

Dissociative Recombination of the Ground State of  $N_2^+$ 

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**Abstract.** Large scale theoretical quantum chemical calculations are reported for the dissociative recombination with an electron of the lowest vibrational level of the ground state of the nitrogen molecular ion. The calculated dissociative recombination rate is  $1.6 \times 10^{-7} \times (T_e/300)^{-0.37} \text{ cm}^3/\text{sec}$  for  $100 < T_e < 1000 \text{ K}$  and is in excellent agreement with prior microwave afterglow experiments but disagrees with recent merged beam results. The dissociation limit yields mostly  $^3\text{S} + ^2\text{D}$  atoms in disagreement with plasma flow tube results. The dominant mechanism for dissociative recombination imparts sufficient energy to the product atoms to allow for escape from the Martian atmosphere.

## Introduction

Dissociative Recombination (DR),



is a major sink for  $N_2^+$  in the Earth's ionosphere [Torr and Torr, 1979]. A long standing problem in aeronomy is that the  $N_2^+$  concentration in ionospheric models is about a factor of two in excess of measured concentrations [Torr and Torr, 1982; Abdou et al., 1984]. An increase in the DR rate coefficient over the laboratory value [Mehr and Biondi, 1969; Zipf, 1980] by a factor of 2-3 has been proposed as a possible resolution of this problem [Abdou et al., 1984].

DR of  $N_2^+$  is an important source of  $N(^2\text{D})$  [Strobel et al., 1976; Rusch et al., 1975], the upper state of the 5200A emission, and atmospheric models report a quantum yield between one and two [Frederick and Rusch, 1977].

DR can impart sufficient kinetic energy to the product atoms to allow for escape from the Martian atmosphere [McElroy, et al., 1976; Fox and Dalgarno, 1980; Fox and Dalgarno, 1983; Fox, 1989]. However, of the possible asymptotes for DR of  $v=0$  with low energy electrons,  $^3\text{S} + ^2\text{D}$ ,  $^3\text{S} + ^2\text{P}$ , and  $^2\text{D} + ^2\text{D}$ , only the first limit can impart enough energy for escape. The energetics also allow DR from  $v=0$  to affect the  $^{15}\text{N}:^{14}\text{N}$  isotope ratio.

Laboratory measurements of the total DR rate have been reviewed by Johnsen [1987, 1989]. A microwave afterglow experiment [Mehr and Biondi, 1969] obtained a total rate of  $1.8(+0.4, -0.2) \times 10^{-7} \times (T_e/300)^{-0.37}$ . Additional microwave afterglow measurements by Zipf [1980] agreed with the earlier results but about 10% of the ions are thought to be vibrationally excited [Johnsen, 1987, 1989]. Merged beam [Mul and McGowan, 1979]

results have been recently corrected by C. Noren, et al. [1989] and are in agreement with the microwave afterglow results but have an exponent for the temperature dependence of -0.5. Earlier shock tube measurements [Cunningham and Hobson, 1972] are in good agreement with the microwave afterglow results. Recent merged beam results [Mitchell and Yousif, 1989; C. Noren, et al., 1989] for the total rate are about a factor of five lower than the microwave afterglow results. A plasma flow tube experiment has reported that recombination of the  $v=0$  level of the ion proceeds to  $N(^2\text{D})$  with a quantum yield higher than 1.85 [Queffelec et al., 1985; Rowe et al., 1989].

We report here the first large scale calculations of the DR cross sections and rates for the  $v=0$  level of the  $N_2^+$  ground state. The important role played by vibrationally excited Rydberg states lying both below and above the  $v=0$  level of the ion is demonstrated.

## Method

The large scale electronic wave function calculations needed for the determination of the potential curves that describe the dissociative routes have been calculated in triple zeta plus polarization, nuclear centered valence Gaussian basis sets. Orbitals have been determined in Complete Active Space Self Consistent Field Calculations (CASSCF) [Siegbahn et al., 1980] and large configuration interaction (CI) wave functions were constructed by taking all single and double excitations from all the CASSCF configurations to the full virtual space [Siegbahn, 1980]. Details of the calculations will be reported separately. In the case of the  $^3\Pi_u$  states this approach leads to wave functions having over a million terms.

The electronic widths needed for calculation of the cross section were obtained using smaller scale wave functions. The method, which has been described elsewhere [Guberman, 1987, 1988, 1989], uses a large set of diffuse Gaussians placed at the molecular midpoint. Rydberg states with high principal quantum numbers,  $n$ , are obtained in Improved Virtual Orbital [Hunt and Goddard, 1969] calculations and the width matrix elements are calculated with the high  $n$  Rydberg wave functions representing the continuum electron.

The cross sections have been calculated using Multichannel Quantum Defect Theory (MQDT) [Guberman and Giusti-Suzor, 1991]. The approach is similar to that used earlier [Giusti, 1980] except that instead of approximating the K matrix as  $K=V$  where  $V$  is the matrix of electronic couplings we now use  $K=V + VGK$  and retain the second order terms in the second term on the right hand side.  $G$  is a Green operator. The approach includes simultaneously both direct recombination [Bates, 1950] in which electron capture only populates the dissociative state and indirect recombination [Bardsley, 1968] in which vibrationally excited

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neutral Rydberg resonance states can be populated prior to predissociation by the dissociative route. Below, we show that interference between direct and indirect recombination leads to considerable structure in the DR cross section. The Rydberg states can be populated by both vibronic excitation (Born-Oppenheimer breakdown) and by second order electronic coupling [Guberman and Giusti-Suzor, 1991]. Both mechanisms are accounted for here.

### Results

The dissociative states involved in the DR of the  $v=0$  level of  $N_2^+$  [Guberman, 1989] are the  $C'^3\Pi_u$  ( $2^3\Pi_u$ ),  $3^3\Pi_u$ ,  $2^1\Sigma_g^+$ , and  $G^3\Delta_g$  states. In the prior discussion [Guberman, 1989], consideration of the primary configurations in these states indicated that the  $^3\Pi_u$  states are likely to have the largest widths for electron capture. These widths have now been calculated in this laboratory and we find that at  $R=2.0$  Bohr the electron capture width for  $C'^3\Pi_u$  is  $0.13\text{eV}$ , compared to  $0.002\text{eV}$  for  $3^3\Pi_u$ . In addition, the calculated width for the  $C'$  state is about 4 orders of magnitude larger than that for  $G^3\Delta_g$  and a factor of about 3 larger than the width for  $2^1\Sigma_g^+$ . Since the direct recombination cross section is approximately proportional to the electron capture width and since the statistical weight for capture into  $^3\Pi_u$  is six times higher than that for  $^1\Sigma_g^+$ , only the  $C'$  state is expected to play an important role in the recombination of  $v=0$ . Therefore, in the calculations reported here we have neglected all of the above states except for  $C'$ , the upper state of the Goldstein-Kaplan bands [Carroll, 1963]. Additional details concerning the calculated widths and the variation with  $R$  will be reported separately. The calculated  $^3\Pi_u$  potential curves are shown in Figure 1. The  $C'$  state consists of the outer well in the lowest adiabatic  $^3\Pi_u$  state (labelled C at the inner minimum) and the repulsive wall of the  $2^3\Pi_u$  state connected in a diabatic manner by the dotted line in Figure 1. There is an avoided crossing between the lowest two adiabatic states near  $R=2.6$  Bohr. A Landau-Zener calculation indicates that for dissociation beginning at the  $v=0$  level of the ion on the  $C'$  ( $2^3\Pi_u$ ) curve, there is an 88% probability that the avoided crossing is traversed leading to  $S + ^2D$  atoms. This is in agreement with Helm and Cosby [1989] who found a 94% probability for traversing the avoided crossing in a diabatic manner after predissociation of a Rydberg state. Therefore, in the calculations reported here we have used a diabatic dissociative  $C'$  curve. The dotted region of the curve shown in Figure 1 is determined by the spline fit between the calculated points at 2.5 Bohr in the upper state and 2.7 Bohr in the lower state. The importance of the  $C'$  state in the DR of  $v=0$  is in agreement with prior results of Michels [1972]. Figure 1 also shows the calculated  $3^3\Pi_u$  and  $4^3\Pi_u$  valence states. The  $3^3\Pi_u$  state crosses the large  $R$  turning point of  $v=0$  but has a very small electron capture width as pointed out above. The  $4^3\Pi_u$  state has a width that is about a factor of 4 lower than that for  $C'$  and will be important in the calculation of DR from  $v=1$ .

The calculated cross sections along the diabatic  $C'^3\Pi_u$  route are shown in Figure 2. The dashed line shows the direct cross section, i.e.

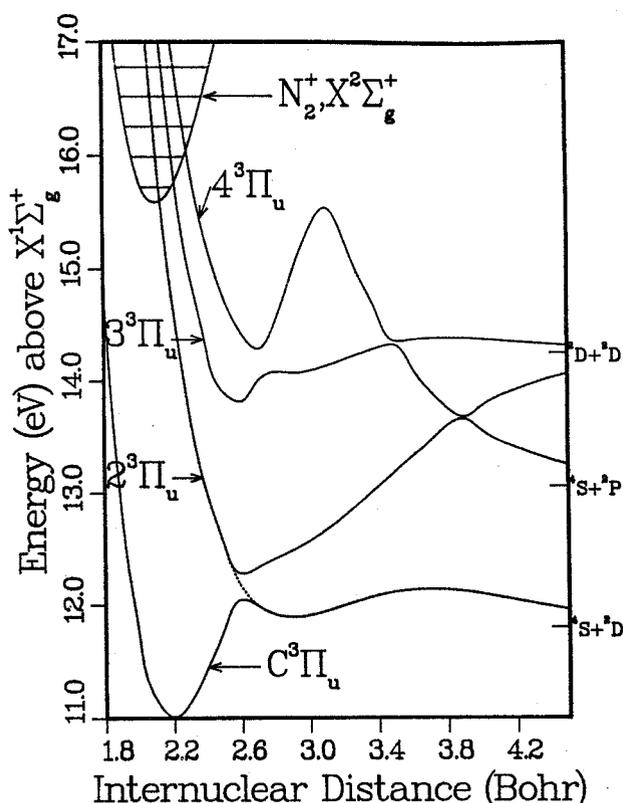


Fig. 1. The calculated  $^3\Pi_u$  potential curves and the ground state ion curve (Lofthus and Krupenie, 1977). The diabatic  $C'^3\Pi_u$  state consists of the  $2^3\Pi_u$  state for  $R \leq 2.5$  Bohr and the lowest  $^3\Pi_u$  state for  $R \geq 2.7$  Bohr connected by the dotted segment.

the cross section in the absence of the intermediate neutral Rydberg resonances. The direct cross section was calculated using Eq.(30) in A. Giusti [1980]. The full cross section is shown as the solid line. The full cross section is below the direct cross section at threshold energies due to an  $n=3$ ,  $v=10$  resonance lying about

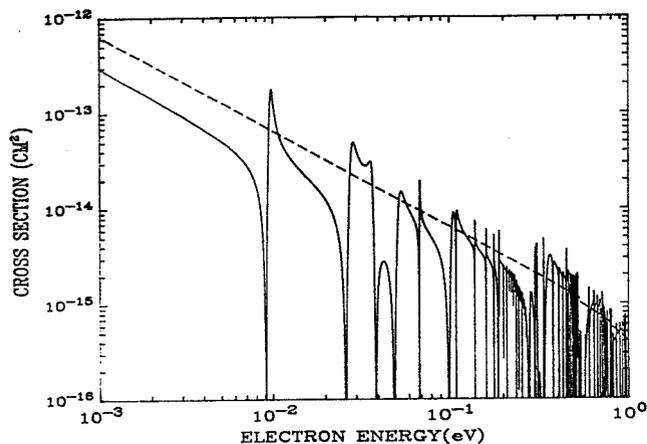


Fig. 2. The DR cross section along the  $C'^3\Pi_u$  state. The direct cross section (dashed line) without the Rydberg resonances and the full cross section (solid line) are shown.

0.15eV below threshold. Near 0.009eV, an  $n=8, v=1$  resonance having a shape characteristic of a positive Fano profile index [Fano, 1961] is seen. The position of this resonance agrees well with the experimental observations of the position of the  $8p^3\Pi_u + 9p^3\Sigma_u^+$  complex [Helm and Cosby, 1988; Sharpe and Johnson, 1986], lying only 0.003eV below the latter. The double peak in the cross section near 0.03eV is due to interference between  $n=4, v=5$  having a positive Fano profile index and  $n=6, v=2$  with a negative profile index. An  $n=5, v=3$  resonance lies very close to  $n=6, v=2$  causing additional interference in the 0.04-0.05eV region. Just below 0.07eV we find a peak due to  $n=9, v=1$  which interferes on the high energy side with  $n=3, v=11$ .

The calculated rates are shown in Figure 3 for both the direct recombination (dashed line) and full recombination including the resonances (solid line). Indirect recombination through the resonances interferes with direct recombination, leading to a full rate that is about 39% below the direct rate at 300K. The full rate is well represented for  $100 < T_e < 1000$  by  $\alpha = 1.6 \times 10^{-7} \times (T_e/300)^{-0.5}$  cm<sup>3</sup>/sec in excellent agreement with the prior microwave results of Mehr and Biondi [1969] and Zipf [1980]. The direct rate has a calculated temperature exponent of -0.50 which is expected for a steep dissociative route. The deviation of the full rate temperature dependence from -0.50 is due to the intermediate Rydberg resonances. The results reported here do not support the recent merged beams [Mitchell and Yousif, 1989; C. Noren, et al., 1989] cross section that is a factor of five lower than the microwave afterglow derived cross sections. However, it is interesting to note that the reported merged beams cross section shows some evidence for resonances near 0.01eV, 0.1eV, and 0.6eV which is near the structure shown in Figure 2.

Because of the 88% probability of dissociating to the  $^4S + ^2D$  limit, the quantum yield for generating  $^2D$  along this route is 0.88. This route yields atoms with 1.72eV kinetic energy. An additional Landau-Zener calculation at the  $R=3.9$  Bohr crossing of the 2 and  $3^3\Pi_u$  curves indicates that the remaining 12% will all go to the  $^2D + ^2D$

limit. This path yields  $^2D$  atoms with a quantum yield of 0.24 and a lower kinetic energy of 0.53eV per atom. Therefore, the total quantum yield for generating  $^2D$  from the  $v=0$  ion level is 1.12. This compares well to the yield calculated by Michels [1972] of 1.08. Coupling of the 2 ( $C'$ ) and  $4^3\Pi_u$  routes via Rydberg states could alter this quantum yield but the effect is expected to be small. This coupling has been neglected here. The potential curves of Figure 1 indicate that recombination of  $v=1$  can produce a significantly different quantum yield for  $^2D$  than DR from  $v=0$  since the  $4^3\Pi_u$  route will have a nonnegligible Franck Condon factor with  $v=1$ . Indeed one can expect an interesting variation of the  $^2D$  quantum yield and the atomic kinetic energies with vibrational excitation. The results reported here do not support the high quantum yield of 1.85 deduced from plasma flow tube experiments [Queffelec, et al., 1985; B. R. Rowe et al., 1989]. However, the high experimental quantum yield may be appropriate to  $v>0$  as discussed above.

Escape from the Martian atmosphere requires that each N atom have 1.74eV kinetic energy [Fox, 1989]. The primary dissociation asymptote found in this study,  $^4S + ^2D$ , leads to N atoms with 1.72eV kinetic energy and enough energy to escape after consideration of the ion translational and electron temperatures. Dissociation to the other asymptotes,  $^2P + ^2D$  and  $^2D + ^2D$  does not provide sufficient energy for escape after DR of the low vibrational levels. Atmospheric escape will have a high probability from  $v=0$  since the mechanism involves the primary DR route for  $N_2^+$ . Furthermore, since  $N^{15}$  requires 1.86eV to escape [Fox, 1989], an isotope enhancement effect will occur from DR of  $v=0$ . The current study shows that DR plays a much more significant role in Martian atmospheric escape and isotope enhancement than that shown by the plasma flow tube experiment.

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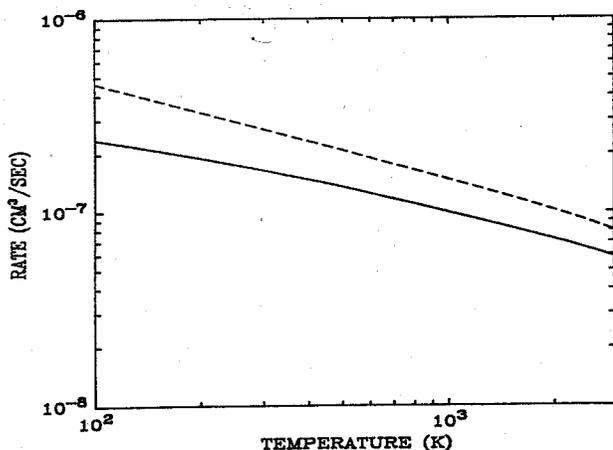


Fig. 3. The DR rate for the cross section shown in Figure 2. The direct rate (dashed line) and the full rate (solid line) are shown.

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