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Experimental and theoretical studies of the monolayer structure of OCS adsorbed on NaCl(001): Coexistence of orientationally inequivalent phases
Adsorption of water on the NaCl(001) surface. II. An infrared study at ambient temperatures

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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.

INTRODUCTION

Thin film water coats the surfaces of many common substances under ambient conditions. In some cases it is a nuisance when, for example, the thin film is responsible for caking of detergent powders.\textsuperscript{1} On the other hand, the thin interface of water on soil particles is essential to maintaining a calcium ion balance to nearby organisms.\textsuperscript{2} Thin film water on ice particles participates in a stew of atmospheric chemical reactions\textsuperscript{3} and is likely involved in cloud electrification.\textsuperscript{4} These three widely disparate examples from myriad other possibilities show the relevance of thin film water to the physical and biological sciences. Yet despite its importance, our understanding of the structure and dynamics of thin film water at the molecular level is rudimentary. In this paper we select as a single example H\textsubscript{2}O on NaCl(001) to show that it is possible to begin to understand, at the molecular level, the properties of thin film water. This understanding is the outcome of collaborative research involving theoretical methods using realistic intermolecular potentials that are described in a companion paper by Engkvist and Stone\textsuperscript{5} and Fourier transform infrared (FTIR) spectroscopy which is the experimental technique we employ.

The emphasis of this paper will be to elucidate the structure and properties of thin film water on well-defined NaCl(001) surfaces under ambient conditions through the interpretation of infrared spectroscopy. In order to prepare for the material to follow we provide an overview of the relevant properties of well-defined NaCl(001) surfaces, water on NaCl(001), and brine. This will be followed by the main body of the paper.

OVERVIEW

NaCl(001) surfaces generated by cleaving single crystals in a dry air environment (the technique we employ) have been studied in many laboratories.\textsuperscript{5–12} The square array of Na\textsuperscript{+} and Cl\textsuperscript{−} ions at the surface offers electric fields within a typical molecular radius (e.g., 300 pm) of up to 10\textsuperscript{9} V m\textsuperscript{−1}.\textsuperscript{8}

These electric fields can hold molecules onto the surface by physisorption\textsuperscript{13} yet for most cases no chemical bonds are broken or formed. For example, secondary ion mass spectroscopy (SIMS) indicates negligible chemical reaction of the surfaces by any constituent of air (e.g., N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2}, H\textsubscript{2}O, etc.).\textsuperscript{14} Transmission electron microscopy (TEM) of gold decorated surfaces reveals smooth terraces bounded by steps of atomic dimensions spaced by 0.1 μm or so.\textsuperscript{7–9} Polarized infrared spectra of adsorbed probe molecules are consistent with the predominance of smooth defect-free terraces on a NaCl(001) face.\textsuperscript{15} Atomic force microscopy (AFM), despite observations that the probe tip can damage the surface, also provides evidence for large smooth terraces.\textsuperscript{10–12,16}

Water on NaCl(001) has been widely studied, but not under conditions that have allowed the molecular structure of the ambient thin film to be revealed. For example, monolayer H\textsubscript{2}O on NaCl(001) has been investigated near 100 K by helium atom scattering (HAS) (Ref. 17) and low energy electron diffraction (LEED).\textsuperscript{18} At these cryogenic temperatures, each water molecule is locked into an energy minimum configuration for times on the order of hours. The resulting structures are monolayer crystalline arrays. By contrast under ambient conditions (e.g., 20–30 °C and 5–20 mbar of water vapor), the lifetime of an adsorbed water molecule is microseconds\textsuperscript{19} and the mobile adlayer structure is an ensemble of many irregular configurations.\textsuperscript{5} Thin film water has also been studied on the surfaces of NaCl crystallites.\textsuperscript{8,20} However, since these defect-rich surfaces are poorly defined, the properties of adsorbed water layers are difficult to describe.

Experiments to explore water adlayers on NaCl(001) under ambient conditions include surface conductivity measurements.\textsuperscript{7} Here conductivity between silver electrodes attached to the NaCl(001) surface was measured as a function of relative humidity (RH). While conductivity rises monotonically in the low humidity regions, a break in the increase occurs near 50% RH. TEM measurements of the gold decorated surface show that step migration is initiated near this value of relative humidity.\textsuperscript{7} A variation of the AFM technique also finds step migration beginning near 50% RH.\textsuperscript{12} Some preliminary infrared studies of water adsorption...
to well defined NaCl(001) surfaces by our group have been published.\textsuperscript{23} There we monitored the adsorption of submonolayer to multilayers of water on NaCl(001) that are the prelude to its dissolution. However, the lack of accompanying theoretical investigations have permitted only speculations regarding adlayer structures. Up to now, theoretical studies have mainly been directed toward the interpretation of cryogenic crystalline adlayers.\textsuperscript{17–24}

An essential prerequisite for the theoretical study of adsorption phenomena is a reliable and accurate description of the surface–adsorbate and adsorbate–adsorbate interactions. Intermolecular potentials for many systems have been constructed successfully by Stone \textit{et al.}\textsuperscript{23,25} using single-molecule properties (distributed multipole moments and polarizabilities) together with intermolecular perturbation theory (IMPT). For the water–water interaction they used the accurate ASP-W4 potential, which has been shown to reproduce accurately energies and structures of water clusters, including many-body effects. For the water–surface interaction they used a similar approach.\textsuperscript{23}

Before accepting these intermolecular potentials to interpret the \textit{dynamic} structures of water adlayers on NaCl(001) under ambient conditions it is useful to appreciate \textit{static} structures that result from 0 K calculations of Engkvist and Stone.\textsuperscript{23} The global minimum for an isolated H\textsubscript{2}O molecule on NaCl(001) places it flat on the surface with its oxygen almost over a Na\textsuperscript{+} ion and its hydrogens pointing toward nearby Cl\textsuperscript{−} ions. Its binding energy, $D_b\textsubscript{\text{\textit{\lambda}}}$, is 40 kJ mol\textsuperscript{−1}. It is relevant to place this energy in the context of H\textsubscript{2}O in the dimer whose binding energy is only 21 kJ mol\textsuperscript{−1}.\textsuperscript{26} Thus in the energy currency of intermolecular water bonding, a single hydrogen bond is only half the binding energy of water in its favorable site on the NaCl(001) surface. Clusters of water on NaCl(001) can benefit both from attractions to the surface and to neighboring molecules. For example, one cyclic tetramer, with each molecule slightly displaced from an underlying Na\textsuperscript{+} ion towards its neighbor, yields a binding energy of 55 kJ mol\textsuperscript{−1} per water molecule. Here the O–O distance is small enough to allow for significant hydrogen bonding resulting in a cluster that is more tightly bound by 60 kJ mol\textsuperscript{−1} than four isolated monomers. The lessons from these calculations are that energy minimization is favored by cluster formation, the clusters usually involve hydrogen bonding and larger clusters tend to give rise to the greatest stabilization. We shall see the importance of these clusters in understanding the low coverage adlayers in the ambient system.

Many stable monolayer structures were also explored at 0 K. For some, water molecules reside principally above Na\textsuperscript{+} and Cl\textsuperscript{−} ion sites. The binding energies for the structures extend from 48 kJ mol\textsuperscript{−1} (least hydrogen bonded) to 55 kJ mol\textsuperscript{−1} (most hydrogen bonded). However, a quantitative comparison to the results we present here for ambient conditions is not appropriate since the theoretical values refer to a minimum of the intermolecular potential well and the thermodynamic results are enthalpies in the range 20–30 °C. In addition the theoretical structures are perfectly ordered, while the ambient adlayers are disordered.

In order to bring these theoretical methods to bear on the ambient water adlayers the multitude of configurations accessible in the range 20–30 °C needs to be sampled. Engkvist and Stone have accomplished this by Monte Carlo simulations described in a companion paper.\textsuperscript{5} We shall make direct use of their results in the interpretation of our spectra.

Brine properties are now considered. As the pressure of water vapor, at say 24 °C, is increased to 23 mbar, beads of brine appear on a salt surface signaling the onset of dissolution.\textsuperscript{27} This pressure marks the deliquescence point at which three phases are present; solid, saturated liquid solution and water vapor. The saturated solution is 5.4 M (Ref. 27), which simple calculation shows to correspond to 5.5 H\textsubscript{2}O molecules per ion. The hydrogen bonding network in neat water is surely altered by the high concentration of ions; yet as we shall see, the spectroscopic signature as reflected in the OH stretching vibrational absorption band is only slightly affected.

**EXPERIMENT**

Vibrational spectra were recorded using a Bruker IFS-66 Fourier transform infrared (FTIR) spectrometer, equipped with a liquid nitrogen cooled InSb (indium antimonide) detector. The resolution was set at 16 cm\textsuperscript{−1} and the monitored frequency region was 4500–2000 cm\textsuperscript{−1}. A background interferogram was collected with 1500 scans. The sample interferogram consisted of 1000 scans (\textsim 3 min). Both the background and sample interferograms were transformed with a four point apodization function and 2× zero filling. Absorbance, $A = \text{log}(I_0/I)$, was plotted as a function of wave number, $\tilde{v}$, using a single-beam sample spectrum intensity, $I$, and the appropriate background intensity, $I_0$. Peak-to-peak noise under these conditions was $A = 5 \times 10^{-5}$. Water vapor features, which can obscure absorbance by the adlayer, were reduced by purging the spectrometer and subtracting out a reference spectrum of water vapor that had been appropriately scaled. The integrated absorbance, $\tilde{A} = \int_{\text{band}} \text{log}(I_0/I) d\tilde{v}$, was obtained by a numerical integration procedure.

For these spectroscopic measurements, 10–15 NaCl crystals were placed in a cylindrical stainless steel cell, a schematic of which is shown in Fig. 1. The 21 mm×21 mm × 10 mm crystals were obtained by cleaving, with a hammer and chisel, larger single crystals of NaCl (Harshaw/Bicron) under a nitrogen purge. Spacers made of 0.1 mm diam Ta wire were sandwiched between the crystals so that the NaCl faces did not touch. Silicon windows (Infrared Optical Products, Inc.) were attached to both ends of the cell, and sealed with Viton O-rings. Copper tubing coiled around the exterior of the cell was attached to a recirculating bath from a variable temperature unit (Julabo, FP50), that was used to control the temperature of the crystals from −30 to 100 °C to within ±1 °C. Temperature was monitored by a thermocouple within the cell. Evacuated chambers (not shown) were attached to either side of the main cell with polished CaF\textsubscript{2} windows (Infrared Optical Products, Inc.) to ease any temperature differential between the cell and room temperature. The entire cell was placed into the spectrometer compartment.
The cell was attached to a vacuum line and pumped with a diffusion pump to a base pressure in the $10^{-6}$ mbar range. The cell and line were baked under vacuum at 100 °C overnight to remove contaminants. The water vapor was obtained from a liquid sample (Sigma, HPLC grade) and further purified by a number of freeze–pump–thaw cycles. Before experiments, the crystal temperature was allowed to equilibrate overnight. Water vapor was then introduced at the desired pressure, as monitored by a Baratron gauge (MKS Instruments, Inc.) accurate to ±10%, and the adlayer of water on the NaCl(001) faces was monitored by transmission spectroscopy.

**RESULTS**

Absorption spectra of water adsorbed to NaCl(001) at 24 °C for a variety of pressures are shown in Fig. 2. The bands are all broad with full width at half-height of typically 350 cm$^{-1}$. At the lowest pressure shown here, 9 mbar, the band is asymmetric, with shading toward lower wavenumbers, and its center at 3515 ± 10 cm$^{-1}$. Increasing pressure causes the band to become more symmetric and to shift to lower wave numbers. Near 13 mbar, the band center, now at 3415 ± 10 cm$^{-1}$, is invariant to further pressure increases. Absorbances change in an involved way with pressure increases. For example, a pressure increase from 9 to 11 mbar results in a doubling of absorbance but an increase by the same increment, from 11 to 13 mbar, results in a fourfold absorbance change. In the discussion to follow we shall quantitatively relate the integrated absorbances, $\hat{A}$, to coverage values, $\Theta$, the number of water molecules per NaCl ion pair at the (001) surface. Coverages are provided in both Figs. 2 and 3 which summarize band center changes. In Fig. 3, the band center increases monotonically with coverage in the submonolayer region, then abruptly increases to its limiting value near $\Theta = 1$.

Spectra shown in Fig. 2 obtained sequentially for increasing pressures are essentially superimposable for corresponding coverages on decreasing pressures. Thus the spectra show negligible hysteresis. Band shapes and centers for comparable coverages are nearly superimposable at different temperatures. This is illustrated in Fig. 4 for near monolayer coverages at 30, 0, and −30 °C. Likewise little difference is observed in the spectra for monolayer water on NaCl(001) near 20 °C and either neat liquid$^{28}$ or 5 M brine$^{29}$ as shown in Fig. 5.

Hundreds of spectra taken over many months from temperatures ranging from −30 to 40 °C were reproducible whether using a single set of crystals for multiple runs or when a new set of crystals was introduced. Visual examination of crystals after use showed no obvious change in the appearance of the surfaces. They remained shiny and clear.

**FIG. 1.** The cell used for transmission FTIR experiments.

**FIG. 2.** Absorption spectra of water adsorbed on NaCl(001) at 24 °C for several pressures and coverage values. The number of NaCl(001) crystal faces for these experiments is $N = 28$.

**FIG. 3.** Band center change with water coverages on NaCl(001) at 24 °C. Data taken on ascending and descending pressures are given by the closed circles and open circles, respectively.
However, we were always careful to maintain water vapor pressures below the deliquescence point where surface degradation (i.e., dissolution) is known to occur.

**DISCUSSION**

Spectroscopic signatures contain information on the environments of water molecules. The OH stretching vibration band systems (the $v_1$, $v_3$ modes) are particularly sensitive probes of hydrogen bonding networks and will be used to surmise adlayer structures on NaCl(001) in our study. The myriad vibrotor features of the gas, with band centers at 3652 and 3756 cm$^{-1}$ (Ref. 31) transform into a single diffuse absorption at 3420 cm$^{-1}$ on condensation to the liquid. This large down shift is accompanied by a correspondingly dramatic increase in the combined $v_1$, $v_3$ integrated cross sections from $8.14 \times 10^{-18}$ cm molecule$^{-1}$ for the gas$^{32}$ to 1.44 $\times 10^{-16}$ cm molecule$^{-1}$ for the liquid.$^{28}$

In their review of a large number of molecular systems, Pimentel and McClelland$^{30}$ demonstrate that as the strength of the hydrogen bonding increases, so does the integrated cross sections for the OH stretching vibration while its frequency decreases. The behavior of neat water on changing from gas to liquid is then typical of more general spectroscopic observations.

Surprisingly, the band center and band shape of water in a 5 M NaCl solution is only subtly different from that of the neat liquid, as comparisons in Fig. 5 show. With the demonstrated spectroscopic response to changes in hydrogen bonding$^{33}$ one might have expected for a 5 M NaCl solution, with each ion associated with 5.5 H$_2$O molecules, more significant changes in band position and shape. Alteration in integrated cross section is correspondingly slight, with 1.39 $\times 10^{-16}$ cm molecule$^{-1}$ for 5 M NaCl (Ref. 29) being only 3.5% lower than neat water. Other salt solutions with different anions and cations can show more profound spectroscopic responses.$^{34}$

In ice, each water molecule participates in four hydrogen bonds with its neighbors so that the randomly broken hydrogen bonds in the liquid are healed on freezing. In keeping with the correlations already established,$^{30}$ the completed hydrogen bonding network in ice results in a band center at 3220 cm$^{-1},^{35}$ downshifted by 200 cm$^{-1}$ from the liquid and, in agreement with the expected trend, a higher integrated cross section, $2.33 \times 10^{-16}$ cm molecule$^{-1}$.

Finally turning to the system at hand, the near coincidence of the spectroscopic signature of thin film water on NaCl(001), at 24 °C and above 12 mbar (Fig. 2), to that of brine or liquid water (Fig. 5) suggests the hydrogen bonding network in the adlayer is liquidlike. Later we shall associate this adlayer with multilayer thin film water. At lower pressures, say below 9 mbar, the band center is shifted to 3500 cm$^{-1}$. This is between the neat liquid value and that of non-hydrogen bonded (e.g., gas phase water) OH vibrations. We shall associate this adlayer with thin film water in submonolayer islands.

Photometry allows quantitative estimation of adlayer coverages from absorbance measurements. The close resemblance of the spectroscopic signatures of bulk water or brine for the higher pressure adlayers on NaCl(001) suggests similarity in hydrogen bonding networks and thus optical properties. In particular we shall assume that their integrated cross sections are equal. The integrated cross section of bulk water at 24 °C was determined from the measured wavenumber-dependent imaginary component, $\kappa$, of the index of refraction$^{37}$ using

$$\bar{\sigma} = \left( \frac{4 \pi}{\rho} \right) \int \kappa \, d \bar{\nu},$$

where $\rho$ is the density of water.

**FIG. 4.** Absorption spectra for monolayer coverages of H$_2$O on NaCl(001) at several temperatures.

**FIG. 5.** Absorption spectra of neat water, brine and monolayer water on NaCl(001) near 24 °C. The neat water data are taken from Ref. 28. The brine data are 5 M NaCl from Ref. 29.
where \( \rho = 3.3 \times 10^{22} \text{ molecules cm}^{-3} \) (Ref. 27) is the molecular density of water and the band integration limits, 2800–3800 cm\(^{-1}\), encompass values of \( \kappa \) to within a few percent of its maximum for this vibrational absorption. The result is \( \bar{\sigma} = 1.4 \times 10^{-16} \text{ cm molecule}^{-1} \). The surface density of adsorbed water, \( S_{\text{H}_2\text{O}} \), is then obtained from a modified Beer–Lambert relationship,

\[
\bar{\sigma} = \frac{N\bar{A}S_{\text{H}_2\text{O}}}{2.303}
\]

with \( N \) as the number of NaCl(001) surfaces and \( \bar{A} \) is the integrated absorbance of the adlayer over the same wave number range used to obtain \( \bar{\sigma} \). Finally the coverage is obtained from

\[
\Theta = \frac{S_{\text{H}_2\text{O}}}{S_{\text{NaCl}}},
\]

where \( S_{\text{NaCl}} = 6.4 \times 10^{14} \text{ cm}^{-2} \), the surface density of ion pairs, calculated for the NaCl(001) face.\(^2\)\(^7\) Using this procedure, coverage values have been assigned to the adlayer spectra in Figs. 2–5. Use of salt solution optical constants, e.g., 5 M NaCl, alter the values of \( \Theta \) by less than 5%.

While we can justify the use of water (or salt solution) optical constants to calculate coverages when the band profiles of the bulk liquid and adlayers are similar, there is a systematic error introduced when the profiles differ as they do in the lower coverage features, which we shall associate with the submonolayer island adlayer. In correlations between integrated cross section and band center for hydrogen bonding systems just reviewed, we anticipate lower values of \( \bar{\sigma} \) for the higher vibrational frequency of the low coverage region. Following this change through Eqs. (1)–(3) we anticipate \( \Theta \) to be underestimated by 10%–35% in the lower coverage region.

Isotherms may be extracted from the pressure dependent adlayer spectra through the photometry analysis just described. Using the spectra shown in Fig. 2, and others as well, we present the 24 °C isotherm in Fig. 6. Coverages obtained from spectra taken on ascending pressures are given by the closed circles while data taken on descending pressures are given by open circles. The slight differences can be ascribed to random errors in obtained values of integrated absorbance values. Thus the isotherm exhibits little if any hysteresis.

Isotherms of water on NaCl crystallites under ambient conditions from other laboratories have been reported.\(^8\),\(^2\)\(^0\) While these isotherm shapes resemble that in Fig. 6 for coverages beyond monolayer, there are qualitative differences in the submonolayer region. These differences can be rationalized by the abundance of defects on the surfaces of the crystallites. Adsorption to defects is expected to be favored over adsorption to the smooth terraces of single crystal NaCl(001) faces.\(^3\)\(^9\) This expectation is consistent with the observations that find a higher water adlayer coverage for a given pressure on NaCl crystallites than on the NaCl(001) faces of single crystals.\(^8\)

Four separate regions can be distinguished in the isotherm of Fig. 6. The low coverage region, with \( \Theta \approx 0.5 \), is characterized by a linear increase in coverage becoming slightly concave at the end of this region. Later we shall identify the low coverage region with islands of water molecules bound to the surface and held together by hydrogen bonds. In the transition region, with 0.5 ≤ \( \Theta \) ≤ 2.5, a sharp (near vertical) rise in coverage is accompanied by pressure increases with an inflection point near \( \Theta = 1.5 \). The transition region will later be proposed to consist of co-existing submonolayer islands and multilayer thin film water structures. The high coverage region, with 2.5 ≤ \( \Theta \) ≤ 3.5, is characterized by a more gentle increase in coverage with pressure. We shall associate the high coverage region with a multilayer bound by a hydrogen bond network resembling that in liquid water. An inflection point near \( \Theta = 3.5 \) signals another upturn in coverage with increasing pressure as the deliquescence point is approached. We shall call coverages with \( \Theta \geq 3.5 \) the presolution region.

In order to present isotherms for NaCl(001) at other temperatures, the wide variation in pressures necessary to produce convenient coverages make use of a logarithmic scale desirable. A sampling of isotherms at −12, 3, and 24 °C is presented in Fig. 7. While the distinct break between the low coverage and transition regions in these isotherms is evident, the logarithmic scale blurs the other regions. The tick marks at the top of this figure indicate deliquescence pressures at the corresponding temperatures.\(^2\)\(^7\) We shall use these and other isotherms to obtain thermodynamic values, but first we shall interpret their shapes.

The shapes of adsorption isotherms have been sources of information on adlayer structures since the interpretations provided by Brunauer et al.\(^4\)\(^0\) in 1940. In the spirit of their analysis, we shall compare the shape of the isotherm of Fig. 6 with isotherms of systems where adlayer structures have been established by infrared spectroscopy, diffraction tech-
Multilayer crystalline CO is formed at \( p/p_0 = 1 \). When the multilayer does form, the original monolayer structure [with CO molecules centered over Na\(^+\) ions and each axis perpendicular to the (001) face\(^13\)] is not appreciably altered.\(^2\) Since the multilayer spectrum is identical to that of the \( \alpha \)-phase of the crystal,\(^43\) the second and higher layers have CO molecules aligned along the diagonals of their cubic unit cell. This structural stability for the CO monolayer with multilayer formation on top is not found for \( \text{H}_2\text{O} \) on NaCl(001) under ambient conditions as we shall see.

Returning to the isotherm of major concern, \( \text{H}_2\text{O} \) on NaCl(001) at 24 °C, there is no similarity with the Langmuir form. The convex shape of the Langmuir form is in contrast to the concavity of the isotherm in Fig. 6, in the low coverage region. Furthermore the ambient water adlayer does not saturate at \( \Theta = 1 \).

While lateral interactions are not important to submonolayer and monolayer CO system at 55 K, as implied by its accurate modeling with a Langmuir isotherm, they do become important below 30 K. This temperature signals a phase transition in which the CO axis becomes tilted.\(^13,44\) To judge whether lateral interactions are important to an adlayer structure, it is helpful to compare \( nW \), where \( n \) is the number of nearest neighbors and \( W \) is the pairwise molecular interaction, with \( RT \).

The quasichemical model treats nearest neighbor lateral interactions through the parameter \( nW/RT \).\(^45\) The form of the resulting isotherm for \( nW/RT = -4 \) (i.e., an attractive interaction), is shown in Fig. 8. This isotherm is concave for low coverages with an inflection point at \( \Theta = 0.5 \). Above half coverage it becomes convex as it approaches saturation at \( \Theta = 1 \). The physical interpretation of the adlayer structure is that at low coverages molecules adsorb randomly and can be treated as a two-dimensional lattice gas. For high coverages lateral interactions are responsible for two-dimensional crystalline island formations. A coexistence region at \( \Theta = 0.5 \) finds both lattice gas and crystal phases in the adlayer. At cryogenic temperatures, several small molecules\(^46–48\) including \( \text{H}_2\text{O} \) (Refs. 17, 18) are well represented by the quasichemical isotherm. For \( \text{CO}_2 \) on NaCl(001) molecular quadrupoles are the chief source of the lateral interaction.\(^47\) Spectroscopic evidence for both lattice gas\(^48\) and two-dimensional crystalline phases\(^47\) of \( \text{CO}_2 \) near 100 K has been found. For \( \text{H}_2\text{O} \) on NaCl(001) near 100 K with the molecules nearly centered over Na\(^+\),\(^17,23\) they are separated too far for hydrogen bonds to form so dipole attraction is the major lateral interaction. For these cryogenic studies half-coverage occurs for \( p/p_0 < 1 \).

There are some qualitative similarities between the quasichemical isotherm of Fig. 8 and that for ambient \( \text{H}_2\text{O} \) on NaCl(001) in Fig. 6. In the low coverage region both show concavity. Both reveal a near vertical rise. However for the quasichemical model, the inflection is at \( \Theta = 0.5 \) while for \( \text{H}_2\text{O} \) on NaCl(001) it is near \( \Theta = 1.5 \). Thus for the room temperature water adlayer, the low and transition coverage regions suggest the importance of lateral interactions but not those necessarily described by lattice gas and island phases.
An analytical model that incorporates multilayer interactions is that of Brunauer, Emmett, and Teller (BET).\textsuperscript{49} The model contains within its parameters the enthalpies of adsorption and bulk condensation. Lateral interactions are ignored (e.g., \( n_w = 0 \)). An example of a BET isotherm (type III from Brunauer\textsuperscript{46}) is shown in Fig. 8. The nature of the model allows multilayer formation as revealed by the asymptotic approach of multilayer formation as \( p \to p_0 \). Despite its denial of lateral interactions, many experimental systems are well represented by the form of the BET isotherm. While the high coverage regions of the BET isotherm form of Fig. 8 is in qualitative agreement with the high coverage and resolution regions of the water isotherm of Fig. 6, representation in the low and transition regions are lacking. (We can actually force a BET isotherm into reasonable quantitative agreement with that in Fig. 6 by fiddling with adjustable parameters. However, fitting data is not the aim of this paper.)

The Langmuir and quasichemical monolayers, both the model and the real systems at cryogenic temperatures we have given as examples, remain stable monolayer structures well beyond saturation pressures. In the case of CO on NaCl(001), pressure increases beyond those required for effective saturation of many orders of magnitude are required before multilayer adsorption is initiated. Thus in these systems clear distinctions among lattice gas, islands, monolayer, and multilayer phases are realizable. This is possible because, at the cryogenic temperatures of these experiments, the free energy differences among the different phases are typically much greater than \( RT \), so they are easily resolved. For the BET isotherm, coverages from submonolayer to multilayer have become blurred as they appear to be for \( \text{H}_2\text{O} \) on NaCl(001) under ambient conditions.

We now summarize comparisons between the water on the NaCl(001) isotherm at 24 °C of Fig. 6 and the model isotherms of Fig. 8. The Langmuir isotherm and the water isotherm appear to have no common features. We conclude that \( \text{H}_2\text{O} \) molecules do not adsorb randomly to NaCl(001) under ambient conditions. The concavity and the sharp rise in the quasichemical isotherm bear qualitative resemblance to the ambient water isotherm. This suggests the importance of lateral interactions in the \( \text{H}_2\text{O} \) adlayer. However, the quantitative mismatch of the inflection points (\( \Theta = 0.5 \) for the quasichemical isotherm and \( \Theta = 1.5 \) in Fig. 6) suggest a different nature of the coexistence phases for the model system and ambient \( \text{H}_2\text{O} \) in NaCl(001). Finally the BET isotherm and adlayer water reveal a similarity but only in the high coverage and resolution regions. Clearly attraction between layers is important. These qualitative comparisons of the model isotherms with that of adlayer \( \text{H}_2\text{O} \) on NaCl(001) appear to be at the limit to the interpretations of the nature of thin film water we can offer from this type of data.

The Monte Carlo calculations of Engkvist and Stone\textsuperscript{5} allow us to deepen our understanding of the thin film molecular structures implied by the observed isotherms. While they provide quantitative information in the form of pair distribution functions, we shall draw from their calculations two configurations corresponding to coverages of \( \Theta = 0.5 \) and \( \Theta = 3.0 \). These are shown in Fig. 9. The exploded views into three distinct layers above the NaCl(001) surface, \( 0 \leq z \leq 360 \text{ pm} \), \( 360 \leq z \leq 640 \text{ pm} \), and \( 640 \leq z \leq 960 \text{ pm} \), provide easier visualization of adlayer structures. These spacings have been guided by the layering revealed by the Monte Carlo distribution functions.

Layer 1 for \( \Theta = 0.5 \) appears a random assemblage of monomers and small clusters. However, the distribution functions actually indicate\textsuperscript{3} that the molecules are not randomly distributed but favor an \( \text{O}–\text{O} \) separation consistent with hydrogen bond formation. Moreover \( \text{H}_2\text{O} \) molecules are more likely over \( \text{Na}^+ \) than \( \text{Cl}^- \) ions. Examination of a number of Monte Carlo configurations suggest that molecules in layer 1 are rather anchored to the underlying ions. The few molecules in layer 2, some directly above molecules in layer 1, suggest the beginning of multilayer formation.

For a coverage of \( \Theta = 3 \), the water molecules are distinctly partitioned into three layers. This is clearly evident in the distribution function that explores molecular positions perpendicular to the (001) face.\textsuperscript{5} The molecules in layer 1 are now influenced by molecules in layer 2 as well as by the substrate below. Thus while 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 \( \text{O}–\text{O} \) separation finds a value near that of liquid water. Thus the adlayer for \( \Theta = 3 \) resembles liquid water.

Thermodynamic analysis of the isotherms follows the procedures laid out by Larher\textsuperscript{50} and discussed by Glachant and Bard\textsuperscript{51}. The equilibrium water vapor pressure above the salt substrate \( p_\Theta \), for coverage \( \Theta \), is expressed by

\[
\ln p_\Theta = \frac{\Delta H_\Theta}{RT} - \frac{\Delta S_\Theta}{R},
\]

where the subscript gives the number of adsorbed layers on the NaCl(001) face so \( \Theta = 1 \) represents a monolayer while \( \Theta = \infty \) represents bulk brine solution. The enthalpy of adsorption is specified for a coverage \( \Delta H_\Theta = U_\Theta - H_\Theta \), with \( U_\Theta \) the molar energy of layer \( \Theta \) and \( H_\Theta \) is the enthalpy of gas phase water. The entropy term is given by \( \Delta S_\Theta = S_\Theta \).
The differential of Eq. (4) evaluated at coverage $\Theta$ is

$$\frac{d(\ln p_{\Theta})}{d(1/T)} = \Delta H_{\Theta}/R,$$  

which can be recognized as a recasting of the Clausius–Clapeyron relationship.

Values of $\Delta H_{\Theta}$ are presented as a function of coverage in Fig. 10. These enthalpies were obtained from the data like those given in Fig. 7 by plotting $\ln p_{\Theta}$ vs $1/T$ and determining (by least squares) the slope for selected values of coverage using Eq. (5). Since these plots reveal no apparent curvature in the region from 10 to 30 °C we take the enthalpy of adsorption to be invariant, within our error limits, in this temperature range. For comparison the dotted line gives the value for heat of condensation of adsorbed water on saturated brine. (The heat of condensation of vapor on neat water, $-44 \text{ J mol}^{-1}$, is to two significant figures the same as on brine.)

We note first that in general, the exothermicity of water condensation to NaCl(001) is greater than in saturated brine (or neat liquid water). The difference being greatest near $\Theta = 1$. This is consistent with the calculations of Engkvist and Stone, which show, for example, that the binding of an isolated molecule of H$_2$O to a Na$^+$ site on NaCl(001) is much greater than H$_2$O to itself in the liquid. Thus water in the monolayer that can participate in surface attraction as well as hydrogen bonding to its neighbors is energetically favored over a liquid phase.

The enthalpy becomes less exothermic at both lower and higher coverages. For submonolayer coverages, e.g., $\Theta < 0.5$, water resides in small islands, bonded to the surface. Molecules within the cluster can hydrogen bond, others at the periphery lack neighbors with which they can bond. At higher coverages, e.g., $\Theta > 2$, molecules in the upper por-

**FIG. 10.** Adsorption enthalpies of water on NaCl(001) as a function of coverage at 24 °C. The dashed vertical line gives the enthalpy of bulk condensation of water.

$-S_a$ where $S_\Theta$ is the entropy at a coverage of $\Theta$ and $S_a$ is the entropy of water vapor. The differential of Eq. (4) evaluated at coverage $\Theta$ is

$$\frac{d(\ln p_{\Theta})}{d(1/T)} = \Delta H_{\Theta}/R,$$

where $\Delta S_a$ is the entropy difference between the saturated brine solution and the adsorbed film on NaCl(001). The equilibrium vapor pressure above a saturated brine solution is $p_a$ and $\Delta H_{\Theta}$ is the enthalpy of vapor condensation onto the salt solution.

The entropy difference between the saturated salt solution and the adlayer, $\Delta S_a$ implies structural information on the thin film. At a coverage of $\Theta = 1$, using $\Delta H_{\Theta} = -44 \text{ kJ mol}^{-1}$ (Ref. 27) and $\Delta H_{\Theta} = -50 \text{ kJ mol}^{-1}$ from Fig. 10, $p_a = 12 \text{ mbar}$ from the isotherm at 24 °C together with $p_a = 10 \text{ mbar}$, and $\Delta H_{\Theta} = -48 \text{ kJ mol}^{-1}$ we find $\Delta S_a = 7 \text{ J K}^{-1} \text{ mol}^{-1}$. The entropy difference has decreased. This is likely due to the configurational entropy of the incompletely filled adlayer. At a coverage beyond monolayer, say $\Theta = 3$, we find $\Delta S_a = 8 \text{ J K}^{-1} \text{ mol}^{-1}$ and again the entropy difference is less but for a different reason. At $\Theta = 3$ much of the adlayer is now removed from the locking influence of the NaCl(001) surface and the thin film is approaching a liquid quality. As $\Theta \to \infty$, as inspection of Eq. (6) shows, $\Delta S_a \to 0$, as indeed it must as thick film saturated brine on NaCl(001) becomes indistinguishable from bulk liquid brine.

We draw from the results of this paper, its companion, the measurements of others and in addition, we offer some speculations.

The phase diagram that describes the crystalline states of thin film solid water on NaCl(001) is complex. At some temperature, not yet determined, these phases melt or sublime. As we move to ambient temperatures we arrive at the disordered phases we have uncovered.
near Na$^+$ ions. The absorptions will be weak not only because of their low surface density but also because of the anticipated low integrated cross sections.$^{32}$

As the coverage increases, to say $\Theta = 0.1$, lateral interactions among adsorbed molecules become important and islands begin to form. We begin to detect this new phase in our spectroscopy as shown in Fig. 3 with a diffuse band centered near 3520 cm$^{-1}$. Both its diffuseness and its higher frequency signal the formation of a hydrogen bonded network. However, hydrogen bonding is essentially lateral and restricted to the available molecules confined to the submonolayer directly above the NaCl(001) face. The band’s 100 cm$^{-1}$ shift from the signature for bulk liquid water suggests an amorphous structuring of the islands. This then is a description of the phase in the low coverage region.

As the islands grow with coverage, the band center moves gradually toward higher wavenumber. An abrupt shift occurs in the band center from between $\Theta = 0.5$ and 1 and comes to rest at 3420 cm$^{-1}$ as documented in Fig. 3. This feature coupled with the near vertical rise in the isotherm between $\Theta = 0.5$ and 2, shown in Fig. 6, we have labeled the transition region. This signals what appears to be a phase transition to liquid like water. The transition region marks a fundamental change in the bonding pattern from lateral hydrogen bonding that complements bonding of the submonolayer to the substrate (low coverage region) to isotropic hydrogen bonding resembling that in liquid water (high coverage region). In the transition region we have a coexistence of adlayer water phases with distinctly different hydrogen bonding patterns.

The near vertical rise of the isotherm in the transition region is reminiscent of a number of other examples in which bonding patterns are abruptly changing. The transformation from a two-dimensional lattice gas to a twodimensional island is described by the quasicontinuous model we have already cited. What is required for our case is a model that accounts for bonding pattern changes from islands to multilayer bonding networks. Percolation theory,$^{52}$ which interprets phase transitions by (idealized) bonding pattern changes in a variety of systems, is perhaps needed here.

The nature of the thin film in the transition region is suggested by the (near) spectroscopic invariance of the absorption band as the temperature is lowered to $-30^\circ $C as shown in Fig. 4. This temperature is well below both the freezing point of neat water, $0^\circ $C, and the eutectic point of saturated brine, $-21^\circ $C, where monoclinic crystals of NaCl·2H$_2$O form.$^{27}$ The invariant spectra in Fig. 4 confirm that no monolayer crystal forms in this temperature range and the thin film remains amorphous (liquid or glassy).

It is not clear how to relate the abrupt change in surface electrical conductivity$^7$ and step migrations$^{7,12}$ near 50% RH [corresponding to 15 mbar at 24$^\circ $C (Ref. 27)] with the isotherm of Fig. 6. Conductivity changes respond to (trace) changes in ion content and mobility within the thin film while the observations of step migrations are following the dynamics of surface defect (i.e., ion) mobility. The spectroscopy is primarily sensitive to hydrogen bonded molecules while the theoretical modeling purposely avoids defects.

As we move to the high coverage region, say $\Theta = 3$, water molecules in layer 1 are bound by both the substrate and molecules above. However, because of the high concentration of water, any molecule in layer 1 is as much influenced by those above it as by those to the sides. Even the substrate below has much less influence on bonding properties. We characterize this a multilayer phase.

The nature of the phase of the presolution region is largely unexplored except for the isotherm segment above $\Theta = 3.5$ in Fig. 6. At some coverage, a significant concentration of ions will become incorporated into the film just before the deliquesce point is reached. Here we must include in addition to H$_2$O within the phase, Na$^+$ and Cl$^-$ ions as additional components. The description of this phase may be somewhat analogous to the exponential growth of thin film water on an ice surface as its melting temperature is approached.$^{53}$ Both experimental and theoretical studies of the presolution region for both NaCl and other soluble solids are needed.

We now speculate on the nature of the final phase of adlayer water on NaCl(001) that will be achieved at the deliquesce point with a saturated brine solution in equilibrium both with water vapor and the underlying surface of crystalline NaCl. Near the interface the ions of the solid surface will have become disordered and intermingled with water molecules. At some distance above this interface, solvated ions will be present. Anions and cations will likely have different (and complex) concentration behavior near the interfacial region.$^{54}$ At some distant displacement from the region, the anion and cation concentrations will approach each other and that of the equilibrium bulk saturated solution. Within this final adlayer phase complex profiles of water, anion, cation concentrations along the $z$-direction are expected. Because of the charge distribution, an intricate electric potential profile is implied between the substrate and the brine substrate in the interfacial region.

The properties of this final adlayer phase as well as the mechanism of dissolution are as yet unexplored.

**AFTERWORD**

The adlayer structures of ambient thin film water on NaCl(001) are varied and complex. Through spectroscopic observations and Monte Carlo calculations we have identified two structures.

At low adlayer coverages, the water molecules making up the submonolayer aggregate into islands. The adlayer stability for this structure is principally achieved by water attraction to the substrate, with lateral hydrogen bonds among neighbors contributing to the island formation. When a critical adlayer concentration is reached, multilayer growth suddenly becomes favorable. In this structure, the bonding arrangement is qualitatively different. Now hydrogen bonding among neighbors is the principle attraction and bonding to the substrate is of secondary importance. The distinct change in bonding networks between these two thin film structures is reflected in the abrupt spectroscopic shift in the band center and the shape of the isotherm.

Both these adlayer structures that comprise the thin film occur at pressures of water vapor well below the deliquesce point, thus solubilization of the NaCl has not occurred.
At higher pressures, as adlayer coverages increase and salt dissolution commences, new adlayer structures will occur.

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