Molecular-Level Processes Governing the Interaction of Contaminants with Iron and Manganese Oxides

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Problem Statement:

•Understanding the fate and transport of contaminants in subsurface environments, and devising effective remediation schemes, requires molecular-level understanding of contaminant-mineral interactions.

•This project is aimed specificially at understanding the interactions of chromate, an important carcinogen in the Hanford site soil, and well-defined iron and manganese oxide mineral surfaces.

•This project specifically addresses redox chemistry and hydroxylation at redox-active mineral surfaces, and the effect of such processes on the fate of redox-active contaminants in the subsurface.

Overall objective:

1. To gain molecular-level understanding of complex aqueous/mineral systems by carrying out controlled experiments on well-defined systems with a constrained number of variables.

Specific Objectives:

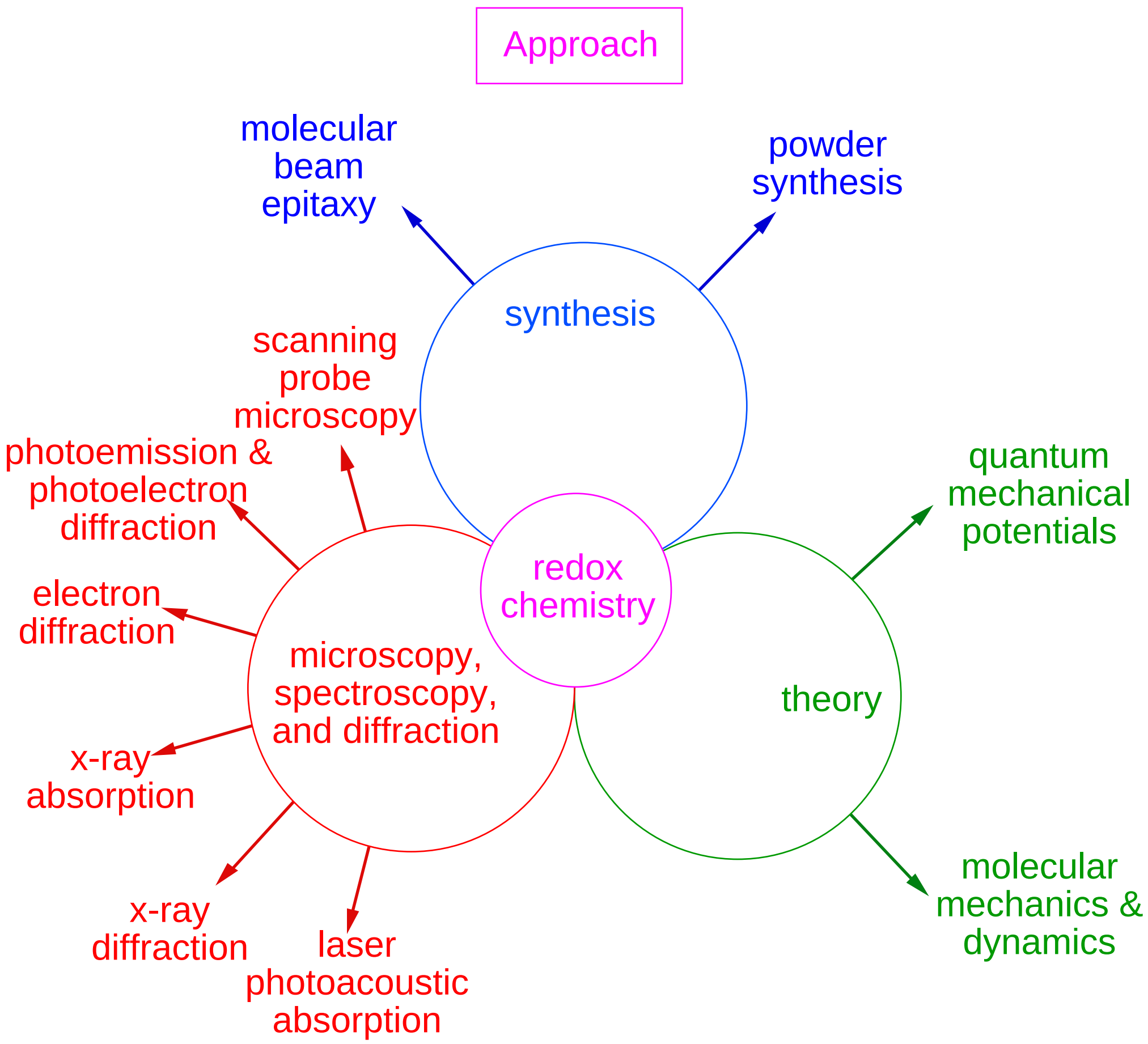
1. Synthesis and characterization of model (i.e. compositionally pure and crystallographically well defined) minerals of iron and manganese .

2. To gain molecular-level understanding of:

    a. pure water and aqueous chromate interactions with model (synthetic) and natural single-crystal iron and manganese oxide and oxyhydroxide surfaces.

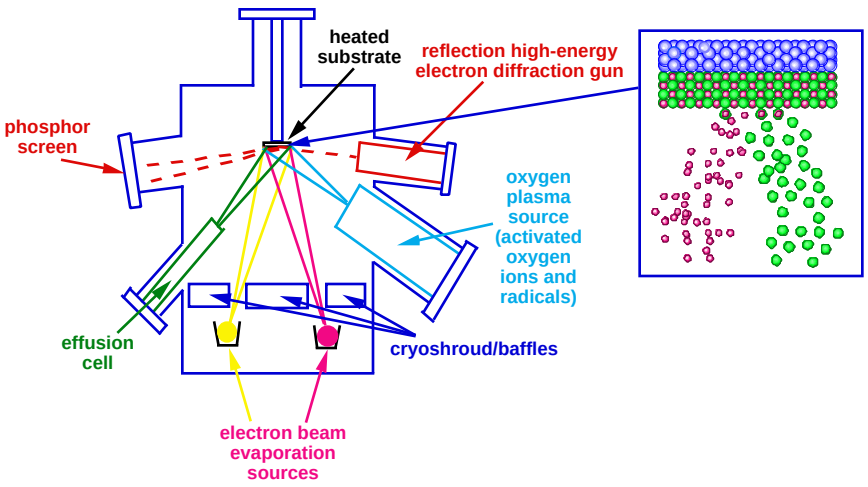
    b. aqueous chromate interactions with more realistic iron and manganese oxide and oxyhydroxide powders.

3. Theoretical prediction of important properties and reaction mechanisms that cannot be measured experimentally.

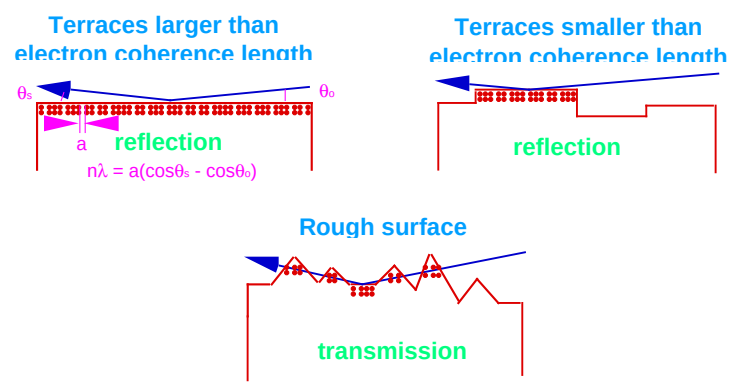

Approach
molecular beam epitaxy
powder synthesis
synthesis
scanning probe microscopy
photoemission & photoelectron diffraction
quantum mechanical potentials
electron diffraction
redox chemistry
microscopy, spectroscopy, and diffraction
theory
x-ray absorption
x-ray diffraction
laser photoacoustic absorption
molecular mechanics & dynamics

Techniques

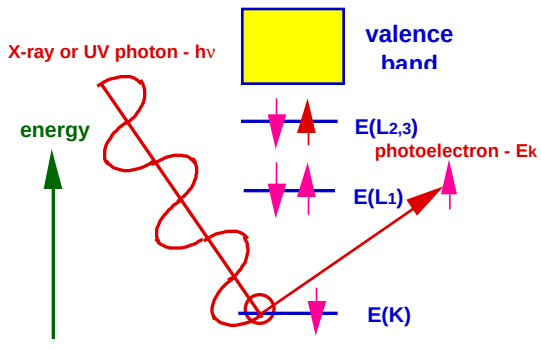
Synthesis of Model Oxide Surfaces by Oxygen-Plasma-Assisted MBE



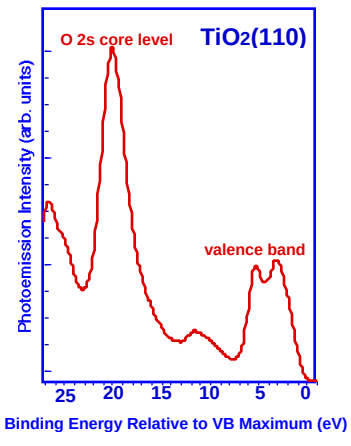
Reflection High Energy Electron Diffraction



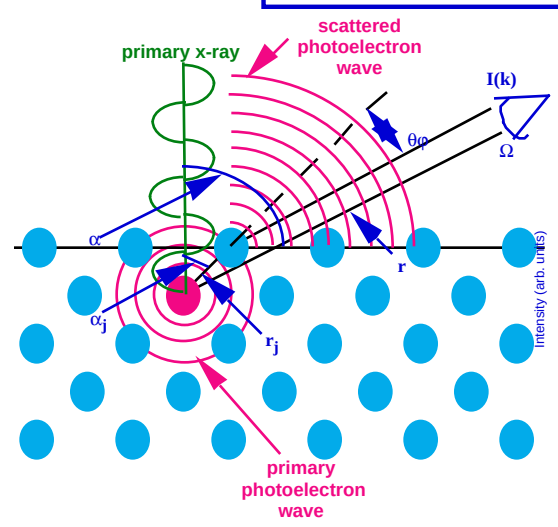
X-ray and UV Photoemission

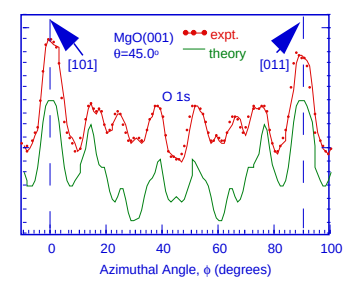


Photoemission -- Ek = hν - E(K)



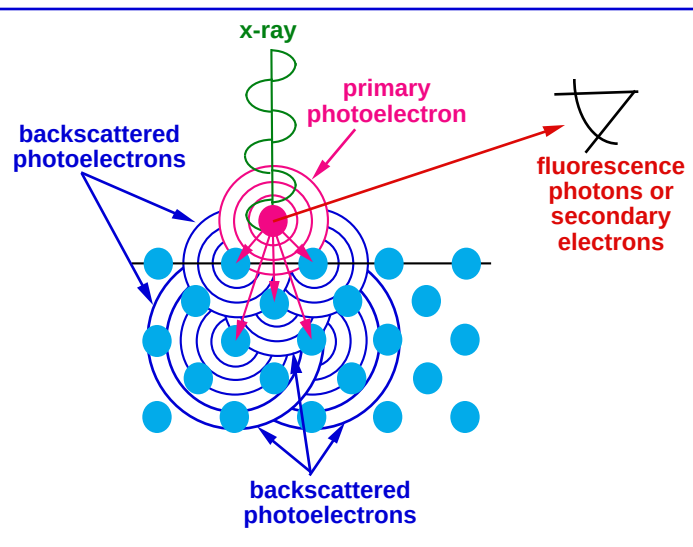
Photoelectron Diffraction



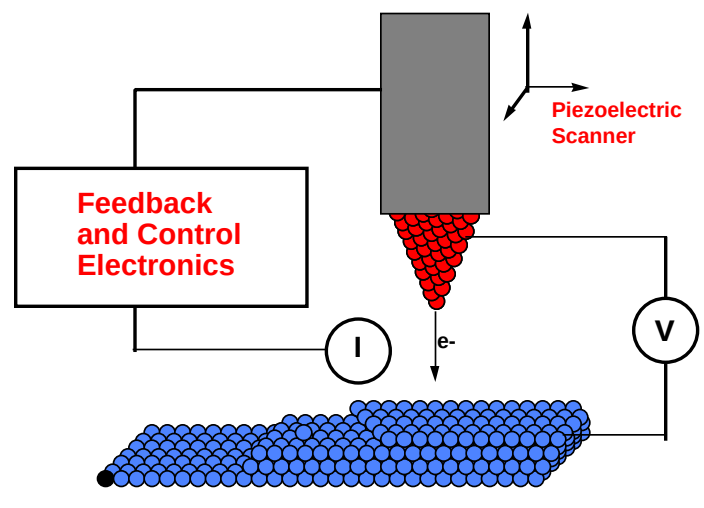


$$I(k) \sim \left|\psi_0(r,\alpha) + \sum \psi_j(r_j,\alpha_j,\theta_j)\right|^2 \quad \psi_j(r_j,\alpha_j,\theta_j) \sim [|f(\theta_j)|/r_j]\exp\{i[kr_j(1-\cos\theta_j)+\gamma(\theta_j)]$$

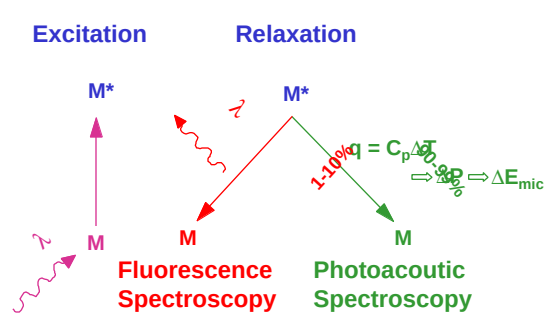
Extended X-ray Absorption Fine Structure (EXAFS)

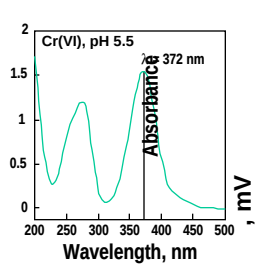


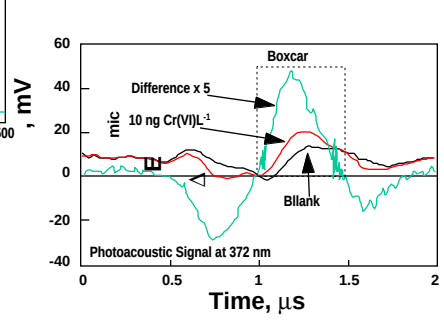
Scanning Tunneling Microscopy



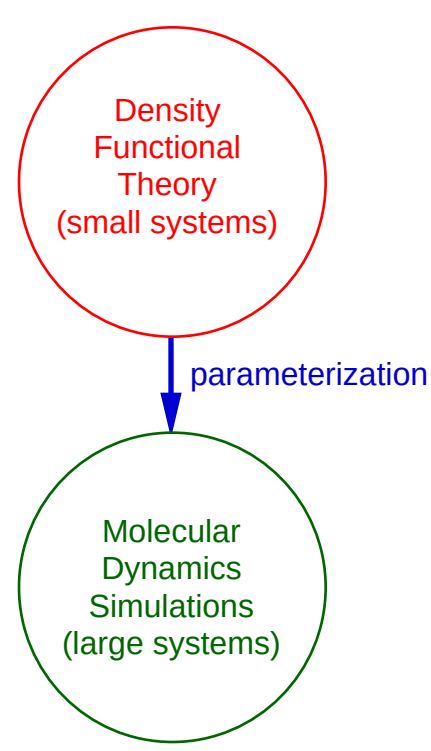
Laser Photoacoustic Spectroscopy



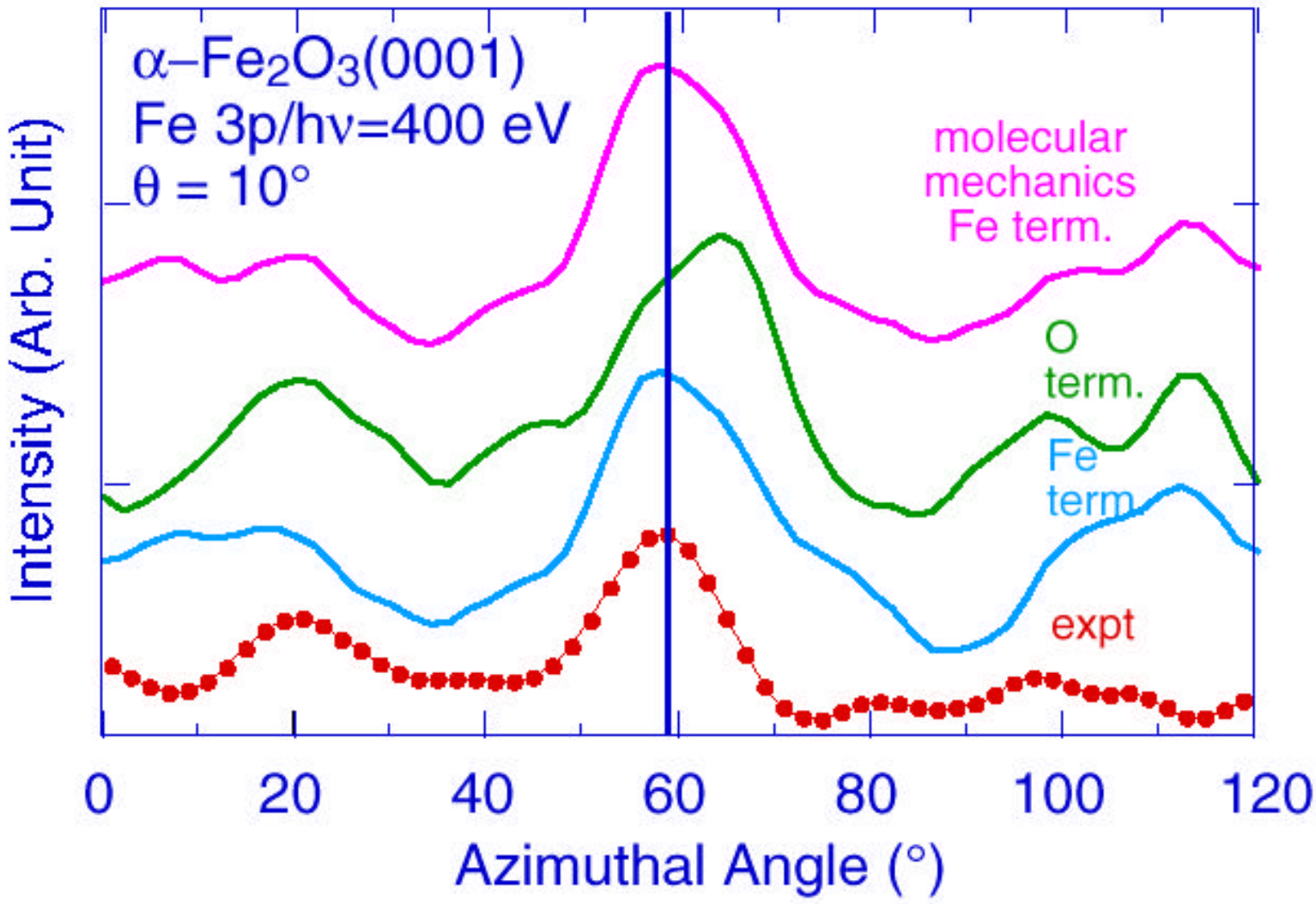




Theoretical Methods Used



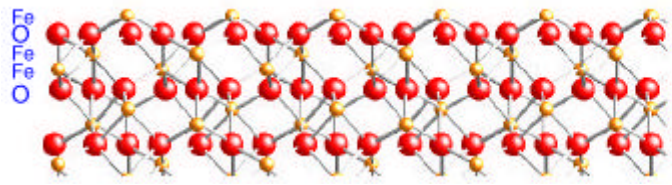
Surface Structure of α-Fe_2O_3(0001)



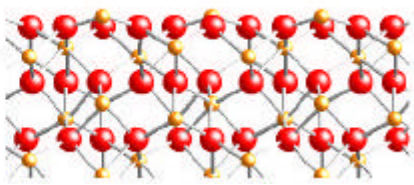
•Obtaining the atomic structure of clean, single-crystal iron oxide surfaces is essential for understanding their respective reactivities with water and chromate.

•Photoelectron diffraction at the LBNL Advanced Light Source reveals that the clean α-Fe 2 O 3 (0001) surface is terminated with a single layer of Fe atoms.

•The percentage relaxations of the first four layers are -41%, +18%, -8% and +47% of the respective bulk values.



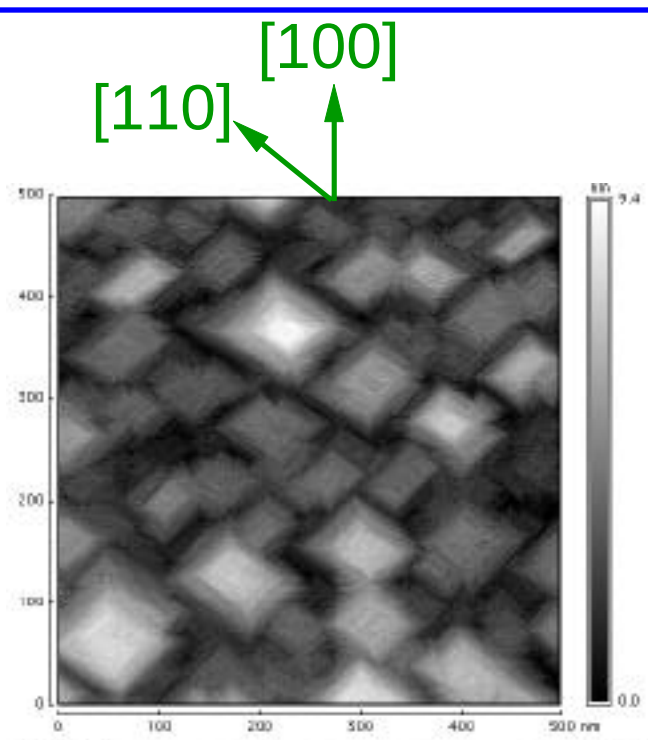
Unrelaxed Bulk Truncation

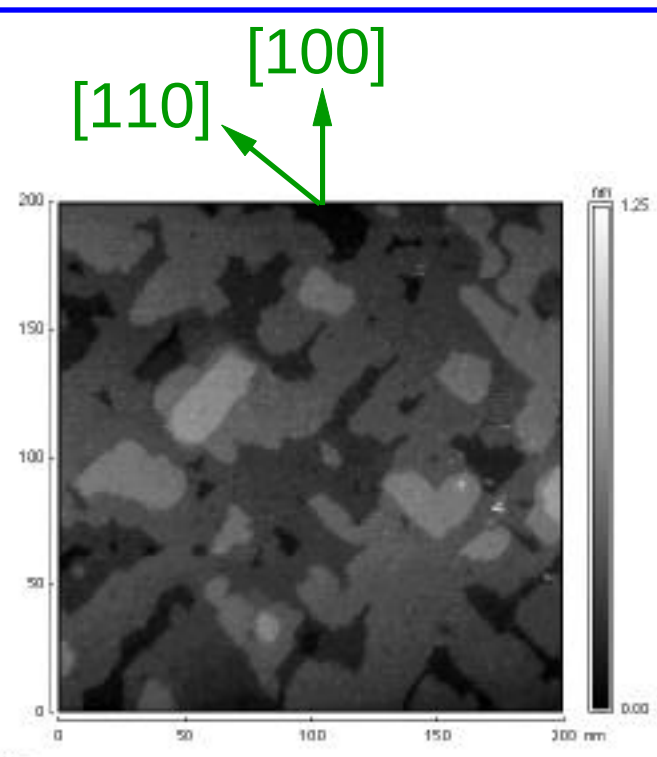


Relaxed Surface

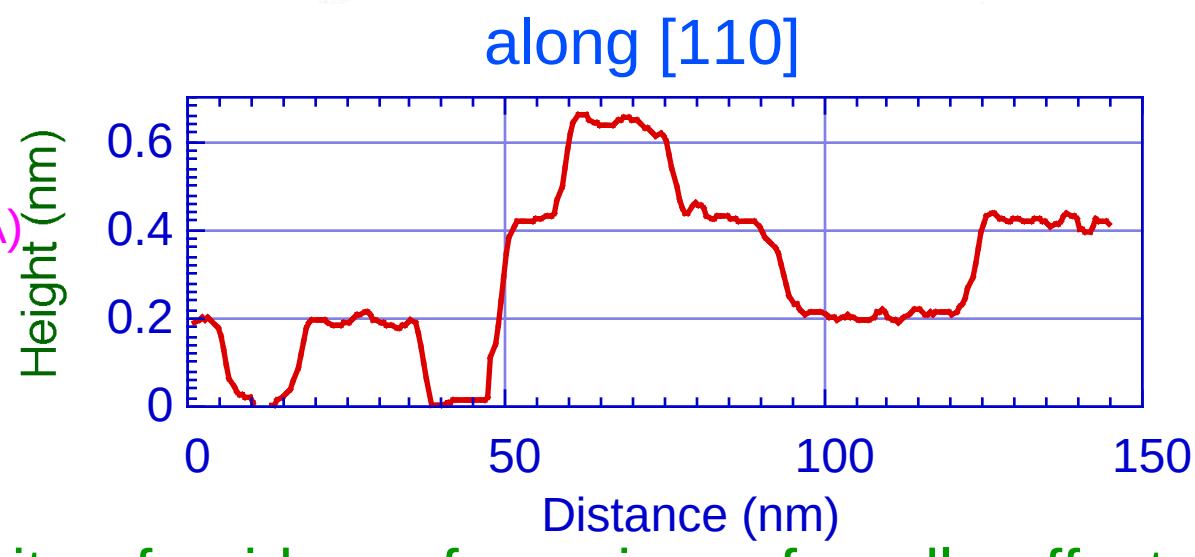
•These top layer relaxations are driven by the associated decrease in surface energy. We have calculated the surface energies of relaxed and bulk-terminated (unrelaxed) α-Fe 2 O 3 (0001) to be 1.64 and 4.24 J m -2 , respectively.

Surface Morphology of $Fe_3O_4(001)$





(sample bias = 1.5 V,
tunneling current = 0.5 nA)



- The initial reactivity of oxide surfaces is profoundly affected by the types and densities of surface defects. Steps are one class of defects that are very active chemically compared to atomically flat terraces.

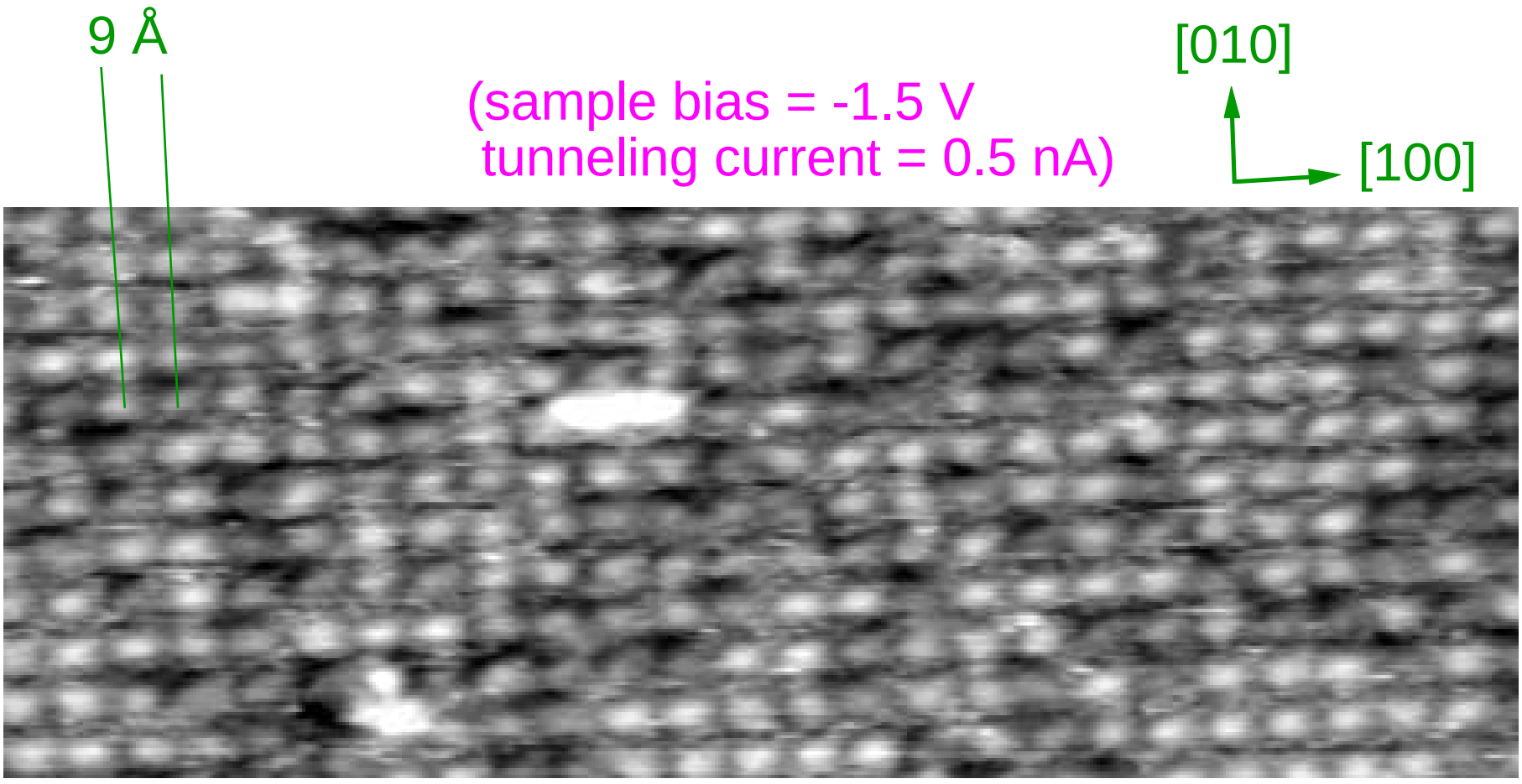
- Dramatic differences in the surface step density of $Fe_3O_4(001)$ can be achieved by using different MBE growth conditions, as seen in these scanning tunneling microscopy (STM) images.

- The resulting step densities (defined as the ratio of the number of atoms at a step edge to the total number in the surface) can vary from as high ~0.20 to lower than 0.05.

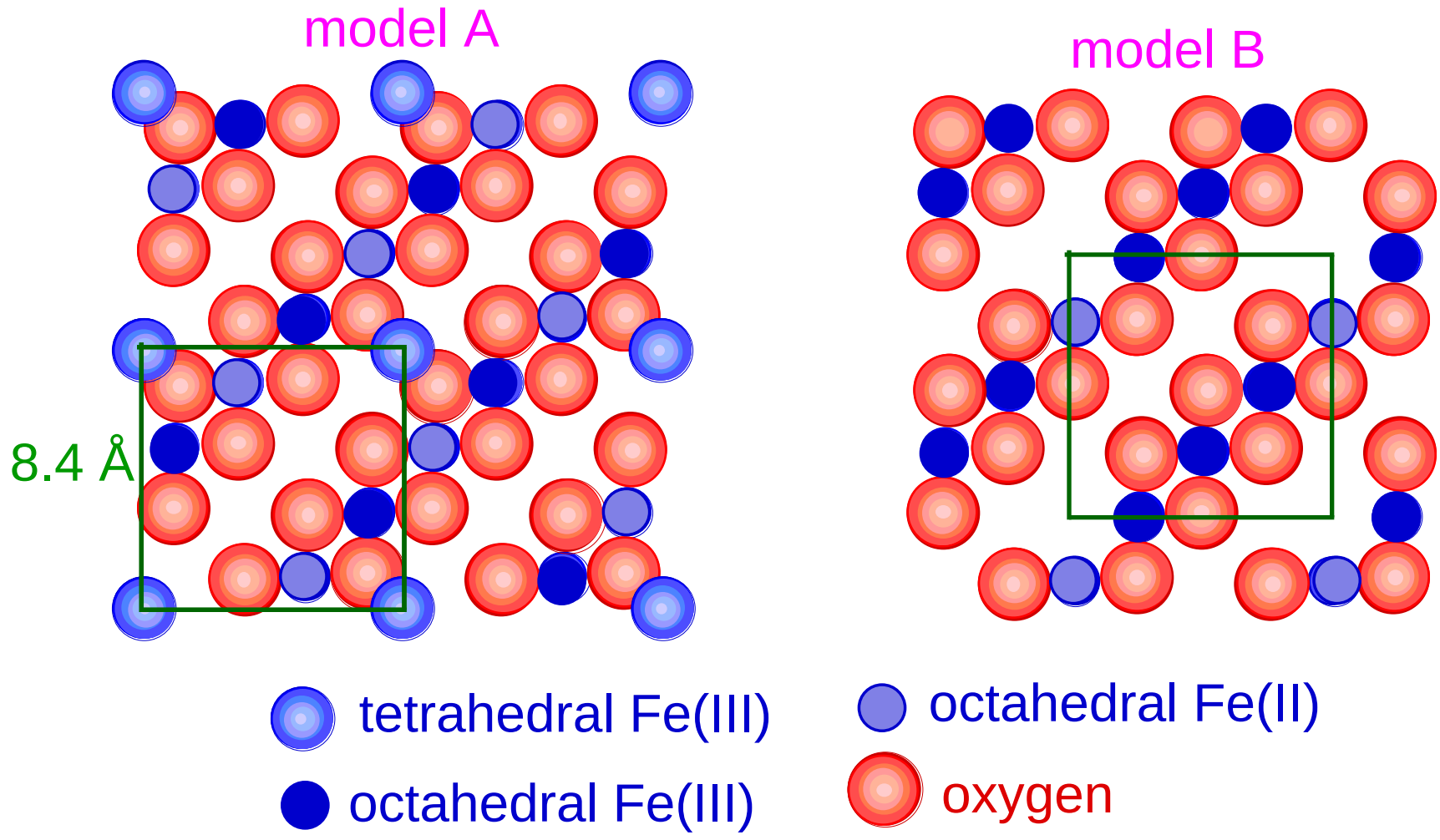
- The ability to systematically vary the step density is crucial to ultimately understanding the role of steps in the redox redox chemistry that occurs on magnetite surfaces.

- The line scan along [110] for the atomically smooth surface reveals single layer high steps of height 2.1Å, indicating that the surface is terminated with *either* a layer of tetrahedral Fe(III), *or* a layer of octahedral Fe(II) and Fe(III), but not both.

Atomically Resolved Image of $Fe_3O_4(001)$

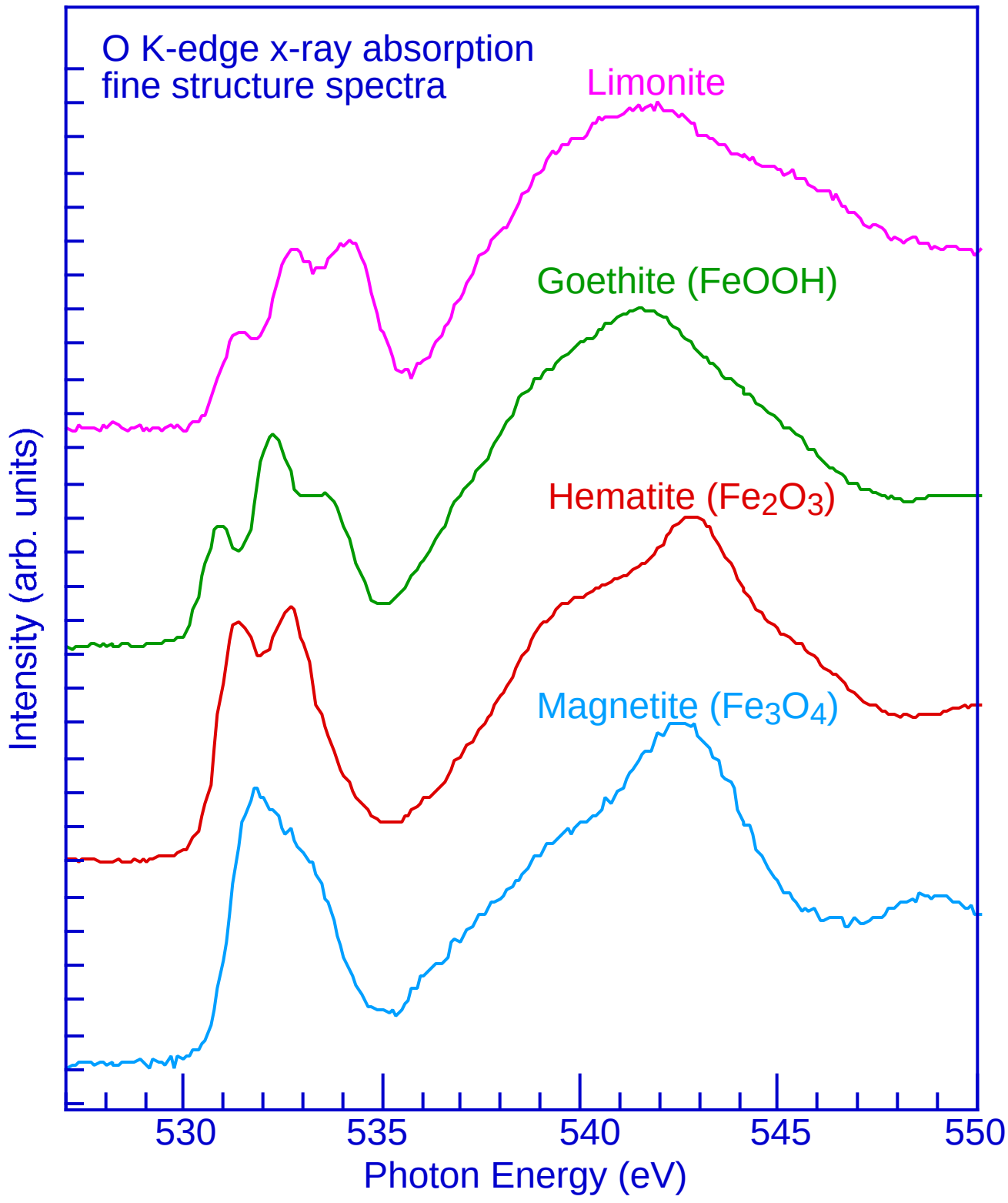


$Fe_3O_4(001)$-($\sqrt{2}$x$\sqrt{2}$)R45



•The reconstruction exhibited by this surface can be explained using formal charge principles which require that the net charge on the surface be zero. Two surface terminations of the correct symmetry satisfy zero formal charge: (i) one-half monolayer of tetrahedral iron (model A), and, (ii) an octahedral iron/oxygen layer with oxygen vacancies (model B). Atomically resolved STM images suggest model A, as seen above, but more work is needed and is in progress.

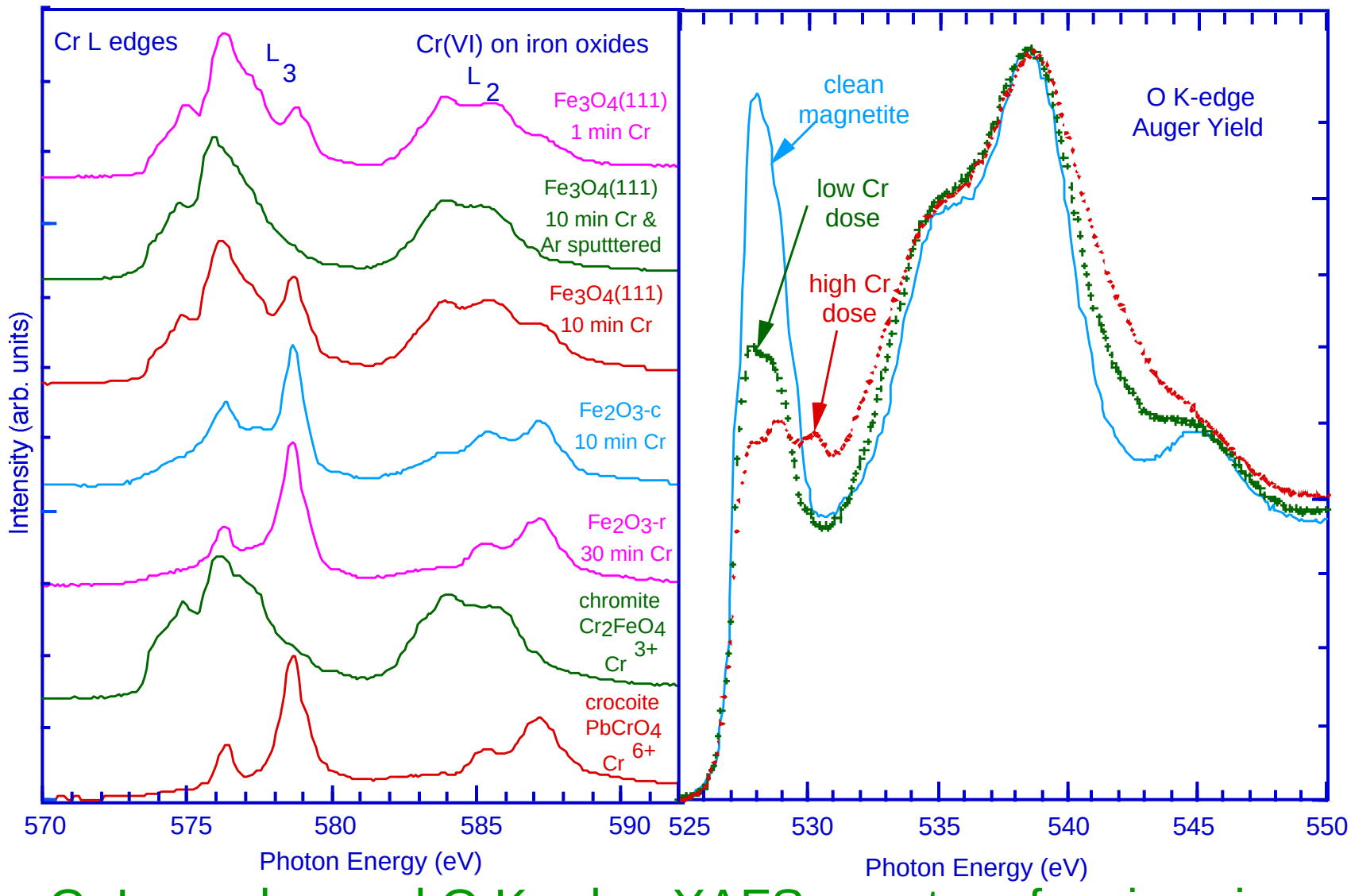
Determining the Iron Oxide Phases Present



- X-ray absorption fine structure (XAFS), done at the Stanford Synchrotron Radiation Laboratory on various bulk iron oxides and oxyhydroxides specimens, reveals unique spectral "fingerprints" for the different structural environments of oxygen.

- Using these reference spectra, we can determine how the surface changes as a result of exposure to aqueous chromate solution.

Redox Chemistry of Chromate with Iron Oxide Surfaces



•Cr $L_{2,3}$-edge and O K-edge XAFS spectra of various iron oxide surfaces exposed to chromate solution reveal the following:

1. Fully oxidized Fe_2O_3 surfaces, which contain no Fe(II), do not reduce chromate at all.

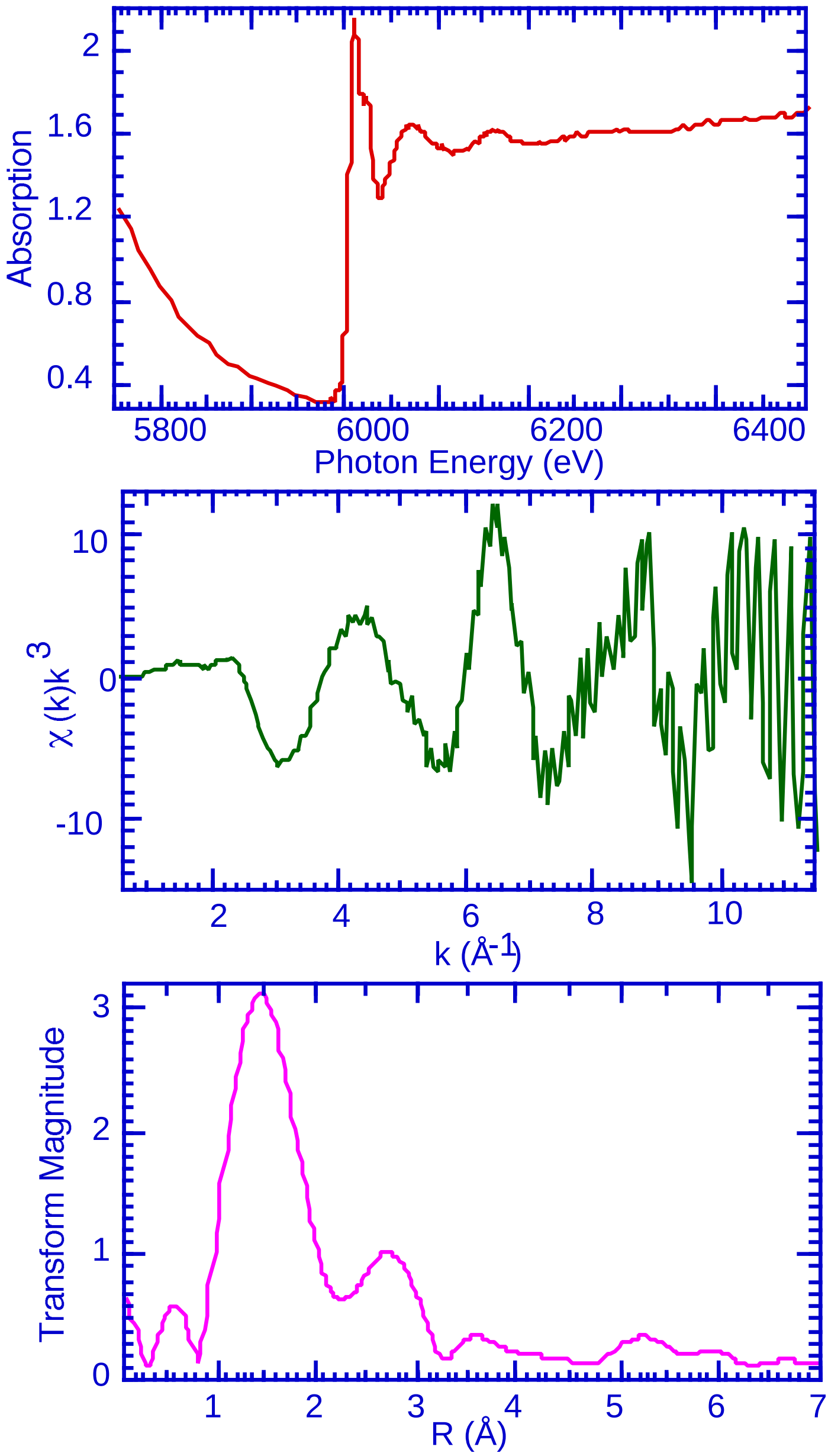
2. Fe_3O_4 surfaces, which contain both Fe(II) and Fe(III), reduce about 80% of Cr(VI) in sorbed chromate to Cr(III). The reaction is:

$$Fe_2^{+3}Fe^{+2}O_4 + Cr^{+6} \text{-->} Fe_2^{+3}O_3 + Cr^{+3}$$

3. Subsequent Ar ion sputtering of Fe_3O_4 surfaces exposed to chromate removes all Cr(VI), but leaves behind Cr(III).

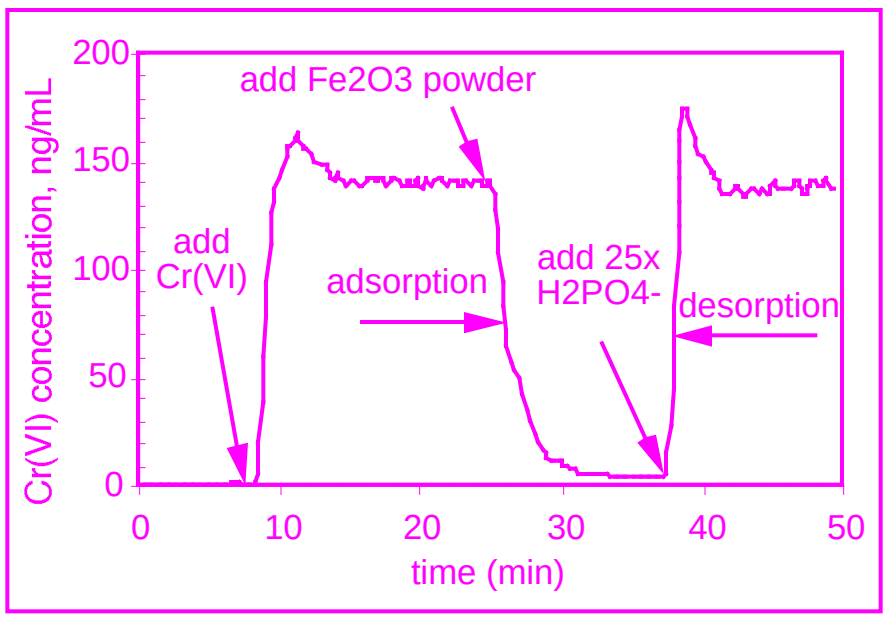
•An important implication of these results is that Cr(III) is expected to be more strongly sorbed than Cr(VI) on magnetite. Thus, once sorbed and reduced to Cr(III), chromate will be substantially immobilized.

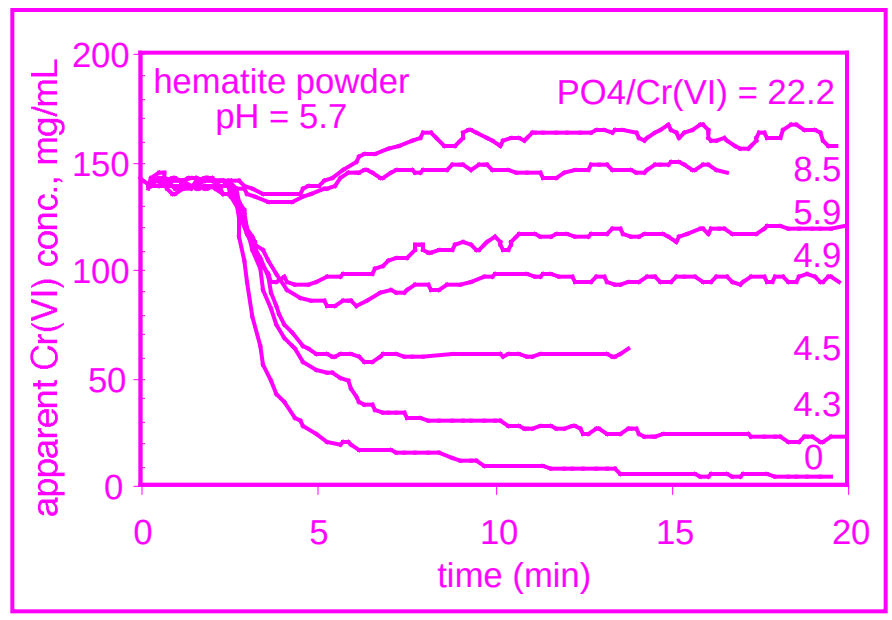
Redox Chemistry of Chromate with Iron Oxide Surfaces



•Grazing-incidence x-ray absorption fine structure (GI-XAFS) spectroscopy of the Cr L edge for chromate on intentionally-reduced α-Fe_2O_3(0001) reveals that near total reduction of Cr(VI) to Cr(III) occurs, similar to what occurs on Fe_3O_4(001).

Kinetics of Chromate Sorption on Iron Oxide Surfaces





•A powerful new tool, laser photoacoustic spectroscopy, has been developed for studies of aqueous adsorption and redox reactions at concentrations typical of environmental conditions. We have used the technique to:

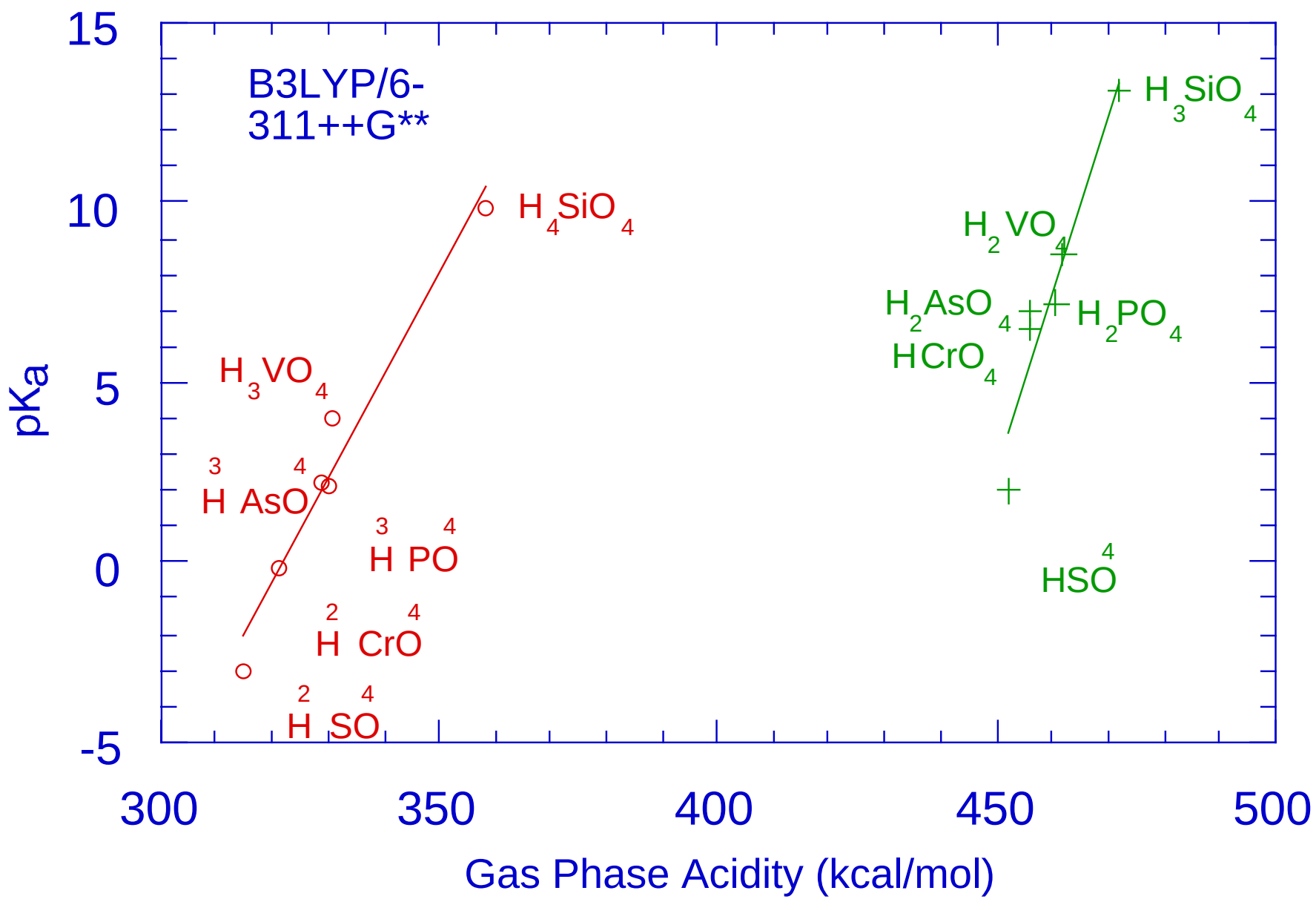
1. Monitor Cr(VI) concentrations *directly, nondestructively,* and at *environmnetally relevant levels.* The detection limit and dynamic range are 1 ppb and 1000, respectively..

2. Determine equilibrium adsorption constants for chromate and naturally occurring competitive oxyanions, such as phosphate, on powdered hematite surfaces. Results demonstrate preferential adsorption of phosphate and chromate on different surface sites in the low concentration regime. Site saturation of either anion leads to competition with the other anion for new adsorption sites.

3. Monitor rates of ion extraction from solution (onto the surface in question) in real time. Current time resolution is a few minutes, but refinements to the experimental apparatus should yield time resolution of a few seconds or faster.

•An important unresolved question -- If phosphate forms strongly-bound, inner-sphere bidentate complexes on a hematite surface and chromate forms a weakly-bound outer-sphere complex, why is so much more phosphate required to displace chromate?

Molecular Modeling of Chromate/ Iron Oxide Interactions



- We have developed a molecular mechanics model to predict the protonation/ deprotonation energetics of the adsorption of oxoacids on solvated Fe oxide surfaces with realistic proton stoichiometries.

- This model was tested against hydrated Fe(II)- Fe(III)- (Cr,P,Si)O_4-H_2O crystal structures with generally good results, yielding lattice constants within 5% of experiment.

- The ability of this model to account for both the structure and protonation energetics in the tetrahedral oxyanions is remarkable and makes the ionic model a feasible option for future investigation of surface complexation reactions using molecular dynamics techniques.

Conclusions

1. Magnetite reduces Cr(VI) in chromate (more toxic and bioavailable) to Cr(III) (less toxic and bioavailable), and Cr(III) is more strongly bound to the surface than chromate.

2. Reaction pathways for redox are not yet understood in detail. However, results suggest that chromate forms outer-sphere, weakly-bound surface complexes, whereas Cr(III) forms inner-sphere, strongly bound surface complexes.

3. Chromate reduction on magnetite is self-limiting due to the formation of an insulating (Fe,Cr) oxyhydroxide-like passivating layer 20-30Å thick.

4. Competitive adsorption between phosphate and chromate on hematite powder does not occur until phosphate concentrations are 4-5 times greater than chromate, suggesting distinct sites for which chromate adsorption is favored.

Future Activities

1. Determination of the effects of defects and organic and inorganic coatings on the reactivity of iron oxide surfaces.

2. Structure determination at hydrated iron oxide surfaces.

3. Effect of substitutional Cr and Al on iron oxide and oxyhydroxide surface redox chemistry.

4. Investigation of Cr(III) oxidation on model manganese oxide surfaces.

5. Determination of kinetics and competitive effects for aqueous reactions of chromate and other common anions (e.g., carbonate and sulfate) with powdered and MBE-grown iron-oxide surfaces.