THERMOPHYSICAL PROPERTIES OF MATERIALS

Computational Study of Interaction of Bromine Ions with Clusters \((O_2)_6(H_2O)_{50}\) and \((O_3)_6(H_2O)_{50}\)

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Abstract.—Interaction of bromine ions with water clusters that have absorbed the molecules of oxygen and ozone is studied using a molecular-dynamics simulation of flexible molecules. The cases of location of \(Br^-\) ions on the surface and in the bulk of the cluster are described. Water clusters with ozone molecules remain stable during their interaction with the \(Br^-\) ions, while oxygen molecules are found to evaporate from the cluster when \(Br^-\) ions appear in its bulk. In the presence of \(Br^-\) ions, the infrared spectra of systems with \(O_3\) molecules are observed to be intensified. The intensities of the IR spectra with \(O_3\) molecules may both increase and decrease depending on the arrangement of the \(Br^-\) ions. The Raman spectra are sensitive to the appearance of \(Br^-\) ions only for systems that contain oxygen molecules. As a result of interaction with the \(Br^-\) ions, the power of IR radiation emitted by the clusters can not only increase, but also decrease.

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INTRODUCTION

Ozone is characterized by instability of its chemical properties (rapid decomposition) and high oxidative activity. A steady vortex forms above the Antarctic in winter, which prevents the admission of ozone-enriched air coming from middle latitudes. Therefore, by spring even a small amount of active chlorine or bromine is able to substantially damage the ozone layer. This vortex is almost absent above the Arctic and, owing to this, drop in ozone concentration is insignificant in the Northern Hemisphere. In the stratosphere, the ozone content is much lower than that of chlorine, but it is more active and induces depletion of a considerable amount of ozone. Additional intrusion of bromine- and chlorine-containing substances into the stratosphere leads to violation of the natural balance in formation and destruction of ozone. This is mainly manifested as an additional factor that causes ozone depletion. Different chlorofluorocarbons have various lifetimes in the atmosphere and different capacities for ozone depletion. The majorly of them are long-living substances which can remain in the atmosphere for many decades and even hundreds of years. The potential of a substance for ozone depletion is determined by the amount of chlorine or bromine atoms in a molecule, its atmospheric lifetime, and the peculiarities of the chemical process required for the decay of this substance. The atomic oxygen required for ozone formation develops during molecular oxygen splitting under the effect of ultraviolet radiation (with a wavelength of <240 nm) above the level of 20 km. These photons can barely penetrate lower than this level, and oxygen atoms are mainly formed during photochemical dissociation of nitrogen dioxide by photons of soft ultraviolet (with a wavelength of <400 nm). The ozone molecule depletion occurs while they enter aerosol particles or arrive at the Earth’s surface, but the main ozone destruction is determined by the cycles of the gas-phase catalytic reactions.

Atmospheric ozone protects living beings, including human beings, from radiation in the ultraviolet, violet, and visible ranges. Ozone forms from common oxygen \(O_2\) when a quantum with a wavelength belonging to the Shumann–Runge absorption bands (ultraviolet; the range is 176–192.5 nm) gets onto the latter. The oxygen molecule becomes excited. In order to transfer to \(O_3\), the excited molecule must first interact with another molecule M to get rid of the energy excess. An oxygen, ozone, impurity, atomic oxygen, or nitrogen molecule can be used as M.

Small water particles in the atmosphere—i.e., clusters—are commonly regarded as condensation nuclei during the formation of clouds. However, the role of atmospheric water clusters in chemical reactions that include \(Br^-\), \(Cl^-\), and \(NO_3^-\) cause ozone depletion have not yet, in fact, been studied. Owing to the atmospheric chemical reactions with \(O_3\), \(O_2\), and \(NO_3^-\), the organic aerosols are known to gradually modify and form complex organic compounds [1–3]. Upon such an oxidation of the organic aerosol surface, a redshift of its infrared absorption spectrum is to be expected [4]. The key question that arises here is how large this shift is and whether it will intensify with an increase of the aerosol lifetime. There are grounds to assume that organic aerosols become even more photochemically active over the years. This is still more
important because of the fact that the surface of the aerosol particles (which traditionally are inorganic, i.e., sea salt, dust, or soot) is very often organic [5–7]. Ozone acts as a key oxidizing agent for atmospheric organic molecules that are formed with unsaturated C–C bonds [8–10]. The products of ozone photolysis (aldehydes, pyroxydes, etc.) mostly have a transverse section of photochemical dissociation in a frequency range of a troposphere window that falls within the wavelengths of λ > 295 nm. In [11] it is shown that atmospheric water clusters are crucial in creating the greenhouse effect. The absorbing capacity of the water clusters with respect to certain atmospheric gases, including oxygen and ozone, is studied in [12–14].

The present study is aimed at examining the interaction of the water clusters that have absorbed the oxygen and ozone molecules and determining the effect of the change of location of bromine ions on the infrared (absorption, emission and reflection) and Raman spectra of ultradispersion systems.

**MOLECULAR DYNAMICS MODEL**

A polarizable flexible version of the water molecular model with the parameters of a TIP4P model is used in this study [13], in which the characteristics of the Lennard–Jones (LJ) part of the potential and the location of a negative charge are changed substantially [15]. As a result, a permanent dipole moment of a molecule corresponds to the experimental value [15]. As a result, a permanent dipole moment of a molecule had a positive electric charge $q_e$ and the side atoms of that molecule carried a negative charge $q_{side} = -0.095e$.

Using high-level ab initio calculations, it was shown [21] that the energetically favorable structure of the $(H_2O)_{20}$ cluster is formed on the basis of a pentagonal prism ($U_{tot} = -(899.4–911.5) \text{ kJ/mol}$) rather than on a dodecahedron ($–(897.0 \text{ kJ/mol})$) or fused cubes ($–889.3 \text{ kJ/mol}$). Molecular dynamics calculations using various empirical potentials are unable as yet to clearly answer which structure of the $(H_2O)_{20}$ cluster corresponds to the lowest energy. The internal energy of the $(H_2O)_{20}$ cluster in the model considered here is $–836.0 \text{ kJ/mol}$.

For the model used in this study, the minimum energy $U_{min} = -19.62 \text{ kJ/mol}$ of a water dimer falls within the space between oxygen atoms of 0.287 nm. These values agree well with the appropriate values ($–20.91 \text{ kJ/mol}$, 0.291 nm) obtained by calculating the electron structure [15]. The experimental value of $U_{min} = -22.6 ± 2.9 \text{ kJ/mol}$ [22].

In order to perform this study, flexible model molecules were used. Flexibility of molecules was created owning to the procedure developed in the framework of the Hamiltonian dynamics in [23, 24]. The essence of this procedure is as follows. Let the atoms $a$ and $b$ in a diatomic molecule be separated with a distance of $u = \|r_a - r_b\|$. 

\[ \Phi(r) = b r_0 \exp[-(e_i + e_j) r_a] - a r_a^2 r_b^4, \]

where the parameters $a$, $b$, and $e_i$ of the potential that describes these interactions are taken from [19].

Coulomb interactions of the $Br^-$ ion with water occurred due to its electric charge $q_{Br^-} = -1e$, where $e$ is the elementary charge. Non-Coulomb interaction between the $Br^-$ ions and the atoms of the $H_2O$, $O_2$, and $O_3$ molecules was determined as the atom–atom interaction according to formula (1) with the parameters of [19]. In [20], for description of the non-Coulomb interaction between the $Br^-$ ions, the Lennard–Jones potential was used. The potentials for the pairs $(Br–Br, Br–O, Br–H)$ of interacting atoms presented by formula (1) are shown in Fig. 1. Each of these potentials has domains of attraction and repulsion. A transition from repulsion to attraction is observed at 0.46, 0.37, and 0.35 nm for the atomic pairs of $Br–Br$, $Br–O$, and $Br–H$, correspondingly. The pair $Br–Br$ has the steepest repulsion branch, and the pair $Br–H$ exhibits the softest repulsion. The atoms of a molecule $O_2$ had no the electric charges. The central atom of the ozone molecule had a positive electric charge $q_{cen} = 0.19e$, and the side atoms of that molecule carried a negative charge $q_{side} = -0.095e$.

![Fig. 1. Potential of non-Coulomb interaction of atomic pairs; $I$—Br–Br, $2$—Br–O, and $3$—Br–H.](image-url)
where $r_a$ and $r_b$ are the vectors determining the positions of the atoms. If the masses of the atoms equal $m_a$ and $m_b$, correspondingly, then their reduced mass is set by the expression

$$\mu = \frac{m_a m_b}{m_a + m_b}.$$  

The length of a bond in a molecule is determined by equilibration of a total potential force

$$f(u) = -\frac{\partial}{\partial u} \nabla \Phi(r)$$  

with the centrifugal force $-\mu \omega^2$. Then for the atoms $a$ and $b$ moving at the rates of $v_a$ and $v_b$, one can write the following equation:

$$-\mu \omega^2 - f(r) \frac{\partial v}{\partial u} = 0,$$

where $\omega = \|v_a - v_b\|/u$ is the angular rate. Using the minimizing of a contribution in the potential energy $U$ from every generalized coordinate, we shall obtain

$$\frac{\partial}{\partial u} H(r, v) = \frac{\partial}{\partial u} \left( \frac{1}{2} \mu \omega^2 v^2 + U(r) \right) = 0.$$  

This method is generalized for molecules of any composition [25].

Simulation of the interaction of the clusters of $(X)_{6}(H_2O)_{50}$, where $X = O_2$ or $O_3$, with the Br$^-$ ions was initiated from the creation of a configuration of an equilibrium water cluster $(H_2O)_{50}$ in the molecular-dynamics calculation that lasted 20 ps with a kinetic energy corresponding to a temperature of 233 K. Later, the cluster $(X)_{6}(H_2O)_{50}$ with the oxygen or ozone molecules aggregated in one region was created. Such an arrangement of $X$ molecules makes it possible to more precisely define the character of the effect of the Br$^-$ ions on them. The cluster $(X)_{6}(H_2O)_{50}$ was equilibrated in the MD calculation that lasted 10 ps at temperature $T = 233$ K. To examine the effect of the Br$^-$ ions on the cluster $(X)_{6}(H_2O)_{50}$, two kinds of boundary conditions (BCs) (free and random) were used. In the case of using the free boundary conditions, the bromine ions were initially located on the beams that emerged from the center of a mass cluster and passed through the centers of the molecules most distant from it. The Br$^-$ ion was located at a 0.6-nm distance from the nearest atom of any peripheral molecules. Using the free BC corresponds to the case of the appearance of slow Br$^-$ ions in the proximity of a water cluster. These ions can form, e.g., under the effect of ionizing radiation on the neutral Br$^-$ ions located in direct proximity to the cluster. The random BC are used to describe situations in which bromine-containing components, such as Br$_2$, BrO, HBr, HBrO, BrONO$_2$, and BrONO, are in the vicinity of the water cluster. Due to the low energy of bonding and rapid photolysis, the bromine ions being liberated under radiation from inorganic bromine may obtain a considerable acceleration and be introduced at random into the water clusters. A molecule breaking can be ascribed to elimination of spin pairing of these electrons that belong to different atoms. Using the random boundary conditions was based on generating new random coordinates for the Br$^-$ ions if it moved away from all atoms of the cluster at a distance exceeding the cutoff radius ($R_{\text{cut}} = 0.9$ nm) of the interactions, with the center of at least one of the molecules being at a closer distance from it, than the 0.6 nm. Thus, in the case of using the free BC, it is suggested that the bromine ions that have already been formed bombard the cluster surface without penetrating into its depth. The calculation of the random BC corresponds to a chemical reaction, i.e., the bromine ions that emerge continuously from the bromine-containing components are capable of randomly appearing at any point of a heterocluster bulk.

The interaction of the cluster $(X)_{6}(H_2O)_{50}$ with the Br$^-$ ions was studied in an ensemble with an exterior thermostat [26] at temperature of 233 K. The molecular-dynamics calculation was carried out at a time step of $\Delta t = 10^{-17}$ s. From this point on, time $t = 0$ will be accepted as the moment of time when the Br$^-$ ions have been added to the $(X)_{6}(H_2O)_{50}$ cluster. The calculation of spectral characteristics was started from the moment of $t = 10^5 \Delta t$ (1 ps) and a total duration of the main calculation was $2.5 \times 10^8 \Delta t$ of time steps.

Let us denote the systems as I−VI for simulation of which the free boundary conditions were used. System I will be $(H_2O)_{50} + 6O_2$, system II will be Br$^-$ + $(H_2O)_{50} + 6O_2$, system III will be 2Br$^-$ + $(H_2O)_{50} + 6O_2$, system IV will be $(H_2O)_{50} + 6O_3$, system V will be Br$^-$ + $(H_2O)_{50} + 6O_3$, and system VI will be 2Br$^-$ + $(H_2O)_{50} + 6O_3$. The systems simulated with the random boundary conditions for the Br$^-$ ions will be denoted as VII and VIII upon a presence of the O$_2$ molecules in them, and as IX and X if O$_3$ molecules are there in the system. There is one Br$^-$ ion in systems VII and IX, and in VIII and X there are two of them.

To integrate the equations of motion of the centers of the masses of molecules, the Gear method of the fourth order was used [27]. The analytical solution of the motion equations for the rotation of molecules was performed using the Rodrigues–Hamilton parameters [28], and the scheme for integrating the motion equations in the presence of rotations corresponded to the approach offered by Zonnenshain [29].

**DIELECTRIC PROPERTIES**

The dielectric permittivity $\varepsilon(\omega)$ as a function of the frequency $\omega$ was represented as the complex value $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. The following equation was used to determine it [30, 31]:
\[ \varepsilon(\omega) - 1 = \frac{1}{\varepsilon_0 - 1} \int_0^\infty \exp(-i\omega t) \frac{dF}{dt} dt \]
\[ = 1 - i\omega \int_0^\infty \exp(-i\omega t) F(t) dt, \]
where \( F(t) \) is the normalized autocorrelation function of a total dipole moment \( M(t) = \sum_{j=1}^N d_i(t) \) of the cluster and \( \varepsilon_0 \) is the static dielectric permittivity.

Raman and infrared spectra of the clusters can be calculated through the autocorrelated functions of polarizability and a dipole moment, correspondingly. A polar molecule is characterized by a permanent polarizability and a dipole moment, correspondingly. Interaction with the neighboring molecules creates the induced dipole moment and polarizability. Interaction with the neighboring molecules \([33]\), where \( \alpha_i, 0 \) are the locations of the centers of mass of the molecule \( i \). Each of the molecules in the model can be regarded as a polarizable point dipole localized in the center of mass of the molecule. The dipole moment \( d_i \) of the molecule \( i \) and its polarizability \( \alpha_i \) are connected due to the interaction with the surrounding molecules \([32]\),

\[ d_i = d_i, 0 + \alpha_i, 0 \sum_{j \neq i} T_{ij} d_j, \]
\[ \alpha_i = \alpha_i, 0 + \alpha_i, 0 \sum_{j \neq i} T_{ij} \alpha_j. \]

Here, \( T_{ij} \) is the tensor of a dipole–dipole interaction:

\[ T_{ij} = \frac{1}{|r_i|} (3\hat{r}_i \hat{r}_j - \mathbf{1}). \]  \( \tag{2} \)

In Eq. (2) \( \hat{r}_i \) is the unit vector in the direction of \( \mathbf{r}_i - \mathbf{r}_j \), where \( \mathbf{r}_i, \mathbf{r}_j \) are the locations of the centers of mass of the molecules \( i \) and \( j \) and \( \mathbf{1} \) is the unit \( 3 \times 3 \) tensor. An anisotropic gas-phase tensor of polarizability \( \alpha_{xx, yy, zz} = \{1.495, 1.626, 1.286\} \) \( \text{Å}^3 \) for the water molecule \([32]\) was used. The oxygen and ozone molecules were characterized by isotropic experimental values of polarizability of 1.57 and 2.85 \( \text{Å}^3 \) \([33]\), and the bromine ions had polarizability of 4.53 \( \text{Å}^3 \) \([20]\). To calculate the induced dipole moments \( d_i \), a standard iterative procedure \([15]\) was used at each of the time steps. The accuracy of determination of \( d_i \) is set in the range of \( 10^{-5} - 10^{-4} \) D.

The cross section of the infrared absorption is determined as follows

\[ \sigma(\omega) = \left( \frac{2}{hv c \rho n} \right) \omega \tanh \left( \frac{h\omega}{2kT} \right) \text{Re} \int_0^\infty d\omega \text{Re} \left\{ M(t) \cdot M(0) \right\}, \]

where \( n \) is the refraction coefficient, \( \varepsilon_\infty \) is the dielectric permittivity of vacuum, and \( c \) is the speed of light.

In the case of the depolarized light, the Raman spectrum \( J(\omega) \) is set by the following expression \([32]\) (scattering at \( \omega < 0 \) is Stokes, and at \( \omega > 0 \) it is anti-Stokes):

\[ J(\omega) = \frac{\omega}{(\omega + \omega_L)^2} \text{Re} \left\{ \int_0^\infty d\omega \text{Re} \left\{ M(t) \cdot M(0) \right\} \right\}, \]

where \( \Pi(t) = \sum_{j=1}^N \{ \alpha_i(t) - \langle \alpha_i \rangle \} \), \( \omega_L \) is the frequency of the exciting laser, \( \Pi_{xx} \) is the \( xx \) component of the value \( \Pi(t) \), the \( x \) axis is directed along a molecular dipole, and \( xy \) is the molecular plane. During simulation, the value of \( \omega_L = 19436.3 \) cm\(^{-1}\) (green line of the argon laser, \( \lambda = 514.5 \) nm) was used.

The frequency dispersion of the dielectric permittivity determines the frequency dependence of the dielectric losses \( P(\omega) \) according to the following equation \([34]\)

\[ P = \frac{\varepsilon''(E^2)/\varepsilon_0}{4\pi}, \]

where \( \varepsilon''(E^2) \) is the mean value of the squared intensity of the electric field and \( \omega \) is the frequency of the emitted electromagnetic wave.

The reflection coefficient \( R \) is determined as the ratio of a mean energy flow reflected from the surface to the incident flow. The reflection coefficient upon a normal incidence of a plane monochromatic wave is defined as follows \([35]\):

\[ R = \left| \frac{\sqrt{|\varepsilon|} - \sqrt{|\varepsilon_0|}}{\sqrt{|\varepsilon|} + \sqrt{|\varepsilon_0|}} \right|^2. \]  \( \tag{3} \)

It is suggested here that the wave incidence occurs from a transparent medium (index 1) into a medium that can be both transparent and nontransparent, i.e., absorbing and scattering (index 2).

The overall number of electrons \( N_{el} \) in a unit of the cluster volume which interact with the external electromagnetic field is set in the following form \([35]\):

\[ N_{el} = \frac{m}{2\pi e^2} \int_0^\infty \omega \varepsilon''(\omega) d\omega, \]

where \( e \) and \( m \) are the charge and the mass of an electron.

RESULTS OF CALCULATIONS

The configurations of the system \((\text{O}_2)_6 + (\text{H}_2\text{O})_{50} + 2\text{Br}^-\) that correspond to the moment of time of 25 ps are shown in Fig. 2. When using the free boundary conditions, both \( \text{Br}^- \) ions moved away from the cluster (Fig. 2a) by the end of
calculations. One of these ions is presented in Fig. 2. As a result of using the random boundary conditions at the moment of \( t = 25 \) ps, both \( \text{Br}^- \) ions are present in the cluster (Fig. 2b). However, three oxygen molecules had left the cluster by that moment of time. When ozone molecules were present in the system instead of oxygen molecules, the \( \text{Br}^- \) ions and \( \text{O}_3 \) molecules remained in the cluster until the moment of \( t = 25 \) ps both in the case of using the free and the random boundary conditions. Perturbation that resulted from the presence of bromine ions in the cluster volume turns out to be sufficient to evaporate a few oxygen molecules from the latter and insufficient for the ozone molecules to leave the cluster.

The real and imaginary parts of the dielectric permittivity determine, correspondingly, the refraction and absorption indices of the considered media. For the dispersion water systems that contain the oxygen molecules, the intensities both of real and imaginary parts of the dielectric permittivity are found to decrease in the frequency range of \( 0 \leq \omega \leq 3500 \text{ cm}^{-1} \) in the presence of one or two \( \text{Br}^- \) ions with the free BC or of one \( \text{Br}^- \) ion when using the random BC. However, when the random BCs are used for two \( \text{Br}^- \) ions, the values of the magnitudes of \( \varepsilon' \) and \( \varepsilon'' \) increase in this range. The values of \( \varepsilon' \) and \( \varepsilon'' \) calculated for the systems that contain ozone are shown in Fig. 3, and the location of their main peaks are listed in Table 1. In this case, the highest values of \( \varepsilon' \) are registered when one \( \text{Br}^- \) ion is present in the system. In the case of using the free BC, the values of \( \varepsilon' \) are higher than when using the random BC (Table 2 shows the correlations between the integral intensities of the spectra). The \( \varepsilon' \) value for the bulk liquid water [36] decreases rapidly with an increase of the frequency and at \( \omega > 600 \text{ cm}^{-1} \) it becomes lower than the similar characteristic of the considered cluster systems. On the whole, between the imaginary parts of the dielectric permittivity, a correlation characteristic for the \( \varepsilon' \) value is preserved. The experimental oscillating function \( \varepsilon''(\omega) \) for the liquid water decays, and at \( \omega > 720 \text{ cm}^{-1} \) it takes lower values than the relevant functions of the cluster systems. Due
### Table 1. Locations of the main peaks in the considered spectra of the systems under study

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<th>Free boundary conditions</th>
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**real part of dielectric permittivity, \(\varepsilon'(\omega)\)**

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**imaginary part of dielectric permittivity, \(\varepsilon''(\omega)\)**

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**absorption spectra of infrared radiation, \(\sigma(\omega)\)**

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**Raman spectra, \(J(\omega)\)**

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**emission spectra of infrared radiation, \(P(\omega)\)**

<p>| | | | | | | | | |</p>
<table>
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to replacement of oxygen molecules by ozone molecules, the dissipation capacity of the infrared radiation increased on the average by 9.5 times when the Br− ions were on the surface of the cluster system and by 2.5 times upon their arising in the bulk of the system (Table 3). This can be ascribed primarily to the appearance of the Coulomb constituent of the interaction (for the O3 molecules), which was absent in the case of the O2 molecules.

The IR-spectra of absorption of the investigated systems are shown in Fig. 4. Figure 4a shows the spectra of the water clusters that have absorbed oxygen, and Fig. 4b shows similar spectra in the case of ozone capture by the water clusters. The Br− appearance inside of the cluster with O2 molecules leads to an increase of the integral intensity of the spectrum (curves 4, 5) and location of the Br− ions from the outside of the aggregate decreases substantially the value.

The correlation between the integral intensities of the systems’ spectra is listed in Table 2. The locations of the main peaks in the IR absorption spectra of the systems under study are shown in Table 1. Figure 4 also depicts the experimental IR absorption spectra of liquid water [38] and gaseous mixture of O2 + O3 [39].

As a result of the ozone absorption, the form of the IR spectrum changes and the spectrum becomes bimodal. Here, a decrease of the integral intensity of IR spectrum due to the location of the Br− ions on the cluster surface does not occur. In all cases after the introduction of the Br− ions into the system, the value increases. Introduction of a second Br− ion causes intensity enhancement of the IR spectrum (Table 3). Table 1 lists the data on the location shifts of the peaks depending on the BC and the number of bromine ions, as well as with respect to the experimental spectra of gaseous ozone [40] and bromine hydride [41].

The Raman spectra for the oxygen-containing systems are presented in Fig. 5a, and those for the ozone-containing system are shown in Fig. 5b. The Raman spectrum of the water–oxygen system without ions has three peaks: the peak at a frequency of 2840 cm−1 is the most intense. The Br− appearance inside of the cluster with O2 molecules leads to a decrease of the integral intensity of the spectra (Table 2), leaving its shapes almost unchanged (curves 2, 3). However, when Br− ions are inside the cluster and can randomly change their places, the J(ω) spectra substantially change (curves 4, 5). One bromine ion that randomly changes its location inside of the cluster is found to transform the Raman spectrum of a system to a spectrum with two symmetrical peaks, and two traveling Br− ions create a single broad peak at 1680 cm−1 (Table 1). The experimental Raman spectra of liquid water [42] and bromine clathratohydrate [43] are indicated by curves 6 and 7 in Fig. 5. In the presence of ozone molecules in a system, the Raman spectrum undergoes no significant changes both in the case of the Br− ions’ location

<table>
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<tr>
<th>System</th>
<th>I (H2O)50 + 6O2</th>
<th>II Br− + (H2O)50 + 6O2</th>
<th>III 2Br− + (H2O)50 + 6O2</th>
<th>VII Br− + (H2O)50 + 6O3</th>
<th>VIII 2Br− + (H2O)50 + 6O2</th>
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<table>
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<th>V Br− + (H2O)50 + 6O3</th>
<th>VI 2Br− + (H2O)50 + 6O3</th>
<th>IX Br− + (H2O)50 + 6O3</th>
<th>X 2Br− + (H2O)50 + 6O3</th>
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<td>1.63</td>
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on the cluster surface and upon penetration of the latter inside of it. All obtained spectra $J(\omega)$ for the systems with the $\text{Br}^-$ ions are close to the Raman spectrum of the system (Fig. 5b, curves 1–5 and Table 1). Curve 8 in Fig. 5b shows the Raman spectra of gaseous ozone [44].

Figure 6 shows the IR radiation power emitted by the cluster systems. For systems with oxygen molecules and $\text{Br}^-$ ions, upon using the free BC, the integral intensity of emission spectra decreases: the more $\text{Br}^-$ ions in the system, the more profound the decrease. Using the random BC in this case causes a mitigation of the value (in the presence of a single bromine ion) and a substantial strengthening of this characteristic (in the presence of two $\text{Br}^-$ ions) (Table 2).

A completely different character of IR radiation emission is observed for the ozone-containing systems. Systems with only one $\text{Br}^-$ ion yield the most intense radiation. In the case of free BC, this radiation is more powerful. The appearance of the second bromine ion decreases the emission power considerably. In the case of the random BC, the emission power on the whole becomes lower than for system IV, which lacks bromine ions (Table 3). This behavior of the $P(\omega)$ function correlates with the value of a number of free electrons $N_e$ that participate in the interaction with electromagnetic radiation. The $N_e$ values for the corresponding systems correlate as $1 : 3.71 : 1.47 : 3.03 : 1.01$. It is noteworthy that systems VI, IX, and X have the lowest mechanical stability.

The reflection spectra $R(\omega)$ of IR radiation for systems III and VI, i.e., with $\text{O}_2$ and $\text{O}_3$ molecules in the presence of two $\text{Br}^-$ ions and the free BC, are shown in Fig. 7. It is seen that the presence of oxygen in the system leads to the $R(\omega)$ spectrum blurring, due to which the integral intensity of the reflection spectrum for system III is 2.36 times higher than that for the corresponding spectrum of system VI. Seven specific peaks created by the water nucleus of the systems are manifested in both cases. However, for system VI containing ozone, these peaks are expressed far more distinctly. Thus, the water clusters that absorb oxygen molecules are found to reflect the incoming IR radiation more uniformly and intensely.
CONCLUSIONS

In this work, a method of a computational simulation is proposed to study the role of water clusters in ozone depletion occurring under the effect of the bromine ions. It was shown that ozone, unlike oxygen, manifests a high stability against desorption which is connected with the change of the Br\(^–\) ion locations in a dispersion water system. The lifetime of the Br\(^–\) ions in the water clusters exceeds substantially the time of location of Cl\(^–\) in the vicinity of these formations. This suggests a more efficient occurrence of chemical reactions with participation of bromine ions. The amount of the Br\(^–\) ions and their location considerably change the values of the real and imaginary parts of dielectric permittivity of cluster systems, but, however, leave unchanged the location of their extreme. For the systems that have absorbed oxygen, the intensities of infrared absorption spectra decrease with Br\(^–\) ions located on the cluster surface and they increase with Br\(^–\) ions in the cluster volume. In the case of the ozone-containing systems, the integral intensity of the IR absorption spectrum grows irrespectively of the location of Br\(^–\) ions in the cluster. In the presence of the bromine ions, the anti-Stokes region of the Raman spectrum decreases its intensity, resulting from the absorption of the oxygen molecules by the water clusters, and almost entirely preserves its form after the absorption of the ozone molecules. The effect of the bromine ions located in the oxygen-containing system on the emission spectrum of IR radiation depends on the ions’ location and on their amount. The ions on the surfaces of the clusters decrease the emission power of these systems, whereas the ions located in the bulk of the clusters may both decrease (one Br\(^–\) ion per cluster) and increase (two Br\(^–\) ions per cluster) the efficiency of radiation. If there is ozone in the system, the power of its IR radiation emission in the presence of the Br\(^–\) ions increases, as a rule. The location of two Br\(^–\) ions in the volume of a cluster is an exception, in which the intensity of the emission spectrum decreases slightly. The spectra of reflection of IR radiation change insignificantly with respect to the amount of the Br\(^–\) ions present in the cluster systems of both types (with oxygen and ozone) if the ions are in the cluster volume. When the Br\(^–\) ions are on the surfaces of clusters, the spectrum of reflection of IR radiation becomes blurred for the oxygen-containing system, while in the case of the ozone-containing system it preserves its form.

Thus, the presence of the Br\(^–\) ions in a system affects primarily the intensity of its spectral character-
istics, while the frequency shifts in IR spectra are determined according to a type of the absorbed molecules by the water system. The data obtained in this study on the IR and Raman spectra of water clusters that contain oxygen, ozone, and bromine can be used in the future to develop an experimental method for investigating of a concentration of the tropospheric ozone and the mechanisms of its depletion, e.g., using lidars. Moreover, experimentators frequently face a problem of identifying the spectra, which turns out to be insolvable very often for a variety of reasons. The computerized experiment makes it possible to immediately create the cluster systems and change their composition, which suggests the feasibility of determining the correlation of the peaks of spectra with different system components. It also becomes possible to analyze a phase state of a system, since the spectra are fairly sensitive to phase transitions.

ACKNOWLEDGMENTS

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