Variable-Temperature Rate Coefficients for the Electron Transfer Reaction \( \text{N}_2^+ + \text{H}_2\text{O} \) Measured with a Coaxial Molecular Beam Radio Frequency Ring Electrode Ion Trap

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Received: June 24, 2010; Revised Manuscript Received: November 5, 2010

The neutral molecule temperature dependence of the rate coefficient for the electron transfer reaction from \( \text{H}_2\text{O} \) to \( \text{N}_2^+ \) is determined using a coaxial molecular beam radio frequency ring electrode ion trap (CoMB-RET) method. The temperature of the \( \text{N}_2^+ \) ions was maintained at 100 K, while the effusive water beam temperature was varied from 300 to 450 K. The result demonstrates the neutral molecule rotational/translational energy dependence on the rate coefficient of an ion–dipole molecule reaction. It is found that the rate coefficient in the above temperature range follows the prediction of the simplest ion–dipole capture model. Use of different buffer gas collisional cooling in both the ion source and the RET reveals the effects of both translational and vibrational energy of the \( \text{N}_2^+ \) ions.

Introduction

In low-Earth orbit, water is one of the major components in the artificial atmosphere around spacecraft.\(^1^{1-3}\) The charge transfer reaction between nitrogen in the atmosphere and water molecules:

\[
\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}^+ \tag{1}
\]

is one of the most important ion–molecule reactions observed in low-Earth orbit associated with shuttle glow. That this reaction is occurring in a highly perturbed nonequilibrium environment regarding both velocity and internal energy distribution is equally intriguing. Meanwhile, ion–H\(_2\)O reactions are ubiquitous in all studies of ion chemistry and mass spectrometry, and therefore a thorough understanding of the dynamics of this reaction is warranted.

There have been a multitude of studies of the rate coefficient for reaction 1 under equilibrium conditions over the years. The kinetic energy dependence of the cross section for this reaction has been studied in the 1960s and more recently by Dressler and co-workers in the 1990s. The relevant electronic energy levels of the electron exchange process for the \( \text{N}_2^+–\text{H}_2\text{O} \) reaction are shown in Scheme 1. If the \( \text{H}_2\text{O}^+ \) product of the reaction is in the \( \text{X}^2\text{B}_1 \) electronic state, there is an exothermicity of 2.96 eV, while production of the \( \text{B}^2\text{B}_2 \) state of \( \text{H}_2\text{O}^+ \) is 1.60 eV endothermic. The energy difference between the \( \text{A}^2\text{A}_1 \) state and the ground state (\( \text{X}^2\text{B}_1 \)) of water ions is 1.00 eV.\(^2^{2,3}\) Turner and Rutherford in the 1960s found that for incident ion energy in the range from 1 to 400 eV using beam techniques, the cross section decreases with increasing collision energy from 30 × 10\(^{-16} \) to 7 × 10\(^{-16} \) cm\(^2\),\(^1\) and the large cross section demonstrates that the reaction takes place at long-range. Using a guided ion beam-gas cell technique, Dressler and his co-workers have shown that the excited product \( \text{A}^2\text{A}_1 \) state of \( \text{H}_2\text{O}^+ \) is populated at low collision energies, while the \( \text{B}^2\text{B}_2 \) state is populated as soon as it becomes energetically accessible, which is above 1.60 eV. At low collision energy, a long-lived complex is formed, which is governed by the long-range ion–dipole interaction, and that at collision energies above 4 eV, a long-lived complex is not involved.\(^2\) The agreement between the average dipole orientation (ADO) model and the \( \text{N}_2^+–\text{H}_2\text{O} \) cross section is good at the lowest meaningful energy (about 0.4–0.8 eV) of their work, while at higher energies, the cross section becomes less dependent on the collision energy because of a direct mechanism that begins to dominate the dynamics.\(^3\)

In this Article, we report a rate study of the \( \text{N}_2^+–\text{H}_2\text{O} \) reaction in a ring electrode trap for collisions between trapped \( \text{N}_2^+ \) ions at fixed temperature and a coaxial \( \text{H}_2\text{O} \) molecular beam with variation of the \( \text{H}_2\text{O} \) beam temperature (CoMB-RET). Using a trapped ion cloud in conjunction with a molecular beam, the relative reactant energy can be easily varied, and the effects of nonequilibrium energetics among the degrees of freedom can be directly investigated.

SCHEME 1: Electronic Energy Levels of \( \text{N}_2^+ + \text{H}_2\text{O} \) Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}^+ )</td>
<td>1.00 (( \text{X}^2\text{B}_1 ))</td>
</tr>
<tr>
<td>( \text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}^+ )</td>
<td>1.60 (( \text{B}^2\text{B}_2 ))</td>
</tr>
<tr>
<td>( \text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{H}_2\text{O}^+ )</td>
<td>1.96 (( \text{A}^2\text{A}_1 ))</td>
</tr>
</tbody>
</table>
2. Experimental Section

In this study, we have employed a new generation coaxial molecular beam ring electrode trap (CoMB-RET), which has been specifically developed to minimize trap interactions with ion source gas or background beam molecule contaminations. The trap in the current configuration is a ring electrode trap, which has been previously described in the literature. This results in long contamination free trap times with very high dynamic range. The instrument, shown schematically in Figure 1, will be described in detail in a future publication, and here we give only a brief introduction, relevant to the current study.

The $\text{N}_2^+$ reactant ions are produced by electron impact in a U-shaped radio frequency trap in the ion source chamber with an $\text{N}_2$ pressure of approximately $1.7 \times 10^{-3}$ Torr. In the storage source, $\text{N}_2^+$ ions relax via charge transfer collisions to the ground electronic state thermalized to the 350 K source temperature. The ions exiting the trap pass through a 90° dc quadrupole bender, which separates the ion stream from the effusive gas exiting the source. The ions are then focused into a double quadrupole mass selector/guide. The quadrupole is operated in RF only mode as a total ion guide because ion source conditions used present only the ion $\text{N}_2^+$. The mass selected ion beam is then turned 90° in a second dc quadrupole bender, bringing it coaxial with the RET trap axis and the axis of the molecular beam.

Ions are injected into the RET at low energy (<0.1 eV) by dropping the entrance guard ring potential. After a 1 ms loading time, the voltage on the trap entrance is increased. The RET is mounted on the end of a thermally regulated liquid He cryostat (Janis model ST-400), which is used in this study to cool the trap to 100 K. Buffer gas admitted to the trap cools to the 100 K wall temperature as do the ions through buffer gas collisions. Use of $\text{N}_2$ buffer in this study provides for extremely efficient ion cooling through resonant electron exchange. Ion storage times in excess of 10 s have been realized limited only by the background impurities within the trap cell.

The ions in the trap are exposed to the transiting $\text{H}_2\text{O}$ molecules from a skimmed effusive molecular beam. The beam source nozzle consists of a 30 mm long $\times$ 0.5 mm ID tube mounted onto the end of a second thermally regulated liquid He cryostat and is backed with 20 Torr of water vapor. The beam expands into a chamber pumped by a 10 000 L/s ($\text{H}_2\text{O}$) cryopump and is skimmed 20 mm downstream via a 0.5 mm orifice conical skimmer (Beam Dynamics). The beam passes through a differential pumping zone (pumped by a 1000 L/s cryopump) and is skimmed a second time at a distance 300 mm from the nozzle by a 2 mm diameter flat aperture and becomes coaxial with the trap. The trapping chamber is pumped by a 500 L/s turbopump. The beam passes through the quadrupole bender and enters the ring electrode trap through a 4 mm inside diameter gate lens. The center of the trap lies 450 mm from the source nozzle. The beam traverses the RET and exits without wall interactions through the 4 mm aperture exit gate lens, followed by a 6 mm aperture differential wall, a differentially pumped (250 L/s) analyzer quadrupole filter/MCP ion detector, and a final 10 mm ID $\times$ 100 mm long tube aperture into a beam dump (pumped by a 70 L/s turbo pump). Here, the molecular beam terminates into the ion source chamber of a residual gas analyzer (RGA; Stanford Research Systems 200). The RGA is used to determine beam flux, which is then calibrated to RET neutral beam density. This is finally cross calibrated against the observed $\text{N}_2^+-$H$_2$O rate at 300 K (both beam source and RET using $k_1 = 2.4 \times 10^{-9}$ cm$^3$ s$^{-1}$). Beam densities of water in the trap in this study range between 4.5 and 8.0 $\times$ 10$^7$ molecules cm$^{-3}$ depending upon source nozzle temperature.

Following exposure of the ion cloud to the water beam, the trap exit gate lens is dropped in potential, and the remaining reactant and newly born product ions are allowed to enter the analysis quadrupole where they are mass selectively filtered and detected using a fast microchannel plate ion counting system. Ion counts versus trapping exposure time is then used to

Figure 1. Schematic of ion-neutral collision apparatus: (1) U-shaped radio frequency trap/electron bombardment ion source; (2) quadrupole bender; (3) ion guide quadrupole; (4) mass selection quadrupole; (5) gas inlet; (6) ring electrode trap; (7) multichannel plate; (8) cryostat; (9) nozzle; (10) skimmer; (11) chopper; (12) cryo-pump; and (13) turbo-pump.
Variable-Temperature Rate Coefficients

This results in the absorption period for rotational transitions of water molecules to be greater than 200 ms for any relevant transitions in our temperature window. In this case, water molecules maintain internal thermal equilibrium at the nozzle wall temperature throughout their transit to the RET. The N$_2$ buffer gas densities employed in the RET are below $1.4 \times 10^{10}$ molecules cm$^{-3}$ (pressure in the trap 5 \times 10^{-7}$ Torr), and thus most water molecules on average transit the RET without either wall or buffer gas collisions. Meanwhile, the reverse reaction need not be considered due to the extreme exothermicity of the forward processes. The result is that the ion cloud presents trap equilibrated ion collisions to a water beam with an internal state distribution, which is thermal at the water nozzle source temperature.

The collision energy is a weighted mean of the translational beam energy and the random ion cloud thermal energy. The appropriate relative center of mass velocity distribution for a low angular divergence skimmed effusive beam–isotropic gas collision system such as this has been shown to be given by:

$$P(g_0) = \{4g_0^2\pi(\alpha_1^2 + \alpha_2^2)^{-3/2}\} \exp[-g_0^2/(\alpha_1^2 + \alpha_2^2)]$$  \hspace{1cm} (5)

where $g_0$ is the relative initial velocity of the ion–molecule collision pair. The quantity

$$\alpha_i = \sqrt{2kT/m_i}$$  \hspace{1cm} (6)

From this, the effective collision temperature is obtained from the moment of the collision energy and is shown to be:

$$T_{eff} = \frac{2\langle E \rangle}{3k} = \frac{m_1T_2 + m_2T_1}{m_1 + m_2}$$  \hspace{1cm} (7)

The internal temperatures of the water molecules and ions remain independently equilibrated to the nozzle temperature ($T_i$) and the trap wall temperatures, respectively. Thus, by varying the nozzle and trap temperatures, it is possible to broadly control the collision energy for a reactive system over independently determined rotational energy distributions.\textsuperscript{11–13}

Figure 2 shows the results of rate measurements of the N$_2^+$ ion cloud with the water beam over trapping times from 0.01 to 3 s. The observed kinetics are clearly first order in water density but do show dependence upon both ion source and RET nitrogen neutral density due to the presence of internally excited nitrogen ions when either buffer density is low. Thus, the ions are clearly prepared in a variety of internally excited states, which upon exiting the ion source chamber are certainly rovibrationally excited. Figure 3a shows the results of a study of the dependence of the observed rate coefficients upon various buffer densities. It is seen that RET trap buffer rapidly translationally cools the injected ions to the 100 K trap wall condition, leading to an increase in rate coefficient consistent with the known inverse temperature dependence of this reaction. Cooling saturation or equilibration as measured by the rate of reaction 1 is observed when the nitrogen buffer/ion collision frequency exceeds approximately 0.2 s. However, it is seen that in the case of He buffer in the RET, the rate coefficient extrapolates at high density to values 30% higher than those for nitrogen cooled ions. This indicates that the He cooled ions represent a distribution of internal states not fully equilibrated.

3. Results and Discussion

The water molecules used as neutral reactants in this study depart the beam nozzle effusively. The molecular velocity distribution in the effusive beam is

$$f(v_x) = 2\sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_x^2}{2kT}\right)$$  \hspace{1cm} (2)

and the average H$_2$O molecule velocity in our work is calculated to be 372 m/s at 300 K and 456 m/s at 450 K, and it takes 1.37–1.68 ms for H$_2$O molecules to travel from nozzle to ion trap. The relevant Einstein A coefficients of the water molecule for rotational transitions are between 0.003 and 16.01 s$^{-1}$,\textsuperscript{7} therefore, the lifetime of spontaneous rotational emission of water molecule is higher than 62 ms,\textsuperscript{7} which is about 37 times greater than the time it takes the H$_2$O molecules to move from nozzle to trap. The relationship between the Einstein A coefficient and B coefficient for absorption is

$$A = \frac{8\pi \hbar v^3}{c^3} - B$$  \hspace{1cm} (3)

and the blackbody energy density function\textsuperscript{10} is

$$\rho_v(T) = \frac{8\pi \hbar v^3}{c^3} \frac{1}{\exp(hv/kT) - 1}$$  \hspace{1cm} (4)

determine the pseudo first-order N$_2^+$ reactant ion loss rate and, from the known water density, the rate coefficient.\textsuperscript{7} See Figure 2.

Figure 2. (a) Plot of trapped ions over the sum of ions as a function of trapping time exposure to a molecular beam water density of 8.80 \times 10^{10} cm$^{-3}$. (●) Normalized number of N$_2^+$ ions, (□) normalized number of H$_2$O$^+$ ions. (b) Plot of N$_2^+$ ions density in the semilog scale versus time. Both plots were in N$_2$ and the average H$_2$O molecule velocity in our work is calculated to 372 m/s at 300 K and 456 m/s at 450 K, and it takes 1.37–1.68 ms for H$_2$O molecules to travel from nozzle to ion trap. The molecular velocity distribution, which is thermal at the water nozzle source temperature.

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to the trap temperature but which are equilibrated using N₂. The known rate of vibrational relaxation \( \nu > 0 \rightarrow \nu = 0 \) of N₂⁺ (\( \nu \)) by N₂ is to be \( 5 \times 10^{-10} \) cm³ s⁻¹; at trap pressure greater than \( 5 \times 10^{-7} \) Torr (100 K) of N₂, the quenching rate is about 200 times the rate of N₂⁺ and H₂O reaction, ensuring reaction of whole vibrationally equilibrated N₂⁺ with H₂O under the beam densities employed. This is confirmed when the rate is measured with \( 1 \times 10^{-6} \) Torr of He in the RET, over a series of measurements where the ion source N₂ density is increased. These data are shown in Figure 3b, demonstrating the relaxation of the rate coefficient to that observed for similar densities of N₂. Because the rf ion trap source has an externally measured temperature of approximately 350 K, the internal temperature of the ions exiting the source at the highest source pressures should not drop below this value. The He in the RET should effectively cool the translational (and presumably rotational) degrees of freedom, but the internal vibrations likely remain at the ion source condition. The fact that the N₂ source pressure (with high RET He pressure) asymptotically relaxes the observed rate to the same values obtained at high RET N₂ pressures suggests that with high densities of He or N₂ in the trap, translation-rotation is efficiently relaxed, but that small variance in the vibrational temperature between 350 and 100 K is not resulting in significant rate change.

The rate coefficients, with RET N₂ relaxed ion populations, for the reaction at effective collision temperatures, \( T_{\text{eff}} \), over a range from 283 to 384 K are shown in Figure 4 and Table 1. In these measurements, the temperature of the internally equilibrated trapped N₂⁺ ions is 100 K, while the beam derived water molecules are in the temperature range from 300 to 425 K.
but with this mass combination and the fact that the N$_2^+$ ions are significantly translationally colder than water, this excellent correlation with simple water temperature (and beam velocity) is not surprising. The quantitative fit to any of the models is not meaningful at this point, however, as the form of eq 4 represents a simple one-dimensional model on collision energy, which cannot differentiate between the nonequilibrium nature of this study. In other words, the excellent agreement with a form linear in $T^{-1/2}$ seen here suggests that the range of the variable space ($T_1$, $T_2$, and the internal temperatures) is not sufficient to differentiate more precise models. However, this study well isolates the one translational energy variable, and the observed excellent correlation with that variable is uncontrollable. This opens the way for further study of both the specific dynamical variables in similar ion–molecule reactions as well reaction systems in natural nonequilibrium environments such as the interstellar medium.17,19

ADO theory assumes that the reaction is dominated by long-range intermolecular forces, and when the ion moves to a certain distance from the molecule, which is beyond the centrifugal barrier, the collision always proceeds with unit efficiency. The rotationally adiabatic capture and centrifugal sudden approximation (ACCSA) theory of D. C. Clary and co-workers is based on a quantum level microcanonical capture model combining the ADO assumptions with rotationally adiabatic capture. Rotationally adiabatic capture assumes that as the ion moves toward the molecule, the initial rotational state $j$ stays on its own adiabatic potential energy curve, and no tunneling through the centrifugal barrier occurs as the reaction proceeds. In the ACCSA model, the ADO rate coefficient formula 3 is determined to be accurate for each rotational state $j$. The constant $C$ in ADO theory becomes a function of $j$, decreasing as $j$ increases. As a result, small values of $j$ will show a stronger temperature dependence, and this will be reflected in the inverse temperature dependence of the ACCSA rate coefficient.19,21 In application, it is found that the ADO theory and ACCSA models predict similar rate coefficients above room temperature, but at low temperature, usually below 200 K, the rate coefficient calculated by ACCSA has a steeper dependence on temperature than ADO theory. In addition, the experiment shows that the ACCSA model works very well for strongly exothermic reaction at low temperature but not as good for slightly endothermic reaction. In the present reaction, although the temperature of N$_2^+$ ions is held at a low value (100 K), only the H$_2$O temperature changes and in a range of around 300 K. It is then not surprising that the simpler ADO model still adequately describes the rate coefficient. The exoergicity of the N$_2^+$ → H$_2$O reaction is 2.96 eV, and it is in the range where ACCSA theory works well. In this case, it is found that even with the energy of N$_2^+$ ions being low, as the rotational and translational energy of the molecular dipole is much higher, the rate coefficient appears to manifest none of the additional temperature sensitivity predicted by ACCSA. Perhaps only when the rotational states of both N$_2^+$ ions and H$_2$O are lower than 200 K will the rate coefficient have steeper dependence on temperature, and using our instrument we can explore this in future reaction studies.

4. Conclusion

The charge transfer rate coefficient of the N$_2^+$ → H$_2$O reaction is determined as a function of water temperature for ions stored in a ring electrode trap. With the temperature of N$_2^+$ ions held at 100 K, the water beam temperature is varied from 300 to 450 K. The result shows that the total energy of the dipolar H$_2$O molecules affects the rate coefficients in a way consistent with the predictions of simple capture models. Different buffer gases nitrogen and helium are used, respectively, in the trap to cool the N$_2^+$ ions to 100 K and the ground rovibrational energy states. Parent nitrogen buffer gas is observed to be a much more efficient internal relaxant than helium buffer in this reaction due to the availability of a (near) resonant electron transfer relaxation mechanism. Such observations should be carefully taken into account when studying low energy ions under conditions where nonequilibrium internal energy distributions may persist.

Acknowledgment. We would like to acknowledge the National Science Foundation for partial support of this work through awards CHE-0618735 and CHE-0513364 and the Office of the Vice President for Research, University of Arizona, for their contributing support. In addition, we must thank Dr. Darin Latimer and Scienix for their assistance with the development of the quadrupole filters. We would also like to thank Prof. Bonner Denton and Paul Wendholt for assistance with this development effort.

References and Notes