

# Resonant Inelastic X-ray Scattering (RIXS) by Using a Crystal Analyzer at the K Pre-edge of Transition Metal Complexes

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## Introduction

The electronic states that form an absorption spectrum are resonantly excited states that subsequently decay. The released energy can either be carried by an electron that is excited into the continuum (resonant Auger effect) or be carried by a photon (resonant x-ray scattering or RXS). A review of the resonant Auger effect was published by Armen [1]. A large body of work on RXS that already exists was reviewed comprehensively by Gel'mukhanov and Ågren as well as Kotani and Shin [2]. In this report, we focus on resonant inelastic x-ray scattering (RIXS) at the transition metal K absorption pre-edges, where only a few studies have been done until now.

## Methods and Materials

After resonant excitation of a 1s electron, the subsequent decay having the highest probability is a radiative 2p-to-1s ( $K\alpha$ ) transition. The 3p-to-1s ( $K\beta$ ) transitions are weaker by a factor of about 8. An expression for the RIXS spectrum  $F(\Omega, \omega)$ , where  $\Omega$  and  $\omega$  are the incident and emitted photon energy, respectively, can be derived from the differential cross section that describes the inelastic x-ray scattering process [2]. It is given by:

$$F(\Omega, \omega) = \sum_f \left| \sum_i \frac{\langle f | T_2 | i \rangle \langle i | T_1 | g \rangle}{E_g - E_i + \Omega - i\Gamma_K} \right|^2 \quad (1)$$

$$\times \frac{\Gamma_L / \pi}{(E_g - E_f + \Omega - \omega)^2 + \Gamma_L^2}$$

The intermediate state  $|i\rangle$  is reached from the ground state  $|g\rangle$  via a transition operator  $T_1$ . In a simplified picture using the atomic configuration, we can write  $|g\rangle = 3d^n$  and  $|i\rangle = 1s3d^{n+1}$ ; that is, a 1s electron is resonantly excited into a 3d orbital (Fig. 1). The intermediate states  $|i\rangle$  in RIXS spectroscopy are the final states in conventional absorption spectroscopy. The spherical ( $SO_3$ ) symmetry of the atomic 3d orbitals branches to the lower symmetry at the metal site.  $T_1$  identifies with the quadrupole transition operator if the

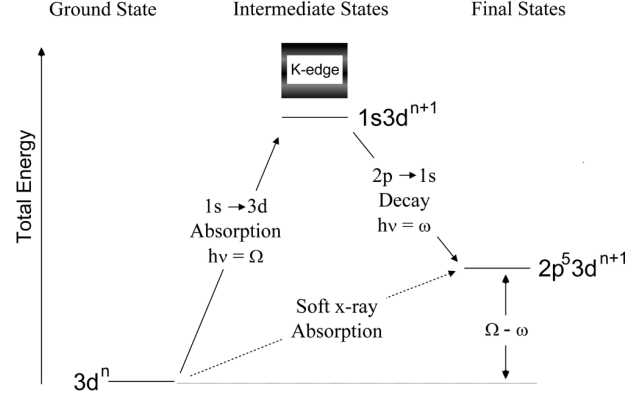


FIG. 1. Energy scheme for 1s2p RIXS in a transition metal ion. The vertical axis indicates the total energy of the electron configuration. For simplicity, atomic configurations are used, and only 1s-to-3d excitations are shown.

scattering atom is in centrosymmetric coordination (e.g.,  $O_h$  symmetry). The final states are reached via a 2p- or 3p-to-1s dipole transition. The electron configurations of the RIXS final states are identical to the soft x-ray L-edge ( $2p^5 3d^{n+1}$ ) and M-edge ( $3p^5 3d^{n+1}$ ) absorption final states.

The incident energy  $\Omega$  as well as the emitted energy  $\omega$  are varied in a RIXS experiment. The recorded intensity is proportional to  $F(\Omega, \omega)$  and is thus plotted versus a 2-D grid. The overall spectra are best displayed in contour plots. In order to assign the total energy of an electronic state to the axes of the contour plots, we use the energy transfer or final state energy  $\Omega - \omega$  as opposed to the emitted energy  $\omega$  (Fig. 1). The energy transfer axis relates to the excitation energy in L-edge and M-edge absorption spectroscopy. The lifetime broadenings  $\Gamma_K$  for the intermediate states and  $\Gamma_f$  ( $f = L, M$ ) for the final states then apply in the  $\Omega$  and  $\Omega - \omega$  direction, respectively. Scans with constant emission energy (CEE) represent diagonal cuts through the  $(\Omega, \Omega - \omega)$  RIXS plane. They are usually plotted versus the incident energy axis and then exhibit a line-sharpening effect when compared to an absorption scan [3, 4].

The spectra were recorded at Bio-CAT beamline

18-ID at the APS. The total incident flux in the first harmonic of the undulator radiation was on the order of  $10^{12}$  to  $10^{13}$  photons/second, depending on the incident energy monochromator crystal. For incident energies below 8 keV, a cryogenically cooled Si(111) double-crystal monochromator was employed. Above 8 keV (Ni K-edge), the Si(400) Bragg reflection was used. The fluorescence spectrometer features up to eight analyzer crystals [5]. The following Bragg reflections were used: Ge(331) for V K $\alpha$ , Ge(333) for Mn K $\alpha$ , Ge(620) for Fe K $\beta$ , and Si(620) for Ni K $\alpha$ . The total data acquisition time needed to record one RIXS plane was 2-4 hours. Careful radiation damage studies were performed for each sample. Radiation-sensitive samples were measured in a He-flow cryostat in an exchange gas surrounding. The RIXS plane was constructed by recording CEE scans (2-30 seconds each in “on-the-fly” mode) for different emission energies. The beam position on the sample was changed with every scan, and the spectra were corrected for variations in sample concentrations.

## Results

The 1s3p RIXS planes in Fe(II) ( $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$ ) and Fe(III) ( $\text{Fe}_2\text{O}_3$ ) in octahedral geometry show the pre-edge shift with oxidation state (Fig. 2). This is well-documented in the literature [6, 7]. The crystal field splitting separates the two peaks for Fe(III) in  $\text{Fe}_2\text{O}_3$  with  ${}^5\text{T}_{2g}$  and  ${}^5\text{E}_g$  symmetry. A theoretical analysis of the multiplet structure yields three 1s-to-3d resonances for Fe(II) in  $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$  with  ${}^4\text{T}_1$ ,  ${}^4\text{T}_2$  and  ${}^4\text{T}_1$  terms [8]. A pronounced asymmetry relative to the diagonal toward larger energy transfer can be observed for the  $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$  complex. This indicates strong (3p,3d) final state interactions. The RIXS spectra indicate that the center resonance with  ${}^4\text{T}_2$  symmetry exhibits the strong final state interactions.

For a detailed analysis of the pre-edge features, it is necessary to subtract the background due to the K main edge. We developed a procedure that fits horizontal cuts through the RIXS plane at constant energy transfer to Voigt line profiles [9]. The fit yields a background plane

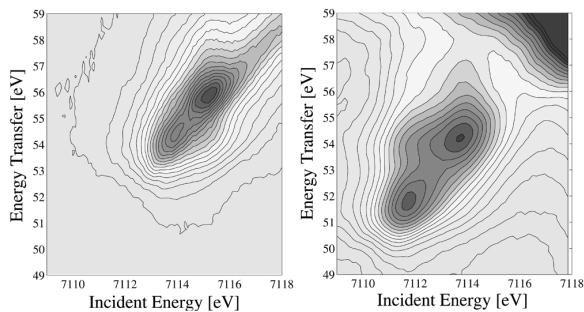


FIG. 2. 1s3p RIXS planes of  $\text{Fe}_2\text{O}_3$  (left) and  $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$  (right).

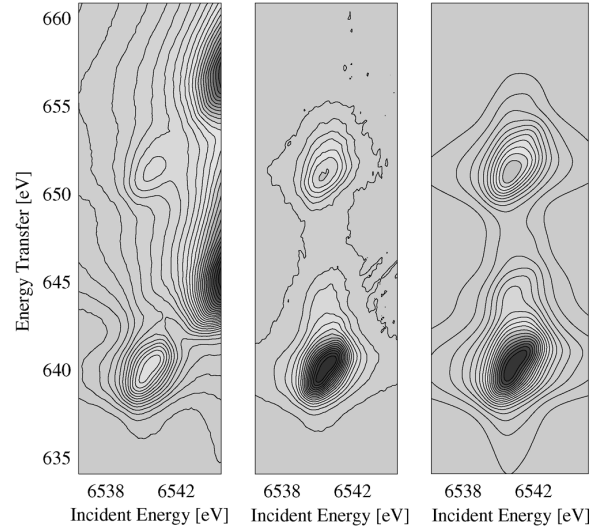


FIG. 3. 1s2p RIXS plane of MnO before (left) and after (center) subtraction of the K main edge together with ligand field multiplet calculations ( $10 Dq = 1.1$  eV). The applied lifetime broadenings are  $\Gamma_K = 1.1$  eV and  $\Gamma_L = 0.5$  eV for the intermediate and final state, respectively, as well as 1.0 eV and 0.8 eV for the instrumental lifetime broadenings of the incident and the emitted x-rays. The features at 640 and 652 eV are the  $2p_{3/2}$  and  $2p_{1/2}$  final states, respectively.

that can be subtracted from the experimental RIXS plane. An example is shown for MnO in Fig. 3, where ligand field multiplet calculations that reproduce the experimental spectral shape after edge subtraction are also shown. The MnO 1s $2p_{3/2}$  RIXS spectra can be fitted to two 1s resonances that are separated by the crystal field splitting similar to  $\text{Fe}_2\text{O}_3$ . This is consistent with 1s-to-3d ligand field multiplet calculations for high-spin Mn(II) in  $\text{O}_h$  symmetry, and it thus indicates that quadrupole transitions contribute to the pre-edge intensity. The  $2p_{3/2}$  final states exhibit a shoulder on the high-energy-transfer side that also appears in soft x-ray L-edge spectroscopy for high-spin Mn(II) compounds.

The K pre-edge of  $\text{VF}_4$  presents a nice example for showing the interplay between crystal field and multiplet splittings. Both splittings have approximately the same magnitude and result in four almost equally separated pre-edge structures (Fig. 4) [10]. The two strong resonances at high incident energies appear to be further split. This could be indicative of the Jahn-Teller splitting in the  $t_{2g}$  orbitals.

## Discussion

RIXS spectroscopy enables the K pre-edge to be separated from the main edge with a considerably higher degree of accuracy than does conventional absorption spectroscopy. This allows for a more

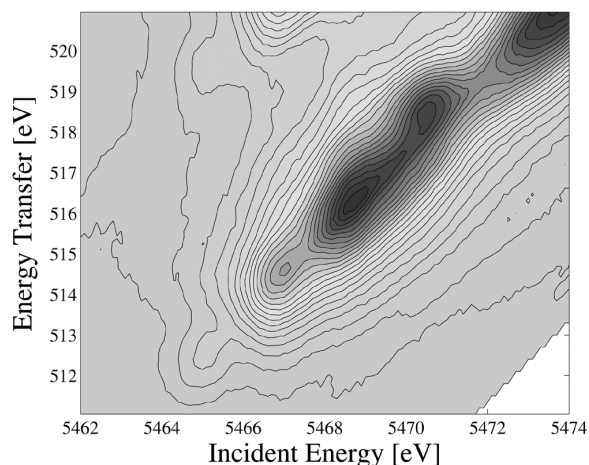


FIG. 4.  $2p_{3/2}$  final states in the  $1s2p$  RIXS plane of  $VF_4$ .

detailed analysis of the spectral features. Quadrupole  $1s$ - $3d$  transitions are important in six-coordinated transition metal complexes. The energy transfer spectra contain information on the electronic structure that is complementary to the  $K$  pre-edge data. The structures are revealed after subtraction of the main edge and give insight into the spin state of the metal center. The pre-edge spectral features cannot be understood without including multiplet splittings in a theoretical analysis.

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