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The Electronic Structure of Mononuclear Manganese Compounds: Insights from Experimental and Theoretical X-ray Absorption Spectroscopy

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As one of the most abundant transition element in earth materials, manganese occurs in different oxidation states and among them, Mn(II), Mn(III), Mn(VI) are the most encountered redox states involved in biochemical process such as photosynthesis. It is a challenging issue to determine the reaction mechanism where the valence of manganese is not straightforward to evaluate with chemistry alone. X-ray absorption spectroscopy (XAS) is an element-specific spectroscopic method that can reflect the electronic structure information of the element. After the absorption of an X-ray photon, a core electron is excited to empty or partially filled orbital which is just below the ionisation threshold, giving an absorption edge. This unique energy provides fingerprint information about the oxidation state, site symmetry, spin state, and crystal field splitting of the targeting materials.

High-Energy Resolution Fluorescence Detected (HERFD) XAS spectra of nine Mn compounds were collected on the ID26 beamline of the ESRF at the temperature of 10 K. In this technique, the emitted energy is tuned to a fluorescence line and the incident energy is scanned through Mn K-edge (6535–6546 eV). The samples present a range of manganese symmetry environments (Oh - octahedral, D4h - distorted octahedral C3v - trigonal bipyramidal), and valences (II, III, and IV). The acquired experimental data was processed using Python codes. The pre-edge features of the XAS are shifted towards higher energy with higher oxidation states, and gain intensity in complexes of lower symmetry.

Theoretical simulations using the *Quanty* package were conducted to obtain deeper insight of pre-edge features. In this work the Hamiltonian included the Coulomb repulsion, spin-orbit coupling, crystal field splitting, and metal 3d ligand orbital hybridization. For compounds having lower symmetry the calculations were done by considering also the hybridization of the 3d and 4p metal orbitals to study the intensity enhancement observed experimentally. Compared with symmetries that present a center of inversion such as Oh, where only the 1s to 3d quadrupole transitions are allowed, in non-centrosymmetric structures the mixing of 4p character gives rise to an enhancement of the pre-edge intensity thanks to the contribution from 1s to 4p dipole transitions.

Resonant Inelastic X-ray Scattering (RIXS) spectra were also measured for these compounds. The resonance occurs when the incident energy is tuned close to an absorption edge, resulting in an energy transfer reduced to a few eV. By interpreting in terms of a second energy transfer axis, one can find new spectral features and this opens up possibilities for more detailed studies of the electronic structure. Data processing and simulations for RIXS measurements will be done in order to reveal more detailed information about electronic configuration concerned in Mn compounds. It would also be interesting to conduct an ab initio calculation by *ORCA* package to compare with the results obtained by *Quanty*.

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