NEGATIVE IONS IN THE LOWER ATMOSPHERE

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Abstract: The chemical compositions of negative ions in the lower atmosphere (0–30 km altitude) at middle latitudes were investigated with two models, one for the lower stratosphere (15–30 km) and the other for the troposphere (0–15 km). The calculated result shows that the predominant ion species are $NO_3^-HNO_3H_2O$ in the height range of 0–10 km and $NO_3^-(HNO_3)_2$ in 10–30 km, and other main negative species have NO_3^- or HSO_4^- cores. In general, the calculated result agrees with the observed one. A possible role of the ions and aerosols generated by the ion-nucleation mechanism is suggested for the Antarctic springtime 'ozone hole' phenomenon.

1. Introduction

The mass spectrometric observations of negative ions in the lower atmosphere have been made since late 1970's (*e.g.*, Arnold and Henschen, 1978; Arijs, 1983), and theoretical studies have been carried out since early 1980's (Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1984, 1986).

As a result of these experimental and theoretical investigations, it was found that the composition of lower atmospheric ions is related to the neutral gases and that ions may grow eventually to aerosol particles. Therefore, it is of worth for climatic and environmental studies to research the ion-nucleation process in the lower atmosphere. In particular, it is important to investigate the relation between ions and aerosols in the stratosphere, the ion-nucleation process in the formation of cloud condensation nuclei (CCN) which result in an acidic precipitation in the troposphere, and the role of ions in the formation of Antarctic springtime 'ozone hole'.

In this paper, the theoretical studies on negative ion compositions in the lower atmosphere are summarized, and a possible role of ion-nucleation in the Antarctic springtime ozone-depletion phenomenon is suggested.

2. Models of Negative Ion Composition

The present theoretical result involves previous studies reported by Kawamoto and Ogawa (1984) in the lower stratosphere (15–30 km) and by Kawamoto and Ogawa (1986) in the troposphere (0–15 km). The adopted models and the computational method are explained in detail by Kawamoto (1987), so the models will be described briefly in the following.

The models include the ionization rate (Q), 100 reactions for ion-neutral reactions

in the troposphere, 96 reactions in the lower stratosphere, recombination coefficient between positive and negative ions (α), attachment coefficient of ions to aerosol particles (β), and the number density of aerosols (Z).

The equilibrium between the production rate Q ($cm^{-3}\ s^{-1}$) and the loss rate of the ion number density $n_{\pm}$ (cm^{-3}) is expressed as

$$Q = \alpha n_{\pm}^2 + \beta Z n_{\pm} \ . \tag{1}$$

Solving eq. (1), the number density of ions is given as

$$n_{\pm} = \frac{-\beta Z \pm \sqrt{(\beta Z)^2 + 4\alpha Q}}{2\alpha} \ . \tag{2}$$

Next, to calculate the fractional abundances of individual negatively-charged species which consist of electrons and negative ions, the equilibrium of production and loss of each species was assumed ($P_i = n_i L_i$). For the employment of the signal flow graph technique (shortened to SFG hereafter), this equilibrium is written as

$$P_i = n_i L_i = \sum_{\substack{j=1 \\ j \neq i}}^{k} r_{ij} n_j + \gamma_i \ , \tag{3}$$

where r_{ij} is considered as the reaction rate (s^{-1}) from j-type to i-type and γ_i is an input of i-species, taking the ionization rate for electrons and zero for the negative ions. This equation can be rewritten as follows by using the relation $P_j = n_j L_j$.
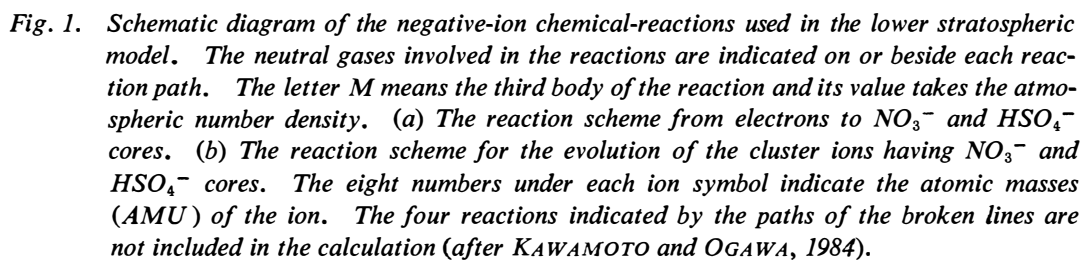
$$P_i = n_i L_i = \sum_{\substack{j=1 \\ j \neq i}}^{k} \left(\frac{r_{ij}}{L_j} \right) P_j + \gamma_i \ . \tag{4}$$
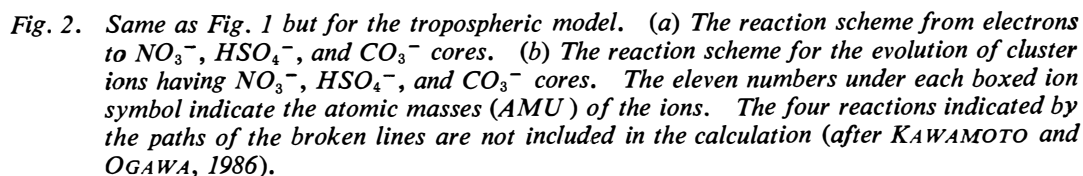
These equations, having the form of eq. (4), construct a linear system which has an input (ionization) and output (production rates of the electrons and negative ions). At this stage, using the SFG technique (HENLEY and WILLIAMS, 1973), we can obtain the value of each production rate (P_i). Refer to WISEMBERG and KOCKARTS (1980) for a detailed explanation. Each concentration n_i is then easily given by using the relation $P_i = n_i L_i$.

In order to carry out the above-mentioned calculation, the values of all r_{ij} are needed. Each r_{ij} is estimated from the reaction rate constant and the concentration of neutral gaseous constituent.

The chemical reaction schemes for the negative ion composition in the lower stratosphere (LS, 15–30 km) and troposphere (TR, 0–15 km) are shown in Figs. 1 and 2, respectively. The reaction schemes shown in Figs. 1a and 2a are considered for the processes of producing the cores of NO_3^-, HSO_4^-, and CO_3^- cores from electrons. The reaction schemes shown in Figs. 1b and 2b are considered for the evolution of cluster ions having these cores.

The height distributions of neutral gases, which were used in the present model calculations, are shown in Figs. 3 and 4. In Fig. 3, the profiles of neutral gases with their number densities larger than $10^{10}\ cm^{-3}$ are shown, and the profiles for minor constituents (smaller than $10^{11}\ cm^{-3}$ in number density) are shown in Fig. 4.
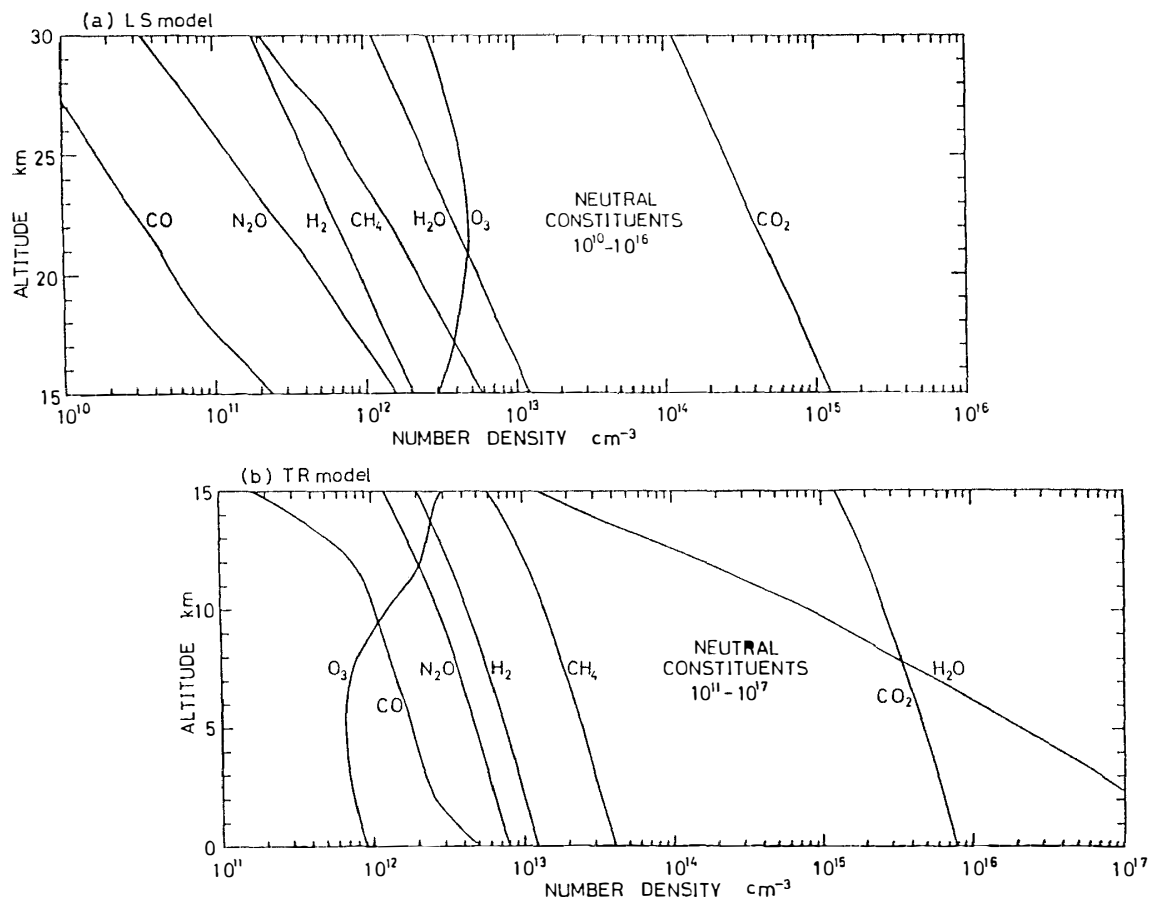
(a)

(b)

Fig. 1.   Schematic diagram of the negative-ion chemical-reactions used in the lower stratospheric
model.   The neutral gases involved in the reactions are indicated on or beside each reac-
tion path.   The letter M means the third body of the reaction and its value takes the atmo-
spheric number density.   (a) The reaction scheme from electrons to NO_3^- and HSO_4^-
cores.   (b) The reaction scheme for the evolution of the cluster ions having NO_3^- and
HSO_4^- cores.   The eight numbers under each ion symbol indicate the atomic masses
(AMU) of the ion.   The four reactions indicated by the paths of the broken lines are
not included in the calculation (after KAWAMOTO and OGAWA, 1984).

(a)

(b)

Fig. 2. *Same as Fig. 1 but for the tropospheric model. (a) The reaction scheme from electrons to NO_3^-, HSO_4^-, and CO_3^- cores. (b) The reaction scheme for the evolution of cluster ions having NO_3^-, HSO_4^-, and CO_3^- cores. The eleven numbers under each boxed ion symbol indicate the atomic masses (AMU) of the ions. The four reactions indicated by the paths of the broken lines are not included in the calculation (after KAWAMOTO and OGAWA, 1986).*

Fig. 3.   Height distributions of the used neutral gaseous constituents larger than 10^{10} cm^{-3} (in LS model) and 10^{11} cm^{-3} (in TR model); except for larger N_2 and O_2, in the lower atmosphere (0–30 km).   (a) The profiles used in the lower stratospheric (LS) model calculation.   (b) The profiles used in the tropospheric (TR) model calculation.

The calculations were made by using the reaction schemes and neutral gas distributions described above.   For details, refer to KAWAMOTO and OGAWA (1984, 1986) and KAWAMOTO (1987).

3.   Results and Discussions

The results of calculated fractional abundances of negative ion species are compared with the results of the observed fractional abundances (VIGGIANO et al., 1983; HEITMANN and ARNOLD, 1983; PERKINS and EISELE, 1984).   Negative ions can be classified into the following three groups: NO_3^- core ions, HSO_4^- core ions, and CO_3^- core and other ions.   The comparisons of negative ions having NO_3^- cores and HSO_4^- cores are shown in Figs. 5 and 6 respectively.   The negative ions which have cores other than NO_3^- or HSO_4^- cores have not yet been detected in the height range of 0–30 km so far.   Therefore, the calculated fractional abundances of species having CO_3^- cores and other ions are shown in Fig. 7.   The characteristics of the three ion groups (NO_3^-, HSO_4^-, and CO_3^- core and others) will be described briefly in the following.
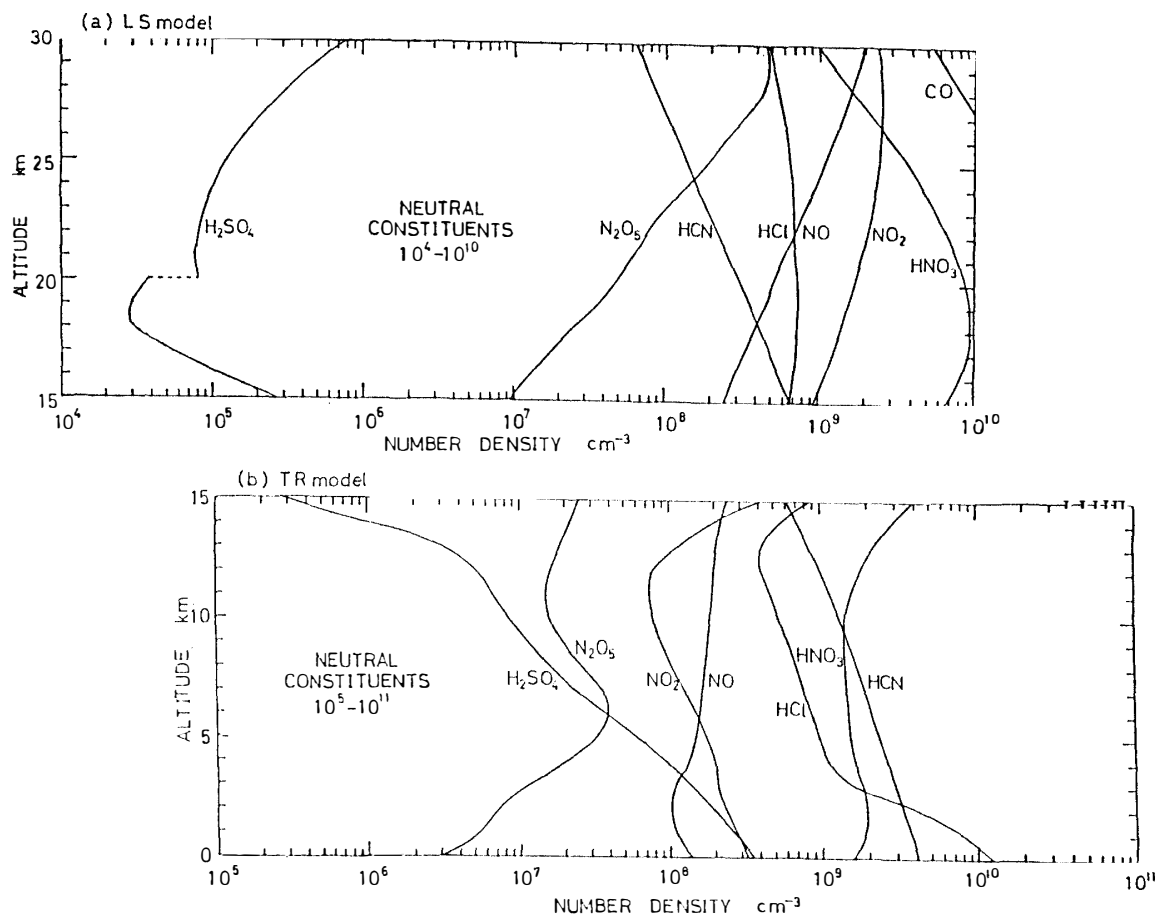
Fig. 4.   Same as Fig. 3 but smaller than 10^{10} cm^{-3} (in LS model) and 10^{11} cm^{-3} (in TR model).

(1) NO_3^- core ions (Fig. 5):   The predominant species are $NO_3^-(HNO_3)_2$ (188 AMU) at 10–30 km altitudes and $NO_3^-HNO_3H_2O$ (143 AMU) at 0–10 km.   The observed fractional abundance of $NO_3^-(HNO_3)_2$ is also dominant in the height range of 9–30 km.   At 4.3 km altitude, the dominant species was $NO_3^-HNO_3$ in the observation.   Since the sampled ambient ions were dried up by N_2 or Ar buffer gas before the mass spectrometric measurement (EISELE, 1983; PERKINS and EISELE, 1984), it is reasonable to assume that $NO_3^-HNO_3H_2O$ ions were measured as $NO_3^-HNO_3$ ions removing H_2O molecules.

The calculated values of $NO_3^-(HNO_3)_3$ (251 AMU) are about one tenth observed ones in fractional abundance.   This may be mainly attributed to the cluster-ion reaction-rate constants supposed by BRASSEUR and CHATEL (1983) and the altitude profile of nitric acid (HNO_3) vapor.

As for the kind of $NO_3^-HNO_3$ (125 AMU), a large discrepancy exists between the calculated and observed values in fractional abundance.   This will be also explained in a similar way as the case for $NO_3^-HNO_3$ in the lower troposphere.   The ion cluster break-up occurs during the ion sampling, removing H_2O and HNO_3 molecules (e.g., ARIJS, 1983; VIGGIANO et al., 1983; HEITMANN and ARNOLD, 1983), and this phenomenon occurs more frequently for the case of higher air density (in the lower atmosphere).
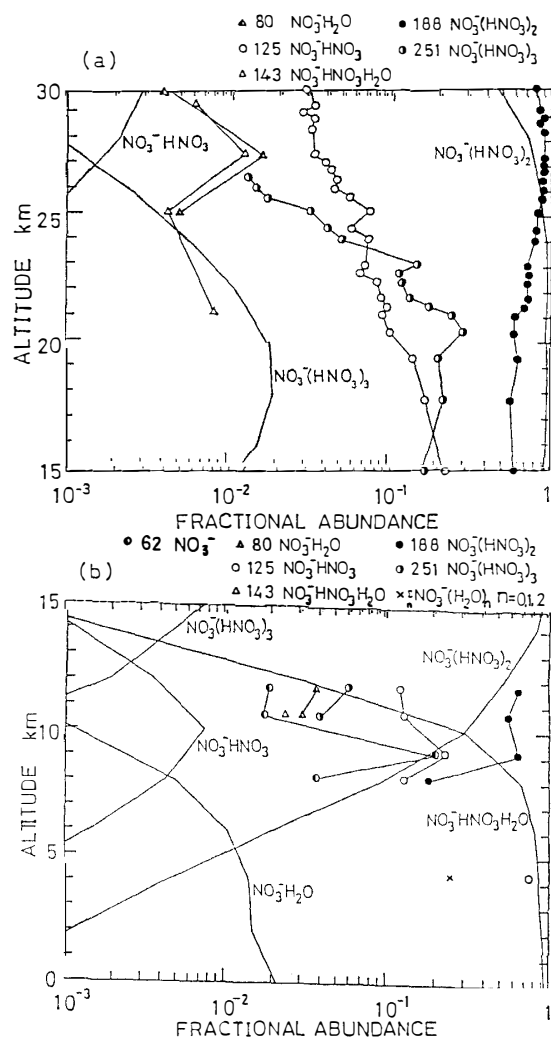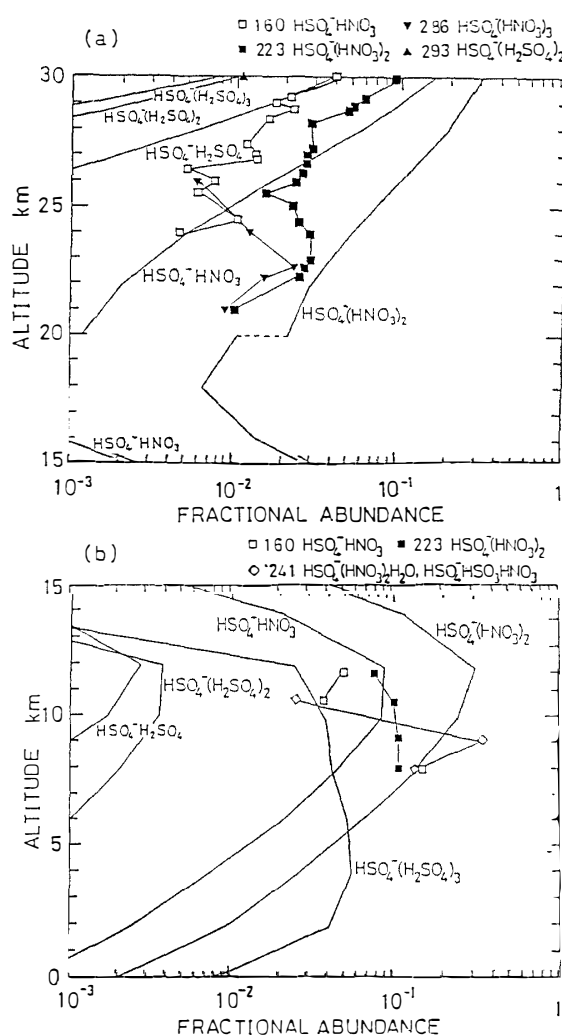
Fig. 5.   **Fig. 6.**

Fig. 5. *Comparison of NO_3^- core ions between the calculated and observed values in fractional abundance. The calculated values are indicated by the solid lines, and the species represented by the lines are written in the figure. The observed values are indicated by the symbols and the species and the masses are written with their symbols over each figure. The observed data are taken from VIGGIANO et al. (1983) for the altitude range of 15–30 km, HEITMANN and ARNOLD (1983) for 8–12 km and PERKINS and EISELE (1984) at 4.3 km. (a) Comparison of the result of the LS model calculation with the observed result in the lower stratosphere (15–30 km altitude). (b) Comparison of the result of the TR model calculation with the observed result in the troposphere (0–15 km altitude).*

Fig. 6. *Same as Fig. 5 but for HSO_4^- core ions. (a) Comparison of the result of the LS model calculation with the observed result in the lower stratosphere. (b) Comparison of the result of the TR model calculation with the observed result in the troposphere. At 4.3 km altitude, the negative ions having HSO_4^- cores have not been detected so far.*

(2) HSO_4^- core ions (Fig. 6): The most abundant ions in this group are $HSO_4^-(H_2SO_4)_3$ (391 AMU) below 6 km altitude and $HSO_4^-(HNO_3)_2$ (223 AMU) above this height. The calculated values of $HSO_4^-HNO_3$ (160 AMU) ions are abundant as secondary and tertiary in the altitude region of 6–30 km and 0–6 km respectively.

(a)

ALTITUDE km

30

25

20

15

HClO$_2^-$ CO$_3^-$

10^{-3} 10^{-2} 10^{-1} 1

FRACTIONAL ABUNDANCE

(b)

ALTITUDE km

15

10

5

0

CO$_3^-$

CO$_3^-$H$_2$O

10^{-3} 10^{-2} 10^{-1} 1
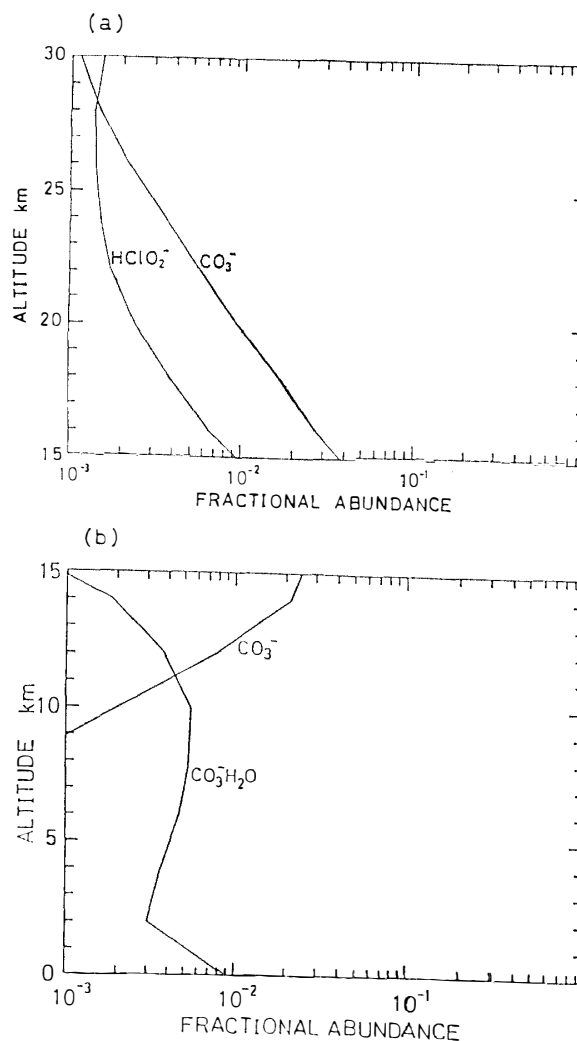
FRACTIONAL ABUNDANCE

Fig. 7. Same as Figs. 5 and 6 but for ions having cores other than NO$_3^-$ and HSO$_4^-$ cores. None of the species in this group has not been detected to date in the lower atmosphere (below 30 km). Therefore, only the calculated values are indicated by the solid lines written with their species. (a) The result in this group of ions by the LS model calculation. (b) The result in this group of ions by the TR model calculation.

The three kinds of ions, HSO$_4^-$(H$_2$SO$_4$)$_n$ ($n=1, 2$, and 3; 195, 293, and 391 AMU respectively), increase in fractional abundance rapidly with height around 30 km altitude.

In the observation, the primary species was HSO$_4^-$(HNO$_3$)$_2$ above 10 km altitude. The HSO$_4^-$HNO$_3$ ions were observed above 8 km. The calculated profiles of these two ions resemble those of the observed. However the calculated abundance of these species is larger than the observed ones. This tendency may be resulted mainly from the theoretical altitude profile of sulfuric acid (H$_2$SO$_4$) vapor by TURCO *et al.* (1979) used in the calculations.

Next, the three kinds of HSO$_4^-$(H$_2$SO$_4$)$_n$ ($n=1, 2$, and 3) species were observed above 30 km and showed the tendency of rapid increase with height (VIGGIANO *et al.*, 1983), being similar to the calculation. These increases may suggest that the conversion from this group of ions to the sulfate aerosol particles occurs above 30 km altitude.

At 4.3 km altitude, the ions having HSO$_4^-$ cores have not yet been detected to date.

(3) CO$_3^-$ core and other ions (Fig. 7): The kinds of ions having CO$_3^-$ cores

and others, being more than 0.1% in fractional abundance, are CO_3^-, $CO_3^-H_2O$, and $HClO_2^-$. The calculated values of these species are at most several percent. This result may agree with the fact that these three species have not been detected in the natural negative ions in the lower atmosphere (below 30 km), considering a detection limit of the present ion mass spectrometer.

4. On the Antarctic Springtime "Ozone Hole"

The Antarctic springtime ozone decrease has been first reported by FARMAN et al. (1985). Since then, a number of theoretical and experimental works have been made for elucidating this phenomenon (e.g. AIKIN and McPETERS, 1986; McELROY et al., 1986; MOUNT et al., 1987; SOLOMON et al., 1986, 1987a, b). CRUTZEN and ARNOLD (1986) proposed a chemical mechanism, which involves ion- and/or aerosol-catalyzed conversion of N_2O_5 and $ClONO_2$ to HNO_3 vapor, for the formation of ozone hole. This was the first work which suggested the roles of ions and/or aerosols in the formation of ozone hole.

From the results of the balloon-borne measurements of ozone and aerosol concentration at McMurdo Station in Antarctica during November of 1985, HOFMANN et al. (1986) reported that the extremely low ozone concentrations were accompanied by the absence of optically active aerosol particles ($r \geq 0.15$ μm) and by the enhancement of condensation nuclei (CN, $r \geq 0.01$ μm).

On the basis of the experimental result obtained by HOFMANN et al. (1986), we suggest here a possible role of condensation nuclei (CN), which have been generated via ion-nucleation caused by the sunlight in Antarctic spring, in the formation of ozone hole. The mechanism, by which CN may be produced and the ozone decrease may occur in the stratosphere, is shown schematically in Fig. 8. In spring of polar regions, the sunlight begins to irradiate the atmosphere, then the sulfuric acid (H_2SO_4) vapor may condense into new aerosol particles via some ion-nucleation mechanism (ARNOLD, 1980, 1982; HOFMANN and ROSEN, 1982, 1983). On the other hand, the increases in various gaseous constituents by which ozone is reduced, such as NO_x and ClO_x, have
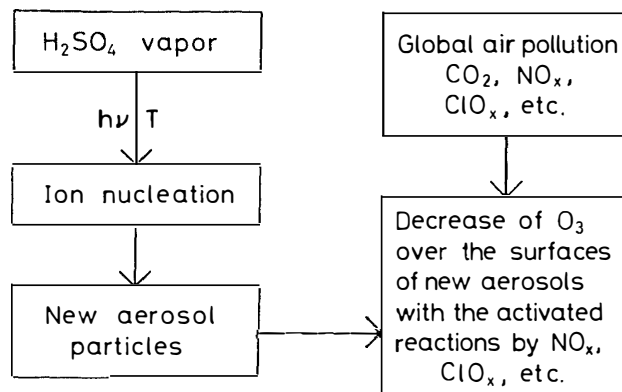

Fig. 8. Schematic diagram of a possible formation of the ozone hole, which is induced by the new aerosol particles generated via some ion-nucleation mechanism, in Antarctic springtime stratosphere.

been extended into the polar regions. The surfaces of new aerosol particles, having a radius smaller than about 0.15 μm, may provide the minor constituents with an effective reaction site for the catalytic reactions of ozone reduction.

5. Conclusion

The chemical compositions of negative ions in the lower atmosphere (0–30 km altitude) were investigated theoretically. From the results of theoretical calculations, the characteristics of negative ion compositions are pointed out as follows;

(1) The natural negative ions in the lower atmosphere have NO_3^- or HSO_4^- cores.

(2) The predominant ion species are $NO_3^- HNO_3 H_2O$ in 0–10 km height region and $NO_3^- (HNO_3)_2$ in 10–30 km.

(3) The rapid increases with height of the kinds of $HSO_4^- (H_2SO_4)_n$ $(n=1, 2, 3)$ ions around 30 km altitude suggest that the conversion from this type of ions to sulfate aerosols occurs in the upper stratosphere.

According to the comparison between theoretical and experimental results, the theoretical values in fractional abundance agrees, in general, with the observed ones. This is quite satisfactory if we consider the instrumental conditions of the ion mass spectrometric measurements.

Further, on the basis of the experiments reported by HOFMANN et al. (1986), we propose a hypothesis which suggests the formation of the springtime ozone decrease in Antarctica (so-called the 'ozone hole'). This idea consists of the two stages. (1) When sunlight begins to irradiate the polar atmosphere in spring, new aerosol particles having the size of condensation nuclei may be formed from the sulfuric acid (H_2SO_4) vapor via some ion-nucleation mechanism. (2) Over the surfaces of these new aerosol particle, the catalytic ozone-loss reactions by the minor gases, such as NO_x and ClO_x, may be activated.

Acknowledgments

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