Coordination Chemistry Reviews xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Recent experimental and theoretical developments in time-resolved X-ray spectroscopies

C.J. Milne [b], T.J. Penfold [a,b], M. Chergui [a,*]

[a] École Polytechnique Fédérale de Lausanne, Laboratoire de spectroscopie ultrarapide, ISIC, FSB-BSP, CH-1015 Lausanne, Switzerland
[b] SwissFEL, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

Contents

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 3 February 2014
Accepted 3 February 2014
Available online xxx

ABSTRACT

Capturing the evolving geometric and electronic structure in the course of a chemical reaction or biological process is the principal aim of time-resolved X-ray spectroscopies. Recent technological and methodological improvements, such as high repetition rate lasers and femtosecond laser-electron slicing have made this a reality. The advent of X-ray free electron lasers introduces a paradigm shift in terms of the temporal resolution of X-ray spectroscopies, and offer exciting possibilities for time-resolved second-order

* Corresponding author. Tel.: +41 21 693 0457/0447; fax: +41 21 693 0365.
E-mail address: majed.chergui@epfl.ch (M. Chergui).

http://dx.doi.org/10.1016/j.ccr.2014.02.013

Keywords:
Time-resolved X-ray spectroscopy
Femtosecond
X-ray free electron laser
Nonadiabatic
Non-linear

X-ray spectroscopies and non-linear X-ray experiments. In parallel, the improved data quality is making it increasingly important to accurately simulate the fine spectroscopic details. This has been the driving force for new theoretical methods permitting a detailed interpretation of the spectra in terms of the geometrical and electronic properties of the system. In this contribution, we discuss recent experimental and theoretical developments in ultrafast X-ray absorption spectroscopies (XAS) and explore the new opportunities they offer.

1. Introduction

Ultrafast studies emerged with the implementation of femtosecond–picosecond linear and non-linear optical spectroscopies [1–3] and had a huge impact on our understanding of chemical reactions, biological functions and phase transitions in materials owing to their ability to probe, in real-time, the nuclear motion within these different types of systems. However, for systems of more than two atoms the link between the optical domain spectroscopic observables and the molecular structure is ambiguous and therefore from the early days of ultrafast spectroscopy much effort was invested to develop methods that achieve both high temporal (on the femtosecond time scale) and spatial (on the order on tenths of an angström) resolution. Towards this goal, various groups adopted diffraction methods based on the use of ultrashort pulses of X-rays [4–6] or electrons [7–10], while others opted for time-resolved X-ray absorption spectroscopy (XAS) [11–17].

XAS is particularly attractive because of its ability to deliver electronic structure as well as geometric information. For the implementation of time-resolved XAS, third generation light sources (i.e. storage rings that generate synchrotron radiation) are most suited because of their wide tuneability, stability and high photon flux. However, the physics of storage rings limits the X-ray pulse duration to 50–100 ps. Nevertheless, several exciting results were gathered on a wide variety of chemical systems [12,13,18–33] and materials [34–37]. The temporal limitation of storage rings has been overcome by the laser-electron slicing scheme [38–41] and the so-called *low-alpha* modes [42,43], albeit at the sacrifice of photon flux. The slicing scheme in particular has made it possible to demonstrate femtosecond XAS of photoexcited molecular species in solution [44–46]. In parallel, the advent of X-ray free electron lasers (X-FELs) is starting to yield the first results in ultrafast XAS [47], which promises to revolutionise the field.

For achieving a full understanding of an experimental spectrum, theoretical simulations are essential. Such analysis has usually been performed using multiple scattering (MS) theory, within the limits of the muffin-tin (MT) potential [48] or using multiplet theory [49,50]. However, while these approaches have provided significant insight into the origin of both static and time-resolved spectra [23,25], the increasing information available from time-resolved spectroscopies means that one must go beyond the present approximations and, in an *ab initio* manner, include the influence of strong electron correlation [51–56], nuclear dynamics beyond the Born-Oppenheimer approximation and non-linear effects [57].

In this contribution, we review some of the most recent advances in both experimental and theoretical approaches for time-resolved XAS. We broaden the scope by discussing some of the new opportunities for time domain core-level spectroscopies such as X-ray emission spectroscopy (XES), and Resonant inelastic X-ray scattering (RIXS) and the potential impact of femtosecond temporal resolution and high fluxes provided by the X-FELs. This review is organised in the following way: In the first section, we recall the basic aspects of core-level spectroscopies. This is followed by a discussion on X-ray sources used for such experiments. A detailed summary of the experimental developments is then presented followed by an examination of theoretical developments.

2. X-ray spectroscopies

2.1. X-ray absorption spectroscopy

An X-ray absorption spectrum (XAS) is characterised by absorption edges, which reflect the ionisation threshold of the different core orbitals, shown schematically in Fig. 1. The physical processes and information content have been presented in detail in a number of books and review papers [58,59,48,50] and we will therefore not discuss them in detail here. Briefly, for a particular edge, an electron is initially excited to empty or partially filled orbitals just below the ionisation potential (IP) yielding information about the unoccupied density of states. The energy of the absorption edge provides information about the oxidation and spin state of the absorbing atom. Just above the edge (<50 eV), in the X-ray Absorption Near-Edge Structure (XANES) region, the low photoelectron energy (i.e. long de Broglie wavelength) implies that the photoelectron undergoes multiple scattering (MS) events. XANES therefore contains information about the three-dimensional structure around the absorbing atom, i.e. bond distances and bond angles. At higher energies, in the Extended X-ray Absorption Fine Structure (EXAFS) region, single scattering (SS) events usually dominate, as the scattering cross section of the photoelectron decreases increasing energy. This region delivers information about coordination numbers and

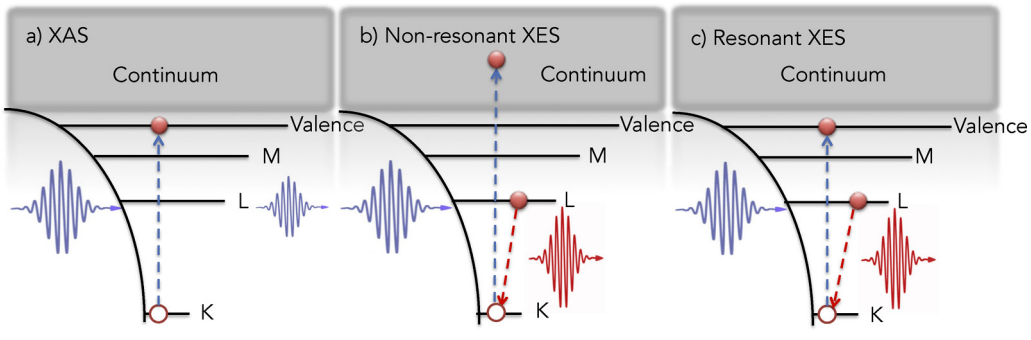

Fig. 1. Schematic energy level diagrams of XAS (a), non-resonant XES (b) and resonant XES (c).

Please cite this article in press as: C.J. Milne, et al., Coord. Chem. Rev. (2014), http://dx.doi.org/10.1016/j.ccr.2014.02.013