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Computer Simulation of the Adsorption of Acetylene by Disperse Aqueous Medium. IR Spectra

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Abstract—Adsorption of acetylene molecules by water clusters at T 230 K was studied by the method of molecular dynamics. Addition of already two C_2H_2 molecules to $(H_2O)_n$ clusters ($10 \le n \le 20$) makes them thermodynamically unstable. With an increase in the acetylene concentration in the disperse aqueous system, the IR absorption by the cluster system in the frequency range $0 \le \omega \le 1000$ cm^{-1} increases. Depending on the number of C_2H_2 molecules per water cluster, the IR reflection by cluster systems can either increase or decrease. The power of the thermal radiation emitted by the clusters considerably increases after the adsorption of C_2H_2 molecules and grows with an increase in the acetylene concentration in the disperse aqueous system.

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Water vapor is the main greenhouse gas of Earth's troposphere, being responsible for up to 95% of the greenhouse effect. Among the main parameters of the capability of molecules to absorb the IR radiation from the planet surfaces are the characteristic frequencies of intramolecular vibrations. The IR absorption spectrum of water vapor has strong bands at 1595 and 3756 cm^{-1} [1]. The spectrum of the thermal radiation of the Earth, corresponding to a temperature of 280 K, virtually ends at about 2500 cm^{-1}. The frequency of the translation vibrations of molecules (in the condensed state) is usually limited: $\omega < 1200$ cm^{-1} [2]. Intramolecular vibrations, as a rule, have higher frequencies.

Hydrogen-bonded water clusters are fairly stable formations. They are capable to take up molecules of other gases. It was found experimentally that water clusters consisting of up to nine atoms can capture and retain a benzene molecule whose molecular weight is approximately a half of the weight of such cluster [3]. Molecular-dynamics simulation demonstrated the possibility of uptake by water clusters of HCl, N_2, Cl_2, CO, CO_2, N_2O, CH_4, and CH_3OH molecules [4–9]. Acetyltne (C_2H_2) is the first member of the homologous series of alkynes. In the IR spectrum of gaseous acetylene, there are two absorption bands. One of the bands (3287 cm^{-1}) belongs to the stretching mode, and the other (729 cm^{-1}), to the doubly degenerate bending mode [10]. A study of the IR absorption by polycrystalline acetylene aggregates is often based on experiments with nonpolarized normally incident light [11]. An IR study revealed the disorientation of acetylene molecules in different layers of a film deposited on the (100) face of a KCl crystal [12]. Being sparingly soluble in water, acetylene should be retained on the surface of an aqueous system [13]. The best adhesion of a linear molecule with a water cluster is attained when the molecular axis is oriented along the tangent to the cluster surface. Here there is an analogy with the adsorption of acetylene on the (100) KCl surface. Ab initio calculations showed that the most energetically favorable site for C_2H_2 molecules on the silicon surface is formed via a bridging structure [14]. In this case, the C atoms of the C_2H_2 molecule are "attached" to the surface via Si–H bonds and are located opposite the same Si_2 dimer.

Precipitates formed in Earth's troposphere, when falling on the surface, ensure the circulation of water. The major fraction of atmospheric water occurs in the ultradispersed state, i.e., in the form of clusters. Cluster formation and capture of greenhouse gases by water clusters exert a certain influence on the greenhouse effect [15]. In this context, it is interesting to study the behavior of acetylene molecules occurring in immediate proximity to water clusters. The role of acetylene as the greenhouse gas in Earth's atmosphere is poorly understood.

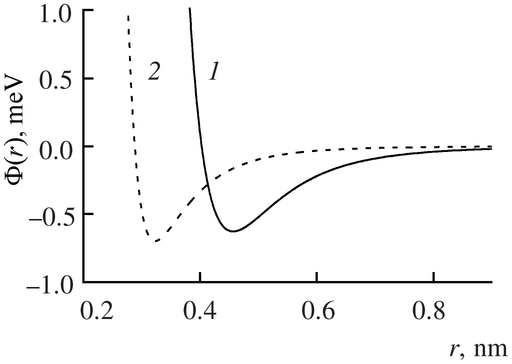

Fig. 1. Dispersion-repulsive term of the atom–atom potential describing C–H interactions: (*1*) model used in this study and (*2*) model used in [22, 23].

The goal of this study was to examine the uptake of acetylene molecules by water clusters, reveal the effect of these linear hydrocarbon molecules on the shape of the IR absorption and reflection spectra of disperse aqueous medium, and elucidate the role of C_2H_2 molecules in dissipation of the energy of the external IR radiation, taken up by the clusters.

COMPUTER MODEL

We took as a basis the well-tested model of liquid water [16] for which the optimal set of parameters of the TIP4P potential has been chosen. Along with the Lennard–Jones and Coulomb interaction, the model takes into account polarization interactions. The first approximation for this model was the potential energy surface obtained by ab initio calculations [17]. For fitting the parameters, we used high-level electronic structure calculations. The calculations were performed using a rigid four-center model of water molecule. The monomer geometry in this model is based on the results of gas-phase studies of water: The O–H bond length is taken equal to 0.09572 nm, and the H–O–H angle, to 104.5°. Fixed charges are assigned to hydrogen atoms and to point M lying on the bisector of the H–O–H angle at a distance of 0.0215 nm from the oxygen atom. The charges (q_H 0.519e, q_M –1.038e) and the position of point M are chosen so as to reproduce both the experimental values of the dipole and quadrupole moments [18] and the energy of the dimer and interatomic distances in it, obtained by ab initio calculations [19]. The characteristic distances of the C_2H_2 molecule are r_{CC} 0.121 and r_{CH} 0.106 nm [20]. The partial atomic charges play an enormous role in analysis of the polarization properties of a molecule. Charges occuring in centers of C and H atoms are q_H 0.094e and q_C –0.094e [21]. These charges are somewhat smaller in the absolute value than those used in [22, 23] in molecular-dynamics simulation of the adsorption of C_2H_2 on the surface of NaCl and KCl crystals. The model used in this study involves calculation of the induced dipole moments of molecules, which allows the polarization effect to be included in the consideration. This model well reproduces the structure and thermodynamic properties of bulk water and of the liquid water–water vapor phase boundary [16]. The optimized potential function also adequately reproduces the structures of water clusters of minimal energy and the binding energy. The validity of this model was confirmed in studies of the interaction of water clusters with N_2O and CH_4 molecules [24]. In this study, the description of the interaction of molecules of a greenhouse gas with water and with each other is based on the potentials calculated in the Gordon–Kim approximation using spherical averaging of the electron densities [21, 25]. The water–acetylene interaction was represented in the form of atom–atom interactions set through the sum of repulsive and dispersion terms:

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

where the parameters a_i, b_i, and c_i describing these interactions were taken from [25]. Despite the fact that the polarizability of the C_2H_2 molecules is 2.6 times higher than that of the H_2O molecules, the induced dipole moment of water molecules, on the average, appears to be two times higher than that of acetylene molecules. This is caused by shorter distance between H_2O molecules, compared to the distance between C_2H_2 and H_2O molecules. The dispersion-repulsive terms of potentials characterizing the C–H atom–atom interaction in this model and in the model used in [22, 23] are compared in Fig. 1. The main difference between the atom–atom potentials used in this study and in [22, 23] is an appreciable shift of the whole potential curve toward longer distances. The slightly sloping long-range attraction branch of the potential used in this study forms a broad potential well and ensures smooth attraction. Also, the potential well of the function $\Phi(r)$ used in this study is deeper for C–C interaction and shallower for H–H interactions, compared to the potentials used in [22, 23].

Initially we performed a molecular-dynamics calculation for water clusters. The final configuration of the water clusters was then used as the initial configuration for the simulation of heteroclusters. In the initial state, the added molecules were arranged so that the minimal distance between the atoms of C_2H_2 molecules and those of water molecules forming the cluster was no less than 0.6 nm. The truncation radius of intermolecular interactions was 0.9 nm. The added linear C_2H_2 molecules were arranged along rays connecting the center of gravity of the water cluster with the centers of gravity of these molecules.

The advantage of the model we used, compared to the simulation method described in [16], is direct integration of motion equations for the rotation of molecules. To integrate the motion equations for centers of gravity of molecules, we used the fourth-order Gere method [26]. Analytical solution of the motion equations for the rotation of molecules was done with Rodrig–Hamilton parameters [27], and the scheme of integration of the motion equations with the occurrence of rotations corresponded to the approach suggested by Sonnenschein [28]. The temperature of the clusters was similar in all the calculations (230 K), and the period covered by the calculation for each cluster was no less than 2.5×10^6 Δt, where the time step Δt was 10^{-17} s. The use of atom–atom potentials, compared to simple effective central potentials, leads to considerably faster accumulation of errors in the trajectory calculations. Therefore, calculations covering more than several millions of time steps become incorrect. The calculations were performed with a Pentium IV computer with a CPU frequency of 3.8 GHz. The calculation covering $10^6\Delta t$ for a cluster of 20 molecules took about 5 h of the computer time.

One of the advantages of the polarizable interaction potential used is that it accounts for the dipole moment of each water molecule as a function of the surrounding charges. To compare the model we used with one of the most popular (SPC) nonpolarizable water models, we calculated the excess (relative to ideal gas) free energy ΔG of a lengthy system (T 273 K) consisting of 54 water molecules in a cell of a cubic shape [29]. The essence of the quick method for calculating ΔG of the cluster is as follows. The method of thermodynamic perturbation and integration for calculating ΔG is based on variation of the interaction between the given molecule and all the other molecules in the system. The expression for the free energy is as follows:

$$G = kT\ln z, \quad z = \int \exp(-U/kT)dX.$$

Calculation by the perturbation method is performed via Boltzmann factor weighing states A and B, at thermal equilibrium of state A:

$$\begin{aligned} z_B/z_A &= \int \exp(-U_B/kT)dX / \int \exp(-U_A/kT)dX \\ &= \langle \exp[-(U_B - U_A)/kT] \rangle. \end{aligned}$$

For example, B may denote a liquid state, and A, an ideal gas. For a gradual transition from one state into another, we can perform integration:

$$\Delta G = \int dG = \int \langle \partial U(\lambda)/\partial \lambda \rangle d\lambda,$$

where U is a function of the parameter λ, varying from U_A to U_B with the variation of λ.

The potential energy is determined as the sum of pair contributions from all pairs of atoms in different molecules, plus nonadditive contribution:

$$U = \Sigma U_{ij} + U_{\mathrm{pol},\lambda},$$

where $U_{\mathrm{pol},\lambda}$ is the polarization energy at the interaction attenuated by the λ factor. Our calculation of the excess free energy in the polarizable model of water differs from the calculations for the nonpolarizable model [30] by the presence of an additional term $U_{\mathrm{pol},\lambda}$. We also used the same functions $f_\alpha(\lambda_\alpha)$ of interaction attenuation as in [30].

The result of this calculation, ΔG –26.9 kJ mol^{-1}, is well consistent with the excess free energy (ΔG –25.1 kJ mol^{-1}) for the nonpolarizable model [30]. In the model we used, the function $\Delta G(t)$ more slowly decreases in the initial period of the calculation and more slowly increases in the final period.

Three types of ultradisperse systems are considered. The first system includes water clusters consisting of 10 to 20 molecules; the second system includes clusters $C_2H_2(H_2O)_i$, i = 10, ..., 20; and the third system includes clusters $(C_2H_2)_2(H_2O)_i$ with the same number of water molecules. Let us denote these systems as I, II, and III, respectively. For a cluster consisting of i impurity molecules and n water molecules, the following statistical weight is assumed:

$$W_{in} = \frac{N_{in}}{N_{i\Sigma}}, \; i\ 0, 1, 2, \; n\ 10, ..., 20,$$

where N_{in} is the number of clusters with i impurity molecules and n water molecules in 1 cm^3, $N_{i\Sigma} = \sum_{n\,10}^{20} N_{in}$. The quantity N_{in} was estimated as follows. Consider the case of nonpolarized light scattering when the path length of the molecules l is much less than the light wavelength λ. The extinction (attenuation) coefficient h of the incident beam is determined, on the one hand, by the Rayleigh formula [31] and, on the other hand, through the scattering coefficient ρ [$h = (16\pi/3)\rho$] [32] in the approximation of scattering at an angle of 90°. Taking into account that $h = \alpha + \rho$, where α is the absorption coefficient, we obtain

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

where c is the velocity of light; ε, dielectric permittivity of the medium; and ω, frequency of the incident wave. All the spectrum characteristics were calculated taking into account the assumed statistical weights W_{in}. The procedure of formation of the cluster system implies their uniform distribution and is valid at low concentration of clusters when they do not interact with each other. The mean concentration of each type of clusters in the examined systems was 12–13 orders of magnitude lower than the Loschmidt number.

ABSORPTION AND REFLECTION COEFFICIENTS AND DIELECTRIC LOSS

The dielectric permittivity $\varepsilon(\omega)$ is a complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. The light absorption at frequency ω at thermodynamic equilibrium in the gas phase of temperature T is characterized by the absorption coefficient α. The quantity α can be determined through the imaginary part of the frequency-dependent dielectric permittivity $\varepsilon(\omega)$ as follows [33]:

$$\alpha(\omega) = 2\frac{\omega}{c}\,\mathrm{Im}[\varepsilon(\omega)^{1/2}].$$

The dielectric permittivity $\varepsilon(\omega)$ was determined from the following equation [34]:

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

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

where ε_0 is the relative dielectric permittivity of the medium and $F(t)$ is the normalized autocorrelation function:

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

where $\mathbf{M}$ is the total dipole moment of the cluster. The quantity ε_0 was calculated from the fluctuations of the total dipole moment [35] as follows:

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

where V is the cluster volume. Along with removal of molecules containing C and H atoms from a C_2H_2 molecule, we considered in this study weakening of all electrostatic interactions owing to the factor $1/\varepsilon_0$, which makes the water clusters more stable.

The reflection coefficient R was determined as the ratio of the mean energy flux reflected from the surface to the incident flux. At normal incidence of a plane monochromatic wave, the reflection coefficient is given by the formula [31].

$$R = \left|\frac{\sqrt{\varepsilon_1}-\sqrt{\varepsilon_2}^{\,2}}{\sqrt{\varepsilon_1}+\sqrt{\varepsilon_2}}\right|. \quad (1)$$

It is assumed here that the wave incidence occurs from a transparent medium (medium 1) into a medium that can be both transparent and nontransparent, i.e., absorbing and scattering (medium 2). The indices at the dielectric permittivity in expression (1) denote the corresponding medium.

The frequency dependence of the dielectric loss $P(\omega)$ can be presented as follows [32]:

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

where $\langle E^2\rangle$ is the mean squared electric intensity and ω is the frequency of the emitted electromagnetic wave.

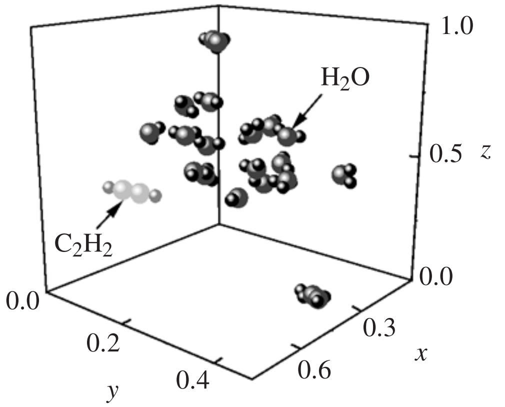

Fig. 2. Configuration of the $C_2H_2(H_2O)_{20}$ cluster corresponding to the instant of time of 25 ps. The molecular coordinates are presented in the units of σ_W = 0.3234 nm (parameter of the Lennard–Jones part of the interaction potential for water).

CALCULATION RESULTS

The C_2H_2 molecules are attracted by water clusters. Finally they acquire orientation of the tangent to the surface of the $(H_2O)_n$ cluster (Fig. 2). Figure 2 shows that the $C_2H_2(H_2O)_n$ cluster has a nonuniform density. The arrangement of water molecules is denser in the vicinity of the C_2H_2 molecule. At the same time, some peripheral water molecules are rather remote from the other H_2O molecules forming the cluster core. Figure 2 shows the variation of the excess free energy ΔG, chemical potential μ, and stability coefficient $(\partial\mu/\partial n)_{V,T}$ as functions of the number n of water molecules in the $(C_2H_2)_2(H_2O)_n$ clusters. As the

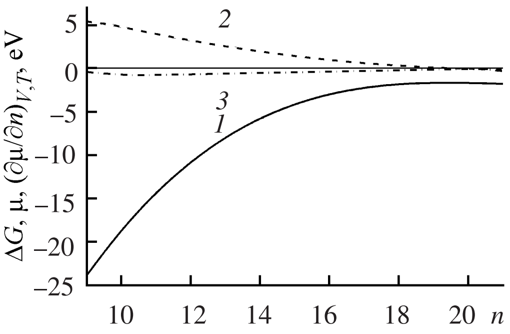

Fig. 3. (*1*) Excess free energy ΔG, (*2*) chemical potential μ, and (*3*) stability coefficient $(\partial\mu/\partial n)_{V,T}$ for clusters containing two C_2H_2 molecules and n water molecules.

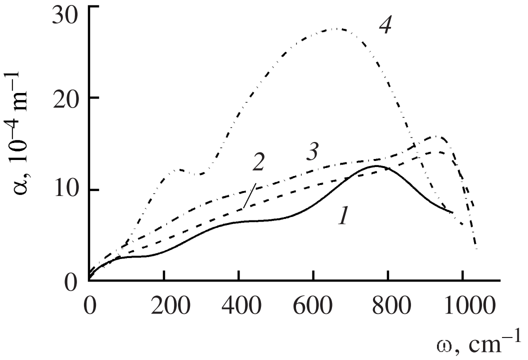

Fig. 4. Calculated coefficient of IR absorption by disperse aqueous systems. System: (*1*) I, (*2*) II, (*3*) III, and (*4*) liquid water (experimental data from [36]).

number of water molecules in clusters increases to 20, ΔG increases and the chemical potential decreases. However, at $n \geq 18$ the dependences flatten out. The stability coefficient $(\partial\mu/\partial n)_{V,T}$ is negative throughout the examined range of variation of n, i.e., the $(C_2H_2)_2 \cdot (H_2O)_n$ clusters are thermodynamically unstable, although the stability of the clusters increases with increasing cluster size. The uptake of methane molecules by the clusters yields more stable aggregates [24]. Water clusters of the size $10 \leq n \leq 20$ are thermodynamically stable until the number of the deposited CH_4 molecules becomes larger than six. The higher stability of the $(CH_4)_i(H_2O)_n$ clusters is associated with the structure of the CH_4 molecule. The tetrahedral shape of the methane molecule is due to tetrahedral orientation of the four hybrid orbitals of the carbon atom (sp^3 hybridization). The electronic structure of the water molecule is also tetrahedral. The CH_4 molecule, compared to C_2H_2, is more easily accommodated in the framework formed by tetrahedral water molecules. In the acetylene molecule, each carbon atom has two hybrid sp orbitals whose axes are collinear, forming an angle of 180°. The C_2H_2 molecule is linear.

On the whole, the IR absorption coefficient for disperse systems containing C_2H_2 molecules is higher than for the disperse system of pure water (Fig. 4). The coefficient α increases with an increase in the number of C_2H_2 molecules in the aqueous system. The principal maximum of the distribution $\alpha(\omega)$ for system I (pure disperse water) is observed at 780 cm^{-1}, and for systems II and III (disperse water with C_2H_2 molecules), at 970 cm^{-1}. The spectrum $\alpha(\omega)$ for bulk water has two maxima at 200 and 700 cm^{-1}. Thus, uptake of acetylene molecules by water clusters enhances the integral intensity I_{tot} of IR absorption. In the case of uptake of methane molecules by water clusters, I_{tot} decreased down to formation of a transparency window in the frequency range $540 \leq \omega \leq 800$ cm^{-1} [37]. In contrast to pure disperse water and to the disperse system containing CH_4 molecules, the IR absorption by systems II and III is more uniform, i.e., the integral intensities of IR absorption by different clusters differ insignificantly (Fig. 5). The difference between the maximal and minimal values of I_{tot} is 36% for system II and 59% for system III. In system III in which each cluster contains two C_2H_2 molecules, an increase in the variation of I_{tot} is accompanied by smoothing of oscillations in the spectra $\alpha(\omega)$.

The IR reflection coefficients of systems I–III are plotted in Fig. 6. After the addition of one C_2H_2 molecule to each water cluster, the integral reflection intensity increases: I_{tot} is 0.28 for system II and 0.23 for system I. The number of peaks in the spectrum R(ω) increases also (from 10 to 16). However, the addition of one more C_2H_2 molecule to each cluster causes $I_{R,tot}$ to decrease (to 0.064). In this case, the peaks of the spectrum $R(\omega)$ become better resolved, and their number reaches 19. An increase in the reflectance of system II is associated with densification of water clusters under the action of acetylene molecules, and a drastic decrease in I_{tot} for system III is due to loosening of the surface of the clusters upon addition of the second C_2H_2 molecule. The IR reflection spectra of separate clusters are characterized by diversity of the integral intensities in the case of both aggregates $C_2H_2(H_2O)_n$ and $(C_2H_2)_2(H_2O)_n$ (Fig. 7). The maximal and minimal values of $I_{R,tot}$ differ by a factor of 7 for the $C_2H_2(H_2O)_n$ clusters and 39 for the $(C_2H_2)_2(H_2O)_n$ clusters. The majority of the spectra R(ω) for the $C_2H_2(H_2O)_n$ clusters show weak frequency dependence, and the function $R(n)$ strongly varies

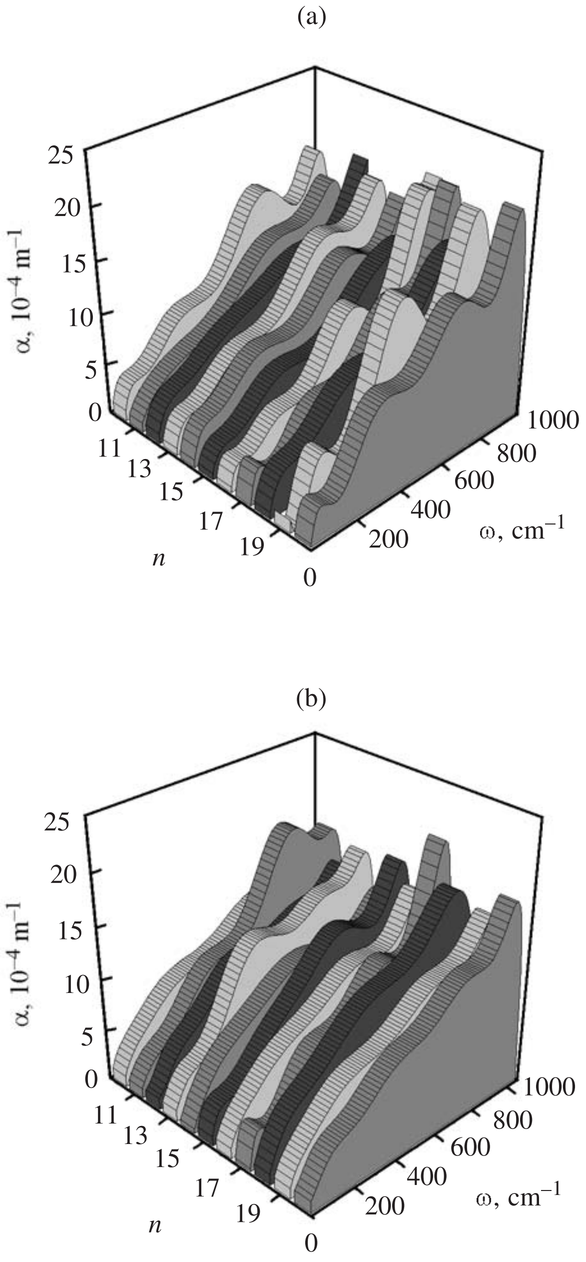

Fig. 5. IR absorption spectra of clusters (a) $C_2H_2(H_2O)_n$ and (b) $(C_2H_2)_2(H_2O)_n$.

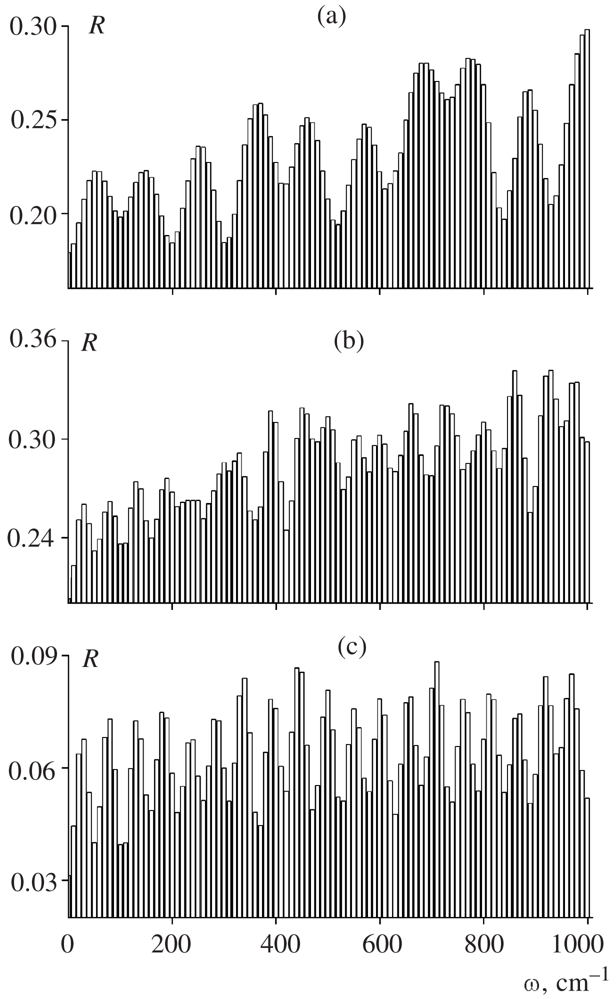

Fig. 6. IR reflection coefficient of disperse aqueous systems. System: (a) I, (b) II, and (c) III.

with the number n of water molecule. The similar pattern is observed with the $(C_2H_2)_2(H_2O)_n$ clusters, but here the dependence $R(\omega)$ is fairly significant.

The clusters accumulate the IR radiation energy and dissipate it. The rate of the dissipation of the accumulated energy, or the radiation power P, of the cluster systems is plotted in Fig. 8a. Pure disperse water has low P (insert in Fig. 8a). The emitted radiation power has a maximum at a frequency of 970 cm^{-1}. After the uptake of C_2H_2 molecules by water clusters, the power of radiation emitted by the disperse systems sharply increases. The larger the number of C_2H_2 molecules captured by the clusters, the higher the radiation power. The maximal values in the spectra $P(\omega)$ for systems I, II, and III are in a ratio of 1 : 12.5 : 17.6. The frequency corresponding to the maximal value of P shifts from 970 cm^{-1} for system II to 910 cm^{-1} for system III.

The maximal values of the radiation power for particular clusters are plotted in Fig. 8b. Clusters of pure water are characterized by extremely low rate of energy dissipation up to the size $n = 18$ (insert in Fig. 8b). For the clusters $(H_2O)_n$ with $n > 18$, the radiation power sharply increases but still remains relatively low compared to that of the clusters containing C_2H_2 molecules. The maximal power of the radiation emitted by water clusters of size $n \leq 18$ that took up one C_2H_2 molecule each is appreciably lower than

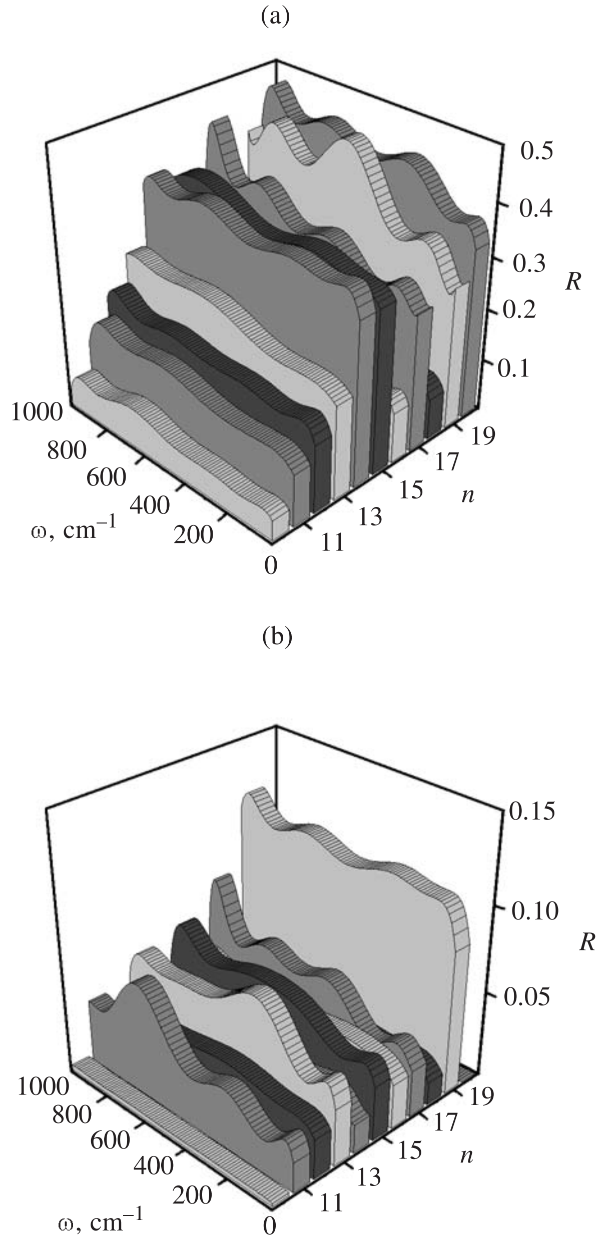

Fig. 7. IR reflection spectra of clusters (a) $C_2H_2(H_2O)_n$ and (b) $(C_2H_2)_2(H_2O)_n$.

P_{max} of the corresponding $(C_2H_2)(H_2O)_n$ clusters. However, at $n > 18$ the pattern becomes opposite. The quantity P_{max} is closely related to structural rearrangements in the clusters. Thus, among clusters of types I, II, and III, the aggregates $(H_2O)_{20}$, $C_2H_2(H_2O)_{20}$, and $(C_2H_2)_2(H_2O)_{11}$ dissipate energy most rapidly.

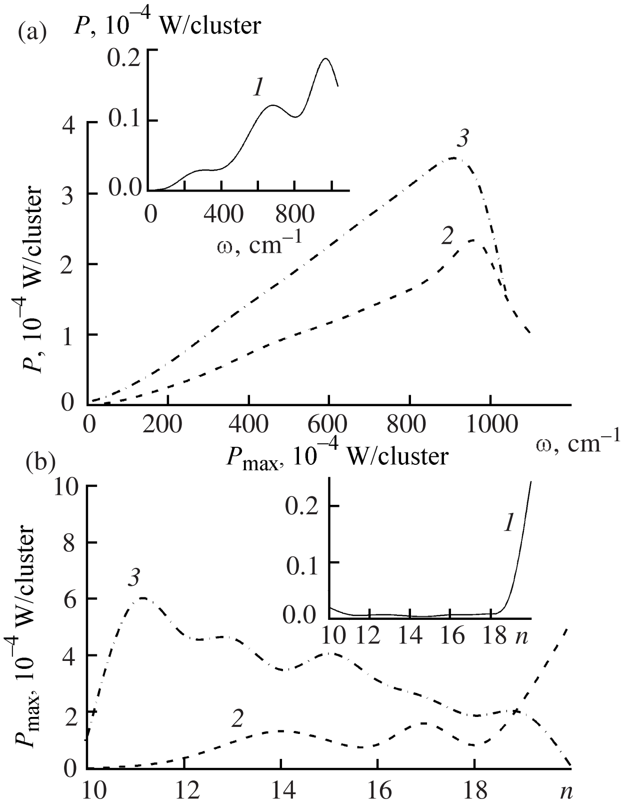

Fig. 8. (a) Power of thermal radiation emitted by disperse systems (*1*) I, (*2*) II, and (*3*) III; (b) maximal rate of energy dissipation as a function of the number of water molecules in clusters (*1*) $(H_2O)_n$, (*2*) $C_2H_2(H_2O)_n$, and (*3*) $(C_2H_2)_2(H_2O)_n$.

Water clusters consisting of 10 to 20 molecules are capable of adsorbing C_2H_2 molecules, but the thermodynamic stability of the clusters is broken, in some cases even on capture of one acetylene molecule and in all the cases on capture of two acetylene molecules. The acetylene molecule in $(C_2H_2)_i(H_2O)_n$ clusters is arranged along the tanget to the aqueous core of the cluster. Addition of acetylene molecules is accompanied by an increase in the IR absorption coefficient of the disperse systems. The coefficient α increases with the number of C_2H_2 molecules captured by the cluster. The frequency of the IR absorption maximum also increases upon uptake of C_2H_2 molecules by the disperse system. The IR reflection by the disperse system is enhanced on addiiton of one acetylene molecule to each cluster but weakens upon capture of the second C_2H_2 molecule. The number of peaks in the spectrum $R(\omega)$ increases and the frequency dependence of the reflection coefficient becomes smoother with an increase in the concentration of C_2H_2 molecules in disperse aqueous systems. The uptake of acetylene molecules by water clusters considerably enhances the power of the radiation emitted by the cluster systems. The rate of dissipation of the accumulated energy increases with an increase in the concentration of C_2H_2 molecules in the system. The highest radiation power among pure water clusters and clusters that captured one and two acetylene molecules is exhibited by the species $(H_2O)_{20}$, $C_2H_2(H_2O)_{20}$, and $(C_2H_2)_2 \cdot (H_2O)_{11}$, respectively.

The capture of acetylene molecules by water clusters enhances the greenhouse effect produced by the dispersion medium owing to an increase in the IR absorption coefficient.

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REFERENCES

1. El'yashevich, M.A., *Atomnaya i molekulyarnaya spektroskopiya* (Atomic and Molecular Spectroscopy), Moscow: Gos. Izd. Fiziko-Matematicheskoi Literatury, 1962.
2. Stern, H.A. and Berne, B.J., *J. Chem. Phys.,* 2001, vol. 115, no. 16, p. 7622.
3. Gruenloh, C.J., Carney, J.R., Hagemeister, F.C., Wood, J.T., and Jordan, K.D., *J. Chem. Phys.,* 2000, vol. 113, no. 6, p. 2290.
4. Galashev, A.E., Pozharskaya, G.I., and Chukanov, V.N., *Kolloid. Zh.,* 2002, vol. 64, no. 6, p. 762.
5. Galashev, A.E., Pozharskaya, G.I., and Chukanov, V.N., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 6, p. 881.
6. Galashev, A.E., Chukanov, V.N., and Pozharskaya, G.I., *Khim. Fiz.,* 2001, vol. 20, no. 9, p. 8.
7. Galashev, A.E. and Chukanov, V.N., *Kolloid. Zh.,* 2004, vol. 66, no. 5, p. 588.
8. Galashev, A.E., Rakhmanova, O.R., and Chukanov, V.N., *Kolloid. Zh.,* 2005, vol. 67, no. 3, p. 308.
9. Brodskaya, E.N., *Kolloid. Zh.,* 2001, vol. 63, no. 1, p. 10.
10. Gribov, L.A., *Teoriya intensivnostei v infrakrasnykh spektrakh mnogoatomnykh molekul* (Theory of Intensities in Infrared Spectra of Polyatomic Molecules), Moscow: Akad. Nauk SSSR, 1963.
11. Dunn, S.K. and Ewing, G.E., *J. Phys. Chem.,* 1992, vol. 96, no. 13, p. 5284.
12. Vogt, J., *Phys. Rev. B,* 2006, vol. 73, no. 8, p. 085418 (1-9).
13. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
14. Silvestrelli, P.L., Toigo, F., and Ancilotto, F., *J. Chem. Phys.,* 2001, vol. 114, no. 19, p. 8539.
15. Chukanov, V.N. and Galashev, A.E., *Perspekt. Energet.,* 2003, vol. 7, no. 7, p. 283.
16. Dang, L.X. and Chang, T.-M., *J. Chem. Phys.,* 1997, vol. 106, no. 19, p. 8149.
17. Sremaniak, L.S., Perera, L., and Berkowitz, M.L., *J. Chem. Phys.,* 1996, vol. 105, no. 9, p. 3715.
18. Xantheas, S., *J. Chem. Phys.,* 1996, vol. 104, no. 21, p. 8821.
19. Feller, D. and Dixon, D.A., *J. Phys. Chem.,* 1996, vol. 100, no. 8, p. 2993.
20. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Leningrad: Khimiya, 1971, vol. 1.
21. Spackman, M.A., *J. Chem. Phys.,* 1986, vol. 85, no. 11, p. 6587.
22. Picaud, S., Hoang, P.N.M., Girardet, C., Glebov, A., Miller, R.E., and Toennies, J.P., *Phys. Rev. B,* 1998, vol. 57, no. 16, p. 10090.
23. Glebov, A.L., Panella, V., Toennies, J.P., Traeger, F., Weiss, H., Picaud, S., Hoang, P.N.M., and Girardet, C., *Phys. Rev. B,* 2000, vol. 61, no. 20, p. 14028.
24. Galashev, A.E., Novruzov, A.N., and Galasheva, O.A., *Khim. Fiz.,* 2006, vol. 25, no. 2, p. 26.
25. Spackman, M.A., *J. Chem. Phys.,* 1986, vol. 85, no. 11, p. 6579.
26. Haile, J.M., *Molecular Dynamics Simulation. Elementary Methods,* New York: Wiley, 1992.
27. Koshlyakov, V.N., *Zadachi dinamiki tverdogo tela i prikladnoi teorii giroskopov* (Problems in Solid State Dynamics and Applied Gyroscope Theory), Moscow: Nauka, 1985.
28. Sonnenschein, R., *J. Comput. Phys.,* 1985, vol. 59, no. 3, p. 347.
29. Galashev, A.E., Chukanov, V.N., and Rakhmanova, O.R., *Metastabil'nye sostoyaniya i fazovye perekhody* (Metastable States and Phase Transitions), Dubrovina, E.N., Ed., Yekaterinburg: NISO Ural'sk. Otd. Ross. Akad. Nauk, 2004, issue 7, p. 180.
30. Hermans, J., Pathiaseril, A., and Anderson, A., *J. Am. Chem. Soc.,* 1988, vol. 110, no. 18, p. 5982.
31. Landau, L.D. and Lifshits, E.M., *Elektrodinamika sploshnykh sred* (Electrodynamics of Continuous Media), Moscow: Nauka, 1982, vol. 8.
32. *Fizicheskaya entsiklopediya* (Physical Encyclopedia), Prokhorov, A.M., Ed., Moscow: Sov. Entsiklopaediya, 1988, vol. 1.

33. Neumann, M., *J. Chem. Phys.,* 1985, vol. 82, no. 12, p. 5663.

34. Bosma, W.B., Fried, L.E., and Mukamel, S., *J. Chem. Phys.,* 1993, vol. 98, no. 6, p. 4413.

35. Bresme, F., *J. Chem. Phys.,* 2001, vol. 115, no. 16, p. 7564.

36. Goggin, P.L. and Carr, C., *Far Infrared Spectroscopy and Aqueous Solutions. Water and Aqueous Solutions,* Bristol: Adam Hilger, 1986, vol. 37, p. 149.

37. Galashev, A.E., Chukanov, V.N., Novruzov, A.N., and Novruzova, O.A., *Teplofiz. Vys. Temp.,* 2006, vol. 44, no. 3, p. 370.