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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 $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ 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 N₂ and O₂ in excess of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. 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.

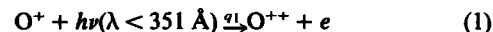
No direct laboratory or theoretical data have been published for the cross section for double photoionization of atomic oxygen, so Victor and Constantinides [1979] derived a plausible cross section by analogy to other measured [Schmidt *et al.*, 1976] and calculated [Carter and Kelly, 1976] systems. 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 $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ 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 N₂, CO₂ and CO can provide sources of N⁺ and C⁺ which, while never dominant, are at some altitudes large enough that they should

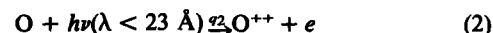
be considered in quantitative studies. Studies which have not included these sources [Nagy *et al.*, 1980; Rusch and Cravens, 1979] have yielded underestimates for the C⁺ and N⁺ concentrations. The O⁺⁺ source is not enough to explain the discrepancy.

PHOTOCHEMISTRY OF O⁺⁺

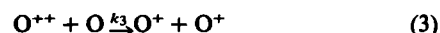
Breig *et al.* [1977], following earlier studies of the terrestrial ionosphere, assumed photoionization of O⁺



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



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



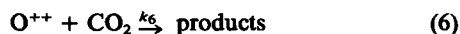
with a rate coefficient of about $10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Recent measurements have established significant destruction rates for O⁺⁺ on molecules. Johnsen and Biondi [1978] and Howorka *et al.* [1979] measured rate constants for the reactions



and obtained values between 1 and $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. 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 1×10^{-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



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



is unknown, but we assume that the reaction 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, $q_1 = 8.7 \times 10^{-8} \text{ s}^{-1}$, 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]. The CO photoabsorption cross sections were taken from *Cook et al.* [1965] for $\lambda > 600 \text{ \AA}$, from *Wight et al.* [1976] for 340 to 600 \AA , from *Cole and Dexter* [1978] for 150 to 340 \AA and from *McGuire* [1968] for $\lambda < 150 \text{ \AA}$.

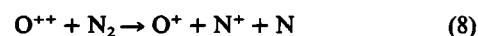
Altitude profiles of the resulting O⁺⁺ production rates from photoionization of O⁺ and double photoionization of O are shown in Figure 1. The rate of Auger ionization is sensitive to the assumed X ray fluxes and is small compared to these two sources. Double photoionization is by far the dominant source of O⁺⁺ in the lower and middle ionosphere, with an optically thin production rate of $7.73 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

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_3 , 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 $k_3 = 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This value is somewhat larger than the upper limit of 1×10^{-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]. This is a large cross section for such an exothermic ion-atom charge exchange process, indicating that a favorable avoided crossing between molecular potential energy curves should exist. An inspection of the separated atom limit energies suggests that the O⁺($2s2p^4 \ ^4P$) excited state may be populated by the charge transfer process leading to $\lambda = 833 \text{ \AA}$ photons. The charge transfer production of 833 \AA photons will be somewhat smaller than that due to direct 2s electron atomic oxygen photoionization. A detailed study of the products of reaction (3) should be carried out. The agreement between the computed and measured O⁺⁺ profiles is excellent except at the lowest altitudes, where the computed densities are too low. Our calculations were done for a solar zenith angle of 45°. The neutral atmosphere measurements [*Niemann et al.*, 1980] are for a solar zenith angle of 18.7°, while the ion data [*Taylor et al.*, 1980] correspond to an 11° solar zenith angle. The computed bottom side O⁺⁺ concentration would increase somewhat with the lower zenith angles appropriate for the measurements. This discrepancy may indicate that the actual double photoionization rate is larger than assumed, but agreement may also be obtained by reducing the rates for reactions (4)–(7) to 1×10^{-9} , which is within the uncertainty of the measurements. The agreement of the profile at higher altitudes is not thereby destroyed because of the decreasing importance of destruction of O⁺⁺ on molecules.

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



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

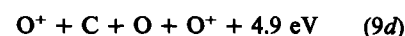
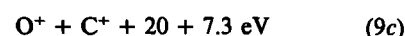
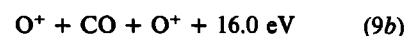
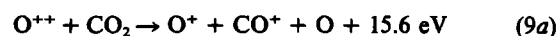


TABLE 1. Loss Mechanisms for O⁺⁺

Reaction	Rate	Reference
O ⁺⁺ + N ₂ → products	$1.6 \pm 0.6 \times 10^{-9}$	<i>Howorka et al.</i> [1979]
O ⁺⁺ + O ₂ → products	$1.7 \pm 0.7 \times 10^{-9}$	<i>Howorka et al.</i> [1979]
O ⁺⁺ + CO ₂ → products	2×10^{-9}	R. Johnson and M. Biondi*
O ⁺⁺ + CO → products	1.6×10^{-9}	This work
O ⁺⁺ + Ar → O ⁺⁺ Ar ⁺	$3.7 \pm 1.5 \times 10^{-10}$	<i>Howorka et al.</i> [1979]
O ⁺⁺ + O → O ⁺ + O ⁺	1.5×10^{-10}	This work

* Private communication (1980).

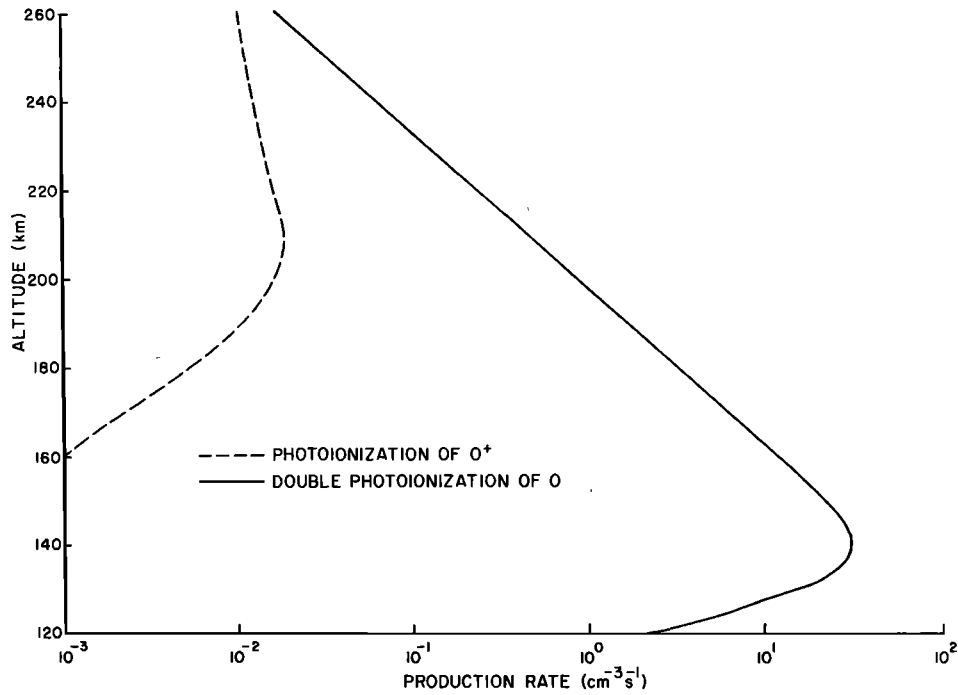
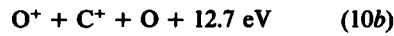
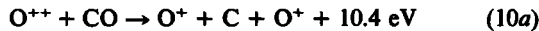


Fig. 1. Sources of O⁺⁺ in the Venusian ionosphere.

and to CO by



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 coefficient

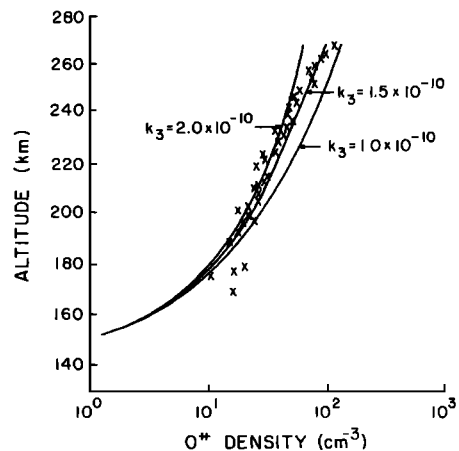


Fig. 2. The O⁺⁺ density in the atmosphere of Venus. The observed data of Taylor *et al.* [1980] are represented by crosses. The solid theoretical curves are labeled by different values of k_3 , the rate coefficient for the destruction of O⁺⁺ by atomic oxygen.

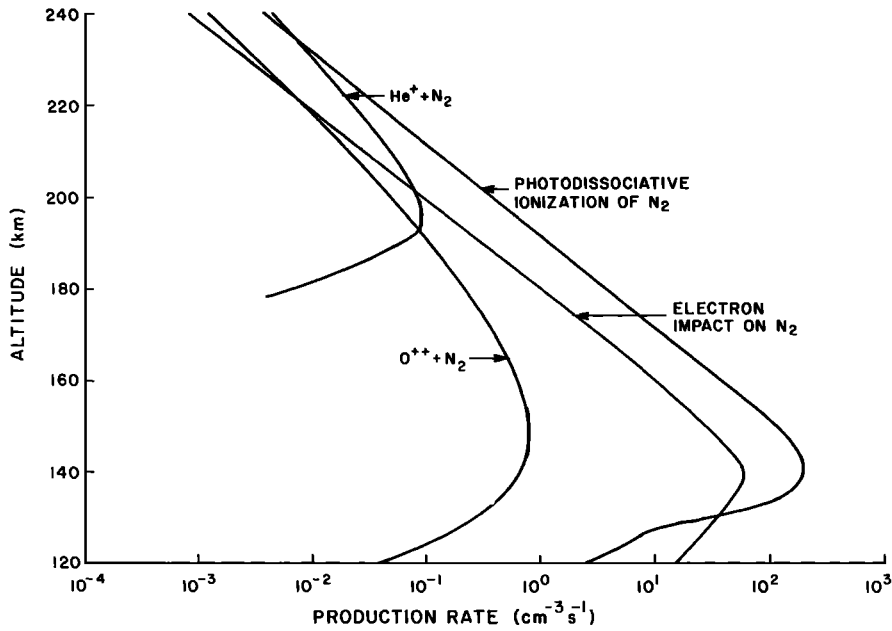


Fig. 3. Sources of N⁺ in the Venusian ionosphere.

cient for reaction (3) of $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, compared to an upper limit of $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ derived by *Victor and Constantinides* [1979] from Atmospheric Explorer data. Below 200 km, loss of O⁺⁺ proceeds mainly by reaction with CO, N₂, and CO₂. 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 N₂, CO, and CO₂ 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.

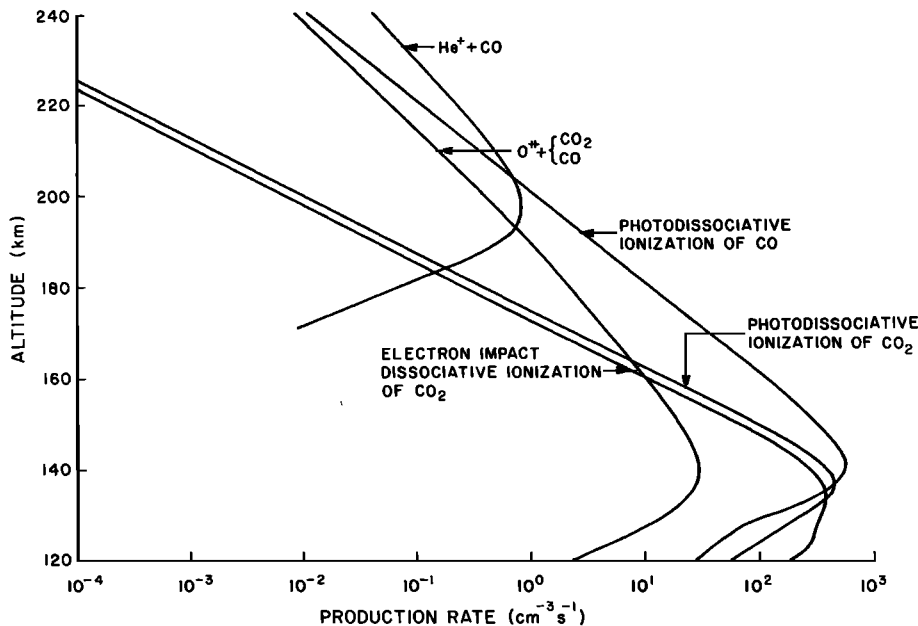


Fig. 4. Sources of C⁺ in the Venusian ionosphere.

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REFERENCES

- Breig, E. L., M. R. Torr, D. G. Torr, W. B. Hanson, J. H. Hoffman, J. C. G. Walker, and A. O. Nier, Doubly charged atomic oxygen ions in the thermosphere, I, Photochemistry, *J. Geophys. Res.*, **82**, 1008–1012, 1977.
- Bauer, S. J., T. M. Donahue, R. E. Hartle, and H. A. Taylor, Jr., Venus ionosphere: Photochemical and thermal diffusion control of ion composition, *Science*, **205**, 109, 1979.
- Carter, S. L., and H. P. Kelly, Double photoionization cross section of ³P carbon, *J. Phys. B*, **9**, 1887, 1976.
- Cole, B. E., and R. N. Dexter, Photoabsorption and photoionization measurements on some atmospheric gases in the wavelength region 50–340 Å, *J. Phys. B*, **11**, 1011, 1978.
- Cook, G. R., P. H. Metzger, and M. Ogawa, Photoionization and absorption coefficients of CO in the 600 to 1000 Å region, *Can. J. Phys.*, **43**, 1706–1722, 1965.
- Fox, J. L., and A. Dalgarno, Ionization, luminosity and heating of the upper atmosphere of Mars, *J. Geophys. Res.*, **84**, 7315–7333, 1979.
- Fox, J. L., and A. Dalgarno, Ionization, luminosity, and heating of the upper atmosphere of Venus, *J. Geophys. Res.*, **86**, in press, 1981.
- Henry, R. J., Photoionization cross sections for N and O⁺, *J. Chem. Phys.*, **48**, 3635, 1968.
- Hinteregger, H. E., EUV fluxes in the solar spectrum below 2000 Å, *J. Atmos. Terr. Phys.*, **38**, 791–806, 1976.
- Hinteregger, H. E., Representation of solar EUV variations for aerometric applications, *Space Res.*, in press, 1981.
- Howorka, F., A. A. Viggiano, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Laboratory studies of O⁺⁺ reactions of ionospheric importance, *J. Geophys. Res.*, **84**, 5941–5942, 1979.
- Johnsen, R., and M. A. Biondi, Measurements of the reaction rates of O⁺⁺ ions with N₂ and O₂ at thermal energy and their ionospheric implications, *Geophys. Res. Lett.*, **5**, 847, 1978.
- Kirby, K., E. R. Constantinides, S. Babeu, M. Oppenheimer, and G. A. Victor, Photoionization and photoabsorption cross sections of thermospheric species: He, O, N₂ and O₂, *At. Nucl. Data Tables*, **23**, 63, 1979.
- McGuire, E. J., Photo-ionization cross sections of the elements helium to xenon, *Phys. Rev.*, **175**, 20–30, 1968.
- Nagy, A. F., T. E. Cravens, S. G. Smith, H. A. Taylor, and H. C. Brinton, Model calculations of the dayside ionosphere of Venus: Ionic composition, *J. Geophys. Res.*, **85**, 7795, 1980.
- Niemann, H. B., W. T. Kasprzak, A. E. Hedin, D. M. Hunten, and N. W. Spencer, Mass spectrometric measurements of the neutral gas composition of the thermosphere and exosphere of Venus, *J. Geophys. Res.*, **85**, 7817, 1980.
- Rusch, D. W., and T. E. Cravens, A model of the neutral and ion nitrogen chemistry in the daytime thermosphere of Venus, *Geophys. Res. Lett.*, **6**, 791–794, 1979.
- Schmidt, V., N. Sandner, H. Kuntzemuller, P. Dhez, F. Willeumier, and E. Kallne, Double ionization of rare gases, II, Ion formation by photon impact, *Phys. Rev. A*, **13**, 1748, 1976.
- Taylor, H. A., H. C. Brinton, S. J. Bauer, R. E. Hartle, P. A. Cloutier, and R. E. Daniell, Global observations of the composition and dynamics of the ionosphere of Venus: Implications for the solar wind interaction, *J. Geophys. Res.*, **85**, 7765, 1980.
- Victor, G. A., and E. R. Constantinides, Double photoionization and doubly charged ions in the thermosphere, *Geophys. Res. Lett.*, **6**, 519–522, 1979.
- Wight, G. R., M. J. Van der Wiel, and C. E. Brion, Dipole excitation, ionization and fragmentation of N₂ and CO in the 10–60 eV region, *J. Phys. B*, **9**, 675–689, 1976.

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