Photoemission from ice and water surfaces: Quasiliquid layer effect

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Photoemission studies of ice and water have been conducted using uv radiation. The photoemission threshold for both ice near −10°C and water near 10°C is about 1950±50 Å, the emission efficiency for liquid water being about half that for ice. Photoemission from ice decreases steadily with decreasing temperature, apparently without shift in threshold, and vanishes below about −160°C. The results suggest that a waterlike phase is stable on the surface of ice at temperatures above −160°C. It is also concluded that hydroxyl ions which are highly concentrated in the surface phase are responsible for the photoactivity.

I. INTRODUCTION

The hypothesis of a liquidlike transition layer on the surface of ice at temperatures below the bulk melting temperature has been the subject of intermittent controversy since it was first proposed by Faraday.[1] The modern revival of interest in the subject dates from the work of Weyl,[2] who developed a qualitative theory for the thermodynamic stability of such a layer. The ensuing experimental studies to examine the question were mainly of a mechanical nature and generally concluded that some type of boundary layer with liquidlike properties does exist. These experiments have been reviewed by Jellinek.[3] Other investigations of a more sensitive nature using techniques such as adsorption,[4] surface conductivity[5] and surface migration kinetics[6,7] have also been conducted, and some of these are reviewed by Fletcher.[8] At present the hypothesis is generally accepted on the basis of this diverse evidence, and the consensus view is that the quasiliquid layer is stable above about −20 ± 10 °C.

The only semiquantitative theoretical treatment of the subject has been developed in stages by Fletcher,[8-11] and concludes that a quasiliquid surface phase is thermodynamically stable at temperatures above about −15 °C, and is characterized by a preferred orientation of the water molecular dipoles that decays with distance below the surface. The treatment also concludes that a diffuse double layer of charged defects is imbedded in the polarized layer, and that the width of the layer increases to hundreds of angstroms as the melting temperature is approached.

Although the available evidence appears to support the quasiliquid layer model, a full confirmation and characterization requires direct measurements of some specific properties. Significant recent studies of this nature have been reported by Kvlividze *et al.*,[12,13] who performed proton magnetic resonance studies on finely divided ice. Their results showed evidence that a liquidlike environment for resonating protons develops on the surface above −10 °C, and the increase in the effect with rising temperature follows closely the widening of the layer as predicted by the theory.

In the present study ice and water were investigated by measuring their photoemission in response to uv radiation. Some much earlier measurements[14] indicate that ice is about two orders of magnitude more photoactive than water. Additionally, it is expected that photoemission should be a surface-specific property due to the very short lifetime expected for free electrons in these phases. The study was intended to investigate the existence and temperature range of stability of any transition phase, and to study its nature by measuring the response to uv radiation of selected wavelengths.

II. APPARATUS

It was required to design an experimental apparatus to generate and measure the photocurrent from ice/water samples. A suitable design is a modification of a Townsend gas discharge apparatus, which consists in essence of a chamber containing two parallel-plate electrodes between which an electric field is maintained, one electrode of which can be irradiated from outside the chamber through an optical port. The irradiated electrode is made the sample and emits photoelectrons which are collected by the other electrode and conducted to instruments outside for measurement. Since it is desired to make the measurements as near to equilibrium as possible, and the equilibrium vapor pressures of ice and water can be appreciable (~1 Torr), vapor processes are expected to influence the current during passage through the vapor phase. Thus, the collecting electric field and interelectrode separation are designed to be variable to permit examination of these processes and establishment of optimum conditions. Additionally, since radiation in the far uv region is strongly absorbed by oxygen, it is necessary to exclude air from the chamber during the measurements by making provision for evacuation or flushing.

The experimental apparatus and measuring circuit are shown schematically in Fig. 1. Lamp radiation, which may be either broadband or monochromatic, passes through window W and mesh electrode A before striking the sample contained in dish C. The external voltage supply establishes the potential difference V across the interelectrode distance d, and the field is maintained normal to the electrodes by guard ring G. The temperature of the chamber is controlled by external cooling, and the sample temperature is measured by thermocouple T imbedded in the sample dish.

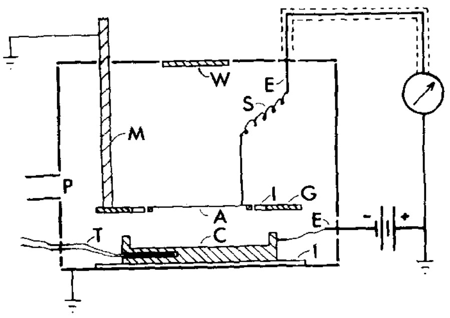

FIG. 1. Schematic representation of the experimental apparatus and measuring circuit, showing the cylindrical brass chamber with O-ring sealed mechanical joints, sample dish *C*, collecting anode *A*, spring connector *S*, electrodes *E*, electrode position adjustment micrometer *M*, teflon insulators *I*, field guard ring *G*, quartz window *W*, evacuation and purge port *P*, thermocouple *T*, and the current measurement instrument and battery potential supply.

All ice and water samples were prepared from distilled water. Before a measurement a sample was surface cleaned *in situ* through sublimation by at least 1 h of continuous chamber evacuation.

The initial stage in the study was to determine the appropriate ranges of V and d. Suitable ranges had been established approximately in an earlier pilot study by Mills[15] using a similar apparatus. Some results obtained from the present study for the most convenient ranges of V and d are shown in Fig. 2, and refer to a sample of ice at $-45\,^\circ$C irradiated in steady light from a "Penray" mercury vapor lamp, and contained in an environment of dry nitrogen at ~ 1 atm. It is apparent that in the ranges $V = 20-40$ V and $d = 0.25-1.0$ cm the photocurrents are the least sensitive to V and d conditions. Since the photocurrents are also large enough for measurement, these may be considered the optimum ranges, and the subsequent results in Figs. 3 and 4 refer to the conditions $V = 30$ V and $d = 0.5$ cm.

The results in Fig. 2 may be understood in a qualitative way by considering electron transport processes in the vapor phase. In principle the processes of current growth by avalanche effects, electron attachment to vapor molecules, and loss of current due to diffusion lateral to the collection field during transit can occur under certain conditions. Avalanche and attachment effects depend upon the parameter V/dp, where p is the pressure. Under the conditions of Fig. 2, calculations show that avalanche processes do not occur unless the voltage is orders of magnitude larger than the optimum range. Even with the saturation vapor pressures of $10^{-3} - 10^{-2}$ atm expected above ice and water near the melting point under continuous evacuation conditions, the region of avalanche effects is well beyond the experimental range. Thus, the exponential current growth characteristic of avalanche effects is not expected to occur. Based on measurements of electron attachment to water vapor molecules,[16] calculations for the present field conditions show that attachment is negligible at 1 atm, but may occur at water and ice vapor pressures near the melting point. Nevertheless, regardless of the degree of attachment, lateral diffusion losses during transport may be substantial. These diffusion losses should be proportional to the mean sidewise drift $(D\tau)^{1/2}$ in the field, where D is the diffusion coefficient for the transporting species and τ is the mean transport time. Thus, it can be shown that the collected current should vary as $1 - CdV^{-1/2}$, where C is a constant characteristic of the vapor and the collection geometry.

Comparing the curves $i(V, d)$ in Fig. 2 with the derived expression, it is seen that diffusion losses may explain qualitatively the observed behavior. If the diffusion loss term is eliminated graphically by extrapolating the data to the infinite collection field conditions i.e., $d \rightarrow 0$ at constant V, a limit function $i^*(V)$ is obtained which is similar in form to the $i(V, d)$ curves and lies just above them. Because of its residual V dependence $i^*(V)$, although corrected for diffusion losses, cannot actually represent the true photocurrent as emitted from the sample. However, for purposes of determining the temperature dependence of the diffusion losses, $i^*(V)$ must suffice as the best available estimate of the true photocurrent. Accordingly, similar extrapolations are carried out for the additional temperatures 20 and $-110\,^\circ$C, and the results show that the ratio $i(V, d)/i^*(V)$, at a given V, is nearly independent of temperature. Thus, although the partial pressure of water vapor within the nitrogen environment of these studies changes by many orders of magnitude over this temperature range, the temperature dependence of the best available estimate of the true photocurrent is well represented by the temperature dependence of the measured photocurrent. In addition it is apparent from the curves that the current losses are comparable in magnitude to the collected current. Therefore it is concluded that the chamber design and experimental conditions are reasonably efficient as well as suitably sensitive and stable.

III. MEASUREMENTS

The investigation divides naturally into two phases which require different conditions of illumination, elec-

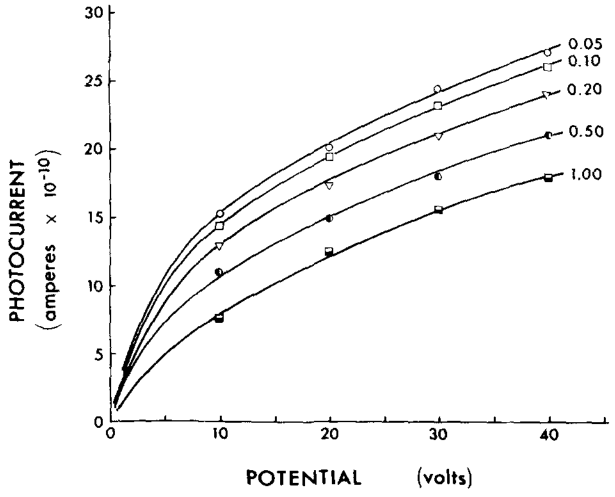

FIG. 2. Photocurrent as a function of collection voltage V for selected values of the interelectrode spacing d (shown in cm as a parameter).

trical equipment and chamber environments. In Sec. III. A the wavelength dependence of the photocurrent was investigated for ice and water near the melting point. In III. B the temperature dependence of the photocurrent was investigated.

A. Wavelength dependence

The wavelength dependence of the photoemission was studied using a deuterium arc lamp (Hilger & Watts model FL 39). The spectral output was calibrated using a photocell and is shown to an arbitrary scale in Fig. 3. The radiation was monochromated using a grating monochromator (Bausch & Lomb 33-86-25-01), whose calibration was confirmed using the 2537 Å peak of the mercury vapor lamp. The wavelength dependence of ice/water samples was examined at several temperatures between − 15 and 15 °C by scanning the range 1750–4100 Å in 100 Å steps. In order to avoid condensation or frost-up on the interior electrodes which causes erratic signal effects, the chamber had to be precooled to just below the lowest temperature of measurement before the sample was inserted. After thermal equilibration the chamber was sealed, evacuated for a minimum of 1 h to allow surface cleaning, and then measurements taken as the chamber was warmed. Variations from this technique could often give inexplicable results. The sample temperature was controlled by judicious control of the temperatures of a glycol–water bath in which the chamber was immersed and of the cold room in which the experiments were performed.

Certain experimental conditions were necessary because the photocurrents from ice/water samples are inherently small. Because the lamp intensity is relatively low, the efficiency of grating monochromators is low, and air is strongly absorbing to uv light, it was necessary to maintain the monochromator and lamp in a dry nitrogen environment during measurements in order to ensure sufficient intensity to generate a measurable level of photocurrent. Similarly, it was necessary to maintain the chamber interior in a partially evacuated condition by continuous evacuation during measurements. Since pumping interferes to some degree with the equilibration of the sample, pumping orifices of several sizes were used to determine this effect. In order to avoid spurious signal effects from instrument drift and noise interference the photocurrent was converted to a 20 Hz square wave by mechanically chopping the light at the monochromator inlet. The square wave signal was measured in conjunction with a reference signal produced synchronously by the chopper in an auxiliary photosensitive circuit using a lock-in amplifier/synchronous detector (P.A.R. model 124).

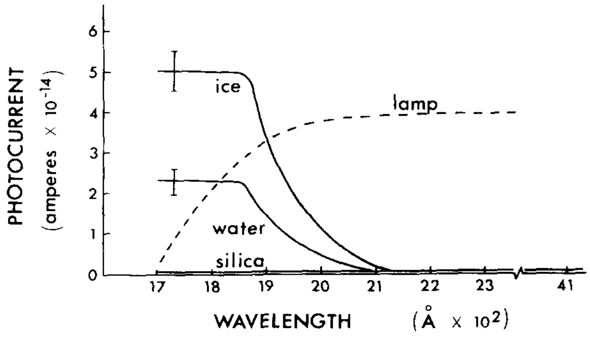

FIG. 3. Photocurrent as a function of the excitation wavelength for samples of ice at − 10 °C, water at 10 °C, and fused silica, as measured under continuous evacuation conditions. The measured lamp spectrum used to calculate these normalized results is shown plotted to an arbitrary scale.

B. Temperature dependence

The photocurrent from ice and water samples was measured as a function of temperature as the chamber was cooled externally. For temperatures above − 25 °C the temperature could be carefully controlled using the glycol–water immersion bath, so thermal equilibrium of the sample was ensured. To reach lower temperatures an intermittent partial immersion of the chamber in liquid nitrogen was employed. Although the cooling rates during the immersion periods were rapid, the thermal mass of the system was sufficient that its temperature remained nearly stationary between immersions, so thermal equilibrium was ensured.

The normal means of maintaining evacuated conditions in the chamber were ineffective at the coldest temperatures. Hence the chamber interior and optical path to the lamp were subjected to a continuous purge of dry nitrogen during measurements to exclude air and to prevent frost condensation due to induced supersaturation during cooling. Broadband measurements were made using the deuterium lamp, and were supplemented by line spectrum measurements using the mercury vapor lamp. The radiation was direct, with frequent checking that a zero light condition corresponded to a zero signal condition. The photocurrents were measured with an electrometer (Keithley model 603) using an input resistance of $10^{10}\,\Omega$.

IV. DISCUSSION OF RESULTS

A. Wavelength dependence

The results of the wavelength dependence studies are shown in Fig. 3. These results were calculated from the photocurrents as measured and the lamp spectrum as shown by normalizing the measured photocurrents to a common intensity basis using the lamp intensity at 2200 Å as an arbitrary standard of intensity. The results show that ice at − 10 °C has a photoemission threshold at 1950 ± 50 Å (6.3 ± 0.2 eV). Water at 10 °C has the same threshold as ice, and has a photoactivity 45 ± 10% as large as ice at the same wavelengths. These are the only significant features of the spectrum in the uv range 1750–4100 Å.

These results were obtained using a 100 Å monochromator bandwith, since smaller slits failed to provide sufficient intensity, and thus about 50 Å of the apparent threshold broadening in Fig. 3 has been disregarded in stating the uncertainty of the threshold. It was found that the absolute values of the photocurrent could vary by as much as a factor of 3 for different samples prepared in the same manner, an effect which was most likely due to differences in the initial purity or the effectiveness of the sublimation surface cleaning. Therefore these results represent a consensus of measurements for several samples which have been standardized to an intermediate value to facilitate comparison, and the uncertainty refers to the data after standardization.

These data have been corrected for the differences in vapor phase current loss at the two temperatures under the constant evacuation conditions. This correction was determined by making photoemission measurements from a copper oxide sample in this temperature range with an off-target source of water vapor present in the chamber, which indicated that the water data must be compensated for a 20% loss relative to the ice data. In general the data should also require correction for the differential reflectivity of ice and water. However, although reflectivity values for uv radiation are unavailable, extrapolation from visible range results for normal incidence[17] indicates that this correction would be unimportant. Since it is possible that background photocurrent may be generated from off-target sources in the chamber due to scattered radiation, a fused silica disc which has about the same reflectivity and transmissivity as water was substituted for the sample and measurements were taken. This study gave an immeasurably small photocurrent as shown in Fig. 3, so the background from this cause is apparently negligible.

Measurements of sample volume loss during evacuation showed that the net evaporative rate through the smallest orifice of about 0.1 mm diameter is about 10 atomic layers/sec at 10 °C. Calculations from this result and the relative vapor pressures predict a loss rate of about 0.1 layers/sec for ice at -10 °C. Since the simultaneous evaporation and condensation rates between the surface and vapor at equilibrium are calculated to be about 10^6 as large as these loss rates, there is little doubt that the surface–vapor equilibrium prevails during the orifice-limited pumping. This conclusion is supported by an inability to prevent frost-up inside the chamber due to induced supersaturation when the chamber containing a water sample was chilled, and also by the differential vapor loss corrections measured under evacuation conditions at different temperatures. However, since the surface position cannot be static during net evaporative conditions, and equilibrium between the surface region and the bulk cannot be assumed. Nevertheless, there was no significant effect on the threshold measurements when pumping orifices from 0.1 to 10 mm were interchanged, so the threshold value extrapolated to a zero evacuation rate is the same as the measured value. Thus, whether or not a quasiequilibrium state prevails in the surface in every respect, it appears that the measured threshold to uv photoexcitation is characteristic of an equilibrium surface state. There was also no difference between results obtained from a preformed, nearly monocrystalline ice disk and the multicrystalline samples formed by *in situ* freezing, so a surface structure peculiar to grain boundaries cannot be responsible for the results.

The threshold values for ice and water indicate that the photoemission requires an energy of 6.3 eV. The electron energy states known to be present in appreciable concentrations in the bulk phases are the molecular bonding orbitals, which have ionization energies greater than 13 eV and the hydroxyl ions (OH^-) present as defects, whose ionization energies are unmeasured. However, the electron affinity of a hydroxyl ion in the vapor phase has been accurately measured[18] as 1.87 eV. Although the network of bonding neighbors in the bulk phase would increase this value, all the intermolecular forces which constitute a hydrogen bond contribute only 0.3 eV, so the network bonded hydroxyl ion is unlikely to have an ionization energy differing much from about 2 eV. The theory predicts that the polarized quasiliquid layer contains an associated diffuse double layer of hydronium and hydroxyl ions which are aligned such that their electric field partially cancels the polarization electric field of the oriented molecular dipoles, and the surface potential results from the net field. Quantitative measurements of the surface potential for water are indecisive even as to sign, and theories have also been inconclusive. However, from studies[19] of heterogeneous nucleation of water droplets it appears that the surface molecules are primarily oriented with their protons directed toward the bulk, which thus produces a surface potential in which the vapor phase is negative relative to the bulk phase. Accordingly the hydroxyl ions in the quasiliquid layer would lie to the bulk side of the double layer and, if these ions are the source of the photoemitted electrons, these electrons would have to surmount the surface potential in order to escape. For a total photoemission energy of 6 eV this potential would need to be about 4 V and of the polarity indicated above. This result does agree with earlier estimates of surface potential in order of magnitude, but there is no specific evidence to support or refute this particular value.

In view of the apparent role of hydroxyl ions in photoactivity, threshold determinations were made for a series of water solutions prepared with NaOH or HCl to exhibit a *p*H range 1–14. It was found that the threshold was unchanged over this acidity range, and that the magnitude of the photocurrent increased by only a factor of 4 as the hydroxyl ion concentration increased by 14 orders of magnitude. Thus it appears that the surface concentration is independent of the bulk concentration over an extremely wide range of bulk concentrations. Since in the highly basic solution of *p*H 14, about 5% of the molecules are ionized, these results would require that the surface region have an even greater proportion of ions. This conclusion is qualitatively consistent with the theory that estimates that the surface region is nearly saturated with ions.

B. Temperature dependence

The results of the temperature dependence studies are shown in Fig. 4. For both lamps the photocurrent from ice appears at about -160 °C and increases steadily to a maximum at the melting point. The water photocurrents are about half as large as for warm ice, in general agreement with Fig. 3. Results for different samples have been standardized to an intermediate value before averaging as discussed above, and the "Penray" results have been rescaled to coincide with the deuterium results at the melting point in order to facilitate the

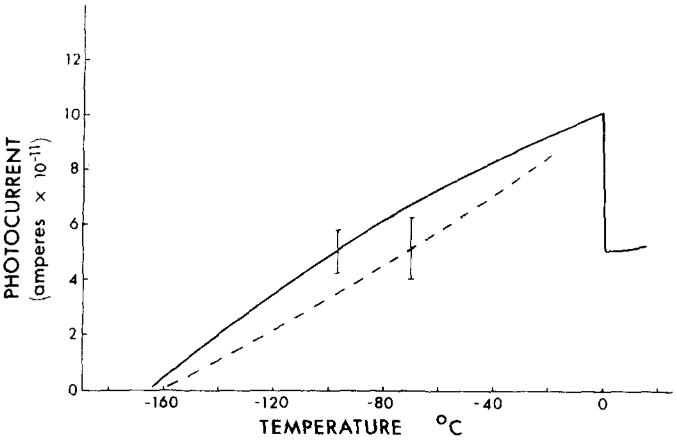

FIG. 4. Photocurrent as a function of temperature using a broadband deuterium lamp (solid line) and a line-spectrum mercury vapor lamp (dotted line).

comparison of their temperature dependences. The uncertainty range indicated in Fig. 4 includes the differences between heating and cooling studies. Studies conducted at different purge rates showed no significant differences, so the surface is apparently maintained in a quasiequilibrium state during purging.

The purpose of comparing results obtained from broadband and line spectrum radiation is to determine if the threshold position changes as a function of temperature. The mercury vapor lamp has a peak at 1849 Å (6.7 eV), which is undoubtedly the stimulant for the measured ice/water photoemission in view of Fig. 3, and another strong peak at 2537 Å (4.9 eV). If the threshold energy shifts down to 4.9 eV, this peak would become photoactive and the difference in photoemission using the two lamps would become quite noticeable. Similarly, if the threshold shifts up to 6.7 eV, the mercury peak at that value would continue to be effective just as when the threshold is maintained at 6.3 eV, but the falling intensity of the deuterium lamp at this shifted value would create a noticeable difference in the results from the two lamps. Although the results from the two lamps in Fig. 4 are not coincident, the differences are within the uncertainties of the measurements. Thus, it appears that the threshold value of 6.3 ±0.2 eV is stationary within a range from 0.4 to −1.4 eV over the whole temperature range.

Since the lamps are located adjacent to the chilled chamber and purge gas stream during these temperature range studies, and the radiation output of gas discharge lamps is known to depend on the lamp envelope temperature, it is conceivable that variation in lamp temperature can contribute to the observed temperature dependence. However, when the envelope temperatures were measured by contact thermometry under the coldest and warmest conditions the difference was only about 15 °C, so this effect is unimportant. In addition, since the electrical conductivity of ice decreases rapidly at low temperature it is conceivable that a significant fraction of the collecting potential is being developed across the ice at low temperatures, which would diminish the collecting field across the vapor and decrease the collected current. This effect was examined by repeating the present measurements using an ice sample doped with 5% HF to be highly conductive at all temperatures. The results were similar to pure ice results, so this effect is unimportant.

In view of this evidence it is reasonable to conclude that the temperature dependence is a real effect associated with the surface, and is caused by changes with temperature of the surface concentration of hydroxyl ions. Since the photocurrent for water differs by only a factor of 2 from warm ice, but differs by orders of magnitude from ice colder than −160 °C, the warm ice surface apparently has properties similar to water and may properly be called quasiliquid. Furthermore, since the threshold energy does not change appreciably as the temperature is decreased, the local bonding about an hydroxyl ion and the interface potential probably remain constant over the whole temperature range. From the earlier conclusions that the hydroxyl ions are highly concentrated in the surface region the mutual interaction of ions should be appreciable, so a constant threshold energy probably indicates that the ions exist at a characteristic volume concentration which is independent of temperature. Accordingly, it is likely that the observed change in the effective concentration of ions with temperature is due to the extensive effect of thickening the quasi-liquid zone, rather than the intensive effect of altering the local concentration of ions.

Thus, the present results indicate that the liquidlike transition layer becomes stable at about −160 °C and thickens progressively to a maximum value at the melting temperature.

V. CONCLUSIONS

From these investigations it has been found that the surface of ice and water near the melting temperature have comparable photoemission efficiencies, in contradiction to much earlier measurements[14] which indicated that the ice photoemission exceeded the water value by two orders of magnitude. The photoemission threshold was found to be 1950 ± 50 Å for both ice and water. The photoactivity of ice is a maximum at the melting point and extends down to about −160 °C. It is concluded that a waterlike transition phase is stable on the surface of ice down to −160 °C, and becomes progressively thinner as the temperature decreases. It is also concluded that hydroxyl ions are the most probable source of the photoactivity and exist at near saturation concentrations in the surface phase.

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