Session 3

Atmosperic Ozone

INITIAL OZONE CREATION MECHANISM IN OXYGEN INCLUDED MIXTURES UNDER KrF LASER EXCITATION.

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The aim of this work is investigation the initial ozone creation mechanism in pure oxygen and its mixtures with inert gases under excimer KrF laser irradiation.
The high pressure kriostats with 1-3cm path length and fluorit windows were used in these experiments. Excitation had been coused by generating pulses of KrF laser (wavelength 248nm, pulse energy 60mJ, duration 10ns, repetition rate under 100Hz). For the investigation of ozone creation phenomena spectral dependence the excitation by the 1st antistokes Raman component of the KrF laser radiation in compressed hydrogen (wavelenth 223nm) was used.
The main results are: measurement of the ozone creation rate dependence on gas pressure and temperature in compressed oxygen , made with two defferent wavelength let conclude that in this case initial ozone creation mechanism is caused by skattering dissociation of oxygen molecules, which is excited from ground state by absorption in the Hertzberg transition.

MEASUREMENTS OF SURFACE AND BOUNDARY LAYER OZONE DURING VARIOUS METEOROLOGICAL CONDITIONS USING VARIOUS METHODS

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Ozone vertical profile measurements on Kola peninsula are presented. The data have been obtained using tetherd balloons up to altitudes of about 0.5 km, tethered sondes up to 120 m and mountainous relief up to 1 km. The observations have been performed at various meterological conditions and seasons. The possibilities of each method are considered.

RECORD OZONE MINIMUM OVER MIDDLE AND HIGH LATITUDES OF THE NORTHERN HEMISPHERE DURING THE WINTER-SPRING SEASONS 1991/92 AND 1992/93

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During the past two winter-spring season total ozone over Europe mad America between 45°N and 65°N reached record minimum values. Ozone deficiencies ranged between about 10% and 12% below the long-term normal and the cumulative ozone decline since winter-spring of 1969/70 was about 14%. Moreover, the number of days in these seasons with ozone values deviating below the long-term mean, beyond statistical expectation, was ten times higher compared to the mean of the pre-1990 period. As to the causes there is evidence that transport of ozone-poor air masses originating from lower latitudes and forced by vertical motions as well as cold air advection (known to have excess ClO content which moved over sun lighted regions, can account for most of the observed low-ozone cases. Both the rates of decline and the prevailing low ozone values, did not reach or even approach the extreme phenomena describing the Antarctic spring ozone hole.

NUMERICAL ESTIMATION OF PERMISSIBLE LEVEL OF THE BACKGROUND AND THE SHAPE OF THE NARROWBAND INTERFERENCE UV LIGHT-FILTERS TO ENSURE A HIGH ACCURACY OF A MEASUREMENT OF ATMOSPHERIC OZONE BY FILTER OZONOMETERS

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The problem is solved by means of model calculations on the electronic computer of the mean (integral) coefficients of ozone absorption for filters with the different spectral transmissions. It was convenient to use this coefficient since it is the parameter that ultimately determines the accuracy and sensitivity of the operation of the instrument. All the necessary spectral functions are taken into account to determine the effective spectral sensitivity of the ozonometer (ESS). As a result of our investigation the following conclusions can be made: the transmission beyond the basic band of the UV filters must not be higher than 10^{-4}-10^{-5} of the transmission in the maximum. In this case ESS remains features of the narrowband system for different measurement conditions. In the other case ESS loses the narrowband features and has a small sensitivity in UV spectral range. That investigation and our earliest works permit to indicate the well-grounded numeral values of all basic spectral parameters for interference light-filters which can be used for accuracy measurement of ozone. Results of measurements of atmospheric ozone by filter ozonometer are discussed in this work too.

COMPARATIVE STUDIES OF OZONE GAS ANALYZERS IN REFERENCE TO THE PROBLEMS OF ATMOSPHERIC MONITORING

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Here are layed out comparative technical data of ozone gas analyzers, which are produced and operate nowadays in Russia and CIS countries for ozone concentration measurements in lower troposphere. Some special features of using of chemiluminescent, optical and electrochemical ozone analyzers are discussed. The recommendations on application of above devices are offered.

OZONE DISTURBANCE BY INTERNAL GRAVITY WAVE AND POSSIBLE OBSERVATION APPEARANCE IN MICROWAVE SOUNDING

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A mechanism of atmospheric ozone disturbance by internal gravity wave (IGW) in a stratified shear flow is proposed. The amplitude and period of ozone density oscillations are found in the vicinity of the critical layer, where the phase velocity of the wave is equal to flow velocity, in the case when the flow pattern near the critical layer is determined by nonlinearity, and viscosity effects are small. It is shown that for reasonable shear flow and IGW parameters the density variation of passive admixtures can be comparable with unperturbed value and the characteristic period of density oscillations is of order of few hours. The numerical estimates of ozone density disturbances and corresponding changes in ozone absorption line observed by millimetre ground-based technique for moderate IGW parameters are presented and compared with experiment.

VARIATIONS IN THE STRATOSPHERIC OZONE IN THE SCANDINAVIAN SECTOR OF THE ARCTIC DURING THE AASE CAMPAIGN AND 1989

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The Airborne Arctic Stratospheric Expedition (AASE) carried out measurements from Jan.3 to Feb.15, 1989. Enhanced levels of chlorine compounds were found in the Arctic stratosphere, and on two single flights ozone decrease of 17% were measured, interpreted as essential features of the Arctic stratosphere, caused by a combined effect of enhanced amounts of chlorine compounds and presence of polar stratospheric clouds. Related model calculations also indicate extended ozone depletion maximizing in late March 1989 and amount to 5-8% in column at 70°N. Ground based ozone measurements, however, show that the most characteristic features during this period are temporal variations and a strong enhancement of ozone, probably due to an extended stratospheric warming. From these measurements it is hard to see any effect of an eventual enhanced burden of stratospheric chlorine, which might show up as an extended and long-lasting decrease of stratospheric ozone, but its eventual existence is masked by the temporal variations.

ESTIMATION OF INFLUENCE OF AEROSOL SINK ON THE LATITUDE DISTRIBUTION OF TROPOSPHERIC OZONE

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The effect of photocatalytic aerosol sink of ozone on ozone latitude concentration profile was estimated from the know one-demensional photochemical model for troposphere. To calculate the latitude profile we used the values of effecience of ozone photocatalytice destruction from [L.S.Ivlev, L.L.Basov, V.S.Sirota, S.P.Smyshlyaev "Photostimulated aerosol sink of atmospheric ozone and methane", J.Ecol.Chem., N1, pp.79-84, 1993]. Comparison of calculated and experimental latitude profiles of tropospheric ozone for European part of the CIS shows that the best correlation between them is obtained when ozone aerozol sink is taken into account.

MICROWAVE MONITORING OF STRATOSPHERIC OZONE OVER NIZHNY NOVGOROD

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Thermal atmospheric emission were observed in spectral line f = 110836 MHz of ozone rotational transition 6(0,6)-6(1,5) above city of Nizhny Novgorod (53.3°N) during February 1992 - March, May 1993. During January - March 1993 measurements were carried out in line f = 142175 MHz of ozone rotation transition 10(0,10)-10(1,9) simultaneously. Another radiometer and different technique of observation were applied. In May 1993 this radiometer was used for ozone measurements over Kiruna (Sweden). Systematic discrepancy of the ozone content above 22 km X(z>22km) obtained from observations of these two lines was less then 10%. Systematic discrepancy of ozone profiles reached 20% for the altitude of z = 35 km. Commensurable seasonal and sporadic components of years variations of X(z>22km) were detected. The greatest sporadic variations took place in March 1992, the smallest variations were in September. In winter X(z>22km) frequently became close to values typical of the Antarctic ozone holes. The influence of the solar proton events on ozone was not manifested on the background of the sporadic component. The comparison of the obtained data and Keating-Young model shows rather good coincidence for the altitude z=50 km and discrepancy for other altitudes (up to 1.5-2.5 times at z = 40 km).

MICROWAVE OBSERVATION OF STRATOSPHERIC OZONE IN KIRUNA

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A series of measurements of stratospheric ozone emission in the line of O rotational transition at 142175 MHz was performed during May 10-22, 1993 in Kiruna (68 N) in a rather unstable weather conditions (including rains, snowfalls etc). The total time of observation during this period was about 100 hours. The experimental set-up includes mm superheterodyne receiver (SSB noise temperature about 3500°K) with conical receiving horn provided single lobe receiving antenna pattern 2 width and multichannel spectrum analyzer covering total band of analysis about 100 MHz. The observational technique gives opportunity to retrieve vertical ozone distribution in the height interval between 20 and 50 km. In the retrieval procedure the data on average temperature and pressure profiles for May 70°N from the Handbook for MAP (1985) have been used. On May 18 the results of mm measurement were compared with ozonosound ECC measurements (up to the height 35 km); a rather close agreement has been revealed in common height interval of measurements (20-35 km). The measured total ozone amount above 20 km was by 1.5-2 time lower than expected from Krueger-Minzner and Keating-Yuong models. Simultaneous measurements performed with the same technique in N.Novgorod (56 N) gave results close to these models.

STRATOSPHERIC OZONE DEPLETION OVER ANTARCTICA DURING OCTOBER 1989 EVENTS

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The depletion of stratospheric ozone was observed over Mirny station (66.5°S, 93°E) by microwave technique nealy simultaneosly with four solar proton events which take place on October 19-25 1989. The decreasing of ozone content above 25 km was also correlated with increasing of riometer absorption which achieved up to 10-20%. Several days later (November 1-5) a rather strong stratospheric ozone depletion was observed, noncorrelated with riometer absorption;to our opinion it may be also related to the same proton events. The decreasing of ozone content above 25 km was 20-30%. These results have obtained during continuous series of observations in which ozone absorption line with the rotational transition frequency 142175 MHz was registred every 25 minutes. Equipment, observation technique and retrieval procedure for vertical ozone distributions are usual and presented elsewhere.

SURFACE OZONE MEASUREMENTS WITHIN THE INDUSTRIAL CITY LIMITS DURING POLAR WINTER PERIOD

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Surface ozone measurements within the city limits are presented. Measurements have been performed by chemiluminescence ozonometer at various sites of industrial and residental areas and in the suburbs as well. The background ozone level is 15-25 ppb.Weak diurnal variation is observed. Decremental ozone concentrations in the city are in some tens of percentage in winter period. The urban plume is extented at least up to 10 km from the city limits.

CHEMILUMINESCENT SENSORS AND OZONE GAS ANALYZERS FOR ATMOSPHERIC MONITORING

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Perspective chemiluminescent ozone sensors and other devices based on chemiluminescent principle of common and specific purposes were worked out and produced during last years in the laboratories of St.Petersburg firm "Optics in ecology" ("OPTEC"). Chemiluminescent ozone sonde LB-01 is supposed to be used for the study of vertical ozone distribution in atmosphere. It operates at the height of up to 50 km. Gas analyzer of ozone microconcentrations (model 308 KI and AD-203) is supposed to be used for the measurement of ozone concentration in lower troposphere. The range of measured ozone concentration is 0,5-500 ppb (V). Time constant for such gas analyser (model AD-203) is 0,05 seconds (when ozone is measured on a background). Gas analysers were tested in 1989-1992 in Atmospheric Environment Service (Canada) on Egbert national station, in Russia, in Kislovodsk and Zelenograd stations of atmospheric monitoring (Academy of Sciences of Russia) and during some international expeditions in Antarctics and North Atlantics.

THE POLAR STRATOSPHERIC OZONE "MINI-HOLES" AND INCREASE OF BIOLOGICALLY ACTIVE UV IN ARCTIC DURING PERIODS OF SOLAR COSMIC RAY EVENTS.

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It is shown that Solar Proton Events of Ground Level Event (GLE) type sometimes cause the ozone total content depletion up to 30%. At the events the area of ozone depletion covers the polar cap mainly in spring hemispheres. This effect is especially dangerous for biological objects in the Nothern hemisphere where many peoples live and work far inside the polar cap. Forbush decreases of galactic cosmic rays (GCR) as well sometimes influence on ozone total content and during "pure" FD (without GLE) can increase the total ozone content (up to 10-15%). When FD and GLE take place simultaneously they could compensate their influence on stratospheric ozone. It is the solar protons in energetic range from 30 to 130 MeV seem to trigger the appearance of ozone "mini-holes" during "pure" GLE events (without Forbush decreases) under favourable conditions for creation of Polar Stratospheric (and aerosol) Clouds. These processes should be considered in terms of temperature balance variations and heterogeneous chemical processes including creation and destroying of aerosol clouds (or Polar Stratospheric Clouds) in the lower atmosphere. There considered variations of UV-B radiation in Arctic during periods of solar cosmic ray events.

ON THE GLOBAL MONITORING OF THE TOTAL OZONE IN THE EARTH ATMOSPHERE.

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Total ozone measurements in the Earth atmosphere from 1924 are discussed. Total ozone averaging data from surface stations for the belt of $30^{o}N$-$60^{o}N$ are in agreement with the last variant (N 6) of TOMS data. For the calibration of cosmic measurements a surface calibbration grid is proposed with disposition along the 30 E meridian and the 19 parallel.

MEASUREMENTS OF SURFACE OZONE IN TROMSO, USING AMERICAN AND RUSSIAN TYPE OZONOMETERS

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Surface ozone measurements are running at The Auroral Observatory, Tromso. In this report measurements throughout the period Nov.17, 1992 to Jan.11, 1993 are given. No diurnal variations can be seen, probably due to the lack of sunlight during the polar night. However, peculiar ozone decreases occur normally during day time when substantial traffic exists in the nearby town, and is considered that the ozone is depleted through reactions with pollutants such as nitric oxides and hydro carbones.
The American ozonometer has provided its reliability through world-wide use, and the Russian ozonometer gives almost identical results. In addition the Russian ozonometer is most usefriendly. The Russian ozonometer is still under development, and our device is a prototype made for testing.

THE PHYSICS OF THE LAMINATION EFFECT IN THE VERTICAL OZONE PROFILES

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The laminar structure in ozone profiles has been first reported thirty years ago and it is characterized by enhanced and depleted ozone layers, especially in the lower stratosphere. In very recent papers laminae were categorized according to their vertical extend (depth), as well as the change in ozone partial pressure inside them (magnitude), using certain criteria to separate genuine laminar features from instrumental noise or large-scale features in the ozone profiles. In this work the investigation of the physical mechanisms which can contribute to the lamination structure of the vertical ozone profiles, is mainly attempted. Furthermore, the identification of the stratosphere-troposphere exchange by exploiting the total-ozone field as deduced from satellite observations, is investigated.

AN IMPACT OF TOTAL OZONE VARIATIONS ON TROPOSPHERIC CARBON MONOXIDE AND METHANE

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Carbon monoxide total column amounts were measured spectroscopically near Moscow in 1971 - 1992 and in Antarctica in 1977 - 1992. In 1970s CO content increased with the time for all the seasons. During the spring months in the Northern Hemisphere a diminution of CO content from year to year after 1982 took place. In the winter months CO contents were rising with the rate of 1 to 2% per year, summer values of CO content were stable after 1982 until now. In Antarctica CO varied in phase with total ozone. It has been noted by many researchers that a slowing down of the methane concentration increase was going on globally during 1980s. These gases have the common chemical sink: a reaction with OH. An increase of concentrations of this tropospheric radical can explain both effects. The OH increase can be associated with total column ozone diminution being observed globally last decade and with an increase of UV radiation. In the report the recent observational data on ozone, methane and carbon monoxide in both hemispheres are presented and/or analyzed.

STRATOSPHERIC WATER VAPOUR MEASUREMENTS WITH BALLOON FLUORESCENT HYGROMETER AT KIRUNA DURING EASOE.

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Optical hygrometer measures in situ water VAPOUR concentration using technique of photofragment (OH) fluorescence during night time. Dissociation of water VAPOUR is provided by VUV krypton lamp (123.6nm). Fluorescence from the electronically exited OH fragments of the air sample near the focus of the optical system is collected by it and detected by photomultiplier which is situated behind the lamp. Total weight of hygrometer is no more than 3 kg and it was used on the main scientific gondola as a "piggy back". Two successful balloon flights for different position of polar vortex were carried out on December 12, 1991 and February 10, 1992. The process of dehydratation has not been observed. The minimum values of water VAPOUR mixing ratio for both flights was 3.2 ppmv. The altitude level of hydropause was 1-2 km higher than tropopause. A slight increase of mixing ratio with altitude up to 6 ppmv at the 25 km level was marked. The measured fine structure in vertical water VAPOUR profiles could be reflection of wave processes (gravity waves) at this altitudes. The calculations based on the Hanson and Mauersberger relationship confirmed that the conditions (temperature and water VAPOUR concentration) for polar stratospheric clouds formation were not suitable in this days.

BALLOON INVESTIGATION OF THE STRATOSPHERIC OZONE AND AEROSOL IN THE ARCTIC REGION DURING EASOE CAMPAIGN.

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Balloon backscattersondes and ECC ozonesondes at polar stations Dikson Isl (73N, 81E), Heiss Isl (81N, 58E), Kiruna (68N, 20E) during EASOE from December 1991 to March 1992 were used. The temperature conditions in the stratosphere were not favorable for PSC's (type1 or type2) formation but stratospheric aerosol (SA) loading was enhanced more than 10 times due to the influence of Pinatubo eruption. Significant amount of SA had been transported to the Arctic before the polar vortex was well developed. Based on simulteneous measurements of backscatter ratio (r) and ozone it was found that strong anticorrelation between aerosol loading and ozone concentration in the lower stratosphere in winter and spring occured if the values of the **r** were more than 8 - 10 (at a 940 nm wavelength). In comparision to the backqround aerosol level in Arctic region a 100 - fold increase of the total surface of aerosol particles in the lower stratosphere (15 - 18 km) was observed. Additional ozone losses could occur due to heterogeneous reactions on volcanic aerosols. Ozone concentration in the lower stratosphere was decreasing concurently with the appearence of dence volcanic layers. At high latitude total ozone was lower than climatic values only at the end of winter 1991-92.

OZONE TOTAL CONTENT VARIATIONS ON POLAR LATITUDES IN RELATION TO SOLAR ACTIVITY AND GEOMAGNETIC DISTURBANCES

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In this work we investigate the relationship between total ozone content and solar activity and geomagnetic disturbances. The research is conducted using extensive data set of polar ozonometric stations of Russia for the period 1972-1988. We use data from 12 stations of the latitude range 64'35 N to 80'37 N. This latitude range is splitted into three zones: polar cap, auroral zone, sub-auroral zone. We choose mid-latitude station Leningrad as a base one. Seasonal run of the total ozone content versus geomagnetic disturbances (AE-index) and solar activity (Wolf numbers) is constructed for all zones mentioned above.