

FEATURE ARTICLE

Thin Film Water

George E. Ewing

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received: May 25, 2004; In Final Form: July 26, 2004

Thin film water is ubiquitous. It coats insulators, even ice, under ambient conditions. And the film can have a profound effect on the physical and chemical properties of the substrates it covers. The direct measurement of thin film water by infrared spectroscopy is described. Our studies can reveal film thicknesses, hydrogen bonding networks, thermodynamic properties, and molecular orientations. Recent examples of our research, with the focus on two model substrates, NaCl and ice, are discussed.

Overview

On a warm humid afternoon, it just begins to rain. A small drop falls on a window pane. It clings there, a rounded cap. Why has it assumed this characteristic shape? Why has not the water spread out to form a uniform sheet on the glass? Or at the other extreme, why does not the drop bead up into a perfect sphere just touching the pane? The answers of course depend on whether the glass surface is hydrophilic or hydrophobic. But perhaps more interesting, the glass surface on this humid day has been prepared by water vapor in the air. Before the rain drop even landed on the glass, it was coated with a thin film of water. The thin film is invisible to the eye, but its presence and properties involve the same collection of interactions that determine the shape of a small drop on the surface of a substrate. Any surface under ambient conditions will be covered by a thin film of water, perhaps a fraction of a monolayer, perhaps many molecular layers. The distance scale of a water film is typically nanometers. Yet this thin film can make a profound effect on the chemical and physical properties of the substrate surface.

There are many fundamental questions on the nature of thin films of water. How thick are they? What are their freezing points and abilities to dissolve molecules and ions? Are water molecules making up the film amorphous or ordered? How are thermodynamic properties affected by the film thickness and the nature of the underlying substrate? What can be said about the hydrogen bonding network within a thin film on a

hydrophobic (nonwetting) or hydrophilic (wetting) surface? How does chemistry within a thin film differ from chemistry in bulk water? In this article we shall offer our approach to addressing these questions.

The properties of ambient thin film water are of great practical importance. Salt particles, thrown up from the earth's oceans, make up one of the most abundant particulate masses in the atmosphere.¹ Water coating their surfaces, sometimes called a quasi-liquid layer, affects chemical reactivity.² A thin film of water on aerosol particles in the atmosphere is a likely prelude to cloud formation.³ Small particles of a variety of solids (e.g., salt, detergents, fertilizers) manufactured annually in millions of metric ton quantities⁴ can cake together in clumps because of adhering water films complicating their handling, packaging and transport.⁵ Thin film water also participates in heterogeneous transformation of solids⁶ and the properties of soils.⁷ Yet despite its relevance, the view of thin film water at the molecular level is incomplete.

Thin film water on ice deserves special consideration. The suggestion that a liquidlike water layer resides on the surface of ice at temperatures near its melting point dates to the work of Michael Faraday.⁸ Interest in this thin water film now variously called the premelting layer, surface melting layer, or quasi-liquid layer, has expanded over the years. Originally confined to understanding the properties of blocks of ice, snow, or glaciers, thin film water on ice is now implicated in the

electrification of clouds⁹ and interpretation of ice cores¹⁰ and is involved in a vast array of environmental phenomena including frost heave, soil freezing, and permafrost.¹¹ Chemical transformation of ice crystals in polar snowpack¹² and stratospheric clouds¹³ affects atmospheric ozone concentrations and is an interfacial phenomenon likely to involve thin film water. Heterogeneous ice nucleation begins at a solid interface with thin film water an intermediary.³ Finally, surface melting is now known to be a general phenomena observed in many solids of which ice is perhaps the most complicated.¹⁴ In short, the study of thin film water on ice continues to be a lively research area.

It is the goal of this article to review our spectroscopic experiments to investigate the properties of thin film water on two model substrates: NaCl and ice.

Some Background

The study of thin water films on insulators started, as did many of the pioneering investigations in surface science, with Irving Langmuir.¹⁵ In 1918 he measured film thicknesses on mica and glass. His procedure, elegant in its simplicity, involved taking many sheets of mica, or cover glass slides, from the ambient laboratory environment and stacking them into a small vial. The adsorbed molecules (principally H₂O) on these surfaces were driven off by heating to 300 °C and captured in a trap cooled with liquid air. The number of water molecules caught, together with the known geometric area of the substrate surfaces, allowed a calculation of thin water film coverages: 2 molecular layers on mica and 4 on glass. If we view these insulator substrates as typical, then we come to expect any insulator surface to have some water molecules stuck to them under ambient conditions.

Work since Langmuir on water adlayers has followed two distinct paths. With the development of ultrahigh vacuum (UHV) technology, thousands of studies of water on metal and nonmetal surfaces have been performed.^{16,17} Typically, water molecules on well-defined surfaces are locked into an ordered structure for long times (hours). The stability and order are dictated by the strength of the adlayer bond or the low temperature of the substrate. For example, a monolayer of H₂O has been prepared on a NaCl(100) surface under UHV conditions.¹⁸ At -130 °C and a water vapor pressure of 10^{-8} mbar, helium atom diffraction has revealed an ordered adlayer with each Na⁺Cl⁻ surface ion pair covered by an H₂O molecule at a specific orientation.

The path less traveled for water adlayer studies is for exploration of ambient thin films. With equilibrium pressures in the mbar pressure range, the scores of surface interrogation techniques, helium atom scattering, low energy electron diffraction, X-ray photoelectron spectroscopy, etc., that depend on the low background pressures of the UHV chambers, fail for water thin film studies. However, four particularly successful general approaches have recently been directed toward the investigation of thin film water: intermolecular force measurements,^{19–22} optical interrogations (both linear, e.g., ellipsometry,^{23–26} and nonlinear, e.g., second harmonic²⁷ and sum frequency generation^{28–30}), molecular simulations,^{31–35} and the infrared approach we shall discuss.

The Monte Carlo calculations of Engkvist and Stone³¹ are examples of molecular simulations that allow us to visualize thin film water at the molecular level as implied by the observed isotherms which we shall later describe. The simulations provide quantitative information in the form of distribution functions such as those shown in Figure 1. The distribution here, $g(z)$, is related to the probability of finding water molecules a distance

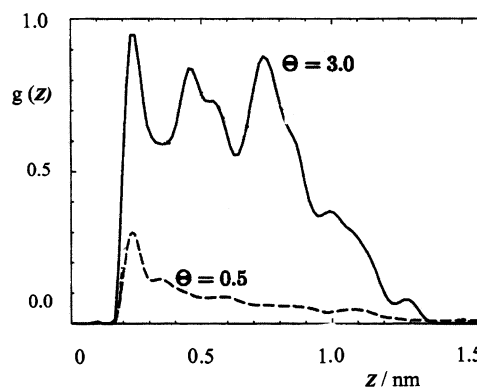


Figure 1. Distribution function $g(z)$ of water molecules at distance z from the NaCl(100) surface at coverages of $\Theta = 0.5$ and $\Theta = 3.0$. Adapted from Engkvist and Stone.³¹

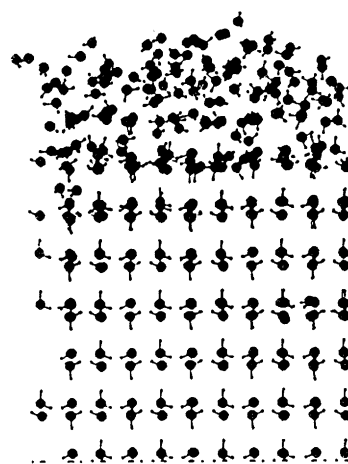


Figure 2. Simulated molecular picture of ice showing surface melting on the basal face at -8 °C. Adapted from Furukawa and Nada.³⁴

z from the NaCl(100) surface. The distribution for $\Theta = 0.5$ might appear as a random assemblage of monomers and small clusters. However, other distribution functions indicate that the molecules are not randomly distributed but favor an O–O separation consistent with hydrogen bond formation. Moreover, H₂O molecules are more likely over Na⁺ than Cl⁻ ions and tend to lie flat against the surface. We emphasize that though the average coverage is $\Theta = 0.5$, the molecules are not solely at the surface but extend beyond it. For a coverage of $\Theta = 3$, the water molecules are distinctly partitioned into three layers as Figure 1 shows. The molecules in the first layer are influenced by molecules in the second layer as well as by the substrate below. Thus although water molecules in the uppermost layer and the layer closest to the surface are only partially surrounded by other molecules, the distribution function that explores the O–O separation finds a value near that of liquid water. Thus the adlayer for $\Theta = 3$ resembles liquid water. This type of molecular simulation has been an essential complement to the interpretation of our spectroscopic measurements.

A molecular dynamics simulation by Furukawa and Nada³⁴ of thin film water on ice near its melting point using the TIP4P potential is reproduced in Figure 2. Using the spacing between water molecules in the ice as a length scale, the disordered region at the surface, thin film water, has a thickness of roughly 1 nm comparable to that for the thin film on NaCl(100) in Figure 1. Other simulations of the ice surface indicate layering of water molecules as well.³⁵

Both of the simulations giving rise to Figures 1 and 2 may be viewed as “snapshots” of molecular configurations. The

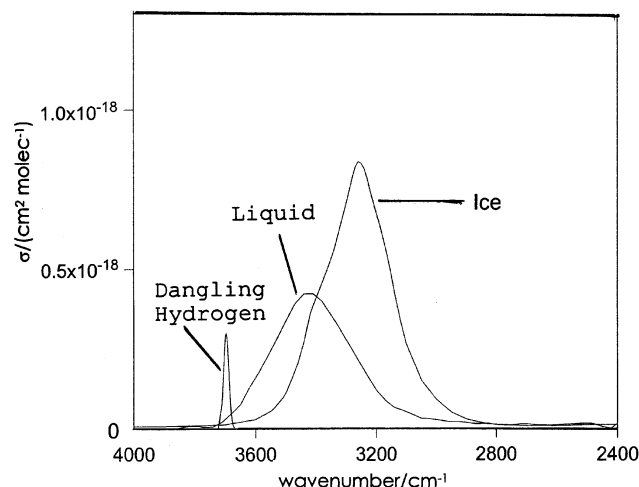


Figure 3. Optical cross sections of water. See text for details.

molecules are in rapid motion, changing positions and orientations on the nanosecond to picosecond time scale. Coverage values of thicknesses are statistical averages. This is then in sharp contrast to the rigid and well-defined adlayers with long lived architectures that are typically obtained in UHV studies.

General discussions of thin films may be found by Israelachvili,²⁰ Adamson and Gast,³⁶ and de Gennes et al.³⁷ We now focus attention on our spectroscopic approach.

Infrared Interrogation

Infrared interrogation of thin film water contains four important levels of information. The first is from the spectroscopic signature that can provide insight into the nature of the hydrogen bonding networks. Second, the extent of the spectroscopic response (absorption, reflection or extinction) yields an estimate of the film thicknesses for construction of isotherms and through them thermodynamic properties. Third, light polarization measurements can be used to determine the orientation of the water molecules. Finally, it is possible to determine concentrations of dissolved molecules in the thin film. Our approach has been to extract the most possible information from each spectroscopic measurement.

Because infrared spectroscopy is our principle probe of thin film water, it is appropriate to review its ability to distinguish both phase differences and hydrogen bonding arrangements. In Figure 3 we compare the optical cross sections, σ ($\text{cm}^2 \text{ molecule}^{-1}$), of liquid water at 27 °C³⁸ with that of ice at -7 °C³⁹ in the region of the ν_1 and ν_3 H₂O stretching vibrational modes. The large shift in the absorption maxima on the liquid to solid phase change, 3400 to 3200 cm^{-1} , is a consequence of different hydrogen bonding arrangements in these states. Normal-mode analysis by Rice and co-workers⁴⁰ and more recently by Buch et al.,⁴¹ as well as qualitative considerations,^{42,43} can account for some of these spectroscopic changes. The sharp feature near 3700 cm^{-1} is due to the dangling hydrogen (d-H) vibration. This vibration is associated with a hydrogen of a water molecule at the vapor interface that does not participate in hydrogen bonding. We have used the (non-hydrogen bonded) gas phase ν_1 and ν_3 oscillator strengths,⁴⁴ scaled by one-half, and assumed a bandwidth of 20 cm^{-1} in keeping with previous surface measurements^{45–47} to generate the d-H band. We note also that all water features throughout the infrared (500–4000 cm^{-1}) undergo significant changes on phase transitions and their optical constants are well-known.^{38,39}

The measurements of thin film water on NaCl(100), BaF₂(111), and mica (100) from our previous work^{48–54} have used trans-

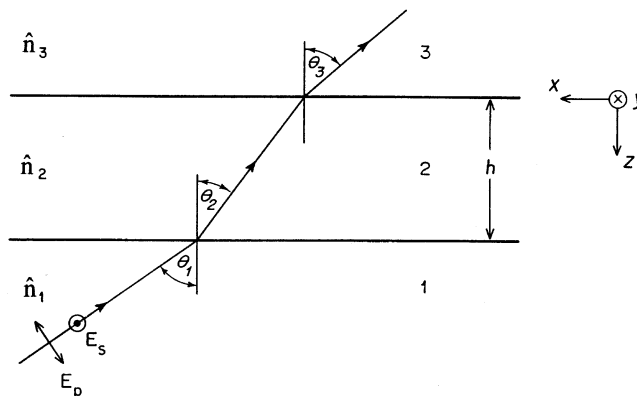


Figure 4. Thin film optics. Adapted from Born and Wolf.⁵⁹

mission/absorption spectroscopy. However, we have gone on to measure spectra in alternative optical configurations^{55–58} that are more appropriate to thin film interrogations.

Figure 4 is adapted from the optical analysis of thin films by Born and Wolf.⁵⁹ For our studies, medium 2 is the thin film water of thickness h and complex refractive index $\hat{n}_2 = n_W + ik_W$ with n_W and k_W the real and imaginary refractive index components of liquid water. The wavenumber dependent k_W component accounts for light absorption. (It is appropriate here to make a connection with another thin film optical interrogation technique—ellipsometry.^{23–26,60} Because the light source is typically in the visible, the transparency of water in this region, i.e., $k_W = 0$, means that information on hydrogen bonding networks and molecular orientation gained from infrared interrogation is inaccessible.) The film is supported by a substrate of medium 1 (e.g., NaCl, Ge, ice, etc.) with its refractive index $\hat{n}_1 = \hat{n}_s$. Above the film, medium 3, is the vapor of such low density that its refractive index is effectively that of vacuum, i.e., $\hat{n}_3 = \hat{n}_v = 1$. In this representation, light approaches from the lower left, with polarization E_p or E_s , through the film and into the vapor. Measurement of the light intensity into region 3 with or without the film present then results in a standard transmission experiment and an *absorbance* profile results. Alternatively, reflection from the substrate/film/vapor interfaces (not shown in Figure 4) can be measured. If the incident angle θ_1 is greater than a critical angle, the reflection is total but attenuated by the presence of an absorbing film. This configuration is the standard attenuated total reflection (ATR) mode.⁶¹ Zhenfeng and Ewing⁵⁵ have recently explored a variation of the reflection experiment in which the incident light is at a value of θ_1 less than the critical angle. In this optical configuration, reflection is not total. Some light escapes at the substrate/film/vapor interfaces, and some is lost by an absorbing film. We have called this attenuated partial reflection (APR). The sensitivity of APR is greater than ATR (for a single reflection) and increases the more the incident angle departs from the critical angle. The optical response, which we call *extinction*, involves both real and imaginary components of the media but can be interpreted. Calculation of thin film extinction (for comparison with observed spectra) is by way of programming the intricate electromagnetic equations⁵⁹ with their appropriate refractive indices as we have done using commercial mathematical software.^{55,56,58}

An important caveat surrounds the quantitative analysis we have described. This involves the assumption that the bulk optical constants are appropriate to thin films. This is certainly not true for water adlayers below monolayer coverage where neither the band center or band shape matches that of the infrared profile in Figure 3. On the other hand, the infrared band

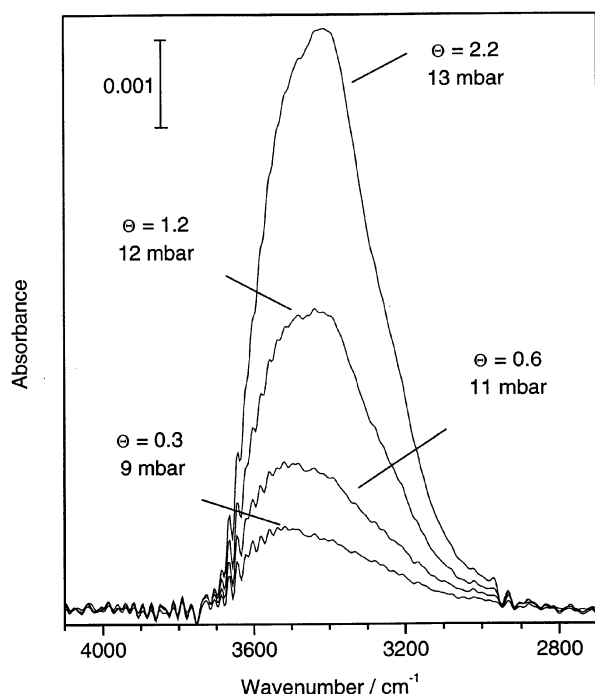


Figure 5. Absorption spectra of thin film water on NaCl(100) at 24 °C. From Foster and Ewing.⁵² Reprinted with permission from the American Institute of Physics. Copyright 2000.

of the low coverage thin film contains information waiting to be analyzed in terms of the hydrogen bonding network it implies. Buch's recent interpretations of Devlin's infrared experiments suggest the promise of this sort of analysis.^{41,62} By measuring extinction with different light polarizations through thin film water, and analysis using simple relationships,⁶³ it is possible to determine the cant of the H₂O molecular plane with respect to the substrate surface plane.

We close this section by noting that although nonlinear optical techniques^{27–30} are valuable for their sensitivity at interfaces, the infrared interrogation we describe explores the entire film: its interfaces and its interior.

Thin Film Water on NaCl(100)

Our infrared approach on this model system, initiated in 1997 by Peters and Ewing,⁵⁴ has provided considerable insight into thin films on well-defined surfaces. For example, the absorption spectrum of thin film water on NaCl(100) at 24 °C, taken from the study of Foster and Ewing,⁵² is shown in Figure 5 for a variety of H₂O gas pressures. The substrate surfaces were prepared by cleaving slabs from a single crystal boule of NaCl and exposing (almost) defect-free (100) faces. A closely spaced stack of 14 slabs was placed in a temperature controlled optical cell, that was set into the sample compartment of a Fourier transform infrared (FTIR) spectrometer and then evacuated. The small spaces between the crystal slabs and the presentation of 28 faces minimized the interfering absorption by the vapor and maximized absorption by adsorbed water. The series of spectra reveal a diffuse absorption associated with the vibrational stretching region of water molecules within the films on the NaCl(100) surfaces.

The close similarity of the water profile in Figure 3 with the 13 mbar spectrum of H₂O on NaCl(100) in Figure 5 is good evidence that the thin film is liquidlike. Use of the optical constants of liquid water and the Beer–Lambert relation has enabled us to determine coverage values as listed in Figure 5 and to construct the isotherm in Figure 6. (A monolayer, $\Theta = 1$,

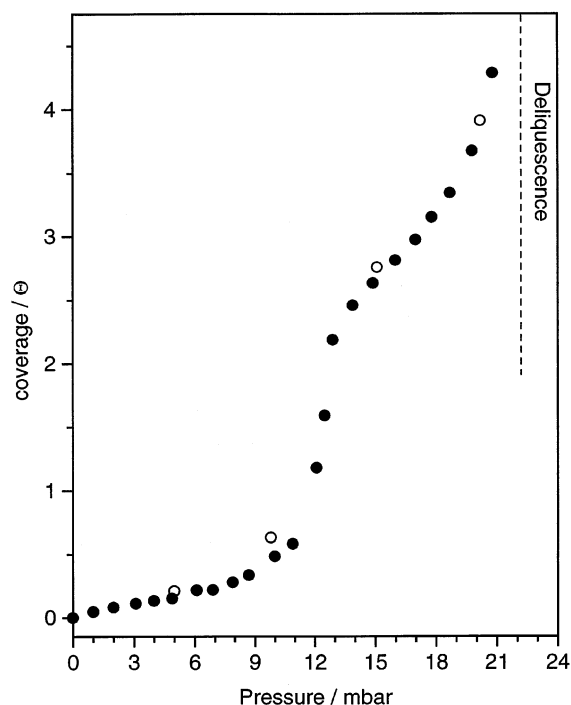


Figure 6. Adsorption isotherm of H₂O on NaCl(100) at 24 °C. The solid circles represent measurements on rising pressures, the open circles on decreasing pressures. From Foster and Ewing.⁵² Reprinted with permission from the American Institute of Physics. Copyright 2000.

corresponds to each Na⁺Cl[−] surface ion pair covered, on average, by an H₂O molecule.) To provide a context with an ambient environment, the water pressure needed to produce a monolayer on NaCl(100) corresponds to 40% relative humidity, a rather arid condition.

The isotherm for water on NaCl(100) reproduced in Figure 6 is rich in detail, its interpretation aided by the Monte Carlo calculations of Engkvist and Stone.³¹ Below a coverage of $\Theta = 0.5$ two-dimensional islands form with H₂O molecules hydrogen bonded both to each other within the island and also to the surface. This bonding structure is consistent with the shift of the adsorption maxima to high wavenumbers in the sub-monolayer spectra of Figure 5. What appears to be a phase transition occurs between $\Theta = 1$ and $\Theta = 3$ where the hydrogen bonding network now extends between layers of molecules as the film thickens. The transition then is from a two-dimensional film to a three-dimensional film. Deliquescence, the spontaneous dissolution of NaCl at 23 mbar,⁶⁴ is signaled in the isotherm by the abrupt increase in coverage above $\Theta = 4$. Interpretations, at a molecular level, of the salt dissolutions are just now being proposed.⁶⁵ Our recent study shows that deliquescence on NaCl(100), like boiling of a liquid, is a nucleated process.⁵⁰

We have measured a family of isotherms. From the changing coverage values with pressure and temperature, we have been able to extract thermodynamic quantities (ΔF , ΔH , ΔS) that characterize thin film water for H₂O on NaCl(100). For example, the enthalpy of vapor condensation to form the monolayer film is $\Delta H = -50$ kJ mol^{−1} or more exothermic than for the condensation to liquid water, which is -44 kJ mol^{−1}.⁶⁴ The monolayer film entropy is 15 J K^{−1} mol^{−1} lower than that of 70 J K^{−1} mol^{−1} for liquid water.⁶⁴ In summary, water molecules are more strongly bound to the NaCl(100) surface than in the liquid and are more ordered.

As a demonstration of the APR reflection method for the study of thin film water consider the design in Figure 7 from the study by Zhenfeng and Ewing.⁵⁵ A prism of NaCl has been

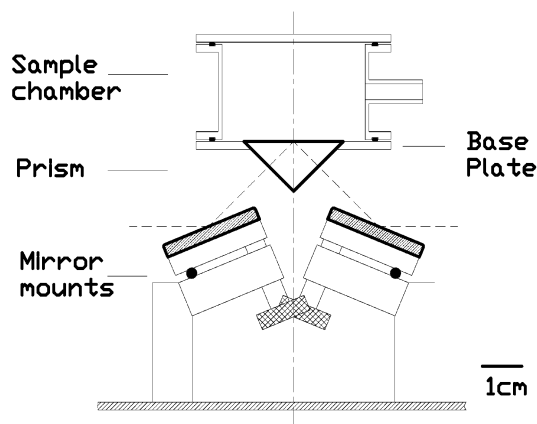


Figure 7. Apparatus for the study of thin film water by infrared extinction spectroscopy. From Zhenfeng and Ewing.⁵⁵

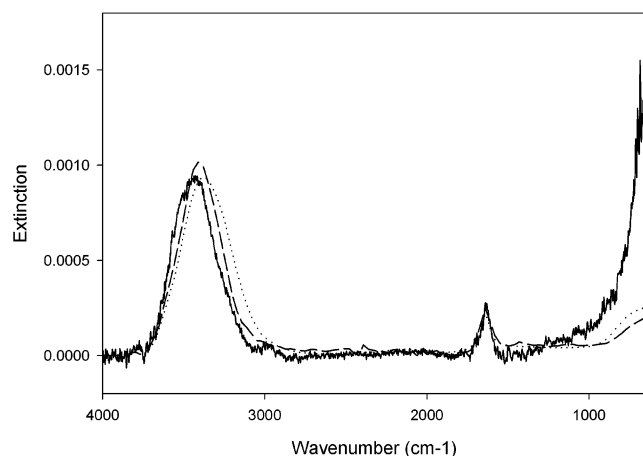


Figure 8. Infrared extinction spectrum of thin film water on NaCl(100). Es polarization was used with incident angle 45°. The solid line is the experimental spectrum at 22 °C and 16 mbar. The dashed line is the calculated spectrum of a 0.4 nm film of brine on NaCl. The dotted line is the calculated spectrum of a 0.4 nm film of water on NaCl. From Zhenfeng and Ewing.⁵⁵

fabricated so that cleavage of its upper surface reveals the (almost) defect free (100) face. Transfer mirrors permit the assembly to be used in the sample compartment of a standard FTIR instrument. Introduction of water vapor into the sample chamber results in the formation of thin film water on the NaCl(100) prism face whose spectrum (the solid line) is shown in Figure 8. The conditions of pressure and temperature are comparable to the $\Theta = 1.2$ coverage in Figure 5. The signal-to-noise for both spectra are comparable as well. This is notable because the data of Figure 5 were taken for films covering 28 NaCl(100) surfaces in the transmission measurement but only a single surface of the prism on the APR experiment. The APR method is thus much more sensitive than transmission spectroscopy. Note that the extinction for monolayer water in Figure 8 is 10^{-3} . Because the noise level of a well-tuned FTIR can approach 10^{-5} , the detection of films at the submonolayer level is realizable. Alternatively, traces of molecules dissolved in a monolayer thin film can be measured and their chemistry monitored. Note also that water vapor interferences above 3400 cm^{-1} in Figure 5 due to absorption between the many crystal slabs are absent in Figure 8.

The measurement for Figure 8 was taken with E_s polarization (electric field perpendicular to the plane of incidence) and calculated spectra using optical constants of bulk water (dotted

line) or brine (dashed line) are shown for comparison. In both cases a reasonable fit of the data is obtained with a film thickness of 0.4 nm. However, significant variations in the band center and band shape are evident. Moreover, measurements of the thin film with E_p polarization (electric field in the plane of incidence) shows extinction differences consistent with H_2O molecule tendency to lie nearly flat at the NaCl(100) surface. This observation is in accord with the predictions of Engkvist and Stone.³¹

Our spectroscopic studies of water on $\text{BaF}_2(111)$ ⁴⁹ or on mica(100)⁵¹ provide qualitatively different thin film behavior. For example, the spectroscopic profile of monolayer water on $\text{BaF}_2(111)$, a diffuse doublet, resembles that expected for an ice bilayer⁶⁶ consistent with the similarities in the $\text{BaF}_2(111)$ and basal face ice lattice constants. Thus although ambient thin film water spectra on NaCl(100) suggest a hydrogen bonding network that is liquid-like, the thin film on $\text{BaF}_2(111)$ appears ice-like even at room temperature.

Thin Film Water on Ice

To investigate the properties of thin film water on ice, we needed to develop special techniques in preparing the substrate: ice itself. A schematic representation of the apparatus developed by Sadtschenko and Ewing⁵⁷ for studies of interfacial melting of ice is given in Figure 9. The upper section of the figure shows the main chamber consisting of the cryogenic reservoir, transfer optics, and vacuum system. A detail of the thin film assembly is illustrated in the lower section of the figure. The ice is grown on the bottom surface of a germanium prism that comprises one wall of a vapor chamber. Water vapor is supplied to the chamber through a solenoid valve. The prism is in thermal contact through its upper surface to a coldfinger at the bottom of the cryogenic reservoir. A custom-built temperature control device allows temperature to be maintained to $\pm 0.01\text{ }^\circ\text{C}$ in the range -30 to $0\text{ }^\circ\text{C}$. An infrared beam from the FTIR spectrometer interrogates the ice.

Below $-10\text{ }^\circ\text{C}$ the observed infrared profile, with the H_2O stretching region band centered near 3200 cm^{-1} , is characteristic of ice. However, on approaching the triple point a shoulder near 3400 cm^{-1} , an infrared signature of liquid water, has appeared. This is shown for $-0.6\text{ }^\circ\text{C}$ in Figure 10 and is our evidence for interfacial melting of ice.

The quantitative analysis of the ice and liquid components has made use of the five layer model in Figure 11: a sandwich of germanium/liquid/ice/liquid/vapor. We have taken as non-adjustable parameters, the bulk indices of refraction of germanium (\hat{n}_s), water (\hat{n}_w), ice (\hat{n}_i), and vapor ($\hat{n}_4 = 1$) taken from literature values^{67,68} and the incident angle ($\alpha_0 = 45^\circ$) defined by the optical path of the incident light. The equations for the optical response of the stratified layers from Born and Wolf⁵⁹ were programmed and the thin film layer thicknesses for water (Z_1 and Z_3) and ice (Z_2) were adjusted to a fit of the spectroscopic extinction. The calculated profiles of the ice and liquid water components are shown for $-0.6\text{ }^\circ\text{C}$ in Figure 10. Their summation (solid line) is in excellent agreement with the observed spectrum (open circles).

The result for a variety of temperatures is shown in Figure 12. We note first that the liquid film disappears below about $-10\text{ }^\circ\text{C}$. By disappear, we mean that the contribution of the liquid component to the overall extinction spectrum becomes less than the sensitivity of our measurements, i.e., less than 0.3 nm or about one monolayer of liquid water. At the high-temperature limit of our measurement, $-0.03\text{ }^\circ\text{C}$, this thickness,

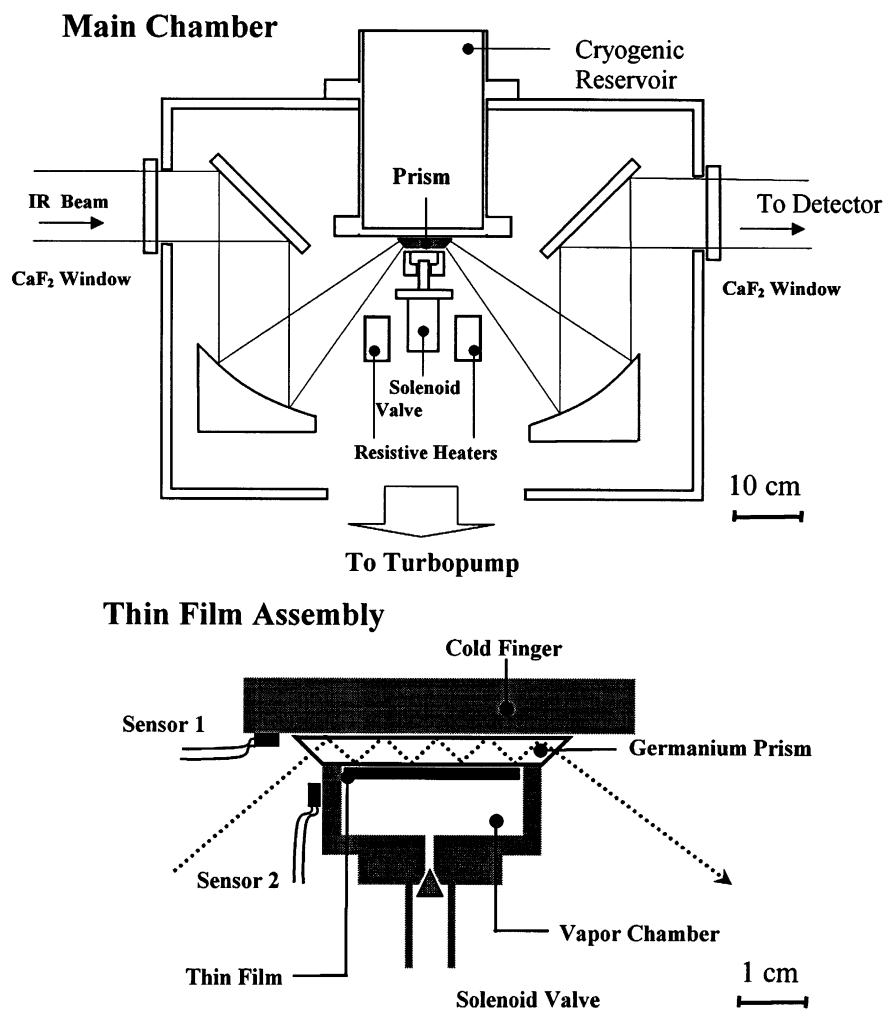


Figure 9. Apparatus for the study of ice by infrared ATR multireflection spectroscopy. Taken from Sadtschenko and Ewing.⁵⁷ Reprinted with permission from the American Institute of Physics. Copyright 2002.

15 nm, corresponds to about 45 monolayers. We believe this work attests to our ability to study surface melting of ice with a powerful technique and it opens the way for further ice surface exploration.

There is *apparent* agreement between our measurement of interfacial melting of ice (see Figure 12) and that calculated by Furukawa and Nada³⁴ (see Figure 2). Both thickness values are 1 nm at $-8\text{ }^{\circ}\text{C}$. Alas, the agreement is likely fortuitous. In the calculations their “sample” is not real ice but a model using the convenient TIP4P potential. Other measurements of surface melting give thickness values an order of magnitude greater⁶⁹ or smaller⁷⁰ than 1 nm at $-8\text{ }^{\circ}\text{C}$.

Unfortunately, in our experiments we did not distinguish the thin film layer at the ice/vapor interface from that at the germanium/ice interface. Our measurement gives the sum of the layers of both interfaces. However, because the evanescent wave that probes the ice on the prism has a penetration depth of the order of tens of nanometers, its extinction is greater for the film at the substrate/ice interface (Z_1 in Figure 9) than the one at the ice/vapor interface (Z_3 in Figure 9). By preparing a thick ice layer (say $1\text{ }\mu\text{m}$) the ice/vapor interface is beyond the reach of the ATR interrogation and only the surface/ice interface is probed. Such an experiment will then provide Z_1 . In another experiment a thin ice layer (say 10 nm) is examined so that both interfaces affect light extinction. Here Z_1 plus Z_3 can be measured. Deconvoluting these separate experiments can then uncover both Z_1 and Z_3 separately. We have described the

analysis and experiments needed to distinguish between these interfaces in a recent publication.⁷¹

What Holds a Thin Film Water Onto a Surface?

We consider first why water vapor at $24\text{ }^{\circ}\text{C}$ and 12 mbar condenses to form a monolayer thin film on NaCl(100) whereas under these conditions bulk water is not thermodynamically favored. That monolayer water on NaCl(100) is more ordered than in the bulk speaks against film stability. However, the large enthalpy of monolayer formation more than makes up for its unfavorable entropy. To appreciate this large enthalpy, we turn first to the energetics of a single water molecule on NaCl(100) and then consider the thin film.

In their analysis of a single H_2O molecule on NaCl(100), Engkvist and Stone⁷² identify four contributions to its bonding energy. Their calculations find the electrostatic energy to be -57 kJ mol^{-1} , repulsion energy at $+43\text{ kJ mol}^{-1}$, induction energy of -13 kJ mol^{-1} , and a dispersion energy of -13 kJ mol^{-1} for a net binding energy of -40 kJ mol^{-1} . It is not surprising that the electrostatic term dominates this assay because of the strong electric field arising from the ionic charges of the substrate. The Coulomb attraction of the dipole of a water molecule next to an isolated Na^+ ion is of the order of -100 kJ mol^{-1} .²⁰ The compensating repulsion of Cl^- ions in the substrate along with the appropriate Ewald summation over all the lattice charges lowers the electrostatic attraction to

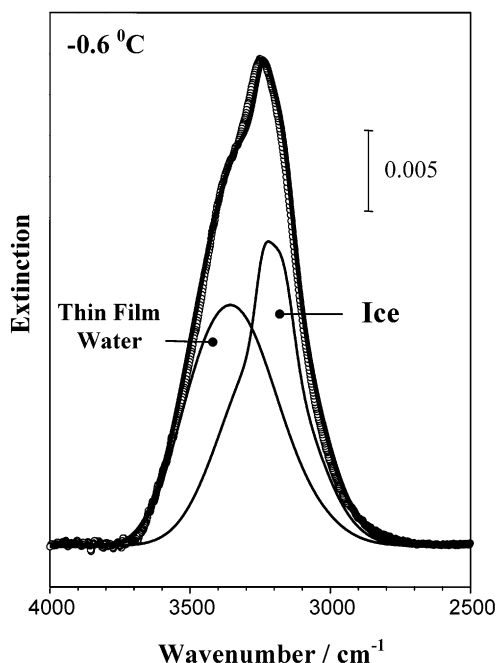


Figure 10. Deconvolution of the ATR spectra of ice into its ice and thin film water components. Taken from Sadtschenko and Ewing.⁵⁷ Reprinted with permission from the American Institute of Physics. Copyright 2002.

-57 kJ mol^{-1} . That the induction energy has a rather large contribution is again the consequence of the ionic substrate that can induce a large dipole in the water molecule drawing it to the surface. Perhaps the most surprising result in the energetics calculation is the significant dispersion contribution. If we consider H_2O and Na^+ isoelectronic to Ne and Cl^- isoelectronic to Ar, the dispersion contribution to the two-body $\text{H}_2\text{O}\cdots\text{Na}^+$ or $\text{H}_2\text{O}\cdots\text{Cl}^-$ interactions should resemble that of a van der Waals complex Ne_2 or NeAr giving an attractive energy of the order of -1 kJ mol^{-1} .⁷³ However, the dispersion attraction of a water molecule on $\text{NaCl}(100)$ involves the many nearby ions at the surface and those of the substrate just below.²⁰ This accounts for the order of magnitude increase in the dispersion attractions of H_2O on a substrate over that in a van der Waals molecule. All insulator substrates, ionic or not, will contribute significant dispersion attractions to water adsorption. The repulsion term will also contribute to energy considerations of water on all substrates.

We now move from the single molecule bound to $\text{NaCl}(100)$, to the film proper. The new energetic term is hydrogen bonding among the water clusters in the film. The energy of a single hydrogen bond estimated from the enthalpy of water condensation is -24 kJ mol^{-1} .⁴³ Because each water molecule can participate in two hydrogen bonds, hydrogen bonding can become the most significant contribution to the energetics of thin film formation.

Water adsorption on other ionic insulators such as $\text{BaF}_2(111)$ ⁴⁹ and mica^{51,60} also yield films of nanometer thicknesses for reasons consistent with the analysis of Engkvist and Stone we have just reviewed. Covalent insulators, for example borosilicate glass,⁷⁴ quartz,⁷⁵ and sapphire (Al_2O_3),⁷⁶ also accommodate nanometer thin film water. In these cases the large electrostatic contribution from the ionic substrates is replaced by strong surface hydrogen bonds for these covalent hydrophilic solids. When the insulator substrate provides neither ionic charges or hydrogen bonding (e.g., polyethylene, Teflon, etc.) then these

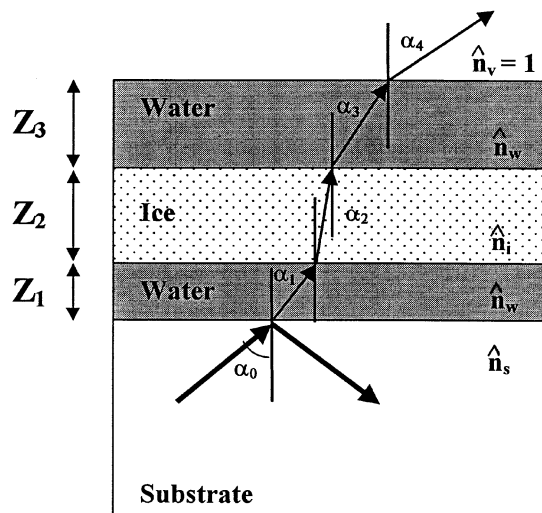


Figure 11. Five layer model for the optical study of interfacial melting of ice. Taken from Sadtschenko and Ewing.⁵⁷ Reprinted with permission from the American Institute of Physics. Copyright 2002.

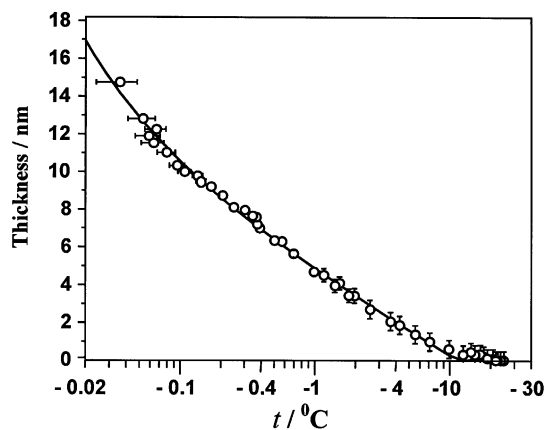


Figure 12. Thin film water thickness on ice as a function of temperature. Taken from Sadtschenko and Ewing.⁵⁷ Reprinted with permission from the American Institute of Physics. Copyright 2002.

hydrophobic solids are expected to support only submonolayers of adsorbed water bound by the ubiquitous dispersion interactions.

Rather than deal with the details of specific water molecule interactions within the film and with the individual particles (atoms, ions, molecules) that make up the substrate, it is possible to take a continuum approach. This is encompassed in the *Lifshitz theory* clearly described by Israelachvili.²⁰ Consider, for example, the three-layer case: substrate, thin film, and vapor. (We might imagine NaCl , thin film water, and its vapor.) Each layer is represented by its bulk dielectric constant and index of refraction. These physical constants, and a few others, are rolled into a number called the Hamaker constant. From the Hamaker constant the form of the isotherm is predicted as well as film thickness as a function of vapor pressure. Though these predictions appear to work for superfluid liquid helium films on a variety of substrates,²⁰ they have fallen short in describing the properties of less exotic thin films.²⁶ Because, as we have discussed for thin film water on $\text{NaCl}(100)$, strong orientational forces are important, a continuum model that is by nature isotropic is expected to be compromised.

To ask the question, "What holds thin film water onto an ice surface?" is related to the question, "What holds water molecules

together to form liquid water or ice?”. Bonding in ice can be approached from quantum mechanics by ab initio methods^{77–79} or using an empirical method employing parametrized intermolecular potential functions.^{80–82} For the purposes of our qualitative interpretation we consider the frequently used TIP4P potential.⁸³ It accounts for the principal electrostatic interactions by assigning two fractional positive charges to the H-atoms in a water molecule and two compensating fractional negative charges to its lone pairs. Dispersion and repulsion are included in two Lennard-Jones terms. The TIP4P potential can account semiquantitatively for the properties of liquid water⁸³ and ice.⁸¹ It is this potential that has been used to account for surface melting on ice by Furukawa and Nada³⁴ that we have illustrated in Figure 2 and in the original simulation by Kroes.³⁵ The presence of thin film water on ice is evident using this simple potential, and it includes the basic terms we have reviewed for thin film water on other insulators. The TIP4P potential describes the same energy terms of interaction in both the thin film and the ice substrate. However, hydrogen bond breaking at the vapor/ice interface leads to premelting and the disorder that characterizes the thin film of water as the melting temperature is approached.

To summarize, we can answer the question, “What holds thin film water onto a surface?” in a qualitative sense by calling on energetic contributions from electrostatic, induction, dispersion, and repulsion terms weighted to accord the nature of the insulator substrate. The characteristic disorder in the thin film is a consequence of symmetry breaking at the film/vapor interface and ambient temperatures.

Some Lessons

Thin films of water coat the surfaces of insulators (even ice) under ambient conditions. These films, on a nanometer scale, are ordered near the surface of their substrates but become disordered at the film/vapor interface. The energetics of thin film formation are a combination of hydrogen bonding within the adlayer, and electrostatic, induction, dispersion and repulsion of water molecules with the substrate. *Caveat lector*: these lessons arise from a handful of experiments and molecular simulations. That they will hold true for the general case will have to await further work using, along with other approaches, the infrared studies we have initiated.

Infrared spectroscopy is a convenient diagnostic for assessing hydrogen bonding networks in thin films, assessing molecular orientations, and determining film thicknesses and thermodynamic properties. Because of the sensitivity of attenuated partial reflection it has the potential for detecting substances dissolved in thin film water as well as monitoring chemical processes.

To bring closure to this article, we go back to the questions raised about water on a window pane in the first paragraph. Experiments are underway in our laboratory to bring techniques of infrared spectroscopy to explore thin film water on silica glass and its crystalline counterpart, quartz.

Acknowledgment. Thanks to those who have been partners in the research described in this article while graduate students, Steve Peters and Zhenfeng Zang, and postdoctoral associates, Dr. Michele Foster and Dr. Vlad Sadchenko. Special thanks to Dr. Anthony J. Stone of Cambridge University for his continuing contributions to our understanding of thin film water through his insight and the calculations by his group. Finally, we acknowledge the sponsorship of the National Science Foundation.

References and Notes

- (1) Warneck, P. *Chemistry of the Natural Atmosphere*; Academic Press: San Diego, 1988.
- (2) DeHann, D. O.; Brauers, T.; Oum, K.; Stutz, J.; Nordmeyer, T.; Finlayson-Pitts, B. J. *Int. Rev. Phys. Chem.* **1999**, *18*, 343–385.
- (3) Pruppacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*; Kluwer Academic Publishers: The Netherlands, 1997.
- (4) *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 2000.
- (5) Tardos, G. I.; Nicolaescu, I. V.; Ahtchi-Ali, B. *Powder Handl. Process.* **1996**, *8*, 7–15.
- (6) Allen, H. C.; Laux, J. M.; Vogt, R.; Finlayson-Pitts, B. J.; Hemminger, J. C. *J. Phys. Chem.* **1996**, *100*, 6371–6375.
- (7) Stumm, W.; Sigg, L.; Sulzberger, B. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*; Wiley: New York, 1992.
- (8) Faraday, M. Royal Institution Discourse, June 7, 1850; *Experimental Researches in Chemistry and Physics*; Taylor and Francis: New York, 1991.
- (9) Dash, J. G.; Mason, B. L.; Wettlaufer, J. S. *J. Geophys. Res.* **2001**, *106*, 20395–203407.
- (10) Rempel, A. W.; Waddington, E. D.; Wettlaufer, J. S.; Worster, M. G. *Nature* **2001**, *411*, 568–572.
- (11) Dash, J. G.; Fu, H.-Y.; Wettlaufer, J. S. *Rep. Prog. Phys.* **1995**, *58*, 115–167.
- (12) Conklin, M. H.; Bales, R. C. *J. Geophys. Res.* **1993**, *98*, 16851–16858.
- (13) Peter, T. *Annu. Rev. Phys. Chem.* **1997**, *48*, 785–822.
- (14) Dash, J. G. *Rev. Mod. Phys.* **1999**, *71*, 1737–1743.
- (15) Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1402.
- (16) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7/6–8*, 211–385.
- (17) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *46/1–8*, 1–308.
- (18) Bruch, L. W.; Glebov, A.; Toennies, J. P.; Weiss, H. J. *Chem. Phys.* **1995**, *1103*, 5109–5120.
- (19) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. *Surface Forces, (Translation from Russian)*; Kisin, V. I., Kitchener, J. A., Eds.; Consultants Bureau: New York, 1987.
- (20) Israelachvili, S. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985.
- (21) Shindo, H.; Ohashi, M.; Tateishi, O.; Seo, A. *J. Chem. Soc., Faraday Trans.* **1992**, *93*, 1169–1174.
- (22) Hu, J.; Xias, X.-D.; Ogletree, D. F.; Salmeron, M. *Science* **1995**, *268*, 267–269.
- (23) Elbaum, M.; Lipson, S. G.; Dash, J. G. *J. Cryst. Growth* **1993**, *129*, 491.
- (24) Beaglehole, D.; Nason, D. *Surf. Sci.* **1980**, *96*, 363.
- (25) Furukawa, Y.; Yamamoto, M.; Kuroda, S. *J. Cryst. Growth* **1987**, *82*, 665.
- (26) Beaglehole, D.; Radlinska, E. Z.; Ninham, B. W.; Christenson, H. K. *Phys. Rev. Lett.* **1991**, *66*, 2084.
- (27) Shang, X.; Benderskii, A. V.; Eissenthal, K. B. *J. Phys. Chem. B* **2001**, *105*, 11578.
- (28) Shen, Y. R. *Solid State Commun.* **1998**, *108*, 399–406.
- (29) Shultz, M. J.; Schnitzer, C.; Simonelli, D.; Baldelli, S. *Int. Rev. Phys. Chem.* **2000**, *19*, 123.
- (30) Becraft, K. A.; Richmond, G. L. *Langmuir* **2001**, *17*, 7721.
- (31) Engkvist, O.; Stone, A. J. *J. Chem. Phys.* **2000**, *112*, 6827–6833.
- (32) Döppenschmidt, A.; Butt, H.-J. *Langmuir* **2000**, *16*, 6709.
- (33) Wassermann, B.; Reif, J.; Matthuias, E. *Phys. Rev. B* **1994**, *50*, 2593.
- (34) Furukawa, Y.; Nada, H. *J. Phys. Chem. B* **1997**, *101*, 6167–6170.
- (35) Kroes, G.-J. *Surf. Sci.* **1992**, *275*, 365.
- (36) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; Wiley: New York, 1997.
- (37) de Gennes, P.-G.; Frochard-Wyatt, F.; Quééré, D. *Capillarity and Wetting Phenomena*; Springer-Verlag: New York, 2003.
- (38) Downing, H. D.; Williams, D. J. *Geophys. Res.* **1975**, *80*, 1656–1661.
- (39) Warren, S. G. *Appl. Opt.* **1984**, *23*, 1206–1225.
- (40) McGraw, R.; Madden, W. G.; Bergren, M. S.; Rice, S. A.; Sceats, M. G. *J. Chem. Phys.* **1978**, *69*, 3483–3496.
- (41) Buch, V.; Delzeit, L.; Blackledge, C.; Devlin, J. P. *J. Phys. Chem.* **1996**, *100*, 3732–3744.
- (42) Pimentel, G. C.; McClelland, A. L. *The Hydrogen Bond*; Reinhold: New York, 1960.
- (43) Eisenberg, D. S.; Kauzmann, W. *The Structure and Properties of Liquid Water*; Oxford University Press: New York, 1969.
- (44) Ikawa, S.-I.; Malda, S. *Spectrochim. Acta* **1968**, *24A*, 655–665.
- (45) Devlin, J. P.; Buch, V. *J. Phys. Chem.* **1995**, *99*, 16534–16548.
- (46) Horn, A. B.; Chesters, M. A.; McCustra, M. R. S.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1077–1078.

- (47) Dai, D.; Peters, S. J.; Ewing, G. E. *J. Phys. Chem.* **1995**, *99*, 10299–10304.
- (48) Ewing, G. E.; Foster, M.; W. Cantrell, W.; Sadtchenko, V. Thin Film Water on Insulator Surfaces. In *Water in Confined Geometries*; Buch, V., Devlin, J. P., Eds.; Springer-Verlag: 2003; pp 179–211.
- (49) Sadtchenko, V.; Conrad, P.; Ewing, G. E. *J. Chem. Phys.* **2002**, *116*, 4293–4301.
- (50) Cantrell, W.; McCrory, C.; Ewing, G. E. *J. Chem. Phys.* **2002**, *116*, 2116–2120.
- (51) Cantrell, W.; Ewing, G. E. *J. Phys. Chem. B* **2001**, *105*, 5434–5439.
- (52) Foster, M.; Ewing, G. E. *J. Chem. Phys.* **2000**, *112*, 6817–6826.
- (53) Peters, S. J.; Ewing, G. E. *J. Phys. Chem. B* **1997**, *101*, 10880–10886.
- (54) Peters, S. J.; Ewing, G. E. *Langmuir* **1997**, *13*, 6345–6348.
- (55) Zhang, Z.; Ewing, G. E. *Anal. Chem.* **2002**, *74*, 2578–2583.
- (56) Sadtchenko, V.; Nutt, D.; Ewing, G. E.; Stone, A. J. *Langmuir* **2002**, *18*, 4632–4636.
- (57) Sadtchenko, V.; Ewing, G. E. *J. Chem. Phys.* **2002**, *116*, 4686–4697.
- (58) Cantrell, W.; Ewing, G. E. *Appl. Spectrosc.* **2002**, *56*, 665–669.
- (59) Born, M.; Wolf, E. *Principles of Optics*, 6th ed.; Cambridge: New York, 1998.
- (60) Beaglehole, D.; Christenson, H. K. *Phys. Chem.* **1992**, *96*, 3395–3403.
- (61) Harrick, N. J. *Internal Reflection Spectroscopy*; Wiley: New York, 1967.
- (62) Devlin, J. P.; Sadley, J.; Buch, V. *J. Phys. Chem.* **2001**, *105*, 974–983.
- (63) Richardson, H. H.; Chang, H.-C.; Noda, C.; Ewing, G. E. *Surf. Sci.* **1989**, *216*,
- (64) *National Research Council (U.S.) International Critical Tables*; McGraw-Hill: New York, 1926.
- (65) Dai, Q.; Hu, J.; Salmeron, M. *J. Phys. Chem. B* **1997**, *101*, 1994–19989.
- (66) Petrenko, V. F.; Whitworth, R. W. *Physics of Ice*; Oxford University Press: Oxford, U.K., 1999.
- (67) Palik, E. O. *Handbook of Optical Constants of Solids*; Academic Press: Orlando, 1985.
- (68) Warren, S. G. *Appl. Opt.* **1984**, *23*, 1206–1225.
- (69) Golecki, I.; Jaccard, C. *J. Phys. C: Solid State Phys.* **1978**, *11*, 4229–4237.
- (70) Pittenger, P.; Fain, S., Jr.; Cochrain, M.; Donev, J.; Robertson, B.; Szuehmneher, A.; Overway, R. *Phys. Rev. B* **2001**, *63*, 134102(1–15).
- (71) Sadtchenko, V.; Ewing, G. E. *Can. J. Phys.* **2003**, *81*, 333.
- (72) Enkvist, O.; Stone, A. J. *J. Chem. Phys.* **1999**, *110*, 12089.
- (73) Parson, J. M.; Siska, P. E.; Lee, Y. T. *J. Chem. Phys.* **1972**, *56*, 1511.
- (74) Saliba, N.; Yang, H.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **2001**, *105*, 10339.
- (75) Derjagvin, B. V.; Churaev, N. V. *Langmuir* **1987**, *3*, 607.
- (76) Al-Abadleh, H. A.; Grassian, V. H. *Langmuir* **2003**, *19*, 8810.
- (77) Fletcher, N. H. *The Chemical Physics of Ice*; Cambridge University Press: Cambridge, 1970.
- (78) Davidson, E. R. *J. Chem. Phys.* **1984**, *81*, 3741.
- (79) Coulson, C. A.; Eisenberg, D. *Proc. R. Soc. London* **1966**, *291*, 454.
- (80) Matsumoto, M.; Saito, S.; Ohmine, I. *Nature* **2002**, *414*, 257.
- (81) Karm, D. A.; Haymet, A. D. J. *J. Chem. Phys.* **1988**, *89*, 6889.
- (82) Buch, V.; Sandler, P.; Sadles, J. *J. Phys. Chem. B* **1998**, *102*, 8641.
- (83) Jorgensen, W. L. *J. Am. Chem. Soc.* **1983**, *79*, 926.