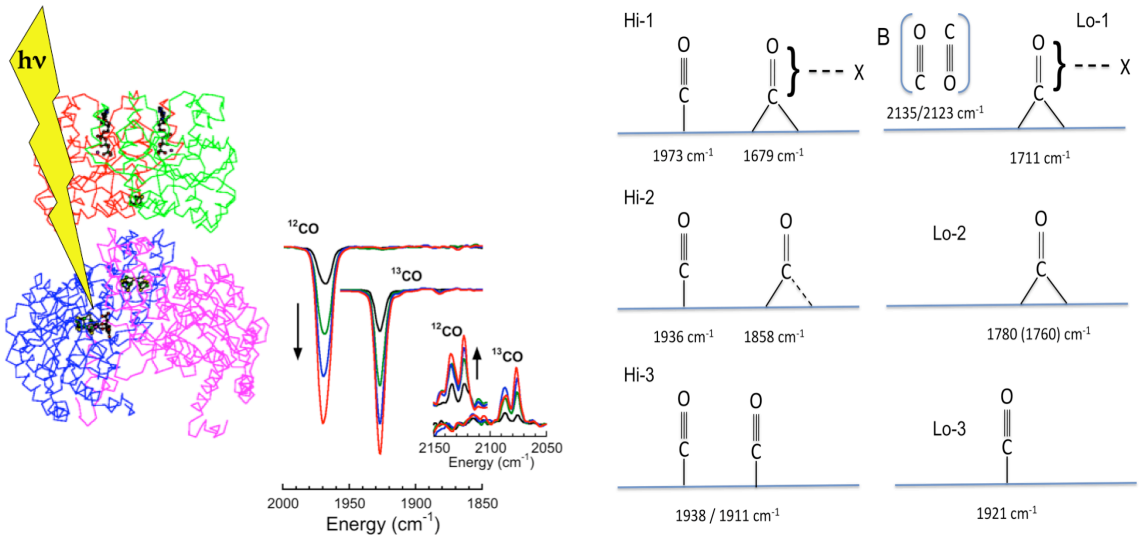
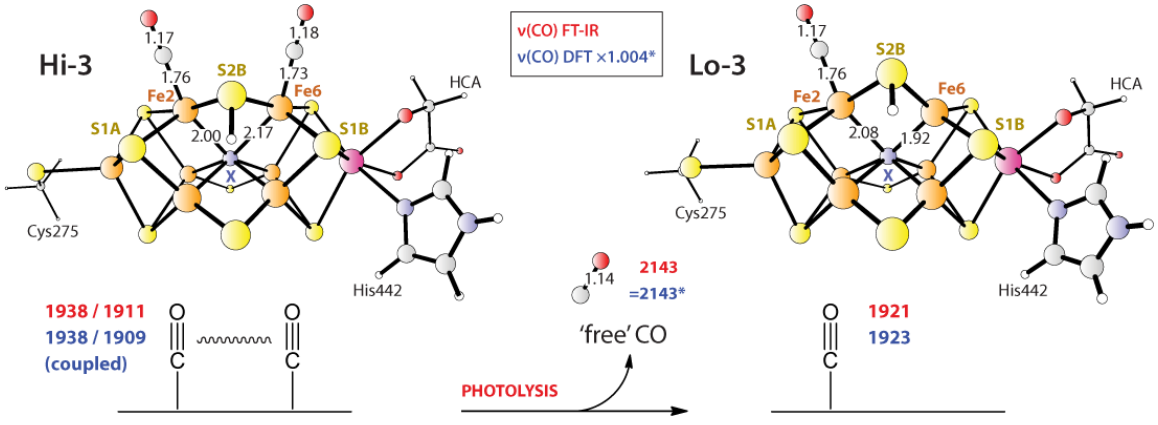
(1)



Fourier-transform infrared-spectroscopy (FT-IR) was used to study the photochemistry of CO-inhibited *Azotobacter vinelandii* Mo nitrogenase using visible light at cryogenic temperatures. With the wild-type, *α*-H195Q and *α*-H195N variant enzymes, three distinct photolabile Hi-CO species (Hi-1, Hi-2, Hi-3) were observed, and turned into three distinct Lo-CO species (Lo-1, Lo-2, Lo-3) separately. Each Hi-CO ↔ Lo-CO pair has different photolysis property, and different temperature dependent recombination dynamics. Different structures were assigned (right-hand figure) with the assistant of normal mode calculations. Hi-3 was confirmed to be an EPR-silent species.

(Yan, L.; Dapper, C. H.; George, S. J.; Wang, H.; Mitra, D.; Dong, W.; Newton, W. E.; Cramer, S. P., "Photolysis of Hi-CO Nitrogenase – Observation of a Plethora of Distinct CO Species using Infrared Spectroscopy", *Eur. J. Inorg. Chem*, **2011**, (2011), 2064-2074)

(2)

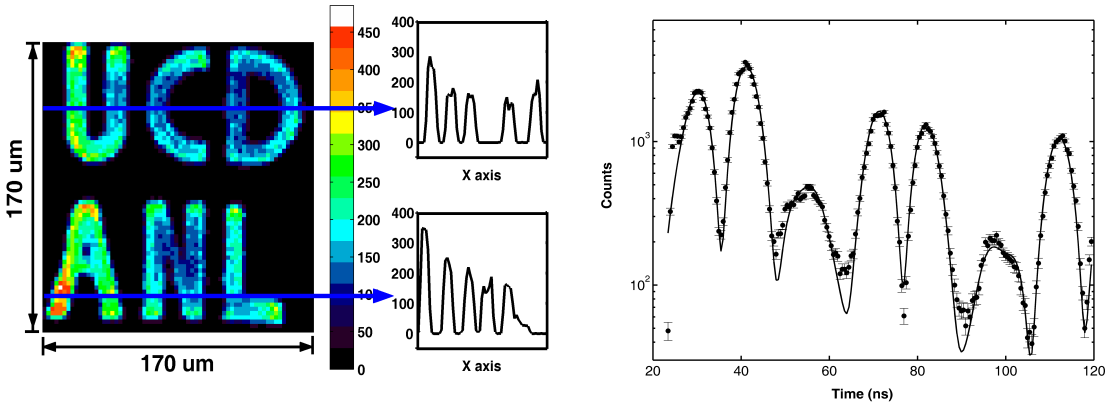


The novel EPR-silent CO-inhibited form (Hi-3) of *α*-H195Q nitrogenase from *Azotobacter*

vinelandii was further studied with FT-IR photolysis. DFT calculations help assign the related Hi-3 and Lo-3 species as terminal CO bound to the FeMo-cofactor active site (shown in Fig.). The Hi-3 bands arise from coupling of two similar CO oscillators. With the mixed 25% $^{12}C^{16}O$ / 75% $^{13}C^{18}O$ isotope gas, the decoupled CO oscillator was observed at 1934 cm^{-1} and ~1917 cm^{-1}. The recombination of Lo-3 to Hi-3 was observed at temperature above 200 K, with the activation energy of ~ 6.5 kJ mol^{-1}.

(Yan, L.; Pelmenschikov, V.; Dapper, C.H.; Scott, A.D.; Newton, W.E.; Cramer, S.P., "IR-Monitored Photolysis of CO-Inhibied Nitrogenase: A Major EPR-Silent Species with Coupled Terminal CO Ligands", (submitted to *Eur. J. Chem.*))

(3)



In cooperation with sector 3 at APS, we have developed Synchrotron Mössbauer microscopy. A 5 μm spatial resolution was achieved, and sub-micrometer resolution is envisioned. Proof-of-principle experiments were performed with the prepared pure ^{57}Fe phantoms (left-hand Fig.). At a certain spot, the hyperfine interactions could be revealed from the decayed time spectrum (right-hand Fig.) in the forward scattering, and the phonon density of state could be obtained with the nuclear resonant vibrational spectroscopy (NRVS) signal in the 4π scattering. Selected meteorite samples were successfully imaged. The potential application to biological samples is under development.

(Yan, L.; Zhao, J.; Divan, R.; Xu, S.; Cai, Z.; Boesenberg, J.S.; Friedrich, J.M.; Cramer, S.P.; Alp, E.E., "Synchrotron Mössbauer Microscopy: A new X-ray imaging modality development", (accepted by *J. of Synchrotron Rad.*))