Core-Hole Clock Spectroscopy
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Introduction
In this short report the main principles of the technique named core-hole-clock spectroscopy is summarized. The method is used to study the charge transfer dynamics at interfaces and surfaces with the lifetime of the core-hole as an internal reference clock to follow the charge transfer process.

Electron transfer processes occur and are most important in many different types of devices and situations such as electrochemistry, optoelectronic devices such as solar cells and LEDs, transistors, catalytic surfaces, molecular electronics and single-electron devices. By using core-hole clock spectroscopy, the dynamics of ultrafast electron transfer can be monitored and due to better understanding of the dynamic process device performance can be improved and developed.

Because of the time scale of the charge transfer process, femtoseconds and below, there are few methods available to study these processes. Besides Core-hole clock, time resolved 2 photon photoelectron spectroscopy, tr-2PPE should be mentioned as an alternative method to follow the charge transfer dynamics but because of their differences they also monitor the process differently.

Experimental details
Core-hole clock spectroscopy is based on the Auger resonant Raman spectroscopy. In normal Auger spectroscopy, the excitation is made far above the absorption threshold. As the excited state relaxes, an Auger electron with constant kinetic energy, independent of the energy of the exciting photons is emitted.

In Auger resonant Raman spectroscopy the energy of the exciting photons approach the core level threshold from above and the initial core excitation is made in resonance, placing the excited electron in an unoccupied state. The excited electron will interact strongly with the remaining system and the process of excitation and decay can not be treated as independent processes anymore which make the kinetic energy of the Auger electron dependent on the energy of the exciting photons. The non-radiative core-hole decay process is called autoionization and it can be divided further into spectator and participator type Auger decay depending on whether the excited electron participates in the decay or remain a spectator localized in its excited position during the decay.

In core-hole clock spectroscopy the initial core excitation is made to an unoccupied state at the adsorbate as illustrated in Figure 1a) and in 1b) and 1c) the spectator and participator decay channels are displayed respectively. In case there is charge transfer from the adsorbate to the substrate at the interface during the lifetime of the core hole as in Figure 1d), a contribution similar to that from normal Auger decay will be present in the spectra with a kinetic energy independent of the excitation energy. Because of the different dispersive behavior of the decay channels, it is possible to estimate the charge
transfer times in relation to the life time of the core-hole from the peak intensities of the different decay processes as the schematic illustration shows in figure 2. The core-hole life time is calculated directly from the relative intensities of the different decay channels according to $\tau_{\text{CT}} = \frac{I_{\text{Raman}}}{I_{\text{CT}}} \times \tau$

Figure 1: Principle of the core-hole clock method\(^1\).

Core-hole life times of inner shell vacancies typically varies between 4 and 6 fs\(^2\) which sets a limit for the time-scale of the method. To access even faster charge transfer processes, the Coster–Kronig decay process of the core-excited state, were the initial and final states are in the same electronic shell and has an atto-second lifetime of the core-hole, could be used as the internal reference clock.

Figure 2. Schematic illustration of how the charge transfer dynamic is estimated from the relative intensities of the decay processes in a spectra\(^1\).
Some scientific results

Core-hole clock spectroscopy has been used successfully in a number of different scientific areas recently with titles such as: Attosecond electron delocalization in the conduction band through the phosphate backbone of genomic DNA\(^3\), Charge-transfer dynamics at model metal-organic solar cell surfaces\(^4\) and Ultrafast charge transfer and atomic orbital polarization\(^5\) just to mention a few with rather different applications. In figure 3 below, the Sulphur KLL autoionization spectra\(^6\) is displayed and is an example of what a measurement could look like and how information is extracted.

![Sulphur KLL autoionization spectra](image)

Figure 3. Decomposition of the Sulphur KL2,3L2,3 autoionization spectra into the atomically localized S2p4 3p+1 final state multiplets (linear dispersion with photon energy), and the charge transfer S 2p4 final states represented by the 1S, 1D normal Auger multiplets at constant kinetic energy\(^6\).

References