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Notes: water and liquid layers

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# Yes

## 2016 Zhu

7 June , Zhao, Wang, Yin, Jia, Yang, Zeng, Yuan

Citations: 1

### Two-dimensional interlocked pentagonal bilayer ice: how do water molecules form a hydrogen bonding network?

The plethora of ice structures observed both in bulk and under nanoscale confinement reflects the extraordinary ability of water molecules to form diverse forms of hydrogen bonding networks. An ideal hydrogen bonding network of water should satisfy three requirements: (1) four hydrogen bonds connected with every water molecule, (2) nearly linear hydrogen bonds, and (3) tetrahedral configuration for the four hydrogen bonds around an 0 atom. However, under nanoscale confinement, some of the three requirements have to be unmet, and the selection of the specific requirement(s) leads to different types of hydrogen bonding structures. According to molecular dynamics (MD) simulations for water confined between two smooth hydrophobic walls, we obtain a phase diagram of three two-dimensional (2D) crystalline structures and a bilayer liquid. A new 2D bilayer ice is found and named the interlocked pentagonal bilayer ice (IPBI), because its side view comprises interlocked pentagonal channels. The basic motif in the top view of IPBI is a large hexagon composed of four small pentagons, resembling the top view of a previously reported "coffin" bilayer ice [Johnston, et al., J. Chem. Phys., 2010, 133, 154516]. First-principles optimizations suggest that both bilayer ices are stable. However, there are fundamental differences between the two bilayer structures due to the difference in the selection among the three requirements. The IPBI sacrifices the linearity of hydrogen bonds to retain locally tetrahedral configurations of the hydrogen bonds, whereas the coffin structure does the opposite. The tradeoff between the conditions of an ideal hydrogen bonding network can serve as a generic guidance to understand the rich phase behaviors of nanoconfined water.

## 2016 Jayaratne

April , Saunders

Citations: 0

### The interaction of ice crystals with hailstones in wet growth and its possible role in thunderstorm electrification

Charge separation during rebounding collisions of ice crystals on hail particles is a probable mechanism of thunderstorm electrification. Modelling of laboratory results successfully predicts the charge structure in thunderclouds under most conditions. An exception is the intense positive ground flashes observed in mid-continental severe storms which contain large hailstones that are generally in wet growth. It is difficult to see how interacting ice crystals may separate from the wet surface of a hailstone without sticking, although some studies have reported charge separation during this process. Our laboratory experiments show that, during ice crystal interactions with a simulated hailstone in wet growth, a small but significant charge transfer occurs during ice crystal interactions. We present evidence to show that the hailstone surface is not uniformly wet and consists of dry zones, particularly at the edges, where ice crystals are most likely to impact, and hypothesize that a small number of ice crystals rebounding off these zones may give rise to the observed charging current. While this may explain wet growth charging in laboratory experiments, we cannot directly extend the findings to natural thunderstorms where hailstones tend to rotate and gyrate as they fall, but they may experience different growth regimes within the cloud.

## 2016 Nagashima

April , Sazaki, Hama, Asakawa, Murata, Furukawa

Citations: 0

### Direct Visualization of Quasi-Liquid Layers on Ice Crystal Surfaces Induced by Hydrogen Chloride Gas

Surface melting of ice crystals forms quasi liquid layers (QLLs) on ice surfaces, and affects a wide variety of natural phenomena. Since QLLs enhance various chemical reactions in ice clouds, the formation of QLLs by atmospheric gases has been studied intensively. However, such studies were performed using spectroscopy techniques, which have low spatial resolution. Here we show the first direct-visualization of QLLs on ice basal faces in the presence of hydrogen chloride (HCl) gas (model atmospheric gas) by advanced optical microscopy, which can visualize individual 0.37 nm-thick elementary steps on ice crystal surfaces. We found that the HCl gas induced the appearances of QLLs with a droplet shape in the temperature range from -15.0 to -1.5 degrees C, where no QLL appears in the absence of HCl gas. This result indicates that HCl gas adsorbed on ice crystal surfaces probably changed the surface structure of ice crystals and then induced the subsequent melting of ice surfaces. We also observed the movement, shape change, and splitting of the droplet QLLs when water vapor was undersaturated. The long-term (1 h) existence of the droplet QLLs under the undersaturated conditions strongly suggests that the droplet QLLs were thermodynamically stable HCl solutions.

## 2016 Asakawa

16 February , Sazaki, Nagashima, Nakatsubo, Furukawa

Citations: 1

### Two types of quasi-liquid layers on ice crystals are formed kinetically

Surfaces of ice are covered with thin liquid water layers, called quasi-liquid layers (QLLs), even below their melting point (0 degrees C), which govern a wide variety of phenomena in nature. We recently found that two types of QLL phases appear that exhibit different morphologies (droplets and thin layers) [Sazaki G. et al. (2012) Proc Natl Acad Sci USA 109(4):1052-1055]. However, revealing the thermodynamic stabilities of QLLs remains a longstanding elusive problem. Here we show that both types of QLLs are metastable phases that appear only if the water vapor pressure is higher than a certain critical supersaturation. We directly visualized the QLLs on ice crystal surfaces by advanced optical microscopy, which can detect 0.37-nm-thick elementary steps on ice crystal surfaces. At a certain fixed temperature, as the water vapor pressure decreased, thin-layer QLLs first disappeared, and then droplet QLLs vanished next, although elementary steps of ice crystals were still growing. These results clearly demonstrate that both types of QLLs are kinetically formed, not by the melting of ice surfaces, but by the deposition of supersaturated water vapor on ice surfaces. To our knowledge, this is the first experimental evidence that supersaturation of water vapor plays a crucially important role in the formation of QLLs.

## 2014 Sellberg

19 June , Huang, McQueen, Loh, Laksmono, Schlesinger, Sierra, Nordlund, Hampton, Starodub, DePonte, Beye, Chen, Martin, Barty, Wikfeldt, Weiss, Caronna, Feldkamp, Skinner, Seibert, Messerschmidt, Williams, Boutet, Pettersson, Bogan, Nilsson

Citations: 97

### Ultrafast X-ray probing of water structure below the homogeneous ice nucleation temperature

Water has a number of anomalous physical properties, and some of these become drastically enhanced on supercooling below the freezing point. Particular interest has focused on thermodynamic response functions that can be described using a normal component and an anomalous component that seems to diverge at about 228 kelvin (refs 1-3). This has prompted debate about conflicting theories(4-12) that aim to explain many of the anomalous thermodynamic properties of water. One popular theory attributes the divergence to a phase transition between two forms of liquid water occurring in the 'no man's land' that lies below the homogeneous ice nucleation temperature (T-H) at approximately 232 kelvin(13) and above about 160 kelvin(14), and where rapid ice crystallization has prevented any measurements of the bulk liquid phase. In fact, the reliable determination of the structure of liquid water typically requires temperatures above about 250 kelvin(2,15). Water crystallization has been inhibited by using nanoconfinement(16), nanodroplets(17) and association with biomolecules(16) to give liquid samples at temperatures below T-H, but such measurements rely on nanoscopic volumes of water where the interaction with the confining surfaces makes the relevance to bulk water unclear(18). Here we demonstrate that femtosecond X-ray laser pulses can be used to probe the structure of liquid water in micrometre-sized droplets that have been evaporatively cooled(19-21) below TH. We find experimental evidence for the existence of metastable bulk liquid water down to temperatures of 227(-1)(+2) kelvin in the previously largely unexplored no man's land. We observe a continuous and accelerating increase in structural ordering on supercooling to approximately 229 kelvin, where the number of droplets containing ice crystals increases rapidly. But a few droplets remain liquid for about a millisecond even at this temperature. The hope now is that these observations and our detailed structural data will help identify those theories that best describe and explain the behaviour of water.

## 2011 Nihonyanagi

26 October , Ishiyama, Lee, Yamaguchi, Bonn, Morita, Tahara

Citations: 146

### Unified Molecular View of the Air/Water Interface Based on Experimental and Theoretical chi((2)) Spectra of an Isotopically Diluted Water Surface

The energetically unfavorable termination of the hydrogen-bonded network of water molecules at the air/water interface causes molecular rearrangement to minimize the free energy. The long-standing question is how water minimizes the surface free energy. The combination of advanced, surface-specific nonlinear spectroscopy and theoretical simulation provides new insights. The complex chi((2)) spectra of isotopically diluted water surfaces obtained by heterodyne-detected sum frequency generation spectroscopy and molecular dynamics simulation show excellent agreement, assuring the validity of the microscopic picture given in the simulation. The present study indicates that there is no ice-like structure at the surface in other words, there is no increase of tetrahedrally coordinated structure compared to the bulk but that there are water pairs interacting with a strong hydrogen bond at the outermost surface. Intuitively, this can be considered a consequence of the lack of a hydrogen bond toward the upper gas phase, enhancing the lateral interaction at the boundary. This study also confirms that the major source of the isotope effect on the water chi((2)) spectra is the intramolecular anharmonic coupling, i.e., Fermi resonance.

## 2011 Gundlach

August , Kilias, Beitz, Blum

Citations: 55

### Micrometer-sized ice particles for planetary-science experiments - I. Preparation, critical rolling friction force, and specific surface energy

Coagulation models assume a higher sticking threshold for micrometer-sized ice particles than for micrometer-sized silicate particles. However, in contrast to silicates, laboratory investigations of the collision properties of micrometer-sized ice particles (in particular, of the most abundant H(2)O-ice) have not been conducted yet. Thus, we used two different experimental methods to produce micrometer-sized H(2)O-ice particles, i.e. by spraying H(2)O droplets into liquid nitrogen and by spraying H(2)O droplets into a cold nitrogen atmosphere. The mean particle radii of the ice particles produced with these experimental methods are (1.49 +/- 0.79) mu m and (1.45 +/- 0.65) mu m. Ice aggregates composed of the micrometer-sized ice particles are highly porous (volume filling factor: phi = 0.11 +/- 0.01) or rather compact (volume filling factor: phi = 0.72 +/- 0.04), depending on the method of production. Furthermore, the critical rolling friction force of F(Roll,ice) = (114.8 +/- 23.8) x 10(-10) N was measured for micrometer-sized ice particles, which exceeds the critical rolling friction force of micrometer-sized SiO(2) particles (F(Roll,SiO2) = (12.1 +/- 3.6) x 10(-10) N). This result implies that the adhesive bonding between micrometer-sized ice particles is stronger than the bonding strength between SiO(2) particles. An estimation of the specific surface energy of micrometer-sized ice particles, derived from the measured critical rolling friction forces and the surface energy of micrometer-sized SiO(2) particles, results in gamma(ice) = 0.190 J m(-2).

## 2010 Nihonyanagi

26 May , Yamaguchi, Tahara

Citations: 99

### Water Hydrogen Bond Structure near Highly Charged Interfaces Is Not Like Ice

Imaginary x((2)) spectra of HOD at air/charged surfactant/aqueous interfaces highly resemble the IR spectrum of the bulk liquid HOD, showing no indication of the "ice-like" structure. Clearly, the hydrogen bond structures at highly charged interfaces are not like ice but very similar to the structure in the bulk.

## 2008 Conde

7 July , Vega, Patrykiejew

Citations: 59

### The thickness of a liquid layer on the free surface of ice as obtained from computer simulation

Molecular dynamic simulations were performed for ice I-h with a free surface by using four water models, SPC/E, TIP4P, TIP4P/Ice, and TIP4P/2005. The behavior of the basal plane, the primary prismatic plane, and of the secondary prismatic plane when exposed to vacuum was analyzed. We observe the formation of a thin liquid layer at the ice surface at temperatures below the melting point for all models and the three planes considered. For a given plane it was found that the thickness of a liquid layer was similar for different water models, when the comparison is made at the same undercooling with respect to the melting point of the model. The liquid layer thickness is found to increase with temperature. For a fixed temperature it was found that the thickness of the liquid layer decreases in the following order: the basal plane, the primary prismatic plane, and the secondary prismatic plane. For the TIP4P/Ice model, a model reproducing the experimental value of the melting temperature of ice, the first clear indication of the formation of a liquid layer, appears at about -100 degrees C for the basal plane, at about -80 degrees C for the primary prismatic plane, and at about -70 degrees C for the secondary prismatic plane.

## 2007 Fridlind

20 December , Ackerman, McFarquhar, Zhang, Poellot, DeMott, Prenni, Heymsfield

Citations: 126

### Ice properties of single-layer stratocumulus during the Mixed-Phase Arctic Cloud Experiment: 2. Model results

Measurements from the US Department of Energy Atmospheric Radiation Measurement Program's 2004 Mixed-Phase Arctic Cloud Experiment (M-PACE) provide a unique opportunity to study poorly understood ice formation processes in mixed-phase stratocumulus. Using meteorological, aerosol, and ice nucleus measurements to initialize large-eddy simulations with size-resolved microphysics, we compare predicted liquid and ice mass, number, and size distribution with observations from a typical flight. We find that ambient ice nuclei appear insufficient by a few orders of magnitude to explain observed ice, consistent with past literature. We also find that two processes previously hypothesized to explain the discrepancy, shatter of freezing drops and fragmentation during ice-ice collisions, were not significant sources of ice based on parameterizations from existing studies. After surveying other mechanisms that have been hypothesized to explain ice formation in mixed-phase clouds generally, we find two that may be strong enough: ( 1) formation of ice nuclei from drop evaporation residuals, a process suggested by sparse and limited measurements to date, and ( 2) drop freezing during evaporation, a process suggested only by inference at this time. The first mechanism can better explain the persistence of mixed-phase conditions in simulations of less vigorous stratus observed during the Beaufort Arctic Storms Experiment ( BASE). We consider conditions under which emission of nuclei from the ocean surface or activation through cloud-phase chemistry could provide alternative explanations for M-PACE observations. Additional process-oriented measurements are suggested to distinguish among ice formation mechanisms in future field studies.

## 2007 Blackford

7 November

Citations: 87

### Sintering and microstructure of ice: a review

Sintering of ice is driven by the thermodynamic requirement to decrease surface energy. The structural morphology of ice in nature has many forms - from snowflakes to glaciers. These forms and their evolution depend critically on the balance between the thermodynamic and kinetic factors involved. Ice is a crystalline material so scientific understanding and approaches from more conventional materials can be applied to ice. The early models of solid state ice sintering are based on power law models originally developed in metallurgy. For pressure sintering of ice, these are based on work on hot isostatic pressing of metals and ceramics. Recent advances in recognizing the grain boundary groove geometry between sintering ice particles require models that use new approaches in materials science. The newer models of sintering in materials science are beginning to incorporate more realistic processing conditions and microstructural complexity, and so there is much to be gained from applying these to ice in the future. The vapour pressure of ice is high, which causes it to sublime readily. The main mechanism for isothermal sintering of ice particles is by vapour diffusion; however other transport mechanisms certainly contribute. Plastic deformation with power law creep combined with recrystallization become important mechanisms in sintering with external pressure. Modern experimental techniques, low temperature scanning electron microscopy and x-ray tomography, are providing new insights into the evolution of microstructures in ice. Sintering in the presence of a small volume fraction of the liquid phase causes much higher bond growth rates. This may be important in natural snow which contains impurities that form a liquid phase. Knowledge of ice microstructure and sintering is beneficial in understanding mechanical behaviour in ice friction and the stability of snow slopes prone to avalanches.

## 2007 Li

12 July , Somorjai

Citations: 92

### Surface premelting of ice

In this review, we summarize the available experimental data from recently developed molecular level techniques on the surface structure, surface premelting layer thickness, and friction of ice. We conclude that surface premelting of ice is responsible for the unique surface properties of the important substance.

## 2006 Dash

July , Rempel, Wettlaufer

Citations: 369

### The physics of premelted ice and its geophysical consequences

The surface of ice exhibits the swath of phase-transition phenomena common to all materials and as such it acts as an ideal test bed of both theory and experiment. It is readily available, transparent, optically birefringent, and probing it in the laboratory does not require cryogenics or ultrahigh vacuum apparatus. Systematic study reveals the range of critical phenomena, equilibrium and nonequilibrium phase-transitions, and, most relevant to this review, premelting, that are traditionally studied in more simply bound solids. While this makes investigation of ice as a material appealing from the perspective of the physicist, its ubiquity and importance in the natural environment also make ice compelling to a broad range of disciplines in the Earth and planetary sciences. In this review we describe the physics of the premelting of ice and its relationship with the behavior of other materials more familiar to the condensed-matter community. A number of the many tendrils of the basic phenomena as they play out on land, in the oceans, and throughout the atmosphere and biosphere are developed.

## 2006 Vrbka

21 September , Jungwirth

Citations: 92

### Homogeneous freezing of water starts in the subsurface

Molecular dynamics simulations of homogeneous ice nucleation in extended aqueous slabs show that freezing preferentially starts in the subsurface. The top surface layer remains disordered during the freezing process. The subsurface accommodates better than the bulk the increase of volume connected with freezing. It also experiences strong electric fields caused by oriented surface water molecules, which can enhance ice nucleation. Our computational results shed new light on the experimental controversy concerning the bulk vs surface origin of homogeneous ice nucleation in water droplets. This has important atmospheric implications for the microphysics of formation of high altitude clouds.

## 2006 Wettlaufer

, Worster

Citations: 109

### Premelting dynamics

When the free surfaces of most solids approach their bulk melting temperatures from below, the molecular structure of the material gives way to a disordered structure with some attributes of both the solid and liquid phases. When the temperature is sufficiently close to that of bulk transition, the surface melts and literally flows as a viscous fluid. This phenomenon, called interfacial premelting, lies at the heart of the microscopic theory of melting of solid matter and captures the interest of condensed matter physicists and physical chemists alike. The process is ubiquitous and responsible for a wide range of consequences in materials with biological, geophysical, and technological significance. Because such systems are often exposed to spatial or temporal variations in thermodynamic forcing, there are a host of fluid mechanical phenomena that result from this underlying melting behavior. The fluid dynamics of unfrozen surfaces holds clues for understanding the bulk behavior of polycrystalline materials, from Earth's mantle to the stratosphere and beyond. In this review we focus on the fluid dynamical consequences of the premelting of solids.

## 2005 Shaw

26 May , Durant, Mi

Citations: 136

### Heterogeneous surface crystallization observed in undercooled water

We report laboratory observations of higher freezing temperatures when an ice-forming nucleus is near the surface of an undercooled water drop than when the nucleus is immersed in the drop. The nucleation rate at the water surface is a factor of 10(10) greater than in bulk water, thereby complementing and providing evidence for homogeneous surface crystallization, which has been hypothesized recently. Interpretation of the data via classical nucleation theory shows that the free energy of formation of a critical ice germ is decreased by a factor of approximately 2 when the substrate is near the air-water interface. Furthermore, the analysis suggests that the jump frequency of molecules from the liquid to the solid may be greatly enhanced at the interface.

## 2004 Duft

4 October , Leisner

Citations: 98

### Laboratory evidence for volume-dominated nucleation of ice in supercooled water microdroplets

We report on measurements of the rate of homogeneous ice nucleation in supercooled water microdroplets levitated in an electrodynamic balance. By comparison of the freezing probability for droplets of radius 49 mum and 19 mum, we are able to conclude that homogeneous freezing is a volume-proportional process and that surface nucleation might only be important, if at all, for much smaller droplets.

## 2004 Koop

Citations: 114

### Homogeneous ice nucleation in water and aqueous solutions

This review provides an introduction to ice nucleation processes in supercooled water and aqueous solutions. Concepts for experimental techniques suitable to study homogeneous ice nucleation are addressed, in particular differential scanning calorimetry of inverse emulsions. Ice nucleation data from aqueous solutions have been analyzed using two approaches, and the interrelations between those are examined. It is argued that the ice nucleation process is driven entirely by thermodynamic quantities and how this can be understood in the context of three proposed theories for supercooled liquid water. Ice nucleation data for pure water droplets surrounded by a gas have been compiled and evaluated; within experimental uncertainty neither a volume dependent nucleation process nor a surface dependent nucleation process is convincingly supported by the analysis. Finally, open questions in the area of supercooled aqueous solutions and ice nucleation are discussed.

## 2002 Parent

15 December , Laffon, Mangeney, Bournel, Tronc

Citations: 60

### Structure of the water ice surface studied by x-ray absorption spectroscopy at the OK-edge

Vapor-deposited H(2)O ice films grown between 38 and 150 K under ultrahigh vacuum conditions have been investigated using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge, in conventional mode-which is bulk sensitive-, and using the photon-stimulated desorption mode (PSD-NEXAFS), which is surface sensitive. By recording simultaneously those two signals, we have evidenced the differences between the surface and bulk electronic and atomic structures, for both amorphous porous ice condensed at 40 K and crystalline ice condensed at 150 K. We have also followed the bulk and surface evolutions of an amorphous ice film annealed from 38 to 147 K. A steep change in the local atomic structure of the bulk is observed, likely related to the high-density amorphous ice-->low-density amorphous ice phase transition between 38 and 55 K. We have shown that the surface of crystalline ice is well ordered, but this order is different from that of the bulk. We have evidenced that the H(2)O-H(2)O intermolecular distance at the surface of ice is always longer than in the bulk, and that this difference increases with temperature, as the thermally induced reordering of the surface proceeds. SCF-Xalpha multiple scattering calculations allow us to figure out those structural differences, both in the bulk and at the surface of amorphous ice, but further calculations are necessary for crystalline ice. We have shown that the PSD-NEXAFS signal is sensitive to the surface morphology that changes with temperature because of the micropores collapse. We have used a model [E. Vichnevetski, A. D. Bass, and L. Sanche, J. Chem. Phys. 113, 3874 (2000)] that quantitatively describes the effect of the surface porosity on the ion yield. The surface of ice at 38 K is well described by a network of vertical cylindrical pores of 20 Angstrom of diameter, separated by 6 Angstrom, collapsing when annealing the film. This model also properly accounts of the peculiar temperature evolution of the PSD signal at the O1s(-1)4a(1)(+1) excitation, and therefore, allows to establish the relation between the PSD-NEXAFS signal and the surface porosity. (C) 2002 American Institute of Physics.

## 2002 Tabazadeh

10 December , Djikaev, Reiss

Citations: 119

### Surface crystallization of supercooled water in clouds

The process by which liquid cloud droplets homogeneously crystallize into ice is still not well understood. The ice nucleation process based on the standard and classical theory of homogeneous freezing initiates within the interior volume of a cloud droplet. Current experimental data on homogeneous freezing rates of ice in droplets of supercooled water, both in air and emulsion oil samples, show considerable scatter. For example, at -33degreesC, the reported volume-based freezing rates of ice in supercooled water vary by as many as 5 orders of magnitude, which is well outside the range of measurement uncertainties. Here, we show that the process of ice nucleus formation at the air (or oil)-liquid water interface may help to explain why experimental results on ice nucleation rates yield different results in different ambient phases. Our results also suggest that surface crystallization of ice in cloud droplets can explain why low amounts of supercooled water have been observed in the atmosphere near -40degreesC.

## 2002 Djikaev

31 October , Tabazadeh, Hamill, Reiss

Citations: 70

### Thermodynamic conditions for the surface-stimulated crystallization of atmospheric droplets

We attempt to explain the experimental and molecular dynamics simulation evidence that suggests that the freezing of atmospheric aerosols occurs beginning at the droplet surface. By using the capillarity approximation, we derive the reversible work of formation of a crystal nucleus in the cases where it forms homogeneously within a (supercooled) bulk liquid and where it forms "pseudoheterogeneously" at the surface. Comparing the works of formation in these two cases, one obtains a condition that must hold in order for pseudoheterogeneous (surface) crystallization to be thermodynamically more favorable than homogeneous (bulk) crystallization. This condition is satisfied when at least one crystal facet is only partially wettable by its own melt.

## 2002 Cho

31 October , Shepson, Barrie, Cowin, Zaveri

Citations: 148

### NMR investigation of the quasi-brine layer in ice/brine mixtures

We report the study of a liquidlike phase that is found in dilute NaCl aqueous solutions frozen at temperatures below the liquid-to-solid-phase transition temperatures of H2O and NaCl.2H(2)O. There is strong evidence that heterogeneous reactions of gases with halides in liquid layers on ice are the source of halogen radicals that destroy the lower tropospheric ozone, and a subeutectic brine phase is thus of particular relevance to discussions of atmospheric composition and its dependence on the chemistry of polar marine ice and snow. The fractions and concentrations of water and NaCl in this subeutectic quasi-liquid phase were measured by H-1 and Na-23 NMR spectroscopy, and the experimental results compared to predictions derived from an equilibrium thermodynamic analysis. The temperature dependence of the salt concentration is well-described by the equilibrium theory for temperature ranges where ideal solution behavior holds; for lower temperatures, where the observed salt concentration increases and deviations from ideality emerge, the predicted concentrations are generally higher than experimental measurements.

## 2002 Granasy

1 October , Pusztai, James

Citations: 56

### Interfacial properties deduced from nucleation experiments: A Cahn-Hilliard analysis

We apply a single-order-parameter Cahn-Hilliard theory to deduce properties of the fluid-crystal interface from nucleation experiments: The two Cahn-Hilliard parameters (the free energy scale and the coefficient of the square-gradient term) are chosen so that the experimentally determined interfacial free energy of nuclei is recovered. The theory is then used to predict the thickness and free energy of the equilibrium planar interface, and other quantities such as the Tolman length and characteristic thickness, which describe the curvature dependence of the interfacial free energy. The accuracy of the method is demonstrated on systems (Lennard-Jones and ice-water) for which these properties are known. Experimental data available for five stoichiometric oxide glasses are then analyzed. The reduced interfacial free energy (Turnbull's alpha) and the interface thickness, we obtained, cover the alpha=0.28-0.51 and the d=0.8-1.6 nm ranges. For oxide glasses we find that alpha scales with n(-1/3), where n is the number of molecules per formula unit. In agreement with computer simulations, the Tolman length is strongly size dependent, while far weaker though still perceptible temperature dependence is observed for the characteristic interface thickness used in Granasy's phenomenological diffuse interface theory. In some cases bulk crystal properties prevail at the center of nuclei, while in other systems the nuclei are ramified, and the local properties significantly deviate from those of the macroscopic crystal. The accuracy of these results rests on a hypothesized temperature independence of the Cahn-Hilliard parameters, an assumption whose validity remains to be seen at large undercoolings.

## 2002 Sadtchenko

15 May , Ewing

Citations: 89

### Interfacial melting of thin ice films: An infrared study

Interfacial melting of ice has been examined by infrared spectroscopy for the first time. Thin ice films, from 10 to 20 nm thick, were prepared on a face of a germanium prism and studied over a range of temperatures just below the triple point. Interrogation was by attenuated total reflection (ATR) spectroscopy. Interfacial melting regions were distinguished from the underlying ice by comparisons of their spectra with the well established infrared signatures of bulk water and ice. Near the triple point, e.g., -0.15 degreesC, the spectroscopic profile of the surface melting region is indistinguishable from that of liquid water. This is compelling evidence that the commonly labeled quasi-liquid layer is indeed like liquid water. The extent of infrared extinction from ice films was used to determine the thickness of the quasi-liquid layers. At -0.03 degreesC the thickness is 15 nm corresponding to 40 monolayers of liquid but at -10 degreesC less than a monolayer remains. We compare our measurements of surface melting with those of others, sometimes finding discrepancies in thickness by two orders of magnitude. The promise of infrared spectroscopy to the further study of interfacial melting of ice is discussed.

## 2002 Bluhm

4 March , Ogletree, Fadley, Hussain, Salmeron

Citations: 159

### The premelting of ice studied with photoelectron spectroscopy

We address the century-old puzzle of the existence of a liquid-like layer at the ice surface near its melting point with new photoelectron spectroscopic tools using synchrotron radiation. Near-edge x-ray absorption shows that a liquid-like film exists at temperatures as low as -20degreesC. Near 0degreesC this film is about 20 Angstrom thick, i.e., six bilayers. With high-pressure x-ray photoelectron spectroscopy, we have further investigated the effect of surface contamination, which is ubiquitous in natural environments, on the state of the ice. Our results show that the premelting of ice can be strongly enhanced by the presence of hydrocarbon contamination.

## 2002 Myers

January , Charpin, Thompson

Citations: 81

### Slowly accreting ice due to supercooled water impacting on a cold surface

A theoretical model for ice growth due to droplets of supercooled fluid impacting on a subzero substrate is presented. In cold conditions rime (dry) ice forms and the problem reduces to solving a simple mass balance. In milder conditions glaze (wet) ice forms. The problem is then governed by coupled mass and energy balances, which determine the ice height and water layer thickness. The model is valid for "thin" water layers, such that lubrication theory may be applied and the Peclet number is small; it is applicable to ice accretion on stationary and moving structures. A number of analytical solutions are presented. Two- and three-dimensional numerical schemes are also presented, to solve the water flow equation, these employ a flux-limiting scheme to accurately model the capillary ridge at the leading edge of the flow. The method is then extended to incorporate ice accretion. Numerical results are presented for ice growth and water flow driven by gravity, surface tension, and a constant air shear.

## 2001 Devlin

15 February , Sadlej, Buch

Citations: 124

### Infrared spectra of large H2O clusters: New understanding of the elusive bending mode of ice

Infrared spectroscopic data for large water clusters, ranging from similar to 100 to 64 000 molecules, have been extended to the O-H stretch and bending mode regions of H2O. The stretch-mode spectra and analysis parallel results reported recently for D2O large clusters. Ambiguities in the current understanding of the bending region of the spectra of amorphous and crystalline ice are addressed using insights derived from the cluster infrared spectra and ab initio reduced-dimensionality models of ice and of the ice surface. The 1400-1700 cm(-1) spectral range, for annealed amorphous ice and crystalline cubic ice at 10 K, is characterized by a broad absorption lacking distinct features assignable to water bending vibrations. The spectra suggest that the bend-mode intensity of the bulk ices is either inherently very weak, diffused through interaction with the librational overtone, or both. However, this is not the case for large water clusters, which display distinct and relatively narrow bands attributed to the bending modes of subsets of surface water molecules. The new computational results suggest a strong but irregular dependence of the bend-mode frequency and band intensity on the strength and tetrahedrality of the hydrogen bonding. The computed intensity does decrease substantially for 4-coordinated vs lower-coordinated waters, but the highest frequency corresponds to double-donor 3-coordinated surface water molecules. A significant decrease of the librational-mode frequency, for those cases for which hydrogen bonding is reduced relative to ice I, is known to reduce the overlap of the bending mode with the librational overtone. Thus, for liquid water, microporous amorphous ice and the ice surface, which deviate strongly from tetrahedral bonding and for which the hydrogen bonding is diminished, the bend-mode absorption assumes a more normal intensity and bandwidth. From this basis a qualitative interpretation is presented of the infrared spectra for the region from similar to 500 to similar to 2400 cm(-1).

## 2001 Wei

19 February , Miranda, Shen

Citations: 226

### Surface vibrational spectroscopic study of surface melting of ice

Surface melting on the (0001) face of hexagonal ice (I(h)) was Studied by sum-frequency vibrational spectroscopy in the OH stretch frequency range. The degree of orientational order of the dangling OH bonds at the surface was measured as a function of temperature. Disordering sets in around 200 K and increases dramatically with temperature. The results show that the disordered (quasiliquid) layer on ice is structurally different from normal liquid water.

## 2000 Maruyama

December , Satoi, Taniguchi, Kawamura, Kodera, Kishimoto, Furukawa

Citations: 4

### X-ray analysis of the structure of premelted layers at ice interfaces

X-ray diffraction patterns of a premelted layer of ice and liquid water were obtained by a glancing-incidence method. Diffuse intensity patterns due to the premelted layer exhibited variation with temperature. Fourier transformation of the intensity curves gave pair-correlation functions, where the first, second and third peaks were observed in the permelted layer and liquid water. This suggests that there is a short range order in their molecular distribution. The average intermolecular distances between the nearest neighbors were 1-2% smaller in the premelted layer than in liquid water.

## 2000 Döppenschmidt

8 August , Butt

Citations: 189

### Measuring the thickness of the liquid-like layer on ice surfaces with atomic force microscopy

Atomic force microscopy was used to study the surface melting of ice in a temperature range above -35 degrees C. The thickness of the liquid-like layer (d) on ice was determined from the jump-in distance of force-versus-distance curves. The layer thickness of ice formed from distilled water was roughly 32 nm at -1 degrees C and 11 nm at -10 degrees C. The temperature dependence of d could best be described by d proportional to -log Delta T, where Delta T is the difference between the melting temperature and the actual temperature. The addition of salt increased the thickness of the liquid-like layer, and the temperature dependency agreed with predictions by Wettlaufer (Phys. Rev. Lett. 1999, 82, 2516).

## 2000 Gao

15 May , Zeng, Tanaka

Citations: 95

### The melting temperature of proton-disordered hexagonal ice: A computer simulation of 4-site transferable intermolecular potential model of water

We report computer simulation results of free energies of proton-disordered hexagonal ice and liquid water at atmospheric pressure with the 4-site transferable intermolecular potential model of water. A new reference system is used to calculate the free energy of the ice phase. The melting point of proton-disordered hexagonal ice at atmospheric pressure is found to be T-m=238(+/- 7) K. This result is consistent with a previous estimation, 230 K < T-m< 250 K, from molecular dynamic simulation of the surface melting of the proton-disordered hexagonal ice [G.-J. Kroes, Surf. Sci. 275, 365 (1992)].

## 1999 Bluhm

15 October , Salmeron

Citations: 65

### Growth of nanometer thin ice films from water vapor studied using scanning polarization force microscopy

Atomic force microscopy (AFM) was used to study the growth and morphology of ice films on the cleavage surface of mica. Measurements performed in contact, as well as in noncontact operation modes of the microscope, allowed us to distinguish the solid and liquid parts of the film. At temperatures below -30 degrees C, supercooled water droplets formed on top of a thin (nanometer range) ice layer in contact with the substrate. After annealing, a contiguous flat film was formed. Between -20 and -10 degrees C and at a relative humidity of similar to 83%, the film consisted of a solid ice layer similar to 7 Angstrom thick, covered by a liquid-like layer 50 +/- 5 Angstrom thick. When the temperature was raised above 0 degrees C, droplets formed, which subsequently evaporated. Comparison of results obtained in the various AFM operation modes allowed us to conclude the existence of a liquid-like layer on the ice surface.

## 1998 Gragson

Citations: 219

14 May , Richmond

### Investigations of the structure and hydrogen bonding of water molecules at liquid surfaces by vibrational sum frequency spectroscopy

The structure and hydrogen bonding of water molecules provides this unique solvent with properties essential to many physical, chemical, and biological processes. The intermolecular hydrogen bonding between water molecules in the bulk medium is disrupted at the surface, imparting the surface with unique structural and thermodynamic properties. We provide an overview of a range of experimental studies from this laboratory in which the structure, orientation, and hydrogen bonding of interfacial water molecules at liquid interfaces are directly probed by resonant vibrational sum frequency spectroscopy. The studies provide insight into the difference in water structure and hydrogen bonding at an air/water interface relative to the interface between two bulk immiscible liquids, namely the CCl4/H2O interface. Also described are studies aimed at understanding. how the presence of a charged alkyl surfactant alters the structure of water at these two interfaces. In both cases field-induced alignment of water molecules in the double layer region is prevalent. This induced alignment has been examined under a variety of experimental conditions. A series of isotopic dilution studies conducted for the first time at liquid surfaces are also described. In these studies the intermolecular and intramolecular coupling of vibrational modes in the water molecules are diminished. The results of these and above-mentioned studies provide valuable information for those interested in developing theoretical descriptions of water at surfaces and interfaces.

## 1998 Mishima

12 March , Stanley

Citations: 471

### Decompression-induced melting of ice IV and the liquid-liquid transition in water

Although liquid water has been the focus of intensive research for over 100 years, a coherent physical picture that unifies all of the known anomalies of this liquid(1-3) is still lacking, Some of these anomalies occur in the supercooled region, and have been rationalized on the grounds of a possible retracing of the liquid-gas spinodal (metastability limit) line into the supercooled liquid region(4-7) or alternatively the presence of a line of first-order liquid-liquid phase transitions in this region which ends in a critical points(8-14). But these ideas remain untested experimentally, in part because supercooled water can be probed only above the homogeneous nucleation temperature T-H at which water spontaneously crystallizes. Here we report an experimental approach that is not restricted by the barrier imposed by T-H, involving measurement of the decompression-induced melting curves of several high-pressure phases of ice in small emulsified droplets. We find that the melting curve for ice IV seems to undergo a discontinuity at precisely the location proposed for the line of liquid-liquid phase transitions(8). This is consistent with, but does not prove, the coexistence of two different phases of (supercooled) liquid water. From the experimental data we calculate a possible Gibbs potential surface and a corresponding equation of state for water, from the forms of which we estimate the coordinates of the liquid-liquid critical point to be at pressure P-c approximate to 0.1 GPa and temperature T-c approximate to 220 K.

## 1997 Peters

20 October , Chung, Cohen

Citations: 89

### Surface melting on small particles

Surface melting on small particles was detected using x-ray diffraction from Pb crystallites of 50 nm diam in ultrahigh vacuum. Since the melting temperature depends on particle size, it can be difficult to distinguish between the melting and surface melting. A sharp crystallite size distribution is obtained by melting the smaller particles while a liquid skin forms on the remaining crystallites. When the sample is cooled slightly, the liquid particles remain liquid while the liquid skin on the crystallites solidifies. In situ x-ray diffraction reveals that the liquid skin thickness changes reversibly.

## 1997 Makkonen

7 August

Citations: 63

### Surface melting of ice

The present theories of surface premelting are based on the assumed mechanism whereby a liquid layer is formed because the free energy of the surface is thus minimized. It is shown experimentally here that this mechanism is not possible in the case of ice, for which surface melting below 0 degrees C is, however, well documented. A mechanism of surface melting, unique for ice, is then proposed. It is based on a concept according to which the surface phase equilibrium temperature differs from that of the bulk material. The new theory predicts the onset temperature of premelting on ice in quantitative agreement with recent experimental data. It also explains regelation of ice and explains why water reaches a density maximum above its freezing point.

## 1997 Petrenko

7 August

Citations: 72

### Study of the surface of ice, ice/solid and ice/liquid interfaces with scanning force microscopy

Contact mode of scanning force microscopy (SFM) and force curves (FC) were used to study the morphology of ice surface in air and in liquid decane and the structure and some physical properties of the interfaces between ice and Si and Si3N4 cantilever tips in the temperature range from -0.4 to -20 degrees C. Evidence for a liquid-like layer on the ice surface came from observation of capillary forces that act on cantilever tips. Intensive mass transport along the ice surface was found at T greater than or equal to -14 degrees C. The FCs were used to determine the adhesion strength of ice to Si and Si3N4 cantilever tips, the corresponding interfacial energies, the thickness of a liquid-like layer, and the density of an electric charge acquired by the tips from the ice surface.

## 1997 Jenniskens

22 July , Banham, Blake, McCoustra

Citations: 185

### Liquid water in the domain of cubic crystalline ice I-c

Vapor-deposited amorphous water ice, when warmed above the glass transition temperature (120-140 K), is a viscous liquid which exhibits a viscosity vs temperature relationship different from that of liquid water at room temperature. New studies of thin water ice films now demonstrate that viscous liquid water persists in the temperature range 140-210 K, where it coexists with cubic crystalline ice. The liquid character of amorphous water above the glass transition is demonstrated by (1) changes in the morphology of water ice films on a nonwetting surface observed in transmission electron microscopy (TEM) at around 175 K during slow warming, (2) changes in the binding energy of water molecules measured in temperature programmed desorption (TPD) studies, and (3) changes in the shape of the 3.07 mu m absorption band observed in,orating angle reflection-absorption infrared spectroscopy (RAIRS) during annealing at high temperature, whereby the decreased roughness of the water surface is thought to cause changes in the selectin rules for the excitation of O-H stretch vibrations, Because it is present over such a wide range of temperatures, we propose that this form of liquid water is a common material in nature, where it is expected to exist in the subsurface layers of comets and on the surfaces of some planets and satellites.

## 1996 Jenniskens

20 December , Blake

Citations: 180

### Crystallization of amorphous water ice in the solar system

Electron diffraction studies of vapor-deposited water ice have characterized the dynamical structural changes during crystallization that affect volatile retention in cometary materials. Crystallization is found to occur by nucleation of small domains, while leaving a significant part of the amorphous material in a slightly more relaxed amorphous state that coexists metastably with cubic crystalline ice. The onset of the amorphous relaxation is prior to crystallization and coincides with the glass transition. Above the glass transition temperature, the crystallization kinetics are consistent with the amorphous solid becoming a ''strong'' viscous liquid. The amorphous component can effectively retain volatiles during crystallization if the volatile concentration is similar to 10% or less. For higher initial impurity concentrations, a significant amount of impurities is released during crystallization, probably because the impurities are trapped on the surfaces of micropores. A model for crystallization over long timescales is described that can be applied to a wide range of impure water ices under typical astrophysical conditions if the fragility factor D, which describes the viscosity behavior, can be estimated.

## 1996 Speedy

1 July , Debenedetti, Smith, Huang, Kay

Citations: 243

### The evaporation rate, free energy, and entropy of amorphous water at 150 K

Measurement of the rates of evaporation of amorphous water (a) and ice (i) near 150 K can be interpreted as giving a measure of their free energy difference, Delta(i)(a)G (150 K) = 1100+/-100 J/mol, which, together with the known enthalpy difference and heat capacity data, suggests a residual entropy difference of Delta(i)(a)S (0) = -0.7+/-2.2 J/(K mol) at absolute zero. Previous theoretical estimates of Delta(i)(a)S (0), which are much larger, did not allow the amorph to be connected with normal liquid water by a reversible thermodynamic path at atmospheric pressure. The present value allows such a connection.

## 1995 DOSCH

1 April , LIED, BILGRAM

Citations: 133

### GLANCING-ANGLE X-RAY-SCATTERING STUDIES OF THE PREMELTING OF ICE SURFACES

The onset of surface melting at {00.1} (''basal''), {10.0} and {11.0} (''nonbasal'') surfaces of hexagonal ice is studied experimentally by glancing-angle X-ray scattering. The preparation of mirror-like single crystal ice surfaces and a special in situ X-ray chamber is described in detail. The X-ray scattering experiments using synchrotron radiation give clear evidence that all the investigated high-symmetry surfaces exhibit surface melting with onset temperatures T-s congruent to -13.5 degrees C for the basal and T-s congruent to -12.5 degrees C for the nonbasal surfaces. The temperature dependence of the thickness of the quasiliquid is presented and discussed in view of various theoretical predictions. In addition we found thermal faceting at nonbasal surfaces as well as a diffuse (''rough'') solid-quasiliquid interface. The thermal properties of the observed surface disorder implies that the correlation length within the socalled ''surface melt'' is much larger than the correlation length in the bulk liquid indicating the presence of significant ''substrate'' interactions.

## 1995 DASH

January , FU, WETTLAUFER

Citations: 488

### THE PREMELTING OF ICE AND ITS ENVIRONMENTAL CONSEQUENCES

Several mechanisms can extend the equilibrium domain of a liquid phase into the solid region of the normal phase diagram. The causes of premelting, which include surface melting, interface curvature and substrate disorder, occur in all types of substances, including H2O. In the case of H2O, premelting can have important environmental consequences, among which are the heaving of frozen ground, breakdown of rock and concrete, sintering of snow, flow of glaciers, scavenging of atmospheric trace gases by snow and ice, and the electrification of thunderclouds. This article reviews the basic mechanisms of premelting and discusses their roles in the environmental phenomena. The principal results of numerous studies are reviewed, and trends in current research are outlined.

## 1994 BAKER

20 May , DASH

Citations: 72

### MECHANISM OF CHARGE-TRANSFER BETWEEN COLLIDING ICE PARTICLES IN THUNDERSTORMS

We derive a theoretical mechanism for the charge transfer between colliding ice and soft hail particles, based on current ideas of surface melting. According to this theory, each of the ice surfaces is covered with a film of quasi-liquid water, whose thickness can be estimated as a function of temperature and local curvature. We show that during contact of two particles, fluid will flow from the thicker to the thinner layer, and we estimate the volume transferred in atmospherically relevant situations. We postulate a charge structure within the surface-melted layer based on observations on similar systems and show that this leads to estimated charge transfers consistent in approximate magnitude and sign with trends observed in the laboratory.

## 1993 CONKLIN

20 September , BALES

Citations: 102

### SO(2) UPTAKE ON ICE SPHERES - LIQUID NATURE OF THE ICE-AIR INTERFACE

The amount Of SO2 gas absorbed by ice of known surface area at equilibrium was used to estimate the volume of liquid water present at the ice-air interface at temperatures from -1 to -60-degrees-C. Calculations were based on Henry's law and acid dissociation equilibrium. The liquid volume is lowest at lower temperatures and ionic strength and under most conditions was greater than the volumes calculated based on freezing-point depression. The equivalent liquid layer thickness, assuming that liquid water is uniformly distributed around the grains, ranged from 3-30 nm at -60-degrees-C to 500-3000 nm at -1-degrees-C. Corresponding ionic strengths for the two temperatures were 1.7-0.0012 M and 0.005-0.00009 M. Lower values were for ice made from distilled water, and higher values were for ice made from 10(-3) M NaCl. Estimated pH values were from 2.9 at -60-degrees-C to 4.1 at -1-degrees-C. Results demonstrate that gas absorption can be used to estimate an equivalent liquid volume and thickness for the ice-air interfacial region. While not directly comparable to physical measurements, the estimated values should be directly applicable to modeling uptake of SO2 and other trace gases by ice. Lack of good thermodynamic data for temperatures below 0-degrees-C is the main limitation to applying this method.

## x 1992 KROES

15 September

Citations: 182

Not available via OU

### SURFACE MELTING OF THE (0001) FACE OF TIP4P ICE

The onset of surface melting of the basal plane (0001) face of TIP4P ice is studied in the temperature range T = 190-250 K using the molecular dynamics (MD) method. The disordering of the surface seen in the calculations can be explained in terms of the disruption of the hydrogen bonding network at the surface. At T = 210 K and lower the surface remains solid-like, as evidenced by non-zero order parameters and no calculable self-diffusion, although the reorientational correlation time (ca. 100 ps) is closer to that of the liquid than that of bulk ice. On the other hand, at T = 230 K (-43-degrees-C) and higher the surface is liquid-like, as shown by low order parameters and a high translational and rotational mobility of the molecules. At all temperatures, there is an orientational preference for the water molecule pointing its protons down, which is in agreement with experiment. The polarisation of the surface increases with increasing temperature. For the transition layer, the calculated reorientational correlation times are in rough agreement with NMR experiments, but for T greater-than-or-equal-to 230 K the calculated self-diffusion coefficients are much higher than the values obtained in NMR experiments.

## 1991 ELBAUM

1 April , SCHICK

Citations: 121

### APPLICATION OF THE THEORY OF DISPERSION FORCES TO THE SURFACE MELTING OF ICE

We apply the theory of Dzyaloshinskii, Lifshitz, and Pitaevskii to ice, water, and vapor at the triple point and find that electromagnetic interactions do not permit a liquid film of macroscopic thickness at the ice-vapor interface. Hence the surface melting of ice is at most incomplete. However, the thickness of the film which is permitted is surprisingly large, with retardation effects setting the scale. Our estimate is about 30 angstrom. Further liquid appears as droplets with a contact angle of about 0.2-degrees. The film thickness decreases rapidly with temperature.

## 1965 Hobbs

30 December 1964

Citations: 29

### The Aggregation of Ice Particles in Clouds and Fogs at Low Temperatures

A previously derived theoretical expression, supported by experimental observations, for the rate of sintering between two ice spheres is applied to the case of adhesion between ice particles down to temperatures of −40C. Appreciable bonding is shown to take place between the particles within 10 seconds of contact even at −40C. The results predicted by the theory are found to be in quantitative agreement with the degree of sintering observed in aggregates of ice particles from natural ice fogs.

## x 1954 NAKAYA

, MATSUMOTO

Citations: 88

Not available via OU

### SIMPLE EXPERIMENT SHOWING THE EXISTENCE OF LIQUID WATER FILM ON THE ICE SURFACE

## End

# Maybe

## 2016 Tong

21 July , Kampfrath, Campen

### Experimentally probing the libration of interfacial water: the rotational potential of water is stiffer at the air/water interface than in bulk liquid

Most properties of liquid water are determined by its hydrogen-bond network. Because forming an aqueous interface requires termination of this network, one might expect the molecular level properties of interfacial water to markedly differ from water in bulk. Intriguingly, much prior experimental and theoretical work has found that, from the perspective of their time-averaged structure and picosecond structural dynamics, hydrogen-bonded OH groups at an air/water interface behave the same as hydrogen-bonded OH groups in bulk liquid water. Here we report the first experimental observation of interfacial water's libration (i.e. frustrated rotation) using the laser-based technique vibrational sum frequency spectroscopy. We find this mode has a frequency of 834 cm(-1), approximate to 165 cm(-1) higher than in bulk liquid water at the same temperature and similar to bulk ice. Because libration frequency is proportional to the stiffness of water's rotational potential, this increase suggests that one effect of terminating bulk water's hydrogen bonding network at the air/water interface is retarding rotation of water around intact hydrogen bonds. Because in bulk liquid water the libration plays a key role in stabilizing reaction intermediates and dissipating excess vibrational energy, we expect the ability to probe this mode in interfacial water to open new perspectives on the kinetics of heterogeneous reactions at aqueous interfaces.

## 2016 Lee

9 June , Bang, Kang

### Surface Charge Layer of Amorphous Solid Water with Adsorbed Acid or Base: Asymmetric Depth Distributions of H+ and OH- Ions

The charge at the surface of water and the resultant surface voltage play an important role in many natural phenomena and technological applications. However, the relationship between surface Charge and the interfacial distribution of H+ and OH- ions remains unclear. We measured the surface voltage produced by an ionized acid or a base at the surface of amorphous solid Water (ASW) using a Kelvin work-function probe and studied the depth distributions of H+ and OH- ions. H+ ions were distributed over a thicker region from the surface than OH- ions, although both ions reside preferentially at the surface. This difference led:to the formation of opposite surface charges in the presence of the acid or base. The deeper penetration of H+ ions is attributed to efficient proton transport, dynamics in the lattice and the resultant dynamic delocalization of protons. The study demonstrates that the asymmetric H+ and OH- distributions may be important to understand, the electrical and acid-base properties of ASW and crystalline ice surfaces and, possibly, those of the liquid water surface as well.

## 2016 Anim-Danso

25 February , Zhang, Dhinojwala

### Surface Charge Affects the Structure of Interfacial Ice

We have conducted studies on the freezing of water molecules next to charged surfaces to elucidate the effect of water orientation on the structure of ice using sum frequency generation spectroscopy. We observed that when water is frozen next to a positively charged sapphire surface, the signal intensity of ice is higher than that of liquid water as so expected from previous theoretical studies. However, when water is frozen next to a negatively charged sapphire surface (using NaOH as pH adjuster), the signal intensity decreases. The same signal attenuation upon freezing is obtained when cesium hydroxide (CsOH) and tetramethylammonium hydroxide (N(CH3)(4)OH) are used as pH adjusters. Since Na+, Cs+, and N(CH3)(4)(+) ions have different hydration properties, the cation specific effect for this attenuation in signal intensity for ice is ruled out. Experiments on a mica surface (inherently negatively charged) also showed similar attenuation in signal intensity for ice as negatively charged sapphire surface. We conclude that the orientation of the water molecules next to a surface plays an important role in the structure of ice. These results have important implications in understanding the strength of ice nucleation and strength of ice adhesion next to charged surfaces.

## 2016 Fransson, T

13 July , Harada, Kosugi, Besley, Winter, Rehr, Pettersson, Nilsson

### X-ray and Electron Spectroscopy of Water

Here we present an overview of recent developments of X-ray and electron spectroscopy to probe water at different temperatures. Photon-induced ionization followed by detection of electrons from either the 0 is level or the valence band is the basis of photoelectron spectroscopy. Excitation between the 0 is and the unoccupied states or occupied states is utilized in X-ray absorption and X-ray emission spectroscopies. These techniques probe the electronic structure of the liquid phase and show sensitivity to the local hydrogen-bonding structure. Both experimental aspects related to the measurements and theoretical simulations to assist in the interpretation are discussed in detail. Different model systems are presented such as the different bulk phases of ice and various adsorbed monolayer structures on metal surfaces.

## 2016 Bryk

, Haymet

### Profiles of electrostatic potential across the water-vapor, ice-vapor and ice-water interfaces

Ice-water, water-vapor interfaces and ice surface are studied by molecular dynamics simulations with the SPC/E model of water molecules having the purpose to estimate the profiles of electrostatic potential across the interfaces. We have proposed a methodology for calculating the profiles of electrostatic potential based on a trial particle, which showed good agreement for the case of electrostatic potential profile of the water-vapor interface of TIP4P model calculated in another way. The measured profile of electrostatic potential for the pure ice-water interface decreases towards the liquid bulk region, which is in agreement with simulations of preferential direction of motion of Li+ and F- solute ions at the liquid side of the ice-water interface. These results are discussed in connection with the Workman-Reynolds effect.

## 2016 Alekseenko

May , Mendig, Schulz, Sinapius, Prykhodko

### An experimental study of freezing of supercooled water droplet on solid surface

Results of experimental investigations of the freezing of immobile water droplet on an aluminum plate are presented. The process was studied with the aid of a high-speed photo camera. The freezing of supercooled water contained in the surface droplet proceeds in a few stages: (i) preliminary heating of water and nucleation of ice microcrystals, (ii) relatively fast formation of the ice-liquid system with a transition to the state of thermodynamic equilibrium near the freezing temperature, and (iii) slow process of complete freezing. The rate and duration of each stage and the time of delay between the moment of action upon the supercooled droplet and the onset of freezing are estimated. Processes of supercooled and nonsupercooled water solidification are compared.

## 2014 Asakawa

July , Sazaki, Yokoyama, Nagashima, Nakatsubo, Furukawa

### Roles of Surface/Volume Diffusion in the Growth Kinetics of Elementary Spiral Steps on Ice Basal Faces Grown from Water Vapor

We measured velocities V-step of lateral displacement of individual elementary steps on an ice basal face, for the first time, by advanced optical microscopy, under various bulk water vapor pressure p(H2O)(infinity). Distances L between adjacent spiral steps exhibited considerable variation under constant p(H2O)(infinity). Hence, we analyzed V-step as functions of L and p(H2O)(infinity). Then we found that (1) under a constant p(H2O)(infinity), V-step decreased with decreasing distances L when L <= 15 mu m and that V-step remained constant when L >= 15 mu m. We named V-step of L >= 15 mu m (isolated steps) V-step(int) and analyzed dependencies of V-step(int) on p(H2O)(infinity). Then we found that (2) the slope of the V-step(int) vs p(H2O)(infinity) plot gradually decreased with increasing p(H2O)(infinity). We proposed a model that took into account both the volume diffusion of water vapor molecules and the surface diffusion of water admolecules on a terrace. Our model could explain result (1) mainly by the competition of adjacent spiral steps for water admolecules diffusing on a terrace but could not explain the result (2) satisfactorily.

## 2014 Domine

, Albert, Huthwelker, Jacobi, Kokhanovsky, Lehning, Picard, Simpson

### Snow physics as relevant to snow photochemistry

Snow on the ground is a complex multiphase photochemical reactor that dramatically modifies the chemical composition of the overlying atmosphere. A quantitative description of the emissions of reactive gases by snow requires knowledge of snow physical properties. This overview details our current understanding of how those physical properties relevant to snow photochemistry vary during snow metamorphism. Properties discussed are density, specific surface area, thermal conductivity, permeability, gas diffusivity and optical properties. Inasmuch as possible, equations to parameterize these properties as functions of climatic variables are proposed, based on field measurements, laboratory experiments and theory. The potential of remote sensing methods to obtain information on some snow physical variables such as grain size, liquid water content and snow depth are discussed. The possibilities for and difficulties of building a snow photochemistry model by adapting current snow physics models are explored. Elaborate snow physics models already exist, and including variables of particular interest to snow photochemistry such as light fluxes and specific surface area appears possible. On the other hand, understanding the nature and location of reactive molecules in snow seems to be the greatest difficulty modelers will have to face for lack of experimental data, and progress on this aspect will require the detailed study of natural snow samples.

## 2013 Limmer

7 June , Chandler

### The putative liquid-liquid transition is a liquid-solid transition in atomistic models of water. II

This paper extends our earlier studies of free energy functions of density and crystalline order parameters for models of supercooled water, which allows us to examine the possibility of two distinct metastable liquid phases [D. T. Limmer and D. Chandler, J. Chem. Phys. 135, 134503 (2011) and preprint arXiv:1107.0337 (2011)]. Low-temperature reversible free energy surfaces of several different atomistic models are computed: mW water, TIP4P/2005 water, Stillinger-Weber silicon, and ST2 water, the last of these comparing three different treatments of long-ranged forces. In each case, we show that there is one stable or metastable liquid phase, and there is an ice-like crystal phase. The time scales for crystallization in these systems far exceed those of structural relaxation in the supercooled metastable liquid. We show how this wide separation in time scales produces an illusion of a low-temperature liquid-liquid transition. The phenomenon suggesting metastability of two distinct liquid phases is actually coarsening of the ordered ice-like phase, which we elucidate using both analytical theory and computer simulation. For the latter, we describe robust methods for computing reversible free energy surfaces, and we consider effects of electrostatic boundary conditions. We show that sensible alterations of models and boundary conditions produce no qualitative changes in low-temperature phase behaviors of these systems, only marginal changes in equations of state. On the other hand, we show that altering sampling time scales can produce large and qualitative non-equilibrium effects. Recent reports of evidence of a liquid-liquid critical point in computer simulations of supercooled water are considered in this light.

## 2012 Sulpizi, M

March , Gaigeot, Sprik

### The Silica-Water Interface: How the Silanols Determine the Surface Acidity and Modulate the Water Properties

Silica is the most abundant metal oxide and the main component of the Earth's crust. Its behavior in contact with water plays a critical role in a variety of geochemical and environmental processes. Despite its key role, the details of the aqueous silica interface at the microscopic molecular level are still elusive. Here we provide such a detailed understanding of the molecular behavior of the silica water interface, using density functional theory based molecular dynamics (DFTMD) simulations, where a consistent treatment of the electronic structure of solvent and surface is provided. We have calculated the acidity of the silanol groups at the interface directly from the DFTMD simulations, without any fitting of parameters to the experimental data. We find two types of silanol groups at the surface of quartz: out-of-plane silanols with a strong acidic character (pK(a) = 5.6), which consequently results in the formation of strong and short hydrogen bonds with water molecules at the interface, and in-plane silanols with a pK(a) of 8.5, forming weak hydrogen bonds with the interfacial water molecules. Our estimate of the quartz point of zero charge (1.0) is found in good agreement with the experimental value of 1.9. We have also shown how the silanols orientation and their hydrogen bond properties are responsible for an amphoteric behavior of the surface. A detailed analysis has identified two species of adsorbed water molecules at the solid liquid interface, which using the language of vibrational spectroscopy can be identified as "liquid-like" and "ice-like" water or, in other words, water molecules forming respectively weak and strong H-bonds with the oxide surface. These two populations of water are in turn responsible for two distinct peaks in the infrared spectrum of interfacial water and thus provide a molecular explanation of the experimental sum frequency generation spectrum recorded in the literature. In the specific case of quartz, we show that the liquid-/ice-like behavior is the result of the silanol groups ability to donate or accept hydrogen bonds with different strengths, which consequently modulates the vibrational properties of the adsorbed water layer.

## 2012 Jung

January , Tiwari, Doan, Poulikakos

### Mechanism of supercooled droplet freezing on surfaces

Understanding ice formation from supercooled water on surfaces is a problem of fundamental importance and general utility. Superhydrophobic surfaces promise to have remarkable 'icephobicity' and low ice adhesion. Here we show that their icephobicity can be rendered ineffective by simple changes in environmental conditions. Through experiments, nucleation theory and heat transfer physics, we establish that humidity and/or the flow of a surrounding gas can fundamentally switch the ice crystallization mechanism, drastically affecting surface icephobicity. Evaporative cooling of the supercooled liquid can engender ice crystallization by homogeneous nucleation at the droplet-free surface as opposed to the expected heterogeneous nucleation at the substrate. The related interplay between droplet roll-off and rapid crystallization is also studied. Overall, we bring a novel perspective to icing and icephobicity, unveiling the strong influence of environmental conditions in addition to the accepted effects of the surface conditions and hydrophobicity.

## 2010 Nilsson

March , Nordlund, Waluyo, Huang, Ogasawara, Kaya, Bergmann, Naslund, Ostrom, Wernet, Andersson, Schiros, Pettersson

### X-ray absorption spectroscopy and X-ray Raman scattering of water and ice; an experimental view

Here we present a review of X-ray absorption spectroscopy and X-ray Raman scattering with the perspective to understand the spectra of water including changes with temperature, mass of the water molecule and presence of monovalent ions. The different detection schemes are discussed and it is concluded that transmission X-ray absorption measurements, using a small area where the thickness is uniform, and X-ray Raman scattering give the most reliable spectra. Different model systems are discussed such as the surface and bulk of ice and various adsorbed monolayer structures on metal surfaces.

## 2009 Fan

27 August , Chen, Yang, Cremer, Gao

### On the Structure of Water at the Aqueous/Air Interface

Vibrational sum frequency spectroscopy (VSFS) and molecular dynamics (MD) simulations were used in concert to investigate the molecular structure and hydrogen bonding of the air/water interface. MID simulations were performed with a variety of water models. The results indicated that only the upper most two layers of water molecules are ordered in this system. There is a strong preference to have the top layer arranged Such that the OH moiety points upward into the air. This orientational preference arises from two factors that involve the maximization of the number of hydrogen bonds formed and the minimization of partial charge that is exposed. Specifically, the lone pairs from oxygen are less likely to face into the air compared with the OH moiety because this would expose more partial charge and, therefore, be unfavorable oil enthalpic grounds. The two-layer interfacial water structure model implies that there should be four distinct types of OH stretches for this system. Namely, one directs upward and another points downward in each layer. Interestingly, VSFS experiments revealed the presence of four OH stretch region peaks at 3 117, 3222, 3448, and 3696 cm(-1). The phases of the 3 117 and 3696 cm(-1) resonances carried a positive sign, which indicates that these features arise from OH groups with protons facing upward toward the air. The other two resonances emanate from OH groups with protons facing downward toward the bulk aqueous solution, On the basis of this, we assign the 3117 cm(-1) peak to the OH moiety from a water molecule in the second layer, which is hydrogen bonded upward toward the top layer. On the other hand, the peak at 3222 cm(-1) should arise from water molecules in the top layer with the OH moiety facing downward to hydrogen bond to the second layer. The 3448 cm(-1) peak arises from hydrogen bonding between water molecules in the second layer and the more disordered water molecules of the bulk liquid. Finally, the peak at 3696 cm(-1) is assigned to the free OH moiety pointing upward in the top layer.

## 2009 Hodgson

30 September , Haq

### Water adsorption and the wetting of metal surfaces

Water adsorption at metal surfaces is governed by a subtle balance between water-water hydrogen bonding and water-metal interactions, which together determine the stability of the water structures formed. This review describes recent experimental and theoretical studies of water and OH/water coadsorption on well-defined single crystal metal surfaces, systems that have seen an upsurge in interest as new results modify our picture of how water adsorbs on metal surfaces. These results reveal that the simple, conventional ice 'bilayer' description of water adsorption, in which water is only marginally distorted from its bulk ice arrangement, is inadequate to describe wetting. Instead, optimisation of the water-metal interaction distorts the local hydrogen bonding geometry of water monolayers significantly from that of bulk ice, with consequent effects on the lateral size and geometry of ice clusters, on the structure of water monolayers and on the wetting of first layer water and growth of ice multilayers. Here we compare adsorption across different metal surfaces, review evidence for the formation of mixed OH/H2O co-adsorption structures and highlight issues that remain uncertain.

## 2009 Mikhailov

, Vlasenko, Martin, Koop, Poschl

### Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations

Interactions with water are crucial for the properties, transformation and climate effects of atmospheric aerosols. Here we present a conceptual framework for the interaction of amorphous aerosol particles with water vapor, outlining characteristic features and differences in comparison to crystalline particles. We used a hygroscopicity tandem differential mobility analyzer (H-TDMA) to characterize the hydration and dehydration of crystalline ammonium sulfate, amorphous oxalic acid and amorphous levoglucosan particles (diameter similar to 100 nm, relative humidity 5-95% at 298 K). The experimental data and accompanying Kohler model calculations provide new insights into particle microstructure, surface adsorption, bulk absorption, phase transitions and hygroscopic growth. The results of these and related investigations lead to the following conclusions:

(1) Many organic substances, including carboxylic acids, carbohydrates and proteins, tend to form amorphous rather than crystalline phases upon drying of aqueous solution droplets. Depending on viscosity and microstructure, the amorphous phases can be classified as glasses, rubbers, gels or viscous liquids.

(2) Amorphous organic substances tend to absorb water vapor and undergo gradual deliquescence and hygroscopic growth at lower relative humidity than their crystalline counterparts.

(3) In the course of hydration and dehydration, certain organic substances can form rubber- or gel-like structures (supramolecular networks) and undergo transitions between swollen and collapsed network structures.

(4) Organic gels or (semi-)solid amorphous shells (glassy, rubbery, ultra-viscous) with low molecular diffusivity can kinetically limit the uptake and release of water and may influence the hygroscopic growth and activation of aerosol particles as cloud condensation nuclei (CCN) and ice nuclei (IN). Moreover, (semi-)solid amorphous phases may influence the uptake of gaseous photo-oxidants and the chemical transformation and aging of atmospheric aerosols.

(5) The shape and porosity of amorphous and crystalline particles formed upon dehydration of aqueous solution droplets depend on chemical composition and drying conditions. The apparent volume void fractions of particles with highly porous structures can range up to similar to 50% or more (xerogels, aerogels).

(6) For efficient description of water uptake and phase transitions of aerosol particles, we propose not to limit the terms deliquescence and efflorescence to equilibrium phase transitions of crystalline substances. Instead we propose generalized definitions according to which amorphous and crystalline components can undergo gradual or prompt, partial or full deliquescence or efflorescence.

We suggest that (semi-)solid amorphous phases may be important not only in the upper atmosphere as suggested in recent studies of glass formation at low temperatures. Depending on relative humidity, (semi-)solid phases and moisture-induced glass transitions may also play a role in gas-particle interactions at ambient temperatures in the lower atmosphere.

## 2008 Buch

22 April , Groenzin, Lit, Shultz, Tosatti

### Proton order in the ice crystal surface

The physics of the ice crystal surface and its interaction with adsorbates are not only of fundamental interest but also of considerable importance to terrestrial and planetary chemistry. Yet the atomic-level structure of even the pristine ice surface at low temperature is still far from well understood. This computational study focuses on the pattern of dangling H and dangling 0 (lone pairs) atoms at the basal ice surface. Dangling atoms serve as binding sites for adsorbates capable of hydrogen-and electrostatic bonding. Extension of the well known orientational disorder ("proton disorder") of bulk crystal ice to the surface would naturally suggest a disordered dangling atom pattern; however, extensive computer simulations employing two different empirical potentials indicate significant free energy preference for a striped phase with alternating rows of dangling H and dangling 0 atoms, as suggested long ago by Fletcher [Fletcher NH (1992) Philos Mag 66:109-115]. The presence of striped phase domains within the basal surface is consistent with the hitherto unexplained minor fractional peaks in the helium diffraction pattern observed 10 years ago. Compared with the disordered model, the striped model yields improved agreement between computations and experimental ppp-polarized sum frequency generation spectra.

## 2008 Quigley

21 Aril , Rodger, PM

### Metadynamics simulations of ice nucleation and growth

The metadynamics method for accelerating rate events in molecular simulations is applied to the problem of ice freezing. We demonstrate homogeneous nucleation and growth of ice at 180 K in the isothermal-isobaric ensemble without the presence of external fields or surfaces. This result represents the first report of continuous and dynamic ice nucleation in a system of freely evolving density. Simulations are conducted using a variety of periodic simulation domains. In all cases the cubic polymorph ice I(c) is grown. The influence of boundary effects on estimates of the nucleation free energy barrier are discussed in relation to differences between this and earlier work.

## 2008 Boxe

, Saiz-Lopez

### Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO(x) release from the Arctic and coastal Antarctic snowpack

We utilize a multiphase model, CON-AIR (Condensed Phase to Air Transfer Model), to show that the photochemistry of nitrate (NO(3)(-)) in and on ice and snow surfaces, specifically the quasi-liquid layer (QLL), can account for NO(x) volume fluxes, concentrations, and [NO]/[NO(2)] (gamma=[NO]/[NO(2)]) measured just above the Arctic and coastal Antarctic snowpack. Maximum gas phase NO(x) volume fluxes, concentrations and gamma simulated for spring and summer range from 5.0x10(4) to 6.4x10(5) molecules cm(-3) s(-1), 5.7x10(8) to 4.8x10(9) molecules cm(-3), and similar to 0.8 to 2.2, respectively, which are comparable to gas phase NOx volume fluxes, concentrations and gamma measured in the field. The model incorporates the appropriate actinic solar spectrum, thereby properly weighting the different rates of photolysis of NO(3)(-) and NO(2)(-). This is important since the immediate precursor for NO, for example, NO(2)(-), absorbs at wavelengths longer than nitrate itself. Finally, one-dimensional model simulations indicate that both gas phase boundary layer NO and NO(2) exhibit a negative concentration gradient as a function of height although [NO]/[NO(2)] are approximately constant. This gradient is primarily attributed to gas phase reactions of NO(x) with halogens oxides (i.e. as BrO and IO), HO(x), and hydrocarbons, such as CH(3)O(2).

## 2006 van den Heever

July , Carrio, Cotton, DeMott, Prenni

### Impacts of nucleating aerosol on Florida storms. Part I: Mesoscale simulations

Toward the end of the Cirrus Regional Study of Tropical Anvils and Cirrus Layer-Florida Area Cirrus Experiment (CRYSTAL-FACE) field campaign held during July 2002, high concentrations of Saharan dust, which can serve as cloud condensation nuclei (CCN), giant CCN (GCCN), and ice-forming nuclei (IFN) were observed over the peninsula of Florida. To investigate the impacts of enhanced aerosol concentrations on the characteristics of convective storms and their subsequent anvil development, sensitivity tests are conducted using the Regional Atmospheric Modeling System (RAMS) model, in which the initialization profiles of CCN, GCCN, and IFN concentrations are varied. These variations are found to have significant effects on the storm dynamics and microphysical processes, as well as on the surface precipitation. Updrafts are consistently stronger as the aerosol concentrations are increased. The anvils cover a smaller area but are better organized and have larger condensate mixing ratio maxima in the cases with greater aerosol concentrations. Cloud water mass tends to increase with increasing aerosol concentrations, with enhanced GCCN concentrations having the most significant influence. Increasing either the GCCN or IFN concentrations produces the most rainfall at the surface whereas enhanced CCN concentrations reduce surface rainfall. Higher IFN concentrations produce ice at warmer temperatures and deeper anvils, but simultaneously increasing the concentrations of CCN and GCCN leads to more supercooled liquid water available for freezing and greater ice mixing ratios. Graupel mixing ratios decrease and hail mixing ratios increase with increasing aerosol concentrations. Higher concentrations of GCCN and IFN result in greater accumulated surface precipitation initially. By the end of the simulation period, however, the accumulated precipitation is the greatest for the case in which the aerosol concentrations are lowest. Such changes in the dynamical and microphysical characteristics of convective storms as a result of the variations in aerosol concentrations have potential climate consequences, both through cloud radiative effects and the hydrological cycle. The impacts of varying CCN, GCCN, and IFN concentrations on the anvils will be discussed more fully in Part II.

## 2006 Andersson

14 February , Al-Halabi, Kroes, van Dishoeck

### Molecular-dynamics study of photodissociation of water in crystalline and amorphous ices

We present the results of classical dynamics calculations performed to study the photodissociation of water in crystalline and amorphous ice surfaces at a surface temperature of 10 K. A modified form of a recently developed potential model for the photodissociation of a water molecule in ice [S. Andersson , Chem. Phys. Lett. 408, 415 (2005)] is used. Dissociation in the top six monolayers is considered. Desorption of H2O has a low probability (less than 0.5% yield per absorbed photon) for both types of ice. The final outcome strongly depends on the original position of the photodissociated molecule. For molecules in the first bilayer of crystalline ice and the corresponding layers in amorphous ice, desorption of H atoms dominates. In the second bilayer H atom desorption, trapping of the H and OH fragments in the ice, and recombination of H and OH are of roughly equal importance. Deeper into the ice H atom desorption becomes less important and trapping and recombination dominate. Motion of the photofragments is somewhat more restricted in amorphous ice. The distribution of distances traveled by H atoms in the ice peaks at 6-7 A with a tail going to about 60 A for both types of ice. The mobility of OH radicals is low within the ice with most probable distances traveled of 2 and 1 A for crystalline and amorphous ices, respectively. OH is, however, quite mobile on top of the surface, where it has been found to travel more than 80 A. Simulated absorption spectra of crystalline ice, amorphous ice, and liquid water are found to be in very good agreement with the experiments. The outcomes of photodissociation in crystalline and amorphous ices are overall similar, but with some intriguing differences in detail. The probability of H atoms desorbing is 40% higher from amorphous than from crystalline ice and the kinetic-energy distribution of the H atoms is on average 30% hotter for amorphous ice. In contrast, the probability of desorption of OH radicals from crystalline ice is much higher than that from amorphous ice.

## 2005 Carignano

December , Shepson, Szleifer

### Molecular dynamics simulations of ice growth from supercooled water

The kinetics of ice growth on the secondary prismatic plane {1 $(2) over bar $ 10} and the basal plane {0001} is studied by Molecular Dynamics simulations. The simulation system initially consists of a slab of ice in contact with a layer of water on one side, and vacuum on the other side. The remaining surface of the water layer is also facing vacuum. The time evolution of the system shows the crystallization of the liquid water and the evaporation of very few molecules at the free surfaces. The ice vapour interfaces are wet on both sides by identical thin layers of liquid water, strongly suggesting that the system has reached its equilibrium state. To analyse the results, we have developed a new method to discriminate whether a molecule belongs to the ice lattice or is in liquid state. Using this method to monitor the number of ice molecules as a function of time, we find that the freezing is much faster on the prismatic plane than on the basal plane. For the prismatic plane, irregularities in the surface of the solid phase are observed during the growing period contrasting with a smooth interface on the basal plane at all times. We studied three different temperatures and found that the rate of crystallization decreases with temperature for the prismatic plane, while no conclusive behaviour was found for the basal plane growth.

## 2005 Nada

15 September , Furukawa

### Anisotropy in growth kinetics at interfaces between proton-disordered hexagonal ice and water: A molecular dynamics study using the six-site model of H2O

Molecular dynamics simulations of interfaces between proton-disordered hexagonal ice and water are carried out at a temperature near the melting point and a pressure of 1 atm using the six-site model of H2O, which was recently proposed for simulation studies of ice and water near the melting point. The simulations are performed for the interfaces of basal, prismatic and {1 1 2 0} planes of ice. The growth process of ice is clearly observed on all planes. It is observed, during growth on the {1 1 2 0} plane, the {1 1 2 0} plane disappears and prismatic planes appear instead. The result suggests that the growth velocity at the interface is larger for the {1 1 2 0} plane than for the prismatic plane. The structure of each interface and growth kinetics at each interface are analyzed on a molecular scale. Simulations show the interfaces of the prismatic and the {1 1 2 0} planes have a geometrically rough structure, whereas the interface of the basal plane has a molecularly flat structure. The simulations also show, that on all planes, growth occurs by reorganization of the hydrogen-bonded network in water near the interface. The reorganization occurs three-dimensionally on the prismatic and the {1 1 2 0} planes, whereas two-dimensionally on the basal plane. The anisotropy in the growth velocity, which is obtained in the present study, is qualitatively consistent with previous experiments. It is shown that the present results on the anisotropy in the interface structure and growth kinetics qualitatively explain the macroscopic shape of ice growing from water in a real system.

## 2005 Donadio

31 March , Raiteri, Parrinello

### Topological defects and bulk melting of hexagonal ice

We use classical molecular dynamics combined with the recently developed metadynamics method [Laio, A.; Parrinello, M. Proc. Natl. Acad. Sci. U.S.A. 2002, 99, 20] to study the process of bulk melting in hexagonal ice. Our simulations show that bulk melting is mediated by the formation of topological defects which preserve the coordination of the tetrahedral network. Such defects cluster to form a defective region involving about 50 molecules with a surprisingly long lifetime. The subsequent formation of coordination defects triggers the transition to the liquid state.

## 2004 Nordlund

1 September , Ogasawara, Wernet, Nyberg, Odelius, Pettersson, Nilsson

### Surface structure of thin ice films

An angular dependent X-ray absorption spectroscopy study of the surface of thin ice films grown on Pt(1 1 1) is presented. Using different probing depths together with spectral calculations based on density functional theory, the spectra are interpreted in terms of the structure of surface, subsurface and bulk regions. It is shown that the crystalline ice is terminated with a large abundance of isotropically distributed free O-H groups and a distorted subsurface.

## 2004 Hong

January , Dudhia, Chen

### A revised approach to ice microphysical processes for the bulk parameterization of clouds and precipitation

A revised approach to cloud microphysical processes in a commonly used bulk microphysics parameterization and the importance of correctly representing properties of cloud ice are discussed. Several modifications are introduced to more realistically simulate some of the ice microphysical processes. In addition to the assumption that ice nuclei number concentration is a function of temperature, a new and separate assumption is developed in which ice crystal number concentration is a function of ice amount. Related changes in ice microphysics are introduced, and the impact of sedimentation of ice crystals is also investigated. In an idealized thunderstorm simulation, the distribution of simulated clouds and precipitation is sensitive to the assumptions in microphysical processes, whereas the impact of the sedimentation of cloud ice is small. Overall, the modifications introduced to microphysical processes play a role in significantly reducing cloud ice and increasing snow at colder temperatures and slightly increasing cloud ice and decreasing snow at warmer temperatures. A mesoscale simulation experiment for a heavy rainfall case indicates that impact due to the inclusion of sedimentation of cloud ice is not negligible but is still smaller than that due to the microphysics changes. Together with the sedimentation of ice, the new microphysics reveals a significant improvement in high-cloud amount, surface precipitation, and large-scale mean temperature through a better representation of the ice cloud-radiation feedback.

## 2003 Raymond

16 January , Tarbuck, Brown, Richmond

### Hydrogen-bonding interactions at the vapor/water interface investigated by vibrational sum-frequency spectroscopy of HOD/H2O/D2O mixtures and molecular dynamics simulations

Vibrational sum-frequency spectroscopy (VSFS) studies of a series of HOD/H2O/D2O mixtures ranging from pure D2O to pure H2O have been performed at the vapor/water interface. The various concentrations allow an iterative fitting procedure to be applied, resulting in a set of resonant peaks which consistently describe the vibrational modes of water molecules present in the interfacial region. The resonant sum-frequency response from the contributing vibrational modes allows more definitive characterization than in previous studies of the bonding interactions between surface water molecules. Comparison of the resonant spectrum of the vapor/H2O interface with the sum-frequency spectrum obtained at the CCl2/H2O interface reveals more similarity between the interfacial hydrogen-bonding environments than previously determined. Recent molecular dynamics simulations of VSF spectra of the vapor/H2O interface are in good agreement with the experimentally obtained spectra, and give insight into the molecular interactions in the interfacial region, as well as an estimate of the interfacial depth probed.

## 2002 Myers

August , Charpin, Chapman

### The flow and solidification of a thin fluid film on an arbitrary three-dimensional surface

A model for the flow of a thin film, with and without solidification, on an arbitrary three-dimensional substrate is presented. The problem is reduced to two simultaneous partial differential equations for the film and solid layer thicknesses. The flow model (with the solidification rate set to zero) is the first such model to describe thin film flow on an arbitrary three-dimensional surface. Various limits are investigated to recover previous models for flow on flat, cylindrical and two-dimensional curved surfaces. With solidification a previous model for accretion on a flat substrate is retrieved. It is shown how the model may be reduced to standard forms, such as solidification on a flat surface, circular and non-circular cylinders, aerofoils and spheres. Numerical solutions are obtained by combining an ADI scheme with a shock capturing method. Results are presented for flow and accretion on a flat surface, aerofoil and sphere.

## 2002 Gay

22 May , Smith, Haymet

### Dynamics of melting and stability of ice 1h: Molecular-dynamics simulations of the SPC/E model of water

Ice 1h is studied by molecular-dynamics simulations using the SPC/E model of water. The simulations were carried out in the constant stress, constant temperature ensemble, over a range of temperature and external pressure. By heating the system at 10 K intervals every 100 ps, we establish an upper bound for the stability of the ice 1h structure at 1 atmosphere to be below 260 K for the SPC/E model. The shape of the crystal lattice does not change significantly from the ideal hexagonal structure of ice 1h, even close to the melting transition. This is significant for future investigations of the ice-water interface using molecular simulations.

## 2002 Matsumoto

28 March , Saito, Ohmine

### Molecular dynamics simulation of the ice nucleation and growth process leading to water freezing

Upon cooling, water freezes to ice. This familiar phase transition occurs widely in nature, yet unlike the freezing of simple liquids(1-3), it has never been successfully simulated on a computer. The difficulty lies with the fact that hydrogen bonding between individual water molecules yields a disordered three-dimensional hydrogen-bond network whose rugged and complex global potential energy surface(4-6) permits a large number of possible network configurations. As a result, it is very challenging to reproduce the freezing of 'real' water into a solid with a unique crystalline structure. For systems with a limited number of possible disordered hydrogen-bond network structures, such as confined water, it is relatively easy to locate a pathway from a liquid state to a crystalline structure(7-9). For pure and spatially unconfined water, however, molecular dynamics simulations of freezing are severely hampered by the large number of possible network configurations that exist. Here we present a molecular dynamics trajectory that captures the molecular processes involved in the freezing of pure water. We find that ice nucleation occurs once a sufficient number of relatively long-lived hydrogen bonds develop spontaneously at the same location to forma fairly compact initial nucleus. The initial nucleus then slowly changes shape and size until it reaches a stage that allows rapid expansion, resulting in crystallization of the entire system.

## 2001 Cheng

8 October , Fenter, Nagy, Schlegel, Sturchio

### Molecular-scale density oscillations in water adjacent to a mica surface

High-resolution specular x-ray reflectivity of the mica(001)-water interface under ambient conditions reveals oscillations in water oxygen density in the surface-normal direction, giving evidence of interfacial water ordering. The spacings between neighboring water layers in the near-surface, strongly oscillatory region are 2.5(2)-2.7(2) Angstrom, approximately the size of the water molecule. The density oscillations extend to about 10 Angstrom above the surface and do not strictly maintain a solvent-size periodicity as that in interfacial liquid metal and hard-sphere molecular liquids. We interpret this oscillatory density profile of the interfacial water as due to the "hard-wall" effect of the molecularly smooth mica surface.

## 2001 Huthwelker

1 June , Lamb, Baker, Swanson, Peter

### Uptake of SO2 by polycrystalline water ice

We have investigated two previous experimental studies (Clapsaddle and Lamb, 1989; Conklin et al. 1989) of SO2 uptake into polycrystalline ice the results of which seem to conflict. Both studies employed porous packed beds prepared by freezing 200-mum-diameter water drops in liquid nitrogen followed by aging. In the absence of oxidation, uptake was measured via frontal chromatography at various temperatures between -60 and -1 degreesC, with SO2 mixing ratios between 15 and 100 ppb. The experiments differed primarily in the ice surface areas and exposure times, yielding purportedly equilibrium surface coverages that differed by more than a factor of 50. The uptake increased with temperature and with a less than linear dependence on partial pressure. Our comparison shows that a kinetic model is needed for interpretation partly explaining the apparent discrepancy between the two investigated uptake experiments. The uptake rates, its amount, and its temperature dependence suggest that SO2 dissociates and diffuses into an internal reservoir for example comprised of veins and nodes, but not into a surface layer as previously hypothesized. Whereas slow diffusion may remain undetected during the relatively short time scales of laboratory experiments, it may dominate trace gas uptake by natural ice. We suggest that dry deposition schemes of SO2 onto snowpacks in climate models should include the kinetics of uptake and account for the temperature and pressure dependencies found in the laboratory studies reviewed here,

## 2001 Kohl

, Mayer, Hallbrucker

### Ice XII forms on compression of hexagonal ice at 77 K via high-density amorphous water

Samples of high-density amorphous water (HDA) were prepared by compression of hexagonal ice (ice Ih) in a piston-cylinder apparatus at 77 K up to 1.8 GPa, recovered at ambient pressure under liquid N(2) and characterized by X-ray diffraction and differential scanning calorimetry. Thereafter HDA samples were reloaded into the piston-cylinder apparatus, compressed at 77 K up to 1.8 GPa, recovered under liquid N(2) and characterized. Formation of ice XII on compression of HDA was observed only when a sudden pronounced pressure drop occurred at pressures greater than or similar to1.1 GPa. Pressure drops below this threshold value, or occurring during the initial compression of ice Ih, did not induce formation of ice XII. Pressure-displacement curves obtained on compression of ice Ih are consistent with formation of ice XII from HDA, and not from ice Ih. We propose that shock waves generated by the pressure drops cause transient local heating up to the temperature range of the ice V domain, and that this induces nucleation and crystal growth of ice XII. The threshold value of approximate to 1.1 GPa pressure necessary for the HDA --> ice XII transition indicates that the density of HDA has to reach a certain minimal value before conversion into ice XII becomes possible. Ice XII could thus be formed via HDA by meteorite impact on the surfaces of icy satellites of the outer planets whenever the temperatures are low.

## 1997 Morgenstern

, Muller, Michely, Comsa

### The ice bilayer on Pt(111): Nucleation, structure and melting

The H2O-adsorption on Pt(111) at 120 K-240 K is investigated by temperature-variable scanning tunneling microscopy. At 140 K the adsorption kinetics of the first bilayer is determined by heterogeneous nucleation at the upper side and the lower side of step edges as well as by homogeneous island nucleation on the terraces. Depending on the preparation conditions the bilayer exhibits three different phases. Phase I can be characterized as an ideal ice bilayer rotated +/-7 degrees with respect to the [112]-direction of the Pt(111)-surface. As a result the STM-images show a Moiree pattern. The second phase, phase IIb, is less dense than phase I and appears to be a regular arrangement of regions of H2O-molecules with the root 3 X root 3 R30 degrees-distance of the Pt(111)-substrate and regions with higher density in between. This leads to two superstructure domains differing in orientation and periodicity from the domains of phase I. Contrary to phase I, the super structure of phase IIb is not a Moiree pattern. The third phase, phase IIa, shows a super structure with the same periodicity as phase IIb, but with a different orientation. It has probably a similar atomic arrangement as phase IIb and is also not a Moiree pattern.

The three solid phases can be transformed into each other either by changing the temperature and/or by applying a H2O-pressure at elevated temperatures. It turns out that solid-solid-phase transformations are only possible. if the ice layer is partially molten. From the pressure dependence of the phase transitions an order of density of the different solid phases can be deduced. It is in agreement with the densities concluded from the structural analysis. All phase transformations can be described consistently, if one assumes that the liquid like phase is denser than the three solid phases. This is analogous to the density anomaly of water in three dimensions. Below 135 K, second layer nucleation takes place. It starts exclusively at special sites of the underlying superstructure. This heterogeneous nucleation leads to a regular array of small clusters. The density of clusters in the second layer is nearly three orders of magnitude higher than the island density in the first bilayer. An analysis of the contrast mechanism for STM-imaging of H2O on Pt(111) leads to the interesting conclusion that the H2O-layer next to the Pt(111)-surface has a metallic conductivity. This is in contrast to 3D-water and may have implications for the description of electron transfer processes in electrochemical experiments.

## 1996 Karcher

1 November , Peter, Biermann, Schumann

### The initial composition of jet condensation trails

Physicochemical processes that generate and transform aerosols in jet aircraft plumes are discussed on the basis of theoretical models and recent observations of young contrails in the upper troposphere. The initial evolution of optical depth and ice water content under threshold contrail formation conditions is studied. Constrained by the measurements, a lower bound is deduced for the number density of ice crystals initially present in contrails. This bound serves as a visibility criterion for young contrails. An analysis of the primary contrail particles (aqueous solution droplets nucleated in situ, emitted insoluble combustion aerosols, and entrained background aerosols) reveals that only soot must be involved as ice forming nuclei if the visibility criterion is to be fulfilled. Possible activation pathways of the soot aerosols are investigated, including an analysis of their wetting behavior and droplet scavenging and heterogeneous nucleation properties. To support these investigations, results of laboratory experiments concerning contact angles of acidic solution droplets on carbonaceous surfaces and the freezing probability of sulfuric acid tetrahydrate are presented. Assuming that the soot particles acquire a liquid coating, heterogeneous freezing rates and their sensitivity on important parameters are studied.

## 1996 Fowler

March , Randall, Rutledge

### Liquid and ice cloud microphysics in the CSU general circulation model .1. Model description and simulated microphysical processes

Microphysical processes responsible for the formation and dissipation of water and ice clouds have been incorporated into the Colorado State University General Circulation Model in order to 1) yield a more physically based representation of the components of the atmospheric moisture budget, 2) link the distribution and optical properties of the model-generated clouds to the predicted cloud water and ice amounts, and 3) produce more realistic simulations of cloudiness and the earth's radiation budget.

The bulk cloud microphysics scheme encompasses five prognostic variables for the mass of water vapor, cloud water, cloud ice, rain, and snow. Graupel and hail are neglected. Cloud water and cloud ice are predicted to form through large-scale condensation and deposition processes and also through detrainment at the tops of cumulus towers. The production of rain and snow occur through autoconversion of cloud water and cloud ice. Rain drops falling through clouds can grow by collecting cloud water, and falling snow can collect both cloud water and cloud ice. These collection processes are formulated using the continuous collection equation. Evaporation of cloud water, cloud ice, rain, and snow are allowed in subsaturated layers. Melting and freezing are included. We also provide a coupling between convective clouds and stratiform anvils through the detrainment of cloud water and cloud ice at the tops of cumulus towers. Interactive cloud optical properties provide the link between the cloud microphysics and radiation parameterizations, the optical depths and infrared emissivities of large-scale stratiform clouds are parameterized in terms of the cloud water and cloud ice paths.

Two annual-cycle numerical simulations are performed to assess the impact of cloud microphysics on the hydrological cycle. In the ''EAULIQ'' run, large-scale moist processes and cloud optical properties are driven by the bulk cloud microphysics parameterization. In the ''CONTROL'' run, condensed water is immediately removed from the atmosphere in the form of rain, which may evaporate as it falls through subsaturated layers. Stratiform ice clouds are not considered in CONTROL. When clouds are present, cloud optical depths and cloud infrared emissivities are dependent on the mean cloud temperatures.

Results are presented in terms of January and July monthly averages. Emphasis is placed on the spatial distributions of cloud water, cloud ice, rain, and snow produced by the cloud microphysics scheme. In EAULIQ, cloud water and cloud ice are more abundant in the middle latitudes than in the Tropics, suggesting that large-scale condensation contributes a major part to the production of condensed water. Comparisons between the simulated vertically integrated cloud water and the columnar cloud water retrievals from satellite microwave measurements over the global oceans indicate a reasonable agreement. Interactions between the cloud microphysics and cumulus convection parameterizations lead to smaller, more realistic precipitation rates. In particular, the cumulus precipitation rate is strongly reduced when compared to CONTROL.

## 1995 DEVLIN

9 November , BUCH

### SURFACE OF ICE AS VIEWED FROM COMBINED SPECTROSCOPIC AND COMPUTER MODELING STUDIES

The structure of the ice surface and its interaction with adsorbates are investigated by several experimental tools, combined with computer modeling. Spectroscopic features characteristic of icy surfaces were identified and assigned. Adsorbate spectroscopy is used to probe both the adsorbate layer and the ice surface structure. These results are potentially informative of basic questions, such as cooperative aspects of H-bonding and the mechanism of ice vaporization, and of diverse practical questions, such as the role of icy particles in atmospheric chemistry and physics as well as the chemistry of interstellar space. Methods are described for the preparation and spectroscopic study of microporous amorphous ice and cubic ice nanocrystals with surface to volume ratios that make it possible to obtain low-noise infrared and Raman spectra of the vibrational modes localized near the surfaces and of the fundamental modes of small molecule adsorbates. The assignment of the bands of several of the surface-localized modes is reported, on the basis of primarily the calculated vibrational excitations for simulated structures of both amorphous and crystalline ice. The usefulness of these spectra is enhanced by conversion to difference spectra that compare high surface area and low surface area samples. Bands have been assigned to each of the three important types of surface water molecules, as revealed by the simulated structures and spectra: molecules with non-H-bonded or dangling-H(D) atoms, molecules with a dangling-O coordination, and 4-coordinated surface water molecules. The experimental difference spectra have also been used to display the influence of small adsorbate molecules on surface-localized vibrations of each type of water molecule. This influence is apparent through the shifting and enhancement of bands of surface-localized modes, the response of the modes of the adsorbate molecules, and the determination of site-selective hears of adsorption of small molecules using the assigned ice modes. Computer modeling in conjunction with ab initio calculations was used to analyze and interpret adsorbate spectra and to elucidate the influence of factors such as the extent of surface disorder on gas-surface interactions. The results suggest significant modification of the ice surface structure with respect to the cubic crystalline interior, toward loss of lateral order.

## 1995 GRANASY

21 September

### DIFFUSE INTERFACE ANALYSIS OF ICE NUCLEATION IN UNDERCOOLED WATER

Experiments on ice nucleation in undercooled water are analyzed in terms of the classical and the diffuse interface theory (CNT and DIT, respectively) of crystal nucleation. It is shown that neither a constant interfacial energy in the CNT nor a constant interface thickness in the DIT can satisfactorily describe the experiments. It has been found that the temperature-dependent interfacial parameters, evaluated by Ewing's model (Ewing, R. H. Philos. Mag. 1972, 25, 779) from the structural information available on undercooled water, yield an improved description both within the framework of the CNT and the DIT. In contrast with the CNT, the DIT is fully consistent with the experiments. Both analyses (CNT and DIT) indicate a bulk (volumetric) heterogeneous nucleation mechanism.

## 1995 ROWLAND

1 June , KADAGATHUR, DEVLIN, BUCH, FELDMAN, WOJCIK

### INFRARED-SPECTRA OF ICE SURFACES AND ASSIGNMENT OF SURFACE-LOCALIZED MODES FROM SIMULATED SPECTRA OF CUBIC ICE

## 1995 DIEHL

May , MITRA, PRUPPACHER

### A LABORATORY STUDY OF THE UPTAKE OF HNO3 AND HCL VAPOR BY SNOW CRYSTALS AND ICE SPHERES AT TEMPERATURES BETWEEN 0-DEGREES-C AND -40-DEGREES-C

A laboratory experiment is described during which the uptake of HNO3 and HCl vapor by dendritic snow crystals and by single crystalline and polycrystalline small ice spheres was studied at ppbv and ppmv gas levels and at temperatures between 0 and -40 degrees C. In one experimental investigation the vapor was allowed to be adsorbed onto the surface of the ice particles. During another experimental investigation the ice particles were allowed to grow from water vapor on fine fibers in the presence of the HNO3 and HCl vapor. The results of our experiments show that under both conditions significant amounts of HNO3 and HCl became scavenged by the ice particles. Scavenging by adsorption was maximum for both vapors at temperatures near 0 degrees C where a quasi-liquid layer exists on the surface of ice. With decreasing temperature the uptake of HNO3 and HCl vapor decreased and kept on decreasing for HCl with further decrease in temperature. In contrast, the uptake of HNO3 reached a minimum near -18 degrees C to increase again strongly with further decrease in temperature. The temperature-dependent uptake of both vapors were explained on the basis of surface melting caused by the vapors. For the case that the ice crystals were growing in an atmosphere supersaturated with respect to ice while simultaneously being exposed to HNO3 or HCl vapor we noted that gas scavenging was less than during simple adsorption by a nongrowing crystal. Our experiments further showed that HNO3 once taken up by an ice particle would not desorb if the ice particle remained at ice saturation. Our experiments also indicated that some of the adsorbed HNO3 and HCl diffuses into the ice particle.

## 1994 SVISHCHEV

15 August , KUSALIK

### CRYSTALLIZATION OF LIQUID WATER IN A MOLECULAR-DYNAMICS SIMULATION

In this Letter we report our success in crystallizing a bulk sample of liquid water in molecular dynamics simulations. In these computer experiments supercooled liquid TIP4P water at 250 K was subjected to a homogeneous static electric field; the resulting polar crystal which forms within 200 ps has the structure of ice I(c). These simulation results suggest that the local electric fields that exist near the surfaces of various materials or within confined geometries can play an important role in promoting the crystallization of liquid water.

## 1992 ABBATT

20 October , BEYER, FUCALORO, MCMAHON, WOOLDRIDGE, ZHANG, MOLINA

### INTERACTION OF HCL VAPOR WITH WATER-ICE - IMPLICATIONS FOR THE STRATOSPHERE

The nature of the interaction of HCl vapor with ice has been investigated, using thermal analysis and FTIR spectroscopy to characterize the ice substrate, and mass spectrometry to measure the concentration of HCl and H2O vapors in the gas phase. The results indicate that a liquid layer is formed rapidly at the ice surface for ice exposed to HCl vapor at partial pressures above those characteristic of the ice - liquid (aqueous HCl solution) equilibrium system. This liquid layer also forms below the eutectic temperature (186 K); that is, it forms even at temperatures at which the liquid is metastable with respect to the formation of HCl trihydrate. For smaller HCl partial pressures such as those prevailing in the stratosphere, the HCl is taken up by the ice surface in amounts corresponding to a large fraction of a monolayer. The chemical reactivity of this surface HCl is very large: Chlorine activation by type II polar stratospheric clouds (consisting of ice particles) should occur efficiently by reaction of the HCl with ClONO2.

## 1992 FECHT

12 March

### DEFECT-INDUCED MELTING AND SOLID-STATE AMORPHIZATION

DESPITE the strong interest in melting over the past 100 years, a general theory for the crystal-liquid transition has not been established 1. Lattice-instability models, which are either vibrational 2, elastic 3, isochoric 4, defective 5 or entropic 6 in nature, all predict a melting point somewhat above the experimentally observed thermodynamic melting temperature, with the ultimate stability limit of a superheated crystal being determined by the equality of crystal and liquid entropies 4,6; this forces regular melting to be a first-order transition. Here I present a model of melting that is driven by the incorporation into the lattice of randomly frozen-in defects. An isentropic condition limits the stability of the crystal as a function of defect concentration; above the glass transition temperature the crystal melts to a liquid, whereas below it 'melting' produces an amorphous solid. This model yields a generic melting diagram with a tunable parameter (defect concentration) that can characterize the static disorder present in solid-state amorphization 7-9, the thermodynamic stability of small clusters 10 and nanocrystalline materials 11, and the frustration present in spin glasses 12 . The model is also relevant to glacial 13, geological 14 and stellar-atmospheric 15 melting processes.

## 1991 SAUNDERS

20 June , KEITH, MITZEVA

### THE EFFECT OF LIQUID WATER ON THUNDERSTORM CHARGING

Laboratory studies have shown that thunderstorm charging caused by the interactions of ice crystals and graupel pellets is affected in sign and magnitude by temperature and cloud liquid water content; the presence of water droplets is a requirement for substantial charge transfer. Relationships showing the dependence of charge transfer on ice crystal size and velocity have previously been reported and now, in a continuation of the laboratory studies, the effect of liquid water content on the charge transfer has been investigated. The experiments show that positive graupel charging occurs at temperatures above a 'charge sign reversal temperature" with negative charging at lower temperatures. The reversal temperature moves to lower temperatures when the liquid water content is increased. However, at low values of liquid water content, the sign of the graupel charging is inverted being positive at low temperatures and negative at higher temperatures. A discussion is presented of the various charge transfer theories. The results are consistent with the idea of two competing mechanisms whose relative success depends on the temperature and liquid water content. Positive graupel charging occurs when the graupel surface grows from the vapor and the crystals interact with a negative surface charge caused by a temperature gradient across the rime ice surface layer. Negative graupel charging occurs when the surface growth effect is swamped by freezing droplets which create either a pseudo contact potential with which the crystals interact, or a positive surface charge, due to dislocations in the rime ice, which is removed during glancing crystal interactions. Relationships between charge transfer, liquid water content, temperature, ice crystal size, and velocity have been determined and the equations may be used in numerical models of the development of thunderstorm electric fields. A one-dimensional model indicates that the charge separation rates noted here are adequate to account for thunderstorm electrification. Use of the equations with cloud parameter values obtained in a thunderstorm research flight, leads to a predicted charge reversal level around -13-degrees-C, which is in agreement with the analysis of the electric field in the thunderstorm studied.

## End

# No

## 2016 Zimmermann

28 May , Kippenberger, Schuster, Crowley

### Adsorption isotherms for hydrogen chloride (HCl) on ice surfaces between 190 and 220 K

The interaction of hydrogen chloride (HCl) with ice surfaces at temperatures between 190 and 220 K was investigated using a coated-wall flow-tube connected to a chemical ionization mass spectrometer. Equilibrium surface coverages of HCl were determined at gas phase concentrations as low as 2 x 10(9) molecules cm(-3) (similar to 4 x 10(-8) Torr at 200 K) to derive Langmuir adsorption isotherms. The data are described by a temperature independent partition coefficient: K-Lang = (3.7 + 0.2) x 10(-11) cm(3) molecule(-1) with a saturation surface coverage N-max = (2.0 +/- 0.2) x 10(14) molecules cm(-2). The lack of a systematic dependence of K-Lang on temperature contrasts the behaviour of numerous trace gases which adsorb onto ice via hydrogen bonding and is most likely related to the ionization of HCl at the surface. The results are compared to previous laboratory studies, and the equilibrium partitioning of HCl to ice surfaces under conditions relevant to the atmosphere is evaluated.

## 2016 Fernandes

30 January , Campos, Cividanes, Simonetti, Thim

### **A**dsorbed water on iron surface by molecular dynamics

The adsorption of H2O molecules on metal surfaces is important to understand the early process of water corrosion. This process can be described by computational simulation using molecular dynamics and Monte Carlo. However, this simulation demands an efficient description of the surface interactions between the water molecule and the metallic surface. In this study, an effective force field to describe the iron-water surface interactions was developed and it was used in a molecular dynamics simulation. The results showed a very good agreement between the simulated vibrational-DOS spectrum and the experimental vibrational spectrum of the iron-water interface. The water density profile revealed the presence of a water double layer in the metal interface. Furthermore, the horizontal mapping combined with the angular distribution of the molecular plane allowed the analysis of the water structure above the surface, which in turn agrees with the model of the double layer on metal surfaces.

## 2016 Schaaf

, Kauffeld

### INDUCTION MELTING BOUNDARY LAYER OF ICE

In many technical applications, ice grows on metallic surfaces. In most applications this effect is unwanted like the icing on heat exchangers, on power lines or the ice building on the wings of airplanes. The ice influences the properties and the lifetime of some components. In other cases metallic surfaces are designed such that ice grows on them, e.g. in many types of ice slurry generators, ice grows on the surface of a heat exchanger.

Whether the icing is a disadvantage or advantage, in a lot of cases deicing is necessary. Deicing purposes the knowledge of the adhesion force between ice and the surface. Typically, the ice is removed from the surface by some means of mechanical or thermal impact. With a scraper or some other tool the ice can be removed mechanically. The scraping force has to be higher than the adhesion force between the ice and the surface. In order to thermally remove the ice, the temperature of the metallic surface has to rise over the melting point of ice.

In this research there is a combination of the mechanical and the thermal method. The thermal energy to heat up the surface is generated with an induction heater. The total heat energy of induction heating depends on the frequency and the amperage for the induction coil. With a high frequency only a thin skin layer of the metallic surface heats up. The surface temperature rises over the melting point of the ice and the ice at the boundary layer melts off. The adhesion force between ice and the metal decreases until there is a complete liquid layer.

The correlation between adhesion force and an induction heating impulse will be shown.

## 2010 Johnston

21 October , Kastelowitz, Molinero

### Liquid to quasicrystal transition in bilayer water

The phase behavior of con. fined water is a topic of intense and current interest due to its relevance in biology, geology, and materials science. Nevertheless, little is known about the phases that water forms even when confined in the simplest geometries, such as water confined between parallel surfaces. Here we use molecular dynamics simulations to compute the phase diagram of two layers of water confined between parallel non hydrogen bonding walls. This study shows that the water bilayer forms a dodecagonal quasicrystal, as well as two previously unreported bilayer crystals, one tiled exclusively by pentagonal rings. Quasicrystals, structures with long-range order but without periodicity, have never before been reported for water. The dodecagonal quasicrystal is obtained from the bilayer liquid through a reversible first-order phase transition and has diffusivity intermediate between that of the bilayer liquid and ice phases. The water quasicrystal and the ice polymorphs based on pentagons are stabilized by compression of the bilayer and are not templated by the confining surfaces, which are smooth. This demonstrates that these novel phases are intrinsically favored in bilayer water and suggests that these structures could be relevant not only for confined water but also for the wetting and properties of water at interfaces.

## 2011 Ho

27 September , Papavassiliou, Lee, Striolo

### Liquid water can slip on a hydrophilic surface

Understanding and predicting the behavior of water, especially in contact with various surfaces, is a scientific challenge. Molecular-level understanding of hydrophobic effects and their macroscopic consequences, in particular, is critical to many applications. Macroscopically, a surface is classified as hydrophilic or hydrophobic depending on the contact angle formed by a water droplet. Because hydrophobic surfaces tend to cause water slip whereas hydrophilic ones do not, the former surfaces can yield self-cleaning garments and ice-repellent materials whereas the latter cannot. The results presented herein suggest that this dichotomy might be purely coincidental. Our simulation results demonstrate that hydrophilic surfaces can show features typically associated with hydrophobicity, namely liquid water slip. Further analysis provides details on the molecular mechanism responsible for this surprising result.

## 2010 Meuler

November , Smith, Varanasi, Mabry, McKinley, Cohen

### Relationships between Water Wettability and Ice Adhesion

Ice formation and accretion may hinder the operation of many systems critical to national infrastructure, including airplanes, power lines, windmills, ships, and telecommunications equipment. Yet despite the pervasiveness of the icing problem, the fundamentals of ice adhesion have received relatively little attention in the scientific literature and it is not widely understood which attributes must be tuned to systematically design "icephobic" surfaces that are resistant to icing. Here we probe the relationships between advancing/receding water contact angles and the strength of ice adhesion to bare steel and twenty-one different test coatings (similar to 200-300 nm thick) applied to the nominally smooth steel discs. Contact angles are measured using a commercially available goniometer, whereas the average strengths of ice adhesion are evaluated with a custom-built laboratory-scale adhesion apparatus. The coatings investigated comprise commercially available polymers and fluorinated polyhedral oligomeric silsesquioxane (fluorodecyl POSS), a low-surface-energy additive known to enhance liquid repellency. Ice adhesion strength correlates strongly with the practical work of adhesion required to remove a liquid water drop from each test surface (i.e., with the quantity [1 + cos theta(rec)]), and the average strength of ice adhesion was reduced by as much as a factor of 4.2 when bare steel discs were coated with fluorodecyl POSS-containing materials. We argue that any further appreciable reduction in ice adhesion strength will require textured surfaces, as no known materials exhibit receding water contact angles on smooth/flat surfaces that are significantly above those reported here (i.e., the values of [1 + cos theta(rec)] reported here have essentially reached a minimum for known materials).

## 2009 Giovambattista

22 Ocotber , Rossky, Debenedetti

### Effect of Temperature on the Structure and Phase Behavior of Water Confined by Hydrophobic, Hydrophilic, and Heterogeneous Surfaces

We perform molecular dynamics simulations of water confined between atomically detailed hydrophobic, hydrophilic and heterogeneous (patchy) nanoscale plates. We study the effects of temperature 220 <= T <= 300 K on confined water's behavior at various pressures -0.2 <= P <= 0.2 GPa and plate separations 0.5 <= d <= 1.6 nm. Combining this with our earlier results on the same system [Giovambattista, N.; Rossky, P. J.; Debenedetti, P. G. Phys, Rev. E: Stat., Nordinear, Soft Matter Phys. 2006, 73, 041604; Giovambattista, N.; Rossky, P. J.; Debenedetti, P. G. J. Phys. Chem. C, 2007,11, 1323], where pressure was varied at constant temperature, allows us to compare water's behavior in nanoscale confinement, upon isobaric cooling and isothermal compression, corresponding to paths of interest in protein denaturation. At a fixed temperature, water confined between hydrophobic plates can form vapor, liquid, or crystal (bilayer ice) phases. depending on the values of P and d. The P-d phase diagrams at T = 300 K and T = 220 K show that cooling, suppresses the vapor phase and stabilizes the liquid and crystal phases. The critical separation d(e)(P), below which vapor forms, shifts to lower values of d and P upon cooling. The density profiles show that, upon cooling, water approaches the hydrophobic plates. Hence, the effective hydrophobicity of the plate decreases as T decreases, consistent with the suppression of the vapor phase upon cooling, However. both the orientation of water's molecules at the interface and the water contact angle on the hydrophobic Surface show practically no temperature dependence. Simulations of water confined by heterogeneous plates decorated with hydrophobic and hydrophilic patches reveal that cooling leads to appreciable blurring of the differences between water densities at hydrophobic and hydrophilic, surfaces. This observation, together with remarkable similarities in confined water's response to isobaric cooling and to isothermal compression, suggests that (fie invasion of hydrophobic cavities by water is all important mechanism underlying both pressure and cold denaturation of proteins,

## 2009 Asay

12 February , Barnette, Kim

### Effects of Surface Chemistry on Structure and Thermodynamics of Water Layers at Solid-Vapor Interfaces

The effects of surface chemistry on the isotherm thickness and structure of the adsorbed water layer as well as the isosteric heat of adsorption and entropy of adsorption were studied using attenuated total reflection infrared spectroscopy. The degree of hydrophilicity seems to distinctively change the structure and thermodynamic properties of the water layers adsorbed on silicon oxide surfaces. On the highly hydrophilic silicon oxide surface covered with silanol groups, the water layer adsorbed at low humidities exhibits the OH stretching peak at 3230 cm(-1) (characteristic of a solid-like water structure), and the isosteric heat of adsorption is much higher than the latent heat of ice sublimation. As the concentration of surface silanol groups decreases, both the initial isosteric heat of adsorption of water and the amount of solid-like water decrease. The water layer adsorbed on the hydrophilic surface at low humidities seems to have much lower entropies than bulk water, while the entropy of the water layer on the partially methylated surface is not much lower than that of bulk water. At high humidities, the liquid water structure becomes dominant in the adsorbed layer. The possible origins of high isosteric heat of adsorption and low entropy are discussed.

## 2009 Vega

, Abascal, Conde, Aragones

### What ice can teach us about water interactions: a critical comparison of the performance of different water models

The performance of several popular water models (TIP3P, TIP4P, TIP5P and TIP4P/2005) is analyzed. For that purpose the predictions for ten different properties of water are investigated, namely: 1. vapour-liquid equilibria (VLE) and critical temperature; 2. surface tension; 3. densities of the different solid structures of water (ices); 4. phase diagram; 5. melting-point properties; 6. maximum in the density of water at room pressure and thermal coefficients alpha and kappa(T), structure of liquid water and ice; 8. equation of state at high pressures; 9. self-diffusion coefficient; 10. dielectric constant. For each property, the performance of each model is analyzed in detail with a critical discussion of the possible reason of each model is analyzed in detail with a critical discussion of the possible reason of the success or failure of the model. A final judgement on the quality of these models is provided. TIP4P/2005 provides the best description of almost all properties of the list, the only exception being the dielectric constant. In second position, TIP5P and TIP4P yield a similar performance overall, and the last place with the poorest description of the water properties is provided by TIP3P. The ideas leading to the proposal and design of the TIP4P/2005 are also discussed in detail. TIP4P/2005 is probably close to the best description of water that can be achieved with a non-polarizable model described by a single Lennard-Jones (LJ) site and three charges.

## 2008 Jinesh

18 July , Frenken

### Experimental evidence for ice formation at room temperature

The behavior of water under extreme confinement and, in particular, the lubrication properties under such conditions are subjects of long-standing controversy. Using a dedicated, high-resolution friction force microscope, scanning a sharp tungsten tip over a graphite surface, we demonstrate that water nucleating between the tip and the surface due to capillary condensation rapidly transforms into crystalline ice at room temperature. At ultralow scan speeds and modest relative humidities, we observe that the tip exhibits stick-slip motion with a period of 0.38 +/- 0.03 nm, very different from the graphite lattice. We interpret this as the consequence of the repeated sequence of shear-induced fracture and healing of the crystalline condensate. This phenomenon causes a significant increase of the friction force and introduces relaxation time scales of seconds for the rearrangements after shearing.

## 2007 Buch

28 November , Tarbuck, Richmond, Groenzin, Li, Shultz

### Sum frequency generation surface spectra of ice, water, and acid solution investigated by an exciton model

A new computational scheme is presented for calculation of sum frequency generation (SFG) spectra, based on the exciton model for OH bonds. The scheme is applied to unified analysis of the SFG spectra in the OH-stretch region of the surfaces of ice, liquid water, and acid solution. A significant role of intermolecularly coupled collective modes is pointed out. SFG intensity amplification observed for acid solutions in the H-bonded OH-stretch region is reproduced qualitatively and accounted for by enhanced orientational preference "into the surface" of the H(2)O bisectors within the hydronium solvation shell.

## 2007 Kahan

1 November , Reid, Donaldson

### Spectroscopic probes of the quasi-liquid layer on ice

Raman spectra of the water OH-stretch region were acquired at air-ice and air-water interfaces at a glancing angle, which allowed observation of surface characteristics. The shapes of the OH-stretch bands indicate that the environment at the air-ice interface is different from that at the air-water interface and from that seen in bulk water. Water spectra measured at the surface of dodecane under low relative humidity indicate that this method is sensitive to fewer than 50 monolayers of water. Changes in the local environment of the surfacial water molecules may be induced by the presence of different solute species, giving rise to changes in the shape of the band. Dissolved sodium chloride disrupts hydrogen bonding in liquid water and has the same effect at the air-ice interface. However, when either HCl or HNO3 is adsorbed from the gas phase onto an ice surface, the opposite effect is seen: Their presence appears to increase the extent of hydrogen bonding at the ice surface. At the same time, shifts in the laser-induced fluorescence spectra of acridine, a fluorescent pH-probe present at the air-ice interface, indicate that dissociation of acids occurs there. These observations suggest that the formation of hydronium ions at the air-ice interface enhances the hydrogen bonding of surfacial water molecules.

## 2007 Buch

1 May , Milet, Vacha, Jungwirth, Devlin

### Water surface is acidic

Water autolonization reaction (H2O)-H-2 -> H3O- + OH- is a textbook process of basic importance, resulting in pH = 7 for pure water. However, pH of pure water surface is shown to be significantly lower, the reduction being caused by proton stabilization at the surface. The evidence presented here includes ab initio and classical molecular dynamics simulations of water slabs with solvated H3O+ and OH- ions, density functional studies of (H2O)(48)H+ clusters, and spectroscopic isotopic-exchange data for D2O substitutional impurities at the surface and in the interior of ice nanocrystals. Because H3O+ does, but OH- does not, display preference for surface sites, the H2O surface is predicted to be acidic with pH < 4.8. For similar reasons, the strength of some weak acids, such as carbonic acid, is expected to increase at the surface. Enhanced surface acidity can have a significant impact on aqueous surface chemistry, e.g., in the atmosphere.

## 2007 Hirunsit

1 February , Balbuena

### Effects of confinement on water structure and dynamics: A molecular simulation study

Classical molecular dynamics simulations are performed to study structural and dynamic properties of water confined within graphite surfaces separated by a distance varying between 7 and 14.5 angstrom, at a constant water density of 1 g/cm(3). Results at 298 K show the formation of a well-ordered structure constituted by water layers parallel to the graphite surfaces. The water molecules in layers in contact with the surface have a tendency to orient their dipole parallel to the surface. Such ice-like structure may have, however, different structural and dynamical properties than those of ice. The time evolution of the calculated mean square displacement reveals that at the smallest separation (7 angstrom) the water mobility is significantly lower than that of low-temperature water (213 K) at the same density; the mobilities become similar at a separation of 8 angstrom although the structure of that confined water is very different from that in low-temperature water. The temperature at which the mobility of water confined between graphite walls separated at 7 angstrom would become similar to that in bulk low-temperature water was found to be 373 K. With respect to the dynamics of confined water, a significant blue shift is observed in the intermolecular vibrational modes associated with the 0(...) 0(...)0 bending and 0(...)0 stretching of molecules linked by hydrogen bonds.

## 2007 Vacha

, Buch, Milet, Devlin, Jungwirth

### Autoionization at the surface of neat water: is the top layer pH neutral, basic, or acidic?

Autoionization of water which gives rise to its pH is one of the key properties of aqueous systems. Surfaces of water and aqueous electrolyte solutions are traditionally viewed as devoid of inorganic ions; however, recent molecular simulations and spectroscopic experiments show the presence of certain ions including hydronium in the topmost layer. This raises the question of what is the pH ( de. ned using proton concentration in the topmost layer) of the surface of neat water. Microscopic simulations and measurements with atomistic resolution show that the water surface is acidic due to a strong propensity of hydronium ( but not of hydroxide) for the surface. In contrast, macroscopic experiments, such as zeta potential and titration measurements, indicate a negatively charged water surface interpreted in terms of preferential adsorption of OH (-). Here we review recent simulations and experiments characterizing autoionization at the surface of liquid water and ice crystals in an attempt to present and discuss in detail, if not fully resolve, this controversy.

## 2007 Richard

1 December , Mercury, Poulet, d'Hendecourt

### Diffuse reflectance infrared Fourier transform spectroscopy as a tool to characterise water in adsorption/confinement situations

We present experimental data acquired by diffuse reflectance infrared spectroscopy in the mid-IR (4000-400 cm(-1)), on micrometric-sized mineral grain powders. The spectral evolution of the OH-stretching band is followed when the adsorbed water film is thinned under dry conditions, from high to low hydration states. The IR bands are found to be characteristic of the degree of adsorption/confinement of the liquid water. The OH-stretching band is shifted toward shorter wavenumbers than in bulk water, showing that a significant portion of adsorbed water has a higher intermolecular bonding energy. Complementary treatment of the kinetics of water desorption, varying with the surface forces in the water film, confirms the relationships of these bands with the constrained water state. We distinguish different water types obeying liquid-liquid interactions (free and capillary water) or dominated by solid-water interactions (confined and adsorbed water). Part of this study is devoted to mesoporous silica MCM-41, of interest due to the restricted geometries of its mesopores (4.7 nm) favouring the confined water state. The methodology allows us to distinguish bulk and adsorbed/confined water, using spectral analysis Coupled with an understanding of the dynamic behaviour of the desorption process.

## 2006 Jinesh

28 April , Frenken

### Capillary condensation in atomic scale friction: How water acts like a glue

We present atomic-scale friction force measurements that strongly suggest that the capillary condensation of water between a tungsten tip and a graphite surface leads to the formation of ice at room temperature. This phenomenon increases the friction force, introduces a short-term memory in the form of an elastic response against shearing, and allows us to "write" a temporary line of ice on a hydrophobic surface. Rearrangements of the condensate are shown to take place on a surprisingly slow time scale of seconds.

## 2005 Gun'ko

30 December , Turov, Bogatyrev, Zarko, Leboda, Goncharuk, Novza, Turov, Chuiko

### Unusual properties of water at hydrophilic/hydrophobic interfaces

The behaviour of water at mosaic hydrophilic/hydrophobic surfaces of different silicas and in biosystems (biomacromolecules, yeast cells, wheat seeds, bone and muscular tissues) was studied in different dispersion media over wide temperature range using H-1 NMR spectroscopy with layer-by-layer freezing-out of bulk water (close to 273 K) and interfacial water (180 < T < 273K), thermally stimulated depolarization current (TSDC) (90 < T < 270 K), infrared (IR) spectroscopy, and quantum chemical methods. Bulk water and water bound to hydrophilic/ hydrophobic interfaces can be assigned to different structural types. There are (i) weakly associated interfacial water (111 NMR chemical shift delta(H) = 1.1-1.7 ppm) that can be assigned to high-density water (HDW) with collapsed structure (CS), representing individual molecules in hydrophobic pockets, small clusters and interstitial water with strongly distorted hydrogen bonds or without them, and (ii) strongly associated interfacial water (delta(H)=4-5 ppm) with larger clusters, nano- and microdomains, and continuous interfacial layer with both HDW and low-density water (LDW). The molecular mobility of weakly associated bound water is higher (because hydrogen bonds are distorted and weakened and their number is smaller than that for strongly associated water) than that of strongly associated bound water (with strong hydrogen bonds but nevertheless weaker than that in ice Ih) that results in the difference in the temperature dependences of the H-1 NMR spectra at T < 273 K. These different waters are also appear in changes in the IR and TSDC spectra. (c) 2005 Elsevier B.V. All rights reserved.

## 2005 Buch

29 September

### Molecular structure and OH-stretch spectra of liquid water surface

Molecular dynamics simulations are used to investigate typical coordination shells of molecules in the liquid water surface, for two potential energy surfaces. The major undercoordinated species found in the surface include three-coordinated H2O with either a dangling-H or a dangling-O atom and two-coordinated H2O with one hydrogen bond via H, and another via O. Vibrational signatures of the different coordinations are calculated. The 3400 cm(-1) band in the surface sum frequency generation (SFG) spectrum is assigned to four-coordinated molecules within the surface layer. The low-frequency wing of the OH-stretch band, near 3200 cm(-1) in the SFG spectrum, is proposed to be due to collective excitations of a relatively small number of intermolecularly coupled O-H bond vibrations.

## 2005 Asay

8 September , Kim

### Evolution of the adsorbed water layer structure on silicon oxide at room temperature

The molecular configuration of water adsorbed on a hydrophilic silicon oxide surface at room temperature has been determined as a function of relative humidity using attenuated total reflection (ATR)-infrared spectroscopy. A completely hydrogen-bonded icelike network of water grows up to three layers as the relative humidity increases from 0 to 30%. In the relative humidity range of 30-60%, the liquid water structure starts appearing while the icelike structure continues growing to saturation. The total thickness of the adsorbed layer increases only one molecular layer in this humidity range. Above 60% relative humidity, the liquid water configuration grows on top of the icelike layer. This structural evolution indicates that the outermost layer of the adsorbed water molecules undergoes transitions in equilibrium behavior as humidity varies. These transitions determine the shape of the adsorption isotherm curve. The structural transitions of the outermost adsorbed layer are accompanied by interfacial energy changes and explain many phenomena observed only for water adsorption.

## 2005 de Meer

15 April , Spiers, Nakashima

### Structure and diffusive properties of fluid-filled grain boundaries: An in-situ study using infrared (micro) spectroscopy

The rate of numerous diagenetic, deformation and metamorphic processes in crustal rock systems ultimately depends on the structure and diffusive properties of water-bearing grain boundaries. We present the first in-situ spectroscopic study of the nature of aqueous films present in mineral interfaces undergoing stress-induced dissolution or 'pressure solution'. Using infrared micro-spectroscopy, we show that during active pressure dissolution of the (111) plane of halite (NaCl) against a CaF2 plate, the confined intercrystalline liquid has an average thickness of 85-185 mn and occupies a rough, non-equilibrium grain boundary structure. The hydrogen bonding of the water within the grain boundary film is modified due to increased polymerization towards ice-like (hard) water. Simultaneous pressure solution I rate measurements show that diffusion within the grain boundary fluid is about one order of magnitude slower than in bulk solution. During active pressure solution of the (100) plane of halite, a similar non-equilibrium gain boundary structure develops but the average thickness of the confined water film is only similar to 40 nm and no evidence is found for modification of the hydrogen bonding of the Water. The difference in hydrogen bonding between the two orientations studied is attributed to differences in surface charge distribution on the (111) and neutral (100) interfaces in NaCl. The difference in mean film thickness is attributed to differences in crystallographically controlled roughness of the dissolving NaCl Surface. If similar grain boundary thickness and diffusivity effects occur in other rock forming minerals, pressure solution in such systems will tend to be interface reaction controlled and may be capable of producing significant seismic anisotropy.

## 2004 Myers

Dec , Charpin

### A mathematical model for atmospheric ice accretion and water flow on a cold surface

A mathematical model is developed to describe ice accretion and water flow on a cold substrate of arbitrary shape. It is shown how the model may be applied to practical substrate shapes, such as flat surface, cylinder and aerofoil. A numerical scheme to solve the governing equations is then described. Results are presented for an aerofoil under conditions appropriate to in-flight icing and for a cylinder in conditions for atmospheric icing.

## 2004 Yang

15 September , Kleehammer, Huo, Sloan, Miller

### Temperature dependence of particle-particle adherence forces in ice and clathrate hydrates

Particle-particle pulloff adherence forces were measured as a function of temperature in the ice/n-decane/ice and tetrahydrofuran (THF) hydrate/n-decane/THF hydrate systems using a newly developed micromechanical testing technique. Experiments using similar to200 mum radius particles were performed at atmospheric pressure over the temperature range 263-275 K. The ice and hydrate particles displayed very similar behavior. While the measured adherence forces had significant variation, the shapes of the cumulative force distribution curves were similar among the different sets of experiments. The measured adherence forces distributions shifted to lower force values as the temperature was decreased from the solid melting temperature. The observed forces and trends were explained by the capillary cohesion of rough surfaces, with the capillary bridging liquid being stabilized below its freezing point by the negative curvature of the bridging liquid/n-decane interface.

## 2004 Finney

29 August

### Water? What's so special about it?

What is so special about water? Why does it have the properties it has, and how might these reasons be relevant to its apparent biological importance? By exploring the structure and dynamics of water, from the isolated molecule and its interactions, through its many crystalline phases and to its so-called anomalous liquid phase, some of its apparently unusual behaviour is rationalized. The way in which it interacts with some relatively simple interfaces is also discussed. As a result of this exploration, a checklist of possible molecular-level reasons for its biological importance is devised.

## 2004 Liu

19 February , Ma, Levering, Allen

### Vibrational Spectroscopy of aqueous sodium halide solutions and air-liquid interfaces: Observation of increased interfacial depth

Air-aqueous sodium halide solution interfaces are examined using vibrational sum frequency generation spectroscopy. Raman and ATR-FTIR (attenuated total reflection Fourier transform infrared) spectroscopies are also used to compare the effects of halide anions on the water structure of the bulk solution to that of the interface. The interfacial water structures for the sodium fluoride and chloride aqueous solutions are found to be similar to the air-water interface, whereas sodium bromide and iodide aqueous solutions cause significant distortion of the hydrogen-bonding network. Analysis of the spectra indicates higher concentrations of bromide and iodide anions in the interfacial region with an increase in interfacial depth.

## 2003 Lawrence

17 February , Skinner

### Ultrafast infrared spectroscopy probes hydrogen-bonding dynamics in liquid water

Time-resolved infrared spectroscopy has the potential to provide unprecedented information about molecular dynamics in liquids. In the case of water, one of the most exciting techniques being developed is transient hole-burning. From experiments on dilute HOD in DO one can obtain the transition frequency time-correlation function for the OH stretch, finding that it decays on a time scale of between 0.5 and 1 ps. In this report we provide a molecular-level interpretation of this spectral diffusion in terms of the dynamics of forming and breaking hydrogen bonds.

## 2002 Devlin

16 May , Uras, Sadlej, Buch

### Discrete stages in the solvation and ionization of hydrogen chloride adsorbed on ice particles

Ionization and dissociation reactions play a fundamental role in aqueous chemistry. A basic and well-understood example is the reaction between hydrogen chloride (HCl) and water to form chloride ions (Cl-) and hydrated protons (H3O+ or H5O2+). This acid ionization process also occurs in small water clusters(1-4) and on ice surfaces(5-17), and recent attention has focused on the mechanism of this reaction in confined-water media and the extent of solvation needed for it to proceed(1-4,9,15-17). In fact, the transformation of HCl adsorbed on ice surfaces from a predominantly molecular form to ionic species during heating from 50 to 140 K has been observed(8,13,14). But the molecular details of this process remain poorly understood. Here we report infrared transmission spectroscopic signatures of distinct stages in the solvation and ionization of HCl adsorbed on ice nanoparticles kept at progressively higher temperatures. By using Monte Carlo and ab initio simulations to interpret the spectra, we are able to identify slightly stretched HCl molecules, strongly stretched molecules on the verge of ionization, contact ion pairs comprising H3O+ and Cl-, and an ionic surface phase rich in Zundel ions, H5O2+.

## 2001 Kim

13 November , Kim, Cremer

### Investigations of water structure at the solid/liquid interface in the presence of supported lipid bilayers by vibrational sum frequency spectroscopy

The structure of water was investigated at the quartz/water interface in the presence of supported lipid bilayers (SLBs) by the use of infrared-visible sum frequency spectroscopy. By varying the pH of the bulk solution and the charge on the SLB, changes in both ice-like and water-like peaks were observed in the OH stretch region with respect to the plain quartz/water interface. The oscillator strengths were most affected by applying charged SLBs, rather than bilayers that did not contain a net charge. Time-dependent studies of the ice-like peak intensity at pH 5.6 during the fusion of lipid vesicles to the bare quartz surfaces revealed that the formation rate of a negatively charged SLB was much slower than that of positively charged and neutral SLBs.

## 2001 Zhu

27 August , Granick

### Viscosity of interfacial water

The effective shear viscosity and frequency-dependent dynamic oscillatory shear spectra of water containing monovalent or divalent ions (ionic strength 25 mM), confined between mica crystals at 1-2 water molecules thickness, oscillated with twist angle with the period expected for the pseudohexagonal surface lattice. The effective viscosity varied by orders of magnitude as the twist angle was changed. Confinement appeared to imprint lateral spatial correlation on the ultrathin liquid, the more so the better the confining lattices were aligned, but the oft-proposed "ice structure" was not observed dynamically.

## 2001 Clegg

12 July , Abbatt

### Uptake of gas-phase SO2 and H2O2 by ice surfaces: Dependence on partial pressure, temperature, and surface acidity

The uptakes of gas-phase SO2 and H2O2 by ice surfaces have been investigated at temperatures from 213 to 238 K and from 10(-7) to 10(-4) Torr partial pressure. These experiments have been conducted in a low-temperature, coated-wall flow tube coupled to an electron-impact, quadrupole mass spectrometer which monitors changes in the SO2 and H2O2 partial pressure. The ice surfaces are formed by freezing liquid water. Unlike the uptakes of strong acids such as HNo3 and HCl, the SO2 and H2O2 uptakes are fully reversible on the time scale of the experiment and the surface coverages are roughly a thousandth of a monolayer at 10(-6) Torr partial pressure and 228 K. The SO2 uptakes scale with the square root of the partial pressure of the SO2 gas, indicating that dissociation of the hydrated form of adsorbed SO2 is occurring on the surface. The H2O2 uptakes scale linearly with the H2O2 partial pressure, indicating that dissociation does not occur. The uptakes are driven by H-bond interactions in this case. Support for these conclusions comes from uptake measurements with ice surfaces which were formed by freezing either acidic or basic aqueous solutions. Although the H2O2 uptakes are independent of pH, the acidic ice surfaces considerably inhibit the SO2 uptake and the basic surfaces enhance the SO2 uptake. The results in this paper are consistent with atmospheric observations which show that both S(IV) and H2O2 have low retention efficiencies after supercooled cloud droplets freeze, whereas the retention efficiency of HNO3 is high. The uptakes are sufficiently small that scavenging of SO2 and H2O2 by ice clouds will not be significant.

## 2001 Sattler

15 Januar , Puxbaum, Psenner

### Bacterial growth in supercooled cloud droplets

It is well known that the atmosphere is a conveyor of microorganisms, and that bacteria can act as ice or cloud condensation nuclei, but clouds have not been considered as a site where organisms can live and reproduce. Here we show that bacteria in cloud droplets collected at high altitudes are actively growing and reproducing at temperatures at or below 0 degreesC. Since similar to 60% of the earth surface is covered by clouds, cloud water should be considered as a microbial habitat.

## 2001 Schreiber

, Ketelsen, Findenegg

### Melting and freezing of water in ordered mesoporous silica materials

The melting and freezing of water in a series of mesoporous silica materials with a hexagonal arrangement of unidimensional cylindrical pores and narrow pore-size distribution (MCM-41 with pore diameters from 2.9 to 3.7 nm, and SBA-15 with pore diameters from 4.4 to 11.7 nm) was studied by differential scanning calorimetry (DSC). A lowering of the melting temperature DeltaT(m)=T-mb-T-m(R) up to 50 K was found for water in pores of decreasing radius R. The melting point data can be represented by a modified Gibbs-Thomson equation, DeltaT(m)(R)=K/(R-t), with K=52 K nm and t=0.4 nm, in agreement with an earlier study of water in MCM-41 materials of pore width 2 to 4 nm. The value of K agrees with an estimate of the Gibbs-Thomson constant based on thermodynamic data for the normal melting point of ice, and the parameter t can be taken as the thickness of a surface layer of non-frozen water at the pore wall. DSC scans of the freezing of H2O and D2O in partially filled pores of SBA-15 reveal a peak pattern depending on the degree of pore filling phi. The different peaks are attributed to different states of the liquid in the pore space, viz. pore water in completely filled regions, and water as an adsorbed film at the pore wall. These two states coexist in a pore filling range phi (min)< phi <1, but only the film state exists at phi < phi (min). The freezing peak of pore water appears to be nucleated by external bulk ice (at phi >1) but exhibits substantial supercooling at phi <1. On the other hand, the peak attributed to the freezing of film water exhibits no significant supercooling and is found at temperatures near 237 K, almost independent of phi and the pore width of the SBA-15 sample. The nature of a further (small) peak near 233 K is not yet understood. Contrary to cooling scans, only one DSC peak is observed in heating scans, independent of the pore filling. This finding indicates that the adsorbed liquid film is metastable relative to the frozen pore liquid.

## 2000 Foster

15 April , Ewing

### Adsorption of water on the NaCl(001) surface. II. An infrared study at ambient temperatures

Water adsorbed on the (001) face of NaCl under ambient conditions has been studied by infrared spectroscopy. From these measurements, combined with recent Monte Carlo calculations, we find evidence of two structures for the adsorbed water. At low coverages, the water molecules aggregate into islands on the surface. When a critical concentration is reached, multilayer growth becomes favorable, creating a thin film on the surface with properties similar to liquid water.

## 1999 Fukuta

15 June , Takahashi

### The growth of atmospheric ice crystals: A summary of findings in vertical supercooled cloud tunnel studies

Measurements of ice crystal growth under free fail in a generation of vertical supercooled cloud tunnels and some static cloud chambers as well as the related theoretical works are summarized.

Growth parameters, that is, mass (m), dimensions, apparent density, and fall velocity (w), show extrema at about -5 degrees, -10 degrees, and -15 degrees C where crystals are predominantly column-needle, isometric, and plate-stellardendrite, respectively. Crystal shape enhances with time (t) at about -5 degrees and -15 degrees C- whereas at -10 degrees C the effect is minimal and crystals show strongest tendency to grow into graupel due to the fail velocity maximum discovered early in the series of present studies. At this temperature, switch-over of growth mode toward graupel occurs more quickly as liquid water content (W-t,) increases. Under a fixed cloud condition, the shape-enhanced crystals hardly grow into graupel and vice versa.

The diffusional growth theory, with Maxwellian surface condition and without ventilation. describes well the behaviors of intermediate size crystals for which m proportional to t(3/2) proportional to (-w)(3/2) proportional to (-z)(3/4), being the fail distance, is identified. Small crystals grow more slowly due to accommodation coefficient effects and larger ones grow faster due to enhanced ventilation; and riming. To include these effects, a generalized growth theory is formulated. r\ simple theory is developed for graupel/hail growth where m proportional to p(u) (3)(W(L)t)(6) proportional to (-z)(3) . P-u being the air density. Based on these relationships, the dominance of diffusional grou th mechanism for precipitation development in,shallow convectively weak, winter clouds and that of graupel/hail-type riming growth in deep, convectively strong, summer clouds is explained.

## 1998 Grundy

25 October , Schmitt

### The temperature-dependent near-infrared absorption spectrum of hexagonal H(2)O ice

Transmission spectra were measured between 1.0 and 2.7 mu m for monocrystalline samples of hexagonal water ice at temperatures between 20 and 270 K. Samples were crystallized from liquid water within closed cells, with thicknesses ranging from 100 mu m to 1.0 cm. The absorption spectrum of ice changes with temperature in several ways. With higher temperature, the shapes of absorption bands become more smoothed, the strengths of some absorption bands decrease, the absorption in continuum wavelengths increases, and the band centers of some absorption bands shift to shorter wavelengths. In this paper we present the new absorption coefficient spectra along with an examination of the different temperature effects. These data should prove extremely valuable for analysis of near-infrared reflectance spectra of low-temperature icy surfaces, such as those of outer solar system satellites, Kuiper Belt objects, Pluto and Charon, comet nuclei, the polar caps of Mars, and terrestrial snow- and ice-covered regions. The data may also be of value in simulating radiative transfer in clouds of ice particles in the atmospheres of planets.

## 1998 Zondlo

16 July , Barone, Tolbert

### Condensed-phase products in heterogeneous reactions: N2O5, ClONO2, and HNO3 reacting on ice films at 185 K

Heterogeneous reactions are important in a wide variety of chemical processes. In many cases reactions on a surface will change both the physical and chemical characteristics of the surface, which in turn will change the surface reactivity toward further gas/surface collisions. As a case study of relevance to the atmosphere, we have investigated the reactions of the NOy species ClONO2, N2O5, and HNO3 on thin ice films representative of water-ice polar stratospheric clouds (type II PSCs). Although these species are known to produce HNO3 upon reacting with the ice surface, the phase, composition, and state of adsorption (physical versus chemical) of the surface reaction product are not known. These reactions were studied using a Knudsen cell reactor to probe heterogeneous reaction rates, mass spectrometry to identify gas-phase reactants and products, and FTIR reflection-absorption spectroscopy to probe the phase and composition of the condensed phase. Under ice frost point conditions at 185 K, each NOy species reacted with ice to form a metastable supercooled H2O/HNO3 liquid layer. Although a crystalline 3:1 H2O:HNO3 hydrate is most thermodynamically stable under these conditions, a supercooled liquid with a composition slightly more dilute than 3:1 H2O:HNO3 continued to grow throughout the NOy exposure period. This product composition is similar to that expected for liquid type Ib PSCs in the atmosphere. ClONO2 and N2O5 reacted with the supercooled H2O/HNO3 liquid layer at 185 K with a reactive uptake coefficient of gamma = 0.003 +/- 0.002 and gamma = 0.0007 +/- 0.0003, respectively. These measured rate coefficients are about 2 orders of magnitude lower than the corresponding reaction rates on pure ice but are comparable to those measured on crystalline nitric acid trihydrate (NAT) or nitric acid dihydrate (NAD) surfaces representative of type Ia PSCs. HNO3 reacted with the supercooled liquid layer with gamma > 0.02. When H2O vapor pressures were decreased to below the ice frost point, the supercooled H2O/HNO3 liquid layer became more concentrated in HNO3 as H2O preferentially desorbed. Only during desorption when stoichiometric ratios of 3:1 or 2:1 H2O:HNO3 were obtained.did the supercooled liquid layer crystallize to NAT or NAD, respectively. These results suggest that water-ice particles in the polar stratosphere may be initially coated with a supercooled H20/HNO3 liquid layer and that heterogeneous nucleation of NAT on ice from either the gas phase or the H2O/HNO3 supercooled liquid phase is slow. The implications of a supercooled H2O/HNO3 liquid layer on ice will be discussed in the context of polar ozone depletion.

## 1997 Zondlo

1 June , Barone, Tolbert

### Uptake of HNO3 on ice under upper tropospheric conditions

The uptake of HNO3 on thin ice films was investigated under upper tropospheric temperature and pressure conditions using a Knudsen cell reactor and FTIR reflection absorption spectroscopy. Two different HNO3 uptake regimes were noted with the critical threshold being the supercooled H2O/HNO3 liquid isotherm at a specific temperature. For H2O/HNO3 partial pressures below the supercooled H2O/HNO3 liquid isotherm, a time-dependent uptake of HNO3 was observed until the HNO3 surface coverage reached approximately one monolayer. The initial uptake coefficient of HNO3 on the ice film was gamma greater than or equal to 0.005 which became progressively smaller until a steady-state uptake coefficient of gamma = 0.0002 +/- 0.0001 was obtained after monolayer coverage of HNO3. In contrast, when H2O and HNO3 partial pressures were greater than the supercooled H2O/HNO3 isotherm, unlimited uptake of HNO3 was observed with an uptake coefficient gamma greater than or equal to 0.005. Under these conditions, the infrared spectra showed the formation and continual growth of a supercooled H2O/HNO3 liquid. By using the best estimates of HNO3 mixing ratios and ice surface area densities in the upper troposphere, two limiting cases of HNO3 uptake are discussed in the context of upper troposeheric chemistry.

## 1997 Peter

### Microphysics and heterogeneous chemistry of polar stratospheric clouds

Liquid and solid particles in polar stratospheric clouds are of central importance for the depletion of stratospheric ozone. Surface-catalyzed reactions on these particles, and diffusion-controlled processes in the bulk of the particles, convert halogens, which derive from compounds of mainly anthropogenic origin, from relatively inert reservoir species into forms that efficiently destroy ozone. The microphysics of these particles under cold stratospheric conditions is still uncertain in many respects, in particular concerning phase transitions such as freezing nucleation and deposition nucleation. Furthermore, there are indications that the rates of key heterogeneous reactions have not yet been established with sufficient accuracy to enable a reliable diagnosis of observed ozone losses by means of global models. The present paper reviews the current (late 1996) knowledge of the physico-chemistry of polar stratospheric clouds and evaluates the remaining uncertainties with respect to their ozone depletion potential.

## 1996 Strambini

February , Gabellieri

### Proteins in frozen solutions: Evidence of ice-induced partial unfolding

From a drastic decrease in the phosphorescence lifetime of tryptophan residues buried in compact rigid cores of globular proteins, it was possible to demonstrate that freezing of aqueous solutions is invariably accompanied by a marked loosening of the native fold, an alteration that entails considerable loss of secondary and tertiary structure. The phenomenon is largely reversible on ice melting although,in some cases, a small fraction of macromolecules recovers neither the initial phosphorescence properties nor the catalytic activity. The variation in the lifetime parameter was found to be a smooth function of the residual volume of liquid water in equilibrium with ice and to depend on the morphology of ice. The addition of cryoprotectants such as glycerol and sucrose profoundly attenuates or even eliminates the perturbation. These results are interpreted in terms of adsorption of protein molecules onto the surface of ice.

## 1994 BENJAMIN

10 October

### VIBRATIONAL-SPECTRUM OF WATER AT THE LIQUID/VAPOR INTERFACE

The infrared spectrum of water molecules at the liquid/vapor interface of pure water and at the liquid/vapor interface of a water-methanol mixture is calculated using molecular dynamics. A comparison with the IR spectrum calculated for bulk water shows a significant population of free OH bonds, in qualitative agreement with a recent experiment by Du et al. [Phys. Rev. Lett. 70, 2313 (1993)]. It is also demonstrated that the free OH IR signal is quenched by a moderate increase in the concentration of methanol in bulk water, which has been recently observed by Du et al. [Science 264, 826 (1994)].

## 1994 KARSTENS

, SIMMER, RUPRECHT

### REMOTE-SENSING OF CLOUD LIQUID WATER

A method is presented to infer cloud liquid water path (LWP in kg/m2) over the ocean from passive microwave measurements of SSM/I. The algorithm to retrieve LWP is based on simulated satellite observations. They are calculated with a radiative transfer model applied to about 3000 radiosonde ascents over the Atlantic Ocean. Since radiosonde observations do not contain direct information about cloud water and ice, these parameters are parameterized based on relative humidity and temperature using modified adiabatic liquid water density profiles. A multiple linear regression is applied water density profiles. A multiple linear regression is applied to the simulated radiances and the calculated LWP to derive the algorithm. The retrieval accuracy based on the regression analysis including instrumental noise is 0.03 kg/m2. Validation of the LWP-algorithm was pursued through a comparison with measurements of a ground-based 33 GHz-microwave radiometer on board of R.V. ''Poseidon'' during the International Cirrus Experiment 1989 at the North Sea (ICE'89). The LWP values agree within the range of uncertainty caused by the different sampling characteristics of the observing systems. The retrieval accuracy for clear-sky cases determined using colocated METEOSAT data over the North Sea is 0.037 kg/m2 and confirms the accuracy estimated from regression analysis for the low liquid water cases.

The algorithm was used to derive maps of monthly mean LWP over the Atlantic Ocean. As an example the Octobers of the 5 years 1987-1991 were selected to demonstrate the interannual variability of LWP. The results were compared with the cloud water content produced by the climate model ECHAM-T2 from the Max-Planck-Institut Hamburg.

Observations during ICE'89 were used to check the accuracy of the applied radiative transfer model. Brightness temperatures were calculated from radiosonde ascents launched during the overpass of DMSP-F8 in cloud-free situations. The channel-dependent differences range from about - 2 to 3 K.

The possibility to identify different cloud types using microwave and infrared observations was examined. The main conclusion is that simultaneous microwave and infrared measurements enable the separation of dense cirrus and cirrus with underlying water clouds. A classification of clouds with respect to their top heights and LWP was carried out using a combination of SSM/I derived LWP and simultaneously recorded Meteosat IR-data during ICE'89.

## 1993 HANSON

25 November , RAVISHANKARA

### UPTAKE OF HCL AND HOCL ONTO SULFURIC-ACID - SOLUBILITIES, DIFFUSIVITIES, AND REACTION

The interaction of HOCl and HCl vapors with liquid sulfuric acid surfaces was studied in a flow tube equipped with chemical ionization mass spectrometry detection. Time-dependent uptake of HCl and HOCl was measured. A methodology for deriving the value of the quantity H square-root D1 (the product of the Henry's law coefficient and the square root of the liquid-phase diffusion coefficient) is discussed. The partial pressures of HCl over HCl-doped sulfuric acid solutions were also measured to directly determine H for HCl (H\*HCl). Using the measured values of H\*HCl and H\*(HCl)square-root D1, the value of D1 for HCl in 50 wt % sulfuric acid was extracted. Values for H(HOCl) and for the second-order rate coefficient for the reaction between dissolved HOCl and HCl were also obtained. The application of these results to modeling stratospheric heterogeneous processes in sulfuric acid aerosols is discussed.

## 1993 DELZEIT

7 October , ROWLAND, DEVLIN

### INFRARED-SPECTRA OF HCL COMPLEXED IONIZED IN AMORPHOUS HYDRATES AND AT ICE SURFACES IN THE 15-90-K RANGE

Cryogenic HCl-ice samples, chosen to maximize the possibility that the primary H2O-HCl interactions will include molecular complexation of HCl with H2O, have been studied by infrared spectroscopy. A thorough review/extension of the spectroscopy of HCl (HBr) amorphous and crystalline hydrate films has revealed the need for a significant reassignment of the published crystalline hydrate infrared spectra. From this reassignment, and new data for the amorphous hydrates, the band position for the stretching mode of HCI (approximately 2550 cm-1), DCI (approximately 1820 cm-1), and HBr (approximately 2220 CM-1) complexed with H2O within the 1:1 amorphous hydrate mixture has been established. This band, together with the spectra of the ionic components of the amorphous hydrate mixtures, has then been used as a probe of the interaction of HCI with the extensive ice surfaces present in samples of gas-phase ice nanocrystals (85 K) and microporous amorphous ice samples prepared at 15 K. This molecular complex band is observed as the dominant spectral feature that emerges as samples of microporous ice, coated with a thin film of HCI, are warmed through the 15-60 K range. However, the major infrared bands that develop upon warming the HCI/amorphous ice system above 60 K, or as ice nanocrystals are exposed to HCI at 8 5 K, are those of the ionic amorphous hydrate mixtures. The results indicate that the limited molecular mobility and activation energy available at temperatures below approximately 50 K result in the kinetic stabilization of the molecular complex of HCI H-bonded to the ice surface oxygen sites, while at temperatures above 60 K, HCI, in the presence of ice, ionizes as it forms amorphous hydrate surface layers, ultimately of a 1:1 composition. This study reveals a qualitatively different ionization behavior of the hydrogen halides within the amorphous hydrate mixture than has been observed for the nitric and perchloric oxyacids (for which ionization is quite limited for the 1:1 composition even into the stable liquid phase): a difference that presumably reflects the very strong hydrogen bonding of H3O+ to multiple neighbor chloride and bromide ions. The identification of the stretching-mode bands of the molecular H(D)X--H2O complex as a useful probe of the extent of ionization within noncrystalline hydrogen halide-water systems is an important byproduct of this study, a study that establishes the strong tendency of ice to form an amorphous ionic hydrate mixture when exposed to HX at temperatures above approximately 60 K.

## 1993 MOLINA

10 September , ZHANG, WOOLDRIDGE, MCMAHON, KIM, CHANG, BEYER

### PHYSICAL-CHEMISTRY OF THE H2SO4/HNO3/H2O SYSTEM - IMPLICATIONS FOR POLAR STRATOSPHERIC CLOUDS

Polar stratospheric clouds (PSCs) play a key role in stratospheric ozone depletion. Surface-catalyzed reactions on PSC particles generate chlorine compounds that photolyze readily to yield chlorine radicals, which in turn destroy ozone very efficiently. The most prevalent PSCs form at temperatures several degrees above the ice frost point and are believed to consist of HNO3 hydrates; however, their formation mechanism is unclear. Results of laboratory experiments are presented which indicate that the background stratospheric H2SO4/H2O aerosols provide an essential link in this mechanism: These liquid aerosols absorb significant amounts of HNO3 vapor, leading most likely to the crystallization of nitric acid trihydrate (NAT). The frozen particles then grow to form PSCs by condensation of additional amounts of HNO3 and H2O vapor. Furthermore, reaction probability measurements reveal that the chlorine radical precursors are formed readily at polar stratospheric temperatures not just on NAT and ice crystals, but also on liquid H2SO4 solutions and on solid H2SO4 hydrates. These results imply that the chlorine activation efficiency of the aerosol particles increases rapidly as the temperature approaches the ice frost point regardless of the phase or composition of the particles.

## 1992 KROES

20 August , CLARY

### STICKING OF HCL AND CLOH TO ICE - A COMPUTATIONAL STUDY

We present results of classical trajectory calculations modeling physical adsorption of HCl and ClOH on single-crystal ice under stratospheric conditions. The adsorption energy that we calculate for adsorption of ClOH on ice (-60 kJ/mol) is in excellent agreement with experiment. On the other hand, the calculated surface coverage of single-crystal ice by HCl is orders of magnitude smaller than the values obtained experimentally for adsorption of HCl on vapor-deposited ice. The results suggest that the high surface coverages found in experiments cannot be due to physisorption alone.

## 1992 TANAKA

15 August , GUBBINS

### STRUCTURE AND THERMODYNAMIC PROPERTIES OF WATER-METHANOL MIXTURES - ROLE OF THE WATER WATER INTERACTION

Thermodynamic properties and structures of water-methanol mixtures at various temperatures have been investigated by means of Monte Carlo simulations and subsequent analyses. The OPLS model by Jorgensen was used for the methanol-methanol interaction and both the Caravetta-Clementi (CC) potential and TIP4P potential by Jorgensen et al. were used for the water-water interaction. We show that the role of water-water interaction is very important in discussing aqueous solutions of alcohols, and examine the origin of the exothermic mixing processes. We have investigated the sensitivity of the temperature dependence of the enthalpy of mixing to the water-water interaction. The CC potential is able to reproduce the temperature dependence observed in experiments, although the absolute values of the mixing enthalpy were larger than the experimental ones. While the TIP4P potential results in better agreement for the excess enthalpy and volume near room temperature, the temperature dependence of the excess enthalpy did not agree with experiment. The difference in the magnitude of the exothermic hydration for different water-water interactions is explained in terms of the energetic stability of the clathrate hydrate compared with ice, on the basis that the structure of water in the vicinity of a methanol molecule is similar to the clathrate hydrate. It is found that the energetic stability of the clathrate hydrate for the CC model is higher than that for TIP4P, and this is responsible for the larger exothermic hydration. The higher stability of the clathrate hydrate structure for the CC potential, in tum, arises from the difference in the pair interaction energy surface between two kinds of potential functions; the minimum energy structure and the flexibility of the hydrogen bonded pair.

## 1992 BUCH

1 March

### GROWTH AND STRUCTURE OF AMORPHOUS ICE CONDENSATES - A COMPUTATIONAL STUDY .2.

Investigation is presented of the static and the dynamic properties of an amorphous cluster (H2O)450 at T almost-equal-to 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.

## 1992 MADER

### THE THERMAL-BEHAVIOR OF THE WATER-VEIN SYSTEM IN POLYCRYSTALLINE ICE

Experimental studies are reported concerning the thermal behaviour of the water-vein system in ice grown in the laboratory from dilute solutions. The temperature versus vein-size behaviour of these samples is determined. The measurements show that the solute, which is concentrated in the veins, remains in the liquid phase during a temperature change. The mass of the solute per unit length of vein M is found to be of the order of M almost-equal-to 10(-8) Mol M-1 for samples grown from singly-distilled water. M is seen to vary with temperature only because of the volume expansion (contraction) on freezing (melting) which causes the liquid to flow along the veins. The effect of these flows on the sample is studied. They are found to provide a mechanism for the transport of impurities along the veins and to and from the sample surface. Samples grown from doubly-distilled water doped with small amounts of NaCl or H2SO4 are studied and are found to display the same general behaviour. However, M is an order of magnitude higher in the H2SO4-doped samples than in either the NaCl-doped samples or the samples grown from singly-distilled water. The approach to equilibrium of distortions in the vein-system geometry is studied. It is suggested that these distortions are due to variations in M along the length of the veins and that equilibration is therefore governed by diffusion of the solutes.

## 1974 Hobbs

22 April , Easter

### The Formation of Sulfates and the Enhancement of Cloud Condensation Nuclei in Clouds

The production of ammonium sulfate by oxidation of dissolved sulfur dioxide in cloud droplets in a wave cloud situation, and the resulting enhancement of cloud condensation nuclei (CCN) released from the cloud on evaporation, have been calculated. The condensational growth of droplets formed on 75 initial CCN sizes is considered simultaneously with the production of sulfates via the Scott-Hobbs mechanism in the droplets in an air parcel moving through a wave cloud. The results show that significant increases in the concentrations of CCN active at 0.5% supersatutation can be produced by SO2 oxidation in wave clouds with short “flow-through” times (4 min) and with concentrations of SO2 and NH3 typical of unpolluted air (1 and 3 ppb, respectively). The sulfate production is found to decrease as the SO2 concentration rises above 10 ppb. This effect is due to the limited buffering capacity of the NH3.

The results of the calculations indicate that the in-cloud production of ammonium sulfate can probably explain previous observations of higher than ambinent CCN concentrations in air from evaporating clouds, and that the rate of production of ammonium sulfate in clouds is sufficiently fast that it is probably the major worldwide source of these particles.

## End

# Unsorted