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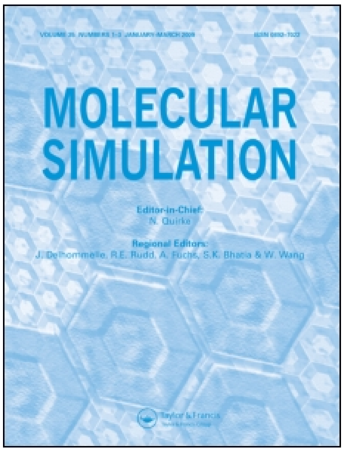

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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First published on: 08 October 2009

To cite this Article Galashev, A. Y.(2010) 'Simulation of hydrocarbon molecules' absorption by ultra disperse water medium', Molecular Simulation, 36: 4, 273 — 282, First published on: 08 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/08927020903307537

URL: http://dx.doi.org/10.1080/08927020903307537

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Molecular Simulation
Vol. 36, No. 4, April 2010, 273–282

Simulation of hydrocarbon molecules' absorption by ultra disperse water medium

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(*Received 17 July 2009; final version received 1 September 2009*)

Uptake of acetylene and ethane molecules by a disperse aqueous system was simulated by molecular dynamics. The cluster $(H_2O)_{20}$ remains stable until the number of the captured C_2H_2 molecules becomes larger than 3 and the number of the C_2H_6 molecules becomes more than 4. Addition of acetylene molecules to the disperse aqueous system increases both the real and imaginary parts of the dielectric permittivity in the frequency range $0 \leq \omega \leq 1000\,\mathrm{cm}^{-1}$. However, capturing of ethane molecules decreases the dielectric permittivity in the same frequency range. The integral IR absorption coefficient of the disperse system containing C_2H_2 and C_2H_6 molecules increases. The heat-radiating power of the clusters decreases upon absorption of ethane molecules and increases when acetylene molecules are added to the water cluster. Absorbed C_2H_2 molecules are aligned with the tangent to the water core of the cluster, thus impeding their penetration into the aggregate and, hence, decreasing the solubility of acetylene.

Keywords: absorption; acetylene; ethane; water clusters

1. Introduction

Hydration of hydrocarbon molecules is accompanied by a hydrophobic effect caused by rearrangement of the hydrogen bond network in the first solvation layer. The extent of the hydrophobic effect can be evaluated from the solubility of the hydrocarbon. The hydrophobic effect is also observed in the dissolution of acetylene and ethane in water. It was shown by a functional group additivity scheme that ethane has the lowest free energy of hydration among saturated hydrocarbons at low temperatures ($T < 244\,\mathrm{K}$) [1]. The functional group contributions were based on almost 1400 experimental points. The hydrogen bonds between two water molecules in the solvation layers of ethane are stronger than those in bulk water [2]. Because of the polarisability of molecules, hydrogen bonds enhance each other, i.e. the H-bonds between water molecules become stronger owing to the electrostatic induction effect of the solvation layer. The stability of the solvation layer is ensured by attainment of a definite distance between the hydrocarbon molecules in solution. At a certain fixed distance (e.g. 0.48 nm for methane), water molecules form a stable cell, accommodating the solute molecules. The stability of the solvation layer is provided by a small number of exchanges between water molecules from the solvation layer and from the bulk.

Absorption of organic molecules by water clusters is still poorly understood. Despite the occurrence of the hydrophobic effect, clusters of water and hydrocarbon molecules can be formed in the gas phase. The results of far-IR studies and DFT calculations are indicative of the formation of benzene–water dimers [3] and $C_6H_6(H_2O)_9$ clusters [4] in a cooling supersonic beam. The H-bond energy in the benzene–water dimer is estimated at 1.9 kcal/mol. The interaction of the benzene ring with $(H_2O)_9$ clusters leads to the formation of one H-bond and to considerable changes in the distances between the oxygen atoms (and in the distances r_{OH} between O and H atoms of different molecules) in the cluster. The absorption of C_6H_6 molecules should also lead to substantial changes in the structure of the whole water cluster. This, in turn, will appreciably affect the spectral characteristics of the ultra dispersed aqueous system, determined by IR spectroscopy. The characteristic frequencies in the absorption spectrum $\alpha(\omega)$ correspond to definite bonds or groups of bonds in a molecule and to a definite steric structure of a molecule. Absorption occurs only when rotation of a molecule leads to changes in the charge distribution in it. In the spectra of the majority of non-polar molecules, the induced translation and rotation spectra are located in the same frequency range and cannot be observed separately. For liquid water, oscillations with the frequency less than $1000\,\mathrm{cm}^{-1}$ correspond to vibration–rotation motion of molecules, whereas the frequencies higher than $1000\,\mathrm{cm}^{-1}$ mainly describe intramolecular vibrations [5]. Computer simulation of the interaction of small water clusters with hydrocarbon molecules was made in [6–10]. In [6], we demonstrated the possibility of uptake of methane molecules by water clusters consisting of 10 and 20 molecules. We found that cluster systems $(CH_4)_i(H_2O)_n$ show virtually no IR absorption in a certain frequency range.

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ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020903307537
http://www.informaworld.com

The goal of this study is to examine the uptake of acetylene and ethane molecules by water clusters, reveal the effect of these hydrocarbon molecules on the shape of the IR absorption spectra of the disperse aqueous system and elucidate the role of C_2H_2 and C_2H_6 molecules in the dissipation of the energy of the external IR radiation, taken up by water clusters.

2. Computer model

Simulation of water clusters was performed with the DC model obtained by correction of the Lennard-Jones (LJ) parameters of the TIP4P interaction potential for water and point of location of the negative charge [11]. In doing so, the charges in the H_2O molecule remain unchanged [12]. The geometry of the H_2O molecule corresponds to the experimental parameters of the water molecule in the gas phase: $r_{OH} = 0.09572\,\text{nm}$, $\angle HOH = 104.5^\circ$ [13]. Fixed charges ($q_H = 0.519e$, $q_M = -1.038e$) are assigned to H atoms and point M lying on the bisector of the HOH angle at a distance of 0.0215 nm from the oxygen atom. The values of charges and the position of point M were chosen so as to reproduce the experimental dipole and quadrupole moments [14,15], and also the dimer energy and characteristic distances in the dimer, obtained by *ab initio* calculations [16]. To point M, we assign the polarisability α_i^p required for calculating the non-additive polarisation energy U_{pol} [17],

$$U_{\text{pol}}(\mathbf{R}_{1\ldots N}) = -\frac{1}{2}\sum_i^N \mathbf{E}_i^0 \mathbf{d}_i^{\text{ind}}, \quad \mathbf{d}_i^{\text{ind}} = \alpha_i^p \mathbf{E}_i, \qquad (1)$$

where $\mathbf{R}_i$ is the radius vector of point M of the *i*th molecule; $\mathbf{E}_i^0$, the Coulomb field strength produced by fixed partial charges; $\mathbf{E}_i$, the field strength in centre *i*, produced both by charges and by interaction of induced dipole moments with these charges; and $\mathbf{d}_i^{\text{ind}}$, the induced dipole moment of molecule *i*.

The dipole tensor is given by the following expression:

$$\mathbf{T}_{ij} = \frac{1}{4\pi\varepsilon_v}\frac{1}{r_{ij}^3}\left[\frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - 1\right],$$

where ε_v is the dielectric permittivity of vacuum and r_{ij} is the distance between points *i* and *j*. To calculate the induced dipole moments, in each time step, we used the standard iterative procedure [11]. The accuracy of the determination of $\mathbf{d}_i$ is set in the range 10^{-5}–10^{-4} D.

The total energy of the interaction between water molecules is given by

$$U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}}.$$

Here, the pair-additive term of the potential is the sum of LJ and Coulomb interactions,

$$U_{\text{pair}} = \sum_i\sum_j \left\{4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{1}{4\pi\varepsilon_v}\frac{q_i q_j}{r_{ij}}\right\},$$

where q is the charge; σ and ε are the parameters of the LJ potential. The short-range LJ potential with the interaction centre assigned to the oxygen atom is responsible for the stabilisation of the short-range order in water clusters.

The additive term of admixture–water and admixture–admixture interactions was represented in the form of atom–atom functions set through the sum of repulsive, dispersion and Coulomb contributions,

$$\Phi(r_{ij}) = b_i b_j \exp[-(c_i + c_j)r_{ij}] - a_i a_j r_{ij}^{-6} + \frac{1}{4\pi\varepsilon_v}\frac{q_i q_j}{r_{ij}},$$

with the parameters a_i, b_i, c_i of the potential describing these interactions taken from [18]. To the C and H atoms in the ethane molecule, we assigned the charges $q_C^{\text{ethane}} = -0.0939e$ and $q_H^{\text{ethane}} = 0.0313e$, respectively. The charges that occur at the centres of C and H atoms of the acetylene molecule are $q_C^{\text{acet}} = -0.094e$ and $q_H^{\text{acet}} = 0.094e$ [18]. The partial atomic charges play an important role in the analysis of polarisation properties of the molecule. The polarisability of the C_2H_2 and C_2H_6 molecules was assigned to its centre of gravity (point M). Using the second expression in formula (1), we determined the induced dipole moments of the acetylene and ethane molecules; its average values were close to the experimental values of 1.05 and 0.3 D [19], respectively.

The C_2H_6 molecule has the most stable staggered conformation [20]. The following interatomic distances in the C_2H_6 molecule are taken: $r_{CC} = 0.154$ and $r_{CH} = 0.11\,\text{nm}$ [19]. The characteristic distances of the linear C_2H_2 molecule are $r_{CC} = 0.121$ and $r_{CH} = 0.106\,\text{nm}$ [19]. The model suggests the calculation of induced dipole moments of molecules, thus making it possible to consider the effect of their polarisation. The polarisability of the acetylene ($3.32\,\text{A}^3$) and ethane ($2.6\,\text{A}^3$) molecules is higher than that of the water molecule ($1.49\,\text{A}^3$) [19]. This model reproduces well the structure and thermodynamic properties of both bulk liquid and the liquid–vapour interface of water [11]. The optimised potential function also makes it possible to adequately reproduce both the structures of water clusters with a minimal energy and the binding energy. The applicability of the model was verified in an investigation of the interaction of water clusters with carbon dioxide, dinitrogen oxide, methane, acetylene and ethane molecules [21].

The trajectories of the centres of gravity of the molecules were determined by the fourth-order Gear method [22].

The time step Δt of the integration was 10^{-17} s, which makes it possible to avoid an increase in the internal energy of the cluster, associated with the accumulation with time of the errors of integration of motion equations, especially of the equations describing the rotation of molecules. Furthermore, longer time step could lead to the destruction of water cluster upon introduction of foreign molecules into the region of the action of molecular forces.

First, in the molecular dynamic calculation by the duration of $2 \times 10^6 \Delta t$, an equilibrium condition at $T = 233$ K for water clusters not containing admixture molecules was reached. The configuration of water cluster corresponding to the moment of time 20 ps was then used as the initial configuration for the modelling of the $(C_2H_2)_i(H_2O)_n$ and $(C_2H_6)_i(H_2O)_n$ systems. The C–C axes of attached C_2H_2 and C_2H_6 molecules were first oriented in the direction of the cluster's centre of mass and the least distance between the atoms in admixture molecules and the atoms of water molecules was of 0.6–0.7 nm. The cut-off radius of all interactions in the model was equal to 0.9 nm. The equilibration of the newly formed system was carried out within a time interval of $0.6 \times 10^6 \Delta t$, and then in the interval of $2.5 \times 10^6 \Delta t$, the necessary physical and chemical properties were calculated.

We consider some types of ultra disperse systems: $(C_2H_2)_j(H_2O)_n$, $(C_2H_6)_j(H_2O)_n$, $(C_2H_2)_i(H_2O)_{20}$, $(C_2H_6)_i(H_2O)_{20}$, $j = 1, 2;\ 10 \le n \le 20,\ 1 \le i \le 6$. It was assumed that cluster containing $i(j)$ admixture molecules and n water molecules has the statistical weight

$$W_{i(j)n} = \frac{N_{i(j)n}}{N_{i(j)\Sigma}}, \quad i = 1, \ldots, 6, \ j = 1, 2,$$

$$n = 10, \ldots, 20,$$

where $N_{i(j)\Sigma} = \sum_{n=10(1)}^{20(6)} N_{i(j)n}$ is the number of clusters with $i(j)$ admixture molecules and n water molecules in 1 cm^3. The $N_{i(j)\Sigma}$ quantity was estimated as follows. Let us consider the case of non-polarised light's dispersion, where the length of the molecules' run l is much less than the λ length of the light wave. The coefficient of the extinction (weakening) h of a falling beam, on the one hand, is defined by the Rayleigh [23] formula, and, on the other hand, is defined through a scattering coefficient ρ ($h = (16\pi/3)\rho$) [24] in the approximation of scattering at a 90° angle. Considering that $h = \alpha + \rho$, where α is an absorption coefficient, we have

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

where c is the light speed; ε is the dielectric permittivity of the medium; and ω is the frequency of the falling wave. Calculation of all spectral characteristics was carried out subject to the accepted statistical weights $W_{i(j)n}$. The procedure of cluster systems' formation supposes the uniform distribution of these formations and it is justified at the 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.

The total dipole moment of the cluster is given by

$$\mathbf{M}(t) = \sum_{i=1}^{N} \mathbf{d}_i(t),$$

where $\mathbf{d}_i(t)$ is the dipole moment of molecule i and N is the number of molecules in the cluster.

The static dielectric constant ε was calculated through fluctuations of the total dipole moment [25],

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

Let us introduce the Fourier–Laplace transform of the normalised autocorrelation function $C(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle \mathbf{M}^2 \rangle$:

$$L_{\mathrm{i}\omega}[C] = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} C(t).$$

The frequency dependence of the dielectric permittivity is presented as a complex quantity $\varepsilon(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega)$, with the real part $\varepsilon'(\omega)$ (dielectric dispersion) and the imaginary part $\varepsilon''(\omega)$ characterising the dielectric loss. The correlation between the frequency-dependent dielectric constant and Fourier–Laplace transform of the time derivative of the function $C(t)$ is given by the following relationship [25]:

$$L_{\mathrm{i}\omega}[-\dot{C}] = \frac{\varepsilon(\omega) - 1}{\varepsilon_0 - 1} = 1 - \mathrm{i}\omega L_{\mathrm{i}\omega}[C].$$

Absorption of electromagnetic waves of a certain frequency by a molecule can occur only in the case when the molecule's dipole moment makes vibrations with the same frequency. The absorption coefficient is proportional to the square vibration amplitude of the dipole moment. Absorption of radiation on ω frequency at thermodynamic equilibrium in the gas phase with temperature T is characterised by the α absorption coefficient. The α quantity was represented through the imaginary part of $\varepsilon(\omega)$ frequency-dependent dielectric permittivity in the form

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

The $P(\omega)$ frequency dependence of dielectric losses was represented [24] as

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

where $\langle E^2 \rangle$ is an average value of the square of the electric field strength and ω is the frequency of emitting electromagnetic wave.

3. Stability criterion

The stability of the absorption of molecules is characterised by the following criterion [26]:

$$\left(\frac{\partial^2 F}{\partial N^2}\right)_{V,T} = \left(\frac{\partial \mu}{\partial N}\right)_{V,T} > 0,$$

where the free energy differential $\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}N$, μ being the chemical potential and N being the number of molecules in the cluster. The excess, relative to an ideal gas, free energy of clusters ΔF was calculated by the procedure suggested in [27]. The essence of the quick method for calculating ΔF of a cluster is as follows. The method of thermodynamic perturbation and integration for calculating ΔF is based on the variation of the interaction between a given molecule and all the other molecules in the system. The expression for free energy is as follows:

$$F = kT \ln z, \quad z = \int \exp(-U/kT)\mathrm{d}X.$$

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

$$z_{\mathrm{B}}/z_{\mathrm{A}} = \frac{\int \exp(-U_{\mathrm{B}}/kT)\mathrm{d}X}{\int \exp(-U_{\mathrm{A}}/kT)\mathrm{d}X} = \langle \exp(-(U_{\mathrm{B}} - U_{\mathrm{A}})/kT) \rangle_{\mathrm{A}}.$$

For example, B may be a liquid and A, an ideal gas. For a gradual transition from one state to another, we can perform the integration,

$$\Delta F = \int \mathrm{d}F = \int \langle \partial U(\lambda)/\partial \lambda \rangle \mathrm{d}\lambda,$$

where U is a function of parameter λ; as λ is varied, U varies from U_{A} to U_{B}.

The potential energy is determined as the sum of the pair contributions from all the pairs of atoms occurring in different molecules, plus the non-additive contribution,

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

where $U_{\mathrm{pol},\lambda}$ is the polarisation energy at the interaction weakened by the λ factor. Our calculation of the excess free energy of water in the polarisable model differs from the calculations for the non-polarisable model [27] by the presence of an additional term, $U_{\mathrm{pol},\lambda}$. We also used the functions $f_\alpha(\lambda_\alpha)$ of interaction weakening, as in [27].

4. The results of calculations

Configurations of (a) $(C_2H_2)_6(H_2O)_{20}$ and (b) $(C_2H_6)_6\,(H_2O)_{20}$ clusters corresponding to the moment of time 25 ps show the absence of stirring of H_2O molecules with C_2H_2 and C_2H_6 molecules even when the number of admixture molecules reaches six (Figure 1). Acetylene molecules are attracted by water clusters. Finally, they get the orientation of a tangent to the $(H_2O)_{20}$ cluster surface. It is reached due to the attraction of C atoms to H atoms of water molecules oriented mainly outwards to the cluster. Thus, H atom, which are on the ends of the C_2H_2 molecule, feel the repulsion from thesurface of the water cluster. In this case, acetylene molecules act as proton acceptors [28]. Also, the bond energy with water clusters is estimated as − 13.8, − 15.4 and − 12.9 kJ/mol for systems $C_2H_6(H_2O)_n$, $(C_2H_6)_2(H_2O)_n$ and $(C_2H_6)_i(H_2O)_{20}$, respectively. These values are coordinated with the estimation of bond energy (− 15.4 kJ/mol) for the acetylene acting as a proton acceptor to amorphous ice [29]. The bond energy for acetylene–water dimer is determined at −(5.0–7.9) kJ/mol (acetylene–proton acceptor) and −(8.7–13.3) kJ/mol (acetylene–proton donor) [30]. Interaction of ethane molecules with water clusters is characterised by higher values of bond energy. These values for systems of $C_2H_6(H_2O)_n$, $(C_2H_6)_2(H_2O)_n$ and $(C_2H_6)_i(H_2O)_{20}$ are − 11.7, − 11.7 and − 6.7 kJ/mol, respectively. If, in general, for the first two systems, the ethane acts as a proton acceptor, then for the last system, it acts as a proton donor (oxygen–hydrogen of ethane pairs gives the lowest energy in the ethane–water interaction). Thus, with the growth of ethane concentration and the amplification of interaction between C_2H_2 molecules, the switching of the bond type from the proton acceptor to the proton donor is

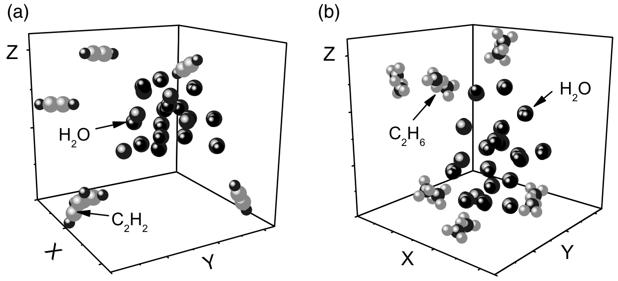

Figure 1. Configurations of (a) $(C_2H_2)_6(H_2O)_{20}$ and (b) $(C_2H_6)_6(H_2O)_{20}$ clusters, corresponding to the moment of time 25 ps.

observed. Bond energy in a complex amorphous ice–ethylene (proton acceptor) is estimated as -15.8 kJ/mol [29]. At atmospheric pressure, the ethylene has the higher solubility in water than ethane. The C_2H_6 molecules are not rejected by water cluster but also do not approach it too close being symmetrically on opposite sides of the cluster.

Theoretical determination of the ground-state geometry of water clusters is a difficult task. As the number of local minima grows exponentially with the number of atoms, finding the global minimum is a real challenge. Exact definition of the cluster configurations with the minimal energy is complicated due to energies, corresponding to the different equilibrium configurations, that are close enough. These configurations frequently differ only in the way of arrangement of atoms of hydrogen in the system of bonds. Already for polytetrahedral clusters from eight molecules, the number of isomers formed due to the hydrogen disorder makes 450, and it is already more than 40,000 of such isomers for similar clusters from 14 molecules [31]. Another difficulty is that the use of various models of water results in clusters with the minimal energy, having various forms. In addition, their structures differ by symmetry [32]. Even with the use of the same model of water, different forms of the $(H_2O)_{20}$ clusters with the minimal energy were received. With the help *ab initio* calculations, using TIP4P potential, Tsai and Jordan [33] have defined such cluster in the form of the fused cube, and by a method of molecular dynamics with the same potential. Wales and Ohmine [34] have found an even lower energy structure for $(H_2O)_{20}$, which consists of three pentagonal prisms sharing three faces. Extensive *ab initio* calculations have been performed for several possible structures of water clusters $(H_2O)_n$, $n = 8$–20 [5]. It is found that the most stable geometries arise from a fusion of tetrameric or pentameric rings. As a result, $(H_2O)_n$, $n = 8$, 12, 16 and 20, are found to be cuboids, while $(H_2O)_{10}$ and $(H_2O)_{15}$ are fused pentameric structures. It is necessary to notice that the adding polarisability in an explicit manner has the effect favouring a reduction in strain energy at the expense of hydrogen bonding [32]. Many-body intermolecular interaction expansions provide a promising avenue for the efficient quantum mechanical treatment of molecular clusters and condensed-phase systems, but the computationally expensive three-body and higher terms are often non-trivial [35].

The neighbourhood already with one ethane molecule changes the structure of water cluster. The C_2H_6 molecules are not detached by the water core of a cluster; however, at the same time, they do not approach the core too closely (Figure 2). In the case of both clusters, every C_2H_6 molecule is adjacent to three water molecules. Also, every C_2H_6 molecule is oriented arbitrarily to the water core of a cluster, i.e. its C–C axis is directed neither at the centre of a cluster mass nor tangentially to the core 'surface'. The presence of a second C_2H_6 molecule changes the shape of the water skeleton of a cluster. This is due to the fact that every ethane molecule adjusts the nearest water molecules of a cluster to its conformation. The C_2H_6 molecules are quite remote from water molecules comparing to the distance between the adjacent H_2O molecules. In general, the surface of the $(C_2H_6)_2(H_2O)_{20}$ cluster turned out to be looser than the surface of the $(C_2H_6)_2(H_2O)_{20}$ cluster. The structures shown in Figures 1 and 2 correspond to the energy close to the minimal one for these clusters under considered conditions.

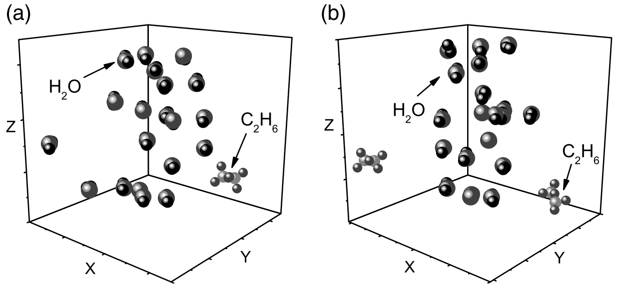

Figure 2. Configurations of the clusters corresponding to a time of 25 ps: (a) $C_2H_6(H_2O)_{20}$ and (b) $(C_2H_6)_2(H_2O)_{20}$ clusters.

The dielectric permittivity describes both the intrinsic properties of water (e.g. excitation spectrum) and the result of its exposure to external electromagnetic radiation. The impact of external factors on the medium alters its state non-locally, i.e. ε experiences both frequency and spatial dispersion. The calculated real ε' and imaginary ε'' terms of the function $\varepsilon(\omega)$ of bare dispersed water (system I) and dispersed water that has adsorbed acetylene (system II) are shown in Figure 3. It is seen that both the real and imaginary parts of $\varepsilon(\omega)$ increase after the capture of C_2H_2 molecules by water clusters. The increase is due to both the polarity of the added molecules (dipole moments of up to 1 D are induced in C_2H_2 molecules) and the consolidation of water clusters as a result of interaction with the C_2H_2 molecules. At $\omega > 35\,\mathrm{cm}^{-1}$, ε' for the systems formed by clusters exceeds that for liquid water [36] (Figure 3(a), curve 3). However, ε'' of system I becomes higher than the value characteristic of liquid water [37] (Figure 3(b), curve 3) at $\omega > 190\,\mathrm{cm}^{-1}$; for system II, this crossover takes place at $\omega > 622\,\mathrm{cm}^{-1}$.

The frequency dependences of the real and imaginary parts of the dielectric permittivity show that addition of C_2H_6 molecules to water clusters leads to a considerable decrease in these characteristics in the entire frequency range (Figure 4). For liquid water, ε' steeply decreases with increasing frequency. At $\omega > 35\,\mathrm{cm}^{-1}$, ε' becomes lower than that for the monodisperse system $(H_2O)_{20}$, and, at $\omega > 250\,\mathrm{cm}^{-1}$, it becomes even lower than that for the system consisting of $(C_2H_6)_i(H_2O)_{20}$ clusters. The function $\varepsilon''(\omega)$ for liquid water also decreases with

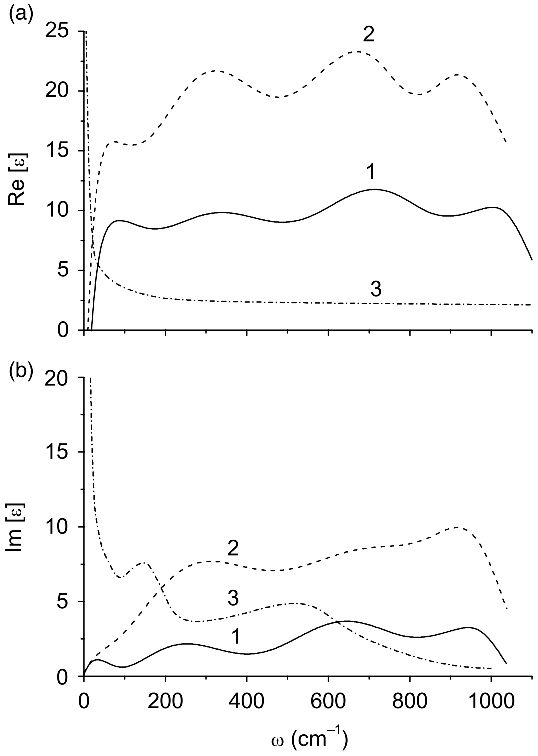

Figure 3. Frequency dependence of (a) the real and (b) the imaginary term of the dielectric permittivity of ultrafinely dispersed systems: 1, $(H_2O)_n$, $21 \le n \le 26$; 2, $(C_2H_2)_i\,(H_2O)_{20}$, $1 \le i \le 6$ and 3, liquid water according to the data reported in (a) [36] and (b) [37].

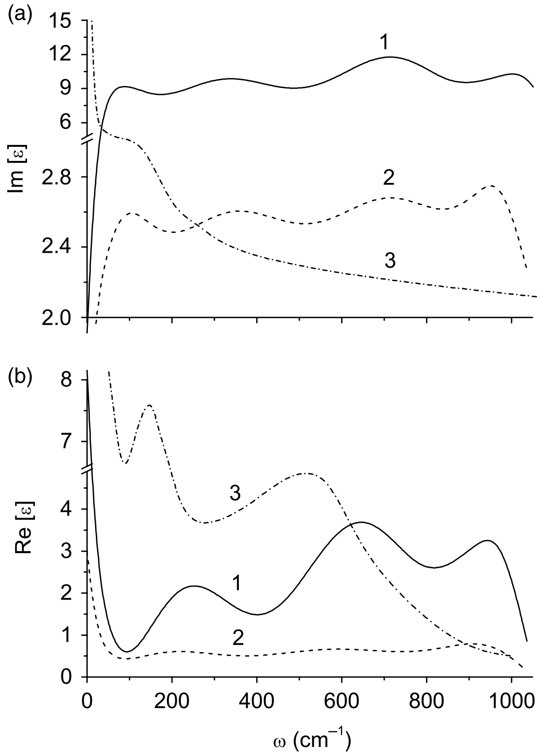

Figure 4. Frequency dependence of (a) the real and (b) the imaginary term of the dielectric permittivity of ultrafinely dispersed systems: 1, monodisperse system $(H_2O)_{20}$; 2, system of $(C_2H_6)_i(H_2O)_{20}$ clusters, $1 \le i \le 6$; 3, liquid water according to the data reported in (a) [36] and (b) [37].

increasing frequency. It undergoes oscillations and then becomes lower than $\varepsilon''(\omega)$ for the $(H_2O)_{20}$ system at $\omega > 260\,\mathrm{cm}^{-1}$ and lower than $\varepsilon''(\omega)$ for the system of $(C_2H_6)_i(H_2O)_{20}$ clusters in a narrow frequency range, $895 \le \omega \le 985\,\mathrm{cm}^{-1}$.

The frequency dependence of $\alpha(\omega)$ IR radiation absorption coefficient of investigated systems is shown in Figure 5. The $\alpha(\omega)$ coefficient for disperse systems containing C_2H_2 molecules is higher than that for the disperse system of pure water (Figure 5(a)). The intensity of the spectrum is increased with the growth of C_2H_2 molecules' number in the water system. The principal maximum of the $\alpha(\omega)$ distribution for the system of pure disperse water falls in the frequency of $780\,\mathrm{cm}^{-1}$, and that for the similar water system with one and two acetylene molecules in each cluster is at $970\,\mathrm{cm}^{-1}$. After absorption from one up to six acetylene molecules by the monodisperse water system, the $\alpha(\omega)$ spectrum becomes strongly oscillating with the principal maximum at $\omega = 920\,\mathrm{cm}^{-1}$. The $\alpha_w(\omega)$ spectrum of bulk liquid water [38] has two maxima at frequencies of $\omega = 200$ and $700\,\mathrm{cm}^{-1}$. The higher integrated intensity of IR radiation absorption for bulk water is caused by its density, which is higher, on average, than the density of water clusters by a factor of 1.4. However, in the presence of hydrocarbon molecules in these clusters, the density is not a determining factor in the absorption of IR radiation. The expansion of the system owing to the attachment of hydrocarbon molecules results in an increase in the number of vibration modes including the $0 \le \omega \le 1000\,\mathrm{cm}^{-1}$ frequency range of the $\alpha(\omega)$ spectrum. The orientation of acetylene molecules on a tangent to the water cluster gives a stable amplification of the integrated intensity of the $\alpha(\omega)$ spectrum with the growth of acetylene concentration. This is promoted by the repulsion of the positive charges of C_2H_2 molecules. The bending band of the $\alpha(\omega)$ spectrum of gaseous acetylene is located at a frequency of $\omega = 730\,\mathrm{cm}^{-1}$ [39]. Thus, the attachment of acetylene molecules by water clusters strengthens the integrated I_{tot} absorption intensity.

Ethane molecules have the more chaotic orientation. This results in a more random change of the vibrations' intensity with the growth of the number of C_2H_6 molecules in clusters. As a consequence, the behaviour of the IR absorption spectrum for these systems is less stable when the number of C_2H_6 molecules changes. After absorption of one ethane molecule, the absorption of external IR

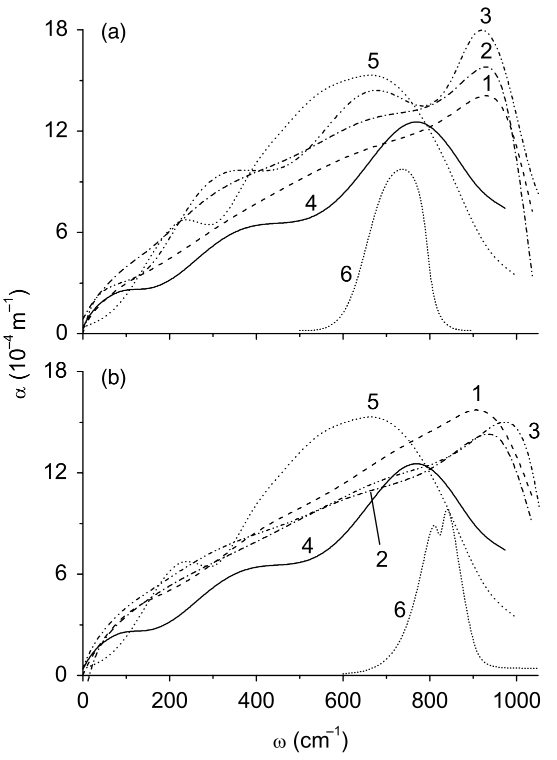

Figure 5. Absorption coefficient of IR radiation for cluster systems: (a) 1, $C_2H_2(H_2O)_n$; 2, $(C_2H_2)_2(H_2O)_n$; 3, $(C_2H_2)_i(H_2O)_{20}$. (b) 1, $C_2H_6(H_2O)_n$; 2, $(C_2H_6)_2(H_2O)_n$; 3, $(C_2H_6)_i(H_2O)_{20}$; 4, $(H_2O)_n$; 5, $\alpha_w(\omega)$ function of bulk water, experiment [38] and 6, experimental spectrum for gaseous hydrocarbon: (a) C_2H_2 and (b) C_2H_6 [39].

radiation in the investigated frequency range by ultra-dispersed water systems is also amplified (Figure 5(b)) and the form of the curve becomes smoother. However, the following addition of C_2H_6 molecules results in some decrease of the IR radiation absorption, at least at frequencies of $\omega > 310\,\text{cm}^{-1}$. The values of the α coefficient for the systems consisting of heteroclusters are higher than that for a cluster system of pure water almost in all frequency ranges (except for the area of $690 \leq \omega \leq 800\,\text{cm}^{-1}$). The principal maximum of the $\alpha(\omega)$ frequency spectrum appears at $\omega = 910\,\text{cm}^{-1}$ ($C_2H_6(H_2O)_n$ system) and $\omega = 973\,\text{cm}^{-1}$ ($(C_2H_6)_2(H_2O)_n$ and $(C_2H_6)_i(H_2O)_{20}$ systems). The part of the $\alpha(\omega)$ spectrum determined by the bending vibrations of gaseous ethane molecules has the doubled maximum in the $810 \leq \omega \leq 840\,\text{cm}^{-1}$ frequency range [39].

Water clusters including clusters absorbing acetylene or ethane molecules are capable of re-emitting the falling IR radiation. Calculations show that the disperse system consisting of pure water clusters has low values of P radiation power, in comparison with the system enriched with acetylene (Figure 6(a)). For the disperse system formed by pure water, two characteristic frequencies of IR radiation are observed: $\omega_1 = 657\,\text{cm}^{-1}$ and $\omega_2 = 973\,\text{cm}^{-1}$. The maximal value of emitted radiation power corresponds to a frequency of $970\,\text{cm}^{-1}$ when only one C_2H_2 molecule is present in the clusters, and to a frequency of $910\,\text{cm}^{-1}$ at the presence of two acetylene molecules in every cluster of the system. After adsorption of the second C_2H_2 molecule by clusters, the radiation power of disperse systems is increased. Moreover, the absorption of ethane molecules by water clusters causes the essential decrease of clusters' P radiation power (Figure 6(a), insert). Arrangement of C_2H_2 molecules on a tangent to a surface of water clusters makes their structure more dense [40]. Due to C atoms, the acetylene molecule is attached to the cluster. Due to H atoms, the molecule keeps a tangent direction to the water cluster and makes it denser. As a rule, $\bar{n}_b$, an average number of hydrogen bonds per molecule, decreases, and $\bar{L}_b$, the H-bond length, increases during the addition of both acetylene and ethane molecules to water clusters [40,41]. When the number of admixture molecules $i < 5$, the value of $\bar{n}_b$ for water clusters with C_2H_2 molecules is higher and $\bar{L}_b$ is lower

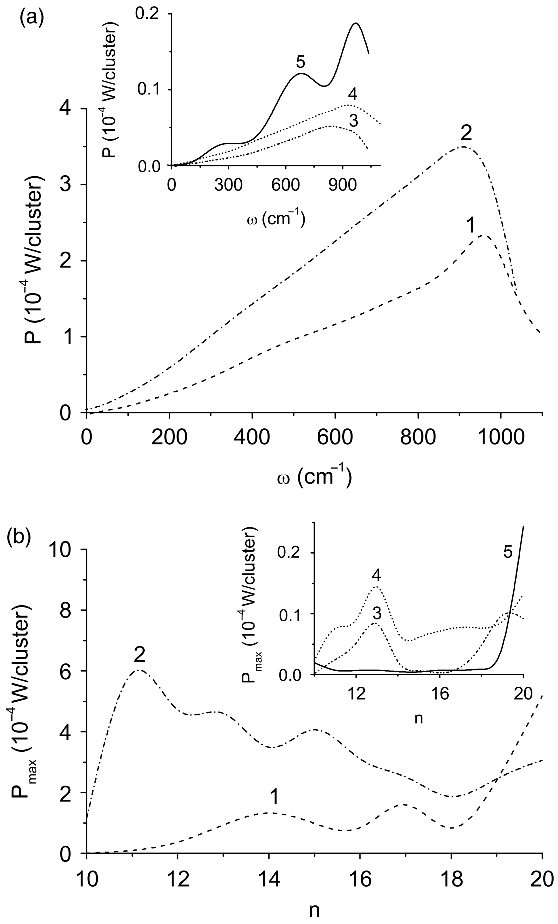

Figure 6. Frequency dependence of (a) $P(\omega)$ IR radiation power and (b) maximum P quantity on n number of water molecules in clusters: 1, $C_2H_2(H_2O)_n$; 2, $(C_2H_2)_2(H_2O)_n$; 3, $C_2H_6(H_2O)_n$; 4, $(C_2H_6)_2(H_2O)_n$; 5, $(H_2O)_n$.

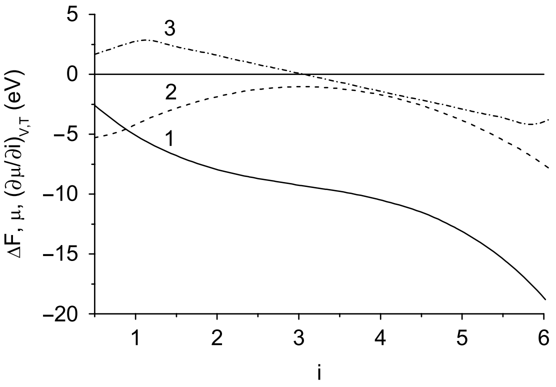

Figure 7. Dependence of 1, the excess free energy ΔF, 2, the chemical potential μ, and 3, the stability coefficient $(\partial\mu/\partial i)_{V,T}$, on the number of C_2H_2 molecules in the $(C_2H_2)_i(H_2O)_{20}$ clusters.

than those for clusters with C_2H_6 molecules. The volume of water clusters with C_2H_2 molecules appears to be 5–10% less than the volume of similar clusters with C_2H_6 molecules. As a result, the D_w self-diffusion coefficient of water molecules in $(C_2H_2)_i(H_2O)_j$ clusters is on average 20–30% lower than that in $(C_2H_6)_i(H_2O)_j$ clusters. The D_a self-diffusion coefficient of C_2H_2 molecules is higher than the D_a value of C_2H_6 molecules by no more than 1%. The decrease of the D_w value causes the amplification of collective vibrations, which, in turn, causes an appreciable amplification of dissipation of absorbed energy. An average $\bar{d}_{cl}$ dipole moment of $(C_2H_2)_i(H_2O)_j$ clusters exceeds the appropriate $\bar{d}_{cl}$ value of $(C_2H_6)_i(H_2O)_j$ clusters on an average by 5%. The ε'' imaginary part of dielectric permittivity of $(C_2H_2)_i(H_2O)_j$ clusters can increase by an order in comparison with the ε'' value of pure water clusters. This causes a sharp amplification of emitted radiation power for the system formed from these clusters. For $(C_2H_6)_i(H_2O)_j$ clusters, the opposite picture is observed, i.e. the ε'' value significantly reduces (up to five times), which causes an appreciable easing of the power of emitted IR radiation by an appropriate cluster system. The $P(\omega)$ spectra for the systems consisting of heteroclusters become smoother than those for the clusters system of pure water. The doubling of C_2H_6 molecules' number in ultra disperse system results in some amplification of radiation power. The principal maxima of the $P(\omega)$ spectra for the systems containing one and two ethane molecules in clusters are located at $\omega = 847$ and $910\,\mathrm{cm}^{-1}$, respectively.

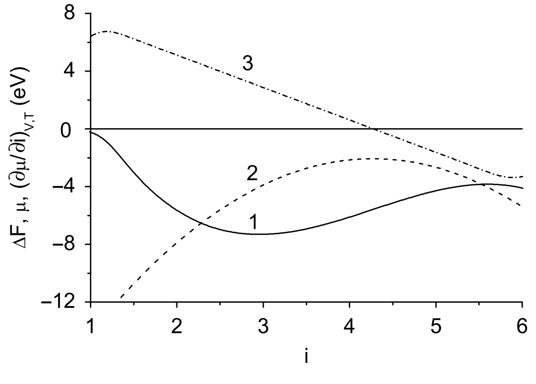

Figure 8. 1, Excess free energy ΔF, 2, chemical potential μ, and 3, stability coefficient $(\partial\mu/\partial i)_{V,T}$, as functions of the number of C_2H_6 molecules in the $(C_2H_6)_i(H_2O)_{20}$ clusters.

The behaviour of the $P_{\max}$ maximal value of clusters in dependence on a number of water molecules containing in clusters is shown in Figure 6(b). Pure water clusters are characterised by an extremely low rate of energy dissipation up to the size $n = 18$ (an insert in Figure 6(b)). For $(H_2O)_n$ clusters with $n > 18$, the radiation power is sharply increased, but still remains low enough in comparison with the similar characteristic of clusters containing C_2H_2 molecules. The maximal values of the radiation power of water clusters adding one C_2H_2 molecule up to the size $n = 18$ are considerably lower than the $P_{\max}$ quantity of $(C_2H_2)_2(H_2O)_n$ clusters. Almost everywhere, the $P_{\max}$ values for clusters of the system where each aggregate contains two ethane molecules exceed the appropriate characteristics of aggregates of the system with one C_2H_6 molecule. At the same time, clusters containing ethane molecules, as a rule, have the higher $P_{\max}$ values than pure water clusters. Water clusters with $n = 10$, 16 and 20 are an exception here.

The factor $(\partial\mu/\partial i)_{V,T}$ [40], which characterises a change in the thermodynamic stability of an aggregate depending on its composition (the number of molecules i in the given case), reflects the cluster stability in the most exact manner. Figure 7 shows a change in the excess free energy ΔF (curve 1), chemical potential μ (curve 2) and thermodynamic stability coefficient $(\partial\mu/\partial i)_{V,T}$ (curve 3) with the addition of C_2H_2 molecules to the $(H_2O)_{20}$ cluster. In general, ΔF decreases with an increase in i, the chemical potential is negative and has the highest value at $i = 3$, and $(\partial\mu/\partial i)_{V,T}$ vanishes to zero after $i = 3$. Thus, the $(H_2O)_{20}$ cluster is thermodynamically stable if it adsorbs at most three C_2H_2 molecules.

Figure 8 shows how the excess free energy ΔF, chemical potential μ and the derivative $(\partial\mu/\partial i)_{V,T}$ for $(C_2H_6)_i(H_2O)_{20}$ clusters vary with i. It is seen that $\Delta F(i)$ has a minimum, and $\mu(i)$, a maximum near $i = 4$. At $i > 4$, the derivative $(\partial\mu/\partial i)_{V,T}$ becomes negative, suggesting the thermodynamic instability of water clusters that took up more than four ethane molecules.

5. Conclusion

Results of the molecular dynamic calculation of hydrocarbon molecules captured by ultra disperse water medium show that the model used provides a good representation of absorption effects as well as structural and dielectric properties. It was established that acetylene molecules are at a tangent to the water core of the $(C_2H_2)_i(H_2O)_n$ clusters. While in $(C_2H_6)_i(H_2O)_n$ clusters, each C_2H_6 molecule is directed to the water core of the aggregate arbitrarily, i.e. its C–C axis is not directed to the cluster's centre of mass and does not have a tangent direction to the aggregate's core. Addition of one acetylene or ethane molecule is accompanied by the increase of IR radiation absorption coefficient of disperse systems. However, during the further increase of admixture molecules' concentration in water clusters, the α coefficient grows in the case of addition of C_2H_2 molecules and decreases at the absorption of C_2H_6 molecules. Also, after adding C_2H_2 or C_2H_6 molecules by disperse water systems, the frequency corresponding to the maximum of IR radiation absorption is also increased. Absorption of acetylene molecules by water clusters results in a significant amplification of the radiation power by cluster systems. Thus, the dissipation rate of acquired energy grows with the increase in C_2H_2 molecules' concentration in the system. Clusters with 20 water molecules not containing or containing only one C_2H_2 molecule and cluster with 11 H_2O molecules capturing two C_2H_2 molecules have the highest radiation power. On the contrary, the ultra disperse system made up of water clusters enriched with ethane molecules loses the emitting power of heat. But with the growth of ethane concentration, the IR radiation power is amplified and the maximum of emitting power is shifted from $n = 19$ to $n = 13$. Examination of the behaviour of the function $(\partial\mu/\partial i)_{V,T}$ shows that the H_2O cluster remains stable until the number of added C_2H_2 molecules exceeds 3 and C_2H_6 molecules exceeds 4.

As a whole, clusterisation and absorption of hydrocarbon molecules by clusters results in a decrease in the greenhouse effect because of the decrease in absorption centres' number of IR radiation and the insufficient amplification of its integral intensity caused by the absorption of C_2H_2 and C_2H_6 molecules.

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