A high resolution and large solid angle x-ray Raman spectroscopy end-station at the Stanford Synchrotron Radiation Lightsource

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We present a new x-ray Raman spectroscopy end-station recently developed, installed, and operated at the Stanford Synchrotron Radiation Lightsource. The end-station is located at wiggler beamline 6-2 equipped with two monochromators-Si(111) and Si(311) as well as collimating and focusing optics. It consists of two multi-crystal Johann type spectrometers arranged on intersecting Rowland circles of 1 m diameter. The first one, positioned at the forward scattering angles (low- q), consists of 40 spherically bent and diced Si(110) crystals with 100 mm diameters providing about 1.9% of 4π sr solid angle of detection. When operated in the (440) order in combination with the Si (311) monochromator, an overall energy resolution of 270 meV is obtained at 6462.20 eV. The second spectrometer, consisting of 14 spherically bent Si(110) crystal analyzers (not diced), is positioned at the backward scattering angles (high- q) enabling the study of non-dipole transitions. The solid angle of this spectrometer is about 0.9% of 4π sr, with a combined energy resolution of 600 meV using the Si (311) monochromator. These features exceed the specifications of currently existing relevant instrumentation, opening new opportunities for the routine application of this photon-in/photon-out hard x-ray technique to emerging research in multidisciplinary scientific fields, such as energy-related sciences, material sciences, physical chemistry, etc. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4704458>]

I. INTRODUCTION

Soft x-ray absorption spectroscopy (XAS), especially in the near-edge region, is a powerful and widely used technique for the structural and chemical characterization of low-Z based systems.¹ The elements C, O, and N are of particular importance as they are abundant and their electronic structure is sensitively influenced by the local chemical environment. Through the symmetry-allowed core electron excitation, the respective density of the lower unoccupied electronic states can be probed (i.e., σ^* and π^*), providing detailed information about the electronic structure and atomic arrangement, with much better than Ångström sensitivity.

Soft XAS can be realized through various detection modes; total electron yield (TEY) and total or partial fluorescence yield (PFY) are the ones most often employed. Although the fluorescence-based modes can result in an information depth of up to several hundreds of nanometers (while the TEY probes the very first few nanometers), soft XAS is in general a surface-sensitive technique. Inner-shell electron energy loss spectroscopy (EELS) is another technique of very high sensitivity that provides XAS equivalent information.^{2,3} However, the very short elastic and inelastic scattering mean free path of energetic electrons restricts the required thickness of the appropriate samples to the nanometer regime. In

all of these techniques, the relatively strong interaction of the probe (soft x-rays or electrons) with matter poses significant limitations to the study of various categories of samples, in particular placing restrictions on the sample environment in vacuum conditions.

X-ray Raman spectroscopy (XRS) is an alternative hard x-ray based technique that can extract soft-XAS information.⁴⁻¹² This hard x-ray photon-in/photon-out technique combines the advantages of a hard x-ray probe with the sensitivity of soft x-ray XAS. In particular it enables bulk studies of low-Z systems under many conditions including extreme pressure/temperature environments, flow tubes, furnaces, liquids, *in situ* cells, etc. In the last decade, the technique moved from demonstration experiments to numerous science applications, most notably the oxygen K-edge studies of water and aqueous solutions under numerous conditions.¹³⁻³¹

The main limitation that hampers the wide applicability of XRS is the very weak Raman cross section, which is on the order of a few barns-as compared to the Mbarns range for conventional XAS. Therefore, to make the technique practical, a large solid angle of the Raman scattered photons has to be collected. To accomplish this, Rowland geometry spectrometers based on multiple perfect-crystal Bragg analyzers that operate in back scattering mode close to 90° have been built by various groups during the last decade.^{10,13,32-40} Yet many of these instruments, in particular those with very

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large efficiency, have a significantly poorer energy resolution (~ 1 -2 eV) as compared to soft x-ray based techniques and EELS (100 meV). The few that are optimized for higher resolution suffer from a much-reduced efficiency.

Here, we present a novel x-ray Raman spectroscopy end-station that was recently developed, installed, and operated in the middle hutch of beamline 6-2 at Stanford Synchrotron Radiation Lightsources (SSRL). The analyzer setup consists of two multi-crystal high energy resolution x-ray spectrometers leading to a wide solid angle of detection, as well as a soft-XAS comparable energy resolution. In addition, the spatial arrangement of the instruments also enables the implementation of XRS studies beyond the dipole approximation, providing insights into non-dipole-allowed electronic excitations (e.g., monopole, quadrupole, or octupole transitions). Some representative first applications of this now operational end-station will be briefly presented and discussed.

II. X-RAY RAMAN SCATTERING AND X-RAY RAMAN INTENSITY

According to the x-ray Raman scattering process, a high-energy incident photon, $\hbar\omega_1$, excites a core electron to an outer unoccupied state while the excess of energy is released with a scattering photon, $\hbar\omega_2$ (Fig. 1). The theoretical description of inelastic x-ray scattering (and thus x-ray Raman scattering too) has been reported in detail elsewhere.^{41,42} The double differential cross section is expressed as

$$\frac{d^2\sigma}{d\Omega_2 d\hbar\omega_2} = r_0^2 \left(\frac{\omega_2}{\omega_1} \right) |\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 S(\mathbf{q}, \omega), \quad (1)$$

with

$$S(\mathbf{q}, \omega) = \sum_f \left| \langle i | \sum_j \exp(-i\mathbf{q} \cdot \mathbf{r}_j) | f \rangle \right|^2 \delta(E_i - E_f + \hbar\omega), \quad (2)$$

where r_0 is the electron radius, $\mathbf{q} = \mathbf{K}_1 - \mathbf{K}_2$ is the momentum transfer, $\hbar\omega = \hbar\omega_1 - \hbar\omega_2$ is the energy loss, $\mathbf{r}_j$ is the core orbital j average radius, and $\mathbf{e}_1, \mathbf{e}_2, \mathbf{K}_1$, and $\mathbf{K}_2$ are the electric field vectors and wavevectors for the incident and the scattered photon, respectively. The above summations run over all possible final unoccupied states (f) and over the number of atomic electrons (j).

The exponential term can be expanded accordingly: $\exp(i\mathbf{q} \cdot \mathbf{r}) = 1 + i\mathbf{q} \cdot \mathbf{r} + \frac{(i\mathbf{q} \cdot \mathbf{r})^2}{2!} + \dots$. As long as the dipole

FIG. 1. A schematic representation of the x-ray Raman scattering process from a 1s initial state. A high-energy incident photon $\hbar\omega_1$ interacts with an atom in the ground state ($|i\rangle$) resulting in a core electron excitation ($|f\rangle$) and an inelastically scattered photon, $\hbar\omega_2$ (all symbols are explained in the text).

approximation condition ($q\mathbf{r} < 1$) is fulfilled, the dynamical structure factor $S(\mathbf{q}, \omega)$ for a given core electron j under the frozen core approximation (i.e., initial and final states are orthogonal) is simplified as follows:

$$S(\mathbf{q}, \omega) \rightarrow \sum_f \mathbf{q}^2 |\langle i | \mathbf{r} | f \rangle|^2 \delta(E_i - E_f + \hbar\omega). \quad (3)$$

The matrix elements of Eq. (3) indicate the equivalence of x-ray Raman scattering and x-ray absorption for this low momentum transfer regime;⁴² it can be shown that $|\langle i | \mathbf{r} | f \rangle|^2 \delta(E_i - E_f + \hbar\omega) \propto \frac{\sigma_j(\omega)}{\omega}$, where σ_j is the photoabsorption cross section for the orbital j .⁴² In addition, accounting for the fact that $\hbar\omega_1$ is much greater than the electron's binding energy and thus the energy loss is not significant ($\hbar\omega_1 \approx \hbar\omega_2$), then $|\mathbf{K}_2| \approx |\mathbf{K}_1| = \hbar\omega_1/c$ and $|\mathbf{q}| \approx (2\hbar\omega_1/c) \sin \frac{\theta}{2}$. In summary, Eq. (1) for a given inner shell electron j , and upon validity of the dipole approximation, can be expressed as

$$\frac{d^2\sigma}{d\Omega_2 d\hbar\omega_2} \propto \mathbf{q}^2 \frac{\sigma_j(\omega)}{\omega} |\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 \approx \frac{\omega_1^2}{\omega} \sigma_j(\omega) \sin^2 \frac{\theta}{2} |\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2. \quad (4)$$

Equation (4) shows the Raman cross section dependences with respect to the various experimental parameters in a quantitative manner, i.e., incident energy ($\sim \omega_1^2$), atomic number (when referring to the same shell, for example for 1s $\frac{\sigma_{1s}(\omega)}{\omega} \sim Z^{-4.7}$), momentum transfer ($\mathbf{q}^2$), and scattering angle ($\sim \sin^2 \frac{\theta}{2} |\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2$) (Ref. 43). It should be noted that for higher momentum transfers ($q\mathbf{r} \sim 1$), as the dipole approximation becomes gradually non-valid, the x-ray Raman scattering cross section calculation turns into a rather more sophisticated procedure.^{42,44,45}

In absolute units, the total x-ray Raman scattering cross section is on the order of a few barns, and therefore thick and relatively high concentrated samples are required for systematic XRS studies. However, for these cases, the corresponding attenuation for the incident and the scattered photons, respectively, has to be considered. In practice, the strong self-attenuation for the incident and scattered radiation pose limitations on the feasibility of XRS studies while at the same time indicates the appropriate energy for the incident radiation (for instance, avoiding strong absorption edges of major matrix element). The emitted x-ray Raman intensity within the energy interval of $d\omega_2$ can be expressed through the following formula:

$$\frac{dI}{d\omega_2} = c I_0 \frac{\Delta\Omega}{4\pi} \frac{d^2\sigma}{d\Omega d\omega_2} \frac{M(\hbar\omega_1; \hbar\omega_2)}{\cos \theta_{in}}, \quad (5)$$

where c is the concentration of the element of interest, I_0 the intensity of the incident radiation, $\Delta\Omega$ the solid angle of detection and $M(\hbar\omega_1; \hbar\omega_2)$ the self-attenuation term, which can be expressed for a reflection or a transmission based geometry, respectively, with the following branching expression

$$M(\hbar\omega_1; \hbar\omega_2) = \begin{cases} \frac{1 - \exp[-\mu_{tot}(\hbar\omega_1; \hbar\omega_2)x]}{\mu_{tot}(\hbar\omega_1; \hbar\omega_2)} \\ (1 - \exp[-\mu_{tot}^r(\hbar\omega_1; \hbar\omega_2)x]) \exp\left[-\frac{\mu(\hbar\omega_2)}{\cos \theta_{out}} x\right] \\ \mu_{tot}^r(\hbar\omega_1; \hbar\omega_2) \end{cases} \quad (6)$$

with

$$\mu_{tot}(\hbar\omega_1; \hbar\omega_2) = \frac{\mu(\hbar\omega_1)}{\cos \theta_{in}} + \frac{\mu(\hbar\omega_2)}{\cos \theta_{out}} \quad (7)$$

and

$$\mu_{tot}^r(\hbar\omega_1; \hbar\omega_2) = \frac{\mu(\hbar\omega_1)}{\cos \theta_{in}} - \frac{\mu(\hbar\omega_2)}{\cos \theta_{out}}, \quad (8)$$

where θ_{in} and θ_{out} are the incident and take-off angle with respect to the sample normal. μ is the sample matrix mass attenuation coefficient for the corresponding energy ($\mu(\hbar\omega) = \sum_n c_n \mu_n(\hbar\omega)$ with n the number of matrix atomic species) and is expressed in the same units as the double differential x-ray Raman cross section (usually cm^2/g). x stands for the thickness of the sample expressed in inverted cross section units.

III. CONCEPTUAL OVERVIEW & TECHNICAL DESCRIPTION OF THE DEVELOPED END-STATION

The x-ray Raman end-station was set up at the 57-pole 0.9T wiggler beamline 6-2 at the Stanford Synchrotron Radiation Lightsource. Beamline 6-2 is equipped with two liquid nitrogen cooled double crystal monochromator options, namely Si(111) ($\phi = 0$) and Si(311) ($\phi = 0$). A collimating and a focusing Rh-coated mirror positioned before and after the monochromator, respectively, deliver monochromatic x-ray photons within an energy range of about 4–18 keV. Under the present SPEAR3 storage ring operational conditions (electron energy of 3 GeV, current 350 mA in top-off mode) and through the Si(311) (Si(111)) monochromator, an incident beam flux of $\sim 4 \times 10^{12}$ photons/s (2×10^{13} photons/s) at 6.5 keV with an energy resolution of about 180 meV (850 meV) and a size of about $100 \times 400 \mu\text{m}^2$ ($v \times h$) is delivered at the sample position (~ 28 m from the source).

The x-ray Raman end-station consists of two Johann type⁴⁶ crystal spectrometers in a Rowland geometry of 1 m (Fig. 2). The first spectrometer is placed along the forward scattering angles in order to allow low-momentum transfer (low- q) measurements, whereas the second one is set at the backward scattering angles (high- q), allowing the study of non-dipole transitions. For the throughput optimization, both spectrometers are based on the concept of the multiple spherically bent analyzers (40 and 14 crystals, respectively) positioned on intersecting Rowland circles.³²

The spectrometers' design aims to optimize the energy resolution that would ultimately required for the x-ray Raman spectroscopy studies; that is, to be comparable to the 1s core-hole lifetime of low-Z atoms. The overall instrumental energy resolution for an apparatus employed for inelastic x-ray scattering is defined by the energy bandwidth of the incident beam, the intrinsic energy resolution of the spectrometer analyzers, as well as various geometrical considerations with respect to the scattering source size and the Bragg angle of operation.

The influence of the various geometrical parameters on Johann-type spectrometers has been reported in detail previously.³² Considering the beamsizes of beamline 6-2, the most crucial geometrical contribution originates from the

FIG. 2. Three dimensional technical drawing of the high-resolution x-ray spectroscopy end-station at beamline 6-2 at Stanford Synchrotron Radiation Lightsource (side perspective and top view). Note: Besides the two x-ray Raman spectrometers located at the forward and the backward scattering angles, the x-ray emission/RIXS spectrometer at beamline 6-2 is also depicted.

effective beam projection along spectrometer's dispersion plane. In order to minimize this contribution, and since the vertical beam size ($\sim 100 \mu\text{m}$) is narrower than the horizontal one ($\sim 400 \mu\text{m}$), both spectrometers were set close to the storage ring plane and in a vertical Rowland circle arrangement. However, the horizontal polarization of the incident beam indicates the maximum scattering intensity along the vertical plane (Eq. (1)). Despite the loss of intensity that facilitates the resolution optimization (detailed calculations for both spectrometers estimate the intensity loss to be of about 40%), the storage ring plane position may also significantly facilitate the experiments and the sampling environments from a practical point of view. Further on, the possibility of implementing appropriate diffraction elements for rotating the beam polarization by $\frac{\pi}{2}$ remains open.

The magnitude of the geometrical contributions within the energy resolution is strongly coupled with the Bragg angle; for the perfect backscattering case, such contributions are minimized ($\cot 90^\circ \rightarrow 0$).³² Here, both spectrometers are designed to operate on a fixed Bragg angle close to backscattering (low- q at 88° and high- q at 87.4°). The angle of 88° for a 1 m Rowland circle defines the minimum distance between detector and sample to be about 70 mm, thus providing

FIG. 3. An inelastic scattering spectrum on an extended energy transfer range from highly ordered pyrolytic graphite using the inverse scanning mode. The elastic peak, the inelastic scattering from the valence electrons, the plasmon and Compton scattering distribution as well as the x-ray Raman scattering from the core 1s electrons can be resolved, indicating at the same time the relative intensity for each of the scattering process. The spectrum was obtained through the 40-crystal XRS spectrometer using the Si(440) reflection at 88° (6462.20 eV). The overall energy resolution (40 crystal analyzers and Si(311) monochromator), as estimated through the elastic peak FWHM, is 270 meV (shown zoomed in the right upper corner inset).

the required space to implement a wide variety of sample environments (cryostats, *in situ* cells, diamond anvil cells, etc.). Since the spectrometers developed here have a fixed analyzing energy, the beamline monochromator is scanned in order to acquire energy transfer measurements for an extended range along the absorption edge of interest (Fig. 3). This standard experimental procedure adopted for x-ray Raman scattering measurements assures a constant solid angle of detection and efficiency of the spectrometer over the whole region of the energy scan. On the other hand, when extended energy-loss ranges are attempted using the latter scanning scheme, deviations in the XRS cross section are imported due to the change of the incident energy and consequently of the momentum transfer (for a given angle of observation); when changes are considered non-negligible, appropriate corrections can be applied (see Eqs. (1) and (4)).

Optimally, the intrinsic energy resolution of the analyzers should be comparable to the respective bandwidth of the incident beam (here about 180 meV at 6.5 keV for the Si(311) monochromator). Dynamical diffraction theory predicts in a very reliable way the reflectivity curves and the Darwin width for perfect flat crystals (see Fig. 4). However, the spherically bent crystals suffer from lattice stress induced perpendicular to the surface. This lattice deformation leads to a significantly broader rocking curve, when compared to the perfect flat crystal case.⁴⁷ Although this degrades the energy resolution, at the same time it also increases the integrated reflectivity, as long as the extinction length is much shorter than the absorption length (i.e., the peak reflectivity is not affected significantly).

FIG. 4. Dynamical diffraction theory calculated Darwin widths for various Si crystal cuts at the backscattering Bragg angle (assuming perfect flat crystals).⁴⁸ Corresponding values for a series of identical Ge crystal cuts are also presented (the labels for the Ge points are omitted, however the correspondence to the respective Si cases is evident).

For the spectrometers designed here, the Si(110) crystal orientation was selected (the Darwin width for a flat Si(440) crystal and for a backscattering reflection, ~ 6.5 keV, is estimated to be about 65 meV). The Si(440) crystals of 4 in. in diameter and bent over a radius of 1 m were found at beamline 6-2 to provide an overall energy resolution of about 500 meV at backscattering (the term *overall* stands for the coupled energy resolution due to the analyzer, the Si(311) monochromator and the source size). The contributions from curving the analyzer are estimated to be of about a factor of 7 greater than the flat crystal case.

To optimize the energy resolution, diced Si(110) spherically bent analyzers (made by XRS TECH) were used. Each diced crystal consists of several thousands of spherically bent parquets of about 1×1 mm² size and a thickness of 0.3 mm bonded on a glass substrate. The parquets cover 75% of each crystal's overall surface, i.e., 100 mm in diameter. The parquets of a diced crystal exhibit a significantly lower lattice deformation when compared to the conventional spherically bent analyzers; in this way, a significantly better performance in terms of energy resolution can be achieved. A few arbitrarily selected XRS TECH diced crystals were examined by SLAC's metrology department, confirming that the optical surface for each 1×1 mm² parquet maintains a bent curvature of 1 m along their overall surface with an accuracy of a few micrometers. Concurrently, the relative position of the parquets on the glass substrate lies on a 1 m sphere with an accuracy of a few micrometers. Elastic peak scans recorded with individual diced Si(440) crystals at beamline 6-2 resulted on an overall resolution for the various crystal within the range of 220–280 meV (at backscattering with the Si(311) monochromator). After unfolding the crystal contribution, an indicative effective Darwin width of about three times greater than the flat crystal case can be extracted (~ 170 meV). This crystal performance matches well with the energy resolution of the monochromator for the energy region at which the beamline exhibits peak performance. In addition, the allowed higher

diffraction orders of the analyzers, e.g., Si(660) and Si(880) enable inelastic x-ray scattering measurements with higher incident energies of about 10 and 13 keV, respectively.

A. Technical description of both spectrometers

The low- q spectrometer consists of 40 diced Si(110) crystal analyzers arranged on a 8×5 stacking array over a 1 m spherical segment; the crystal's active surface results in an overall solid angle of the spectrometer of $\sim 1.9\%$ of 4π sr (Fig. 2). This instrument is set along the forward scattering angles regime with its center lying at 40° in order to meet, as much as possible, the dipole approximation condition and thus to enable soft-XAS equivalent studies. When using a single detector, the angular opening of the spectrometer of about 50° , averages over a relatively wide range of momentum transfers (for instance, for the Si(440) reflection, the spectrometer surface corresponds to momentum transfers within 0.4–1.7 a.u.). In order to avoid non-dipole contributions the largest momentum transfers need to be kept within the dipole approximation. Alternately, it is possible to perform q -dependent measurements, by directing individual columns of the spectrometer into multiple individual detectors. The advantage of the single detector setup is a higher signal to noise ratio.

The high- q spectrometer consists of 14 crystal analyzers arranged in two 7-crystal arrays as seen in Fig. 2. Currently, the spectrometer is using conventional spherically bent Si(110) crystals of 100 mm diameter. The center of the spectrometer is set at 145° with respect to the direction of the incident beam and has an angular opening of about 40° ; for the Si(440) crystal reflection, the spectrometer's angular opening corresponds to momentum transfers in the range of 3.0–3.4 a.u.

For aligning purposes, each analyzer is mounted on an adjustable module. This module integrates three rotational motors coupled on corresponding lead screws with a total linear range of two inches (Fig. 5). The lead screws' tips are in contact with kinematic mounts positioned at the backside of the crystal support plate. Two constant force springs ensure a tight contact between the motor tips and the crystal. Two motors are used for the angular alignment of the crystal (for the pitch and the yaw, respectively) whereas a third motor, when operates simultaneously with the other two, results in a linear motion along the crystal's normal direction. Since the motion points are located at the back-side of each crystal support, the rotation axes are not defined on the crystal surface center and thus a crystal displacement accompanies each angular motion of the analyzers. Nonetheless, accounting for the required range of motion, the displacement (in the range of a few tens of micrometers) is negligible for a 1 m Rowland circle geometry. For the motors' motion control, an in-house developed FPGA-based driver and multiplexer box is used.

For both spectrometers, the analyzed x-rays are recorded by means of two silicon drift detectors (energy resolution FWHM of about 150 eV at 5.9 keV). This way, in most cases, the analyzed signal can be resolved from the diffused scattering and the fluorescence of surrounding materials, thus considerably improving the signal to background ratio. In ad-

FIG. 5. Three-dimensional mechanical drawing of the crystals adjustable module. Three rotational stepping motors provide all the required angular and translational motions for crystal alignment.

dition, as the overall experimental station operates at atmospheric pressure, a polypropylene bag filled with helium is used to minimize both the attenuation and the diffused scattering of the x-rays as they propagate from the sample to the analyzers and then toward the detector.

B. Deviations from the exact Johann geometry for multirow spectrometers operating on a fixed energy

According to the concept of the Rowland geometry, for a given source and detector position only a circular set of points fulfill the exact Rowland condition. The Johann spectrometers are accompanied by the so-called Johann aberration, i.e., moving along the dispersion plane of the analyzer, and away from the perfect Rowland circle position, the incident angle increases gradually. Nonetheless, for near backscattering geometries (close to 90°), and for crystals of a few inches of diameter, even the outermost crystal areas can analyze the energy of interest due to the minor variation of the angle of incidence, the crystal's Darwin width, and the finite source size.

For multirow spectrometers, the Johann aberration indicates that crystals cannot be set along an extended spherical segment. The crystals that lie away from the row that intersects the exact Rowland circle plane have to be tilted along their dispersion plane in order to meet a common Bragg angle condition. On the other hand, given the fixed position of the sample, the detector footprint of those crystals off the exact Rowland circle plane would be shifted slightly (Fig. 6(b)). As long as the shift is not prominent, the detector's extended active surface (usually is several tens of mm^2) can compensate this misalignment. However, a tight collimation of the detector's active surface is mandatory for minimizing the signal to diffused background ratio. That is a point of high importance, especially for the detection of very low cross section processes such as x-ray Raman scattering. For

FIG. 6. A Monte Carlo ray tracing study for the 40-crystal XRS spectrometer at 88° . (a) The blue circle indicates the set of points that lie on the exact Rowland plane for 1 m Johann geometry and for the given source and detector position. The green vertical circles depict the overlapping Rowland circles for spectrometer mid-row crystals. Red and blue lines represent the trajectories of the scattered and the analyzed photons, respectively. (b) Detector plane footprints for all the crystal analyzers. The footprint shifts gradually for the crystal rows lying away from the Rowland plane. The broadening of the footprints originates from Johann aberration, the crystal Darwin width, and are also due to the finite beamsizes ($100 \times 400 \mu\text{m}^2$), which has been explicitly taken into consideration.

efficient detector collimation, the footprints for all analyzers have to be set as close as possible to one another (to move the footprint of a crystal vertically, the crystal has to move slightly along its normal direction; although it has to be expected that this is at the expense of focus size and energy resolution). In the present case, the detector's active surface for both spectrometers were masked using $1 \times 5 \text{ mm}^2$ ($v \times h$) entrance slits. From a practical point of view, all crystals were initially positioned with millimeter accuracy on their nominal positions (i.e., along a 1 m spherical surface); then, through iterative adjustments, their optimum spatial and angular position was established individually as the detected count rates were maximized and the elastic peak scan for each one of them was overlapped.

IV. FIRST RESULTS AND DISCUSSION

The overall response functions of the two instruments, i.e., the convolution of the monochromator and spectrom-

(a) Normalized 1s x-ray Raman cross sections

(b) X-ray Raman intensities from bulk samples

FIG. 7. Relative x-ray Raman scattering cross sections (a) and intensities (b) for the 1s shell of low Z atoms. The values have been extracted through the dipole approximated Eq. (4) for forward scattering angle of 45° . The momentum transfer for Si-440 (660) is about 1.3 (2.0) a.u. It should be noted that the lightest elements (Li, B) would eventually deviate significantly from the dipole approximation especially in the case of the Si(660);⁴⁹ their values are only indicative.

ters' energy resolution, can be evaluated through elastic scattering scans. However, due to the different angular dependence of the elastic scattering when compared to the x-ray Raman (originating by the horizontal polarization of the incident beam), the contribution of the individual analyzers is slightly biased (the crystals closer to the forward direction exhibit a higher contribution). Nonetheless, the very similar response of the crystals indicates that the actual response for the x-ray Raman process is not expected to deviate substantially from the one suggested by elastic scattering. Adopting this procedure, the overall energy resolution for the

FIG. 8. (a) Angular dependent carbon 1s x-ray Raman spectra from HOPG (Compton background contribution has been subtracted for ease of presentation). As the HOPG c -axis gets perpendicular to the average $\mathbf{q}$ transfer vector, a maximum π^* to σ^* ratio is observed (red curve); the ratio is gradually decreasing as the c -axis is rotated with steps of 10° (average momentum transfer $q_{av} = 1.3$ a.u.). For comparison purposes all spectra are normalized at the sharpest σ^* feature (Si(440) reflection). (b) X-ray Raman scattering of Oxygen 1s electrons as measured on liquid water (Si(440) reflection, $q_{av} = 1.3$ a.u.). (c) Li metal 1s XRS raw spectrum (Si(440) reflection, $q_{av} = 0.9$ a.u.). (d) Fe-L_{2,3} XRS from a LiFePO₄ battery cathode (Si(660) reflection, $q_{av} = 2.1$ a.u.). For all measurements the Si(311) monochromator was used.

low- $\mathbf{q}$ and the high- $\mathbf{q}$ spectrometer for the Si(440) (Si(660)) analyzers' reflection, through the Si(311) monochromator, was found to be 0.27 eV (0.50 eV), and 0.60 eV (1.4 eV), respectively. For all cases, the shape of the response functions can be well-described with Gaussian distributions.

In Fig. 7, we present in a relevant scale the dependence of the x-ray Raman cross section for the 1s state of various low atomic number elements for incident photon energies that correspond to the Si(440) and Si(660) reflections of the spectrometers. The calculations are based on the dipole-approximated Eq. (4). In addition, respective calculations for the expected intensities from corresponding bulk mono-elemental targets are presented as obtained for a reflection geometry case through Eq. (5) (the relative changes for the amongst the different crystal cuts reflectivity as well as the beamline 6-2 transmission has been taken into account). For all calculations a geometrical configuration of $\theta_{in} = 80^\circ$ and $\theta_{out} = 55^\circ$ (i.e., forward scattering angle of 45°) was used. All points have been normalized to the corresponding values of carbon for the Si(440) reflection case. In this

way estimations for expected experimental XRS count rates from various sample cases can be attempted. However, from an experimental point of view, it should be noted that the Compton scattering distribution would also be a part of the overall detectable signal. In this way, reliable estimations for experimental measurements time (i.e., to estimate the signal to noise ratio) would ultimately require also an estimation for the corresponding Compton profile for the given sample matrix.

A few examples of XRS spectra measured with the low- $\mathbf{q}$ 40 crystal spectrometer are presented within Fig. 8. In Fig. 8(a), a series of carbon 1s spectra from a highly oriented pyrolytic graphite (HOPG) sample are shown. The various spectra correspond to different angles of incidence for the incident beam with respect to the HOPG surface with steps of 10° . When the c -axis of the HOPG is perpendicular to the spectrometer's average momentum transfer vector, a maximum π^* to σ^* intensity ratio is observed. On the other hand, as the c -axis orientation is changing with respect to the $\mathbf{q}$, this ratio is gradually decreasing in favor of the

FIG. 9. Comparison between carbon 1s XRS spectra from a polycarbonate as measured with low- and the high- q spectrometers using the Si(311) monochromator (mean average momentum transfer for the low and high- q spectra is 1.3 a.u. and 3.2 a.u. respectively). The area of high- q spectrometer's spectrum has been normalized to the respective low- q area. Compton background contribution has been subtracted for ease of presentation.

σ^* transition that becomes dominant when the c -axis approaches the q orientation. It is worth noting that the instrument's energy resolution (~ 270 meV) permits to resolve in detail the spectral features along the complex σ^* region, whereas the required measuring time for each of the C spectra is less than 5 min. The signal to background ratio for the highest π^* case is about 20. In Fig. 8(b) an oxygen 1s spectrum is shown as obtained from liquid phase of water; again, a very high quality spectrum can be obtained in less than 10 min. The 1s XRS spectra of Li measured on a bulk metallic Lithium target is shown in Fig. 8(c). The spectrum has been obtained using only the three lowest- q columns of the 40-crystal spectrometer in order to reduce the Compton background within the Li 1s energy transfer regime, as well as to assure that the dipole approximation ($qr < 1$) remains valid for such a light element. In Fig. 8(d), an XRS spectra of Fe $2p_{3/2}$ and $2p_{1/2}$ obtained from a LiFePO₄ charged battery cathode material is shown. Due to the strong photo-absorption of the incident beam from the Fe 1s when the spectrometer operates at the Si(440) reflection, the Si(660) was used to realize this measurement. In Fig. 9, a comparison of a carbon XRS spectra from a polycarbonate bulk material between the high- and low- q spectrometers is shown (acquisition time was less than 5 min).

V. SUMMARY AND CONCLUSIONS

Described here is a new x-ray Raman spectroscopy end-station recently developed, installed, and now operated at the SSRL. The apparatus consists of two multi-crystal Johann spectrometers arranged on a Rowland circle of 1 m. A large acceptance 40-crystal spectrometer is positioned along the low momentum transfer direction (forward scattering angles) providing soft XAS alike information with an overall energy resolution down to 270 meV at 6462.20 eV through the implementation of diced Si(110) crystal analyzers. Concurrently, a second 14-crystal spectrometer positioned at the

high- q regime (backward scattering angles) can provide further insights into the electronic transitions beyond the dipole approximation.

The large acceptance, as well as the high energy resolution of this experimental station, overcomes some important limitations that limited the wide applicability of x-ray Raman spectroscopy (i.e., very weak interaction cross sections and low energy resolution compared to the corresponding soft XAS based studies). These capabilities are expected to open up new directions on the applicability of this hard x-ray photon-in/photon-out technique on various emerging scientific fields. Systematic studies of aqueous or diluted samples as well as *in situ* cells in various conditions (high T/P) become now feasible, leading to improved research related to next-generation batteries, photovoltaics, hydrogen storage materials, etc. Further on, the high energy resolution of the end station (~ 270 meV at low- q) could also render the present end-station as a powerful tool to reveal new insights related to low-energy non-dipole transitions in atoms and molecular systems through q -dependent studies within the low- q regime.^{50–58} Moreover, XRS from semicore levels of heavy elements studied with the present instrument will give improved resolution of the overlapping multiplet features – an important improvement for broader application of XRS to f-electron systems.^{59–62}

The continuous progress with the x-ray optics as well as the availability of modern undulator radiation beamlines, such as the anticipated new undulator beamline at SSRL dedicated to high resolution x-ray spectroscopy, will further boost this technique to a wide range of applications. For example, it will become feasible to perform XRS based extended x-ray absorption fine structure (EXAFS) studies on small samples in realistic acquisition times. Moreover, the combination of this, and related instrumentation, with the recently available x-ray free electron laser sources, such as the Linac Coherent Light Source (LCLS) at SLAC, is expected to provide further unexplored opportunities in fields that profit from an ultra-fast, ultra-bright x-ray probe.

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