HEAT AND MASS TRANSFER
AND PHYSICAL GASDYNAMICS

A Computer Study of the Absorption of Infrared Radiation by Systems of Molecular Clusters

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Abstract—The method of molecular dynamics is used to investigate the process of absorption of N_2O and CH_4 molecules by water clusters and to determine the frequency spectra of permittivity for systems consisting of clusters mixed in different ratios, namely, $(H_2O)_n$, $(N_2O)_i(H_2O)_{10}$, and $(CH_4)_i(H_2O)_{10}$. IR-radiation absorption spectra for these systems are calculated and analyzed; the radiation power scattered by these systems and the tangent of dielectric loss angle are determined. The inclusion of anharmonicity of phonon oscillation makes it possible to explain the origin of characteristic frequencies appearing in IR spectra of mixtures of cluster systems. The capture of molecules of greenhouse gases by an ultradisperse aqueous medium affects the ability of this medium to absorb terrestrial radiation, i.e., reduces the greenhouse effect.

INTRODUCTION

The atmosphere of the Earth is a complex dynamic system protecting the biosphere. One of the important factors affecting the terrestrial radiation balance is the greenhouse effect, whose increase is associated both with increasing solar activity and with increasing content of gases exhibiting pronounced radiative properties in the atmosphere. A marked effect is made on the formation of fields of thermal radiation by H_2O vapors, as well as by atmospheric gases such as CO_2, N_2O, CH_4, and others. The processes occurring in the atmosphere are characterized by both geological (up to 10^6 years) and lower (up to 10^3 years) time scales. The variation of the concentration of greenhouse gases such as CO_2, N_2O, and CH_4 is a "fast" process. Such processes may cause significant unfavorable changes of climate. However, phenomena are also observed in the atmosphere, which hold back the fast development of climatic processes. The clustering of greenhouse gases may be classed with such phenomena.

In this study, an attempt is made for the first time to apply the theory of anharmonicity of crystal IR spectra to systems of molecular clusters. It is our objective to determine the possibility of using this theory for predicting the variations in the position of the first IR peaks for different cluster systems. In a harmonic approximation, the modes which form the frequency spectrum are independent. An IR spectrum represented by rotational and vibrational-rotational modes may exhibit an intermode anharmonicity caused by the presence of polyatomic molecules of different sorts in the vibrational system. An analogy is observed here with internal vibrations in complex polyatomic molecules for which Fermi resonances are quite probable even in the case of a low excitation level, i.e., a strong interaction between the levels of close-in-value energies characterizing vibrational states. When the condition $\hbar\omega \ll kT$ of validity of the classical theory does not hold, the anharmonicity effect may be reduced to a random exchange of quanta between harmonic oscillators simulating a system of molecules. The methods of computer simulation (Monte–Carlo and molecular dynamics) make it possible to directly investigate the anharmonicity due to the interaction of modes.

This paper deals with a molecular-dynamic study of the impact made by clustering of H_2O vapors and atmospheric gases CH_4 and N_2O on the greenhouse effect.

COMPUTER MODEL

Used as the basis is the well-tested model of liquid water [1] for which an optimized set of parameters of TIP4P potential was selected. The first approximation

for this model was provided by the potential energy surface obtained as a result of *ab initio* calculations [2]. High-level computations of electron structure were used for fitting the parameters. The calculations involved the use of a rigid four-center model of water molecule. The monomer geometry in this model is based on the data of investigation of the gas phase of water: the length of O–H bond is taken to be 0.09572 nm, and the angle H–O–H – 104.5°. Fixed charges are assigned to hydrogen atoms and point M lying on the bisectrix of angle H–O–H at a distance of 0.0215 nm from the oxygen atom. The values of charges ($q_H =$ $= 0.519e$, $q_M = -1.038e$) and the position of point M are selected such that both the experimentally obtained values of dipole and quadrupole moments [3] and the *ab initio* calculated energy of dimer and its characteristic distances [4] would be reproduced. The model presumes the calculation of induced dipole moments of molecules, which enables one to include into treatment the effect of their polarization. This model reproduces well the structure and thermodynamic properties of massive water, as well as of the water-vapor interface [1]. The optimized potential function further enables one to adequately reproduce the structures of water clusters with minimal energy and the binding energy. We extended the range of validity of this model by introducing into treatment the interaction of water molecules with molecules of nitrous oxide and methane. The description of interaction of molecules of greenhouse gases with water and with one another was based on atom-atom potentials calculated in the Gordon–Kim approximation using the spherical averaging of electron densities [5, 6].

First the molecular-dynamic calculation for water clusters was performed. In what followed, the final configuration of $(H_2O)_{10}$ cluster was used as initial for simulating heteroclusters. In the initial state, the molecules being added were positioned such that the minimal spacing between atoms of impurity molecule and atoms of water molecule, which form the cluster, would be at least 0.6 nm. The cut-off radius of intermolecular interactions was equal to 0.9 nm. In the case of $(N_2O)_i(H_2O)_{10}$ systems, the added linear molecules of N_2O were located along the rays connecting the center of mass of $(H_2O)_{10}$ cluster with centers of mass of these molecules. In the case of $(CH_4)_i(H_2O)_{10}$ systems, the CH_4 molecules were located at the sites of imaginary bcc lattice threading the cluster. In both

instances, the impurity molecules were located beyond the cluster.

Yet another advantage of the employed model over the method of simulation used by Dang and Chang [1] is the direct integration of the equation of motion for rotation of molecules. This procedure is necessary for correct calculation of the autocorrelation function of the total dipole moment of cluster, which is used for determining the IR spectrum. The equations of motion of centers of mass of molecules were integrated using the fourth-order Gear method [7]. The Rodrigues–Hamilton parameters were used for analytical solution of the equations of motion for rotation of molecules [8], and the scheme of integration of the equations of motion in the presence of rotation corresponded to the approach suggested by Sonnenschein [9]. The cluster temperature was the same throughout the calculations (233 K), and the duration of calculation for each cluster was at least $3 \times 10^6 \Delta t$, where the time step $\Delta t =$ $= 10^{-17}$ s. The calculations were performed using a Pentium-IV computer with the processor clock frequency of 3.2 GHz. About seven hours of computer time was required for the calculation procedure with a duration of $10^6 \Delta t$ for a cluster of 20 molecules.

The investigation of water clusters was started with a dimer. For the model employed by us, the minimum of energy $U_{min} = -19.62$ kJ/mol of water dimer falls on the interatomic spacing of 0.287 nm. These values agree well with the respective values (–20.91 kJ/mol, 0.291 nm) obtained by way of calculating the electron structure [1]. The experimentally obtained value is $U_{min} = -22.6\pm2.9$ kJ/mol [3]. For the configuration which represents the minimum of total energy, the contribution by polarization energy amounts to approximately 17% of total energy. One of the advantages of the employed polarization potential of interaction is the possibility of explaining the value of dipole moment of each water molecule depending on the charges surrounding this molecule.

In order to compare the model employed by us with one of the most popular (SPC) nonpolarizable models of water, the excess (with respect to ideal gas) free energy ΔF of an extended system ($T = 273$ K) represented by 54 water molecules in a cubic cell was calculated [10]. The result of this calculation ($\Delta F = -26.9$ kJ/mol) agrees well with the value of excess free energy ($\Delta F = -25.1$ kJ/mol) for a nonpolarizable model [11]. In the model employed by us, the function $\Delta F(t)$ exhibits a slower decrease in the initial

stage of calculation and a slower increase in the closing stage.

Ultradisperse systems of three types were considered in order to reveal the impact of absorbed molecules of nitrous oxide and methane on the greenhouse effect. The first such system consists of water clusters of two to 20 molecules, the second system contains $(H_2O)_{10}$ clusters which absorbed from one to ten molecules of N_2O, and the third system contains $(H_2O)_{10}$ clusters which absorbed as many CH_4 molecules. We will number these systems I, II, and III in the order of succession.

DIELECTRIC PROPERTIES

Up to now, the molecular-dynamic calculations of permittivity of aqueous medium were performed either for a system with periodic boundary conditions [12, 13] or for water clusters [14]. In this study, a computer model is used for the first time for investigating the impact made by impurities on the dielectric properties of water clusters. We will further analyze IR spectra of disperse systems consisting of clusters and heteroclusters of different size and composition. We will consider the case of scattering of unpolarized light, where the molecular path l is much shorter than the light wavelength λ. The extinction (attenuation) factor h of incident beam is determined, on the one hand, by the Rayleigh formula [15] and, on the other hand, in terms of the scattering factor $\rho\left(h = \dfrac{16\pi}{3}\rho\right)$ [16] at an angle of 90°. In view of the fact that $h = \alpha + \rho$, where α is the absorption factor, we have

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

Here, N is the number of scattering centers per cm^3, c is the light velocity, ε is the permittivity of the medium, and ω is the incident wave frequency.

The basis for heteroclusters is provided by the aggregate $(H_2O)_{10}$, because water clusters of smaller size may form unstable heteroclusters by way of addition of N_2O or CH_4 molecules [17]. Accordingly, systems II and III of $(N_2O)_i(H_2O)_{10}$ and $(CH_4)_i(H_2O)_{10}$ clusters are formed in such a manner that a cluster containing i impurity molecules would have the statistical weight

$$W_i = N_i/N_\Sigma, \quad i = 1, ..., 10,$$

where N is the number of clusters with i impurity molecules per cm^3, and $N_\Sigma = \displaystyle\sum_{i=1}^{10} N_i$. Similar weights were used for $(H_2O)_i$ clusters which make up system I. In what followed, all spectral characteristics were calculated in view of adopted statistical weights W_i. The procedure of formation of cluster systems presumes a uniform distribution of these systems and is valid for a low concentration of clusters; therefore, they do not interact with one another. The average value of concentration of clusters of each type in the investigated systems is 12 or 13 orders of magnitude lower than the value of Loschmidt number.

The static permittivity ε_0 was calculated in terms of fluctuations of total dipole moment $\mathbf{M}$ [13],

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

The total dipole moment of cluster was calculated by the formula

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

In which $\mathbf{r}_i(t)$ is the vector indicating the location of atom i at the instant of time t; Z is the electric charge located at the center of atom; the subscript "+" indicates ions which carry a positive electric charge (H, N), and the subscript "–" indicates negative ions (O, C); and N is the number of molecules in cluster. The permittivity $\varepsilon(\omega)$ was represented as complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ which was determined using the equation [13, 18]

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

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

Here, the function $F(t)$ represents the normalized autocorrelation function of the total dipole moment of cluster,

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

The frequency dispersion of permittivity defines the frequency dependence of dielectric loss $P(\omega)$ in accordance with the expression [16]

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

where $\langle E^2 \rangle$ is the average value of the square of electric field intensity, and $\tan\delta = \varepsilon'/\varepsilon''$ is the tangent of dielectric loss angle.

The IR radiation absorption cross section was preassigned by the expression [14]

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

where ε_v is the permittivity of vacuum, $\hbar = h/2\pi$, h is the Planck constant, and n is the refractive index independent of frequency ω.

CALCULATION RESULTS

During the calculation, all impurity molecules appearing in the range of action of atom-atom potentials were added to water clusters. The addition of an impurity molecule is a strong perturbation which causes structure transformation of the entire aggregate. The interaction of polar (N_2O) molecules with a water cluster differs from that of nonpolar (CH_4) molecules. Polar molecules (given their small amount) tend to penetrate into the cluster and mix with water molecules, while nonpolar molecules, on the contrary, only surround the cluster and develop a new surface layer. When the number of N_2O molecules is commensurable with the number of water molecules in the cluster, they do not fully mix with H_2O molecules: part of them go deep into the cluster, while the other molecules remain on the cluster surface. This distribution of impurity is apparently associated with the effect of interaction between N_2O molecules proper. Note that the geometric dimensions of CH_4 and N_2O molecules are approximately the same. The structure of equimolecular heteroclusters is given in Fig. 1, where the configurations of $(N_2O)_i(H_2O)_{10}$ and $(CH_4)_i(H_2O)_{10}$ clusters are shown. One can see that both clusters have a significantly irregular structure. The core of clusters consists largely of water molecules; however, N_2O molecules may also be present. Correlation is observed in the orientation of N_2O and H_2O molecules; CH_4 molecules are disoriented.
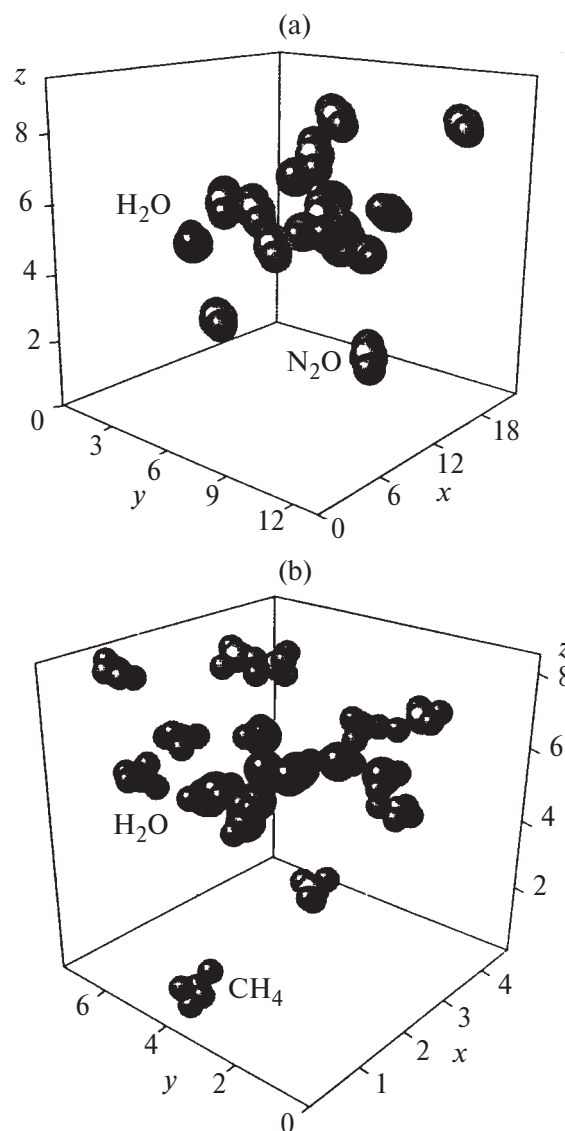
Fig. 1. Configurations of clusters: (a) $(N_2O)_{10}(H_2O)_{10}$ and (b) $(CH_4)_{10}(H_2O)_{10}$, corresponding to the instant of time of 20 ps.

The real ε' and imaginary ε'' parts of permittivity are not independent. For real positive frequency, the correlation between these parts is described by the Kramers–Kronig dispersion relations [15]. The value of ε' affects significantly the energy density of the electromagnetic field propagating in the medium, and ε'' defines the dissipation of electromagnetic energy in matter. Figure 2 gives the calculated values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for cluster systems I, II, and III along with the respective values of ε' and ε'' for liquid water obtained as a result of molecular-dynamic calculation using the TIP4P model of water [19] and experimentally [20]. The permittivity (both ε' and ε'') of an ultradisperse aqueous system containing CH_4 mole-
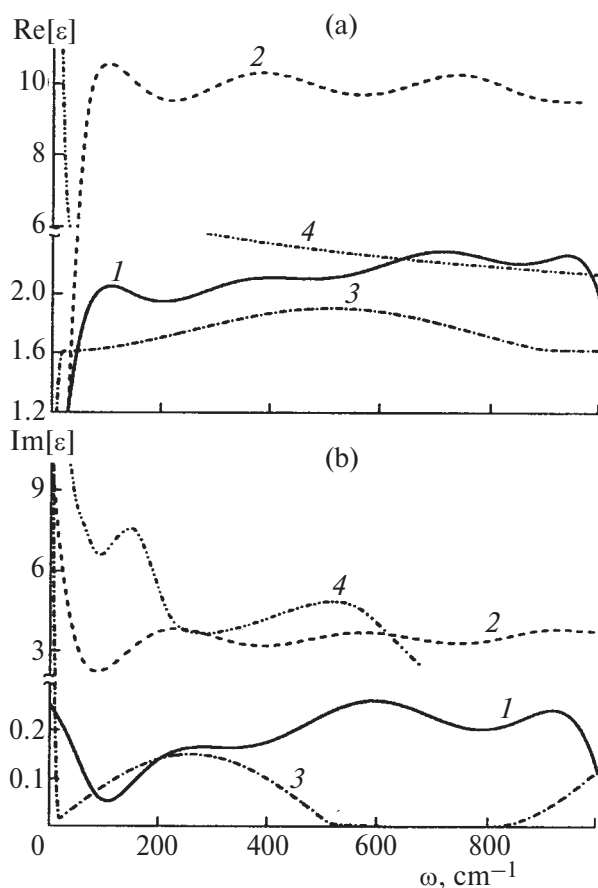
Fig. 2. The frequency dependence of (a) real and (b) imaginary parts of permittivity for systems: (*1*) $(H_2O)_n$ (I), (*2*) $(N_2O)_i(H_2O)_{10}$ (II), (*3*) $(CH_4)_i(H_2O)_{10}$ (III); (*4*) liquid water – (a) [19], (b) [20].

Fig. 3. (a) The frequency dependence of dielectric loss and (b) the tangent of dielectric loss angle for systems: (*1*) I (in the inset), (*2*) II, (*3*) III.

cules (system III) decreases for all frequencies in the range $0 \leq \omega \leq 1000$ cm^{-1} compared to the respective value in the case of ultradisperse system of "pure" water (system I). Moreover, a transparency window, where $\varepsilon''(\omega) = 0$, is observed in the frequency range $640 \leq \omega \leq 790$ cm^{-1}. For system II including N_2O molecules, on the contrary, the permittivity increases significantly, so that its real part (curve *2*, Fig. 2a) at $\omega > 40$ cm^{-1} exceeds ε' for liquid water (curve *4*, Fig. 2a). Note that, after the addition to clusters $(H_2O)_{10}$ of impurity molecules (both CH_4 and N_2O), the $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ curves become smoother (with a smaller number of extrema) than the respective characteristics of system I.

The greenhouse effect produced by atmospheric gases consists in the absorption of thermal radiation of the Earth by these gases and subsequent dissipation of
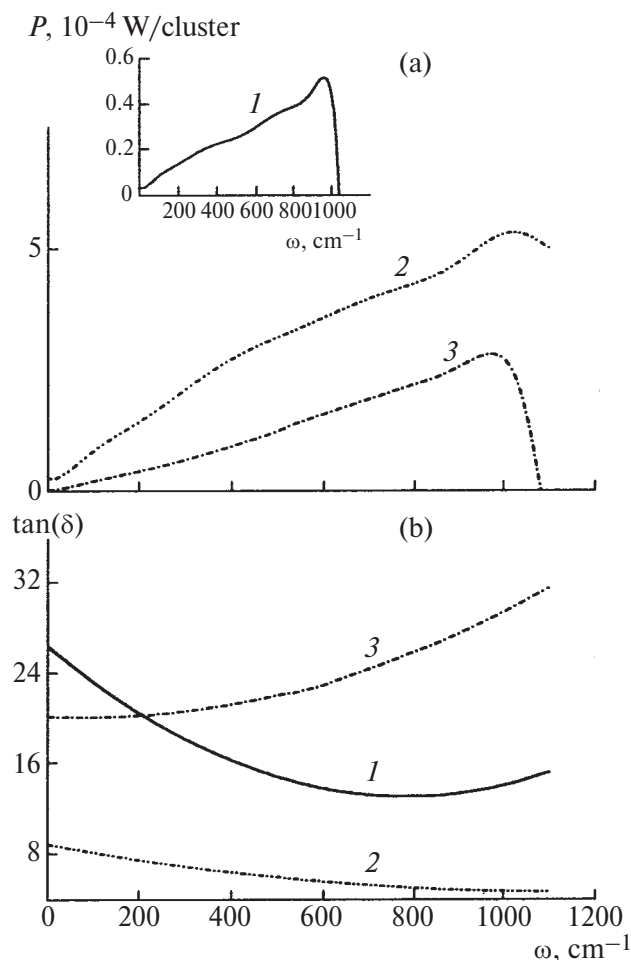
absorbed energy. The frequency distribution of power dissipated by clusters is given in Fig. 3a. One can see that the addition of both CH_4 and N_2O molecules to water clusters causes a significant increase in the rate of energy dissipation. The energy of absorbed IR radiation is dissipated most rapidly by system II with the maximum of dissipation at a frequency of 1036 cm^{-1}. Similar to the clusters which absorbed CH_4 molecules, water clusters exhibit the highest rate of dissipation of stored energy at frequency $\omega = 974$ cm^{-1}. The function $\tan\delta(\omega)$ for systems I and II decreases monotonically (Fig. 3b). The $\tan\delta(\omega)$ curve for system I exhibits a close-to-parabolic shape with a minimum at frequency $\omega = 784$ cm^{-1}. For cluster system II, the function $\tan\delta(\omega)$ decreases monotonically, and for system III increases, with increasing frequency. Therefore, the presence of CH_4 and N_2O molecules in
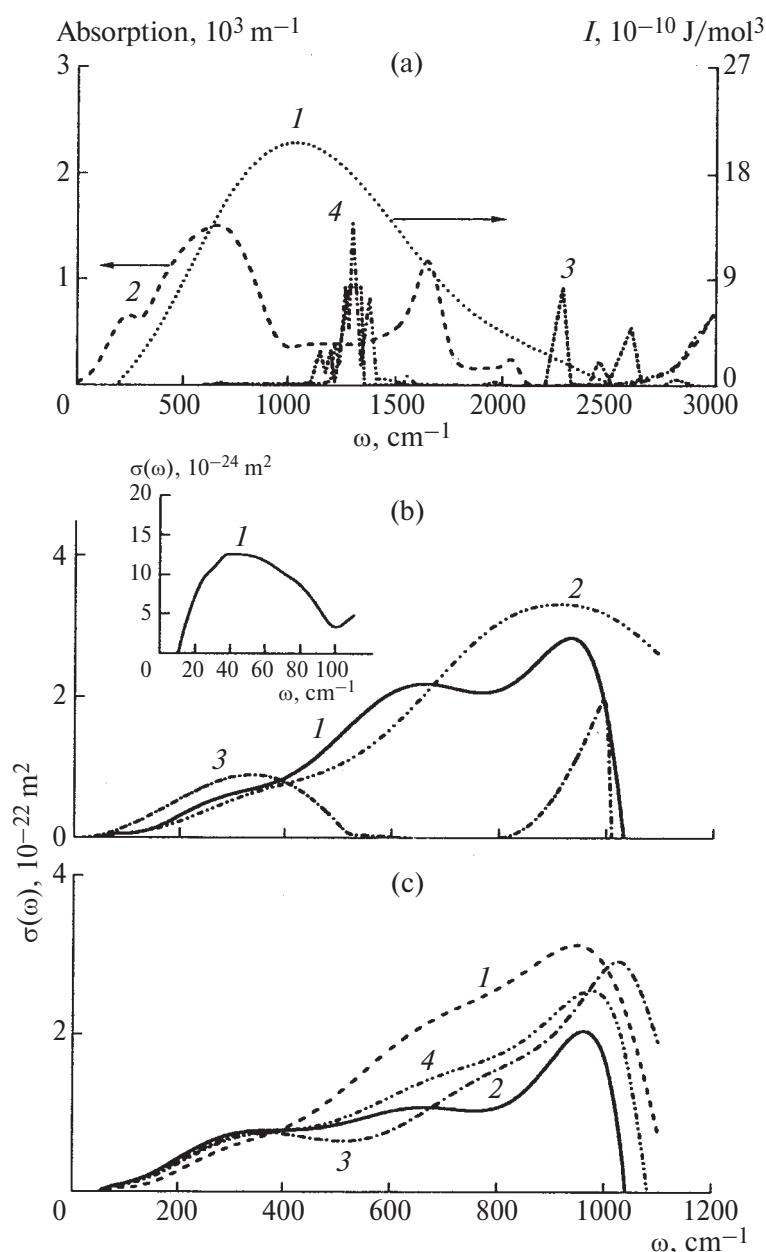
Fig. 4. IR absorption spectra. (a): (*1*) spectrum of thermal radiation of the Earth at $T = 280$ K; (*2–4*) experimental spectra for liquid water [21], gaseous N_2O and CH_4 [22], with the right-hand ordinate relating to spectrum *1*, and the left-hand ordinate – to spectra *2–4*; (b): (*1*) system I, (*2*) II, (*3*) III, the inset shows the initial region of spectrum of system I on an enlarged scale; (c) spectra for systems mixed in equal proportions: (*1*) mixture of systems I and II, (*2*) I and III, (*3*) II and III, (*4*) I, II, and III.

an ultradisperse aqueous system results in a significant variation of the pattern of dissipation of energy absorbed by clusters.

Figure 4a gives the spectrum of terrestrial thermal radiation along with the experimentally obtained spectra of absorption of IR radiation by liquid water and gaseous N_2O and CH_4. The spectrum for water covers almost the entire frequency range of terrestrial

radiation and demonstrates the maximal significance of atmospheric moisture in developing the greenhouse effect. IR spectra of systems I, II, and III are given in Fig. 4b. The spectrum for ultradisperse system of "pure" water has two pronounced peaks at $\omega = 974$ and 661 cm^{-1}, while IR spectra for aqueous systems containing N_2O and CH_4 molecules exhibit one maximum in the frequency range $0 \leq \omega \leq 1000$ cm^{-1}.

These peaks fall on the frequencies of 911 and 340 cm^{-1}, respectively. Note that the IR spectrum of system I exhibits yet another peak at $\omega_{rot} = 36$ cm^{-1}, which is caused by rotations of H_2O molecules. The initial part of spectrum of system I on a larger scale is shown in the inset in Fig. 4b. In the frequency range under consideration, the integral intensity of absorption of IR radiation by system II increases slightly; for system III, on the contrary, this intensity decreases appreciably relative to the respective characteristic of system I. In the frequency range $500 \leq \omega \leq 800$ cm^{-1}, cluster system III transmits freely the energy of thermal radiation (absorption factor $\alpha = 0$). The calculation results enable one to construct IR spectra of clusters of various ultradisperse aqueous systems. We will restrict our consideration to the absorption spectra of four more media which represent 50% of mixture of system I+II (curve *1*, Fig. 4c), I+III (curve *2*), and II+III (curve *3*), as well as equimolar (33.3%) mixture of I+II+III (curve *4*). The spectrum of the first one of these media (curve *1*) inherits the principal maximum of system I (at 974 cm^{-1}) and the weak maximum of the same system (at 36 cm^{-1}). The spectrum of the second medium (curve *2*) is characterized by three maxima, two of which (at 974 and 661 cm^{-1}) are defined by system I, and the third one (at 348 cm^{-1}) – by system III. The spectrum of the third medium (curve *3*) has two maxima; the location of the lower of these maxima (at 348 cm^{-1}) is close to the point of localization of the maximum of system III, and the principal maximum corresponds to a higher frequency (1036 cm^{-1}) than the principal maximum of system II. The IR spectrum for the fourth medium (curve *4*) has one maximum (at 974 cm^{-1}) which corresponds to the same frequency as the principal maximum of similar spectrum of system I. Therefore, the emergence of two new frequencies ($\omega = 348$ and 1036 cm^{-1}) in the IR spectra of two of four media under consideration cannot be interpreted rigorously on the basis of harmonic analysis of IR spectra. The variation of characteristic frequencies of IR spectra may be linked to the anharmonicity of vibrational processes present in the systems.

ANALYSIS OF ABSORPTION SPECTRA OF CLUSTER SYSTEMS

We will consider the energy exchange between photons which represent an incident electromagnetic wave and phonons, i.e., collective vibrations of molecules in clusters. The most probable events of this process are as follows [23]: 1) photon absorption with frequency ω (or energy $\hbar\omega$), which causes production of two phonons with the same frequency ω_1 propagating in opposite directions (according to the law of conservation of energy, $\hbar\omega = 2\hbar\omega_1$ or $\omega = 2\omega_1$); 2) photon absorption with frequency ω, which results in the emergence of two phonons with different frequencies ω_1 and ω_2 (in so doing, $\omega = \omega_1 + \omega_2$); and 3) annihilation of one phonon and production of another phonon for which $\omega = \omega_1 - \omega_2$ and $\omega_1 \neq \omega_2$. The exchange of energy of electromagnetic radiation with clusters is a substantially anharmonic process. In so doing, both mechanical anharmonicity is observed, which is associated with the emergence of terms of the third and higher orders in the expansion of potential function, and optical anharmonicity caused by the interaction between dipole moments. The anharmonicity renders the process of interaction between electromagnetic radiation and clusters more complex and less determinate. In particular, the thus produced phonon will be characterized by a set of frequencies in a certain range rather than by a single frequency.

The most probable result of interaction of IR radiation with clusters, as well as with crystals [24], is the emergence of two phonons of the same frequency (event 1). It is with this event that we identify the frequency $\omega = 974$ cm^{-1} of localization of the principal peak of the IR spectrum of system I. Then the mathematical expectation of the frequency of emerging phonons is defined by the quantity $\omega_1 = 487$ cm^{-1}. Second by the frequency of realization is event 2, when the energy of absorbed photon is distributed nonuniformly between excited phonons. To this event is ascribed the emergence of the second peak in the IR spectrum of system I at frequency $\omega = 661$ cm^{-1}. Hence the frequency $\omega_2 = \omega - \omega_1 = 174$ cm^{-1} is determined. The third event, when the localization of the peak in IR spectrum falls on the frequency $\omega_1 - \omega_2$, is the least probable one. In this case, the location of expected peak falls on $\omega = 313$ cm^{-1}. In the IR spectrum of system I, only the inflection point of the $\sigma(\omega)$ curve is

located in the neighborhood of this frequency (at 348 cm^{-1}). The spectrum of individual vibrations of centers of molecular mass in clusters for system I has a maximum at $\omega = 0$ and an inflection point at $\omega =$ = 364 cm^{-1}. At the found frequency ω_{rot} (= 36 cm^{-1}), the molecular rotational spectrum in clusters exhibits an intensity that is almost four times that of translational spectrum [25]; therefore, the motion of rotational type at a frequency of 36 cm^{-1} may be taken to be the main anharmonic contribution. Then the minimal values of frequency of expected phonons ($\omega_i' = \omega_i - \omega_{rot}$) will be $\omega_1' = 451$ cm^{-1} and $\omega_2' =$ = 138 cm^{-1}, and the maximal values – $\omega_1'' =$ = 523 cm^{-1} and $\omega_2'' = 210$ cm^{-1}.

The molecules of N_2O and CH_4 added to $(H_2O)_{10}$ cluster assume the vibration frequency of a core of H_2O molecules. However, the values of this frequency are not strictly defined by those of frequencies of basic phonons of aqueous system I and may vary because of anharmonicity. In so doing, ω_1 may increase to a value of 523 cm^{-1}. In this case, the most typical photon frequencies (locations of maxima in IR spectra) will correspond to the values of $\omega = 2\omega_1'' =$ = 1046 cm^{-1} and $\omega = \omega_1'' - \omega_2 = 349$ cm^{-1}. These values agree adequately with the values (1036 and 348 cm^{-1}) of characteristic frequencies of IR spectra of media formed of systems I+II and II+III.

CONCLUSIONS

This study resulted in determining the dielectric properties of finely divided mixtures of clusters of greenhouse gases, which make up different systems, depending on the composition. We considered the interaction of these systems with the electric field of IR radiation averaged over volumes which significantly exceed scale nonuniformities. An ultradisperse mixture manifests itself relative to such field as a homogeneous and isotropic medium with the effective value of permittivity corresponding to its average value over the volume of the system. Both the real and imaginary parts of permittivity vary significantly depending on the composition of clusters which make up the system. In so doing, the absorption of polar molecules (N_2O) by clusters causes an increase in permittivity, and the absorption of nonpolar molecules

(CH_4) causes a decrease in permittivity at frequencies $\omega > 200$ cm^{-1}. Ultradisperse aqueous systems effectively scatter and absorb IR radiation. The rate of dispersion of radiant energy increases with frequency both for clusters of "pure" water and for clusters which absorb impurity molecules. Of the clusters considered by us, the aggregates which absorbed N_2O molecules exhibit the highest rate of energy dissipation. After the absorption of molecules of greenhouse gases by clusters, the shape of IR spectra for mixtures formed of them varies such that the anharmonicity of phonons must be taken into account for interpreting the observed peaks. The absorption of nonpolar molecules by clusters causes a decrease in integral absorption of IR radiation I_{tot}, and the addition of polar molecules may somewhat increase this absorption. However, this increase cannot compensate for the contributions to I_{tot} by the same free (prior to their capture by clusters) molecules. Therefore, the capture of molecules of greenhouse gases by water clusters causes a decrease in the overall value of I_{tot} and, consequently, a reduction of greenhouse effect.

ACKNOWLEDGMENTS

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