

AN AUTOCATALYTIC CYCLE FOR OZONE PRODUCTION  
IN THE LOWER STRATOSPHERE INITIATED  
BY GALACTIC COSMIC RAYS

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**Abstract**

Being poorly known, the ion chemistry of the lower stratosphere is generally ignored, or treated as similar to that of the middle atmosphere, by the current chemistry-climate modes. Some recent achievements in atmospheric chemistry have motivated us to re-assess the ionization efficiency of galactic cosmic rays (GCR) and ion-molecular reaction initiated by them. We reveal that near to the maximum of the GCR absorption, the energetically allowed ion-molecular reactions form an autocatalytic cycle for continuous  $O_3$  production in the lower stratosphere. The amount of the produced ozone is comparable to the values of the standard winter time  $O_3$  profile. This is an indication that GCR are responsible for a greater part of the lower stratospheric ozone variability than is assumed currently.

**Key words:** lower stratospheric ozone, galactic cosmic rays, climate

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**Introduction.** It is broadly accepted that stratospheric ozone  $O_3$  is produced by the photolysis of oxygen molecules by solar UV radiation (shorter than 242 nm) into oxygen atoms and their rapid attraction by oxygen molecules, i.e.  $O_2 + O + M \rightarrow O_3 + M$  [1]. Having a relatively short lifetime, the  $O_3$  is not uniformly mixed through the atmosphere and its distribution is controlled by chemical and dynamical processes in the atmosphere [2]. In the upper stratosphere, the ozone distribution is determined by a balance between production and destruction from catalytic cycles involving hydrogen, nitrogen and halogen radical species – the essence of the concept for photochemical equilibrium of the upper stratospheric  $O_3$ . In the middle and especially the lower stratosphere, the role of the dynamics

(i.e. the stratospheric Brewer–Dobson circulation) is supposed to have a dominant role for the formation of the observed winter-spring time  $\text{O}_3$  maximum in extra-tropics [2]. However, the recent multi-model’s experiments of GREWE [3] show that the local production is much more important for the extra-tropical stratospheric ozone balance than the tropical ozone transported by the Brewer–Dobson circulation.

This result immediately raises the question “What is the source of ozone production at these latitudes and altitudes?” It is worth noting that except by solar UV radiation, the molecular oxygen could be dissociated also by the corpuscular radiation of different origin (solar, galactic or extragalactic). Moreover, some recent achievements indicate that ion-molecular reactions, initiated by highly energetic particles, may be a source of atmospheric ozone [4, 5]. Our initial step to estimate the impact of the galactic cosmic rays (GCR) in the total ozone balance [6] shows that they could describe the greatest part of the ozone variability (55%) – more than those described by equivalent effective stratospheric chlorine (46%), or atmospheric circulation (38%). In this paper we estimate the efficiency of the GCR ionisation of the main atmospheric compounds and their ion-molecular reactions. It is shown that in the lower stratosphere GCR initiate an autocatalytic cycle for continuous  $\text{O}_3$  production, determining a great part of the ozone variability at these levels.

**2. Ion chemistry model of the lower stratospheric  $\text{O}_3$ .** Since the famous work of CHAPMAN [7], the stratospheric ozone, has been thought to be produced by the UV band of solar radiation, which dissociates the molecular oxygen  $\text{O}_2$  in two oxygen atoms  $\text{O}$ , thus forcing a three-body reaction of ozone formation:  $\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$ . The lower stratosphere, however, is less affected by the solar UV radiation, because the latter is strongly absorbed by the ozone aloft. The intensity and frequency of solar UV radiation, able to penetrate at these levels, is substantially decreased and it cannot dissociate anymore the molecular oxygen – a critical compound for the ozone formation. Another difference in the lower stratospheric chemistry (compared to the middle atmosphere) is the substantially reduced amount of the ozone depleting nitric oxide  $\text{NO}$  molecules, the main source of which is the oxidation of nitrous oxide  $\text{N}_2\text{O}$  by atomic oxygen [8] – due to the severely reduced density of oxygen atoms at these levels.

The other potential source of nitrogen oxides  $\text{NO}_x$  are GCR [9]. However, according to [10] the dissociative-ionization of nitrogen molecule by electron impact (i.e.  $\text{N}_2 + e^- \rightarrow \text{N}^+ + \text{N} + e^- + 24.34 \text{ eV}$ ) is very unlikely, by electrons with energies less than 30 eV. Having in mind that the mean energy of formation of electron-ion pair is  $\sim 35 \text{ eV}$  [11], it becomes clear that GCR’s channel for creation of  $\text{NO}_x$  molecules is highly ineffective. The primary ionization of  $\text{N}_2$  by electron impact ( $\text{N}_2 + e^- \rightarrow \text{N}_2^+ + 2e^- + 15.58 \text{ eV}$ ) demands less energy, but the created nitrogen cation  $\text{N}_2^+$  very rapidly exchange its charge with molecular oxygen ( $\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2^+ + 3.5 \text{ eV}$ ) [8, 12]. Consequently, in the lower stratosphere the

ozone destructive chemistry by nitrogen oxides could be really ignored in the  $O_3$  chemistry models of this region. The  $HO_x$  (H, OH,  $HO_2$ ) chemistry is also unimportant for the  $O_3$  balance, because of the minimum density profile in the  $H_2O$  vapour at this level (in the whole tropo-stratospheric system) and the inability of penetrating solar UV to dissociate  $O_2$ ,  $H_2O$  or  $H_2$  at these altitudes [8, 12].

Our chemical model includes the following energetically possible in the lower stratosphere reactions:

- (1)  $O_2 + e^- \rightarrow O_2^+ + 2e^- + 12.07 \text{ eV}$
- (2)  $O_2 + e^- \rightarrow O^+ + O + 2e^- + 18.69 \text{ eV}$
- (3)  $N_2 + e^- \rightarrow N_2^+ + e^- + 15.58 \text{ eV}$
- (4)  $O_3 + e^- \rightarrow O_3^+ + 2e^- + 12.75 \text{ eV}$
- (5)  $O_3 + e^- \rightarrow O_2^+ + O + 2e^- + 13.125 \text{ eV}$
- (6)  $O_3 + e^- \rightarrow O^+ + O_2 + 2e^- + 15.2 \text{ eV}$
- (7)  $O_3 + e^- \rightarrow O_2 + O + e^- + 3.773 \text{ eV}$
- (8)  $O_3^+ + e^- \rightarrow O_2^+ + O + e^- + 0.64 \text{ eV}$
- (9)  $O_3^+ + e^- \rightarrow O^+ + O_2 + e^- + 2.19 \text{ eV}$
- (10)  $O_3^+ + M \rightarrow O + O + O + \sim 0 \text{ eV}$
- (11)  $O_2^+ + O_2 + M \rightarrow O_4^+ + M + 3.5 \text{ eV}$
- (12)  $O_2^+ + e^- \rightarrow O + O + 5.12 \text{ eV}$
- (13)  $O_4^+ + O \rightarrow O_2^+ + O_3 + 5.6 \text{ eV}$
- (14)  $O_4^+ \rightarrow O_3^+ + O + 0.82 \text{ eV}$
- (15)  $O_4^+ \rightarrow O_2^+ + O_2 + 1.26 \text{ eV}$
- (16)  $N_2^+ + O_2 \rightarrow O_2^+ + N_2 + 3.5 \text{ eV}$
- (17)  $N_2^+ + O_2 \rightarrow NO + NO^+ + 4.45 \text{ eV}$
- (18)  $O^+ + O_2 \rightarrow O_2^+ + O + 1.5 \text{ eV}$

The energy on the right side is the activation energy of the reactions [13] in electron-volts (eV).

The main derivatives from a direct ionization and ion-molecular reactions producing ozone in our ion chemistry model are  $O_4^+$ ,  $O_3^+$ ,  $O_2^+$ ,  $O^+$  and O. Atomic oxygen rapidly reacts with  $O_2$  creating ozone, i.e.:  $O + O_2 + M \rightarrow O_3$ . The charge exchange of  $O^+$  with  $O_2$  forms O and  $O_2^+$ , while the  $O_2^+$  is the main source for creation of tetraoxygen cation  $O_4^+$  (see reaction (11)). After the work of CACACE et al. [4] it becomes clear that the latter dissociates very quickly in two different channels. One of them produces  $O_3^+$  and O (reaction (14)) and according to [4] may be a source of ozone in the atmosphere, while the other restores the  $O_2^+$  cations (reaction (15)). The ozone cation  $O_3^+$  is weakly bound and easily dissociates by photon absorption, collision or recombination. According to [14] the  $O_3^+$  also undergoes efficient charge exchange with molecular oxygen  $O_2$  to yield neutral  $O_3$ . However, the dissociative recombination of ozone cation to three oxygen atoms (reaction (10)), according to [15] is less energy demanding and occurs with

a very high probability. For the prevailing conditions in the lower stratosphere (i.e. ground state ozone cations and lower energetic electrons) reaction (10) occurs in 94% of cases [15]. Consequently, dissociation of one tetraoxygen cation (via reaction (14)) is a source of four ozone molecules. The amount of  $O_4^+$  cations is restored by reaction (11), while  $O_2^+$  cations are continuously produced by GCR. Thus reactions (11), (14), (15) and (10) form an *autocatalytic cycle* for continuous  $O_3$  production in the lower stratosphere, having a maximum at the level of strongest absorption of GCR (known as Pfofzer maximum).

What concerns the quenching of  $N_2^+$ , BANKS AND KOCKARTS [12] pointed out that production of nitric oxide NO by means of reaction (17) is not competitive to the charge exchange between  $N_2^+$  and  $O_2$  (reaction (16)), since the former requires a double bond breakage. Therefore, we exclude (17) from our further estimations.

### 2.1. Primary ionization of main atmospheric constituents by GCR.

The efficiency of the direct ionization of  $N_2$ ,  $O_2$  and  $O_3$  – calculated by the Maxwell–Boltzmann distribution (see eq. M1), are given on Table 1. It can be seen that despite the lower ionization potential of  $O_2$  (compare reactions (1) and (3)), the efficiency of the  $N_2$  ionization is 2.88 times greater because of its higher number density (remember that the ratio of nitrogen to oxygen molecules in the lower atmosphere is  $N_2/O_2 \approx 3.7$ ).

Comparison of our estimations for the efficiencies of electron impact ionization of  $N_2$ ,  $O_2$  and  $O$ , with corresponding values given in [16], shows almost identical values for  $N_2$  and slightly higher values for  $O_2$  and  $O$ , i.e. 0.206 against 0.176 for  $O_2^+$  and 0.154 against 0.076 for  $O^+$ . It is worth to note, however, that in our model the partitioning between all reactions (1÷7) is assessed simultaneously, while in [16] only the partitioning between (1) and (2) is estimated. For the mesospheric levels, the authors of [16] have partitioned a production of  $N_2^+$  from the dissociative-ionization of  $N_2$  (i.e.  $N_2 + e^- \rightarrow N^+ + N + 24.34$  eV), which has not been taken in consideration in our lower stratospheric model, because the output of  $N^+$  cations is practically impossible by the electrons with energies below 30 eV [10]. Having in mind that the mean energy of the secondary electrons produced by GCR is  $\sim 35$  eV [11], the appearance of  $N^+$  cations in the lower stratosphere is highly improbable. Additionally, the amount of NO at these levels is very small [8], which makes the possibility for ionisation of the products of the reaction:  $NO + e^- \rightarrow N + O$  very unlikely.

T a b l e 1

Efficiency of electron impact fractional ionization of  $N_2$ ,  $O_2$  and  $O_3$ ; numbers in brackets indicate the number of chemical reaction

|            | $O_2$       |                 | $N_2$       | $O_3$       |                   |           |                 |
|------------|-------------|-----------------|-------------|-------------|-------------------|-----------|-----------------|
| Products   | $O_2^+$ (1) | $O^+$ , $O$ (2) | $N_2^+$ (3) | $O_3^+$ (4) | $O_2^+$ , $O$ (5) | $O^+$ (6) | $O$ , $O_2$ (7) |
| Efficiency | 0.206       | 0.154           | 0.594       | 0.009       | 0.009             | 0.008     | 0.014           |

The efficiencies of  $O_3^+$  and  $O_2^+$  dissociation, and the formation of  $O_4^+$  are given on Table 2. The statistically derived efficiency of  $O_3^+$  dissociation (based on the activation energies of the reactions) gives almost equal probability for occurrence of reactions (8), (9) and (10). The experimental measurements [15] show, however, that for prevailing conditions in the lower stratosphere, i.e. ground state ozone cations and low energetic electrons, reaction (10) occurs in 94% of all cases. This means that the dissociation of one ozone cation is a source for production of three new ozone molecules.

## 2.2. Production of ozone creating substances ( $O_2^+$ , $O^+$ , $O$ , $O_4^+$ ).

The source of  $O^+$  in the lower stratosphere is described by reactions (2), (6) and (9). Using the efficiency for the occurrence of each reaction, listed on Tables 1 and 2, the production term of  $O^+$  is equal to:

$$(19) \quad P(O^+) = (0.154 + 0.008 + 0.003)Q = 0.165Q,$$

where  $Q$  denotes the density of electron/ion pairs [ $\text{cm}^{-3}$ ] produced by GCR.

Examination of reactions (1÷18) shows that the  $O_2^+$  production term includes reactions (1), (5), (8) and (18). The restoration of  $O_2^+$ , through dissociation of  $O_4^+$  (reaction (15)), is not included in the balance equation because the density of the short-lived  $O_4^+$  is unknown (we will calculate it from the estimated concentrations of  $O_2^+$  produced in our model). The fast process of charge exchange between  $O^+$  and  $O_2$  allow us to define the amount of  $O_2^+$ , formed through reaction (18), as  $P(O^+)$ . Moreover, the  $N_2^+$  – produced via reaction (16) – is almost immediately converted in  $O_2^+$  through a charge exchange (e.g. [12, 8] and references therein). So the quantity of  $O_2^+$ , produced through reaction (16), has been included in the  $P(O_2^+)$  term as  $P(N_2^+)$ , given on Table 1. Thus the balance equation for the produced  $O_2^+$  via the reactions (1), (5), (8) and (18) has the form

$$(20) \quad P(O_2^+) = (0.206 + 0.009 + 0.0032 + 0.166 + 0.594)Q = 0.978Q.$$

Similarly, the production term of atomic oxygen is calculated using reactions (2), (5), (7), (8), (10).

$$(21) \quad P(O) = (0.154 + 0.009 + 0.014 + 0.0032 + 3 \times 0.0033)Q = 0.1901Q.$$

T a b l e 2

Efficiencies of electron impact dissociation of  $O_3^+$  and  $O_2^+$ , and formation of  $O_4^+$ ; numbers in brackets indicate the number of chemical reaction

|            | $O_3^+$         |           |        | $O_2^+$ |              |
|------------|-----------------|-----------|--------|---------|--------------|
| Products   | $O_2^+$ , O (8) | $O^+$ (9) | O (10) | O (12)  | $O_4^+$ (11) |
| Efficiency | 0.0032          | 0.003     | 0.0033 | 0.099   | 0.11         |

The calculated profiles of  $O_2^+$ ,  $N_2^+$  and  $O^+$  are given in Fig. 1. Comparison with mid-latitude  $O_3$  profile by the US standard atmosphere [17] shows that the maximum of  $O_2$ ,  $N_2$  and  $O$  cations' profiles almost coincides with the maximum of ozone density. It is obvious, however, that the products of *direct ionization* by GCR are orders of magnitude less than  $O_3$  density and could not be responsible for distortion of its profile. Below will be estimated the amount of ozone produced by the autocatalytic cycle in the lower stratosphere.

The ozone production within the autocatalytic cycle is constrained by the density of the existing  $O_4^+$ . In order to estimate the efficiency of reaction (11), producing  $O_4^+$ , we have assumed that after a collision with energetic electron or ion,  $O_2^+$  receives at least 20% of the energetic particle's energy. The mean energy of the secondary electron/ion pair (formed in the atmosphere by GCR) is estimated to be  $\sim 35$  eV [11]. Therefore the estimated reactants' temperature of reaction (11) is  $\sim 7$  eV.

Applying the Saha equation (eq. M3) we have calculated the amount of  $O_4^+$  produced from reaction (11), by GCR with energy  $E = 2.5$  GeV. The resulted profile is shown in Fig. 2. Note that the maximum of calculated  $O_4^+$  profile is comparable to the maximum ozone density, which naturally raises the ques-

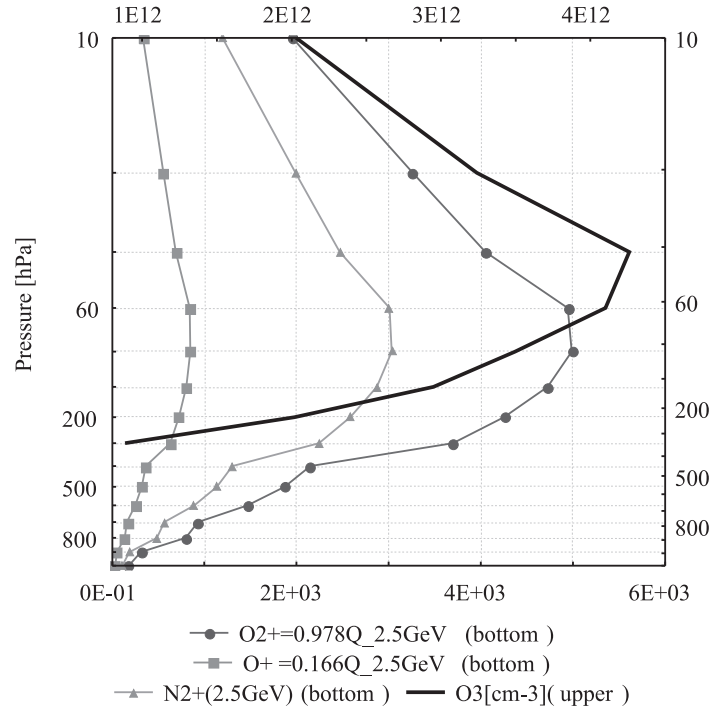


Fig. 1. Vertical profiles of  $O_2^+$ ,  $N_2^+$ ,  $O^+$  concentrations in  $[cm^{-3}]$  produced by GCR in our ion chemistry model, compared with the standard mid-latitude  $O_3$  profile of the US Stand Atmosphere

tion: If the density of tetraoxygen is so high, why has it not been measured till now? The answer could be found in the works [4, 14, 18], which show that due to the very short life span of  $O_4^+$  complex, there is *continuous cycling* between  $O_2^+$ ,  $O_4^+$  and  $O_3^+$  cations. Moreover, in the upper and middle stratosphere the accumulation of  $O_4^+$  is prevented by the pressure dependence of the intensity of  $O_4^+$  formation (decreasing with a pressure decrease) [4]. Additionally, the higher affinity of  $H_2O$  vapour to  $O_2^+$  [18], leads to a formation of the water clusters in the upper stratosphere, but not of  $O_4^+$ . The maximum in calculated  $O_4^+$  profile corresponds to the maximum of ionization, created by GCR (i.e. Pfotzer maximum). It is placed near to the tropopause – the driest levels of the lower and middle atmosphere, where the influence of the  $H_2O$  vapour is severely reduced.

**2.3. Ozone production by the autocatalytic cycle.** By the use of the Saha equation we have calculated the value of branching ratio between reactions (14) and (15) to be 0.505/0.495. The efficiency of reaction (13), producing also ozone, is very low (due to its higher activation energy) and practically has no impact in variations of  $O_3$  profile. Taking into account that reaction (10) is not

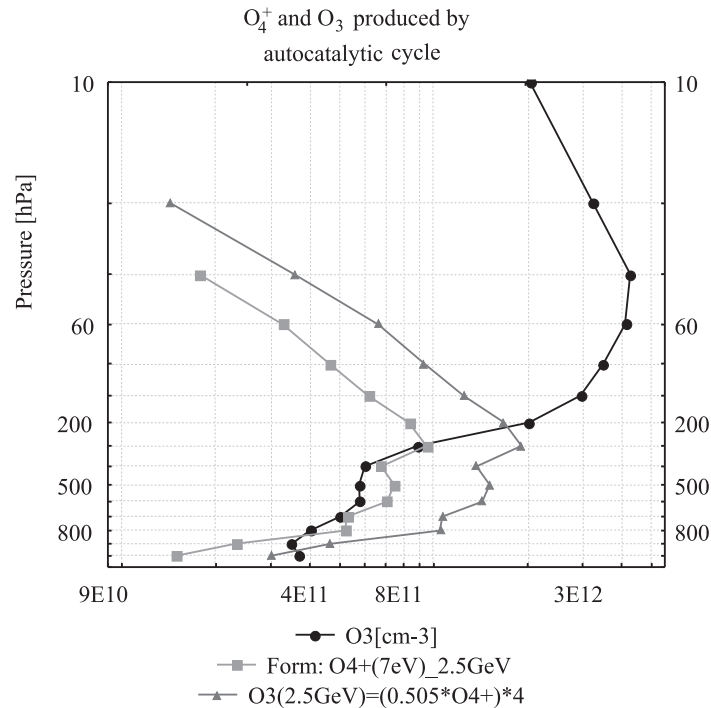


Fig. 2. Vertical profiles of  $O_4^+$  calculated by the use of the Saha equation, and  $O_3$  produced through reactions (14) and (10). Note that the amount of ozone produced by the autocatalytic cycle in the lower stratosphere is comparable with the standard mid-latitude  $O_3$  profile; densities are in  $[cm^{-3}]$

energy demanding and occurs in 94% of the observed cases [16], we have calculated the amount of ozone, produced through the autocatalytic cycle, by the formula

$$(22) \quad \text{O}_3\text{prod} = (0.505 \times \text{O}_4^+) \times 4,$$

where the multiplication by factor 4 reflects the number of O<sub>3</sub> molecules produced by reactions (14) and (10). The resulting O<sub>3</sub> profile from our ion chemistry model is shown in Fig. 2. Comparison with the ozone profile from the US Standard Atmosphere [17] shows that the ozone in the lower stratosphere and upper troposphere could be strongly influenced by the ion chemistry initiated by GCR.

**3. Data and methods of analysis.** The profile of the electron/ion pair production rate by 2.5 GeV galactic cosmic rays is taken from [19–22] for a period of solar minimum. The electron concentration (N<sub>e</sub>) has been calculated by the formula  $Q = \alpha_{eff} \cdot (N_e)^2$ , where the effective recombination coefficient is taken from [23], and  $Q$  is the electron production rate of GCR. The mean vertical profiles of the main atmospheric constituents (O<sub>2</sub>, N<sub>2</sub> and O<sub>3</sub>) are taken from [17].

The efficiency of atmospheric constituents' ionization from the secondary electrons and ions (produced by GCR) is calculated using the Maxwell–Boltzmann distribution (a well established approach in quantum statistics):

$$(M1) \quad \frac{N_i^+}{N} = \frac{g_i \exp(-\Delta E_i/kT)}{\sum_{j=1} g_j \exp(-\Delta E_j/kT)},$$

where  $N_i^+$  and  $N$  are the number density of ionized molecules of type  $i$  and the total neutral density;  $\Delta_i$  is the ionization potential of the  $i$ -th molecule,  $T$  is the mean temperature of secondary electrons converted to their mean energy  $E_e = 35$  eV by the formula:  $kT = 2/3E_e$ ;  $g_i$  are the weighting factors accounting for the fractional ratio of each constituents to the total atmospheric number density, i.e.  $g_{N_2} = 0.77$ ,  $g_{O_2} = 0.2299$  and  $g_{O_3} = 0.0001$ . The sum in the denominator is called partition function.

The efficiency of the ion-molecular or ion-atomic reactions of the type



has been calculated by the use of Saha equation

$$(M3) \quad \frac{[A^+][B]}{[C^+][D]} = \left[ \frac{2\pi \frac{m(A^+)m(B)}{m(C^+)m(D)} \cdot kT}{h^2} \right]^{3/2} \cdot \frac{Z(A^+)Z(B)}{Z(C^+)Z(D)},$$



where  $m(i)$  denotes the mass of the reactant or product;  $k$  is the Boltzmann const.;  $T$  is the temperature of the reaction;  $h$  is the Plank const.;  $Z(i)$  is the partition function of the corresponding reactant or product. The right side of eq. M3 is also known as the *equilibrium rate of reaction* (M2).

**4. Conclusions.** Unlike the upper and middle stratosphere, the factors controlling  $O_3$  variability in the lower stratosphere is highly uncertain. The ozone depletion during 1980s and 1990s, and its current recovery, is thought to be driven by: (i) the increased concentration of halogen substances in the stratosphere and (ii) the long-term changes in the lower stratospheric circulation ([<sup>2</sup>] and references therein). The causes for changing circulation, including trends in AO/NAO (Arctic Oscillation/North Atlantic Oscillation) indices, remain, however, unclear (as pointed in the same report). This means that at least 50% of the ozone variability in the lower stratosphere is still not explained. Moreover, recent modelling show that the  $O_3$  distribution in the extra-tropics is formed mainly from the local production, while the impact of the tropical ozone, transported by stratospheric dynamics, is substantially smaller [<sup>3</sup>]. During winter conditions, when the amount of solar UV radiation at middle and high latitudes is strongly reduced, the only alternative source of  $O_3$  at these latitudes are highly energetic galactic cosmic rays (GCR) capable of penetrating into the lower stratosphere and troposphere. However, the influence of GCR on the lower stratosphere has been ignored for a long time, though to be negligible at these levels [<sup>24</sup>].

Through reassessment of the efficiency of main atmospheric constituents' ionization by GCR and the ion-molecular reactions between the most abundant ions and neutrals, we have shown an existence of an autocatalytic cycle for continuous  $O_3$  production in the lower stratosphere and upper troposphere (near the level of maximal absorption of GCR, known as Pfofzer maximum). The quantity of  $O_3$ , produced by the positive ion chemistry, has the same order of magnitude as the mid-latitude steady-state ozone profile. This is an indication that the lowermost ozone profile could be substantially distorted by the highly energetic particles.

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