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Computer simulation of the cluster destruction of stratospheric ozone by bromine*

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The interaction of $(Br^-)_i(H_2O)_{50-i}$, $0 \le i \le 6$ clusters with oxygen and ozone molecules is investigated by the method of molecular dynamics simulation. The ozone molecules as well as the bromine ions do not leave the cluster during the calculation of 25 ps. The ability of the cluster containing molecular oxygen to absorb the infrared (IR) radiation is reduced in the frequency range of $0 \le \omega \le 3500$ cm^{-1} when the number of the bromine ions in the cluster grows. The intensity of the Raman spectrum is not changed significantly when the Br^- ions are added to the ozone-containing system. The power of the emitted IR radiation is increased when the number of bromine ions grows in the oxygen-containing system. The data obtained in this study on the IR and the Raman spectra of the water clusters that contain ozone, oxygen, and Br^- can be used to develop an investigation of the mechanisms of ozone depletion.

Keywords: bromine ion, water cluster, ozone, infrared and Raman spectra

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1. Introduction

Bromine is one of the most active destroyers of the stratospheric ozone layer, which forms an invisible shield around the Earth protecting it from the biologically damaging ultraviolet rays of the Sun. In the stratosphere, the bromine concentration is much lower than that of chlorine. Nevertheless, the bromine is more active and causes more effective depletion of the ozone (by 45–69 times).[1] The additional intrusion of bromine- and chlorine-containing substances into the stratosphere leads to the violation of the natural balance of formation and destruction of the ozone. This is mainly manifested as an additional factor that causes ozone depletion. Under the action of sunlight, the organobromine compounds are destroyed to form free bromine atoms in the atmosphere, which are highly effective in ozone depletion (in the bound state, chlorine and bromine do not destroy ozone). On one hand, the ozone ability to absorb the biologically dangerous Sun ultraviolet radiation is most valuable. On the other hand, however, the ozone irritates and inflames our lungs, which is one of the reasons why exercising in polluted places can exacerbate asthma and other health problems. Small water particles in the atmosphere, i.e., clusters, are commonly regarded as the condensation nuclei during the formation of clouds. The depletion of ozone occurs not only because of the halogens (bromine or chlorine atoms), the clusters and the small water droplets also make the contribution. However, the atmospheric chemical reactions including water clusters and bromine ions that cause the ozone depletion have not been studied yet.

Bromine can be dissolved easily in water (35 g/L in water), carbon disulfide, and other organic solutions. When added to water, bromine forms hypobromous acid. Hypobromous acid is a weak acid. It partly dissociates to form hydrogen ions and hypobromite ions. The ratio of hypobromous acid and hypobromite ions is determined by the pH value of the water. When the pH value is between 6.5 and 9, both hypobromous acid and hypobromite ions can be found in the water. The bromine reacts with the other substances in the water to form bromine-containing substances. These substances are disinfectants and do not give off odors. In nature, bromine can be found as bromide salts or organic bromine substances. These substances are produced by several sea organisms. Bromine is mostly found in soluble salts in seawater, salt lakes, and ocean.

At present, Raman and infra-red spectra are the main characteristic tools used to find the concentrations of atmospheric gases representing health haz-

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ard in the troposphere and the stratosphere. Infrared spectroscopy provides a method to determine the internal geometrical structures of molecules. Near-infrared spectroscopy has been used to evaluate acute lung injuries.[2] Extensive studies to characterize the mutant hemoglobin by NMR spectroscopy, X-ray diffraction, and molecular dynamics simulations have been executed.[3−5]

The goal of the present work is to investigate the interaction of bromine ions with cold water clusters when the contact with ozone and oxygen molecules is observed, to determine the influences of the bromine ions on the infrared absorption spectra and on the Raman spectra of the cluster systems, to calculate the power spectra of the emitted radiation, and to investigate the mechanisms of ozone destruction.

2. Molecular dynamics model

In the present work, the polarizable variant of the advanced TIP4P model of water is used.[6] In this case, the parameters of the Lennard–Jones (LD) parts of the potential and the site of negative charge are changed. As a result, the permanent dipole moment of the water molecule corresponds to the experimental value in the gas phase (1.848 D).[7] The distance between atoms in the oxygen molecule is 0.12074 nm.[8] The geometry of the ozone molecule is determined by an isosceles triangle, the length of equal sides is 0.1278 nm, and the angle between them is 116.8°. The total energy is represented as a sum of kinetic, potential, and polarization energies. In the case of water–water interactions, the pair part of the potential is the sum of the Lennard–Jones and the Coulomb contributions. The non-Coulomb part of water–oxygen (ozone) and oxygen (ozone)–oxygen (ozone) interactions is represented as a sum of repulsive and dispersive contributions[9,10]

$$\Phi(r_{ij}) = b_i b_j \exp[-(c_i + c_j) r_{ij}] - a_i a_j r_{ij}^{-6}, \quad (1)$$

where a_i, b_i, c_i are the potential parameters describing the interactions, which are taken from Ref. [11], and r_{ij} is the distance between atoms i and j.

The Coulomb interaction of Br^- ion with water molecules is taken into account due to its electric charge $q_{Br^-} = -e$, where e is the elementary charge. The non-Coulomb Br^-–H_2O interaction is determined as the Lennard–Jones one with parameters taken from Ref. [12]. For Br^- ions and also for ions and atoms of O_2 or O_3 molecules, both the Coulomb interaction and the atom–atom interactions determined by Eq. (1) are considered. The central atom of the ozone molecule has a positive electric charge $q_{cen} = 0.19e$, and the side atoms of the O_3 molecule each carry a negative charge $q_{side} = -0.095e$. The atoms of the O_2 molecule have no electric charge.

Flexible models of molecules are considered. The flexibility of the molecules is created using the procedure developed within the framework of Hamiltonian dynamics.[13,14] We consider the diatomic molecule. Let atoms a and b in a molecule be separated by the distance

$$q = \|\boldsymbol{r}_a - \boldsymbol{r}_b\|, \quad (2)$$

where $\boldsymbol{r}_a$ and $\boldsymbol{r}_b$ are vectors representing the positions of the atoms. The corresponding velocities are denoted by $\boldsymbol{v}_a$ and $\boldsymbol{v}_b$, and the reduced mass is written as

$$\mu = \frac{m_a m_b}{m_a + m_b}. \quad (3)$$

The size of the molecule with atoms a and b is determined by the equality condition of potential $f(q) = -(\partial \boldsymbol{r}/\partial \boldsymbol{q})\nabla \Phi(\boldsymbol{r})$ and centrifugal $-\mu q \omega^2$ forces

$$-\mu q \omega^2 - f(\boldsymbol{r}) \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{q}} = 0, \quad (4)$$

where $\omega = \|\boldsymbol{v}_a - \boldsymbol{v}_b\|/q$ is the angular velocity. From the condition of the minimal contribution to potential U from each generalized coordinate, we have

$$\frac{\partial}{\partial q_i} H(\boldsymbol{r}, \boldsymbol{v}) = \frac{\partial}{\partial q_i} \left(\frac{1}{2} \mu_i q_i^2 \omega_i^2 + U(\boldsymbol{r}) \right) = 0. \quad (5)$$

This method is generalized to molecules of any composition.[15]

The simulation of the interaction of the $(Br^-)_i(H_2O)_{50-i}$ clusters with the gas environment containing i H_2O molecules and six O_2 or O_3 molecules begin with the creation of configuration from the equilibrium $(H_2O)_{50}$ water cluster in the molecular dynamics calculation with the kinetic energy corresponding to the temperature of 233 K. We use this value according to the following thoughts: the maximum of isothermal compressibility of the supercooled water is observed at 233 K,[16] and hence it has the lowest mechanical stability determined by $1/(V\beta_T)$. The cluster inheriting properties of the liquid water should also be the least stable at 233 K. Therefore, the successful simulation at this temperature assumes the opportunity to obtain the stable clusters at the other temperatures ($T > 233$ K). Big water clusters including $(H_2O)_{50}$ (with transversal size about 3.5 nm) are present in clouds. Water clusters

containing more than 10 molecules are injected to the atmosphere by spacecrafts at heights from 10 km up to 30 km (i.e., at $T < 230$ K). These clusters can exist for a very long time, because the evaporation energy of the molecules makes up the most part of the whole cluster energy.[17] Particles of a sea salt and the ice from the sea can be sources of bromine in the atmosphere. Due to the high concentration of bromides, the reaction of bromides with the ozone on the surface of the sea salt particle goes more intensively than that in a bulk water medium.[18] The inorganic Br_y bromine is released from the precursor components in the bottom part of the stratosphere. Big water clusters with high concentrations of bromine ions can be formed here with high probability. The coordinate system connected with the cluster center of mass is used to determine the positions of bromine ions in the cluster. The virtual sphere around the water cluster is drowned. The water molecules that are closer than the other ones to the points of exit from the sphere of the coordinate axes are found. Each of these molecules (from 1 up to 6) moves outside along the appropriate coordinate axis at the distance of 0.7 nm from the former position of its center of mass. The Br^- ion is placed instead of replacing the water molecule. The number of bromine ions corresponds to the number of the replaced water molecules. The interaction of $(Br^-)_i(H_2O)_{50-i}$ cluster and water, ozone or oxygen molecules is investigated at 233 K. The cut-off radius of the molecular interactions in the model is 0.9 nm. The use of the cut-off radius in the case of water–water interactions is explained by the necessity to save other parameters of potential constructed for simulating both clusters and bulk systems. The potential function cut-off for the other interactions in the system under consideration has not been carried out. Six O_2 or O_3 molecules are placed close to the bottom part of the cluster. The time step of the molecular dynamics calculation is $\Delta t = 10^{-17}$ s, which helps to save the integrity of the cluster. The time step for the simulation of clusters is smaller by one order than that for the system with periodic boundary conditions. The calculation of spectral characteristics begin at the moment $t = 10^5\Delta t$ (1 ps). The full duration of calculation is 2.5×10^6 time steps (25 ps). The relaxation time in the bulk water is 10 ps.[19] The relaxation in the clusters happens more quickly. Consequently, 25 ps is sufficient both for the calculations of spectral characteristic and thermodynamic quantities.

The motion equations for the centers of mass of the molecules are integrated by using the Gear fourth-order method.[20] Equations for the rotational motion of molecules are analytically solved using the Rodrigous–Hamilton parameters.[21] The integration scheme for the rotational motion equations corresponds to the approach proposed by Sonnenschein.[22]

3. The formation of ultradisperse systems from clusters

Let us consider the case of unpolarized light dispersion, where the length of the molecule l is much smaller than the wavelength of the light λ. The extinction coefficient (weakening) of a beam η on one hand is defined by the Rayleigh formula[23]

$$\eta = \frac{2\omega^4}{3\pi c^4}\frac{(\sqrt{\varepsilon}-1)^2}{N}, \tag{6}$$

on the other hand, it is defined through a scattering coefficient ρ ($\eta = 16\pi\rho/3$)[24] in the approximation of scattering at angle 90°. Considering that $\eta = \alpha + \rho$, where α is the absorption coefficient, we have

$$N = \frac{2\omega^4}{3\pi c^4}\frac{(\sqrt{\varepsilon}-1)^2}{\alpha}\left(1-\frac{3}{16\pi}\right), \tag{7}$$

where N is the number of scattering centers in 1 cm^3, c is the velocity of light, ε is the dielectric permittivity of the medium, and ω is the frequency of the wave.

We will form the heterocluster system so that a cluster containing i admixture molecules and n water ones has the statistical weight

$$W_{in} = \frac{N_{in}}{N_\Sigma}, \quad i = 1,\ldots,6;\ n = 50, \tag{8}$$

where N_{in} is the number of clusters with i admixture molecules and 50 water ones in 1 cm^3, $N_\Sigma = \sum_{i=1}^{6} N_{in}$, and i can vary from 1 to 6. The similar weights have been used for pure water clusters. In that case, $i = 0$, and n is between 10 and 50 with $\Delta n = 5$, so the top index is equal to 9. According to this scheme, the ultradisperse system consisting of water clusters, bromine ions, and oxygen or ozone molecules are formed. The calculations of all spectral characteristics will be held in accordance with the accepted statistical weights of W_{in}.

The procedure of cluster system formations assumes the uniform distribution of these formations, and it is justified at low cluster concentrations. The clusters do not interact with each other. The average concentration of each type of cluster in the system under investigation is less than the Loschmidt number by 12–13 orders.

4. Dielectric properties

The dielectric permittivity $\varepsilon(\omega)$ is represented by a complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega)$, and it is defined according to the following equation:[25]

$$\frac{\varepsilon(\omega)-1}{\varepsilon_0-1} = -\int_0^\infty \exp(-\mathrm{i}\omega t)\frac{\mathrm{d}\,F}{\mathrm{d}\,t}\,\mathrm{d}\,t = 1-\mathrm{i}\omega\int_0^\infty \exp(-\mathrm{i}\omega t)F(t)\,\mathrm{d}\,t, \quad (9)$$

where $F(t)$ is a normalized autocorrelation function of the total dipole moment of a cluster $\boldsymbol{M}(t) = \sum_{j=1}^{N} \boldsymbol{d}_j(t)$, and ε_0 is the static dielectric constant.

It is possible to calculate Raman and infrared spectra of the clusters through the autocorrelation functions of polarizability and dipole moment correspondently. The polar molecule is characterized by permanent (gas phase) dipole moment $\boldsymbol{d}_{i,0}$ and by polarizability tensor $\boldsymbol{\alpha}^{\mathrm{p}}_{i,0}$. The induced dipole moment and polarizability of molecule i lead to the interaction with the neighboring molecules. In the model, each molecule can be considered as a polarizable dot dipole located at the molecule center of mass. The dipole moment $\boldsymbol{d}_i$ of molecule i and its polarizability $\boldsymbol{\alpha}^{\mathrm{p}}_i$ are connected due to the interaction with the surrounding molecules[25]

$$\boldsymbol{d}_i = \boldsymbol{d}_{i,0} + \boldsymbol{\alpha}^{\mathrm{p}}_{i,0}\sum_{j\neq i}\boldsymbol{T}_{ij}\boldsymbol{d}_j, \quad (10)$$

$$\boldsymbol{\alpha}^{\mathrm{p}}_i = \boldsymbol{\alpha}^{\mathrm{p}}_{i,0} + \boldsymbol{\alpha}^{\mathrm{p}}_{i,0}\sum_{j\neq i}\boldsymbol{T}_{ij}\boldsymbol{\alpha}^{\mathrm{p}}_j. \quad (11)$$

Here $\boldsymbol{T}_{ij}$ is the tensor of dipole–dipole interaction

$$\boldsymbol{T}_{ij} = \frac{1}{|r_{ij}|^3}\left(3\hat{\boldsymbol{r}}_{ij}\hat{\boldsymbol{r}}_{ij} - \mathbf{1}\right), \quad (12)$$

where $\hat{\boldsymbol{r}}_{ij}$ is a unit vector in the $\boldsymbol{r}_i - \boldsymbol{r}_j$ direction, $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ are the positions of the centers of mass of i and j molecules, respectively, and $\mathbf{1}$ is a unit 3×3 tensor. For the water molecule, the anisotropic gas phase tensor of polarizability $\alpha_{xx,yy,zz} = \{1.495, 1.626, 1.286\}$ Å^3 is used.[25] The ozone molecules are characterized by the isotropic experimental value of polarizability of 2.85 Å^3, and the oxygen ones have the polarizability of 1.57 Å^3.[26] The bromine ions have the polarizability of 4.53 Å^3.[18] For the calculation of the induced dipole moments, the standard iterative procedure is used in each time step.[6] The accuracy of $\boldsymbol{d}_i$ definition is set in the range of 10^{-5}–10^{-4} D.

The infrared absorption is given in the form[25]

$$\sigma(\omega) = \left(\frac{2}{\varepsilon_{\mathrm{v}} c\hbar n}\right)\omega\tanh\left(\frac{\hbar\omega}{2kT}\right) \times \mathrm{Re}\int_0^\infty \mathrm{d}\,t\mathrm{e}^{\mathrm{i}\omega t}\left\langle \boldsymbol{M}(t)\cdot\boldsymbol{M}(0)\right\rangle, \quad (13)$$

where ε_{v} is the vacuum permittivity, $\hbar = h/2\pi$, h is Planck's constant, n is a refractive index independent of frequency ω, and $\boldsymbol{M}(t)$ is the normalized autocorrelation function of the total dipole moment of cluster.

In the case of depolarized light, the Raman spectrum is set by the equation[25]

$$J(\omega) = \frac{\omega}{(\omega_{\mathrm{L}}-\omega)^4}\left(1-\mathrm{e}^{-\hbar\omega/kT}\right) \times \mathrm{Re}\int_0^\infty \mathrm{d}\,t\mathrm{e}^{\mathrm{i}\omega t}\left\langle \Pi_{xz}(t)\Pi_{xz}(0)\right\rangle, \quad (14)$$

where

$$\Pi(t) \equiv \sum_{j=1}^{N}\left[\boldsymbol{\alpha}^{\mathrm{p}}_j(t) - \left\langle\boldsymbol{\alpha}^{\mathrm{p}}_j\right\rangle\right], \quad (15)$$

ω_{L} is the frequency of the exciting laser, Π_{xz} is the xz component of $\Pi(t)$, axis x is directed along a molecular dipole, and xy is a molecular plane. We set $\omega_{\mathrm{L}} = 19436.3$ cm^{-1} (green line of argon laser, $\lambda = 514.5$ nm).

The frequency dependence of dielectric losses can be represented as[24]

$$P = \frac{\varepsilon''\langle E^2\rangle\omega}{4\pi}, \quad (16)$$

where $\langle E^2\rangle$ is the average value of the square of the electric field strength, and ω is the frequency of the emitted electromagnetic wave.

5. Results

The configurations of the $(\mathrm{Br}^-)_6(\mathrm{H_2O})_{44} + 6\mathrm{O_2} + 6\mathrm{H_2O}$ system corresponding to the moments of 1 ps and 25 ps are shown in Fig. 1. The Br^- ions replace the water cores by the moment of 1 ps. On the contrary, the water molecules surrounding the cluster come closer to the core (Fig. 1(a)). As a result, a complete cluster consisting of 50 $\mathrm{H_2O}$ molecules, 6 $\mathrm{O_2}$ molecules, and 6 Br^- ions is formed. However, the $\mathrm{O_2}$ molecules and the Br^- ions leave the cluster with the time being. By the end of calculation (25 ps), the $(\mathrm{Br}^-)_6(\mathrm{H_2O})_{50}(\mathrm{O_2})_6$ cluster has lost 2 $\mathrm{O_2}$ molecules and 3 Br^- ions. The evaporating bromine ion is shown in the bottom part of Fig. 1(b). On the contrary, in the case of ozone-containing system, $\mathrm{O_3}$ and $\mathrm{H_2O}$ molecules are adsorbed on the cluster surface during the calculation time. They form a new cluster together with the Br^- ions. It should be noted that the

bromine ions save their positions close to the cluster surface during the whole calculation.

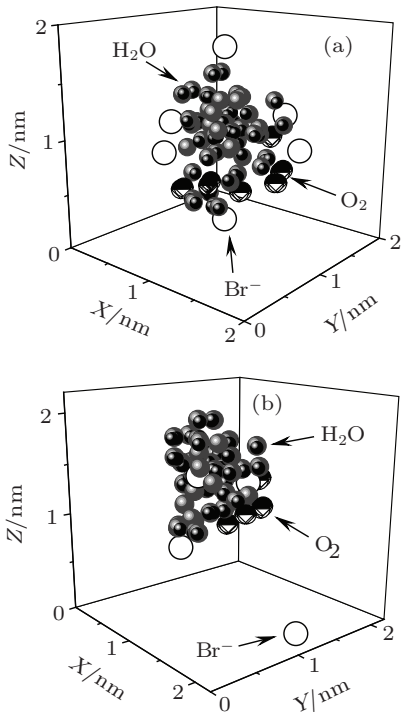


Fig. 1. Configurations of $6O_2 + (H_2O)_{50} + 6Br^-$ system corresponding to the moments of (a) 1 ps and (b) 25 ps.

The relative dielectric permittivity shows by how many times the interaction between the charges in a homogeneous medium is less than that in the vacuum. Water is a very good solvent for ions. The high dielectric permittivity of water, an effective screening of the Coulomb potential of the dissolved ions, is observed. It prevents the aggregation of opposite charge ions. The Br^- ions degenerate when they are placed uniformly on a cluster surface. According to the traditional beliefs, the water molecules solvate anions in such a way that the hydrogen atoms are turned in the direction of the anion. In a water solution, the bromine ion does not allow two water molecules of the first hydration layer to be moved.[27] In the case of Na^+ and K^+ ion hydration, the number of attached ions to the water molecule is equal to three. It is possible to expect that the bonding of water molecules by ions will result in effects similar to the temperature lowering. The real and the imaginary parts of the complex dielectric permittivity of water grow when the temperature drops (experiment at the frequencies of 0.915–2.45 GHz).[28] The water molecules in a big cluster screen the Br^- ions, reducing their electrostatic repulsion to a minimum. The low movement velocity of the water molecules in the hydrate layers strengthens their reaction to the electric field. It is expressed in a growth of the dielectric permittivity quantity. The real and the imaginary parts of the dielectric permittivity for $(Br^-)_i(H_2O)_{50} + 6O_3$, $0 \le i \le 6$ systems are presented in Fig. 2. The values increase with the increase of the Br^- ions in the cluster. The integral intensities of $\varepsilon'(\omega)$ spectra correlate as 1 : 0.82 : 1.76 : 2.01 : 1.94 : 1.24 : 2.18 (Fig. 2(a)). The integral intensities of the corresponding $\varepsilon''(\omega)$ spectra have the following correlation: 1 : 0.48 : 2.41 : 2.78 : 2.73 : 1.58 : 3.08 (Fig. 2(b)). The real part ε' characterizes the reserved energy of the system when the electric field influences. The imaginary part ε'' or the factor of dielectric loss influences on the absorption and attenuation of energy. It is the main characteristic for the definition of dielectric properties. According to the theory,[29] low frequencies up to $\omega = 1000\ \mathrm{cm}^{-1}$ (a peak at $430\ \mathrm{cm}^{-1}$ in $\varepsilon''(\omega)$ spectrum in our calculations) describe the relaxation processes in the heteroclusters when the dipoles have an opportunity to follow the changes of the applied field.

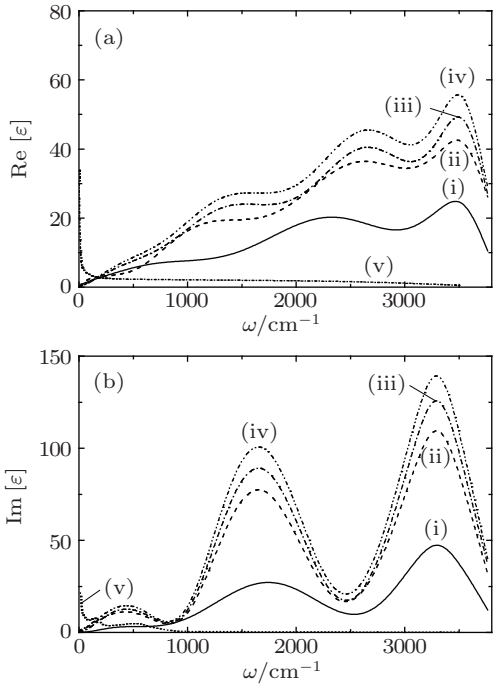


Fig. 2. Frequency dependences of (a) real and (b) imaginary parts of dielectric permittivity of systems: (i) $(H_2O)_{50} + 6O_3$, (ii) $(Br^-)_2(H_2O)_{50} + 6O_3$, (iii) $(Br^-)_4(H_2O)_{50} + 6O_3$, and (iv) $(Br^-)_6(H_2O)_{50} + 6O_3$. Curve (v) in panel (a) is the MD simulation result for the bulk water,[30] while curve (v) in panel (b) gives the experimental result for the liquid water.[31]

However, the contribution of this mode to the general picture is insignificant. Medium frequencies up to $\omega = 2500$ cm^{-1} (the maximum at 1700 cm^{-1} in our calculations) characterize the resonant processes in the systems and the fast libration (rotation) of the molecule motion. The libration motions replace the rotation degrees of freedom when the gas phase goes to the condensed one. The addition of bromine ions changes only the rate of rotation of the molecular motions. Therefore, the rotation motions will take place almost in all collided molecule pairs. The increase of the rotation motions results in the amplification of $\varepsilon''(\omega)$ spectrum intensity in the investigated frequency range. The peak at $\omega = 3300$ cm^{-1} (high frequencies, $\omega > 2500$ cm^{-1}) corresponds to the bonded water molecules in the system. In our case, the intensity of this peak is essentially increased, but it does not change its location in the process of Br^- ion addition to the cluster. Thus, the high-frequency share of the absorption in the IR spectrum considerably increases. It points to a strong influence of water skeleton on the dielectric properties of heteroclusters. The $\varepsilon'(\omega)$ of the liquid water[30] decreases rapidly when the frequency grows. It already takes lower values than that for the investigated systems at $\omega > 200$ cm^{-1}. The $\varepsilon''(\omega)$ of water obtained from the experiment[31] behaves almost in a similar way. Its value becomes lower than that for the systems under investigation at $\omega > 650$ cm^{-1}. When two and four Br^- ions are added to the oxygen-containing system, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ change significantly. However, when the number of bromine ions increases up to 6, they restore to values which are typical for the system without Br^- ions.

The absorption spectra of IR radiation of the cluster systems containing oxygen molecules are shown in Fig. 3. The intensities of the IR spectra decrease when the number of bromine ions increases in the system. The integral intensities of the IR spectra for the systems with O_2 molecules correlate as 1 : 0.71 : 0.71 : 0.56 : 0.42 : 0.52 : 0.42. The location of the principal maximum of the IR spectrum does not change significantly with the increase of Br^- ion number in the system. The wide first peak locating at $\omega = 1858$ cm^{-1} for the $(H_2O)_{50} + 6O_2$ system has blue shifted by ~ 50 cm^{-1} in the IR spectrum of the $(Br^-)_2(H_2O)_{50} + 6O_2$ system, and it is transformed to a shoulder for the $(Br^-)_4(H_2O)_{50} + 6O_2$ and the $(Br^-)_6(H_2O)_{50} + 6O_2$ systems. The experimental IR spectrum for gaseous O_2 has the sharp maximum at $\omega = 45$ cm^{-1}.[32] The area of high intensity in the experimental spectrum of gaseous bromine hydride is in the frequency range of 2300 cm$^{-1} \leq \omega \leq$ 2700 cm^{-1}.[33] The local minimum of this IR spectrum at the frequency of 2500 cm^{-1} coincides with a local minimum of the appropriate spectra of the disperse systems. The increase of the number of bromine ions up to six results in disappearing of the first peak of the $\sigma(\omega)$ spectrum. Nonpolar O_2 molecules create effect of dilution owing to the decrease of the total dipole moment magnitude. The Br^- ions perturb the internal electric field of a cluster and accelerate the attenuation of the autocorrelation function of its dipole moment magnitude $d_{\rm cl}$. As a result, the IR spectrum intensity of the oxygen-containing system decreases when the number of bromine ions grows.

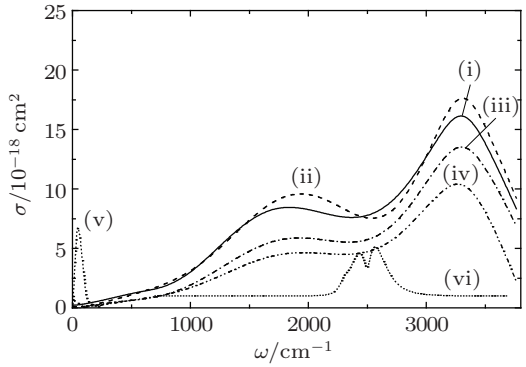


Fig. 3. Infrared absorption spectra of systems: (i) $(H_2O)_{50} + 6O_2$, (ii) $(Br^-)_2(H_2O)_{50} + 6O_2$, (iii) $(Br^-)_4(H_2O)_{50} + 6O_2$, and (iv) $(Br^-)_6(H_2O)_{50} + 6O_2$. Curve (v) is the experimental spectrum of gaseous O_2,[32] while curve (vi) gives the experimental spectrum of gaseous bromine hydride.[33]

The intensity of the $\sigma(\omega)$ spectrum increases when the Br^- ions are added to the cluster in the ozone-containing systems (Fig. 4). The growth of intensity in the IR absorption spectrum stops when the number of the attached Br^- ions is 4. The integral intensity of the $\sigma(\omega)$ spectrum for the system with six Br^- ions is lower than that for the system with four Br^- ions. The correlation between the integral intensities of IR spectra for systems with O_3 molecules is 1 : 1.33 : 3.37 : 6.97 : 6.85 : 8.91 : 6.31. The grouped polar O_3 molecules create a poorly varying electric field, which orders the dipole moments of the water molecules. As a result, the magnitude $d_{\rm cl}$ essentially increases and the intensity of the IR spectrum grows when the number of Br^- ions in the system rises. The amplification of perturbation due to the addition of more than 4 Br^- ions to the cluster

results in a faster attenuation of the autocorrelation function of the dipole moment $d_{\rm cl}$. As a consequence, the evolved $i = 4$ intensity of the IR spectrum of the ozone-containing system starts to reduce. The initial increase of the $\sigma(\omega)$ spectral intensity for these systems correlates with the maximum location of the IR spectrum of gaseous O_3 (1000 $\rm cm^{-1}$).[34] The most intensive absorption band with a maximum at the frequency of 3304 $\rm cm^{-1}$ is characterized by the valence symmetric vibrations of the O–H bonds of the water molecules (3450 $\rm cm^{-1}$ for bulk water, experiment[35]). The short displacement into the red area of the $\sigma(\omega)$ spectrum for the systems with bromine ions can be explained by the change of the hydrogen bond structure caused by the addition of bromine ions to the system. The wide band in the range of 1700–1900$\rm cm^{-1}$ is formed when the Br^- ions are added to the system. It testifies the formation of –Br$\cdots$H–O– associates. The growth of the intensity of this peak in the process of bromine ion addition testifies the increase of strength of these hydrogen associates.

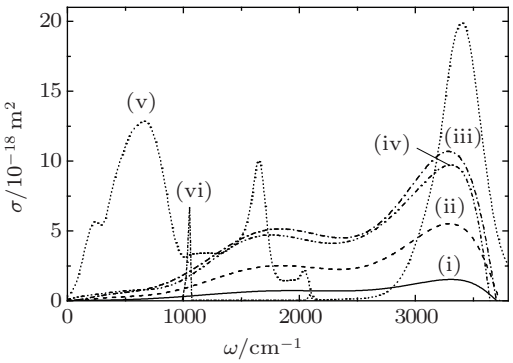


Fig. 4. Infrared absorption spectra of systems: (i) $(H_2O)_{50}+6O_3$, (ii) $(Br^-)_2(H_2O)_{50}+6O_3$, (iii) $(Br^-)_4(H_2O)_{50}+6O_3$, (iv) $(Br^-)_6(H_2O)_{50}+6O_3$; Curve (v) is the $\sigma(\omega)$ spectrum of the bulk water obtained in experiment,[35] curve (vi) is the experimental spectrum of gaseous O_3.[34]

The Raman $J(\omega)$ spectra of $(H_2O)_{50}+6O_3$ and $(Br^-)_6(H_2O)_{50}+6O_3$ systems containing ozone molecules together with the appropriate experimental spectra of liquid water,[36] gaseous O_3,[37] and clathrate hydrate of crystal bromine[38] are shown in Fig. 5. The Raman spectra of the $(Br^-)_i(H_2O)_{50}+6O_3$, $1 \le i \le 5$ systems differ a little from the appropriate spectrum of the $(H_2O)_{50}+6O_3$ system (curve (i)). The integral intensity of the $J(\omega)$ spectrum for the system containing 6 Br^- ions (curve (ii)) is lower by a factor 4.3 compared to that for the system without the Br^- ion. The location of the principal maximum of the Raman spectrum for the ozone-containing system is displaced toward high frequencies with respect to the peak location of the appropriate spectrum for bromine clathrate hydrate and to low frequencies with respect to the location of the principal maximum of the experimental spectrum of liquid water. The first peak of the $J(\omega)$ spectra for the $(Br^-)_i(H_2O)_{50}+6O_3$, $0 \le i \le 6$ systems is in a frequency range determined by the locations of peaks for gaseous O_3. The $J(\omega)$ spectrum for the $(Br^-)_6(H_2O)_{50}+6O_2$ system (curve (iii)) as well as the Raman spectra for the other oxygen- and bromine-containing systems are close to the Raman one of the $(H_2O)_{50}+6O_2$ system (curve (i)). The integral intensity of the Raman spectrum for the system containing 6 bromine ions is differ only by a factor 1.1 from that characteristic of the system without the Br^- ions. The principal maximum of the $J(\omega)$ spectra for the systems with oxygen molecules (3228 $\rm cm^{-1}$) is located between the main peaks of the Raman spectra for liquid water (3322 $\rm cm^{-1}$) and for clathrate hydrate of crystal bromine (3100 $\rm cm^{-1}$).

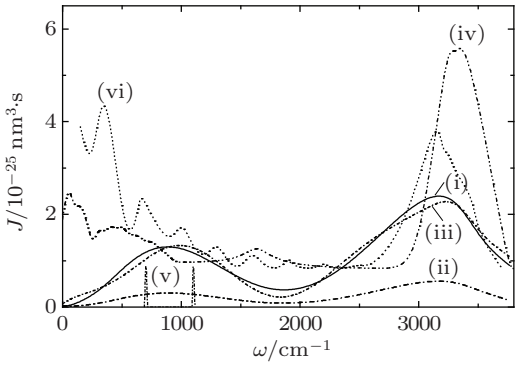


Fig. 5. Raman spectra for systems: (i) $(H_2O)_{50}+6O_3$, (ii) $(Br^-)_6(H_2O)_{50}+6O_3$, (iii) $(Br^-)_6(H_2O)_{50}+6O_2$, (iv) bulk water at $T = 293$ K (experiment[36]), (v) gaseous ozone (experiment[37]), and (iv) bromine clathrate hydrate at 266 K (experiment[38]).

The average polarizability per molecule $\bar{\alpha}^{\rm p}$ goes down in comparison with the simulated $\alpha^{\rm p}$ magnitude for water cluster at the addition of nonpolar molecules having lower polarizability $\alpha^{\rm p}$ (0.793 Å^3) than the $\alpha^{\rm p}$ magnitude (1.49 Å^3) for molecules of liquid water. The presence of Br^- ions renders a weak influence on the behavior of the autocorrelation function of fluctuation of the polarizability. As a result, we have similar Raman spectra of the investigated systems containing oxygen. The other situation arises for the systems containing ozone. The polar molecules of ozone have higher polarizability ($\alpha^{\rm p} = 2.7$ Å^3) than the water ones. Therefore, the $\bar{\alpha}^{\rm p}$ magnitude is higher than $\alpha^{\rm p}$ for the water cluster. The disordering of the dipole

moments amplifies with the increase of the number of the Br^- ions, and the polarizability is smoothly reduced. The fluctuation of $\alpha^{\rm p}$ is lower than that for the systems with oxygen. As a result, the intensity of the $J(\omega)$ spectrum for the systems containing ozone is reduced when the number of the Br^- ions increases.

The power of the emitted IR radiation by the clusters with O_3 molecules is shwon in Fig. 6(a). The intensity of the $P(\omega)$ spectrum considerably increases after the addition of three and more Br^- ions to the cluster. The spectral integral intensities of the $(Br^-)_i(H_2O)_{50} + 6O_3$, $0 \le i \le 6$ systems under investigation have the following correlation: 1 : 0.74 : 0.87 : 5.27 : 5.25 : 6.10 : 6.63. The principle maximum of the $P(\omega)$ spectrum is insignificantly displaced to low frequencies ($\sim$ 30 cm^{-1}) after the addition of more than three bromine ions to the ozone-containing cluster. When the Br^- ions are added to the system with O_3 molecules, the low-frequency peak in the vicinity of frequency 1760 cm^{-1} appears. The clusters emit the weakest radiation at frequencies of $\omega < 1000$ cm^{-1}.

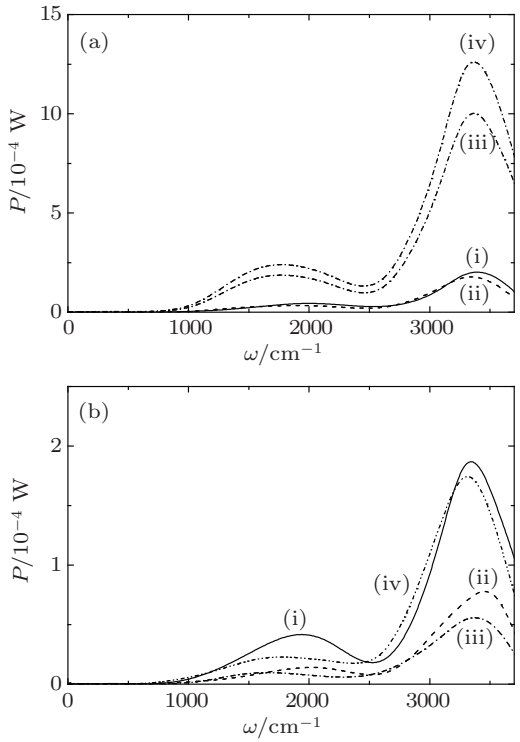


Fig. 6. Frequency dependences of IR radiation power $P(\omega)$ for systems containing (a) O_3 or (b) O_2 molecules and (i) 0 Br^-, (ii) 2 Br^-, (iii) 4 Br^-, (iv) 6 Br^- ions.

For the oxygen-containing systems, the intensities of the $P(\omega)$ spectra decrease (Fig. 6(b)). However, the intensity starts to increase when the ultradisperse system with O_2 molecules contains 5 and 6 bromine ions. When there are two and four Br^- ions interacting with the oxygen molecules in the system, the location of the principle maximum of the $P(\omega)$ spectrum has a small shift ($\sim$ 40–50 cm^{-1}) into the area of high frequencies. When the number of the bromine ions is equal 6, the shift to the low frequencies ($\sim$ 25 cm^{-1}) is observed. The presence of the Br^- ions results in smearing the first peak of the $P(\omega)$ spectrum and decreasing its intensity.

The time dependences of the ion numbers in chlorine- and bromine-containing systems are shown in Fig. 7. These dependences are obtained with the assumption that if the ion moves away from the nearest molecule by a distance more than 2 nm, then it does not influence the system state. Only four, two, and one bromine ions surround the $6O_2 + (H_2O)_n$ system by the time moment of 25 ps. When the system is surrounded by the same amount of chlorine ions, it loses them completely at the moment of 3 ps.[39] Thus, the bromine ions stay near to the cluster surface much

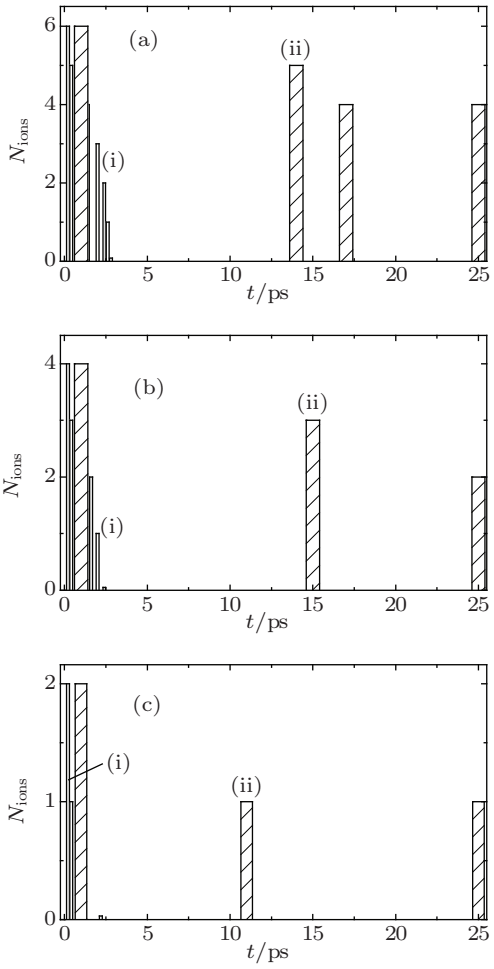


Fig. 7. Time dependences of the numbers of (i) Cl^- ions and (ii) Br^- ions interacting with the $6O_2 + (H_2O)_{50}$ system when there are (a) six, (b) four, and (c) two ions in the water cluster.

longer (by the order) than the chlorine ones. Therefore, the Br^- ions are much more effective than the Cl^- ions in splitting the O_3 molecules in the atmosphere.

The destruction of the ozone molecule occurs easily. The length of the O_3 molecule is longer than that of the oxygen one. The bond energy (52 kJ/mol) of the third oxygen atom is almost five times smaller than that between the other two oxygen atoms in the O_3 molecule. As a result, the strength of the ozone molecule is lower than that of the oxygen one. The intramolecular bond in oxygen is much stronger than that in ozone. In all states (gaseous, liquid, and solid), O_2 is a paramagnetic substance, and its dissociation energy is 496 kJ/mol. The disintegration energy of water to simple substances is 484 kJ/mol. The dissociation energy of N_2 (the most widespread molecule in the atmosphere) is 945 kJ/mol. The oxygen molecule is much more chemically active than the nitrogen one. The high energy collisions of the Br^- ions with O_2 and O_3 molecules are recorded in our calculations. The ozone destruction takes place when the cluster has 3 or more bromine ions.

6. Conclusion

The important role of bromine in the chemistry of the troposphere is defined first of all by its influence on the contents of ozone. The destruction of ozone begins with the photolysis of the molecular compound containing Br^-. As a result, the atomic bromine is formed. Bromine destroys ozone according to the well known cycle including BrO_x and HO_x components. The ozone destruction can be caused not only by chlorine components fluorine and bromine, but also by the microparticles of water and ice, which activate this process. Atomic oxygen is an initial product of the ozone destruction. At the same time, the O_2 molecule is considerably stronger, and it is not disintegrated under the action of UV radiation in the stratosphere.

It is shown in the present work that water clusters can keep the Br^- ions from interacting with environmental moleculars oxygen and ozone. During the whole MD calculation of duration 25 ps, the bromine ions contact with water and ozone molecules. The bromine ions show a low desorption even at high concentrations. It testifies that in the disperse water medium, the Br^- ions influence considerably stronger (owing to the increase of contact time) on the ozone destruction than the Cl^- ones.[40] The water cluster can attract a high concentration of Br^- ions around itself. In this case, the bromine ions get high kinetic energy because of the electrostatic repulsive. The high-energy bromine ion colliding with an oxygen molecule can remove it easily from the system. The intensity of the infrared absorption spectrum of the disperse water system with ozone molecules considerably increases when the Br^- ions are in the system. The absorption activity decreases consistently during the addition of the Br^- ions to the water cluster. The larger the number of the bromine ions in the clusters is, the weaker the intensity grows. At high concentrations of Br^- ions, the growth of the absorptive intensity stops. The strong reduction of the Raman spectrum intensity of the disperse system with ozone molecules is observed at high concentrations of Br^- ions. In the case of a system containing ozone, the increase of the bromine ion concentration in the clusters results in an essential amplification of the IR radiation emitted power by that system. On the contrary, the increase of the Br^- ion number in the systems with oxygen molecules results in the decrease of the power of the emitted IR radiation by the clusters. In water clusters absorbing oxygen and ozone molecules, the bromine ions have considerably longer life time than the chlorine ones.

References

[1] Sinnhuber B M, Sheode N, Sinnhuber M, Chipperfild M P and Feng W 2006 *Atmos. Chem. Phys. Discuss* **6** 6497
[2] Shibata S, Ohdan H, Noriyuki T, Yoshioka S, Asahara T and Dohi K 1999 *Am. J. Respir. Crit. Care Med.* **160** 317
[3] Kim H W, Shen T J, Sun D P, Ho N T, Madrid M and Ho C 1995 *J. Mol. Biol.* **248** 867
[4] Puius Y A, Zou M, Ho N T, Ho C and Almo S C 1998 *Biochemistry* **37** 9258
[5] Kim H W, Lee C H, Jung S and Won Y 2001 *Bull. Korean Chem. Soc.* **22** 253
[6] Dang L X and Chang T M 1997 *J. Chem. Phys.* **106** 8149
[7] Benedict W S, Gailar N and Plyler E K 1956 *J. Chem. Phys.* **24** 1139
[8] Nikolskiiy B P 1971 *The Chemists Book* (Leningrad: Himiya) p. 204
[9] Galashev A E, Rakhmanova O R and Chukanov V N 2005 *Rus. J. Chem. Phys.* B **24** 90
[10] Spackman M A 1986 *J. Chem. Phys.* **85** 6579
[11] Spackman M A 1986 *J. Chem. Phys.* **85** 6587
[12] Perera L and Berkowitz M L 1991 *J. Chem. Phys.* **95** 1954
[13] Lemberg H L and Stillinger F H 1975 *J. Chem. Phys.* **62** 1677
[14] Rahman A, Stillinger F H and Lemberg H L 1975 *J. Chem. Phys.* **63** 5223
[15] Berendsen H J C, Postma J P M, van Gunsteren W F, DiNola A and Haak J R 1984 *J. Chem. Phys.* **81** 3684
[16] Bartell L S 1997 *J. Phys. Chem.* **101** 7573

[17] Vostrikov A A, Dyubov D Y and Drozdov S V 2008 *Letters to JTP* **34** 87
[18] Hunt S W 2004 *J. Phys. Chem.* A **108** 11559
[19] Skripov V P and Koverda V P 1984 *Spontaneous Crystallization of Supercooled Liquids* (Moscow: Nauka) p. 230
[20] Haile J M 1992 *Molecular Dynamics Simulation Elementary Methods* (New York: Wiley) p. 490
[21] Koshlaykov V N 1985 *Problems of Solid Body Dynamics and Applied Theory of Gyroscopes* (Moscow: Nauka) p. 286
[22] Sonnenschein R J 1985 *Comp. Phys.* **59** 347
[23] Landau L D and Lifshitz E M 1982 *Electrodynamics of Continuous Media* (Moscow: Nauka) p. 620
[24] Prokhorov A M 1988 *Physical Encyclopedia* (Moscow: Sovetskaya Entciklopediya) p. 702
[25] Bosma W B, Fried L E and Mukamel S J 1993 *Chem. Phys.* **98** 4413
[26] Huiszoon C 1986 *Mol. Phys.* **58** 865
[27] Marcus Y 1987 *Pure Appl. Chem.* **59** 1093
[28] Komarov V V and Tang J 2004 *Microw. Opt. Tech. Lett.* **42** 419
[29] Komarov V V, Wang S and Tang J 2005 *Encyclopedia RF Microwave Engineering* (New York: Wiley) p. 3693
[30] Neumann M 1986 *J. Chem. Phys.* **85** 1567
[31] Angell C A and Rodgers V 1984 *J. Chem. Phys.* **80** 6245
[32] Robichaud D J, Hodges J T, Brown L R, Lisak D, Maslowski P, Yeung L Y, Okumura M and Miller C E 2008 *J. Mol. Spectrosc.* **248** 1
[33] Kozintzev V I, Belov M L, Gorodnichev V A and Fedotov U V 2003 *Laser Optical Acoustic Analysis of Multicomponent Gas Mixtures* (Moscow: MSTU named N.E. Bauman) p. 352
[34] Goggin P L and Carr C 1986 *Water and Aqueous Solutions* (Boston: Adam Hilger) p. 149
[35] Upschulte B L, Green B D, Blumberg W A and Lipson S J 1994 *J. Phys. Chem.* **98** 2328
[36] Vallee P, Lafait J, Ghomi M, Jouanne M and Morhange J F 2003 *J. Molec. Struct.* **651–653** 371
[37] Andrews L and Spiker R C 1972 *J. Phys. Chem.* **76** 3208
[38] Goldschleger I U, Kerenskaya G, Janda K C and Apkarian V A 2008 *J. Phys. Chem.* A **112** 787
[39] Galashev A E, Rakhmanova O R, Novruzova O A and Galasheva A A 2009 *Colloid Journal* **71** 734
[40] Galashev A E and Rakhmanova O R 2011 *Rus. J. Phys. Chem.* B **5** 197