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O++ in the Venusian Ionosphere

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It is shown that the revised photochemical theory for O++ in the earth’s ionosphere, where double photoionization of O is the dominant source, is consistent with recent O++ measurements on Venus. A rate coefficient of $1.5 \times 10^{-10}$ cm$^3$ s$^{-1}$ for O++ + O is obtained, and the possible importance of O++ chemistry on minor atomic ions and airglow emissions is explored.

INTRODUCTION

The ion mass spectrometer aboard the Pioneer Venus Orbiter has measured significant concentrations of O++ in the Venusian ionosphere [Taylor et al., 1980]. During the day, the density ranges from about 10 cm$^{-3}$ at 170 km to over 100 cm$^{-3}$ near 300 km. O++ has also been measured in the terrestrial ionosphere by mass spectrometers on the Atmospheric Explorer satellites [Breig et al., 1977]. Our understanding of the photochemistry of O++ on the earth has changed significantly recently by the identification of the dominant sources and sinks. Johnsen and Biondi [1978] and Howorka et al. [1979] have measured reaction rates for O++ destruction by the molecules N$_2$ and O$_2$ in excess of $10^{-9}$ cm$^3$ s$^{-1}$. Such large laboratory destruction rates imply an additional large source of O++ to explain the observed atmospheric concentrations. Victor and Constantinides [1979] have shown that double photoionization of outer shell electrons is the missing source, which at most altitudes is up to several orders of magnitude more efficient than the previously identified sources: photoionization of O* and Auger stabilized k shell ionization of O by X rays.

No direct laboratory or theoretical data have been published for the cross section for double photoionization of atomic oxygen, so Victor and Constantinides [1979] derived a plausible cross section by analogy to other measured [Schmidt et al., 1976] and calculated [Carter and Kelly, 1976] systems. The O++ ion concentration data for the terrestrial ionosphere are consistent with the derived cross section except at low altitudes where the measured concentration, which is very small, exceeds the calculated values.

In this work we present the results of a photochemical study of O++ in the Venusian ionosphere. As with the earth, we find harmony between the theoretical and observed densities of O++ when the large double photoionization source is used. Also, the possible discrepancy between theory and observation at lower altitudes appears smaller on Venus than on the earth. From the high altitude O++ data for Venus, we have derived a rate coefficient of $1.5 \times 10^{-10}$ cm$^3$ s$^{-1}$ for the reactions of O++ with atomic oxygen which is reasonably consistent with the crude upper limit obtained on the earth by Victor and Constantinides [1979]. The calculations show that with the additional large source of O++, reactions of O++ and N$_2$, CO$_2$ and CO can provide sources of N* and C* which, while never dominant, are at some altitudes large enough that they should be considered in quantitative studies. Studies which have not included these sources [Nagy et al., 1980; Rusch and Cravens, 1979] have yielded underestimates for the C* and N* concentrations. The O++ source is not enough to explain the discrepancy.

PHOTOCHEMISTRY OF O++

Breig et al. [1977], following earlier studies of the terrestrial ionosphere, assumed photoionization of O*

$$O^* + hv(\lambda < 351 \text{ Å}) \rightarrow O^{++} + e \quad (1)$$

as the major source of O++. The X ray Auger process, in which the ion produced by k shell ionization decays by ejection of an outer shell electron

$$O + hv(\lambda < 23 \text{ Å}) \rightarrow O^{++} + e \quad (2)$$

is a minor source. These sources can account for the observed densities if destruction proceeds only by charge transfer of O++ to atomic oxygen

$$O^{++} + O \rightarrow O^{++} + O^* \quad (3)$$

with a rate coefficient of about $10^{-11}$ cm$^3$ s$^{-1}$. Recent measurements have established significant destruction rates for O++ on molecules. Johnsen and Biondi [1978] and Howorka et al. [1979] measured rate constants for the reactions

- $O^{++} + N_2 \rightarrow$ products \hspace{1cm} (4)
- $O^{++} + O_2 \rightarrow$ products \hspace{1cm} (5)

and obtained values between 1 and $2 \times 10^{-9}$ cm$^3$ s$^{-1}$. With such large destruction rates, a very large additional source of O++ is required to explain the observed densities. Victor and Constantinides [1979] have shown that double photoionization of outer shell electrons is the desired missing source. Although cross sections for this process have not been reported, they estimate a plausible cross section by analogy to other measured and calculated systems [Schmidt et al., 1976; Carter and Kelly, 1976] and found that a ratio of O++/O* cross sections of 10% could satisfactorily account for the data. The source is large because it arises from the major high altitude neutral species rather than an ion and the threshold at 254 Å allows a much larger and more intense region of the solar spectra to be productive. Agreement was best if a crude upper limit of $1 \times 10^{-10}$ was used for the rate coefficient for reaction (3).

Using the cross sections for double photoionization of atomic oxygen derived by Victor and Constantinides [1979], we
have computed the O** densities in the Venusian ionosphere. In addition to reaction with N₂, O₂ and O, loss of O** on Venus should occur by charge transfer to CO₂ and CO. The rate coefficient for the reaction

\[ \text{O}^{**} + \text{CO}_2 \rightarrow \text{products} \]

has been recently measured and found to be about \( 2 \times 10^{-9} \, \text{cm}^3 \, \text{s}^{-1} \) (R. Johnsen and M. Biondi, private communication, 1980). The rate of the reaction with CO

\[ \text{O}^{**} + \text{CO} \rightarrow \text{products} \]

is unknown, but we assume that the rate proceeds at about the same rate as that with the isoelectronic molecule N₂. O** has been found to react at about the gas kinetic rate with almost all molecules. The relevant reactions of O** and their rates are summarized in Table 1.

**THE MODEL**

The model atmosphere is based on the measurements of the Pioneer Venus Orbiter for daytime conditions. The neutral densities were taken from Niemann et al. [1980]. Density profiles for He⁺ and O⁺ were taken from Taylor et al. [1980]. We used the F79050 solar fluxes of Hinteregger [1981] which apply to February 19, 1980. The high solar activity \( F_{10.7} \approx 200 \) at the time of Pioneer Venus precludes the use of previous reference spectra [Hinteregger, 1976] which apply to periods of low solar activity \( F_{10.7} \approx 74 \).

For photoionization of O⁺ we used the ionization rate for optically thin conditions, \( q_1 = 8.7 \times 10^{-4} \, \text{s}^{-1} \), derived from cross sections of Henry [1968] by Breig et al. [1977] and scaled for Venus. Photoionization of O⁺ is unimportant except above 250 km where attenuation of incoming radiation is negligible. Absorption of radiation was taken into account for double photoionization of atomic oxygen. The photoabsorption and photoionization cross sections for N₂ and O have been tabulated by Kirby et al. [1979]. The cross sections used for CO₂ are the same as those employed by Fox and Dalgarno [1979].

**RESULTS**

Using these production rates and the loss processes shown in Table 1, O** densities were computed and are presented in Figure 2 for three values of \( k_s \), the rate coefficient for charge transfer of O** to atomic oxygen. Because atomic oxygen increasingly dominates the neutral atmosphere above 150 km, reaction of O** with O becomes the major loss process above 200 km. The best fit is obtained for \( k_s = 1.5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \). This value is somewhat larger than the upper limit of \( 1 \times 10^{-10} \) derived by Victor and Constantinides [1979], but uncertainties involved in extrapolation of the measured densities to higher altitudes and in the solar fluxes at the time of the measurement limit the accuracy of this number to the order of about 50%. The photochemical model itself may not be appropriate at the highest altitudes considered [Bauer et al., 1979].

The products of the reactions of O** with O₂, N₂, CO₂ and CO are not known. The large amount of available energy renders dissociative ionization processes more probable than simple charge transfer. O** lies 35.1 eV above the ground state of O⁺. The reaction

\[ \text{O}^{**} + \text{N}_2 \rightarrow \text{O}^+ + \text{N}^+ + \text{N} \]

is exothermic by 10.9 eV. Charge transfer to CO₂ may proceed by

\[ \text{O}^{**} + \text{CO}_2 \rightarrow \text{O}^+ + \text{CO}^+ + \text{O} + 15.6 \, \text{eV} \]

\[ \text{O}^+ + \text{CO} + \text{O}^+ + 16.0 \, \text{eV} \]

\[ \text{O}^+ + \text{C}^+ + 20 + 7.3 \, \text{eV} \]

\[ \text{O}^+ + \text{C} + \text{O} + \text{O}^+ + 4.9 \, \text{eV} \]

**TABLE 1. Loss Mechanisms for O**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O** + N₂ → products</td>
<td>1.6 ± 0.6 \times 10^{-9}</td>
<td>Howorka et al. [1979]</td>
</tr>
<tr>
<td>O** + O₂ → products</td>
<td>1.7 ± 0.7 \times 10^{-9}</td>
<td>Howorka et al. [1979]</td>
</tr>
<tr>
<td>O** + CO₂ → products</td>
<td>2 \times 10^{-9}</td>
<td>R. Johnson and M. Biondi*</td>
</tr>
<tr>
<td>O** + CO → products</td>
<td>1.6 \times 10^{-9}</td>
<td>This work</td>
</tr>
<tr>
<td>O** + Ar → O** + Ar⁺</td>
<td>3.7 ± 1.5 \times 10^{-10}</td>
<td>Howorka et al. [1979]</td>
</tr>
<tr>
<td>O** + O → O⁺ + O⁺</td>
<td>1.5 \times 10^{-10}</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Private communication (1980).
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and to CO by

\[ \text{O}^{++} + \text{CO} \rightarrow \text{O}^+ + \text{C} + \text{O}^+ + 10.4 \text{ eV} \]  \hspace{1cm} (10a)

\[ \text{O}^+ + \text{C}^+ + \text{O} + 12.7 \text{ eV} \]  \hspace{1cm} (10b)

These reactions may produce important quantities of C+ and N+. In Figure 3 the major sources of N+ [Fox and Dalgarno, 1981] are compared to that due to reaction of O++ with N2, with the likely assumption that every reaction produces N+. Photodissociative ionization of N2 dominates in the lower ionosphere and charge transfer from He+ becomes more important near 230 km. Reaction (8) is an insignificant source of N+ below 200 km, but at higher altitudes it becomes comparable to electron impact on N2 and even exceeds photodissociative ionization above 270 km. The sources of C+ are shown in Figure 4. The profile due to charge transfer from O++ is an upper limit, since it assumes that every reaction produces a C+. As for N+, photodissociative ionization and charge transfer from He+ are the most important sources. Above 200 km, however, charge transfer from O++ is of the same order of magnitude as these sources and above 260 km it even exceeds photodissociative ionization of CO. Dissociative ionization of CO2 is less important than charge transfer from O++ above 160 km. It is clear that reaction of O++ with molecules may be an important, although not dominant, source of atomic ions and should not be ignored in computations of the minor ion chemistry. Ionospheric models which ignore this source have thus far yielded underestimates for the steady state densities of N+ and C+ [Nagy et al., 1980; Rusch and Cravens, 1979]. O++ also reacts with Ar to produce Ar+, but the source is small compared to photoionization and electron impact ionization.

The large exothermicity of reactions (8)-(10) indicates that the products in these reactions are probably produced in excited states. Thus dissociative charge transfer from O++ may be a source of metastable species and airglow emissions. For instance, reactions (10a) and (10b) may produce excited states of C and C+. Computed values for the C I 1329, 1657 and 1561 Å dayglow emissions on Venus and Mars are low compared to the measured values [Fox and Dalgarno, 1979, 1981]. Reaction (10) could contribute a source comparable to electron impact or photodissociation of CO2 but probably less than dissociative ionization of CO.

CONCLUSIONS

We have shown that the O++ profile in the Venusian ionosphere may be explained in terms of the same sources which are operative on the earth. The major source is double photoionization of atomic oxygen. Because charge exchange with atomic oxygen is the only important loss mechanism for O++ above 200 km, we have been able to derive a rate coeffi-

Fig. 2. The O++ density in the atmosphere of Venus. The observed data of Taylor et al. [1980] are represented by crosses. The solid theoretical curves are labeled by different values of \( k_3 \), the rate coefficient for the destruction of O++ by atomic oxygen.
cient for reaction (3) of $1.5 \times 10^{-16}$ cm$^3$ s$^{-1}$, compared to an upper limit of $1 \times 10^{-16}$ cm$^3$ s$^{-1}$ derived by Victor and Constantinides [1979] from Atmospheric Explorer data. Below 200 km, loss of O$^{++}$ proceeds mainly by reaction with CO, N$_2$, and CO$_2$. The computed densities appear to be somewhat low near 170 km, but because of the uncertainty in the rate constants for loss of O$^{++}$ on molecules, we cannot conclude that the source assumed is too small or that an additional low altitude source must be present. The computed and measured profiles for the earth also diverge at low altitudes, but the magnitude of the discrepancy there is more serious. In general, the cross sections for double photoionization derived by Victor and Constantinides [1979] for the earth adequately reproduce the density profile observed in the Venusian ionosphere.

Reaction of O$^{++}$ with N$_2$, CO, and CO$_2$ may be an important source of C$^+$ and N$^+$ in the upper ionosphere, although charge transfer from He$^+$ still dominates at high altitudes. Nonetheless, inclusion of this source may decrease the discrepancy between the measured and computed densities of these minor ions in Venusian ionospheric models.
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REFERENCES


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