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A. Hotzel, E. Knoesel, Martin Wolf, G. Ertl, "Controlled modification of surface state lifetimes by physisorbed adsorbates," Proc. SPIE 3272, Laser Techniques for Surface Science III, (30 April 1998); doi: 10.1117/12.307125

SPIE.

Event: Optoelectronics and High-Power Lasers and Applications, 1998, San Jose, CA, United States

Controlled Modification of Surface State Lifetimes by Physisorbed Adsorbates

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ABSTRACT

Femtosecond time-resolved two-photon photoemission (2PPE) is used to study the influence of physisorbed xenon and oxygen adlayers on the lifetime of image potential states and interfacial quantum well states on Cu(111). Adsorption of 0 to 3 layers of Xe leads to a pronounced *increase* of the $n = 1$ image state lifetime from 22 fs to 300 fs, respectively. However, for adsorbate heterostructures consisting of one monolayer (ML) O₂ on top of Xe spacer layers with variable thickness it is found that the lifetime of an oxygen induced quantum well state (0.35 eV below E_{vac}) *decreases* from 650 fs to 90 fs when the number of spacer layers is raised from 1 ML to 5 ML. The results can be semiquantitatively reproduced by a model calculation which accounts for the modified image potential due to the Xe and O₂ adlayers. The changes of the lifetimes are explained by the differences in the penetration of the excited state wave function into the Cu substrate.

Keywords: Ultrafast surface dynamics, femtosecond time-resolved photoemission, quantum well states, physisorption, xenon, oxygen, Cu(111) single crystal

1. INTRODUCTION

The dynamics of electronic excitations at surfaces and interfaces are of fundamental importance for a wide range of phenomena, e.g., for the performance of electronic devices, the interaction of molecules with surfaces including charge transfer processes as well as in photo- or electron stimulated desorption and dissociation. In the latter processes of electronically induced adsorbate reactions the lifetime of the excited state is the key quantity, which governs both the cross sections and the dynamics of the reaction, but remains most often an unknown parameter [1, 2]. Attempts to measure the excited state lifetime of chemisorbed species at metals directly in the time domain were so far only partially successful [3] (except for a single system: Cs/Cu(111) [4]). This suggests to investigate model systems to elucidate the interaction of excited electronic states at surfaces with the underlying substrate [5] and to explore possibilities to control the ultrafast electron dynamics at surfaces [6]. Image potential states at metals [7, 8] provide an ideal testing ground, because they are conceptually simple and it has been demonstrated that their lifetimes can be modified by adsorbates [9-11] as well as by temperature induced binding energy shifts [12].

In this paper we report a systematic study of the influence of physisorbed adsorbate overlayers on Cu(111) on the dynamics of image states and adsorbate induced quantum well states. For rare gas adsorption the lifetime is found to increase with increasing number of overlayers, a trend which has been observed also for alkane and heptane overlayers on Ag(111) and for Xe/Ag(111) [10, 13]. The slower relaxation rates observed for thicker layers can be attributed to a shift of the electron probability density away from the metal/adsorbate interface which leads to a reduced wave function penetration into the bulk where the excited electron population can decay into electron hole pair excitations in the metal [11]. For systems

with a repulsive electron affinity (like heptane) a model invoking a tunneling barrier has been proposed [10, 13] while for xenon a dielectric continuum model which incorporates the formation of the Xe conduction band seems more appropriate [14]. On the other hand, for molecules like O₂ with a low lying negative ion resonance near the vacuum level we find that new adsorbate induced quantum well states are formed, which exhibit an unexpected dependence of their lifetimes on the 'spacer' layer thickness. In heterostructures consisting of Xe and O₂ the lifetime of an oxygen induced quantum well state is maximum when the O₂ molecules are adsorbed on one monolayer of Xe but decreases upon further increase of the number of Xe spacer layers. This is attributed to the different contributions of an O₂ molecular resonance to the quantum well state in the adsorbate heterostructure [15]. A calculation of the bulk penetration of the quantum well states using a one-dimensional model potential yields good agreement with the experimentally observed trends.

2. EXPERIMENTAL

The time-resolved two-photon photoemission (2PPE) experiments were performed in an UHV chamber equipped for photoelectron spectroscopy combined with a Ti:Sapphire femtosecond laser system, as described elsewhere [12]. In the two color 2PPE setup tunable femtosecond UV pulses (60 - 75 fs, $h\nu_{\text{pump}} = 3.6 - 4.8$ eV) are used to excite electrons into normally unoccupied image potential or quantum well states from where they are subsequently probed by a second laser pulse (60 - 75 fs, $h\nu_{\text{probe}} = 1.8 - 2.4$ eV). The photoemitted electrons are detected in time-of-flight spectrometer along the surface normal (at $k_{\parallel} = 0$). The lifetime of the intermediate state is determined from the analysis of time-resolved 2PPE spectra as a function of the time delay between the UV ($h\nu_{\text{pump}}$) and visible ($h\nu_{\text{probe}}$) pulses (see figure 1). Details of the data analysis, which is based on a density matrix formalism, are discussed elsewhere [12, 16].

The Cu(111) crystal is mounted on a He-cryostat and can be cooled to 25 K. The Xe monolayer (ML) coverage was prepared by exposing the surface to a dose exceeding 1 ML at 30 K and subsequent annealing to 65 K, whereupon the

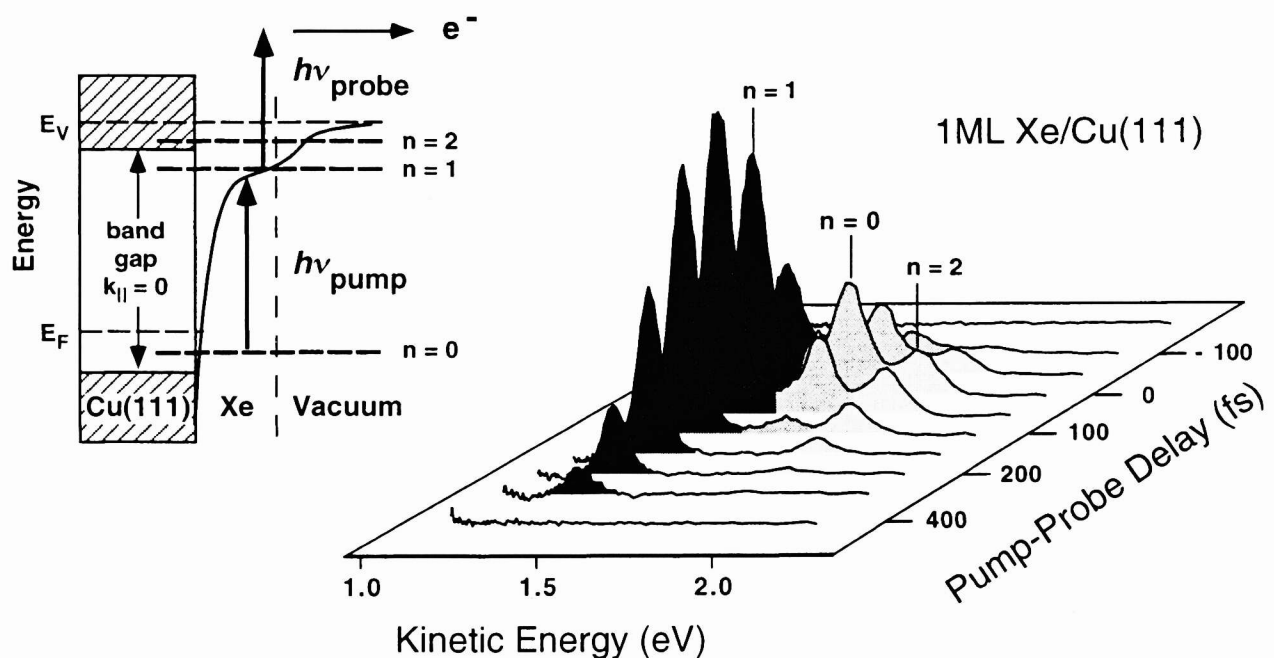


Figure 1: Time-resolved 2PPE spectra of surface and image states for 1ML Xe/Cu(111). The inset shows a schematic energy diagram of the Cu(111) surface at $k_{\parallel} = 0$, indicating the excitation from the occupied ($n = 0$) surface state to the unoccupied $n = 1$ and $n = 2$ image potential states with $h\nu_{\text{pump}}$ and $h\nu_{\text{probe}}$, respectively.

desorption of the second and further layers are monitored with a quadrupole mass spectrometer. The Xe bilayer was prepared by controlled dosing at 57 K. In this way, well-ordered Xe monolayer and bilayer coverages were obtained, which were checked by their characteristic 2PPE spectra. Xenon multilayers were prepared by controlled dosing at 50 K. O₂ was dosed on top of the Xe adlayers at 28-31 K. It was verified that after thermal desorption of the O₂ layer by heating to 40 K, the previous 2PPE spectra of the Xe-covered surface were reproduced. This, together with the sharp features observed in the 2PPE spectra, served as a test for well-defined adlayers. The O₂ and Xe coverages were analyzed after the 2PPE measurements by temperature-programmed desorption [15].

3. DYNAMICS OF IMAGE STATES: XENON ADLAYERS ON Cu(111)

Figure 1 (inset) shows a schematic energy diagram of the electronic structure of Cu(111) for zero parallel momentum ($k_{\parallel} = 0$). At a substrate temperature of 25 K the projected *sp*-band gap at $k_{\parallel} = 0$ extends from 0.9 eV below the Fermi level to 4.15 eV above E_f . With increasing temperature the lattice expands and the width of the gap becomes smaller. Recently we have shown that due to this temperature dependence of the bulk band structure the lifetime and energetic position of the first image state on Cu(111) becomes also temperature dependent [12]. At 25 K the $n = 1$ state is located at 4.10 eV above E_f (i.e. clearly inside the gap) and we determine a lifetime of 22 ± 3 fs. At higher temperatures the image state begins to overlap with the band edge and its lifetime decreases to 14 ± 3 fs at 350 K. Note that the $n = 1$ lifetime of 18 fs reported in a previous study was measured at 90 K [5, 11].

The surface and image potential states are found to persist upon adsorption of one monolayer of xenon (see figure 1) and the lifetimes of the $n = 1$ and $n = 2$ states increase with respect to bare Cu(111). With increasing number of Xe layers we observe a pronounced rise of the lifetimes up to 300 ± 50 fs for the $n = 1$ state and 90 ± 10 fs for the $n = 2$ state for 3 ML Xe (see figure 2). Furthermore, the binding energy of the $n = 1$ ($n = 2$) state with respect to the vacuum level decreases (increases) from 0.80 eV (0.21 eV) on the bare surface to 0.38 eV (0.27 eV) for 3 ML Xe/Cu(111). The different trends in

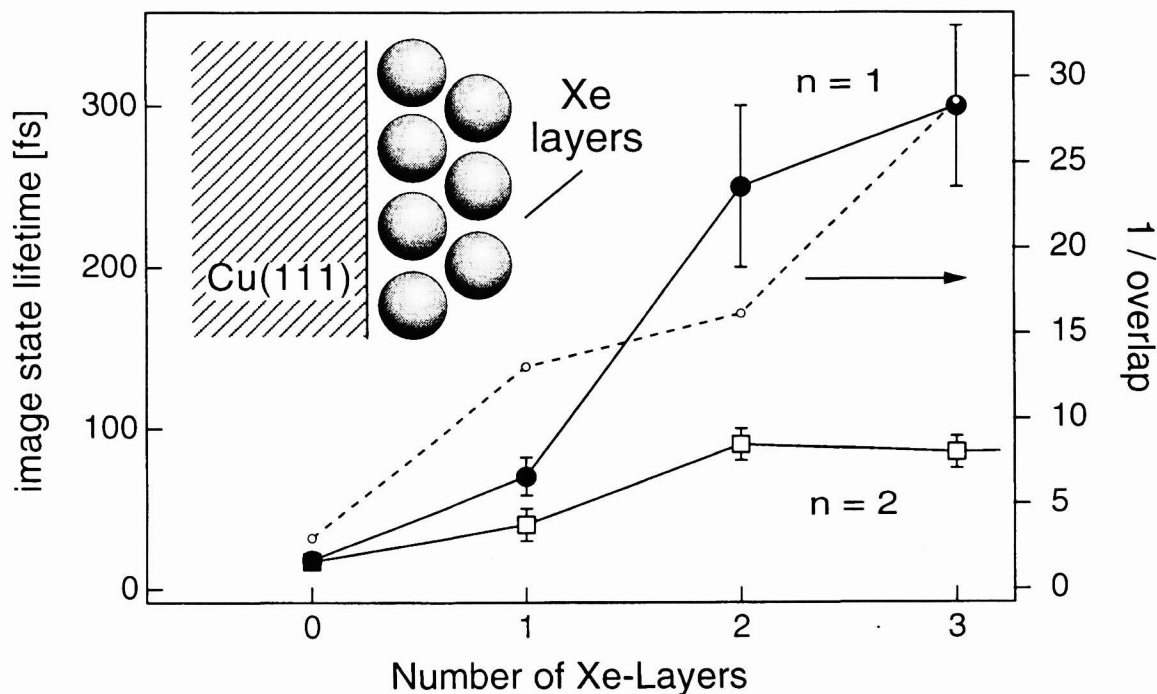


Figure 2: Lifetime of the $n = 1$ (●) and $n = 2$ (□) image potential states on Xe covered Cu(111) versus number of Xe over-layers. The dashed line (- o -) shows the inverse of the calculated wave function overlap in the substrate (see Fig. 3).

the binding energies of the $n = 1$ and $n = 2$ state indicates the formation of quantum well states, as discussed below. Similar results were also observed for Xe/Ag(111) by Harris and coworkers [13, 14]. Note that the $n = 2$ state exhibits a shorter lifetime compared to the $n = 1$ state in contrast to the expectation of a n^3 scaling of the lifetime of the Rydberg series of image states [17]. This may be explained by the fact that the $n = 2$ state is energetically degenerate with bulk states for Xe coverages ≤ 1 ML, but it shifts slightly below the band edge for coverages ≥ 2 ML.

To explain the pronounced increase in lifetimes with Xe coverage one has to consider that the dominant relaxation pathway of photoexcited electrons in the image state is given by inelastic scattering processes with electrons in substrate. Hence the penetration of the image state wave function into the crystal volume and its overlap with bulk state determines the coupling to substrate excitations and its lifetime [18]. There are several factors which influence the wave function overlap with the bulk. First, the damping of the image state wave function inside the metal depends critically on the energetic position within the band gap. In a one-dimensional two-band approximation of the bulk band structure (in the direction normal to the surface) the electron wave vector k has a non-vanishing imaginary part, $Im(k)$, for energies inside the gap (see figure 3) [8]. When the image state binding energy approaches the gap edge $Im(k)$ becomes small and thus the wave function penetration increases resulting in a shortening of the lifetime.

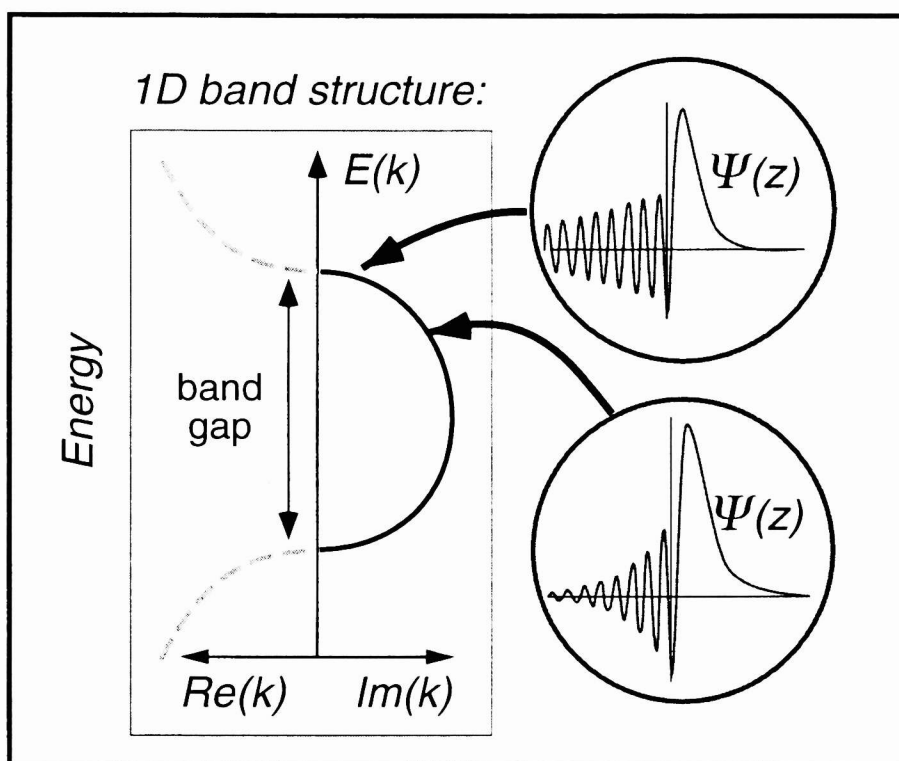


Figure 3: Complex band structure (schematic) indicating the real ($Re(k)$) and imaginary ($Im(k)$) part of the electron wave vector k in the direction normal to the surface. The increase of $Im(k)$ towards the center of the gap leads to a stronger damping of the image state wave function inside the crystal. The smaller probability density in the metal substrate reduces the rate of inelastic scattering with bulk electrons and leads to longer lifetime of the image state.

Upon adsorption of 1 ML Xe on Cu(111) the work function is reduced by 0.5 eV to 4.4 eV; however with further adsorption, it changes only slightly. The observed increase in the $n = 1$ lifetime upon adsorption of the *first* Xe layer arises predominantly from the downward shift of the image state towards the center of the gap due to the decrease of work function

(see figure 3) [5, 11]. However, to explain the *further* increase of the lifetime for coverages above 1ML the changes of the image potential due to the dielectric properties of the rare gas layer and the position of the Xe affinity level must be taken into account.

In the following we will, therefore, consider the rare gas overlayers as a dielectric slab in front of a semi-infinite metal (approximated by the nearly free electron (NFE) model). The modification of the image potential of the bare metal by the dielectric (rare gas) layer results (1) in a lowering of work function, which shifts the energetic position of the electronic states with respect to the bulk band structure (see above), (2) screening of the image potential inside the layer, which is also shifted with respect to the vacuum by the electron affinity, E_A , of the rare gas layer, (3) build up of an image potential at the dielectric/vacuum interface (see reference [14]). Treating the dielectric as a continuum without considering its atomic structure would result in unphysical singularities at the metal/dielectric and dielectric/vacuum interface. However, the polarization of the xenon can only occur on a finite length scale of the order of one atomic layer and we thus interpolate the image potential at the dielectric/vacuum interface (see figure 4, lowest panels). The analytic expression for the potential, $V(z)$, inside the Xe slab and in the vacuum is given by formulas (2-9) from reference [14]. Since the polarizability of neighboring

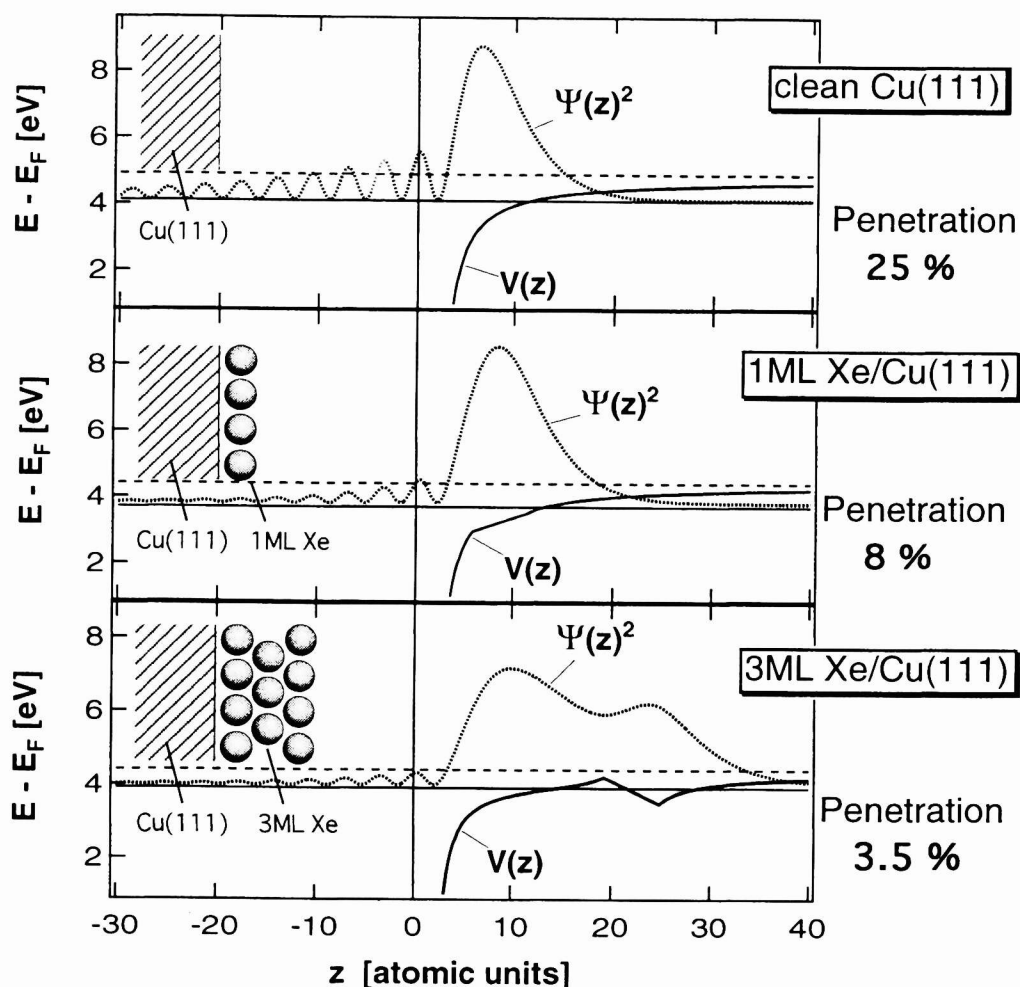


Figure 4: One dimensional model potentials $V(z)$ and calculated probability densities $\Psi(z)^2$ for 0, 1 and 3 monolayers of Xe on Cu(111). With increasing number of overlayers the electron density shifts away from the metal substrate and hence the overlap with bulk states is reduced.

Xe atoms is the origin for the dielectric constant ϵ being >1 and for the increase of the electron affinity in bulk xenon compared to a free atom or a monolayer slab, we assume that for the first three Xe layers the values of E_A and $(\epsilon-1)$ are smaller than the bulk values. This treatment differs from Ref. [14] but appears necessary to reach reasonable agreement with the experimental findings. We assume that E_A and $(\epsilon-1)$ scale with 1/6, 1/3 and 2/3 for 1, 2 and 3 layers, respectively (see [19]). The scaling factors were chosen to give the best reproduction of the measured binding energies and lifetimes both for Xe/Cu(111) and for the O₂/Xe/Cu(111) system (see below).

We can reproduce the experimental observed changes of the image state binding energies and lifetimes within our proposed model in a semi-quantitative way. Hereby we calculate the wave function by matching the solution of the nearly free electron (NFE) model decaying exponentially into the Cu crystal with the numerical solutions of Schrödinger's equation for the potential, $V(z)$, on the Xe/vacuum side (see figure 4). Valid solutions are the bound states which decay exponentially towards the vacuum side. The parameters for the NFE model describing the Cu(111) substrate are -8.6 eV for the bottom of the sp-band and -0.9 eV and 4.15 eV for the lower and upper edge of the band gap with respect to E_F . The vacuum energy is set to 4.9 eV for clean Cu(111) and to 4.4 eV for Xe/Cu(111). The thickness of a Xe layer is $6.76 a_0$ ($= 3.58 \text{ \AA}$) and we use a bulk value of $\epsilon = 2.2$ for the dielectric constant (calculated from the Clausius-Mossotti relation) and $E_A = 0.4$ eV for the electron affinity. Figure 4 shows the calculated probability densities $\Psi(z)^2$ for 0, 1 and 3 monolayers of Xe on Cu(111). At higher coverage the center of gravity of the probability density clearly shifts away from the metal. Hence the bulk overlap (i.e. the part of $\Psi(z)^2$ inside the crystal at $z < 0$) decreases from 25% to 8% to 3.5 % for 0, 1 and 3 Xe layers, respectively.

The inverse values of the calculated bulk overlap of the $n = 1$ image state are plotted together with the measured lifetimes for 0 to 3 ML Xe in figure 2. Comparing with the experiment we find good agreement with the experimentally observed trend of the lifetimes. Note, because the $n = 2$ image state is degenerate with bulk states (< 2 ML) the above treatment is not applicable. De Andres has calculated for image states on Cu(111) that a bulk overlap of 10 % corresponds to a lifetime of $\hbar/19.4 \text{ meV} = 34 \text{ fs}$ [18]. Albeit this calculation underestimates the measured lifetimes by more than a factor of two, the quasi linear dependence of the lifetime with the inverse overlap is fully consistent with the experiments. We also find that the trends of the calculated binding energies for the $n = 1$ and $n = 2$ states are nicely reproduced by our calculation (not shown). With increasing Xe coverage all states with $n \geq 2$ shift downwards in energy towards the conduction band minimum of solid Xe, which indicates the formation of quantum well states within the Xe slab [14].

4. ADSORBATE HETEROSTRUCTURES: O₂/Xe/Cu(111)

The above experiments as well as previous studies [13, 20] on the influence of rare gas overlayers on electronic lifetimes suggest that the dynamics of excited states at metals can be modified in a controlled way. To gain further insights into surface (photochemical) reactions it seem appealing to extend these studies beyond chemically inert rare gas layers and to investigate also systems with low lying molecular resonances. Here we present a study of the electron dynamics of a heterogeneous multilayer systems of xenon and molecular oxygen. Our goal is to achieve a coupling of the relatively long-lived image potential state with an O₂ negative-ion resonance by suitable variation of the spatial and energetic resonance conditions between the O₂ molecule and the Cu(111) surface (see fig. 5). This may allow to change the resonance lifetime in a controlled way. We choose O₂ because its lowest-lying negative-ion resonance ($X^2\Pi_g$, which corresponds to the population of an antibonding π^* orbital with an additional electron) lies near the vacuum energy. Upon adsorption close to a metal surface its resonance energy will be shifted downwards due to the image charge attraction and will thus be energetically close to typical binding energies of image states.

Figure 5 shows the result for a O₂/Xe/Cu(111) heterostructure consisting of 1ML O₂ on top of 1 ML Xe. We observe a single unoccupied state with a binding of 0.36 eV below the vacuum level. The crosscorrelation traces show that the life-

time of this state is substantial longer (650 fs) as compared to the lifetime of 70 fs of the $n = 1$ image state for 1 ML Xe/Cu(111). The origin of this unoccupied oxygen induced state and its extraordinary long lifetime may be attributed to the formation of the O_2 $^2\Pi_g$ negative-ion resonance. However, using this interpretation one might expect that increasing the number Xe spacer layers would result in further decoupling of the resonance from the metal and hence lead to a further increase of its lifetime. However, as demonstrated in figure 6 (left panel) the lifetime of the O_2 induced state is found to *decrease* from 650 fs to 90 fs when the number of Xe spacer layers is raised from 1 ML to 5 ML. The binding energy with respect to the bulk band edge is nearly constant between 1 ML to 5 ML, indicating that the changes in lifetime do not originate from a shift of the energetic position with respect to the bulk band structure (see figure 3)

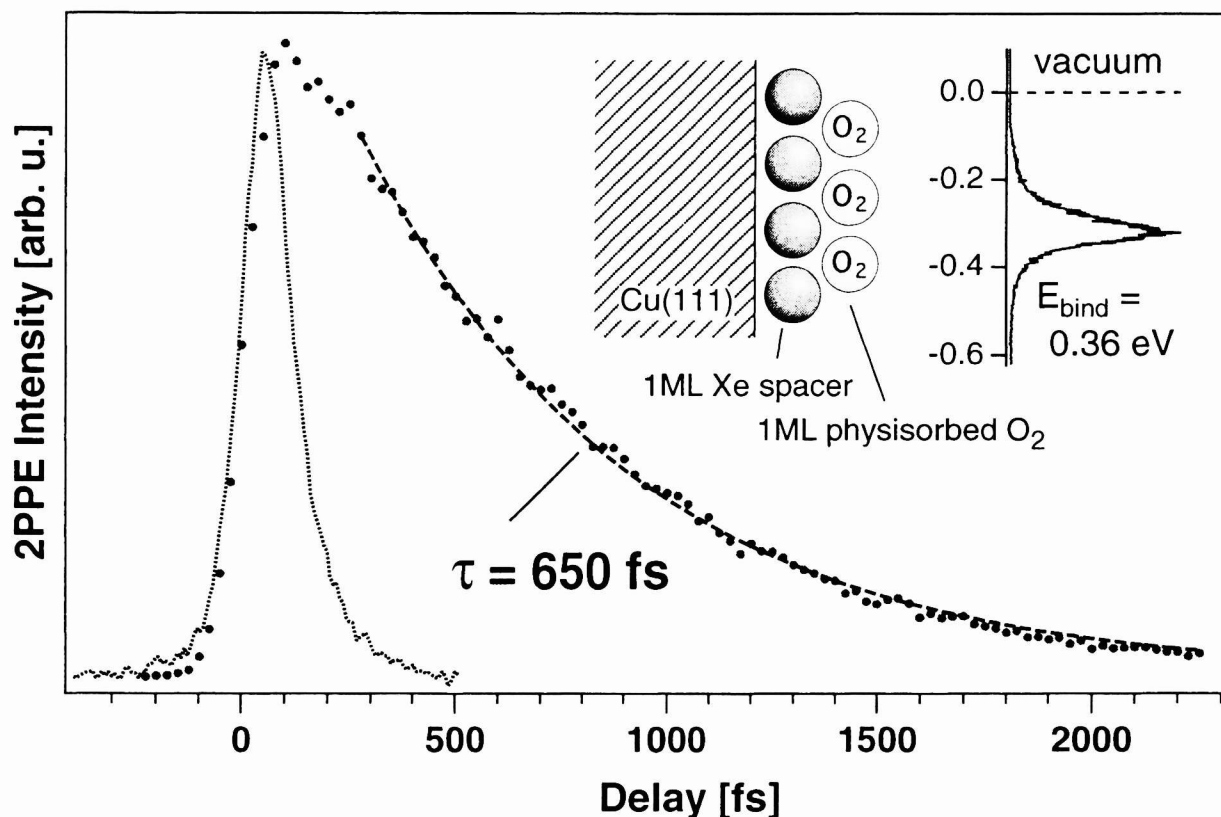


Figure 5: 2PPE Crosscorrelation traces of the $n = 1$ image state on 1ML Xe/Cu(111) (dotted line) and of an unoccupied, O_2 induced state observed for 1ML O_2 adsorbed on top of 1ML Xe/Cu(111) (●) which exhibits a lifetime of 650 fs. The inset shows the O_2 /Xe/Cu(111) heterostructure and the corresponding 2PPE spectrum.

For the interpretation of this extraordinary behavior in the O_2 /Xe/Cu(111) heterostructures we assume that a coupling of the modified image potential states in the Xe quantum well with an O_2 resonance leads to varying degrees of hybridization between both states. We can reproduce the observed decrease in lifetimes within simple one-dimensional model by adding a potential supporting a resonance to the Xe/Cu(111) potential described above. The oxygen potential is modeled heuristically by a square well of 3 eV depth and $3.6 a_0$ ($= 1.91 \text{ \AA}$) width, which is joined on both sides to a potential $V(z) = 2 \text{ Ry} * a_0^2 / (z-z_0)^2$ corresponding to the centrifugal barrier for $l = 2$ (z_0 being the center of the well). To model O_2 adsorbed on n ML Xe, the oxygen potential is centered at the position of the $(n+1)$ -th Xe layer and superimposed to the

potential of $n+1$ layers Xe. The resulting potentials are shown in figure 6 for a spacer layer thickness of 1 ML and 3 ML. Further details of the calculations are published elsewhere [15].

In figure 6 we show the calculated squared wave functions $\Psi(z)^2$ of the lowest-lying bound state for O_2 on 1 ML and 3 ML Xe, respectively. The calculations reproduce the proposed higher amount of resonance character of the state for 1 ML Xe. It can also be seen that the calculated $\Psi(z)^2$ for $O_2/1$ ML Xe has less overlap with the Cu bulk than in the case of 3 Xe layers. This agrees well with the experimentally observed trend in the lifetimes as shown in the left panel of fig. 6.

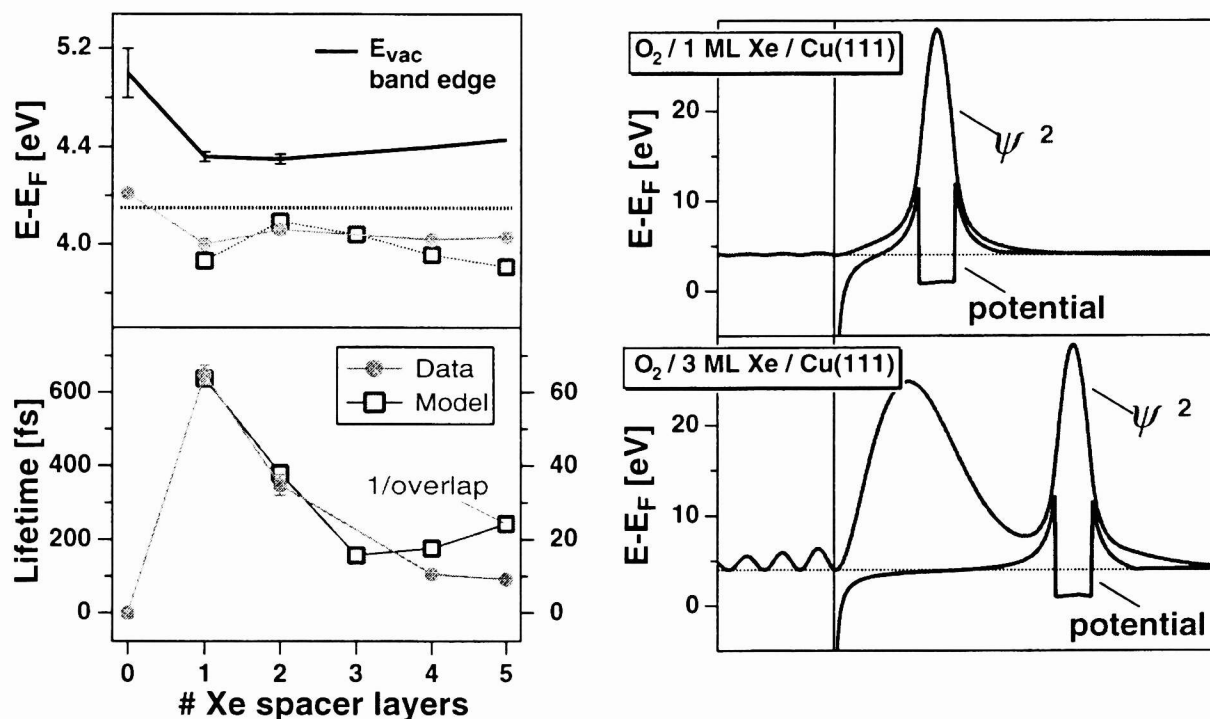


Figure 6: Left panel: Binding energies and lifetimes of the oxygen induced state in the $O_2/Xe/Cu(111)$ heterostructures as a function of Xe spacer layer thickness. The dots (●) indicate experimental data and the open squares show the results of the model calculation (see text). Right panel: One dimensional model potentials and calculated probability densities $\Psi(z)^2$ for 1ML O_2 adsorbed on 1ML and 3 ML Xe/Cu(111).

5. CONCLUSIONS

Our time-resolved 2PPE studies for Xe overlayers on Cu(111) show that the lifetimes of image states increase with the number of adsorbate overlayers. In contrast to these observations and to previous 2PPE studies of physisorbed adlayers we observe for the $O_2/Xe/Cu(111)$ system a pronounced *decrease* of the lifetime with increasing number of Xe spacer layers. We propose that this extraordinary behavior is due to varying degrees of coupling (hybridization) between an image potential state and an adsorbate molecular resonance. These results open the perspective to tailor the lifetimes of electronic states at surfaces by the combination of rare gas layers and molecular resonances. This would allow to control photostimulated adsorbate reactions, which are driven by the formation (mostly short lived) negative ion resonances. The recently developed techniques of coherent 2PPE spectroscopy will provide further insights in the elementary processes of such reactions [6].

ACKNOWLEDGMENT

The authors would like to thank K. Ishioka for experimental help in part of this work. We acknowledge valuable discussions with D. Menzel, W. Wurth and U. Höfer.

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