Shining Light on Metalloenzyme Catalysis

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In this study we demonstrate the potential of time-resolved multiple probe spectroscopy (TRMPS) at Ultra to provide unique insight into proton-coupled electron transfer reactions in biology. By exploiting an intrinsically photosensitive step during the [NiFe] hydrogenase catalytic cycle, we are able to track the movement of a proton (H^+) relative to electron transfer on mechanistically-relevant timescales. The TRMPS method is sufficiently sensitive to allow detection of low-intensity transient intermediates in dilute (*ca* mM) biological samples. Here we have established proof-of-concept methodologies that will allow detailed interrogation of biological proton-coupled electron transfer via photodissociation of intrinsic or extrinsic ligands at metalloenzyme active sites. Proton-coupled electron transfer is ubiquitous in nature, and underpins the efficiency of metalloenzymes that catalyse thermodynamically 'difficult' reactions under ambient conditions using earth-abundant metals.

A deep understanding of metalloenzyme mechanisms is needed in order to inspire a new generation of catalysts for sustainable, 'green' energy-conversion processes.

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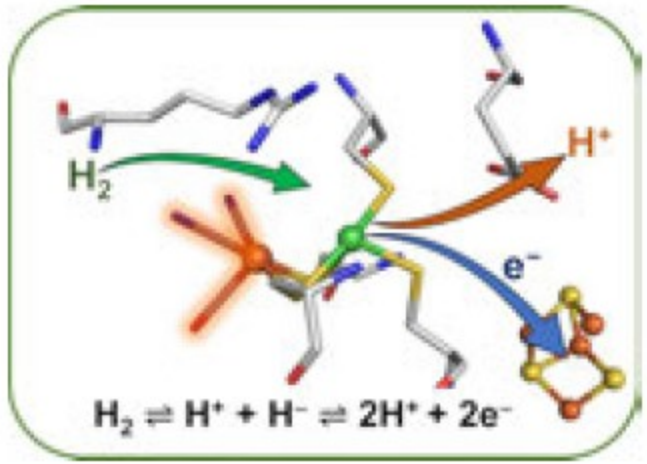

Activation of H_2 by [NiFe] hydrogenase enzymes is reliant upon the highly coordinated movement of protons (H^+) and electrons (e^-), and serves as a paradigm for studying biological proton-coupled electron transfer.