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A Remeasurement of the Products for Electron Recombination of N_2H^+ Using a New Technique: No Significant NH + N Production[†]

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A remeasurement of the product distribution from dissociative electron-ion recombination (DR) of N_2H^+ has been made using a new technique. The technique employs electron impact to ionize the neutral products prior to detection by a quadrupole mass analyzer. Two experimental approaches, both using pulsed gas techniques, isolate and quantify the DR products. In one approach, an electron-attaching gas is pulsed into a flowing afterglow to transiently quench DR. Results from this approach give an upper limit of 5% for the NH + N product channel. In the second approach, the reagent gas N_2 is pulsed. The absolute percentages of products were monitored versus initial N_2 concentration. Results from this approach also give an upper limit of 5% for NH + N production. This establishes that N_2 + H is the dominant channel, being at least between 95 and 100%, and that there is no significant NH production contrary to a recent storage ring measurement that yielded 64% NH + N and 36% N_2 + H. Possible reasons for this dramatic difference are discussed.

Introduction

Dissociative electron-ion recombination (DR) is very important, since it is a dominant loss process in many plasma media such as interstellar gas clouds,[1] cometary coma,[2,3] planetary atmospheres,[2,4] combustion flames,[5] and others. In particular, the recombination of N_2H^+ is very important

$$N_2H^+ + e \rightarrow N_2 + H + 8.47\ \text{eV} \qquad (1a)$$

$$\rightarrow NH + N + 2.25\ \text{eV} \qquad (1b)$$

since N_2H^+ has been detected in multiple places in the ISM (e.g., dark clouds that are precursor sites to high mass star formation[6] and in areas of preprotostellar collapse[7]), and rotational emission lines from both N_2H^+, (1-0) and (3-2), and N_2D^+, (2-1) and (3-2), have been used to search for massive prestellar cores.[8] DR of N_2H^+ is perhaps the most studied of all recombinations[9−17] in both the flowing afterglow (FA) and the storage ring (SR) and has been reviewed recently.[18,19] Studies have been made to determine the rate coefficient, α_e, of this DR as a function of temperature and quantitatively determine the products (both ground and excited state). The former FA study determined that α_e was essentially independent of temperature.[17] In the latter, FA experiments involving optical emission from this DR have yielded electronically excited N_2 as a product by identification of various vibrational bands of the $N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)$ transition.[13] Emissions from excited-state NH were also searched for. Vibrational bands (0,0) and (1,1) of the spin-forbidden $NH(a^1\Delta) \rightarrow NH(X^3\Sigma^-)$ transition are in the experimental accessible wavelength range and have appreciable Franck−Condon factors, yet these were not observed.[13] Other earlier FA studies using vuv absorption of L_α to detect H atoms implied that the product channel to N_2 + H was very dominant.[9] However, recent studies in an SR by Geppert et al. gave product channels of 36% (N_2 + H) and 64% (NH + N); these include both ground and excited states.[16] This is a surprising result given that breaking the N≡N triple bond is the dominant pathway, which was not observed in the previous results of Adams et al.[9,13] Additional spectroscopic data were published the same year as the SR results and determined the total emission intensity from the excited-state product N_2(B, $v' \geq 1$), which was translated to a quantitative product yield of 18 ± 9% for N_2 from this DR. However, this does not resolve the conflict between the earlier measurements.[15] The use of an independent technique to directly measure the products of this recombination is desperately needed to resolve the discrepancy; such a technique is presented here.

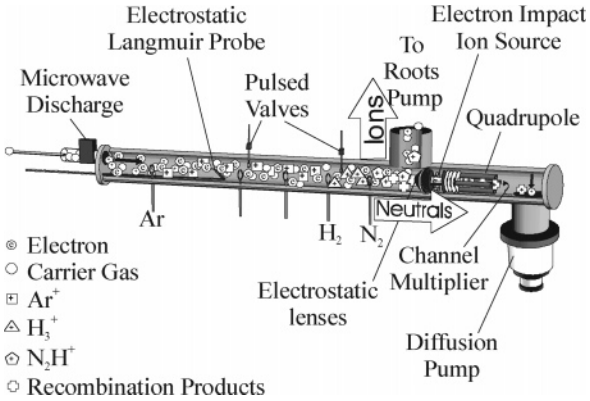

Figure 1. Diagram of FA modified to quantitatively determine the products of DR. This shows the various reagent gas inlet ports, pulsed valves (attaching gas or reagent gas added), electrostatic lenses that block ions from entering the detection system, electron impact ion source, and the quadrupole mass filter.

Experimental Section

A brief overview of this new technique is presented here; a detailed explanation will be given elsewhere.[21] The technique

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involves two basic experimental approaches, both of which utilize a flowing afterglow (FA) plasma. These differ in the means of determining the products, with the method of production of the recombining ions being common. The plasma source is a microwave discharge He plasma operating at 1.4 Torr (4.0 Torr for second method), thus creating a He_2^+/e^- dominant plasma (Figure 1). The He is of 99.997% purity and is further purified with two liquid nitrogen-cooled sieve traps. Downstream from the cavity, about 2mTorr of Ar (99.999% purity) is added to the flow, which destroys He^m and increases the ionization number density (i.e., electron density, [e], increases). Further downstream from the introduction of Ar, sufficient H_2 (99.999% purity further purified by a liquid nitrogen-cooled sieve trap) is added to rapidly generate a H_3^+/e^- dominant plasma, and this readily proton transfers to N_2 (99.999% purity) added just downstream of H_2, forming the recombining ion of interest, N_2H^+. Equations 2−6 summarize the chemical reactions leading to N_2H^+ production:

$$He^+ + He + He \rightarrow He_2^+ + He \quad k = 2.0 \times 10^{-31}\ cm^6\ s^{-1}\ {}^{22} \tag{2}$$

$$He_2^+ + Ar \rightarrow Ar^+ + 2He \quad k = 2.0 \times 10^{-10}\ cm^3\ s^{-1}\ {}^{23} \tag{3}$$

$$Ar^+ + H_2 \rightarrow ArH^+ + H \quad k = 8.6 \times 10^{-10}\ cm^3\ s^{-1}\ {}^{23} \tag{4}$$

$$ArH^+ + H_2 \rightarrow H_3^+ + H \quad k = 6.3 \times 10^{-10}\ cm^3\ s^{-1}\ {}^{23} \tag{5}$$

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2 \quad k = 1.6 \times 10^{-9}\ cm^3\ s^{-1}\ {}^{23} \tag{6}$$

It should be noted that a small amount of He^+ still exists at the point of N_2 addition, ∼9% of the H_3^+, which reacts readily with N_2 to form N^+ (60%) and N_2^+ (40%),[23] in which N^+ does not recombine with electrons and reacts slowly with H_2 (1.5×10^{-10} $cm^3\ s^{-1}$); this N^+ obviously will not affect the measurements. The N_2^+ that is formed reacts rapidly with H_2 to yield N_2H^+. Also, note that the reagent gases flow rates are measured by a capillary system, and thus accurate number densities of each gas can be introduced in the FA. In the case of the very small N_2 additions, a 0.2% mix of N_2 in He was used. Note that, in these studies, very pure gases were used to minimize N_2 impurities. In any case, impurities in the flow tube would not be pulsed and would not be detected as recombination products. The N_2H^+ thus produced then recombines forming neutral products, which are either thermalized via collisions with the He carrier gas or by radiative relaxation. The ions and neutrals in the flow tube can be detected by a downstream quadrupole mass filter/ion detection system, which can separately monitor either ions or neutrals from the plasma as dictated by the operating mode of the experiment. Plasma ions are detected in the conventional way. Neutrals that exist in the plasma can be monitored by ionizing them with an electron impact (EI) ionization source just upstream of the quadrupole mass filter (Figure 1). In this case, application of appropriate potentials to the electrostatic lenses just upstream of the EI ionization source prevents plasma ions and electrons from entering the detection system, eliminating interference from plasma ions while monitoring neutrals. These neutrals have multiple sources that are a combination of unreacted reagent gases, products of upstream ion−molecule reactions, and products of DR. The central part of the technique is to distinguish the recombination products from these other sources, and this has been done in two ways.

1. Electron-Attaching Gas Method. In this approach, a rapidly electron-attaching gas (e.g., CCl_4)

$$e + CCl_4 \rightarrow Cl^- + CCl_3 \tag{7}$$

is pulsed into the flow tube. When the attaching gas is present, the electrons are scavenged generating anions (Cl^-) and DR is quenched. Thus, the difference between ion counts from ionized neutrals with the pulsed gas being out (*A*) versus in (*B*) is a positive signal ($S = A - B$) from the products of DR. The use of an electron-attaching gas to identify signal originating from DR has been very successful previously to identify spectroscopic emissions from excited-state products of DR.[24] In the present use of this technique, the concentration of attaching gas and flow conditions are optimized so that quenching of DR is maximized with the effect of ion−ion recombination between N_2H^+ and the anion (Cl^-) being minimized. This is achieved by monitoring the modulated electron density with a Langmuir probe at the point of introduction of the attaching gas. For an optimum situation, ∼80−90% of the electron density is destroyed, which ensures that the signal from DR products is large enough to give a good statistical representation of the product distribution in a reasonable time (<250 s). Since typical room-temperature reaction rate coefficients, α_i, for ion−ion recombination (iir) are an order of magnitude (or more)[25] smaller than the room-temperature DR rate coefficient for N_2H^+, the effects of iir can be kept to ≤8−9% relative to the DR products. Even so, there is a potential for some overlap between products of iir and products of DR. Note that the products of iir would appear as a negative signal (i.e., *S* negative), since for this *A* will be smaller than *B*. No such negative signal has been observed in any of our experiments, and this is unlikely to be a significant source of error. Even so, to eliminate this possibility, the second experimental approach was applied.

2. Pulsed Reagent Gas (RG) Method. In this experimental technique, the RG (N_2), a N_2 mix (0.2% N_2 in He), was pulsed into the flow, generating a N_2H^+/e^- plasma. Note that the reaction sequence is the same as the previous method.

The difference between N_2 out (*A*) versus that in (*B*) creates a signal ($S = A - B$) that is a fraction of unreacted N_2 (f_1) plus a fraction of products of DR (f_2). If only N_2H^+ exists, there is no residual N_2, then all of the signal would be from DR products. At a higher N_2 concentration, there will be some fraction (f_1) of signal from unreacted N_2 with the remaining fraction (f_2) of signal being due to products from DR of N_2H^+. To identify the contribution of each fraction and to maximize f_2 and minimize f_1, the initial concentration of N_2, $[N_2]_0$, was varied around the magnitude of [e] (∼3.0×10^{10} molecules/cm^3) at the position where N_2 is injected while monitoring energetically allowed products of the DR. This should yield a transition from the EI pattern of N_2 which occurs at high concentrations of N_2 ($[N_2]_0 \gg [e]$ and $f_1 \gg f_2$) to some fractional mixture of the EI pattern of unreacted N_2 and products of DR, $[N_2]_0 < [e]$, and f_2 is optimized so its contribution can be observed as a deviation from the EI pattern. To model the fractional contributions of f_1 and f_2 over the concentration range of N_2, a chemical model of the reactive system was constructed that calculated the absolute percent monitor ion signals versus $[N_2]_0$ (the values of $[N_2]_0$ used in the model encompass the experimental range of concentrations). A series of possible product distributions were used, and the model results were compared to the experimental data to determine the agreement. The product distribution in the model was then varied to maximize the agreement.

Results

1. Electron-Attaching Gas Method. In the electron impact ionization and quadrupole mass analysis, N_2^+, NH^+, and N^+

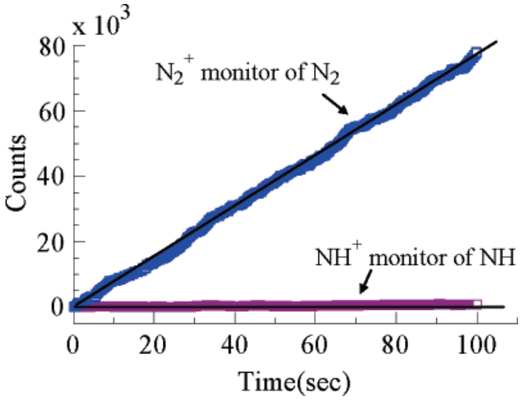

Figure 2. Integrated signals of the ion monitors N_2^+ and NH^+ for the possible products, N_2 and NH, from DR of N_2H^+. Signals were obtained from the difference between the two channels, *A* and *B*. The difference was created by pulsing in a rapidly electron-attaching gas (CCl_4), which quenches DR recombination.

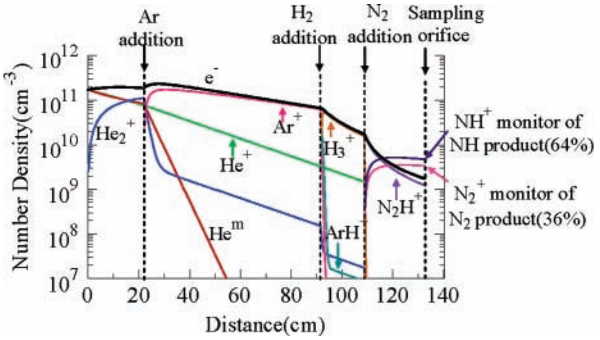

Figure 3. Kinetic model of the plasma dynamics as a function of distance down the flow tube from the microwave discharge source, represented at 0 cm. There are three gas additions points for argon, hydrogen, and nitrogen to generate the ion of interest, N_2H^+. The product channel percentages used in this model are taken from Geppert et al.[16] Therefore, the appearance of the N_2^+ and NH^+ ions, which are monitor ions for the N_2 and NH products of DR, can be seen as N_2H^+ recombines with electrons. If this product distribution were valid, then the NH^+ monitor ion would be very evident.

serve as monitors of the N_2, NH, and N DR products, respectively. The signals of these ions were integrated over time to build up statistically significant signals, whether it be from direct ionization of the DR products or from dissociative EI ionization of a larger molecule (i.e., N_2 fragments to 14% N^+ signal). For this study, a very significant N_2^+ signal was observed, with no NH^+ signal (Figure 2), but with some N^+ fragmentation signal (not shown).

Figure 2 shows the integrated signal of monitor ion N_2^+ building up over time from EI ionization of recombination product N_2, while the signal from NH^+ remains at zero.

Not shown in Figure 2 is the N^+ signal; this signal is attributed only to the dissociative ionization of N_2 that occurs with 70 eV electrons in the EI source and thus mirrors the N_2^+ signal. Signals from the EI dissociative ionization process and parent ionization process give information on the fragmentation pattern (cracking pattern) of the N_2 molecule. Detailed knowledge of such fragmentation is essential so that the observed ion signal can be corrected for the effect of fragmentation, yielding the true DR product distribution. Fortunately, this information is readily available for many stable molecules such as N_2 in the NIST database.[26] However, data for unstable molecules such as radicals are generally not available. Fragmentation patterns of some radical species can be obtained if the relative ionization cross sections of fragment ions to parent ions are available in the literature.[27] This information is available for the NH radical,[28] giving the fragmentation pattern as 78% NH^+ and 22% N^+. Thus, if NH is a product from the DR of N_2H^+, a NH^+ signal should be observed. The fact that it was not seen is in stark contrast to SR results where NH is reported as the major product channel (64%).[16] To ensure that our experimental data were properly interpreted, a model of the chemistry in the flow tube was also constructed. This replicates the experimental conditions described in the Experimental Section for the electron-attaching gas method and is shown in Figure 3. In Figure 3, the results from Geppert et al.[16] are used to show the expected formation of products of DR. It is clearly seen that the NH^+ monitor dominates over the N_2^+ monitor by 1.5−2 times and that if NH is a 64% channel then it would have readily been detected.

2. Pulsed Reagent Gas Method. To confirm the absence of a NH channel and corroborate the results of the electron-attaching gas method, this additional experiment technique was used. Note that, in this technique, there are two extreme situations with a crossover between them. In the limit $[N_2]_0 \gg [e]$, the ion signals observed should be the EI fragmentation pattern of N_2. In the opposite limit, $[N_2]_0 < [e]$, the ion signals should be a mix of the EI ionized products of DR and some N_2 fragmentation pattern. The N_2 fragmentation pattern contributes because as less N_2 is introduced into the FA this increases the reaction time for the proton transfer between H_3^+ and N_2. Thus, the time for this reaction to go to completion becomes longer than the residence time in the flow tube, and this leaves some unreacted reagent gas that gets sampled.

The crossover between these limits occurs when $[N_2]_0$ is somewhere close to [e], ∼3.0×10^{10} molecules/cm^3, in the flow tube at the point of introduction of the N_2 reagent gas. The model for this, using the results of Geppert et al.,[16] is given together with our experimental results (Figure 4a).

The dashed lines represent the modeled results, the solid lines with the symbols are the experimental results, and the dashed vertical line, ∼3.0×10^{10} molecules/cm^3, is the electron number density in the FA at the N_2 introduction point, measured with a movable Langmuir probe. Note that, the experimental data at the lowest concentration has a much larger amount of error (∼14%) than any of the other points. This is because as $[N_2]_0$ is reduced, so is the detected signal, which makes it difficult to obtain data that have error <10% in the final product distribution within any reasonable amount of time when $[N_2]_0$ is below ∼8×10^9 molecules/cm^3. The ability to detect $[N_2]_0$ at lower concentrations is possible by the pulsing technique, where any impurities in the FA are constant, thus subtracted by $S = A - B$. The detection limit is the ratio of signal to background, in this case 10^{-3}.[21] Concerning the other data points, the error decreases dramatically (<1%) at highest $[N_2]_0$ concentrations such that error bars are smaller than the symbol size.

The experimental data in Figure 4a is the same as that in Figure 4b, but the model shown uses a 98% N_2 + H product and a 2% NH + N product.

Discussion

1. Electron-Attaching Gas Method. The experimental results from the electron-attaching gas method show a large buildup of the N_2^+ signal. This signal is due to the DR product N_2 and cannot be from the unreacted N_2 neutrals in the flow tube since these are not modulated. This was confirmed by experiments[21] with the DR of CO^+ and HCO^+. From previous work, the major HCO^+ DR product channel is known to be CO + H,[13,29] but for CO^+ the only possible channel is the dissociation to

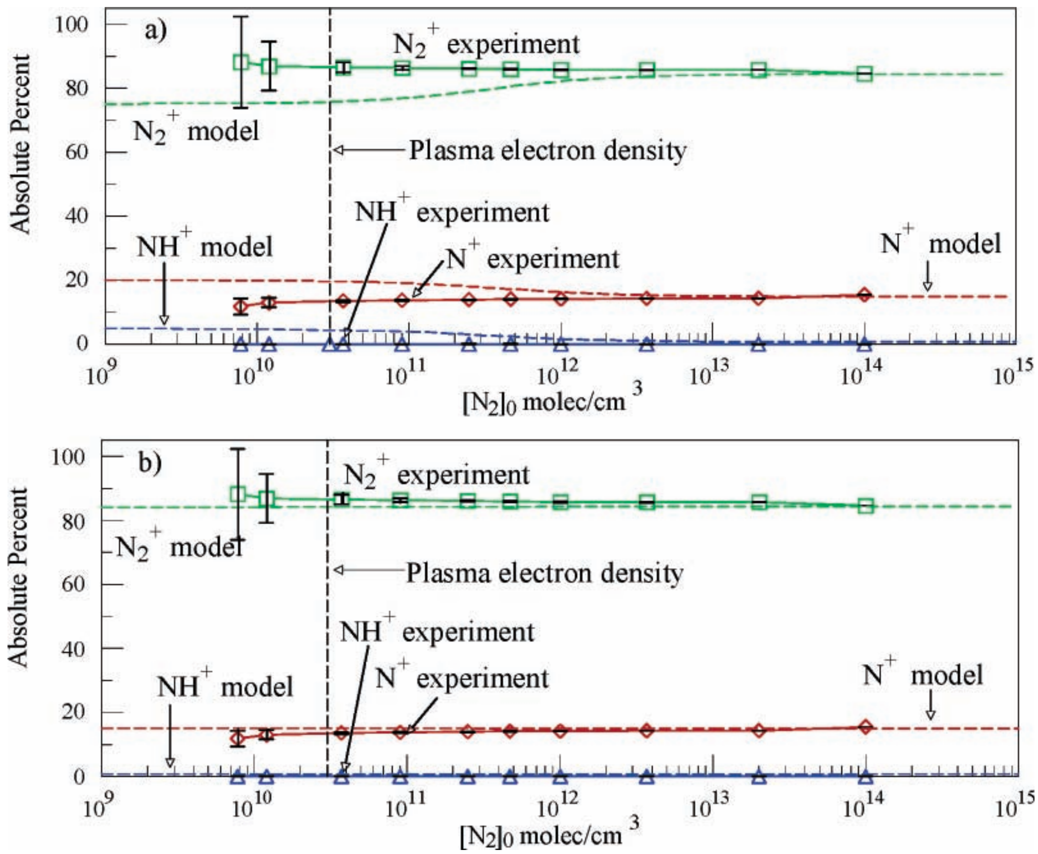

Figure 4. Absolute ion percentages of the monitor ions, model and experiment, as a function of initial N_2 concentration. The solid lines with open symbols represent the same experimental data in both (a) and (b). The dashed lines represent the kinetic model results using two different values for the absolute DR product percentages: (a) using N_2 (36%) and NH (64%) and (b) using N_2 (98%) and NH (2%). The model from (b) agrees with the experimental data far better than the model from (a).

C + O.[30−32] With these results in mind, there should not be a CO^+ signal, the monitor ion for CO, in the CO^+ DR, but it should be very substantial in the HCO^+ DR. This is exactly what is seen in the data presented in Figure 5.

In the case of DR for HCO^+, the buildup of the CO^+ monitor ion is not due to unreacted CO in the flow tube since there is no such buildup of the CO^+ monitor in the DR of CO^+. Thus, all this buildup is due to the product CO in the DR of HCO^+. This confirms that any signal from the unreacted reagent gas is completely subtracted out. This is also true for the N_2H^+ recombination, and the signal thus originates from the N_2 product of the DR.

From the lack of any NH^+, there cannot be any NH in the DR. However, it must be established that there are no loss processes for NH or reverse mass discrimination, which would prevent its observation. First, there are several possible reactive loss processes of NH by radical−radical reactions:

$$NH + NH \rightarrow N_2 + H_2 \quad k = 1.6 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}\ ^{33} \tag{8a}$$

$$NH + H \rightarrow N + H_2$$
$$k = 7.6 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}\ ^{34(\text{theoretical value at 400 K})} \tag{8b}$$

$$NH + N \rightarrow N_2 + H \quad k = 2.5 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}\ ^{35} \tag{8c}$$

Also, diffusive loss of NH (reactive loss on the walls of the flow tube) is a possibility; this is treated as 100% loss in the model described below. In addition to these losses, products from ion−ion recombination need to be considered because a signal from this process in one of the possible products will reduce the observed signal attributed to that product in DR. All of these situations, except for the effects from iir, have been consider in the model shown in Figure 3, and yet the model, with 64% NH + N channel assumed, shows a dominance of NH product, not seen in our experiment. In the model, which treats all loss processes, the predicted loss of NH is less than one-third, yet NH is still 1.4 times larger than N_2 so there would be no problem detecting NH if it were present.

The effects of iir need special attention. The reaction sequence below is considered:

$$N_2H^+ + Cl^- \rightarrow N_2H + Cl + 5.30\ \mathrm{eV} \tag{9a}$$

$$\rightarrow N_2 + H + Cl + 4.86\ \mathrm{eV} \tag{9b}$$

$$\rightarrow N_2 + HCl + 9.34\ \mathrm{eV} \tag{9c}$$

$$\rightarrow NH + NCl + 2.05\ \mathrm{eV} \tag{9d}$$

$$\rightarrow NH + N + Cl - 1.41\ \mathrm{eV} \tag{9e}$$

The production of channel d or e would take away from the NH product in the DR process; channel 9e is endothermic and is not considered further. This leaves channel 9d as the only channel that could take signal away from the DR NH product channel, but for channel 9d to occur there must be an intimate interaction between N_2H^+ and Cl^-, specifically a bond between the Cl and one of the nitrogen atoms must form for this channel to be exothermic. This is contrary to the mechanism usually assumed for iir, which is electron transfer at long range when there is a curve crossing.[36] In addition, the point at which the neutral product curve, NH + NCl, crosses the ion−ion attractive Coulombic potential is around 5.2 Å, which is well away from

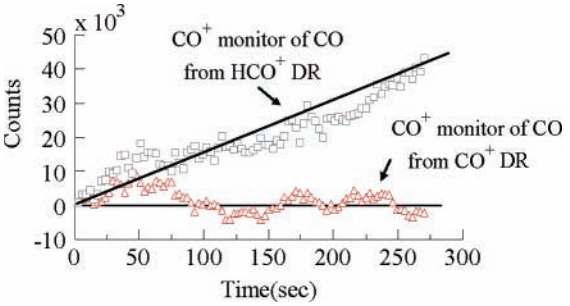

Figure 5. Integrated signal of monitor CO^+ for CO originating from the DR of HCO^+ and DR of CO^+. (□) CO^+ monitor for DR of HCO^+, which previous experimental FA and SR results have shown CO as a major product. (△) CO^+ monitor for DR of CO^+, which cannot yield CO as a product since the recombination is dissociative. It is clear that there is signal buildup in the DR of HCO^+ and not in the DR of CO^+, which indicates that no background CO reagent gas is being counted as signal for the products of recombination. This is showing that the technique is performing exactly as expected.

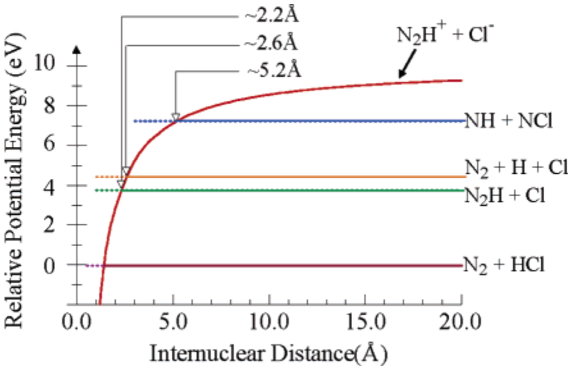

Figure 6. Ion−ion attractive Coulombic potential. $N_2H^+ + Cl^-$ crosses the neutral product curve, $N_2 + H + Cl$ near 2.6 Å. The NH + NCl product curve crosses near 5.2 Å. This is well away from the equilibrium bond length of NCl (1.61 Å) and seems unlikely that this channel will occur.

the equilibrium bond length of NCl (1.61 Å) and seems unlikely that this channel will occur (Figure 6).

This will bring the relative percent of eq 9d to DR below the previously mentioned 8−9% (iir percentage relative to DR). In addition, there was no signal from possible neutral products Cl, HCl, or NCl coming from iir, and since the neutrals HCl and NCl have zero background, they would easily have been detected.

The last effect that needs to be addressed is the possibility of mass discrimination against NH; this can be taken into account by comparing the relative amount of N_2^+ signal to that of N^+ and comparing the results to the NIST electron impact fragmentation pattern. Then, since there is little difference in mass discrimination of masses differing by only 1 amu (N^+ and NH^+), the effects of mass discrimination on NH product can easily be taken into account. For this experiment, there was not any mass discrimination against N^+.

After evaluating the experimental data in this method and modeling the experimental conditions, we concluded that there was not a significant NH depletion due to any of the possible loss processes for NH discussed above. Thus, there is no experimental evidence for NH production with the DR channel to N_2 + H being 95−100% and the NH + N channel 0−5%. To further assess the influence of iir and also validate the DR channel magnitudes, the second experimental approach needs to be considered.

2. Pulsed Reagent Gas Method. Since iir does not occur here, it will not affect the chemistry in this experimental approach; the signal is due to either excess neutral N_2 from unreacted reagent gas or products of DR of N_2H^+. To ascertain the amount of signal originating from DR, a model was employed in which the magnitudes of the products from DR were varied until the model output matched the experimental data. Note that all of the NH loss processes considered in the model for electron-attaching gas technique were included. In addition, contributions of ^{15}N to the ^{14}NH channel are incorporated. Two possible variants are shown in Figure 4. In part a, the values obtained by Geppert et al.[16] are used. Here, the model predicts a clear change from high $[N_2]_0 \approx 1 \times 10^{15}$ molecules/cm^3 to low $[N_2]_0 \approx 1 \times 10^9$ molecules/cm^3, as the N_2^+ ion signal decreases and the NH^+ signal increases. Note that these results for the model disagree with the experimental results. We also noticed that the absolute percentage for N_2^+ at low initial $[N_2]_0$ concentration never reaches the 36% that is given by Geppert et al.[16] This is due to two factors. The first is caused by remaining N_2 still contributing to the signal and thus bringing the percent of N_2^+ signal up. This results in the absolute percentage of the monitors (NH^+ and N^+ for NH and N, respectively) being lower, since the absolute percent of products is the amount of signal for each channel normalized to the total signal from all channels. The second factor is that the modeled results are intended to replicate the results coming directly from the experiment, before corrections for fragmentation effects have been made.

Figure 4b is the magnitude of products that best matched the experimental data, with N_2 + H being 98% and NH + N being 2%. Excellent agreement can be seen between the model and the experimental data, and in both the experimental data and the model we noticed that the change in products is small between the two extreme concentrations. This is expected since the major product from DR of N_2H^+ is N_2, giving almost the same absolute product percentage as electron impact fragmentation.

Comparing these experimental data to the modeled result, we concluded that the DR product channel going to N_2 + H is 95−100% and the NH + N channel is limited to 0−5%. Another product that has not been addressed thus far is the H atom. This product is difficult to quantitatively measure due to a large mass discrimination relative to other products; such a measurement was not necessary since both channels were already monitored.

Conclusions

On the basis of our two experimental techniques and the modeling of each technique, we have considered all of the possible concerns, yet these results are still in sharp contradiction to the results published by Geppert et al.[16] It is not known why there should be such a drastic difference between these FA and SR experimental data. An exhaustive effort has been made to consider all possible sources of error in the present FA experiments, and we believe that all of these have been taken into account. Considering the results from Geppert et al.,[16] there is some concern about the operation of the hot filament ion source with the N_2/H_2 mixtures. It is known from their work that there is contamination of N_2H^+ due to the $^{14}N^{15}N$ isotope, but this is assessed as only 8% as measured by a mass spectrometer. It may be possible that with the large extraction voltages there is a short residence time in the ion source and that $^{14}N^{15}N^+$ is preferentially extracted before the N_2^+ reaction with H_2 takes place

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \quad (10)$$

It is of great concern that a large room-temperature rate coefficient is used for reaction 10 with a source operating at high temperatures (1000−2000 K),[37] especially since there is evidence for a decrease in rate coefficient as temperature increases for ion−molecule reactions of similar type (i.e., hydrogen abstraction). For example, the reaction

$$CH_4^+ + H_2 \rightarrow CH_5^+ + H \quad (11)$$

has been reported to have negative temperature dependence with a rate coefficient approaching 10^{-11} cm^3 s^{-1} at 1000 K.[38] To our knowledge, there has been no study of the rate for the $N_2^+ + H_2$ reaction above room temperature. It is thus unclear how much of the N_2^+ is reacting with the H_2 before mass 29 is injected in the ring and if any modeling of the chemistry in the ion source was undertaken.

It is interesting to note that in the case of HCO^+, even where enough energy is available to break the CO partial triple bond, there is a large CO + H channel (88%) and small C + OH and CH + O channels (6% for both)[29] as detected in storage ring measurements. Note that although the CH + O channel is observed it is endothermic by ∼0.2 eV. In this experiment, the isotopic forms ^{13}CO and D are used to allow the $D^{13}C^{16}O^+$ ion to be preferentially selected. This eliminates the possibility of injecting a different isotopic species of the same mass as the ion of interest.

In summary, in the present study, there is no experimental evidence for a significant NH product from direct measurements of the ground-state neutral DR products. The two experiments techniques adopted in this study are consistent, with N_2 as the major product having limits of 95−100% for the electron-attaching gas method and 95−100% for the pulsed reagent gas method.

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Note Added in Proof. It has come to our attention that, as a consequence of our experiments, the storage ring measurements have been repeated (Larsson, M., Department of Physics, Stockholm University, Stockholm, Sweden, private communication, 2007). The storage ring channel to NH + N is now considered to be much smaller.

References and Notes

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