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Research paper

Quantifying covalent interactions with resonant inelastic soft X-ray scattering: Case study of Ni^{2+} aqua complex

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ABSTRACT

We analyze the effects of covalent interactions in Ni 2p3d resonant inelastic X-ray scattering (RIXS) spectra from aqueous Ni^{2+} ions and find that the relative RIXS intensities of ligand-to-metal charge-transfer final states with respect to the ligand-field final states reflect the covalent mixing between Ni 3d and water orbitals. Specifically, the experimental intensity ratio at the Ni L_3-edge allows to determine that the Ni 3d orbitals have on average 5.5% of water character. We propose that 2p3d RIXS at the Ni L_3-edge can be utilized to quantify covalency in Ni complexes without the use of external references or simulations.

1. Introduction

Covalency, understood as the sharing of electrons between atomic centers [1], is a fundamental concept that is essential for understanding and predicting basic chemical properties ranging from molecular structures to reactivity and biological function. However, direct experimental determination of covalency, i.e. contributions of atomic orbitals from different atomic centers to a molecular orbital (MO), is a generally a difficult task. Here we demonstrate how resonant inelastic X-ray scattering (RIXS) at a 3d transition metal L-edge can be employed to experimentally derive quantitative information on covalent interactions by revealing the atomic compositions of the chemically relevant frontier orbitals. We test our concept by deriving the covalent contributions to the solute-solvent interactions of Ni^{2+} ions in aqueous solution. The interactions of Ni^{2+} with the solvent water molecules can be well described by considering the first solvation shell only [2] with octahedral arrangement of the water ligands. The highly polar coordinative bonding between Ni and the water ligands in the resulting prototypical Werner-type $[Ni(H_2O)_6]^{2+}$ complex is characterized by weak covalent interactions of the ligand-to-metal charge-transfer type ideally serving for a case study [3–5].

Recently, triggered by the development of soft X-ray techniques on liquids and solutions, a number of X-ray absorption spectroscopy (XAS), photoelectron and Auger electron spectroscopy studies have addressed 3d-transition-metal ions in water [2,6–12]. Given the intrinsic sensitivity to local charge distributions, these studies emphasized the covalent effects in metal-solute bonding. This sensitivity of X-ray spectroscopy methods to ligand environment is frequently utilized not only by soft X-ray, but also by hard X-ray techniques [13–18]. However, quantitative determination of the orbital specific covalent contributions is in practice often beyond the experimental capabilities. Particularly investigations at the transition metal absorption edges require typically elaborate electronic structure calculations and spectral simulations in order to disentangle the inter-atomic covalent effects from intra-atomic and core-hole relaxation effects [8,19–24], although significant advancements with regard to density functional and wavefunction based computational methods have been made in recent years [25–29].

In contrast to sophisticated computational methods, a relatively simple method to derive quantitative information about the

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metal-ligand covalency from more experimental grounds has been developed by Solomon and co-workers [30]. They derived a formula based on the molecular orbital theory to describe the intensity of ligand K-edge XAS pre-edge feature:

$$I_{XAS} \propto \alpha^2 n_h (1-k)^2 |\langle \phi_{L1s}|\hat{D}|\phi_{Lnp}\rangle|^2 \tag{1}$$

Here α^2 is metal-ligand covalency (defined as the ligand content in the MO corresponding to the pre-edge feature), n_h is number of holes in the respective MO manifold, k describes the contribution of the other ligand atoms to the MO and the last term is a square of the atomic transition dipole moment. The aim of this letter is to derive an analogues expression for metal 2p3d RIXS in order to fully exploit the information content embedded in the RIXS spectral intensities.

In our previous experimental work we analyzed in detail the metal-centered ligand-field (LF) RIXS final states at the Ni L_3 and L_2 edge [31]. Crystal field multiplet (CFM) and restricted active space self-consistent field (RASSCF) calculations presented there did not include ligand-to-metal charge-transfer (LMCT) final states due to computational limitations. In contrast, the present theoretical study concentrates on the LMCT peaks. Our objective is to relate the relative RIXS intensity of LF and LMCT peak to the degree of covalency of the Ni^{2+}-water bond, apply it to the experimental spectrum from Ref. [31] and carry out additional charge transfer multiplet (CTM) calculations which include both LF and LMCT final states.

2. Theory

RIXS spectra were simulated by multiplying absorption and emission transition moments (two-step approximation) as retrieved from the CTM calculations [32–34]. Exact diagonalization was utilized to calculate the valence- and core-excited states [35]. The following convolution scheme was applied (values for the FWHM are given): 0.35 eV Gaussian broadening taking into account the monochromator bandwidth, 0.5 eV (1.0 eV) Lorentzian lifetime broadening at the L_3 (L_2) edge for core-excited states, and 1.2 eV Gaussian broadening of RIXS spectra to account for the spectrometer resolution. An additional 0.5 eV Gaussian broadening of both X-ray absorption and RIXS spectra was used to account for inhomogeneous broadening. Polarization effects were not included in the simulation of the RIXS spectra (in Ref. [31] we found these are small in horizontal polarization).

3. Results and discussion

Water $3a_1(a_{1g} + e_g + t_{1u})$ orbitals are involved in σ-bonding with the Ni $3d(e_g)$, $4s(a_{1g})$ and $4p(t_{1u})$ orbitals whereas water $1b_1(t_{2g} + t_{2u})$ and Ni $3d(t_{2g})$ orbitals exhibit π-interactions in $[Ni(H_2O)_6]^{2+}$ [4,5]. The leading covalent contribution has been identified as the mixing between Ni 3d and the water $3a_1$ and $1b_1$ orbitals [5,36]. The most relevant MOs for the present investigation are the bonding (e_g,t_{2g}) nominal ligand and antibonding (e_g^*,t_{2g}^*) nominal Ni MOs as displayed in Fig. 1(a).

The principle of utilizing L-edge RIXS for probing covalency in 3d transition-metal complexes is illustrated in Fig. 1(b) and (c). Resonant excitation to unoccupied nominal Ni 3d MOs at the Ni L-edge is followed by scattering to the LF final states of the $(e_g^*, t_{2g}^*)^8$ configuration or by scattering to the LMCT final states of the $(e_g,t_{2g})^9(e_g^*,t_{2g}^*)^9$ configuration (Fig. 1(b)) [31].

In first approximation the intensities of the LF and LMCT RIXS peaks reflect the Ni 3d composition of the (e_g^*,t_{2g}^*) and (e_g,t_{2g}) MOs, respectively (Fig. 1(c)). Because these MOs are the antibonding and bonding combinations of Ni 3d and water $3a_1$ and $1b_1$ orbitals resulting from the corresponding covalent orbital mixings, the relative intensities of LF and LMCT RIXS peaks can be expected to correlate with the magnitude of these mixings, i.e. the covalency in the complex.

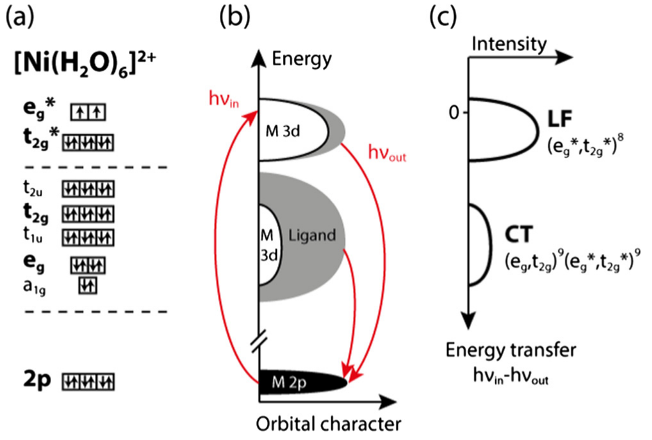

Fig. 1. (a) Schematic molecular orbital (MO) diagram for the hexaaqua $[Ni(H_2O)_6]^{2+}$ complex. Bold letters are used for the orbitals relevant for the present investigation. e_g/e_g^* and t_{2g}/t_{2g}^* MOs form two sets of bonding/antibonding orbitals, governing the covalent interaction. (b) Schematic depiction of the resonant inelastic X-ray scattering (RIXS) process in a transition-metal complex. The metal 3d and ligand characters of the MOs are shown in white and grey, respectively. For $[Ni(H_2O)_6]^{2+}$ these are Ni 3d and water $3a_1/1b_1$ characters in the nominal metal e_g^* and t_{2g}^* and nominal ligand e_g and t_{2g} MOs. $h\nu_{in}$ and $h\nu_{out}$ denote the incident and the emitted photon energies. (c) Schematic RIXS spectrum with RIXS intensities versus energy transfer. The peak denoted LF corresponds to RIXS final states assigned to valence-excited ligand-field states [states of the $(e_g^*,t_{2g}^*)^8$ configuration for $Ni^{2+}(aq)$] and the peak denoted CT corresponds to RIXS final states assigned to ligand-to-metal charge-transfer states [$(e_g,t_{2g})^9(e_g^*,t_{2g}^*)^9$ configuration for $Ni^{2+}(aq)$]. The intensities of LF and CT peaks reflect the metal 3d (Ni 3d) character of the MOs [(e_g^*,t_{2g}^*) and (e_g,t_{2g})].

The qualitative considerations outlined above are scrutinized as follows. Within the framework of LCAO-MO theory the covalent bonding between atoms is described in terms of mixing of atomic orbitals at different atomic sites. In case of metal-centered complexes such as $[Ni(H_2O)_6]^{2+}$ we can describe the bonding between the metal and the ligands as a mixing of the symmetry adapted metal orbitals with ligand group orbitals (LGO) formed by a symmetry adapted mixing of the equivalent ligand orbitals. Mixing of one metal orbital with one LGO results in a pair of bonding and antibonding MOs:

$$\psi = \alpha\phi_M + \sqrt{1-\alpha^2}\phi_L$$

$$\psi^* = \sqrt{1-\alpha^2}\phi_M - \alpha\phi_L$$

where ψ is a bonding and ψ^* an antibonding MO, ϕ_M is an atomic metal orbital and ϕ_L is a LGO. The parameter α^2 describes the magnitude of mixing between the metal orbital and the LGO and can be interpreted as the relative contribution of ligand orbitals to the antibonding MO (or the relative amount of metal orbitals in the bonding MO). We have followed here the same definition of covalency as used by Solomon et al. [19,30].

Within approximations detailed below (most importantly the one-electron and the frozen-orbital approximations), the dipole transition matrix elements involving decay from the ψ and ψ^* MOs to an atomic metal 2p core orbital ϕ_{M2p} can be written as:

$$\begin{aligned} |\langle\psi|\hat{D}|\phi_{M2p}\rangle|^2 &= \alpha^2|\langle\phi_{M3d}|\hat{D}|\phi_{M2p}\rangle|^2 \\ |\langle\psi^*|\hat{D}|\phi_{M2p}\rangle|^2 &= (1-\alpha^2)|\langle\phi_{M3d}|\hat{D}|\phi_{M2p}\rangle|^2 \end{aligned} \tag{2}$$

where ϕ_{M3d} is a metal 3d orbital, ϕ_{M2p} is a metal 2p core orbital and D is the dipole transition operator. The above equations indicate that the transition probabilities are proportional to the 3d character