

## EFFECT OF INTERNAL AND TRANSLATIONAL ENERGY ON THE $\text{NH}_3^+(\nu) + \text{D}_2$ ION-MOLECULE REACTION

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Using 2+1 multiphoton ionization,  $\text{NH}_3^+$  is prepared in selected levels of the  $\nu_2$  bending mode ( $\nu = 0-7$ ) and the  $\text{NH}_3^+(\nu) + \text{D}_2$  reaction is studied as a function of the center-of-mass collision energy (1–10 eV). The exchange channel ( $\text{NH}_2\text{D}^+ + \text{HD}$  or  $\text{H} + \text{D}$ ) is enhanced by ion vibrational excitation whereas the addition channel ( $\text{NH}_3\text{D}^+ + \text{D}$ ) is almost unaffected.

### 1. Introduction

Studies of ion-molecule reactions are frequently concerned with the measurement of reaction cross sections and product branching ratios as a function of the ion collision energy and sometimes with the ion's internal energy [1]. Experiments in the latter category have been especially limited owing to the implicit lack of control over the internal states of the ions when they are prepared by such standard techniques as electron impact ionization. Recent developments in the field of multiphoton ionization photoelectron spectroscopy (MPI-PES) suggest that MPI can now be exploited as a powerful new means for preparing high densities of internally state-selected reagent ions for chemical dynamics studies [2–5]. Indeed, this is an obvious extension of the classic study of Chupka and co-workers [6] on  $\text{H}_2^+(\nu) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ , in which different vibrational levels of  $\text{H}_2^+$  were selected by one-photon vacuum ultraviolet (VUV) photoionization of  $\text{H}_2$ .

The present study uses MPI to investigate the ion-molecule reactions of state-selected  $\text{NH}_3^+$  ions with  $\text{D}_2$ :



This reaction system has been previously investigated by Henglein and co-workers [7], who used  $\text{NH}_3^+$  reagent ions prepared in an unknown state distribution by electron impact. The energy range covered was from 0.4 to 10 eV in the center of mass. They found product intensity contour maps which suggest that an impulsive, spectator-stripping mechanism is operative in  $\text{NH}_3^+ + \text{D}_2$  reactive collisions, and which ruled out the existence of a long-lived collision complex. At lower energies, thermal studies with vibrationally unselected  $\text{NH}_3^+$  indicate that the rate constant for reaction (1a) with  $\text{D}_2$  is  $3 \times 10^{-13} \text{ cm}^3/\text{s}$  [8], and with  $\text{H}_2$   $5 \times 10^{-13} \text{ cm}^3/\text{s}$  [9], showing that this exothermic reaction proceeds at a remarkably slow rate compared to the predicted Langevin value of  $1.5 \times 10^{-9} \text{ cm}^3/\text{s}$ . Indeed, Fehsenfeld et al. [9] found a 90 meV activation barrier, which has been corroborated by ultra-low-energy studies employing an ion trap [10].

The energetics of the different pathways (1a)–(1c) are illustrated in fig. 1. As has been demonstrated in the preceding Letter [2], 2+1 MPI via the  $\tilde{\text{C}}'$  state can prepare  $\text{NH}_3^+(\tilde{\text{X}}, \nu)$  with a vibrational "purity" exceeding 80%, making this ion an ideal candidate for vibrationally state-selected ion-molecule reactions. In this Letter we address the question of how the product ion distribution into the respective channels (1a)–(1c) is influenced by both the collision energy and the vibrational state of the  $\text{NH}_3^+$  ions. The motivation for such a study is to ascertain in what manner internal motions may affect reactivity. It is worth stressing that a number of photoionization [1,11–14], flowing

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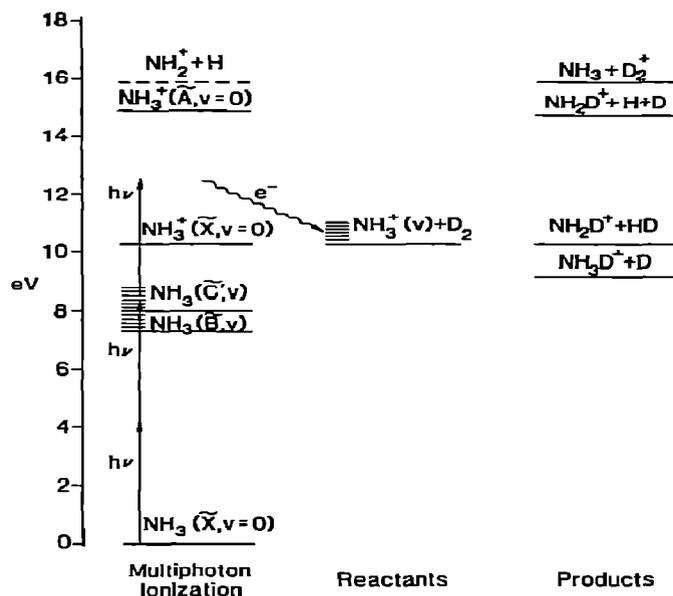


Fig. 1. Energetics of the  $\text{NH}_3^+ + \text{D}_2$  ion-molecule reaction. The 2+1 MPI scheme used to prepare the vibrational state of the ammonia ion is also shown.

afterglow [15] and ion cyclotron resonance [16] experiments have implicated beyond any reasonable doubt that internal excitation of molecular ions can influence markedly the rates of ion-molecule reactions.

## 2. Experimental

A schematic diagram of our apparatus for carrying out the reactive studies is shown in fig. 2. Briefly, state-selected  $\text{NH}_3^+$  ions are prepared by multiphoton ionization of a skimmed and collimated pulsed beam of  $\text{NH}_3$  seeded 1:20 in argon (Lasertechnics LPV-1 pulsed valve, 0.1 mm nozzle, and 6 psi total backing pressure). Laser wavelengths in the range 280–320 nm, at pulse energies of 2–9 mJ, are used to ionize ammonia in a 2+1 process resonantly enhanced by vibronic levels of the  $\text{NH}_3$  B and C' Rydberg states. The vibrational state selection in each case is established by separate photoelectron measurements which are reported in the preceding Letter [2]. The extensive rotational cooling and collisionless conditions in the ammonia beam are essential in order to achieve the highest possible ion densities while avoiding vibrational relaxation of the ions prior to reaction. Typically the pressure in the ionization chamber with the beam operating is  $8 \times 10^{-8}$  Torr. Under these conditions, undesirable ion-molecule reactions in the source region are effectively suppressed.

The UV light is focused by a 25 cm focal length lens so as to intersect the ammonia beam between the initial pair of electrodes of an ion optics system. An electric field of 3 V/cm maintained between these electrodes extracts, and a following Einzel lens collimates the photoions into a beam at an energy of 50 eV. A series of cylinder lenses then provides some further acceleration of the beam before it enters a reaction chamber through a 4 mm aperture.

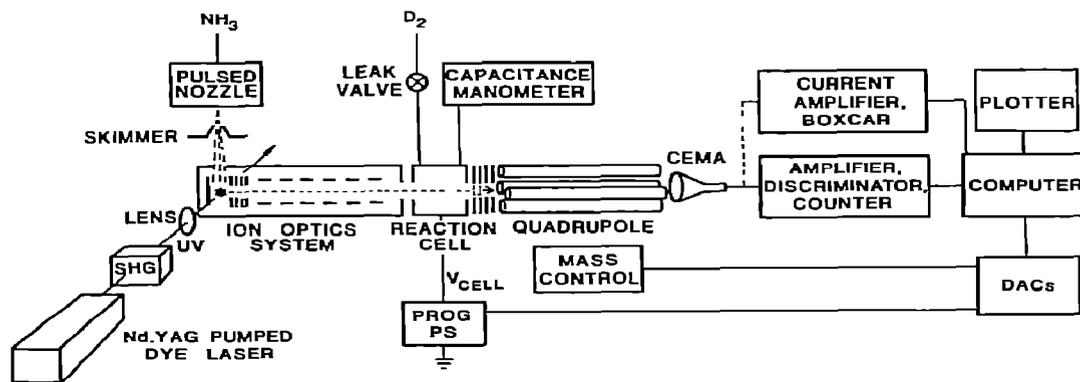


Fig. 2. Schematic of the experimental apparatus.

This chamber, which is separately pumped to minimize cross-contamination of the ionization and reaction regions, houses deceleration optics which inject the ion beam at controlled translational energy into a field-free scattering cell. The latter is a stainless-steel cylinder 15.5 mm long, with entrance and exit aperture 2.54 and 3.81 mm in diameter, respectively, located some 50 cm from the ionization volume. The low conductance of the cell apertures makes it possible to maintain a pressure of several mTorr of  $D_2$  inside the cell, as determined by a capacitance manometer (MKS Baratron with 220 BHS head), while the pressure outside is  $4 \times 10^{-6}$  Torr. The  $D_2$  is introduced to the cell through a leak valve (Granville Phillips). By careful adjustment of the potentials applied to the final elements of the decelerator, the  $NH_3^+$  laboratory collision energy can be tuned over a wide range (typically 3–50 eV) simply by changing the cell potential. Retarding potential measurements are performed to calibrate the energy scale.

Ion–molecule reaction products and unreacted primary ions ( $NH_3^+$ ) are then recollimated by a series of lenses, pass through a quadrupole mass filter (Extranuclear, with model 10 High Q head), and are subsequently detected by a channel electron multiplier array (CEMA, FTD 2002, Galileo Electro-optics). Owing to the grossly different signal levels which are encountered for primary and product ions in this experiment, the respective ion signals are processed in one of two different ways. When the mass spectrometer is tuned to  $m/e = 17$  ( $NH_3^+$ ), the CEMA is operated in an analog mode and its output fed to a current amplifier (Keithley 427) and boxcar (PAR 162/164). Product ions are measured by a standard pulse-counting apparatus including an amplifier (Ortec 574), discriminator (Ortec 436) and counter (Ortec 776). Rates as high as 50 counts/laser shot are observed in some of the runs reported here. In order to perform automatic scans over a range of  $NH_3^+$  collision energies, a computer system interfaced to the experiment controls the reaction cell potential, and programs the quadrupole mass while simultaneously monitoring either the boxcar or the counter output.

Considerable attention has been given to the issue of product ion collection efficiency. The favorable kinematics of this heavy plus light reaction ensures that the products are strongly forward scattered. Calculations further suggest that both reaction products are

being collected without bias towards either one. Experimentally, the reaction cell geometry has been varied and pulsed extraction potentials have also been applied to the cell. However, use of the latter method is complicated by the perturbing effect of the pulses on the incident ion energy. Since this has not yet been fully characterized, we have elected not to use this technique in the present work.

### 3. Results

By selecting the appropriate ionizing wavelength, ion–molecule reactions could be carried out using  $NH_3^+$  ions prepared with as many as ten quanta of the out-of-plane bending mode excited [2]. The vibrational frequency of the  $\nu_2$  bending mode in  $NH_3^+$  is 120 meV, determined from peak spacings in the high-resolution photoelectron study of Weiss and Lawrence [17]. At each wavelength used, we first checked the mass purity of the ion beam impinging on the scattering cell with the quadrupole mass filter. At our laser energies, the percentage of the incident ion flux attributable to  $^{14}NH_3^+$  was found to be wavelength dependent, and ranged from 93% to 99.99%. The ion  $NH_2^+$  ( $m/e = 16$ ), whose yield was greater at shorter wavelengths, accounted for the balance, excluding a minor contribution which was also observed at mass 18. Wavelength scans taken with the quadrupole mass filter tuned to this mass revealed virtually identical spectra to those recorded for  $^{14}NH_3^+$ , except for a small red-shift which increased with increasing  $\nu$  in both the  $\tilde{B}$  and  $\tilde{C}'$  progressions. The sizes of the shifts we observed are consistent with the 0.59% lowering of the bending frequency expected for  $^{15}NH_3$  by the Redlich–Teller product rule [18]. Our data presented here are corrected for this residual mass 18 contribution from  $^{15}NH_3^+$  in the incident beam.

At a pressure of 1.0 mTorr of  $D_2$  in the scattering cell, product ions were observed at both masses 18 ( $NH_2D^+$ ) and 19 ( $NH_3D^+$ ). In agreement with the earlier study, we did not observe the ion  $NH_2D_2^+$  ( $m/e = 20$ ), which strongly argues against an intermediate complex mechanism for this reaction [7]. Typical raw data are shown in fig. 3a for a collision energy scan employing  $NH_3^+$  ( $2\nu_2$ ) reagent ions. The center of mass energy scale in this figure was derived by multiplying the laboratory energy by the factor 0.19, the ratio of the

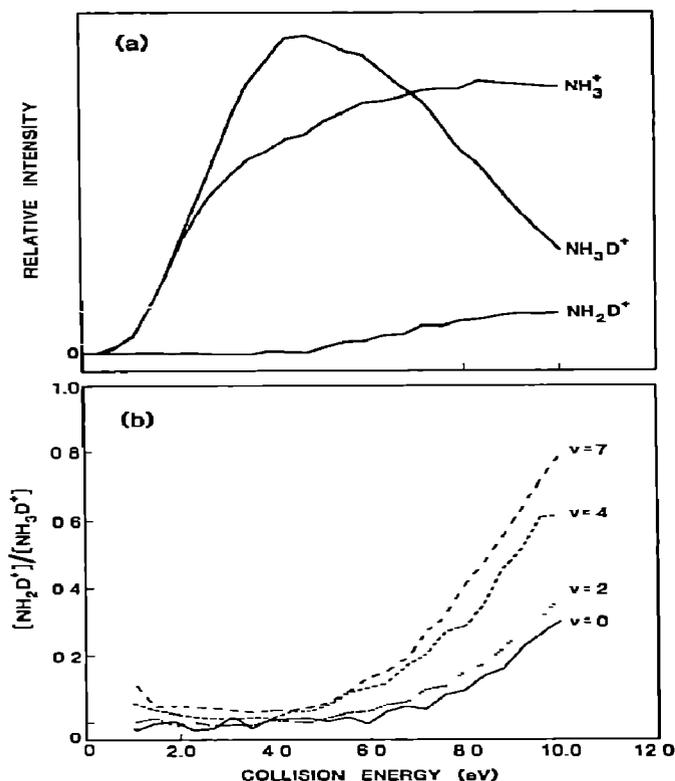


Fig. 3. The addition ( $\text{NH}_3\text{D}^+$ ) and exchange ( $\text{NH}_2\text{D}^+$ ) product channels as a function of  $\text{NH}_3^+(\nu)$  internal and translational energy for the reaction  $\text{NH}_3^+ + \text{D}_2$ : (a) raw data for 2+1 MPI via  $\tilde{\text{C}}'(2)$ , with the  $\text{NH}_3^+$  trace rescaled for comparison; and (b)  $\text{NH}_2\text{D}^+/\text{NH}_3\text{D}^+$  branching ratios obtained for different vibrationally state-selected  $\text{NH}_3^+$  ions.

mass of  $\text{D}_2$  to the combined mass of the reagents. Also shown for comparison is the incident  $\text{NH}_3^+$  transmission function, recorded with no  $\text{D}_2$  in the scattering cell. Approximately 7500 product counts were registered at the peak of the  $\text{NH}_3\text{D}^+$  trace in this experiment, in which the total attenuation of the  $\text{NH}_3^+$  beam was about 5%.

It can clearly be seen from fig. 3a that the addition channel (1a) leading to  $\text{NH}_3\text{D}^+$  dominates at low energies over processes (1b) and (1c), which produce  $\text{NH}_2\text{D}^+$ . In fact in this run we did not observe *any*  $\text{NH}_2\text{D}^+$  ions below an energy of 4.5 eV. The translational energy dependences of the two product ion signals are also markedly different. The  $\text{NH}_3\text{D}^+$  yield displays a pronounced maximum and then falls off at

higher energies, even as the  $\text{NH}_3^+$  flux continues to increase slightly. In contrast, the  $\text{NH}_2\text{D}^+$  product curve shows a clear energy threshold, above which the yield actually increases. It is interesting to note that the onset of the latter and the turnover of the former occur at approximately the same energy (4.5 eV), suggesting that internally excited  $\text{NH}_3\text{D}^+$  is dissociating to yield  $\text{NH}_2\text{D}^+$ .

A series of different laser dyes were required to generate the wavelengths necessary to investigate the effects on the reaction of varying the vibrational energy in the reagent  $\text{NH}_3^+$  ion. As a result, the laser energies, and hence the primary ion beam intensities in each separate experiment were inevitably not the same. In order to compare actual product counts from one run to the next, the following normalization procedure was adopted. For each reagent ion vibrational state studied, a data set similar to that shown in fig. 3a was recorded, in each case with the same  $\text{D}_2$  pressure in the reaction cell. Within a particular data set, checks were made to ensure that the same laser energy was used to record primary and product ion signals. Data sets obtained in this manner were then scaled to bring the respective primary ion transmission curves into coincidence, thus referencing the product ion signals to constant primary ion beam intensity.

After normalization, we found that the  $\text{NH}_3\text{D}^+$  yield curves as a function of translational energy for the ion vibrational states  $\nu = 0-7$  were superimposable, at least to within 10% upto 5 eV. Because this small difference lies within our present ability to hold the laser energy and cell pressure constant during a data set, we conclude that the reaction cross section for  $\text{NH}_3\text{D}^+$  production is insensitive to vibrational energy deposited in the  $\nu_2$  mode of the  $\text{NH}_3^+$  ion in this energy range. However, between 5 and 10 eV the data sets diverge slightly, showing a smaller amount of  $\text{NH}_3\text{D}^+$  for the higher vibrational level.

The situation is different for the exchange product,  $\text{NH}_2\text{D}^+$ . In fig. 3b we show the  $\text{NH}_2\text{D}^+/\text{NH}_3\text{D}^+$  branching ratios for the reagent ion vibrational states  $\nu = 0, 2, 4$  and 7, prepared using the vibronic levels  $\tilde{\text{C}}'(0)$ ,  $\tilde{\text{C}}'(2)$ ,  $\tilde{\text{C}}'(4)$  and  $\tilde{\text{B}}(7)$ . In these experiments, the contributions from  $\text{NH}_3^+$  to the total reagent ion flux are  $\approx 0\%$ , 0.1%, 0.7% and 0.9%, respectively. Even at these seemingly insignificant levels of contamination, it is important to consider the possibility of a contribution to the mass 18 product signal from the

competing process  $\text{NH}_2^+ + \text{D}_2 \rightarrow \text{NH}_2\text{D}^+ + \text{D}$ , because the cross section for the exchange reaction (1b) is small. At present, we can only qualitatively estimate a correction for this contribution. The procedure we use is to compare our observed  $\text{NH}_2\text{D}^+/\text{NH}_3\text{D}^+$  ratios at a given energy to the measured  $\text{NH}_2^+/\text{NH}_3^+$  ratio in the incident beam, after scaling the latter by the cross section ratio for H atom addition to  $\text{NH}_2^+$ , versus that for H atom addition to  $\text{NH}_3^+$  [7]. The difference between these two quantities is the corrected branching ratio which can be associated with reactions of  $\text{NH}_3^+$  in the complete absence of  $\text{NH}_2^+$ . The effect of this on the data in fig. 3b is insignificant for the high-energy region, but does reduce the indicated branching ratios for the  $\nu = 4$  and  $\nu = 7$  runs slightly between 1 and 4 eV. Even when this is taken into account, our data indicate that  $\text{NH}_2\text{D}^+$  production is being observed below 4 eV for high vibrational states of the reagent ion  $\text{NH}_3^+$ . We reiterate that  $\text{NH}_2\text{D}^+$  is completely absent at these translational energies in the low  $\nu$  experiments. Finally, although all the branching ratio curves show an increase at higher energies, we observe higher net yields of  $\text{NH}_2\text{D}^+$  in the high  $\nu$  runs than are seen at low  $\nu$ .

#### 4. Discussion

Based on energetics, both the addition ( $\text{NH}_3\text{D}^+$ ), and exchange ( $\text{NH}_2\text{D}^+$ ) channels are possible in studies on  $\text{NH}_3^+ + \text{D}_2$  conducted at low collision energies, and indeed both product ions were observed in this and the earlier work [7]. As shown in fig. 1, charge transfer is not expected to play an important role in these experiments, owing to the large difference in ionization potentials between  $\text{NH}_3$  (10.18 eV) and  $\text{D}_2$  (15.47 eV).

The addition channel (1a) is estimated to be exothermic by approximately 1.07 eV, by analogy to the hydrogen atom transfer reaction  $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$ . The heat of formation of  $\text{NH}_4^+$  is 6.44 eV, calculated from the mean of the reported values (8.92 eV) [19] for the proton affinity of ammonia. Although the ion  $\text{NHD}_2^+$  could conceivably also contribute to the product ion signal at  $m/e = 19$ , we can rule out this possibility since we detect  $\text{ND}_3\text{H}^+$ , but not  $\text{NDH}_2^+$ , in similar experiments we have performed with the isotopes  $\text{ND}_3^+$  and  $\text{H}_2$ . Neglecting small differences in zero-point

energies of reactants and products, the exchange channel (1b) is thermoneutral. The product ion  $\text{NH}_2\text{D}^+$  at  $m/e = 18$  can also arise via the overall process (1c), which is endothermic by the bond dissociation energy of HD, i.e. 4.51 eV.

Our experiments have shown that the addition channel (1a) leading to the  $\text{NH}_3\text{D}^+$  product ion is hardly affected by  $\nu_2$  excitation in the  $\text{NH}_3^+$  reagent ion. This result is consistent with the rather general expectation that internal energy effects are not likely to be significant for exothermic reactions [1]. On the other hand, substantial translational and internal energy effects on the reaction rate can be anticipated for endothermic processes, or systems with activation barriers beyond the reaction energy. In such cases, both the energetic and dynamical features of the potential energy surface govern the relative importance of translational or internal energy in promoting a particular reaction. As we have found in this study, in the case of reactions (1b) and (1c), both forms of energy can play an important role.

The turnover behavior which we observe in the  $\text{NH}_3\text{D}^+$  yield, and the accompanying rise in  $\text{NH}_2\text{D}^+$  production between the energies of 4.5 and 10 eV, can be attributed, in part, to an increase in the internal energy in the  $\text{NH}_3\text{D}^+$  product ion as the  $\text{NH}_3^+$  translational energy is increased. For an ideal stripping reaction, the energy coupled into the product ion internal degrees of freedom depends in a simple manner on the masses of the reactants and products, the collision energy, and the reaction energy [20,21]. Applying this model to process (1a), we calculate the  $\text{NH}_3\text{D}^+$  product internal energy to be 55% of the c.m. collision energy plus the exoergicity (1.07 eV) and the vibrational energy of the  $\text{NH}_3^+$  reagent. Thus at sufficiently high collision energies, the  $\text{NH}_3\text{D}^+$  product ion can dissociate to  $\text{NH}_2\text{D}^+ + \text{H}$ . The effect of increased translational energy and of increased vibrational energy in  $\text{NH}_3^+$  is therefore to turn on reaction (1c) at the expense of (1a). Indeed, when the branching ratio is plotted against the estimated total  $\text{NH}_3\text{D}^+$  internal energy, as calculated by the spectator stripping model, the data sets merge.

We also have evidence for production of  $\text{NH}_2\text{D}^+$  via reaction (1b) at energies below 4.5 eV, where process (1c) is not energetically accessible. While we find reaction (1b) to be affected by vibrational motion in the  $\text{NH}_3^+$ , it is not markedly influenced by translational

energy. This channel, while insignificant for low to moderate vibrational excitation, becomes possible even at low translational energies for highly vibrationally excited  $\text{NH}_3^+$  ions. Clearly, further work is necessary to quantify this behavior. This will be possible after we incorporate a second mass filter into our apparatus to permit mass selection of the reagent ion beam.

The exchange reaction (1b) requires D—D bond cleavage, and the formation of the two new bonds, N—D and H—D. As a single non-bonding electron occupies the  $p_z$  orbital on the nitrogen atom in  $\text{NH}_3^+$ , this reaction can be imagined to occur in collisions in which the  $\text{D}_2$  molecule approaches the vibrating ion out-of-plane. In two idealized, extreme cases, one could then envisage the  $\text{D}_2$  molecule to be oriented either along the  $\text{C}_3$  axis, or perpendicular to it. The latter case would seem to be preferable in terms of forming the new N—D bond, and allowing interaction of the freed D atom with a hydrogen atom in the ion, forming molecular HD. One might then think of this process as proceeding via a four-center, four-electron mechanism. Vibrational excitation of the ammonia ion along the approach coordinate promotes this reaction.

A more detailed discussion of the reaction dynamics for the three channels (1a)—(1c) under study would be greatly aided by the calculation of the  $\text{NH}_3^+ + \text{H}_2$  reaction surface, a calculation which should be tractable. Nevertheless, the present study demonstrates that MPI can indeed be used to explore ion—molecule reactions as a function of the translational and internal energy of the reagent ion. Such investigations can help to reveal the detailed dynamics of the various collision processes which occur in this large and important class of reactions.

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