \quad \Delta H = 4.90\ \text{eV}. \qquad (4b)\end{array}$$

Owing to the difference in ionization potentials between CH_3 and NH_3, bond scission to form NH_3^+ ($m/e = 17$) is higher in energy. Any decomposition along the $CH_3 + NH_3^+$ channel is masked experimentally by the unreacted $NH_3^+ (v)$ primary ion beam signal at mass 17 so that the branching ratio between reactions 4(a) and 4(b) could not be determined. These decomposition mechanisms are supported by deuterium substitution of the ammonia ion to produce $CH_3\text{–}ND_3^+$, which subsequently undergoes 1,2-elimination of molecular HD to form $CH_2{=}ND_2^+$ ($m/e = 32$) and bond scission to form CH_3^+ ($m/e = 15$). There is no experimental evidence for isotope exchange in the condensation product or during its decomposition. The energies of the C–H and N–H bond are sufficiently different as to prevent facile rearrangement and there is likely to be an energy barrier analogous to the 3.56 eV barrier calculated for the 1,2-hydrogen shift in methylamine.[17] Elimination of molecular H_2 is experimentally observed to proceed exclusively across the C–N bond. Collin and Franklin have calculated that the CH_3NH^+ product of 1,1-elimination of molecular hydrogen from the amine group is 1.4 eV higher in energy than the $CH_2NH_2^+$ product of 1,2-elimination.[18]

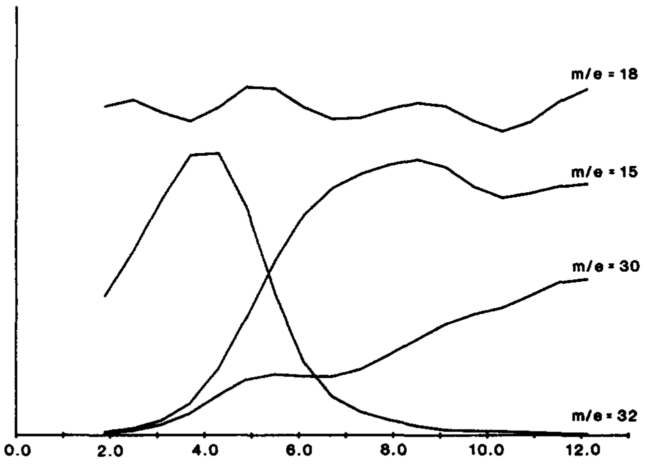


FIG. 3. Kinetic energy dependence of the CH_3^+ ($m/e = 15$), NH_4^+ ($m/e = 18$), $CH_2{=}NH_2^+$ ($m/e = 30$), and $CH_3\text{–}NH_3^+$ ($m/e = 32$) product ion signals for $NH_3^+ (v = 0) + CH_4$ (1 mTorr).

A minor peak also appears at mass 16 in the mass spectra of both the $NH_3^+ (v) + CH_4$ and $ND_3^+ (v) + CH_4$ reaction systems due to direct charge transfer from the ammonia ion to the methane to form CH_4^+ ($m/e = 16$):

$$NH_3^+ (v) + CH_4 \rightarrow NH_3 + CH_4^+, \quad \Delta H = 2.52\ \text{eV}. \qquad (5)$$

While a peak at this mass could also be attributed to collisional fragmentation of the $NH_3^+ (v)$ primary ion at high kinetic energies to form NH_2^+ ($m/e = 16$) + H, no corresponding ND_2^+ peak ($m/e = 18$) appears in the mass spectrum of the $ND_3^+ + CH_4$ system [Fig. 2(b)] to corroborate this mechanism.

A contribution to the observed CH_3^+ ($m/e = 15$) signal could conceivably come from electron transfer to form CH_4^+, followed by loss of a neutral H atom. However, it is unlikely that the CH_4^+ can be produced with sufficient internal excitation by the removal of an electron to cause its subsequent decomposition. The kinetic energy dependence of the condensation reaction product signals suggests that the CH_3^+ appears via reaction 2(b) at the expense of the $CH_3\text{–}NH_3^+$.

There is no evidence of proton transfer occurring in the mass spectrum of the $ND_3^+ (v) + CH_4$ system, despite the fact that there is sufficient energy available for formation of CH_4D^+ ($m/e = 18$). The CH_5^+ (CH_4D^+) ion has been shown to exist, but there may be an energetic barrier or kinetic constraints which prevent it from being formed and surviving to be detected in this reaction system.

Figure 4 shows the effect of the $NH_3^+ (v)$ vibrational quantum state on the hydrogen atom abstraction channel [reaction (1)] for $v = 0$ to 9. Vibrational enhancement κ is defined as the fractional change in the product signal relative to the product signal for the $v = 0$ level of the ion,

$$\kappa = [I(v) - I(0)]/I(0). \qquad (6)$$

Thus κ is equal to the relative cross section minus one. Positive values represent an increase in the product ion signal with vibrational excitation of the ion, while negative values represent a decrease with vibration. When $\kappa = 0$, the cross section does not depend on the vibrational excitation of the reagent ion. The data indicate that increasing excitation of the ν_2 umbrella-bending mode of the ammonia ion enhances the formation of the NH_4^+ ion uniformly over the ion kinetic energies studied. At $v = 9$, this effect is to nearly double the amount of NH_4^+ observed. Since the enhancement changes with the vibrational excitation and does not vary as much with the kinetic energy, the effect appears to be dynamic in nature, rather than energetic. Hydrogen atom abstraction presumably occurs with the planar NH_3^+ ion approaching the methane in such a fashion that the nitrogen $2p_z$ orbital projects out toward the hydrogen atoms on the methane. Transfer of one of the methane hydrogen atoms can then proceed directly between the N···H–C atomic centers. Although the equilibrium geometry is still planar, excitation of the NH_3^+ umbrella-bending mode acts to deform the ion out-of-plane. Since the final geometry of the NH_4^+ product has a tetrahedral structure, increased vibrational excitation of the planar $NH_3^+ (v)$ primary ion (H–N–H bond angle = 120°) improves the geometric overlap with the tetrahedral product (H–N–H bond angle = 109°). Classically, nearly seven quanta of vibrational excitation are required to give an average angle of deformation equal to the tetrahedral N–H product angle. In addition, increasing deformation of the NH_3^+ apex angle has the effect of pushing the nitrogen $2p_z$ orbital further out in space on the opposite side of the molecule from the instantaneous position of the three hydrogen atoms. This would make the transfer of the H atom from the methane to this orbital more favorable during the portion of the NH_3^+ vibration that the hydrogen atoms are furthest away. The steric hindrance caused by the hydrogen atoms on the ammonia is lessened during this half of the vibrational period, but this effect may be somewhat counteracted by greater steric hindrance during the half of the period that the hydrogen atoms are on the methane side of the nitrogen.

The vibrational energy of the NH_3^+ is likely to be fully retained in the NH_4^+ product ion. If the internal energy of the ion cannot be easily accommodated into the additional degrees of freedom of the product, increasing vibrational excitation would promote the reverse reaction resulting in the production of less NH_4^+. In the direct atom abstraction of a hydrogen atom, the combined ν_2 vibration of the NH_3^+ and the motion of the H atom along the ammonia C_3 molecular axis maps directly onto the triply degenerate ν_3 vibrational mode of the NH_4^+ product.[19] A linear combination of the ν_{3a}, ν_{3b}, and ν_{3c} vibrational modes produces a vibration with the appropriate threefold symmetry to readily accommodate the umbrella-bending motion of the NH_3^+ without requiring that the energy be rapidly randomized throughout the molecule.

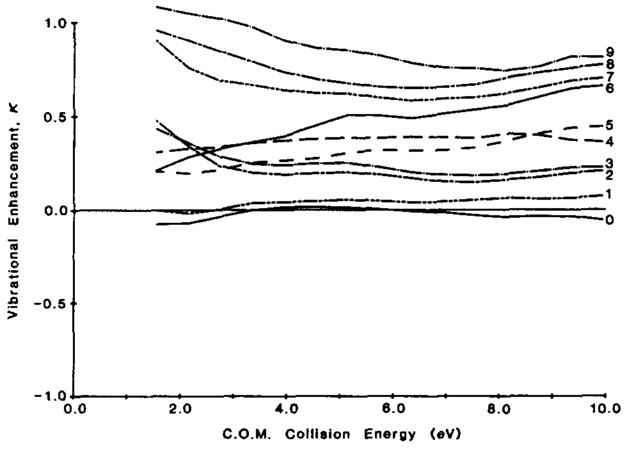


FIG. 4. Vibrational enhancement of the $NH_3^+ (v) + CH_4 \rightarrow NH_4^+ + CH_3$ reaction for $v = 0$ to 9. The reproducibility of the $v = 0$ curve demonstrates the experimental error associated with the scatter in the data points and the normalization between the vibrational data sets.

As observed in the $NH_3^+ (v) + D_2$ system,[10] the hydrogen atom abstraction product is expected to decompose by loss of an H or D atom when it is formed with internal excitation exceeding the N–H bond dissociation energy of ≈ 4.5 eV. In the $ND_3^+ (v) + CH_4$ reaction system, the ND_2H^+ ion produced by an analogous mechanism would appear at mass 19, but no ions at this mass are observed experimentally. For reaction (1), the fractional contribution of the collision energy to the NH_4^+ (NH_3D^+) product ion internal energy based on a simple spectator stripping model is only 0.11. If this model is valid for the ammonia-d_3-ion–methane system, collision energies above 40 eV for $ND_3^+ (v = 0)$ and above 32 eV for $ND_3^+ (v = 8)$ would be necessary to impart sufficient energy to the ND_3H^+ to cause it to undergo unimolecular decomposition. It is not surprising then that ND_2H^+ is not observed in the 2–10 eV kinetic energy range in this study.

The effect of vibrational excitation of the $NH_3^+ (v)$ ion on the condensation reaction channel must be examined by decomposing the process into its two component parts: (1) the initial formation of the $CH_3–NH_3^+$ ion, and (2) the subsequent unimolecular decomposition of the $CH_3–NH_3^+$ complex if it is produced with sufficient internal excitation in the formation reaction. If the $CH_2{=}NH_2^+$ and CH_3^+ products observed in this experiment come entirely from reaction (3) and reaction (4), then the sum of the $CH_3–NH_3^+$, $CH_2{=}NH_2^+$, and CH_3^+ ion signals must equal the total amount of $CH_3–NH_3^+$ initially formed at any particular kinetic energy regardless of whether or not it had subsequently decomposed. Figure 5 shows the effect of vibrational excitation of the $NH_3^+ (v)$ ion on the formation of $CH_3–NH_3^+$ by plotting the relative change in the sum of these three signals relative to the $v = 0$ signal for $v = 0$ to $v = 9$. Any change in the total amount of $CH_3–NH_3^+$, $CH_2{=}NH_2^+$, and CH_3^+ is sufficiently small that it is less than the experimental uncertainty of $\pm 10\%$ associated with normalization of the data sets for the different ion vibrational states and could not be detected. Vibrational excitation of the $NH_3^+ (v)$ primary ion does not seem to influence the formation of the $CH_3–NH_3^+$.

Once the formation of the $CH_3–NH_3^+$ is established as being independent of the $NH_3^+ (v)$ vibrational quantum state, the effect of the vibrational energy on its subsequent decomposition can be readily treated. Figure 6 shows a plot of the CH_3^+, $CH_2{=}NH_2^+$, and $CH_3–NH_3^+$ ion signals as a percentage of the total amount of $CH_3–NH_3^+$ before decomposition (the sum of the CH_3^+, $CH_2{=}NH_2^+$, and $CH_3–NH_3^+$ ion signals) for $NH_3^+ (v = 0)$ and

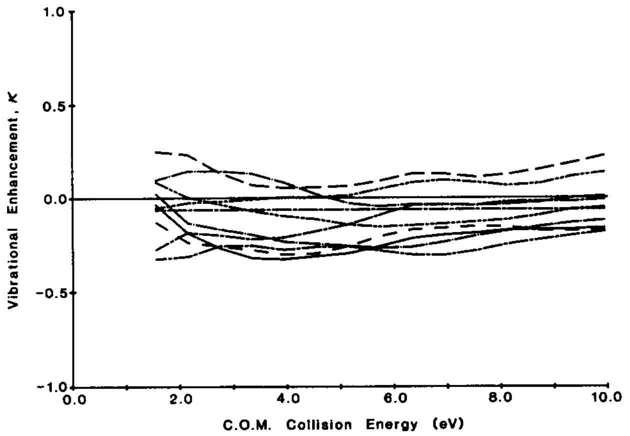


FIG. 5. Vibrational enhancement of the NH_3^+ (v) + $CH_4 \rightarrow CH_3$-NH_3^+ + H reaction for $v = 0$ to 9. The curves show no dependence on the ion vibrational level within the ± 10% experimental uncertainties; therefore the curves corresponding to different vibrational levels are not labeled.

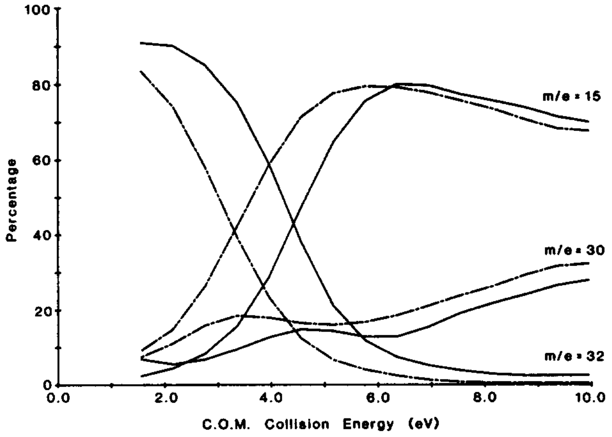
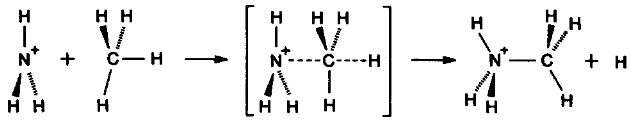


FIG. 6. Vibrational energy dependence of the CH_3-NH_3^+ ($m/e = 32$), CH_2=NH_2^+ ($m/e = 30$), and CH_3^+ ($m/e = 15$) ion signals as a percentage of the sum of the ion signals for these three ions. The solid line is for the reaction NH_3^+ ($v = 0$) + CH_4 and the dashed line for NH_3^+ ($v = 8$) + CH_4. Because the collection efficiency varies with the ion, the important features are the relative changes of m/e = 15, 30, and 32, not the absolute changes.

NH_3^+ ($v = 8$). Vibrational excitation of the NH_3^+ (v) ion at a given collision energy promotes decomposition of the CH_3-NH_3^+ product ions through both the vicinal elimination of H_2 and the C–N bond scission. The effect is to shift the appearance curves for the CH_3^+ and CH_2=NH_2^+ to lower ion kinetic energy by an amount comparable to the amount of vibrational energy added to the ion. It is interesting to note that the fractional contribution of the collision energy predicted by the spectator stripping model[20] for the internal energy of the CH_3-NH_3^+ product ion is 0.97, suggesting that the NH_3^+ (v) vibration and kinetic energy make nearly equivalent contributions to the total internal energy of the product ion. The similarity in the variation in the H_2 elimination and bond scission decomposition product signals with NH_3^+ (v) vibrational quantum state indicates that the initial vibrational energy of the ion is rapidly randomized in the product. Dynamical effects resulting from the umbrella-bending motion of the hydrogen atoms on the ammonia would be expected to influence these two channels to a different degree because the transition states for the two processes are very different.

Huntress, Bowers, and co-workers have examined the bond scission and H_2 elimination decomposition pathways of CH_3-NH_3^+ as a function of internal excitation by reacting H_3^+ ions with methylamine.[15,21] They observed little hydrogen scrambling and predominantly 1,2-elimination of molecular hydrogen. The results are consistent with the existence of a 2.6 eV energy barrier in the CH_2-NH_2^+ + H_2 decomposition channel.[15] If the energy of the barrier is added to the enthalpies of reactions (2) and (3), this indicates that 3.6 eV of collision energy is necessary in the NH_3^+ (v) + CH_4 system to reach the dissociation threshold. This is in agreement with our experimental observations of a 3–4 eV onset for both the bond scission and H_2-elimination decomposition channels in the NH_3^+ (v) + CH_4 system.

A barrier to the formation of CH_3-NH_3^+ may also exist which would explain the absence of CH_3-NH_3^+ condensation reactions in the thermal energy studies on this system despite the fact that the reaction is exothermic.[1-3] In spite of the low count rates that limit our ability to examine the kinetic energy dependence at low energies, we do observe an increase in the CH_3-NH_3^+ formation in the 1–2 eV range with increasing reagent translational energy, suggestive of a small energy barrier. If the mechanism for the condensation reaction between the ammonia ion and methane proceeds by a nucleophilic-type attack of the nitrogen along one of the methane C_3 axes, then a small energy barrier would be expected to be associated with the penetration of the ammonia ion and inversion of the methyl group hydrogen atoms at the pentacoordinate carbon center as the hydrogen atom on the opposite side of the attack is expelled, i.e., an S_N2-type mechanism:



(7)

Excitation of the ammonia ν_2 vibrational mode would not be expected to provide dynamical assistance in overcoming the barrier associated with the methyl group inversion, and there is no direct experimental evidence that stereochemical inversion takes place in this system. Nevertheless, nucleophilic displacement reactions involving anions and neutral molecules have been observed experimentally in the gas phase by several groups.[22-28] Brauman and co-workers have developed statistical models to estimate the central barrier height on a double-minimum potential energy surface for several of these anion–neutral reactions, including some involving S_N2 displacement at methyl centers.[28] Calculations of a barrier in the NH_3^+ + CH_4 system do not appear in the literature. No dependence of the reaction cross section on the initial ion vibrational state is observed within the experimental uncertainties, indicating that the transition state is sufficiently short-lived that the vibrational energy does not have time to become statistically distributed among the degrees of freedom of the intermediate and the reaction proceeds by a direct mechanism.

CONCLUSIONS

In summary, direct hydrogen atom abstraction is the dominant reaction pathway for the $NH_3^+ (v) + CH_4$ system in the kinetic energy range studied. Vibrational excitation of the NH_3^+ umbrella-bending mode enhances the abstraction reaction by improving the dynamics of the transition into the NH_4^+ product channel. The $CH_3–NH_3^+$ condensation product appears at low kinetic energy and its formation is unaffected by the initial ion vibrational state. There is evidence for a small barrier associated with the displacement reaction to form this product ion, and the reaction mechanism may be of the S_N2-type. At higher energies, the $CH_3–NH_3^+$ ion decomposes by 1,2-elimination of molecular hydrogen across the C–N bond and by C–N bond scission. The vibrational energy of the ammonia ion is randomized in the condensation product before decomposition and makes a significant energetic contribution to the internal energy of the complex. The appearance of the $CH_2{=}NH_2^+$ product is consistent with previous reports of a 2.6 eV energy barrier in the $CH_3–NH_3^+$ decomposition channel.

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