

Vibrationally state-selected reactions of ammonia ions. III. $\text{NH}_3^+(\nu) + \text{ND}_3$ and $\text{ND}_3^+(\nu) + \text{NH}_3$

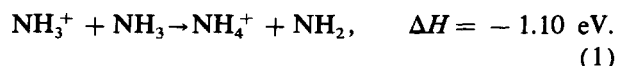
William E. Conaway, Takayuki Ebata,^{a)} and Richard N. Zare
Department of Chemistry, Stanford University, Stanford, California 94305

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The role of vibrational excitation of the ν_2 umbrella-bending mode of ND_3^+ ($\tilde{X}, \nu = 0$ to 10) and NH_3^+ ($\tilde{X}, \nu = 0$ to 9) on the reaction with NH_3 and ND_3 is examined over the 2 to 12 eV center-of-mass kinetic energy range. Isotopic substitution permits the investigation of charge transfer, proton/deuteron transfer, and neutral atom abstraction. The charge transfer channel is moderately enhanced by excitation of the ammonia ion ν_2 vibrational mode. The proton/deuteron channel is suppressed by vibrational excitation of the ion at low kinetic energies. The hydrogen/deuterium atom abstraction channels show nearly a factor of 6 vibrational enhancement relative to NH_3^+ ($\nu = 0$). The ion vibrational and translational energy play inequivalent roles in the reactions, indicating that nonstatistical factors are important in the transition from reactant to product channels. A simple dynamical model is offered to explain both the proton/deuteron transfer and the neutral atom abstraction reactions; it is based on the argument that vibrational motion along the particle transfer coordinate promotes reaction while vibrational motion perpendicular to the transfer coordinate hinders reaction.

INTRODUCTION

Experimentally, the ammonia ion–ammonia neutral reaction system (see Table I for a summary of relevant energetics) has been studied quite extensively by numerous workers without regard to the role played by the individual quantum states of the reagent molecules on the reactivity.^{1–21} The dominant reaction observed in these non-state-selected studies is the formation of the NH_4^+ product ion:

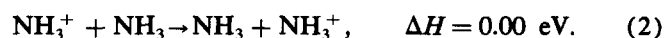


For this reaction, the reported literature values for the thermal energy reaction rate constant cluster around $1.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, close to the value of $2.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ calculated for the classical average dipole orientation (ADO) collision rate constant.^{22,23} The close agreement of the reaction cross section and the collision cross section indicates that the reaction occurs with near unit efficiency at thermal energies.

Several workers have noted that the formation of NH_4^+ in reaction (1) can proceed by either proton transfer from the ion to the neutral or by abstraction of a hydrogen atom from the neutral by the incident ion. The results of Huntress *et al.*¹¹ using ion cyclotron double resonance ejection techniques on a 1:1 mixture of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ indicated that proton transfer is the predominant reaction mechanism. A later study in the same laboratory¹⁷ found that the hydrogen atom abstraction reaction does occur in addition to the proton transfer reaction and that the ratio for $k_{\text{HAA}}/k_{\text{PT}}$ for these channels is 0.28. Recent data of Adams *et al.*²¹ using the selected ion flow tube (SIFT) technique in the system $\text{ND}_3^+ + \text{NH}_3$ showed that hydrogen atom abstraction is a nonnegligible reaction pathway, amounting to a significant

fraction (15%) of the product ions in their study.

In addition to the formation of NH_4^+ , Huntress *et al.*¹¹ observed the symmetric charge transfer reaction in ammonia and set an upper limit of $4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ on the rate constant for this channel:



The charge transfer reaction was not observed to occur at thermal collision energies, but it was found to occur for translationally excited NH_3^+ ions (laboratory kinetic energies above 1 eV). At 35–40 eV laboratory kinetic energies, the amount of charge transfer product and proton transfer product observed were nearly equal.

Condensation products have also been seen in the reaction of ammonia ions with neutral ammonia, albeit with very low reaction cross section. Protonated hydrazine, N_2H_5^+ , produced by the formation of a N–N bond and the ejection of a hydrogen atom

TABLE I. Thermodynamic data for the $\text{NH}_3^+ + \text{NH}_3$ reaction system.

M	$\Delta H_f^\circ(M)$
H	2.239 ^a
H ⁺	15.837
NH ₂	1.70
NH ₂ ⁺	13.10
NH ₃	–0.478
NH ₃ ⁺	9.70
NH ₄ ⁺	6.42 ^b
N ₂ H ₃ ⁺	10.05 ^c
N ₂ H ₄ ⁺	9.71
N ₂ H ₅ ⁺	8.10 ^d

All units are eV. Values are from Rosenstock (Ref. 24), unless otherwise noted.

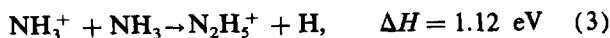
^a Reference 25.

^b Based on a proton affinity for NH_3 of 206 kcal/mol (Ref. 26).

^c Reference 27.

^d Based on a proton affinity for N_2H_4 of 204.7 kcal/mol (Ref. 28).

^{a)} Present address: Department of Chemistry, Tohoku University, Sendai 980, Japan.

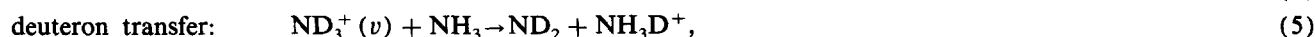
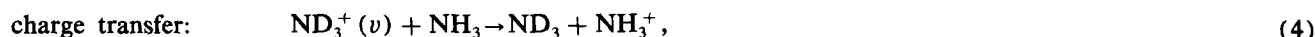


has been observed in several studies^{3,7} and the reaction rate constant for this process determined to be $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, about 1000 times less than reaction (1).

The effect of vibrational excitation of the ν_2 umbrella-bending mode of the ammonia ion in its reaction with neutral ammonia to form NH_4^+ has been investigated in several previous experimental studies. The pioneering work of Chupka and Russell²⁹ utilized single-photon vacuum ultraviolet photoionization to produce $\text{NH}_3^+(v)$ ions in selected vibrational quantum states from $v = 0$ up to $v = 10$. They observed a factor of 2 decrease in the relative cross section with increasing vibrational energy in the ion at several kinetic energies. The absolute rate constant for proton transfer [reaction (1)] was measured by Sieck *et al.*³¹ using a Lyman- α photoionization source at 121.6 nm to produce $\text{NH}_3^+(v)$ ions exclusively in the $v = 0$ vibrational ground state. They determined the value of k to be $2.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $v = 0$ and to decrease with increasing photon energy, in qualitative agreement with the results of Chupka and Russell. Baer and Murray,³² using the photoion-photoelectron coincidence (PIPECO) technique to study the re-

actions of ammonia ions, confirmed the experimental results of Chupka and Russell for the vibrational dependence of the proton transfer reaction and presented additional vibrationally state-specific results for the charge transfer channel. They observed a factor of 3 increase in the relative cross section for symmetric charge transfer [reaction (2)] with increasing vibrational excitation up to $v = 10$ at all kinetic energies examined in the study. Most recently, Pijkeren *et al.*³³ have extended the internal-energy selected measurements of proton transfer to lower kinetic energy and found the relative cross section for proton transfer to decrease by slightly less than a factor of 2 with vibrational excitation of the ion.

In the present tandem quadrupole mass spectrometer study, we have investigated the effect of vibrational excitation of the ν_2 umbrella-bending mode of the ammonia ion in both the $\text{ND}_3^+(v) + \text{NH}_3$ and $\text{NH}_3^+(v) + \text{ND}_3$ reaction systems. Deuterium labeling of either the ammonia ion or ammonia neutral reaction molecules provides an unequivocal means of distinguishing the product of the charge transfer reaction [reaction (4)] from the unreacted primary ion beam and the products of the proton/deuteron transfer reaction [reaction (5)] from the neutral atom abstraction reaction [reaction (6)]:



In addition, isotopic labeling of the reaction molecules permits examination of the influence of the mass of the transferred particle on the effect of the ion vibrational quantum state. Vibrational states from $v = 0$ to 10 are produced in the umbrella-bending mode of the $\text{ND}_3^+(v)$ ion (one ν_2 quantum $\approx 93 \text{ meV}$) and up to $v = 9$ of the $\text{NH}_3^+(v)$ ion (one quantum $\approx 120 \text{ meV}$) using vibrationally quantum state-selective resonance enhanced multiphoton ionization. The relative reactivity of the ammonia ion in each of the above reaction channels as a function of vibration state is examined over a 2 to 12 eV center of mass collision energy range.

EXPERIMENTAL

The vibrationally state-selected resonance enhanced ionization technique and the tandem quadrupole mass spectrometer have been discussed in detail in previous publications.^{34,35} Anhydrous ammonia- h_3 (Matheson, 99.99% purity) and ammonia- d_3 (MSD Isotopes, 99 atom% isotopic purity) were used without further purification for both the supersonic ion beam nozzle source and the static gas reaction cell. The gas lines to the reaction cell were baked out and purged with the reagent gas to prevent unwanted hydrogen/deuterium isotope exchange with water molecules on the walls. Mass selection in the first stage of the tandem quadrupole mass spectrometer provided additional control over isotopic contamination of the reagent ion beam.

The mass spectrum observed in the reaction $\text{NH}_3^+(v = 2) + \text{ND}_3$ is shown in Fig. 1 for both low (2.5 eV) and high (10 eV) center-of-mass collision energies. The deuterium atom abstraction product, NH_3D^+ ($m/e = 19$), is the dominant ion observed at low collision energy. The charge transfer product, ND_3^+ ($m/e = 20$), dominates the product ion mass spectrum at high energy. The proton transfer product, ND_3H^+ ($m/e = 21$), is clearly distinguished from the deuterium atom abstraction product. The $m/e = 22$ mass peak shown in Fig. 1 is likely to be ND_4^+ , formed by charge transfer followed by a secondary collision of ND_3^+ with the ND_3 scattering gas. Its small count rate is consistent with such a process. Product ions resulting from condensation reactions and, at higher kinetic energies, condensation reactions followed by unimolecular decomposition of the internally excited condensation product by elimination or bond scission are observed at the high mass end of the spectrum, but the ion count rates are too small to permit examination of the effect of the reactant ion vibrational state in these particular reactions.

It is interesting to note that at thermal collision energies the proton transfer channel appears to dominate, being something like five times larger than the hydrogen atom abstraction channel, based on the work of Huntress and Pinizzotto¹⁷ and of Adams, Smith, and Paulson.²¹ On the other hand, the data in Fig. 1 at 2.5 and 10 eV seems to imply that the hydrogen atom abstraction channel dominates by a fac-

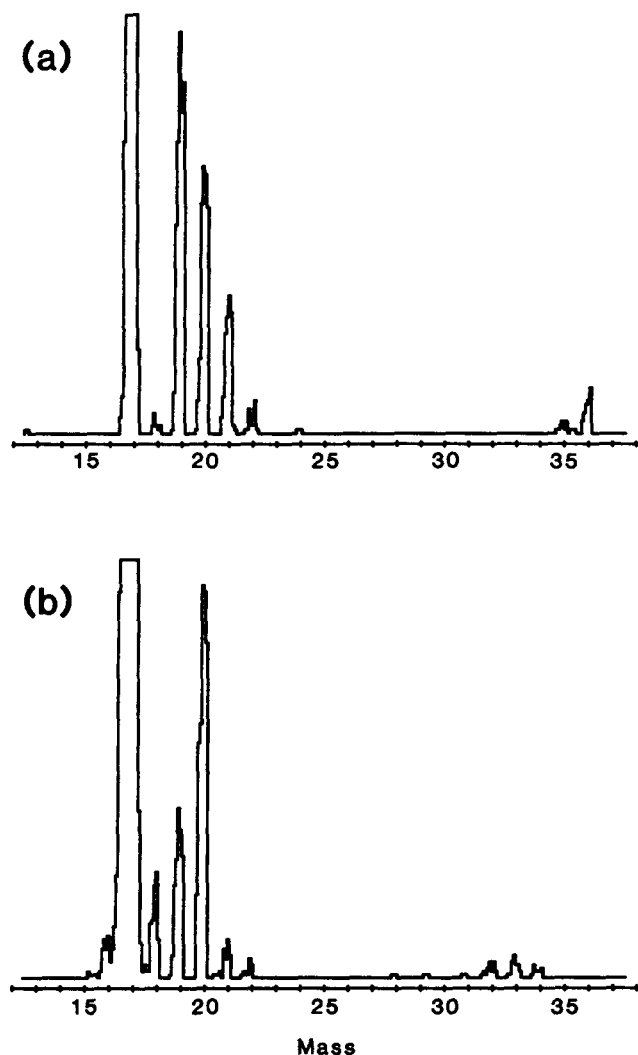


FIG. 1. Reaction product mass spectrum for the reaction $\text{NH}_3^+(v=2) + \text{ND}_3$ (a) at a collision energy of 2.5 eV and (b) at a collision energy of 10 eV.

tor of 3. However, because the two mechanisms sharply differ, we are biased in our collection efficiency for the products of the hydrogen atom abstraction channel, and we are reluctant to use our data to compare the relative contributions from the two channels.

The collection efficiency of our apparatus may change with collision energy and with the mass of the product ion. Therefore we report only relative cross sections for reactions with different vibrational states of the NH_3^+ (ND_3^+) ion as a function of the collision energy. We define the vibrational enhancement κ as the fractional change in the product ion signal relative to the product signal for the $v=0$ level of the ion, $\kappa = [I(v) - I(0)]/I(0)$. Positive values of κ indicate that the reaction under study is enhanced by vibrational excitation of the reagent ion, while negative values of κ indicate that it is suppressed. When $\kappa = 0$, the reaction is independent of reagent ion vibrational excitation.

Although quantitative information from the data on the variation of the reaction cross section with kinetic energy is not reliable in our apparatus owing to the variation in the product ion collection efficiency with product ion kinetic energy, general trends in the data can be observed. The deu-

terium atom abstraction product signal increases up to a maximum at 5 eV, then decreases at higher energies. The proton transfer product signal decreases systematically as the collision energy increases. The charge transfer product ion signal increases with collision energy. At intermediate collision energies, condensation products appear at masses 35 and 36 as either an H or D atom is ejected in the collision and a nitrogen–nitrogen bond is formed to yield a protonated hydrazine molecule. At higher collision energies, the products ions appearing at masses 35 and 36 give way to products at masses 32, 33, and 34 which arise from ejection of additional H or D atoms in the collision or from decomposition by the elimination of molecular H_2 , HD, or D_2 from the condensation products formed with excess internal excitation. Isotopic scrambling of the H and D atoms appears to occur readily in the protonated hydrazine product ions, in contrast to the results observed for the $\text{NH}_3^+(v) + \text{CH}_4$ system.³⁵ The peak assigned to NH_2D^+ ($m/e = 18$) is formed by the decomposition of the deuterium atom abstraction product or the condensation products at the collision energies above a 4 eV appearance threshold. Some fragmentation of the $\text{NH}_3^+(v)$ primary ion is observed at high energy and appears as NH_2^+ at mass 16.

VIBRATIONAL EFFECTS ON CHARGE TRANSFER

Results

We observe an increase in the amount of charge transfer product as the number of vibrational quanta in the ν_2 umbrella-bending mode of the ammonia ion is increased. The relative charge transfer cross section in the $\text{ND}_3^+(v) + \text{NH}_3$ system (Fig. 2) grows by a factor of 1.5 to 2 for $\text{ND}_3^+(v=10)$ over the 2–12 eV collision energy range. The relative cross section of the $\text{NH}_3^+(v) + \text{ND}_3$ system shows similar behavior with ion vibrational excitation, increasing by a factor of 1.5 for $\text{NH}_3^+(v=9)$, compared to $\text{NH}_3^+(v=0)$. Within the experimental errors, the trend toward increasing relative cross section with vibrational quantum state is

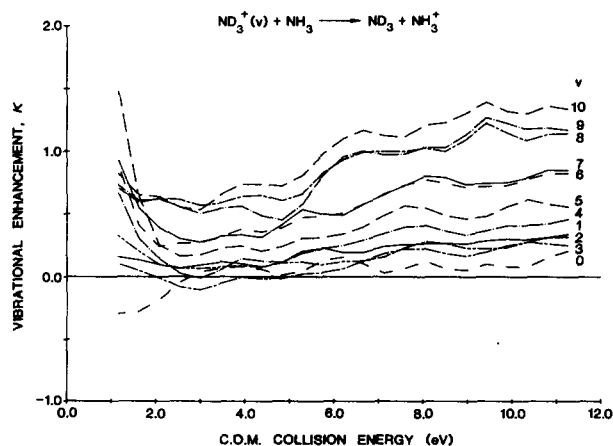


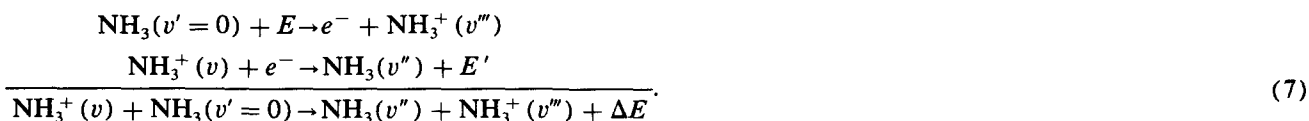
FIG. 2. Vibrational dependence of the relative cross section of the charge transfer reaction between $\text{ND}_3^+(v)$ and NH_3 for $v=0$ through $v=9$. The reproducibility of the $v=0$ curve indicates the magnitude of the error associated with the scatter in the data points and the normalization between the vibrational data sets.

smooth and shows no sign of behavior attributable to accidental resonant overlap of vibrational energy levels. Compared to the symmetric $\text{NH}_3^+(v) + \text{NH}_3$ system, the different vibrational frequency of the ν_2 mode [720 cm^{-1} in $\text{NH}_3^+(v)$ vs 950 cm^{-1} in $\text{NH}_3^+(v)$] arising from the deuterium substitution on one of the reactants in the $\text{ND}_3^+(v) + \text{NH}_3$ and $\text{NH}_3^+(v) + \text{ND}_3$ systems acts to shift the vibrational levels out of resonance. This permits the examination of the role of nonresonant channels in the charge transfer process. In addition, the shift in vibrational frequency is accompa-

nied by a shift in the maximum of the Franck–Condon envelope from $v = 5$ for $\text{NH}_3(v = 0) \rightarrow \text{NH}_3^+$ to $v = 7$ for $\text{ND}_3(v = 0) \rightarrow \text{ND}_3^+$.

Discussion

The symmetric charge transfer reaction in the ammonia ion–ammonia system can be thought of as consisting of the two half-reactions:

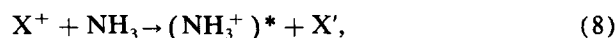


It is interesting to consider the effect of vibrational excitation of the reagent ion in charge transfer reactions in terms of the Franck–Condon overlap factors for each half-reaction and the size of the energetic mismatch ΔE between the vibrational energy levels for the two halves of the reaction. Resonant charge transfer channels, such as $\text{NH}_3^+(v = 4) + \text{NH}_3(v = 0) \rightarrow \text{NH}_3(v = 0) + \text{NH}_3^+(v = 4)$, have an energy mismatch of 0 eV. Nonresonant channels, such as $\text{NH}_3^+(v = 4) + \text{NH}_3(v = 0) \rightarrow \text{NH}_3(v = 1) + \text{NH}_3^+(v = 3)$, have a nonzero energy mismatch arising from the difference in vibrational frequency in the neutral and in the ion and from the anharmonicities in the potential energy surfaces. This nonzero energy mismatch is made up in the change in translational energy of the two molecules before and after the exchange of the electron. Assuming that the collision cross section is independent of the vibrational quantum state of the ion, the overall charge transfer cross section is expected to increase with increasing Franck–Condon overlap factors and decreases with increasing energy mismatch. Recently these two effects have been considered in some detail for the $\text{NH}_3^+ + \text{NH}_3$ symmetric charge transfer system using a multistate impact parameter treatment.³⁶ It was found that nonresonant channels dominate and that the cross section dependence on vibrational excitation of the reagent ion could be successfully modeled.

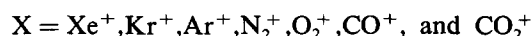
In atom–diatom reaction systems, it is reasonably straightforward to discuss vibrational effects in terms of Franck–Condon transitions and vibrational energy level mismatches since only one vibrational mode exists to be excited. However, in the polyatomic systems, the situation is complicated by the greater number of vibrational modes that can be excited in the molecule and the higher density of vibrational states available to accommodate an energy mismatch. A rigorous theoretical treatment of the effect of ion vibration on charge transfer cross section must include a full multidimensional Franck–Condon analysis covering all $3N-6$ normal vibrational coordinates of the polyatomic molecule.

In the tetratomic ammonia system, such an analysis would entail consideration of all six vibrational coordinates in the four distinct vibrational modes. An assumption can be

made that only the ν_2 umbrella-bending mode participates in the charge transfer exchange. This simplification is justified based on the results of photoionization experiments which indicate that the ν_2 mode is the predominant mode excited when the electron is removed from the nonbonding $2p_z$ orbital on the nitrogen atom. The electron–ion recombination reaction presumably occurs by the reverse process, with the electron entering the nitrogen atom $2p_z$ orbital, again, only involving excitation of the ν_2 vibrational mode. However, such vibrational exclusivity may not be applicable when considering chemical ionization in the ammonia system. Experimental work by Marx and co-workers³⁷ and by Bowers and co-workers³⁸ on



where



indicate that charge transfer does not necessarily occur to states with the largest Franck–Condon overlap factors and that the distribution of the internal energy in the ammonia ion varies greatly with the choice of X^+ . Several vibrational levels of the ammonia ion are populated and there is a significant conversion of reaction energy into kinetic energy. The ion can absorb small amounts of reaction energy to match up with nearby, nonresonant, vibrational levels in the ammonia ion.

In their state-specific studies of symmetric charge transfer in the $\text{NH}_3^+(v) + \text{NH}_3$ system, Baer and Murray³² observed a factor of 3 increase in the reaction cross section from $v = 0$ to $v = 9$ over a 1 to 100 eV kinetic energy region. No vibrational enhancement was observed at 3000 eV collision energy. This is slightly more than the factor of 2 enhancement in the cross section which we observe over the same kinetic energy range for the deuterium-labeled systems. Their results are discussed in terms of the multistate impact parameter theory of charge transfer based upon the Franck–Condon factors and the vibrational overlap mismatch between the reactant ion and neutral molecule. The observed vibrational enhancement is much less than the factor of 30 variation in the Franck–Condon factors between $v = 0$ and

$v = 5$ for resonant charge transfer considering only the ν_2 vibrational mode. The discrepancy between the experimental enhancement and the Franck–Condon factors can be rationalized if (1) excitation of nonresonant vibrational levels is important, (2) vibrational modes other than the ν_2 mode play a role in the reaction, or (3) Franck–Condon factors alone are insufficient to describe the charge transfer mechanism. The classical model of charge transfer between an ion and a neutral molecule involves the electron hopping back and forth repeatedly between the two molecules during the time that they interact. The model proposed by Baer and Murray suggests that the reaction probability varies with impact parameter b . For b less than the critical Langevin impact parameter b_L , the electron makes a sufficient number of hops that the probability of the electron being associated with either molecule is split evenly between the two molecules. Beyond b_L , the electron makes fewer hops and the reaction probability (i.e., the probability that the electron makes an odd number of hops) is proposed to decrease exponentially at a rate empirically determined from the experiment data for the various ion vibrational states. In this model, the initial internal energy of the ion is important only for those collisions occurring with impact parameters greater than b_L . They suggest that energetically nonresonant charge transfer channels are important in determining the observed variation in relative cross section with the initial $\text{NH}_3^+(v)$ vibrational state.

While the small difference between the results of Baer and Murray and our results can be attributed to the difference in experimental conditions (i.e., state-selection efficiency, ion kinetic energy spread), it may also be due to the elimination of the resonant charge transfer channels in the mixed isotope system. The $v = 0$ vibrational state is likely to be the only vibrational state in exact energetic resonance. If charge transfer of the $v = 0$ state is enhanced by this resonance while the remainder of the vibrational levels are not, this could account for the difference in the observed results. Our results for the deuterated ammonia systems neither directly support nor conflict with the empirical model based on impact parameters proposed by Baer and Murray. The results do indicate, however, that nonresonant vibrational

levels must be considered in addition to resonant channels in charge transfer reactions.

It would be instructive to examine charge transfer in the $\text{NH}_3^+(v) + \text{NH}_3$ reaction system in addition to the two deuterium-labeled reaction systems in order to directly compare the role of resonant charge transfer and nonresonant charge transfer under similar experimental conditions. At present, it is experimentally too difficult to distinguish with sufficient accuracy the NH_3^+ product ions from the $\text{NH}_3^+(v)$ reactant ions based on temporal considerations of the ion pulses alone. However, $^{15}\text{NH}_3$ might be used in the future to give the necessary mass discrimination between the reactant and product ions and provide additional data for these studies.

VIBRATIONAL EFFECTS ON PROTON/DEUTERON TRANSFER

Results

The effect of vibrational excitation on $\text{ND}_3^+(v)$ ion on the transfer of D^+ to NH_3 to form NH_3D^+ is shown in Fig. 3. We observe up to a factor of 2 decrease in the relative reaction cross section in going from $v = 0$ to $v = 10$ at a collision energy of 1.5 eV. This effect becomes less pronounced with collision energy for all vibrational levels and, within experimental uncertainty, disappears for energies above 5 eV. In the $\text{NH}_3^+(v) + \text{ND}_3$ system, there is a factor of 2.5 decrease for $v = 9$ at 1.5 eV, disappearing for energies above 8 eV. The main difference observed between proton and deuteron transfer in these systems is that the effect of vibrational excitation of the ion begins to become less important at lower kinetic energy for the D^+ transfer reaction as compared to the H^+ transfer reaction. The greater mass of the deuteron can contribute more internal excitation of the NH_3D^+ product ion from the energy of the collision than the lighter proton can contribute for the ND_3H^+ product ion. The greater amount of internal excitation of the product as a function of collision energy appears to work against the enhancement achieved by vibrational excitation of the incident ion, either by making the backreaction to products more favorable or by opening up decomposition pathways.

Discussion

In their pioneering work on the $\text{NH}_3^+(v) + \text{NH}_3$ system, Chupka and Russell observed a factor of 2 decrease in the relative cross section for the formation of NH_4^+ when $v = 10$ is compared to $v = 0$. However, their experimental methodology did not permit control over the magnitude of and spread in the collision energy. Moreover, Chupka and Russell were not able to distinguish between NH_4^+ ions formed as a result of hydrogen atom abstraction or as a result of proton transfer. Consequently, the comparison of their results with the present study leaves unresolved several ambiguities. Unlike the work of Chupka and Russell, Baer and Murray³² were able to study the proton transfer reaction channel in the $\text{NH}_3^+(v) + \text{NH}_3$ system without interference from the hydrogen atom abstraction channel. Using the photoion–photoelectron coincidence (PIPECO) technique, they found a factor of 2 decrease in the relative cross section for $\text{NH}_3^+(v = 0)$ at a 0.1 eV center-of-mass collision energy.

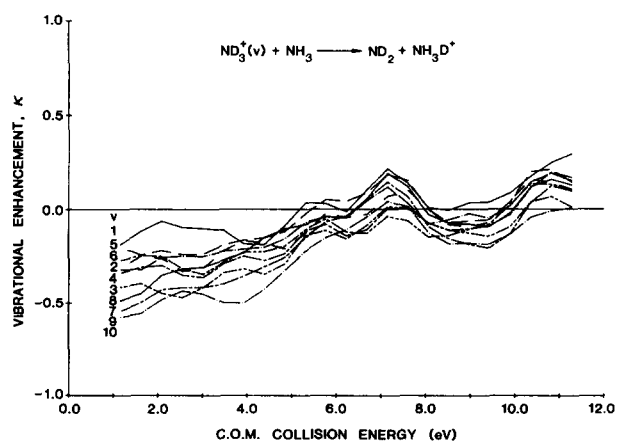


FIG. 3. Vibrational dependence of the relative cross section of the deuteron transfer reaction between $\text{ND}_3^+(v)$ and NH_3 for $v = 0$ through $v = 10$.

The effect of vibrational suppression was even more dramatic at a collision energy of 1.0 eV, where they observed a factor of 10 decrease in the NH_4^+ product ion yield with nine quanta of vibrational excitation in the incident ammonia ions.

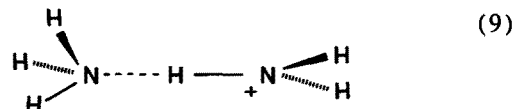
As shown in Fig. 3, the decrease in the relative cross section with increasing vibrational quantum state at the low collision energies is in qualitative agreement with the results of the previous studies on proton transfer in the $\text{NH}_3^+(v) + \text{NH}_3$ system. The lack of exact quantitative agreement may be due to the effect of deuterium labeling of the reactants, or it may be due to the contributions from high energy ions arising in the nonnegligible energy spread in the ion beam in our apparatus. The lack of a vibrational effect at the higher collision energies could be due to a change in the mechanism of the reaction or it may reflect the fact that as the molecules approach each other faster, vibrations begin to appear frozen on the time scale of the interaction and the distinction between $v = 0$ and $v = 10$ in the transfer of the proton/deuterium disappears.

The original explanation of Chupka *et al.* for the decrease in the relative reaction cross section with increasing vibrational excitation was based on statistical phase space considerations. This assumed that the reaction proceeded through a long-lived $(\text{NH}_3)_2^+$ complex and that vibrational excitation of the ion made it more probable that the complex would fall apart back into the $\text{NH}_3^+ + \text{NH}_3$ reactant channel rather than forward into the $\text{NH}_4^+ + \text{NH}_2$ product channel. Later detailed calculations for this system by Chesnavich and Bowers³⁰ indicated that the phase space of the reactant and product channels does not vary with reactant internal energy by an amount sufficient to be consistent with the observed experimental results. For small amounts of vibrational excitation ($E_v \leq 1.5$ eV, $v \leq 13$), the $\text{NH}_3^+(v)$ vibrational level is not expected to greatly influence the decomposition of the complex. Only at large values of E_v does the relative cross section begin to deviate significantly from unity.

Van Pijkeren *et al.*³³ have interpreted the decrease in the relative cross section with increasing ion vibrational quantum state in terms of a modified statistical phase space model in which the dynamical constraints of the reaction restrict the number of accessible final states. The model employs an adjustable parameter s related to the number of reduced degrees of freedom present in the intermediate complex participating in the process of statistical energy redistribution. They then assume that the number of participating degrees of freedom decrease with increasing kinetic energy to accommodate the kinetic energy results of Baer and Murray. The model can be successfully made to fit the experimental data and claims to bridge the gap between the direct and complex reaction mechanisms. However, no direct dynamical information can be extracted from s , the value of the reduced number of participating degrees of freedom.

In general, reactions which occur through weakly bound complexes do not proceed statistically. The binding energy of $(\text{NH}_3)_2^+$ complex has been determined experimentally to be 0.79 eV.³⁹ Chesnavich and Bowers have suggested that the proton transfer reaction proceeds directly rather than through a long-lived complex and that dynamical

constraints in the reaction mechanism were the cause of the observed decrease in the reaction cross section with ion vibrational excitation. They proposed a mechanism in which the transfer of the proton in the transition state occurs directly between the nitrogen atom of the vibrationally excited ammonia ion and the lone pair electrons on the nitrogen atom of the neutral ammonia molecule:



The ν_2 umbrella-bending motion of the ion produces molecular motion of the nitrogen and hydrogen atoms perpendicular to the direction of the H^+ transfer. Thus, Chesnovitch and Bowers argued that the vibrational energy of this motion is not expected to couple strongly to the $\text{N}-\text{H}\cdots\text{N}$ reaction coordinate.

This argument can be taken a step further. Tomoda and Kimura⁴⁰ have performed *ab initio* calculations on the equilibrium structure of the $(\text{NH}_4^+ \cdot \text{NH}_2)$ complex and determined that the linear $\text{N}-\text{H}-\text{N}$ configuration represents the lowest energy structure for this system. Based on the reaction scheme shown in scheme (9), the increase in the energy of the transition state complex as the ion geometry becomes more and more nonplanar makes the transfer of the proton less favorable and results in a decrease in the amount of NH_4^+ product ion formed, in agreement with the experimental data of this and previous studies. Hence we conclude that vibrational excitation of the ν_2 mode of the ammonia ion interferes with the ability of the $(\text{NH}_4^+ \cdot \text{NH}_2)$ complex to maintain a linear $\text{N}-\text{H}-\text{N}$ configuration and suppresses the formation of products.

VIBRATIONAL EFFECTS ON NEUTRAL ATOM ABSTRACTION

Results

The effect of the incident ion internal energy on hydrogen atom abstraction in the $\text{NH}_3^+(v) + \text{NH}_3$ system has not been studied previously due to its small cross section at thermal energies, mass interference from the proton transfer channel, and/or from temporal interference from the unreacted primary ion beam. Full deuteration of either the ammonia ion or the ammonia neutral molecule permits unambiguous mass discrimination of the proton/deuteron transfer and neutral atom abstraction channels.

The effect of vibrational excitation of the ν_2 mode of the $\text{ND}_3^+(v)$ ion on hydrogen atom abstraction from NH_3 is shown in Fig. 4. There is a strong vibrational enhancement with increasing vibrational quantum state which peaks at a collision energy of 4 eV. The increase is smooth and, within the experimental error, shows no sign of accidental resonances or perturbations. The vibrational excitation of $\text{NH}_3^+(v)$ on deuterium atom abstraction from ND_3 shows a very similar enhancement effect, reaching a factor of 5 for $v = 8$ at 4 eV, then decreasing rapidly at the higher collision energies. The greater mass of the deuterium atom can contribute more internal excitation of the NH_3D^+ product ion

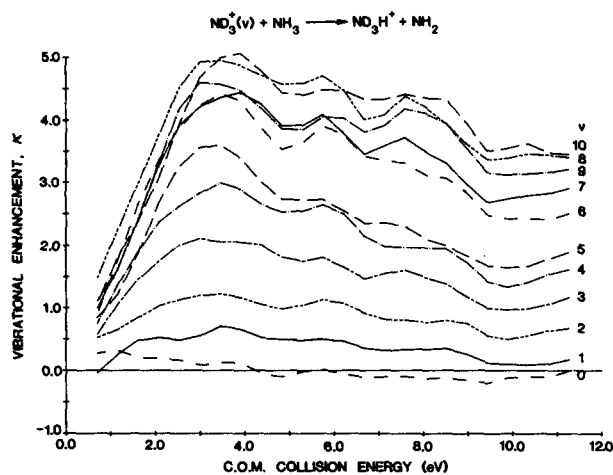


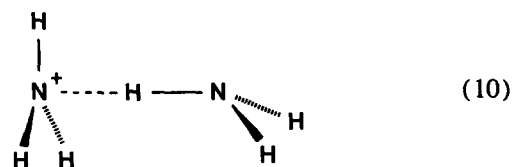
FIG. 4. Vibrational dependence of the relative cross section of the hydrogen atom abstraction reaction between $\text{ND}_3^+(v)$ and NH_3 for $v = 0$ through $v = 10$.

from the collision than the lighter hydrogen atom can for the ND_3H^+ product ion. The greater amount of internal excitation of the product as a function of collision energy appears to work against the enhancement achieved by vibrational excitation of the incident ion.

Discussion

Owing to the slow variation of the relative cross section with collision energy, it may be strongly argued that the vibrational enhancement of the neutral atom abstraction reactions is not simply caused by an increase in the sum of the kinetic and internal energy of the primary ions, but by the dynamical interactions between the two molecules during the atom transfer. As in the analogous case of proton transfer, the statistical phase space theory indicates that the neutral atom abstraction reactions should be independent of the ion internal energy if it were to proceed statistically through a long-lived complex. The lack of agreement suggests that this reaction proceeds by a direct mechanism.

In the proton/deuteron transfer reaction between $\text{NH}_3^+(v) + \text{NH}_3$, Su and Bowers⁴¹ proposed a transition state [scheme (9)] in which the vibrational motions of nuclei of the ion are directed perpendicular to the motion associated with transfer of the H^+ to the neutral ammonia molecule. In the same paper, they propose a transition state for hydrogen atom abstraction in the $\text{NH}_3^+(v) + \text{H}_2\text{O}$ system in which the vibrational motions of the nuclei of the ion are directed along the motion associated with transfer of the hydrogen atom to the ammonia ion. Vibration in the ion is expected to couple strongly into the $\text{N-H}\cdots\text{N}$ reaction coordinate. Further, Su and Bowers suggest that excitation of the ν_2 umbrella-bending mode pushes the geometry of the $\text{NH}_3^+(v)$ ion more toward the tetrahedral geometry of the NH_4^+ product ion. Thus, a strong vibrational enhancement of hydrogen atom abstraction is expected, although none was observed experimentally in the $\text{NH}_3^+(v) + \text{H}_2\text{O}$ system. We propose that a similar transition state describes the hydrogen atom abstraction in the $\text{NH}_3^+(v) + \text{NH}_3$ system:



Vibrational excitation of the ν_2 mode of the ammonia ion produces molecular motion of the nitrogen and hydrogen atoms along the direction of hydrogen atom transfer, similar to the hydrogen atom abstraction reaction in the $\text{NH}_3^+(v) + \text{CH}_4$ system.³⁵ Vibration increasingly deforms the time-averaged structure of the ion away from its planar equilibrium structure and toward the bent structure characteristic of the NH_4^+ product geometry. The improvement is the geometric overlap between the reactant NH_3^+ and product NH_4^+ structures is expected to enhance the hydrogen atom transfer cross section. The vibrational enhancement results of the present study support this simple dynamical interpretation of hydrogen atom transfer from neutral ammonia to NH_3^+ .

In contrast to the transition state proposed for proton transfer [scheme (9)], the dipole of the neutral ammonia molecule in the transition state proposed for hydrogen atom abstraction [scheme (10)] is directed away from the nearby charge on the ion as the two particles approach. This structure represents only a local minimum energy configuration, with the proton transfer transition state in which the dipole is aligned more in the direction of the ion representing the global minimum. As in the average dipole orientation (ADO) model, the dipole never completely locks in on the charge, but instead takes on an average value between the completely randomized limiting case and the completely locked limiting case.

Vibrational excitation plays an opposite role in reaction scheme (10) than in reaction scheme (9). In scheme (10) the vibrational motion is along the reaction coordinate and promotes reaction, whereas in scheme (9), vibrational motion is directed perpendicular to the reaction coordinate and hinders reaction. Thus, one dynamic model provides a unifying interpretation for the effects of ammonia umbrella bending mode vibration on reactivity for proton/deuteron transfer and for hydrogen/deuterium abstraction.

CONCLUSIONS

The proton/deuteron transfer channel and the neutral atom abstraction channel provide unique insight into the coupling of the ammonia ion vibrational motion into the reaction coordinate for each mechanism. The fact that the vibrational energy and translational energy of the ion affect the relative reaction cross section to different extents indicates that these reactions are better described by a dynamical rather than a statistical model. Both dynamical and structural features of the transition state appear to play a role in determining which mechanism is operative and whether it is suppressed or enhanced by vibration in the ion. In the case of proton transfer, motion of the nuclei of the ion perpendicular to the direction of transfer hinders the formation of

NH_4^+ , while for hydrogen abstraction, the same motion perpendicular to the direction of hydrogen transfer favors formation of the NH_4^+ product ion.

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