Dephasing of Image-Potential States on Cu(100) upon CO Adsorption Measured by Femtosecond Two-Photon Photoemission Spectroscopy

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Abstract. The relaxation dynamics of the image-potential states of Cu(100) under the influence of CO adsorption is investigated by time-resolved Two-Photon Photoemission Spectroscopy (2PPE). Pure dephasing due to elastic scattering leads to a fast decay of quantum-beat patterns of energetically close-lying image states at already very low CO coverages. For higher CO exposure an increase in structural order is correlated with a decrease in pure dephasing rates.

1. Introduction

An electron located at distance z in front of a metal surface is attracted by its image charge located at -z. The resulting image potential in front of the surface gives rise to a series of Rydberg-type unoccupied bound states converging towards the vacuum energy E_{vac} ($E_n \approx E_{vac}$ - 0.85eV / n^2) if there are no available bulk states (see Ref. 1). For increasing quantum number n the center of the wavefunction shifts more and more away from the surface, leading to a reduced overlap of the wavefunction with unoccupied bulk states which act as energy-decay channels (electron-electron scattering). For Cu(100) the lifetimes T_1 of the image-state population have been measured for $n \leq 6$ with time-resolved 2PPE (Ref. 2).

In this paper we focus on quasielastic scattering, which does not change the population of the image-potential states but destroys the coherence between the involved states (pure dephasing time T_2^*). We investigate the influence of disorder on the quasielastic-scattering channel and minimize a possible effect of quasielastic electron-phonon scattering (Ref. 3) by reducing the sample temperature down to 90 K. Adsorption of CO on Cu(100) allows to control the surface order (revealed by linewidth in spot-profile LEED analysis).

2. Experimental Methods

The method of choice for investigating the dynamics of image-potential states is the time-resolved Two-Photon-Photoemission Spectroscopy (Refs. 1-4). In our case the states are populated by the frequency-tripled light of a Ti-sapphire-Laser (Coherent, MIRA 900) (4.5 eV, 70 fs) and ionized by the fundamental (1.5 eV, 45 fs after optical compression). The number of electrons photoemitted normal to the surface is measured as a function of kinetic energy with a hemispherical analyzer (energy resolution = 40 meV, acceptance angle = 0.6°). Time-resolved pump-probe experiments are accomplished by varying the delay between excitation and ionization pulses.

From the exponential decay of the photoemission signal, the population relaxation time T_1 can be deduced. Within the framework of optical Bloch-equations population decay time T_1 and pure dephasing time T_2^* both contribute to the intrinsic linewidth $\Gamma = \hbar(1/T_1+2/T_2^*)$. In order to suppress short-lived offresonant excitations, which broaden the linewidth, one has to delay the probe pulse with respect to the pump pulse by about 100 fs.

3. Results and Discussion

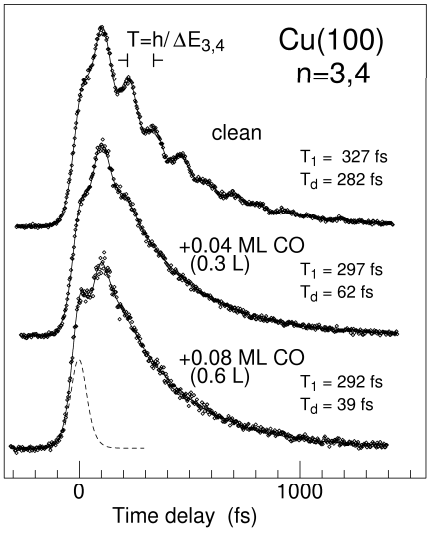

Fig. 1. Quantum-beat pattern showing a coherent superposition of the n = 3 and n = 4 states. Adsorption of CO leads to a rapid decay of the quantum-beat pattern (T_d), whereas the overall exponential decay (T_1) remains almost unchanged.

The effect of pure dephasing on the relaxation dynamics of image-potential states can be directly seen in Fig. 1 when one excites a coherent superposition of several states (Ref. 2). This is achieved, when the energy difference of the excited states gets comparable to the linewidth of the excitation pulse (30 meV). For the clean sample the 2PPE signal of the n = 3 state shows an exponential decay (T_1 = 327 fs) as a function of pump-probe delay. Superimposed on this decay is a quantum-beat pattern between the n = 3 and n = 4 states. The beat period T corresponds to the energy difference $\Delta E = h/T$ = 35 meV of these states.

Adsorption of 0.04 monolayers (ML) CO only slightly alters the exponential decay time (T_1 = 297 fs), but dramatically increases the damping of the quantum-beat structure, which can be explained in terms of rapid pure

dephasing of the involved states: CO molecules initially adsorb randomly on the Cu(100) surface. Thus disorder is produced leading to elastic scattering, which destroys the coherence between the involved states.

Figure 2 shows a series of energy-resolved spectra of the states n = 1, 2, 3 as a function of CO exposure. The linewidth of the n = 1 state varies non-monotonically with CO exposure. Part of the overall linewidth increase can be explained by the increase of the inverse lifetime ($\hbar/T_1$). The lifetime T_1 decreases from 40 fs (clean surface) to 10 fs at 3.5 L and stays constant at higher coverages. The CO molecules offer additional unoccupied states ($2\pi^*$) acting as decay channels for the image-state electron.

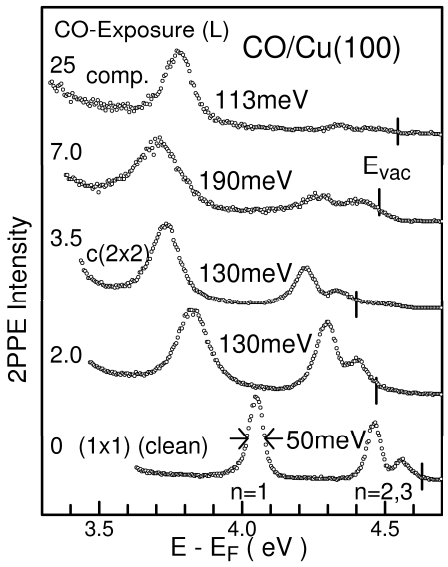

Fig. 2. Series of energy-resolved spectra as a function of CO exposure (1L = 10^{-6}Torr s). The spectra at 0 L, 3.5 L and 25 L correspond to the well-ordered (1x1), c(2x2) and compressed surface structures, respectively.

We interpret the difference between Γ and $\hbar/T_1$ in terms of pure dephasing rate, which shows pronounced minima at 0 L, 3.5 L and saturation-exposure. LEED analysis reveals that these exposures correspond to the well-ordered surface structures (1x1) (clean sample), c(2x2) and the c($7\sqrt{2}\times\sqrt{2}$)R45° compressed structure.

In conclusion, we have shown, that one can distinguish between energy relaxation and pure phase relaxation (pure dephasing) of image-potential states and that the structural order correlates with pure dephasing. We attribute the latter to quasielastic scattering due to the disorder of the surface.

References

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