Review Article

1s2p RIXS Calculations for 3d Transition Metal Ions in Octahedral Symmetry

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We present a series of 1s2p resonant inelastic X-ray scattering (RIXS) calculations for 3d transition metal ions in octahedral symmetry covering each ground state between $3d^0$ and $3d^9$. The calculations are performed in octahedral (O_h) symmetry using the crystal field multiplet theory. We discuss the crystal field effects and the selection rules with respect to the 1s2p RIXS pre-edge and compare their final state energies with the corresponding 2p X-ray absorption spectrum (XAS). The calculations provide a detailed understanding of 1s2p RIXS and serve as a basis for the future analysis of experimental spectra and also as a starting point for calculations that add additional channels including the nonlocal peaks.

1. Introduction

Throughout the past decades, X-ray *absorption spectroscopy* (XAS) as well as X-ray *emission spectroscopy* (XES) has played an important role towards the study of the electronic structure of transition metal complexes. The advent of synchrotron light sources has made high flux and high-resolution measurements accessible to researchers worldwide. Especially, the second order *resonant inelastic* X-ray *scattering* (RIXS) process, where the X-ray emission spectra are measured as a function of the incident X-ray energy, has proven to be a valuable instrument with respect to the investigation of the electronic structure. Such resonant measurements are nowadays routinely performed at the synchrotrons around the world.

Here, we will focus on 1s2p RIXS measurements at the K preedge of the 3d transition metals, where a 1s core electron is promoted into the 3d band (electric quadrupole 1s XAS) and the subsequent $K\alpha_{1,2}$ decays (electric dipole 2p XES) are observed, which yields a two-dimensional RIXS map. In the following, such spectra will be referred to as 1s2p RIXS. In 2p XAS on the other hand, an electron is promoted from

the 2p shell via a dipole transition into the 3d level. Both types of spectra, the two-dimensional 1s2p RIXS (1s XAS, 2p XES) and the one-dimensional 2p XAS, are illustrated in Figure 1.

We limit our discussion of 1s2p RIXS to the pre-edge excitonic states, and we will not discuss the 1s2p RIXS plane related to excitations at the main edge and at higher energies. The 1s2p RIXS plane related to excitations at the edge can be explained from a convolution of the 1s XAS spectral shape and the 1s2p nonresonant XES spectral shape [1, 2].

Most transition metal compounds show a pre-edge structure in K-edge absorption (1s XAS) which relates to the local and nonlocal electronic structure as well as the symmetry of the system under study. Usually, the shape of the pre-edge is associated with the quadrupole transitions from the 1s shell into the *local* 3d orbitals.

In the case of inversion symmetry, local 4p3d mixing is forbidden by symmetry, but a nonlocal mixing of the local 4p orbitals with the 3d orbitals of the neighbouring ligands ($\rightarrow$ nonlocal) can alter the pre-edge structure and produce additionally the so-called *nonlocal peaks* [3–8] (e.g., TiO_2 [3] and CrO_2 [9]).

FIGURE 1: Scheme (a) illustrates the different pathways in the two-step 1s2p RIXS process, composed of the 1s XAS (K pre-edge) and 2p XES ($K\alpha$ decays) transitions and the direct 2p XAS ($L_{2,3}$ -edge). The term scheme (b) illustrates the analogy between the energy transfer E_T in 1s2p RIXS and 2p XAS.

When there is no inversion symmetry, the quadrupole ($1s \rightarrow 3d$) and dipole ($1s \rightarrow 4p$) peaks can mix locally in the pre-edge leading to an additional dipole contribution to the quadrupole peaks. For example, distortions or vibrational excitations can break the local inversion symmetry of O_h leading to some local dipole character in the pre-edge [10–12]. In addition, the tail of the much stronger dipole character of the main edge ($1s \rightarrow 4p$) overlaps, but the X-ray emission due to this tail absorption can be subtracted from the 1s2p RIXS spectra. Due to this, the exact quadrupole and dipole contributions in the K pre-edge can be difficult to distinguish in experimental spectra. An exact analysis of such cases would go beyond the scope of the present paper, but it will be mentioned when relevant.

The motivation for 1s2p RIXS has its origin mainly in two aspects:

- (1) High-resolution wavelength-dispersive detection of the $K\alpha$ emission enables for the so-called *high-energy resolution fluorescence-detected* (HERFD) spectra. The advantage here is the effective suppression of the core-hole lifetime broadening due to the two-step 1s XAS $\rightarrow$ 2p XES process.
- (2) The final state configuration $1s^2 2p^5 3d^{N+1}$ is identical in 1s2p RIXS and 2p XAS, which enables to access “ $L_{2,3}$ -edge information” with hard X-rays. However, it shall be noted that the different selection rules (quadrupole versus dipole) and the inclusion of an intermediate state in 1s2p RIXS can lead to significant differences in the spectra.

In this context, we are comparing the two-step 1s2p RIXS process with the direct 2p XAS ($L_{2,3}$ -edge) spectra for 3d transition metal compounds. Based on the crystal field theory (CFT), we calculated at least one spectrum for each $3d^N$ ground state, where $N \in \{0, \dots, 9\}$. We aim to give an overview of the general structure of 1s2p RIXS for the $3d^N$ transition metal series to illustrate their specific behaviour,

but the calculated spectra shall also serve as a reference for future analysis.

In 1s2p RIXS, the 1s core hole created in 1s XAS interacts only weakly with the valence electrons. Since the 1s shell has no orbital momentum L , there is no spin-orbit coupling with the other open shells. As we will see, this is important when comparing 1s2p RIXS with 2p XAS [13]. The consequences on the outcome of the spectra will be discussed throughout this paper.

The paper is organised as follows. In Section 2, we describe the theoretical background of the calculation of 1s2p RIXS and the resulting selection rules. In Section 3, we give the computational details. In Section 4, we analyse the 1s2p RIXS of three didactic cases in more detail, and in Section 5, we describe a series of the remaining $3d^N$ cases including a short discussion of related experiments.

2. Theory

The necessary background being the theoretical framework and the computational tools used in this study are described in the following.

2.1. 1s2p RIXS with Kramers-Heisenberg. In 1s2p RIXS experiments, the incident energy is tuned around a resonance related to a $1s \rightarrow 3d$ transition (1s XAS). This excitation is followed by a subsequent radiative $2p \rightarrow 1s$ decay (2p XES). The emitted photons are detected with a wavelength-dispersive detector (crystal analyser) reaching in the hard X-ray range sub-eV resolutions. Often this translates into a bandwidth of less than the lifetime broadening of the spectral features under study. This is often referred to as the *RIXS sharpening effect* overcoming the core-hole lifetime broadening which is related to the RIXS cross-section [14, 15].

The RIXS process is described as a two-step photon-in photon-out scheme in which the incident photons undergo an inelastic scattering around a core resonance followed by a characteristic X-ray emission. The theoretical modelling of the 1s2p RIXS cross-section σ is achieved with

TABLE 1: Russell-Saunders term symbols for the $3d^N$ free ion configurations giving the number of states, the corresponding number of energy levels, and the terms for the given configuration. Note that d^N gives the same terms as d^{10-N} . A more detailed list can be found in *Core Level Spectroscopy of Solids* [13] (p. 103).

Config	States	Energy levels	Ground term	Excited terms
$3d^1, 3d^9$	10	1	2D	—
$3d^2, 3d^8$	45	5	3F	$^2P, ^1G, ^1D, ^1S$
$3d^3, 3d^7$	120	8	4F	$^4P, ^2H, ^2G, ^2F, ^2D, ^2P$
$3d^4, 3d^6$	210	16	5D	$^3H, ^3G, ^2^3F, ^3D, ^2^3P, ^1I, ^2^1G, ^1F, ^2^1D, ^2^1S$
$3d^5$	252	16	6S	$^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2^2G, ^2^2F, ^3^2D, ^2P, ^2S$

the *Kramers-Heisenberg* formula for the second order quantum process which includes the 1s XAS, 2p XES, and interference effects [14–19]:

$$\frac{d^2\sigma}{d\Omega d\omega} = \sum_{|f\rangle} \left| \sum_{|n\rangle} \frac{\langle f | \hat{T}_2 | n \rangle \langle n | \hat{T}_1 | i \rangle}{E_i - E_n + \hbar\Omega + i(\gamma_n/2)} \right|^2 \quad (1)$$

$$\times \frac{\gamma_f/2\pi}{(E_i - E_f + \hbar\Omega - \hbar\omega)^2 + \gamma_f^2/4},$$

with incident photons of energy $E_{\text{in}} = \hbar\Omega$, the inelastically scattered photons of energy $E_{\text{out}} = \hbar\omega$, and the energy transfer $E_T = \hbar\Omega - \hbar\omega$. The two-step process relates to the two transition operators, $\hat{T}_1$ for the quadrupole 1s XAS and $\hat{T}_2$ for the dipole 2p XES, describing the 1s2p RIXS cross-section σ as the transition from the initial state $|i\rangle$ into the final states $|f\rangle$ via all possible intermediate states $|n\rangle$ of the system with energies E_i , E_f and E_n , respectively. And finally, γ_n and γ_f are the natural line widths of the intermediate and final states. This means that the 1s XAS is naturally broadened by the intermediate state lifetime γ_n and 2p XES is naturally broadened by the final state lifetime γ_f [15, 20].

2.2. Crystal Field Theory: Local Model. We recapitulate briefly the aspects of the framework of the crystal field theory that are important for the present paper. Further details can be found in other references [13, 21]. The initial, intermediate, and final states $|i\rangle$, $|n\rangle$, and $|f\rangle$, respectively, are described each by the corresponding Hamiltonian $\mathcal{H}$:

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{e/N} + \mathcal{H}_{e/e} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{CF}}, \quad (2)$$

where $\mathcal{H}_{\text{kin}} = \sum_N p_i^2/2m$ is the kinetic energy of the electrons with the momentum p and mass m , $\mathcal{H}_{e/N} = \sum_N -Ze^2/r_i$ is the electrostatic interaction of the electron i of charge e with the nucleus at radius r_i and charge Z , $\mathcal{H}_{e/e} = \sum_{\text{pairs}} e^2/r_{ij}$ is the electron-electron Coulomb interaction which is determined by the direct Coulomb repulsion and the Coulomb exchange interaction described by the Slater integrals F^k and G^k , respectively, and $\mathcal{H}_{\text{SO}} = \sum_N \zeta(r_i) l_i \cdot s_i$ is the spin-orbit interaction on every open shell. These first four terms, together with a given ground state $|\psi\rangle$, describe the isolated atom in each state [21].

The electron-electron interactions of an electronic configuration give rise to multiple term symbols. The term

symbol indicates a total orbital moment $\mathcal{L}$, total spin moment $\mathcal{S}$, and total angular moment $\mathcal{J}$, with $|\mathcal{L} - \mathcal{S}| \leq \mathcal{J} \leq |\mathcal{L} + \mathcal{S}|$. This is the $\mathcal{L}\mathcal{S}$ coupling scheme or *Russell-Saunders coupling*, which will be used throughout the present paper (Table 1). In the absence of spin-orbit coupling, all terms with the same $\mathcal{L}$ and $\mathcal{S}$ have the same energy, giving an energy level that is $(2\mathcal{L} + 1)(2\mathcal{S} + 1)$ -fold degenerate. When spin-orbit coupling is included, $\mathcal{L}$ and $\mathcal{S}$ lose their meaning and the terms are split in energy according to their $\mathcal{J}$ value, each with a degeneracy of $2\mathcal{J} + 1$. One can assign to these states a so-called Russell-Saunders term symbol $^{2\mathcal{S}+1}X_{\mathcal{J}}$, where X is representing the orbital momentum $\mathcal{L}$; for values of 0, 1, 2, and 3, one writes S, P, D, and F, respectively [21, 22]. For example, a single electron in an s shell is given as $^2S_{1/2}$, and a single electron in a p shell is represented as $^2P_{1/2}$ and $^2P_{3/2}$.

The term symbol describes the symmetry aspects, but it does not say anything about its relative energy [14]. The electron-electron repulsion and the spin-orbit coupling define the relative energy of the different terms within a configuration. Here, *Hund's rules* offer a convenient way to determine the state lowest in energy (max $\mathcal{S}$, max $\mathcal{L}$, and max $\mathcal{J}$ if more than 1/2 is filled, otherwise min $\mathcal{J}$) [21].

The total number of states per configuration is calculated via the *binomial coefficients* [21]:

$$3d^N : \quad \binom{10}{N} = \frac{10!}{N! \cdot (10 - N)!},$$

$$1s^1 3d^{N+1} : \quad \binom{2}{1} \cdot \binom{10}{N+1} = 2 \cdot \frac{10!}{(N+1)! \cdot (10 - (N+1))!},$$

$$2p^5 3d^{N+1} : \quad \binom{6}{1} \cdot \binom{10}{N+1} = 6 \cdot \frac{10!}{(N+1)! \cdot (10 - (N+1))!}. \quad (3)$$

The crystal field multiplet Hamiltonian $\mathcal{H}_{\text{CF}}$ extends the atomic Hamiltonian with an electrostatic field created by the neighbouring atoms in the solid state. Because a large range of systems consist of a transition metal ion surrounded by six neighbouring atoms, where these neighbours are positioned at each corner of an octahedron centred around the transition metal atom, we will focus on the case of the cubic crystal field. The neighbours form a so-called octahedral field, which belongs to the O_h point group. Thus, we discuss all ions throughout this paper in

TABLE 2: Branching of the $\mathcal{S}$, $\mathcal{L}$, and $\mathcal{J}$ atomic terms in an octahedral crystal field ($O_3 \rightarrow O_h$) [28] (p.262). The first columns can be either the orbital momentum, the total spin $\mathcal{S}$, or the total angular momentum $\mathcal{J}$. The g for *gerade* and the u for *ungerade* must be added to indicate the parity.

O_3 $\mathcal{S}, \mathcal{L}, \text{ or } \mathcal{J}$	$\rightarrow$	O_h Term symbol
0 (S)	$\rightarrow$	A_1
1 (P)	$\rightarrow$	T_1
2 (D)	$\rightarrow$	$E \oplus T_2$
3 (F)	$\rightarrow$	$T_1 \oplus T_2 \oplus A_2$
4 (G)	$\rightarrow$	$A_1 \oplus E \oplus T_1 \oplus T_2$
5 (H)	$\rightarrow$	$E \oplus 2 T_2 \oplus T_2$
6 (I)	$\rightarrow$	$A_1 \oplus T_1 \oplus E \oplus 2 T_2 \oplus A_2$
7	$\rightarrow$	$2 T_2 \oplus E \oplus 2 T_2 \oplus A_2$
8	$\rightarrow$	$A_1 \oplus 2 T_1 \oplus 2 E \oplus 2 T_2$
1/2	$\rightarrow$	$E_{1/2}$
3/4	$\rightarrow$	$F_{3/2}$
5/2	$\rightarrow$	$F_{3/2} \oplus E_{5/2}$
7/2	$\rightarrow$	$E_{1/2} \oplus F_{3/2} \oplus E_{5/2}$
9/2	$\rightarrow$	$E_{1/2} \oplus 2 F_{3/2}$
11/2	$\rightarrow$	$E_{1/2} \oplus 2 F_{3/2} \oplus E_{5/2}$
13/2	$\rightarrow$	$E_{1/2} \oplus 2 F_{3/2} \oplus 2 E_{5/2}$
15/2	$\rightarrow$	$E_{1/2} \oplus 3 F_{3/2} \oplus E_{5/2}$

an octahedral symmetry (O_h). We are aware that this is not necessarily true for all 3d transition metal ions (e.g., CrO_2 (Cr^{4+}) and TiO_2 (Ti^{4+}) have tetragonal (D_{4h}) symmetry; Fe_2O_3 (Fe^{3+}) has C_3 symmetry). However, we make this simplification since we are aiming to present and discuss the elementary differences for each case in an analogue and comparable way.

In a single-electron picture, in a spherical environment, the 3d orbitals are degenerate. In O_h , the cubic crystal field induces the splitting of the five 3d orbitals into two symmetrically different groups: (1) the 3-fold t_{2g} orbitals (xy , xz , and yz), which point in between the six metal-ligand bonds and thus participate in π bondings with the surrounding ligands, and (2) the 2-fold e_g orbitals (z^2 and $x^2 - y^2$), which point along the metal-ligand bonds and therefore relate to σ bondings. The splitting between the e_g and t_{2g} orbitals is defined by the strength of the crystal field and is described by the parameter $10Dq$ [13].

The symmetry of the multielectronic term changes from spherical symmetry (O_3) to octahedral symmetry (O_h) causing the $\mathcal{L}$ term (S, P, D, etc.) to branch to an O_h irreducible representation (IRREP): S (O_3) branches into an A_1 (O_h) symmetry state, P (O_3) branches into a T_1 (O_h) symmetry state, and D (O_3) branches into T_2 (O_h) and E (O_h) symmetry states. Because the point group O_3 (resp., O_h) contains the inversion, a parity information should be added for *gerade* or *ungerade* to the term, + or - for the atomic (spherical) terms, and g or u for the crystal field terms. The $3d^N$ initial state and the intermediate state $1s^1 3d^{N+1}$ in 1s2p RIXS

are gerade (g), and the final state $2p^5 3d^{N+1}$ is, due to the open 2p shell, ungerade. In the following, the parity of the spherical term will be omitted for simplicity. All the branchings are given in Table 2, which we will use extensively throughout this paper.

The relative energies of the O_h IRREPs are calculated by adding the effect of the cubic crystal field $10Dq$ to the atomic state energies. The diagrams of the relative energies with respect to the cubic crystal field, often without spin-orbit coupling, are known as *Tanabe-Sugano diagrams*. More generally, we will call them *energy level diagram* (ELD). They will appear in the context of the quadrupole 1s XAS because the ELD for any intermediate state in 1s2p RIXS with a $1s^1 3d^{N+1}$ electron configuration is the same as the diagram for a $1s^2 3d^{N+1}$ configuration times the $^2A_{2g}$ term to include the 1s core hole.

When spin-orbit coupling (SOC) and crystal field are both to be included, there are in principle two ways to derive the term symbols: (1) by first deriving the branching of the uncoupled atomic terms (with $\mathcal{L}$ and $\mathcal{S}$) in O_h symmetry and then by deriving the spin-orbital coupling or (2) by first deriving the atomic $\mathcal{J}$ quantum number in the $\mathcal{L}.\mathcal{S}$ coupling scheme and then deriving the branching of the $\mathcal{J}$ value in the O_h point group. Both methods yield identical final results and the identical ground state for a given Hamiltonian (see, e.g., Figure 2).

The order in which the derivation should be done is related to the relative weights of the spin-orbit coupling and crystal field terms in the Hamiltonian. In the initial state of 1s2p RIXS, the 3d spin-orbit coupling ζ_{3d} is small (a few tens of meV) compared to the usual values of crystal field splitting $10Dq$ (a few eV). As a result, in cases with neglectable spin-orbit interaction, the mixing between the spin and the orbital momenta is weak and thus $\mathcal{L}$ and $\mathcal{S}$ can still be used to describe the initial state. Similarly, for the intermediate state, the 1s core hole with $\mathcal{L} = 0$ does not have spin-orbit coupling. Therefore, in these cases, the $\mathcal{L}.\mathcal{S}$ coupling is achieved after the crystal field branching. (See Xu et al. [23] for details on $\mathcal{L}.\mathcal{S}$ coupling.)

In the present paper, we are focusing on the 3d transition metal ions represented by a series of cases with a ground state electron configuration ranging from $3d^0$ to $3d^9$. Depending on the number of 3d electrons, the value of the total spin $\mathcal{S}$ varies between 0 (minimum) and 5/2 (maximum). The branching for each value of $\mathcal{S}$ in O_h is given in Table 2. The $\mathcal{L}.\mathcal{S}$ -coupled term, also called $\mathcal{J}$ value IRREP, in O_h symmetry is obtained from the direct product of the $\mathcal{L}$ IRREP and the $\mathcal{S}$ IRREP. For this calculation, the direct product tables Tables 3, 4, and 5 can be used. Note that the total orbital multiplicity is always maintained, for example,

$$\underbrace{T_{1g}}_{\text{(Size=3)}} \otimes \underbrace{T_{2g}}_{\text{(Size=3)}} = \underbrace{A_{2g}}_{\text{(Size=1)}} \oplus \underbrace{E_g}_{\text{(Size=2)}} \oplus \underbrace{T_{1g}}_{\text{(Size=3)}} \oplus \underbrace{T_{2g}}_{\text{(Size=3)}}. \quad (4)$$

Total size: $3 \times 3 = 9$ Total size: $1 + 2 + 3 + 3 = 9$

On the contrary, in the final state configuration, the strong spin-orbit coupling ζ_{2p} of the 2d hole (a few eV)

FIGURE 2: Initial state term schemes for Cu^{2+} ($3d^9$) illustrating the effect of the 3d SOC ζ_{3d} and O_h crystal field $10Dq$ and the resulting splittings of the atomic ground state term 2D .

TABLE 3: Direct products of representations (product table) in O_h symmetry.

O_h	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{1g}	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{2g}		A_{1g}	E_g	T_{2g}	T_{1g}
E_g			$A_{1g} \oplus A_{2g} \oplus E_g$	$T_{1g} \oplus T_{2g}$	$T_{1g} \oplus T_{2g}$
T_{1g}				$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$	$A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$
T_{2g}					$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$

TABLE 4: Direct products of representations (cont.) in O_h symmetry (dipole).

O_h	A_{1u}	A_{2u}	E_u	T_{1u}	T_{2u}
A_{1g}	A_{1u}	A_{2u}	E_u	T_{1u}	T_{2u}
A_{2g}	A_{2u}	A_{1u}	E_u	T_{2u}	T_{1u}
E_g	E_u	E_u	$A_{1u} \oplus A_{2u} \oplus E_u$	$T_{1u} \oplus T_{2u}$	$T_{1u} \oplus T_{2u}$
T_{1g}	T_{1u}	T_{2u}	$T_{1u} \oplus T_{2u}$	$A_{1u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$	$A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$
T_{2g}	T_{2u}	T_{1u}	$T_{1u} \oplus T_{2u}$	$A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$	$A_{1u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$
A_{1u}	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{2u}		A_{1g}	E_g	T_{2g}	T_{1g}
E_u			$A_{1g} \oplus A_{2g} \oplus E_g$	$T_{1g} \oplus T_{2g}$	$T_{1g} \oplus T_{2g}$
T_{1u}				$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$	$A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$
T_{2u}					$A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}$

TABLE 5: Direct products of representations (cont.) in O_h symmetry (SOC). Note that in this table, the parity (*g*: gerade; *u*: ungerade) was omitted here as the table can be used for either case. For accurate labelling, the parity has to be added to the term symbol, where *gerade* times *gerade* equals *gerade* and *gerade* times *ungerade* equals an *ungerade* term symbol.

O_h	$E_{1/2}$	$E_{5/2}$	$F_{3/2}$
A_1	$E_{1/2}$	$E_{5/2}$	$F_{3/2}$
A_2	$E_{5/2}$	$E_{1/2}$	$F_{3/2}$
E	$F_{3/2}$	$F_{3/2}$	$E_{1/2} \oplus E_{5/2} \oplus F_{3/2}$
T_1	$E_{1/2} \oplus F_{3/2}$	$E_{1/2} \oplus F_{3/2}$	$E_{1/2} \oplus E_{5/2} \oplus 2F_{3/2}$
T_2	$E_{5/2} \oplus F_{3/2}$	$E_{1/2} \oplus F_{3/2}$	$E_{1/2} \oplus E_{5/2} \oplus 2F_{3/2}$
$E_{1/2}$	$A_1 \oplus T_1$	$A_2 \oplus T_2$	$E \oplus T_1 \oplus T_2$
$E_{5/2}$		$A_1 \oplus T_1$	$E \oplus T_1 \oplus T_2$
$F_{3/2}$			$A_1 \oplus A_2 \oplus E \oplus 2T_1 \oplus T_2 \oplus T_2$

is dominant. This induces a strong mixing between the spin and orbital momenta and resulting in $\mathcal{L}$ and $\mathcal{S}$ not being good quantum numbers anymore. Instead, the total angular momentum $\mathcal{J}$ must be used to describe the final states. The effect of the O_h crystal field is added as the corresponding branching of the atomic $\mathcal{J}$ value IRREP. The branching for each value of $\mathcal{J}$ is also given in Table 2. The obtained IRREPs are either A_{1u} , T_{1u} , E_u , T_{2u} , or A_{2u} for integer $\mathcal{S}$ or $\mathcal{J}$. And they are $E_{1/2u}$, $F_{3/2u}$, and $E_{3/2u}$ for half-integer values of $\mathcal{S}$ or $\mathcal{J}$.

As we will see across the $3d^N$ series, the information of $\mathcal{L}$, $\mathcal{S}$, and $\mathcal{J}$ is important for the description of the ground state of the initial state electron configuration when comparing the one-step 2p XAS with the two-step 1s2p RIXS selection rules (see Section 2.3). Therefore, in an O_h crystal field, we will indicate the uncoupled atomic term (with $\mathcal{L}$ and $\mathcal{S}$) along with the total angular momentum $\mathcal{J}$ value IRREP using the following notation: $^{2\mathcal{S}+1}\mathcal{L}[\mathcal{J}]$.

We illustrate this here with an example for Ni^{2+} ($3d^8$) with the atomic ground state term 3F (O_3).

$${}^3F \xrightarrow{O_h} {}^3A_{2g} + {}^3T_{1g} + {}^3T_{2g}. \quad (5)$$

Note that the spin multiplicity should be kept and is part of the term symbol because spin-orbit coupling is not yet included. The ${}^3A_{2g}$ symmetry represents in this case the state being the lowest in energy, and it is therefore the ground state term. In the next step, we derive the total angular momentum $\mathcal{J}$ IRREPs in the $\mathcal{L}\mathcal{S}$ coupling scheme ($\mathcal{S} = 1 \rightarrow \otimes T_{1g}$) for the three terms derived in (5):

$${}^3A_{2g} \otimes T_{1g} = T_{2g} \quad (\text{splitting of the } {}^3A_{2g} \text{ term due to } 3d \text{ SOC}), \quad (6)$$

$${}^3T_{1g} \otimes T_{1g} = A_{1g} + E_g + T_{1g} + T_{2g} \quad (\text{splitting of the } {}^3T_{1g} \text{ term due to } 3d \text{ SOC}), \quad (7)$$

$${}^3T_{2g} \otimes T_{1g} = A_{2g} + E_g + T_{1g} + T_{2g} \quad (\text{splitting of the } {}^3T_{2g} \text{ term due to } 3d \text{ SOC}). \quad (8)$$

In (6), we find the T_{2g} total angular momentum IRREP as the ground state for the example $3d^8$ in an octahedral crystal field. To summarise all this information in a condensed form, we write

$${}^3A_{2g}[T_{2g}]. \quad (9)$$

This translates as a *term without SOC with $\mathcal{S}$ and $\mathcal{L}$ [term with SOC using $\mathcal{J}$]*.

In other words, in (9), the term ${}^3A_{2g}$ is *before* the inclusion of SOC, where the spin multiplicity is 3 and the orbital momentum is given as A_{2g} . And the T_{2g} term is the symmetry *after* spin-orbit interaction has been included (also identified as $\mathcal{J}$ value IRREP).

Finally, we note that charge transfer effects (e.g., the interaction with a $3d^{N-1}\underline{L}$ configuration) are neglected but their relative importance will be discussed where appropriate throughout the $3d^N$ series.

2.3. Selection Rules. The selection rules are the constraints that define the possibility of a transition between two states with a given transition operator. In other words, for 1s2p RIXS, the selection rules are the conditions for which the matrix elements $\langle f|\hat{T}_2|n\rangle$ and $\langle n|\hat{T}_1|i\rangle$ in the Kramers-Heisenberg equation (1) are nonzero. The operators $\hat{T}_1$ and $\hat{T}_2$ describe the interaction of the photon with matter. They are defined by the interaction Hamiltonian $\mathbf{p} \cdot \mathbf{A}$, where $\mathbf{p}$ is the momentum of the photon and $\mathbf{A}$ is the vector potential (e.g., the amplitude) of the electromagnetic field of the light. The electromagnetic interaction term is $(\varepsilon \cdot \mathbf{p})e^{i\mathbf{k}\cdot\mathbf{r}}$, where ε is the polarisation of the photon and $\mathbf{k}$ is the propagation vector of the photon. In a multipole expansion, the $e^{i\mathbf{k}\cdot\mathbf{r}}$ term can be decomposed in a Taylor series (the selection rules can be

derived from the decomposition of the electron dipole/quadrupole transition matrix element into angular and radial parts using the Wigner-Eckart theorem [13, 24], where the triangular relations of the symbol determine the selection rules) which leads to the electric dipole and the electric quadrupole terms [25]. Further details can be found in *Core Level Spectroscopy of Solids* [13] and elsewhere [16, 24, 25].

Due to the electric dipole operator being the first-order term of this decomposition, the result is that the $\mathcal{J}$ quantum number can only change by a value of 0 or 1. Thus, the electric dipole selection rule translates to $\Delta\mathcal{J} = +1, 0, \text{ or } -1$. Because the electric quadrupole operator is the second-order term of this decomposition, the resulting selection rule translates to $\Delta\mathcal{J} = -2, -1, 0, +1, \text{ or } +2$.

However, when the spin-orbit coupling is neglected (or weak), the orbital momentum $\mathcal{L}$ and the spin momentum $\mathcal{S}$ can still be considered good quantum numbers. In this case, the transitions are spin-conserving ($\Delta\mathcal{S} = 0$) and only $\mathcal{L}$ changes. Due to the fact that light carries an orbital momentum of $|\mathcal{L}| = 1$, this implies for electric dipole transitions $\Delta\mathcal{L} = +1$ or -1 . For the second-order term, the electric quadrupole transitions, this implies $\Delta\mathcal{L} = +2, 0, \text{ or } -2$ [21].

As a result, the transition operator $\hat{T}_1$ of the 1s XAS absorption step promoting an electron from 1s to 3d ($\Delta\mathcal{L} = +2$) is an electric quadrupole term, and this step is forbidden as an electric dipole transition. On the contrary, the transition operator $\hat{T}_2$ for the 2p XES decay from 2p to 1s ($\Delta\mathcal{L} = -1$) is an electric dipole term. Similarly, the transition operator $\hat{T}$ of the 2p XAS absorption step from 2p to 3d ($\Delta\mathcal{L} = +1$) is also an electric dipole term.

These selection rules, defined in spherical symmetry, translate into the point group symmetry of the absorbing ion. In cubic symmetry (O_h), the selection rules of each operator depend on its symmetry properties. The electric dipole operator (first-rank tensor) behaves as the $\mathcal{J} = 1$ IRREP (O_3) and branches into T_{1u} in O_h . The electric quadrupole operator (second-rank tensor) behaves as a $\mathcal{J} = 2$ IRREP (O_3) and branches in O_h into $T_{2g} \oplus E_g$ (see Table 2). The transition matrix element between two states $|i\rangle, |f\rangle$ with the IRREPs Γ_i and Γ_f and the transition operator $\hat{T}$ is nonzero if the direct product $\Gamma_i \otimes \Gamma_{\hat{T}}$ contains Γ_f , where $\Gamma_{\hat{T}}$ is the IRREP of the transition operator. In other words, the final state IRREPs Γ_f accessible via the transition operator $\hat{T}$ are given by the direct product $\Gamma_i \otimes \Gamma_{\hat{T}}$. The selection rules are derived from the direct product tables for the O_h point group (see Tables 3, 4, and 5) and give the symmetry of the accessible states.

The selection rules will be commented in more detail for each case of the $3d^N$ series throughout this paper. Magnetic and natural dichroisms, which are a property from the crystal and not from the point group of the absorbing transition metal ion [26], will not be discussed here.

3. Calculations and Computational Details

All calculations are done using the framework of the crystal field multiplet theory, which is a multielectronic, semiempirical approach initially developed by Thole et al. [27] and further established by Butler and Cowan [28, 29]. It takes into

TABLE 6: Summary of the different notations in O_h symmetry. T/S/K: Tanabe/Sugano/Kamimura, though Sugano also uses a variation of this notation as shown. The CTM4XAS program uses mostly the Butler notation, though the .ora-file translation is listed for ease of use.

Altmann	Mulliken	T/S/K	Sugano	Koster/Bethe	Butler	CTM4XAS
A_1	A_1	A_1	A_1	Γ_1	0	0
A_2	A_2	A_2	A_2	Γ_2	$\tilde{0}$	$\wedge 0$
E	E	E	E	Γ_3	2	2
T_1	T_1	T_1	T_1	Γ_4	1	1
T_2	T_2	T_2	T_2	Γ_5	$\tilde{1}$	$\wedge 1$
$E_{1/2}$	E'	E or E_1	$E_{1/2}$	Γ_6	1/2	SO
$F_{3/2}$	U'	G	$G_{3/2}$	Γ_8	3/2	S1
$E_{5/2}$	E''	E' or E_2''	$E_{5/2}$	Γ_7	$\tilde{1/2}$	$\wedge S0$

TABLE 7: Summary of the ground state terms, number of microstates, and crystal field values (10Dq) for all ions used in our calculations.

GS	Ion	Ground state terms			Number of MS		Total GS $\binom{10}{N}$	10Dq	
		O_3 HS	O_h HS	LS	HS	LS		HS	LS
$3d^0$	Ti^{4+}	1S	$^1A_{1g}[A_{1g}]$		1		1	0 eV & 2.1 eV	
$3d^1$	Ti^{3+}	2D	$^2T_{2g}[F_{3/2g}]$		6		10	1.5 eV	
$3d^2$	Cr^{4+}	3F	$^3T_{1g}[E_g]$		9		45	2.1 eV	
$3d^3$	Cr^{3+}	4F	$^4A_{2g}[F_{3/2g}]$	$^3T_{1g}[A_{1g}]$	4	9	120	1.5 eV	
$3d^4$	Mn^{3+}	5D	$^5E_g[A_{1g}]$	$^2T_{2g}[E_{5/2g}]$	10	6	210	1.5 eV	
$3d^5$	Fe^{3+}	6S	$^6A_{1g}[F_{3/2g}]$	$^1A_{1g}[A_{1g}]$	6	1	252	1.5 eV	
$3d^6$	Fe^{2+}	5D	$^5T_{2g}[T_{2g}]$	$^2E_g[F_{3/2g}]$	15	4	210	0.9 eV	
$3d^7$	Co^{2+}	4F	$^4T_{1g}[E_{1/2g}]$		12		120	0.9 eV	
$3d^8$	Ni^{2+}	3F	$^3A_{2g}[T_{2g}]$		3		45	0.9 eV	
$3d^9$	Cu^{2+}	2D	$^2E_g[F_{3/2g}]$		4		10	0 eV & 3.0 eV	

account all the 3d-3d, 1s-3d, and 2p-3d electronic Coulomb interactions, as well as the spin-orbit coupling ζ on every open shell of the absorbing atom (e.g., 2p SOC ζ_{2p} and 3d SOC ζ_{3d} in 1s2p RIXS).

The 2p XAS and 1s2p RIXS spectra were calculated using Quanty which uses second quantisation and the Lanczos recursion method for the exact diagonalisation and Green functions to calculate the spectra [30–32]. This method enables to avoid the explicit calculation of the intermediate and final states, which are only defined with their respective Hamiltonian. Each of these many-body states is described by a linear combination of Slater determinants [31]. The atomic electronic interactions are parametrised by the Slater integrals, which are reduced to 80% of the Hartree-Fock values. The latter has empirically proven to correspond to the actual atomic values. For the spin-orbit coupling parameters ζ_{2p} , ζ_{3d} , the Hartree-Fock calculated values are used. All calculations are done in octahedral symmetry (O_h), and the crystal field is defined by the crystal field parameter 10Dq. The same value is used for the initial, intermediate, and final states. The influence of the crystal field splitting is investigated by varying the parameter 10Dq from 0 eV up to a few eV. The symmetry IRREPs of the labels of the final states in the O_h point group are obtained using the CTM4XAS program [33].

(Table 6 shows a general list of different notations to translate between them.) The natural broadenings $\gamma_n = 0.5$ eV and $\gamma_f = 0.25$ eV for the intermediate state and final state, respectively, were applied.

All RIXS intensities are given as calculated by Quanty. They reflect the total absorption as the sum over the five quadrupole basis components and the three dipole emission polarisations and thus imply an isotropic spectrum. When needed, one can in fact also compute the scattered photons as the percentage of the incident beam in dependency of a given experimental setup. The 2p XAS spectra are scaled for the best comparison for each case. The energies E_{in} and E_{out} are given by Quanty relative to the centre of gravity for each of the three states in 1s2p RIXS, being the $3d^N$, $1s^13d^{N+1}$, and $2p^53d^{N+1}$ configurations, respectively. Thus, also the $E_T = 0$ eV position of the energy transfer $E_T = E_{in} - E_{out}$ is based on the centre of gravity and E_T does not reflect the real energy transfer.

More details on the method can be found elsewhere [13, 30–32, 34] and the references therein. The calculations are performed for a temperature of $T = 300$ K as described in the following.

3.1. $T = 300$ K Approximation: Boltzmann Distribution. The multielectronic ground state at ambient condition is

FIGURE 3: Initial state term schemes of Ti^{3+} ($3d^1$) illustrating the effect of the 3d SOC and an O_h crystal field $10Dq$ on the splittings of the atomic ground state term 2D .

a linear combination of an ensemble of $\mathcal{N}$ microstates ψ_i with $i \in \{0, \dots, \mathcal{N} - 1\}$. In general, the Coulomb and spin-orbit interactions as well as crystal field effects can induce a mixing of different states, leading to complex multielectronic states involving many microstates. For example, a $3d^5$ configuration has in total 252 microstates, but only $\mathcal{N} = 6$ microstates form in high spin the atomic multielectronic ground state 6S (O_3) (Table 7).

However, at absolute zero ($T = 0$ K), formally, only the state ψ_0 lowest in energy is populated. Thus, the calculated spectra result from a linear combination of each contributing state, weighted according to their respective population, because for temperatures $T > 0$ K higher states are also partially occupied. The population is described with the *Boltzmann distribution*.

It gives the population probability p_i for each state ψ_i in dependency of its relative energy $E_i - E_0$, with $E_0 = E(\psi_0)$ being the energy of the lowest microstate ψ_0 , and absolute temperature T . It is given (with Boltzmann constant k_B) as

$$p_i = \frac{1}{a} \exp \left[-\frac{E_i - E_0}{k_B T} \right], \quad (10)$$

with

$$a = \sum_{i=0}^{\mathcal{N}} \exp \left[-\frac{E_i - E_0}{k_B T} \right]. \quad (11)$$

In the present case, the eigenvalues calculated with Quanta from $\mathcal{H}|\psi\rangle = E|\psi\rangle$ give the energies E_i for each microstate ψ_i , which are used in (10) and (11) to compute the coefficients p_i for the Boltzmann linear combination of each multielectronic ground state.

For example, Ti^{3+} ($3d^1$) has the atomic ground state 2D with $\mathcal{N} = 10$ microstates. In other words, the single 3d electron can be in 10 different states. In an O_h crystal field, this ground state branches without 3d spin-orbit interaction into two crystal field terms: $^2D \xrightarrow{O_h} ^2T_{2g} \oplus ^2E_g$.

The term $^2T_{2g}$ represents the multielectronic ground state in an O_h crystal field, formed as a linear combination of $\mathcal{N} = 6$ microstates. For $3d^1$, the $^2T_{2g}$ term is the lowest in energy as can be seen in the single electronic picture: $|t_{2g}^1 e_g^0\rangle$, as opposed to the 2E_g with $|t_{2g}^0 e_g^1\rangle$ in 4 possible microstates.

Furthermore, it should be noted that the $\mathcal{N}$ microstates forming the multielectronic ground state are a priori not degenerate. For Ti^{3+} , the lowest 10 microstates are in fact partially degenerate. With 3d spin-orbit interaction included, the microstates are spread in a 4 : 2 : 4 ratio, corresponding to the terms $F_{3/2}$, $E_{5/2}$, and $F_{3/2}$, respectively. In other words, the lowest four microstates ψ_0, ψ_1, ψ_2 , and ψ_3 are degenerate in energy ($E_0 = E_1 = E_2 = E_3$), and the two states ψ_4 and ψ_5 are degenerate ($E_4 = E_5$), as well as the remaining 4 microstates ψ_6, ψ_7, ψ_8 , and ψ_9 ($E_6 = E_7 = E_8 = E_9$). Hence, the 10 microstates, which are related to the atomic multielectronic ground state 2D (O_3) and are split by the crystal field and spin-orbit interaction, are spread over three different energy levels. However, the six microstates forming the $^2T_{2g}$ (O_h) term are only spread over two different energies (see Figure 3).

Note, if not stated otherwise, we only use the lowest crystal field ground state for the Boltzmann linear combination (e.g., $^2T_{2g}$ for Ti^{3+}); the next multielectronic term higher in energy (e.g., 2E_g for Ti^{3+}) is neglected. This approximation relates to the fact that in general the second multielectronic term has a relatively small contribution in most cases.

4. Didactic Examples

In this section, we discuss three model systems as didactic examples in detail before the results for the remaining $3d^N$ series (with $N \in \{1, \dots, 7\}$) which are discussed in a more summarising manner (Section 5). Here, we will emphasise the elementary differences between the atomic (O_3) and the crystal field (O_h) cases to illustrate the effects with respect to the selection rules. Furthermore, we compare the results due to the different possible pathways in the direct one-step 2p XAS and the two-step 1s2p RIXS and the corresponding spectra.

As didactical examples, we use the following three cases:

- (i) $3d^9 \text{Cu}^{2+}$: single open shell with only a single hole in each state
- (ii) $3d^0 \text{Ti}^{4+}$: two peaks in the 1s XAS split by the crystal field $10Dq$
- (iii) $3d^8 \text{Ni}^{2+}$: a common model system often used in education

FIGURE 4: Atomic case: term scheme (with SOC; no crystal field) comparing the two-step (1s XAS, 2p XES) 1s2p RIXS and the one-step 2p XAS pathways for Cu^{2+} . The sum over all $\mathcal{J}$ multiplicities ($2\mathcal{J} + 1$) yields the total number of microstates per configuration.

FIGURE 5: Calculated atomic 1s2p RIXS map with 2p XES projection for an isolated Cu^{2+} ($3d^9$). Notice the 2p XAS ($L_{2,3}$ -edge) (dashed red) has only one peak, because only the final state with $\mathcal{J} = 3/2$ can be populated. See also Figure 7.3 in *Core Level Spectroscopy of Solids* [13].

We aim to assign the symmetry labels to the relevant peaks in the 1s2p RIXS spectra and compare the 2p XES to the well-understood $L_{2,3}$ -edge (2p XAS) spectra [35].

4.1. $3d^9$: Divalent Copper Cu^{2+} —Crystal Field Effects Altering the Selection Rules. In this part, we investigate the elementary differences between 1s2p RIXS and 2p XAS for a divalent copper ion Cu^{2+} with a $3d^9$ ground state. Each successive step of the 1s2p RIXS process has an electronic configuration with only one open shell and a single hole in the 3d, 1s, and 2p shells, respectively.

We first describe the atomic case of an isolated ion without any crystal field. The electronic configuration of the initial state of Cu^{2+} is $1s^2 2p^6 3d^9$. In spherical symmetry (O_3), the 3d spin-orbit coupling (SOC) ζ_{3d} induces the splitting of the 10-fold degenerate ground state 2D (10 microstates) into two multielectronic states $^2D_{5/2}$ (O_3) and $^2D_{3/2}$ (O_3), defined by $\mathcal{J} = 5/2$ (ground state) and $\mathcal{J} = 3/2$, respectively. These two states are separated in energy by $\Delta E = 5/2\zeta_{3d}$.

The electronic configuration of the 1s2p RIXS intermediate state of Cu^{2+} is $1s^1 2p^6 3d^{10}$, which corresponds to the 2-fold degenerate state $^2S_{1/2}$ (O_3) with $\mathcal{J} = 1/2$. The electronic configuration of the final state in 2p XAS and 1s2p RIXS of Cu^{2+} is $1s^2 2p^5 3d^{10}$, which splits due to the 2p spin-orbit coupling ζ_{2p} into $\mathcal{J} = 3/2$ (lowest energy state) and $\mathcal{J} = 1/2$ separated by $3/2\zeta_{2p}$. This is summarised in the scheme in Figure 4.

Since the ground state of the initial state is $\mathcal{J} = 5/2$, the electric dipole absorption operator (2p XAS) enables only to reach the $\mathcal{J} = 3/2$ final state ($\Delta\mathcal{J} = -1$). In 1s2p RIXS, the selection rules of the electric quadrupole absorption for 1s XAS ($\Delta\mathcal{J} = -2$) enable to reach the intermediate state $\mathcal{J} = 1/2$. The subsequent electric dipole emission (2p XES) enables to reach both $\mathcal{J} = 1/2$ and $\mathcal{J} = 3/2$ final states. As a result, for an isolated Cu^{2+} ion in spherical symmetry, the 2p XAS shows only one peak, while the 1s2p RIXS shows two peaks. The resulting spectra are shown in Figure 5.

In the vertical direction, the $K\alpha_1$ and $K\alpha_2$ decays (2p XES) appear as two separate peaks. These two peaks are separated by the 2p SOC $\zeta_{2p} \approx 13.5$ eV, corresponding to the two resonant emission transitions from the intermediate state with $\mathcal{J} = 1/2$ to the final states with $\mathcal{J} = 1/2, 3/2$.

4.1.1. Considering a Cubic (Octahedral) Crystal Field. When the absorbing ion is embedded in a solid state, one has to take

FIGURE 6: Multielectronic term scheme for $3d^9 \text{Cu}^{2+}$ comparing the 1s2p RIXS and direct 2p XAS pathways. Where SOC ($\mathcal{S} = 1/2$) $\rightarrow \otimes E_{1/2}$ is included, the spin multiplicity is omitted.

into account the crystal field potential created by the surrounding atoms. In the following, we will assume an octahedral (O_h) crystal field described by the parameter $10Dq$. In a single electron picture, this crystal field induces the splitting of the 3d orbitals into t_{2g} and e_g . In the multielectronic formalism (neglecting the 3d spin-orbit coupling in first approximation), the 2D term of the initial state branches in the O_h point group into the 2E_g ($|t_{2g}^6 e_g^3\rangle$) and ${}^2T_{2g}$ ($|t_{2g}^5 e_g^4\rangle$) terms. Thus, the multielectronic ground state (at $T = 0$ K) is 2E_g (O_h). The intermediate state term 2S (O_3) branches in an octahedral crystal field into ${}^2A_{1g}$ (O_h) symmetry.

In the O_h point group, the electric quadrupole 1s XAS operator has T_{2g} and E_g symmetries. We derive the selection rules from the *product table* (Table 3) for the first step of the 1s2p RIXS process.

$$\begin{aligned} {}^2E_g \otimes T_{2g} &= {}^2T_{1g} \oplus {}^2T_{2g}, \\ \underbrace{{}^2E_g}_{1s^2 3d^9} \otimes \underbrace{E_g}_{1s \text{ XAS}} &= \underbrace{{}^2A_{1g} \oplus {}^2A_{2g} \oplus {}^2E_g}_{\text{Accessible states}}. \end{aligned} \quad (13)$$

From (13), it becomes obvious that many symmetries are in principle accessible via 1s XAS from the multielectronic ground state symmetry 2E_g (O_h). In spite of the fact that many symmetries are in principle reachable via a quadrupole 1s XAS transition starting from the ground state symmetry 2E_g (O_h), the electronic structure of a Cu^{2+} ion only offers ${}^2A_{1g}$ (O_h) symmetry leading to a single peak in the 1s XAS projection.

While spin-orbit coupling was neglected in this last step, it must be included in the description of the final state with the 2p core hole to understand the complete 1s2p RIXS process and to be able to compare it with the 2p XAS. Using the $\mathcal{L}\mathcal{S}$ -coupled terms obtained above in the atomic case, we derive their respective branchings in the octahedral crystal field (O_h).

The initial ground state ${}^2D_{5/2}$ (O_3) branches in octahedral symmetry (O_h) into $E_{5/2g} \oplus F_{3/2g}$ (O_h). The ground state at $T = 0$ K is ${}^2E_g[F_{3/2g}]$ (O_h). The effects of the 3d spin-orbit coupling ζ_{3d} and the O_h crystal field parameter $10Dq$ are illustrated in Figure 2.

The intermediate state term ${}^2S_{1/2}$ (O_3) branches in an octahedral crystal field (O_h) into $E_{1/2g}$ (O_h). The final states

${}^2P_{3/2}$ (O_3) and ${}^2P_{1/2}$ (O_3) branch into $F_{3/2u}$ (O_h) and $E_{1/2u}$ (O_h), respectively. In octahedral symmetry, the electric dipole operator has T_{1u} symmetry and thus, using the product table (Table 5), we find the reachable final states in the subsequent electric dipole emission (2p XES):

$$E_{1/2g} \otimes T_{1u} = E_{1/2u} \oplus F_{3/2u}. \quad (14)$$

The direct 2p XAS starts from the $F_{3/2g}$ ground state yielding with the T_{1u} IRREP the reachable final state terms:

$$F_{3/2g} \otimes T_{1u} = E_{1/2u} \oplus E_{5/2u} \oplus 2F_{3/2u}. \quad (15)$$

Altogether, this demonstrates that the crystal field enables both final states to be probed by 2p XAS and 1s2p RIXS. This is summarised in the scheme in Figure 6 and the corresponding calculated spectrum is shown in Figure 7.

The RIXS projections for various values of $10Dq$ show almost no difference in both directions (XAS and XES). It is noteworthy that the 2p XAS ($L_{2,3}$ -edge) approaches the two peaks in the 2p XES projections for large $10Dq$ values. This is due to the crystal field ($10Dq$) affecting the spin-orbit interaction altering the 2p XAS selection rules.

In other words, the L_2 -edge probes in 2p XAS the amount of $\mathcal{J} = 3/2$ character in the ground state. In the atomic case ($10Dq = 0.0$ eV) with spherical symmetry (O_3) and at absolute zero $T = 0$ K, the ion is pure $\mathcal{J} = 5/2$ ($D_{5/2}$). In octahedral O_h symmetry, on the other hand, an increasing crystal field (scaled via $10Dq$) mixes more and more $\mathcal{J} = 3/2$ character from the $D_{3/2}$ into the ground state, resulting in a continuous visible increase of the L_2 peak in 2p XAS.

And finally, it can be seen that the single-particle limit with two peaks is reached in both cases, 1s2p RIXS and 2p XAS, respectively. The intensity ratio of the two peaks of 2:1 is given by the degeneracy of the ${}^2P_{1/2}$ (O_3) and ${}^2P_{3/2}$ (O_3) final states.

4.1.2. 1s2p RIXS Experiments of $3d^9$ Systems. Experimental 1s2p RIXS spectra of CuO have been published by Hayashi et al. [2]. They show the 1s2p X-ray emission spectra from excitation energies before the K-edge, through the edge to the continuum. As such, they observe the transition from resonances in the Lorentzian tails to nonresonant 1s2p XES. At the excitation energy at the pre-edge, the two-peaked 1s2p

FIGURE 7: Calculated 1s2p RIXS map for $10Dq=3.0$ eV with 2p XES projection for Cu^{2+} ($3d^9$) for $10Dq=3.0$ eV. The 2p XES appears identical to the 2p XAS. The mixing induced by the crystal field symmetry breakdown enables to populate the $J = 1/2$ and $J = 3/2$ final states in direct 2p XAS.

RIXS spectrum is visible, in addition to the background from the edge [2].

4.2. $3d^0$: Tetravalent Titanium Ti^{4+} —1s XAS Peaks Split by $10Dq$. In the following, we discuss the differences between 2p XAS and 1s2p RIXS for the case of tetravalent titanium (Ti^{4+}). Here, the initial state configuration $1s^2 2p^6 3d^0$ has no partially filled shells. This is interesting because the resulting selection rules are straightforward: the nature of the probed final states reflects the nature and symmetry of the transition operators. The transition into the intermediate state promotes a 1s electron into the 3d band yielding a $1s^1 2p^6 3d^1$ electron configuration. The final state in 1s2p RIXS and 2p XAS is in this case $1s^2 2p^5 3d^1$.

FIGURE 8: Splitting of the intermediate state spin singlet and triplet terms $^1,^3D$ due to 3d SOC ζ_{3d} for a Ti^{4+} ion into D_1 , D_2 , and D_3 . States accessible in 1s XAS ($J = 2$) are shown in blue. However, the existing terms with $J = 1$ or 3 cannot be populated and will therefore not contribute to the spectrum.

$$\begin{aligned}
 1s2p \text{ RIXS: } 1s^2 2p^6 3d^0 &\xrightarrow[1s \text{ XAS}]{\Delta J = \pm 2} 1s^1 2p^6 3d^1 \xrightarrow[2p \text{ XES}]{\Delta J = 0, \pm 1} 1s^2 2p^5 3d^1, \\
 2p \text{ XAS: } 1s^2 2p^6 3d^0 &\xrightarrow[2p \text{ XAS}]{\Delta J = 0, \pm 1} 1s^2 2p^5 3d^1.
 \end{aligned}
 \quad (16)$$

The $3d^0$ case enables to describe the effect of the crystal field on the intermediate state, the interferences in the 1s2p RIXS process, and the more complex multi-electronic effects in the final state. It provides an extent to $L_{2,3}$ -edge considerations of $3d^0$ ions previously described in [35].

4.2.1. Atomic Case with Spin-Orbit Coupling. We start again with the case of an isolated Ti^{4+} ion ($3d^0$) where the effect of the solid state, that is, the crystal field, is neglected. The initial state configuration of Ti^{4+} is $1s^2 2p^6 3d^0$. Since all shells are full, $\mathcal{S} = 0$ and $\mathcal{L} = 0$. The $\mathcal{L}, \mathcal{S}$ -coupled total angular momentum is thus $J = 0$, and the initial state symmetry is the *totally symmetric* term 1S_0 .

The electronic configuration of the intermediate state in 1s2p RIXS of Ti^{4+} is $1s^1 2p^6 3d^1$, corresponding to the total orbital angular momentum $\mathcal{L} = 2$ and total spin angular

momentum $\mathcal{S} = 0$ or $\mathcal{S} = 1$ giving the Russel-Saunders terms 1D and 3D ($2 \cdot 10 = 20$ microstates). Considering the spin-orbit interaction in the $\mathcal{L}, \mathcal{S}$ coupling scheme, one obtains $J = 2$ for the 1D term and $J = 1, 2$, and 3 for the 3D term (Figure 8). The splitting of these four terms (1D_2 , 3D_1 , 3D_2 , and 3D_3) is defined by the 3d SOC ζ_{3d} and exchange interaction G_{sd}^2 , which are both small (32 meV and 46 meV, resp.). The calculated energy splitting is $\Delta E = 92$ meV and is beyond the reach of current experimental resolution and not resolved in our calculations discussed here.

The electric quadrupole transition of the 1s XAS enables to reach the intermediate states with $J = 2$, though here 3d SOC ζ_{3d} is small and transitions to the spin triplet term 3D_2 will be weak, such that the 1s XAS is dominated by the transition in the spin singlet term 1D_2 .

The final state electronic configuration is $1s^2 2p^5 3d^1$ with two partially filled shells that have to be accounted for: the 2p and the 3d shell. The total orbital angular momentum $\mathcal{L}$ of the final state electronic configuration is $\mathcal{L} = 1, 2$, and 3. The total spin angular momentum $\mathcal{S}$ of the final state electronic configuration is $\mathcal{S} = 0, 1$. This gives in the atomic case the spin singlet and triplet terms $^1,^3P$, $^1,^3D$, and $^1,^3F$.

FIGURE 9: Splitting of the final state terms $^{1,3}P$, $^{1,3}D$, and $^{1,3}F$ due to spin-orbit coupling for Ti^{4+} .

FIGURE 10: Calculated 1s2p RIXS map with 2p XES projection and the 2p XAS ($L_{2,3}$ -edge) for an isolated Ti^{4+} ($3d^0$) ion in O_3 symmetry.

As previously described by de Groot et al. [35], when spin-orbit interaction is neglected, the selection rules for the electric dipole transition in 2p XAS with $\Delta\mathcal{S} = 0$ and $\Delta\mathcal{L} = \pm 1$ allow only to reach the singlet 1P term from the 1S initial state, leading to one peak only (the L_2 -edge). The L_3 -edge, corresponding to transitions into the spin triplet term 3P , would have zero intensity. But in fact the strong 2p spin-orbit coupling ζ_{2p} in the final state ($\mathcal{J}$ is used) leads to three peaks, two of them forming the L_2 - and L_3 -edges, and a third weak peak related to triplet transitions.

The derivation of the total angular momentum $\mathcal{J}$ of the final state electronic configuration in the $\mathcal{L}\mathcal{S}$ coupling scheme yields the term symbols illustrated in Figure 9.

The direct electric dipole transition in 2p XAS with $\Delta\mathcal{J} = 0, \pm 1$ ($\mathcal{J} = 0 \rightarrow \mathcal{J} = 0$ forbidden) starts for Ti^{4+} from the total symmetric term 1S_0 , which allows to reach all final states with $\mathcal{J} = 1$ (P_1 and D_1 , marked with a red circle in Figure 9). The L_2 - and L_3 -edges are separated by the 2p spin-orbit coupling ζ_{2p} corresponding to transitions into the 1P_1 (L_2 -edge) and 3D_1 (L_3 -edge) terms. More precisely, from the squared matrix elements, we find that the second peak is dominated by 3D_1 contribution of 60%, adding 36% of 1P_1 and 4% of 3P_1 character. The small third peak in the 2p XAS, at $E_T \approx -5$ eV in Figure 10, is related to transitions into the 3P_1 terms. Though the resolution chosen in our calculations does not reveal them as individual peaks, the direct Coulomb and exchange terms are not negligible. As discussed by de Groot et al. [35], they lead to a splitting of the $L_{2,3}$ -

edge into three absorption lines including a redistribution of the intensities.

In the 1s2p RIXS process, the 2p XES decays with $\Delta\mathcal{J} = 0, \pm 1$ starting from the intermediate states with $\mathcal{J} = 2$ (D_2) and enables to reach the final states $P_{1,2}$, $D_{1,2,3}$, and $F_{2,3}$ with $\mathcal{J} = 1, 2$, and 3 (terms shown in green Figure 9). Therefore, all $\mathcal{J}$ values except 0 and 4 are reachable.

With this, one can draw for Ti^{4+} the atomic term scheme with spin-orbit coupling for the two-step 1s2p RIXS and the one-step 2p XAS process as shown in Figure 11.

The intermediate state is the key element when comparing the direct 2p XAS and 1s2p RIXS. It enables to access additional terms in the 1s2p RIXS final state, adding multiple visible peaks in the energy transfer direction as shown in Figure 10. But in both cases, $\mathcal{J} = 0$ and 4 are not possible to reach.

In summary, so far, we have discussed the effect of the spin-orbit coupling in the atomic case in spherical symmetry (O_3), but neglecting any crystal field. With the above, one can describe the 1s XAS with only one visible peak due to transitions into the 1D_2 intermediate state term. The 3d spin-orbit coupling ζ_{3d} and exchange interaction G_{sd} lead to small splittings which are not visible in this plot. Furthermore, the small 3d SOC may induce some mixing adding weak transitions into the 3D_2 term.

The splitting of the 2p XAS is dominated by the large 2p SOC ζ_{2p} separating the L_2 -edge from the L_3 -edge, for example, the spin singlet and the triplet states. The 2p XES on the other hand consists of transitions from the intermediate

FIGURE 11: Atomic term scheme with spin-orbit coupling for Ti^{4+} ($3d^0$) comparing the two-step (1s XAS, 2p XES) 1s2p RIXS and the one-step 2p XAS pathways. The two 1s XAS transitions are separated by the small 3d SOC, Coulomb, and exchange interactions; hence, the splitting is small. The direct dipole transitions in 2p XAS can only populate the final states with $\mathcal{J} = 1$, while the dipole decays in 2p XES can reach final states with $\mathcal{J} = 1, 2$, and 3. However, terms with $\mathcal{J} = 0$ or 4 cannot be populated in either case and thus do not contribute to the spectrum. Nonaccessible terms are omitted for clarity.

FIGURE 12: Branching of the intermediate state terms 1D and 3D of Ti^{4+} ($3d^0$) due to 3d SOC and an O_h CF. Symmetries accessible in the quadrupole 1s XAS step (GS $\rightarrow$ IS) are shown in blue.

state with $\mathcal{J} = 2$ IRREP (mostly 1D_2) into the final states with $\mathcal{J} = 1, 2$, and 3 IRREPs resulting multiple visible peaks in the energy transfer direction. All final state terms are also split by the exchange and direct Coulomb interactions, G_{pd} and F_{pd} , respectively.

4.2.2. Considering an O_h Crystal Field. We now consider the effect of an octahedral O_h crystal field. The totally symmetric initial state term 1S_0 branches in O_h into $^1A_{1g}[A_{1g}]$. Formal consideration of an O_h crystal field and 3d spin-orbit interaction leads to the branching of the intermediate state terms 1D and 3D into eight terms. The scheme in Figure 12 illustrates these branchings of the terms due to an O_h crystal field and the 3d spin-orbit interaction ζ_{3d} ($\mathcal{S} = 0 \rightarrow \otimes A_{1g}$ and $\mathcal{S} = 1 \rightarrow \otimes T_{1g}$).

In spite of several available intermediate state terms, starting from the initial state $^1A_{1g}$ and using the T_{2g} and E_g IRREPs, representing the quadrupole 1s XAS operator, and the *product table* (Table 3) reflecting the orbital

momentum selection rules, one finds the accessible intermediate state symmetries.

$$\begin{array}{ccc} ^1A_{1g} & \otimes & T_{2g} = ^1T_{2g}, \\ \underbrace{^1A_{1g}}_{1s^2 3d^0} & \otimes & \underbrace{E_g}_{1s \text{ XAS}} = \underbrace{^1E_g}_{\text{Accessible terms}}. \end{array} \quad (17)$$

In other words, from the *totally symmetric* ground state A_{1g} (O_h), only the E_g (O_h) and T_{2g} (O_h) symmetries can be reached in the intermediate state via a quadrupole 1s XAS transition. Hence, for sufficiently large values of $10Dq$, relative to the broadenings used in a calculation (or the experimental resolution in a measurement), two distinct peaks can be observed in the 1s XAS projection (Figure 13). Because the 3d spin-orbit coupling ζ_{3d} is small, the transitions to the spin singlet intermediate states are dominating (i.e., matrix elements are the largest), while the transitions via the $J = 2$ IRREP from triplet 3D should be weak. The 1s

FIGURE 13: Calculated 1s XAS projections of a 1s2p RIXS for Ti^{4+} ($3d^0$) scaling the octahedral crystal field parameter $10Dq$ from 0.1 eV to 3.0 eV with an energy level diagram as overlay. The splitting of the 3d level into the two peaks T_{2g} and E_g due to the crystal field is visible.

XAS is dominated by transitions to the E_g and T_{2g} terms from the 1D_2 .

In an O_h crystal field, the final state IRREPs with $\mathcal{F} = 0, 1, 2, 3$ and 4 (see Figure 11) branch, respectively, into the $\mathcal{L}\mathcal{S}$ -coupled terms: A_{1u} , T_{1u} , $E_u \oplus T_{2u}$, $A_{2u} \oplus T_{1u} \oplus T_{2u}$, and $A_{1u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$. The 2p XES in 1s2p RIXS from the two intermediate state terms T_{2g} and E_g via the electric dipole operator, described by the T_{1u} IRREP, leads to

$$\begin{aligned} T_{2g} \otimes T_{1u} &= A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}, \\ \underbrace{E_g}_{1s^1 3d^1} \otimes \underbrace{T_{1u}}_{2p \text{ XES}} &= \underbrace{T_{1u} \oplus T_{2u}}_{\text{Accessible final states}}. \end{aligned} \quad (18)$$

It is noteworthy here that only the intermediate state with T_{2g} symmetry can access in the 2p XES decay the A_{2u} and E_u final state symmetries. The T_{1u} and T_{2u} final state terms are however accessible from both T_{2g} and E_g intermediate state symmetries. Furthermore, we note that the intermediate state symmetry A_{1u} is not reachable as the final state symmetry and will therefore not contribute to the 2p XES spectrum.

On the other hand, in 2p XAS, the possible final states must have T_{1u} symmetry; otherwise, the transition matrix element equals zero. As can be seen from the branchings of $\mathcal{F}$ (O_3) in and octahedral crystal field (Table 2), the T_{1u} IRREP can be reached not only from the $\mathcal{F} = 1$ IRREP but also from the $\mathcal{F} = 3$ and $\mathcal{F} = 4$ IRREPs.

This results in only seven possible T_{1u} IRREPs in O_h symmetry, or in other words, only seven final states are reachable among the 60 available. The 2p XAS spectrum consists, in principle, of seven lines, as can be seen in Figure 14, where

the calculated spectra for Ti^{4+} ($3d^0$) for a crystal-field splitting of $10Dq = 2.1$ eV are shown. While only spin singlet states would be reached in the absence of 2p SOC, the consideration of the strong spin-orbit coupling in the final state induces a mixing of the spin singlet and triplet states. This weakens the spin selection rule $\Delta S = 0$ allowing also transitions into former spin triplet states (e.g., $^3T_{2u}$, $^3T_{1u}$, 3E_u , and $^3A_{2u}$).

This enables to draw the electronic term scheme in Figure 15 illustrating the different pathways in 1s2p RIXS and 2p XAS for $3d^0 \text{Ti}^{4+}$ in O_h symmetry. The accessible 1s2p RIXS final state terms are given in (18), while, as discussed above, the 2p XAS can only reach final states with T_{1u} symmetry ($A_{1g} \otimes T_{1u} = T_{1u}$).

Similarly to the $3d^9$ case (Cu^{2+}) discussed in Section 4.1, comparing the final states, it becomes clear once again that the key elements are the intermediate states from which the 2p XES decays and thus enables to reach more final states when compared to the direct 2p XAS.

This overall results in the 1s2p RIXS maps shown in Figure 14. The total RIXS map is decomposed into the E_g and T_{2g} quadrupole absorption components. The selective absorption towards each intermediate state is obtained. Experimentally, this dichroic behaviour has been observed for Ti^{4+} in cubic oxides such as the prototypal SrTiO_3 [36]. The 1s2p RIXS spectra calculated for each of the two absorption peaks are shown (Figure 14(a)), and the 60 final states are labelled with their total angular IRREP (Figure 14(b)). This enables to see that both, the 1s2p RIXS and 2p XAS, probe the T_{1u} final state symmetry. We further observe that within the four main peaks in 2p XAS, the first peaks of the L_3 (at $E_T \approx -3.5$ eV) and of the L_2 (at $E_T \approx 2$ eV) are stronger via the T_{2g} absorption channel of the 1s2p RIXS than the E_g and vice-versa: the second peaks of the L_3 ($E_T \approx -1$ eV) and of the L_2 (at $E_T \approx 4.5$ eV) are stronger via the E_g absorption channel of the 1s2p RIXS than via the T_{2g} . This can be understood in a single electron picture with the crystal field splitting of the final state: the lower states of the L_3 -edge contain the 3d single electron in the t_{2g} orbitals while the higher energy states have the 3d electron in the e_g orbitals and similarly for the L_2 -edge [37].

4.2.3. 1s2p RIXS Experiments of $3d^0$ Systems. Experimental 1s XAS spectra (e.g., HERFD) of titanium oxides in the solid state often show more than two peaks in the pre-edge, which contradicts the result shown in Figure 13. The reason is that there are additional dipole transitions at energies overlapping with the quadrupole prepeaks. These dipole peaks are related to so-called *nonlocal* peaks, where the 4p states from the absorbing ion mix with the 3d states of the neighbouring ions [3]. In addition, we note that for high valent ions such as Ti^{4+} , charge transfer is important for the detailed description of the 2p XAS and 1s2p RIXS spectral shapes [37].

Experimental 1s2p RIXS experiments have been published on TiO_2 by Glatzel et al. [38] and Kas et al. [39]. The 1s2p RIXS planes show the quadrupole pre-edges and the nonlocal peaks. The 1s2p RIXS cross-section at the first quadrupole peak shows three peaks in qualitative agreement

FIGURE 14: (a) Calculation of the 1s2p RIXS spectra for Ti^{4+} ($3d^0$) with $10Dq = 2.1$ eV separated into the quadrupole components Y_l^m (with $m = 0, 1$ and $l = 2$) in spherical symmetry. They translate into the T_{2g} and E_g IRREPs describing the quadrupole 1s XAS transitions. The term scheme insets illustrate the corresponding pathways. (b) The corresponding 2p XES projections onto the energy transfer axis for the two quadrupole components and the calculated 2p XAS ($L_{2,3}$ -edge).

FIGURE 15: Multielectronic term scheme comparing the 2p XAS and the 1s2p RIXS pathways. The two quadrupole 1s XAS transitions with T_{2g} and E_g symmetry lead to two different intermediate state symmetries. The subsequent dipole decays (2p XES) with T_{1u} symmetry yield multiple 1s2p RIXS final state symmetries. The direct 2p XAS ($L_{2,3}$ -edge) transition with T_{1u} symmetry can on the other hand only access the T_{1u} symmetry in the final state. Noncontributing states are omitted for clarity.

FIGURE 16: Atomic term scheme with spin-orbit coupling for Ni^{2+} comparing the two-step (1s XAS, 2p XES) 1s2p RIXS and the one-step 2p XAS pathways. Here, it should be noted that the two IS terms are only separated by the small 3d SOC ζ_{3d} . Note that the final state is similar to Ti^{4+} . Nonaccessible terms (e.g., final states with $J = 0$) are omitted for clarity.

with the t_{2g} calculation in Figure 14. Bagger et al. analysed the quadrupole and dipole RIXS separately [1]. We note that the ionic limit as calculated in Figure 14 is likely to be reached by 1s2p RIXS experiments at the K-edge on divalent calcium systems (Ca^{2+}), including octahedral CaO and cubic CaF_2 .

4.3. $3d^8$: Divalent Nickel Ni^{2+} —Single Peak in 1s XAS. In this part, we investigate the elementary differences between 2p XAS and 1s2p RIXS for a divalent nickel ion (Ni^{2+} , $3d^8$). As we will show, the electronic configurations of the different steps of 1s2p RIXS present strong analogies with the case of Ti^{4+} ; the main difference being the nature of the initial state. We start again with the atomic case by deriving the $\mathcal{J}$ values as IRREPs.

$$\begin{aligned}
 \text{1s2p RIXS: } 1s^2 2p^6 3d^8 &\xrightarrow[1s \text{ XAS}]{\Delta\mathcal{J}=\pm 2} 1s^1 2p^6 3d^9 \xrightarrow[2p \text{ XES}]{\Delta\mathcal{J}=0, \pm 1} 1s^2 2p^5 3d^9, \\
 \text{2p XAS: } 1s^2 2p^6 3d^8 &\xrightarrow[2p \text{ XAS}]{\Delta\mathcal{J}=0, \pm 1} 1s^2 2p^5 3d^9.
 \end{aligned}
 \quad (19)$$

The electronic configuration of the initial state of Ni^{2+} is $1s^2 2p^6 3d^8$ with two holes in the 3d shell. The multielectronic interactions lead to 45 states spread across the terms 3F , 3P , 1G , 1D , and 1S [13]. In spherical symmetry (O_3), the atomic ground state is 3F ($\mathcal{L} = 3$ and $\mathcal{S} = 1$). The 3d spin-orbit coupling $\zeta_{3d} \approx 0.1$ eV induces the splitting of the 3F term into the three terms:

$$^3F \xrightarrow{3d \text{ SOC}} ^3F_2, ^3F_3, ^3F_4. \quad (20)$$

From those three IRREPs with $\mathcal{J} = 2, 3$, and 4, the 3F_4 term with $\mathcal{J} = 4$ is the ground state term symbol.

The electronic configuration of the intermediate state in 1s2p RIXS of Ni^{2+} is $1s^1 2p^6 3d^9$ (one hole in the 1s shell and one hole in the 3d shell) which translates into the two terms 1D and 3D ($2 \cdot 10 = 20$ microstates). It is noteworthy that this is identical to the intermediate state of Ti^{4+} described above (Section 4.2) due to the *electron-hole equivalency*. The 3d spin-orbit interaction splits the two terms into the 1D_2 (for $\mathcal{S} = 0$) and 3D_1 , 3D_2 , and 3D_3

(for $\mathcal{S} = 1$) Russell-Saunders terms. The resulting splittings distribute the four terms in energy over $\Delta E \approx 0.25$ eV for which the 1s XAS will appear only as a single peak due to the resolution chosen in our calculations, analogue to the Ti^{4+} atomic case.

The difference in the 1s XAS step in 1s2p RIXS between the $3d^8 \text{Ni}^{2+}$ and $3d^0 \text{Ti}^{4+}$ cases arises from the spin multiplicity of the initial state. In both cases, the electric quadrupole absorption leads to a $\mathcal{J} = 2$ intermediate state. However, because of the small 3d spin-orbit coupling ($\zeta_{3d} = 0.1$ eV), the spin multiplicity is mostly conserved in the transition and the absorption from the spin triplet initial state of Ni^{2+} leads to the 3D_2 state. For Ti^{4+} on the other hand, mainly, the 1D_2 term is reached.

The electronic configuration of the final state in 2p XAS and 1s2p RIXS of Ni^{2+} is $1s^2 2p^5 3d^9$. This is again strictly analogue to the final state of Ti^{4+} . The final state configuration corresponds to several atomic terms ($^1, ^3P$, $^1, ^3D$, and $^1, ^3F$) which are split further due to the strong 2p spin-orbit coupling $\zeta_{2p} = 11.5$ eV. The total symmetry final state terms are represented with integer $\mathcal{J}$ values ranging from $\mathcal{J} = 0$ to $\mathcal{J} = 4$. The detailed splittings are given above in Figure 9 in Section 4.2.

Only the final state terms with $\mathcal{J} = 1, 2$, and 3 are formally accessible in the 1s2p RIXS from the intermediate state with $\mathcal{J} = 2$ via 2p XES decays ($\Delta\mathcal{J} = 0, \pm 1$). The direct 2p XAS (with $\Delta\mathcal{J} = 0, \pm 1$) on the other hand can only reach the final state terms with $\mathcal{J} = 3$ or $\mathcal{J} = 4$ from the ground state with $\mathcal{J} = 4$. Altogether, the selection rules for the atomic case can be summarised as

$$\begin{aligned}
 \text{1s2p RIXS: } \mathcal{J} = 4 &\xrightarrow[1s \text{ XAS}]{\Delta\mathcal{J}=\pm 2} \mathcal{J} = 2 \xrightarrow[2p \text{ XES}]{\Delta\mathcal{J}=0, \pm 1} \mathcal{J} = 1, 2, 3 \\
 \text{2p XAS: } \mathcal{J} = 4 &\xrightarrow[2p \text{ XAS}]{\Delta\mathcal{J}=0, \pm 1} \mathcal{J} = 3, 4.
 \end{aligned}
 \quad (21)$$

This is also illustrated in the combined term scheme shown in Figure 16.

The calculated 1s2p RIXS of an isolated Ni^{2+} ion (O_3) is compared to the 2p XAS in Figure 17. The transitions are labelled with the dominant contribution of the

FIGURE 17: Calculated 1s2p RIXS for an isolated Ni^{2+} ion ($3d^8$) representing the atomic case. The projection of the total 1s2p RIXS map onto the energy transfer axis is shown together with the 2p XAS ($L_{2,3}$ -edge) in dashed red and the corresponding stick spectrum.

corresponding final state terms. The four peaks in the 2p XAS (three in the L_3 and one in the L_2) correspond to the $\mathcal{J} = 3$ and $\mathcal{J} = 4$ IRREPs. It is noteworthy here that the 3F_4 final state term is special in the sense, that it can be accessed only in 2p XAS, but its population via 1s2p RIXS is forbidden. Hence, in 2p XAS, the peak at $E_T \approx -4$ eV is related to the $\mathcal{J} = 4$ IRREP (dominated by 3F_4), while in 1s2p RIXS the peak at $E_T \approx -4$ eV in the 2p XES decay relates to transitions into the final state IRREP $\mathcal{J} = 2$ (mostly 1D_2). In other words, though it seems that the same peak at $E_T \approx -4$ eV appears in the 2p XAS as well as in the 2p XES decay in 1s2p RIXS, it is in each case related to a *different* final state IRREP.

Closer inspection of the sticks reveals that the 3F_3 term does not appear as a dominant contribution, but instead, the 1F_3 term appears twice. This is due to the fact that the atomic terms lose their meaning when spin-orbit interaction is included. Then $\mathcal{J} = 3$ becomes the identifying IRREP which is formally a linear combination of 1F_3 , 3D_3 , and 3F_3 . Here, it happens to be the case that the 1F_3 contribution is dominant in two $\mathcal{J} = 3$ IRREPs.

As expected, the $\mathcal{J} = 0$ IRREP (dominated by the 3P_0 term), as well as the $\mathcal{J} = 1$ IRREP (3P_1 and 3D_1 terms), has no contribution to the 2p XAS spectrum. Furthermore, also, transitions into the $\mathcal{J} = 2$ IRREPs (P_2 , F_2 , and F_2 terms) are not appearing in 2p XAS.

In the 2p XES decay, on the other hand, the $\mathcal{J} = 2$ IRREPs have a much stronger contribution to the spectrum. Those peaks, related to the final state IRREPs $\mathcal{J} = 2$, show in this example the largest difference between the 2p XAS and 2p XES as can be seen in Figure 17.

4.3.1. Considering an O_h Crystal Field. The crystal field splitting in O_h symmetry of the atomic terms of the initial state configuration of Ni^{2+} ($1s^2 2p^6 3d^8$) is well-known and described with the Tanabe-Sugano diagram. The ground state atomic term symbol 3F splits into $^3A_{2g}$, $^3T_{2g}$, and $^3T_{1g}$ and gives $^3A_{2g}$ as the octahedral crystal field ground state. The inclusion of the 3d spin-orbit coupling ($\mathcal{S} = 1 \rightarrow \otimes T_{1g}$) translates the ground state term as $^3A_{2g} \otimes T_{1g} = T_{2g}$. Thus,

FIGURE 18: 1s XAS projections of the calculated 1s2p RIXS map for Ni^{2+} ($3d^8$) showing only one peak as the T_{2g} term is not reachable. The red lines indicate the energy levels of the intermediate state.

the crystal field ground state of $3d^8 \text{ Ni}^{2+}$ including 3d spin-orbit interaction is $^3A_{2g}[T_{2g}](O_h)$.

The crystal field splitting of the 1s2p RIXS intermediate state of Ni^{2+} is analogue to Ti^{4+} as the $^1,^3D$ terms split into $^1,^3E_g \oplus ^1,^3T_{2g}$. From the ground state symmetry $^3A_{2g}$ (neglecting 3d SOC), the 1s XAS IRREPs T_{2g} and E_g enable to reach only $^3T_{1g}$ and 3E_g intermediate state symmetries:

$$^3A_{2g} \xrightarrow{\otimes T_{2g}} ^3T_{1g}, \quad (22)$$

$$^3A_{2g} \xrightarrow[\text{1sXAS}]{\otimes E_g} ^3E_g. \quad (23)$$

In other words, the intermediate state term $^3T_{2g}$ cannot be reached by the electric quadrupole 1s XAS absorption.

FIGURE 19: Multielectronic term scheme for Ni^{2+} ($3d^8$) comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Populating the T_{2g} intermediate state would require a two-electron transition in $3d^8$.

Hence, only the $1s$ XAS IRREP E_g leads to an existing intermediate state symmetry: $3E_g$. This is illustrated in Figure 18. As a result, the $1s$ XAS projection of the total $1s2p$ RIXS map will consist only of transitions into the $3E_g$ intermediate state symmetry, because the quadrupole $1s$ XAS transition into the $3T_{2g}$ intermediate state term is forbidden. We note that the spin singlet and triplet intermediate states are only separated by a few meV by the $3d$ spin-orbit, Coulomb, and exchange interactions (e.g., $\zeta_{3d} \approx 0.1$ eV). Therefore, the $1s$ XAS transitions appear as a single peak due to the resolution chosen in our calculations.

The single peak observed in the $1s$ XAS step for Ni^{2+} ($3d^8$) is the first important difference with Ti^{4+} ($3d^0$), which arises from the different nature of the initial state term. This can be further understood in a single electron picture: since the two holes of the initial state of Ni^{2+} are in the e_g orbitals, the excited $1s$ electron can only go to the empty e_g orbitals ($3E_g$ intermediate state). On the contrary, in the case of Ti^{4+} (Section 4.2), both e_g and t_{2g} orbitals are empty leaving both E_g and T_{2g} intermediate state symmetries accessible.

When the crystal field ($10Dq$) is large with respect to the other electronic interactions, such as the $3d$ spin-orbit interaction ζ_{3d} , the $1s$ XAS step of the $1s2p$ RIXS can be described well with the noncoupled IRREPs ($\mathcal{L}$ and $\mathcal{S}$ are good quantum numbers). However, when the crystal field is weak or when the electronic interactions are stronger, such as the ζ_{2d} spin-orbit, it is necessary to use the $\mathcal{L}\mathcal{S}$ -coupled terms. The spin-orbit coupling translates the intermediate state terms into the same total angular symmetry terms as for Ti^{4+} (see Figure 12). From this, it is evident that the intermediate state offers four different symmetries A_{2g} , E_g , T_{1g} , and T_{2g} from which the $2p$ XES decays can occur.

The branching in the octahedral symmetry of the final state of Ni^{2+} is again analogue as Ti^{4+} (see Section 4.2). Those terms translate in an O_h crystal field to the *ungerade* symmetries: A_{1u} , A_{2u} , E_u , T_{1u} , and T_{2u} . The dipole

$2p$ XES decays in $1s2p$ RIXS from the intermediate state terms give

$$E_g \xrightarrow{\otimes T_{1u}} T_{1u} \oplus T_{2u}, \quad (24)$$

$$T_{1g} \xrightarrow{\otimes T_{1u}} A_{1u} \oplus E_u \oplus T_{1u} \oplus T_{2u}, \quad (25)$$

$$T_{2g} \xrightarrow[2p \text{ XES}]{\otimes T_{1u}} \underbrace{A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}}_{\text{Accessible FS terms}}. \quad (26)$$

From that, we find that in $2p$ XES all final state symmetries can be reached. However, for $2p$ XAS, the dipole transition (T_{1u}) starts from the T_{2g} ground state.

$$T_{2g} \xrightarrow[2p \text{ XAS}]{\otimes T_{1u}} \underbrace{A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}}_{\text{Accessible FS terms}}. \quad (27)$$

From that, we find that the reachable $2p$ XAS final states can have A_{2u} , E_u , T_{1u} , or T_{2u} symmetry. In other words, all intermediate terms, except those with A_{1u} , can be reached in $2p$ XAS. This is identical to the third case of the RIXS as described above in (26). However, the difference between the transition matrix elements of XAS and RIXS can result in different intensities.

The comparison between the $2p$ XAS and $1s2p$ RIXS selection rules is summarised in the scheme in Figure 19.

Comparing this case with the case of Ti^{4+} in an O_h crystal field enables to highlight the crucial influence of the ground state symmetry.

We conclude with the calculated $1s2p$ RIXS maps and a comparison with the corresponding $2p$ XAS as shown in Figure 20.

The calculations reveal two aspects: first, we notice the direct $2p$ XAS and the $2p$ XES final state spectra appear to have a similar appearance. This can be explained with the term scheme in Figure 19 illustrating that the $2p$ XES and the direct $2p$ XAS probe similar final state terms. Second,

FIGURE 20: Calculated 1s2p RIXS for the ion Ni^{2+} ($3d^8$) for $10Dq = 0.9$ eV. As can be seen in the map reflecting the quadrupole IRREP T_{2g} (top row, left), the contribution to the spectrum is nonzero because of the small 3d spin-orbit interaction leading to a weak mixing of the states. However, its contribution is about 186 times weaker and thus neglectable in first approximation.

we note that the intensity of the contribution to the 1s2p RIXS via the quadrupole T_{2g} IRREP is two orders of magnitude weaker than the contribution via E_g 1s XAS IRREP. According to the strict $\mathcal{L} = \pm 2$ selection rule (e.g., when neglecting 3d spin-orbit coupling), no transitions arise from the T_{2g} absorption. However, the 3d spin-orbit interaction ζ_{3d} is in fact nonzero, though small. Hence, when looking at the total angular momentum IRREPs of the intermediate states (e.g., the terms including SOC) and the 1s XAS selection rules shown in (22), it appears that some intermediate states can be probed by the T_{2g} operator. In other words, the small but nonzero 3d spin-orbit coupling ζ_{3d} induces some mixing such that the contributions to the spectrum via the 1s XAS IRREP T_{2g} will be nonzero but weak. A direct comparison of the two 1s XAS transitions with T_{2g} and E_g symmetries shows that the T_{2g} spectrum multiplied by 186 is almost identical to the E_g spectrum (Figure 20).

4.3.2. 1s2p RIXS Experiments of $3d^8$ Systems. Experimental 1s2p RIXS spectra of $3d^8$ NiF_2 and molecular Ni^{2+} complexes have been published by Glatzel et al. [14, 40]. Within the resolution of the measurement, the NiF_2 spectrum is exactly reproduced by the crystal field calculation [14].

5. 1s2p RIXS for Other $3d^N$ Configurations

In this section, the remaining $3d^N$ configurations ($N \in \{1, \dots, 7\}$) are discussed in a more condensed manner. Furthermore, for the systems with a $3d^4$, $3d^5$, $3d^6$, and $3d^7$ ground state, a high spin (HS) and a low spin (LS) case is presented. This is due to the fact that the crystal field splitting energy ($10Dq$) and the pairing energy in those cases are competing. In other words, for sufficiently large values of $10Dq$, the ground state changes from high spin to low spin. Subsequently, this affects the possible transitions within those systems and hence the resulting spectra will have a different appearance [13].

FIGURE 22: Multielectronic term scheme for Ti^{3+} ($3d^1$) comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Where SOC is included, the spin multiplicity is omitted as its meaning is lost in that case.

${}^2{}^4F$, ${}^2{}^4P$, 2G , and 2S (Table 1). Because the Coulomb exchange G_{sd} is small, the splitting between the doublet and the quartet spin states is small and beyond the accessible energy resolution.

Using Table 2, one finds the branchings of the atomic states in an O_h crystal field. The resulting O_h term symbols for a $1s^1 3d^2$ configuration are ${}^{2,4}A_{2g}$, ${}^{2,4}T_{2g}$, ${}^{2,4}T_{1g}$, ${}^2A_{1g}$, and 2E_g . The energy splitting of these O_h crystal field terms is qualitatively similar to the Tanabe-Sugano diagram of $3d^2$. In the particular case of Ti^{3+} , the result of the calculation is given in Figure 21 where the $1s$ XAS projections are shown together with the crystal field terms assigned.

Because the $3d$ spin-orbit coupling is weak, one can neglect it in first approximation; the spin conservation leads to the $1s$ XAS being dominated by transitions into the spin doublet states, while the matrix elements of the transition to the spin quartet terms are much smaller. In the following, we will therefore focus on the doublet spin states.

$${}^2T_{2g} \xrightarrow{\otimes T_{2g}} {}^2A_{1g} \oplus {}^2E_g \oplus {}^2T_{1g} \oplus {}^2T_{2g}, \quad (37)$$

$$\underbrace{{}^2T_{2g}}_{\text{GS}} \xrightarrow[1s \text{ XAS}]{\otimes E_g} \underbrace{{}^2T_{1g} \oplus {}^2T_{2g}}_{\text{Reachable IS terms}}. \quad (38)$$

This shows, in an O_h crystal field, starting from the ${}^2T_{2g}$ ground state, the $1s$ XAS operators T_{2g} and E_g enable to reach all even terms except the ${}^2A_{2g}$ IRREP. This results in numerous multiplet states reached in the intermediate state of $1s2p$ RIXS. The $1s$ XAS projections in Figure 21 show the splitting of the peaks due to the scaling of the crystal field parameter $10Dq$. We note that the ${}^2A_{2g}$ (2F) does not get any intensity in the absorption step of $1s2p$ RIXS in agreement with the $1s$ XAS selection rules as found in the expressions given in (37) and (38).

The previous didactic examples (Section 4) demonstrated the necessity to consider the $\mathcal{L}\mathcal{S}$ -coupled terms to describe the $2p$ XES transitions to the final state in

$1s2p$ RIXS and the $2p$ XAS. In the intermediate state, the O_h total symmetry IRREPs of the doublet spin states are obtained by coupling the reachable orbital IRREPs with the spin IRREP ($\mathcal{S} = 1/2 \rightarrow \otimes E_{1/2g}$):

$$\begin{aligned} A_{1g} \otimes E_{1/2g} &= E_{1/2g}, \\ E_g \otimes E_{1/2g} &= F_{3/2g}, \\ T_{1g} \otimes E_{1/2g} &= E_{1/2g} \oplus F_{3/2g}, \\ T_{2g} \otimes E_{1/2g} &= E_{5/2g} \oplus F_{3/2g}. \end{aligned} \quad (39)$$

The result shows that all three odd total symmetric IRREPs $E_{1/2g}$, $F_{3/2g}$, and $E_{5/2g}$ are thus reachable in the intermediate state. In other words, all three odd IRREPs are contributing to the $2p$ XES decays.

The final state configuration $1s^2 2p^5 3d^2$ contains $6 \cdot 45 = 270$ microstates due to the hole in the $2p$ shell. The atomic term symbols span from S to H with spin doublets and quartets and $\mathcal{J}$ values ranging from $1/2$ to $11/2$ [13]. In an O_h crystal field, these terms branch into the three IRREPs $E_{1/2u}$, $F_{3/2u}$, and $E_{5/2u}$ (Table 2).

The $2p$ XES dipole transition IRREP T_{1u} gives the transitions from the three intermediate state symmetries into all three final state symmetries as given in (33), (34), and (35).

For the direct $2p$ XAS, as mentioned above, the two ground state terms $F_{3/2g}$ and $E_{5/2g}$ are to be considered due to the small splitting. This leads with the dipole transition IRREP T_{1u} also to all three final state symmetries:

$$\begin{aligned} E_{5/2g} &\xrightarrow{\otimes T_{1u}} E_{5/2u} \oplus F_{3/2u} \\ F_{3/2g} &\xrightarrow[2p \text{ XAS}]{\otimes T_{1u}} E_{1/2u} \oplus 2F_{3/2u} \oplus E_{5/2u}. \end{aligned} \quad (40)$$

It becomes obvious that the selection rules enable to reach all three final state IRREPs in both cases: $2p$ XAS and $1s2p$ RIXS. This is summarised in the combined term scheme shown in Figure 22.

FIGURE 23: Calculated 1s2p RIXS spectrum for Ti^{3+} ($3d^1$) for $10Dq = 1.5$ eV shown together with some selected CIE slices. The stick spectrum at the bottom illustrates the distribution of the three final state terms $E_{1/2u}$, $F_{3/2u}$, and $E_{5/2u}$ with respect to the emissions.

Although it seems that all the final state symmetries can be reached in both cases, 2p XAS and the 2p XES in 1s2p RIXS, the calculated spectra shown in Figure 23 demonstrate that the RIXS intermediate state enables to select some specific final states.

According to the combined term scheme in Figure 22, the intermediate states T_{1g} , T_{2g} , and E_g enable to reach all final state symmetries. The calculated 1s2p RIXS together with some CIE slices is shown in Figure 23. However, due to the first term ${}^2T_{1g}$ corresponding to the excitation of the 1s

The second term ${}^2T_{1g}$ (from 2P atomic term symbol) corresponds to the absorption to the e_g orbitals and is consequently probed by the E_g absorption operator and corresponds to the “ e_g ” part of the final states. The intermediate state ${}^2A_{1g}$ (from 2S atomic term symbol) only gives a very weak absorption via the T_{2g} quadrupole operator in agreement with the selection rules as given in (37).

5.1.1.1. 1s2p RIXS Experiments of $3d^1$ Systems. Experimental 1s2p RIXS spectra of $3d^1V^{4+}$ ions in TiO_2 have been measured by Bordage [41]. However, the experimental resolution does not allow to compare the data in detail with the calculations as shown in Figure 23.

$$\begin{array}{l}
1s2p \text{ RIXS} : 1s^2 2p^6 3d^2 \xrightarrow{1s \text{ XAS}} 1s^1 2p^6 3d^3 \xrightarrow{2p \text{ XES}} 1s^2 2p^5 3d^3, \\
2p \text{ XAS} : 1s^2 2p^6 3d^2 \xrightarrow{2p \text{ XAS}} 1s^2 2p^5 3d^3.
\end{array}
\quad (41)$$

The initial state electron configuration $1s^2 2p^6 3d^2$ corresponds to the atomic ground state term $^3F(O_3)$ with 45 microstates. It translates into an O_h crystal field (without 3d SOC) into a $^3T_{1g}$ ground state symmetry with 9 microstates. By including 3d SOC ζ_{3d} , we find the further splittings of the $^3T_{1g}$ ground state term ($S = 1 \rightarrow \otimes T_{1g}$):

From these terms, E_g lies lowest in energy; hence, the ground state is ${}^3T_{1g}[E_g](O_h)$.

Because the 3d SOC is weak, the spin is conserved leading to the 1s XAS transitions being dominated by transitions into the spin triplet states, while the matrix elements of the transition to the spin quintet terms are weak. Thus, we will focus on the spin triplet symmetries.

$${}^3T_{1g} \xrightarrow[1s \text{ XAS}]{\otimes E_g} \underbrace{{}^3T_{1g} \oplus {}^3T_{2g}}_{\text{Accessible IS terms}}. \quad (44)$$

For the 2p XES decays in 1s2p RIXS, however, the inclusion of SOC is again required. Using the T_{1g} IRREP ($S=1 \rightarrow \otimes T_{1g}$) and the direct product table (Table 3), one finds the intermediate state symmetries including 3d

FIGURE 25: Multielectronic term scheme for Cr^{4+} ($3d^2$) comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Where SOC is included, the spin multiplicity is omitted as its meaning is lost in that case.

SOC ζ_{3d} as also shown in the combined term scheme in Figure 25.

$$\begin{aligned}
 {}^3A_{2g} \otimes T_{1g} &= T_{2g}, \\
 {}^3E_g \otimes T_{1g} &= T_{1g} \oplus T_{2g}, \\
 {}^3T_{1g} \otimes T_{1g} &= A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}, \\
 {}^3T_{2g} \otimes T_{1g} &= A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{2g}.
 \end{aligned} \tag{45}$$

The subsequent $2p$ XES starts from any of the intermediate state symmetries found in expression (45). The possible $2p$ XES final state symmetries are all even symmetries as given in expressions (28), (29), (30), (31), and (32).

The final state ($1s^2 2p^5 3d^3$) contains $6 \cdot 120 = 720$ microstates due to the hole in the $2p$ shell spanning $\mathcal{J}$ from 0 to 7. In an O_h crystal field, these terms branch into the five total symmetry IRREPs A_{1u} , A_{2u} , E_u , T_{1u} , and T_{2u} . In other words, all existing FS symmetries can be reached in the $2p$ XES.

Also for $2p$ XAS, spin-orbit interaction is crucial. Thus, starting from the ${}^3T_{1g}[E_g]$ (O_h) ground state and using the T_{1u} IRREP, we find that only T_{1u} and T_{2u} IRREPs are reached, which makes a drastic difference between $2p$ XAS and $1s2p$ RIXS. The selection rules for a $3d^2$ ground state system are summarised in Figure 25 showing all reachable symmetries.

According to the electric quadrupole selection rules derived in (43), the A_{2g} and E_g intermediate state symmetries are only reachable via the quadrupole T_{2g} IRREP. This is confirmed in Figure 26 (RIXS maps) where the low energy peak at $E_{in} = -2.25$ eV appears only in the RIXS map corresponding to the T_{2g} IRREP. The t_{2g} and e_g components appear well separated with (i) the t_{2g} components probed by the T_{2g} absorption giving two intense and narrow peaks at $E_T \approx -6.5$ eV and (ii) the e_g components probed by the E_g absorption leading to a larger group of final states spread in energy between $E_T = -5$ eV and 0 eV. Furthermore, it can be noted that the X-ray emission spectra ($2p$ XES) are here overall very rich. The

corresponding sticks in Figure 26 illustrate how dense the reachable final states are distributed. We observe that the $2p$ XAS and $1s2p$ RIXS differs mainly in the low energy final states: the $1s2p$ RIXS enhances the final states below $E_T \approx -2.5$ eV to which the $2p$ XAS transition matrix elements are weak. We note that the $1s2p$ RIXS spectra which are the closest to the $2p$ XAS spectrum are those obtained at the higher energy transfers at $E_T > 0$ eV.

Considering now the quantitative influence of the natural broadening as the principal limit of any experimental spectrum, it becomes clear that an experimental separation of the final states is impossible. However, high-resolution RIXS measurements enable to extract CIE slices similar to the illustrated examples shown in Figure 26.

And finally, in Figure 27, we show the $2p$ XES projections of the calculated $1s2p$ RIXS to illustrate its evolution when the crystal field value $10Dq$ is scaled from $10Dq = 0.1$ eV, ..., 3 eV.

5.2.1. $1s2p$ RIXS Experiments of $3d^2$ Systems. Experimental $1s2p$ RIXS spectra of $3d^2$ CrO_2 have been published by Zimmermann et al. [9]. Analysis of the magnetic circular dichroism (MCD) of the $1s2p$ RIXS revealed that the pre-edge structure that is visible in the $1s2p$ RIXS plane is dominated by a nonlocal contribution. The MCD data reveals the real quadrupole peak, but due to its low intensity and limited resolution, it does not allow to compare the quadrupole peak to the spectra calculated in Figure 26.

5.3. $3d^3$ Ground State System, for Example, Cr^{3+} . The electronic configurations involved for a $3d^3$ ion are summarised below:

$$\begin{aligned}
 1s2p \text{ RIXS : } 1s^2 2p^6 3d^3 &\xrightarrow[1s \text{ XAS}]{\Delta \mathcal{J}=\pm 2} 1s^2 2p^6 3d^4 \xrightarrow[2p \text{ XES}]{\Delta \mathcal{J}=0,\pm 1} 1s^2 2p^5 3d^4, \\
 2p \text{ XAS : } 1s^2 2p^6 3d^3 &\xrightarrow[2p \text{ XAS}]{\Delta \mathcal{J}=0,\pm 1} 1s^2 2p^5 3d^4.
 \end{aligned} \tag{46}$$

FIGURE 26: Calculated 1s2p RIXS spectrum for Cr^{4+} ($3d^2$) for $10Dq = 2.1$ eV. Note that the A_{2g} intermediate state symmetry is in agreement with the selection rules only populated via the T_{2g} 1s XAS IRREP. The slices have been scaled to a comparable intensity to enhance their character better. The bottom plot compares the integrated incident energy (IIE) 2p XES with the 2p XAS ($L_{2,3}$ -edge).

FIGURE 27: Effect of the O_h crystal field on the 2p XES projections of the calculated 1s2p RIXS spectra for Cr^{4+} ($3d^2$).

For $3d^3$ systems such as Cr^{3+} , the initial state configuration $1s^2 2p^6 3d^3$ (120 microstates) translates in O_h to a ${}^4A_{2g}$ ground state (4 microstates). With 3d SOC ($\mathcal{S} = 3/2 \rightarrow \otimes F_{3/2g}$), the ground state of a $3d^2$ ion is thus ${}^4A_{2g}[F_{3/2g}]$ (O_h) (Table 5).

The intermediate state terms (420 microstates) contain spin sextets, quartets, and doublets and orbital momentum ranging from S to I. They split in the O_h crystal field as the Tanabe-Sugano diagram of $3d^4$ systems. Those terms, neglecting 3d spin-orbit interaction, branch into multiple O_h terms:

$${}^{6,4,2}T_{2g}, {}^{6,4,2}E_g, {}^{4,2}T_{1g}, {}^{4,2}A_{2g}, \text{ and } {}^{4,2}A_{1g} \quad (47)$$

For 1s XAS, the weak spin-orbit coupling in the 3d shell results in spin-conserving transitions from the ground state ${}^4A_{2g}$ to the spin-quartet intermediate states with quadrupole IRREPs ${}^4T_{1g}$ and 4E_g :

$$\begin{aligned} {}^4A_{2g} &\xrightarrow{\otimes T_{2g}} {}^4T_{1g}, \\ {}^4A_{2g} &\xrightarrow{\otimes E_g} {}^4E_g. \end{aligned} \quad (48)$$

This illustrates, though many symmetries exist in the intermediate state, only the transitions into the T_{1g} and E_g symmetries contribute to the spectrum as can be seen in Figure 28.

Again, as detailed throughout the examples above for the 2p XES decays, consideration of 3d SOC is again required. Hence, we give the splitting of the two reachable intermediate state terms ${}^4T_{1g}$ and 4E_g due to SOC ($\mathcal{S} = 3/2 \rightarrow \otimes F_{3/2}$):

$$\begin{aligned} {}^4T_{1g} \otimes F_{3/2g} &= E_{1/2g} \oplus E_{5/2g} \oplus 2 \cdot F_{3/2g}, \\ {}^4E_g \otimes F_{3/2g} &= E_{1/2g} \oplus E_{5/2g} \oplus F_{3/2g}. \end{aligned} \quad (49)$$

FIGURE 28: 1s XAS projections of a calculated 1s2p RIXS spectrum for Cr^{3+} ($3d^3$) with ELD.

Here, it is noteworthy that both IS terms (${}^4T_{1g}$ and 4E_g) are branching into the same three symmetries: $E_{1/2}$, $E_{5/2}$, and $F_{3/2}$.

The final state ($1s^2 2p^5 3d^4$) contains $6 \cdot 210 = 1260$ microstates due to the hole in the 2p shell. The atomic term symbols, obtained by coupling the $3d^4$ atomic terms with 2P , span from S to K with spin doublets, quartets, and sextets and $\mathcal{J}$ values from 1/2 to 15/2. A detailed list can be found in the book *Core Level Spectroscopy of Solids* [13] (p. 103). The important information is that these $\mathcal{J}$ values branch in O_h into the three odd IRREPs $E_{1/2u}$, $F_{3/2u}$, and $E_{5/2u}$.

As derived in (49), the 2p XES decays in 1s2p RIXS start from either of the three intermediate state symmetries $E_{1/2g}$, $E_{5/2g}$, and $F_{3/2g}$ and can reach $E_{1/2u}$, $E_{5/2u}$, and $F_{3/2u}$ final state IRREPs. The transitions are again given in (33), (34), and (35).

The direct 2p XAS final state terms are similar though it starts from the $F_{3/2g}$ ground state symmetry.

$$F_{3/2g} \xrightarrow{\otimes T_{1u}} E_{1/2u} \oplus E_{5/2u} \oplus 2F_{3/2u}. \quad (50)$$

Altogether, the reachable final state terms are the same in 1s2p RIXS and the direct 2p XAS, the selection rules, and the corresponding transitions yield different results.

The selection rules are summarised in the term scheme shown in Figure 29.

The calculated 1s2p RIXS maps and some CIE slices together with the corresponding 1s XAS for Cr^{3+} ($3d^3$) for a crystal field of $10Dq = 1.5$ eV are shown in Figure 30. As can be seen from the corresponding RIXS maps, from the A_{2g} ground state symmetry, the quadrupole T_{2g} IRREP populates only states with T_{1g} symmetry, while the quadrupole E_g IRREP populates only intermediate states with E_g symmetry. The ${}^4T_{1g}$ (4H) intermediate state symmetry corresponds to the electronic configuration with four 3d electrons in the t_{2g} orbitals, and as a result, the corresponding final states

FIGURE 29: Multielectronic term scheme for Cr^{3+} ($3d^3$) comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Where SOC is included, the spin multiplicity is omitted as its meaning is lost in that case.

(between $E_T \approx -5$ eV and -2.5 eV) are reached in the RIXS. These states correspond to spin-quartet final states and are weak in $2p$ XAS. The first 4E_g IRREP intermediate state ($E_{in} \approx -0.6$ eV) leads to the final states between $E_T \approx -5$ eV and -2.5 eV, which correspond to the e_g part of the final states with $(t_{2g})^3(e_g)^1$. The other 4E_g intermediate state symmetries at $E_{in} \approx 2.35$ eV and 3.5 eV lead to higher energy final states, where it is the RIXS spectrum of 4E_g ($E_T \approx 3.5$ eV) that resembles more to $2p$ XAS. This is consistent with the fact that the atomic term of this intermediate state is similar to the atomic term of the ground state (4F) leading to similar $1s2p$ RIXS and $2p$ XAS spectra.

5.3.1. $1s2p$ RIXS Experiments of $3d^3$ Systems. Examples for $3d^3$ systems are Cr^{3+} and Mn^{4+} . Experimental $1s2p$ RIXS spectra of a number of Cr^{3+} ($3d^3$) systems have been published by Frommer et al. [42]. Thomas et al. (unpublished) compare Cr(III)(acac) and Cr_2O_3 with $1s2p$ RIXS crystal field multiplet calculations, equivalent to Figure 30. Cr(III)acac is well reproduced by the crystal field multiplet calculations. In the case of Cr_2O_3 , additional intensity due to the nonlocal peak overlaps with the second pre-edge peaks in the $1s$ XAS. Experimental $1s2p$ RIXS spectra of MnO_2 have been published by Glatzel et al. [43]. Mn^{4+} is a covalent system dominated by charge transfer. As such, the $1s2p$ RIXS is dominated by fluorescence and the $1s2p$ RIXS resonances calculated here are not visible as separate features.

5.4. $3d^4$ Ground State System, for Example, Mn^{3+} . The electronic configurations involved in this example are summarised below:

This is the first case in which the crystal field splitting energy ($10Dq$) and the pairing energy are competing. Thus, as shortly discussed in the introduction notes for Section 5, the ground state can have a high spin or low spin configuration.

5.4.1. $3d^4$ System in High Spin (Quintet Ground State). The initial state electronic configuration is $1s^2 3d^4$ (210 micro-states) having in high spin the atomic ground state term 5D . In the O_h crystal field, the 5D ground state splits into the $^5E_g(|t_{2g}^2 e_g^2\rangle)$ and $^5T_{2g}(|t_{2g}^3 e_g^1\rangle)$ terms, where 5E_g is the lowest in energy. The inclusion of spin-orbit interaction ($\mathcal{S} = 2 \rightarrow \otimes (E_g \oplus T_{2g})$) yields the following splittings in the initial state:

$$^5E_g \otimes (E_g \oplus T_{2g}) = (A_{1g} \oplus A_{2g} \oplus E_g) \oplus (T_{1g} \oplus T_{2g}). \tag{52}$$

The ground state 5E_g splits due to $3d$ SOC into several symmetries from which the term A_{1g} is the lowest in energy; hence, the ground state is $^5E_g[A_{1g}] (O_h)$.

The intermediate state with $1s^1 3d^5$ ($2 \cdot 252 = 504$ micro-states) corresponds to the atomic terms of $3d^5$ coupled with the $1s$ core hole. This gives spin multiplicities ranging from 1 to 7. Using Table 2, one finds the branchings of the atomic states in an O_h crystal field which are analogue to the Tanabe-Sugano diagram of $3d^5$. Because the $1s$ XAS is spin-conserving, only quintet intermediate states are reached in the absorption from the quintet high spin ground state (5E_g). The atomic quintet terms are 5S , 5D , 5F , 5G , and 5P which correspond to the crystal field terms $^5A_{1g}$, $^5A_{2g}$, 5E_g , $^5T_{1g}$, and $^5T_{2g}$.

Starting from the 5E_g ground state term, Table 3 gives the reachable intermediate state symmetries:

$$^5E_g \xrightarrow{\otimes T_{2g}} ^5T_{1g} \oplus ^5T_{2g}, \tag{53}$$

$$\underbrace{^5E_g}_{\text{GS}} \xrightarrow[1s \text{ XAS}]{\otimes E_g} \underbrace{^5A_{1g} \oplus ^5A_{2g} \oplus ^5E_g}_{\text{(Accessible IS in high spin)}}. \tag{54}$$

FIGURE 30: Calculated 1s2p RIXS spectrum for $3d^3\text{Cr}^{3+}$ for $10Dq = 1.5$ eV.

The result is that all quintet intermediate state symmetries can be reached in 1s XAS. This is confirmed in Figure 31 where in high spin only terms with a quintet

component contribute to the spectrum. Furthermore, it can be seen that the high spin configuration is maintained up to a crystal field of $10Dq \approx 2.8$ eV.

FIGURE 32: Multielectronic term scheme for Mn^{3+} ($3d^4$) in high spin comparing the 1s2p RIXS and direct 2p XAS pathways. Where SOC is included, the spin multiplicity is omitted.

For the 2p XES decay, we find again from expressions (28), (29), (30), (31), and (32) that all even symmetries (A_{1u} , A_{2u} , E_u , T_{1u} , and T_{2u}) can be reached. In 2p XAS, starting from the A_{1g} total symmetry term and using the T_{1u} IRREP, we find that only T_{1u} final state IRREPs can be reached. The selection rules are summarised in the combined term scheme in Figure 35.

An example calculation for the low spin case ($10Dq = 3.9$ eV) of Mn^{3+} ($3d^4$) is shown in Figure 36.

This example is the first case here in which the crystal field energy ($10Dq$) and the pairing energy are competing to induce a low spin configuration for sufficiently large values of $10Dq$. In the present case of Mn^{3+} ($3d^4$), we see the high spin to low spin transition at around $10Dq \approx 2.85$ eV as is observable in the 1s XAS and 2p XES projections (Figures 31 and 37, resp.).

One difference between the low spin and high spin Mn^{3+} is the spin state of the ground state. The result is that in the HS, the 1s XAS absorption reaches the spin-quintet IS while in the LS case, it reaches the spin-triplet IS. This results in different final states being probed regardless of the effect of the crystal field. In the low spin case, the intermediate state is separating the two quadrupole components T_{2g} and E_g (Figure 26 top row). Although the projected 1s2p RIXS and the 2p XAS present close intensities across the final states, the calculations show that by choosing the 1s2p RIXS incident energy E_{in} , one can select specific intermediate states.

We observe that the quadrupole T_{2g} IREEP can reach only one ${}^3T_{2g}$ (3I) intermediate state symmetry, while it cannot be reached with the quadrupole E_g operator. This is consistent with the corresponding electron configuration of the ${}^3T_{2g}$ IRREP in the 3d shell: $|t_{2g}^5 e_g^0\rangle$.

The quadrupole E_g IRREP enables to reach only the intermediate state spin-triplets at higher energy. Consequently, it appears that in the case of low spin Mn^{3+} , depending on the

RIXS intermediate states that are probed, one can enhance either the transitions into the t_{2g} orbitals of the final states or the transitions into the e_g orbitals.

5.4.3. 1s2p RIXS Experiments of $3d^4$ Systems. Experimental 1s2p RIXS spectra of a number of Mn^{3+} ($3d^4$) systems have been published by Glatzel et al. [43] for Mn_2O_3 and also for a series of molecular complexes that serve as reference systems for photosystem II. The pre-edge 1s2p RIXS resonances can be separated well from the main peak. The 1s2p RIXS plane of Mn(III)acac [43] is similar to the calculated plane in Figure 36.

5.5. $3d^5$ Ground State System, for Example, Fe^{3+} . In this part, we present the elementary differences for the case of an Fe^{3+} ion ($3d^5$) (Mn^{2+} analogue). First, we gather the relevant information analogue to the previous cases which are again summarised in a combining term scheme illustrating the transition paths in 1s2p RIXS (1s XAS, 2p XES) and 2p XAS. The electronic configurations involved in this case are summarised below:

$$\begin{aligned}
 1s2p \text{ RIXS : } 1s^2 2p^6 3d^5 &\xrightarrow[1s \text{ XAS}]{\Delta\mathcal{F}=\pm 2} 1s^1 2p^6 3d^6 \xrightarrow[2p \text{ XES}]{\Delta\mathcal{F}=0, \pm 1} 1s^2 2p^5 3d^5, \\
 2p \text{ XAS : } 1s^2 2p^6 3d^5 &\xrightarrow[2p \text{ XAS}]{\Delta\mathcal{F}=0, \pm 1} 1s^2 2p^5 3d^6.
 \end{aligned} \tag{59}$$

Also in $3d^5$ ground state systems like Fe^{3+} or Mn^{2+} , high spin to low spin transitions can be observed. Thus, for large values of $10Dq$, the ground state changes from ${}^6A_{1g}$ for $|t_{2g}^3 e_g^2\rangle$ to ${}^2T_{2g}$ for $|t_{2g}^5 e_g^0\rangle$.

5.5.1. Fe^{3+} ($3d^5$) in High Spin (Sextet Ground State). The initial state configuration $1s^2 3d^5$ (252 microstates) has in high spin the ground state term 6S (Table 1) branching in O_h into a ${}^6A_{1g}$ symmetry (6 microstates). The spin-orbit interaction

FIGURE 33: Calculated 1s2p RIXS map for Mn^{3+} ($3d^4$) with a crystal field for $10Dq = 1.5$ eV reflecting the high spin case. As can be seen by the two RIXS maps (top row, left and middle), the contributions are in agreement with the predicted symmetries found in (51) and (52).

($\mathcal{S} = 5/2 \rightarrow \otimes [F_{3/2g} \oplus E_{5/2g}]$) yields the following splittings of the ground state term:

$${}^6A_{1g} \otimes [F_{3/2g} \oplus E_{5/2g}] = F_{3/2g} \oplus E_{5/2g}. \quad (60)$$

Here, the term $F_{3/2g}$ lies the lowest in energy; thus, the ground state is ${}^6A_{1g}[F_{3/2g}]$ (O_h). However, the splitting is small (few meV) and thus also the $E_{5/2g}$ term would contribute weakly in a measurement.

FIGURE 34: 1s XAS projection of a calculated 1s2p RIXS map for Mn^{3+} ($3d^4$) in low spin.

FIGURE 35: Multielectronic term scheme for Mn^{3+} ($3d^4$) in low spin comparing the 1s2p RIXS and direct 2p XAS pathways. Where SOC is included, the spin multiplicity is omitted.

The intermediate state with $1s^1 3d^6$ ($2 \cdot 210 = 420$ microstates) gives the atomic terms with spin multiplicity from 0 to 6 and orbital momentum from S to I. The O_h crystal field splits these terms analogue to the classic Tanabe-Sugano diagram of $3d^6$. In 1s XAS, due to the weak 3d SOC starting from the ${}^6A_{1g}$ ground state, only sextet spin terms ${}^6T_{2g}$ and 6E_g arising from the only atomic sextet spin term 6D are reached (Table 3):

The corresponding 1s XAS projections for a $3d^5$ system with $10Dq$ between 0.1 eV and 4.2 eV are shown in Figure 38. It is noteworthy that this situation presents some similarities with the case of $3d^0$ (Ti^{4+}). In both cases, the excited 1s electron can go into either the t_{2g} orbitals or the e_g orbitals. The drastic difference is that for $3d^5$, all spin-up orbitals are full in the total symmetric IRREP ${}^6A_{1g}$ (O_h).

For the 2p XES decay, spin-orbit interaction is again crucial; hence, we include 3d spin-orbit coupling ($\mathcal{S} = 5/2 \rightarrow \otimes [F_{3/2g} \oplus E_{5/2g}]$) for the reachable intermediate state terms:

$$\begin{aligned} {}^6T_{2g} \otimes [F_{3/2g} \oplus E_{5/2g}] &= (E_{1/2g} \oplus E_{5/2g} \oplus 2F_{3/2g}) \\ &\quad \oplus (E_{1/2g} \oplus F_{3/2g}), \\ \underbrace{{}^6E_g}_{\text{Reachable IS}} \otimes [F_{3/2g} \oplus E_{5/2g}] &= (E_{1/2g} \oplus E_{5/2g} \oplus F_{3/2g}) \oplus F_{3/2g}. \end{aligned} \quad (62)$$

Due to the spin ($\mathcal{S} = 5/2$) and the resulting splittings, all three odd IRREPs ($E_{1/2g}$, $E_{5/2g}$, and $F_{3/2g}$) appear more than once. Thus, the 2p XES can decay from any of the three IRREPs $E_{1/2g}$, $E_{5/2g}$, or $F_{3/2g}$. As given in (33), (34), and (35), the dipole IRREP T_{1u} also enables to reach all three odd symmetries $E_{1/2u}$, $E_{5/2u}$, and $2F_{3/2u}$ in the final state.

The direct 2p XAS on the other hand starts from the $F_{3/2g}$ ground state term; hence, the reachable final state symmetries are identical to those found in (35). In other words, the direct 2p XAS reaches the same final states as the 2p XES decays from the $F_{3/2g}$ intermediate state symmetry. The resulting overall selection rules for $3d^5$ in high

FIGURE 36: Calculation of 1s2p RIXS and 2p XAS for Mn^{3+} ($3d^4$) for $10Dq = 3.9$ eV (low spin).

spin are summarised in the combined term scheme in Figure 39.

The calculated 1s2p RIXS maps shown in Figure 40 confirm the selection rules as summarised above. The two

RIXS maps corresponding to the two quadrupole IRREPs T_{2g} and E_g (Figure 40 top row, left and middle) confirm that the intermediate states are probed selectively according to the quadrupole transition operator. This means that

FIGURE 39: Multielectronic term scheme for Fe^{3+} ($3d^5$) high spin comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Where SOC is included ($\mathcal{S} = 5/2$), the spin multiplicity is omitted.

relate to the difference of the intermediate state population via the first $1s$ XAS step. Again, the intermediate state plays the decisive role.

For $2p$ XAS, starting from the $E_{5/2g}$ ground state, only two final state terms are reachable:

$$\underbrace{E_{5/2g}}_{\text{GS}} \xrightarrow[2p \text{ XAS}]{\otimes T_{1u}} \underbrace{E_{1/2u} \oplus F_{3/2u}}_{\text{Accessible FS terms}}. \quad (66)$$

The results of the selection rules as discussed above are summarised in the combined term scheme shown in Figure 42.

The calculated $1s2p$ RIXS map for a low spin case ($10Dq = 3.9$ eV) is given in Figure 43.

In the left RIXS map in Figure 43(a), it appears that the quadrupole IRREP T_{2g} enables to reach only the first fully symmetric ${}^2A_{1g}$ intermediate state symmetry. This term corresponds in the single electron picture to a $|t_{2g}^6 e_g^0\rangle$ configuration of the $3d$ shell where all the t_{2g} orbitals occupied. The spin doublet emerges solely from the core hole in the $1s$ shell.

The $2p$ XES decay reaches two final states corresponding to the t_{2g} orbital full and a hole in the $2p$ shell, relating to one in the L_3 and one in the L_2 . In the multielectronic picture, these two peaks correspond to the ${}^2A_{1g} \otimes {}^2P$ final states (see Figures 43 and 44). It is noteworthy that this peak is not reached in the L_2 -edge via the $2p$ XAS. This can be explained in the single electron picture of the initial state, which contains only one hole in the t_{2g} orbitals. The L_2 -edge does not get a peak because it would require a spin-flip to fill the t_{2g} hole with an electron from the $2p$ shell. In $1s2p$ RIXS, these two peaks arise only from the decay of the $2p$ shell electron into the $1s$ shell, which is possible for both L_3 and L_2 . The higher energy range of the final states is reached via the intermediate state probed by the quadrupole E_g IRREP ($1s$ XAS operator).

5.5.3. $1s2p$ RIXS Experiments of $3d^5$ Systems. Examples of $3d^5$ systems include Mn^{2+} and Fe^{3+} . Experimental $1s2p$ RIXS spectra of MnO have been published by Kas et al. [39]. Compared with the calculations in Figure 40, the intensity ratio of the T_{2g} and the E_g peak is inverted in the experiment, with the E_g peak at [6540, 638] eV having the largest intensity. The same observation can be made for the Fe^{3+} systems Fe_2O_3 and iron impurities in MgO [14]. The tetrahedral Fe^{3+} contains a single $1s2p$ RIXS feature, reproduced by the calculations. $1s2p$ RIXS of a series of iron minerals has been published by Vercamer in his PhD thesis [44]. The $1s2p$ RIXS spectrum of octahedral low spin compounds Fe(III)(tacn) and Fe(III)cyanide has been measured and reproduced in multiplet calculations by Lundberg et al. [45].

5.6. $3d^6$ Ground State System, for Example, Fe^{2+} . In this part, we present the elementary differences between $1s$ XAS and $1s2p$ RIXS for the case of Fe^{2+} ($3d^6$; Co^{3+} analogue). As in the previous case(s), first, we gather the relevant informations which are summarised in a combining term scheme illustrating the transition paths in $1s2p$ RIXS ($1s$ XAS, $2p$ XES) and $1s$ XAS. The electronic configurations involved are summarised below:

$$\begin{aligned} 1s2p \text{ RIXS: } 1s^2 2p^6 3d^6 &\xrightarrow[1s \text{ XAS}]{\Delta\mathcal{J}=\pm 2} 1s^1 2p^6 3d^7 \xrightarrow[2p \text{ XES}]{\Delta\mathcal{J}=0, \pm 1} 1s^2 2p^5 3d^7, \\ 2p \text{ XAS: } 1s^2 2p^6 3d^6 &\xrightarrow[2p \text{ XAS}]{\Delta\mathcal{J}=0, \pm 1} 1s^2 2p^5 3d^7. \end{aligned} \quad (67)$$

As in the previous case, the crystal field splitting energy ($10Dq$) and the pairing energy are in competition in a $3d^6$ configuration. Thus, for sufficiently high values of $10Dq$, the ground state changes from high spin ${}^5T_{2g}$ for $|t_{2g}^4 e_g^2\rangle$ to low spin ${}^1A_{1g}$ for $|t_{2g}^6 e_g^0\rangle$.

5.6.1. Fe^{2+} ($3d^6$) in High Spin (Quintet Ground State). The initial state electronic configuration is $3d^6$ (210 microstates) with the atomic ground state term 5D (25 microstates). In

FIGURE 40: Calculated 1s2p RIXS spectrum for Fe³⁺ (3d⁵) for 10Dq = 1.5 eV (high spin).

an O_h crystal field, the 5D term splits into ${}^5T_{2g}$ for $|t_{2g}^4 e_g^2\rangle$ and 5E_g for $|t_{2g}^3 e_g^3\rangle$. The inclusion of spin-orbit interaction ($\mathcal{S} = 2 \rightarrow \otimes (E_g \oplus T_{2g})$) yields the following splittings:

$${}^5T_{2g} \otimes (E_g \oplus T_{2g}) = A_{1g} \oplus E_g \oplus 2T_{1g} \oplus 2T_{2g}. \quad (68)$$

Here, the term T_{2g} lies the lowest in energy; thus, the ground state is ${}^5T_{2g}[T_{2g}] (O_h)$.

The intermediate state electron configuration $1s^1 3d^7 3d^7$ ($2 \cdot 120 = 240$ microstates) yields the atomic terms ${}^{1,3,5}F$, ${}^{1,3,5}P$, ${}^{1,3}D$, ${}^{1,3}G$, and ${}^{1,3}H$ (Table 1). Using Table 2, one finds the branchings of the atomic states in an O_h crystal field which are analogue to the Tanabe-Sugano diagram of $3d^7$.

FIGURE 41: Low spin 1s XAS projections ($10Dq = 3.3$ eV to 4.2 eV) for Fe^{3+} ($3d^5$) with ELD. In the single electron picture the 3d shell has either $|t_{2g}^6 e_g^0\rangle$ for ${}^2A_{1g}$ or $|t_{2g}^5 e_g^1\rangle$ for ${}^4T_{1g}$ and ${}^4T_{2g}$, respectively.

FIGURE 42: Multielectronic term scheme for Fe^{3+} ($3d^5$) low spin comparing the 1s2p RIXS and direct 2p XAS pathways. Where SOC is considered, the spin multiplicity was omitted.

Because the 1s XAS is spin-conserving, only quintet intermediate states are reached in the absorption, corresponding to the crystal field terms derived from 5F and 5P : ${}^5A_{2g}$, ${}^5T_{2g}$, ${}^5T_{1g}$, and ${}^5T_{1g}$, respectively. For 1s XAS, starting from the ${}^5T_{2g}$ ground state term, the reachable high spin intermediate state terms are

$$\begin{aligned} {}^5T_{2g} &\xrightarrow{\otimes T_{2g}} {}^5A_{1g} \oplus {}^5E_g \oplus {}^5T_{1g} \oplus {}^5T_{2g}, \\ \underbrace{{}^5T_{2g}}_{\text{GS}} &\xrightarrow[\text{1s XAS}]{\otimes E_g} \underbrace{{}^5T_{1g} \oplus {}^5T_{2g}}_{\text{Reachable IS (high spin)}}. \end{aligned} \quad (69)$$

The reachable intermediate state terms of Fe^{2+} ($3d^6$) in high spin are therefore ${}^5T_{1g}$ and ${}^5T_{2g}$. In other words, though the ${}^5A_{1g}$ and 5E_g symmetries are formally reachable in 1s XAS, the intermediate state does not offer this IRREP to be populated. Furthermore, though an ${}^5A_{2g}$ IRREP exists, the quadrupole selection rules do not allow it to be reachable in 1s XAS (see Figure 45). However, the small 3d SOC

may induce some mixing enabling also weak transitions into this IRREP.

Adding SOC ($\mathcal{S} = 2 \rightarrow \otimes (E_g \oplus T_{2g})$) to the reachable IS terms leads to the splittings in the IS:

$$\begin{aligned} {}^5A_{1g} \otimes (E \oplus T_2) &= E \oplus T_2, \\ {}^5T_{1g} \otimes (E_g \oplus T_{2g}) &= (T_{1g} \oplus T_{2g}) \oplus (A_{2g} \oplus E_g \oplus T_{1g} \oplus T_{2g}), \\ {}^5T_{2g} \otimes (E_g \oplus T_{2g}) &= (T_{1g} \oplus T_{2g}) \oplus (A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g}). \end{aligned} \quad (70)$$

We find the decays in 1s2p RIXS can occur from all integer symmetries (A_{1g} , A_{2g} , E_g , T_{1g} , and T_{2g}).

The final state electron configuration $1s^2 2p^5 3d^7$ contains $6 \cdot 120 = 720$ microstates due to the hole in the 2p shell spanning $\mathcal{J}$ from 0 to 7. In an O_h crystal field, these terms branch into the five integer total symmetry IRREPs A_{1g} , A_{2g} , E_g , T_{1g} , and T_{2g} . The 2p XES decays can occur from any of the populated intermediate state terms; thus, the accessible final state terms are again derived with the dipole T_{1u} IRREP as given in (28), (29), (30), (31), and (32). In short, all “ungerade” integer IRREPs are reachable in the final state of 2p XES.

FIGURE 44: 2p XES projections for Fe^{3+} ($3d^5$) for $10Dq = 0.1$ eV to 4.2 eV. The high spin to low spin transition between $10Dq \approx 3.0$ eV and 3.3 eV also induces visible changes in the 2p XES. The most notable is the appearance of the two peaks related to the first ${}^2A_{1g}$ intermediate state symmetry around $E_T < -5$ eV and $E_T \approx 7$ eV.

FIGURE 45: 1s XAS projections of the calculated 1s2p RIXS spectrum for Fe^{2+} ($3d^6$) showing the high spin to low spin transition just above $10Dq \approx 1.8$ eV.

In 2p XAS, starting from the T_{2g} total symmetry IRREP term and using the T_{1u} IRREP, the reachable final states are again identical to the 2p XES final state term reachable from the T_{2g} intermediate state IRREP as given (32).

Altogether, this enables to draw the term scheme for Fe^{2+} ($3d^6$) in high spin as shown in Figure 46.

The result of the calculation for high spin Fe^{2+} ($3d^6$) for $10Dq = 0.9$ eV is shown in Figure 47.

We note that the quadrupole T_{2g} IRREP (left RIXS map in Figure 47(a)) is dominated by transitions into the ${}^5T_{2g}$

intermediate state symmetry, while the quadrupole E_g IRREP (middle RIXS map in Figure 47(a)) leads mostly into the T_{1g} intermediate state IRREPs. As predicted above, the 1s XAS spectra gain their intensity only from two intermediate state symmetries, the ${}^5T_{1g}$ and ${}^5T_{2g}$ IRREPs. The ${}^5A_{2g}$ intermediate state symmetry does not contribute to the spectrum as can be seen in Figure 45.

5.6.2. Fe^{2+} ($3d^6$) in Low Spin (Singlet Ground State). For a sufficiently large crystal field splitting ($10Dq$), a $3d^6$ electronic configuration results in a low spin configuration with all t_{2g} orbitals fully occupied ($|t_{2g}^6 e_g^0\rangle$). This corresponds to the totally symmetric ground state term ${}^1A_{1g}$ (1 microstate) derived from the atomic term 1I (Table 1). The inclusion of spin-orbit interaction ($\mathcal{S} = 0 \rightarrow \otimes A_{1g}$) gives the total ground state as ${}^1A_{1g}[A_{1g}] (O_h)$.

The intermediate state electron configuration $1s^1 3d^7$ is still the same as in the high spin case. However, for high crystal fields ($10Dq$), the order of the intermediate state energy levels is different in low spin. In the low spin case, the initial state being a spin singlet, the spin-conserving 1s XAS will only reach spin singlet intermediate states (Table 3):

$$\begin{aligned} & {}^1A_{1g} \xrightarrow{\otimes T_{2g}} {}^1T_{2g}, \\ & \underbrace{{}^1A_{1g}}_{\text{GS}} \xrightarrow[\text{1s XAS}]{\otimes E_g} \underbrace{{}^1E_g}_{\text{Reachable IS}}. \end{aligned} \quad (71)$$

Although there are ${}^1T_{2g}$ and 1E_g IRREPs existing in the intermediate state, only the 1E_g derived from the 1G atomic term can be reached. This can be understood from the $\Delta\mathcal{L} = \pm 2$ quadrupole selection rule, which allows only to reach the 1G atomic term ($\mathcal{L} = 4$) from the 1I atomic ground state term ($\mathcal{L} = 6$). The quadrupole 1s XAS formally can, according to the selection rules, only reach the ${}^1T_{2g}$ and 1E_g IRREPs from this term. But finally, the transition to the ${}^1T_{2g}$ intermediate state symmetry would imply a two-electron transition from $|t_{2g}^6 e_g^0\rangle$ to $|t_{2g}^5 e_g^2\rangle$, which has a very low probability. Hence, only the 1E_g IRREP from the 1G atomic term is populated thus adding intensity to the 1s XAS spectrum as visible in Figure 48.

For the 2p XES decays in 1s2p RIXS, spin-orbit interaction in the intermediate state must be considered ($\mathcal{S} = 0 \rightarrow \otimes A_{1g}$) leading the identities:

$$\underbrace{{}^1E_g}_{\text{reachable IS}} \otimes A_{1g} = E_g. \quad (72)$$

The final state electron configuration $1s^2 2p^5 3d^7$ is again identical to the high spin case regardless of the crystal field effects, offering the five total symmetry IRREPs A_{1u} , A_{2u} , E_u , T_{1u} , and T_{2u} . The 2p XES decaying from the populated intermediate state term E_g can reach with the dipole IRREP T_{1u} the final state terms T_{1u} and T_{2u} as given in (30).

FIGURE 46: Multielectronic term scheme for Fe^{2+} ($3d^6$) (high spin) comparing the 1s2p RIXS and 2p XAS pathways. Where SOC is considered, the spin multiplicity is omitted as its meaning is lost.

On the contrary, the 2p XAS, starting from the total symmetric A_{1g} ground state symmetry, can reach only the T_{1u} final state IRREP.

This again enables altogether to draw the combined term scheme comparing the two-step 1s2p RIXS with the direct dipole 2p XAS pathways in Figure 49.

The resulting calculated 1s2p RIXS for Fe^{2+} ($3d^6$) is shown in Figure 50. As already discussed, the 1s2p RIXS is dominated by the E_g intermediate state symmetry. As can be seen, the quadrupole T_{2g} IRREP has overall a negligible contribution to the total RIXS. From the term scheme in Figure 49, one can furthermore derive that the difference between the integrated 2p XES (IIE) and the direct 2p XAS emerges from the T_{2u} final state IRREP which can only be reached in 1s2p RIXS.

5.6.3. 1s2p RIXS Experiments of $3d^6$ Systems. $3d^6$ systems include Fe^{2+} and Co^{3+} . A large number of experimental 1s2p RIXS spectra of Fe^{2+} systems have been published. Vercamer measured a large series of Fe^{2+} minerals in his PhD thesis [44]. The tetrahedral and octahedral Fe^{2+} oxides/minerals have been studied and reproduced by multiplet calculations [5, 17, 46]. Guo et al. [47] studied low spin Fe^{2+} cyanide complexes. Lundberg et al. [45] compared these experiments to the tacn complex and reproduced the spectra from multiplet calculations. Leidel et al. [48] studied iron hydrogenase complexes. Vanko et al. [49] studied the time evolution of the 1s2p RIXS planes. The static spectra of the low spin systems $[\text{Fe}(\text{terpy})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ and the laser-excited spectrum of $[\text{Fe}(\text{terpy})_2]^{2+}$ show a partial transition to a high spin ground state as is confirmed in the calculations.

In case of Co^{3+} , all measured systems were low spin $^1A_{1g}$. Vanko et al. [7] compared an isolated Co^{3+} complex with a series of cobalt oxides. They nicely show the presence of the nonlocal peaks as a function of the Co-O-Co angle.

5.7. $3d^7$ Ground State System, for Example, Co^{2+} . In this part, we present the elementary differences between 1s2p RIXS and 2p XAS for the case of Co^{2+} ($3d^7$). First, we gather the relevant information analogue to the previous cases which are again summarised in the combining term scheme in Figure 39 term scheme illustrating the transition paths involved (Figures 51 and 52). The electronic configurations involved are summarised below:

$$\begin{aligned}
 1s2p \text{ RIXS} : 1s^2 2p^6 3d^7 &\xrightarrow[1s \text{ XAS}]{\Delta\mathcal{F}=\pm 2} 1s^1 2p^6 3d^8 \xrightarrow[2p \text{ XES}]{\Delta\mathcal{F}=0, \pm 1} 1s^2 2p^5 3d^8, \\
 2p \text{ XAS} : 1s^2 2p^6 3d^7 &\xrightarrow[2p \text{ XAS}]{\Delta\mathcal{F}=0, \pm 1} 1s^2 2p^5 3d^8.
 \end{aligned} \tag{73}$$

Also, a $3d^7$ system encounters, for sufficiently high values of $10Dq$, a change of the ground state from $^4T_{2g}$ for $|t_{2g}^5 e_g^2\rangle$ (high spin) to 2E_g for $|t_{2g}^6 e_g^1\rangle$ (low spin).

5.7.1. Co^{2+} ($3d^7$) in High Spin (Quartet Ground State). For the initial state configuration $3d^7$ (120 microstates), the high spin ground state term symbol is 4F (Table 1), which branches in O_h into $^4T_{1g}$, $^4T_{2g}$, and $^4A_{2g}$, where the $^4T_{1g}$ term with 12 microstates is the lowest in energy. The inclusion in spin-orbit interaction ($\mathcal{S} = 3/2 \rightarrow \otimes F_{3/2g}$) yields the subsequent splitting of $^4T_{1g}$ term:

$$^4T_{1g} \otimes F_{3/2g} = E_{1/2g} \oplus E_{5/2g} \oplus 2F_{3/2g}. \tag{74}$$

The ground state $^4T_{1g}$ splits due to 3d SOC into the three odd symmetries $E_{1/2g}$, $E_{5/2g}$, and $F_{3/2g}$ from which the term $E_{1/2g}$ is lowest in energy; hence, the combined ground state is $^4T_{1g}[E_{1/2g}] (O_h)$.

FIGURE 47: Calculated 1s2p RIXS spectra and slices for Fe^{2+} ($3d^6$) for $10Dq = 0.9$ eV (high spin).

The intermediate state electron configuration is $1s^1 3d^8$ ($2 \cdot 45 = 90$ microstates). The atomic terms are $^2 4F$, $^2 4P$, $^2 S$, $^2 D$, and $^2 G$ (Table 1). Using Table 2, one finds the branchings of the atomic states in an O_h crystal field which are

analogue to the Tanabe-Sugano diagram of $3d^8$. The spin-conserving 1s XAS reaches only spin quartet intermediate states, which corresponds to the crystal field terms issued from 4F and 4P : $^4 A_{2g}$, $^4 T_{2g}$, $^4 T_{1g}$, and $^4 T_{1g}$, respectively.

FIGURE 48: 1s XAS projections of the calculated 1s2p RIXS spectrum for Fe^{2+} ($3d^6$) showing low spin part above $10Dq \approx 1.8$ eV only. It reveals only the E_g symmetry is giving a significant contribution.

FIGURE 49: Multielectronic term scheme for Fe^{2+} ($3d^6$) in low spin comparing the 1s2p RIXS and direct 2p XAS pathways. We note its similarity to the Ti^{4+} ($3d^0$) case shown in Figure 15.

Starting from the high spin ground state term ${}^4T_{1g}$, the two quadrupole IRREPs give the reachable intermediate state terms:

$${}^4T_{1g} \xrightarrow{\otimes T_{2g}} {}^4A_{2g} \oplus {}^4E_g \oplus {}^4T_{1g} \oplus {}^4T_{2g}, \quad (75)$$

$$\underbrace{{}^4T_{1g}}_{\text{GS}} \xrightarrow{\otimes E_g} \underbrace{{}^4T_{1g} \oplus {}^4T_{2g}}_{\text{(Accessible low spin IS)}}. \quad (76)$$

The reachable 1s XAS intermediate state terms in high spin are therefore ${}^4A_{2g}$, ${}^4T_{1g}$, and ${}^4T_{2g}$. Here, it shall be noticed that an E_g symmetry would be reachable by the quadrupole selection rules, but the intermediate state does not offer any (quartet) 4E_g symmetries. The 1s XAS projections displayed in Figure 53 confirm these findings.

Applying the 3d spin-orbit interaction ($\mathcal{S} = 3/2 \rightarrow \otimes F_{3/2g}$) to the three reachable terms yields the splittings in the intermediate state:

$$\begin{aligned} {}^4A_{2g} \otimes F_{3/2g} &= F_{3/2g}, \\ {}^4T_{1g} \otimes F_{3/2g} &= E_{1/2g} \oplus E_{5/2g} \oplus 2 \cdot F_{3/2g}, \\ {}^4T_{2g} \otimes F_{3/2g} &= E_{1/2g} \oplus E_{5/2g} \oplus 2 \cdot F_{3/2g}. \end{aligned} \quad (77)$$

The result is that all three half-valued IRREPs appear more than once and hence the 2p XES can decay from any of these terms.

The final state ($1s^2 2p^5 3d^8$) contains $\cdot 6 \cdot 45 = 270$ microstates due to the hole in the 2p shell spanning $\mathcal{J}$ from 1/2 to 11/2. In an O_h crystal field, these terms branch into the three total symmetry IRREPs $E_{1/2u}$, $E_{5/2u}$, and $F_{3/2u}$. The 2p XES starts from either $E_{1/2g}$, $E_{5/2g}$, or $F_{3/2g}$, and we find ((33), (34), and (35)) that all three odd terms are also reachable in the 1s2p RIXS final state.

The 2p XAS on the other hand, starting from the $E_{1/2g}$ ground state term, can only reach the $E_{1/2u}$ and $F_{3/2u}$ final state terms (Table 4).

A summary of the findings above is shown below as a combined term scheme in Figure 51.

We conclude this part with the corresponding calculations of the 1s2p RIXS for Co^{2+} ($3d^7$) for a crystal field energy of $10Dq = 0.9$ eV which is shown in Figure 54.

It can be noted that the RIXS map for the quadrupole T_{2g} IRREP (Figure 54(a), left) is dominated by the 1s XAS transitions into the ${}^4A_{2g}$ intermediate state symmetry which corresponds in the single electron picture to a $|t_{2g}^6 e_g^2\rangle$ configuration. However, as given in expression (75), it has also contributions into the two T_{1g} intermediate state symmetries

FIGURE 50: Calculated 1s2p RIXS spectrum for Fe^{2+} ($3d^6$) for $10Dq = 3.0$ eV (low spin).

though they are weak with respect to the A_{2g} contribution. The stick spectrum here is not as dense as in some of the cases discussed above, and this enables to identify also some of the reachable final state terms. For example, the strong peak at $E_T \approx -4.5$ eV relating to the decay from the ${}^4A_{2g}$

intermediate state symmetry corresponds to the two final state terms $E_{1/2u}$ and $F_{3/2u}$. This can be understood considering that the ${}^4A_{2g}$ branches due to SOC into a $F_{3/2g}$ intermediate state symmetry, which can reach the above two final state terms via the dipole T_{1u} IRREP.

FIGURE 51: Multielectronic term scheme for Co^{2+} ($3d^7$) in high spin comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Also, the spin multiplicity was omitted where the spin-orbit interaction is included.

FIGURE 52: Multielectronic term scheme for a Co^{2+} ion ($3d^7$) in low spin comparing the $1s2p$ RIXS and direct $2p$ XAS pathways. Where SOC is included, the spin multiplicity is omitted.

The quadrupole IRREP E_g on the other hand shows only contributions into the ${}^4T_{1g}$ and ${}^4T_{2g}$ intermediate state symmetries as predicted in expression (76).

And finally, it should be noted that the $1s$ XAS projections in Figure 53 show with increasing crystal field energy $10Dq$ the branching of the 4F into the three IRREPs 4A_2 , ${}^4T_{2g}$, and ${}^4T_{1g}$, while the atomic term 4P translates in an O_h crystal field only into a ${}^4T_{1g}$ symmetry.

5.7.2. Co^{2+} ($3d^7$) in Low Spin (Doublet Ground State). At high crystal field energies, the $3d^7$ initial state gives the low spin ground state term 2E_g (4 microstates) arising from the atomic term 2F which corresponds to the electronic configuration $|t_{2g}^6 e_g^1\rangle$. The inclusion of spin-orbit interaction ($\mathcal{S} = 1/2 \rightarrow \otimes E_{1/2g}$) yields the subsequent splittings:

$${}^2E_g \otimes E_{1/2g} = F_{3/2g}. \quad (78)$$

Hence, the combined ground state is ${}^2E_g[F_{3/2g}] (O_h)$.

The intermediate state configuration $1s^1 3d^8$ is still the same as in the high spin case; however, the higher crystal field results in different energies for the intermediate state energy levels. In the low spin case, the initial state being a spin doublet, the spin-conserving $1s$ XAS only reaches spin doublet intermediate state terms (Table 3), which correspond to the crystal field terms issued from 2S , 2P , 2D , 2F , and 2G and ${}^2A_{1g}$, ${}^2A_{2g}$, 2E_g , ${}^2T_{1g}$, and ${}^2T_{2g}$. The quadrupole $1s$ XAS starts from the low spin ground state term 2E_g revealing the reachable terms:

$$\begin{aligned} {}^2E_g &\xrightarrow{\otimes T_{2g}} {}^2T_{1g} \oplus {}^2T_{2g}, \\ \underbrace{{}^2E_g}_{\text{GS}} &\xrightarrow[\text{1s XAS}]{\otimes E_g} \underbrace{{}^2A_{1g} \oplus {}^2A_{2g} \oplus {}^2E_g}_{\text{Reachable IS}}. \end{aligned} \quad (79)$$

FIGURE 53: 1s XAS projections of a calculated 1s2p RIXS spectrum for Co^{2+} ($3d^7$) with ELD. It confirms that in high spin only the quartet terms 4F and 4P contribute to the 1s XAS. The high spin to low spin transition appears at approximately $10Dq \approx 2.2$ eV.

Thus, according to the quadrupole selection rules, from the 2E_g ground state, the 1s XAS transitions can reach all existing spin doublet IRREPs in the intermediate state. However, because in the low spin initial state all t_{2g} orbitals are occupied, 1s XAS transitions can only go into the e_g orbitals via the quadrupole E_g IRREP. The transitions into the t_{2g} orbitals with the quadrupole T_{2g} IRREP are less probable as they require a two-electron transition. In other words, the matrix elements of the quadrupole E_g IRREP are larger than those of the quadrupole T_{2g} IRREP. The resulting 1s XAS projections for the low spin case are shown in Figure 55.

For the 1p XES decays, the inclusion of 3d SOC ($\mathcal{S} = 1/2 \rightarrow \otimes E_{1/2g}$) is again required, leading to the following splittings of the five reachable terms in the intermediate state:

$$\begin{aligned}
 ^2A_{1g} \otimes E_{1/2g} &= E_{1/2g}, \\
 ^2A_{2g} \otimes E_{1/2g} &= E_{5/2g}, \\
 ^2E_g \otimes E_{1/2g} &= F_{3/2g}, \\
 ^2T_{1g} \otimes E_{1/2g} &= E_{1/2g} \oplus F_{3/2g}, \\
 ^2T_{2g} \otimes E_{1/2g} &= E_{5/2g} \oplus F_{3/2g}.
 \end{aligned} \tag{80}$$

Hence, the 2p XES decays in 1s2p RIXS can occur from any of these three total angular momentum IRREPs $E_{1/2g}$, $E_{5/2g}$, or $F_{3/2g}$.

The final state electron configuration $1s^2 2p^5 3d^8$ is again identical to the high spin case regardless of the crystal field

effects, offering the three total angular momentum IRREPs $E_{1/2u}$, $E_{5/2u}$, and $F_{3/2u}$. For the 2p XES decaying from the populated intermediate state terms, using the T_{1u} IRREP (Table 4) again reveals that all three final state IRREPs are also reachable. Furthermore, in 2p XAS, starting from the $F_{3/2g}$ ground state symmetry, also, all three final state IRREPs are reachable (Table 4).

The results according to the selection rules as discussed above are again summarised in a combined term scheme as displayed in Figure 52.

Again, we conclude with an example calculation for a Co^{2+} ion ($3d^7$ ground state configuration) with $10Dq = 3.0$ eV reflecting the low spin case as shown in Figure 56.

It is noteworthy that the quadrupole IRREP T_{2g} here is very weak (10^{-3}) with respect to the E_g IRREP. This can again be explained with the very small matrix elements for the two-electron transition that is required to create a hole in the t_{2g} orbitals, because the quadrupole IRREP T_{2g} populates the intermediate state symmetries T_{1g} and T_{2g} , which both require a hole in the t_{2g} level.

This is also confirmed by the total RIXS map (Figure 56(a), right) showing that the overall result is dominated by the transitions into the three intermediate state symmetries $^2A_{2g}$, 2E_g , and $^2A_{1g}$, while the $^2T_{1g}$ and $^2T_{2g}$ intermediate state symmetries are negligible due to the reason given above.

However, as predicted by the selection rules for the quadrupole IRREPs, T_{2g} and E_g as shown in Figure 56 confirm the predicted reachable terms as found in expression (79).

5.8. 1s2p RIXS Experiments of $3d^7$ Systems. A 300 meV resolution 1s2p RIXS experiment on CoO was published by

FIGURE 54: Calculated 1s2p RIXS spectrum for Co^{2+} ($3d^7$) for $10Dq = 0.9$ eV (high spin).

Kurian et al. [50]. The increased resolution revealed new details in the pre-edge fine structure, and it was possible to study the effect of interference effects on the 1s2p RIXS plane.

6. Concluding Remarks

We have presented first three didactic cases, being the Cu^{2+} ($3d^9$), Ti^{4+} ($3d^0$), and Ni^{2+} ($3d^8$), respectively, for

FIGURE 55: 1s XAS projections of the calculated 1s2p RIXS maps for a Co^{2+} ion ($3d^7$) with $10Dq = 2.4$ eV to 3.3 eV (low spin only).

which detailed descriptions were given. For those cases, we included also an atomic calculation without a crystal field to illustrate the effect an octahedral crystal field has. The didactic cases were chosen as these cases have a low number of microstates involved (e.g., having an almost full or almost empty 3d shell). Though the effort would be significantly larger, when needed, one can further separate the 2p XES transitions for the more complex cases discussed in Section 5. For example, calculations with an unrealistic low natural broadening (e.g., 1–2 meV) would enable to do a detailed fingerprint comparison with the stick spectra allowing to assign the peaks.

Altogether, we illustrated the effects of an octahedral crystal field and the selection rules for an example ion for every $3d^N$ ground state case (with $N = \{0, \dots, 9\}$). Here, we provide a few selected examples of calculations. For an even better illustration, one can for example combine the calculated RIXS maps or combine many slices into short movie clips where one or more parameters (e.g., $10Dq$ or SOC) are scaled. For the crystal field parameter $10Dq$, such scaling would relate to the corresponding *Tanabe-Sugano diagram* which is also shown throughout this paper for the 1s XAS projections.

Another important aspect is the mixing of the states induced by spin-orbit or exchange interactions, as well as the crystal field. Although we have assigned labels to many states involved in the transitions, those labels represent only the dominant contribution to each state. In reality, most states are not pure in their nature as it was also mentioned for several cases throughout this paper. As can be seen for example in the Cr^{3+} , Mn^{3+} , or Fe^{3+} cases, the stick spectra show a very dense distribution of states. To give a detailed insight into the structure of the spectra, we have used a rather small Lorentzian broadening, while any Gaussian broadening was omitted for all calculations. Hence, when a realistic natural broadening is assumed and an experimental broadening is also considered, one can hardly separate the transitions visible in one of the complex spectra. Due to the often very small splittings in many cases, the states appear as a band rather than discrete states. The difference between the final states probed in 1s2p RIXS versus 2p XAS is emphasised for each $3d^N$ case.

The computational effort is for the complex cases quite time-consuming, especially when aiming for high-resolution spectra which are needed when the broadenings are small. However, this effort is justified as it helps to get a better understanding of RIXS spectra and they can in some cases be also useful to determine for example the spin state (high spin versus low spin).

With increasing computational power being available in the future, also Monte Carlo-like calculations can become a favourable approach, as one can for example calculate “all RIXS spectra” for a sufficient section of the parameter space and then select the best fit. However, it is safe to assume that for most ions such calculations will yield multiple results making the combination with additional information, especially for more complex cases, necessary. Although we show the importance of the multielectronic excitations in the 1s2p RIXS, the emerging first-principle estimation of the crystal field parameters will open new opportunities for the modelling of experimental data.

For each case of the $3d^N$ series, we have discussed the 1s2p RIXS crystal field calculation in the light of the available experimental data. With few exceptions, 1s2p RIXS experiments are to date performed with an experimental resolution of 500 meV or more. This resolution does not allow a competitive comparison with 2p XAS regarding the details of the electronic structure parameters as discussed here. The constant improvements of the experimental resolution in hard X-ray spectroscopy enable to acquire a better experimental spectrum where natural broadenings are approached as the ultimate limit. An overall experimental resolution of 200 meV would be necessary to improve upon the determination of the parameters. Tetra-valent systems are dominated by nonlocal dipole transitions that overwhelm the quadrupole pre-edges. This makes the analysis of 1s2p RIXS complicated. The best systems to study the details of the 1s2p RIXS resonances are ionic divalent systems.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

FIGURE 56: Calculated 1s2p RIXS spectrum for Co^{2+} ($3d^7$) for $10Dq = 3.0$ eV (low spin).

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