Application of X-ray Near-edge Absorption Spectroscopy on Fe(II) Spin Crossover Complexes

Hsin-Chin Huang (黃信嘉)[1], Chou-Fu Sheu (許朝富)[1], Jyh-Fu Lee (李志甫)[2], Jin-Ming Chen (陳錦明)[2], and Yu Wang (王瑜)[1]

[1]Department of Chemistry, National Taiwan University, Taipei, Taiwan
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

The changes in spin state or electronic configuration of iron(II) were investigated by Fe K and L-edge absorption spectroscopy, which is very sensitive not only to the oxidation state but also to the electronic density distribution around the metal center. Previous studies with K- and L-edge absorption spectroscopy have established the spectroscopic fingerprints of HS and LS iron(II) spin-crossover complexes.[1-3] From high spin (HS) to low spin (LS), the spin configuration changes from $(e_g^2)(t_{2g}^4)$ S=2 to $(e_g^0)(t_{2g}^6)$ S=0. The unoccupied of the anti-bonding character e_g orbital causes the shortening of Fe-ligand bond length (～0.2 Å).

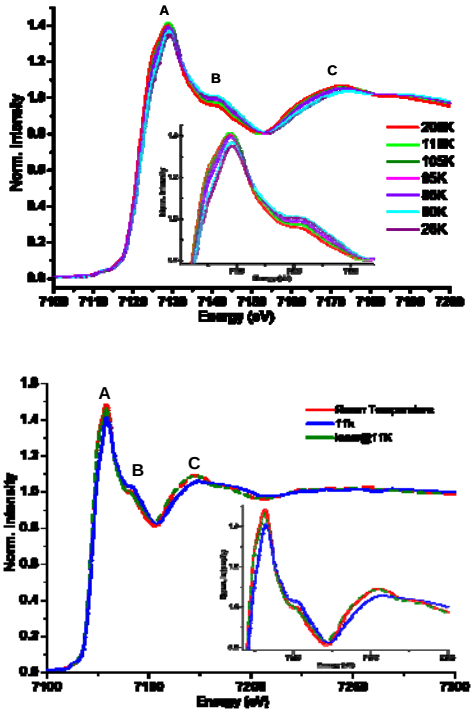

Fig. 1: Thermal dependent XANES measurement of $\{[Fe^{II}(\mu_4\text{-bpt})(abpt)][(ClO_4)]\}_n$ **(1)** (Top)； excitation of Fe(II) from LS to HS-2(LIESST) achieved by irradiating with an 532nm laser.(bottom) Ligand bpt stands for 3,5–di-2-pyridyl-4-H-1, 2, 4 triazole. Abpt = 4–amino-3,5–di–2–pyridyl–4-H-1,2,4 triazole.

From several different complexes with HS and LS state at room temperature determined previously by magnetic measurement, typical spectra of six-coordinated Fe(II) complexes (FeN_6) is well-characterized. Using a 1-D chain SCO compound $\{[Fe^{II}(\mu_4\text{-bpt})(abpt)][(ClO_4)]\}_n$ **(1)** with $T_{1/2}$ = 97 K for thermal dependent and LIESST(induced by light irradiation at low temperature) XANES measurement, the significant differences in HS and LS can be clearly seen (Fig. 1). Undergoing spin transition from HS to LS, the intensity of the main resonance (A) is weaker slightly and the peak position of (B) is shift to higher energy. Also the broad feature (C) arising from scattering of the photoelectron by the nearest-neighbor shell is also shift to higher energy due to the shortening of Fe-ligand distances in the LS state.

The preliminary result of iron K-edge XANES on Fe(II) spin crossover complexes demonstrates the power on characterization the oxidation and spin state. In complicated system with ferro- or antiferromagnetic interaction existing between unpaired electron, the metal spin state can only be determined unambiguously in the aid of x-ray absorption or Mossbauer spectroscopy.

The Fe L-edge is even a better tool for probing electronic configuration in comparison with the Fe K-edge. It involves in an electric dipole transition from *2p* to non-fully occupied *3d* valence orbitals. The features of Fe L-edge absorption are the sensitivity to the nature of the absorbing atom and the corresponding occupancy in the electronic configuration and the local symmetry around the target atom of the complex. The Fe L-edge absorption profiles are extremely sensitive to the *d* orbital populations and the corresponding electron density distribution.

A series of Fe L-edge absorption spectra of **(1)** were measured at various temperatures, among which selected ones are shown in Fig. 2. The shift in energy, change in structure of the principal spectral features, and the different branching ratio between the HS and LS states agree well with the experimental data and the result of multiplet calculation of $[Fe^{II}(phen)_2(NCS)_2]$ (phen=1,10-phenanthroline).[3]

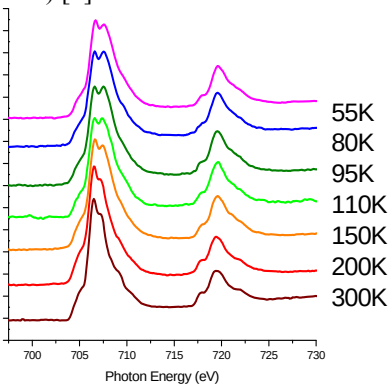

Fig. 2: Temperature dependent Fe L-edge absorption spectra of $\{[Fe^{II}(\mu_4\text{-bpt})(abpt)][(ClO_4)]\}_n$ **(1)**.

Reference

[1] V. Briois, C. Cartier dit Moulin, P. Sainctavit, C. Brouder, and A.-M. Flank, J. Am. Chem. Soc. **117**, 1019 (1995).
[2] C. Cartier dit Moulin, P. Rudolf, A.-M. Flank, and C. T. Chen, J. Phys. Chem. **96**, 6196 (1992).
[3] J. J. Lee, H. S. Sheu, C. R. Lee, J. M. Chen, J. F. Lee, C. C. Wang, C. H. Huang, and Y. Wang, J. Am. Chem. Soc. **122**, 5742 (2000).