nature reviews methods primers

https://doi.org/10.1038/s43586-024-00366-8

Supplementary information

X-ray absorption spectroscopy

In the format provided by the authors and unedited

Nature Reviews Methods Primer: X-ray Absorption Spectroscopy: Supplementary Information

Christopher T Chantler[1*], Grant Bunker[2*], Paola D'Angelo[3*] and Sofia Diaz-Moreno[4*]

[1*]Physics, The University of Melbourne, Elgin Street, Parkville, 3010, Victoria, Australia.
[2]Department of Physics, Illinois institute of Technology, 3105 S. Dearborn St., Chicago, IL 60616, Illinois, USA.
[3]Department of Chemistry, University of Roma 'La Sapienza', P.le A. Moro 5, Rome, 00185, Rome, Italy.
[4]Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, Oxfordshire, United Kingdom.

*Corresponding author(s). E-mail(s): chantler@unimelb.edu.au; bunker@iit.edu; p.dangelo@uniroma1.it; sofia.diaz-moreno@diamond.ac.uk;

Photoelectric absorption (PE) can be represented by a transition amplitude A^{pe} and a cross-section in barns per atom σ_{pe} [1, 2] (1 barn = 10^{-24} square cm). In first order, $A^{m=pe} = \langle f|H^{m=pe}|i\rangle$ where $H^{m=pe}$ is the interaction Hamiltonian for a physical process m, i is the initial state and f is the final state. $\sigma_m = A_m^2$ (conventionally barns per atom). Using $[\mu/\rho]_m = \frac{\sigma_m}{uA}$ with u the atomic mass unit and A the relative atomic mass, yields the common formula.

Early developments used a plane wave photoelectron instead of a curved wave or Green(s) function approach, with key improvements to phase offsets from scattering [3]. Early work used point scattering from nuclei [4]; later work used muffin-tin potentials around each atom to yield scattering from electron orbitals [5, 6]; more recent work uses full-potential scattering from a density functional theoretical basis; in principle all electron density can contribute in each order. Early work predicted only two-leg paths, or single scattering paths ($i_{max} = 1$ [7]); recent work predicts 3-, 4- and more -leg paths (i.e. double, $i_{max} = 2$, triple, $i_{max} = 3$, or more scattering from different atomic sites before recombining at the origin [5, 8, 9]). Early, it was claimed that a few dominant single-scattering paths are sufficient but higher-order and multiple-legged paths have been seen to be significant in many data sets and to aid in explaining experimental data and distinguishing between hypotheses of structure. The many-body reduction factor $S_0^2(k)$ was introduced later; although initial derivation and discussion recognised that it should be k-dependent, it is almost always fitted as a constant S_0^2 in analysis. Major current variations depend upon the approximations made to simplify the relativistic wavefunction and potential.

The cumulant approach expands the atomic distribution function $g(R)$ following $\langle x\rangle = \frac{\int dRxg(R)}{\int dRg(R)}$ so without the Gaussian assumption $e^{-2\sigma_j^2 k^2}$ and hence can in principle observe anisotropy and bonding. $\chi(k) \propto \left\langle e^{ikR_j}\right\rangle$ with $\left\langle e^{ikR_j}\right\rangle = exp\left[\Sigma_n = 1^{\infty}\frac{(2ik)^n}{n!}C_n\right]$ where the cumulant terms are $C_1 =< r >; C_2 =< r^2 > - < r >^2; C_3 =< r^3 > -3 < r^2 >< r > +2 < r >^3; C_4 =< r^4 > -3 < r^2 >^2 -4 < r^3 >< r > +12 < r >^2 < r >^2 -6 < r >^4; \ldots$ and note the main change is the potentially non-zero values for C_3 and C_4. In more detail, the distribution function can be investigated, like crystallography, as a tensor.

Case study: Fast oxidation reactions in solution

Conventional XAFS experiments performed with double crystal monochromators impose limitations on the time resolution of the collected data, due to the fact that the monochromator crystals have to be mechanically scanned. To overcome these restrictions, the energy dispersive XAS (EDXAS) mode has been developed. [10] This collection mode exploits a polychromator to spatially diverge the incoming white beam and, together with a CCD-based detector, allows the collection of XAS spectra with millisecond dwell times. Owing to the detector geometry, the entire spectrum is collected at the same time over a specific energy range. Recently, EDXAS has been coupled with UV-vis spectroscopy to study the reactivity of a $[\text{N4Py}\cdot\text{Fe}^{\text{IV}}(\text{O})]^{2+}$ non-heme iron-oxo complex (N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine) with different organic substrates in acetonitrile solution solution (Figure 6b in the main document). [11] This combined approach is particularly compelling, as it allows

one to overcome the potential interferences from the species present in solution by shifting the point of view to the metal cation with XAS, while also obtaining mechanistic insights orthogonal to those yielded by UV-vis spectroscopy. In this study, Fe K-edge XAS spectra were measured for the oxidation of a series of differently substituted thioanisoles by $[N4Py{\cdot}Fe^{IV}(O)]^{2+}$ with a time resolution down to 120 ms. This reaction produces the corresponding methyl phenyl sulfoxides and the reduced complex $[N4Py{\cdot}Fe^{II}(O)]^{2+}$. The shift in the Fe K-edge onset energy E_0 over time was then calculated in order to obtain pseudo-first-order rate constants. The obtained rate constants were found to be identical to those determined by the simultaneously collected UV-vis data, showing the potential of EDXAS in cases where the investigated metal ion is silent in the UV-vis region. Additionally, it was observed that the EDXAS data provide sufficient resolution to detect a different behaviour in the oxidation kinetics of the many substrates. The reaction kinetics was in fact found to correlate with the electron withdrawing or donating nature of the ring substituents, reflecting the electrophilic character of the oxidizing complex.

References

[1] Chantler, C. T. Theoretical Form Factor, Attenuation, and Scattering Tabulation for Z=1–92 from E=1–10 eV to E=0.4–1.0 MeV. *Journal of Physical and Chemical Reference Data* **24**, 71–643 (1995).

[2] Chantler, C. T. Detailed tabulation of atomic form factors, photoelectric absorption and scattering cross section, and mass attenuation coefficients in the vicinity of absorption edges in the soft X-ray (Z = 30-36, Z = 60-89, E = 0.1-10 keV)–addressing convergence issue. *Journal of Physical and Chemical Reference Data* **29**, 597–1056 (2000).

[3] Gurman, S. J. The small atom approximation in EXAFS and surface EXAFS. *J Phys C* **21**, 3699–3717 (1988).

[4] Stern, E. A. Theory of the extended x-ray-absorption fine structure. *Physical Review B* **10**, 3027–3037 (1974).

[5] Lee, P. A. & Pendry, J. B. Theory of the extended x-ray absorption fine structure. *Phys. Rev. B* **11**, 2795–2811 (1975).

[6] Natoli, C. R. Multichannel multiple scattering theory with general potentials. *Phys Rev B* **42**, 1944–1968 (1990).

[7] Ashley, C. A. & Doniach, S. Theory of extended X-ray absorption edge fine structure (EXAFS) in crystalline solids. *Physical Review B* **11**, 1279–1288 (1975).

[8] Gurman, S. J., Binstead, N. & Ross, I. A rapid, exact, curved-wave theory for EXAFS calculations: II The multiple-scattering contributions. *J Phys C* **19**, 1845–1861 (1986).

[9] Rehr, J. J. & Albers, R. C. Theoretical approaches to X-ray absorption fine structure. *Phys Rev B* **41**, 8139–8144 (1990).

[10] Matsushita, T. & Phizackerley, R. P. A fast x-ray absorption spectrometer for use with synchrotron radiation. *Jpn. J. Appl. Phys.* **20**, 2223 (1981).

[11] Capocasa, G. *et al.* Coupled x-ray absorption/uv-vis monitoring of fast oxidation

reactions involving a nonheme iron-oxo complex. *J. Am. Chem. Soc.* **141**, 2299–2304 (2019).