Angular dependence and powder average of resonant inelastic X-ray scattering

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Resonant inelastic X-ray scattering (RIXS) is a synchrotron-based spectroscopy that has seen growing interest across a range of scientific disciplines beyond fundamental physics. The interpretation of experimental RIXS data requires theoretical calculations based on the Kramers–Heisenberg formula. However, due to the dependence of RIXS on both the incident and scattered photon properties, a tractable treatment of the angular dependence in this formula has been lacking. In this work, within the electric dipole approximation, we determine the number of fundamental spectra contributing to the RIXS cross-section for all crystallographic point groups. We then derive a general expression for the RIXS cross-section of isotropic samples such as un-textured powders, homogeneous glasses or liquids, explicitly accounting for the polarization and propagation directions of both the incident and scattered photons. Simplified forms of the RIXS expressions are subsequently obtained for most common point groups. Finally, we demonstrate the applicability of our formalism through a case study of uranium $3d4f$ RIXS.

Resonant inelastic X-ray scattering (RIXS) has proven to be extremely useful to investigate the properties of materials [1, 2]. The riches of RIXS come from the fact that it depends on the energy of the incident and scattered beams, as well as on the polarization and direction of the incident and scattered beams with respect to the sample, which allows access to more spectral information [3–6]. To this end, instrumental capabilities have been implemented at synchrotron beamlines, providing the ability to control the polarization of the incident beam, vary the scattering angle, and perform polarization analysis of the scattered radiation [7–9].

While most of these studies are performed on single crystals, the number of studies on isotropic samples like powders has been growing thanks to the application of RIXS by new scientific communities, e.g. chemistry [2, 10], catalysis [11], high-pressure [12], actinides [13]. These communities exploit RIXS to go beyond conventional X-ray Absorption Spectroscopy (XAS) through the use of High Energy Resolution Fluorescence Detection (HERFD). This approach, which involves taking a constant-emission-energy cut in the RIXS plane, overcomes the limitations imposed by core-hole lifetime broadening and reveals otherwise hidden spectral features. A remarkable example is provided by the actinide M edges, where the application of HERFD-XAS has reopened a very active field of investigation on these complex compounds [14, 15]. However, the interpretation of experimental RIXS data often requires theoretical calculations. The Kramers-Heisenberg formula [16, 17] has been implemented in various computational methods, from semi-empirical ligand field multiplet calculations [18] to more advanced *ab-initio* calculations [19, 20].

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In a previous work [21], we investigated the dependence of RIXS on the polarization and direction of the incident and scattered beams for a sample without considering the effect of sample symmetry. We also derived explicit formulas for the polarization and angular dependence of an isotropic powder sample. However, the remaining challenge is that computational methods do not use an isotropic sample as input but the non-isotropic structural model of the system of interest (e.g. the point group symmetry of the absorbing atom for semi-empirical multiplet calculations, a cluster around the absorber or the unit cell of a crystal for *ab-initio* methods). In standard XAS computation, the spectra computed using the model system can easily be related to the experimental isotropic spectrum [22]. However for RIXS, the coupling between the incident photon and the scattered photon makes this connection more challenging.

The purpose of this article is two-fold. Firstly, we discuss the effect of a sample (molecule or crystal) symmetry on the angular and polarization dependencies and secondly we determine the minimal number of calculations (or single-crystal measurements) required to compute these dependencies for an isotropic powder sample in the electric dipole approximation for the incident and scattered beams. These derivations are performed in the impurity approximation, meaning that we neglect the interferences between the scattering events of different atoms. In the following, the coordinates (x, y, z) are in the standard orthonormal reference frame for point group operations as defined by Altman and Herzig [23].

This paper is divided into six parts. In part I, we demonstrate the well-known fact that the RIXS cross-section for electric dipole transitions is based on 81 spectra, and we prove that this number can be reduced further down to $n_G \leq 81$ fundamental spectra by taking symmetry into account. In part II, we use spherical tensors to understand n_G and provide specific considerations about circular dichroism and site symmetry. In part III, we determine n_G and the relations between RIXS matrix elements for several symmetry groups as well as for the case of a spherically symmetric sample. In part IV, we derive the RIXS cross-section formula for a powder sample without taking the symmetry into account and then in part V, we give the final RIXS cross-section formula for an isotropic sample knowing the symmetry of the absorber for most point groups. Finally, in part VI, we draw some predictions for the experimental observations and we apply these formulas to selected examples to highlight the impact on the computed result.

I. RIXS CROSS SECTION AND SAMPLE SYMMETRY

The starting point of this analysis is the Kramers-Heisenberg formula [16, 17] for RIXS

$$\frac{r_e^2}{m^2}\frac{\omega_s}{\omega}\sum_F\Big|\sum_N\frac{\langle F|\epsilon_s^*\cdot\mathbf{P}\mathrm{e}^{-i\mathbf{k}_s\cdot\mathbf{r}}|N\rangle\langle N|\epsilon\cdot\mathbf{P}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}|I\rangle}{E_I-E_N+\hbar\omega+i\gamma}\Big|^2 \times\delta(E_F+\hbar\omega_s-E_I-\hbar\omega),$$

where m is the electron mass, r_e is the classical electron radius: $r_e=e^2/(4\pi\epsilon_0 mc^2)$, $|I\rangle$, $|N\rangle$, $|F\rangle$ are the initial, intermediate and final (possibly many-body) states, respectively, γ is the total width of the intermediate state $|N\rangle$, $\mathbf{P}$ and $\mathbf{r}$ are the momentum and position operators. The incident and scattered photons are characterized by the pulsation, wavevector and polarization vectors $\omega,\mathbf{k},\epsilon$ and $\omega_s,\mathbf{k}_s,\epsilon_s$, respectively. Note that ϵ_s^* is the complex conjugate of ϵ_s.

In the present paper we limit ourselves to the RIXS cross-section due to electric dipole transitions [21]:

$$\sigma(\epsilon_s,\epsilon) = \frac{r_e^2}{\hbar^2}\frac{\omega_s}{\omega}\sum_F\Big|\sum_N\frac{(E_I-E_N)(E_N-E_F)}{E_I-E_N+\hbar\omega+i\gamma} \times\langle F|\epsilon_s^*\cdot\mathbf{r}|N\rangle\langle N|\epsilon\cdot\mathbf{r}|I\rangle\Big|^2\delta_E, \quad (1)$$

where $\delta_E=\delta(E_F+\hbar\omega_s-E_I-\hbar\omega)$.

A. Group action

It will be convenient to use the concept of an action of a group on a set. Consider for example the group $G=O(3)$ of (linear) isometries, where an element g of G is represented by an orthogonal matrix g_{ij} (i.e. a rotation matrix possibly multiplied by an inversion). With g we can operate on: *i)* a vector $\mathbf{r}$, *ii)* a function $f(\mathbf{r})$, *iii)* a quantum state $|\phi\rangle$, *iv)* a sample s, etc.

In general, the action of an operation g on a set X is a transformation of any element x of X into an element y of X, denoted by $y=g\triangleright x$. In our examples: *i)* X is the space $\mathbb{R}^3$ of 3-dimensional vectors $\mathbf{r}$, *ii)* X is the space of functions $f(\mathbf{r})$ on $\mathbb{R}^3$, *iii)* X is the Hilbert space $\mathcal{H}$ of quantum states $|\phi\rangle$ of the system, *iv)* X is the set S made of a sample s with all its possible orientations (note that we can rotate an object but we cannot mechanically invert it).

An action of a group G on a set X is a *group action* if the successive action of two arbitrary group elements is compatible with the group product : $g'\triangleright(g\triangleright x)=(g'\cdot g)\triangleright x$, where $g'\cdot g$ is the product in G, and if all elements x of X are stable under the action of the identity element e of G (i.e. $e\triangleright x=x$). In case *i)* the action of an isometry g on a vector $\mathbf{r}$ is $g\triangleright\mathbf{r}=g\mathbf{r}$ (i.e. product of the matrix g_{ij} by the vector $\mathbf{r}$). In case *ii)* the action of a rotation on a function $f(\mathbf{r})$ is [24]

$$(g\triangleright f)(\mathbf{r}) = f(g^{-1}\mathbf{r}), \quad (2)$$

where g_{ij}^{-1} is the inverse matrix of g_{ij}. For case *iii)*, we consider the action of an isometry on a quantum state which is an eigenstate of a Hamiltonian H with energy E. To take energy degeneracy into account, consider a basis $|\psi_1\rangle,\dots,|\psi_n\rangle$ of the eigenstates of H with energy E. If G is a symmetry group of H (i.e. $g\triangleright H=H$ for all $g\in G$), we know that every element g of G transforms a state of H into a state with the same energy. More precisely, Wigner showed that there is a unitary matrix $U(g)$ such that:[25]

$$g\triangleright|\psi_i\rangle = \sum_{j=1}^n U(g)_{ji}|\psi_j\rangle, \quad (3)$$

where $U(g)_{ji}$ is required instead of $U(g)_{ij}$ for $g\triangleright|\psi_i\rangle$ to be a (linear) group action:

$$\begin{aligned} g'\triangleright(g\triangleright|\psi_i\rangle) &= \sum_{j=1}^n U(g)_{ji}(g'\triangleright|\psi_j\rangle) \\ &= \sum_{j=1}^n\sum_{k=1}^n U(g)_{ji}U(g')_{kj}|\psi_k\rangle \\ &= \sum_{k=1}^n\big(U(g')U(g)\big)_{ki}|\psi_k\rangle. \end{aligned}$$

This action is a group action if and only if $U(g')U(g)=U(g'\cdot g)$ (i.e. U is a unitary representation of G).

Consider now the projection onto the space of states of energy E:

$$P(E) = \sum_{j=1}^n|\psi_j\rangle\langle\psi_j|.$$

From the action of g on $|\psi_j\rangle$ of Eq. (3) and the unitarity of $U(g)$, we deduce that $P(E)$ is invariant under the action of g:

$$g\triangleright P(E) = \sum_{j,k,l}U(g)_{kj}|\psi_k\rangle\langle\psi_l|U(g)_{lj}^* = P(E). \quad (4)$$

These preliminaries enable us to calculate various actions of groups of isometries on the RIXS cross-section.

B. Action of an isometry on the cross-section

We calculate the action of isometries on the RIXS cross-section in two ways: by acting on the states seen as a function of $\mathbf{r}$ as in Eq. (2) and then by acting on the states by a unitary representation as in Eq. (3).

We want to determine how the transition matrix element $\langle\phi|H_I|\psi\rangle = \int d\mathbf{r}\phi^*(\mathbf{r})\epsilon\cdot\mathbf{r}\psi(\mathbf{r})$ transforms under the action of a general isometry g. We show that

$$g \triangleright \langle\phi|H_I|\psi\rangle \;=\; \int d\mathbf{r}\phi^*(g^{-1}\mathbf{r})\epsilon\cdot\mathbf{r}\psi(g^{-1}\mathbf{r}). \qquad (5)$$

This statement is not as trivial as it looks because we must disentangle the action of g on H_I from its action on the unperturbed Hamiltonian H_0. First recall that the Hamiltonian of an electron in an electromagnetic field is $H = (\mathbf{p} - e\mathbf{a})^2/2m + V + ev$, where $\mathbf{p} = -i\hbar\nabla$, $\mathbf{a}$ is the vector potential and v the electric potential. Time-dependent perturbation theory for an incident electromagnetic wave described by the vector potential $\mathbf{a}\cos(\omega t)$ leads to the calculation of matrix elements such as $\langle\phi|H_I|\psi\rangle$, where $H_I = -e\mathbf{p}\cdot\mathbf{a}/m$ and $|\phi\rangle$ and $|\psi\rangle$ are eigenstates of $H_0 = \mathbf{p}^2/2m + V$ [22]. Within this model, acting with isometry g on the sample amounts to transforming the potential $V(\mathbf{r})$ into the potential $V'(\mathbf{r}) = (g \triangleright V)(\mathbf{r}) = V(g^{-1}\mathbf{r})$, as in Eq. (2). The Hamiltonian of the transformed sample in the original reference frame is $H_0' = \mathbf{p}^2/2m + V'$ and we go from the momentum transition operator $-e\mathbf{p}\cdot\mathbf{a}/m$ to the electric dipole one by using $[\mathbf{r}, H_0] = [\mathbf{r}, H_0'] = (\hbar^2/m)\nabla$. Therefore, g does not act on the transition operator, which is still $\epsilon\cdot\mathbf{r}$.

To determine the eigenstates of H_0', we observe that a change of coordinates $\mathbf{r} \to \mathbf{r}' = g^{-1}\mathbf{r}$ transforms H_0 into $g \triangleright H_0 = (\mathbf{p}')^2/2m + V(\mathbf{r}')$, where $\mathbf{p}' = g^{-1}\mathbf{p}$. The orthogonality of g implies that $(\mathbf{p}')^2 = \mathbf{p}^2$ and $g \triangleright H_0 = H_0'$. Thus, the eigenstates of H_0' are the eigenstates of $g \triangleright H_0$, which are $\phi(\mathbf{r}') = \phi(g^{-1}\mathbf{r})$. This completes the proof of Eq. (5). Note that the result is still valid if H_0 contains a two-body Coulomb interaction.

Starting from Eq (5), we change variables $\mathbf{r} = g\mathbf{r}'$ and notice that $d\mathbf{r} = d\mathbf{r}'$ (g being an orthogonal matrix, the Jacobian of the transformation is $|J| = |\det g| = 1$) to replace a transformation of the sample by a transformation of the transition operator and then a transformation of the polarization vector:

$$g \triangleright \langle\phi|\epsilon\cdot\mathbf{r}|\psi\rangle \;=\; \langle\phi|\epsilon\cdot(g\mathbf{r})|\psi\rangle = \langle\phi|(g^{-1}\epsilon)\cdot\mathbf{r}|\psi\rangle,$$

because g, as a linear isometry, conserves scalar products. The physical interpretation of this result is that the action of an isometry on a sample gives the same result as the action of the inverse isometry on the measurement device (represented by ϵ).

Thus, the action of an isometry g on the sample transforms the cross-section into $g \triangleright \sigma(\epsilon_s, \epsilon) = \sigma(g^{-1}\epsilon_s, g^{-1}\epsilon)$, that it will be more convenient to write

$$g^{-1} \triangleright \sigma(\epsilon_s, \epsilon) \;=\; \sigma(g\epsilon_s, g\epsilon), \qquad (6)$$

where we recall that we only assume g to be an isometry (i.e. an arbitrary element of $O(3)$) and not necessarily a symmetry of the sample. This property will be crucial in the following derivations. Note that Eq. (6) has no equivalent for antiunitary elements g of a magnetic group [26].

C. Action of a symmetry on the cross-section

We consider now only isometries g which are symmetries of the sample. By this we mean the point group of the space group of a crystal or the point group of a molecule. If the site of the absorbing atom has a lower symmetry group, then this subgroup must be used for the calculation of the spectrum, but the average over the different sites recovers the full point group [27].

For example, if the system is represented by the Hamiltonian $H_0 = \mathbf{p}^2/2m + V$, we assume that $(g \triangleright V)(\mathbf{r}) = V(g^{-1}\mathbf{r}) = V(\mathbf{r})$ and the action of g on the states of the system is described by Eq. (3).

To compute the action of g on $\sigma(\epsilon_s, \epsilon)$, we expand the modulus square in Eq. (1) for a given value of E_I, E_N, $E_{N'}$ and E_F (the presence of $E_{N'}$ being due to the fact that the sum over N is inside the modulus, as in Eq. (10)), and we replace the sum over states of energy E by a projector $P(E)$ to obtain terms of the type.

$$T \;=\; \langle I|\epsilon^*\cdot\mathbf{r}P(E_{N'})\epsilon_s\cdot\mathbf{r}P(E_F)\epsilon_s^*\cdot\mathbf{r}P(E_N)\epsilon\cdot\mathbf{r}|I\rangle.$$

For simplicity, we considered a non-degenerate initial state $|I\rangle$. If it is degenerate, we must average over initial states (this also is how we take temperature effects into account) and T becomes

$$\frac{1}{n_I}\mathrm{Tr}\Big(P(E_I)\epsilon^*\cdot\mathbf{r}P(E_{N'})\epsilon_s\cdot\mathbf{r}P(E_F)\epsilon_s^*\cdot\mathbf{r}P(E_N)\epsilon\cdot\mathbf{r}\Big),$$

where n_I is the degeneracy of the initial state. By using the invariance of $P(E)$ under the action of a symmetry operation g (see Eq. (4)), we see that $g \triangleright T = T$, so that

$$g \triangleright \sigma(\epsilon_s, \epsilon) \;=\; \sigma(\epsilon_s, \epsilon). \qquad (7)$$

Equations (6) and (7) lead us to the invariance

$$\sigma(\epsilon_s, \epsilon) \;=\; \sigma(g\epsilon_s, g\epsilon), \qquad (8)$$

for every symmetry operation g of the sample. These symmetry operations form a group G. In other words, for any isometry of the absorbing atom point group, the RIXS cross-section is the same when the incident and scattered polarizations are rotated with this same operation.

D. Symmetry reduction of the cross-section

To investigate the effect of symmetry on the RIXS cross-section we rewrite its definition Eq. (1) as:

$$\sigma(\epsilon_s, \epsilon) \;=\; \sum_{imjn} \epsilon_{si}^*\epsilon_m\epsilon_n^*\epsilon_{sj}a_{im,jn}, \qquad (9)$$

where ϵ_m and ϵ_n run over the three Cartesian coordinates of ϵ and the same for ϵ_s, and

$$\begin{aligned} a_{im,jn} &= \frac{r_e^2}{\hbar^2}\frac{\omega_s}{\omega}\sum_F\sum_{N,N'}\frac{(E_I-E_N)(E_N-E_F)}{E_I-E_N+\hbar\omega+i\gamma} \\ &\times\frac{(E_I-E_{N'})(E_{N'}-E_F)}{E_I-E_{N'}+\hbar\omega-i\gamma}\langle F|r_i|N\rangle\langle N|r_m|I\rangle \\ &\times\langle I|r_n|N'\rangle\langle N'|r_j|F\rangle\delta_E, \end{aligned} \quad (10)$$

where r_i, r_m, r_j and r_n run over the Cartesian coordinates of $\mathbf{r}$. From this definition we see that $a_{im,jn}$ is Hermitian (i.e. $a^*_{im,jn} = a_{jn,im}$), so that $a_{im,jn}$ has a priori 81 components.

In the presence of non-trivial symmetry, relations exist between different $a_{im,jn}$ and we call *fundamental spectra* a set of real or imaginary parts of some $a_{im,jn}$ from which all non-zero $a_{im,jn}$ (and thus all RIXS spectra) can be computed. This is similar to the fundamental spectra defined by Thole and Van der Laan for photoemission [28]. A specific $a_{im,jn}$ will provide one fundamental spectrum if it is real or purely imaginary and two fundamental spectra if it has non-zero real and imaginary parts.

We shall see in section IV B that the invariance property of Eq. (8) implies

$$a_{im,jn} = \sum_{i'm'j'n'} N_{imjn,i'm'j'n'}a_{i'm',j'n'}, \quad (11)$$

where

$$N_{imjn,i'm'j'n'} = \frac{1}{|G|}\sum_{g\in G} g_{ii'}g_{mm'}g_{jj'}g_{nn'}. \quad (12)$$

In section IV B we prove that, thanks to the average of G in Eq. (12), the left hand side of Eq. (11) has all the symmetries of the group G even if $a_{i'm',j'n'}$ has no symmetry. In other words, the invariance under G is entirely due to the properties of $N_{imjn,i'm'j'n'}$.

We give now the practical method to determine the symmetries of $a_{im,jn}$, which can easily be implemented with standard symbolic computing packages.

- Compute $N_{imjn,i'm'j'n'}$ by Eq. (12).
- Transform $N_{imjn,i'm'j'n'}$ into a 81×81 matrix denoted by N^G. For this, associate a number k between 1 and 81 to each quadruple (i,m,j,n). For example $k = n+3(j-1)+9(m-1)+27(i-1)$ and define $N^G_{kk'} = N_{imjn,i'm'j'n'}$.
- Compute the number n_G of fundamental spectra of $a_{im,jn}$, which is the rank of N^G and also the trace of N^G since N^G is a projection (i.e. $(N^G)^2 = N^G$ and $(N^G)^\dagger = N^G$).
- Gather in the rectangular matrix L^G the different non-zero lines of N^G (i.e. if the same line appears several times in N^G it appears only once in L^G). Let n_L be the number of lines of L^G (note that $n_L \geq n_G$).
- Compute the null space of the transpose of L^G, which gives you $n_L - n_G$ relations between lines by which you can write these lines in terms of n_G independent ones.
- For each line L of L^G, identify the index k of the lines of N^G which are equal to L and transform back k into (i,m,j,n) to express this equality of lines as an equality between some $a_{im,jn}$.

For the example of D_{6h}, we shall see that the rank of N^G is $n_G = 10$, the number of its non-zero lines is 21, the number of different non-zero lines of N^G is $n_L = 11$ and there is one relation between lines.

We can also determine the numbers $n_{\rm Re}$ and $n_{\rm Im}$ of non-zero real and imaginary fundamental spectra by noticing that the matrix P representing the permutation $(imjn) \to (jnim)$ commutes with N and satisfies $P^2 = 1$. From $Pa_{im,jn} = a_{jn,im} = a^*_{im,jn}$ we see that the number of independent real and imaginary parts in the tensor $a_{im,jn}$ are $n_{\rm Re} = {\rm Tr}\big((1+P)N/2\big)$ and $n_{\rm Im} = {\rm Tr}\big((1-P)N/2\big)$, respectively, with $n_{\rm Re}+n_{\rm Im} = n_G$.

Table I gives for each crystallographic point group, the number of matrix elements $a_{im,jn}$ which are not zero by symmetry, the number n_L of matrix elements which are different (in the sense that any matrix element is equal to one of those) and the number n_G of fundamental spectra (in the sense that any matrix element can be written as a linear combination of those). The symbol $\simeq$ in Table I means that, if the standard reference frame [23] is used (in particular the high symmetry axis is along the z axis), then all the matrix elements $a_{im,jn}$ of these two groups enjoy the same relations. The only difficulty comes from the case of C_{3v} which has two usual reference frames [23]: the $1A$ parameters or the $1B$ parameters. With $1B$ parameters (where the mirror plane is perpendicular to the x axis), the matrix elements $a_{im,jn}$ have the same relations as those of C_{3v} and D_3 (see Section III F). With $1A$ parameters (where the mirror plane is perpendicular to the y axis), the matrix elements have different relations (see Section III G).

Several other examples will be given below.

II. ALTERNATIVE WAY TO THE FUNDAMENTAL SPECTRA

In this section we show that the number of fundamental spectra can be understood and obtained by hand using spherical tensors. We first define spherical parameters and then we use them to calculate circular dichroism and to compute the average cross-section over equivalent sites in a crystal or a molecule.

TABLE I. Number of possibly non-zero matrix elements (i.e. that do not vanish by symmetry), number n_L of different matrix elements, number n_G of fundamental spectra and number $n_{\rm Im}$ of imaginary components for all crystallographic point groups, $SO(3)$ and $O(3)$. For an isotropic sample, n_S is the number of spectra needed to calculate the full angular dependence and n_C is the number of spectra needed to calculate the angular dependence when the polarization of the scattered beam is not measured, as explained in Section V. The meaning of $\simeq$ is explained at the end of Section I D.

Point groups	$\neq 0$	n_L	n_G	$n_{\rm Im}$	n_S	n_C
$C_1\simeq C_i$	81	81	81	36	21	15
$C_2\simeq C_s\simeq C_{2h}$	41	41	41	16	17	13
$D_2\simeq C_{2v}\simeq D_{2h}$	21	21	21	6	15	12
$C_4\simeq S_4\simeq C_{4h}$	41	31	21	8	10	7
$D_4\simeq C_{4v}\simeq D_{2d}\simeq D_{4h}$	21	11	11	2	9	7
$C_3\simeq S_6$	73	47	27	12	11	7
$D_3\simeq D_{3d}$, C_{3v}	37	19	14	4	8	6
$C_6\simeq C_{3h}\simeq C_{6h}$	41	31	19	8	9	6
$D_6\simeq C_{6v}\simeq D_{3h}\simeq D_{6h}$	21	11	10	2	8	6
$T\simeq T_h$	21	7	7	2	5	4
$O\simeq T_d\simeq O_h$	21	4	4	0	4	3
$SO(3)\simeq O(3)$	21	4	3	0	3	2

A. Definition of spherical parameters

Instead of fundamental spectra, we can define the *spherical parameters* S^{abc}_γ, which were defined in [21] by

$$S^{abc}_\gamma = \sum_{\alpha,\beta}\sum_{\mu\nu\mu'\nu'} (1\mu' 1\nu|a\alpha)(1\mu 1\nu'|b\beta)(a\alpha b\beta|c\gamma) \times A_{i\mu'}A_{m\nu}A_{n\mu}A_{j\nu'}\, a_{im,jn}, \quad (13)$$

(corresponding to $S^{g_1 g_2 a}_L$ in Ref. 21), where a and b take the values 0, 1, 2 and c runs from $|a-b|$ to $a+b$, so that c takes values from 0 to 4.

For the example of a sample with symmetry O, T_d or O_h, the non-zero spherical parameters of this approach are

$$\begin{aligned} S^{000}_0 &= a_{11,11} + 2a_{11,22},\\ S^{110}_0 &= -\sqrt{3}(a_{12,12} - a_{12,21}),\\ S^{220}_0 &= \frac{1}{\sqrt{5}}(2a_{11,11} - 2a_{11,22} + 3a_{12,12} + 3a_{12,21}),\\ S^{224}_4 &= S^{224}_{-4} = \sqrt{\frac{5}{14}}\,S^{224}_0\\ &= \frac{1}{2}(a_{11,11} - a_{11,22} - a_{12,12} - a_{12,21}). \end{aligned}$$

The relation between the components of the spherical tensor S^{224} is a well-known consequence of cubic symmetry [22]. It illustrates the fact that several spherical parameters S^{abc}_γ can be proportional. Of course, the number of independent spherical parameters is the same as the number of fundamental spectra.

The relation $a_{jn,im} = a^*_{im,jn}$ implies

$$(S^{abc}_\gamma)^* = (-1)^{a+b+c+\gamma} S^{abc}_{-\gamma},$$

which shows that S^{abc}_0 is real if $a+b+c$ is even and purely imaginary if $a+b+c$ is odd.

To describe the action of an isometry g on the spherical parameters S^{abc}_γ, we first note that any isometry can be written $g = (-1)^{n_g}R$, where R is a rotation matrix and $n_g = 0$ or 1 if $\det g = 1$ (g is said to be even) or -1 (g is said to be odd), respectively. The rotation R will be called the *rotation part* of g.

The fact that the columns of matrix A can be considered as polarization vectors leads to the group action

$$g^{-1} \triangleright S^{abc}_\gamma = \sum_{\gamma'=-c}^{c} S^{abc}_{\gamma'} D^c_{\gamma'\gamma}(R),$$

where R is the rotation part of g and where $D^c_{\gamma'\gamma}(R)$ is the Wigner rotation matrix whose arguments are the same Euler angles as those of R. The part $(-1)^{n_g}$ of g disappears because the group action involves a product of four g.

When the symmetry group G is only made of even isometries, building group invariants from $a_{im,jn}$ reduces to building group invariants from spherical harmonics Y^γ_c and the number $n_G(c)$ of such invariants is given by the number of fully symmetric representations (denoted A_{1g} or A_1 or A) of G indicated in the section "Subduction from $O(3)$" of Altmann and Herzig's tables [23]. These group invariants can also be obtained explicitly by considering the group averages

$$\langle Y^\gamma_c \rangle = \frac{1}{|G|}\sum_{g\in G} Y^{\gamma'}_c D^c_{\gamma'\gamma}(R).$$

These averages for $c = 2$ and 4 were constructed in Ref. [22].

The spherical tensor decomposition described by Eq. (13) can be summarized by

$$\begin{aligned} \mathbf{1}^{\otimes 4} &= (\mathbf{1}^{\otimes 2})^{\otimes 2} = (\mathbf{0}\oplus\mathbf{1}\oplus\mathbf{2})^{\otimes 2}\\ &= (3\times\mathbf{0})\oplus(6\times\mathbf{1})\oplus(6\times\mathbf{2})\oplus(3\times\mathbf{3})\oplus\mathbf{4}, \quad (14) \end{aligned}$$

which means that $a_{im,jn}$ can be seen as the sum of three spherically symmetric tensors, six tensors of rank 1, six tensors of rank 2, three tensors of rank 3 and one tensor of rank 4. The total number of fundamental spectra is then the weighted sum of the numbers $n_G(c)$:

$$n_G = 3n_G(0) + 6n_G(1) + 6n_G(2) + 3n_G(3) + n_G(4).$$

The procedure must be modified when some elements g of G are odd, which is the case of the groups that are not in the first position in a line of Table I. Indeed, Altmann and Herzig's tables are constructed such that an inversion cancels all spherical tensors of odd rank, whereas it has no effect on the RIXS tensor. Therefore, these tables must be used with a group G' derived from G as follows. Since G contains an odd element, G can be written as the union of a set G^+ of even elements and a set G^- of odd elements. Since the inversion I commutes with all rotations and satisfies $I^2 = 1$, we see that G^+ is a subgroup of G and has the same number of elements as G^-. If I is an element of G^-, then $IG^- = G^+$, where IG^- is the set of $-g_{ij}$ with $g \in G^-$. In that case we take $G' = G^+$ (because the average Eq. (12) over G is the same as the average over G^+). If I is not an element of G^-, then $G' = G^+ \cup IG^-$ is a group without odd elements, which has the same number of elements as G and such that G^+ is a subgroup of G'. The number n_G of fundamental spectra of G is then the weighted sum of $n_{G'}(c)$. In Table I the first group of each line is the G' for all groups of that line.

Conversely, if the spherical parameters are constructed as linear combinations of Y_c^γ for all c such that $n_{G'}(c) \neq 0$, they can be transformed into relations for $a_{im,jn}$ by inverting Eq. (13):

$$a_{im,jn} = \sum_{a\alpha b\beta c\gamma} \sum_{\mu\nu\mu'\nu'} (1\mu' 1\nu|a\alpha)(1\mu 1\nu'|b\beta)(a\alpha b\beta|c\gamma) \times A^*_{i\mu'} A^*_{m\nu} A^*_{n\mu} A^*_{j\nu'} S^{abc}_\gamma. \quad (15)$$

B. Circular dichroism and permutation symmetry

Circular dichroism is the difference between the spectra obtained from left- and right-polarized incident beams. This is now a well-established technique [26, 29–31].

Circular dichroism in RIXS measures the difference

$$\Delta\sigma(\epsilon_s, \epsilon) = \sigma(\epsilon_s, \epsilon) - \sigma(\epsilon_s, \epsilon^*). \quad (16)$$

By Eq. (9) we see that

$$\Delta\sigma(\epsilon_s, \epsilon) = \sum_{imjn} \epsilon^*_{si} \epsilon_m \epsilon^*_n \epsilon_{sj} (a_{im,jn} - a_{in,jm}).$$

Circular dichroism is usually normalized with respect to the average of $\sigma(\epsilon_s, \epsilon)$ and $\sigma(\epsilon_s, \epsilon^*)$ which is obtained by $(a_{im,jn} + a_{in,jm})/2$. The basic remark of this section is to notice that $a_{in,jm}$ is obtained from $a_{im,jn}$ by the permutation $(imjn) \to (injm)$.

We saw by Eq. (15) that

$$a_{im,jn} = \sum_{abc\gamma} Y^{ab}_{imjn}(c, \gamma) S^{abc}_\gamma,$$

where

$$Y^{ab}_{imjn}(c, \gamma) = \sum_{\alpha\beta} \sum_{\mu\nu\mu'\nu'} (1\mu' 1\nu|a\alpha)(1\mu 1\nu'|b\beta)(a\alpha b\beta|c\gamma) \times A^*_{i\mu'} A^*_{m\nu} A^*_{n\mu} A^*_{j\nu'}.$$

The determination of circular dichroism in RIXS by $a_{im,jn} - a_{in,jm}$ amounts to the calculation of $Y^{ab}_{imjn}(c, \gamma) - Y^{ab}_{injm}(c, \gamma)$. The quantity $Y^{ab}_{injm}(c, \gamma)$ is obtained from $Y^{ab}_{imjn}(c, \gamma)$ by the permutation $(imjn) \to (injm)$. Spherical tensor recoupling techniques allow us to write this permutation in terms of $9j$-symbols [32, p. 70]

$$Y^{ab}_{injm}(c, \gamma) = \sum_{d,e} \Pi_{abde} \begin{Bmatrix} 1 & 1 & a \\ 1 & 1 & b \\ d & e & c \end{Bmatrix} Y^{de}_{imjn}(c, \gamma),$$

where

$$\Pi_{abde} = \sqrt{(2a+1)(2b+1)(2d+1)(2e+1)}.$$

To describe the sum over d, e, recall that Eq. (14) describes the multiplicity of rank c in the tensor decomposition of $\mathbf{1}^{\otimes 4}$. This multiplicity is $T(c) = 3, 6, 6, 3, 1$ for $c = 0, 1, 2, 3, 4$, respectively, where $T(c)$ is the number of pairs (a, b), a and b taking values in $\{0, 1, 2\}$, such that the triangle rule $|a - b| \leq c \leq a + b$ is satisfied. For example, for $c = 2$, the 6 pairs are $(a, b) = (0, 2), (1, 1), (1, 2), (2, 0), (2, 1), (2, 2)$. The sum over d, e is the sum over these $T(c)$ pairs.

Other permutations have a physical meaning: the measurement of the circular dichroism of the scattered beam is obtained by the permutation $(imjn) \to (jmin)$, the interchange of the incident and scattered beam is described by the permutation $(imjn) \to (njmi)$, which can be obtained by combining the permutations

$$Y^{ab}_{jnim}(c, \gamma) = (-1)^c Y^{ab}_{imjn}(c, \gamma),$$
$$Y^{ab}_{mijn}(c, \gamma) = (-1)^a Y^{ab}_{imjn}(c, \gamma),$$
$$Y^{ab}_{imnj}(c, \gamma) = (-1)^b Y^{ab}_{imjn}(c, \gamma).$$

In conclusion, every permutation of $(imjn)$ in $Y^{ab}_{imjn}(c, \gamma)$ can be expressed as a linear combination of $Y^{de}_{imjn}(c, \gamma)$. In group theoretical parlance, for each $c = 0, \ldots, 4$, the spherical tensors $Y^{ab}_{imjn}(c, \gamma)$ form a $T(c)$-dimensional representation of the symmetric group S_4 of permutations of four elements. The decomposition of these $T(c)$ tensors into irreducible representations of S_4 allows us to pick up the permutation symmetry required for the physical quantity of interest (circular dichroism of the incident or scattered beam, average spectrum of the incident or scattered beam, etc.).

Recall that S_4 is a group of order 24 with 5 irreducible representations: two of them are one dimensional (the trivial representation denoted by (4) and the sign representation denoted by (1,1,1,1)), one is two-dimensional (denoted by $(2, 2)$) and two are three-dimensional (the standard representation denoted by $(3, 1)$ and the product of the sign and standard representations denoted by $(2, 1, 1)$). An explicit calculation gives us the decomposition of $T(c)$-dimensional representation generated by

$Y^{ab}(c)$ into irreducible representations of S_4:

$$\begin{aligned}3\times\mathbf{0} &= (4)\oplus(2,2),\\ 6\times\mathbf{1} &= (3,1)\oplus(2,1,1),\\ 6\times\mathbf{2} &= (4)\oplus(3,1)\oplus(2,2),\\ 3\times\mathbf{3} &= (3,1),\\ \mathbf{4} &= (4).\end{aligned}$$

This combination of point group and permutation symmetries was also found useful in the calculation of Coulomb matrix elements [24].

The conclusion of this discussion is that all linear operations that are carried out on the 81 matrix elements of $a_{im,jn}$ can be encapsulated into equivalent linear operations on the (generally) much less numerous spherical parameters S^{abc}_γ.

A last useful relation is

$$Y^{ab}_{imjn}(c,\gamma)^* = (-1)^{c+\gamma}Y^{ab}_{imjn}(c,-\gamma).$$

C. From site to point group symmetry

In general, the point symmetry group G of a molecule or crystal generates several equivalent sites. Consider a scattering atom at site A with coordinates $\mathbf{R}_A$. Its local symmetry group H is the set of elements g of G such that $g\mathbf{R}_A = \mathbf{R}_A$. The number of fundamental spectra for the RIXS of this atom is that of H. Since our formulation is independent of the translation between atoms, the scattering cross section of the full molecule or crystal is computed as the average of the cross-sections of the equivalent atoms.

Here again, the use of spherical parameters will be particularly convenient. The transition from site symmetry to point group was discussed in detail for the case of X-ray absorption spectroscopy [27] and much of that discussion holds for RIXS. If $S^{abc}_\gamma(A)$ are the spherical parameters of site A, then the spherical parameters $S^{abc}_\gamma(B)$ corresponding to an equivalent site B obtained from A by the transformation $\mathbf{r}_B = g\mathbf{r}_A$ (plus a possible translation) where g is an element of G which is not in H, are [27, Eq. (24)]

$$S^{abc}_\gamma(B) = \sum_{\gamma'=-c}^{c} S^{abc}_{\gamma'}(A)D^c_{\gamma'\gamma}(R^{-1}),$$

where R^{-1} is the inverse of the rotation part of g. And the spherical parameters of the full molecule or crystal is

$$S^{abc}_\gamma = \frac{1}{n}\sum_{g\in K}\sum_{\gamma'=-c}^{c} S^{abc}_{\gamma'}(A)D^c_{\gamma'\gamma}(R^{-1}), \quad (17)$$

where K is a set of representatives of the coset of H in G, i.e. a set of elements of G that transform $\mathbf{r}_A$ into all the sites equivalent to A (up to possible translations), and n is the number of elements of K.

To illustrate the difference between the fundamental spectra and the spherical parameters approaches, consider a site with symmetry D_4 in a cubic crystal. We choose as coset representatives the identity, the rotation of $2\pi/3$ around the (111) axis and the rotation of $2\pi/3$ around the $(\bar{1}1\bar{1})$ axis, but the result does not depend on the representatives. The relation between the fundamental spectra of O and D_4 is

$$\begin{aligned}a^O_{11,11} &= \frac{2}{3}a^{D_4}_{11,11} + \frac{1}{3}a^{D_4}_{33,33},\\ a^O_{11,22} &= \frac{1}{3}a^{D_4}_{11,22} + \frac{2}{3}\,\mathrm{Re}(a^{D_4}_{11,33}),\\ a^O_{12,12} &= \frac{1}{3}a^{D_4}_{12,12} + \frac{1}{3}a^{D_4}_{13,13} + \frac{1}{3}a^{D_4}_{31,31},\\ a^O_{12,21} &= \frac{1}{3}a^{D_4}_{12,21} + \frac{2}{3}\,\mathrm{Re}(a^{D_4}_{13,31}).\end{aligned}$$

So we need to determine 9 components (among the 11 of D_4) to build the 4 components of O. Only the imaginary parts of the fundamental spectra of D_4 are not required.

The spherical parameters for D_4 are 3 parameters $S^{aa0}_0(D_4)$ with $a = 0, 1$ and 2, 6 parameters $S^{ab2}_0(D_4)$ with $(ab) = (02), (11), (12), (20), (21), (22)$ and two parameters $S^{224}_0(D_4)$ and $S^{224}_4(D_4) = S^{224}_{-4}(D_4)$.

The spherical parameters of the crystal with symmetry O obtained from the average of Eq. (17) is then the three parameters $S^{aa0}_0(O) = S^{aa0}_0(D_4)$ which are the same as those of D_4 because a spherical tensor of rank 0 is invariant under rotation, the six parameters S^{ab2}_0 vanish because no invariant of O can be constructed from $c = 2$ and we do not have to calculate them, and the non-zero spherical parameters are

$$\begin{aligned}S^{224}_4(O) &= S^{224}_{-4}(O) = \sqrt{\frac{5}{14}}\,S^{224}_0(O)\\ &= \frac{5}{12}S^{224}_4(D_4) + \frac{\sqrt{70}}{24}S^{224}_0(D_4).\end{aligned}$$

Therefore, we only have to calculate 5 spherical parameters of D_4 (instead of 9) to obtain the 4 spherical parameters of O.

III. RIXS CROSS-SECTION FOR VARIOUS POINT GROUPS

We give now the full determination of the fundamental spectra and of the relations between the $a_{im,jn}$ (defined in Eq. (10)) for several symmetry groups.

A. Case C_1 or C_i

If the symmetry group is C_1 or C_i no $a_{im,jn}$ is constrained to be zero by symmetry and the only relation between them is $a_{jn,im} = a^*_{im,jn}$, so that there are nine real fundamental spectra (i.e. $a_{im,im}$) and the other fundamental spectra can be grouped into 36 complex terms. The number of fundamental spectra is indeed

$$n_G = 3\times 1 + 6\times 3 + 6\times 5 + 3\times 7 + 9 = 81.$$

B. Case C_2, C_s or C_{2h}

If the symmetry group is C_2 or C_s, then $a_{im,jn}$ is zero if exactly one or exactly three of the indices $imjn$ are equal to 3. There are 16 terms where none of the indices $imjn$ are equal to 3, 24 terms where exactly two of the indices $imjn$ are equal to 3 and one term $imjn = 3333$. The only relation between matrix elements is $a_{jn,im} = a^*_{im,jn}$.

$$n_G = 3\times 1 + 6\times 1 + 6\times 3 + 3\times 3 + 5 = 41.$$

C. Case D_2 or C_{2v} or D_{2h}

If the symmetry group is D_2 or C_{2v} or D_{2h}, the matrix elements a_{imjn} which are not zero by symmetry can be written as nine fundamental spectra ($a_{im,im}$ for i and m equal 1,2,3) that are always real and 12 ones that can be grouped into 6 complex parameters

$$\begin{aligned} a_{11,22} &= a^*_{22,11},\ a_{11,33} = a^*_{33,11},\ a_{12,21} = a^*_{21,12}, \\ a_{22,33} &= a^*_{33,22},\ a_{23,32} = a^*_{32,23},\ a_{13,31} = a^*_{31,13}. \end{aligned}$$

$$n_G = 3\times 1 + 6\times 1 + 6\times 3 + 3\times 3 + 5 = 41.$$

D. Case C_4 or S_4 or C_{4h}

If the symmetry group is C_4 or S_4 or C_{4h}, we have seven real fundamental spectra

$$\begin{aligned} a_{13,13} &= a_{23,23},\quad a_{12,21} = a_{21,12}, \\ a_{12,12} &= a_{21,21},\quad a_{11,22} = a_{22,11}, \\ a_{11,11} &= a_{22,22},\quad a_{31,31} = a_{32,32}, \\ & a_{33,33}, \end{aligned}$$

two imaginary fundamental spectra

$$a_{23,13} = -a_{13,23},\quad a_{32,31} = -a_{31,32},$$

and six complex fundamental spectra

$$\begin{aligned} a_{22,21} &= -a_{11,12} = a^*_{21,22} = -a^*_{12,11}, \\ a_{22,12} &= -a_{11,21} = a^*_{12,22} = -a^*_{21,11}, \\ a_{21,33} &= -a_{12,33} = a^*_{33,21} = -a^*_{33,12}, \\ a_{23,31} &= -a_{13,32} = a^*_{31,23} = -a^*_{32,13}, \\ a_{33,11} &= a_{33,22} = a^*_{11,33} = a^*_{22,33}, \\ a_{31,13} &= a_{32,23} = a^*_{13,31} = a^*_{23,32}. \end{aligned}$$

$$n_G = 3\times 1 + 6\times 1 + 6\times 1 + 3\times 1 + 3 = 21.$$

E. Case D_4 or C_{4v} or D_{2d} or D_{4h}

If the symmetry group is D_4 or C_{4v} or D_{2d} or D_{4h}, there are seven real fundamental spectra

$$\begin{aligned} a_{13,13} &= a_{23,23},\quad a_{31,31} = a_{32,32},\quad a_{12,21} = a_{21,12}, \\ a_{12,12} &= a_{21,21},\quad a_{11,22} = a_{22,11},\quad a_{11,11} = a_{22,22}, \\ & a_{33,33}, \end{aligned}$$

and four complex parameters corresponding to eight fundamental spectra

$$\begin{aligned} a_{13,31} &= a_{23,32} = a^*_{31,13} = a^*_{32,23} \\ a_{11,33} &= a_{22,33} = a^*_{33,22} = a^*_{33,11}. \end{aligned}$$

$$n_G = 3\times 1 + 6\times 0 + 6\times 1 + 3\times 0 + 2 = 11.$$

F. Case D_3 or D_{3d} or C_{3v} with $1B$ reference frame

If the symmetry group is D_3 or D_{3d} or C_{3v} with $1B$ reference frame, the fundamental spectra are six real parameters

$$\begin{aligned} a_{13,13} &= a_{23,23},\quad a_{31,31} = a_{32,32},\quad a_{12,21} = a_{21,12}, \\ a_{12,12} &= a_{21,21},\quad a_{11,22} = a_{22,11},\quad a_{33,33}, \end{aligned}$$

and four complex parameters

$$\begin{aligned} a_{11,32} &= a_{12,31} = a_{21,31} = -a_{22,32} \\ &= a^*_{31,12} = a^*_{31,21} = a^*_{32,11} = -a^*_{32,22}, \\ a_{11,23} &= a_{12,13} = a_{21,13} = -a_{22,23} \\ &= a^*_{13,12} = a^*_{13,21} = a^*_{23,11} = -a^*_{23,22}, \\ a_{11,33} &= a_{22,33} = a^*_{33,11} = a^*_{33,22}, \\ a_{13,31} &= a_{23,32} = a^*_{31,13} = a^*_{32,23}, \end{aligned}$$

with the remaining non-zero matrix elements

$$a_{11,11} = a_{22,22} = a_{11,22} + a_{12,12} + a_{12,21}.$$

$$n_G = 3\times 1 + 6\times 0 + 6\times 1 + 3\times 1 + 2 = 14.$$

G. Case C_{3v} with $1A$ reference frame

If the symmetry group is C_{3v} with $1A$ reference frame, the fundamental spectra are six real parameters

$$\begin{aligned} a_{13,13} &= a_{23,23}\quad a_{31,31} = a_{32,32}\quad a_{12,21} = a_{21,12}, \\ a_{12,12} &= a_{21,21},\quad a_{11,22} = a_{22,11},\quad a_{33,33}, \end{aligned}$$

and four complex parameters

$$\begin{aligned} a_{12,23} &= a_{21,23} = a_{22,13} = -a_{11,13} \\ &= a^*_{13,22} = a^*_{23,12} = a^*_{23,21} = -a^*_{13,11}, \\ a_{12,32} &= a_{21,32} = a_{22,31} = -a_{11,31} \\ &= a^*_{31,22} = a^*_{32,12} = a^*_{32,21} = -a^*_{31,11}, \\ a_{33,11} &= a_{33,22} = a^*_{11,33} = a^*_{22,33}, \\ a_{31,13} &= a_{32,23} = a^*_{13,31} = a^*_{23,32}, \end{aligned}$$

with the remaining non-zero matrix elements

$$a_{11,11} = a_{22,22} = a_{11,22} + a_{12,12} + a_{12,21}.$$

$$n_G = 3 \times 1 + 6 \times 0 + 6 \times 1 + 3 \times 1 + 2 = 14.$$

H. a_{imjn} for D_6, C_{6v}, D_{3h} and D_{6h}

If the symmetry group is D_6, C_{6v}, D_{3h} or D_{6h}, we see from the decomposition of Eq. (14) that we have ten fundamental spectra (three coming from tensors of rank 0, six from tensors of rank 2 and 1 from the tensor of rank 4). The first six real ones are:

$$\begin{aligned} a_{11,22} &= a_{22,11}, \quad a_{12,12} = a_{21,21}, \quad a_{12,21} = a_{21,12}, \\ a_{13,13} &= a_{23,23}, \quad a_{31,31} = a_{32,32}, \quad a_{33,33}, \end{aligned}$$

The other four are grouped into two complex parameters

$$\begin{aligned} a_{11,33} &= a_{22,33} = a^*_{33,11} = a^*_{33,22}, \\ a_{13,31} &= a_{23,32} = a^*_{31,13} = a^*_{32,23}. \end{aligned}$$

The remaining non-zero matrix elements $a_{im,jn}$ are

$$a_{11,11} = a_{22,22} = a_{11,22} + a_{12,12} + a_{12,21}.$$

$$n_G = 3 \times 1 + 6 \times 0 + 6 \times 1 + 3 \times 0 + 1 = 10.$$

I. a_{imjn} for T or T_h

If the symmetry group G is T or T_h, the explicit calculation of the matrix $N^G_{kk'}$ shows that there are 21 non-zero $a_{im,jn}$ that can be expressed in terms of 7 fundamental spectra. Three of them are real

$$\begin{aligned} a_{11,11} &= a_{22,22} = a_{33,33}, \\ a_{12,12} &= a_{23,23} = a_{31,31}, \\ a_{13,13} &= a_{21,21} = a_{32,32}, \end{aligned}$$

and the remaining four can be grouped into two complex numbers:

$$\begin{aligned} a_{11,22} &= a_{22,33} = a_{33,11} = a^*_{11,33} = a^*_{22,11} = a^*_{33,22}, \\ a_{12,21} &= a_{23,32} = a_{31,13} = a^*_{13,31} = a^*_{21,12} = a^*_{32,23}. \end{aligned}$$

$$n_G = 3 \times 1 + 6 \times 0 + 6 \times 0 + 3 \times 1 + 1 = 7.$$

J. a_{imjn} for O_h or O or T_d

If the symmetry group G is O_h or O or T_d, the explicit calculation of the matrix $N^G_{kk'}$ shows that there are 21 non-zero $a_{im,jn}$ that can be expressed in terms of 4 real fundamental spectra:

$$\begin{aligned} a_{11,11} &= a_{22,22} = a_{33,33}, \\ a_{11,22} &= a_{11,33} = a_{22,33} = a_{22,11} = a_{33,11} = a_{33,22}, \\ a_{12,12} &= a_{13,13} = a_{23,23} = a_{21,21} = a_{31,31} = a_{32,32}, \\ a_{12,21} &= a_{13,31} = a_{23,32} = a_{21,12} = a_{31,13} = a_{32,23}. \end{aligned}$$

They are real because, for instance, $a^*_{im,jn} = a_{jn,im}$ implies $a^*_{12,21} = a_{21,12} = a_{12,21}$.

$$n_G = 3 \times 1 + 6 \times 0 + 6 \times 0 + 3 \times 0 + 1 = 4.$$

An alternative mathematical approach to this question was proposed by Perla Azzi and coll. [33] for the elastic tensor, which is also a fourth-rank tensor, but with a different symmetry with respect to the interchange of indices. They also investigated the distance with respect to cubic symmetry.

K. a_{imjn} for spherical samples

For a spherical sample (e.g. an atom), we cannot use directly the average given by Eq. (12) because the number $|G|$ of rotations in infinite. However, since $SO(3)$ is a compact group, the average is obtained as a normalized integral over Euler angles α, β and γ [34]:

$$N_{imjn,i'm'j'n'} = \langle g_{ii'} g_{mm'} g_{jj'} g_{nn'} \rangle. \tag{18}$$

To compute this spherical average, we write each rotation matrix g in terms of the Wigner rotation matrix $D^1_{\mu\mu'}$, for which averages over angles are well known.

The relation giving the Cartesian basis (e_x, e_y, e_z) in terms of the spherical basis (e_{-1}, e_0, e_{+1}) is

$$\begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} e_{-1} \\ e_0 \\ e_{+1} \end{pmatrix}, \tag{19}$$

where the 3×3 matrix will be denoted by A. Thus, the rotation matrix g is related to the Wigner rotation matrix D^1 by

$$g_{ij} = \sum_{\mu\mu'} A_{i\mu} A^*_{j\mu'} D^1_{\mu\mu'}. \tag{20}$$

This way, the spherical average of Eq. (18) is reduced to the angular average of a product of four Wigner matrices (implicitly) expressed in terms of Euler angles:

$$\begin{aligned} N' &= \langle D^1_{\mu_1,\mu'_1} D^1_{\mu_2,\mu'_2} D^1_{\mu_3,\mu'_3} D^1_{\mu_4,\mu'_4} \rangle \\ &= \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma D^1_{\mu_1,\mu'_1} \\ &\quad \times D^1_{\mu_2,\mu'_2} D^1_{\mu_3,\mu'_3} D^1_{\mu_4,\mu'_4}. \end{aligned}$$

To compute this, we write the product of two Wigner matrices as a sum of Wigner matrices [32, p. 84] weighted by Clebsch-Gordan coefficients, then we use the angular average of a product of two Wigner matrices [32, p. 96] and obtain

$$N' = \sum_{b=0}^{2} \frac{(-1)^{\beta'-\beta}}{2b+1} (1\mu_1, 1\mu_2|b\beta)(1\mu_1', 1\mu_2'|b\beta') \times(1\mu_3, 1\mu_4|b-\beta)(1\mu_3', 1\mu_4'|b-\beta'),$$

where $\beta = \mu_1 + \mu_2 = -\mu_3 - \mu_4$ and similarly for β'. By multiplying with A and A^* and summing over μ_j we find 21 non-zero $a_{im,jn}$ that can be expressed in terms of 3 fundamental spectra

$$\begin{aligned} a_{11,22} &= a_{11,33} = a_{22,33} = a_{22,11} = a_{33,11} = a_{33,22}, \\ a_{12,12} &= a_{13,13} = a_{23,23} = a_{21,21} = a_{31,31} = a_{32,32}, \\ a_{12,21} &= a_{13,31} = a_{23,32} = a_{21,12} = a_{31,13} = a_{32,23}. \end{aligned}$$

The remaining non-zero matrix elements are

$$a_{11,11} = a_{22,22} = a_{33,33} = a_{11,22} + a_{12,12} + a_{12,21}.$$

If we compare with a cubic sample, we see that the first fundamental spectrum of a cubic sample becomes the sum of the three other ones in the spherical case.

With these parameters, we recover the fact [21] that angular dependence of a RIXS spectrum of a powder is entirely determined by coefficients of $|\epsilon\cdot\epsilon_s|^2$ and $|\epsilon\cdot\epsilon_s^*|^2$.

If we put these coefficients $a_{im,jn}$ in the RIXS cross-section of Eq. (9), we find that for general (i.e. possibly non normalized) ϵ and ϵ_s the RIXS cross-section of a powder is

$$\sigma(\epsilon_s, \epsilon) = a_{11,22}|\epsilon\cdot\epsilon_s^*|^2 + a_{12,21}|\epsilon\cdot\epsilon_s|^2 + a_{12,12}||\epsilon||^2||\epsilon_s||^2. \quad (21)$$

This is a linear combination of the three possible spherically symmetric polynomials of degree four that can be constructed from two complex vectors ϵ and ϵ_s. For normalized polarization vectors, we recover the fact [21] that the angular dependence of a RIXS spectrum of a powder is determined by the coefficients of $|\epsilon\cdot\epsilon_s|^2$ and $|\epsilon\cdot\epsilon_s^*|^2$.

If the polarization of the scattered beam is not measured, we can average over its normalized polarizations perpendicular to the unit vector $\widehat{\mathbf{k}}_s$ along the scattered beam [21] to obtain

$$\sigma(\widehat{\mathbf{k}}_s, \epsilon) = \frac{1}{2}(a_{11,22} + 2a_{12,12} + a_{12,21})||\epsilon||^2 - \frac{1}{2}(a_{11,22} + a_{12,21})|\epsilon\cdot\widehat{\mathbf{k}}_s|^2. \quad (22)$$

IV. RIXS MEASUREMENT OF A POWDER

In this section we deal in detail with the way RIXS measurements of an isotropic sample depend on the polarizations (and indirectly on the directions) of the incident and scattered beams.

For X-ray absorption spectra, it is well known that the spectrum $\langle\sigma_{\rm XAS}\rangle_{\rm powder}$ of a powder does not depend on polarization and can be calculated as the average of three spectra $\sigma_{\rm XAS}(\epsilon)$ calculated for a single crystal with a polarization vector ϵ along x, y and z [35]:

$$\langle\sigma_{\rm XAS}\rangle_{\rm powder} = \frac{\sigma_{\rm XAS}(\epsilon_x) + \sigma_{\rm XAS}(\epsilon_y) + \sigma_{\rm XAS}(\epsilon_z)}{3}.$$

Moreover, if the sample has cubic symmetry, then all three spectra are identical and only one spectrum must be computed to obtain $\langle\sigma_{\rm XAS}\rangle_{\rm powder} = \sigma_{\rm XAS}(\epsilon_x)$.

For a magnetic powder the calculation of an X-ray absorption spectra needed a 302-point Lebedev quadrature [36]. For electron scattering spectra the situation is more complex and an average over orientations required a 590-point Lebedev quadrature [37]. Moreover, a Lebedev quadrature averages a function $f(\theta, \phi)$ of the two angles θ and ϕ whereas we need to average spectra $f(\alpha, \beta, \gamma)$ depending on the three Euler angles that describe the orientation of the sample.

In this section, we write the RIXS spectrum of a powder as a weighted sum of RIXS spectra of a single crystal (or oriented molecule) with different incident and scattered polarizations. Since RIXS calculations can be computationally expensive, we look for the minimum number of such spectra wich turns out to be 21, and even of 15 spectra if the polarization state of the scattered beam is not measured. In the next section, we show that the symmetry of the sample further decreases this number.

A. Spherical tensor analysis

We know [21] that the polarization dependence of the RIXS cross-section of an isotropic (e.g. powder) sample could entirely be described, in the electric dipole approximation, by three parameters denoted S_0, S_1 and S_2, defined in Eq. (25) and related to $S^{gg0}_{L_0}$ of Ref. 21 by $S_g = \sqrt{2g+1}\, S^{gg0}$.

The general formula for arbitrary polarization of the incident beam and polarization detection of the scattered beam is

$$\sigma(\epsilon_s, \epsilon) = -\frac{S_1}{6} + \frac{S_2}{10} + \Big(\frac{S_1}{6} + \frac{S_2}{10}\Big)|\epsilon\cdot\epsilon_s|^2 + \Big(\frac{S_0}{3} - \frac{S_2}{15}\Big)|\epsilon\cdot\epsilon_s^*|^2.$$

We previously stressed [21] that the polarization ϵ_s of the scattered beam is characterized by the measurement device and several experimental setups were devised to explicitly measure the polarization of the scattered beam [38–42]. From the theoretical point of view [39, 43] the crystal analyzers with (or without) explicit polarization detection can be considered as a polarization filter and when we say that the polarization is not measured, we mean that this filter gives the same weight to all polarization directions.

So, if the polarization of the scattered beam is not measured, the cross section becomes

$$\sigma(\widehat{\mathbf{k}}_s,\epsilon) \;=\; C_0 + C_1\big(|\epsilon\cdot\widehat{\mathbf{k}}_s|^2 - 1/3\big), \qquad (23)$$

where $\widehat{\mathbf{k}}_s$ is the unit vector along the scattered beam and

$$C_0 = \frac{S_0}{9} - \frac{S_1}{9} + \frac{S_2}{9},\;\; C_1 = -\frac{S_0}{6} - \frac{S_1}{12} - \frac{S_2}{60}. \qquad (24)$$

The term $-1/3$ in Eq. (23) is used to isolate C_0, which is the RIXS cross-section when all scattered beams are collected [21]. In other words, C_0 is the RIXS cross-section that would be measured with a detector (emission spectrometer) that would cover all directions in space.

The coefficients S_b are defined by

$$S_b \;=\; \sum_{imjn} X_{im,jn}(b) a_{im,jn}, \qquad (25)$$

with

$$X_{im,jn}(b) \;=\; \sum_{\beta=-b}^{b} (-1)^{b-\beta} \sum_{\mu\nu\mu'\nu'} (1\mu'1\nu|b\beta) \times(1\mu1\nu'|b-\beta) A_{i\mu'}A_{m\nu}A_{n\mu}A_{j\nu'}, \qquad (26)$$

where the matrix elements of A (defined in Eq. (19)) appear because the original definition of $S^{bb0}_{L_0}$ in [21] was in terms of spherical components $\mathbf{r}^{(1)}_\mu$ and we work now with Cartesian components r_n. $X(b)$ is also related to the tensor of Section II B by $X(b) = \sqrt{2b+1}Y^{bb}(0,0)$. We changed the normalization to avoid the cluttering of square roots in formulas and tables, but $X(b)$ are no longer orthonormal for the Hilbert-Schmidt scalar product:

$$\sum_{imjn} X_{im,jn}(b) X^*_{im,jn}(b') \;=\; (2b+1)\delta_{bb'}. \qquad (27)$$

Because of the definition of $X(b)$ as a coupling of spherical tensors, the matrix elements $X_{im,jn}(b)$ enjoy the same relations as $a_{im,jn}$ for a spherical sample (see Section III K). In addition to the permutation symmetries discussed in Section II B, we note that each $X(b)$ is real-valued and the three tensors $X(b)$ commute in three ways

$$\sum_{kl} X_{im,kl}(b) X_{kl,jn}(b') \;=\; \sum_{kl} X_{im,kl}(b') X_{kl,jn}(b),$$
$$\sum_{kl} X_{km,ln}(b) X_{km',ln'}(b') \;=\; \sum_{kl} X_{km,ln}(b') X_{km',ln'}(b),$$
$$\sum_{kl} X_{ik,jl}(b) X_{i'k,j'l}(b') \;=\; \sum_{kl} X_{ik,jl}(b') X_{i'k,j'l}(b),$$

and they are related to the spherical average of product of rotation matrices in Eq. (18) by

$$N_{imjn,i'm'j'n'} \;=\; \sum_{b=0}^{2} \frac{1}{2b+1} X_{im,nj}(b) X_{i'm',n'j'}(b),$$

which means that $X(b)$ are eigenstates of N for the eigenvalue 1, taking into account the normalization of Eq. (27).

We are now in a position to describe the problem at hand. We want to compute S_b for $b = 0, 1, 2$ and Eq. (25) suggests that, in the absence of symmetry, we need to determine the 81 fundamental spectra of $a_{im,jn}$. Moreover, some computer programs do not directly calculate $a_{im,jn}$, but cross-sections $\sigma(\epsilon_s,\epsilon)$ related to $a_{im,jn}$ by Eq. (9). Thus, we wish to find a certain number L of pairs of polarization vectors $(\epsilon_{sl},\epsilon_l)$ such that

$$S_b \;=\; \sum_{l=1}^{L} \rho_l(b)\sigma(\epsilon_{sl},\epsilon_l),$$

where $\rho_l(b)$ is the weight of $\sigma(\epsilon_{sl},\epsilon_l)$ for S_b and we would like to minimize the number L of calculations.

As proved in Eq. (29), a generalization of the polarization identity requires 16 calculations of $\sigma(\epsilon_s,\epsilon)$ to calculate each $a_{im,jn}$. Therefore, a brute force approach would require $L = 16 \times 81 = 1296$ calculations of cross-sections to compute the three parameters of the RIXS of a powder. We shall reduce this number to $L = 21$.

B. Generalized polarization identity

The polarization identity is a relation between

$$f(\mathbf{u},\mathbf{v}) \;=\; \sum_{mn} u^*_m a_{mn} v_n,$$

where a_{mn} is a (finite dimensional) complex matrix, and $\phi(\mathbf{u}) = f(\mathbf{u},\mathbf{u})$. Namely

$$f(\mathbf{u},\mathbf{v}) \;=\; \frac{1}{4}\sum_{k=0}^{3}(-i)^k \phi(\mathbf{u}+i^k\mathbf{v}).$$

Our case is more complicated because we must define

$$f(\mathbf{u},\mathbf{u}';\mathbf{v},\mathbf{v}') \;=\; \sum_{imjn} u^*_i v^*_m a_{im,jn} u'_j v'_n, \qquad (28)$$

and $\phi(\mathbf{u},\mathbf{v}) = f(\mathbf{u},\mathbf{u};\mathbf{v},\mathbf{v})$, so that $\sigma(\epsilon_s,\epsilon) = \phi(\epsilon_s,\epsilon^*)$. A lengthy but straightforward calculation proves the generalized polarization identity that we need:

$$f(\mathbf{u},\mathbf{u}';\mathbf{v},\mathbf{v}') \;=\; \frac{1}{16}\sum_{m=0}^{3}\sum_{n=0}^{3}(-i)^{m+n} \times\phi(\mathbf{u}+i^m\mathbf{u}';\mathbf{v}+i^n\mathbf{v}'). \qquad (29)$$

An immediate consequence of this identity is that the invariance of the cross-section (and therefore of ϕ) implies the invariance of f. Indeed, Eq. (8) implies

$$\begin{aligned}\phi(g\mathbf{u}+i^m g\mathbf{u}';g\mathbf{v}'+i^n g\mathbf{v}') &= \phi\big(g(\mathbf{u}+i^m\mathbf{u}');g(\mathbf{v}'+i^n\mathbf{v}')\big)\\ &= \phi(\mathbf{u}+i^m\mathbf{u}';\mathbf{v}'+i^n\mathbf{v}'),\end{aligned}$$

and then, by the polarization identity,

$$f(g\mathbf{u}, g\mathbf{u}'; g\mathbf{v}, g\mathbf{v}') \;=\; f(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}'), \qquad (30)$$

for every g in the invariance group G of the sample. This identity extends the invariance of the function $\sigma(\epsilon_s, \epsilon)$ of two vectors ϵ_s and ϵ to the invariance of a function f of four vectors.

Similarly, Eq. (7) implies that, for any isometry g

$$(g^{-1} \triangleright f)(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}') \;=\; f(g\mathbf{u}, g\mathbf{u}'; g\mathbf{v}, g\mathbf{v}'). \qquad (31)$$

C. Symmetrization

We are now ready to prove that the left hand side of Eq. (11) has all the symmetries of the group G even if $a_{i'm',j'n'}$ has no symmetry. More generally, we prove that, if f has no invariance whatsoever, then the average $\overline{f}$ defined by

$$\overline{f}(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}') \;=\; \frac{1}{|G|}\sum_{g\in G} f(g\mathbf{u}, g\mathbf{u}'; g\mathbf{v}, g\mathbf{v}').$$

is invariant under any operation g of the invariance group G of the sample. This statement will be clear to the group theory experts, because the right hand side is just the projection onto the fully symmetric representation of G, but let us show it. Let $h \in G$ be an element of the symmetry group. By linearity of the action

$$(h^{-1} \triangleright \overline{f})(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}') = \sum_{g\in G} \frac{(h^{-1} \triangleright f)(g\mathbf{u}, g\mathbf{u}'; g\mathbf{v}, g\mathbf{v}')}{|G|}.$$

Now we can use Eq. (31), which is valid even if h is not a symmetry of f:

$$(h^{-1} \triangleright \overline{f})(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}') = \sum_{g\in G} \frac{f(hg\mathbf{u}, hg\mathbf{u}'; hg\mathbf{v}, hg\mathbf{v}')}{|G|}.$$

Any element g can be written in a unique way as $g = h^{-1}g'$ and g' runs over G when g runs over G. Thus,

$$\begin{aligned}(h^{-1} \triangleright \overline{f})(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}') \;&=\; \sum_{g'\in G} \frac{f(g'\mathbf{u}, g'\mathbf{u}'; g'\mathbf{v}, g'\mathbf{v}')}{|G|} \\ &=\; \overline{f}(\mathbf{u}, \mathbf{u}'; \mathbf{v}, \mathbf{v}').\end{aligned}$$

Since this is true for any $h \in G$, $\overline{f}$ is invariant under G even if f is not. Besides, if f is already invariant under G, then $\overline{f} = f$.

D. Singular value decomposition

To decrease the number of calculations, we write a sort of singular value decomposition of $X(b)$:

$$X_{im,jn}(b) \;=\; \sum_{k=1}^{9} \lambda^k(b) U^k_{ij} (V^k_{mn})^*, \qquad (32)$$

where it will turn out that the 3×3 matrices U^k and V^k do not depend on b. If we can diagonalize U^k and V^k as

$$\begin{aligned} U^k_{ij} \;&=\; \sum_{r=1}^{3} \mu^{kr} u^{kr}_i (u^{kr}_j)^*, \\ V^k_{mn} \;&=\; \sum_{s=1}^{3} \nu^{ks} v^{ks}_m (v^{ks}_n)^*, \end{aligned}$$

we obtain by definition (25) of S_b:

$$S_b \;=\; \sum_{k,r,s} \lambda^k(b) \mu^{kr} \nu^{ks} \phi((\mathbf{u}^{kr})^*, \mathbf{v}^{ks})). \qquad (33)$$

Equation (33) is already an improvement because the sum over k, r, s involves 81 cross-sections $\phi((\mathbf{u}^{kr})^*, \mathbf{v}^{ks})$ instead of 1296, but further progress is possible.

To implement this singular value decomposition, we define three 9×9 matrices $M(b)$ by $M(b)_{3(i-1)+j,3(m-1)+n} = X_{im,jn}(b)$:

$$M(0) \;=\; \frac{1}{3}\mathrm{Id}_9,$$

$$M(1) \;=\; \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \end{pmatrix},$$

and

$$M(2) \;=\; \frac{1}{6}\begin{pmatrix} 4 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 3 \\ 0 & -2 & 0 & 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 3 & 0 & -2 & 0 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & -2 & 0 & 3 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 & 0 & -2 & 0 \\ 3 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 4 \end{pmatrix}.$$

These matrices commute and are real symmetric, so the singular value decomposition turns out to be a diagonalization of $M(b)$ (this would not be the case if quadrupole transitions were taken into account) and a common set of real "eigenvectors" U^k and $V^k = U^k$ can be chosen for the three $X(b)$. Since all U^k are real we can write

$$X_{im,jn}(b) \;=\; \sum_{krs} \lambda^k(b) \mu^{kr} \mu^{ks} u^{kr}_i u^{ks}_m (u^{kr}_j)^* (u^{ks}_n)^*.$$

TABLE II. Eigenvalues $\lambda^k(b)$ of $M(b)$ for $b = 0, 1, 2$ corresponding to their common eigenvectors U^k. The last line indicates whether U^k is symmetric (+) or antisymmetric (−).

b	U^1	U^2	U^3	U^4	U^5	U^6	U^7	U^8	U^9
0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
2	$\frac{5}{3}$	$-\frac{5}{6}$	$-\frac{5}{6}$	$-\frac{5}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$
	+	−	−	−	+	+	+	+	+

We further observe in Table II that each U^k is either symmetric or antisymmetric, so the eigenvalues μ^{kr} for a given k are either all real or all purely imaginary and

$$X_{im,jn}(b) = \sum_{krs} \lambda^k(b)\mu^{kr}\mu^{ks}(u_i^{kr})^*(u_m^{ks})^* u_j^{kr} u_n^{ks}. \quad (34)$$

Thus,

$$S_b = \sum_{krs} \lambda^k(b)\mu^{kr}\mu^{ks}\phi(\mathbf{u}^{kr}, \mathbf{u}^{ks}).$$

The eigenvalues $\lambda^k(b)$ are given in Table II and the nine matrices U^k are

$$U^1 = \frac{1}{\sqrt{3}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad U^2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$U^3 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad U^4 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$U^5 = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad U^6 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$U^7 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad U^8 = \frac{1}{\sqrt{6}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$U^9 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Matrices U^k for $k = 1, 5$ and 8 are already diagonal, so we can take for eigenvectors $\mathbf{u}^{kr}$ (for $k = 1, 5$ and 8) the same real unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ along the x, y and z axes, respectively. This means that we can calculate $k = 1, 5$ and 8 with the same 9 values of $\phi(\mathbf{e}_p, \mathbf{e}_q)$, where p and q take the values x, y and z, even if only four of them are useful for $k = 5$ because of its zero eigenvalue.

For $k = 2, 3$ and 4, each U^k is a real antisymmetric matrix, its two non-zero eigenvalues are $\mu^{kr} = \pm\imath/\sqrt{2}$, the corresponding eigenvectors are of the form $\mathbf{u}^{kr} = \boldsymbol{\pi}^{\pm}_{pq} = (\pm\imath\mathbf{e}_p + \mathbf{e}_q)/\sqrt{2}$ (i.e. $\boldsymbol{\pi}^{\pm}_{yz}$ for $k = 2$, $\boldsymbol{\pi}^{\pm}_{xz}$ for $k = 3$, $\boldsymbol{\pi}^{\pm}_{xy}$ for $k = 4$) and we have to calculate 4 different $\phi(\mathbf{u}^{kr}, \mathbf{u}^{ks})$ for each k.

For $k = 6, 7$ and 9, each U^k is a real symmetric matrix, its two non-zero eigenvalues are $\mu^{kr} = \pm 1/\sqrt{2}$, the corresponding eigenvectors are of the form $\mathbf{u}^{kr} = \mathbf{e}^{\pm}_{pq} = (\pm\mathbf{e}_p + \mathbf{e}_q)/\sqrt{2}$ (i.e. $\mathbf{e}^{\pm}_{yz}$ for $k = 6$, $\mathbf{e}^{\pm}_{xz}$ for $k = 7$, $\mathbf{e}^{\pm}_{xy}$ for $k = 9$) and we have again to calculate 4 different $\phi(\mathbf{u}^{kr}, \mathbf{u}^{ks})$ for each k.

Therefore, the total number of cross-sections to calculate is reduced from 81 to $9 + 3 \times 4 + 3 \times 4 = 33$.

E. Further reduction

To proceed with the reduction, we define the fourth-rank tensors $(\mathbf{u}, \mathbf{v})$ with components

$$(\mathbf{u}, \mathbf{v})_{imjn} = u_i^* v_m^* u_j v_n,$$

and we write Eq. (34) in a more general form:

$$X_{im,jn}(b) = \sum_l \rho_l(b)(\mathbf{u}_l, \mathbf{v}_l)_{imjn}, \quad (35)$$

where l enumerates the krs indices, $(\mathbf{u}_l, \mathbf{v}_l)$ is a fourth-rank tensor and $\rho_l(b) \in \mathbb{R}$ is its weight. After reduction, Eq. (35) will still be valid whereas Eq. (34) will not.

By examining the 33 fourth-rank tensors in Eq. (34), we observe the following linear relations

$$\sum_{r,s\in\{p,q\}} (\mathbf{e}_r, \mathbf{e}_s) = \sum_{\eta,\eta'\in\{+,-\}} (\boldsymbol{\pi}^{\eta}_{pq}, \boldsymbol{\pi}^{\eta'}_{pq}),$$
$$\sum_{r,s\in\{p,q\}} (\mathbf{e}_r, \mathbf{e}_s) = \sum_{\eta,\eta'\in\{+,-\}} (\mathbf{e}^{\eta}_{pq}, \mathbf{e}^{\eta'}_{pq}),$$

where $(p, q) = (y, z), (x, z)$ and (x, y). These 6 linear relations would enable us to remove six fourth-rank tensors $(\mathbf{u}_l, \mathbf{v}_l)$. However, we can further reduce them by observing that $(\mathbf{u}^+, \mathbf{u}^-)$ and $(\mathbf{u}^-, \mathbf{u}^+)$ always have the same weight in the calculation of $X(b)$ by Eq. (34) for any $\mathbf{u} = \boldsymbol{\pi}_{pq}$ and $\mathbf{u} = \mathbf{e}_{pq}$. Therefore, we can use

$$\sum_{\eta=\pm} (\boldsymbol{\pi}^{\eta}_{pq}, \boldsymbol{\pi}^{-\eta}_{pq}) = \sum_{r,s\in\{p,q\}} (\mathbf{e}_r, \mathbf{e}_s) - \sum_{\eta=\pm} (\boldsymbol{\pi}^{\eta}_{pq}, \boldsymbol{\pi}^{\eta}_{pq}),$$
$$\sum_{\eta=\pm} (\mathbf{e}^{\eta}_{pq}, \mathbf{e}^{-\eta}_{pq}) = \sum_{r,s\in\{p,q\}} (\mathbf{e}_r, \mathbf{e}_s) - \sum_{\eta=\pm} (\mathbf{e}^{\eta}_{pq}, \mathbf{e}^{\eta}_{pq}),$$

to remove 12 tensors $(\mathbf{u}_l, \mathbf{v}_l)$ instead of 6 and we are finally left with 21 fourth-rank tensors.

Our final result is

$$S_b = \sum_{l=1}^{21} \rho_l(b)\phi(\mathbf{u}_l, \mathbf{v}_l) = \sum_{l=1}^{21} \rho_l(b)\sigma(\mathbf{u}_l, \mathbf{v}_l^*), \quad (36)$$

TABLE III. Value of the weight $\rho_l(b)$ of $\sigma(\mathbf{u}_l, \mathbf{v}_l^*)$ for the minimal 21 fourth-rank tensors $(\mathbf{u}_l, \mathbf{v}_l)$ to calculate S^{bb0} by Eq. (36) as well as C_0 and C_1 in Eq. (23). The basis unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ are along the three axes of $\mathbb{R}^3$, $\boldsymbol{\pi}^{\pm}_{mn} = (\pm i\mathbf{e}_m + \mathbf{e}_n)/\sqrt{2}$ and $\mathbf{e}^{\pm}_{mn} = (\pm\mathbf{e}_m + \mathbf{e}_n)/\sqrt{2}$.

l	$(\mathbf{u}_l, \mathbf{v}_l)$	$\rho_l(0)$	$\rho_l(1)$	$\rho_l(2)$	C_0	C_1
1	$(\mathbf{e}_x, \mathbf{e}_x)$	1/3	−1	−1/3	1/9	1/30
2	$(\mathbf{e}_x, \mathbf{e}_y)$	0	−1	0	1/9	1/12
3	$(\mathbf{e}_x, \mathbf{e}_z)$	0	−1	0	1/9	1/12
4	$(\mathbf{e}_y, \mathbf{e}_x)$	0	−1	0	1/9	1/12
5	$(\mathbf{e}_y, \mathbf{e}_y)$	1/3	−1	−1/3	1/9	1/30
6	$(\mathbf{e}_y, \mathbf{e}_z)$	0	−1	0	1/9	1/12
7	$(\mathbf{e}_z, \mathbf{e}_x)$	0	−1	0	1/9	1/12
8	$(\mathbf{e}_z, \mathbf{e}_y)$	0	−1	0	1/9	1/12
9	$(\mathbf{e}_z, \mathbf{e}_z)$	1/3	−1	−1/3	1/9	1/30
10	$(\boldsymbol{\pi}^+_{yz}, \boldsymbol{\pi}^+_{yz})$	−1/3	1/2	5/6	0	0
11	$(\boldsymbol{\pi}^-_{yz}, \boldsymbol{\pi}^-_{yz})$	−1/3	1/2	5/6	0	0
12	$(\boldsymbol{\pi}^+_{xz}, \boldsymbol{\pi}^+_{xz})$	−1/3	1/2	5/6	0	0
13	$(\boldsymbol{\pi}^-_{xz}, \boldsymbol{\pi}^-_{xz})$	−1/3	1/2	5/6	0	0
14	$(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^+_{xy})$	−1/3	1/2	5/6	0	0
15	$(\boldsymbol{\pi}^-_{xy}, \boldsymbol{\pi}^-_{xy})$	−1/3	1/2	5/6	0	0
16	$(\mathbf{e}^+_{yz}, \mathbf{e}^+_{yz})$	1/3	1/2	1/6	0	-1/10
17	$(\mathbf{e}^-_{yz}, \mathbf{e}^-_{yz})$	1/3	1/2	1/6	0	-1/10
18	$(\mathbf{e}^+_{xz}, \mathbf{e}^+_{xz})$	1/3	1/2	1/6	0	-1/10
19	$(\mathbf{e}^-_{xz}, \mathbf{e}^-_{xz})$	1/3	1/2	1/6	0	-1/10
20	$(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy})$	1/3	1/2	1/6	0	-1/10
21	$(\mathbf{e}^-_{xy}, \mathbf{e}^-_{xy})$	1/3	1/2	1/6	0	-1/10

for the tensors and the weights given in Table III.

We can also write C_0 and C_1 in the angular dependence of Eq. (23) directly in terms of 15 cross-sections:

$$C_0 = \frac{1}{9}\sum_{pq}\sigma(\mathbf{e}_p, \mathbf{e}_q), \quad (37)$$

$$C_1 = \frac{1}{12}\sum_{pq}\sigma(\mathbf{e}_p, \mathbf{e}_q) - \frac{1}{20}\sum_{p}\sigma(\mathbf{e}_p, \mathbf{e}_p) - \frac{1}{10}\sum_{p<q}\big(\sigma(\mathbf{e}^+_{pq}, \mathbf{e}^+_{pq}) + \sigma(\mathbf{e}^-_{pq}, \mathbf{e}^-_{pq})\big), \quad (38)$$

where p and q run over $\{x, y, z\}$ and $p < q$ over $\{xy, yz, xz\}$.

V. RIXS FOR A POWDER WITH SYMMETRY

We can now combine the discussion of the influence of the symmetry of the sample and the number of $\phi(\epsilon_s, \epsilon)$ required to calculate the spectrum of a powdered material when the material itself has a symmetry.

The basic idea is quite simple. If G is the symmetry group of the material, we compute $\phi(\mathbf{u}_l, \mathbf{v}_l)$, where

$$\phi(\mathbf{u}_l, \mathbf{v}_l) = \sum_{imjn} u^*_{li} v^*_{lm} a_{im,jn} u_{lj} v_{ln},$$

for the 21 pairs of polarizations $(\mathbf{u}_l, \mathbf{v}_l)$ of Table III in terms of the n_G fundamental spectra of $a_{im,jn}$. This gives us a linear relation between $\phi(\mathbf{u}_l, \mathbf{v}_l)$ and the fundamental spectra described by a $n_G \times 21$ matrix whose null space represents the relations between different $\phi(\mathbf{u}_l, \mathbf{v}_l)$. For the example of a cubic material, the expression of $\phi(\mathbf{u}_l, \mathbf{v}_l)$ in terms of the four fundamental spectra $a_{11,11}$, $a_{11,22}$, $a_{12,12}$ and $a_{12,21}$ is

$$\begin{aligned}
\phi(\mathbf{e}_p, \mathbf{e}_q) &= a_{12,12} + \delta_{pq}(a_{11,11} - a_{12,12}),\\
\phi(\boldsymbol{\pi}^{\pm}_{pq}, \boldsymbol{\pi}^{\pm}_{pq}) &= \frac{1}{2}(a_{11,11} - a_{11,22} + a_{12,12} + a_{12,21}),\\
\phi(\mathbf{e}^{\pm}_{pq}, \mathbf{e}^{\pm}_{pq}) &= \frac{1}{2}(a_{11,11} + a_{11,22} + a_{12,12} + a_{12,21}),
\end{aligned}$$

for p and q equal to x, y and z. The relations between $\phi(\mathbf{u}_l, \mathbf{v}_l)$ is then $\phi(\mathbf{e}_p, \mathbf{e}_p) = \phi(\mathbf{e}_x, \mathbf{e}_x)$ for all p, and for all $q \neq p$: $\phi(\mathbf{e}_p, \mathbf{e}_q) = \phi(\mathbf{e}_x, \mathbf{e}_y)$, $\phi(\boldsymbol{\pi}^{\pm}_{pq}, \boldsymbol{\pi}^{\pm}_{pq}) = \phi(\boldsymbol{\pi}^{\pm}_{xy}, \boldsymbol{\pi}^{\pm}_{xy})$ and $\phi(\mathbf{e}^{\pm}_{pq}, \mathbf{e}^{\pm}_{pq}) = \phi(\mathbf{e}^{\pm}_{xy}, \mathbf{e}^{\pm}_{xy})$. For a powder of a cubic sample only four calculations are required to compute the full angular dependence of RIXS. This number reduces to three when the polarization state of the scattered beam is not measured, because $\phi(\boldsymbol{\pi}^{\pm}_{pq}, \boldsymbol{\pi}^{\pm}_{pq})$ is not needed.

We list now the fundamental spectra required to calculate the RIXS spectum of a powder of a sample with various symmetry groups. For all crystallographic point groups, the minimal number of spectra n_S and n_C needed to compute S_b and (C_0, C_1), respectively, is given in Table I.

A. For O, T_d and O_h symmetry groups

In the previous paragraph, we showed that $\phi(\mathbf{u}_l, \mathbf{u}_v)$ can take only four different values. Thus, Eq. (36) becomes:

$$\begin{aligned}
S_0 &= \sigma(\mathbf{e}_x, \mathbf{e}_x) + 2\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) - 2\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}),\\
S_1 &= -3\sigma(\mathbf{e}_x, \mathbf{e}_x) - 6\sigma(\mathbf{e}_x, \mathbf{e}_y)\\
&\quad + 3\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) + 3\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}),\\
S_2 &= -\sigma(\mathbf{e}_x, \mathbf{e}_x) + \sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) + 5\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}).
\end{aligned}$$

The most general polarization dependence of a powder of cubic sample can be obtained from the calculation of four spectra:

$$\begin{aligned}
\sigma(\epsilon_s, \epsilon) &= \big(\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) - \sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy})\big)|\epsilon \cdot \epsilon_s^*|^2\\
&+ \big(\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) + \sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy})\\
&\quad - \sigma(\mathbf{e}_x, \mathbf{e}_x) - \sigma(\mathbf{e}_x, \mathbf{e}_y)\big)|\epsilon \cdot \epsilon_s|^2\\
&+ \sigma(\mathbf{e}_x, \mathbf{e}_y)||\epsilon||^2||\epsilon_s||^2.
\end{aligned}$$

For polarization vectors normalized to unity and when the polarization of the scattered beam is not measured, three calculations are enough:

$$C_0 = \frac{\sigma(\mathbf{e}_x,\mathbf{e}_x)+2\sigma(\mathbf{e}_x,\mathbf{e}_y)}{3},$$
$$C_1 = \frac{\sigma(\mathbf{e}_x,\mathbf{e}_x)+5\sigma(\mathbf{e}_x,\mathbf{e}_y)-6\sigma(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy})}{10}.$$

B. For D_3, D_{3d}, C_{3v}, D_6, C_{6v}, D_{3h} and D_{6h}

For the groups D_3, D_{3d} or C_{3v}, the relations between $\phi(\mathbf{u}_l,\mathbf{v}_l)$ are not the same as those for D_6, C_{6v}, D_{3h} or D_{6h}, but the differences compensate each other and the same final formulas for S_b are obtained. Indeed, the relations between $\phi(\mathbf{u}_l,\mathbf{v}_l)$ for D_3 are:

$$\begin{aligned}
\phi(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}) &= \frac{1}{2}\big(\phi(\mathbf{e}^-_{yz},\mathbf{e}^-_{yz})+\phi(\mathbf{e}^+_{yz},\mathbf{e}^+_{yz})\big),\\
\phi(\mathbf{e}^-_{xz},\mathbf{e}^-_{xz}) &= \phi(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
\phi(\mathbf{e}^-_{xy},\mathbf{e}^-_{xy}) &= \phi(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy}) = \phi(\mathbf{e}_y,\mathbf{e}_y) = \phi(\mathbf{e}_x,\mathbf{e}_x),\\
\phi(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^+_{xz}) &= \frac{1}{2}\big(\phi(\boldsymbol{\pi}^-_{yz},\boldsymbol{\pi}^-_{yz})+\phi(\boldsymbol{\pi}^+_{yz},\boldsymbol{\pi}^+_{yz})\big),\\
\phi(\boldsymbol{\pi}^-_{xz},\boldsymbol{\pi}^-_{xz}) &= \phi(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^+_{xz}),\\
\phi(\boldsymbol{\pi}^-_{xy},\boldsymbol{\pi}^-_{xy}) &= \phi(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^+_{xy}),\\
\phi(\mathbf{e}_z,\mathbf{e}_y) &= \phi(\mathbf{e}_z,\mathbf{e}_x),\\
\phi(\mathbf{e}_y,\mathbf{e}_z) &= \phi(\mathbf{e}_x,\mathbf{e}_z),\\
\phi(\mathbf{e}_y,\mathbf{e}_x) &= \phi(\mathbf{e}_x,\mathbf{e}_y),
\end{aligned}$$

while for D_6 they are

$$\begin{aligned}
\phi(\mathbf{e}^-_{yz},\mathbf{e}^-_{yz}) &= \phi(\mathbf{e}^+_{yz},\mathbf{e}^+_{yz}) = \phi(\mathbf{e}^-_{xz},\mathbf{e}^-_{xz}) = \phi(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
\phi(\boldsymbol{\pi}^-_{yz},\boldsymbol{\pi}^-_{yz}) &= \phi(\boldsymbol{\pi}^+_{yz},\boldsymbol{\pi}^+_{yz}) = \phi(\boldsymbol{\pi}^-_{xz},\boldsymbol{\pi}^-_{xz}) = \phi(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^+_{xz}),\\
\phi(\mathbf{e}^-_{xy},\mathbf{e}^-_{xy}) &= \phi(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy}) = \phi(\mathbf{e}_y,\mathbf{e}_y) = \phi(\mathbf{e}_x,\mathbf{e}_x),\\
\phi(\boldsymbol{\pi}^-_{xy},\boldsymbol{\pi}^-_{xy}) &= \phi(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^+_{xy}),\\
\phi(\mathbf{e}_z,\mathbf{e}_y) &= \phi(\mathbf{e}_z,\mathbf{e}_x),\\
\phi(\mathbf{e}_y,\mathbf{e}_z) &= \phi(\mathbf{e}_x,\mathbf{e}_z),\\
\phi(\mathbf{e}_y,\mathbf{e}_x) &= \phi(\mathbf{e}_x,\mathbf{e}_y).
\end{aligned}$$

When the polarization state of the scattered beam is not measured we need six calculations:

$$\begin{aligned}
C_0 &= \frac{2}{9}\big(\sigma(\mathbf{e}_x,\mathbf{e}_x)+\sigma(\mathbf{e}_x,\mathbf{e}_y)+\sigma(\mathbf{e}_x,\mathbf{e}_z)+\sigma(\mathbf{e}_z,\mathbf{e}_x)\big)\\
&\quad+\frac{\sigma(\mathbf{e}_z,\mathbf{e}_z)}{9},\\
C_1 &= -\frac{2}{15}\sigma(\mathbf{e}_x,\mathbf{e}_x)+\frac{\sigma(\mathbf{e}_x,\mathbf{e}_y)+\sigma(\mathbf{e}_x,\mathbf{e}_z)+\sigma(\mathbf{e}_z,\mathbf{e}_x)}{6}\\
&\quad+\frac{\sigma(\mathbf{e}_z,\mathbf{e}_z)}{30}-\frac{2}{5}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}).
\end{aligned}$$

For the full spectra we need eight calculations.

$$\begin{aligned}
S_0 &= \frac{4}{3}\sigma(\mathbf{e}_x,\mathbf{e}_x)+\frac{1}{3}\sigma(\mathbf{e}_z,\mathbf{e}_z)-\frac{2}{3}\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad-\frac{4}{3}\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+\frac{4}{3}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
S_1 &= -\sigma(\mathbf{e}_x,\mathbf{e}_x)-2\sigma(\mathbf{e}_x,\mathbf{e}_y)-2\sigma(\mathbf{e}_x,\mathbf{e}_z)\\
&\quad-2\sigma(\mathbf{e}_z,\mathbf{e}_x)-\sigma(\mathbf{e}_z,\mathbf{e}_z)+\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad+2\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+2\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
S_2 &= -\frac{1}{3}\sigma(\mathbf{e}_x,\mathbf{e}_x)-\frac{1}{3}\sigma(\mathbf{e}_z,\mathbf{e}_z)+\frac{5}{3}\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad+\frac{10}{3}\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+\frac{2}{3}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}).
\end{aligned}$$

C. For D_4, C_{4v}, D_{2d} and D_{4h}

For the groups D_4 or C_{4v} or D_{2d} or D_{4h} the relations between $\phi(\mathbf{u}_l,\mathbf{v}_l)$ are

$$\begin{aligned}
\phi(\mathbf{e}^-_{yz},\mathbf{e}^-_{yz}) &= \phi(\mathbf{e}^+_{yz},\mathbf{e}^+_{yz}) = \phi(\mathbf{e}^-_{xz},\mathbf{e}^-_{xz}) = \phi(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
\phi(\boldsymbol{\pi}^-_{yz},\boldsymbol{\pi}^-_{yz}) &= \phi(\boldsymbol{\pi}^+_{yz},\boldsymbol{\pi}^+_{yz}) = \phi(\boldsymbol{\pi}^-_{xz},\boldsymbol{\pi}^-_{xz}) = \phi(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^+_{xz}),\\
\phi(\mathbf{e}^-_{xy},\mathbf{e}^-_{xy}) &= \phi(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy}),\\
\phi(\boldsymbol{\pi}^-_{xy},\boldsymbol{\pi}^-_{xy}) &= \phi(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^+_{xy}),\\
\phi(\mathbf{e}_x,\mathbf{e}_x) &= \phi(\mathbf{e}_y,\mathbf{e}_y),\\
\phi(\mathbf{e}_z,\mathbf{e}_y) &= \phi(\mathbf{e}_z,\mathbf{e}_x),\\
\phi(\mathbf{e}_y,\mathbf{e}_z) &= \phi(\mathbf{e}_x,\mathbf{e}_z),\\
\phi(\mathbf{e}_y,\mathbf{e}_x) &= \phi(\mathbf{e}_x,\mathbf{e}_y).
\end{aligned}$$

When the polarization state of the scattered beam is not measured we need seven calculations:

$$\begin{aligned}
C_0 &= \frac{2}{9}\big(\sigma(\mathbf{e}_x,\mathbf{e}_x)+\sigma(\mathbf{e}_x,\mathbf{e}_y)+\sigma(\mathbf{e}_x,\mathbf{e}_z)+\sigma(\mathbf{e}_z,\mathbf{e}_x)\big)\\
&\quad+\frac{\sigma(\mathbf{e}_z,\mathbf{e}_z)}{9},\\
C_1 &= \frac{1}{15}\sigma(\mathbf{e}_x,\mathbf{e}_x)+\frac{\sigma(\mathbf{e}_x,\mathbf{e}_y)+\sigma(\mathbf{e}_x,\mathbf{e}_z)+\sigma(\mathbf{e}_z,\mathbf{e}_x)}{6}\\
&\quad+\frac{\sigma(\mathbf{e}_z,\mathbf{e}_z)}{30}-\frac{1}{5}\sigma(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy})-\frac{2}{5}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}).
\end{aligned}$$

For the full spectra we need nine calculations.

$$\begin{aligned}
S_0 &= \frac{2}{3}\sigma(\mathbf{e}_x,\mathbf{e}_x)+\frac{1}{3}\sigma(\mathbf{e}_z,\mathbf{e}_z)-\frac{2}{3}\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad-\frac{4}{3}\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+\frac{2}{3}\sigma(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy})+\frac{4}{3}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
S_1 &= -2\sigma(\mathbf{e}_x,\mathbf{e}_x)-2\sigma(\mathbf{e}_x,\mathbf{e}_y)-2\sigma(\mathbf{e}_x,\mathbf{e}_z)\\
&\quad-2\sigma(\mathbf{e}_z,\mathbf{e}_x)-\sigma(\mathbf{e}_z,\mathbf{e}_z)+\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad+2\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+\sigma(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy})+2\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}),\\
S_2 &= -\frac{2}{3}\sigma(\mathbf{e}_x,\mathbf{e}_x)-\frac{1}{3}\sigma(\mathbf{e}_z,\mathbf{e}_z)+\frac{5}{3}\sigma(\boldsymbol{\pi}^+_{xy},\boldsymbol{\pi}^-_{xy})\\
&\quad+\frac{10}{3}\sigma(\boldsymbol{\pi}^+_{xz},\boldsymbol{\pi}^-_{xz})+\frac{1}{3}\sigma(\mathbf{e}^+_{xy},\mathbf{e}^+_{xy})+\frac{2}{3}\sigma(\mathbf{e}^+_{xz},\mathbf{e}^+_{xz}).
\end{aligned}$$

D. For T or T_h

For the groups T and T_h the relations between $\phi(\mathbf{u}_l, \mathbf{v}_l)$ are

$$\begin{aligned}
\phi(\mathbf{e}^-_{yz}, \mathbf{e}^-_{yz}) &= \phi(\mathbf{e}^+_{yz}, \mathbf{e}^+_{yz}) = \phi(\mathbf{e}^-_{xz}, \mathbf{e}^-_{xz}) = \phi(\mathbf{e}^+_{xz}, \mathbf{e}^+_{xz}) \\
&= \phi(\mathbf{e}^-_{xy}, \mathbf{e}^-_{xy}) = \phi(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}), \\
\phi(\boldsymbol{\pi}^-_{yz}, \boldsymbol{\pi}^-_{yz}) &= \phi(\boldsymbol{\pi}^+_{yz}, \boldsymbol{\pi}^+_{yz}) = \phi(\boldsymbol{\pi}^-_{xz}, \boldsymbol{\pi}^-_{xz}) = \phi(\boldsymbol{\pi}^+_{xz}, \boldsymbol{\pi}^+_{xz}) \\
&= \phi(\boldsymbol{\pi}^-_{xy}, \boldsymbol{\pi}^-_{xy}) = \phi(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^+_{xy}), \\
\phi(\mathbf{e}_x, \mathbf{e}_x) &= \phi(\mathbf{e}_y, \mathbf{e}_y) = \phi(\mathbf{e}_z, \mathbf{e}_z), \\
\phi(\mathbf{e}_x, \mathbf{e}_y) &= \phi(\mathbf{e}_y, \mathbf{e}_z) = \phi(\mathbf{e}_z, \mathbf{e}_x), \\
\phi(\mathbf{e}_y, \mathbf{e}_x) &= \phi(\mathbf{e}_z, \mathbf{e}_y) = \phi(\mathbf{e}_x, \mathbf{e}_z).
\end{aligned}$$

We need five calculations for the full spectrum

$$\begin{aligned}
S_0 &= \sigma(\mathbf{e}_x, \mathbf{e}_x) + 2\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) - 2\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}), \\
S_1 &= -3\sigma(\mathbf{e}_x, \mathbf{e}_x) - 3\sigma(\mathbf{e}_x, \mathbf{e}_y) - 3\sigma(\mathbf{e}_y, \mathbf{e}_x) \\
&\quad +3\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) + 3\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}), \\
S_2 &= -\sigma(\mathbf{e}_x, \mathbf{e}_x) + \sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy}) + 5\sigma(\boldsymbol{\pi}^+_{xy}, \boldsymbol{\pi}^-_{xy}).
\end{aligned}$$

And we need four calculations if the polarization state of the scattered beam is not measured:

$$\begin{aligned}
C_0 &= \frac{\sigma(\mathbf{e}_x, \mathbf{e}_x) + \sigma(\mathbf{e}_x, \mathbf{e}_y) + \sigma(\mathbf{e}_y, \mathbf{e}_x)}{3}, \\
C_1 &= \frac{\sigma(\mathbf{e}_x, \mathbf{e}_x)}{10} + \frac{\sigma(\mathbf{e}_x, \mathbf{e}_y) + \sigma(\mathbf{e}_y, \mathbf{e}_x)}{4} - \frac{3\sigma(\mathbf{e}^+_{xy}, \mathbf{e}^+_{xy})}{5}.
\end{aligned}$$

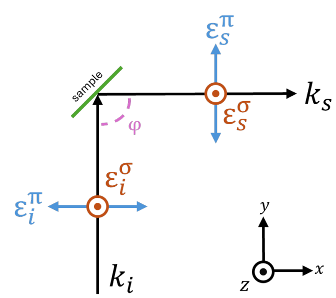

FIG. 1. Schematic showing an overview of experiment configuration. Parallel and perpendicular polarization vectors are denoted as π and σ respectively. The incident and scattered photon momentum are denoted as $\widehat{\mathbf{k}}_i$ and $\widehat{\mathbf{k}}_s$ respectively. The angle of scattered photon detection is given by φ.

VI. APPLICATIONS

A. General experiment considerations

In a RIXS experiment, depending on the energy range of the scattered photon, detection is achieved using an emission spectrometer that can either utilize grazing incidence diffraction gratings for soft X-rays or crystal analyzers for hard X-rays. The sample, crystal analyzer, and detector sit within a Rowland circle.

With reference to Figure 1, the incoming incident beam is denoted by $\widehat{\mathbf{k}}_i$ and the emitted fluorescence photons ($\widehat{\mathbf{k}}_s$) that are scattered by the sample are energy discriminated using crystal analyzers, before detection, at an angle φ with respect to $\widehat{\mathbf{k}}_i$. The crystal analyzer is usually positioned at 90°, with respect to the incoming incident beam ($\widehat{\mathbf{k}}_i$), and serves as the reference point from which additional crystal analyzers can be positioned either side.

The derivations for powder samples from the present paper lead to several general experimental conclusions:

- the RIXS cross-section measured with incident vertical polarization and standard φ=90° horizontal scattering geometry is identical to the RIXS cross-section measured with incident vertical polarization and back-scattering horizontal geometry.
- in hard X-ray RIXS, the use of multiple crystal analyzers leads to the summation of different RIXS spectra unless the each of their intensity is detected individually using a 2D detector. Theoretical modeling should then be performed accordingly using the provided formulas.
- for cubic samples, four spectra need to be computed to obtain the correct RIXS cross-section of a powder, contrary to standard XAS where only one spectrum is needed.

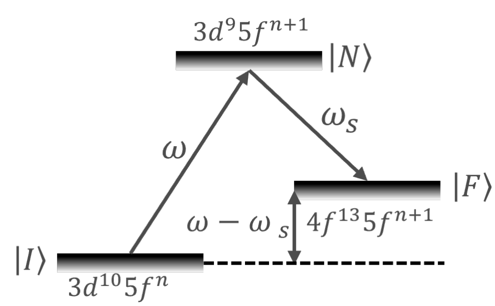

FIG. 2. Schematic of $3d4f$ RIXS, depicting the correlation between incident (ω), emitted (ω_s), and transferred (ω - ω_s) energies, and the corresponding electronic configurations of the initial $|I\rangle$, intermediate $|N\rangle$, and final $|F\rangle$ states.

B. Case study: actinide $3d4f$ RIXS

The formulas derived within section V have been applied to a selection of actinide compounds, previously published and measured using $3d4f$ RIXS. It is to be emphasized though, that the derivations are applicable to all RIXS measurements, regardless of which absorption and emission lines are probed.

With respect to actinide X-ray spectroscopy, $3d4f$ RIXS is a photon-in photon-out inelastic scattering process of which a $3d$ core electron is resonantly excited into

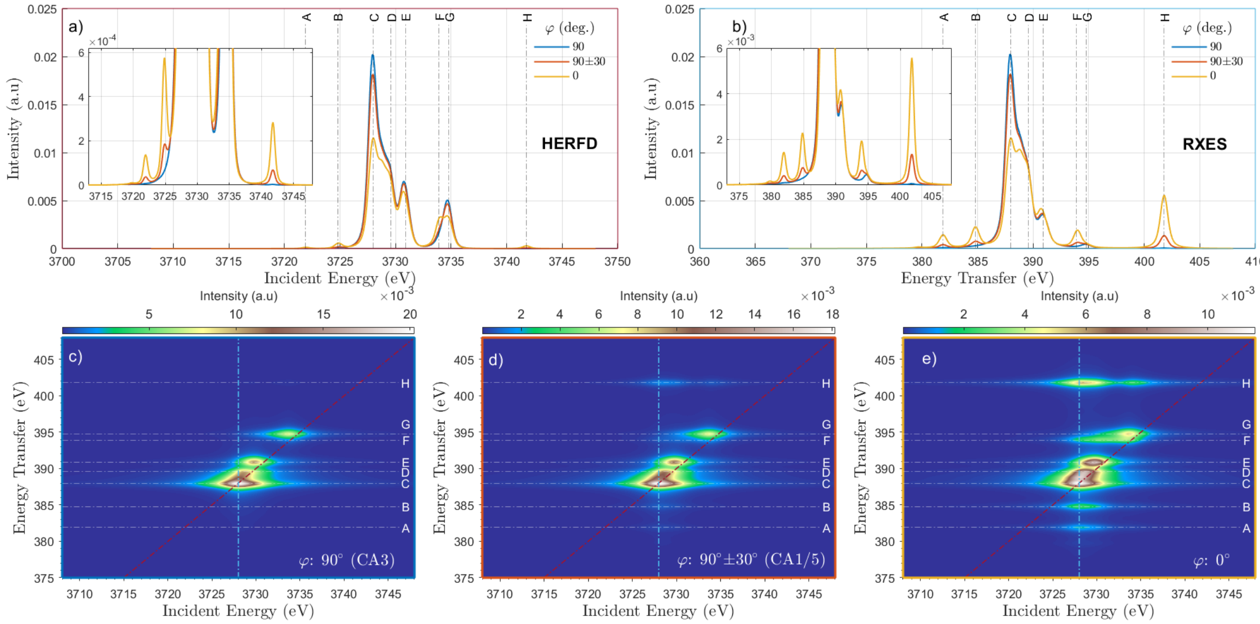

FIG. 3. $U^{VI}O_2Cl_4{}^{2-}$ a) simulated HERFD cuts through $3d4f$ RIXS maps (c-e), inplot is same as (a) but with limited y axis. b) simulated RXES cuts through RIXS maps (c-e), inplot is same as (b) but with limited y axis. c-e) simulated uranium $3d4f$ RIXS maps at different crystal analyzer (CA) positions φ; 90°, 90°±30°, and back-scattering case of 0°. HERFD (red dash) and RXES (blue dash) cuts are represented as the diagonal and vertical cuts in the maps. White horizontal lines (c-e) and black vertical lines (a-b) correlate to the most prominent peaks present.

the unoccupied valence $5f$ states, while simultaneously detecting fluorescence photons emitted from a $4f \to 3d$ decay. The complete $3d4f$ RIXS process is shown in Figure 2.

Actinide $3d4f$ RIXS falls within the tender X-ray region. As such, performing these measurements does not require ultra-high vacuum environments but are yet capable of providing high resolution spectra, exposing spectral features that are otherwise hidden by the large core-hole lifetime broadening if measuring hard X-ray spectroscopy or conventional XAS. This balance of experiment conditions and spectral resolution lends itself as a quintessential technique for probing actinides. Due to this reasoning, $3d4f$ RIXS is increasingly being utilized as the technique to probe the valence actinide $5f$ orbitals to investigate and gain insights into actinide electronic structure, local coordination, redox, and their subsequent role in covalency [44–56].

However, due to the relative short divergence of φ from the reference crystal analyzers positioned at $\varphi = 90°$, we show in Figures 3-5 that $3d4f$ RIXS measurements performed using these emission spectrometer orientations miss the wealth of information that could otherwise be revealed if the crystal analyzers are positioned towards more extreme back-scattering geometries, (φ: 90°→ 0°).

To emphasize the contrast of additional information that can be extracted by $3d4f$ RIXS, a systematic selection of three uranium compounds, previously published and measured, with common U oxidation states and varying local point-group symmetry have been chosen as case studies, namely; $U^{VI}O_2Cl_4{}^{2-}$ (D_{4h})[47], $Sr_3U^{VI}O_6$ (O_h)[47], and $U^{IV}O_2$ (O_h)[57], where U^{VI} and U^{IV} have $5f^0$ and $5f^2$ ground state electronic structures, respectively. We will consider as typical instrument a five-crystal analyzer spectrometer, as has been developed on several beamlines [58–62].

In Figure 3(c-d), the simulated RIXS maps correspond to crystal analyzers positioned at φ=90° and 90°±30°, this is representative of most divergent positions of typical five-analyzers emission spectrometers which typically have crystal analyzers at these positions and φ= 90°±15°, which we do not account for. In order to further highlight the contrast in the possible spectra obtainable, Fig. 3(e) correlates to $\varphi = 0°$ and reflects when an emission spectrometer would be orientated in a back-scattering geometry.

From these simulated $3d4f$ RIXS maps, constant emission energy (CEE) cuts can be taken (Figure 3(a)), which are representative of experimentally obtained HERFD-XAS spectra, and correspond to the diagonal red-dash cuts through the $3d4f$ RIXS maps at the maximum of the N_6 (M_β) emission line. Characteristic spectral features of the CEE cut, peaks **C-E, G**, are associated to the main whiteline transition and the large $5f$ D_{4h} ligand field splitting, carrying sensitivity to the incoming incident energy. It is observed that when φ is varied from 90°→ 0°, the intensity of these peaks are seemingly not perturbed, with the exception to the whiteline, peak

C, which readily decreases in intensity when approaching back-scattering geometries.

Similarly, constant incident energy (CIE) cuts, Figure 3(b), represented as vertical blue-dash cuts through the simulated $3d4f$ RIXS maps are representative of resonant X-ray emission spectroscopy (RXES) measurements, carrying sensitivity to the final state of the $3d4f$ RIXS process. As the example presented concerns U^{VI}, the remaining non-characterized intensity present in the simulated RIXS maps and prominently extracted in the CIE cuts, peaks **A-B, F, H**, arise from inter-shell $4f^{13}5f^1$ spin-exchange interactions, and commonly referred to as satellites. The intensity of these peaks increases drastically as a function of φ (90 °→0°). It is also noted that the current most divergent crystal analyzer positions (φ: 90°±30°) of typical five-analyzer spectrometer would be potentially adequate to capture partial intensity of these features in experiment conditions, depending on signal-noise and other experiment considerations.

Upon comparing simulations presented here using the derivations of section V with the simulations previously published [47], some key points are made. The authors previously modeled their experimental HERFD-XAS spectra of $U^{VI}O_2Cl_4{}^{2-}$ using an X-ray absorption ligand field multiplet model that considers the $5f$ ligand field splitting, $3d^95f^1$ repulsion and spin-exchange interactions, and spin-orbit coupling. Their best simulation of the $U^{VI}O_2Cl_4{}^{2-}$ HERFD data most noticeably required a scaling the $3d$-$5f$ Slater integrals to 50% of their atomic values. Conversely, what we present is that by employing a ligand field multiplet model that encompasses the entire $3d4f$ RIXS process, implying additional consideration in the simulations to include the $4f^{13}5f^1$ repulsion and spin-exchange interactions and their respective spin-orbit coupling constants, and that of which employs the equations for D_{4h} in section V, we are able to come close to reproducing the fine structure in their spectra. The key factor though is that in the simulations we present, the Slater integrals were solely scaled, conventionally, to 80% of their atomic value [63], with no other scaling required. Solely by accounting for the position of the crystal analyzers with respect to φ and the inclusion of our derivations when calculating the $3d4f$ RIXS spectra, we are, in general, able to now provide a method that more accurately simulates experimental data.

Maintaining a uranium $5f^0$ electronic configuration but changing the symmetry from $U^{VI}O_2Cl_4{}^{2-}$ D_{4h} to $Sr_3U^{VI}O_6$ O_h, the results are similar in nature. Figure 4(a-b) show simulated $3d4f$ RIXS maps of $Sr_3U^{VI}O_6$ in both extreme, perpendicular (φ=90°) and back-scattering (φ=0°), geometries. It is clear that the experiment orientation has a limited sensitivity to peaks **B-D**, and can be attributed to the $5f$ ligand field splitting. Contrarily, peaks **A** & **E** carry significant sensitivity to the $4f$-$5f$ inter-shell spin-exchange interactions in the final state of $3d4f$ RIXS. Another perspective of analyzing the sensitivity of peak intensity, peaks **A-E**, as a function of φ is shown in Figure 4(c). The intensity of the peaks is shown on the radial axis of the polar plot, while the angular axis shows φ, typical five-crystal analyzer φ positions are shown as a reference emission spectrometer configuration. When measuring perpendicular to the incident beam ($\varphi = 90°$), the intensity of peaks **A** and **E** approach 0 and would not be observed experimentally, whilst all other features are at their maxima. Conversely, at $\varphi = 0°$, this relation is inverted such that the satellite intensities are at their respective maxima and peaks **B-D** are at their lowest.

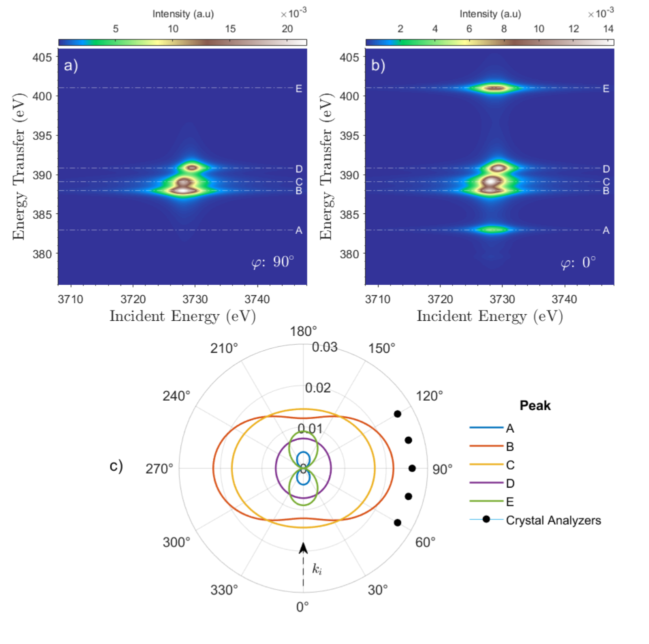

FIG. 4. $Sr_3U^{VI}O_6$ a-b) simulated uranium $3d4f$ RIXS maps at a) φ=0° and b) φ=90° with respect to the incident beam, $\hat{\mathbf{k}}_i$. c) Polar plot of features **A**-**E**. The angular axis is representative of φ and the radial axis is the peak intensity. Example positions of crystal analyzers are indicated by black dots.

Maintaining O_h symmetry but diverging from U^{VI} $5f^0$ ($Sr_3U^{VI}O_6$) to U^{IV} $5f^2$ ($U^{IV}O_2$) ground state electronic configuration subsequently results in Figure 5. Prior to characterizing the features present in the simulations, starting from a $5f^2$ ground state electronic structure, this subsequently leads to an intermediate $|N\rangle$ $3d^95f^3$ and final $|F\rangle$ $4f^{13}5f^3$ state electronic configuration during the RIXS process. With particular emphasis to the final state electronic configuration, it consequently leads to necessity to consider $4f$-$5f$ and $5f$-$5f$ inter-shell spin-exchange and repulsion interactions. Comparing between Figures 4(c) and 5(c), where the experiment geometry is perpendicular to the incoming beam ($\varphi = 90°$), peaks **A** and **E** would each now have observable intensity in U^{IV} experimental $3d4f$ RIXS measurements. The same observations as before, with reference to Figure 5(c), are observed when the crystal analyzers are orientated perpendicular to the incoming beam ($\varphi = 90°$), the main whiteline intensity and features **B-D** arising from the $5f$ ligand field splitting are most intense. Additionally

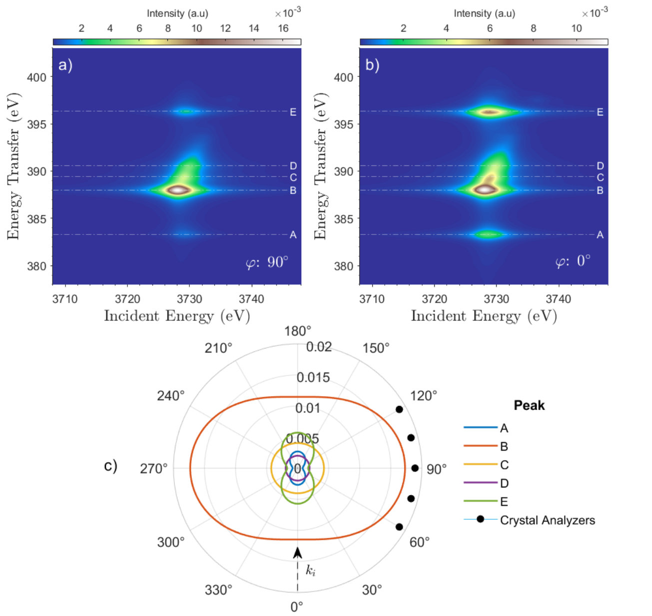

FIG. 5. $U^{IV}O_2$ a-b) simulated uranium $3d4f$ RIXS maps at a) φ=0° and b) φ=90° with respect to the incident beam, $\widehat{\mathbf{k}}_i$. c) Polar plot of features **A**-**E**. The angular axis is representative of φ and the radial axis is the peak intensity. Example positions of crystal analyzers are indicated by black dots.

secluded within these peaks, however, is intensity that originates from $5f$-$5f$ repulsion interactions, although it is proposed that φ carries minor influence on the intensity of these features. Although, when approaching back-scattering geometry (φ: 90°→0°), the satellites corresponding to inter-shell $4f$-$5f$ spin-exchange interaction are most prominent, following the same trends as U^{VI}.

As previous authors have used the energy position and intensities of the satellites to gain information into the effective value of Slater integrals to further derive insights into chemical bonding, we show however that the implication from these examples, such satellites present in $3d4f$ RIXS, and others, can serve as an anchor for determining the correct scaling of Slater integrals, as solely the intensity of these features are perturbed as function of φ, not their energetic positioning, which only changes as a consequence of scaling.

To further elaborate on the sensitivity of $3d4f$ RIXS to inter-shell $5f$-$5f$ repulsion and $4f$-$5f$ spin-exchange interactions, a series of $An^{IV}O_2$ (An = Th, Np, Pu) in cubic symmetry (O_h) as previously published[57] have been simulated as example cases where the ground state $5f$ electron occupancy changes from $5f^0$ to $5f^3$ to $5f^4$ respectively. These can be found in the supplementary information.

VII. CONCLUSION AND PROSPECTS

In this work, we provided a general method —applicable to all point group symmetries— to express a RIXS spectrum in terms of its fundamental spectra. In other words, we determined the minimal number of spectra that must be measured or calculated in order to fully access all the spectral information contained in a sample. The analysis was carried out within the electric dipole approximation for both the incoming and outgoing photons.

A direct application of this approach is the derivation of simple and practical expressions for the RIXS spectrum of isotropic samples with the most common sample symmetries (cubic, tetrahedral, hexagonal, trigonal, and tetragonal). We expect that these easy-to-use formulas will stimulate new experimental measurements, in particular by exploring the dependence on the scattering angle and the polarization of the outgoing beam, which for example could help to enhance elusive spectral features by choosing more appropriate experimental configurations. Accounting for this dependence may also lead to a reexamination, and possibly a reinterpretation, of existing data in the literature.

To illustrate the derivations, we show that there is a significant angular dependence in actinide $3d4f$ RIXS by simulating previously reported literature. In each of these examples, it is shown that final-state RIXS satellite intensities are significantly perturbed as a function of the spectrometer geometry. As actinide X-ray measurements are performed on isotropic powder samples, we have shown that it is crucial to use the formulas presented within the present paper to correctly simulate satellite intensities and subsequently obtain the correct effective scaling for Slater integrals. Furthermore, from an experiment perspective, we highlight that ideal experiment conditions should use a 2D detector for RIXS measurements. This would facilitate spectrometer designs to have a large divergence with respect to $\widehat{\mathbf{k}}_s$, and allow for the individual analysis of the scattered photon intensity from each crystal analyzer.

The present work can also be used to determine the minimum number of experimental spectra that must be measured to extract all the information available from RIXS spectroscopy.

A natural extension of this work, which is currently in progress, concerns the case of an electric quadrupole approximation for the incoming photon combined with an electric dipole approximation for the outgoing photon. This situation is relevant to many experiments on transition metals. Another perspective is to include the dipole–quadrupole interference term for the incoming photon, which gives rise to the XNCD effect in RIXS.

VIII. ACKNOWLEDGEMENTS

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Appendix A: Ligand field multiplet simulations

Multiplet simulations of the $3d4f$ RIXS planes were carried out using Quanty Version 0.7 beta [65]. To emphasize the features, a slightly narrower broadening was used than that previously published, such that a Lorentzian broadening of 3 eV and 0.5 eV for the $3d^9$ and $4f^{13}$ core-hole lifetimes, and a Gaussian broadening of 0.5 eV, associated to experimental resolution. As Quanty is semi-empirical, a modular Hamiltonian was be constructed consisting of the $5f$ ligand field splitting, electron-electron interactions, and spin-orbit coupling in the initial, intermediate, and final electronic configurations of $3d4f$ RIXS. A small magnetic field was applied on the Z axis. The on-site energy of regarding the $5f$ ligand field splitting were the same as previously reported [47, 57]. All electron-electron interactions, associated to the Coulomb inter-shell repulsion & spin-exchange interactions, were scaled at 80% of the Hartree-Fock value. Spin-orbit coupling constants were kept at a scaling of 100%. No scaling has been applied regarding the intensity of the simulated RIXS maps.

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