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Cluster Mechanism of the Atmosphere Ozone Destruction by Bromine Ions

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Abstract—Interaction of bromine ions absorbed by water cluster with adsorbed oxygen and ozone molecules has been investigated by the molecular dynamics method. It was shown that the part of O_2 molecules was removed from the system by evaporating Br^- ions, while all O_3 molecules and Br ions were kept in the system during 25 ps. The increase the concentration of the Br^- ions in the clusters resulted in a reduction of the absorption intensity and emission in IR spectra at the presence of oxygen, whereas the absorption intensity in the appropriate IR spectra of ozone-containing systems increased with the growth of a number of the Br^- ions. Raman spectra of oxygen-containing systems were poorly sensitive to the concentration of the Br^- ions but the absorption intensity of Raman spectra for systems with ozone considerably decreased with the growth of a number of bromine ions.

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The sun rays consist of the visible spectrum, and rays invisible to our eyes, such as, infra-red (IR) and ultraviolet (UV) ones. A necessary condition for normal life is getting a wave with a length of 8–14 mm (IR rays). Ozone in the stratosphere protects the Earth's inhabitants from a harmful ultraviolet sun radiation. The concentration of ozone in the stratosphere is 1000 times higher than in the lower layer of the Earth's atmosphere, i.e. the troposphere. The appearance of polar stratospheric clouds (PSCs) impacts the ozone depletion. The PSCs are formed during the cold months of the Antarctic and Arctic winter when stratospheric temperatures fall below –193°K (at altitudes from 10 to 25 km). At low temperatures the mixture of nitric acid and water containing in clouds turns into large pieces of ice with dissolved HNO_3. Chlorine- and bromine-containing substances are responsible for the ozone depletion. Being in a bound state, chlorine and bromine don't destroy ozone. Arctic spring sunlight transforms molecular forms of chlorine and bromine into the ionized atomic chlorine and bromine. Ionization process of molecular bromine by UV radiation lasts approximately for 0.085 ± 0.015 ps. The first molar ionization energy of bromine, which characterizes the process of obtaining an atom with one lost electron, is 1139.9 kJ mol^{-1}, for chlorine this quantity is equal to 1254.9 kJ mol^{-1}. A catalytic cycle, driven by light, which destroys ozone starts extremely fast. Atomic chlorine and bromine react with ozone converting it into oxygen. It leads to formation of oxides of halogens. Oxides of ClO and BrO being destroyed, chlorine or bromine are released, proceeding to destroy ozone. One atom of Cl or Br can destroy up to 10000 molecules of ozone. Ozone depletion potential of bromine is estimated as 60-fold to chlorine.

Greenhouse gases (GHGs) have the ability to absorb or capture the infrared radiation and move it upward due to absorption of radiation energy emitted by the Earth's surface. GHG re-emit the absorbed energy quickly. Approximately 50% of re-emitted energy goes back to the Earth's surface. This energy would be lost if it had not been "caught" by greenhouse gases. Due to GHGs, the Earth's surface is heated up, while stratosphere is becoming colder thus creating more favorable conditions for ozone depletion.

Ozone is constantly produced and destroyed in a natural cycle, so the total amount of ozone should not change greatly. When the ozone production and destruction are balanced, ozone levels remain stable.

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Such situation existed during few last decades. Large increase of chlorine and bromine in stratospheric disturbs this balance. Thus, ozone is destroyed faster than it is formed. Therefore, the amount of ozone starts to fall to a lower level until it reaches a new balance. The global stratospheric ozone levels fell slightly from 1969 to 1986. At this rate, the stratospheric ozone has decreased by 1.7–3.0% between 30º and 64º north latitudes. Ozone strongly decreased during winter at high latitudes, in summer it decreased to a lesser extent. The concentration of ozone in the troposphere increased by about 1 % year^{-1} over the last 20 years. The reduction of ozone in stratospheric exceeds the increase of its mass in the troposphere.

The presence of radicals NO_x has a significant impact on the ozone content. The natural source of stratospheric NO_x is nitrous oxide N_2O known as laughing gas. The surface concentration of N_2O is about 0.31 ppmv. The measurements indicate the increase of N_2O concentration approximately 0.2 to 0.3 % year^{-1}. This gas is not regarded as reactive, but its lifetime is more than 150 years. As a result, it reaches the stratosphere, where, due to the ultraviolet photolysis, it is mostly converted into nitrogen and oxygen. However, a small fraction of N_2O reacts with oxygen atoms. This reaction is the main supplier of natural NO_x in the stratosphere. The stratospheric ozone is destroyed by nitric oxide NO molecules. Bromine considerably depletes ozone in the Earth's atmosphere. However, it was not clear up to now, what role in this process water clusters formed from water vapor play. It was shown in papers [1–3] that the lifetime of the Cl ions in water clusters and the time of interaction of these ions with absorbable clusters of ozone molecules are sufficient for the cleavage reaction of ozone. Water clusters play the role of traps for Cl ions and ozone molecules. Infrared spectra appear as a result of vibrational (and partly rotational) motion of molecules, namely, as a result of transitions between the vibrational levels of the electronic main state of molecules. Infrared radiation is absorbed by many gases at frequency typical for each of them. According to Raman, the combinational scattering (CS) of light is the inelastic scattering of optical radiation on the molecules of substance (solid, liquid or gaseous) accompanied by a noticeable change of its frequency. Raman and infrared spectroscopy are intermutual methods. Non-polar molecules produce intense Raman bands, but weak IR signals.

The purpose of the present study is to analyze the interaction of Br ions in water clusters with ozone and oxygen molecules. The purpose of the study also includes the determination of the impact of Br ions on the spectral characteristics of cluster systems including IR and Raman spectra.

MODEL

Dynamics of the system was implemented with the potential of intermolecular interaction of water-water [4] and the description of the interaction of oxygen-oxygen and oxygen-water system in the form of the sum of repulsive and dispersive contributions calculated in Gordon-Kim approximation [5, 6]. Coulomb interaction of the Br^- ion with water is achieved by its electric charge $q_{Br^-} = -1e$, where e is elementary charge. Non-Coulomb interaction between bromine ions Br^-, atoms of H_2O, O_2 and O_3 molecules and bromine ions, is defined as the atom-atom interaction in accordance with [5]. Atoms of the O_2 molecule do not demonstate electric charges. The central atom of the ozone molecule has a positive electric charge $q_{cen} = 0.19\ e$, while the side atoms of the molecule are negative charged $q_{side} = 0.095\ e$.

Flexible models of molecules were considered based on balancing entire potential power of centrifugal force $\mu u \omega^2$ [7], where $u = \|r_a - r_b\|$ are absolute difference vectors determining the positions of atoms a and b in a single molecule, and $\mu = \frac{m_a m_b}{m_a + m_b}$ is a reduced mass, $\omega = \|v_a - v_b\|/u$ is angular velocity.

Modeling the interaction of clusters $(Br^-)_i\,(H_2O)_{50-i}$ with six molecules of X, where X = O_2 or O_3 started with the creation of configuration of the equilibrium water cluster $(H_2O)_{50}$ in molecular-dynamic model at 233°K. Next, $(Br^-)_i(H_2O)_{50-i}$ clusters were formed. To determine the position of bromide ions in the cluster, the coordinate system ascribed to the center of mass of water cluster was used. Being circumscribed a virtual sphere from the center of mass around the water cluster, water molecules have been found, located nearer to the point where they exit from the scope of the coordinate axes. Each of these molecules (from 1 to 6) is moved outward along the corresponding coordinate axis to a distance of 0.7 nm from the previous position of its mass center. The place of a removed molecule is occupied by ion Br^-. The number of ions corresponds to the number of removed molecules. Molecular-dynamic calculation is made with a time step of $\Delta t = 10^{-17}$ s. Hereafter, time when the X molecules are added to the cluster $(Br^-)_i\,(H_2O)_{50-i}$ is counted for time t = 0. Duration of basic calculation is 2.5×10^6 Δt time steps. To integrate the equations of motion of molecules mass centers the fourth-order Gear method

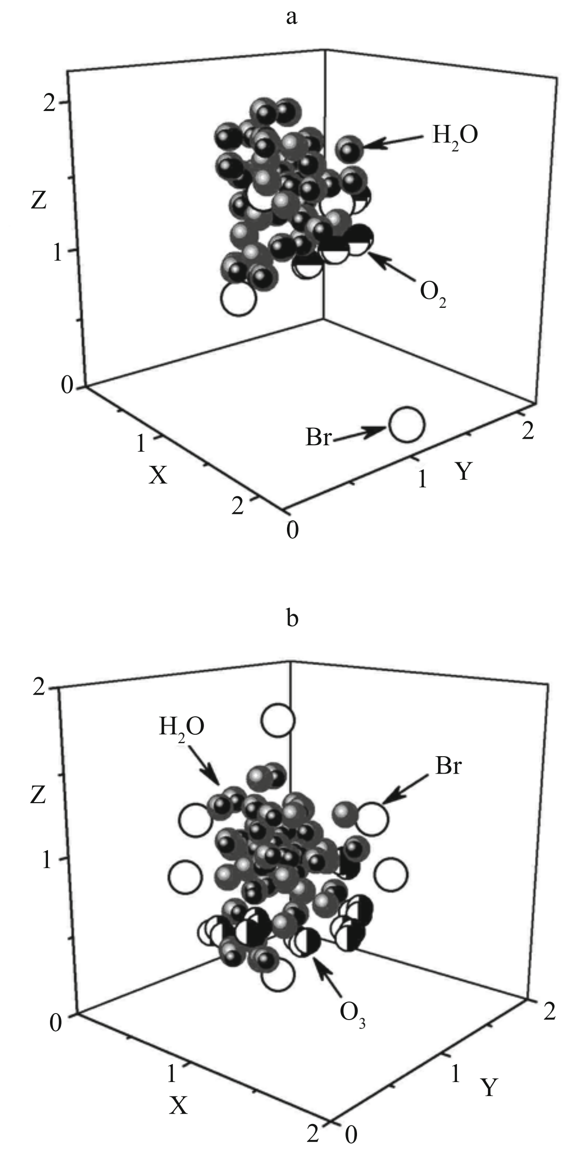

Fig. 1. The system configurations $(Br^-)_6(H_2O)_{44}+6H_2O+6X$ relating to the time moment 25 ps: (a) is $X=O_2$, (b) is $X=O_3$. The coordinates of the molecules are given in nm.

[8] was used. Analytical solution of the equations of motion for rotation of the molecules was carried out using the Rodrigues-Hamilton parameters [9], while a scheme for integrating the equations of motion in the presence of rotations corresponded to the aproach proposed by Sonnenschein [10]. Calculation of IR and Raman spectra was made on the basis of the method described in [11–13], and the spectra of emission and reflection were defined according to [14–16]. The method of constructing of hybrid polyhedron was described in [17].

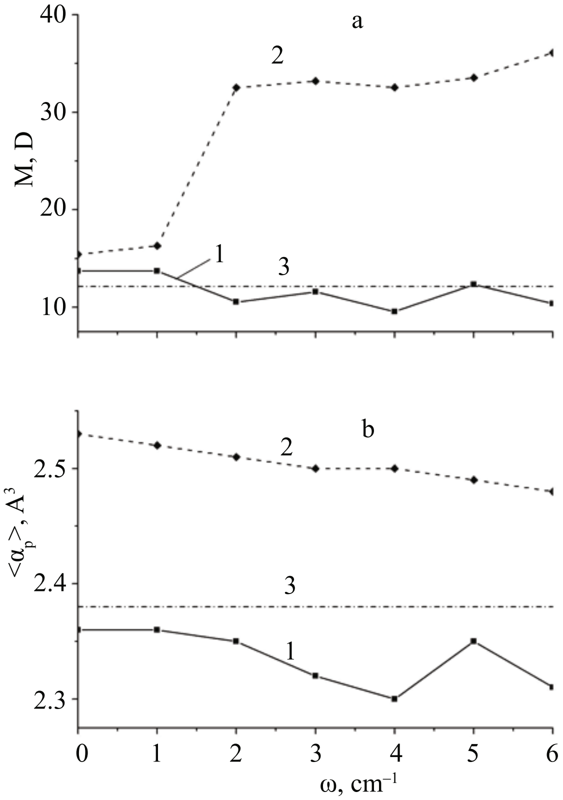

Fig. 2. The total dipole moment of the cluster (a) and average polarizability of a molecule (b) depending on the number i of ions Br^- in a water cluster after adsorption of admixture molecules X: 1 is O_2, 2 is O_3; 3 are values M (a) and $\bar{\alpha}_p$ (b) for the cluster $(H_2O)_{50}$.

RESULTS OF CALCULATION

Configuration of cluster systems $6Br^-(H_2O)_{44} + 6H_2O + 6X$ received by the end of calculation, i.e. to the moment of time 25 ps is shown in Fig. 1. Here, X means the O_2 molecules (Fig. 1a) or O_3 molecules (Fig. 1b). In both cases there are six molecules of water fixed to the cluster $6Br^-(H_2O)_{44}$, which originally locate near it. When oxygen is present in the system, three of six Br ions leave the cluster. One of these ions is shown presented at the bottom of the Fig. 1. Along with removed ions, three O_2 molecules evaporate, while the other three O_2 molecules join the cluster. The presence of ozone molecules makes the effect different. Each of six O_3 molecules is adsorbed by the cluster. In this case, six Br ions come to the surface of the cluster but do not remove too far from it, so that they could be treated as evaporated. The evaporated ions or molecules include those, for which the non-Coulomb interaction with other molecules is lost, due to the cutting of the corresponding interaction potential at a distance of 0.9 nm. That sort of ions or molecules never get back into cluster.

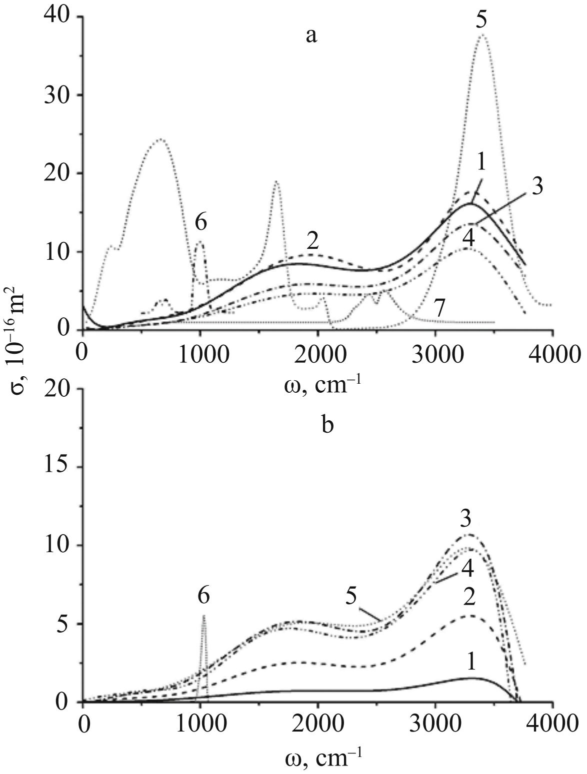

Fig. 3. The absorption spectra of IR radiation for systems $(Br^-)_i(H_2O)_{50-i} + iH_2O + 6X$: (a) is $X=O_2$, (b) is $X=O_3$; 1 is $i=0$, 2 is $i=2$, 3 is $i=4$, 4 is $i=6$. (a): 5 is a function *σ(ω)* of the bulk liquid water, experiment [18], 6 is experimental spectrum for gaseous mixture O_2+O_3 [20], 7 is *σ(ω)* spectrum of gaseous HBr, experiment [19]; (b): 5 is function *σ(ω)* of cluster $(H_2O)_{50}$, 6 is experimental spectrum of gaseous O_3 [21].

The complete change of the total dipole moment M of the cluster with the increase of Br ions is shown in Fig. 2a. Adsorption of O_2 molecules by the cluster in the absence of Br ions increases the value of M by 13% (curve 1). This value of M remains stable with the presence of a Br ion in the cluster. However, further increase of bromide ions tends to reduce the dipole moment of the cluster below the level (line 3), that corresponds value of M for the cluster $(H_2O)_{50}$ having no impurities. In the absence of Br^- (curve 2) the dipole moment M increases by 27% after adsorption of O_3 molecules by the water cluster. Adsorption of one Br ion by the above mentioned cluster gives even a slight increase of M (1%). The value of M increases in a step (twofold compared to the previous value) after absorption of the second Br ion. The value of M tends to moderate growth by a further increase of bromide ions in the cluster. The presence of polar molecules of O_3 in the cluster causes strong perturbation of the internal electric field with two Br ions presented, whereas at the absorption of oxygen even six Br ions do not significantly perturb the molecular field.

The average per molecule polarizability $\overline{\alpha}_p$ depending on the amount of presented Br ion in the cluster is shown in Fig. 2b. The adsorption of O_2 molecules causes the decrease of $\overline{\alpha}_p$ magnitude, while the accession of molecules O_3 to the cluster increases this value. Generally, increase of bromide ions in the cluster leads to decrease of $\overline{\alpha}_p$ (except with $i > 4$ in systems with oxygen molecules).

In the IR and Raman spectroscopy the same molecular vibrations are observed and, consequently, of the same frequency. Various types of elementary processes determine the intensity or activity of molecular vibration at the realization of both spectroscopic techniques. The intensity of the absorption in the IR spectrum is directly proportional to the square of the first derivative of the dipole moment of its internuclear distance. Such polar molecules like H_2O have intense bands in the IR spectrum. The Raman spectra manifest those vibrations where polarizability of the molecule changes. The intensity of the Raman lines is proportional to the square of the derivative of the polarizability of the molecule on the internuclear distance. Vibrations of nonpolar homonuclear molecules like O_3 are active only in Raman spectra. Frequency and intensity of the normal vibrations are determined by weight and type of atoms bonding force and atomic array of atoms (length and angles of bonds). Changing the structure of the cluster, adsorbed Br ions affect the intensity of the IR spectrum and to a lesser extent influence the intensity of the Raman spectrum.

IR absorption spectra *σ(ω)* of some systems above mentioned are shown in Fig. 3. Attachment of six oxygen molecules to the cluster $(H_2O)_{50}$ increases 2.3 times the integrated intensity of I_{tot} of infrared radiation absorption. However, Br ions (equivalent to the desorption of water molecules) being absorbed by water cluster, the value I_{tot} is not increased. When four or more Br ions are present the values I_{tot} decrease during oxygen absorption. In other words, the increase of Br ions in disperse aqueous system with molecular oxygen, usually causes a decrease in the intensity of the *σ(ω)* spectrum, depending on the number of Br ions in the cluster. In this case, however, the location of the main peak of the IR spectrum does not change, and the peak with second intensity deformes to the shoulder. The location of the main peak is shifted (~100 cm^{-1}) to low frequencies with respect to the main peak of the experimental IR spectrum of liquid water [18]. Localization of the

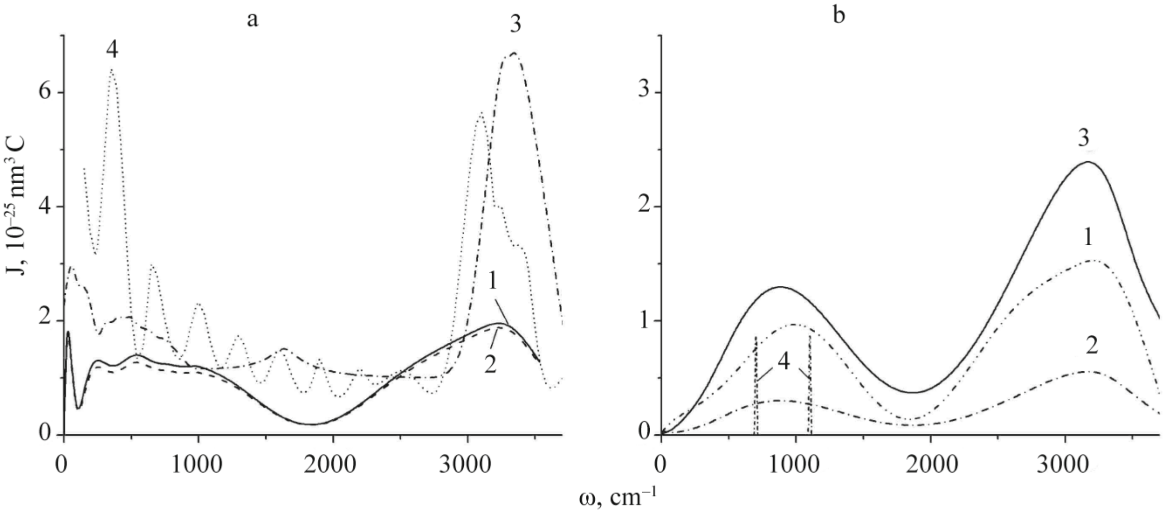

Fig. 4. Raman spectra: (1–2) of systems $(Br^-)_i(H_2O)_{50-i}+ iH_2O + 6X$; (a) is $X=O_2$, (b) is $X=O_3$; 1 is $i=0$, 2 is $i=6$; (a): 3 is liquid water at 293°K, experiment [22], 4 is clathrate hydrate bromine at 266°K, experiment [23]; (b): 3 is cluster $(H_2O)_{50}$, 4 is gaseous O_3, experiment [24].

minimum between two peaks of the cluster systems spectra $\sigma(\omega)$ is on the interval of maximum intensity of experimental IR spectrum of gaseous bromine hydride [19]. The rapid rise in the intensity in the spectra of these systems corresponds to the position of the main peak of the experimental IR spectrum of gaseous mixture of O_2+O_3 [20]. Diametrically opposed transformation of the spectrum $\sigma(\omega)$ occurs when the number of Br ions in the cluster changes when ozone is present in the system. Attachment of O_3 molecules to the cluster $(H_2O)_{50}$ results in reduced quantities I_{tot} 7.3 times. This decline becomes less evident with increasing number of Br ions in the cluster. In other words, the adsorption of ozone increases the values of I_{tot}, if the water cluster consistently attaches Br ions. Thus, two Br ions being present, the intensity of the IR spectra upon adsorption of ozone decreases 2.1 times, while the presence of four Br ions in the cluster decreases the value of I_{tot} only 1.07 times. If the number of Br ions exceeds four, the intensity of the spectra $\sigma(\omega)$ is stopped. At changing the number of Br ions in the cluster, the location of the main peak of the IR spectrum remains practically stable corresponding approximately to 3300 cm^{-1}. Here, as with oxygen present in the the system, a red shift of the main peak of the spectrum with respect to the localization of the main peak of the experimental IR spectrum of liquid water is also observed. The minimum separating the peaks of the spectra $\sigma(\omega)$ of cluster systems is in the region of the greatest intensity of the IR spectrum of gaseous bromine hydride. The rapid increase in the intensity of the spectra $\sigma(\omega)$ of these systems is in the frequency range, where the peak of the IR spectrum of gaseous ozone is localized [21]. Nonpolar molecules of O_2 create the effect of "diluting" resulting in decrease of the value of the cluster total dipole moment. Br ions perturb the internal electric field of the cluster accelerating the decay of the autocorrelation function of magnitude M. As a result, the intensity of the infrared spectrum decreases with increasing number of bromide ions. Polar O_3 molecules, being bunched, create a slowly varying electric field, which regulates the dipole moments of water molecules. As a result, the M value increases significantly and the intensity of the infrared spectrum increases with the number of Br ions in the system. The disturbance, being increased by adding of more than four Br ions into cluster, leads to more rapid decay of the autocorrelation function of the dipole moment M. As a consequence, the infrared spectrum intensity of aqueous ozone system, increased at $i = 4$, begins to decline.

Spectra $J(\omega)$ of anti-Stokes Raman scattering are shown in Fig. 4. Adsorption of six oxygen molecules leads to an increase 1.6 times of the integrated intensity J_{tot} of Raman spectrum of the cluster $(H_2O)_{50}$. In the presence of oxygen, the spectrum of $J(\omega)$ slightly changes the intensity and shape at variation the number of Br ions in the cluster. Thus, at absorption of six Br ions by water-oxygen system the value J_{tot} decreases only by 7.1%. In systems containing up to six Br ions, a red shift of core peak by ~110 cm^{-1} is observed with respect to the location of the main peak of the experimental Raman spectrum of liquid water [22] and the blue shift by ~130 cm^{-1} with respect to the localization of the signified peak in the corresponding experimental spectrum of clathrate hydrate bromine [23]. Addition

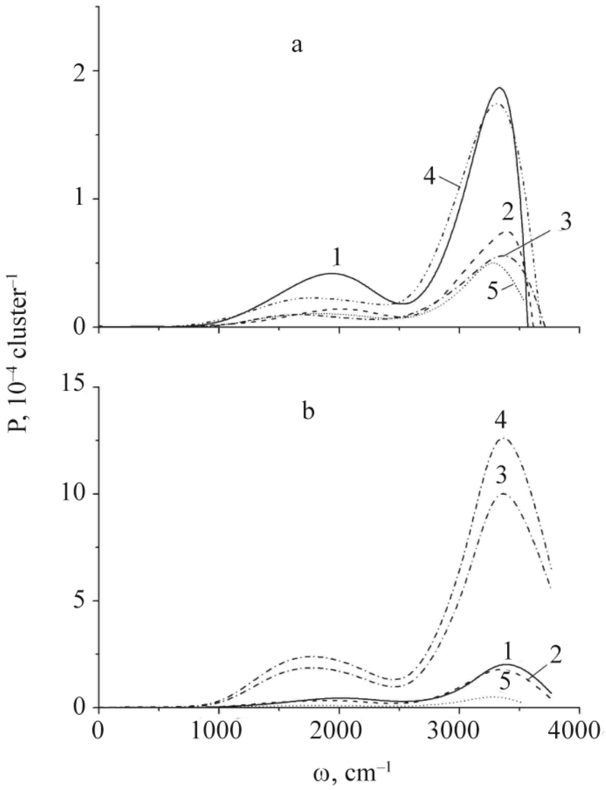

Fig. 5. Emission spectra of the IR radiation of the systems $(Br^-)_i(H_2O)_{50-i}+iH_2O+6X$: (a) is X=$O_2$, (b) is X=$O_3$, 1– i =0, 2 is i=2, 3 is i =4, 4 is i=6; 5 is function *J(ω)* of the cluster $_i(H_2O)_{50}$.

of six ozone molecules leads to a weakening 1.5 times of the integrated intensity J_{tot} of cluster $(H_2O)_{50}$. The number of Br ions in the cluster greatly affects the form of spectra *J(ω)* of the cluster systems containing ozone. Spectra *J(ω)* significantly reduce its intensity by increasing the number of Br ions. The value J_{tot} in the presence of six Br ions in the water-ozone system is 4.3 times lower than at their absence. Red and blue (at 170 and 20 cm^{-1}) shifts in the position of the maximum of the Raman spectrum of the cluster system are observed with respect to the peaks of the experimental spectra of water and clathrate hydrate bromine. The location of the first (less intense) peak spectra *J(ω)* for the cluster systems containing ozone reaches the interval separating the two peaks corresponding to the experimental spectrum of gaseous ozone [24]. Nonpolar molecules of O_2 having a lower polarizability α_p (0.793 Å^3) than the quantity α_p (1.49 Å^3) for the molecules of liquid water being added to water clusters, the average polarizability of the molecule $\bar{\alpha}_p$ decreases as compared with the calculated value α_p for water cluster. The presence of Br ions slightly affects the behavior of the autocorrelation function of the polarizability fluctuations. As a result, similar Raman spectra of the studied systems containing oxygen are observed. For systems containing ozone the situation is different. Polar ozone molecules have a higher polarizability ($\bar{\alpha}_p$ = 2.7 Å^3) than a water molecule. So, the value of $\bar{\alpha}_p$ is higher than α_p for water cluster. The increase of Br ions number leads to the growth of disorder of the dipole moments and polarizability values gradually reduce. Herein, fluctuations of the α_p value is lower than for systems with oxygen. As a result, with the increase of Br ions, the intensity of the spectrum *J(ω)* for the systems containing ozone decreases.

Adsorption of the oxygen molecules and as well as ozone by the cluster $(H_2O)_{50}$ enhances the integrated intensity P_{tot} emission spectra of IR radiation. Moreover, the addition of six O_3 molecules increases 3.8 times the value of P_{tot}, while adding of six O_3 molecules to the cluster it increases 4.1 times (Fig. 5)The emission spectra of cluster systems significantly change their intensity by varying the number of Br ions in the cluster solution. In addition, as a rule, the intensity of the emission is reduced in the presence of oxygen in the system and increases, when the clusters adsorb ozone. For example, in the presence of six Br ions the spectrum *P(ω)* reduces 1.1 times the integrated intensity during the adsorption of oxygen and increases in 6.4 times, when ozone is attached. In general, the location of the main peak of the emission spectrum slightly shifts (up to ~20 cm^{-1}) to higher frequencies by adding bromide ions in the oxygen system and in a minor way (up to ~35 cm^{-1}) to lower frequencies for the system containing ozone. The maximum reduction in the intensity of emission spectra for the systems with oxygen occurs in the presence of four Br ions in the cluster, while the maximum increase of this characteristic is observed for the systems with ozone in the presence of six Br ions in the cluster.

As a result, the adsorption of O_2 and O_3 molecules by the cluster $(H_2O)_{50}$ leads to a weakening of the effective coefficient of $\bar{R}$ reflection of the infrared radiation. Thus, the attachment of six oxygen molecules results in reduction 23.0% of ratio $\bar{R}$, while the capture of the same number of ozone molecules leads to a decrease 13.6% of $\bar{R}$. Replacement of six $(H_2O)_{50}$ molecules with Br ions causes additional decrease 1.3% of R in case of adsorption of six molecules by the cluster, and, conversely, increase 9.5% of $\bar{R}$ at the attachment of the same number of O_3 molecules. Reflectance spectra of the systems with originally six Br ions in the clusters are shown in Fig. 6. These spectra have a large number of sharp peaks (15 peaks can be distinguished) showing a high surface irregularity. In general, the systems containing ozone have higher reflectivity. The average

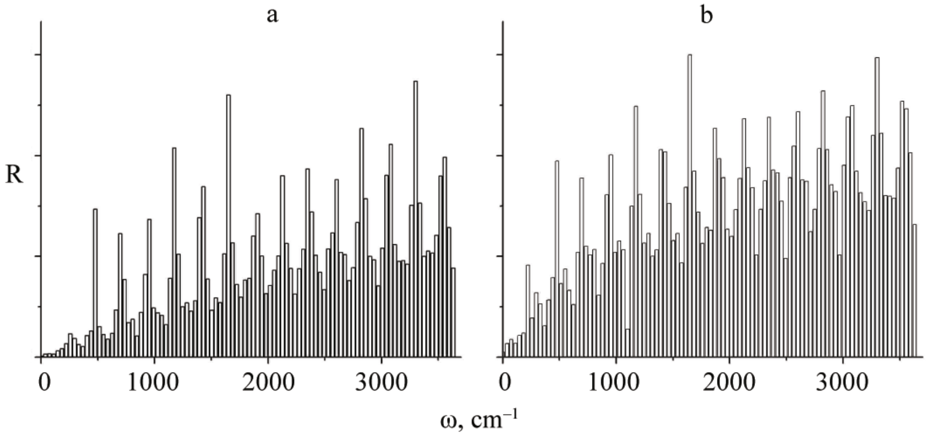

Fig. 6. Reflectance IR spectra of the systems $(Br^-)_6(H_2O)_{44}$+ $6H_2O + 6X$: (a) is $X=O_2$, (b) is $X=O_3$.

reflectance of water-ozone system in the presence of six Br ions is 1.6 times higher than for a similar system with oxygen.

The adsorption of oxygen or ozone molecules in the presence of Br ions affects the structure of water component of the cluster. Hydrogen bond in a water core of the cluster will be determined by the number of bonds per H_2O molecule and by the length of the hydrogen bond. These characteristics are based on the construction of hybrid polyhedra with the oxygen atom in the centre of each of them, and the environment, forming the face, is formed from hydrogen atoms. In addition, the energy criterion of hydrogen bond is used, i.e. two molecules of H_2O are considered to be hydrogen bonds if the energy of their interaction is not higher than –12.55 kJ mol^{-1} [25]. The number of bonds n_b molecule^{-1} varies nonmonotonic with increasing number of i ion containing in the system (Fig. 7a). The strongest changes in the function of $n_b(i)$ occur when cluster adsorbs ozone molecules. In this case the value n_b varies in the range of $3.45 \le n_b \le 4.20$. The highest value n_b is observed when $i = 6$, and the lowest at $i = 0$. In the range of $3 \le i \le 5$ n_b values differ slightly from the values of n_b at $i = 0$. When oxygen is absorbed by the cluster, the values n_b generally increase with the raise of Br ions. Besides, the maximum value n_b is observed at $i = 4$, fluctuations of the $n_b(i)$ function are more moderate. The average length L_b of OH hydrogen bond fluctuates more strongly, when oxygen presents in the system (Fig. 7b). The minimum value of L_b is observed at $i = 1$, max at $i = 0$. Dependence of $L_b(i)$ in the case of

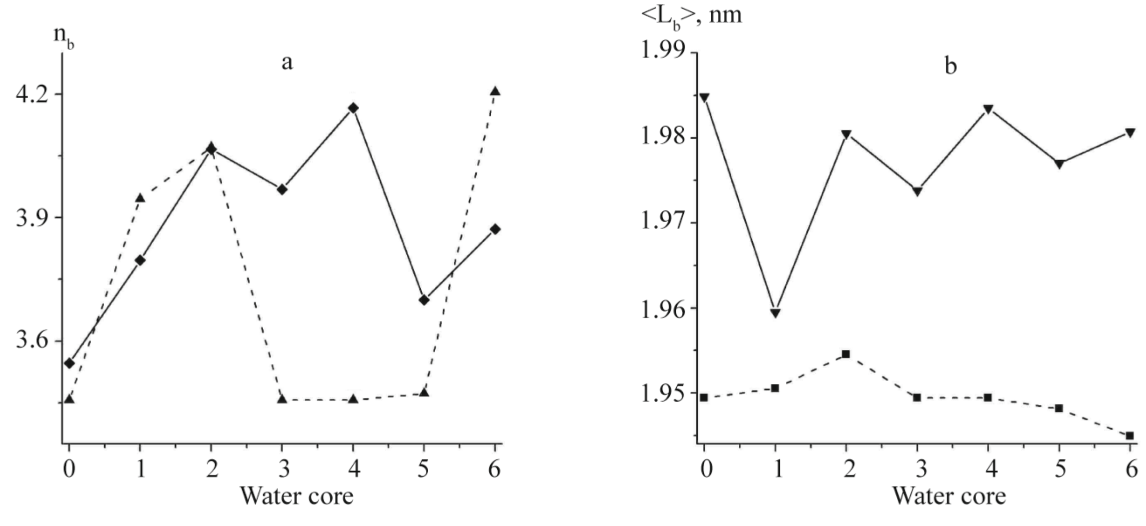

Fig. 7. Dependence: (a) is the average number of hydrogen bonds per water molecule, and (b) is the average bond length on the amount of bromine ions i in the systems $(Br^-)_i(H_2O)_{50-i}$+ $iH_2O + 6X$: 1 is $X = O_2$, 2 is $X = O_3$.

ozone adsorption is more gradual than, when oxygen is joined by a cluster. Here, maximum is observed at $i = 2$, and minimum value of L_b corresponds to the value of $i = 6$. Thus, the capture of polar O_3 molecules by water clusters creates stronger fluctuations in the number of hydrogen bonds and more weak changes in the average bond length, than in the case when nonpolar O_2 molecules are added to the cluster.

CONCLUSION

Catalytic cycles caused by the appearance of an active atomic chlorine and bromine contribute to the rapid destruction of ozone. The ozone hole currently covers a geographic area slightly larger than Antarctica, and stretches nearly 10 km in height in the lower layer of the stratosphere. During the last 50 years the moisture content in the stratosphere has doubled up. Ozone concentration usually ranges between 0.02 and 0.03 ppmv in the lower atmospheric layer of the Earth troposphere. Air pollution can act as catalysts, making it possible for sunlight to form ozone. Tropospheric ozone is harmful, it can damage plant and lung tissue. The troposphere contains about 75% of the mass of the atmosphere and 99% of its water vapor and aerosols. Decrease of temperature and water vapor content within the troposphere depends on height. Water vapor plays a major role in regulating the temperature of the air, as it absorbs solar energy and thermal radiation from the planet's surface. The concentration of water vapor depends on the latitude. In tropics humidity can reach 3% but it decreases significantly in direction to the polar regions.

The presented study shows that water clusters can absorb ozone, and block its molecules on the surface for considerable time. Clusters of polar molecules attract Br ions. Thus, some favorable conditions for the reaction of bromine with ozone appear on the surface of water cluster, that leads to the destruction of the latter. The maximum ozone concentration is observed at the height of 20–25 km. The layer formed by ozone is called the ozonosphere. The temperature at such heights is ~218–228° K. Under such conditions water vapor can be condensed to form ice. The reaction of ozone destruction by bromine also takes place on the ice surface. Increase of humidity of the stratosphere is highly undesirable, as it enhances the process of ozone destruction. In the troposphere, most of the clusters are concentrated up to a height of 2.5 km, while drops are mainly located at the height of 3 km. The crystals are generally located higher than 3 km. The higher to the troposphere, the lower the air temperature falls (6°K 1000 m^{-1}), since the air heating is caused mainly by sun reflected from the earth's surface. Therefore, the temperature at a height of 2.5 km varies by ~ 257 ± 20° K, depending on time of the year. Under these conditions, clusters and droplets are in liquid state, and the destruction of ozone by active bromine takes place on their surface. Therefore, increase of troposphere humidity up to a certain level contributes to its cleansing from the harmful ozone. The current average humidity at the surface (~ 11 g m^{-3}) may increase 55%, while doubling the total quantitative properties of humidity in the atmosphere.

The presented study reveals the following changes in the spectral dispersion of the water system, that adsorbed ozone, when changing the content of Br ions. The intensity of the infrared absorption spectra significantly increases in proportion to the number of Br ions within a cluster. Raman spectra of dispersed water-ozone systems significantly reduce their intensity with increasing number of Br ions. Emission spectra of the infrared radiation greatly increase the intensity only at high concentrations of Br ions in the clusters. Ability of dispersed water-ozone system to reflect infrared radiation increases with increasing amounts of dissolved Br ions. In general, such systems have a higher reflectivity than similar systems in the presence of oxygen. Bromine ions in the clusters impact the nature of hydrogen bonds in water-ozone, as well as in water-oxygen system. The number of H-bonds is a nonmonotonic function of the content of Br ions, and the average OH-bond length at variation of the number of Br ions fluctuates with oxygen in the system and tends to decrease with increasing number of Br ions in the ozone-containing system.

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