

New Developments in Advanced X-ray Spectroscopy and Their Applications

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Abstract

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Physics

X-ray spectroscopy is a non-destructive, element-specific probe that gives information on electronic structure and local coordination geometry. It describes a family of X-ray spectral techniques including X-ray absorption fine structure (XAFS), X-ray emission spectroscopy (XES), High Energy Resolution Fluorescence Detected (HERFD), and non-resonant X-ray Raman Scattering (XRS), which are utilized across multiple fields of science, including chemistry, physics, and materials science. However, the full diagnostic potential of these techniques is often limited by optical constraints, particularly in spherically bent crystal spectrometers. Additionally, persistent analytical bottlenecks exist in unmixing multi-phase experimental spectra when no extensive reference libraries are available.

To address the optical limitation, this dissertation presents a comprehensive theoretical and experimental development of asymmetric operation for spherically bent crystal analyzers (SBCAs)

under Rowland geometry. By accessing different crystal planes through hkl hopping, a single SBCA can cover a broad energy range that includes the K-edge absorption and emission spectra of 3d transition metals. Furthermore, through extensive geometric ray-tracing simulations and experiments, we show that operating near the Johann Normal Alignment (JNA) condition systematically suppresses or eliminates Johann error, the major source of energy-resolution compromise in a Rowland-geometry SBCA spectrometer. The new operation method of a Rowland spectrometer preserves high energy resolution and large collection solid angles while enhancing sample clearance for specialized environments in XAFS, XES, HERFD, and XRS imaging applications.

Complementing these hardware advances, this work introduces "spectral harvesting", a novel geometric data analysis framework for non-reference-based spectral decomposition. Operating within latent space generated with the aid of Principal Component Analysis (PCA), the algorithm enforces a suite of physics- and chemistry-motivated constraints to systematically filter unphysical latent space regions and establish an Area of Feasible Solutions (AFS). Pure phase candidates are selected through subsequent maximum-volume simplex fitting within the reduced AFS, effectively reducing sensitivity to rotational ambiguity that is commonly faced by standard matrix-based decomposition algorithms such as Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS).

Together, the instrumental and analytical developments established in this dissertation significantly expand the operational scope, spectral resolution, and spectral decomposition accuracy of modern X-ray spectroscopy, providing robust methodologies for both laboratory bench-top instruments and synchrotron beamline spectrometers.

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GLOSSARY

IXS	inelastic X-ray scattering
XRS	X-ray Raman scattering
NRIXS	nonresonant inelastic X-ray scattering
RIXS	resonant inelastic X-ray scattering
XAS	X-ray absorption spectroscopy
XAFS	X-ray absorption fine structure
EXAFS	extended XAFS
XANES	X-ray absorption near-edge structure
HERFD	high energy resolution fluorescence detection
VtC XES	valence-to-core X-ray emission spectroscopy
SBCA	spherically bent crystal analyzer
JNA	Johann normal alignment
AFS	area of feasible solutions
PCA	principal component analysis
MCR-ALS	multivariate curve resolution-alternating least squares
SIMPLISMA	simple-to-use interactive self-modeling mixture analysis
LCA	linear combination analysis
TTA	target transformation analysis
$\mu(E)$	absorption coefficient, where $I_T = I_0 e^{-\mu t}$
I_0, I_T	incident and transmitted X-ray intensity

t	thickness of absorbing material
$\chi(k)$	EXAFS fine-structure oscillation, where $\mu(E) = \mu_0(E)(1 + \chi(E))$
$\chi(R)$	Fourier transform of $\chi(k)$
$\mu_0(E)$	smooth single-atom background absorption coefficient
k	photoelectron wave vector magnitude, where $k = 2\pi/\lambda$
λ	wavelength of the incident photon or photoelectron wave
$E_0^{(h,k,l)}$	Bragg diffracted photon energy at a nominal $\theta_B = 90^\circ$
θ_B	Bragg angle, where $E(\theta_B) = E_0^{(h,k,l)} / \sin \theta_B$
α	asymmetry angle, denoting the angle between $\vec{G}_{hkl}$ and $\vec{G}_0$
$\vec{G}_0$	crystal surface normal reciprocal lattice vector
$\vec{G}_{hkl}$	asymmetric diffraction plane reciprocal lattice vector
$\hat{n}$	physical optical wafer surface normal vector
θ_M	mechanical analyzer angle, defined via $\theta_M = \theta_B + \alpha$
α_J	asymmetry angle required for JNA, defined by $\alpha_J = 90^\circ - \theta_B$
ρ, d	source-to-analyzer and analyzer-to-detector chord lengths
D	Rowland circle diameter or radius of curvature of the SBCA wafer
f_m, f_s	vertical meridional line focus distance and horizontal sagittal line focus distance
R	bending radius of curvature of the spherically bent crystal wafer
h_m, w_s	vertical beam height at focus f_m and horizontal width at focus f_s

d_{xtal}	active visual analyzer face diameter
γ	sagittal angular size of the crystal analyzer as viewed from the source
f_{cc}	distance from the crystal face to the minimum circle of confusion
D_{SDD}	active sensing element face diameter of a silicon drift detector
σ_{resp}	total standard deviation metric evaluated to track energy response variance
c_i	pure-phase concentration profile weight, where $\sum_{i=1}^N c_i = 1$
N	total number of primary principal components or constituent pure phases

Chapter 1

Background on X-ray Spectroscopy

X-ray spectroscopy is a broad term for a set of techniques that exploit the interaction of X-rays with matter to study the structure and properties of materials. This field of science has been under continuous development since the discovery of X-rays in the early 1900s. Although its theory is grounded in physics, its applications span a wide range of disciplines, including chemistry, geoscience, biology, and others. In simple terms, X-ray spectroscopy can be described as a two-step process: atomic excitation by an incident photon, followed by relaxation via the emission of a photon or an electron to conserve energy. These processes give rise to distinct types of spectroscopy which will be covered in detail in this chapter. To do so, we begin with the first interaction in this chain, i.e., the photoelectric effect and X-ray absorption spectroscopy.

1.1 X-ray Absorption Spectroscopy (XAS)

To start, recall Fermi's Golden rule, which describes the transition rate of a quantum system from one energy eigenstate i to a final state f due to a weak perturbation [1],

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \delta(E_f - E_i), \quad (1.1)$$

where H' is the perturbing Hamiltonian that produces transitions between the initial $|i\rangle$ and final $|f\rangle$ state, and the delta function ensures energy conservation. In the case of a photoelectric process, the perturbing Hamiltonian is due to the electromagnetic field and takes the form $H' = \frac{e\vec{A} \cdot \vec{p}}{m}$, and

$|i\rangle$ and $|f\rangle$ are the state of the electrons of the absorbing atom, Eq. 1.1 can then be written as

$$\Gamma_{i \rightarrow f} \propto |\langle f | \vec{A} \cdot \vec{p} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega). \quad (1.2)$$

Note that the argument in the delta function now consists of the energies of the final state (E_f) with a core-hole, the initial state (E_i), and the incident photon ($\hbar\omega$).

Using Eq. 1.2, we can further calculate the probability of photon absorption (through exciting an electron), which is what governs absorption spectroscopy. To do so, we first realize that the vector potential $\vec{A}$ takes the form $A_0 e^{i\vec{k} \cdot \vec{r}} \hat{\epsilon}$. Since the spatial extent of an orbital is typically much smaller than the wavelength of light needed for the photoelectric effect to occur, we have $\vec{k} \cdot \vec{r} \ll 1$ and the vector potential can be approximated as $A_0(1 - i\vec{k} \cdot \vec{r})\hat{\epsilon}$. We typically refer to these two terms as the electric dipole and quadrupole terms. Together with the commutator expression $\vec{p} = \frac{im}{\hbar}[H, \vec{r}]$, Eq. 1.2 can be written as

$$\Gamma_{i \rightarrow f} \propto |\langle f | (1 - i\vec{k} \cdot \vec{r})\hat{\epsilon} \cdot (H\vec{r} - \vec{r}H) | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (1.3)$$

$$= (E_f - E_i)^2 |\langle f | (1 - i\vec{k} \cdot \vec{r})\hat{\epsilon} \cdot \vec{r} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega). \quad (1.4)$$

With the dipole approximation, $\vec{A}$ is constant over the length scale of an orbital; Eq. 1.4 turns into,

$$I_{XAS} \approx (\hbar\omega)^2 |\langle f | \hat{\epsilon} \cdot \vec{r} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega). \quad (1.5)$$

If we further approximate that the matrix element can be rewritten into a single-electron form by

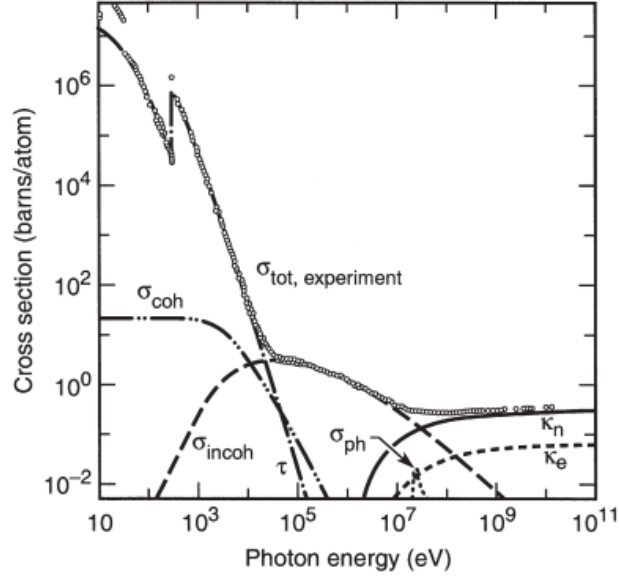


Figure 1.1: Photon cross section of carbon through various processes. The curve labeled τ is the photon absorption cross section we calculated above, which follows a $1/E^3$ relation. The other cross sections listed are from coherent scattering (σ_{coh}), incoherent scattering (σ_{incoh}), photonuclear absorption (σ_{ph}), nuclear pair production (κ_n), and electronic pair production (κ_e). [2]

removing all inactive electrons, the series of delta functions then identifies with the density of states (ρ), and the X-ray absorption cross-section becomes

$$I_{XAS} \approx (\hbar\omega)^2 |\langle \varepsilon | \hat{\epsilon} \cdot \vec{r} | e \rangle|^2 \rho, \quad (1.6)$$

where ε is the free electron wave function and e is a core wavefunction.

In Fig. 1.1, we show a plot of the photon cross section of carbon through various processes [2]. The curve labeled τ is the photon absorption cross section, which often exhibits a $1/E^3$ trend with sharp rises when the incident photon energy exceeds the electron binding energy. These sharp rises correspond to the excitation of a core electron to the continuum and are referred to as an absorption edge. Depending on the core orbital, absorption edges can be further categorized as

K, L, M, etc. Eq. 1.6 describes the physics of photon absorption and forms the basis of X-ray Absorption Spectroscopy (XAS).

Experimentally, an absorption spectrum is produced by measuring the so-called absorption coefficient (μ) defined by the Beer-Lambert Law

$$I_T = I_0 e^{-\mu t}, \quad (1.7)$$

where I_T and I_0 are the transmitted X-ray intensity and incident X-ray intensity, respectively, and t represents the thickness of the absorbing material. The absorption coefficient μ is a direct measure of the absorption probability, and its variation with incident X-ray energy is what we refer to as XAS.

Ever since the discovery of X-rays in the late 19th century, tremendous efforts have been devoted to experimentally recording the X-ray absorption spectrum [5]. Many attempts were made, but they later proved faulty [6–9]. In 1918, Wilhelm Stenström, a doctoral student at Lund University in Sweden working under Manne Siegbahn’s supervision, presented a set of data in his thesis [3] which he claimed to be the M-series absorption spectrum of thorium (Fig. 1.2). His photographically recorded spectral image, along with a graphically rendered spectrum, was considered to be possibly the first published evidence of a true X-ray absorption spectrum showing edge steps. This finding was later supported by Walther Kossel in his seminal theoretical paper [4]. Stenström’s work provided the initial evidence of X-ray absorption features, but due to limitations in energy resolution, absorption fine structure was still undiscovered. The field of X-ray Absorption Fine Structure (XAFS) was unexplored until Hugo Fricke presented the K-series spectra of tran-

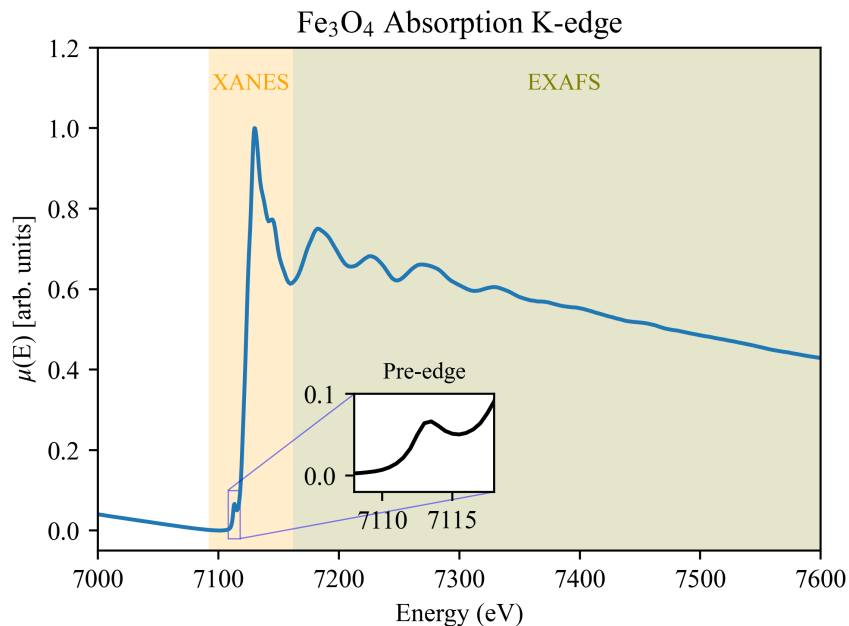


Figure 1.3: A Fe K-edge XAS spectrum of Fe_3O_4 reproduced from the data on the Canadian Light Source XAS Database, illustrating the three regions of interest: pre-edge, XANES, and EXAFS.

sition metals measured on high-resolution photographic plates [10] in which he experimentally observed oscillations in the absorption spectra. It was at that point that the scientific community became aware of the fine structure and acknowledged XAFS as an important branch of science.

Since then, XAFS has become an important tool across all fields of science for obtaining atomic-level information, which we discuss in detail in the remainder of this section. To do so, it is useful to divide the spectrum into three energy ranges: pre-edge, X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS). This is illustrated in Fig. 1.3, where we use a Fe_3O_4 Fe K-edge spectrum as an example. The XANES region typically corresponds to the energy range up to ~ 50 eV above the edge, while EXAFS focuses on the oscillations past ~ 50 eV. The pre-edge region, as part of XANES, refers to the region ~ 20 eV below the absorption edge.

T_d		O_h	
p	d	p	d
A_1	$x^2 + y^2 + z^2$	A_{1g}	$x^2 + y^2 + z^2$
A_2		A_{2g}	
E	$(2z^2 - x^2 - y^2, x^2 - y^2)$	E_g	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	(R_x, R_y, R_z)	T_{1g}	(R_x, R_y, R_z)
T_2	(x, y, z) (xz, yz, xy)	T_{2g}	(xz, yz, xy)
		A_{1u}	
		A_{2u}	
		E_u	
		T_{1u}	(x, y, z)
		T_{2u}	

Table 1.1: List of irreducible representations and relating $p - d$ orbitals in T_d (tetrahedral) and O_h (octahedral) point groups. [11]

1.1.1 Pre-edge Features

Pre-edge features are spectral features that occur before the absorption edge, typically within a 20 eV window below it. The spectral signal in this region corresponds to electron excitation from the core electronic state to unoccupied states just above the Fermi level, and is extremely sensitive to the local symmetry of atomic structure. To understand this, one must first refer back to the matrix element, $\langle \varepsilon | \hat{e} \cdot \vec{r} | e \rangle$, presented in Eq. 1.6, which describes the probability of electric dipole transitions. Note that for a symmetrical integral range, the integrand must be even to produce a non-zero integral. This implies that $|\varepsilon\rangle$ and $|e\rangle$ must be in opposite symmetry in order for the transition to be allowed. The s, p, d orbitals are even, odd, even functions for the inversion of axes, meaning the $s - p$ transition will be allowed but not the $s - d$. This is often referred to as the dipole selection rule ($\Delta l = \pm 1, \Delta j = 0, \pm 1$).

Using the $3d$ transition-metal K-edge as an example, states just above the Fermi level are pre-

dominantly d states, so excitation from the $1s$ core to these states is nominally not dipole-allowed. However, such transitions are allowed by electric quadrupole coupling, which is typically much weaker than dipole coupling. However, experimental observations show that some $3d$ transition-metal K-edge spectra exhibit a strong pre-edge feature, which is due to hybridization between p and d orbitals. To understand when $p-d$ hybridization is allowed, we refer to the Table. 1.1 reproduced from Yamamoto (2008) [11]. The point groups T_d and O_h listed in this table represent tetrahedral and octahedral atomic structures, respectively. Under each point group, p and d orbitals are further sorted into different irreducible representations based on their symmetry. In order for $p-d$ orbitals to hybridize, they need to have the same symmetry. For example, in T_d point group, both $p_{x,y,z}$ and $d_{xz,yz,xy}$ orbitals have T_2 symmetry. Group theory then predicts that $p-d$ hybridization can occur in tetrahedral-structured materials. On the other hand, in the O_h point group, no p and d orbitals share the same symmetry, meaning there will be no dipole transitions induced by hybridization in octahedral-structured materials [12, 13]. In Fig. 1.4, we show FEFF-simulated Cr K spectra of CrO_3 and Cr_2O_3 , which have tetrahedral and octahedral geometry around the Cr, respectively. One can see that the pre-edge feature is much more prominent in the tetrahedral sample, as predicted by group theory. In the octahedral sample, the pre-edge peak intensity is weak and likely due to quadrupole transitions alone or to sample structural distortion. In summary, the most common use of the pre-edge feature is to probe the local coordination geometry and track structural distortions surrounding the absorbing atom.

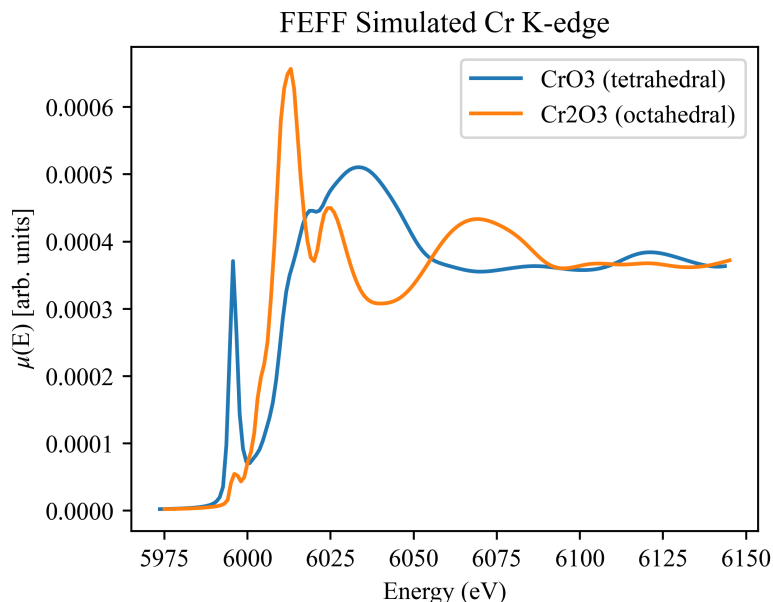


Figure 1.4: FEFF simulation of Cr K-edge of CrO_3 (tetrahedral) and Cr_2O_3 (Octahedral). The tetrahedral sample exhibits a much stronger pre-edge peak intensity due to stronger $p - d$ hybridization, as predicted by group theory.

1.1.2 X-ray Absorption Near-edge Structure (XANES)

XANES provides rich, element-specific insights into oxidation states, coordination geometries, and electronic structures. These capabilities make it an essential tool for species identification, particularly in tracking changes during phenomena such as phase transitions. To facilitate this identification, experimental spectra are typically compared against those of well-characterized reference standards, which are often readily available online from multiple synchrotron and theoretical databases. For a more complex multi-phase sample, one can reconstruct the experimental data by linearly combining known references to infer the phase contributions, or use principal component analysis when less prior knowledge is available.

As mentioned above, XANES is a useful tool for identifying oxidation states. This information is most prominently reflected in the absorption edge location. Recall that the absorption edge

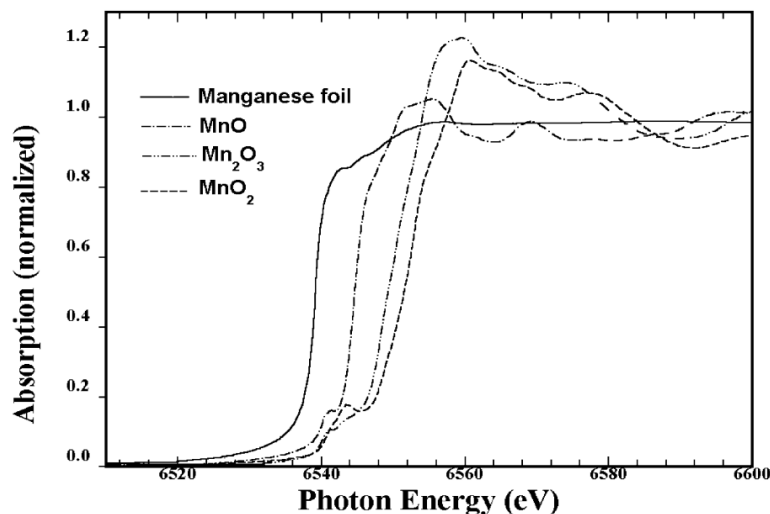


Figure 1.5: From Stueben et al. [14] The Mn XANES spectra of a collection of Mn oxides with different oxidation states. The edge energy tends to shift to higher values as the oxidation state increases, due to slight changes in core-electron binding energies.

energy reflects the binding energy of the core-level electron that is responsible for the absorption process. With increasing oxidation state, the nuclear shielding weakens due to the reduced number of outer electrons. This results in stronger Coulomb attraction between the nucleus and the core electrons, increasing the core-level binding energy. In Fig. 1.5, we show a figure extracted from Stueben et al. [14], where Mn XANES from different Mn compounds is presented. Note that these compounds are ordered in increasing oxidation state (Mn, Mn(II), Mn(III), Mn(IV)), and there is a clear trend of upshift in edge energy with increasing oxidation states. Experimentally, the absorption edge has been defined to be either the first maximum of the first derivative of the absorption spectrum, or the energy where μ reaches half of its edge-step. Studies have shown that oxidation state and edge energy often show a linear relationship [15–17].

The white line, named after the early days of X-ray spectroscopy when spectra were recorded on photographic plates, is the sharp feature just above the edge. As discussed above, its location

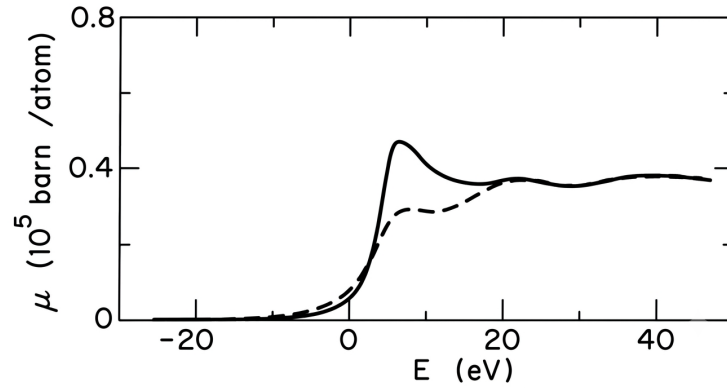


Figure 1.6: Figure reproduced from Brown et al. showing L_2 (dashed) and L_3 (solid) edges of Pt metal. The two edges are shifted in energy so that they line up, and the L_2 edge is multiplied by a factor of 2.22 to have the extended region overlap with L_3 . [18]

depends strongly on the oxidation state and is a direct probe of the number of empty states in the low-lying band with appropriate symmetry. For example, Fig. 1.6 shows that Pt exhibits a strong white line in the L_3 spectrum (solid) but not in the L_2 spectrum (dashed). This is because the only unoccupied d states in the Pt atom are $d_{5/2}$. Since L_3 probes the transition $p_{3/2} \rightarrow d_{5/2}$ whereas L_2 probes $p_{1/2} \rightarrow d_{5/2}, s_{1/2}$ according to the dipole selection rule, only L_3 Pt spectrum can exhibit white line feature [18].

As discussed in detail later in the EXAFS section, the fine structure oscillation in XAFS is caused by interference between outgoing and scattered incoming photoelectrons, and such interference exists in both the XANES and EXAFS regions. However, the physics underlying them differs slightly between these two regions. In the XANES region, the ejected photoelectrons have energies in the range of 10 to 40 eV. In this energy range, the probability for the photoelectron to excite a plasmon is relatively low. Excitation of a plasmon causes photoelectrons to lose coherence and hence do not show interference or fine structure. This means that low-energy photoelectrons can

undergo multiple scattering without losing coherence, whereas high-energy photoelectrons mostly only experience single scattering events before losing coherence. Due to multiple scattering paths among neighboring atoms across several shells, XANES is highly sensitive to stereochemical coordination, oxidation state, and electronic structure [19–22], and can serve as a strong fingerprint of nanostructure [23].

1.1.3 Extended X-ray Absorption Fine Structure (EXAFS)

As mentioned earlier, considerable effort was invested in accurately measuring XAS in the early 1900's. What we have not mentioned is that the theory development to describe the fine structure was also undergoing some dramatic changes and iterations. In the early stage of theory development in the 1920's, Kossel suggested that the near-edge fine structure is related to the transition of the ejected K-electron into the discrete optical levels of an atom [4]. Later in the 1930's, experimental improvements enabled measurements to extend to hundreds of eV beyond the main edge, and it was observed that metals with the same crystal structure exhibit similar fine-structure oscillations, suggesting that EXAFS is connected to long-range order in solids. Kronig proposed that the photoelectron is Bragg reflected by the crystal lattice [24]. He claimed that the forbidden photoelectron energy due to Bragg diffraction corresponds to the minimum observed in the EXAFS oscillation. His long-range order theory successfully describes several features in EXAFS, including (i) similar fine structure for similar crystal structures, (ii) r^{-2} dependence, and (iii) increasing separation between oscillation maxima with energy from the edge.

However, as Hanawalt pointed out [25], Kronig's long-range order theory fails for amorphous

materials, so Kronig also developed the short-range order theory [26] to accommodate that. Kronig's short-range order theory laid the foundation of modern EXAFS, and a breakthrough came with the development of the "EXAFS equation" by Lytle, Stern, and Sayers [27, 28]. The EXAFS equation provides a mathematical framework for modeling the effects of physical properties, such as interatomic distances, coordination numbers, and structural distortions, thereby making EXAFS a quantitative tool.

The EXAFS equation uses point-scatterer theory to describe the fine-structure oscillation, $\chi(E)$, in an XAFS spectrum. Mathematically, we can decompose an XAFS spectrum $\mu(E)$ as

$$\mu(E) = \mu_0(E)(1 + \chi(E)), \quad (1.8)$$

where $\mu_0(E)$ is the absorption coefficient of a free atom, with no effect from its neighboring atoms. Point-scatterer theory states that the oscillation $\chi(E)$ arises from interference between the outgoing and scattered photoelectrons due to neighboring atoms. One can imagine it to be an outgoing circular wave interfering with its own reflection, implying that taking the Fourier transform of $\chi(E)$ could give us information about the distance of the neighboring scatterer atoms.

The complete form of the EXAFS equation reads as follows, and the definition of each variable is listed below:

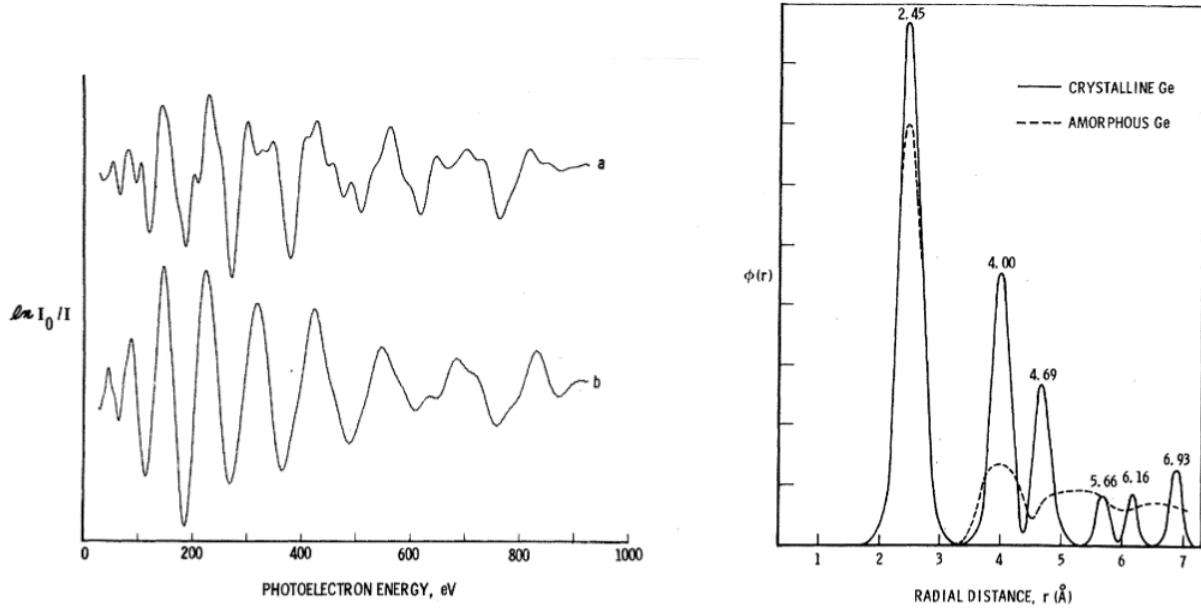
$$\chi(k) = -kf(k)\sum_j[N_j\frac{e^{-\gamma_j r_j}}{r_j^2}]e^{-\sigma_j^2 k^2/2}\sin(2kr_j + 2\eta(k)). \quad (1.9)$$

- $k = 2\pi/\lambda$: photoelectron wave vector

- $f(k)$: electron scattering factor (Fourier transform of the scattering potential)
- r_j : distance from the absorbing atom to the j th coordination shell
- N_j : number of atoms at r_j
- $e^{-\gamma r_j}$: photoelectron scattering range
- σ_j^2 : mean square displacement of atoms in j th shell
- $\eta(k)$: phase shift of the photoelectron caused by the absorbing atom potential

To intuitively understand Eq. 1.9, first note that the summation indicates that the contributions from each shell add like a classical wave interference calculation. The N_j/r_j^2 factor properly scales the reflection amplitude from each shell by the number of scatterers and takes into account the r^{-1} dependence of spherical waves. Two exponential terms describe damping, where $e^{-\gamma r_j}$ accounts for extrinsic losses (plasmon excitation) described earlier, with γ related to the electron mean free path, and $e^{-\sigma_j^2 k^2/2}$ is the Debye-Waller factor term measuring the structural disorder due to thermal and quantum vibrations. The sine factor at the end models the interference, and the factor $2r_j$ arises from the distance the scattered wave must travel to return to the absorbing atom. Multiplying this distance by k yields the phase shift accumulated during the travel. An additional phase shift arising from the electric potential is included in the $2\eta(k)$ term.

In Fig. 1.7, we show experimental results for χ and its Fourier transform. Both crystalline and amorphous forms of Ge EXAFS were measured, and the single atom background μ_0 was subtracted using post-measurement analysis, and the resulting EXAFS oscillation $\chi(E)$ is plotted in Fig. 1.7(a). By performing the Fourier transform on χ , we get the radial structure function $\phi(r)$ in Fig. 1.7(b), where the peaks relate to the interatomic distance with respect to the absorbing atom,



(a) Crystalline (top) and amorphous (bottom) Ge $\chi(E)$.

(b) Fourier transform of the data in (a).

Figure 1.7: Figures extracted from Sayers et al. [27]. Experimentally measured (a) EXAFS oscillation $\chi(E)$ and (b) $\phi(R)$ on crystalline and amorphous Ge samples.

but where phase-shift corrections are still needed. Notice that the crystalline sample shows defined, narrow peaks, whereas the amorphous sample has only the first distinct peak and a broadened feature beyond the first shell.

1.2 X-ray Emission Spectroscopy (XES)

As discussed in the previous section, XAS is a powerful tool to non-destructively study sample material, but the physics does not stop there. After X-ray absorption, the atom resides in an excited state with a core hole. The de-excitation can happen in two ways. The first decay channel is the Auger process, in which an electron from a higher energy level drops to fill the core hole, and a (separate) Auger electron is ejected to conserve energy. The second decay channel is X-ray

emission, in which a photon is emitted instead. In an emission process, the emitted photon has energy equal to the difference between the core-hole energy level and the higher energy level that participates in the transition. Unlike XAS, which maps the unoccupied states via absorption, X-ray Emission Spectroscopy (XES) provides information about the occupied states. It is a bulk-sensitive, photon-in, photon-out technique that provides a direct view of local orbital structures and chemical bonding and is used across various scientific fields. [29–39]

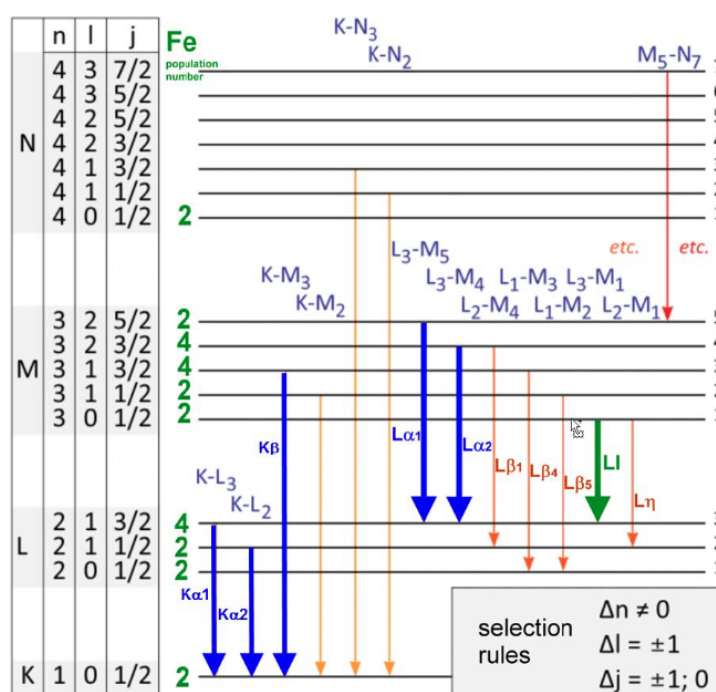


Figure 1.8: Figure reproduced from Andrade et al [40]. A variety of energy levels and selection rules for electron transitions in an atom.

Similar to the absorption spectrum, XES can be categorized into K, L, M, etc. series, depending on the final-state orbital of the emission transition. Fig. 1.8 shows the atomic energy levels and summarizes some transitions in the K, L, M, and N series. Notice there are two different notations presented in Fig. 1.8. The IUPAC notation marks the initial and final orbital of the transition ex-

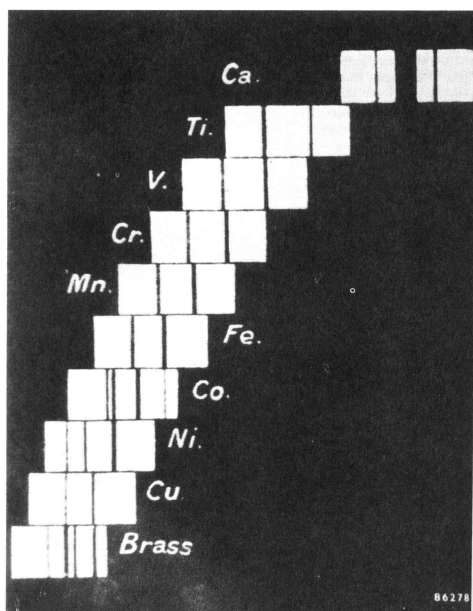


Figure 1.9: Photographic recording of $K\alpha$ and $K\beta$ emission lines for a range of elements collected by Moseley. [41]

plicitly (ex. $K - L_3$, $L_3 - M_4$, etc.), whereas the Siegbahn notation (ex. $K\alpha_1$, $K\alpha_2$) uses Greek letters to group transitions based on the higher transition orbital. In the rest of this section, we will use mainly the Siegbahn notation.

Another similarity between XES and XAS is that they are both element-specific techniques. This is first demonstrated by Moseley in 1913, when he found that the frequency of the emitted X-ray ν is dependent on atomic number Z through Moseley's law $\nu = A(Z - b)^2$, where A and b are constants depending on the type of emission line (K, L, etc). Fig. 1.9 shows a range of $K\alpha$ and $K\beta$ lines collected by Moseley on different transition metals ordered by their atomic number, where a clear dependence of emission energy and Z can be seen.

Although Fig. 1.8 only shows core-to-core transition, XES can also probe valence electrons through valence-to-core (VTC) transitions, which is extremely useful for investigating molecular bonding. However, emission intensity decreases drastically in outer-shell transitions, posing

significant experimental difficulty. For this exact reason, many XES experiments on core-to-core transitions center around the $K\alpha$ and $K\beta$ emission lines (the term "line" comes from the use of photographic plates in the early days). Hence, in this section, we focus on the physics underlying X-ray $K\alpha$, $K\beta$, and VTC spectra.

1.2.1 $K\alpha$ XES

The $K\alpha$ emission line originates from the transition between the L ($n = 2$) and K ($n = 1$) shells. The dipole selection rule in l restricts the transitions between these two shells to only $2p_{3/2} \rightarrow 1s_{1/2}$ and $2p_{1/2} \rightarrow 1s_{1/2}$, which are labeled $K\alpha_1$ and $K\alpha_2$ respectively. As mentioned previously, due to the strong overlap between the $1s$ and $2p$ wavefunctions, the transition intensity is strongest out of all emission lines.

As explained in the XAS section, changes in oxidation state alter the screening effect at the core levels, resulting in shifts in their energies. This causes the absorption edge to shift with the oxidation state. In the case of XES, since different orbitals are affected differently by outer electron screening, the energy level shift is not uniform. As a result, the energy difference between energy levels, which determines the emission energy, shifts with the oxidation state [29].

Other than oxidation state, $K\alpha$ lines are also highly sensitive to the local spin state (the number of unpaired electrons), particularly in transition metals and rare-earth elements. Using $3d$ metal as an example, the $2p$ core hole in the final state of the emission process interacts with the $3d$ electrons via $3d - 2p$ exchange interaction. This exchange coupling splits and distorts the energy levels (also called multiplet splitting), resulting in a broadened $K\alpha$ spectral shape. In high-spin

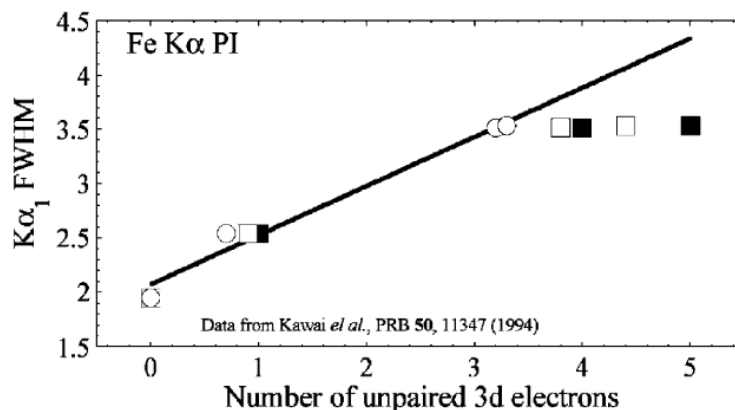


Figure 1.10: Reproduced from Kawai et al [42]. $K\alpha_1$ FWHM of various Fe compounds vs. number of unpaired 3d electrons. The number of unpaired electrons is derived in three ways: (i) filled square: nominal Fe oxidation state, (ii) open square: effective ground-state number of unpaired 3d electrons, (iii) circle: effective 1s excited-state number of unpaired 3d electrons.

states, the number of unpaired electrons is high, and their spins are aligned parallel. Under this configuration, the remaining core electrons experience a strong magnetic exchange coupling, and the multiplet splitting is therefore large, increasing the width of the $K\alpha$ peak. On the other hand, when under a low-spin state where the exchange coupling is minimized, $K\alpha$ will be relatively sharper. In Fig. 1.10, we show a collection of $K\alpha_1$ FWHM from various Fe compounds. The FWHM is plotted against the number of unpaired 3d electrons in these Fe compounds, and a near-linear dependence is observed.

1.2.2 $K\beta$ XES

Though $K\beta$ intensity is not as strong as the $K\alpha$ line, it is much more sensitive to oxidation and spin state. $K\beta$ emission line corresponds to the transition between the 3p and 1s level, and under spin orbit splitting, $K\beta$ line further divides into two groups of emission lines: $K\beta$ main lines and $K\beta$ satellite lines (see Fig. 1.11). The $K\beta$ main lines group consists of $K\beta_{1,3}$ and $K\beta'$,

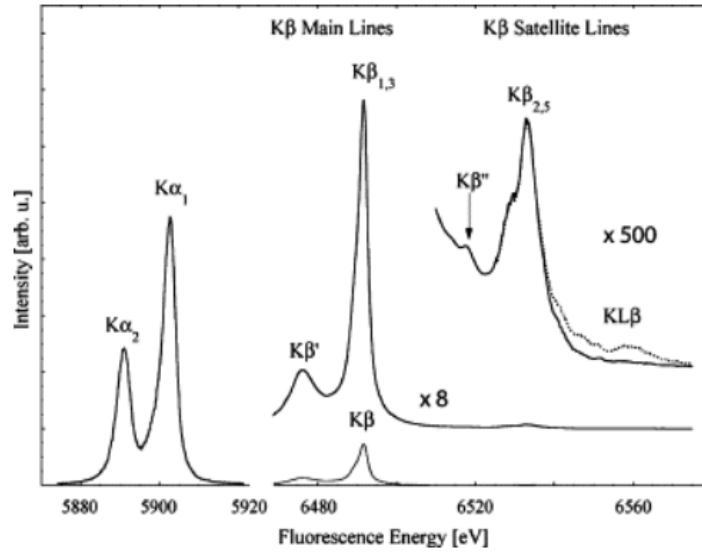


Figure 1.11: Reproduced from Glatzel and Bergmann [35], the K shell emission lines of MnO.

which correspond to the main $3p \rightarrow 1s$ transition and the splitting off due to exchange interaction. If one observes closely, one can see that the $K\beta_{1,3}$ is slightly asymmetric. This shoulder on the lower-energy side arises from a spin flip in the metal valence shell. This spin flip originates from many-body effects. When a $3p \rightarrow 1s$ transition occurs, a second electron in the $3d$ shell responds to the change in electron configuration by changing its spin orientation relative to the other valence electrons [43]. The satellite lines group includes $K\beta_{2,5}$, corresponding to the transition from the highest occupied valence orbital to $1s$, and $K\beta''$, often known as the "crossover peak", occurring when an electron is localized mostly on the ligand's innermost valence shell. Our discussion here will focus on the $K\beta$ main lines labeled in Fig. 1.11.

As discussed earlier in the section on $K\alpha$ features, exchange coupling causes splitting of the final-state core level and depends on the spin state. As valence spin decreases, the $3d-3p$ exchange interaction (if using $3d$ transition metal as an example again) becomes weaker. Consequently, the

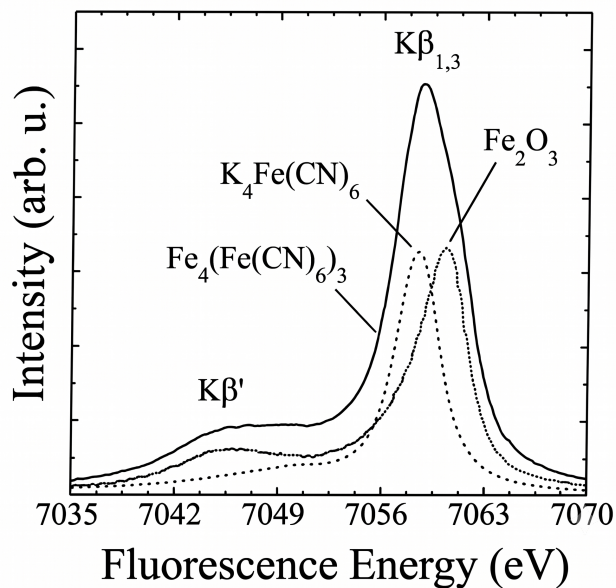


Figure 1.12: Reproduced from Glatzel et al. [44]. $K\beta$ spectra of Fe_2O_3 (dotted) and $\text{K}_4\text{Fe}(\text{CN})_6$ (dashed line). These two Fe compounds have spins $5/2$ and 0 , respectively, resulting in different $K\beta_{1,3}$ peak positions. $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ (solid line), on the other hand, has mixed spin and hence has an intermediate $K\beta_{1,3}$ peak location.

$K\beta'$ and $K\beta_{1,3}$ lines move towards each other with $K\beta'$ merging into $K\beta_{1,3}$ line at spin zero. Since the $K\beta$ line regards the $3p$ orbital, which is closer to the valence shell compared to the $2p$, as in the $K\alpha$, the effect of exchange coupling is much stronger, rendering the $K\beta$ a much more effective probe for spin states. Through similar reasoning, in more covalent compounds, unpaired electrons are sparsely distributed between the metal ion and the ligand, resulting in a reduced effect of exchange coupling. Moreover, the spin state is often correlated with the oxidation state; $K\beta_{1,3}$ can also contain oxidation-state information. In Figure 1.12, we show an example of three Fe compounds with different spins.

1.2.3 Valence-to-core XES

Valence-to-Core XES (VTC XES) probes the transitions of electrons from the highest occupied orbital into a deep core hole. Since the energy difference between these states is typically close to the binding energy, VTC peaks are often observed within a 100 eV range below the absorption edge energy. Because valence electrons are the ones directly participating in chemical bonding, VTC XES provides a direct map of the local ligand environment and electronic structure. In the discussion below, we will use transition metals as an example; however, the physics behind VTC XES generalizes to all species.

The $K\beta_{2,5}$ and $K\beta''$ peaks shown in Fig. 1.11 represent the K-edge VTC transitions in $3d$ transition metals. While a transition from the $3d$ valence level to the $1s$ core state is dipole-forbidden by selection rules, VTC intensity becomes observable due to metal-ligand orbital hybridization. When the metal ion bonds with ligands featuring valence p -orbitals, the $3d$ valence electrons acquire ligand or metal p -character, making the $3d \rightarrow 1s$ transition dipole-allowed. As a result, the VTC intensity is highly sensitive to metal-ligand covalency and localized bond lengths, providing a specialized structural probe that distinguishes it from other forms of XES. Orbital hybridization explains the physics behind the main VTC $K\beta_{2,5}$ peak, whereas the weaker $K\beta''$ line (or often called the cross-over peak) located at lower energy originates from ligand ns to metal $1s$ transition. The location of the $K\beta''$ line depends on the ligand's atomic s shell binding energy, hence can be used as a ligand identification tool [31–34].

To see these effects experimentally, we first show Mn VTC with three different ligands (Cl, Br, and I) in Fig. 1.13. An upward energy shift of $K\beta''$ is observed as moving down the halogen

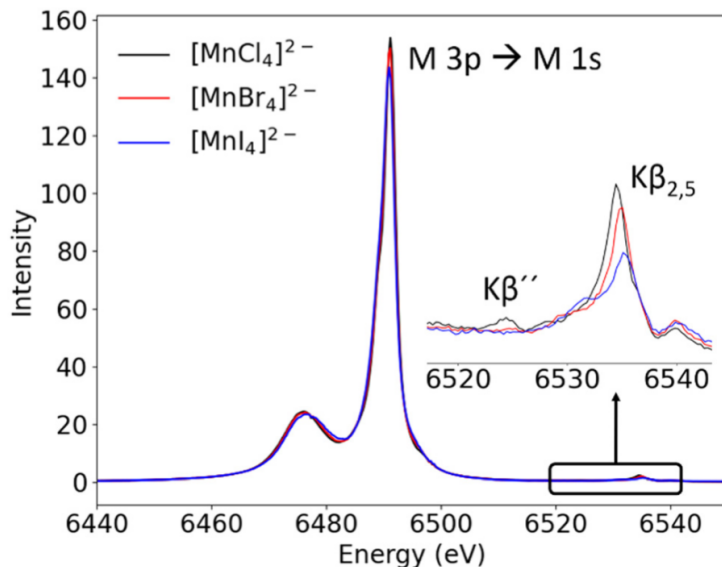


Figure 1.13: Reproduced from Roemelt et al [30]. Comparison of Mn VTC XES for Mn compounds with three different ligands from the halogen group. The shift in $K\beta''$ corresponds to different ligand s shell binding energy, and the intensity change in the $K\beta_{2,5}$ reflects the overlap of the wavefunction between metal d and ligand p orbitals.

group (from Cl to I). This is because the higher ns orbital is less tightly bound to the nucleus compared to the lower ns orbital, meaning that the energy difference between the ligand ns and metal $1s$ level is higher, which is reflected in the $K\beta''$ location. Also note that the $K\beta_{2,5}$ intensity decreases as one moves toward iodine, which indicates a smaller extent of pd mixing. Since a higher np orbital wavefunction, as in the iodine case, is spatially dispersed and highly diffused, the electron density is diluted over the overlapping region of the ligand np and metal valence orbital wavefunctions, meaning smaller pd mixing.

In Fig. 1.14, we show the dependence of VTC XES on the metal ion, where multiple transition metal VTCs with the same ligand are compared. As the transition metal atomic number (Z) increases from Mn to Cu, a decrease in the overall integrated VTC XES intensity is observed [30]. The physics dictating this attenuation can be traced to the effects of increasing nuclear charge on

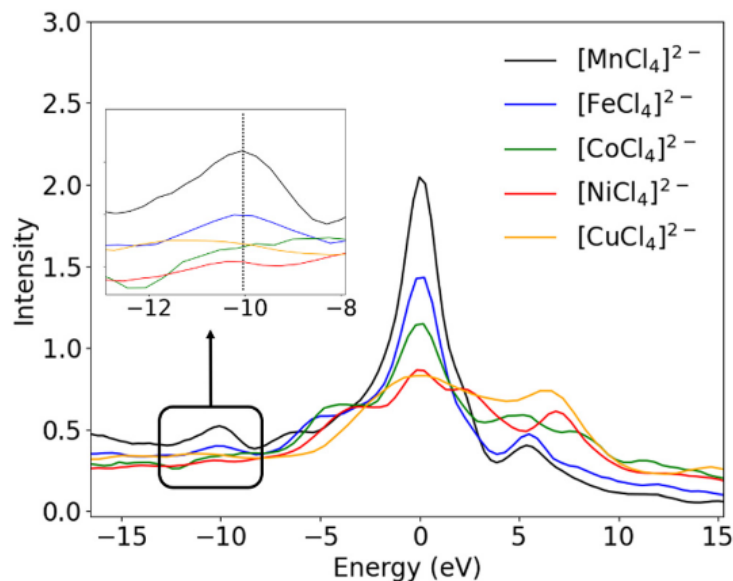


Figure 1.14: Reproduced from Roemelt et al [30]. Normalized VTC XES for different tetrachloride compounds with different $3d$ metals. All $K\beta_{2,5}$ maxima are aligned at 0 eV. The integrated VTC intensity decreases as the metal atomic number increases.

the spatial extent of the metal wavefunctions. As Z increases, the greater nuclear attraction causes a severe contraction and electrostatic stabilization of both the metal core and valence shells. Crucially, this contraction is most pronounced for the deep core metal $1s$ orbital, which shrinks much more tightly than the outer valence states. While the degree of metal p -character mixed into the ligand-dominated molecular orbitals remains robust, the severe spatial contraction of the core $1s$ wave function drastically diminishes the intrinsic metal $np \rightarrow 1s$ transition [30]. Since VTC intensity depends on this core-dependent transition probability, the systematic reduction of the intrinsic transition dipole moment across the series results in a drastically reduced oscillator strength, as clearly captured by the diminishing intensity toward Cu.

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Chapter 2

Background on Spectrometer and Asymmetric Operation

2.1 History of X-ray Spectrometer

Upon the discovery of X-rays by Wilhelm Conrad Röntgen in 1895 [1], scientists began to expand their experiments beyond utilizing optical and ultraviolet light, exploring the regime of very short wavelengths. The short wavelength of this newly discovered radiation enables studies of even finer microstructure than before, sparking a surge of scientific discovery. One of the most important findings in X-ray science was the discovery of Bragg's Law by William H. Bragg and Lawrence Bragg, who systematically studied the diffraction of X-rays by crystals (Fig. 2.1), which eventually led to winning the Nobel prize in physics in 1915 [2].

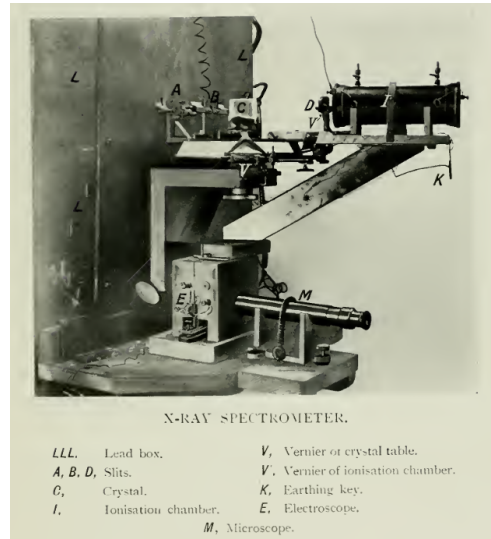


Figure 2.1: The original Bragg spectrometer. Taken from Bragg, W. H. and Bragg, W. L. X-rays and crystal structure. [2]

Astonishingly, this pivotal finding by Braggs can be explained by a simple but elegant equation written as

$$E(\theta_B) = E_0^{(h,k,l)} / \sin \theta_B, \quad (2.1)$$

where $E(\theta_B)$ is the diffracted photon energy by the specified crystal plane with Miller indices

(h, k, l) at the given Bragg angle θ_B , and $E_0^{(h,k,l)}$ is the Bragg diffracted photon energy at $\theta_B = 90 \text{ deg}$. In short, Bragg's Law describes how photons diffracted by a crystal are spatially dispersed across different angles according to their energy, effectively monochromatizing a white X-ray beam. This laid the foundation of modern X-ray spectrometers and X-ray science.

In 1913, the same year Braggs published their finding on X-ray diffraction by crystals, both J. Herweg [3] (first) and M. de Broglie [4] (slightly later) reported the discovery of a series of lines right above the absorption edges of heavy metals, which they claimed to be the absorption spectrum. Although the two experimental setups differed slightly, they both employed Bragg diffraction from crystals and recorded the absorption spectrum with photographic plates. The following year, 1914, Herweg and de Broglie separately published their spectra (Fig. 2.2) [5, 6], and their claim that the X-ray absorption spectrum had been detected and properly recorded was subject to peer review. Unfortunately, the scientific community later discredited both of them. Herweg's results were shown by G.E.M. Jauncey not to obey Moseley's Law, and de Broglie's results were determined to be the fluorescence lines from Ag and Br in the photographic plate emulsion, and further progress in the field was temporarily halted. Nonetheless, the use of Bragg's Law in X-ray spectrometers for monochromatization was well established at this time.

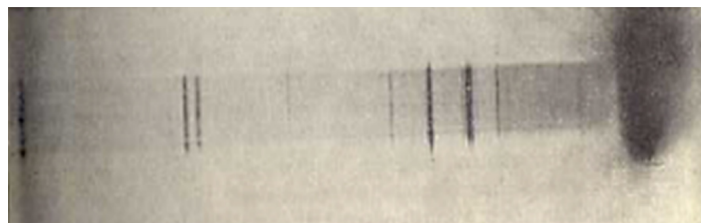


Figure 2.2: The platinum absorption spectrum published by de Broglie and Lindemann, in which the additional lines were later concluded to arise from the fluorescence emission of Ag and Br in the photographic plate emulsion. [6]

In the coming years, the need for more quantitative, finely resolved instrumentation for X-ray spectroscopy has greatly advanced the development of X-ray spectrometers. Some of the most immediate scientific impact of such development were the correction and structuring of the periodic table by Henry Moseley using the uniqueness of each element's X-ray fluorescence line [7, 8], and the first "true" observation of an X-ray absorption edge and fine structure [9, 10] enabled by Manne Siegbahn's work on intra-atomic transition [11]. The development of X-ray science and instrumentation is tightly bound by nature, and it was roughly at this stage that the principle of the Rowland circle emerged in the context of X-ray spectroscopy.

2.2 Rowland and Rowland Geometry

Henry A. Rowland (1848–1901), who served as the founding professor of physics at Johns Hopkins University and as the first president of the American Physical Society, is best remembered for his development of the curved optical gratings and the associated circular geometry named in his honor [12]. This work in the 1880's unlocked the full potential of the Rowland grating and achieved perfection in both engineering and fabrication aspects. In addition, he distributed his gratings, which were universally accepted as having the best performance in collection efficiency and resolving power, to other scientists at no charge. The accessibility of high-quality optics has facilitated advances in micro-scale science, and its impact is still evident in modern optical spectroscopies.

To understand how Rowland optics operate, one must first learn about the Rowland circle. Although the original invention by Rowland involved optical gratings, which differ slightly from

the case described below, they share the same idea. It starts with a simple geometric fact that given two common endpoints, all inscribed angles in a circle are equivalent (Fig. 2.3(a)). On top of that, in an orientation where the common endpoints are vertically symmetric, as shown in Fig. 2.3(a), the angle bisector of all inscribed angles converges at the bottom of the circle. Recall that Bragg's Law (Eq. 2.1) requires the incident and the diffracted angle to be equivalent. This means if we were to place a crystal at the tip of each inscribed angle, with its diffraction plane perpendicular to the angle bisector, rays emitted from one common end points (marked as "Source" in Fig. 2.3(b)) will be diffracted and converged at the other end point (marked as "Detector" in Fig. 2.3(b)) with the same Bragg angle. From Eq. 2.1, one can see that there is a one-to-one relationship between the Bragg angle and the energy of the diffracted ray. In other words, if moving the source and the detector symmetrically up and down along the Rowland circle, the spectrometer can control what energy of the diffracted ray that enters the detector (Fig. 2.3(c)). As discussed previously, Bragg diffraction has been widely used in monochromatizing X-ray beams. Rowland circle geometry provides additional point-to-point focusing, greatly enhanced collection efficiency, and energy resolution as mentioned above.

In the 1930s, Jesse DuMond used this idea to build the first Rowland Circle X-ray spectrometer with an array of flat crystals [13]. He used fifty flat calcite crystals, each individually mounted on separate 1/4-inch cylindrical holders, and aligned them precisely along a half-meter radius Rowland circle (Fig. 2.4). Although their approach was highly successful, they acknowledged that the handling and orientation of the crystals posed substantial challenges. Fortunately, this issue has been overcome in today's Rowland spectrometer by the advent of curved-crystal optics, which will

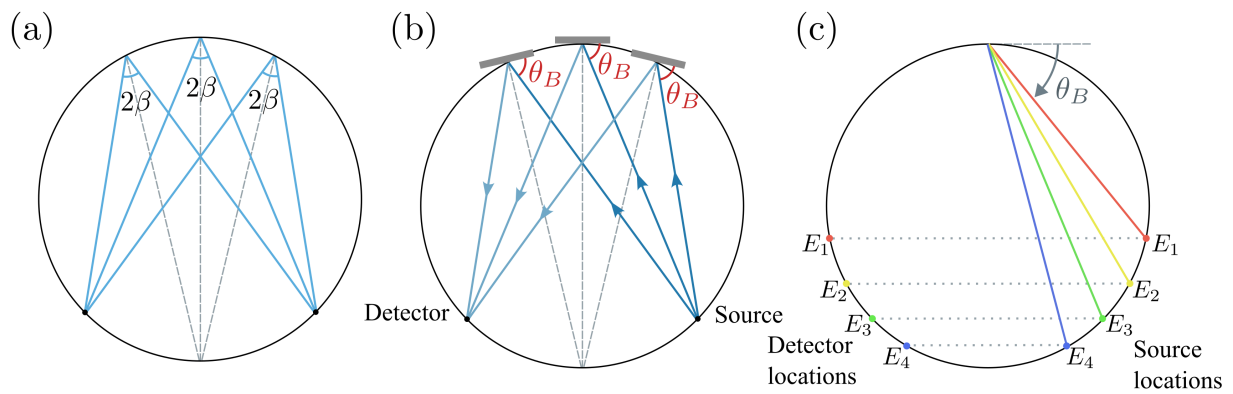


Figure 2.3: (a) The Rowland circle. Inscribed angles in a circle with common endpoints are all equivalent. The angle bisectors of the inscribed angle converge at the bottom of the circle. (b) If placing diffraction crystals at the tip of each inscribed angle, with the diffraction plane perpendicular to the angle bisector, Bragg's Law will be satisfied. Rays emitted from a common endpoint (Source) will be diffracted and converge at the other endpoint (Detector) at the same Bragg angle. (c) By moving the source and detector symmetrically along the Rowland circle, the spectrometer can control what energy of the diffracted ray enters the detector.

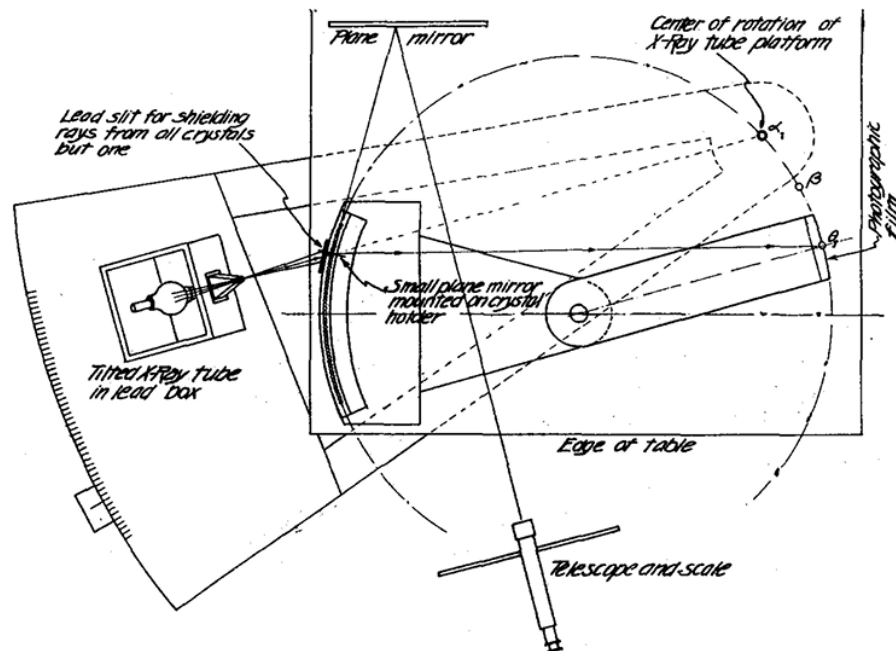


Figure 2.4: Sketch of the first Rowland Circle X-ray spectrometer by Jesse DuMond. Figure taken from his paper "The Multiple Crystal X-ray Spectrograph" (1930) [13].

be discussed in detail in the next section.

2.3 Bent Crystal Spectrometer: Johann and Johansson Optics

Recall from Fig. 2.3, for Rowland geometry to work, the reflection crystal plane normal vectors have to point towards the bottom center of the circle. Notice that if we bend a single piece of crystal so that its radius is twice that of the Rowland circle, and center it around the circle's bottom center point, this condition will always be satisfied. To position the crystal plane at the correct location on the Rowland circle, the inner curve of such a bent crystal is then ground to match the circle curvature as shown in Fig. 2.5(a). Such crystals are called Johansson crystal analyzers [14]. However, Johansson crystals are difficult and expensive to manufacture, mainly due to the extra grinding process. Because of this, the Johann crystal analyzer comes into favor. Johann crystals are simply bent, which greatly reduces manufacturing difficulty and cost but also introduces energy broadening known as the Johann error. As shown in Fig. 2.5(b), since the analyzer surface deviates from the curvature of the Rowland circle, the inscribed angles are no longer constant. This deviation is particularly exacerbated towards the edges of the analyzer. The deviation in Bragg angle means that the diffracted rays entering the detector are no longer monochromatic but span a range of energies. This energy broadening, the so-called Johann error, degrades spectral resolution and is particularly severe at lower Bragg angles.

In Fig. 2.6, we show ray tracing simulations to visualize Johann error. The circular image represents the surface of a Si(551) Johann analyzer with a 50 cm bent radius, oriented in a way so that the Rowland circle (or Rowland plane) lies horizontal and extends in and out of the page. The

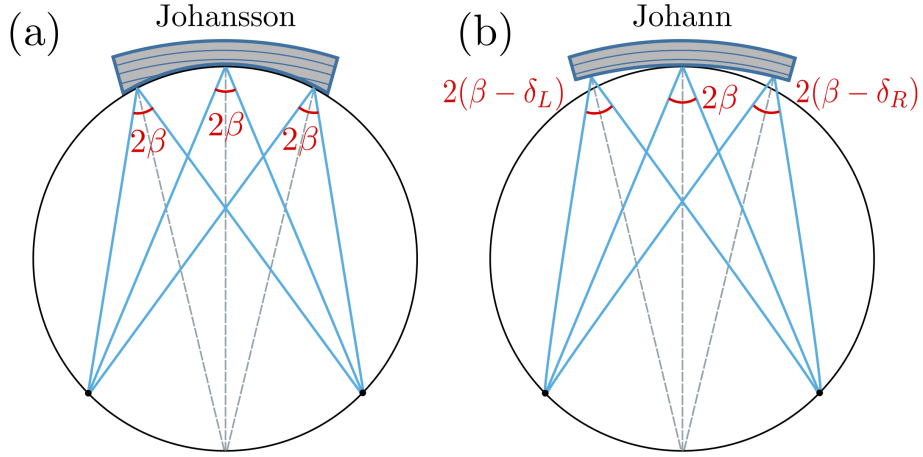


Figure 2.5: (a) Johansson crystal analyzer. The crystal is bent to a radius twice that of the Rowland circle, and the surface is ground to match the curvature of the circle. Bragg angle, $\theta_B = 90^\circ - \beta$, is constant across the crystal surface. (b) Johann crystal analyzer. The crystal is simply bent, causing a deviation in the Bragg angle toward the edges of the crystal, degrading energy resolution.

color corresponds to the energy deviation from the set Rowland circle energy. In Fig. 2.6(a), the Bragg angle is set to be 75° , and we see $|\Delta E|$ increases monotonically when approaching the edges of the analyzer. Also, notice that the energy deviation is always negative. In Fig. 2.6(b), the Bragg angle is now set to 60° , and as mentioned before, the energy deviation is much worse than that in the 75° case.

In this section, we introduced two types of bent-crystal analyzers, i.e., Johansson and Johann optics, and explained the cause of the Johann error. Although Johann error has long been recognized, Johann optics remains dominant in bent crystal spectrometers. There are two common ways to reduce Johann error. The first is to mask the edges of the analyzer, thereby rejecting rays with energy deviations from entering the detector. The other is to operate at a larger Rowland radius; the reduced angular size of the analyzer results in smaller $\delta_{R,L}$ as denoted in Fig. 2.5(b). Unfortunately, both solutions significantly reduce collection efficiency, and this is the condition we have

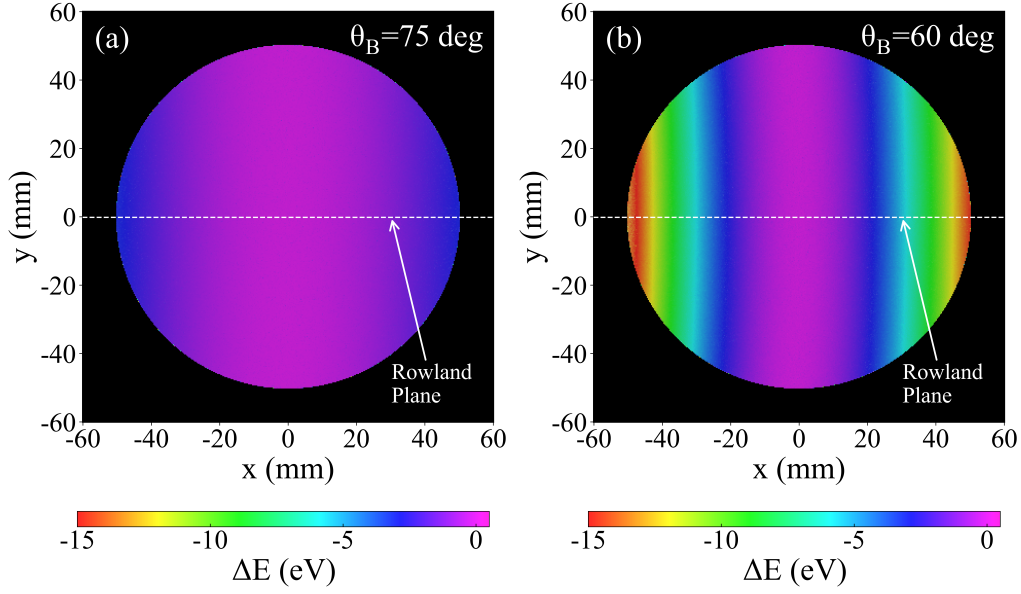


Figure 2.6: Ray tracing simulation showing Johann error on a spherically bent Si(551) crystal analyzer, with a bent radius of 50 cm. (a) When the Bragg angle is set to 75 deg, the edges of the analyzer diffract rays that are about 0.25 eV below the set spectrometer energy. (b) At a lower Bragg angle (65 deg), the effect of Johann error is much worse.

been contending with. In the later sections, we introduce a novel approach to mitigating Johann error. This methodology serves as a cornerstone of the dissertation.

2.4 Modern Examples of Rowland Spectrometer with Spherically Bent Crystal Analyzer (SBCA)

Thus far, we have introduced the operating principles of the Rowland circle and Johann optics, as well as the major obstacles to such instruments. What we have not mentioned is that Johann optics can be further categorized into cylindrically, spherically, and toroidally bent crystal analyzers. A cylindrical crystal analyzer is merely bent about an axis perpendicular to the Rowland plane, satisfying Rowland geometry in 1-dimension. On the other hand, a toroidally bent crystal

analyzer has a second bending axis that is in the Rowland circle, satisfying Rowland geometry on multiple Rowland circles that share the same source/detector position and θ_B . However, the most commonly used analyzer in hard X-ray science, and hence the focus of this thesis, is the spherically bent crystal analyzer (SBCA), in which the crystal surface is bent spherically about a single center point at a radius twice that of the Rowland circle.

The usage of SBCA with the Rowland geometry is diverse. This includes synchrotron X-ray light source endstations that perform X-ray Raman Scattering (XRS) [15–17], X-ray Emission Spectroscopy (XES) [18–20], and High Energy Resolution Fluorescence Detected (HERFD) [21–25]. These instruments provide a useful combination of a larger collection solid angle and fine energy resolution, and conduct important science across various fields, including, but not limited to, chemistry, biochemistry, condensed matter physics, materials science, geoscience, and environmental science [26–32]. On top of these synchrotron usages, SBCAs are also the most commonly used X-ray optics of laboratory-based X-ray Absorption Fine Structure (XAFS) and X-ray Emission Spectroscopy (XES) [33–40]. The emergence of such relatively inexpensive laboratory-based instruments offers greater accessibility to X-ray spectroscopy without compromising any data quality. Below, we provide a brief overview of some of these state-of-the-art Rowland Spectrometers with SBCA.

In Fig. 2.7, we show the X-ray Raman Spectrometer at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Raman spectroscopy takes advantage of the following fact: when the momentum transfer q is small in an inelastic scattering process, the double-differential scattering cross section is proportional to the X-ray absorption coefficient, meaning the absorption

spectrum can be obtained by monitoring the inelastically scattered photon [15]. This is particularly useful when studying low-Z material or weakly bound shells, since instead of dealing with high air absorption, one can obtain the absorption spectrum of such samples with penetrating hard X-rays. The ESRF Raman spectrometer has six cone-shaped analyzer-detector vacuum vessels, which can be moved to the desired momentum-transfer location for each experiment. In each analyzer-detector vacuum vessel, there is an array of 12 SBCA with a 1-meter bent radius at the base, whose foci coincide with the detector at the tip of the vessel. Note that four rows of analyzer represent four distinct Rowland Planes with common source and detector positions, and each column of analyzer sits at a slightly different Bragg angle. The sample is located outside the analyzer-detector vessel, typically very close to the vessel tip. This is because X-ray Raman Spectrometers commonly suffer from the Johann error, which requires operating at a near-90-degree Bragg angle and a large Rowland circle radius. As a result, these instruments are often immense in scale ($4\text{ m} \times 3.2\text{ m}$ for the ESRF spectrometer) and have low count rates due to a reduced collection solid angle.

Next, we show the HERFD spectrometer at the National Synchrotron Light Source II (NSLS-II), New York (Fig. 2.8). The high energy resolution provided by the Rowland geometry enables precise monitoring of photons from a specific emission line produced after absorption, which can then be used to infer the absorption spectrum without the effects of core-hole lifetime broadening. This is particularly useful when studying high-Z materials and deep core-level edges. Compared to the Raman spectrometer, the HERFD setup is relatively simple. There is no optical motion during a scan, as the spectrometer energy is fixed to a single X-ray emission channel throughout the experiment. The HERFD setup at NSLS-II features a five-analyzer array, with each analyzer

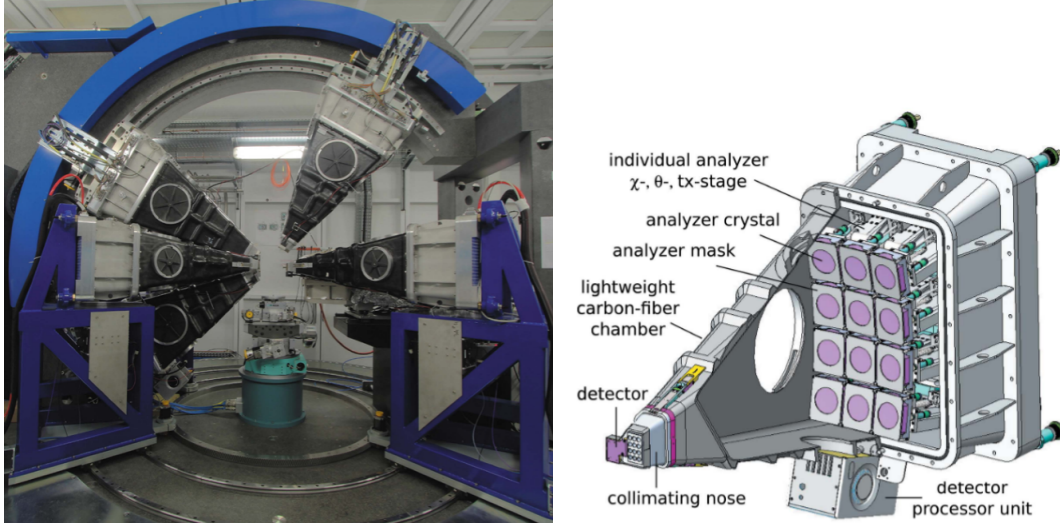


Figure 2.7: (Left) The X-ray Spectrometer at ESRF ID20. It features 6 sets of independently movable crystal chambers, each of which hosts a 12-crystal array. All SBCAS are on a 1 m Rowland circle. (Right) A schematic view of one of the twelve analyzer-detector vessels. [17]

on a separate vertical Rowland plane, but all sharing a common detector and sample positions. Though, depending on the chosen emission channel, typically count rates in a HERFD experiment are significantly better than those in a Raman scan. This is the reason why a much smaller number of SBCA is required.

Lastly, we show a laboratory-based Rowland geometry spectrometer at the University of Washington that is capable of doing both absorption and emission spectroscopy (Fig. 2.9) [41]. The physics behind these types of spectroscopy was covered in the previous chapter; hence, we focus here only on introducing the instrument. The CAD rendering in Fig. 2.9 is showing the XAS configuration. On the left side is a 100 W Pd-anode X-ray source mounted on a stationary platform. The SBCA and the detector are mounted on a goniometer that controls the Bragg angle. Furthermore, the goniometer and the detector are mounted on separate linear motorized stages to ensure that the source and detector are positioned on the Rowland circle. This instrument can also

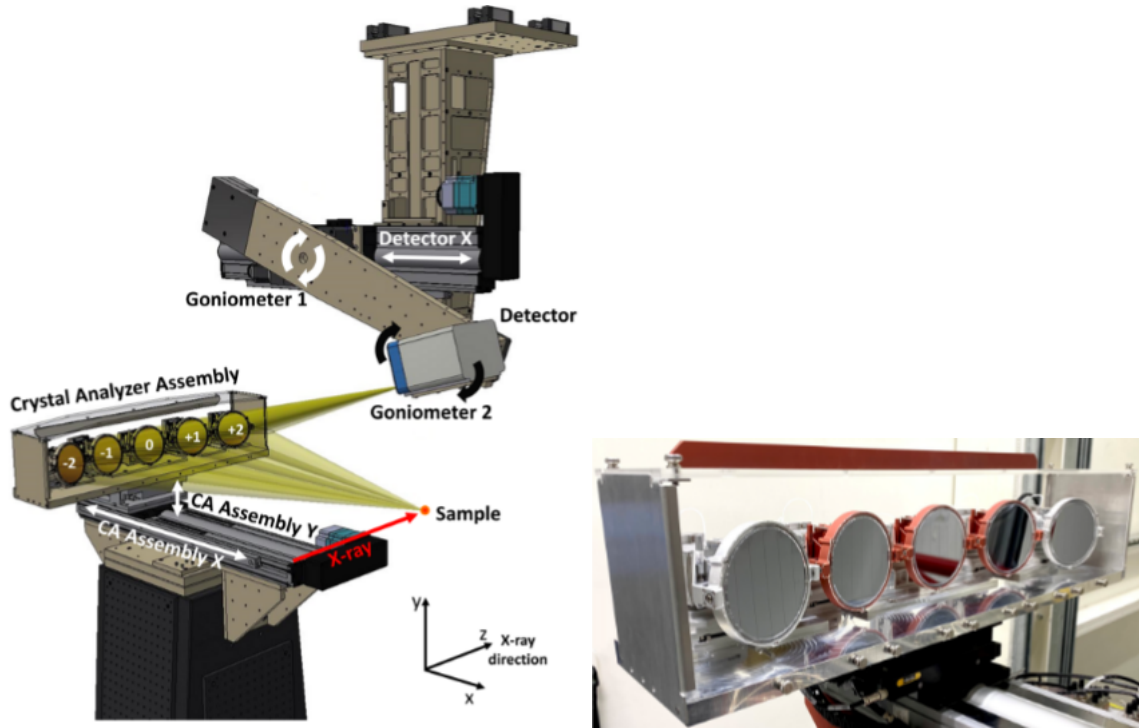


Figure 2.8: (Left) A schematic diagram showing the HERFD spectrometer at NSLS-II Inner Shell Spectroscopy beamline (8-ID). Though all components are stationary during a scan, the five-analyzer array and the detector are mounted on motorized stages to reach different emission channels. (Right) A photo showing the five-analyzer array. Such an array greatly increases the HERFD spectrometer’s count rate. [25]

be configured for XES, with a much more powerful source at 2 kW. This laboratory-based Rowland spectrometer is compact and enclosed in a stainless steel radiation enclosure of approximately $2\text{ m} \times 1.5\text{ m} \times 1\text{ m}$ (picture on the right in Fig. 2.9). One important point to note is that this spectrometer is the first dedicated asymmetric Rowland-geometry spectrometer. In the next section, we will discuss in detail the asymmetric operation of the Rowland circle.

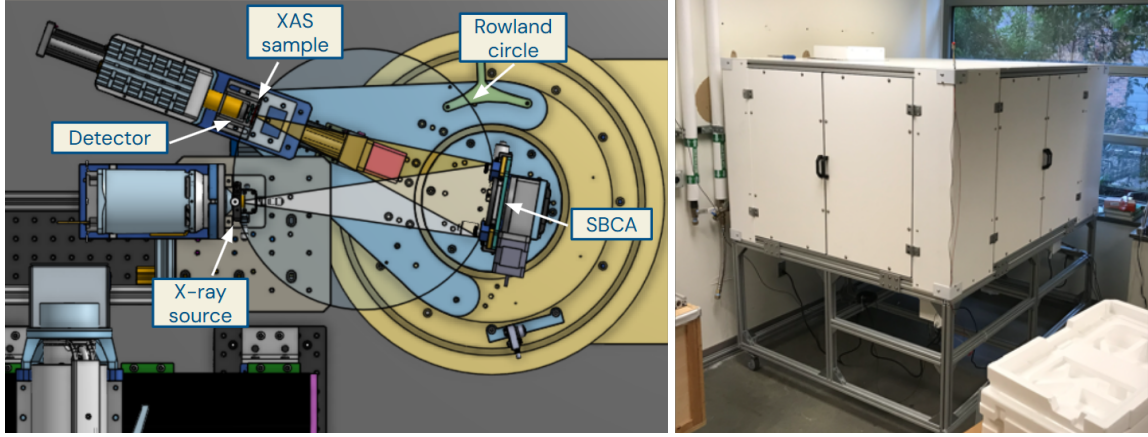


Figure 2.9: (Left) Top-view CAD rendering of the laboratory-based Rowland spectrometer configured for XAS. (Right) Radiation enclosure of the spectrometer.[41]

2.5 A Missed Opportunity: Asymmetric Operation

In this section, we propose a new way to operate SBCA in a Rowland circle. This method of operation comes with two key advantages. First, with strategic selection, one can effectively limit or even eliminate the Johann error described in section 2.3 without any masking. Second, we are no longer limited to the nominal crystal-plane cut for a given analyzer, allowing a single SBCA to span a wider energy range by choosing different reflection planes. We call this operating method the asymmetric operation.

The asymmetric operation exploits the fact that a given crystal structure can have multiple crystal planes, each denoted by its unique Miller indices. Fig. 2.10 shows an example of various crystal planes in a body-centered cubic (BCC) crystal structure. Commercial SBCAs are cut to a variety of planes to achieve different d-spacings, accommodating different energy ranges. Traditionally, SBCAs are used symmetrically, that is, Bragg diffraction is done using the plane that the crystal is cut to, as shown in Fig. 2.11(a). However, diffraction is not limited to this single plane;

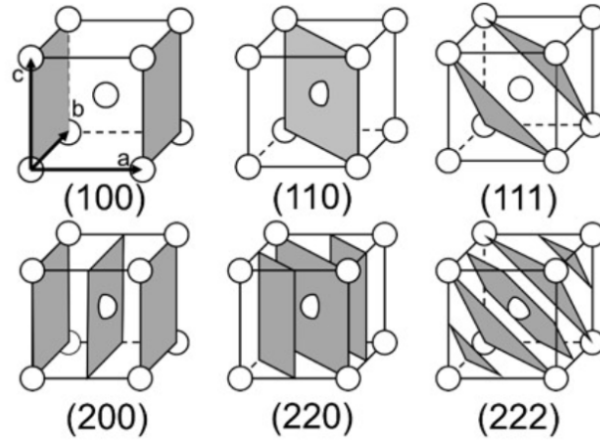


Figure 2.10: Example of various crystal planes of a BCC crystal structure, each denoted by a unique set of Miller indices.[42]

in fact, it can be done using any crystal plane inside that very same SBCA. In Fig. 2.11(b), we show how Bragg's Law is still satisfied through asymmetric diffraction.

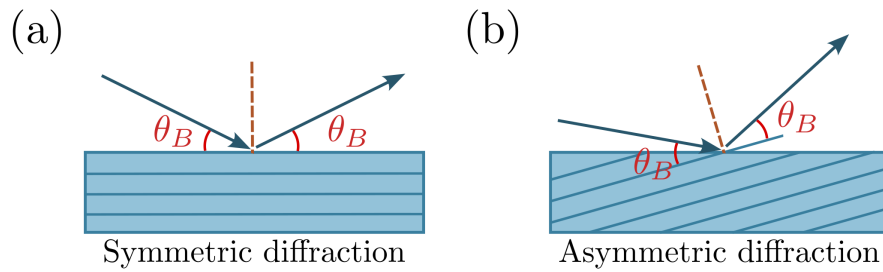


Figure 2.11: (a) Symmetric diffraction used traditionally by most SBCAs, where the diffraction plane is parallel to the surface of the crystal. (b) Bragg's Law can still be satisfied if using any other plane in the same crystal, diffracted asymmetrically.

To see how asymmetric diffraction can be used in a Rowland circle, first recall that under the symmetric case, the angle of incidence equals the angle of reflection ($i = r$) as shown in Fig. 2.12 (a). Note that all incident rays emanate from one point on the circle and all diffracted rays converge on another point on the circle. In Fig. 2.12 (b), we define α to be the angle between the symmetric diffraction plane (or the crystal cut plane) and the chosen asymmetric diffraction

plane (marked as red). With the source location unchanged, this constant angle offset α gives a new incident angle $i' = i - \alpha$. Tracing out the diffracted ray at an angle $r' = i'$, we see that all diffracted rays still converge at one (though different as before) point on the Rowland circle due to the equivalent inscribed angle theorem (Fig. 2.12 (c)). This shows SBCA is capable of doing asymmetric diffraction on a Rowland circle.

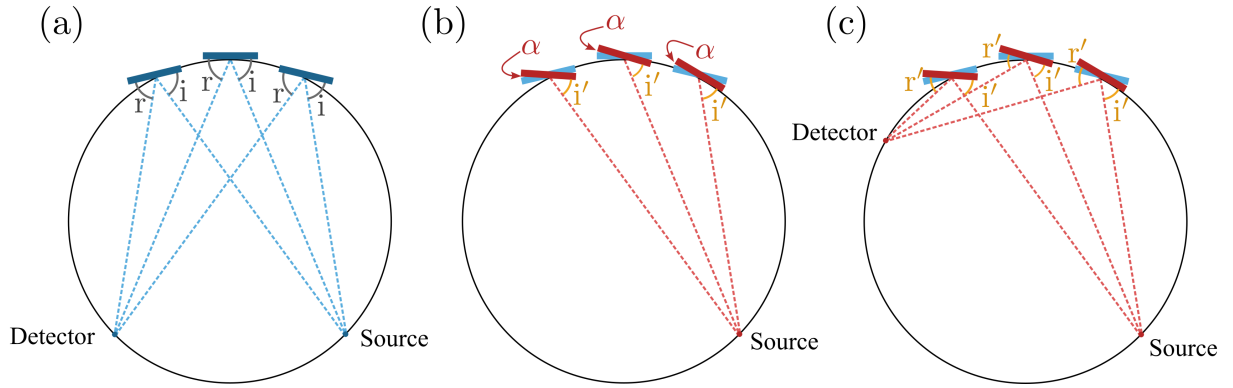


Figure 2.12: (a) Recall symmetric geometry where the diffraction plane is parallel to the crystal surface, and the incident angle is equal to the diffraction angle ($i = r$). (b) When using an asymmetric diffraction plane which makes an angle α with the crystal surface, with the source location unchanged, the new incident angle is $i' = i - \alpha$. (c) The diffracted rays are at an angle $r' = i'$ required by Bragg's Law, which must also converge at one point due to the equivalent inscribed angle theorem.

Next, we will show how asymmetric operation can effectively reduce Johann error. Before that, we first define some parameters, as shown in Fig. 2.13. We denote the SBCA surface plane, or the symmetric crystal plane, with normal vector G_0 . Similarly, an asymmetric diffraction plane with Miller indices hkl is defined by G_{hkl} . As mentioned above, α is the angle in the Rowland plane between these two planes, or equivalently, the angle between G_0 and G_{hkl} . θ_B still denotes the Bragg angle under asymmetric diffraction; the only difference in asymmetric operation is that we define a new angle $\theta_M = \theta_B + \alpha$ (M stands for mechanical), denoting the incident ray angle

with respect to the crystal surface.

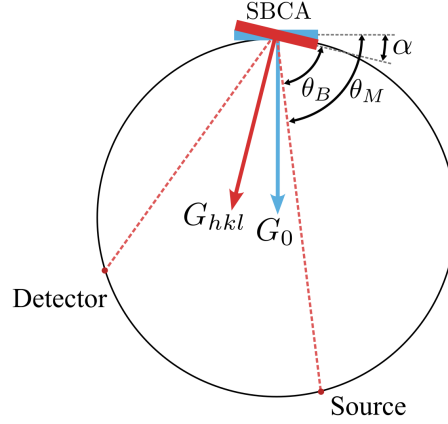


Figure 2.13: The symmetric diffraction plane is denoted by normal vector G_0 , and similarly G_{hkl} for the asymmetric one with Miller indices hkl . α is the angle between G_0 and G_{hkl} in the Rowland plane, and the incident angle with respect to the crystal surface is marked as $\theta_M = \theta_B + \alpha$.

In Fig. 2.14 we show one specific and important configuration in asymmetric operation, that is, when $\theta_M = \theta_B + \alpha = 90^\circ$. For a given θ_B , we define such α as α_J , i.e. $\alpha_J = 90^\circ - \theta_B$. We call this configuration the Johann Normal Alignment (JNA). On the right is an enlarged view of a crystal element on an SBCA. Note that since $\alpha_J = 90^\circ - \theta_B$ and the angle between $\vec{G}_0$ and $\vec{G}_{hkl}$ is α_J by definition, the incident X-ray impinges the crystal element in the direction of $\vec{G}_0$, that is, normal to the crystal surface. Since this is true for all crystal elements on the SBCA, θ_B is the same anywhere on the crystal surface, meaning Johann error does not exist under JNA configuration. It is also worth noting that this configuration happens when the X-ray source is right at the sphere center of the SBCA, as shown on the left side of Fig. 2.14.

In summary, asymmetric operation can utilize a large set of reflection planes within a single SBCA. This reduces the cost of needing multiple crystals and provides convenience when reaching a wider energy range by hopping between different hkl planes. Moreover, by strategically selecting

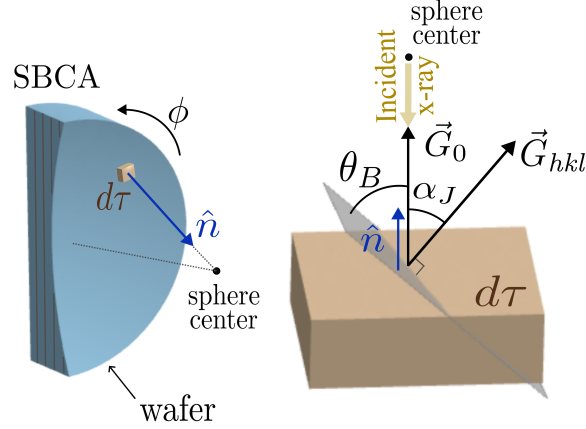


Figure 2.14: Graphical representation of the Johann normal alignment (JNA). The left figure shows a sectional view of the SBCA, and all crystal element ($d\tau$) normal vectors point towards the sphere center of the SBCA. The right figure shows one specific crystal element, where the incident X-ray is along the crystal normal and maintains a constant angle α_J with respect to $\vec{G}_{hkl}$.

planes that are close to $\theta_M = 90$ deg within the desired energy range, Johann error can be greatly suppressed. In the following chapters, we first show how asymmetric operation is performed on a laboratory spectrometer (Chapter 3), and then provide a broad survey of the instrument's performance through extensive ray-tracing simulations (Chapter 4). Lastly, in the remaining chapters, we shift our focus from spectrometer design and performance study to a new analytical method for processing mixed-phase XAS spectra.

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Chapter 3

Asymmetric Rowland Circle Geometries for Spherically Bent Crystal Analyzers in Laboratory and Synchrotron Applications

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3.1 Abstract

Spherically bent crystal analyzers (SBCAs) are the dominant high-resolution hard X-ray optic in the ongoing rebirth of laboratory-based X-ray absorption fine structure (XAFS) and X-ray emission spectroscopy (XES) as well as in synchrotron methods such as high energy resolution fluorescence detection (HERFD) and non-resonant X-ray Raman scattering (XRS). In the overwhelming majority of cases, SBCAs are implemented in a ‘symmetric’ configuration on the Rowland circle, wherein the diffracting crystal plane is nominally coincident with the analyzer surface. We report here comprehensive investigations of ‘asymmetric’ operation of SBCA on the Rowland circle, wherein the diffracting crystal plane is not coincident with the optical surface of the analyzer. First, we have developed a laboratory spectrometer for XAFS and XES that is specialized for asymmetric SBCA operation. We find several benefits, including the capacity to use a single SBCA over a very wide energy range via ‘hkl hopping’ and the frequent ability to eliminate Johann error, the most prevalent energy-broadening mechanism when using SBCA symmetrically on the Rowland circle. Second, we expand these ideas to synchrotron facilities with a demonstration study of HERFD and XRS where asymmetric operation also provided advantage. Our results suggest that large-array systems for HERFD augmented with an additional mechanical degree of

freedom could streamline user operation and also indicate benefits to XRS in the asymmetric configuration, where larger solid angle, larger sample-to-detector distance, and decreased Johann error can be achieved simultaneously.

3.2 Introduction

Spherically bent crystal analyzers (SBCAs), specifically those with Johann-type profiles [1], are hard X-ray optics that provide a useful combination of large collection solid angle and fine energy resolution. This has resulted in their extensive use in the ongoing rebirth of laboratory-based X-ray absorption fine structure (XAFS) and X-ray emission spectroscopy (XES) [2–10] in addition to their historical and continued use as workhorse optics for high-resolution photon-in photon-out X-ray spectroscopy at synchrotron facilities [11–18]. With infrequent but valuable exceptions [19–22], such applications have been in a ‘symmetric’ Rowland circle configuration wherein the diffracting plane is nominally coincident with the surface of the SBCA diffracting wafer.

Here, we propose that asymmetric operation of SBCA on the Rowland circle is an underutilized opportunity. The basic parameters for asymmetric Rowland circle operation are defined in Fig. 3.1. In the figure, note the asymmetry angle α , the need for a ‘mechanical’ analyzer angle θ_M , and the inequality of the chord lengths ρ and d when $\alpha \neq 0$. The usual theorem for equality of inscribed angles still holds when $\alpha \neq 0$ so that the optic still functions as a monochromator in the Rowland plane, barring Johann error which will be discussed in detail later. Out-of-plane astigmatism at large α can become considerable, but we find that is not a significant limitation on

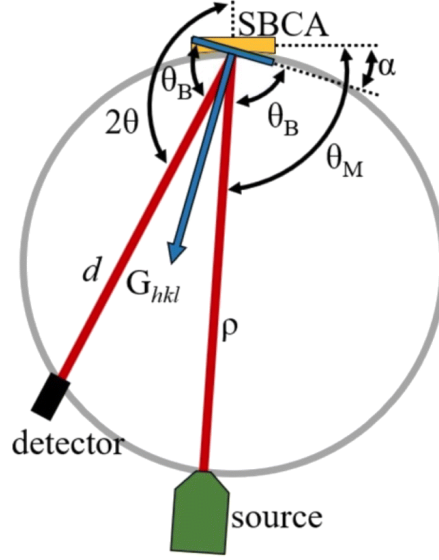


Figure 3.1: Diagram of spectrometer components during asymmetric operation in the reference frame of the SBCA. α denotes the angle between the diffracting plane for the reflection G_{hkl} and the plane at the optic's surface (nominally normal to the reciprocal lattice vector G_0). Note the chord lengths d and ρ differ when $\alpha \neq 0$.

energy resolution. It is not difficult to derive the dependence of the parameters in Fig. 3.1 on the Bragg angle, θ_B , and α , specifically.

$$\begin{aligned}
 \rho &= D \sin(\theta_B + \alpha) \\
 d &= D \sin(\theta_B - \alpha) \\
 2\theta &= 2\theta_B \\
 \theta_M &= \theta_B + \alpha
 \end{aligned} \tag{3.1}$$

where D is the diameter of the Rowland circle or equivalently the radius of curvature of the Johann SBCA.

With this background established, we address the potential advantages of asymmetric operation as a central principle in spectrometer design. We denote by G_0 the reciprocal lattice vector

normal to the wafer surface and assume the wafer miscut is small. Choosing G_0 is equivalent to choosing which wafer material and orientation to use in the optic, and it determines the useful energy range in symmetric operation – Bragg angles below 60 degrees generally suffer degraded energy resolution due to Johann error and source-size broadening. While analyzer harmonics sometimes enable high-resolution access to a few distinct energy ranges [23], both laboratory instruments and synchrotron facilities typically fabricate or acquire a suite of SBCAs having a variety of G_0 vectors.

Asymmetric operation modifies these considerations. Any single crystal has a multitude of additional crystal planes at various angles to the surface. Each allowed reflection capable of diffraction in an asymmetric configuration gives an additional useful energy range dependent on its own d-spacing. Hence, as a first advantage, we show that asymmetric operation of a single SBCA can permit high-resolution performance for photon energies from 5 keV through 10 keV and beyond with no gaps in the energy range. The good performance of many different reflections of various Miller indices (hkl) from a single analyzer is a major result of the present study, and we find it appropriate to introduce the term ‘ hkl hopping’ when a monochromator jumps between different Miller indices of a single SBCA to adjust energy range or to improve energy resolution, which we now address.

The second advantage of asymmetric operation is the minimization or even elimination of Johann error for SBCAs; prior work by Suortti and others for curved analyzers on the Rowland circle as well as asymmetric applications in other fields and other classes of optics motivates and supports this inquiry [21, 22, 24–35]. Briefly, Johann analyzers possess a radius of curvature

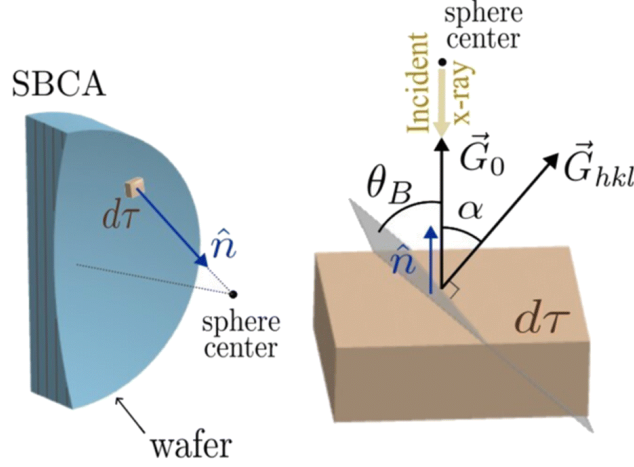


Figure 3.2: An infinitesimal single crystal element (right) of a spherically bent crystal analyzer (left), demonstrating a geometric argument for the elimination of Johann error in asymmetric Rowland geometries when the source is close to the sphere-center of the SBCA curved wafer.

for the diffracting wafer that is equal to the diameter of the desired Rowland circle. This yields the necessary surface orientations but results in small displacements between the wafer surface and the Rowland circle at the analyzer edges with corresponding errors in the Bragg angle upon moving away from the analyzer center. There is consequently a characteristic low energy tail in the analyzer's energy response function [12].

The underlying principle for suppression of Johann error via asymmetric operation is illustrated in Fig. 3.2. As shown, consider the special case where all incident X-rays have an incoming path exactly normal to each infinitesimal crystallite that makes up the SBCA surface, i.e., the special case where a point source is located at the sphere center of the curved analyzer wafer surface. The key observation is that for every point on the analyzer surface, the angle between an arbitrarily chosen reciprocal lattice vector $\vec{G}_{hkl}$ and the incident X-ray is the same everywhere on the surface. Hence, in this special case the Bragg angle is the same at every point on the surface and Johann error from the lack of coincidence between the edges of the analyzer and the Rowland circle is

eliminated. More generally, asymmetric operation allows operation with the source closer to the sphere center than is often possible symmetrically, and hence with decreased Johann error. We illustrate this later with XANES and XES measurements.

Finally, a third benefit comes from those special geometries that are expected to fully eliminate Johann error, as described by Fig. 3.2. Non-resonant X-ray Raman scattering (XRS), i.e., the non-resonant inelastic X-ray scattering from semicore levels, gives a hard X-ray analog to electron energy loss spectroscopy and allows X-ray spectroscopy on low-energy shells while using high-energy photons. This capability has seen sufficient demand that several dedicated facilities have been constructed at synchrotron facilities [11, 14, 36–38]. However, the extremely small cross-section for inelastic scattering from the semicore levels makes all XRS spectrometers subject to severe competition between the collection solid angle and the energy resolution. The best practice to date has been to use banks of 1 m curvature SBCA as close as possible to a backscatter geometry in symmetric Rowland operation, together with considerable diligence to reject background scatter [12, 14, 17, 18]. That being said, achieving highest energy resolution still requires analyzer masking to reduce Johann error; in some cases, small off-circle broadening is accepted as a compromise that aids with clearance between detector and the beam spot on the sample [13]. The more recently available 0.5 m curvature SBCA having four times the solid angle of the older optics have not been used for XRS because their larger angular size results in far larger Johann error in symmetric operation. On the other hand, the Johann-rejection strategy of Fig. 3.2 provides a possible path toward simultaneously attaining large solid angle, fine energy resolution, and large clearance between sample and detector. XRS measurements are performed in so-called inverse-scanning mode

where a single energy is chosen for the outgoing (analyzed) photon while the incident monochromator is scanned to create the necessary range of energy losses: the spectrometer must have low Johann error at only a single energy.

In this paper we address all three of these proposed benefits. We describe a new laboratory-based XAFS and XES hard X-ray spectrometer specifically designed to enable easy exploration of asymmetric Rowland geometries. With this instrument we demonstrate hkl hopping over a broad energy range and also demonstrate the minimization of Johann error through choice of the favorable special geometry with the source near the spherical center of the analyzer. These benefits also appear in our preliminary synchrotron studies, where we use asymmetric reflections to access the otherwise inconvenient $\text{Zn } K\alpha_1$ for high-energy resolution fluorescence detection (HERFD) X-ray absorption spectroscopy and also use an optimal asymmetric configuration for XRS via an 0.5 m radius SBCA. This ensemble of results across laboratory and synchrotron venues supports the hypothesis that asymmetric operation of SBCA has been underutilized and suggests directions for further inquiry.

3.3 Laboratory Spectrometer Design and Operation

We now present the six main spectrometer systems in order: the X-ray enclosure, X-ray sources, the detector and its subassembly, the optic, the motorization of the primary Rowland circle degrees of freedom, the additional motorized degree of freedom used to rotate many different desired reflections into the Rowland plane, and the overall control software.

The spectrometer is housed in a steel enclosure, approximately 1.8 m wide by 1.5 m deep by

1.3 m tall. The slightly oversized enclosure provides ample space for special sample environments in the future such as a cryostat or additional equipment such as a potentiostat for operando electrochemical measurements. The computer-aided design (CAD) rendering in Fig. 3.3 shows the design of the spectrometer and its key components in Rowland circle geometries configured for XAFS and XES measurements in Fig. 3.3(a) and (b), respectively. In XAFS mode (Fig. 3.3(a)), a 100 W X-ray source (Varex VF-80 Pd-anode tube) with variable width entrance slits to adjust apparent source size is placed on-circle via manual slide. In XES mode (Fig. 3.3(b)), a 3 kW X-ray source (Varex OEG-76H W-anode tube) with a preliminary 1 mm fixed-width entrance slit on the sample enclosure is placed on-circle via manual slide. A kinematic feature at the fixed source

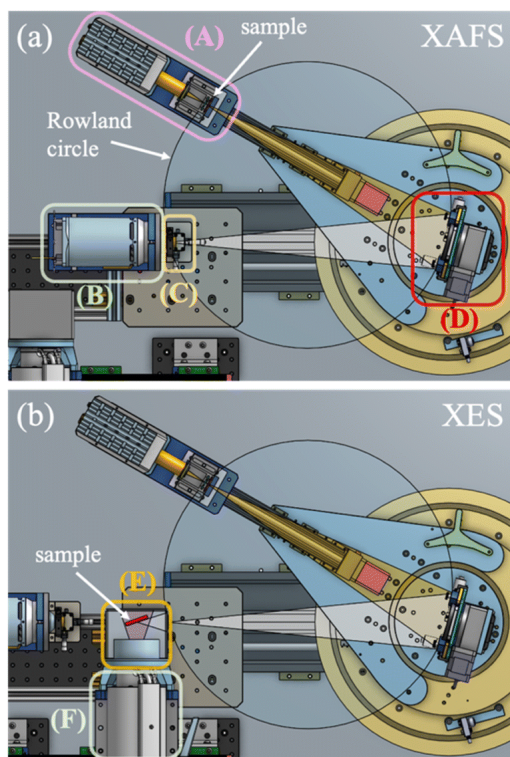


Figure 3.3: Top-view CAD renderings of the spectrometer configured for (a) XAFS and (b) XES measurements. The key components are outlined with boxes and labeled as follows: (A) detector, (B) 100 W XAFS source, (C) adjustable-width XAFS entrance slit, (D) crystal analyzer and optic tower, (E) XES sample enclosure and entrance slit, and (F) 3 kW XES source.

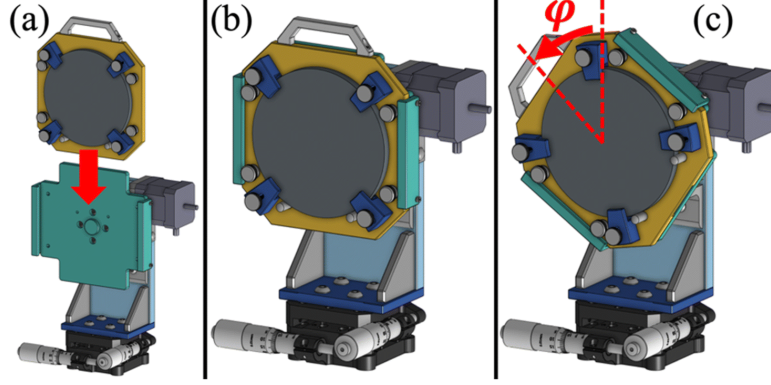


Figure 3.4: (a) An optic cartridge is loaded into the optic tower subassembly. (b) The fully assembled motorized optic tower concentrically indexes the crystal on a motorized rotation stage. (c) The motorized azimuthal (ϕ) degree of freedom allows for tilt-free correction of crystal miscut and for automated asymmetric operation.

location ensures precise placement of radiation entrance slits on circle. A 100 W X-ray tube with a tungsten anode, but otherwise identical to the XAFS-mode source, was used for commissioning in XES measurements (not shown in the figure).

The detector is a silicon drift detector (SDD) with 150 mm² area sensing element (KETEK AXAS M-1) mounted on a motorized linear stage (Velmex XSlide) to adjust the detector-analyzer chord length. The optics are 0.5 m radius of curvature SBCAs (XRS Tech). The chord lengths and angular positioning of the detector and optic are motorized. The optic and detector subassemblies are concentrically mounted on the θ and 2θ rotation stages, respectively, of a repurposed goniometer from a commercial X-ray diffraction instrument (Bruker D8 Advance). The θ and 2θ stages of the goniometer are independent, allowing for the α offsets required in asymmetric operation. The entire goniometer-detector-optic subassembly is mounted on a motorized linear stage (Velmex tandem BiSlide) to adjust source-analyzer chord length, ρ .

For automated asymmetric operation, an additional motorized degree of freedom we refer to

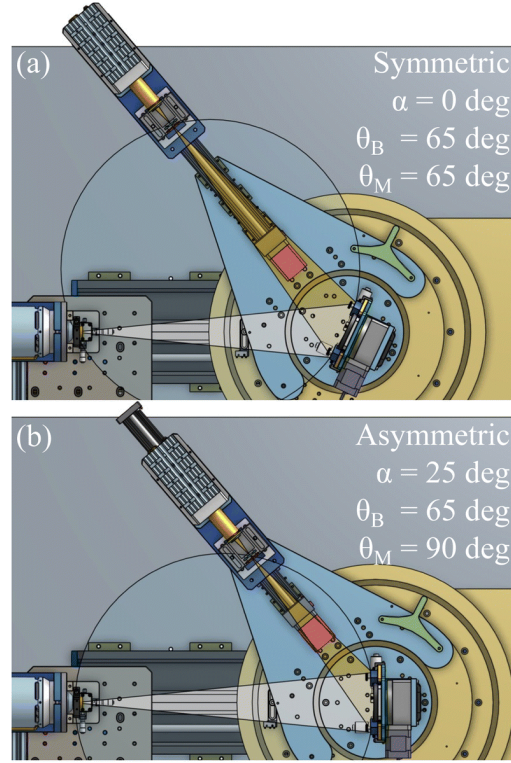


Figure 3.5: (a) Symmetric spectrometer operation at $\theta_B = 65$ deg in XAFS mode. (b) Asymmetric spectrometer operation at the same θ_B with $\alpha = 25$ deg, placing the source diametrically from the optic resulting in a monochromatic diffracted beam with no Johann broadening.

as the ‘clock angle’ or ϕ is required in the optic subassembly. This additional degree of freedom also enables motorized tilt-free correction of crystal miscut [39]. CAD renderings of the optic cartridge, the full optic tower assembly, and the ϕ rotation stage and direction are shown in the three panels of Fig. 3.4. The cartridge mounts concentrically on a small, motorized rotation stage (Velmex B5990TS). The fine adjustment x–y stage at the base of the optic tower aligned the optic on the rotation axis of the goniometer during spectrometer commissioning.

Recalling from the introduction the requirements for asymmetric Rowland configurations, the spectrometer achieves these geometries by using independent rotation and linear stages. Representative symmetric and asymmetric configurations are shown in CAD renderings in Fig. 3.5. Specif-

ically, Fig. 3.5(a) shows a typical symmetric operation at an unfavorable θ_B far from backscatter, whereas Fig. 3.5(b) shows an asymmetric configuration at the same θ_B but satisfying the condition of $\theta_B + \alpha = 90$ deg, the configuration that is expected to eliminate Johann error, recall Fig. 3.2. It is important to note Fig. 3.5(a) and (b) could be at radically different energies because of the different d -spacings for G_0 and G_{hkl} . The purpose of the figure is to demonstrate the difference in geometries in these different diffracting conditions. Note that the chord lengths between source-and-analyzer and analyzer-and-detector become unequal when $\alpha \neq 0$.

The spectrometer control software consists of two main components. First, a library of routines was written in Python (Jupyter) to generate ASCII files with component-by-component instructions for each step in any desired spectrometer scan. Second, LabView software was written to interpret the scan definition files and execute the desired measurements by commanding the motors and reading the detector. The LabView software can define measurement projects that perform sequences of measurements each parametrized by a different scan definition file including for successive scans using different G_{hkl} . For both XAFS and XES, the energy is scanned by stepping the crystal angle θ_M and satisfying the Rowland circle geometry at a particular Bragg angle by driving the ρ , detector, and 2θ stages.

3.4 Methods

Ray tracing simulations are generated using the xrt Python package [40]. The ray tracing calculations use a $250\ \mu\text{m}$ by $250\ \mu\text{m}$ area source and a 100 mm diameter, 0.5 m SBGA in both symmetric and asymmetric Rowland circle configurations, thus approximating the experimental con-

ditions. Calculations for the location of asymmetric reflections and their resulting energy ranges were performed in home-written software in Python (Jupyter).

XES and XAFS measurements were taken with the laboratory-based instrument described in Section 3.3 using only a 100 W source in both configurations. Studies were selected to demonstrate instrument capabilities to characterize the advantages of asymmetric operation. For XAFS, standard metal reference foils of Cu and Ni (EXAFS Materials) were used. To demonstrate the extended energy range afforded by asymmetric operation, a multi-component transition metal oxide sample was prepared for XES. Equal masses of V_2O_3 , MnO, FeO, NiO, CuO, ZnO, and $SrTiO_3$ were dry milled together to homogeneously mix the sample. The multi-component powder was enclosed in a polyimide pouch for XES study.

XRS and HERFD-XANES measurements were performed at sector 25-ID of the Advanced Photon Source. This used a Si(111) double crystal monochromator and a set of Kirkpatrick–Baez mirrors to achieve an approximately $100\ \mu\text{m}$ by $100\ \mu\text{m}$ spot size on the sample. The monochromator was not detuned, and the resulting expected energy resolution is 1.2–1.3 eV at 8700 eV. An Eiger S 500K camera (Dectris Corp.) was used to measure the X-rays analyzed by the SBCA (XRS Tech) and an SDD (Hitachi, Vortex) was used to measure total fluorescence yield in the HERFD study. The HERFD sample was a ZnO film with embedded Ge nanocrystals, prepared by sequential sputtering of ZnO and Ge targets under reactive ZnO growth conditions [41]. The XRS sample was an 0.9 mm diameter cylinder of randomly oriented graphite in a low-Z binder (mechanical pencil lead). For both studies the incident flux was $\sim 3 \times 10^{12}$ ph per s.

3.5 Results and Discussion

3.5.1 The Asymmetric Rowland Geometry in the Laboratory

We begin by illustrating a central motivation of asymmetric operation, i.e., the large number of crystal planes that are available and the consequently wide energy range that can be accessed with fine energy resolution for a single SBCA. See Fig. 3.6. In panel (a) we show the calculated locations for a large number of asymmetric reflections for a Si(551) analyzer in terms of the asymmetry angle α (radial direction in the polar plot) and the clock angle ϕ (azimuthal direction in the polar plot). Note that the $G_0 = (551)$ reflection itself is at the center of the polar plot. In panel (b) we show an experimental survey of the (α, ϕ) space at $\theta_B = 82^\circ$ and find excellent agreement with the calculations of panel (a). In addition, as shown by the color scale indicating the dominant energy detected at a given location, we observe that a very large energy range can likely be patched together by hkl-hopping between different asymmetric configurations. This type of study is readily performed in the laboratory because of the very broad bremsstrahlung spectrum of X-ray tubes. Panels (c) and (d) show analogous calculations and experimental results for a Si(221) analyzer. Miller indices in panels (b) and (d) were identified by consistency between the theoretical (α, ϕ) polar plot with all allowed reflections and the results of converting the observed energy of an experimental reflection to the sum of squared indices by Bragg's law.

In both Fig. 3.6(b) and (d) an azimuthal smearing is seen in the experimental results at large values of α near the borders of the pole plots. When at large asymmetries the chord length d from the SBCA to the detector becomes much smaller than the vertical radius of curvature of the analyzer, resulting in a significant vertical (perpendicular to the Rowland plane) extension and en-

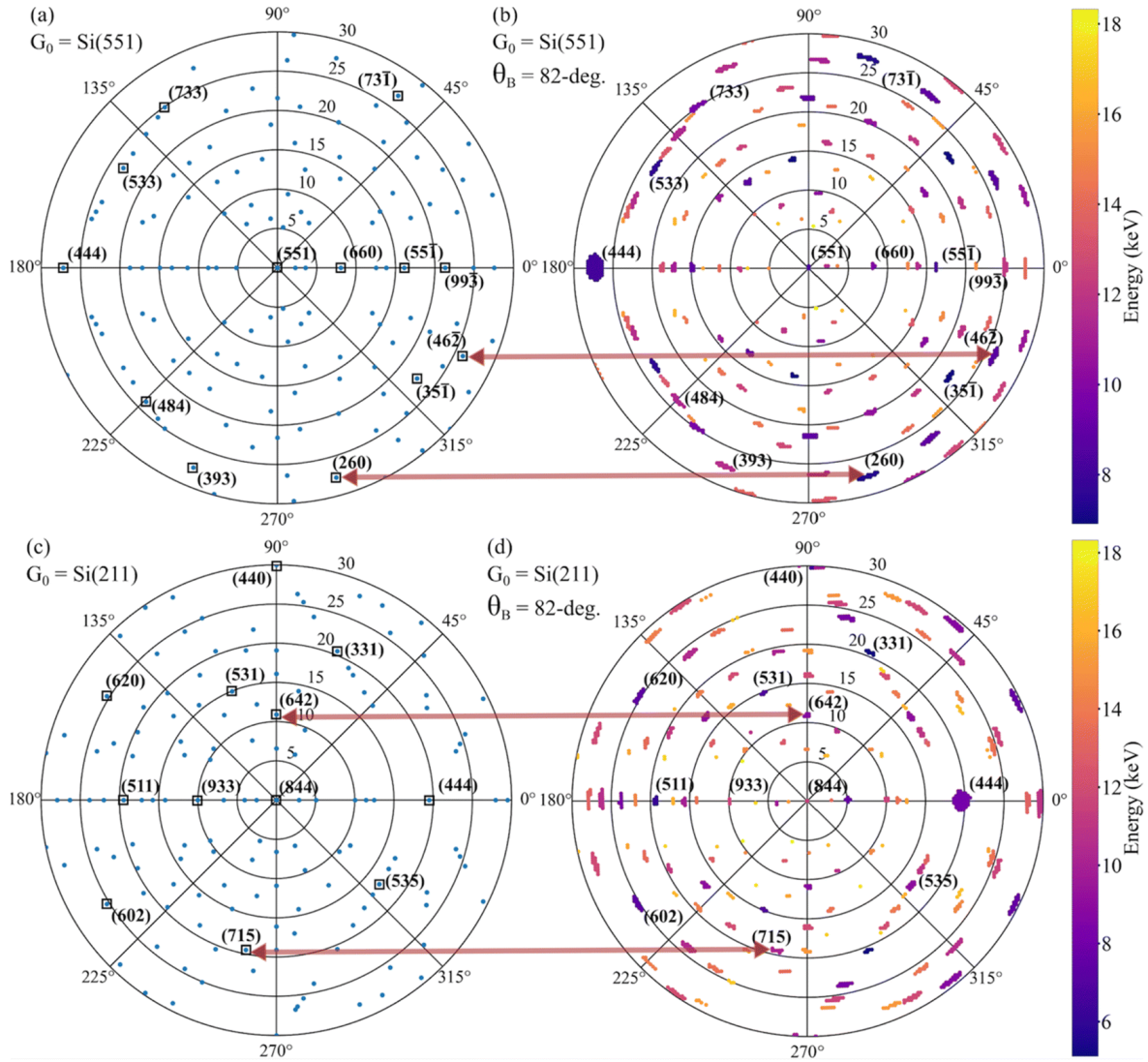


Figure 3.6: Polar plots in (α, ϕ) for calculated and measured reflections. (a) Calculated values of selected asymmetric reflections of a Si(551) analyzer. (b) Experimental data for Si(551) SBCA obtained by sampling phi-alpha space values at a fixed Bragg angle. (c) Calculated values of asymmetric Si(211) reflections. (d) Experimental data for Si(211) SBCAs. A threshold on reflection intensity was implemented to remove background in experimental data.

largement of the sagittal defocusing of the analyzed X-rays. The loss of intensity that occurs when the analyzed beam height is larger than the active diameter of the spectrometer's SDD is a confounding factor that leads to a trade-off between analyzed flux and the experimental convenience of asymmetric operation.

In Fig. 3.7 we compare the energy ranges of a conventional suite of SBCA operating symmetrically and the accessible diffraction planes of a single SBCA operated asymmetrically. This is investigated for the energy range of absorption edges and emission lines of the 3d transition metals. A comprehensive energy range is possible with a single analyzer operating asymmetrically and a suitable reflection is nearly always available that is close to the special condition (with the source moderately close to the analyzer spherical center) for a given emission or absorption edge. Hence, both a large energy range and high energy resolution should be expected with the Si(551) analyzer studied in the right panel of Fig. 3.7. We emphasize that there are complicated trade-offs between energy range coverage and analyzed flux (due to the vertical extent of the analyzed beam, described above), and we do not claim that Si(551) is necessarily optimal, although it does illustrate a favorable case for the argument being made here.

We next access a series of planes of the Si(551) SBCA on the amalgam XES, see Fig. 3.8. We measure $K\alpha$, $K\beta$, and valence-to-core (VTC) emission en masse with a single analyzer, demonstrating an expanded energy range through hkl hopping. The optimal reflections for the study are given in the left-hand side of Table 3.1; the experimental reflections used differ modestly in some cases. Fifteen emission lines spanning ~ 5 keV to ~ 14 keV were collected across seven elemental species using nine unique diffraction planes from the Si(551) analyzer. By comparison, under sym-

metric operation at useful Bragg angles the Si(551) crystal has an energy range of only $\sim 8.2\text{--}9.3$ keV and the same emission measurements would require a considerable number of separate Si optics, even if somewhat inferior Bragg angles were employed.

Having established the comprehensive advantage of a greatly increased energy range, we now address the proposed second benefit of asymmetric operation: an enhanced energy resolution compared to symmetric cases through elimination of Johann error when $\theta_B + \alpha = \theta_M$ is approximately 90 deg. Ray tracing simulations in Fig. 3.9 show the reduction of Johann error when approaching this special condition. Fig. 3.9(a) shows an equatorial full-range broadening of ~ 9 eV at the analyzer edge of an SBCA at $\theta_B = 65$ deg. Fig. 3.9(b), at the same photon energy, shows less than

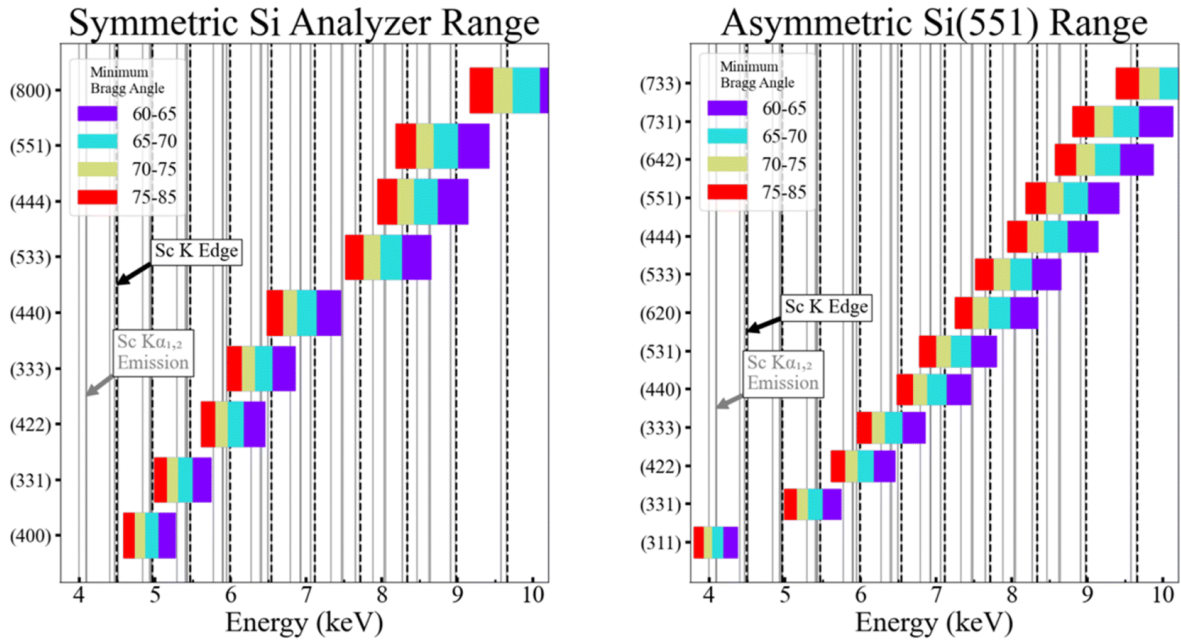


Figure 3.7: (Left) Diagram of the energy range achievable operating symmetrically with the Si SBCAs commonly used for transition metal XAS and XES: $G_0 = (100)$, (110) , (111) , (211) , (331) , (533) , (551) . The vertical gray lines indicate emission lines and the vertical black dashed lines indicate K-edges between 4 and 10 keV. (Right) Diagram of the energy range achievable operating asymmetrically with a Si(551) SBCA. Duplicate reflections, those that cover the exact same energy range at the same Bragg angle are omitted for clarity.

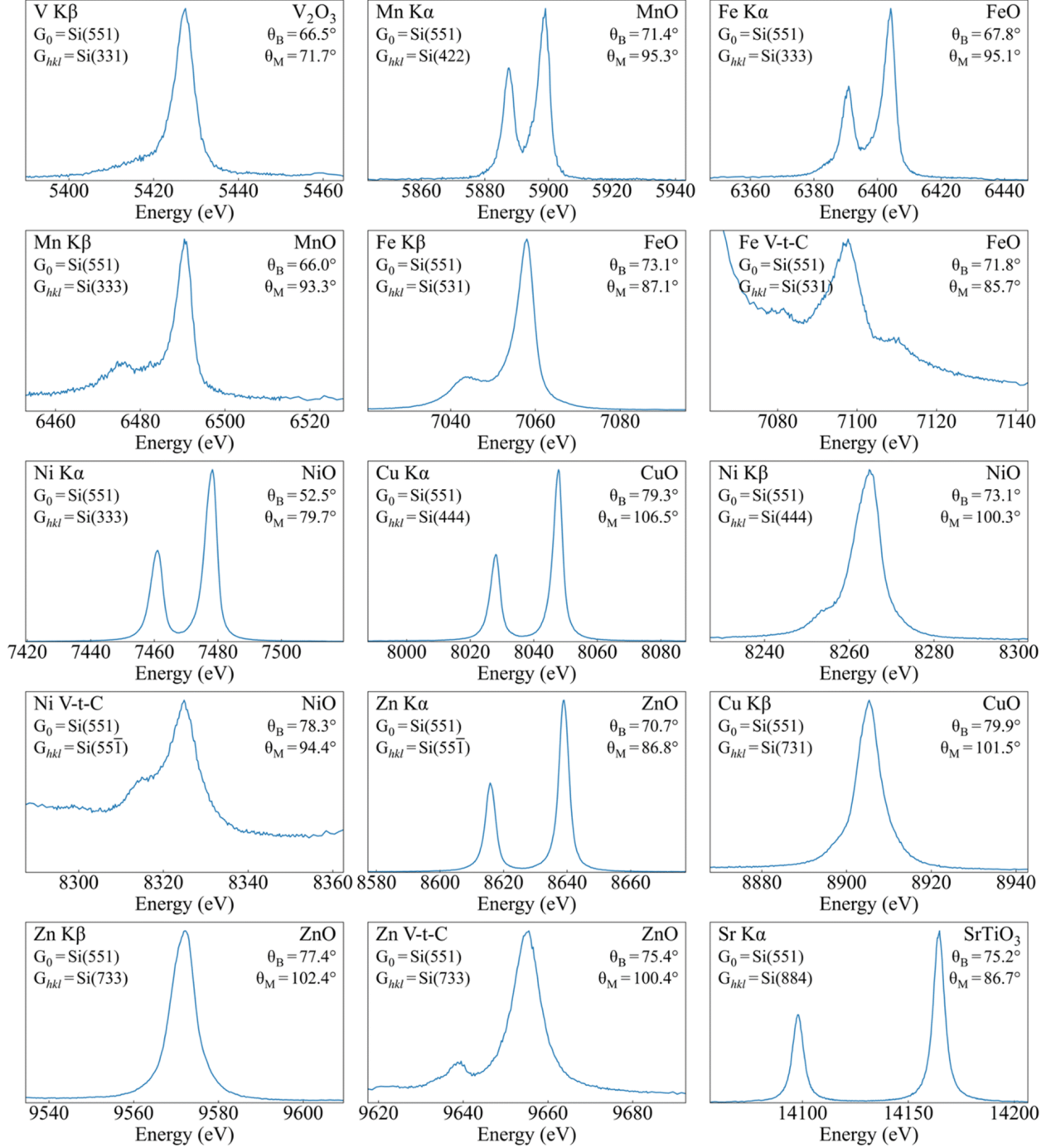


Figure 3.8: Emission lines measured asymmetrically with a Si(551) analyzer, arranged in order of ascending energy, presented with no background subtraction. The Bragg angle required to select the nominal energy of the emission line is given for each scan.

Table 3.1: Optimal asymmetric reflections for $G_0 = \text{Si}(551)$ and best symmetric counterparts for 3d transition metal XES, where both Si and Ge analyzers are considered for the symmetric case. For each emission line, the configuration expected to have the least Johann error is given in bold.

Emission	Energy (eV)	G_{hkl}	θ_B	α	θ_M	Best Si symm. analyzer	θ_B	Best Ge symm. analyzer	θ_B
V $K\beta$	5428	(33 $\bar{1}$)	66.47	21.31	87.78	(331)	66.47	(422)	81.49
Mn $K\alpha$	5900	(422)	71.44	23.84	95.28	(422)	71.44	(511) or (333)	74.81
Mn $K\beta$	6492	(333)	66.04	27.21	93.25	(440)	84.06	(531)	86.94
Fe $K\alpha$	6405	(333)	67.85	27.21	95.06	(511) or (333)	67.85	(440)	75.42
Fe $K\beta$	7059	(531)	73.11	13.97	87.08	(531)	73.11	(620)	79.04
Ni $K\alpha$	7480	(620)	74.87	27.67	102.54	(620)	74.87	(533)	73.87
Ni $K\beta$	8267	(55 $\bar{1}$)	80.49	16.1	96.59	(551) or (711)	80.49	(642)	82.7
Cu $K\alpha$	8046	(444)	79.45	27.21	106.66	(444)	79.45	(551) or (711)	76.55
Cu $K\beta$	8904	(731)	80.03	21.61	101.64	(731) or (553)	80.03	(800)	79.91
Zn $K\alpha$	8637	(642)	81.57	13.34	94.91	(624)	81.57	(553) or (731)	77.04
Zn $K\beta$	9570	(733)	77.56	24.95	102.51	(733)	77.56	(555) or (751)	82.57
Sr $K\alpha$	14161	(884)	75.35	11.42	86.77	(777) or (11 5 1)	77.77	(991)	81.09
Sr $K\beta$	15825	(12 6 2)	78.13	18.25	96.38	(13 3 3) or (995)	80.53	(13 5 3) or (11 9 1)	80.6

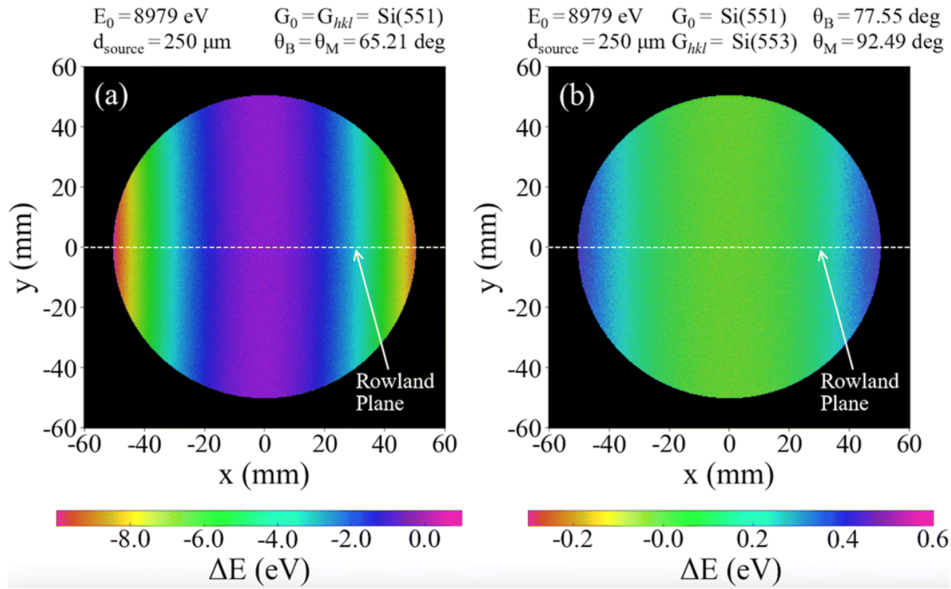


Figure 3.9: (a) XRT ray traced simulation of a Si(551) operated symmetrically far from backscatter, demonstrating Johann error as lower diffracted energies on the left and right sides of the crystal. (b) The same photon energy when using the asymmetric $G_{hkl} = (553)$ reflection with the same analyzer. The crystal is optically near backscatter, resulting in elimination of Johann error.

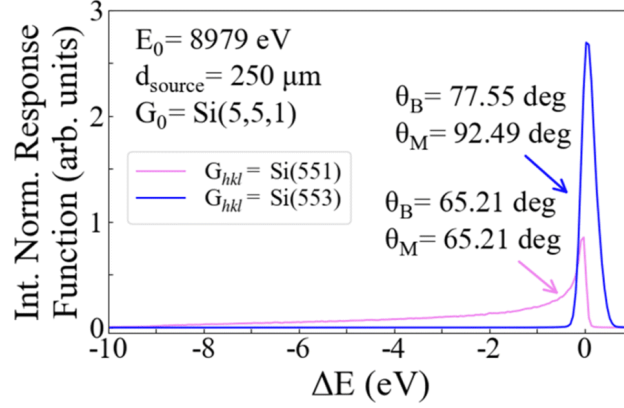


Figure 3.10: Symmetric and asymmetric energy response functions corresponding to Fig. 3.9 (a) and (b), demonstrating the reduction of Johann error.

10% as much broadening (with an opposite sign) for $\theta_B = 77.5$ deg and $\alpha = 14.9$ deg.

The ray tracing results show the availability of an asymmetric plane at the same energy as its conventional symmetric counterpart but with improved energy resolution via reduction of Johann broadening. This is further illustrated in Fig. 3.10, which shows the energy response functions corresponding to cases (a) and (b) of Fig. 3.9. The general consideration that Johann error is smallest when the source is near to the SBCA sphere center is also investigated in Table 3.1, where the most favorable cases with respect to this condition are shown in bold for each emission line. The asymmetric option from even the single favorable case of a Si(551) analyzer are always quite close to the best choices among Si or Ge analyzers used symmetrically and is generally better by this metric.

To show this Johann error reduction in practice, Cu and Zn $K\beta$ XES on the amalgam sample were measured using both (somewhat unfavorable) symmetric and (rather favorable) asymmetric configurations. Fig. 3.11(a) and (b) shows significant difference in the width and symmetry of the characteristic emission. The symmetric spectrum is broadened with a tail primarily because of

Johann error, as well as some contribution from source size broadening. Asymmetric reflections with θ_M near backscatter have improved energy resolution through elimination of Johann error. The effect is more evident in Fig. 3.11(b) as the symmetric Zn measurement is far from backscatter at $\theta_B = 58$ deg, so broadening is more pronounced. The standard deviation of the energy response function calculated via ray tracing in the asymmetric case of the Zn measurement was 0.6 eV, compared to 4.6 eV in the symmetric case. The broadening in the asymmetric case is largely from source size effects.

To further investigate energy resolution effects, we performed transmission mode XANES and EXAFS studies on metal reference foils in symmetric and asymmetric SBGA configurations. Fig. 3.12 shows Cu XANES, selected for the well-known shoulder feature in its rising edge, measured symmetrically and asymmetrically with and without analyzer masking and compared to synchrotron data. Johann error both broadens and shifts the spectra, as shown in the unmasked symmetric case having $\theta_B = \theta_M = 65.2$ deg at the absorption edge, and analyzer masking improves the energy resolution of the symmetric data. However, the asymmetric spectra are unaffected by analyzer masking as Johann error is eliminated in the optical configuration with $\theta_B = 77.5$ deg and $\theta_M = 92.5$ deg, and the asymmetric spectra shows superb energy resolution with no loss of information compared to the synchrotron reference data.

Next, the Ni K-edge EXAFS was measured symmetrically and asymmetrically using the Si(551) analyzer and reflections $G_0 = (551)$ and $G_{hkl} = (55\bar{1})$ and compared to synchrotron data. The raw EXAFS and $\chi(k)$ are shown in Fig. 3.13(a) and (b). There is again no loss in information between synchrotron and laboratory XAFS. The symmetric and asymmetric results are identical

here because the Johann broadening in the symmetric case has little effect for spectrally broad features over the large energy range studied.

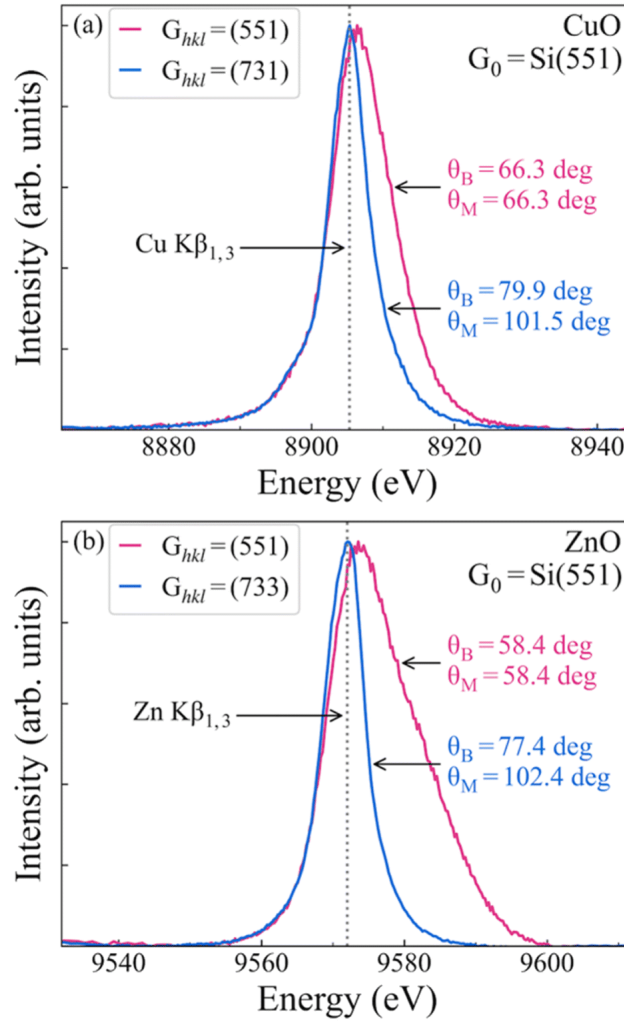


Figure 3.11: $K\beta_{1,3}$ emission spectra of (a) Cu and (b) Zn. Spectra were collected using the Si(551) SBCA symmetrically and with the most optimal asymmetric plane. Further from backscatter, the symmetric reflection analyzer response function broadens due to Johann error. On the other hand, the asymmetric reflection response function is narrow because of a mechanical analyzer angle, θ_M , close to 90 deg.

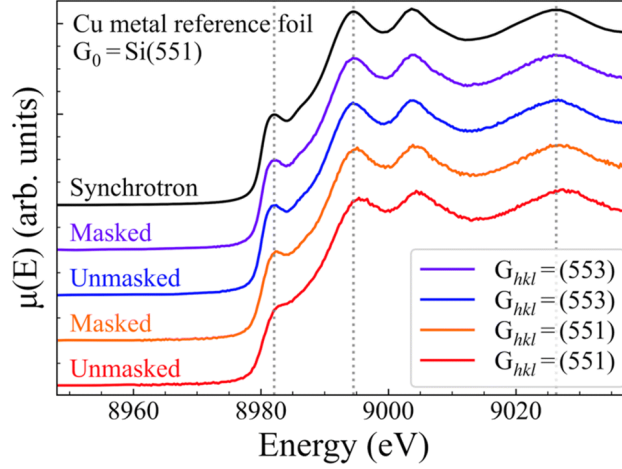


Figure 3.12: Cu K XANES measured using a Si(551) analyzer symmetrically and $G_{hkl} = (553)$ reflection asymmetrically, compared to synchrotron results. At 8978.9 eV, $\theta_B = \theta_M = 65.2$ deg symmetrically whereas $\theta_B = 77.5$ deg and $\theta_M = 92.5$ deg. The asymmetric configuration eliminates Johann error by operating mechanically at near backscatter. Masking the edges of the analyzer removes Johann broadening in the symmetric case, whereas masking in the asymmetric case shows no appreciable difference in energy resolution. Spectra are offset for clarity of presentation.

3.5.2 Synchrotron Measurements

Having demonstrated some benefits of asymmetric Rowland geometry in laboratory X-ray spectroscopy, we extend the discussion to synchrotron X-ray measurements. Fig. 3.14 shows the asymmetric Rowland geometry of the monochromator for a HERFD-XANES measurement, tuned to the Zn $K\alpha_1$ emission energy for a study of a ZnO thin film. Note that while Si(642) is the preferred symmetric analyzer, it is an uncommon SBCA and in our case did not exist at any of the several beamlines performing XES or HERFD at our synchrotron, whereas the Si(211) is relatively common for its (422) harmonic to study XES for vanadium. Fig. 3.15 shows the HERFD-XANES collected using the asymmetric $G'_{hkl} = (642)$ reflection of a Si(211) SBCA compared to total fluorescence yield (TFY) results, and shows significant suppression of the Zn K-shell lifetime broadening. This result supports the use of asymmetric configurations for HERFD and XES at syn-

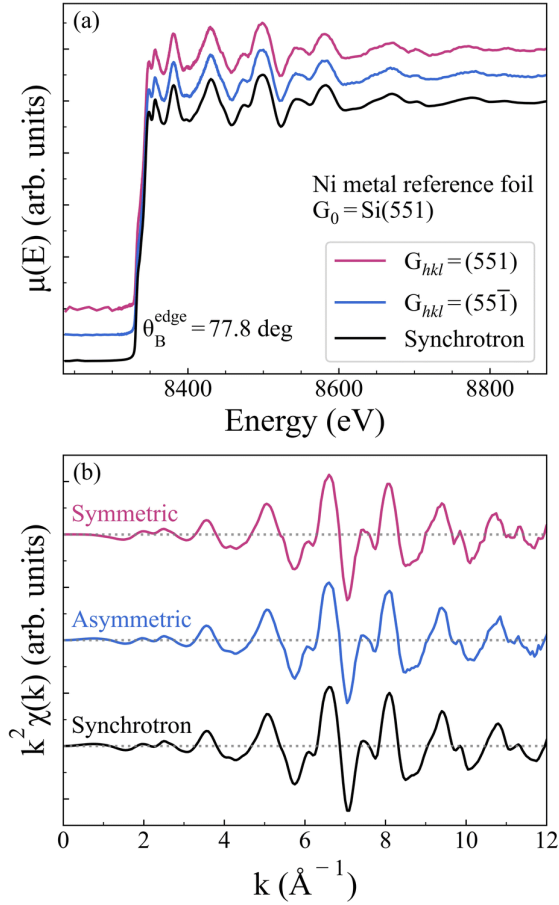


Figure 3.13: (a) Ni K XAFS measured using a Si(551) analyzer symmetrically and with the $G_{hkl} = (55\bar{1})$ reflection asymmetrically, compared to synchrotron results. Both spectra show agreement with synchrotron data. Spectra are offset for clarity of presentation. (b) The background subtracted EXAFS oscillations.

chrotron light sources. The addition of ‘clock angle’ degrees of freedom to the common designs for multi-SBCA arrays for HERFD [42, 43] would therefore allow hkl -hopping with increased user convenience, i.e., when a single analyzer is favorable for all user-desired emission lines in a given study, jumping between the different energy ranges would not require changing the SBCA and retuning.

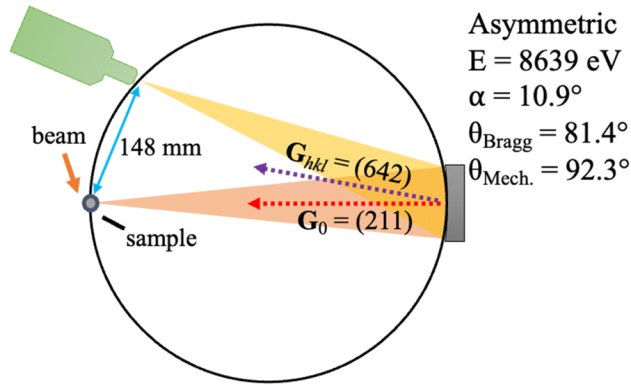


Figure 3.14: The asymmetric configuration implemented for HERFD-XANES measurements. Note the longer source-detector chord length (blue arrows), allowing greater flexibility in special sample environments and less size constraints than a symmetric counterpart.

We now move to our last study, a demonstration of XRS with an SBCA in an asymmetric configuration. Here we again used the Si(211) analyzer asymmetrically accessing the $G_{hkl} = (642)$ reflection, approximately satisfying the condition $\theta_B + \alpha = \theta_M = 90 \text{ deg}$ at 8702.9 eV. The elastic line, measured by scanning the Si(111) double crystal monochromator, is shown in Fig. 3.16. The shape and (near) symmetry of the elastic peak illustrates a favorable energy response function for the experimental realization. The FWHM is 1.25 eV, which is comparable to the expected resolution of the Si(111) double crystal monochromator without second-crystal detuning, i.e., the analyzer is adding little broadening in this configuration. In addition, the source/sample-detector chord length of $\sim 150 \text{ mm}$ is quite large compared to that for synchrotron XRS spectrometers. This

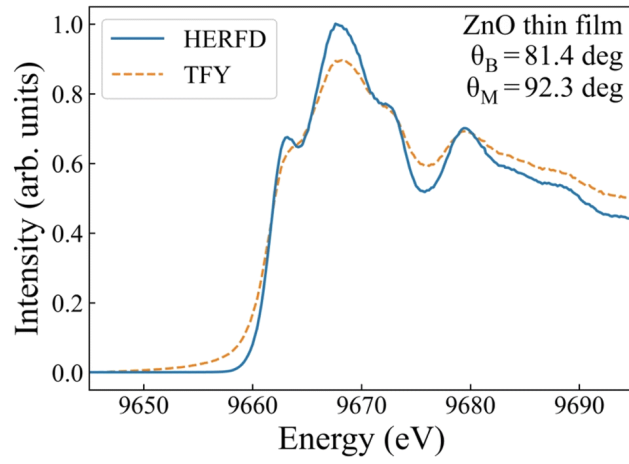


Figure 3.15: Zn HERFD-XANES measured with $G_{hkl} = (642)$ of a Si(211) SBCA.

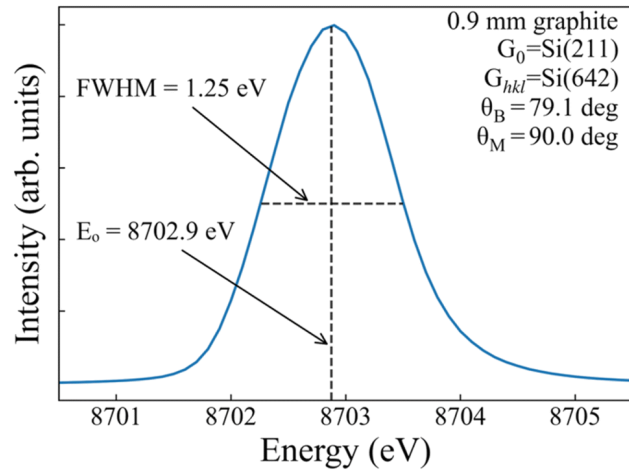


Figure 3.16: Elastic lines measured using a Si(211) analyzer asymmetrically $G_{hkl} = (642)$, demonstrating Johann error elimination and narrowing of the analyzer response function when operated asymmetrically.

is beneficial due to the easier rejection of stray scatter and the larger clearance for special sample environments. This configuration is best used with a focused beam to avoid source broadening, given the ~ 81 deg Bragg angle. We note that asymmetric operation of curved analyzers have been used before to accommodate unequal source-analyzer and analyzer-detector chords required by ancillary equipment [35, 44]. However, here we make use of asymmetric operation to get high energy resolution and large analyzer solid angle together with good sample-to-detector clearance. Similar resolutions are reported in a prior XRS study using the von Hamos (non-Rowland) configuration [45], but it should be noted that contemporary XRS end stations overwhelmingly use arrays of SBCAs [12, 14, 17, 18]. The resulting wide energy scan of the inelastic X-ray scattering and the C K-edge XRS itself are shown in Fig. 3.17, main panel and inset, respectively. The results indeed agree with the well-known spectrum for graphite. While these results are preliminary, they build on the strength of the prior demonstrations in this paper and strongly suggest the use of 0.5 m radius SBCA in XRS measurement, especially when a study requires focusing and thus makes source broadening irrelevant.

We note one detail missing from our present study: 0.5 m SBCAs are typically sliced for strain relief, which raises the question of whether the XRS imaging modality that is now in common use [46, 47] may exhibit some degradation. This is an important topic for further study.

3.6 Conclusions

We investigate the merits of asymmetric Rowland geometries of spherically bent crystal analyzers (SBCAs) for laboratory based XAFS and XES as well as for synchrotron studies of high

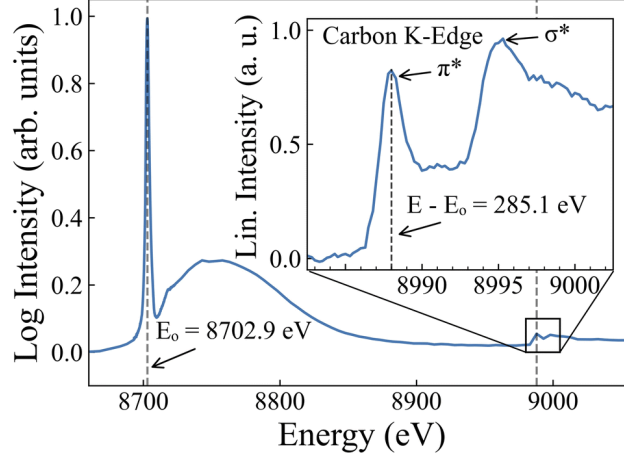


Figure 3.17: XRS of graphite showing elastic, inelastic, and XRS features of C K-edge. Measured with Si(211) using $G_{hkl} = (642)$. The analyzer was mechanically at backscatter with a Bragg angle of 79.1 deg. The elastic peak FWHM is approximately 1.3 eV.

energy resolution fluorescence detection (HERFD) and X-ray Raman scattering (XRS). Several benefits of asymmetric operation are demonstrated. First, a single SBCA employed asymmetrically can use hkl hopping to access a large range of crystal planes and corresponding d -spacings, greatly extending the useful energy range with fine energy resolution compared to conventional symmetric operation. Second, by satisfying the condition that the source be at least relatively near to the SBCA sphere center, asymmetric Rowland geometries can mitigate or eliminate Johann error. Third, asymmetric Rowland geometries can significantly increase the clearance between sample and detector when the nominally perfect sphere-center geometry can be used. The combination of suppressed Johann error, larger solid angle (by use of the 0.5 m SBCA enabled by the elimination of Johann error), and large source-detector distance makes asymmetric operation an especially appealing paradigm for the design of future XRS end stations.

3.7 Conflicts of Interest

There are no conflicts to declare.

3.8 Acknowledgments

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Chapter 4

A Ray Tracing Survey of Asymmetric

Operation of the X-ray Rowland Circle

Using Spherically Bent Crystal Analyzers

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4.1 Abstract

The Spherically Bent Crystal Analyzer (SBCA) is a widely adopted hard x-ray optic, renowned for its good energy resolution and large collection solid angle. It is frequently employed in synchrotron-based techniques like Resonant Inelastic X-ray Scattering (RIXS) and X-ray Emission Spectroscopy (XES), as well as in the rebirth of laboratory-based X-ray Absorption Fine Structure (XAFS) and XES, and its predominant use has been in ‘symmetric’ operation on the Rowland circle. The recent study of Gironda *et al.* (*J. Anal. At. Spectrom.*, 2024, **39**, 1375) emphasizes the benefits of ‘asymmetric’ SBCA operation, demonstrating the use of multiple crystal reflections from a single SBCA to broaden its accessible energy range. Furthermore, Gironda *et al.* demonstrate that asymmetric operation frequently mitigates energy broadening intrinsic to Johann optics and propose that under a specific Rowland circle configuration, designated here the Johann Normal Alignment (JNA), such broadening is eradicated altogether. We report extensive ray tracing simulations and new experimental results to scrutinize the impact of asymmetric configurations on energy broadening and detector plane defocusing. We find that the performance of asymmetric SBCA operation generally exceeds its symmetric counterpart in energy resolution when no analyzer masking is used and, with strategic detector placement, the decrease in detection efficiency due to defocusing can be minimized. Spectroscopic imaging is adversely affected

by the detector plane blurring, but rejection of scattering from special environment windows in X-ray Raman imaging is still feasible, and high imaging quality can be recovered by Johann-like analyzer edge masking. These results help inform future, more common implementations of asymmetric reflections with SBCA in several synchrotron applications and in laboratory-based XAFS and XES.

4.2 Introduction

The spherically bent crystal analyzer (SBCA) is one of the most widely used hard X-ray optics due to its favorable combination of fine energy resolution and large collection solid angle [1]. SBCAs are used in synchrotron x-ray light source endstations that perform Resonant Inelastic X-ray Scattering (RIXS) [2–4], X-ray Emission Spectroscopy (XES) [5–7], and X-ray Raman Scattering [8–10]. SBCAs are also the most commonly used X-ray optic in the ongoing rebirth of laboratory-based X-ray Absorption Fine Structure (XAFS) and X-ray Emission Spectroscopy (XES) [11–18].

This broad and successful implementation of SBCAs has almost exclusively used “symmetric” operation on the Rowland circle (see Figure 4.1a and 4.1b). The exceptions have come from small corrections in wafer miscut for laboratory spectrometers [14], rare cases in synchrotron inelastic x-ray scattering when a desired SBCA orientation was not available but could be accessed with modest deviation from the nominal surface planes of an available SBCA [19], and in the recent work of Gironda *et al.* [20].

In Gironda *et al.* [20], it was demonstrated that an asymmetric operation of the SBCA on

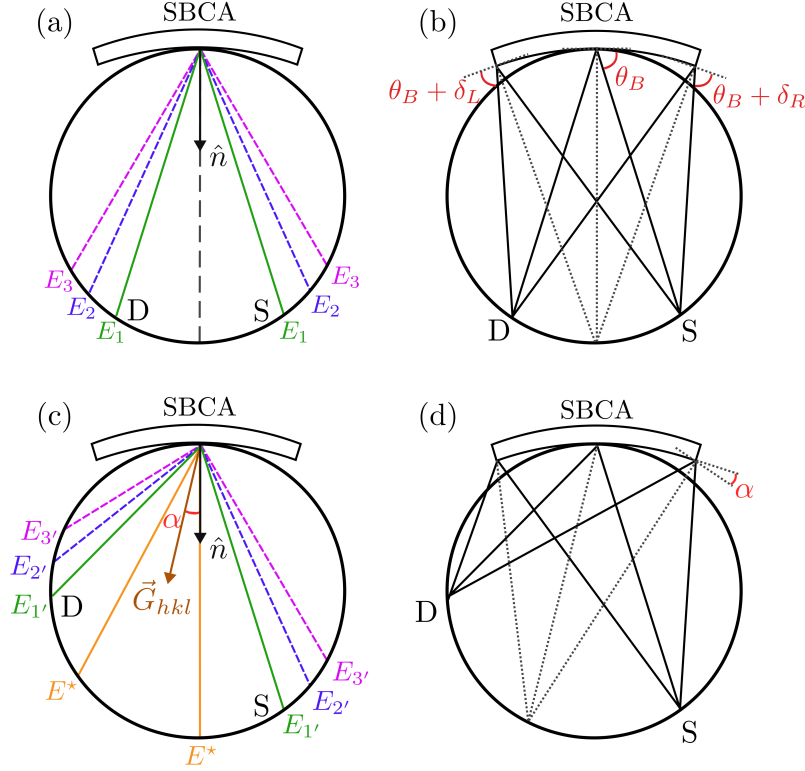


Figure 4.1: (a) By positioning the source (S) and detector (D) symmetrically on the Rowland circle, the detector selects the energy to be detected through Bragg diffraction. (b) By setting the SBCA bent radius to be twice as the Rowland circle, all diffracted rays from the analyzer are (approximately) focused onto the detector. (c) When operating asymmetrically a new reflection plane $\vec{G}_{hkl}$ is introduced. The E^* lines mark the configuration where $\theta_B + \alpha = 90$ deg. (d) The diffracted rays are still approximately focused onto the detector, with slight blurring which will be discussed later in this paper.

the Rowland circle offers significant advantages that may have been underutilized. In particular, it provides the opportunity to harness a multitude of crystal reflections from a single analyzer, thus widening the energy range accessible using any single SBCA and enabling a natural automation to access a wide energy range without the need for exchanging and aligning multiple SBCA. Moreover, when properly configured, asymmetric operation can greatly reduce, and sometimes fully eliminate, energy broadening from so-called Johann error.

The source of the Johann error is due to the diffractive crystal being spherically bent to twice the radius of the Rowland circle, resulting in a gap between the crystal periphery and the Rowland circle (Figure 4.1b). This causes a Bragg angle deviation at the analyzer edges in the Rowland plane and consequent energy broadening. When operating asymmetrically (Figure 4.1c and 4.1d), a new angular parameter α is introduced which is defined to be the angle between the SBCA wafer normal and the lattice vector, $\vec{G}_{hkl}$, of the chosen new reflection (or equivalently the angle between the crystal face and the selected reflection plane). It should be noted that the crystal normal vector continues to be oriented toward the bottom of the Rowland circle, and $\vec{G}_{hkl}$ bisects the incident and the reflected rays. When an additional mechanical degree of freedom, ϕ , is added to rotate the SBCA about its own cylindrical axis the spectrometer user can then bring any desired $\vec{G}_{hkl}$ into the Rowland plane. This is the basis of the demonstration in Gironda *et al.* of performance over a wide energy range with a single SBCA. While overlapping signals from unfortunate combinations of different asymmetric reflections is possible, the pole-plot style maps of Gironda *et al.* using a broadband source show that this is a rare occurrence.

As discussed previously by Suortti *et al.* [21], when $\theta_B + \alpha = 90^\circ$ the source coincides precisely with the sphere center of the SBCA (see E^* lines in Figure 4.1c and see Figure 4.2). For a given θ_B , we define such α as α_J , i.e. $\alpha_J = 90^\circ - \theta_B$. In this conceptually important configuration and ignoring bending strains, the incident X-ray beam impinges normally at all points on the wafer surface with a constant angle θ_B between the incident ray and the chosen reflection plane (Figure 4.2). As a result, a Bragg angle of $90^\circ - \alpha_J$ is maintained at every point on the spherically curved wafer face of the optic, effectively eliminating the Johann error. We call this

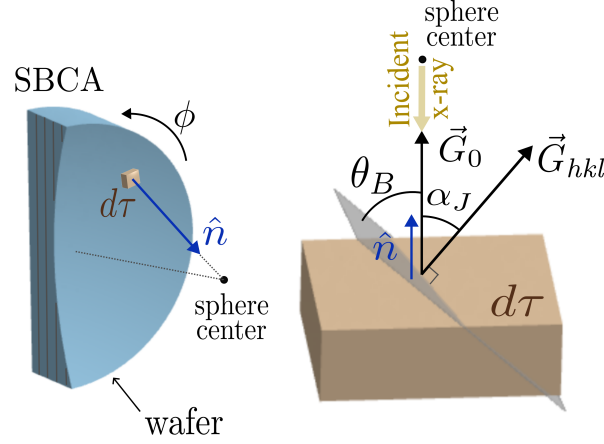


Figure 4.2: Graphical representation of the Johann normal alignment (JNA). The left figure shows a sectional view of the SBCA and all crystal element ($d\tau$) normal vectors point towards the sphere center of the SBCA. The right figure shows one specific crystal element, where incident x-ray is along the crystal normal and maintains a constant angle α_J with respect to $\vec{G}_{hkl}$.

optimal configuration the Johann Normal Alignment, henceforth JNA.

While Girona *et al.* [20] showed a successful utilization of asymmetric operation in improving energy resolution through a series of experimental results, we go beyond that here. In this paper, we present an extensive geometric ray tracing study of asymmetric Rowland circle operation of SBCA's under conditions immediately relevant for experiments both in the laboratory and at the synchrotron. We focus on two key issues. First, we examine the energy response function of SBCAs as a function of experimental configuration with an emphasis on suppression of Johann error. We find that the Johann error is completely suppressed at JNA, and we provide a broad survey of the benefit of asymmetric operation on energy resolution. Second, we use a purely geometrical calculation (hence ignoring penetration and analyzer strain effects [22, 23]) to address what may be the largest drawback to asymmetric operation of SBCA, i.e., the poorer focus on the detector and especially the increased sagittal defocusing. We discuss the effects of this defocusing under

two cases, namely the decrease in detection efficiency due to limited detector sensor area and the degradation in spatial resolution when doing X-ray Raman Imaging. While initially worrisome, we confirmed from simulation and experiment that this unwanted sagittal defocusing can be controlled by appropriate SBCA masking. These results directly inform the case-specific decision of best practice for asymmetric operation constrained by the available detector size, and thus seek to improve future experiment design using SBCA in asymmetric configurations.

4.3 Method

To computationally implement the Rowland geometry, we use the open-source ray tracing software XRay Tracer (xrt) [24]. Though the xrt package has the capability to calculate x-ray diffracted by deformed crystal, we found that the stress and strain effect has minimal influence on our results (contributes less than 0.5 eV of broadening when at symmetric $\theta_B = 60$ deg, and 0.2 eV when under JNA). We expect this effect to be even smaller when analyzers with strain relief cuts are used. Hence, our simulation is purely geometric. A typical run of simulation includes three distinct optical elements: an x-ray source, a SBCA, and a detector. The source is circular with a diameter of 50 μm , characterized by a flat energy distribution spanning a specified energy range. The number of incident rays ranges from 5M to 50M between studies. The SBCA is a Si(551) analyzer, possessing a bend radius of 500 mm and a crystal face diameter of 100 mm; these sizes match SBCA's most often used in synchrotron and laboratory applications. The detector has a circular face, featuring an active area of 150 mm^2 ; this matches the dimensions of the widely employed KETEK AXAS-M detector. The spatial placement of these components on the Rowland

circle (with a radius of 250 mm) is determined by the prescribed θ_B and α .

For the discussion of imaging capability under asymmetric operation, we include two sets of detector plane results. The first set of images are taken using an in-lab spectrometer at University of Washington [20] which operates on Rowland geometry with a 500 mm Rowland circle diameter and 100 mm diameter SBCAs. This in-lab spectrometer uses a 100 W X-ray source (Varex VF-80 Pd anode tube) which has an effective source size of about 1 mm, and a Si(551) analyzer for our particular measurement. The detector plane images are collected (exposure time 500 seconds) using a camera with a sensor area of 14 mm $\times$ 14 mm and a pixel size of 55 μ m.

The second set of images are taken at sector 25-ID-D of the Advanced Photon Source. That beamline has a Si(111) double-crystal monochromator feeding into a Kirkpatrick-Baez mirrors to deliver a beam with a 100 μ m (V) $\times$ 200 μ m (H) spot size onto a 4 μ m thick Co foil. The Co $K\alpha_1$ fluorescence was the source for an 0.5-m radius SBCA Rowland circle system. This used the 531 reflection of a Si (211) SBCA, with $\theta_B = 77.06$ deg and $\alpha = 14.96$ deg. The detector plane image is captured by an Eiger S 500 K pixelated area detector with pixel size of 75 μ m.

4.4 Results and Discussion

4.4.1 Johann Error Characterization

In Figure 4.3, a sequence of crystal analyzer face images is depicted at various α for $\theta_B = 75$ deg. The coloration in these images signifies the energy deviation from the energy E_0 due to Johann error. Under symmetric operation ($\alpha = 0$ deg), the energy deviation reaches -3 eV at the

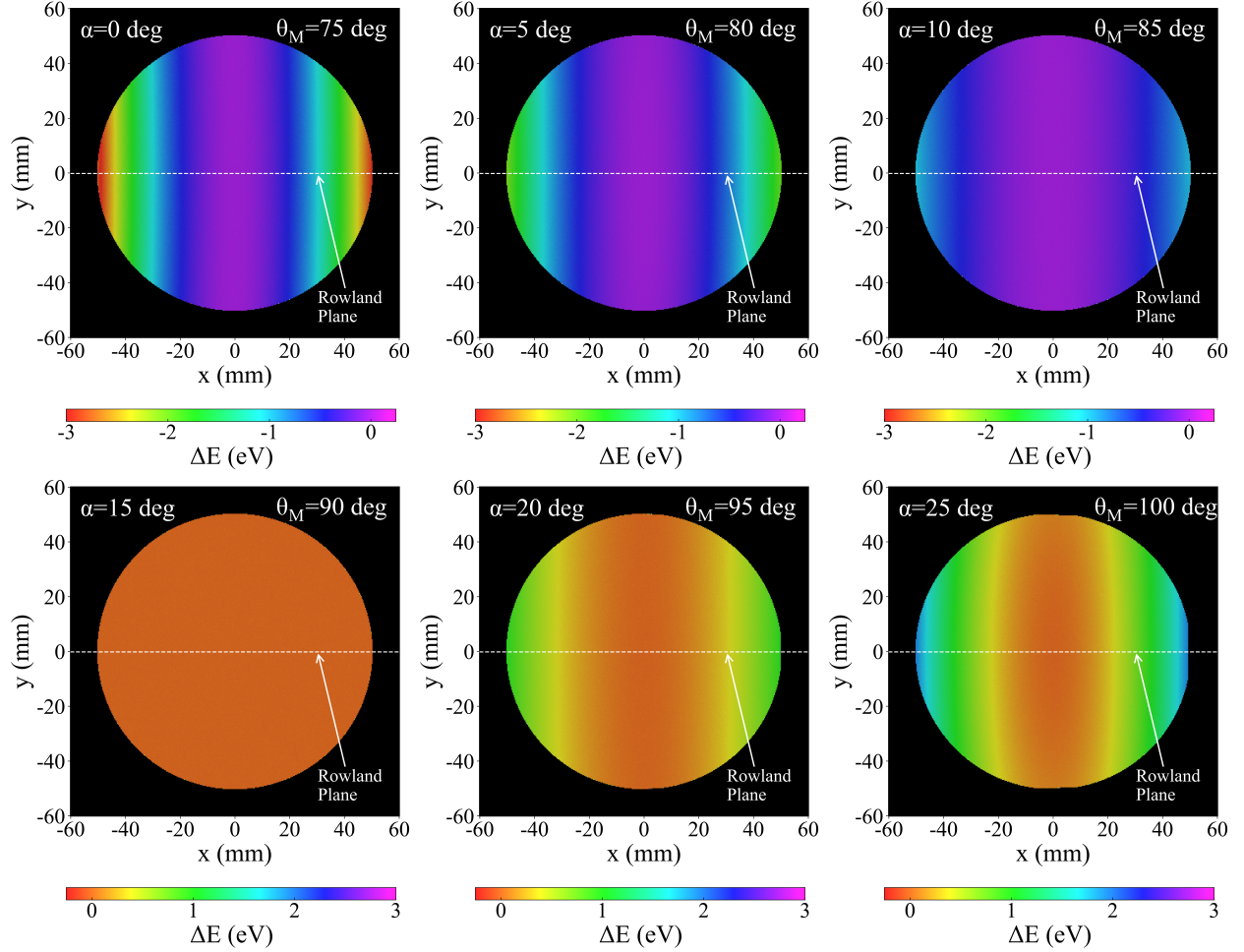


Figure 4.3: Crystal analyzer face images of a Si(551) analyzer operating at $\theta_B = 75^\circ$ (corresponding to $E_0 = 8439 \text{ eV}$) and multiple values of the asymmetry α . The mechanical angle of the spectrometer is indicated by θ_M , which is defined through the relation $\theta_M = \theta_B + \alpha$. The simulation employs a source size of $50 \mu\text{m}$. At $\alpha = \alpha_J = 15^\circ$ the Johann error is eliminated.

crystal edge. Conversely, at $\alpha = \alpha_J = 15 \text{ deg}$ (where α_J is the required angle for achieving JNA for a given θ_B), the energy deviation approaches zero and displays a uniform distribution. As α surpasses α_J , Johann error re-emerges, but manifesting a positive energy deviation. As a reminder, the improved energy resolution at JNA was demonstrated experimentally in Gironda *et al.*, such as by very high resolution measurement of Cu XANES with different Bragg reflections, θ_B , and asymmetries α . [20]

In Figure 4.4 we show the energy response functions corresponding to the analyzer face images presented in Figure 4.3. At $\alpha = \alpha_J = 15 \text{ deg}$ the response function is symmetrical about 0 eV with a FWHM of approximately 0.04 eV attributed to source size broadening. For $\alpha < \alpha_J$ the response functions display a low-energy tail, whereas for $\alpha > \alpha_J$ they instead exhibit a high-energy tail.

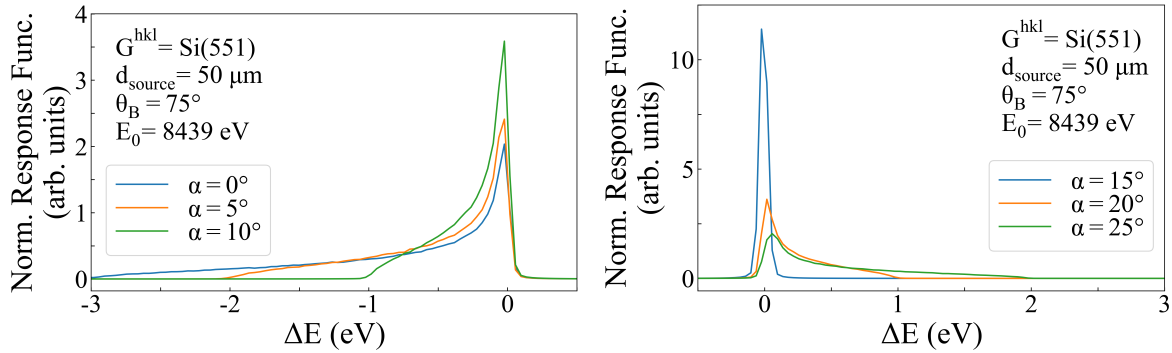


Figure 4.4: Integral normalized response functions corresponding to each crystal face images shown in Figure 4.3.

In Figure 4.5 we show the standard deviation of the response function (σ_{resp}) as a function of α . The standard deviation decreases from 0.77 eV when $\alpha = 0 \text{ deg}$ (symmetric operation) to 0.12 eV at JNA when $\alpha = \alpha_J = 90 \text{ deg} - \theta_B$. Recall that the broadening for $\alpha = \alpha_J$ is due to the finite source size.

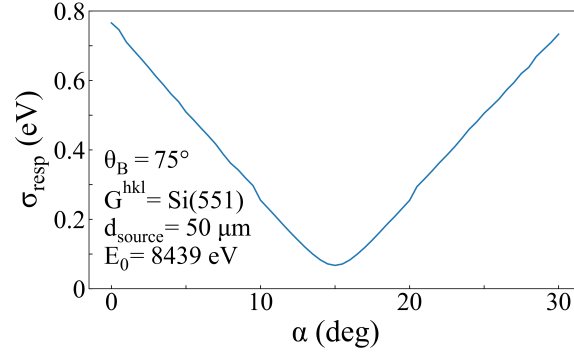


Figure 4.5: Standard deviation of the response functions as a function of α , when θ_B is 75 deg. A Si(551) analyzer is used which gives $E_0 = 8439$ eV.

In Figure 4.6 we provide a more complete exploration of energy broadening in the 2-D space of θ_B and α . Note that σ_{resp} exhibits a minimum along the dashed line where $\alpha + \theta_B = 90$ deg. Also note that σ_{resp} remains small, i.e. around the range of an eV, within the range of $\alpha + \theta_B > 80$ deg. However, σ_{resp} increases rapidly when $\alpha + \theta_B$ drops below 80 degrees. With this we can provide a recommendation range of θ_B and α when running an experiment with an unmasked analyzer to maximize solid angle.

On the other hand, if an experiment requires $\alpha + \theta_B < 80$ deg then masking the analyzer edges should be considered, just as is commonly done for symmetric operation. Hence, we repeat the simulation of Figure 4.4 with a 30-mm-wide analyzer mask (see Figure 4.7), which gives 38% of the active area compared to the unmasked case. Unsurprisingly, we observe the response function standard deviations are greatly reduced for all α compared to Figure 4.4, except when $\alpha = \alpha_J = 15$ deg where the response function is unchanged.

In conclusion, through examining the response functions under various cases, we see that the energy resolution is greatly improved through asymmetric operation, especially when α is close to α_J . Applying a mask to the SBCA edges in the Rowland plane, as often done in symmetric case,

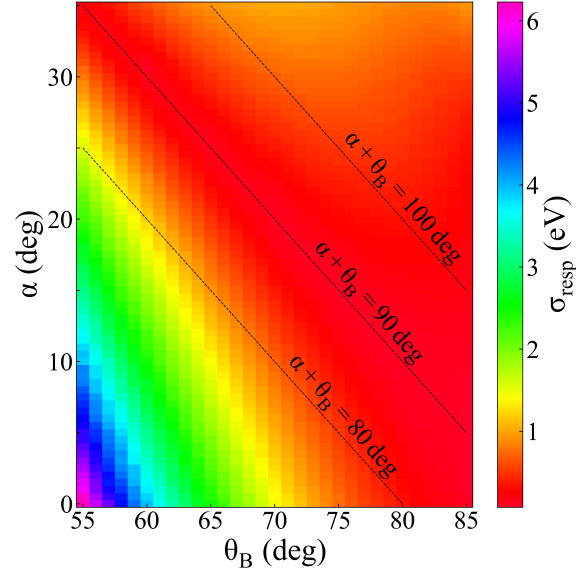


Figure 4.6: Standard deviation of the response function (σ_{resp}) as a function of α and θ_B , presented as a 2-D density map.

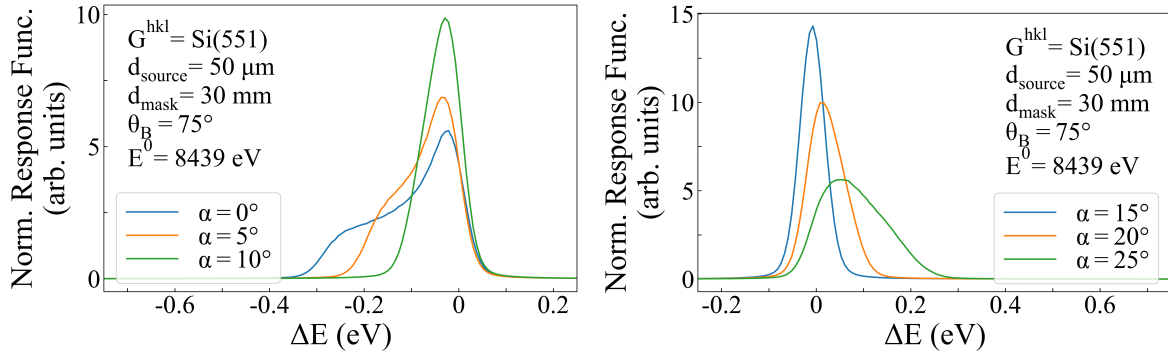


Figure 4.7: Integral normalized response functions at $\theta_B = 75$ deg and selected values for α . The simulation parameters are the same as in Figure 4.4 but with a 30-mm wide analyzer mask.

further reduces the energy broadening. This facilitates the use of multiple reflection planes within a single SBCA without the concern of compromising energy resolution.

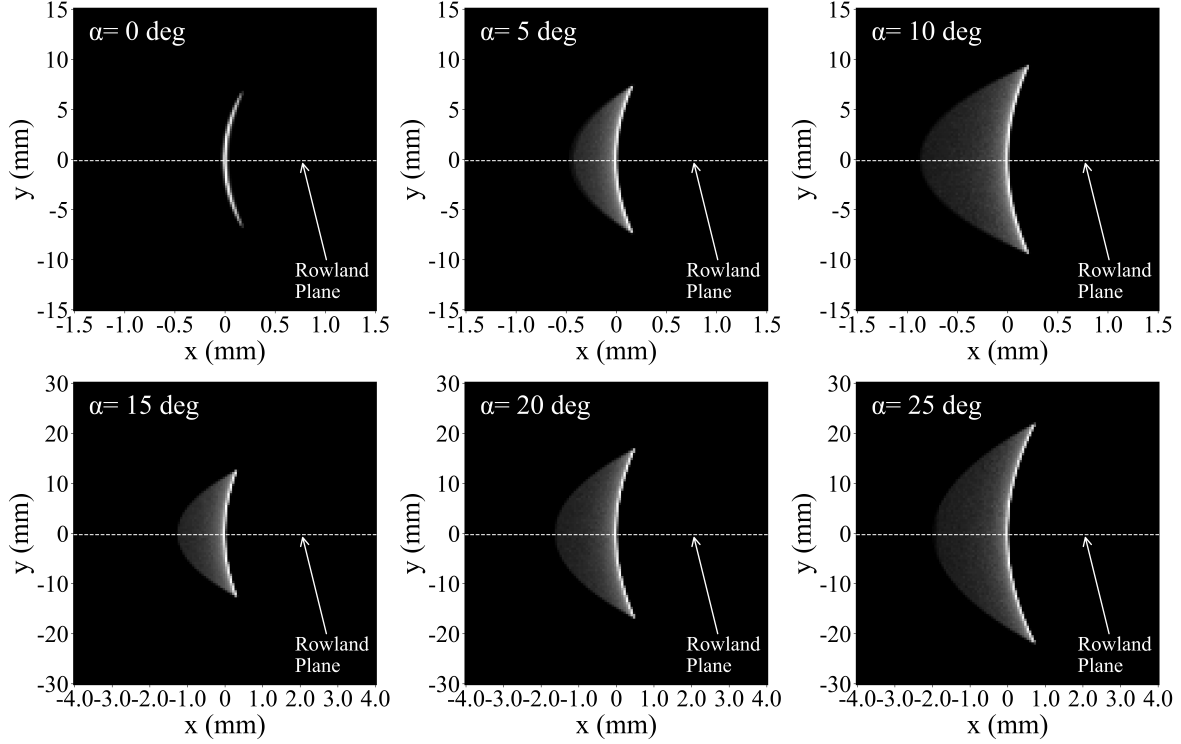


Figure 4.8: Detector plane images at the indicated values of α when $\theta_B = 75$ deg. A noticeable defocusing in the vertical direction can result in decreased detection efficiency because of finite detector size.

4.4.2 Detection Efficiency Study

While SBCA-based spectrometers can use many different detectors, the strong background rejection of silicon drift detector (SDD) makes them the most popular choice. In the context of asymmetric operation, the typical SDD active diameter ($D_{SDD} = 13.8$ mm) raises the issue of signal losses. The key issue is shown in Figure 4.8 where intensity maps are shown for the detector plane at the Rowland circle at $\theta_B = 75$ deg and various α . As α increases, both the width and especially the height of the detected beam increase.

Figure 4.9 shows this broadening effect of the detector image experimentally. In the left column, we show the detector plane images collected from the in-lab spectrometer. Due to the

limited sensor size, images were stitched to capture the full beam. Note that horizontal dark lines in the experimental results are due to the analyzer strain-relief cut, not image stitching. Both images were taken at $\theta_B = 75$ deg, and the crystal reflections used were 551 and 553 for the symmetric and asymmetric case, respectively. The column on the right shows the corresponding simulations. One can see that the beam height agrees well between simulation and experiment, while the extent of sagittal broadening appears to be slightly less significant because of the difficulty in detecting weak signals at the tail in the experimental case.

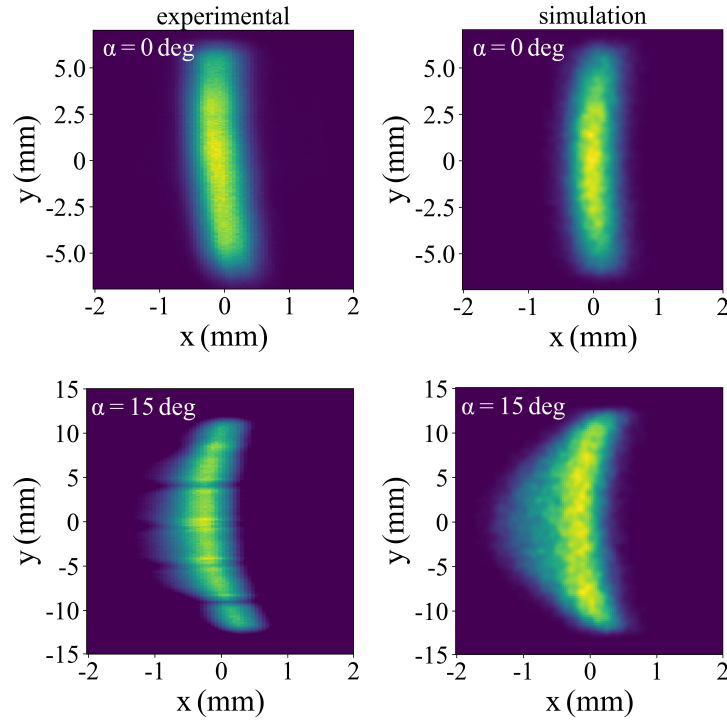


Figure 4.9: A comparison between experimental (left) and simulated (right) detector plane image under symmetric (top) and asymmetric (bottom) configuration. All images are taken at $\theta_B = 75$ deg with a Si(551) analyzer. The 553 reflection was used for the asymmetric case. The effective source size is about 1 mm.

Fortunately, as we will show next, the signal loss due to sagittal broadening can be improved by strategically placing the detector behind the Rowland circle. To explore how detection efficiency

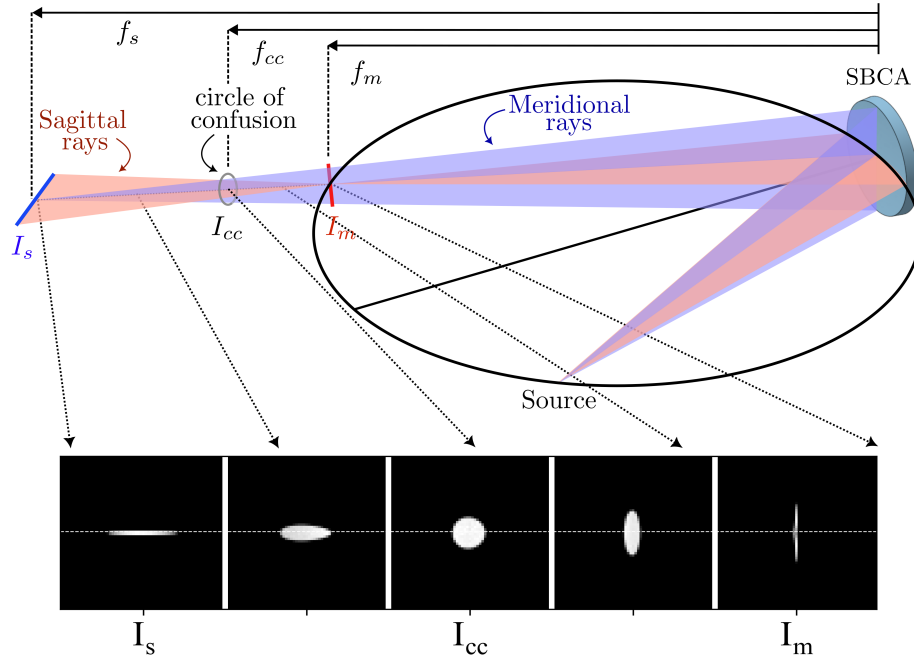


Figure 4.10: Astigmatic imaging errors of an SBCA result in a vertical line focus (I_m) from the meridional rays on the Rowland circle and a horizontal line focus (I_s) from the sagittal focus behind the circle. The position of the circle of confusion (I_{cc}) is where the beam height equals the beam width. The detector images at I_m , I_{cc} , and I_s (with $\theta_B = 75$ deg and $\alpha = 0$ deg) are shown at the bottom, with additional images at the midpoints of each segment.

can be optimized through detector placement, we first present a geometrical explanation on how beam shape changes from the point behind the Rowland circle.

While Johann crystal analyzers offer good on-circle focusing in the Rowland plane when employing a point source, as illustrated in Figure 4.1 (b) and (d), the vertical focusing exhibits a finite height, see Figure 4.10. This is because the SBCA focal point in the meridional plane is behind the Rowland circle, consequently resulting in a vertical (meridional) line focus of the point source on the Rowland circle and a horizontal (sagittal) line focus positioned behind it.

The distance from the vertical focus (I_m) to the crystal is represented as f_m , whereas the corresponding distance for the horizontal focus (I_s) is labeled as f_s . Under symmetrical configuration,

these distances have been well studied [25], and similar calculations for the asymmetric case give

$$f_m = R \sin(\theta_B - \alpha) \quad (4.1)$$

and

$$f_s = -\frac{R \sin^2(\theta_B + \alpha)}{\sin(\theta_B - \alpha) \cos(2(\theta_B + \alpha))} \quad (4.2)$$

where R is the radius of curvature. The beam height at the vertical focus (h_m) and the width at the horizontal focus (w_s) are

$$h_m = 2(f_s - f_m) \tan\left(\frac{d_{xtal}}{2f_s}\right) \quad (4.3)$$

and

$$w_s = 2(f_s - f_m) \tan\left(\frac{\gamma}{2}\right) \quad (4.4)$$

where γ is the sagittal angular size of the analyzer viewed from the source and d_{xtal} is the analyzer diameter.

Using these expressions, we then can define the distance f_{cc} from the crystal face to the minimum circle of confusion (CC) at location I_{cc} , i.e. where the beam height equals the beam width

$$f_{cc} = f_m + \frac{h_m(f_s - f_m)}{h_m + w_s}. \quad (4.5)$$

The analytical results inform the ray tracing needed for a fully quantitative picture.

In Figure 4.11 we extend the series of detector images presented in Figure 4.10 to the asymmetric case, where $\alpha = 15$ deg (middle column) and $\alpha = 25$ deg (right most column). Notice in all

cases, the beam spot is most compatible with the circular SDD active region near I_{cc} , suggesting that repositioning the detector strategically could improve detection efficiency.

To find the optimal detector location, we examine the detection efficiency (with detector diameter equals D_{SDD}) under symmetric and asymmetric configurations when $\theta_B = 75^\circ$ as a function of detector location (Figure 4.12). The SBCA bent radius is set to be 500 mm and with a crystal face diameter of 100 mm. The position of I_m (red), I_s (green) and I_{cc} (blue) is marked with dashed lines. An additional black line (I_{SDD}) at 68.4 mm marks the location where the beam horizontal width is equal to the circular detector sensor diameter.

We find the maximum efficiencies typically are at detector positions near I_{cc} , as suggested earlier, and often occurs at a location slightly in front of I_{SDD} in all cases. Since the location of I_{SDD} does not depend on θ_B and α , the results suggest I_{SDD} as a pragmatic static location for detector placement when utilizing asymmetric configuration.

To give a more holistic view, we quantitatively examine the effect of detector position on detection efficiency under asymmetric operation when the detector active area diameter equals D_{SDD} . Again, the issue here is the possible mismatch between the SDD active region size and the often larger dimension of the analyzed beam at the detector face. In Figure 4.13, we show the detection efficiency at I_{SDD} in the 2-D space of α and θ_B , in which we observe that the detection efficiency exhibits an oval contour. We have also shown labeled points for the best analyzer selection (Si or Ge) for the $3d$ transition metal $K\alpha_1$ emission lines (with Scandium omitted due to its infrequent appearance in XES studies). Table 4.1 gives the emission lines and associated analyzers, Bragg angles asymmetries, and reflections. While a full treatment of analyzer selection is outside of the

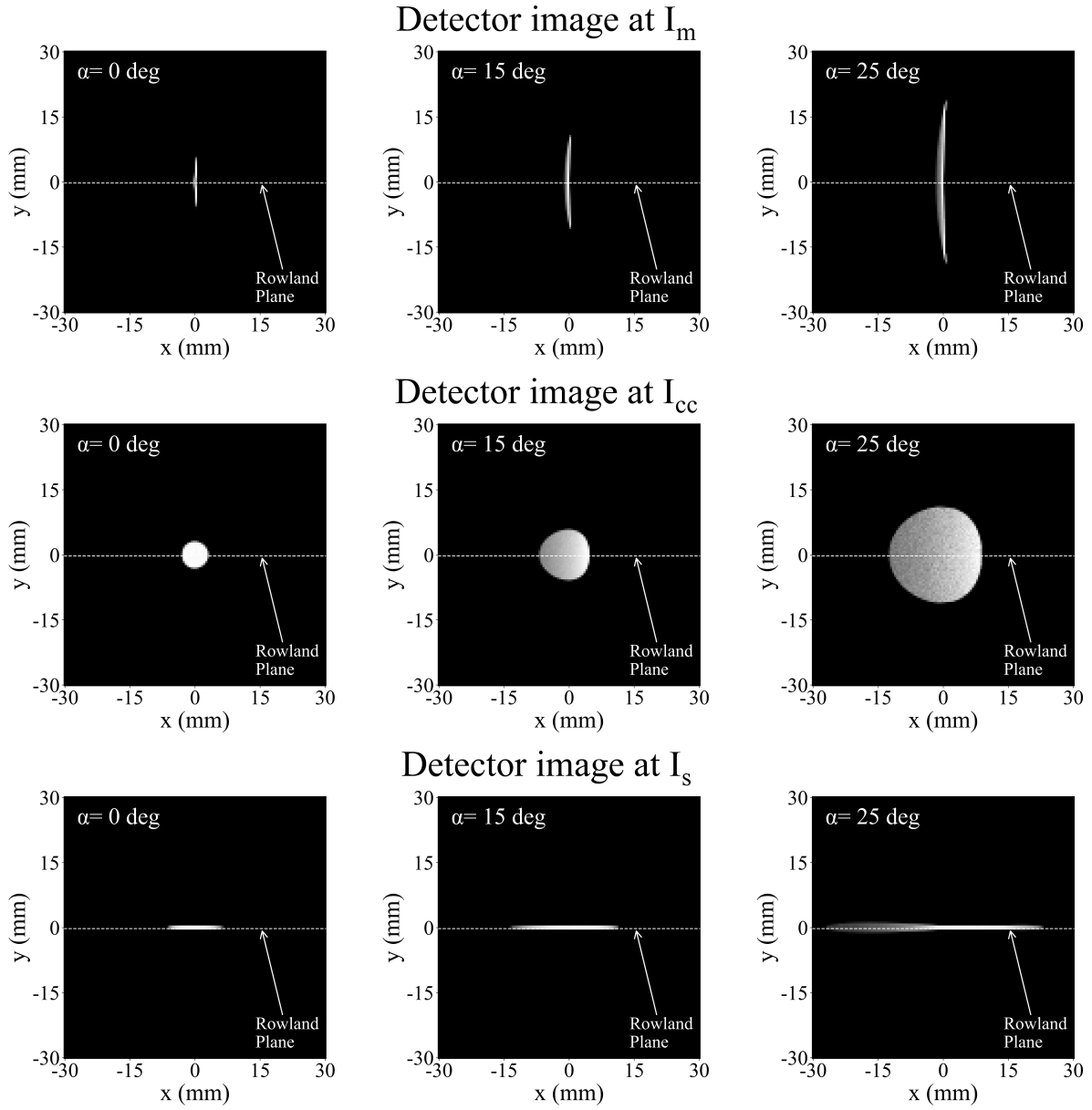


Figure 4.11: Detector plane images at $\theta_B = 75$ deg and $\alpha = 0, 15$, and 25 deg. Each row from top to bottom correspond to I_m , I_{cc} , and I_s respectively.

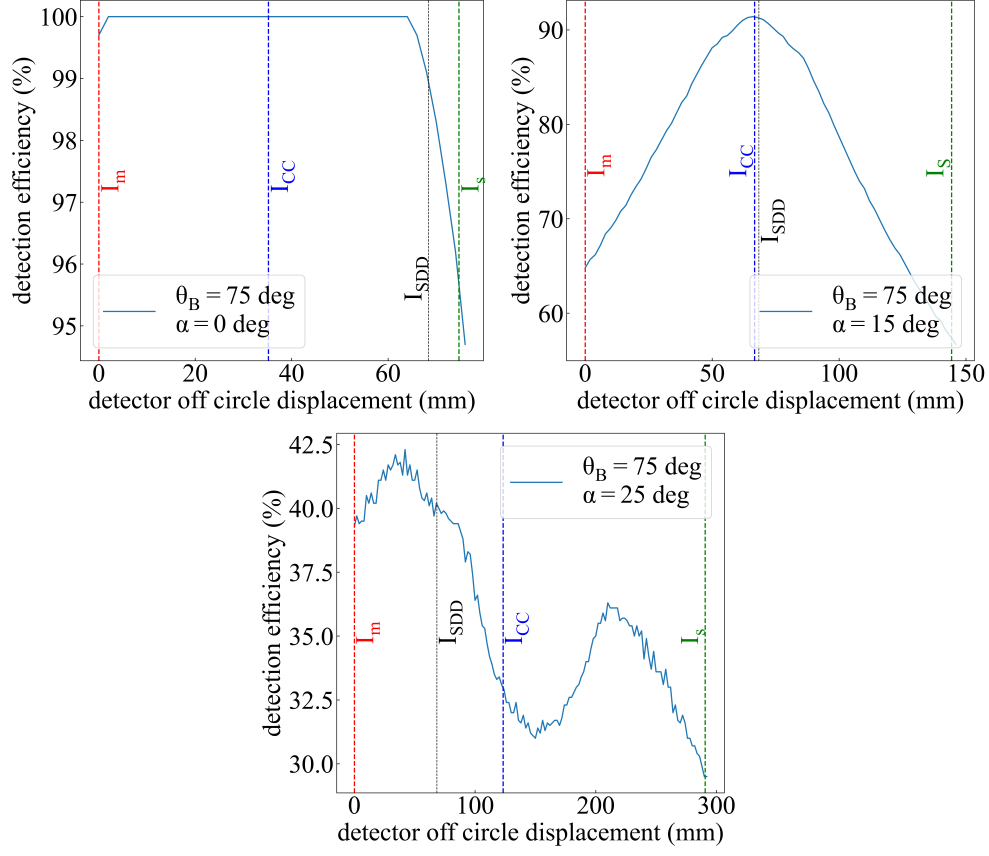


Figure 4.12: Efficiency of detector with diameter $D_{SDD} = 13.8$ mm as a function of the detector off-circle position, evaluated under both symmetric and asymmetric configuration at $\theta_B = 75$ deg.

scope of the present paper and is discussed elsewhere [26], we have included the ‘best’ performing reflection for context: typical losses are less than 30% for lower-energy emission lines, while the plethora of possible d -spacings as energy increases makes asymmetric operation lossless in terms of detection efficiency effects.

4.4.3 Asymmetric Operation In X-ray Raman Imaging

X-ray Raman scattering (XRS), sometimes also grouped under the term nonresonant inelastic x-ray scattering, uses hard x-rays to measure the x-ray absorption spectrum for weakly bound

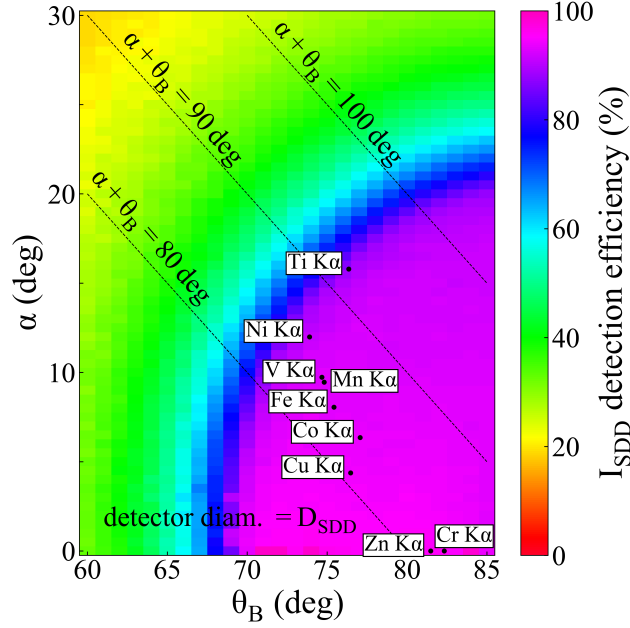


Figure 4.13: The detection efficiency for a detector with an active area diameter D_{SDD} positioned at I_{SDD} . Labeled points indicate the best analyzer selection for the $3d$ transition metal $K\alpha_1$ emission lines, where θ_B , α , G_0 , and G_{hkl} for each emission line is detailed in Table 4.1. Here $R = 500$ mm and $d_{xtal} = 100$ mm.

shells [27, 28]. This comes with three main advantages, all accruing from the use of high energy incident photons. First, the higher penetrating power of hard x-rays ensures truly bulk-like measurement without risk of self-absorption effects. Second, the high penetrating power, again, greatly simplifies and in some cases uniquely enables the measurement in special sample environments of the XAS spectrum for low-energy edges. These uses have been most prominent in high pressure studies using diamond anvil cells [29, 30]. Finally, the large momentum transfers available from inelastic scattering of the incident photon allows tuning of selection rules, enabling measurement of a plethora of final state orbital angular momenta [31].

However, these scientific benefits of XRS are inhibited by its very weak signal, requiring not just very high intensity synchrotron beamlines but also multianalyzer spectrometers seeking to

Table 4.1: Associated analyzers, Bragg angle symmetries, and reflections for the labeled points in Figure 4.13.

Emission	Energy (eV)	θ_B	α	G_{hkl}	G_0
Ti $K\alpha$	4510	76.35	15.79	Ge(400)	Ge(511)
V $K\alpha$	4952	74.67	9.73	Ge(331)	Ge(553)
Cr $K\alpha$	5416	82.33	0	Ge(422)	Ge(422)
Mn $K\alpha$	5899	74.82	9.45	Ge(511)	Ge(311)
Fe $K\alpha$	6404	75.43	8.05	Ge(440)	Ge(551)
Co $K\alpha$	6930	77.07	6.35	Si(531)	Si(642)
Ni $K\alpha$	7478	73.9	11.99	Ge(533)	Ge(642)
Cu $K\alpha$	8048	76.47	4.37	Ge(711)	Ge(511)
Zn $K\alpha$	8639	81.48	0	Si(642)	Si(642)

maximize the collection solid angle. A complete discussion of such instrument design is outside the scope of this manuscript, but we note that the careful considerations of Huotari *et al.*[10] illustrate well the reasons behind not just the continued use of 1-m radius of curvature optics but also the fact that even those optics are often masked to remove (or decrease) Johann error at some cost in collection solid angle.

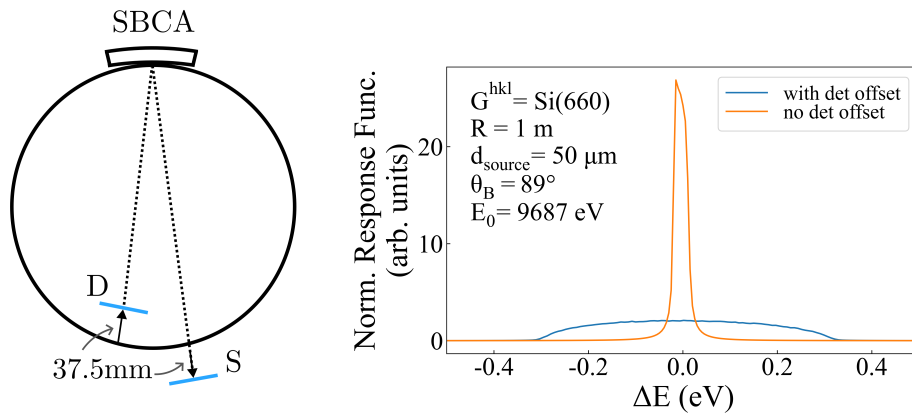


Figure 4.14: (Top) To gain more sample clearance and still maintaining focus when operating at higher θ_B , the source and the detector is displaced off the Rowland circle symmetrically by 37.5 mm. (Bottom) Response functions at $\theta_B = 89$ deg when $R = 1$ m and: (i) the source and the detector is displaced off the Rowland circle by 37.5 mm (blue); (ii) no detector and analyzer offsets is applied (orange).

One use of XRS is Raman imaging, or direct tomography [32]. It uses the fact that an extended source gives an extended image to generate images with both spectral and spatial information. In the work of Huotari *et al.*[10], they reported that the state-of-the-art Raman imaging is constrained to near backscattering Bragg angles due to the energy broadening caused by Johann error and analyzer strains. To obtain more sample clearance but maintain quality of focus on the detector plane, the source and the detector are displaced off the Rowland circle, which introduces another source of energy broadening (see Figure 4.14). At $\theta_B = 89^\circ$ with Si(660) 1-m radius SBCA, our ray tracing shows the energy broadening due to a 75 mm detector offset is 0.52 eV. This is much larger than source sizes for any typical focused beam, and is a large part of the error budget.

Together with the maximization of the collection solid angle, these issues motivated Gironda *et al.*[20], to make use of the JNA configuration with the much larger, 0.5-m radius of curvature SBCA. There, they make a first claim that the full solid angle of the newer optics (four times that of the traditional 1-m radius optics, even before masking) can be effectively used in XRS. Moreover, by utilizing the JNA configuration, operation at lower θ_B is allowed hence more sample clearance is obtained and no detector offset is required. This asserts a new paradigm for the design of such spectrometers: a small cluster of the larger, more tightly curved optics in JNA configurations will give a mechanically simpler and more cost-effective alternative to traditional designs while also increasing spectrometer solid angle and exhibiting good energy resolution.

For bulk measurements, i.e., homogeneous sample not in special samples environments, the argument of Gironda *et al.*[20], is persuasive. However, as admitted by those authors, a significant portion of XRS studies are performed in special sample environments where the XRS imaging

methods that either reject the background inelastic x-ray scattering from sample chamber windows [10] or even complete spatial mapping of the XRS spectrum across a chemically inhomogeneous sample [32]. We have previously mentioned (see Section 4.4.2 and Figure 4.8) the larger aberrations of the analyzed radiation on the nominal detector plane when working asymmetrically on the Rowland circle. Here, we address the consequences of those aberrations on XRS imaging applications.

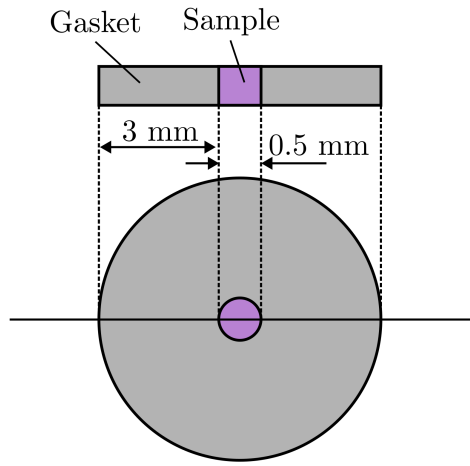


Figure 4.15: A schematic diagram for a typical diamond anvil cell used in X-ray Raman imaging, where the top shows a sectional view seen in the Rowland plane, with a top-down view shown at the bottom. The sample with a 0.5 mm diameter is placed at the center of a gasket.

This is illustrated by means of a case study of a typical diamond anvil cell used in x-ray Raman imaging, as shown in Figure 4.15 [30]. We simulate this extended source under JNA at $\theta_B = 80 \text{ deg}$ with multiple $50 \text{ }\mu\text{m}$ sources spaced across the beampath through the gasket and sample. As shown in Figure 4.16, the detector-plane image produced by the sample (left panel) and the gasket (right panel) are examined separately. The red line defines the boundary of the suggested range of interest (ROI). It is taken to be the region where the pixel intensity is greater

than 45% of the maximum intensity from the sample, and it captures roughly 75% of the sample signal.

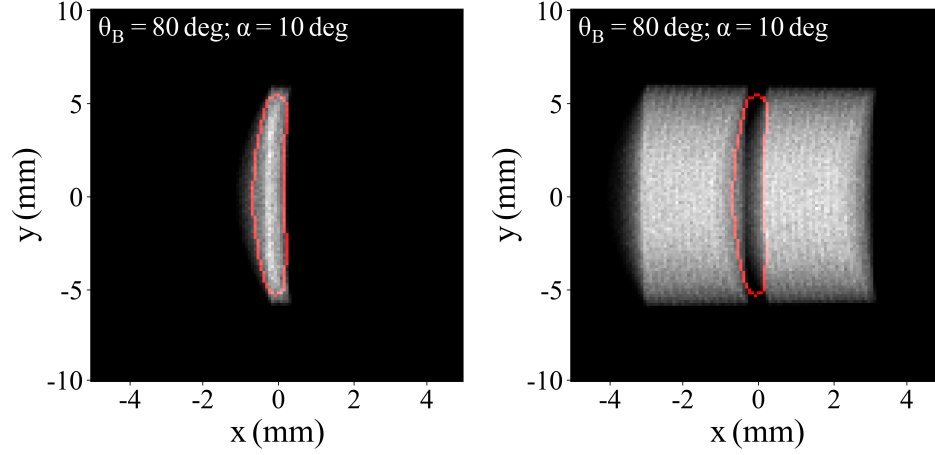


Figure 4.16: Detector image from the sample (left) and the gasket (right) under JNA when operating at $\theta_B = 80 \text{ deg}$. The region outlined with the red indicates the ROI when calculating signal intensity. Note that the texture in the images is solely artifacts from plotting due to low image resolution.

To quantify the contamination of sample signal by the photons scattered from the gasket, we first calculate the percentage of the sample signal (57%) and percentage of the environment signal (43%) with respect to the total intensity (all within the given ROI), then the sample to environment signal ratio is found to be 1.3. This shows that asymmetric operation at $\theta_B = 80 \text{ deg}$ (with $R = 50 \text{ cm}$) still maintains a high signal-to-environment ratio even with the detector image blurring, while the sample clearance increases from 8.2 cm (when using symmetric geometry with source and detector offset) to about 17 cm.

Although asymmetric operation offers advantages for XRS, it also presents limitations. When the sample environment shares the same element as is being studied in the sample, their signal peaks coincide in the Raman spectra. In such instances, any contamination from the environment

is likely prohibitive. Similar concerns arise when using XRS to spatially map an extended, inhomogeneous sample [10].

Luckily, appropriate analyzer masking can effectively reduce the extent of sagittal broadening as shown in Figure 4.17, where we show synchrotron results (top row) and corresponding simulations. Recall that here we have $\theta_B = 77.06$ deg and $\alpha = 14.96$ deg. A series of images were taken with different analyzer masks covering the edges of the analyzer along the Rowland plane, and the illumination width ranges from full illumination to 30 mm. The middle row shows its simulated counterpart. Notice that these images have shadows which we have not seen in previous studies, which is due to the fact that the detector placement is not normal to the reflected beam off the analyzer for this instrument. Also note that the rotation of the experimental images are due to small misalignment of the source in the direction perpendicular to the intended Rowland plane, and the slightly thicker width is a result of the detector being slightly off circle. The bottom row is showing the simulated images with 6 mm displacement of the detector out of the Rowland circle, and 10 mm of source displacement perpendicular to the Rowland plane. They agree well with the experimental data. In any event, we see that masking effectively reduces sagittal broadening in both the simulated and experimental results, which greatly benefit the use of asymmetric operation in Raman imaging. These results show that there is a beneficial trade-off between solid angle and imaging capability for XRS, and support the use of JNA configurations for XRS imaging.

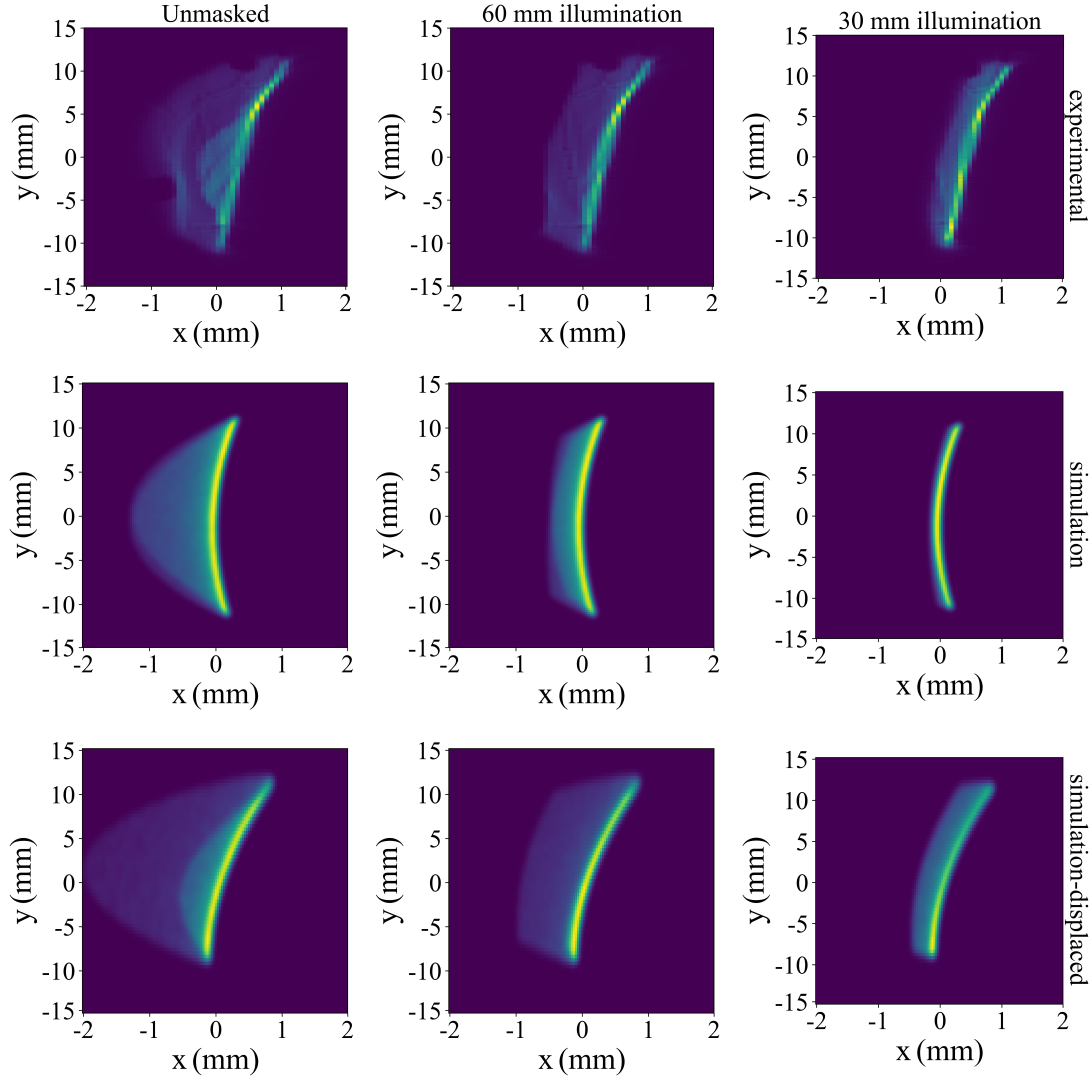


Figure 4.17: Experimental (top) and simulated (middle) images shown how masking the edges of the analyzer (along the Rowland plane) can effectively reduce sagittal broadening. The slight rotation and thicker width of the experimental result are due to small misalignment of the source and the detector. The bottom row shows the simulated images with 6 mm displacement of the detector out of the Rowland circle, and 10 mm for the source in direction perpendicular to the Rowland plane.

4.5 Conclusion

The recent Gironda *et al.* study gave a convincing experimental argument that asymmetric operation of spherically bent crystal analyzers (SBCAs) was an underutilized opportunity. Here,

we have gone beyond that work in several directions. First, the conceptual rationale for the possible elimination of Johann error in asymmetric operation has been made quantitative. Specifically, we find a significant reduction in Johann error when operating asymmetrically, with complete elimination observed under the Johann Normal Alignment (JNA). We provide detailed insights into the standard deviation of the response functions (σ_{resp}) across a wide range of θ_B and α , offering guidelines on best practice for asymmetric operation.

Second, we explore the optimization of detector placement to mitigate signal losses resulting from sagittal image broadening under asymmetric operation. We propose a static location, I_{SDD} , for detector placement, and show that the detection efficiency remains close to maximum for a given θ_B and α under this arrangement.

Third, we extend our analysis to the effect of sagittal defocusing on X-ray Raman imaging, emphasizing the importance of spatial resolution, particularly in applications requiring sample environment signal rejection. Through the examination of a typical diamond anvil cell under JNA at $\theta_B = 80$ deg, we demonstrate that the signal-to-background ratio remains useful at 1.3, while increasing the sample clearance to about 17 cm (with a half-meter Rowland radius). The benefit of asymmetric operation is even clearer when effective analyzer masking is applied, where sagittal broadening is significantly reduced, highlighting the effectiveness of asymmetric operation in maintaining signal integrity and gaining sample clearance.

In conclusion, our findings highlight the underutilization of asymmetric operation despite its manifold benefits. We foresee a widespread adoption of this approach in both synchrotron and laboratory settings in the near future. Moving forward, further research should extend beyond

purely geometric calculations. Moreover, guidelines on the selection of analyzers and reflections that suit typical experimental constraints are needed [26]. With continued investigation, we can unlock the full potential of asymmetric operation, enhancing the capabilities of X-ray spectroscopy and imaging methods.

4.6 Author contributions

Conceptualization, G. T. S.; formal analysis, Y. C.; software, Y. C.; investigation, Y. C., A. J. G. and Y. S.; methodology, Y. C. and G. T. S., project administration, G. T. S.; writing - original draft, Y. C.; writing - review & editing, Y. C. and G. T. S.; funding acquisition, G. T. S. and A. D. T.; supervision, G. T. S.

4.7 Conflicts of interest

There are no conflicts to declare.

4.8 Acknowledgments

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Chapter 5

Spectral Harvesting: A New Geometric Approach to Spectral Decomposition of X-ray Absorption Spectrum

This chapter is based on a manuscript under preparation with the following authors: Yeu Chen and Gerald T. Seidler.

5.1 Abstract

X-ray absorption spectroscopy (XAS) is a powerful, element-specific analytical technique used across diverse disciplines and capable of tracking multiphase chemical transformations [1–28]. However, isolating unknown pure-phase profiles from an experimental mixture ensemble is a challenging inverse problem, analogous to the classic cocktail party problem in signal decomposition [29]. Traditional methods, such as Linear Combination Analysis (LCA) and Target Transformation Analysis (TTA), approach this problem by relying heavily on *a priori* reference libraries, which are frequently unavailable for novel, transient, or highly disordered systems [30, 31]. Conversely, unsupervised methods like Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) require no prior knowledge and utilize simple physical constraints, such as non-negativity of spectral and concentration profiles and unity summation of concentrations [32]. However, MCR-ALS suffers from severe rotational ambiguity and numerical instability when the constituent pure-phase spectra exhibit weak linear independence [32]. Although the rotational ambiguity problem could likely be improved by imposing additional physical constraints on the candidate pure-phase spectra, the structure of the matrix-based algorithm makes it difficult.

Here, we present "spectral harvesting" [33], a new method for imposing a wide range of physically and chemically motivated prior information. By applying more rigorous physical constraints on absorption spectra to filter out unphysical regions in the Principal Component Analysis (PCA)

latent space, our algorithm then performs geometric simplex fitting to isolate pure-phase candidates from the mixture.

Using simulated and experimental datasets, we demonstrate that this geometric approach avoids the initialization sensitivity and rotational ambiguity of MCR-ALS. Additionally, using multiple case studies, we discuss how algorithm performance is affected by input criteria such as oxidation-state shifts, linear dependence of the data, and detailed spectral features.

5.2 Introduction

X-ray absorption spectroscopy (XAS) is a powerful, non-destructive analytical technique that provides element-specific electronic and structural information about a target compound. This capacity has made XAS a cornerstone diagnostic tool across diverse scientific disciplines, proving particularly invaluable for operando investigations of active chemical systems [1–28]. Because XAS acts as a targeted probe of local chemical changes at a specific atomic site, it can track transient states in real time [1, 2, 6, 7, 9, 15, 18, 20, 26]. Coupled with the exceptional photon flux delivered by modern synchrotron facilities, operando XAS yields dense, high-resolution datasets that map intricate, multi-phase chemical trajectories as reactions unfold.

There are two questions that are commonly asked when studying multi-phase chemical reactions: (i) what is the rate of the reaction, and (ii) what chemical phases are involved. To address the first question, we first note that the experimentally measured absorption spectrum is a linear combination of all chemical phases of the selected element present in the sample, and the weighting of each component is directly related to the mole fraction of each phase. If all phases present in the

reaction are known, one can perform Linear Combination Analysis (LCA) using known reference spectra to deduce the mole fraction of each phase at different stages of the reaction [34–37]. Hence, addressing the second question is often most crucial for understanding a chemical reaction, as we frequently lack a complete picture of all the chemical phases that emerge during such a reaction.

As described above, each of the experimental spectra $\mu(E)$ can be written as a linear combination of a set of N *pure* spectra (or phases) s_i as

$$\mu(E) = \sum_{i=1}^N c_i s_i, \quad (5.1)$$

where c_i are the mole fractions of each of the pure phases. Here, a pure phase means a spectrum from a single chemical compound. For example, a reaction converting CuO to Cu₂O will have absorption spectra from CuO and Cu₂O as two pure phases, with $N = 2$. Experimentally, an ensemble of $\mu(E)$ will be collected, and one common goal is to infer the pure phases s_i from the experimental ensemble.

The standard starting point to tackle such a problem is Principal Component Analysis (PCA) [38]. To understand how PCA works, we first note that Eq. 5.1 can be written in matrix form as

$$X = SC^T, \quad (5.2)$$

where the columns of X and S are experimental and pure phase spectra, respectively, and the columns of C^T contain the related concentrations of each of the experimental spectra. The PCA

algorithm performs singular value decomposition (SVD) on the matrix X and rewrites it as

$$X = U\Sigma V^T, \quad (5.3)$$

where U and V are two square unitary matrices and Σ is a diagonal rectangular matrix. Matrix U contains in its columns the eigenvectors of the covariance matrix associated with X , which are the so-called principal components (PCs), and the diagonal elements of Σ are the singular values and are related to the variances associated with the dataset's principal components. The matrix V^T shows on its rows the eigenvectors of $(XX^T)^T$, which can be interpreted as the projections of X over the entire set of principal components. The variance of a PC is a quantitative measure of how much physical information or variability a specific component captures from the experimental dataset. By default, the PCA algorithm outputs PCs in decreasing order of variance. There are standard procedures for determining the minimum number of PCs (called primary principal components) needed to fully explain the experimental set [39–41]. These PCs are then used as basis vectors to span the latent space, a simplified mathematical subspace where multidimensional data is reduced to its most informative principal directions.

For an experimental dataset involving N linearly independent pure phases, the primary PCs will be the set $PC_0, \dots, PC_{N-1}$, where PC_0 is the average of all experimental spectra and always has a weighting of one, leaving $N - 1$ tunable variables in the latent space. The reduction in dimensionality comes from the fact that for every experimental spectrum, the mole fraction weighting in Eq. 5.1 sums up to one ($\sum_{i=1}^N c_i = 1$). This imposes a constraint on the N -th pure-phase component, reducing the dimensionality by one.

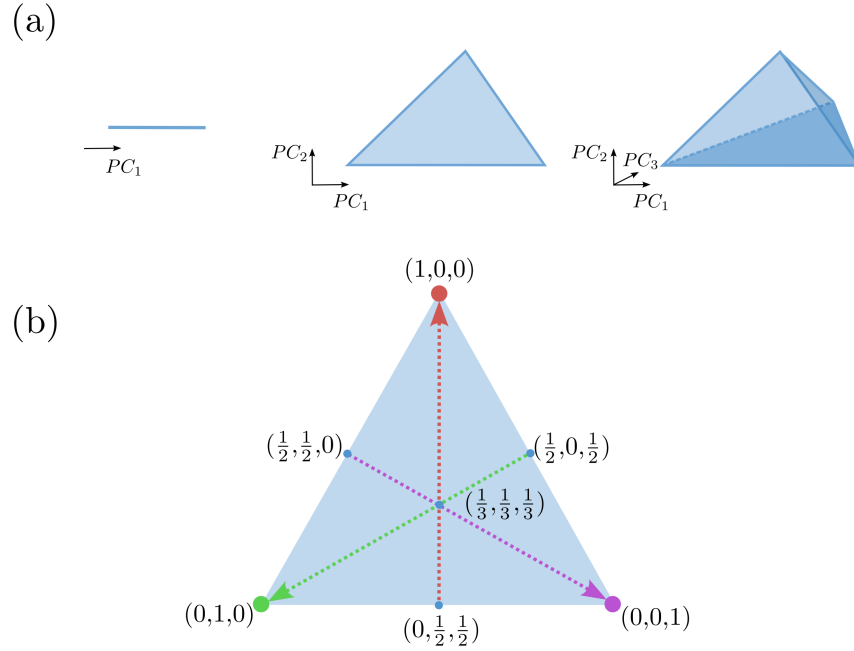


Figure 5.1: (a) Demonstrating simplex in one (line segment), two (triangle), and three (tetrahedron) dimensions. (b) Using 2-D simplex as an example, the pure phases reside on the vertices of the triangle, and any spectrum outside of the simplex represents a negative concentration of at least one of the pure phases and cannot be physical. Spectra that lie within the triangle satisfy $\sum_{i=1}^N c_i = 1$ and $c_i \geq 0$, and the contribution from each phase can be inferred from three axes drawn, where the arrow corresponds to the transition from zero to 100 percent contribution of the corresponding phase. This concept can be generalized to simplices in all dimensions.

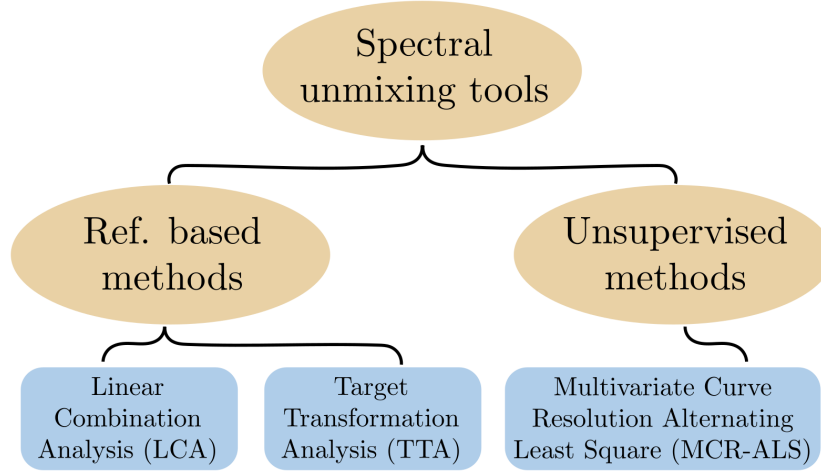


Figure 5.2: Common methods for performing spectral decomposition.

Another useful fact $\sum_{i=1}^N c_i = 1$ provides is that it imposes a constraint on where experimental spectra can lie in the $(N - 1)$ -D latent space for any possible combination of c_i 's. This region forms a $(N - 1)$ -D simplex as illustrated in Fig. 5.1 (a) [42]. Any spectrum outside this region corresponds to at least one negative c_i and hence cannot be physical. Using a 3-phase system as an example, the physical region is a 2-D triangle in which the pure phases reside at the three vertices. In Fig. 5.1 (b), we show the three pure phases with different colored dots, and the corresponding axis pointing towards the vertex represents the progression from zero to 100 percent contribution of that phase. This concept generalizes to simplexes in all dimensions.

Current methods for identifying pure phases fall into two main categories: those based on partial knowledge of the pure phases [42] and those that require no prior knowledge (Fig. 5.2). The best-known method in the first category is the Target Transformation Analysis (TTA), in which spectra from a candidate set of pure phases are tested individually to determine whether they can be reconstructed from the primary PCs [6, 30]. In other words, TTA assesses whether the test

spectrum lies in the latent space spanned by the primary PC's or not. Obviously, TTA requires strong prior knowledge of the system and can be sensitive to slight differences between the test and the true pure-phase spectra. For a system without well-established reference standards, TTA will not be suitable.

The second category, also called the Multivariate Curve Resolution (MCR) Approach [7–28] aimed to realize the decomposition in Eq. 5.2 from the sole information derived from the original data matrix X along with some simple physical constraints on the decomposed matrices S and C (non-negativity on both S and C and unity summation on C). The MCR approach involves an iterative process to refine the pure phase and concentration matrices, effectively rotating the pure-phase orthogonal basis in the N -D spectral space until a solution that satisfies the non-negativity and unit-summation constraints is found.

Currently, the most commonly used MCR algorithm is the Alternating Least Squares (MCR-ALS) method [7–28, 43–46]. After PCA is performed, the MCR-ALS algorithm first estimates a set of spectra profiles (S), with the number of spectra equal to the number of primary PC. This initial estimate of S is most commonly obtained using the "simple-to-use interactive self-modeling mixture analysis" (SIMPLISMA) [47], which selects the most linearly independent spectra from the experimental set. The ALS optimization loop assumes the current spectral shapes are correct and calculates C that satisfies

$$C = X^T S (S^T S)^{-1}. \quad (5.4)$$

Since real-world concentration is non-negative and sums to unity, the MCR-ALS algorithm forces all negative values in C to zero and normalizes the concentration set. With this new concentration

profile C_{new} , a new spectra set S_{new} is then calculated using

$$S_{new} = XC_{new}(C_{new}^T C_{new})^{-1}, \quad (5.5)$$

followed by the same non-negativity constraint applied to S_{new} . At the final step of the iteration, the residual, $\varepsilon = X - S_{new}C_{new}^T$, is then evaluated. If the residual is smaller than a preset threshold, the iteration stops, and the pure phases are the spectra contained in S_{new} ; if the residual is greater than the threshold, the iteration starts again to obtain an updated set of $S_{new}C_{new}^T$. The MCR approach can be effective but is sensitive to the initial estimate in the iterative process. Hence, MCR can sometimes suffer from the so-called "rotational ambiguity", where more than one solution of $S_{new}C_{new}^T$ exists that satisfies the non-negativity and unit-summation constraints, and a poor choice of initial guess can lead the algorithm to select an incorrect set of solutions. This often happens when the experimental data set has weak linear independence [32].

To better understand the rotational ambiguity associated with MCR-ALS, we visualize the MCR-ALS solution in both spectral and latent spaces. Using a three-phase problem as an example, in Fig. 5.3 (a) we show the MCR-ALS pure phases in a 3-D spectral space. The three axes represent the true pure phases, and the linearly independent vector set $\vec{s}_i$ represents the identified pure phases obtained through MCR-ALS. The experimental data lie on a 2-D plane (P) due to the $\sum_{i=1}^N c_i = 1$ constraint, where c_i are the concentration profiles with respect to the pure phase. Since $c_{i,new}$ (concentration profiles with respect to the MCR-ALS-identified pure phase) also satisfy unit summation, all spectra reconstructed using $\vec{s}_i$ also lie in a 2-D plane P_{new} . Since both P and P_{new} contain all experimental data, $P = P_{new}$, and the MCR-ALS-identified pure phases must lie on the

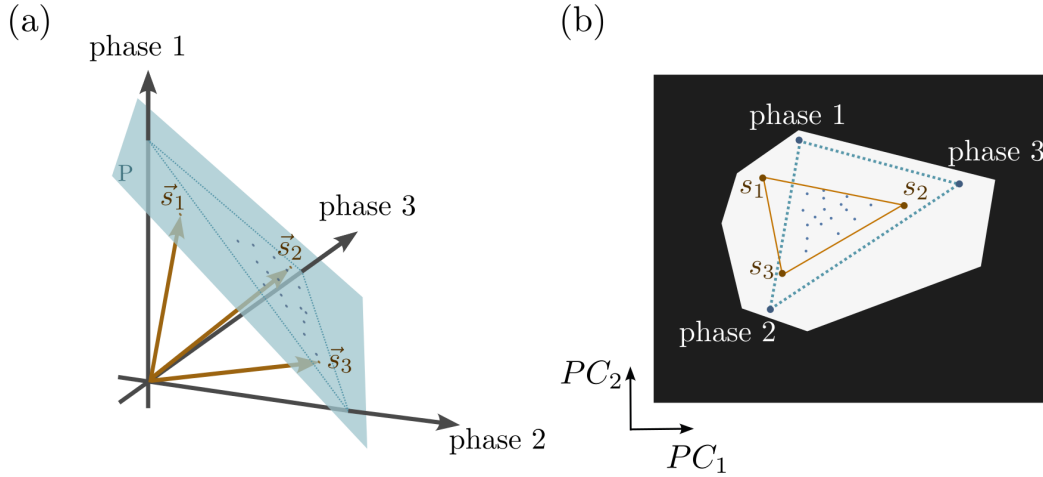


Figure 5.3: Visualizing MCR-ALS results in spectral and latent space using a three-phase example. (a) In the 3-D spectral space with axes representing each of the pure phases, all experimental data lie on a 2-D plane P . The MCR-ALS-identified pure phases are a set of linearly independent vectors $\vec{s}_i$ that span the same spectral space, with tips lying on the plane P . (b) Physicality map showing the non-negative spectral region (white) in the 2-D latent space. The true pure phases form a 2-D simplex (dashed blue line), and all experimental data lie within this region. The MCR-ALS algorithm requires that the identified pure phases (s_i) remain within the non-negative region, with the triangle formed by the vertices s_i enclosing all experimental data.

plane P .

Moving on to lower dimensions, Fig. 5.3 (b) shows the non-negative region (white) in the reduced 2-D latent space. This is called the Area of Feasible Solutions (AFS), a region that must contain the solutions to the pure phases (s_i). The true pure phases are marked with blue dots, and all experimental data must also be contained in the simplex formed by these pure phases (dashed line). Since s_i can reconstruct all experimental spectra with all positive concentrations, the 2D simplex formed by s_i must also contain all experimental data points. However, any simplex that lies within the AFS and encloses all experimental data can be an MCR-ALS solution, meaning that if all experimental data are clustered about a point, the MCR-ALS solution simplex can freely rotate about that point. One possible way to reduce rotational ambiguity is to further limit the

AFS by imposing additional physical constraints based on partial knowledge of the system. With a series of additional physical constraints, one can even reduce the AFS closely to the true physical region, and then identifying the pure phases becomes purely a geometric problem.

The idea of utilizing reduced AFS is a relatively novel approach in XAS spectral decomposition. In recent work done by Timoshenko et al. [48], an AFS is generated with the aid of supervised machine learning. The machine learning model was trained by scanning through all relevant compounds on the Materials Project database and performing XANES simulations on all of these structures. Such a model is then used to evaluate candidate spectral samples within the latent space, assigning a physical plausibility score that guides global optimization algorithms toward realistic pure-phase solutions. While effective, this data-driven framework relied heavily on extensive computational databases and element-specific neural network training sets to establish spectral plausibility scores. In any event, Timoshenko et al. successfully showed that using additional spectral constraints to reduce the AFS is the effective solution to rotational ambiguity.

In this paper, we propose "spectral harvesting" [33], a geometric approach for improving pure-phase identification that directly addresses the unique challenges of unmixing complex XAS datasets by imposing a series of physical constraints. Instead of using artificial intelligence to apply these constraints, as Timoshenko et al. did, we exploit human intelligence to apply physics- and chemistry-driven spectral constraints. By superimposing the AFS from a set of physicality tests, the algorithm isolates true pure-phase candidates via multi-dimensional simplex fitting. Because spectral harvesting directly targets the geometric simplex vertices of the AFS boundary, it drastically reduces the dependence on experimental data sets. Consequently, our algorithm retains

stability when evaluating weakly linearly independent data and effectively minimizes rotational ambiguity inherent in the conventional MCR methods. Additionally, the AFS generated by the spectral harvesting algorithm can be used as an aid to other spectral decomposition algorithms, such as LCA, MCR-ALS, or some machine learning frameworks, allowing users to provide more physical insight into the phase identification process. Our spectral harvesting software provides an intuitive graphical user interface (GUI) and is designed to be adaptive to different chemical systems by allowing users to define their own physical constraints. The package is currently open-sourced on GitHub at <https://github.com/HelenChen86/MySpecFarm> [33].

In the remainder of this work, we outline the workflow of our spectral harvesting algorithm and the formulation of a set of pre-defined general physical constraints in the Method section, followed by a systematic evaluation of the algorithm’s performance across several case studies using both simulated and experimental datasets in the Results and Discussion section. Through these examples, we demonstrate that weak linear independence has a smaller effect on our framework compared to the standard MCR-ALS and discuss how specific spectral criteria influence the optimization boundaries.

5.3 Method

In Fig. 5.4, we present a workflow diagram for our latent-space pure-phase spectral harvesting algorithm. The algorithm has three parts: (i) input data generation, (ii) AFS reduction through physical constraints, and (iii) pure-phase candidate extraction. Component (i) is solely for simulation purposes; if real experimental data is used, only standard spectral pre-processing is required,

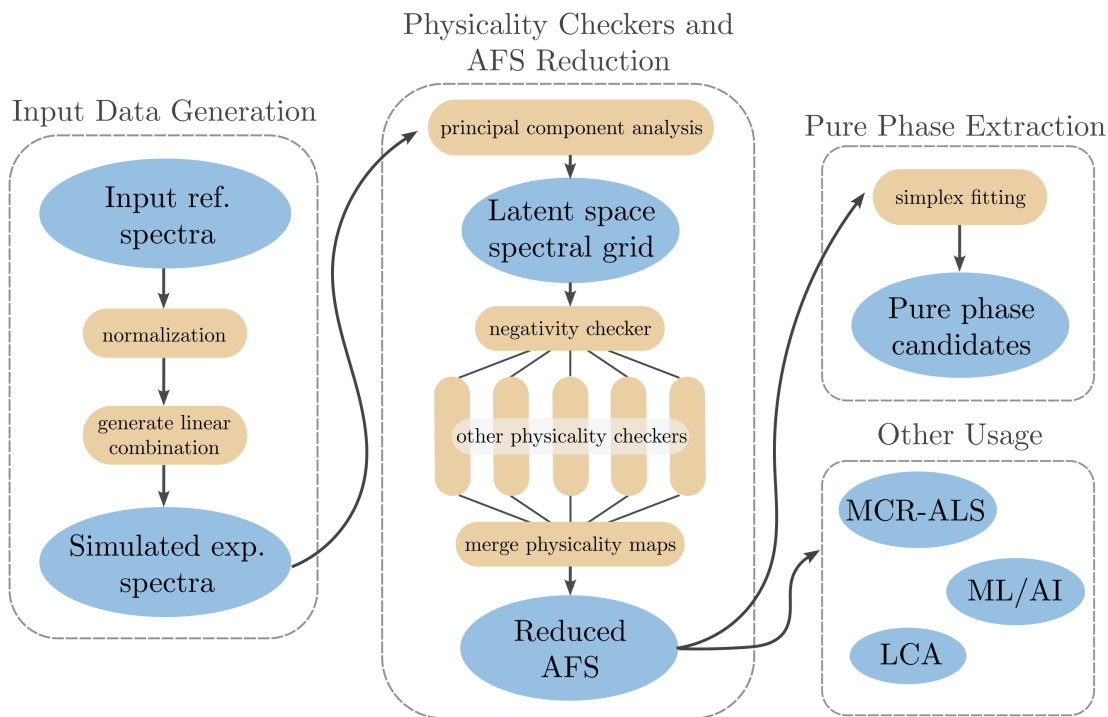


Figure 5.4: Workflow diagram of the latent space pure phase harvesting algorithm.

such as normalization and pre- and post-edge flattening. Each of these components is discussed in detail in this section.

5.3.1 Input Data Generation

The input data set for the spectral harvesting algorithm consists of spectra that are linear combinations of a set of pure phases with non-negative component weights that sum to one. For most of the studies in this paper, we artificially construct the input spectrum set by linearly combining Cu K-edge synchrotron absorption spectra from different Cu compounds, subject to the unity-concentration summation constraint. The pure-phase reference spectra are obtained from the Canadian Light Source XAS database (unless noted separately) and are normalized and pre- and

post-edge flattened using Larch [49] before linear-combination processing. The generated input spectrum set from linear combinations consists of 20 to 40 spectra, and the weighting of each phase can be evenly distributed or skewed depending on the study.

We also use experimentally collected mixed-phase Cu K spectra measured at beamline X16C of the National Synchrotron Light Source at Brookhaven National Lab, as presented by Wang et al. [1]. The sample was prepared by brushing fine CuO powder onto adhesive Kapton tape, then loaded into an in situ flow cell and heated to 260 C°. The sample was then exposed to a flowing 5% CO/95% He gas mixture, and X-ray absorption spectra were repeatedly recorded in transmission mode. For real experimental data, each spectrum should be normalized and flattened before being fed into the spectral harvesting algorithm. For convenience, we refer to both simulated and experimentally collected input spectrum sets as "experimental spectra" in this paper. A special note will be included when the actual experimental spectra are used.

5.3.2 Physicality Checkers and Latent Space Reduction

The experimental spectra are first processed by PCA, and an appropriate set of primary PCs is then selected to define the dimensionality of the latent space. The latent space is then scanned by a series of standard general-physicality checkers, which output binary maps outlining the AFSs. These binary maps are then merged with a logical AND to produce the final reduced AFS. This process is illustrated in Fig. 5.5. The basic usage of the spectral harvesting GUI will be to define a single AFS applicable to all pure phases. A more advanced usage will be defining additional AFS that are phase-specific through user-defined checkers. A detailed explanation of handling multiple

AFSs is included later in the section.

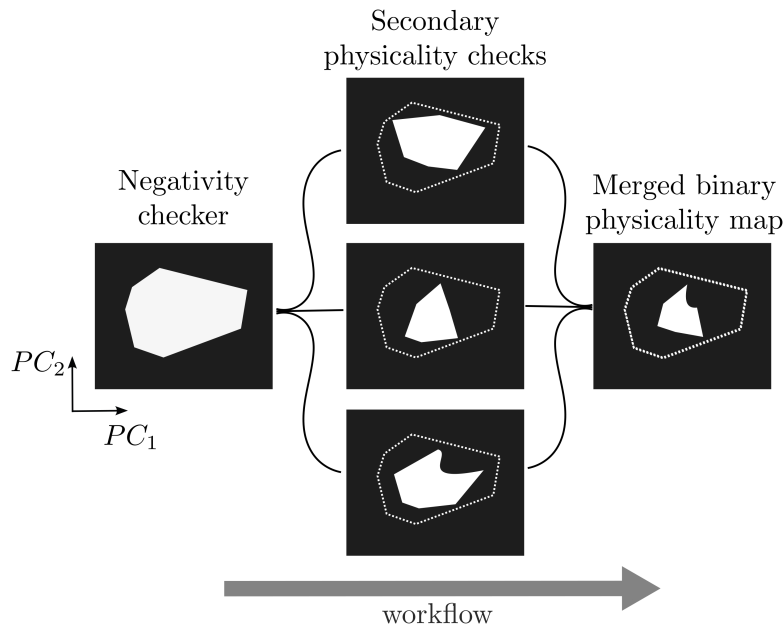


Figure 5.5: Workflow diagram illustrating how physicality checkers reduce latent space to only the physical region recognized by the user (i.e. AFS). This particular example has a 2-D latent space (i.e., three pure phases). The negativity checker serves as the primary physicality test. The user can choose to operate only within the non-negative region for all subsequent tests to reduce calculation time.

Below, we describe each physicality check in detail, accompanied by figures. These figures show the AFS generated by the checker on the left and an example set of PC-reconstructed spectra along the color arrow on the right. These spectra are evenly spaced in the latent space and span from physical (solid line) to unphysical (dashed line) regions. In general, these predefined physicality checkers can operate in two modes: "data-driven defaults" (derived directly from the experimental dataset's statistical bounds) and "physics-driven Boundaries" (derived from fundamental spectroscopic constraints). Default settings are designed to be permissive baseline rules that prevent optimization runaway without discarding any physical input spectrum.

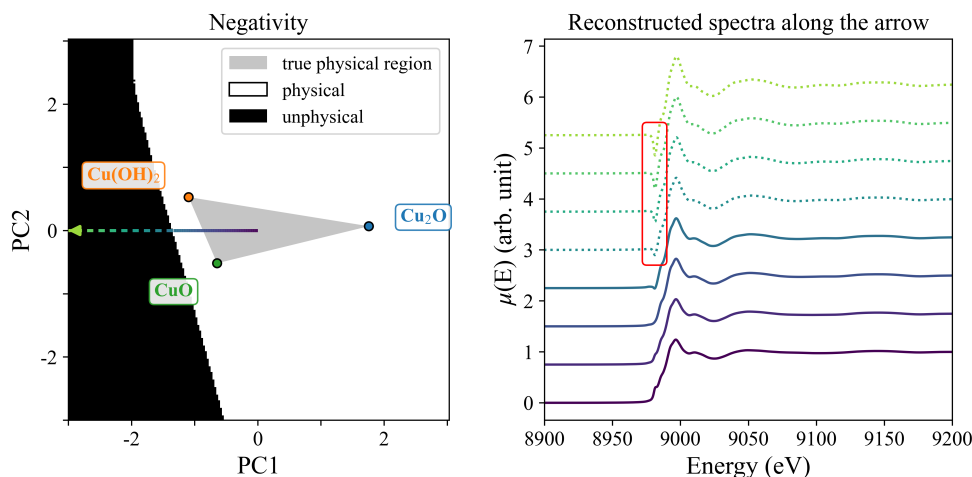


Figure 5.6: Negativity physicality map and example spectrum set. The portion where spectra go negative is boxed in red.

Negativity checker (Fig. 5.6) The negativity checker rejects any spectrum with negative values; it is the first physicality test used by the spectral harvesting algorithm and is a primary constraint in MCR-ALS. The negativity checker is the only required physicality test in the GUI, and it defines the latent-space spectral grid point and search region for all subsequent physicality tests. The user can choose to perform subsequent physicality tests only within the non-negative region, which could greatly reduce processing time when using some computationally heavy secondary tests. To avoid over-constraining due to negative spectral values from experimental noise or imperfect pre-edge flattening, the algorithm first performs nearest-neighbor smoothing and only rejects negative values that are persistent (i.e., consistently negative across a threshold number of data points). A `neg_slack` value can also be given to allow slightly negative spectral values.

Edge onset dip checker (Fig. 5.7) One major way to trigger the negativity checker is to subtract a near-edge feature from the edge onset. The features in this energy range are either a pre-edge peak or a white line, so the resulting feature will be a sharp, narrow dip on the smoother rising

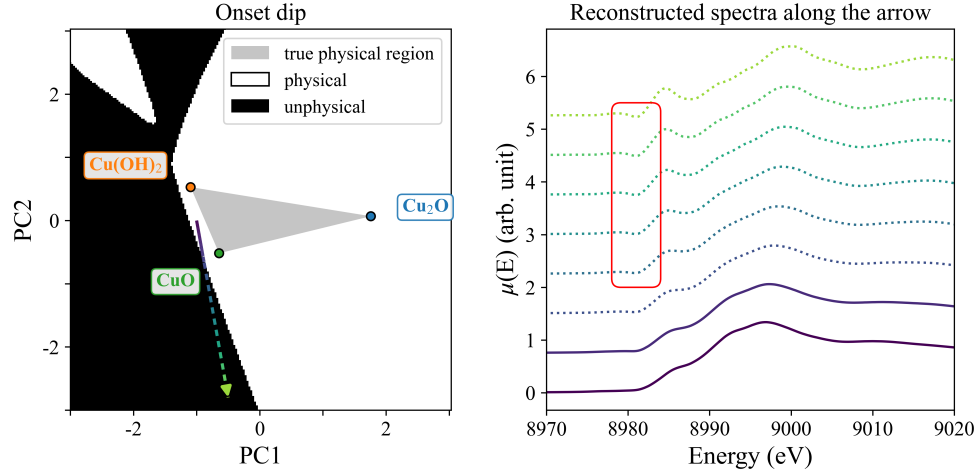


Figure 5.7: Edge onset dip physicality map and example spectrum set. The portion with an unphysical dip on the Lorentzian rising edge is boxed in red.

Lorentzian. Since absorption mode should be additive in this energy range, such a dip renders the spectrum unphysical. The edge-onset dip checker can detect such a dip even before the spectral value becomes negative. This function takes a search range and smooths the spectrum within that range to reduce the effects of noise. Then, the checker will search for an inverted peak based on the set minimum prominence and maximum peak width. Any spectra with an identified peak in this range will be excluded from the AFS.

White line amplitude checker (Fig. 5.8) Outside of the true physical region, though $\sum_{i=1}^N c_i = 1$ is still true, at least one c_i will be negative and $|c_i|$ does not have an upper bound. In such cases, spectral oscillation from one pure phase can be amplified if no opposing cancellation exists from other pure phases. For example, when one spectrum in the pure phases has a white line with a weighting much greater than one, if the pure phase that goes negative does not have a white line, the resulting spectrum can have an unrealistic intensity just above the edge. The white line amplitude checker imposes closed bounds on μ oscillation amplitude by taking the threshold to

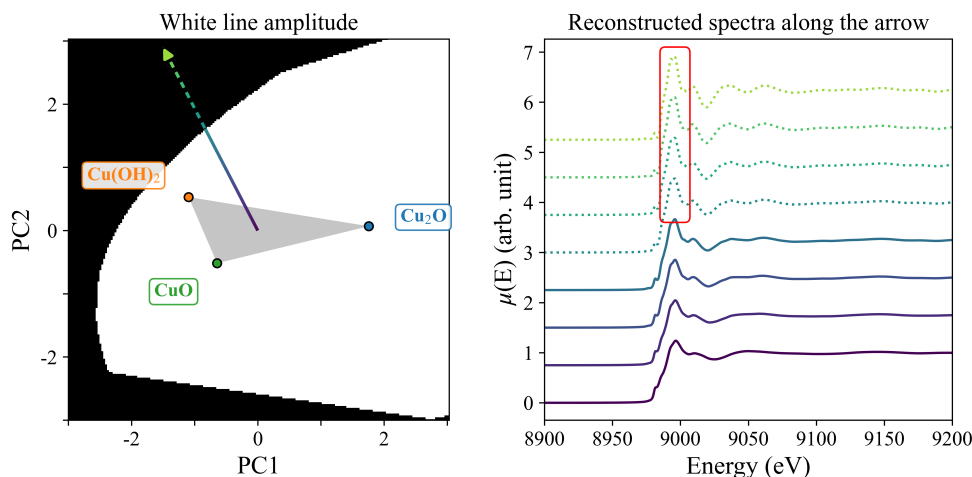


Figure 5.8: White line amplitude physicality map and example spectrum set. The portion where the white line intensity increases significantly is boxed in red.

be the maximum white line amplitude in the experimental data. This threshold is tunable via an absolute tolerance. Physically, the white line intensity is governed by the number of valence states in the conduction band, so if the user self-selects a physicality threshold, they are advised to consult reference spectra of similar chemical composition to gauge which parameter value is appropriate. This is particularly important when the chemical reaction is strongly weighted toward one phase. In such cases, data-driven default parameter values might unknowingly reject a potential pure phase.

μ oscillation decay checker (Fig. 5.9) The EXAFS oscillation from different pure phases can sometimes interfere constructively. With $|c_i|$ not having an upper bound as one of c_i goes negative, this can render the oscillation amplitude unphysical. One way to identify this type of constructive interference is to observe the decay rate of μ . All absorption spectra exhibit exponential decay of oscillation amplitude with energy; however, for an unphysical spectrum, damping becomes small due to some combination of unphysically large $|c_i|$ and unreal constructive interference. The μ oscillation decay checker finds the smallest exponential decay constant that encompasses all

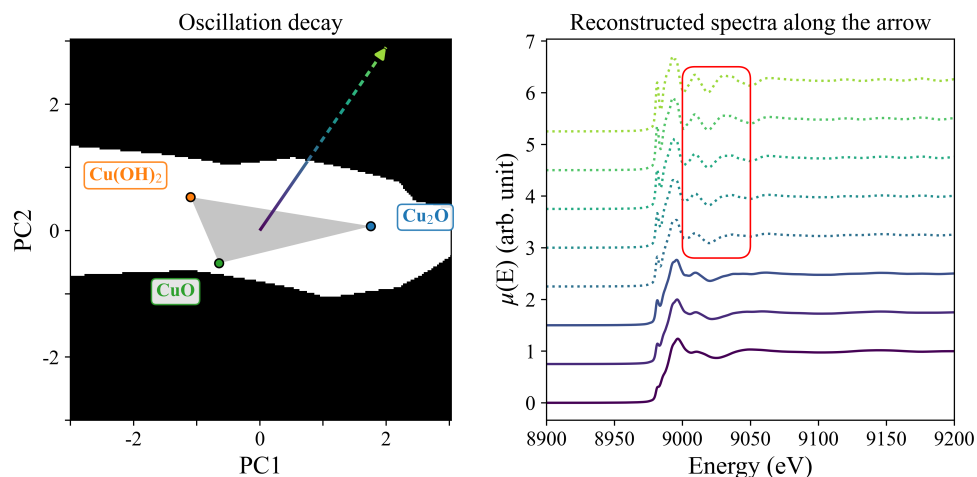


Figure 5.9: μ oscillation decay physicality map and example spectrum set. The region where damping in μ slows is boxed in red. The oscillation amplitude in mu is much greater in the same energy range compared to the solid-line spectra.

experimental data and uses that number to reject any spectra that have a slower decay rate. Again, the damping of EXAFS oscillation is governed by physical properties such as the Debye-Waller effect. If users wish to define the parameter values themselves, more detailed, system-specific theoretical calculations of the decay rate should be performed.

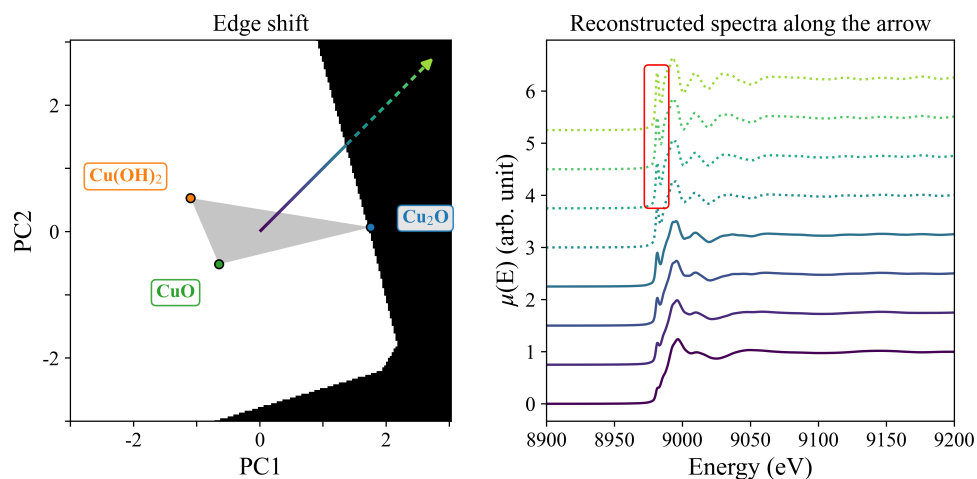


Figure 5.10: Edge shift physicality map and example spectrum set. The region where the pre-edge feature intensity increases sufficiently to be mislabeled as an edge is boxed in red.

Edge shift checker (Fig. 5.10) When one of the pure phases has a pre-edge feature or an edge shoulder, unphysical weightings can amplify these features. This results in a spectrum that appears to have the edge shifted down in energy. Physically, a change in edge location is related to a change in the binding energy of the core electron that is probed; the possible edge energy hence must be bounded. The edge shift checker takes a threshold value and identifies any spectral feature that crosses it as an edge. The edge energy is then calculated using the half-edge step method. The algorithm automatically determines the range of edge energy spanned by experimental spectra, and the edge shift checker defines a spectrum with an edge in this energy window as physical. This window can be adjusted by extending the boundary symmetrically if desired.

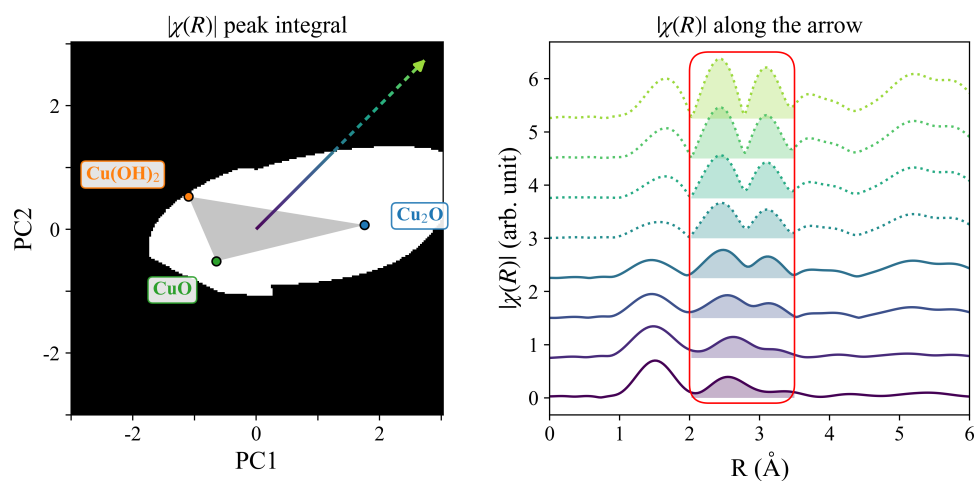


Figure 5.11: $|\chi(R)|$ peak integral physicality map and example spectrum set. The checker imposes an upper bound on the integral value in a given R range. For this particular example, choose to monitor the second and third shell peaks boxed in red.

$|\chi(R)|$ peak integral checker (Fig. 5.11) The last standard physicality check is by examining $|\chi(R)|$. The amplitude and area integrals of $|\chi(R)|$ correspond directly to the coordination number and hence should have an upper bound. When unphysical weighting causes the oscillation am-

plitude in $\chi(k)$ to increase, the Fourier transform will reflect this increase in the peak integrals of each shell. The $|\chi(R)|$ peak integral checker calculates the integral of $|\chi(R)|$ in a selected R range, and rejects spectra with an integrated value greater than some set threshold value. If desired, the user can run a FEFF simulation on a similarly structured compound to gauge what a reasonable $|\chi(r)|$ peak integral is. Otherwise, the threshold value should be set based on the input spectra. For this example, we choose to monitor the second- and third-shell peaks. This is because, oftentimes, all pure phases have similar first-shell bond lengths, meaning that the oscillation in $\chi(k)$ due to first-shell ligands mostly coincides in momentum space. When phases coincide, any unphysical weighting of one phase will be canceled out by the other due to the unity sum of the weights. This results in the first peak amplitude not changing much in $|\chi(R)|$. On the other hand, the second and third shells are more likely to have different bond lengths between phases and therefore will not have this problem.

In Table.5.1, we summarize all predefined standard physicality checkers, along with descriptions of the physical constraints that motivate them. Parameters commonly used in the GUI relating to that checker are also listed in the table.

User-defined physicality checks Depending on the system, users might wish to use additional system-specific physicality tests to truncate the latent space. The spectral harvesting software allows users to easily define custom Python functions to achieve this. The user can input a Python function that returns a truth value when given a reconstructed spectrum in the form of μ , $\chi(k)$, or $|\chi(R)|$; the software will then evaluate the function at the given latent space grid point and output the custom-defined physicality map. In Table 5.2, we summarize the physics- and chemistry-driven

Physicality check	Constraining factor ¹ & Motivation ²	Parameters
Negativity	1. Negative spectral value. 2. $\mu < 0 \rightarrow$ transmitted beam intensity is larger than incident beam intensity in an absorption process.	• <code>PC_coeff_range</code> : latent space search range. • <code>res</code> : latent space grid resolution. • <code>smoothing_window_ev</code> : μ smoothing window width. • <code>neg_slack</code> : negative floor adjustment. • <code>min_neg_points</code> : consecutive sub-floor points required for rejection.
Onset dip	1. Narrow dip on the Lorentzian edge onset. 2. Absorption mode must be additive in pre-edge energy range.	• <code>onset_lower/upper_energy</code> : search window in eV. • <code>onset_dip_prominence</code> : minimum prominence of identified dip. • <code>onset_dip_max_width_ev</code> : maximum width of identified dip. • <code>smoothing_window_ev</code> : pre-smoothing before detection.
White line amplitude	1. Large white line amplitude. 2. Limited number of unoccupied states in the conduction band.	• <code>search_lower_bound</code> : check oscillation amplitude above this eV. • <code>tolerance</code> : absolute slack above the auto amplitude base.
μ oscillation decay	1. Slow damping in extended μ oscillation. 2. Damping rate must agree with the Debye-Waller effect and attenuation due to extrinsic losses.	• <code>search_lower_bound</code> : check amplitude decay rate above this eV. • <code>tolerance</code> : slack on the allowed decay constant.
Edge shift	1. Large shift of edge energy from the experimental average. 2. Limited shift of binding energy due to changes in valence electron configuration.	• <code>threshold</code> : μ level defining the edge crossing. • <code>tolerance</code> : eV slack added to the experimental edge window.
$ \chi(R) $ peak integral	1. Large $\chi(R)$ peak integral. 2. Coordination number must have an upper bound.	• <code>r_min/max</code> : integrating R range. • <code>tolerance</code> : slack above the max experimental first-shell integral.

Table 5.1: Overview of the spectral harvesting physicality checkers.

motivations that aid the definition of current and possible additional physicality checkers.

Property category	Physical and chemical properties
Envelope Constraints	• Binding Energy Limits: Core shifts reflect changes in electrostatic shielding and absorption edges must lie within bounds dictated by achievable formal oxidation states. • State Density Limits: Pre-edge and near-edge intensities map to unoccupied orbital densities and cannot exceed finite orbital degeneracy. • Scattering Amplitudes: EXAFS oscillations $\chi(k)$ and Fourier-transformed radial peak integrals $\chi(R)$ are physically capped by coordination numbers and atomic scattering factor. • Additive Cross-Sections: Photoabsorption is purely additive in the pre-edge region, and subtracting misaligned edges creates unphysical negative dips on the smooth Lorentzian rising edge.
Selectivity Constraints	• Ligand Radial Distances: Distinct interatomic bond lengths yield localized first-shell peaks at unique radial distances in $\chi(R)$. • Z-Dependent Phase Shifts: Photoelectron back scattering phase shifts $\delta(k)$ are unique to scatterer. • Symmetry & Selection Rules: Local geometry dictates allowed orbital mixing. • Higher-Shell Order: Strong higher-order shell spectral features exist in $\chi(R)$ collinear or near-collinear aligned atomic structure, which often comes with highly ordered crystal structures and heavy scattering atoms. • Extremal Redox States: Terminal reaction intermediates (e.g., fully reduced vs. fully oxidized species) define the physical boundary vertices of the latent-space AFS.
Basic Physics	• Lattice Damping: Thermal vibrations and structural disorder physically bound the Debye-Waller factor ($e^{-2k^2\sigma^2}$), dictating EXAFS oscillation damping. • Monotonic Kinetics: Species evolution requires continuous and monotonic (for single-step reaction) concentration profiles during reaction pathways. • Stoichiometric Anchors: Known initial reactants and final products establish grounded physical boundary anchors that enclose all transient mixtures.

Table 5.2: Physical and chemical properties that can be used to define physicality checkers.

5.3.3 Simplex Fitting

After all AFSs have been generated and merged using a logical AND, the resulting latent space is passed through a simplex-fitting algorithm. Assuming there is no over-constraining at each physical check, all experimental data and the simplex representing the true physical spectrum region should be contained in the AFS. If the AFS closely resembles the physical simplex, pure phases can be identified by acknowledging the vertices of a simplex with minimum volume that is contained in the AFS. To further restrict and prevent potential rotational ambiguity, the maximum simplex volume fitting algorithm requires that all experimental data lie within the fitted maximum volume simplex.

In some cases, users might have additional knowledge applicable only to certain phases. The software allows users to define secondary AFSs, and during the simplex fitting step, each vertex can be assigned to a different AFS region. This feature is often used with custom-defined physicality checkers, and we show an example in one of the case studies.

One additional feature of the pure-phase candidate identification process is the Minimum-Volume Transformation [42, 50], in which the fitted simplex minimizes its volume in the latent space while containing the data cloud. The Minimum-Volume Transformation is known to perform well when the true pure phases are included in the input spectra, or when all pure phases have at least one concentration profile that is close to 100 percent. When the input spectrum set is weakly linearly independent, Minimum-Volume Transformation can suffer from rotational ambiguity, similar to that in MCR-ALS. Note that this method does not account for any AFS. We make this feature available as an alternative that can be useful for cross-referencing in certain cases.

5.4 Results and Discussion

5.4.1 Case study 1: Two-phase Cu oxides (CuO and Cu₂O)

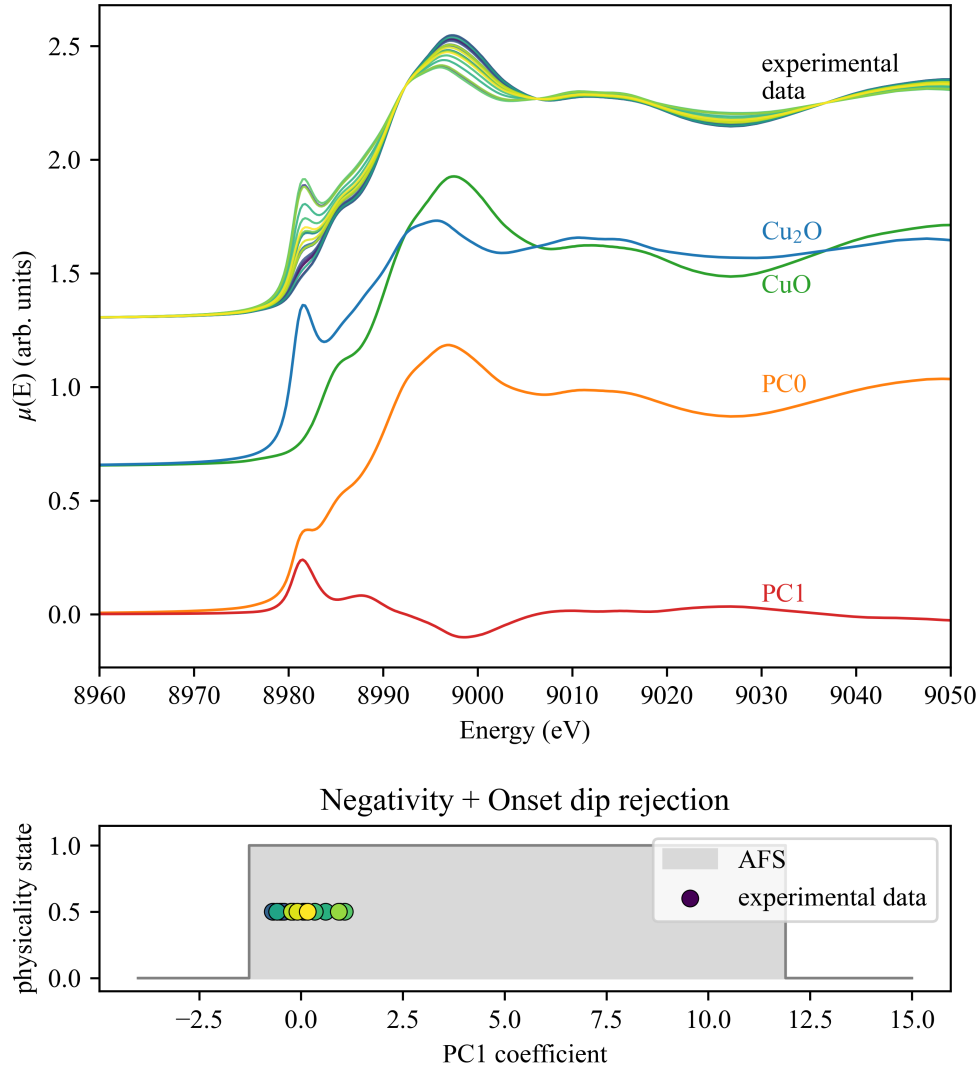


Figure 5.12: (Top) Three sets of spectra from top down are: simulated experimental data set through random linear combination of reference spectra, CuO and Cu₂O reference spectra, and primary PCs. (Bottom) Negativity map generated by the spectral harvesting algorithm. The gray region is where the reconstructed spectrum has no negative values and unphysical edge onset dip. The experimental data are marked using dots on the negativity map.

The first case study is a simple two-phase problem with two different Cu oxides. 20 experi-

mental spectra are generated by randomly mixing CuO and Cu₂O reference spectra (Fig. 5.12 top). The primary physicality check is non-negativity, and the only other check we add is the onset dip rejection. The resulting AFS is shown in Fig. 5.12 (bottom).

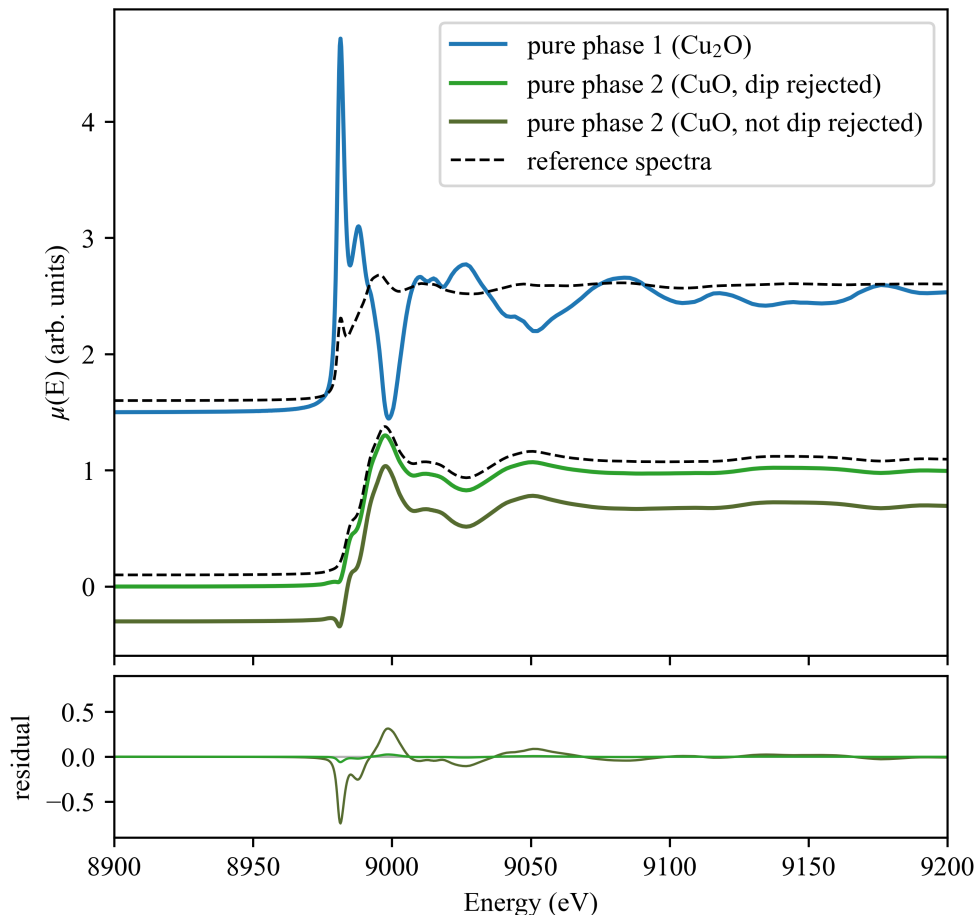


Figure 5.13: Candidate pure phases identified by only imposing the negativity checker (with and without the edge onset dip rejection). The higher-oxidation-state pure phase (CuO) can be well identified by the algorithm when only the negativity constraint is applied, especially when dip rejection is added. The residuals of the two candidate CuO phases (with and without dip rejection) are plotted below. The lower-oxidation-state pure phase, on the other hand, cannot be identified correctly.

In Fig. 5.13, we show the candidate pure phases identified through maximum simplex fitting. For a 1-D latent space case, the candidate pure phases are simply the physical boundary endpoints.

Even though the identified phase 1 is clearly non-physical, the identified pure phase 2 closely matches the CuO reference, particularly when the onset dip rejection is included. We find that this is often true for a two-phase problem in which the pure phases have mismatched edge energies, especially when the lower-oxidation-state phase (hence the lower edge-energy spectrum) exhibits a strong pre-edge feature. The physical reason the negativity checker successfully selects the higher-oxidation-state phase is illustrated in Fig. 5.14.

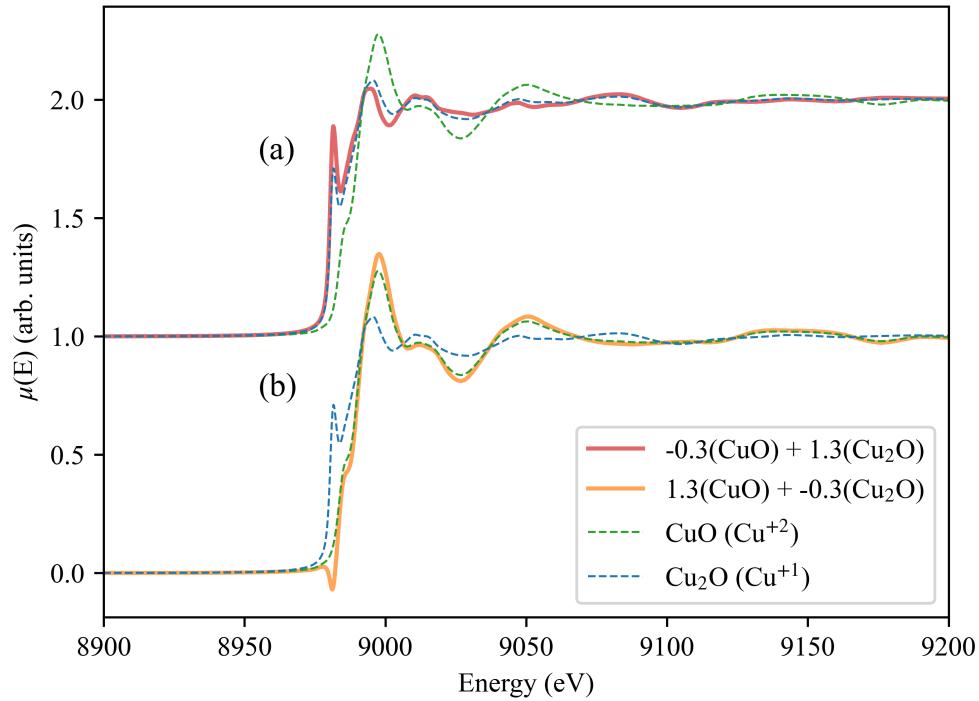


Figure 5.14: Linearly combining two oxidation state spectra (CuO and Cu₂O) with one of the spectra having negative weighting. (a) When the higher-oxidation-state spectrum (CuO) is weighted negatively, the resulting spectrum still looks 'physical'. (b) On the other hand, when the lower-oxidation-state spectrum (Cu₂O) is weighted negatively, the resulting spectrum shows a negative dip just before the edge.

In Fig. 5.14, we show two linear combinations of CuO and Cu₂O spectra with one phase having negative coefficients. Though the coefficients still sum to unity, the negative coefficients

render these spectra unphysical. Linear combination (a) has a slight negative weighting on CuO (the pure phase spectrum with a higher edge energy) while combination (b) has the same negative weighting but on Cu₂O instead.

When the lower-oxidation-state spectrum (Cu₂O) is weighted negatively, the resulting spectrum will have negative values immediately before the onset of the higher-oxidation-state spectrum (CuO). This is due to the misalignment of the absorption edge, where the higher-oxidation-state spectral value is effectively zero between the onsets of the two pure phases and thus cannot cancel any negative contribution from the lower-oxidation-state spectrum.

Hence, the negativity spectral value constraint is sensitive to negative contributions from the lower-oxidation-state pure phase, implying that the weighing of the lower-oxidation-state pure phase will be capped to near zero. This leaves the weighting of the higher-oxidation-state spectrum close to one at the non-negativity boundary. Capping the lower-oxidation-state weighting to zero using negativity checkers works particularly well when the lower-oxidation-state spectrum contains any pre-edge feature. When there is no pre-edge feature and the edge onset is smooth, one will need to rely more on the unphysical dip-rejection feature in the negativity checker to achieve the same result.

5.4.2 Case study 2: Three-phase Cu reduction ($\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$)

Next, we look at a three-phase Cu reduction process involving transitions between Cu oxides to Cu metal. The data used is a collection of Cu K spectra presented in Wang et al. [1] (Fig. 5.15). The spectra were collected sequentially during the transition of Cu from CuO to Cu₂O, then to Cu

metal, with scan number 1 indicating the start of the reaction.

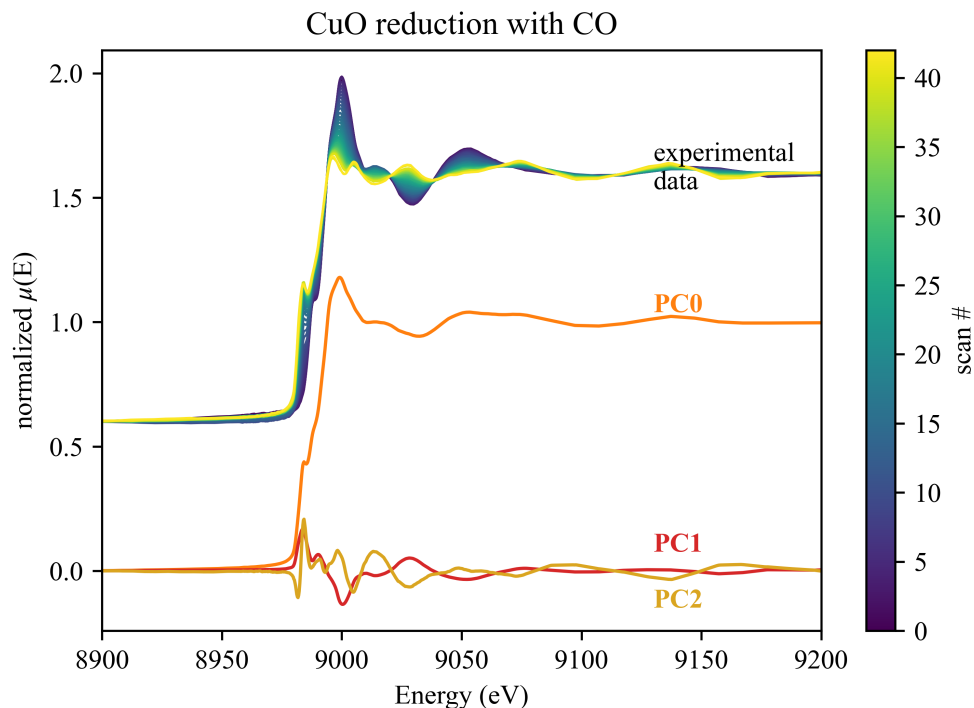


Figure 5.15: Cu K EXAFS recorded during the reduction process by Wang et al. [1] Each scan was performed sequentially, with scan number 1 marking the beginning of the reaction. The CuO powder was reduced under a constant flow of CO gas, transitioning from CuO to Cu₂O and then to Cu. The primary PCs are presented below the experimental spectra.

We process the Cu spectral set, performing all the physicality checks described in the methods section. The AFS (white region) generated by each checker is shown in Fig. 5.16, with experimental spectra marked. For a true chemical reaction, the measured spectra trace a linear trajectory in latent space. The left endpoint corresponds to the start of the reaction and, in our case, represents the pure CuO phase. It is also the highest-oxidation-state pure phase out of three. Recall the case study with two different oxidation-state pure phases; the higher oxidation state can be well recovered by identifying the 1-D AFS boundary. Although in 2-D latent space the highest-oxidation-state pure phase cannot be directly extracted from the endpoint as in the 1-D case, the

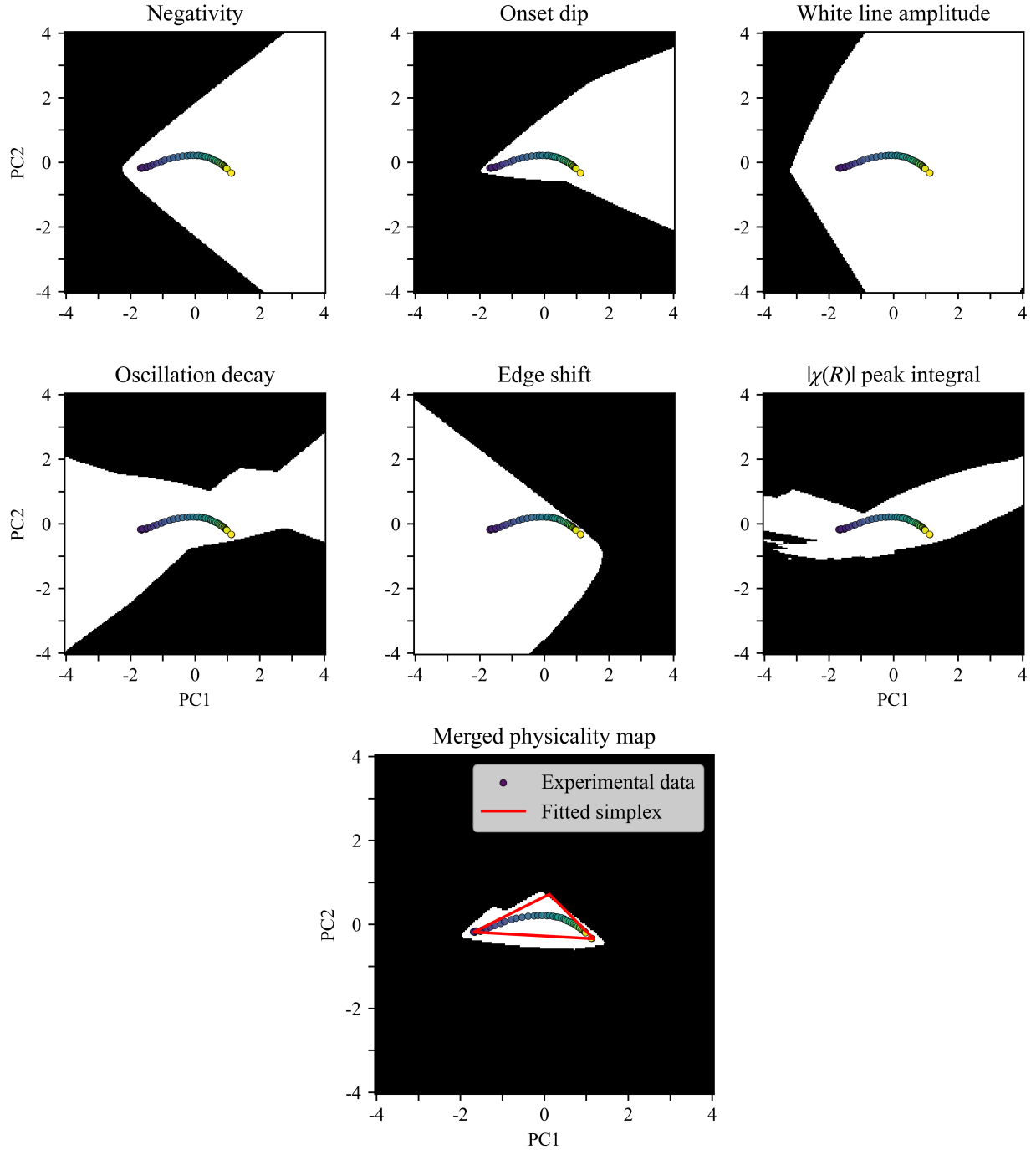


Figure 5.16: Physicality maps showing the AFS defined by all checkers mentioned in the method section. The merged map is shown at the bottom, with a fitted maximum-volume simplex overlay on top. Note that we use the knowledge that this transition starts and ends on a pure phase to help anchor the fitted simplex.

CuO phase sits in a "corner" in the non-negative region, following the same argument we gave earlier. This is true when only one pure phase has the highest edge energy. If there were two Cu^{2+} phases present as pure phases, negativity checkers would not be able to reduce the AFS to a corner around one of them. Another important point is that we use the fact that this chemical reaction starts and ends on a pure phase to help anchor two vertices of the fitted simplex.

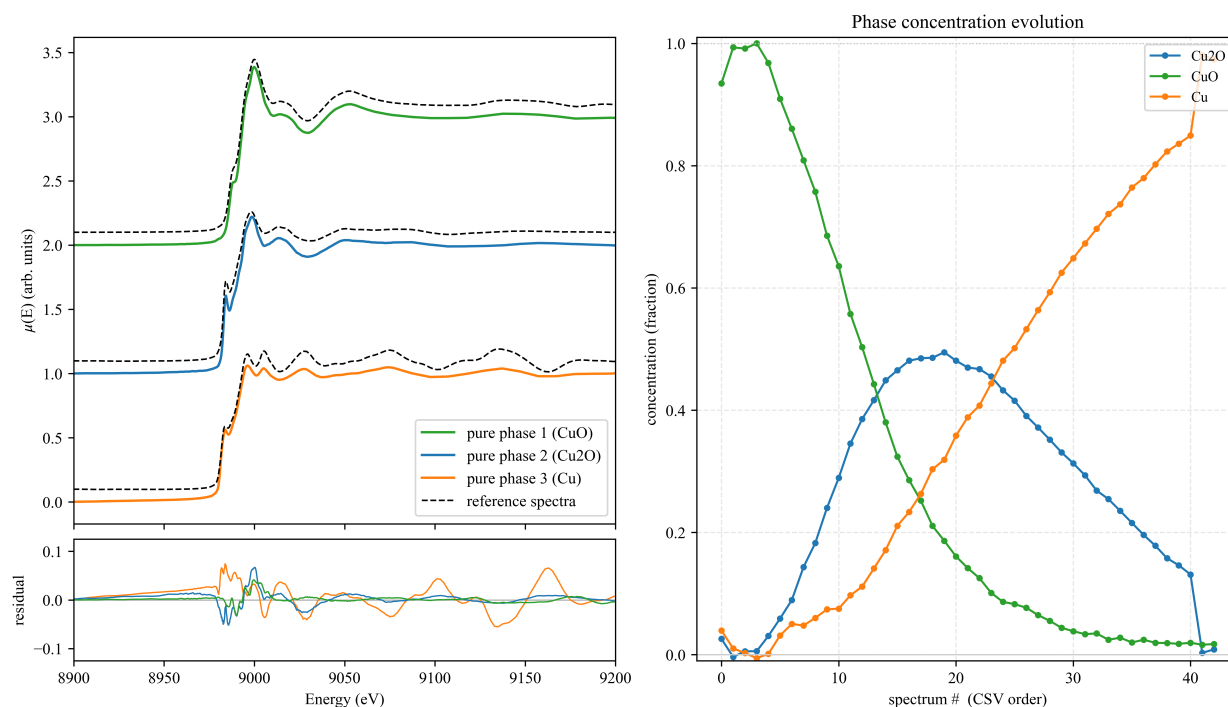


Figure 5.17: (Left) Three phases identified by spectral harvesting in Cu reduction reaction. The synchrotron references are included as dotted lines. The pure phases identified overall show a good match with the references, except in the extended region. This is because the synchrotron references are collected at room temperature, while our Cu reduction process is performed at 260 °C. (Right) Concentration evolution in time when reconstructing experimental spectra using the identified pure phase candidates.

In Fig. 5.17, we compare the pure phases identified by the spectral harvesting algorithm with synchrotron references and see that they agree overall (left). The deviation in the extended region can be due to the Debye-Waller effect. Since the experiment was performed at 260°C,

the amplitude is expected to be damped in the extended region compared to the reference spectra measured at room temperature. Additionally, we show the evolution of the concentration profile of each pure phase candidate over time on the right side of Fig. 5.17. Such evolutions can be used to validate the identified pure phase candidate, since in a real chemical reaction the concentration evolution should be smooth and monotonically increasing or decreasing. In this particular example, we do see such a trend except for minor fluctuations at the beginning and the end of the reaction. Such fluctuations are likely due to experimental instability when starting and ending the chemical reaction.

For comparison, we show the pure phase candidates and the concentration evolution when using the Minimum-Volume Transformation in Fig. 5.18. Notice that the pure-phase candidates do not vary much from those identified through maximum-volume simplex fitting. The concentration evolution profile, on the other hand, recognizes a heavier weighting on the Cu_2O phase around the midpoint of the reaction, which in fact is closer to what is claimed in Wang et al. [1].

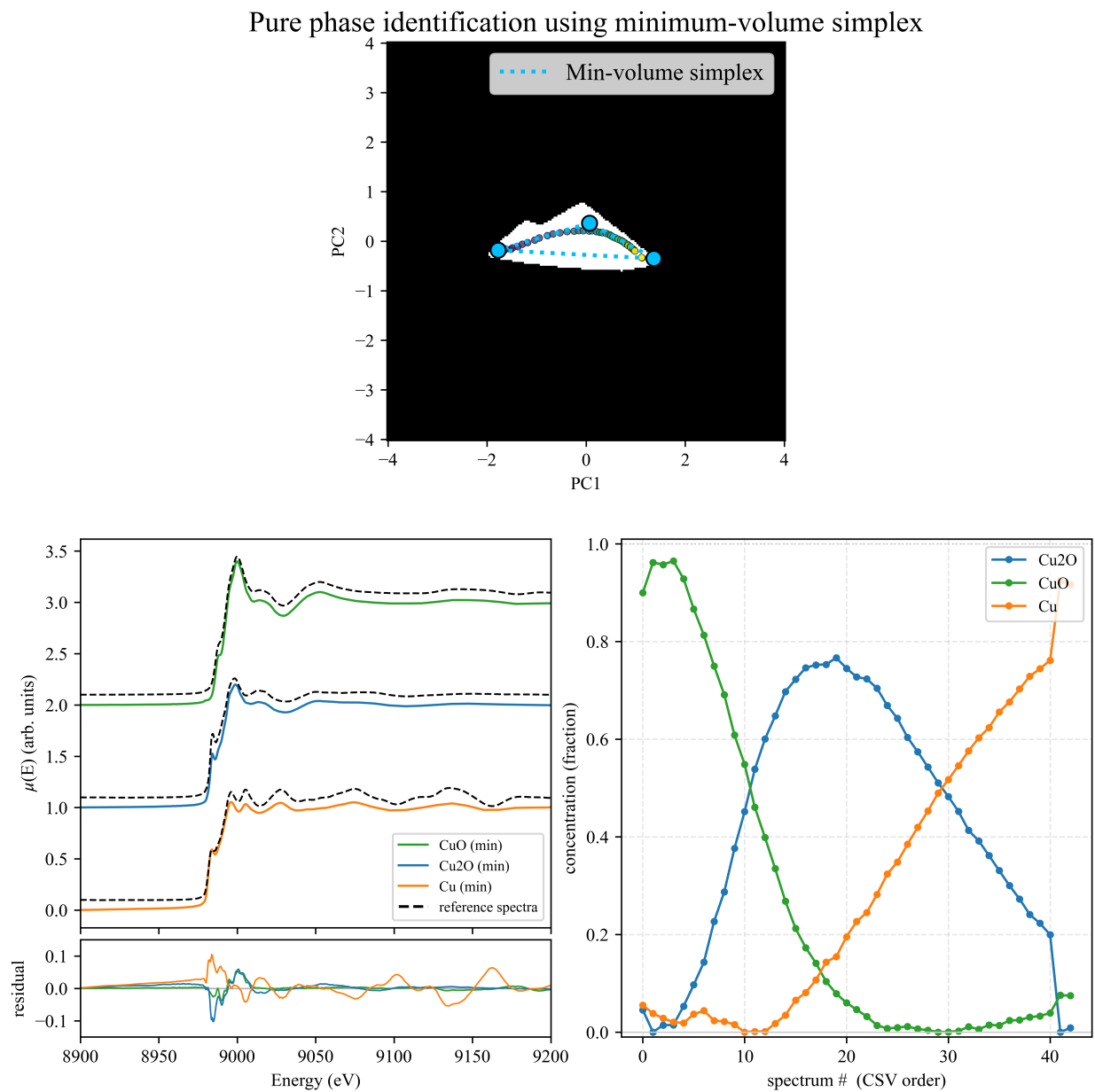


Figure 5.18: Pure phase identification results by using Minimum-Volume Transformation.

5.4.3 Case study 3: Three-phase problem with weakly linearly independent data set (Cu_2O , CuO , $\text{Cu}(\text{OH})_2$)

In this case study, we examine a weakly linearly independent three-phase dataset comprising CuO , Cu_2O , and $\text{Cu}(\text{OH})_2$. These simulated spectra deviate only slightly from the three-phase average and hence cluster around PC0 in the latent space. We show this spectral set along with all the physicality maps in Fig. 5.19.

In Fig. 5.20, we show the pure-phase identification results from both the spectral harvesting and MCR-ALS algorithms. Fig. 5.20 (a) shows our identified pure phases through maximizing simplex volume within the AFS shown at the top. This AFS is obtained through merging all the individual AFSs in Fig. 5.19. The identified pure phases and maximum volume simplex are marked in red, and the true pure phases used to generate the dataset are labeled in separate colors. The white dashed line shows the boundary where the reconstructed spectral profile turns negative; it is equivalent to the negativity AFS shown in Fig. 5.19. We also include the minimum-volume simplex marked in light blue. As expected, since this data set does not contain spectra with a strong weight of any of the true pure phases, the minimum-volume simplex differs strongly from the true physical simplex. Below the physicality map are the identified phases at the simplex vertices, along with the true pure phases. Though not exact, we still observe a favorable recovery of the pure phases using the spectral harvesting algorithm. Since the simplex fitting algorithm uses the experimental spectra to anchor the fitted simplex by requiring all experimental data to be enclosed, the fit result will still depend on the experimental data itself. In ideal cases, if the AFS reduces to nearly match the true physical region, maximum simplex fitting can still recover the true

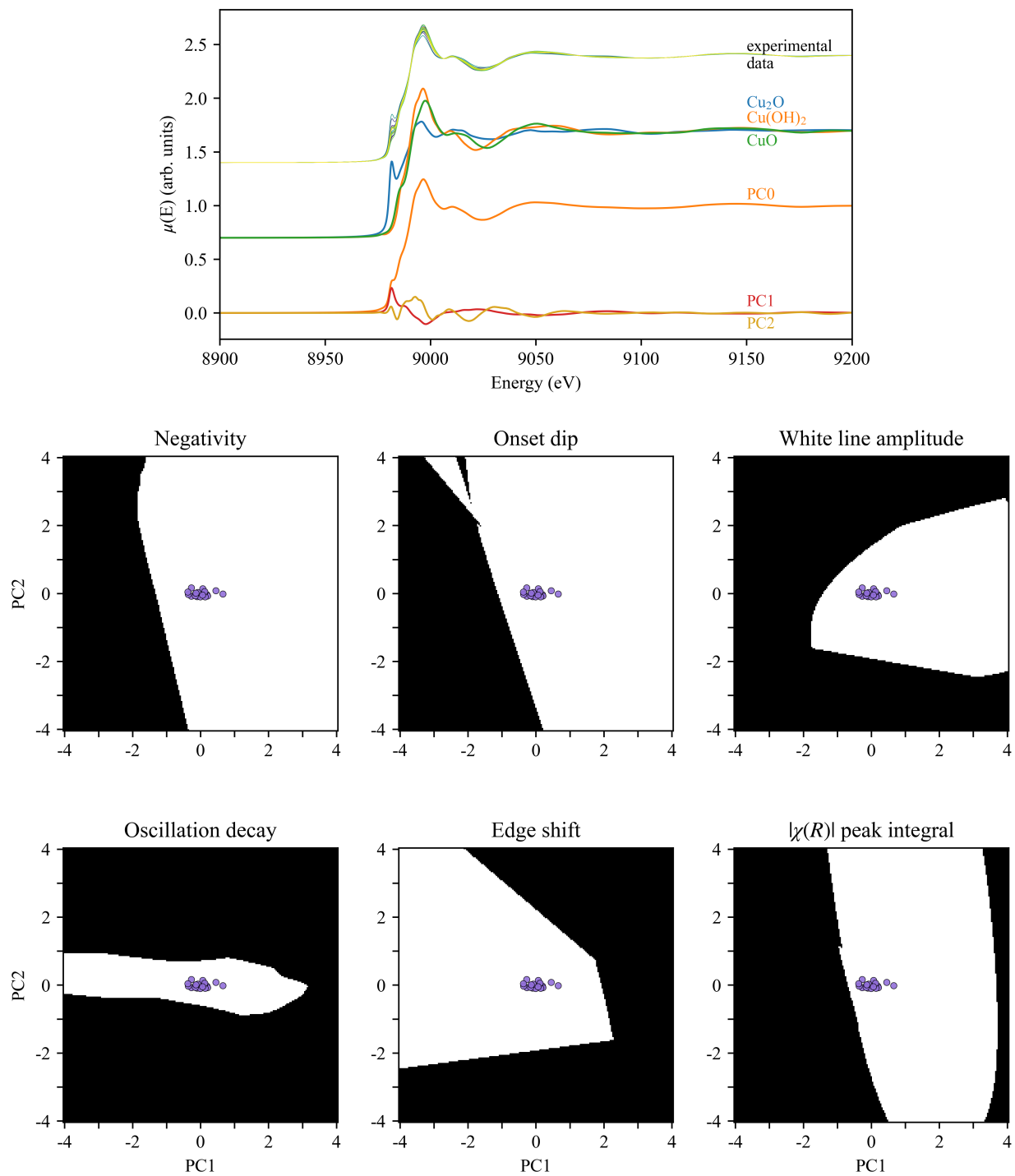


Figure 5.19: Weakly linearly independent three-phase spectral set and physics maps showing the AFS defined by all checkers.

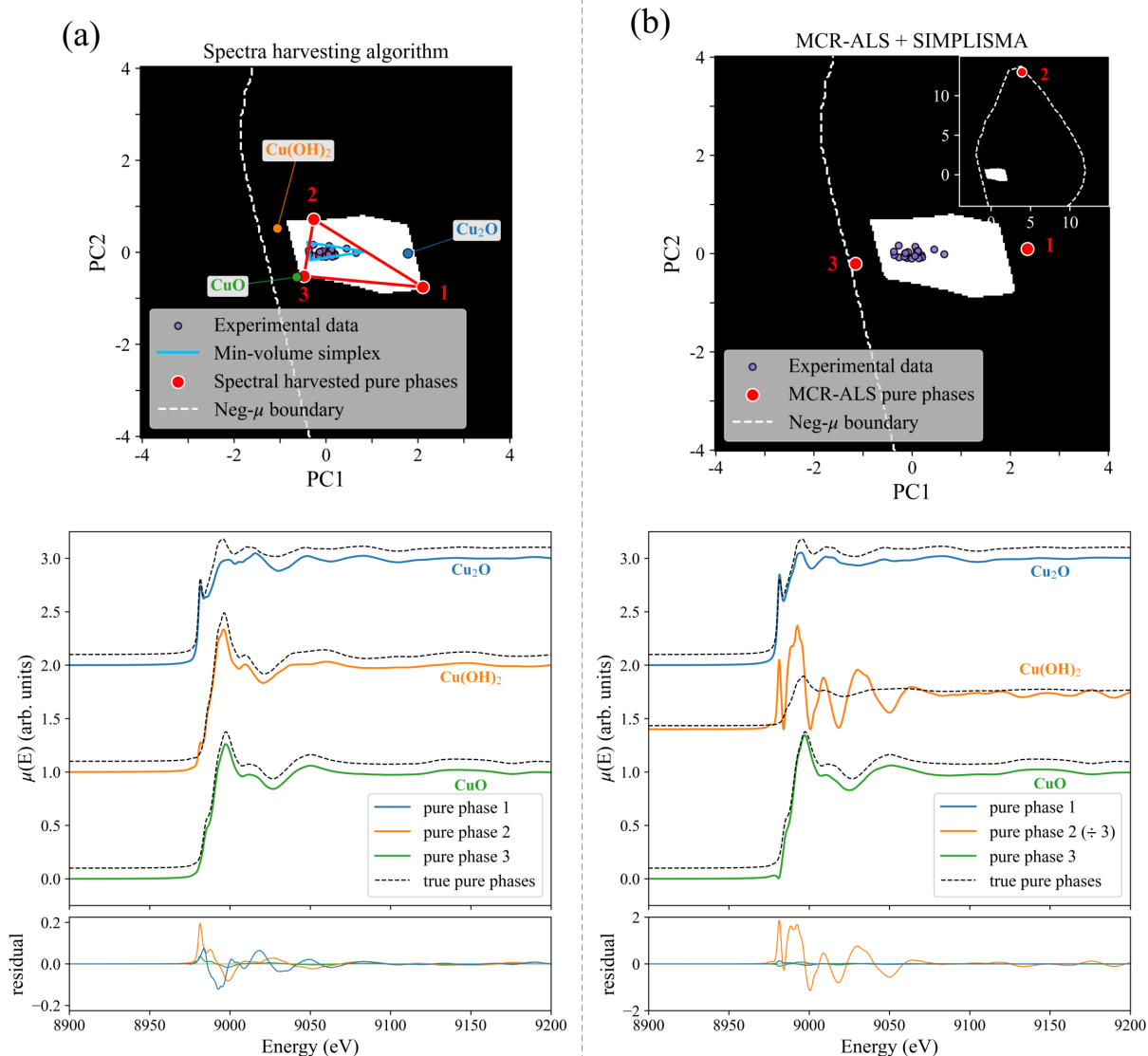


Figure 5.20: Comparison of the pure phases identified through (a) our spectral harvesting algorithm and (b) the standard MCR-ALS method with SIMPLISMA selected initial guess. The top half of the figure shows the merged AFS from Fig. 5.19, and the boundary of the non-negativity region is marked with a white dashed line. Note that both AFS are produced by the spectral harvesting algorithm. We show the same AFS in (b) solely for visualizing MCR-ALS results in the same latent space. The experimental data are marked in purple, and the identified pure phases from each algorithm are marked in red. For the MCR-ALS panel, an additional inset is included to show a wider region of the latent space. On the lower half, the identified pure phases are plotted with the true pure phase, and the residual is shown at the bottom. Note that the MCR-ALS Cu(OH)_2 spectra set is scaled down by a factor of three for better presentation. We see MCR-ALS phase 2 diverges to the boundary of the non-negativity region due to a poor choice of the initial guessed spectral profile from SIMPLISMA.

physical region with no effect from the experimental set distribution. However, this is often not the case, as demonstrated here. Although we reduce the AFS significantly to almost recover the true physical region, a slight rotation between the true and fitted simplex still exists. This could have been avoided if the experimental data set had extended further toward the pure phases, or, in other words, had been more linearly independent.

In Fig. 5.20 (b), a similar plot is presented for the MCR-ALS results. Note that the merged AFS shown here is generated by the spectral harvesting software, not the MCR-ALS algorithm. We repeat the same map on the MCR-ALS case just for visualizing MCR-ALS-identified pure phases in the same latent space. In addition to the physicality map, we added an inset to show a wider range of the latent space. Note that all the MCR-ALS-identified pure phases lie within the non-negative region but differ dramatically from those shown in Fig. 5.20 (a), especially for pure phase 2. This is because the initial spectral profile determined by SIMPLISMA was, unfortunately, not a good choice. As we discussed earlier, the success rate of MCR-ALS strongly depends on the starting spectra. This example shows the limitation of the standard MCR-ALS method and provides a side-by-side comparison between MCR-ALS and our spectral harvesting method. If additional physicality constraints can be applied during MCR-ALS's iterative process, any divergence like phase 2 can be at least capped in a more sensible region (i.e., within the AFS defined by spectral harvesting).

5.4.4 Case study 4: Three-phase problem with different ligands (Cu_2O , Cu_2S , and $\text{Cu}(\text{OH})_2$)

In this case study, we examine a three-phase problem with two different ligands: O and S. The simulated input spectra and AFS from the standard physicality checker are shown in Fig. 5.21.

In the first figure on the left of Fig. 5.22, we show the merged AFS along with the reference pure phases and fitted simplex. We see good overlap between the reference and candidate pure phases for $\text{Cu}(\text{OH})_2$, but not for the other two. To improve the fit, we use the fact that the ligands in this example are either oxygen or sulfur. Since Cu-O has a shorter bond length compared to Cu-S, the O-ligand phase will have its first peak location in $|\chi(R)|$ at a smaller R compared to the S-ligand phase. In the middle of Fig. 5.22, we show the calculated $|\chi(R)|$ for the reference pure phases Cu_2O and Cu_2S . The O-ligand phase has its first peak at about 1.3 Å, and the S-ligand phase has its first peak at about 1.9 Å. With this information, we define a custom physicality check to require $|\chi(R)|$ to exhibit a local maximum within the R range between 1.7 Å and 2.1 Å, and to have an integrated value greater than 0.16 in this range. This checker is meant to select out spectra with a strong weight of the S-ligand phases, and the resulting AFS is shown as a shaded gray area in the physicality map on the right of Fig. 5.22. From this visualization of the experimental data distribution, we see that there is only one S-ligand phase, which is towards the right side of the primary AFS. The simplex fitting step then requires at least one of the simplex vertices to be contained in the gray area, and the simplex to be contained in the white primary AFS, the AFS that is applicable to all three pure phases. The resulting simplex and vertices are drawn in red.

In Fig. 5.23, we show the spectra identified from simplex fitting alongside the true reference

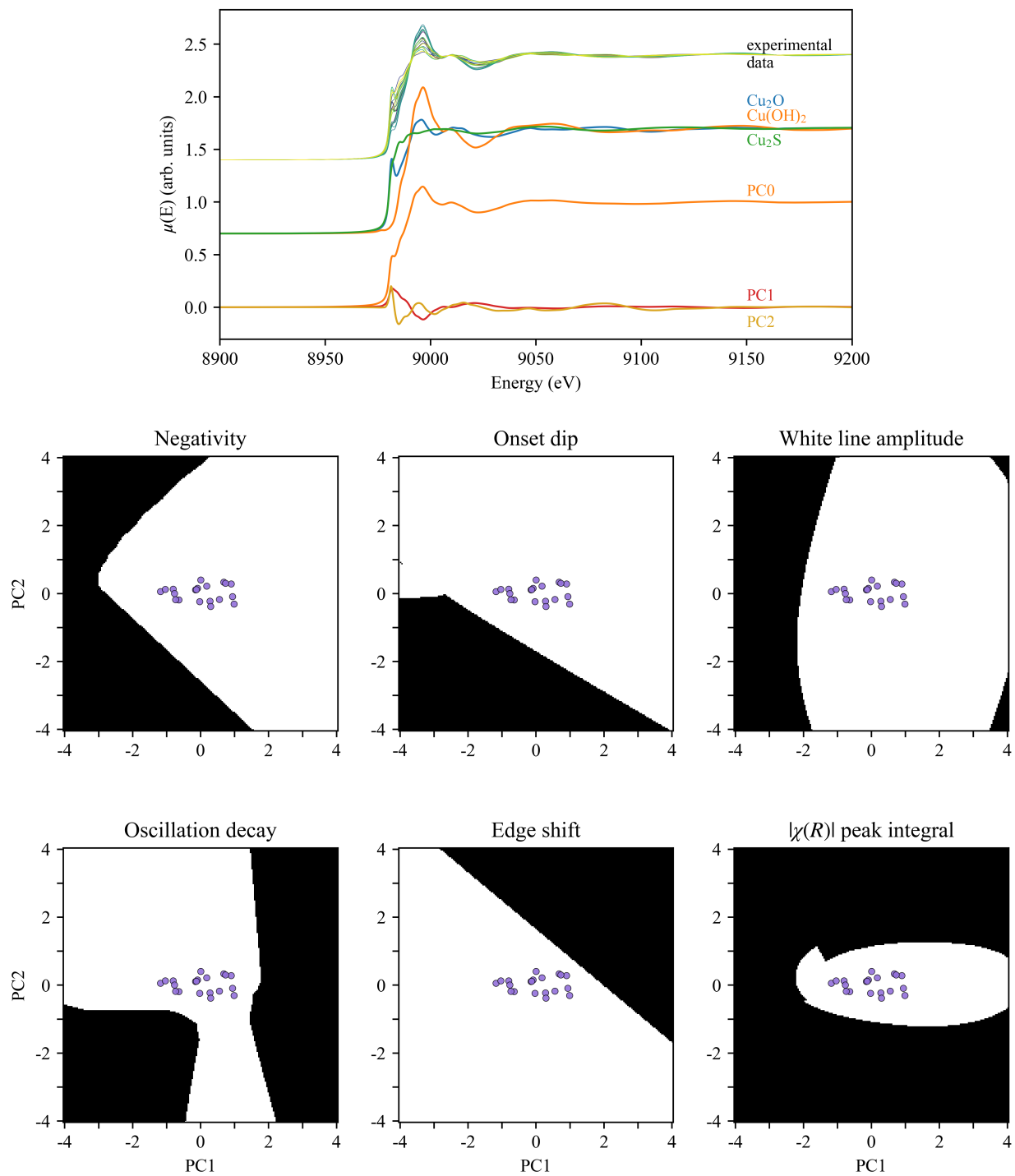


Figure 5.21: A three-phase spectral set with two different types of ligands (Cu_2O , Cu_2S , and $\text{Cu}(\text{OH})_2$) and physics maps showing the AFS defined by all checkers.

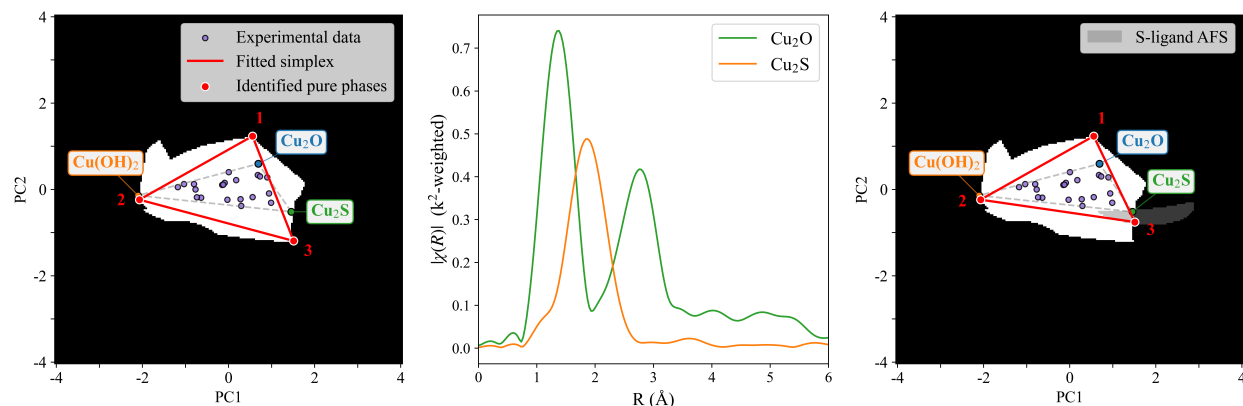


Figure 5.22: (Left) Merged AFS along with reference pure phases and fitted simplex. (Middle) Calculated $|\chi(R)|$ on two reference phases with different ligands, demonstrating how the bond length reflects in the $|\chi(R)|$ first-shell peak. (Right) Same merged AFS with an additional secondary AFS to select out the S-ligand phase. The fitted simplex now requires phase 3 to be contained in the S-ligand AFS.

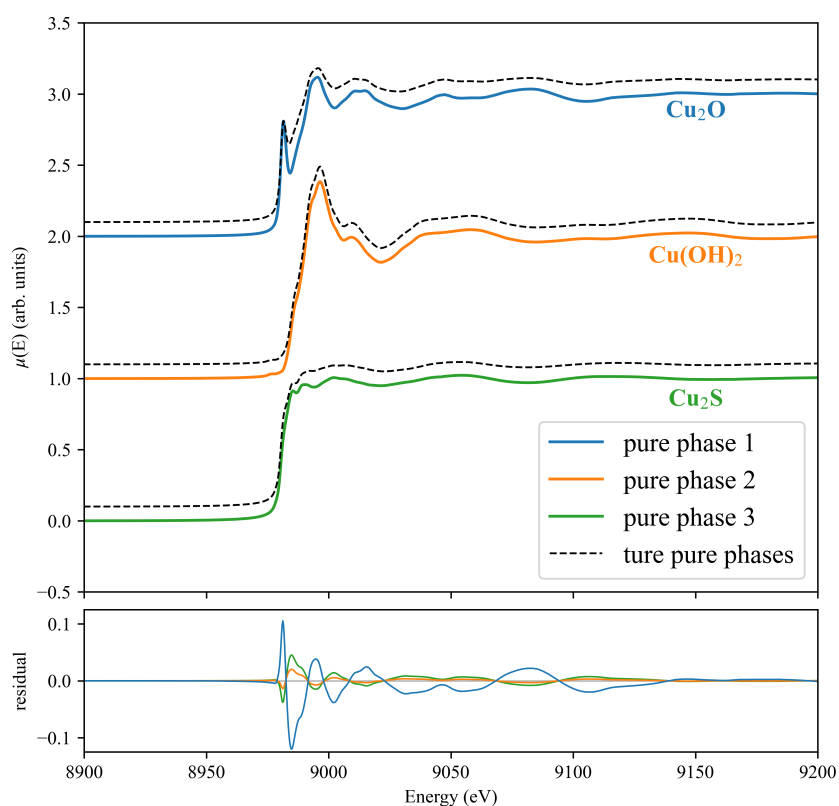


Figure 5.23: Cu_2O , $\text{Cu}(\text{OH})_2$, and Cu_2S pure phase identified by spectral harvesting algorithm with the aid of secondary AFS. We see a good recovery of the $\text{Cu}(\text{OH})_2$ and Cu_2S phases, and slightly worse performance on the Cu_2O phase.

spectra. We see a good recovery of the $\text{Cu}(\text{OH})_2$ and Cu_2S phase, and slightly worse performance on the Cu_2O phase. This case study demonstrates one usage of a custom physicality checker and secondary AFS.

5.5 Conclusion

In this chapter, we introduced "spectral harvesting," a new geometric framework designed to overcome the core limitations of traditional spectral unmixing techniques for X-ray absorption spectroscopy. By imposing physics- and chemistry-driven constraints on the spectra and leveraging the intrinsic geometry of PCA latent space to isolate constituent pure phases, spectral harvesting is much less susceptible to rotational ambiguity than the standard spectral unmixing method MCR-ALS.

The strength of this approach lies in its ability to seamlessly incorporate system-specific physical and chemical constraints. Through a customizable suite of physicality checkers such as non-negativity, white-line amplitude capping, oscillation decay rates, and coordination number, the algorithm systematically prunes unphysical regions of the latent space to establish a tightly bounded AFS. Max-volume simplex fitting within this reduced AFS enables robust recovery of pure-phase spectral profiles, even for weakly linearly independent datasets where the standard MCR-ALS method diverges. We also propose that a simple integration of reduced AFS generated by the spectral harvesting algorithm with the current standard MCR-ALS package pyMCR [51] could be a straightforward approach to prevent extreme divergence, as shown in case study 3, when appropriate initial guess spectra are not readily available.

Through both simulated benchmarks and experimental operando reduction studies, we demonstrated that spectral harvesting provides a stable, objective, and reproducible workflow for unmixing complex multi-phase systems without requiring prior reference standards. Furthermore, the generated AFS maps offer invaluable diagnostic value, providing other spectral unmixing tools with a way to incorporate additional physical knowledge, thereby further improving their performance.

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