EXAFS 50 SYMPOSIUM

CELEBRATING 50 YEARS OF DEVELOPMENT OF EXAFS INSTRUMENTATION, THEORY, DATA ANALYSIS & APPLICATIONS

OCTOBER 30-31, 2023

Hosted by Brookhaven National Laboratory

XAFS-2023 Short Course, Nov. 1-3, 2023

Sponsors:
Chemistry Division, BNL
Stony Brook University
Users Executive Committee, NSLS-II

S. Peters (BNL)
speters@bnl.gov
A. Frenkel (SBU/BNL)
frenkel@bnl.gov

Short Course on X-ray Absorption Fine Structure: Advanced Topics in Data Analysis and Modeling

Brookhaven National Laboratory — Chemistry Division

BNL administrator:
Sarah Peters
(speters@bnl.gov)

Stony Brook University

Instructors:

Alexei Kuzmin (U. Latvia)

Janis Timoshenko (Fritz Haber Inst.)

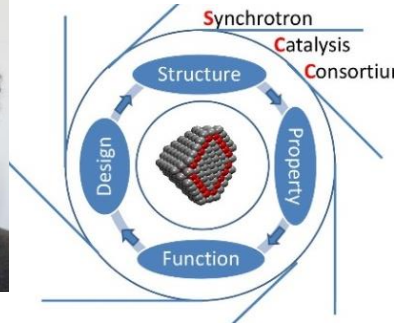
Prahlad Routh (SBU)

Nicholas Marcella (UIUC/BNL)

Ryuichi Shimogawa

(Mitsubishi Chem/SBU)

Anatoly Frenkel (SBU/BNL)



Financial support

Brookhaven National Laboratory
Stony Brook University
UEC, NSLS-II
Synchrotron Catalysis Consortium

U.S. DEPARTMENT OF ENERGY

XAFS course, Brookhaven National Laboratory, Nov 1-3, 2023

Internet

Connect to Corus

Updated Account Details	
Guest Username:	20231023000
Guest Password:	633905
Account Status:	Active
Account Activation:	Monday, 23 October 2023, 12:33 PM
Account Expiration:	Account will expire at Friday, 03 November 2023, 8:00 PM
Sponsor's Name:	oauth2:TEST

Food

Google: BNL food services

Micro-marts
24-hour micro-marts with self-purchase, ready-to-eat food and beverage options are located in the lobbies of Building 400

Lunch:
The Artisan (Wednesday, Thursday, Friday)
At the cafeteria in Berkner Hall

Mobile Food Vendors
Food trucks are on site for lunch from 11 a.m. to 1 p.m. at Berkner Hall

Dinner:
Locations of multiple restaurants and take out places are in BNL food services web page
Delivery: give your location in the lab, phone #, and make sure the driver has N.Y. driver license for getting into the lab.

Agenda at a glance

Wednesday, Nov 1

9:00am **A. Frenkel** *Welcoming remarks*

9:20am **J. G. Chen** *Synchrotron Catalysis Consortium (SCC)*

9:50am **A. Frenkel** *Introduction and overview of XAFS*

10:30am *Break + photo*

11:00am **A. Kuzmin** *The use of Molecular Dynamics simulations for the interpretation of EXAFS spectra*

12:00pm *Adjourn for lunch*

1:00pm J. **Timoshenko** *Obtaining 3D structure from EXAFS spectra. Part 1: Wavelet transform analysis*

1:30pm **J. Timoshenko** *Obtaining 3D structure from EXAFS spectra. Part 2: Reverse Monte Carlo simulations and evolutionary algorithm*

2:30pm **P. K. Routh** *Resolving spectral mixtures: linear combination fitting, principal component analysis and MCR-ALS*

3:30pm *Break*

4:00pm **N. Marcella** *Machine Learning Analysis of XANES and EXAFS*

5:00pm **Q & A:** *Instructors and participants*

6:00pm *Adjourn for dinner*

Friday, Nov. 3

9:00 Data analysis practicum

Instructors: J. Timoshenko, A. Kuzmin, P. Routh, N. Marcella, R. Shimogawa, A. Frenkel

12:00pm *Break for Lunch*

1:00pm Data analysis practicum

Instructors: J. Timoshenko, A. Kuzmin, P. Routh, N. Marcella, R. Shimogawa, A. Frenkel

Discussion for all groups

5:00pm *Adjourn*

Thursday, Nov 2

9:00am **A. Frenkel** *EXAFS data analysis and modeling of mono- and bimetallic nanoparticles (demonstration)*

10:00am **J. Timoshenko** *Software demonstration. Part 1: Wavelet transform analysis*

10:30am *Break*

11:00am **J. Timoshenko** *Software demonstration. Part 2: Reverse Monte Carlo simulations and evolutionary algorithm*

12:00pm **A. Kuzmin** *Software demonstration for Molecular Dynamics simulations of EXAFS spectra: Part 1*

12:30pm *Adjourn for lunch*

1:30pm **A. Kuzmin** *Software demonstration for Molecular Dynamics simulations of EXAFS spectra: Part 2*

3:00pm **P. Routh** *Python for XAFS (Colab, plotting, etc.)*

3:30pm **P. Routh** *Software demonstration for PCA and MCR-ALS*

4:00pm *Break*

4:30pm **N. Marcella** *Software demonstration for machine learning applications.*

5:30pm **Q & A:** *Instructors and participants*

6:00pm *Adjourn for dinner*

1. MD-EXAFS
2. RMC-EXAFS
3. PCA/MCR-ALS
4. ML-EXAFS

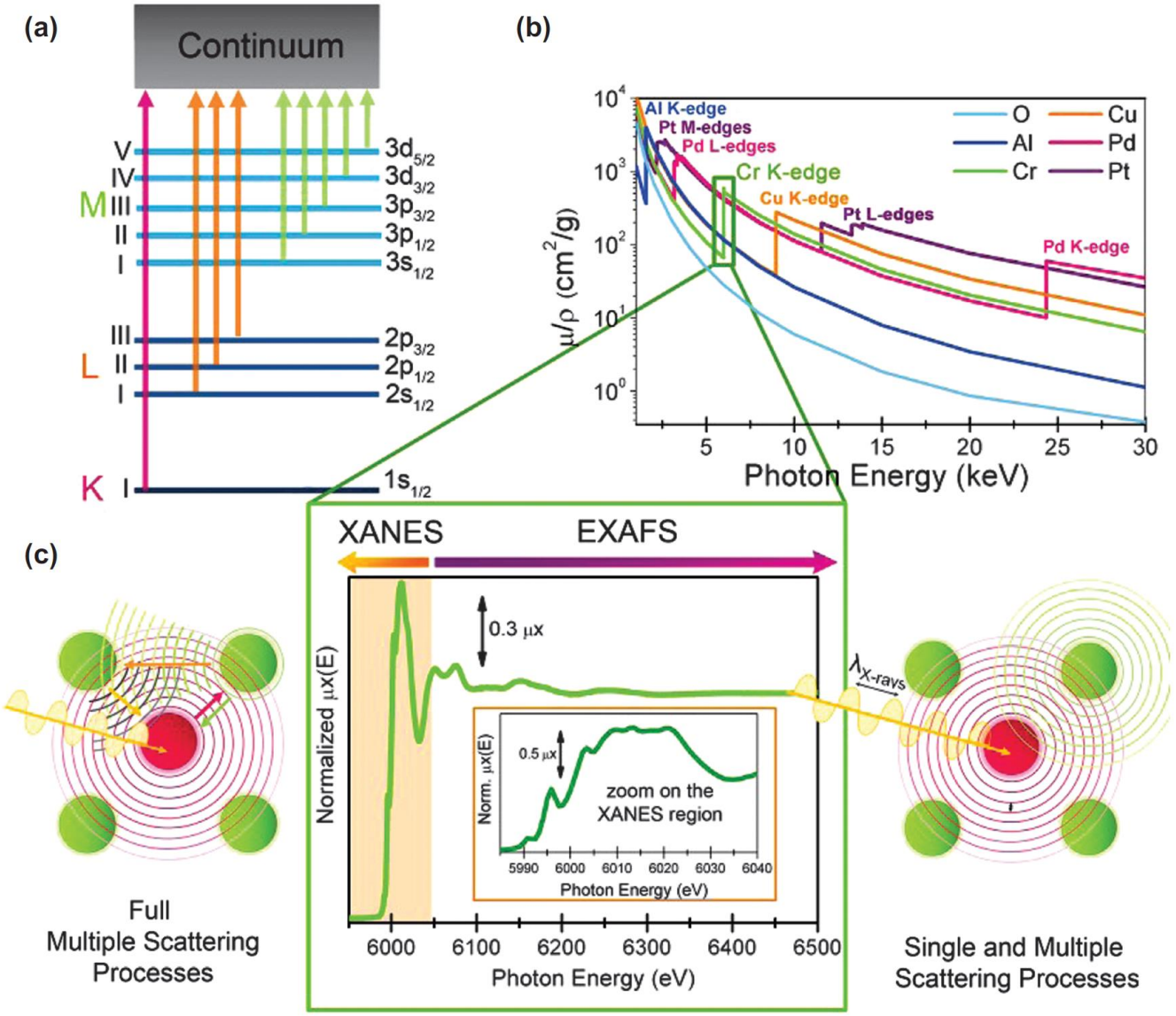
Introduction and overview of XAFS

Anatoly Frenkel

Materials Science and Chemical Engineering,
Stony Brook University
Division of Chemistry, Brookhaven National Laboratory
Synchrotron Catalysis Consortium

Anatoly.Frenkel@stonybrook.edu

Absorption Coefficient and Fine Structure



XANES

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$$

$$H' = \vec{p} \cdot \hat{\varepsilon} e^{i\vec{k}\cdot\vec{r}}$$

$$\rho(r, r', E) = \sum_f |f\rangle\langle f| \, \delta(E_f - E)$$

EXAFS

$$E = E_0 + \frac{p^2}{2m}$$

$$p = \hbar k = \frac{h}{\lambda}$$

$$\psi_f = \psi_{out} + \psi_{sc}$$

$$\psi_{sc} \sim f(k) \frac{e^{ikr_j}}{r_j} \frac{e^{ik|\vec{r} - \vec{r_j}|}}{|\vec{r} - \vec{r_j}|}$$

$$\chi(k) = S_0^2 \sum_i N_i F_i(k) e^{-2\sigma_i^2 k^2} e^{-\frac{2r_i}{\lambda(k)}} \frac{\sin[2kr_i + 2\delta_l(k) + \theta_i(k)]}{kr_i^2}$$

X-ray Absorption Fine Structure (XAFS)

X-ray Absorption Near Edge Structure (XANES)

Near Edge X-ray Absorption Fine Structure (NEXAFS)

Extended X-Ray Absorption Fine Structure (EXAFS)

Information in XAFS data:

- Local atomic geometry
- Identities of nearest neighbors
- Coordination numbers of nearest neighbors
- Interatomic distances relative to the absorber
- Bond length disorder (static and dynamic)
- Charge states of absorbing elements

Different levels of XAFS skill sets ≡ different levels of XAFS short courses

Beginners

- ❑ Synchrotrons, beamlines
- ❑ Sample preparation
- ❑ Fundamentals of XAFS
- ❑ Theory of XANES
- ❑ Theory of EXAFS
- ❑ Basic principles of data analysis: XANES and EXAFS
- ❑ Software demonstration
- ❑ Data analysis practicum
- ❑ Beamline experiments (optional)

Intermediate

- ❑ Fundamentals of XAFS
- ❑ Theory of XANES
- ❑ Theory of EXAFS
- ❑ Software demonstration
- ❑ Multiple scattering
- ❑ Complex systems
- ❑ Disordered systems
- ❑ New developments in analysis
- ❑ New developments in data modeling
- ❑ In situ/operando
- ❑ Data analysis practicum

Advanced

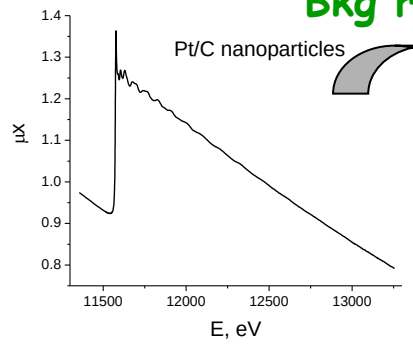
- ❑ MD-EXAFS
- ❑ RMC-EXAFS
- ❑ Wavelet Transform
- ❑ ML-EXAFS
- ❑ HERFD, RIXS
- ❑ Polarization dependence
- ❑ Pre-edge features
- ❑ Software demonstration
- ❑ Data analysis practicum

2023: in person

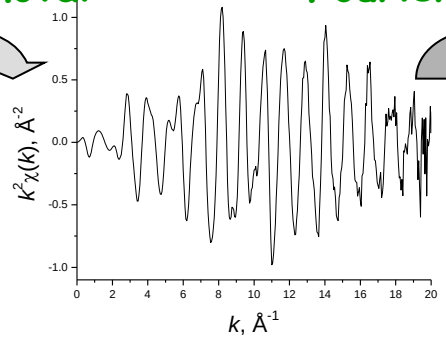
Basic EXAFS data analysis

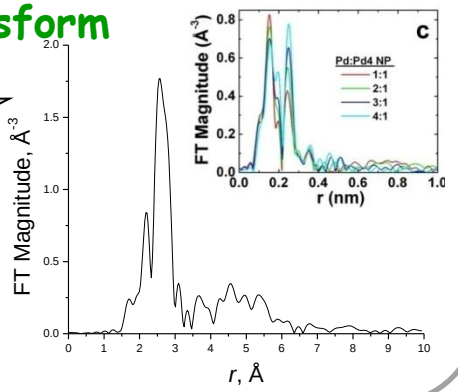
I. Processing and visual examination of the data

Bkg removal



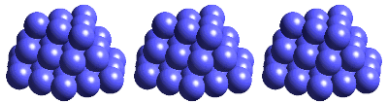
Fourier Transform

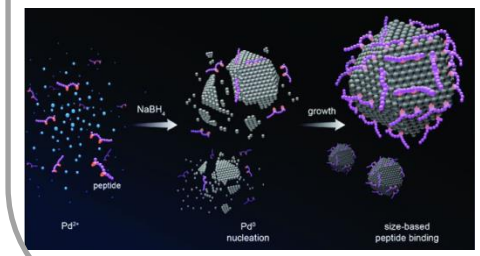




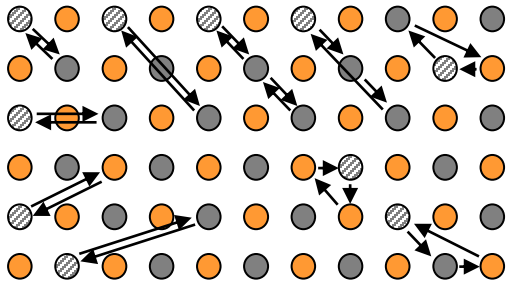
II. Deciding on the model and refinement parameters

Structural modeling
(different for homogeneous and heterogeneous systems)

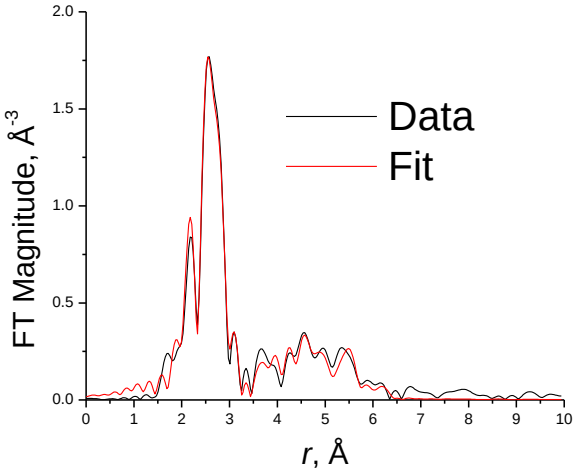




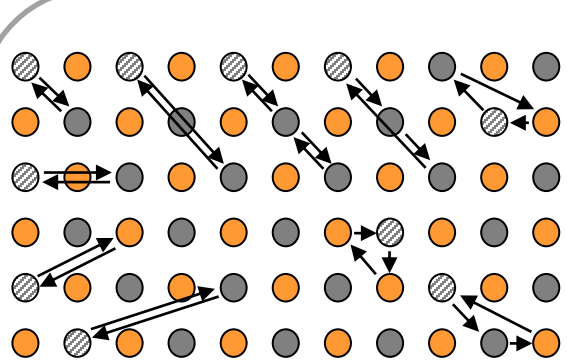
Path expansion and FEFF modeling
f(k), δ(k), λ(k)

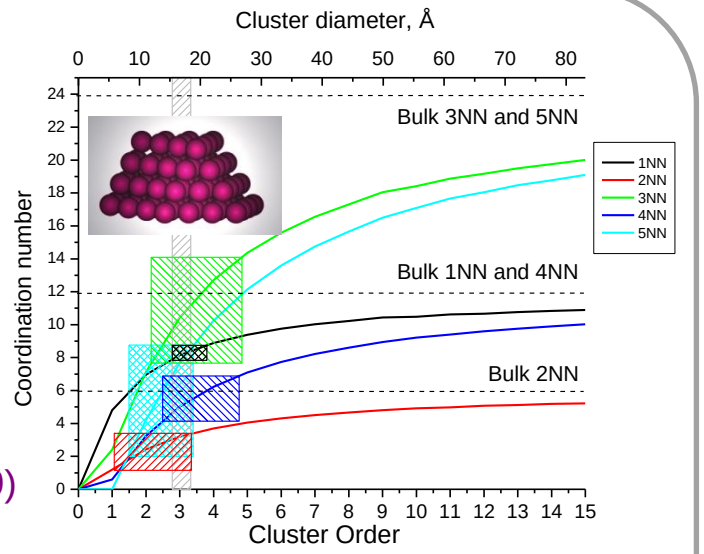


III. Fitting theoretical EXAFS signal to the data



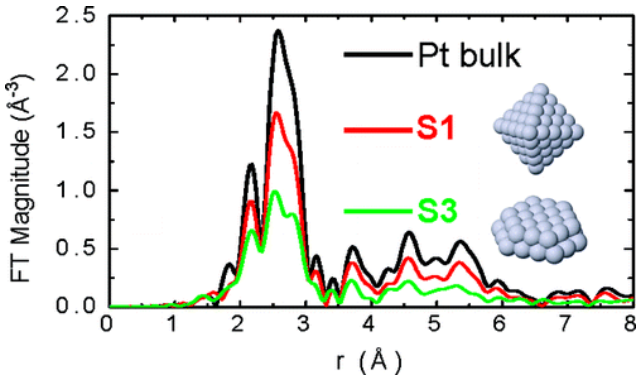
Multiple Scattering (MS) in EXAFS: Nanoparticles



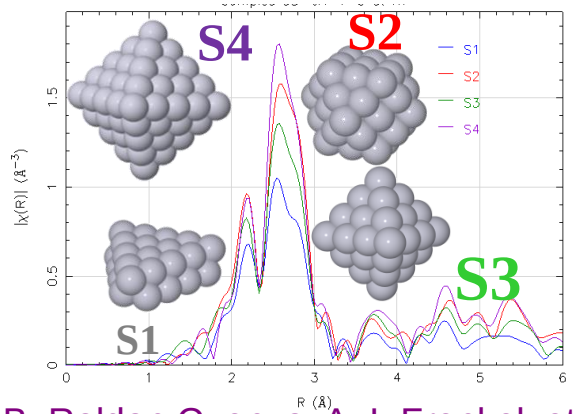


A. I. Frenkel,
J. Synchrotron Rad., **6**, 293 (1999)

A. I. Frenkel, C. W. Hills, and R. G. Nuzzo,
J. Phys. Chem. B **105**, 12689 (2001).



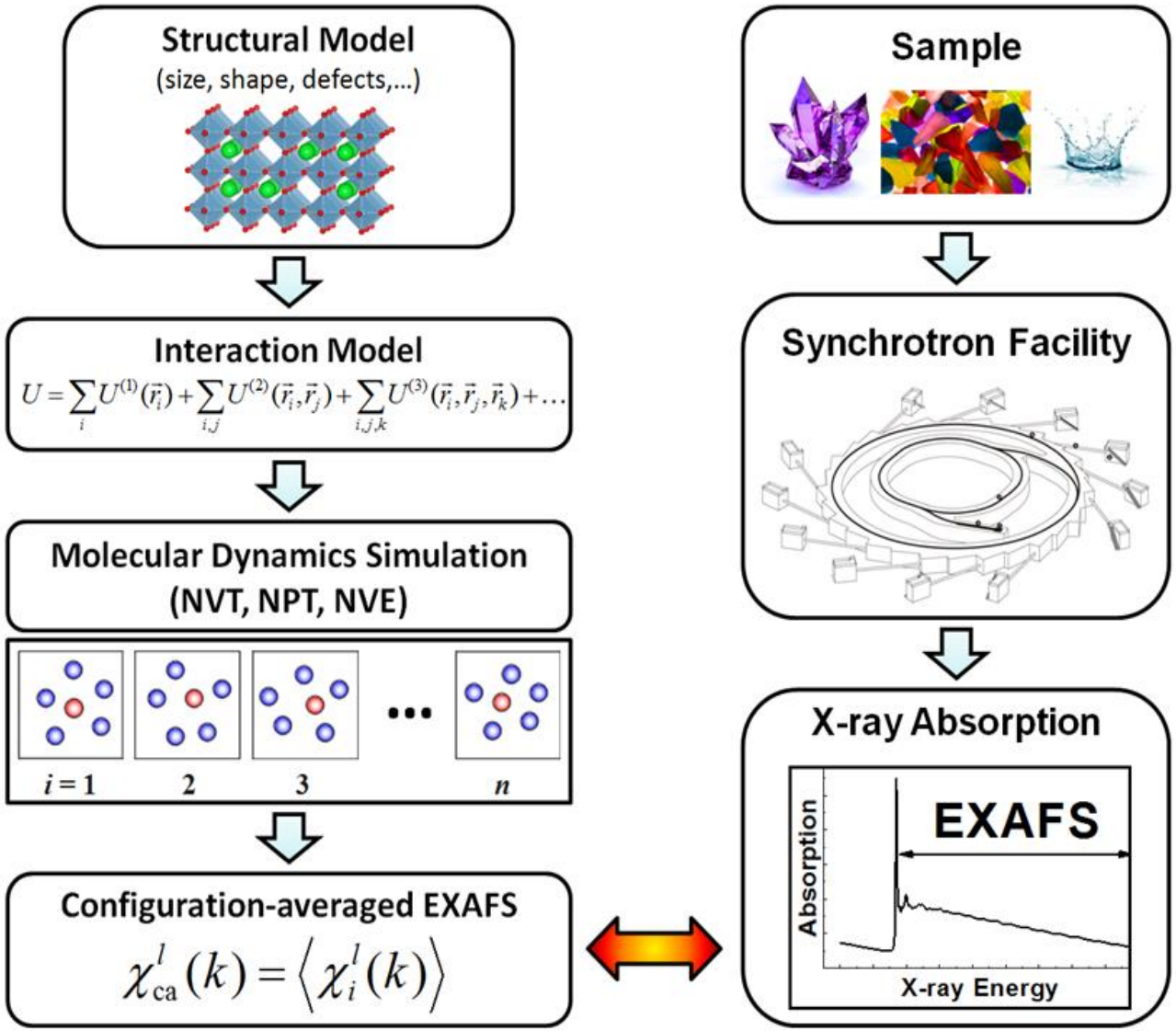
B. R. Cuenya et al,
J. Am. Chem. Soc. **132**, 8747 (2010)



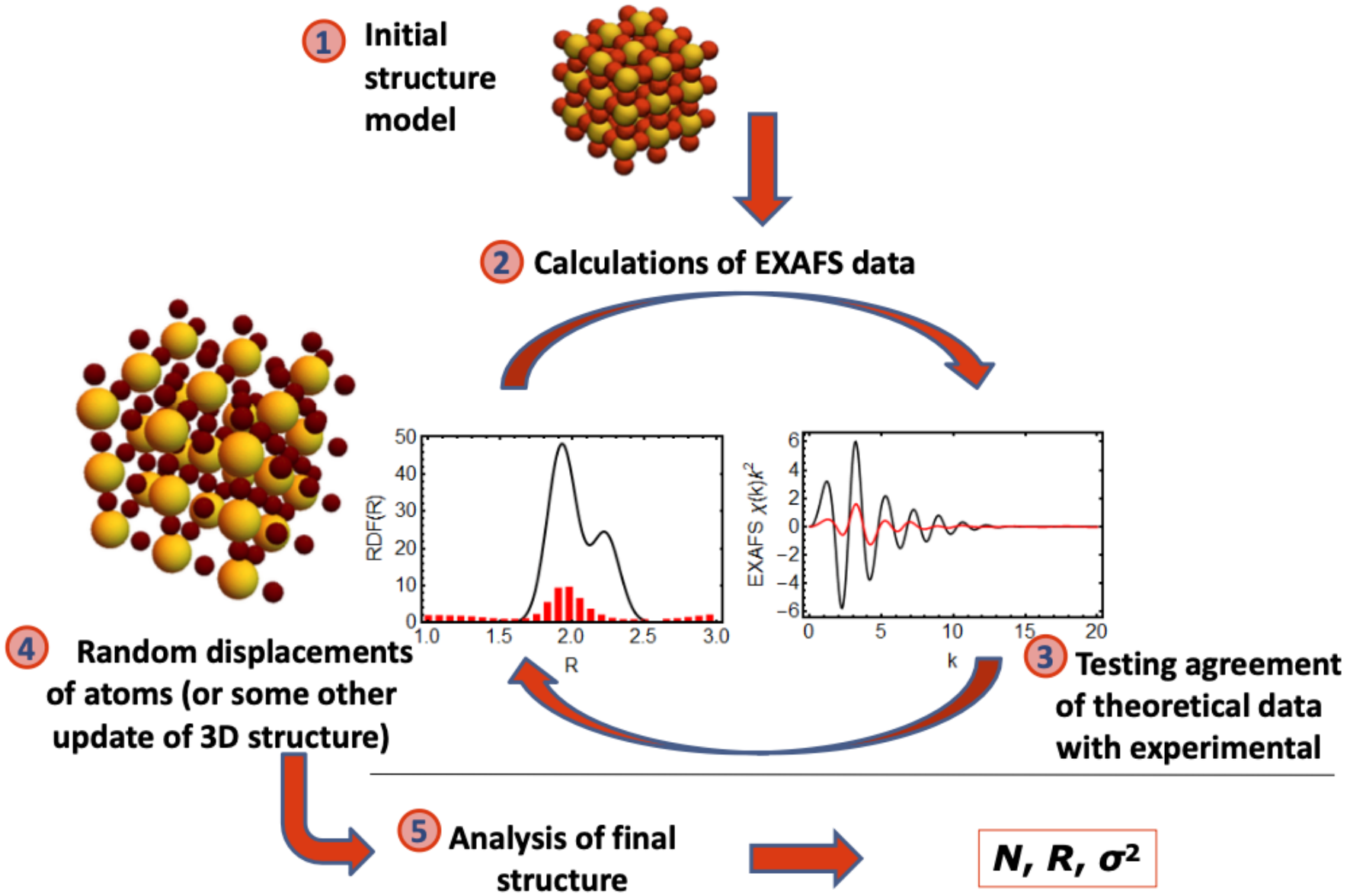
B. Roldan Cuenya, A. I. Frenkel, et al,
Phys. Rev. B. **82**, 155450 (2010)

MS EXAFS: a gateway to advanced analysis:
MD-EXAFS,
RMC-EXAFS,
ML-EXAFS

Advanced analysis: Molecular Dynamics (MD) – EXAFS (A. Kuzmin)



Advanced analysis: Reverse Monte Carlo (RMC) – EXAFS (J. Timoshenko)

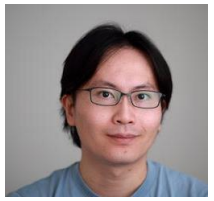


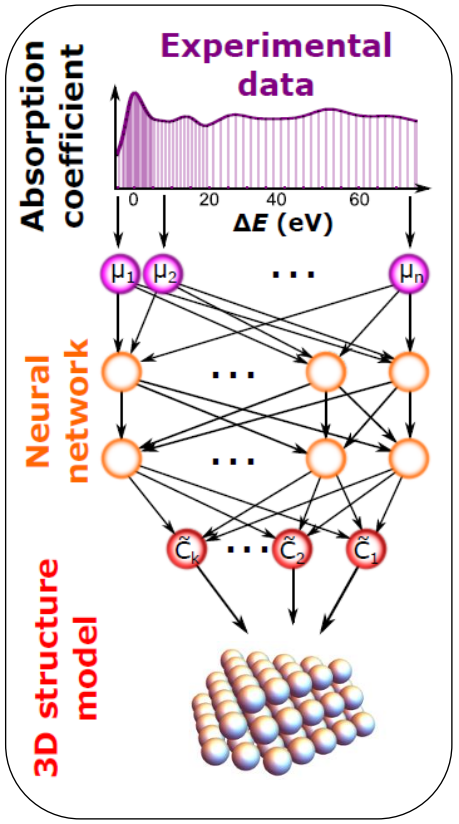
In the last decade: increased interest to XANES for advanced characterization:

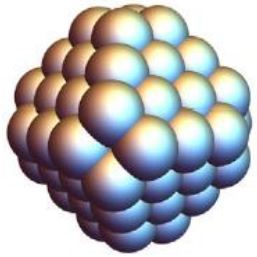
- Machine learning-assisted inversion of XANES
- Speciation of heterogeneous mixtures using XANES

From Spectrum to Structure: using Machine Learning (N. Marcella, P. Routh, R. Shimogawa)

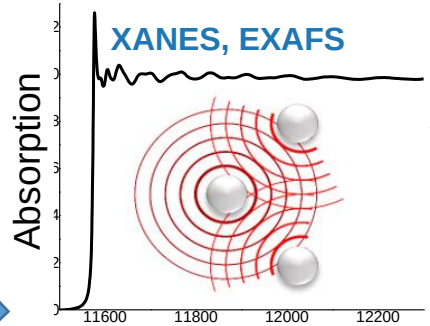


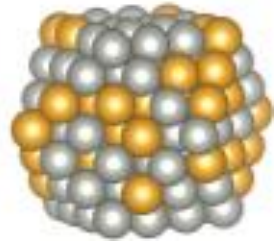


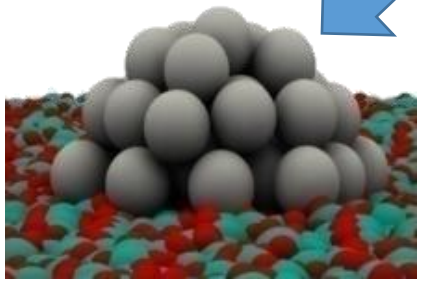


Nanoparticles

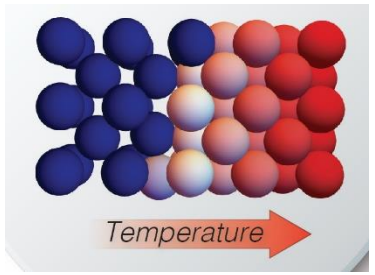




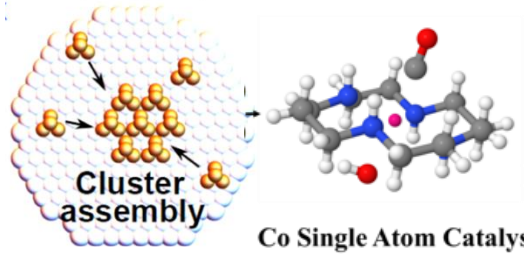
Restructuring of bimetallic catalysts



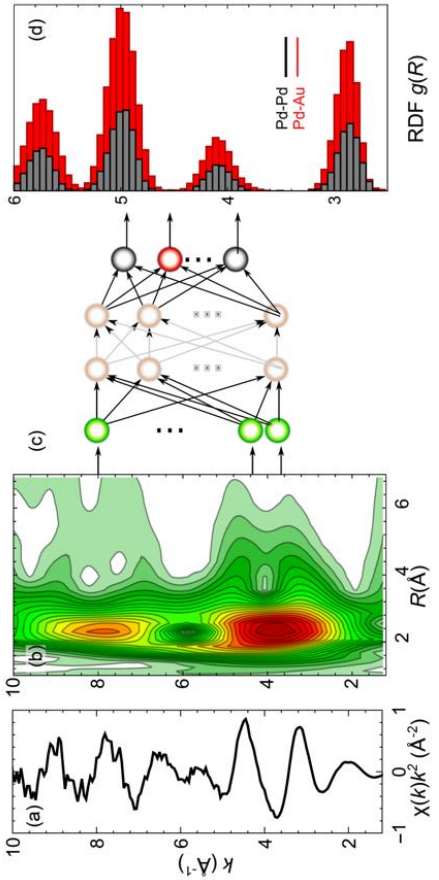
Shape changes

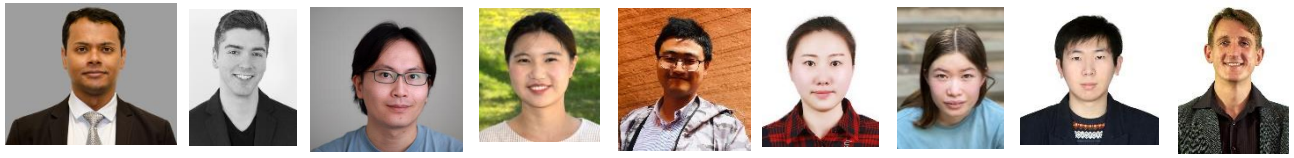


Transformations



Co Single Atom Catalyst



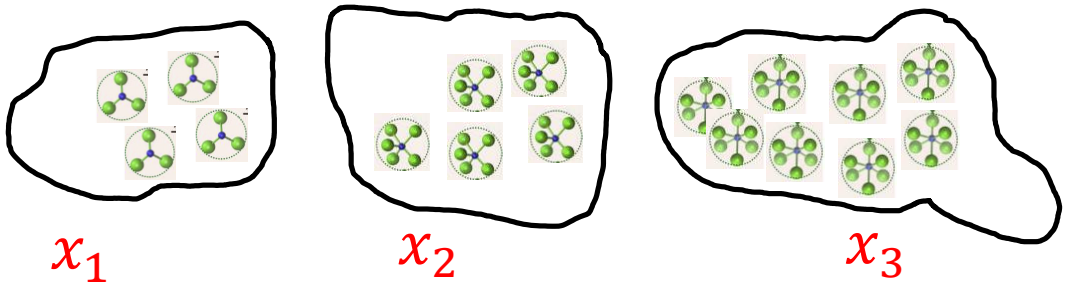


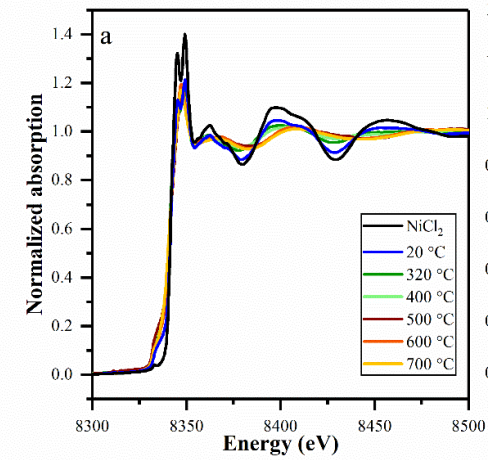
N. Marcella, P. Routh, S. Xiang,
K. Zheng, Y. Xiang, S. D'Halleweyn,
R. Shimogawa, Y. Liu, J. Timoshenko

Speciation of metal complexes (Prahlad Routh)

$$M = x_1 M_1 + x_2 M_2 + x_3 M_3 + \cdots$$
$$x_1 + x_2 + x_3 + \cdots = 1$$

$$\mu(E) = x_1 \mu_1 + x_2 \mu_2 + x_3 \mu_3 + \cdots$$



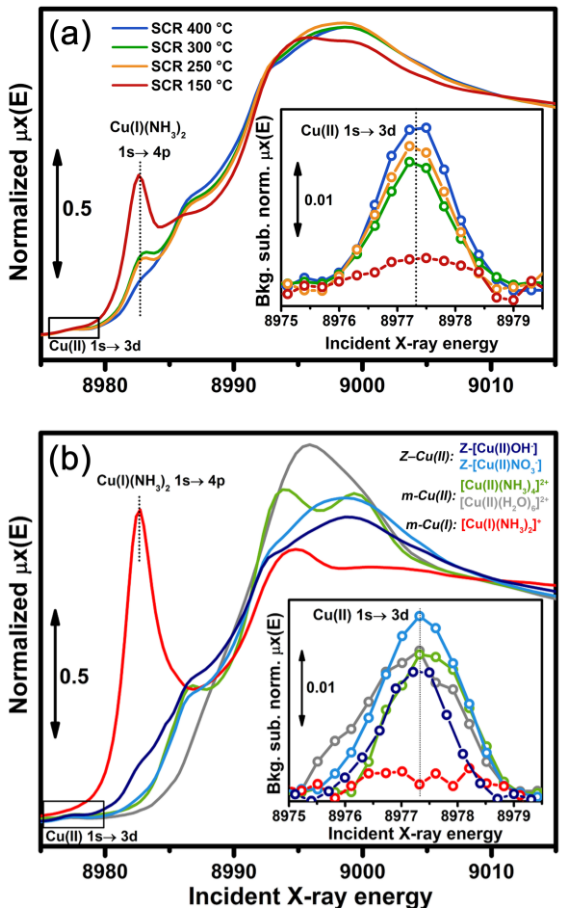


- ❖ Linear combination fitting
- ❖ Principal component analysis
- ❖ MCR-ALS
- ❖ Under development:

MCR-ALS + Machine Learning

Linear Combination Fitting

$$\mu(E) = x_1\mu_1 + x_2\mu_2 + x_3\,\mu_3 + \cdots$$

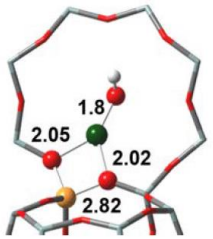
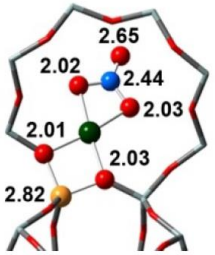
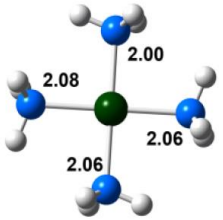
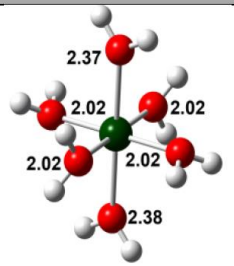
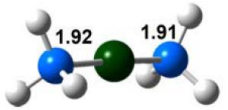


500 ppm NO, 500 ppm NH_3
10% O_2, 5% H_2O

JACS Communication
pubs.acs.org/JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

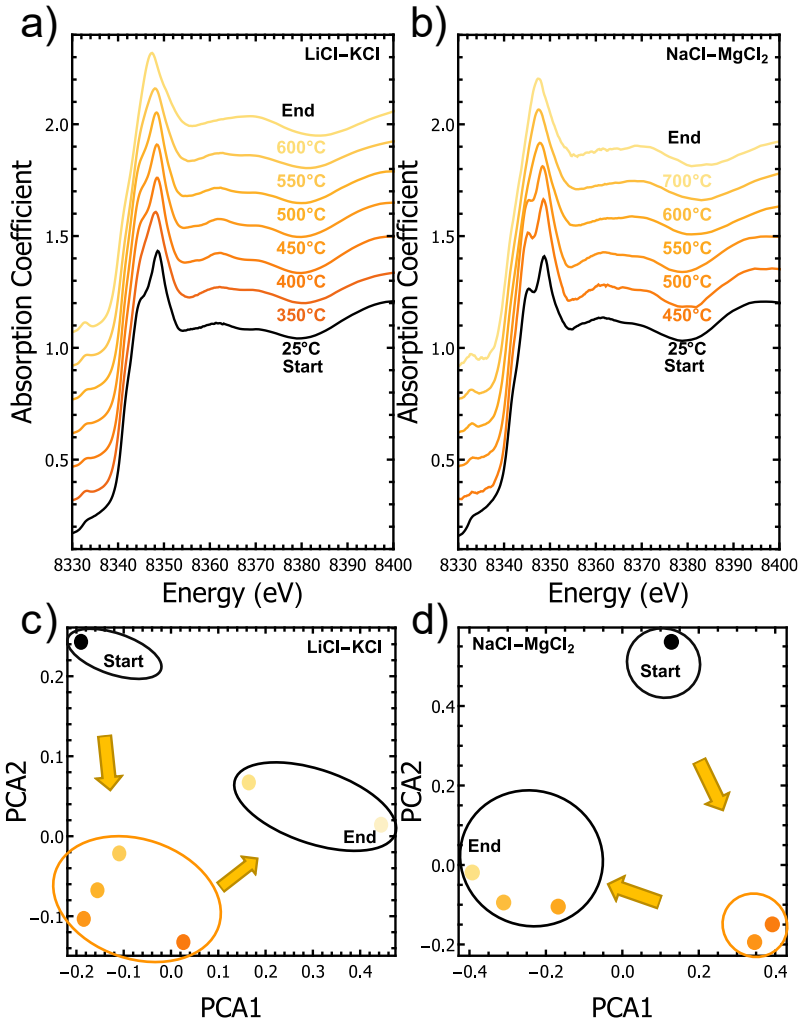
The Cu-CHA deNO$_x$ Catalyst in Action: Temperature-Dependent NH_3-Assisted Selective Catalytic Reduction Monitored by Operando XAS and XES

Kirill A. Lomachenko,[†,‡] Elisa Borfecchia,[*,†] Chiara Negri,[†] Gloria Berlier,[†] Carlo Lamberti,[†,‡] Pablo Beato,[§] Hanne Falsig,[§] and Silvia Bordiga[†]

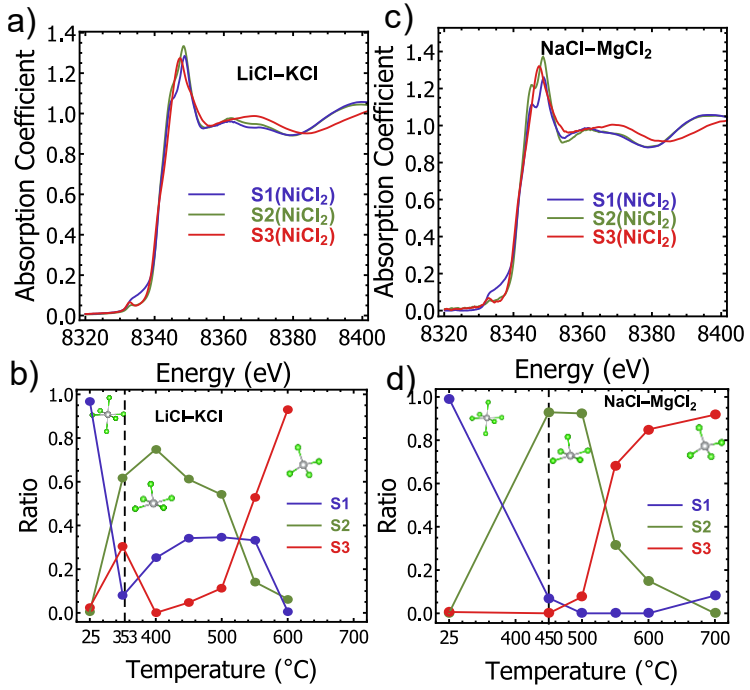
Cu-type	*Z-Cu(II)*		*m-Cu(II)*		*m-Cu(I)*
(Dominant) Cu-species	Z-[Cu(II)OH$^-$]	Z-[Cu(II)NO_3^-](*)	$[Cu(II)(NH_3)_4]^{2+}$	$[Cu(II)(H_2O)_6]^{2+}$(**)	$[Cu(I)(NH_3)_2]^+$
Molecular geometry					
XAS data collection conditions	50%O_2/He 400 °C	1000 ppm NO/10%O_2/He 200 °C	Solution phase RT	Solution phase RT	Solution phase RT
Pertinent Cu-CHA *in situ* states	50%O_2/He 400 °C ca. 80% total Cu	1000 ppm NO/10%O_2/He 200 °C	1200 ppm NH_3/He 200 °C ca.75% total Cu	Hydrated, RT ca. 100% total Cu	1000 ppm NO/ 1200 ppm NH_3/He 200 °C ca. 100 % total Cu

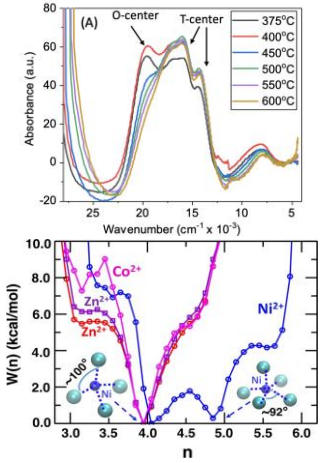
Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS)

$$\mu(E) = x_1\mu_1 + x_2\mu_2 + x_3\,\mu_3 + \cdots$$



- Number of pure species obtained (3, scree test of the PCA)
- Mixing fractions of the unique species and their pure spectra obtained (MCR-ALS)
- Ni-Cl complexes identified (UV-Vis, validation with AIMD)





Information in XAFS data:

- Identities of nearest neighbors
- Local atomic geometry
- Coordination numbers of nearest neighbors
- Interatomic distances relative to the absorber
- Bond length disorder (static and dynamic)
- Charge states of absorbing elements

Materials properties

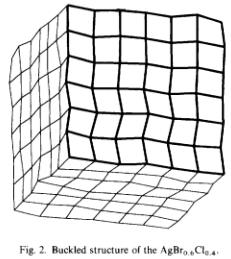
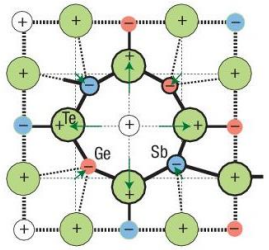


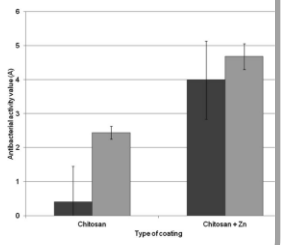
Fig. 2. Buckled structure of the $AgBr_{0.4}Cl_{0.4}$.

Physica B **208 & 209** , 334 (1995).



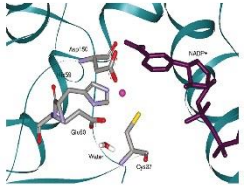
Nature Materials, **3**, 703-708 (2004).

J. Mater. Chemistry **22**, 7028-7035 (2012)

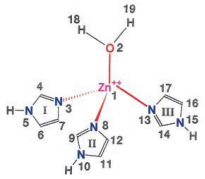


J. Mater. Chem. B **1**, 1968-1976 (2013)

Structural biology

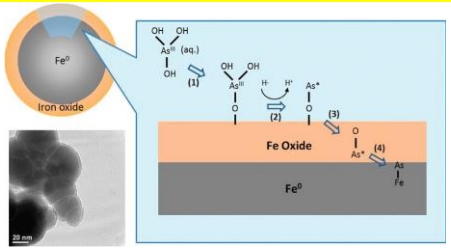


Nat. Struct. Biology, **10** , 98-103 (2003).



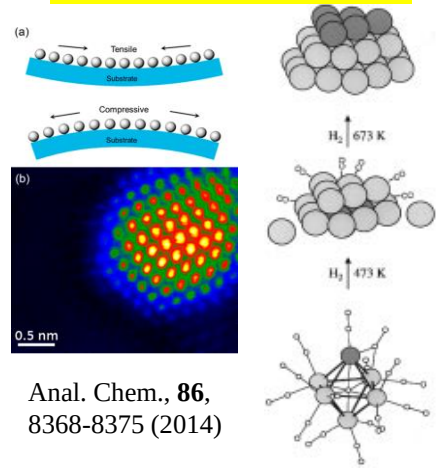
J. Biological Chemistry, **44** , 34335-34343 (2000).

Environmental science



Environ. Sci. Technol. **46**, 7018-7026 (2012)

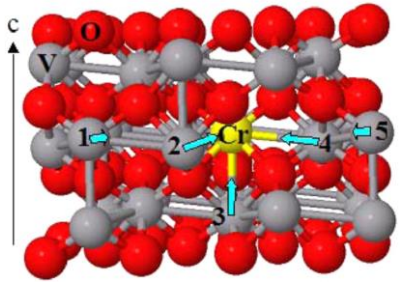
Catalytic mechanisms



Anal. Chem., **86**, 8368-8375 (2014)

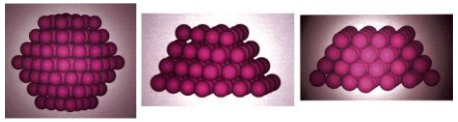
J. Am. Chem. Soc., 120, 1998

Phase transitions

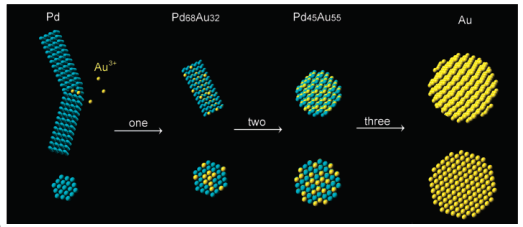


Phys. Rev. Lett. **97**, 195502 (2006).

Nanoparticles

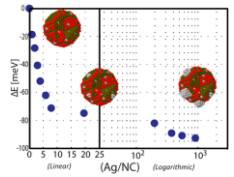


J. Phys. Chem. B, **105,** 12689-12703 (2001).

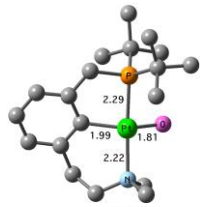


J. Am. Chem. Soc. **130**, 1093-1101 (2008).

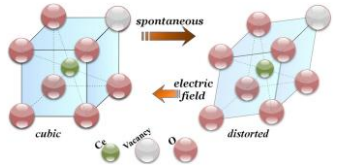
Novel materials



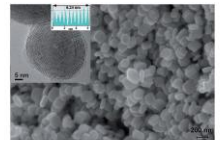
ACS Nano **9**, 10790-10800 (2015)



Nature **255**, 1093-1096, 2008.



App. Phys. Lett.**106**, 042904 (2015)



Angew. Chem. Int. Ed. **51**, 1148-1151 (2012)

Resources

IFEFFIT Mailing List
https://millenia.cars.aps.anl.gov/mailman/listinfo/ifeffit

IXAS: The International X-ray Absorption Society
https://xrayabsorption.org/

SCC: Synchrotron Catalysis Consortium at BNL:
https://you.stonybrook.edu/scc2/

Hands-on session