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# Time-resolved X-ray photoelectron spectroscopy techniques for the study of interfacial charge dynamics

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### ABSTRACT

X-ray photoelectron spectroscopy (XPS) is one of the most powerful techniques to quantitatively analyze the chemical composition and electronic structure of surfaces and interfaces in a non-destructive fashion. Extending this technique into the time domain has the exciting potential to shed new light on electronic and chemical dynamics at surfaces by revealing transient charge configurations with element- and site-specificity. Here, we describe prospects and challenges that are associated with the implementation of picosecond and femtosecond time-resolved X-ray photoelectron spectroscopy at third-generation synchrotrons and X-ray free-electron lasers, respectively. In particular, we discuss a series of laser-pump/X-ray-probe photoemission experiments performed on semiconductor surfaces, molecule-semiconductor interfaces, and films of semiconductor nanoparticles that demonstrate the high sensitivity of time-resolved XPS to light-induced charge carrier generation, diffusion and recombination within the space charge layers of these materials. Employing the showcase example of photo-induced electronic dynamics in a dye-sensitized semiconductor system, we highlight the unique possibility to probe heterogeneous charge transfer dynamics from both sides of an interface, i.e., from the perspective of the molecular electron donor and the semiconductor acceptor, simultaneously. Such capabilities will be crucial to improve our microscopic understanding of interfacial charge redistribution and associated chemical dynamics, which are at the heart of emerging energy conversion, solar fuel generation, and energy storage technologies.

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## 1. Introduction

Since the first demonstration of X-ray photoemission spectroscopy (XPS) by Siegbahn and co-workers in 1957 [1], the method has found widespread application in many areas of research and industry due to its capability to derive quantitative information on the atomic composition and electronic structure of solid and liquid surfaces. In particular, in the fields of surface physics and interfacial chemistry, it has been developed into a powerful spectroscopic tool that does not only reveal the presence of small traces of atomic species on a surface based on their characteristic electron binding energies, but also provides insight into their chemical environment. The latter manifests itself in so-called “chemical shifts” of the photoemission lines, which relate to the fact that the exact inner-shell binding energy of an atom sensitively depends on the

available electronic charge that can screen a specific core-hole vacancy [2,3].

Extending XPS into the time domain holds great promise to capture not only the final products of photophysical processes and chemical reactions, but would additionally allow access to the microscopic dynamics underlying, for example, (photo-)catalytic processes including short-lived intermediate states. The history of time-dependent XPS studies traces back approximately twenty five years [4,5] and may, traditionally, be divided into two broad categories, which either use fast data acquisition or pump/probe techniques. Enabled by the high X-ray brilliance available at third generation synchrotron light sources and the development of efficient electron energy analyzers and detectors, chemical reactions between molecules adsorbed from the gas phase onto metal surfaces have been followed on a few-second timescale by fast sequential data acquisition [4,6,7]. However, this approach is generally restricted to the study of relatively slow reactions, since the time resolution in the experiments is limited by the minimum time needed to record an XPS spectrum with a sufficiently high signal-to-noise ratio [8]. By restricting the collection of fast XPS signals

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to a single binding energy, Höfert et al. [9] recently demonstrated the possibility to follow adsorption and desorption kinetics of CO from Pt(111) with a temporal resolution of 500  $\mu\text{s}$  through averaging over hundreds of individual XPS time scans [9]. However, this approach requires precise prior knowledge of the evolution of the full XPS spectrum as function of process parameters, which may render the characterization of short-lived precursor states difficult.

Over the past  $\sim 15$  years, time-resolved X-ray techniques have been introduced that make use of the pulsed time structure of X-rays emitted by synchrotron radiation facilities within a pump–probe scheme [10–19]. In this approach, a “pump” pulse initiates electronic and/or nuclear dynamics inside a target and their time evolution is monitored by a second, delayed X-ray “probe” pulse. In principle, the pump pulse can be any stimulus acting on the sample, such as a voltage [20], magnetic [21–23] or photon pulse [10,13–15,24,25] as long as it is precisely synchronized to the probing X-rays. The time resolution within these experiments reaches the picosecond [11,14,15,26–29] and even femtosecond [25,30–32] regime.

We note that the vast majority of synchrotron-based time-resolved X-ray spectroscopy studies of photo-induced chemical and interfacial dynamics have, so far, not been based on XPS. Instead, the transient response of a sample to optical excitation has mostly been probed via the time-dependence of the X-ray fluorescence emitted from or X-ray intensity transmitted through the sample [11,14,15,28,29]. These time-resolved X-ray absorption spectroscopy (XAS) techniques have been successfully applied to uncover intra-molecular spin- and charge dynamics in isolated and solvated molecules [26,27], and have recently been extended to probe charge transfer dynamics in dye-sensitized semiconductor nanoparticles [28,29]. A time resolution of a few tens of picosecond, which is governed by the duration of the electron bunches in the storage ring, is routinely obtained in these experiments. A number of complementary time-domain X-ray techniques, such as femtosecond time-resolved XES [33–36] and high-field streaking experiments [37–39], have also been successfully applied by several groups to study ultrafast electronic and chemical dynamics in solid and liquid phase systems. We refer the reader to the cited references and other contributions to this special issue for a more detailed discussion of these techniques.

Despite the distinct advantages offered by the high surface sensitivity of XPS compared to the more bulk-sensitive XAS techniques in the investigation of surface and interfacial chemistry, the development of time-resolved XPS at synchrotron facilities is still in an early stage. Up to now, it has been used almost exclusively to study the dynamics of transient surface photovoltage (SPV) phenomena at surfaces and interfaces of elemental semiconductors and metal oxides [5,16,19,40–47]. First pioneering experiments have also addressed magnetization dynamics in thin films by taking advantage of the X-ray magnetic linear dichroism effect in photoemission [24]. However, one of the key capabilities of XPS – the detection of chemical shifts – has so far barely been exploited in the time-domain.

Generally, a transient charge redistributions around a probed atom is expected to induce a dynamical chemical shift of the corresponding core-level photoemission lines similar to time-dependent shifts of the absorption edges observed in time-resolved XAS experiments [29,48]. In a recent pump–probe photoemission experiment performed with extreme ultraviolet (XUV) radiation produced by high-harmonic generation (HHG), the UV-induced electronic response in a self-assembled monolayer of iodophenylphenol on a Si(100) substrate could be followed on a few-picosecond timescale by selectively probing the inner-shell photoelectrons emitted from an iodine marker atom incorporated in the organic film [49]. Similar setups have been used to track the laser-induced bond-reconfiguration of oxygen atoms on a metal surface and the

build-up of the SPV response in semiconductors with femtosecond resolution [50,51]. Although these studies clearly demonstrate the prospects of time-resolved XPS to provide atomic-site specific real-time access to complex interfacial electron dynamics, HHG light sources still suffer from a limited energy range of the emitted radiation ( $\leq 200$  eV [52]), which currently restricts their application to a relatively narrow range of inner-shell orbitals and model systems. HHG with significantly higher photon energies has been demonstrated, albeit with average intensities and/or pulse repetition rates that are, usually, too low for XPS applications [53]. New HHG techniques, however, are emerging rapidly and it appears to be only a matter of time until table-top femtosecond XPS setups will become available [54].

We note that HHG-based time-resolved photoemission spectroscopy (PES) on valence electrons is a fast expanding field of research. As opposed to XPS involving core-level transitions, however, valence PES does, generally, not provide atomic site specificity, which is a central motivation for the work presented herein. Therefore, we refer the reader to the rich literature on time- (and angle-) resolved valence PES for an overview of its history and current trends (see e.g. [55–60] and references therein).

In this contribution, we discuss some possibilities offered by time-resolved XPS at third-generation synchrotrons and X-ray free-electron laser (FEL) facilities, which combine pico- and femtosecond temporal resolution, respectively, with a photon energy range covering the XUV, soft- and hard-X ray regions of the electromagnetic spectrum. Experimental implementations and associated challenges are described, in particular, for a picosecond time-resolved XPS apparatus recently commissioned at the Advanced Light Source (ALS) [12], and for a femtosecond time-resolved XPS experiment performed at the Linac Coherent Light Source (LCLS) [61]. Opportunities for sub-nanosecond time-resolved XPS using constant wave (CW) X-ray light sources will also be outlined [62]. Particular emphasis will be given to the ability of time-resolved XPS to follow charge carrier relaxation based on the transient SPV effect at semiconductor surfaces and buried interfaces. The light-induced electron injection and recombination dynamics at interfaces formed by N3 dye molecules (bis(isothiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylato)-ruthenium(II), see Fig. 7) adsorbed on films of ZnO nanoparticles are used to illustrate how dynamic chemical shifts in combination with SPV responses can provide comprehensive microscopic insight into transient electronic charge configurations in technologically pertinent hybrid systems.

## 2. Experimental techniques and instrumentation

X-ray FELs and synchrotron radiation facilities provide X-ray pulses that differ not only in their duration but also by orders of magnitude in repetition rates and pulse energies. The differences in pulse characteristics pose different challenges for the implementation of photoemission techniques at these facilities. In the following, we discuss strategies and schemes that have been adopted to take advantage of their characteristic beam properties in time-resolved XPS experiments.

### 2.1. High-repetition rate pump–probe XPS at synchrotron radiation facilities

The intrinsically pulsed nature of synchrotron radiation provides an opportunity for pump–probe studies with pulse repetition rates in the MHz range. The time resolution is, generally, limited by the duration of the electron bunches in the storage ring, which are typically in the range of 30–100 ps [14–16,19] but may be reduced to few-ps [63,64] or even sub-ps regimes [25,65] using special (“low

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