



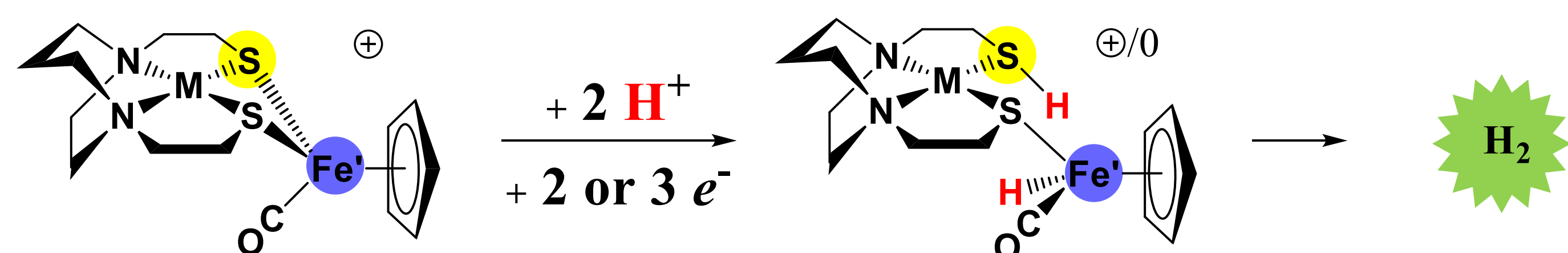
Hemi-labile Bridging Thiolates as Proton Shuttles in Bioinspired H₂ Production Electro-catalysts

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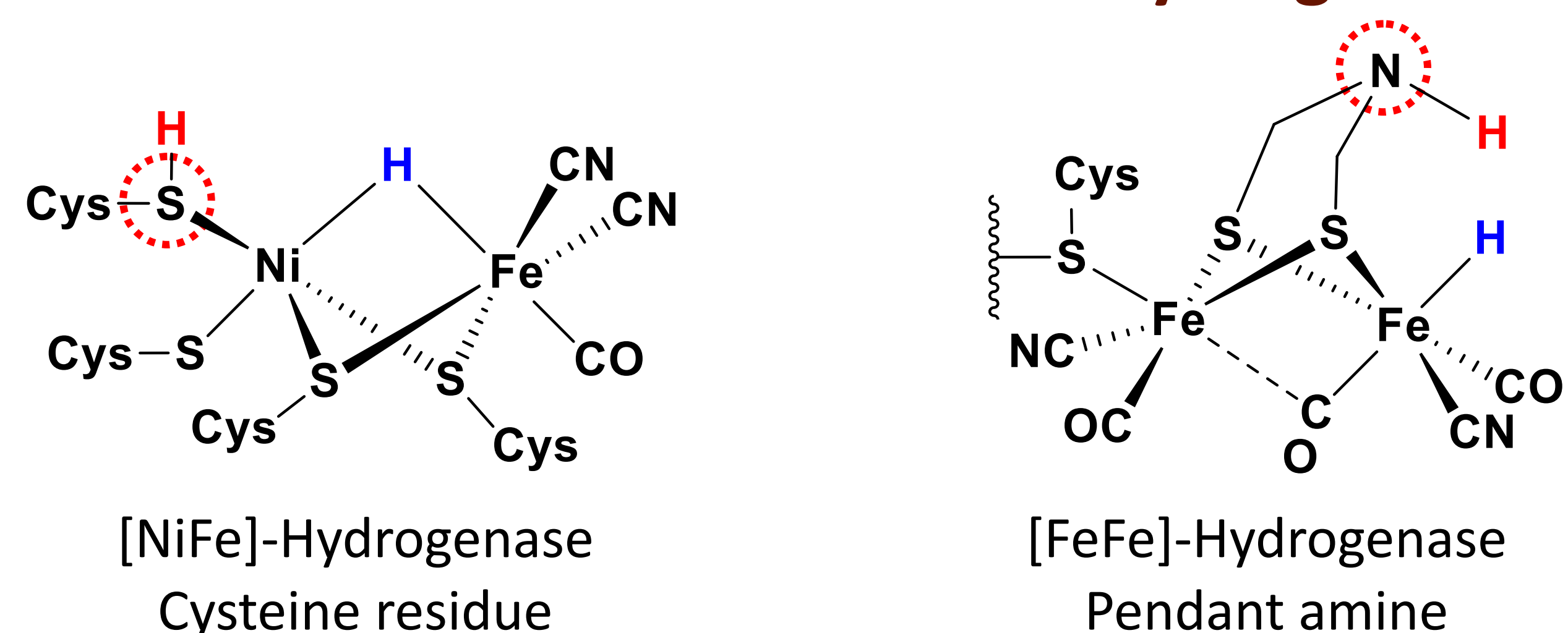


Abstract

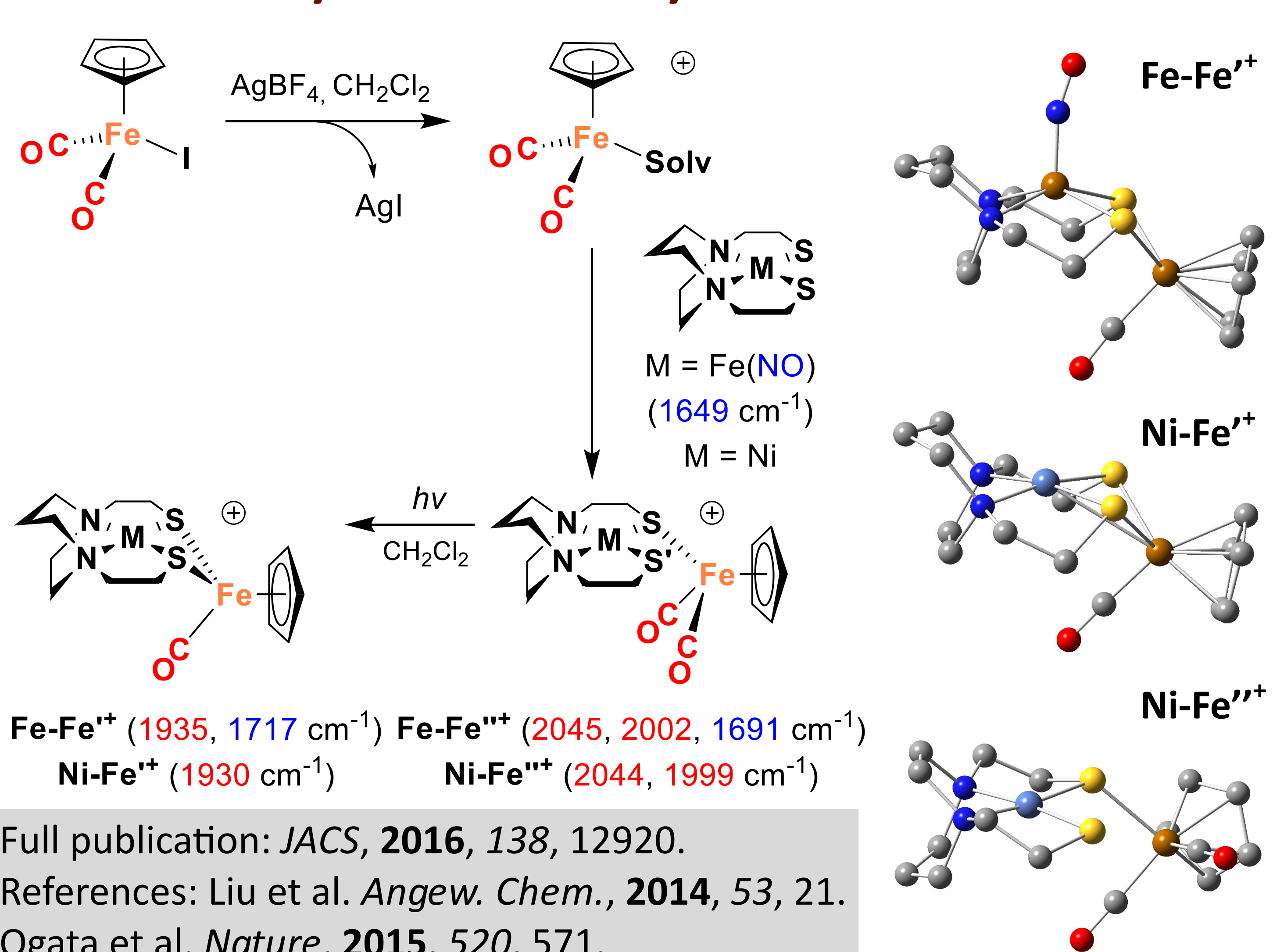
The coupling of a proton and a hydride to form H₂ in the active sites of either [FeFe]- or [NiFe]-hydrogenase, is assisted by an intramolecular base as the proton shuttle. Our synthetic model, [M(N₂S₂)Fe(CO)Cp]⁺ (M = Ni or Fe(NO)), though it lacks an apparent base, may dissociate its S-Fe' bond (Hemi-lability) to create a Lewis pair and act as an electro-catalyst for H₂ production. After two protonations and two/three reductions, the proton on S and the hydride on Fe' are propitiously orientated and their spatial proximity facilitates the subsequent coupling. Such a coupling reaction and its barrier are dependent on the oxidation states and may occur by either a [ECEC] or an E[CECE] mechanism.



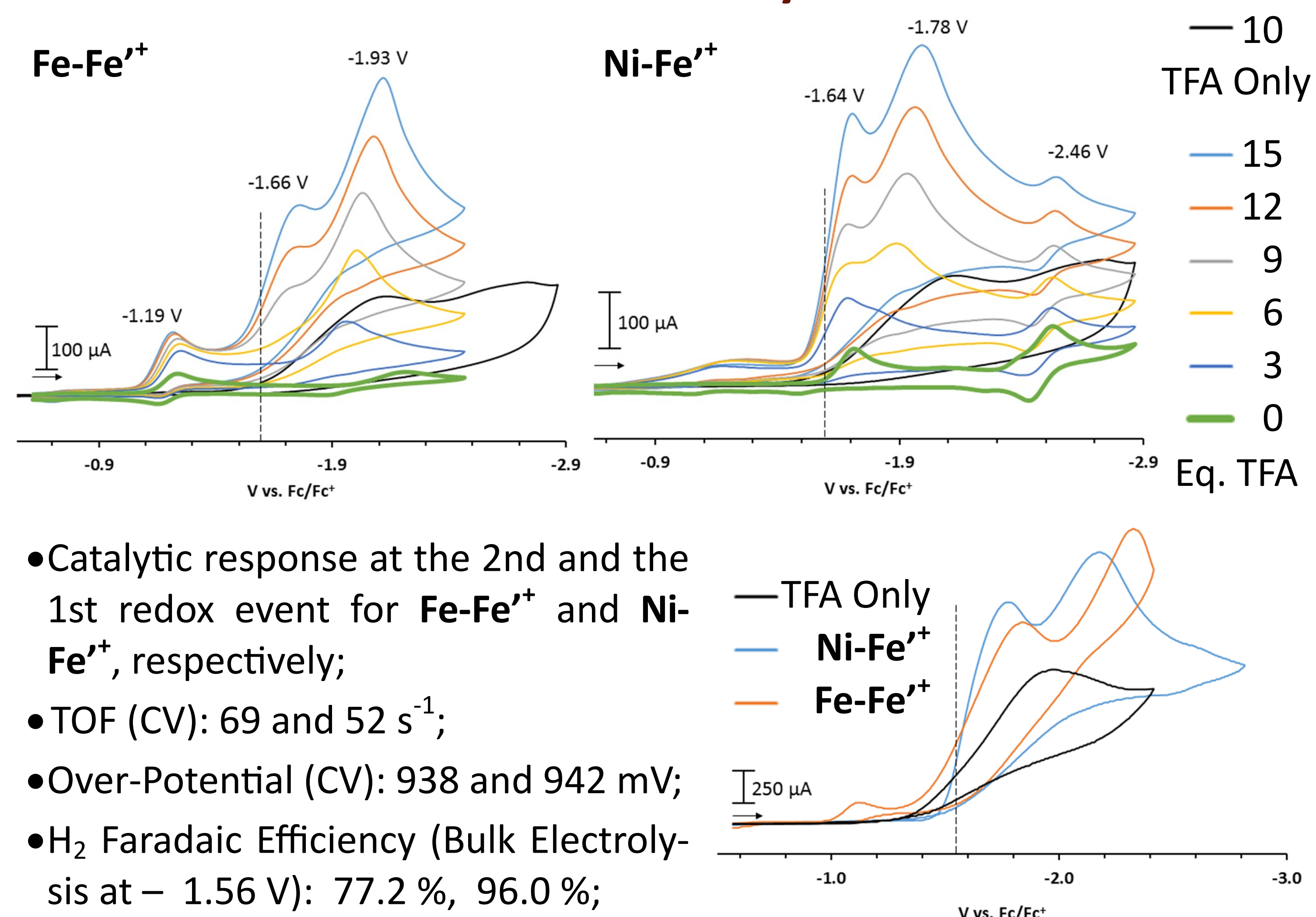
Introduction: Proton Shuttles in Hydrogenase



Synthesis and Crystal Structure

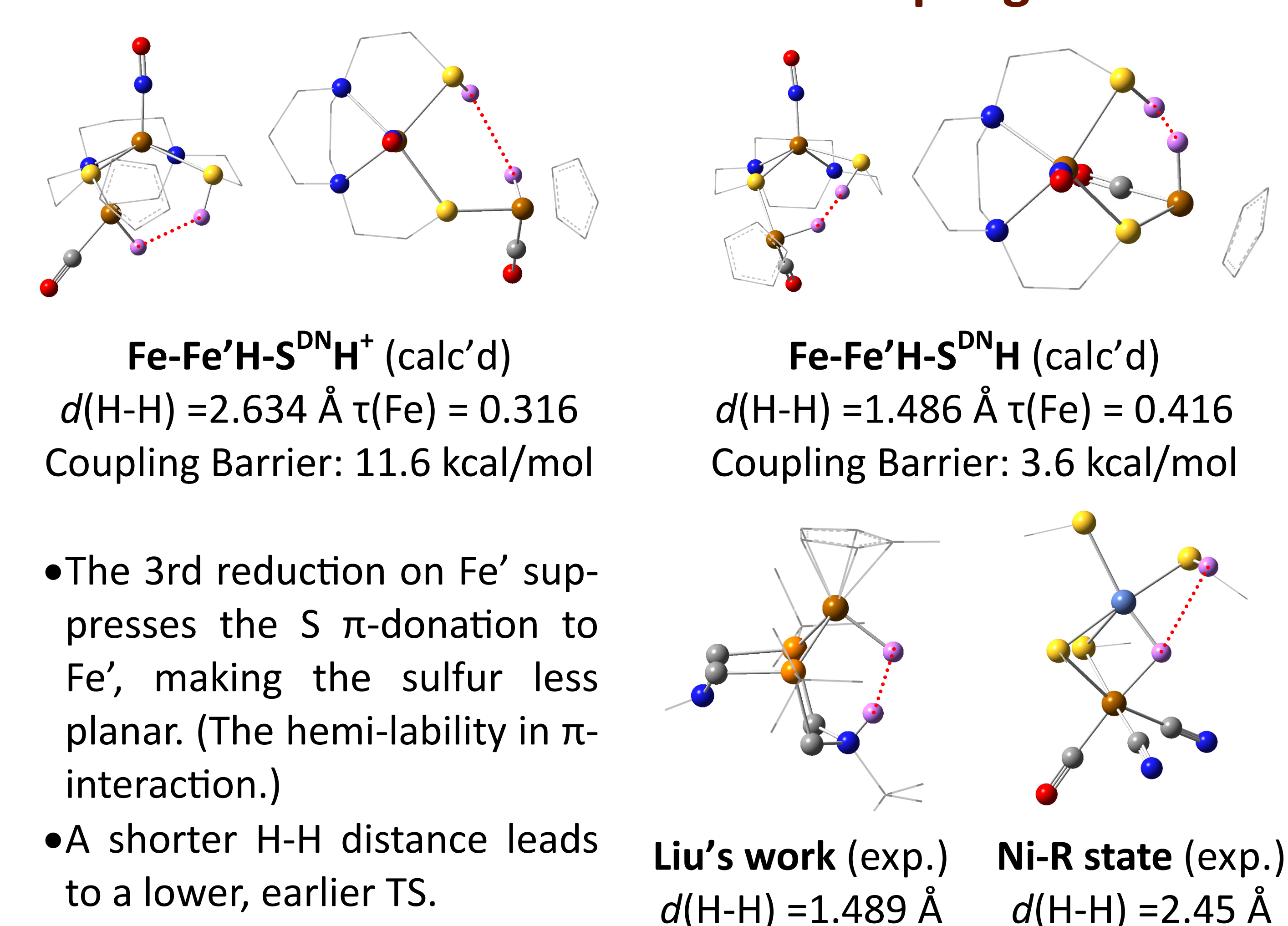


Electrochemistry



- Catalytic response at the 2nd and the 1st redox event for Fe-Fe²⁺ and Ni-Fe²⁺, respectively;
- TOF (CV): 69 and 52 s⁻¹;
- Over-Potential (CV): 938 and 942 mV;
- H₂ Faradaic Efficiency (Bulk Electrolysis at -1.56 V): 77.2 %, 96.0 %;

Calculated H-H Distance and Coupling Barrier



Mechanism of H₂ Production with the Lewis Pair Created by S-Fe' Bond Rupture

