Ultrafast charge transfer and atomic orbital polarization

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The role of orbital polarization for ultrafast charge transfer between an atomic adsorbate and a substrate is explored. Core hole clock spectroscopy with linearly polarized x-ray radiation allows to selectively excite adsorbate resonance states with defined spatial orientation relative to the substrate surface. For c(4 × 2)/S/Ru(0001) the charge transfer times between the sulfur 2s-13p*1 antibonding resonance and the ruthenium substrate have been studied, with the 2s electron excited into the 3p^2 state along the surface normal and the 3p^2* state in the surface plane. The charge transfer times are determined as 0.18±0.07 and 0.84±0.23 fs, respectively. This variation is the direct consequence of the different adsorbate-substrate orbital overlap. © 2007 American Institute of Physics.

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INTRODUCTION

While in free atoms all orbitals are isotropic due to rotational invariance, certain orientations may be preferred if symmetry is broken, e.g., by another atom or a surface, and orbitals can be polarized along a direction, opening the way for localized interactions. This orbital polarization should, in particular, play a role in charge transfer (CT) processes from an atomic adsorbate to a substrate, because an enhanced coupling as a result of larger overlap between adsorbate and substrate states will lead to a shorter charge transfer time \( \tau_{CT} \). Ultrafast CT processes in the range of a few femtoseconds are of importance in a number of fields, such as heterogeneous catalysis,\(^1\) solar energy conversion,\(^2,3\) and molecular electronics.\(^\text{4,5}\)

In order to experimentally explore the influence of orbital polarization on CT, we have to prepare excited states in an oriented system, which have defined symmetry and thus spatial orientation at selected atomic centers. On a surface we can create these atomically and spatially defined excited states with resonant x-ray absorption using polarized radiation and exploiting symmetry selection rules. As a model system we chose the c(4 × 2)/S/Ru(0001) system, resonantly exciting a sulfur 2s electron into a resonance with a strong contribution from the 3p orbitals at the same site and controlling the symmetry (\( p_x, p_y, \) or \( p_z \)) of the excited electronic state by the polarization of the exciting radiation. For this system calculations\(^6\) have predicted a dependence of CT times on orbital polarization.

To investigate CT from these oriented excited states the core hole clock method\(^7-20\) is uniquely suited as it offers orbital selectivity\(^21\) and a temporal resolution that can be pushed down to the attosecond regime by selecting core holes decaying via ultrafast Coster-Kronig processes.\(^6\) In time resolved two-photon photoemission, another tool for investigating surface dynamics,\(^22-24\) the adsorbate resonance is commonly populated by hot electrons, created in the substrate by an optical pulse. Thus states of different orbital polarization cannot be selected as starting points for the CT. Therefore in this work we apply the core hole clock method to determine the influence of orbital polarization on ultrafast charge transfer, finding that CT is faster from orbitals exhibiting larger overlap with the substrate.

EXPERIMENT

The experiments were performed at beamline I511-1 at the MAXlab synchrotron facility in Lund, Sweden. The experimental end station is designed for surface experiments in ultrahigh vacuum, and was operated at a base pressure of 2 × 10^{-10} mbar. Its analysis chamber is equipped with a Scienta SES R4000 electron energy analyzer.
The Ru(0001) substrate was cleaned by cycles of Ar ion sputtering, exposure to 4.5 L of oxygen (1 L = 1.33 × 10⁻⁶ mbar s) and annealing at 1570 K for 30 s. Absence of O and C contaminations was verified by x-ray photoelectron spectroscopy. On the clean substrate a S monolayer was prepared by dosing 300 L of H₂S with the substrate held at 550 K and subsequent annealing at 850 K for 30 s. With this procedure, H₂S dissociates completely and the remaining sulfur forms a c(4×2) structure on Ru(0001) with S atoms on hcp and fcc sites.²⁵

The specimen was exposed to synchrotron light at grazing incidence of 7° in two different geometries, with the electric field vector normal or parallel to the substrate surface. Figure 1 shows sketches of the setups. In the left panel the synchrotron radiation is polarized perpendicular to the surface. If the photon energy is chosen around the S 2s²⁻13p⁺↑ antibonding resonance, the excitation of a sulfur 2s electron into an electronic state with strong 3p⊥ character, with its main symmetry axis along the surface normal, is preferred (out of plane). We refer to this state hereafter as 3p⊥ state. In the right panel the light is polarized parallel to the surface and therefore, with the proper choice of photon energy, the 2s electron is excited into a 3p∥ state, with its symmetry axis oriented along the surface plane (in plane).

The electron analyzer was placed in the plane of light polarization and at an angle of 45° to the surface normal in both cases. The autoionization spectra were obtained at a pass energy of 100 eV with a 200 μm slit, resulting in an instrument resolution of 25 meV.

X-ray absorption (XAS) spectra were recorded in partial electron yield mode at a kinetic energy range from 37 to 45 eV with photon energies around the S 2s⁻¹3p⁺↑ resonance from 224 to 233 eV at a bandwidth of 80 meV. The photon energy was tuned across the same resonance to measure autoionization spectra. During exposure to synchrotron light the sample was scanned to prevent radiation damage of the S layer.

RESULTS AND DISCUSSION

Figure 2 gives an overview of the autoionization spectra after subtraction of the substrate background, recorded in out-of-plane and in-plane geometries, respectively. The bright feature in the top left corner corresponds to the S 2p₁/₂ and 2p₃/₂ photoionization lines resulting from S atoms in the hcp and fcc sites of c(4×2)/S/Ru(0001). Because of color scale saturation the spin-orbit splitting of 1.1 eV is not visible in the plot. This feature also incorporates the participant states of autoionization, where the initially excited electron takes part in the Coster-Kronig decay. All other states in the plot are spectator states. The features denoted L and l are Auger resonant Raman channels at constant binding energies of 170.4 and 180.5 eV, respectively. Here the spectator electron is still located at the atomic center when the autoionization happens. L corresponds to the 2p⁻¹3p⁻¹⁺³p⁺↑↑ final state and l to the 2p⁻¹3s⁻¹3p⁺↑↑ final state. It has to be noted that L can also be reached as a photoionization satellite, according to the shake-up monopole selection rule. D and d appear at constant kinetic energy of 50.6 and 40.4 eV and resemble normal Auger decay features. These states occur when the spectator electron is transferred to the substrate before the Auger transitions. This is best described as a two-step process: energy is transferred to the substrate and the corresponding feature shows no dispersion. The elec-
Electronic configuration for $D$ is $2p^{-3}3p^{-1}\text{deloc}^{-1}$ and for $d$ it is $2p^{-1}3s^{-1}\text{deloc}^{-1}$ where deloc denotes a delocalized substrate state.

To determine the charge transfer time $\tau_{CT}$ quantitatively one has to focus on the $l$ and $d$ states because these can be reached via resonant excitation and subsequent autoionization only, while $L$ and $D$ also contain contributions from shake-up photoionization. Using the lifetime of the S 2s core hole $\tau=0.5\text{ fs,}^{28}$ $\tau_{CT}$ can be calculated via

$\tau_{CT} = \tau \frac{f}{1-f}$,

where the Raman fraction $f=l/(l+d),^{13}$ with $l$ and $d$ being the total intensities of the corresponding channels. In this treatment we determine the charge transfer time $\tau_{CT}$ of sulphur bound in the hcp and fcc sites of $c(4\times2)\text{S}/\text{Ru}(0001)$ equally.

In Fig. 3 contour plots of the autoionization spectra of channels $l$ and $d$ for both geometries are shown. Qualitatively it is apparent that CT is faster in out-of-plane geometry, as the delocalized state $d$ dominates the corresponding spectrum, while for in-plane polarization the intensities of $l$ and $d$ are similar.

To determine $\tau_{CT}$ quantitatively, a phenomenological fit with fixed spin-orbit split Voigt line shapes was applied to the spectra corresponding to photon energies directly above resonance. The line shapes were determined far below resonance ($L,l$) and far above, respectively, ($D,d$), where the
TABLE I. Fixed parameters of the phenomenological fit.

<table>
<thead>
<tr>
<th></th>
<th>$l$</th>
<th>$L$</th>
<th>$d$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>180.45</td>
<td>170.37</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Kinetic energy (eV)</td>
<td>...</td>
<td>...</td>
<td>40.4</td>
<td>50.6</td>
</tr>
<tr>
<td>Lorentz width (eV)</td>
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<td>0.8</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Gaussian width (eV)</td>
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<td>3.0</td>
<td>4.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Splitting (eV)</td>
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<td>1.1</td>
<td>3.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Ratio</td>
<td>0.46</td>
<td>0.46</td>
<td>0.59</td>
<td>1</td>
</tr>
</tbody>
</table>

features are well isolated from each other. They were found to be identical in both geometries, and are summarized in Table I, together with their binding and kinetic energies. The shapes were kept fixed across the resonance to reduce the number of free fitting parameters.

It has to be emphasized that, while the spin-orbit character of the localized states is not surprising and practically identical with the splitting of the photoionization lines, the “spin-orbit” splitting and ratio of the delocalized states are purely phenomenological. A precise simulation of this feature would have to include the substrate band structure. However, a simple model of two peaks at the splitting and ratio noted in Table I fits to the data reasonably well. On the right of Fig. 2 exemplary fits for both geometries are shown.

The determined intensities of $l$ and $d$ were used to calculate the CT times. At the bottom of Fig. 3 the result is depicted; error bars include the standard deviation of the fit and a systematical error due to the two different sites occupied by S. The S-L$_3$ edge XAS spectra are also shown to visualize the energetic position of excitation relative to the resonance.

The absorption maximum for out-of-plane geometry is shifted toward higher energies relative to the in-plane case as a result of larger overlap between the adsorbate and substrate states, leading to an increased splitting between the bonding and antibonding combinations of the adsorbate states involving the S 3$p$. The out-of-plane resonance is broadened in comparison to the in-plane resonance, which is due to a stronger contribution of the substrate bands in the out-of-plane adsorbate state in comparison to the in-plane state. In a time-dependent picture this results in enhanced charge transfer in the out-of-plane orbital polarized resonance.

For out-of-plane polarization CT times have been reported earlier as 0.32±0.09 fs just above resonance, decreasing to 0.11±0.06 fs at large detuning. For the same excitation geometry we find here 0.18±0.07 and 0.16±0.06 fs close above resonance and for large detuning, respectively. While the results are within error bars, a difference could also arise due to the different detection geometry, as in our previous work the detector was tilted by 45° towards the light source, while here it is placed in a plane normal to the beam. Furthermore, in this work the fitting approach is more detailed, determining the phenomenological line shape for each state off resonance, while in our earlier work the same shape was used for all lines. In general channel separation by fitting becomes difficult when they overlap on resonance, especially if the channels’ intensities are very similar, resulting in a larger error close to resonance.

While we find a $\tau_{\mathrm{CT}}$ of 0.18±0.07 fs for out-of-plane geometry just above resonance, we determine a $\tau_{\mathrm{CT}}$ of 0.84±0.23 fs for in-plane excitation at the same energetic position, decreasing to 0.44±0.07 fs for large detuning, compared to 0.16±0.06 fs in the out-of-plane case. The density and character of substrate states have been identified as the main reason for the energy dependence of $\tau_{\mathrm{CT}}$. The observed decrease of CT with increasing detuning may be related to the change of the band structure of Ru(0001) at ~2 eV above the Fermi energy from being dominated by states with a strong contribution from the localized Ru 4$d$ orbitals below to display more dispersive and delocalized states with main $sp$ character. As expected, CT is much faster for out-of-plane polarization than for the in-plane case, due to the larger overlap of the wave function and therefore stronger coupling between adsorbate and substrate states.

The theoretical prediction, of faster CT by larger overlap has been confirmed by our experiments. The calculated values of $\tau_{\mathrm{CT}}$ were 0.63 fs for the out-of-plane polarization and 1.15 fs for the in-plane case, with a very weak dependence on the S adsorption site (fcc or hcp). Thus, the CT from the 3$p^1_3$ state was predicted to proceed 1.8 times faster than that from the 3$p^1_2$ state. The polarization effect found in the experiment is even more pronounced. The measured ratio between the CT times for the out-of-plane and in-plane symmetries varies from 4.7 directly above the resonance to 2.8 at large detuning. The difference in the computed and experimentally measured CT times can be attributed, at least partially, to the approximations made to simplify the calculation: (i) density functional theory was used to describe an excited state; (ii) the influence of the core hole was neglected, giving rise to a shift of the resonance energy of ~0.4 eV; (iii) the CT time was estimated from the time evolution of the population of wave packets with different symmetry, however, the initial excitation process from the S 2$s$ level was not taken into account. In addition, it is difficult to make accurate estimations of the decay constant of very fast decay processes due to the quadratic dependence of the wavepacket population at short times and the appearance of oscillations associated with the coherent evolution of the wavepacket. Thus the CT time for the out-of-plane symmetry might be overestimated. Taking into account all this, the semiquantitative agreement between the theoretical calculations and the experiments is somewhat remarkable and makes us quite confident about the robustness of the effect presented here.

CONCLUSION

In conclusion we have verified that the charge transfer time from a sulfur atom adsorbed to a ruthenium substrate depends strongly on the orientation of the intermediate electronic state with $p$ symmetry relative to the surface. If electrons are promoted to a state with a strong contribution from the S 3$p$ orbital oriented along the surface normal ($3p^1_3$ state), the CT happens within 0.18±0.07 fs, while for orientation parallel to the surface ($3p^1_2$ state), we find 0.84±0.23 fs, both at photon energies directly above the absorption resonance. These findings are supported by calcula-
tions that reproduce the strong dependence of the CT time on the symmetry of the resonance wave function. In general, this type of investigation allows obtaining a detailed picture of the symmetry-dependent coupling of adsorbate states to the surface even in cases where these states overlap energetically.

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