



Resonant soft X-ray emission for studies of molecules and solids

Joseph Nordgren, Jan-Erik Rubensson*

Uppsala University, Dept. of Physics and Astronomy, Box 516, SE 751 20 Uppsala, Sweden

ARTICLE INFO

Article history:

Available online 24 November 2012

Keywords:

Soft X-ray emission
Synchrotron radiation
RIXS
X-ray Raman spectroscopy

ABSTRACT

Resonant inelastic X-ray scattering (RIXS) has emerged as a powerful method for the study of the electronic structure of matter in various phases and ambient conditions. The selectivity offered by resonant excitation and polarization control in RIXS experiments offers rich information on excitations in molecules, liquids, and solids. The photon-in photon-out nature of RIXS makes it an interesting method in the study of ultra-high brightness FEL radiation interaction with matter. The present work offers an introductory review on the sub-keV RIXS, including some historic comments.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

X-ray spectroscopy offered an experimental basis for the exploration of the electronic structure of matter from the early 20th century, and over the years X-ray spectroscopy has been widely used both for elemental analysis in a great variety of applications, and as a method for basic research in physics and chemistry. Already around 1920 one observed the chemical sensitivity of X-ray spectra (chemical shifts) [1,2]. Valence band soft X-ray emission spectroscopy was used for the exploration of the electronic structure of solids during the next decades, and it became a widespread tool in materials physics and chemistry study, see e.g. reviews in [3,4]. Starting in the mid-sixties soft X-ray emission spectroscopy was used to study molecular orbitals in molecules in low resolution using artificial crystal Bragg diffraction [5–7], and later on employing grating diffraction for high resolution studies [8–11].

The introduction of synchrotron radiation sources has advanced X-ray emission as a spectroscopic tool for electronic structure studies by allowing selective and resonant excitation, starting in the mid-eighties [12–17]. The ability to excite X-ray emission by means of a monochromatic and tunable photon source opened new avenues for spectroscopic study. In particular, the third generation sources, notably the Advanced Light Source at Berkeley and the ESRF in Grenoble became facilitators to pave the way for a new form of X-ray spectroscopy in the mid-nineties, *resonant inelastic X-ray scattering spectroscopy* (RIXS). Evidence of resonant inelastic X-ray scattering had been observed in 1974 by C. Sparks [18], and a few years later by Eisenberger et al. [19], but it did not become much exploited until a decade later. Since the mid-nineties, there has been a rapidly growing community exploring the electronic

structure of various systems, often of complex nature, based on resonant inelastic scattering of soft and hard X-rays. RIXS instrumentation has become an increasingly common spectroscopic tool at synchrotron radiation facilities world-wide, and it is presently also being incorporated at the free electron laser facilities (FEL) built or under construction.

2. Properties of soft X-ray emission spectroscopy

X-ray emission spectra (XES) possess inherent local character due to the involvement of core electrons. For valence-core transitions (K_{β} , L_{β} , etc.) this means probing of the valence band at the site of a particular atomic species. Soft X-ray transitions are furthermore governed by electric dipole selection rules that impose restrictions on the states involved. This provides selectivity with respect to orbital symmetry. For molecules this is used to describe molecular orbitals in terms of atomic orbital composition (LCAO, linear combinations of atomic orbitals), and for solids in terms of partial densities of states, to describe the electronic structure of the bands. Soft X-ray emission thus offers a means to determine the composition of the molecular orbitals in the study of complex multi-component materials.

In addition to the local character and symmetry probing capability of conventional X-ray emission, the use of tunable synchrotron radiation for excitation provides further means to obtain detailed information about electronic structure. The first stage of the emission process, the X-ray absorption, can be seen as a selection of a particular atomic species of a multi-component system, or even a specific chemical site of an element. In the subsequent de-excitation, or X-ray emission, the local and symmetry selected contribution to the electronic structure emerges as an emission spectrum, see Fig. 1.

With tunable synchrotron radiation X-ray emission at specific chemical sites of a compound can be excited, since atoms in

* Corresponding author.

E-mail address: jan-erik.rubensson@fysik.uu.se (J.-E. Rubensson).

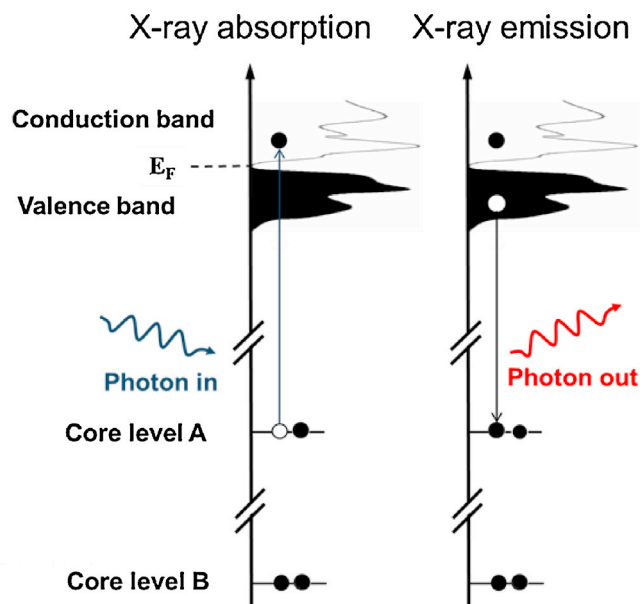


Fig. 1. Diagram of RIXS as a two-steps process, X-ray absorption and X-ray emission.

different chemical environments usually have different X-ray absorption energies. An illustrating example of how this can provide detailed information about chemical bonding is offered by an XES study of an adsorbate system, N_2 molecules adsorbed on a Ni(111) surface [20]. Since the molecule is adsorbed perpendicular to the surface the two nitrogen atoms of the molecule experience different chemical surrounding, leading to different X-ray absorption cross section distributions. This is seen as a shift in the X-ray absorption edge energy. By tuning the exciting radiation to one or the other of these edges, one can excite X-ray emission pertaining to one or the other nitrogen atoms. The respective spectra then reflect local components of atomic orbital contribution to the molecular orbitals. Furthermore, by using the angular distribution of dipole radiation a more detailed picture emerges. As σ -orbitals do not radiate along the molecular axis, while π -orbitals do, one can separate the π -orbital contribution in the spectra by recording the emission perpendicular to the surface. Knowing the π -contribution then allows the σ -orbital contribution to be established by recording emission parallel to the surface. Altogether, a detailed picture of the bonding can be obtained. For further study of soft X-ray emission spectra of chemical bonding of adsorbate systems, see e.g. [21].

The example above is a case of resonant excitation of X-ray emission used to obtain site selectivity. The process is often and intuitively seen as a two-step process where the first step is the X-ray absorption and the second step is the emission. The absorption step offers site selectivity, and the emission probes the local electronic structure at the particular site selected. It is important to note that in many cases resonant X-ray emission cannot be treated in terms of two consecutive, disconnected steps, but rather one has to regard the entire process as one scattering process where the excitation and emission steps are interlinked in an inelastic scattering process. This has a number of important consequences for X-ray emission as a spectroscopic tool, adding means of obtaining detailed information, which is presently being exploited for various applications.

3. RIXS spectroscopy

Resonant inelastic X-ray scattering, or RIXS, is a photon-in photon-out process where one can measure the change in energy and momentum of the scattered photon. The change in energy and

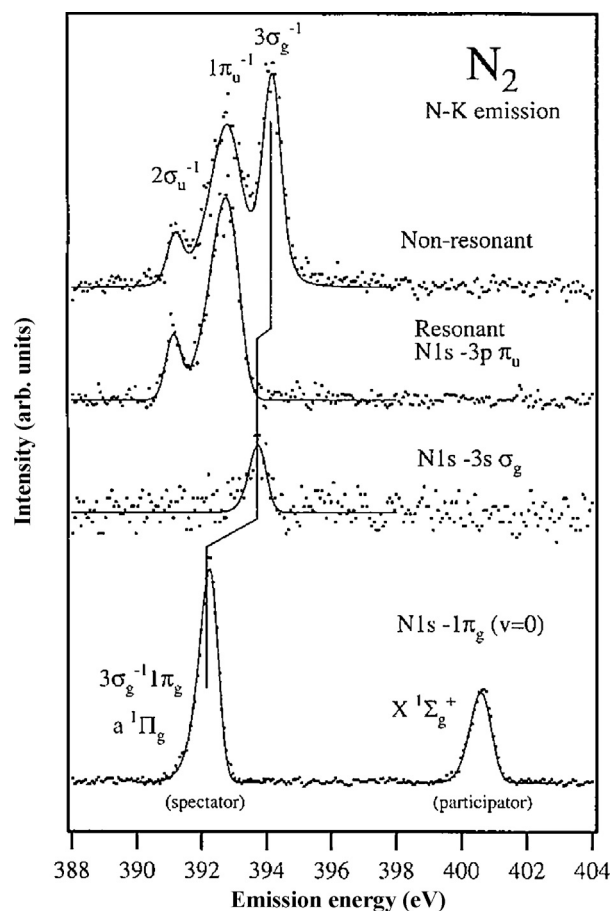


Fig. 2. NK RIXS spectra of gaseous N_2 , excited at different photon energies, corresponding to different orbital symmetries.

momentum is taken up by the material under study as intrinsic excitations such as electronic, magnetic or lattice excitations and this provides a means to study the material properties at the atomic scale. This means that the electronic excitations observed as energy loss features in RIXS spectra obey two-photon selection rules as opposed to visible and IR absorption spectra.

Molecules with inversion symmetry have served as a show-case for demonstrating the power of dipole selection rules, dictating that interaction with one photon must change the parity of the state. Often this selection rule is assumed to be valid also for individual orbitals. In Fig. 2 are shown NK emission spectra of free N_2 molecules, excited at different excitation energies, and the effect of the two-photon electric dipole selection rules come out in a distinct way [22]. The three outermost orbitals of the nitrogen molecule, $3\sigma_u$, $2\pi_u$, and $1\sigma_g$ all appear as final states in the NK emission spectrum excited in a non-resonant manner, i.e. without exciting a core electron to a state with defined inversion symmetry. When tuning the excitation to a *gerade* resonance, the emission spectrum only shows *gerade* molecular orbitals, whereas when excitation is made to *ungerade* states only *ungerade* final states appear. Thus, even in transitions involving core holes, which we tend to think of as localized at a specific atomic site, seemingly breaking the inversion symmetry, the parity selection rules appear to be strict.

Molecular RIXS spectroscopy greatly benefits from high energy resolution [23–26], giving deeper insights into the selectivity in the RIXS process. It turns out that one must be cautious when applying the parity selection rule to individual orbitals. For the oxygen molecule it is found that the core hole and the excited electron may swap parity during the process. In contrast to the common

Download English Version:

<https://daneshyari.com/en/article/5396147>

Download Persian Version:

<https://daneshyari.com/article/5396147>

[Daneshyari.com](https://daneshyari.com)