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Greenhouse effect of clusterization of CO_2 and CH_4 with atmospheric moisture

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Abstract Carbon dioxide and methane are major compounds involved in global warming. The process of CO_2 and CH_4 molecules absorption by water clusters was investigated by the molecular dynamics method. The frequency spectra of dielectric permittivity for systems consisting of $(H_2O)_n$, $(CO_2)_i(H_2O)_{10}$ and $(CH_4)_i(H_2O)_{10}$ clusters mixed in various proportions were determined. The IR radiation absorption spectra of these systems were calculated and compared. Also, the radiating power of these systems was established. The capture of greenhouse gases' molecules by ultra disperse water media reduces the ability of the media to absorb the Earth's radiation, i.e., it reduces the greenhouse effect.

Keywords Absorption · Carbon dioxide · Dielectric permittivity · Greenhouse effect · IR spectra · Methane · Molecular dynamics · Water clusters

Introduction

The Earth is naturally warmed to some extent by atmospheric gases, principally water vapor, in what is often called a greenhouse effect. The Earth maintains its energy balance in part by absorption of the outgoing longwave radiation in the atmosphere, which causes warming. The current level of warming is on the order of 33°K (Peixoto and Oort 1992). Of course, this increase in temperature is not caused simply by absorption of radiation by the gases themselves. Much of the 33°K effect is caused by the Earth's adaptation to higher temperatures, which includes secondary effects such as increased water vapor, cloud formation, and changes in albedo or surface reflectivity caused by melting and aging of snow and ice. Accurately calculating the relative contribution of each of these components presents major difficulties. The global increase in the concentration of carbon dioxide (CO_2), methane (CH_4) and nitrogen oxides (NO_x) becomes a more important factor in the Earth's thermal balance. The gaseous components of atmosphere are effectively detected by the spectral method of analysis that has a high sensitivity and selectivity. The control over gaseous components' content in the atmospheric air can be carried out by laser methods both directly in the pollution zone, and at a significant distance. However, on the basis of spectroscopic data it is impossible to establish the influence of atmospheric gases' clusterization on the greenhouse effect. The content of water clusters in the atmosphere is experimentally proved and can be considered theoretically. The known physical monitoring methods do not allow determining the absorption ability of such clusters. If water clusters absorb greenhouse gases molecules (such as CO_2, CH_4, NO_x) and bond them then the ability of absorbed molecules to rotate and interact with the Earth's thermal radiation changes. In other words, the clusterization of greenhouse gases should influence the thermal balance of the planet. It is possible to investigate the probability of greenhouse gases' heteroclusters formation and their interaction with infra-red (IR) radiation by computer modeling method.

The aim of the present work is to investigate the process of CO_2 and CH_4 molecules' absorption by water clusters, to calculate and compare IR radiation absorption spectra of various ultra disperse water systems, and to determine the dissipated radiation power of these systems within the framework of the molecular dynamic model.

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Experimental

The modified potential TIP4P (Dang and Chang 1997) and rigid four-centered water molecule model are used in the present work. The model is designed to calculate the induced dipole moments of molecules, including the consideration for their polarization effect. The description of greenhouse gases molecules' interaction with water and also between themselves is based on atom-to-atom potentials calculated in the Gordon–Kim approximation with the usage of spherical average of electronic densities (Spackman 1986).

First, the molecular dynamic calculation for water clusters was undertaken. The final $(H_2O)_{10}$ cluster configuration was used further as the initial configuration for heteroclusters' modeling. In the case of $(CO_2)_i(H_2O)_{10}$ systems the added linear CO_2 molecules were placed along the beams, connecting the cluster $(H_2O)_{10}$ center of the mass to these molecules' centers of the mass. And for $(CH_4)_i(H_2O)_{10}$ systems the CH_4 molecules were placed in the knots of imaginary BCC lattice piercing the cluster. In both cases, the admixture molecules were situated outside the cluster at a distance of 0.6–0.7 nm from the nearest water molecules' atoms. The temperature of clusters was the same during all calculations (233°K), and the duration of calculation for each cluster lasted for not less than $2 \times 10^6 \Delta t$, where time step was $\Delta t = 10^{-17} c$.

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

1. an area filled with water clusters of the size from 2 up to 20 molecules;
2. a medium consisting of $(H_2O)_{10}$ clusters, which absorbed from 1 up to 10 CO_2 molecules;
3. a set of $(H_2O)_{10}$ clusters that absorbed a similar quantity of CH_4 molecules;

We will designate these systems by numbers I, II and III, respectively.

The basis of heteroclusters consists of the cluster $(H_2O)_{10}$ because the water clusters of smaller sizes can form unstable heteroclusters by joining CO_2 or CH_4 molecules (Galashev and Chukanov 2004). The systems II and III consisting of $(CO_2)_i(H_2O)_{10}$ and $(CH_4)_i(H_2O)_{10}$ clusters are formed in such a way that a cluster containing i admixture molecules has a statistical weight

$$W_i = \frac{N_i}{N_\Sigma},\ i = 1\ldots10, \qquad (1)$$

where N_i is the number of clusters with i admixture molecules in 1 cm^3, determined with a help of Rayleigh's formula (Landau et al. 1984) $N_\Sigma = \sum_{i=1}^{10} N_i$. Similar weights were used for $(H_2O)_i$ clusters forming the system I. Further, the calculation of all the spectral characteristics was carried out with consideration of the accepted statistical weights W_i.

The static dielectric constant ε was calculated through fluctuations of full dipole moment $\mathbf{M}$ (Bresme 2001)

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

The dielectric permittivity $\varepsilon(\omega)$ was represented by complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ for definition of which the equation (Bresme 2001, Neumann 1985) was used

$$\frac{\varepsilon(\omega) - 1}{\varepsilon - 1} = -\int_0^\infty \exp(-i\omega t)\frac{dF}{dt}dt$$
$$= 1 - i\omega \int_0^\infty \exp(-i\omega t) F(t) dt, \qquad (3)$$

where $F(t)$ is the normalized autocorrelation function of cluster's full dipole moment

$$F(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\left\langle \mathbf{M}^2 \right\rangle}. \qquad (4)$$

The frequency dispersion of dielectric permittivity determines the frequency dependence of dielectric losses $W(\omega)$ according to the expression (Prokhorov 1988)

$$W = \frac{\varepsilon' < E^2 > \omega}{4\pi} \mathrm{tg}\ \delta, \qquad (5)$$

where $<E^2>$ is an average value of square of electric field strength, $tg\ \delta = \varepsilon'/\varepsilon''$ is the tangent of the dielectric loss angle.

The cross section of IR radiation absorption was set in the form (Bosma et al. 1993)

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

where ε_v is a dielectric permittivity of vacuum, c is the velocity of light, $\hbar = h/2\pi$, h is Plank constant, n is refraction coefficient and it does not depend on the frequency.

Results and discussion

The configurations of $(CO_2)_i(H_2O)_{10}$ and $(CH_4)_i(H_2O)_{10}$ clusters, (relating to the time moment 30 ps) are represented in Fig. 1. It is apparent that water cluster absorbs CO_2 molecules as well as CH_4 molecules. A complete mix of water molecules with carbon dioxide (Fig. 1a) takes place, while methane molecules practically do not penetrate inside the cluster (Fig. 1b) instead remaining on the surface.

In the case of bulk water it is supposed that movements with frequency less than 1,200 cm^{-1} correspond to the librations of molecules, and frequencies higher than 1,200 cm^{-1} generally describe intramolecular vibrations (Stern and Berne 2001). The frequency dependence of real and imaginary parts of dielectric permittivity of systems I, II and III in the frequency range of $0 \leq \omega \leq 1{,}000$ cm^{-1} is shown in Fig. 2. One may observe, that with the addition of CO_2 molecules to the water system a substantial increase of $\varepsilon'(\omega)$ spectrum intensity (Fig. 2a) takes place, thus the situation of maximal intensity peak ($\omega_1 = 973$ cm^{-1}, system I) shifts to the region of lower frequencies ($\omega_1 = 90$ cm^{-1}, system II). In the case of system III, when CH_4 molecules are being added to the water cluster, the character of $\varepsilon(\omega)$, the real part dependency significantly changes: the curve has only one maximum at $\omega_1 = 510$ cm^{-1}. In this case the $\varepsilon'(\omega)$ value at the maximum point appeared to be minimal among the considered systems. The imaginary part $\varepsilon(\omega)$ behaves itself similarly (Fig. 2b). The values of $\varepsilon''(\omega)$ function for system II considerably exceed $\varepsilon''(\omega)$ quantities for systems I and III. In the observed frequency range the $\varepsilon''(\omega)$ function for system III has only one maximum at $\omega = 250$ cm^{-1}. At this point the $\varepsilon''(\omega)$ function is characterized by a lower value, than the $\varepsilon''(\omega)$ intensity for other systems. The maximum of $\varepsilon''(\omega)$ function for system I, represented by water clusters, is referred to the frequency $\omega = 594$ cm^{-1}, and for system II (consisting of water clusters with molecules CO_2) it shifts to the left and appears at $\omega = 215$ cm^{-1}. Curve 4 at Fig. 2a, b reflect $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ dependences for the liquid water, receiving by TIP4P model (Neumann 1986) and in the experiment (Angell and Rodgers 1984) accordingly. With the frequency growth the $\varepsilon'(\omega)$ value of the system I (water clusters) approaches to the values of the liquid water corresponding characteristic, however, $\varepsilon''(\omega)$ for the system I at the considered frequency the range is much below that for the liquid water.

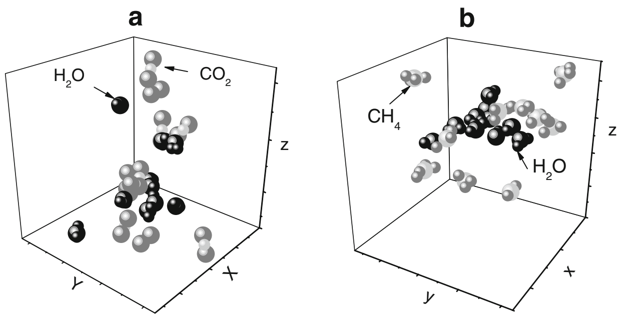

Fig. 1 Configurations of clusters: **a** $(CO_2)_{10}(H_2O)_{10}$, and **b** $(CH_4)_{10}(H_2O)_{10}$. The instant of time is 20 ps

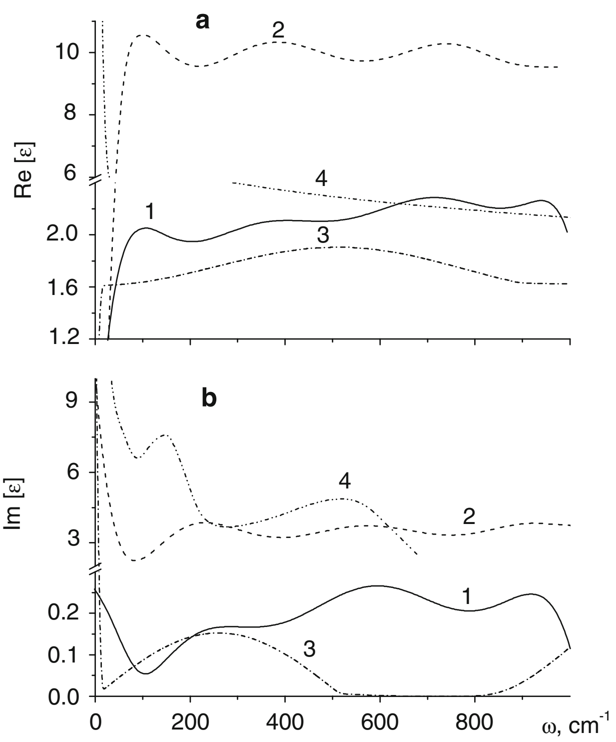

Fig. 2 Dependences on frequency real (**a**) and imaginary (**b**) parts of dielectric permittivity for systems: *1* (I), *2* (II), *3* (III), *4* liquid water: and **a** (Neumann 1986), **b** (Angell and Rodgers 1984)

Figure 3 represents the frequency dispersion $W(\omega)$ of the dielectric losses of three considered systems. For the systems I and II the energy dissipation occurs at the identical range of frequencies: $0 \leq \omega \leq 600$ cm^{-1}, and for the system III this range extends up to 1,050 cm^{-1}. The spectrum with the greatest intensity of induced radiation belongs to the water system (system I), and with the least, to the system formed by $(CH_4)_i(H_2O)_{10}$ clusters (i.e., system III). The most active emission frequencies for systems I, II, III are 184, 342 and 973 cm^{-1} accordingly. System I has the highest dissipation speed. The relation of the maximum value of this value of the water system to the appropriate value of the system II is 3.4, and the relation for the systems I and III is equal to 10.7, i.e., the speed of energy dispersion absorbed by clusters decreases with the attachment of CO_2 molecules to pure water clusters and decreases even more with the absorption of CH_4 molecules by water clusters.

The IR spectrum for the system of pure water clusters is compared to the spectrum of the Earth's thermal radiation in Fig. 4a, with the appropriate experimental spectral characteristics for gaseous CO_2 (Hertzberg 1949) and CH_4 (Kozintzev et al. 2003), and also for the liquid water (Goggin and Carr 1986). The most intensive absorption band for the spectrum of gaseous CO_2: $\omega = 650$ cm^{-1}, and for CH_4

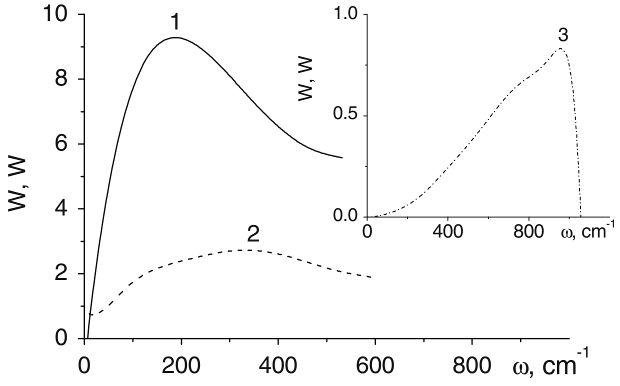

Fig. 3 Frequency dependence of dielectric losses for systems: *1* I, *2* II, *3* III (in an *inset*)

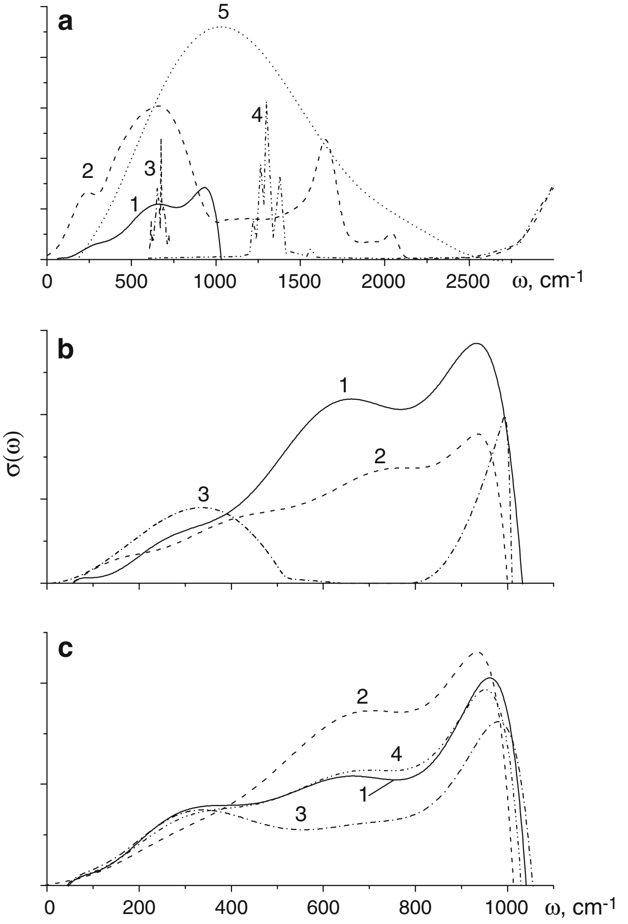

Fig. 4 IR absorption spectra: **a** *1* $(H_2O)_n$, *2*, *3*, *4* experimental spectra for liquid water (Goggin and Carr 1986), gaseous CO_2 (Hertzberg 1949) and CH_4 (Kozintzev et al. 2003), *5* a spectrum of thermal radiation of the Earth at $T = 280$ K; **b** *1* system I, *2* II, *3* III; **c** IR spectra for the systems mixed in equal proportions: *1* a mix of systems II and III, *2* I and II, *3* I and III, *4* I, II and III

$\omega = 1{,}340\ \text{cm}^{-1}$. The $\sigma(\omega)$ function received from experiment with massive water at the frequency range of $0 \leq \omega \leq 1{,}000\ \text{cm}^{-1}$ has two maxima, the main one of which corresponds to the frequency $\omega_1 = 700\ \text{cm}^{-1}$, and the low-frequency maximum is at 200 cm^{-1}. The main part of deformation vibrations in the CO_2 molecule take place with the frequency of 667 cm^{-1} which is close to the characteristic frequency of the molecule's librations in the liquid water. The frequency range of intramolecular vibrations in the CH_4 molecule situates outside the area of considered frequencies ($0 \leq \omega \leq 1{,}000\ \text{cm}^{-1}$). The addition of CO_2 molecules to $(H_2O)_{10}$ cluster (the system II) results in the reduction of IR spectrum intensity [Fig. 4b (curve 2)] at the constant site of the main peak, $\omega_1 = 973\ \text{cm}^{-1}$. In the case of the system III as a whole, a strong decrease in absorption intensity is observed, and in the range of $650 \leq \omega \leq 790\ \text{cm}^{-1}$ frequencies the window of transparency is created where the falling radiation is not being absorbed by the system at all. Thus, the most susceptible to IR radiation frequency shifts to the left and equals 340 cm^{-1}. In the Fig. 4c, the absorption spectra of the systems received by mixing of medium I, II and III in identical proportions are presented. The curve 1 represents the IR spectrum of 50% mixture (by the number of clusters) of systems II and III, the curves 2 and 3 reflect the spectra of a similar mixture of the systems I–II and I–III accordingly, and the curve 4—a spectrum of 33.3%—the mixture of systems I, II and III. The IR spectra for mixtures are received by finding the arithmetic average of the spectrum intensity of the systems I, II and (or) III. This procedure is lawful for the "model of orientated clusters" where clusters in the system do not influence each other. If the system contains two admixture components, i.e., CO_2 and CH_4 (curves 1 and 4) then it is difficult to define the mixture composition on the basis of spectra structure as they are close to each other. If the system definitely contains only one of the admixture components then the presence of this component can identify the IR spectrum of the mixture. We shall emphasize, however, that in the cases of 1 and 4 of the concentration of impurities differ more than twice, and the spectra of such systems are practically identical.

Thus, dielectric properties of water clusters are determined not only by the polarity of absorbed molecules, but also by the shape of impurity molecules and the distribution of electric charge in them. Impurity molecules with more symmetric charge distributions and shapes favor the increase in the time of reorientation of molecules in clusters. Dielectric relaxation in a water cluster, which has captured a highly symmetric foreign molecule, occurs in the vicinity of a single sufficiently low frequency.

Conclusion

There are many environmental problems coming from the increased concentration of greenhouse gases in Earth's atmosphere. Several signs indicate that we have begun changing Earth's climate: increased water vapor in the atmosphere, glaciers and polar ice caps appear to be melting, and sea levels have risen. These increases in sea level can increase the salinity of freshwater throughout the world, and cause coastal lands to be washed under the ocean.

The radiating factors influence the climate of the planet by the means of greenhouse effect change. In the absence of greenhouse gases, the Earth would be 33° cooler than it is today, or about 255 K. Of these greenhouse gases, water is by far the most important. Water has multiple effects on infra-red radiation, through its vapor phase and through its condensed phases. A process of clusterization is accompanied by a sharp reduction of number of scattering centers. The condensation heat emitted during cloud formation warms up the atmosphere. However, during the $(H_2O)_{10}$ cluster average time of life ~ 20 ps the anti-greenhouse effect, calculated for IR radiation with the frequency of $1{,}600\ \mathrm{cm}^{-1}$, loses 5–6 times more heat than the heat of condensation of 10 molecules. During the analysis of absorption spectrum of atmospheric IR radiation it is necessary to consider the fact that the intensity of spectral bands can be disproportional to the concentration of the gas component as it takes place when the component is entrained by the ultra disperse water medium. The absorption by atmospheric water clusters' (CO_2, CH_4) components considerably change the IR spectra of clusters and therefore weakening the greenhouse effect of the atmosphere.

The results of the investigation regarding the absorption and dispersion (re-emission) of electromagnetic waves by ultra disperse water systems point towards the importance of considering the effect of greenhouse gases' clusterization for estimations of the greenhouse effect. The resonant absorption and electric dipole radiation render the strongest influence on the greenhouse effect.

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