Ultrafast Electron Dynamics in C_6F_6/Cu(111) after Localized or Delocalized Excitation

P. S. Kirchmann[1], P. Loukakos[1], U. Bovensiepen[1], M. Wolf[1], S. Vijayalakshmi[2], F. Hennies[2], A. Pietzsch[2], M. Nagasono[2], A. Föhlisch[2], and W. Wurth[2]

[1] Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany, e-mail: patrick.kirchmann@physik.fu-berlin.de
[2] Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany

Abstract. Using optical and core-hole excitation, we study relaxation dynamics of excited electrons at C_6F_6/Cu(111) interfaces as a function of adsorbate coverage. Differences in the coverage dependence of charge transfer times obtained by time-resolved photoemission and core-hole spectroscopy indicate different delocalization processes of the excited electron wave packet in the C_6F_6 resonance.

Ultrafast electron transfer across interfaces represents an elementary step in many electro- and photo-chemical processes such as solar energy conversion in Graetzel cells [1]. Furthermore, applications in organic devices and molecular electronics [2] require a comprehensive understanding of charge carrier dynamics in ultrathin organic molecular films. The decay rates of excited electronic states at solid interfaces are governed by the wave function overlap of the excited state in the adlayer with the delocalized states of the substrate [3, 4]. In the limit of strong electronic coupling charge transfer may occur even on an attosecond time scale as has been demonstrated for S/Ru(001) [5].

Here we investigate ultrafast electron transfer by two complementary methods, namely time-resolved two-photon photoemission (2PPE) [6] and the core-hole-clock (CHC) spectroscopy [4]. We compare both approaches for the same molecular system using optical (valence band) and soft x-ray (core-level) excitation into the π^*-LUMO resonance of hexafluorobenzene (C_6F_6) adsorbed on Cu(111). C_6F_6 is an aromatic molecule with a delocalized π-electron system similar to benzene, which serves as a model system for electron transfer across the organic/metal interface.

In 2PPE spectroscopy we study the dynamics of electron transfer in the π^*-LUMO resonance in C_6F_6/Cu(111) using a frequency-doubled pump pulse ($h\nu_1 = 4.26$ eV) and the time-delayed fundamental pulse ($h\nu_2 = 2.13$ eV) as a probe, each with pulse durations < 30 fs. The kinetic energy of the photoemitted electrons is analyzed by a time-of-flight spectrometer. The C_6F_6 layers were adsorbed at substrate temperatures of 140-160 K to prepare the desired coverage $\theta = 1$-10 monolayers (ML) [7]. For CHC measurements identically prepared layers were investigated using soft x-ray radiation at the beam line UE56/1(SGM) of the synchrotron facility BESSYII in Berlin, Germany. The high-resolution autoionization spectra were recorded with a hemispherical electron analyzer.

C_6F_6 adsorbed on Cu(111) exhibits several unoccupied states below the vacuum level which can be probed by 2PPE [7, 8]. The present study focuses on the electron transfer dynamics in the lowest unoccupied molecular (LUMO) state with

π^*-symmetry. In the 2PPE process delocalized electrons from the metal substrate are excited into the π^*-resonance by the pump pulse $h\nu_1$ (see Fig. 1 a). The decay of the transient electron population in the excited LUMO state is monitored by photoemission induced by a time-delayed probe pulse $h\nu_2$. Analysis of the transient population of the π^*-resonance by a rate equation model yields the decay times as a function of C_6F_6 coverage show in Fig. 1 (center). The lifetimes of the π^*-resonance are found to increase strongly from 7 ± 3 fs for $\theta = 1$ ML to 37 ± 3 fs for $\theta \geq 3$ ML [9].
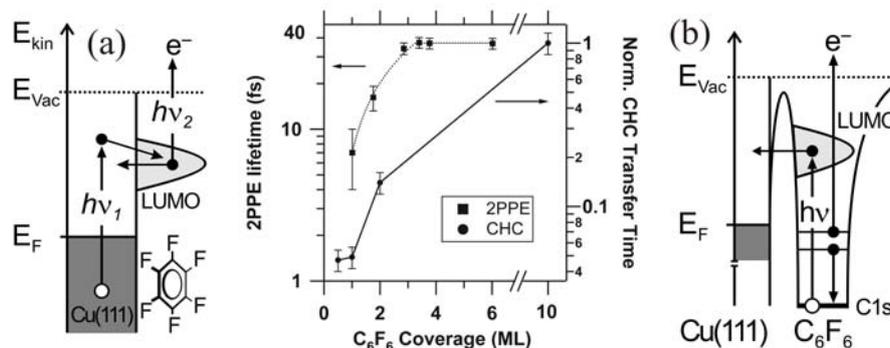

Figure.1. (a) Schematic illustration of time-resolved 2PPE. A laser pulse $h\nu_1$ excites electrons from the metal substrate into unoccupied states of the adsorbate where the transient electron population is probed by a second time-delayed probe pulse $h\nu_2$. (b) Scheme of the core-hole-clock (CHC) method. A localized C1s core electron is resonantly excited into molecular resonance where it may transfer to the substrate or stay localized in the resonance on the time scale of the core-hole decay. The comparison of the different relaxation channels yields the electron transfer time by comparison to the core-hole lifetime (see text). Center panel: Coverage dependence of lifetimes obtained by the 2PPE and CHC methods. The decay times for CHC are normalized to multilayer coverage (see text). The solid lines guide the eye.

With the core-hole-clock method the ultrafast charge transfer processes occurring during the natural core-hole lifetime on a femto- to attosecond timescale become accessible [4, 5, 10, 11]. In the experiment a core electron is excited to a bound adsorbate resonance by narrow-band soft x-ray radiation. This core-excited state will decay primarily by autoionization (Auger processes), whereby different decay channel must be considered: (i) If the resonance electron has already transferred to the substrate when the decay occurs, the normal Auger decay leads to autoionization with constant kinetic energy when the x-ray photon energy is tuned across the resonance. (ii) In the spectator channel the core excited electron stays localized at the adsorbate during the core-hole lifetime and the kinetic energy of the outgoing electron disperses with photon energy. In the participator channel (iii) the resonance electron decays back to the core hole, which is a competing channel to the charge transfer to the substrate. The charge transfer time can be determined from the ratio of the decay channels [10]. The analysis of the autoioni-

Patrick S. Kirchmann

zation spectra requires thus a careful consideration of all different relaxation channels.

For molecular systems like C_6F_6/Cu(111) the separation of normal Auger channels and spectator and participator channels is complicated, which hinders the evaluation of absolute values for charge transfer times. A comparison to gas phase results where no charge transfer is possible and thus normal Auger is not present allows to extract the coverage dependence of the charge transfer channels (see Fig. 1, center). The differences in the coverage dependence obtained by the 2PPE and CHC technique suggests that different physical mechanisms play a role when comparing delocalized (valence band) and localized (core-level) excitations. To determine the absolute charge transfer times analysis of the spectral weights of the different autoionization channels in gas phase measurements are currently underway.

In summary, we have studied ultrafast charge transfer dynamics of the LUMO π*-resonance of C_6F_6 on Cu(111) using optical and core-hole excitation as a function of adsorbate coverage. The observed differences in the coverage dependence of charge transfer times obtained by 2PPE and CHC spectroscopy indicate different delocalization processes of the excited electron wave packet in the molecular resonance. Future time-resolved soft x-ray experiments open the perspective to observe such electron packet motion after a core level excitation directly in the time domain.

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