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Quantitative Interpretation of X-ray Absorption Near Edge Structure

Continuation Progress Report for 1st year 9/15/98-9/14/99

DE-FG03-97ER45718/A000, P.I. John J. Rehr

Co P.I.'s: Dr. Simon Bare, UOP LLC; Dr. Joachim Stöhr, IBM-Almaden

I. Personnel Associated with this Grant

A. Prof. John J. Rehr (P.I.); Dr. Simon Bare, Dr. Joachim Stöhr (Co P.I.'s)

B. Dr. Alexei L. Ankudinov (Postdoctoral Research Associate)

C. Alexei Nesvizhskii (Graduate Research Assistant)

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II. Summary of Proposed Topics and Rationale for Research Project

We proposed to develop two industrial research collaborations, designated A and B below, which further develop and apply our new FEFF8 x-ray spectroscopy code to achieve a quantitative interpretation of x-ray absorption near edge structure (XANES) in materials of interest in energy research:

A) Quantitative interpretation of XANES for heterogeneous catalysts and disordered materials.

This work is carried out in collaboration with Dr. Simon Bare of the UOP LLC Research Center. The tools and extensions proposed include the generalization of FEFF for configurational averages, and tools for analyzing XANES including electronic structure such as densities of states, charge transfer, etc. These will be tested by the analyses of a number of materials of particular interest to UOP. Examples include Pt salts and bimetallic clusters, both on alumina. We also proposed studying similar catalysts using *in situ* XANES combined with FEFF calculations to better elucidate the role of Cl in these modified catalysts.

B) Quantitative interpretation of white-lines in XANES

This work is carried out in collaboration with Dr. Joachim Stöhr of IBM-Almaden Research. We proposed to develop a quantitative interpretation of the edge peaks known as "white lines" in XANES, particularly in transition metals and magnetic materials. A second goal of this collaboration is to achieve a quantitative treatment of the X-ray absorption "sum rules"

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III. Significant Results from the 1st Grant Year

A) The work of Dr. Ankudinov focused largely on Project A with UOP. Regular visits are an important part of the effort; the P.I. and the Postdoctoral Research Associated have each visited UOP during the first six months of the grant and further visits are planned. In accordance with our proposed research we have made efforts to improve preliminary versions of our FEFF8 code for XANES calculations and we have carried out applications of interest to our UOP collaborator. The significant advantage of FEFF8 over other XANES codes is that it simultaneously determines both XANES and electronic structure (i.e., local density of electron states or LDOS), thus permitting an interpretation of XANES in terms of electronic properties and charge transfer. A major accomplishment during this grant period was the successful automation of various subroutines to make the FEFF8 code faster, more robust and user friendly for industrial research. In particular the self-consistent potentials were automated using the Broyden algorithm and the Lorentzian broadening of calculated spectra was replaced by a more reliable complex energy plane integration. In addition an algorithm for configuration averages over the XAFS spectra, which is needed in this collaboration, was incorporated. Fortunately the spherical potential approximation used in FEFF8 usually works reasonably well, even in non-symmetric systems. Thus in general, the present FEFF8 code now leads to a good agreement between calculated XANES and experiment in a wide class of systems.

Several applications of FEFF8 were then initiated for systems of specific interest to UOP. To study the effects of Cl in the Pt XANES spectra, calculations of XANES for $(\text{NH}_4)_2\text{PtCl}_4$, $(\text{NH}_4)_2\text{PtCl}_6$ and K_2PtCl_6 crystals both for Pt L_3 and Cl K edge spectra. Remarkably the FEFF8 calculations are in good agreement with the observed experimental XANES for these systems [Fig. 1]. More importantly, the analysis of calculated XANES in terms of LDOS allowed us to interpret the small peak next to the white line in the Pt L_3 spectra as directly due to the presence of Cl, since the peak is found to be coincident with the unoccupied 3d DOS of Cl.

Fig 1. Calculations for $(\text{NH}_4)_2 \text{PtCl}_4$ with (dashes) and without (short dashes) d states on Cl vs experiment (solid) and the dDOS of Cl (dots). This clearly demonstrates that the origin of the second peak in XANES is due to unoccupied d states of Cl.

This finding may turn out to be of great importance for catalyst investigations, since the size of the peak provides a direct way of monitoring the amount of Cl attached to Pt during chemical reactions with XANES. We plan to publish these results in a joint paper [A.I. Ankudinov, S. R. Bare, and J. J. Rehr, (in preparation)].

The determination of catalyst cluster size using XANES is also of practical interest to UOP. An analysis of this problem with FEFF8 improves on earlier studies, (e.g., using the FEFF7 code), since the self-consistent potentials generally give much more quantitative XANES calculations. In a preliminary attempt to analyze the effects of cluster size we made several simulations for Pt clusters of various shapes and sizes and noted significant changes

in XANES vs configuration. These results are highly encouraging, and we are confident that such simulations can be used to correlate Pt cluster shape and size distributions with features in XANES experiment. We expect this investigation also to lead to a joint paper. In summary, our calculations to date have already proved to be important for catalysis applications at UOP, and we plan to submit at least two joint papers with our UOP collaborators by September 1999.

B) The work in our collaboration with IBM-Almaden has initially focused on quantifying the relation between white lines and the d-hole count in 3d transition metals. It is well known that the intensity of the white line of $L_{3,2}$ edges in XANES of 3d transition metals is correlated with the number of unoccupied d states. This relation has been extensively used by experimentalists for studying charge transfer in catalysis and in XMCD in transition metals and alloy systems. However, the accuracy of this correlation is limited because the actual number of d-holes is not known accurately and because of ambiguities in the subtraction of the background intensity, many-body effects, etc. Therefore, it is important to establish a more direct and reliable way of determining the hole count from XANES. To this end we have developed a quantitative procedure based on the new self-consistent FEFF8 code. The method is based on the formal similarity between the absorption coefficient $\mu(E)$ and the projected density of states $\rho(E)$

$$\mu(E) = \mu_0(E)[1 + \chi'(E)]; \quad \rho(E) = \rho_0(E)[1 + \chi(E)].$$

where $\chi(E)$ is the fine structure. In other words if $\chi \approx \chi'$, $\rho \propto \mu$, i.e., the XANES is proportional to the unfilled dDOS. Therefore, an experimental estimate for the density of unoccupied states (holes) ρ_{expt} can be obtained from XANES, simply by multiplying the absorption coefficient by the smoothly varying ratio $\rho_0(E)/\mu_0(E)$, i.e., $\rho_{\text{expt}}(E) \approx [\rho_0(E)/\mu_0(E)]\mu(E)$. Although χ and χ' differ slightly due to self-energy corrections, we find that it is a good approximation to neglect this difference. The result is illustrated in Fig. 2. Note that the unfilled d DOS from experiment (dots) closely agrees with d DOS from theory (short dashes).

Fig. 2. Experimental L₃ XANES of Cu (solid); theoretical ratio of dDOS/XANES (long dashes); theoretical dDOS from FEFF8 (short dashes), and the theoretical estimate of unfilled dDOS (dots) obtained from the experimental XANES.

III. Plans for the 2nd Year

A) UOP Collaboration

One of our priorities in the 2nd year is to further improve the FEFF8 code as necessary for this collaboration. In particular we aim to improve the potentials used in the FEFF8 code, adding corrections that go beyond the spherical approximation. Such non-spherical corrections may be important in cases where the structure around an atom is highly anisotropic, such as molecules or catalysts in which some atoms are located on surfaces. Our proposed approach is based on overlapping, non-spherical potentials, as discussed in a recently submitted preprint, "Multiple Scattering Theory for Overlapping

Potentials," by A. L. Ankudinov, submitted to J. Math Phys (February 1999). We believe that a full potential development of FEFF8 based on such an extension may be necessary to achieve a fully quantitative interpretation of XANES, which is important to both of our industrial collaborators. The next phases of the UW-UOP collaboration will focus on two applications:

- (1) Understanding the sensitivity of the Pt L_3 and L_2 edge XANES to Pt cluster size and morphology. The size and shape of supported metal clusters determines their catalytic activity. We hope to understand the fundamental parameters that affect the Pt XANES as the cluster size and shape are varied. This work will involve a careful study of the various ways of implementing configurational averages in XANES. In addition we plan to use FEFF to study the effect of adsorbed hydrogen on the Pt XANES of these clusters, as there have been conflicting reports in the literature on the interpretation of this effect. Improved potentials will likely be necessary to draw definitive conclusions in this case.
- (2) Using FEFF to calculate the Pt L_3 and L_2 edge XANES of bimetallic clusters. In many catalytic processes the reactivity of Pt has to be attenuated in some way, and this is often accomplished industrially by alloying with a second element, e.g. Sn or Re. We plan to combine experimental XANES data with FEFF calculations to develop an in-depth fundamental understanding of the modification of Pt with other metals in supported catalysts.

B) IBM Collaboration

We now plan to apply a similar procedure to that developed for relating the DOS to the XANES, to check the validity of different sum rules derived for XAS and XMCD. In particular, we propose to check procedures for evaluating the sum rules in systems simulated with FEFF8 and its generalizations. The sum rules connect the integrated intensity of the absorption spectra with the orbital and spin moments, thus providing a practical and unique way for studying magnetic properties of transition- and rare-earth-metal systems. However, these sum rules were obtained theoretically for very simple model systems, and many important questions on their practical applicability remain unresolved. These sum rules can now be directly tested by simulations on more realistic systems with FEFF8.

CURRENT AND PENDING SUPPORT-JOHN J. REHR, PI

A. Current Support

1. Spin-Dependent X-ray Spectroscopy Theory
 - a. Supporting Agency: Department of Energy
 - b. Amount: \$184,995
 - c. Period covered: Nov 15, 1996 - Nov 14, 1999
 - d. Percentage of effort: 30% academic year,* 100% two summer months
 - e. Location of research: Univ. of Washington
2. XAFS Simulations in Biological Systems
 - a. Supporting Agency: National Institutes of Health (Subcontract from SSRL NIH Biotechnology Resource)
 - b. Amount: \$201,330 (\$14,200 in 1999-2000)
 - c. Period covered: Mar 1, 1995 - Feb 28, 2000
 - d. Percentage of effort: 30% academic year,* 100% one summer month
 - e. Location of research: Univ. of Washington
3. University-Industry Grant: Quantitative Interpretation of XANES
(Collaboration between U. Washington, UOP LLC, and IBM-Almaden)
 - a. Supporting Agency: Department of Energy
 - b. Amount: \$276,000
 - c. Period covered: Sep 15, 1998 - Sep 14, 2001
 - d. Percentage of effort: 30% academic year,* 100% one summer month
 - e. Location of research: Univ. of Washington

B. Pending Support: None

C. Transfer of Support: None

D. Other agencies this proposal submitted to: None

* Note: Because of partial overlap of the activities of these grants, the net percentage of effort will not exceed 50% during the academic year and 100% during the summer.

Year 2: 9/1/99 - 8/31/2000

ORGANIZATION University of Washington				Budget Page No: Year 2 of 3	
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR John J. Rehr, P.I.				Requested Duration: 36 (Months)	
A. SENIOR PERSONNEL: P/PI, Co-PIs, Faculty and Other Senior Associates (List each separately with title; A.6. show number in brackets)			DOE Funded Person-mos.		Funds Requested by Applicant
			CAL	ACAD	SUMR
1.					
2.					
3.					
4.					
5.					
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)					
7. () TOTAL SENIOR PERSONNEL (1-6)					
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (1) POST DOCTORAL ASSOCIATES (4 months on UOP)			8.00		\$30,476
2. () OTHER PROFESSIONAL (TECHNICIAN, PROGRAMMER, ETC.)					
3. (1) GRADUATE STUDENTS 11 MOS. AT \$1362					\$14,982
4. () UNDERGRADUATE STUDENTS					
5. () SECRETARIAL - CLERICAL					
6. () OTHER					
TOTAL SALARIES AND WAGES (A+B)					\$45,458
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 21% Post-Doc, 8% Grad Student					\$7,599
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)					\$53,057
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM.)					
TOTAL PERMANENT EQUIPMENT					
E. TRAVEL			1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)		\$646
			2. FOREIGN		
TOTAL TRAVEL					\$646
F. TRAINEE/PARTICIPANT COSTS					
1. STIPENDS (Itemize levels, types + totals on budget justification page)					
2. TUITION & FEES					
3. TRAINEE TRAVEL					
4. OTHER (fully explain on justification page)					
TOTAL PARTICIPANTS () TOTAL COST					
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES					
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION					\$1,000
3. CONSULTANT SERVICES					
4. COMPUTER (ADPE) SERVICES					\$655
5. SUBCONTRACTS					
6. OTHER Mail, Long Distance, Copying (\$500) and Tuition (\$7,097)					\$7,597
TOTAL OTHER DIRECT COSTS					\$9,252
H. TOTAL DIRECT COSTS (A THROUGH G)					\$62,955
I. INDIRECT COSTS (SPECIFY RATE AND BASE) 52% of \$55,858 (Tuition Exempt)					
TOTAL INDIRECT COSTS					\$29,046
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)					\$92,001
K. AMOUNT OF ANY REQUIRED COST SHARING FROM NON-FEDERAL SOURCES					
L. TOTAL COST OF PROJECT (J+K)					\$92,001

2 March, 1999

Dr. Manfred Leiser
Division of Materials Sciences, ER-132
Office of Basic Energy Sciences
Department of Energy
Germantown, MD 20874-1290

DOE University-Industry Collaboration
"Quantitative Theory and Interpretation of X-ray Absorption Near Edge
Structure"
DOE Grant DE-FG03-98ER45718/A000

Dear Dr. Leiser:

This letter is in support of renewed funding from DOE for the titled project in the collaboration between Prof. John J. Rehr (University of Washington) and Dr. Simon R. Bare (UOP LLC). I am strongly encouraged, and excited, by the initial results from the collaboration and I look forward to continued progress over the next funding year. The data generated through this collaboration will have a significant impact on our understanding of the local structure of supported heterogeneous catalysts and this, together with reactivity data on these same materials, will allow us to understand structure-activity relationships.

The combination of theory and experiment provides a unique and powerful insight into the molecular level structure of supported Pt catalysts under reaction conditions. I know of no other method to obtain this level of detail and understanding of these catalysts. I believe that the only way to make a significant breakthrough in this area of catalysis, which has been well-studied, is to truly understand the fundamentals of the catalyst preparation and activation. The data generated from this collaboration will provide us with this fundamental knowledge.

Dr. Alexei Ankudinov, the talented postdoctoral associate working with Prof. Rehr has had an extremely positive impact on the project. His previous familiarity with the problem has meant that he was able to "hit the ground running", and is proving to be most productive. He has already visited UOP for two days, and will be visiting again in the next couple of weeks. The close collaboration between Dr. Ankudinov, Prof. Rehr and myself has contributed to the early successes of this research.

The initial problem we are addressing is to determine if the new self-consistent FEFF8 code can be used to provide insight in to the local structure of supported platinum catalysts, a major class of heterogeneous catalysts used industrially in many different

hydrocarbon processing reactions. The goal is to understand the near edge structure at the Pt L₃-edge and Cl K-edge of such catalysts. We have observed that in catalysts prepared from chloroplatinic acid a small but obvious feature was present in the Pt L₃-edge XANES spectrum at ~15 eV above the main absorption edge. This feature diminishes and finally disappears as the catalyst is heated in hydrogen causing decomposition and reduction of the Pt-Cl complex on the alumina surface. The FEFF8 calculations have demonstrated that this resonance is indeed due unequivocally to the presence of a chlorine atom at a bonding distance away from the Pt. This is critical information as we now have a tool to use to determine under reaction conditions (XANES is a photon-in/photon-out spectroscopy, so can be used in situ) whether there is indeed chlorine directly bonded to the Pt particles. The new self-consistent FEFF8 code is also being used to calculate the XANES spectrum at the chlorine K-edge of several Pt-Cl complexes, and the initial results are very encouraging. At the Cl K-edge there is an intense pre-edge peak present if the Cl is bonded to an open d-shell transition metal. We hope to use the intensity and position of this peak as a measure of the strength of the Pt-Cl interaction, in addition to learning something about the local geometry of the Pt-Cl complex.

The next phases of the collaboration will focus on the sensitivity of the Pt L₃ and L₂-edge XANES to Pt cluster size and morphology and on the XANES of bimetallic clusters, as described in more detail in the Renewal request. We plan to combine experimental XANES data with new self-consistent FEFF8 code calculations to develop an in-depth fundamental understanding of the modification of Pt with other metals in supported catalysts.

In conclusion, I am fully supportive of this enabling research work. UOP will continue to provide partial funding for the project for 1999. UOP will not only use the knowledge gained to increase our understanding of proprietary processes, but also to enhance our recognition by publishing the results in peer-reviewed journals.

Sincerely,

A handwritten signature in black ink, appearing to read 'Simon R. Bare', with a long horizontal flourish extending to the right.

Simon R. Bare, Ph.D.
R&D Associate
E-mail: srbare@uop.com