UC Santa Cruz
UC Santa Cruz Previously Published Works

Title

In situ/operando soft x-ray spectroscopy of chemical interfaces in gas and liquid environments

Permalink

Journal

ISSN

Authors

Yang, Feipeng
Feng, Xuefei
Liu, Yi-Sheng
et al.

Publication Date

2021-08-01

DOI

Peer reviewed

In situ/*operando* soft x-ray spectroscopy of chemical interfaces in gas and liquid environments

Feipeng Yang, Xuefei Feng, Yi-Sheng Liu, Per-Anders Glans, and Jinghua Guo

Feipeng Yang, Advanced Light Source, Lawrence Berkeley National Laboratory, USA; feipeng_yang@lbl.gov

Xuefei Feng, Advanced Light Source, Lawrence Berkeley National Laboratory, USA; xuefeifeng@lbl.gov

Yi-Sheng Liu, Advanced Light Source, Lawrence Berkeley National Laboratory, USA; ysliu2@lbl.gov

Per-Anders Glans, Advanced Light Source, Lawrence Berkeley National Laboratory, USA; paglans@lbl.gov

Jinghua Guo, Advanced Light Source, Lawrence Berkeley National Laboratory, USA; jguo@lbl.gov

Many energy-storage and energy-conversion systems are based on the complexity of material architecture, chemistry and interfacial interactions. To understand and thus ultimately control the energy applications calls for *in situ*/*operando* characterization tools. Over the years, *in situ*/*operando* soft x-ray spectroscopy has been developed for the studies of gas molecules, molecular liquids, catalytic, and electrochemical reactions. Soft x-ray spectroscopy offers electronic structure characterization of materials in energy conversion, energy storage, and catalysis regarding functionality, complexity of material architecture, and chemical interactions. It has been shown how to use the powerful in situ/operando soft x-ray spectroscopy characterization techniques of interfacial phenomena and how to reveal the mechanism of charge transfer and chemical transformation of solid/gas and solid/liquid interfaces of energy storage and catalytic materials in a realistic environment. It has been demonstrated how to overcome the challenge that soft x-rays cannot easily peek into the high-pressure catalytic or liquid

electrochemical reactions. The unique design of *in situ*/*operando* soft x-ray spectroscopy instrumentation and fabrication principle and examples of experiments are presented.

Keywords: electronic structure, energy storage, interface, *operando*, spectroscopy, x-ray fluorescence

Introduction

Interfacial phenomena are crucial in a verity of energy devices and chemical reactions. For example, Li ion batteries, catalysis, and photoelectrochemical cells. The functionalities of such energy devices under operational conditions are determined by the chemical reactions and charge transfer process happened at the solid/liquid or solid/gas interfaces.

In general, electronic structure ultimately determines the properties of matter, and it is therefore natural to anticipate that a description of the electronic structure of functionalized systems will lead to a progress in energy science and technology, not inferior to the one we have seen in recent years. Soft x-ray spectroscopy has some basic features that are important to consider. Soft x-ray originates from an electronic transition between a localized core state and a valence state. As a core state is involved, elemental selectivity is obtained because the core levels of different elements are well separated in energy, meaning that the involvement of the inner level makes this probe localized to one specific atomic site around which the electronic structure is reflected as a partial density-of-states contribution. The participation of valence electrons gives the method chemical state sensitivity and further, the dipole nature of the transitions gives particular symmetry information. Additionally, the substantial penetration of soft x-rays offers bulk-sensitivity probing.

Synchrotron based x-ray absorption spectroscopy (XAS) became an important tool as early as the 1990s for the characterization of materials as well as for fundamental studies of atoms, molecules, adsorbates, surfaces, liquids, and solids. The particular assets of XAS spectroscopy are its element specificity and chemical sensitivity. O K-edge and $3d$-transition-metal L-edge XAS was first utilized for measuring the covalent mixing of the metal $3d$ and oxygen $2p$ states in a series of $3d$-transition-metal oxides[1–3] and high-T_c superconducting properties exhibited cuprates.[4] XAS was also a most fundamental probe of the electronic and geometric structure of molecules. In addition, high-resolution XAS can detail the chemical bonding and vibrational structures of molecules.[5, 6]

Synchrotron radiation sources producing intensive tunable monochromatized x-ray beams have opened up new possibilities for soft x-ray emission spectroscopy (XES). The possibility to select the energy of the excitation has created an extra degree of freedom compared to the traditional spectroscopy pursued with high-energy electron or characteristic x-ray excitation. The energy selectivity makes it possible to perform resonant excitation (i.e., exciting to particular

empty states).[7–9] The introduction of selectively excited soft x-ray emission has opened a new field of study by disclosing many new possibilities of resonant inelastic soft x-ray scattering (RIXS). With this technique one can measure resonantly excited Ti L-edge and N K-edge signals in TiN[10] and site selectivity in high-T_c superconducting materials,[10–12] low-energy excitations in correlated materials,[13] femtosecond dynamics[14] and chemical bonding mechanism[15–17] by detuning from, for example, resonance.

Soft x-ray absorption and consequent decay through x-ray emission at the C K-edge was assumed to be two independent one-photon processes. However, resonant inelastic scattering from diamond suggested the presence of a correlation between the absorption and emission processes.[11] Such energy dependence at the C K-edge was also observed from the x-ray fluorescence of condensed C_{60}, and the strong intensity modulation of constituent spectra is detected with varying excitation energy up to 10 eV above threshold.[18] A recent work from Feng et al. observed the exciton–photon coupling (EPC) with two different phonons in graphite and a significantly different coupling strength was reported for the first time.[19] The C K-edge at different detection geometry has also been investigated using the high-resolution spectrometer (hrRIXS) and high-throughput spectrometer (htRIXS) with the emitted x-ray photons detected at 90° and 160° relative to the incident photon beam, respectively. The difference in the RIXS features is attributed to the different momentum transfer between the spectrograph geometries.[20]

Characterization of soft x-ray spectroscopy

Soft x-ray absorption spectroscopy provides information about the unoccupied states. The atomic nature of the core hole implies elemental and chemical selectivity. The probability of such a transition is related to the x-ray absorption cross section. The core vacancy left by the excited core-level electron is filled by an electron from the valence orbital, thereby soft x-ray emission also gives direct information about the chemical bonding. An interest in the technique is presently booming due to the advent of third generation synchrotron radiation sources started in the middle of 1990s.
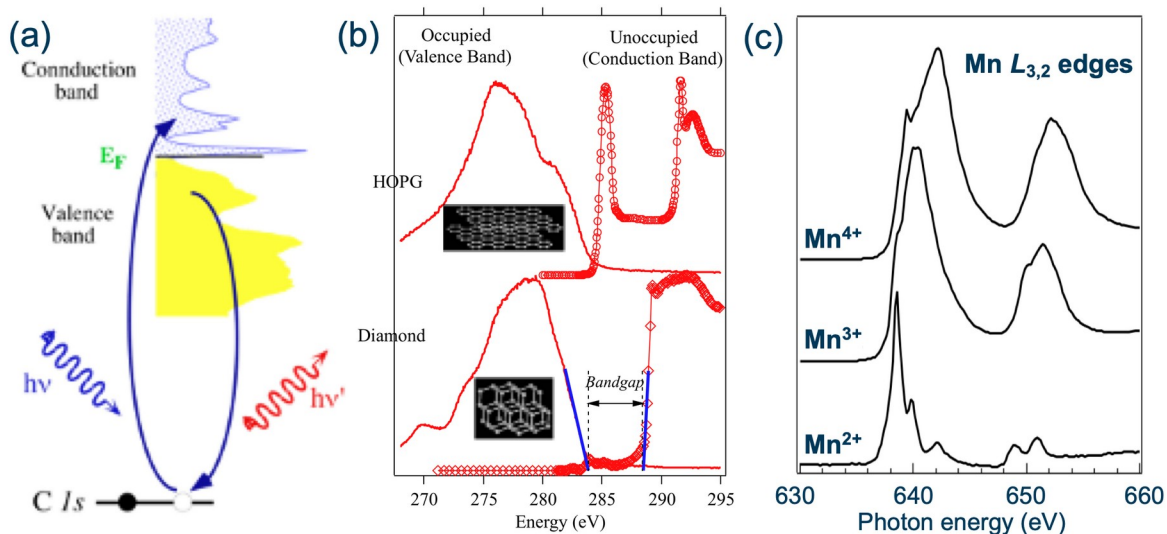
Figure 1. The energy diagram of x-ray absorption and emission excitation processes (a); the C K-edge x-ray absorption and emission spectra of graphite and diamond (b); the Mn L-edge x-ray absorption spectra of Mn at the different oxidation states (c).

For example, in carbon K-edge absorption, the carbon 1s electron is excited to empty electronic states in the carbon conduction band (shown in **Figure 1**a), and the dipole selection rule provides a tool to study locally the C $2p$ character of the unoccupied valence band. Figure 1b displays the XAS of graphite and diamond, both are made of pure carbon atoms. Carbon has an atomic number of 6 and has a $1s^2 2s^2 2p^2$ configuration in the electronic ground state. The atoms in the diamond structure are tetrahedrally bonded to their four nearest-neighbors using linear combinations of $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals in a sp^3 configuration. So, the XAS spectrum of diamond presents a spectral of σ* character rising from 289 eV. In contrast, in the graphite structure, strong in-plane bonds are formed between a carbon atom and its three nearest-neighbors from $2s$, $2p_x$, and $2p_y$ orbitals; this bonding arrangement is denoted by sp^2. The remaining electron with a p_z orbital provides only weak interplanar bonding, but it is responsible for the semimetallic electronic behavior in graphite. Thus, the XAS spectrum of graphite presents a spectral of π* at 285 eV and σ* character rising from 291.5 eV. Figure 1c shows an example for the XAS study of $3d$ transition-metal compounds. The Mn L-edge XAS spectra of different Mn compounds show different spectral profiles in corresponding to the different oxidation states. The main L_3 peak positions (and centroids) for these Mn oxides are 638.5 eV

(Mn^{2+}), 640.2 eV (Mn^{3+}), and 642.0 eV (Mn^{4+}) suggesting a higher energy shift for higher oxidation states, respectively, which provides additional spectral information beyond the chemical shifts. In addition to the inherent elemental selectivity of x-ray spectra, energy selective excitation allows separation of features that pertain to different atoms of a sample. Emission from chemically nonequivalent sites of the same atomic species can be separated as shown in the Figure 1b.

The intensity of these secondary electrons or the photons can be measured as a function of incoming photon energy. This will reflect the absorption cross section as the intensity of the secondary electrons/emitted photons are proportional to the absorbed intensity. Because of the short mean free path of electrons, the total-electron-yield (TEY) detection method is very surface sensitive (typically under 5 nm). If the out coming photons are detected, the x-ray absorption under total-fluorescence-yield (TFY) detection becomes bulk probing (about 100–200 nm) due to the comparatively larger attenuation lengths.

The emission is originating from an electronic transition between a valence state and a localized core state. The energy of the emitted x-ray is equal to the difference in energy of the two states. The involvement of the inner level makes this probe localized to one specific atomic site around which the electronic structure is reflected as a partial density of states (DOS) contribution. Chemical sensitivity is obtained when the resolution of the detected emission lines is high enough to resolve fine structure. The line shapes are determined by the valence electron distribution and the transitions are governed by dipole selection rules. For solids essentially a partial DOS mapping is obtained.
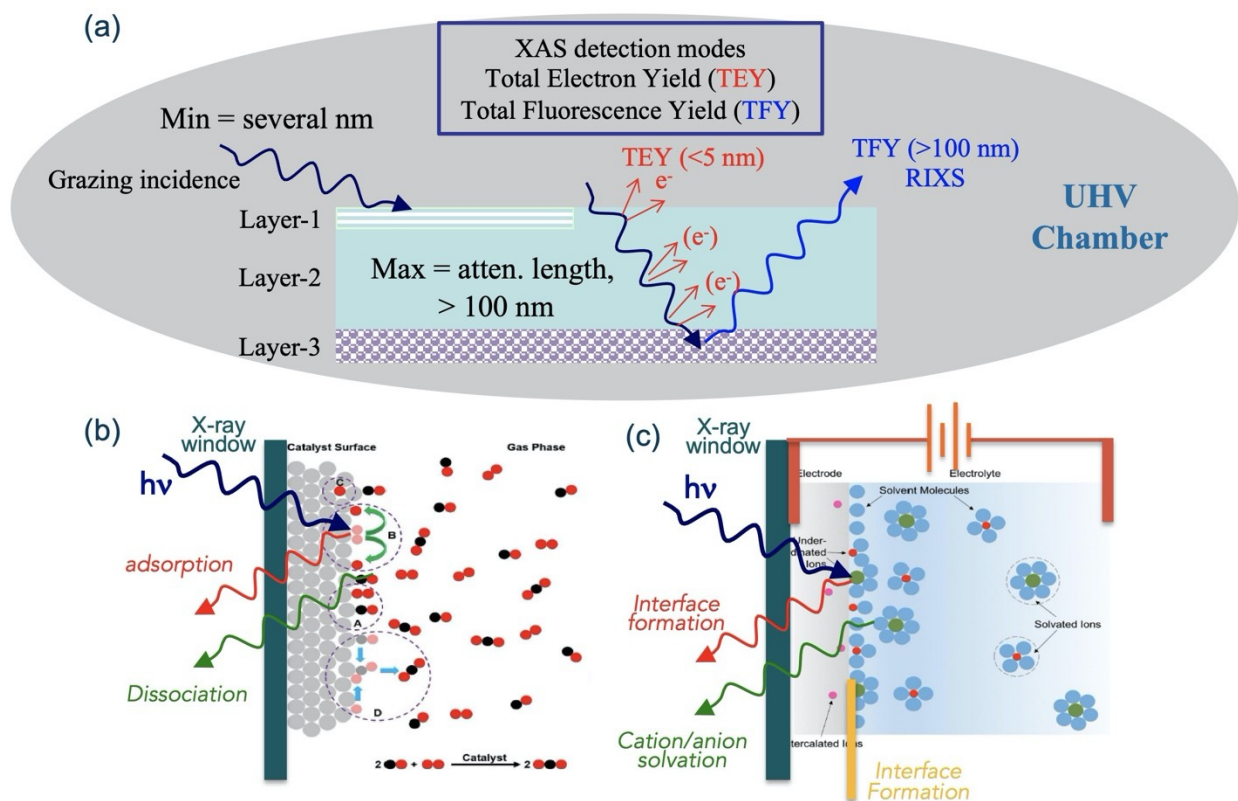
Figure 2. (a) The experimental sample schemes and electron/fluorescence yields being detected for XAS and XES measurements. Schematics of the experimental setup for (b) gas/solid interface catalysis studies and (c) solvation and desolvation studies at the liquid/solid interface.

Soft x-ray spectroscopy characterization can also be surface or bulk sensitive depending on the selected experimental geometries. When the incident angle of the excitation x-ray is set to be <5 degrees to the surface, the XAS and XES signals from the surface (as the layer-1 in **Figure 2**a) are enhanced. For an example, in such an experimental scheme, the monolayer of O_2 and CO molecules on the top of Ni(100) surface or Cu(100) surface were studied by XES.[21] In the XES study, the intensity ranging from the main feature to the sharp edge at the Fermi level reveals that there is strong hybridization of the O $2p$ states with the Ni $3d$ band, while the Cu $3d$ band is found deeper below the Fermi level (≈2 eV) than the Ni $3d$ band. With selective resonant excitations, XES reveals the details of the surface chemical bond and provides direct evidence for interaction effects: N_2 and C_6H_6 molecules adsorbed on Ni (100), and it was found that that all outer and inner valence orbitals of the molecule change due to the surface interaction.[22] The use of x-ray transmission windows such as SiN allows the probing of gas/solid interface (Figure

2b) and liquid/solid interface (Figure 2c) under operando conditions, which will be introduced in later sections.

Resonant x-ray emission is a good candidate for investigating the symmetry problem. This is because the discrete nature of core-excited states prepares the symmetry for the emission step, and the dipole character of the absorption or emission then leads to simple selection. First-row molecules, such as N_2 and O_2, are ideal candidates, because the possible symmetry breaking depends only on electronic structure and electronic motion. The results provide direct evidence that the inversion symmetry is not broken in the core-excited states. Furthermore, the experiments themselves demonstrate a new experimental technique of broad applicability for studies of electronic structure and excitation dynamics in free atoms and molecules. As shown in **Figure 3**, high resolution RIXS spectra excited as indicated in the inset at the $1s^{-1}1\pi*$ resonance in gas phase O_2 are dominated by a vibrational progression in the 0–2 eV and a structure in the 6.5–8 eV energy-loss range, corresponding to transitions to the electronic ground state. The vibrational intensities associated with the electronic ground state allow for an accurate determination of the development of the vibrational wave packet in the intermediate state and its crucial parameters. [23, 24]
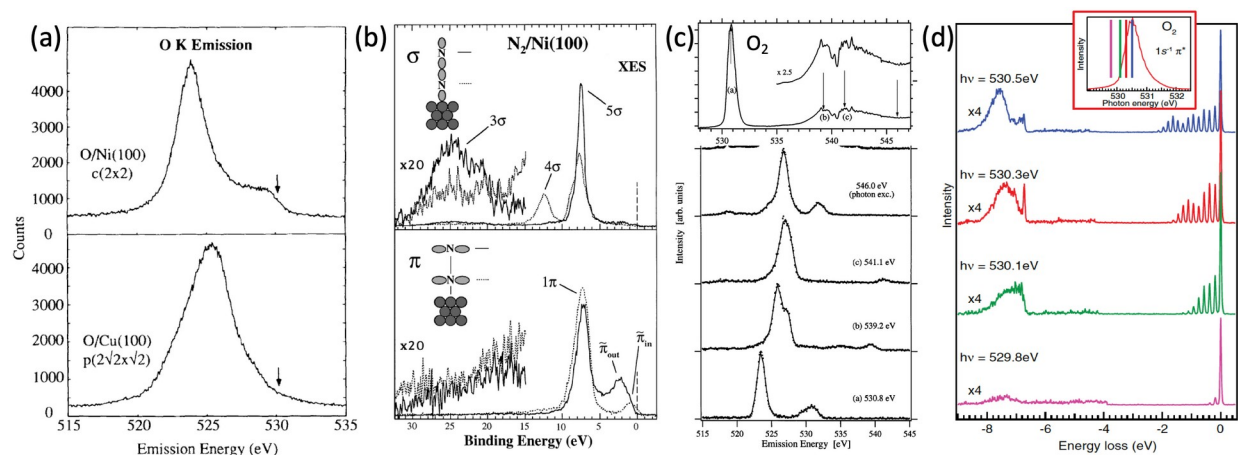

Figure 3. Soft x-ray spectroscopy experimental study of monolayer of O_2 adsorbed on Ni(100) and Cu(100) (a); N_2 and C_6H_6 molecules adsorbed on Ni (100) (b); resonant XES of O_2 molecules (c); and high resolution RIXS of O_2 (d). [23, 24]

The basic bulk probing of soft x-ray spectroscopy is a very useful asset in materials research, as very often the decisive structure for a certain property lies buried in an interface or below a capping layer. For example, in a study of Si(100) buried in GaAs (similar scheme to the layer-3 in Figure 2a), it has been demonstrated that it is in fact possible to extract detailed information about DOS.[25] By irradiating the sample with a bright source, it is possible to detect characteristic fluorescence from buried layers. The ability to probe a buried structure with respect to the chemical bonding to the surrounding matrix is applied to one monolayer (ML) of Si buried at 100 Å depth in a GaAs matrix. In the Si L-emission spectra from three different samples, 1 ML, 3 ML and bulk Si, Si local, *s* and *d* partial DOS are extracted. Clearly detectable differences as compared to the bulk Si DOS are observed. And the theoretical calculations showed good agreement with the experimental spectra and allowed for a quantitative analysis.[26] The layer thickness and the distribution over atomic sites were concluded to be very important for the total spectra. With proper experimental setup, XAS and XES from solid/gas and solid/liquid interfaces can be probed under *operando* conditions.

In situ/operando study of samples under gas and liquid environment

In contrast to hard x-ray absorption measurements, soft x-ray requires ultra-high vacuum (UHV) conditions which are required in this photon energy range. Additionally, many soft x-ray and electron detectors are operated under UHV conditions. Thus, soft x-ray absorption and emission spectroscopy in materials research has been commonly performed on solid-state samples in UHV conditions since 1980s.[1–4]
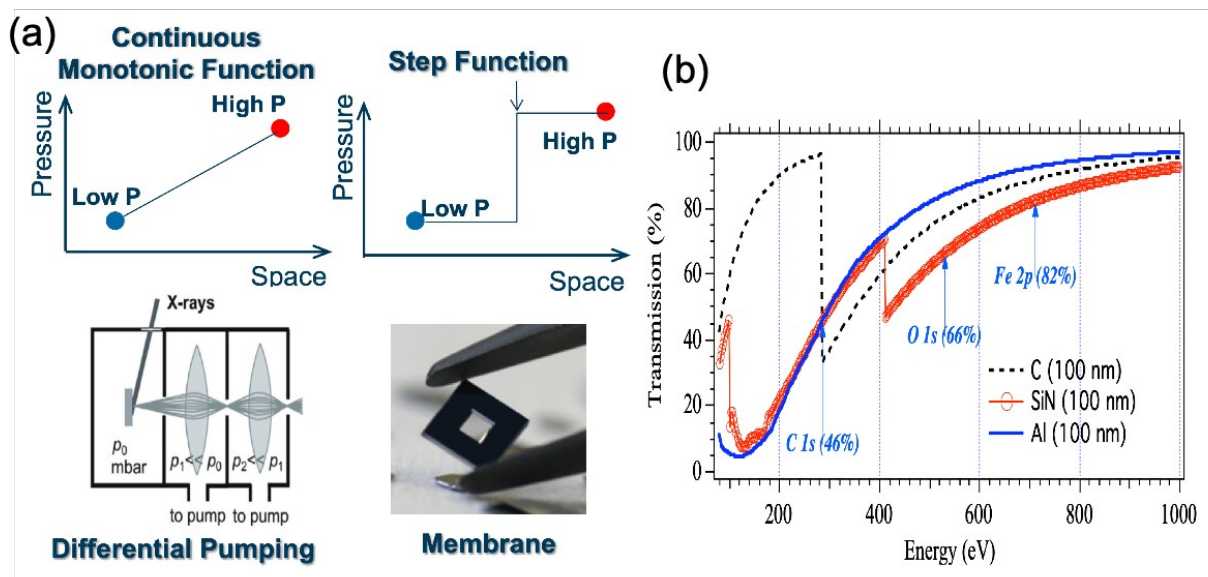
Figure 4. (a) Instrument development to handle the gas and liquid samples under UHV conditions including differential pumping to provide a pressure change as a continuous function or using an x-ray transmission membrane window to provide a pressure change as a step function. (b) The transmission (%) of membrane windows made from C, SiN, or Al as a function of energy (eV).

As demonstrated in **Figure 4**, there has been extensive instrumentation development to handle the gas and liquid samples under vacuum conditions for soft x-ray experimental studies. In general, it has been two main schemes: (1) using differential pumping capability to provide a continuous pressure change in a monotonic function with two or more stages.[27–29] (2) using an x-ray transmission membrane window to provide a pressure change in a step function with a commonly used silicon nitride window.[24]

The soft x-ray spectroscopic view of local hydrogen-bonding structures in liquid water has been a hot scientific topic over the years. Various experimental methods to handle the liquid water samples were developed: (1) sample is kept in Helium atmosphere at a pressure of 760 Torr, and is separated from the high vacuum of the beamline by a Si_3N_4 window, for which liquid water was obtained by water flowing over a metal plate with the surface of the water film;[30] (2) liquid water is realized in a liquid jet produced using fused silica nozzles;[31] (3) ice and water samples were condensed from vapor onto a cooled copper substrate. The samples were

investigated in the temperature range of −40 to 0°C;[32] (4) liquid water was contained in a silicon nitride membrane window sealed cell.[33–37]

The soft x-ray-transmission-window based gas cell design enabled the potential of gas-phase RIXS that has long been recognized by the early studies: O_2-gas molecule,[24] CO_2-gas molecule,[14] and C_2H_2, C_2H_4, and C_2H_6–gas molecules.[38] The high-resolution RIXS allows for well-resolved vibrational progressions and then observation of the spatial quantum beat effect in vibrational RIXS of molecular oxygen.[23, 39]

## Cell schemes for the characterization of surfaces and interfaces

The large attenuation length makes soft x-ray spectroscopy a tempting choice for studying buried interfaces and modifications of solid surfaces and thin films in gas atmosphere and liquid environment. As the schematic shown in **Figure 5**, different geometries were used to probe the gas/solid and liquid/solid interface due to the different mean free path of soft x-rays in gas and liquid phase. For gas/solid interfaces, a thin solid sample is deposited on the substrate while for the probing of liquid/solid interfaces, a thin solid sample is fabricated on the x-ray transmission membrane window.

The concept has been used in various experimental systems, including electrochemical corrosion, Mg battery, photoelectrochemical devices, and nanoparticle oxidation. In the study of electrochemical corrosion of copper in aqueous $NaHCO_3$ solution, an *in situ*/*operando* flow liquid cell was used.[40] The body of the cell made from a UHV compatible polymer, polyether ether ketone (PEEK), a Si_3N_4 membrane held by a silicon frame separated the electrolytes in the flow liquid cell from the UHV (10^{-9} Torr) in the endstation. A thin copper film with a Cr adhesive layer was deposited on the Si_3N_4 membrane and Pt and Ag wires are used as the counter and pseudo-reference electrode. Such a setup enables the probing of Cu L-edge XAS during the cyclic voltammetry (CV) and opens the way for *in situ* investigations in batteries and catalysis. In a separate work, a static liquid cell was used to observe the electrochemical deposition of magnesium form $[Mg_2(\mu\text{-}Cl)_3\cdot6(OC_4H_8)]^+$ under *operando* conditions.[41] *Operando* condition XANES disclosed the presence of an interfacial Mg intermediate at the electrode/electrolyte interface below the equilibrium Mg/Mg^{2+} potential. Additionally, for the first time, *operando* substrate-film-cell assembly as a photoelectrochemical cell was reported in the oxygen K-edge near edge x-ray absorption fine structure (NEXAFS). Two different electron hole transitions in

hematite of a PEC photoanode were probed under *operando* conditions, and the Fe $3d$ hole is proved also to be active for H_2O activation, though it is less energetic than the O $2p$ hole.[42] As an example for the gas/solid interface, the x-ray absorption spectroscopy investigations of Co nanoparticle reaction in the presence of gases at atmospheric pressure has been demonstrated with examples of Co and H_2 Fischer–Tropsch reactions.[43]
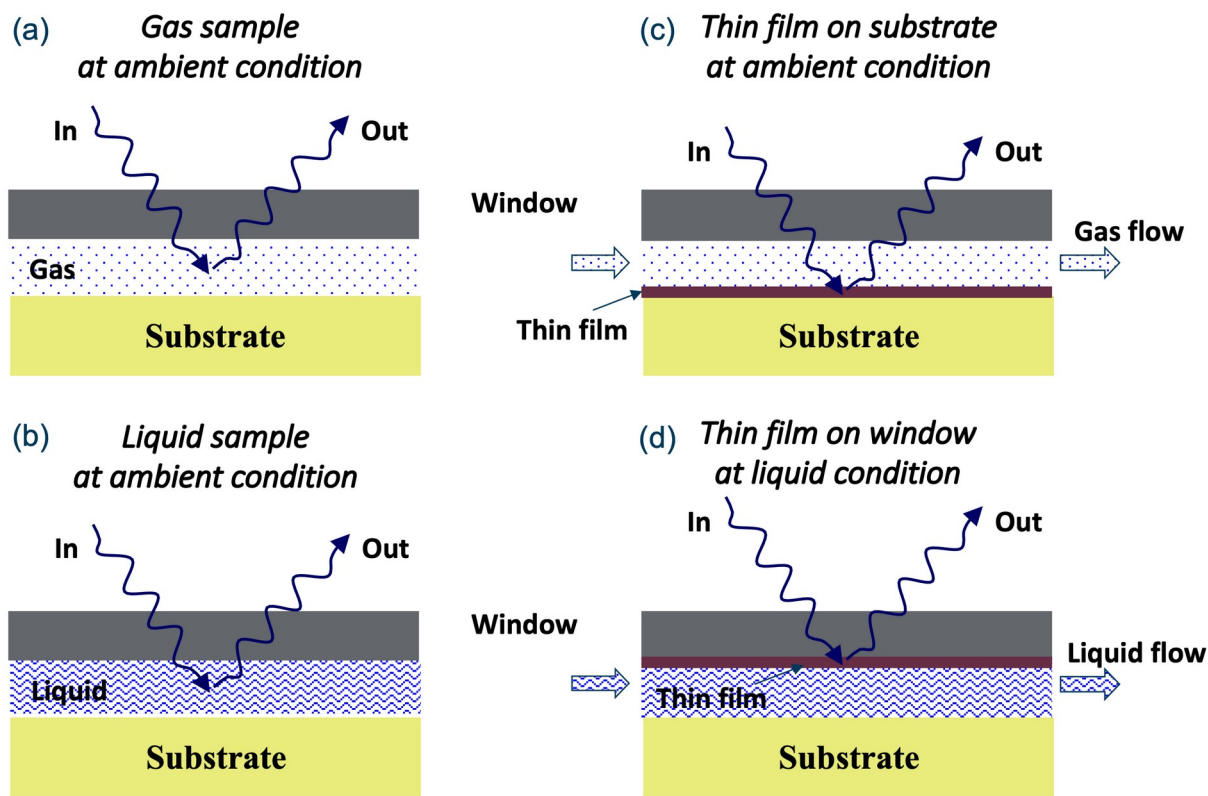
Figure 5. Thin solid film fabricated on the substrate for the probing of gas/solid interface (a, c) and deposited on the x-ray transmission membrane window for the detection of liquid/solid interface (b, d).
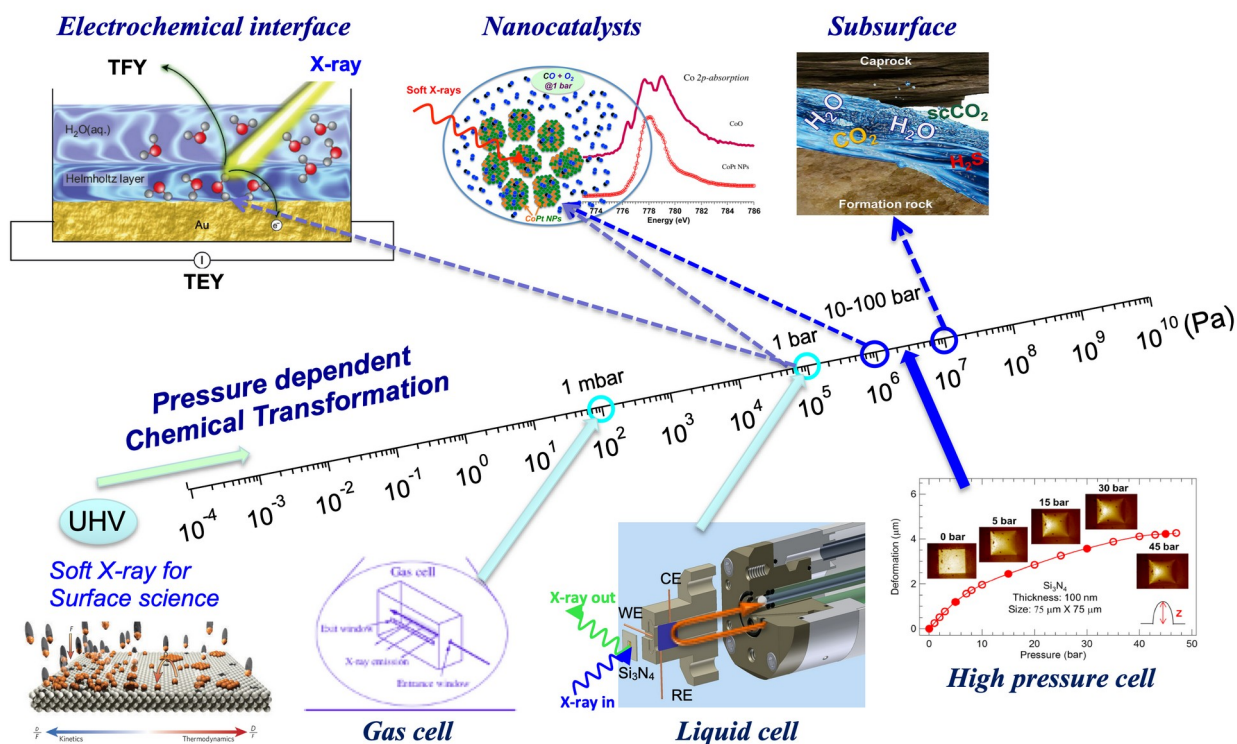
Figure 6. Schematic diagram of the scientific issues and the required environments for pressure dependent studies. [40, 44]

As previously discussed, in the past decades, different techniques such as flow cell and liquid jet, have been developed to overcome the incompatibility between the vacuum requirement for soft x-ray studies and the (near-)ambient pressure reaction environments. These approaches enable the scientists to understand more about the relations between the electronic structure and the performance of materials. As shown in **Figure 6**, a pressure of ~1 bar can be reached with the SiN-membrane-window-based flow cells. However, since plenty of important chemical and physical processes such as many catalytic reactions occur at higher pressure, extending the capabilities of current instruments especially in the pressure range of operation is becoming more urgent.

Novel liquid flow systems have been developed and a pressure of ~100 bars have been reached. Ca L-edge soft x-ray absorption spectra of 5M $CaCl_2$ aqueous solution at 1 to 41 bars have been collected.[44] The results show that the burst pressure of the membrane is strongly dependent on the size and thickness of the windows. For instance, as shown in the lower right of Figure 6, the pressure of ~45 bars can be reached with a 100-nm-thick, 75 μm × 75 μm Si_3N_4

membrane window. Additionally, a thicker silicon wafer substrate and the optimized mounting of wafer with less deformation can also help to reach a higher pressure.

Summary

In summary, *in situ*/*operando* soft x-ray spectroscopy is an irreplaceable technique to understand and ultimately control the energy storage or conversion, catalysis and electrochemical reactions. The elemental sensitivity nature and the large attenuation length makes soft x-rays suitable for the probing of buried interfaces, at both gas/solid and liquid/solid interfaces. Such interfacial phenomena are of critical significance in the understanding of the mechanism of charge transfer in energy-storage and catalytic reactions, and the probing of the species is only possible under *operando* conditions. Through the design of *in situ*/*operando* instruments with capabilities to probe such interfaces at (near-)ambient pressure and at higher pressures, the intermediate species can be resolved at their realistic working condition, benefiting the future design of novel catalysts and energy-storage devices.

Acknowledgments

Figure captions

Figure 1. The energy diagram of x-ray absorption and emission excitation processes (a); the C K-edge x-ray absorption and emission spectra of graphite and diamond (b); the Mn L-edge x-ray absorption spectra of Mn at the different oxidation states (c).

Figure 2. (a) The experimental sample schemes and electron/fluorescence yields being detected for XAS and XES measurements. Schematics of the experimental setup for (b) gas/solid interface catalysis studies and (c) solvation and desolvation studies at liquid/solid interface.

Figure 3. Soft x-ray spectroscopy experimental study of monolayer of O_2 adsorbed on Ni(100) and Cu(100) (a); N_2 and C_6H_6 molecules adsorbed on Ni (100) (b); resonant XES of O_2 molecules (c); and high resolution RIXS of O_2 (d).

Figure 4. (a) Instrument development to handle the gas and liquid samples under UHV conditions, including differential pumping to provide a pressure change as a continuous function or using an x-ray transmission membrane window to provide a pressure change as a step function. (b) The transmission (%) of membrane windows made from C, SiN, or Al as a function of energy (eV).

Figure 5. Thin solid film fabricated on the substrate for the probing of gas/solid interface (a, c) and deposited on the x-ray transmission membrane window for the detection of liquid/solid interface (b, d).

Figure 6. Schematic diagram of the scientific issues and the required environments for pressure dependent studies.

Author biographies

Feipeng Yang is a postdoctoral fellow in the group of Dr. Jinghua Guo at the Advanced Light Source, Lawrence Berkeley National Laboratory performing soft x-ray spectroscopic studies on energy materials as part of the Joint Center for Energy Storage Research (JCESR) Hub. He obtained his Ph.D. degree from the Department of Polymer Science, The University of Akron, in 2018. His current research focuses on the beyond lithium-ion battery materials using *in situ*/*operando* soft x-ray core-level spectroscopies. Yang can be reached by email at (feipeng_yang@lbl.gov).

Xuefei Feng is a project scientist at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory as part of the Joint Center for Energy Storage Research Hub. He obtained his Ph.D. degree from the University of Science and Technology, China, in 2014. After two years of postdoctoral fellow research at the Shanghai Institute of Microsystem and Information Technology, Chinese Academic of Sciences, China, he joined at ALS as a postdoctoral researcher in 2016. His research interest is scientific instrument development for *in situ*/*operando* soft x-ray spectroscopic study on energy materials. Feng can be reached by email at (xuefeifeng@lbl.gov).

Yi-Sheng Liu is a project scientist at the Advanced Light Source, Lawrence Berkeley National Laboratory. His research interests include the study of energy materials through *in situ* and *ex situ* soft x-ray spectroscopies. They also focus on the development of *in situ* soft x-ray capabilities applied to energy materials especially for metal ion batteries and hydrogen storage. Liu can be reached by email at (ysliu2@lbl.gov).

Per-Anders Glans is a research scientist at the Advanced Light Source, Lawrence Berkeley National Laboratory. His research includes photoemission, as well as photon-in, photon-out techniques such as soft x-ray absorption, soft x-ray emission, and resonant inelastic x-ray scattering. He is currently focusing on a high-resolution soft x-ray beamline with associated x-ray emission spectrometer. Glans can be reached by email at (paglans@lbl.gov).

Jinghua Guo is a senior scientist and RIXS Program Lead at the Advanced Light Source, Lawrence Berkeley National Laboratory, an adjunct professor in the Department of Chemistry and Biochemistry at the University of California, Santa Cruz, and a Fellow of the American Physical Society. His research on soft x-ray spectroscopy has recently been honored with the Materials Research Society Innovation in Materials Characterization Award "for pioneering *in situ*/*operando* soft x-ray spectroscopy characterization of interfacial phenomena in energy, catalysis, and chemical materials science." His work has garnered more than 26,500 citations by July 2021, leading to an h-index of 85. Guo can be reached by email at jguo@lbl.gov.

Conflict of interest
On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. F.M.F. de Groot, M. Grioni, J.C. Fuggle, J. Ghijsen, G.A. Sawatzky, H. Petersen, "Oxygen 1s x-ray-absorption edges of transition-metal oxides," *Phys. Rev. B* **40**, 5715 (1989).

2. F.M.F. de Groot, J.C. Fuggle, B.T. Thole, G.A. Sawatzky, "L2,3 x-ray-absorption edges of d0 compounds: K+, Ca2+, Sc3+, and Ti4+ in Oh (octahedral) symmetry," *Phys. Rev. B* **41**, 928 (1990).

3. F.M.F. de Groot, J.C. Fuggle, B.T. Thole, G.A. Sawatzky, "2*p* x-ray absorption of 3*d* transition-metal compounds: An atomic multiplet description including the crystal field," *Phys. Rev. B* **42**, 5459 (1990).

4. C.T. Chen, F. Sette, Y. Ma, M.S. Hybertsen, E.B. Stechel, W.M.C. Foulkes, M. Schulter, S.-W. Cheong, A.S. Cooper, L.W. Rupp, B. Batlogg, Y.L. Soo, Z.H. Ming, A. Krol, Y.H. Kao, "Electronic states in $La_{2-x}Sr_xCuO_4+\delta$ probed by soft-x-ray absorption," *Phys. Rev. Lett*. **66**, 104 (1991).

5. F.X. Gadea, H. Köppel, J. Schirmer, L.S. Cederbaum, K.J. Randall, A.M. Bradshaw, Y. Ma, F. Sette, C.T. Chen, "Vibronic coupling and core–hole localization in K-shell excitations of ethylene," *Phys. Rev. Lett*. **66**, 883 (1991).

6. Y. Ma, C.T. Chen, G. Meigs, K. Randall, F. Sette, "High-resolution K-shell photoabsorption measurements of simple molecules," *Phys. Rev. A* **44**, 1848 (1991).

7. J. Nordgren, P. Glans, K. Gunnelin, J. Guo, P. Skytt, C. Såthe, N. Wassdahl, "Resonant soft x-ray fluorescence spectra of molecules," *Appl. Phys*. **65**, 97 (1997).

8. A. Kotani, S. Shin, "Resonant inelastic x-ray scattering spectra for electrons in solids," *Rev. Mod. Phys*. **73**, 203 (2001).

9. L.J.P. Ament, M. van Veenendaal, T.P. Devereaux, J.P. Hill, J. van den Brink, "Resonant inelastic x-ray scattering studies of elementary excitations," *Rev. Mod. Phys*. **83**, 705 (2011).

10. J.-E. Rubensson, N. Wassdahl, G. Bray, J. Rindstedt, R. Nyholm, S. Cramm, N. Mårtensson, J. Nordgren, "Resonant behavior in soft x-ray fluorescence excited by monochromatized synchrotron radiation," *Phys. Rev. Lett*. **60**, 1759 (1987).

11. S.M. Butorin, J.-H. Guo, L.-C. Duda, N. Wassdahl, J. Nordgren, E.Z. Kurmaev, S.P. Tolochko, "Electronic structure of $La_{2-x}Sr_xNiO_4+\delta$ studied by soft x-ray absorption and emission spectroscopies," *Phys. C Supercond*. **235**, 1047 (1994).

12. J.-H. Guo, S.M. Butorin, N. Wassdahl, P. Skytt, J. Nordgren, Y. Ma, "Electronic structure of La$_{2-x}$Sr$_x$CuO$_4$ studied by soft-x-ray-fluorescence spectroscopy with tunable excitation," *Phys. Rev. B* **49**, 1376 (1994).

13. S.M. Butorin, D.C. Mancini, J.-H. Guo, N. Wassdahl, J. Nordgren, M. Nakazawa, S. Tanaka, T. Uozumi, A. Kotani, Y. Ma, K.E. Myano, B.A. Karlin, D.K. Shuh, "Resonant x-ray fluorescence spectroscopy of correlated systems: A probe of charge-transfer excitations," *Phys. Rev. Lett*. **77**, 574 (1995).

14. P. Skytt, P. Glans, J.-H. Guo, K. Gunnelin, C. Såthe, J. Nordgren, F. Kh. Gel'mukhanov, A. Cesar, H. Ågren, "Quenching of symmetry breaking in resonant *inelastic x-ray scattering by detuned excitation," *Phys. Rev. Lett*. **77**, 5035 (1996).

15. J.-H. Guo, P. Glans, P. Skytt, N. Wassdahl, J. Nordgren, Y. Luo, H. Ågren, Y. Ma, T. Warwick, P. Heimann, E. Rotenberg, J.D. Denlinger, "Resonant excitation x-ray fluorescence from C60," *Phys. Rev. B* **52**, 10681 (1995).

16. L. Qian, M. Nyberg, Y. Luo, J.-E. Rubensson, A.V. Talyzine, C. Såthe, D. Ding, J.-H. Guo, H. Högberg, T. Kämbre, U. Jansson, J. Nordgren, "Bonding mechanism in the transition-metal fullerides studied by symmetry-selective resonant x-ray inelastic scattering," *Phys. Rev. B* **63**, 085418 (2001).

17. M. Nyberg, Y. Luo, L. Qian, J.-E. Rubensson, C. Såthe, D. Ding, J.-H. Guo, T. Käämbre, J. Nordgren, "Bond formation in titanium fulleride compounds studied through x-ray emission spectroscopy," *Phys. Rev. B* **63**, 115117 (2001).

18. Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P.D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, S.D. Kevan, "Soft-x-ray resonant inelastic scattering at the C K edge of diamond," *Phys. Rev. Lett*. **69**, 2598 (1992).

19. X. Feng, S. Sallis, Y.-C. Shao, R. Qiao, Y.-S. Liu, L. C. Kao, A.S. Tremsin, Z. Hussain, W. Yang, J. Guo, Y.-D. Chuang, "Disparate exciton–phonon couplings for zone-center and boundary phonons in solid-state graphite," *Phys. Rev. Lett*. **125**, 116401 (2020).

20. R. Qiao, Q. Li, Z. Zhuo, S. Sallis, O. Fuchs, M. Blum, L. Weinhardt, C. Heske, J. Pepper, M. Jones, A. Brown, A. Spucces, K. Chow, B. Smith, P.-A. Glans, Y. Chen, S. Yan, F. Pan, L.F.J. Piper, J. Denlinger, J. Guo, Z. Hussain, Y.-D. Chuang, W. Yang, "High-efficiency *in situ* resonant inelastic x-ray scattering (iRIXS) endstation at the Advanced Light Source," *Rev. Sci. Instrum*. **88**, 033106 (2017).

21. N. Wassdahl, A. Nilsson, T. Wiell, H. Tillborg, L.-C. Duda, J.H. Guo, N. Mårtensson, J. Nordgren, J.N. Andersen, R. Nyholm, "Soft x-ray emission studies of adsorbates," *Phys. Rev. Lett*. **69**, 812 (1992).

22. A. Nilsson, M. Weinelt, T. Wiell, P. Bennich, O. Karis, N. Wassdahl, J. Stöhr, M.G. Samant, "An atom-specific look at the surface chemical bond," *Phys. Rev. Lett*. **78**, 2847 (1997).

23. F. Hennies, A. Pietzsch, M. Berglund, A. Föhlisch, T. Schmitt, V. Strocov, H.O. Karlsson, J. Andersson, J.-E. Rubensson, "Resonant inelastic scattering spectra of free molecules with vibrational resolution," *Phys. Rev. Lett*. **104**, 193002 (2010).

24. P. Glans, K. Gunnelin, P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, H. Ågren, F. Kh. Gel'mukhanov, T. Warwick, E. Rotenberg, "Resonant x-ray emission spectroscopy of molecular oxygen," *Phys. Rev. Lett*. **76**, 2448 (1996).

25. P.O. Nilsson, J. Kanski, J.V. Thordson, T.G. Andersson, J. Nordgren, J. Guo, M. Magnuson, "Electronic structure of buried Si layers in GaAs(001) as studied by soft-x-ray emission," *Phys. Rev. B* **52**, R8643 (1995).

26. S. Mankefors, P.O. Nilsson, J. Kanski, K. Karlsson, "*Ab initio* calculations of soft-x-ray emission from Si(100) layers buried in GaAs," *Phys. Rev. B* **58**, 10551 (1998).

27. K.R. Wilson, B.S. Rude, T. Catalano, R.D. Schaller, J.G. Tobin, D.T. Co, R.J. Saykally, "X-ray spectroscopy of liquid water microjets. *J. Phy.s Chem. B* **105**, 3346 (2001).

28. K.R. Wilson, B.S. Rude, J. Smith, C. C,"appa, D.T. Co, R.D. Schaller, M. Larsson, T. Catalano, R.J. Saykally, "Investigation of volatile liquid surfaces by synchrotron x-ray spectroscopy of liquid microjets," *Rev. Sci. Instrum*. **75**, 725 (2004).

29. D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, "A differentially pumped electrostatic lens system for photoemission studies in the millibar range," *Rev. Sci. Instrum*. **73**, 3872 (2002).

30. S. Myneni, Y. Luo, L.Å. Näslund, M. Cavalleri, L. Ojamäe, H. Ogasawara, A. Pelmenschikov, P. Wernet, P. Väterlein, C. Heske, Z. Hussain, L. G. M. Pettersson, A. Nilsson, "Spectroscopic probing of local hydrogen-bonding structures in liquid water," *J. Phys. Condens. Matter*. **14**, L213 (2002).

31. K.R. Wilson, M. Cavalleri, B.S. Rude, R.D. Schaller, A. Nilsson, L.G.M. Pettersson, N. Goldman, T. Catalano, J.D. Bozek, R.J. Saykally, "Characterization of hydrogen bond acceptor molecules at the water surface using near-edge x-ray absorption fine-structure spectroscopy and density functional theory," *J. Phys. Condens. Matter*. **14**, L221 (2002).

32. H. Bluhm, D.F. Ogletree, C.S. Fadley, Z. Hussain, M. Salmeron, "The premelting of ice studied with photoelectron spectroscopy," *J. Phys. Condens. Matter*. **14**, L227 (2002).

33. J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, J. Nordgren, "X-ray emission spectroscopy of hydrogen bonding and electronic structure of liquid water," *Phys. Rev. Lett*. **89**, 137402 (2002).

34. J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D.K. Shuh, H. Ågren, J. Nordgren, "Molecular structure of alcohol-water mixtures," *Phys. Rev. Lett*. **91**, 157401 (2003).

35. O. Fuchs, M. Zharnikov, L. Weinhardt, M. Blum, M. Weigand, Y. Zubavichus, M. Bär, F. Maier, J.D. Denlinger, C. Heske, M. Grunze, E. Umbach, "Isotope and temperature effects in liquid water probed by x-ray absorption and resonant x-ray emission spectroscopy," *Phys. Rev. Lett*. **100**, 027801 (2007).

36. T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L.G.M. Pettersson, A. Nilsson, S. Shin, "High resolution x-ray emission spectroscopy of liquid water: The observation of two structural motifs," *Chem. Phys. Lett*. **460**, 387 (2008).

37. Y. Harada, T. Tokushima, Y. Horikawa, O. Takahashi, H. Niwa, M. Kobayashi, M. Oshima, Y. Senba, H. Ohashi, K.T. Wikfeldt, A. Nilsson, L.G.M. Pettersson, S. Shin, "Selective probing of the OH or OD stretch vibration in liquid water using resonant inelastic soft-x-ray scattering," *Phys. Rev. Lett*. **111**, 193001 (2013).

38. K. Gunnelin, P. Glans, J.-E. Rubensson, C. Såthe, J. Nordgren, Y. Li, F. Gel'mukhanov, H. Ågren, "Bond-length-dependent core hole localization observed in simple hydrocarbons," *Phys. Rev. Lett*. **83**, 1315 (1999).

39. A. Pietzsch, Y.-P. Sun, F. Hennies, Z. Rinkevicius, H.O. Karlsson, T. Schmitt, V.N. Strocov, J. Andersson, B. Kennedy, J. Schlappa, A. Föhlisch, J.-E. Rubensson, F. Gel'mukhanov, "Spatial quantum beats in vibrational resonant inelastic soft x-ray scattering at dissociating states in oxygen," *Phys. Rev. Lett*. **106**, 153004 (2011).

40. P. Jiang, J.-L. Chen, F. Borondics, P.-A. Glans, M.W. West, C.-L. Chang, M. Salmeron, J. Guo, "*In situ* soft x-ray absorption spectroscopy investigation of electrochemical corrosion of copper in aqueous $NaHCO_3$ solution," *Electrochem. Commun*. **12**, 820 (2010).

41. T.S. Arthur, P.-A. Glans, M. Matsui, R. Zhang, B. Ma, J. Guo, "Mg deposition observed by *in situ* electrochemical Mg K-edge x-ray absorption spectroscopy," *Electrochem. Commun*. **24**, 43 (2012).

42. A. Braun, K. Sivula, D. K. Bora, J. Zhu, L. Zhang, M. Grätzel, J. Guo, E.C. Constable, "Direct observation of two electron holes in a hematite photoanode during photoelectrochemical water splitting," *J. Phys. Chem. C* **116**, 16870 (2012).

43. C. Escudero, P. Jiang, E. Pach, F. Borondics, M.W. West, A. Tuxen, M. Chintapalli, S. Carenco, J. Guo, M. Salmeron, "A reaction cell with sample laser heating for in situ soft X-ray absorption spectroscopy studies under environmental conditions," *J. Synchrotron. Radiat*. **20**, 504 (2013).

44. R. Qiao, Y. Xia, X. Feng, J. Macdougall, J. Pepper, K. Armitage, J. Borsos, K.G. Knauss, N. Lee, A. Allézy, B. Gilbert, A.A. MacDowell, Y.-S. Liu, P.-A. Glans, X. Sun, W. Chao, J. Guo, "Soft x-ray spectroscopy of high pressure liquid," *Rev. Sci. Instrum*. **89**, 013114 (2018).