Theoretical Simulation of Resonant Inelastic X-Ray scattering in Transition Metal Oxides

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Introduction

Resonant inelastic x-ray scattering (RIXS) belongs to a family of experimental techniques known as spectroscopy which are useful for studying valence electron states (VES).

RIXS is a second-order optical process, where first a core electron is excited by an incident x-ray photon. This is known as **x-ray absorption spectroscopy** (XAS).
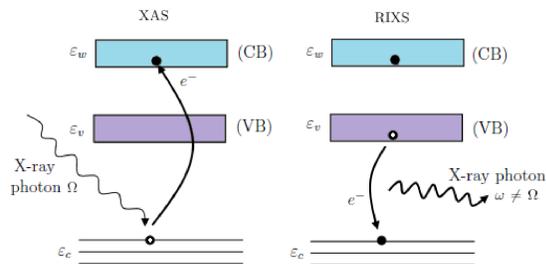
This is followed by the excited state decaying by emitting an x-ray photon to fill the core hole.

This project aims to simulate XAS and RIX spectra for TiO_2 with and without defects. Understanding the properties of defects in TiO_2 may hold the key for advancing in certain technologies.

Theory

In TiO_2 XAS, a 2p core hole is created. Thus, the final state contains a partly filled core state ($2p^5$) and a partly filled valence state ($3d^1$).

$$2p^6\,3d^0 \longrightarrow 2p^5\,3d^1$$

A strong overlap between the 2p-hole and 3d-hole radial wave functions split the XAS final states. These final states created through splitting are known as atomic multiplets.

For simulations in this project, atomic multiplets were calculated first using a quantum mechanical description, where only the interactions within the absorbing atom are considered.

Crystal field parameters 10Dq, Ds, and Dt are then incorporated to describe the breaking of degeneracy's of electronic orbital states due to a static electric field produced by a surrounding charge distribution.

Two types of symmetries were imposed by the crystal field parameters. The first was octahedral symmetry (O_h) and the second was the more distorted tetragonal symmetry (D_{4h}).

O_h symmetry is cubic in shape, however, as can be seen in the unit cell of TiO_2, there is a stretching along the lattice vector indicated by the yellow line. D_{4h} symmetry allows one to describe this shape better.
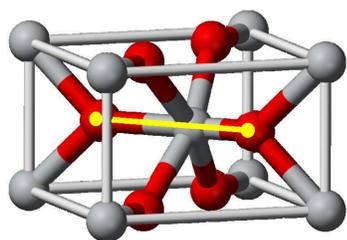
Finally, charge transfer effects, which describe the effects of charge fluctuations in the initial and final states are taken into consideration. This allows the use of more than one configuration so that ligand bonds can be accounted for [3]. Δ below is the charge transfer energy.
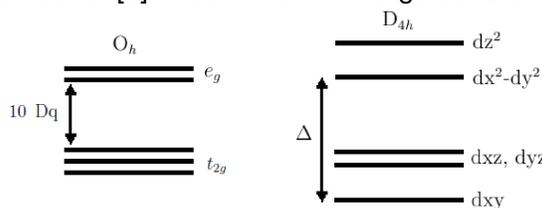
In the case of RIXS, the entire process can be considered as a set of atomic transitions from a ground state $|g\rangle$ to an intermediate state $|i\rangle$ to a final state $|f\rangle$ of energies E_g, E_i, and E_f respectively. The scattering cross section can then found by the Kramers-Heisenberg equation:

$$\sigma(\Omega, \omega) \propto \sum_j \left[\sum_i \frac{\langle j|T|i\rangle\langle i|T|g\rangle}{E_g + \Omega - E_i - i\Gamma_i} \right]^2 \times \delta(E_g + \Omega - E_j - \omega)$$

T represents the radiative transition and Γ_i is the broadening due to the intermediate state core-hole lifetime [1].

Method

Simulations were carried out using software called

CTM4XAS

which combined a number of programs to compute the different step required to simulate XAS and RIXS spectra.
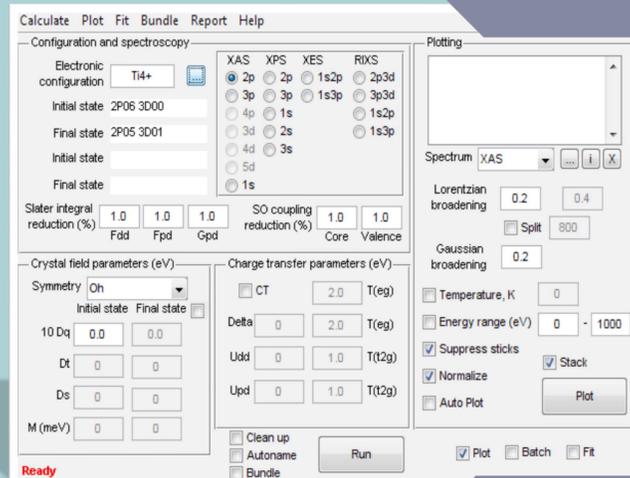
Results

Octahedral Symmetry:
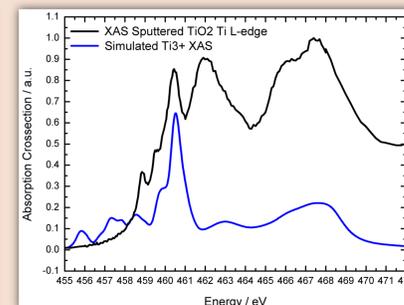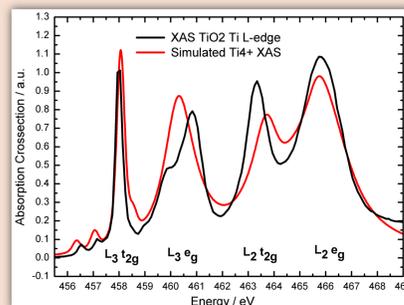
Tetragonal Symmetry:
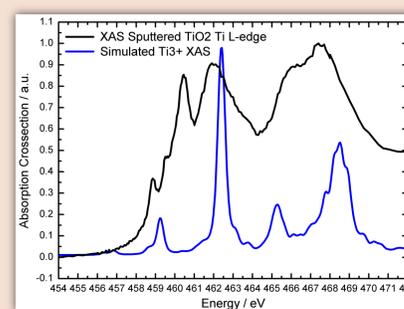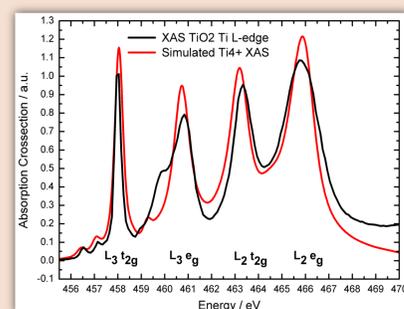
RIXS:
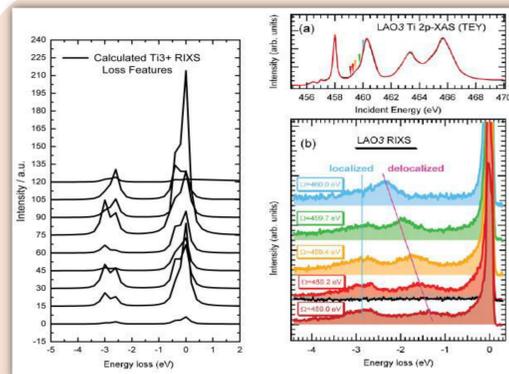
Each graph contains the theoretical spectra calculated using the CTM4XAS program compared against the equivalent experimental spectra that one is modelling [2].

Conclusions

As one can see, although simulated XAS spectra for Ti^{4+} compare well against experimental data, there appears to be little correlation between parameters used for Ti^{4+} and Ti^{3+}. Therefore, this is not an ideal approach to model sputtered TiO_2.

RIXS simulations were able to model experimental data to a certain degree, however, they could be improved upon by a using a lower symmetry crystal field such as C_{4v}.

Acknowledgements

Refrences:
[1] Akio Kotani and Shik Shin "Resonant Inelastic X-Ray Scattering Spectra for Electrons in Solids", Rev. Mod. Phys. 73, (2001), pp. 203-342.
[2] E. Stavitski and F.M.F. De Groot, "The CTM4XAS program for EELS and XAS spectral shape analysis of transition metal L-edges", Micron 41, (2010), pp. 687-694.