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Computational Study of Carbon Monooxide Absorption by Ultradisperse Systems. Emission Spectra

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Abstract—Molecular dynamics was used to study absorption of carbon monoxide molecules by water clusters combined into two groups (2–10 and 11–20 water molecules) on the basis of their statistical weights. Spectral characteristics of the clusters in the frequency range $0 \le \omega \le 1000$ cm^{-1} were established. Within this range, the integral IR adsorption intensity of both systems increases with addition of CO molecules. The IR emission power increases significantly after a cluster has absorbed one CO molecule but decreases with the absorption of a further CO molecule. A similar situation is observed with the number of electrons "active" toward external electromagnetic radiation. As the smallest clusters containing two CO molecules grow by adding water molecules, the IR emission power decreases. In other cases, these changes are of a periodical character.

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Carbon monoxide enters the atmosphere with equal probability from both natural and antropogenic sources. The average time of existence of this gas in the atmosphere is about 0.1 year. Under the action of hydroxyl it is oxidized to carbon dioxide. The role of CO consumer in the human organism belongs to globins, viz. water-soluble respiratory proteins. In the atmosphere, CO can be absorbed by a disperse aqueous medium [1]. Polar molecules like water are good proton donors, and this fact opens new up new possibilities for catalytic reactions. In part, carbon monoxide can enhance the catalytic activity of nanosized gold clusters and can be oxidized to carbon dioxide by H_2O molecules.

Interaction of molecules and atoms with the surface of crystalline and amorphous ice have been studied by means of atomic and molecular beams [2, 3]. Interactions leading to chemical reactions on ice surface are of great significance in astrochemistry and the chemistry of the atmosphere. Similar investigations have been conducted by means of computer modeling [4–6]. Al-Halabi et al. [7] have studied adhesion of CO molecules on the surface of amorphous and hexagonal ice with varying the energy of these molecules. Interaction of CO molecules with water clusters in the Earth's atmosphere still remains poorly studied.

Like CO_2, carbon monoxide is a greenhouse gas. It absorbs the heat radiation energy and transforms it into the kinetic energy and also creates conditions for chemical reactions for molecules of other gases. These internal energy changes and transformations occur on the background of heat deficiency. The heat obtained from molecular motion or chemical reaction is dissipated by convection to other atmospheric areas. The heat energy created in the atmosphere is transmitted, due to heat conduction and convection, to the Earth and oceans, and, in part, to space. Thus, the heat is not accumulated and stored in the atmosphere. Greenhouse gases do not prevent heat transfer by precipitation. Carbon monoxide, like water, belong to thermally and chemically stable molecules capable of inducing emission spectra. In radiating clusters, the substance exists in the thermodynamic equilibrium with respect of all degrees of freedom, that is, the state of clusters can be related to a certain temperature. The energy lost by clusters by emission is continuously compensated for by absorption of external IR radiation. As a result, clusters produce steady-state emission spectra.

The purpose of this work was to obtain the IR adsorption and emission spectra of systems formed by water clusters with one or two CO molecules, to reveal

changes in the integral intensity of these IR spectra, and to assess the loss of thermal emission power, caused by cluster formation.

Computational model. Water clusters were modeled using an improved interaction potential TIP4P for water and a rigid four-center model of a water molecule [8]. The geometry of such molecule corresponds to its experimental gas-phase parameters: r_{OH} 0.09572 nm, HOH angle 104.5° [9]. Fixed charges (q_H 0.519 e, q_M –1.038 e) are assigned to the H atoms and to the point M on the HOH bisector line at the distance of 0.0215 nm from the oxygen atom. The charges and position of the M point are taken to reproduce the experimental dipole and quadrupole moments [10, 11], as well as the ab initio energy of the dimer and characteristic distances in it [12]. The short-range order in water clusters is stabilized largely by the short-range Lennard–Jones potential whose interaction center is placed on the oxygen atom. Induced dipole moments in each time step are computed using a common iteration procedure [8]. The precision in $\mathbf{d}_i$ is set in the range from 10^{-5} to 10^{-4} D.

Atom–atom carbon monoxide–water interactions are defined via the sum of the repulsion, dispersion, and Coulomb contributions.

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

Here the a_i, b_i, and c_i parameters of the potential describing the above interactions are taken from [13]. It is suggested that the charges in the centers of the C and O atoms are q_C 0.139 e and q_O –0.139 e. The interatomic distance in the CO molecule is r_{CO} 0.1282 nm. The molecular polarizability of CO is 2.0 Å^3, which is larger than that of the water molecule (1.49 Å^3) [14].

The trajectories of the mass centers of the molecules were determined by the fourth-order Gear method [15]. The time increment Δt for integration was taken to be 10^{-17} s. Initially a $2\times10^6\Delta t$ s molecular dynamics computation was used to prepare the equilibrium state at T 233 K for water clusters containing no admixture molecules. The configuration of the water cluster at the time moment 20 ps was further used as the starting configuration for modeling the $(CO)_i(H_2O)_n$ system. Added CO molecule was initially located so that the minimum distance between its atoms and those of the water molecule was ca. 0.5 nm. The CO molecule was located along the line connecting the mass center of the $(H_2O)_n$ cluster with its own mass center. The cutting radius for all interactions in the system was taken equal to 0.9 nm. Equilibration of the newly formed system was carried out for $0.6\times10^6\Delta t$ and then all necessary physicochemical properties were computed for $2.5\times10^6\Delta t$. Analytical solution of the motion equations for molecular rotation was carried out using the Rodrigues–Hamilton parameters [16], the scheme of integration of the motion equations in the presence of rotations corresponds to the approach proposed in [17]. Computations were carried out on a PENTIUM-IV computer with the tact frequency of the four-nuclear processor of 2.67 GHz. One computation with the duration $10^6\Delta t$ for the $(CO)_2(H_2O)_{20}$ cluster took about 10 h operating time of one nucleus of the processor.

Dielectric properties. We studied six types of ultradisperse systems combined into two groups. The first group consisted of clusters with 10 or less water molecules, and the second group included larger clusters containing 11 to 20 water molecules. The first group was formed by systems I–III. System I was represented by water clusters comprising 2 to 10 water molecules, system II consisted of clusters $CO(H_2O)_n$ (n = 2, …, 10), and system III contained a set of clusters $(CO)_2(H_2O)_n$ with the same number of water molecules. It was assumed that a cluster containing i molecules of carbon monoxide and n water molecules has the following statistical weight:

$$W_{in} = N_{in}/N_{i\Sigma},$$
$$i = 0, 1, 2; n_1 = 2, \ldots, 10; n_2 = 11, \ldots, 20.$$

Here N_{in} is the number of clusters containing i molecules of the admixture and n water molecules in 1 cm^3, $N_{i\Sigma} = \sum_{n=2(11)}^{10(20)} N_{in}$. The N_{in} value was estimated as follows. Let us consider the case of scattering of nonpolarized light when the path length l of molecules is much shorter than the light wavelengh λ. The extinction coefficient h of the incident ray is defined, on the one hand, by the Rayley's formula [18], and, on the other hand, via the scattering coefficient ρ (h = 16πρ/3) [19] in the approximation of scattering at the angle of 90°. Taking into account that $h = \alpha + \rho$, where α is the absorption coefficient, we obtain the following equation:

$$N_{in} = \frac{2\omega^4}{3\pi c^4}\frac{(\sqrt{\varepsilon} - 1)^2}{\alpha}[1 - (3/16\pi)].$$

Here c is the light velocity; ε, dielectric constant of the medium; and ω, incident wave frequency. All

spectral characteristics were computed with accounting for the accepted statistical weights W_{in}. The procedure of formation of cluster systems assumes uniform distribution of these species and is valid at a low concentration of clusters, when they do not interact with each other. The average concentration of each type of clusters in the studied systems is lower by 12–13 orders of magnitude than the Loschmidt's number.

The total dipole moment $\mathbf{d}_{cl}$ of a cluster was calculated along the formula:

$$\mathbf{d}_{\text{cl}}(t) = Z_{+}\sum_{i=1}^{2N}\mathbf{r}_i(t) + Z_{-}\sum_{j=1}^{N}\mathbf{r}_j(t)$$

Here $\mathbf{r}_i(t)$ is the vector pointing to the location of ith atom at the time moment t; Z, electric charge located either in the center of the atom or in the point M; index "+" relates to hydrogen or carbon atoms bearing a positive charge and "–," to oxygen atoms; and N, number of molecules in the cluster.

The static dielectric constant ε_0 was calculated via fluctuations of the total dipole moment $\mathbf{d}_{\text{cl}}$ [20]:

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

Here V is the volume of the cluster and k, Boltzmann's constant.

The dielectric constat $\varepsilon(\omega)$ as a function of the frequency ω was represented by a complex value $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, which was calculated by the following equation [20, 21]:

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

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

$$F(t) = \frac{\langle\mathbf{d}_{\text{cl}}(t)\cdot\mathbf{d}_{\text{cl}}(0)\rangle}{\langle\mathbf{d}_{\text{cl}}^2\rangle}.$$

The IR absorption signal was taken in the form [22]:

$$\sigma(\omega) = \left(\frac{m}{\varepsilon_v c\hbar n}\right)\omega\text{th}\left(\frac{\hbar\omega}{2kT}\right)\text{Re}\int_0^\infty dt e^{i\omega t}\langle\mathbf{d}_{cl}(t)\cdot\mathbf{d}_{cl}(0)\rangle.$$

Here ε_v is the dielectric constant in a vacuum; c, light velocity; $\hbar = h/2\pi$, where h is the Planck's constant; and n, refractive index independent of the frequency ω.

The frequency dispersion of dielectric constant defines the frequency dependence of dielectric loses $P(\omega)$ according to the following equation [19]:

$$P = \frac{\varepsilon'' < E^2 > \omega}{8\pi}.$$

Here $<E^2>$ is the average squared electric field intensity and ω, frequency of emitted electromagnetic wave.

The total number of electrons N_{el} interacting with external electromagnetic field in the cluster unit volume is defined as follows [18]:

$$N_{\text{el}} = \frac{m}{2\pi^2 e^2}\int_0^\infty \omega\varepsilon''(\omega)d\omega.$$

Here e and m are the electron charge and mass, respectively.

Motions with a frequency below 1200 cm^{-1} correspond to molecular librations and those with a frequency above 1200 cm^{-1} relate largely to intramolecular vibrations [23]. As far as the model used does not include intramolecular vibrations, in the analysis of frequency-dependent characteristics we restricted ourselves to the frequency range $0 \le \omega \le 1000\ \text{cm}^{-1}$.

Computation results. The configurations of the $CO \cdot (H_2O)_{20}$ cluster related to the time moments 0 and 25 ps are depicted in Fig. 1. As seen, with time the CO molecule penetrates the cluster and comes into contact with several water molecules at once. At the same time, several water molecules move out fairly far from the cluster center. In an H_2O–CO complex inside the cluster, the exchange of the free and bound hydrogen atom of one and the same water molecule is hindered. Hydrogen bonding between CO and another water molecule is more probable here. Figure 2 compares the computed IR spectra of systems I–VI with the corresponding experimental spectra of gaseous CO [24] and liquid water [25]. After adding to water clusters of one and then one more CO molecule the integral IR absorption intensity J_{tot} increases 2.3- and 3.9-fold for cluster systems with $n \le 10$ and 1.3- and 4.1-fold for systems with $n > 10$, respectively. Note that the J_{tot} value increases as the cluster size in the system grows. Thus, the J_{tot} value for system IV consisting of rather large clusters ($11 \le n \le 20$) is higher by a factor of 1.9 than for system I ($2 \le n \le 10$). Thus, irrespective of whether a system comprises small

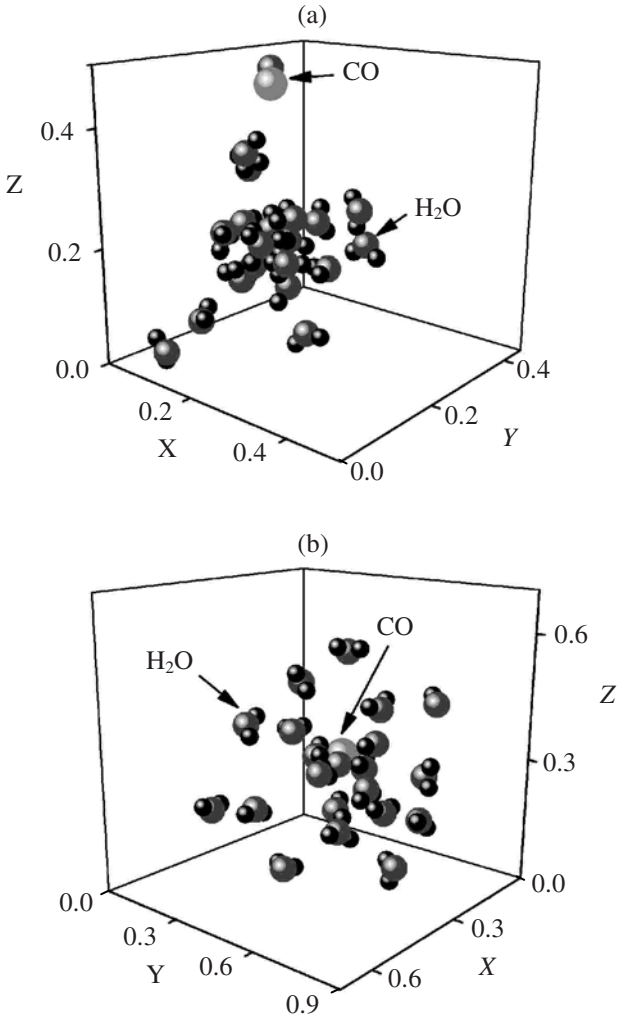

Fig. 1. Configurations of the $CO(H_2O)_{20}$ cluster corresponding to the time moments: (*a*) 0 and (*b*) 25 ps. Molecular coordinates are in nm.

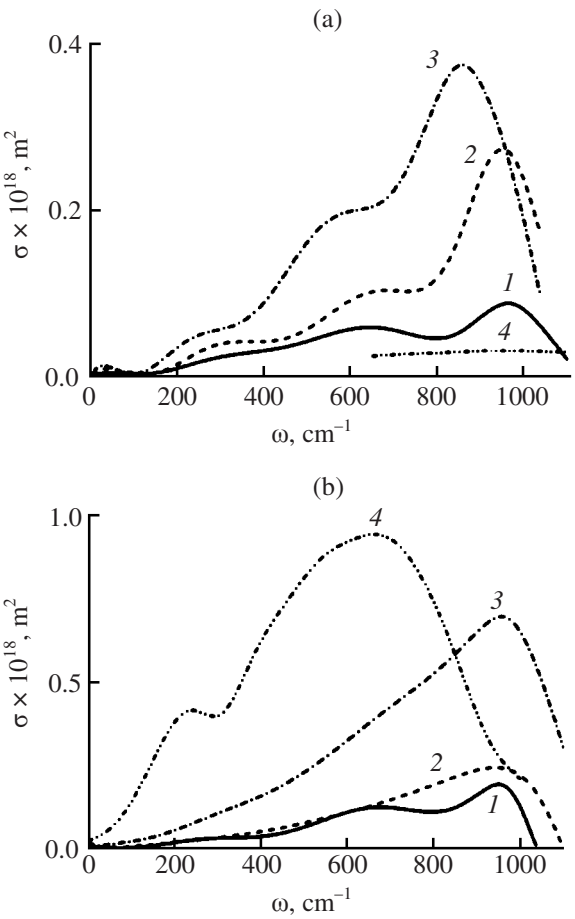

Fig. 2. IR absorption spectra of (a) systems containing clusters with 2 to 10 water molecules: (*1*) clusters $(H_2O)_n$, (*2*) $(CO)(H_2O)_n$, (*3*) $(CO)_2(H_2O)_n$, and (*4*) gaseous CO, experiment [24]; (b) cluster systems with clusters containing 11 to 20 water molecules: (*1*) clusters $(H_2O)_n$, (*2*) $(CO)(H_2O)_n$, (*3*) $(CO)_2(H_2O)_n$, and (*4*) liquid water, experiment [25].

or large clusters, i.e. regardless of cluster size, the absorption of CO enhances its IR absorption, and the enhancement is the stronger the more CO molecules are absorbed by the system. However, CO absorption shifts the IR absorption maximum of a system of small water clusters to lower frequencies and has almost no effect on that of a system of large clusters (system VI). The experimental IR absorption spectrum of gaseous CO is defined within a narrow frequency range and has no features. The main IR absorption maximum of liquid water has a lower frequency (700 cm^{-1}) as compared with the respective value for utradisperse systems.

The emission power of clusters is increased by an absorbed CO molecule (Fig. 3). However, when the CO concentration in a cluster system is doubled, the emission power slightly decreases. The ratio of the integral emission intensities is 1:3.07:3.01 for systems I–III and 1:2.39:2.35 for is, for systems IV–VI. The self-diffusion coefficient D_w of water molecules for small-cluster systems II and III is, on average, 4% lower than that for large-cluster systems V and VI. Decreased D_w favors enhanced collective vibrations, which, in its turn, enhances dissipation of the absorbed energy. The static dielectric constant ε_0 for systems II and III is, on average, 14% lower than the respective value for systems V and VI. However, the situation with the imaginary dielectric constant ε" is reversed: The ε" for small-cluster systems is 12% higher than that for large-cluster ones. As a result, the emission power of systems II and III is enhanced to a greater

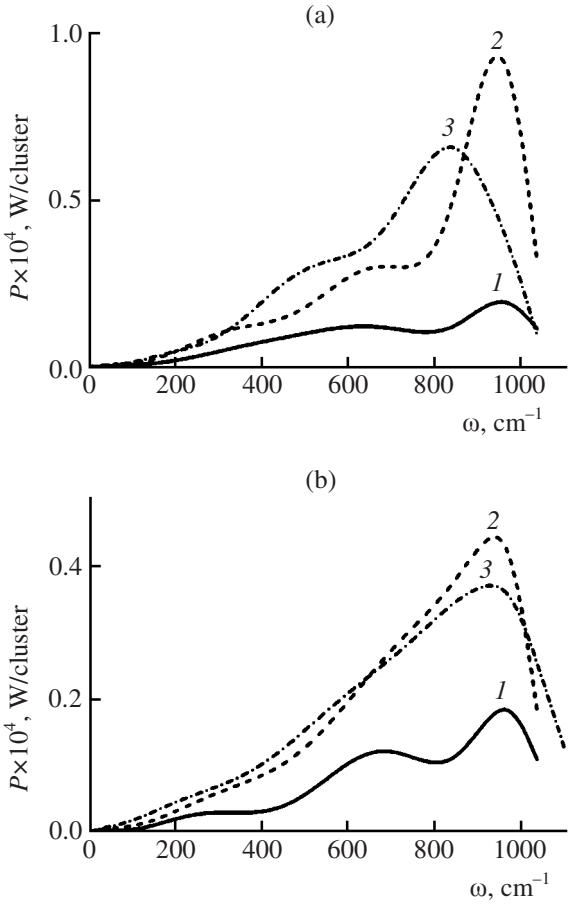

Fig. 3. Frequency dependence of IR emission power for systems (a) I–III and (b) IV–VI: (*1*) I and IV, (*2*) II and V, and (*3*) III and VI.

extent than in the case of systems V and VI. The absorption of one CO molecule and its further penetration in a water cluster favors a thicker structure of the latter. The second absorbed CO molecule loosens the cluster and decreases ε" value. The ε" values for systems III and VI fall 1.8- and 2.4-fold, respectively. As a result, the integral emission intensity for systems III and VI turns to be lower compared to systems II and V, respectively. Among system I–III clusters, the highest peak [that is, corresponding to the main maximum on the $P(\omega)$ plot] emission power has the cluster $CO(H_2O)_8$, among system IV–VI clusters, $(CO)_2(H_2O)_{17}$.

Clusters produce nonblackbody radiation, and the emission power spectrum depends on the temperature and on the type and state of the substance. According to the simplest theory [26], on optical excitation a molecule passes from its ground state with the energy E_1 into a discrete state of higher level with the energy E_i, absorbing a photon $\hbar\omega = E_i - E_1$. The excited molecule can release its energy by emitting a photon or by giving it up to another molecule via interaction with it. Commonly, on optical excitation the emission frequency is lower than the absorption frequency. Just such a relation between the emission and absorption frequencies provides positions of the main peaks in the $\sigma(\omega)$ and $P(\omega)$ plots for systems I, III, and VI. However, with systems II, IV and V, the main maxima in the $\sigma(\omega)$ and $P(\omega)$ plots coincide, that is, these cluster systems produce resonance emission with the frequencies 946, 958, and 936 cm^{-1}, respectively. External IR radiation interacts with a cluster via the electronic subsystem of its constituent molecules.

The number of electrons involved to the interaction with external electromagnetic field commonly increases after a disperse water system has absorbed one CO molecule (Fig. 4). However, like with the emission power, the number of "active" electrons decreases after addition to each cluster of the second CO molecule. The ratio between full numbers of "active" electrons in systems I–III is 1:13.8:6.4 and in systems IV–VI, 1:4.2:1.7.

The relative change in the integral IR emission power of one cluster as a function of its size is shown in Fig. 5. For system II (curve *1*), the $[I_{tot}^{(n+i)} - I_{tot}^{(2+i)}]/I_{tot}^{(2+i)}$ value (n is the number of water molecules and i , number of admixture molecules) at $i = 1$ is positive always, except for $\Delta n = 4$ and 8. This means that the emission power of clusters $CO(H_2O)_n$ is commonly higher than that of the $CO(H_2O)_2$ cluster, due to added water molecules. For clusters $(CO)_2(H_2O)_n$, (system III, curve), the picture is opposite: adding 1 to 8 water molecules to $(CO)_2(H_2O)_2$ attenuates the emission power. For systems V and VI (curves *3* and *4*), as the cluster grows by adding water molecules, the $[I_{tot}^{(n+i)} - I_{tot}^{(11+i)}]$ difference changes sign. In other words, the emission power of growing cluster can be either higher or lower than that of the respective parent cluster $CO(H_2O)_{11}$ or $(CO)_2(H_2O)_{11}$. Therewith, the emission power of system V clusters is aiienuated at $3 < \Delta n < 5$ and that of system VI clusters, at $\Delta n < 5$.

Thus, we showed CO absorption strongly affects spectral characteristics of water clusters. Adding to any cluster one CO molecule produces significantly increases the integral IR absorption intensity J_{tot} in the case of the small-cluster systems and exerts a slightly weaker effect on the J_{tot} of larger cluster systems. Doubling the number of CO molecules in both small and large clusters produces further significant increase

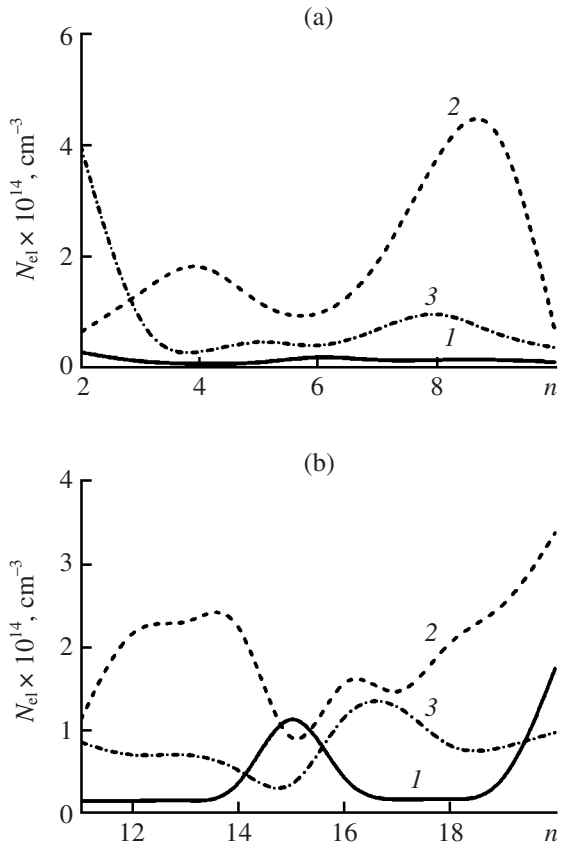

Fig. 4. Number of electrons interacting with external electromagnetic radiation. For the numerical notation, see legend to Fig. 3.

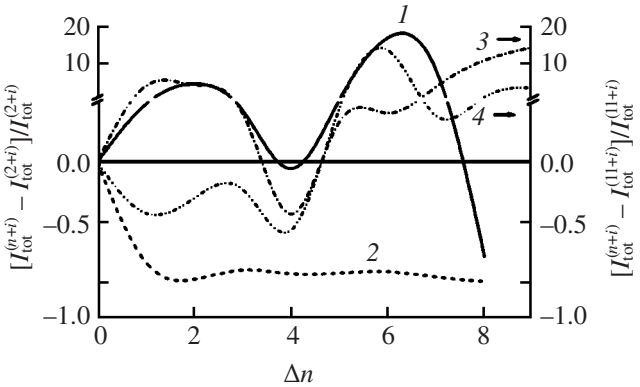

Fig. 5. Relative changes in the integral intensity of IR emission power on varying the number of water molecules in a cluster by Δ*n*. System: (*1*) II, (*2*) III, (*3*) V, and (*4*) VI.

in J_{tot}. The integral IR emission intensity of both small and large clusters increases significantly after absorption of the first CO molecule but weakens after absorption of the second CO molecule. The same trend is observed with the number of electrons involved to interaction with external electromagnetic radiation. The integral IR emission power of small clusters containing one CO molecule generally increases as the cluster grows by adding water molecules. When the number of CO molecules in each small cluster equals two, I_{tot} decreases as the cluster grows. In the case of larger clusters, I_{tot} undergoes periodical changes with cluster growth, irrespective of whether the cluster contains one or two CO moleulce chages occurs periodical changes in with growing both at the presence one or two CO molecules.

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