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Zachary Mathe
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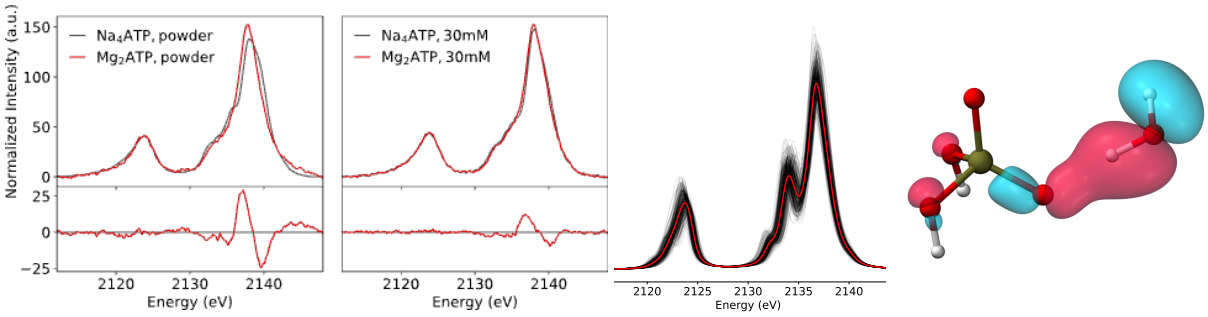
Phosphorus X-ray emission spectroscopy & multimodal calculations probe subtle interactions in solids and solutions

Zachary Mathe, Olivia Stepanic, Sergey Peredkov, Ragnar Bjornsson,* Serena DeBeer*
Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany.

Phosphorus is ubiquitous in biochemistry, being found in the phosphate groups of nucleic acids, nicotinamide redox carriers and the energy-transferring systems of adenine nucleotides (e.g. ATP). Kβ X-ray emission spectroscopy (XES) of phosphorus, which probes the P-O valence orbital space, has remained largely unexplored, with our 2021 study being the first application of the technique to biomolecules.[1] Inorganic phosphates and phosphate biomolecules were measured, both as powders and aqueous solutions in a continuous flow cell. P Kβ spectra are found to offer a detailed view of phosphate valence electronic structure and the local chemical environment, reporting on subtle non-covalent effects such as hydrogen bonding and ionic interactions.



In addition to the published experimental work, we present in-depth DFT calculations using plane-wave-optimized periodic structures and AIMD trajectories to model the effects of hydrogen bonding interactions. These protocols allow for highly accurate calculation of P Kβ X-ray emission spectra and understanding of the structural origins of spectral features. Combined X-ray spectroscopy and DFT calculations show great promise for future application to enzymatic catalysis and energy transfer processes.

References

(1) Mathe, Z. et al. *Chem. Sci.* **2021**. doi:10.1039/D1SC01266E.