

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.

The band of ν_{1+3} combination vibration of isotopically mixed ozone adsorbed on silica (aerosil) is split into six components grouped in two triplets, which belong to molecules with central atoms either ^{16}O , or ^{18}O [5]. 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 any more and the same ν_{1+3} band is split in 8 components.

DFT calculation of models of titania clusters with chemisorbed ozone bound to coordinately unsaturated Ti^{4+} cations reproduces well the structure of the ν_{1+3} band, as seen from the Fig. 1, 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].

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 the pressure increase evidences for ozone catalytic decomposition already at $-196\text{ }^\circ\text{C}$. On CeO_2 the reaction can have the explosive character even at liquid nitrogen temperature as if the coverage is sufficient [6]. Fast reactions of ozone with coadsorbed molecules such as ethylene adsorbed on silica also start easily at $-196\text{ }^\circ\text{C}$ [9]. With mono- or dichloroethenes ozone re-

acts slower, and with tetrachloroethene on titania it does not react even at ambient temperature [10]. The reaction, however, can be stimulated by UV radiation.

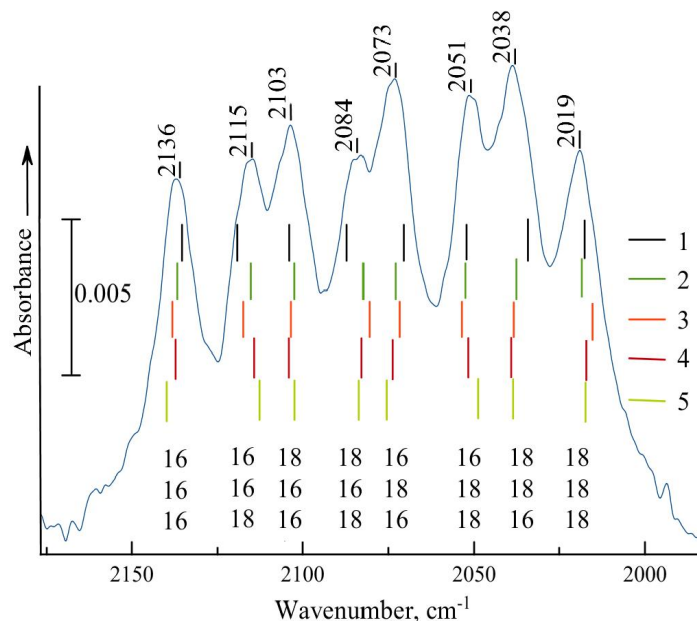


FIGURE 1. Experimental spectrum of a 50 % ^{18}O isotopic mixture of ozone chemisorbed on TiO_2 (solid curve) and the calculated frequencies of the ν_{1+3} combination mode of 8 ozone isotopomers forming a monodentate or bidentate complexes with different TiO_2 clusters (1–5). From ref. [8]

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 2 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.

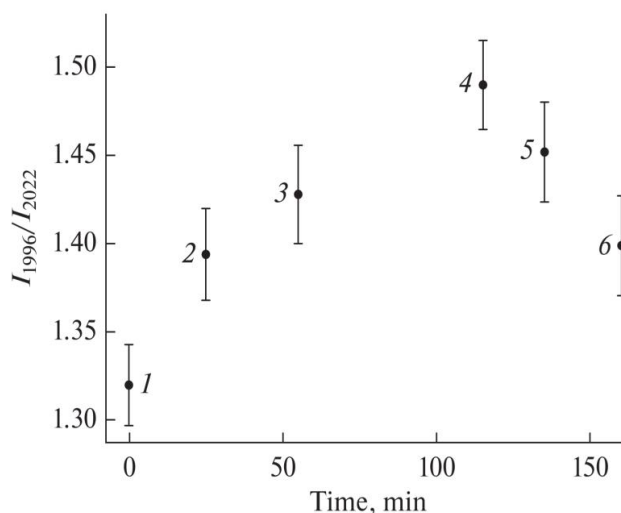


FIGURE 2. Changes in the ratio of the integral intensities of the absorption bands at 1996 and 2022 cm^{-1} in the IR spectrum of ozone on irradiation at 2030–2020 cm^{-1} for 0 (1), 25 (2), 55 (3) and 115 min (4) and subsequent irradiation at 2200 cm^{-1} for 20 (5) and 45 min (6). From ref. [4].

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

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