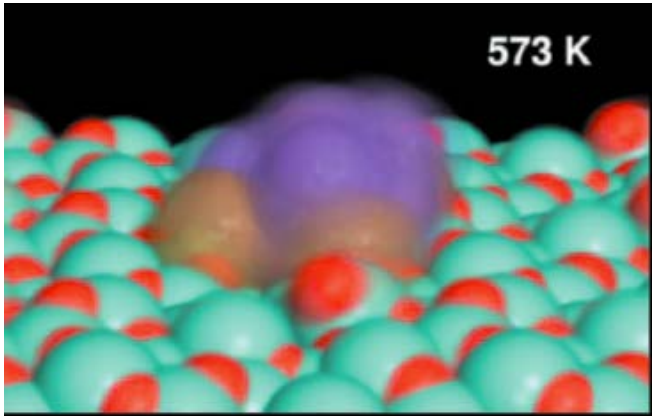
IV. Calculations of X-ray Spectra in Real-space and Real-time

J. J. Rehr



Calculations of X-ray Spectra in Real-space and Real-time

Goal: Real-space, real time Theory of XAS

Talk: Mostly real-time

- I. RT-TDDFT and XAS
- II. Many-body effects – S_0^2 and satellites
- III. Vibrational & non-equilibrium properties

”The real-time formalism

is a gift of god“

W. Kohn

Motivation

Why real-time?

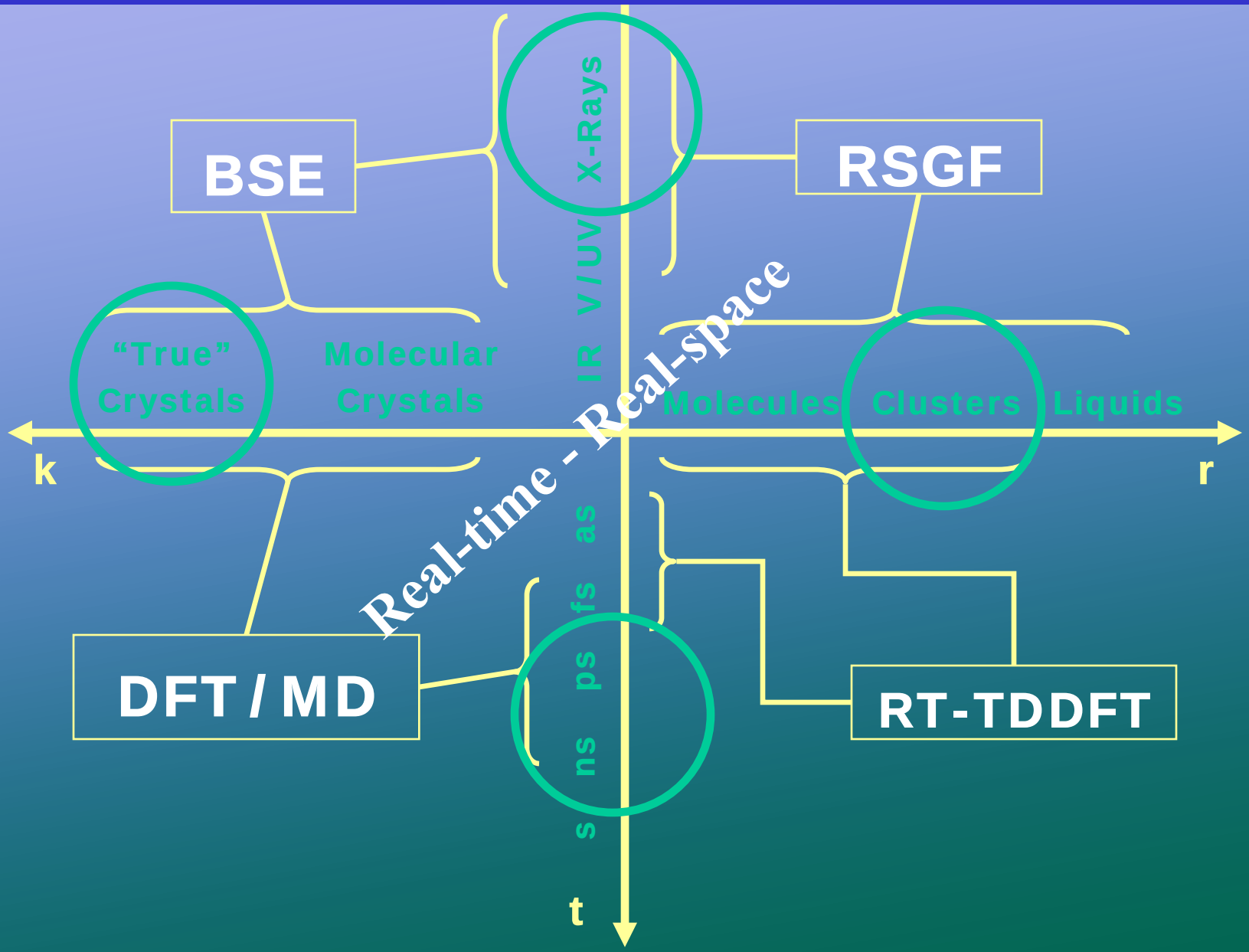
XFEL pulsed x-ray sources (FLASH, LCLS)

Pump-probe experiments

Interest in time-dependent response

Non-equilibrium systems

Theoretical challenge: many length & time-scales



A. Real-time approach for XAS

PHYSICAL REVIEW B 86, 115107 (2012)

Local time-correlation approach for calculations of x-ray spectra

A. J. Lee, F. D. Vila, and J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195, USA
(Received 26 June 2012; published 7 September 2012)

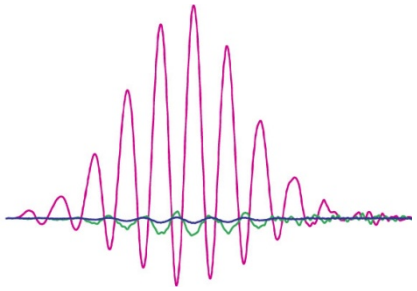
We present a local time-correlation function method for real-time calculations of core level x-ray spectra (RTXS). The approach is implemented in a local orbital basis using a Crank-Nicolson time-evolution algorithm applied to an extension of the SIESTA code, together with projector augmented wave (PAW) atomic transition matrix elements. Our RTXS is formally equivalent to ΔSCF (Δ self consistent field) Fermi's golden rule calculations with a screened core-hole and an effective independent particle approximation. Illustrative calculations are presented for several molecular and condensed matter systems and found to be in good agreement with experiment. The method can also be advantageous compared to conventional frequency-space methods.

Time-correlation function formalism

$$\mu(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} G_c(t)\langle\psi(t)|\psi(0)\rangle\theta(\omega+\epsilon_c-E_F). \qquad (1)$$

Equivalent to single-particle Fermi golden rule

Real-time engine: RT-TDDFT



THE JOURNAL OF CHEMICAL PHYSICS **127**, 154114 (2007)

Real-time time-dependent density functional theory approach for frequency-dependent nonlinear optical response in photonic molecules

Y. Takimoto, F. D. Vila, and J. J. Rehr[a)]
Department of Physics, University of Washington, Seattle, Washington 98195, USA

(Received 11 July 2007; accepted 4 September 2007; published online 19 October 2007)

We present *ab initio* calculations of frequency-dependent linear and nonlinear optical responses based on real-time time-dependent density functional theory for arbitrary photonic molecules. This approach is based on an extension of an approach previously implemented for a linear response using the electronic structure program SIESTA. Instead of calculating excited quantum states, which can be a bottleneck in frequency-space calculations, the response of large molecular systems to time-varying electric fields is calculated in real time. This method is based on the finite field approach generalized to the dynamic case. To speed the nonlinear calculations, our approach uses Gaussian enveloped quasimonochromatic external fields. We thereby obtain the frequency-dependent second harmonic generation $\beta(-2\omega;\omega,\omega)$, the dc nonlinear rectification $\beta(0;-\omega,\omega)$, and the electro-optic effect $\beta(-\omega;\omega,0)$. The method is applied to nanoscale photonic nonlinear optical molecules, including *p*-nitroaniline and the FTC chromophore, i.e., 2-[3-Cyano-4-(2-{5-[2-(4-diethylamino-phenyl)-vinyl] - thiophen-2-yl} - vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile, and yields results in good agreement with experiment.

*K. Yabana and G. F. Bertsch, Phys. Rev. B **54**, 4484 1996.

RT-TDDFT Formalism

- **Yabana and Bertsch** Phys. Rev. B **54**, 4484 (1996)

$$i\frac{\partial \Psi}{\partial t} = H(t)\,\Psi \qquad H = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r},t) + V_H[\rho](\mathbf{r},t) + V_{xc}[\rho](\mathbf{r},t)$$

- Direct numerical integration of TD Kohn-Sham equations

$$\Psi(t) = T\,\exp\left(-i\int_0^t H(t')dt'\right)\Psi(0)$$

- The response to external field is determined by applying a **time-dependent electric field** $\Delta H(t) = -\boldsymbol{E}(t)\cdot\boldsymbol{x}$.

- Optical properties determined from **total dipole moment**:

$$\mathbf{p}(t) = \int \rho(\mathbf{r},t)\,\mathbf{r}\,d^3\mathbf{r}$$

Can be more powerful and more EFFICIENT than Frequency space

Numerical Real-time Evolution

$$|\psi(t)\rangle = \sum_j |j\rangle c_j(t) \equiv \boldsymbol{c(t)}$$

- Ground state density ρ_0, **overlap matrix *S*,** and ***H(t)*** at each time-step evaluated with SIESTA

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)c(t)$$

Coefficients of Orbitals

- Crank-Nicholson time-evolution: **unitary**, **time-reversible**

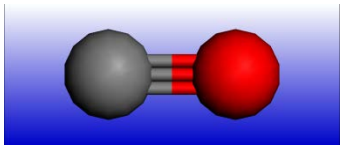
Stable for long time-steps !

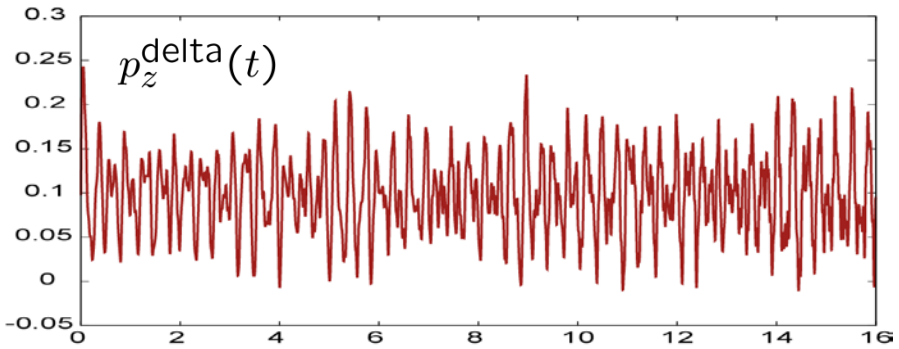
$$c(t+\Delta t) = \frac{1 - iS^{-1}H(\bar{t})\Delta t/2}{1 + iS^{-1}H(\bar{t})\Delta t/2}c(t) + \mathcal{O}(\Delta t^2), \quad \boldsymbol{\bar{t} = t + \Delta t/2}$$

- Adiabatic GGA exchange-correlation (PBE) functional

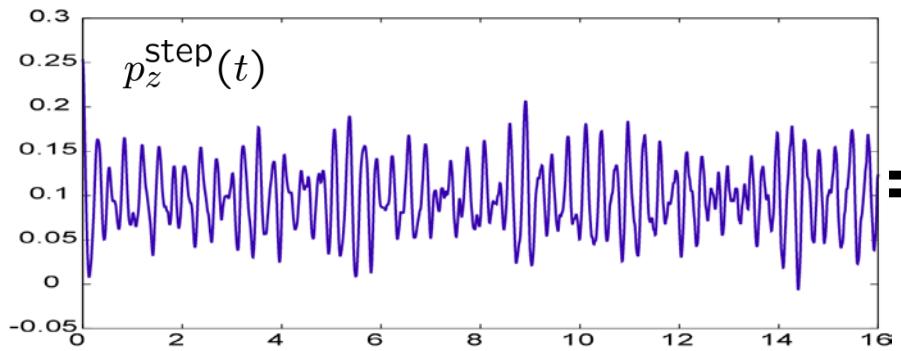
Example: CO molecule Linear Response

- Delta Function
  (Unit Impulse at *t=0*)

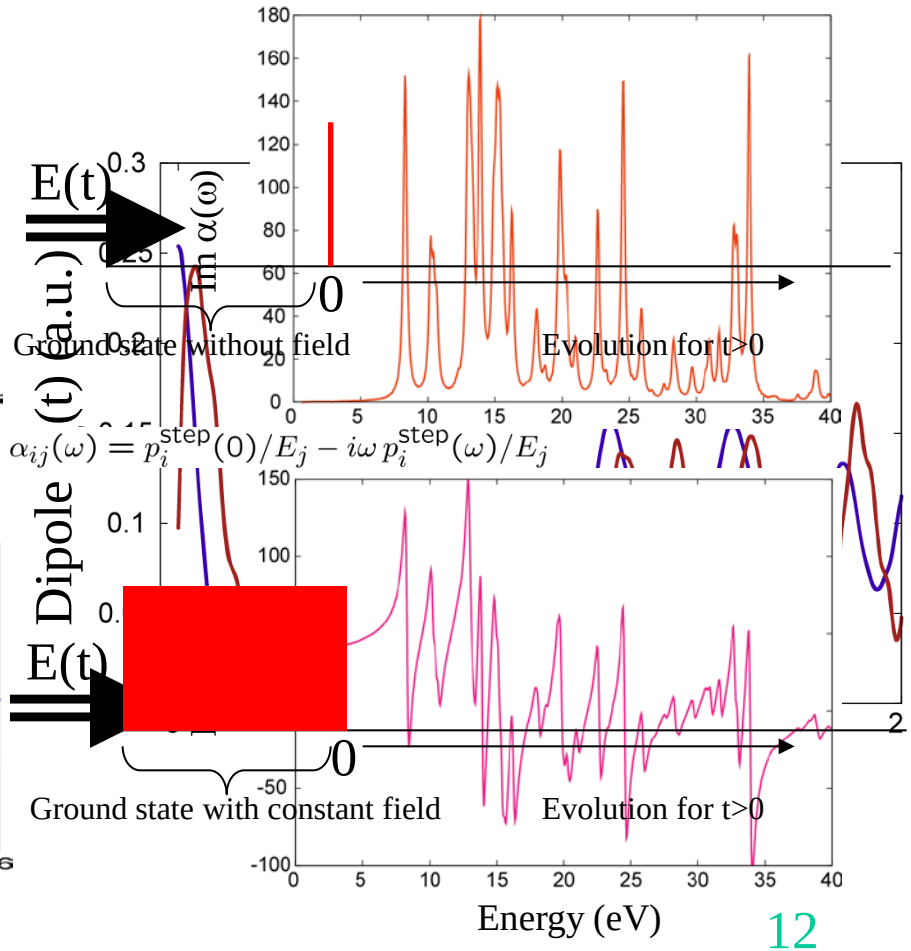




(Turn-off Constant E at *t=0*)

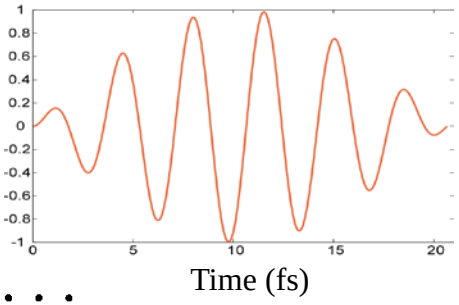


$\alpha_{ij}(\omega) = p_i^{\mathrm{delta}}(\omega)/E_j$



Shaped pulses and non-linear response

- Nonlinear expansion in field *E(t)* including time lag in response



$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

$$\begin{aligned} p_i(t) = \quad & \mu_i^0 + \int dt_1\, \chi_{ij}^{(1)}(t-t_1)E_j(t_1) \\ & + \int dt_1 \int dt_2\, \chi_{ijk}^{(2)}(t-t_1, t-t_2)E_j(t_1)E_k(t_2) \\ & + \int dt_1 \int dt_2 \int dt_3\, \chi_{ijkl}^{(3)}(t-t_1, t-t_2, t-t_3)E_j(t_1)E_k(t_2)E_l(t_3) \\ & + \cdots \end{aligned}$$

¿ **How to invert the equation for nonlinear response ?**

Shaped pulses and non-linear polarizability

- Define $\boldsymbol{E_j(t) = F(t)E_j}$ and response $p_i(E)$

$$p_i(t) = \mu_i^0 + p_{ij}^{(1)}(t)E_j + p_{ijk}^{(2)}(t)E_jE_k + \cdots$$

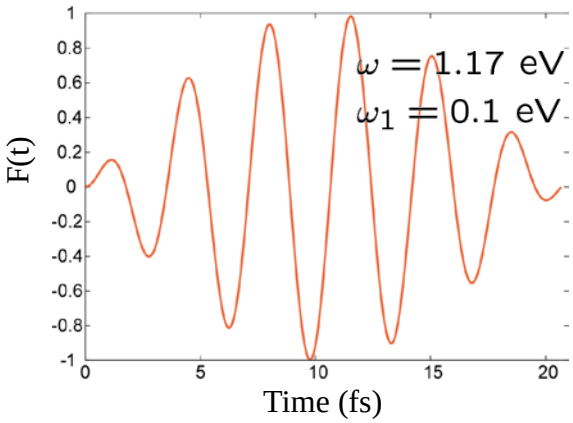
where $p^{(1)}$ represents linear response, $p^{(2)}$ non-linear quadratic response, ….

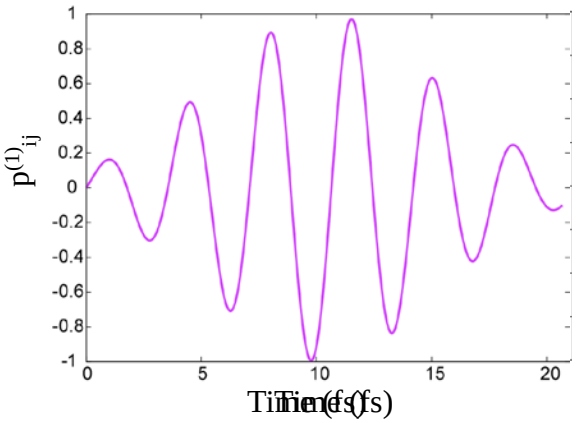
- Quadratic response function $\chi^{(2)}$

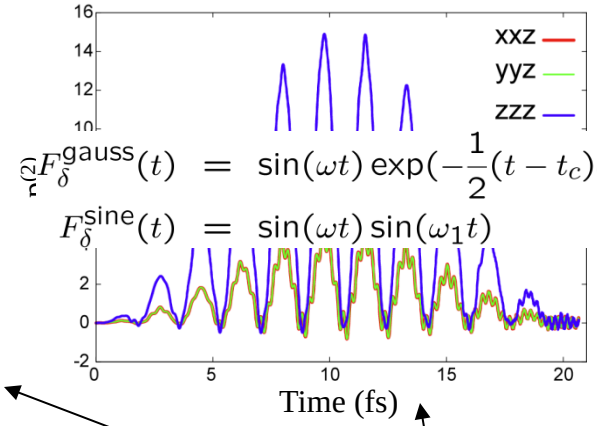
$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \; \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$

Shaped pulses and non-linear response $F_\delta(t)$

- Sine wave enveloped by another sine wave or Gaussian

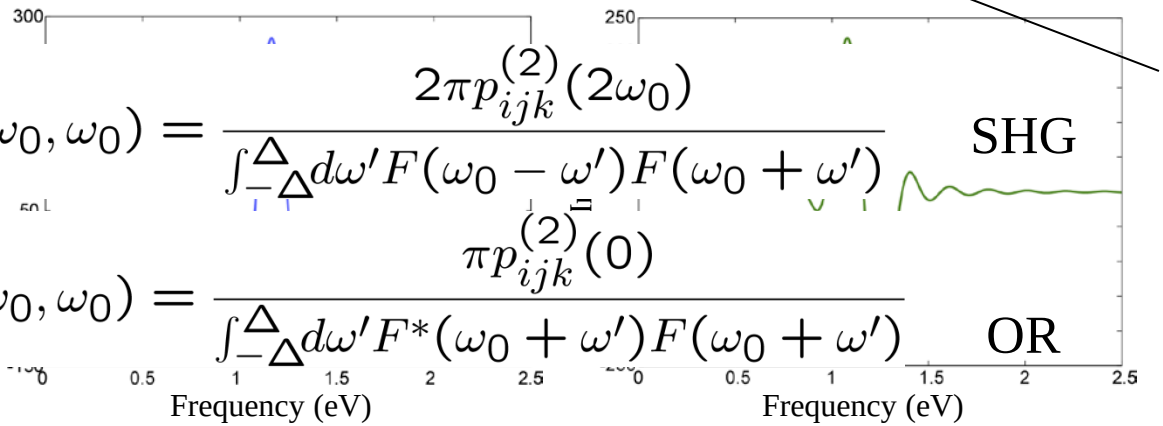






$$\chi^{(2)}_{ijk}(-2\omega_0;\omega_0,\omega_0) = \frac{2\pi p^{(2)}_{ijk}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0-\omega')F(\omega_0+\omega')} \quad \text{SHG}$$

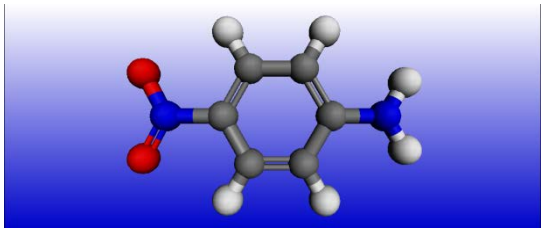
$$\chi^{(2)}_{ijk}(0;-\omega_0,\omega_0) = \frac{\pi p^{(2)}_{ijk}(0)}{\int_{-\Delta}^{\Delta} d\omega' F^*(\omega_0+\omega')F(\omega_0+\omega')} \quad \text{OR}$$

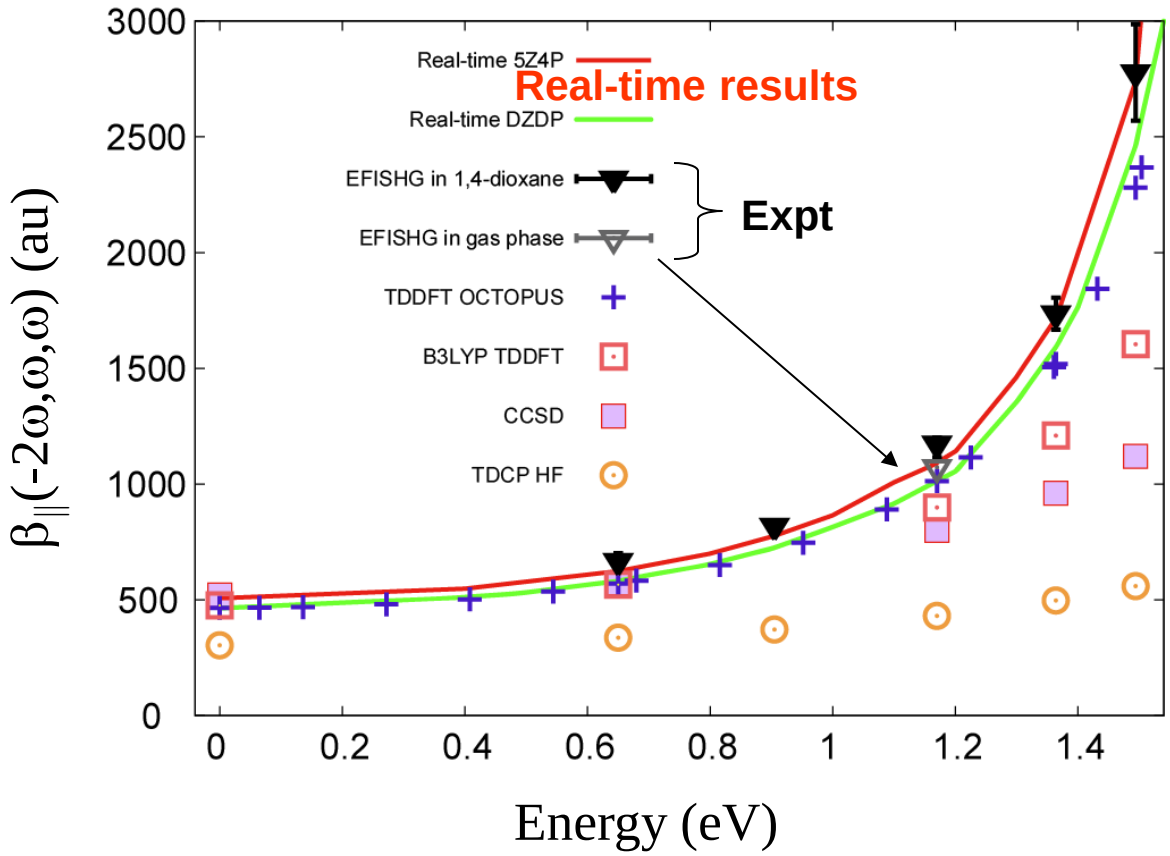


Linear and Nonlinear response of CO

Example: non-linear SHG in pNA

- Comparison with other methods





Application to XAS: RTXS Equations

XAS Absorption Fermi golden rule, ΔSCF, FSR)

$$\mu(\omega) = \sum_k |\langle c|d|k\rangle|^2 \delta_\Gamma(\omega + \varepsilon_c - \varepsilon_k)\theta(E - E_F)$$

FT

$$\mu(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} G_c(t)\langle\psi(t)|\psi(0)\rangle\theta(\omega + \varepsilon_c - E_F)$$

Core Hole Green's Function

$$G_c(t) = i\exp[i(\varepsilon_c + i\Gamma)t]$$

Autocorrelation Function

$$\langle\psi(t)|\psi(0)\rangle = \sum_{jj'}\langle c|d^\dagger|j\rangle U_{jj'}(t,0)\langle\tilde{j}'|d|c\rangle$$

$$\langle\psi(0)|\psi(t)\rangle \begin{cases} |\psi(0)\rangle = d|c\rangle \\ |\psi(t)\rangle = U(t,0)|\psi(0)\rangle \end{cases}$$

$$U(t,0) = T\exp\left[-i\int_0^t dt\, H(t)\right]$$

Crank-Nicolson RT-TDDFT

$$|\psi(t)\rangle = \sum_j |j\rangle c_j(t)$$

$$\bar{t} = t + \Delta/2 \qquad \mathbf{U}(t+\Delta,t) = \frac{\mathbf{1} - \mathbf{S}^{-1}\mathbf{H}(\bar{t})\Delta/2}{\mathbf{1} + \mathbf{S}^{-1}\mathbf{H}(\bar{t})\Delta/2}$$

$$H_{jj'} = \langle j|h_H + v_{ch} + \Sigma|j'\rangle$$

Interpretation of correlation function

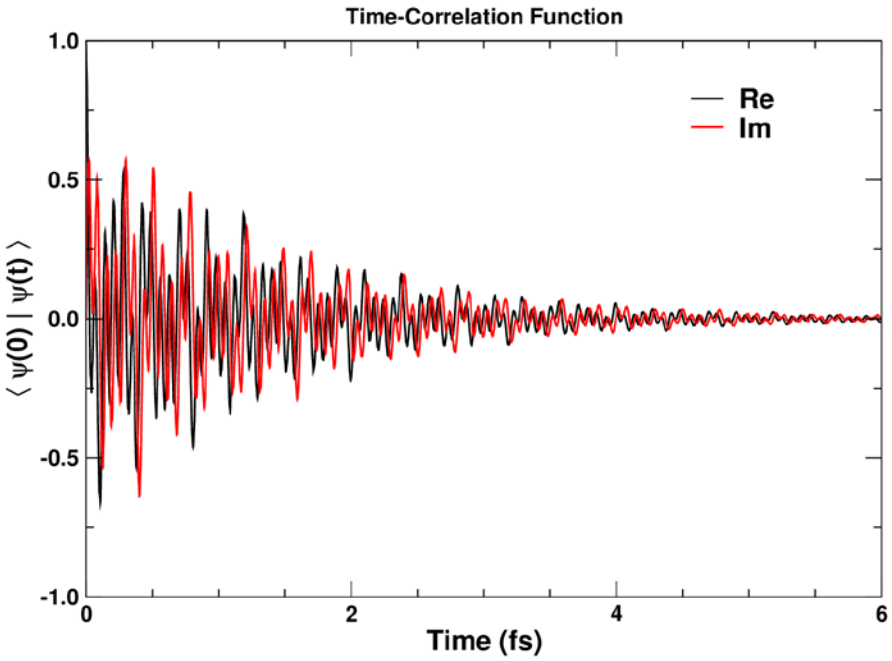
*p*DOS = *FT* of $\langle\psi(0)|\psi(t)\rangle$ for seed state $|\psi(0)\rangle$

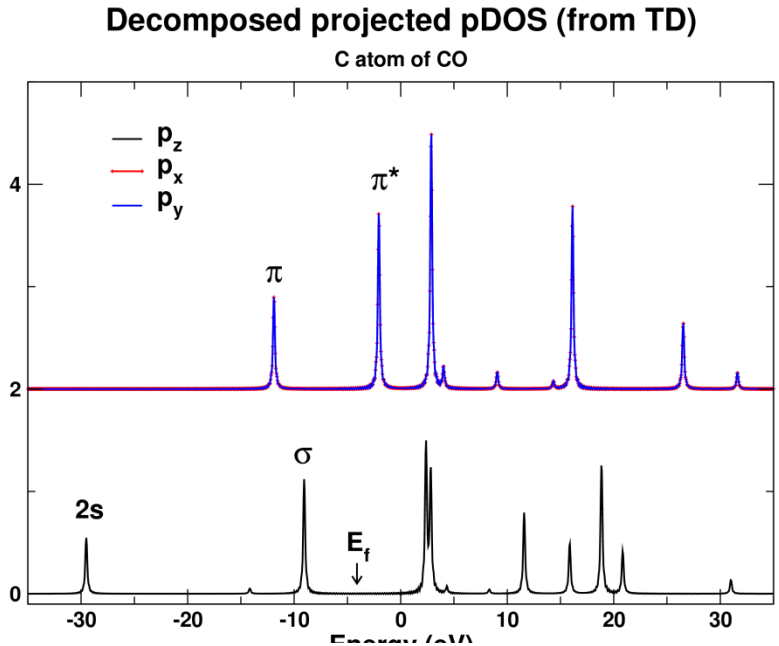
$$\rho_\psi(\omega) = -\frac{1}{\pi|\psi|^2|}\,\mathrm{Im}\int_0^\infty dt\, e^{i\omega t}\langle\psi(t)|\psi(0)\rangle$$

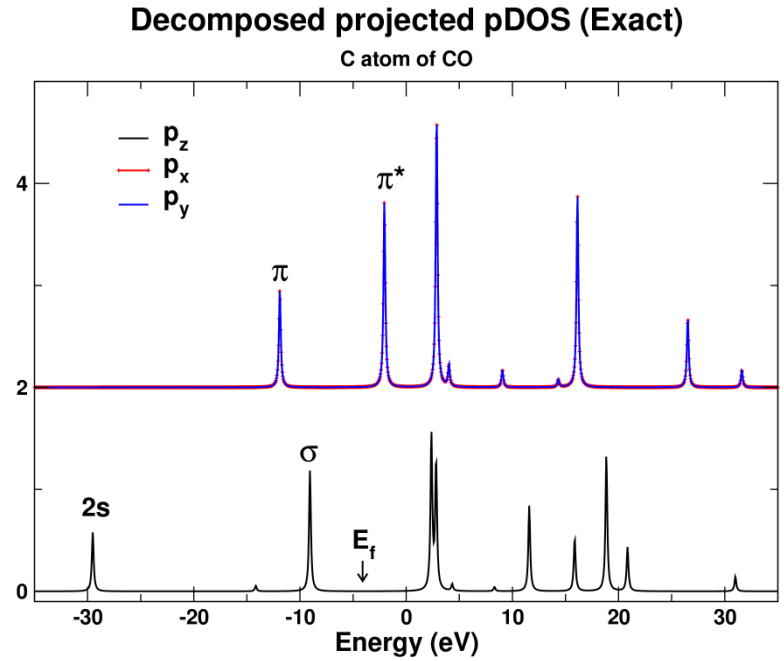
$$|\psi_+(0)\rangle \equiv \mathcal{P}\,|\psi(0)\rangle = \mathcal{P}\,d(x)|c\rangle$$

Example

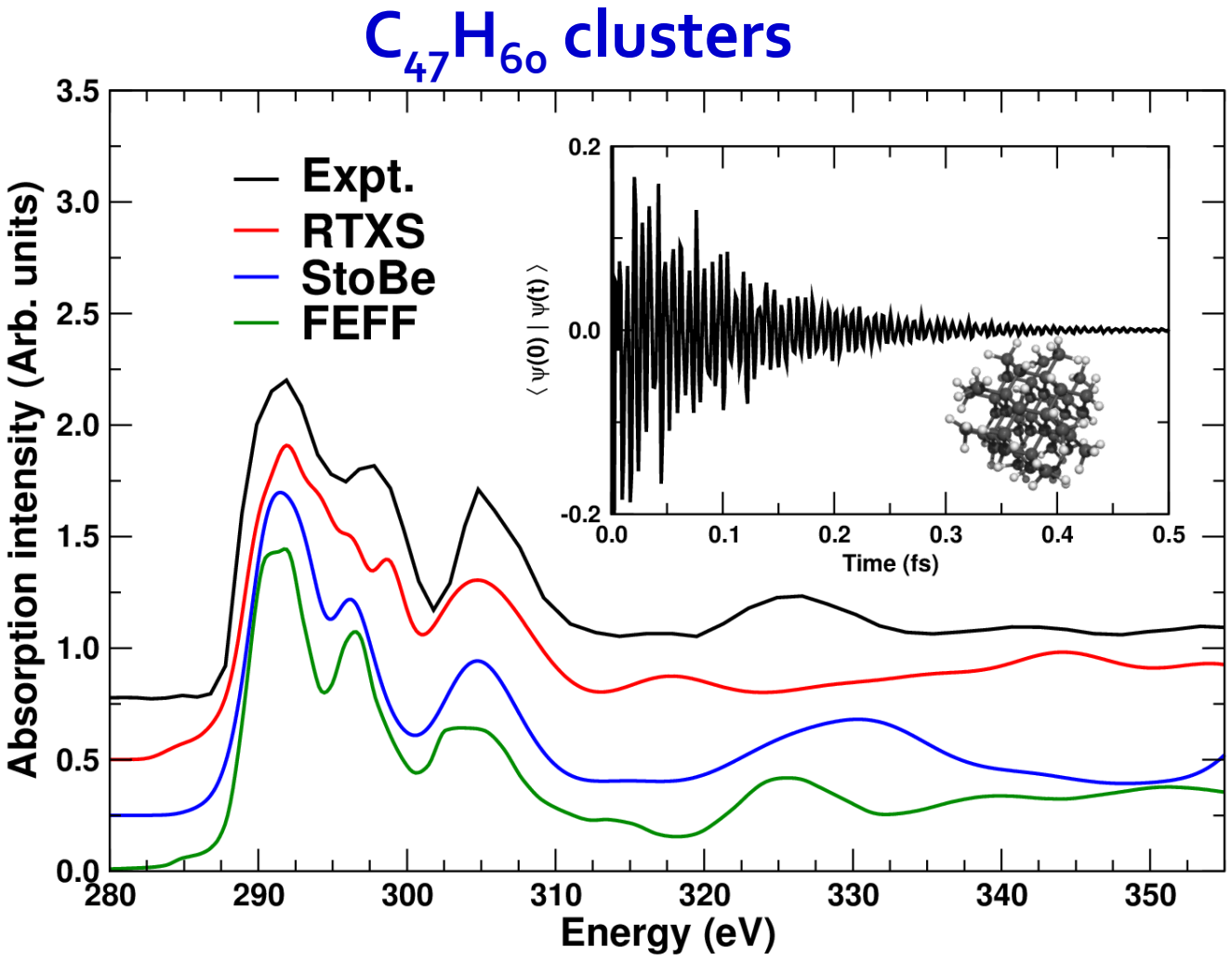
C K-edge of CO







Example: C K-edge XAS of Diamond cluster



B. Real-time approach for many-body effects

1. Intrinsic losses - due to sudden core-hole

Formalism: Cumulant expansion for core-hole Green's function

$$G_c^+(t) = e^{i\epsilon_c t} e^{C(t)} \theta(t)$$

Many body effects implicit in **"cumulant"** ***C(t)***

*D. Langreth Phys Rev B 1, 471 (1970)

Reviews and references

J. Phys.: Condens. Matter 11 (1999) R489–R528

On correlation effects in electron spectroscopies and the *GW* approximation

Lars Hedin

Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden

THE JOURNAL OF CHEMICAL PHYSICS **143**, 184109 (2015)

Dynamical effects in electron spectroscopy

Jianqiang Sky Zhou,[1,2,a)] J. J. Kas,[2,3] Lorenzo Sponza,[4] Igor Reshetnyak,[1,2] Matteo Guzzo,[5] Christine Giorgetti,[1,2] Matteo Gatti,[1,2,6] Francesco Sottile,[1,2] J. J. Rehr,[2,3] and Lucia Reining[1,2]

[1]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM-IRAMIS, Université Paris-Saclay, F-91128 Palaiseau, France*

[2]*European Theoretical Spectroscopy Facility (ETSF)*

[3]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*

[4]*Department of Physics, King's College London, London WC2R 2LS, United Kingdom*

[5]*Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany*

[6]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette, France*

Cumulant expansion properties

$$G_k(t) = e^{i\epsilon_k^0 t} e^{C(t)}$$

$$C(t) = \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2}$$

Landau formula for $C(t)$

Excitation spectra $\beta_k(\omega) = \frac{1}{\pi} |\mathrm{Im}\, \Sigma_k(\omega + \epsilon_k)|$

GW Σ

Spectral Function

$$A_k(\omega) = \int \frac{dt}{2\pi} e^{i(\omega - \epsilon_k)t} \exp\left\{ \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2} \right\}$$

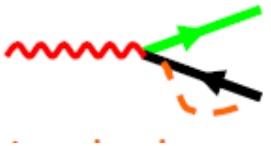
*For diagrammatic expansion of higher order terms, see e.g.
O. Gunnarsson et al., Phys. Rev. B **50**, 10462 (1994)

Intrinsic losses: CT excitations RT-TDDFT cumulant

PHYSICAL REVIEW B **91**, 121112(R) (2015)

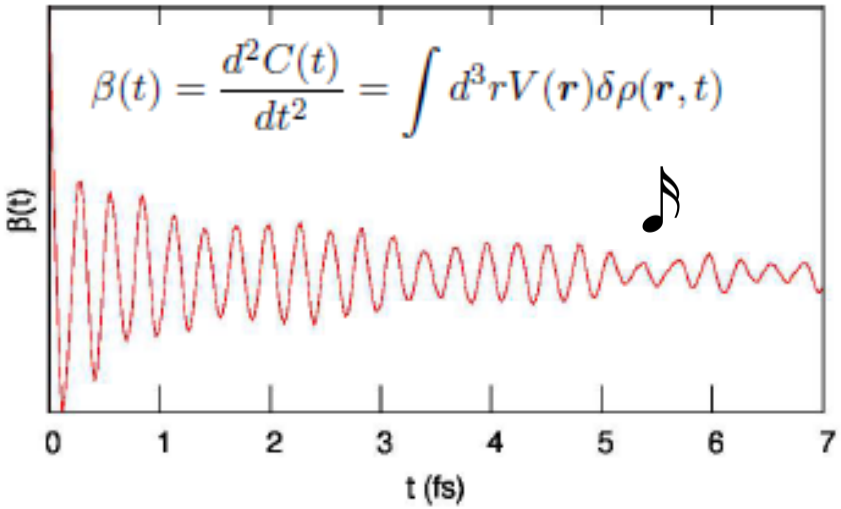
Real-time cumulant approach for charge-transfer satellites in x-ray photoemission spectra

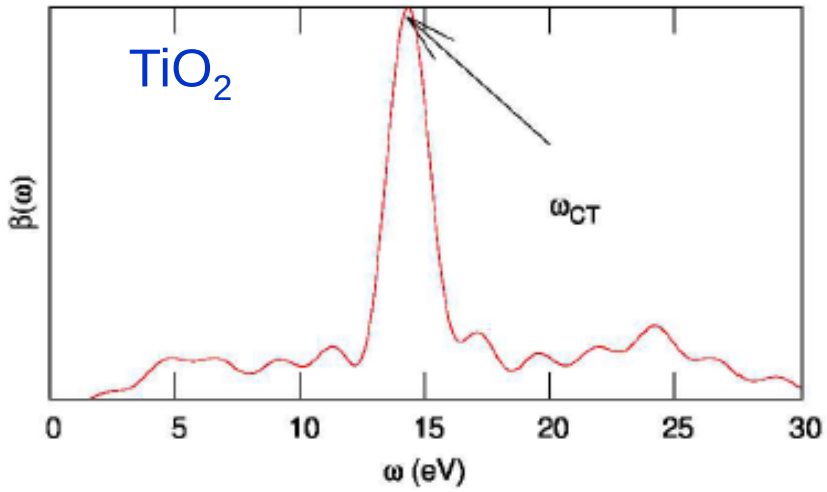
J. J. Kas,[1] F. D. Vila,[1] J. J. Rehr,[1] and S. A. Chambers[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*



Langreth cumulant in time-domain*

$$C(t) = \sum_{q,q'} V_q^* V_{q'} \int d\omega S(q,q',\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$



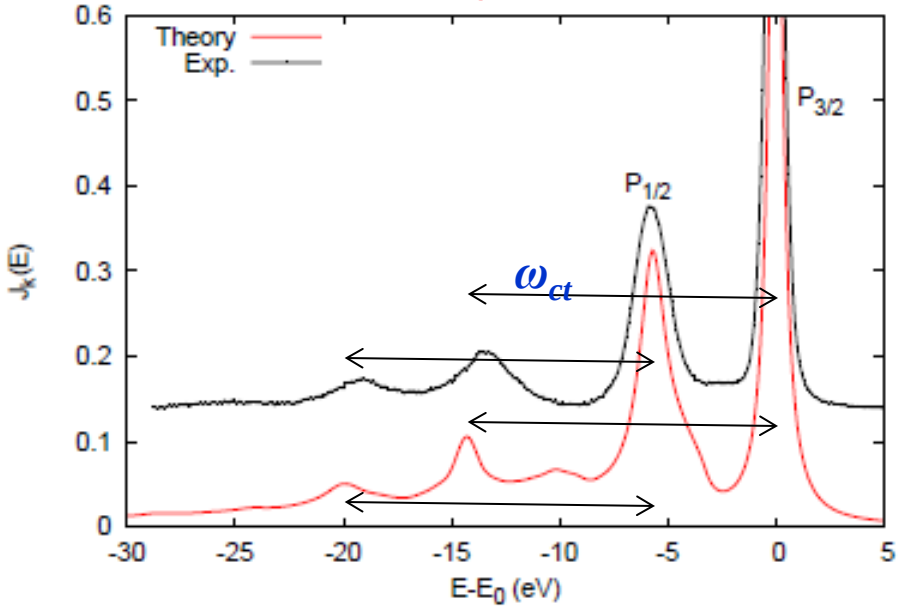


*D. C. Langreth, Phys. Rev. B **1**, 471 (1970)

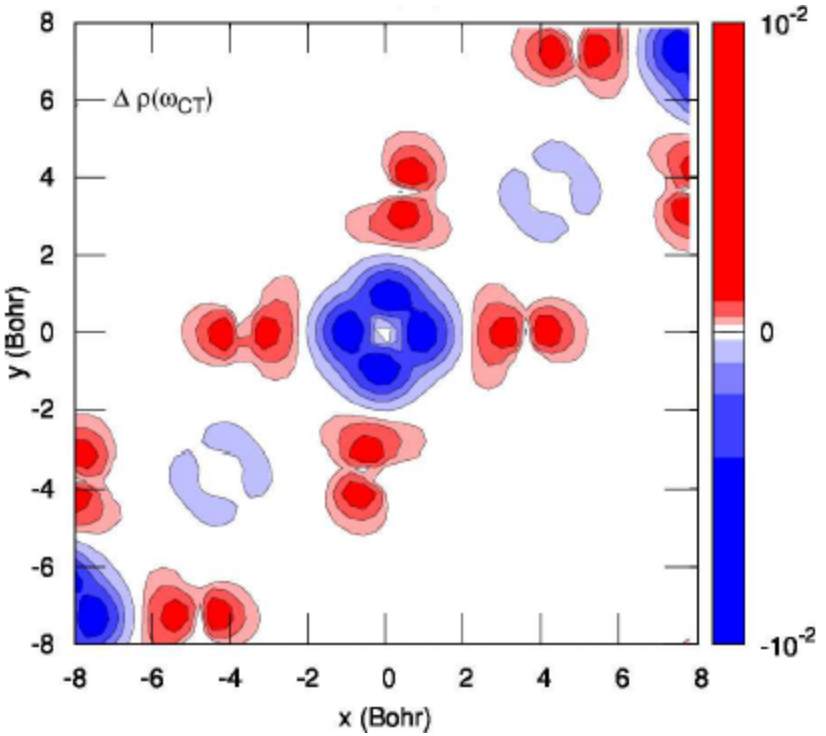
Real-space interpretation – RT-TDDFT cumulant

RT TDDFT Cumulant

Theory vs XPS



Charge transfer fluctuations

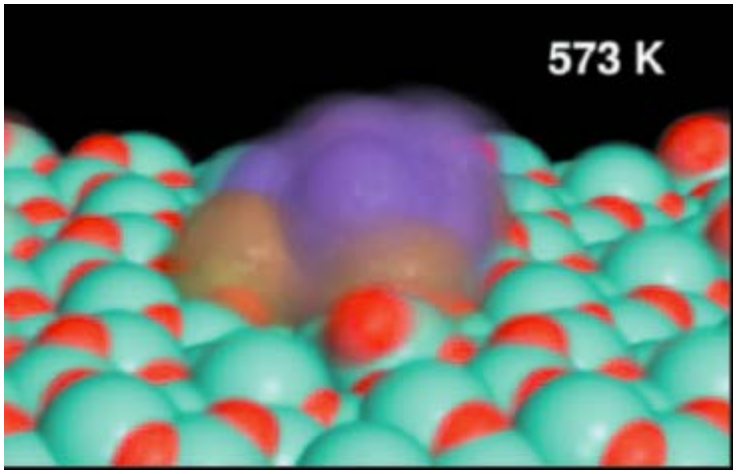


Interpretation: satellites arise from oscillatory charge density fluctuations between ligand and metal at frequency ~ ω_{CT} due to turned-on core-hole

C. Real-time approach for vibrations and non-equilibrium systems

1. XAS Debye-Waller factors

2. DFT/MD approach for nanocatalysts



1. Real-time EXAFS Debye-Waller factors

PHYSICAL REVIEW B **85**, 024303 (2012)

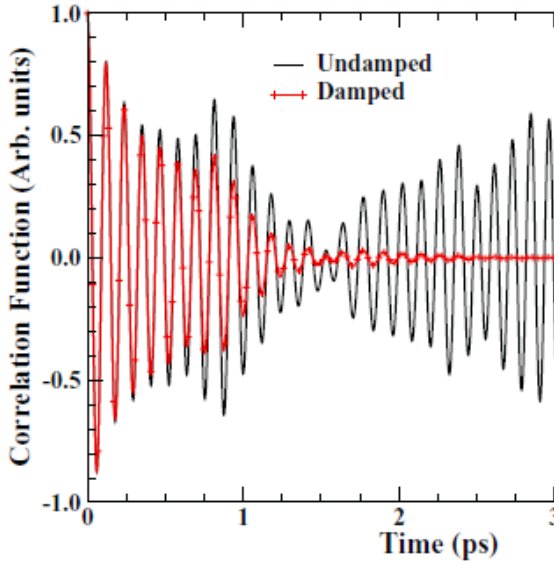
X-ray absorption Debye-Waller factors from *ab initio* molecular dynamics

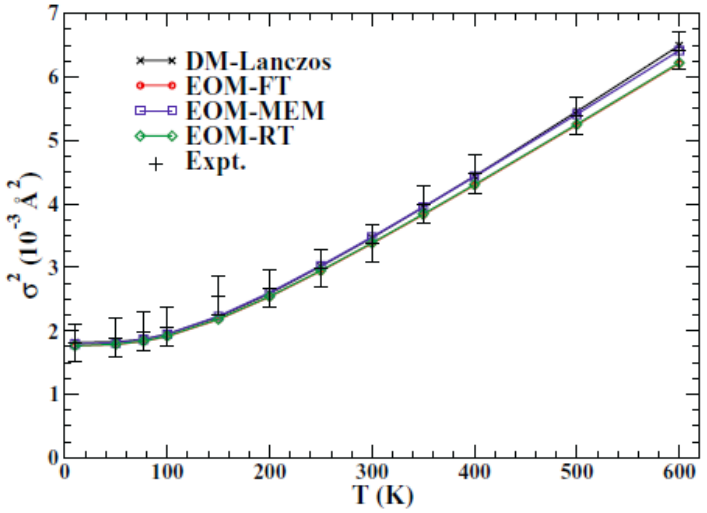
F. D. Vila, V. E. Lindahl, and J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195, USA
(Received 30 August 2011; revised manuscript received 11 January 2012; published 25 January 2012)

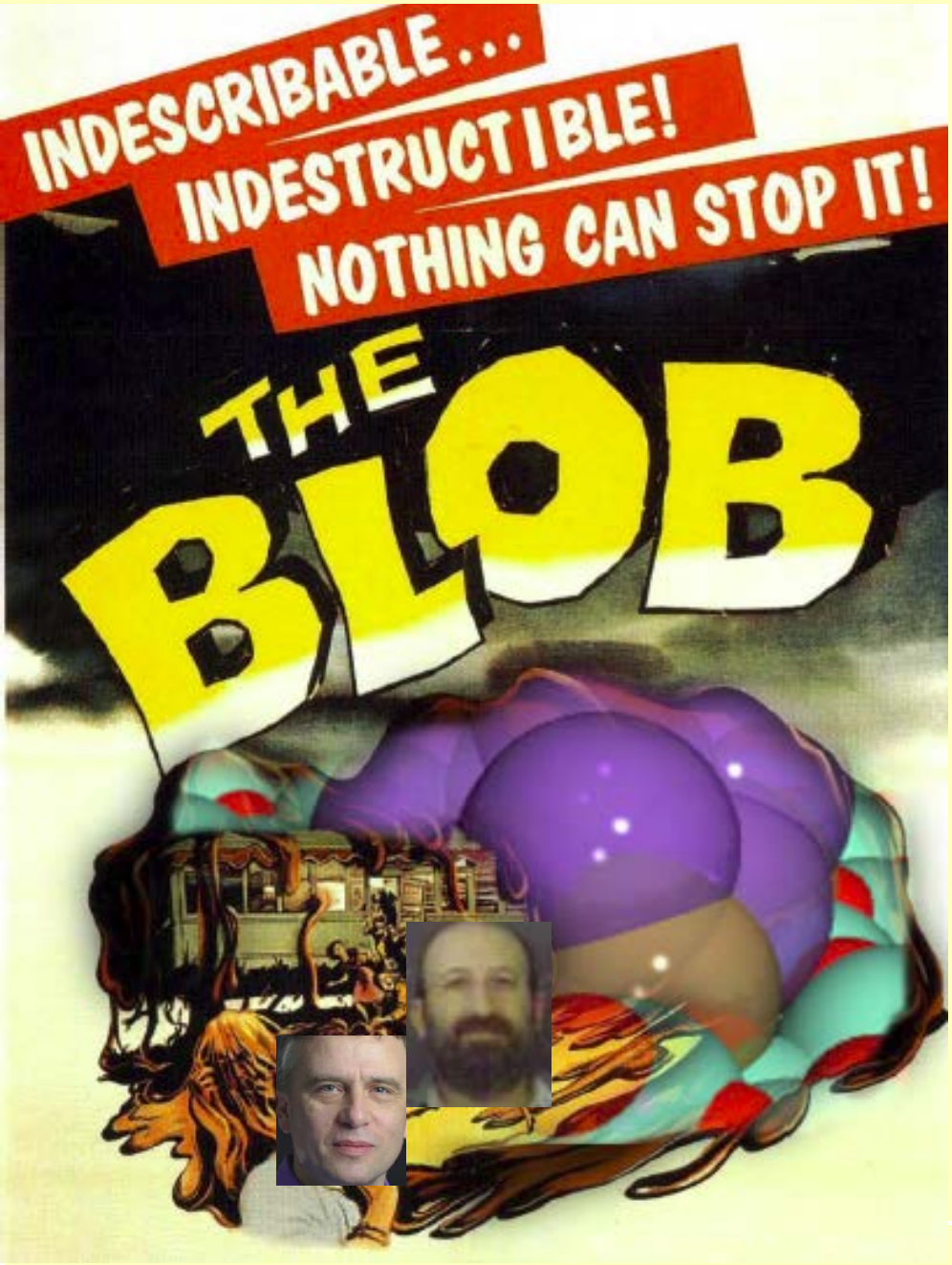
An *ab initio* equation of motion method is introduced to calculate the temperature-dependent mean-square vibrational amplitudes σ^2 which appear in the Debye-Waller factors in x-ray absorption, x-ray scattering, and related spectra. The approach avoids explicit calculations of phonon modes, and is based instead on calculations of the displacement-displacement time correlation function from *ab initio* density functional theory molecular dynamics simulations. The method also yields the vibrational density of states and thermal quantities such as the lattice free energy. Illustrations of the method are presented for a number of systems and compared with other methods and experiment.

Displacement-displacement Autocorrelation function

$$\sigma_R^2(T) = \frac{\hbar}{\mu_R \pi} \int_0^{t_{\max}} dt \langle Q_R(t) | Q_R(0) \rangle \times \ln \left[\left(2 \sinh \frac{\pi t}{\beta \hbar} \right)^{-1} \right] e^{-\varepsilon t^2}$$







a Sequel

2. Non-equilibrium systems

A theoretical horror story

Starring

Fernando Vila
&
Anatoly Frenkel

with

J. Kas, S. Bare & S. Kelly

Directed by J. J. Rehr

a DOE CSGB Production

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

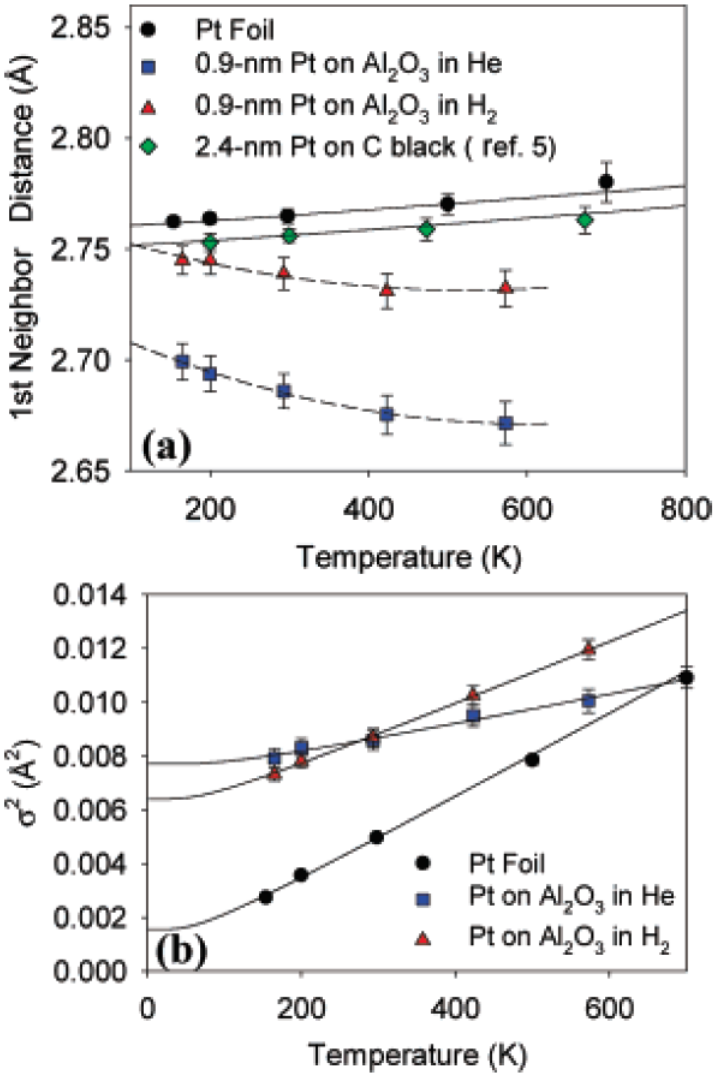
- **Pt-Pt nn**

  Negative Thermal Expansion

  & Bond expansion in H_2

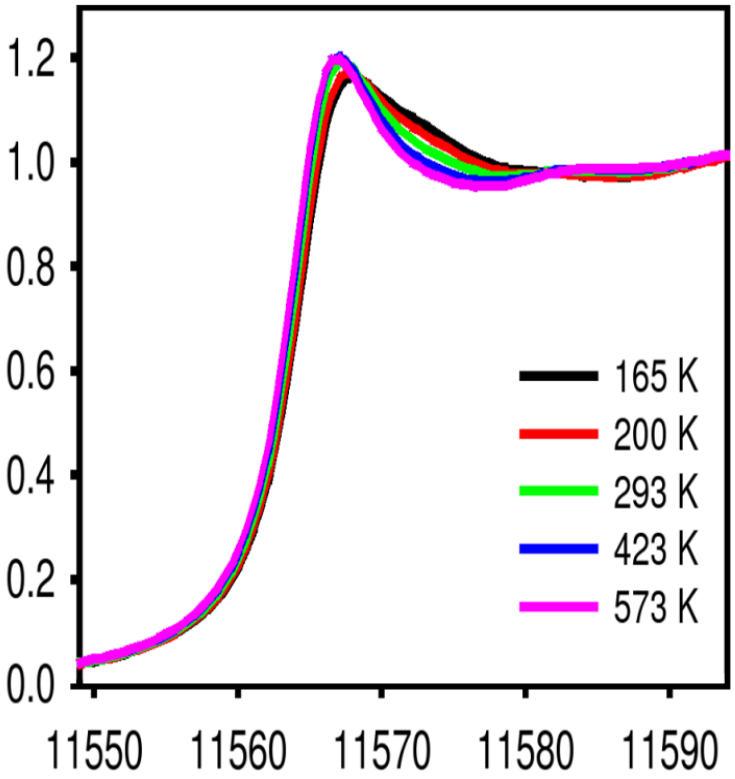
- **Anomalous Pt-Pt disorder**

NOT bulk-like !



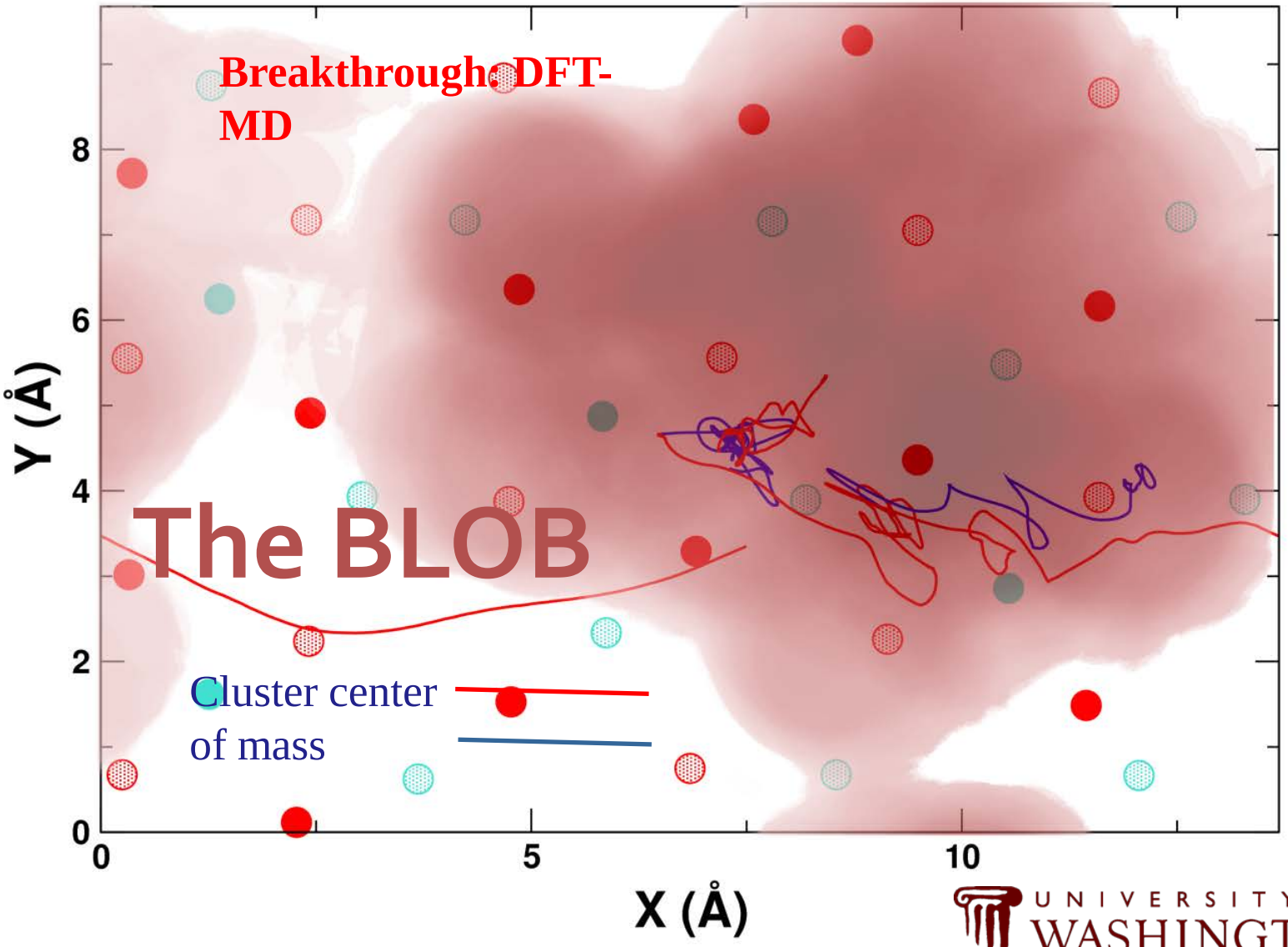
More Anomalous properties* $Pt_{10}/\gamma Al_2O_3$

- **Increased edge intensity**
- **Redshift of XANES with increasing T (charge effects)**
- **Standard theory fails!**



What's going on?

Blob footprint @ 573 K



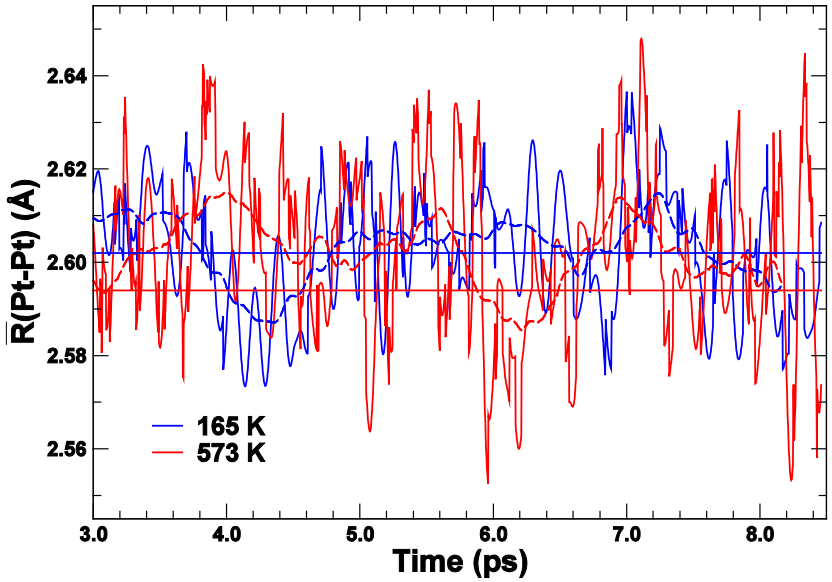
UNIVERSITY OF WASHINGTON

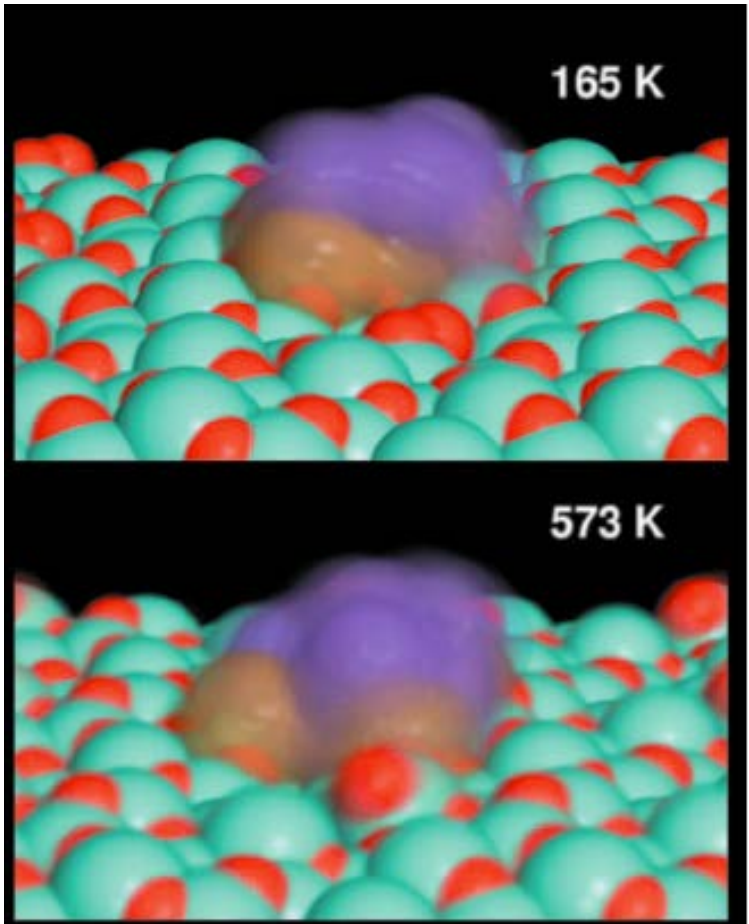
PHYSICAL REVIEW B 78, 121404(R) (2008)

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

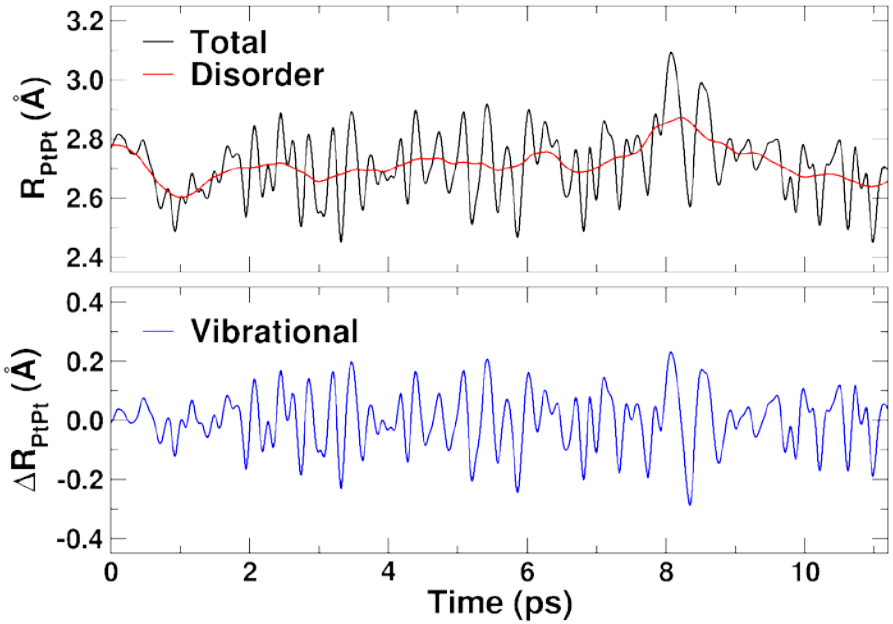
F. Vila,[1] J. J. Rehr,[1,*] J. Kas,[1] R. G. Nuzzo,[2] and A. I. Frenkel[3]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[3]*Department of Physics, Yeshiva University,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

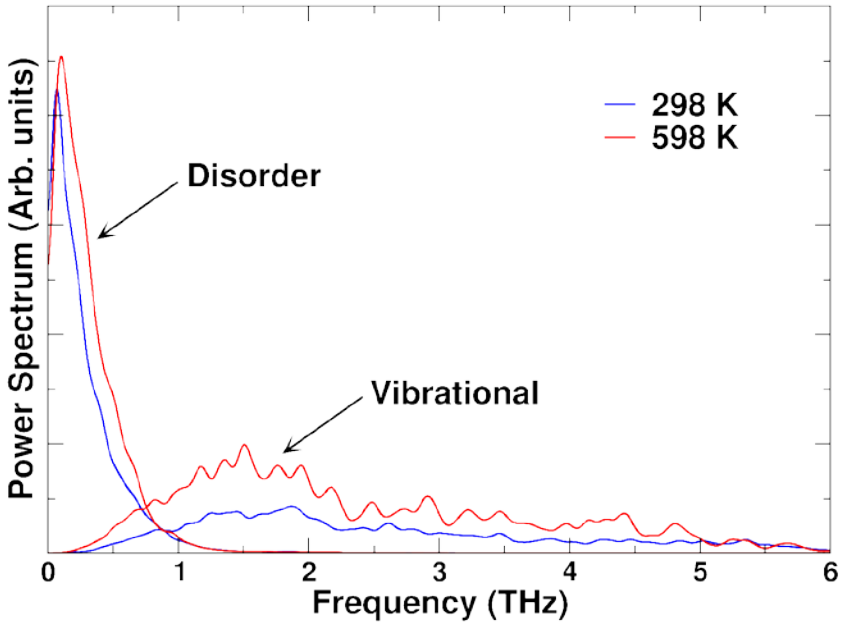
Fuzzy "structure"





Dynamic Disorder: Anomalous Behavior





Decomposition into Vibrational and Disorder components

Vibrational – Normal behavior (THz - 200-400 fs periods)

Dynamic disorder – Large, chaotic, sub THz

CONCLUSIONS

Real-time, real-space formalism - powerful alternative to frequency and k-space methods

- Linear and non-linear optical and x-ray response to monochromatic and pulsed sources
- Many-body effects: multi-electron excitations, plasmon and charge-transfer satellites
- Vibrational and non-equilibrium effects

Acknowledgments

Supported by DOE BSE DE-FG02-97ER45623

Thanks to

J.J. Kas
J. Vinson
T. Fujikawa
S. Story
M. Verstraete
L. Reining
K. Gilmore
F. Vila
S. Biermann
J. Sky Zhou
G. Bertsch
L. Campbell
E. Shirley
M. Guzzo
C. Draxl