

# Computer-Aided Study of Oxygen Absorption by Water Clusters. IR Spectra of Heteroclusters

O. A. Novruzova<sup>a</sup>, V. N. Chukanov<sup>a</sup>, and A. E. Galashev<sup>b</sup>

<sup>a</sup> Institute of Industrial Ecology, Ural Division, Russian Academy of Sciences,  
ul. Sof'yi Kovalevskoi 20-a, Yekaterinburg, 620219 Russia

<sup>b</sup> Institute of Thermal Physics, Ural Division, Russian Academy of Sciences,  
ul. Amundsena 106, Yekaterinburg, 620016 Russia

Received January 24, 2006

**Abstract**—Spectral characteristics of  $(\text{H}_2\text{O})_m$ ,  $(\text{O}_2)_m(\text{H}_2\text{O})_n$ , and  $(\text{O})_i(\text{H}_2\text{O})_n$  cluster systems, where  $m \leq 2$ ,  $i \leq 4$ , and  $10 \leq n \leq 50$ , are studied with the molecular dynamics method using a flexible molecule model. The IR absorption spectra are changed substantially as a result of  $\text{O}_2$  molecule dissociation, and in the presence of atomic oxygen in the clusters, the spectra are characterized by a deep minimum at  $520 \text{ cm}^{-1}$ . The absorption of oxygen causes a marked reduction in reflection coefficient  $R$  of monochromatic IR radiation. The number of peaks in the  $R(\omega)$  spectra decreases to two in the case of molecular oxygen absorption and is no larger than four in the case of atomic oxygen absorption. The absorption of atomic oxygen by the clusters is also accompanied by a significant increase in the dissipation of energy accumulated by the clusters. This effect weakens when molecular oxygen is absorbed. An increase in atomic oxygen concentration in the clusters renders their radiation harder.

**DOI:** 10.1134/S1061933X06040107

## INTRODUCTION

The mass fraction of oxygen in water is 0.89. Water can be a natural source of oxygen. Oxygen is produced from water in the upper atmosphere of the Earth above the ozone layer. The UV radiation of the Sun plays a key role in this process. Water is decomposed to yield atomic and molecular oxygen and hydrogen. Hydrogen, which is lighter than air, leaves Earth's atmosphere, while oxygen remains [1]. Sometimes it is believed that water in the dispersed state possesses absorption properties similar to those of the bulk water. Calculations performed under this assumption by the molecular orbital method predict the formation of a hydrate with structure **I** in a polyhedral cluster composed of 14 water molecules and captured an oxygen molecule [2].

Water clusters formed through hydrogen bonding are quite stable. They exhibit a high ability of absorbing other gas molecules. As was experimentally established, water clusters with sizes less than nine atoms can capture and retain a benzene molecule whose molecular mass amounts to half the mass of such a cluster [3]. Using the molecular dynamics method, it was revealed that water clusters can absorb  $\text{HCl}$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CH}_3\text{OH}$  molecules [4–9]. Oxygen is low-soluble in water. At 293 K, one oxygen molecule is dissolved in approximately 300 water molecules. The absorption of oxygen molecules by water clusters was investigated using the rigid TIP4P model [10]. Upon the addition of oxygen molecules, the

absorption coefficient of electromagnetic radiation by water clusters decreases, and the reflection coefficient rises. The effect of oxygen absorption on the spectral characteristics of water clusters must be more clearly disclosed when flexible molecule models are used.

The goal of this work was, using a flexible molecule model, to study the capture of molecular and atomic oxygen by water clusters, to determine the effect of oxygen absorption by aqueous dispersed medium on the IR absorption and reflectance spectra, and to establish how the radiation power of the cluster systems is changed in this case.

## COMPUTER MODEL

Widely used SPC [11], SPC/E [12], TIP3P, and TIP4P [13] computer models of water molecules describe the properties of ice and water in gas phases much better than those of liquid water. The modified TIP4P model of water [14] was used in this study. The dynamics of a system of molecules is realized using the potential of water–water intermolecular interaction [15] and describing oxygen–oxygen and oxygen–water interactions as a sum of repulsive and dispersive contributions [16]:

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

where parameters  $a_i$ ,  $b_i$ , and  $c_i$  of the potential describing these interactions are taken from [17]. The interatomic distance in the  $\text{O}_2$  molecule is  $r_{\text{OO}} = 0.12074 \text{ nm}$  [18].

It is assumed [19] that the use of polarizable flexible models enables one to markedly better describe the properties of liquid phases. Rigorous flexible models of water cannot be just classical, but they must take into account quantum effects. However, the account of the quantum effects increases the volume of the calculations by, at least, an order of magnitude and makes the simulation ineffective.

Flexible models were developed within the framework of Hamilton's dynamics [20, 21]. Let us consider a two-atom molecule. Let the distance between  $a$  and  $b$  atoms in a molecule be

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

where  $\mathbf{r}_a$  and  $\mathbf{r}_b$  are vectors denoting the locations of the atoms. Let us designate their velocities as  $\mathbf{v}_a$  and  $\mathbf{v}_b$  and write the reduced mass as

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

The size of a molecule represented by  $a$  and  $b$  atoms is estimated from the equality between total potential force  $\mathbf{f}(\mathbf{q}) = -\frac{\partial \mathbf{r}}{\partial \mathbf{q}} \nabla \Phi(\mathbf{r})$  and the centrifugal force  $-\mu q \omega^2$ , so that

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

where  $\omega = \|\mathbf{v}_a - \mathbf{v}_b\|/q$  is the angular velocity. By minimizing the contribution of each generalized coordinate to potential energy  $U$ , we arrive at

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

This method may be generalized to the molecules of any composition [19].

We began to investigate oxygen absorption by water clusters with constructing a configuration composed of an equilibrium water cluster and surrounding oxygen molecules or atoms. Initial equilibrium configurations of water clusters were developed in separate molecular dynamic calculations, assuming that the kinetic energy of the molecules constituting the cluster corresponded to 233 K. Initially, the center of mass of free (one or two) oxygen molecules was placed at a distance of 0.6–0.7 nm from the nearest atom of the water cluster so that each atom of the oxygen molecule occurred in the field of molecular interaction. The cut-off radius of all interactions in the model was 0.9 nm. A linear  $O_2$  molecule was oriented along a ray connecting its center with the center of mass of the cluster. When two molecules were added to the cluster, they were located along the same ray, but on the opposite sides of the cluster. When the absorption of oxygen atoms by the cluster was simulated, the principle of the initial location of the atoms was the same, except for the fact that the orientation should not be preset. In the case of four oxygen atoms,

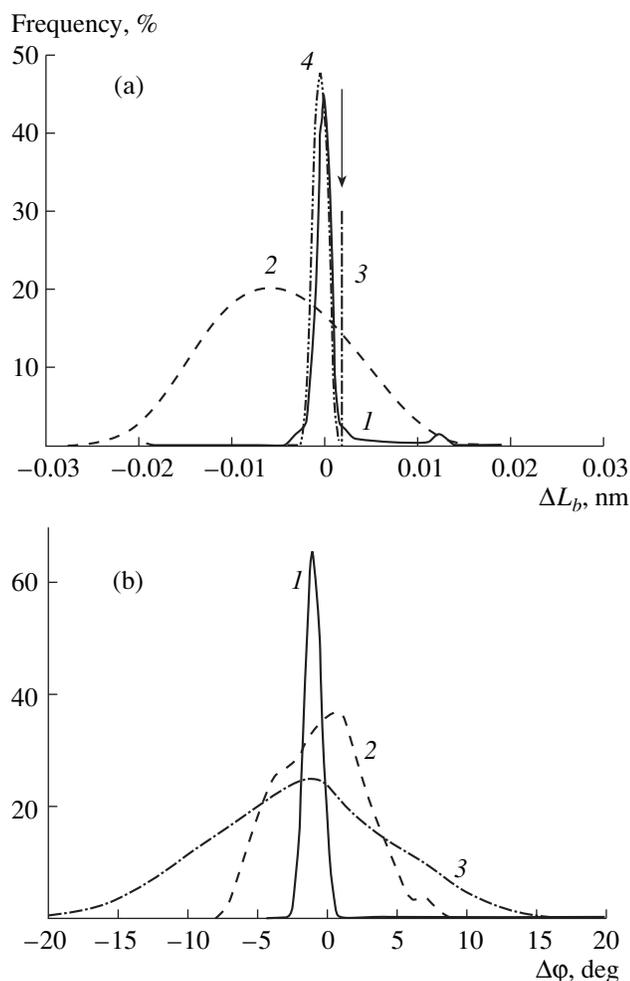
they were located on the lines intersecting at a right angle. The point of intersection coincided with the center of mass of the cluster. Each atom was located on its own ray originating from this center. This symmetric location of molecules and atoms provided conditions for the uniform action of impurity on the cluster and minimized the interaction between free molecules ( $O_2$ ) or atoms (O). A newly formed system was equilibrated within a time interval of  $0.6 \times 10^6 \Delta t$ , where the time step is  $\Delta t = 10^{-17}$  s. Then, necessary physicochemical properties were calculated within an interval of  $2 \times 10^6 \Delta t$ . The equations for the motion of the centers of mass of the molecules were integrated by the Gear fourth-order method [22]. Equations for rotational motion of molecules were analytically solved using the Rodrig–Hamilton parameters [23]. The integration scheme for equations of motion involving rotation corresponded to the approach proposed by Sonnenschein [24]. The calculations were carried out with a PENTIUM-IV computer operating at a processor clock frequency of 3.8 GHz.

#### PHYSICAL PROPERTIES OF THE FLEXIBLE MOLECULE MODEL

An appreciable advantage of flexible water molecule models is the fact that they make it possible to study the effects of temperature, pressure, and local environment of molecules and ions on such parameters as dipole moments and vibration frequencies. Their application for the simulation of aqueous systems is particularly useful for the interpretation of the influence of chemical composition, as well as for revealing structural features and more rigorous determination of thermodynamic properties.

In [25], the flexible BJH (Bopp–Jancso–Heinzinger) model of water was used to analyze intramolecular stretching and deformation vibrations in water in the supercritical state. Upon a rise in water density, a red shift was observed in stretching vibration frequencies of water with respect to corresponding characteristics of the gaseous phase, and a blue shift was revealed in deformation vibrations. These data are consistent with the pattern of experimental Raman spectra [26, 27].

Characteristics of the flexible model used in this work and the BJH model of water are compared in Fig. 1, where the deviations of the intramolecular length of OH bond and the HOH angle from the corresponding values for an isolated water molecule ( $L_b^f(\text{OH}) = 0.09572$  nm and  $\angle(\text{HOH})^f = 104.52^\circ$ ) are presented. The distribution of the deviations of length  $L_b$  for  $H_2O$  and  $O_2$  molecules in  $(O_2)_2(H_2O)_n$  clusters is characterized by a sharp peak. The deviation of average length  $\bar{L}_b$  of the intramolecular bond from the  $L_b^f$  value is equal to zero for  $H_2O$  molecules and is slightly shifted ( $\Delta \bar{L}_b = \bar{L}_b - L_b^f = 0.001$  nm) toward shorter



**Fig. 1.** The distributions of the deviations of intramolecular bond (a) lengths and (b) angles from the corresponding parameters of free molecules: (1, 4) the model used in this work for  $\text{H}_2\text{O}$  and  $\text{O}_2$  molecules, respectively, in the  $(\text{O}_2)_2(\text{H}_2\text{O})_{50}$  cluster, (2) the model used in this work for  $\text{H}_2\text{O}$  molecules in the  $(\text{O})_4(\text{H}_2\text{O})_{50}$  cluster, and (3) the BJH model of water molecules in the supercritical state [25].

than  $L_b^f$  distances (Fig. 1a) for  $\text{H}_2\text{O}$  molecules. However, for  $(\text{O})_4(\text{H}_2\text{O})_n$  cluster, the distribution of OH bond lengths becomes quite broad, and its maximum shifts to the left by  $\approx 0.007$  nm. For the BJH model of water, the average value of  $L_b$  is 0.09755 nm. This value is denoted by the arrow in Fig. 1a, because the character of the  $L_b$  distribution was not presented in [25]. The deviation of HOH angle from  $\angle(\text{HOH})^f$  for the models under consideration is shown in Fig. 1b. In the case of  $(\text{O}_2)_2(\text{H}_2\text{O})_{50}$  cluster, the angular distribution is characterized by a sharp peak localized at  $\approx 103^\circ$ . Corresponding distribution for  $(\text{O})_4(\text{H}_2\text{O})_{50}$  cluster is diffused, less symmetric, and has a maximum in the vicinity of  $\approx 106^\circ$ . The angular distribution for the BJH model of water with a maximum at  $100.78^\circ$  is characterized by even larger dispersion. As the density of this system

increases, the average length of the OH bond becomes greater and the HOH angle decreases. Average permanent dipole moment  $\bar{d}$  of water molecule in the BJH model increases from  $\bar{d}^f = 1.86$  to 1.97 D. In the flexible molecule model under examination, the  $\bar{d}$  value also rises from  $\bar{d}^f = 1.85$  to 2.02 and 1.97 D for  $(\text{O}_2)_2(\text{H}_2\text{O})_{50}$  and  $(\text{O})_4(\text{H}_2\text{O})_{50}$  clusters, respectively.

## DIELECTRIC PROPERTIES

Let us consider the scattering of unpolarized light, when free path  $l$  of molecules is much shorter than light wavelength  $\lambda$ . Extinction (reduction) coefficient of an incident beam is determined, on the one hand, by the Rayleigh equation [28] and, on the other hand, by the scattering coefficient  $\rho$  ( $h = \frac{16\pi}{3}\rho$ ) [29] under the approximation of a scattering angle of  $90^\circ$ . Taking into account that  $h = \alpha + \rho$ , where  $\alpha$  is the absorption coefficient, we have

$$N = \frac{2\omega^4 (\sqrt{\epsilon} - 1)^2}{3\pi c^4 \alpha} \left(1 - \frac{3}{16\pi}\right), \quad (6)$$

where  $N$  is the number of scattering sites in  $1 \text{ cm}^3$ . Here,  $c$  is the speed of light,  $\epsilon$  is the medium permittivity, and  $\omega$  is the frequency of incident wave.

Let us define the following types of ultradispersed systems: **I** is a region filled with water clusters with sizes from 10 to 50 molecules, **II** is a medium composed of  $(\text{H}_2\text{O})_n$  clusters that absorbed one  $\text{O}_2$  molecule, **III** is a system consisting of  $(\text{O}_2)_2(\text{H}_2\text{O})_n$  aggregates, **IV** is a set of  $(\text{H}_2\text{O})_n$  clusters that absorbed two O atoms each, and **V** is a set of  $(\text{O})_4(\text{H}_2\text{O})_n$  species.

Let us organize systems **II–V** in such a manner that a cluster containing the  $i$  molecules (atoms) of an impurity and an  $m$  water molecules would have a statistical weight of

$$W_{im} = \frac{N_{im}}{N_\Sigma}, \quad i = 1(2)\dots 2(4), \quad (7)$$

$$m = 10, 15, \dots, 50,$$

Here,  $N_{im}$  is the number of clusters containing  $i$  impurity molecules (atoms) and  $m$  water molecules in  $1 \text{ cm}^3$  and  $N_\Sigma = \sum_{k=1}^9 N_k$ , where  $k$  characterizes the set of  $i$  and  $m$  subscripts. For example, at  $k = 1$ ,  $m$  is always equal to 10, while  $i$  may be 1, 2 or 4. Similar weights were used for  $(\text{H}_2\text{O})_n$  clusters forming system **I**. Hereafter, all spectral characteristics are calculated with account of assumed weights  $W_{im}$ .

Static dielectric constant  $\epsilon_0$  was calculated from the fluctuations of total dipole moment  $\mathbf{M}$  [30]:

$$\epsilon_0 = 1 + \frac{4\pi}{3VkT} [\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2]. \quad (8)$$

The total dipole moment of a cluster is calculated according to the equation

$$\mathbf{M}(t) = Z_H \sum_{i=1}^{2N} \mathbf{r}_i(t) + Z_O \sum_{j=1}^N \mathbf{r}_j(t), \quad (9)$$

where  $\mathbf{r}_i(t)$  is a vector denoting the location of atom  $i$  at instant  $t$ ;  $Z$  is the electrical charge located in the center of the atom; subscripts H and O refer to hydrogen and oxygen atoms, respectively; and  $N$  is the number of water molecules in the cluster.

Permittivity  $\epsilon(\omega)$  was represented as complex quantity  $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ , which was defined using the equation [31, 32]

$$\begin{aligned} \frac{\epsilon(\omega) - 1}{\epsilon_0 - 1} &= - \int_0^{\infty} \exp(-i\omega t) \frac{dF}{dt} dt \\ &= 1 - i\omega \int_0^{\infty} \exp(-i\omega t) F(t) dt, \end{aligned} \quad (10)$$

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

$$F(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle \mathbf{M}^2 \rangle}. \quad (11)$$

Coefficient  $\alpha$  of external IR radiation absorption can be defined via the imaginary part of frequency-dependent permittivity  $\epsilon(\omega)$  as [33]

$$\alpha(\omega) = 2 \frac{\omega}{c} \text{Im}[\epsilon(\omega)^{1/2}]. \quad (12)$$

Reflection coefficient  $R$  is defined as the ratio of the average energy flux reflected by the surface to the incident flux. For a normal incidence of the plane monochromatic wave, the reflection coefficient is calculated by the equation [28]

$$R = \left| \frac{\sqrt{\epsilon_1} - \sqrt{\epsilon_2}}{\sqrt{\epsilon_1} + \sqrt{\epsilon_2}} \right|^2. \quad (13)$$

Here, it is assumed that the incidence of wave occurs from the transparent medium (medium 1) to the medium, which can be transparent or opaque, i.e., absorbing or scattering (medium 2). Subscripts at the permittivity in Eq. (13) refer to the corresponding media.

Frequency dispersion of the permittivity determines the frequency dependence of dielectric loss  $P(\omega)$  according to the equation [29]

$$P = \frac{\epsilon' \langle E^2 \rangle \omega}{4\pi} \tan \delta, \quad (14)$$

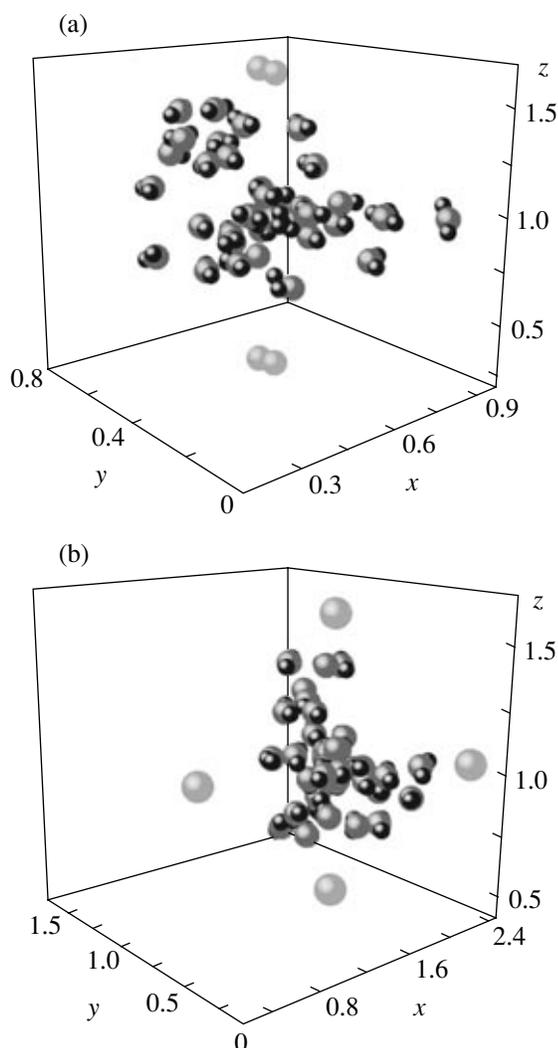
where  $\langle E^2 \rangle$  is the average squared electric field strength and  $\tan \delta = \epsilon''/\epsilon'$  is the dielectric loss tangent.

## RESULTS OF CALCULATIONS

The configurations of a cluster composed of 40 water molecules that has absorbed two O<sub>2</sub> molecules or four oxygen atoms are presented in Figs 2a and 2b, respectively. It is seen that, in the course of time (the configuration is presented for a time of 20 ps), the orientation of O<sub>2</sub> molecules has changed, and their axes are directed tangential to the cluster surface. This is caused by the attraction between each atom of the O<sub>2</sub> molecule and hydrogen atoms (of neighbor water molecules) that are directed toward O<sub>2</sub> molecules. Absorbed O atoms partly pull some water molecules out of the cluster; however, the latter does not lose its integrity.

The coefficient of IR radiation absorption increases with frequency for the system of pure water clusters and for systems of clusters that have absorbed one (system **II**) or two (system **III**) oxygen molecules (Fig. 3a). Spectrum  $\alpha(\omega)$  for the bulk water [34] is markedly more intense than these distributions for disperse systems. The main IR absorption bands are observed for liquid water at  $\omega_1 = 200$  and  $\omega_2 = 700$  cm<sup>-1</sup>. Absorption of oxygen molecules increases the absorption coefficient of system **II** at frequencies  $\omega \leq 730$  cm<sup>-1</sup> and that of system **III** at  $\omega \leq 400$  cm<sup>-1</sup>. In other cases, the  $\alpha$  values are decreased. The  $\alpha(\omega)$  spectra for systems of clusters that absorbed oxygen molecules show characteristic vibrations, while only one distinct peak at  $\omega_{\max} = 847$  cm<sup>-1</sup> is present in a similar spectrum of system **I**, and absorption maxima are observed at  $\omega_{\max} = 770$  and 830 cm<sup>-1</sup> for systems **II** and **III**, respectively.

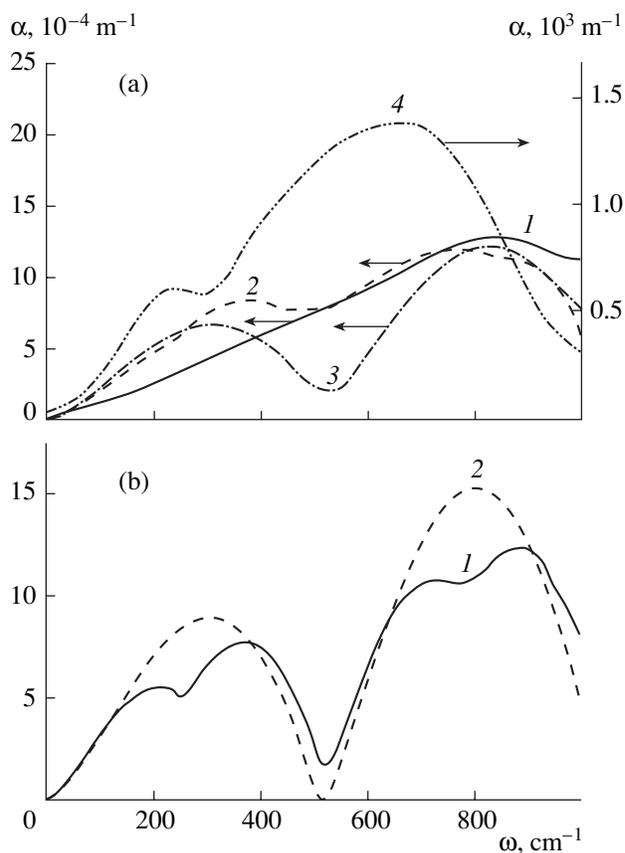
The IR absorption spectra of systems **IV** and **V** containing atomic oxygen demonstrate two characteristic maxima separated by a deep minimum (Fig. 3b). When water clusters capture two oxygen atoms (system **IV**), the peaks in the  $\alpha(\omega)$  spectrum are splitted; i.e., each peak has two local maxima and one minimum. When clusters capture four oxygen atoms (system **V**), only two broad peaks appeared in the  $\alpha(\omega)$  spectrum with an even deeper minimum between them. For system **IV**, the most intense IR absorption bands are observed at  $\omega_1 = 210$ ,  $\omega_2 = 370$ ,  $\omega_3 = 730$ , and  $\omega_4 = 890$  cm<sup>-1</sup>, while those for system **V** are at  $\omega_1 = 310$  and  $\omega_2 = 810$  cm<sup>-1</sup>. A most pronounced decline in the IR adsorption for systems containing atomic oxygen is observed at the frequency  $\omega = 520$  cm<sup>-1</sup>. The integral intensity of IR absorption in the  $0 \leq \omega \leq 1000$  cm<sup>-1</sup> frequency range somewhat rises after the addition of one O<sub>2</sub> molecule or



**Fig. 2.** Configurations of (a)  $(\text{O}_2)_2(\text{H}_2\text{O})_{40}$  and (b)  $(\text{O})_4(\text{H}_2\text{O})_{40}$  clusters corresponding to time of 20ps. Coordinates of molecules (atoms) are presented in nanometers.

two O atoms and slightly decreases after the addition of two  $\text{O}_2$  molecules or four O atoms.

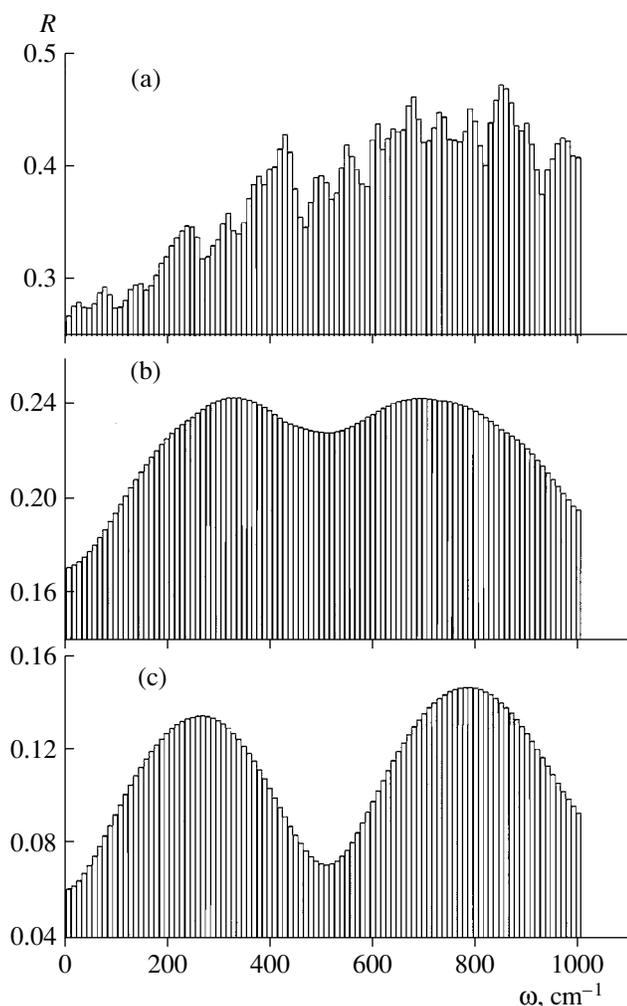
The reflection coefficient for monochromatic plain electromagnetic wave substantially changes upon the absorption of oxygen molecules by water clusters. The pattern of  $R(\omega)$  spectra also changes (Fig. 4). Pure water clusters exhibit a tendency toward an increase in the reflection coefficient with a rise in the frequency of incident wave (Fig. 4a). Intramolecular vibrations, more “spherical” surface, and the outward orientation of hydrogen atoms [35] of surface molecules predetermine quite a large value of the reflection coefficient for system **I**. The capture of one oxygen molecule by each cluster leads, on average, to almost a twofold reduction in the  $R$  value. Moreover, the peaks in the  $R(\omega)$  spectrum become smoothed (Fig. 4b). Two broad peaks remain at  $\omega_1 = 330$  and  $\omega_2 = 690 \text{ cm}^{-1}$ . The addition of one oxygen molecule leads to the rearrangement in the



**Fig. 3.** Frequency dependences for the coefficient of IR absorption by molecular systems of clusters. Panel (a): (1–3) systems **I–III**, respectively, and (4) bulk water (experiment [34]) and panel (b): coefficient  $\alpha$  for systems (1) **IV** and (2) **V** of water clusters that absorbed atomic oxygen.

structure of the whole aggregate and its surface becomes “more rough.” The addition of another (second) oxygen molecule to each cluster causes a further decrease in the reflection coefficient (Fig. 4c): the peaks become almost resolvable, and the integral intensity of reflected radiation decreases. The peaks also change their positions:  $\omega_1 = 270$  and  $\omega_2 = 785 \text{ cm}^{-1}$ . The latter peak becomes more intense than the former one.

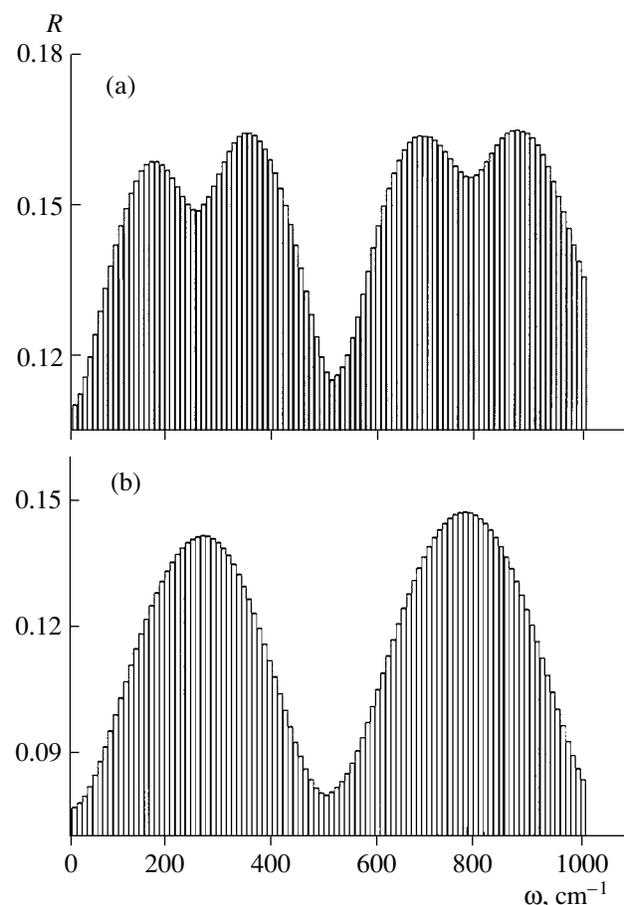
The absorption of atomic oxygen by water clusters also leads to noticeable changes in reflection coefficients and the pattern of  $R(\omega)$  spectra (Fig. 5). A decline in coefficient  $R$  for system **IV** is more pronounced than that for system **II**. When each cluster absorbs two oxygen atoms, the  $R(\omega)$  spectrum demonstrates four peaks divided into two groups by a deep minimum at a frequency of  $510 \text{ cm}^{-1}$  (Fig. 5a). Maxima of these peaks fall on  $\omega_1 = 160$ ,  $\omega_2 = 360$ ,  $\omega_3 = 680$ , and  $\omega_4 = 870 \text{ cm}^{-1}$  frequencies. The addition of two more oxygen atoms to each cluster decreases the number of peaks to two in the  $R(\omega)$  distribution for system **V** (Fig. 5b). The peaks are localized in the vicinity of the local minima of the  $R(\omega)$  spectra of system **IV**, at  $\omega_1 = 260$  and  $\omega_2 = 770 \text{ cm}^{-1}$ . The integral reflection intensity for system **V** is lower



**Fig. 4.** Frequency dependences of the reflection coefficient of monochromatic plane electromagnetic wave by different cluster systems: (a) **I**, (b) **II**, and (c) **III**.

than that for system **IV**, but it is somewhat higher than that for system **III**.

Clusters that acquired energy from external IR radiation dissipate the energy to the environment. Dissipated power  $P$  increases with a rise in the radiation frequency achieving a maximum at  $\omega = 973 \text{ cm}^{-1}$  for system **I** of pure water clusters and at  $910$  and  $973 \text{ cm}^{-1}$  for systems **II** and **III**, respectively (Fig. 6). If, being captured by water clusters, oxygen molecules remain non-dissociated, the rate of the dissipation of the accumulated energy does not increase substantially. The absorption of a second oxygen molecule by the clusters leads to a rise in the radiation power only in the vicinity of the fundamental radiation frequency. The absorption of atomic oxygen by water clusters causes a noticeable increase in  $P$ . Moreover, the larger the number of oxygen atoms captured by the dispersed aqueous system, the higher the principal peak in the  $P(\omega)$  spectrum. This peak grows at the expense of a reduction in the emis-



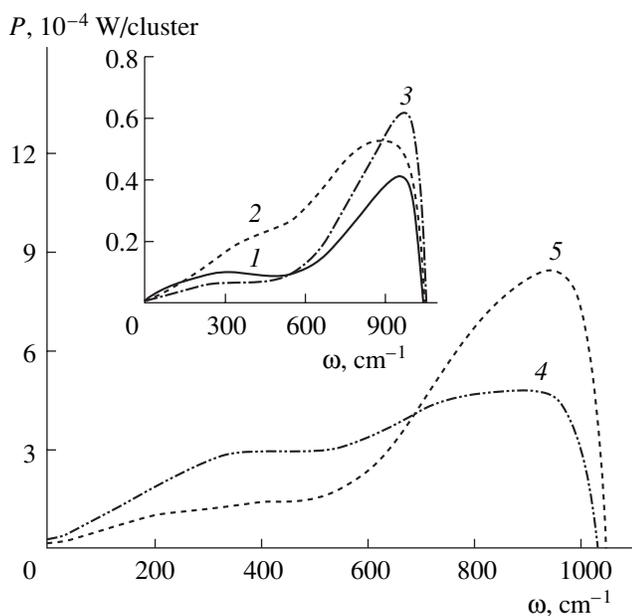
**Fig. 5.** Frequency dependences for the coefficients of reflection of monochromatic plane electromagnetic wave by systems (a) **IV** and (b) **V** of clusters that absorbed atomic oxygen.

sion intensity at low frequencies; that is, the higher the concentration of atomic oxygen in the clusters, the harder and the more powerful radiation they emit. The principal peaks of the  $P(\omega)$  spectra are located at  $\omega = 910$  and  $973 \text{ cm}^{-1}$  for systems **IV** and **V**, respectively.

## CONCLUSIONS

The flexible water molecule model used in this study appeared to be sensitive to the type of impurities contained in clusters. The effect of molecular oxygen is reduced mainly to a decrease in the average intramolecular HOH angle, while the presence of atomic oxygen leads to the reduction in the average length of intramolecular OH bonds and a slight increase in the average HOH angle in water molecules. However, even when the atomic oxygen is absorbed by the clusters, the dispersion of angle deviations is lower than that in the BJH model describing the supercritical state of water.

At frequencies  $\omega > 250 \text{ cm}^{-1}$ , the use of the water molecule flexible model leads to higher absorption



**Fig. 6.** Frequency dependence of the power of energy dissipation of IR radiation by different cluster systems (I–V) I–V, respectively.

coefficients than the rigid water molecule model of the same type [10]. Moreover, the integral intensity of IR absorption in the  $0 \leq \omega \leq 1000 \text{ cm}^{-1}$  frequency range increases by 31 %. Even more substantial changes are observed for the reflection coefficient of monochromatic IR radiation. The integral reflection intensity for the plane wave increases by factor of 14 compared to the rigid model. On the contrary, the average rate of the dissipation of accumulated energy turns out to be nine-fold lower for a system of clusters composed of flexible molecules than for a similar system of rigid molecules.

The pattern of absorption and reflectance spectra for systems of water clusters that captured oxygen depends to a high extent on the state of the absorbed gas (molecular or atomic). The pattern of the frequency dependence for the absorption coefficient greatly changes when the atomic oxygen is added to water clusters, while the addition of molecular oxygen more weakly affects the pattern of this dependence. The reflection coefficient for plane monochromatic electromagnetic wave decreases, when water clusters capture both molecular and atomic oxygen. If oxygen dissociates in the clusters, the decrease in the  $R$  value is more pronounced. The concentration of absorbed atomic oxygen influences not only the  $R$  value, but also the number of peaks in the  $R(\omega)$  spectrum, with this number decreasing upon a rise in the concentration. On the contrary, when a second oxygen molecule is captured by water clusters, the number of peaks in the  $R(\omega)$  spectrum is not reduced. However, as the  $\text{O}_2$  concentration increases, the peaks in the  $R(\omega)$  spectrum become more distinct. The addition of oxygen to water clusters accelerates the dissipation of stored energy. The power of

this radiation rises to the highest extent when the clusters absorb atomic oxygen. The higher the concentration of atomic oxygen, the harder the radiation emitted by the clusters.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-02-17322.

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