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Geppert, W. D., Thomas, R., Semaniak, J., Ehlerding, A., Millar, T.J., Osterdahl, F., Af Ugglas, M., Djuric, N., Paat, A., & Larsson, M. (2004). Dissociative Recombination of N₂H⁺ Evidence for Fracture of the N-N bond. *Astrophysical Journal*, 609, 459-464.

Published in:
Astrophysical Journal

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DISSOCIATIVE RECOMBINATION OF N_2H^+ : EVIDENCE FOR FRACTURE OF THE N–N BOND

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Received 2003 August 26; accepted 2004 February 27

ABSTRACT

Branching ratios and absolute cross sections have been measured for the dissociative recombination of N_2H^+ using the CRYRING ion storage ring. It has been found that the channel $\text{N}_2\text{H}^+ + e^- \rightarrow \text{N}_2 + \text{H}$ accounts for only 36% of the total reaction and that the branching into the other exoergic pathway, $\text{N}_2\text{H}^+ + e^- \rightarrow \text{NH} + \text{N}$, consequently amounts to 64%. The cross section of the reaction could be fitted by the expression $\sigma = (2.4 \pm 0.4) \times 10^{-16} E^{-1.04 \pm 0.02} \text{ cm}^2$, which leads to a thermal reaction rate of $k(T) = (1.0 \pm 0.2) \times 10^{-7} (T/300)^{-0.51 \pm 0.02} \text{ cm}^3 \text{ s}^{-1}$, in favorable agreement with previous flowing afterglow Langmuir probe measurements at room temperature, although our temperature dependence is very different. The implications of these measurements for the chemistry of interstellar clouds are discussed. A standard model calculation for a dark cloud predicts a slight increase of N_2H^+ in the dark clouds but a five- to sevenfold increase of the NH concentration as steady state is reached.

Subject headings: astrochemistry — ISM: molecules — methods: laboratory

1. INTRODUCTION

Dissociative recombination (DR) is one of the most important destruction mechanisms of molecular ions, especially in environments with low number densities such as the interstellar medium or the upper layers of planetary atmospheres. In many systems, the high kinetic energy release of the DR reaction can enable different fragmentation pathways of the intermediate neutral molecule. Knowledge of the branching ratios of the different pathways is therefore crucial to accurately model large reaction networks in these media (Millar et al. 1988). It was predicted that the bond or bonds disrupted in the DR reaction are those involving significant positive partial charges on the ion and that simultaneous breakage of several bonds is unlikely (Bates 1986, 1987). Recent research into the DR of many molecular species, however, has shown that many reactions do not follow this prediction. For example, unexpected pathways like ruptures of the C–C bond in the DR of hydrocarbon ions and three-body breakups in triatomic molecules are, in fact, very common, and branching ratios turn out to be far less predictable than previously assumed (Larsson & Thomas 2001).

N_2H^+ is one of the most ubiquitous and important interstellar molecular ions. It has been predicted and detected in a multitude of astronomical environments, e.g., in dark and translucent interstellar clouds (Turner 1974, 1995), protostellar cores (Caselli et al. 2002), and photodissociation regions (Fuente et al. 1993), as well as in ionospheres of planets and their satellites (Krasnopolsky 2002; Ip 1990). The ion also serves as a tracer for N_2 , which is elusive to direct

astronomical observation (Herbst et al. 1977). N_2H^+ can also protonate other molecules, such as water and unsaturated hydrocarbons, which are present in interstellar space (Milligan et al. 2002). Furthermore, N_2H^+ has been detected in microwave discharge plasmas (Fujii et al. 2002).

The DR of N_2H^+ possesses two exoergic reaction channels, where the quoted energetics refer to the rovibronic ground states of the reaction participants:

The branching ratio of the DR of N_2H^+ is important for answering the question of whether all of the nitrogen in dense clouds is stored in the form of N_2 , as has been argued for the diffuse cloud NGC 2264 (van Dishoeck et al. 1992). N_2 is inert to reactions with neutral molecules but can react with proton donors (such as H_3^+) to form N_2H^+ :

If the branching ratio of pathway (1a) were 1.0, as has hitherto been assumed, N_2 lost through protonation would be fully recovered by DR. This paper presents a measurement of the branching ratios for the DR reaction of N_2H^+ at collision energies relevant to the interstellar medium.

2. EXPERIMENTAL

The DR experiments have been performed at the heavy-ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm University. The experimental procedure has been described in detail elsewhere (Neau et al. 2000) and is only briefly summed up here. N_2H^+ ions were produced in a hot filament Penning discharge ion source (Nielsen m/57) from a hydrogen-nitrogen mixture. After the ions were extracted from the source at 40 keV, they were mass selected, injected into the ring, and accelerated to 3.31 MeV translational energy. The stored ion beam was merged with a monoenergetic electron beam in an electron cooler, the length of the interaction region

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FIG. 1a

FIG. 1b

FIG. 1.—(a) Energy spectrum of the neutral fragments of the dissociative recombination of N_2H^+ (signal from the surface barrier detector) with the grid (transmission = 0.297) in place. The solid line shows the data, whereas the double-Gaussian fitting curves are shown as dashed lines and the total fit as a dotted line. (b) Energy spectrum of the neutral fragments of the dissociative recombination of N_2H^+ with the grid removed. The solid line shows the data, whereas the double-Gaussian fitting curves are shown as dotted lines and the total fit as dashed line.

being 0.85 m. During the first 4 s after acceleration, the electron and the ion beam were kept at the same average velocity to allow heat transfer from the ion to the electron beam in order to reduce the translational temperature of the ions, which results in an increase of their density in phase space. Furthermore, such storage time enables radiative vibrational cooling of the ions.

Neutral products generated by DR reactions in the electron cooler leave the ring tangentially and were detected by an energy-sensitive silicon surface barrier detector (SBD) with a diameter of 34 mm mounted at a distance of 3.85 m from the center of the interaction region. A background signal due to neutral products emerging from collisions of the ions with residual gas was also present; this was measured with the relative translational energy of ions and electrons tuned to 1 eV, where the DR cross section is very low and neutral fragments are therefore almost exclusively produced by rest gas collisions. This background was subsequently subtracted from the total SBD signal.

2.1. Branching Ratios

The fragments produced by a DR event reached the detector within a very short time interval compared with the integration time of the detection system. The pulse height of the SBD signal was therefore proportional to the kinetic energy carried by the products of the reaction, and therefore to the mass. To measure the branching ratios of the two DR channels, a metal grid with a transmission $T = 0.297 \pm 0.015$ was inserted in front of the detector (Neau et al. 2000). Particles stopped by the grid do not reach the detector, and DR events where one of the fragments has been stopped by the grid results in a signal whose amplitude is proportional to the detected fragment's kinetic energy. The registered DR spectrum therefore splits into a series of peaks with different energies, the intensities of which can be expressed in terms of the branching ratios and the probabilities of the particles passing the grid. For example, the intensity of the 2N peak emerging from reaction (1a) is

proportional to $T(1 - T)\alpha$, with α being the branching ratio of reaction (1a) and $T(1 - T)$ the probability of only the N_2 fragment passing the grid. The energy spectrum of the DR reaction is shown in Figure 1a. The different signal peaks are well resolved but slightly asymmetric. This asymmetry originates from the SBD and increases at higher energies (masses). The peaks were therefore fitted to double-Gaussian functions. As can easily be seen in Figure 1a, the final fitting curve is almost indistinguishable from the data.

Owing to the high-energy release of reaction (1a), some of the hydrogen atoms produced by this pathway might receive a large transversal velocity relative to the propagation direction and therefore miss the detector. This reduces the contribution of reaction (1a) to the $2N + H$ energy channel to $T^2(1 - L)\alpha$, where L is the H-atom loss factor. Conversely, the 2N energy channel is augmented to $T(1 - T)(1 - L)\alpha + T\alpha L$. Using the transmission probabilities mentioned above, the following matrix equation is formulated for the relative intensities of the different energy (mass) channels:

$$\begin{bmatrix} T^2(1 - L) & T^2 \\ T(1 - T)(1 - L) + TL & 0 \\ 0 & T(1 - T) \\ 0 & T(1 - T) \\ T(1 - T)(1 - L) & 0 \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0.151 \\ 0.204 \\ 0.263 \\ 0.262 \\ 0.121 \end{pmatrix}, \quad (3)$$

where α and β are the branching ratios of reaction channels (1a) and (1b), respectively. Clearly the matrix is overdefined, since there are more equations than variables, and therefore a least-squares fit was employed to solve the matrix. To evaluate the loss of the hydrogen atoms, two different methods have been applied. First, an energy spectrum was measured with the grid removed, and this is depicted in Figure 1b. Since for this

case $T = 1$ and $\alpha + \beta = 1$, it can easily be worked out from the above matrix that the ratio between the 2N peak and the 2N + H peak is

$$I_{2N}/I_{2N+H} = \alpha L/(1 - \alpha L). \quad (4)$$

By iteratively solving the matrix with a certain loss and calculating L according to equation (4), the loss of H atoms, L , was determined to be 0.32 and the branching ratios α and β were found to be 0.36 ± 0.05 and 0.64 ± 0.05 , respectively. The loss factor can also be determined from the ratio between the intensity of the 2N channel and the H channel in the measurement with the grid in, which is given by $1 + L/(1 - T)$ ($1 - L$). From this equation, $L = 0.33$ is obtained, which agrees well with the result of the other method.

2.2. Absolute Cross Section and Thermal Reaction Rate

During cross section measurements, the relative translational energy between the ions and the electrons was continuously varied between 1 and 0 eV. This was achieved by changing the cathode voltage of the electron cooler over 1 s from a high value corresponding to a center-of-mass energy of 1 eV, the electrons being faster than the ions, down to a low value also corresponding to 1 eV but where the electrons were slower than the ions. Thus, a voltage corresponding to a center-of-mass energy of 0 eV is reached during the scan. Before the measurement was started, 4 s of cooling, with the electrons tuned to 0 eV collision energy, was carried out. The signal from the SBD was monitored by a single-channel analyzer selecting the signal from all fragments reaching the detector simultaneously and thereafter recorded by a multichannel scaler, yielding the number of counts versus storage time and, therefore, at a given relative translational collision energy.

The experimental DR rate coefficient in the electron cooler is expressed by the formula

$$\langle v_{cm}\sigma \rangle = \left(\frac{dN}{dt} \right) \frac{v_i v_e e^2 r^2 \pi}{I_i I_e l}, \quad (5)$$

where dN/dt is the number of counts per unit time, v_i and v_e are the electron and ion velocities, respectively, r_e is the radius of the electron beam, l is the length of the interaction region, and I_e and I_i are the electron and ion current, respectively. Simultaneously with this measurement, the ion current was monitored using an AC integrating current transformer in combination with a neutral particle/channeltron detector installed in the end of one of the straight sections of the ring. Continuous registration of neutral products of the ion–rest gas collisions also allowed the decay of the ion beam to be monitored during each injection. The following corrections to the measured data had to be performed: (1) The voltage of the electron cooler cathode (and therefore v_e) had to be corrected for space charge effects. (2) The measured rate coefficient $\langle \sigma v_{cm} \rangle$ had to be adjusted because of the toroidal effect (Lampert et al. 1996). This toroidal effect stems from the zones at both ends of the interaction region where the electron beam is bent into or out of the ion beam. In these regions, the transversal electron velocity is higher than in the merged interaction region, leading to larger collision energies. (3) Since the electron beam has (in contrast to the ion beam) a non-negligible energy spread, the measured reaction rate $\langle \sigma v_{cm} \rangle$ has to be deconvoluted according to the formula

$$\langle v_{cm}\sigma \rangle = \int_{-\infty}^{+\infty} v_e f(v_e) \sigma(v_e) d^3 v_e, \quad (6)$$

FIG. 2.—Cross section of the dissociative recombination of N_2H^+ as a function of collision energy. The dashed line shows the best fit with $\sigma = 1.96 \times 10^{-16} E^{-1.07} \text{ cm}^2$.

where $f(v_e)$ is the velocity distribution. (4) Drag force effects (Mowat 1998) were neglected because of the relatively large weight of the investigated ion. The obtained cross section, as a function of the collision energy, is presented in Figure 2. These data are best fitted by the expression $\sigma = (2.4 \pm 0.1) \times 10^{-16} E^{-1.04 \pm 0.02} \text{ cm}^2$. The thermal reaction rate can be deduced from the cross sections by applying the following formula:

$$k(T) = \frac{8\pi m_e}{(2\pi m_e kT)^{3/2}} \int_0^{+\infty} E \sigma(E) e^{-E/kT} dE, \quad (7)$$

where m_e is the mass of the electron. From the resulting rate constants the (comparatively) very small contribution to the data due to charge transfer processes with the rest gas had to be subtracted. Since the cross section of the DR is very low at 1 eV collision energy and the rest gas collisions are independent of the electron velocity, the neutral particles measured at this energy were assumed to be due solely to charge transfer. The temperature dependence of the rate can be fitted by the equation $k(T) = (1.0 \pm 0.1) \times 10^{-7} (T/300)^{-0.51 \pm 0.02} \text{ cm}^3 \text{ s}^{-1}$. This agrees favorably with the value of $1.7 \times 10^{-7} (T/300)^{-0.90} \text{ cm}^3 \text{ s}^{-1}$ obtained in a flowing afterglow Langmuir probe (FALP) experiment (Smith & Adams 1984), at least at room temperature.

3. DISCUSSION

The most striking feature is the high branching ratio of the N–N breakup channel. Notwithstanding the great importance of N_2H^+ in the interstellar medium, no detailed investigation of the DR branching ratio of this molecule has been previously reported, although it was briefly mentioned that the DR branching ratio of reaction (1a) was close to 1 (Adams et al. 1990). Several reasons could account for the prominence of channel (1b). First of all, the possibility of highly excited rotational or vibrational states of the parent ion has to be discussed. The lifetimes of excited states of N_2H^+ have recently been investigated by Heninger et al. 2003. Their calculations yielded a lifetime of 123.1 and 530.1 ms for the ν_2 and ν_3 normal modes, respectively. Both theoretical and experimental studies of the ν_1 mode yielded a lifetime of 1.1 ms (Heninger et al. 1994; Keim et al. 1990).

In addition, the lifetime of different single-mode and combination vibrational levels have been experimentally measured. No lifetime longer than 200 ms has been found. Since the storage time of the ions in the ring is 4 s, vibrationally excited states cannot account for the unexpected branching ratios. High rotational excitation of the ion, on the other hand, would favor the loss of H because of the higher centrifugal force experienced by the hydrogen atom. However, it was found in an infrared spectroscopy study (Kabbadj et al. 1994) that N_2H^+ ions created in a discharge of a mixture of helium, nitrogen, and hydrogen at low pressures are much colder rotationally than vibrationally. Second, the existence of an exit barrier for reaction (1a) has to be investigated. Ab initio calculations predicted a barrier of 10 kcal mol⁻¹ for the $\text{N}_2\text{H} \rightarrow \text{N}_2 + \text{H}$ dissociation (Gu et al. 1998). Such a barrier is marginal compared with the electron affinity of N_2H^+ ; therefore this threshold can easily be surmounted by the system. No information about a barrier in the $\text{N}_2\text{H} \rightarrow \text{NH} + \text{N}$ exit channel is available, although the dominance of this channel indicates that even if such a barrier exists, it is not insurmountable.

Third, since the DR cross section is almost exactly inversely proportional to the collision energy and no resonances are detected, a significant contribution of indirect mechanisms (via N_2H Rydberg states) to the reaction is quite unlikely. This is in contrast to neutralization reactions of N_2H^+ by metal atoms, where the involvement of a highly excited, probably $n = 3$, Rydberg level of the N_2H radical has been observed (Selgren et al. 1989). Furthermore, deuteration has been observed to have a considerable effect on the vibrational distribution of the N_2 product from the DR reaction, suggesting the possible contribution of a tunneling mechanism (Butler et al. 1997).

Finally, there is a possible contamination of the N_2H^+ ion beam by $^{14}\text{N}^{15}\text{N}^+$, which has the same mass and would, if undergoing DR, also lead to products with masses 14 and 15. Although the natural abundance of ^{15}N is only 0.36%, this problem is aggravated by the fact that the ionization cross section of N_2 is about 3 times as large the one of H_2 (Dose et al. 2000; Hudson et al. 2003) under the electron impact energy employed in the present experiment (~ 160 eV). On the other hand, N_2^+ reacts very efficiently with H_2 to form N_2H^+ and H (de Gouw et al. 1995), which leads to an increase in the $\text{N}_2\text{H}^+ / ^{14}\text{N}^{15}\text{N}^+$ ratio. To get insight into this ratio, a mass spectrum was taken under the conditions employed in the experiment and the $^{14}\text{N}^{15}\text{N}^+$ contamination was worked out from the ratio between the $^{14}\text{N}_2^+$ peak and the one at $m/z = 29$, assuming equal ionization cross sections for the different isotopomers of the nitrogen molecule ion. This yielded a maximal contamination of 8% of the N_2H^+ ion beam with $^{14}\text{N}^{15}\text{N}^+$ under the experimental conditions. Since the DR cross sections of N_2^+ and N_2H^+ are very similar (Peterson et al. 1998), isotopic contamination cannot considerably change the experimental result.

Considering direct mechanisms, the question arises as to which doubly excited state is formed. If the electron enters an antibonding orbital of the $\text{N} \equiv \text{N}$ triple bond and excites one of the bonding electrons to an antibonding level, the $\text{N}-\text{N}$ bond will be considerably weakened and a rupture of the $\text{N}-\text{N}$ bond more likely. It should be noted here that the fracture of multiple bonds has also been observed in other systems. For example, in the somewhat related DR of C_2H_2^+ a considerable contribution of the $\text{CH} + \text{CH}$ product channel has been found (Derkatch et al. 1999).

4. ASTROPHYSICAL IMPLICATIONS

Two important astrophysical implications of the measured branching ratios can be inferred: (1) the role of the title reaction in the production of NH in interstellar clouds and (2) its contribution in destroying N_2H^+ in these environments.

The NH radical was first detected through its optical absorption at 335.8 nm in diffuse interstellar clouds by Meyer & Roth (1991), with column densities typically an order of magnitude or more greater than those predicted by the most comprehensive chemical models of such sources (van Dishoeck & Black 1986). In their models, however, nitrogen chemistry was initiated by the unusual reaction

which is now known not to proceed. Instead, the chemistry of nitrogen-bearing molecules in diffuse clouds must be initiated through the cosmic-ray ionization of N atoms, followed by the slightly endothermic reaction (Adams et al. 1984)

followed by successive fast reactions with H_2 to form NH_2^+ and NH_3^+ . The reaction of NH_3^+ with H_2 is relatively slow with a rate coefficient of around 2×10^{-13} cm³ s⁻¹ at the temperatures of diffuse clouds (Adams & Smith 1984), so dissociative recombination rather than reaction with H_2 is the dominant loss for NH_3^+ . This produces NH and NH_2 , whose photodissociation also produces NH. Wagenblast et al. (1993) investigated detailed diffuse cloud chemical models that ignored the $\text{H}_3^+ + \text{N}$ reaction and found that the abundance of NH calculated was a factor of 30 or so less than that observed. They suggested that the NH detected in diffuse clouds owed its origin to grain surface chemistry, either directly or indirectly as a photodissociation product of grain-produced NH_3 . This conclusion is somewhat unsatisfactory given our lack of knowledge in quantifying surface chemistry and given that NH is the only molecule detected in diffuse clouds, with the exception of H_2 , for which grain-surface rather than gas-phase synthesis seems necessary.

Our new branching channel to NH from N_2H^+ provides a new route to NH in diffuse clouds, which may dominate its formation and remove the discrepancy with observation. Unfortunately, published diffuse cloud models do not tabulate N_2 and N_2H^+ abundances, so we cannot answer this point; detailed calculations on diffuse cloud chemistry are required.

We have, however, been able to test the effect of the new branching ratios on models of the chemical evolution of dark clouds having $T \sim 10$ K, $n(\text{H}_2) \sim 10^4$ cm⁻³, and a cosmic ionization rate of 5×10^{-17} s⁻¹ using a standard model (Markwick et al. 2000). In this calculation we have adopted a value for C/H of 7.3×10^{-5} , a value used in many calculations of dark cloud chemistry and about a factor of 2 less than the average value of $(1.4 \pm 0.2) \times 10^{-4}$ observed in the gas phase of seven diffuse interstellar clouds (Sofia et al. 1997). Table 1 and Figure 3 summarize our results for some of the N-bearing species. RATE99 refers to the standard branching widely adopted, all recombinations leading to N_2 with the total dissociative recombination rate coefficient taken from Smith & Adams (1984), which gives a value at 10 K of 3.63×10^{-6} mol⁻¹ cm³ s⁻¹. The results show that the dissociative recombination of N_2H^+ to yield NH provides a significant new route to NH formation, with the fractional abundance of this molecule increasing by about 5 at early time and a

TABLE 1
FRACTIONAL ABUNDANCE OF SELECTED SPECIES

SPECIES	EARLY TIME (3.16×10^5 yr)		STEADY STATE	
	RATE99	This Work	RATE99	This Work
N.....	4.12(−5)	4.13(−5)	3.16(−5)	3.31(−5)
NH.....	3.46(−11)	1.99(−10)	3.56(−10)	2.44(−9)
N_2	7.55(−7)	7.10(−7)	5.54(−6)	4.80(−6)
N_2H^+	1.89(−11)	4.38(−11)	2.53(−10)	4.50(−10)
NH_3	4.06(−9)	3.92(−9)	4.56(−8)	4.03(−8)

factor of 7 at steady state. Since N_2H^+ has a relatively low proton affinity, it can also be destroyed in proton transfer reactions with neutral molecules, the most important of which is CO. In RATE99, dissociative recombination dominates because of the large value of the dissociative recombination rate coefficient. With our new rate coefficients, which are about a factor of 6 slower at 10 K, the abundance of N_2H^+ increases by about a factor of 2. The fractional abundances of N_2H^+ and NH_3 observed in TMC-1 of $(1.2-5) \times 10^{-10}$ and $(1.1-2) \times 10^{-8}$, respectively (Pratap et al. 1997; Ohishi & Kaifu 1998) agree very well with those derived here in Table 1.

Dissociative recombination of N_2H^+ will be a more significant source of NH in clouds in which CO is depleted. One such cloud is L1544, for which a depletion of CO greater than 98% has been inferred (Caselli et al. 2003). It has long been recognized that such “depleted cores” will have a very high fractionation in H_2D^+/H_3^+ for the same reason (Brown & Millar 1989). If N_2 , because of its greater volatility, remains in the gas phase while CO is depleted, then the abundances of both N_2H^+ and N_2D^+ can be large, as can their fractionation. Indeed, in L1544, $N_2D^+/N_2H^+ \sim 0.2$ (Caselli et al. 2002) and $H_2D^+/H_3^+ \sim 2$ (Caselli et al. 2003), the largest ratio known. The physical conditions in L1544 also lead to efficient multiple deuteration; Roberts et al. (2003) find that the abundances of D_2H^+ and D_3^+ are larger than that of H_3^+ .

The presence of abundant N_2H^+ and N_2D^+ in depleted cores means that dissociative recombination to NH and ND dominates over loss through proton transfer to N_2 . A number of consequences follow: (1) dissociative recombination is essentially the only effective route to NH and ND, and their production rates and fractional abundances will be much larger than previously calculated; (2) the fractionation in ND/NH should reflect that in N_2D^+/N_2H^+ , that is, be larger than 0.1; and (3) incomplete recycling of N_2H^+ to N_2 will eventually lead to the freezeout of nitrogen as NH and ND accrete on to the dust grains. Some evidence for this latter process comes from the work of Bergin et al. (2002), who show that the abundance of N_2H^+ (and by inference N_2) decreases in the central, high-extinction core of the B68 dark cloud.

Dissociative recombination of N_2H^+ and N_2D^+ could lead to detectable quantities of NH and ND in depleted cores. Unfortunately, the lowest rotational transition of NH lies near 1 THz and is inaccessible from the ground. However, ND does have observable lines. Its submillimeter spectrum has been measured by Saito & Goto (1993), who showed that the $N = 1-0$ transition, which is split into fine and hyperfine components, lies in the 490–550 GHz range. In particular, the $N, J = 1, 0-0, 1$ transition has six hyperfine transitions

FIG. 3.—Calculated evolution of abundances of some N-bearing species in a dark molecular cloud with $T \sim 10$ K and $n(H_2) \sim 10^4$ cm $^{-3}$ using a standard model employing the widely adopted RATE99 rate coefficient for the dissociative recombination of N_2H^+ (dashed lines) and using the results obtained in this work (solid lines).

near 490.95 GHz, close to the $^3P_1-^3P_0$ transition of C I. A search for ND in depleted cores having strong N_2D^+ lines—L1544, B68, and IRAS 16293E are examples—might prove rewarding.

Another important question is the importance of the DR reaction in the breakdown of N_2H^+ and, consequently, of N_2 . In the photodissociation region NGC 7023, a decline in the fractional abundance of N_2H^+ with decreasing visual extinction has been detected (Fuente et al. 1993). In this environment, dissociative recombination is seen as the main destruction pathway for N_2H^+ . In this light, it is also interesting to compare the abundance of N_2H^+ and HCO^+ in small translucent clouds, such as Clemens-Barvainis (CB) objects, which have been surveyed recently (Turner 1995). Whereas HCO^+ is found in all of the CB objects investigated, N_2H^+ is only abundant in one of them (CB 17), which also exhibits an unusually large column density. The authors ascribe this to the absence of photoprocesses in the “dark” regions with highest $A_{v,0}$. However, since the DR of HCO^+ (unlike in N_2H^+) almost exclusively leads to $CO + H$ (W. D. Geppert et al. 2004, in preparation), HCO^+ lost through DR can therefore be recovered by protonation of CO. The different DR branching ratios for HCO^+ and N_2H^+ might therefore explain the different abundances of these two ions in these objects. We hope that further astronomical observations of other systems will clarify this point.

The authors want to thank the Swedish Research Council for funding. W. D. Geppert acknowledges the European Union (EU) for granting a Marie Curie Individual Fellowship under the EU program “Improving Human Potential,” contract number HMPF-CT-200201583. Support from the EU IHP Research Training Network program under contract HPRN-CT-2000-0142 is also acknowledged. Astrophysics at UMIST is supported by a grant from PPARC. The authors also want to thank the staff at Manne Siegbahn Laboratory for excellent technical assistance.

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