Chemical Physics 493 (2017) 49–55

Contents lists available at ScienceDirect

Chemical Physics

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

Electronic structure of Fe, α-Fe_2O_3 and $Fe(NO_3)_3 \times 9\ H_2O$ determined using RXES

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ARTICLE INFO

Article history:
Received 16 January 2017
In final form 10 June 2017
Available online 17 June 2017

Keywords:
RXES
Iron
X-ray spectroscopy
FEFF
Density of states

ABSTRACT

Resonant X-ray emission spectroscopy (RXES) technique was applied to probe electronic states of three Fe compounds: Fe, α-Fe_2O_3 (hematite) and $Fe(NO_3)_3 \times 9\ H_2O$ (ferric nitrate) around Fe K-absorption edge with simultaneous detection of Kβ and valence-to-core transitions. We show that deep insights on the valence and conduction band position, such as main orbital contribution to band-gap formation and ligand orbital contributions, can be retrieved from RXES data. Moreover applicability of Kβ and valence-to-core RXES measurements to extract band gap energies is demonstrated. Obtained results were supplemented with *ab initio* calculations allowing precise determination of orbital contributions to the measured spectral features. Good agreement with experimental results has shown that proposed approach is promising tool in further applications.

1. Introduction

Iron is the most abundant element in environment from 4th group of elements' periodic table [1]. It occurs mainly in forms of insoluble oxides and it is present in form of natural compounds as well as in many pollutants [2]. Iron is also crucial microelement for life. However, many iron compounds involved in cell cycles are also sources of free radicals in ascorbate anions oxygenation reaction by Fe(III) ions [3]. One of the well-known harmful reactions in biological systems is the Fenton reaction [4]. Fe(II) ions decompose hydrogen peroxide which naturally occurs inside cells and produce hydroxyl radicals. Subsequently the radicals damage cellular structures around, since they are one of the most active so called Reactive Oxygen Species (ROS). Many metalloenzymes important from industrial, healthcare or medical point of view are provided with catalytic active sites based on iron atoms. Among many examples of such proteins one can mention Fe-Only Hydrogenase [4] or catalase [5]. Enzymes are extremely powerful catalysts in very complicated chemical reactions therefore revealing electronic properties of their active sites as well as their local geometry is essential to understand the mechanism of enzymatic reactions. Moreover there is also need of revealing any existing intermediate states in enzymatic reactions. Many techniques has been applied including XRD [6] or Mossbauer spectroscopy [7] with good quality results on Fe containing enzymes, however each of mentioned techniques were focused either on structure, local spin state or oxidation state.

Oxide forms of iron are represented by rhombohedral hematite α-Fe_2O_3, γ-Fe_2O_3 which has cubic structure and magnetite Fe_3O_4 $Fe^{(III)}[Fe^{(II)}Fe^{(III)}]O_4$ with spinel cubic inversed structure [8]. Iron oxides have been studied using multiple techniques, including X-ray methods like XAS [9], XES [10], or even RIXS (Resonant Inelastic X-ray Scattering) [11]. From electronic point of view, pure iron is a conductor whereas iron oxides are considered to be semiconductors. Band gap between valence and conduction bands for hematite was estimated to be 2.2 eV [12] however either in case of doping or different sizes and shapes of α-Fe_2O_3 structures it can be significantly altered [13–16]. This properties of iron(III) oxide form was recently used to develop new type of water oxidizing system based on α-Fe_2O_3 thin film as photoanode with >40% of efficiency [17].

X-ray spectroscopies are well-established methods used to investigate electronic structures of aforementioned systems. XAS was already widely used in iron K-edges studies applied to iron oxides and proteins. This included the application of XANES (X-ray Absorption Near Edge Spectroscopy) pre-edge analysis of iron (III) oxide [18] in order to get information about local symmetry changes, as well as edge shift examination in purpose of studying changes in iron oxidation state [19]. On the other hand more information can be provided by application of Extended X-ray Absorption Fine Structure spectroscopy (EXAFS). Using this technique one can obtain data about structure, local symmetry and nearest

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http://dx.doi.org/10.1016/j.chemphys.2017.06.002

neighbours [20]. EXAFS however, is unable to distinguish between scattering signal from light atoms such as C, N and O, which appears to be almost identical. This problem weakens EXAFS utility in metalloprotein catalytic active sites study. Yet EXAFS could be used as a valuable supporting technique in protein active site structure study as it was in case of nitrogenase [21]. The non-resonant X-ray Emission Spectroscopy experiments have been done on α-Fe_2O_3 to study spin state of hematite [22] as well as on more complicated complexes and organocomplexes of ferrous and ferric compounds [10,23]. It was shown that XES spectroscopy is able to distinguish, unlike EXAFS, nearest neighbours also in case of low mass atoms like C, N and O and as well as spin state of studied system [24]. Valence-to-core region, the highest energy-range part of XES spectrum, showed high sensitivity both to ligand type and local geometry [22–24].

Due to the existence of high flux and brilliance light sources emerging nowadays and development of new X-ray spectrometers [25–29], the resonant X-ray emission spectroscopy (RXES) can be employed as complementary tool to obtain comprehensive electronic information about sample. This method provides full electronic information about the element of interest because of simultaneously recording XES and XAS spectra and thus occupied and unoccupied electronic states of scattering atom [25]. For example, recently these type of measurements were successfully applied to the studies of mechanism of action of platinum-based antitumor compounds [26]. RXES is a coherent process: X-ray photon absorption and core-hole creation as well as following decay transitions are occurring quasi-simultaneously in the sub-femtosecond time range [25]. Subsequently, lifetime broadening of detected electronic states is reduced which allows to access electronic details that are unavailable in classical XAS and XES experiments.

Three iron compounds with different electronic properties: conducting, semi-conducting and insulating were studied. The differences in Kβ XES mainline and in valence-to-core region were identified. The observed spectral differences are related to different electronic structure and properties of samples. Spectra features were identified with support of *ab initio* calculations based on FMS (Full Multiple Scattering) approach [27]. Theoretical XAS and XES spectra as well as density of states were calculated and compared with experimental data allowing for identification of both orbital contributions and electronic band-gaps. Obtained results have not only validated selected set of parameters and structures but also pointed out that this approach may be extended over standard solid state physics approach to more interdisciplinary and biophysical aspects.

2. Materials and methods

2.1. Sample preparation

Powders of hematite α-Fe_2O_3 and iron (III) nitrate (V) nonahydrate (both from Sigma-Aldrich) were pressed into pellets of approximately 2 mm thick. Iron foil of 0.5 mm thick was used as reference material and for calibration.

2.2. RXES measurements

RXES data were recorded at the Swiss Light Source in Paul Scherrer Institut, Villigen Switzerland at SuperXAS (X10DA) beamline operating on superbending magnet. Photon flux on the sample was approximately 1×10^{12} *ph/s*. Beam was collimated by bent mirror and focused by toroidal mirror, both coated with Rh and Pt. Energy selection was performed using a Si(111) double crystal monochromator. Data were acquired using dispersive von Hamos geometry X-ray spectrometer with 2D PILATUS X-ray detector with 1D array segmented-type focusing crystal. The spectrometer geometry is described elsewhere [28]. Incident energy range was set from 7100 eV to 7150 eV with 1 eV step size. Emission spectra were acquired in the range from 6800 eV to 7160 eV, however final results were crop to emission energy range of 6.97–7.12 keV since rest of range was background. Energy resolution of each measurement was estimated from full width at half maximum (FWHM) of Gaussian function fitted to the elastic peak. We found the total energy resolution to be 1.5(5) eV for the measured samples, where 1.1(1) eV is contribution from X-ray emission spectrometer and 1.0 (5) eV corresponds to incidence beam width given by Si(111) monochromator. The estimated total 0.5 eV error results from both error contributions.

2.3. Methodology of data analysis

XAS probes unoccupied valence bands above Fermi level of an atom. Through the process of X-ray photon absorption the core electron is being promoted above Fermi energy level. Then, this intermediate excited state of an atom decays by electronic transition involving electron from upper core level or valence shell with simultaneous emission of fluorescence X-ray photon. Because of dipole selection rules involved in the absorption transitions, the K-edge XAS signal is proportional to p-projected density of unoccupied states (DOS). Therefore XAS allows to access information about oxidation state, coordination environment and valence band structure. On the contrary, the K-edge XES probes occupied valence states of an atom. One can gather information about electronic structure of an atom, spin states and contributions to valence-to-core region originating from ligands, pronounced as Kβ'' lines [26,29].

RXES is based on X-ray-in X-ray-out experiment that simultaneously acquires both XAS and XES data. As an example, in Fig. 1 we plot RXES plane of bulk α-Fe_2O_3 (hematite) recorded around Fe K-edge and with detection of Kβ and valence-to-core X-ray emission signals. In general, depending on excitation energy, three regions in RXES plane may be distinguished: off-resonant, resonant and non-resonant. These are schematically marked in Fig. 1a. The off-resonant regime is located for incidence X-ray energy set far below the absorption threshold. At such excitation energies the XES spectrum shows asymmetric shape with an intensity cut-off on high-energy side (Fig. 1c). As reported, the shape of high energy resolution off-resonant spectra (HEROS) is being equivalent to XAS signals. Moreover, HEROS spectra exhibit more detailed structure being independent on core-hole broadening and self-absorption effects [30,31]. However, as may be noticed from RXES plane, the off-resonant regime is characterized by low transition yields that limits the HEROS application to concentrated samples. For incidence X-ray energy tuned close to absorption edge, the weak pre-edge resonances and following rising edge features are detected. In this resonant regime, the density of unoccupied states determines the XES shape and intensity. The resonant excitations in 3d metals may be of both, dipole and quadrupole character and are very sensitive to chemical environment of scattering atom [32]. As the incidence X-ray energy increases, the shape of XES spectrum becomes constant and only total area intensity is modulated by absorption coefficient of the sample. This non-resonant regime is used for determination of occupied electronic states based on measured XES signals. Fig. 1d shows the non-resonant XES spectrum in which two distinctive regimes are observed: the core-to-core Kβ emission (3p->1 s transition) and weak satellite lines on lower energy side (transitions from valence orbitals to 1 s core-hole) [33]. The valence-to-core transitions involve outmost electronic orbitals and provide deep insight knowledge on