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Photoemission from Sodium on Ice: A Mechanism for Positive and Negative Charge Coexistence in the Mesosphere

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Photoemission from sodium deposited on ice films is described. Deposition of 0.02 ML of sodium is found to dramatically reduce the threshold for photoemission from the ice film to (2.3 ± 0.2) eV. Thus, the cross-section for photoemission reaches $>10^{-18}$ cm^2 in the visible region of the spectrum. It is proposed that the initial state is a solvated electron on the ice surface, which is supported by optical transmission spectroscopy. The potential significance of these results in understanding unexplained charging phenomena in the mesosphere is discussed.

Introduction

Electron- and photon-induced processes in water ice are of central importance in understanding the physics and chemistry of the earth's and planetary atmospheres.[1−5] In this letter, we report the photoemission of sodium-doped ice films and find a dramatic decrease in the threshold for photoemission, compared to the water ice substrate. These data are potentially of great significance in understanding charging phenomena and particle coagulation in the upper atmosphere. Polar mesospheric (also known as noctilucent) clouds (PMCs) comprise submicron-sized ice particles that form at altitudes between 82 and 86 km during summer at high latitudes, when temperatures fall below 150 K.[6,7] PMCs were first reported during 1885 over middle and northern Europe.[8] Since then, the clouds have been observed more frequently, and their brightness has increased,[9] leading to speculation that they are an early warning of climate change in the upper atmosphere.[10] PMCs can be observed optically but also give rise to intense high-frequency radar backscatter, termed the polar mesospheric summer echo (PMSE).[11] It is believed that PMSEs are caused mainly by ice particles with radii less than 10 nm, which are negatively charged by the attachment of electrons. The radar is then scattered from the sharp gradient in the free electron density around the cloud.[11] Although rocket-borne measurements have confirmed that there is usually a "bite-out" in the electron density profile at the altitude of a PMC, charged particle collectors on rockets have also shown that on rare occasions PMC particles are *positively* charged, with an enhanced cloud of electrons around them.[12,13]

Photoionization of ice particles is clearly one potential mechanism for the generation of positively charged particles. However, at heights below 100 km in the atmosphere, there is insufficient intensity in the solar spectrum of photons of energy greater than the work function of ice (8.7 eV[14]) to account for the observed charge density.[15] Indeed, attempts to simulate the experimental observations required the particles to have a work function on the order of 2.5 eV,[15] much too low for pure water ice. In fact, PMCs occur in the same altitude range as metal atoms, such as Na and Fe, which ablate from the 20−50 tonnes of interplanetary dust that enters the atmosphere each day.[16] This stimulated us to investigate the photoemission of metal-doped ice films. In this letter, we describe measurements of photoemission from sodium adsorbed on ice, a system which has been the subject of intense interest recently.[17−19] We find that the effect of sodium deposition is to reduce dramatically the photoemission threshold of ice, to (2.3 ± 0.2) eV, resulting in a very substantial cross-section for photoemission on irradiation in the visible and near-UV region. The potential consequences of this observation for understanding the chemistry of the mesosphere are briefly considered.

Experimental Section

Photoelectron energies were measured with an electron time-of-flight spectrometer. The substrate was a Cu(111) surface, and the spectrometer was calibrated relative to the work function and the surface state, observed through two-photon excitation.[20] The irradiation source was a pulsed dye laser pumped by a Nd:YAG laser which was synchronized to the electron time-of-flight detection. The work function of the detector was determined as 4.52 eV. Further details of the spectrometer are described elsewhere.[21]

To obtain the photoemission cross-section, which is essential in analyzing the significance of the observations in the atmosphere, a number of corrections to the measured electron count are required. The collection solid angle of the spectrometer was first corrected for the acceleration potential between the sample and the spectrometer entrance. The electron count was then corrected for the open area ratio (0.6) of the microchannel plate. The absolute quantum detection efficiency of microchannel plates in the low electron energy range has not been measured. We assumed a value of 0.4. From the corrected detection solid angle and the electron count, the electron

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emission into the full solid angle was obtained. The sample was positively biased to measure the work function below that of the spectrometer.

The substrate was cooled to 90 K, and water was deposited at a rate of 50 langmuir/min. Photoemission from the Cu(111)/H_2O surface was studied as a function of coverage with a fixed irradiance of 0.3 mJ cm^{-2} at 3.80 eV. Two effects were observed with increasing coverage. First, the work function decreased monotonically, from 4.9 eV at 0 ML to 3.9 eV at 4 ML (1 ML = 1 monolayer). This was reported previously by Bovensiepen et al.[22] No further change in work function was seen for additional deposition up to at least 15 ML. Second, the yield of photoelectrons decreased dramatically with increasing coverage, by at least a factor of 100 between 0 and 15 ML. This is consistent with previous measurement of the thickness-dependent transmission of low-energy photoelectrons through water ice.[23] To better simulate the conditions pertaining to PMCs, the thickness of the ice film was increased to 3000 ML and heated (0.3 K s^{-1}) to a temperature of 160 K, to yield the cubic phase.[24,25] The sample was then recooled to 90 K. At these thicknesses, photoemission from the Cu(111)/ice film was only detectable at very high irradiance, >10 mJ.cm^{-2}, even for incident photon energies in excess of 3.9 eV. This is expected; photoelectrons generated at the Cu(111)/ice interface will be trapped in the ice film and eventually recombine with the substrate.[26]

Sodium was deposited onto the annealed ice film using a sodium getter at a rate of 0.02 ML/min. The deposition rate was calibrated using the published dependence of the work function of the Cu(111) surface on sodium coverage.[27] All photoemission measurements reported below were made with 0.02 ML of sodium freshly deposited onto the ice film. The effect of deposition was a dramatic enhancement in the yield of photoelectrons. For example a $\sim 10^5$-fold enhancement in the photoemission yield, compared to the bare ice surface, was observed for incident photon energies of 2.9 eV. The observation of a linear dependence of the photoelectron yield on laser power[21] suggests a single-photon photoionization mechanism in the doped film, consistent with the large cross-section. Thus, we can immediately conclude that the cross-section for photoemission of an ice film on irradiation with visible radiation is dramatically enhanced by deposition of 0.02 ML of sodium. The energy of electrons emitted from weakly conducting samples can be affected by positive charging during the photoemission process. The average number of electrons detected in our experiments was between 0.2 and 0.5 per laser pulse. Repeated measurements in a broader intensity range up to ~1.5 electrons per laser pulse did not exhibit any distortion or shifting of the measured bands outside the observed experimental uncertainty of the energy scale.

Results and Discussion

The photon energy dependence of the photoelectron energy distribution is presented in Figure 1. At low photon energy (<3 eV), a narrow distribution is observed with an upper energy defined by the incident photon energy and a threshold defined by the vacuum level. From these data, the photoemission threshold for the surface can be determined as (2.3 ± 0.2) eV. As the photon energy is increased, the photoelectron energy distribution shifts to higher energy and broadens (Figure 1). At all photon energies, the measured energy distribution is observed to be somewhat asymmetric. The photon energy dependence of the photoemission cross-section, σ, was also measured (Figure 2). Weak photoemission ($\sigma < 10^{-20}$ cm^2) was observed for photon energies as low as 2.1 eV, but the cross-section increased sharply around 2.6 eV to a value of 10^{-18} cm^2 and reached a plateau at that value between 2.9 and 3.6 eV. At photon energies between 3.6 and 4.6 eV, the cross-section decreases by an order of magnitude.

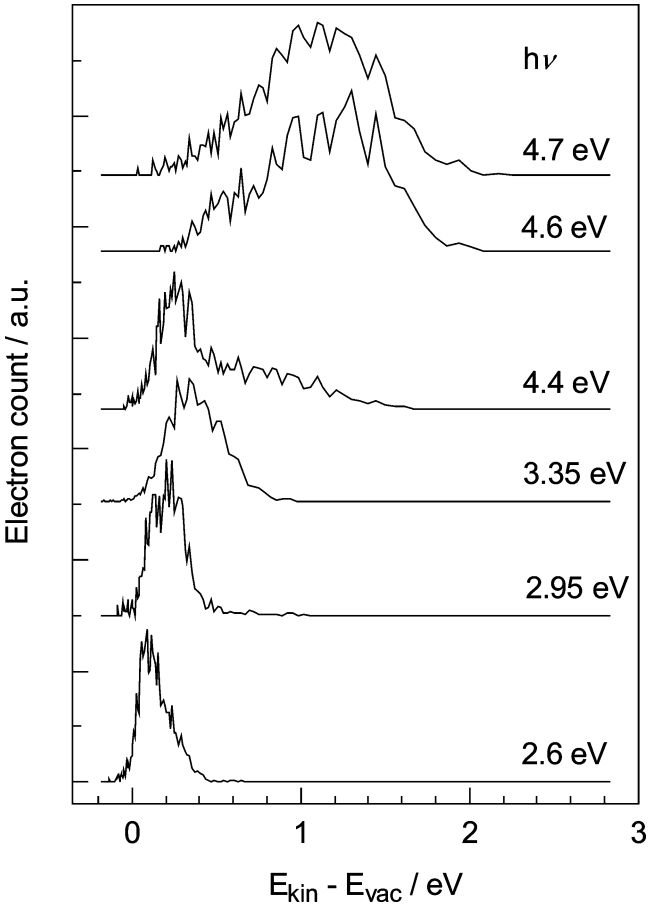

Figure 1. Photoelectron spectra for a 3000-ML-thick ice film on Cu(111) with 0.02 ML freshly deposited sodium, measured as a function of incident photon energy.

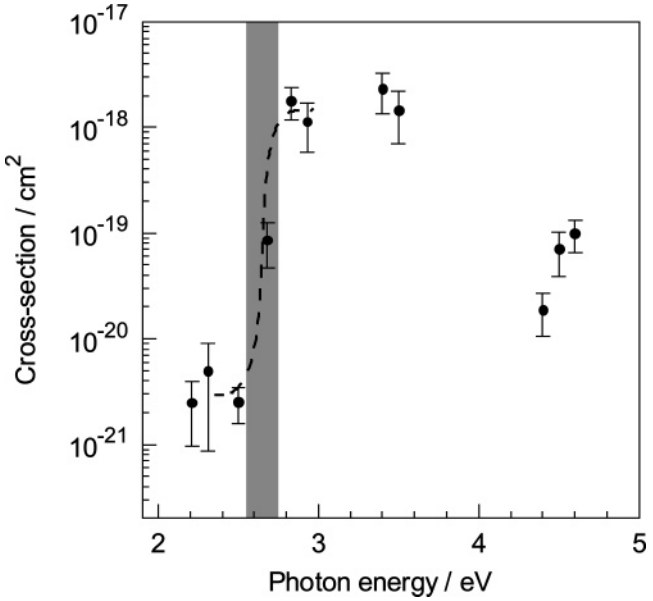

Figure 2. Photoemission cross-section for 0.02 ML of Na deposited on 3000 L of ice, measured as a function of incident photon energy. The corresponding cross-section for the undoped film was $<10^{-22}$ cm^2.

Such a dramatic effect of a low coverage of sodium on the photoemission cross-section of the surface cannot be explained

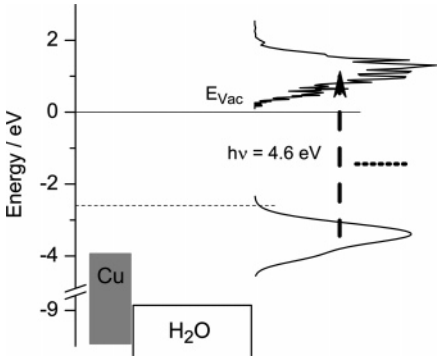

Figure 3. The initial state for photoemission is located between the Fermi level of the Cu(111)/H_2O interface (3.9 eV) and the vacuum level. Photons of increasing energy sample deeper within the width of the initial state. The energy of the bound excited state observed in the optical transmission spectrum is indicated by the dotted level. The dashed line indicates the photoemission threshold derived from the wavelength dependence of the cross-section.

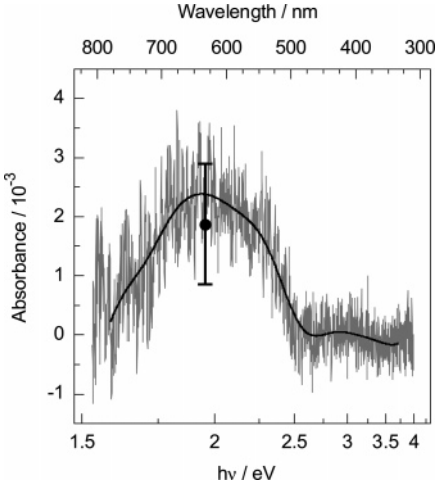

Figure 4. Optical transmission spectrum of a thick annealed ice film with 0.2 MLof freshly deposited sodium. The single point with an error bar was obtained by a HeNe laser in a two-beam setup.[21]

by the conventional picture of work function lowering through the formation of a dipole layer; the decrease of the work function of the Cu(111) surface upon the deposition of 0.02 ML of Na is only ~0.5 eV, far below the shift observed here.[27,28] In addition, the photoemission yield from the Na on ice surface is independent of film thickness above 20 ML. Thus, we assign the enhanced photoemission observed to the formation of a new electronic state on adsorption of a sodium atom at the vacuum−ice interface, which can itself undergo photoionization. The photon energy dependence locates the new state at around 3 eV below the vacuum level. This is illustrated schematically in Figure 3. The Fermi level of the Cu(111) substrate covered by 3000 L of water is located at 3.9 eV (i.e., assuming no further shift beyond 4 ML coverage). It is further assumed that the deposition of sodium atoms on the surface of the thick (3000 ML) ice film does not further shift the substrate work function. The new electronic state induced by sodium adsorption has a width of 0.9 eV (Figure 1). As the incident photon energy decreases, the time-of-flight distribution shifts to lower energies and narrows (Figure 1). This effect arises because less of the width of the initial state is sampled (Figure 3). The initially slow increase of the photoemission cross-section with increasing photon energy before the rapid increase at 2.6 eV (Figure 2) suggests that the high-energy edge of the initial state is not characterized by a sharp cutoff. This in turn suggests an inhomogeneous distribution of sites for the state formed by sodium adsorption.

To investigate the nature of the initial state, we recorded the optical transmission of 0.2 ML sodium deposited on a 3000-ML-thick ice film, itself deposited on a sapphire substrate. The higher sodium coverage was necessary to induce a measurable change in optical transmission. The spectrum (Figure 4), extending from 2.7 eV to beyond 1.5 eV, is centered at 1.9 eV. The fact that this transition occurs at energy below the photoemission threshold indicates that it involves a bound excited state (also indicated in Figure 3). The spectrum bears a striking resemblance to that of the solvated electron formed in γ-irradiated crystalline ice.[29,30] Formation of an electron on doping ice with Na is consistent with measurements of the metastable impact electron spectra and UV photoemission of sodium on ice at 130 K, which revealed the formation of solvated Na^+ ions (at the higher Na coverage of 0.5 ML).[31] It is also consistent with quantum chemical calculations, which show the 3s electron density to be highly delocalized and available for electron transfer.[21] The photoemission threshold for the solvated electron in water clusters has also been determined to be at 2.4 eV, close to our experimentally determined threshold for sodium-doped ice.[32] On the basis of these data, we propose that the sodium atom is ionized on the surface, and photoemission arises from photodetachment of the resultant electron solvated near the surface. We have also observed that the initial state is a metastable one; the photoemission yield decreases with time, at a rate of $(4 \pm 0.4) \times 10^{-4}$ s^{-1} at 93 K, increasing at higher temperature.[21] This may arise from chemical reaction of the defect, for example, by formation of the hydroxyl radical, which requires a much higher photon energy for photodetachment.[32]

In conclusion, we have demonstrated using photoelectron spectroscopy that doping an ice film with only 0.02 ML coverage of sodium dramatically lowers the photon energy required for photoemission, from 8.7 to 2.3 eV. The cross-section for photoemission reaches $>10^{-18}$ cm^2 $atom^{-1}$ in the visible region of the spectrum. This may have significant implications for chemistry in the mesosphere. When integrated over the solar actinic flux in the mesosphere, the photoionization lifetime of a Na atom adsorbed on an ice particle is about 10 s, compared with 5×10^4 s for a Na atom in the gas phase.

Detailed modeling of photoionization in the mesosphere is in progress,[21] and we report preliminary results here. When PMCs are present, the background layer of Na atoms is largely removed below 86 km, because uptake of metal atoms on the ice particles is faster than the average injection rate of fresh Na from meteoric ablation.[33] Thus, photoelectric emission from ice particles would not normally be significant. However, a layer of positively charged ice particles would be the transient response to a fresh trail of Na atoms produced by the ablation of a relatively large meteoroid. For example, a 1000 μg meteoroid, moving at the average infall velocity of about 20 km s^{-1}, will ablate in the 80−90 km region.[16] This will initially produce a Na atom concentration roughly 50 times larger than the background daytime concentration of 10^3 cm^{-3} at 83 km. Using the cross-section determined above and adapting a model of ice particles suspended in a plasma,[15] we have shown that a layer of positively charged particles will form in less than 60 s, through uptake of Na and resulting photoelectric emission. The layer will persist for about 15 min as a patch of roughly 100 m dimension. Meteoroids smaller than about 500 μg will not produce enough Na atoms to generate a net population of positively charged particles. However, we have not included here possible photoelectric emission caused by the adsorption

of other more abundant meteoric metal atoms, such as Fe and Mg. On average, two 500 μg or larger meteoroids will enter an area of 100 m radius each day.[34] Thus, the probability of a rocket-borne instrument observing a layer of positive particles is about 0.02, in accord with the few occasions on which such layers have been reported.[12,13]

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