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STUDIES OF THE CHEMISTRY OF VIBRATIONALLY AND ELECTRONICALLY EXCITED SPECIES IN PLANETARY UPPER ATMOSPHERES

Grant NAGW-506

Final Report

For the period 1 October 1983 through 30 September 1984

Principal Investigator
Dr. Jane L. Fox

November 1984

Prepared for
National Aeronautics and Space Administration
Washington, D. C. 20546

Smithsonian Institution
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Cambridge, Massacusetts 02138

The Smithsonian Astrophysical Observatory
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We have been looking into the vibrational distribution of O_2^+ in the atmospheres of Venus and Mars to compare them to that found on the Earth. Vibrationally excited O_2^+ on Venus is formed in charge transfer reactions and lost in dissociative recombination. The vibrational levels are interchanged in quenching reactions and fluorescent scattering. In order to compute the vibrational distribution, we needed to compute the excitation rates and transition probabilities for fluorescent scattering in the second negative system of $O_2^+(A^2\Pi_u \rightarrow X^2\Pi_g)$. Because the potential curves for the X and A states of O_2^+ have minima at very different internuclear distances, excitations from the X state can populate very high vibrational levels of the A state, which may then decay to high vibrational levels of the X state. Published values of the transition probabilities included only about ten levels of each state. This was completely inadequate for our purposes, so we recomputed the wavefunction and energies for 61 vibrational levels of the $X^2\Pi_g$ state, and 34 vibrational levels of the $A^2\Pi_u$ state, and the oscillator strengths for all of the transitions between these levels. We then computed the transition probabilities for the A→X transitions, and excitation rates for absorption of a solar photon using our oscillator strengths and the solar fluxes of Vernazza et al. (1976). (See attached preprint).

We have calculated the vibrational distribution of $O_2^+(X^2\Pi_g)$ and $O_2^+(A^2\Pi_u)$ in the daytime Venusian ionosphere for models which are based on Pioneer Venus data. We find that at low altitudes quenching limits the fraction vibrationally excited to less than 5%. At high altitudes the vibrational distribution approaches that assumed for the reaction:

$$O^+ + CO_2 \rightarrow O_2^+(v) + CO \ . \qquad (1)$$

We have assumed that the reaction proceeds by the formation of a collision complex so that the available energy is statistically distributed among the degrees of freedom of the complex. This is probable for low energy encounters. Thus we have assumed that all of the available vibrational levels are populated equally in (1) and the relative population of each of vibrational levels 0 to 5 of O_2^+ approaches .16 at high altitudes.

The fraction of O_2^+ vibrationally excited at the exobase, about 200 km, depends on the assumed value for the rate coefficient for quenching of $O_2^+(v)$ by atomic oxygen:

$$O_2^+(v) + O \rightarrow O_2^+(v-1) + O \quad . \qquad (2)$$

The rate coefficient for reaction (2) has not been measured. We first assume that the reaction proceeds with a rate coefficient of $1 \times 10^{-10} cm^3 s^{-1}$ and that the vibrational quantum number changes by only one in each reaction. For this model, 49% are vibrationally excited at the exobase. This will affect the exothermicity of the reaction:

$$O_2^+ + e \rightarrow O + O$$

both because the average vibrational energy is near 0.4eV at the exobase and because the dissociative recombination may proceed through different channels for different vibrational energy levels (Guberman private communication, 1983). Thus the hot oxygen corona will be affected by the vibrational distribution of $O_2^+(v)$ at the exobase and therefore the hot hydrogen corona will also be affected by scattering with O atoms. (See attached preprint of a paper given at the XXVth COSPAR meeting and submitted for publication in Advances in Space Research).

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No. 1978

RADIATIVE LIFETIMES OF THE SECOND NEGATIVE SYSTEM OF O_2^+

R.W. Wetmore
Guelph Waterloo Centre for Chemistry, Guelph, Ontario

and

J. L. Fox and A. Dalgarno
Harvard-Smithsonian Center for Astrophysics

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Radiative lifetimes of the second negative system of O_2^+

R.W. Wetmore[+], J.L. Fox and A. Dalgarno

Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138
[+]Guelph Waterloo Centre for Chemistry, Guelph, Ontario

Abstract. The dipole moment of the $A^2\Pi_u - X^2\Pi_g$ transition of O_2^+ is calculated as a function of internuclear distance using ab initio methods. The band absorption oscillator strengths and band transition probabilities of the second negative system are derived and the resulting lifetimes are compared with experimental data. The high-lying v" levels of the ground state may decay into low-lying v' levels of the excited state. The corresponding radiative lifetimes are calculated.

Introduction

The upper electronic state of the second negative system of O_2^+ can be populated by the absorption of solar radiation in the daytime and twilight atmospheres and in cometary atmospheres by ground state O_2^+ ions and by electron impact with molecular oxygen during auroras. Absorption band oscillator strengths and spontaneous band emission probabilities are needed to determine the vibrational population of O_2^+ ions in the ionsphere and to calculate the emission spectrum in the dayglow, in auroras, and in comets.

Measurements have been carried out by Jeunehomme (1966), Fink and Welge(1968) and Erman and Larsson (1977) of the radiative lifetimes of vibrational levels of the $A^2\Pi_u$ state. The measurements show little variation with the vibrational quantum number and range from about 650 ns to 1000 ns depending upon the experimental technique. We present here the results of ab initio calculations of the electronic wave function of the $X^2\Pi_g$ and $A^2\Pi_u$ states and of the electronic dipole transition moment. Using empirical RKR potential energy curves we obtain the vibrational wave functions by numerical integration of the radial equation of nuclear motion and we calculate the absorption oscillator strengths and the transition probabilities for individual bands of the second negative system. By summing over the final states, we determine radiative lifetimes for comparison with the measurements.

2. Theory

If $\psi_i(\underline{r}|R)$ is the electronic wave function of the ground $X^2\Pi_g$ state at an internuclear distance R, where $\underline{r}$ represents collectively the position vectors $\underline{r}_j$ of the electrons, and $\psi_f(\underline{r}|R)$ is the electronic wave function of the excited $A^2\Pi_u$ state, the transition electric dipole is given in a.u. by

$$D(R) = \langle \psi_X(\underline{r}|R) | \sum_j z_j | \psi_A(\underline{r}|R) \rangle \qquad (1)$$

where the sum is over all the electrons, the z-axis of coordinates lies along the internuclear axis, and the integration is over the coordinate space of all the electrons. The diagonal matrix elements of the electronic Hamiltonian define the potential energy curves $V_X(R)$ and $V_A(R)$. The corresponding vibrational wave functions $\chi_{v''}(R)$ and $\chi_{v'}(R)$ are the regular normalised solutions of the equations

$$\left\{\frac{d^2}{dR^2} + 2\mu\left[E_{v''} - V_X(R)\right]\right\}\chi_{v''}(R) = 0$$

and

$$\left\{\frac{d^2}{dR^2} + 2\mu\left[E_{v'} - V_A(R)\right]\right\}\chi_{v'}(R) = 0$$

where μ is the reduced mass in units of the electron mass, and $E_{v''}$ and $E_{v'}$ are the vibrational eigenvalues in atomic units of respectively the $X^2\Pi_g$ and $A^2\Pi_u$ states.

The absorption band oscillator strengths $f_{v'v''}$ are given by

$$f_{v'v''} = \frac{2}{3}(E_{v'} - E_{v''})|(\chi_{v''}|D|\chi_{v'})|^2$$

and the spontaneous emission transition probabilities are given by

$$A_{v'v''} = 2.03 \times 10^{-6}\ \nu^3_{v'v''}|(\chi_{v''}|D|\chi_{v'})|^2\ s^{-1}$$

where $\nu_{v'v''}$ is the transition frequency in cm^{-1}. The radiative lifetime of level v' is given by

$$\tau_{v'} = 1/\sum_{v''=0}^{v''_m} A_{v'v''} \quad .$$

Because the $X^2\Pi_g$ and $A^2\Pi_u$ states separate to the same limit, the summation over v" is limited and includes only those vibrational levels of the ground state $v'' \leq v''_m$ which lie below the v' level of the excited state.

The radiative lifetimes of the higher vibrational levels of the ground $X^2\Pi_g$ state are given by

$$\tau_{v''} = 1/\sum_{v'=0}^{v'_m} A_{v''v'}$$

where v'_m is the quantum number of the highest level of the $A^2\Pi_u$ state that lies below the v" level of the $X^2\Pi_g$ state.

3. Calculations

Electronic eigenfunctions of several low-lying states of O_2^+ have been determined for $1.5a_o \leq R \leq 6.5a_o$ by Beebe, Thulstrup and Andersen (1976) and Honjou et al. (1978) using minimal basis-set self-consistent field (SCF) procedures supplemented by full valence configuration-interaction (FVCI). We have extended their calculations using larger SCF and CI bases, the details of which will be given elsewhere (Wetmore and Dalgarno 1984). The CI bases used contained between 1169 and 2500 configuration state functions. The resulting transition dipole moment is listed in table I for separations between 1.8 a_o and 10.0 a_o.

For the potential functions $V_X(R)$ and $V_A(R)$ we adopted the RKR values (Krupenie 1972) extended to large distances by the asymptotic polarization term $-\frac{1}{2}\alpha R^{-4}$ where $\alpha = 5.28\ a_o^3$ is the polarizability of atomic oxygen (Kelly 1966).

The calculated lifetimes of the $A^2\Pi_u$ state for vibrational levels v' between 0 and 7 are compared in table II with the experimental values. The theoretical lifetimes are consistent with the experiments in showing little variation with vibrational level. The theoretical lifetimes of about 790 ns lie between the values of about 660 ns measured by Jeunehomme (1966) and 710 ns measured by Fink and Welge (1968) and the values around 1000 ns measured by Erman and Larsson (1977). The uncertainty in the calculated dipole moment is probably about 10%, and hence in the calculated lifetimes about 20%, and does not permit a choice between the different measurements.

The calculated lifetimes of the other vibrational levels of the $A^2\Pi_u$ state are listed in table III. The lifetimes increase slowly but steadily with v' to a value of 17.4μs for v' = 33.

The theoretical data for the individual emission bands are presented in table IV as absorption oscillator strengths $f_{v'v''}$ for v' and v" ≤ 7. The table includes semi-empirical values of Erman and Larsson derived using the r-centroid method. The agreement is close with the exception of some of the weak transitions where the values are sensitive to the variation of the dipole moment with R.

With our adopted potential energy curves, levels v" ≥ 30 of the $X^2\Pi_g$ state lie above the v' = 0 level of the $A^2\Pi_u$ state and can decay by electric dipole radiation. The calculated lifetimes are given in table V for v" ≤ 39. For higher v" the lifetimes are in the range $10^4 - 10^3$s.

The lifetimes of the vibrational levels corresponding to electric quadrupole emission are not known for O_2^+. For H_2^+, they range between 2 x 10^6s and 5 x 10^5s (Posen, Dalgarno and Peck 1983). Those for O_2^+ may be somewhat longer so that the lifetimes of the higher levels are significantly shortened by emission into the $A^2\Pi_u$ state.

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Table 1

Dipole moment D(R) of the $A^2\Pi_u - X^2\Pi_g$ transition of O_2^+.

$R(a_o)$	D(R) (a.u.)
1.8	0.122
2.12	0.155
2.5	0.198
3.0	0.316
3.5	0.620
4.0	1.121
5.0	2.129
6.0	2.788
7.5	3.615
10.0	4.873

Table II

Lifetimes of vibrational levels v' of the
$A^2\Pi_u$ state of O_2^+ in ns

v'	Jeunehomme	Fink and Welge	Erman and Larsson	Theory
0	676±56		1020±70	779
1	620±60		1050±70	782
2	664±65		1030±70	784
3	676±65	710±60	1020±70	789
4	655±40	710±60	1000±70	793
5	680±35	710±60	980±70	799
6	646±70		990±70	806
7			1000±70	815

Table III

Calculated lifetimes τ in s of the vibrational levels v' of the $A^2\Pi_u$ state of O_2^+.

v'	τ(s)	v'	τ(s)	v'	τ(s)
8	8.24(-7)	17	1.20(-6)	26	3.45(-6)
9	3.36(-7)	18	1.29(-6)	27	4.11(-6)
10	8.53(-7)	19	1.41(-6)	28	4.98(-6)
11	8.79(-7)	20	1.55(-6)	29	6.13(-6)
12	9.11(-7)	21	1.73(-6)	30	7.71(-6)
13	9.48(-7)	22	1.94(-6)	31	9.90(-6)
14	9.95(-7)	23	2.20(-6)	32	1.30(-5)
15	1.05(-6)	24	2.52(-6)	33	1.74(-5)
16	1.12(-6)	25	2.93(-6)		

Table IV

Absorption oscillator strengths $f_{v'v''} \times 10^4$

v'/v"	0	1	2	3	4	5	6	7
0	6.9(-5)	1.3(-3)	0.011	0.061 *0.1*	0.238 0.2	0.697 *0.7*	1.60 *1.6*	2.93 *2.9*
1	5.5(-4)	6.8(-3)	0.065 *0.1*	0.295 *0.3*	0.914 *1.0*	2.02 *2.1*	3.25 *3.3*	3.71 *3.8*
2	2.3(-3)	0.032	0.203 *0.2*	0.753 *0.8*	1.82 *1.9*	2.90 *3.1*	2.92 *3.1*	1.52 *1.7*
3	7.1(-3)	0.085 *0.1*	0.449 *0.5*	1.35 *1.5*	2.45 *2.7*	2.60 *2.9*	1.26 *1.4*	0.031 *0.1*
4	0.017	0.178 *0.2*	0.707 *0.9*	1.88 *2.1*	2.47 *2.7*	1.50 *1.7*	0.107 *0.2*	0.520 *0.5*
5	0.035	0.316 *0.3*	1.16 *1.3*	2.17 *2.4*	1.92 *2.2*	0.440 *0.6*	0.168 *0.1*	1.40 *1.4*
6	0.063 *0.1*	0.494 *0.5*	1.51 *1.7*	2.13 *2.4*	1.11 *1.4*	5.4(-3)	0.835 *0.8*	1.38 *1.5*
7	0.103 *0.1*	0.698 *0.8*	1.75 *2.0*	1.80 *2.1*	0.420 *0.5*	0.190 *0.2*	0.127 *1.4*	0.687 *0.8*

[*] The empirical values of Erman and Larsson are in italics.

Table V

Lifetimes of vibrational levels v" of the ground $X^2\Pi_g$ state

v"	τ(s)
30	5.7×10^5
31	7.5×10^4
32	1.1×10^5
33	1.5×10^5
34	9.0×10^3
35	3.7×10^3
36	3.9×10^3
37	1.4×10^4
38	4.4×10^4
39	3.1×10^4
--	- - - - -
59	1.5×10^4

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The O_2^+ Vibrational Distribution in the Venusian Ionosphere

J. L. Fox

Harvard-Smithsonian Center for Astrophysics
Cambridge, Massachusetts 02138

O_2^+ is the major ion in the lower ionosphere of Venus, even though O_2 is not an important neutral constituent (Taylor et al. 1980). O_2^+ is formed in the reactions

$$O + CO_2^+ \rightarrow CO + O_2^+(v) + 1.33\text{eV} \quad , (1)$$

and

$$O^+ + CO_2 \rightarrow CO + O_2^+(v) + 1.20\text{eV} \ . \quad (2)$$

Reaction (1) is the major source below and reaction (2) above 150km. The ions produced in these reactions will probably be vibrationally excited. Reaction (1) can populate up to v=6. For reaction (2), vibrational levels up to v=5 are energetically allowed. O_2^+ is lost mainly by dissociative recombination

$$O_2^+(v) + e \rightarrow O(^3P,^1D) + O(^3P,^1D,^1S) \quad (3)$$

The potential curves published by Guberman (1983) show that the repulsive state of O_2 through which the dissociative recombination occurs will vary with the vibrational level of the O_2^+. Thus the rate of reaction (3), the electronic states of the O atoms produced and hence the total exothermicity will also depend on the vibrational level of the ion. Guberman (private communication) has found that the $O(^1S)$ yields for O_2^+ in the v=1 and v=2 states are considerably enhanced over that for v=0. If the production rates of $O(^1S)$ and $O(^1D)$ are affected, the airglow intensities of lines originating in these levels will also be affected.

Abreu et al. (1983) have examined data from the visible airglow experiment on Atmosphere Explorer-E and have found that the quantum yield of O(^{1}S) (0.09-0.23) varies with the ratio of the electron density to the atomic oxygen density. This ratio is a measure of the vibrational excitation of O_2^+ in the terrestrial ionosphere (Bates and Zipf, 1981).

Dissociative recombination of O_2^+ is the major source of hot oxygen atoms in the upper atmosphere of Venus (Nagy et al., 1981). The energy distribution of these atoms will depend on the exothermicity of reaction (3). One mechanism for the escape of hydrogen from Venus is collision of H atoms with hot O atoms (McElroy et al., 1982; Kumar et al., 1983). The predicted escape rate will therefore depend on the channel assumed for reaction (3).

In this paper, we calculate the vibrational distribution of O_2^+ in the ionosphere of Venus for a model based on data from the Pioneer Venus neutral mass spectrometer (Hedin et al., 1983; Neimann at al., 1980). This model is essentially the same as that described by Fox (1982a,b). The calculation of the ion densities includes both chemistry and diffusion. The relative populations of the vibrational levels are computed assuming photochemical equilibrium and are valid to about 230km. We included vibrational levels v=0 to v=60 of the ground state $X^2\Pi_g$ of O_2^+, and v=0 to v=33 of the $A^2\Pi_u$ state.

The $X^2\Pi_g$ State

The sources and sinks of O_2^+ in the Venusian ionosphere are summarized in Table 1. Reactions (1) and (2) far exceed photoionization and electron impact ionization of O_2 as sources of O_2^+. $O^+(^2D)$ may also react with CO_2, although only the rate coefficient for charge transfer of fast $O^+(^2D)$ has been measured (Moran and Wilcox, 1978). $O^+(^2D)$ has been found to react at near gas-kinetic rates in collisions with several molecules (cf. Glosick et al., 1978; Rowe et al., 1980). We assume that the reaction occurs with a rate coefficient of $8\times10^{-10}cm^3s^{-1}$, near that for N_2 and CO, and that the products are CO + O_2^+, as they are for reaction of $O^+(^4S)$. The vibrational distribution of the O_2^+ produced in these reactions is unknown. We assume that the available levels are all populated with equal probability.

As sources of $O_2^+(v=1)$, reactions (1) and (2) are of similar magnitude up to 150km. Above that altitude, reaction (2) dominates. Dissociative recombination is the major loss process for O_2^+ over the entire altitude range of interest. The value of the dissociative recombination coefficient will vary with the vibrational level of the ion, but no measurements or calculations of the magnitude of the difference exist. We therefore assume that the rate coefficient measured by Mul and McGowan (1979) applies to all the vibrational levels.

In addition to the processes which cause net production or loss of O_2^+, there are processes which interchange the vibrational levels. They are presented in Table 2. Fluorescent scattering of sunlight in the second negative system of O_2^+ is such a process. We have computed new excitation rates and transition probabilities from the dipole moment computed by Wetmore et al. (1984). For solar fluxes, we used the values presented by Vernazza et al. (1976).

Vibrationally excited $O_2^+(v>0)$ may be quenched in collisions with atoms or molecules. The rate coefficient for quenching by CO_2 and several other molecules has been reported by Böhringer et al. (1983) for v=1 and v=2. We assume that the rates for higher levels are equal to that for v=2. $O_2^+(v>0)$ may also be quenched by atomic oxygen (reaction 12). Our standard model assumes that the rate coefficient is $1 \times 10^{-10} cm^3 s^{-1}$ for all v, but we also explore the consequences of larger or smaller values. In these reactions, we assume that the vibrational level of the O_2^+ changes by only one quantum, as one would expect for vibration-translation (V-T) energy transfer (Böhringer et al., 1983)

At low altitudes, quenching is more important as a source or sink for v=1 than the reactions which cause net production or loss of O_2^+. The vibrational distributions at low altitudes will not directly reflect the distributions produced in reactions (1) or (2).

The computed relative populations of vibrational levels v=0-2 and v>3 for altitudes from 115 to 250km are shown in Fig. 1. Below 140km quenching limits the fraction vibrationally excited to less that 5%. At high altitudes, the populations of vibrational levels 0 to 5 approach 0.16 , since the major O_2^+ production mechanism, reaction (2), is assumed to produce each of those levels with equal probability. The fraction found in the ground state decreases gradually above 140km. The rate of this reduction depends on the assumed value for quenching of $O_2^+(v)$ by atomic oxygen (reaction 12). Figure 2 also shows altitude profiles of the fraction found in v=0 for quenching coefficient k_{12} of $1x10^{-11}cm^3s^{-1}$ and $6x10^{-10}cm^3s^{-1}$. A quenching coefficient of $6x10^{-10}cm^3s^{-1}$ should be considered an upper limit, since this value is essentially gas kinetic. The results of Abreu et al. (1983), however, probably exclude values this large.

Table 4 gives the fractional population in v=0 to 9 at 205km for each of the models considered. In the standard model, 59% are vibrationally excited at that altitude. If k_{12} is reduced to $1x10^{-11}cm^3s^{-1}$, the fraction vibrationally excited increases to 79%; if k_{12} is increased to $6x10^{-10}cm^3s^{-1}$ fraction in v>0 decreases to 22%. We also consider a model in which the vibrational level produced in reactions (1) and (2) is always the highest level possible. This assumption should give an upper limit to the fraction vibrationally excited. Table 5 shows that for this assumption, 90% of the O_2^+ are in v>0, and for v=1 to 5, the fraction in each level increases with the vibrational quantum number.

Fluorescent scattering in the second negative system of O_2^+ is important as a source of v≥6. The only other production mechanism for these levels is reaction of $O^+(^2D)$ with CO_2, which may produce $O_2^+(X^2\Pi_u)$ in vibrational levels up to v=24 and possibly $O_2^+(a^4\Pi_u)$ up to v=3, although production of the $a^4\Pi_u$ state would involve a spin change. The second negative band system is weak and spread over a large wavelength range. Figure 2 shows the integrated overhead intensities summed in 50Å bins from 1800Å to 9000Å. The total intensity is about 640R.

Discussion

The vibrational distribution of O_2^+ on Venus is significantly different from that on Earth (Fox and Dalgarno, 1984). On Earth, the major production mechanisms are photoionization and electron impact ionization and the reaction

$$O^+ + O_2 \rightarrow O_2^+ (v \leq 7) + O .$$

The vibrational distribution of O_2^+ produced in ionization of O_2 is determined by Franck-Condon factors and is different from the statistical distribution assumed for the charge transfer reactions. The presence of O_2 as a quencher is also important for Earth. In general quenching of a molecular ion by its parent neutral is efficient. Because the reaction occurs by symmetric charge transfer, the change in v is not limited to one quantum number. The final state of the $O_2^+(v)$ will be influenced by Franck-Condon factors for $O_2 \rightarrow O_2^+$. At high altitudes on Earth the distribution of $O_2^+(v)$ approaches 50% vibrationally excited. Both the rate of dissociative recombination of $O_2^+(v)$ and the final electronic states of the O atoms produced will be influenced by the vibrational level of the ion. The major source of both $O(^1S)$ and $O(^1D)$ in the Venusian thermosphere is photodissociation of CO_2 (Fox and Dalgarno, 1981). The peak of this source occurs at altitudes (115km) at which $O(^1D)$ atoms are quenched. The total dissociative recombination rate is comparable to or exceeds the production of $O(^1D)$ due to all other sources for altitudes above 140km. Thus we expect the branching ratio for $O(^1D)$ production in dissociative recombination of O_2^+ to influence the intensity and lineshapes of the 6300Å O(^{1}D → ^{3}P) emission.

O(^{1}S) is not as readily quenched and the density of this species peaks near 115km. The dissociative recombination rate exceeds the production of O(^{1}S) only for altitudes above 130km. Thus, although we do not expect the total overhead intensity of the emissions from O(^{1}S) at 5577Å and 2972Å to be greatly affected by the value of the yield of O(^{1}S) in (3), the volume emission rate above 130km will reflect the yield if it is significant.

Nagy et al. (1981) predicted the presence of a hot oxygen corona around Venus analogous to the terrestrial oxygen corona (Yee et al., 1980). The major source of hot oxygen atoms was found to be dissociative recombination of O_2^+. The exothermicity of the reaction and therefore the energies of the O atoms produced will depend on the vibrational state of the O_2^+ ion. At 205km, the average vibrational energy is .38eV in the standard model.

If the product atoms are in the O(^{3}P) and O(^{1}D) states, the energy released is 5.0eV, so the addition of 0.38eV will not be significant. If, however, the products are O(^{1}S)+ O(^{1}D), the exothermicity is only 0.83eV for $O_2^+(v=0)$. The addition of one or two quanta of vibrational energy may significantly change the energy distribution of the O atoms produced. Killeen and Hays (1983) examined line profile measurements of the oxygen green line in the terrestrial ionosphere and concluded that the O(^{1}S) + O(^{1}D) channel is favored over the O(^{1}S) + O(^{3}P) channel by a factor of four. This is in agreement with the theoretical prediction of Guberman (1983) that the major channel for production of O(^{1}S) is through the repulsive $^1\Sigma_u^+$ state of O_2 which dissociates into one O(^{1}S) and one O(^{1}D). If so, the line profile of the 5577Å emission should reflect the vibrational state of the O_2^+ ion.

More important to the total exothermicity however, is the possibility that the reaction proceeds through different channels for different initial vibrational levels of O_2^+.

McElroy et al. (1982) proposed that the escape of hydrogen from Venus is caused by collisions of thermal H atoms with hot O atoms produced in

$$O_2^+ + e \rightarrow O(^1D) + O(^3P) + 5.1eV .$$

Kumar et al. (1983) have evaluated the source and found that it is important in the current atmosphere, but that charge exchange of hot H^+ with H dominated in the past. Table 3 shows that near the exobase, the O_2^+ is considerably vibrationally excited. If recombination in different vibrational levels proceeds through different channels, the energies of the oxygen atoms will change and therefore the hydrogen escape rate due to this source will be affected.

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Figure Captions

1. Relative populations of O_2^+ in v=0, 1, 2, and v>3 over the altitude range 115 to 250km.
2. Integrated overhead intensities of the second negative bands of $O_2^+(A^2\Pi_u - X^2\Pi_g)$. The intensities are summed in 50Å bins.

Table I. Sources and Sinks of O_2^+ in the Venusian thermosphere

	Reaction	Rate $(cm^3 s^{-1})$	Reference
1	$O + CO_2^+ \rightarrow O_2^+(v \leq 6) + CO$	1.64×10^{-10}	Fehsenfeld et al. 1970
2	$O^+ + CO_2 \rightarrow O_2^+(v \leq 5) + CO$	9.4×10^{-10}	Smith et al. 1978
3	$O_2^+ + e \rightarrow O + O$	$1.9 \times 10^{-7}(300/T_e)^{0.5}$	Mul and McGowan 1978
4	$O^+(^2D) + CO_2$ $\rightarrow O_2^+(X^2\Pi_g v \leq 24 ; a^4\Pi_u v \leq 3) + CO$	See Text	
5	$O_2^+ + NO \rightarrow NO^+ + O_2$	4.8×10^{-10}	Smith et al. 1978
6	$O_2^+ + N \rightarrow NO^+ + O$	1.2×10^{-10}	Fehsenfeld 1977
7	$O_2^+ + N(^2D) \rightarrow NO^+ + O$	1.8×10^{-10}	Goldan et al. 1966
8	$O_2^+ + N(^2D) \rightarrow O_2 + N^+$	4.0×10^{-10}	estimate of Dalgarno 1970
9	$O_2^+ + C \rightarrow CO^+ + O$ $\rightarrow C^+ + O_2$	5×10^{-11} 5×10^{-11}	Prasad and Huntress 1980

Table 2. Processes that interchange the vibrational levels of O_2^+

	Fluorescent scattering:		Rate(cm^3s^{-1})	Reference
10	$O_2^+(X^2\Pi_g;\ v) + h\nu \rightarrow O_2^+(A^2\Pi_u;\ v')$		see text	
11	$O_2^+(A^2\Pi_u; v') \rightarrow O_2^+(X^2\Pi_g;\ v'') + h\nu$		see text	
	Quenching:			
12	$O_2^+(v) + O \rightarrow O_2^+(v-1) + O$		$1x10^{-10}$	see text
13	$O_2^+(v) + CO_2 \rightarrow O_2^+(v-1) + CO_2$	v=1	$1x10^{-10}$	Böhringer et al 1983
		v=2	$2x10^{-10}$	
14	$O_2^+(v) + CO \rightarrow O_2^+(v-1) + CO$	v=1	$4.4x10^{-11}$	
		v=2	$6.5x10^{-11}$	

Table 3. Vibrational distributions of O_2^+ at 205km in the Venusian ionosphere for several models. The numbers given are the fraction in each vibrational level.

vibrational level	Model: 1	2	3	4	5
0	.41	.20	.78	.10	.61
1	.15	.17	.064	.059	.062
2	.14	.17	.054	.090	.068
3	.12	.16	.043	.14	.075
4	.098	.15	.030	.22	.082
5	.062	.13	.017	.35	.090
6	.0053	.0057	.0019	.017	.0048
7	.0033	.0022	.0014	.0050	.0017
8	.0027	.0017	.0012	.0047	.0015
9	.0021	.0013	.0010	.0036	.0012
10	~.01				

Model:

1. Standard model: $k_{12} = 1\text{x}10^{-10}\,\text{cm}^3\text{s}^{-1}$.
2. k_{12} reduced to $1\text{x}10^{-11}\,\text{cm}^3\text{s}^{-1}$.
3. k_{12} increased to $6\text{x}10^{-10}\,\text{cm}^3\text{s}^{-1}$.
4. Production of O_2^+ in reactions (1) and (2) is assumed to populate the highest vibrational levels possible.
5. Same as 4 but with k_{12} increased to $6\text{x}10^{-10}\,\text{cm}^3\text{s}^{-1}$.

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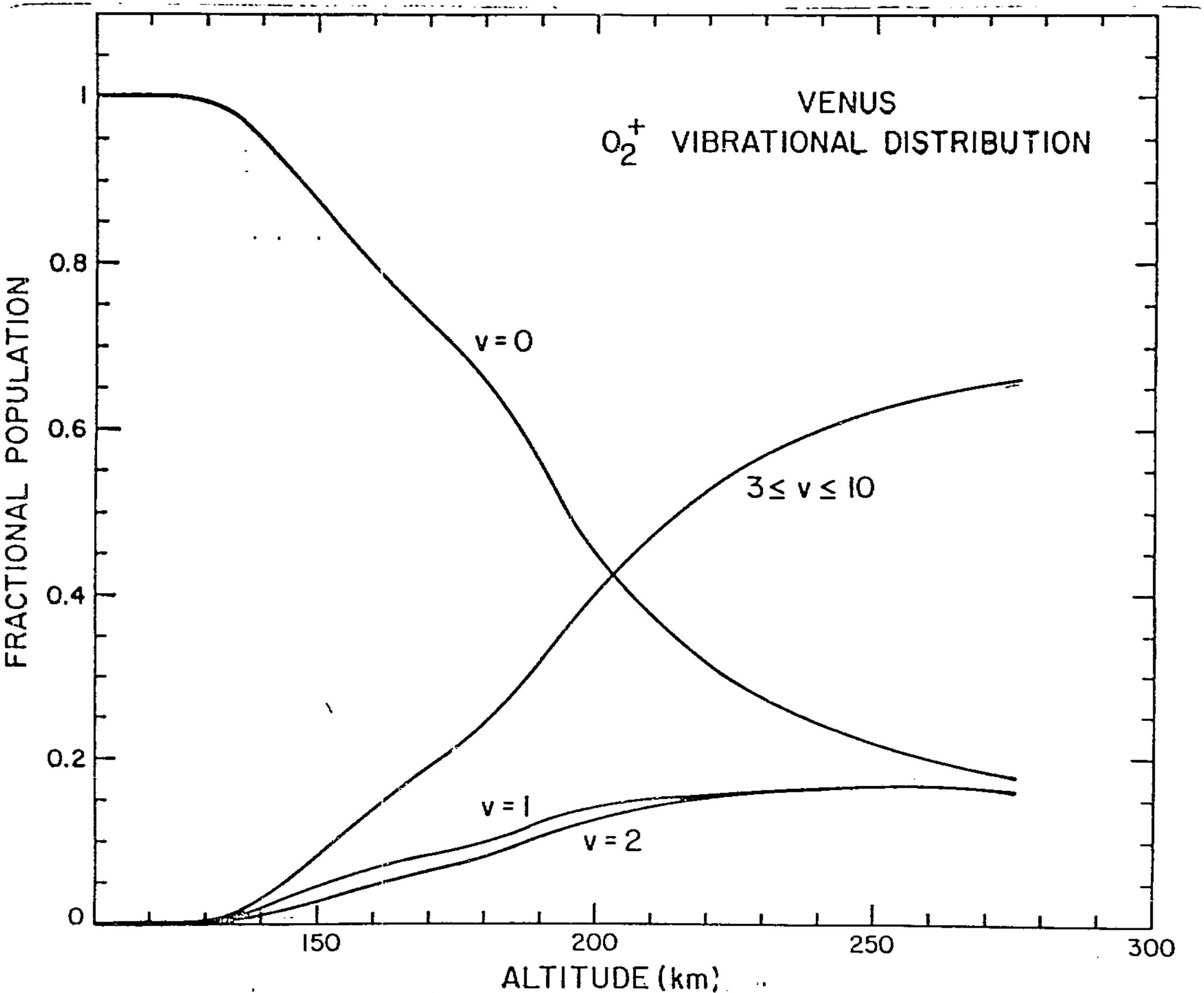
VENUS
O_2^+ VIBRATIONAL DISTRIBUTION
FRACTIONAL POPULATION
1
0.8
0.6
0.4
0.2
0
150
200
250
300
ALTITUDE (km)
v = 0
3 ≤ v ≤ 10
v = 1
v = 2

Figure 1

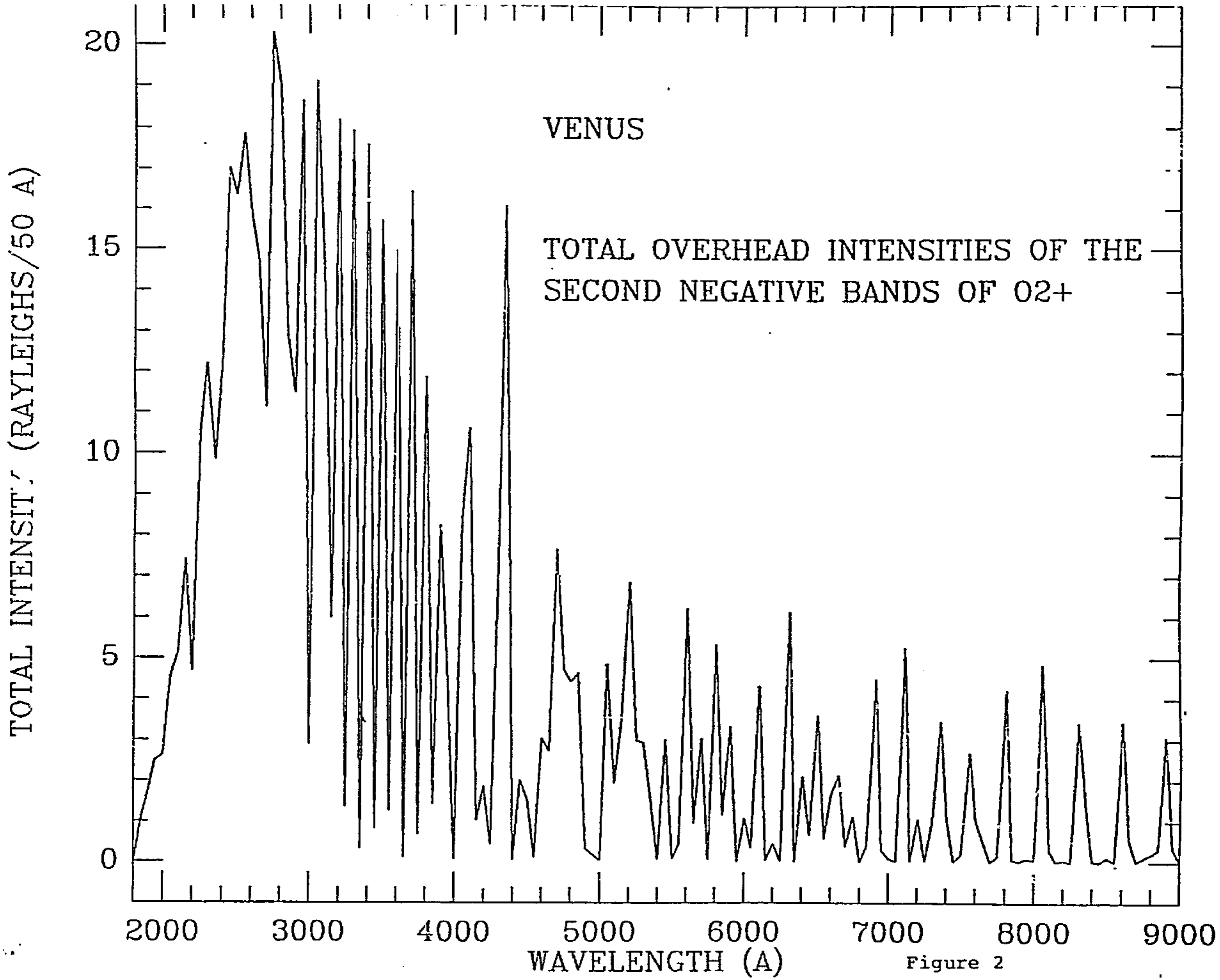
VENUS
TOTAL OVERHEAD INTENSITIES OF THE SECOND NEGATIVE BANDS OF O2+
TOTAL INTENSITY (RAYLEIGHS/50 A)
20
15
10
5
0
2000
3000
4000
5000
6000
7000
8000
9000
WAVELENGTH (A)

Figure 2