Lifetime Effects of Xenon Adsorption on the Image-Potential States of Ru(0001)

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Abstract. The electron dynamics of the image-potential states of clean and Xe-covered Ru(0001) surfaces was investigated by means of time-resolved two-photon photoemission. Xe adsorption is observed to reduce the coupling of the first image-potential state to the metal and lead to lifetimes that increase from 11 fs in case of the clean surface to 125 fs for a double layer of Xe. The results are discussed within the framework of a tunnelling model wherein the Xe 6s-derived electron affinity level determines the barrier height.

The quantum yield of most electronically induced adsorbate reactions on metal surfaces is exceedingly small, because the primary excitation delocalizes into the bulk within a few femtoseconds or even on a sub-femtosecond timescale. Within the commonly employed Menzel-Gomer-Readhead model, these small yields depend exponentially on the excited state lifetime [1]. In order to be able to exploit some of the unique properties of two-dimensional adsorbate layers for time-domain experiments [2] it will thus be necessary to reduce the coupling between adsorbate and bulk electronic states. This may be accomplished by the use of rare-gas spacer layers [3]. As a model system to study related coupling issues we have investigated the relatively long-lived image-potential states [4,5] that are mainly located in the vacuum above a Ru(0001) surface and report here how there relaxation behavior depends on xenon adsorption.

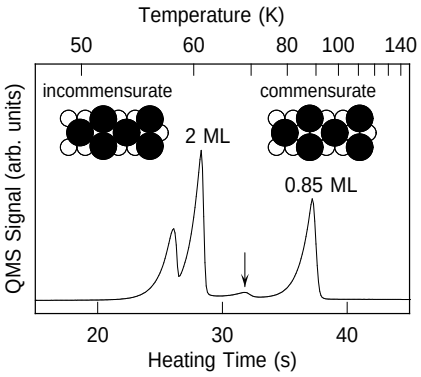

Fig. 1. Temperature programmed desorption of Xe from Ru(0001)

The experiments were performed by time-resolved two-photon photoemission (2PPE). Electrons were excited into the normally unoccupied image-potential states by 80-fs UV pulses ($\hbar\omega_a = 4.95\,\mathrm{eV}$). They were photoemitted by subsequent 40-fs IR pulses ($\hbar\omega_b = 1.65\,\mathrm{eV}$) and detected energetically resolved in a hemispherical analyzer. The Xe layers were prepared with temperature programmed desorption (TPD). The TPD spectra (Fig. 1) show the desorption of the second and

the first monolayer (ML) as two prominent peaks; the small maximum in between arises from a phase transition from the incommensurate close-packed monolayer to the commensurate $\sqrt{3}\times\sqrt{3}$-superstructure with a coverage of 0.85 ML [6].

The 2PPE spectra recorded with zero delay between UV and IR pulses are plotted in Fig. 2. The binding energy of the lowest image-potential state ($n = 1$) increases from -0.64 eV to -0.74 eV after adsorption of the commensurate and incommensurate monolayers; it decreases again slightly to -0.71 eV after adsorption of the bilayer. Image-potential states with higher quantum numbers ($n = 2, 3$) can be seen from the Xe-covered surfaces as well, because the decrease of the workfunction by 0.6 eV upon Xe adsorption enables their excitation with the UV pump photons. The lifetime of the $n = 1$ state on clean ruthenium was determined from a peak shape analysis to be 11 fs and served as a reference for the time-domain experiments. The 2PPE cross-correlation curves (Fig. 3) exhibit a strong increase in lifetime upon Xe adsorption. 36 fs, 52 fs and 125 fs were obtained for the commensurate and the incommensurate monolayer and the bilayer, respectively.

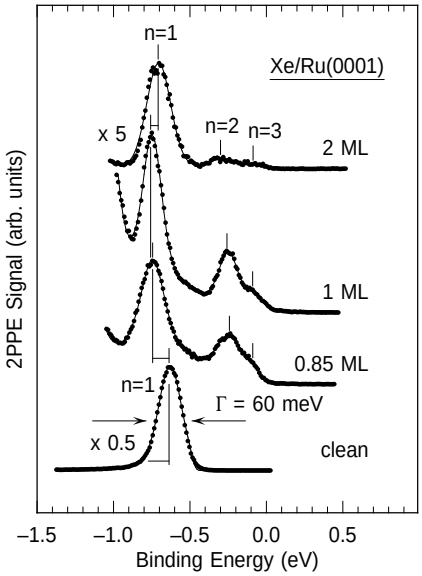

Fig. 2. 2PPE Spectra from clean and Xe covered Ru(0001) recorded at normal emission and an analyzer resolution of 40 meV.

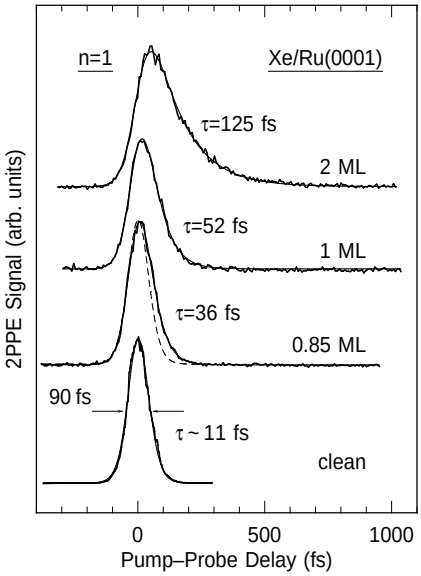

Fig. 3. 2PPE cross-correlation traces from the $n = 1$ state for different Xe coverages. At positive delays the UV pump pulses arrive before the IR probe pulses

The observed behavior can be interpreted in a picture where the Xe layers form a repulsive barrier for electrons in the $n = 1$ state [7]. For all Xe layers we investigated, the binding energy of this state lies below the electron affinity of bulk Xe, which is 0.5–0.55 eV below the vacuum level. Thus, the wavefunction of the $n = 1$

state is mainly located in the vacuum above the Xe layer and gets exponentially damped when transversing this barrier. The measured increase in lifetime upon completing the second monolayer can be explained by a thicker tunneling barrier. An estimate from plane waves tunneling through a rectangular barrier, with a Xe/Xe layer spacing of 3.6 $\AA$, is in good agreement with our experimental results.

In contrast to Ag(111) and Cu(111) surfaces [7,8], the $n = 1$ energy on clean Ru(0001) lies close to the center of the band gap. The effect that the lowering of the work function upon Xe adsorption shifts the image-potential states towards the gap center and thereby increases the bulk barrier [8] can thus be neglected in the case of Ru(0001). The significant longer lifetime of the incommensurate as compared to the commensurate monolayer can be understood qualitatively from the fact that the interaction of an excess electron with the closed Xe valence shell is repulsive. As the Xe coverage is 15% higher in the incommensurate phase, the enhanced interatomic overlap is likely to cause an upshift of the electron affinity and thus to increase the barrier height.

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