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Monte Carlo studies of water monolayer clusters on substrates: Hexagonal AgI[a]

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A Monte Carlo procedure is used to study the stability and structure of small water clusters adsorbed on model basal and prism faces of hexagonal AgI. Effective pair potentials for the H_2O–AgI interaction [B. N. Hale and J. Kiefer, J. Chem. Phys. **73**, 923 (1980)] and the revised central force potentials for the H_2O–H_2O interaction [F. H. Stillinger and A. Rahman, J. Chem. Phys. **68**, 666 (1978)] are used to determine average internal cluster binding energy and average cluster–substrate binding energy for water clusters containing 6, 24, and 44 water molecules at temperatures 240, 265, and 298 K. The results (using an effective substrate point charge of $0.4e$) give between 5 and 6 kcal/mol per molecule for each of the above average binding energies. The iodine exposed basal AgI face organizes the H_2O into five- and six-membered rings centered around the exposed I atoms. The prism face appears less effective in promoting ring structure and gives, in general, lower average internal cluster binding energies. The basal AgI face positions the water molecules (in H_2O–substrate high binding sites) about 2.8 A apart while the water–water interactions orient the H_2O dipole moments into configurations favorable for hydrogen bonding. The resulting six-membered ring structure is similar to that in ice I_h (crinkled) basal face layers, and appears to be qualitatively the same for all the temperatures studied.

I. INTRODUCTION

This and previous studies of H_2O on model AgI substrates[1,2] have been motivated by an attempt to understand ice nucleation on substrates and in particular to explain the effectiveness of hexagonal silver iodide as an ice nucleating agent.[3] It has long been thought that this effectiveness is due to the small latice mismatch of hexagonal AgI with ice I_h. However, silver iodide is generally considered to be hydrophobic and there is some indication that the pure AgI substrate does not nucleate ice as efficiently as does the contaminated substance.[4] It appears that one must consider water clustering on the hydrophobic substrate and examine the effect of surface defects, distribution of hydrophilic sites, and the complementary role of lattice mismatch in ice formation. These effects we have attempted to model on a microscopic scale using effective pair potentials for the H_2O–AgI interaction[1] and the revised central force potentials for the H_2O–H_2O interactions of Stillinger and Rahman.[5] Our first studies modeled the adsorption of one and two water molecules on the AgI substrates and included some preliminary investigations of the effects of iodine vacancies, impurity atoms on the (basal) substrate, and simple two and four atomic layer ledges on the basal (iodine exposed) AgI face.[1,2] Similar methods have been applied to modeling one and two water molecules on (rigid) basal and prism faces of ice I_h.[6,7]

Ice nucleation on the AgI substrate necessarily involves the interaction among adsorbed water molecules, as well as the interaction of the H_2O with the substrate. Toward this end, we have extended our model to small water clusters using the Metropolis Monte Carlo technique to examine the equilibrium properties of the adsorbed water. Although the calculations are fully three-dimensional, the resulting clusters are monolayer in character due to the strength of the binding to the AgI substrate. The present work examines the stability and structure of equilibrated clusters containing 6, 24, and 44 water molecules on the basal face and 6 and 24 water molecules on the AgI prism face. In these studies, the substrate is rigid and smooth and contains no defects.

In Sec. II we present the model and discuss features of the H_2O–AgI effective pair potentials. In Sec. III are results of the Metropolis Monte Carlo studies on the 6, 24, and 44 water molecule clusters on the basal face at temperatures of 240, 265, and 298 K and the 6 and 24 molecule water clusters on the prism face of AgI at 265 K. Comments and concluding remarks are given in Sec. IV.

II. THE MODEL SYSTEM AND THE MONTE CARLO PROCEDURE

The silver iodide substrate is modeled by an infinite array of point charge atoms in the wurtzite structure. The lattice parameter $a = 4.58$ and $c = 7.49$ A and an effective charge on the Ag and the I atoms of $0.4e$ are used. The details and parameters of the H_2O–AgI potentials are identical with those given in Ref. 1 except for the value of effective substrate atomic charge. Some simplifications in the evaluation of the potential have been made and will be discussed. The water molecule is represented by the three point charge model of Stillinger and Rahman[5] and when interacting with the substrate is attributed a point polarizability and a Lennard-Jones core.[1] Both the water molecules and the substrate remain internally rigid throughout the calculations. For these studies, the H–O–H bond angle and

TABLE I. Average internal cluster binding energy per molecule $\langle -V_c/N \rangle$ average cluster-substrate binding energy $\langle -V_s/N \rangle$, and the average total binding energy per molecule $\langle -V_{tot}/N \rangle$ for N-molecule water clusters adsorbed on the model AgI basal and prism faces. N_{mc} is the number of Monte Carlo steps in the run and A_c is the constraining area for the cluster. Uncertainties are standard deviations in 100 K (50 K) interval averages for the basal (prism) face results.

T (K)	N	N_{mc}	AgI face	$\langle -V_c/N \rangle$ (kcal/mol)	$\langle -V_s/N \rangle$ (kcal/mol)	$\langle -V_{tot}/N \rangle$ (kcal/mol)	A_c (Å^2)
240	6	700 K	Basal	4.85 ± 0.02	6.29 ± 0.04	11.14 ± 0.06	400
	24	500 K	Basal	6.04 ± 0.06	5.93 ± 0.03	11.97 ± 0.09	400
253	6	800 K	Basal	4.76 ± 0.03	6.23 ± 0.05	10.99 ± 0.08	400
265	1		Basal	...	7.90 ± 0.03	7.90 ± 0.03	∞
	6	700 K	Basal	4.57 ± 0.12	6.25 ± 0.03	10.82 ± 0.15	400
		720 K	Basal	4.68 ± 0.06	6.51 ± 0.10	11.19 ± 0.16	280
	6	200 K	Prism	3.96 ± 0.14	5.36 ± 0.09	9.38 ± 0.23	113
	24	600 K	Basal	5.85 ± 0.09	5.90 ± 0.01	11.75 ± 0.10	400
	24	300 K	Prism	5.31 ± 0.21	5.85 ± 0.24	11.16 ± 0.45	415
	44	600 K	Basal	4.96 ± 0.06	5.75 ± 0.03	10.71 ± 0.09	∞
		460 K	Basal	5.19 ± 0.10	5.67 ± 0.09	10.86 ± 0.19	400
298	6	700 K	Basal	4.43 ± 0.06	6.12 ± 0.04	10.55 ± 0.10	400
	24	500 K	Basal	5.51 ± 0.12	5.71 ± 0.05	11.22 ± 0.17	400
	44	600 K	Basal	5.40 ± 0.05	5.81 ± 0.05	11.21 ± 0.10	400

the O–H bond length are 104.5° and 0.96 A, respectively.

In order to facilitate long Monte Carlo runs in which the AgI–H$_2$O interaction potential must be evaluated many times, four substrate potential grids are generated and used for oxygen-substrate separation distances up to 5 A. These grids represent the Coulomb, the Lennard-Jones, and the two inductive terms in the potential.[1] A linear interpolation is used between grid points. In the grid for the second inductive term (the contribution from polarization of the substrate atoms) the H$_2$O has its dipole moment directed perpendicular to the surface plane. The interpolation from this grid is multiplied by $[1 + (\hat{p} \cdot \hat{z})^2]/2$, where $\hat{p}$ is along the actual H$_2$O dipole moment direction and $\hat{z}$ is perpendicular to the surface. Beyond 5 A, the potential is essentially uniform in xy planes and a five point Lagrange interpolation is used in the z direction. For H$_2$O center-of-mass-substrate surface plane separation distances greater than 10 A, the potential is set equal to zero. These simplifications introduce relatively small errors in the H$_2$O–AgI interaction potential energy and greatly reduce the computation time.

The adsorbed clusters are constrained to a substrate surface area A_c, as shown in Table I. The equilibrium cluster properties are found to be relatively insensitive to A_c as long as A_c is not too small.

In the previous studies of the water monomer on the silver iodide model substrates[1,2] it was found that the magnitude of the optimal adsorption energy is primarily dependent on the value of Q_n, the effective substrate atomic charge. The value of $0.6e$ gives average optimal adsorption energies for the H$_2$O on the model AgI

equal to about 20 kcal/mol. This value is large, both for physical adsorption and in comparison with optimal binding energies of the water molecule on the rigid ice substrates[6,7] using the revised central force potentials for water.[5] Some comparison is possible with experiment if one considers the heat of adsorption of water on AgI at low coverages. The isosteric heat of adsorption approaches the average binding of the single water molecule to the substrate in the low coverage limit. In Fig. 1 is plotted the isosteric heat of adsorption vs H$_2$O coverage on AgI from the data of Corrin and Nelson,[8]
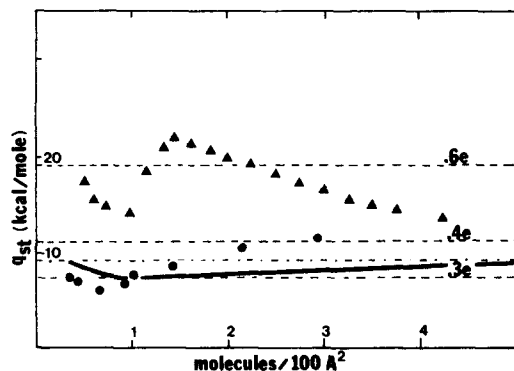
FIG. 1. The experimental isosteric heat of adsorption q_{st} for H$_2$O on AgI from the data of Corrin and Nelson (Ref. 8) (▲), Hall and Tompkins (Ref. 9) (●), and Tcheurekdjian, Zettlemoyer, and Chessick (Ref. 10) (—). The dashed lines are average maximal binding energies of a single water molecule on the model prism face of AgI as calculated for $Q_n = 0.6$, 0.4, and $0.3e$ (Ref. 1). The dot–dashed line is a similar average for a single water molecule on the rigid prism face of ice (Ref. 7), using Stillinger's revised central force potentials (Ref. 5).

Hall and Tompkins,[9] and Tcheurekdjian, Zettlemoyer, and Chessick.[10] Using our model potentials we have calculated average optimal binding energies of the water molecule to the model AgI substrate for $Q_n = 0.6$, 0.4, and $0.3e$. The averages are calculated from Boltzmann weighted sums over the maximal binding energies at the grid points described in Ref. 1. These grid points span a representative region of the substrate from which the entire maximal binding energy surface can be generated. The resulting average optimal monomer binding energies are shown as dashed lines; the dot–dashed line shows a similar average for the water monomer on the rigid ice substrate.[6,7] A judicious choice for Q_n appears to be $0.4e$ and we assume this value in the following calculations.

A Metropolis[11] Monte Carlo procedure similar to that of Barker and Watts[12] and Abraham[13] is used to examine the effect of the substrate in structuring and stabilizing the water clusters on the model silver iodide substrates. In particular we calculate the canonical ensemble averages of the internal (H_2O–H_2O) cluster potential energy V_c and the cluster substrate potential energy V_s. The structure factor for the effective two-dimensional lattice formed by the adsorbed H_2O is also examined. In Fig. 2 are shown the average $|V_c|$ and $|V_s|$ (per molecule) at $T = 265$ K for the six molecule water cluster adsorbed on the model (iodine exposed) basal AgI face, as a function of Monte Carlo step number. It is noted that equilibrium is established after about 100 K (K = 1000) steps and the initial 100 K steps are ignored in obtaining cumulative averages.

III. RESULTS FOR WATER CLUSTERS ON THE MODEL AgI BASAL AND PRISM FACES

In the previous study of a six water molecule vapor cluster relaxing in the presence of the model basal AgI substrate we found the relaxed cluster to be monolayer
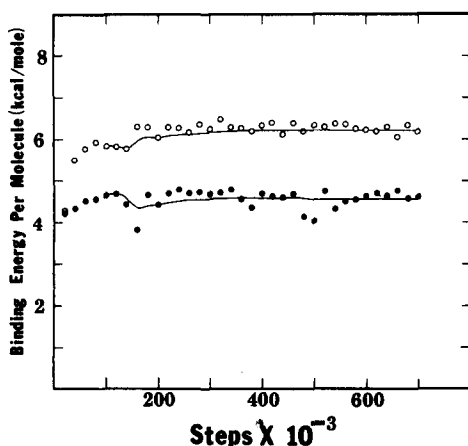

FIG. 2. The cumulative average (solid line) and the average over the previous 20 K steps (O) of the cluster-substrate binding energy per molecule for the six molecule water cluster on the model (iodine exposed) AgI basal face at temperature 265 K vs Monte Carlo step number. The points (●) are averages over the previous 20 K steps of the internal (H_2O–H_2O) cluster binding energy; the solid line through these points is the cumulative average. A_c is 400 Å².
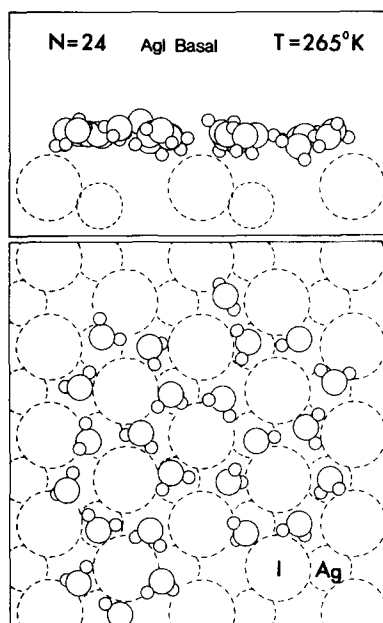

FIG. 3. Snapshot of the 24 water molecule cluster on the model (iodine exposed) AgI basal face after 500 K Monte Carlo steps at 265 K. The upper (lower) view is parallel (perpendicular) to the plane of the substrate. Large (small) dashed circles indicate iodine (silver) atoms in the substrate. The Ag atoms in the second layer are 0.94 Å below the surface plane passing through the center of the exposed iodine atoms. A_c is 400 Å².

in character.[2] Similar studies of a 24 molecule ice cluster near the AgI substrate produced an equilibrated "monolayer" cluster. Hence in these studies the initial configurations for the Monte Carlo simulations are monolayer in structure but with the water molecules placed in sites with random orientation with respect to the surface. On the model (iodine exposed) basal AgI face the 6, 24, and 44 molecule clusters are studied at temperatures 240, 265, and 298 K. A snapshot of the 24 molecule cluster equilibrated at 265 K (after 500 K steps) is shown in Fig. 3. This particular configuration has an internal (V_c) potential energy of -5.78 kcal/mol per molecule and a cluster-substrate (V_s) potential energy of -5.97 kcal/mol per molecule. The upper (lower) part of Fig. 3 shows a view of the cluster parallel (perpendicular) to the substrate surface plane. The average H_2O center-of-mass-surface plane separation distance is 2.7 A. The lower view shows the hexagonal arrangement of the substrate surface atoms and the preference for the cluster to form five- and six-membered rings centered around the exposed I atoms. The H_2O adsorption sites are close to those found for the maximally bound water monomer on the same substrate.[1] Figure 4 shows a similar snapshot of the 44 water molecule cluster on the model AgI basal face at 265 K—after 460 K Monte Carlo steps.

On the model prism face of AgI, the six and 24 molecule water clusters are equilibrated at 265 K. A snapshot of the 24 molecule cluster after 300 K Monte Carlo steps is shown in Fig. 5. This cluster structure can be compared with that of the 24 molecule cluster on the
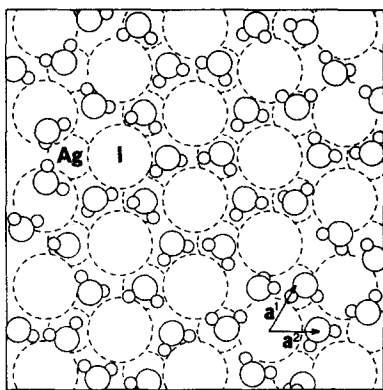
FIG. 4. Snapshot of the 44 water molecule cluster on the model (iodine exposed) basal AgI face after 460 K Monte Carlo steps at 265 K. In the initial configuration for this run each H_2O is in a site located by $\bar{a}^1$ or $\bar{a}^2$ with a dipole moment directed into the surface plane. A_c is 400 Å^2.

basal face in Fig. 3. One notes some five- and six-membered ring structure in the cluster on the model prism face—but to a lesser degree than on the model basal face. On the model prism face, the water molecules also tend to bond closer to the substrate: this reflects the low density of surface plane substrate atoms. Results for all the clusters studied are given in Table I. The clusters on the model prism face of AgI appear to have smaller binding energies—both for the internal cluster binding $(-V_c)$ and for the cluster-substrate binding $(-V_s)$.

As a means of investigating the degree to which the basal face clusters form six-membered rings commensurate with the substrate symmetry, we have calculated $S(\bar{k}^1)$ and $S(\bar{k}^2)$ for the reciprocal lattice vectors $\bar{k}^i$ corresponding to the two-dimensional lattice with lattice vectors $\bar{a}^1$ and $\bar{a}^2$ (see Fig. 4). $S(\bar{k})$ is given by

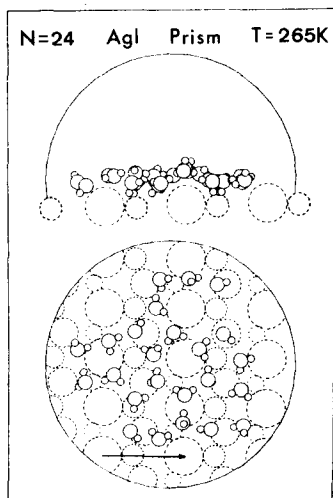$$S(\bar{k}) = N^{-1} \left| \sum \exp(i\bar{k} \cdot \bar{r}_j) \right|^2 , \qquad (1)$$

FIG. 5. Snapshot of the 24 water molecule cluster on the model prism face of AgI after 300 K Monte Carlo steps at 265 K. The upper (lower) view is parallel (perpendicular) to the substrate surface plane. The arrow is in the c axis direction.
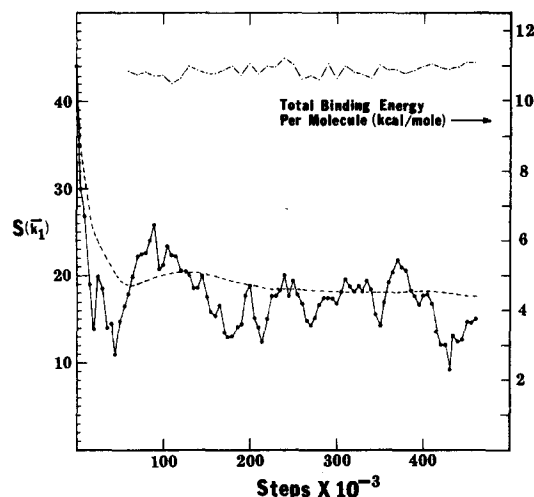

FIG. 6. The cumulative average (- - -) and instantaneous values (●) of $S(\bar{k}^1)$ as a function of Monte Carlo step number for 44 water molecules on the model AgI basal face at 265 K. Corresponding instantaneous values of the total binding energy of the cluster are given by the dot–dashed curve. A_c is 400 Å^2.

where $\bar{r}_j$ is the position vector of the center-of-mass of the jth molecule and N is the number of molecules. If all the molecules are in lattice sites S will be equal to N. However, this is rarely the case and one looks for S of the order of N. S/N represents roughly the fraction of atoms in lattice sites. In this calculation we have investigated only the two-dimensional symmetry of the clusters: no lattice vectors with components in the z direction are considered.

The structure factor $S(\bar{k}^1)$ for the 44 water molecule cluster on the model (iodine exposed) basal face of AgI is shown in Fig. 6. For this calculation, the initial configuration is chosen such that each H_2O is in a lattice site (defined by $\bar{a}^1$ and $\bar{a}^2$ in Fig. 4) with dipole moment directed along $-\hat{z}$ (toward the substrate). The cumulative average of $S(\bar{k}^1)$ is plotted as a function of Monte Carlo step number in Fig. 6 and shows the initial relaxation from the perfect lattice to a structure with $S/N \simeq 0.4$. The configuration at the end of the run is shown in Fig. 4. For this run $S(\bar{k}^2)/N$ after 460 K Monte Carlo steps is 0.5. Figure 6 also shows instantaneous values for $S(\bar{k}^1)$ and the corresponding instantaneous values of the total binding energy of the cluster. The relatively large value for $S(\bar{k}^1)/N$ indicates the preference for the adsorbed water molecules to be in sites on the model substrate which were found to be optimal bonding sites for the water monomer.[1] The large fraction of adsorbed molecules in a two-dimensional lattice commensurate with the substrate symmetry indicates the significant role the substrate plays in stabilizing the cluster.

IV. COMMENTS AND CONCLUSIONS

We have studied small H_2O clusters adsorbed on model substrates of silver iodide, using a Metropolis Monte Carlo technique and effective pair potentials for the H_2O-H_2O[5] and H_2O-AgI[1] interactions. The clusters on the (iodine exposed) basal AgI face have internal cluster

(H_2O-H_2O) binding energies and H_2O-substrate binding energies per molecule which are comparable: each of these quantities ranges from 5–6 kcal/mol per molecule. The model AgI basal face appears to organize the adsorbed water molecules into five- and six-membered rings centered around the exposed I atoms. The prism face of AgI as modeled appears to be less effective in promoting such ring structures, however the internal binding energies are only slightly less than for the basal face clusters. Cluster-substrate binding energy also appears to be less on the prism face. A structure factor analysis of the six-membered ring structure on the model AgI basal face indicates that for the 44 molecule water cluster about half of the H_2O molecules are in maximal binding energy sites found for the single adsorbed H_2O.[1] The latter structure factor study used lattice vectors for the underlying AgI substrate and indicates the role of the substrate in positioning the adsorbed H_2O. Slight variations on the AgI lattice vectors produced structure factors which were smaller.

These studies are preparatory to an investigation of critical cluster size on the model substrate.[14] Presently, calculations of differences in free energy between the n and $n-1$ molecule adsorbed water clusters on the model AgI substrate are underway. Preliminary results indicate that at $T = 265$ K the critical cluster contains less than six water molecules. The future studies will also investigate the effect of smaller effective substrate atomic charge and of deviations from the experimental AgI lattice constants.

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