Dielectric Characteristics of $O_2(H_2O)_i$ and $(O_2)_2(H_2O)_i$ Clusters. Computer-Aided Experiment

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Abstract—Absorption of oxygen molecules by water clusters with sizes of $10 \leq i \leq 50$ is studied by the molecular dynamics method using the modified TIP4P model. It is revealed that the total dipole moment of the clusters nonmonotonically increases with their sizes. Absorption of O_2 molecules tends to raise the static permittivity of the ultradispersed medium formed by the clusters. The real and imaginary parts of the permittivity of water clusters with absorbed O_2 molecules are aperiodic functions of frequency. The permittivity components turn out to be nonmonotonic functions of cluster sizes. The IR absorption and reflectance spectra are calculated for clusters of pure water and aggregates with absorbed O_2 molecules. After the addition of oxygen molecules, the absorption coefficient of the clusters decreases, while the reflection coefficient increases. It is concluded that the capture of oxygen molecules by atmospheric moisture may reduce the greenhouse effect.

INTRODUCTION

The selection of interaction potential can play a key role when modeling water clusters, because the presence of free boundaries admits the formation of diverse structures. A wide spectrum of the potentials, from *ab initio* to entirely empirical ones, is encountered in the published literature. A feature common to these potentials is their very complex potential surfaces. Special procedures are required for the determination of the global energy minima of such surfaces. It was established [1] that the structure of a pentagonal prism is the most energetically favorable for clusters composed of ten molecules. The pentagonal prism may also serve as a basic element for clusters composed of 20 and 30 molecules. If larger clusters have been formed on the basis of unit cells, the formation of linear structures would be preferable. However, real large water clusters have a noncyclic structure and a nonlinear shape. The structure of bulk water is also noncyclic.

Oxygen is low soluble in water. At 293 K and normal atmospheric pressure, one liter of water contains only 6.2 ml of oxygen. Because of the absence of a permanent dipole moment, oxygen molecules do not have rotational spectra. However, when two molecules collide with each other, their electron shells are deformed, thus leading to the appearance of a dipole moment. Oxygen starts to noticeably absorb the IR radiation at a high frequency of the collisions, for example, in a dense gas [2]. The molecular density is higher in clusters than in the compressed gas; therefore, it may be expected that oxygen molecules captured by water clusters acquire new spectral properties. However, the main effect created by oxygen molecules in water clusters consists in significant changes in the kinetic parameters and structure of the clusters. The activation energy of the diffusion of O_2 molecules in water is close to zero [3]. An easily diffusing oxygen molecule collides with water molecules in a cluster and increases their characteristic vibration frequency, thus affecting the IR absorption and reflectance spectra.

The goal of this work was to investigate the absorption of oxygen molecules by water clusters and to determine the effect of absorbed oxygen molecules on the spectral characteristics of water clusters.

COMPUTER MODEL

The modified TIP4P model of water [4, 5] was used in this work. The dynamics of a system is governed by the motion of molecules at relatively simple interactions. The potential of water–water intermolecular interaction, geometrical parameters of water molecules, the method for integration of equations of motion, and the procedure of molecular-dynamic calculations are identical to those used in [6]. The oxygen–oxygen and oxygen–water interactions can be represented as a sum of repulsive and dispersive contributions [7]:

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

where parameters a_i, b_i, and c_i of the potential describing these interactions were taken from [8]. The interatomic distance in an O_2 molecule is $r_{OO} = 0.12074$ nm [9].

Molecular-dynamic calculations performed using different empirical potentials so far cannot answer the question which structure of a water cluster containing ten and more molecules corresponds to the minimum energy. High-level *ab initio* calculations suggested [10] that the $(H_2O)_{20}$ cluster with the most energetically favorable structure is formed on the basis of a pentagonal prism (U_{tot} varies from –9.32 to –9.44 eV) rather than a dodecahedron (–8.67 eV) or fused cubes (–9.21 eV). According to the proposed model, the internal energy of the $(H_2O)_{20}$ cluster is equal to –8.66 eV.

Time step Δt of integration was 10^{-17} s. The equilibrium state of water clusters at $T = 233$ K was originally established by a molecular dynamics calculation lasted for $10^6 \Delta t$ interval. Further evolution time for each $(H_2O)_i$ cluster amounted to 20 ps, that is, $2 \times 10^6 \Delta t$. At the next stage of modeling, an O_2 molecule was introduced into the range of intermolecular forces of cluster molecules. The center of an O_2 molecule was placed at a point arbitrarily selected on a sphere surrounding a water cluster. The O_2 molecule was oriented arbitrarily. The distance between atoms of admixture molecule and atoms of the nearest water molecule was no less than 0.6 nm. The cut-off radius of all interactions in the model was 0.9 nm. The newly formed system was equilibrated within a time interval of $0.6 \times 10^6 \Delta t$; then required physicochemical properties were calculated within an interval of $2 \times 10^6 \Delta t$.

The calculations were performed with a PENTIUM-IV computer operating at a processor clock frequency of 3.2 GHz. The calculation with time $10^6 \Delta t$ for cluster composed of 20 molecules took about 7 h of computer time.

CALCULATION OF THE ABSORPTION AND REFLECTANCE SPECTRA

The total dipole moment **M** of a cluster was calculated by the equation

$$\mathbf{M}(t) = Z_+ \sum_{i-1}^{2N} \mathbf{r}_i(t) + Z_- \sum_{j=1}^{N} \mathbf{r}_j(t), \qquad (2)$$

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 "+" and "–" refer to positively charged hydrogen atoms and negatively charged oxygen atoms, respectively; and N is the number of molecules in the cluster.

Static permittivity ε_0 was calculated from fluctuations of total dipole moment **M** [11]:

$$\varepsilon_0 = 1 + \frac{4\pi}{3VkT}[\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2], \qquad (3)$$

where V is the cluster volume and k is Boltzmann' constant.

Permittivity $\varepsilon(\omega)$ was presented as a function of frequency ω by complex value $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, which was defined using the equation [11, 12]

$$\frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} = -\int_0^\infty \exp(-i\omega t)\frac{dF}{dt}dt$$

$$= 1 - i\omega \int_0^\infty \exp(-i\omega t)F(t)dt, \qquad (4)$$

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

$$F(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle \mathbf{M}^2 \rangle}. \qquad (5)$$

The IR absorption signal was set in the following form [13]:

$$\sigma(\omega) = \left(\frac{2}{\varepsilon_v c \hbar n} \right)$$

$$\times \omega \tanh\left(\frac{\hbar\omega}{2kT} \right) \mathrm{Re} \int_0^\infty dt e^{i\omega t} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle, \qquad (6)$$

where ε_v is the permittivity of vacuum, c is the speed of light, $\hbar$ is the Planck constant, and n is the refractive index independent of frequency ω.

Reflection coefficient R is determined as the ratio of the average energy flux reflected by the surface to the incident flux. For a normal incidence of a plane monochromatic wave, the reflection coefficient is calculated by the equation [14]

$$R = \left| \frac{\sqrt{\varepsilon_I} - \sqrt{\varepsilon_{II}}}{\sqrt{\varepsilon_I} + \sqrt{\varepsilon_{II}}} \right|^2. \qquad (7)$$

Here, it is assumed that the incidence of wave occurs from a transparent medium (medium I) to a medium, which can be transparent or opaque, i.e., absorbing and scattering (medium II). Subscripts at the permittivity in Eq. (7) refer to the corresponding media.

Motions with frequencies below 1200 cm^{-1} correspond to librations of molecules, while frequencies above 1200 cm^{-1} are mainly attributed to intramolecular vibrations [15]. Because intramolecular vibrations are absent in the used model, when analyzing frequency-dependent parameters, we confine ourselves to the $0 \leq \omega \leq 1000$ cm^{-1} frequency range.

CALCULATION RESULTS

The configuration of the $(O_2)_2(H_2O)_{30}$ cluster at a time of 26 ps is presented in Fig. 1. By this time, one oxygen molecule has approached water molecules at a
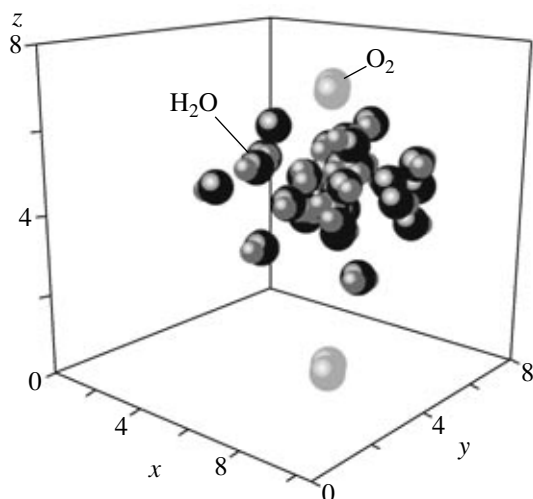
Fig. 1. Configuration of the $(O_2)_2(H_2O)_{30}$ cluster corresponding to a time 26 ps.

Fig. 2. Total dipole moment M of clusters as a function of their sizes i: (*1*) $(H_2O)_i$, (*2*) $O_2(H_2O)_i$, and (*3*) $(O_2)_2(H_2O)_i$.

sufficiently short distance and is retained on the cluster surface, while another molecule is at a longer distance from the surface. Oxygen molecules do not tend to penetrate into the cluster but only surround it that is typical of the clusters in hydrophobic solutions [16].

Total dipole moment M is presented in Fig. 2 as a function of cluster size i. When i was varied from 10 to 50, the magnitude of M increased by a factor of 2.1, 1.8, and 3.0 for clusters of pure water and clusters absorbed one and two O_2 molecules, respectively. It is seen that oxygen molecules in a cluster affect the orientation of dipole moments of water molecules and, in the long run, the total dipole moment of a cluster. The value of M rises with i in an oscillating rather than a monotonic mode. The highest peaks of M are observed at $i = 40$ and 30 for clusters of pure water and those containing oxygen atoms, respectively. In the aforementioned range of i, the $M(i)$ function demonstrates three peaks for $(H_2O)_i$ and $O_2(H_2O)_i$ clusters and two peaks for $(O_2)_2(H_2O)_i$ clusters. In the latter case, the peak at $i = 20$ degenerates into a shoulder.

The absorption of oxygen molecules causes an increase in static permittivity ε_0 (Fig. 3). For example, the ε_0 value of a cluster containing 50 water molecules rises by factor of 5.2 and 1.9 after the absorption of one or two O_2 molecules, respectively. As the number of molecules in a cluster increases, the ε_0 value varies nonmonotonically. For clusters of all types under consideration, function $\varepsilon_0(i)$ has a peak at $i = 40$. After one oxygen molecule is absorbed, the peak at $i = 20$ shifts to $i = 30$, and then returns to its initial position ($i = 20$) when the water cluster absorbs second O_2 molecule.

The real and imaginary parts of permittivity ε of $O_2(H_2O)_i$ clusters are shown in Fig. 4. In the $0 \leq \omega \leq 1000$ cm^{-1} frequency range, the largest ε' and ε'' values are observed for clusters containing 10 and 20 water molecules. These values considerably vary with cluster sizes. Functions $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are oscillating. As a
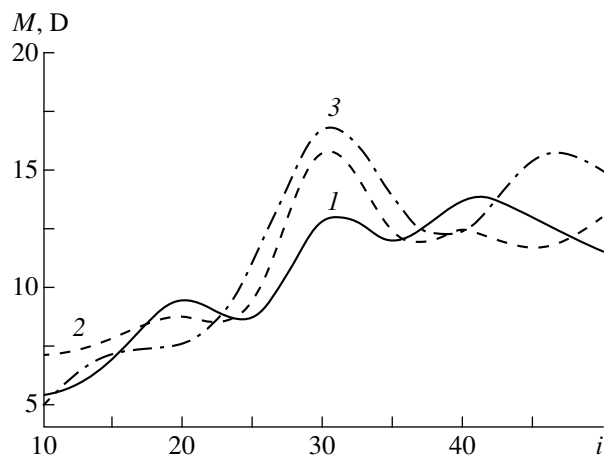
rule, the oscillations of the $\varepsilon''(\omega)$ function are more pronounced. The largest values of $\varepsilon'(\omega)$ function at $i = 10$, 20, 25, and 40, and of $\varepsilon''(\omega)$ function at all i values, except for $i = 25$ and 35, fall on frequency $\omega = 1000$ cm^{-1}, which is limiting for the $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ spectra because of the absence of internal degrees of freedom in the molecular models. In other cases, principal maxima of the $\varepsilon'(\omega)$ function are localized within the 724 cm$^{-1} \leq \omega \leq 881$ cm^{-1} frequency range; the largest values of the $\varepsilon''(\omega)$ function at $i = 25$ and 35 appeared at frequency $\omega = 978$ and 809 cm^{-1}, respectively.

The IR spectra, reflecting the cross sections of the absorption for $O_2(H_2O)_i$ and $(O_2)_2(H_2)_i$ clusters, are illustrated in Fig. 5. The intensity of the IR spectra of water clusters absorbed one or two O_2 molecules is low at cluster sizes $i < 30$. Clusters $O_2(H_2O)_{30}$ and $(O_2)_2(H_2O)_{30}$ are characterized by the highest-intensity IR spectra. The numbers and the heights of the peaks in the IR spectra vary irregularly with a further increase in
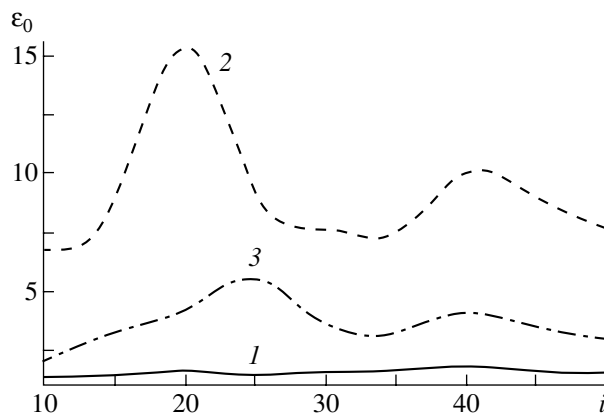

Fig. 3. Static permittivity ε_0 of clusters as a function of their sizes i: (*1*) $(H_2O)_i$, (*2*) $O_2(H_2O)_i$, and (*3*) $(O_2)_2(H_2O)_i$.

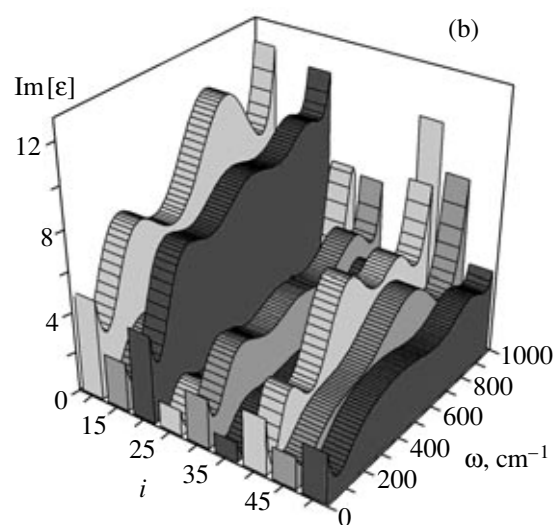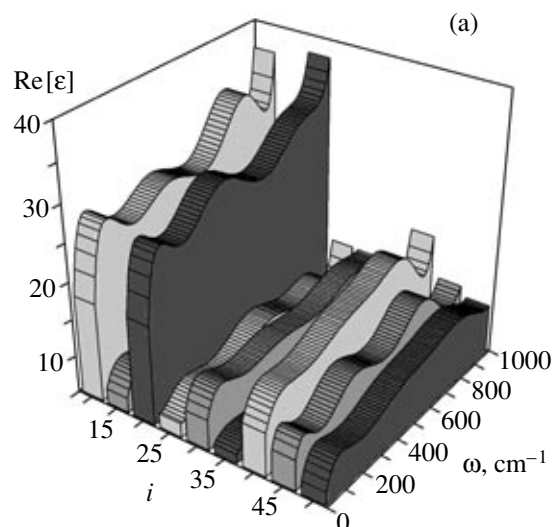**Fig. 4.** (a) Real and (b) imaginary parts of permittivity of $O_2(H_2O)_i$ clusters.

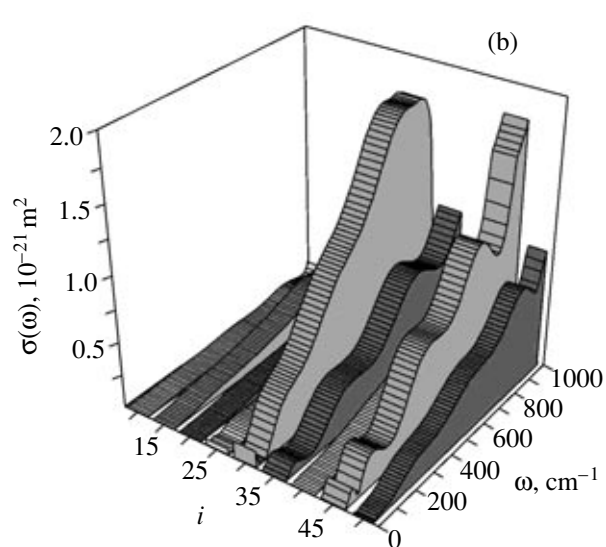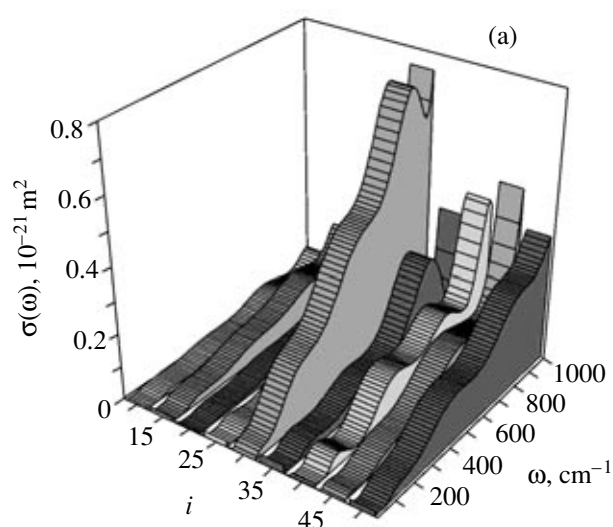**Fig. 5.** The IR absorption spectra of (a) $O_2(H_2O)_i$ and (b) $(O_2)_2(H_2O)_i$ clusters.

the cluster size. Similarly to the $\varepsilon''(\omega)$ function, the highest intensities for the majority of the IR spectra are observed at the frequency $\omega = 1000$ cm^{-1}; for higher frequencies, the spectra were not calculated. For clusters containing one absorbed oxygen molecule, the localization of the principal maximum at $\omega < 1000$ cm^{-1} is revealed at sizes $i = 10, 20, 25, 30,$ and 40; for clusters containing two O_2 molecules, it is revealed only at $i = 30$. Note that, in general, the intensities of IR spectra for clusters absorbed two oxygen molecules are substantially higher than for clusters with only one O_2 molecule. Thus, the addition of second oxygen molecule to a cluster increases the absorption of IR radiation.

The IR reflectance spectra of water clusters captured one (Fig. 6a) or two (Fig. 6b) oxygen molecules differ in the intensities and patterns. As a rule, the reflectance

coefficient decreases upon the absorption of second O_2 molecule by a cluster. The most pronounced decrease (almost ninefold) in coefficient R is observed for the cluster containing ten water molecules. In general, cluster reflectance spectra are not significantly changed with the frequency. As a rule, the highest-to-lowest intensity ratio for the same reflectance spectrum does not exceed two. The minima of these spectra are quite shallow, and the principal maximum, most often, falls on the 736 cm$^{-1} \leq \omega \leq 918$ cm^{-1} frequency range. Thus, the ability to reflect the IR radiation decreases after the addition of the second O_2 molecule to a cluster. An exception is the cluster with the number of water molecules $i = 25$, for which the addition of the second oxygen molecule does not cause a noticeable reduction in the intensity of reflectance spectrum.
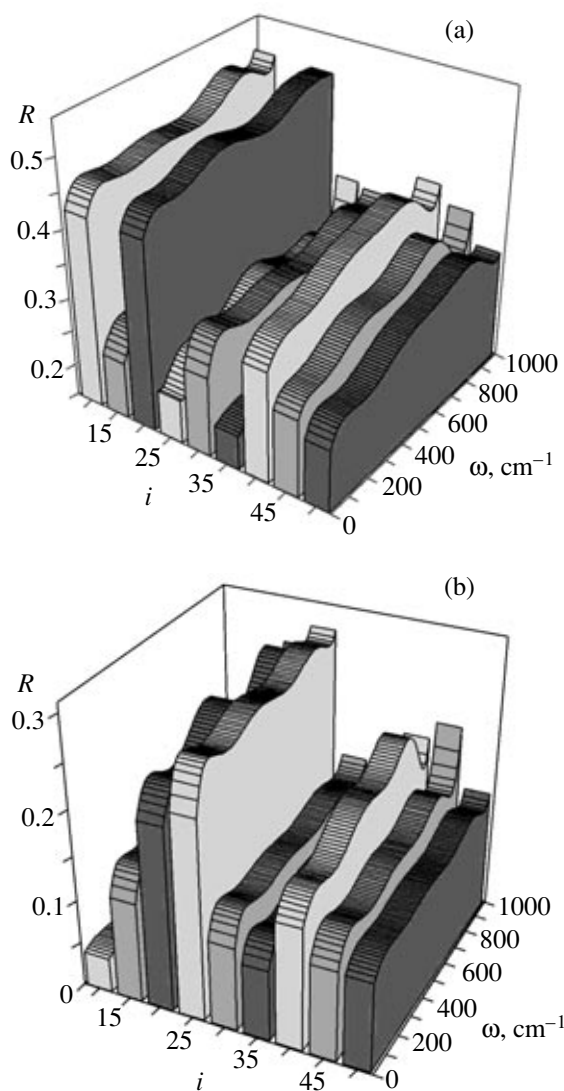
Fig. 6. The IR reflectance spectra of (a) $O_2(H_2O)_i$ and (b) $(O_2)_2(H_2O)_i$ clusters.

CONCLUSIONS

It is known from experiments that oxygen can be adsorbed on various surfaces, in particular, on Pt (111) [17] and GaAs (110) surfaces [18] in both molecular and atomic states. Physical adsorption proceeds at low, whereas dissociative chemisorption, at elevated temperatures. Characteristic vibration frequencies of oxygen atoms in face-centered cubic and hexagonal close-packed lattices are equal to 690 and 710 cm^{-1}, respectively. The frequency of vibrations related with the internal stresses in an oxygen molecule is 1556 cm^{-1} [19]. The internal vibrations arise in an oxygen molecule because of a low dipole activity developed upon physical adsorption. It was established that, on a Pt (111) surface saturated with oxygen, characteristic frequencies of O_2 molecule vibrations are equal to 700 and 875 cm^{-1} [17]. Absorption of two oxygen molecules leads to the localization of the characteristic vibration

frequency of the total dipole moment of clusters within the 738 cm$^{-1} \leq \omega \leq 882$ cm^{-1} range that is in good agreement with the range of the most probable vibration frequencies of oxygen molecules adsorbed on the Pt (111) surface.

As was determined from the mean-square displacement of molecules, self-diffusion coefficient D_{O_2} of O_2 molecules that approached the cluster at a distance of about 0.3–0.4 nm is larger than diffusion coefficient D_{H_2O} of water molecules in the cluster, so that the D_{O_2}/D_{H_2O} ratio averaged over number i equal to 2.2 at $T = 233$ K. This is consistent with the behavior of oxygen in supercritical water [3]. The main result of cited work is the fact that, when the temperature decreases, the local density around water molecules rises, thus hindering their diffusion. At the same time, there is a deficiency of molecules in the environment of O_2 that increases with a decrease in temperature. This forces O_2 molecules to move faster than H_2O molecules. The diffusion coefficient ratio $D_{O_2}/D_{H_2O} = 1.7$ at $T = 647$ K.

The addition of one oxygen molecule to each water cluster leads, on average, to a 3.8-fold reduction in integral intensity I_{tot} of the IR absorption spectrum. The addition of another O_2 molecule to each cluster increases I_{tot}, on average, by 2.3 times. However, average integral parameter $\bar{I}_{tot}$ obtained in this way still remains 1.6-fold lower than this parameter for clusters of pure water. Oxygen is not a gas causing the greenhouse effect, because it does not substantially contribute to the absorption of Earth's thermal radiation. Nevertheless, it can participate in the development of greenhouse effect. The absorption of oxygen by ultradispersed aqueous medium in the amount of one molecule per a cluster may reduce the greenhouse effect. At the same time, a twofold rise in the oxygen concentration in water clusters leads to the opposite effect. However, even in this case, the greenhouse effect created by pure dispersed aqueous system is not achieved.

Thus, just a physical interaction of oxygen with atmospheric moisture may reduce the greenhouse effect. In connection to this, it is of interest to study the effect of absorption of atomic oxygen and ozone by water clusters on the absorption of IR radiation by these clusters.

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