Ultrafast electron dynamics studied with time-resolved two-photon photoemission: intra- and interband scattering in $\text{C}_6\text{F}_6/\text{Cu}(1\,1\,1)$

P S Kirchmann, P A Loukakos, U Bovensiepen and M Wolf

Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin-Dahlem, Germany
E-mail: wolf@physik.fu-berlin.de

New Journal of Physics 7 (2005) 113
Received 21 January 2005
Published 29 April 2005
Online at http://www.njp.org/
doi:10.1088/1367-2630/7/1/113

Abstract. The advances in femtosecond laser techniques facilitate the investigation of ultrafast electron dynamics at surfaces directly in the time-domain. We employ time-resolved two-photon-photoemission (2PPE) spectroscopy to study the electron dynamics of the unoccupied electronic states in hexafluorobenzene ($\text{C}_6\text{F}_6$) on Cu(1\,1\,1) serving as a model system for charge transfer across organic–metal interfaces. Our coverage-dependent study reveals a lifetime of the lowest unoccupied molecular resonance of 7\,fs for a single monolayer (ML) which increases to 37\,fs above 3\,ML coverage. We find that the population build-up of the excited state is delayed by a characteristic time of about 10\,fs with respect to the exciting laser pulse. By angle-resolved 2PPE spectroscopy, the mechanism of the delayed population rise is identified as intraband relaxation in the adsorbate band structure. The actual electron-transfer to the metal substrate occurs through interband scattering between the molecular resonance and substrate states on comparable timescales. Therefore the present study demonstrates that relaxation of hot electrons at molecule–metal interfaces include—even in the presence of strong electronic molecule–substrate interaction—also decay channels within the adlayer.

1 Author to whom any correspondence should be addressed.
1. Introduction

Direct and inverse photoelectron spectroscopies facilitate comprehensive information on the static electronic structure of condensed matter. In addition, femtosecond time-resolved investigations in combination with first principle calculations of electronic excitations led recently to a profound understanding of electronic relaxation processes at metal surfaces [1]–[3]. These studies have focused mainly on low-index noble metal surfaces like Cu(1 0 0) or Cu(1 1 1) which exhibit pronounced surface and image potential states (IPS). Such two-dimensional electronic band structures constitute well-defined model systems to study the ultrafast dynamics of elementary scattering processes and have been investigated extensively over the last decade. The field has certainly benefited from the high surface sensitivity of photoelectron studies as well as from complementary techniques like scanning tunnelling spectroscopy [1, 4] and high-resolution valence band photoemission spectroscopy [1, 5]. However, most of the recently achieved insight into the dynamics of image potential states is based on time-resolved photoemission, employing femtosecond Ti:sapphire laser sources.

Two-photon photoemission (2PPE) spectroscopy is a second-order process. Electrons are excited by a short laser pulse from below the Fermi level $E_F$ to bound intermediate states below the vacuum level $E_{\text{vac}}$. Subsequently, these hot electrons are probed by excitation into the continuum of final states as illustrated in figure 1 (top panel). Early investigations by Fauster and Steinmann [6, 7] employed tunable dye lasers where the pump and probe steps were mediated by the identical laser pulse with nanosecond pulse duration and later, in bichromatic 2PPE, by a fundamental pulse $h\nu$ and its second harmonic $2h\nu$, respectively. The first femtosecond time-resolved 2PPE studies have been performed on IPS of Ag(1 0 0) and Ag(1 1 1) by Schoenlein et al using a combination of a colliding-pulse mode-locked ring dye laser and a copper-vapour laser amplifier operating at 8 kHz resulting in 55 fs pulse duration [8]. The advent of high-repetition ($\sim$80 MHz) mode-locked Ti:sapphire oscillators delivering ultrashort laser pulses of 50 fs enabled Aeschlimann and co-workers to investigate the relaxation time of photoexcited bulk electrons on Cu(1 0 0) [9]. The electronic lifetime was found to decrease rapidly with increasing electronic excess energy in qualitative agreement with Fermi liquid theory. Fann et al examined the dynamics of electron thermalization after excitation with intense femtosecond-laser pulses in Au films by employing time-resolved direct photoemission and analysis of the transient non-equilibrium electron distributions [10].

In recent years, scattering processes involved in the relaxation of quasi-particle excitations have been studied in great detail for bare low-index metal surfaces. Hot electrons generated by absorption of a femtosecond-laser pulse relax through various elastic and inelastic scattering processes via electron–electron, electron–phonon or electron–defect interactions. The damping
rate or the inverse lifetime $\Gamma = \tau^{-1}$ of IPS is proportional to $\langle \Psi_i | \text{Im}(W) | \Psi_f \rangle$ [1], whereby the lifetime is determined by the wave function overlap of initial states $\Psi_i$ (representing the IPS) with final states $\Psi_f$ (i.e. bulk states) and the screened electron–electron interaction $W$. Optical Bloch equations have been employed to describe the temporal evolution of the electron populations and coherences. Simple rate equations are justified in the limit of non-resonant excitation schemes due to inelastic scattering events. However, resonant optical excitation followed by relaxation through elastic scattering leading to dephasing requires an analysis by Bloch equations [2]. Electron momentum resolved studies identified intraband decay within one dispersing IPS band which competes with interband decay from the IPS into bulk states. Additional scattering centres introduced by adatoms allowed a detailed investigation of defect-induced quasi-elastic scattering. These processes have already become important at minute coverages [1, 3, 11]. At stepped copper surfaces, even asymmetric scattering rates have been observed for up- and downstairs electron momentum whereby the upstairs direction is favoured [3].

Upon adsorption of the highly polarizable rare gases, the IPS retain their character localized along the surface normal and delocalized parallel to the surface. As shown for the adsorption of Xe, a dielectric layer basically acts as a spacer layer and decouples the modified IPS from metal substrate states. Consequently, lifetimes generally increase [12] as accounted for by the dielectric continuum model (DCM) at least qualitatively [13]. The DCM, however, neglects the atomic (or molecular) structure of the adsorbate. It has been shown for Ar/Cu(1 0 0) that the heavier (i.e. more polarizable) rare gases present limiting cases where the DCM applies, but for a general description the atomic or molecular polarization is required to describe the experimentally determined lifetimes [14].

In general, the dynamics of electronic excitations at molecule–metal interfaces play an important role in various physical and chemical phenomena [15]. Electron transport across nanoscale junctions, interfacial electron transfer in electrochemistry, hot-electron mediated surface photochemistry, electron injection in dye-sensitized solar cells and charge injection in organic light-emitting diodes are all based on charge-transfer processes across interfaces. Molecules or atoms adsorbed on single crystal metal surfaces under ultrahigh vacuum (UHV) conditions constitute well-suited model systems to investigate the mechanism of electron transfer from metallic substrate states to unoccupied adsorbate resonances and, subsequently, back to the metal. In these systems, the electronic metal–molecule coupling is usually strong, and electron transfer occurs on femtosecond timescales. So far investigations have been focused on metal substrates with large sp-band gaps around the $\bar{\Gamma}$-point like Cu(1 1 1) or Ag(1 1 1) which can hinder effective charge transfer between adsorbate states and the metal. Lifetimes of 10–55 fs depending on temperature (adsorbate geometry) have been obtained for Cs/Cu(1 1 1) where the antibonding sp-state of the alkali atom is excited [16]. This long lifetime made it possible to study the laser-induced adsorbate motion by a binding–energy shift with time and non-exponential decay dynamics [17]. On the other hand, for the $2\pi^\ast$ resonance in CO/Cu(1 1 1), only an upper lifetime limit of 5 fs has been reported [18]. Thus, electronic lifetimes (also referred in this context as charge transfer times) are determined by the wave function overlap and the screened Coulomb interaction as demonstrated for the dynamics of IPS. In case of adsorbate resonances on metal surfaces, the interaction is furthermore strongly dependent on the symmetry of the excited state, as has been shown by Gauyacq [19]. Hotzel et al combined the concept of decoupling IPS from the metal by Xe adsorption and intraband decay dynamics [20]. They investigated N$_2$ molecules adsorbed on Xe/Cu(1 1 1) and identified the observed intraband scattering originating from electron–phonon interaction within the nitrogen adlayer on picosecond timescales.
A favourable example of a molecular resonance with an experimentally well accessible lifetime is $\text{C}_6\text{F}_6$/Cu(111). Hexafluorobenzene is an organic molecule with a molecular structure similar to $\text{C}_6\text{H}_6$; however, the large electronegativity of fluorine decreases the electron density in the carbon backbone and leads to an electron affinity of 0.64 eV for free $\text{C}_6\text{F}_6$ compared to $-1.14$ eV for gas phase benzene [21]. A first spectroscopic investigation of the $\text{C}_6\text{F}_6$/Cu(111) system by Vondrak and Zhu using single-colour 2PPE resulted in the observation of an unoccupied molecular resonance (named peak A) derived from the lowest unoccupied molecular resonance (LUMO) at about 3 eV above $E_F$ [22]. Our subsequent investigation [23] agrees with this study and reports for coverages above 4 ML, a second broad resonance (named peak B) several 100 meV above the LUMO. Also the lifetimes $\tau_A$, $\tau_B$ of both resonances have been studied and were found to increase with coverage from $\tau_A(1 \text{ ML}) = 7(3) \text{ fs}$ to $\tau_B(5 \text{ ML}) = 32(8) \text{ fs}$. Although the time-resolution of this experiment was limited by the laser pulse duration of 65 fs, a delayed rise of the time-dependent electron population had to be included in the data analysis. The rise time agreed within experimental error bars with $\tau_B$ which suggested an indirect population of state A by relaxation (interband scattering) from the higher lying state B.

In this paper, we report new results on ultrafast electron transfer dynamics in $\text{C}_6\text{F}_6$/Cu(111) obtained with an improved time resolution of 30 fs. We identified the delayed rise to originate from an intraband decay process within the molecular resonance A, which is delocalized parallel to the interface. Thereby, we show that ultrafast relaxation dynamics at molecule–metal interfaces consist not only of charge transfer processes between the substrate and adsorbate, but also relaxation processes within the molecular adsorbate band structure that cannot be neglected.

### 2. Experimental setup and data analysis

To access the ultrafast electron transfer dynamics and scattering processes, time- and angle-resolved two-photon photoemission (2PPE) is employed. The experimental setup combines an ultrahigh vacuum (UHV) chamber (base pressure $<10^{-10}$ mbar) for sample preparation and photoelectron spectroscopy with a tunable femtosecond laser system. The Cu(111) crystal was prepared with repetitive cycles of argon ion sputtering at kinetic ion energies of 700 eV and successive annealing at 670 K for 5 min. The surface quality was inspected with low-energy electron diffraction (LEED) and the preparation was continued until sharp, low background LEED images from the Cu(111) surface were obtained. Within the resolution limits of Auger electron spectroscopy no O or C contamination was observed. Also, the work function, energetic positions, linewidths and lifetimes of the Cu(111) surface (SS) and IP state were monitored by 2PPE to confirm the surface quality. According to earlier investigations, this is a very sensitive surface characterization method because, e.g., terrace steps lead to increased scattering rates [3]. $\text{C}_6\text{F}_6$ was adsorbed on Cu(111) at substrate temperatures of 140–160 K depending on the desired coverage. The substrate temperatures were chosen appropriately to prevent the adsorption of subsequent layers, as has been reported earlier [23]. Thermal desorption spectroscopy (TDS) was routinely used to determine the adsorbate coverage ($\Theta$) from the integrated desorption yield, recorded at the mass of the most prominent $\text{C}_6\text{F}_6$-fragment (CF+, 31 amu). $\text{C}_6\text{F}_6$ coverages were investigated between 0.5 and 6 ML, where 1 ML coverage is defined by saturation of the monolayer desorption feature between 165 and 205 K in TDS [24]. All 2PPE measurements were performed at a substrate temperature of 100 K.
For the 2PPE experiments, a regenerative amplifier (Coherent RegA 9050) operating at 200 kHz repetition rate is employed, which generates pulses with a duration (FWHM) of 55 fs at a centre wavelength of 800 nm (1.55 eV). The RegA output beam pumps two optical parametric amplifiers (OPAs), operating in the near-infrared (1100–1300 nm and 1.13–0.95 eV) and visible (470–730 nm and 2.64–1.70 eV) spectral regimes. Subsequent doubling and quadrupling of the OPA output allows to generate photon energies in the visible (2.25–1.91 eV) and near ultraviolet (UV) (4.51–3.82 eV) range. The extensive tunability allows us to carefully tune the laser photon energies to specific resonances of the molecule–metal interface and to follow their dynamics. The dispersion introduced by the optical path to both the visible and the UV pulses is pre-compensated with the use of prism pair compressors, thus resulting in nearly Fourier-transform-limited pulses with durations as short as 28 fs (FWHM) at the position of the sample. The UV pulses are temporally delayed with respect to the visible pulses and are then focused onto the sample surface with polarizations parallel to the plane of incidence (p-polarization). The beam spots exhibit a Gaussian profile with a diameter of 100–150 µm, resulting in typical fluences of 100 µJ cm⁻² for the visible and of 20 µJ cm⁻² for the UV light.

To elucidate time-resolved 2PPE spectroscopy and the data analysis, we present in figure 1 2PPE data for the clean Cu(1 1 1) surface. In this experimental scheme (figure 1, top panel-right), the first laser pulse at photon energy \( h\nu_1 \) (4.68 eV) pumps the system by exciting electrons from occupied states at or below the Fermi level to unoccupied intermediate states. The dynamics of the electron population of these intermediate states are then probed with a second, time-delayed pulse with photon energy \( h\nu_2 \) (2.34 eV) that excites electrons from the intermediate states to final state energies above the vacuum level (\( E_{\text{vac}} \)). The generated photoelectrons are analysed in a time-of-flight (TOF) spectrometer. The intermediate state energy is determined as \( E - E_F = E_{\text{kin}} + \Phi - h\nu_{\text{probe}} \), where \( h\nu_{\text{probe}} \) is the probing photon energy and \( \Phi \) the sample work function.\(^3\) In addition, angle-resolved studies access the component of the electron momentum parallel to the surface: \( \hbar k_{\parallel} = \sin \alpha \sqrt{2m_e E_{\text{kin}}} \), where \( m_e \) is the free-electron mass and \( \alpha \) is the emission angle with respect to the surface normal.

In figure 1, a false colour representation of the photo-emission intensity represents the electron distribution as a function of both time delay (horizontal axis) and energy (vertical axis). To visualize low intensities, white contour lines (1, 5 and 10% of the maximum intensity) are appended to the colour-coded figure. Depending on the sequence of the laser pulses (or formally, the sign of the delay), the dynamics are probed either near \( E_F \) or at higher intermediate state energies (see figure 1, top panel). Positive delays correspond to populating intermediate electronic states \( (n = 1, n = 2 \text{ IPS}) \) with the UV light pulses \( (h\nu_1) \), while the visible pulses \( (h\nu_2) \) subsequently probe the excited electron population. On the other hand, for negative delays electrons are excited to intermediate states close to the Fermi level (e.g. hot electrons, d-band) with visible pulses \( (h\nu_2) \) and are subsequently probed by the UV pulses \( (h\nu_1) \). Therefore, the scaling on the right and left vertical axes (figure 1, main panel) depends on the sign of the delay axis and \( E - E_F \) \((E^* - E_F)\) denotes the intermediate energy scale for states pumped with the UV (visible) pulses. To obtain the pump-induced two-colour 2PPE signal, the corresponding one-colour 2PPE signal due to multiphoton absorption in the presence of either pump and probe

\(^2\) The laser pulse duration is inferred from the width of the cross correlation traces of the photoelectron yield assuming a sech²(\( t \)) pulse envelope. See also \(^{25}\).

\(^3\) The kinetic energy \( E_{\text{kin}} \) is routinely corrected for the contact potential difference of the sample and spectrometer.
Figure 1. 2PPE intensity (colour map) as a function of pump probe delay (horizontal axis) and intermediate state energy referred to $E_F$ (vertical axis) from clean Cu(1 1 1) with photon energies of $h\nu_1 = 4.68$ eV for the UV and $h\nu_2 = 2.34$ eV for the visible laser pulses. Top panel: the excited electron distribution is probed with $h\nu_1$ at negative delays, while at positive delays it is probed with $h\nu_2$ thus resulting in two intermediate state energy scales (left and right) given by $E^{(\ast)} - E_F = E_{\text{kin}} + \Phi - h\nu_{1,2}$. Middle panel: 2PPE spectrum obtained at zero time delay exhibiting peaks from the occupied SS and unoccupied $n = 1$ IPS of Cu(1 1 1). The signature of the onset of the d-band states of Cu(1 1 1) located at $\sim 1.8$ eV below $E_F$ is best seen as a small feature in the 1 and 5% contour lines around $E^{(\ast)} - E_F \sim 0.6$ eV. Bottom panel: cross correlations at different intermediate state energy intervals of 100 meV full width. Due to the finite lifetime of the excited electron population, the cross correlation of the $n = 1$ IPS ($\bullet$, $E - E_F = 4.12$ eV) shows a delayed ($\Delta t = 18$ fs) peak maximum with respect to the SS ($\blacktriangle$, $E - E_F = 4.27$ eV), which determines zero time delay and gives the laser pulse envelope. Since the hot electron distribution is probed with $h\nu_1$ the temporal traces taken at two different energies close to $E_F$ ($\blacktriangle$, $E^{(\ast)} - E_F = 0.47$ eV and $\bigcirc$, $E^{(\ast)} - E_F = 0.27$ eV) decay towards negative delays.
alone have been subtracted from all spectra presented here. This background is typically in the order of 10% of the total signal.

The two-dimensional data sets as shown in figure 1 can be analysed in two different ways: either by extraction of time-dependent 2PPE spectra as given exemplarily by the spectrum at \( \Delta t = 0 \) in the right panel of figure 1 or by the time-dependent photoelectron yield integrated over energy intervals centred on the state of interest (typically 100 meV full width). The latter procedure provides the temporal evolution of the electron population, referred to as cross correlation traces as shown in the bottom panel of figure 1. Returning to figure 1, we briefly discuss the main features of the time-resolved 2PPE spectra.

(i) The hot electron distribution appears at energies in the vicinity of the low-energy cutoff (secondary edge) at \( E^* - E_F = 0.24 \text{ eV} \) and extends to \( E^* - E_F = 2.34 \text{ eV} \) \( (E_F + h\nu_2) \). Since these electrons are pumped with the visible light \( (h\nu_2) \) and their dynamics are probed with the UV light \( (h\nu_1) \), the intermediate state energy axis is given by \( E^* - E_F \). The population decay is observed towards negative time delays \( (\Delta t < 0) \) as is shown by the cross correlation traces in the bottom panel of figure 1. For details we refer to earlier work on this topic [26].

(ii) The \( n = 1 \) image potential state of the Cu(1 1 1) surface [27, 28] with a binding energy of 0.82 eV (with respect to \( E_{\text{vac}} \)) appears at \( E - E_F = 4.12 \text{ eV} \) and is populated by \( h\nu_1 \). Its cross correlation exhibits a delayed \( (\Delta t = 18 \text{ fs}) \) peak maximum with respect to the corresponding trace of the SS, which reflects the finite lifetime of the excited electron population [27, 28] as well as the non-instantaneous population build-up at \( k_\parallel = 0 \) [28, 29]. The peak maximum shift of 18 fs at 100 K is in very good agreement with previous studies [28].

(iii) The occupied SS of Cu(1 1 1) with a binding energy of 0.41 eV below \( E_F \) appears at \( E^* - E_F = 1.93 \text{ eV} \) and \( E - E_F = 4.27 \text{ eV} \), since it can be pumped and probed with both sequences of visible and UV light. At \( k_\parallel = 0 \), the detected electrons can originate from the SS only by a non-resonant two-photon process \( (h\nu_1 + h\nu_2) \) involving a virtual intermediate state, since the Cu(1 1 1) surface exhibits a band gap at \( k_\parallel = 0 \) in the projected surface band structure [28]. This excitation process occurs quasi-instantaneously and therefore the temporal envelope of the SS reflects the cross correlation of pump and probe pulses at the sample position and thus defines the time zero of the experiment [28].

3. Results and discussion

To introduce the results on C\textsubscript{6}F\textsubscript{6} adsorbed on Cu(1 1 1), we present in figure 2 the coverage-dependent 2PPE spectra at zero delay for coverages up to \( \Theta = 6 \text{ ML} \). Adsorption of 1 ML C\textsubscript{6}F\textsubscript{6} on Cu(1 1 1) leads to a significant reduction in the intensity of the SS and the \( n = 1 \) IPS of the bare Cu(1 1 1) surface, however both peaks can still be clearly discerned. A pronounced adsorbate-induced feature marked ‘A’ appears at \( E - E_F = 3.13(1) \text{ eV} \) for \( \Theta = 1 \text{ ML} \). This feature originates from the LUMO of C\textsubscript{6}F\textsubscript{6} but is also influenced by the image potential in front of the Cu(1 1 1) surface, as discussed previously [22, 23]. State A shifts to lower energies with increasing coverage and remains basically at constant energy \( E - E_F = 2.82(2) \text{ eV} \) for \( \Theta > 3 \text{ ML} \) [23]. For \( \Theta \geq 3 \text{ ML} \) another feature named ‘B’ appears at \( E - E_F = 3.24(2) \text{ eV} \).
which broadens considerably at $\Theta = 6 \text{ ML}$, but is located at a very similar energy. The shift of the low-energy cutoff in the 2PPE spectra reflects the lowering of the work function $\Phi$ from 4.95(1) eV for the clean Cu(1 1 1) surface to 4.63(1) eV for 1 ML coverage which does not change significantly upon further adsorption of C$_6$F$_6$.

As pointed out previously [23], the unoccupied adsorbate-induced states A and B are localized along the surface normal but delocalized parallel to the surface. The dispersion and thus the delocalization of state A parallel to the surface increases with coverage resulting in an electron effective mass $m_{\text{eff}} \approx m_e$ for $\Theta \geq 5 \text{ ML}$, whereas state B remains more localized with $m_{\text{eff}} \geq 2m_e$. Therefore, these states will be treated as quasi-free electron bands in the following.

To investigate the charge transfer dynamics in C$_6$F$_6$/Cu(1 1 1), femtosecond time-resolved 2PPE was employed. In figure 3 a false-colour representation of the energy- and time-resolved photoelectron yield detected in normal emission is presented exemplarily for 3 ML coverage. Both states A and B decay towards positive time delays, which confirms the above assignment of a population with the UV ($h \nu_1 = 4.26 \text{ eV}$) and probing with the visible ($h \nu_2 = 2.13 \text{ eV}$) pulses. State B is obviously only slightly higher in energy ($\sim 300 \text{ meV}$) compared to A but decays significantly faster than A (about four times, see figure 5). This observation differs fundamentally from electron dynamics of IPS at metal surfaces where the lifetime increases due to the decrease in the wave function penetration into the bulk with the quantum number ($n$) [1, 7]. The shorter
Institute of Physics

DEUTSCHE PHYSikalische Gesellschaft

Figure 3. Energy- and time-resolved 2PPE intensity (colour map) of 3 ML C₆F₆/Cu(1 1 1) recorded in normal emission. State A exhibits a maximum shifted to positive delays by Δt = 28 fs due to a finite lifetime of the excited electrons and a population decay towards positive delays. State B reveals a remarkably fast response with a peak shift of only 6 fs.

lifetime of state B suggests a stronger coupling with the Cu substrate and points to different symmetries of states A and B. Note that charge transfer dynamics are also determined by the orbital character of the molecular states as shown by Gauyacq et al in the comparison of Cs and CO on Cu(1 1 1) [19]. From the difference in the dynamics of states A and B, we therefore conclude that both resonances cannot be regarded as IPS but are derived from molecular states of C₆F₆. This conclusion is consistent with previous Xe-overlayer experiments [23] which show that states A and B must be predominantly localized within adsorbate layers and cannot be considered as IPS.

To analyse the decay quantitatively, we acquire cross correlation traces of state A for various coverages. This is shown in figure 4 on a linear and logarithmic scale in the left and right panel, respectively. The analysis of the cross correlation signals within a rate equation model yields the corresponding decay times [23]. Note that information on time zero and the laser pulse duration cannot be obtained through the SS on C₆F₆ covered surfaces, but is retrieved from the clean Cu(1 1 1) surface after thermal desorption of the adlayer. In addition, this pulse characterization has been cross-checked by comparison with the cross correlation signal from short-lived states at energies E − E_F = 4.1 eV. There, the lifetimes of 1–3 fs are considerably shorter [30, 31] than the pulse duration confirming the time zero derived on clean Cu(1 1 1).

Inspecting the transient population of peak A, we identify in figure 4(a) a peak maximum at Δt = 28 fs due to the population build-up within the pulse duration and the subsequent population...
Figure 4. (a) Cross correlation obtained from the SS of Cu(1 1 1) (∗) providing time zero of the pump–probe delay and the temporal laser pulse envelope from a fit (——) of a sech² pulse-shape. The cross correlation of state A at 6 ML C₆F₆/Cu(1 1 1) shows a delayed (Δt = 28 fs) peak maximum and a subsequent decay. The dotted line is an attempt to fit its temporal evolution with a single exponential decay mechanism which describes neither the position of the peak maximum nor the slope of the decay. The fit shown with a full line additionally includes a delayed rise mechanism and reproduces the data satisfactorily. (b) Semi-logarithmic presentation of cross correlations of state A obtained for various coverages. The positive delay of the peak maxima increases while the decay rate decreases with coverage. Both changes reflect the increase in the lifetime of the excited state electron population. The rise and decay times are extracted from fits (——) of a delayed rise mechanism. The non-vanishing intensity for negative delays is attributed to hot electrons pumped by the visible and probed by the UV laser pulses [26, 30, 31]. In the fits, this is taken into account by a second single exponential decay for Δt < 0.
excited electron population as already discussed by Gahl et al [23]. Due to the improved time resolution of the present investigation, we are now able to unambiguously identify the population mechanism. The population dynamics including a delayed rise mechanism is given by

\[
\frac{dN(t)}{dt} = \frac{\tilde{N}(t)}{\tau_{AR}} - \frac{N(t)}{\tau_{AD}}. \tag{1}
\]

Therein \(N(t)\) denotes the electron population of state A that is probed in the final step of the 2PPE process. \(\tilde{N}(t)\) is the transient electron population initially excited to an energetically higher lying state which is not probed in normal emission (at \(k_\parallel = 0\)). A possible mechanism would comprise electrons in state A at \(k_\parallel \neq 0\) which may relax via intraband scattering towards \(k_\parallel = 0\) or an interband scattering mechanism of electrons decaying from state B into A. The first term in (1) leads to a non-instantaneous build up of \(N(t)\) with a maximum at \(\Delta t > 0\). This results in a further delay of the maximum in the transient population and a subsequently faster decay. The free parameters of rise and decay times are given by the lifetimes \(\tau_R\) and \(\tau_{AD}\), respectively. The resulting fits are shown with solid lines in figure 4 and obviously reproduce all experimental data in an excellent manner, even over three orders of magnitude of the photoelectron intensity.

Taking into account the coverage-dependent investigations, we find that all transient populations of state A require a fit based on a delayed rise mechanism as well as a coverage dependence of both time constants. The peak maximum in the cross correlation traces shifts

\[4 \text{ The transient electron population of the additional higher lying state is given by } d\tilde{N}(t)/dt = -(1/\tau_{AR} + 1/\tau_D)\tilde{N}(t). \]

Here, \(1/\tau_{AR}\) represents the decay rate due to the filling of state A at \(k_\parallel = 0\) and \(1/\tau_D\) denotes the decay rate via interband scattering into the bulk. In order to achieve convergence in the fits, \(1/\tau_D\) had to be assumed to be negligible compared to the inverse rise time \(1/\tau_{AR}\).
to later delays with increasing coverage, from 11 fs for 1 ML C_6F_6/Cu(111) to 28 fs for Θ > 3 ML. The quantitative analysis performed by fitting equation (1) to the time-resolved data results in the characteristic times τ_{AR} and τ_{AD} that are summarized in figure 5 as a function of coverage.

We have also obtained cross correlation curves for state B. We find that in contrast to A, a single exponential decay is sufficient to reproduce the temporal evolution of the population in state B (not shown). The resulting lifetimes τ_B are included in figure 5. The decay times for state A increase from 7 fs for Θ = 1 ML to 37 fs for 3 ML. Up to 6 ML, the decay time τ_{AD} of state A remains constant within the experimental accuracy (±3 fs), while τ_{AR} on the other hand exhibits a smaller, but constant increase from 7 fs for 1 ML to 13 fs for 6 ML. A similar trend is observed for the decay time τ_B of state B which increases from 9 fs for 3 ML to 12 fs for the highest coverage.

The necessity to implement a delayed rise asks for a mechanism to populate state A. We start the discussion by assuming that the finite timescale τ_{AR} for the population build-up could be attributed to electrons initially excited to higher lying energies which decay towards the bottom of the band of state A where they are finally probed at k_∥ = 0. As identified previously [20, 29], this can be caused by two very fast relaxation channels of the surface resonance. Firstly, intraband relaxation along k_∥ of electrons, which are initially excited at k_∥ ≠ 0 and decay within the band of state A to the bottom (arrow (2) in figure 6(b)), may lead to a delayed rise. Secondly, interband scattering of electrons from the higher lying state B or from bulk states into state A (arrow (3) in figure 6(b)) provides another possible mechanism. The fact that the rise time of the peak A corresponds to the decay time of state B could be an indication for the interband scattering mechanism as was proposed earlier [23]. However, as we explain in the following, angle-dependent investigations provide evidence that not the interband decay leads to the delayed rise, but intraband scattering along k_∥ within state A.

To identify the origin of the delayed rise, 2PPE spectroscopy has been carried out using the tunability of the visible OPA. Thereby, the occupied SS of Cu(111) acts as the initial state. By tuning the photon energies from below the transition between the SS and state A to energies above the transition to state B, an increase in the intensity of state A is expected if interband scattering B → A was operative. However, apart from an increase in the intensity of state B, we observe a constant intensity of state A when we cross the resonantly enhanced transition from the SS to state B (not shown). Thus we exclude an interband scattering mechanism B → A as the origin of the delayed rise. Note also that for Θ < 2 ML state B is not observed in 2PPE and is therefore unlikely to act as an additional higher lying state in interband scattering. The observed coincidence of the electron decay time of state B and build-up time in state A is thus considered to be accidental.

To test the intraband scattering mechanism, angle-dependent and time-resolved 2PPE measurements have been carried out. With this method we are able to probe the dynamics of electrons which are excited from well-defined, non-zero values of k_∥ into state A (figure 6(b)). If the intraband scattering indeed contributes to the population evolution of state A, we expect the population build-up to be faster with increasing k_∥ values. To realize this experiment, probe pulses are generated with the infrared OPA with an energy of hν_2 = 2.15 eV and combined with the frequency-doubled RegA output at 3.09 eV as a pump so that the probe photon energies can be set independently of the pump. The photon energy hν_1 = 3.09 eV has been chosen for two reasons. Firstly, this photon energy is insufficient to populate state B. Secondly, state A can be populated only at non-zero k_∥ values as indicated by the solid arrow in figure 6(b). For a
Institute of Physics / DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

Figure 6. (a) Cross correlations of state A for 3 ML C₆F₆/Cu(1 1 1) detected at various emission angles and electron momenta as indicated. The delay of the peak maximum decreases with increasing emission angle, i.e. with increasing $k_\parallel$ of the probed electron population. This indicates a systematic decrease of the excited state lifetime with increasing $k_\parallel$. (b) Scheme of the excitation, relaxation and detection processes in C₆F₆/Cu(1 1 1). (1) Interband decay from state A to SS of Cu(1 1 1). (2) Intraband decay within state A. (3) Interband decay from state B to state A.

The photon energy of $h\nu_1 = 3.09$ eV, only electrons from the occupied SS with $k_\parallel \approx 0.18$ Å⁻¹ can be pumped into state A. Populating state A at greater $k_\parallel$ values is impossible due to lack of occupied states, while at smaller $k_\parallel$ values the energy difference between the SS and state A increases and cannot be overcome. A drawback of this approach is the decreased temporal resolution due to the duration (55 fs) of the 3.09 eV pulses.

The cross correlation traces of state A for 3 ML C₆F₆/Cu(1 1 1) obtained in this manner for $k_\parallel$ between zero and 0.13 Å⁻¹ are shown in figure 6(a). The trace at $k_\parallel = 0$ exhibits a delayed peak maximum at $\Delta t = 16$ fs which shifts to $\Delta t = 5$ fs for $k_\parallel = 0.06$ Å⁻¹. At $k_\parallel = 0.13$ Å⁻¹, the peak maximum is located at zero time delay indicating an almost vanishing lifetime of the excited state. Therefore, at this point in k-space (i.e. close to excitation at $k_\parallel \approx 0.18$ Å⁻¹), no delayed contribution to the population is observed because we essentially probe only the decay of the population. Thus we identify the intraband decay as the dominant mechanism of the delayed rise of the population of state A. Although a quantitative analysis of the cross correlation traces in

New Journal of Physics 7 (2005) 113 (http://www.njp.org/)
terms of rise and decay times is inhibited by the significantly longer pulse duration, we are still able to qualitatively identify the influence of intraband decay as demonstrated in figure 6(a).

The delayed population build up at \( k_{\parallel} = 0 \) requires a filling by electrons which are initially excited to higher lying electronic states and subsequently decay towards the centre of the surface Brillouin zone on a finite timescale (see figure 6(b)). From the angle-dependent experiments, it is clearly evident that this filling mechanism is provided by the intraband relaxation of electrons excited into the delocalized band of state A, which then relax towards the band bottom along \( k_{\parallel} \). The timescale of the intraband scattering determined by \( \tau_{AD} \approx 10 \text{ fs} \) is much below any low-energy vibrational mode of C_6F_6 [32], which suggests that the intraband scattering is linked to electron–electron interactions either within the adlayer itself or with the Cu substrate. In the latter case, the underlying mechanism should be the same as for the interband decay into the bulk and a similar coverage dependence of both characteristic times \( \tau_{AR} \) and \( \tau_{AD} \) would be expected, which is not observed (see figure 5). To resolve this issue, additional high-resolution angular- and time-resolved 2PPE experiments must be conducted to quantitatively determine the intraband scattering rate in C_6F_6/Cu(1 1 1) as a function of \( k_{\parallel} \) and adsorbate coverage.

4. Conclusions and outlook

Summarizing, we have investigated the ultrafast electron dynamics at the C_6F_6/Cu(1 1 1) interface by femtosecond time and angle-resolved two-photon photoelectron spectroscopy. In accordance with earlier investigations, we find two molecular resonances at 2.82 and 3.24 eV above the Fermi level for a coverage >3 ML. At lower coverage, only the resonance A closer to \( E_F \) is observed at higher energies \( (E - E_F = 3.13 \text{ eV} \text{ at } 1 \text{ ML}) \). The decay dynamics of the states A and B were analysed by rate equation models. We find that three time constants are required to describe the population dynamics, a decay time for A and B (\( \tau_{AD} \) and \( \tau_{B} \)) and a rise time \( \tau_{AR} \) accounting for the delayed population build-up in state A. \( \tau_{AD} \) increases in a low coverage range up to 3 ML to a maximum value of 37 fs and remains constant for higher coverage. The origin of the delayed population build up in state A has been identified by angle-resolved studies to originate from intraband scattering within the band of state A. Our results highlight the potential of time- and momentum-resolved studies in revealing decay mechanisms at molecular–metal interfaces, which will play a key role in future molecular electronic devices.

The adsorbate–substrate system C_6F_6/Cu(1 1 1) represents a promising test case for ultrafast electron transfer dynamics suggesting a comparison with other experimental methods like resonant Auger–Raman spectroscopy (‘core-hole-clock’ method) [33]. This would provide a critical test of different experimental approaches and allow further insights into the underlying principles of charge transfer dynamics.

Acknowledgments

We thank C Gahl for fruitful discussions and L Ungureanu for experimental support. PAL gratefully acknowledges financial support from the European Community (no MEIF-CT-2003-501826). This work has been funded by the Deutsche Forschungsgemeinschaft through SPP 1093.

5 The absence of a delayed peak maximum for the cross correlation trace at \( k_{\parallel} = 0.13 \text{ Å}^{-1} \) due to charge transfer into the substrate is attributed to the decreased temporal resolution in this particular experiment.
References

[1] Echenique P M, Berndt R, Chulkov E V, Fauster Th, Goldmann A and Höfer U 2004 Surf. Sci. Rep. 52 219
[2] Petek H and Ogawa S 1997 Prog. Surf. Sci. 56 239
[3] Weinelt M 2002 J. Phys.: Condens. Matter 14 R1099
[4] Kliewer J, Berndt R, Chulkov E V, Silkin V M, Echenique P M and Crampin S 2000 Science 288 1399
[5] Reinert F, Nicolay G, Schmidt S, Ehm D and Hüfner S 2001 Phys. Rev. B 63 115415
[6] Steinmann W 1989 Appl. Phys. A 49 365
[7] Fauster T and Steinmann W 1995 Electromagnetic Waves: Recent Developments in Research vol 2, ed P Halewi (Amsterdam: Elsevier)
[8] Schoenlein R W, Fujimoto J G, Eslesy G L and Capeheart T W 1988 Phys. Rev. Lett. 61 2596
[9] Schmuttenmaer C A, Aeschlimann M, Elsayed-Ali H E, Miller R J D, Mantell D A, Cao J and Gao Y 1994 Phys. Rev. B 50 R8957
[10] Fann W S, Storz R, Tom H W K and Bokor J 1992 Phys. Rev. B 46 13592
[11] Olsson F E, Borisov A G, Persson M, Lorente N, Kazansky A K and Gauyacq J P 2004 Phys. Rev. B 70 205417
[12] Wolf M, Knoesel E and Hertel T 1996 Phys. Rev. B 54 R5295
[13] McNeill J D, Lingle R L Jr, Ge N-H, Wong C M, Jordan R E and Harris C B 1997 Phys. Rev. Lett. 79 4645
[14] Marina D C, Ramseyer C, Borisov A G, Teillet-Billy D, Gauyacq J P, Bertholdt W, Feulner P and Höfer U 2002 Phys. Rev. Lett. 89 046802
[15] Zhu X-Y 2004 Surf. Sci. Rep. 56 1
[16] Bauer M, Pawlik S and Aeschlimann M 1999 Phys. Rev. B 60 5016
[17] Petek H, Weida M J, Nagano H and Ogawa S 2000 Science 288 1402
[18] Bartels L, Meyer G, Rieder K-H, Velic D, Knoesel E, Hotzel A, Wolf M and Ertl G 1998 Phys. Rev. Lett. 80 2004
[19] Gauyacq J P, Borisov A G and Rašeev G 2001 Surf. Sci. 490 99
[20] Hotzel A, Wolf M and Gauyacq J P 2000 J. Phys. Chem. B 104 8438
[21] Chowdhury S, Grimsrud E P, Heinis T and Keharle P 1986 J. Am. Chem. Soc. 108 3630 and references therein
[22] Vondrak T and Zhu X-Y 1999 J. Phys. Chem. B 103 3349
[23] Gahl C, Ishioika K, Zhong Q, Hotzel A and Wolf M 2001 Faraday Discuss. 117 191
[24] Ishioika K, Gahl C and Wolf M 2000 Surf. Sci. 454–456 73
[25] Rulliere C 1998 Femtosecond Laser Pulses (Berlin: Springer)
[26] Knoesel E, Hotzel A and Wolf M 1998 Phys. Rev. B 57 12812
[27] Knoesel E, Hotzel A and Wolf M 1998 J. Electron Spectrosc. Relat. Phenom. 88–91 577
[28] Hertel T, Knoesel E, Wolf M and Ertl G 1996 Phys. Rev. Lett. 76 535
[29] Berthold W, Höfer U, Feulner P, Chulkov E V, Silkin V M and Echenique P M 2000 Phys. Rev. Lett. 88 056805
[30] Knorrer R, Bennemann K H, Burgermeister R and Aeschlimann M 2000 Phys. Rev. B 61 9427
[31] Bürgi L, Jeandupeux O, Brune H and Kern K 1999 Phys. Rev. Lett. 82 4516
[32] Braden D A and Hudson B S 2000 J. Phys. Chem. A 104 982
[33] Wurth W and Menzel D 2000 Chem. Phys. 251 141

New Journal of Physics 7 (2005) 113 (http://www.njp.org/)