SECOND EXPERIMENT ON THE INVESTIGATION OF THE CONSTANTS OF ION-MOLECULE REACTIONS DIRECTLY IN THE IONOSPHERE

GEOPHYSICS

1968

SovietRxiv

Abstract

Full Text

UDC 551.510.535:541.124.13

GEOPHYSICS

A. D. DANILOV, V. K. SEMENOV

SECOND EXPERIMENT ON THE INVESTIGATION OF THE CONSTANTS OF ION-MOLECULE REACTIONS DIRECTLY IN THE IONOSPHERE

(Presented by Academician E. K. Fedorov on 14 VIII 1967)

Ion-molecule reactions play a major role in the ionization-recombination cycle of processes in the Earth' s ionosphere. In [1] it was shown that laboratory measurements give a considerable scatter (by an order of magnitude and more) in the values obtained for the constants γ of the principal ion-molecule reactions:

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

$$O^+ + O_2 \rightarrow O_2^+ + O. \tag{2}$$

As a result, it is unclear what values γ_1 and γ_2 should be used for ionospheric studies.

In [2] a method was briefly described for studying the constants of the two principal ionospheric ion-molecule reactions (1) and (2) by releasing fixed portions of gas in the immediate vicinity of the analyzer of a radio-frequency mass spectrometer during rocket flight; the results of the first experiment of this kind, carried out with the BB instrument (air release) in 1962 at an altitude of about 400 km, were also presented. For the ratio of the constants of reactions (1) and (2), the estimate obtained was

$$\gamma_2/\gamma_1 \gtrsim 10. \tag{3}$$

In March 1967, at noon in the middle latitudes of the European part of the USSR, a geophysical rocket was launched carrying an MX6407M radio-frequency mass spectrometer for studying the ionic composition of the atmosphere and a BB-2 instrument. The instrument consisted of a glass cylinder with air, of volume about 500 cm^3, and an opening-and-ejection device. The geometry of

Fig. 1. Diagram of the placement of the BB cylinder and the mass spectrometer during the experiment. 1 —upper plate of the instrument compartment; 2 —glass cylinder with air; 3 —analyzer of the MX6407M mass spectrometer

Figure 1: Fig. 1. Diagram of the placement of the BB cylinder and the mass spectrometer during the experiment. 1 —upper plate of the instrument compartment; 2 —glass cylinder with air; 3 —analyzer of the MX6407M mass spectrometer

the experiment is shown schematically in Fig. 1. The cylinder was fitted with a “nose”with a capillary, which was opened at a specified moment at the prescribed altitude. Gas flowed out through the capillary for 7 sec, after which the cylinder was ejected from the instrument by means of a special device in order to preserve the vacuum purity of the subsequent mass-spectrometric measurements. Before the nose was opened, the air in the cylinder was at atmospheric pressure; the diameter of the capillary was 0.7 mm.

The release of air in the experiment described was carried out near the top of the rocket trajectory, at an altitude of about 170 km. A sharp change was recorded in the character of the ion spectrum registered by the mass spectrometer, confirming operation of the BB instrument. The start of the air release (opening of the nose) and its end (ejection of the cylinder) were monitored through a special telemetry channel.

As the analysis of the spectra obtained showed, in the first seconds after the beginning of the air release the gas cloud was so dense that it practically completely shielded the mass spectrometer from the surrounding atmosphere; therefore, in the first spectrum there are no peaks either of atmospheric ions or of ions caused by neutral particles of the released—

gas. For the analysis, the second spectrum was taken, where shielding by the cloud particles was already significantly weaker and rather well pronounced ion peaks are observed. The magnitude of the shielding was estimated from the peak of the ion O^+. Since the released gas contained no particles of atomic oxygen, it was assumed that the mass-16 peak in spectrum No. 2 was due to the concentration of atmospheric O^+ ions, reduced by the shielding effect. Comparison of the intensity $I^{(2)}(O^+)$ recorded in spectrum No. 2 with the value $I_{\text{atm}}(O^+)$ recorded by the mass spectrometer several seconds before the start of operation of the BB instrument showed that the shielding coefficient K was 1.76. Accordingly, the intensities of the peaks of NO^+ and O_2^+ ions recorded in the spectrum before release were reduced by a factor of 1.76. The quantities thus obtained, $I^{(2)}_{\text{atm}}(NO^+)$ and $I^{(2)}_{\text{atm}}(O_2)$, were interpreted as the contribution to the intensity of the mass 30 and 32 peaks in spectrum No. 2 due to atmospheric ions NO^+ and O_2^+, taking account of the shielding effect.

Fig. 1. Diagram of the placement of the BB cylinder and the mass spectrometer

during the experiment. 1 —upper plate of the instrument compartment; 2 —glass cylinder with air; 3 —analyzer of the MX6407M mass spectrometer.

The difference between the actually recorded intensity of these peaks in spectrum No. 2, $I^{(2)}(NO^+)$ and $I^{(2)}(O_2^+)$, and the quantities $I^{(2)}_{\text{atm}}(NO^+)$ and $I^{(2)}_{\text{atm}}(O_2^+)$ was interpreted as the result of ion-molecular reactions between the molecules N_2 and O_2 of the released air and atmospheric oxygen ions:

$$I^{(2)}_{\text{BB}}(NO^+) = I^{(2)}(NO^+) - I^{(2)}_{\text{atm}}(NO^+); \tag{4}$$

$$I^{(2)}_{\text{BB}}(O_2^+) = I^{(2)}(O_2^+) - I^{(2)}_{\text{atm}}(O_2^+). \tag{5}$$

Since the lifetime of particles in the retarding field of the mass-spectrometer analyzer is small, as in work (2) it was assumed that the intensities of the NO^+ and O_2^+ ion peaks caused by operation of the BB instrument are proportional to the rate of formation of these ions as a result of ion-molecular reactions. Taking into account only the two principal reactions (1) and (2), this leads to the following expression for the ratio of their constants γ_1 and γ_2:

$$\gamma_2/\gamma_1 = I_{\text{BB}}(O_2^+)[N_2]_{\text{air}}[O^+]_{\text{atm}}/I_{\text{BB}}(NO^+)[O_2]_{\text{air}}[O^+]_{\text{atm}}, \tag{6}$$

where $[N_2]_{\text{air}}/[O_2]_{\text{air}}$ is the ratio of the concentrations of nitrogen and oxygen molecules in the released air, equal to 3.7, and $[O^+]_{\text{atm}}$ is the concentration of atomic oxygen ions in the surrounding atmosphere. The value of the ratio of the peaks $I^{N_2}_{\text{BB}}(O_2^+)/I^{N_2}_{\text{BB}}(NO^+)$ in this experiment, after accounting for the contribution of atmospheric ions and the influence of the shielding effect, was found to be 2.7, which gives the ratio of the constants γ_2/γ_1 in (6) equal to 10.

At present, however, laboratory data on the constants of ion-molecular reactions lead to the conclusion that, in addition to processes (1) and (2), the following reactions may also take part in the formation of NO^+ and O_2^+ ions from neutral N_2 and O_2 molecules:

$$N_2^+ + O_2 \to NO^+ + NO; \tag{7}$$

$$O_2^+ + N_2 \to NO^+ + NO; \tag{8}$$

$$N^+ + O_2 \to NO^+ + O; \tag{9}$$

$$N_2^+ + O_2 \to O_2^+ + N_2; \tag{10}$$

$$N^+ + O_2 \to O_2^+ + N. \tag{11}$$

Reactions (7) and (8) are of low efficiency (γ_7 and $\gamma_8 \ll 10^{-13}$ $\text{cm}^3 \cdot \text{sec}^{-1}$ (^{3})) and cannot compete with reaction (1). Estimates based on the relative concentrations of the ions $[N_2^+]/[O^+]$ and $[N^+]/[O^+]$, recorded in the spectrum before the release, show that reaction (10), for a value $\gamma_{10} \approx 10^{-10}$ $\text{cm}^3 \cdot \text{sec}^{-1}$ (^{4}), also makes no substantial contribution to the formation of NO^+ ions under the experimental conditions, whereas the contribution of reactions (9) (to the formation of NO^+) and (11) (to the formation of O_2^+) is significant and must be taken into account. Such an allowance, with values of the constants $\gamma_9 \approx \gamma_{11} \approx 5 \cdot 10^{-10}$ $\text{cm}^3 \cdot \text{sec}^{-1}$, taken in accordance with laboratory measurements (^{4}), was made and led to a refinement of the obtained ratio of constants: $\gamma_2/\gamma_1 = 1.3 \cdot 10$. Allowance for possible measurement errors makes it possible to consider that the experimental results give the following interval of values for the desired ratio of constants:

$$\gamma_2/\gamma_1 = (1.0 - 1.5) \cdot 10. \tag{12}$$

The value obtained refers to an altitude of about 170 km, which under daytime quiet conditions is characterized, according to (^{5}), by a temperature ≈ 1000°K. The value found for γ_2/γ_1 agrees with the results of the first experiment with the BB instrument (^{2}), where it was obtained that $\gamma_2/\gamma_1 \gtrsim 10$. Analysis of ionospheric estimates, which pertain mainly to greater heights in the ionosphere (the F_2 region), showed (^{1}) that there the ratio of the constants of reactions (1) and (2) is approximately 10, with an accuracy to within a factor of 1.5–2. Comparison of the results of the laboratory experiments of Fehsenfeld et al. (^{6,7}), which are at present regarded as the most reliable, leads to the ratio $\gamma_2/\gamma_1 = 1.3 \cdot 10$ at a temperature of the order of 300°K. In comparing these values of γ_2/γ_1 with one another, however, caution is necessary, since the question of the temperature dependence of the constants of ion-molecular reactions has not yet been resolved.

It should be noted that the present experiment, despite the good agreement of the obtained ratio γ_2/γ_1 with the data of Fehsenfeld et al., does not settle the question of the applicability of laboratory values of the constants to ionospheric studies. If a significant number of excited O_2 and N_2 molecules, participating in the reactions under discussion, exist in the upper atmosphere, the actual rates of these reactions may differ substantially from those obtained in the laboratory. In the experiment described, the rate of interaction of O^+ with unexcited gas molecules is also studied, since the lifetime of these molecules after leaving the cylinder is very short. However, the participation in the reactions under study of real atmospheric ions, with the ion temperature corresponding to the given altitude, brings the experimental conditions closer to the real conditions in the ionosphere. This makes it possible, by carrying out several gas releases at different heights (with different T_i), to obtain the dependence of the constants under study on the ion temperature. In addition, measurements at heights with different ratios [N^+]/[O^+] will make it possible, without specifying laboratory values for γ_9 and γ_{11}, to find all the constants of interest to us. Although the reproducibility of laboratory experiments is incomparably higher than that of such single experiments, it appears that the latter may be useful for understanding the extent to which laboratory measurements of the quantities γ are applicable to ionospheric studies, and also for filling some of the gaps that still exist in laboratory data.

Institute
of Applied Geophysics

Received
26 VII 1967

CITED LITERATURE

1. A. D. Danilov, DAN, **169**, 332 (1966).
2. A. D. Danilov, S. P. Yatsenko, *Cosmic Research*, **2**, 276 (1964).
3. G. G. Volpi et al., *J. Chem. Phys.*, **39**, 518 (1963).
4. E. E. Ferguson, *J. Geophys. Res.*, **70**, 4323 (1965).
5. M. Nicolet, *Aeronomy*, M., 1964.
6. E. C. Fehsenfeld et al., *Planetary and Space Science*, **13**, 579 (1965).
7. E. C. Fehsenfeld et al., *Planetary and Space Science*, **13**, 219 (1965).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.