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GENERAL ASPECTS OF HIGH ENERGY CHEMISTRY

Molecular Dynamics Simulation of Ion Sputtering of a Sodium Chloride Solution

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Abstract—The sputtering of an aqueous solution of sodium chloride with a concentration of 0.5 mol/L under bombardment by 1–20 positive ions with initial energies of 50–500 eV has been simulated by a molecular dynamics method. It has been found that the transfer of solute cations and anions to a gas phase requires a threshold energy of bombardment. It has been shown that the solute components occurred in the gas phase both as hydrated ions and in the form of ion pairs in the composition of water clusters. As the energy input into the cell reached ~0.33 eV/particle, the clusters of five or more water molecules were predominantly sputtered.

Keywords: water, ion sputtering, liquid cathode, transfer processes, simulation, molecular dynamics, clusters
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INTRODUCTION

A study of gas discharges excited in liquids and in contact with them is currently a priority line in the physics of plasma and plasma chemistry [1, 2]. In particular, this is related to prospects for the practical applications of these discharges; among them are the decomposition of organic pollutants in water and the disinfection of water [3–5], the modification of polymeric materials [6–8], the application of coatings [9], the formation of micro- and nanostructures [10–12], and the quantitative spectral analysis of solutions for metal ion contents [13–16].

The action of gas-discharge plasma on water and aqueous solutions is accompanied by the transfer of components from a liquid phase into plasma [17, 18]. A change in the composition of plasma leads to changes in its properties and in the rates of processes occurring in it.

Several hypotheses were proposed to explain the mechanisms of the transfer of liquid cathode components into the gas phase. It is assumed that this process is similar to cathode sputtering in reduced-pressure discharges with metal electrodes [19]. An analogy between the transfer of solute components into the gas phase under the action of a discharge a matrix assisted laser desorption/ionization (MALDI) process was hypothesized [20, 21]. It was assumed [22, 23] that a substance is transferred as microdroplets, which evaporate in the plasma, and the ions of a solute undergo desolvation and neutralization. There is also a hypothesis on the contribution of solution electrosputtering under the action of a strong electric field [24].

The use of a transfer coefficient, a quantity analogous to a cathode sputtering coefficient, was proposed for the quantitative characterization of the process. The transfer coefficient is equal to the number of particles passed from the solution into the gas phase per ion incident on the solution surface [17, 18]. The transfer coefficients (s) for solvent (water) molecules and solute components were experimentally determined in studies of discharges with solutions of acids, alkalis, and alkali or alkaline earth metal salts as a cathode [17, 18, 25, 26]. The values of s = 300–500 molecule/ion and s = 0.001–0.1 particle/ion were obtained for water and solute components, respectively. It was established that the transfer of solute components comes into play at a threshold discharge current (a threshold intensity of the ion bombardment of a liquid cathode) [26]. It was found that the threshold intensity values depend on the masses of hydrated cations in solution, and the transfer coefficients increase with the intensity of ion bombardment.

The use of computer simulation in a study of the interaction of plasma with solutions was reported [2]. The processes of the interaction of ions with water were simulated with the use of a classical molecular dynamics method [27, 28]. It was shown that the transfer coefficients of water varied from 100 to 500 molecule/ion depending on the bombarding ion energy (50–500 eV), and the energy consumed for the transfer of a molecule was ~1.5 eV/molecule [27]. Minagawa et al. [28] determined the penetration depth of an ion with an initial energy from 10 to 100 eV into a liquid cathode and the temperature acquired by water as a result of the energy loss by the ion.

The aim of this work was to study the process of the ion sputtering of a more complex system—an aqueous solution of sodium chloride—using a classical molecular dynamics method. In particular, the simulation should give answers to questions on the form in which solute components are transferred into a gas phase and whether the energy threshold of the process is possible.

SIMULATION PROCEDURE

The molecular-dynamic simulation was executed with the use of the Gromacs 4.5.4 program package [29] in the all-atom force field OPLS-AA [30], which takes into account both interactions between the molecules of water and between the molecules of water and ions. In the description of interactions between the molecules of water, the SPC/E model was used [31], and a combined potential, which represented the sum of Coulomb and Lennard-Jones interactions, was used for describing the interactions of Na^+ and Cl^- ions with one another and with water. The Lennard-Jones parameters for each pair of the interacting particles of different types were determined taking into account the Lorentz–Berthelot combination rule with the parameters proposed by Chandrasekhar et al. [32].

The simulation was conducted in the NVE ensemble. This is the statistical ensemble of an isolated macroscopic system with the constant values of volume, number of particles, and energy. Newton's equations were integrated with the aid of the Verlet algorithm [33]. The total simulation time was 50 ps. Electrostatic interactions were considered with the use of the PME-Switch algorithm [34, 35]. Bond lengths in the molecules were limited with the aid of the LINCS algorithm [36]. This limitation assumes that atoms in the molecule of water remained bound in the course of simulation.

A cell with periodic boundary conditions in the form of a parallelepiped with the sizes $x \times y \times z =$ $4.9596 \times 4.9596 \times 9.9192$ nm^3 contained 8112 water molecules, 80 Na^+ ions, and 80 Cl^- ions, which correspond to the concentration of sodium chloride solution of 0.5 mol/L and the solution density of 1026.8 of kg/m^3 at $T = 298$ K. Figure 1 shows the general view of the cell.

A vacuum layer with a thickness of 9.9192 nm was located above the layer of water with a thickness of 80.0808 nm in the cell. A layer of atoms with a thickness of 3.0 nm, which remained unchanged in the course of the entire simulation, was added at the bottom of the layer of water. This allowed us to avoid a shift of the center of mass of the system caused by momentum transfer from the incident ion to the molecules of water.

The initial cell after construction was equilibrated in the NVT ensemble over the time of 500 ps with a time step of 1 fs. A constant temperature was maintained with the aid of a Nose–Hoover thermostat [37, 38]. The equilibration was determined based on the potential energy and temperature and energy fluctuations in the course of simulation.

The bombarding ions had an atomic mass of 23 and a charge of +1. Calculations were performed for the cases when 1, 5, 8, 9, 13, and 20 ions with energies from 50 to 500 eV simultaneously impinged upon the surface of solution. Thus, the energy put into the cell on ion bombardment was varied.

The following geometric criteria were used in the calculation of the number of hydrogenous bonds in the water: distances between oxygen atoms should be $R_{OO} \le 0.33$ nm, distances between the oxygen atom of one molecule and a hydrogen atom of another should be $R_{OH} \le 0.24$ nm, and an angle between the planes of the molecules should be $\alpha \le 30°$ [39]. The results of the simulation were visualized using the Visual Molecular Dynamics (VMD 1.9.1) software [40]. The results were averaged based on five calculations for each particular system.

RESULTS AND DISCUSSION

The radial distribution functions (RDFs) of water (Fig. 2a) and mixed RDFs of NaO_w, ClH_w, and ClO_w (the subscript w indicates that the atom belongs to the molecule of water) (Fig. 2b) were calculated for the confirmation of the correctness of the initial cell equilibration. The functions obtained are consistent with published data [41–43].

The values of interatomic distances (r_{max}), which correspond to RDF maximums for NaO_w and ClO_w, correspond to the radii of hydrated ions, and areas under RDF curves make it possible to determine the numbers of the nearest particles, which surround a given ion, that is, the coordination number (CN) for sodium and chloride ions:

$$CN = 4\pi\rho_\beta \int_0^{r_1} g_{\alpha,\beta}(r) r^2 dr,$$

where ρ_β is the density of particles of this kind around the central atom α, and r_1 is the radius of the first coordination sphere.

The calculated values of r_{max} and CN are consistent with published data [42–44] within the accuracy of the analysis (Table 1). According to the results of the simulation, ion bombardment leads to the destruction of the network of hydrogen bonds and the sputtering of water. As a result, a cavity with a volume from 0.31 nm^3 (at the incident ion energy $\varepsilon_0 = 250$ eV) to 1.97 nm^3 (at $\varepsilon_0 = 500$ eV) is formed at the surface of solution. The penetration depths of ions into solution were 0.8 and 1.3 nm at ion energies of 50 and 100 eV, respectively

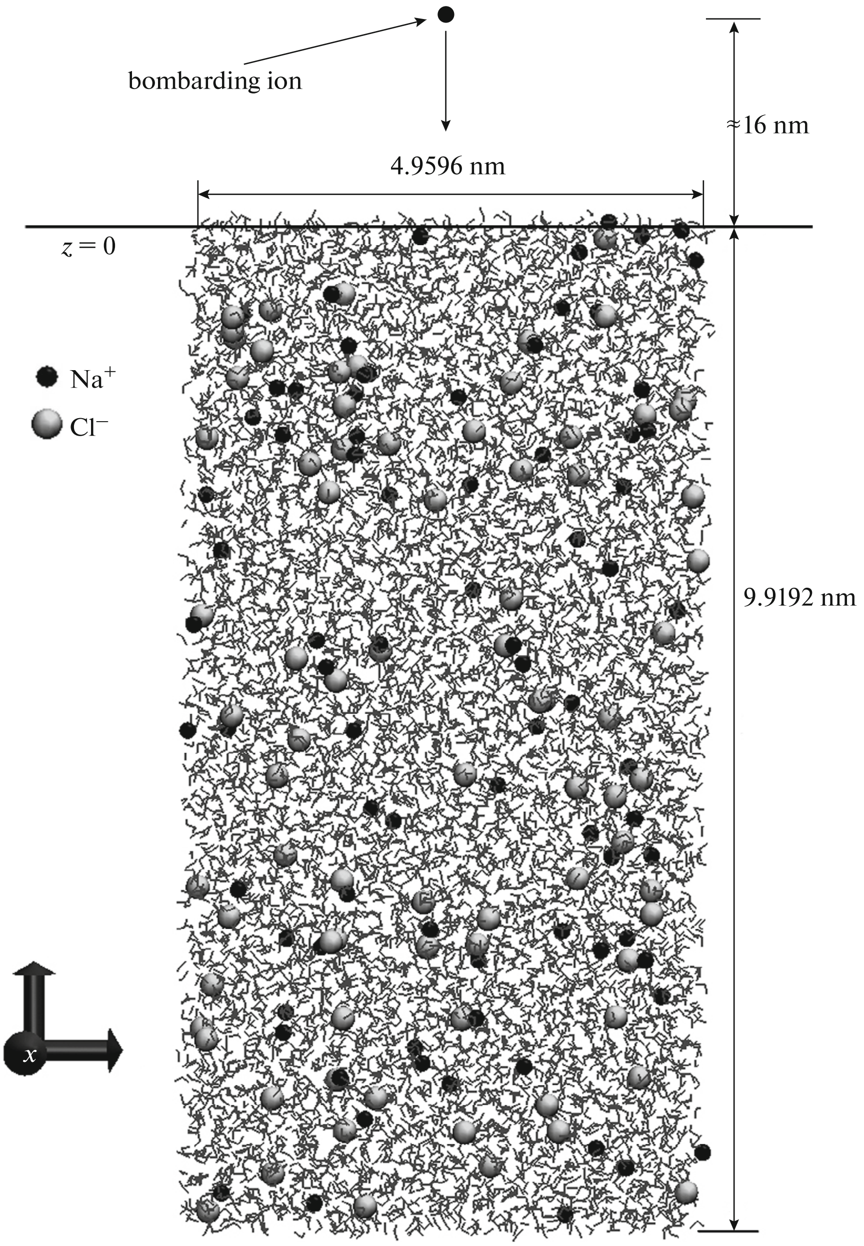

Fig. 1. Initial geometry of the cell containing 8112 water molecules, 80 Na^+ ions, and 80 Cl^- ions.

(Table 2); these results are consistent with data published by Minagawa et al. [28], who found that the ion path in water is 0.7–1.5 nm at an initial ion energy of 10–100 eV.

At a relatively low energy input in the cell (0.14–0.25 eV/particle), the separate molecules of water were predominantly released into the gas phase. An increase in the number of bombarding ions and the energy input in the system leads to an increase in the penetration depth of ions into the liquid phase to 7.5 nm (Table 2) and to the appearance of dimers and trimers from water molecules in the gas phase.

As a threshold value of energy input (0.3 eV/particle) is reached, not only the molecules of water but also solute components (both in the form of hydrated cations and anions and as ion pairs in the composition of water clusters) are released into the gas phase. The fraction of separate hydrated ions can be as high as 30%. The occurrence of the threshold energy of bombardment at which the transfer of solute components is observed is consistent with experimental data [26].

As an example, Fig. 3 shows a cluster containing 3 sodium ions, 3 chloride ions, and 28 water molecules. The molecules of water in the cluster are united by means of hydrogen bonds, whose parameters satisfy

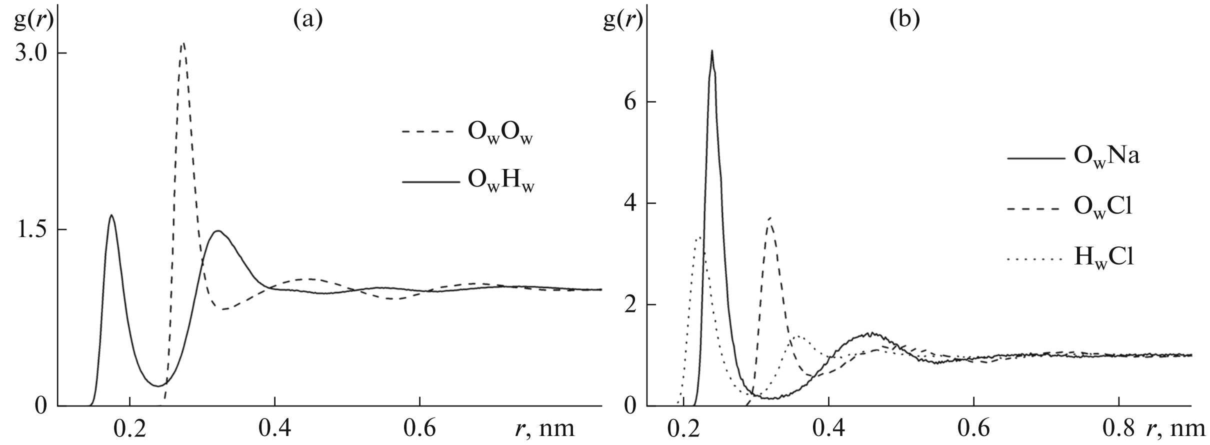

Fig. 2. Radial distribution functions of the oxygen (O_w) and hydrogen (H_w) atoms of water around (a) the oxygen atoms of water and (b) sodium and chloride ions at 298 K.

the geometric criterion. Not only the number of sputtered molecules of water but also the fractions of molecules in the composition of clusters increase with the energy input (Fig. 4). About 20% water molecules occurred as the constituents of water clusters in the gas phase at an energy input of ~0.33 eV/particle in the cell. The maximum fraction of water clusters in the gas phase reaches 45%, and a third of them consist of clusters containing seven or more molecules of water (Fig. 5).

Transfer coefficients were found based on the determination of the numbers of particles knocked out of the solution with the use of atomic coordinates at the final point of the time evolution of the system. In the calculations, we assumed that particles with the coordinates $z > 0$ occurred in the gas phase ($z = 0$ is the coordinate of the initial phase boundary, which remained constant in the course of the simulation). Table 2 summarizes transfer coefficients for the molecules of water. These values are consistent with published data. Thus, the transfer coefficients calculated by Nikiforov [27] in the molecular-dynamic simulation of water sputtering under the action of an incident ion with energies from 300 to 500 eV were 150–450 molecule/ion. Previously, we experimentally found [26] that the transfer coefficients of water in a discharge with the electrolytic cathode of a solution of sodium chloride (c = 0.5 mol/L) compose 300–450 molecule/ion.

The transfer coefficients calculated for the ions of sodium and chloride upon the simultaneous incidence of 13 and 9 ions with initial energies of 200 and 300 eV onto the liquid phase surface were 0.307 and 0.333 particle/ion, respectively. The experimental values of s = 0.258–0.395 were found for Cl^- ions at discharge currents of 30–50 mA [26]; these values are consistent with the results of calculations (Table 2). In the case of Na^+ ions, the calculated values were higher than the experimental ones (s = 0.019–0.152). The difference can be explained by the fact that a strong electric field in the cathodic discharge region prevents the release of positively charged particles into the gas phase, but it is not braking for neutral and negatively charged particles.

Table 1. Calculated values of r_{max} and the coordination numbers of ions

Parameter	Calculated results	Published data
$r_{max}(O_wH_w)$, nm	0.176	0.182 ± 0.005 [41]
$r_{max}(O_wO_w)$, nm	0.274	0.281 ± 0.004 [41]
$r_{max}(O_wNa)$, nm	0.240	0.235 ± 0.008 [41]
$r_{max}(O_wCl)$, nm	0.320	0.318 ± 0.005 [42, 43]
$r_{max}(H_wCl)$, nm	0.222	0.212 ± 0.006 [42, 43]
CN (Na^+)	5.35	5–6 [42, 43]
CN (Cl^-)	6.75	6–8 [42, 43]

CONCLUSIONS

Thus, the results of the simulation by a classical molecular dynamics method in accordance with experimental data show a threshold character of solute transfer under the action of the ion bombardment of solution. It was established that the ion sputtering led to the release of both hydrated ions and ion pairs as the constituents of water clusters into the gas phase. As the energy input in the cell reached ~0.33 eV/particle, the clusters of five or more water molecules, including those containing solute ions, were predominantly sputtered.

Table 2. Average values of the ion paths in a liquid phase (λ_i) and the transfer coefficients of water molecules $s(H_2O)$ and solute components (s_i) calculated by a molecular dynamics method

Number of incident ions	Ion energy, eV	E, eV/particle	λ_i, nm	$s(H_2O)$, molecule/ion	s_i, particle/ion
1	50	0.0061	0.8 ± 0.1	15 ± 2	–
1	100	0.0121	1.3 ± 0.2	37 ± 4	–
1	250	0.0302	2.0 ± 0.2	50 ± 5	–
5	300	0.1814	5.5 ± 0.3	270 ± 10	–
8	300	0.2901	7.2 ± 0.2	310 ± 15	0.125
8	500	0.4835	7.7 ± 0.3	480 ± 35	0.251
9	300	0.3264	7.5 ± 0.3	405 ± 20	0.333
13	200	0.3143	7.0 ± 0.2	280 ± 25	0.307

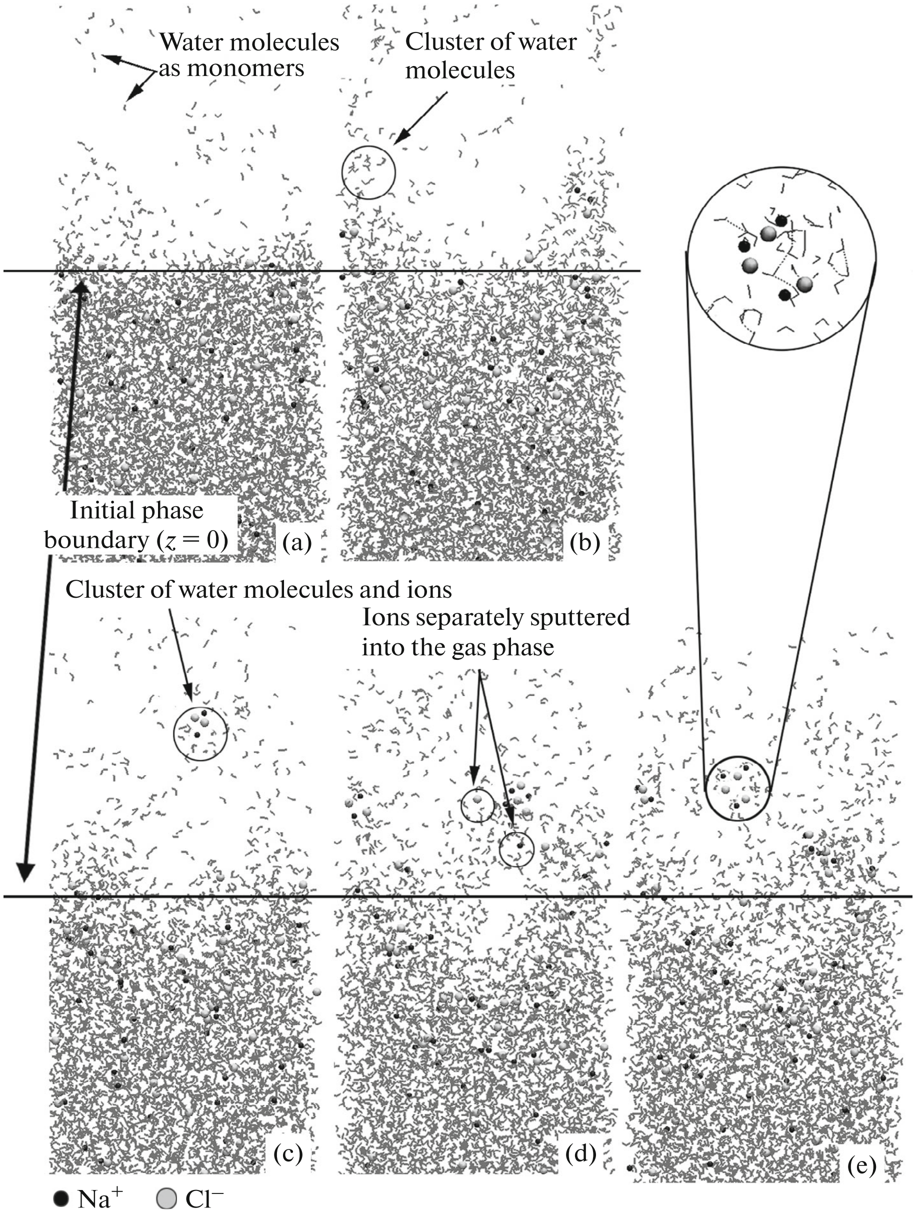

Fig. 3. States of the cell 10 ps after the incidence of (a) 1, (b) 5, (c) 9, (d) 13, or (e) 20 ions onto the surface.

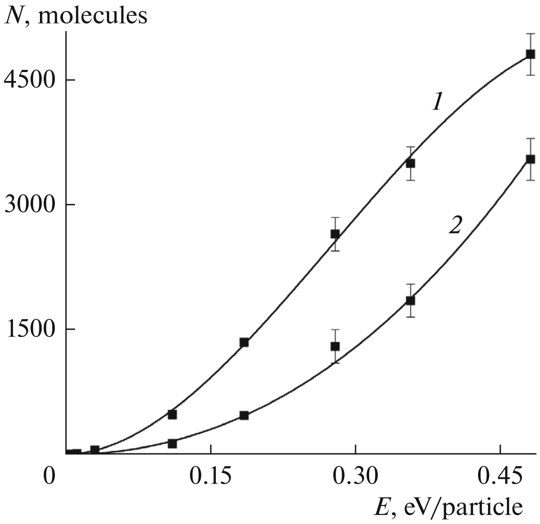

Fig. 4. (*1*) Number of water molecules in the gas phase and (*2*) number of water molecules as the constituents of clusters as functions of input energy (E) in the cell on ion bombardment.

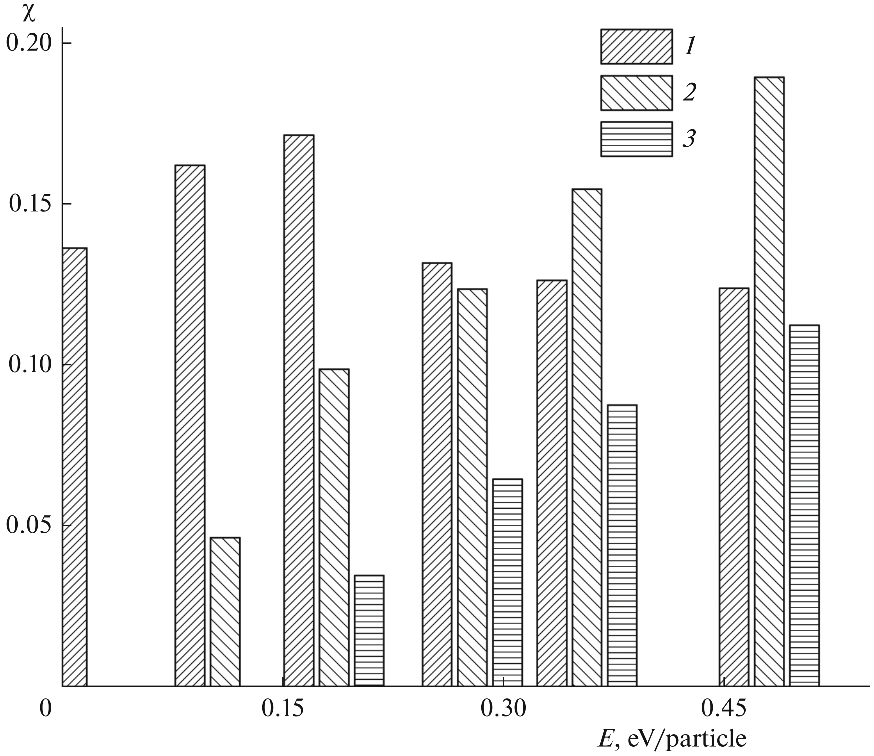

Fig. 5. Mole fraction (χ) of water molecules in the clusters occurring in the gas phase: (*1*) three or four molecules in a cluster, (*2*) five to seven molecules in a cluster, and (*3*) more than seven molecules in a cluster.

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