

# L-edge X-ray Absorption Spectroscopy of Some Ni and NiFe Complexes

Hongxin Wang [1], Weiwei Gu [1], Ping-Chang Lin [1], Anthony T. Young [2],  
Elke Arenholz [2], and Stephen P. Cramer [1, 3]

[1] Department of Applied Sciences, University of California, Davis, CA 95616,

[2] Advanced Light Source Division and [3] Physical

Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

## INTRODUCTION

NiFe hydrogenase catalyzes the formation / consumption of molecular hydrogen and is one of the most important Ni enzymes.[1] It is interesting not only for its biological importance but also for its potential relevance to bio-energy applications in the future.[2] Sulfur ligated Ni and NiFe complexes [3,4] are often useful in modeling the active Ni sites for the corresponding hydrogenases. Geometric structure and electronic structure are the two major interesting aspects concerning metal complexes. For studying electronic structure of 3d metal complexes, L-edge X-ray absorption spectroscopy (XAS) has demonstrated several advantages [5] over the usual K-edge measurement. These features include a rich and theoretically interpretable multiplet due to the strong interaction between 2p hole and 3d electrons, a direct probe of the metal-ligand bonding orbital (3d), a dipole-allowed 2p → 3d transition, and a better X-ray energy resolution. For these reasons, L-edge absorption spectroscopy is one of the best methods available now to study electronic structure for various inorganic and bioinorganic complexes.[5] In the work described in this abstract, we have measured and analyzed Ni L-edge absorption spectra for six Ni and NiFe complexes which mimic hydrogenase active site.

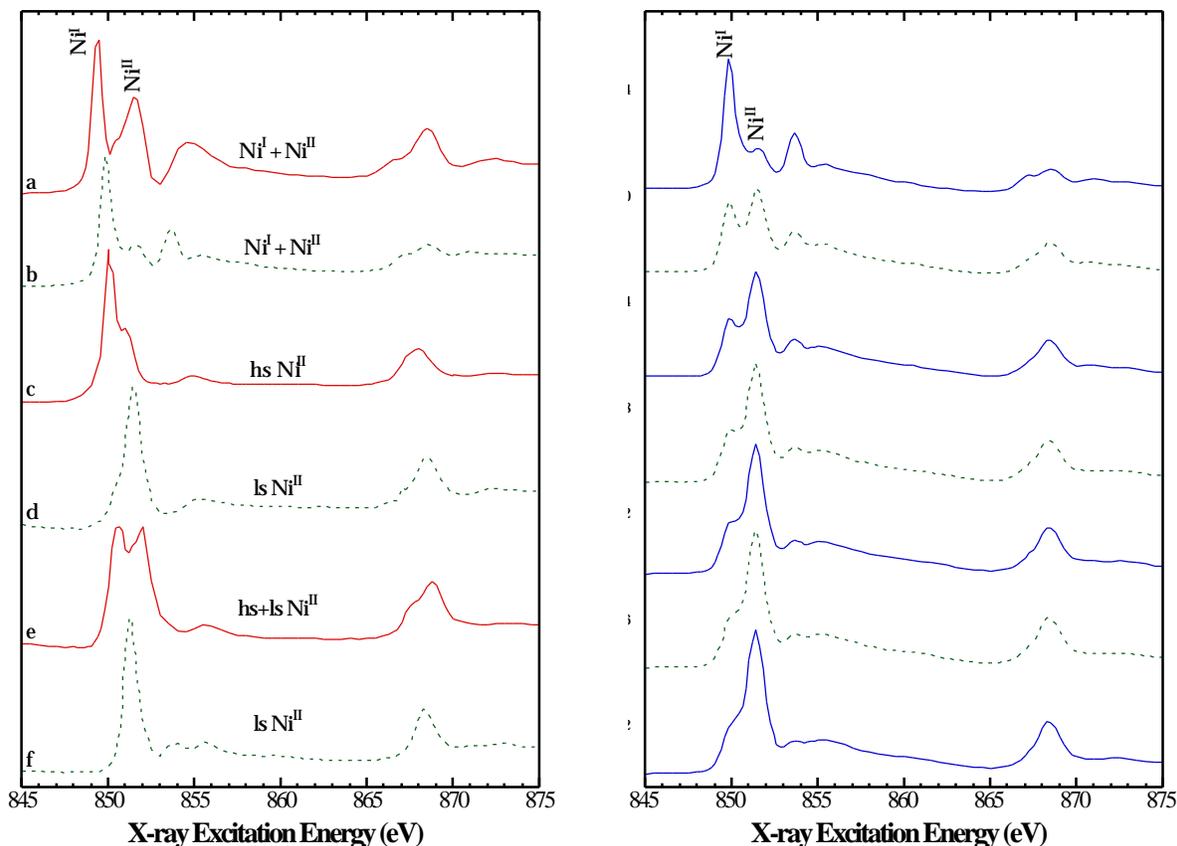
## EXPERIMENTS

In this experiment, we measured the L-edge XAS for a series of Ni and NiFe compounds: **a)**  $[\text{PhTt}]^{\text{tBu}}\text{Ni}^{\text{I}}\text{P}(\text{CH}_3)_3$ ; **b)**  $[\text{PhTt}]^{\text{tBu}}\text{Ni}^{\text{I}}\text{CO}$ ; **c)**  $[\text{PhTt}]^{\text{tBu}}\text{Ni}^{\text{II}}\text{Cl}$ ; **d)**  $[\text{K}_2\text{-PhTt}]^{\text{tBu}}\text{Ni}^{\text{II}}\text{CH}_2\text{S}^{\text{tBu}}$ ; **e)**  $[\text{Fe}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}(\text{CN})\text{Ni}^{\text{II}}(\text{CH}_3)(\text{dppe})]$ ; and **f)**  $[\text{Fe}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}(\text{NO})\text{Ni}^{\text{II}}\text{Cl}(\text{dppe})]$ . The samples (**a-d**) were obtained from Riordan's lab [3] while (**e-f**) were obtained from Evans' lab.[4] L-edge spectra were measured at ALS beamline 4.0.2 (a magnetic spectroscopy undulator beamline), which has an energy range of 50-1800 eV and a resolving power of  $>5,000$ . The measurement chamber was maintained at a vacuum of  $5 \times 10^{-9}$  torr. A thin (1000Å) aluminum window was also placed in between the beamline and the measurement chamber. While the monochromator was scanned across the intended energy region, the total electron yield from the samples was measured using a Galileo 4716 channeltron electron multiplier.[6] The incident beam intensity was measured via a gold grid, and used to normalize the total electron yield signal. The scans were recorded with a step size of 0.1 eV and an integration time of 1 s/pt. The spectral resolution is at about 0.2 eV. Each final spectrum was the sum of 3 such scans from different sample spots. The relative energy position was calibrated to be within 0.1 eV for different scans during our measurement.

## RESULTS AND DISCUSSION

The figure below in the left panel shows the L-edge absorption spectra for all six Ni/NiFe complexes studied here. From the rich multiplet,  $\text{Ni}^{\text{I}}$  vs.  $\text{Ni}^{\text{II}}$  and low spin (ls) vs. high spin (hs)  $\text{Ni}^{\text{II}}$  are clearly resolvable. The samples **a** and **b** exhibit a  $\text{Ni}^{\text{I}} + \text{Ni}^{\text{II}}$  feature. The main  $L_3$  peaks are clearly from  $\text{Ni}^{\text{I}}$ . The second  $L_3$  peaks are the residual ls  $\text{Ni}^{\text{II}}$ . The third peaks are the typical contribution from S or other ligands (in all the spectra). The sharp third peak in **b** could be the

transition to the orbital with CO character. **c** is a typical hs Ni<sup>II</sup>, **d** and **f** are typical ls Ni<sup>II</sup> while **e**) has mixed ls and hs Ni<sup>II</sup>.



**Figure 1** Left panel: L-edge X-ray absorption spectra of six Ni/NiFe complexes studied in this work (**a-f** are listed in experimental section). Right panel: L-edge X-ray absorption spectra of sample **b**, with out moving irradiation spot, to see the changes under constant X-ray radiation.

We also measured seven sequential L-edge spectra of **b** at one sample spot (with each scan taking 6 minutes). As shown in the right panel, the intense X-ray beam could cleave the Ni-CO bond and decrease the third peak. Meanwhile, Ni also changed from Ni<sup>I</sup> (or hs Ni<sup>II</sup>) to ls Ni<sup>II</sup>. More theoretical studies are needed to clarify the related issues.

These model studies show that Ni L-edge spectra are very sensitive to the Ni oxidation states and spin states. The spectroscopy should be very useful to investigate the Ni active site in different redox forms of NiFe hydrogenases. With a polarization control, high photon flux and an energy resolving power of >5,000, ALS beamline 4.0.2 will be the best for our future L-edge XAS and XMCD studies on NiFe hydrogenases.

This project has been funded by NIH grant GM-44380. Advanced Light Source is supported by US Department of Energy, Office of Basic Energy Sciences. We also thank Prof. C. Riordan at the University of Delaware (Newark, DE) and Prof. D. Evans at the John Innes Center (Colney, UK) for the Ni / NiFe samples.

Principal investigator: Stephen P. Cramer, Physical Biosciences Division, Ernest Orlando Lawrence Berkeley National Laboratory. Contact: Hongxin Wang Email: hongxin@popper.lbl.gov. Telephone: 510-486-6094.

## REFERENCES

1)Fontecilla-Camps, J. C. *Struct. Bonding* **1998**, *91*, 2-30.

- 2) Hall, D. O. and House, J. I. *Biomass & Bioenergy* **1994**, *6*, 11-30.
- 3) Schebler, P. J.; Mandimutsira, B. S.; Riordan, C. G.; Liable\_Sands, L. M.; Incarvito, C. D. and Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 331
- 4) Davies, S. C.; Evans, D. J.; Hughes, D. L.; Longhurst, S. and Sanders, J. R., *Chem. Commun.*, **1999**, 1999, 1935.
- 5) Wang, H.-X.; Peng, G.; Miller, L. M.; Scheuring, E. M.; George, S. J.; Chance, M. R.; Cramer, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 4921.
- 6) Wang, H.-X.; Ge, P.; Riordan, C. G.; Brooker, S.; Woome, C. G.; Collins, T.; Melendres, C. A.; Ggraudejus, O.; Bartlett, N. and Cramer, S. P. *J. Phys. Chem. B*, **1998**, *102*, 8343