Ultrafast Charge Transfer Times of Chemisorbed Species from Auger Resonant Raman Studies

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We demonstrate that high resolution autoionization studies for core excitations under Auger resonant Raman (ARR) conditions can be used to extract extremely fast charge transfer (CT) relaxation times for chemisorbed molecules on a metal surface. For the O $1s$ and C $1s$ bound resonances of CO on Ru(0001), ARR behavior is almost completely suppressed; from its small remnant detectable by its linear dispersion with photon energy, CT times below 1 fs can be determined. For CO on a Xe spacer, only dispersive Raman-type decay is seen; i.e., no CT occurs. [S0031-9007(98)05348-4]

Quite generally, resonant excitation of a core electron to a bound state by photon absorption leads to neutral core excited states which subsequently decay via autoionization (or resonant Auger decay). If such an excitation is performed with photons with a bandwidth lower than the width corresponding to the respective core-hole lifetime, two distinct effects are observed: The energy of the resonant Auger electrons shows linear dispersion with photon energy, and the linewidth of the respective decay channels is no longer influenced by the natural linewidth of the core hole.

These effects, commonly termed Auger resonant Raman (ARR) effects, are based on the coherence between excitation and decay of the core-hole state [1]. They were first observed in the x-ray energy range by Brown *et al.* [2] in 1980. Since then they have received considerable attention in atomic and molecular electron spectroscopy, because they allow the obtaining of spectroscopic information on excited atomic or molecular states with unprecedented detail [3]. The bulk of published ARR studies so far concern isolated noble gas atoms [4–6], which are well understood theoretically [1,7]. ARR spectroscopy of molecules is much more complicated and informative because of the influences of nuclear dynamics during core-hole decay [8,9], and lifetime-vibrational interference effects in resonantly excited decay spectra [10,11].

In this paper, we will describe the first observation of these effects for a chemisorbed molecule on a surface. We will demonstrate how their presence or absence for coupled systems like adsorbates on a surface can be used to determine the lifetime of extremely fast decaying (sub-femtosecond) electronic adsorbate resonances. Besides the fact that the lifetime of excited adsorbate states is an important unknown for the understanding of all photochemical processes, we note that there is a general connection of the surface coupling thus observed with the adsorbate bond. We believe that our approach can be generalized and may also have significance for other fields, such as semiconductor physics.

It has been shown recently that, for atoms physisorbed on metal surfaces with a resonance state lying energetically above the Fermi level, the resonant Auger spectrum obtained under ARR conditions consists of two types of decay channels, coherent Auger Raman type and incoherent normal Auger type [12,13], in contrast to the case of isolated atoms where only coherent Raman-type channels are observed. To explain this observation, a model has been developed which takes the localization of the resonantly excited electron into account. If the resonantly excited electron stays spatially localized at the site of the core hole up to its decay, the decay channels exhibit the ARR effect. When the coherence of excitation and decay is lost because of charge transfer of the excited electron into the substrate *before* core-hole decay, the subsequent decay spectra do not show the ARR effect.

Therefore, the ratio of Raman versus non-Raman channels can be used to determine the lifetime (or inversely the charge transfer rate) of the excited electron with respect to the core-hole lifetime. Because the core-hole lifetime, which is usually in the femtosecond regime, is used as an "internal clock," the time scale of the transfer process can be determined in the femtosecond to sub-femtosecond regime. Assuming that the core-hole lifetime is nearly independent of the chemical environment and the transfer time is inversely proportional to the absolute square of the transition matrix element, the charge transfer time τ_{CT} can be calculated as $\tau_{CT} = \tau_\Gamma / (f^{-1} - 1)$, where f is the branching ratio f of the Raman-type decay channels, and τ_Γ is the core-hole lifetime [14,15]. With this method, shorter times can be resolved than in typical time-resolved pump/probe laser experiments.

The charge transfer rate depends sensitively on the coupling between adsorbate and substrate and on the local density of unoccupied substrate states. The latter dependence is the reason for the observed energy dependence of the fraction of the dispersive Raman-type decay channels across a resonance [12,13].

It has been shown previously that in the case of strongly coupled chemisorbates the decay spectra of resonant and nonresonant excitations are essentially equal and independent of primary energy, which means that the resonant excitation decays via very fast charge transfer into the

fully relaxed core-hole ground state [16–18]. Until now, the fraction of coherent decay channels (termed Raman channels above) of strong chemisorbates was assumed to be too small to be observable. The incoherent normal Auger decay channels were considered to be so dominant that they would cover up all potential decay channels from unrelaxed excited core-hole states. However, we will show that, with excitation under ARR conditions, even small contributions with Raman-type behavior become discernible, because their linear dispersion with excitation energy sets them off from the normal predominant Auger contributions.

X-ray absorption (NEXAFS) and resonant Auger experiments were performed at the ELETTRA storage ring in Trieste (Italy) at the SuperESCA beam line, using a modified SX-700 monochromator with a flux of 10^{12} photons/s at a resolution of 5000. This experimental station consists of a standard ultrahigh vacuum chamber equipped with a spherical sector electron analyzer (VSW CLASS150, 16-channel detector), which was used for taking the decay spectra. NEXAFS was measured by collecting secondary electrons with a partial yield detector. For the measurements of chemisorbed CO at the O $1s$ edge, the photon bandwidth was 100 meV and the analyzer resolution about 250 meV. For physisorbed CO, NEXAFS and Auger spectra were recorded at the C $1s$ resonance with resolutions of monochromator and analyzer of about 50 and 60 meV, respectively. The sample was cooled by a homebuilt vertical liquid He cryostat with a base temperature below 10 K, and cleaned and annealed by standard procedures. The saturated chemisorbed CO monolayer was prepared by exposing the sample to 10 L CO (where 1 L $= 10^{-6}$ Torr s) and heating to 200 K [19]. For the physisorbed CO layer, first 10 L Xe (to produce a Xe bilayer) was dosed, followed by 1 L CO, producing a dilute CO monolayer. All preparations were controlled with high resolution x-ray photoelectron spectroscopy measurements.

CO is *the* prototype molecular chemisorbate on metal surfaces and has been amply investigated also by x-ray absorption [20,21], Auger [22], and autoionization [23,24] spectroscopies. On Ru(0001), as on many other d metals, chemisorbed CO is oriented vertically with the carbon atom attached to the surface [25]. The interaction with the partly filled d band splits the primarily unoccupied CO 2π level into occupied bonding and unoccupied antibonding 2π-$d\pi$ hybrid states [26,27]; in addition, the interaction with the d metal leads to an increase of the 5σ binding energy because of repulsion in the σ space [26].

Figure 1 (inset) shows the NEXAFS spectrum of the saturated monolayer of CO on Ru(0001) at the oxygen K edge. With a total linewidth of about 2 eV, the $2\pi^*$ resonance at 532.6 eV of the chemisorbed molecule is much broader than the 2π resonance of gas phase CO with a linewidth of 1.2 eV [28]. Because of the strong hybridization of the 2π valence orbital, the resonantly excited electron can delocalize very quickly (i.e., hop

into the substrate), so that the electron in this orbital is decoupled from the core hole. Hence, the linewidth of the $2\pi^*$ resonance is strongly influenced by the lifetime of the excited $2\pi^*$ electron, which is considerably reduced by the fast charge transfer (CT) process [21]. However, because this width can contain other than lifetime effects, both homogeneous (mainly broadened vibrational structure) and inhomogeneous, it cannot be directly used to obtain CT times.

At the lower energy side of the $2\pi^*$ resonance, a small shoulder with a photon energy of 530.8 eV can be found. The Ru(0001) crystal has a high density of unoccupied d states in a narrow energy range above the Fermi level, which couple to the CO via its strong hybridization with the metal. The energetic position of this so-called Fermi level step [29] implies that the center of the $2\pi^*$ resonance lies about 1.8 eV above the Fermi level.

The resonant Auger decay spectra after excitation with finely varied photon energies at the high energy side of the $2\pi^*$ resonance are shown in Fig. 1. The direct photoemission contributions as deduced from off-resonance measurements are subtracted; only the resonantly enhanced features are displayed. At kinetic energies below 520 eV, dominant decay channels into final states with two holes in the valence shell of CO are observed. It is obvious that the energies of these decay channels are not influenced by the photon energy; only their intensities are. Hence, these dominant decay channels, which follow the charge transfer process, show normal Auger-type, nondispersive behavior. Therefore, we conclude that they start from the same screened core-hole ground state *after* the charge transfer process. So far, they were the only channels seen in resonant as well as nonresonant decay [16–18].

Now, however, two small resonantly enhanced peaks with kinetic energies higher than 520 eV are observed, which show roughly linear dispersion with photon energy, as can be seen plotting the decay spectra versus binding energy (BE) (see right side of Fig. 1) where they appear at constant binding energy. These coherent resonant decay lines, which can be assigned to $4\sigma^{-1}$ and $5\sigma^{-1}/1\pi^{-1}$ states at BE's of about 11 and 8 eV [30], result from decay channels where the resonantly excited $2\pi^*$ electron does not relax into the metal before the core-hole decay, but takes part in the resonant Auger decay ("participant" lines). Because of the overwhelming intensity of the normal Auger channels, we cannot determine the dispersive Raman-type transitions leading to states with two holes in the valence shells (with the resonantly excited $2\pi^*$ electron acting as a "spectator") which must lie below the dominant nondispersive decay channels. However, taking the ratio of participant and spectator channels from our measurements of physisorbed CO mentioned below, which was found to be about 1:7, we can estimate the total ratio of Raman to Auger channels. We find a fraction of at most 10% for the Raman channels. With an assumed O $1s$ core-hole lifetime of about 6 fs [28] and the
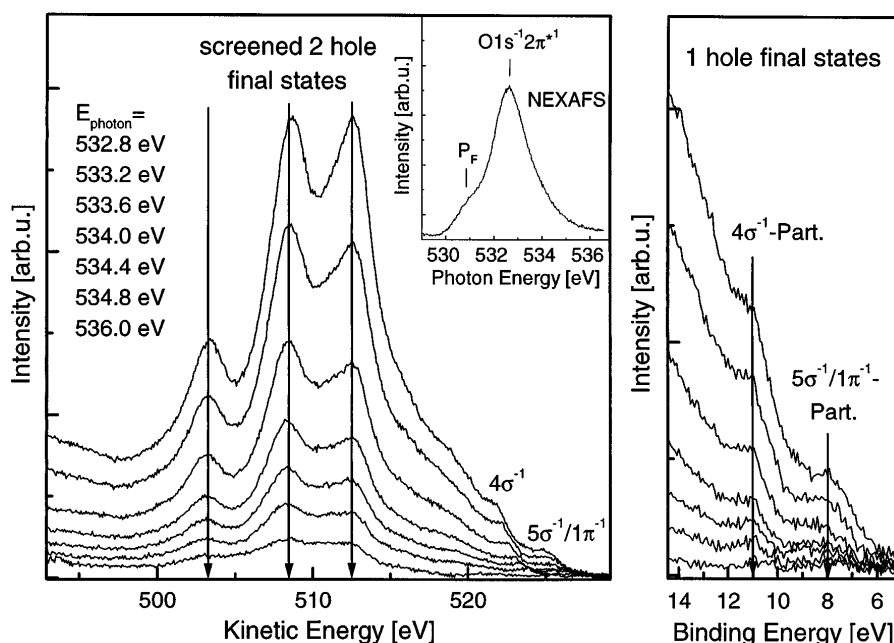
FIG. 1. O $1 \rightarrow 2\pi^*$ photoabsorption (inset) of the saturated CO monolayer on a Ru(001) surface (P_F indicates the position of the Fermi level), and O *KLL* resonant Auger spectra (after subtraction of the photoemission background) at the O $1s \rightarrow 2\pi^*$ resonance. The photon energy (narrow-band excitation) varies across the resonance as given. The plot against kinetic (left part) energies emphasizes the Auger channels; that against binding energies (right part), the Raman channels.

formula given above, the charge transfer time can be estimated to be of the order of 0.6 fs. The absolute accuracy of this value is low (possibly up to $\pm 50\%$) because of the overwhelming strength of the Auger channels. We note that the situation would be much improved for less extreme branching into the Auger and Raman channels, which for the same ultrafast transfer times could be achieved utilizing core holes with much faster decay times.

Figure 2 shows that the charge transfer probability depends also on the excitation energy. The intensity ratios of the $4\sigma^{-1}$ and $5\sigma^{-1}/1\pi^{-1}$ decay channels to the decay to the screened $4\sigma^{-1}4\sigma^{-1}$ hole state (503.2 eV) are plotted versus photon energy. While there is still a background problem, these relative values are more accurate than the absolute one. Note that the lower part of the resonance is missing since, in the range below 532.0 eV, the Raman channels are still hidden below the (stationary) Auger channels. The ratios increase strongly with photon energy above the maximum of the resonance. Hence, also, the charge transfer time increases with photon energy, or with distance of the resonance energy from the Fermi level. The most likely explanation is the density of unoccupied d states of ruthenium, which, as mentioned, is highest just above the Fermi level and decreases to higher energies, leading to a decline of the charge transfer probability with increasing photon energy.

Similar, although less resolved, results have been obtained for x-ray absorption and resonant Auger decay spectra of chemisorbed CO at the C $1s$ edge and are com-

patible with the same conclusions. They are not shown here, therefore.

We have found the opposite extreme to be realized in the corresponding results for CO molecules physisorbed on a Xe bilayer. Because of the very weak surface bond, the electronic properties of such (rather disordered [17]) layers are essentially unchanged compared to the isolated molecule. Correspondingly, the vibrationally resolved
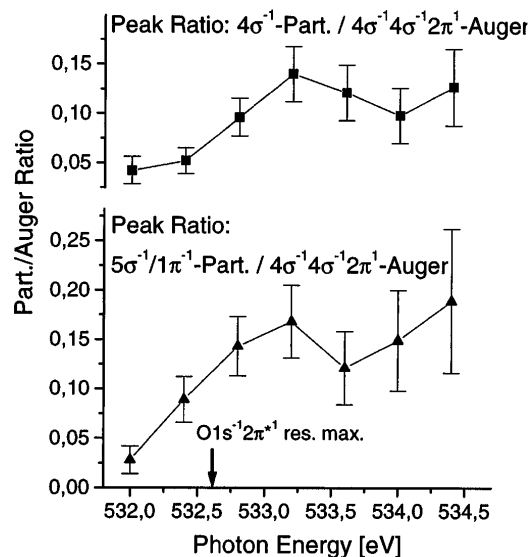

FIG. 2. Variation of the Raman/Auger intensity ratios as a function of photon energy, for the 4σ (top) and the $5\sigma/1\pi$ (bottom) participants. The Auger decay line at 503.2 eV has been taken as representative of the Auger lines.

C $1s^{-1}2\pi^{*1}$ NEXAFS spectrum (not shown here for space reasons) is found to be nearly identical to gas phase data [31]. We find an inherent Lorentzian linewidth of 95 meV which excludes any contributions from intermolecular decay processes, as seen for chemisorbed CO. Not surprisingly, therefore, the autoionization spectra also essentially represent the gas phase data, the main difference being that no vibrational fine structure can be resolved in them, in spite of our sufficiently high overall resolution. Detailed analysis for the clearly set-off participant lines revealed that, compared to the isolated gas phase molecules, these spectra contain mainly additional Gaussian, but also some Lorentzian broadening. We interpret the Gaussian contribution by inhomogeneous effects of next-neighbor screening: Polarization screening will vary with the (variable) number of surrounding molecules and their distances in the disordered layer. A possible reason for the Lorentzian broadening could be the delocalization of the final state valence hole by hopping to neighboring molecules, which corresponds to a weakly developed two-dimensional band structure. Because of the overall broadening of the final states we cannot observe any line narrowing effect [3] in the decay spectra. Resonant Auger spectra for photon energies detuned mainly below the maximum of the $2\pi^{*}$ resonance with $\Delta v = 0$ clearly exhibit the linear shift of kinetic energy with photon energy expected for Raman behavior of molecules decoupled from the surface; i.e., no influence of charge transfer can be detected. While the Xe spacer layer will also reduce the charge transfer rate [32], the primary reason for this behavior is that now the resonance lies energetically below the Fermi level (as shown by comparison of the resonance energy and the core hole binding energy). Hopping processes as seen for chemisorbed CO are then not possible on simple energetic grounds, so that we cannot determine the separate influence of coupling, contrary to the case of adsorbed argon [32]. The detailed results, as well as other interesting details pertaining to the interference of core decay with vibrational motion in the intermediate state (which suggest subtle influences of the weak surface bond on these processes) not of importance in the present context, will be reported elsewhere [33].

In conclusion, we have shown that, after resonant core excitation even of a strongly chemisorbed system, coherent Raman-type decay channels—signalling the absence of charge transfer processes into the underlying metal substrate during core-hole lifetime—can be detected under ARR conditions. This makes it possible to estimate very fast charge and energy relaxation transfer processes of adsorbates on a sub-femtosecond time scale, using the core-hole lifetime as an internal clock. For chemisorbed CO on Ru(0001) at most 10% of coherent decay channels can be detected even though normal Auger decay channels after the hopping of the excited electron vastly dominate. The transfer time of the resonantly excited $2\pi^{*}$ electron is then around 0.6 fs; it varies across the resonance. Physisorbed CO on a Xe spacer layer on Ru(001) behaves essentially like gas phase CO and shows no charge transfer into the metal, which is due to the fact that now the resonance lies below the Fermi level.

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