

Growth and structure of amorphous ice condensates: A computational study. II

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Citation: *The Journal of Chemical Physics* **96**, 3814 (1992); doi: 10.1063/1.461886

View online: <http://dx.doi.org/10.1063/1.461886>

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Growth and structure of amorphous ice condensates: A computational study. II

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(Received 23 October 1991; accepted 25 November 1991)

Investigation is presented of the static and the dynamic properties of an amorphous cluster $(\text{H}_2\text{O})_{450}$ at $T \approx 10$ K. The cluster was obtained in a simulation of slow condensation of gaseous water molecules, and is used here to obtain insights into molecular properties of low temperature amorphous ice deposits. The cluster is shown to contain a substantial fraction of molecules of hydrogen bond coordination less than 4. Low coordinated configurations are formed during condensation in a highly selective fashion, i.e., some configurations are strongly favored over others. Condensation dynamics is investigated, in an effort to clarify a link between molecular mechanisms of condensation and the resulting metastable structure. Physical reason is suggested for the experimentally measured very large surface area of the amorphous ice deposits.

I. INTRODUCTION

Amorphous ice [H_2O (as)] is an interesting example of a glassy solid whose structure is determined by formation dynamics. Amorphous ice is obtained by slow condensation of water vapor on a cold surface.¹ At low temperatures the condensing molecules are insufficiently mobile to relax to the low energy crystalline structure, and the resulting solid is energy rich and amorphous. Low temperature (10–77 K) deposition results in a microporous form of H_2O (as) of a large surface area with respect to gas absorption.^{2,3}

In a recent series of studies we have employed the molecular dynamics computer simulation technique⁴ to study formation, structure and dynamics of this glassy hydrogen-bonded substance. The present article summarizes some new results on the subject, obtained from the analysis of a model amorphous ice cluster $(\text{H}_2\text{O})_{450}$ at $T \approx 10$ K. The main objective is to explore the connection between the dynamics of the condensation process, and the resulting molecular properties of the amorphous ice condensate.

Recent experimental data show that low temperature H_2O (as) deposits contain a significant amount of partially coordinated water molecules, i.e., molecules with less than four hydrogen bonds. Some of such molecules have “dangling” OH bonds, i.e., OH bonds in which the H atom is not hydrogen bonded. The dangling bonds have a characteristic spectroscopic signature in the infrared, which was recently investigated in detail by Devlin and collaborators.⁵ Another recent set of experimental data, of Johari *et al.*,⁶ on the dielectric behavior of H_2O (as) also suggests presence of low-coordinated water molecules on the H_2O (as) surface. I examine in this study the type of low-coordinated molecules found in our H_2O (as) model, and demonstrate the important role of such molecules in the growth process of amorphous ice.

This article is organized as follows: In Sec. II methodological aspects are discussed. Section III describes structural and dynamic properties of the simulated $(\text{H}_2\text{O})_{450}$ cluster.

Section IV focuses on condensation dynamics and its relation to the structure of the cluster. Summary is presented in Sec. V.

II. METHODOLOGICAL ASPECTS

A. Calculation of a simulated H_2O (as) cluster

The calculations of Secs. III and IV are performed on a 450 molecule amorphous ice cluster, obtained by a simulation protocol described in Ref. 4(b). Briefly, the calculation was designed to simulate (within the constraints of the computer resources) the experimental formation process of amorphous ice, i.e., slow condensation of water vapor. Classical equations of motion were solved for a sequence of H_2O molecules impinging at random on the cluster and sticking to its surface; the cluster kept growing as a result. (The initial cluster nucleus contained ten water molecules and was obtained by relaxing a piece of a cubic ice structure.) The molecules were found to stick to the cluster with unit probability. Each sticking trajectory was continued for 8–14 ps. The water molecules were assumed rigid. The pairwise TIPS2 intermolecular potential⁷ was employed with cutoff of 11 Å. The trajectory was integrated using the Verlet algorithm, in which the SHAKE procedure was incorporated to keep the bonds rigid.⁸

The temperature of the cluster was defined as twice the mean kinetic energy per degree of freedom, divided by the Boltzmann constant. Each sticking trajectory was associated with a T jump due to release of binding energy of the new molecule to the cluster. [In the laboratory experiments on H_2O (as) condensation, the binding energy is carried away by a metal substrate. The metal was not included explicitly in the calculation due to computer time limitations.] The molecular velocities within the cluster were rescaled after each sticking trajectory by a constant factor to represent cooling back to the initial temperature, which was 10 K. Thus the

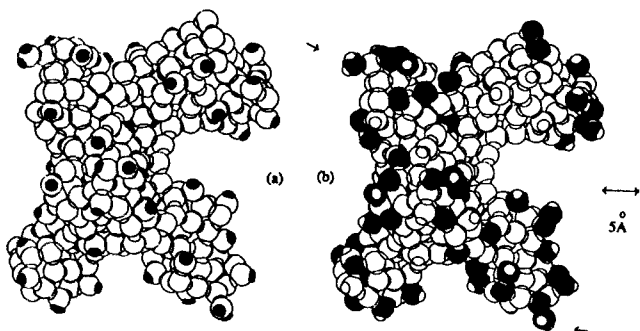


FIG. 1. The $(\text{H}_2\text{O})_{450}$ amorphous ice cluster. (a) Dangling H atoms marked in black. (b) Dangling O atoms marked in black. A dangling H atom does not participate in a hydrogen bond, a dangling O atom participates in one hydrogen bond. Two one-coordinated molecules are marked by arrows.

present computational protocol introduces fluctuations in temperature of the simulated amorphous ice cluster. The T jump after a sticking event decreased of course with the size of the cluster, and beyond cluster size of ~ 50 molecules it became less than 30 K. For sticking trajectories of molecules number 128–450, the final T value of a trajectory was in the range 12–27 K. Thus most of the simulation of the condensation process, leading to the formation of the $(\text{H}_2\text{O})_{450}$ cluster, was in the temperature range between 10 and 27 K. The cluster structure used in the present analysis is the last structure of a condensation trajectory of the 450th molecule; the cluster temperature in the end of this trajectory was 13 K. The shape of the final 450 molecule cluster is shown in Fig. 1.

In Sec. III, the analysis is presented of 116 sticking trajectories out of the ensemble leading to the formation of the $(\text{H}_2\text{O})_{450}$ cluster. The ensemble is composed of condensation trajectories of molecules number 332–450 (with the exception of molecules 434, 435, and 436). Emphasis was made on the type of bonding formed by the newly attached molecules to the cluster surface. The temperature of the impinging molecules was 10 K. The initial distance of an impinging molecule to the nearest cluster molecule was 10 Å. [Detailed choice of initial conditions for each trajectory is described in Ref. 4(b).] The duration of the trajectories in this group was either 10 or 14 ps. Specifically, a trajectory was terminated after 10 ps unless the final potential energy of the newly attached molecule was above -5.2 kcal/mol, in which case the trajectory was run for additional 4 ps to allow extra time for relaxation. Each trajectory was examined at 1 ps intervals. A first structure in which the impinging molecule was found hydrogen bonded to the surface was stored and used to examine initial bonding of the molecule to the surface. The average time of the initial bonding, from the initiation of the trajectory, was 3.9 ps (standard deviation: 1.0 ps). I also examined the bonding of the newly attached molecules to the surface in the last structure of each trajectory (which corresponded to $t = 10$ ps in 87 trajectories, and to $t = 14$ ps in 29 trajectories).

Molecular motions in the final $(\text{H}_2\text{O})_{450}$ cluster are discussed in the end of Sec. III. For the purpose of this discus-

sion, an extended 165 ps classical trajectory was evaluated for the $(\text{H}_2\text{O})_{450}$ cluster. The initial conditions of this run were designed to eliminate slight global rotation of the cluster which was generated by the sticking trajectories. (In the simulation of the cluster growth, this rotation was not eliminated, since its period was several orders of magnitude larger than a time scale of a sticking trajectory. In the extended 165 ps trajectory, global rotation was eliminated to facilitate analysis of local molecular motions.) The initial coordinates were adopted from the last structure of a sticking trajectory of molecule number 450. The initial velocities were set to zero, to ensure zero angular momentum. A relaxing trajectory was then run for 1 ps; during this period the molecules acquired nonzero velocities because the initial structure was not at minimum; the final kinetic temperature was 6.7 K. Velocity scaling and an additional relaxing trajectory were used to reset the kinetic temperature to 8.4 K. The corresponding velocities were used as initial conditions for the 165 ps trajectory. Structures along the trajectory were analyzed at 5 ps intervals. Gradual heating of the cluster during the trajectory run was obtained because of the use of 11 Å cutoff for the TIPS2 potential. The cutoff introduces a noise component to the forces exerted on a water molecule, resulting in deviations from conservation of energy, and in heating; a 20 ps trajectory run was found to be associated with heating by 3 deg. To avoid excessive rise in temperature during the 165 ps trajectory, the velocities were rescaled every 5 ps; the scaling factor was chosen so that the initial value of the total energy was recovered after rescaling. The resulting average temperature in this run was 8.4 K, with variance of 0.65 K.

B. Definition of a hydrogen bond

Analysis of hydrogen-bond network in a disordered system requires mathematical definition of an H bond. In this

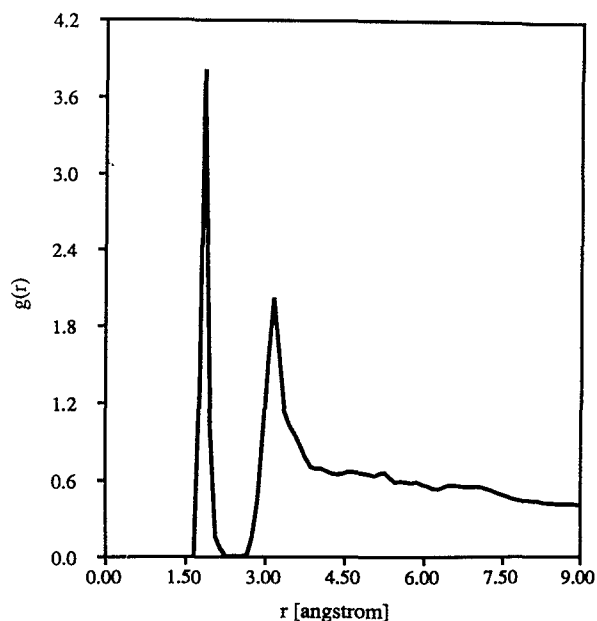


FIG. 2. Radial distribution function of distances between O atoms and H atoms in the $(\text{H}_2\text{O})_{450}$ cluster (excluding the chemically bonded pairs). Resolution is 0.1 Å for $r < 3.4$ Å, and 0.2 Å for $r > 3.4$ Å.

study two water molecules are defined as hydrogen bonded if one of the intermolecular $O\cdots H$ distances is less than 2.3 Å. Figure 2 shows $g_{O\cdots H}$, the radial distribution function of distances between O atoms and H atoms in the $(H_2O)_{450}$ cluster. [Definition of $g_{O\cdots H}$ of the cluster is given in Ref. 4(b) Eq. (3)]. The first sharp peak is followed by a dip which is 3 orders of magnitude of the value at the first peak. It thus appears reasonable to define pairs of molecules contributing to the first peak as "hydrogen bonded."

Other definitions of a hydrogen bond are commonly employed in the literature.^{7,9} These include a geometric definition based on $O\cdots O$ distance, that is a pair of H_2O is defined H bonded if the $O\cdots O$ distance is within the first peak of the radial distribution function g_{OO} . We do not employ this definition since in our H_2O (as) models a small number of pairs of molecules can be found with short $O\cdots O$ distance, but with very weak or even repulsive interaction [see Ref. 4(b), Fig. 3]. This problem does not occur with a definition based on the $O\cdots H$ distance.

Another commonly employed definition of the H bond is based on the distribution of the pair interaction energies between molecules. This distribution for the $(H_2O)_{450}$ cluster is shown in Fig. 3. The usual convention is to use the energy corresponding to the dip in the plot (-2.9 kcal/mol in our system) as a criterion; thus pairs of molecules with interaction energy less than the "dip" energy are defined as hydrogen bonded. However, the dip in the distribution is several percent of the maximum value at -5.5 kcal/mol, and thus the separation between the "bonded" and the "nonbonded" pairs of molecules is (in my view) less sharply defined than in the $O\cdots H$ based geometric definition. Also, the $O\cdots H$ based definition appears more intuitively pleasing for defining dangling bonds and dangling atoms—thus a dangling H atom is defined as the one that does not have an O atom in

close vicinity. It should be noted that although the $O\cdots H$ based geometric definition is used throughout this paper, the use of the energy definition yields similar results. That is because out of total of 836 H bonds which are found in the cluster according to the $O\cdots H$ criterion, 819 bonds satisfy also the energy criterion. The remaining 17 bonds correspond to pair interaction energies in the range $(-1.37) \sim (-2.83)$ kcal/mol; the average value of -2.3 kcal/mol is not that far from the -2.9 kcal/mol cutoff of the energy criterion.

III. MOLECULAR PROPERTIES OF THE MODEL H_2O (as) CLUSTER

A. Structural properties of the $(H_2O)_{450}$ cluster

In the discussion below I use a snapshot of the cluster in the end of the sticking trajectory of a molecule number 450. Dynamic properties are discussed in Sec. III B; there the cluster is shown to be quite rigid, which further supports the validity of using a single snapshot for discussing structural properties.

The average number of hydrogen bonds per molecule in our $(H_2O)_{450}$ cluster (shown in Fig. 1) is 3.72. Figure 4 shows the number of hydrogen bonds per molecule, averaged over consecutive groups of 20 molecules. The molecules are indexed by the order of arrival to the cluster. It is seen that the 20 molecules which arrived last have on the average 2.45 H bonds per molecule, and that the average coordination increases gradually towards 4 as the "age" of the molecules in the cluster increases. From this plot, a typical molecule sticking to the surface appears to start with

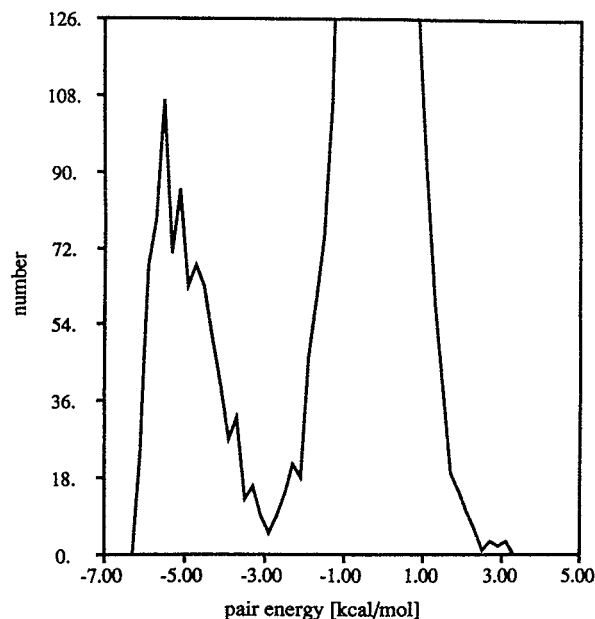


FIG. 3. Histogram of interaction energies between pairs of molecules in the $(H_2O)_{450}$ cluster; energy grid of 0.2 kcal/mol.

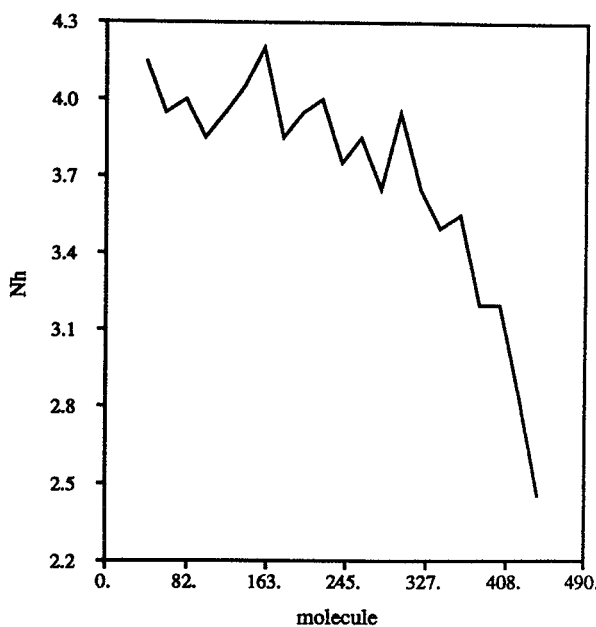


FIG. 4. Number of hydrogen bonds per molecule, averaged over consecutive groups of 20 molecules in the $(H_2O)_{450}$ cluster. Molecules are indexed by the order of arrival to the cluster.

TABLE I. Properties of molecules of different coordinations in the $(\text{H}_2\text{O})_{450}$ cluster.

Type of coord. ^a	Number ^b	\bar{E}_{pot} ^c (kcal/mol)	\bar{R} ^d (Å)	$N_{\text{min}} - N_{\text{max}}$ ^e	\bar{N} ^f
O	2	- 6.7 (0.1)	24.0 (0.2)	446,447	
OH	30	- 13.2 (1.6)	18.0 (3.5)	237-450	394 (56)
OOH	30	- 19.0 (1.6)	15.5 (3.7)	104-442	348 (90)
OHH	59	- 17.7 (1.7)	15.0 (4.6)	24-444	298 (106)
OOHH	302	- 23.3 (1.9)	12.3 (4.6)	2-443	185 (115)
OOOHH	27	- 27.6 (1.8)	12.1 (2.4)	1-370	182 (106)

^a Notation such as OOH means molecule with two hydrogen bonds via oxygen, and one via hydrogen.

^b Number of molecules of given coordination within the cluster.

^c Average potential energy; standard deviation in parentheses.

^d Average distance from the center of mass of the cluster; standard deviation in parentheses.

^e Range of indices; molecules are indexed consecutively by arrival order to the cluster.

^f Average index; standard deviation in parentheses.

coordination 2 or 3 and to acquire eventually (during the growth of the cluster) the usual coordination 4.

The range of the hydrogen bond coordinations in the $(\text{H}_2\text{O})_{450}$ cluster extends from 1 to 5. The number of molecules of various coordinations, and their properties are given in Table I. Notation such as OOH means "molecule with two hydrogen bonds via oxygen, and one via hydrogen." While 302 out of the 450 molecules are the in usual 4-coordinated OOHH configuration, there is also a substantial and interesting population of other coordinations, most notably 119 2- and 3-coordinated molecules. Table I shows that the lower is the coordination, the higher is the average distance from the cluster center of mass; also lower coordinated molecules correspond, on the average, to later arrivals to the cluster.

The most striking feature of these results is a clear indication of the selectivity of the condensation process. Thus the only kind of 2-coordinated molecules found in the cluster is the asymmetrically connected OH category; the OO and HH configurations are absent. Also, the OHH connected 3-coordinated molecules are twice as abundant as the OOH connected molecules; despite the fact that the OHH molecules have, on the average, higher potential energy. Thus condensation dynamics appears to favor some molecular configurations at the expense of others. More detailed analysis of the relation between condensation dynamics and the resulting molecular structure is presented in the next section.

Recent spectroscopic studies^{5(a),5(c)} in conjunction with initial computational analysis^{5(b)} indicated presence of two kinds of dangling OH bonds within 10 K amorphous ice deposits (evidenced by a pair of infrared OH stretch absorption features). In accord with these results, our simulated cluster contains two major types of dangling bonds—the ones belonging to the 30 2-coordinated OH-connected molecules, and the ones belonging to the 30 3-coordinated OOH-connected molecules. "Dangling OH bonds" are defined by the presence of a dangling H atom; i.e., in a dangling OH bond an H atom is not hydrogen bonded. In addition to 64 dangling H atoms (4 in 1-coordinated molecules, 30 in 2-coordinated, and 30 in 3-coordinated), the cluster contains 91 dangling O atoms, i.e., O atoms involved in only one hy-

drogen bond (2 in 1-coordinated molecules, 30 in 2-coordinated, and 59 in 3-coordinated OHH molecules). The dangling H and O atoms are marked in Fig. 1. It is shown in the next section that the dangling atoms play a major role in the condensation process of amorphous ice.

The 27 5-coordinated molecules within the cluster are all OOOHH connected. One may note that in 9 out of 27 5-coordinated molecules, one of the hydrogen bonds does not satisfy the energy criterion for bonding; that is, although the $\text{O} \cdots \text{H}$ distance is short (< 2.3 Å), but the interaction energy is above $- 2.9$ kcal/mol (see end of Sec. II for discussion of the geometric and the energy criteria for hydrogen bonding). Presence of 5-coordinated molecules was revealed in our previous study of a smaller 116-molecule cluster; it was shown there that such molecules disappear upon simulated annealing.^{4(c)} The existence of 5-coordinated molecules in low temperature simulated clusters can be accounted for as follows. TIPS2 pair potential used in this study is a sum of the Lennard-Jones interaction centered on the O atoms, and of the Coulombic interactions between charges; in each molecule two positive charges are placed on the H atoms, and one negative charge near the O atom. Thus to hydrogen bond to a water molecule, an O atom of another molecule must approach the vicinity of one of the positive charges on the H atoms. On the other hand, an H atom can approach from anywhere on the O side of the water molecule. Thus the bonding to an O atom is less directional than the bonding to an H atom of a water molecule, and this lack of directionality appears to allow for occasional formation of three bonds to an oxygen atom of a water molecule. One may note that although the above description is in terms of the TIPS2 potential, the nondirectionality of hydrogen bonding to O atoms in water appears to be well established, independently of the TIPS2 model; see, e.g., the review by Stillinger.⁹ There is evidence from other studies indicating presence of 5-coordinated molecules in condensed forms of H_2O ; such molecules were invoked, for example, to explain the unusual behavior of the self-diffusion coefficient in liquid water.¹⁰

Past studies^{1(c),1(l),4} have shown that the structure of H_2O (as) combines significant ordering along the hydrogen

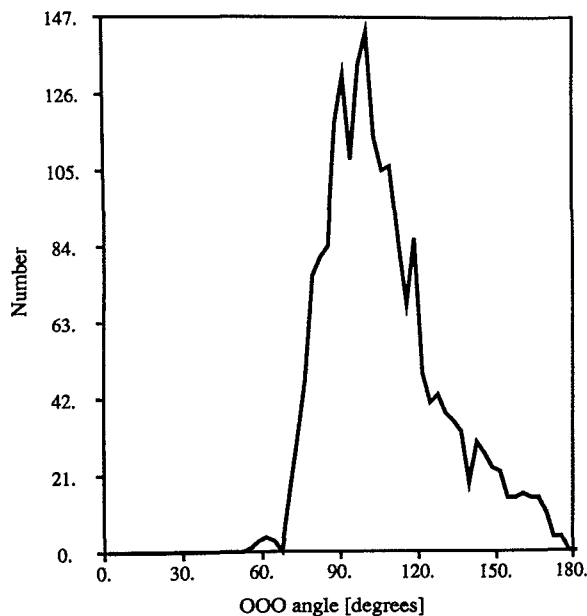


FIG. 5. Histogram of all OOO angles between adjacent hydrogen bonds in the $(\text{H}_2\text{O})_{450}$ cluster; grid of 3 deg.

bond axis, with significant angular disorder. That is, the distribution of $\text{O}\cdots\text{H}$ and $\text{O}\cdots\text{O}$ distances in hydrogen-bonded pairs of molecules is sharp (see Fig. 1), while the distribution of OOO angles between adjacent hydrogen bonds is broad. Additional information on this angular disorder is provided in Figs. 5–7, and in Table II. The global OOO angle distribution in the cluster is shown in Fig. 5. It is of interest to note that the peak is at 101° , below the tetrahedral value of 109° . The distribution is asymmetric, with a high angle wing, and therefore the average OOO angle (107°) is higher than the peak value.

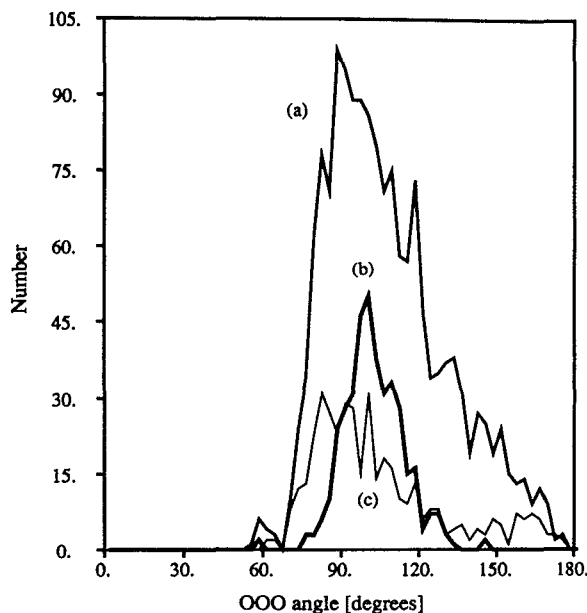


FIG. 6. Histogram of OOO angles between adjacent hydrogen bonds in the $(\text{H}_2\text{O})_{450}$ cluster; grid of 3 deg. (a) $\text{OH}\cdots\text{OH}\cdots\text{O}$ angles; (b) $\text{O}\cdots\text{HOH}\cdots\text{O}$ angles; (c) $\text{OH}\cdots\text{O}\cdots\text{HO}$ angles.

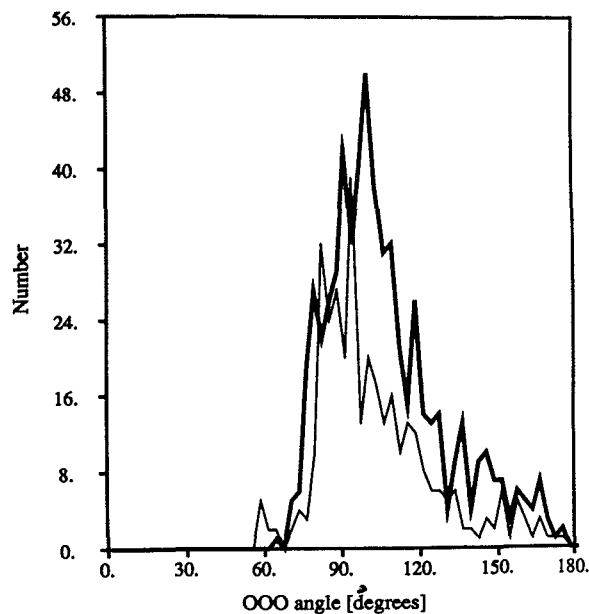


FIG. 7. Histogram of OOO angles between adjacent hydrogen bonds in the $(\text{H}_2\text{O})_{450}$ cluster; grid of 3 deg. Thick line—central molecules number 151–250. Thin line—central molecules number 351–450.

OOO angles come in three varieties: (a) $\text{OH}\cdots\text{OH}\cdots\text{O}$; (b) $\text{O}\cdots\text{HOH}\cdots\text{O}$; (c) $\text{OH}\cdots\text{O}\cdots\text{HO}$; the respective distributions are shown in Fig. 6 (see also Table II). In accord with the discussion given above, distribution (b) is significantly narrower than the other two, and thus bonding via an H atom of a central molecule is much more directional than bonding via O. Thus the angular disorder originates mostly from nondirectionality of hydrogen bonding via the O atom.

Figure 7 shows the OOO angular distribution for central molecules number 151–250, and for central molecules number 351–450. (A central molecule means “a molecule at the center of the OOO angle.”) It is seen that the angles between adjacent hydrogen bonds tend to be larger for the “old” molecules than for the “new” ones. Possible reasons are discussed in the next section.

Table II gives details of the OOO-angle distribution for molecules of all coordinations (coordination refers to a central molecule of OOO). All the distributions span roughly the same angular range and have peaks in the 89° – 101° range. The OHH distribution has an extra peak at 120° value, corresponding apparently to a triangular rather than pyramidal arrangement of the three bonds; a peak at 120° is also visible in Fig. 6(a) in the $\text{OH}\cdots\text{OH}\cdots\text{O}$ angle distribution. The 5-coordinated distribution has a small peak at very high values (161°) in addition to a larger peak at 89° ; presence of both large and small OOO angles in this overcrowded arrangement is not unexpected.

B. Dynamic properties of the $(\text{H}_2\text{O})_{450}$ cluster

Dynamic properties were studied using a 165 ps trajectory for the $(\text{H}_2\text{O})_{450}$ cluster at $T \approx 8.4$ K; structures were examined on a 5 ps time grid. Data on the dynamics of molecules

TABLE II. Properties of distributions of various types of OOO angles between adjacent hydrogen bonds; angles in degrees.

Type of angle	Number ^a	Peak	Average	Standard deviation	Range
All angles	2379	101	107	22	56–176
O···HOH···O	388	101	102	12	57–146
OH···O···HO	413	83–101	105	26	60–175
OH···OH···O	1578	89	108	23	56–177
OH ^b	30	80~120	100	17	58–144
OOH ^b	90	95	97	16	60–150
OHH ^b	177	101, 119	106	18	59–170
OOHH ^b	1812	101	107	22	56–176
OOOHH ^b	270	89, 161	106	28	58–175

^a Number of angles of a given type.

^b Coordination of the central molecule in the OOO angle; notation as in Table I, footnote a.

of different coordinations in the $(\text{H}_2\text{O})_{450}$ cluster are summarized in Table III. We first note that the distribution of the molecular coordinations *averaged over the trajectory* is very similar to the corresponding distribution for a single snapshot of the cluster, given in Table I. Moreover, similar values are obtained for the mean potential energies of the different coordinations from a single snapshot, and from the trajectory average. These results provide support for the use of a single snapshot in the analysis of the structural properties in Sec. III A above.

We further found that only 13 out of 450 cluster molecules underwent hydrogen bonding changes during the 165 ps trajectory. The bonding changes were *not* associated with large displacements; all the 13 molecules were within a distance of 0.1–0.5 Å from their initial positions in the end of the trajectory. The coordination of the 13 molecules (averaged over the trajectory) was in the range 2.2–4.8; for 9 out of the 13 molecules the bonding change occurred more than once dur-

ing the trajectory, suggesting local oscillatory bonding fluctuations, rather than (say) a single stabilization event.

Inspection of Table III shows that the range of motion of the water molecules decreases with increasing coordination. 3-, 4-, and 5-coordinated molecules undergo only small fluctuations in coordinates during the trajectory. Atomic displacements between consecutive trajectory structures are of order of 0.2 Å, and angular displacements are 3~6 deg. For 2-coordinated molecules the displacements are larger by about a factor of 2 than for 3-coordinated molecules. Root mean square displacements in coordinates of 2–5-coordinated molecules over the 160 ps time interval are very similar to the displacements averaged over 5 ps intervals; suggesting that molecular motions can be described as oscillations on a time scale which is much shorter than 5 ps. This conclusion is confirmed by inspection of plots of molecular coordinates as a function of time. (Oscillations of some molecules contain a conspicuous low frequency component, on a time scale

TABLE III. Summary of dynamic properties of the $(\text{H}_2\text{O})_{450}$ cluster; angles in degrees, distances in Å, energies in kcal/mol.

\bar{n}_h^a	mol. ^b	Δr_5^c	Δr_{165}^d	Δr_{\max}^e	ϕ_5^f	ϕ_{165}^g	ϕ_{\max}^h	θ_5^i	θ_{165}^j	θ_{\max}^k	\bar{E}^l
1	2	0.88	1.46	2.38	48.90	96.78	170.26	25.07	23.04	62.95	6.64
2	30	0.39	0.43	1.88	11.02	11.95	40.92	10.63	10.53	36.59	13.26
3	90	0.21	0.23	0.95	4.60	4.73	24.44	5.30	5.79	25.26	18.24
4	302	0.16	0.17	0.78	3.25	3.22	21.11	3.87	4.00	15.08	23.85
5	26	0.14	0.16	0.49	2.97	3.30	9.21	3.29	3.65	9.34	27.88

^a Coordination averaged over a 165 ps trajectory, binned over unit intervals; e.g., entry three corresponds to average coordination between 2.5 and 3.5.

^b Number of molecules of given average coordination.

^c Root mean square displacement of atomic coordinates between consecutive structures, averaged over atoms of molecules of a given coordination and over all the 5 ps time intervals.

^d Root mean square displacement of atomic coordinates between two structures at $t = 5$ ps and $t = 165$ ps, averaged over atoms of molecules of a given coordination.

^e Largest atomic displacement obtained for a molecule of a given coordination in a 5 ps time interval.

^f Root mean square angular displacement of the HH molecular axes between consecutive structures, averaged over all molecules of a given coordination and over all 5 ps time intervals.

^g Root mean square angular displacement of the HH molecular axes between two structures at $t = 5$ ps and $t = 165$ ps, averaged over molecules of a given coordination.

^h Largest angular displacement of an HH axis obtained for a molecule of a given coordination in a 5 ps time interval.

ⁱ Like f, for orientations of molecular bisectors.

^j Like g, for orientations of molecular bisectors.

^k Like h, for orientations of molecular bisectors.

^l Potential energy averaged over a trajectory.

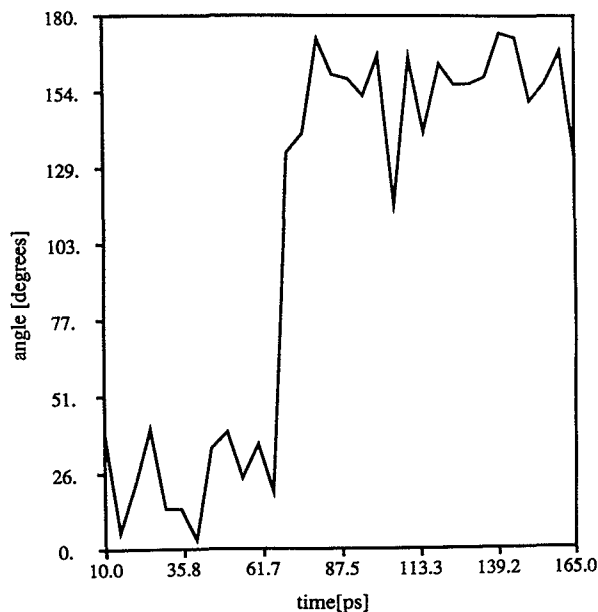


FIG. 8. Angle between the HH axis of a 1-coordinated molecule at time t of the trajectory, and the HH axis of the same molecule in the initial structure.

of several ps. This component could be a reason that the 160 ps displacements are slightly larger than the 5 ps displacements.)

The dynamics of the two 1-coordinated molecules in the cluster is exceptional; the motion of the 1-coordinated molecules can be described as hindered rotation around the molecular bisector. The orientation of the HH axis of one of such molecules as a function of time is shown in Fig. 8. A flip in the orientation in the middle of the trajectory is apparent. Two such flips occur in the trajectory of the second molecule. One may note that the relatively large rms displacement in atomic coordinates of the 1-coordinated molecules in Table III is due mostly to the flipping H atoms; the rms displacements of the O atoms are of order of 0.3 Å only.

IV. CONDENSATION DYNAMICS AND ITS RELATION TO MOLECULAR STRUCTURE

The objective of the present analysis is to understand better the dynamics of the condensation process, and to try to link condensation dynamics to the structural features of the H_2O (as) cluster described in Sec. III. In this section analysis is presented of an ensemble of 116 condensation trajectories contributing to the formation of the $(\text{H}_2\text{O})_{450}$ cluster. (More computational details on the calculation of these trajectories can be found in Sec. I A.) For each trajectory we examined the type of hydrogen bonding formed by an impinging molecule to the surface upon initial attachment (which occurs typically at $t = 3\sim 5$ ps of a sticking trajectory), and at the end of a sticking trajectory (at $t = 10$ ps or at $t = 14$ ps). We also examined configurations of "connectors," i.e., of surface molecules which participate in bonding of an impinging molecule in a sticking trajectory. (More precisely, a connector molecule is defined as a cluster

TABLE IV. Molecular configurations of newly attached molecules in 116 sticking trajectories: (a) initial attachment; (b) attachment in the last configuration of the trajectory; see beginning of Sec. IV for details. Notation as in Table I.

Configuration	Number of traj. ^a	Number of traj. ^b
O	45	8
H	29	0
OH	34	73
HH	3	0
OO	1	1
OOH	2	15
OHH	2	16
OOHH	0	2

molecule which is hydrogen bonded to a new molecule at the end of a trajectory.) Tables IV–VI show the combined results for the 116 trajectories.

Table IV shows the distribution of molecular configurations of newly attached molecules on the surface. Most (64%) of the impinging molecules were initially hooked to the surface via a single bond, either via an H or via an O atom; about 30% were initially hooked via two bonds in an asymmetric OH configuration. Over the period of several ps after the initial attachment, a large majority of newly bonded 1-coordinated molecules acquired additional hydrogen bonds. Thus in the end of the 116 trajectories most (63%) of new molecules were 2 coordinated in the OH configuration, and 27% were 3 coordinated in either the OOH or the OHH configuration.

One may note the low mobility of the molecules during the attachment process. Thus in 111 out of 116 trajectories, all the bonds formed during initial attachment were preserved during subsequent trajectory (and subsequent bonding to the surface). In four of the remaining trajectories, only one of the initially formed two bonds was broken during the subsequent trajectory. Only in one trajectory a complete change in bonding of a new molecule occurred (i.e., an initially formed hydrogen bond disappeared during the following trajectory).

One may try to link the above bonding mechanism to the low values of OOO angles between adjacent hydrogen bonds, obtained for newly attached molecules in the $(\text{H}_2\text{O})_{450}$ cluster (see Sec. III A and Fig. 7). A typical molecule forms initially one bond to the surface, and then acquires additional bonds in the immediate vicinity. This mechanism is expected to favor bonding to the nearest sites which are within the range of the motion of the newly attached molecule; resulting in the relatively low angles between adjacent hydrogen bonds of the new molecule. The molecule then "ages" in the cluster, while attaching additional molecules from the gas phase. The angles between the new bonds and the old bonds of the "aging" molecule are not confined to be small. Therefore the OOO angle distribution shifts to higher values for "older" cluster molecules as seen in Fig. 7.

Table V shows the total number and the type of bonds formed by the 116 impinging molecules to the surface mole-

TABLE V. Total number of bonds formed by impinging molecules in 116 sticking trajectories; for computational details see Sec. II A.

Type of bond	Number of bonds ^a	Number of bonds ^b
O ^c	87	133
O/d H ^d	75	97
H ^e	75	126
H/sO ^f	59	89

^a Bonds formed by impinging molecules upon initial attachment events to the surface.

^b Total number of bonds formed by impinging molecules in the end of 116 sticking trajectories.

^c Bonding via oxygen atom of a sticking molecule.

^d Bonding via oxygen atom of a sticking molecule, to a dangling H atom on the surface; subgroup of (c).

^e Bonding via hydrogen atom of a sticking molecule.

^f Bonding via hydrogen atom of a sticking molecule to a dangling (1-coordinated) O atom; subgroup of (e).

cules. It is evident from the table that dangling H and O atoms play a major role in the condensation process—they serve as attachment sites for the impinging molecules. Specifically, 83% of bonds formed by impinging molecules upon initial attachment to the surface were to dangling H or O atoms on the surface. (Dangling H atom means here “H atom which was unattached in an initial structure of a trajectory,” and dangling O atom means “1-coordinated O in an initial structure.”) Ability of a new molecule to rearrange bonds seems to increase somewhat during formation of additional bonds, following the initial attachment; and thus somewhat smaller proportion (72%) of new bonds formed in the end of the 116 trajectories was to atoms which were dangling in the initial structure of a trajectory.

Table VI provides data on connector molecules on the cluster surface. The dangling H atoms are available predominantly in surface molecules in OH and OOH configurations. Dangling O atoms are available in OH and OHH configurations. The OH surface molecules bind the impinging molecules more efficiently (by about a factor of 2) to their dangling H atoms than to their dangling O atoms. Moreover, 2-coordinated surface molecules appear to bind new molecules more effectively than the 3-coordinated ones; this can

be seen from the fact that the ratio between the binding events to OH/OHH/OOH connector molecules is 80:68:45 (see Table VI), whereas the ratio between the numbers of OH/OHH/OOH molecules in the final (H₂O)₄₅₀ cluster is 30:59:30 (see Table I). The latter result also suggests somewhat higher efficiency of binding of new molecules to OOH than to OHH surface connectors.

Several percent of the bond-forming events proceeded via attachment of an H atom of an impinging molecule to a 2-coordinated O atom on the surface, which thus became 3-coordinated (and the corresponding connector molecule became 5-coordinated). In a sense, these 2-coordinated O atoms can also be considered as dangling, since they were sufficiently exposed to allow for the formation of a third hydrogen bond.

I also examined the bonding changes occurring in connector molecules during sticking trajectories; specifically, comparison was carried out between hydrogen bonds of connector molecules in the initial and the final structure of each trajectory. From the point of view of a typical connector molecule, attachment of a new molecule is a relatively simple event: In 55% of bond formation events by new molecules, a surface molecule did not undergo any additional bonding changes, except for attachment of the new molecule. In 34% of bonding events a single hydrogen bond exchange took place during attachment, i.e., formation of the bond to a new molecule by the connector molecule was accompanied by breaking of one of the old hydrogen bonds of the connector. The remaining 11% of bonding events were associated with other (mostly more complicated) bonding changes in the connectors. However, in none of the trajectories did the connector molecule lose all of its old hydrogen bonds as a result of a sticking event.

A common event occurring during collision trajectories is “triangular” bonding—i.e., bonding of a new molecule to a pair of hydrogen-bonded molecules on the surface. Such bonding occurs either without breaking of the old bond (“addition”) or via bond breaking (“insertion”). Among 116 trajectories, there are 31 trajectories with one insertion, 20 with one addition, 3 with double insertion, and 1 with one insertion + one addition. The addition events generate rings of three molecules on the surface; such rings are likely to

TABLE VI. Distribution of configurations of connector molecules. Connector molecules are surface molecules which participated in bonding of the impinging molecules in the end of the 116 trajectories. (a) Distribution of configurations of connectors before attachment; (b) distribution of configurations after attachment.

Initial configuration	Number initial ^a	Final OH	Final OOH	Final OHH	Final OOOH	Final OOOHH
O	2	1	1
OH ^a	80	23	17	34	5	...
OOH	45	...	3	7	35	...
OHH	68	2	2	10	54	...
OOHH	60	1	49	10
OOOHH	4	2	2
Final configuration		26	23	52	145	12

^a One OH connector ends as HH.

contribute significantly to the low angle wing of the OOO angle distributions shown in Figs. 5–7. The insertion events are expected to occur preferentially to strained surface bonds, such as the ones in three-molecule rings. Opening of small rings via insertion may contribute to the shift in OOO angle distribution to higher values with the age of the water molecules in the cluster, as seen in Fig. 7.

With the above results in mind, one may attempt to understand the distribution of the molecules of the different coordinations within the $(\text{H}_2\text{O})_{450}$ cluster (see Table I and Sec. III) in terms of the condensation dynamics. Formation of molecules of the different coordinations is discussed below:

(a) *1-coordinated molecules*: While the 1-coordinated configuration is formed frequently during initial attachment of an impinging molecule, this configuration appears unstable, and in most cases disappears during several picoseconds after the initial attachment. The relatively large range of motion of 1-coordinated molecules (see Sec. III B and Table III) appears sufficient to promote formation of additional bonding to neighboring molecules. The two 1-coordinated molecules which survived in the $(\text{H}_2\text{O})_{450}$ cluster are both at tips of protruding portions of the cluster surface—see Fig. 1. At such tip locations the probability of finding an additional bonding partner by a 1-coordinated molecule may be particularly low.

(b) *2-coordinated molecules*: The presence of OH-bonded 2-coordinated molecules in the $(\text{H}_2\text{O})_{450}$ cluster can be now linked to the condensation dynamics; since the impinging molecules are typically attached to the surface in the OH configuration. The attachment in the OH configuration is associated with two major microscopic sticking mechanisms. One is sticking via hydrogen bond insertion—in such events one surface O atom, and one H atom become available for bonding of a new molecule. Formation of 18 out of the 73 new OH configurations in Table IV is associated with such insertion events. A more important source of OH configurations is attachment to the appropriate double binding sites available on the cluster surface. Thus in 50 of the trajectories, a new molecule forms an OH configuration by attachment to a pair of dangling atoms—an O atom and an H atom—present on the cluster surface.

Clear preference for the formation of the 2-coordinated OH configurations with respect to either OO or HH in condensation trajectories is quite striking; I can explain it only partially. A possible reason is unavailability of symmetric pairs of binding sites at a distance appropriate for symmetric double bonding. For example, OO bonding of a new molecule would be promoted by a presence of a pair of dangling H atoms at a distance appropriate for second nearest neighbor molecules; and Coulombic repulsion could possibly prevent formation of such like pairs of binding sites. To examine this idea, I calculated (a) the ranges of $\text{H}\cdots\text{H}$, $\text{O}\cdots\text{H}$, and $\text{O}\cdots\text{O}$ distances for adjacent hydrogen bonds; (b) the number of pairs of dangling atoms within these ranges in the $(\text{H}_2\text{O})_{450}$ cluster. The results were: 8 $d\text{H}/d\text{H}$ binding sites, 12 $d\text{O}/d\text{O}$ binding sites, and 53 $d\text{H}/d\text{O}$ binding sites ($d\text{H}$, $d\text{O}$ denote dangling atoms). Thus there are 2.7 times more asymmetric binding sites than the symmetric ones; however, in the ensemble of the 116 trajectories there were 73 trajec-

tories that ended in the asymmetric OH configuration, and only 1 trajectory that ended in the symmetric (OO) configuration. Thus there appear to be additional factors contributing to the preference for OH configuration with respect to either OO or HH; for the moment I do not know what they are.

(c) *3-coordinated molecules*: As noted in Sec. III, in the final $(\text{H}_2\text{O})_{450}$ cluster there are twice as many OHH connected 3-coordinated molecules than OOH connected molecules; the question is why. One may note that the average potential energy of the less abundant species OOH is lower by 1.3 kcal/mol than that of the more abundant OHH species (see Table I). Preferential formation of the OHH configuration by impinging molecules does not seem to be the reason; since among 116 trajectories examined, about the same number of impinging molecules ended in OOH configuration as in OHH (see Table IV). Rather, the preference for OHH seems to be related to subsequent evolution of molecules, after the attachment. Two contributions to this effect were identified: (i) Most of the 2-coordinated OH connectors are converted to 3-coordinated upon attachment of impinging molecules. However (as noted above), binding to an H atom of a surface OH molecule is more efficient than binding to an O atom, and as a result this process produces more OHH configurations than OOH configurations. (ii) As noted before, OHH molecules attach new molecules somewhat less efficiently than OOH. Better ability of OHH to survive within the cluster is also evidenced by the fact that in the $(\text{H}_2\text{O})_{450}$ cluster the OHH molecules are, on the average, older than the OOH molecules (see Table I). In fact on graphic displays of the $(\text{H}_2\text{O})_{450}$ cluster some of the OHH molecules appear “buried” within the cluster. Also the OOO angle distribution around OHH molecules contains an extra peak near 120° (see Sec. III and Table II). All these findings suggest that better ability of OHH to survive condensation may be associated with its ability to form triangular rather than pyramidal configuration of three hydrogen bonds. Specifically, the bonding via O atom of an OHH molecule may occur in plane of the two bonds via H (see discussion in Sec. III on the enhanced angular flexibility of the bonds via O, with respect to the bonds via H). This triangular bonding may then make formation of the fourth bond via O to another molecule less favorable (since it would be associated with a particularly small angle between adjacent hydrogen bonds), enhancing the ability of an OHH molecule to survive in the cluster. On the other hand, such triangular configuration is not expected to be favored by OOH molecules, as confirmed by the absence of peak near 120° in the OOO angle distribution around such molecules.

(d) *4-coordinated molecules*: Table IV shows that an impinging molecule only rarely forms four bonds during sticking. Formation of 4-coordinated molecules is thus a more complicated and prolonged process. A most significant source of 4-coordinated molecules which I identified is conversion of 3-coordinated molecules to 4-coordinated during attachment of new molecules from the gas phase (see Table VI).

(e) *5-coordinated molecules*: The only source of such molecules which I identified is attachment of newly impinging

molecules to 4-coordinated surface molecules. Most (eight out of ten) 5-coordinated molecules thus formed were not generated during initial hookup of an impinging molecule, but rather during subsequent trajectory following the initial hookup. One may then try to link formation of 5-coordinated molecules to low molecular mobility during condensation. An initially hooked molecule can form additional bonds to neighboring molecules only; and occasionally the most accessible binding site available in the vicinity corresponds to a 2-coordinated O atom which is sufficiently exposed to allow for additional bonding.

V. SUMMARY AND FINAL COMMENTS

The objective of this study was to advance molecular level understanding of low temperature amorphous ice deposits. A $(\text{H}_2\text{O})_{450}$ amorphous ice cluster was generated by simulation of slow condensation of gaseous H_2O , a process by which amorphous ice is generated in the laboratory. Investigation is presented of the structural and the dynamic properties of the cluster at ~ 10 K, and of the condensation trajectories contributing to the cluster growth. Link is explored between condensation dynamics and the resulting structural features.

Condensation is shown to be highly selective, promoting formation of specific molecular configurations. A typical impinging molecule sticks to the surface in an OH configuration (i.e., in a configuration with one hydrogen bond through an O atom, and another through H). The symmetrically connected 2-coordinated configurations OO and HH are formed only rarely during a sticking event. The initially 2-coordinated surface molecules acquire additional hydrogen bonds via attachment of new molecules from the gas phase. Formation and survival of the 3-coordinated OHH configurations is favored over that of the OOH configurations. The old cluster molecules are mostly 4 coordinated; but some 5-coordinated molecules are formed as well in the OOOHH configuration. Some of the structural features of the cluster (e.g., presence of 5-coordinated OOOHH configurations, and preference for OHH configurations over OOH configurations) was linked to the lack of directionality of hydrogen bonding via an O atom of a water molecule (as opposed to directional bonding via H atoms). The range of motion of the cluster molecules increases with decreasing coordination. 2–5-coordinated molecules perform oscillatory motions, while the two 1-coordinated molecules which were found in the cluster perform hindered rotations.

The most conspicuous feature of the condensation process is the low mobility of molecules during a sticking event. A typical impinging molecule is hooked via a hydrogen bond to the surface, and then forms additional bond(s) to molecules in the immediate vicinity. The surface molecules either do not undergo any bonding changes except for attaching

the new molecule, or lose one of their old bonds as a result of the attachment event.

The present study suggests a physical reason (or one of the reasons) for the very large surface area of low T amorphous ice deposits. New molecules are attached preferentially to dangling atoms on the surface, i.e., to unbonded H atoms, and to O atoms with only one hydrogen bond. The dangling atoms belong to surface molecules of low coordination. Such surface molecules tend to stick out of the surface (see Fig. 1 and Table I). The molecules which become attached to the dangling atoms stick out even more, and having coordination less than four serve as binding sites for additional incoming molecules. This type of process is expected to propagate formation of surface protrusions, contributing to very significant surface roughness, and to the large surface area. The process seems related to the well known model of diffusion limited aggregation.¹¹ (Unfortunately, the cluster is too small to derive meaningful fractal dimension.)

ACKNOWLEDGMENTS

The support of the National Science Foundation Grant No. CHE-9022055 and of the Petroleum Research Fund Grant No. 23685-AC6, administered by the American Chemical Society, is gratefully acknowledged. The author is a Camille and Henry Dreyfus Teacher-Scholar.

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