

Molecular dynamics study of the greenhouse gases clusterization

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(Received 24 February 2006; in final form 29 July 2006)

Absorption of CO₂, CH₄ and N₂O molecules by water clusters has been investigated by the molecular dynamics method. The frequency spectra of dielectric permittivity for systems consisting of (H₂O)_n, (CO₂)_i(H₂O)₁₀, (CH₄)_i(H₂O)₁₀ and the (N₂O)_i(H₂O)₁₀ clusters have been defined. The calculation and analysis of IR radiation absorption spectra for these systems have been carried out. The analysis of inharmoniousness of phonon oscillations allows an explanation of the origin of characteristic frequencies appearing in the IR spectra. The influence of cluster compositions on the reflection coefficient of transverse electromagnetic wave from the cluster surface was considered. The capture of greenhouse gas molecules by an ultra disperse aqueous medium reduces the ability of the medium to absorb the Earth's radiation and thus reduces the greenhouse effect.

Keywords: Atmosphere; Water; Cluster; Absorption and reflection spectra

1. Introduction

Earth's atmosphere is a complicated dynamic system protecting the biosphere. One of the essential factors influencing the Earth's radiation balance is the greenhouse effect, whose amplification is bound not only with rising solar activity but also with the magnification of the gases possessing radioactive properties in the atmosphere. A significant influence on formation of thermal radiation fields is rendered by H₂O vapors and also by atmospheric gases such as CO₂, CH₄, N₂O and others. A change of the greenhouse gases concentration can cause unfavorable climatic changes. However, in the atmosphere there are phenomena which slow down rapid development of climatic processes. One may link the clusterization of greenhouse gases to a number of such phenomena. The present article focuses on the molecular dynamic study of the influence of the H₂O vapor and CO₂, N₂O, CH₄ atmospheric gases clusterization on the greenhouse effect.

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2. Computer model

The molecular dynamic (MD) calculations are carried out with the help of modified potential TIP4P [1] and the rigid four-centered model of water molecule [2–4]. The model supposes calculation of induced dipole moments of molecules which allows inclusion for viewing their polarization effect. The description of greenhouse gases molecules interaction with water and also between them is based on an atom–atom potential calculated in the Gordon–Kim approximation with the application of spherical average of electronic densities [5, 6].

First, the molecular dynamic calculations for water clusters were carried out. The final $(\text{H}_2\text{O})_{10}$ cluster configuration was then used as the initial configuration for heteroclusters modeling. In the initial state the joined molecules were placed so that the minimum distance between the atoms of admixture molecule and the atoms of water molecules forming a cluster were not less than 0.6 nm. All considered interactions were cut off at a distance of the 0.9 nm. In the case of $(\text{CO}_2)_i(\text{H}_2\text{O})_{10}$ and $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$ systems the added linear CO_2 and N_2O molecules were placed along the beams, connecting $(\text{H}_2\text{O})_{10}$ cluster's center of mass with those molecules centers of mass. For $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ systems the CH_4 molecules were placed in the knots of imaginary BCC lattice piercing the cluster. In all cases the admixture molecules were situated outside the cluster.

The Geer method of fourth order was used for the integration of the motion equations of the molecules' centers of the mass [7]. The analytical solution of motion equations for molecules' rotation was carried out with a help of the Rodrigues–Hamilton parameters [8]. Scheme of equations of motion integration at presence of rotation corresponded with the approach offered by Sonnenschein [9]. The temperature of clusters was the same during all of the calculations (233 K) and the duration of calculation for each cluster was not less than $3 \cdot 10^6 \Delta t$, where time step was $\Delta t = 10^{-17}$ s. The calculations were completed on PENTIUM-IV computer with 3.2 GHz processor clock frequency. Approximately 7 h of computer time were required to complete a calculation of $10^6 \Delta t$ duration of cluster with 20 molecules.

In order to determine the influence of absorbed carbon dioxide, nitrous oxide and methane molecules on the greenhouse effect, four types of ultra disperse systems were considered:

- (1) an area filled with water clusters of the size from 2 up to 20 molecules,
- (2) a medium consisting of $(\text{H}_2\text{O})_{10}$ clusters, which absorbed from 1 up to 10 CO_2 molecule,
- (3) a set of $(\text{H}_2\text{O})_{10}$ clusters that absorbed similar quantity of CH_4 molecules,
- (4) a system of $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$, $i = 1, \dots, 10$ clusters.

We will number those systems as I, II, III and IV.

The static dielectric constant ε_0 was calculated through the fluctuations of total dipole moment \mathbf{M} [10] as

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

where V is cluster's volume.

The dielectric permittivity $\varepsilon(\omega)$ is represented by a complex variable $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, to define which the following equation was used [11, 12]:

$$\frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} = - \int_0^\infty \exp(-i\omega t) \frac{d\Omega}{dt} dt = 1 - i\omega \int_0^\infty \exp(-i\omega t) \Omega(t) dt, \quad (2)$$

where $\Omega(t) = \langle \mathbf{M}(0)\mathbf{M}(t) \rangle / \langle \mathbf{M}(0)^2 \rangle$ is a normalized autocorrelation function of cluster's total dipole moment.

The IR absorption signal was given in the form [12]

$$\sigma(\omega) = \left(\frac{2}{\varepsilon_v c \hbar n} \right) \omega \tanh\left(\frac{\hbar\omega}{2kT} \right) \text{Re} \int_0^\infty dt e^{i\omega t} \langle \mathbf{M}(t)\mathbf{M}(0) \rangle, \quad (3)$$

where ε_v is the vacuum permittivity, c is the velocity of light, $\hbar = h/2\pi$, h = Planck's constant, n is a non dependant on frequency ω refractive index.

The reflection coefficient R is defined as a ratio of an average flow of energy, reflected from a surface, to a falling flow. At the normal falling of a monochromatic wave the reflection coefficient is given by the formula [13]

$$R = \frac{|\sqrt{\varepsilon_I} - \sqrt{\varepsilon_{II}}|^2}{|\sqrt{\varepsilon_I} + \sqrt{\varepsilon_{II}}|^2}. \quad (4)$$

We assume that a wave is transmitted from a transparent medium (medium I) to medium, which can be either transparent or non-transparent i.e. absorbing and scattering (medium II). In expression (4) indices of dielectric permittivity denote a medium.

Let us consider the case of unpolarized light dispersion where the length of the molecules l is much less than the length λ of the light wave. The coefficient ξ of the extinction (weakening) of a falling beam on the one hand is defined by the Rayleigh [13] formula and on the hand is defined through a scattering coefficient ρ ($\xi = 16\pi\rho/3$) [14] in the approximation of scattering at 90° angle. Considering that $\xi = \alpha + \rho$, where α is an absorption coefficient, we have

$$N = \frac{2\omega^4}{3\pi c^4} \frac{(\sqrt{\varepsilon} - 1)^2}{\alpha} \left(1 - \frac{3}{16\pi} \right), \quad (5)$$

where N is the number of the scattering centers in 1 cm^3 . Here c is a velocity of light, ε is a dielectric permittivity of the medium and ω is a frequency of a falling wave.

The basis of heteroclusters consists of a $(\text{H}_2\text{O})_{10}$ cluster, as water clusters of a smaller size can form unstable heteroclusters by joining CO_2 , N_2O or CH_4 molecules [15]. The systems II, III and IV, consisting of $(\text{CO}_2)_i(\text{H}_2\text{O})_{10}$, $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ and $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$ clusters, are formed in such a way that a cluster containing i molecules of admixture had a statistical weight

$$W_i = \frac{N_i}{N_\Sigma}, \quad i = 1, \dots, 10, \quad (6)$$

where N_i is the number of clusters with i admixture molecules in 1 cm^3 , $N_\Sigma = \sum_{i=1}^{10} N_i$. Similar weights are used for $(\text{H}_2\text{O})_i$ clusters forming the system I. Further, the calculation of all spectral characteristics was carried out considering the accepted statistical weights W_i . The procedure of cluster system formation supposes

even the distribution of these formations and is justified at low clusters concentration. Due to this they do not interact among themselves. The average value of each type of clusters concentration in the investigated systems is less than a Loschmidt number by 12–13 orders.

3. Results

The structure of equimolecular heteroclusters is shown in figure 1 with configurations of $(\text{CO}_2)_{10}(\text{H}_2\text{O})_{10}$ and $(\text{CH}_4)_{10}(\text{H}_2\text{O})_{10}$ clusters. One can observe that both clusters have significantly irregular structure. Moreover, CO_2 molecules intermix with H_2O molecules and CH_4 molecules gather in one group forming heterocluster surface. The correlation in orientation of the CO_2 and H_2O molecules can be observed while

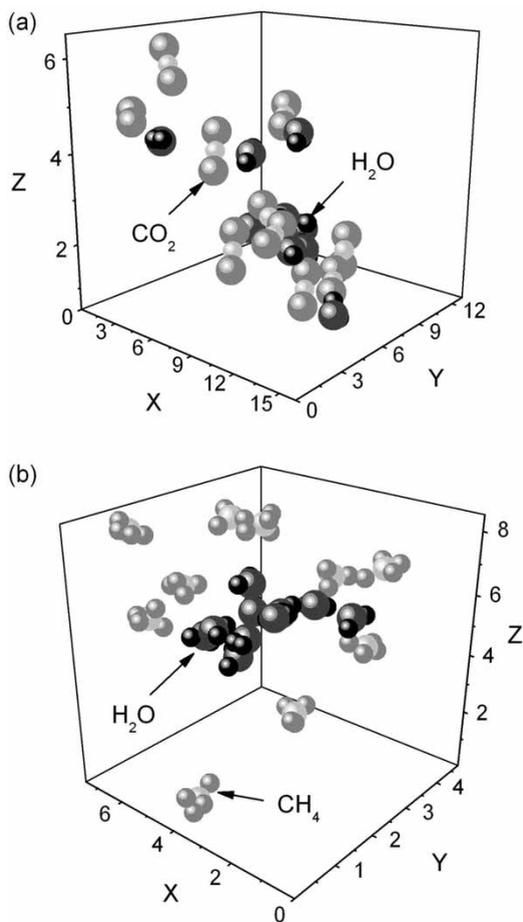


Figure 1. Configurations of clusters: (a) $(\text{CO}_2)_{10}(\text{H}_2\text{O})_{10} > (\text{N}_2\text{O})_{10}(\text{H}_2\text{O})_{10}$, (b) $(\text{CH}_4)_{10}(\text{H}_2\text{O})_{10}$, corresponding to the moment of time 30 ps coordinates of molecules are presented in angstroms.

CH_4 molecules are disoriented. The rigid molecule model used in this work does not allow considering intramolecular oscillations taking place, as a rule, at frequencies $\omega > 1000 \text{ cm}^{-1}$. In this article the frequency range of $0 \leq \omega \leq 1000 \text{ cm}^{-1}$ was investigated, describing the oscillatory and rotary movements of molecules.

The real ϵ' and imaginary ϵ'' parts of dielectric permittivity are not independent. For real positive frequency the connection between them can be described with the help of Cramer–Cronig dispersion relations [13]. The value ϵ' significantly influences the energy's density of spreading in medium electromagnetic field and ϵ'' defines the electromagnetic energy's dissipation in a substance. The calculated values of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ for I, II, III and IV cluster systems together with corresponding ϵ' and ϵ'' liquid water values obtained by molecular dynamic calculations with TIP4P water model application [16], as well as obtained in experiment [17], are shown in figure 2. The dielectric permittivity (both ϵ' and ϵ'') of ultra disperse aqueous system containing CH_4 molecules (the system III) is reduced at all frequencies within the range $0 \leq \omega \leq 1000 \text{ cm}^{-1}$ in correlation with corresponding values of “pure” water ultra disperse system (the system I). Moreover, the transparency window can be observed in the frequency range of $640 \leq \omega \leq 790 \text{ cm}^{-1}$ where $\epsilon''(\omega) = 0$. On the contrary, for the systems II and IV, including CO_2 and N_2O molecules, the dielectric permittivity significantly increases, so that its real part (curves 2 and 4, figure 2a) at $\omega > 50 \text{ cm}^{-1}$ exceeds the ϵ' value for liquid water (curve 5, figure 2a). One may

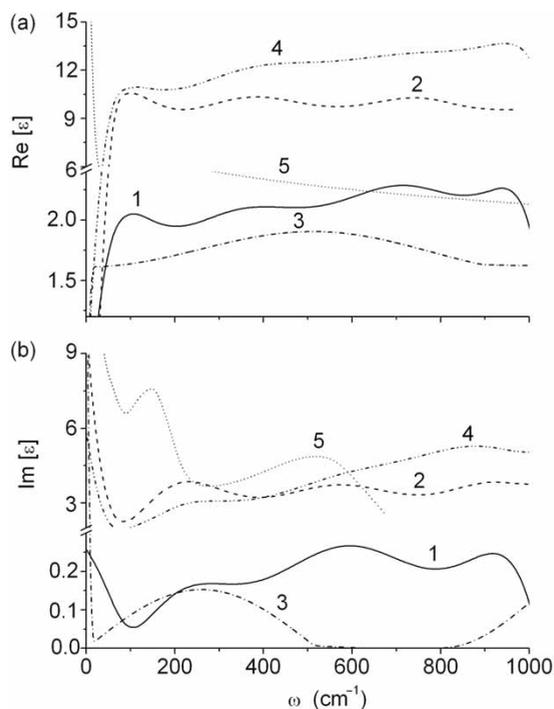


Figure 2. Frequency dependences of (a) real and (b) imaginary parts of the dielectric permittivity for systems: 1 – $(\text{H}_2\text{O})_n$ (I), 2 – $(\text{CO}_2)_i(\text{H}_2\text{O})_{10}$ (II), 3 – $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ (III), 4 – $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$ (IV), 5 – liquid water: (a) MD with using TIP4P water model [16], (b) experiment [17].

observe that after the addition of the admixture molecules to $(\text{H}_2\text{O})_{10}$ clusters, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ the dependences become smoother (with a smaller number of extremes), than corresponding characteristics of system I.

The greenhouse effect caused by atmospheric gases is in fact the absorption of the Earth's thermal radiation by them and a subsequent dissipation of the absorbed energy. The $\sigma(\omega)$ spectrum of Earth's thermal radiation, together with experimental IR radiation absorption spectrum of liquid water, is shown in figure 3(a). The spectrum for water overlaps practically all of the Earth's radiation frequency range and indicates the greatest significance of atmospheric moisture in greenhouse effect creation. The experimental IR spectra of gaseous CO_2 , N_2O and CH_4 absorption are represented in figure 3(b). In the investigated frequency range the locations of the main spectrum peaks for gaseous N_2O and CH_4 coincide. These spectra represent a landmark for the location of changes of relevant IR-spectra peaks during the transition from clusters of pure water to heteroclusters. IR spectra of systems I, II, III and IV presented in figure 3(c) are calculated by method described in [15]. The spectra for ultra-disperse systems of "pure" water and the $(\text{CO}_2)_i(\text{H}_2\text{O})_{10}$ clusters

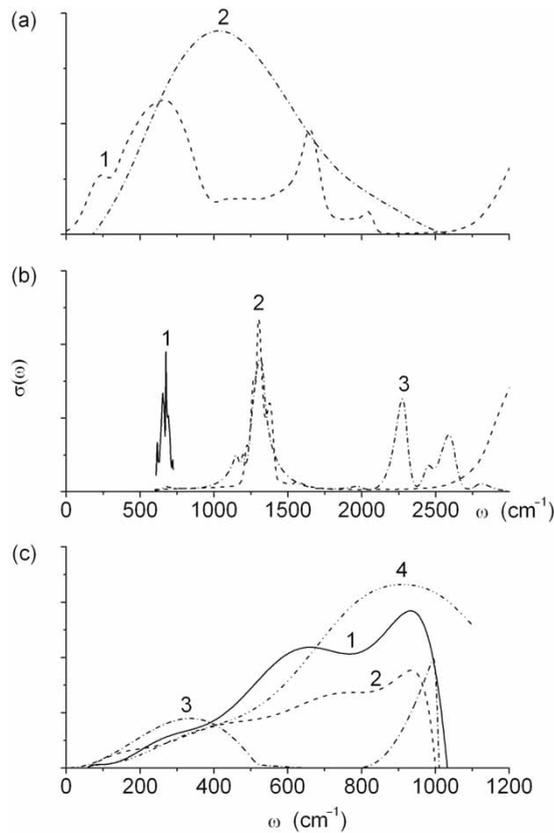


Figure 3. IR absorption spectra, (a) 1 – experimental spectrum for liquid water [18], 2 – spectrum of thermal radiation of the Earth at $T=280\text{ K}$; (b) 1, 2, 3 – experimental spectra for gaseous CO_2 [19], CH_4 and N_2O [20] correspondingly; (c) 1 – system I, 2 – II, 3 – III, 4 – IV.

system have two peaks, the main of which situates at $\omega = 974$ (I) and 960 cm^{-1} (II), and the second peak at 661 cm^{-1} (I) and 724 cm^{-1} (II) is less expressed. The IR spectra in the frequency range of $0 \leq \omega \leq 1000 \text{ cm}^{-1}$ related with aqueous systems containing N_2O and CH_4 molecules are characterized by one peak. These peaks are situated respectively at the 911 and 340 cm^{-1} frequency. In the observed frequency range the integral intensity of IR radiation absorption by systems II and III significantly decreases. On the contrary, for the system IV this value slightly increases in comparison with the corresponding characteristic of system I.

Let us consider energy exchange between photons representing falling electromagnetic wave and phonons — collective oscillations of molecules in clusters. The most probable events of this process are [21]:

- (1) the absorption of photon with frequency ω (or $\hbar\omega$ energy) with a birth of two phonons with the same ω_1 frequency extending in opposite directions under the law of energy conservation $\hbar\omega = 2\hbar\omega_1$ or $\omega = 2\omega_1$,
- (2) the absorption of photon with frequency ω causes appearance of two phonons with different frequencies ω_1 and ω_2 , where $\omega = \omega_1 + \omega_2$,
- (3) the absorption of photon, the collapse of one phonon and the emergence of another with $\omega = \omega_1 - \omega_2$, $\omega_1 \neq \omega_2$.

The exchange of electromagnetic radiation energy with clusters is an essentially unharmonious process. Due to this the emerged phonon can be characterized not only by one frequency but by a number of frequencies from the appointed interval.

The most probable result of IR radiation interaction with clusters, as well as with crystals [21], is the appearance of two phonons of the same frequency (event 1). We especially refer to this event at $\omega = 974 \text{ cm}^{-1}$ frequency of the main IR spectrum peak of the system I. Then the frequency expected for appearing phonons is defined by $\omega_1 = 487 \text{ cm}^{-1}$ value. The event 2 should be the second one according to the frequency occurrence where absorbed photon energy distributes among excited phonons in uneven portions. To this event we can attribute the emergence of the second IR spectrum peak in the system I at $\omega = 661 \text{ cm}^{-1}$ frequency. The frequency $\omega_2 = \omega - \omega_1 = 174 \text{ cm}^{-1}$ can be thus derived. The third event of the system I, where the frequency of IR-spectrum peak localization is defined by $\omega_1 - \omega_2$, is the least probable. In this case the location of expected peak is given by $\omega = 313 \text{ cm}^{-1}$. In the IR spectrum of the system I in the vicinity of this frequency (at 348 cm^{-1}) there is only one inflection point of dependence $\sigma(\omega)$. It is possible to estimate the influence of admixture molecules on clusters' phonons, and consequently, on corresponding IR spectra by inharmonic contributed by them. In the case of CO_2 molecules the interaction of clusters with IR radiation gives events 1 and 2, and the inharmoniousness is characterized by the quantities $\Delta\omega_1 = \omega_1(\text{II}) - \omega_1(\text{I}) = -7 \text{ cm}^{-1}$, $\omega_2(\text{II}) - \omega_2(\text{I}) = 70 \text{ cm}^{-1}$ (II: $\omega_1 = 480 \text{ cm}^{-1}$ and $\omega_2 = 280 \text{ cm}^{-1}$). The event 1 with phonon frequency $\omega_1 = 455.5 \text{ cm}^{-1}$ takes place at interaction of IR radiation with $(\text{N}_2\text{O})_f(\text{H}_2\text{O})_{10}$ clusters, and the inharmoniousness is defined by the value $\Delta\omega_1(\text{IV}) = 31.5 \text{ cm}^{-1}$. From the minimum unharmonious effect estimation it follows that for $(\text{CH}_4)_f(\text{H}_2\text{O})_{10}$ clusters the realization of event 3 with phonon frequencies $\omega_1 = 650 \text{ cm}^{-1}$ and $\omega_2 = 310 \text{ cm}^{-1}$ leading to a quantity of inharmoniousness $\Delta\omega_2(\text{III}) = 136 \text{ cm}^{-1}$, is more probable. Thus, according to the quantity of contributed inharmoniousness (from greater to smaller) the admixture molecules locate as CH_4 , CO_2 , N_2O .

Under the influence of external IR radiation a rapid change of refraction index dispersion takes place in clusters. It causes sharp oscillations in the reflection spectrum. The values of clusters' reflection coefficient R strongly depend on aggregates' composition. Clusters of pure water in the range of $2 \leq i \leq 10$ sizes have the lowest reflection coefficient of a value not exceeding 0.1. The transition from one cluster size to another is connected with considerable change in $R(\omega)$ spectrum shape. The addition of CO_2 molecules to $(\text{H}_2\text{O})_{10}$ cluster causes significant increase in R coefficient; in most cases this value is greater than 0.3. The addition or exception to $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$ an admixture molecule can change R -value many times (figure 4a). Hence, at $\omega = 1000 \text{ cm}^{-1}$, R value for water cluster with 5 N_2O molecules is 12.6 times higher than that for a cluster with 6 molecules of this admixture. The dependence of R coefficient on frequency for $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$ clusters is insignificant

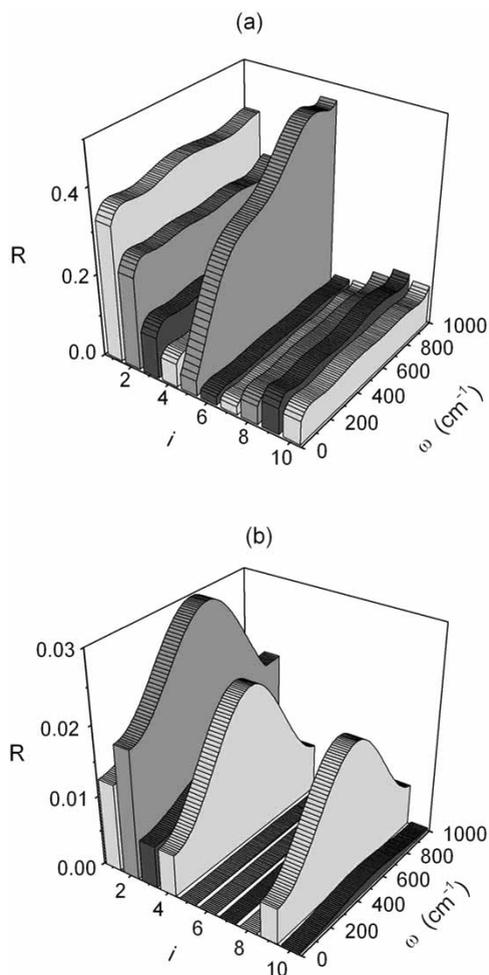


Figure 4. Reflection coefficient of transverse electromagnetic wave falling normally to a surface of cluster: (a) $(\text{N}_2\text{O})_i(\text{H}_2\text{O})_{10}$, (b) $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ depending on a composition i and frequency ω of wave oscillations.

except for a cluster with $i = 5$, where R vary from 0.036 at $\omega = 10 \text{ cm}^{-1}$ up to 0.465 at $\omega = 1000 \text{ cm}^{-1}$ value. $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ clusters exhibit the same instability of R coefficient with the change of composition (figure 4b). In this case the distinction between R -values for clusters of a various composition is even more significant. Clusters with number i of CH_4 molecules equal to 4–8 and 10 have especially low R -values. Cluster with two CH_4 molecules has the highest values of reflection coefficient. The quantity R for $(\text{CH}_4)_i(\text{H}_2\text{O})_{10}$ clusters strongly depends on frequency. The function $R(\omega)$ is characterized by one maximum which location varies within $500 \leq \omega \leq 540 \text{ cm}^{-1}$ range depending on number of molecules. Let us note, that in the case of CH_4 admixture the average value R is almost by an order of magnitude smaller than that for the CO_2 and N_2O admixtures. It is caused by the fact that linear molecules, by penetrating into water clusters, create rather dense formations. The adsorption of CH_4 hydrophobic molecules leads to loosening of heteroclusters structure and to formation of strong scattering surface.

4. Conclusion

Investigations of the dielectric properties of finely dispersed mixtures of greenhouse gas clusters specified depending on composition in various systems have been described. The interaction of these systems with IR radiation electric field, averaged to a degree that significantly exceeds the discontinuity scale, has been investigated. In relation to such fields the ultra disperse mixture presents itself as a homogeneous and isotropic medium with an effective value of dielectric permittivity. Both the real and imaginary parts of the dielectric permittivity vary significantly depending on the clusters included into the system. Also, absorption of the CO_2 and N_2O molecules by clusters increases and absorption of CH_4 molecules decreases the value of the dielectric permittivity at frequencies $\omega > 200 \text{ cm}^{-1}$. It seems reasonable to say that CO_2 , N_2O and CH_4 molecules added to $(\text{H}_2\text{O})_{10}$ cluster accept the frequency oscillation of the H_2O molecule skeleton. However, the values of this frequency are not strictly defined by frequencies of basic phonons of aqueous system I and can vary due to inharmoniousness. The composition of cluster causes significant influence on the reflection coefficient. The linear (CO_2 , N_2O) admixture molecules increase and spherical symmetric hydrophobic CH_4 molecules, surrounding cluster, reduce the R -value. Ultra disperse aqueous systems effectively scatter and absorb IR radiation. The addition of non-polar molecules (CO_2 , CH_4) to clusters leads to a decrease in the integral absorption of IR radiation I_{tot} and the addition of polar molecules (N_2O) can slightly strengthen this absorption. However, this strengthening cannot compensate the contributions in I_{tot} of the same free (before they were captured by clusters) molecules. Thus, the capture of greenhouse gases molecules by water clusters leads to a decrease of the average I_{tot} value and therefore, a reduction of the greenhouse effect.

Acknowledgment

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

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