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Abstract

Full Text

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MOLECULAR IONS IN THE UPPER ATMOSPHERE

(Presented by Academician E. K. Fedorov, December 26, 1960)

Data on the ionic composition of the upper atmosphere, obtained by V. G. Istomin on geophysical rockets ([1]) and the third Soviet artificial Earth satellite ([2,3]), have made it possible to consider a number of processes in which these ions participate. In ([4]) it was shown that the mechanism of formation of NO^+ ions by the charge-transfer reaction

$$O^+ + N_2 \rightarrow NO^+ + N \tag{1}$$

and of the disappearance of NO^+ ions by the dissociative-recombination reaction

$$NO^+ + e \rightarrow N + O \tag{2}$$

well explains the observed concentration ratio $[NO^+]/[O^+]$. A number of authors ([5,6]) believe that O_2^+ ions are formed in the atmosphere as a result of charge transfer of atomic oxygen ions with O_2 molecules:

$$O^+ + O_2 \rightarrow O_2^+ + O. \tag{3}$$

Fig. 1. *a*—rate of disappearance of O_2^+ ions; *b*—rate of formation of O_2^+ ions by reaction (3); *v*—rate of formation of O_2^+ ions by reaction (5).

However, the fact that O_2^+ ions are observed up to altitudes of 400 km, whereas molecular oxygen should be completely dissociated above 200 km, casts doubt on whether the charge-transfer mechanism is responsible for the formation of O_2^+ ions at all altitudes where these ions are observed. If reaction (2) is responsible

Fig. 2. Variation with altitude of the ratio $[N_2^+]/[N^+]$. 1 —calculated curve; 2 —data of V. G. Istomin.

Figure 2: Fig. 2. Variation with altitude of the ratio $[N_2^+]/[N^+]$. 1 —calculated curve; 2 —data of V. G. Istomin.

for the formation of O_2^+ ions, then at all altitudes it must compensate the disappearance of these ions by the reaction

$$O_2^+ + e \rightarrow O + O. \tag{4}$$

Ion concentrations were obtained experimentally in the work of V. G. Istomin, electrons in the work of K. I. Gringauz ([7]), and molecular oxygen in the work of Byram et al. ([8]). On the basis of these concentrations and the values of the rate coefficients of reactions (3) and (4), discussed in detail in ([4]) and equal to 10^{-10} and 10^{-6} $cm^3 \cdot sec^{-1}$, respectively, the rate of formation of O_2^+ ions by reaction (3) and of disappearance of these ions by reaction (4) was calculated.

The results of the calculations, shown in Fig. 1 (curves a and b), show that reaction (3) can provide the required rate of formation of O_2^+ ions only up to altitudes of 150-160 km, while higher up the rate of this reaction falls sharply because of the decrease in the concentration of O_2 due to dissociation.

Similarly, the possibility of explaining the formation of O_2^+ ions by direct photoionization of O_2 molecules is eliminated, since at altitudes of 300-400 km there cannot be a sufficient quantity of undissociated oxygen molecules.

It appears that, in order to explain the presence of O_2^+ ions at great altitudes, one should seek a mechanism for their formation that does not depend on the concentration of O_2 molecules. Such a mechanism may be the radiative recombination reaction of neutral and ionized oxygen atoms:

$$O + O^+ \rightarrow O_2^+ + h\nu. \tag{5}$$

There are no definite data on the magnitude of the rate coefficient of this reaction. Therefore it makes sense to consider only the variation with altitude of the rate of formation of O_2^+ ions as a result of this reaction. The value of [O] was taken from density data ([9,10]), under the assumption that at the altitudes considered oxygen is completely dissociated and that the effects of diffusive separation may be neglected:

$$[O] = \frac{1}{5}\frac{r\rho}{m_0},$$

where m_0 is the mass of the oxygen atom in grams.

Fig. 2. Variation with altitude of the ratio $[N_2^+]/[N^+]$. 1 —calculated curve; 2 —data of V. G. Istomin.

The results of the calculations, shown in Fig. 1 (curve 6), indicate that the variation of the rate of formation of O_2^+ ions by reaction (5) is close to the variation of the disappearance of these ions. For the absolute values of the rates to coincide, the rate coefficient of reaction (5) must be equal to $5 \cdot 10^{-11}$ cm$^3 \cdot$ sec^{-1}. Thus, reaction (5), provided that the rate coefficient of this reaction is sufficiently high, can explain the existence of O_2^+ ions at great altitudes.

It is natural to consider the possibility of the formation of N_2^+ ions by a charge-transfer reaction analogous to (1) and (3):

$$N^+ + N_2 \rightarrow N_2^+ + N. \tag{6}$$

With a rate coefficient γ of the order of 10^{-10} cm$^3 \cdot$ sec^{-1}, the rate of formation of N_2^+ ions by this reaction at altitudes greater than 200 km is 5-10 times higher than the rate of direct photoionization. The disappearance of N_2^+ ions should occur by the reaction of dissociative recombination

$$N_2^+ + e \rightarrow N + N. \tag{7}$$

From the equilibrium condition for these reactions, the ratio $[N_2^+]/[N^+]$ was obtained, which can be compared with the observed one. The concentration of N_2 was taken from experimental density values ([10]), analogously to (4). The results of the calculations are given in Fig. 2, 1. In Fig. 2, 2 are shown the values of the ratio $[N_2^+]/[N^+]$ obtained by V. G. Istomin. The agreement in the course of the theoretical and observed curves shows that the choice of reactions (6) and (7) for considering the formation and disappearance of N_2^+ ions is correct and that it is precisely these reactions that are responsible for the existence of these ions at altitudes of 200-500 km. For agreement of the absolute values of the calculated and observed—

of the given values of $[N_2^+]/[N^+]$, the quantity γ must be equal to $4 \cdot 10^{-10}$ cm$^3 \cdot$ sec^{-1}, which agrees with the available data on the magnitude of the rate coefficient of charge-exchange reactions.

Thus, the impression is created that, of the 5 types of ions in the upper atmosphere, only 2 atomic ions, O^+ and N^+, are "primary," i.e., are formed as a result of direct photoionization, whereas the molecular ions are the product of secondary reactions in which atomic ions take part. In recombination processes, on the contrary, the leading role belongs to molecular ions, since they very rapidly combine with electrons in reactions of dissociative recombination, the rate coefficient of which has been investigated experimentally ([11,12]) and is equal to 10^{-6} cm$^3 \cdot$ sec^{-1}. The number of molecular ions present in the atmosphere at a given altitude determines the effective recombination coefficient of electrons α', which is usually defined as

Fig. 3. Change with altitude of the ionization intensity. Points—values of j calculated from (11); curve—absorption exponent for $\sigma = 5 \cdot 10^{-17}$ cm^2.

Figure 3: Fig. 3. Change with altitude of the ionization intensity. Points—values of j calculated from (11); curve—absorption exponent for $\sigma = 5 \cdot 10^{-17}$ cm^2.

Fig. 3. Change with altitude of the ionization intensity. Points—values of j, calculated from (11); curve—absorption exponent for $\sigma = 5 \cdot 10^{-17}$ cm^2.

$$\frac{dn_e}{dt} = \alpha' n_e n_i, \tag{8}$$

where n_i is the total number of ions (equal to n_e) and dn_e/dt is the rate of disappearance of electrons per unit volume per second. Indeed, since the rate coefficient of dissociative recombination reactions is 6 orders of magnitude higher than the rate of radiative recombination reactions, the disappearance of electrons at altitudes of 100–500 km occurs mainly by reactions (2), (4), (7). Then the rate of disappearance of electrons in 1 cm^3 in 1 sec is equal to the sum of the rates of these reactions:

$$\frac{dn_e}{dt} = \{[NO^+] + [O_2^+] + [N_2^+]\} n_e \alpha^* = [M^+] n_e \alpha^*. \tag{9}$$

Comparing (8) and (9), we obtain $\alpha^* n_e [M^+] = \alpha' n_e^2$, whence

$$\alpha' = \alpha^* \frac{[M^+]}{n_e}, \tag{10}$$

where α^* is the rate coefficient of dissociative recombination reactions.

In the case where molecular ions constitute the overwhelming majority of the total number of ions (for example, at $H = 100$ km), the ratio $[M^+]/n_e$ is practically equal to 1, and the effective recombination coefficient of electrons must be of the order of the coefficient α^*. At altitudes where molecular ions are practically absent, electron recombination will be determined by radiative recombination reactions and will have an effective coefficient close to 10^{-12} cm$^3 \cdot$ sec^{-1}.

At the altitudes of the E and F layers, formula (10) leads to values (see Table 1) 2 orders of magnitude larger than those presently accepted ([13]); however, these values are in good agreement with new data on the high intensity of the ionizing radiation of the Sun in the ultraviolet region of the spectrum ([14,15]).

Table 1

H, km	120	140	160	180	200	250	300	350	400
$\alpha^1 \cdot 10^6$	1.0	0.97	0.89	0.76	0.58	0.17	0.04	0.02	0.01

Knowledge of the total rate of disappearance of ions makes it possible to consider the change in the ionization intensity in the upper atmosphere. Starting from the condition of equilibrium,

$$V_{\text{dis}} = [\text{M}^+] n_e \alpha^* = V_{\text{form}} = [M] j, \qquad j = \sigma_i n_{\text{qu}}, \tag{11}$$

where $[M]$ is the total concentration of particles in 1 cm^3 at the given altitude, j is the ionization coefficient, σ_i is the ionization cross section, and n_{kv} is the flux of ionizing radiation; it is not difficult to calculate j for each altitude.

In the calculations, the atmospheric model used in considering the formation of the ions NO^+, O_2^+, and N_2^+ was adopted.

The results of the calculations, shown in Fig. 3, indicate that the altitude dependence of the value of j, obtained from (11), is well represented by an absorption exponential:

$$j = j_\infty e^{-\tau}, \qquad \tau = N\sigma,$$

where j_∞ is the ionization coefficient outside the atmosphere; τ is the optical thickness; N is the number of neutral particles in the atmospheric column above the given level; and σ is the absorption cross section, with $\sigma = 5 \cdot 10^{-17}$ cm^2. The high value obtained for σ (several times greater than the maximum absorption cross section of solar ultraviolet by atmospheric constituents) indicates stronger absorption of the ionizing agent in the Earth' s atmosphere than has hitherto been assumed.

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Note: Figure translations are in progress. See original paper for figures.