Negative cluster ion formation from water ice in high electric fields

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Abstract

The first experimental observation of negative water ion clusters by field desorption is presented. Ions of the form \((\text{H}_2\text{O})_n^{-}\cdot\text{OH}^-\), with \(n = 1–8\), are detected. The ions are produced by desorbing thin layers of water ice from a metal substrate in the presence of a high electric field by increasing the temperature of the substrate. The electric field strength is below the minimum field required for detectable electron emission from the clean metal substrate surface. Ion emission occurs from localized areas of the surface, and an electrohydrodynamic ion emission mechanism is proposed.

Key words: Field desorption microscopy; Field electron emission; Negative water cluster ions; Amorphous ice

1. Introduction

The study of negative hydrated ions is of great interest. Hydrated ions play an important role in the earth’s atmosphere [1] and in biological systems [2]. In addition, the solvated hydroxyl ion \((\text{H}_2\text{O})_n^{-}\cdot\text{OH}^-\) \((n \geq 1)\) holds a key position in the chemistry of aqueous solutions [3]. Negative ions can be created by electrical discharges in gases, ion sputtering, charge exchange [4], low energy electron impact [5], and by field-ionization [6]. Water clusters of the form \((\text{H}_2\text{O})_n^{-}\cdot\text{OH}^-\) \((n \geq 1)\) have been the subject of a number of theoretical studies [2,7,8], and have been observed experimentally [9–14]. In this study, field desorption is used for the first time to form these species.

Although the study of negative ions and ion clusters is of fundamental scientific interest, the creation of negatively charged molecules by field ionization has only been investigated by few authors and for selected ion species [6]. The difficulty in producing negatively charged ions by field ionization arises from the fact that an electron must first tunnel from a metal or semiconductor into an atom or molecule adsorbed on its surface. The negatively charged surface species can then field-desorb. Most molecules, however, have an electron affinity that is too small to capture an electron in the presence of an electric field that is high enough to extract electrons from the conductive substrate. As a result, a commonly employed technique to produce negative ions by applying an electric field is to extract pre-formed ions from condensed liquid and solid layers [15]. In most cases, an aqueous polymer matrix is used to dissolve the sample that will be ionized [15]. Ions from salts, acids, and polyhydroxy compounds have been found by negative field-desorption. In our study, ions are not pre-formed in the con-
densed phase prior to the application of an electric field. A frozen layer of water ice is desorbed by increasing its temperature while a high electric field is present, producing negatively charged water clusters. Our experimental approach resembles thermal desorption spectroscopy where the temperature of an adsorbate is raised in a controlled way (with no electric field applied) to desorb neutral species [16,17].

2. Experimental details

A field emitter tip is used to create an electric field high enough to desorb species from its apex. The tip is formed by electrochemical etching of a wire to produce a needle-like specimen. In this experiment, after subsequent annealing of the specimen in vacuum (to clean and smooth its surface [18]), its apex radius of curvature $R$ is $\approx 200$ nm. When a negative voltage is applied to the tip, the magnitude of the electric field at its apex is given by [19]:

$$F \approx \frac{V}{5R}$$  \hspace{1cm} (1)

The field emitter tip is mounted onto a wire loop and placed in a UHV chamber at $\approx 10^{-9}$ Torr. The tip is cooled to 80 K by a cold finger filled with liquid nitrogen, but it can be heated by passing an electric current through the wire loop. Water vapor is introduced into the system. The vapor is obtained by evaporation from a triply distilled and thoroughly degassed liquid water reservoir kept at 300 K, which is connected to the main chamber via all metal UHV equipment. The water vapor is composed of mostly monomers of non-dissociated H$_2$O molecules, which condense onto the cold tip [20]. They form an amorphous ice layer that is essentially free of pre-formed ions [21]. In a typical experiment, the layer thickness is $\approx 10$ nm. After the ice layer is formed the water vapor is pumped away and a negative voltage, $V = 2$ kV, is applied to the tip to produce an electric field of $\approx 20$ MV cm$^{-1}$. In the presence of the field, a current is passed through the wire loop, which increases the temperature of the tip at an initially constant rate. A temperature is eventually reached sufficient to initiate field desorption of the water layer. Negatively charged ions are produced and are accelerated radially away from the tip. They can either be focused and analyzed in a mass spectrometer, or they can be directed toward an imaging detector to produce a highly magnified image of the desorption event [22]. A detailed description of the apparatus used for this experiment has been given elsewhere [23,24].

The mass spectrometer used is a Wien filter. Its straight line system and its focusing properties allow species with different mass-to-charge ratios to appear as a series of bright focused spots along a horizontal line on a channel electron multiplier array (CEMA). They appear separated from each
other by a certain distance depending on the parameters of the Wien filter, so that each spot can be assigned to a unique mass-to-charge ratio [25].

3. Results and discussion

Figure 1(a) shows a mass spectrum of water ice field-desorbed from an iridium tip by increasing its temperature as described above. Desorption occurs ≈ 30 s after the tip begins to increase in temperature, and it commences for 5 to 10 s. The detected ions are identified as \((\text{H}_2\text{O})_n\cdot\text{OH}^-\) \((n = 1–8)\). When a digital analysis of the intensity of each spot in Fig. 1(a) (corresponding to a different mass-to-charge ratio) is performed, the relative abundance of each ion species is obtained. The result is shown in Fig. 1(b). Notice that the ionic cluster with \(n = 2\) is most abundant.

In negative field ionization experiments conducted previously, negative ions were often detected in the presence of strong electron emission [26–28]. In those cases, a gas or vapor was introduced into the vacuum system to provide species to be ionized. With electron emission present, secondary positive ions can be produced by electron impact, which may then form negative ions by surface sputtering [29]. Additionally, negative ions could be created directly by collision of low energy electrons with neutral molecules near the tip surface [5]. This implies that field ionization may not have been the only mechanism that led to the formation of negative ions. In our experiment, the absence of electron emission during the removal of the ice layer when negative cluster ions are observed proves that field desorption is the only mechanism that leads to the production of these ions.

To ensure that the detected ionic clusters are hydroxyl ions and not ions of the form \((\text{H}_2\text{O})_{n+1}\), the experiment is also performed with a mixture of 50% \(\text{H}_2\text{O}\) and 50% \(\text{D}_2\text{O}\). Four mass peaks are observed for the negative water cluster ion with \(n = 1\); these have the intensities expected from a statistical distribution of H and D in field ionization mass spectra of water [30]. Therefore, possible formation of HDO in the gas phase or on the UHV chamber walls prior to vapor deposition does not influence the mass calibration. The formation of \((\text{H}_2\text{O})_{n+1}\) ions or other contaminant ion species is thereby ruled out.

The negatively charged water clusters are likely to be created by field dissociation of the frozen water at the ice-vacuum interface according to the relation [31]

\[
(\text{H}_2\text{O})_{n+2} \rightarrow \text{H}_2\text{O} \cdot \text{H}^+ + (\text{H}_2\text{O})_n \cdot \text{OH}^-
\]

with the positive \(\text{H}^+\) ion being solvated in the bulk of the ice. This mechanism is very similar to the formation of positive ionic clusters of the form \((\text{H}_2\text{O})_{n+1}\cdot\text{H}^+\) under inverted (“positive”) field conditions [24,32]. However, with a negative voltage applied to the tip as reported here, negative ions are accelerated away from the surface into vacuum, while the remaining \(\text{H}^+\) ions conduct the positive charge through the ice layer to the ice–metal interface where charge exchange can occur. Ice is a protonic conductor [21], so that this mechanism seems likely. A similar charge transport mechanism has been suggested for negative field ionization applied to matrix mixtures containing salt. When salt is present, the cation can travel through the matrix to the metal surface where it can corrode the surface or be released as a gas [15].

An alternative mechanism for the negative ion production at the ice–vacuum interface such as electron tunneling from the metal to the ice surface seems unlikely because of the initial great thickness of the ice layer \((\approx 100 \text{ Å})\). An electronic conduction through the ice is not likely to occur either because of its large band gap between valence and conduction band [33].

Since field desorption is a thermally activated process, the temperature of the ice needs to be raised well above 80 K to initiate desorption at a field strength of \(\approx 20 \text{ MV cm}^{-1}\). We estimate that the desorption of the physisorbed ice occurs in the temperature interval between 140 and 160 K. The lower limit of 140 K is deduced from a comparison with previous experiments (under inverted field conditions), where a minimum electric field of \(\approx 40 \text{ MV cm}^{-1}\) is required to desorb the ice layer at this temperature [24]. Thin layers of ice are known to sublime rapidly in vacuum at tempera-
tures of \(\approx 160\) K, setting an upper limit to the temperature range \([17]\). The temperature could not be directly measured because of experimental difficulties associated with the negative field-desorption mode. The abundance of the negative ionic water clusters shown in Fig. 1(b) is surprisingly similar to the abundance observed for positively charged water clusters with the same number of oxygen atoms field-desorbed at 140 K \([24]\). This is an indication that the dynamics of both processes are closely related, since water clusters of the form \((\text{H}_2\text{O})_{n+1}\) \(\cdot \) \(\text{H}^+\) and \((\text{H}_2\text{O})_n\) \(\cdot \) \(\text{OH}^-\) appear to resemble each other with respect to their structure and enthalpies of formation \([34,35]\).

Figure 2(a) shows a field ion micrograph that was taken during a desorption event. Ion emission occurs from highly localized emission regions on the apex of the ice-covered tip. With increasing temperature, these emission centers constantly change their position to new locations. During this process, no electron emission is detected. At some temperature, ion emission ceases, and moderately strong field-electron emission is observed in a ring-like pattern (Fig. 2(b)). (Electron emission can be distinguished from ion emission by applying a small magnetic field.) If the temperature is increased further to a temperature below \(\approx 700\) K, the electron emission pattern disappears. If the electric field at the apex of the tip is increased at this point, a slightly contaminated, four-fold electron emission pattern of a (001) iridium surface is observed \([19,36]\).

The localized ion emission observed in Fig. 2(a) is interpreted as a combination of two effects.

(i) The water molecules at the apex have a certain mobility above the annealing temperature of amorphous ice at \(\approx 110\) K \([37]\). This mobility enables them to exhibit "liquid-like" behavior at the surface. In the presence of the field, electrohydrodynamic instabilities can form, leading to ion emitting cusps \([38]\) as suggested by the appearance of the image.

(ii) The (reversible) glass transition temperature of water is at \(\approx 135\) K. If amorphous ice is heated above this temperature, it turns into a highly viscous liquid \([39]\) which is able to form ion emitting cusps under the influence of the high electric field.

After the physisorbed ice layer is desorbed, electron emission occurs through a thin layer of water. While the electron work function for amorphous ice is high \([33]\) and therefore prevents electron emission, the remaining adsorbed water obviously exhibits some spatial non-uniformity, which may enhance the electric field, leading to appreciable electron emission. Ring patterns of electron emission have been observed previously on water covered field emitters and have been associated with either electron optical reflections by isolated charged surface molecules or the formation of little hemispherical water droplets that are shadowed by the emitted electrons \([40]\). When the tip temperature is increased to below \(\approx 700\) K, the ring-like electron emission pattern disappears because most of the remaining water is removed from the
metal surface as indicated by the four-fold electron emission pattern of the (001) iridium surface at higher fields.

4. Conclusions

This study demonstrates that negative ionic clusters of water molecules can be created by a pure field desorption mechanism. Although this study has been limited to condensed water layers, the technique could be applied to other condensed layers to produce other negative ions (or ionic clusters), species that may be difficult to create by other means. A prerequisite is a species with an electron affinity that is high enough to ensure that field detachment of an electron cannot occur [6]. It is expected that the electrical conductivity of the condensed layer will also play a role in the process; and perfect insulating layers will not be usable. A drawback of the method is that it produces only short lasting ion signals of rather weak intensity, which are characteristics of most other single-tip field ion sources.

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6. References