EXPLORATIONS COSMIQUES

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-asses 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 then 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 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.
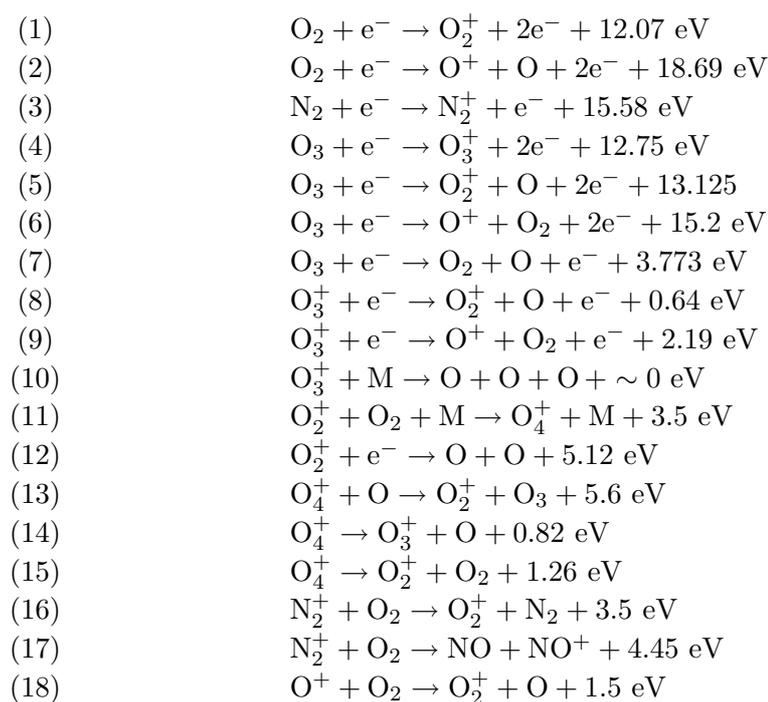
This result immediately raises the question "What is the source of ozone production at these latitudes and altitudes?" It is worth noting that except by solar UV radiation, the molecular oxygen could be dissociated also by the corpuscular radiation of different origin (solar, galactic or extragalactic). 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 O_3 production, determining a great part of the ozone variability at these levels.

2. Ion chemistry model of the lower stratospheric 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 O_2 in two oxygen atoms O, thus forcing a three-body reaction of ozone formation: $O_2+O+M \rightarrow O_3+M$. 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 NO molecules, the main source of which is the oxidation of nitrous oxide N_2O by atomic oxygen [8] – due to the severely reduced density of oxygen atoms at these levels.

The other potential source of nitrogen oxides NO_x are GCR [9]. However, according to [10] the dissociative-ionization of nitrogen molecule by electron impact (i.e. $N_2+e^- \rightarrow N^++N+e^-+24.34$ 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$35 eV [11], it becomes clear that GCR's channel for creation of NO_x molecules is highly ineffective. The primary ionization of N_2 by electron impact ($N_2+e^- \rightarrow N_2^++2e^-+15.58$ eV) demands less energy, but the created nitrogen cation N_2^+ very rapidly exchange its charge with molecular oxygen ($N_2^++O_2 \rightarrow N_2+O_2^+ + 3.5$ 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) $O_2 + e^- \rightarrow O_2^+ + 2e^- + 12.07$ eV
(2) $O_2 + e^- \rightarrow O^+ + O + 2e^- + 18.69$ eV
(3) $N_2 + e^- \rightarrow N_2^+ + e^- + 15.58$ eV
(4) $O_3 + e^- \rightarrow O_3^+ + 2e^- + 12.75$ eV
(5) $O_3 + e^- \rightarrow O_2^+ + O + 2e^- + 13.125$
(6) $O_3 + e^- \rightarrow O^+ + O_2 + 2e^- + 15.2$ eV
(7) $O_3 + e^- \rightarrow O_2 + O + e^- + 3.773$ eV
(8) $O_3^+ + e^- \rightarrow O_2^+ + O + e^- + 0.64$ eV
(9) $O_3^+ + e^- \rightarrow O^+ + O_2 + e^- + 2.19$ eV
(10) $O_3^+ + M \rightarrow O + O + O + \sim 0$ eV
(11) $O_2^+ + O_2 + M \rightarrow O_4^+ + M + 3.5$ eV
(12) $O_2^+ + e^- \rightarrow O + O + 5.12$ eV
(13) $O_4^+ + O \rightarrow O_2^+ + O_3 + 5.6$ eV
(14) $O_4^+ \rightarrow O_3^+ + O + 0.82$ eV
(15) $O_4^+ \rightarrow O_2^+ + O_2 + 1.26$ eV
(16) $N_2^+ + O_2 \rightarrow O_2^+ + N_2 + 3.5$ eV
(17) $N_2^+ + O_2 \rightarrow NO + NO^+ + 4.45$ eV
(18) $O^+ + O_2 \rightarrow O_2^+ + O + 1.5$ 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 Pfotzer 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 ~ 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

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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:

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

where Q denotes the density of electron/ion pairs [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

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

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

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

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

Products	O_3^+			O_2^+	
	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 ~35 eV [11]. Therefore the estimated reactants' temperature of reaction (11) is ~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-
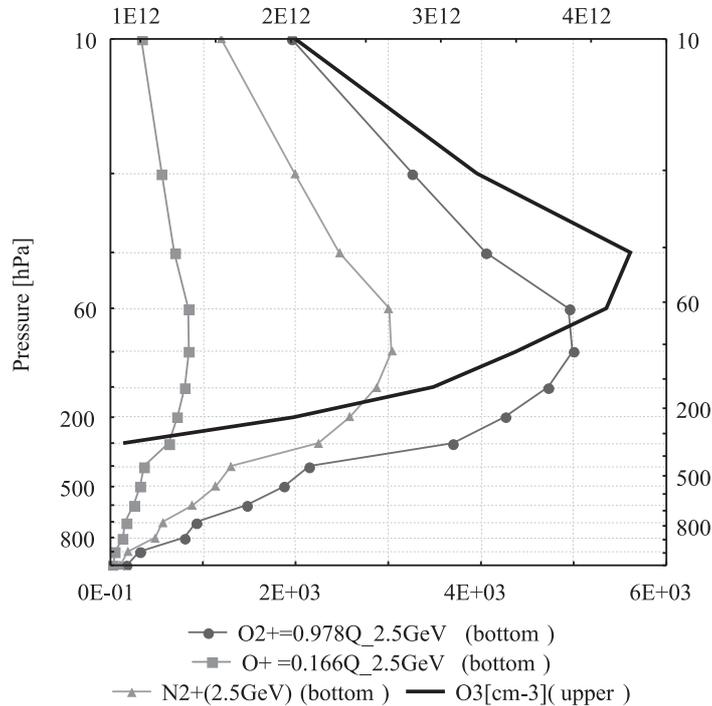

Fig. 1. Vertical profiles of O_2^+, N_2^+, O^+ concentrations in [cm^{-3}] produced by GCR in our ion chemistry model, compared with the standard mid-latitude O_3 profile of the US Stand Atmosphere

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
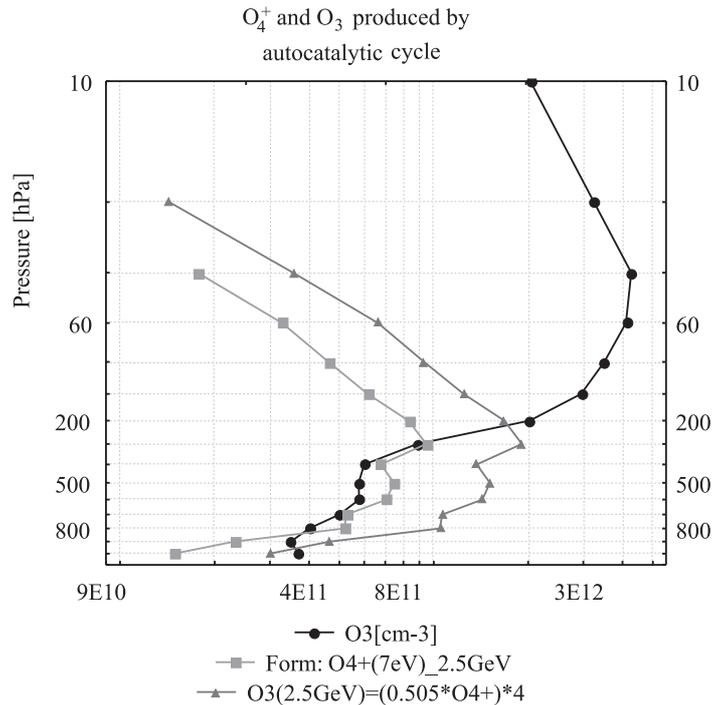

Fig. 2. Vertical profiles of O_4^+ calculated by the use of the Saha equation, and O_3 produced through reactions (14) and (10). Note that the amount of ozone produced by the autocatalytic cycle in the lower stratosphere is comparable with the standard mid-latitude O_3 profile; densities are in $[cm^{-3}]$

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

$$(22) \qquad O_3 prod = (0.505 \times O_4^+) \times 4,$$

where the multiplication by factor 4 reflects the number of O_3 molecules produced by reactions (14) and (10). The resulting O_3 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 (Ne) has been calculated by the formula $Q = \alpha_{eff}.(N_e)^2$, 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_2, N_2 and O_3) 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):

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

where N_i^+ and N are the number density of ionized molecules of type i and the total neutral density; Δ_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. $g_{N2} = 0.77$, $g_{O2} = 0.2299$ and $g_{O3} = 0.0001$. The sum in the denominator is called partition function.

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

$$(M2) \qquad A^+ + B \rightarrow C^+ + D$$

has been calculated by the use of Saha equation

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

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 ([2] 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 [3]. 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 [24].

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 Pfotzer 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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