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MOLECULAR MODEL FOR ICE NUCLEATION AND GROWTH

Final Report

August, 1981

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PROJECT SUMMARY

The research was directed toward the development and testing of molecular models for ice nucleation and growth. Subsequent research will continue to refine the models and apply them to examine specific properties which influence ice processes in the natural atmosphere and under low gravity conditions. Specific short range goals were to apply and compare two distinct but complimentary techniques, the semi-empirical quantum mechanical approach (see Attachment I) and the central field empirical pair potential model (see Attachment II). The former technique was used to study ionic, configurational and impurity defects in the ice surface while the latter concentrated on studying the effects of kinks, ledges and vacancies on the absorption of water molecules from the vapor.

In addition to static calculations of the energetics of the water monomer-ice surface interaction, molecular dynamics studies were initiated. These dynamics studies did not model the ice surface directly but used small aggregates of water molecules to examine the time evolution and temperature dependence of structure in hydrogen bonded systems (see Attachment I, section 2). Molecular dynamics simulations of collisions also provide information about "sticking coefficients" and the role of energy transfer in the absorption process.

Results of the calculations of monomer-ice surface interactions conclude that many adsorption sites exist on the ice surfaces and that the barriers between "bonding sites" are relatively low. Thus the surface of ice is exceedingly complex and these multiple

attractive sites suggest the probability of a liquid-like layer at ordinary temperatures.

Both the quantum mechanical and the empirical potential results indicate that bonding on the prism face of ice I_h is preferentially above lattice sites. However, for the basal surface the two techniques differ in their prediction of the most stable absorption sites. The quantum mechanical calculations again predict that bonding to a lattice site is preferred while the empirical potential predicts a greater stability for absorption between lattice sites. The source of this disagreement has not been resolved. Since the differences are not large, careful consideration of proton orientations, effects of unshielded long range forces in the empirical model and correlation effects in the quantum model may be required. Then too, surface relaxation effects were not considered and these may alter the predictions as to the magnitude of the monomer interaction with different surface sites. In addition, the molecular dynamics and Monte Carlo calculations are beginning to provide information about the effects of surface relaxation, temperature and collision energy transfer processes on the monomer-surface binding, all of which may alter the predictions of the static calculations.

The major results of the molecular dynamics simulations are i) cluster and/or surface modes play a primary role in the absorption process, ii) the flexibility of the hydrogen bond serves to decrease the energy required for structural interconversion, iii) the rapid distribution of added energy in a hydrogen bonded system leads to aggregate stability which greatly exceeds that predicted by static energy calculations and iv) as a result of iii) additional mechanisms for dissociation or evaporation processes in the nucleation kinetics should be considered.

The results obtained during the course of this contract and summarized in attachments I and II show that molecular models for nucleation and growth of ice have been developed and have been successful in providing insight into these processes. Many questions still remain and refinements of the models are needed, but the work to date demonstrates the viability of the molecular approach.

N81-33423 D1

ATTACHMENT I

FINAL TECHNICAL REPORT

A MOLECULAR MODEL FOR ICE NUCLEATION AND GROWTH

NAS8 - 31150

December 15, 1977 -- June 30, 1981

Patricia L. M. Plummer

CONTENTS

I. Quantum Mechanical Studies of Water Interactions with Ice Surfaces

In the continuing effort to analyze the effect of microscopic properties of the surface on the nucleation and growth of ice, quantum mechanical calculations of a model ice surface interacting with a water monomer were undertaken. The initial calculations which examined several possible bonding sites on the basal and prism faces are reported in ref. 1, (Plummer, 1978). The conclusions of this study were that the strength of the bonding of a monomer to the surface was roughly the same for both the basal and prism faces but that residence times and diffusion rates on the two faces could be substantially different. The presence of many local minima suggests that surface diffusion will be a primary mechanism for surface cluster formation and growth.

In these calculations the surface-monomer interaction was modeled using a thirteen molecule ice cluster with the molecules arranged as for a basal or prism face of ice I_h. The technique used to evaluate the stability of different surfaces and configurations was a semiempirical quantum mechanical method known by the acronym CNDO/2$^{(2)}$. The ice cluster used to represent the basal surface is shown in Figs. 1 and 2. The oxygens represented by filled circles lie 0.9 Å below the plane.

Fig. 1. Perspective drawing of the basal surface of ice I_h (BA).

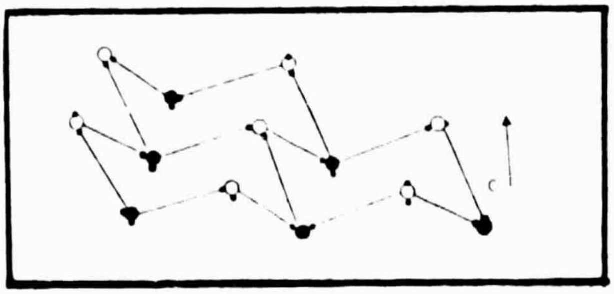
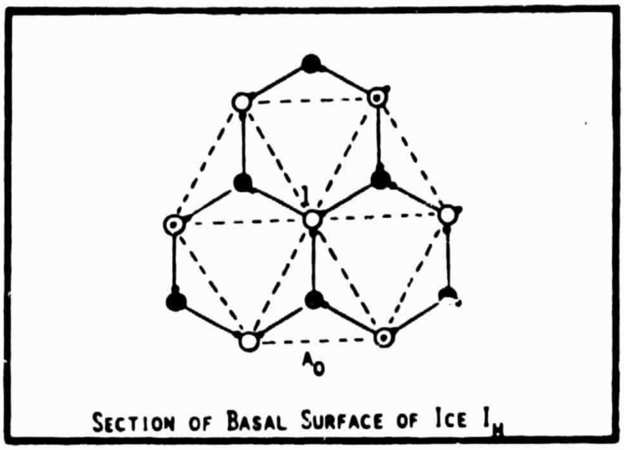
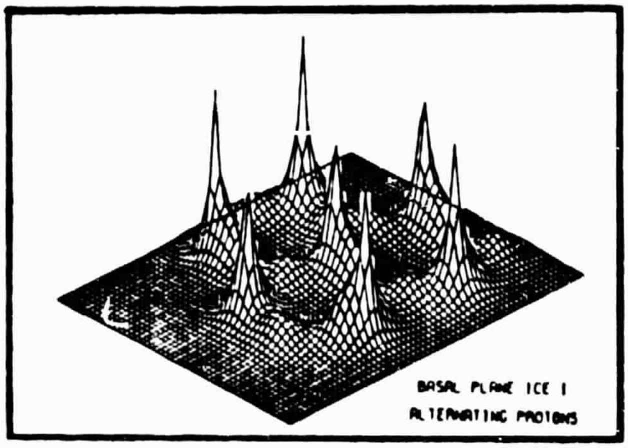


Fig. 2. Section (~60 A^2) of the basal surface of ice I_h showing proton configurations for an alternating (BA) surface. Primary bonding site is indicated by 1; dashed lines connect coplanar molecules and illustrate the hexagonal symmetry of the lattice.



In order to better visualize the ice surface as viewed by an approaching water monomer, electron density plots were generated. Such a plot is shown in Fig. 3 for the basal face with the same proton configuration as shown in Figs. 1 and 2.

Fig. 3. Electron density map of the basal surface of ice I_h. The magnitude of the density in the plane of the upper level of molecules is represented by the height of the peaks. Total area of the density map is 180 A^2; grid points are .25 A apart. Perspective is 30° above plane and 45° clockwise from the orientation depicted in Fig. 2.



Several possible bonding sites were investigated for the basal face. The results are discussed further in ref. 1 and summarized in Table I.

TABLE I

Summary of Results for Basal (BA) Surface-Energy Calculations as a Function of Site

Site	Energy (kcal/mole)	Frequency (cm^{-1})
Primary basal		
a) 180	-7.98	280
b) 0°	-7.50	
Second layer	-4.05	180
Ring Center	-4.45	
Bridge Site	-6.79	190

Other neutral surfaces were also studied: a prism surface, two polarized basal surfaces and an optimal basal surface. The prism surface illustrating the proton configuration is given as Fig. 4.

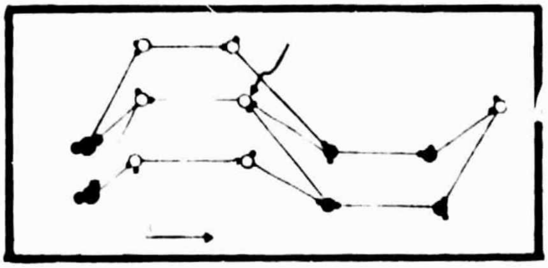


Fig. 4. Perspective drawing of the 13 molecules used to represent the prism face of ice I_h. The primary site is indicated by the arrow.

The other basal surfaces examined differ from Fig. 1 only in proton configuration. The polarized surfaces had all of the protons in the upper level pointing either up (BU) or down (BD). The optimal basal surface had the upper protons alternating as in Fig. 1 but the second level protons were reoriented so as to produce the most stable configuration for the surface itself (BOPT). The binding energy of a monomer to the central site for these surfaces is given in Table II.

TABLE II

Summary of Results of Monomer-Surface Interaction Energy as a Function of Surface Configuration

Site	Binding Energy (kcal/mole)
Basal primary site	
a) BA	-7.98
b) Optimal (BOPT)	-7.46
c) Proton up (BU)	-7.62
d) Proton down (BD)	-7.13
Prism	
a) Primary	-7.35
b) Bridge site	-3.88

In addition to the neutral ice surfaces, the effect of including defects in the surface was examined. The first defects considered were ionic defects such as ion pairs which would be formed by proton tunneling. The calculations attempt to simulate the condition of an incoming water monomer reacting with a surface ion site before recombination can take place. Two initial cases having the ions on adjacent lattice sites were considered, one having a positive surface site and the other a negative surface site. A further case modeled a second tunneling event which produces a "separated" ion pair and a surface having both a positive and a negative site. The results for the ion defect surface studies are summarized in Table III.

TABLE III

Summary of Results for Energy Calculation for Monomer Interactions with Defect Surfaces

Site	Binding Energy (kcal/mole)	Frequency (cm^{-1})	Rotational Barrier (kcal/mole)
Primary basal	-7.98	280	.50
Defect ion pairs			
a) Positive site	-5.07	130	.20
b) Negative site	-24.34	300	.67
c) Separated ion pair	-37.46	380	-
Configurational Defects			
a) L-defect	-7.0	-	
b) D-defect	-6.8	-	

The effect of incorporating other ions in the ice surface on an approaching monomer are very similar to the results for separated ion pairs with a Na^+ impurity behaving very much like a hydrodium ion and a Cl^- impurity like a hydroxyl ion. These results are only indicative rather than conclusive because the ice lattice was not allowed to relax about the impurity ion. It might be expected that this relaxation might be substantial because the small sizes of the impurity ions.

The other types of defects modeled were the so-called configurational defects or D- and L- defects. These types of defects occur when a molecular rotation becomes "frozen in" by the incorporating of additional lattice members. In such defects, there are either two (D-type) or no (L-type) protons lying along the normal hydrogen bond. Since such defects occur between oxygen layers they are not as close to an incoming monomer and therefore the initial effect on the interaction is considerably less than for either a polar surface or ion defect. However the influence of the configurational defect would be expected to be greater for secondary bonding sites and for surface diffusion because of the lattice relaxation about the defect. These results are also given in Table III.

I.. Molecular Dynamics Studies

The quantum mechanical calculations described in the previous paragraphs served to provide much information about the monomer - ice surface but at an effective temperature of zero kelvin. To examine the effects of non-zero temperatures and also to examine time-dependent phenomena, a series of molecular dynamics studies were undertaken. Because of the complexity of the ice problem, these studies were carried out for small clusters of water molecules. Using clusters rather than a model for bulk ice, the importance of different energy transfer processes, molecular motions, and molecular orientations, including proton positions could be examined. Since almost all cluster molecules were also "surface molecules" the effects being studied are more related to surface than bulk processes.

In the first series of studies (see the attached preprint[3] and the dissertation of T. S. Chen) the structure and stability of a twenty molecule clathrate was investigated. The interaction potential used was a central field pair potential[4]. The equations are given below.

$$V_{OO}(R) = \frac{144.538}{R} + \frac{26758.2}{R^{8.8591}} - .25\,\mathrm{EXP}[-4(R-3.4)^2] - .25\,\mathrm{EXP}[-1.5(R-4.5)^2]$$

$$V_{OH}(R) = -\frac{72.269}{R} + \frac{6.23403}{R^{9.19912}} - \frac{10}{1+\mathrm{EXP}[40(R-1.05)]} - \frac{4}{1+\mathrm{EXP}[5.49305(R-2.2)]}$$

$$V_{HH}(R) = \frac{36.1345}{R} + \frac{18}{1+\mathrm{EXP}[40(R-2.05)]} - 17\,\mathrm{EXP}[-7.62177(R-1.45251)^2]$$

The molecules were initially arranged on the vertices of a regular dodecahedron (Fig. 5).

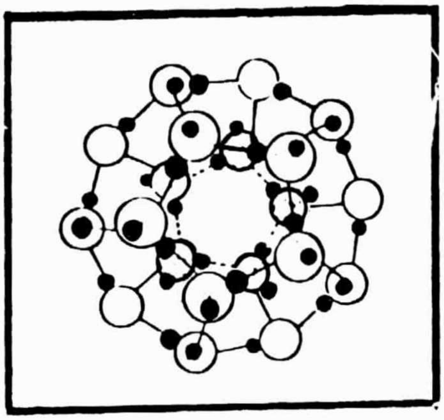


Fig. 5. Symmetric proton configuration for the clathrate (pentagonal dodecahedron).

In this cluster all of the water molecules participate in three bonds, as in a fully bonded surface layer. The stability of the structure was examined as a function of temperature, proton arrangement and method of energy addition to the system. It was found that the cluster was remarkably stable to dissociation even under conditions of extreme heating. The structure or hydrogen-bonding pattern was disrupted above 250K but an evaporation event did not occur until much higher temperatures. The excess energy was absorbed by disruption of the hydrogen bond structure (melting) with bonds continually breaking and reforming. When dissociation finally occurred, it was not through the evaporation of a single molecule but via the loss of clusters containing two or more molecules. Upon examination of the mechanisms for energy transmittal through the cluster, the molecular dynamics shows that the energy does not build up in the low frequency modes, which would lead to dissociation but rather is transmitted by the librational modes throughout the cluster. This transfer of energy takes place extremely rapidly (< .02 psec) and appears to account for the remarkable stability of the hydrogen bonded system. The method of break-up of the cluster suggests that usual nucleation kinetics model which allows for decay by only one molecule should be re-examined if this trend is observed for other cluster sizes as well.

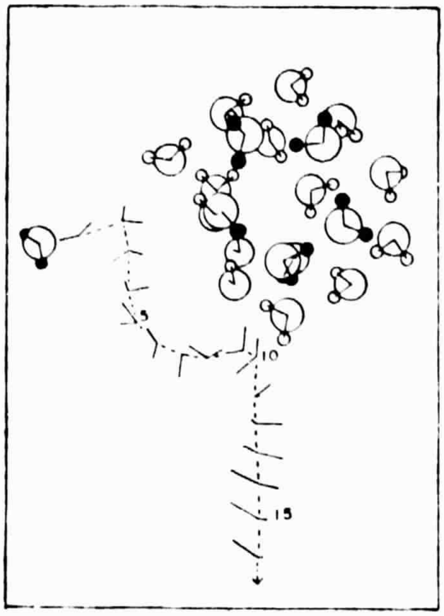
To begin to model the nucleation and growth processes a second set of studies of collision and scattering simulation between the clathrate and a monomer were undertaken. Four types of collision processes were modeled. The random proton structure was used and the initial cluster temperature was ~ 225K.

1) A virtual collision was simulated by giving one cluster molecule extra translational energy--of the order of 2.5 kcal/mole. In this process the injected energy was directed toward the center of mass of the cluster, and the energy redistribution mechanisms were studied. The sudden transfer of energy to a single molecule did not, as has been speculated, disrupt the cluster structure significantly nor did it result in the loss of a molecule. The energy was rapidly transferred to adjacent molecules and was absorbed by the cluster. Subsequent observations revealed a radial distribution function relatively unchanged from its initial form before the virtual collision. There was no evidence for any "build-up" of energy which could result in the evaporation of a molecule.

2) A virtual evaporation was simulated by instantaneously removing one molecule from the cluster. The remaining molecules were left unaltered. Surprisingly, the cage-like structure did not collapse and there was no extensive rearrangement of the remaining bonds. The cage expanded somewhat, however, and the radial distribution showed loss of definition in the third and subsequent peaks. Much of the nearest neighbor and five-membered ring structure of the original cluster remained intact.

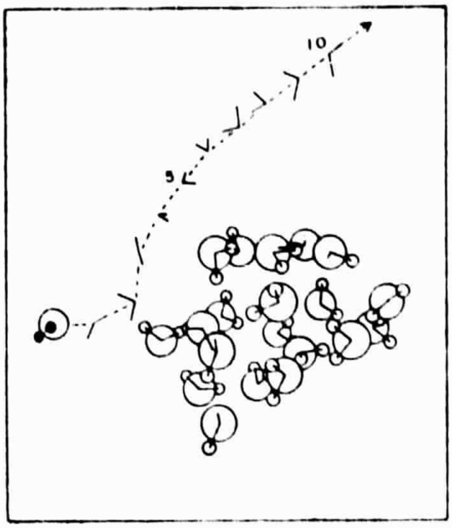
3) An additional collision was simulated by introducing a water molecule as a projectile with an average kinetic energy for the temperature under study, and with impact parameters of 0, 5 and 10 A. (The cluster radius was about 5 A.) In the first of these collisions the incoming monomer was allowed to transfer energy internally but not to the cluster, which was held rigid. Collision with a rigid cluster attempted to mimic a collision with a very cold cluster and also to examine the ability of the projectile to accommodate to the cluster in an attempt to maximize the interaction. The results of these collisions are shown in Figs. 6, 7 and 8. As the attraction between the cluster and the monomer increased there was a corresponding increase in the monomer librational energy and decrease in monomer translational energy--reflecting accommodation of the monomer to the cluster. In all cases, the monomer eventually escaped. At an impact parameter of 0 A (Fig. 6) the monomer bounced once before escaping.

Fig. 6. Collision sequence of a monomer with a rigid 20 molecule cluster. The number alongside the trajectory is elapsed time in units of 1,000 Δt. The impact parameter, b, is OA.



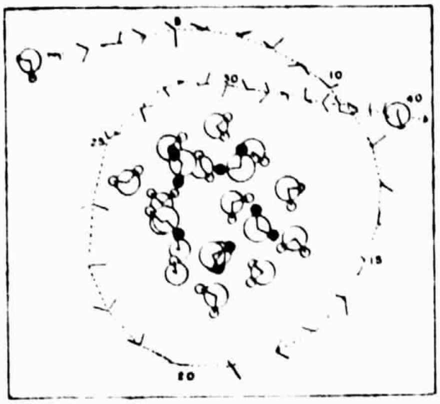
At 5 A (Fig. 7) the monomer scatters off the cluster.

Fig. 7. Collision of a monomer with a rigid clathrate (b = 5 A).



At 10 A an orbiting collision was observed (Fig. 8).

Fig. 8. Collision of a water monomer with a rigid cluster (b = 10 A). The lines along the trajectory indicate the changing monomer orientations.



In the latter case the interaction energy was large--in excess of that required for bond formation. However, large oscillations in the librational energy introduced reorientation to a weaker interaction configuration and the monomer subsequently escaped.

4) This study was the same as case 3 but now included the full dynamics of the target cluster as well as the projectile. Again initial impact parameters of 0 A, 5 A or 10 A were used. For all impact parameters, the impinging monomer was incorporated into the cluster--indicating that energy transfer from the monomer to the cluster molecules was an efficient process. The interaction

energies (between the monomer and cluster) ranged from 7 to 16 kcal/mole, or 1.5 to 3 hydrogen bonds. The cluster structure was altered under the influence of the monomer even when the interaction energy was small (less than one kcal/mole). In the addition process, the cluster absorbs about 10 to 15% of the initial monomer energy. Figures 9 and 10 indicate two "snapshot" views of the monomer-cluster absorption process for the 0 A impact parameter case.

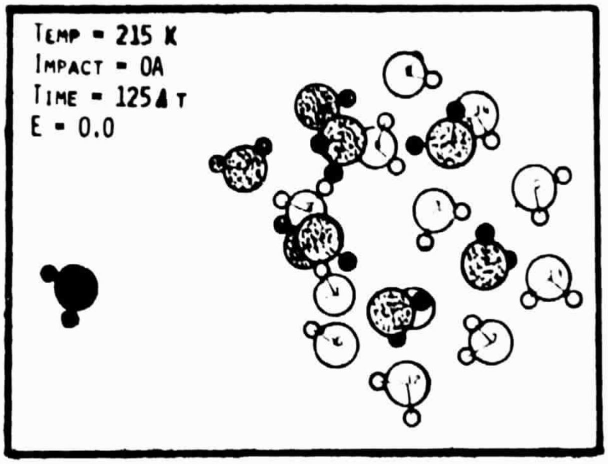


Fig. 9. "Snapshot" drawing of the monomer and cluster configurations. The impact parameter is 0 A, t=0.

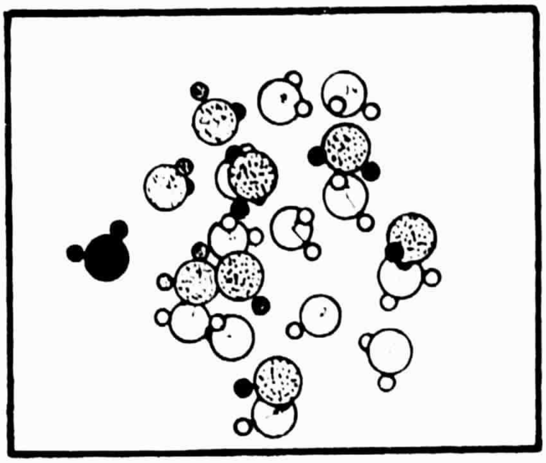


Fig. 10. Subsequent view of the monomer and cluster configurations for the case with impact parameter equal to 0 A, t=1 psec.

For all impact parameters the results indicated that once a bond was formed (when the average interaction potential exceeds 4 kcal/mole) the monomer reorients within about 100 intramolecular vibrations to form a second bond with the cluster.

A third series of molecular dynamic studies was made on even smaller water aggregates. Clusters containing five water molecules were used to examine the rate and temperature dependence of structure interconversion. First a series of different hydrogen bonding clusters were cooled to determine which geometries were the most stable at low temperatures (1-5 K). These structures are shown in

Fig. 11.

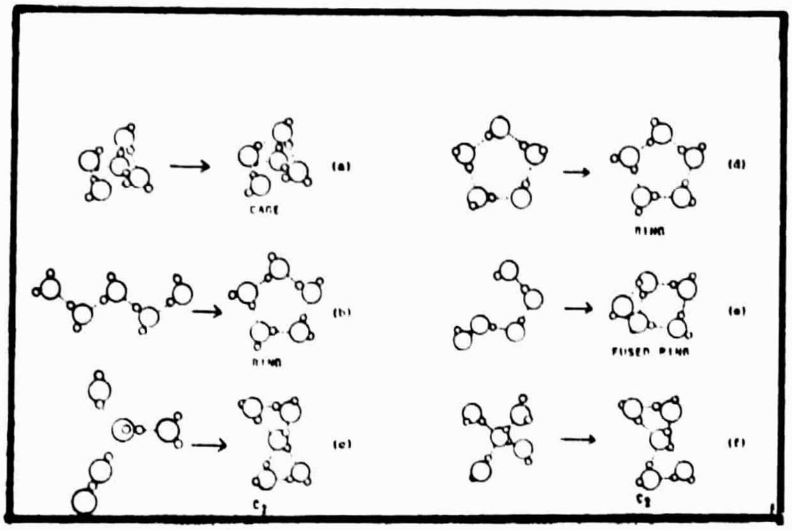


Fig. 11. Optimization of various water pentamer structures. On the left side of the arrow are initial configurations. On the right side of the arrow are optimized configurations.

Then a series of heating and equilibrium runs were undertaken as indicated in the flow chart in Fig. 12.

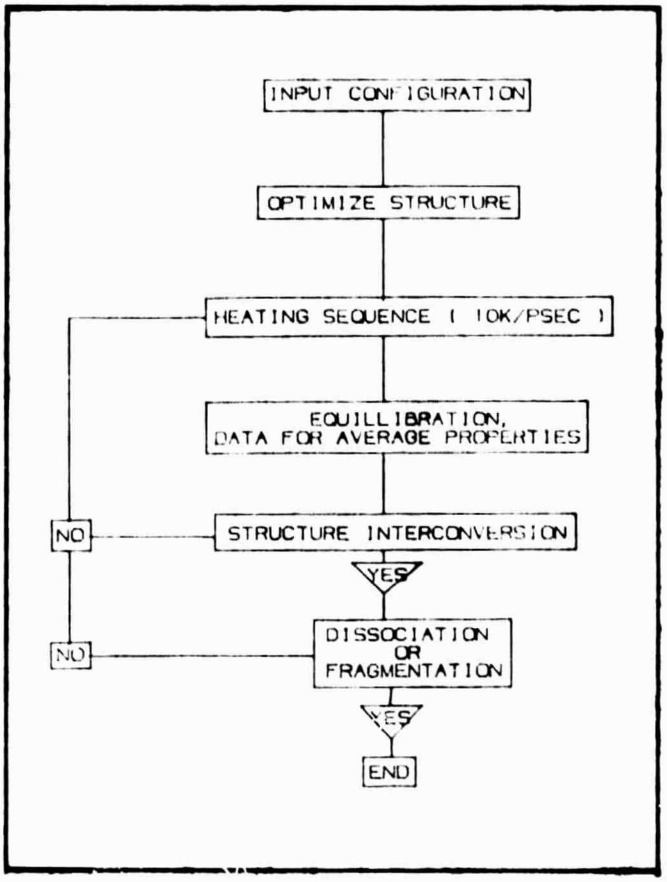


Fig. 12. Flow chart for structure stability simulations.

It was found that the cage structure was the most stable at low temperatures. However, the barriers between the "stable structures" were sufficiently high that no interconversions occurred below about

70 K. Thus we conclude that at low temperatures, the configuration space is not ergodic and all such "stable" structures must be included in statistical studies.

As expected, at the low temperatures, the energy of the hydrogen bonds dominate the free energy for the aggregate. As the temperature is increased, the entropy term becomes increasingly more important resulting in the transition from the cage to the fused ring to the ring structure. The conversion process is indicated in Fig. 13 by a plot of the radial distribution function as a function of temperature for these structures.

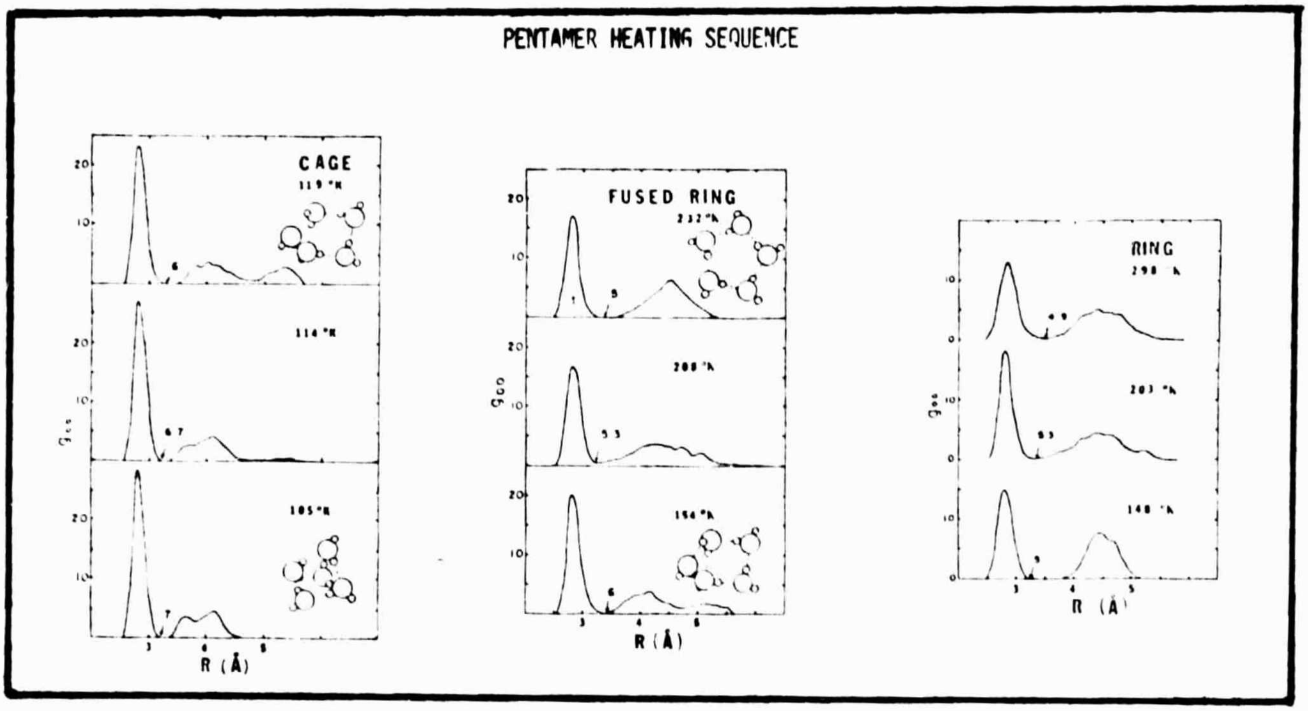


Fig. 13. The plots show the change in the 0-0 distribution as the case structure is heated and undergoes conversion first to a fused ring and then to a ring.

Fig. 14 shows the energy vs. temperature for two structures, C_2 and ring.

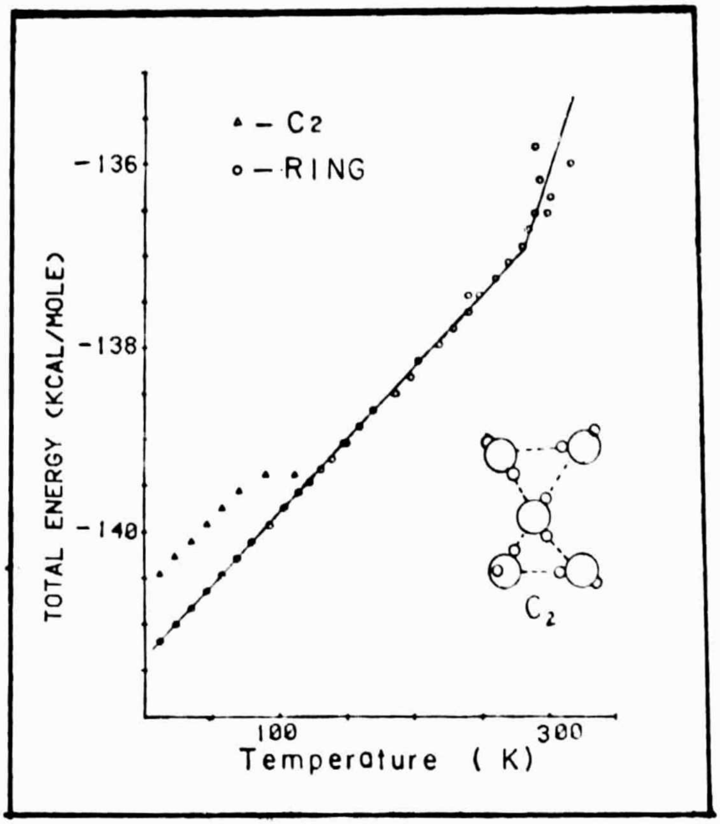


Fig. 14. The total energy of the ring pentamer as a function of temperature is plotted. The structure or bonding pattern remains essentially unchanged from 2 K to 280 K. Above 290 K structures having fewer total hydrogen bonds or "dangling" molecules are observed with increasing frequency. The change in slope around 300 K corresponds to fragmentation of the ring and possibly can be considered as a transition from dense to a gas phase. The other points on the curve show the transition of another pentamer structure, C2, to the ring at approximately 100 K. The C2 structure formed on cooling a tetrahedral pentamer.

Above 290K structures having fewer total hydrogen bonds or "dangling" molecules are observed with increasing frequency. The change in slope around 300K corresponds to fragmentation of the ring and possibly can be considered as a transition from a dense to a gas phase. For the ring the fraction of hydrogen bonds having a specific length at 20K and 297K are shown in Fig. 15. From this and the frequency spectra at the same temperatures (Fig. 16, 17) it is seen that although the average structure is still a ring at the higher temperatures, the hydrogen bonds are becoming very "fluid" and an increasing amount of energy is contained in the librational motions. As was seen before the case of the larger clusters, a buildup of energy in the librational modes leads to a disruption of the hydrogen bonding structure.

Fig. 15. Plot of the fraction of O-O separation at a given distance for the ring pentamer at 20 K and 297 K.

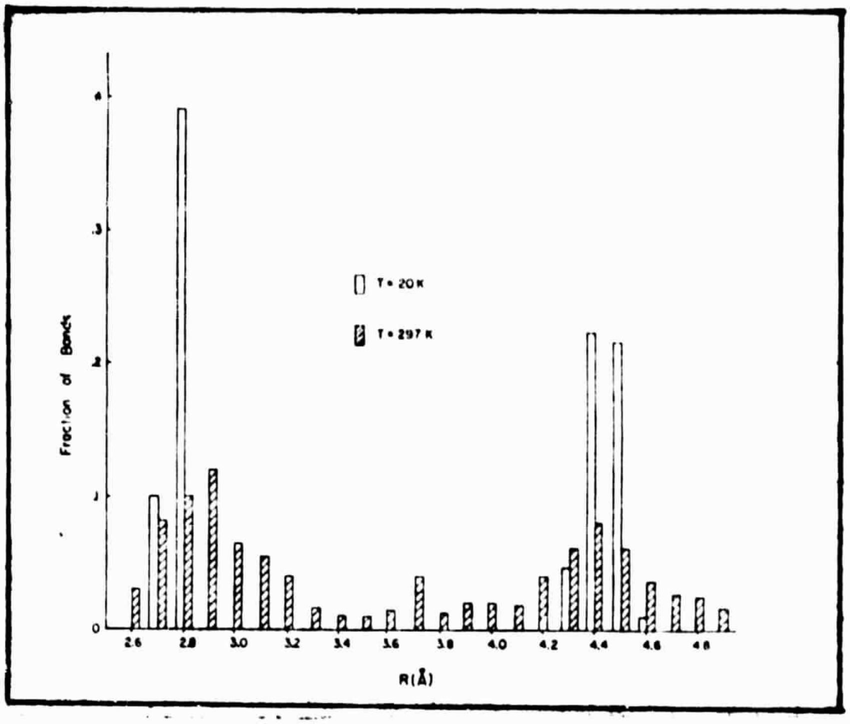


Fig. 16. Frequencies associated with group cluster motions of the pentamer ring at 20 K.

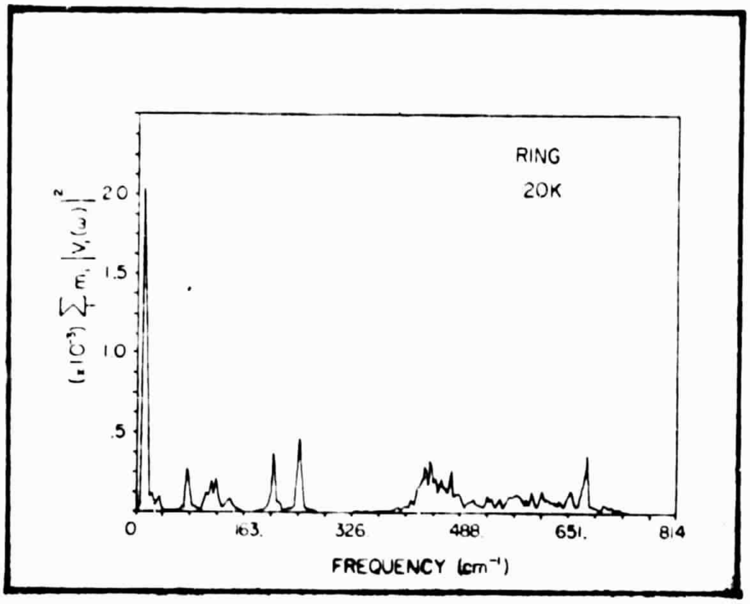
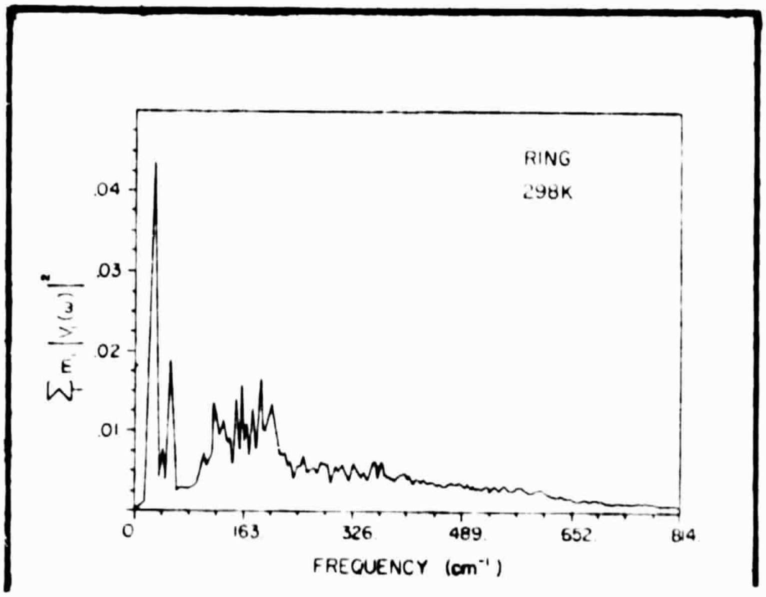


Fig. 17. Same as 16 but at 297. Note the change of scale on the vertical axis.



Detailed analysis of these motions at higher temperatures has shown how readily certain structural changes and proton switching reactions can occur, even when the energy present is less than that required to break a hydrogen bond. This is illustrated in Fig. 18 which shows the librational motion which results in exchanging the hydrogen participating in the hydrogen bond with the non bonded hydrogen and in Fig. 19 which shows the energy components for the exchange.

Fig. 18. The sequence of orientations observed for proton switching reaction in a pentamer ring at ~ 220 K.

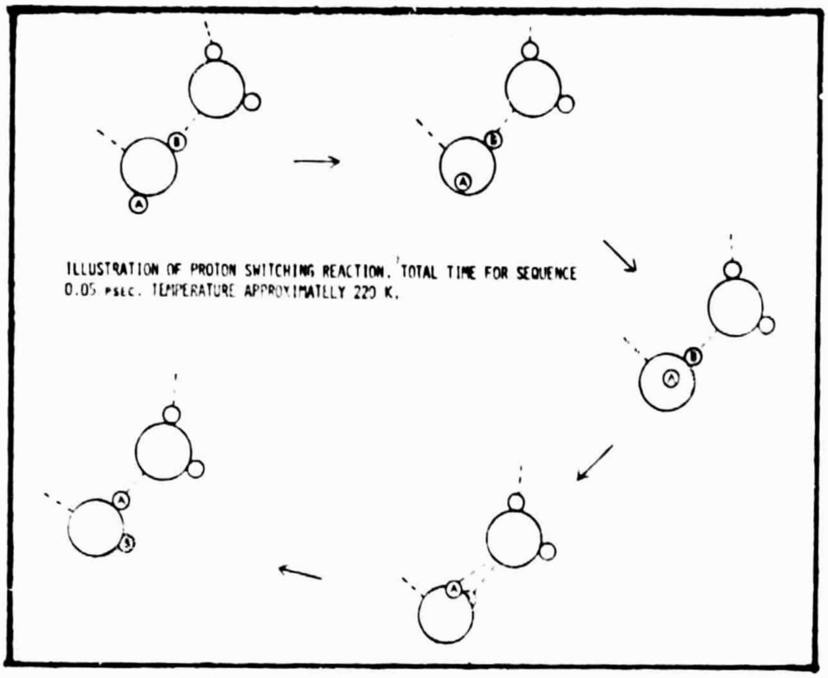
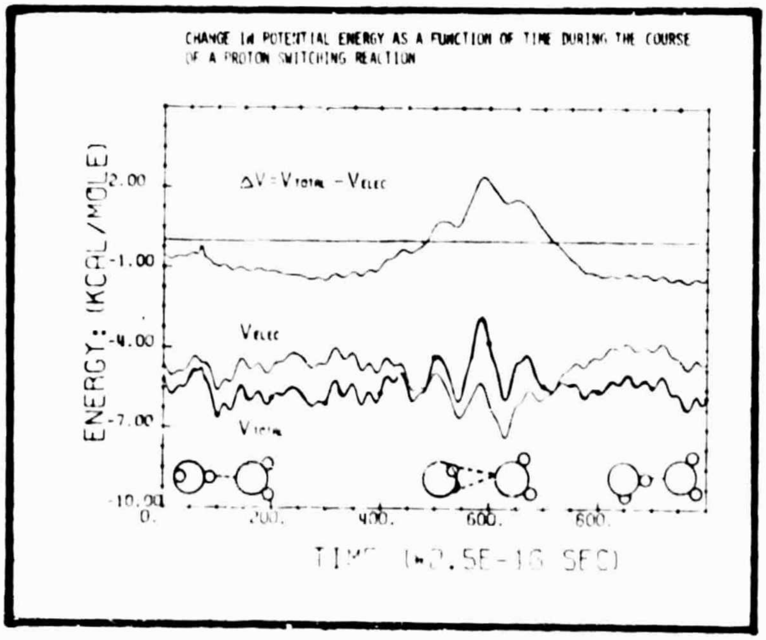


Fig. 19. Plot of energy vs. time for the electrostatic and total potential energy during a proton switching reaction.



Thus the energy required for the switch was 3 kcal/mole rather than 7 kcal/mole. Such switching reactions and cooperative effects serve to substantially alter the energy requirements for structure interconversions and hence for diffusional motion and surface aggregation.

In a further attempt to assess the ease of structural changes during the growth of an aggregate, collision studies between a monomer and/or pentamer were made. Typical results are shown in Figs. 20 and 21.

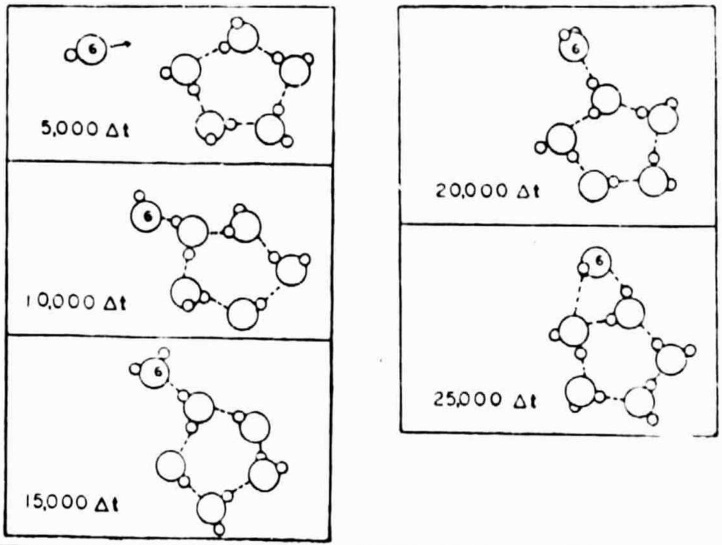


Fig. 20. Collision sequence of monomer with pentamer. Impact parameter 6 A.

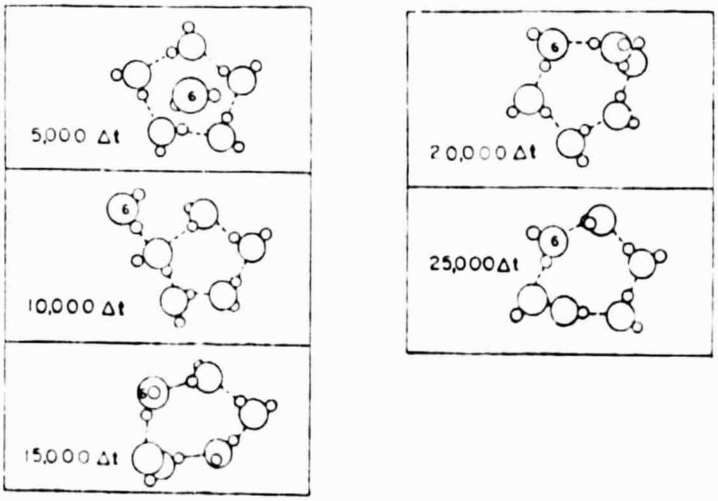


Fig. 21. Collision sequence of monomer with ring pentamer. Initial monomer position 6 A above ring. Impact parameter 0 A.

The incoming monomer initially had an energy equal to the average energy of a cluster molecule. Trajectories examined were i) in the plane of the cluster at impact parameter OA and ii) 6A and iii) perpendicular to the plane of the cluster with impact parameter of OA. Here again the monomer was captured and quickly formed a second hydrogen bond with the cluster. Ring enlargement reactions were observed with the perpendicular trajectory indicating the transition from a 5 to a 6 member ring readily occurs.

III. Summary of Results

These studies have provided the techniques for studying the molecular dynamics of a water molecule colliding with an ice surface. Such studies can examine the kinetic factors needed to evaluate the nucleation rate expressions. They can also be used to examine the structure of the surface as a function of time. It is hoped that they can quantify the idea of a "liquid-like" layer on the ice surface: at what temperature does it begin to form, how disordered is the surface, through how many layers does the disorder (liquid layer) persist? In addition, the molecular dynamics has the potential of evaluating the importance of the binding sites identified by the static calculations to the formation of critical embryos and in the crystal growth process.

These studies of the specific features of the interactions of water molecules with ice surfaces and clusters have provided the following:

1) There are many sites on the basal and prism faces of ice at which the monomer is at least quasi-bound.

2) The magnitude of the bonding on the basal and prism sites is the same but the barriers for moving between the sites appear to be lower for the basal face. This would suggest a difference in activity for the two faces which could well be temperature dependent.

3) The molecular dynamics of vapor phase clusters has shown that a variety of configurations for a given size cluster can co-exist. It is expected that this effect would be enhanced for embryos on a surface.

4) The dynamic studies of monomer-cluster scattering suggest the possibility of larger absorption coefficients, of the order of one.

5) The monomer-cluster scattering experiments have also shown that cluster structure can be substantially changed (for example from a five to a six member ring) and that only a small percent of the monomer energy needs to be transferred to the cluster for absorption to take place.

Thus this work with the molecular model has shown both the feasibility and importance of the approach, has provided insights as to the importance of specific effects and has provided potentials and algorithms for use in the further studies of the formation and growth of ice.

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V. ORAL PRESENTATIONS

"Model Calculations of Water Interactions with an Ice Surface", Nucleation Symposium, American Chem. Soc., New Orleans, LA, March, 1977.

"Application of Semiempirical Quantum Mechanics to the Study of Nucleation Processes on Surfaces", 10th Midwest Theoretical Chemical Conference, Argonne National Laboratory, May, 1977.

"Molecular Orbital Calculations of Water Ice Surface Interactions", International Conference on the Physics and Chemistry of Ice, Cambridge, England, September, 1977.

"Stability and Structure of Prenucleation Embryos", A Molecular Dynamics Study of Water Clusters", with T. S. Chen, 9th International Conference on Nucleation and Aerosols, Galway, Ireland, September, 1977.

"Properties of Active Ice Nuclei: Theoretical Studies of Water Surface Interactions", 9th International Conference on Nucleation and Aerosols, Galway, Ireland, September, 1977.

"Water Clusters: A Molecular Dynamics Study", with T. S. Chen, Nucleation Symposium, American Chemical Society, Anaheim, California, March, 1978.

"Molecular Dynamics Study of Small Water Aggregates", with T. S. Chen, Midwest Theoretical Chemistry Conference, Purdue, Ind., May, 1979.

"Molecular Dynamics Study of Small Water Aggregates III", with T. S. Chen, MASAU Physics Conference, Columbia, MO, May, 1979.

"Molecular Dynamics Study of Cluster Growth and Stability", with T. S. Chen, 53rd Colloid and Surface Science Symposium, Amer. Chem. Soc., Rolla, MO, June, 1979.

"Molecular Modeling and Molecular Dynamics in Water-Ice Systems", Colloquium, Washington Univ., Jan., 1980, invited.

"Molecular Dynamics Study of Small Water Aggregates IV: Structure and Stability of Water Pentamers", with T. S. Chen, 54th Colloid and Surface Science Symposium, Lehigh University, PA, June, 1980.

"Molecular Dynamics Studies of Ice", Nucleation Symposium, American Chemical Society, San Francisco, August, 1980.

"Molecular Dynamics Simulations of a Hydrogen Bonded System", Horizons in Hydrogen Bond Research, Sanga Saby, Sweden, August, 1980.

"Dynamics of Hydrogen Bonded Systems", with T. S. Chen, Texas Conference on Chemical Dynamics, Univ. of Texas-Austin, March, 1981.

VI. PUBLICATIONS

"Molecular Orbital Calculations of Water-Ice Surfaces Interactions", P.L.M. Plummer, J. of Glaciology, 21, 565 (1978)*.

"CNDO Calculations on the Structure of a Liquid Sodium Carboxcylate-Carboxylic Acid Compound", B. Bendiksen, S. E. Friberg and P.L.M. Plummer, J. Colloid and Interface Sci., 72, 495 (1979).

"Fundamental Studies on Vapor Phase Water Clusters", J. L. Kassner, Jr., D. E. Hagen B. N. Hale, P. L. M. Plummer, J. L. Schmitt, L. H. Lund, R. A. Zalabsky, R. E. Thurman, L. E. Stoddard, T. S. Chen, R. C. Miller, P. C. P. Yue, R. J. Anderson and M. Daee, Atmospheric Water Vapor, ed. by A. Deepak, T. Walkerson, and L. Runke, Academic Press, (1980) p. 613.

"Molecular Dynamics Study of Water Clusters", P. L. M. Plummer, Proceedings: Workshop on Stochastic Molecular Dynamics, NRCC, No. 6, 47 (1980).

"Stability and Structure of Prenucleation Embryos: A Molecular Dynamics Study of Water Clusters", T. S. Chen and P. L. M. Plummer, Proceedings of the IX International Conference on Nucleation, Summer (1981).*

*Copies attached

VII. CONFERENCES ATTENDED AND OTHER ACTIVITIES

Session Chairman: Symposium on Nucleation Theory and Experiment, ACS, March, 1977.

Session Rapportuer: International Conference on Physics and Chemistry of Ice, England, September, 1977.

Co-Organizer: Nucleation Symposium, Spring Meeting of American Chemical Society, 1977.

CAUSE Proposal Review Panel, Washington, D.C., January, 1978.

Invited participant: Symposium in honor of Robert Mulliken, Chicago, IL. October, 1978.

Session Chairman: Zettlemoyer Symposium on Nucleation, 53rd Colloid and Surface Science Symposium, June, 1979.

NSF Women in Science, Proposal Review Panel, Washington, D. C., February, 1979, panel leader.

Co-Organizer: Zettlemoyer Symposium on Nucleation; Symposium on Light Scattering; Symposium on Aerosols, Annual meeting of Colloid and Interface Science Division of ACS, June, 1979.

Invited participant: Workshop on Stochastic Molecular Dynamics, sponsored by NRCC, Woods Hole, Mass., July, 1979.

Invited participant: Workshop on Computational Methods for Molecular Structure Determination: Theory and Technique, sponsored by NRCC and QCPE, Indiana Univ., August, 1979.

Conference on Atmospheric Water Vapor; Vail, CO, September, 1979.

Invited participant: Horizons in Hydrogen Bond Research, Sanga-Saby, Sweden, August, 1980.

NSF Women in Science, Proposal Review Panel, Washington, D. C., February, 1981, panel leader.

Conference Organizer, VI International Symposium on Physics and Chemistry of Ice, to be held 2-6 August, 1982, Rolla, MO.

Editorial Advisory Board: Journal of Colloid and Interface Science, 1980-1983.

VIII. PERSONNEL AND DEGREES AWARDED

Senior Personnel

Dr. Patricia L. M. Plummer

Graduate Students and Degrees Earned

T. S. Chen, Ph.D., Physics, December, 1980

Dissertation: "A Molecular Dynamics Study of the Stability of Small Prenucleation Water Clusters", (copy attached)

D2

N81-33424

ATTACHMENT II

FINAL TECHNICAL REPORT

A MOLECULAR MODEL FOR ICE NUCLEATION AND GROWTH

NAS8 - 31150

December 15, 1977 -- June 30, 1981

Barbara N. Hale

CONTENTS

I. STUDIES OF THE WATER MOLECULE BONDING TO ICE SURFACES

Our attention was focused on the microscopic aspects of ice crystal growth habit and ice nucleation because of the essential role these processes play in cloud microphysics and because of the absence of reliable macroscopic models. At a 1978 Workshop on Ice and Snow Crystal Growth, Weickmann[1] reviewed the great variety of ice crystal growth habits and commented on the lack of a unified explanation which could incorporate: the role of a transition (or liquid like) layer on the ice surfaces; the role of supersaturation with respect to ice at water saturation values as a function of temperature; the role of two dimensional nucleation processes on the basal and prism faces of ice.

During the grant period we have developed a program to examine the basic interaction of the water monomer with a variety of ice surfaces. These studies were intended to give a molecular description of the bonding and diffusion of H_2O on ice substrates with experimental values for lattice constants and structure. A companion study is being made on the interaction of the water molecule (and clusters of water molecules) on the basal and prism face of silver iodide[2,3,4]. The latter work is funded by grant from the National Science Foundation.

In the first set of studies, molecular arrays of point charge water molecules are generated to represent the basal and prism faces of hexagonal ice. The adsorbed water monomer and the water molecules in the ice surfaces interact via the H_2O-H_2O potentials of Stillinger and Rahman[5].

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

$$V_{OH}(r) = \frac{72.269}{r} + \frac{6.23403}{r^{9.19912}} - \frac{10}{1+\exp\{40(r-1.05)\}} - \frac{4}{1+\exp\{5.49305(r-2.2)\}} \; ; \tag{2}$$

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

where H and O refer to the hydrogen and oxygen components of the water molecule, and r is the separation distance between the atoms in the subscripts of V. These potentials have been tested for application to liquid water systems. Further discussion of the potentials can be found in the literature[6].

The prism (basal) faces of ice are represented by 100 (50) water molecules arranged in four (two) layers of 25 molecules each in the hexagonal ice I_h structure. Lattice parameters are a = 4.519 A and c = 7.330 A, and each water molecule (with oxygen on a lattice point) is surrounded tetrahedrally by four water molecules 2.76 A distant. All H_2O are rigid with H-O-H bond angle equal to 109.5° and OH distance euql to 0.9584 A. The hydrogens in the model substrate are arranged so that the top surface layer has water molecules with dipole moment projection alternately into and out of the surface plane. Basal ice faces with positive and negative surface polarization have also been modelled[7]. The ice substrate models are finite in size to avoid complicated Ewald summations and to prevent divergences associated with periodic polarized unit cells. The adsorbed water molecule interacts with all the ice substracte molecules, but is constrained with its center of mass projection over a small region about 30 A^2 in area in the center of the array. Since we are interested in the qualitative features of the interactions and not exact magnitudes of binding energies the finite ice model serves adequately. Larger arrays have been examined and found to produce the same qualitative results.

A 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 described above. The upper and lower terrace (basal faces) are negatively polarized and the prism face polarization is the same as that described above. Proton configurations for all of the ice substrate models can be seen in the figures displaying the results.

The maximal binding energy surfaces are generated by minimizing the potential energy of the adsorbed water molecule at a set of grid points about 0.25 A apart and covering the "adsorption" region in the center of the arrays. The center of mass of the water monomer is held with fixed (x,y) projection onto the grid point, and the center of mass height above the substrate, z, and the monomer Euler angles (α,β,γ) are varied until the interaction potential energy is minimized. The minimization is done with subroutine VA04A of the Harwell subroutine library.[8]

Results for the water monomer on the prism (basal) face are shown in Fig. 2a (b) in the form of contour density plots. Shading in the plots indicates regions of higher binding energy for the adsorbed water monomer. Circles on the plots indicate location and proton arrangement of H_2O molecules in the first and second layer of the ice substrate. The largest maximal binding energy site on the two faces is on the prism face (10.2 kcal/mole) and is located in the center of the six membered ring shown in the upper part of the figure. The smallest binding energy is also on the prism face (2.7 kcal/mole)--directly over molecules in the second layer. An interesting view of all the four ice substrates studied is shown in Fig. 1 where the minimal potential energy of the adsorbed water monomer is plotted three dimensionally. Wells in the potential surface indicate regions of large binding energy. Small dots indicate positions of ice substrate molecules in the first layer. In order to examine the effect of extended regions of larger or smaller binding energies, an average maximal binding energy is calculated for each model substrate byweighting the value at each grid point with a Boltzman factor. The averages for the prism and basal faces are 8.9 and 8.3 kcal/mole, respectively. For the negatively and positively polarized basal faces the results are 7.0 and 6.7 kcal/mole, respectively. Thus the prism face of ice appears to be more attractive to the adsorbed water molecule than the basal faces. The energy

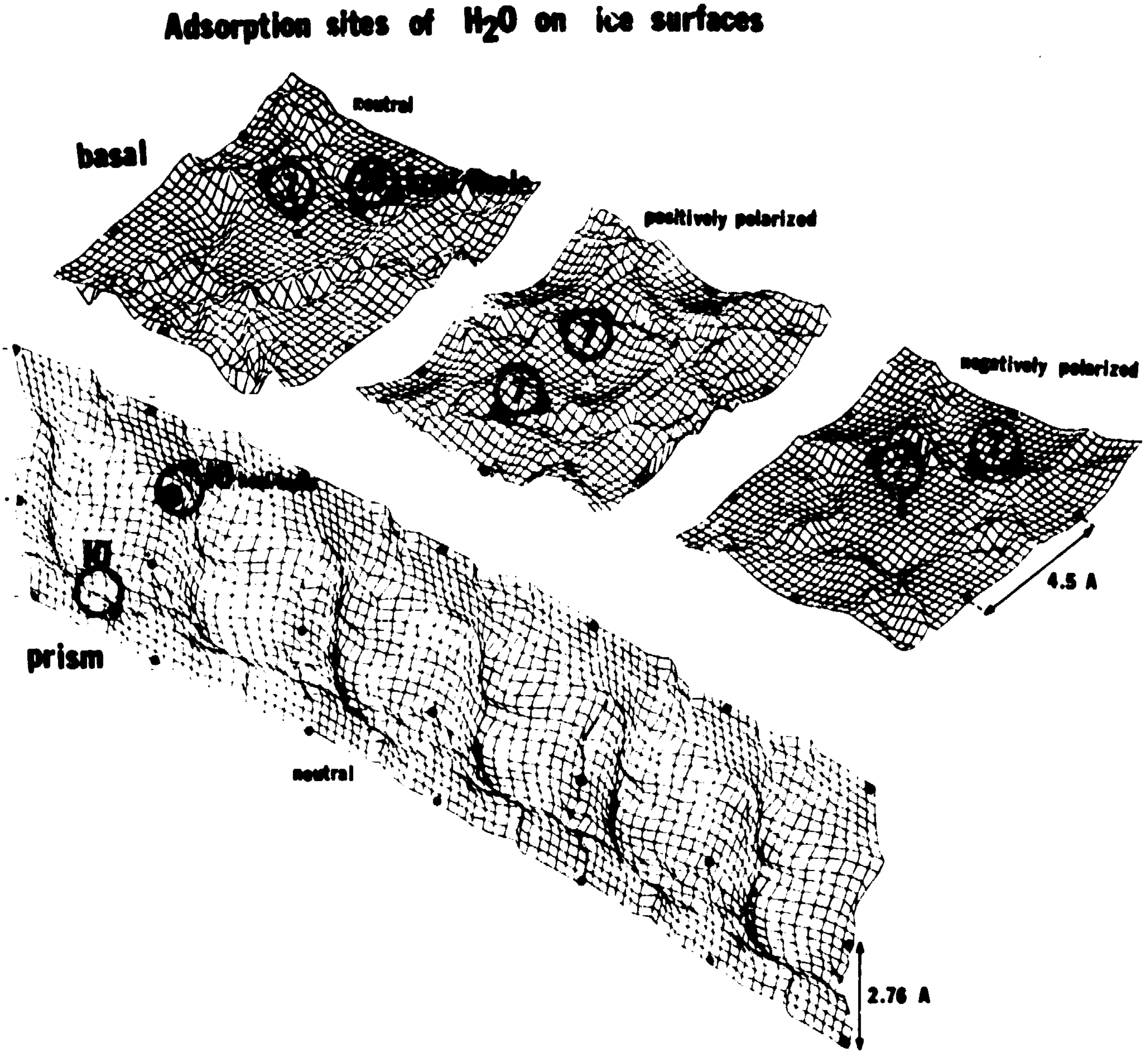

Fig. 1. **Perspective views of the minimal potential energy surfaces of the adsorbed** water monomer on the basal and prism faces of ice. Sample H_2O configurations with maximal binding energies (in kcal/mole) are indicated. Small dots on the contours show positions on first layer ice substrate water molecules.

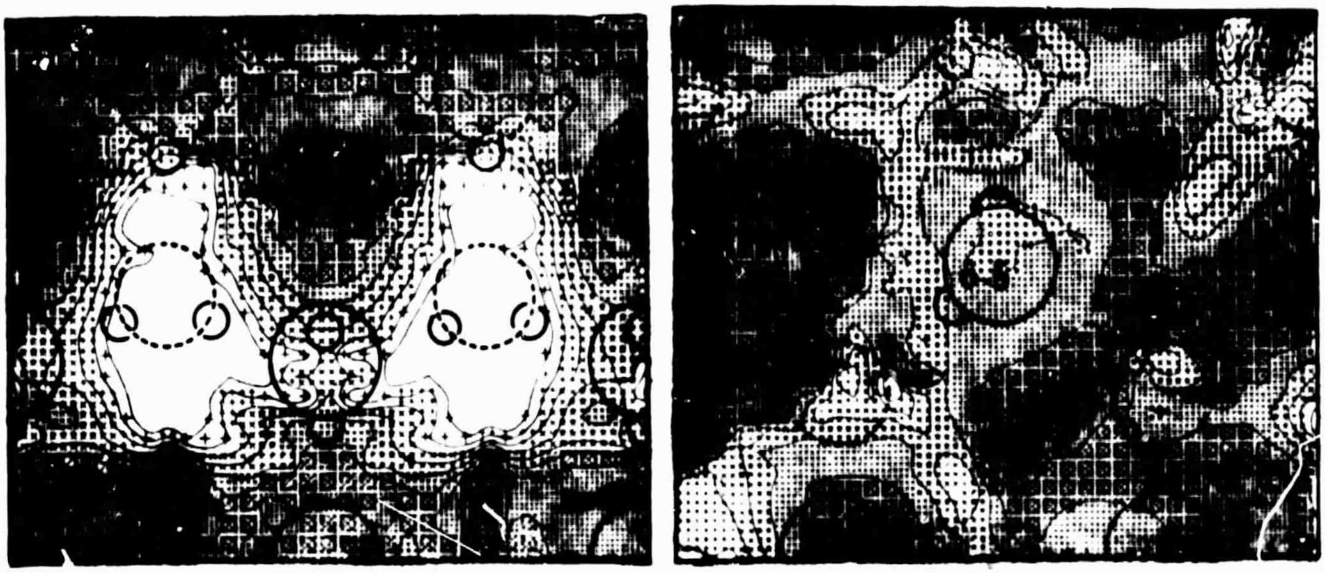

Fig. 2. The maximal binding energy of the water molecules above sites on the (a) prism face and (b) unpolarized basal face of ice I_h. The H_2O molecules in the z = 0 plane are indicated by solid circles; z = -0.9 A plane molecules are indicated by dashed circles. The smallest binding energy contours are 5.0 kcal/mole for the prism face and 6.5 kcal/mole for the basal face. Neighboring contours differ by 0.5 kcal/mole. The largest maximal binding energies are 9.5 and 10.2 kcal/mole for the basal and prism faces, respectively.

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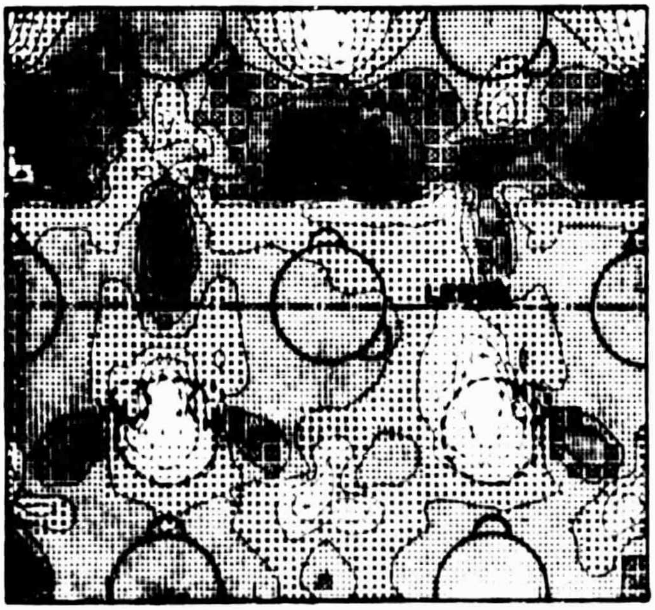

Fig. 3. The maximal binding energy contours for the water monomer above sites on the basal face ledge. Solid circles on and below the dashed line of the ledge are molecules in the first layer of the upper terrace. The lower terrace is at z = -7.33 A, and located in the upper portion of the figure.

barriers to diffusion from grid point to grid point on the maximal binding energy surfaces are 3.0 and 2.5 kcal/mole for the prism and basal surfaces, respectively. Diffusion barriers for the basal faces appear to be independent of the surface polarization.

Maximal binding energy for the water monomer adsorbed on the ice basal face ledge is 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 without the ledge. The maximal binding energy is 10.2 kcal/mole and only slightly larger than that found for the optimal binding configuration on the smooth prism face. The potential energy surface and some optimal bonding configurations are shown in Figs. 4a and 4b.[9]

The main features of the maximal binding energy contours are: (1) potential energy "troughs" which appear to pass around and between first layer ice substrate molecules; (2) a preference for water monomer adsorption on the prism face and above basal face ledges; (3) smaller diffusion barriers on the basal faces; and (4) a complexity of preferred adsorption sites with the adsorbed H_2O greatly affected by neighboring surface proton arrangement. The results of this model present a somewhat different view of H_2O attaching to an ice substrate, and point out the difficulties in modelling the H_2O - ice substrate system with the assumption that molecules adsorb directly above substrate molecules in bulk ice configurations. This calculation indicates that a more complicated situation could prevail--particularly at low monomer concentrations--and hints at the very real possibility of a quasi-liquid like layer on the surface of ice. It is also noted that two dimensional ice clusters forming on the rigid (low temperature) ice surface could assume considerable distortion along the cluster periphery. Since it is the edge energy that determines the energy of formation of the cluster on the substrate, two dimensional nucleation (with some modifications) could once again be a possibility. This was suggested some time ago by Bartley[10]. Future

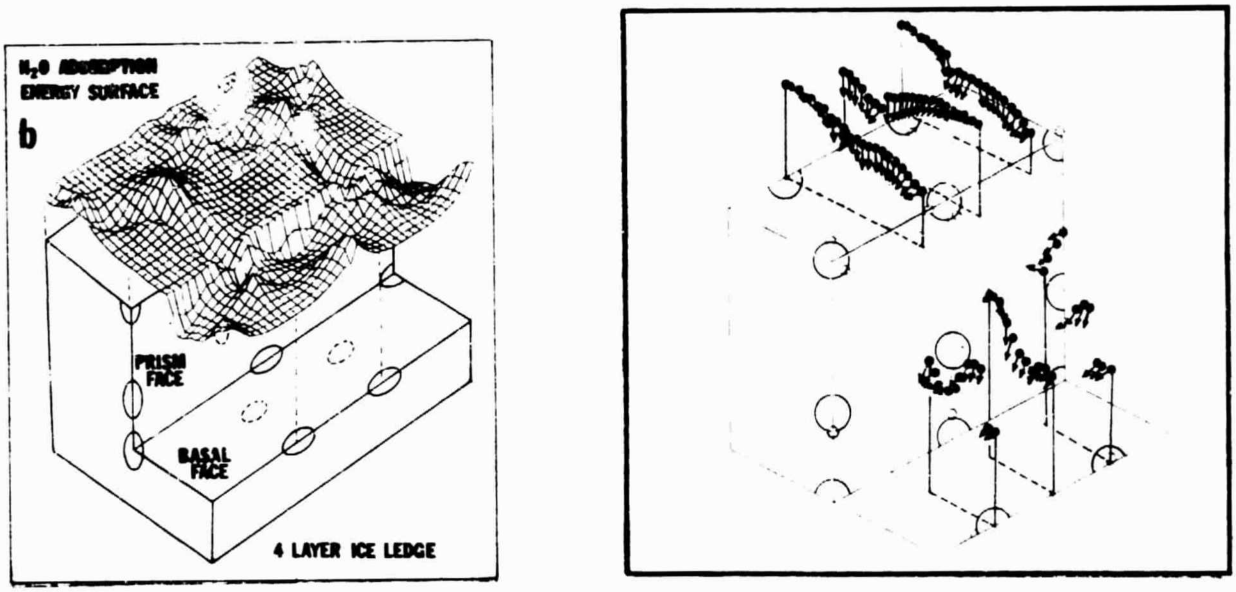

Fig. 4. (a) The minimal potential energy surface for the water monomer adsorbed on the basal ice face with a four layer ledge. (b) Some optimal bonding configurations for the water molecule in three "walks" over the four layer ledge. Dipole porjections onto the plane of the paper are shown.

work will investigate binding energies of adsorbed ice clusters and attempt to determine critical cluster sizes.[11]

II. MOLECULAR DYNAMICS STUDIES OF THE WATER MONOMER AND SMALL WATER CLUSTERS ON THE BASAL FACE OF ICE

These initial studies of the water monomer and a six molecule water cluster on the basal face of ice were begun in order to examine the diffusion rates and the stability of small water aggregates on the ice surface. The basal face ice surface (neutrally polarized) is constructed as in reference 9 , and the water molecules interact via the Stillinger potentials.[5,6] Molecular dynamics is used to follow the development of the water monomer and the six molecule cluster. In Fig. 5 is shown a six-molecule water cluster in the process of breaking up after having been placed on the ice surface in an extended bulk ice lattice configuration. The six membered ring cluster was placed on the surface with zero kinetic energy, but at a position slightly offset from a relative minimum in the interaction potential energy. The displacement from the relative minimum was small--amounting to about 3% of the total binding energy of the cluster to the surface. This deviation in potential is about 1 kT at a temperature of 260 K, and is of the order of thermal fluctuations of the cluster. Figure 5 shows the water molecules diffusing to sites on the ice surface which are optimal adsorption sites. These optimal adsorption sites were studied in the static studies of the water monomer interacting with the ice surfaces.[3,9] We are presently extending these studies to allow the ice surface molecules to move and to study the exchange of energy between the cluster molecules and the ice surface. The results to date indicate that the six membered ring (ice-like) structure is not stable on the ice surface for times small compared to the time between collisions with adsorbed surface monomers. A study of the optimal binding energy surfaces for the adsorbed water monomer has indicated that molecules on the periphery of the surface clusters will find stronger binding to the surface at "interstitial" sites in distorted bonding configurations.[3] Since the six-membered ring cluster is composed entirely of "edge" molecules, it is not surprising that the structure is unstable

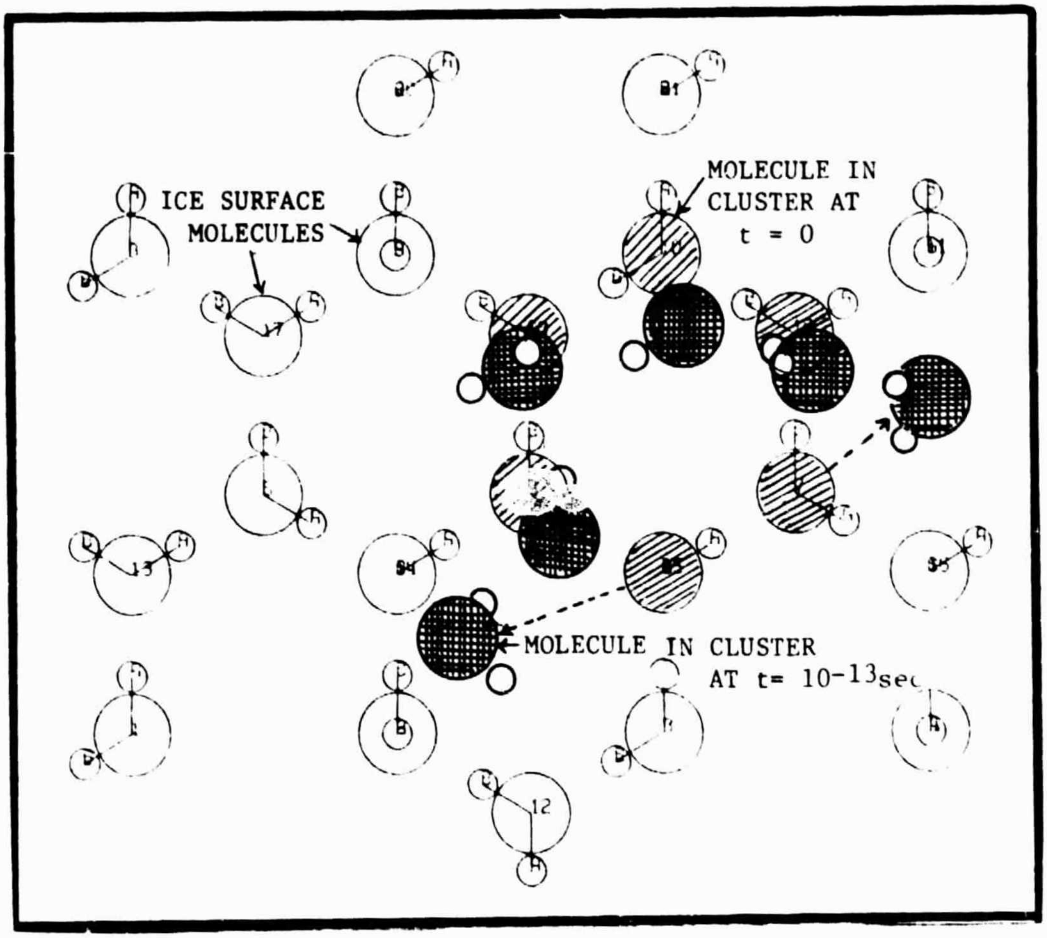

Fig. 5. A six-membered ring water cluster adsorbed on the basal face of ice. ○ circles represent water molecules in the ice substrate; ▨ molecules in the cluster at time t=0; ▦ molecules in the "cluster" at t = 10^{-13} sec.

on the ice surface. We are presently developing computer programs to look at larger ice-like clusters on the ice substrates to investigate the dependence of stability on cluster size.

III. STUDIES OF A PERIODIC ICE STRUCTURE USING THE STILLINGER POTENTIALS

These studies were undertaken in order to examine the equilibrium ice structure resulting from the Stillinger potentials[5,6]. For this investigation, a 192 molecule ice sample was generated which has zero dipole, quadrupole and octupole moments.[13] The ice sample also has a hydrogen arrangement which allows the 192 molecules to form a "unit cell" for application of periodic boundary conditions. The latter conditions are necessary for simulations of bulk ice.

The ice sample was allowed to relax to its equilibrium configuration (at 0°K) and the corresponding lattice constants for the hexagonal ice structure were recorded. The internal O-H distances and H-O-H bond angles were also allowed to vary. These parameters were then used to generate a new unit cell for the periodic ice structure.[13] In the next phase of this study the unit cell in the minimal energy ice structure was allowed to equilibriate at 20°K using a Metropolis Monte Carlo method [12]. Figure 6 shows one layer of the unit cell after 50 thousand steps. The darkened molecules represent the initial configuration. There is considerable relaxation at the surface of this large ice sample--reflecting the deficiency of nearest neighbors in the surface molecules.

Present studies are examining the relaxation of the periodic ice structure using the Monte Carlo method at 20°K. The results indicate that the initial minimization, which produced values 2.78 A, 0.97 A, and 101° for the O-O separation distance in the hexagonal ice, the O-H distance internal to the H_2O molecule, and the H-O-H angle internal to the water molecule, respectively, is consistent with a full Monte Carlo equilibration at 20°K. That is, the Stillinger potentials support a hexagonal ice structure at this temperature with the above constants generating the lattice constants and the internal H_2O parameters. Subsequent work will investigate the temperature range in which this structure is stable and examine the relaxed surface of the sample cleaved along basal and prism planes.

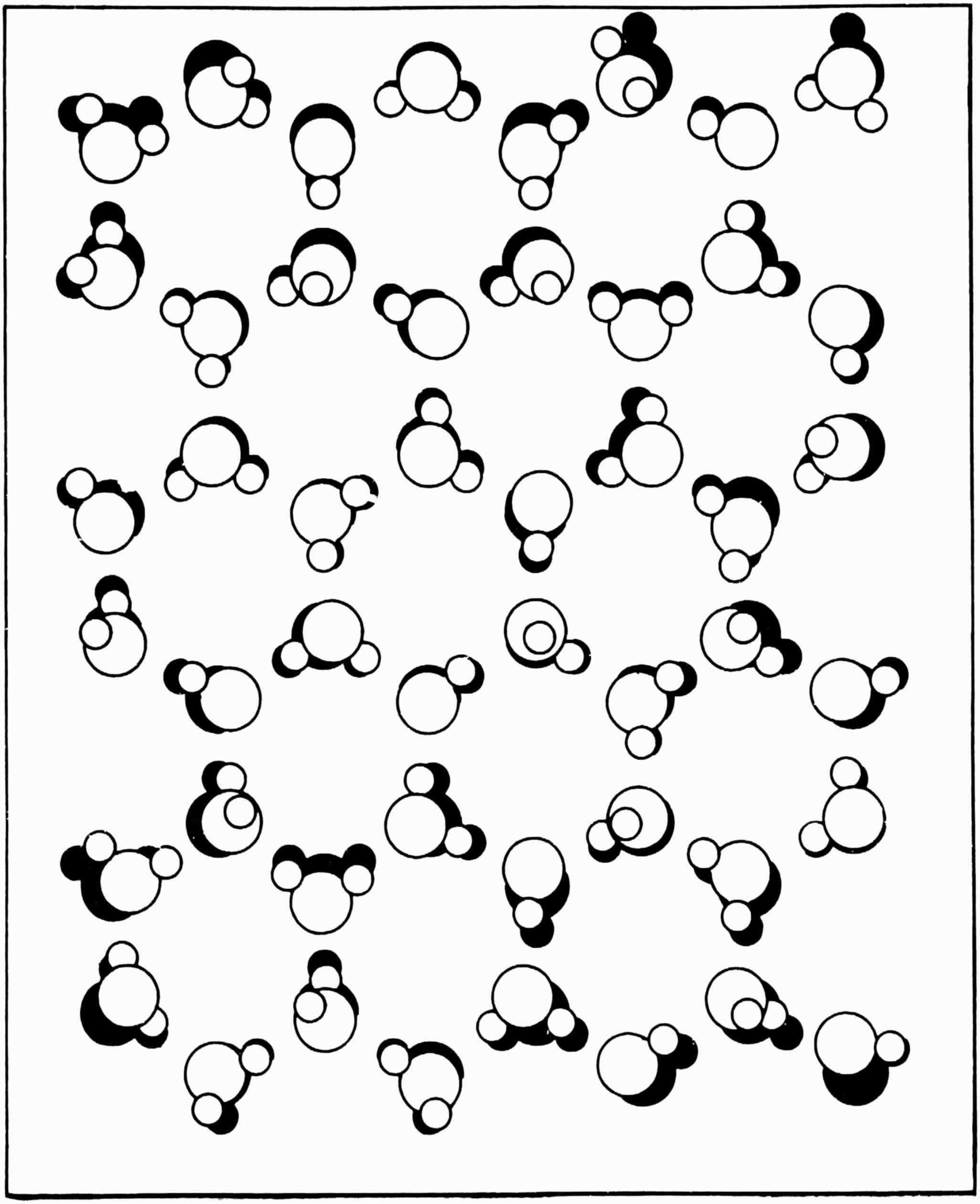

Fig. 6. One layer of the basic cell of the ice sample after 50 thousand Monte Carlo steps at 20°K. The darkened molecules indicate the initial configurations.

IV. COMPANION STUDIES OF WATER ON AN ICE NUCLEATING AGENT

Under National Science Foundation Grants ATM77-12614 and ATM80-15790 a companion study of ice nucleation on silver iodide has been carried out. The objectives have been to determine critical cluster sizes, and nucleation rates for water and ice on hexagonal AgI, to examine the properties of water layers on the same substrate and to determine which substrate features promote ice formation. For results on these studies we refer the reader to the attached copies of references 2, 3 and 4. The studies primarily indicate a preference for monolayer water clusters containing five and six membered rings. Diffusion rates on the basal AgI faces were found to be larger than on the prism face and binding to the substrate was preferred on the prism face--at sites not directly above first or second layer substrate atoms.

An example of a two layer water cluster on the AgI basal face is shown in Fig. 7. The upper part of the figure shows the layering (viewed parallel to the basal face) and the lower portion shows the predominance of five and six membered rings centered on the exposed iodine atoms. This figure was generated from a Metropolis Monte Carlo simulation of 88 water molecules adsorbed on AgI at 265°K. Similar studies of water layers on the ice substrates are being developed--using the periodic ice sample described in the previous section. Critical cluster sizes on the AgI basal and prism faces are also being studied -- using the technique described in reference 11.

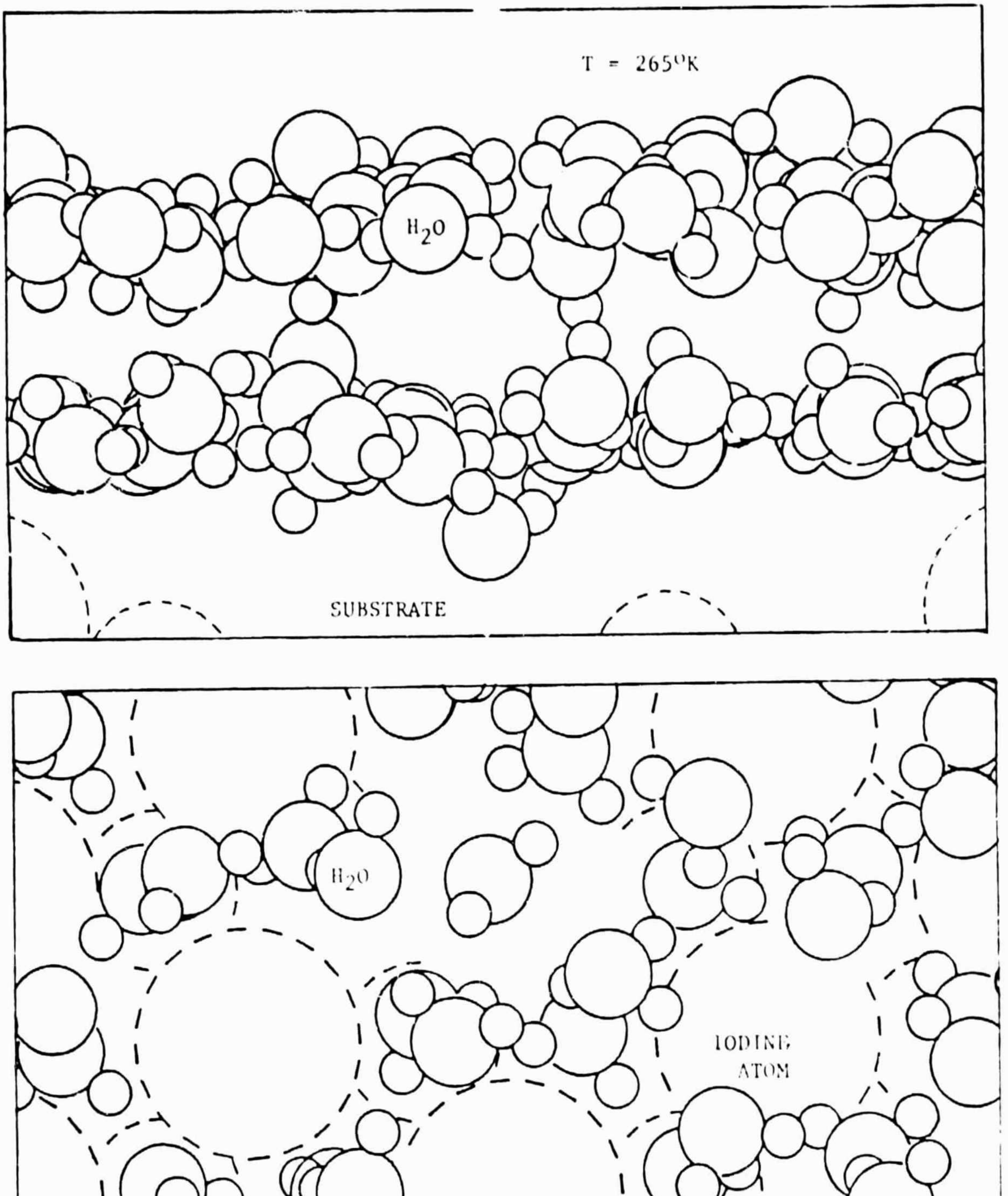

Fig. 7. Snapshot of a two layer water system on the basal face of silver iodide. Top view is parallel to the substrate; bottom view is looking down on the basal face. Evidence of six-membered ring structure is seen in the top layer of water molecules.

V. PUBLICATIONS DURING THE GRANT PERIOD

"The Water Monomer on the Basal Plane of Ice I_h: an Effective Pair, Central Force Potential Model of Static Interaction", J. Kiefer and B. Hale, J. Chem. Phys. 67, 3206 (1977).

"Studies of Water on AgI Surfaces: an Effective Pair Potential Model", J. Kiefer and B. Hale, J. Chem. Phys. 73, 923 (1980).

"Theoretical Studies of Water Adsorbed on Silver Iodide", B. Hale, J. Kiefer, S. Terrazas, and R. Ward, J. Phys. Chem. 89, 1473 (1980).

"The Water Monomer on Surfaces of Ice I_h: Comparison of the Basal and Prism Faces", B. Hale, J. Kiefer, and C. Ward, J. Chem. Phys., 75, (August 15, 1981).

"A Monte Carlo Method for Approximating Critical Cluster Size in the Nucleation of Model Systems", B. Hale and R. Ward, submitted to J. Statistical Physics.

"Monte Carlo Studies of Water Monolayer Clusters on Surfaces: AgI Basal Face", R. Ward, J. Holdman and B. Hale, submitted to J. Chem. Phys.

VI. PAPERS PRESENTED AND MEETINGS ATTENDED

ORAL PRESENTATIONS

"The Water Monomer on the Basal Planes of Ice and AgI: An Effective Pair Potential Study", Jerry Kiefer and Barbara Hale, Paper Presented at the Ninth International Conference on Atmospheric Aerosols, Condensation and Ice Nuclei, September 1977, Galway, Ireland.

"An Effective Pair Potential Study of the Interaction of a Water Monomer with the Basal Plane of Ice I_h", B. N. Hale and J. Kiefer, Paper Presented at the Symposium on the Physics and Chemistry of Ice, Cambridge, England, September 1977.

"The Water Monomer on Ice and AgI", U.M.R. Physics Colloquium, October 1977.

"Two-dimensional Nucleation and Studies of H_2O on the AgI and Ice Substrates", Ice Crystal Growth Habit Workshop, Boulder, Colorado, February 1978.

"Bonding and Diffusion of the Water Molecule on the Substrates of β-AgI and Ice", Nucleation Symposium, American Chemical Soc. Meeting, Anaheim, California, March, 1978.

"The Water Molecule on Surfaces of AgI", Colloquium, University of Washington, Seattle, Washington, May 1978.

"Effect of AgI Surface Structure on the Adsorption of H_2O Molecules", talk presented at the Gordon Conference on Chemistry at Interfaces, Meriden, N.H., July, 1978.

"Theoretical Studies of Water Adsorbed on Silver Iodide", with Jerry Kiefer, Sergio Terrazas and Richard Ward, 53rd Colloid and Surface Science Symposium, Rolla, Missouri, June 11-13, 1979.

"Molecular Modelling of Water on Silver Iodide", Seminar, Calspan Corp., Buffalo, N.Y., July 1979.

"Theoretical Studies of H_2O on Surfaces of β-AgI", Colloquium, Carnegie Mellon University, October, 1979.

"Monte Carlo Studies of Clusters of Water Molecules Adsorbed on Silver Iodide: Cluster Stability and Structure", R. Ward, S. Terrazas, and B. Hale, 54th Colloid and Surface Science Symposium, Lehigh University, June 1980.

"Monte Carlo Studies of H_2O Clusters on an Ice Nucleating Agent: AgI", Nucleation Symposium, Am. Chem. Soc. Meeting , Las Vegas, August 1980, with R. Ward and J. Holdman.

"Monte Carlo Studies of Water Clusters on Silver Iodide Substrates", Poster Paper presented at the Gordon Conference on Water and Aqueous Solutions, Plymouth, NH, July, 1980, with R. Ward, J. Holdman and W. Joubert.

"A Lattice Gas Model for Adsorption on AgI", S. Terrazas and B. Hale, Missouri Academy of Sciences Meeting, St. Joseph, MO, April, 1981.

OTHER ACTIVITIES

WMO/IAMAP Scientific Conference on Weather Modification, Tashkent, U.S.S.R., October, 1973.

Ice Nucleation Workshop, Laramie, Wyoming, June, 1975.

International Cloud Physics Conference, Boulder, Colorado, July, 1976.

Second WMO Scientific Conference on Weather Modification, Boulder, Colorado, August, 1976.

Nucleation Symposium, American Chem. Soc. Meeting, New Orleans, March, 1977.

Midwest Solid State Conference, Purdue University, October, 1977.

NSF Review Panel for Proposals on Women in Science, January, 1977.

Ice Crystal Growth Habit Workshop, Boulder, Colorado, February, 1978.

American Chemical Society Meeting, Anaheim, California, March, 1978.

Gordon Conference on "Chemistry at Interfaces", Meriden, New Hampshire, July, 1978.

Visit to Institut for Experimental Physics, University of Vienna, September, 1978.

Gordon Conference on Water and Aqueous Solutions, Plymouth, NH, July 1980.

American Chemical Society Meeting, Las Vegas, August, 1980.

VII. SENIOR PERSONNEL INVOLVED IN THE PROJECT

Dr. Barbara Hale
Dr. Richard Ward
Dr. Peter Deutsch

VIII. GRADUATE STUDENTS AND DEGREES EARNED

1. Jerry Kiefer (Ph.D. in Physics, September 1979)
   Dissertation: "Effective Function Models of the Water-Surface Interaction: Ice and AgI"

2. Sergio M. Terrazas (Ph.D. in Physics, December 1981)
   Dissertation: "Adsorption of Water Molecules on Substrates"

3. Phillip Barton (Ph.D. in Physics - candidate)

IX. UNDERGRADUATE STUDENTS INVOLVED IN THE PROJECT

1. David Lataigne (Summer 1979)

2. Wayne Joubert (Summers, 1980, 1981)

3. Jon Holdman (Summers, 1980, 1981; Academic years, 1980-81 and 1981-82)

X. SUMMARY OF PROGRESS

During the grant period we have developed molecular models for the water molecule's environment on the positively, negatively and neutrally polarized ice I_h basal faces,[7] on the neutrally polarized ice I_h prism face,[9] and on a negatively polarized ice basal face with a four-molecular layer ledge.[9] The water monomer was found to adsorb more strongly on the prism face than on the basal faces of ice--at sites not directly above molecules in the first or second layer of the (rigid) ice I_h substrate. The basal face four layer ledge served to expose favorable sites on the prism face and to promote attachment of the H_2O at the base of the step. Diffusion rates for the monomer were found to be slightly larger on the basal faces.[7,9] These results, together with the multiplicity of relative maxima found in the binding energy for H_2O adsorbed on ice, indicate a rather complex environment for the adsorbed water. The latter is consistent with the existence of a liquid-like layer on the ice surfaces.[1] Molecular dynamics studies of the decay of a six membered ring ice structure on the (rigid) ice basal further strengthen this hypothesis. A 192 molecule periodic ice structure was generated which has zero dipole, quadrupole and octupole moments.[13] The sample was allowed to relax to an equilibrium hexagonal ice lattice using the Stillinger central force potentials. The optimal lattice constant values were determined, together with optimal values for the H_2O internal O-H distance and H-O-H bond angle.[13] This energy minimized periodic ice structure is presently being studied via Metropolis Monte Carlo methods to determine stability as a function of temperature. The surface of this ice structure will be applied to studies of the stability and structure of basal and prism ice surface layers and subsequently to studies of ice crystal growth habit and nucleation of ice layers. During the grant period four articles have been published in refereed journals,[2,3,7,9] two articles have been submitted for publication,[4,11] one manuscript is in preparation,[13] and 15 papers have been presented .

XI. REFERENCES

1. H. Weickmann, "A Review of Snow Crystal Gorwth and Its Relationship to Precipitation Systems", paper presented at the Workshop on Ice And Snow Crystal Growth Boulder, Colorado, February 1978

2. B. Hale, J. Kiefer, S. Terrazas and R. Ward, J. Phys. Chem. 84, 1473 (1980)

3. B. Hale and J. Kiefer, J. Chem Phys. 73, 923 (1980)

4. R. Ward, J. Holdman and B. Hale," Monte Carlo Studies of Water Monolayer Clusters on Surfaces: AgI Basal Face", to be published.

5. F. H. Stillinger and A. Rahman, J. Chem. Phys. 68, 666 (1978); 60, 1545 (1974)

6. F. H. Stillinger and A. Rahman, J. Chem. Phys. 60, 1545 (1974) and references contained therein.

7. J. Kiefer and B. Hale, J. Chem. Phys. 67, 3206 (1977).

8. M.J. Powell, Comput. J. 7, 155 (1964).

9. B. Hale, J. Kiefer and C. Ward, J. Chem. Phys. 75, 1991 (1981).

10. D. Bartley, J. Chem Phys. 65, 1876 (1976); 66, 1063 (1977).

11. B. Hale and R. Ward, "A Monte Carlo Method for Approximating Critical Cluster Size in the Nucleation of Model Systems", submitted to J. Stat. Physics

12. N. Metrolopis, A. W. Rosenbluth, M.N. Rosenbluth, A. Teller and E. Teller, J. Chem. Phys. 21, 1087 (1953).

13. P. Deutsch, B. Hale and R. Ward, to be published.