

Spectral Characteristics of Water Clusters upon Interaction with Oxygen Molecules and Chlorine Ions

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Abstract—The interactions of a $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system with two, four, or six Cl^- ions are studied by the molecular dynamics method. The integral intensity of IR and Raman spectra decreases with an increase in the number of Cl^- ions surrounding the system. The values of real and imaginary parts of dielectric permittivity increase with the rise in the frequency reaching maxima in the $850 \leq \omega \leq 950 \text{ cm}^{-1}$. As a result of interactions between ions and the formed $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster, the pattern of the reflection spectrum of IR radiation becomes smoother. The interaction between $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system and Cl^- ions leads to the substantial increase in the power of emitted radiation. With time, Cl^- ions gradually leave the interaction zone with the system. Maximum residence time of the last ion near the system boundary does not exceed 3 ps. Cl^- ions located closer to O_2 molecules do not penetrate into the depth of an $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster.

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INTRODUCTION

Water clusters have been rather extensively studied by computer simulation [1–4]. These studies give grounds for understanding the formation of hydrogen bonds in systems with a small number of water molecules. The system formed by water and dissolved substance is more complex. Interactions between substance and water or hydration occur during dissolution. The reversible addition of water molecules to ions, atoms, or molecules of another substance occurs over the course of hydration. Small polar molecules are easily hydrated by polar water molecules. Gaseous oxygen does not have permanent dipole moment; i.e., oxygen molecules are apolar. However, the polarizability of oxygen molecule ($\alpha_{\text{O}_2} = 1.57 \text{ \AA}^3$) is higher than for water molecule ($\alpha_{\text{H}_2\text{O}} = 1.45 \text{ \AA}^3$) [5]. Oxygen is one of the most abundant elements on Earth. About the half of the Earth's crust consists of components containing oxygen and one-fifth of the atmosphere is composed of oxygen. Molecular oxygen is dissolved in liquid water in amount of about 6 ml/l ($T = 300 \text{ K}$). Clusters are capable of absorbing molecules of many apolar substances including oxygen [6–8]. The study of molecular clusters yields a unique possibility to investigate the transition from the gas phase to condensed phases and gives insight into intermolecular interactions between absorbed substance and water. Oxygen physically absorbed by clusters weakly interacts with water molecules.

The solution of Schrödinger equation for electrons and nuclei in water clusters is complicated due to following circumstances. First, the number of atoms

involved in calculations increases with cluster size and the accuracy of calculations quickly becomes uncontrollable. Second, the obtained potential energy surface possesses the set of minima that makes the interpretation and the reproducibility of potential surface more complicated and prevents subsequent dynamic study. Therefore, increased attention in the study of energetics and structure of water-containing clusters is given to computer simulation methods, such as molecular dynamics (MD) and Monte Carlo simulation.

Physical and chemical absorption of oxygen on surface (111) of platinum was well studied in physical experiment [9]. Calculations of potential energy surface indicate the existence of energy minima for both face-centered and face-centered close-packed lattices, as well as for the intermediate positions of O_2 molecules [10]. For water clusters, it was of interest to study the competitive process of hydration between oxygen molecules and hydrophobic ions, e.g., Cl^- . This process can occur in the Earth's troposphere where water clusters, which are formed upon a decrease in temperature, encounter oxygen molecules and chlorine ions. Chlorine is a relatively heavy element and approximately 20000 times less common than oxygen.

In the upper atmosphere in the presence of short-wave ultraviolet radiation, a number of reactions occur with the participation of chloromethanes, particularly the action of photons with wavelengths of 190–225 nm leads to the photolysis of chloromethanes to form several tens of different compounds and radicals, e.g., by the following scheme:



In principle, the reaction is not stopped at this stage and $\text{CF}_x\text{Cl}_{3-x}$ molecules can be further decomposed photochemically to once again form free chlorine. Chlorine also appears in the atmosphere in consequence of chemical plants effluents and waste incineration.

Chlorine is chemically very active due to the low energy of dissociation of Cl_2 molecules into atoms and high affinity of electrons for chlorine atom. High-energy electrons propagating in the atmosphere ionize neutral atoms and molecules and excite their energy levels. Oxygen exists in the atmosphere in the form of allotropic modifications O_2 and O_3 (ozone). In all states (gas, liquid, and solid), O_2 is paramagnetic and has very high energy of dissociation (496 kJ/mol). Chlorine forms a number of oxides with oxygen, which are unstable and explosive in pure form. It was established by computer simulation that the Cl^- ion, in contact with small $(\text{H}_2\text{O})_4$ water cluster, behaves differently than Na^+ ion [11]. The main distinctive feature of the formation of $\text{Cl}^-(\text{H}_2\text{O})_4$ complex is the fact that $(\text{H}_2\text{O})_4$ cluster is located on the one side of the ion. In case of $(\text{H}_2\text{O})_{20}$ cluster, the Cl^- ion is also displaced by hydrogen bonds to the surface of aggregate [12].

The aim of this work is to study the effect of Cl^- ions surrounding aggregates formed from $(\text{H}_2\text{O})_{50}$ water cluster and six oxygen molecules on the dielectric properties of these aggregates, including Raman spectra, as well as to establish the possibility of the solvation of Cl^- ions with water cluster containing oxygen.

MOLECULAR DYNAMICS MODEL

In this work, we used the variant of polarizable molecules in the modified TIP4P model of water [13]. In that work, Dang and Chang substantially changed the parameters of the Lennard-Jones (LD) part of the potential so that coefficients in terms that characterize repulsion and attraction decrease by 2.5- and 2.9-fold, respectively. In addition, the localization center of negative charge is far from the center of oxygen atom by a distance of 0.0215 nm instead of 0.015 nm as before. This made it possible to correct the permanent dipole moment of water molecule to 1.848 D, which corresponds the experimental value of this parameter in the gas phase. The dynamics of the system of molecules was implemented with the intermolecular water–water interaction potential [14] and the description of oxygen–oxygen and oxygen–water interactions in the form of the sum of repulsion and attraction contributions [15]

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

where a_i , b_i , and c_i are parameters of potential describing these interactions are taken from [16].

The Cl^- ion in the model was characterized by the electric charge $q_{\text{Cl}^-} = -1e$, where e is elementary electric charge. As in the case of water molecule, the Cl^- ion

possesses one center of Lennard-Jones interaction. Parameters of LD potential describing Cl^- –O interactions are taken from [17]. In addition to Coulombic interactions, atom–atom interactions between Cl^- ions calculated by formula (1) with parameters used in [16] were also taken into account.

Flexible models of molecules were considered. The flexibility of molecules was created using the procedure developed within the framework of Hamiltonian dynamics [18, 19]. We consider the diatomic molecule. Let atoms a and b in a molecule be separated by the distance

$$q = |\mathbf{r}_a - \mathbf{r}_b|,$$

where \mathbf{r}_a and \mathbf{r}_b are vectors that determine the positions of atoms. Corresponding velocities are denoted by \mathbf{v}_a and \mathbf{v}_b , and the reduced mass is written as

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

The size of molecule presented by atoms a and b is determined from the equality condition by the values of

potential $\mathbf{f}(\mathbf{q}) = -\frac{\partial \mathbf{r}}{\partial \mathbf{q}} \nabla \Phi(\mathbf{r})$ and centrifugal $(-\mu q \omega^2)$ forces so that

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

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

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

This method is generalized to molecules of any composition [20].

The simulation of interactions of the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system with Cl^- ions started by creating a configuration of an equilibrium $(\text{H}_2\text{O})_{50}$ water cluster and surrounding oxygen molecules. Initial equilibrium configurations of water clusters were constructed in the preliminary molecular dynamics calculations; the kinetic energy of molecules constituting the cluster corresponded to 250 K. The interactions of water cluster with oxygen molecules and chlorine ions were studied at the same temperature. Initially, the center of free oxygen molecule was positioned at a distance of 0.6–0.7 nm from the nearest center of water molecule constituting the cluster. Moreover, the linear O_2 molecule was characterized by a random orientation. As a result, each oxygen molecule appeared in the field of molecular interaction. The cut-off radius of molecular interactions in the model was 0.9 nm. Six O_2 molecules were added to the bottom part of the cluster. The fairly compact arrangement of O_2 molecules promotes the elucidation of their effect on the behavior of Cl^- ions added to $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system. Molecular dynamics calculations were performed with

a time step of $\Delta t = 10^{-17}$ s. Here and below, time $t = 0$ is assumed to be the moment at which oxygen molecules and chlorine ions approached the water cluster. The calculation of spectral characteristics started with moment $t = 10^5 \Delta t$ (1 ps) and the total duration of calculations was $2.1 \times 10^6 \Delta t$ time steps. The $(\text{O}_2)_6 (\text{H}_2\text{O})_{50}$ cluster was formed during $\sim 3 \times 10^5 \Delta t$ time steps, irrespective of the presence of Cl^- ions. The attainment of stable values of total dipole moment of $(\text{O}_2)_6 (\text{H}_2\text{O})_{50}$ cluster and stable bond length distribution testified to the formation of this aggregate. Ions approached $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system pairwise and arranged on coordinate axes on different sides of the system at a distance of no shorter than 0.6 nm from any atom of the nearest molecule. The motion equations for the centers of mass of the molecules were integrated by the Gear fourth-order method [21]. Equations for the rotational motion of molecules were analytically solved using the Rodrig–Hamilton parameters [22]. The integration scheme for rotational motion equations corresponded to the approach proposed by Sonnenschein [23]. The calculations were carried out with a Pentium-IV four-core computer operating at a processor clock frequency of 2.83 GHz.

DIELECTRIC PROPERTIES

Permittivity $\epsilon(\omega)$ as a function of frequency ω was represented as complex value $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, which was defined by the equation [24, 25]

$$\begin{aligned} \frac{\epsilon(\omega) - 1}{\epsilon - 1} &= - \int_0^\infty \exp(-i\omega t) \frac{dF}{dt} dt \\ &= 1 - i\omega \int_0^\infty \exp(-i\omega t) F(t) dt, \end{aligned} \quad (2)$$

where the $F(t)$ function is the normalized autocorrelation function of the total dipole moment of cluster

$$F(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle \mathbf{M}^2 \rangle},$$

where

$$\mathbf{M}(t) = \sum_{j=1}^N \mathbf{d}_j(t)$$

presents the sum of dipole moments of individual molecules.

Using the Drude–Lorentz model for describing the motion of electrons in a molecule, we obtain the fol-

lowing expressions for real ϵ' and imaginary ϵ'' parts of the permittivity of dielectric [26]:

$$\begin{aligned} \epsilon' &= 1 + \frac{\omega_p^2(\tilde{\omega}_0^2 - \omega^2)}{(\tilde{\omega}_0^2 - \omega^2) + \omega^2 v^2}, \\ \epsilon'' &= \frac{\omega_p^2 v \omega}{(\tilde{\omega}_0^2 - \omega^2) + \omega^2 v^2}, \end{aligned} \quad (3)$$

where $\omega_p^2 = 4\pi N q^2/m$, N is the number of oscillators in a system, q is the electric charge of oscillating atom, m is its mass, $\tilde{\omega}_0^2 = \omega_0^2 - \omega_p^2/3$, ω_0 is the resonance angular frequency of normal oscillation, and mv is the coefficient accounting for the decay of oscillations in the motion equation of oscillator, where $v = 10^{14} \text{ cm}^{-1}$. As ω_0 , we used the frequency corresponding to the principal maximum of IR spectrum. The ϵ' and ϵ'' values determined from expressions (3) were used to compare with analogous characteristics calculated directly by Eq. (2).

Changes in the vibrational state of molecules take place upon the action of a laser on the sample, which begins to emit radiation with changed wavelength (Raman scattering). Any substance that also permanently emits the Rayleigh radiation occurs without a substantial change in the wavelength. Raman spectroscopy makes it possible to analyze substance in any state, i.e., in liquid, gas, and solid states with particle sizes larger than 1 μm . In the Raman spectrum of the cluster, along with lines corresponding to the frequencies of incident light, there are lines that conform to the combinations (sums and differences) of these frequencies with frequencies of normal vibrations of molecules. Raman and IR spectra can be calculated via the autocorrelation functions of the polarizability and dipole moment, respectively. A polar molecule is characterized by permanent dipole moment $\mathbf{d}_{i,0}$ and polarizability tensor $\boldsymbol{\alpha}_{i,0}$. Interaction with neighbor molecules gives rise to induced dipole moment due to the polarizability of i th molecule. In the model, each molecule can be considered to be a polarizable point dipole in the center of the mass of molecule. Dipole moment \mathbf{d}_i of molecule i and its polarizability $\boldsymbol{\alpha}_i$ are connected due to interactions with surrounding molecules as follows [27]:

$$\mathbf{d}_i = \mathbf{d}_{i,0} + \boldsymbol{\alpha}_{i,0} \sum_{j \neq i} \mathbf{T}_{ij} \mathbf{d}_j, \quad (4)$$

$$\boldsymbol{\alpha}_i = \boldsymbol{\alpha}_{i,0} + \boldsymbol{\alpha}_{i,0} \sum_{j \neq i} \mathbf{T}_{ij} \boldsymbol{\alpha}_j. \quad (5)$$

Here, \mathbf{T}_{ij} is the tensor of dipole–dipole interaction

$$\mathbf{T}_{ij} = \frac{1}{|r_{ij}|^3} (3\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} - 1). \quad (6)$$

In Eq. (6), $\hat{\mathbf{r}}_{ij}$ is the unit vector in direction $\mathbf{r}_i - \mathbf{r}_j$, where \mathbf{r}_i and \mathbf{r}_j are positions of the centers of the mass of mol-

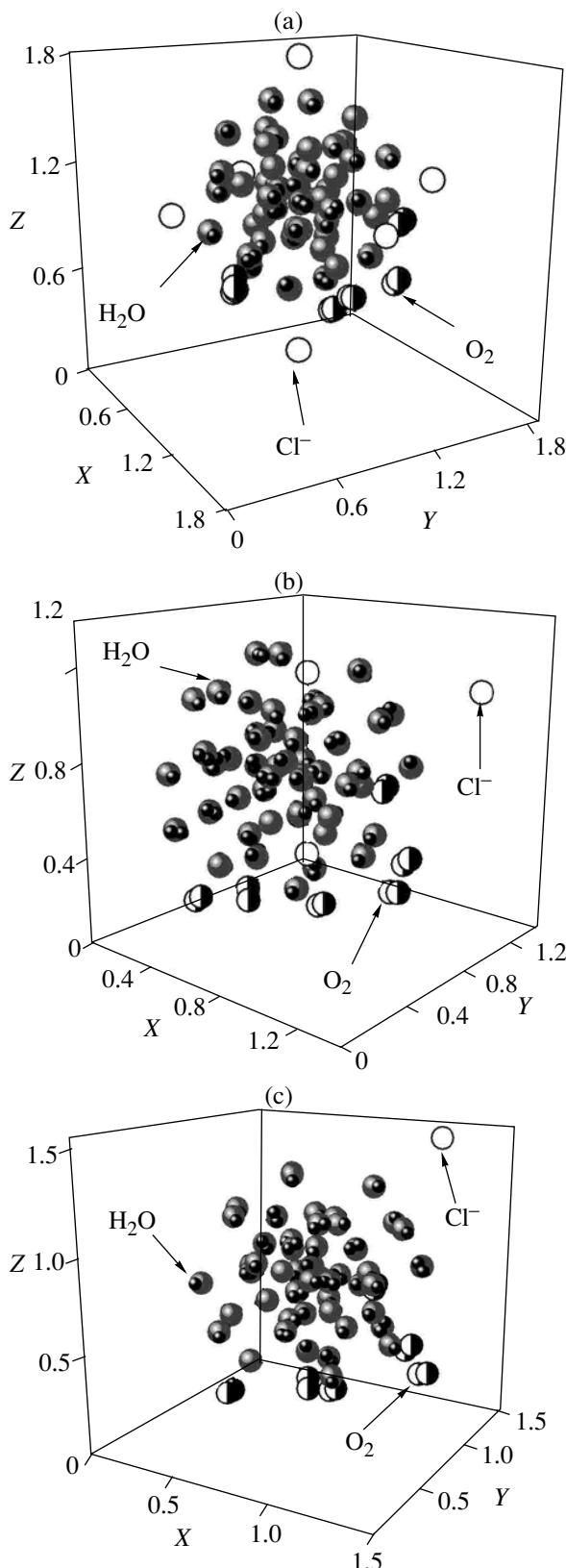


Fig. 1. Configurations of $(\text{O}_2)_6 + (\text{H}_2\text{O})_{50} + 6\text{Cl}^-$ system at different times: (a) 0, (b) 2.2, and (c) 3 ps, respectively. Coordinates of molecules are indicated in nm.

ecules i and j ; the unit 3×3 tensor is denoted by $\mathbf{1}$. For the water molecule, we used anisotropic diagonal polarizability tensor $\alpha_{xx,yy,zz} = \{1.495, 1.626, 1.286\} \text{ Å}^3$ [28]. The oxygen molecule was characterized by the experimental isotropic value of polarizability $\alpha = 1.57 \text{ Å}^3$ [5].

Equations (4) and (5) for \mathbf{d}_i and $\boldsymbol{\alpha}_i$ can be solved by the reversal of matrix using $\mathbf{d}_{i,0}$ and $\boldsymbol{\alpha}_{i,0}$ on the right-hand side of equations. This calculation procedure gives \mathbf{d}_i and $\boldsymbol{\alpha}_i$ values, which agree with the values of corresponding parameters obtained by the iteration [29]. Once dipole moments of molecules are determined, the cross section of absorption of IR radiation is set as follows:

$$\sigma(\omega) = \left(\frac{2}{\epsilon_v c \hbar n} \right) \omega \tanh \left(\frac{\hbar \omega}{2kT} \right) \operatorname{Re} \int_0^\infty dt e^{i\omega t} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle,$$

where n is the frequency-independent refractive index, ϵ_v is the electric constant, and c is the speed of light.

In the case of depolarized light, the Raman spectrum $J(\omega)$ is set by expression [27]

$$J(\omega) = \frac{\omega}{(\omega_L - \omega)^4} (1 - e^{-\hbar\omega/kT}) \times \operatorname{Re} \int_0^\infty dt e^{i\omega t} \langle \Pi_{xz}(t) \Pi_{xz}(0) \rangle,$$

where

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

ω_L is the frequency of exciting laser, Π_{xz} presents the xz -component of $\Pi(t)$ value, the x axis is directed along the molecular dipole, and the xy plane is the molecular plane.

The frequency dispersion of permittivity determines the frequency dependence of dielectric losses $P(\omega)$ in accordance with the expression [30]

$$P = \frac{\epsilon'' \langle E^2 \rangle \omega}{4\pi},$$

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

Let us define systems I–IV as $(\text{H}_2\text{O})_{50}$ clusters with six neighbor oxygen molecules that do not have chlorine atoms in the interaction zone at time moment $t = 0$, as well as clusters with two, four, and six Cl^- ions in this zone.

RESULTS OF CALCULATIONS

The configurations of $6\text{O}_2 + (\text{H}_2\text{O})_{50} + 6\text{Cl}^-$ system corresponding to time moments 0, 2.2, and 3 ps are

shown in Fig. 1. It can be seen that, at the initial time moment, six Cl^- ions uniformly surround the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system and, 3 ps later, only one ion remains near the formed $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster. Due to the corresponding orientation of water molecules (hydrogen outward) and polarization interaction, Cl^- ions are drawn into the cluster. The character of the interaction of each ion with the cluster is determined by both the position of the ion relative to the nearest water molecules in the cluster and the presence of other Cl^- ions. The ions located nearer to the water molecules than to oxygen molecules are first incorporated into the system. The ions are characterized by short contact time (~ 0.1 ps) with the molecules that constitute the cluster. During the time of collisions, the relative energy of $\text{H}_2\text{O} + \text{Cl}^-$ system is transformed into the vibrational energy of water molecules and the kinetic energy of Cl^- ion, which receives an impulse directed outward with respect to cluster. Ions that are brought into contact with water molecules are the first to leave the system. The Cl^- ion drawn apart from the nearest molecule to a distance exceeding 2 nm hardly affects the state of the cluster at all. One of the ions was drawn apart from the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system to a distance exceeding 2 nm after as little as 0.4 ps, whereas four more ions were moved to the same distances during 2.5 ps. The O_2 molecules present on the surface form an interlayer between H_2O molecules in the system and ions. The interaction between the Cl^- ion and water molecules screened by oxygen molecules becomes weaker. Because of this, the ion nearest to oxygen atoms moves inside the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system with considerable delay. In the case of a system surrounded by six Cl^- ions at time $t = 0$, this event occurs within 2 ps when only four ions are remained near the system. The ion passed through O_2 molecules is left in the boundaries of $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system for a longer time than other ions. To some extent, this is promoted by oxygen molecules, which prevent the escape of ion from the system. Direct contact between oxygen molecules and the Cl^- ion is not established; therefore, chlorine is not oxidized.

In other cases, the remoteness of Cl^- ions from the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system was also observed. For example, for the $6\text{O}_2 + (\text{H}_2\text{O})_{50} + 2\text{Cl}^-$ system, one of the ions departed from the molecular system to a distance of $r > 2$ nm 0.6 ps after the beginning of calculation, while the other ion retained its position near this system to time of 2.6 ps.

The average electric potential $\Phi(r)$ created by molecules in the sphere with radius r is calculated by the formula [31, 32]

$$\Phi(r) = a \left[\sum_{j, r_j < r} q_j/r + \sum_{j, r_j > r} q_j/r_j \right],$$

where $a = 1$ in the centimeter-gram-second system of units and $a = 1/4\pi\epsilon_0$ in the SI system and ϵ_0 is the electric constant.

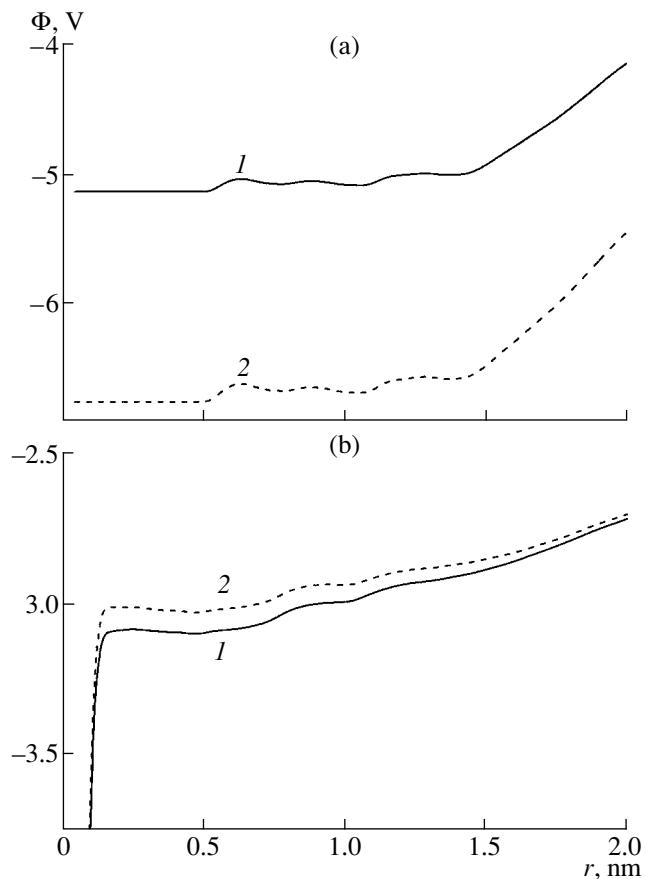


Fig. 2. Electric potential referred to the center of the mass of (a) O_2 and (b) H_2O molecules for $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system surrounded by (1) two or (2) six Cl^- ions.

The electric potential $\Phi(r)$ created by internal charges of molecules is presented in Fig. 2. For the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system, potential $\Phi(r)$ determined in the center of mass of O_2 molecule, in the initial presence of two Cl^- ions near this system (Fig. 2a, curve 1), is characterized by much larger values compared to the analogous characteristic for the same system in the presence of six Cl^- ions in the vicinity of its boundary at time $t = 0$ (Fig. 2a, curve 2). However, for the $\Phi(r)$ potential, which is established in the center of mass of water molecules, the situation is different: the system surrounded by six Cl^- ions at the initial time is characterized by larger values of $\Phi(r)$ function. Apparently, this is associated with the fact that stronger initial compression of $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system imparted by six Cl^- ions allowed O_2 molecules that had previously been drawn rather far from water molecules to be brought into closer and more energy advantageous contact with H_2O molecules. This resulted in a decrease in the values of $\Phi(r)$ function constructed for the centers of O_2 molecules. In turn, the action of six Cl^- ions on a system also resulted in drawing together water molecules that were already in close contact. This caused additional repulsion between molecules and led to an increase in the value

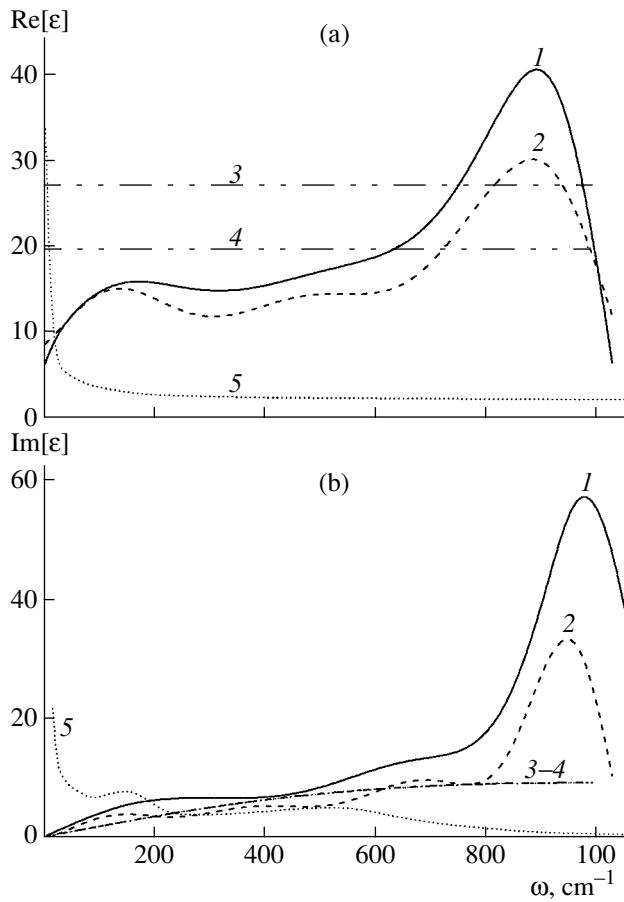


Fig. 3. (a) Dependences of (a) real and (b) imaginary parts of permittivity on frequency for systems (1, 3) I and (2, 4) III; (1, 2) MD calculation, (3, 4) calculation by formulas (3), and (5) (a) MD calculation for bulk liquid water [33] and (b) experimental data for liquid water [34].

of $\Phi(r)$ function referred to the centers of H_2O molecules.

The presence of Cl^- ions near the $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster resulted to a decrease in the value of dipole moment. Moreover, the \mathbf{M} value is the lower the larger amount of Cl^- ions interacts with the cluster. Calculated real ϵ' and imaginary ϵ'' parts of permittivity for systems I–IV, in general, are increasing frequency functions. Figure 3 shows these functions for systems I and III. The positions of principal maximum of $\epsilon'(\omega)$ function for systems I–IV fall at frequencies of 895, 937, 963, and 973 cm^{-1} , respectively. Analogous characteristics of $\epsilon''(\omega)$ function are 889, 930, 915, and 973 cm^{-1} , respectively. The presence of Cl^- ions decreases both the integral intensity of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ spectra and the intensity of the principal peak of these functions. The ϵ' values decrease with an increase in the number of Cl^- ions, which initially surrounded the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system. Decrease in $\epsilon'(\omega)$ value is caused by greater approach of O_2 and H_2O molecules under the action of larger number of ions at the initial calculation stage. In other words, here, we deal with the effect of the dilution of

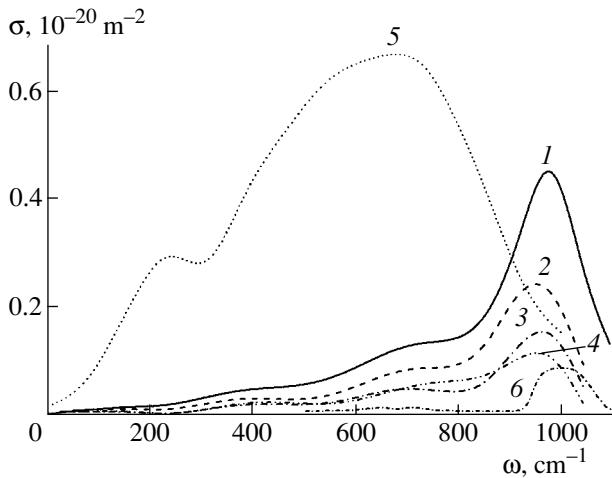


Fig. 4. IR absorption spectra for different systems: (1) I, (2) II, (3) III, (4) IV, (5) experimental $\sigma(\omega)$ function of bulk liquid water [35], and (6) experimental spectra for gaseous $\text{O}_2 + \text{O}_3$ mixture [36].

the cluster composed of polar molecules by apolar molecules. Figure 3 also demonstrates the $\epsilon'(\omega)$ and $\epsilon''(\omega)$ dependences calculated by formula (3) and relevant characteristics for bulk liquid water. The thus determined real part of the permittivity of studied samples is characterized by an extremely weak frequency dependence (Fig. 3a). The frequency dependence of imaginary ϵ'' of the permittivity is identical for all studied clusters (Fig. 3b, curves 3 and 4); i.e., according to formula (3), the dependences of the energy dissipation of IR radiation on Cl^- ions are not observed. Liquid water exhibits much steeper descending frequency dependence of ϵ' and ϵ'' values (curve 5). Furthermore, the $\epsilon''(\omega)$ dependence for water passes through two small maxima localized at 147 and 530 cm^{-1} .

Calculated IR absorption spectra for systems I–IV are compared in Fig. 4 with the corresponding experimental spectrum for bulk liquid water. The IR spectrum for liquid water demonstrates two peaks at 200 and 690 cm^{-1} [35]. The spectrum of the gaseous oxygen–ozone mixture has one distinct peak at 996 cm^{-1} [36]. For $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ systems, peaks in the vicinity of 400 and 700 cm^{-1} are either extremely low or are not seen at all. As a result of the effect of Cl^- ions, the principal peak shifts from its position at $\omega = 970 \text{ cm}^{-1}$ to the vicinity of frequency 950 cm^{-1} . Integral intensity I_{tot} of IR radiation is the lower, the larger amount of Cl^- ions is involved into the reaction with $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system. For example, the I_{tot} value for system IV (with six Cl^- ions) appeared to be 3.1-fold smaller than relevant characteristic of system I (containing no Cl^- ions).

The interaction between Cl^- ions and the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system was expressed in the compaction of the surface of formed cluster; as a result, four broad peaks in the reflection spectrum of plane electromagnetic wave became more distinct and the roughness of

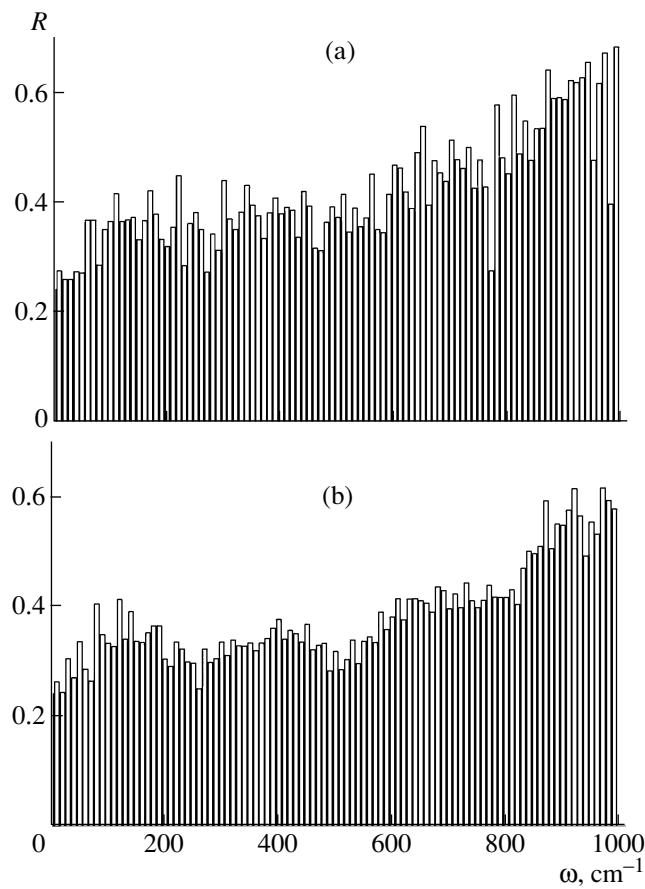


Fig. 5. IR reflection spectra for $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster, which represents at time $t = 0$ systems (a) I and (b) III.

the spectrum diminished considerably (Fig. 5). Maxima of IR reflection spectra are positioned in the vicinity of frequency bands of 140, 407, 686, and 915 cm^{-1} . In the presence of Cl^- ions, the integral intensity of IR radiation, I_{ref} , lowers. In case of four Cl^- ions acting on a system, the I_{ref} decreased by 8.8%.

IR emission spectra $P(\omega)$ are characterized by the presence of a principal band in the $800 \leq \omega \leq 1000 \text{ cm}^{-1}$ frequency range (Fig. 6). The integral intensity I_{rad} of emission spectra of systems under consideration increases significantly in the presence of Cl^- ions. The ratio of I_{rad} values for systems I–IV is equal to 1 : 68 : 51 : 79.

Raman spectra calculated for $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ systems are compared in Fig. 7 with a corresponding experimental spectrum of pure water placed into a quartz tube and excited with light (wavelength of 514.5 nm) [37]. The Raman spectrum for liquid water is characterized by low-frequency peaks at $\omega = 60$ and -30 cm^{-1} , as well as by a peak near 170 cm^{-1} . The peak at 60 cm^{-1} is formed by the bending of hydrogen bonds between water molecules; the peak at 170 cm^{-1} appears due to bond stretching [27]. Stokesian and anti-Stokesian parts in this spectrum are asymmetric, which is

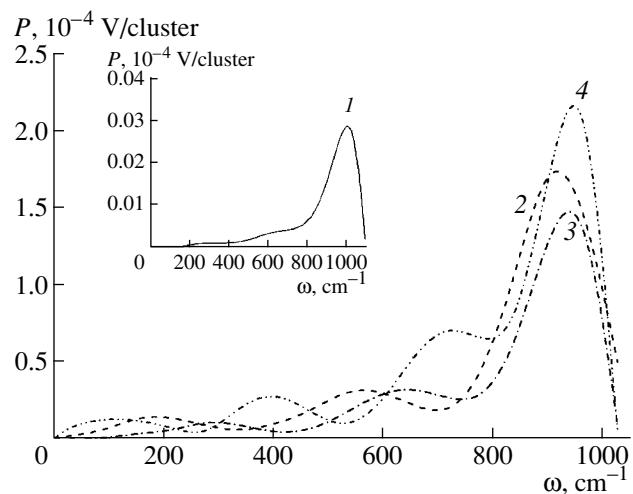


Fig. 6. IR emission spectra for $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster in the absence of Cl^- ions (1) at time $t = 0$ and upon interaction with (2) two, (3) four, and (4) six Cl^- ions.

explained by the effect of photoluminescence. The computer model is free of this effect. Therefore, the left- and right-hand sides of the spectrum are symmetric with respect to zero. In the absence of Cl^- ions, the pattern of Raman spectrum for $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system is more similar to the spectrum of pure water than the corresponding spectra of system excited by ions. The position of principal Raman peak of systems refers to frequency 26 cm^{-1} . Other peaks in the Raman spectrum of system I are characterized by low resolution. The first peak of $J(\omega)$ spectrum for $(\text{H}_2\text{O})_{50}$ cluster in SPC/E model corresponds to frequency 25 cm^{-1} [27]. However, in the presence of Cl^- ions, peaks conforming to frequency combinations are pronounced the stronger, the larger amount of ions participates in interaction. Characteristic frequencies of Raman spectrum change their positions due to interaction between $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system and Cl^- ions. The system without Cl^- ions has three characteristic frequencies in the Raman spectrum ($255, 547$, and 762 cm^{-1}), the system with two Cl^- ions has four characteristic frequencies ($168, 475, 757$, and 946 cm^{-1}), and the system with four Cl^- ions has three frequencies ($168, 490$, and 920 cm^{-1}). The Raman spectrum for water pentamer is characterized by typical peaks at 200 and 245 cm^{-1} bands [27]. Peaks in the Raman spectra of $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ systems in the $168 \leq \omega \leq 255 \text{ cm}^{-1}$ frequency range can be assigned to the collective vibrations in rings formed by water molecules.

The time dependence of the number of ions in the vicinity of $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system is reflected by histograms shown in Fig. 8, which are plotted under the assumption that, if the Cl^- ion moves away from the nearest water molecule to a distance exceeding 2 nm, it no longer affects the state of the system. A $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system originally surrounded by six Cl^- ions loses them by 3.2 ps, while systems with four or two

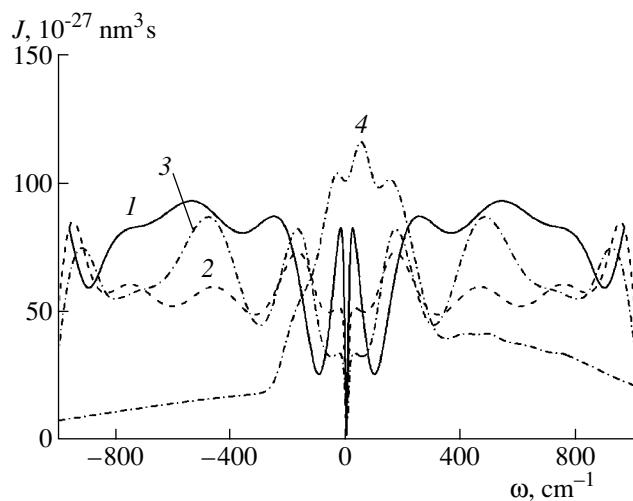


Fig. 7. Raman spectra for systems (1) I, (2) II, (3) III, and (4) experimental data for liquid water [37].

ions get rid of these ions by 2.8 ps. Thus, in each case, the $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster barely interacts with Cl^- ions by time $t = 3.2$ ps.

CONCLUSIONS

The appearance of neighbors near $(\text{H}_2\text{O})_{50}$ cluster (in the form of O_2 molecules and Cl^- ions) resulted in the hydration of O_2 molecules to form $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster. Upon the action of the group of Cl^- ions on $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system and then on the $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster, the ions periodically enter the $(\text{H}_2\text{O})_{50}$ cluster and escape from the interaction zone. Interaction with water molecules leads to the generation of negative electric potential around oxygen molecules. The depth of the potential well increases with the number of surrounding Cl^- ions. Chlorine ions act oppositely on water molecules; i.e., Cl^- ions tend to increase potential Φ centered on water molecules. The presence of Cl^- ions near the $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system decreases both the values of real and imaginary parts of permittivity, as well as the integral intensity of absorption and reflection IR spectra. The interaction between $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system and Cl^- ions causes substantial increase in the power of IR radiation emitted by aggregates and decreases the intensity of the first low-frequency peak in the Raman spectrum. In this case, peaks of the Raman spectrum become more pronounced at higher frequencies.

Chlorine ions are drawn with time into $(\text{O}_2)_6(\text{H}_2\text{O})_{50}$ cluster and accommodate there, as a rule, during no less than 1 ps. With a close approach, Cl^- ions should enter into chemical reaction with water molecules. This effect is not considered in the model used in this work. It is known that, in the reaction between chlorine and water, oxygen is released and hydrogen chloride is formed. The latter once more forms chlorine during photosynthesis with carbon dioxide. In atmosphere

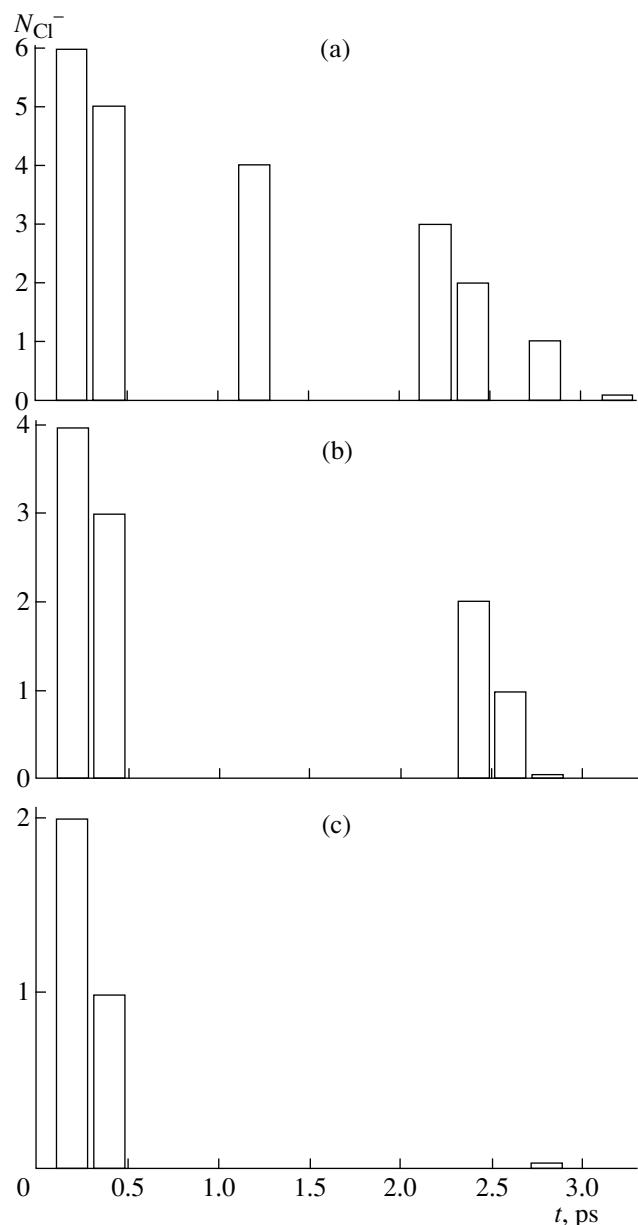


Fig. 8. Time dependences of the number of Cl^- ions interacting with $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system at the initial presence of (1) six, (2) four, and (3) two Cl^- ions near this system.

with stable chemical state, electrons are attached to chlorine atoms to form Cl^- and $\text{H}_3\text{O}^+\text{Cl}^-$ ions (ozone-destructing agents). Due to the fact that each Cl^- ion captured by $6\text{O}_2 + (\text{H}_2\text{O})_{50}$ system resides in this system for a short time (~ 1 ps) and presents near its boundary, the solvation of ions is not observed.

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