Negative Ion Densities in Chemical Equilibrium in the *D* Region

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Abstract

Assuming the distributions of minor constituents in the upper mesosphere, an estimate is made of the negative ion densities in chemical equilibrium with the observed electron density. The result shows that the negative ion composition in the region above 80 km is essentially same as in the *E*-region. But in the region below 70 km, negative ions, such as CO_3^- , NO_2^- , and NO_3^- , of high electron affinities are shown to be relatively abundant, especially during the night. The result may possibly account for the characteristic growth of the *D*-region electron density at sunrise. A discussion of the sequences of negative ions in the *D* region leads to the conclusion that O_3 and CO_2 play an important role in determining the abundance of these negative ions of high electron affinities.

1. Introduction

Since *Reid* (1961) suggested, in his quantitative study of a polar cap absorption event, the presence of negative ions other than O_2^- in the *D*-region, a greater attention has been paid to the processes in which various kinds of negative ions are produced. Observational information from various techniques indicates that there must be a considerable amount of negative ions of high electron affinities and their photodetachment can be caused only by the solar radiation in the UV range (*Hultqvist*, 1966). *Bowhill and Smith* (1966) have measured the electron density profiles at sunrise and suggested that NO_2^- is the very likely negative ion dominating the behaviors of the *D*-region at sunrise. Based on the electron density profiles measured by *Mechtly and Smith* (1968) at solar zenith angles of 108° , 96° , 94° , and 85° , *Sechrist* (1968) has concluded that the screening height for the solar radiation causing photodetachment of electrons from negative ions in the *D* region is about 50 km above the sea-level and hence the wavelength of the radiation concerned is shorter than 2900 Å. This implies that the electron affinity of these negative ions must exceed 4.3 eV. This paper describes the sequences of negative ions in the *D*-region under the assumption of the density distribution of minor constituents, and an estimate is made of the ion density distributions of various species in chemical equilibrium.

2. Chemical Reactions

In this paper, the atmosphere is assumed to be composed of N_2 and O_2 with traces of minor constituents such as O , O_3 , CO_2 , N , NO , and NO_2 . The height distribution of each of the constituents in the region concerned is assumed as shown in Fig. 1. The concent-

Fig. 1 Height distributions of neutral constituents. The condition during the daytime is drawn as full lines. As for N , NO , and NO_2 , the nighttime condition is shown by dashed lines.

rations of some of the constituents may change drastically during the night, and these are illustrated by the dashed lines. The atmosphere model thus employed here is based on the theoretical results for O , N , NO , and NO_2 obtained by *Hesstvedt* (1969), and *Hesstvedt and Jansson* (1969) who take into account the effect of vertical eddy diffusion, and on the observational result for O_3 reported by *Smith* (1969).

Reaction in which negative ions such as NO_2^- and NO_3^- are created have been studied by various workers (*Fehsenfeld et al.* (1967), *Reid* (1969), and *Keneshea* (1969)). According to these studies, the following processes should be considered in this paper. The rate coefficients which are adopted from the DASA Reaction Rate Handbook are listed in the paper by *Keneshea* (1969), and they are referred to on the right-hand sides of the respective formulae for the processes.

Primary negative ions are created though the following attachment processes;

and

In the presence of O , O_2 , O_3 , N , NO , NO_2 , and CO_2 , these negative ions are subjected to the charge transfer reactions, and the resulting ions are also followed by the other transfer processes. The charge transfer reactions considered in this paper are listed below.

The negative ions thus produced are lost through collisional detachment, photodetachment, or ionic recombination processes. The detachment processes due to collisions considered here are

The photodetachment processes are

In view of the spectrum of the solar radiation, a little contribution to the photodetachment is expected from the wavelength range below 2000 Å. As far as the range exceeding 2000 Å is concerned, the solar radiation is thought to be almost independent of altitude and incident angle in the region above the shielding height. Thus, the photodetachment rates are assumed to be roughly constant throughout the region concerned.

Various kinds of positive ions may exist in the D-region, and they are neutralized with negative ions through recombination processes. Although a dominant component of positive ions is presumably NO^+ in the D region, this paper introduces a symbolic positive ion XY^+ which is assumed to behave as a representative positive ion possessing mean characteristics of the positive ions in the region concerned. Therefore, the ionic recombinations are expressed as follows;

The rate coefficients are assumed to be those for the processes in which only concern is NO^+ . To complete the description of the loss processes of positive ions, the dissociative recombination of XY^+ ,

should be considered in estimating the positive ion density in equilibrium.

3. Equilibrium Ion Densities

When the transport effect is neglected, the number densities of the various kinds of positive and negative ions involved in the processes described above can be estimated on the basis of the observed electron density. If the number density is denoted by a chemical symbol in the parentheses for each of the constituents, the densities are given, in the equilibrium condition, by

$$(O^-) = \frac{\{\beta_1(O) + \beta_3(O_3)\}(e) + k_3(O)(O_2^-)}{r_1(O) + r_2(O_2) + r_3(NO) + k_9(O_3) + k_{10}(NO_2) + \mu_1 + \alpha_1(XY^+)}, \quad (1)$$

$$(O_2^-) = \frac{\{k_1(O_2) + k_2(N_2) + \beta_2\}(O_2)(e) + (O)\{k_6(O_3^-) + k_7(CO_3^-) + k_8(NO_3^-)\}}{r_4(N) + r_5(O) + k_3(O) + k_4(O_3) + k_5(NO_2) + \mu_2 + \alpha_2(XY^+)}, \quad (2)$$

$$(O_3^-) = \frac{(O_3)\{k_4(O_2^-) + k_9(O^-)\}}{k_6(O) + k_{11}(NO) + k_{12}(NO_2) + k_{13}(CO_2) + \mu_3 + \alpha_3(XY^+)}, \quad (3)$$

$$(CO_3^-) = \frac{k_{13}(CO_2)(O_3^-)}{k_7(O) + k_{14}(NO) + \mu_4 + \alpha_4(XY^+)}, \quad (4)$$

$$(NO_2^-) = \frac{(NO_2)\{k_{10}(O^-) + k_5(O_2^-) + k_{12}(O_3^-)\} + k_{14}(NO)(CO_3^-)}{k_{15}(O_3) + \mu_5 + \alpha_5(XY^+)}, \quad (5)$$

$$(NO_3^-) = \frac{k_{11}(NO)(O_3^-) + k_{15}(O_3)(NO_2^-)}{k_8(O) + \mu_6 + \alpha_6(XY^+)}, \quad (6)$$

and the charge neutrality implies

$$(XY^+) = (e) + (O^-) + (O_2^-) + (O_3^-) + (CO_3^-) + (NO_2^-) + (NO_3^-). \quad (7)$$

For a daytime condition, the equilibrium ion densities computed by machine are shown in Fig. 2. The assumed profile of the electron density is based on the result obtained by *Mechtly and Smith* (1968) at the solar zenith angle of 85° . In the region above 75 km, the ratio of the negative ion density to the electron density, λ , is smaller than unity, and only O_2^- and O^- are the major components of the negative ions as is the case in the *E*-region. Below 75 km, however, λ increases rapidly with decreasing height, being about 100 at 60 km and about 10^4 at 50 km. The relative abundances of O_2^- and CO_3^- increase markedly in this region. Thus, the lowermost region of the ionosphere is characterized by the predo-

minance of ionic components.

During the night, the electron density has not yet been measured with a sufficient accuracy in the region below 80 km. Therefore, the profile of the electron density is assumed as shown in Fig. 3. The profile above 80 km is based on the result measured at $\chi=108^\circ$ by *Mechtly and Smith* (1968). In the absence of the photodetachment processes, the equilibrium ion densities on the basis of the nighttime atmosphere model are shown in

Fig. 2 Equilibrium density distributions of electrons, positive ions, and the various kinds of negative ions during the daytime. The electron density profile is based on the result obtained by the direct measurement by *Mechtly and Smith* (1968).

Fig. 3 Equilibrium density distribution of electrons, positive ions, and the various kinds of negative ions during the night when photodetachment processes are absent. The electron density profile above 80 km is based on the direct measurement by *Mechtly and Smith* (1968) at $\chi=108^\circ$, but an assumption is made for the profile below 80 km.

Fig. 3 which differs from the daytime result in many aspects. First, the relative concentration of NO_2^- is much more abundant during the night than during the daytime. Below 70 km, NO_2^- and CO_3^- are shown to be the most dominant constituents of the negative ions. The NO_3^- concentration is also increased remarkably during the night as compared with the daytime result. The ratio, λ , is much larger during the night than during the daytime, being about 10^3 at 60 km and more than 10^6 at 50 km. Hence, a majority of the negative charges created shortly before sunset is considered to be stored in the form of NO_2^- during the night.

4. Discussions

Although the results given in the preceding section should contain uncertainties resulting from the assumption of the atmospheric model and from the adopted values for the rate coefficients, a conclusion is reached that CO_3^- , NO_2^- , and NO_3^- are the important ions in the *D* region, especially at lower altitudes. The electron affinities of these ions have not yet been known precisely, but are thought to be greater than 4 eV. Consequently, the wavelengths of the solar radiation causing the photodetachment of electrons from these ions should be shorter than 2900 Å. Such a radiation in the UV range must be strongly absorbed by ozone in the atmosphere. Hence, the behavior of the lower *D* region at sunrise must be largely controlled by the shielding effect of the ozone layer. Fig. 4 is a reproduction of the observed results (*Mechtly and Smith, 1968*) showing the growth of the electron density profile at sunrise. The shielding effect of O_3 was studied by *Sechrist* (1968) and the lowest height of the ray path was found to be 45–55 km. Thus, the remarkable increase in the electron density in the region from 70 km up to 85 km at $\chi=94^\circ$ is

Fig. 4 The electron density profiles observed directly by means of rockets at solar zenith angles of 108° , 96° , 94° , and 85° at Wallops Is., Virginia (After *Mechtly and Smith, 1968*).

Fig. 5 Diagram showing the negative ion sequences at 90 km-level. The dominating processes are shown by heavy lines. The dashed-and-dotted lines indicate the processes which are important only during the day-time.

Fig. 6 Diagram showing the negative ion sequences at the 70 km-level. The heavy lines have the same meaning as in Fig. 5.

presumably ascribed to the photodetachment of CO_3^- , NO_2^- , and NO_3^- by the solar UV radiation grazing the upper ozone layer. According to our estimate, the minimum height of the ray path is thought to be 54 km.

Next, the sequences of negative ions are shown schematically in Figs. 5 and 6. The neutral component involved in the reactions is indicated on the line showing the sequence. Photodetachment or collisional detachment is denoted by *PD* or *D* in circles, and recombination by *R*. Examining numerically, the heavy lines are drawn so as to indicate the processes which are more than a hundred times as important as the remaining processes concerned in determining the density of ion given in a box. The heavy dashed-and-dotted lines are important only during the daytime. Fig. 5 illustrates the sequences at the 90 km-level. It is understandable from the diagram that the only major negative ions at this level are O^- and O_2^- which are almost in chemical equilibrium with the electron density. At the 70 km-level, however, O^- and O_2^- are in equilibrium not only with electrons but also with O_3^- which in turn balances CO_3^- and its sequences. Thus, in the lower part of the *D* region, O_3^- , CO_3^- , NO_2^- , and NO_3^- should be dominant as well as O^- and O_2^- . In general, the production of O_3^- is controlled by the ozone concentration. Hence, the total concentration of high electron affinity ions such as CO_3^- , NO_2^- , and NO_3^- is essentially dependent upon the O_3 and CO_2 concentrations. On the other hand, CO_2 is also an important constituent as the absorber of the solar radiation in the micron range causing the heating of the mesosphere. Thus, it is noted here that a greater attention should be paid to the

aeronomy pertaining to CO_2 . This paper assumes the CO_2 concentration to be $1/10^4$ of the total air concentration at these altitudes, in view of the possibility of dissociation of CO_2 into CO and O .

5. Conclusions

The processes producing negative ions, such as CO_3^- , NO_2^- , and NO_3^- , having high electron affinities are studied in this paper. The distribution of the equilibrium ion densities are shown in Fig. 2 for the daytime and in Fig. 3 for the nighttime condition. From the standpoint of the ion composition, the region above 85 km is concluded to be essentially the lower part of the E layer where electrons, O^- , and O_2^- are in chemical equilibrium. In the lower D region below 75 km, however, the ion composition is quite different from that in the higher region. The relative abundances of CO_3^- , NO_2^- , and NO_3^- increase rapidly with decreasing altitude, being the major ionic constituents in the lower D region. This tendency is much more pronounced during the nighttime. Therefore, the growth of the D region at sunrise is presumably explained by the photodetachment of electrons from negative ions, such as CO_3^- , NO_2^- , and NO_3^- , of high electron affinities by the solar radiation in the UV range which grazes the upper part of the ozone layer. The minimum height of the ray path is estimated to be about 54 km from the data obtained by Mechtly and Smith (1968). The diagrams showing the sequences of the negative ions suggest the importance of the aeronomy involving CO_2 as well as O_3 .

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