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UPPER ATMOSPHERIC EXCITATION PROCESSES.(U)
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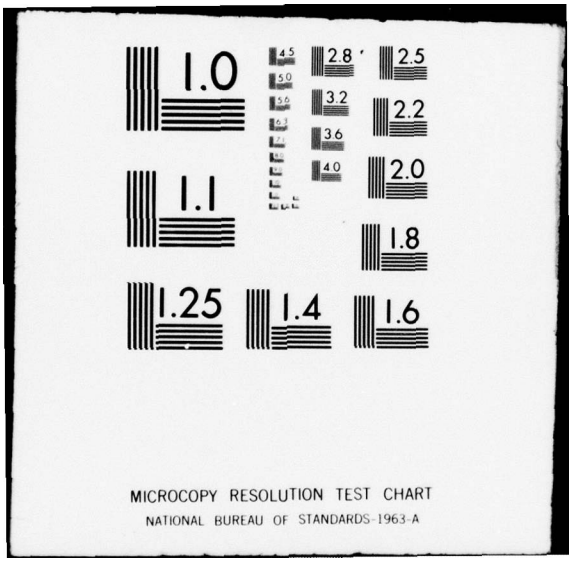
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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 3920 — 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* UPPER ATMOSPHERIC EXCITATION PROCESSES	5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) A. W. Ali, R. H. Kummler*, F. R. Gilmore** and J. W. McGowan†	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem H02-27D Project ~~HD 0 1043~~
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Nuclear Agency Washington, DC 20305	12. REPORT DATE February 27, 1979
	13. NUMBER OF PAGES 127
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT *(of this Report)* Approved for public release; distribution unlimited.	
17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*	
18. SUPPLEMENTARY NOTES This research was sponsored by the Defense Nuclear Agency under Subtask S99QAXHD411, work unit 15 and work unit title Reaction Rates Essential to Propagation. (Continues)	
19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)* Excited states — Reaction rates Excitations and deexcitations Disturbed atmosphere Quiescent atmosphere	
20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)* A review of the excitation and deexcitation processes relevant to the disturbed and the quiescent upper atmosphere is presented along with the current reaction rate coefficients.	

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18. Supplementary Notes (Continued)

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CONTENTS

UPPER ATMOSPHERIC EXCITATION PROCESSES

1. INTRODUCTION

The atmosphere from the sea level to higher altitudes (~ 1000 km) is an arena where large number of physical and chemical reactions occur almost on a continuous basis. These reactions are due to the natural response of the atmosphere as it absorbs energy from the sun under quiet or disturbed conditions. Disturbed atmospheric conditions arise from sun flares, electron and proton precipitations, and man made explosive devices. The absorption of energy by the constituents of the atmosphere results, generally, in a large number of excited states; these excited states are either radiative with short lifetimes or metastable. They are neutral and ionic and are atomic and molecular in nature. They all play an important role in the atmosphere in the ultimate degradation of the energy absorbed. The excited metastable species play significant roles in the physics and the chemistry of the atmosphere.

This report deals with the excitation and deexcitation of the atmospheric species by discussing their internal degrees of freedom and the mechanisms responsible for their excitations. The report also provides the appropriate and current rate coefficients for the excitations considered. It, therefore, puts certain emphasis on excited states and their reactions in the quiescent and disturbed atmosphere. The role of the excited state reactions in laboratory as well as in the at-

Note: Manuscript submitted November 27, 1978.

mosphere were considered previously to be of minor consequence relative to ground state reactions. However, it is now recognized that both in the laboratory and the atmosphere small numbers of excited metastable species can have large effects on total reaction rates and consequently affect the steady state conditions as well as the relaxation of highly disturbed conditions.

The role of specific excited states in the quiescent and disturbed atmosphere, and in the laboratory work, has been considered, in part, in many journal articles and books[1-15]. Excited state species and their energy transfer to other species have attracted further attention with the advent of lasers[16]. Recent studies have depicted the role of excited states in specific parts of the atmosphere, e.g., the stratosphere[17], and the quiescent ionosphere[18]. More general considerations to the role of excited states in the atmosphere, as a whole, under quiescent and disturbed conditions have also appeared[19,20].

2. EXCITATION MECHANISMS

The excitation of the radiative or metastable states can proceed through several well known physical processes. These processes are presented below with specific, but not exhaustive, examples.

2.1 PHOTOABSORPTION

We use this term broadly to include the photodissociation, dissociative ionization, photoionization as well as absorption resulting in electronic and vibrational excitation:

$$h\nu + O_2 \rightarrow O + O^* \qquad (1)$$

$$h\nu + O_2 \rightarrow O^* + O^+ + e \qquad (2)$$

$$h\nu + N_2 \rightarrow N_2^+ (X,A,B) + e \qquad (3)$$

$$h\nu + O\,(^3P) \rightarrow (^3S) \qquad (4)$$

$$h\nu + NO \rightarrow NO^{\ddagger} \qquad (5)$$

The notations used here, which will be utilized hereafter, are as follows: The excited species are designated by a star whenever the state is not specifically identified. For the vibrational excitation, the symbol ‡ is used. Furthermore, whenever the state of a species is not given, its ground state is implied.

2.2 CHARGED PARTICLE IMPACT

This includes the electron and the proton impact excitations and are very similar in nature to the photoabsorption processes discussed in section 1.1, that is:

$$e + O_2 \rightarrow O + O^* \qquad (6)$$

$$e + O_2 \rightarrow O^+ + O^* + 2e \qquad (7)$$

$$e + N_2 \rightarrow N_2^+(X,A,B) + 2e \qquad (8)$$

$$e + N(^4S) \rightarrow N(^4P) + e \qquad (9)$$

$$e + N_2 \rightarrow N_2^{\ddagger} + e \qquad (10)$$

2.3 CHARGE EXCHANGE AND ION-MOLECULE REARRANGEMENT PROCESS

Charge exchange processes which result in the production of excited states, of interest to this chapter, are generally exothermic in nature. For our purposes we give examples of resonant and non-resonant assyme-

tric reactions, e.g.,

$$O^+(^2D) + N_2 \rightarrow N_2^+(A,v) + O \qquad (11)$$

$$N_2^+ + N \rightarrow N^+ + N_2^\ddagger \qquad (12)$$

In Reaction (12), the excess energy may end up in other degrees of freedom of the reaction products, such as kinetic, vibrational or electronic mode.

The ion molecule rearrangement processes are also exothermic, and the excess energy of the reaction can be partitioned into other degrees of freedom of the reaction products. An example of ion-molecule rearrangement reaction is:

$$O^+ + N_2 \rightarrow NO^+ + N \qquad (13)$$

2.4 NEUTRAL PARTICLE AND NEUTRAL PARTICLE REARRANGEMENT COLLISIONS

Excitation under this general category arises from collisions between atoms, atoms and molecules where the translational energy is converted into vibrational or electronic modes of the collision products, e.g.:

$$O + N_2 \rightarrow N_2^\ddagger + O \qquad (14)$$

or when the internal energy of an excited neutral is transferred to the other partner by exciting its electronic and or vibrational modes, e.g.:

$$O(^1D) + N_2 \rightarrow N_2^{\ddagger} + O(^3P) \quad (15)$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2\,(b^1\Sigma,\ v\leq 2) \quad (16)$$

The neutral particle rearrangement collisions lead into excitations of the reaction products in the same manner as above, however, the reaction products are different due to atom-atom interchange, e.g.:

$$N(^2D) + O_2 \rightarrow NO^{\ddagger} + O \quad (17)$$

2.5 DISSOCIATIVE RECOMBINATION

The dissociative recombination of molecular ions, especially the atmospheric ions, produce excited state species, e.g.:

$$N_2^+ + e \rightarrow N(^4S) + N(^2D) \quad (18)$$

and

$$NO^+ + e \rightarrow N(^2D) + O(^3P) \quad (19)$$

2.6 DEEXCITATION PROCESSES

The deexcitation of an excited state follows, in principle, the inverse process of the excitation and its rate coefficient is obtained from the excitation rate coefficient through the principle of detailed balance.

3. LIFETIMES, EMISSIONS AND ENERGY STORED IN THE EXCITED STATES

The dominant neutral species of the quiescent atmosphere are: N_2,

O_2, and O . There are a large number of minor species, however. Those most relevant to the purposes of this chapter are: CO_2, O_3, H_2O, OH, NO and NO_2. During the quiescent and the disturbed atmosphere, ionic species will be present and their densities clearly depend on the altitude and the strength of the disturbance. Additionally, a large number of excited states appear under disturbed and undisturbed conditions, they store part of the incident energy which in turn is emitted in various spectral wavelengths, transferred into kinetic and or vibrational degrees of freedom.

The atmospheric species and their excited states, especially the metastable states, are given in Table 1. This table gives the excitation energies, lifetimes and the references relevant to the atomic data for each species. For lifetimes it is necessary to distinguish between the effective lifetime, τ_e, which allows for collisional deexcitations and the collision free radiative lifetimes, τ_o. These lifetimes are related through the reactive collision frequency,

$$\frac{1}{\tau_e} = \frac{1}{\tau_o} + \sum_i k_i . n_i . \qquad (20)$$

where k_i is the rate coefficient (cm^{+3} sec^{-1}) by which the excited species inelastically scatter from another species of density n_i (cm^{-3}). Much of what is known about radiative lifetimes of the longer lived species is summarized in Table 1.

Grotrian energy diagrams of the atmospheric species of interest are given in Figures 1 and 2. In energy transfer, resonance or near

resonance reactions can play a significant role depending upon the details of potential energy surface associated with the interaction considered[12,21-24].

In Table 1, the excited state species are predominantly electronic in nature. However, the ground state vibrational excitations of major and minor atmospheric species play an equally important role in the emission and the degradation of the energy absorbed. The relevant data for the vibrational modes, energy spacings, emitted radiation and their transition rates are presented in Table 2.

4. EXCITATIONS AND DEEXCITATIONS IN N_2

4.1 EXCITATIONS AND DEEXCITATIONS OF N_2 GROUND STATE VIBRATIONAL LEVELS

An appreciable amount of the energy deposited in the atmosphere comes to rest in the vibrational excitation of nitrogen. This excitation arises through several physical and chemical processes which are: the radiative transitions from higher-lying excited states[61], e.g.:

$$N_2\ (A^3\Sigma,v) \rightarrow N_2\ (X^1\Sigma_g^+,v) + h\nu, \tag{21}$$

chemical reaction[6,7], e.g.:

$$NO(X^2\pi) + N(^4S) \rightarrow N_2\ (X^1\Sigma_g^+,\ v > 0 + O(^3P) \tag{22}$$

energy transfer[10,82-87], e.g.:

$$O(^1D) + N_2\ (X^1\Sigma_g^+,\ v=0) \rightarrow O(^3P) + N_2\ (X^1\Sigma_g^+,v > 0) \tag{23}$$

and by electron impact[88,89], e.g.:

$$e + N_2\ (X^1\Sigma_g^+,\ v=0) \rightarrow e + N_2\ (X^1\Sigma_g^+,v) \tag{24}$$

This last process is very efficient, with a large cross section[90], and has attracted considerable experimental[88,89] and theoretical[91-93] investigations. One of these calculations[93] reproduces the experimental results very satisfactorily[94]. The ground state vibrational excitation arises through a temporary negative ion[88-92], $N_2^-\ (^2\pi)$, which in turn

decays into eight individual vibrational states (v=1→8). These individual cross sections, excited by electron impacts, have been resolved experimentally[88], as a function of the energy of the incident electron. The deexcitation of the vibrational levels by electrons have also been observed[95]. To obtain the excitation rate coefficients, these cross sections[88] have been integrated with the electron velocity over an electron Maxwellian velocity distribution[96]. These rates, shown in Figure 3 are also given in Table 3. Similar rates have been obtained by others[97]. Thus, to calculate the energy deposited by electrons in the vibrational mode of N_2, one must consider the threshold energies for each individual level and not the threshold energy for the temporary negative ion as done by some workers[98,99].

A number of chemical reactions have been reported in which vibrational excited products have been identified[13,100-102], however, Reaction (22) is the only one thus far studied in detail[6,7,86] which gives $N_2^{\ddagger}$ as a product. One fourth of the exothermic energy of Reaction (22) is converted into vibrational energy[86].

As for the vibrational excitation through the energy transfer from $O(^1D)$, it was speculated earlier[10] that a significant amount of $O(^1D)$ energy will be transferred to N_2, especially since the excitation energy of $O(^1D)$ coincides with the excitation of N_2 (x, v=7). This near resonance concept has been utilized in the calculation of the vibrational temperature in the ambient atmosphere[85]. However, because of the significance of this energy transfer, Reaction (23) has been studied by several workers[82,83,86,87]. The most recent experimental analysis[87] indicate that only 30% of the internal energy of $O(^1D)$ is trans-

ferred to N_2 as vibrational energy.

The vibrational excitation of N_2 through the radiative cascade (Reaction 21) clearly depends on the excitation of the N_2 ($A^3\Sigma$) state and the population densities of its vibrational levels. Transitions from these vibrational levels to the N_2 ground state vibrational levels will contribute to the total vibrational energy of N_2.

The deexcitation of the vibrational energy, in principle, should follow the reverse of the excitation processes discussed earlier. Thus, the deexcitation by electron impact through the superelastic collisions can be calculated from the corresponding excitation rates, given in Table 3, via the principle of detailed balance. Vibrationally excited molecules, however, transfer their energies to the vibrational levels of other molecules through energy transfer (vibration-vibration, VV) or to the kinetic energy of molecules or atoms (vibration-translation,VT). These VV and VT quenching processes are thought to be well understood[1] [103-106]. According to Callear[105], the N_2 ($v=1\rightarrow0$) transition, at room temperature, requires 10^{10} collisions. However, the number of collisions required for V-T transfer is considerably less when the relaxation proceeds via the atom exchange[107-110]. The probability of vibrational energy transfer increases with increasing temperature and decreasing vibrational spacings. Usually the deexcitation of higher vibrational levels is a step by step, ladder-descending process. For most conditions $\Delta v = \pm 1$ but for higher levels and/or high kinetic temperatures, transitions with $\Delta v > 1$ can also occur[111-112].

The VT data for many molecules have been summarized by Millikan and White[113]. Data for vibrational-transitional energy transfer are

usually presented as a relaxation time-pressure product, $p\tau$, where τ is the e-folding time of the vibrational energy, ϵ, according to

$$\frac{d\epsilon}{dt} = \frac{1}{\tau}\left[\epsilon_{eq} - \epsilon\right] \tag{25}$$

at constant translational temperature and in the absence of sources. The rate constant can easily be obtained from the $p\tau$ product, such that

$$k = (P\tau M)^{-1} \tag{26}$$

where M is the density of the deactivating agent at pressure, P. Furthermore, the rate constant for the deexcitation of the first vibrational level k_{10} is

$$k_{10}\, M = \left[\tau(1-e^{-h\nu/kT})\right]^{-1} \tag{27}$$ *

where $h\nu$ is the vibrational energy spacing. For higher vibrational level deexcitations, on the other hand, one may utilize the following relation:

$$k(v=n) = n\, K(v=1) = n\, k_{10} \tag{28}$$

The quenching of the vibrationally excited N_2 by oxygen atom have been measured over a wide range of kinetic temperature[114-116] indicating that oxygen is an effective quencher. Furthermore, the meas-

*k in Equation (27) is the usual Boltzmann constant.

ured deexcitation rate at low kinetic temperatures exceeds considerably the calculated rate[117].

The vibrational-vibrational energy transfer to other atmospheric molecules, are either non-resonant or near resonant processes. As a deexcitation mechanism for the vibrational energy of N_2 the process excites vibrational modes of other molecules. This transferred energy results in infrared radiation whenever the molecule that acquires the energy has a permanent dipole moment. The N_2 vibrational energy transfer to CO_2 is well known from the advent of the CO_2 laser[118]. For the quiescent and disturbed atmosphere, the VT and VV energy transfer rate processes from N_2 to other atmospheric "species" are presented in Table 4.

The deexcitation of the vibrational energy through the energy transfer to electronic excitations of atoms is also possible. Hunten[122] has argued that the excitation of the Sodium D-line in auroras below 100 Km is likely to be the result of energy transfer from vibrationally excited nitrogen. This reaction has been observed in the laboratory[123] and the cross section has been measured[124] as 10^{-15} cm^2, although it is doubtful that vibrationally excited nitrogen exists below the turbopause[83,125-127].

The emphasis on the N_2 vibrational temperature stems from the fact that the degree of vibrational excitation significantly affects certain reactions, the most important of which is

$$N_2^{\ddagger}(X^1\Sigma,v) + O^+(^4S) \rightarrow NO^+ + N(^4S) \qquad (29)$$

This reaction depends upon the vibrational temperature[128,129] as well as the ion kinetic temperature[130] and plays an important role in the deionization process of the quiescent and the disturbed ionosphere. It was suggested earlier by Schmeltekoff, et al[128], that Reaction (29) would enhance the loss of electrons in the ionosphere, due to the enhanced formation of NO^+. Several workers have shown that this is the case in the quiescent ionosphere, the auroral arcs (see for example Refs. 84, 85,125,126,131 and 132) and atmospheres disturbed by nuclear bursts[133].

Finally the processes, discussed above, that control the vibrational excitation as a function of altitude are shown in Figure 4. These rates are obtained[125,126] using atmospheric densities given in Ref. 134.

4.2 EXCITATION AND DEEXCITATION OF THE ($A^3\Sigma_u^+$) STATE

The nitrogen molecule possesses a number of triplet states, e.g., $A^3\Sigma$, $B^3\pi$, $C^3\pi$, etc. which can be excited from the ground state of the molecule by electron impacts[135-144]. The $A^3\Sigma$ state at 6.2 eV is the lowest of the electronic states and is metastable with a lifetime of 1 sec[31]. Its emission consists of the well known Vegard-Kaplan band system. In addition to its excitation by electron impact from the ground state of the molecule, it can be populated by cascade from higher-lying triplet states, especially from $B^3\pi$ and $C^3\pi$ states. The electron impact excitation cross sections of these triplet states have been calculated[145,146]. Measured cross sections exist for $A^3\Sigma$ state[139,140], $B^3\pi$ state[139-142], and $C^3\pi$ state[129,142-144]. However, the shapes and the peak values of these cross sections, whether experimental or theoretical, are not in good agreement with each other[147]. A case in point

is the peak cross section of the $A^3\Sigma$ state with values of 5.25 (Ref. 140), 3.00 (Ref. 139), 12.00 (Ref. 146) and 15 (Ref. 145) in units of 10^{-15} cm^2. However, using the average of the experimental cross sections as a limit, the rate coefficient for the electron impact excitation of the $A^3\Sigma$ state is given in Figure 5. This rate is obtained[148] using the calculated cross section[145] averaged with the electron velocity over a Maxwellian electron velocity distribution.

The significance of the $A^3\Sigma$ state is apparent in the highly disturbed atmosphere and in the auroral displays. Apart from the electron impact excitation and cascade from higher N_2 triplet states, the following near resonant charge exchange transfer reaction should be considered in the excitation of the $A^3\Sigma$ state

$$N_2^+(X) + NO \rightarrow N_2(A) + NO^+ \qquad (30)$$

This reaction has a measured rate coefficient[149-151] of 3.3×10^{-10} cm^3 sec^{-1}.

The deexcitation of the $A^3\Sigma$ state proceeeds through the superelastic collisions with electrons, and by quenching collisions with atmospheric species. Quenching by the ground state nitrogen is small[152,153]. However, it has been observed[154] that nitrogen atoms effectively quench the A-state through atom interchange:

$$N + N_2(A) \rightarrow N_2(X) + N \qquad (31)$$

In the atmosphere, on the other hand, Hunton and McElroy[10] have found

that oxygen atoms could provide the necessary quenching. Most recently Vallance Jones and Gattinger[155] have obtained the A-state quenching by oxygen atom in the aurora with a rate coefficient of 7.5×10^{-11} cm^3 for v=o level. Part of the A-state quenching by oxygen results in the excitation of the $O(^1S)$ state, according to:

$$N_2(A) + O \rightarrow N_2(X) + O(^1S) \qquad (32)$$

with a rate coefficient[156] of 3×10^{-12} cm^3 sec^{-1}. Metallic species like, Na, Fe, Hg, Ba, etc. are also effective quenchers for the A-state through Penning ionization[11,157,158]. Finally a summary of available quenching date for $A^3\Sigma$ state by atmospheric species is given in Table 5.

4.3 HIGHER-LYING STATES IN NITROGEN

Among the many other metastable states of nitrogen, only one more state, the $a^1\Pi$ state will be discussed. This state with a lifetime of 0.1 msec, has attracted some theoretical[146] and considerable experimental[139,140,163-166] attention concerning its excitation cross section by electron impact. The most recent electron impact excitation cross section[166] for $a^1\Pi$ state agrees very well with an earlier measurement[140] from threshold up to incident electron energy of 40 eV. The excitation threshold for $a^1\Pi$ state is 8.5 eV which coincides with a metastable state observed by Cermak[167] to lead to associative ionization of the type

$$N_2^* + NO \rightarrow N_2NO^+ + e \qquad (33)$$

However, the product N_2NO^+ has not been identified as yet in the D-region mass spectral studies.

4.4 EXCITATIONS AND DEEXCITATIONS OF N_2^+ STATES

4.4.1 EXCITATIONS AND DEEXCITATIONS OF $B^2\Sigma$ STATE

The 3914 Å band, which corresponds to the (0,0) transition of the first negative bands system ($B^2\Sigma \rightarrow X^2\Sigma$), is one of the strongest emissions in the aurora, twilight glow, day glow and in the highly disturbed atmosphere. The primary sources of excitation of $N_2^+(B^2\Sigma)$ state in the ionosphere are the ionization of N_2 by solar radiation[168],

$$N_2 + h\nu(>18.7 \text{ eV}) \rightarrow N_2^+(B^2\Sigma) + e \qquad (34)$$

by energetic electrons

$$N_2 + e \rightarrow N_2^+(B^2\Sigma) + 2e \qquad (35)$$

and resonance scattering of solar radiation[169] at 3915 Å off ambient N_2^+ ions:

$$N_2^+ + \frac{hc}{\lambda} \rightarrow N_2^+(B^2\Sigma) \qquad (36)$$

To these one must add the electron impact excitation from the ground state of the ion, especially by low energy electrons[170]:

$$N_2^+ + e \rightleftarrows N_2^+(B^2\Sigma) + e \qquad (37)$$

In auroras, only Reaction (35) is likely to be an important source of excitation. Indeed the efficiency of converting the electron energy into (0,0) transition in air via Reaction (35) is constant and has a value [177] of 5.2×10^{-3}, independent of electron energy above 100 eV, and plays an important role in determining the auroral strength. In highly disturbed atmosphere, on the other hand, Reactions (34) and (37) are important excitation sources in addition to Reaction (35). The electron impact ionization cross section leading to $N_2^+(B, v=o)$ as one of the few ionization continua of N_2 (Reaction 35) has been measured by many investigators[172-175] and is well established. Using the measured cross-section[173], averaged with the electron velocity over an electron Maxwellian velocity distribution, the electron impact excitation rate coefficient for (0,0) band is obtained[148], and is given in Figure 6. The excitation cross section for the (0,0) band emission from the ground state of the ion has also been measured[170,176,177]. However, there is a large disagreement among the first two measurements[170,176] and the most recent one[177]. The peak cross sections by Lee and Carlton[170], and Dashchenko, et al[176], are 44 and 22 times as large as that measured by Crandall, et al[177]. A rate coefficient measurement for the excitation of (0,0) transition[178] indicated that the Lee and Carlton cross section [170] may be large by a factor of 40. This makes the recently measured cross section perhaps the most reliable. The corresponding electron impact excitation rate coefficients is presented in Figure 6 obtained from the deexcitation rates of Crandall, et al[177].

One of the important deexcitation processes of $N_2^+(B,v=o)$ state

is its quenching by N_2. The quenching cross section by N_2 has been measured[175,179,180], and the corresponding rate coefficient for thermal temperatures is $\sim 4.4 \times 10^{-10}$ cm^3/sec. In a highly ionized medium, however, the superelastic collisions of the B-state with electrons will constitute an additional source for its deexcitation. Wallace and McElroy[181] have discussed the relative importance of the preceeding reactions on the 3914 Å emission in the quiescent ionosphere. They show that above 100 to 150 km, resonance scattering is the major source of 3914 Å radiation. At higher densities, however, resonance charge exchange such as

$$N_2^+(B^2\Sigma) + O_2(X^3\Sigma) \rightarrow N_2(X^1\Sigma) + O_2^+(b^4\Sigma) \qquad (38)$$

may be significant. Reactions of this type would produce additional $O_2^+(b \rightarrow a)$ first negative band emission and $O_2^+(a^4\pi)$ metastable ions. Because of the near resonance nature of the reaction, it may proceed at a faster rate in comparison with the charge exchange with N_2^+ in its ground state. More recently, Sharp[182] has analyzed the twilight air glow from rocket measurements and pointed out, not unexpectedly, that 90% of the 3914 Å emission is due to solar photon scattering off $N_2^+(X)$, while solar photoionization leading to $B^2\Sigma$ state produces less than 10% of the emission.

4.4.2 EXCITATION AND DEEXCITATION OF $A^2\pi$ STATE

The excitation of the $A^2\pi$ state of N_2^+, which results in the well known Meinel band emission (A→X), in the aurora, ambient and disturbed ionosphere, proceeds through the same mechanisms as those for $N_2^+(B)$

state. However, an additional excitation source via the near resonance charge exchange:

$$O^+(^2D) + N_2 \rightarrow N_2^+(A,\ v=1) + O \qquad (39)$$

has been advanced by Omholt[183]. Hunten[184] has observed that (1,0) and (1,2) bands of the Meinel system often have anomalously high intensities in the aurora, which could be attributed to the preferential excitation of the first vibrational level according to Reaction (39). Reaction (39) is one of the important deionization processes that transfers an atomic ion into a molecular one. The dissociative recombinations of the atmospheric molecular ions with electrons proceed much faster than the atomic ion radiative recombination. The cross section for Reaction (39) has been measured[185] and is quite large, since it is a near resonant process, leading to a reaction rate coefficient $\sim 10^{-9}$ cm^3/sec.

Observations of the normal auroras indicate that the Meinel band system is one of the strongest emissions[186] which have been also detected in day glow[187]. The electron impact ionization cross section leading to $A^2\pi$ state has been measured[188]. Using currently available data on excitation cross sections, transitions and quenching rates, Cartwright, et al[189], have calculated the auroral emission of the Meinel band relative to that of the first-negative bands system. Comparison of these calculations with the measured data is in reasonable accord.

The excitation of the Meinel band, by electron impacts from the ground state of the ion, have not been measured. This process becomes

important in highly disturbed atmosphere as a cooling process for the electrons.

The deexcitation processes of the Meinel band system should proceed through superelastic collisions with low energy electrons and via quenching by N_2 and O_2. The quenching rate of the A-state vibrational levels by N_2 and O_2 have been measured by several workers[188,190,191]. However, the agreement between their results is not good. Average values[189] for quenching of v=1 level by N_2 and O_2 are 4.5 X 10^{-10} cm^3/sec respectively.

The charge transfer

$$N_2^+(A) + O_2 \rightarrow N_2 + O_2^+(a^4\pi) \qquad (40)$$

may be another loss mechanisms of the $A^2\pi$ state since the reaction is a near resonance one.

Other excited states of N_2^+ have been observed, especially the metastable states $^4\Sigma$ and $^4\Delta$. These states have been found[49,192] to form N_3^+ through the reaction:

$$N_2^+(^4\Sigma \text{ or } ^4\Delta) + N_2 \rightarrow N_3^+ + N \qquad (41)$$

Finally, it should be remarked that the electron impact excitation of molecular nitrogen and oxygen do not populate the vibrational levels according to the Franck-Condon factors. Studies near ionization threshold[193,194] show that vibrational levels are produced indirectly

via autoionizing states. The importance of autoionization can be seen in the case of $N_2^+(X)$ where the Franck-Condon factors for transitions from N_2 (X, v=o) to $N_2^+(X,v)$ decrease by nearly an order of magnitude for each successive vibrational level of the ion, while for electrons with energy not far above the ionization-potential, Fineman, et al[195], have demonstrated that the populations of the v=o and v=1 levels are nearly equal.

5. EXCITATIONS AND DEEXCITATIONS IN N

The nitrogen atom has two low-lying metastable states of interest. These are $N(^2D)$ and $N(^2P)$ and are excited through several mechanisms. The $N(^2D)$ state which is the upper level for the 5200 Å day glow is excited by the dissociative recombinations

$$N_2^+(X) + e \rightarrow N(^4S) + N(^2D) \qquad (42)$$

and

$$NO^+(X) + e \rightarrow N(^2D) + O \qquad (43)$$

The branching ratios of these reactions have recently been calculated. Michels' calculations[196] show that the products of the NO^+ dissociative recombination are ~ 100% $N(^2D)$ and 100% $N(^4S)$. $N(^2D)$ and $N(^2P)$ are excited by electron impacts from the ground state of the nitrogen atom, N^4S, that is

$$e + N(^4S) \rightarrow N(^2D, {}^2P) + e \qquad (44)$$

The cross sections for these excitations have been calculated[199-203]. However, the most recent calculation[203] is the most accurate, since it considers many relevant factors such as polarization of the target, higher lying configurations, etc., which were neglected by previous calculations. Using these cross sections[203], the excitation rate coefficients for the low lying levels of nitrogen atom has been obtained[204] for a Maxwellian electron velocity distribution. These rate coefficients are presented in Figure 7 as a function of the electron temperature and are tabulated in Table 6 with the corresponding deexcitation rate coefficients.

Several charge exchange and ion-atom interchange reactions, in ambient and highly disturbed ionosphere, also produce $N(^2D)$ and $N(^2P)$. Below is a few examples taken from a larger set of reactions[205] where only exothermic processes were considered in addition to the condition of the conservation of the total spin:

$$N_2^+(^2X) + O(^3P) \rightarrow NO^+(^1\Sigma) + N[^2D, ^2P] \quad (45)$$

$$N_2^+(^2X) + O(^1D) \rightarrow NO^+(^1\Sigma) + N[^2D, ^2P] \quad (46)$$

$$N^+(^3P) + O_2(^3\Sigma) \rightarrow O_2^+(^2\pi) + N(^2D) \quad (47)$$

From Atmospheric Explorer data analysis, Reaction (45) is found[206] to be the main process for producing $N(^2D)$ in the normal ionosphere, and that the reaction product is 100% $N(^2D)$. Finally, the electron impact

dissociation and dissociative ionization of N_2 also produce $N(^2D)$, e.g.,

$$e + N_2 \rightarrow N^+ + N(^2D) + 2e \quad (48)$$

$$e + N_2 \rightarrow N(^2D) + N \quad (49)$$

however, even though novel experiments have been conducted in dissociation[207] and metastable detections[208], exact branching ratios to delineate the productions of $N(^2D)$ from Reactions (48) and (49) are not currently available.

The deexcitations of $N(^2D)$ and $N(^2P)$ proceed by superelastic collisions with low energy electrons. However, a major loss mechanism for $N(^2D)$, in daytime, aurora and highly disturbed atmosphere, is in its reaction with O_2 to form NO

$$N(^2D) + O_2 \rightarrow NO + O \quad (50)$$

The coefficient for Reaction (50) has been measured[209,210] and is $\sim 6 \times 10^{-12}$ cm^3 sec^{-1}. $N(^2D)$ is also lost through the following reaction

$$N(^2D) + N_2O \rightarrow N_2 + NO \quad (51)$$

which has a room temperature reaction rate coefficient[209,211] of 1.6×10^{-12} cm^3 sec^{-1}. A recent measurement by Davenport, et al[212] gives the quenching rate coefficient of $N(^2D)$ by atomic oxygen as

1.8×10^{-12} cm^3 sec^{-1}. This rate is larger by a factor of 3 compared to a value estimated in the real atmosphere by Rush, et al[213]. A summary of the quenching rate coefficients of $N(^2D)$ by atmospheric species of interest is given in Table 7.

6. EXCITATIONS IN N^+

The atomic nitrogen ion has two low lying metastable states which are important in highly ionized atmosphere. These are $N^+(^1D)$ and $N^+(^1S)$ and are excited through the photoionization of the atomic metastable states $N(^2D)$ and $N(^2P)$. The photoionization cross sections for these processes have been calculated by Henry[214].

The metastable states $N^+(^1D)$ and $N^+(^1S)$ are also excited by electron impacts with the ground state of the ion, $N^+(^3P)$, where the relevant near threshold collision strengths have been calculated by Henry, et al[201], and Saraph, et al[215]. These collision strengths are in good agreement and are utilized[204] to obtain the corresponding deexcitation rate coefficients for a Maxwellian electron velocity distribution and are given in Table 8. The corresponding excitation rate coefficients can be obtained through the principle of the detailed balance.

In addition to the above processes, $N^+(^1D)$ and $N^+(^1S)$ are excited by the electron impact dissociative ionization of N_2 and several plausable[205] charge exchange processes such as

$$N_2^+(^2\Sigma) + N(^2D) \rightarrow N_2(^1\Sigma) + N^+(^1D) \qquad (52)$$

and

$$N_2^+(^2\Sigma) + N(^2P) \rightarrow N_2(^1\Sigma) + N^+(^1S) \qquad (53)$$

The deexcitation and loss processes of $N^+(^1D)$ and $N^+(^1S)$ are by superelastic collisions with electrons and by charge exchanges and ion-atom interchanges[205] such as

$$N^+(^1D) + O_2(^3\Sigma) \rightarrow O_2^+(^4\pi) + N(^4S) \quad (54)$$

$$N^+(^1S) + NO(^2\pi) \rightarrow NO^+(^3\Sigma) + N(^2P) \quad (55)$$

However, no quantitative measurements are available for reactions (52 through 55).

7. EXCITATIONS AND DEEXCITATIONS IN O_2

7.1 GROUND STATE VIBRATIONAL EXCITATIONS OF O_2

Excitations of the vibrational levels of O_2 in the atmosphere have been reviewed[10,108,216]. The following reaction

$$O + O_3 \rightarrow O_2(a^1\Delta) + O_2^{\ddagger} \quad (56)$$

has been found[217] to be efficient and excites O_2 into higher vibrational levels. Electron impacts with the ground state of the molecule leads also into vibrational excitations[218,219]. These cross sections are generally much narrower and smaller in magnitude in comparison with the vibrational excitations of N_2. The electron impact excitation rate coefficient, obtained[220] using measured cross section is shown in Figure 8 for an electron Maxwellian velocity distribution. High energy ions ($\geq$ 10 eV) are found[221] to excite vibrational levels of O_2 via

$$O^+ + O_2 \rightarrow O^+ + O_2^{\ddagger} \qquad (57)$$

The significance of the vibrationally excited O_2 is in the role it plays in enhancing the rate of processes such as

$$O_2 + e \rightarrow O^- + O \qquad (58)$$

where it is found that the cross section for reaction (58) depends strongly on the temperature[194,222,223] of O_2. As the equilibrium temperature of O_2 is increased from 300 to 2100 °K, both the energy of the maximum cross section and the threshold are shifted downwards. O'Malley [224] interpreted these results as being due to the vibrational excitation of O_2. Chen, however, has shown that rotational excitations must also be important[225].

The vibrationally excited O_2 is quenched by atmospheric species and a summary of quenching coefficients is given in Table 9. Using these data and atmospheric densities and temperatures[134], the deactivation rate (sec^{-1}) for $O_2^{\ddagger}(v=1)$ is given in Figure 9 as a function of altitude.

7.2 ELECTRONIC EXCITATION IN O_2

7.2.1 EXCITATION OF O_2 ($a^1\Delta$)

Perhaps the most abundant metastable state in the upper atmosphere is the ($a^1\Delta_g$) state of oxygen molecule. This state is the upper level where (0,0) transition band to the ground state of the molecule gives rise to the infrared atmospheric emission at 1.27μ. Its abundance

[229,330] at 50 km during the day is ~ 10^{10} cm^{-3} and it is attributed to the photodissociation of the ozone by the solar radiation in the Hartley continuum[229,231].

$$O_3 + h\nu(\text{Hartley continuum}) \rightarrow O + O_2(a^1\Delta) \qquad (59)$$

The quantum yields for the photolysis (Reaction 59) are given as a function of wavelength[232], in Table 10.

Other excitation mechanisms for $O_2(a^1\Delta)$ are:

$$O(^3P) + O_3 \rightarrow O_2 + O_2(a^1\Delta) \qquad (60)$$

with a rate coefficient[233] of 4.5 X 10^{-15} cm^3 sec, and by electron impacts

$$e + O_2(X^3\Sigma) \rightarrow O_2(a^1\Delta) + e \qquad (61)$$

The cross section for the last reaction has been measured[234] and calculated[235] using Born Approximation. Swider[236] has suggested the exothermic reaction

$$O_2^+ + NO \rightarrow NO^+ + O_2(^1\Delta) \qquad (62)$$

to be of relevance in auroras.

The altitude profile of $a^1\Delta$ using rocket measurements of the

1.27μ radiation[230,237] is well understood in terms of its production mechanism during daytime. However, the nighttime measurements[238] call for additional reactions such as

$$O + O + M \rightarrow O_2(a^1\Delta) + M \tag{63}$$

and

$$O + HO_2 \rightarrow O_2(a^1\Delta) + OH \tag{64}$$

The last mechanism has been suggested[239] as an additional source for the night glow.

The singlet metastable state, $a^1\Delta$, is quite stable and its behavior has been documented[249]. Furthermore, it is quenched by atmospheric species, O_2, N_2, O, O_3 and in a highly disturbed atmosphere by low energy electrons. Data on the quenching of $a^1\Delta$ have shown excellent agreement[241]. The most reliable values (excluding the data in Ref. 242) are given in Table 11. It is obvious from these data that molecular oxygen is the dominant quenching partner in the normal atmosphere, a fact confirmed by Evans' interpretation of $O_2(a^1\Delta)$ emission in the atmosphere[230].

Other loss mechanisms for $a^1\Delta$ has been suggested, such as

$$O_2^- + O_2(a^1\Delta) \rightarrow 2O_2 + e \tag{65}$$

operating in polar-cap absorption events[248] and in the disturbed atmos-

phere[249]. Subsequent investigations have verified the rapidity of the reaction[250,251] which has a rate coefficient ~ 2 X 10^{-10} cm^3 sec^{-1}, and have indicated that

$$O^- + O_2(^1\Delta) \rightarrow O_3 + e \qquad (66)$$

is rapid as well, with a rate coefficient of 3 X 10^{-10} cm^3 sec^{-1}.

The deexcitation detachment reacitons are significant for disturbed atmosphere in which an anomalously high, 1.27μ, emission are found, presumably due to $O_2(^1\Delta)$[252,254].

Another channel through which $O_2(a^1\Delta)$ may be quenched is radiative O_2 dimer formation[240,255].

$$2O_2(a^1\Delta) \rightleftarrows O_4^* \rightarrow 2O_2(X^3\Sigma) + h\nu(6340,\ 7030\ \text{Å}) \qquad (67)$$

The same reaction leads to the excitation of $b^1\Sigma$ state[255,256].

$$2O_2(a^1\Delta) \rightarrow O_2(b^1\Sigma) + O_2(X^3\Sigma) \qquad (68)$$

However, the rate coefficient[257] for Reaction (67) is 2 X 10^{-17} cm^3 sec^{-1} which indicates that Reactions (66) and (67) may not be of importance in the normal atmosphere.

7.2.2 EXCITATION OF $b^1\Sigma$

The metastable state $b^1\Sigma$ which is the upper level for the O_2 atmospheric band emission ($b^1\Sigma \rightarrow X^3\Sigma$) can be excited in the same manner

as $a^1\Delta$. It is excited from the ground state of the molecule

$$e + O_2(X^3\Sigma) \rightarrow O_2(b^1\Sigma) + e \tag{69}$$

whose cross section has been measured[234]. It can be excited through the photolysis of the ozone by solar radiation:

$$h\nu + O_3 \rightarrow O_2(b^1\Sigma) + O, \tag{70}$$

by three body reaction

$$O + O + M \rightarrow O_2(b^1\Sigma) + M \tag{71}$$

and by

$$O + O_3 \rightarrow O + O_2(b^1\Sigma) \tag{72}$$

However, two additional mechanisms produce the $b^1\Sigma$ state, which are Reaction (68) and through the energy transfer[258,259]:

$$O(^1D) + O_2(X^3\Sigma) \rightarrow O(^3P) + O_2(b^1\Sigma) \tag{73}$$

The rate coefficient for Reaction (73) has been measured[259] to be 9×10^{-11} cm^3 sec^{-1}, which may be important in auroras[260]. Reaction (73) has been identified by Seaton[261] to be resonant with v=2 of $O_2\ b^1\Sigma$

state. However, recent observations[262] of the atmospheric band in auroras indicate emission from higher vibrational levels $v \geq 5$. This suggests processes of energy transfer from $O(^1S)$ and $N(^2D)$ and also $O(^1D)$ with higher kinetic energies to populate[262] $v \geq 4$.

The quenching of $b^1\Sigma$ state proceeds via low energy electrons in the highly disturbed and normal atmosphere. It is also quenched by N_2 and O_2 with (1.5 - 2.5) X 10^{-15} cm^3 sec^{-1} (Refs. 263,264) and 1.5 X 10^{-16} cm^3 sec^{-1} (Refs. 14, 263), respectively.

7.2.3 EXCITATIONS OF O_2 $(A^3\Sigma)$ STATE

The $A^3\Sigma$ state of oxygen molecule, is metastable and is the upper level of the forbidden Herzberg bands transitions. In the normal atmosphere and in laboratory afterglow measurements, it is believed that the dominant excitation of this state is due to the three-body process[265,266]

$$O + O + M \rightarrow O_2(A^3\Sigma) + M \qquad (74)$$

The rate coefficient for Reaction (74) has been measured[267] with $M = N_2$ and has a value of $\sim 10^{-37}$ cm^6/sec, for low pressure ($N_2 < 10^{16}$ cm^3/sec). In a highly disturbed atmosphere, the electron impacts with O_2 should excite the $A^3\Sigma$ state, however, no realistic cross section for this process exists. The quenching of $A^3\Sigma$ state by atmospheric species is not well known.

8. EXCITATION AND DEEXCITATION IN ATOMIC OXYGEN

The atomic oxygen has two low-lying metastable states. These are $O(^1S)$ and $O(^1D)$ and are the upper levels for the well known and documented emissions at 5577 and 6300 Å, respectively. In addition,

the resonance line at 1304 Å has been of considerable interest as an ultraviolet emission in the atmosphere. A detailed excitation mechanism of these states is given below:

8.1 EXCITATIONS AND DEEXCITATIONS OF $O(^1D)$

The ^1D state of oxygen emits the forbidden red lines (6300 and 6364 Å) which are prominent in the aurora, dayglow, nightglow, twilight and highly disturbed atmosphere. In the dayglow the major source of $O(^1D)$ is the photodissociation in the Schumann-Runge cominuum[268]:

$$O_2 + h\nu\ (> 7.1\ eV) \rightarrow O(^3P) + O(^1D) \qquad (75)$$

Below 80 km the photolysis of the ozone (see Table 10) contributes heavily to the production of $O(^1D)$. *In higher altitudes* $O(^1D)$ *is produced* by the dissociative recombination

$$O_2^+ + e \rightarrow O(^1D) + O \qquad (76)$$

and by electron collision with the ground state of oxygen;

$$e + O(^3P) \rightarrow O(^1D) + e \qquad (77)$$

Processes (76 and 77) are important contributers to ^1D in auroras and highly disturbed atmosphere as well as during the normal atmosphere. The dissociative recombination (Reaction 76) have a measured and reliable rate coefficient over a wide range of the electron temperature[269].

Its room temperature value is 2.2×10^{-7} cm^3 sec^{-1}. The branching ratio for the products of Reaction (76) has been measured in afterglows[270,271] and these results are given in Table 12.

The electron impact excitation cross sections for the ground state configuration which includes ^1D and ^1S have been calculated[199-201,272]. The last calculation is the most recent and accurate and its cross sections are utilized to obtain[204] the relevant excitation cross sections. These rates are shown as a function of the electron temperature in Figure 10 and are tabulated in Table 13.

The ^1D state also arises under electron impacts with O_2 through the dissociation and the dissociative ionization of the molecule. However, no quantitative data in this area is available. Data from flowing afterglow experiments[267] suggest that the deactivation of $O(^1S)$ by $O(^3P)$ could give rise to $O(^1D)$,

$$O(^1S) + (^3P) \rightarrow 2O(^1D) \text{ or } O(^1D) + O(^3P) \qquad (78)$$

whose importance in the nightglow has been discussed by Hunten and McElroy[10]. However, this reaction and its most current rate coefficients will be discussed in the next section in conjunction with the deactivations of $O(^1S)$.

The $O(^1D)$ is quenched by collisions with various atmospheric atoms and molecules. In highly ionized atmosphere, superelastic collisions with low energy electrons deexcite $O(^1D)$ effectively. Much of the older quenching data are discussed by Hunten and McElroy[10], who conclude that molecular nitrogen is the most efficient, with a rate coefficient

$k \simeq 8 \times 10^{-11}$ cm^3 sec^{-1}. This value is supported by the work of Carleton, et al[273], and by that of McGarth and McGarvey[274], who found that the rate for nitrogen as a quencher exceeds that for oxygen. Zipf[14] has reviewed this subject and concurs in the view that nitrogen is the major atmospheric quenchant. However, in a recent review[275], the quencing rate coefficients of $O(^1D)$ by N_2 and O_2 are given as 5.5×10^{-11} cm^3 sec^{-1} and 7.5×10^{-11} cm^3 sec^{-1}, respectively.

In addition to the normal collisional quenching, $O(^1D)$ undergoes chemical quenching in its reactions with minor atmospheric species, especially in th3 stratosphere. The importance of these reactions have been demonstrated by Hunt[276] in the D-region and by Hampson[277] in the stratosphere. Hampson, for example, showed that in the stratosphere the free radicals OH and HO_2 are present only because of the reaction of $O(^1D)$ with the water vapor

$$O(^1D) + H_2O \rightarrow 2OH \qquad (79)$$

This reaction has a rate coefficient[278] of 6×10^{-10} cm^3 sec^{-1} or 3.5×10^{-10} cm^3 sec^{-1}. Hunt[276] showed that the ozone concentration, in agreement with measured values, could be derived only if several $O(^1D)$ reactions involving hydrogen and water were taken into consideration. These are Reactions (79) and

$$O(^1D) + H_2 \rightarrow OH + H \qquad (80)$$

which has a rate coefficient[280] of 3×10^{-10}. Assuming a rate coeffi-

cient of 10^{-11} cm^3 sec^{-1} for Reaction (80) Hunt arrived at $O(^1D)$ densities of 10^3-10^4 between 40 and 100 km. This value is probably too large because of his assumed value for Reaction (80), however, the general conclusion that even small concentrations of $O(^1D)$ are extremely important, persists even when turbulent transport is taken into account[281,282]. In addition to Reactions (79) and (80), other chemical quenching reactions involving $O(^1D)$ in the stratosphere are

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \qquad (81)$$

and

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (82)$$
$$\rightarrow 2NO$$

with rate coefficients[283] of 3×10^{-10} cm^3 sec^{-1} and 1×10^{-10} cm^3 sec^{-1}, respectively. These reactions clearly demonstrate the importance of $O(^1D)$ in the stratosphere, its importance have also been noted in the tropospheric chemistry[284-286]. A summary[287] of $O(^1D)$ quenching reactions and their rate coefficients is presented in Table 14. However, in a highly ionized atmosphere the population density of $O(^1D)$ will also be affected by a host of charge exchange and ion-atom intercharge reactions[205] of which a few examples are:

$$N_2^+ + O(^1D) \rightarrow N_2(^1\Sigma) + O^+(^2D) \qquad (83)$$

$$N^+(^3P) + O(^1D) \rightarrow N(^2D) + O^+(^4S) \quad (84)$$

$$N^+(^1S) + O_2(^1\Delta) \rightarrow NO^+(^1\Pi) + O(^1D) \quad (85)$$

8.2 EXCITATIONS AND DEEXCITATIONS OF $O(^1S)$

In 1931 Chapman[288] suggested that $O(^1S)$ may be formed in the nightglow by the reaction

$$O(^3P) + O(^3P) + O(^3P) \rightarrow O(^1S) + O_2 \quad (86)$$

where among the collision partners available to O_2, only energy transfer to $O(^3P)$ could generate $O(^1S)$. This implicitly assumed an initial step in which the stabilized excited O_2 had sufficient energy to excite $O(^3P)$ to $O(^1S)$. Such a mechanism, quite belatedly, was proposed by Barth and Hildenbrandt[289], that is

$$O(^3P) + O(^3P) + M \rightarrow O_2^* + M \quad (87)$$

$$O_2^* + O(^3P) \rightarrow O_2 + O(^1S) \quad (88)$$

Donahue, et al[290], have advocated the abandonment of the Barth two step mechanism. However, more recently Slanger and Black[291] using new data on the production of $O(^1S)$ combined with current altitude profiles of 5577 Å intensities and $O(^3P)$ concentrations, make persuasive arguments in favor of the two step mechanism. They indicate that the ex-

cited molecular oxygen may be $O_2(A^3\Sigma)$. The reaction rate coefficient for the overall production of $O(^1S)$, i.e., Reactions (87) and (88), have been measured recently[291] as a function of the kinetic temperature and found to be $1.4 \times 10^{-30} \exp(-1300/RT)$. This should be compared with the three-body process, Reaction (86), which has a rate coefficient[292] at 300 °K, of 4.8×10^{-33} cm^6 sec^{-1}. Additional three-body reactions forming $O(^1S)$ are:

$$O(^3P) + O(^3P) + N(^4S) \rightarrow O(^1S) + NO \qquad (89)$$

and

$$N(^4S) + N(^4S) + O(^3P) \rightarrow N_2 + O(^1S) \qquad (90)$$

They have[292] the following rate coefficients: 2.56×10^{-31} cm^6 sec^{-1} and 1.3×10^{-30} cm^6 sec^{-1}, respectively.

The $O(^1S)$ is also excited through the dissociative recombination of O_2^+, (see Reaction 76 and Table 12). Excitations of $O(^1S)$, in a highly ionized atmosphere, proceeds by electron impacts with the ground state of oxygen and $O(^1D)$, in addition to the above processes (see Figure 10 and Table 13 for the rate coefficients).

During the daytime, however, the photodissociation of O_2

$$O_2 + h\nu \ (\lambda < 1332 \text{ Å}) \rightarrow O + O(^1S) \qquad (91)$$

contributes[293] appreciably to the 5577 Å emission below 150 km with the major contribution to $O(^1S)$ being the photo-dissociation of O_2 in the wavelength range 1205-1292 Å. However, Hays and Sharp[294] have suggested that absorption near the ionization threshold $\lambda \simeq 1027$ Å is mainly responsible for the photo-dissociation. In measuring the quantum yield of $O(^1S)$ through the photo-dissociation of O_2 over a wavelength range 850-1300 Å. Lawrence and McEwan[295] have concluded that Reaction (91) is more efficient around 1050 Å and that the photo-dissociative excitation around Lyman β (1025.7 Å) provides the major fraction of $O(^1S)$.

The $O(^1S)$ is quenched by the atmospheric species and by superelastic collisions with low energy electrons in a highly disturbed atmosphere. Early auroral measurements of the green lines[296] have found the effective lifetime of 5577 Å to be shorter than its natural lifetime. This clearly attributed to the quenching of $O(^1S)$ by several atmospheric species where currently the corresponding rate coefficients have been measured by many workers and some as a function of the kinetic temperature. The quenching of $O(^1S)$ by $O(^3P)$ (see Reaction 78) had an early measurement with a value[267] of 1.38×10^{-13} cm^3 sec^{-1}. This old value is now superseded by a much larger value[292], e.g., 7.5×10^{-12} cm^3 sec^{-1} at 300 °K and $5.0 \times 10^{-11} \exp(-610/RT)$ cm sec^{-1} (see Ref. 291). The quenching of $O(^1S)$ by O_2

$$O(^1S) + O_2 \rightarrow O(^3P) + O_2 \qquad (92)$$

has the following rate coefficients: $4.0 \times 10^{-12} \exp(-1730/RT)$ cm^3

sec^{-1} (Ref. 297) and 4.9×10^{-12} exp(- 1700/RT) cm^3 sec^{-1} (Ref. 298). This last value is smaller by 20% at room temperature, compared to an earlier measurement by Stuhl and Welge[299]. The quenching rate coefficient[298] of $O(^1S)$ by N_2 is $< 5 \times 10^{-17}$ cm^3 sec^{-1}. A summary of the quenching rate coefficients of $O(^1S)$ by major and minor atmospheric species, is given[287] in Table 15.

9. EXCITATIONS AND DEEXCITATIONS IN O^+

The atomic oxygen ion has two low-lying metastable states; $O^+(^2D)$ and $O^+(^2P)$. They play important roles in the chemistry of the quiescent and the disturbed atmosphere. They are produced in the dayglow through the direct photoionization of the oxygen atom

$$O + h\nu \rightarrow O^+(^4S, ^2D, ^2P) + 2e \qquad (94)$$

Quantative branching ratios for Reaction (94) are not available, however, estimates can be made using photoionization cross sections as a guide. These excited states can also be produced[301] by electron impacts on O_2. Stebbings[301] indicate that for 100 eV electrons on O_2 the fraction of excited O^+ is 25% of the ions produced.

In addition to these processes, $O^+(^2D)$ and $O^+(^2P)$ also arise through the electron impacts with the ground state of the ion, $O^+(^4S)$, e.g.,

$$e + O^+(^4S) \rightarrow O^+(^2D, ^2P) + e \qquad (95)$$

The relevant near threshold collision strengths for processes (95) have been calculated[201,302]. Using these collision strengths, the deexcitation rate coefficients have been calculated[204] for a Maxwellian electron velocity distribution. These coefficeints are presented in Table 16. The excitation rates can be obtained through the principle of detailed balance.

The quenching of ^2D proceeds through superelastic collisions (see Table 16) especially for a highly ionized atmosphere. However, an important loss mechanism for $O^+(^2D)$ is its near resonance charge exchange with N_2 and O_2.

$$O^+(^2D) + N_2 \rightarrow N_2^+(A,\ v=1) + O(^3P) \qquad (39)$$

$$O^+(^2D) + O_2 \rightarrow O_2^+(v=o, a^4\Pi) + O(^3P) \qquad (96)$$

$$\rightarrow O_2^+(A^2\Pi\ v=o) + O(^3P) \qquad (97)$$

These processes have large rate coefficients[185,192] $\sim 3 \times 10^{-10}$ cm^3 sec^{-1}. Reaction (39), discussed earlier, may enhance infrared emissions in the Meinel bands[183,184]. However, Reaction (97) may result in visible radiation from the second negative bands of O_2^+. Near resonance Reactions (39) and (97) have been suggested as new laser sources[303].

The importance of Reactions (39), (96) and (97) for the atmospheric deionization is very obvious, where atomic ions are converted into molecular ions which have much faster rates in dissociatively recombing with the free electrons.

$O^+(^2P)$ which emits radiation at 7319 Å in its decay to $O^+(^2D)$, is quenched by low energy electrons (see Table 16), however, its quenching by atmospheric species is not well known. In the recent Atmospheric Explorer C Satellite experiments, dayglow measurements of the surface emission at 7319 Å have been analyzed[304] indicating that quenching by N_2 may have a rate coefficient as large as 5×10^{-10} cm^3 sec^{-1}.

10. EXCITATION BY PROTON IMPACT

This section is devoted to the effect of the proton precipitation in the atmosphere. The precipitation of energetic protons disturbs the atmosphere resulting in what is generally called the proton aurora. Proton auroras are different from electron auroras in their emissions and their lesser vertical extent because of the energy range of the ions in the atmosphere.

Atomic hydrogen lines, H_α 6564 Å and H_β 4861 Å, were first discovered by Vegard[305] in the auroral spectrum. These spectral lines were attributed[305] to hydrogen or proton showers. The displacement of H_β towards the blue was interpreted as protons with large velocities neutralized in their collisions with atmospheric atoms or molecules. Reviews of proton precipitations and hydrogen line emissions[306] indicate that typical protons have energies of 1-100 KeV.

The hydrogen line emissions are excited by the following processes :

$$H^+ + M \rightarrow H(n) + M^+ \qquad (98)$$

where the charge exchange leaves the hydrogen atom in either the ground

or excited states. The hydrogen atoms thus created have very high velocities and travel in straight lines causing ionization and excitations:

$$H + M \rightarrow H^+ + M^* + e \qquad (99)$$

$$H + M \rightarrow H(n\ ) + M^* \qquad (100)$$

$$H + M \rightarrow H(n\ ) + M^+ + e \qquad (101)$$

There are considerable experimental data for hydrogen line emissions due to collisions of protons with N_2, as reviewed recently by McNeal and Birely[307]. The measured emission cross sections are basically for excited states of n=2, 3 and 4 with representative emissions of Lyman α, H_α and H_β.

However, in addition to the hydrogen line emissions in the proton aurora, the collisions of the protons and hydrogen atoms with atmospheric atoms and molecules excite well known atomic and molecular emissions. Among the most prominant excitations are the Meinel and the first negative bands of N_2^+, that is;

$$H^+ + N_2 \rightarrow H^* + N_2^+ (A^2\Pi) \qquad (102)$$

and

$$H^+ + N_2 \rightarrow H^* + N_2^+ (B^2\Sigma) \qquad (103)$$

The cross sections for the excitation of the Meinel bands (Reaction 102) by protons and hydrogen atoms on N_2 have been measured by Birely and Johnson[308], in the energy range of 0.5-25 KeV. These measurements indicate that both H and H^+ make comparable contributions to the Meinel bands emission. The cross sections for the first negative bands emission by proton and hydrogen atom impacts on N_2 (Reaction 103) also have been measured[309,310,311] for incident energies of 1-25 KeV. For energies above 25 KeV, measured cross sections for Reaction (103) exist[312,313] up to 100 KeV. However, for proton impacts alone, the 3914 Å emission cross section, beyond 20 KeV, have been measured[314,315] up to 1000 KeV.

Excitations of other electronic emissions in N_2 by proton impacts have been studied in the laboratory. Measurements exist for N_2 ($B^3\pi$-$A^3\Sigma$) first positive band[308] and for N_2 ($C^3\pi$-$B^3\pi$) second positive band[309] emissions.

As for excitations in O_2 experimental data are limited in terms of the energy range and electronic states. Some data exist for the excitation of the Schumann-Runge continuum[316,317] and the ($b^4\Sigma \rightarrow A^4\pi$) emission[318] of O_2^+. Furthermore, the proton impact dissociation of O_2

$$H^+ + O_2 \rightarrow H^+ + O(^3P) + O(^1D) \qquad (104)$$

and

$$H^+ + O_2 \rightarrow H^+ + O(^3P) + O(^3P) \qquad (105)$$

have been measured over a limited energy range[316,317] where part of the

dissociation process results in the excitation of the 6300 Å oxygen red line. However, using certain scaling laws, Edgar, et al[319] have obtained proton excitation cross sections for 0 and 0_2 from electron impact excitations. Their scaling approach gives good results in comparison with some measured cross sections[309].

11. METALLIC SPECIES

Alkali atoms, Na, K etc., are present in the atmosphere in small quantities and are concentrated, generally, in the E- and D-regions. Emission from Na and K have been measured in the twilight[320] from which their altitude profiles can be inferred. Sodium ions have been measured [321] by rocket born spectrometer and other metallic ions are found to be present[322,323] in the D- and E-regions. Metallic ions like Mg^+, Fe^+ are maintained by ablating meteroroids[234]. However, other metallic atoms and ions are introduced into the atmosphere as a result of nuclear detonations.

The alkali atoms are excited during the daylight by the absorption and the resonance scattering of the solar radiation. During the night time their emission results from chemical reactions. However, a detailed chemistry of the alkalis in their reaction with atmospheric species is not well understood[325], as yet. Many of these metallic ions may be in excited states, especially the energetic ions created as a result of nuclear detonations. For Na^+, Fe^+, Al^+ and a few other metallic ions Fogel[326] and Layton[327] have shown that excitation has a marked effect upon the cross sections measured at kilovolt energies. Thus, it could be said that a large number of reaction rates involving metallic

atoms and their ions with atmospheric species remain unknown. This includes reacitons when the species are in ground states as well as in excited states.

12. REACTION RATES FOR REACTIONS INVOLVING EXCITED STATES

This report ends with a summary of reaction rates and cross sections where excited states are involved. The summary given in Table 17 provides a considerable portion of the information available in this area with emphasis on atmospheric species. The temperature at which measurements were made are given with the appropriate references and the types of experiments used to obtain the data.

REFERENCES

1. Armstrong, E.B. and A. Dalgarno, Eds., The Airglow and Aurora, Pergamon Press, London (1956).
2. Zelikoff, M., Ed., The Threshold of Space, Pergamon Press, New York (1957).
3. Ratcliffe, J.A., Ed., Physics of the Upper Atmosphere, Academic Press, New York (1960).
4. Chamberlin, J.W., Physics of the Aurora and Airglow, Academic Press New York (1961).
5. Cadle, R.D., Ed., Chemical Reactions in the Lower and Upper Atmosphere, Interscience Publishers, New York (1961).
6. Phillips, L.F. and H.I. Schiff, J. Chem. Phys. 36, 1509, 3283 (1962).
7. Morgan, J.E., L.F. Phillips and H.I. Schiff, Disc. Faraday Soc. 33, 118 (1962).
8. Bates, D.R., Disc. Faraday Soc. 37, 21 (1964).
9. Hines, C.L., et al, Eds., Physics of the Earth's Upper Atmosphere, Prentice Hall, Englewood Cliffs, NJ (1965).
10. Hunten, D.M. and M.B. McElroy, Revs. Geophys. 4, 303 (1966).
11. Muschlitz, E.E., in Molecular Beams, J. Ross, Ed., Interscience Publishers, New York (1966), p. 171.
12. Wright, A. and C. Winkler, Active Nitrogen, Academic Press, New York (1968).
13. Gilmore, F.R., E. Bauer and J.W. McGowan, J. Quant. Spect. Rad. Transfer 9, 157 (1969).
14. Zipf, E.C., Jr., Can. J. Chem. 47, 1863 (1969).

15. Donavan, R.J. and D. Husain, Chem. Revs. 70, 489 (1970).

16. Shuler, K.E. and W.R. Bennett, Eds., Appl. Opt. Suppl. 2, Chemical Lasers (1965).

17. Taylor, R.L., Can. J. Chem. 52, 1436 (1974).

18. Vlasov, M.N., J. Atm. Terr. Phys. 38, 807 (1976).

19. McGowan, W.J., R.H. Kummler and F.R. Gilmore, Chapt. 20, Defense Nuclear Agency Reaction Rate Handbook, DNA 1948 H (1974), Bortner and Baurer Eds., published by DASIAC.

20. McGowan, W.J., R.H. Kummler and F.R. Gilmore, "The Excited State in Chemical Physics", J. W. McGowan, Ed. Wiley & Sons, Inc. (1975).

21. Laidler, K.J., Chemical Kinetics of Excited States, Oxford University Press, London (1965).

22. Bates, D.R., Ed., Atomic and Molecular Processes, Academic Press, New York (1962).

23. Ford, U. and W. Lichten, Phys. Rev. Lett. 14, 627 (1965).

24. Bauer, E., E.R. Fisher and F.R. Gilmore, J. Chem. Phys. 51, 4173 (1969).

25. Wiese, W.L., M. Smith and B.M. Glenon, Atomic Transition Probabilities, Vol. 1, National Bureau of Standards Reference Data Systems Report NSRDS-NBS-4 (1966).

26. Lawrence, G.M. and B.D. Savage, Phys. Rev. 141, 67 (1966).

27. Omholt, A., Planet. Space Sci. 2, 246 (1960).

28. Garstang, R.H., Mon. Not. Roy Astron. Sci. 111, 115 (1951).

29. Nicolaides, C., O. Sinanoglu and P. Westhaus, Phys. Rev. A 4, 1400 (1971).

30. Lawrence, G.M., Can. J. Chem. 47, 1856 (1969); Phys. Rev. A 2, 397 (1970).

31. Shemansky, D., J. Chem. Phys. 51, 689 (1969).

32. Shemansky, D. and N.P. Carleton, J. Chem. Phys. 51, 682 (1969).

33. Shemansky, D. and A.L. Broadfoot, J. Quant. Spect. Rad. Transfer 11, 1385 (1971).

34. Jeunehomme, M., J. Chem. Phys. 45, 1805 (1966).

35. Hollstein, M., D.C. Lorents, R. Peterson and J.R. Sheridan, Can. J. Chem. 47, 1858 (1969).

36. Wu, H.L. and W. Benesch, Phys. Rev. 172, 31 (1968).

37. Covey, R. and W. Benesch, Bull. APS 18, 575 (1973).

38. Gilmore, F.R., Unpublished (1971).

39. Shemansky, D.E., J. Chem. Phys. 51, 5487 (1969).

40. Borst, W.L. and E.C. Zipf, Phys. Rev. A 3, 979 (1971).

41. Bennett, R.G. and F.W. Dalby, J. Chem. Phys. 31, 434 (1959).

42. Hesser, J.E., J. Chem. Phys. 48, 2518 (1968).

43. Johnson, A.W. and R.G. Fowler, J. Chem. Phys. 53, 65 (1970).

44. Dotchin, L.W., E.L. Chapp and D.J. Pegg, J. Chem. Phys. 59, 3960 (1973).

45. Freund, R.S., J. Chem. Phys. 50, 3734 (1969).

46. Holland, R.F. and W.B. Maier, J. Chem. Phys. 56, 5229 (1972).

47. Peterson, J.R. and J.J. Mosely, J. Chem. Phys. 58, 172 (1973).

48. Cartwright, D.C., J. Chem. Phys. 58, 178 (1973).

49. McGowan, J.W. and L. Kerwin, Can. J. Chem. 42, 2086 (1964).

50. Frosch, R. and G. Robinson, J. Chem. Phys. 41, 367 (1964).

51. Lefebvre-Brion, H. and F. Guerin, J. Chem. Phys. 49, 1446 (1968).

52. Jeunehomme, M., J. Chem. Phys. 45, 4433 (1966).

53. Bubert, H. and F.W. Froben, Chem. Phys. Lett. 8, 242 (1971).

54. Weinstock, E.M., R.N. Zare and L.A. Melton, J. Chem. Phys. 56, 3456 (1972).

55. Jeunehomme, M. and A.B.F. Duncan, J. Chem. Phys. 41, 1692 (1964).

56. Edquist, O., et al, Ark. Fys. 40, 439 (1970).

57. Mathis, R.F., B.R. Turner and J.A. Rutherford, J. Chem. Phys. 49, 2051 (1968).

58. Maier, W.B. and R.F. Holland, J. Chem. Phys. 51, 1286 (1969).

59. Schwartz, S. and H. Johnston, J. Chem. Phys. 51, 1286 (1969).

60. Keyser, L., S. Levine and F. Kaufman, J. Chem. Phys. 54, 355 (1971).

61. Nicholls, R., Ann. Geophys. 20, 144 (1964).

62. Badger, R.M., A.C. Wright and R.F. Whitlock, J. Chem. Phys. 43, 4345 (1965).

63. Miller, J.H., R.W. Boese and L.P. Giver, J. Quant. Spectr. Rad. Transfer 9, 1507 (1969).

64. Childs, W. and R. Mecke, Zeits Phys. 68, 344 (1931).

65. Degen, V., Can. J. Phys. 46, 783 (1968).

66. Jarmain, W.R. and R.W. Nicholls, Proc. Phys. Soc. 90, 545 (1967).

67. Jeunehomme, M., J. Chem. Phys. 44, 4253 (1966).

68. Fink, E.H. and K.H. Welge, Z. Naturforsch. 23 a, 358 (1968).

69. Copeland, G.E., J. Chem. Phys. 54, 3482 (1971).

70. Fairbairn, H.R., J. Chem. Phys. 60, 521 (1974).

71. James, T.C., J. Chem. Phys. 55, 4118 (1971).

72. Johnson, C.E. and R.I. Van Dyke, Jr., J. Chem. Phys. 56, 1506 (1972).

73. Wentink, T., Jr., E.P. Marram, L. Isacson and R.J. Spindler, AFWL-TR-67-30 Nov. 1967.

74. Isacson, L., E.P. Marram and T. Wentink, Jr., Appl. Optics 8, 235 (1969).

75. Bennett, R.G. and E.W. Dalby, J. Chem. Phys. 32, 1716 (1960).

76. Fink, E.H. and K.H. Welge, J. Chem. Phys. 46, 4315 (1967).

77. Jeunehomme, M., J. Chem. Phys. 42, 4086 (1965).

78. Bennett, R.G. and E.W. Dalby, J. Chem. Phys. 36, 399 (1962).

79. Moore, J.H., Jr. and D.W. Robinson, J. Chem. Phys. 48, 4870 (1968).

80. Gilmore, R.F., Chapt. 10, Defense Nuclear Agency Reaction Rate Handbook, DNA 1948 H (1972), Bortner and Baurer, Eds., DASIAC DoD Nuclear Information and Analysis Center GE-TEMPO, Santa Barbara, CA.

81. Kennealy, J.P. and F.P. Del Greco, Chapt. 11, DNA Reaction Rate Handbook, DNA 1948 H (1972), Bortner and Baurer, Eds., DASIAC DoD Nuclear Information and Analysis Center GE-TEMPO, Santa Barbara, CA.

82. Fisher, E.R. and E. Bauer, J. Chem. Phys. 57, 1966 (1972).

83. Bauer, E., R.H. Kummler and M.H. Bortner, Appl. Optics 10, 1861 (1971).

84. Walker, J., Planet. Space Sci. 16, 321 (1968).

85. Walker, J., R.S. Stolarski and A.F. Nagy, Ann. Geophys. 25, 831 (1969).

86. Black, G.R., L. Sharpless and T.G. Slanger, J. Chem. Phys. 58, 4792 (1973).

87. Slanger, T. and G. Black, J. Chem. Phys. 60, 468 (1974).

88. Schulz, G.J., Phys. Rev. 116, 114 (1959) ibid, 125, 229 (1962), ibid, 135, A988 (1964).

89. Ehrhardt, H. and K. Willman, Z. Physik, 204, 462 (1967).

90. Englehardt, A.G., A.V. Phelps and C.G. Risk, Phys. Rev. 135, A1566 (1964).

91. Herzenberg, A. and F. Mandl, Proc. Roy. Soc. A270, 48 (1962).

92. Chen, J.C.Y., J. Chem. Phys. 40, 3507 (1964), Phys. Rev. 146, 61 (1966).

93. Britwistle, D.T. and A. Herzenberg, J. Phys. B 4, 153 (1971).

94. Schulz, G.J., Rev. Mod. Phys. 45, 378 (1973).

95. Burrow, P.D. and P. Davidovitz, Phys. Rev. Lett. 21, 1789 (1968).

96. Ali, A.W., U.S. Naval Research Laboratory, Plasma Dynamics Technical Note 24 (1970) and NRL Report 7578 (1973).

97. Abraham, G. and E.R. Fisher, Wayne State University Report RIES 70-01 (1970).

98. Green, A.E.S. and C.A. Barth, J. Geophys. Res. 70, 1083 (1965).

99. Green, A.E.S., Ed., The Middle Ultraviolet, John Wiley and Sons, New York (1966) p. 165.

100. Shuler, K.E., T. Carrington and J.C. Light, p. 81 of Ref. 16.

101. Polanyi, J.C., J. Quant. Spect.ad. Transfer 3, 471 (1963).

102. Herschbach, D., p. 128 of Ref. 16.

103. Herzfeld, K.F. and T.A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, Academic Press, New York (1959).

104. Rapp, D. and T.E. Sharp, J. Chem. Phys. 38, 2641 (1963).

105. Callear, A.B., p. 145, Ref. 16.

106. Takayangi, K. in Advances in Atomic and Molecular Physics, D.R. Bates and I. Estermann, Eds., Academic Press, New York (1965) Vol. 1, p. 149.

107. Bates, D.R., J. Atm. Terrest. Phys. 6, 171 (1955).

108. Dalgarno, A., Planet. Space Sci. 10, 19 (1963).

109. Clark, T.C., S.H. Garnett and G.B. Kistiakowsky, J. Chem. Phys. 52, 4694 (1970).

110. Garnett, S.H., G.B. Kistiakowsky and B.V. O'Grady, J. Chem. Phys. 51, 84 (1969).

111. Bauer, E. and F.W. Cummings, J. Chem. Phys. 36, 618 (1962).

112. Treanor, C.E., J. Chem. Phys. 43, 532 (1965).

113. Millikan, R. and D. White, J. Chem. Phys. 39, 3209 (1963).

114. Breshears, W.D. and P.F. Bird, J. Chem. Phys. 48, 4768 (1968).

115. McNeal, R.J., M.E. Whitston, Jr., and G.R. Cook, Chem. Phys. Lett. 16, 507 (1972).

116. McNeal, R.J., M.E. Whitston and G.R. Cook, J. Geophys. Res. 79, 1527 (1974).

117. Fisher, E.R. and E. Bauer, J. Chem. Phys. 57, 1966 (1972).

118. Patel, C.K.N., Phys. Rev. Lett. 12, 588 (1964).

119. Taylor, R. and S. Bitterman, Revs. Mod. Phys. 41, 26 (1969).

120. Fisher, E.R. and R.H. Kummler, J. Chem. Phys. 49, 1075 (1968).

121. Breig, E.M. Brenner and R. McNeal, J. Geophys. Res. 78, 1225 (1973).

122. Hunten, D.M., J. Atm. Terres. Phys. 27, 583 (1965).

123. Starr, W.L., J. Chem. Phys. 43, 73 (1965).

124. Fite, W.L., W.R. Henderson, H.F. Krause and J.E. Mentall, Fifth Int. Conf. Phys. Electronic Atomic Collisions, Leningrad, USSR (1967).

125. Jamshidi, E., E.R. Fisher and R.H. Kummler, J. Geophys. Res. 78,

6151 (1973).

126. Kummler, R.H. and M.H. Bortner, Space Res. 12, 711 (1972).

127. Kumer, J.B. and T.C. James, J. Geophys. Res. 79, 638 (1974).

128. Schmeltekopf, A.L., F.C. Fehsenfeld, G.I. Gilman and E.E. Ferguson Planet. Space Sci. 15, 401 (1967).

129. Schmeltekopf, A.L., E.E. Ferguson and F.C. Fehsenfeld, J. Chem. Phys. 48, 2966 (1968).

130. Johnsen, R. and M.A. Biondi, J. Chem. Phys. 59, 3504 (1973).

131. Thomas, L. and R.B. Norton, J. Geophys. Res. 15, 401 (1967).

132. Newton, G.P., J.C.G. Walker and P.H.E. Meiyer, J. Geophys. Res. 79, 3807 (1974).

133. Whitten, R. and A. Dalgarno, Planet. Space Sci. 15, 1419 (1967).

134. COSPAR International Reference Atmosphere, North-Holland Publishing Co., Amsterdam (1965).

135. Lichten, W., Phys. Rev. 120, 848 (1960).

136. Olmstead, J., A.S. Norton and K. Street, J. Chem. Phys. 42, 2321 (1965).

137. Foner, S.N. and R.L. Hudson, J. Chem. Phys. 37, 1662 (1962).

138. Winters, H.F., J. Chem. Phys. 43, 926 (1965).

139. Brinkmann, R.T. and S. Trajmar, Ann. Geophys. 26, 201 (1970).

140. Borst, W.L., Phys. Rev. A 5, 648 (1972).

141. Stanton, P.N. and R.M. St. John, J. Opt. Soc. Am. 59, 252 (1969).

142. Shemansky, D.E. and A.L. Broadfoot, J. Quant. Spect. Rad. Transfer 11, 1401 (1971).

143. Jobe, J.D., F.A. Sharpton and R.M. St. John, J. Opt. Soc. Am. 57, 106 (1967).

144. Burns, D.J., F.R. Simpson and J.W. McConkey, J. Phys. B 2, 52 (1969).

145. Cartwright, D.C., Phys. Rev. A 2, 1331 (1970) and Aerospace Report TR-0059 (9260-01)-6 (1970).

146. Chung, S. and C.C. Lin, Phys. Rev. A 6, 988 (1972).

147. Ali, A.W., "Auroral Emission and Inelastic Electron Collision Processes in Air", NRL Memo Report 2724 (1973).

148. Ali, A.W. and A.D. Anderson, "Low-Energy Electron Impact Rate Coefficients for Some Atmospheric Species", NRL Report 7432 (1972).

149. Turner, B.R., J.A. Rutherford and R.F. Stebbings, J. Geophys. Res. 71, 4521 (1966).

150. Goldan, P.O., et al, J. Chem. Phys. 44, 4095 (1966).

151. Fehsenfeld, F.C., D.B. Dunken and E.E. Ferguson, Planet. Space Sci. 18, 1267 (1970).

152. Noxon, J.F., J. Chem. Phys. 36, 926 (1962).

153. Zipf, E.C., Jr., Bull. Am. Soc. 9, 185 (1964).

154. Young, R.A., Can. J. Chem. 44, 1171 (1966).

155. Vallance Jones, A. and R.L. Gattinger, J. Geophys. Res. 81, 497 (1976).

156. Meyer, J.A., D.W. Sester and D.H. Steadman, Astrophys. J. 157, 1023 (1969).

157. Kenty, C., J. Chem. Phys. 23, 1555 (1955).

158. Cermak, V., J. Chem. Phys. 44, 1318 (1966).

159. Young, R.A., G. Black and T.G. Slanger, J. Chem. Phys. 50, 303 (1969).

160. Young, R.A. and G.A. St. John, J. Chem. Phys. 48, 895 (1968).

161. Thrush, B.A., J. Chem. Phys. 47, 3691 (1967).

162. Wray, K., J. Chem. Phys. 44, 623 (1966).

163. Ajello, J., J. Chem. Phys. 53, 1156 (1970).

164. Aarts, J.F.M. and F.J. DeHeer, Physica, 52, 45 (1971).

165. Holland, R.F., J. Chem. Phys. 51, 3940 (1969).

166. Finn, T.G. and J.P. Doering, J. Chem. Phys. 64, 4490 (1976).

167. Cermak, V., J. Chem. Phys. 43, 4527 (1965).

168. Saha, M.N., Proc. Roy. Soc. Ser. A 160, 155 (1937).

169. Wulf, O.R. and L.S. Deming, J. Geophys. Res. 43, 283 (1938).

170. Lee, A.R. and N.P. Carleton, Phys. Lett. 27A, 195 (1968).

171. Shemansky, D.E., T.M. Donahue and E.C. Zipf, Quant. Spect. Rad. Transfer 20, 905 (1972).

172. Borst, W.L. and E.C. Zipf, Phys. Rev. A 1, 834 (1970).

173. McConkey, J.W., J.M. Woolsey and D.J. Burns, Planet. Space Sci. 15 1332 (1967).

174. Srivastava, B.N. and I.M. Mirza, Trans. Am. Geophys. Un. 48, 73 (1967).

175. Hirsh, M.N., E. Poss and P.N. Eisner, Phys. Rev. A 1, 1615 (1970).

176. Dashchenko, I.P. Zapesochnyi and A.I. Imre, Opt. Spectros. 35, 970 (1973).

177. Crandall, D.H., W.E. Kauppila, R.A. Phaneuf, P.O. Taylor and G.H. Dunn, Phys. Rev. A 9, 2545 (1974).

178. McLean, E.A., A.W. Ali, J.A. Stamper and S.O. Dean, Phys. Lett. A 38, 209 (1972).

179. Brocklehurst, B. and F.A. Downing, J. Chem. Phys. 46, 2976 (1967).

180. Davidson, G. and R. O'Neil, American Science and Engineering Report No. AFCRL-67-0277, Cambridge, MA (1968).

181. Wallace, L. and M.B. McElroy, Planet. Space Sci. 14, 677 (1966).

182. Sharp, W.E., Jr., Geophys. Res. 79, 1569 (1974).

183. Omholt, A., J. Atmosph. Terrest. Phys. 10, 320 (1957).

184. Hunten, D.M., Ann. Geophys. 14, 167 (1958).

185. Stebbings, R.F., B.R. Turner and J.A. Rutherford, J. Geophys. Res. 71, 771 (1966).

186. Vallance Jones, A., Space Sci. Rev. 11, 776 (1971) ibid 12, 258 (1971).

187. Wallace, L. and A.L. Broadfoot, Planet. Space Sci. 17, 975 (1969).

188. Pendleton, W.R., Jr. and L.D. Weaver, Final Technical Report, ARPA Order 1691, Contract F 33657-71-C-0174, Advanc. Res. Proj. Agency, Washington, DC, July (1973).

189. Cartwright, D.C., W.R. Pendleton, Jr. and L.D. Weaver, J. Geophys. Res. 80, 651 (1975).

190. Mitchell, K.B., J. Chem. Phys. 53, 1795 (1970).

191. Gray, D.D., T.D. Roberts and J.L. Morack, J. Chem. Phys. 57, 4190 (1972).

192. Gilmore, F.R., Rand Cp. Report RM-4034-1-PR (1966).

193. McGowan, J.W., et al, Phys. Rev. Lett. 14, 620 (1964).

194. Fite, W.L. and R.T. Brackmann, Proc. Sixth Int. Conf. Ionization Gases, North-Holland Publishing Co., New York (1963) Vol. 1, p.21.

195. Fineman, M.A., et al, Proc. Fourth Int. Conf. Phys. Elect. Atomic Collisions, Science Bookcrafters, Inc., New York (1965), p. 425.

196. Michels, H.H., "Theoretical Study of Dissociative Recombination

Kinetics", AFWL-TR-73-288 (1974).

197. Kley, D., G.M. Lawrence and E.J. Stone, J. Chem. Phys. 66, 4157 (1977).

198. Michels, H.H., H.J. Kolker and G. Peterson, "Theoretical Analysis of Dissociative Recombination in N_2^+", Proc. High Alt. Nuclear Effects Symp. SRI (1971).

199. Seaton, M.J., in "The airglow and Aurora", E.B. Armstrong and A. Dalgarno, Ed., Pergamon Press, London (1956).

200. Smith, K., R.J.W. Henry and P.G. Burke, Phys. Rev. 157, 51 (1967).

201. Henry, R.J.W., P.G. Burke and A.L. Sinfailam, Phys. Rev. 178, 218 (1969).

202. Ormonde, S., K. Smith, B.W. Torres and A.R. Davies, Phys. Rev. A 8 262 (1973).

203. Berrington, K.A., P.G. Burke and W.D. Robb, J. Phys. B, Atom. Mol. Phys. 8, 2500 (1975).

204. Ali, A.W., "Electron Impact Rate Coefficients for the Low Lying Metastable States of O, O^+, N and N^+", NRL Memo Report 3371 (1976).

205. Ali, A.W., "Charge Exchange and Ion-Molecule Rearrangements in the Disturbed E and F Regions - Implications for Optical Emissions and Deionization", NRL Memo Report 3165 (1975).

206. Rush, D.W., W.E. Sharp and P.B. Hays, J. Geophys. Res. 80, 13 (1975).

207. Winters, H.F., J. Chem. Phys. 44, 1472 (1966).

208. Wells, W.C., W.L. Borst and E.C. Zipf, Phys. Rev. A 14, 695 (1976).

209. Lin, C.L. and F. Kaufman, J. Chem. Phys. 55, 3760 (1971).

210. Slanger, T.G., B.J. Wood and G.J. Black, J. Geophys. Res. 76,

8430 (1971).

211. Black, G., T.G. Slanger, G. St. John and R.A. Young, J. Chem. Phys. 51, 116 (1969).

212. Davenport, J.E., T.G. Slanger and G. Black, J. Geophys. Res. 81, 12 (1976).

213. Rush, D.W., A.I. Stewart, P.B. Hays and J.H. Hoffman, J. Geophys. Res. 80, 2300 (1975).

214. Henry, R.J.W., Astrophys. J. 161, 1153 (1970).

215. Saraph, H.E., M.J. Seaton and J. Shemming, Proc. Roy. Soc. (London) 89, 27 (1966).

216. Dalgarno, A. and M.B. McElroy, Planet. Space Sci. 14, 1321 (1966).

217. Gilpin, R.H., H.I. Schiff and K.H. Welge, J. Chem. Phys. 55, 1087 (1971).

218. Schulz, G. and J.T. Dowell, Phys. Rev. 128, 174 (1962).

219. Spence, D. and G. Schulz, Phys. Rev. A 2, 1802 (1970).

220. Hyman, E., Naval Research Lab., Private Communications (1971).

221. Cosby, P. and T. Moran, J. Chem. Phys. 52, 6157 (1970).

222. Stebbings, R.F., et al, General Atomic Division (General Dynamics Corporation) Report DASA 1708 (1965).

223. Fite, W.L., R.T. Brackmann and W.R. Henderson, Proc. Fourth Int. Conf. Phys. Electron Atomic Collisions, Science Bookcrafters, Inc. New York (1965) p. 100.

224. O'Malley, T.F., Phys. Rev. 155, 59 (1967).

225. Chen, J.C.Y. and J.L. Preacher, Phys. Rev. 163, 103 (1967).

226. Kovacs, M.A. and M.A. Mack, Appl. Phys. Lett. 20, 487 (1972).

227. Kiefer, J.H. and R.W. Lutz, Eleventh Symp. (Int.) on Combustion,

The Combustion Institute, Pittsburgh, PA (1967) p. 67.

228. Bauer, S.H. and S.C. Tsang, Phys. Fluids 6, 182 (1963).

229. Vallance Jones, A. and R.L. Gattinger, Planet. Space Sci. 11, 961 (1963).

230. Evans, W.F., D.M. Hunten, E.J. Llewellyn and A. Vallance Jones, J. Geophys. Res. 73, 2885 (1968).

231. Jones, I.T.N. and R.P. Wayne, J. Chem. Phys. 51, 3617 (1969).

232. Hampson, R., W. Braun, R. Brown, D. Garvin, J. Herron, R. Huie, M. Kurylo, A. Laufer, J. McKinley, H. Okabe, M. Sheer and W. Tsang, J. Phys. Chem. Reference Data 2, 267 (1973).

233. Fluegge, R.A. and D. Headrick, Cornell Aeronautic Lab. Report DASA 2551 (1970).

234. Trajmar, S., D.C. Cartwright and W. Williams, Phys. Rev. A 4, 1482 (1971).

235. Julienne, P.S. and M. Krause, J. Res. Nat'l. Bur. Stand. 76A, 661 (1972).

236. Swider, W., J. Geophys. Res. 79, 3221 (1974).

237. Evans, W.F.J., E.J. Llewellyn and A. Vallance Jones, Ann. Geophys. 26, 167 (1970).

238. Evans, W.F.J., E.J. Llewellyn and A. Vallance Jones, J. Geophys. Res, 77, 4899 (1972).

239. Wood, H.C., Ph-D Thesis, University of Saskatchewan, Canada (1972).

240. Trozzalo, A.M., Ed., Int. Conf. Singlet Molecular Oxygen and Its Role in Environmental Sciences , Ann. NY Academy Sci. 171, Art. 1 (1970).

241. Clark, I.D. and R.P. Wayne, Proc. Roy. Soc. A314, 111 (1969).

242. Winer, A. and K. Bayes, J. Phys. Chem. 70, 302 (1966).

243. Clark, I.D. and R.P. Wayne, Chem. Phys. Lett. 3, 93 (1969).

244. Findlay, F., C. Fortin and D. Snelling, Chem. Phys. Lett. 3, 204 (1969).

245. Steer, R.P., R.A. Ackerman and J.N. Pitts, Jr., J. Chem. Phys. 51, 843 (1969).

246. Clark, I.D. and R.P. Wayne, Chem. Phys. Lett. 3, 405 (1969).

247. McNeal, R.J. and G.R. Cook, J. Chem. Phys. 47, 5385 (1967).

248. Megill, L.R. and J.B. Hasted, Planet. Space Sci. 13, 339 (1965).

249. Kummler, R.H. and M.H. Bortner, GE Company TIS Report R67SD20 (1967).

250. Fehsenfeld, F.C., D.L. Albritton, J.A. Burt and H.I. Schiff, Can. J. Chem. 47, 1793 (1969).

251. Kummler, R.H. and M.H. Bortner, p. 237, Ref. 240.

252. Noxon, J., J. Geophys. Res. 75, 1879 (1970).

253. Megill, L., A. Despain, D. Baker and K. Baker, J. Geophys. Res. 75, 4775 (1970).

254. Schiff, H.I., J. Haslett and L. Megill, J. Geophys. Res. 75, 4363 (1970).

255. Arnold, S.J., N. Finlayson and E.A. Ogryzlo, J. Chem. Phys. 44, 2529 (1966).

256. Young, R.A. and G. Black, J. Chem. Phys. 42, 3740 (1965).

257. Derwent, R.G. and B.A. Thrush, Trans. Far. Soc. 67, 2036 (1971).

258. Young, R.A., G. Black and T.G. Slanger, J. Chem. Phys. 49, 4758 (1968).

259. Noxon, J., J. Chem. Phys. 52, 1852 (1970).

260. Wallace, L. and J.W. Chamberlain, Planet. Space Sci. 2, 60 (1959).

261. Seaton, M.J., J. Atm. Terr. Phys. 4, 295 (1953).

262. Vallance Jones, A. and R.L. Gattinger, J. Geophys. Res. 79, 4821 (1974).

263. Becker, J.H., W. Groth and U. Schurath, Chem. Phys. Lett. 8, 259 (1971).

264. Wallace, L. and D.M. Hunten, J. Geophys. Res. 73, 4813 (1968).

265. Chamberlain, J.W., Astrophys. J. 121, 277 (1955).

266. Degen, V., J. Geophys. Res. 77, 6213 (1972).

267. Young, A. and G. Black, J. Chem. Phys. 44, 3741 (1966).

268. Watanabe, K., Adv. Geophys. 5, 153 (1958).

269. Mehr, F.J. and M.A. Biondi, Phys. Rev. 181, 264 (1969) and references therein.

270. Zipf, E.C., Jr., Bull. Am. Phys. Soc. 12, 225 (1967).

271. Zipf, E.C., Jr., Bull. Am. Phys. Soc. 15, 418 (1970).

272. Thomas, L.D. and R.K. Nisbet, Phys. Rev. A 11, 170 (1975).

273. Carleton, N.P., F.J. LeBlanc and O. Oldenberg, Bull. Am. Phys. Soc. 11, 503 (1966).

274. McGrath, W.D. and J.J. McGarvey, Planet. Space Sci. 15, 427 (1967).

275. Garvin, D., "Chemical Kinetics Data Survey" IV, Nat'l Bureau of Standards, NBSIR-73-203 (1973).

276. Hunt, B.G., J. Geophys. Res. 71, 1385 (1966).

277. Hampson, J., Canadian Armament Research and Development Establishment T.N. 1627/64 (1964).

278. Paraskevopoulos and R.J. Cvetanovic, Chem. Phys. Lett. 9, 603 (1971).

279. Garvin, D. and R. Hampson, Proc. of the Second Conf. on the Climatic Impact Assessment Program, A. Broderick, Ed., U.S. Dept. of Transportation Report DOT-TSC-OST, 73-4 (1973).

280. Crutzen, P.J., J. Geophys. Res. 76, 7311 (1971).

281. Hesstvedt, E., Geophys. Norveg. 27, 1 (1967).

282. Anderson, J., Ph.D. Dissertation, University of Colorado (1970).

283. Nicolet, M. in Ref. 279.

284. Kummler, R.H., M.H. Bortner and T. Baurer, Environm. Sci. Tech. 3, 248 (1969).

285. Kummler, R.H. and T. Baurer, J. Geophys. 78, 5306 (1973).

286. Chemeides, W. and J.C.G.Walker, J. Geophys. Res. 78, 8751 (1973).

287. Garvin, D. and R. Hampson, NBS Report NBSIR 74, 430 (1974).

288. Chapman, S., Proc. Roy. Soc. A132, 353 (1931).

289. Barth, C.A. and A.F. Hildenbrandt, J. Geophys. Res. 66, 985 (1961).

290. Donahue, T.M., B. Guenther and R.J. Thomas, J. Geophys. Res. 78, 6662 (1973).

291. Slanger, T.G. and G. Black, Planet. Space Sci. 25, 79 (1977).

292. Felder, W. and R.A. Young, J. Chem. Phys. 56, 6028 (1972).

293. Schaeffer, R.C., P.D. Feldman and E.C. Zipf, J. Geophys. Res. 77, 6828 (1972).

294. Hays, P.B. and W.E. Sharp, J. Geophys. Res. 78, 1153 (1973).

295. Lawrence, G.M. and M.J. McEwan, J. Geophys. Res. 78, 8314 (1973).

296. Evans, W.F.J. and A. Vallance Jones, Can. J. Phys. 43, 697 (1965).

297. Slanger, T.G., B.J. Wood and G. Black, Chem. Phys. Lett. 17, 401 (1972).

298. Atkinson, R. and K.H. Welge, J. Chem. Phys. 57, 3689 (1972).

299. Stuhl, F. and K.H. Welge, Can. J. Chem. 47, 1870 (1969).

300. Dalgarno, A., R.J.W. Henry and A.L. Stewart Planet. Space Sci. 12, 235 (1964).

301. Stebbings, R.F., in "Advances in Atomic and Molecular Physics", Bates and E. Stermann, Ed., Vol. 4 (1968), Academic Press, NY.

302. Czyzak, S.J., T.K. Krueger, P. de A.P. Martins, H.E. Saraph and M.J. Seaton, Mon. Nat. R. Astron. Soc. 148, 361 (1970).

303. Ali, A.W., Appl. Optics 12, 2243 (1973).

304. Walker, J.C.G., D.G. Torr, P.B. Hays, D.W. Rush, K. Docken, G. Victor and M. Oppenheimer, J. Geophys. Res. 80, 1026 (1975).

305. Vegard, L., Nature 144, 1089 (1939).

306. Eather, R.H., Rev. Geophys. 5, 207 (1967).

307. McNeal, R.J. and J.H. Birely, Rev. Geophys, Space Phys. 11, 633 (1973).

308. Birely, J.H. and P.A. Johnson, Geophys. Res. Lett. 1, 113 (1974).

309. Birely, J.H., Phys. Rev. A 10, 550 (1974).

310. McNeal, R.J. and D.C. Clark, J. Geophys. Res. 74, 5065 (1969).

311. Hoffman, J.M., G.J. Lockwood and G.H. Miller, Phys. Rev. A 11, 841 (1975).

312. DeHeer, F.J. and J.F.M. Aarts, Physica 48, 620 (1970).

313. Dahlberg, D.A., D.K. Anderson and I.E. Dayton, Phys. Rev. 164, 20 (1967).

314. Dufay, M., J. Desesquelles, M. Druetta and M. Eidelsberg, Ann. Geophys. 22, 614 (1966).

315. Robinson, J.M. and H.B. Gilbody, Proc. Phys. Soc. (London) 92, 589 (1967).

316. Moore, J.H., J. Geophys. Res. 77, 5567 (1972).

317. Park, J.T., F.D. Schowengerdt and D.R. Schoonover, Phys. Rev. A 3, 679 (1971).

318. Hughes, R.H. and D.K.W. Ng, Phys. Rev. 136, A1222 (1964).

319. Edgar, B.C., H.S. Porter and A.E.S. Green, Planet. Space Sci. 23, 787 (1975).

320. Hunten, D.M., Space Sciences Rev. 6, 493 (1967).

321. Narcisi, R.S., Ann. Geophys. 22, 224 (1966).

322. Narcisi, R.S. and A.D. Bailey, J. Geophys. Res. 7, 3687 (1965).

323. Narcisi, R.S., C.R. Philbrick, M.A. MacLeod and N.W. Rosenberg, Eos Trans. AGU 53, 462 (1972).

324. Narcisi, R.S., in "Physics and Chemistry of Upper Atmosphere", B. M. McCormak, Ed., Reidel Publishing Co., Boston (1973).

325. Kvifte, G., p. 158 in Ref. 324.

326. Fogel, M., Ya. Sov. Phys. Usp 3, 390 (1960).

327. Layton, J.K., J. Chem. Phys. 47, 1869 (1967).

328. Moiseiwitsch, B. and S. Smith, Rev. Mod. Phys. 40, 238 (1968).

329. McGowan, J.W., J.F. Williams and E.K. Corley, Phys. Rev. A 180, 132 (1969).

330. Fite, W.L., R.F. Stebbings and R.T. Brackmann, Phys. Rev. 116, 356 (1959).

331. Lichten, W. and S. Schulz, Phys. Rev. 116, 1132 (1959); Lichten, W., Phys. Rev. Lett. 6, 12 (1961).

332. Hils, D., H. Kleinpoppen and H. Koschmieder, Proc. Phys. Soc. 89, 35 (1966).

333. Zapesochnyi, I.P. and L.L. Shimon, Soviet Optics Spect. 19, 268

(1965).

334. Holt, H.K. and R. Krotkov, Phys. Rev. 144, 82 (1966).

335. Ingraham, J.C. and S.C. Brown, Phys. Rev. 138, A1015 (1965).

336. Phelps, A.V., Phys. Rev. 99, 1307 (1955).

337. Chaney, E.L. and L.G. Christophorou, J. Chem. Phys. 51, 883 (1969).

338. Basco, N. and R.A.W. Norrish, Disc. Faraday Soc. 33, 99 (1962).

339. March, R.S. Furnival and H.I. Schiff, Photochem. Photobiol. 4, 971 (1965).

340. Anlauf, K., D. Maylotte, J. Polanyi and R. Berstein, J. Chem. Phys. 51, 5716 (1969).

341. Polanyi, J., D. Tardy, J. Chem. Phys. 51, 5717 (1969).

342. Polanyi, J.C., Applied Optics 10, 1717 (1971) and many other articles on specific reactions in the same issue.

343. McFarland, M., D.L. Albritton, F.C. Fehsenfeld, E.E. Ferguson and A.L. Schmeltekopf, J. Chem. Phys. 59, 6620 (1973).

344. Bauer, E. and F.W. Cummings, J. Chem. Phys. 36, 618 (1962).

345. King, A.B. and C. Gatz, J. Chem. Phys. 37, 1566 (1962).

346. Kenty, C., J. Chem. Phys. 37, 1567 (1962).

347. Broida, H.P., J. Chem. Phys. 36, 444 (1962).

348. Cher, M. and C. Hollingsworth, Can. J. Chem. 47, 1937 (1969).

349. Fehsenfeld, F.C., A.L. Schmeltekopf, D.B. Dunkin and E.E. Ferguson ESSA Technical Report REL 135-AL3, Boulder, Colorado (1969).

350. Pradel, P., F. Roussel, A.S. Schlatchter, G. Spiess and A. Vallance, Phys. Rev. A 10, 797 (1974).

351. Bauer, E. and M. Salkoff, J. Chem. Phys. 33, 1202 (1960).

352. Sester, D.W. and B.A. Thrush, Proc. Roy. Soc. A 288, 275 (1965).

353. Carabetta, R.A. and W.E. Kaskan, Eleventh Int. Symp. on Combustion The Combustion Institute, Pittsburg, PA (1967) p. 321.

354. Bates, D.R., Earth is a Planet, University of Chicago Press, Chicago (1960) p. 576.

355. Belles, F.E. and M.R. Lauver, J. Chem. Phys. 40, 415 (1964).

356. Ali, A.W. and W.W. Jones, "Towards Shorter Wavelength Lasers and Breaking the 1000 Å Barrier - III (Recombination)", NRL Memo Report 3015 (1975).

Table 1. Radiative lifetimes and transitions for principal atmospheric species

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
ATOMS AND ATOMIC IONS				
$N(^4S^o)$	Ground State			
$(^2D^o_{\frac{3}{2}})$	6.1×10^4	$^4S^o \leftarrow {}^2D^o_{3/2}$; 5200 (nebular)	2.38	25
$(^2D^o_{\frac{1}{2}})$	1.4×10^5	$^4S^o \leftarrow {}^2D^o_{5/2}$; 5201	2.38	25
$(^2P^o)$	13	$^2D^o \leftarrow {}^2P^o$; 10,396; 10,404	1.19	25
$(3s\ ^4P)$	2.5×10^{-9}	$^4S^o \leftarrow {}^4P$; 1200, 1201	10.31	25,26
$N^+(^3P)$	Ground State			
(^1D)	250	$^3P \leftarrow {}^1D$; 6584, 6548	1.89	25
(^1S)	0.90	$^1D \leftarrow {}^1S$; 5755	2.15	25
$O(^3P)$	Ground State			
(^1D)	148	$^3P \leftarrow {}^1D$; 6300, 6364 (red lines)	1.96	25,27,28
(^1S)	0.80	$^1D \leftarrow {}^1S$; 5577 (green line)	2.22	25,29

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
ATOMS AND ATOMIC IONS (Cont'd.)				
$O(3s\ ^5S^o)$	0.0006	$^3P \leftarrow ^5S^o$; 1356, 1359	9.13	25
$(3s\ ^3S^o)$	1.8×10^{-9}	$^3P \leftarrow ^3S^o$; 1302,1305,1306	9.51	25,30
$O^+(^4S^o)$	Ground State			
$(^2D^o_{\frac{3}{2}})$	5.9×10^3	$^4S^o \leftarrow ^2D^o_{3/2}$; 3726 (nebular)	3.33	25
$(^2D^o_{\frac{5}{2}})$	2.1×10^4	$^4S^o \leftarrow ^2D^o_{5/2}$; 3729	3.32	25
$(^2P^o_{\frac{1}{2}})$	5.4	$^2D^o \leftarrow ^2P^o_{1/2}$; 7319,7330 (auroral)	1.69	25
$(^2P^o_{\frac{3}{2}})$	4.2	$^2D^o \leftarrow ^2P^o_{3/2}$; 7319,7330	1.69	25
DIATOMIC MOLECULES AND MOLECULAR IONS[a]				
$N_2\ (X^1\Sigma_g^+)$	Ground State			
$(A^3\Sigma_u^+)$	1.3 (F_2); 2.7 (F_1,F_3)	A → X (Vegard-Kaplan)	6.2	31,32,33
$(B^3\Pi_g)$	8.0×10^{-6}	B → A; 10,510 (first positive)	1.2	33,34,35

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
ATOMS AND ATOMIC IONS (Cont'd.)				
N_2 ($W^3\Delta_u$)	1.0×10^{-3} (v=2)	W → X W → B	7.4 0.003	36,37
($B'^3\Sigma_u^-$)	10^{-5} est.	B' → B (Y Bands)	0.8	38
($a'^1\Sigma_u^-$)	≥ 0.04	a' → X (Wilkinson)	8.4	
($a^1\Pi_g$)	1.4×10^{-4} $1.15 \pm 0.20 \times 10^{-4}$	a → X; 1450 (Lyman-Birge-Hopfield)	8.6	39,40
($w^1\Delta_u$)	10^{-4} est.	w → a; 36,400	0.3	38
($C^3\Pi_u$)	4.0×10^{-8}	C → B; 3371 (second positive)	3.7	41,42,43,44
($E^3\Sigma_g^+$)	2.0×10^{-4}	E → A,C	5.7,0.8	40,45
N_2^+ ($X^2\Sigma_g^+$)	Ground State			
($A^2\Pi_u$)	1.7×10^{-5} (v=3)	A → X; 11,036 (Meinel)	1.0	35,44,46-48
($B^2\Sigma_u^+$)	5.9×10^{-8}	B → X; 3914 (first negative)	3.2	42,43,44
($^4\Sigma_u^+$)	Mod. Long	$^4\Sigma_u^+$ → X	~ 6	38,49

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
DIATOMIC MOLECULES AND MOLECULAR IONS (Cont'd.)				
NO($X^2\Pi$)	Ground State			
($a^4\Pi$)	156, 93, 35 msec.	a → X	4.7	50
	~ 0.16 (Ω = 5/2)			51
($A^2\Sigma^+$)	2.0×10^{-7}	A → X; 2265 (γ bands)	5.5	52,53,54
($B^2\Pi$)	3.6×10^{-6}	B → X; (β bands)	5.6	52,55
NO^+($X^1\Sigma^+$)	Ground State			
($a^3\Sigma^+$)	Long	a → X	6.4	56,57
($b^3\Pi$)	1.4×10^{-4}	b → a	0.9	58
($w^3\Delta$)	~ 10^{-4} est.	w → b	0.3	38
NO_2 ($^2B_1$) [b]	5.5×10^{-5} to 9.0×10^{-5}	$A^2B_1 \rightarrow X^2A_1$		59,60
O_2 ($X^3\Sigma_g^-$)	Ground State			
($a^1\Delta_g$)	3.9×10^3	a → X; 12,680 (infrared atmospheric)	0.98	28,61,62

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
DIATOMIC MOLECULES AND MOLECULAR IONS (Cont'd.)				
O_2 ($b\,^1\Sigma_g^+$)	12	b → X; 7619 (atmospheric)	1.63	61,63,64
($c\,^1\Sigma_u^-$)	Long	c → X; 2856 (Herzberg II)	4.0	65
($C\,^3\Delta_u$)	Long	C → X(Herzberg III) C → a	~ 4.2	38
($A\,^3\Sigma_u^+$)	0.03	A → X: 2856 (Herzberg I) A → b; 4586 (Broida-Gaydon)	4.3	66
($B\,^3\Sigma_u^-$)	4.2×10^{-8}	B → X: 2030 (Schumann-Runge)	6.1	61
O_2^+($X\,^2\Pi_g$)	Ground			
($a\,^4\Pi_u$)	Long	a → X; 6026	4.0	38
($A\,^2\Pi_u$)	7×10^{-7}	A → X (second negative)	5.0	67,68
($b\,^4\Sigma_g^-$)	1.1×10^{-6}	b → a; 6026 (first negative)	2.1	67,68,70
CO($X\,^1\Sigma_g^-$)	Ground State			

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
DIATOMIC MOLECULES AND MOLECULAR IONS (Cont'd)				
CO($a^3\Pi$)	$\sim 10^{-2}$ (dep. on J)	a → X (Cameron bands)	6.0	71,72
($a'^3\Sigma^+$)	10^{-5} (v=4)	a' → a (Asundi bands) a' → X (Birge-Hopfield)	~ 0.9 ~ 6.9	73,74
($d^3\Delta$)	6.0×10^{-6}	d → a (triplet bands)	1.5	73
$CO^+(X^2\Sigma^+)$	Ground			
($A^2\Pi$)	3.8×10^{-6}	A → X (comet tail)	2.6	68,46
CH($X^2\Pi$)	Ground			
($A^2\Delta$)	5×10^{-7}	A → X	2.9	75,76
($B^2\Sigma$)	4×10^{-7}	B → X	3.2	76
CN($X\Sigma^+$)	Ground			
($A^2\Pi$)	7×10^{-6} (v=1)	A → X (red bands)	1.1	77

Table 1. (Cont'd.)

Species and State	Mean Radiative Lifetime (sec)	Principal Transition; λ (in A); Name of Transition	Approx. ΔE_{if} (eV)	References
DIATOMIC MOLECULES AND MOLECULAR IONS (Cont'd)				
$CN(B^2\Sigma^+)$	8×10^{-8}	B X; 3883 (violet bands)	3.2	78,79

NOTES:

[a]The quoted lifetime is for the v=o level, and the wavelength and energy are for the (0,0) transition.

[b]This tiatomic molecule is included at this point for the sake of continuity with the NO and NO^+ species preceding.

Table 2. Ground state vibrational data for atmospheric molecules

Molecule and Vibrational Spacing	Energy ∿(eV)	Principal Transition λ(μ)	Lifetime (sec)	Reference
N_2				
v=1	0.29		Long	80
O_2				
v=1	0.19		Long	80
NO				
v=1	0.23	5.3	8.3×10^{-2}	80
v=2	0.46	2.68	1.3	81
CO				
v=1	0.26	4.6	2.9×10^{-2}	80
v=2	0.52	2.35	1.0	81
OH				
v=1	0.44	2.8	8.2×10^{-2}	80
v=2	0.88	1.4	1.8×10^{-1}	81
O_3 (a)	v_1	v_2	v_3	
Vib. sp.	0.14	0.09	0.13	80
λ(μ)	9.6	14.0	9.0	81
τ(sec)	9.2×10^{-2}	3.7	8.0	81

Table 2. (Cont'd.)

Molecule and Vibrational Spacing	Energy (eV)	Principal Transition $\lambda(\mu)$	Lifetime (sec)	Reference
CO_2 [a]	v_1	v_2	v_3	
vib. sp.	0.17	0.08	0.29	80
$\lambda(\mu)$		15.0	4.26	81
τ(sec)		3.6	2.5×10^{-3}	81

[a]The vibrational information is arranged according to the modes of oscillation and do not conform to the headings of the table.

Table 3. Electron impact excitation rate coefficients for eight vibrational levels of N_2

T_e/X_v	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0.1	1.98(-14)	1.49(-16)	6.28(-17)	1.57(-17)	5.58(-18)	1.37(-18)	2.27(-19)	2.51(-20)
0.2	4.01(-12)	1.48(-12)	8.81(-13)	4.16(-13)	2.16(-13)	1.14(-13)	3.28(-14)	7.81(-15)
0.3	5.63(-11)	2.82(-11)	1.83(-11)	1.05(-11)	6.20(-12)	4.13(-12)	1.45(-12)	4.31(-13)
0.4	2.08(-10)	1.14(-10)	7.59(-11)	4.76(-11)	3.02(-11)	2.24(-11)	8.71(-12)	2.85(-12)
0.5	4.38(-10)	2.52	1.68(-10)	1.11(-10)	7.33(-11)	5.77(-11)	2.39(-11)	8.26(-12)
0.6	6.96(-10)	4.11	2.74	1.88	1.27(-10)	1.04(-10)	4.47	1.60(-11)
0.7	9.43(-10)	5.66	3.77	2.65	1.82	1.52	6.76	2.47
0.8	1.16(- 9)	7.04	4.67	3.35	2.32	1.98	9.00(-11)	3.33
0.9	1.34	8.20	5.41	3.96	2.75	2.38	1.10(-10)	4.12
1.0	1.48	9.12	5.99	4.45	3.11	2.72	1.27	4.80
1.1	1.58	9.84(-10)	6.43	4.85	3.38	2.99	1.42	5.37
1.2	1.66	1.04(- 9)	6.75	5.15	3.60	3.20	1.53	5.83
1.3	1.71	1.08	6.96	5.39	3.75	3.37	1.62	6.19
1.4	1.74	1.10	7.09	5.56	3.86	3.48	1.69	6.46
1.5	1.76	1.12	7.16	5.67	3.93	3.57	1.74	6.65

Table 3. (Cont'd.)

T_e/X_V	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
1.6	1.77	1.12	7.17	5.75	3.96	3.62	1.77	6.78
1.7	1.76	1.12	7.15	5.79	3.97	3.65	1.79	6.86
1.8	1.75	1.12	7.09	5.81	3.96	3.66	1.80	6.89
1.9	1.73	1.11	7.00	5.80	3.94	3.65	1.80	6.89
2.5	1.56	1.02(- 9)	6.26	5.51	3.61	3.45	1.71	6.46
3.0	1.39	9.21(-10)	5.57	5.15	3.36	3.20	1.58	5.88
3.5	1.24	8.29	4.93	4.77	2.93	2.95	1.44	5.29
4.0	1.11(- 9)	7.47	4.38	4.43	2.64	2.73	1.32	4.74
4.5	9.95(-10)	6.74	3.90	4.12	2.38	2.55	1.21	4.24
5.0	8.96(-10)	6.11(-10)	3.49(-10)	3.84(-10)	2.16(-10)	2.39(-10)	1.12(-10)	3.80(-11)

Numbers in parenthesis indicate powers of 10 by which the entries are to be multiplied.

Where no parenthesis are given the entries are multiplied by the power of 10 for the preceding entries.

Table 4. Energy transfer from $N_2^{\ddagger}$

Level	Collision Partner	Probable Product	Rate Constant	Temperature Range (K)	References
1	N_2	Kinetic energy	$\ll 10^{-20}$	300	17,119,120
1	N_2	Kinetic energy	8.5×10^{-7} Exp$(-273/T^{1/3})$	1000-5000	17,119
1	N_2	$N_2^{\ddagger}$ (Resonant VV)	3×10^{-13}	300	120
1	O_2	Kinetic energy	$\ll 10^{-20}$	300	17
1	O_2	Kinetic energy	8.5×10^{-7} Exp$(-273/T^{1/3})$	1000-5000	17
1	O_2	$O_2^{\ddagger}$ (V-V Nonresonant)	1.74×10^{-10} Exp$(-124/T^{1/3})$	200-5000	17
1	O	Kinetic energy	1.2×10^{-13} Exp$(-23/T^{1/3})$	300-5000	114-116,121
1	CO_2	$CO_2^{\ddagger}$ (001) VV-Nonresonant	1.71×10^{-6} Exp$(-175/T^{1/3})$ + 6.0×10^{-14} Exp$(15.3/T^{1/3})$	200-2000	17
1	NO	$NO^{\ddagger}$ (Nonresonant-VV)	1.5×10^{-16}		120

TABLE 5. Quenching data for N ($A^3\Sigma_u^+$)

Quenchant	Rate Constant ($cm^3\ sec^{-1}$)	Reference
N_2	$< 3 \times 10^{-19}$	152
	$\sim 10^{-19}$	14
O_2	2.5×10^{-12}	156
		159
O	$\leq 3 \times 10^{-11}$	10
	5×10^{-11}	14
	7.5×10^{-11}	155
N	5×10^{-11}	160
	5×10^{-12}	161
	5×10^{-11}	162
NO	7×10^{-11}	160

Table 6. Electron impact excitation and deexcitation rate coefficients for the low lying states of nitrogen atom

T_e(eV)	$^4S - ^2D$	$^4S - ^2P$	$^2D - ^2P$
0.1	8.0 (-20)[a]	2.6 (-25)	2.10 (-14)*
	6.3 (-10)[b]	5.5 (-10)	5.7 (- 9)
0.2	1.54 (-14)	2.03 (-17)	1.16 (-11)
	8.6 (-10)	7.5 (-10)	7.8 (- 9)
0.3	1.25 (-12)	1.11 (-14)	9.78 (-11)
	1.35 (- 9)	1.1 (- 9)	8.9 (- 9)
0.5	4.2 (-11)	1.47 (-12)	6.0 (-10)
	1.9 (- 9)	1.2 (- 9)	1.0 (- 8)
0.7	1.98 (-10)	1.63 (-11)	1.1 (- 9)
	2.34 (- 9)	1.8 (- 9)	1.0 (- 8)
1.0	6.38 (-10)	8.91 (-11)	2.05 (- 9)
	2.7 (- 9)	2.1 (- 9)	1.1 (- 8)
1.2	1.08 (- 9)	1.73 (-10)	2.56 (- 9)
	3.1 (- 9)	2.29 (- 9)	1.16 (- 8)
1.5	1.52 (- 9)	3.38 (-10)	3.24 (- 9)
	2.9 (- 9)	2.4 (- 9)	1.2 (- 8)
2.0	2.27 (- 9)	6.54 (-10)	4.1 (- 9)
	2.9 (- 9)	2.6 (- 9)	1.2 (- 8)
3.0	3.31 (- 9)	1.23 (-9)	5.18 (- 9)
	2.9 (-9)	2.7 (- 9)	1.3 (- 8)

Table 6. (Cont'd.)

T_e(eV)	$^4S - ^2D$	$^4S - ^2P$	$^2D - ^2P$
5.0	4.5 (- 9)	1.99 (- 9)	6.2 (- 9)
	2.90 (- 9)	2.7 (- 9)	1.3 (- 8)
7.0	5.26 (- 9)	2.36 (- 9)	6.5 (- 9)
	2.9 (- 9)	2.6 (- 9)	1.3 (- 8)
10.0	5.85 (- 9)	2.4 (- 9)	6.5 (- 9)
	2.9 (- 9)	2.3 (- 9)	1.2 (- 8)
15.0	5.97 (- 9)	2.49 (- 9)	6.1 (- 9)
	2.79 (- 9)	2.1 (- 9)	1.1 (- 8)
20.0	4.96 (- 9)	2.28 (- 9)	5.47 (- 9)
	2.2 (- 9)	1.8 (- 9)	9.7 (- 9)

*Numbers in parenthesis indicate the power of ten by which the entries are multiplied.

[a]Excitation rate coefficient.

[b]The corresponding deexcitation rate coefficient.

Table 7. Quenching of $N(^2D)$

Quenching Species	Rate Constant ($cm^3\ sec^{-1}$)	Reference
O_2	6×10^{-12}	209,210
N_2	1.6×10^{-14}	209
O	1.8×10^{-12}	211
	6×10^{-13}	212
NO	7.0×10^{-11}	209
e	See Table 6	204

Table 8. Deexcitation rate coefficients for the low lying metastable states of N^+ (T_e in units of eV).

Transition	Deexcitation Rate Coefficients (cm^3 / sec)
$^1D - {}^3P$	$4.8 \times 10^{-8} (T_e)^{-1/2}$
$^1S - {}^3P$	$3.2 \times 10^{-8} (T_e)^{-1/2}$
$^1S - {}^1D$	$3.3 \times 10^{-8} (T_e)^{-1/2}$

Table 9. Deactivation of $O_2^{\ddagger}$ (v=1)

Reaction	Rate Coefficient (cm^3 sec^{-1})	T Range °K	References
$O_2^{\ddagger} + M \rightarrow O_2 + M$	4.81×10^{-8} $Exp(-170/T^{1/3})$	200-5000	17,113,119,226
$M = N_2$ or O_2			
$O_2^{\ddagger} + O \rightarrow O_2 + O$	6.88×10^{-9} $Exp(.76.75/T^{1/3})$	200-2000	17,227
	1.7×10^{-10} $Exp(-4000/T)$	2000-4000	228
$O_2^{\ddagger} + H_2O \rightarrow O_2 + H_2O^{\ddagger}$	3.6×10^{-10} $Exp(-60.69/T^{1/3})$	200-5000	17,119

Table 10. Summary of evaluated photochemical data (Ref. 232)

	Quantum Yield, $\phi(\lambda)$	Wave-Length λ nm	Wavelength Range nm, for Absorption Coefficients
$O_3 + h\nu$ (vis) $\rightarrow O + O_2$	1	450-750	440-850
$O_3 + h\nu$ (uv) $\rightarrow O\ (^1D) + O_2\ (^1\Delta)$	1	250-310	200-360
	0	> 310	
$\rightarrow O\ (^1D) + O_2\ (^3\Sigma_g^-)$	0	< 350	
$\rightarrow O\ (^3P) + O_2$ (Singlet)	0	< 310	
	~1	310-350	
$\rightarrow O$ (total) $+ O_2$	1	250-350	
$\rightarrow O\ (^1D) + O_2\ (^1\Sigma_g^+)$	0	250-350	
$\rightarrow O\ (^3P) + O_2\ (^3\Sigma_g^-)$	0	250-350	

Table 11. Quenching data for $O_2(^1\Delta_g)$

Quenching Species	Rate Constant ($cm^3\ sec^{-1}$)	References
O_2	2.4×10^{-18}	241
	2.2×10^{-18}	243
	2.2×10^{-18}	244
	2.2×10^{-18}	245
	$2.2(\frac{T}{300})^{0.8} \times 10^{-18}$	232
N_2	$<1.1 \times 10^{-19}$	230
CO_2	3.9×10^{-18}	241
H_2O	1.5×10^{-17}	241
Ar	$\leq 2.1 \times 10^{-19}$	241
O	$\leq 1.3 \times 10^{-16}$	246
N	$(2.8 \pm 2) \times 10^{-15}$	246
O_3	3×10^{-15}	247

Table 12. Dissociative recombination of O_2^+ with electrons (Ref. 269, 271)

$O_2^+ + e \rightarrow O^* + O^{**}$	Product Ratio	Rate constant[a] ($cm^3\ sec^{-1}$) for Production at 300 K
Total O (^1S)	0.1	2.1×10^{-8}
Total O (^1D)	0.9	1.9×10^{-7}
Total O (^3P)	1	2.1×10^{-7}

Table 13. Electron impact excitation and deexcitation rate coefficients for the low lying states of oxygen atom

T_e(eV)	$^3P - {}^1D$	$^3P - {}^1S$	$^1D - {}^1S$
0.1	1.92 (-18)[a]	1.78 (-28)	2.25 (-19)*
	1.1 (- 9)[b]	2.1 (- 9)	2.2 (-13)
0.2	5.28 (-14)	1.96 (-19)	1.76 (-14)
	1.7 (- 9)	2.1 (- 9)	3.9 (-11)
0.3	1.76 (-12)	2.10 (-16)	8.07 (-13)
	2.2 (- 9)	2.1 (- 9)	2.3 (-10)
0.5	3.28 (-11)	6.04 (-14)	1.52 (-11)
	2.9 (- 9)	2.3 (- 9)	8.7 (-10)
0.7	1.21 (-10)	7.25 (-13)	5.4 (-11)
	3.5 (- 9)	2.5 (- 9)	1.5 (- 9)
1.0	3.43 (-10)	4.93 (-12)	1.38 (-10)
	4.4 (- 9)	2.9 (- 9)	2.3 (- 9)
1.2	5.20 (-10)	1.06 (-11)	1.97 (-10)
	4.8 (- 9)	3.1 (- 9)	2.7 (- 9)
1.5	7.94 (-10)	2.32 (-11)	2.76 (-10)
	5.2 (- 9)	3.4 (- 9)	3.1 (- 9)
2.0	1.21 (- 9)	5.15 (-11)	3.98 (-10)
	5.8 (- 9)	3.7 (- 9)	3.6 (- 9)

Table 13. (Cont'd.)

T_e(eV)	$^3P - {}^1D$	$^3P - {}^1S$	$^1D - {}^1S$
3.0	1.84 (- 9)	1.16 (-10)	5.30 (-10)
	6.3 (- 9)	4.2 (- 9)	3.9 (- 9)
5.0	2.52 (- 9)	2.21 (-10)	7.16 (-10)
	6.7 (- 9)	4.6 (- 9)	4.5 (- 9)
7.0	2.73 (- 9)	2.8 (-10)	7.76 (-10)
	6.5 (- 9)	4.6 (- 9)	4.6 (- 9)
10.0	2.80 (- 9)	3.3 (-10)	7.5 (-10)
	6.1 (- 9)	4.5 (- 9)	4.2 (- 9)
15.0	2.58 (- 9)	3.8 (-10)	6.9 (-10)
	5.3 (- 9)	4.5 (- 9)	3.7 (- 9)
20.0	2.23 (- 9)	3.7 (-10)	6.4 (-10)
	4.4 (- 9)	4.1 (- 9)	3.4 (- 9)

* Numbers in parenthesis indicate the power of ten by which the entries are multiplied.

[a] Excitation rate coefficient.

[b] The corresponding deexcitation rate coefficient.

Table 14. Reaction rate constants for $O(^1D)$ loss (Ref. 287)

Reaction	Temp. Range/K	Reaction Rate Constant k/cm^3 molecule$^{-1}S^{-1}$	Reliability of log k
$O(^1D_2) + O_2 \rightarrow O_2(^1\Sigma_g^-) + O(^3P)$	298	7.4×10^{-11} cm^3 molecule^{-1}S^{-1}	$\pm$0.1
$O(^1D_2) + O_3 \rightarrow O_2(^3\Sigma_g^-) + O_2$ (?) (a)	298	$5.3 \times 10^{-10}(k_a + k_b)k_a/k_b \sim 1$	$\pm$0.3
$\rightarrow O_2 + 2\,O(^3P)$ (b)	298		
$O(^1D_2) + NO \rightarrow NO + O(^3P)$	298	1.7×10^{-10}	$\pm$0.3
$O(^1D_2) + NO_2 \rightarrow NO + O_2$	298	2.8×10^{-10}	$\pm$0.1
$O(^1D_2) + N_2 \rightarrow N_2 + O(^3P)$	298	5.4×10^{-11}	$\pm$0.15
$O(^1D_2) + N_2 + M \rightarrow N_2O + M$	298	2.8×10^{-36} cm^6 molecule^{-2}S^{-1}	
$O(^1D_2) + N_2O \rightarrow N_2 + O_2$ (a)	298	1.1×10^{-10} cm^3 molecule^{-1}S^{-1}	$\pm$0.1
$\rightarrow 2\,NO$ (b)	298	1.1×10^{-10}	$\pm$0.1
$O(^1D_2) + NH_3 \rightarrow NH_2 + HO$	298	(Probably about 3×10^{-10} No measurements available)	
$O(^1D_2) + H_2 \rightarrow HO + H$	298	2.9×10^{-10}	$\pm$0.1
$O(^1D_2) + H_2O \rightarrow 2\,HO$	298	3.5×10^{-10}	$\pm$0.1

Table 14. (Cont'd.)

Reaction	Temp. Range/K	Reaction Rate Constant k/cm^3 molecule$^{-1}S^{-1}$	Reliability of log k
$O(^1D_2) + H_2O_2 \rightarrow HO + HO_2$	298	$> 3 \times 10^{-10}$	
$O(^1D_2) + CO \rightarrow CO + O(^3P)$	298	7.7×10^{-11}	± 0.1
$O(^1D_2) + CO_2 \rightarrow CO_2 + O(^3P)$	298	1.8×10^{-10}	± 0.1
$O(^1D_2) + CH_4 \rightarrow CH_3 + HO$ (a) $\rightarrow CH_2O + H_2$ (b)	298	$4.0 \times 10^{-10}(k_a + k_b)k_a/k_b=10$	± 0.1
$O(^1D_2) + C_2H \rightarrow C_2H_5 + HO$ (a) $\rightarrow CH_3 + CH_2OH$ (b)	298	4.8×10^{-10} $(k_a + k_b)$	± 0.1

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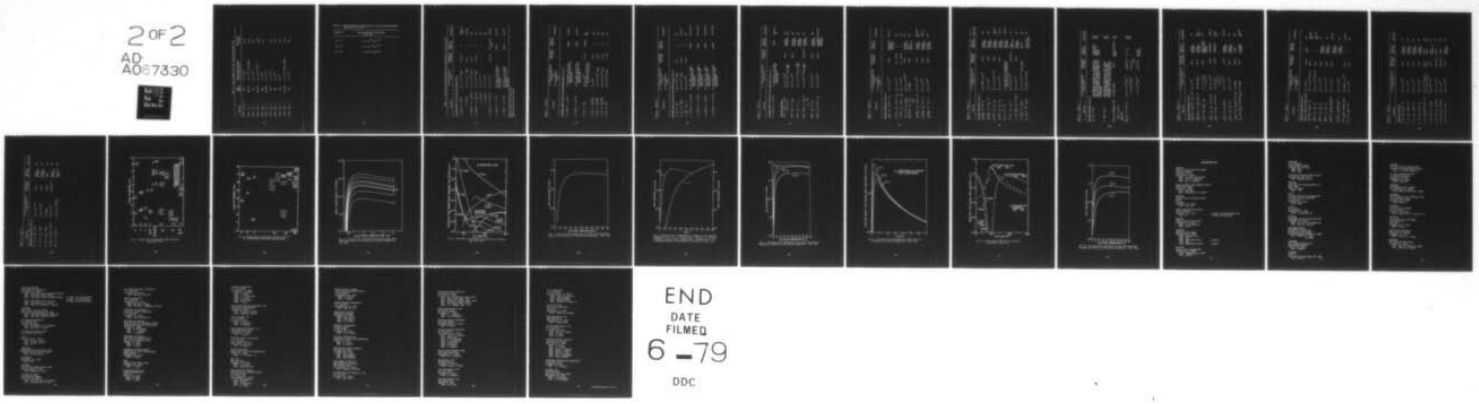

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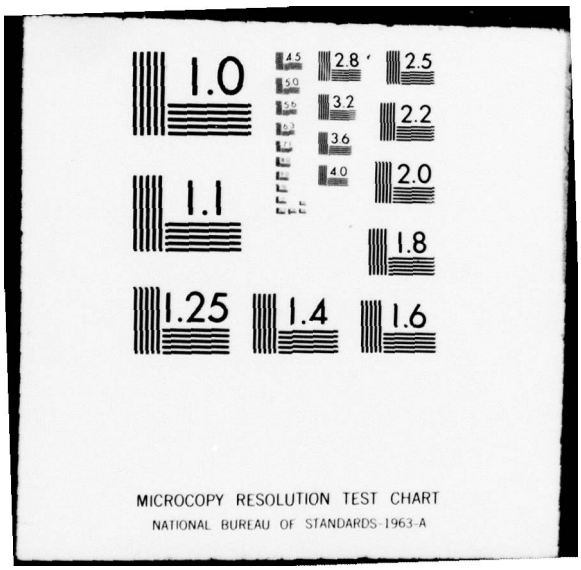
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Table 15. Rate constants for $O(^1S)$ deactivation (Ref. 287)

Reaction	Temp Range/K	Reaction Rate Constant k/cm^3 molecule$^{-1}S^{-1}$	Reliability of log k
$O(^1S) + O(^3P) \rightarrow ?$	300	7.5×10^{-12}	± 0.2
$O(^1S) + O_2 \rightarrow ?$	200-377	$4.3 \times 10^{-12} \exp(-850/T)$	± 0.15
$O(^1S) + O_3 \rightarrow ?$	300	5.8×10^{-10}	± 0.7
$O(^1S) + NO \rightarrow ?$	200-291	3.2×10^{-11} $(T^{0.5})$	± 0.05
$O(^1S) + NO_2 \rightarrow ?$	300	5×10^{-10}	± 0.2
$O(^1S) + N_2 \rightarrow ?$	200-380	$<5 \times 10^{-17}$	
$O(^1S) + N_2O \rightarrow ?$	300	1.4×10^{-11}	± 0.1
$O(^1S) + NH_3 \rightarrow ?$	300	5×10^{-10}	± 0.2
$O(^1S) + H_2O \rightarrow ?$	300	$>10^{-10}$	± 0.1
$O(^1S) + CO_2 \rightarrow ?$	200-450	$3.1 \times 10^{-11} \exp(-1320/T)$	± 0.15
$O(^1S) + CH_4 \rightarrow ?$	300	2×10^{-11}	± 0.4

Table 16. Deexcitation rate coefficients for the low-lying metastable states of O^+ (T_e in eV)

Transition	Deexcitation Rate Coefficient (cm^3 /sec)
$^2D - {}^4S$	$1.3 \times 10^{-8} (T_e)^{-1/2}$
$^2P - {}^4S$	$6.3 \times 10^{-9} (T_e)^{-1/2}$
$^2P - {}^2D$	$2.4 \times 10^{-8} (T_e)^{-1/2}$

Table 17. Excitation and deexcitation rate coefficients or cross sections

Reaction	(2) Cross-Section (cm^2)	Temperature or Energy	Type of Experiment	References
ELECTRON-IMPACT EXCITATION AND DEEXCITATION				
$e + H(1S) \rightarrow e + H(2P)$	(2) 7×10^{-17} (max)	10-50 eV	b	328[a],329, 330
$\rightarrow e + H(2S)$	(2) 1.4×10^{-17} (max)	12 eV	b	331,332
$e + Na(3^2S) \rightarrow e + Na(3^2P)$	(2) 2×10^{-15} (max)	10 eV	b	333
$e + He(1^1S) \rightarrow e + He(2^3S)$	(2) 3×10^{-18} (max)	20.6 eV	b	234
$\rightarrow e + He(2^1S)$	(2) 1×10^{-18}		b	334
$\rightarrow e + He(2^3P)$	(2) 3×10^{-18}			334
$e + He(2^1S) \rightarrow e + He(2^3S)$	(2) 3×10^{-14}	0.025 eV	Static afterglow	335,336
$e + N(^2D) \rightleftarrows e + N(^4S)$	See Table 6 for Temperature Dependent Rate Coefficients		Theory	203,204
$e + N(^2P) \rightarrow e + N(^4S)$	See Table 6 for Temperature Dependent Rate Coefficients		Theory	203,204

[a]Review article for ^2P excitation

[b]Beams and fast-flowing systems

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$) or (2) Cross-Section (cm^2)	Temperature or energy	Type of Experiment	References
ELECTRON-IMPACT EXCITATION AND DEEXCITATION (Cont'd.)				
$e + O(^1D) \rightarrow e + O(^3P)$	(1) See Table 13 for Temperature Dependent Rate Coefficients		Theory	272,204
$e + O(^1S) \rightarrow e + O(^3P)$	(1) See Table 13 for Temperature Dependent rate Coefficients		Theory	272,204
$e + N_2 \rightarrow e + N_2^{\ddagger}$	(2) 6×10^{-16}	2.3 eV	b,theory	88
	(1) See Table 3 for Excitation Rate Coefficients			88,7
$e + N_2 \rightarrow e + N_2(A^3\Sigma)$	(2) (3-5)	10 eV	b	139
$e + N_2 \rightarrow e + N_2(B^3\Pi)$	(2) 6.0×10^{-17} (max)	10 eV	b	140
$e + N_2 \rightarrow e + N_2(C^3\Pi)$	(2) 4.0×10^{-17} (max)	17 eV	b	139
$e + CO \rightarrow e + CO^{\ddagger}$	(2) 8×10^{-16} (max)	1.75 eV	b	88

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$) or (2) Cross-Section (cm^2)	Temperature or energy	Type of Experiment	References
ELECTRON-IMPACT EXCITATION AND DEEXCITATION (Cont'd.)				
$e + H_2 \rightarrow e + H_2^{\ddagger}$	(2) 6×10^{-17} (max)	2 eV	b	88
$e + N_2 \rightarrow 2e + N_2^+(B)$	(2) 2×10^{-17} (max)	100 eV	b	173,174
$e + N_2O^{\ddagger} \rightarrow N_2 + O^-$	(2) 8.3×10^{-18}	2.3 eV	b	337
$e + N^+(^3P) \rightleftarrows e + N^+(^1D)$	(1) See Table 8 for Temperature Dependent Rate Coefficients		Theory	214,215,204
$e + N^+(^3P) \rightleftarrows e + N^+(^1S)$	(1) See Table 8 for Temperature Dependent Rate Coefficients		Theory	214,215,204
$e + N^+(^1D) \rightleftarrows e + N^+(^1S)$	(1) See Table 8 for Temperature Dependent Rate Coefficients		Theory	214,215,203
$e + O^+(^4S) \rightleftarrows e + O^+(^2D)$	(1) See Table 16 for Temperature Dependent Rate Coefficients		Theory	214,204,302

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$)	Temperature or Energy	Type of Experiment	References
ELECTRON-IMPACT EXCITATION AND DEEXCITATION (Cont'd.)				
$e + O^+(^2D) \rightleftarrows e + O^+(^2P)$	(1) See Table 16 for Temperature Dependent Rate Coefficients		Theory	214,204, 302
TWO BODY REACTIONS				
$O(^1S) + O(^3P) \rightarrow O(^1D) + O(^1D \text{ or } ^3P)$	(1) 7.5×10^{-12}	300 K	Flowing afterglow	292
	(1) $5.0 \times 10^{-11}\ Exp(-\frac{610}{RT})$			291
$O(^1S) + N_2O \rightarrow O + N_2O$	(1) 1.4×10^{-11}	300 K	Flowing afterglow	287
$O(^1S) + O_2 \rightarrow O + O_2$	(1) $4.0 \times 10^{-13}\ Exp\ (-\frac{1730}{RT})$		Flowing afterglow	297
$O(^1S) + CO_2 \rightarrow O + CO_2$ or $O_2 + CO$	(1) $3.1 \times 10^{-11}\ Exp(-\frac{1320}{T})$	200-450 °K	Flowing afterglow	287
$O(^1S) + N_2 \rightarrow O + N_2$	(1) $< 5 \times 10^{-17}$	300 K	Flowing afterglow	287
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	(1) 5.4×10^{-11}	300 K	Atmospheric Flowing afterglow	287,275

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$) or (2) Cross-Section (cm^2)	Temperature or energy	Type of Experiment	References
TWO BODY REACTIONS (Cont'd.)				
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	(1) 7.5×10^{-11}	300 K	Atmospheric, Flowing afterglow	287,275
$O^+(^2D) + N_2 \rightarrow O(^3P) + N_2^+$	(2) $\sim 3 \times 10^{-15}$	0.5 - 100 eV	b	185
$O^+(^2D) + O_2 \rightarrow O(^3P) + O_2^+$	(2) $\sim 3 \times 10^{-15}$	0.5 - 100 eV	b	185
$O + O_3 \rightarrow O_2 + O_2(a^1\Delta_g)$	(1) $4.5 \times 10^{(-15\pm2)}$	300 K	Flowing afterglow	233
$O_2^{\ddagger}(X, v\leq 17) + O_3 \rightarrow 2O_2 + O(^1D)$	(1) Large	300 K	Flash photolysis	338
$O_2(a^1\Delta_g) + O_2 \rightarrow O_2(X) + O_2$	(1) 2.4×10^{-18}	300 K	Flowing afterglow	241 thru 245
$O_2(a^1\Delta_g) + O_2^- \rightarrow 2O_2 + e$	(1) 2×10^{-10}	300 K	Flowing afterglow	250,251
$O_2(a^1\Delta_g) + O^- \rightarrow O_3 + e$	(1) 3×10^{-10}	300 K	Flowing afterglow	250

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient (cm^3 sec^{-1})	Temperature or energy	Type of Experiment	References
TWO-BODY REACTIONS (Cont'd.)				
$O_2(a^1\Delta_g) + N \rightarrow NO + O$	(1) $(2,8^{\ddagger}2) \times 10^{-15}$	300 K	Flowing afterglow	245
$O_2(b^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$	(1) 6×10^{-13}	300 K	Flowing afterglow	339
$O_2(b^1\Sigma) + N_2 \rightarrow O_2 + N_2$	(1) $(1.5\text{-}2.5) \times 10^{-15}$	300 K	Flowing afterglow	14,263, 264
$O_2(b^1\Sigma) + O_2 \rightarrow O_2 + O_2$	(1) 1.5×10^{-16}	300 K	Flowing afterglow	14,263
$O_2^+ + e \rightarrow O^* + O^{**}$	(1) See Table 12 for Temperature Dependent Rate Coefficients		Flowing afterglow	269,271
$N(^2D) + O_2 \rightarrow NO + O$	(1) $4 \times 10^{-13} T^{1/2}$	236-365 K	Flash photolysis	210
$N + NO \rightarrow N_2^{\ddagger}(X, v\approx 8) + O(^3P)$	(1) 2.2×10^{-11}	300 K	Flowing afterglow	152
$N + N_2(X) \rightarrow N + N_2(A)$	(1) $1.9 \times 10^{-6} T^{-3/2} \exp(-E_{XA}/kT)$		Shocks	162
$N_2 + N_2(X) \rightarrow N_2^* + N_2(A)$	(1) $k(N_2) \leq 0.01\ k(N)$		Active discharge, Shocks	162

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$)	Temperature or energy	Type of Experiment	References
TWO-BODY REACTIONS (Cont'd.)				
$A^{\ddagger} + B \rightarrow A + B^{\ddagger}$	Considerable literature is available on this type of reaction. The general agreement of vibrational energy transfer associated with lower vibrational levels is encouraging.		Flames, Flash photolysis, Shocks, Theory	105 106 119
$A + BC^{\ddagger} \rightarrow AB + C$	Considerable literature on this subject of a non-atmospheric nature has been generated by Polanyi at the University of Toronto. (Cf. the listed references)			340 341 342
$NO\ (A,\ v=x) + N_2\ (X,\ v=o)$ $\rightarrow NO\ (A,\ v=x-1) + N_2^{\ddagger}\ (X, v=1)$	(1) Very large	300 K	Flash photolysis, Theory	105 106
$N_2^{\ddagger}(X,v) + O^+ \rightarrow NO^+ + N$	(1) $3.1 \times 10^{-14}(T_a)^{-1.0}$	$T_a \leq 0.065$ eV	$T_a = T_{vib}$	129 130 343
	$1.2 \times 10^{-10}(T_a)^{2.0}$	$0.065 \leq T_a \leq 0.67$		
	$8.5 \times 10^{-11}(T_a)^{1.2}$	$T_a > 0.67$ eV	Flowing afterglow	

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient (cm^3 sec^{-1})	Temperature or energy	Type of Experiment	References
TWO-BODY REACTIONS (Cont'd.)				
$N_2^{\ddagger}(X,v\geq 7) + N_a(3^2S) \rightarrow N_2 + Na^*$	(1) $\sim 10^{-10}$	300 K	Flowing afterglow	124
$N_2^{\ddagger}(X,v=1) + M \rightarrow N_2(X,v=o) + M$	(1) See Table 2	300 K	Flowing afterglow	See Table 2
$N_2(A) + N_2 \rightarrow N_2(X) + N_2$	(1) $< 3 \times 10^{-19}$ $\sim 1 \times 10^{-19}$	300 K	High pressure chemical reactions	152
$N_2(A) + O_2 \rightarrow N_2 + (O_2 \text{ or } 2O)$	(1) 2.5×10^{-12}	$\sim$ 300 K	Atmospheric	156,159
$N_2(A) + O \rightarrow N_2 + O \text{ or } NO + N$	(1) 3×10^{-11} 5×10^{-11} 7.5×10^{-11}	$\sim$ 300 K	Atmospheric	10,14, 155
$N_2(A) + N \rightarrow N + N_2^{\ddagger}(X)$	(1) 5×10^{-11}	$\sim$ 300 K	Flowing afterglow	160,162
$N_2(A) + NO \rightarrow N_2 + NO$	(1) 7×10^{-11}	300 K	Flowing afterglow	160
$N_2(a,v) + N_2 \rightarrow N_2(a,v'<v) + N_2$	(1) Large	1000 K	Theory	344
$N_2 + Ba \rightarrow N_2(X) + Ba^+(6\,^2P_{3/2}) + e$	(1) Large	300 K	b, Static afterglow	157,345, 346

Table 17. (Cont'd.)

Reaction	(1) Reaction Coefficient ($cm^3\ sec^{-1}$) or (2) Cross-Section (cm^2)	Temperature or energy	Type of Experiment	References
TWO-BODY REACTIONS (Cont'd.)				
$OH^{\ddagger}(X,v')+OH^{\ddagger}(X,v)\rightarrow OH(A)+OH(X)$	(1) $\sim 10^{-10}$	~ 300 K	Flames	347
$N_2^+(A^2\Pi_u) + O_2 \rightarrow N_2 + O_2^+$	(1) 7.0×10^{-10} for $\bar{v}=1$	300 K	b	188 thru 191
$N_2^+(A) + N_2 \rightarrow N_2^+ + N_2$	(1) 4.5×10^{-10} for $\bar{v}=1$	300 K	b	188 thru 191
$N_2^+(B) + N_2 \rightarrow N_2^+ + N_2$	(1) 4.4×10^{-10}	300 K	Static afterglow	175
$N_2^+(B) + O_2 \rightarrow N_2^+ + O_2$	(1) 7.0×10^{-10}	300 K	Static afterglow	175
$He(2^3S) + N_2 \rightarrow He(1S)+N_2^+(B)+e$	(1) 1.4×10^{-10}	300 K	b Flowing afterglow	123,348
$He(2^3S) + O_2 \rightarrow He(^1S)+O_2^{+*} +e$	(1) 5.0×10^{-10}		Flowing afterglow	348
$He^+ + N_2(X) \rightarrow He+N_2^+(C,v=3)$	(2) Large 4×10^{-10}	300 K	b	129,349
$H^+ + Cs \rightarrow H(2P) + Cs^+$	(2) 6×10^{-15}	1 KeV	b	350

Table 17. (Cont'd.)

Reaction	(3) Reaction Coefficient ($cm^6\ sec^{-1}$)	Temperature or energy	Type of Experiment	References
THREE-BODY REACTIONS				
$N + N + N_2 \rightarrow N_2(B) + N_2$	(3) 1.4×10^{-33}	300 K	Flowing afterglow	267
$N + O + N_2 \rightarrow NO(B) + N_2$	(3) 1×10^{-34}	300 K	Flowing afterglow	267
$O + O + N_2 \rightarrow O_2(A) + N_2$	(3) 2.1×10^{-37}	300 K	Flowing afterglow	267
$O + O + N_2 \rightarrow O_2(b) + N_2$	(3) 1.7×10^{-37}	300 K	Flowing afterglow	267
$O + O + O_2 \rightarrow O_2(A, v=9,10) + O_2$	(3) 1×10^{-33} (v=9)	1000 K	Theory	351
	(3) 5.5×10^{-33} (v=10)	1000 K	Theory	351
$O + O + CN \rightarrow O_2 + CN(A)$	(3) $10^{-31} - 10^{-30}$	300 K	Flash photolysis	352
$O + O + Na \rightarrow O_2 + Na^*(^2P)$	(3) 1.5×10^{-29}	1250-1500 K	Flames	353
$H + H + Na \rightarrow H_2 + Na^*(^2P)$	(3) 5×10^{-31}	1250-1500 K	Flames	353
$N + N + O \rightarrow N_2 + O(^1S)$	(3) 1.3×10^{-30}	~ 300 K	Flowing afterglow	292

Table 17. (Cont'd.)

Reaction	(3) Reaction Coefficient ($cm^6\ sec^{-1}$)	Temperature or energy	Type of Experiment	References
THREE-BODY REACTIONS (Cont'd.)				
$N + 0 + 0 \rightarrow NO + 0(^1S)$	(3) 2.5×10^{-31}	300 K	Flowing afterglow	292
$0 + 0 + 0 \rightarrow 0_2 + 0(^1S)$	(3) 4.8×10^{-33}	300 K	Flowing afterglow	292
$0 + 0 + 0 \rightarrow 0_2 + 0(^1D)$	(3) Large	300 K	Theory	354
$H + H_2 + 0_2 \rightarrow H_20 + OH$ (A)	(3) 5×10^{-37}	1000-1900 K	Static afterglow	355
$H^+ + e + e \rightarrow H(n) + e$	(3) $9.5 \times 10^{-29} \frac{n^4}{T_e^2}$		Theory, T_e in eV	356

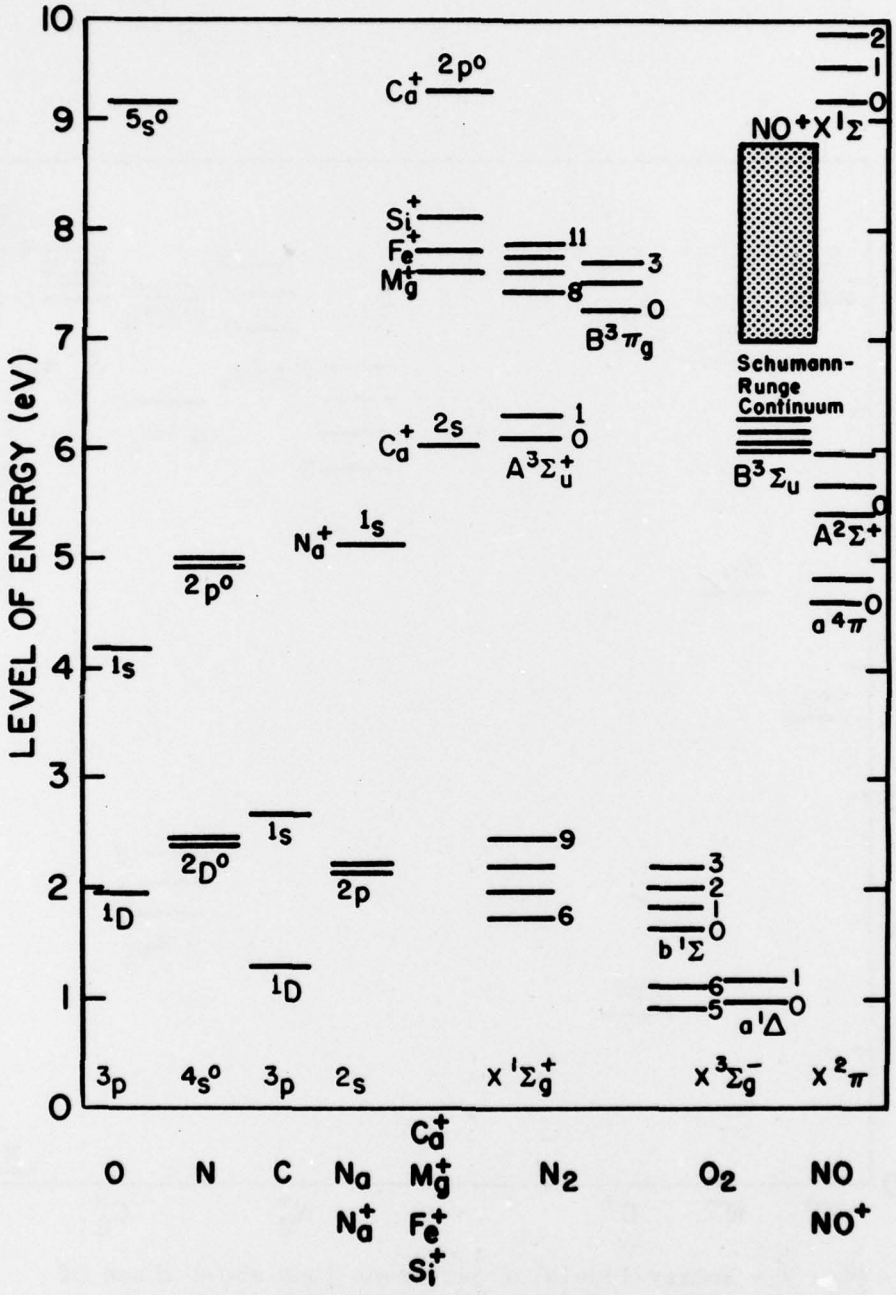

Fig. 1 - Energy levels of pertinent atoms, molecules and metallic ions.

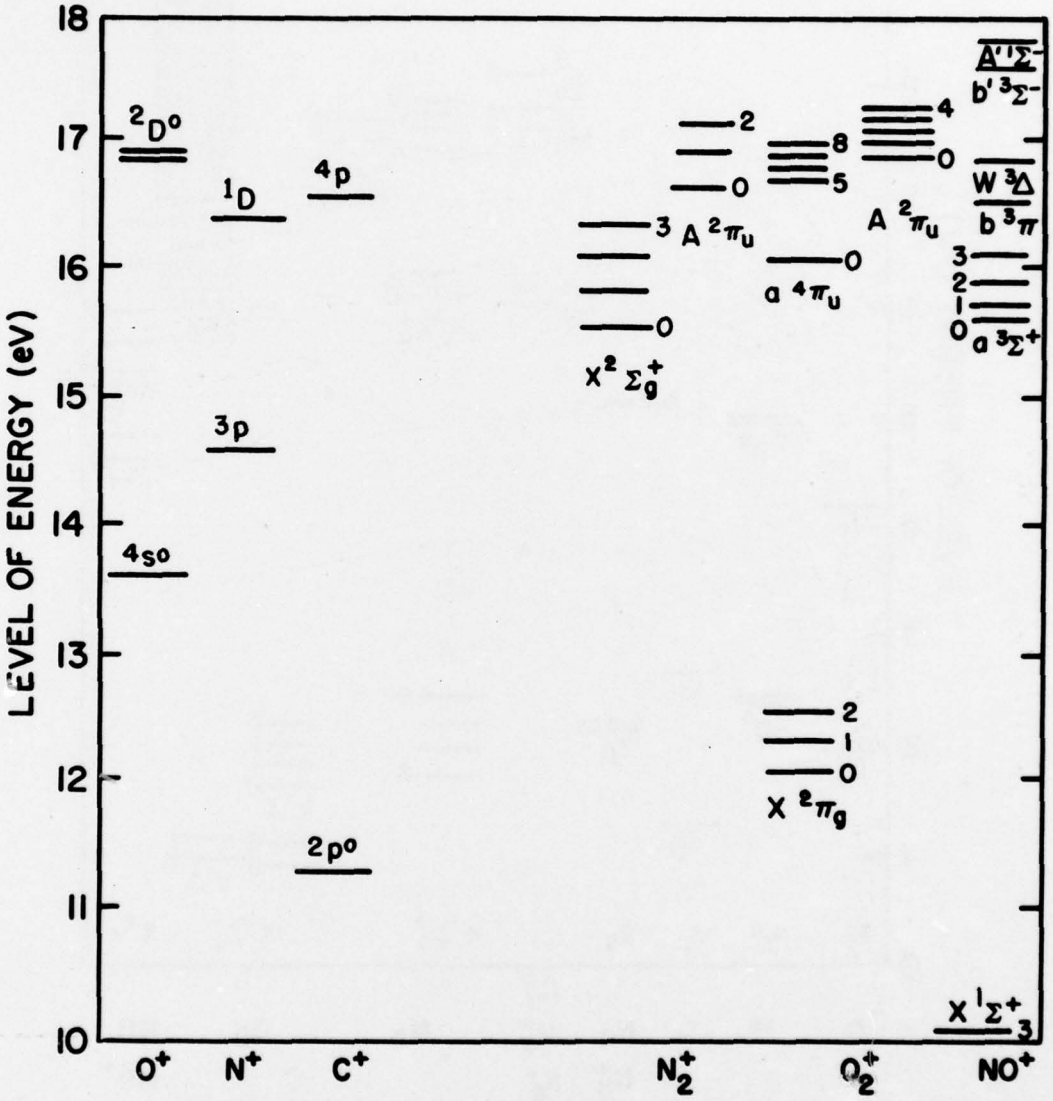

Fig. 2 - Energy levels of pertinent ions above those of the corresponding ground state neutral species.

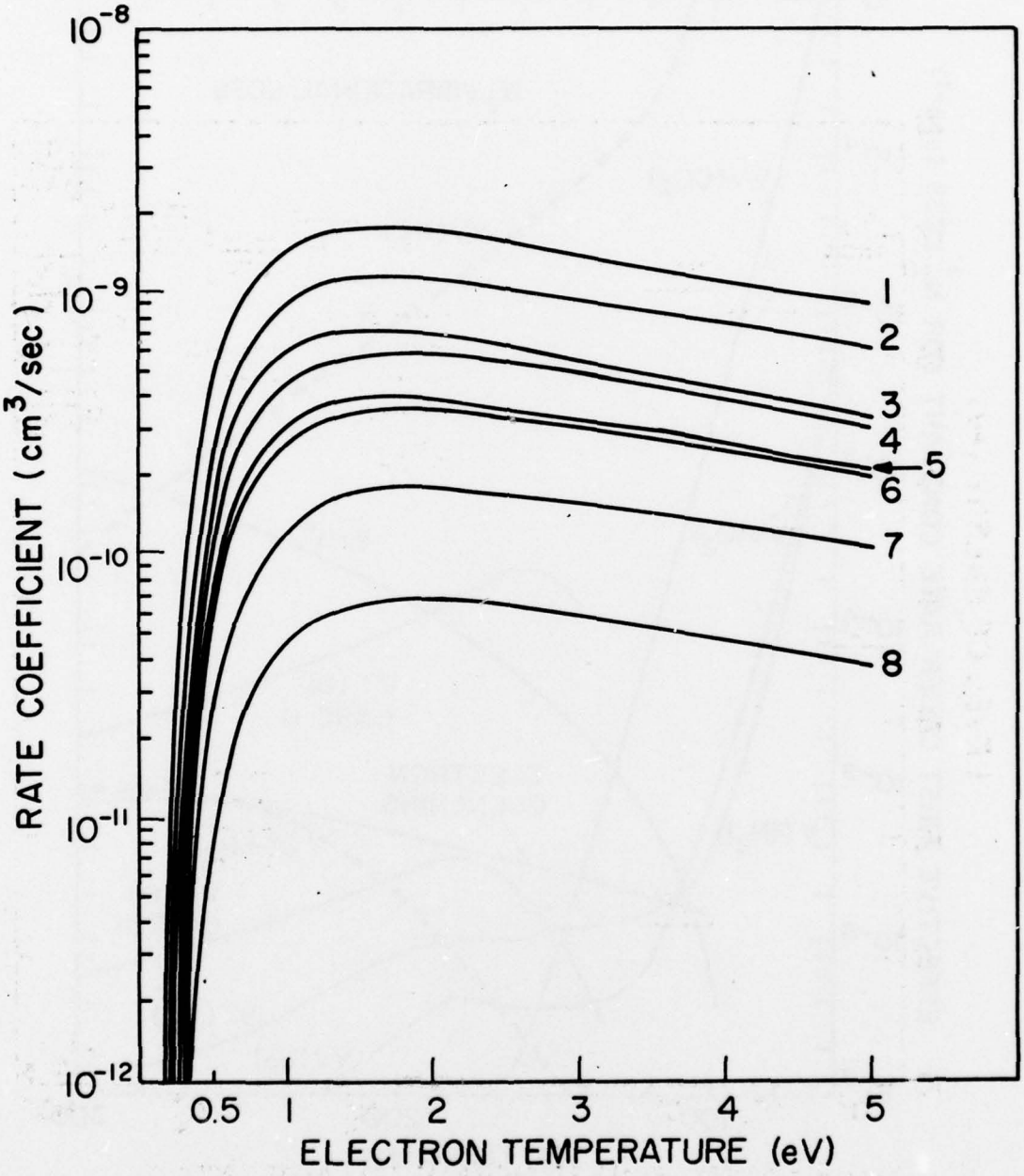

Fig. 3 - Excitation rate coefficients of eight N_2 ground state vibrational levels as a function of the electron temperature. (Ref. 204).

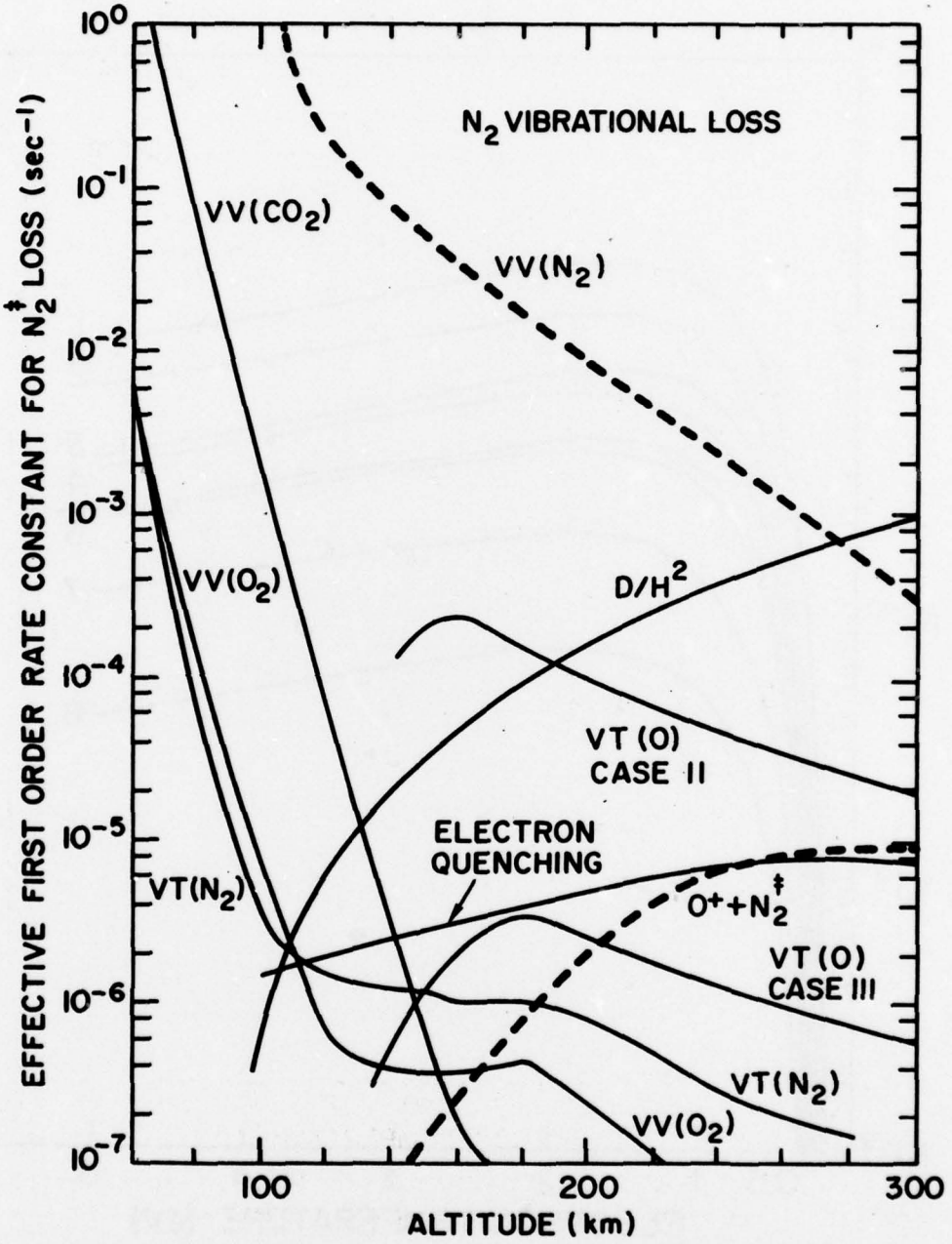

Fig. 4 - Loss Rates of N_2 vibration as a function of altitude. (Ref. 125 & 126).

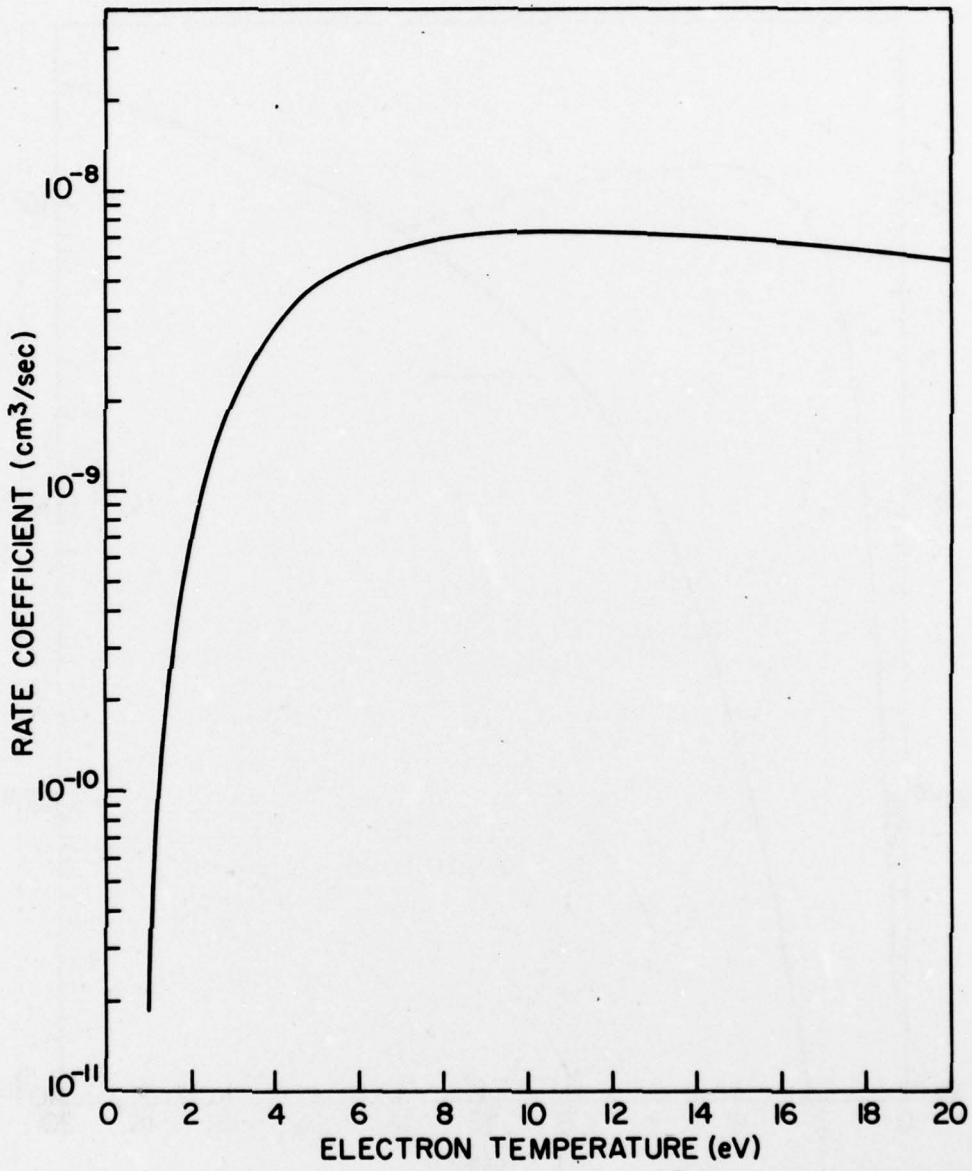

Fig. 5 - Excitation rate coefficient of N_2 ($A^3\Sigma$) from the ground state of N_2 as a function of the electron temperature. (Ref. 148).

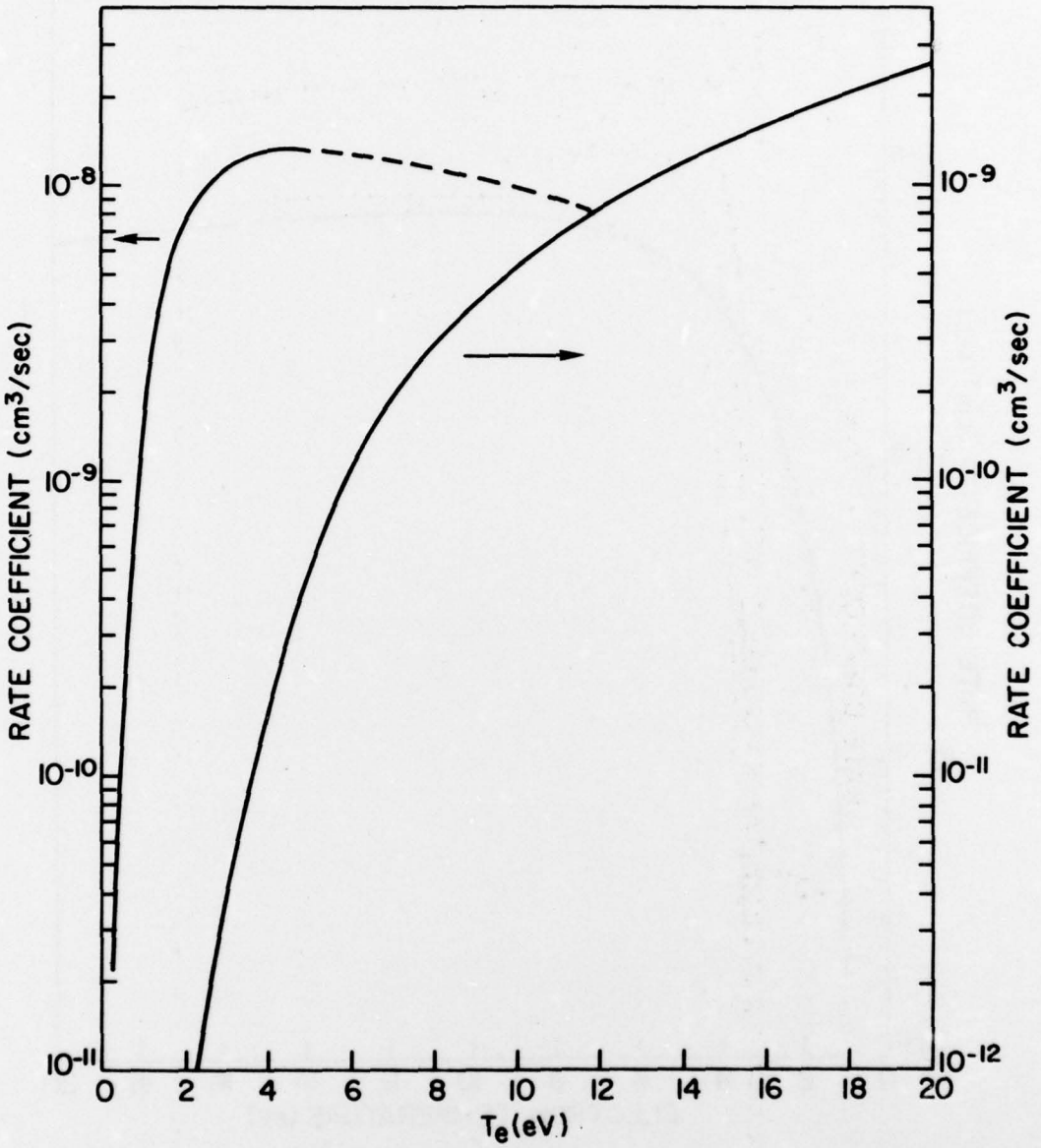

Fig. 6 - Excitation rate coefficients as a function of the electron temperature for $e + N_2 \rightarrow e + N_2^+ (B,0)$ and $e + N_2^+ (X) \rightarrow e^- + N_2^+ (B,0)$, indicated as curves a and b, respectively. The dashed part of (b) is obtained from Ref. (178) adjusted to the results of Ref. (177).

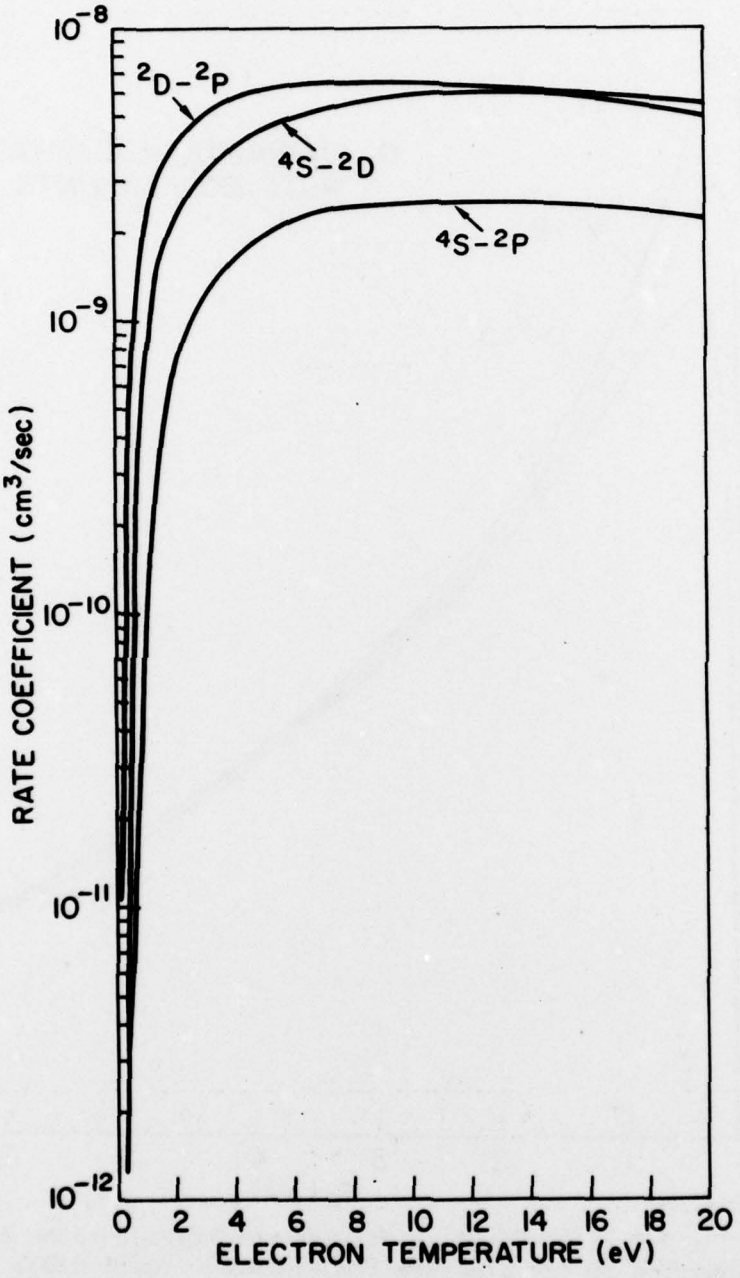

Fig. 7 - Excitation rate coefficients for the low lying states of nitrogen as a function of the electron temperature. (Ref. 204).

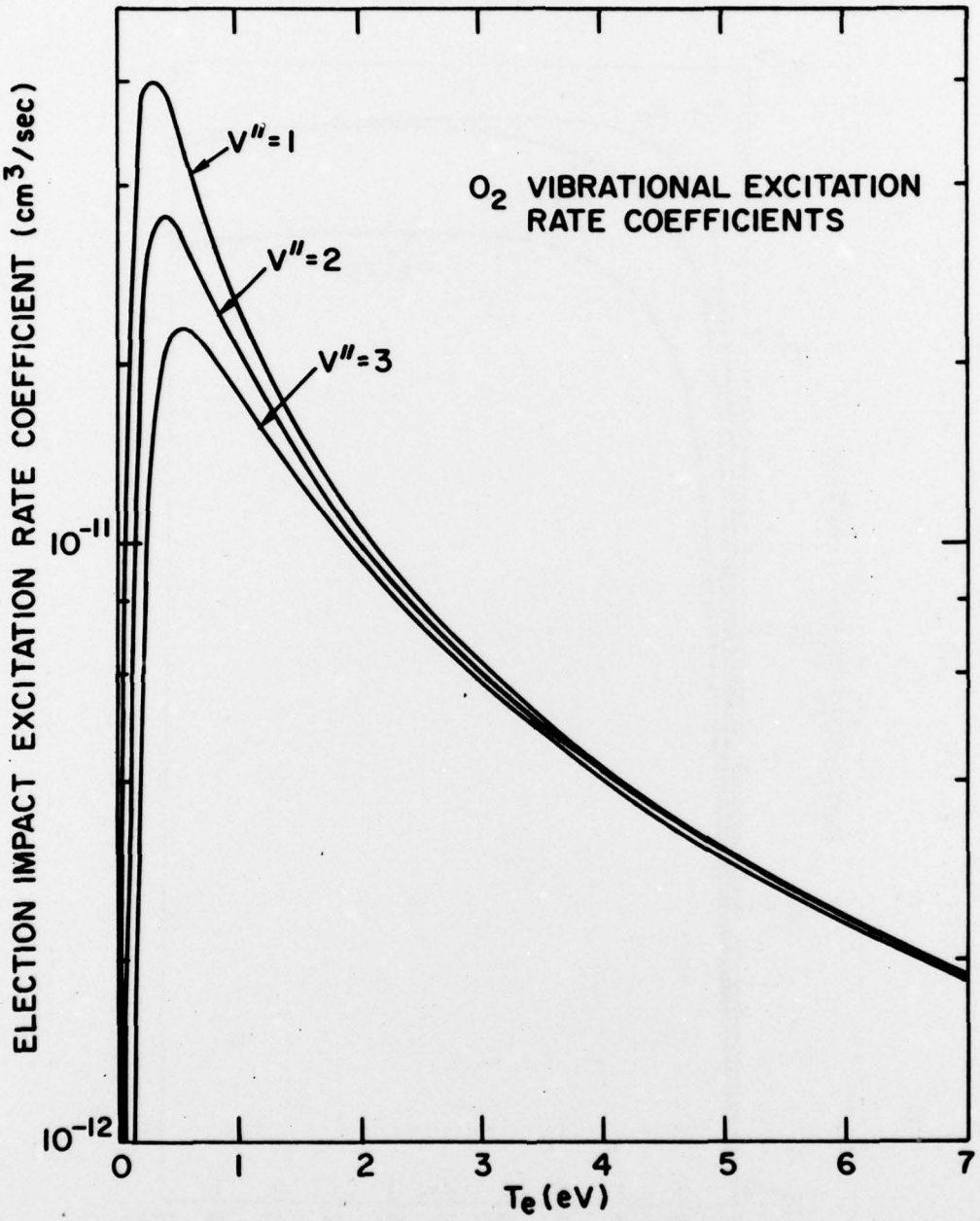

Fig. 8 - O_2 ground state vibrational excitation rates as a function of the electron temperature. (Ref. 220).

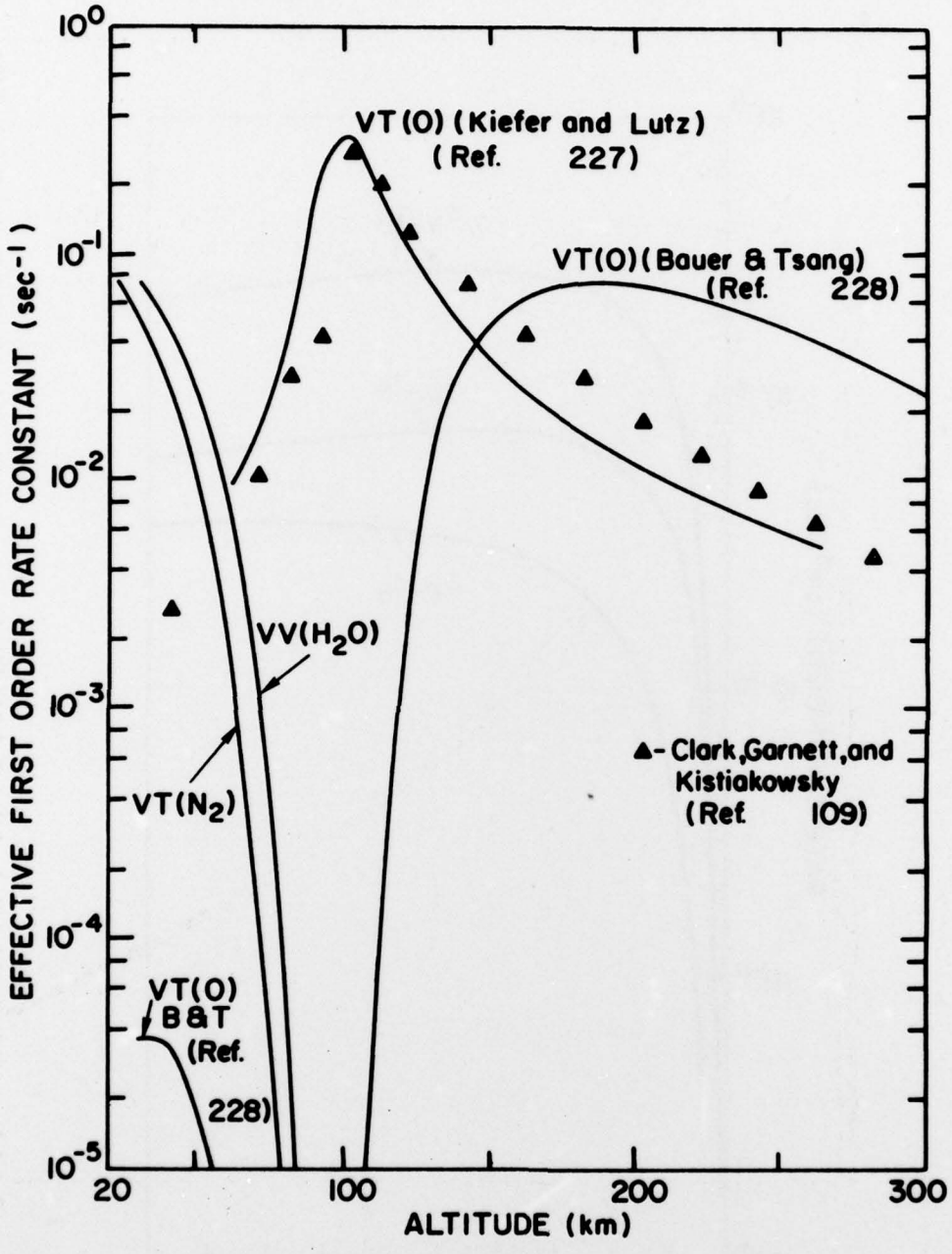

Fig. 9 - Deactivation of $O_2^{\ddagger}$ (v=1) as a function of altitude. (Ref. 134).

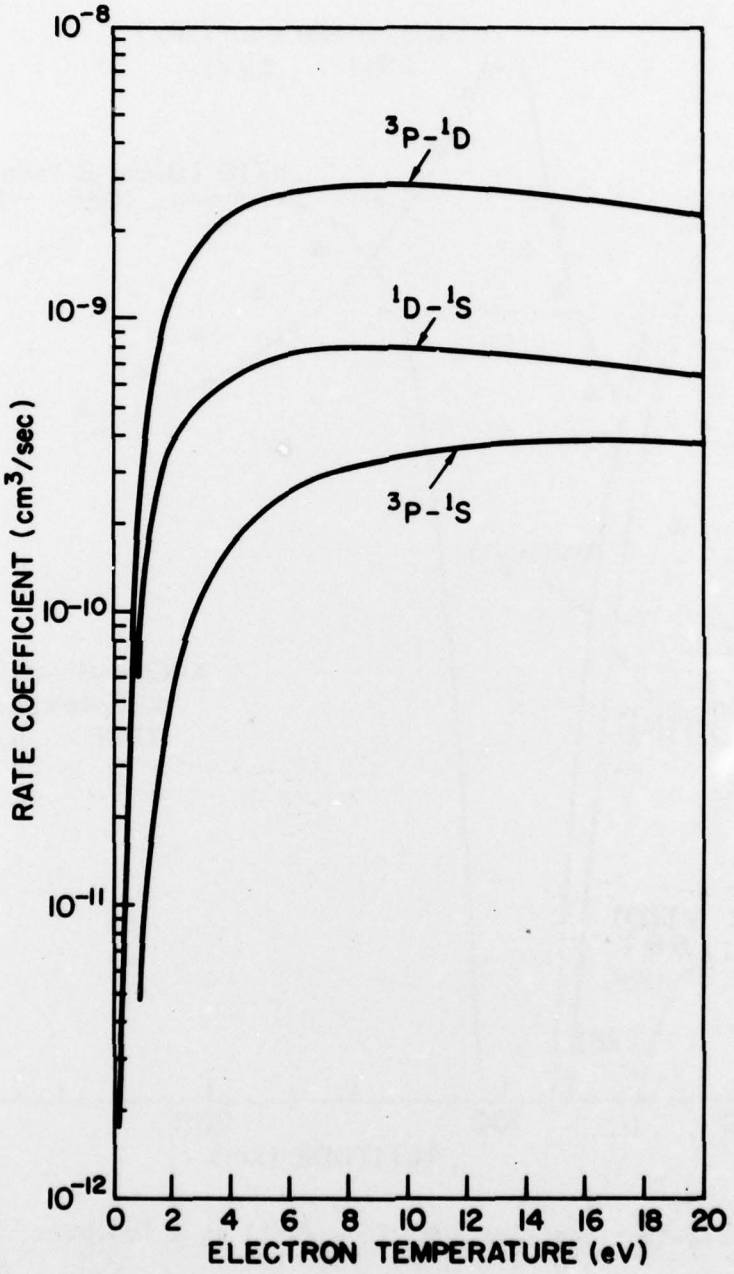

Fig. 10 - Excitation rate coefficients for the low lying states of oxygen as a function of the electron temperature. (Ref. 204).

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