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The water monomer on the prism face of ice and above a four layer ice basal face ledge: An effective pair potential model^{a)}

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A previous study of the water monomer on the basal faces of ice is extended to consider the interaction of the water molecule with a rigid prism face of ice and with an ice basal face ledge. The effective central force H₂O-H₂O potentials of Stillinger and Rahman are used to generate maximal binding energy surfaces for the H₂O adsorbed on the sample substrates. The results indicate that the prism face of ice binds the water molecule more strongly than the basal faces, and the step on the basal face serves to expose high binding sites on the prism face and multiple bonding configurations at the base of the ledge. Bonding on all the substrates is preferred at sites not directly above water molecules in the first or second layer. Average maximal binding energies on the prism and ledge surfaces are 9 kcal/mol compared to a value of 8 kcal/mol on the (unpolarized) basal face. Optimal bonding configuration for the adsorbed water moment are also presented. Barriers to diffusion between maximal binding sites are 2.5 and 3.0 kcal/mol on the basal and prism faces, respectively.

I. INTRODUCTION

In this paper we present calculations of the maximal binding energy surfaces for a water molecule adsorbed on a rigid prism face of ice I_h , and above a four-layer ice basal face ledge. The motivation for this work is to compare the environment of the H₂O molecule on the basal and prism faces of ice and to examine the distortions in the maximal binding energy surfaces in the presence of a simple surface defect. This work began with a similar study of maximal binding energy surfaces for H₂O on three sample ice basal faces,¹ and is continuing with studies of water monomers and water clusters adsorbed on the basal and prism faces of hexagonal silver iodide.²⁻⁴ These investigations are directed toward understanding the role of substrate features in promoting ice formation on the surfaces of effective ice nucleating agents. The goal of our initial studies of a single water molecule on the substrates is to examine the qualitative effects of surface structure, surface defects, and substrate impurities on the adsorption of the water monomer. A comparison of the results for the ice and silver iodide substrates gives insight into characteristics of ice nucleating agents and provides a means of scaling the AgI-H₂O interaction potential functions for realistic representation of an hydrophobic substrate. The specific long range goals are to determine critical cluster sizes and estimate ice nucleation rates on well characterized sample substrates.

In Sec. II we present the ice prism face and four-layer ledge models and the interaction potentials. Calculations and results for the maximal binding energy surfaces and optimal binding configurations are presented in Sec. III. Discussion and conclusions are in Sec. IV.

II. THE MODEL SUBSTRATES AND THE INTERACTION POTENTIALS

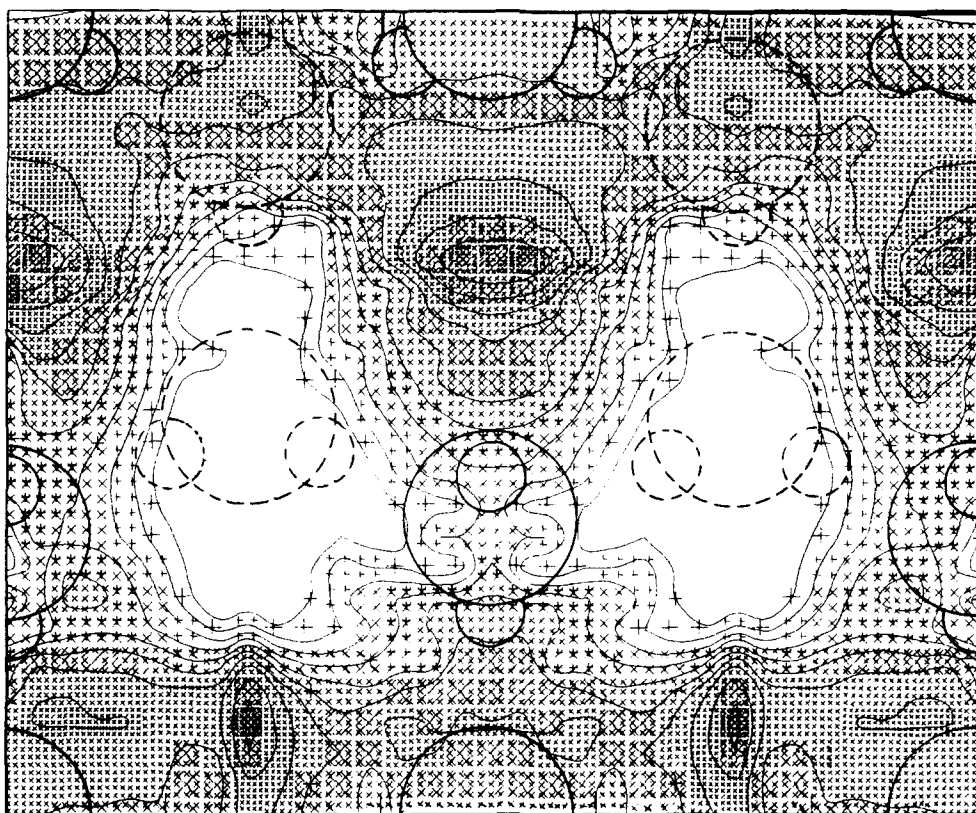
The prism face is represented by 100 water molecules arranged in four layers of 25 molecules each in the hexagonal ice I_h structure. Lattice parameters for the ice are $a = 4.519 \text{ \AA}$ and $c = 7.330 \text{ \AA}$, and each water molecule with its oxygen on a lattice point is surrounded tetrahedrally by four water molecules 2.76 \AA distant. All H₂O are rigid with H-O-H bond angle equal to 109.5° and OH distance equal to 0.9584 \AA . The hydrogens in the prism model are arranged so that the top surface layer has water molecules with dipole moment projection alternately into and out of the prism plane. (See Fig. 1.) This configuration of dipole moments is assumed so that the ice prism face mimics the nonpolar prism face of hexagonal silver iodide. The adsorbed water molecule interacts with all the ice substrate molecules but is constrained with its center-of-mass projection over a $4.52 \times 7.33 \text{ \AA}^2$ area in the center of the array.

The four-layer ledge on the ice basal face is represented by 120 water molecules arranged in four layers of 15 molecules each and based on two layers of 25 molecules each. The step is 7.33 \AA high. Lattice constants and internal H₂O structure are as described above. The upper and lower terrace basal faces are negatively polarized (to mimic the iodine exposed AgI basal face) and the prism face polarization is as described above. Proton configuration for the basal face terraces are shown in Fig. 2. On the basal face ledge, the adsorbed water monomer center of mass projection is constrained to a rectangular region ($4.52 \times 7.79 \text{ \AA}^2$)—the long dimension of which is perpendicular to the prism face of the step.

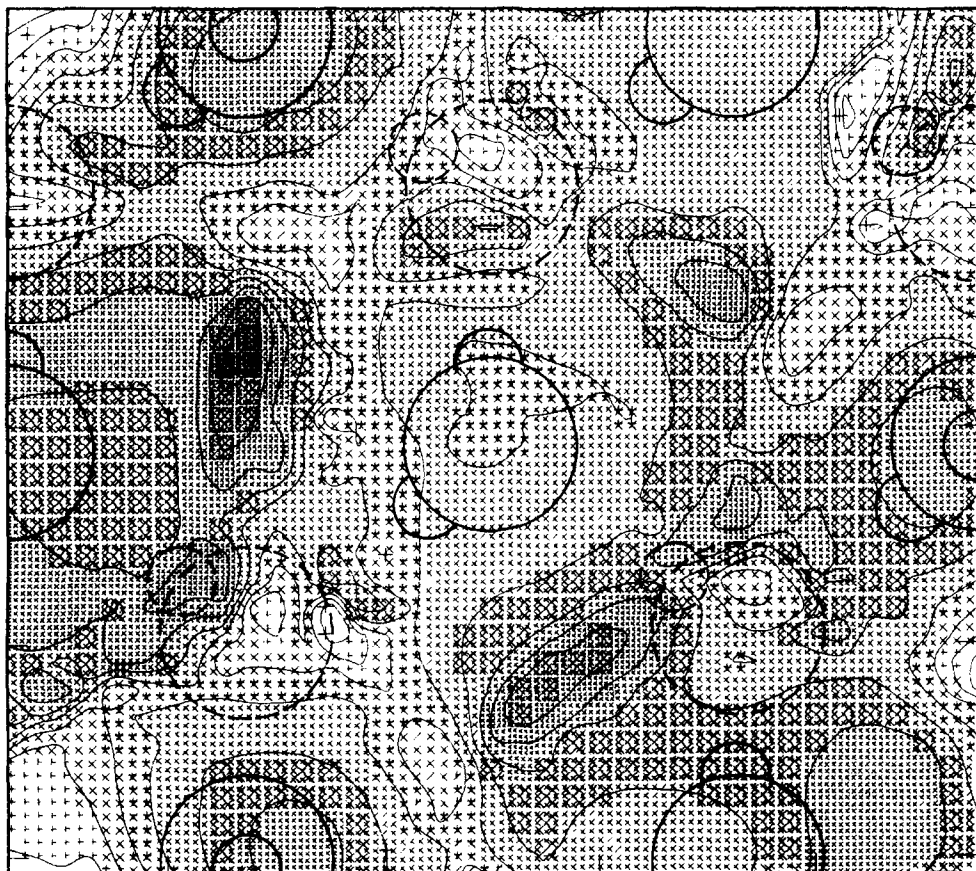
The center of mass of the water molecule is assumed to coincide with the position of the negative charge, $-2q$, and the hydrogen positions are at the two positive charge sites, q . In the central force model of Stillinger and Rahman,⁵ $q = 0.32983e$ and the interaction potential for OO, OH, and HH are given by the following functions of

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(a)



(b)

FIG. 1. The maximal binding energy of the water molecule above sites on the (a) prism face and (b) unpolarized basal face of ice I_h . The H_2O molecules in the $z=0$ plane are indicated by solid circles; $z=-0.905$ Å plane molecules are indicated by dashed circles. The smallest binding energy contours are 5.0 kcal/mol for the prism face and 6.5 kcal/mol for the basal face. Neighboring contours differ by 0.5 kcal. The largest maximal binding energies are 9.5 and 10.2 kcal/mol for the basal and prism faces, respectively.

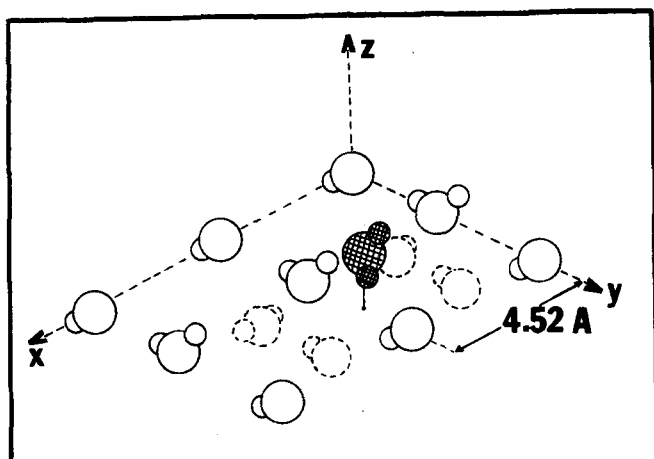


FIG. 2. Configuration of the H_2O molecule in its maximal binding site on the prism face of ice. Solid (dashed) circles indicate configurations of the H_2O molecules in the first (second) layer of the ice substrate. The center of mass of the optimally bound water monomer is 1.7 \AA above the $z = 0$ plane.

the separation distance r :

$$V_{\text{HH}}(r) = \frac{36.1345}{r} + \frac{18}{1 + \exp[40(r - 2.05)]} - 17 \exp[-7.62177(r - 1.45251)^2], \quad (1)$$

$$V_{\text{OH}}(r) = -\frac{72.269}{r} + \frac{6.23403}{r^{9.19912}} - \frac{10}{1 + \exp[40(r - 1.05)]} - \frac{4}{1 + \exp[5.49305(r - 2.2)]}, \quad (2)$$

$$V_{\text{OO}}(r) = \frac{144.538}{r} + \frac{26758.2}{r^{8.8591}} - 0.25 \exp[-4(r - 3.4)^2] - 0.25 \exp[-1.5(r - 4.5)^2]. \quad (3)$$

Further discussion of the potential functions is found in Stillinger and Rahman.⁵

III. CALCULATIONS AND RESULTS

The maximal binding energy surfaces are generated by minimizing the potential energy of the adsorbed water monomer at a set of grid points about 0.25 \AA apart and covering the rectangular regions centered on the array. The center of mass of the adsorbed water monomer is held with fixed projection (x, y) onto the grid point, and the center of mass-substrate separation distance (z) and monomer Euler angles (α, β, γ) are varied until the interaction potential energy is minimized. The minimization is done with subroutine VAO4A of the Harwell subroutine library.⁶

Results for the water monomer on the prism face of ice are shown in Fig. 1(a). In this contour density plot, shading in the figure indicates regions of higher binding energy for the monomer. Circles superimposed on the contour plot show the location and proton arrangements of H_2O molecules in the first and second layer of the ice substrate. The largest maximal binding energy site (10.2 kcal/mol) is located in the center of the six membered ring in the upper part of the figure. A smaller region of high binding energy (about 9.5 kcal/mol) is found in the center of the six membered rings in the

lower portion of the figure. The smallest binding energy site is over molecules in the second layer (2.7 kcal/mol). Results for the (unpolarized) basal face using Eqs. (1)–(3), are shown in Fig. 1(b). This basal face has dipole moments of the top layer of molecules alternately directed into and out of the surface plane. In order to examine the effect of extended regions of larger or smaller binding, an average maximal binding energy $\langle E_B \rangle$ is calculated for the surface regions shown in Fig. 1 using the following expression:

$$\langle E_B \rangle = \frac{\sum -V_i \exp(-V_i/kT)}{\sum \exp(-V_i/kT)}, \quad (4)$$

where V_i is the minimal potential energy at the i th grid point. The averages for the prism and basal faces are 8.9 and 8.3 kcal/mol , respectively. The application of Eq. (4) to the negatively and positively polarized basal face results¹ gives 7.0 and 6.7 kcal/mol , respectively. Thus the prism face of ice appears to be more attractive to the adsorbed water monomer than the basal faces. Energy barriers to monomer surface diffusion between largest maximal binding energy sites are 3.0 and 2.5 kcal/mol for the prism and basal face results shown in Fig. 1. The diffusion barrier for the basal faces was found to be independent of the chosen surface polarization.

In the largest maximal binding energy site on the ice prism face, the water monomer is close to the surface ($z = 1.7 \text{ \AA}$) and has the orientation indicated in Fig. 2. The water monomer configuration for maximal binding directly over the prism face $z = 0$ plane molecules is characterized by larger substrate-monomer separation distances ($z = 2.8 \text{ \AA}$) and dipole moment orientations strongly dependent on the surface molecule proton arrangement. We note that the next layer of molecules in the ice structure would not have an H_2O in the monomer configuration shown in Fig. 2. The optimally bound H_2O on the ice prism face has monomer substrate separation distances ranging from 1.7 to 2.9 \AA in this model, depending on the adsorption site.

The results for the adsorbed water monomer above the four-layer basal face ice ledge are shown in Fig. 3. The largest maximal binding energy site is at a position about halfway up the step—in a configuration close to that observed for optimal binding on the prism face. The exposed prism face of the ledge dominates the bonding of the water molecule in the region of the step and produces an optimal binding energy of 10.2 kcal/mol . Dipole moment projections and center of mass-substrate separation distances for the optimal bonding configurations of the water monomer along three sample "paths" are shown in Fig. 4. The energy barrier to diffusion away from the base of the step through the optimal bonding configurations is 3 kcal/mol . The effect of the ledge appears to be primarily to expose favorable bonding sites on the prism face.

IV. COMMENTS AND CONCLUSIONS

The results of these calculations indicate that the ice prism face binds the adsorbed water monomer more strongly than the basal faces studied earlier.¹ However, the maximal binding energies found on samples of the

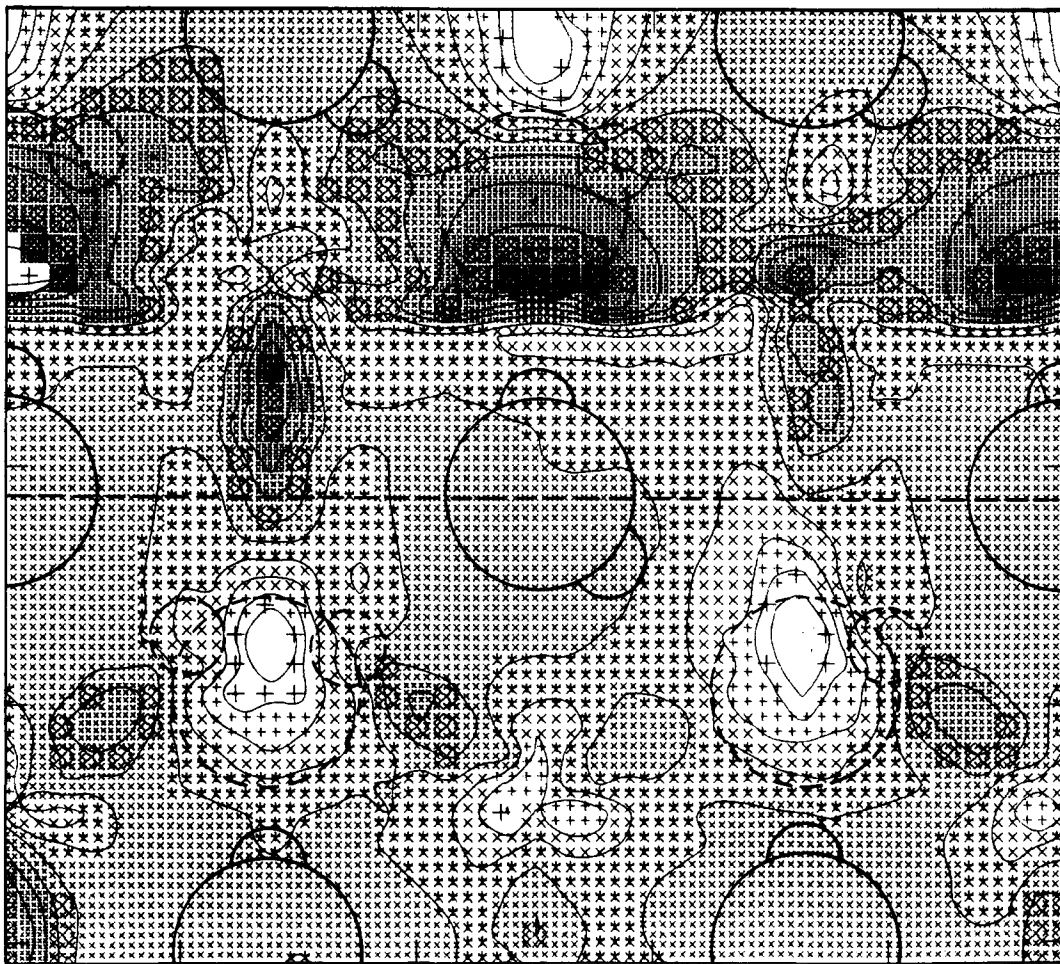


FIG. 3. The maximal binding energy of the water molecule above sites on the basal face ledge. The dashed line marks the ledge and the lower terrace is in the upper part of the figure. Solid circles are H_2O molecules in the $z=0$ and $z=-7.33$ planes; dashed circles are in the $z=-0.905$ and $z=-8.235$ planes. The smallest binding energy contour is 5.0 kcal/mole and neighboring contours differ by 0.5 kcal/mol. The largest binding energy is 10.2 kcal/mol at the base of the ledge.

two faces differ by less than 1 kcal/mol and indicate that ice substrate proton configurations play a major role in orienting and optimally binding the adsorbed water monomer. The ice prism face also provides a wide range of optimal binding energies and bonding configurations and gives rise to a larger energy barrier to diffusion for the monomer on the optimal energy surface shown in Fig. 1(a). The ice basal face ledge serves to expose favorable bonding sites on the prism face at the base of the ledge and provides maximal binding energies comparable to those found on the prism face. On all of the ice surfaces studied there is a multiplicity of relative maxima in the monomer binding energy at a given center-of-mass projection—indicating the complexity of the interaction and the strong dependence on proton configurations in the ice substrate. The irregularities in the optimal binding energy contours suggest that the bonding patterns of H_2O in partially filled ice surface layers could be highly disordered. Recent studies of H_2O molecules on the basal face of hexagonal AgI indicate that adsorbed water clusters have relatively stable five and six-membered ring structures, due apparently to the under-

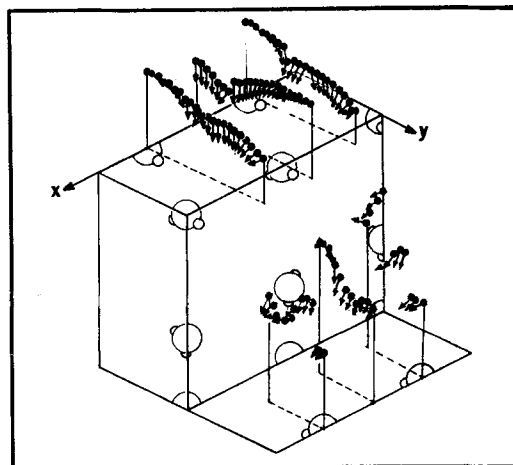


FIG. 4. Optimal bonding configurations of the H_2O molecule above the basal face ledge of ice. Solid circles indicate the center of mass for the adsorbed H_2O and arrows show dipole moment projections into the plane of the paper. The xy plane is parallel to the basal faces of the ledge. Open circles indicate positions of H_2O molecules in the ice substrate.

lying symmetry and lattice constants of the AgI.^{3,4} The primary similarity between the present studies and those of H₂O on AgI is a preference for the adsorbed H₂O to bond to the substrate at sites not directly above substrate molecules (atoms) in the first or second layer. Future studies will examine water clusters on the rigid ice substrate and relaxation of the ice surface layers.

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