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PHOTON STIMULATED FIELD DESORPTION OF HYDROGEN FROM RHODIUM

W. Drachsel, S. Jaenicke, A. Ciszewski*, J. Dösselmann and J.H. Block
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, F.R.G.

Abstract

Using synchrotron radiation (40-120 eV) from the BESSY storage ring, photon stimulated field desorption of hydrogen from a rhodium emitter was observed. The yield of photon-stimulated H$_2^+$ and H$^+$, discriminated by a time-of-flight technique, displayed a strong photon energy dependence: a broad maximum at 70 eV was found; the onset correlated with 4p$_3$ and 4p$_1$ core level excitations of rhodium, whereas the 4s-excitation caused no increase.

The excitation transfer from the substrate to the adsorbate most probably takes place via metal Auger electrons (XESD mechanism). From the temperature dependence of the desorption yield it is concluded that only field-adsorbed H$_2$ can be desorbed following photon-excitation of the rhodium. The occurrence of H$^+$ as a desorbing species is attributed to field-dissociation and especially at high photon flux, also to photo-dissociation of H$_2^+$.

1. Introduction

The observed enhancement of field desorption by irradiation with photons of suitable energy can be described by two concepts [1]: a. as photon-assisted field desorption or b. as field-assisted photon-stimulated desorption. To clarify the underlying mechanism it is essential to measure the dependence of the enhancement on photon energy and field strength. For the excitation of valence and core levels in the substrate as well as in the adsorbate, synchrotron radiation provides an ideal tunable light source. Laser excitation so far was only successful in special cases. Ethylene was desorbed from a silver surface in the presence of a field in a one-photon process [2], and enhanced field evaporation of silicon was observed in what appeared to be a multi-photon excitation [3].

Here, the observation of a threshold in the photon-stimulated field desorption of hydrogen from rhodium is reported and arguments for a desorption model are given.

* on leave from Institute of Experimental Physics, University of Wroclaw, PL-50 205 Wroclaw
2. Experimental

The experiments were performed at the BESSY storage ring using a toroidal grating monochromator (40-120 eV). The apparatus has been described elsewhere [4]. Briefly, it consists of a field ion microscope, where the tip to screen distance (−10 cm) also serves as the flight path for time of flight (ToF) mass analysis (fig. 1). Monochromatized synchrotron radiation (SR) was focused onto the emitter tip. The flight times of the desorbed ions were recorded at the repetition rate of the SR-light pulses of 5 MHz at BESSY.

The relative light intensity was monitored via the photo current from a gold coated glass disc. The etched rhodium tip was cleaned in vacuum by repeated annealing and field evaporation using neon as image gas.

For a good signal to noise ratio it is mandatory to work at pressures less than 2 × 10⁻⁹ mbar. Hydrogen from a pressure can (Messer Griesheim, purity better than 99.999%) was introduced with open main valve to the pumps.

![Fig. 1 - Experimental arrangement of the 10 cm ToF-field ion microscope](image)

3. Results

Previous experiments with "white" SR light [5] had shown that it is possible to obtain photon assisted field desorption from field emitters despite the small target area of 10⁻¹⁰ cm². For measurements with monochromatic light with a 10⁻³ fold lower intensity, the optimum signal-to-noise ratio must be used, which is achieved at a hydrogen pressure of 2 × 10⁻⁹ mbar (at 80 K). The hydrogen desorption signal from the rhodium emitter surface depends under these conditions linearly on the pressure, whereas at higher pressure the hydrogen coverage and therefore also the desorption signal saturate. The competing field-ionization rate, which is responsible for the random background in the ToF spectra grows always linearly with the pressure.
Fig. 2 a-c Time-of-flight spectra of hydrogen from Rhodium at $p = 2 \cdot 10^{-10}$ mb, $F = 20$ V/nm, $T = 80$ K at 3 different photon energies

Fig. 3 a-c Spectral dependence of the hydrogen yield at 3 different field strengths, $p = 2 \cdot 10^{-10}$ mb, $T = 80$ K
In fig. 2a, an original ToF-spectrum for the "white" SR light illumination is presented with the Rh tip held at 80 K. Under the same conditions, the spectral measurements at 25 nm and 18 nm are shown in fig. 2b and 2c. Over the energy range of 40-120 eV, desorption spectra were taken at three field strengths, which are shown in fig. 3a-c. The hydrogen intensity in these plots represents the sum of the H$_2^+$ and H$^+$ signals above the background, taken from ToF-spectra. The desorption rate is corrected for changes of gas pressure and light intensity. To obtain the photon flux, the current from the gold diode was converted using the data of Saloman [6].

By varying the width of the entrance slit to the monochromator, the photon flux at the tip could be changed. A linear relationship between photon flux and desorption signal, indicative for a single photon process, was observed (fig. 4).

4. Discussion

In fig. 2 some characteristic differences between ToF spectra taken with "white" and monochromatic illumination become evident. Gas-phase photo-ionization, which appears as a broad band around 210 nm with white light is virtually absent under monochromatic irradiation. The H$^+/\text{H}_2^+$ ratio changes from 0.6 with monochromatized light to 1.1 with white light, indicating additional photo-dissociation of desorbing H$_2^+$ under intense illumination. The count rates of the desorbed ions remain almost unchanged when going from illumination at 18 nm to white light, even though the photon flux is here about 400 times higher. Obviously, under the intense illumination almost the complete coverage of H$_2$ is removed from the surface. This is also indicated by the reduction of the background signal.

The pressure was adjusted so that the desorption signal did not yet saturate. Under these conditions the normalized hydrogen yield reflects the true desorption cross section as a function of photon energy. As is seen from fig. 3, varying the field strength between 30 and 36 V/nm influences neither the threshold at appx. 50 eV nor the shape of the desorption band. Steps in the desorption yield correlate with the rhodium 4$p_{3/2}$ and 4$p_{1/2}$ core excitations, whereas the 4$s$ excitation does not show up in the desorption spectrum.
These features are consistent with the model of Knotek and Feibelman (KF) as well as the XESD model proposed by Jaeger et al. In both models the initial step is the creation of a core hole at a metal atom. If this hole is filled by a valence electron of the adsorbate, the KF mechanism applies. Additional ejection of Auger electrons can increase the oxidation state of the adsorbed molecule by two or three units, so that ionic desorption becomes possible. In XESD, the core hole is filled by a metal electron. Thereby Auger electrons of sufficient energy are generated which can lead to the desorption of adsorbed molecules.

The KF mechanism will only be active when all paths for intramolecular Auger processes are blocked. This is not the case, when desorption from a metal surface is to be considered, where a large number of mobile electrons is available in the conduction band. In addition, there is little orbital overlap between the metal atom and the adsorbed hydrogen molecule. Let us now consider the influence of the high electrostatic field. It was found that desorption starts at kink sites, and the electric field will certainly reduce the electron density at such protruding atoms. Also, the valence electrons of the field-adsorbed H$_2$ will be pulled towards the metal surface. Nevertheless this field effect should not be sufficient to alter the desorption mechanism to such degree that the KF-mechanism becomes dominant.

Ernst determined that an electron energy above 40 eV is necessary for electron-stimulated field-desorption. The Rh 4p Auger electrons have just about this energy. They can therefore lead to an efficient desorption. Since the absorption coefficient of the metal increases steeply at the 4p edge, the number of photo-electrons which are created near the surface will increase sharply. The XESD mechanism therefore explains the onset behaviour of the desorption yield.

Discussing PSD, Menzel pointed out that structures in the desorption yield sometimes coincide incidentally with inner core transitions in the metal. He could explain the observed spectrum for CO desorption from Ru with the assumption of multiple valence-excitations in the adsorbate, which lead to long living, highly correlated excited electronic states. The fact that the H$_2^+/H^+$ ratio is governed only by the field strength does not favour this model for our case, because following a multiple valence excitation in H$_2$ one expects a high degree of dissociation.

To decide which model describes correctly the photon-stimulated field desorption, further experiments with different substrates as well as adsorbates are needed. So far it could be demonstrated that the primary step is a one-photon excitation. This primary excitation takes place in the bulk of the metal substrate. We prefer the XESD-model to explain the excitation transfer to the adsorbate. However, there is at least one other desorption mechanism active. This is apparent in fig. 3, where a low, but distinct desorption yield is seen below the threshold at ~50 eV. The threshold for this low-energy process has not yet been determined. It lies at energies below 10 eV, because the desorption signal was still observed after inserting a LiF window into the light beam. This low-energy desorption mechanism is tentatively attributed to a direct valence excitation of the field-adsorbed hydrogen.

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References

10. R. Smoluchowski, Phys. Rev. 60 (1941) 661.