

# Identifying and Characterizing Sulfur Radicals in Biology: Probing Radical Intermediates in Proteins with X-ray Absorption Methods

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Sulfur-centered radicals are emerging as an important functional moiety in biological processes, including catalysis, cell signaling, redox buffering, and oxidative damage. A significant hurdle towards the investigation of sulfur-centered radicals has been the availability of selective tools for their identification. We are exploring the strengths and limitations of using Sulfur K-edge X-ray Absorption Spectroscopy (XAS) as a new spectroscopic probe for such species. Cysteine radicals, for example, exhibit a strong electric dipole allowed S 1s→3p pre-edge transition, whose energy and intensity reflects the electronic nature of the singly-occupied orbital in this species. The effect of environmental factors such as hydrogen-bonding can be probed directly using this methodology. The basic framework for this methodology is developed and applied to some examples of biological relevance. Theoretical models that allow for simulation of these spectroscopic methods are explored and evaluated by comparison with experimental data.