

The influence of ozone concentration on the lower ionosphere – modelling and measurements during the 29–30 October 2003 solar proton event

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Abstract. A numerical model of D-region ion chemistry is used to study the influence of the ozone concentration in the mesosphere on ion-composition and electron density during solar proton events (SPE). We find a strong sensitivity in the lower part of the D-region, where negative ions play a major role in the ionization balance. We have chosen the strong SPE on 29–30 October 2003 when very intense proton fluxes with a hard energetic spectrum were observed. Deep penetration into the atmosphere by the proton fluxes and strong ionisation allows us to use measurements of electron density, made by the EISCAT 224 MHz radar, starting from as low as 55 km. We compare the electron density profiles with model results to determine which ozone concentration profiles are the most appropriate for mesospheric altitudes under SPE conditions. We show that, during daytime, an ozone profile corresponding to depletion by a factor of 2 compared to minimum model concentrations for quiet conditions (Rodrigo et al., 1986), is needed to give model electron density profiles consistent with observations. Simple incorporation of minor neutral constituent profiles (NO, O and O₃) appropriate for SPE conditions into ion-chemistry models will allow more accurate modeling of electron and ion densities during such events, without the need to apply a complete chemical model calculating all neutral species.

Keywords. Atmospheric composition and structure (Middle atmosphere – composition and chemistry) – Ionosphere (Ion chemistry and composition; Polar ionosphere)

1 Introduction

Minor neutral constituents play a significant role in the processes controlling the ionization balance in the lower ionosphere. They are, as a rule, input parameters into theoretical models which compute ion composition, electron density (N_e), and other ionosphere characteristics. Both experimental data and the results of theoretical investigations demonstrate a large variability in minor constituents, in particular, in the ozone concentration [O₃] at the altitude of the mesosphere. Theoretical investigations allow us to understand the nature of and reasons for such variability. Models of the minor constituents in the mesosphere have revealed the processes controlling photochemical and dynamical sources and sinks of each component. They have shown that the number density of the minor neutral constituents depends on solar illumination, geomagnetic activity, ionization sources, season, downward transport, turbulence, molecular and eddy diffusions and other factors. To obtain accurate numerical estimations of parameters describing the structure of the ionosphere during any specified geophysical situation, it is very important to incorporate, into the model, reasonable height profiles of the minor neutral components that are appropriate to the given geophysical conditions. The influence of the concentration of nitric oxide on the N_e height-profile has been considered by Verronen et al. (2002). The role of the atomic oxygen concentration in forming the electron density profile during a solar proton event (SPE) has been investigated, in particular, by Osepian et al. (2008). Ondraskova et al. (2008) have considered the influence of solar illumination on the ion-chemistry and N_e profile, comparing modelled responses between polar night and polar day. Although they briefly mention the role of ozone they do not make any



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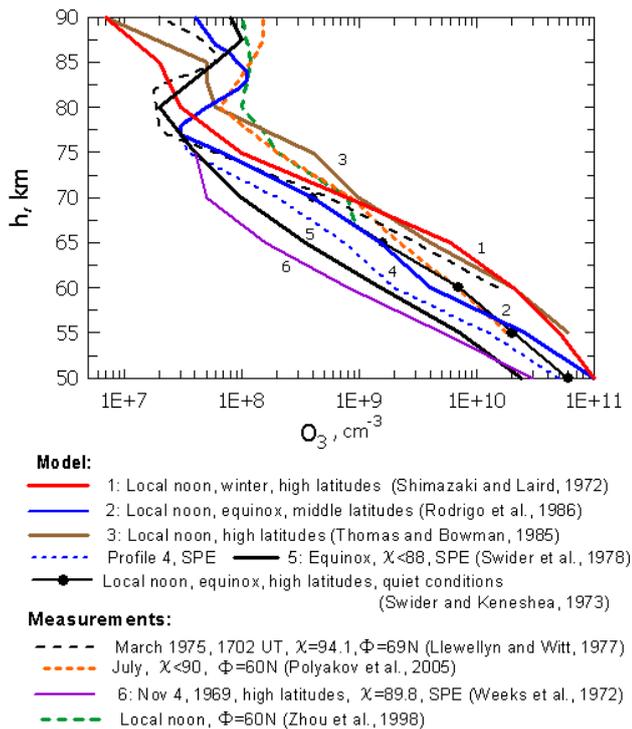


Fig. 1. Examples of the height distribution of the ozone concentration in the D-region obtained from measurements and from theoretical studies.

quantitative study of the sensitivity of the N_e profile to the ozone profile.

In this study, we use numerical modelling to investigate the role of ozone in the ionization balance at different mesospheric altitudes and the influence of the ozone concentration, $[O_3]$, as it changes due to the effects of solar proton precipitation, on the height distribution of the ion and electron densities during the SPE on 29–30 October 2003, also known as one of the “Halloween Storms”. We use a theoretical model of the D-region and available height profiles of ozone in the mesosphere, measured or deduced with different diffusive-photochemical models. For calculation of the ionization rates we use code developed by Kirkwood and Osepian (1995) with input data on the differential solar proton fluxes in the energy range 2.4–300 MeV measured by the satellites GOES-10 and GOES-11 (<http://spidr.ngdc.noaa.gov/spidr/index.jsp>). Then we combine the results of the modelling with measurements of electron density in the lower ionosphere made by the EISCAT 224 MHz radar (geographic coordinates 69.6° N, 19.3° E) to determine which ozone concentration profiles are most appropriate for mesospheric altitudes in conditions of solar proton precipitation. We use the theoretical model of the ionisation-recombination cycle of the D-region which was developed by Smirnova et al. (1988), Kirkwood and Osepian (1995), Osepian and Smirnova (1997). Tests of the model have shown that it

reproduces both N_e absolute values and the shape of N_e -profiles measured by the EISCAT radar during auroral activity, for altitudes above 70–75 km (Osepian et al., 1996; Kirkwood et al., 2001) and during SPE at altitudes above 65–70 km (Osepian et al., 2008).

In Sect. 2 we present a brief review of modern knowledge concerning the height distribution of ozone concentration in the mesosphere for different geophysical conditions. In Sect. 3 we examine the influence of the ozone concentration on the ion composition and electron density in the mesosphere. We estimate the efficiency of the reactions in the processes of transformation of primary negative O_2^- and O^- ions into intermediate complex ions O_3^- , O_4^- , NO_4^- , NO_3^- and NO_3^- to understand the role of reactions with ozone in the ionisation balance at each altitude during SPE. Comparison of theoretical and experimental N_e -profiles then allows us to estimate ozone concentrations which correspond to SPE.

2 Height profiles of ozone in the mesosphere

Ozone is continually formed and destroyed in the mesosphere. Figure 1 presents examples of the height distribution of the O_3 concentration in the mesosphere during daytime, obtained from measurements and as a result of theoretical studies. Measurements show substantial diurnal variations at mesospheric altitudes with maximum concentrations at nighttime and a secondary peak above 80 km (Llewellyn and Witt, 1977; Weeks et al., 1972, 1978; Wilson and Schwartz, 1981; Ulwick et al., 1987; Zommerfelds et al., 1989; Zhou et al., 1998; Sandor et al., 1997; Gumbel et al., 1998; Fussen et al., 2000; Kaufmann et al., 2003; Polyakov et al., 2005; Kyrölä et al., 2006).

The height distribution of the O_3 -density in the mesosphere, its seasonal and diurnal variations and the secondary peak have been explained by theoretical investigations and by modelling (Shimazaki and Laird, 1970, 1972; Ogawa and Shimazaki, 1975; Swider et al., 1978; Keneshea et al., 1979; Thomas and Bowman, 1985; Rodrigo et al., 1986; Sandor et al., 1997; Marsh et al., 2003; Jackman et al., 1995, 2005). The primary chemical production mechanism for odd oxygen in the thermosphere and mesosphere is photodissociation of molecular oxygen. Chemical losses occur either through the Chapman (oxygen-only) reactions or through catalytic cycles involving NO_x or HO_x radicals. The major cycles relevant for odd oxygen are summarized in Tables 1–2. The most important reactions for a pure oxygen atmosphere are Reactions (R1–R8) (Table 1). Reactions (R1–R5) constitute net production and losses for odd oxygen. Reactions (R6–R8) regulate partitioning between atomic oxygen and ozone within the odd oxygen family. Because of very rapid photolysis (Reaction R3 in Table 1) ozone concentration is low during the day but ozone reforms during both day and night by the 3-body Reaction (R4).

Theoretical investigations have shown that, in addition to the photochemical schemes and reactions presented in Table 1, catalytic reactions involving hydrogen species (Table 2) as well as turbulent mass transport are important.

At the altitudes where O and H have high abundances, catalytic cycles lead to more rapid odd oxygen loss than through the Chapman reactions only. For example, in the lower mesosphere odd oxygen is lost in catalytic reaction cycles (R4) and (R9) (Table 2):

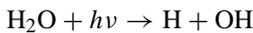


The cycle (R6) and (R8) (Table 2):



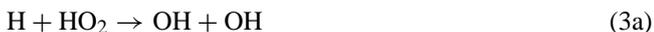
becomes important in the middle and upper mesosphere.

Near 75–80 km odd hydrogen is produced primarily from photolysis of water vapor:



and therefore varies in proportion to H_2O . Below this region OH is produced by Reaction (R5) (Table 2) with $\text{O}(^1\text{D})$ which itself is produced from O_3 photolysis. Thus Reactions (R5) (Table 2), (R3) (Table 1) link OH production to the ozone amount: an increase in OH will decrease ozone and so decrease the amount of OH density. Since OH and HO_2 are chemically active they are present in fairly low concentrations in quiet conditions.

During precipitation of solar protons (SPE), the concentration of the odd hydrogen constituents, H, OH and HO_2 increases. In particular, Solomon et al. (1981) pointed out that below 80 km nearly 2 odd hydrogen particles are formed per ionization and the subsequent reactions:



produce OH and HO_2 . The transformation of precursor ions O_2^+ and NO^+ to intermediate hydrated clusters (Swider and Keneshea, 1973; Frederick, 1976; Solomon et al., 1981; Reid, 1977; Reid et al., 1991), with further clustering and dissociative recombination of water cluster ions, increases OH and H concentrations below the transition height in the mesosphere (the transition height being the height where the concentration of cluster ions equals the concentration of molecular ions). After the onset of a strong SPE these changes can become greater than 100% (McPeters and Jackman, 1995; Jackman et al., 1995, 2005; Verronen et al., 2006).

During SPE the concentration of NO in the mesosphere is also increased strongly owing to dissociation and dissociative ionization of the nitrogen molecule N_2 by relativistic protons and its dissociation by secondary electrons (Crutzen et al., 1975; Porter et al., 1976; Rusch et al., 1981; Jackman et al., 2005; Verronen et al., 2002; Lopez-Piortas et al., 2005). As

a result of enhanced concentration of NO and hydrogen radicals, the catalytic cycles (Eqs. 1–2) become important in the mesosphere and lower thermosphere and as a consequence they lead to a change of the O_3 and O densities. The character of the odd oxygen component variations under conditions of very strong solar proton precipitation depends on height, season, solar illumination and intensity of the corpuscular ionization source (Swider and Keneshea, 1973; Swider et al., 1978; Solomon et al., 1983; McPeters and Jackman, 1985; Smirnova et al., 1990; Seppälä et al., 2006, 2004; Jackman et al., 2005; Rohen et al., 2005; Verronen et al., 2005). Note that the last 4 of these studies include the same solar proton event as we study here.

Height profiles of ozone in the mesosphere deduced in different diffusive-photochemical models for daytime, quiet conditions are presented in Fig. 1 by curves 1–3 (Shimazaki and Laird, 1972; Rodrigo et al., 1986; Thomas and Bowman, 1985). Deviations in the concentration of ozone between O_3 -profiles 1–3 can be explained by differences in accounting for solar radiation intensity in different wavelength ranges, in absorption cross sections, in values of eddy diffusion coefficient, in concentration of atomic oxygen and other species, in rate constants of reactions and in other factors applied in the model studies. Nevertheless, at altitudes below 78–77 km, the range of theoretical O_3 -profiles is close to the range of experimental values of the ozone concentration. In the upper mesosphere, above 80 km, in several cases, the observed ozone abundance is larger than predicted by the photochemical models.

As has been mentioned above, even moderate SPE can cause ozone depletion of 30–70%. According to Jackman et al. (2005), during the very strong SPE on 28–30 October 2003, changes in the concentration of NO and hydrogen radicals were significant and have also led to destruction of ozone. The hypothetical O_3 -profile 4 in Fig. 1 represents the height distribution of ozone decreased below 80 km altitude by a factor 2 compared with the minimum model O_3 -concentrations for quiet conditions (Swider and Keneshea, 1973; Rodrigo et al., 1986). The O_3 -profiles 5 and 6 represent O_3 concentrations in the mesosphere obtained in a neutral chemistry model for the SPE-disturbed D-region (Swider and Keneshea, 1973; Swider et al., 1978) and measured by Weeks et al. (1972) during the SPE in November 1969.

3 Influence of the ozone concentration on the ion composition and electron density in the mesosphere

To investigate the role of the ozone concentration in determining the ion composition and electron density profiles at mesospheric altitudes, we use a theoretical scheme describing the main ionic transformation processes and ion-chemical reactions. This forms the basis of the theoretical chemical model applied in the present study and is described detail in Osepian et al. (2008).

Table 1. Principal reactions for formation and destruction of odd oxygen.

No	Reactions	Rate coefficient, $\text{cm}^3 \text{s}^{-1}$, $\text{cm}^6 \text{s}^{-1}$ (DeMore, 1994; Sander et al., 2003)
(R1)	$\text{O}_2+h\nu(<1750 \text{ \AA})\rightarrow\text{O}({}^3\text{P})+\text{O}({}^1\text{D})$	4.10×10^{-6}
(R2)	$\text{O}_2+h\nu(1750\text{--}2050 \text{ \AA})\rightarrow\text{O}({}^3\text{P})+\text{O}({}^1\text{D})$	1.87×10^{-7}
(R3)	$\text{O}_3+h\nu(<3100 \text{ \AA})\rightarrow\text{O}_2({}^1\Delta_g)+\text{O}({}^1\text{D})$	9.63×10^{-3}
	$\text{O}_3+h\nu(3100\text{--}3600 \text{ \AA})\rightarrow\text{O}_2({}^1\Delta_g)+\text{O}({}^3\text{P})$	1.25×10^{-4}
(R4)	$\text{O}({}^3\text{P})+\text{O}_2+\text{M}\rightarrow\text{O}_3+\text{M}$	$6.6\times 10^{-34}\times(300/T)^{2.3}$
(R5)	$\text{O}+\text{O}+\text{M}\rightarrow\text{O}_2({}^1\Delta_g)+\text{M}$	$4.7\times 10^{-33}\times(300/T)^{2.0}$ $9.2\times 10^{-34}\times(470/T)$
(R6)	$\text{O}({}^3\text{P})+\text{O}_3\rightarrow\text{O}_2+\text{O}_2$	$1.9\times 10^{-11}\times\exp(-2300/T)$ $8.0\times 10^{-12}\times\exp(-2060/T)$
(R7)	$\text{O}({}^1\text{D})+\text{O}_3\rightarrow\text{O}_2+\text{O}_2$	2.65×10^{-10}
(R8)	$\text{O}({}^1\text{D})+\text{O}_3\rightarrow\text{O}_2+2\text{O}({}^3\text{P})$	2.65×10^{-10}
(R9)	$\text{N}({}^4\text{S})+\text{O}_3\rightarrow\text{NO}+\text{O}_2$	5.7×10^{-13}
(R10)	$\text{O}_3+\text{NO}+\text{M}\rightarrow\text{NO}_2+\text{O}_2$	$2.0\times 10^{-12}\times\exp(-1400/T)$
(R11)	$\text{O}_3+\text{NO}\rightarrow\text{NO}_2+\text{O}_2$	$9.0\times 10^{-13}\times\exp(-1200/T)$ $2.0\times 10^{-12}\times\exp(-1400/T)$
(R12)	$\text{O}_3+\text{NO}_2\rightarrow\text{NO}_3+\text{O}_2$	$1.2\times 10^{-13}\times\exp(-2450/T)$

Table 2. Reactions of odd oxygen with hydrogen species in the mesosphere.

No.	Reactions	Rate constants, $\text{cm}^3 \text{s}^{-1}$, $\text{cm}^6 \text{s}^{-1}$ (DeMore, 1994; Sander et al., 2003)
(R1)	$\text{O}+\text{H}_2\rightarrow\text{OH}+\text{H}$	$8.5\times 10^{-20}\times T^{0.7}\times\exp(-3160/T)$
(R2)	$\text{O}({}^3\text{P})+\text{H}_2\rightarrow\text{OH}+\text{H}$	$2.5\times 10^{-17}\times T^2\times\exp(-3801/T)$ $3.0\times 10^{-14}\times T\times\exp(-4480/T)$
(R3)	$\text{O}+\text{H}_2\text{O}_2\rightarrow\text{OH}+\text{HO}_2$	$1.4\times 10^{-12}\times\exp(-2000/T)$
(R4)	$\text{O}+\text{HO}_2\rightarrow\text{OH}+\text{O}_2$	$3.0\times 10^{-11}\times\exp(-200/T)$
(R5)	$\text{O}({}^1\text{D})+\text{H}_2\text{O}\rightarrow\text{OH}+\text{OH}$	2.2×10^{-10}
	$\text{O}({}^3\text{P})+\text{H}+\text{M}\rightarrow\text{OH}+\text{M}$	3.0×10^{-32}
(R6)	$\text{O}+\text{OH}\rightarrow\text{O}_2+\text{H}$	$2.2\times 10^{-11}\times\exp(-120/T)$
(R7)	$\text{O}+\text{OH}+\text{M}\rightarrow\text{HO}_2+\text{M}$	1.4×10^{-31}
(R8)	$\text{O}_3+\text{H}\rightarrow\text{OH}+\text{O}_2$	$1.4\times 10^{-10}\times\exp(-470/T)$
(R9)	$\text{O}_3+\text{OH}\rightarrow\text{HO}_2+\text{O}_2$	$1.6\times 10^{-12}\times\exp(-940/T)$
(R10)	$\text{O}_3+\text{HO}_2\rightarrow\text{OH}+2\text{O}_2$	$1.1\times 10^{-14}\times\exp(-500/T)$ $1.1\times 10^{-13}\times\exp(-1250/T)$

Computations of the ionospheric parameters have been made during the SPE on 29 and 30 October 2003 at about local noon (at 1000 UT, $\chi=82.8^\circ$ and 83°), for different values of O_3 concentration (the O_3 -profiles 1–6 in Fig. 1). Input values for nitric oxide (curve 1) and atomic oxygen (curve 2) for the autumn season are presented in Fig. 2.

The NO-profile has been deduced for the SPE on October 1968 in the model by Verronen et al. (2002). The concentration of nitric oxide is substantially larger than [NO] in quiet conditions. The effect of solar proton precipitation on atomic oxygen consists in depletion of [O]. The O-profile (curve 2)

is taken from results of a neutral chemistry model for the SPE on 2 November 1969, using the methods described by Swider and Keneshea, (1973) and Swider et al. (1978).

For comparison we present the O-profile (curve 3) obtained for winter daytime mesosphere during the SPE on 17 January 2005 (Osepian et al., 2008). In both cases [O] is less than [O] in quiet conditions.

In our model we have incorporated changes of the odd oxygen concentration with zenith angle during twilight as in the simulation results by Turco and Sechrist (1972). We have further assumed a diurnal variation of the NO and NO_2

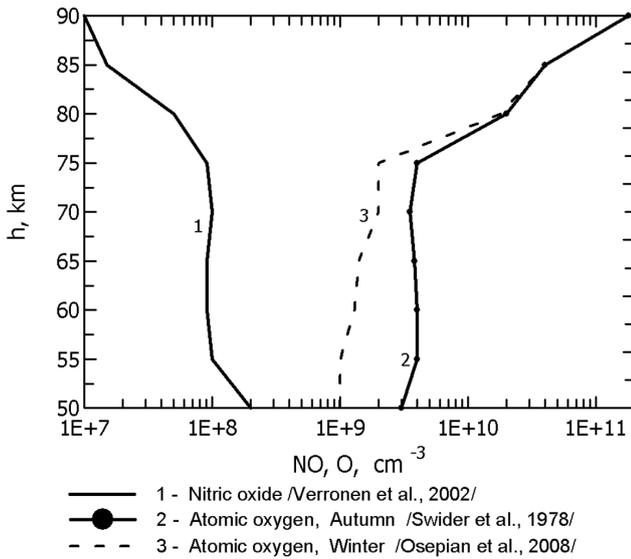


Fig. 2. Input values for nitric oxide (curve 1, Verronen et al., 2002) and atomic oxygen: curve 2 is for the autumn season (Swider et al., 1978) and curve 3 is for winter daytime (Osepian et al., 2008).

concentrations at altitudes below 70 km accordingly to the investigation results by Ogawa and Shimazaki (1975).

3.1 Efficiencies of ion-molecular reactions forming complex negative ions in the lower ionosphere

Variations of the O_3 concentration are especially important for the negative ion chemistry. The primary negative O_2^- and O^- ions participate in a complicated series of fast ion-molecular reactions with neutral constituents which produce different negative ions in the lower ionosphere, in particular, intermediate complex O_3^-, O_4^-, NO_4^- ions (Table 3).

The intermediate ions O_3^-, O_4^-, NO_4^- rapidly appear and disappear but they play a key role in formation of NO_3^- and NO_3^- ions. To understand the role of the ozone concentration in the ionisation balance at each altitude during SPE we have estimated the efficiencies of the ion-molecular reactions in the processes of transformation of primary negative O_2^- and O^- ions into intermediate complex ions $O_3^-, O_4^-, NO_4^-, NO_3^-$ and NO_3^- .

We use V_{eff} to denote the efficiency of individual reactions, e.g. for the efficiency of reaction $NO_4^- + O_3 \rightarrow O_3^- + NO_2 + O_2$, $V_{eff} = 1.3 \times 10^{-10} [O_3]$. The efficiency of this reaction is equal to the product of the rate constant k , $cm^3 s^{-1}$, and ozone concentration $[O_3]$, cm^{-3} , i.e. it is the frequency of the reaction, V_{eff}, s^{-1} .

As an example, in Fig. 3 we show efficiencies of the reactions in which O_3^- ions are produced and lost. The main reactions producing O_3^- ions are reactions forming O_3^- from O_2^- and O^- :

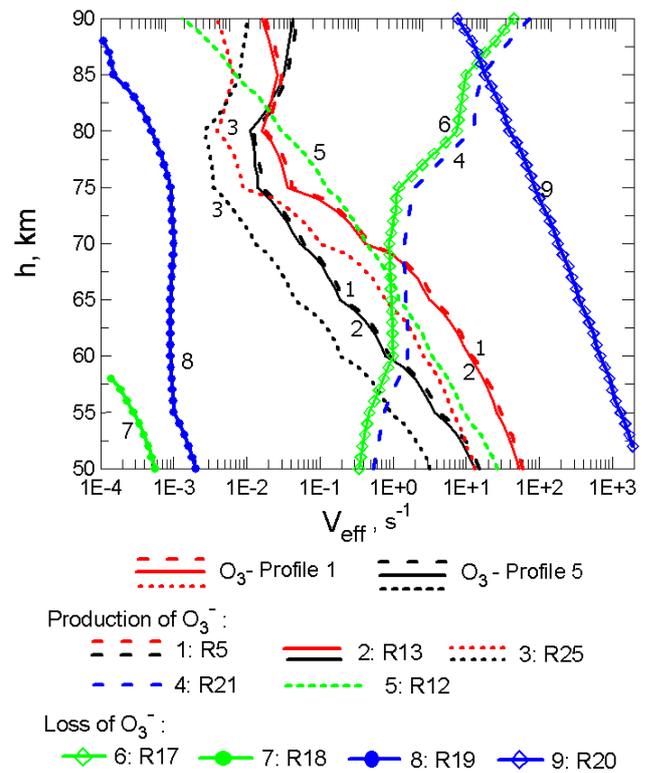
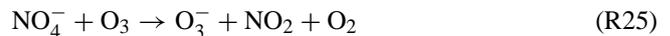


Fig. 3. Height profiles of the efficiencies of reactions for the O_3^- ion production and loss. Red and black lines correspond to ozone profiles 1 and 5, respectively, in Fig. 1. See text Sect. 3.1 for the various reaction paths R_n .



The efficiencies of these 3 reactions, calculated for O_3^- profiles 1 and 5, are given by curves 1, 2 and 5. The efficiencies of the reaction forming O_3^- from NO_4^-



are shown by curves 3. Efficiency of the reaction forming O_3^- from O_4^-



is given by curve 4.

Losses of the O_3^- ions via reactions with participation of NO_y are small:



At altitudes below 85 km the O_3^- ions rapidly disappear in a reaction with NO_2 :

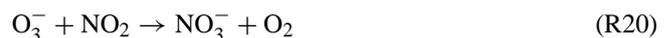


Table 3. Ion-molecular reactions forming complex negative ions from O_2^- and O^- .

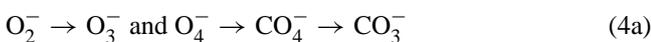
Reactions	Rate coefficient, $cm^3 s^{-1}$, $cm^6 s^{-1}$ (Albritton, 1978)
(R1) $O_2^- + O_2 \rightarrow e + O_2 + O_2$	$3.0 \times 10^{-10} (300/T)^{-0.5} \exp(-5590/T)$
(R2) $O_2^- + N_2 \rightarrow e + O_2 + N_2$	$1.9 \times 10^{-120} (300/T)^{-1.5} \exp(-4990/T)$
(R3) $O_2^- + O \rightarrow e + O_3$	1.5×10^{-10}
(R4) $O_2^- + O_2(^1\Delta_g) \rightarrow e + O_2 + O_2$	2.0×10^{-10}
(R5) $O_2^- + O_3 \rightarrow O_3^- + O_2$	6.0×10^{-10}
(R6) $O_2^- + CO_2 + O_2 \rightarrow CO_4^- + O_2$	$2.0 \times 10^{-29} (300/T)^{5.0}$
(R7) $O_2^- + O_2 + O_2 \rightarrow O_4^- + O_2$	$4.0 \times 10^{-31} (300/T)^{5.0}$
(R8) $O_2^- + H_2O + O_2 \rightarrow O_2^- \cdot H_2O + O_2$	$1.6 \times 10^{-28} (300/T)^{3.0}$
(R9) $O_2^- + h\nu \rightarrow e + O_2$	$\rho_1 = 0.33 s^{-1}$
(R10) $O^- + O_2(^1\Delta_g) \rightarrow e + O_3$	2.0×10^{-10}
(R11) $O^- + CO_2 + O_2 \rightarrow CO_3^- + O_2$	$3.1 \times 10^{-28} (300/T)^{5.0}$
(R12) $O^- + O_2 + O_2 \rightarrow O_3^- + O_2$	$9.0 \times 10^{-31} (300/T)^{5.0}$
(R13) $O^- + O_3 \rightarrow O_3^- + O$	5.3×10^{-10}
(R14) $O^- + O \rightarrow e + O_2$	1.9×10^{-10}
(R15) $O^- + NO \rightarrow e + NO_2$	1.6×10^{-10}
(R16) $O^- + H_2O \rightarrow OH^- + OH$	1.4×10^{-10}
(R17) $O_3^- + O \rightarrow O_2^- + O_2$	2.5×10^{-10}
(R18) $O_3^- + NO_2 \rightarrow NO_3^- + O_2$	2.8×10^{-10}
(R19) $O_3^- + NO \rightarrow NO_2^- + O_2$	1.0×10^{-11}
(R20) $O_3^- + NO_2 \rightarrow NO_3^- + O_2$	4.0×10^{-10}
(R21) $O_4^- + O \rightarrow O_3^- + O_2$	4.0×10^{-10}
(R22) $O_4^- + CO_2 \rightarrow CO_4^- + O_2$	4.3×10^{-10}
(R23) $O_4^- + NO \rightarrow NO_3^- + O_2$	2.5×10^{-10}
(R24) $O_4^- + H_2O \rightarrow O_2^- \cdot H_2O + O_2$	1.5×10^{-9}
(R25) $NO_4^- + O_3 \rightarrow O_3^- + NO_2 + O_2$	1.3×10^{-10}
(R26) $NO_4^- + O \rightarrow CO_3^- + O_2$	1.4×10^{-10}
(R27) $CO_3^- + NO \rightarrow NO_2^- + CO_2$	1.1×10^{-10}
(R28) $CO_3^- + NO_2 \rightarrow NO_3^- + CO_2$	2.0×10^{-10}
(R29) $NO_3^- + O_2 \rightarrow O_3^- + CO_2$	6.0×10^{-15}
(R30) $NO_3^- + O \rightarrow O_2^- + CO_2$	1.1×10^{-10}

Above 85 km the O_3^- ions again transform to O_2^- ions through the reaction



It is clear that variations of the ozone concentration affect the composition of negative ions mainly at altitudes below 70 km.

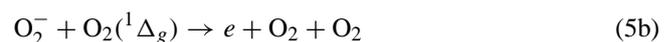
In our theoretical model the efficiencies of reactions included in the paths (Eq. 4a, b) forming intermediate negative ions O_3^- , O_4^- , NO_4^- from the primary ions O_2^- and O^- and their transformations into NO_3^- ions:



are substituted by effective parameters $B(O_2^-)$, $B(O^-)$. They are described by the expressions (A4) and (A5) in the Appendix of Osepian et al. (2008). The efficiencies of both

channels calculated for O_3^- -profiles 1 and 5 are shown by curves 1 and 2 in Fig. 4. First of all, note that the efficiency of reactions in the chain (Eq. 4b), $B(O^-)$, is greater than the efficiency of the path (Eq. 4a), $B(O_2^-)$, especially in the model with low $[O_3]$. The influence of the ozone concentration on the efficiency of both paths becomes significant below 75 km. The efficiency of the path (4a), $B(O_2^-)$, depends on the ozone concentration to a larger extent than $B(O^-)$.

The efficiencies of the main reactions which lead to losses of the O_2^- and O^- ions through channels (4a), (4b) (curves $B(O_2^-)$ and $B(O^-)$) and through reactions which do not produce negative ions (curves 2, 3):



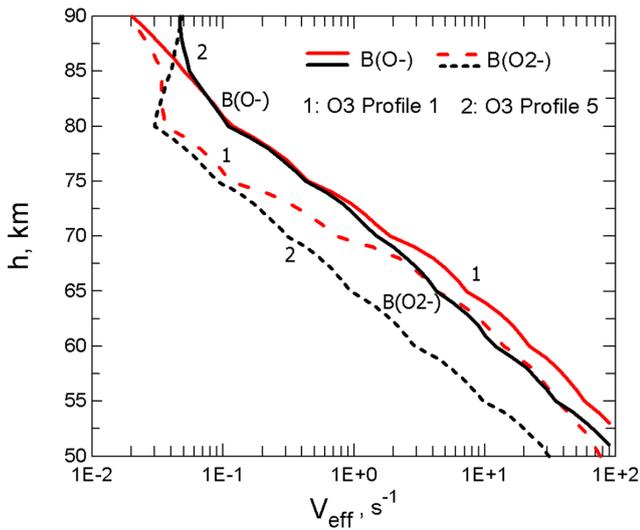


Fig. 4. Height profiles of the sum of the efficiencies, $B(O_2^-)$, and $B(O^-)$, of the reaction chains described by Eqs. (4a) and (4b). Red and black lines correspond to ozone profiles 1 and 5, respectively, in Fig. 1.

and



are compared in Fig. 5. The results of computations show that, in the model with low $[O_3]$ concentration (O₃-profile 5), negative ions are mainly formed from the O⁻ ion since the efficiency of the path (4b), $B(O^-)$, is greater than $B(O_2^-)$ and the efficiency of reactions (6a, b). This process dominates at altitudes up to 73 km. Production of complex negative ions from O₂⁻ takes place only at altitudes below ~58 km owing to the high efficiency of Reaction (5b). In the model with high $[O_3]$ (O₃-profile 1) the path (4a) becomes effective at altitudes up to ~70 km. In both cases, at altitudes above 73 km, formation of complex negative ions is broken, mainly due to processes of associative detachment (Eqs. 5a, 6a).

3.2 Ion composition and electron density for different concentrations of ozone

It is clear that the height distribution in the mesosphere of negative ions depends mainly on the O and O₃ concentrations. Figure 6 (upper panel) demonstrates the influence of ozone concentration on the height distribution in the mesosphere of the main negative ions, O₂⁻, O⁻, CO₃⁻ and NO₃⁻. It is seen that variations of ozone concentration lead to redistribution of the ion species abundances. A decrease of O₃ concentration in the mesosphere strongly reduces the efficiency, $B(O_2^-)$, of Reaction (8a) forming CO₃⁻ ions. In the model with low $[O_3]$ (O₃-profile 5), the number density of O₂⁻ ions

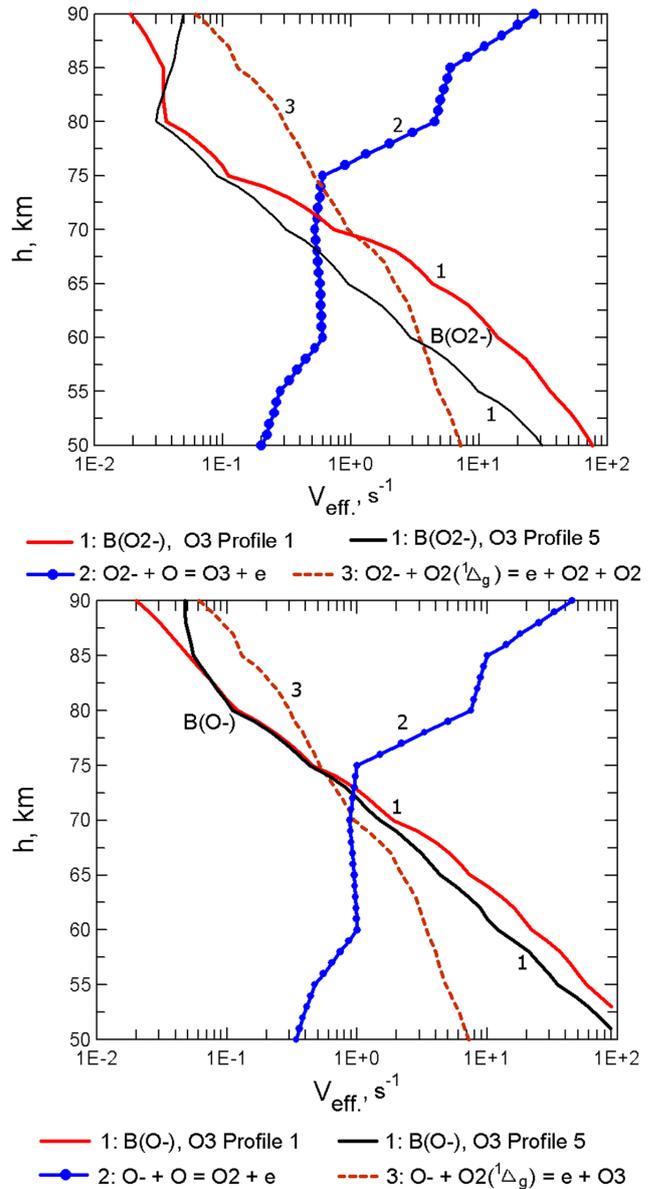


Fig. 5. Upper panel: height profiles of the efficiencies of the reactions which lead to losses of the O₂⁻ ion. Lower panel: height profiles of the efficiencies of the reactions which lead to losses of the O⁻ ion. Curves 1 are efficiency of the channels $B(O_2^-)$ and $B(O^-)$ for the O₃-profile 1 and 5. Curves 2 and 3 are efficiencies for reactions which do not produce negative ions.

at altitudes below 70 km is higher, but $[CO_3^-]$ and $[NO_3^-]$ are lower than in the model with high $[O_3]$ (O₃-profile 1).

Figure 6 (lower panel) shows the height distribution in the mesosphere of the main positive molecular ions, O₂⁺, NO⁺, and clusters, CL1⁺, CL2⁺, computed for the O₃-profiles 1 and 5. Hydrated clusters in the form of O₂⁺.X and NO⁺.X, with recombination coefficient $\alpha \sim 2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$, are combined into a Cluster₁⁺ family (CL1⁺). The proton

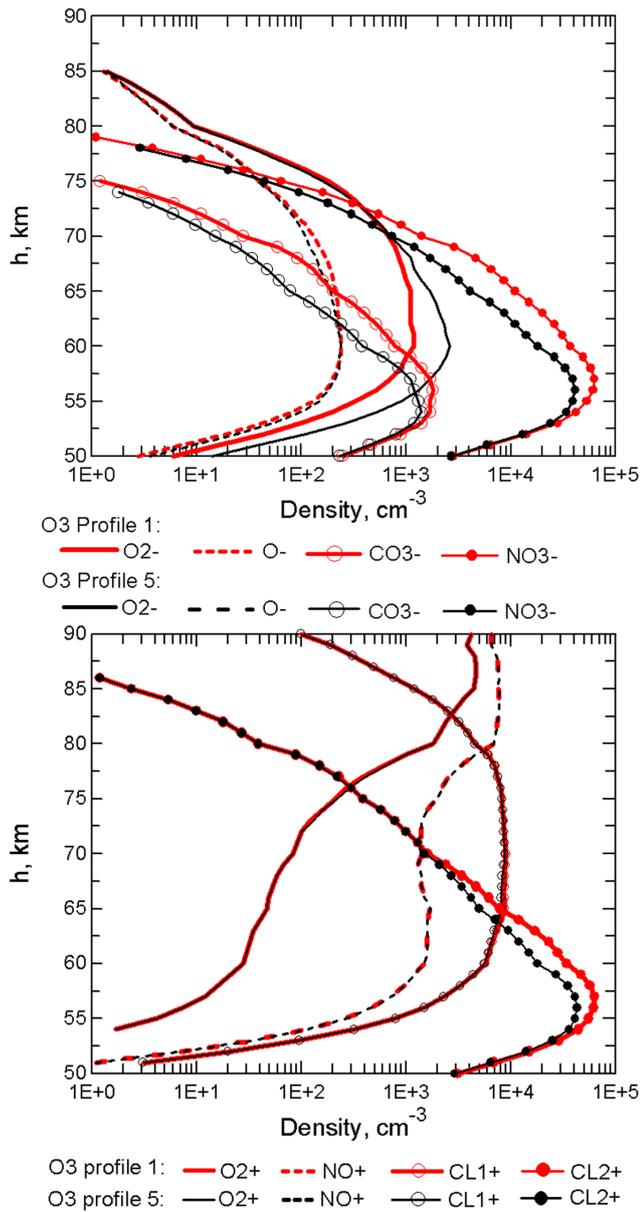


Fig. 6. Upper panel: height distribution of the main negative ions O_2^- , O^- , CO_3^- and NO_3^- for different profiles of ozone concentration O_3 -profile 1 (red) and O_3 -profile 5 (black). Lower panel: height distribution of the main positive molecular ions O_2^+ , NO^+ , and clusters $CL1^+$, $CL2^+$, computed for the O_3 -profiles 1 (red) and O_3 -profile 5 (black).

hydrates, which are created from $CL1^+$, are combined into a Cluster $_2^+$ family ($CL2^+$) with $\alpha \sim 1 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$. It is seen that a decrease of $[O_3]$ by an order magnitude does not affect the number density of ions $CL1^+$, NO^+ and O_2^+ and only very slightly influences $[CL2^+]$ below 68 km. Cluster ions dominate over the simple molecular ions NO^+ and O_2^+ up to 79 km altitude in all cases. The concentration of the cluster

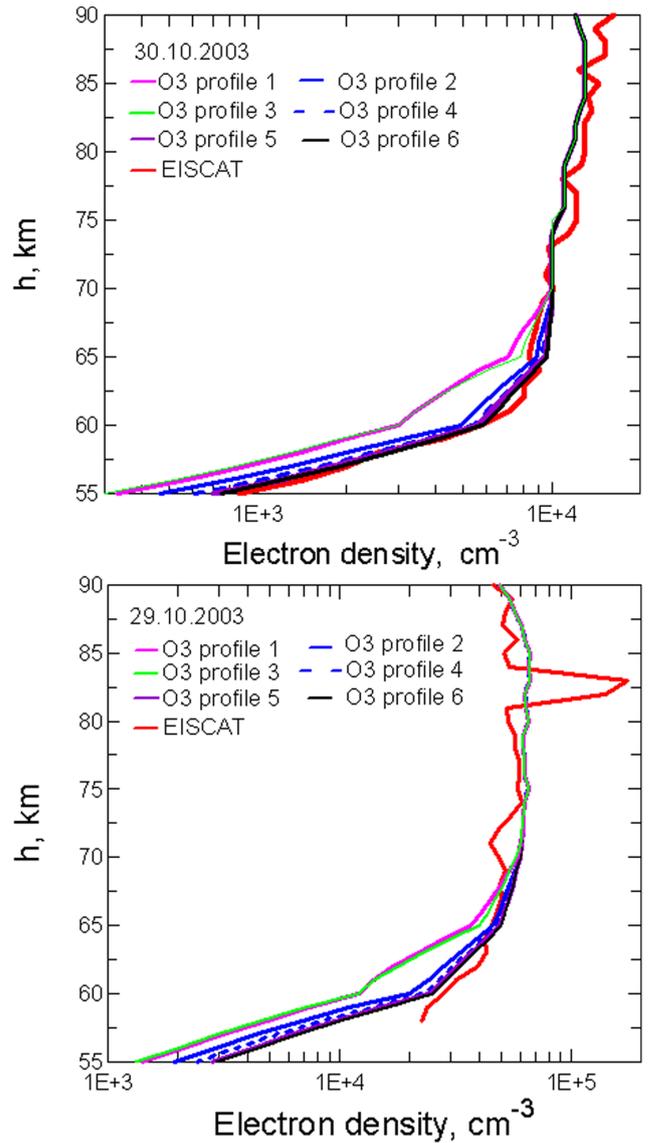


Fig. 7. Upper panel: The effect of different ozone concentrations (O_3 -profiles 1–6) on the theoretical value of electron density at different altitudes for the SPE on 30 October 2003 at solar zenith angle 83.2° . Lower panel: The effect of different ozone concentrations (O_3 -profiles 1–6) on the value of theoretical electron density at different altitudes for the SPE on 29 October 2003 at solar zenith angle 82.8° . Red curves are experimental (EISCAT) electron density profiles.

ion family, $CL1^+$, is almost constant inside the height interval 57–78 km and then, above 78 km, it decreases rapidly as a result of the decrease in the water vapour concentration. Under SPE conditions (high $[NO]$), the major ion at altitudes above 79 km is NO^+ . The cluster ion family $CL2^+$ dominates at altitudes below 63–62 km.

Figure 7 shows the influence of the ozone concentration on the value of electron density at the different altitudes in

the mesosphere. The theoretical N_e -profiles have been calculated on the basis of the O_3 -profiles 1–6. Results of the calculations are presented for the SPE on 30 October 2003 at 10:00 UT, solar zenith angle (χ)=83.2°, (upper panel), and on 29 October 2003 at 10:00 UT, χ =82.8°, (lower panel). First of all note that differences in the O_3 concentration observed at altitudes above 70 km are not reflected in the value of electron density in the upper mesosphere. Effects of $[O_3]$ on the electron density occur only in the lower mesosphere where negative ions play the main role in the ionization balance. Maximum changes of N_e take place in the height range 55–65 km. Here a decrease of $[O_3]$ by about an order of magnitude (O_3 -profiles 1–4) causes enhancement of the electron density by a factor ~ 1.5 –2. The maximum deviations in $[O_3]$, between our hypothetical O_3 -profile 4 and the O_3 -profile 5 taken from the neutral chemistry model by Swider and Keneshea (1973) and the O_3 -profile 6 from Weeks et al. (1972), are about a factor 2 and a factor ~ 4.5 , respectively. It is seen that they do not lead to such large differences in the value of N_e . The maximum changes in N_e are a factor 1.2 or less.

Over the SPE period 28–30 October 2003, the most intensive fluxes of solar protons were measured on 29 October between 05:00 UT–12:00 UT. It can be seen in Fig. 8 (black curves) that the measured values of cosmic noise absorption, A_M , differ very strongly between 29 and 30 October. A_M is the absorption measured by the vertical beam of the 38 MHz IRIS riometer at Kilpisjärvi, ~ 100 km SW of EISCAT, scaled to 30 MHz by multiplying by the factor $38^2/30^2$. Red curves show absorption at 30 MHz calculated on the basis of experimental (EISCAT) N_e -profiles, A_E .

Absorption is calculated using the Appleton-Hartree formula deduced from classical magneto-ionic theory:

$$A = 0.46 \int \frac{N_e(h)v_{ef}(h)}{(\omega \pm \omega_L)^2 + v_{ef}^2(h)} dh \quad (7)$$

where ω is the angular frequency of the radiowaves, $\omega_L = \Omega_e \cos \vartheta$, where Ω_e is the electron gyro-frequency, ϑ is the angle between the wave vector and geomagnetic field line, N_e is the electron density at the altitude h , $v_{ef}(h)$ is the effective collision frequency of electrons with neutral particles. We use a radiowave frequency of 30 MHz since this is a common standard for riometers and allows easy comparison with other publications.

For $v_{ef}(h)$ we use the expressions deduced by Banks (1966) from the measurements results of electron cross sections for momentum transfer with the neutral particles of the atmosphere (N_2 , O_2 , O):

$$v_{ef} = v(N_2) + v(O_2) + v(O) \quad (8)$$

$$v(N_2) = 2.33 \times 10^{-11} \cdot [N_2] \cdot (1 - 1.21 \times 10^{-4} T_e) \cdot T_e \quad (9a)$$

$$v(O_2) = 1.82 \times 10^{-10} \cdot [O_2] \cdot (1 + 3.6 \times 10^{-2} \cdot T_e^{1/2}) \cdot T_e^{1/2} \quad (9b)$$

$$v(O) = 2.8 \times 10^{-10} \cdot [O] \cdot T_e^{1/2} \quad (9c)$$

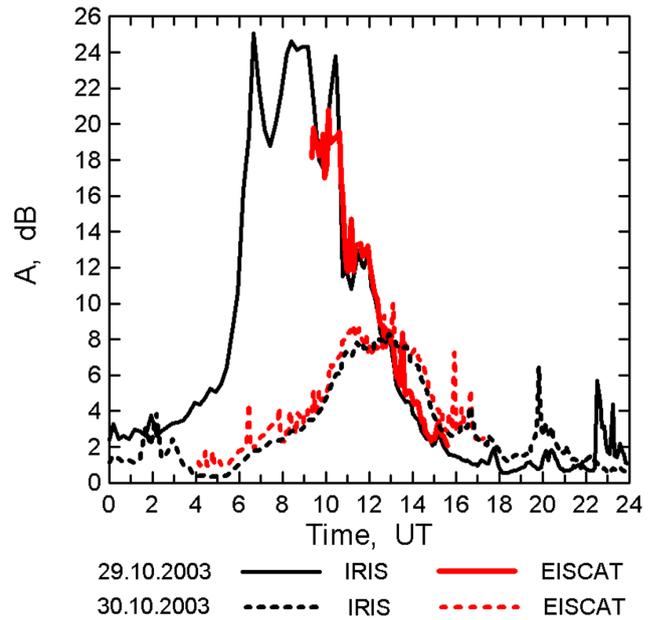


Fig. 8. Comparison of time series of the measured values of cosmic noise absorption from the IRIS riometer at Kilpisjärvi (black curves) with absorption calculated on the basis of experimental (EISCAT) N_e -profiles (red curves). The solid lines are on 29 October 2003, the dashed lines are on 30 October 2003. Absorption is given for a frequency of 30 MHz.

where $[N_2]$, $[O_2]$, $[O]$ are concentrations of N_2 , O_2 molecules (from the NRLMSISE-00 model of the neutral atmosphere, described by Picone et al., 2002) and of the atomic oxygen O (for SPE -from Osepian et al., 2008). Under condition of the thermal equilibrium ($T_e = T$) the expressions (Eq. 8 gives values of $v_{ef}(h)$ very close to

$$v_{ef}(h) = 2.5v_m(h) \quad (10)$$

where $v_m(h)$ is expressed by Thrane and Piggott (1966) in terms of the atmospheric pressure P :

$$v_m(h) = 6.38 \times 10^5 \cdot P(h) \quad (11)$$

Note also that for the cases which we consider, at 10:00 UT, the values of A_M and A_E almost coincide ($A_M = 17.4$ dB, $A_E = 17.8$ dB on 29 October 2003; $A_M = 4.5$ dB, $A_E = 5.0$ dB on 30 October 2003). Therefore in Fig. 7 we compare our theoretical N_e -profiles with N_e -profiles measured by the incoherent scatter method to find which O_3 -profile best represents the SPE conditions. At 10:00 UT on 30 October, ionisation rates (Fig. 9) and electron densities were much smaller than at the same time on 29 October. In both cases model N_e -profiles based on the O_3 -profiles 4, 5 and 6 match each other and are close to experimental values of electron density at all mesospheric altitudes.

In Fig. 10 we show N_e -profiles measured and calculated for other ionization rates and zenith angles (30 October 2003, 09:00 UT, $\chi = 84.6^\circ$ upper panel; 12:30 UT, $\chi = 85.8^\circ$ lower

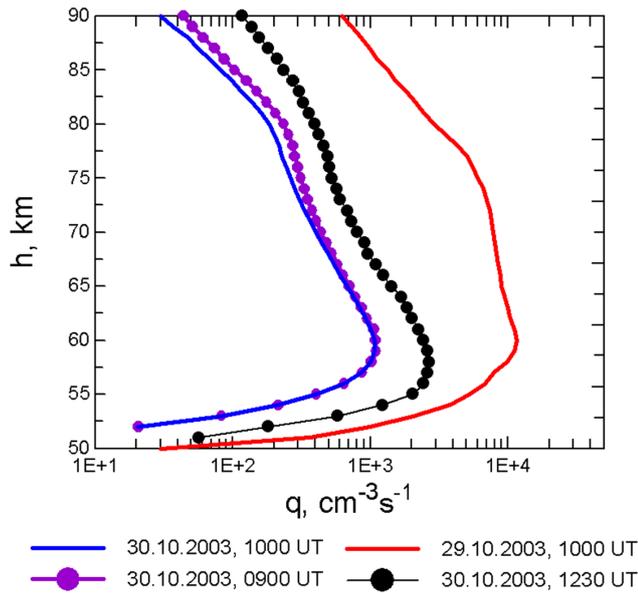


Fig. 9. Comparison of the ionisation rates on 29 October at 10:00 UT and on 30 October at 09:00, 10:00 and 12:30 UT.

panel) using O₃-profiles 1, 4, 5 and 6. In these cases it is also seen that there is good agreement between experimental and model N_e -profiles for O₃-profiles 4, 5 and 6.

It is clear that very large ionization rates in the lower ionosphere caused strong ozone destruction. Concentrations of ozone consistent with the measured electron densities during the SPE on 29–30 October 2003 are low compared to available O₃-profiles during quiet conditions, both those measured and those deduced in diffusion-photochemical models. The O₃-profile 4 in Fig. 1 represents the maximum values of [O₃] in the autumn noon mesosphere needed for reproduction of experimental N_e -profiles in conditions of strong solar proton precipitation.

Figure 11 shows changes in the O₃ concentration with changes in solar zenith angle, as used in our model calculations. The O₃-profile 4 (local noon and $\chi < 86^\circ$) is shown here by the red line. Our computations of electron density at other zenith angles ($87^\circ < \chi < 95^\circ$) have also shown good agreement between model and experimental values.

4 Conclusion

We have examined the influence of the ozone concentration on the height distribution of ion composition and electron density in the mesosphere during the SPE on 29 and 30 October 2003. Variations of [O₃] primarily affect the negative ion chemistry. The efficiencies, $B(\text{O}_2^-)$ and $B(\text{O}^-)$, of the reactions forming intermediate negative ions, O₃⁻, O₄⁻, CO₄⁻, CO₃⁻, from primary negative ions O₂⁻ and O⁻ depend on O₃ concentration at altitudes below 75 km. This dependence is stronger for path (3.5a), i.e. $B(\text{O}_2^-)$.

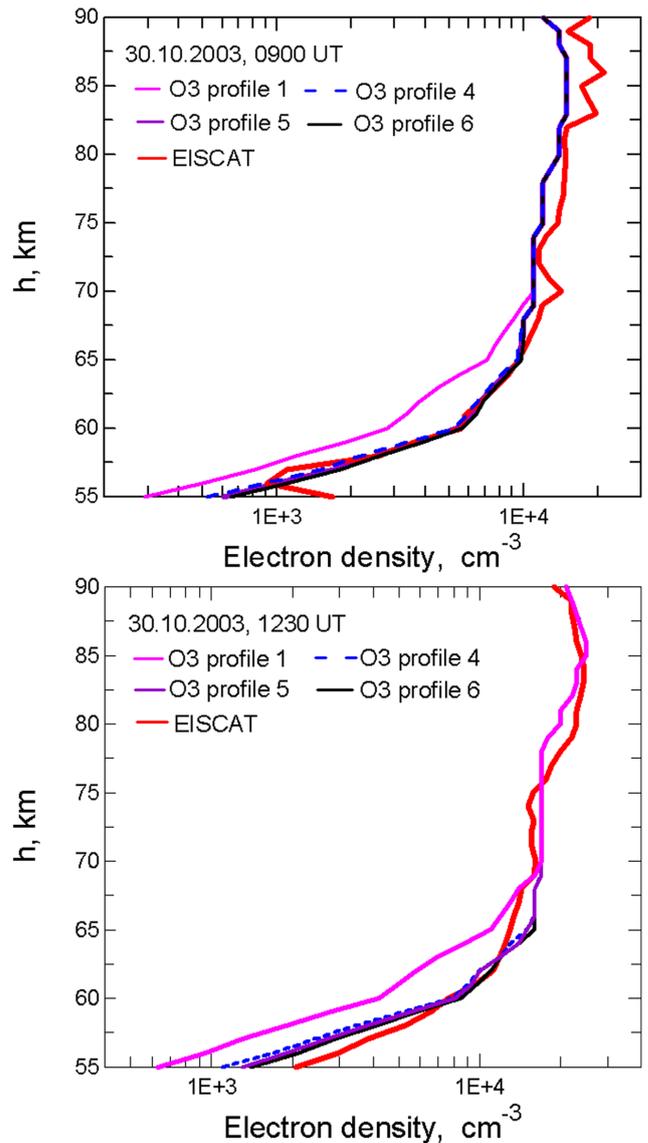


Fig. 10. Upper panel: electron density profiles measured and calculated on 30 October 2003 at 09:00 UT for zenith angle 84.6° . Lower panel: electron density profiles measured and calculated on 30 October 2003 at 12:30 UT for zenith angle 85.8° . The O₃-profiles 1, 4, 5 and 6 are used to obtain the modeled profiles.

In the model with low [O₃], the probability of production of intermediate ions from O₂⁻ ions is much smaller than in the model with high [O₃]. Moreover, the boundary, h_B , of the region where O₂⁻ ions participate mainly in the production of complex negative ions, drops with decreasing [O₃] from $h_B \approx 68$ km to $h_B \approx 58$ km if [O₃] decreases by an order of magnitude. Above h_B the losses of O₂⁻ ions occur due to the high efficiencies for reactions of O₂⁻ with excited oxygen O₂(¹ Δ_g) and atomic oxygen, which results in enhancement of the electron density. In our model computations, the path

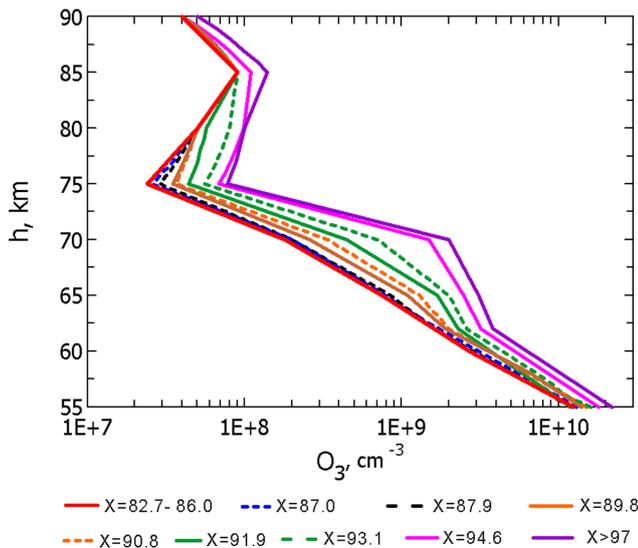


Fig. 11. Height profiles of the O_3 concentration as a function of the solar zenith angle. The O_3 -profile 4 (local noon and $\chi < 86^\circ$) is shown by the red line.

(4b), forming intermediate negative ions from O^- ions, is more effective than the path from O_2^- ions, $B(O^-) > B(O_2)$, and this path dominates up to $h_B \approx 73$ km, even in the model with low $[O_3]$. At $h > 73$ km, O^- ions rapidly disappear through the reaction of associative detachment with atomic oxygen.

Thus variations of ozone concentration lead to redistribution of the negative ion species abundance. In the model with low $[O_3]$, the number density of the O_2^- ions is higher, but $[CO_3^-]$ and $[NO_3^-]$ are lower than in the model with high $[O_3]$. As a result at heights below 70 km, the total number density of negative ions decreases and electron density increases. The maximum changes of N_e take place within the height range 55–65 km.

Comparison of electron density profiles calculated by our numerical model, with the N_e -profiles measured by the EISCAT incoherent scatter radar during the strong SPE on 29–30 October 2003, have given us the possibility to find which O_3 -profiles (at local noon and at zenith angles $87^\circ < \chi < 95^\circ$) are consistent with experimental N_e values. The result is presented in Fig. 11. It should be noted that the noon O_3 -profile 4, which we find is needed for an adequate fit to the experimental N_e values during the very strong SPE on 29–30 October 2003, is close to the O_3 -profile deduced for full daytime in the neutral chemistry model by Swider and Keneshea (1973) and used by Swider et al. (1978) in the ion-chemistry model for the strong SPE during 2–5 November 1969. Deviations in $[O_3]$ concentration between our study and Swider and Keneshea (1973), by about a factor 2, would result in changes of electron density less than 5–10%. Further decrease of the O_3 concentration would not lead to a noticeable effect on the ionization balance in the lower ionosphere.

Note also that the effects of the SPE-related O_3 concentration depletion on the height distribution of ion and electron density occurs only in the lowermost part of the ionosphere, below 70 km. This is different from the effect of atomic oxygen concentration which influences electron densities at all mesospheric altitudes (Osepian et al., 2008).

Summarizing, we have shown that reasonably accurate information on the height profile of the minor neutral constituent ozone is necessary for accurate modelling of the effective recombination coefficient, and hence the electron density profile, in the lower part of the D-region where negative ions dominate. We have shown that an ozone profile corresponding to strong depletion is needed to give model N_e -profiles consistent with observations during the strong SPE on 29–30 November 2003. Mesospheric ozone depletion was observed directly during this event (Rohen et al., 2005) and is likely a common feature of reasonably strong SPE. Simple incorporation of minor neutral constituent profiles (NO , O and O_3), appropriate for SPE conditions, into ion-chemistry models will allow more accurate modeling of electron and ion densities during such events, without the need to apply a complete chemical model calculating all neutral species.

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