



Radiative lifetimes for $^{29}\text{N}_2^+$ and implications for planetary escape and isotope enrichment



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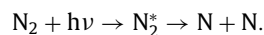
ABSTRACT

The Viking missions to Mars found that $^{15}\text{N}/^{14}\text{N}$ is enhanced by a factor of 1.62 compared to Earth and it was suggested that the cause was dissociative recombination (DR) of N_2^+ . The high kinetic energy imparted to N in DR drives atmospheric escape. More recent models of the Martian ionosphere show that much of the N_2^+ is vibrationally excited. If DR of vibrationally excited $^{29}\text{N}_2^+$ is important, the energetics are such that the isotope enhancement would be greatly reduced. Here I show that at the Mars exobase electron temperature and density, the excited vibrational levels of $^{29}\text{N}_2^+$ radiate before they can recombine. The isotope enhancement arising from DR is due entirely to DR of $^{28}\text{N}_2^+$ with a small contribution to ^{14}N escape arising from DR of the ground vibrational level of $^{29}\text{N}_2^+$.

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1. Introduction

After the early Mariner Mars mission found no atmospheric N_2 (Barth et al., 1969), the questions arose: “Mars: Is Nitrogen Present?” (Dalgarno & McElroy, 1970) and “Mars: Has Nitrogen Escaped?” (Brinkmann, 1971). In order to reconcile the Mariner data with the N_2 density expected from surface outgassing, Brinkmann (1971) suggested that energetic N atoms had escaped the planet via photodissociation in which solar radiative excitation of N_2 is followed by predissociation, i.e.



Brinkmann (1971) also briefly mentioned that dissociative recombination (DR) of N_2^+ could contribute, i.e.



McElroy (1972) suggested DR of N_2^+ and the solar wind as sources of fast N and recognized that the products of DR can have kinetic energies that are high enough for atmospheric escape. Using the N_2 potential curves of Michels (1976) which showed that the important escape channel on the right side of Reaction (1) is not that which generates ground state atoms but instead $\text{N}(^4\text{S}) + \text{N}(^2\text{D})$, McElroy et al. (1976) suggested that an enhancement of ^{15}N over ^{14}N , as observed by the Viking 1 mission, could occur from DR or electron impact. The importance of

the $\text{N}(^4\text{S}) + \text{N}(^2\text{D})$ asymptote is confirmed by more recent theoretical calculations (Guberman 2012, 2013, 2014). A model (Nier & McElroy, 1977) based upon data returned from the Viking missions found that $^{15}\text{N}/^{14}\text{N}$ at Mars is larger than it is at Earth by a factor of 1.62 ± 0.16 and is much larger than the analogous factor observed for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ (Nier & McElroy, 1977). They attributed the enhancement to escape of ^{14}N . McElroy et al. (1977) and later Fox & Hać (1997) showed that diffusive separation in the gravitational field of Mars does not account for the high degree of isotope enrichment. Taking $\text{N}(^4\text{S}) + \text{N}(^2\text{D})$ as the main dissociative channel, Wallis (1978) found that ^{15}N from DR of $^{29}\text{N}_2^+$ had a 23.7% probability of escape but ^{14}N from DR of $^{28}\text{N}_2^+$ had a 46.1% probability if all recombination arises from the ground vibrational level of these ions. A later model (Fox & Dalgarno 1983) including improved N_2^+ densities identified DR as the major escape mechanism. Fox (1993) found that DR is the dominant escape mechanism at high solar activity and that DR and photodissociation are of comparable importance at low solar activity. Fox and Hać (1997) determined the escape fraction of ^{15}N and ^{14}N atoms arising from DR and took into account the thermal spread of ion and electron energies. They reported 15% and 29% escape probabilities for ^{15}N and ^{14}N respectively, about 63% of the Wallis (1978) values. They found that the isotope enhancement decreased as ν increased.

The enhancement for the $\nu = 0$ ion arises because of the difference in Reaction (1) atomic kinetic energies for the $^{28}\text{N}_2^+$ and $^{15}\text{N}^{14}\text{N}^+$ ions, assuming that the DR rate constants are similar. The energetic difference arises mostly from conservation of energy and

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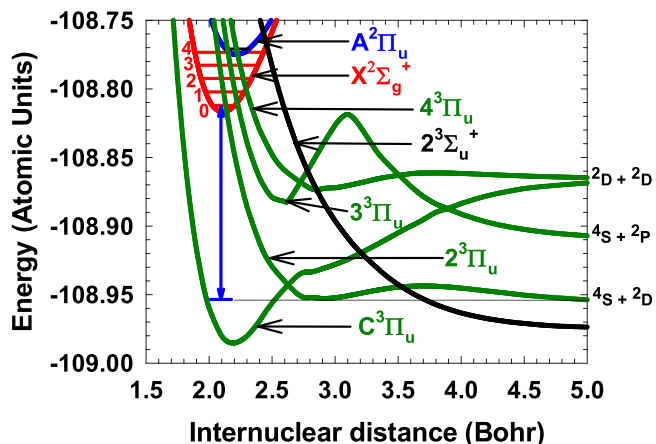


Fig. 1. Major potential energy curves of N_2 (green and black) describing the atmospheric escape of N from the DR of N_2^+ . The lowest 5 vibrational levels of the ion ground state (red) are shown with the first excited ion state (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

momentum by the DR products. From the $v = 0$ ion level at low electron energies, the energetics allow ^{14}N to escape from the Martian exobase but not the ^{15}N (see below). A model (Fox & Dalgarno 1983) found that at the exobase, 40% of the recombining N_2^+ is vibrationally excited. As the ion vibrational excitation increases, the atomic kinetic energies of Reaction (1) increase and isotope enrichment decreases. For excited vibrational levels, the rate of radiative relaxation (Wu, 1952; Ellison, 1962) can be competitive with the rates of the DR reactions. Excited vibrational levels of homonuclear diatomic ions have very long lifetimes because of the absence of a dipole moment. However, isotopomers of these ions possess a dipole moment and radiate with lifetimes of the order of seconds (Wu, 1952; Ellison, 1962). The $^{29}N_2^+$ lifetimes have not appeared in the literature. In this paper, I show that the calculated decay lifetimes of $^{29}N_2^+$ excited vibrational levels are short enough so that at Mars vibrational excitation does not affect the degree of isotope separation.

The focus upon DR here should not be interpreted to mean that DR is the only important escape and isotope enhancement mechanism. Many of the models have included additional mechanisms such as photon and electron impact dissociative ionization, ion-molecule reactions and pickup ion sputtering (Jakosky et al., 1994). However, the models uniformly show that DR is a major if not the dominant mechanism for N isotope fractionation and escape.

It is beyond the scope of this paper to present a detailed model of Martian isotope enhancement. Instead, it is suggested that vibrational radiative transitions of $^{29}N_2^+$ need to be included in future models of the Martian ionosphere. The DR routes and energetics for isotope enhancement are in the next Section. Section 3 has the calculation of the radiative transition lifetimes. The implications of these results for Martian escape are in Section 4. Section 5 has the conclusions.

2. Mechanism

The major potential curves (see Guberman (2012, 2013, 2014)) that govern the DR escape mechanism are shown in Fig. 1. The states of the separated atoms are shown on the right side of the Figure. Additional dissociative states contribute to the total DR rate constant but are not involved in escape either because the rate constants are too small (see Guberman (2012, 2013, 2014)) or insufficient energy is imparted to the product atoms to allow for escape from the Martian exosphere. Dissociation proceeds by capture of an electron by the ion ground state (red in Fig. 1)

into one of the neutral dissociative states (green and black), by capture of the electron into a neutral Rydberg level (not shown) followed by predissociation along the dissociative routes and by other mechanisms described previously (Guberman, 2003, 2007). The highest energy release from DR of the $X^2\Sigma_g^+$ vibrational levels would occur if there were a favorable dissociative route leading to two ground state (4S) atoms. Analysis of all potential dissociative routes (Michels, 1976; Guberman, (2012, 2013, 2014)) shows that such a route is not present. The highest kinetic energy imparted to the dissociating atoms from $v = 0$ occurs by dissociation to the first excited limit, $N(^4S) + N(^2D)$. Because the ion ground state has doublet spin symmetry only singlet and triplet spin states can be formed by electron capture. However, the $N(^4S) + N(^2D)$ limit cannot form singlet molecular states. Among the remaining states, $W^3\Delta_u$, $G^3\Delta_g$, $2^3\Pi_u$, $B^3\Pi_g$, $1^3\Sigma_g^+$ and $2^3\Sigma_u^+$, prior calculations (Guberman, 1991, 2012, 2013, 2014) have shown that only the $2^3\Pi_u$ and $4^3\Pi_u$ states contribute more than 1×10^{-8} cm³/sec to the total $v = 0$ rate constant for electron temperatures between 100 and 3000 K. Four $^3\Pi_u$ states are shown (green) in Fig. 1. Dissociation from $v = 0$ to $^4S + ^2D$ atoms releases a total energy corresponding to the vertical double arrowed blue line. The total released is slightly different (0.002 eV) for the isotopomers because the vibrational levels of $^{29}N_2^+$ are lower in the potential well than those of $^{28}N_2^+$. The kinetic energy imparted to each atom is governed by conservation of energy and momentum. At the Martian exobase (200 km), the electron energy used in models is about 0.172 eV (2000 K) (Fox & Hać 1997). The recent MAVEN mission found a mean energy of 0.084 eV at 200 km (Ergun et al., 2015) and reaches the 0.172 eV value at about 250 km. The energetics given below are for the 0.172 eV value. The MAVEN value does not change the escape scenario with the exception of a slight change in escape altitude for ^{15}N from $v = 1$ of $^{29}N_2^+$ (see Section 2.2 below). Escape from the exobase requires 1.844 eV for ^{15}N and 1.722 eV for ^{14}N (Fox & Hać 1997).

2.1. $^{28}N_2^+$

From $v = 0$ of $^{28}N_2^+$ at zero electron energy, dissociation to $^4S + ^2D$ atoms releases 1.719 eV/atom. Adding half the electron energy at the exobase yields a release of 1.805 eV/atom and these atoms escape as can the more energetic atoms arising from DR of $v = 1 - 4$ (if the ion does not radiate prior to DR, see below). For $v = 4$, $2^3\Sigma_u^+$ (shown as the black curve in Fig. 1) provides an additional route to $^4S + ^2D$. DR from $v = 0 - 3$ to the next highest asymptote, $N(^4S) + N(^2P)$ does not impart enough kinetic energy for escape. However, from $v = 4$, 1.736 eV is imparted to each atom arising from $^{28}N_2^+$ DR to $N(^4S) + N(^2P)$. This limit gives rise to triplet and quintet spin states. The latter cannot be DR routes from the doublet ion. The only routes with large enough rate constants (Guberman, 2014) are dissociative paths with multiple curve crossings that start along the $2^3\Pi_u$, $3^3\Pi_u$, and $4^3\Pi_u$ curves.

The potential curves in Fig. 1 are shown in a diabatic representation in which curves of the same electronic symmetry are allowed to cross. At such a crossing, the dissociating atoms can remain on the same potential curve or jump to the intersecting curve. In diabatic passage through a crossing, the motion of the dissociating atoms is described by the same potential curve on both sides of the crossing, i.e. the electrons do not readjust. In adiabatic passage, the motion jumps to the intersecting potential curve and the electron cloud adjusts to the new potential. At intersections between curves of different electronic symmetry, the motion of the dissociating atoms remains on the initial curve because the interaction that connects the curves is very small.

DR to $^4S + ^2D$ atoms initially proceeds along the $2^3\Pi_u$ curve and passes diabatically through a crossing near 2.6 a_0 with $C^3\Pi_u$.

Table 1

DR rate constants (cm³/sec)* of N₂⁺ to the 4S+2D limit along the 2³Π_u state (multiplied by the applicable Landau-Zener factor) for vibrational level *v* at 2000 K electron temperature. For *v* = 4, the 2³Σ_u⁺ contribution is given and the 3³Π_u contribution is for all the mechanisms discussed in the text, not just for 2³Π_u.

<i>v</i>	²⁸ N ₂ ⁺	²⁹ N ₂ ⁺
0	0.55	0.60
1	0.072	0.060
2	0.20	0.23
3	0.21	0.22
4	0.12(³ Π _u) + 0.062(³ Σ _u ⁺)	0.11(³ Π _u) + 0.057(³ Σ _u ⁺)

*Multiply the listed rate constants by 10⁻⁷. For *v* = 4, the rate constant is the sum of the 3³Π_u and 3³Σ_u⁺ values.

The Landau-Zener probability (Landau, 1932; Zener, 1932), *P*, for staying on the diabatic dissociative state at a crossing of potential curves is given by:

$$P = e^{-\frac{4\pi^2|\beta|^2}{\hbar v|\alpha|}} \quad (2)$$

where β is 1/2 of the energy difference between the adiabatic curves (Guberman, 2014) at the avoided crossing, α is the difference in the slopes of the diabatic curves at the crossing and *v* is the velocity of the atoms at the crossing. The velocity is determined by the conservation laws and differs for the isotopomers. For *v* = 0, the calculated DR rate constant (Table 1) along 2³Π_u discussed below is multiplied by *P* = 0.880 to get the appropriate rate for DR to this limit. (Guberman, 1993). For *v* = 1, 2, 3 and 4, *P* is 0.886, 0.889, 0.893 and 0.895, respectively.

None of the other 3³Π_u curves can reach the 4S+2D limit with the exception of C³Π_u (with a crossing at 2.6 a₀) which has a very small rate constant and is neglected. As pointed out above, in addition to 2³Σ_u⁺, escape can occur via several pathways from *v* = 4 to N(4S)+N(2P). First, capture into the curve labeled 2³Π_u followed by transfer to C³Π_u at the R = 2.6 a₀ crossing followed by transfer to 3³Π_u at the R = 3.9 a₀ crossing can induce escape. The Landau-Zener probability for the first transfer is *P* = 0.10 and that for the second is *P* = 0.001 giving a negligible total rate constant for both isotopomers. Second, capture can occur into 3³Π_u followed by a diabatic path (remaining on 3³Π_u) through three crossings to N(4S)+N(2P). Starting from the inner most crossing, the product of the rate constant (Guberman, 2014) and the Landau-Zener factors are 0.17 × 10⁻⁸ cm³/sec × 0.79 × 0.99 × 1.0 = 0.013 × 10⁻⁷ cm³/sec. Third, capture can proceed as in the second example except that at the 2.7 crossing an adiabatic jump can occur to 4³Π_u followed by an adiabatic jump back to 3³Π_u followed by a diabatic traversal of the crossing with the C state. The product of the rate constant (Guberman 2014) and the Landau-Zener factors are 0.17 × 10⁻⁸ cm³/sec × 0.21 × 0.01 × 1.0 = 0.000035 × 10⁻⁷ cm³/sec and this pathway can be neglected. The fourth pathway starts from *v* = 4 on 4³Π_u and traverses the 2.7, 3.5 and 3.9 crossings diabatically, adiabatically and diabatically, respectively. The product of the rate constant (Guberman, 2014) and the Landau-Zener factors are 0.14 × 10⁻⁷ cm³/sec × 0.79 × 0.01 × 1.0 = 0.0011 × 10⁻⁷ cm³/sec. Lastly, the fifth pathway traverses the 2.7, 3.5 and 3.9 crossings adiabatically, diabatically and diabatically, respectively. The product of the rate constant (Guberman 2014) and the Landau-Zener factors are 0.14 × 10⁻⁷ cm³/sec × 0.21 × 0.99 × 1.0 = 0.029 × 10⁻⁷ cm³/sec. For *v* = 4, the 3³Π_u rate constant in Table 1 includes all 5 pathways. These 5 pathways from *v* = 4 to N(4S)+N(2P) will interfere with each other. The interference is neglected here.

In summary, for escape of ¹⁴N from ²⁸N₂⁺ there is one route from *v* = 0 - 4 along 2³Π_u, five pathways from *v* = 4 to N(4S)+N(2P) along the 3³Π_u routes and a single route along 2³Σ_u⁺ from *v* = 4 to N(4S)+N(2D).

2.2. ²⁹N₂⁺

For ²⁹N₂⁺, conservation of energy and momentum requires that after dissociation ¹⁴N will have more kinetic energy than ¹⁵N. DR of *v* = 0 to the 4S+2D limit at 0.172 eV electron energy gives ¹⁵N with 1.742 eV and ¹⁴N with 1.866 eV of kinetic energy. (Lofthus & Krupenie 1977; Moore, 1949) Therefore, from the *v* = 0 ion, DR of ²⁹N₂⁺ imparts sufficient energy for ¹⁴N atoms to escape but not ¹⁵N. Escape is along the 2³Π_u diabatic curve. From *v* = 0, insufficient energy is imparted for escape from the 4S+2P limit. From *v* = 1, dissociation to the 4S+2D limit gives ¹⁴N with 2.00 eV and ¹⁵N with 1.870 eV and both isotopes escape. However, for the Mavén electron energy of 0.084 eV, 1.958 eV and 1.828 eV are imparted to ¹⁴N and ¹⁵N respectively. ¹⁴N escapes but at 200 km ¹⁵N needs an additional 0.016 eV. But ¹⁵N can escape near 210 km because of both the decrease in the escape energy (Fox and Hac, 1997) and the increase in the MAVEN electron energy relative to 200 km. At both electron energies at 200 km, the isotopes escape from DR of *v* = 2 - 4 via the 4S+2D limit but escape via the 4S+2P limit along the five 3³Π_u paths discussed above is energetically possible only from *v* = 4 for ¹⁴N. Both isotopes escape from *v* = 4 along 3³Σ_u⁺.

Therefore an isotope discrimination effect from this mechanism is due to DR from *v* = 0 at the exobase. Without radiative relaxation, the higher the degree of ion vibrational excitation, the less will be the isotope enhancement. But if these excited levels radiate prior to DR, vibrational excitation cannot diminish the isotope enhancement.

These conclusions are only meaningful if the DR rate constants for all *v* are similar for ²⁸N₂⁺ and ²⁹N₂⁺. Calculations done in this laboratory show that the DR rate constants differ by less than 20% for all *v* (see Table 1).

3. Radiative lifetimes

Prior calculations on the radiative lifetimes of the isotopomers of H₂⁺, O₂⁺ and CO⁺ have been reported (Amitay et al., 1994) but ²⁹N₂⁺ was not included.

The ²⁹N₂⁺ dipole moment is nonzero because the center of charge, which is at the midpoint of the internuclear axis, does not coincide with the center of mass. An oscillating electric field arises from the motion of the center of charge relative to the center of mass due to vibration. It has been shown (Wu, 1952; Ellison, 1962) that for the isotopomers of charged homonuclear molecules, the dipole moment operator, μ , is

$$\mu(R) = (1/2)eR(M_a - M_b)/(M_a + M_b)$$

where *e* is the electron charge, *R* is the internuclear distance and for ²⁹N₂⁺ *M*_a and *M*_b are the masses of ¹⁵N and ¹⁴N. For ²⁸N₂⁺, where *M*_a = *M*_b, $\mu = 0.0$. The calculation of the vibrational level lifetimes requires the calculation of the matrix elements of *R* over the vibrational wave functions in the ²⁹N₂⁺ ground state:

$$\mu_{v'v} = \langle \chi_{v'} | R | \chi_v \rangle$$

where χ_v is the vibrational wave function of the *v*th level. The χ_v were determined numerically by the method of Cooley (1961) using a grid of 0.001 a₀ between 1.0 and 8.0 a₀. The 2³Σ_g⁺N₂⁺ ground state potential consisted of the RKR derived points near the minimum (Lofthus & Krupenie 1977) and configuration interaction (CI) values at other distances (Guberman, 2007).

The lifetimes of the levels are given by the reciprocal of the Einstein emission coefficient, *A*_{*v*′*v*} (Guberman & Dalgarno, 1992), where *v* and *J* denote the upper vibrational and rotational levels, respectively. If $\mu_{v'v}$ is expressed in atomic units and the transition energy, ΔE , is expressed in cm⁻¹ the Einstein coefficient (sec⁻¹) for

Table 2
Lifetimes* (secs) of rovibrational levels of $^{29}\text{N}_2^+$.

J	v				
	0	1	2	3	4
0		45.1	22.4	15.5	12.0
1	2.15(7)	45.1	22.4	15.5	12.0
2	2.24(6)	45.1	22.4	15.5	12.0
3	6.18(5)	45.1	22.4	15.5	12.0
4	2.51(5)	45.1	22.4	15.5	12.0
5	1.26(5)	45.1	22.4	15.5	12.0
6	7.18(4)	45.0	22.4	15.5	12.0
7	4.47(4)	45.0	22.4	15.5	12.0
8	2.97(4)	45.0	22.4	15.5	12.0
9	2.07(4)	44.9	22.4	15.5	12.0

* (n) denotes $10^{\pm n}$.

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$\Delta J = +1$ (R branch) is given by

$$A_{vJ}^R = 2.0259 \times 10^{-6} \times \frac{(J+1)^2}{(J+1)(2J+1)} \times M \times \sum_{v'=0}^{v-1} \mu_{v'v}^2 \Delta E_{vJ'vJ+1}^3$$

where $M = \left[\frac{M_A - M_B}{2(M_A + M_B)} \right]^2$. For $\Delta J = -1$ (P branch),

$$A_{vJ}^P = 2.0259 \times 10^{-6} \times \frac{J^2}{(J)(2J+1)} \times M \times \sum_{v'=0}^v \mu_{v'v}^2 \Delta E_{vJ'vJ-1}^3$$

Since the ion ground state is of Σ symmetry there is no $\Delta J = 0$ (Q branch). The lifetime, τ_{vJ} , is given by $\tau_{vJ} = 1/(A_{vJ}^R + A_{vJ}^P)$. The lifetimes (see Table 2) of rotational levels in $v = 0$ are very long due to the small value of ΔE^3 . In addition, rotational change has a negligible effect upon transitions from $v > 0$. The lifetimes of the excited levels range from 45 to 12 sec. Note that the $v = 5$ lifetime is much shorter than those in Table 2 due to an allowed transition to $v = 0$ of $A^2\Pi_u$ and $v = 5$ will radiate before DR can occur at typical planetary atmosphere electron densities. The fast radiative decay of excited vibrational levels of $^{34}\text{O}_2^+$ relative to those for $^{32}\text{O}_2^+$ has already been reported in a model of the vibrational distribution of O_2^+ in the Mars ionosphere (Fox, 2011; Fox & Hać, 2010).

4. Escape at Mars

The assessment of escape of ^{15}N arising from DR of vibrationally excited $^{29}\text{N}_2^+$ requires comparison of the lifetimes of radiative transitions and of DR which does and does not lead to escape. The electron density at the Mars exobase (200 km) is 10^4 cm^{-3} . (Cui et al., 2015) The electron temperatures considered here are 2000 K (0.172 eV) (Fox & Hać, 1997) and 975 K (0.084 eV) at 200 km. (Ergun et al., 2015) As discussed above, the DR rate constants for both isotopomers are of similar magnitude. The rate constants for escape (Table 1) at 2000 K vary from 0.23×10^{-7} to $0.60 \times 10^{-8} \text{ cm}^3/\text{sec}$ with lifetimes from 4300 sec to 17,000 sec. At 975 K, calculations analogous to those in Table 1 show that the rate constants vary from 0.87×10^{-7} to $0.70 \times 10^{-8} \text{ cm}^3/\text{sec}$ with lifetimes from 1100 sec to 14,000 sec.

Since the lifetimes in Table 2 are mostly more than an order of magnitude shorter than the time for escape via DR, nearly all of the $v \geq 1$ population of $^{29}\text{N}_2^+$ will decay by light emission before escape from DR can occur. Only a negligible amount of ^{15}N can arise from DR of excited vibrational levels and a very small amount can arise from $v = 0$ due to the high energy tail of the electron energy distribution.

The total DR rate constant (Guberman, 2014) for $1 \leq v \leq 4$ is between 2 and 5 times the escape DR rate constant and is also too small to affect the conclusions reached here.

The excited vibrational levels, i.e. $v=1 - 4$ of $^{28}\text{N}_2^+$ have very long radiative lifetimes because the dipole transition moment in the ground state of $^{28}\text{N}_2^+$ is zero. Although magnetic dipole or quadrupole lifetimes for excited vibrational levels in the ground state of N_2^+ have not been reported, they may be shorter (Herzberg, 1950) than the time for DR. In that case, DR via excited vibrational levels of $^{28}\text{N}_2^+$ will play no role in escape.

5. Conclusions

Calculations reported here of the radiative lifetimes of vibrational levels in the $^{29}\text{N}_2^+$ ground state coupled with calculations of the DR rate constants of the lowest 5 vibrational levels of $^{29}\text{N}_2^+$ and $^{28}\text{N}_2^+$ support the early proposals (Brinkmann, 1971; McElroy, 1972) that DR of N_2^+ can account for the isotope enhancement of ^{15}N relative to ^{14}N . The excited vibrational levels of $^{29}\text{N}_2^+$ decay radiatively near the Martian exobase before they can undergo DR and play no role in isotope enhancement. Since the energetics prohibit escape of ^{15}N by DR of the ground vibrational level, DR of $^{29}\text{N}_2^+$ does not contribute to ^{15}N escape. The isotope enhancement is due to DR of $^{28}\text{N}_2^+$ with a smaller contribution from DR of the ground vibrational level of $^{29}\text{N}_2^+$ to ^{14}N escape. The lifetimes and DR rate constants reported here should be included in future quantitative models of Martian ^{14}N escape.

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