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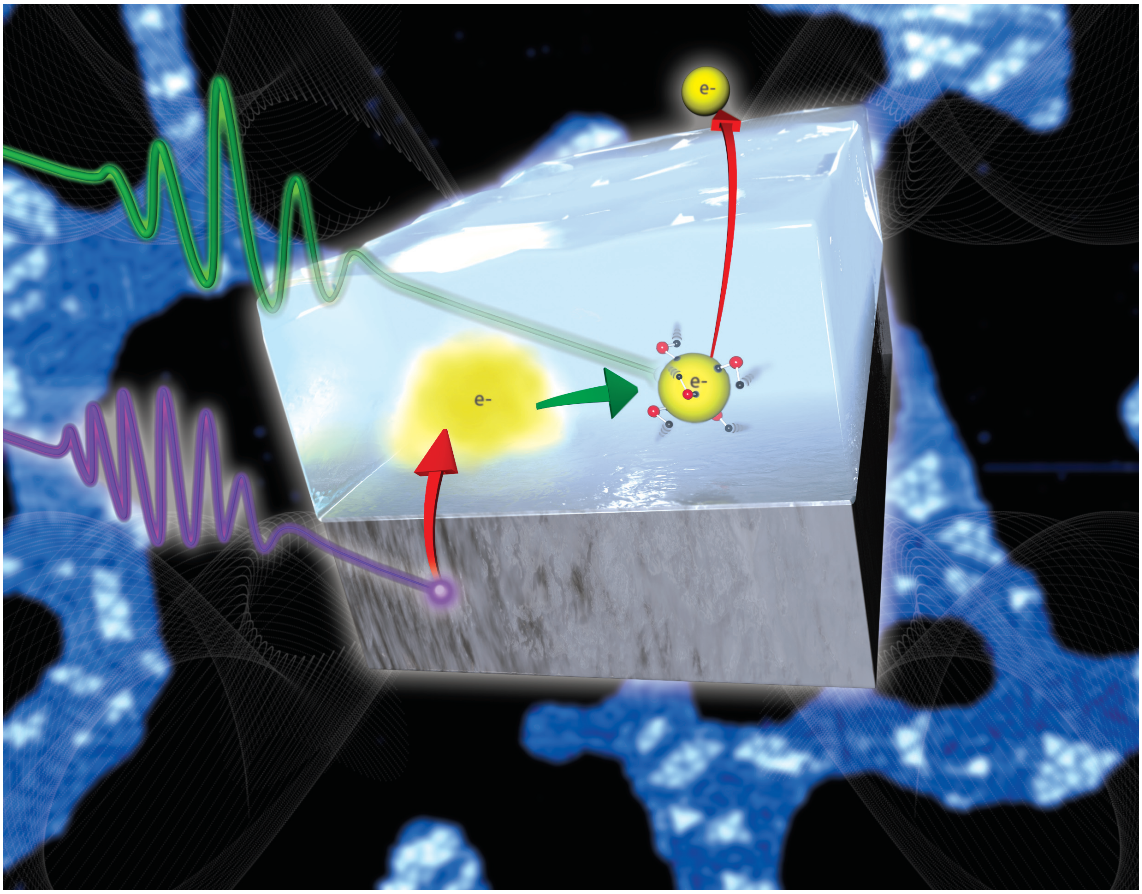

Ultrafast charge transfer at surfaces accessed by core electron spectroscopies†

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Charge transfer at surfaces, which is very important for surface photochemistry and other processes, can be extremely fast. This *tutorial review* shows how high resolution correlated excitation/decay spectroscopies of core excitations can be used to obtain charge transfer times at surfaces around or below 1 fs. Some results are described in more detail, and their meaning and theoretical modelling are discussed. A brief comparison to laser methods shows that there are differences in the processes they look at.

1. Introduction

Charge exchange and charge transfer are at the heart of chemical interactions. The chemical bond is strongly correlated with these processes, and in the hopping picture of bonding even the ground state of chemical systems is related to them, although they cannot be observed directly there. Looking at chemical dynamics, charge transfer (CT) is a very important basic aspect; it often governs the elementary interaction processes of electronically excited states. So it is a very important aspect of chemical dynamics in general.

Therefore CT is a very old research subject. Slow intramolecular charge transfer—in the range of ms to ns, so that the internal atomic motions are much faster—can be treated by approaches assuming local equilibrium and averaging over all coordinates. With the advent of methods to observe much faster processes it became clear that there are many CT processes which can reach into the range of vibrational motion or to even shorter times. In particular at surfaces, *i.e.* between substrates and adsorbed atoms and molecules, the characteristic CT times can be considerably shorter than any atomic motion. That this must be the case had been concluded indirectly already several decades ago, when, in order to explain observations on the modification of electronically induced dissociation and desorption processes (DIET, desorption induced by electronic excitations[1–3]) on metal surfaces it was necessary to invoke that charge and energy transfer can go close to completion within a single pass of an excited atom or molecule through the (repulsive or attractive) excited state potential[3,4] at a surface, so that the fate of a potentially bond-breaking electronic excitation—broken bond or quenched excitation—is determined extremely rapidly. A decade ago, it was shown that the use of short, intense laser pulses opens a new mode of bond breaking; multiple repetitive excitation–de-excitation cycles of the same adsorbate can then occur within a single short laser pulse, which can lead to bond breaking even under conditions of fast excitation quenching (DIMET, desorption induced by multiple electronic excitations, or friction-like energy transfer[5]). All these results could only be explained by charge and energy transfer occurring on the timescale of order 1 fs or even below. Since the development of ultrafast laser methods (laser pump–probe (LPP) measurements such as optical transients or TR-2PPE, time-resolved two-photon photoemission),[6–8] CT times in the time range of vibrational motion and even lower became accessible. There are many very interesting systems which have properties in this range, which are also of considerable practical importance.[8]

For well-characterised adsorbates on single crystal surfaces the described indirect evidence from investigations of bond-breaking events by electronic excitations had made it obvious that on such timescales even ultrafast laser methods, as available at that time (the early 1990s), could not give direct access to the elementary processes. It was therefore very helpful when more than a decade ago the range around some fs and even below 1 fs became accessible through the use of the decay time of a core hole as internal time standard, in the so-called core hole clock (CHC) method.[9,10] The past decade has also seen the rapid improvement of LPP methods by the optimisation of

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techniques, *e.g.*, by stroboscopic detection.[6] And very recently the development of few-cycle or even half-cycle laser sources[11] is promising to give access to yet faster processes. Nevertheless, the CHC method, which made sub-femtosecond time determination possible already 10 years ago,[12] still is a very interesting contender. While, hopefully, there may soon be results obtained more directly and with more variability of systems and parameters, at present the CHC method still accesses the fastest processes.[13] Furthermore, its physics is of considerable general interest, and the systems and situations it examines are different in many respects from those of LPP techniques in the valence region, so that it can be expected to remain interesting in its own right besides LPP.

In this *tutorial review*, I will give an overview of the principles of the use of correlated excitation/decay spectroscopies of adsorbate core levels for the detection of ultrafast charge transfer at surfaces on timescales in the range between a few tens to some tenths of a femtosecond. The range of these short time scales covers the variation typical for excited states from physisorbed to chemisorbed atoms and molecules on metal and semiconductor surfaces, with their variation from weak to strong coupling to the substrate. Some typical results and their interpretations will be given, and model calculations will be sketched. Finally I will briefly discuss the similarities and differences compared to LPP experiments.

2. Description of the CHC method

Core holes can be created by primary electrons, photons, or ions. Such holes in a deep level are short-lived (0.1 to 10 fs). They decay either by emission of a photon, a dipole transition (X-ray fluorescence) in which an electron from a higher occupied level fills the core hole and the energy difference goes into the emitted photon; or by emission of an electron which takes up the energy difference for a second electron falling into the core hole. The latter process, termed Auger decay or internal conversion, is a monopole transition. Auger spectra usually contain many lines, as the Coulomb matrix element does not possess strong selection rules, so that the combinations of most occupied levels give a line. Generally, deep core holes (excitation energy more than some keV; K-shells of most atoms, and other shells depending on nuclear charge) decay mainly by photon emission, while shallow core holes (up to about 1 keV) decay predominantly by Auger electron emission. Here we will deal with Auger emission, because the low energy of these electrons with relatively short exit depth from a solid make them a surface-sensitive probe. It should be kept in mind, though, that most arguments which we will make can be carried over to X-ray fluorescence, albeit now weighted towards the volume.

Core hole creation by photoabsorption in an atom or molecule can be done either non-resonantly—removing the core electron concerned into the vacuum—or resonantly—bringing it into a bound, normally unoccupied state, *e.g.* the LUMO (see Fig. 1). The first leads to a primary ion, the latter to a neutral species with high internal excitation. For an isolated atom or molecule Auger decay depends on this charge state (Fig. 1). Auger decay of a core ion (c^{-1}) leads to a multitude of 2-hole (2h) states, where the final state holes are distributed over the previously filled orbitals. Auger decay of a neutral core-excited particle (c* or $c^{-1}e$) leads to two types of final state. One type contains the same 2h states but with the excited electron remaining in the excited level as a spectator. The kinetic energy spectrum of the electrons emitted when these 2-hole–1-electron (2h1e) states are formed is similar to the Auger spectrum of the same system, but with all lines uniformly shifted to higher kinetic energies. This "spectator shift" is caused by the screening action of the excited electron on the two holes which eases their creation, so that the kinetic energies of the emitted decay electrons shift to higher values (by a constant value for all lines). In the other type of decay, the participator (or participant) decay, the excited electron participates as one of the electrons of Auger decay, and the end product is a 1-hole (1h) state (Fig. 1).

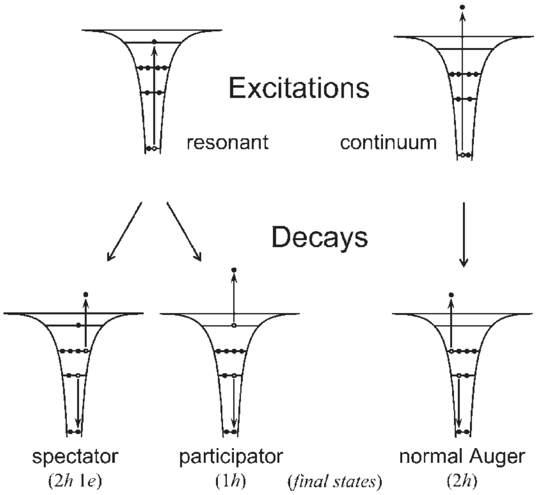

Fig. 1 Sketch of the various core hole excitation and decay processes in an atom. Top row: resonant absorption of a photon of fitting energy can lead to a neutral $c^{-1}e$ state, while higher photon energies lead to core ionisation and emission of a photoelectron. Bottom row: decay of the neutral $c^{-1}e$ state proceeds either by an Auger process with the excited electron remaining in the LUMO (final state: 2h1e), or to one under participation of the excited electron (to a 1h state). Decay of the core-ionised state (right) by normal Auger process leads to a 2h state.

These various transitions are the basis of well-known electron spectroscopies. The total removal of a core electron with its detection is the basis of X-ray photoelectron spectroscopy (XPS, or ESCA); the resonant absorption, detected in various ways, that of X-ray absorption spectroscopy (XAS). The normal Auger electron spectroscopy (AES), leaving behind 2h states, has already been mentioned. The energies of the "participator" (or "participant") decay events to 1h states correspond to the well-known 1h energies found by photoelectron spectroscopy (UPS); this measurement is therefore also termed resonant photoemission. The 2h1e spectator states correspond to UPS shake-up energies, *i.e.* states reached by UPS with an additional internal excitation. In both cases, however, Coulomb matrix elements are operative rather than dipole matrix elements as in the various photoelectron spectroscopies.

On this basis we can now see the principle of the CHC method, which is quite simple (see Fig. 2). A core hole is created by photon absorption in an adsorbate resonantly, *i.e.*

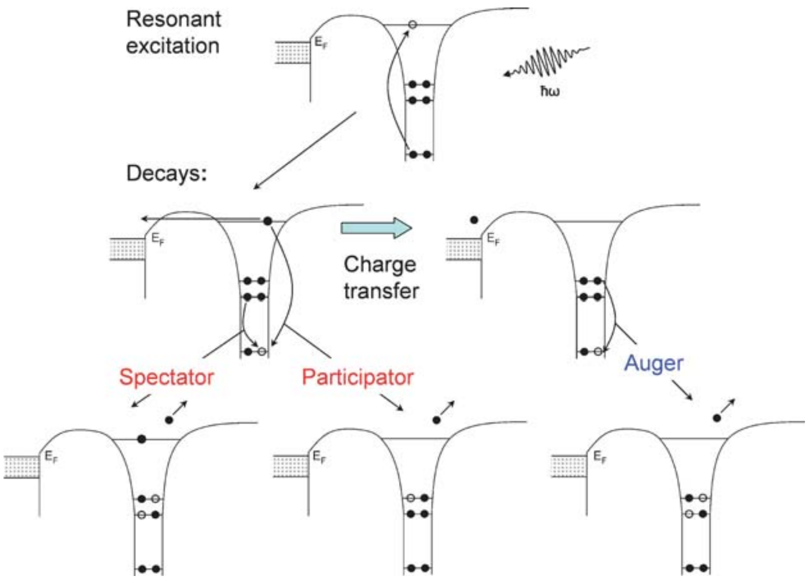

Fig. 2 Sketch of the principle of the CHC method. Narrow band resonant photon absorption in an atom or molecule adsorbed on a surface leads to a $c^{-1}e$ state which, if undisturbed during core hole life time, will decay *via* spectator or participator decay (see Fig. 1). However, if the excited electron is delocalised from the atom containing the core hole, *e.g.* by charge transfer into the substrate as indicated, then the state at core hole decay resembles that reached by continuum excitation (see Fig. 1), so that normal Auger decay leads to 2h final states. The 2h1e states and the 2h states with the same holes involved differ by the screening action of the excited electron in the former; the corresponding electron spectra exhibit the "spectator shift" to higher kinetic energies for the former. The two sets of spectra and consequently the occurrence of charge transfer before or after core hole decay can thus be distinguished.

putting the electron taken from the adsorbate core level into an unoccupied orbital of the adsorbate, and the decay of the core hole is observed by measuring the emitted electrons. As understandable from the outline above, the energies of these decay electrons will be different depending on whether the excited electron is still localised on that atom at the instant of core hole decay, or whether it has been transferred away (usually to the bulk; see below) before hole decay. These two possible decay modes lead to two different sets of spectra; the branching ratio into the two final states, as determined from the ratio of the integrals of the two sets, gives directly the inverse of the ratio of the two related time constants. Since the decay times for the various core holes do not vary much with surroundings and are quite well known, the CT time constant can be derived.

In a simplified semi-quantitative version, which can be performed even with rather broadband excitation, one can compare the decay spectra from an adsorbate system after continuum and resonant excitation. If they are clearly different, with the expected spectator shift setting them off from each other, then negligible charge transfer has happened between core excitation and decay. However, if these two sets of spectra are the same, the excited electron in the resonant case must have been transferred away from the core-excited adsorbate *before* the core hole had been refilled. In the latter case the CT time must be considerably faster than core hole refilling. Indeed, already 20 years ago[14] it was found that CO adsorbed on transition metal surfaces such as Ru or Ni possessed the same decay spectra no matter whether the initial core excitation had been done resonantly or non-resonantly. This fact was interpreted as showing that the charge transfer of the excited electron (produced by resonant excitation) was much faster than the core hole decay time (here about 6 fs), so that in both cases a "nude" (except for screening, see below) core cation was the initial state of core decay. For a more weakly bound (and therefore presumably more weakly coupled) adsorbate such as argon atoms it could be shown that the decay spectra were clearly different for resonant or continuum excitation.[15,16] Furthermore, for resonant excitation the decay spectra consisted of two components, a certain fraction corresponding to normal Auger as in the continuum excitation case, while the other part consisted of resonant decay spectra, *i.e.* to states containing the excited electron on its original atom at the instance of core hole refilling. While this was obvious, the disentangling of the two components was not so easy since both consist of several peaks.

Great progress was therefore made when narrow band synchrotron radiation (SR) with good intensities became available from the third generation of storage rings working as light sources for soft X-ray SR. The bandwidths were now narrow enough that several measurements could be performed within the width of the resonant absorption peak. Then energy conservation requires that for the case that the resonance has not evolved by the instant of core hole decay, *i.e.* the resonant electron is still localised on the atom with the core hole, the decay spectra will shift with changed photon energy, $h\nu$. An increment $\Delta h\nu$ will lead to the same increment in the kinetic energy of the emitted electron; the difference ($h\nu$ − KE), usually termed binding energy BE, will stay constant. However, if the excited electron has been transferred to the substrate before core hole decay, then it will take any excess energy $\Delta h\nu$ with it and the initial state of decay will always be the same. The KEs of these "true" Auger electrons behave in the way known from Auger spectroscopy: they are independent of how (in particular by what photon energy) they have been created. The fact that the two spectral components shift differently when $h\nu$ is tuned through the resonance (one staying at constant BE, the other at constant KE) can then be used to unequivocally separate those two components.

To reiterate, Fig. 2 summarises the basics of the method. The quantitative measurement starts with a core-to-bound excitation by absorption of a soft X-ray photon of narrowly defined energy, *i.e.* by taking an electron from a core level to an empty bound state, usually (but not necessarily) to the LUMO. The core hole in this resulting $c^{-1}e$ state can be filled from the valence shell either before or after the excited electron has been delocalised (usually this means: transferred into the substrate; but see the discussion below). In the first case 2h1e (and 1h) valence states is the result which shows up by "Raman lines" (the reason for this nomenclature will become obvious below), *i.e.* by spectator + participator lines, whose KE shift with $h\nu$ and whose BE stay constant. In the second case the resulting "Auger lines", corresponding to 2h valence states, have constant KE, independent of the exciting $h\nu$ (see Fig. 3). Plotting the results either as f(KE) or f(BE) for varied $h\nu$, one or the other component can then be separated. Once the separate components are available, each spectrum can be integrated. The integrated intensities of the two components represent the important result.

The extraction of CT times can be made by considering the core hole decay and the charge transfer as two independent rate processes (1 or 2), each with its characteristic exponential decay (rate constant $k_{1,2}$, or decay time $\tau_{1,2}$). Then the ratio of the total numbers of events through the two channels, $N_{1,2}$, (each of which is proportional to the integral, $I_{1,2}$, of its spectral components, $P_{1,2}$) is proportional to the ratio of the rate coefficients $k_{1,2}$, or inversely proportional to that of the corresponding decay times $\tau_{1,2}$:

$$I_{1,2} = I(P_{1,2}(E))\mathrm{d}E;\ I_1/I_2 = k_1/k_2 = \tau_2/\tau_1$$

For a certain atom and level, the core hole lifetimes, τ_{ch}, do not vary much with the chemical environment of the atom and can be taken from tables.[17] The CT time, τ_{CT}, can then be obtained directly from the ratio of the integrated spectral components:

$$\tau_{\mathrm{CT}} = (I_{\mathrm{Auger}}/I_{\mathrm{Raman}})\tau_{\mathrm{ch}}$$

where "Raman" denotes the spectator + participator component (see below). Since it is usually not possible to safely extract a spectral component smaller than $\sim$10% of the majority channel, the accessible range of τ_{CT} is from about ten times to one tenth of τ_{ch}. For a core hole lifetime of, say, 5 fs, a range from $\sim$0.5 to $\sim$50 fs is then accessible. Obviously, a shorter core hole lifetime shifts this accessible range to shorter CT times. It should be mentioned that often the so-called Raman fraction, $f_{\mathrm{Raman}} = I_{\mathrm{Raman}}/(I_{\mathrm{Raman}} + I_{\mathrm{Auger}})$ has been used instead of the direct ratio. The CT time constant is then $\tau_{\mathrm{CT}} = \tau_{\mathrm{ch}}(1/f_{\mathrm{Raman}} - 1)$. There is no advantage to this, and the result is the same, of course.

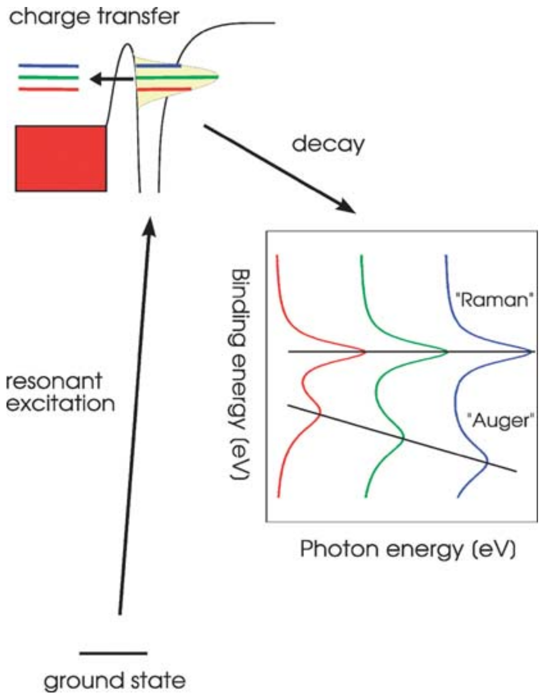

Fig. 3 Depiction of the branching of the de-excitation paths of a resonant core excitation of an adsorbate atom, into core hole decay before CT (leading to Raman lines) and CT before core hole decay (leading to Auger lines). The corresponding decay electrons of the former possess constant binding energy, those of the latter constant kinetic energy, upon varied exciting photon energy. As indicated by the coloured lines, the exciting bandwidth can be about 15 times smaller than the resonance width.

Because of the narrow photon bandwidth, a number (of order 10 to 20) of such measurements can be fit into the line width of the absorption peak. This can lead to additional certainty of the decomposition, since fitting all decay spectra with the same parameter set is a good test for consistency of the data. More importantly, the obtained dependence of the CT time on the exact excitation energy, albeit on a rather narrow range (the width of the excitation resonance, usually around 0.5 eV or a bit higher), yields interesting information about the mechanism of the process, as will be shown below.

3. A digression: Auger resonant Raman processes

In the description above a very simple account of the important processes has been given. While this turns out to be a good representation, the situation was not so clear from the start. Since very interesting physics is involved, it is worth while to discuss the connected questions, even though in the end we will discard any important influence on our topic.

The conditions which are used in these measurements, primarily because they make the disentanglement of contributions easy, are to use an exciting photon bandwidth which is narrow compared to the lifetime width of the resonant core-to-bound excitation. These conditions are usually termed Auger resonant Raman (ARR) conditions. In isolated systems (atoms, molecules) they lead to very interesting effects.[18,19] One consequence is that the entire process, from the initial (ground) state to the final state after core hole decay, is one coherent process. For the intermediate (core-excited) state, energy conservation needs not to be fulfilled.

There are a number of theoretical descriptions for that situation (see for instance ref. 18 and 19, and references therein). A conceptually appealing picture which is based on an explicitly time-dependent formalism[19] will be used here. If the exciting band width is narrower than the resonance width, then according to the Heisenberg uncertainty principle the preparation of the excited state takes longer than its decay. This can be described as the gradual build-up of the final (decay) state by pumping the system into it *via* the intermediate state. Since the excitation takes longer than the decay, the "spectrum formation time" is at most the core hole decay time; it is the relevant time if the excitation takes place exactly on-resonance. If the excitation is detuned from the centre of the resonance, this available time is shortened. The classical analogy of a forced oscillator driven off-resonance is quite illustrative: the main impulse will be delivered in a very short time after starting to pump; after that, increasing destructive interference has the effect that vanishing contributions to the final spectral density are delivered, even though the pumping action continues. The consequence is that only on-resonance will the decay spectrum be fully characteristic of the core excitation/decay sequence. Detuning will lead to deviations—the more detuned from the resonance maximum the exciting wavelength is, the more the decay spectrum resembles that of a *direct* excitation from initial (ground) to final (decay) states. In atoms the main effect is that of "line narrowing"; due to energy conservation the widths of the decay lines are not given by the lifetime width of the intermediate state, but by the narrow exciting band width. More distinct consequences can occur in molecules. For vibrational excitations coupled to the core hole excitation, a strong dependence on the exact excitation energy can result ("vibrational collapse" or its opposite, *i.e.*, disappearance or appearance of vibrational structure upon detuning, depending on the relative arrangement of the potential energy curves of the molecular states involved[18,19]). For dissociative excitations,[18,20] detuning can select the state monitored: for resonant excitation which makes the maximum time available during core hole lifetime, the state imaged in the decay spectrum is close to or entirely that after dissociation, while detuning emphasises early stages of the process close to the molecular situation. An important feature of these evolutions is that the detuning effects are symmetric around the resonance—there is no difference between positive or negative detuning (however, interference effects with direct photoemission can happen in the wings of the resonance[18]).

One might well think that such an effect could influence what one sees in the present case of charge transfer. If it were generally true that detuning from the resonance corresponds to a shortening of the time span over which the evolution of the system is examined, one might expect that detuning would lead to a strengthening of the Raman channel, because that is the one dominating at time zero. Experimentally, this does not seem to be correct: there are many results which are very asymmetric around the resonance (see below), while if the detuning effect would be dominant, they should be symmetric.[21] The excitation in the resonance maximum would correspond to the longest time of evolution possible, *i.e.* the strongest admixture of charge transfer, while detuning should shift the weight to a stronger admixture of Raman, non-CT components. One could argue that there might be other stronger effects (*e.g.* band structure effects, see below) in various systems, but the detuning effect could still be active as well. A theoretical examination,[22] while not being able to give a full quantitative representation due to the difficulties of describing a system in which discrete excitations are coupled to a structured continuum, showed that this is not the case. In a simplified conceptual argument, the reason is that the detuning effects are based on a coherent evolution of the entire process, because they effectively constitute interference effects. In our case, however, only the Raman part can evolve coherently and undisturbed—for that path the excited atom or molecule does not even know about its being adsorbed on a surface, and the Auger Raman picture does apply. Charge transfer *before* core hole decay, however, destroys this necessary coherence of excitation and decay—not only charge and energy, but also phase are transported into the continuum of the substrate. So the phase relations are lost and no interference between the two channels can occur. In reverse, this is in fact a prerequisite of the simple rate approach given above. This approach requires two independent competing processes, in which no common phases occur.

It is interesting to note that decoupling an adsorbate sufficiently from the substrate indeed brings back the features of molecular Auger resonant Raman processes. For N_2 adsorbed directly on a metal surface, the usual CT behaviour was obtained (see below), while for a multilayer of N_2[23] the essential ARR vibrational detuning behaviour[18,19] was recovered, apart from some broadening (probably partly inhomogeneous, partly due to the lifetime of the final states and/or kinetic energy acquired in the process, see below). This shows that indeed the Raman part of a surface species evolves as in an isolated particle, while the introduction of CT destroys coherence for that path. The Raman part constitutes a one-step process, while the Auger part is due to a two-step process in the spectroscopic sense. This also has the consequence that it makes sense to assign the exact energy of excitation to the energy at which the excited electron is transferred: the two-step process requires energy conservation even for the intermediate state.

We note again that identical effects can be observed if the core hole decay is monitored by X-ray emission rather than by Auger electrons (resonant inelastic X-ray scattering, RIXS).[18] The fact that the observation of decay electrons is much preferable for surface species is due to two reasons: (1) emitted electrons are much more surface specific than emitted X-rays; and (2) for the relevant core energies (up to 1 or 2 keV) the ratio Auger decay/radiative decay is strongly in favour of the Auger path. On the other hand, the observation of RIXS is preferable if bulk properties are to be investigated. Note that the relevant core hole lifetime is always given by the sum of all decays.

4. Results and interpretation

4.1 Some typical CT results

The first[24] and overall the largest number of experiments[9,10] conducted under Auger Raman conditions as described have been done using adsorbed argon layers. This is due to a favourable combination of parameters for this adsorbate: the

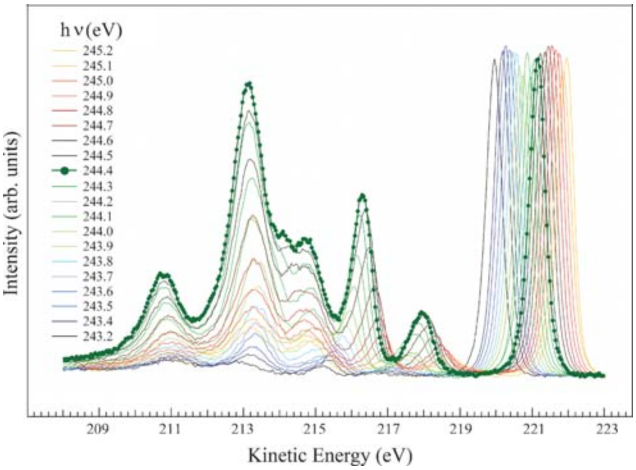

Fig. 4 Raw data of decay electron spectra of core-excited Ar adsorbed on n-Si(100)–H for a 2 eV wide range of photon energies around the resonance at 244.4 eV, plotted on a kinetic energy scale. The data show the true background. Electron energies are still slightly off calibration, and data not yet normalised in intensity. The large peak on the right is the Ar 3s photoemission feature.

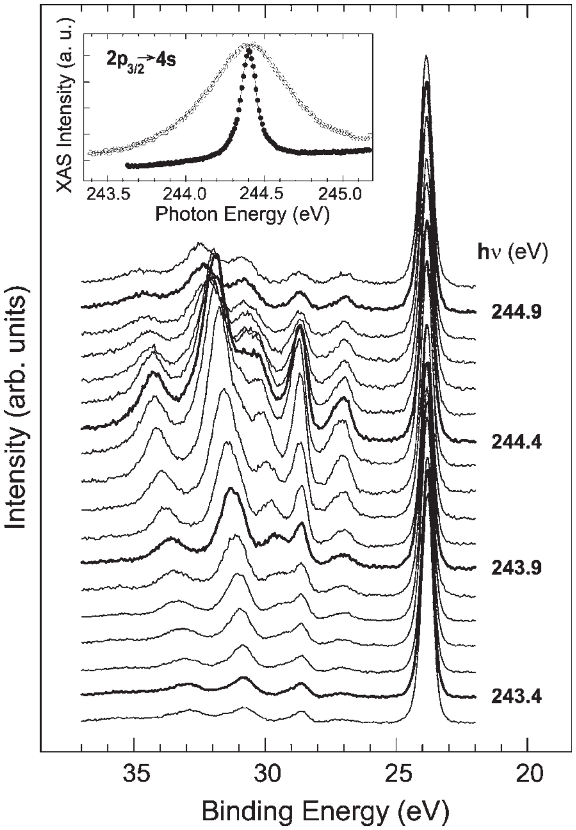

Fig. 5 Data of Fig. 4 after energy adjustment by calibration, and intensity normalisation (see text), plotted now on a binding energy scale to emphasise Raman decay lines with constant binding energy. The large peak on the right is the Ar 3s photoelectron peak (its resonant contribution is negligible in this case). Insert: The photoabsorption peak of the resonant Ar 2p$_{\frac{3}{2}}$ excitation in the free atom (narrow curve) and the adsorbed Ar (broad curve).

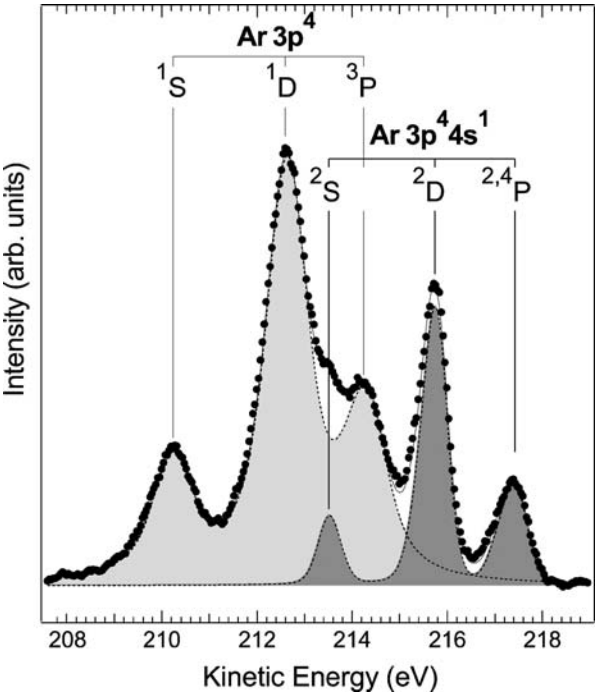

Fig. 6 Example for decomposition of the overlapping Auger and Raman spectra, here for Ar on n-Si(100)–H at resonance (data from Fig. 5). The reliability of such a decomposition derives from the fact that spectra at all photon energies for one set are fitted with the same energy and width parameters, with energy spacings and shifts of Auger and Raman components as expected (the widths of Auger peaks are wider than those of Raman peaks but again constant), and that for many sets of spectra for different samples the same fit parameters are used. From ref. 25.

Ar atom has a conveniently located core level, the 2p$_{\frac{3}{2}}$ level at about 245 eV, from where an electron can be easily excited to the empty 4s level with very narrow bandwidth (at or below 40 meV for the usual third generation SR sources). Its lifetime, about 5.5 fs,[17] is in the range of CT processes for weakly coupled systems, so that it is a good match for the weak (essentially van der Waals) bond between Ar and a metal surface, which leads to weak coupling. Thus the CT times are expected to be just in the right range and in particular not too short. Due to the approximate validity of the equivalent core approximation according to which a neutral core-excited atom of nuclear charge Z has valence properties roughly like an atom with a nuclear charge $Z + 1$, the intermediate Ar ($c^{-1}4s$) atom can, to first order, be viewed as a neutral K atom—albeit at the distance of the adsorbed Ar in the ground state. The excited Ar atom will essentially not move during the time before CT or core decay (even though it may experience a "kick" during this time if the potential energy curve of the intermediate state has a sufficient gradient. This could possibly lead to its desorption, but this will happen after the core excitation/decay sequence. So the spectroscopy will not be influenced, other than giving the final states of decay larger widths). Furthermore, it is easy to modify the coupling of adsorbed Ar to the surface by well-defined underlayers of other rare gases or chemisorbed species, as will be shown.

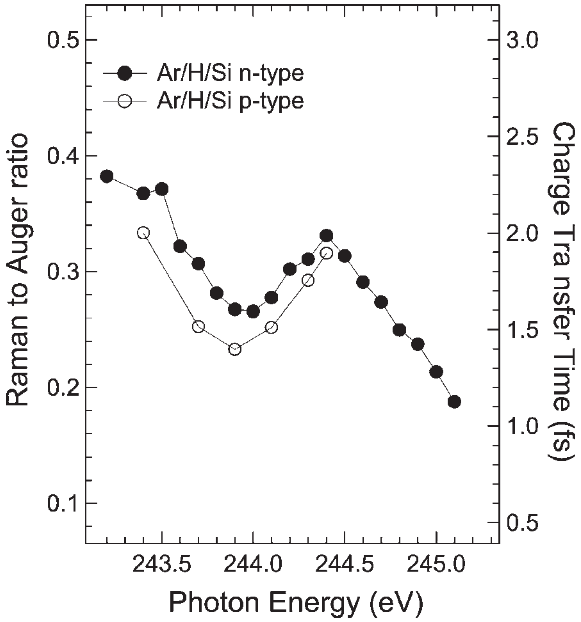

Fig. 7 Collection of the results of Raman/Auger ratio and CT times for Ar on Si(100)–H, for both p- and n-type materials, from analyses as shown in Fig. 6. After ref. 25.

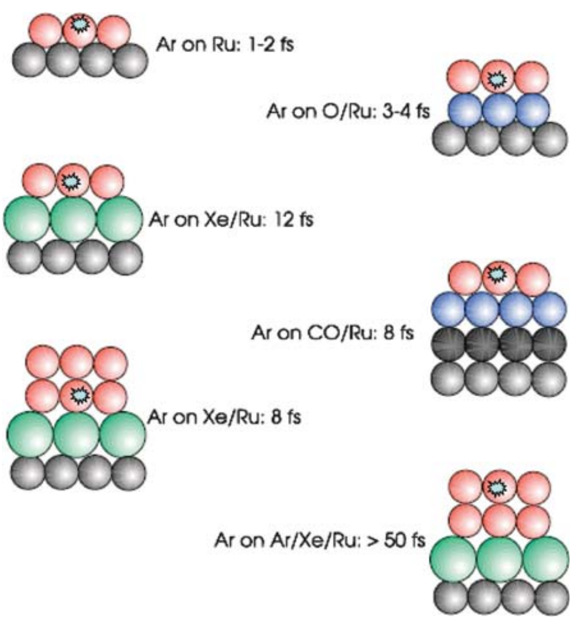

Fig. 8 Tuning of the CT coupling by spacer layers. Data for the CT times from core-excited adsorbed Ar directly on a transition metal surface (Ru(0001); top left), and on various well-defined spacer layers are shown. The values given are the CT times at resonance except for the top two cases, where the variation through the tuning range is given. The location of the core excitation is indicated by a star. Note the two lowest cases which concern the identical layer structure, but in the left case Ar in the lower layer is core-excited, and in the right case that in the top layer, leading to an at least 6-fold CT time. After ref. 9.

Fig. 4 shows a set of raw decay electron data for Ar adsorbed on an n-Si(100) surface with a monohydride layer, H–Si(100), resonantly excited into the $2p_{\frac{3}{2}}^{-1}4s$ state.[25] This is a particularly clean case since there is almost no background on which the decay spectra ride (on metal surfaces and even on clean Si this background is usually considerably larger and a satellite tail exists at the low KE side, due to easy coupling of the decay electrons to low energy excitations). The large peak on the right is the Ar 3s photoelectron peak (while in general it would be expected to contain a resonant participator contribution, this is negligible here[25]). The data are plotted on the KE (kinetic energy) scale, so that Auger peaks (resulting from core hole decay *after* CT) stay at the same energy while Raman peaks (core hole decay *faster* than CT) and the 3s photoelectron peak move with changed photon energy; the latter peaks stay put on a binding energy scale. Already here it can be seen that the two peaks at lowest KE must be Auger peaks and the two at highest KE are Raman peaks; the range in between must contain a mixture. There are still slight variations of the energy scales of photons and electrons and of the intensity (due to fluctuations of light intensity) in these raw data; these can easily be removed by calibrations carried out in parallel. In Fig. 5 this has been done, and the small background is subtracted; now the spectra are plotted on the binding energy scale which emphasises the Raman peaks at constant BE. The insert in the figure shows the absorption spectrum of the $2p_{\frac{3}{2}}^{-1}4s$ resonance through which the photon energy is tuned to obtain the decay spectra, and a comparison to that of isolated Ar in the gas phase which is much narrower. It has been easy to find a single set of energy and width parameters with which *all* spectra (including those on p-type Si(100)) can be resolved into their two components. Fig. 6 shows an example of this decomposition. By integrating the components and intensity ratios, CT times are obtained. We note that n- and p-type surfaces behaved similarly, the only difference being a shift of about 1 eV between the KE of the decay spectra, as expected for flat band conditions under intense irradiation.

To test the influence of the surface conditions, similar measurements have also been done on clean Si(100) surfaces (n- and p-type), albeit not as extensively. On the clean Si surface the spectra were clearly more strongly weighted to the Auger contribution, which shows that on this surface CT is even faster. There are some interesting differences in the detailed energies (photoelectron and decay energies) between the two surfaces which are consistent with different screening on the two types of surface. The reader is referred to ref. 25 for details.

The evaluation of all sets of measurements on H–Si(100) (n- and p-dopings) resulted in the behaviour shown in Fig. 7. The CT times are in the low fs range, with the value at resonance at about 2 fs, as for many metals (see below). Comparing this to the broadening of the absorption spectrum by about a factor 5 for Si–H (Fig. 5), it becomes obvious that the latter contain some inhomogeneous broadening in addition to the effective lifetime decrease by CT. The structure seen in the CT times *vs.* energy will be discussed below. CT times on clean Si (not shown) are about a factor 2 faster.

Fig. 8 compiles results for a number of Ar layers on top of other well-defined adsorbates.[10] Such "spacer" layers obviously lead to considerable increases of the CT times which must be mainly due to the larger separation from the surface (see below). On different metal surfaces, a considerable variation of CT times has been found, with values between 1.5 and 6 fs on resonance.[10,24,26,27] In particular a difference of almost a factor of 2 between two different faces of Cu[27] is noteworthy. We will discuss this in section 4.4. Another interesting point to note which is important in connection with the mechanism of CT is that in many cases the energy dependence is unexpected: in quite a few cases the CT times increase with increasing excitation energy,[26] *i.e.* with the excitation approaching the vacuum level. This is at variance with a picture of CT being due to simple tunnelling through a barrier into a continuum, and also with any influence of an Auger–Raman type effect (see above). Before we discuss these points some other results are summarised.

4.2 Sub-femtosecond charge transfer

Already 10 years ago[12] it was found that CT from resonantly excited chemisorbed CO (using the O1s core level) was extremely fast, in agreement with the earlier[14] semi-quantitative conclusion from mentioned comparison of resonant and non-resonant decay spectra of CO adsorbed on transition metal surfaces. So it was not surprising that the Raman contribution was difficult to extract even from measurements with narrow band excitation because the spectator Raman and the (much stronger) Auger spectra strongly overlapped; therefore only the weak participator Raman peaks could be seen unobstructed (see Fig. 9). While the extracted CT times (about 0.6 fs for CO[12]) therefore contains a larger error than for Ar, the early conclusion of extremely fast CT for chemisorbed CO, obtained from comparison of resonant and continuum core excitation,[14] is clearly corroborated. Since no core levels with shorter decay times are available in these light atoms, no improvement is accessible for these strongly coupled systems.

Shorter timescales are accessible with better accuracy if core levels with shorter lifetime are contained in the system investigated. This has been shown for adsorbed sulfur using the S 2s core level with its very short lifetime (about 0.5 fs[17]) due to Coster–Kronig decay.[13] The CT time on resonance for an electron excited into the S 3p level was found to be about 400 as. Subsequent work[28] has shown that a difference of up to a factor of 4 exists for the CT times between the electron being excited into the 3p orbital parallel ($p_{x,y}$) and perpendicular (p_z) to the surface (see Fig. 10), with the latter at 0.2 fs.

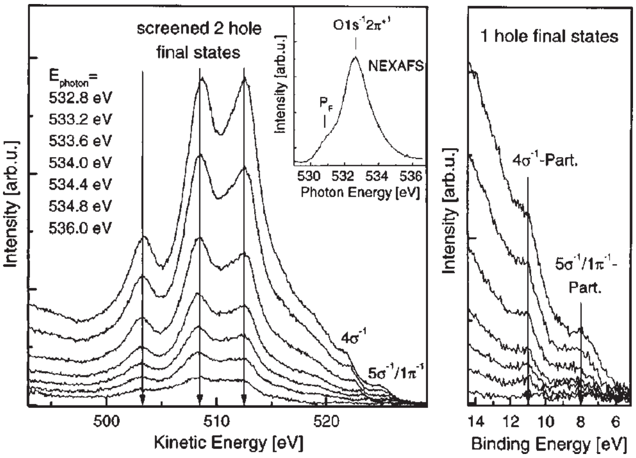

Fig. 9 Sub-femtosecond CT from chemisorbed CO on Ru(0001). In this case the predominant Auger channel, which qualitatively shows that the CT is much faster than core hole decay, makes the overlapping spectator Raman contribution not observable. A semi-quantitative CT value can be derived from the participator Raman channel which shows resonant behaviour (detail in the right panel). For details see ref. 12. From ref. 12.

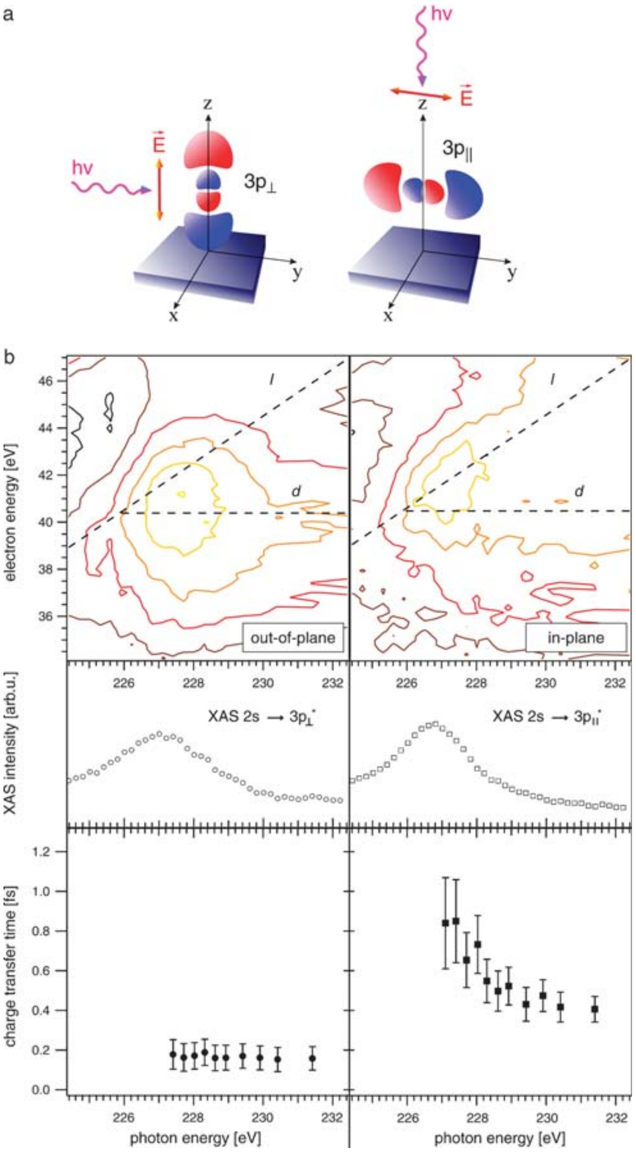

Fig. 10 Effect of orbital polarisation for CT times in the sub-femtosecond range. CHC measurements for S/Ru(0001) using the very short-lived S 2s excitation were conducted with different polarisation of light, chosen such that the excited electron is put either into the 3p orbital perpendicular or into that parallel to the surface (a); (b), from top: the corresponding decay electron distribution for varied photon energy (horizontal lines indicate constant KE, *i.e.* Auger lines, while inclined lines indicate constant binding energy, *i.e.* Raman lines); the absorption peaks; and the CT times for these two polarisations. The much faster CT (by up to a factor of 4) for the better overlapping perpendicular orbital is obvious. Reprinted with permission from ref. 28. Copyright 2007, American Institute of Physics.

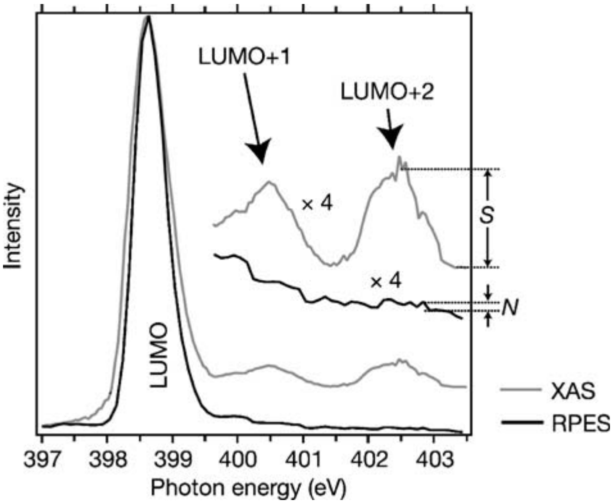

Fig. 11 Comparison of absorption peaks and intensity of resonant photoemission (RPES, *i.e.* participator lines), as indicated, for excitation into the LUMO and the LUMO + 1 and +2, for a monolayer of bi-isonicotinic acid on TiO_2. The large RPES line at the LUMO stems from the fact that the LUMO lies within the TiO_2 band gap, making coupling very weak, while LUMOs + 1 and +2 lie in regions of large empty density of states which leads to fast CT and correspondingly low RPES intensity. From ref. 29. Reprinted by permission from Macmillan Publishers Ltd: *Nature*, 2002.

4.3 Other surface systems

In recent years the CHC method has also been used for the investigation of more complicated molecules and of questions of practical interest, albeit in many cases with semi-quantitative results due to the complications for large molecules. Some examples are given in the following.

The first case of a CHC investigation of a large molecule was that of bi-isonicotinic acid on a TiO_2 surface as a model substance for solar cell surfaces.[29] It used resonant C1s excitation to 3 different unoccupied orbitals (UMOs) and found very different delocalisation times (see Fig. 11) which were explained by band structure influences. For the LUMO which lies energetically in the substrate band gap strong localisation was observed; while for the LUMO + 2 in the energy range of large empty substrate DOS the fastest delocalisation (below 3 fs) was concluded from the very small resonant decay signal. For Fe–tetraphenylporphyrin on MoS_2 very large differences were found for CT times for a LUMO localised on the phenyl rings (3–6 fs), compared to one on the porphyrin ring (30 fs), again demonstrating the influence of the location of the excited electron orbital.[30] For layers of a self-assembled monolayer (SAM) of a terphenylthiol on Au, a strong change in the CT time was derived from the strength of the resonant signal when the rings were partly fluorinated, suggesting that the fluorination localises the excited state electrons; and for 4-fluorobenzenethiol monolayers, a strong influence of the actual molecular orientation on the surface (standing up or lying down) on CT was detected: a change of the molecular orientation by 30° switched the CT coupling from negligible to ultrafast (<6 fs) CT.[31] It should be noted that in the case of large molecules with several overlapping UMOs the distinction between Auger and spectator decays *via* constant KE *vs.* constant BE can be softened,[30,31] so that analysis of data is more difficult.

A more quantitative approach with clear localisation of the charge to be transferred was possible in the investigation of smaller, aliphatic thiol SAMs of varied backbone length (2 *vs.* 16 methylene groups, C2 and C16) on Au by the use of a suitable end-group, a nitrile group.[32] Use of the nitrile group as the location of core excitation has the advantages that a clear starting point of the CT process is defined, and that their decay spectra possess well separated Raman and Auger components, in particular for N1s excitation. While for energetic reasons no CT is possible for the long SAM (the energy of the excited electron is below the Au Fermi level), for the short SAM a CT time from the nitrile group to the substrate of about 15 fs was found.[32] This is in surprisingly good agreement with calculations for single molecule conductance of this SAM. It should be noted that, in particular for weakly adsorbed species and large molecules with a low-lying UMO, the case of energetic blockade of CT from the molecule to the substrate is not infrequent, as here for the C16 chain: the created core hole pulls the LUMO below the Fermi level of the substrate. In such cases the reverse transfer (from substrate to molecule) can occur which, however, was not observed for the C16 SAM—not surprising considering the quite long chain. Such a reverse CT, which can be interpreted as a screening event of the adsorbate core hole, has been seen for physisorbed N_2 where a characteristic time of 9 fs was derived for this reverse CT; this result represented the first quantitative use of the CHC method.[33]

In this connection it should be realised that the final states of core hole decay are partially screened by polarisation, even if nominally they correspond to 2h or 2h1e states, at least on metal and semiconductor surfaces. The core exciton state reached by the core-to-bound excitation is self-screened, *i.e.* the core hole is screened by the excited electron residing on the same atom or atom group. If that electron jumps away, the formed "naked" core hole state will be screened by the surroundings (substrate and co-adsorbates) at a time scale which is short compared to all the time scales discussed here. For an essentially van der Waals-bound species such as an Ar atom, the screening is done mainly by polarisation of the substrate electrons, which for a metal can be represented by an image charge in the substrate for the distances involved. In addition there is also some screening by polarisation of the surrounding ground state adsorbates. Since this image charge is in reality formed by charge accumulation at the interface whose formation can be seen as superimposed surface plasmons, its formation time is given by the surface plasmon frequency, *i.e.* is in the range of 0.1 fs. For a chemisorbed species the screening is mostly done by charge transfer into a screening orbital formed close to the Fermi level by pulling down DOS by the core hole. The rate of this (reverse) CT is given by the width of the orbital doing the chemisorption interaction, *i.e.* again much faster than the CT observed. As to the decay processes, the Raman final states (which are 2h1e states) are effectively 1h valence states screened roughly as the c^{-1} states. The Auger final states are 2h valence states whose screening energy is about 3 times that of 1h states, at least for polarisation screening. Corresponding shifts have been seen in Ar on Si(100), as mentioned above.[25]

4.4 What are and what determines the CT times?

The use of the term CT time is sometimes controversial. It could as well be replaced by calling the measured time a delocalisation time. The method measures the branching of the final state into one of two well-defined final states, where for one the excited electron is located on the atom containing the core hole, while the other does not. How the evolution of one to the other proceeds, for instance how the initially strongly localised excited electron density spreads while still localised on the core hole atom, is not addressed by the measurement; it might become accessible by time-dependent attosecond measurements with half-cycle X-ray pulses.[11] For the process which must occur between the two alternatives either nomenclature, CT or delocalisation, appears appropriate.

As to what determines the CT/delocalisation time, it is clear that it will depend both on the location of the source orbital, as shown on some examples above, and on the receiving state, *i.e.* where the excited electron is being transferred to. As to the latter, we will start by assuming that CT puts the locally excited electron into the substrate. Naively one would then expect that the CT times of an excited electron on an adsorbed atom (say, core-excited Ar or S) would mainly be determined by tunnelling of the excited electron into the substrate. This would result from a picture in which the excited electron would sit on the atomic well and be separated from the metal (or semiconductor) continuum by a barrier of finite width and height (see Fig. 2). In all cases of strong influences of layers which represent insulators in the relevant region, *i.e.* underlayers (spacers), or multilayers, the main influence is indeed likely to be the distance from the surface, *i.e.* the thickness of a true tunnelling barrier.

Looking at a simple atom such as Ar, sitting directly on a metal surface, the relevant parameter (distance being fixed) should then be the barrier height. Upon changing the excitation level by tuning the photon energy upwards, tunnelling should become exponentially faster when going closer to the vacuum level with the excited electron. However, this case is rarely found. As mentioned above, the opposite variation—decrease of the transfer rate with increasing energy—is often found, or a clear structure is seen as for Ar on H–Si(100) (see Fig. 7). The importance of band structure has already been mentioned for some cases above. More quantitatively, it has been shown in several investigations that the surface-projected density of states (SpDOS) of suitable symmetry, into which the excited electron can be transferred, is of utmost importance. The very different behaviour of Ar on Cu(100) and Cu(111)[27] has been explained quantitatively by the very different empty surface band structure of these faces; in particular the slower CT (by a factor of 2) for the Cu(111) case has been traced back to the large band gap on this surface. A detailed first principles calculation of CT has been developed recently[34] which also bears out the connection between CT and empty band structure. It has been applied to the well-documented case of core-excited Ar on Ru(0001).[10] Very good agreement with the experimental values was found, and the counterintuitive increase of the CT time with increasing energy was traced back to the existence of a surface projected band gap of the substrate. For the very fast CT of S on Ru(0001) mentioned above,[13,28] a calculation on similar grounds resulted in good agreement with the measured behaviour, including the strong dependence of the CT time on the polarisation-selected LUMO (see Fig. 10). This polarisation dependence also stresses that the overlap of the suitably selected SpDOS with the donor orbital is the decisive quantity. In the case of Ar on Si(100) a connection to the empty band structure is one possibility which is being tested, although other influences may contribute to the unexpectedly fast CT in this case.[25] The work in ref. 34 showed that for high-lying resonances, the picture of tunnelling through a true barrier is not very appropriate, as in the intermediate state the levels mix as in adsorbate binding. A better conceptual picture is then that of coupled electronic levels (in chemical terms hybridisation), so that fast charge transfer corresponds to strong coupling. It should be noted, however, that this is not a real difference of the underlying physics: in all cases the overlap of electronic wave functions of favourable symmetry determine the probability of transfer. Also, it does not mean that one should better talk of level widths than of CT times—after all, these two expressions, corresponding to a stationary and a time-dependent picture, signify the same situation. Furthermore, the corresponding level widths would have to be those giving the homogeneous (life-time) width; however, in most cases investigated so far influences of inhomogeneous broadening and vibrational structure have been seen or cannot be excluded.

The overriding influence of the SpDOS of appropriate symmetry is proof that in all those cases CT indeed puts the electron into the substrate. It will mainly be expected on well characterised single crystal surfaces with well defined band gaps, and for closely coupled simple source atoms. But as shown above, on substrates with absolute gaps their influence is visible even for large molecules, which can lead to selection of CT for certain UMOs. While, due to the more complex and overlapping decay spectra, the interpretation will probably not be possible in as much detail, a wealth of more informative details can be expected from further applications of the CHC method to large molecules.

Another important parameter determining CT times is clearly geometry, be it the actual (and possibly changeable, switchable) arrangement of a complex molecule relative to a surface, or be it the localisation of the orbital into which the excited electron has been injected. Here the most important strength of the CHC method comes to fruition, the strong localisation of the intermediate state following from the overlap of the core orbital with the selected UMO. Again, many clever applications in addition to those described above are conceivable and will certainly be realised in the near future. In particular, it would appear very interesting to measure CT times for switchable molecules as important for molecular electronics.

The third effect is obviously what could be called the spacer effect, *i.e.* the consequence of increasing the tunnelling distance, whether by an inert intermediate layer, the extension of a distancing chain, or by mere geometrical effects. There is then overlap with what has been called geometry in the preceding paragraph—there is not much difference between an increased tunnelling distance due to filling in an insulating material or due to a geometry which forces the molecule to intersperse empty space between the localised electron and the medium into which it is delocalised by CT.

All these considerations apply to the case that CT brings the excited electron directly into the substrate. In the case of a core-excited atom on a metal or semiconductor surface, with the excited electron in an UMO between Fermi and vacuum level, the delocalisation indeed usually transfers the electron into the substrate, as corroborated by the described band structure influences. However, it is conceivable that the primary delocalisation of the electron away from "its" atom with core hole—the effect leading to the observed change of the decay spectrum of this core hole—is a delocalisation *within* the adsorbate layer, to be transferred to the substrate only later. The CHC method will record the first transfer of the initially localised electron away from its source core hole. For Ar layers a lateral delocalisation is not possible because the neutral Ar neighbours have no DOS at the energy of the excited electron. The Ar layer has in fact negative electron affinity, and the core exciton is a bound state only because of the core hole charge. In a layer of large, strongly polarisable molecules this is not necessarily the case any more. All that is necessary to delocalise the excited electron within the layer (the core hole remains localised on the original atom, of course) is that the screening energy of the surroundings to the core hole "denuded" by delocalising "its" excited electron is sufficient to cancel the binding energy of the localised core exciton—which will often be possible in a complex, easily polarisable molecular layer. So in such cases the path taken by the excited electron is not given *a priori*, and the connection to other connected properties, *e.g.*, single molecule conductance, may not be simple to analyse. Nevertheless, the examples given above of CT within a self-assembled monolayer, or the dependence of CT on the conformation of a large molecule on a surface, show the potential of this type of investigation. It can be hoped that such research will lead to improved insight in molecular electronics, be it to get a better handle on switching behaviour, or on single molecule conductance.

5. Comparison to other CT measurements

Most measurements of ultrafast dynamics are nowadays done by LPP techniques.[6–8] Therefore it is worthwhile to briefly discuss the similarities and differences between these and the present method.

There have been discussions whether the CHC method should be considered as a time domain or frequency domain method. Obviously no information from peak widths and similar frequency information enters in the CHC case. On the other hand, in a strict definition it could be considered a frequency domain method because of the extended pump time (see above). It does use time comparison, though, and in a looser definition, it can be seen as a special pump–probe method: The excitation by photon absorption is the pump event, and the core hole decay is the probe which is exponentially distributed; integration over many processes is necessary to define the result. Things are in fact more complicated. Because of the narrow exciting bandwidth compared to the width corresponding to decay, the processes (excitation and de-excitation by core hole decay or CT) occur simultaneously, and the decay might in fact not be simply exponentially distributed. In the theoretical work on Ar/Ru,[35] some evidence for deviations from that simple decay law have been found. However, these points appear less important than some other differences.

If LPP results are compared to those obtained by the CHC method, it has to be remembered that the latter uses an atomically localised core excitation as the start: both hole and excited electron are initially localised on the same atom. LPP measurements, on the other hand, up to now look at a valence excitation. The level from which the excited electron was taken is often a surface band of the substrate; the holes are left in the substrate and evolve there independently. If the state receiving the hot electron is localised on an atom or molecule, the excited state essentially corresponds to a (screened) negative adsorbate ion of the ground state adsorbate, but it can also be a band state (see below). For CHC, on the other hand, we have already pointed out above that the core excited atom is roughly equivalent to a $(Z + 1)$ atom, as suggested by the equivalent core approximation, and that the excited electron is initially atomically localised. So comparison of CHC results of adsorbed Ar should not be made with LPP of adsorbed Ar, but rather of adsorbed K. This will still not be a good comparison, not only because of the shortcomings of the equivalent core approximation, but also because the K atom has to be put at the site and distance of the adsorbed Ar; it is much better than the Ar comparison. In the same sense, N_2 corresponds to NO, and CO corresponds to either NO or CF depending on which atom has been core-ionised; and CHC of a molecule such as C_6F_6 has to be compared to either C_5NF_6 or to C_6F_5Ne. No such direct comparison seems to have been made to date.

These considerations apply if the laser-induced excitation is, as the CHC excitation, localised on an atom or molecule. Generally, this will be the case only for very low coverages of the adsorbate, a situation which has been realised in some,[35] but not in the majority of measurements. For higher coverages and in particular for a monolayer, the excited states will couple, and for a periodic adsorbate layer LPP puts the excited electron into a LUMO band, *i.e.* into a delocalised state, and it does so in a coherent way. Dephasing of this coherent, delocalised excitation may then be more important than its transfer into the substrate. For laser experiments with intense fs pulses there may be additional effects from strong filling of this LUMO band and consequent electron interactions; however, such effects can be avoided in 2PPE measurements by the design of experiments.[35] The CHC experiments work at very low excitation densities, with less than 1 core-excited atom in the probe area within the relevant $\sim$10 fs.

So it appears that CHC and LPP measurements not only use different excitations, but also look at different physical processes. One may ask which of the excitation modes is the more "realistic" one, *i.e.* corresponds better to interesting properties of the system. There it appears that the localised, low density CHC method is closer to reality if the latter consists of localised charge transport (molecular conductance; STM measurements or similar). On the other hand the delocalised excitations by

LPP methods will correspond closer to reality in semiconductor systems and *e.g.* laser-induced molecular switching.

These considerations show that comparisons of CHC and (valence) LPP for the same or even for core-equivalent systems may not be very relevant; it is better to treat each method with its appropriate theory, and select the one which corresponds better to the envisioned application. A direct comparison between CHC and LPP for the identical process will become possible when half-cycle soft X-ray pulses will be available on a routine basis and applicable to surface systems—a situation which appears to be just around the corner.[36] The intensity of these pulses will be very low, and they will be usable for core hole excitation, so that the situation will be close to that in CHC experiments. Since they will then also probe the CT from single, localised core excitations, their results should be directly comparable to CHC results, but with more flexibility and direct probing. It will then be possible to check whether there is a difference introduced solely by the method of measurement. Because of the extremely short time delays which can be continuously varied, even the evolution of the core-excited state itself in, say, a large molecule might become accessible. These possibilities appear very exciting.

6. Conclusions

The core hole clock method is a very suitable method to measure local charge transfer (or delocalisation) times between adsorbates and substrates in the range around and below 1 fs. Recent publications have shown quite convincingly which parameters determine the CT times measured, and have resulted in interesting details about large adsorbed molecules. The physical situation which is imaged by this method is quite different from fs LPP techniques such as time-resolved 2PPE, so that comparison is not simple. So there is room and need for both approaches, and the future should be bright for both. Direct pump–probe measurements with half-cycle soft X-ray pulses will be a very important new addition to the arsenal of methods in this realm of surface physics.

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