

Understanding hydrogen oxidation and evolution reactions are key to developing new technologies towards the goal of a future hydrogen economy. With contemporary artificial catalysts, transformations of hydrogen are achieved by expensive and scarce metals such as platinum, ruthenium, or iridium. In nature, these reactions are facilitated by cheap and abundant transition metal cofactors – such as nickel and iron – in the hydrogenase metalloenzymes with the catalysis of these enzymes involving transient Fe-H intermediates. Determining the strength of these Fe-H interactions and their binding moieties are key to understanding their reactivity and providing a framework to develop biomimetic technology. Unfortunately, Fe-H bonds are not easily probed by conventional infrared or Raman vibrational spectroscopies. Here we have utilized ^{57}Fe nuclear resonance vibrational spectroscopy (NRVS) which probes the vibrational sidebands of the Mössbauer transition and affords a highly selective probe for the normal modes of ^{57}Fe . Probing Fe-H bonds are a challenge for ^{57}Fe NRVS, however for nearly a decade we have improved sample preparation, analysis methods, computational approaches, and experimental conditions to obtain high quality observations of weak signals. Collectively these developments, and studies of Fe-H model systems and enzymes, have afforded us unprecedented insights into the nature and reactivity of hydrogenases.