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Proceedings of International Conference "Atmosphere, ionosphere, safety" (AIS-2023) include materials reports on: (1) — response analysis of the atmosphere — ionosphere to natural and manmade processes, various causes related geophysical phenomena and evaluate possible consequences of their effects on the human system and process; (2) — to study the possibility of monitoring and finding ways to reduce risk. Scientists from different countries and regions of Russia participated in the conference. Attention was given to questions interconnected with modern nanotechnology and environmental protection. Knowledge of the factors influencing the atmosphere and ionosphere can use them to monitor natural disasters and to establish the appropriate methods on this basis.

Content of the reports is of interest for research and students specializing in physics and chemistry of the atmosphere and ionosphere.

ELEMENTARY PROCESSES IN THE UPPER ATMOSPHERE AND IONOSPHERE

MECHANISMS OF OZONE INTERACTION WITH MODEL AEROSOLS

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Ozone transformations in heterogeneous processes are of significant interest due to the problems of ozone layer protection and water purification from organic contaminants. Despite that, only few works deal with ozone adsorption studied by IR spectroscopy so far (see [1] and references therein). Here we summarize the results obtained in our group concerning the mechanisms of ozone adsorption and ozonolysis of adsorbed molecules studied by low-temperature FTIR spectroscopy [2] and modeled by DFT calculations. It was established that photoreactions of ozone in the atmosphere are sensitive to isotopic composition of oxygen [3], and it is not excluded that our recent data on resonance vibrational excitation of adsorbed ozone for isotope separation [4] have something to do with the heterogeneous processes in the atmosphere, that is why we report here also some of these results.

Figure 1 shows the band of ν_{1+3} combination vibration of usual and ^{18}O -enriched ozone adsorbed on silica (aerosil), studied in [5]. Symbols near the components denote the isotopic composition, e.g. 668 means that the molecule contains two atoms of ^{16}O and one ^{18}O , which here is in terminal position. One can see that the band of isotopically mixed ozone is split into six components grouped in two triplets, which belong to molecules with central atoms either ^{16}O , or ^{18}O . This means that in this case of weak adsorption the molecule keeps its symmetry, and two terminal atoms remain equivalent or almost equivalent. This is not a case for ozone chemisorbed on CeO_2 [6] or TiO_2 [7,8], where chemisorbed ozone was shown to be bound via terminal oxygen atom and the molecule is not symmetric anymore.

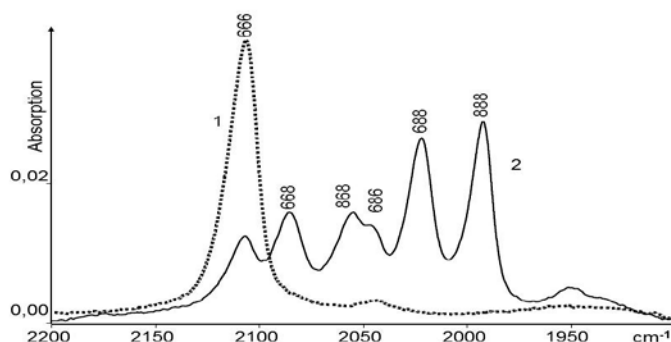


FIGURE 1. IR spectrum of SiO_2 pretreated at 923 K after adsorption of $^{16}\text{O}_3$ (1), and isotopically mixed ozone with 67% of $^{18}\text{O}_3$ (2) at 80 K.

Figure 2 shows the deconvoluted spectrum of isotopically mixed ozone chemisorbed on TiO₂, where the same ν_{1+3} band is split in 8 components, as it should be if the shifts caused by substitution of each atom are different. While the bands at highest and lowest wavenumbers corresponding to ¹⁶O₃ and ¹⁸O₃ have for the used enrichment value (43%) the highest and lowest relative intensities, the remaining two groups of bands with intensities 0.17 - 0.13 and 0.10 - 0.09 (the shares of total integrated intensity of the band) belong to molecules containing 1 or two atoms of ¹⁸O isotope.

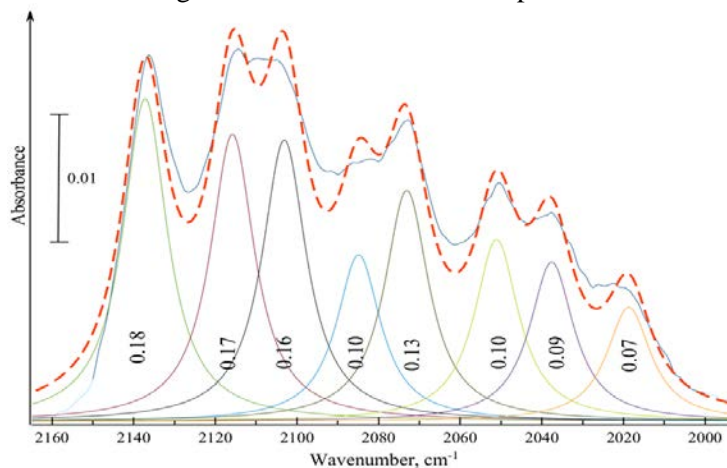


FIGURE 2. The band of ν_{1+3} combination of ozone (43% of ¹⁸O) chemisorbed on TiO₂ (solid curve) represented by a sum of 8 Gaussians (dashed line). Figures inside of each Gaussian indicate its relative area. From ref. [8].

DFT calculation of models of titania clusters with chemisorbed ozone bound to coordinately unsaturated Ti⁴⁺ cations reproduces well the structure of the ν_{1+3} band, as seen from the Fig. 3, although the exact positions of the bands is not reproduced, and the distance between ν_1 and ν_3 bands turns to be overestimated. This does not enable us to make a final choice between the monodentate and non-symmetric bidentate or bridged structures [8].

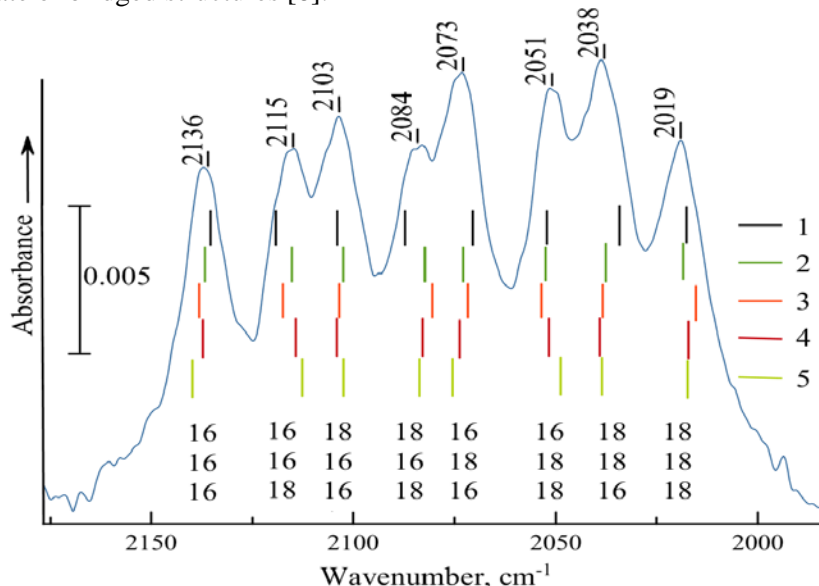


FIGURE 3. Experimental spectrum of a 50% ¹⁸O isotopic mixture of ozone chemisorbed on TiO₂ (solid curve) and the calculated frequencies of the ν_{1+3} combination mode of 8 ozone isotopomers forming a monodentate or bidentate complexes with different TiO₂ clusters (1-5). From ref. [8]

While ozone adsorbed on SiO_2 is rather stable and can be kept in the cell with the sample at ambient or low temperatures for hours or days, in the presence of TiO_2 or CeO_2 pretreated in vacuum at about 450°C , in the cooled cell the pressure increase evidences for ozone catalytic decomposition which occurs already at -196°C and accelerates on raising the temperature. On the high surface area CeO_2 the reaction can have the explosive character even at liquid nitrogen temperature as soon as the coverage is sufficient [6]. Fast reactions of ozone with coadsorbed molecules such as ethylene adsorbed on silica also start easily at -196°C [9]. With mono- or dichloroethenes ozone reacts slower, and with tetrachloroethene on titania it does not react even at ambient temperature [10]. The reaction, however, can be stimulated by UV irradiation.

High reactivity of adsorbed ozone gives us an idea that the vibrational excitation of adsorbed ozone by resonant absorption at the frequency of certain isotopologue can lead to its selective interaction with coadsorbed species or to decomposition. The attempts to stimulate selective desorption of different molecules from isotopic mixtures were not successive so far (see, e.g., ref. [11]), apparently, because of fast vibrational energy exchange in the adsorbed layer by the mechanism of resonance dipole-dipole interaction [12]. One can suppose that the rate of such a process can be lowered if we choose properly the molecule, use low surface coverages and, finally, try to stimulate the process, which is irreversible [13]. Ozonolysis reactions and its decomposition meet well the latter requirement. Attempts to stimulate ozonolysis of cis-dichloroethylene adsorbed on titania have shown that it does occur, but the bands of products overlap and are too broad to detect any isotopic selectivity.

The first results of laser-induced ozone decomposition on TiO_2 are more promising. Figure 4 shows the effect of sample irradiation at certain wavenumbers upon the intensity ratio of bands in the spectrum of adsorbed isotopically mixed ozone. Irradiation at $2030\text{--}2020\text{ cm}^{-1}$ leads to the insignificant but clearly observed changes. The relative intensity of the band at the frequency of which irradiation is performed decreases, while at irradiation outside the ozone absorption bands, the intensity ratio gradually returns to its original value, apparently as a result of the continuing adsorption of ozone.

We believe that the above data could be helpful for understanding the processes at the surface of solid atmospheric aerosol particles.

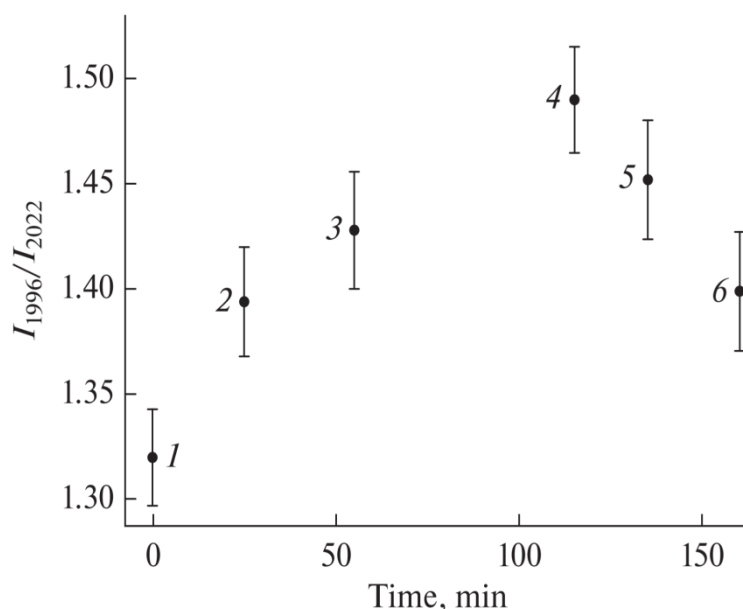


FIGURE 4. Changes in the ratio of the integral intensities of the absorption bands at 1996 and 2022 cm^{-1} in the IR spectrum of ozone on irradiation at $2030\text{--}2020\text{ cm}^{-1}$ for 0 (1), 25 (2), 55 (3) and 115 min (4) and subsequent irradiation at 2200 cm^{-1} for 20 (5) and 45 min (6). From ref. [4]

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DISSOCIATION DYNAMICS OF CH₃CHOO CRIEGEE INTERMEDIATES IN THE ATMOSPHERE OF THE EARTH

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Carbonyl oxides, also known as Criegee Intermediates, are formed during the ozonolysis of alkenes, which are the typical anthropogenic air pollutants. Initially their role in the chemistry of the Earth's atmosphere has been studied by Rudolf Criegee in the early 1950s [1,2]. Due to the presence of the biradical >C-O-O group, these compounds are chemically very active. When interacting with various substances present in the atmosphere, they produce many active substances such as OH radicals,