Metal Active Sites -- from Enzymes to Surfaces

Dawn M. Sabel   Final Seminar   August 10, 1993

A large portion of spectroscopy centers on metals and their role in reactivity. The work presented here involves the study of both biological and surface reactivity.

In recent years, the Mo activated site of Mo hydroxylases has come under intense scrutiny [1-4]. Degradation studies indicate that the Mo is located in a low molecular weight cofactor which consists of a pterin ring with a di-thiolene side chain (Figure 1) and chelation
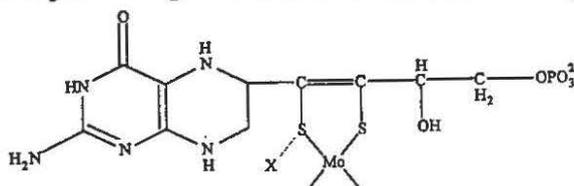
of the Mo is considered to occur through the di-thiolene linkage [5-9]. A number of EXAFS [1, 3, 10] and EPR [1, 4] studies have been performed on the molybdoenzymes, yet uncertainty involving the number, type and geometry of the ligands at the Mo active site persists. Crystal structures for the molybdoenzymes are not known and optical studies are hindered by the presence of strongly absorbing chromophores. The isolation of *Rhodobacter sphaeroides* [11] and *Rhodobacter capsulatus* [12] DMSO reductase has allowed for the study of the Mo active site in its native form since these strains do not contain additional prosthetic groups. However, a lack of understanding about the electronic nature of simple model systems, such as $[MoOCl_4]^-$, has limited the insight that may be gained from the direct study of the enzymes [13-16].

The assignment of the electronic spectra of the $[MOCl_4]^-$ (M = Cr or Mo) and $[WOCl_4(H_2O)]^-$ compounds was made using magnetic circular dichroism (MCD) spectroscopy. Because of their similar MCD spectra, assignments for these complexes were made with respect to the $[MoOCl_4]^-$ spectrum (Figure 2). The two lowest energy transitions are assigned to the d_{xy} to d_{xz},d_{yz} and d_{xy} to $d_{x^2-y^2}$ transitions, respectively. The next three features are due to charge transfer excitations from the non-bonding Cl p_π orbitals to the d_{xy} orbital. The feature of ca. 34,000 cm^{-1} is tentatively assigned to the d_{xy} to d_{z^2} ligand field
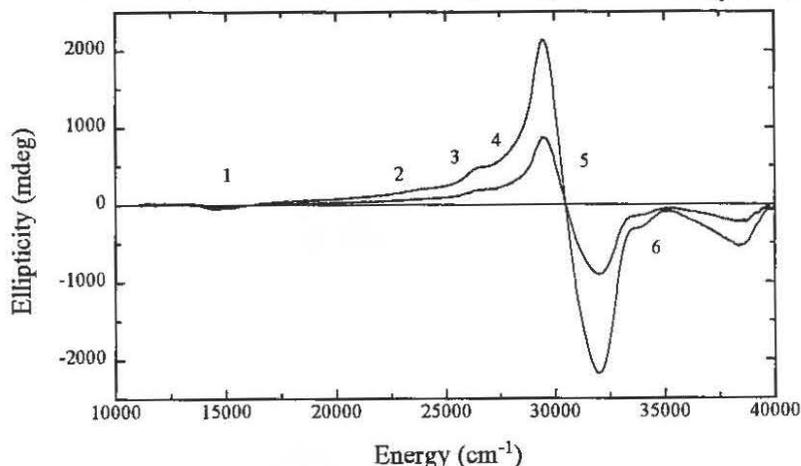

transition. Using these assignments, it was experimentally confirmed that low energy charge transfer transitions are responsible for the inverted EPR signals that characterize these complexes and the molybdoenzymes [1, 4, 17, 18]. MCD characterization of $[MoO(SPh)_4]^-$

and *Rhodobacter sphaeroides* DMSO reductase was also performed. The spectra collected for the enzymes are consistent with thiol coordination although further analysis needs to be done on the system.

Reactions may also occur on metal surfaces in electrochemical systems. Recent advances in *in situ* techniques such as atomic force and scanning tunneling microscopies (AFM and STM) and glancing incidence X-ray spectroscopy (GIXS) allow the surface structure of these systems to be studied in detail [19]. Much of the work done to date has centered on the underpotential deposition, UPD, of a metal adatom on a substrate. These systems often display behavior different from that of either metal. The UPD process is readily controlled and coverage of a monolayer or less of the deposited metal is easily obtained. However, alloy formation may occur in some systems even in the UPD region [20-22]. Such systems are characterized by stable bimetallic phases involving the adatom and substrate or high degrees of miscibility between the two metals.

One system that displays both of these properties in the UPD region is Cd deposited on Ag(111) [23, 24]. AFM studies have shown that at potentials immediately following the first UPD peak (-890 mV vs. Hg/Hg_2SO_4) but before alloy formation, the Cd forms a $\sqrt{3} \times \sqrt{3}$ R30° adlattice on the Ag(111) surface. Polarization at potentials more negative than -1.04 V causes alloy formation in this system. The dissolution process was followed as more positive potentials were applied and AFM images of this process are shown below. At -1.04 V, the

a   b   c
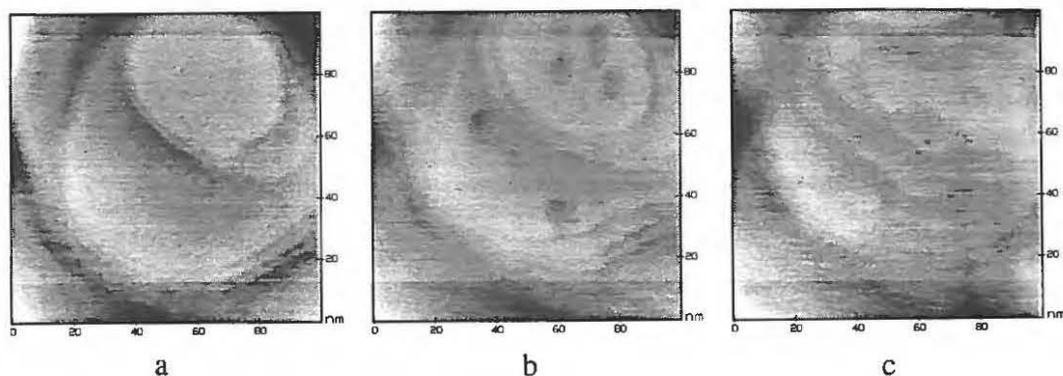
surface is smooth and consists of a number of plateau-like features (Figure 3a). At -800 mV (Figure 3b) the surface roughens and pits form. Application of more positive potentials completely removes the Cd from the Ag(111) surface (Figure 3c). Similar behavior has been noted in the dissolution of Ag from dilute Ag/Au alloys and indicates that the dealloying or corrosion process involves the formation of surface pits on the nanometer scale which have the ability to diffuse across the surface, thus allowing for subsurface dissolution [25, 26].

References

1.   Coughlan, M. P ., Ed.; *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon Press: New York, 1980.

2.   Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Ed.* **1985**, *62*, 943.

3.   Sykes, A., Ed.; *Advances in Inorganic and Bioinorganic Mechanisms*; Academic Press: London, 1983; Vol. 2.

4.   Spiro, T., Ed.; *Molybdenum Enzymes*; Wiley-Interscience: New York, 1985.

5. Johnson, J. L.; Hainline, B. E.; Rajagopalan, K. V. *J. Biol. Chem.* **1980**, *255*, 1783.

6. Johnson, J. L.; Rajagopalan, K. V. *Proc. Natl. Acad. Sci. USA* **1982**, *79*, 6856.

7. Johnson, J. L.; Hainline, B. E.; Rajagopalan, K. V.; Arison, B. H. *J. Biol. Chem.* **1984**, *259*, 5414.

8. Kramer, S. P.; Johnson, J. L.; Ribeiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* **1987**, *262*, 16357.

9. Gruber, S.; Kilpatrick, L.; Bastian, N. R.; Rajagopalan, K. V.; Spiro, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 8179.

10. Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59.

11. Bastian, N. R.; Kay, C. J.; Barber, M. J.; Rajagopalan, K. V. *J. Biol. Chem.* **1991**, *266*, 45.

12. McEwan, A. G.; Ferguson, S. J.; Jackson, J. B. *Biochem. J.* **1991**, *274*, 305.

13. Deeth, R. J. *J. Chem. Soc., Dalton Trans.* **1990**, 365.

14. Collison, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2999.

15. Gray, H. B.; Hare, C. R. *Inorg. Chem.* **1962**, *1*, 363.

16. Deeth, R. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1895.

17. Garner, C. D.; Hillier, I. H.; Mabbs, F. E.; Taylor, C.; Guest, M. F. *J. Chem .Soc., Dalton Trans.* **1976**, 2258.

18. Garner, C. D.; Hill, L. H.; Mabbs, F. E.; McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1202.

19. Bard, A. J.; Abruna, H. D.; Chidsey, C. E.; Faulkner, L. R.; Feldberg, S. W.; Itaya, K.; Majda, M.; Melroy, O.; Murray, R. W.; Porter, M. D.; Soriaga, M. P.; White, H. S. *J. Phys. Chem.* **1993**, *97*, 7147.

20. Jovic, V. D.; Jovic, B. M.; Despic, A. R. *J. Electroanal. Chem.* **1990**, *288*, 299.

21. Schultze, J. W.; Koppitz, F. D.; Lohrengel, M. M. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 693.

22. Hassan, M. Z.; Untereker, D. R.; Bruckenstein, S. *J. Electroanal. Chem.* **1973**, *42*, 161.

23. Schwitzgebel, G. *Z. Phys. Chem. NF* **1975**, *95*, 15.

24. Schwitzgebel, G.; Michael, P.; Zohdi, Y. *Acta Metall.* **1975**, *23*, 1551.

25. Oppenheim, I. C.; Trevor, D. J.; Chidsey, C. E. D.; Trevor, P. L.; Sieradzki, K. *Science* **1991**, *254*, 687.

26. Sieradzki, K.; Corderman, R. R.; Shukla, K.; Newman, R. C. *Phil. Mag.* **1989**, *59*, 713.