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Probing the [FeFe]-hydrogenase subsite using muon spectroscopy

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In the drive to replace fossil fuels with sustainable alternatives, achieving the reversible interconversion of protons and dihydrogen is a crucial target. The reaction can be carried out readily using platinum-based systems, but the cost and availability of this precious metal preclude scaling such approaches. In nature, the [FeFe]-hydrogenase enzymes have evolved to perform the very same task at rates that rival platinum electrodes. These systems feature a large protein component in addition to a core bioinorganic unit, the {2Fe2S} subsite. To enable us to produce practical catalysts we need to mimic the chemistry carried out by the enzyme: the natural system itself is too large and sensitive for wide-scale use. Thus understanding the chemistry of the {2Fe2S} subsite is vital.

Central to the hydrogen chemistry carried out by the subsite is its interaction with protons. Probing the solution kinetics and electrochemisty of model systems allows us to understand key reactivity of iron hydrides on a timescale as short as one second. However, much of the most interesting behaviour of these models occurs on much shorter timescale. For example, the location of the primary protonation sites is still an open question, with terminal and bridging hydrides possible candidates along with the sulphur, carbonyl and cyanide ligands. Muonium, as a 'light'analogue of H·, offers the means of studying the structure and dynamics of such chemistry on the nanosecond timescale. The use of the avoided level cross (ALC) technique has now allowed to identify two sites for primarily muonation in this model in the solid stat, with density functional theory (DFT) assignment strongly implicating competing bridging and terminal binding. This unique insight opens up the possibility of new reaction pathways in both models and the enzyme as well as demonstrating the wider importance of muon techniques in studying reactive organometallic systems.

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