RECOMBINATION COEFFICIENT OF SMALL IONS IN THE LOWER STRATOSPHERE

Y. Morita

Research Institute of Atmospheric, Nagoya University
Toyokawa, Aichi 442

Abstract. The total ion-ion recombination coefficient up to the lower stratospheric heights was calculated from the balloon borne measurements of ion pair production rate and positive polar conductivity. The height dependence of recombination coefficient agrees reasonably well with the presently accepted theoretical concepts. The crossover from three-body to two-body recombination coefficient occurs at an altitude of around 23 km.

1. Introduction

In the earlier letter the author presented the results of balloon borne Atmospheric Electrical Measurements Workshop hosted by the Atmospheric Physics Group of the University of Wyoming. The comparison on positive polar conductivity profiles and the dependence of ion pair production rate on the solar activity at the stratospheric heights was discussed briefly (Morita, 1981). In this letter the profile of total ion-ion recombination coefficient will be presented by using the measured values of ion pair production rate and positive polar conductivity in the summer of 1978.

2. Measurements

If favorable values of ion pair production rate and small ion density are obtained by making the simultaneous measurements at the same location, the total ion-ion recombination coefficient can be calculated. It is also possible to calculate the recombination coefficient by using electric conductivity instead of small ion density provided the ion mobility reduced to STP retains the constant value up to the stratospheric heights. Two simultaneous balloon measurements of ion pair production rate and positive polar conductivity were conducted on July 30 (W-183) and on Aug. 4 (W-186, 188), 1978 over Laramie, Wyoming. Fig.1 shows the profiles of ambient ion pair production rate obtained from the flights of W-183 and 188. The full line below 28 km indicates an average profile of the two measurements and above 28 km it presents only the measurement of W-183. The agreement of the two profiles is reasonably good. The profiles of positive polar conductivity for the flights of W-183 and 186 are shown in Fig.2. Similarly to the measurements of ion pair production rate the continuous line is an average profile of the two flights. The agreement of the two profiles is quite good and an excellent agreement is obtained above 20 km.

3. Results and Discussions

The small ion density was calculated from the average conductivity profile shown in Fig.2. The average mobility of small ion is inversely proportional to atmospheric density. Usually the value lies between $(1.0 - 2.0) \times 10^{-4} \text{ m}^2/\text{Volt} \cdot \text{sec.}$ at ground level and increases by a factor of about 100 times at an altitude of 30 km. The ion mobilities of positive ions in the stratosphere have been measured by several investigators. There was, however, considerable disagreement between the results reported by the investigators and the mobility measurements differ by more than an order of magnitude at 30 km altitude (e.g. Meyerott et al., 1980). This is probably

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Fig.1. Ambient ion pair production rate profiles over Laramie, Wyoming.

Fig.2. Positive polar conductivity profiles over Laramie, Wyoming.

Fig.3. Small ion density profile calculated from the measurements of positive polar conductivity. See text for details.

due to a difficulty in ion mobility measurements in the stratosphere. Though considerable different values of ion mobility have been obtained in the stratosphere, the reduced mobility of $1.3 \times 10^{-4} \text{ m}^2/\text{Volt}\cdot\text{sec.}$ is assumed in this calculation. This assumption is supported by the measurements of Morita et al. (1971) and Rosen et al. (1982). Morita et al. obtained the constant reduced ion mobility of $1.3 \times 10^{-4} \text{ m}^2/\text{Volt}\cdot\text{sec.}$ from the balloon borne simultaneous measurements of electric conductivity and small ion density. Recent measurements of Rosen et al. indicate the values of reduced positive ion mobility are relatively constant with altitude to about 30 km. The calculated small ion density profile is shown in Fig.3.

Assuming a simple theory of small ion equilibrium under steady state conditions in the aerosol-free atmosphere, the total ion-ion recombination coefficient α is given by the well known equation $\alpha = q/n^2$, where q and n are the ion pair production rate and small ion density. The ambient ion pair production rate profile in Fig.1 and the small ion density profile in Fig.3 were used in the present calculation. Open circles in Fig.4 present the calculated recombination coefficient from the measured two parameters. Also shown in Fig.4 is the Thomson three-body recombination coefficient (α_{3b}) as described by Loeb (1955). As the three-body recombination coefficient depends on temperature, the mean temperature profile of the three flights was used in the calculation. The three-body recombination coefficient is shown by normalizing the value at ground level to $1.4 \times 10^{-6} \text{ cm}^3/\text{sec.}$ obtained from the experimental measurements of Nolan (1943). This surface value is thought to be the most reliable by several investigators (e.g. Hoppel, 1969). The three-body recombination theory has been refined

Fig.4. A comparison of recombination coefficient profiles.
See text for details.

and developed by several workers (Natanson, 1959; Bricard, 1965; Hoppel, 1969; and others). They are not mutually in entire agreement and do not show serious significant differences.

At higher altitudes the recombination process is thought to be controlled by a two-body reaction. The two-body recombination coefficient is independent of pressure but depends on temperature. The range of experimental values of three-body coefficient lies between $(1-2) \times 10^{-6}$ cm³/sec. at ground level and $(10^{-6} - 10^{-7})$ cm³/sec. for two-body coefficient (Hake et al., 1973). The combined three- and two-body recombination coefficient (α_{3b+2b}) is shown in Fig.4, in case that the value of 1.0×10^{-7} cm³/sec. is chosen as the two-body recombination coefficient. The three-body recombination coefficient in Fig.4 decreases more rapidly than the combined recombination coefficient with increasing altitude above the tropopause. The values of present experimental recombination coefficient (open circles) follow the three-body coefficient in the altitude between 6 and 20 km, and they are fit for the combined coefficient above 25 km. This suggests that the "crossover" from three-body to two-body recombination starts from above 23 km. Hake et al. (1972) constructed plausible upper and lower limits for the profile of combined recombination coefficient based on the estimates of several investigators (e.g. Cole and Pierce, 1965; Shreve, 1970; and others). The limits are also shown as broken lines in Fig.4. The crossover from three-body to two-body in the estimation of Hake et al. is at 15 km on the upper limit and it is at 25 km for the lower limit. Recent measurements of Gringel (1978) indicated that the crossover began in an altitude around 20 km. Thus the variation of present experimental total ion-ion recombination coefficient above 6 km is reasonable. However, below 5 km the

disagreement with the theoretical concepts is quite evident. The calculation reported here does not include the influence of aerosol on the small ion density. The apparent large values of recombination coefficient could be attributed to the attachment of ions to aerosols in the lower troposphere. At this time of the measurements, stratospheric aerosol concentration was in a background level (Hofmann and Rosen, 1981) and the attachment loss of small ions to aerosols in the stratosphere was negligible compared with ion-ion recombination.

The three-body recombination coefficient depends on ionic mass. The ionic mass in the troposphere and lower stratosphere is not yet precisely known. Recent mass spectrometric measurements in the stratosphere indicate the existence of two major positive and negative ion species (Arijs et al., 1981; Arnold et al., 1981; Henschen and Arnold, 1981; and others). The positive ions are thought to be proton hydrates, $H^+(H_2O)_n$, and non proton hydrates, $HX^+(H_2O)_m$. The negative ions in the stratosphere are now believed to be $NO_3^-(HNO_3)_n$ and $HSO_4^-(H_2SO_4)_l(HNO_3)_m$. It is expected to exist more complex ions in the troposphere and lower stratosphere. Two-body recombination process also depends on the ionic composition. The values of rate coefficient for two-body recombination measured by Moseley et al. (1972) are $(1-5) \times 10^{-7}$ cm³/sec. for unclustered positive and negative ions. Recent laboratory experiment made by Smith et al. (1981) shows that the values are $(5-7) \times 10^{-8}$ cm³/sec. for the reaction of $H^+(H_2O)_4$ and $H^+(H_2O) \cdot (CH_3CN)_3$ with several negative ion species observed in the stratosphere. The laboratory experiments, however, have not been carried out all ion species existing in the stratosphere. Present our knowledge in this regard is limited for troposphere and lower stratosphere, and the details have not been worked out. It thus is necessary to determine the height dependence of "total ion-ion recombination coefficient" from the reliable experimental measurements of atmospheric electrical elements as mentioned above.

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References

- Arijs, E., D.D. Nevejans, P. Frederick, and J. Ingels, Negative ion composition measurements in the stratosphere, *Geophys. Res. Lett.*, **8**, 121-124, 1981.
- Arnold, F., R. Fabian, E.E. Ferguson, and W. Joos, Mass spectrometric measurements of fractional ion abundances in the stratosphere - negative ions, *Planet. Space Sci.*, **29**, 195-203, 1981.
- Bricard, J., Action of radioactivity and pollution upon parameters of atmospheric electricity, *Problems of Atmos. Space Electr.* ed. by S.C. Coroniti, Elsevier Publishing Co., London, 82-118, 1965.
- Cole, R.K. Jr., and E.T. Pierce, Electrification in the earth's atmosphere for altitudes between 0 and 100 km, *J. Geophys. Res.*, **70**, 2735-2749, 1965.
- Gringel, W., K.H. Käsela, and R. Mühleisen, Recombination rates of small ions and their attachment to aerosol particles, *Pageoph.*, **116**, 1101-1113, 1978.
- Hake, R.D. Jr., E.T. Pierce, and W. Viezee, Stratospheric electricity, Final report, SRI Project 1724, Stanford Res. Inst., Menlo Park Calif., 140, 1973.
- Henschen, G., and F. Arnold, Extended positive ion composition measurements in

- the stratosphere - Implications for neutral trace gases, *Geophys. Res. Lett.*, 8, 999-1001, 1981.
- Hofmann, D.J., and J.M. Rosen, On the background stratospheric aerosol layer, *J. Atmos. Sci.*, 38, 168-181, 1981.
- Hoppel, W.A., Application of three-body recombination and attachment coefficients to tropospheric ions, *Pageoph.*, 75, 158-166, 1969.
- Loeb, L.B., Basic processes of gaseous electronics, The university of California Press., 545, 1955.
- Meyerott, R.E., J.B. Reagan, and R.G. Joiner, The mobility and concentration of ions and the ionic conductivity in the lower stratosphere, *J. Geophys. Res.*, 85, 1273-1278, 1980.
- Morita, Y., H. Ishikawa, and M. Kanada, The vertical profiles of the small ion density and the electric conductivity in the atmosphere in 19 km, *J. Geophys. Res.*, 76, 3431-3436, 1971.
- Morita, Y., Recent measurements of electric conductivity and ion production rate in the lower stratosphere, *Res. Lett. Atmos. Electr.*, 1, 49-52, 1981.
- Moseley, J.T., W. Aberth, and R. Peterson, Two-body mutual neutralization rates of $O_2^+ + O^-$, $NO^+ + O^-$, and $Na^+ + O^-$ obtained with merged beams, *J. Geophys. Res.*, 77, 255-259, 1972.
- Natanson G.L., The theory of volume recombination of ions, *Soviet Physics Tech. Phys.*, 4, 1263-1269, 1959 (Engl. translation).
- Nolan, P.J., The recombination law for weak ionization, *Proc. Roy. Irish Acad.*, 49A, 67-90, 1943.
- Rosen, J.M., D.J. Hofmann, W. Gringel, J. Belinski, S. Michinowshi, Y. Morita, T. Ogawa, and D. Olson, Results of an international workshop on atmospheric electrical measurements, *J. Geophys. Res.*, 87, 1219-1227, 1982.
- Shreve, E.L., Theoretical derivation of atmospheric ion concentrations, conductivity, space charge density, electric field and generation rate from 0 to 60 km, *J. Atmos. Sci.*, 27, 1186-1194, 1970.
- Smith, D., N.G. Adams, and E. Alge, Ion-ion mutual neutralization and ion-neutral switching reactions of some stratospheric ions, *Planet. Space Sci.*, 29, 449-454, 1981.

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