Soft X-ray Fluorescence Spectroscopy

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Soft X-ray fluorescence (SXF) spectroscopy is X-ray fluorescence (XRF) spectroscopy for low- and middle-atomic-number elements whose X-ray absorption edges are in the soft X-ray (SX) region. Electron beams have been used as excitation probes for (nonresonant or normal) SXF spectroscopy in laboratories. In addition, synchrotron radiation (SR) beams have been utilized as excitation probes, enabling selective excitation near the X-ray absorption threshold. Selectively excited SXF involves soft X-ray scattering, which can be regarded as a resonant soft X-ray emission (SXE) spectroscopy. SXF and SXE spectroscopies provide element-, orbital-, and symmetry-specific information. Thus, they are powerful tools for chemical analysis and materials characterization.

In this article, the principles of SXF/SXE spectroscopies and instrumentation focused on gratings are described. Examples of nonresonant (normal) SXF and resonant SXE spectroscopies are shown, and details of the spectral profiles are explained. Resonant SXE spectroscopy of liquid water and operando observations of the electrode reactions are also demonstrated as advanced chemical analyses.

1 INTRODUCTION

SXF is XRF in the SX region and is taken as an extension from about 250 eV (below the carbon K absorption edge) to several keV. The SX region, which extends to the extreme ultraviolet (EUV) region of 30–250 eV, is characterized by the presence of a primary atomic resonance and absorption edges of low- and intermediate-atomic-number (Z) elements. XRF is an X-ray photon emitted from the atom with an energy equal to the energy difference between the initial states with a core hole and the final states in which the core hole is filled by electrons from valence orbitals. XRF is, therefore, based on the electric dipole transition and obeys the selection rule. Hence, XRF provides element- and orbital-specific information and has been utilized as a novel chemical analysis method.

For SXF, some experimental difficulties are attributed to the low fluorescence yield. Consequently, SXF spectroscopy has been achieved in laboratories by energetic electron (E)-beam excitations. E-beam-excited SXF was measured from the 1930s(2,3) to the 1970s. Many works on E-beam-excited SXF are summarized in the literature. However, even with the E-beam excitation, the SXF intensity is weak, and selective excitation near the absorption threshold is difficult via E-beam excitation.

The advent of SR-beam excitations opens new possibilities for SXF spectroscopy. The highly brilliant SR beam can overcome the low fluorescence yield and provide selective excitations with high-energy resolutions. In particular, selective excitations have been used as a new probe for SX scattering. Thus, the term ‘SXE spectroscopy with SR-beam excitation’ is nowadays used in a wider sense than SXF spectroscopy.

This article describes the principles of SXF/SXE, instrumentation of SX spectroscopy(5) using gratings, applications of SXF/SXE spectroscopies, and advanced applications of SXE spectroscopy.(6)
2. SOFT X-RAY FLUORESCENCE SPECTROSCOPY

2.1 Principle of X-ray Fluorescence

According to the Bohr model, the atomic energy levels \( E_n \) in a one-electron model are described as

\[
E_n = -\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2n^2} \quad (n = 1, 2, 3, \ldots)
\]

where \( e \) is the electron charge, \( m \) the mass of an electron, \( Ze \) the nuclear charge, \( \varepsilon_0 \) the permittivity of free space, and \( \hbar \) is Planck’s constant divided by \( 2\pi \). This model can explain radiation only when an electron transitions from an initial state \( (n_1) \) to another final state \( (n_f) \) with characteristic energies as

\[
\hbar\omega = E_i - E_f = -\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2} \left( \frac{1}{n_1^2} - \frac{1}{n_f^2} \right)
\]

Modern quantum theory describes a particle’s motion in terms of a wavefunction \( \Psi(r, t) \), which obeys Schrödinger’s wave equation as

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r, t)\Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}
\]

where \( m \) is the particle mass, \( V(r) \) the potential energy, and \( \nabla \) the vector gradient. The solution of Schrödinger’s equation for a one-electron atom assumes a time dependence, which is expressed as

\[
\Psi(r, t) = \Psi(r)e^{-iE/t}\hbar
\]

in a potential as

\[
V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}
\]

The time-independent term of \( \Psi(r) \) can be described with separable functions in spherical coordinates as

\[
\Psi(r) = \Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)
\]

where \( \theta \) is the angle from the z-axis and \( \phi \) the angle around the z-axis. The functions of \( R(r) \), \( \Theta(\theta) \), and \( \Phi(\phi) \) introduce quantum numbers of \( n \), \( l \), and \( m_l \), respectively. Here, \( n \) is the principal quantum number associated with the radial coordinate and takes an integer value \( n = 1, 2, 3, \ldots \). The orbital quantum number \( l \) associated with the \( \theta \)-coordinate is related to the angular momentum by \( L = \sqrt{l(l+1)}\hbar \), and takes an integer value of \( l = 0, 2, \ldots, n-1 \). The magnetic quantum number \( (m_l) \) associated with the continuity of the wavefunction in the angle \( \phi \) is related to the z-component angular momentum by \( L_z = m_l\hbar \), and takes an integer value of \( m_l = -l, -l+1, \ldots, 0, \ldots, l \). Furthermore, the total angular momentum quantum number \( j \) is determined by the vector sum of the orbital and spin \( (s) \) angular momentum, \( j = l+s, l+s-1, \ldots, |l-s| \).

The binding energy of electrons in an atom can be described as a combination of the quantum numbers \( n, l, \) and \( j \). Figure 1 shows the binding energy levels described with the K-shell \((n = 1)\), L-shell \((n = 2)\), M-shell \((n = 3)\), \ldots, as a function of the atomic number. The energy of each shell increases as \( Z \) increases. For example, the K-shell ranges from 13.6 eV for a hydrogen atom to approximately 100 keV for a uranium atom. Such a wide energy range of the inner shells corresponds to an energy range from EUV to hard X-rays (~100 keV). In this range, SX covers the inner shells of low Z atoms and shallow shells of middle Z atoms. SX spectroscopy, which uses SX as a diagnostic probe, can extract electronic structure information for low and middle Z atoms.

Figure 2 shows the electronic transition processes of an inner shell excitation. When high-energy probes such as electrons or X-rays strike an electron in an inner orbital with a binding energy lower than the probe energy, the electron can be ejected from the inner orbital and jump into the vacuum level (ionization). In the ionization, a vacancy is formed in the inner orbital (core hole).

The core hole state is unstable. Two processes can revert the atom to the original state. One process is the fluorescent X-ray emission. An electron in an outer orbital is transferred to fill the core hole. The energy difference
between the initial and final states of the transferred electron can be given as a fluorescent X-ray emission. The other process is the Auger electron emission. The energy difference by the transferred electron can be given as an electron emission in the valence band. Hence, fluorescent X-ray emission and Auger electron emission are competitive processes for the relaxation of an unstable core hole state.

The probability of a transition between two states in an atom is proportional to the square of the quantum mechanical dipole matrix element as

$$-er_{id} = -e \int \Psi_i^* r \Psi_f dr$$  \hspace{1cm} (7)

where $\Psi_i$ and $\Psi_f$ are wavefunctions for the initial and final states, respectively. If the integral is zero, there is no transition. That is, the transition is not allowed. When $r$ is an odd function of the coordinates, the initial and final wavefunctions must have opposite parity for a non-zero integral. The parity of the wavefunctions is found to alternate with increasing $l$, leading to selection rules for allowed transitions as

$$\Delta l = \pm 1$$ \hspace{1cm} (8)

In addition, the total angular momentum ($j$) must satisfy

$$\Delta j = 0, \pm 1$$ \hspace{1cm} (9)

These allowed transitions lead to the characteristic X-ray emission as XRF. A fluorescent X-ray emission followed by ionization is called a nonresonant (or normal) X-ray emission. On the other hand, an X-ray emission caused by the excitation of an inner electron into a specific unoccupied level is called a resonant X-ray emission. Electronic transitions of the resonant X-ray emission are described later.

### 2.2 Properties of Soft X-ray Spectroscopy

The energy of XRF is determined by the energy difference between the inner orbital in which a core hole is formed and the outer orbital in which an electron is transferred to the core hole. Figure 3 shows the X-ray energy of the $K$, $L$, and $M$-emission lines as functions of $Z$ compared to the fluorescence yield ($\omega_{KL}$) for the $K$- and $L$-emissions.(7) When the upper limit of SX energy is approximately 4 keV, the maximum $Z$ is 20 for the $K$-line (Ca) and 53 for the $L$-line (I). Hence, SX fluorescence spectroscopy can be used for low $Z$ and/or middle $Z$ atoms.
Figure 3  Energy of fluorescent X-rays (a) and fluorescence yield of $K$ and $L$ emissions (b) as functions of atomic number ($Z$).

The corresponding fluorescence yields are weak. The yields are less than 20% for the $K$-emission and less than 10% for the $L$-emission. The weak fluorescence yield of SXF experimentally requires intense probes for ionization and highly efficient X-ray detectors. Early works\(^{(2,3)}\) on SXF in the 1930s–1960s used electron beams for the excitation probe and detectors of photographic detection, gas proportional counters, and photomultipliers. Advances in synchrotron SX sources and high sensitivity area detectors have made greatly advanced SXE spectrometers. Details will be described later.

Figure 4  Mass absorption coefficients $\mu$ of nitrogen and oxygen in the X-ray region.

The absorption of X-rays in matter can be expressed by the Beer–Lambert Law. The intensity of transmitted X-rays ($I$) is described as

$$I = I_0 e^{-\mu \rho L} \tag{10}$$

where $I_0$ is the initial intensity of the incident X-rays. The parameters $\mu$, $\rho$, and $L$ are the absorption mass coefficient, density, and thickness of the target matter, respectively. Based on Equation (10), the penetration length of X-rays in matter can be defined as $1/\mu$.

Figure 4 shows $\mu$ of nitrogen and oxygen in the X-ray region.\(^{(8)}\) $\mu$ in the SX region is higher than that in the hard X-ray region. The $K$ absorption edges of nitrogen and oxygen are at 410 and 540 eV, respectively. Hence, SX can be strongly adsorbed in atmospheric air. For example, the penetration length of a 1 keV X-ray in air under standard conditions is approximately 2 mm. Therefore, instrumentation for SX spectroscopy should be designed for use in high vacuum conditions.

Reflective optics such as mirrors and dispersive optical elements of crystals and gratings are generally used in SX spectrometers. Hence, the reflectivity of the optical elements should be carefully considered for designing highly efficient SX spectrometers. Figure 5 shows the reflectivity in the SX region of a gold (Au)-coated mirror with the grazing angles of 1–10°. The calculations were performed using Henke’s data.\(^{(9,10)}\) As the reflectivity drastically decreases as the grazing angle increases, an SX spectrometer should usually be designed with grazing angles less than 3°.
3 INSTRUMENTATION OF SOFT X-RAY EMISSION SPECTROSCOPY USING GRATINGS

3.1 Gratings for a Soft X-ray Emission Spectrometer

3.1.1 Grating Formula

Large lattice spacing crystals are typically used for dispersive optics in the spectral range of 1–4 keV, while gratings are used below 1 keV. Here, we focus on a grating spectrometer.

Diffraction gratings are used to monochromatize X-rays based on a well-known grating formula

\[ \sin \alpha + \sin \beta = \frac{m \lambda}{\delta} \]  

(11)

where \( \alpha \) is the incident angle, \( \beta \) the diffraction angle, \( m \) the spectral order, \( \lambda \) the wavelength of the diffracted X-ray, and \( \delta \) the groove width of the grating.

3.1.2 Rowland Mount Grating

In the optical design of a spectrometer, aberration corrections are important to achieve high-resolution spectroscopy. For grazing-incidence grating optics, the Rowland circle mount using a spherical grating is a typical optical mount. Figure 6 shows the Rowland circle, which was first reported in 1883.\(^{11}\) Figure 7 shows the geometry of the Rowland circle mount. On a spherical grating with a curvature radius of \( R \), the Rowland circle is in contact at the grating center (\( G \)) with a diameter (\( R \)). When a point source (\( P \)) and a focal point (\( F \)) are located on the circle, and the following conditions are satisfied, rays emitted from \( P \) are diffracted by the grating and focused at \( F \) without a Coma aberration

\[ r = R \cos \alpha, \quad r' = R \cos \beta \]  

(12)

where \( r = \overline{PG}, \quad r' = \overline{GF} \). \( \alpha \) is the incident angle and \( \beta \) the diffraction angle.

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**Figure 5** Calculated reflectivity of an Au mirror in the soft X-ray region.

**Figure 6** Rowland circle first published in Ref. 11. If a source of light exists on the circle, the reflected image and all the spectra will be focused on the same circle. \( A \) is the slit, \( C \) is the eyepiece, and \( B \) is the grating with its center of curvature at \( C \). Geometry satisfies as \( r = \rho \cos \mu \) and \( R = \rho \cos \nu \). (Reproduced with permission from Ref. 11. © Taylor & Francis, 1883.)

**Figure 7** Geometry of the Rowland circle mount of a spherical grating.
3.1.3 Varied Line Spacing Grating

In the 1980s, other aberration-corrected gratings, which can focus diffracted rays sharply onto a plane almost normal to the rays, were invented by using computer-controlled ruling engine.\(^{(12,13)}\) An aberration-corrected grating is a varied line spacing grating (VLSG). Figure 8 shows the basic idea of varied line spacing for flat-field focusing. At a grating center \((x = 0)\), the grating formula of \(\sin \alpha_0 + \sin \beta_0 = m \lambda / \delta_0\) is satisfied. When the ray emitted from a point source illuminates position \(x = w\) on the grating, the diffracted ray focuses on the same position for the diffracted center ray with the varied line spacing \(\delta_w\) as

\[
\delta_w = \frac{m \lambda}{\sin \alpha_w + \sin \beta_w} \tag{13}
\]

where

\[
\alpha_w = \tan^{-1} \frac{r \sin \alpha_0 - w}{r \cos \alpha_0} \tag{14}
\]

\[
\beta_w = \tan^{-1} \frac{r' \sin \beta_0 - w}{r' \cos \beta_0} \tag{15}
\]

Figure 9 shows the design specifications for a flat-field concave grating and the calculated focal curves with various incident angles and wavelengths\(^{(13)}\). The focal curve profile strongly depends on the incident angle and wavelength. However, the curve can be approximated as a flat line with specific parameters. If an area detector is placed along the focal plane, the spectrograph of the diffracted rays can be obtained without aberrations.

Figure 10 shows an example of the E-beam-excited SXF spectrometer, which employs the Rowland circle mounting, developed in the 1960s\(^{(14)}\). The grating has a 2 m curvature radius and 1152 mm\(^{-1}\) grooves with an incident angle of 87.5°. The spectrometer was pumped to a 10\(^{-6}\) Torr vacuum. High-resolution SXF of Li K, Be K, B K, Al L, and Si L were measured by the spectrometer.

Figure 11 shows examples of SR-beam-excited SXE spectrometers by applying the Rowland circle mounting, which were designed by Nordgren\(^{(15)}\), Callcott\(^{(16)}\), and Shin\(^{(17)}\) in the 1980s–1990s for high-resolution SXE spectroscopy. All three employ highly brilliant SR from an undulator or a wiggler as the excitation source. They
Figure 10  E-beam-excited SXF spectrometer developed in the 1960s with Rowland circle mounting. (a) Shows block diagrams of the spectrometer. (b) Shows the original chart record for the Be K emission. OK and CK emissions are also recorded on the left side of the Be K emission peak.\(^{(14)}\) (Reproduced with permission from O. Aita and T. Sagawa, Soft X-ray emission spectra of light elements. I. Li, Be, B, Al and Si, J. Phys. Soc. Jpn., 27, 164–175 (1969). © The Physical Society of Japan, 1969.)

employed grazing-incidence optics with a fixed entrance slit, spherical gratings, and a two-dimensional area detector composed of microchannel plates (MCPs). The optics are mechanically aligned on the Rowland circle. Nordgren’s spectrometer installed in a wiggler beamline at HASYLAB covers a 50–1240 eV range with an energy resolution \(E/\Delta E\) of 2000–400 by three gratings. Their grooves (curvature radius and incident angle) are 300 mm\(^{-1}\) (3 m, 84.6\(^\circ\)), 400 mm\(^{-1}\) (5 m, 87.4\(^\circ\)), and 1200 mm\(^{-1}\) (5 m, 88.1\(^\circ\)). Callcott’s spectrometer installed in an undulator beamline at ALS covers a 40–1000 eV range by four gratings of 600 mm\(^{-1}\) (5 m, 86\(^\circ\)), 1500 mm\(^{-1}\) (5 m, 86\(^\circ\)), 600 mm\(^{-1}\) (10 m, 88\(^\circ\)), and 1500 mm\(^{-1}\) (10 m, 88\(^\circ\)). Shin’s spectrometer installed in an undulator beamline at the Photon Factory covers a 30–1200 eV range with \(E/\Delta E\) of 2000–520 by three gratings of 600 mm\(^{-1}\) (5 m, 85.98\(^\circ\)), 1200 mm\(^{-1}\) (7 m, 87.13\(^\circ\)), and 2400 mm\(^{-1}\) (10 m, 87.99\(^\circ\)). Using tunable energy SR-excitations, they researched the photon-in/photon-out SXE spectroscopy, as described later.
Figure 11 (Continued).
3.2.3 Synchrotron Radiation-beam-excited Varied Line Spacing Grating Soft X-ray Emission Spectrometer

VLSG has also been applied to an SR-SXE spectrometer\(^{18-20}\) to achieve both high efficiency and high-energy resolutions. Figure 12 shows an example of the VLSG spectrometer for SR-beam-excited SXE spectroscopy\(^{19}\) installed in a SX beamline at SPring-8. The spectrometer does not have an entrance slit, and the incident beam is focused to less than 5 μm at the sample position, corresponding to the source point for the grating. Cylindrical VLSG is adopted in the spectrometer. The curvature radius is 8939.89 mm, and the average groove density is 2000 mm\(^{-1}\). A back-illuminated charge-coupled device (CCD) detector, which has 2048 × 2048 pixels where each pixel size is 13.5 × 13.5 μm\(^2\), is placed along the focal plane. To improve the spatial resolution, the super-resolution-reconstruction method is used for the image processing on the CCD. The entrance-slitless optics, well-focused beam, cylindrical VLSG, and super-resolution-reconstruction CCD system enable high efficiency and high-resolution SXE spectroscopy.

To perform at a higher energy resolution and a higher efficiency, advanced VLSG SXE spectrometers have been developed\(^{21-25}\). In the entrance slitless optics, well-focused incident SR beams directly affect the energy resolution and efficiency. Figure 13(a) shows the refocusing mirror system for incident SR beams and the focused beam spot profile. The refocusing system with a VLSG SXE spectrometer is installed at the SPring-8.
mirror system, composed of two plane elliptical mirrors, is aligned in a Kirkpatrick–Baez (K–B) configuration.\(^{(26)}\) Using the K–B mirrors, the SR beam can be focused with a size of 1.6\(\mu\)m\(^V\) \(\times\) 13\(\mu\)m\(^H\). The small focus on a sample enables ultrahigh resolution SXE spectroscopy.

Figure 13(b) shows the measured SXE spectra in the N K region of \(h\)-BN and in the Mn L region of MnO. The clearly separated peak profiles indicate an ultrahigh resolution \(E/\Delta E\) of 10,000–8000 in the 350–750 eV range. Such an ultrahigh resolution SXE spectrometer can explore the fine structure analysis by element/symmetry-specific electronic, vibrational, magnon, spinon, and orbiton excitations.

3.2.4 E-beam-excited Varied Line Spacing Grating Soft X-ray Fluorescence Spectrometer Combined with a Transmission Electron Microscope

An E-beam-excited VLSG SXF spectrometer attached to a transmission electron microscope (TEM) has recently been developed.\(^{(27–30)}\) The SXF spectrometer combined with TEM enables microscopic analysis with high-resolution SXF. In addition, the combination of electron energy loss spectroscopy (EELS) in TEM and SXF provides electronic structural information of unoccupied orbitals and occupied orbitals, respectively.

Figure 14(a,b) shows a schematic of the TEM/SXE system and the measured SXF of the 400 nm diameter \(h\)-BN and \(c\)-BN samples. An energy resolution of 0.4 eV is sufficient to distinguish their spectral differences. Figure 14(c,d) shows another TEM/SXE system, which employs W/B\(_4\)C multilayer-coated (MLC) VLSG for the higher energy region and the measured SXE spectra of KNbO\(_3\). Using the MLC-VLSG, Nb L\(_{\beta 1}\) and K L\(_{\alpha,\beta}\) peaks can be detected. This confirms that MLC-VLSG improves the efficiency in the 2–4 keV region. Such a laboratory SXF/TEM system is a powerful microspectroscopic tool for bandgap analysis in small areas.

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**Figure 12** (a) Shows a schematic of the VLSG SXE spectrometer. (b) Shows the optical parameters of the spectrometer where \(r = 300\) mm, \(r' = 500\) mm, \(\alpha = 87.5^\circ\), and \(\theta = 47.42^\circ\).\(^{(19)}\) (Reproduced from T. Tokushima, Y. Harada, H. Ohashi, Y. Senba, and S. Shin, High performance slit-less spectrometer for soft X-ray emission spectroscopy, Rev. Sci. Instrum., 77, 063107 (2006) doi: http://dx.doi.org/10.1063/1.2204623, with the permission of AIP Publishing.)
Figure 13  (a) The optical layout of the refocusing mirror system. (b) The measured focused spot profile at the sample position. (c) The N K-emission of h-BN and Mn L-emission of MnO measured with the SXE system.\textsuperscript{(21)} (Reproduced from Y. Harada, M. Kobayashi, H. Niwa, Y. Senba, H. Ohashi, T. Tokushima, Y. Horikawa, S. Shin, and M. Oshima, Ultrahigh resolution soft X-ray emission spectrometer at BL07LSU in SPring-8, Rev. Sci. Instrum., 83, 013116 (2012) doi: http://dx.doi.org/10.1063/1.3680559, with the permission of AIP Publishing.)
4 SOFT X-RAY EMISSION SPECTRA OF LIGHT ELEMENT MATERIALS

4.1 Nonresonant (Normal) Soft X-ray Emission

XRF is the radiative process of the electric dipole transition. The XRF spectral distribution can be described as the well-known Fermi’s golden rule. However, the K emission of light elements can be approximately described by the density of states (DOS) of the ground states because the core levels are compact and have distinct binding energies. In addition, the dipole selection rules governing a one-electron transition assure that the spectra are selective for the angular momentum state.

Nonresonant (normal) XRF provides information about the partial density of state (PDOS) of the valence bands. This selectivity of the nonresonant XRF is useful for electronic structure analysis and/or chemical analysis of materials. Figure 15 demonstrates the nonresonant SXF of various carbon compounds relative to the calculated PDOS of C2p and C2s orbitals. The C K spectra were measured by a Rowland mount spectrometer with monochromatized 320 eV SR-beam excitation. Compared to the E-excitation, the monochromatized SR-beam excitation has advantages, including less sample damage and suppression of the bremsstrahlung background. The spectral profile of each compound can be reproduced by the C2p-DOS because the C K emission is caused by the K(1s−1)V(2p) transition. Such a combination of XRF and theoretical analysis has been utilized for chemical analysis.

4.2 Anisotropy of Soft X-ray Emission

The XRF of ordered molecules exhibits a take-off angle-dependent profile due to dipole selection rules. Figure 16 shows the take-off angle-dependent C K emission spectra of highly oriented pyrolytic graphite (HOPG) measured...
at take-off angles of 15–75° and a 320 eV SR-beam excitation.\(^{(32)}\) In the higher take-off angle direction, the higher energy portion, which can be assigned to the π orbital, increases. HOPG is formed with the hexagonal carbon layers by sp\(^2\) carbon atoms and the layers piled up due to van der Waals forces. In such an ordered crystal structure, π orbitals are perpendicular to the layer plane, and σ orbitals are parallel to the plane. The C K emission caused by the 1s\(^{−1}\)–2p transition induces an anisotropic emission intensity distribution. In the emission normal to the planes, an emission from only σ orbitals can be observed. In contrast, an emission from both σ and π orbitals can be observed parallel to the plane direction. Such an emission intensity distribution \(I(E, \theta)\) can be described with the intensity components of σ and π orbitals \(I_{\sigma, \pi}(E)\) as

\[
I(E, \theta) = I_{\sigma}(E) \left(1 + \cos^2\theta \right) + I_{\pi}(E)\sin^2\theta
\]

where \(\theta\) is the take-off angle measured normal to the plane.\(^{(33)}\) Similar angle-dependent XRF has been observed in hexagonal boron nitride (h-BN).\(^{(34)}\) Figure 17 shows the B K and N K emission spectra measured with take-off angles of 15–75°, compared to the σ and π components of B2p- and N2p-DOS. The spectral intensities are normalized by the 182 eV main peak intensity in the B K emission and the 392.5 eV peak intensity in the N K emission. The excitation energies of SR beams are 220 eV for B K and 430 eV for N K. In both B K and N K emission spectra, the higher energy portions increase in the higher take-off angle direction. This behavior agrees with the anisotropic σ and π orbitals in B 2p and N 2p DOS. Such an angle-dependent XRF can separate the states with different symmetries.
The angle-dependent XRF can also be applied to determine the structure of adsorbed molecules on a substrate.\textsuperscript{(35-37)} The adsorbed structure of CO on Ni(100) surface was investigated by the angle-dependent C K and O K XRF.\textsuperscript{(35)} Figure 18(a) shows the schematic of the molecular orientation of CO with respect to the $E$ vector for the emitted X-rays. In the C K and O K emissions from CO adsorbed perpendicular to the substrate surface, it can be considered that emissions from only $\pi$ orbitals can be observed in the normal emission mode, whereas emissions from both $\sigma$ and $\pi$ orbitals can be observed in the grazing emission mode.

Figure 18(b) shows the grazing and nonresonant C K and O K emission spectra and the UPS spectrum of CO adsorbed on Ni(100) substrate in the c(2×2) structure. The 4$\sigma$ state is observed only in the O K grazing emission because the grazing emission is sensitive to $\sigma$ orbitals, which are hybridized with O2p and C2s orbitals. The 5$\sigma$ and 1$\pi$ states are observed in both the C K and O K emissions. The 5$\sigma$ peak is only observed in the grazing emission mode, while the 1$\pi$ peak is maximized in the normal emission. Such spectral profiles can clarify CO molecule adsorbed perpendicular to the Ni(100) substrate.

4.3 Resonant Soft X-ray Emission

4.3.1 Resonant Transition Processes

Energy-tunable SR beams enable selective excitation near the threshold for XRF. Figure 19 shows a schematic of the excitation of inner electrons into unoccupied orbitals near threshold and decay processes of the core hole. In the near threshold excitation, photon-in and photon-out processes are often coupled and can be described as inelastic scattering. The scattering is called resonant inelastic X-ray scattering (RIXS).

In the RIXS process, an electron–hole pair is created in the final state. The energy loss $\Delta E$ needed to create an electron–hole pair is observed in the emitted X-ray as

$$\Delta E = \hbar \omega_\text{in} - \hbar \omega_\text{out} = (E_e - E_h)_f$$

(17)

where $(E_e - E_h)_f$ is the energy of the electron–hole pair in the final state. In the energy distribution of RIXS in crystalline materials with delocalized states, the scattering process conserves the crystalline momentum. The wavevectors of the electron and hole states $\mathbf{k}_e$ and $\mathbf{k}_h$, and the incident and emitted photons $\mathbf{q}_\text{in}$ and $\mathbf{q}_\text{out}$ are conserved as

$$\mathbf{k}_e + \mathbf{q}_\text{in} = \mathbf{k}_h + \mathbf{q}_\text{out}$$

(18)
Figure 18  (a) A schematic of the molecular orientation of CO with respect to the E vector for the emitted light. (b) The grazing and normal C and O K emission spectra and a UPS spectrum of CO on Ni(100) in the \(c(2 \times 2)\) structure.\(^{(35)}\) (Reproduced with permission from Ref. 35. © American Physical Society, 1995.)

Figure 19  Excitation of the inner electron into unoccupied orbitals near threshold and decay processes of the core hole as RIXS and REXS.

Figure 20  Excitation process of the inner electron just below the absorption threshold and decay process as Raman scattering.

For SX scattering, \(q \ll k\) because the X-ray wavelength is much larger than the atomic spacing. Hence, \(k\)-conserving inelastic scattering as \(k_e \approx k_h\) is observed in the SX region. The \(k\)-conserving RIXS in graphite is described later. On the other hand, in atomic systems or insulators with localized states in the conduction band, the localized electron behaves in core exciton states. Relaxation of the core exciton states results in resonant elastic X-ray scattering (REXS). REXS can be observed in trigonal coordination boron compounds, which will be described later.
In an excitation below the threshold, inelastic X-ray scattering can also be observed (Figure 20). The energy loss is observed as the Raman scattering due to the localized valence exciton state on which an electron is bound to a valence hole in the final state. Thus, the Raman scatterings are observed at a constant energy displacement from the elastic peaks of incident X-rays.

4.3.2 Resonant Inelastic X-ray Scattering

Figure 21 shows the C K-emission spectra of graphite selectively excited near the threshold from 284 eV for RIXS to 400 eV for the nonresonant emission.\(^{(38)}\) The dispersive spectral profile depends on the excitation energy near the threshold and corresponds to the band structure. This demonstrates \(k\)-conserving scattering. Figure 22 shows the Raman shift of graphite, which is selectively excited below a threshold to 275.5 eV. The horizontal axis is converted from the photon energy to the Raman shift (energy displacement from the elastic peaks). The spectra excited below 284.1 eV exhibit the same profile. This profile reflects the \(\sigma\)-\(p\) DOSs, produced by the energy loss of the electronic Raman excitations from the \(\sigma\)-\(p\) valence bands to a localized valence exciton derived from the \(\pi^*\)-\(p\) conduction band states.

RIXS is a powerful tool to investigate the electronic structure and/or band structure and RIXS has been applied to many functional materials for characterization and electronic structure analysis, including Li K\(^{(40,41)}\), Be K\(^{(42)}\), B K\(^{(43–50)}\), C K\(^{(51–59)}\), N K\(^{(60,61)}\), O K\(^{(62–67)}\), F K\(^{(68–71)}\), thresholds of light element materials, and L\(^{(72–97)}\) and M\(^{(98–103)}\) thresholds of metal elements.

4.3.3 Resonant Elastic X-ray Scattering

Figure 23 shows the selectively excited B K emission of boron oxide (\(B_2O_3\)).\(^{(104)}\) \(B_2O_3\) is an insulating material with a localized \(\pi^*\) state near 193 eV. At a 193 eV excitation, a strong elastic peak has been observed, which is REXS. REXS can also be observed in \(h\)-BN\(^{(45,105)}\) because the \(\pi^*\) state of \(h\)-BN is strongly localized at 192 eV. Thus, REXS can be utilized to detect trigonal coordination boron.
5 ADVANCED CHEMICAL ANALYSIS USING SOFT X-RAY EMISSION SPECTROSCOPY

5.1 Chemical Bonding of Liquid Water

As mentioned in Section 2.2, experiments for SXE are generally performed under a high vacuum. Thus, samples, even liquid or wet ones, should be stable in a vacuum. On the other hand, the long probing depth of SX, which is longer than the electrons in photoemission spectroscopy, is an advantage for bulk analysis.

SXE studies on liquid water solutions have been performed using water cells. The water cell has a thin window, which separates the liquid and the vacuum, and the incident SX beam and the emitted SX beam from the liquid sample can transmit the window. Silicon nitride with a thickness of several hundred nanometers is typically used for the window.

Figure 24(a) shows the SR-excited SXE in the O region of liquid water and water molecules (water vapor) compared to the theoretically calculated molecular orbitals and DOSs. The liquid water model for the calculation is a cluster composed of 26–28 water molecules, generated by molecular dynamic simulations.

The measured SXF spectral profiles can be assigned mainly to the $1b_1$, $3a_1$, and $1b_2$ orbitals. The $1b_1$ orbital is the ‘lone pair’ orbital, and the $1b_2$ and $3a_1$ orbitals are responsible mainly for OH bonding. The spectral profile of liquid water is very similar to that of a water molecule. However, a slight difference is observed at the $3a_1$ structure, which depends on the chemical states of hydrogen bonding.

Figure 24(b) shows the resonant and nonresonant SXE spectra of liquid water compared to the calculated spectra for various symmetry models. The nonresonant SXE spectrum agrees with the SYM model, suggesting that the electronic structure of water molecules has four hydrogen bonds. On the other hand, the resonant spectrum agrees with the D-ASYM model, suggesting that one hydrogen bond is broken. This study demonstrates the powerful potential of RIXS to investigate the electronic structures and local structures of liquid systems.
5.2 Operando Observation of Electrode Reactions

Utilizing SXE advantages such as being a powerful tool for electronic structure analysis and its bulk-sensitive long observation length, SR-excited SXE has recently been applied to operando observations of chemical reactions. For polymer electrolyte fuel cells (PEFCs), it has strongly been required to determine the active site of the oxygen reduction reaction (ORR) and to directly clarify the reaction mechanism at carbon-based catalysts. Consequently, operando SXE observations have been conducted on carbon-based catalysts prepared by pyrolyzing a mixture of iron phthalocyanine (FePc) and phenolic resin (PhRs).\(^{111}\)

Operando SXE measurements in the Fe L region have been performed at SPring-8 using a vacuum compatible membrane electrode assembly (MEA) cell. Figure 25(a,b) shows the MEA cell structure. The vacuum environment of the beamline with an SXE spectrometer is separated by a 150 nm thick SiC membrane from the MEA in the atmosphere. The transmission of the incident and emitted X-ray near 710 eV to the SiC membrane is 57%. An O-ring, SiC membrane, PTFE gaskets with Au foil, and the MEA are sandwiched between a vacuum flange and the MEA cell. The MEA cell has four gas channels and two guides for the electrodes. The electric potential between both electrodes can be manipulated by a Potentio/Galvanostat.

Figure 25(c) shows the operando Fe L SXE spectra excited at 710.0 eV for MEA samples under O\(_2\) or N\(_2\) flows and with operation voltages of 0.4 or 1.0 V plotted as the energy loss from an elastic peak at 710 eV. The main peak around 3.5 eV reflects a nonresonant Fe L emission from metallic iron as Fe or Fe\(_3\)C. The peak at 1.5 eV observed under N\(_2\) gas is significantly reduced under O\(_2\) gas. This suggests that oxygen adsorbs on an iron site with a planar ligand coordination, such as Fe–N\(_x\) embedded into the sp\(^2\) carbon network. This finding has not been observed in ex situ measurements, demonstrating the capability of operando SXE measurements for dynamic reaction analysis.

6 CONCLUSION

SXF is a useful method to analyze the electronic structure of light element materials and middle Z materials. Since the advent of SR, SXF spectroscopy has advanced to SXE spectroscopy using highly brilliant SR as an energy-tunable excitation source. SXE essentially provides element-, orbital-, and symmetry-specific information for valence band and electronic transitions. Sophisticated high-energy-resolution SXE spectrometers allow fine information to be extracted from various functional materials not only in basic research fields of physics,
Figure 25 (a, b) The schematics of the MEA cell for operando SXE measurements; exploded (a) and cross-sectional assembled views. (c) The operando Fe L SXE spectra of the multi-FePc/PhRs catalyst.\(^{(111)}\) (Reproduced with permission from Ref. 111. © Elsevier, 2013.)
chemistry, electronics, energy science, and life science but also in industrial technology. In addition, operando SXE technology utilizing the long observation length of SX enables direct observations of chemical reactions in the atmosphere. Such advanced SXE instrumentation and analytical methods, including theoretical analysis, will open unexplored research fields.

**ABBREVIATIONS AND ACRONYMS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CCD</td>
<td>Charge-coupled Device</td>
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<tr>
<td>DOS</td>
<td>Density of State</td>
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<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme Ultraviolet</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
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<tr>
<td>K–B</td>
<td>Kirkpatrick–Baez</td>
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<tr>
<td>MCP</td>
<td>Microchannel Plate</td>
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<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
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<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
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<tr>
<td>PDOS</td>
<td>Partial Density of State</td>
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<tr>
<td>PEFC</td>
<td>Polymer Electrolyte Fuel Cell</td>
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<tr>
<td>REXS</td>
<td>Resonant Elastic X-ray Scattering</td>
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<tr>
<td>RIXS</td>
<td>Resonant Inelastic X-ray Scattering</td>
</tr>
<tr>
<td>SR</td>
<td>Synchrotron Radiation</td>
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<tr>
<td>SX</td>
<td>Soft X-ray</td>
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<td>SXE</td>
<td>Soft X-ray Emission</td>
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<td>SXF</td>
<td>Soft X-ray Fluorescence</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<tr>
<td>VLSG</td>
<td>Varied Line Spacing Grating</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
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**REFERENCES**


39. Y. Muramatsu, unpublished data


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