J. Phys. Chem. A **2005,** *109,* 7181−7186 **7181**

Mechanisms of Electron-Ion Recombination of N_2H^+/N_2D^+ and HCO^+/DCO^+ Ions: Temperature Dependence and Isotopic Effect

Viktoriya Poterya, Jason L. McLain, Nigel G. Adams,* and Lucia M. Babcock

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received: April 14, 2005; In Final Form: June 20, 2005

The temperature dependencies of the rate coefficients, α_e, for electron-ion dissociative recombination (DR) of N_2H^+/N_2D^+ and HCO^+/DCO^+ ions with electrons have been measured over the range 100−500 K. Also, optical emissions have been detected at ∼100 K from the $N_2(B^3\Pi_g)$ electronically excited products of N_2H^+/N_2D^+ recombination. The measurements were carried out using the classic FALP technique combined with an optical monochromator. For N_2H^+, there was no variation of α_e with temperature above 200 K, with an average value of $\alpha_e(N_2H^+) = 2.8 \times 10^{-7}$ cm^3 s^{-1}. The temperature variation for $T \sim 100-300$ K observed for $\alpha_e(HCO^+)$ is similar to that of N_2H^+ ions for $T \sim 300-500$ K. The smaller rate coefficient measured for DCO^+ and N_2D^+ ions shows the influence of an isotope effect. The substantial enhancement of the vibrational level, $v' = 6$, from the N_2B state for N_2H^+ recombination over N_2D^+ recombination is consistent with previous result at 300 K and implies the influence of a tunneling mechanism of DR.

Introduction

The dissociative recombination (DR) of N_2H^+ and HCO^+ is a subject of astrophysical importance.[1,2] These ions have substantial dipole moments (3.4 and 3.3 D[3], respectively) and are easily detected in interstellar space by pure rotational transitions. These emissions are frequently used to probe the structure of molecular clouds, particularly in star formation regions.[4] Both ions have a simple chemistry of formation via fast proton transfer

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2$$

Since H_3^+ is the most abundant ion known in interstellar media, N_2H^+ and HCO^+ are widespread. In molecular clouds of intermediate density, N_2H^+ and HCO^+ are destroyed by proton transfer to abundant molecules with larger proton affinities. However, in low-density interstellar regions, DR is an important destruction mechanism.

Originally two basic pathways for DR (the direct and indirect mechanisms) were considered. In 1950, the first theoretical explanation for recombination of molecular ions with electrons was proposed by Bates.[5] This direct mechanism of DR proceeds when the electron is captured by the molecular ion into a resonant doubly excited state, which tends to dissociate into fragments within a very short time. Quite a few experimental results could be explained by this theory.[6−8] It is now accepted that the rate coefficient for the direct mechanism can be written as $\alpha_e(T_e) = \alpha_{e0}(T_e/300)^{-0.5}$, where α_{e0} is the rate coefficient of recombination at 300 K and T_e is the electron temperature. Later, the indirect mechanism was postulated by Bardsley.[9] In this recombination mechanism, the electron is initially captured into an excited Rydberg state which predissociates into neutral fragments due to the coupling to the same repulsive doubly excited state as in the direct mechanism. The $\alpha_e(T)$ for the indirect mechanism was shown to generally vary as $\alpha_{e0}(T/300)^{-1.5}$ where T is the electron and ion temperature. Usually both modes can occur together causing interference and affecting the rate coefficient of DR either in a destructive[10] or constructive[11] way.

According to several afterglow experimental results[12,13] and the results of the present paper, the rate coefficient, α_e, for DR of N_2H^+ with electrons can be represented as $(2.5 \pm 0.4) \times 10^{-7}$ cm^3 s^{-1} at room temperature. Earlier infrared spectroscopy results by Amano[14] gave a surprisingly high rate of recombination of 7×10^{-7} cm^3 s^{-1}. On the contrary, recent storage ring (SR) measurements of cross section for DR[15] yield a thermal α_e of 1×10^{-7} cm^3 s^{-1}, which is lower than FA results but approaches the earlier afterglow value[16] of 1.7×10^{-7} cm^3 s^{-1}.

However, there is no complete knowledge of the branching ratio of the dissociative channels. The large exothermicity of N_2H^+ recombination (8.5 eV) is frequently deposited in the N_2 product giving the possibility of populating several electronically excited states.[13,17] In particular, the presence of channel 1c has been identified experimentally as well as channel 1g:

$$N_2H^+ + e^- \rightarrow N_2(X^1\Sigma_g^+) + H + 8.49\text{ eV} \tag{1a}$$

$$\rightarrow N_2(A^3\Sigma_u^+) + H + 2.32\text{ eV} \tag{1b}$$

$$\rightarrow N_2(B^3\Pi_g) + H + 1.14\text{ eV} \tag{1c}$$

$$\rightarrow N_2(W^3\Delta_u) + H + 1.13\text{ eV} \tag{1d}$$

$$\rightarrow N_2(B'^3\Sigma_u^-) + H + 0.33\text{ eV} \tag{1e}$$

$$\rightarrow N_2(a'^1\Sigma_u^-) + H + 0.09\text{ eV} \tag{1f}$$

$$\rightarrow NH(X^3\Sigma^-) + N + 2.25\text{ eV} \tag{1g}$$

For channel 1c, an absolute yield of the $N_2(B^3\Pi_g)$ state of greater than 19% has been determined recently.[13] It was concluded, however, that the observed yield could be enhanced by transitions to the N_2B state from other excited states formed in the recombination event, and so it may only give an upper limit to the branching ratio for this channel. For channel 1g, recent storage ring data show their presence with a probability

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* To whom correspondence should be addressed. Telephone: (706)-542-3722. Fax: (706)-542-9454. E-mail: adams@chem.uga.edu.

10.1021/jp051945b CCC: $30.25 © 2005 American Chemical Society
Published on Web 07/23/2005

of 65%;[15] the observation of this latter channel is surprising since it requires breaking of a multiple bond.

The rate coefficient for DR of HCO^+ has been the subject of controversy between the theory and experiment for several years. There are several possible exothermic channels for this recombination:

$$HCO^+ + e^- \rightarrow CO(X^1\Sigma^+) + H + 7.45\ \text{eV} \qquad (2a)$$

$$\rightarrow CO(a^3\Pi_r) + H + 1.41\ \text{eV} \qquad (2b)$$

$$\rightarrow CO(a'^3\Sigma^+) + H + 0.53\ \text{eV} \qquad (2c)$$

$$\rightarrow C + OH(X^2\Pi_i) + 0.75\ \text{eV} \qquad (2d)$$

$$\rightarrow O + CH(X^2\Pi) + 0.19\ \text{eV} \qquad (2e)$$

The laboratory studies[16,18−22] resulted in a rate of recombination close to 2×10^{-7} cm^3 s^{-1} that is typical for simple polyatomic ions.[23] However, the absence of a favorable curve crossing, according to ab initio computations,[24] would not allow fast direct recombination to proceed. The problem was solved by Bates[25] who included several ground core Rydberg states in the calculations and deduced a rate coefficient of order of magnitude 10^{-7} cm^3 s^{-1}. In this way, HCO^+ recombination was the first example showing that a crossing of the ion potential curve by a repulsive curve near the minimum was not necessary for the rate coefficient to be large.

This modification of indirect recombination that occurs for the HCO^+ ion proceeds through several intermediate Rydberg states. In this mechanism, called multistep indirect recombination, the electron is captured into the Rydberg state R(n, υ) followed by a sequence of transitions to other Rydberg states R(n′, υ') by quantum tunneling. The final step involves a single electron radiationless transition to the repulsive state followed by dissociation. A close energy match of the initial state of the ion with discrete states of the neutral molecule facilitates tunneling and can result in large recombination rate coefficients. The calculated temperature variation[25] for recombination of HCO^+ driven by a tunneling mode can follow a $T^{-1.5}$ dependence; however, it was noted that this cannot be accepted as a prediction. For example, the theoretical results obtained for HeH^+ recombination, which has repulsive potential curve lying to the small internuclear separation side of the molecular ion curve and below the Rydberg states, gives a dependence of α_e on temperature of $T^{-0.47}$ for the temperature range 200−400 K.[26]

According to the recent recombination review papers,[7,23,27,28] in contrast to simple direct recombination, the indirect mode can occur by a multitude of pathways. For example, to explain the measured low-energy resonances for the OH^+ ion recombination cross section,[11] a different type of indirect mechanism was proposed. In this case, indirect recombination is considered to proceed through the capture of an electron into Rydberg states having electronically excited ion cores. Such transitions involve the Rydberg levels with vibrational quantum number $\upsilon = 0$, which have a high Franck−Condon overlap and consequently a high electron capture probability. It is worthwhile noting that, in Bardsley's indirect mechanism, Rydberg levels will have $\upsilon = \upsilon_i + 1$, where υ_i is the vibrational quantum number of the recombining molecular ion.

Related to this, an interesting feature was observed for the N_2^+ recombination. The experimental measurements[29,30] of α_e and theoretical calculations,[10] based on the direct mechanism, show good agreement. However, calculations[10] involved both the direct mechanism and an indirect mechanism involving ground-state ion core Rydberg states produced a rate of recombination which is about 40% below the rate of "pure" direct recombination. When extended calculations[31] with excited core Rydberg states were made, the α_e becomes about 10% bigger than that for the direct and the indirect mechanism with ground-state ion core Rydberg states. Furthermore, calculations[10] showed that, when both direct and indirect recombinations interfere, the temperature variation of $\alpha_e(N_2^+)$ is weaker ($T^{-0.37}$) than the $T^{-0.5}$ dependence calculated for the direct mechanism by itself. This is in the direction observed in the present studies.

Because of the lack of information about the potential surfaces for the N_2H^+ molecular ion, the Rydberg states, and the dissociative neutral states, only speculations based on the experimental results can indicate the recombination mechanism involved. A theoretical approach to estimating the degree of excitation distributed in the products of recombination was first developed by Bates,[32] and measurements were carried out to check the theory for N_2H^+ and HCO^+ recombinations.[33,34] It was inferred in a detailed study[34] that the significant enhancement of the vibrational level ($\upsilon' = 6$) of the N_2B state for N_2H^+ recombination over N_2D^+ recombination can be ascribed to a tunneling mode of DR.

In a recent study, new data on the temperature dependence of the rate coefficients for the recombination of a series of hydrocarbon molecular ions were obtained using a temperature variable flowing afterglow technique with an electrostatic Langmuir probe (FALP).[8] The temperature dependencies of the rate coefficients were found to be consistent with the theoretical predictions of simple direct and indirect DR. The present results extend these temperature dependence studies to include N_2H^+ and HCO^+; however, they show no well-defined evidence for a temperature-dependent behavior. The temperature effect on the final vibrational state distributions for N_2B was examined further for N_2H^+ and N_2D^+ recombination. Since both the temperature dependence and final state product distributions can differ with change of the recombination mechanism, results of the present study can greatly contribute to the theory of DR.

Experiment

A full description of the FALP technique can be found in several publications[35,36] and will not be repeated here. For this particular study, a copper jacket, which had copper tubes brazed to it, was clamped around the flow tube. Liquid nitrogen flowing through the tubes was used for cooling to temperatures as low as 80 K, and resistive heaters were used for temperatures up to 600 K. The copper jacket covered most of the flow tube to ensure sufficient thermal conductivity to produce a uniform temperature. A vacuum chamber around the flow tube provided thermal insulation and kept the temperature stable during experimentation.

Primary He^+ ions were created by a microwave discharge in a helium carrier gas. A decaying plasma composed of the primary ions then reacted with gases added further downstream. Argon was usually added several centimeters downstream of the discharge to destroy helium metastable atoms, He^m. Operation at 1.8 Torr pressure caused the rapid formation of He_2^+ ions from He^+ via three-body association. These He_2^+ ions were then converted into Ar^+ ions via reaction with the added argon. Hydrogen was introduced through a port further downstream to create H_3^+ ions via a sequence of well-known ion−molecule reactions.[17] Since these ions exchange a proton very fast with addition of CO or N_2, this rapidly formed the ions under study. To form DCO^+ and N_2D^+, deuterium gas was substituted for hydrogen. A quadrupole mass spectrometer located further downstream in the flow provided quantitative information concerning the plasma composition.

To determine the recombination rate coefficient, the electron number density was measured as a function of distance along the flow tube using a Langmuir probe.[37] From the linear fit of the $1/[e]_z$ data, the recombination coefficient (α_e) was evaluated using the formula[38]

$$\frac{1}{[e]_z} = \frac{1}{[e]_{z0}} + \alpha_e \frac{z}{\upsilon_i}$$

where $[e]_z$ is electron density as a function of axial position, z, in the flow tube and υ_i is the ion flow velocity. The temperature dependencies of the rate coefficients were determined in a series of separate measurements in which the temperature of the flow tube was kept at various constant values in the range 100−500 K. Since the whole gas was in thermal equilibrium with the flow tube walls, both electrons and ions had the same temperature.

Experiments were also carried out to quantitatively detect optical emission from the recombinations of N_2H^+ and N_2D^+ ions at 100 K. Since the present study was focused on a comparison between the results at different temperatures, the detection of the emission at 100 K was carried out under experimental conditions similar to the previous study at 300 K[34] providing fast formation of N_2H^+/N_2D^+ ions. Sufficient amounts of N_2 were added to quench any residual excitation in the recombining molecular ions by proton transfer. It was verified previously[17] that full relaxation can be achieved in this way before recombination occurs. Furthermore, a recent afterglow study[13] suggested that collisions with He carrier gas and Ar were sufficient to provide vibrational relaxation of N_2H^+. After recombination occurred, the emitted photons were focused into an entrance slit of an atmospheric pressure monochromator by a quartz lens. This was situated in a side tube of the flow tube directly opposite the region where the reactant gas entrance port for N_2 was located. Since recombination is fast, and the radiative lifetime of the monitored N_2B state is short,[39] this arrangement allows detection of emissions within a time period of several microseconds after recombination. This time corresponds to a transit distance of 0.25 mm along the flow tube equivalent to the image of an N_2B state molecule passing across the entrance slit of the monochromator. Such a short time excludes the collisional relaxation of the N_2B state and decreases the probability of transitions from other electronically excited states into this state. The monochromator was equipped with a 1800 groove mm^{-1} diffraction grating, and a slit width of 0.25 mm was used providing rotational resolution of the lines. Dispersed emissions exiting the monochromator were detected by a photomultiplier with an S20 photocathode, and the output pulses were counted using a gated photon counter (SR 400).

Results

1. Temperature Dependence Results. The rate coefficients for the recombination of the N_2H^+ and HCO^+ ions obtained at five different temperatures are depicted in the Figure 1. It can be seen that, over the range of the temperatures studied, the $\alpha_e(T)$ variations do not simply obey the power laws of the order of $T^{-0.5}$ or $T^{-1.5}$ associated with the direct or indirect mechanisms. The recombination of N_2H^+ ion can be characterized by an almost constant α_e with an average of 2.8×10^{-7} cm^3 s^{-1} for $T > 200$ K. A slightly higher value of α_e has been obtained at $T = 100$ K, and data below 300 K give a power law of at least −0.35. Keeping in mind the lack of points in the low-temperature region, the temperature dependence might be steeper and thus approaching that predicted by the direct mechanism dependence ($T^{-0.5}$). Indeed as can be seen in Figure 2 our temperature dependence for $T < 300$ K is in a good agreement with the data previously obtained by Adams et al.,[16] Amano,[14] and Smith et al.[12] and closely approaches the storage ring α_e temperature dependence[15] which follows $T^{-0.5}$ power law, although the absolute storage ring α_e values are lower and the Amano's results are larger than the other experimental determinations.

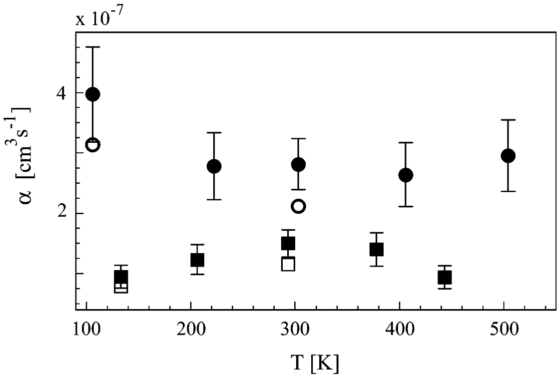

Figure 1. The temperature dependencies of rate coefficients for DR, α_e, of N_2H^+/ N_2D^+ (full/open circles) and HCO^+/DCO^+ (full /open squares) ions with electrons. Error bars shown represent accuracy to within ±15% at 300 , and ±20% at all other temperatures.

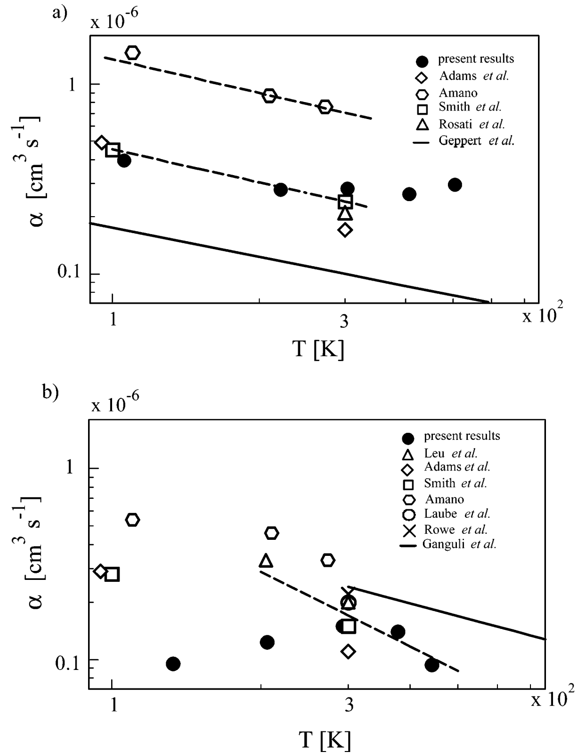

Figure 2. The temperature dependencies of α_e for DR of (a) N_2H^+ and (b) HCO^+. Present data are depicted together with the previous results. Dashed lines are approximate fits of the experimentally obtained α_e values.

For HCO^+ ions, it is difficult to explain the small decrease in the rate coefficient with decreasing temperature below 300 K. The initial measurements were complicated by the presence of some C^+ ions, which have a tendency to lower the rate of recombination. Since C^+ is produced by the reaction of CO with He^+, the He pressure in the flow tube was increased to 2.5 Torr

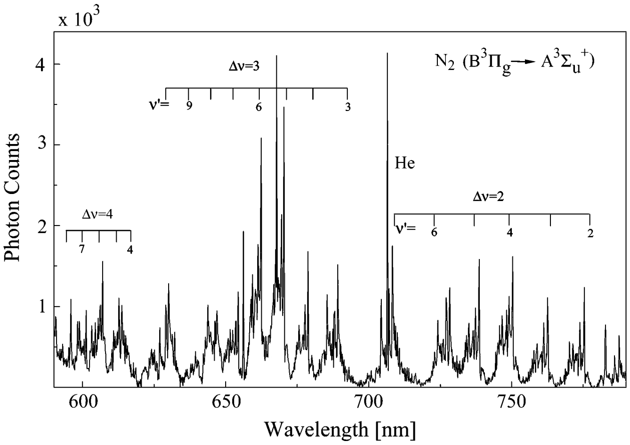

Figure 3. Spectrum of N_2 ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) emission resulting from the dissociative electron recombination of N_2H^+ ions with electrons at 100 K.

at $T > 300$ K to accelerate the three body association reaction resulting in more rapid formation of He_2^+. At low temperatures, the pressure was kept at 1.8 Torr, which according to chemical kinetic modeling gives a number density high enough to eliminate the C^+ effect. Consistent with this, the ion mass spectra obtained at 100 K did not show the presence of a C^+ peak. Thus it is unlikely that the low values of α_e were significantly affected by the presence of C^+. Indeed, α_e at 300 K is consistent with previous results. At $T < 300$ K, $\alpha_e(HCO^+)$ exhibits temperature behavior which can be ascribed to neither a direct nor an indirect mechanism of DR. This temperature dependence contradicts the results of Leu et al.,[18] Adams et al.,[16] and Smith et al.[12] where α_e for $T < 300$ K has a tendency to increase with reducing temperature. However, at $T > 200$ K, the decrease of α_e values of Leu et al. and Amano with increasing temperature is consistent with our data and can be fitted by the T^{-1} power law as indicated by a dashed line in Figure 2(b). The stationary afterglow data by Ganguli et al.[19] show slightly weaker temperature dependence, although in their experiment only the temperature of electrons was varied. To define more accurately temperature dependence at $T > 300$ K, more measurements are needed.

The recombination rate coefficients for DCO^+ and N_2D^+ ions with electrons measured at 300 and 100 K are slightly lower than α_e for their hydrogenated form. Thus, for example the ratios of $\alpha_e(HCO^+)/\alpha_e(DCO^+)$ are 1.3 and 1.2 at 300 and 100 K, respectively. Coincidently, the ratios of $\alpha_e(N_2H^+)/\alpha_e(N_2D^+)$ are very close to $\alpha_e(HCO^+)/\alpha_e(DCO^+)$ being 1.3 and 1.26 at 300 and 100 K, respectively.

2. Analysis of Emission Results. The spectrum obtained in the range 580−800 nm from the recombination of N_2H^+ ions with electrons at 100 K (Figure 3) was used to determine the N_2B state vibrational population. From the original data, a small background signal was subtracted. Since the emissions occurred over a large spectral range, corrections were made to take into account the differing transmission efficiencies of the focusing lenses, the windows, the monochromator, and the photomultiplier with wavelength. All lines were identified as $N_2(B^3\Pi_g \rightarrow A^3\Sigma_u^+)$, except for a single He line originating from scattered radiation from the microwave discharge source.

The spectra obtained for both N_2H^+ and N_2D^+ ions have similar features to those obtained previously at 300 K,[34] and this facilitated identification of the lines. As in other studies,[40] checks were carried out to ensure that the detected emission originated only from recombination of the ion of interest. Here, the electron number density was varied by moving the microwave discharge source to change the diffusive loss of the electrons and thus the electron density prior to recombination. Since the rate of generation of excited products of DR and consequently the emission intensities, I, are proportional to $[e]^2$, a log−log plot of I versus [e] is expected to have a slope of 2. This dependence was closely followed for at least an order of magnitude decrease in [e] indicating that at least 90% of the emissions resulted from DR (Figure 4).

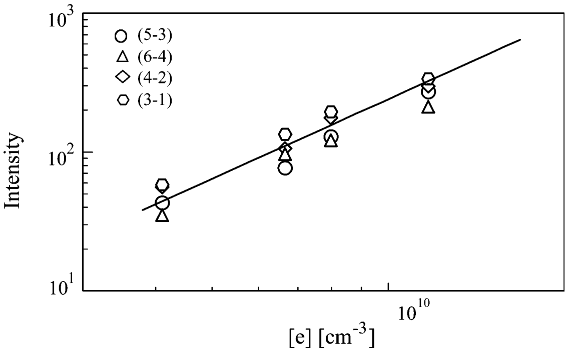

Figure 4. A ln−ln plot of the detected emissions in several bands originating from N_2H^+ recombination against electron density, [e]. Legend shows the studied transitions (v'-v). The slope of the solid line is 1.9 indicating a dependence on $[e]^2$ as expected.

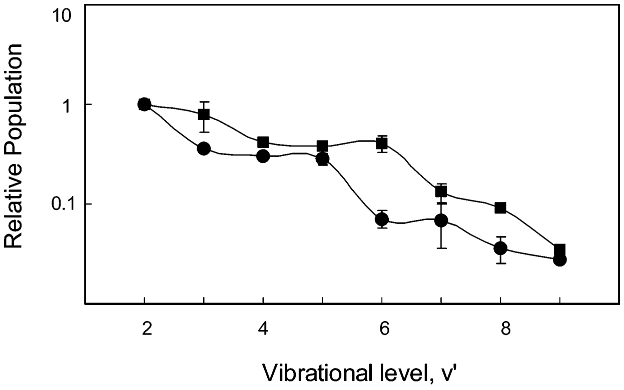

Figure 5. Relative vibrational populations for the N_2 ($B^3\Pi_g$) state generated in the recombinations of N_2H^+ and N_2D^+ (squares and circles, respectively) at 100 K.

The calculations of the relative population distributions were carried out by integration of the count rates, I, under each vibrational band (v', v') divided by the Franck−Condon factors calculated previously[34]

$$I(v',v'') \propto \nu^3 N(v')(\mathrm{FCF})$$

where $N(v')$ is the population of vibrational level v', FCF is the Franck−Condon factor, and ν is the frequency of the transition.

Figure 5 shows a comparison between the relative vibrational populations of the N_2B state obtained in the recombinations of N_2H^+ and N_2D^+ ions at 100 K. The population distributions were normalized to the lowest level $v' = 2$ from which emissions could be observed. This was because the spectrum was restricted to wavelengths below 800 nm due to the upper limit to the wavelength detectable by the photomultiplier. Since the populations of most of the individual vibrational levels were calculated from several transitions, errors can be determined and are given for each data point. A bigger error occurred for $v' = 3$ due to overlap of the (3,0) and (8,6) bands.

The results at the low temperature exhibit a similar behavior to the data previously obtained at 300 K.[34] For N_2H^+, vibrational

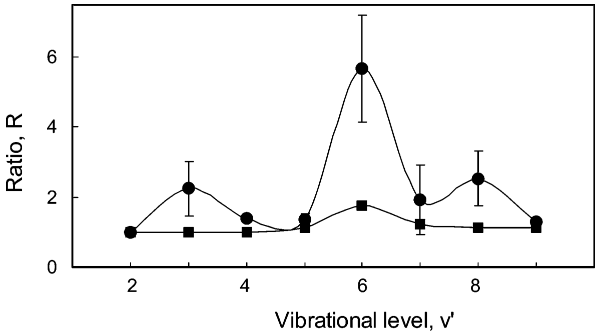

Figure 6. Comparisons between ratios *R* generated in the recombinations of N_2H^+ and N_2D^+ at 100 K (circles) and *R* obtained from results generated in the recombinations of N_2H^+ and N_2D^+ at 300 K (squares).[34]

levels up to $v' = 6$ are populated with a significant decrease in the populations for $v' > 6$ where population of the levels is endothermic. The populations of higher levels decrease gradually as the v' increases for both N_2H^+ and N_2D^+ recombining ions. Note that a significant decrease occurred at a slightly lower level (for $v' = 5-6$) for N_2D^+ than for N_2H^+. Comparison of the ratios of the vibrational populations for N_2H^+ and N_2D^+ at 100 K, and those previously[34] determined at 300 K, is given in Figure 6. For both temperatures, the striking feature is that $v' = 6$ from the N_2B state are populated more extensively at the temperature of 100 K than those detected at 300 K by about a factor of 3. There also seems to be some evidence for small enhancements for $v' = 3$ and 8.

Discussion

Theoretical calculations have been made previously for the recombination of HCO^+ ions, but here there are discrepancies between several different calculations of the potential surfaces. The earlier ab initio computations of Talbi et al. indicated the presence of a crossing point of the $HCO^+(X^1\Sigma^+)$ near its minimum by the repulsive state $HCO(X^2\Sigma^+)$. The same type of computations made later by Kraemer and Hazi dismissed the recombination of HCO^+ by the direct mechanism because their repulsive HCO $(X^2\Sigma^+)$ potential lies at a smaller C−H separation than the inner wall of the HCO^+ $(X^1\Sigma^+)$ potential. Bates postulated a new multistep indirect mechanism and applied it to HCO^+ recombination. Recombination, driven by this new mechanism,[25] even despite the no favorable curve crossing, predicts a large α_e, which is comparable with the experimental results.[16,18−21] Later calculations by Le Padellec et al.,[22] however, again show the presence of a crossing with the repulsive potential surface of HCO $(X^2\Sigma^+)$ near the minimum of the ion potential surface. Thus, the large value of the rate coefficient does not distinguish between the noncrossing Kraemer and Hazi curves with the Bates mechanism and the Le Padellec curves with the direct mechanism. Data on the temperature dependence of $\alpha_e(HCO^+)$ do not clarify the situation. The early afterglow α_e data of Ganguli et al. give a temperature dependence of $T_e^{-0.69}$ above 300 K consistent with the present data above room temperature; however, this is a much smaller temperature dependence than the $T_e^{-1.2}$ calculated by Le Padellec et al. from merged beam data (note that this might be influenced to some degree by the onset of an additional product channel above ~0.3 eV). The combined afterglow data are consistent with the direct mechanism with a favorable curve crossing; however, since the temperature dependence is not known for the Bates mechanism with no favorable crossing, no definite conclusion can be reached. With regards to the products of DR, the direct mechanism should result in formation of the $CO(^1\Sigma^+)$ state. The $CO(a^3\Pi)$ state as a product of HCO^+ recombination was detected spectroscopically[17,41] with an absolute yield of 30%, which included cascading from higher states.[41] Additionally, the detected Cameron band emissions from $CO(a^3\Pi)$ in the Red Rectangle was concluded to originate from recombination of HCO^+.[42] Chemical modeling[42] based on the assumption that HCO^+ recombination forms a $CO(a^3\Pi)$ product with a probability of 100% gave a calculated emission in good agreement with astronomical observations. This is in contradiction to the earlier theoretical calculations of the CO product vibrational distribution for direct HCO^+ recombination[43] which predicted that only an insufficient amount of vibrational energy available in $CO(a^3\Pi)$ can be converted into infrared radiant energy. Although a remark was made, that if HCO^+ recombination proceeds via Bates' multistep mechanism, initial CO excitation may occur during tunneling transition into the Rydberg state of Π symmetry. Thus, the question remains whether the direct mechanism is dominant for low-energy recombination and how significant is the indirect mechanism. Quantitative determination of the relative abundances of the $CO(^1\Sigma^+)$ and $CO(a^3\Pi)$ states is needed.

There are some theoretical (and also experimental) data available for the structure and energy levels of N_2H^+/N_2D^+ ions[44] and the N_2H neutral molecule;[45] however, there is no information about the relative position of the potential surfaces or of the Rydberg states. The energy of the ground state of N_2H^+ $(v = 0)$ can range from 8.32 to 8.67 eV according to proton affinity calculations.[46] This energy matches certain vibrational levels of the $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\ \Sigma_u^-$, and $a'^1\Sigma_u^-$ states of the free N_2 molecule in the dissociated N_2H (consideration of this is given by Adams and Babcock[17]). The potential energy diagram for these states has been deduced by Rosati et al.[13] Even though the equilibrium separations of N_2 in all of these states lie within the 0.2 Å $(0.378a_0)$ to the right of the equilibrium N−N separation[44] in N_2H^+ $(v = 0)$, taking into account three-dimensional behavior, it is impossible to predict whether the asymptotes of the corresponding N_2H states will cross N_2H^+ surface.

The effect of the elevated temperature on the populations of the three fundamental modes of N_2H^+ ions was considered. At $T = 500$ K, only the bending mode can be accessed with a population of 10% of the ions in the ground state. Note that two stretching modes have vibrational energies too big to be populated at this temperature.

To explain the observed small temperature dependence, we suggest that recombination of N_2H^+ resulting in the formation of the channel $N_2(B^3\Pi_g) + H$ can be driven by the tunneling recombination mechanism initially proposed by Bates for the HCO^+ recombination. The almost zero temperature dependences obtained for the N_2H^+ and HCO^+ recombinations might imply a common mechanism. It was shown in Figure 6 that there is a very noticeable enhancement of the population of the $N_2(B^3\Pi_g)$ $(v' = 6)$ for N_2H^+ recombination over N_2D^+ recombination at 300 K and especially at 100 K. Since the energy of N_2H^+ $(v = 0)$ approaches the energy of $N_2(B^3\Pi_g)$ $(v' = 6)$ (~8.56 eV), this accidental resonance makes quantum tunneling very likely to happen if there is a potential barrier between the N_2H^+ surface and the asymptote of $N_2(B^3\Pi_g)$+H. The even stronger enhancement of $v' = 6$ at 100 K than obtained previously at 300 K allows us to suggest that $N_2H^+ + e^-$ system at 100 K has an even closer energy match to the $N_2(B^3\Pi_g)$ $(v' = 6)$ state increasing the "transparency" of the potential barrier by accidental resonance and facilitating the recombination.

In addition to the resonance at $v' = 6$, it is necessary to explain the presence of enhancements of $v' = 3$ and 8 and the reduced enhancements for other v' levels. However, since detailed potential curve and energies of vibrational levels in

N_2H^+ are not currently available, such a discussion can only be qualitative. Here, a repulsive curve can be pictured for each vibrational level of the N_2B state giving a varying form of the potential barrier. For products with an energy equal to that of the ion equivalent to $v' = 6$ level there would be an unbound potential curve with wave function associated with each v' level. These curves will be overlapped by the wave function for the $v = 0$ level of the ion, after penetration through the tunneling barrier. So, if the overlap is positive the channel will be enhanced, and if the overlap is negative the channel will be depressed. It does appear that positive overlap is achieved for $v' = 3$ and 6 and a negative or small overlap for $v' = 1$, 2, 4, and 5. The presence of $v' = 7$ and 8 although small indicates the presence of small vibrational excitation in the ion with a more positive overlap for $v' = 8$ than $v' = 7$.

It was pointed out previously[13] that the $N_2(B^3\Pi_g)$+H channel may not be the only channel, and the other channels leading to the triplet ($A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\ \Sigma_u^-$) states of N_2 may be present as well. It is possible that, at $T > 300$ K, other resonances may open up to different channels smoothing over the temperature dependence. It is surprising that recent measurements of the cross sections[15] for N_2H^+ recombination do not show the presence of resonances. Their experimental α_e perfectly follows the direct mechanism power law although this temperature dependence ($T^{-0.5}$) is weaker than any previous SR data for polyatomic molecular ions.[23]

The present work shows that recombination of N_2H^+ and HCO^+ is a factor of 1.3 larger than their deuterated analogues. This is consistent with a tunneling mechanism discussed by Bates[7] where D tunneling is much less efficient than H tunneling allowing more time for autoionization. This is especially relevant for the N_2H^+/N_2D^+ recombination where there is a resonance with the $v' = 6$ state of the N_2B recombination product (for HCO^+/DCO^+ the observations are not inconsistent with a tunneling mechanism, but the data are not so compelling).

Conclusion

The measured rate coefficients for the recombination of HCO^+ and N_2H^+ ions are in good agreement with afterglow values previously obtained.[12,13,16,18−21] The deuterated ions revealed smaller rate coefficients of recombination by about a factor of 1.3. The measured rate coefficients for DR of N_2H^+ and HCO^+ ions exhibit behavior with little temperature dependence. The α_e measured for HCO^+ exhibit behavior with a tendency to a virtually temperature-independent recombination for 100−300 K that is similar to the 200−500 K temperature range N_2H^+ results. This similar independence of temperature suggests that the recombination of both ions may be driven by the same, or a similar, mechanism; this does not appear to be either of those (direct and indirect) commonly accepted. Quantum tunneling is implicated from the spectral emissions studies for N_2H^+/N_2D^+ recombinations. Since it is not known how this will affect the temperature dependence, theoretical input is greatly needed here.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant No. 0212368.

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