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PHOTON INDUCED FIELD DESORPTION OF WATER CLUSTERS

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Abstract—Synchrotron radiation is used to study the photon induced field desorption from a water covered field emitter. Above a threshold photon energy of 7.1 eV, the desorption of a variety of water clusters \((H_2O)_n.H^+\), \(n=1,...,15\) is observed. This threshold energy, which corresponds with the optical absorption maximum of liquid water, is found to be independent of cluster size and substrate material. The abundance of clusters decrease roughly exponentially with increasing cluster size and depends also on substrate temperature and photon energy. The analysis of the cluster distribution reveals an energy increment of 9 meV per water molecule which seems to be correlated to the frustrated translation energy of water molecules on metals. Basic RRK-theory arguments can be applied to explain the cluster distribution.

I. INTRODUCTION

The formation of water clusters has been observed in the past by many workers using a variety of techniques. In field-ionization mass spectroscopy studies for example, water clusters have been seen in the mass spectra [1]. The formation of protonated water species on the emitter surface is assumed [2]. The goal of this study is to determine weather an electronic excitation of the adsorbate can stimulate the desorption of water clusters. Therefore, experiments with synchrotron light were carried out with field emitters exposed to water vapor.

II. EXPERIMENTAL SETUP

The measurements were carried out at the HIGITI monochromator at the HASYLAB beamline in Hamburg. This monochromator covers an energy range from 6 to 30 eV. Silver field emitter tips were made from Ø 0.1 mm wires and etched in 50% KCN. A very low residual gas pressure of \(5\times10^{-11}\) mbar was necessary to measure at very low coverages. Triply distilled water was continuously dosed in the UHV-chamber in a pressure range from \(10^{-9}\) to \(10^{-7}\) mbar. The experimental setup has been described elsewhere [3]. It consists of a field ion microscope, where the tip to screen distance of 10 cm also serves as the flight path of the time-of-flight (ToF) mass analysis (Fig. 1).
The synchrotron light was focused onto the emitter tip which was cooled by an cold finger filled with liquid nitrogen. In addition, a helium–displex–system was used for cooling, and in this case a minimum surface temperature of 54 K was reached. The flight time of the desorbed ions is measured in a reverse mode, which means that the clock is started when a particle is detected and stopped by the bunch marker signal which is in phase with the synchrotron light pulse. The relative light intensity was monitored via the photo current on a gold coated glass disc. To improve the S/N-ratio, each spectrum was collected at least for 300 s.

III. RESULTS AND DISCUSSION

At a dosing pressure of $10^{-10}$ mbar, only a submonolayer of water is established at an emitter temperature of 54 K. Under these conditions only a small amount of $\text{H}_3\text{O}^+$ and $(\text{H}_2\text{O})_2\cdot\text{H}^+$ were observed. The appearance of $(\text{H}_2\text{O})_2\cdot\text{H}^+$ indicates that protonated dimers already exist on the surface even at a relatively low coverage. If we increase the water coverage by dosing at a higher water pressure of appr. $10^{-8}$ mbar, protonated water clusters $(\text{H}_2\text{O})_n\cdot\text{H}^+$ with $n$ ranging up to 15 are desorbed (Fig 2).
Autoprotolysis of water facilitates the field desorption, so that only a relative low field strength of \( \approx 20 \text{ V/nm} \) was necessary. These findings are similar to earlier measurements with Ni, Mo and Ir as substrates [4].

To investigate the underlying excitation, the photon energy was varied, and the results are shown in Fig. 3. The desorption yield shows a sharp onset above 7.1eV (\( \lambda=175\text{nm} \)) independent of the cluster size as was found in our early work [4]. This onset coincides with the main band in the absorption spectrum of super-cooled water [6]. In ref. [6], the electronic excitation in the liquid water is explained as arising from an exciton formation, or from a fragmentation of the water to electronically excited H\(^+\) and OH\(^-\). The linear dependence of the desorption yield on the photon intensity (Fig. 4) further confirms the view of a one-photon-excitation.

Fig. 3.: Photon energy dependence.  
Fig. 4.: Light intensity dependence of the ion yield  
(trimere, \( \lambda = 100 \text{nm} \))

To determine the nature of the transformation of this ‘impact energy’ of the light into the vibrational energy necessary to overcome the activation barrier for desorption, the substrate temperature was varied. The cluster yields are normalized against the trimere yield in the following plots. Fig. 5.a. shows such a set of normalized spectra for 4 different substrate temperatures (80–140K). With increasing temperature, the total yield decreases by two or three orders of magnitude as evidenced by the increase of the statistical noise in the desorption yield. Much more instructive is the drastic change in the cluster distribution. Bigger clusters are much more favoured at higher temperatures than at lower temperatures, as seen for example in fig. 5.a. comparing the spectrum at 80 K and 140 K.

Remarkable is the relative dominance of the tetramere cluster in the spectra, also seen in fig. 2.. This cluster is theoretically considered to be a rather stable configuration, where H\(_3\)O\(^+\) is linked to three water molecules by hydrogen bonds [5]. The low yields of monomers and dimers in the spectra and their disappearance at higher temperatures has to be explained, since in contrast the most abundant species in SIMS–experiments from ice layers is the monomere [7]. For field desorption experiments, the monomere is lower in abundance then the ‘stable’ tetramere at low field strength; at high fields, the relation reverses. Laser induced field desorption experiments by Tsong [1 c.] and by our group [12] confirm this tendency. The low ‘extraction’ yield of monomers and dimers might be
explained by the high solvation energy of the proton. This means for the process of field desorption, which is thought to proceed at equilibrium condition, the removal of a proton surrounded of at least three water molecules (if available) is energetically favoured. In dynamic SIMS, however, the desorption process is far from equilibrium and thermodynamic arguments do not hold.

Further information is obtained by plotting the relative cluster yields versus inverse surface temperature in an 'Arrhenius plot' (fig. 5.). The \( \ln (I_{n}/I_{3}) \) can be approximated by straight lines with increasing slope with increasing cluster size. The calculated energies normalized to the trimere process are plotted versus cluster size for two different voltages (for the same conditions otherwise) in fig. 6.

**Fig. 5.a.:** ToF-MS at different surface temperatures. Yields normalized for \((H_2O)_3H^+\). \(8 \cdot 10^{-8} \text{mbar}, 5 \text{kV}, \text{white VUV-light.}\)

**Fig. 5.b.:** Data versus inverse temperature.

**Fig. 6.:** Activation energy dependence on cluster size.
It is striking that these energies increase continuously with increasing cluster size. The addition of a water molecule to a cluster requires about 9 meV. This could be due to the energy barrier for translational transport of a water molecule on the surface (H$_2$O on metals ≈ 20–50 meV [9]) which is lowered by the field, as also shown in fig. 6. The absolute rates for photon stimulated desorption however have the opposite tendency to the relative rates; with increasing temperature, they decrease drastically, which is interpreted as a reduction of water coverage by thermal field desorption. The overall field desorption rate, which is reflected in the background count rate of the spectra, is indeed increasing in this temperature interval.

The photon stimulated emission of water cluster ions from a multilayer on an emitter tip by field desorption is a rather complicated process. A general theory, applicable for this type of ‘reaction’ was developed by Rice, Ramsperger and Kassel (RRK) [8]. In the RRK-theory, the decomposition of an energized species $M^*$ proceeds via an activated transition state $M^\#$ according to the scheme

$$M^* \rightarrow M^\# \rightarrow \text{products}.\,$$

The ‘impact’ energy in $M^*$ is distributed over the 3n–6 vibration modes into $M^\#$, leading to the fragmentation. In comparing this reaction scheme with our case, the excitation in the water multilayer ($h\nu > 7.1$ eV) delivers the impact energy which is converted into vibrational energy localized in a subsystem of water molecules and which leads to the ejection of one fragment (the cluster) by energy fluctuations. One consequence of the RRK–theory is that the yield of fragments in which more bonds have to be broken increases if the impact energy increases. The influence of the photon energy on the cluster distribution is indicated already in fig. 3. The predominance of tetramer near the threshold energy is not seen at photon energies above 15 eV. In terms of the RRK–theory, this means that at higher impact energy the energy differences determining the stabilities of a configuration are overridden.

![Graph showing relative cluster distribution at different photon energies.](image-url)

Fig. 7.: Relative cluster distribution at different photon energies.
As the decrease in yield is nearly exponential with cluster size (as also seen in fig. 2), the normalized yield \( \frac{I_n}{I_1} \) versus \( n \) is plotted in fig. 7. to demonstrate the change of cluster distribution with impact energy. This demonstrates that the yields of larger clusters are greater at higher photon energy than at threshold. An exact numerical evaluation of this data within the frame work of the RRK-theory has not been done so far, as this requires more detail about the as yet unknown structure of the water clusters on the surface. If this structure were determined, the energies of the cluster formation could be evaluated better.

IV CONCLUSIONS

The photon stimulated field desorption of water clusters \((H_2O)_nH^+\) from a metal field emitter exposed to water vapor is understood as an emission of protonated water clusters, occuring by energy fluctuation after the impact energy is transferred locally to vibrational modes. The RRK-theory gives a qualitatively good discription of the results, and a quantitative evaluation is still lacking. In order to explain occasional high losses in ion energy in the spectra, Anway [10] proposed a whisker model for the water growth which later was also used by Jaenicke [11]. The RRK-theory is compatible with such a growth model, provided the crossection of such a whisker structure is at least some molecules wide (mono–molecular wide whiskers are excluded). A similar energy loss was not observed in our experiments, but the energy resolution of our 10cm ToF-mass spectrometer is not appropriate for a conclusive statement on this point. The change of cluster distribution with temperature is due to a better transport of \( H_2O \)–molecules with increasing temperature. At higher temperatures, the overall higher field desorption rate causes the thickness of the water layer to diminish and this with the absolute cluster rate falls too.

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