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Studies of the role of metastables and doubly ionized species in the  
chemical and thermal structure of the Venusian and Martian Ionospheres.

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## 1. Introduction

Metastable species are long-lived excited states which are abundant in the low-pressure, far from equilibrium environment of planetary upper atmospheres. Their chemistry is very different from that of ground state atoms and molecules. Because reaction rates of these species have been difficult to measure in the laboratory, the influence of metastable chemistry on the structure of planetary upper atmospheres has not been fully explored. Doubly ionized species, especially  $O^{++}$  have also been ignored in most models.  $O^{++}$  has, however been detected by the ion mass spectrometers aboard Pioneer Venus. The goal of this work is to apply our growing knowledge of metastables and of doubly ionized species to the atmospheres of Mars and Venus, and, in conjunction with the Pioneer Venus data to construct models which will increase our understanding of these atmospheres, and of the elementary molecular processes which determine their structures.

## 2. Construction of Models.

Models of the upper atmospheres of Mars and Venus have been constructed using Viking and Pioneer Venus Data. The neutral densities, with the exception of  $NO$ ,  $N(^4S)$ ,  $N(^2D)$  and  $N(^2P)$ , have been taken from the measured values, along with the neutral, ion and electron temperatures. Using solar fluxes measured by Hinteregger (1976) and relevant cross sections, the production rates of ions and neutral fragments by photo- and electron impact processes are computed. These production rates are combined with chemical production and loss along with one dimensional transport including eddy diffusion, molecular and ambi-polar diffusion, and thermal diffusion, to determine the densities of ions and odd nitrogen species. It is necessary to include transport in the calculations because the range in which photochemical equilibrium is valid is very narrow.

### 3. $O^{++}$ chemistry.

• Double photoionization of atomic oxygen has recently been shown to be the dominant source of  $O^{++}$  in the earth's atmosphere (Victor and Constantinides, 1979). Furthermore, the reaction rates for loss of  $O^{++}$  on molecules have recently been measured. (Howorka et al., 1979; Johnsen and Biondi, 1978). This new information, along with the cross section derived by Victor and Constantinides (1979) has been applied to the Venusian ionosphere to determine  $O^{++}$  densities and to derive a rate for charge transfer of  $O^{++}$  to  $O$  (Fox and Victor, 1981). Reaction of  $O^{++}$  with  $N_2$ ,  $CO_2$  and  $CO$  was found to be an important, but not dominant source of the fragment ions,  $C^+$  and  $N^+$ . Reaction of  $O^{++}$  with  $N_2$  might also be a source of  $N(^2D)$  although this source is found to be small compared with other chemical sources, such as the reaction



In the Martian ionosphere the reaction



is a significant source of escaping nitrogen atoms. Escape rates of the order of  $5 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$  are possible. This source was not included by Fox and Dalgarno (1980), because the relevant data for  $O^{++}$  sources and sinks were not available.

### 4. $N(^2D)$ Chemistry

The reaction



has been shown to be the most important source of  $N^+$  in the terrestrial

ionosphere. (Constantinides et al. 1979). This process is also important in the Venusian atmosphere, but is less important than photo-dissociative ionization of  $N_2$ .  $N(^2D)$  may also react with  $CO_2^+$  to produce  $N^+$  and  $CO_2$ . For a reaction rate near  $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , the source is large, dominating reaction with  $O^+$  at low altitudes. This reaction may also produce  $NO^+$  or  $CO^+$ . Production of  $CO^+$  is small compared to other chemical sources.

Dalgarno (1970) estimated the reaction rate for



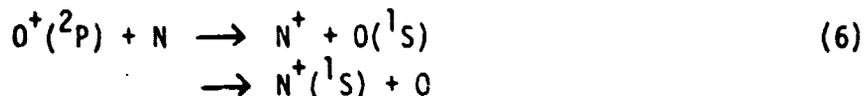
as  $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . If the reaction rate for this process is in fact this large, this reaction is an important source of  $N^+$ , of the same order of magnitude as photo production.

#### 5. $O^+(^2D)$ and $O^+(^2P)$ Chemistry

$O^+(^2D)$  is produced with about one-third efficiency in photoionization and electron-impact ionization of atomic oxygen. Its lifetime is long, about 3.6 hours.  $O^+(^2D)$  and a higher excited state,  $O^+(^2P)$  may react with atomic nitrogen to produce  $N^+$ . Dalgarno (1979) placed an upper limit on the reaction



of  $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , although he indicated that the rate was probably much smaller. If the rate were this large, the source would be important in the Venusian atmosphere. Torret et al (1975) have derived a rate of  $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for the reaction

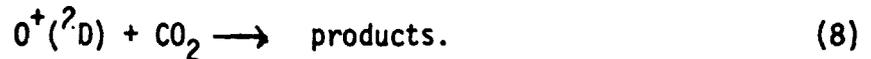


from AE observation of the 5577 Å line. A reaction rate this large yields a source of  $N^+$  comparable to photoproduction.

The reaction



is an important source of  $N_2^+$ . Recent measurements have shown that the rate for this reaction is larger than previously believed (Johnson and Biondi 1980; Rowe et al. 1980). This reaction is the dominant chemical source of  $N_2^+$ . The impact of this reaction depends on the rate of the reaction



If the rate coefficient for this process is as rapid as that of (7), production of  $N_2^+$  is significantly decreased. Nonetheless, for Mars production of  $N_2^+$  and subsequent dissociative recombination produces a larger escape rate than that computed by Fox and Dalgarno (1980).

The rate for charge transfer of  $O^+(^2D)$  to CO has been measured by Glosik et al. (1978). This reaction constitutes the most important chemical source of  $CO^+$  in the Venusian ionosphere.

## 6. Atomic Carbon

The Dayglow intensities associated with neutral and ionized carbon are difficult to explain, partly because the processes producing excited states of C and  $C^+$  have not been measured. Reaction of  $O^{++}$  with  $CO_2$  and CO has been proposed as a possible source (Fox and Victor, 1981) but further calculations show the source to be small. Photo-dissociation of CO produces a substantial fraction of fluorescent fragments (Lee et al. 1975). Calculations show this to be a large but not dominant source.

## 7. Summary

• Preliminary calculations employing models based on pioneer Venus data have shown that the chemistry of metastables and doubly ionized species is important in the ionospheres of Mars and Venus. Production of  $N^+$  in metastable reactions is particularly important, and it explains the discrepancy between the measurements and earlier models (Nagy et al. 1981). Production of  $CO^+$  is also affected. Reactions of  $O^{++}$  and  $O^+(^2D)$  with  $N_2$  have important consequences for the escape rate of atomic nitrogen from the Martian atmosphere.

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