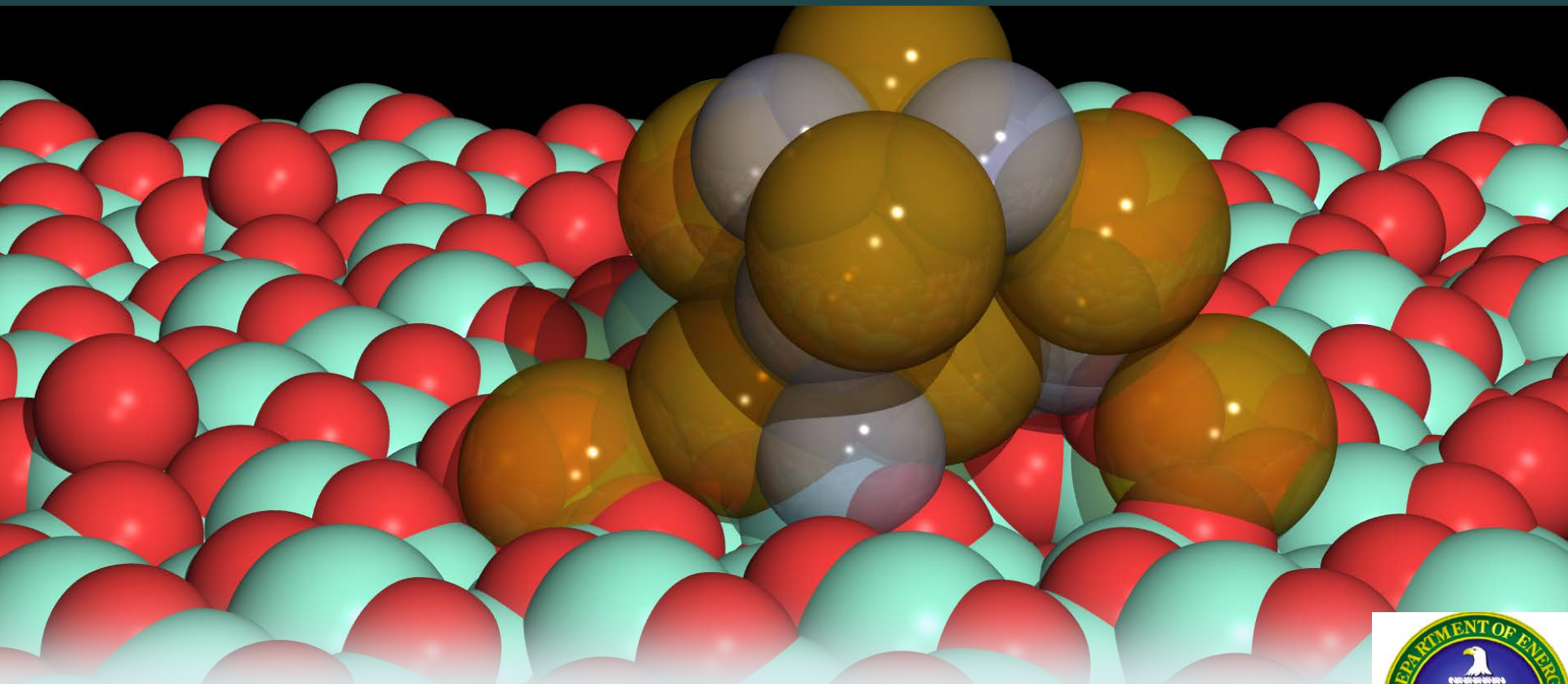
REU Seminar University of Washington 27 July, 2015

Theory, Interpretation and Applications of X-ray Spectra*

J. J. Rehr et al.



UNIVERSITY OF WASHINGTON

A theoretical horror story

Starring

Fernando Vila
&
Anatoly Frenkel

with

J. Kas, S. Bare & S. Kelly

Directed by J. J. Rehr

a Sequel

Part I: Application

Operando theory of nanocatalysts:

Structure, thermal properties, catalytic activity

Pt Clusters on γ-Al_2O_3

Theoretical Challenge: Anomalous properties* of $Pt_{10}/\gamma Al_2O_3$

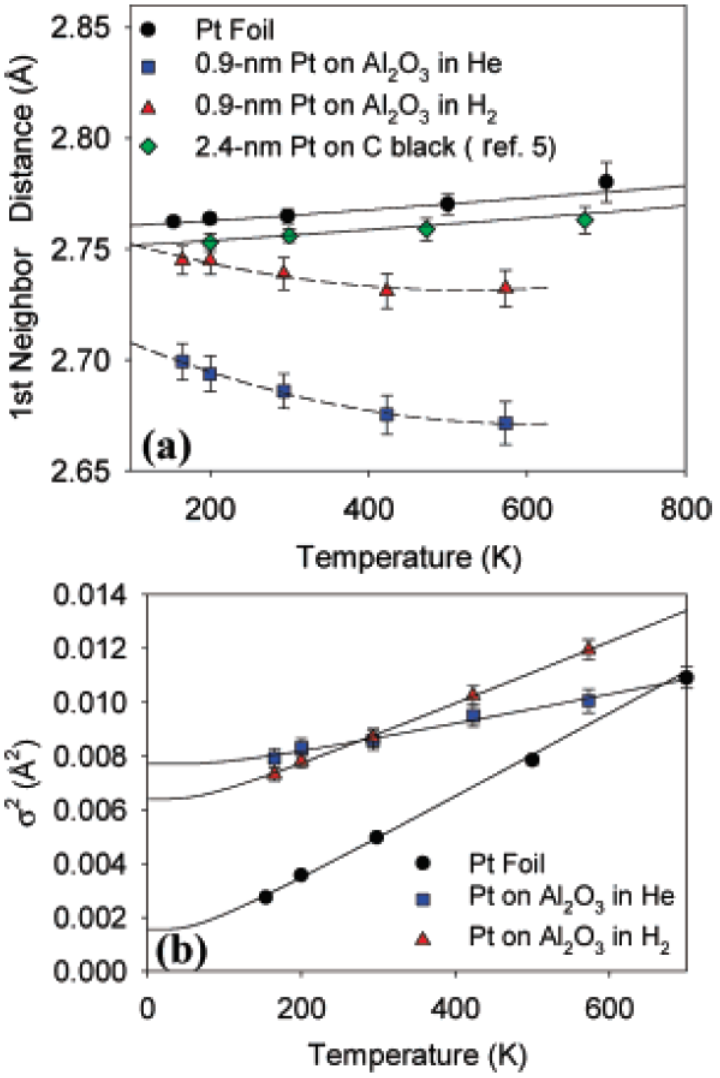
- Pt-Pt nn

  Negative Thermal Expansion

  & Bond expansion in H_2

- Anomalous Pt-Pt disorder

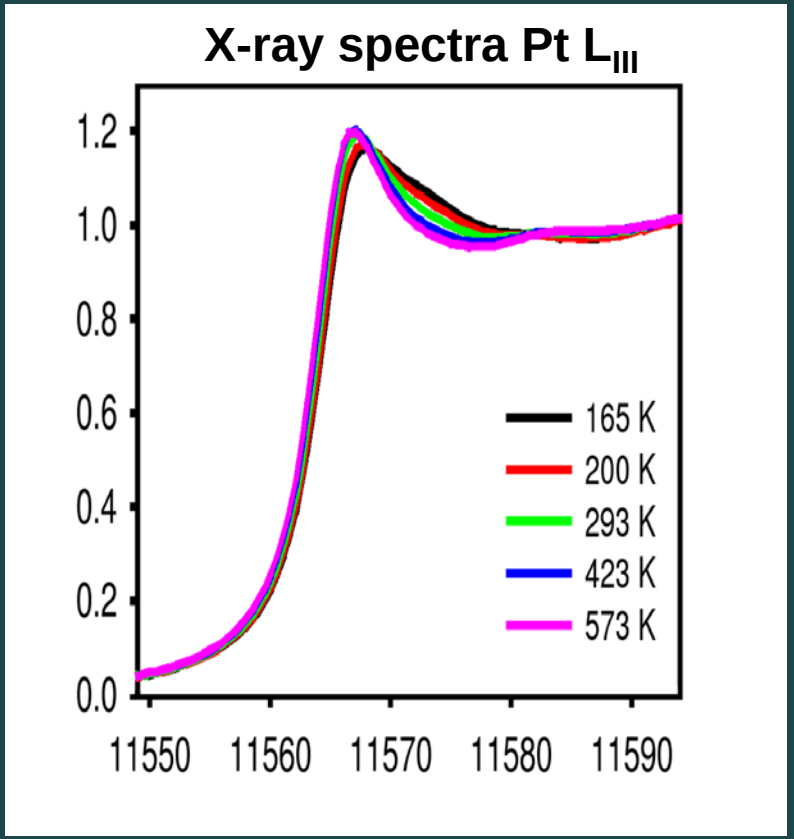
NOT bulk-like !



*J.H. Kang, L. D. Menard, R. G. Nuzzo, and A. I. Frenkel. JACS 2006, *128*, 12068

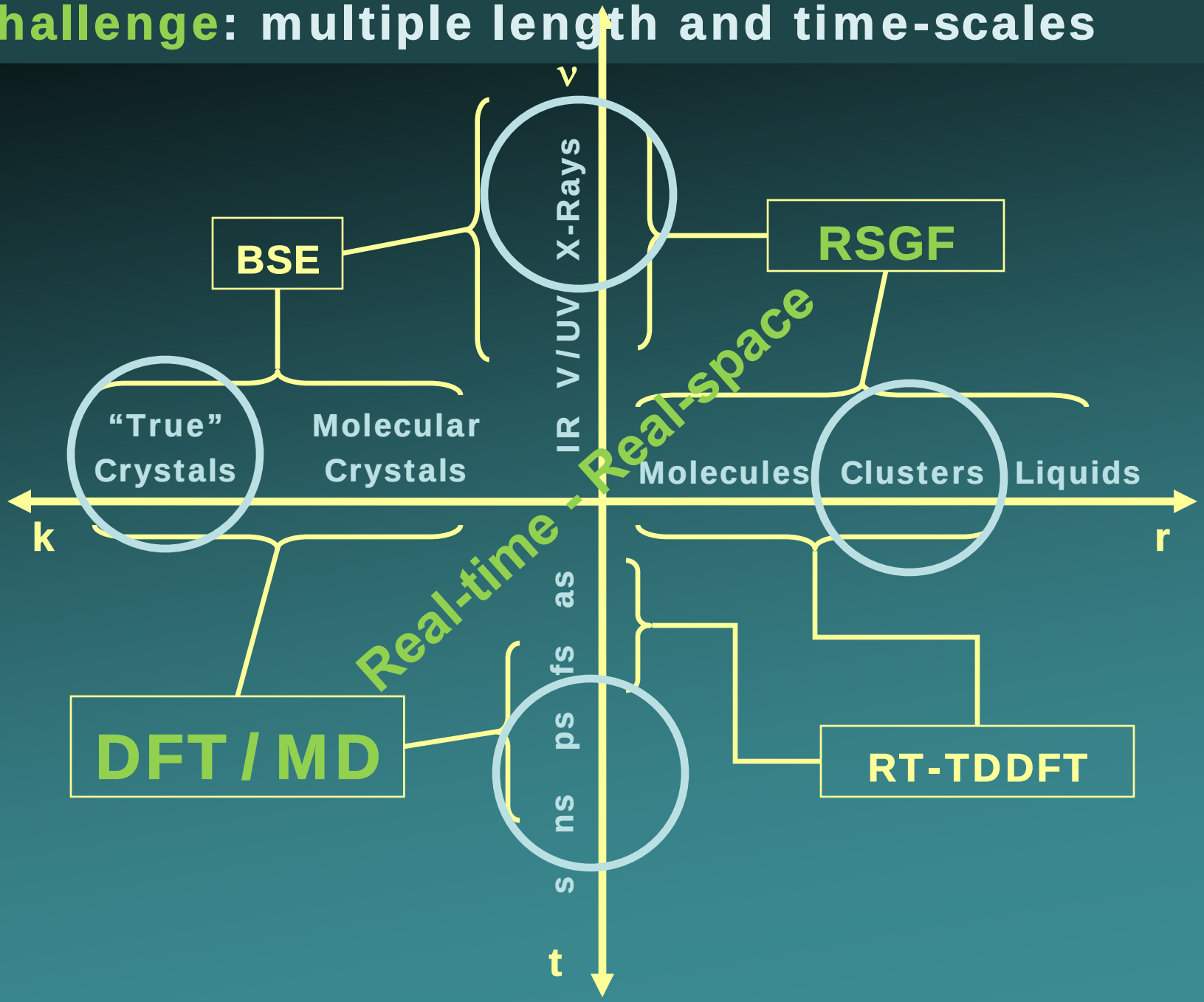
More Anomalous properties* $Pt_{10}/\gamma Al_2O_3$

- Increased edge intensity
- Redshift of XANES with increasing T
- **Standard analysis fails!**



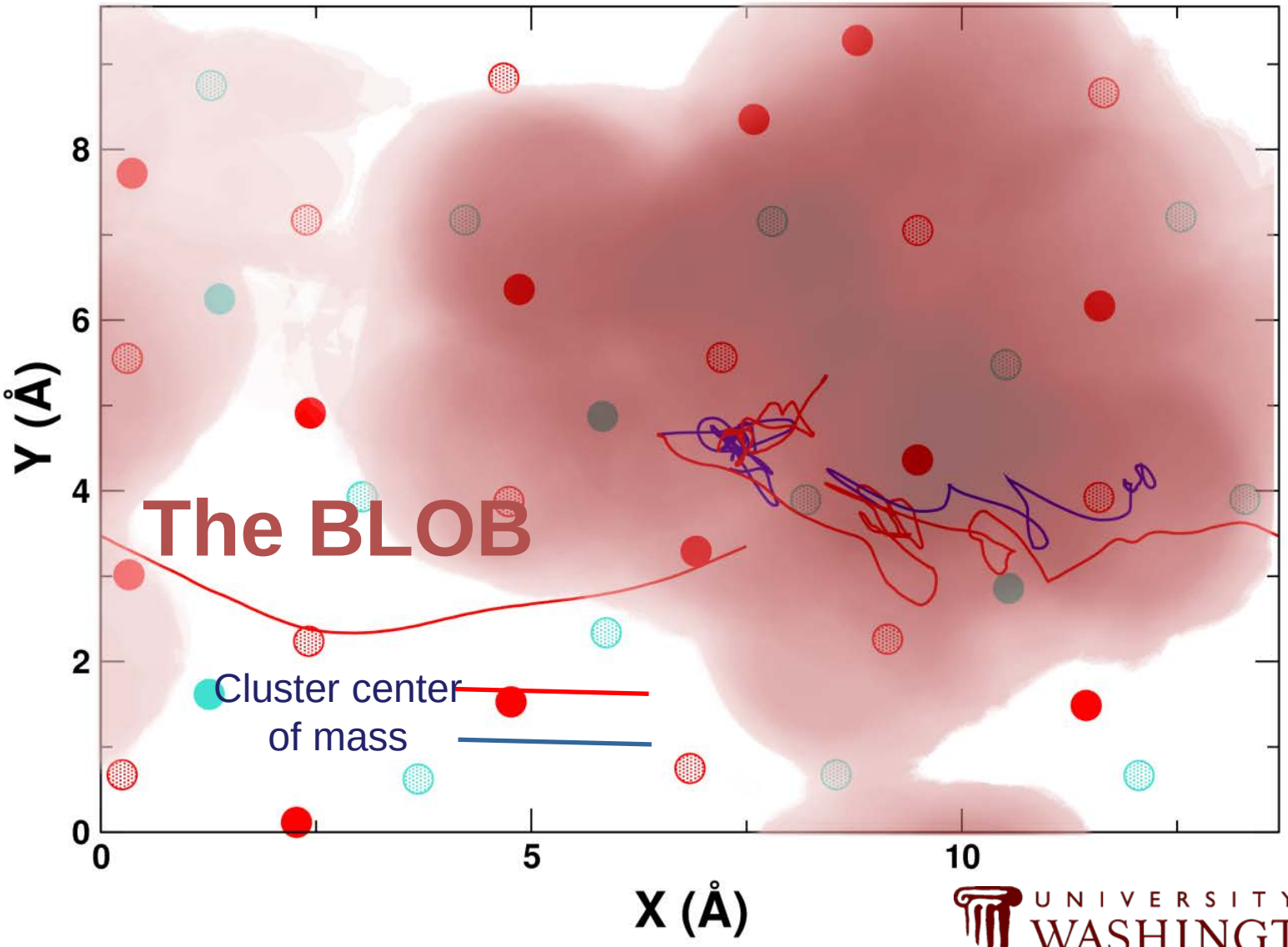
*J.H. Kang, L. D. Menard, R. G. Nuzzo, and A. I. Frenkel. JACS 2006, *128*, 12068

Challenge: multiple length and time-scales



What's going on?

Blob footprint @ 573 K



UNIVERSITY OF WASHINGTON

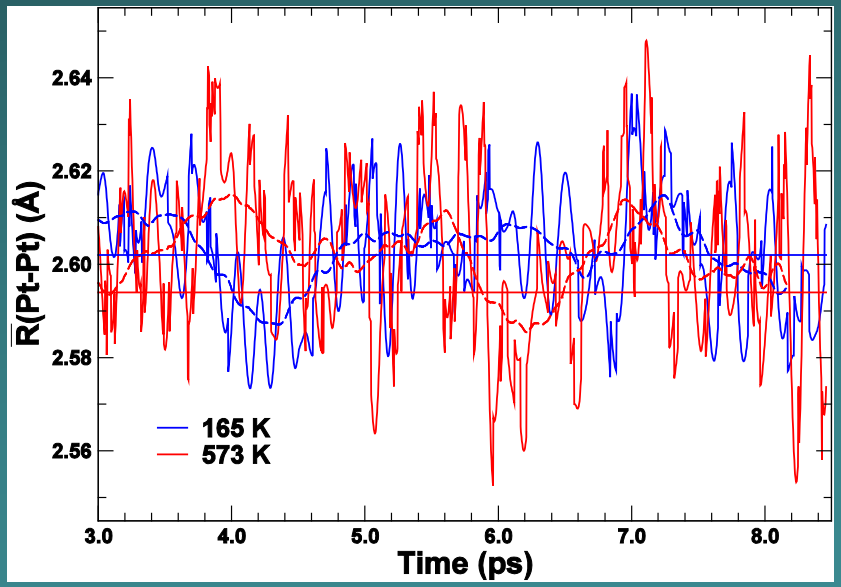
PHYSICAL REVIEW B 78, 121404(R) (2008)

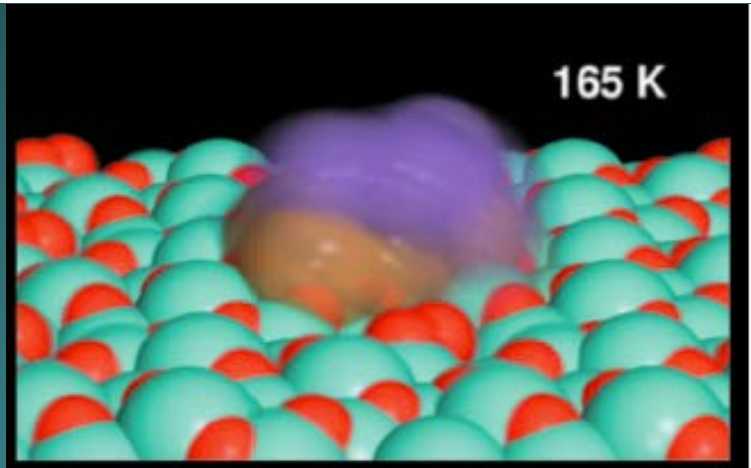
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

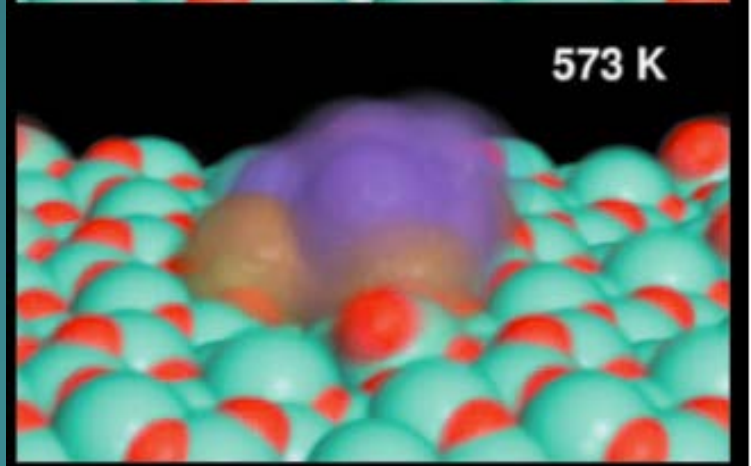
F. Vila,[1] J. J. Rehr,[1,*] J. Kas,[1] R. G. Nuzzo,[2] and A. I. Frenkel[3]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[3]*Department of Physics, Yeshiva University, New York, New York 10016, USA*
(Received 24 July 2008; published 11 September 2008)

Fuzzy "structure"

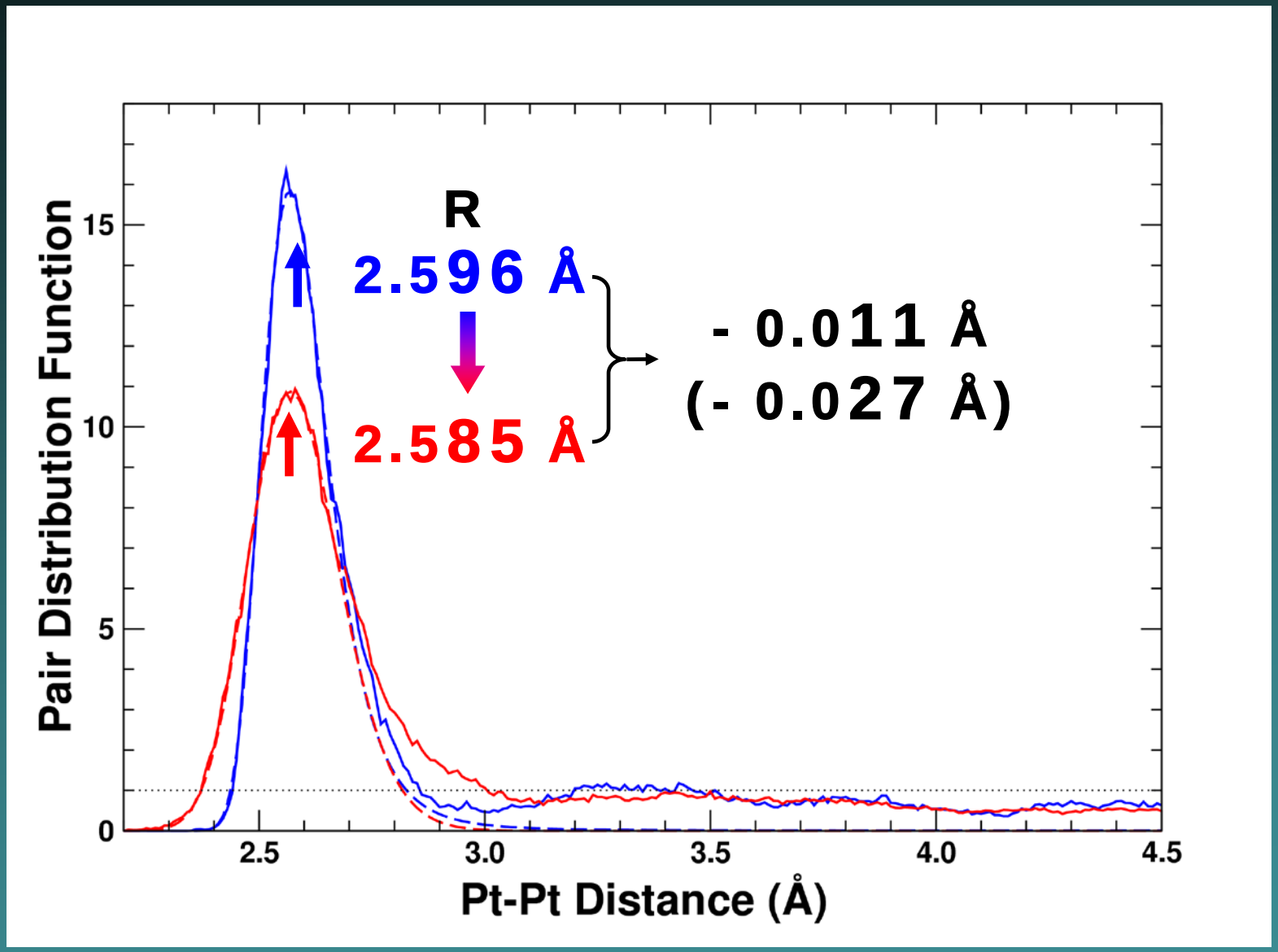
DFT/MD nn distance



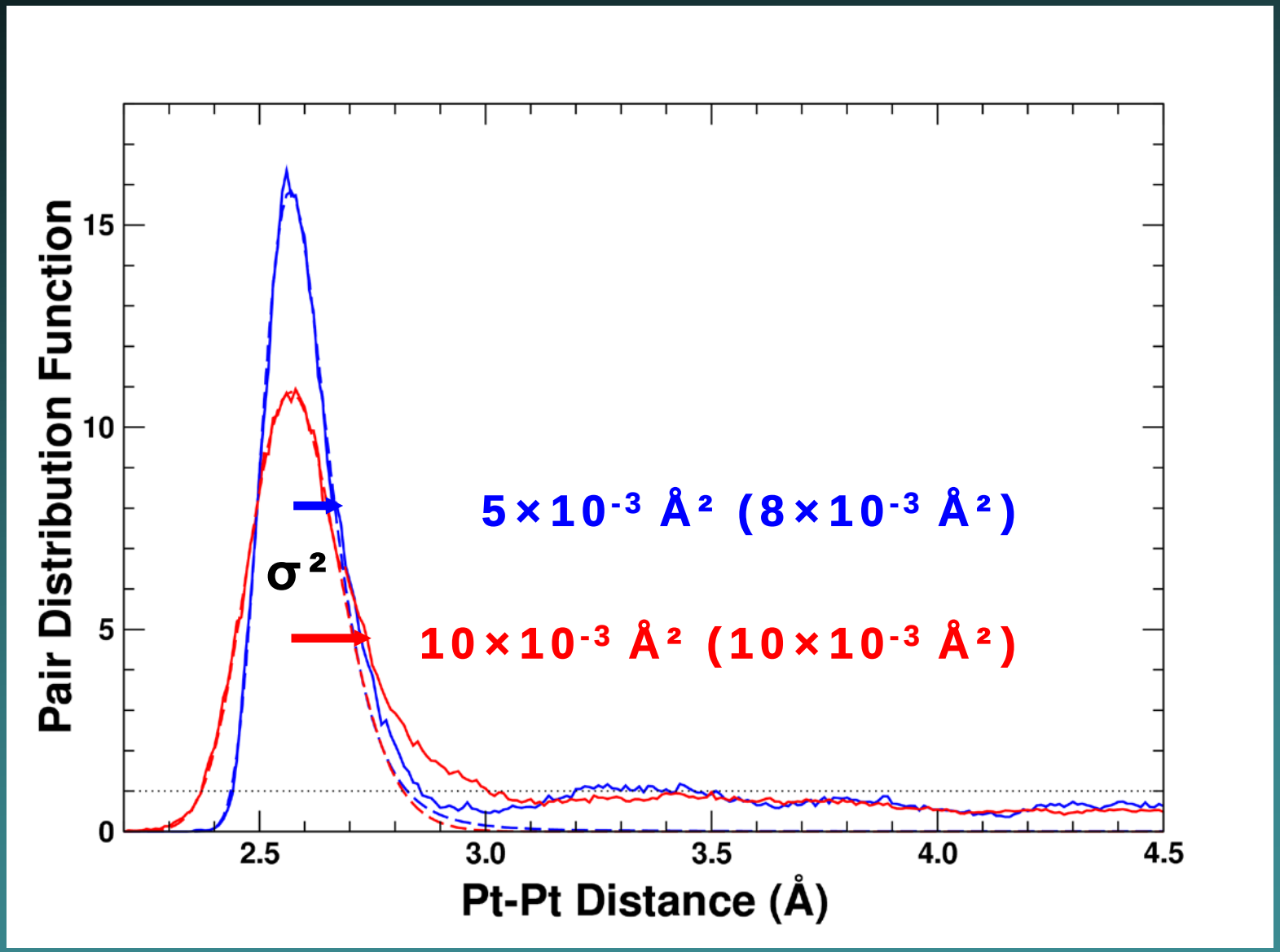




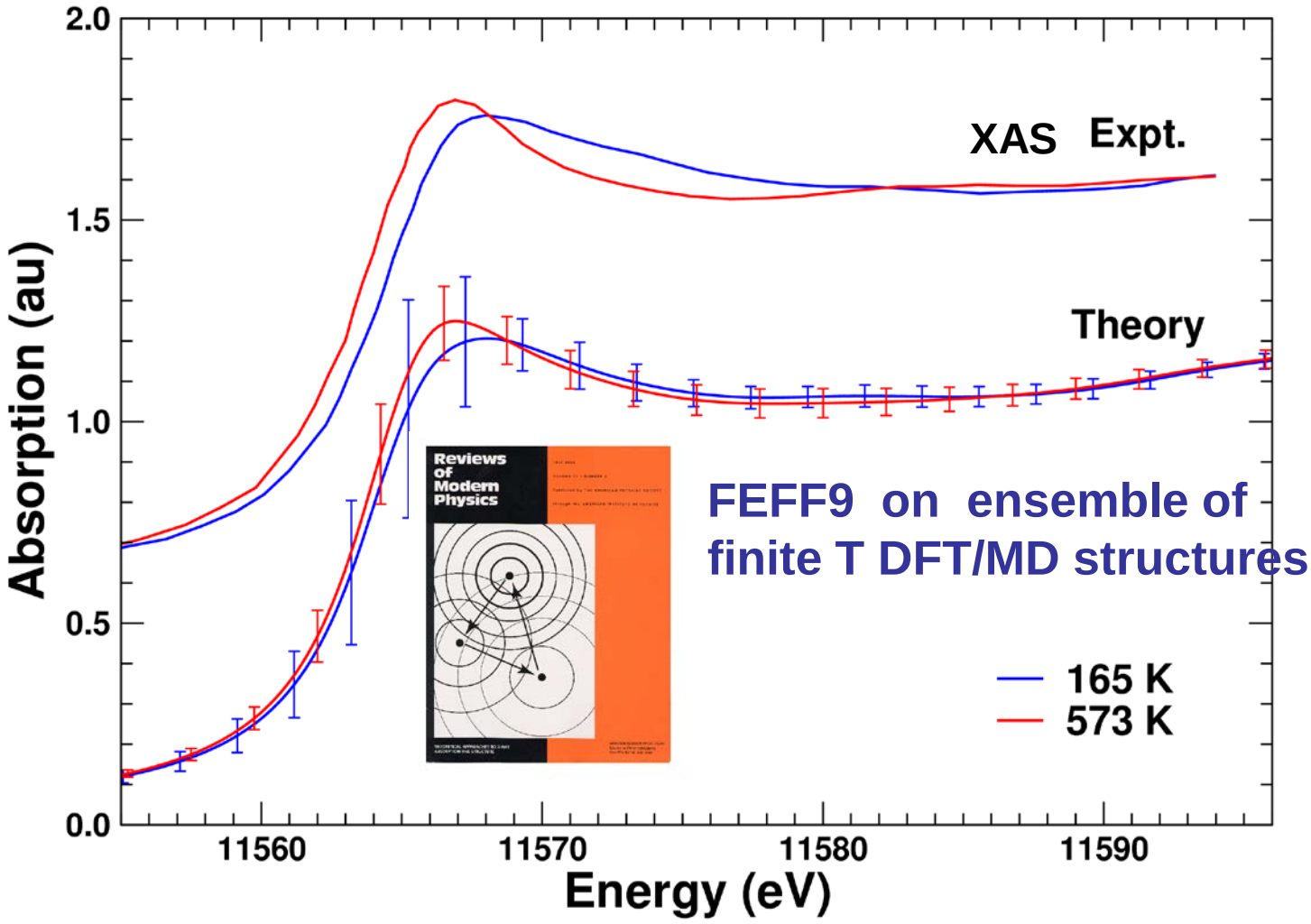
Negative Thermal Expansion Explained



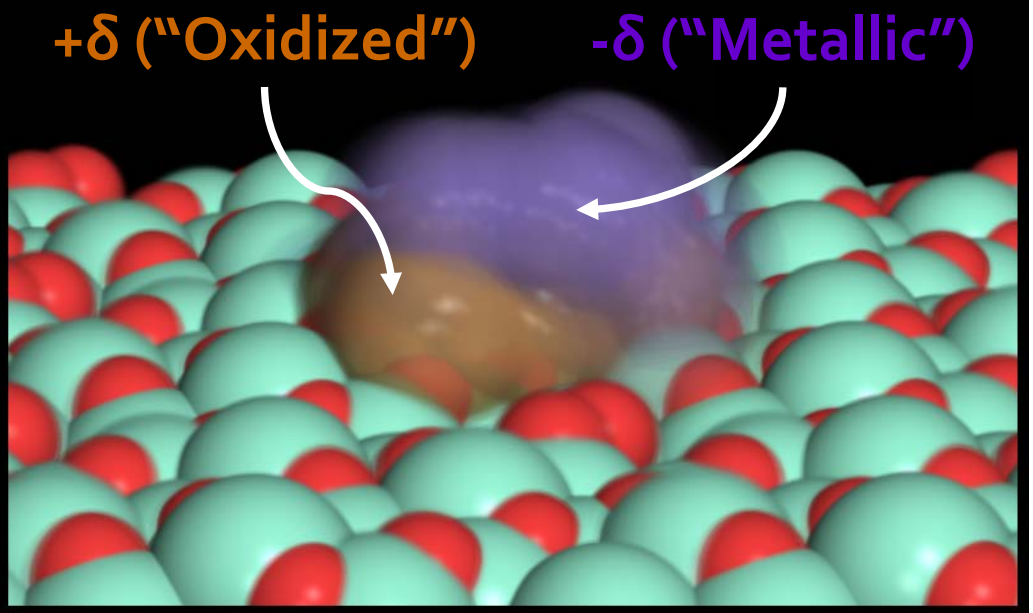
High Pt-Pt Disorder Explained



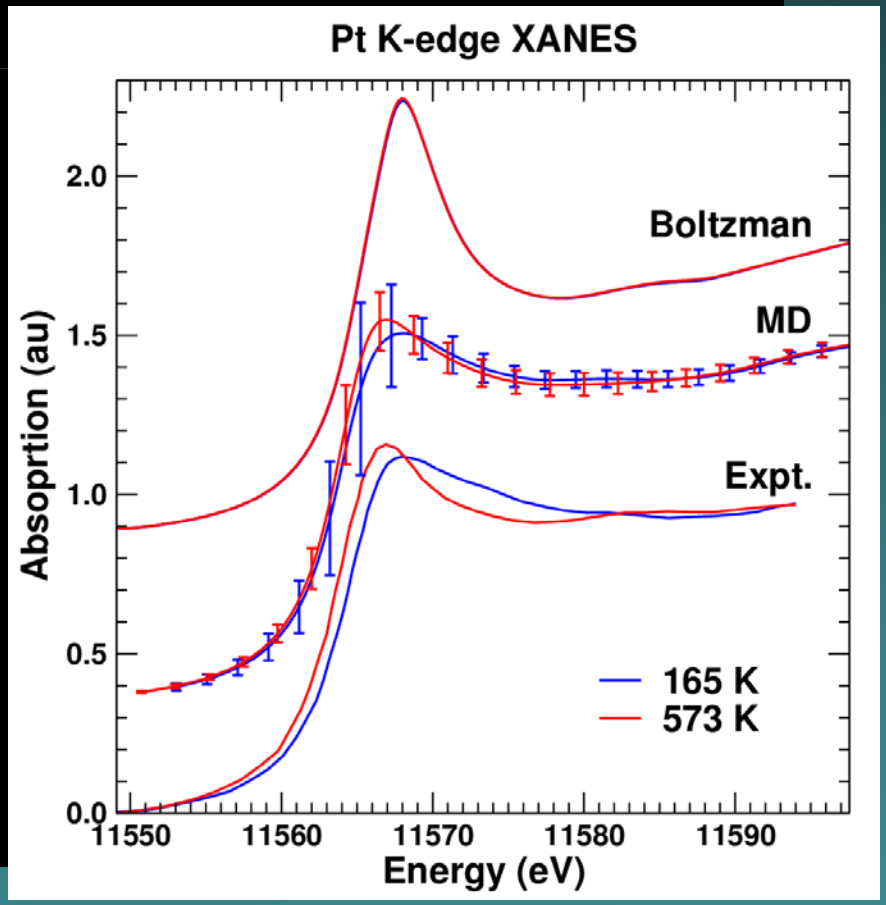
Increased intensity and redshift explained



Dynamic structural disorder

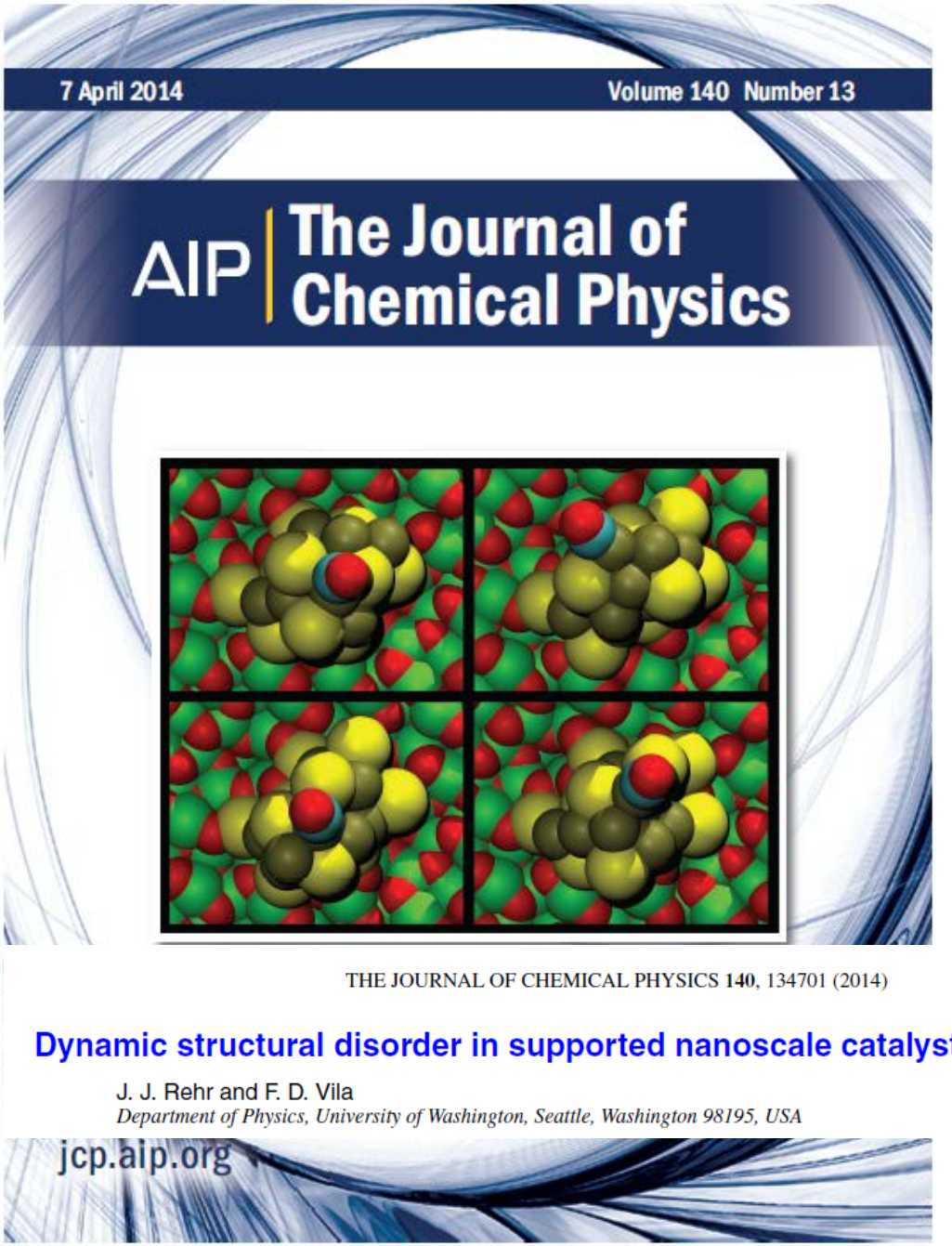


Pt_{10} on γ-Al_2O_3 @ 165 K



Need Operando AIMD dynamics* to reproduce experiment

*F. Vila, J. J. Rehr, J. Kas,R. G. Nuzzo, and A. I. Frenkel, Phys. Rev. B **78**, 121404(R), 2008



Conclusion

Must consider dynamic structure to understand the nano-scale

Part II: Theory and Interpretation of X-ray Spectra

- **GOALS**: *ab initio* theory

  Accuracy ~ experiment

- **TALK**:

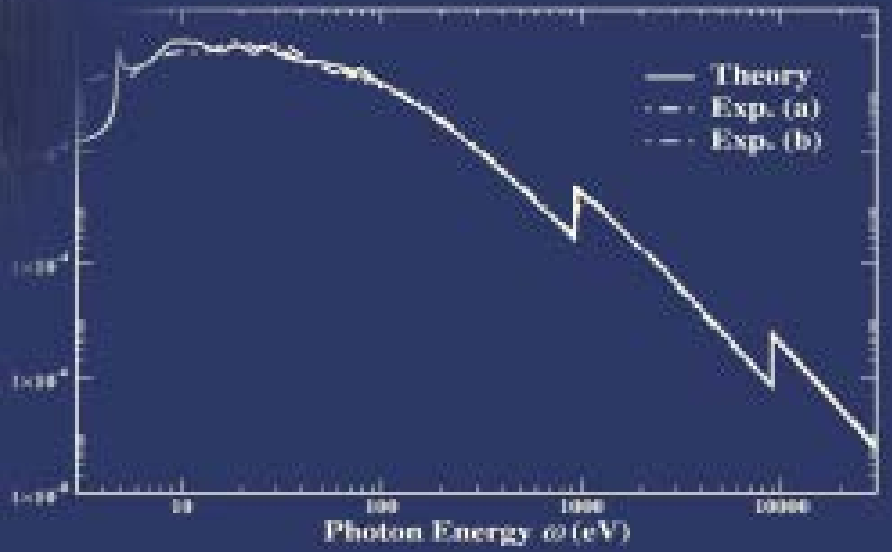
I. Introduction — History

II. Real-space Green's function theory — FEFF codes

III. Improvements — XAS, Optical spectra, etc, …

GOAL – Theoretical X-rayBeamline

$$\mu \propto -\frac{1}{\pi}\,\mathrm{Im}\,\langle i|d\,G(\omega)\,d^{\dagger}|i\rangle$$



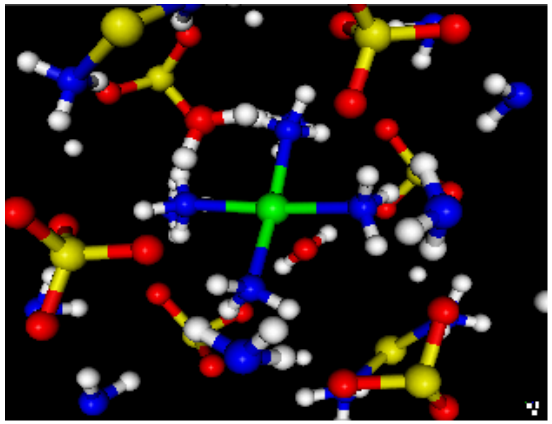
Rehr Group

Questions we want to answer:

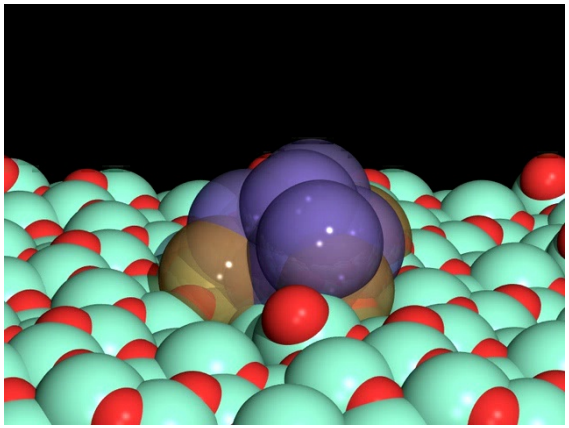
What are the *structure* and *dynamics* ?

and other *physical properties* ?

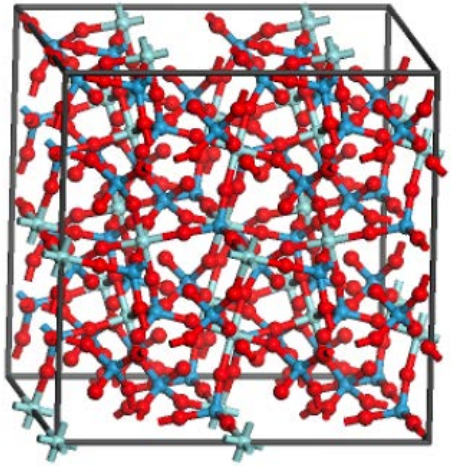
of complex systems ?



$Cu(NH_3)_4SO_4H_2O$

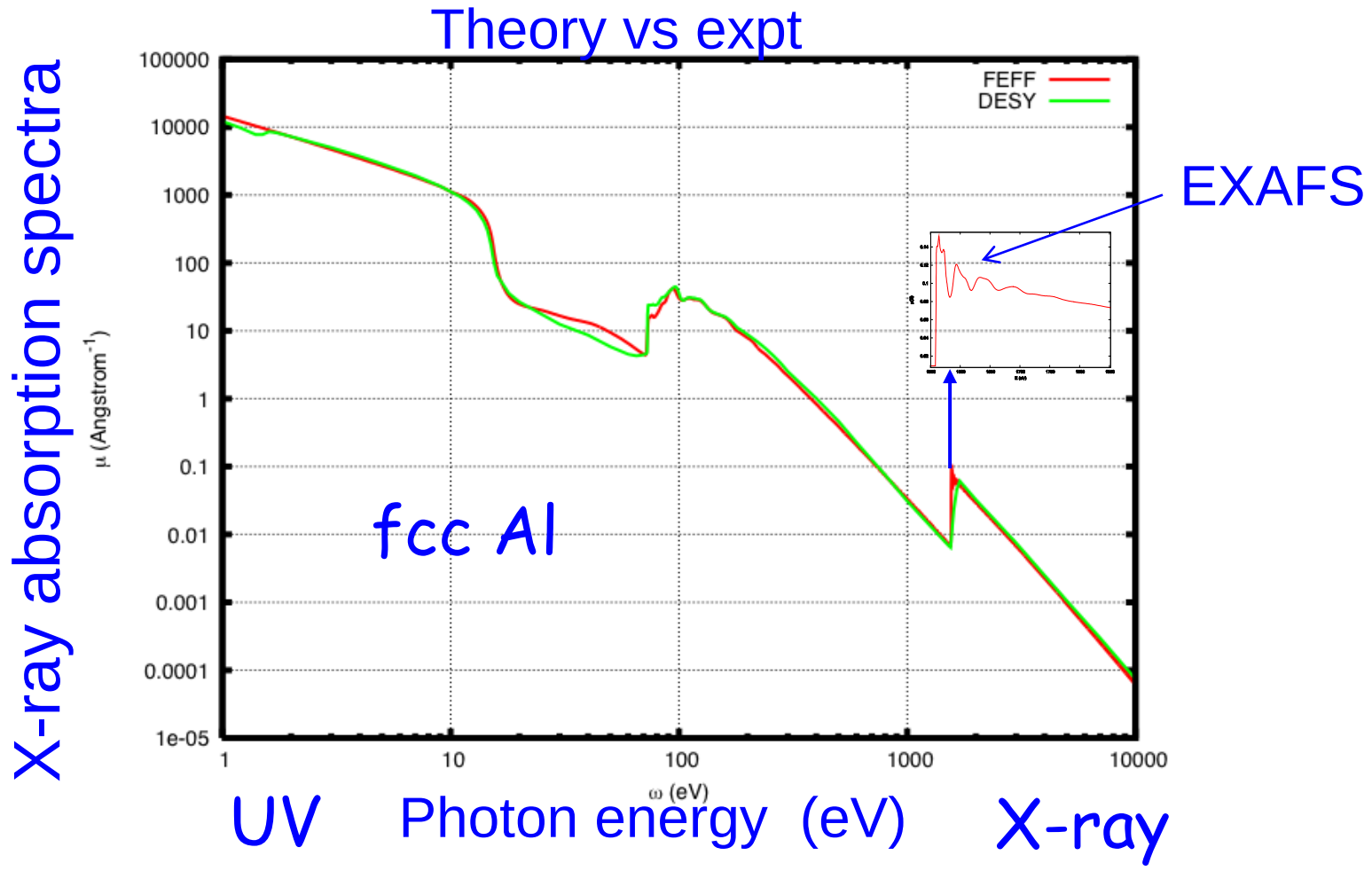


$Pt/\gamma\text{-}Al_2O_3$



Zirconium Tungstate

Experiment: X-ray Spectroscopy

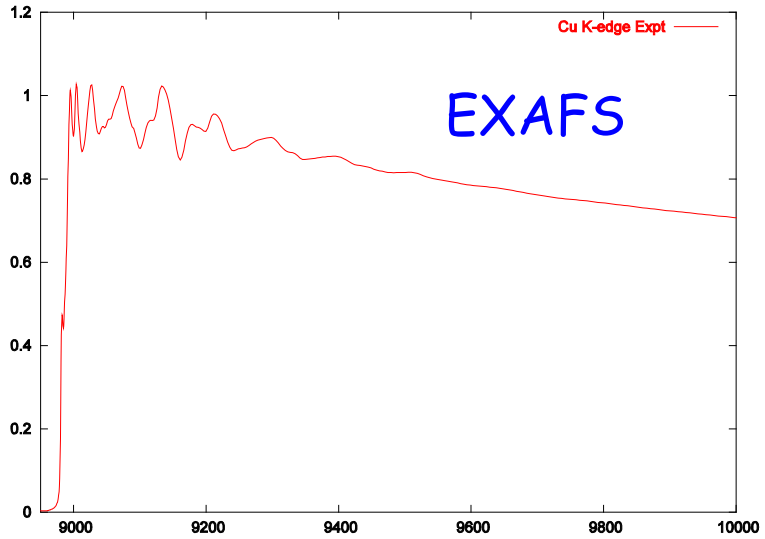


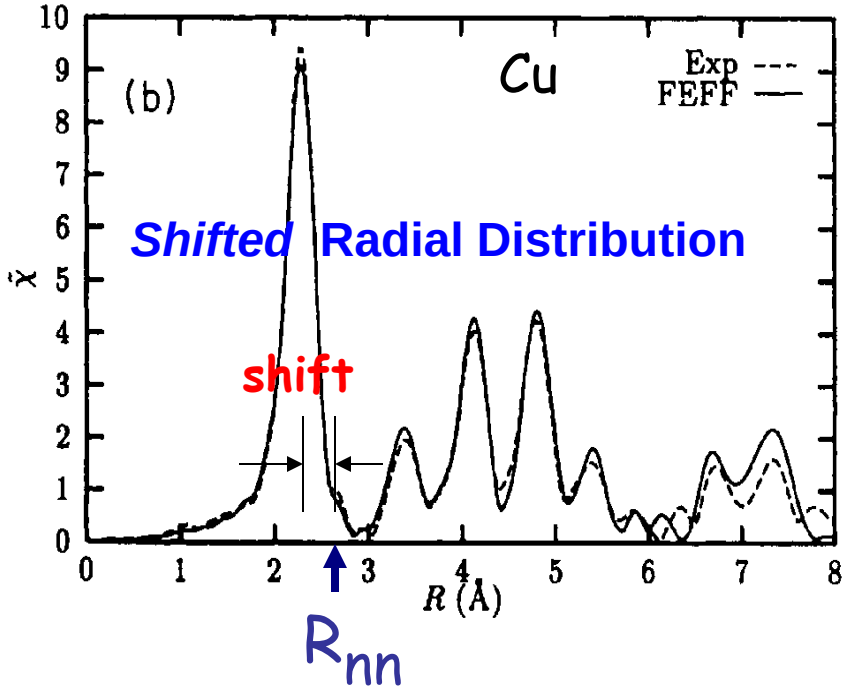
? What's in a spectrum ?

Historical interpretation of EXAFS*

*Stern Sayers Lytle, UW **1971**

Short range order theory → EXAFS Fourier Transform





→ X-ray Microscope!

BUT need to calibrate experiment with “Standard”

”Can you write an equation

for the theory?”

P.A.M. Dirac

(to R. Feynman)

Answer: Exact EXAFS Equation*

Effective Scattering Amplitude f_{eff}

$$\chi(k) = S_0^2 \sum_R \frac{|f_{\mathrm{eff}}(k)|}{kR^2} \sin(2kR+\Phi_k) e^{-2R/\lambda_k} e^{-2\sigma^2 k^2}$$

S_0^2 Many body amplitude factor

λ_k Mean free path

σ^2 Mean square vib amplitude

EXAFS measures **local structure & disorder**

Distance R Coordination N Disorder σ^2

*JJR, RC Albers, CR Natoli, EA Stern, Phys Rev B**34**, 4350 (1986)

BUT: need many parameters !

Question: Can the EXAFS parameters

$$k \quad f_{\mathbf{eff}} \quad \Phi_k \quad \sigma^2 \quad \lambda_k \quad S_0^2$$

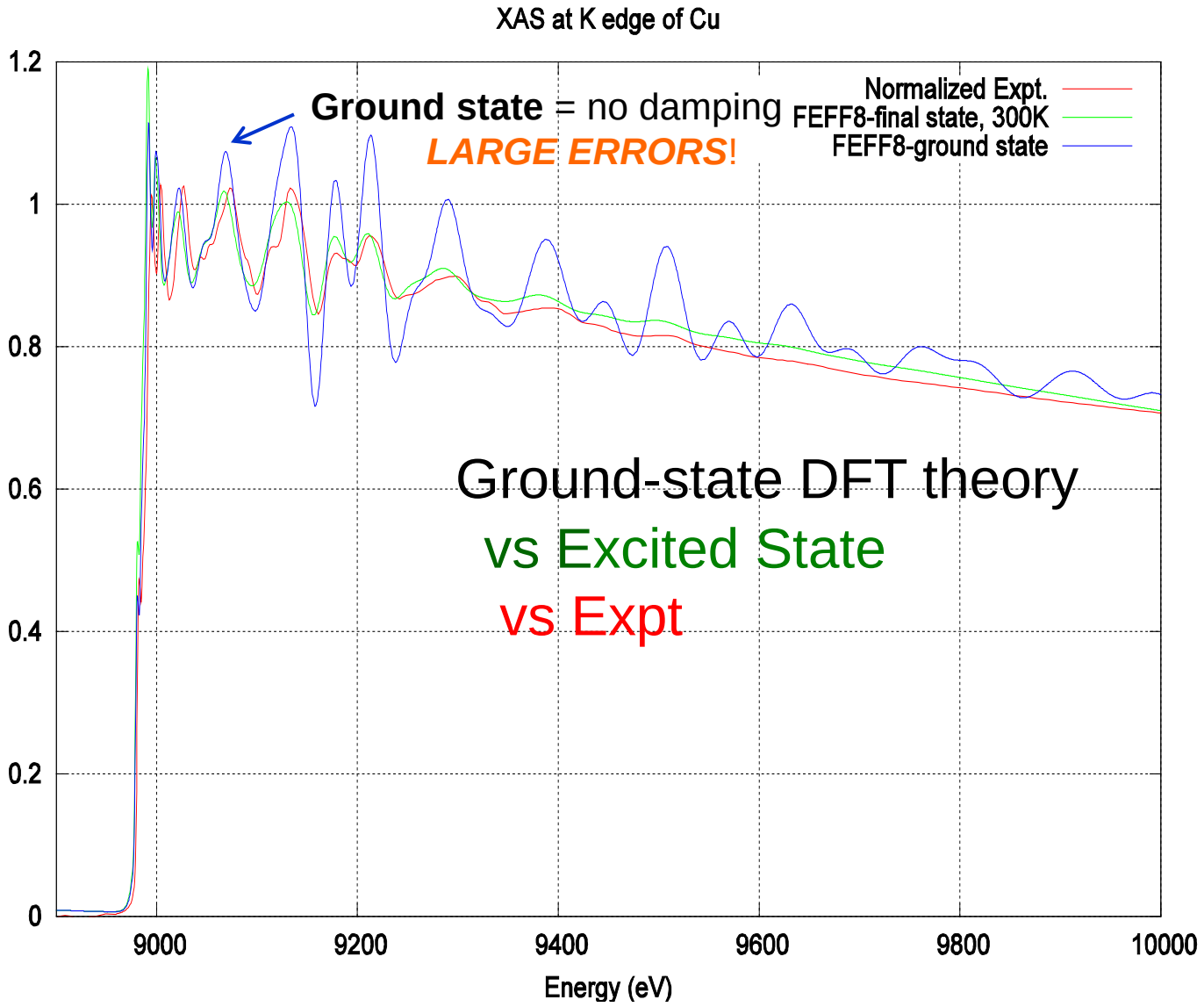
be calculated theoretically **?**

Answer 1

"I always thought it was easier to measure x-ray absorption than to calculate it."

Hans Bethe
ca 1980

Gotcha: Standard theory fails!



Why?

Fermi Golden Rule for XAS $\mu(\omega)$

$$\mu(\omega) \sim \Sigma_f |\langle \psi_f | d | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Too many quasi-particle final states ψ_f

$$\left[\frac{p^2}{2m} + V'_{coul} + \Sigma(E)\right] \psi_f = E_f \psi_f$$

Final state rule

$$V'_{coul} = V_{coul} + V_{core-hole}$$

Non-hermitian **self-energy** $\Sigma(E)$

(replaces DFT Vxc)

Answer 2 (JJR)* "Now** it is often easier to calculate x-ray absorption than to measure it"

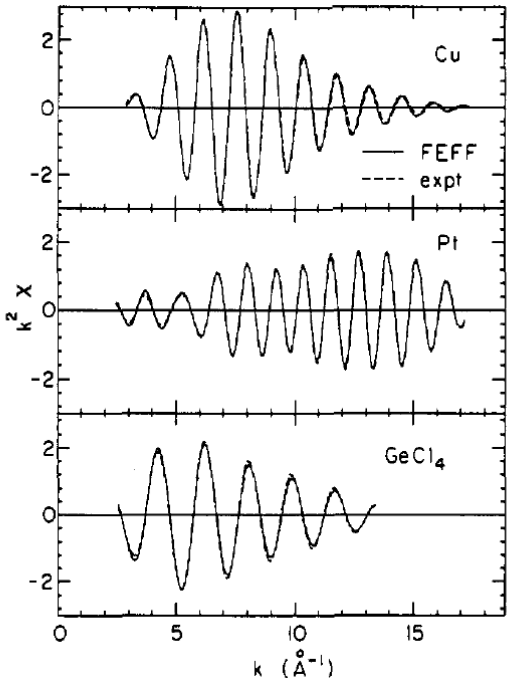
(**if structure is known)

Theoretical X-ray Absorption Fine Structure Standards

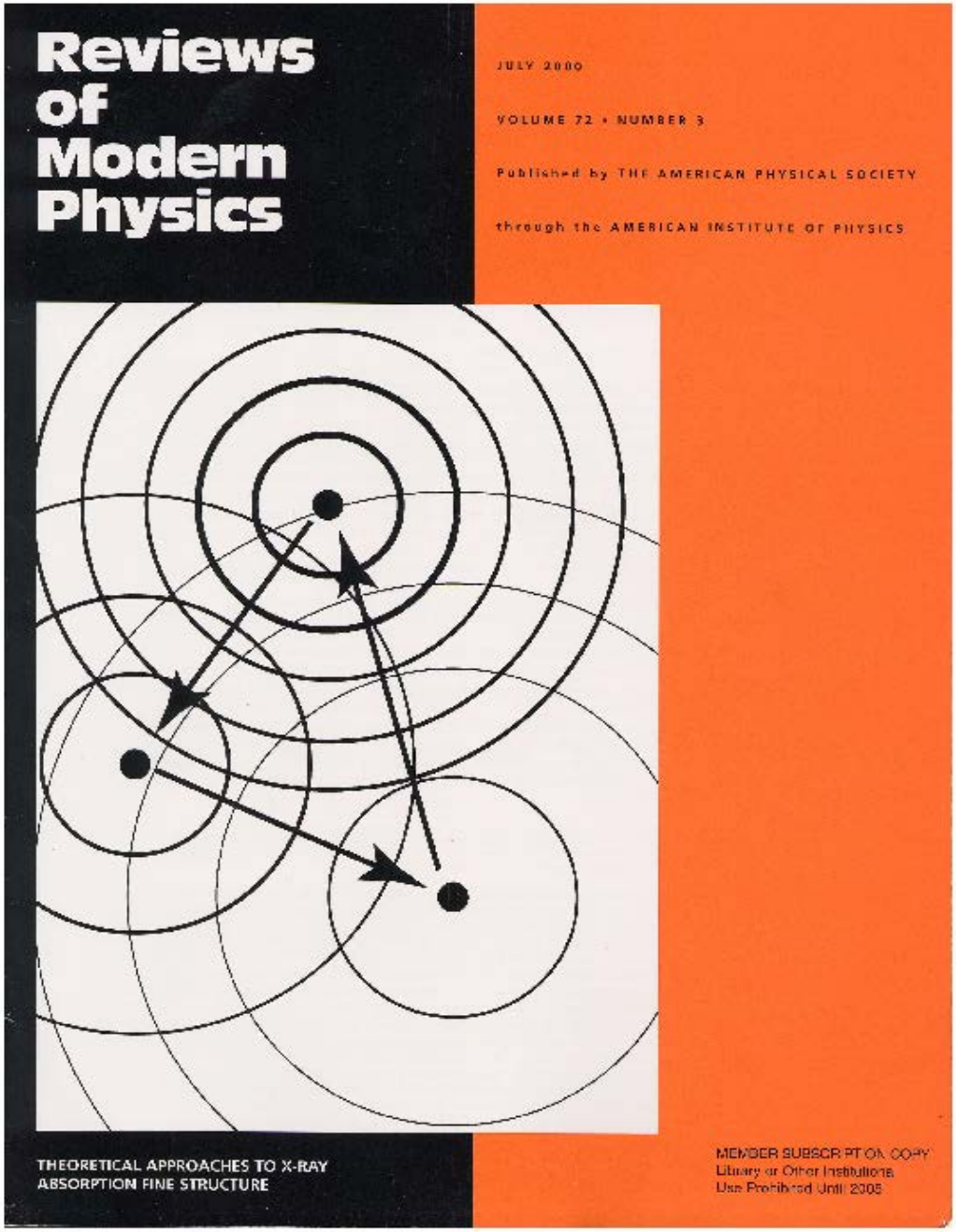
J. J. Rehr,*,† J. Mustre de Leon,†,‡ S. I. Zabinsky,† and R. C. Albers§

Contribution from the Department of Physics, FM-15, University of Washington, Seattle, Washington 98195, and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545. *Received November 13, 1990*

Abstract: Theoretical X-ray absorption fine structure (XAFS) standards are developed for arbitrary pairs of atoms throughc the periodic table ($Z \leq 94$). These standard XAFS spectra are obtained from *ab initio* single-scattering XAFS calculatio using an automated code, FEFF, which takes into account the most important features in current theories: (i) an exact treatm of curved-wave effects; (ii) approximate molecular potentials derived from relativistic atoms, (iii) a complex, energy-dependc self-energy; (iv) a well defined energy reference. FEFF also yields tables of XAFS phases and amplitudes as well as mean-fi paths. Sample results are presented and compared with experimental results and with earlier work. We find that these theoreti standards are competitive with experimental standards, permitting XAFS analysis at lower wavenumbers and yielding distar determinations typically better than 0.02 Å and coordination numbers typically better than 20%. These standards also prov theoretical tests of chemical transferability in XAFS.



** 10 years later - JACS **113**, 5136 **(1991)**



How? (10 more years)

Quantitative

XAS theory

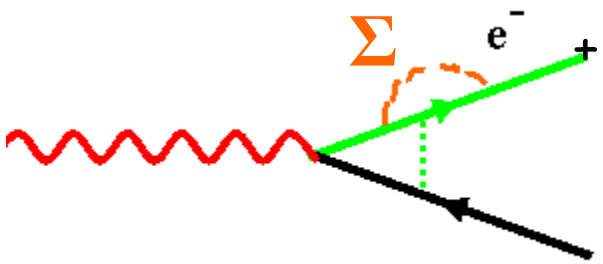
FEFF

J. J. Rehr & R.C. Albers

Rev. Mod. Phys. **72**, 621 (2000)

http://leonardo.phys.washington.edu/feff/

Theoretical Tricks: Green's functions



- Real-space **Green's function** Theory
- Mean free path, Self-energy Σ
- Screened core-hole

Real-space Green's Function Theory

Golden rule via Wave Functions

$$\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2 \delta(E-E_f)$$

Paradigm shift

Golden rule via Green's Functions $\mathbf{G} = 1/(E - h - \Sigma)$

$$\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

No sums over final states !

What's a Green's function?

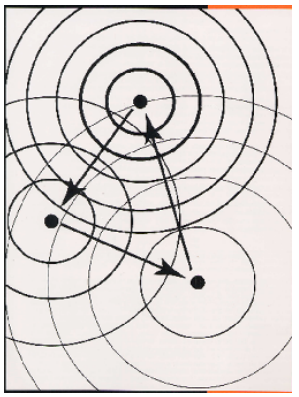
Wave function in QM $H\,\Psi = E\,\Psi$

$\Psi(r)$ = Amplitude to find particle at r

Green's function $(H - E)\,G = -\,\delta(r-r')$

$G(r,r',E)$ = *aka Propagator*

= Amplitude to go from r to r'



Multiple-scattering theory of G

$$\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

$$G = G^0 + G^0 t G^0 + G^0 t G^0 t G^0 + \cdots$$

(MS path expansion - geometric series)

Path

$$= [1 - G^0 t]^{-1} G^0 \qquad \text{“full MS”}$$

Full MS

Ingredients:

G_0 free propagators ***t*-matrix** $= e^{i\,\delta_l}\,sin\,\delta_l\,\boldsymbol{\delta}_{RR'}\boldsymbol{\delta}_{ll'}$

Implementation: FMS FEFF code

PHYSICAL REVIEW B VOLUME 58, NUMBER 12 15 SEPTEMBER 1998-II

Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure

A. L. Ankudinov
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

B. Ravel
Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

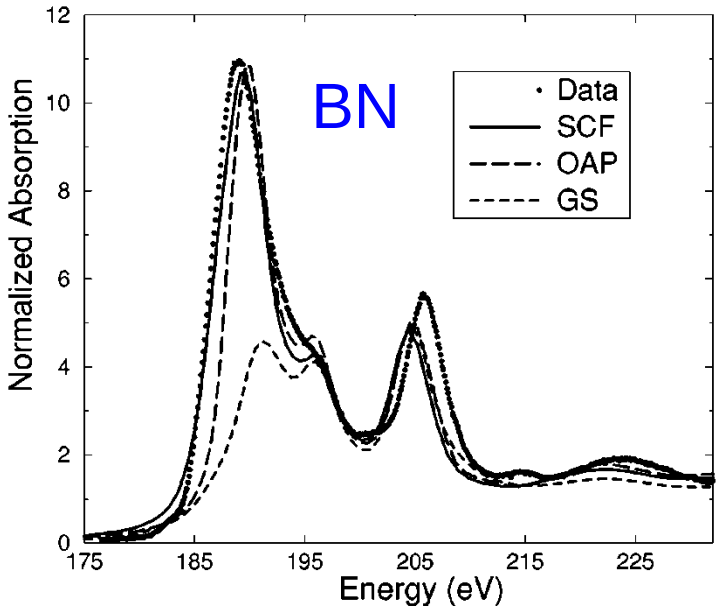
J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560

S. D. Conradson
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexic

89 atom cluster

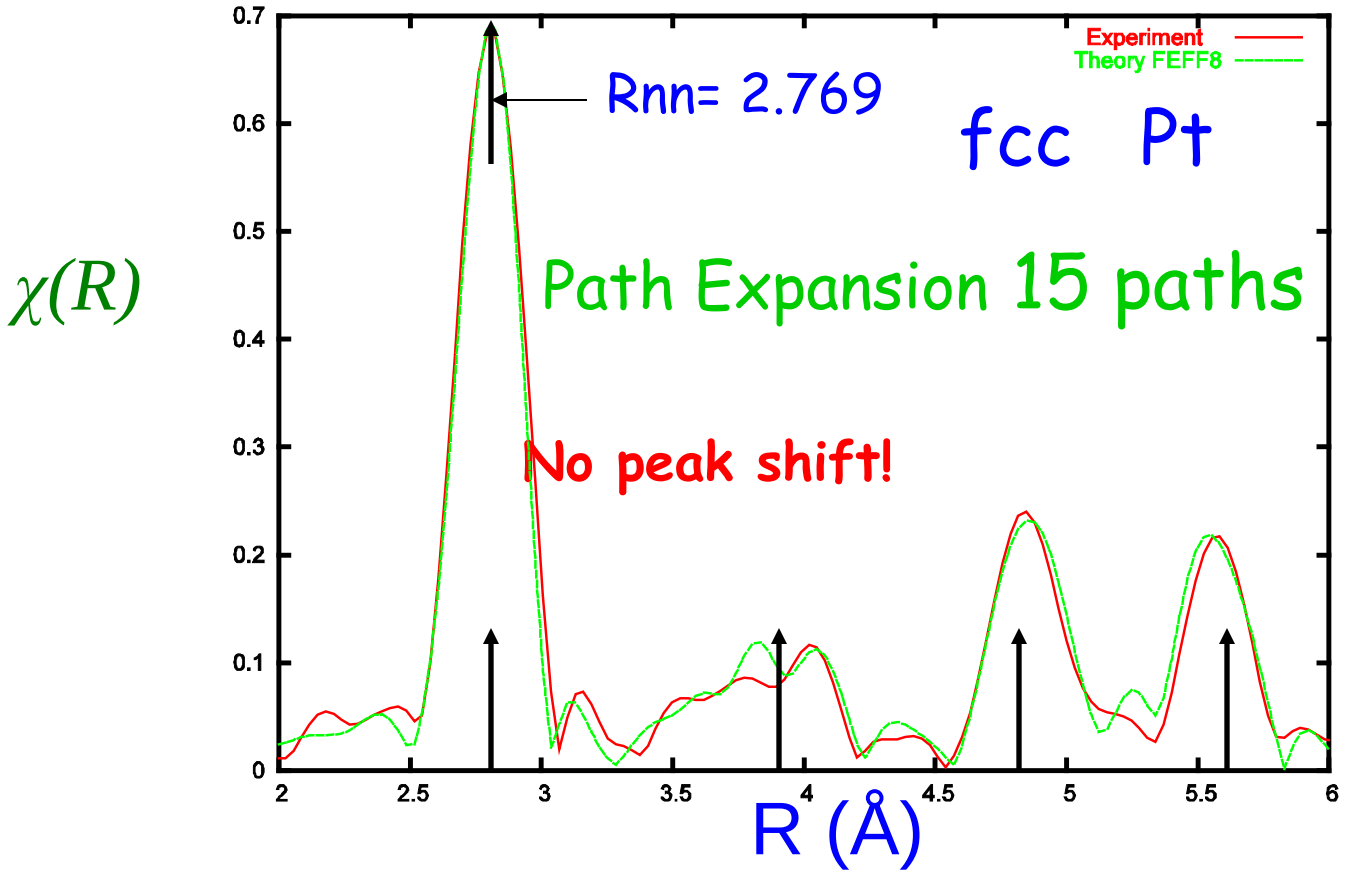
Core-hole, SCF potentials

Essential!



Example: Pt EXAFS – MS path expansion

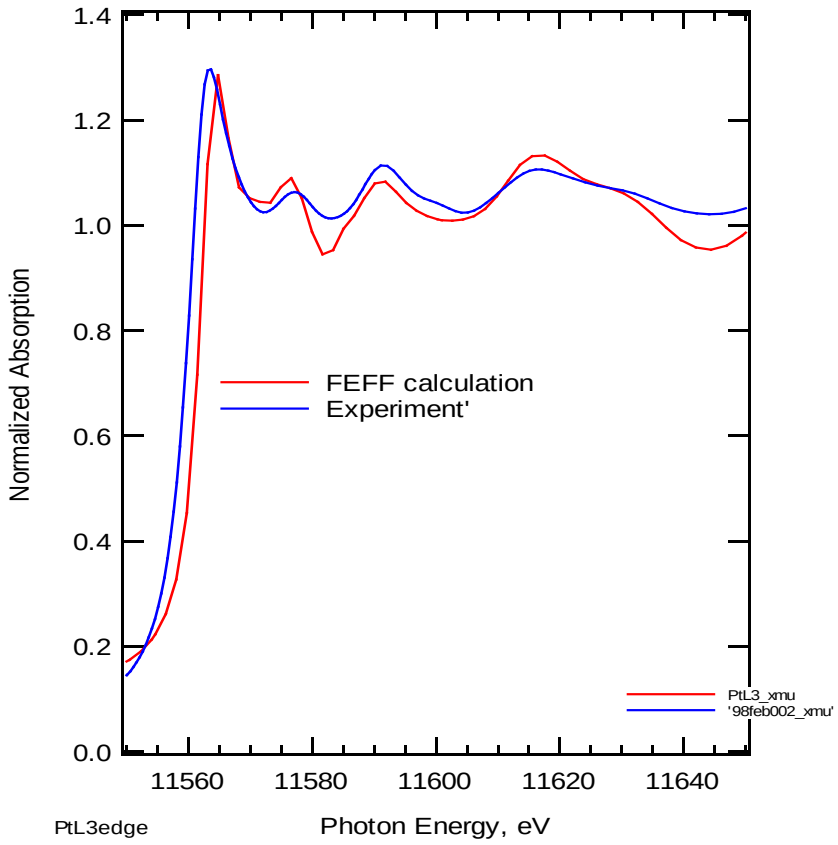
Phase Corrected EXAFS Fourier Transform *



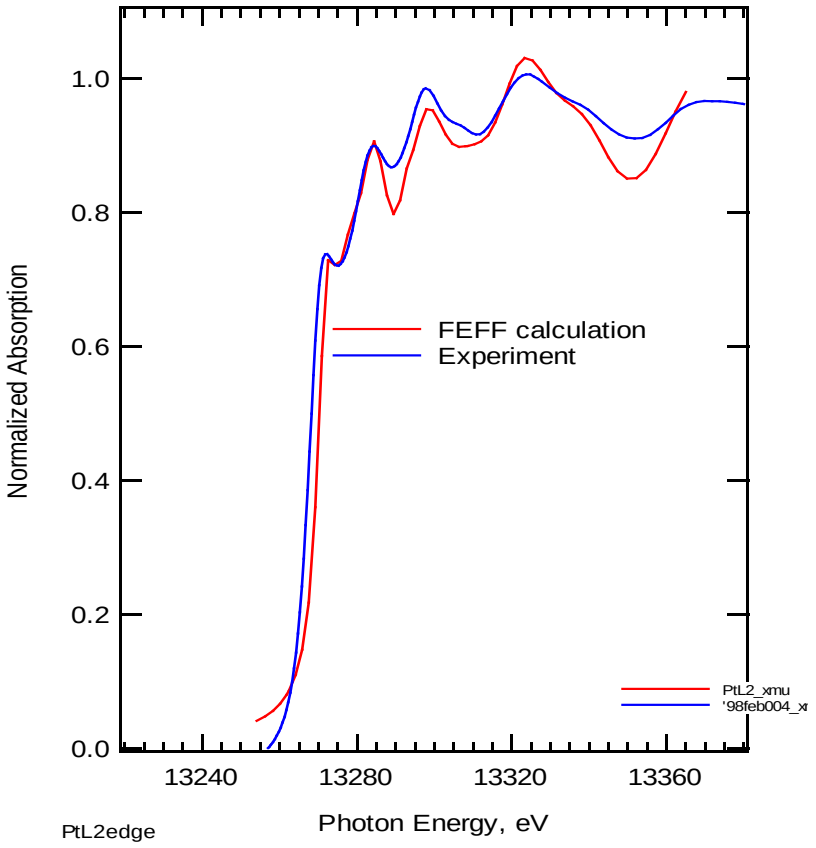
Theoretical phases → accurate distances to < 0.01 Å

Example: Pt XANES full multiple-scattering

Pt L_3-edge



Pt L_2-edge (S. Bare, UOP)



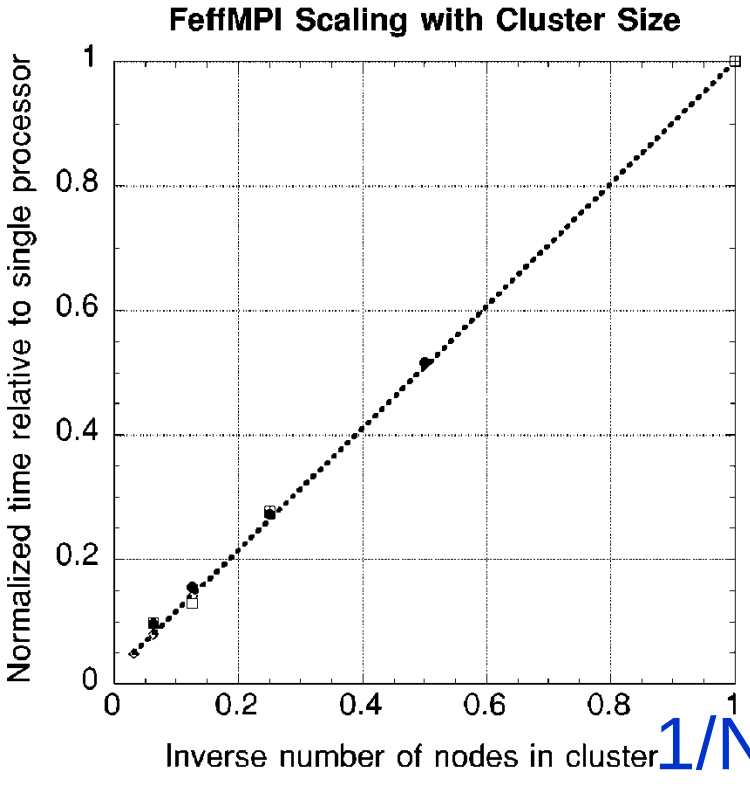
- Good agreement: *Relativistic* FEFF8 code reproduces all spectral features, ***including absence of white line at L_2-edge***.
- Self-consistency essential: position of Fermi level strongly affects white line intensity.

Green's Functions and Parallel Computation

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

A. L. Ankudinov,[1] C. E. Bouldin,[2] J. J. Rehr,[1] J. Sims,[2] and H. Hung[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



$1/N_{CPU}$

$$\mu(E) \sim -\tfrac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

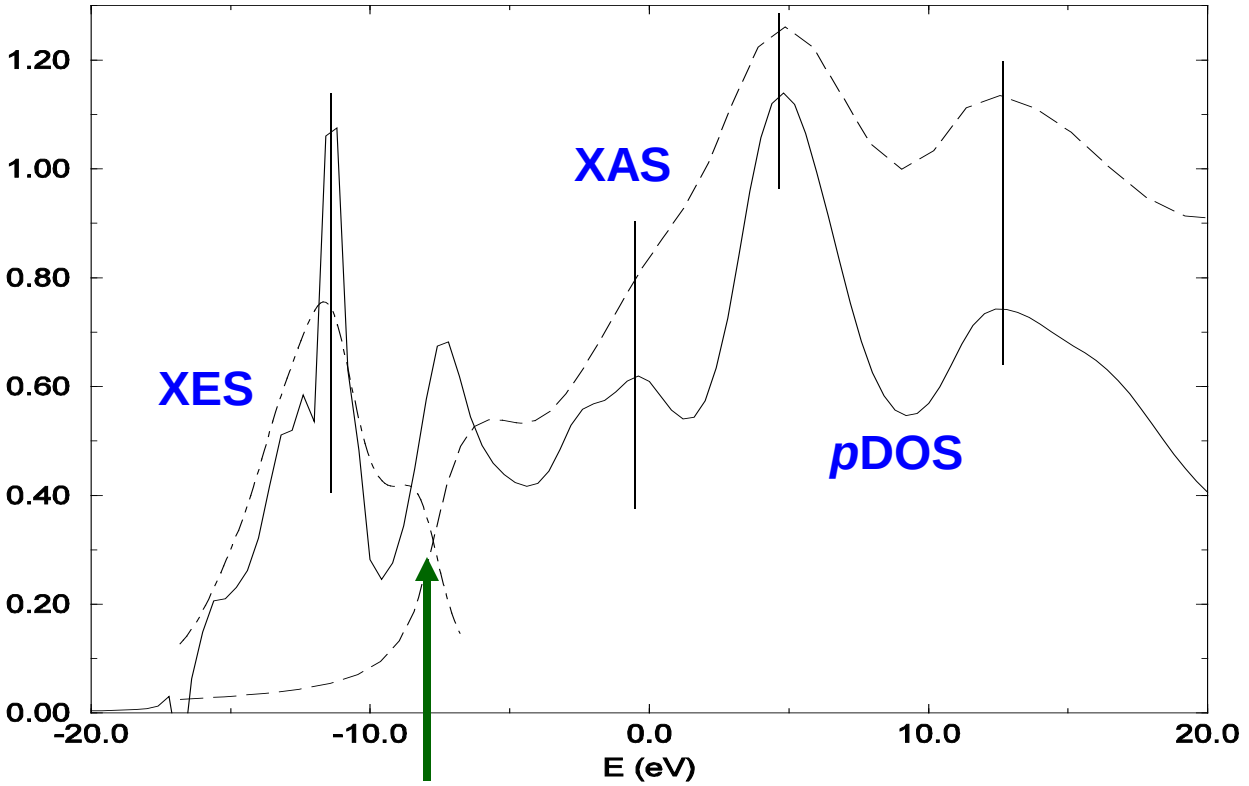
Energy E
is just a parameter !

"Natural parallelization"

Each CPU does one energy

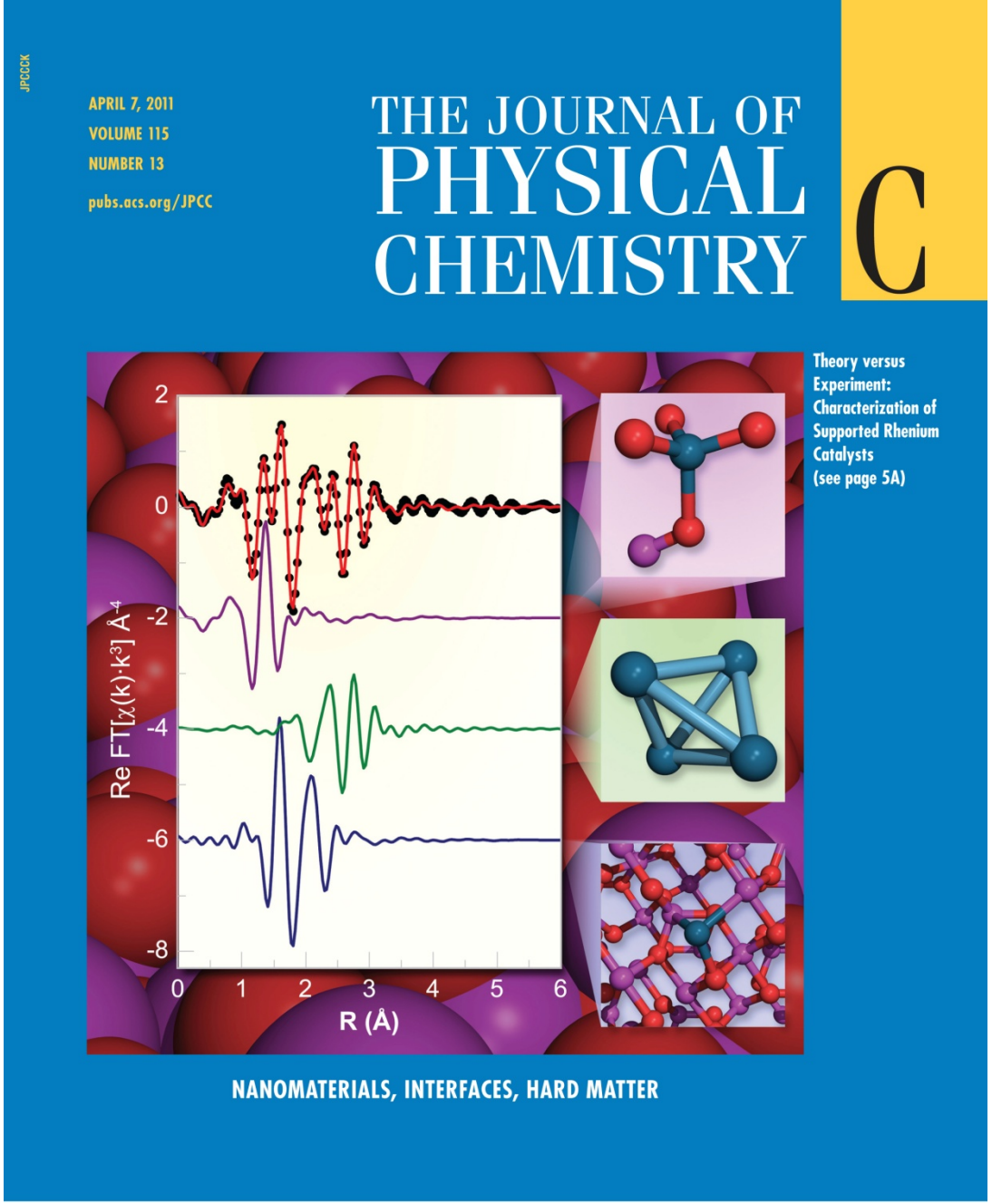
Interpretation of XANES : Excited State Electronic Structure

Cu *p*DOS vs XAS and XES



Fermi energy E_F

Final state energy E



Application

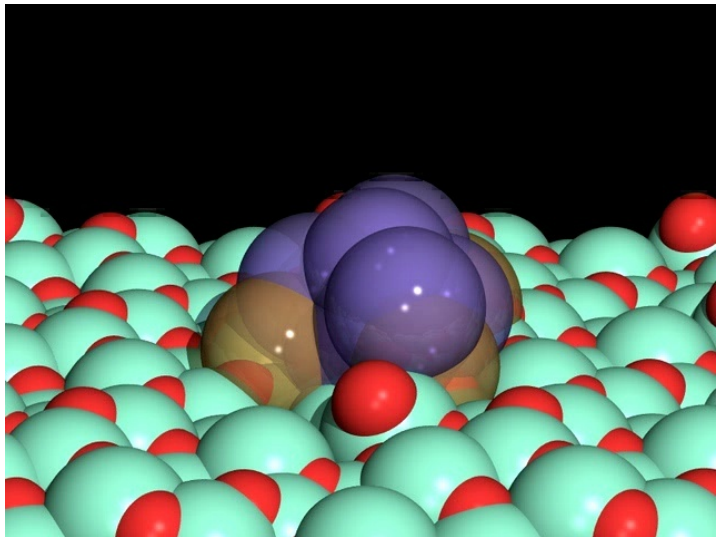
EXAFS analyis of Re-catalysts

Simon R. Bare, et al., J. Phys. Chem. 115, 5740 (2011)

Application: Pt catalysts

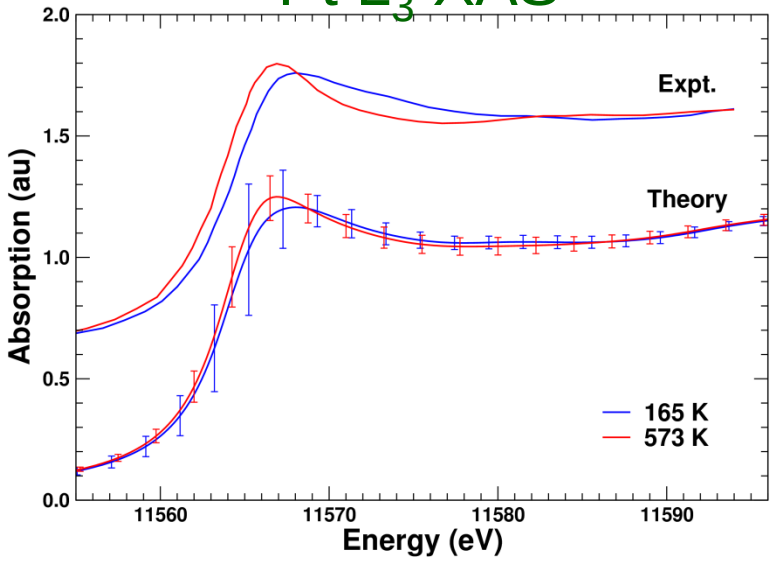
$Pt_{10}/\gamma\text{-}Al_2O_3$

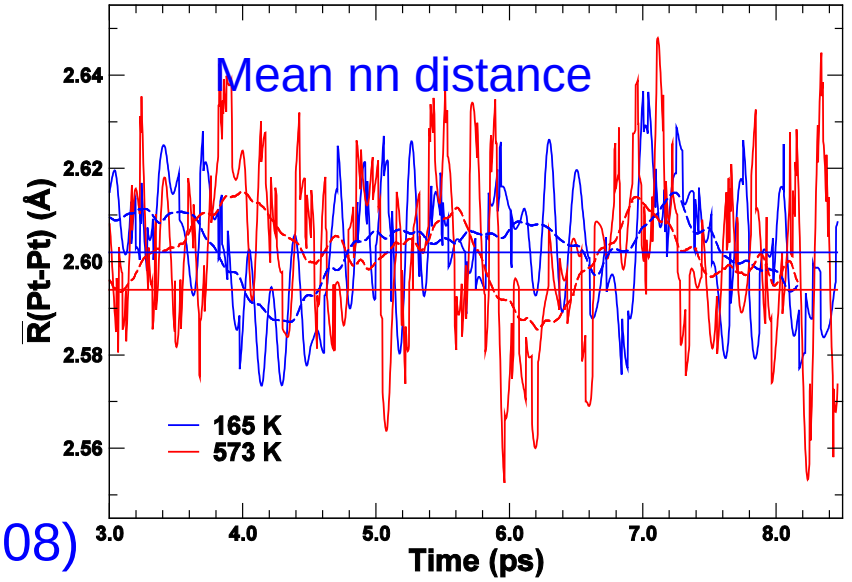
Finite Temp, Real-time DFT/MD calculations of supported Pt nano-catalysts*



2500 3 fs time-steps

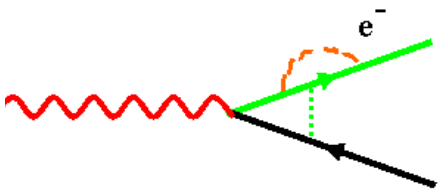
Pt L_3 XAS





*F. Vila et al. Phys Rev B**78**, 121404(R) (2008)

What's Next: Even better theory

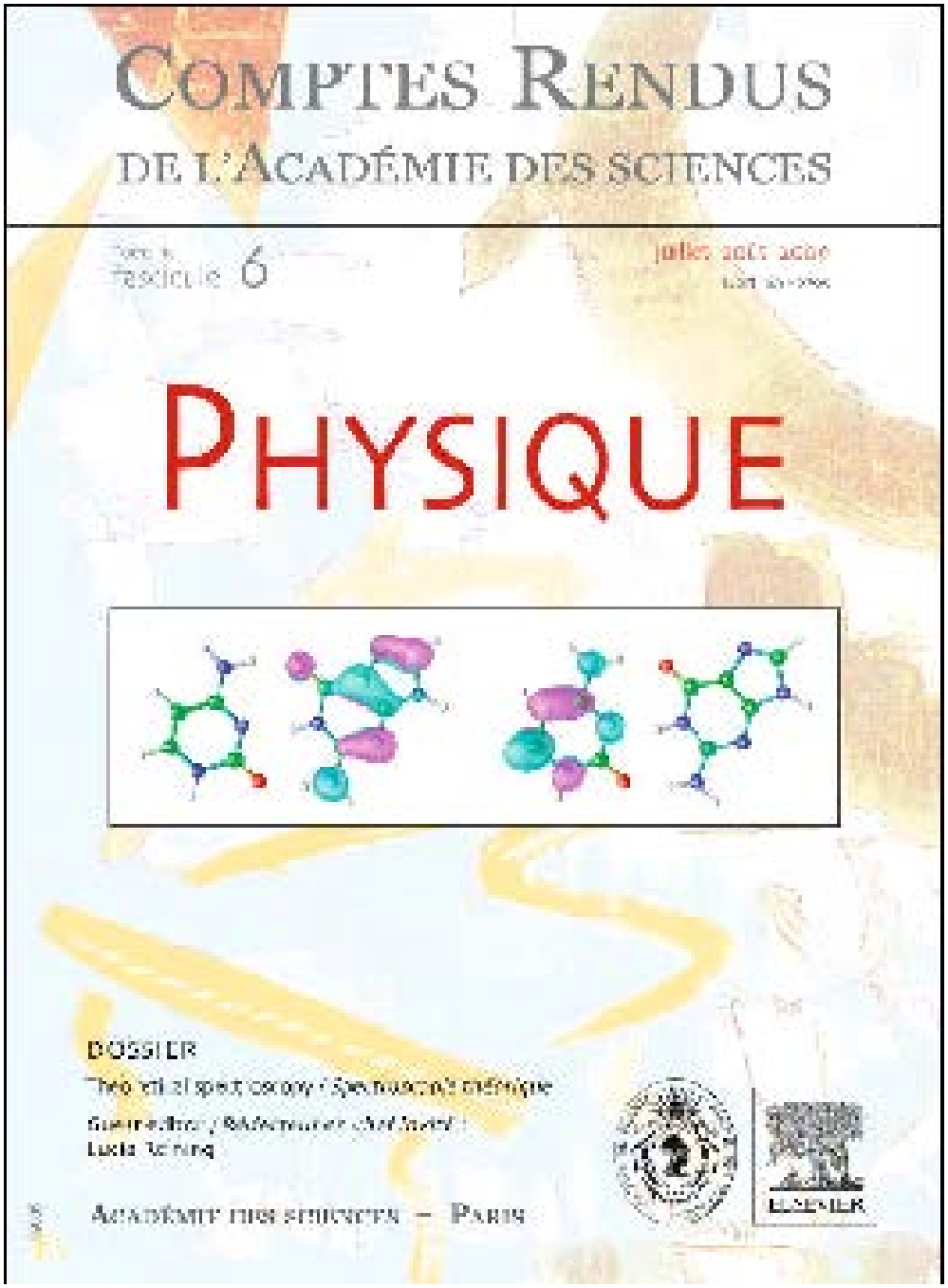


A. Other spectra: NIXS, RIXS, Optical, Compton

B. *Ab initio* mean free paths λ_k

C. *Ab initio* Debye Waller factors σ^2

D. Multi-electron excitations S_0^2



(10 more years)

Quantitative XAS

FEFF9

JJR et al., Comptes Rendus Physique **10**, 548 (2009)

in Theoretical Spectroscopy

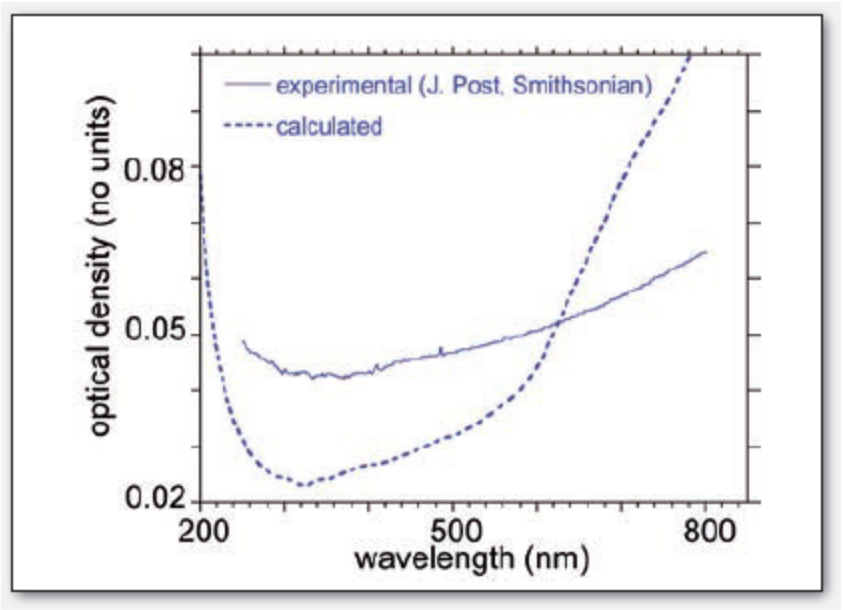
L. Reining (*Ed*) (2009)

Application: Optical Spectra

The Rediscovery of the 'French Blue' diamond

François Farges [1,2], John Vinson, John J. Rehr [3] and Jeffrey E. Post [4] - DOI: 10.1051/epn/2012103
[1] Laboratoire de minéralogie et de cosmochimie du Muséum (LMCM) and CNRS UMR 7160 - Muséum national d'Histoire naturelle - Paris - France.
[2] Dept. of Environmental and Geological Sciences - Stanford University, CA 94305-2115 - USA.
[3] Dept. of Physics - University of Washington - Seattle, WA 98195-1560 - USA.
[4] Department of Mineral Sciences - Smithsonian Institution - Washington, DC 20560 - USA.

▸ **FIG. 2:** Optical spectroscopy spectrum measured for the 'Hope' diamond (courtesy of Smithsonian Institution, Washington, DC, USA) together with a computer spectrum assuming a boron atom inside a 69-carbon atom cluster.

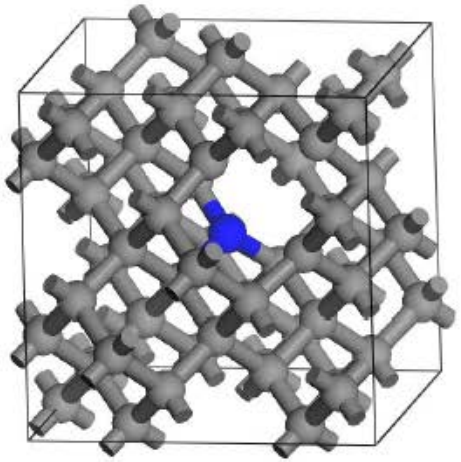


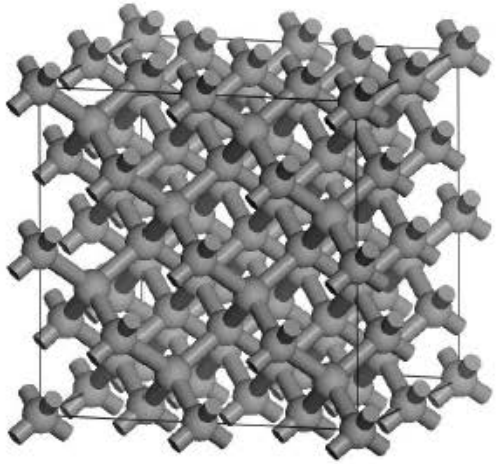
Europhysics News 43, 1 (2012)

Optical Absorption of N-Doped Diamond

Presentation by: Winnie H. Liang

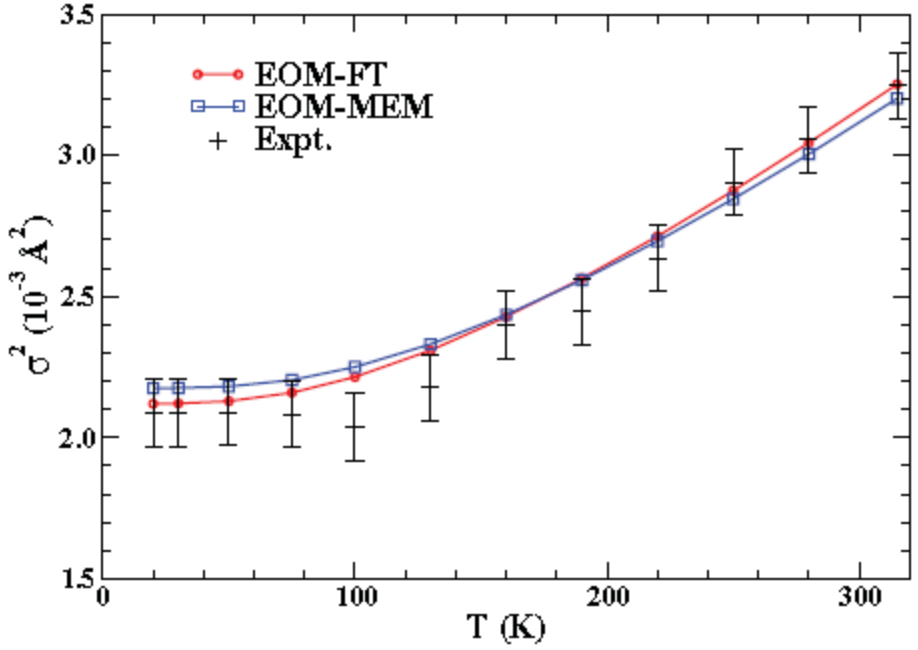
INT REU: University of Washington 2014

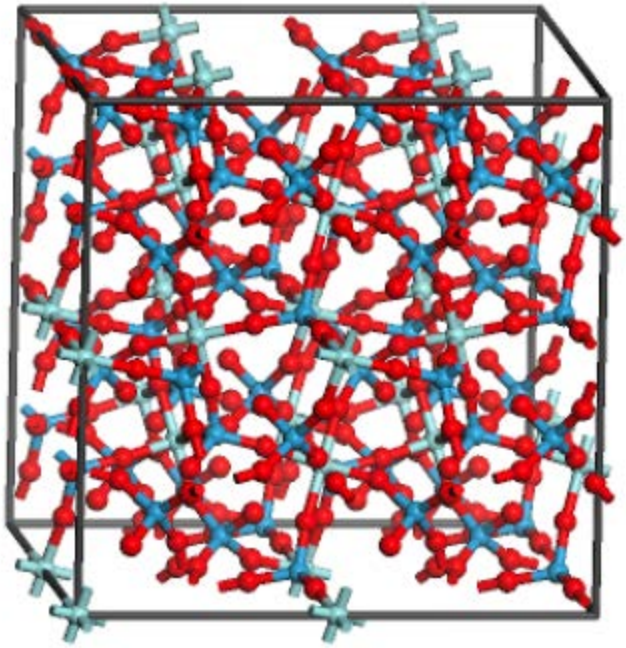




Debye-Waller factors σ^2 in Zr tungstate

Mean square vibration amplitudes





+ Easy to use GUI for everyone – JFEFF

New Developments in FEFF: FEFF9 and JFEFF

Proceedings of XAFS 15 in press 2012

Kevin Jorissen and John J. Rehr

Department of Physics, University of Washington, Seattle, WA 98195, USA

kevinjorissen.pdx@gmail.com

Abstract. The ab initio core-level spectroscopy code FEFF9 has seen many new developments in recent years. We describe the addition of new physics and new features designed to calculate more accurate spectra. We also present the user-friendly Java-based GUI JFEFF that simplifies running FEFF on platforms ranging from personal computers to high-performance parallel systems and virtual cloud platforms.

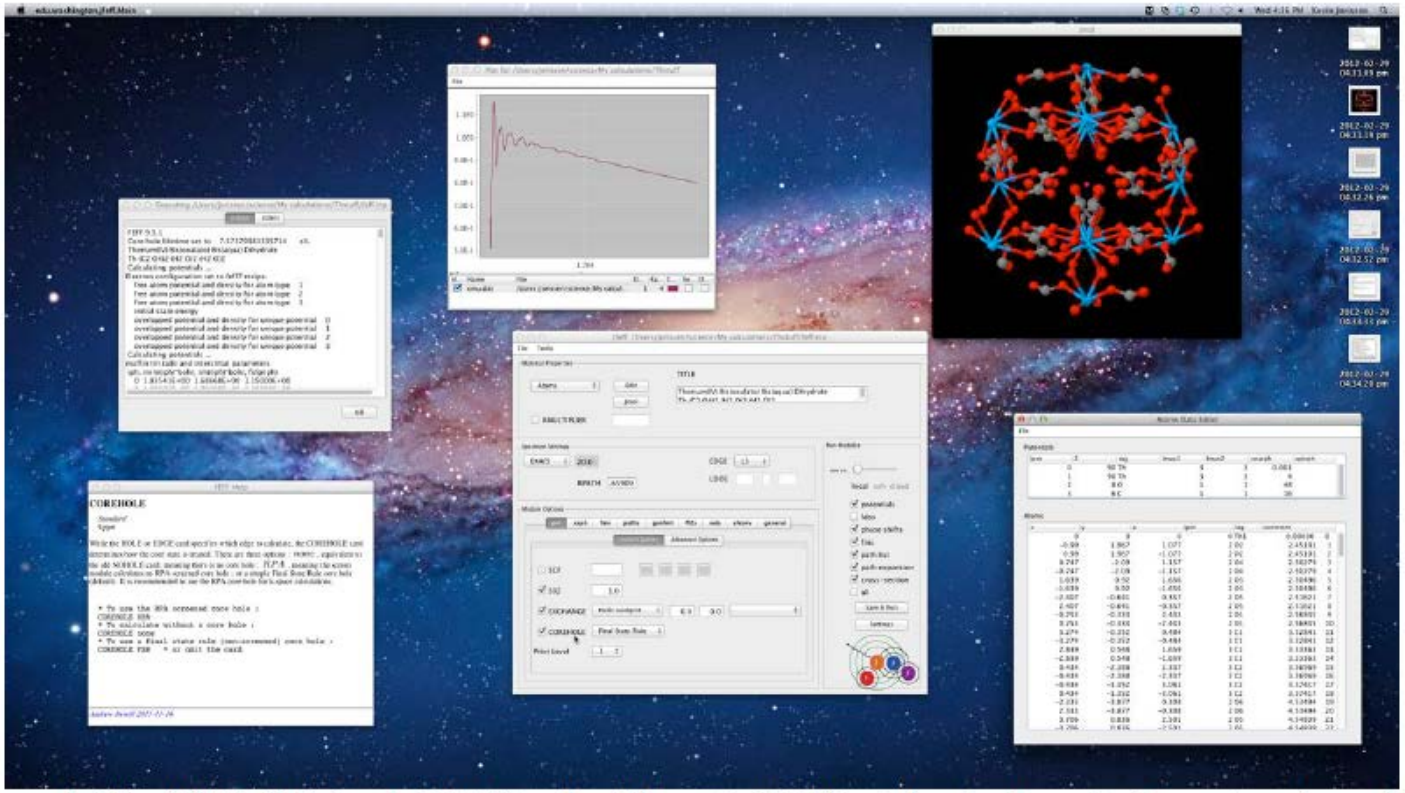


Figure 1 The JFEFF GUI for the FEFF9 code. The main JFEFF window is shown in the centre. Around it

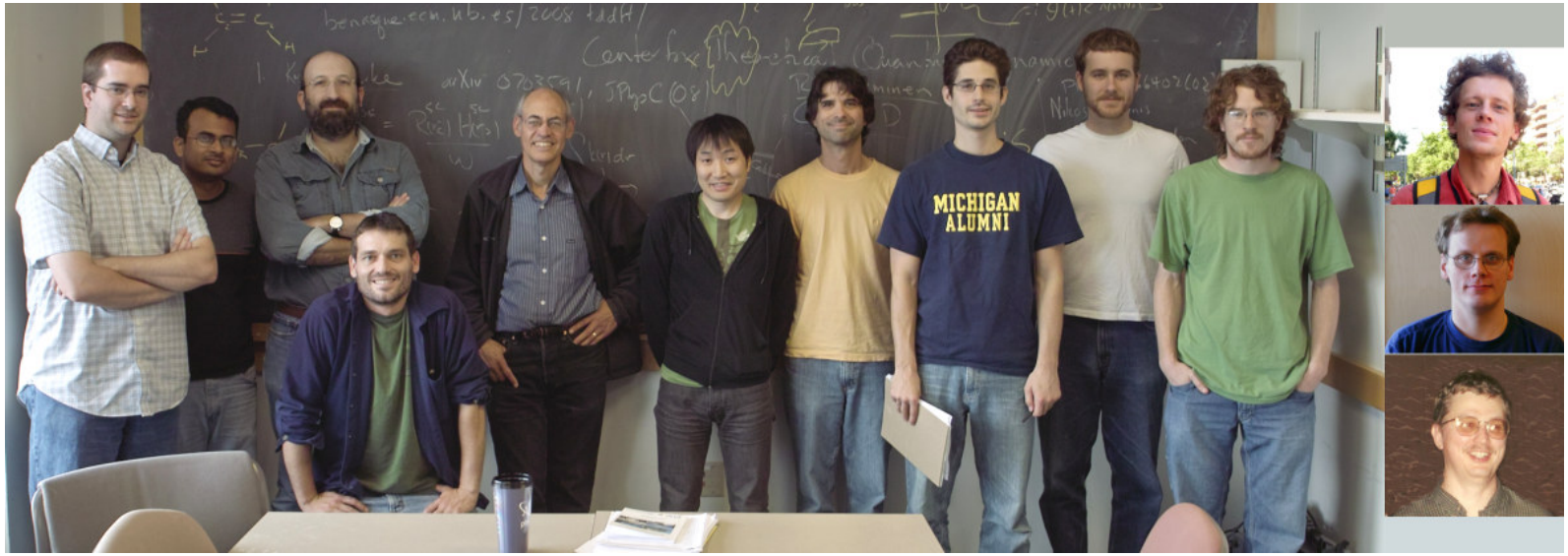
Acknowledgments

Rehr Group

- J. Kas (UW)
- F. Vila (UW)
- J. Vinson (UW)
- K. Jorissen (UW)
- T. Ahmed (UW)
- S. Williams
- E. Clevac

Key collaborators

E. Shirley (NIST)
A. Soininen (U. Helsinki)
A.L. Ankudinov (STM)
R.C. Albers (Los Alamos))



Supported by DOE-BES

That's all folks!