



Dynamics of Some He and Ar Clathrate Hydrates. Computer Simulation Study

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Abstract

Molecular dynamics simulation of solid solutions of He and Ar in ice II at $T \sim 200$ K has shown that amplitudes of water molecule oscillations diminish when noble gas atoms fill the cavities of the hydrogen-bonded framework. The effect of Ar atoms is more pronounced. Slow diffusion of He along trigonal axis is observed when not all the cavities are filled. He and Ar atoms exert little effect on frequencies of translational and librational vibrations of the water molecules. Type II empty gas hydrate framework (CSII) is quite stable at T 200 K. Amplitudes of oscillations of water molecules which occupy different crystallographic positions are different. Filling of the cavities in the CSII framework with Ar atoms causes diminution of the amplitudes of water molecule vibrations, and difference between amplitudes of vibration of molecules occupying different positions becomes less pronounced. Large cavities in the CSII framework can accommodate two Ar atoms without distortion. No diffusion of guest Ar atoms was observed at 200 K in CSII framework.

Introduction

Argon hydrate was obtained by P. Villard in 1896 soon after the discovery of argon itself [1]. Its composition was found to be close to $\text{Ar} \cdot 6\text{H}_2\text{O}$. The chemical nature of noble and other gas hydrates was not clear until the end of the 40s of the XX century when von Stackelberg [2] established the crystal structure of many of them. It turned out that gas hydrates belong to inclusion compounds in which the host is hydrogen bonded network formed by water molecules and gas atoms or molecules are the guests. It has been believed for a long time that Ar hydrate crystallises in so-called CSI structure (46 water molecules in primitive cubic unit cell with $a \sim 12$ Å). It was only in 1984 that strong evidence of the fact that argon clathrate crystallises in the CSII structure (136 water molecules in face-centred cubic unit cell with $a \sim 17$ Å) was given [3, 4]. It is well established now that at moderately low pressure the stable form of argon clathrate hydrate has the CSII structure [5–8].

Studies of the Ar-water system under higher pressure have shown that several other argon hydrates exist [7, 9–11]. The CSIII (H) hexagonal phase exists between 460 and 770 MPa [7]. The structure of the tetragonal phase stable at the pressure 770–950 MPa has been determined [11].

Helium is known to be unable to form clathrate hydrates based on the water frameworks built from the convex polyhedra with a great number of pentagonal faces. It was shown rather long ago that He can be dissolved in hexagonal ice Ih [12, 13]. Later [14, 15] it was found that He solubility in ice II is much higher. It was proposed to call this solid solution helium clathrate hydrate. One of the consequences

of the formation of the solid solution of some gas in ice II is impossibility of ice III formation when the temperature and gas pressure are within the field of ice III stability. In our neutron scattering study of heavy water under argon pressure we did not observe formation of ice III [5, 6]. Mixtures of ice Ih and CSII clathrate and of ice II and CSII clathrate were observed at 100 and 300 MPa of Ar, respectively. This led us to the conclusion that Ar can enter the ice II cavities [5]. In this work crystal chemical argumentation in favour of this hypothesis is given. Possibility of formation of Ar solid solution in ice II is also discussed by Dyadin and his co-authors [7].

Host and guest dynamics of clathrate hydrates was studied experimentally, theoretically, and by computer simulation. Incoherent inelastic neutron scattering (IINS) [16–20], NMR [21–25] and dielectric spectroscopy [21, 26] can be mentioned among the experimental methods providing information about clathrate hydrate dynamics. IINS studies of ice II and its He solid solutions [17, 18] have shown that He exerts only a slight effect on the water framework dynamics. Dong and co-authors [18] as well as Belosludov and co-authors [27] performed He clathrate lattice dynamics calculations. Results of neutron scattering by SCII Ar hydrate are presented in several papers [5, 6, 19].

Several molecular dynamics simulation studies of clathrate hydrates have been performed during the last years [28–31]. In our simulation of aqueous systems we gave particular attention to dependence of dynamical characteristics of water molecules on their local environment. Among other systems we studied crystalline [32, 43, 46] and amorphous [33–35] forms of ice. The same interaction model and simulation algorithm were used in the present study, in which

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we simulated dynamics of empty CSII framework, of ice II framework filled with He and Ar atoms, and CSII framework filled with Ar atoms. Results of our simulations of the empty ice II framework have been published earlier [32, 36].

Simulated systems and computational procedure.

As in our other works [32–36, 43, 46], dynamics of the studied systems was simulated in the NVE (microcanonical) ensemble. Periodic boundary conditions were applied. Geometry of water molecules remained constant during the simulation. The equations of motion were integrated using the Verlet algorithm [37] and Grivtsov–Balabayev method of treating constraint equations for bonds of fixed lengths [38]. The total energy per molecule was conserved during the run with an accuracy better than 0.002 kcal/mol.

Water–water intermolecular interactions were described by the atom-atom potential functions proposed in [40]. These functions were used earlier to study the structure and dynamics of stable and metastable water [36, 39, 47], of the hydration of DNA fragments [40–42], dynamics of crystalline and amorphous ices [32–35, 43, 46]. The water molecule in this system of potential functions is a rigid triangle with O–H distances equal to 0.98 Å and tetrahedral H–O–H angle. The main contribution to the interaction energy is due to electrostatic interactions between point charges on the atoms:

$$q_{\text{H}} = 0.34, q_{\text{O}} = -0.68 \text{ (electron charge units).}$$

Non-Coulombic interactions are calculated by formula:

$$E = B/r^{12} - A/r^n, \quad (1)$$

$n = 10$ for O··H interactions and $n = 6$ for H··H and O··O interactions (in the latter case the formula is the classical Lennard–Jones one).

Interactions of water molecules with He and Ar atoms were calculated with the Lennard–Jones 6–12 formula. Parameters of the functions given in [44] were taken as the bases. We performed molecular dynamics simulation of crystalline and liquid argon at 100 K. Density of the crystalline phase was found to be 1.699 g/cm³ at pressure 92 MPa, while density of liquid argon at this temperature and pressure 73 MPa was 1.489 g/cm³. These values are close to the experimental ones [45]. Interaction of a He atom with water molecules of ice Ih and ice II cavities and of an Ar atom with water molecules of ice II and CSII cavities has been also calculated. After these calculations, the parameters of the potential functions taken from the book by Kaplan [44] were slightly changed. They are given in Table 1. Justification of our choice of the parameters describing gas–gas and gas–water interaction will be given elsewhere.

All simulated systems were rectangular boxes containing 576 (ice II framework) and 1088 (CSII framework) water molecules with periodic boundary conditions. Dimensions of the boxes were 22.487, 25.965, 25.012 Å in the case of ice II and 34,334 Å (doubled lattice constant of argon hydrate at

Table 1. Parameters of potential functions

Interaction	A	B	σ	r_0	ϵ
O··O	200	410000	3.56	4.0	0.0244
O··H	3760*	9760	1.61	1.76	2.136
H··H	40	3800	2.14	2.40	0.105
Ar··Ar	1473	22766190	3.40	3.81	0.238
Ar··O	1078	1314830	3.27	3.68	0.218
Ar··H	300	116470	2.70	3.03	0.194
He··He	22.65	4317	2.56	2.87	3.03
He··O	359	187350	2.84	3.18	0.172
He··H	41	6736	2.34	2.62	0.628

* $n = 10$, for all other pairs of atoms $n = 6$.

Energy in kcal/mol, distance in Å.

$r = \sigma$, $E = 0$; $r = r_0$, $E = -\epsilon$.

$P = 300$ MPa [5, 6] in the case of CSII framework. Ice II box contained 96 cavities, CSII box contained 64 large (hexakaidecahedral) and 128 small (dodecahedral) cavities. In this paper results on the ice II framework with half and all the cavities filled by He and Ar atoms as well as on empty CSII and CSII framework in which all the small and large cavities are filled by one Ar atom will be presented. Simulation of the CSII framework with several large cavities filled with two Ar atoms was also done. Dynamics of the simulated systems is characterised by dependence of mean square displacement of centres of mass of water molecules and of guest atoms on time $\langle \Delta r^2 \rangle(t)$ and by density of vibrational states (DOS) of water molecule centres of mass and of water hydrogen and guest atoms. Velocity autocorrelation functions were calculated during the simulation and their Fourier transformation gave rise to DOS of corresponding centres of mass or atoms. Trajectories 40 ps long were generated to obtain dynamic characteristics of the systems based on an ice II framework and of an empty CSII framework and 60 ps long to obtain these characteristics for filled CSII framework. 40 ps trajectories were divided in 40 fragments 1 ps each, so the reported $\langle \Delta r^2 \rangle(t)$ and DOS mean functions were obtained by averaging over 40 such segments. As the period of Ar oscillations in large CSII cavities proved to be longer than 1 ps, 60 ps trajectory obtained for this system was divided into 20 segments 3 ps each. Kinetic energy in all simulated systems corresponded to temperature of about 200 K.

Results and discussion

He and Ar solid solutions in ice II

Water molecules occupy two crystallographically different positions in the ice II framework. Molecules of the first type form almost flat six-membered rings. Rings formed by the second type molecules are puckered and their configuration is close to that of six-membered rings found in the structures of ices Ih and Ic. Hydrogen bonds between molecules of the first type are shorter than the bonds between molecules of the second type. Rings of these two kinds are placed above one another in the ice II crystal structure forming rather wide

Table 2. Maximum values of $\langle r^2 \rangle(t)$, \AA^2 , water molecule centres of mass, $T \sim 200$ K

Type of molecule	Ice II					CSII	
	Empty	He 50%	He 100%	Ar 50%	Ar 100%	Empty	Ar 100%*
1	0.2094	0.2011	0.1896	0.1694	0.1274	0.3526	0.2886
2	0.2328	0.2082	0.1985	0.1703	0.1463	0.3651	0.2897
3	–	–	–	–	–	0.3864	0.2922
All	0.2116	0.2048	0.1941	0.1699	0.1368	0.3584	0.2891

* One Ar atom in each cavity (large and small).

channels going along the trigonal axis. We have found earlier that the amplitude of oscillations of the molecules of the first type is less than the corresponding value of the molecules of the second type [32, 43]. As to density of vibrational states, a difference between two types of the molecules was also found and can account for subtle peculiarities of the experimental spectra derived from IINS experimental data [43].

Filling of the cavities by noble gas atoms leads to decrease of amplitude of molecular centre of mass oscillations. As $\langle \Delta r^2 \rangle$ is an attenuating function of time and 1 ps is too short a period of time to determine exact values of amplitude of vibrations, we use the value of the first maximum of this function to characterise these amplitudes. The maximum values of $\langle \Delta r^2 \rangle (r_{\max}^2)$ are some 25% higher than the values at infinite time. As is seen in Table 2, filling of the cavities of the ice II framework gives rise to decreasing r_{\max}^2 values. Difference in r_{\max}^2 values for molecules of different crystallographic types becomes negligible when half of the cavities is filled either with He or Ar atoms but is more pronounced when all the cavities are filled (Table 2, Figures 1a, 2a, 3 and 4). It is quite natural, because when only part of the cavities are filled, diversity of local environment of water molecules is much wider as compared to the cases when no or all the cavities contain guest molecules. Diversity of types of local environments of water molecules in partially filled frameworks cannot be reduced to two crystallographically different types of molecules in the empty framework.

Argon atoms diminish amplitude of water molecule vibrations much stronger than helium atoms (Table 2). Average square amplitudes of oscillations of helium atoms are twice as great as those of water molecules. It is of interest that amplitude of He atom oscillations along trigonal axis (z-axis, Figures 1b and 2b) is greater than amplitudes of oscillations along x- and y-axes, when 50% of cavities are filled and is less than along x- and y-axes when all the cavities are filled. Detectable diffusion of helium atoms along the z-axis (along the channels) is observed in partially filled framework (Figures 1a and 1b). No diffusion of helium in ice II framework is seen when all the cavities are filled (Figure 2). We did not detect diffusion of argon atoms in ice II at $T \sim 200$ K either when the framework is partially or totally filled (Figures 3 and 4). Amplitudes of argon atom vibrations are a little less than of water molecule centres of mass.

Entering of He and Ar atoms in an ice II framework produces rather little effect on the density of vibrational states

of water molecule centres of mass and hydrogen atoms in conformity with the IINS experiment [17–19]. As degree of filling increases, main peaks slightly shift to higher frequencies. This shift is better pronounced in Ar solid solutions in ice II. As to vibrations of guest atoms, they are highly anisotropic and depend on degree of filling (Figures 5, 6, 7, and 8). No detectable distortion of the ice II framework on entering noble gas atoms was observed.

Empty CSII and Ar hydrate with this structure

Empty CSII framework proved to be stable in the course of our simulation. There are three crystallographically different water molecules in this structure. Unlike ice II, CSII framework is disordered with respect to positions of protons. This means that the actual number of non-equivalent water molecules is greater. When we compared dynamics of proton-ordered ice IX and of its proton-disordered analogue ice III [46], we found that proton disordering slurs the difference in dynamic properties of water molecules whose oxygen atoms occupy different crystallographic positions. Nevertheless, $\langle \Delta r^2 \rangle(t)$ curves for three types of water molecules of empty CSII framework are noticeably different (Figure 9 and Table 2, two right columns). It is worth mentioning that the most symmetrically surrounded molecules (those sharing six faces of four pentagonal dodecahedra) have the highest amplitudes of vibrations. When in each large and small cavity one argon atom is placed, this difference in $\langle \Delta r^2 \rangle(t)$ curves becomes less pronounced (Table 2). Densities of vibrational state for centres of mass and hydrogen atoms are only slightly affected by the presence of argon atoms in the cavities (Figure 11). Two translational bands with maxima at about 8.3 meV (67 cm^{-1}) and 41 meV (330 cm^{-1}) and two librational bands with maxima at about 57 meV (460 cm^{-1}) and 71 meV (570 cm^{-1}) are present in the simulated spectra of both empty and filled CSII frameworks.

There is an appreciable difference in the dynamics of argon atoms in small and large cavities (Figure 10). Square amplitude (r_{\max}^2) of argon in large cavity is about 4.2 \AA^2 , while this quantity is only 0.8 \AA^2 for argon in small cavity. Our procedure does not allow to determine accurately DOS at low frequency. Period of oscillations of argon atoms in a large cavity can be estimated as about 1.5 ps and of argon atoms in a small cavity as about 0.6 ps.

There is strong belief that hexakaidecahedral cavity accommodate two argon atoms. We placed two argon atoms in

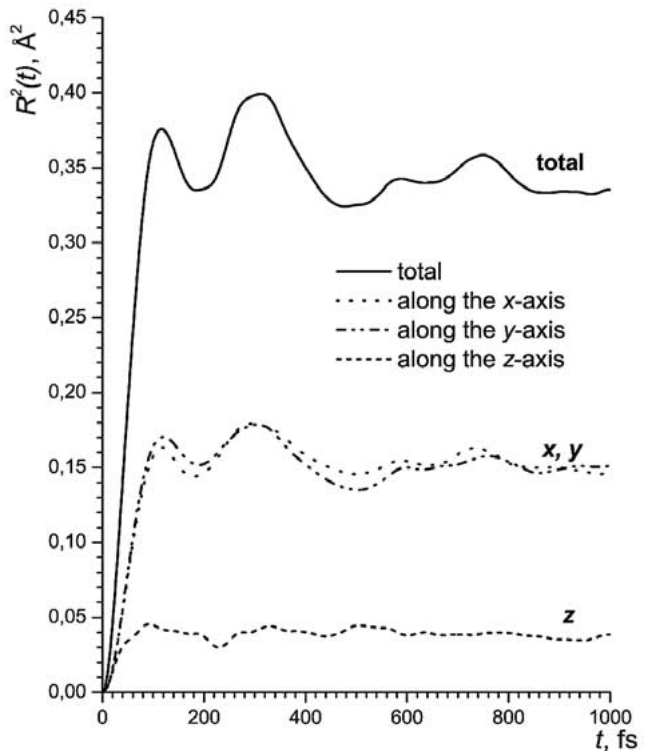
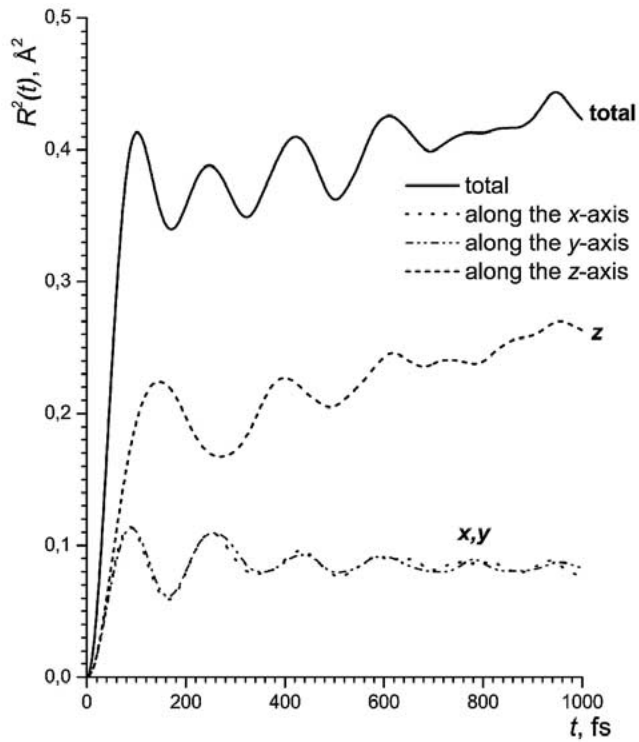
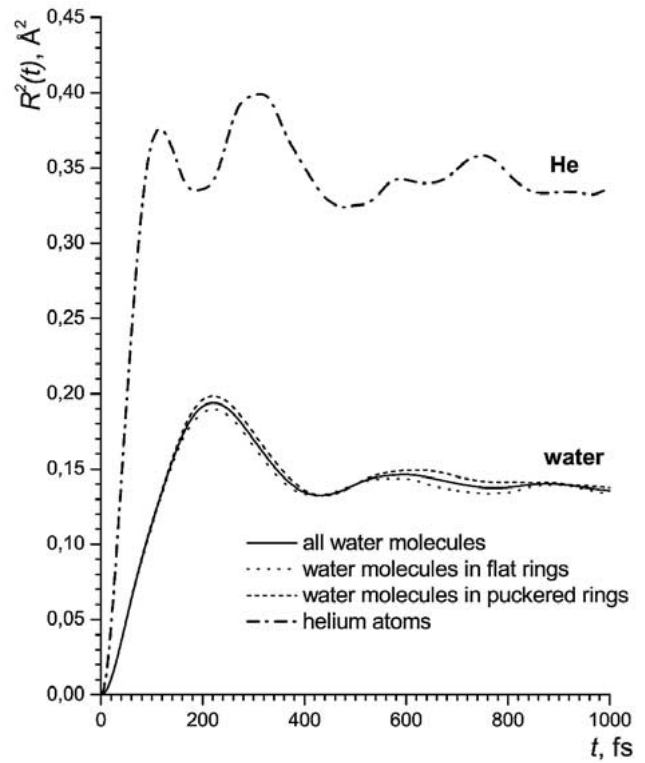
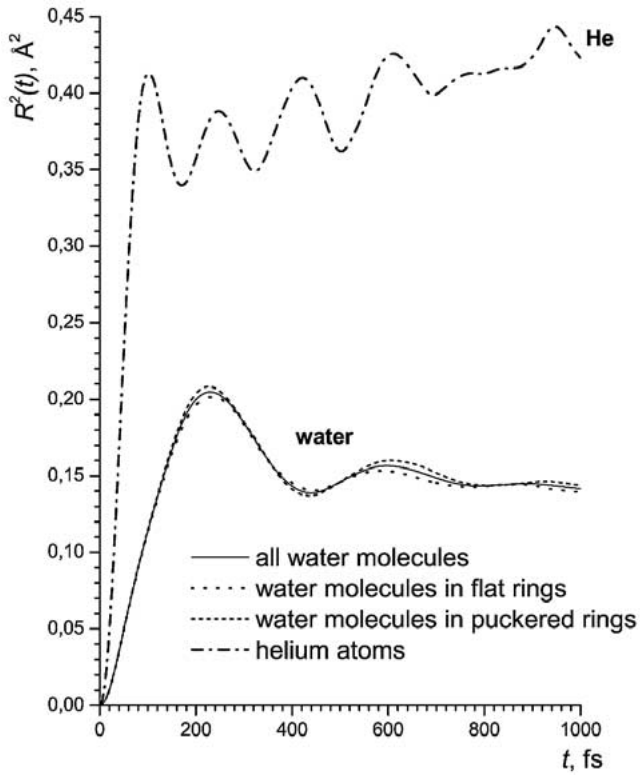


Figure 1. He clathrate hydrate based on the ice II framework with 50% of cavities filled with He atoms. Time dependence of mean square displacements. (a) He atoms and centres of mass of water molecules occupying various crystallographic positions. (b) He atoms along different directions. Diffusion along z-axis is seen.

Figure 2. The same as Figure 1. All the cavities are filled with He atoms. No diffusion of He atoms.

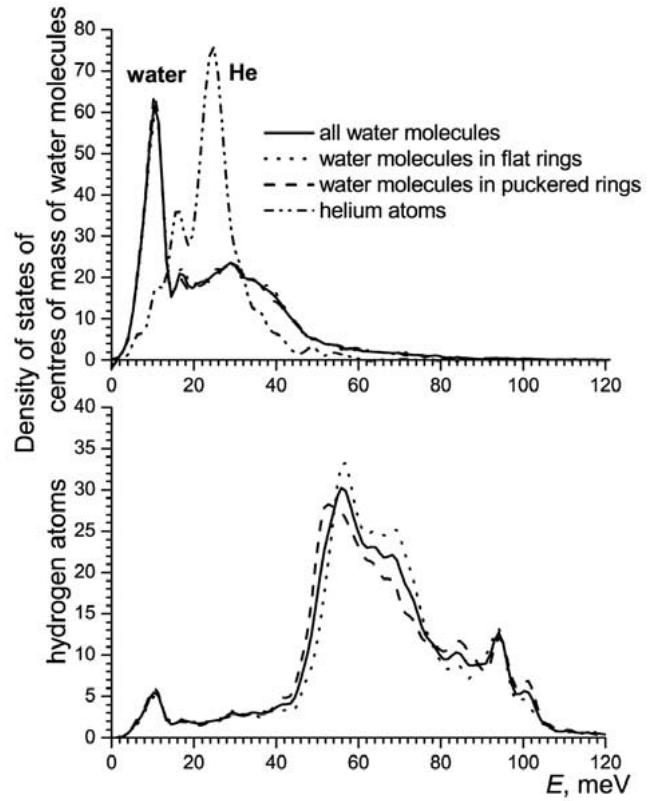
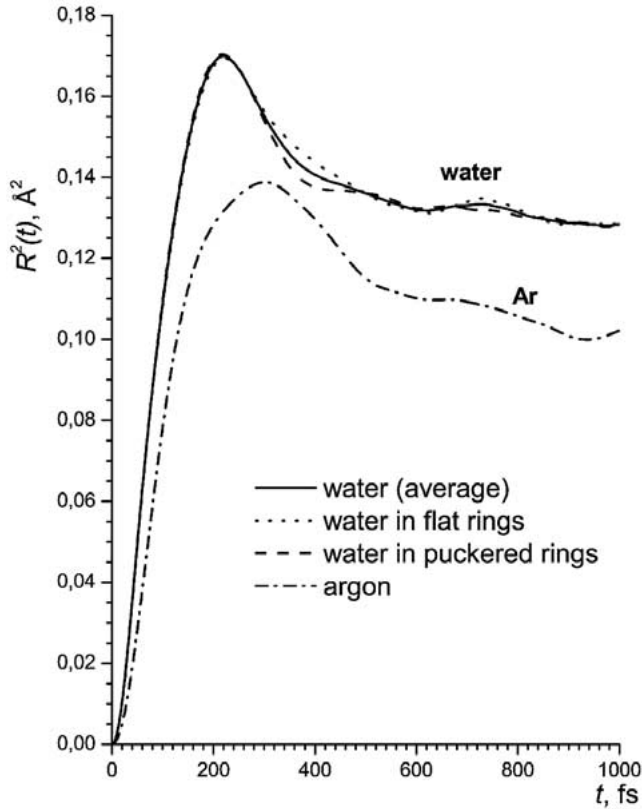


Figure 3. The same as Figure 1a and Figure 2a for hypothetical ice II Ar clathrate with 50% of cavities filled.

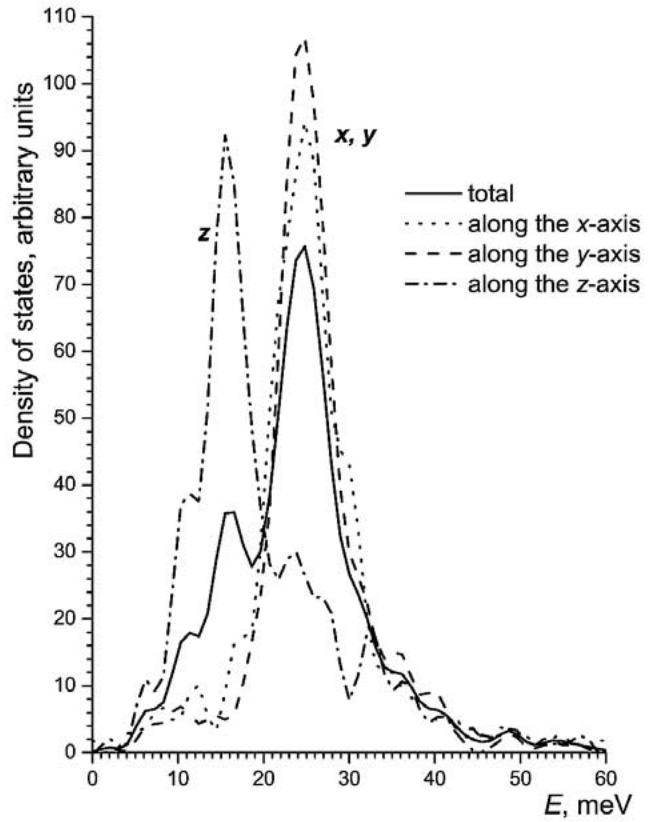
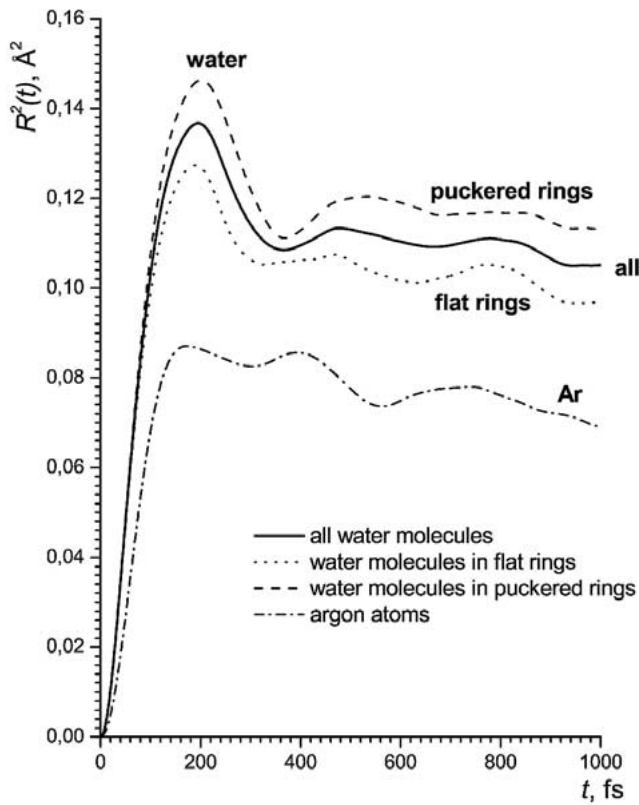


Figure 5. He clathrate hydrate based on the ice II framework with 50% of cavities filled with He atoms. (a) Densities of states of centres of mass and He atoms (top) and of hydrogen atoms (bottom). (b) Densities of state of He atoms along different directions.

Figure 4. The same as Figure 3 for all the cavities filled.

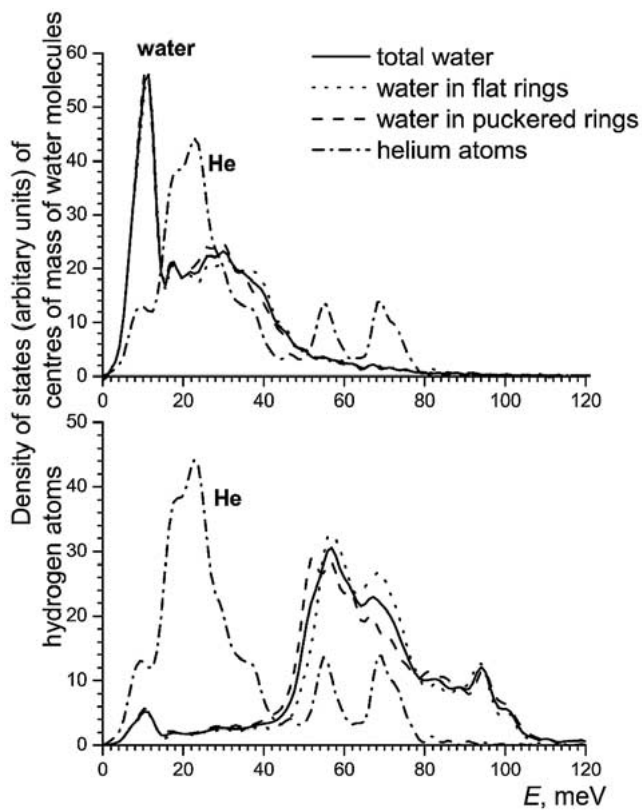


Figure 6. The same as Figure 5. All the cavities are filled with He atoms.

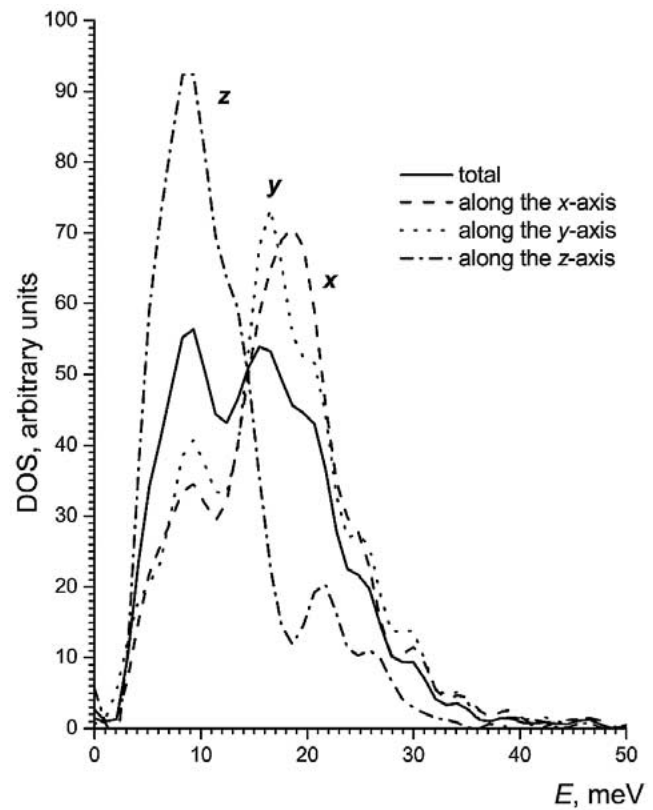
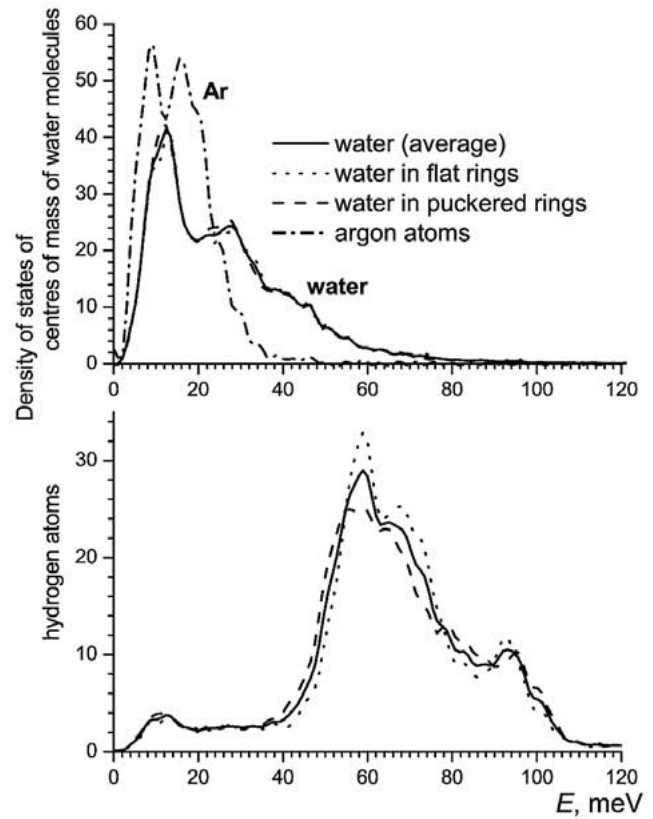


Figure 7. The same as Figure 5 for Ar clathrate with 50% of cavities filled.

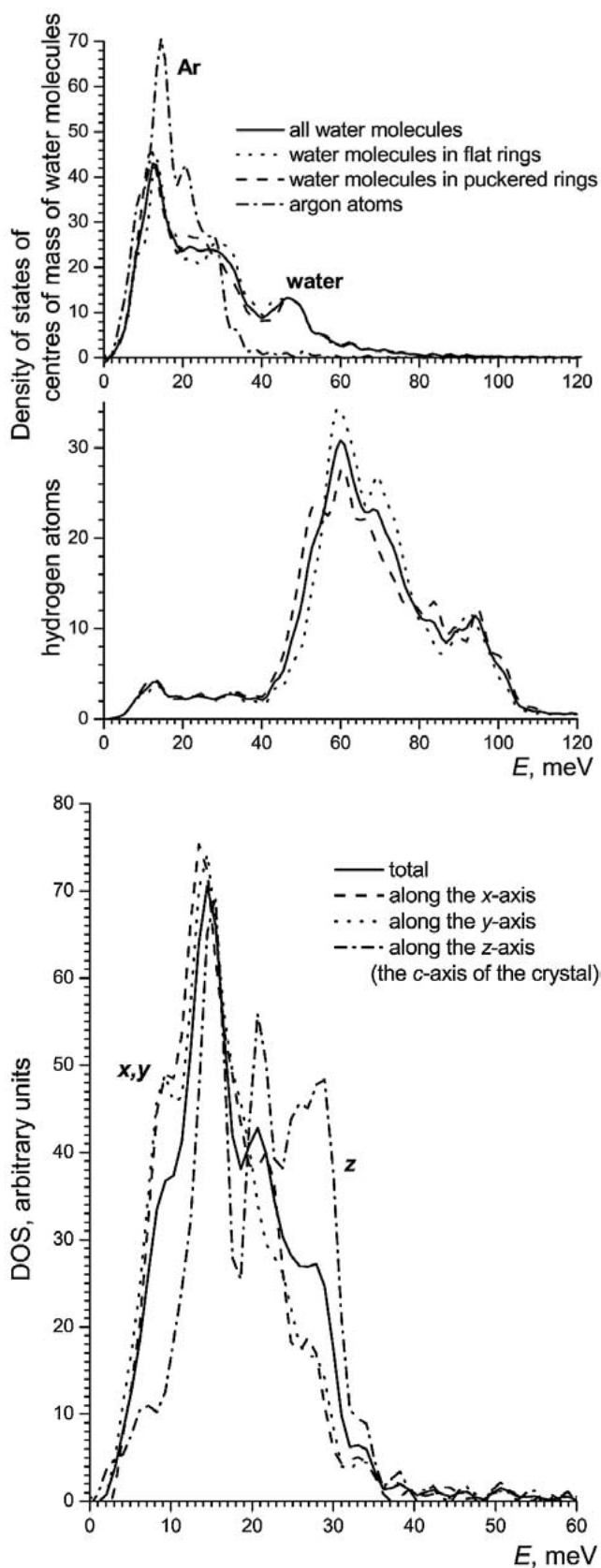


Figure 8. The same as Figure 5 for Ar clathrate with all the cavities filled.

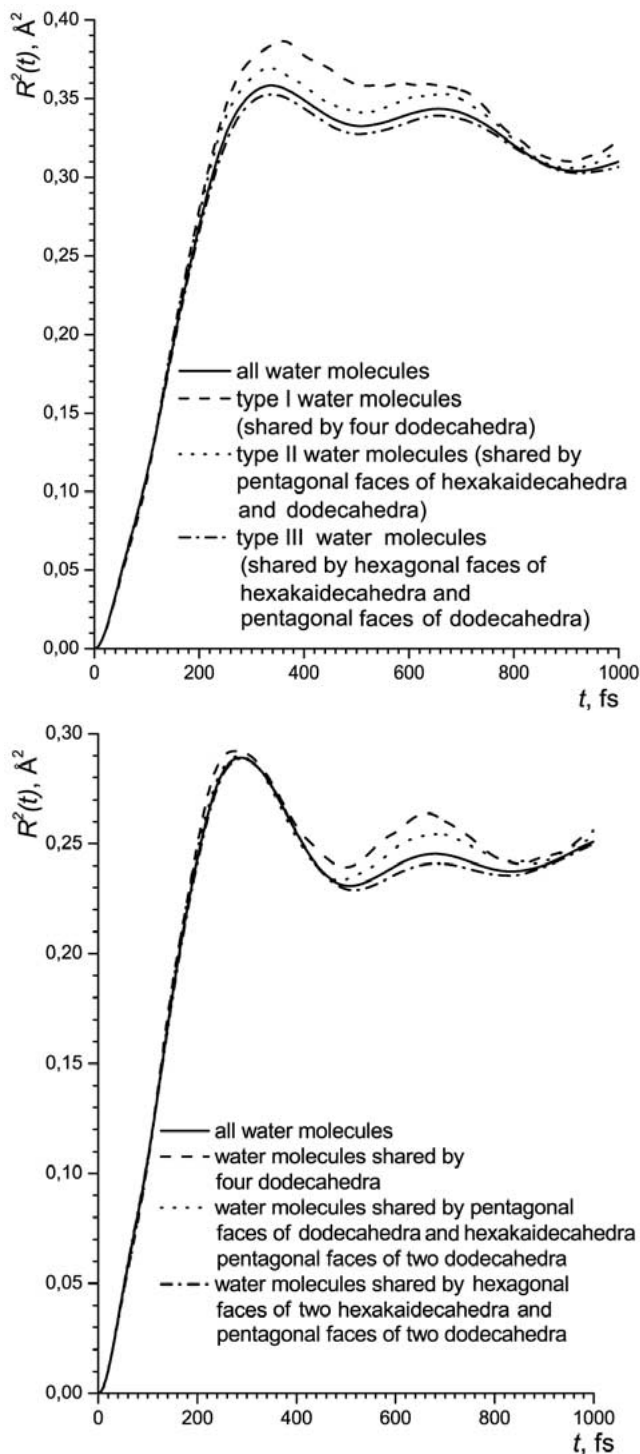


Figure 9. CSII framework. Time dependence of mean square displacements of centres of mass of water molecules occupying various crystallographic positions. (a) Empty framework. (b) Each cavity is filled by one Ar atom.

some of large cavities. They did not distort the geometry of the cavity, nor did they migrate to another cavity. Number of such atoms was too small to obtain good statistics for calculating $\langle \Delta r^2 \rangle(t)$ or DOS. We shall give here an example of their behaviour in the cavity (Figure 12). Mean Ar—Ar distance is 3.4 Å and period of oscillation of this distance is about 0.3 ps. Distance between argon atoms in the Wil-

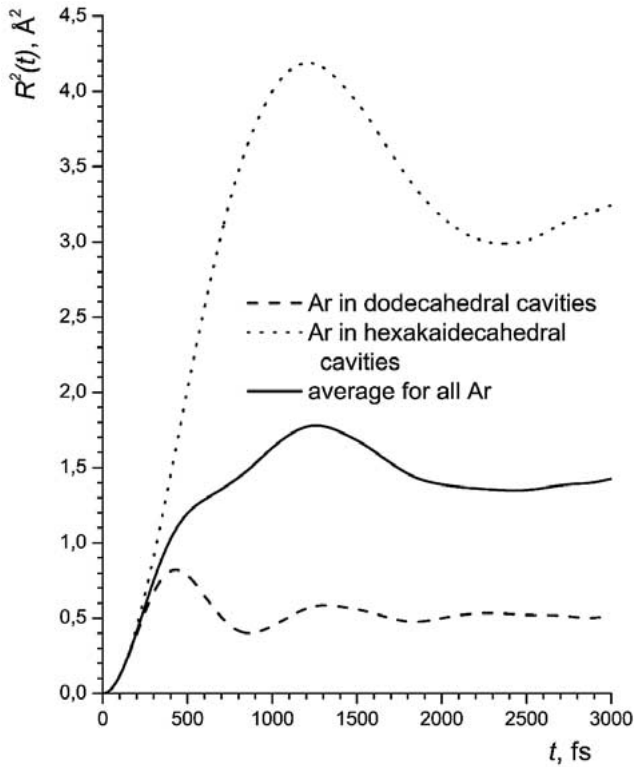


Figure 10. Mean square displacement of Ar atoms in large and small CSII cavities. One Ar atom in each cavity.

liams' "tetrakaidecahedron" ($4^25^86^4$) in the structure of the tetragonal $\text{Ar} \cdot 3\text{H}_2\text{O}$ hydrate was found to be 3.25 \AA [11].

Conclusions

Molecular dynamics computer simulation has shown that filling of the cavities in the ice II framework with He and Ar atoms results in diminution of the amplitudes of water molecule vibrations but only slightly affects the frequencies of water translational and librational oscillations. Ar atoms do not noticeably distort the ice II structure. Slow diffusion of He atoms along trigonal axis is observed when half of the voids are filled. No diffusion is seen when all the voids are filled with He atoms or when half or all of them are filled with Ar atoms at 200 K. Empty CSII framework is quite stable at this temperature. Ar atoms placed in large and small cavities of this framework produce a similar effect on water molecule dynamics as has been found for ice II framework. No Ar atom diffusion was detected at 200 K. Two Ar atoms can be placed in the large cavity of CSII framework without its distortion. The frequency of their oscillations is much greater than of single molecules.

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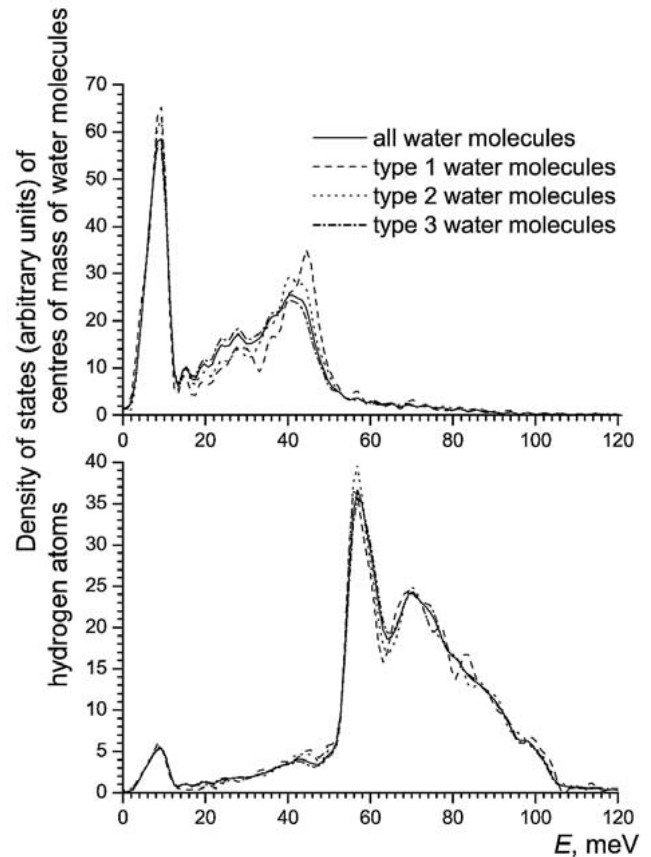
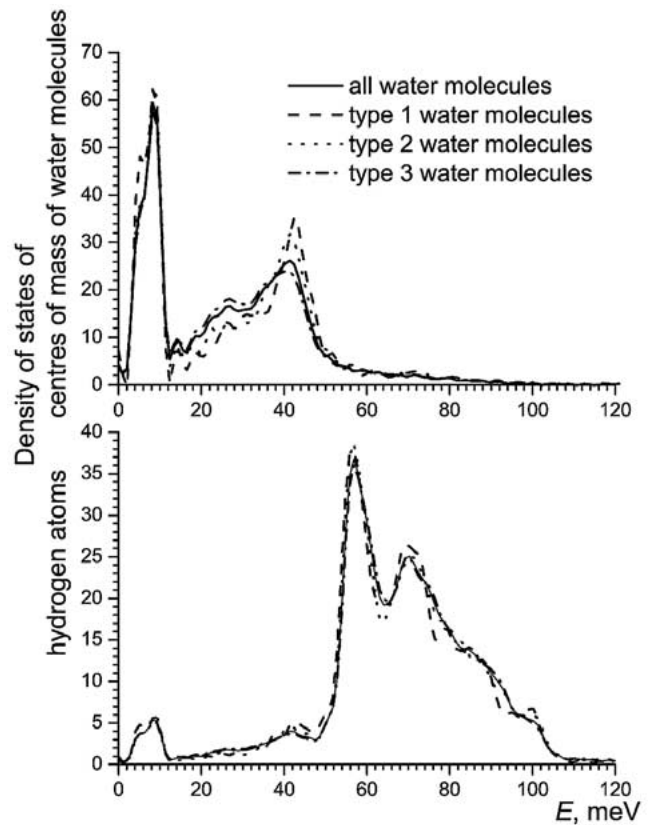


Figure 11. CSII framework. Densities of states of water molecule centres of mass (top) and of hydrogen atoms (bottom). (a) Empty framework. (b) Each cavity is filled by one Ar atom.

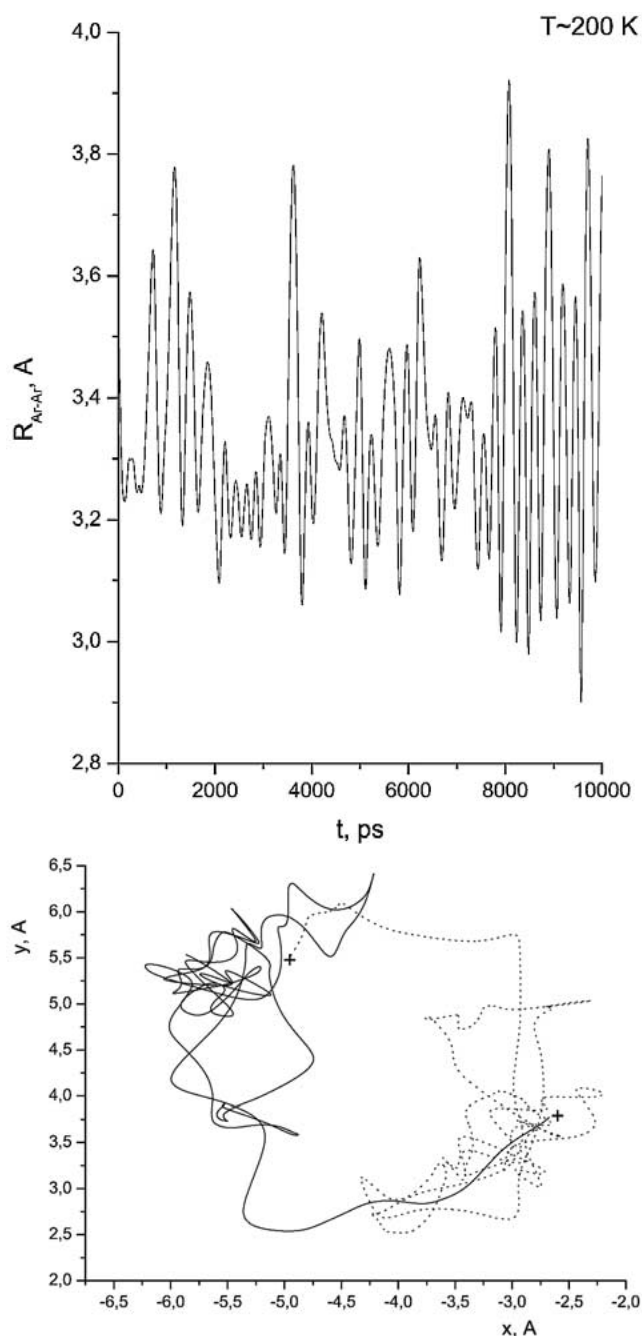


Figure 12. Dynamics of two Ar atoms in one large cavity of CSII framework. (a) Time dependence of the distance between Ar atoms. (b) Projection of their trajectories (10 ps long) on the xy plane. Positions of the atoms in the beginning of the simulation is marked by the crosses.

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