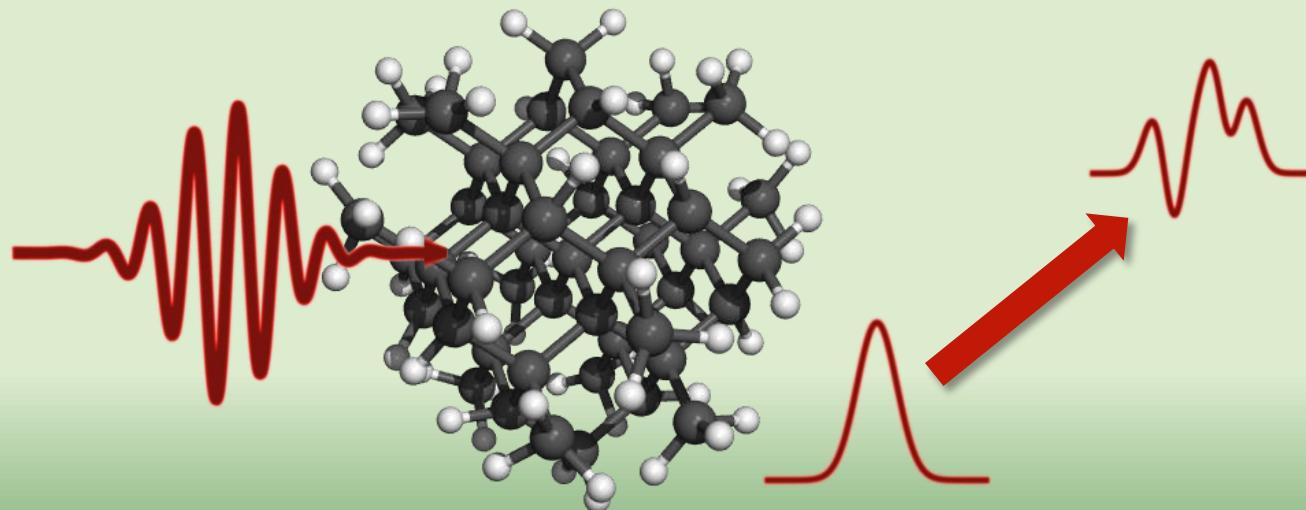


# RT-SIESTA: Real-time linear and non-linear response for optical and core spectroscopies

**F. D. Vila, Y. Takimoto, A. J. Lee, J. J. Kas, J.J. Rehr**

*Department of Physics, University of Washington*

Vanderbilt University, Nashville, Mar 10 2014



# Why TDDFT?

Don't really need to convince you...

## But why real time?

Can be **more efficient** than frequency space (large systems)

Very **versatile** (pulses, transport, etc)

More “physical/**realistic**”

Easy access to **NLO properties**

# Background Theory

# Real-Time Time Dependent DFT

Direct numerical integration of the time-dependent Kohn-Sham equations in a time-dependent external electric field:

$$i \frac{\partial \Psi}{\partial t} = H(t) \Psi \quad \Psi(t) = T \exp \left( -i \int_0^t H(t') dt' \right) \Psi(0)$$
$$H = -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}, t) + V_H[\rho](\mathbf{r}, t) + V_{xc}[\rho](\mathbf{r}, t)$$

Optical properties are determined from the total dipole moment:

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

$$\chi_{ij}^{(1)}(\omega) = \delta p_i(\omega) / E_j(\omega) = \alpha_{ij}(\omega) \quad \sigma(\omega) \sim \omega \operatorname{Im} \langle \alpha(\omega) \rangle$$

Linear Response

Absorption

# Numerical Real-Time Evolution

The ground state density  $\rho_0$ , overlap matrix  $S$  and Hamiltonian matrix  $H(t)$  evaluated at each time-step using **SIESTA**:

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

Orbital coefficients

Accurate and stable evolution using Crank-Nicolson propagator:

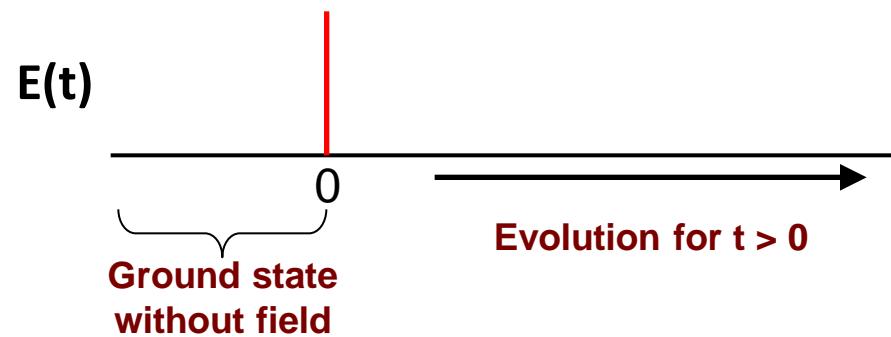
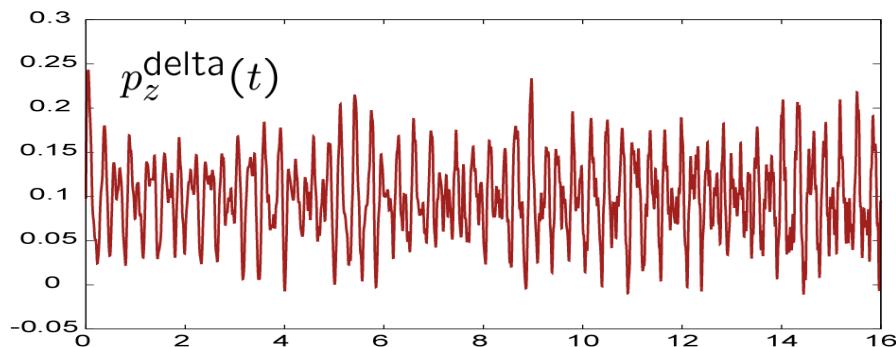
$$c(t + \Delta t) = \frac{1 - iS^{-1}H(\bar{t})\Delta t/2}{1 + iS^{-1}H(\bar{t})\Delta t/2} c(t) + \mathcal{O}(\Delta t^2)$$

Soler *et al.* J. Phys.: Condens. Matter 14, 2745 (2002)

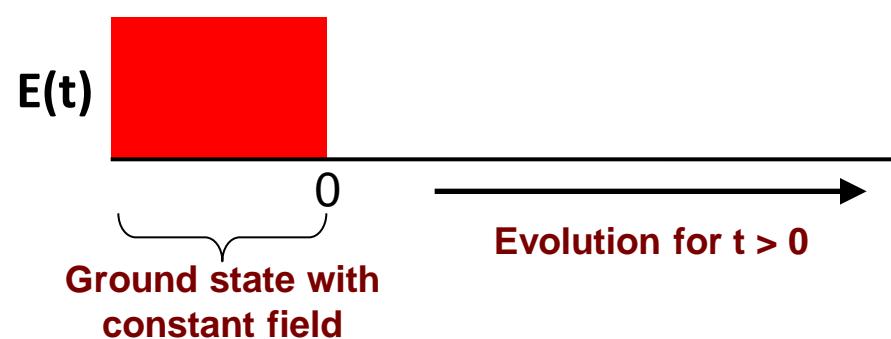
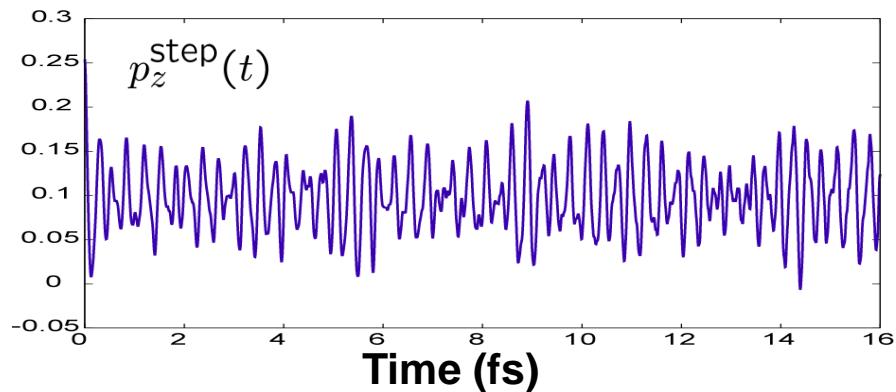
Tsolakidis *et al.* Phys. Rev. B 66, 235416 (2002)

# Optical Absorption in CO

Delta Function (Unit Impulse at t=0)

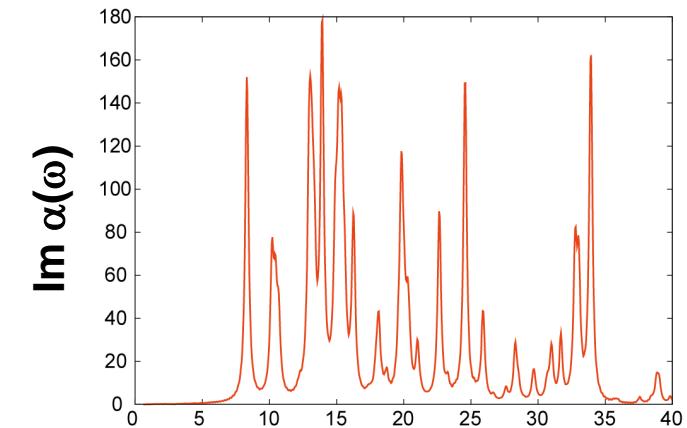
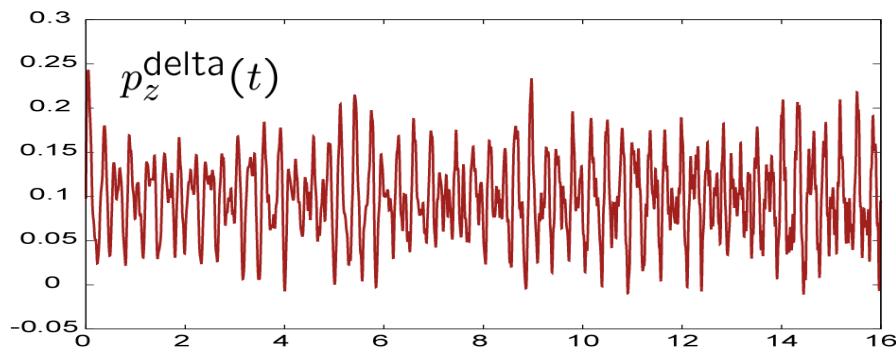


Step Function (Turn-off Constant E at t=0)

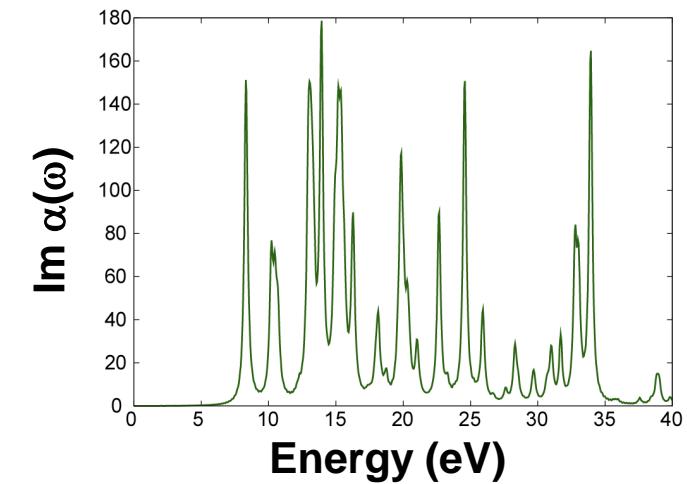
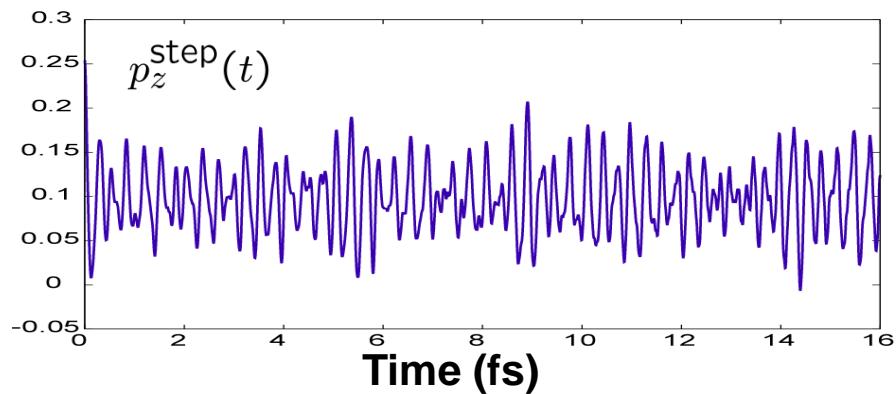


# Optical Absorption in CO

Delta Function (Unit Impulse at t=0)

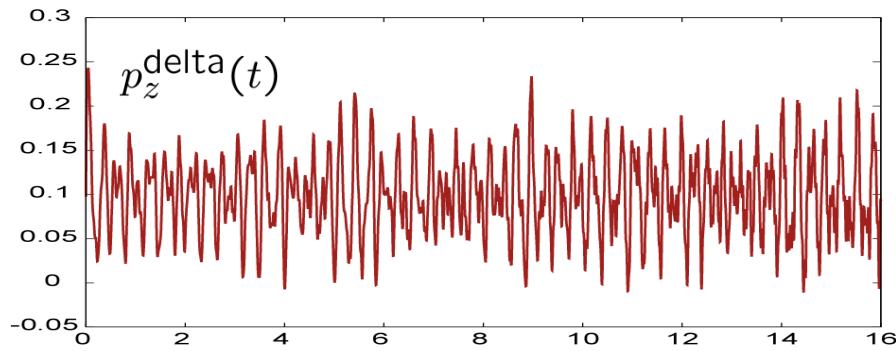


Step Function (Turn-off Constant E at t=0)

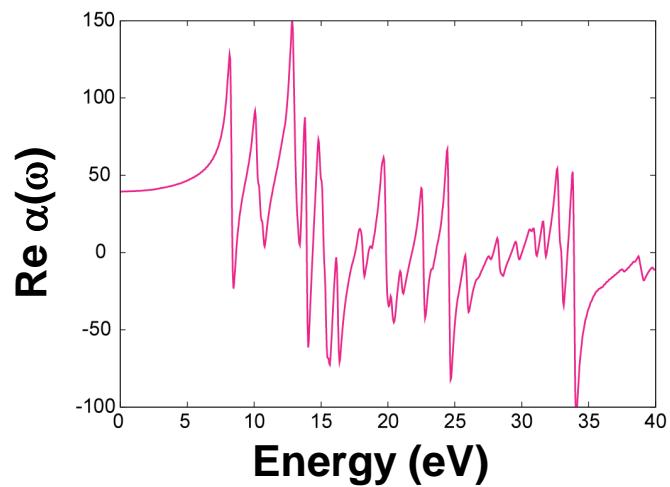
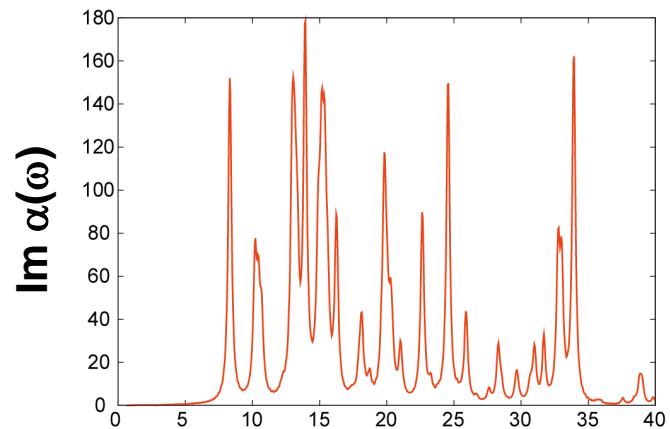
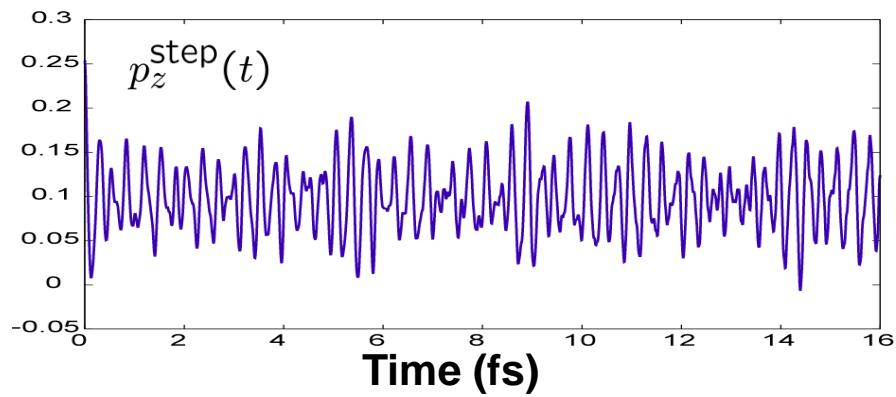


# Optical Absorption in CO

Delta Function (Unit Impulse at t=0)

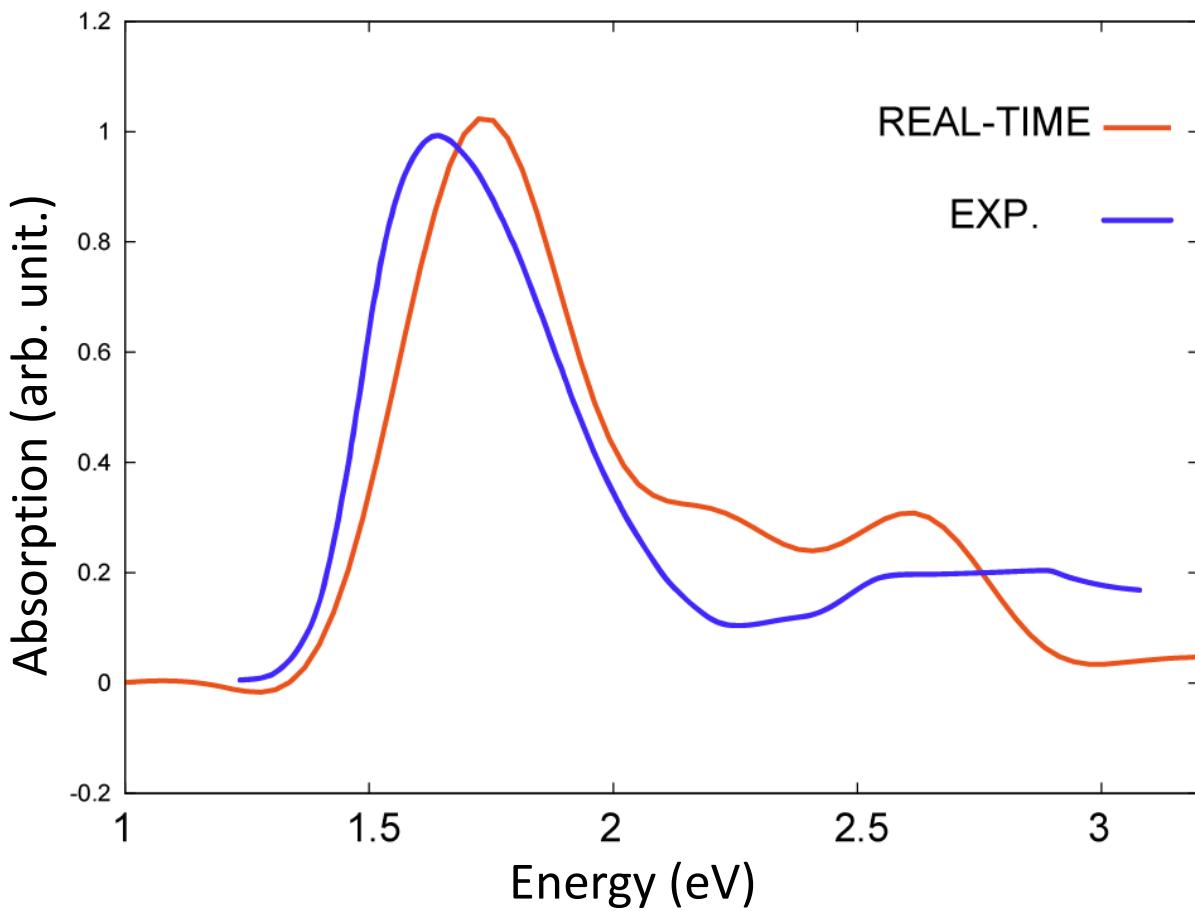
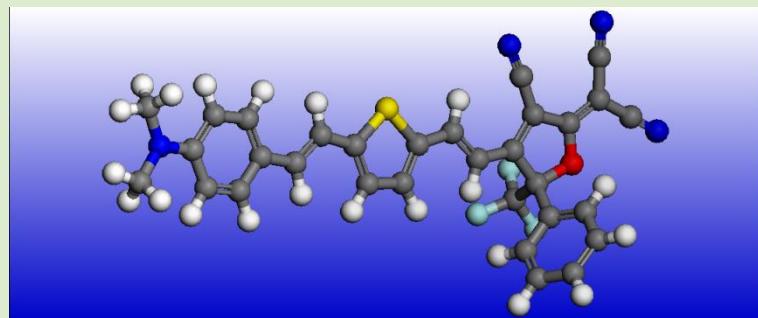


Step Function (Turn-off Constant E at t=0)



# Linear response: Chromophores

# NLO chromophore: YLD\_156



Real-time (gas)  
absorption peak

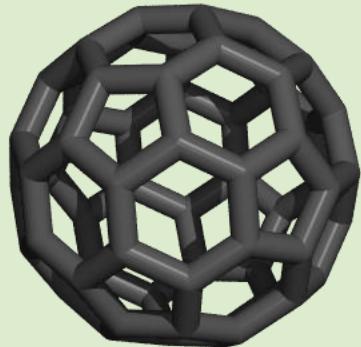
$$\omega_0 = 1.72 \text{ eV}$$
$$(\lambda_0 = 721 \text{ nm})$$

Expt. ( $\text{CHCl}_3$ )  
absorption peak

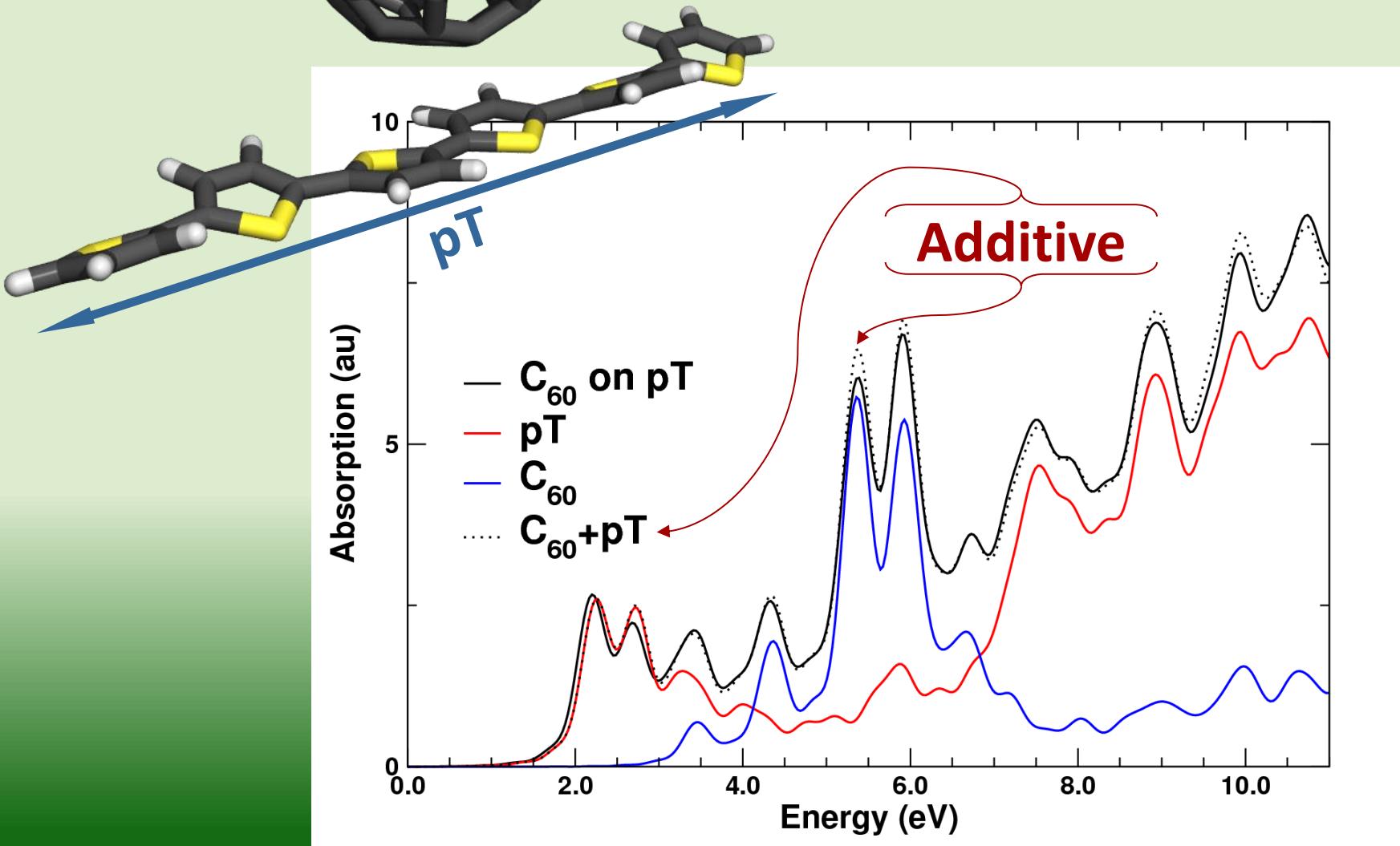
$$\omega_0 = 1.65 \text{ eV}$$
$$(\lambda_0 = 753 \text{ nm})$$

# Linear response: Organic solar cell components

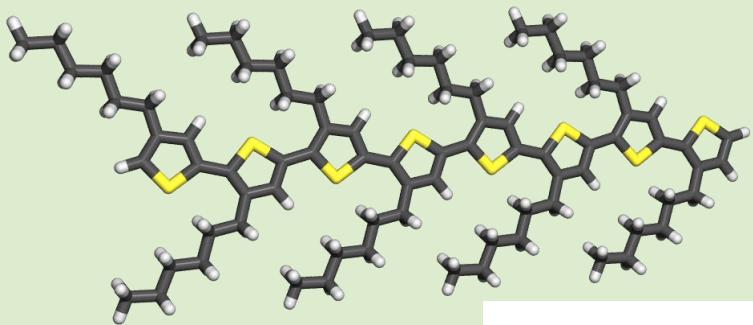
$C_{60}$



# Interaction Between pT and $C_{60}$



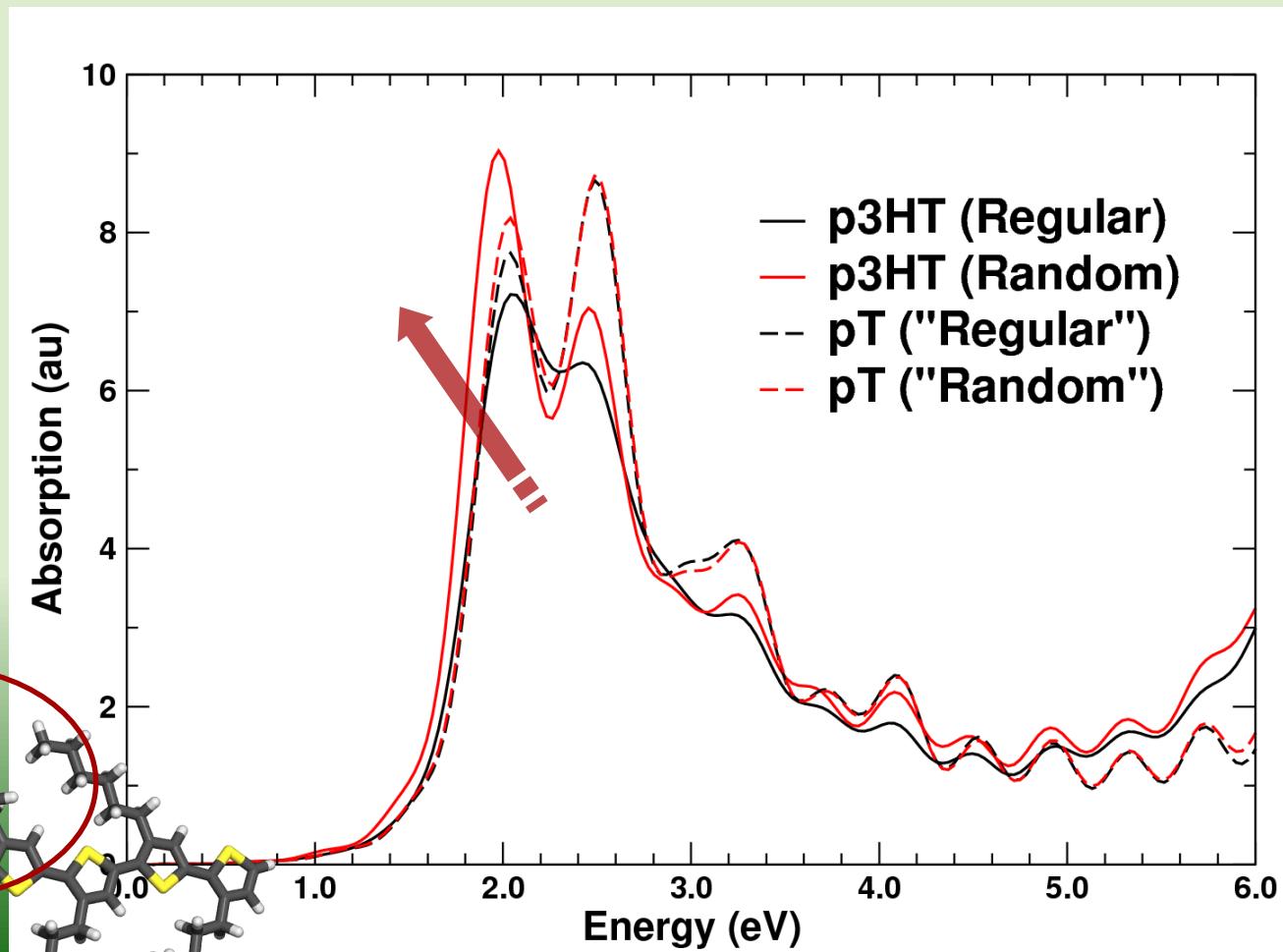
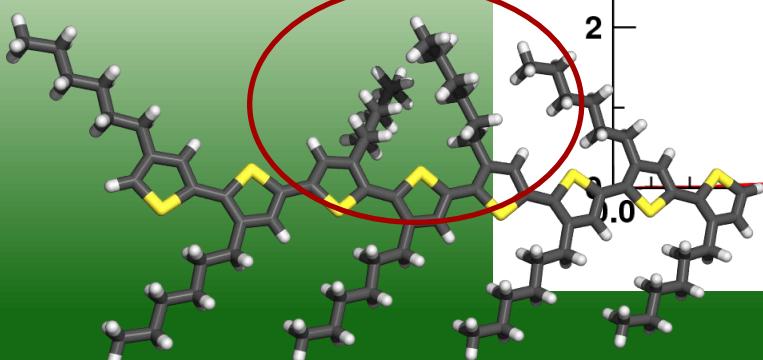
# Effect of Hexyl Chains in p3HT



p3HT  
(Regular)

↓ Redshift

p3HT  
(Random)



# Nonlinear optical properties

# Real time Nonlinear Response

## Nonlinear expansion

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

Must take into account **response time**:

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

How do we invert to get nonlinear response function?

# **Static Nonlinear Polarizabilities: FFPT**

**For static response we use Finite Field Perturbation Theory (FFPT):**

$$p_i = \mu_i^0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots$$

**Then either finite-differences stencil or fitting to extract tensor components:**

$$\beta_{i,jj} = [-p_i(-2E_j) + 16p_i(-E_j) - 30p_i(0) + 16p_i(E_j) - p_i(2E_j)]/24E_j^2$$

# *Dynamic Nonlinear Polarizabilities*

Time dependent  $E_j(t)$  as  $F(t)E_j$ , and define time-dependent formula:

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

where:       $p^{(1)}$  linear response  
                 $p^{(2)}$  non-linear quadratic response

...

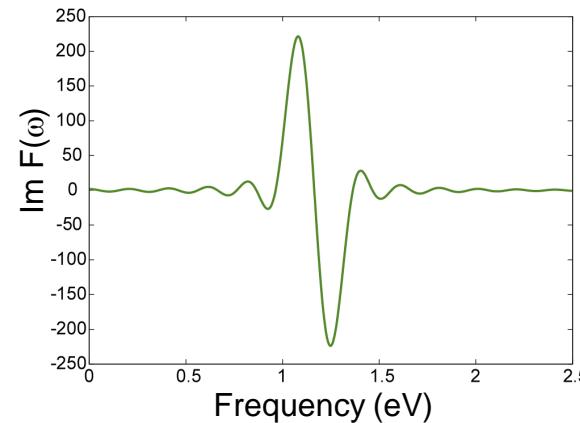
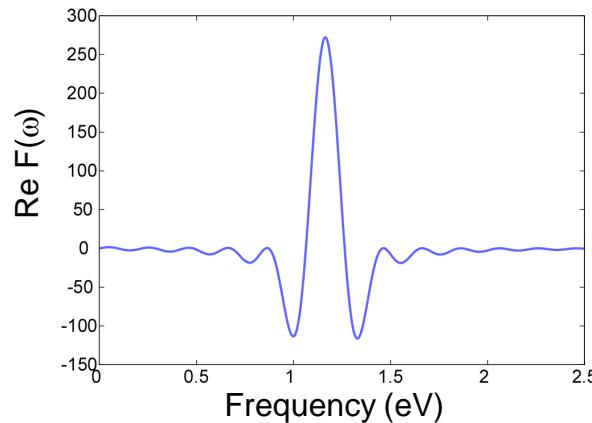
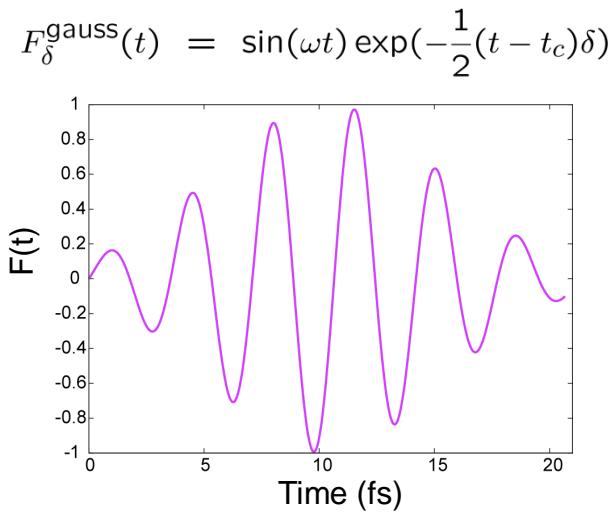
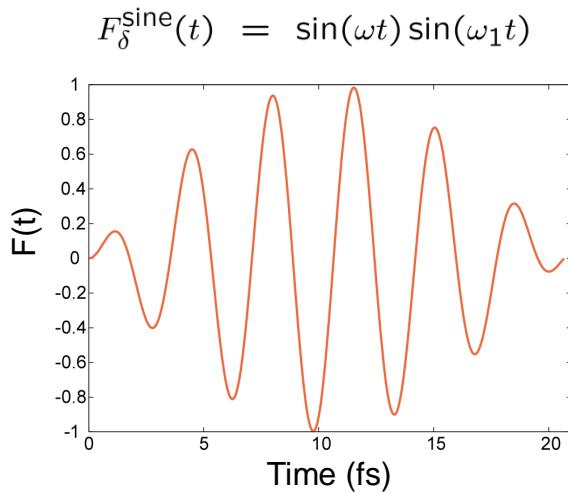
The quadratic response  $\chi^{(2)}$  is related to  $p^{(2)}$  by:

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

# Dynamic Nonlinear Response with Quasi-monochromatic Field $F_\delta$

$F_\delta$ : Sine wave with sine or Gaussian envelope

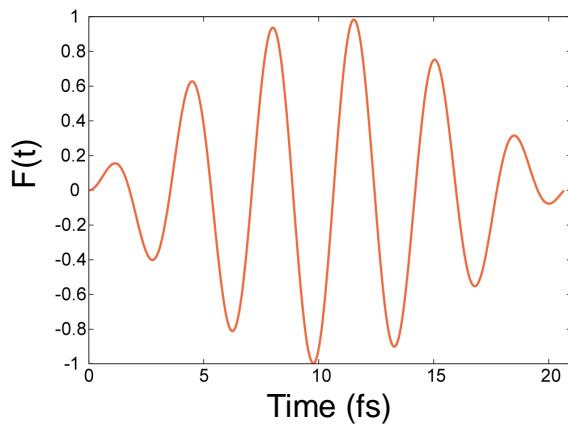
$$\begin{aligned}\omega &= 1.17 \text{ eV} \\ \omega_1 &= 0.1 \text{ eV}\end{aligned}$$



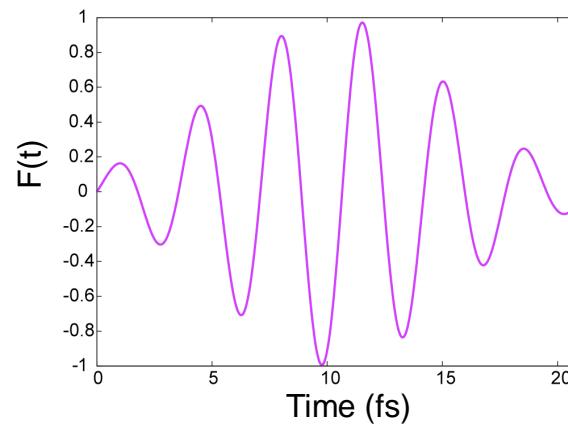
# Dynamic Nonlinear Response with Quasi-monochromatic Field $F_\delta$

$F_\delta$ : Sine wave with sine or Gaussian envelope

$$\begin{aligned} \omega &= 1.17 \text{ eV} \\ \omega_1 &= 0.1 \text{ eV} \end{aligned}$$



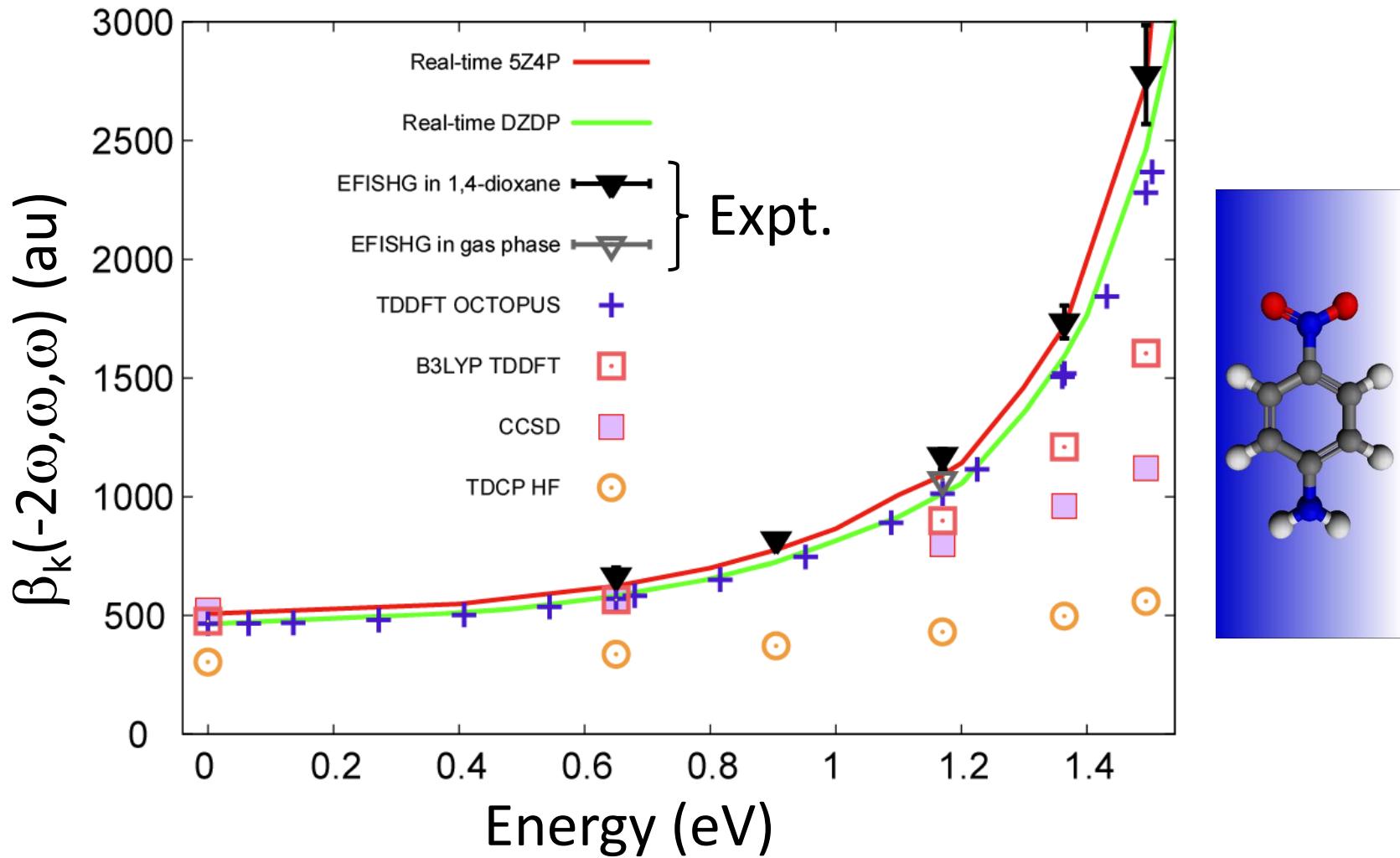
$$F_\delta^{\text{gauss}}(t) = \sin(\omega t) \exp\left(-\frac{1}{2}(t - t_c)\delta\right)$$



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

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

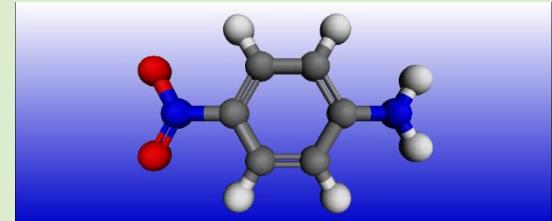
# Second Harmonic Generation (SHG) in pNA



# Solvent effects

# “Local” Solvent Effect

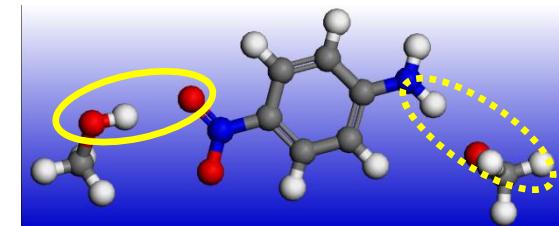
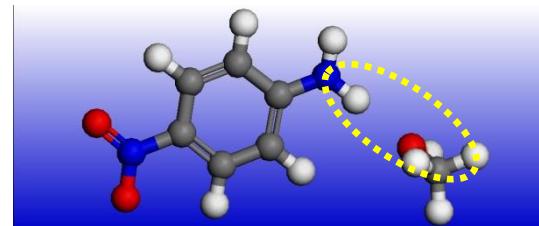
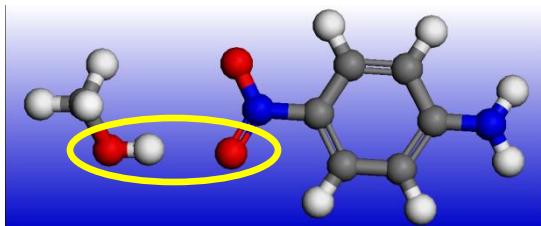
Study of local contact with  
methanol (polar) or chloroform (non-polar)



$$\beta_{\text{HRS}} \ 798.6 \ (\text{au})$$
$$\omega = 1.17 \ \text{eV}$$

$$\beta_{\text{HRS}}(-2\omega; \omega, \omega)$$

$$1900 \pm 100$$



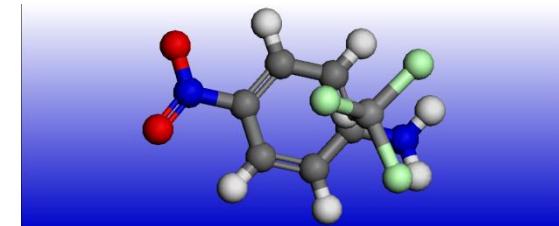
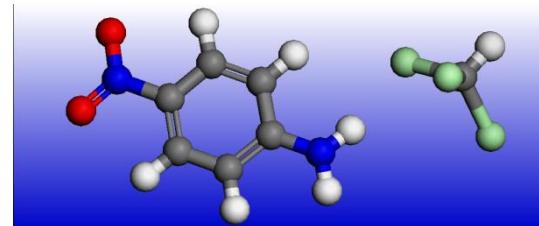
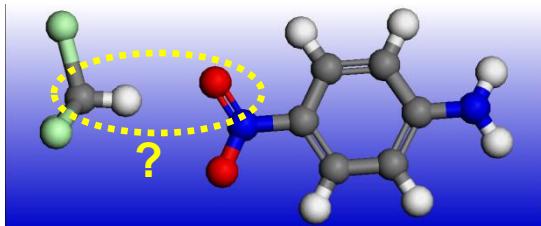
$$\text{Expt.}$$

$$\beta_{\text{HRS}} \ 1556 \ (21.3)$$

$$869.3 \ (19.9)$$

$$1812 \ (31.4)$$

$$1400 \pm 40$$

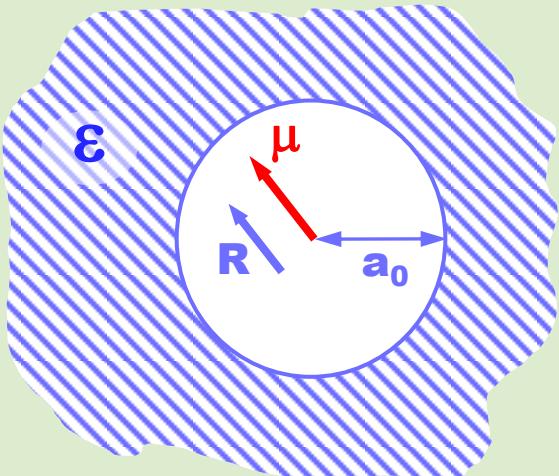


$$\beta_{\text{HRS}} \ 1081 \ (10.8)$$

$$797.5 \ (8.79)$$

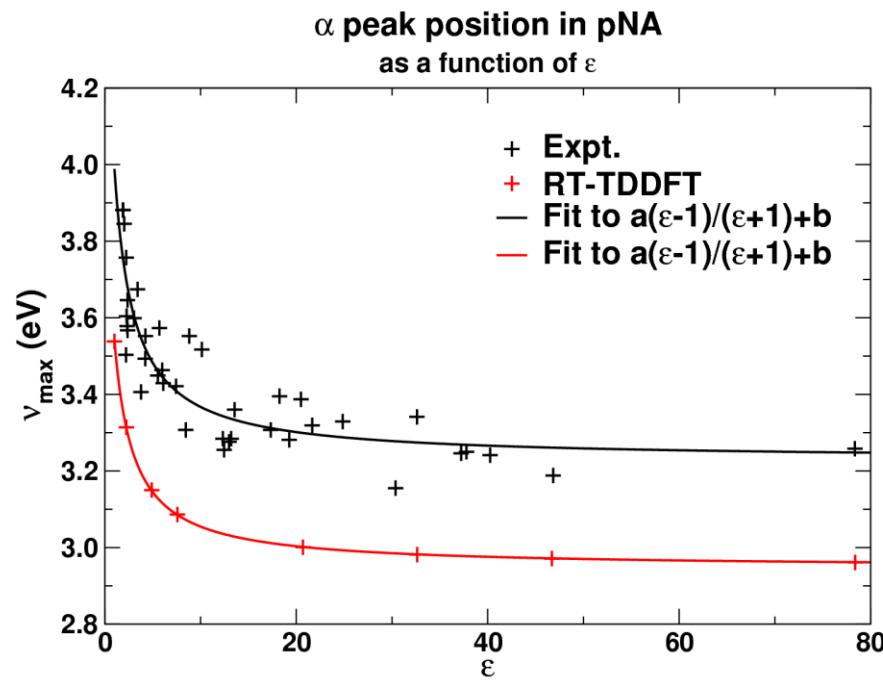
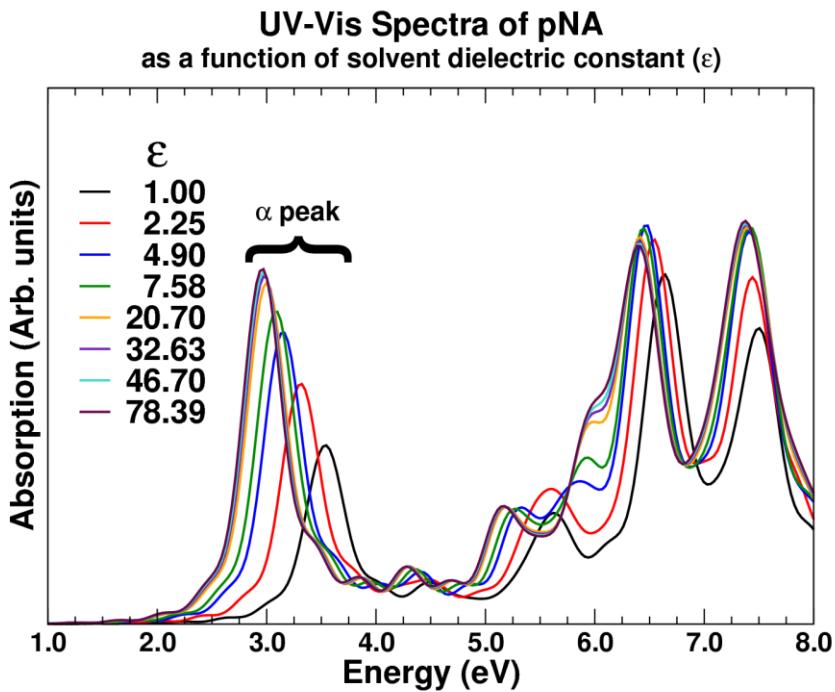
$$746.1 \ (6.36)$$

# Onsager Solvation Model

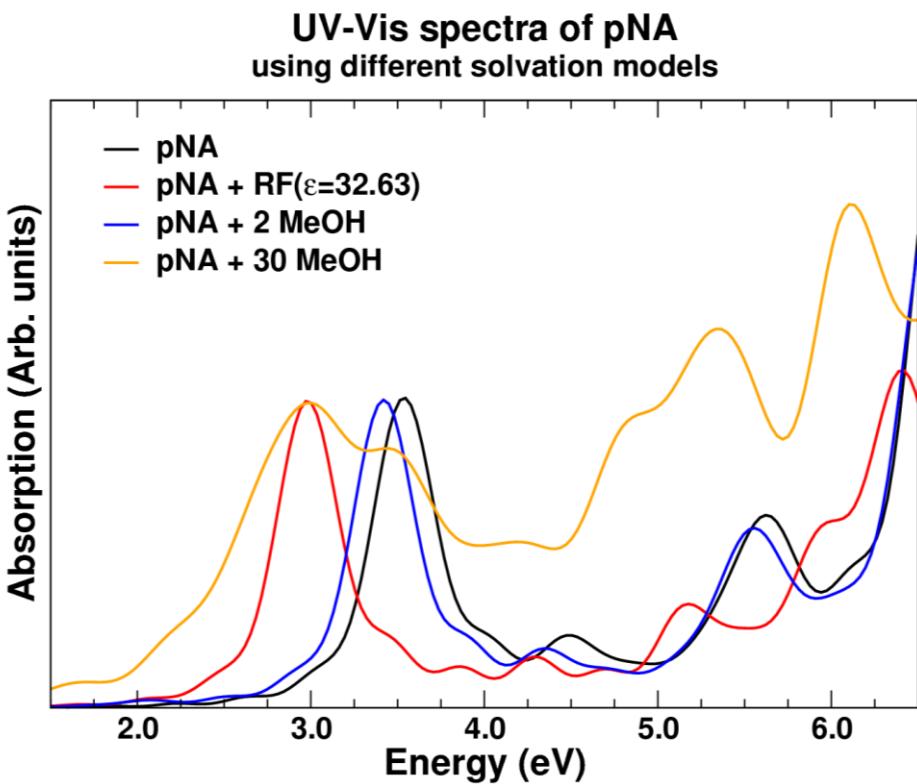
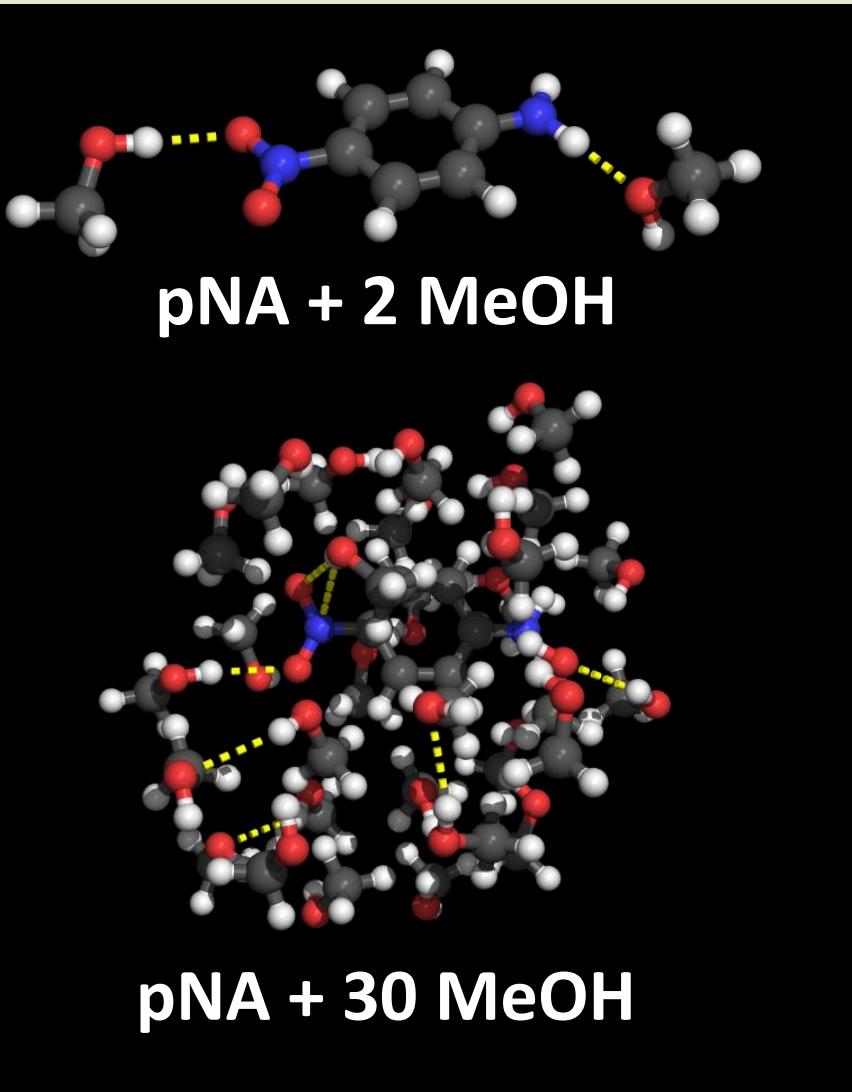


Spherical cavity of radius  $a_0$  in  
dielectric medium

Computational effort equivalent to  
vacuum calculation



# Explicit vs Reaction Field Solvation



# **Current Developments**

**Improve scaling**

**Add nuclear motion**

**Steady state transport**

## **Summary**

**(Fairly) Efficient implementation of RT-TDDFT paradigm**

**Full spectrum in one calculation**

**Easy nonlinear response**

**Very versatile**

# Real-time core spectroscopy

# Why Use a TD Approach for Core Spectra?

XS traditionally calculated with Fermi's Golden Rule (FGR) using wavefunctions or real-space Green's functions (RSGF)

Currently:

New experimental pulsed sources (XFEL, LCLS) and pump-probe experiments

Increased interest in time-dependent (TD) response

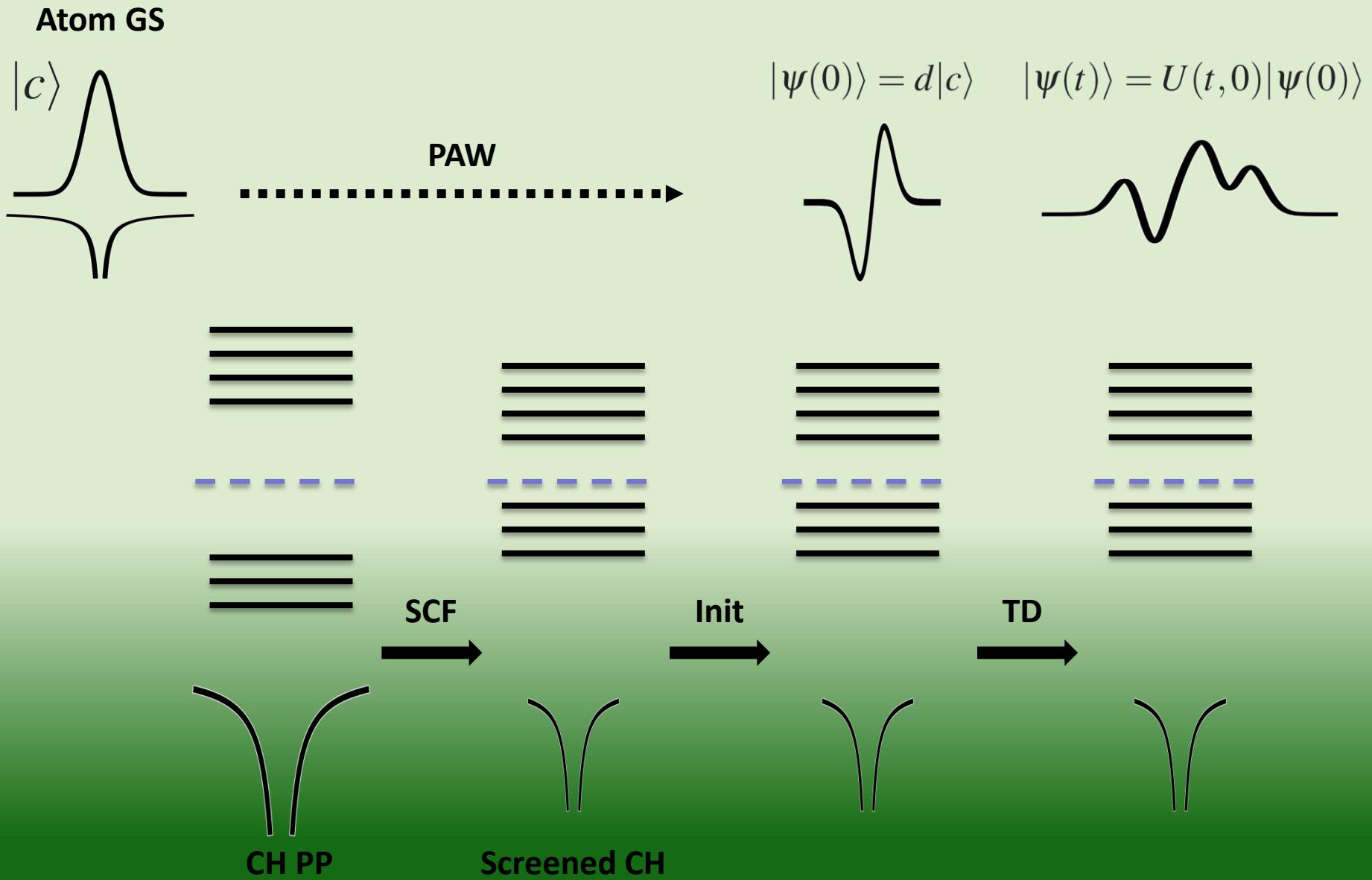
Our approach:

Compute response using TD autocorrelation function

Goal:

TD x-ray response, including core hole (CH) dynamics

# Real-Time X-Ray Spectroscopy (RTXS)



# RTXS Equations

## XAS Absorption (FGR, $\Delta$ SCF, FSR)

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

↓ FT

$$\mu(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty dt e^{i\omega t} \underbrace{G_c(t)}_{\text{Core Hole Green's Function}} \underbrace{\langle \psi(t)|\psi(0)\rangle}_{\text{Autocorrelation Function}} \theta(\omega + \varepsilon_c - E_F)$$

### Core Hole Green's Function

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

### Autocorrelation Function

$$\underbrace{\langle \psi(t)|\psi(0)\rangle}_{\text{Autocorrelation Function}} = \sum_{jj'} \langle c|d^\dagger|j\rangle U_{jj'}(t,0) \langle j'|d|c\rangle$$

$$\langle \psi(0)|\psi(t)\rangle \begin{cases} |\psi(0)\rangle = d|c\rangle \\ |\psi(t)\rangle = U(t,0)|\psi(0)\rangle \end{cases} \longrightarrow U(t,0) = T \exp \left[ -i \int_0^t dt H(t) \right]$$

### Crank-Nicolson

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

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

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

# Computational Details

Implemented on RT-SIESTA with:

Real-time propagation

PAW for dipole matrix elements (based on UW OCEAN)

SIESTA details:

TZDP basis

Norm conserving PP

150 Ry grid cutoff

Experimental structures

TD:

Simulation time ~1-5 fs with 0.01 fs steps

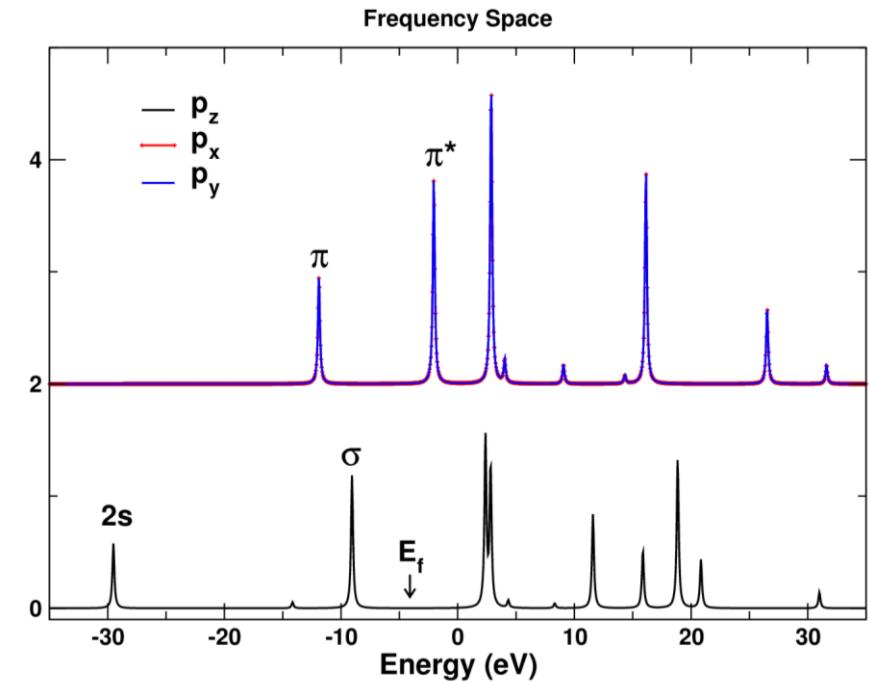
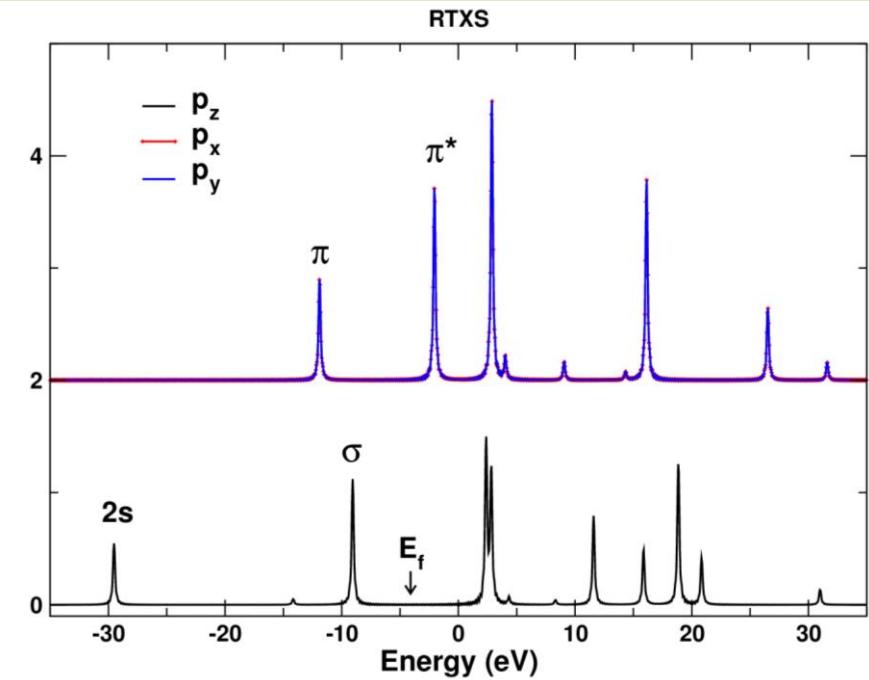
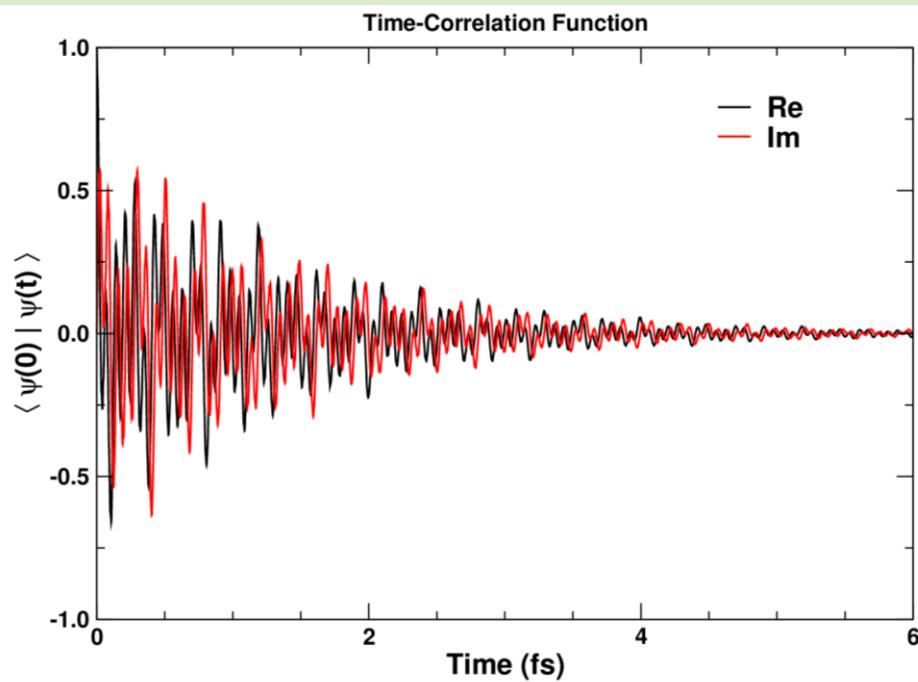
Broadening and  $E_c$  shift to match experiment

Comparisons with:

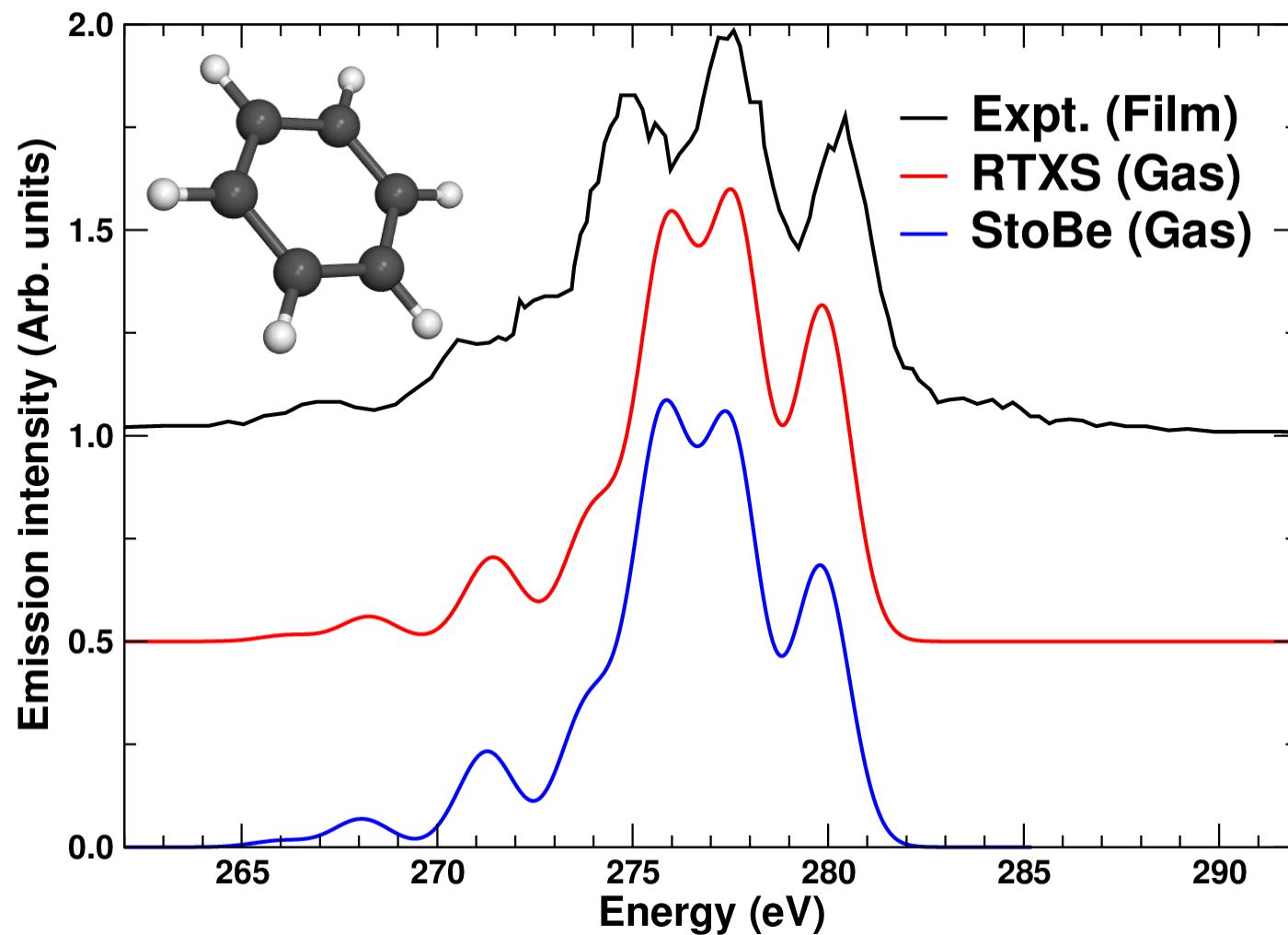
StoBe (GTO-based FGR, TST CH approximation)

FEFF (Real Space Multiple Scattering, FSR)

# Autocorrelation Function and C pDOS for CO

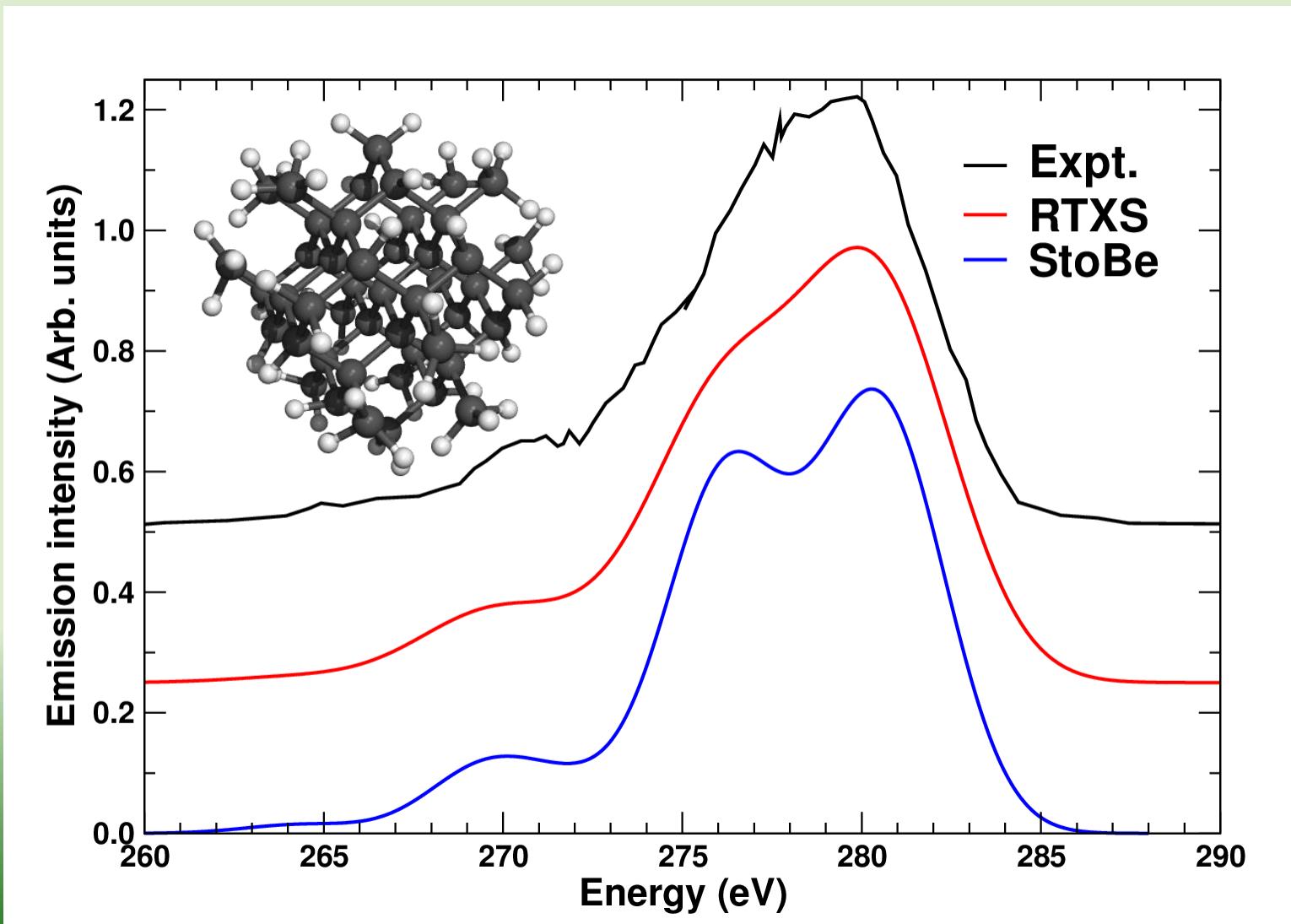


# C K $\alpha$ XES of C<sub>6</sub>H<sub>6</sub>

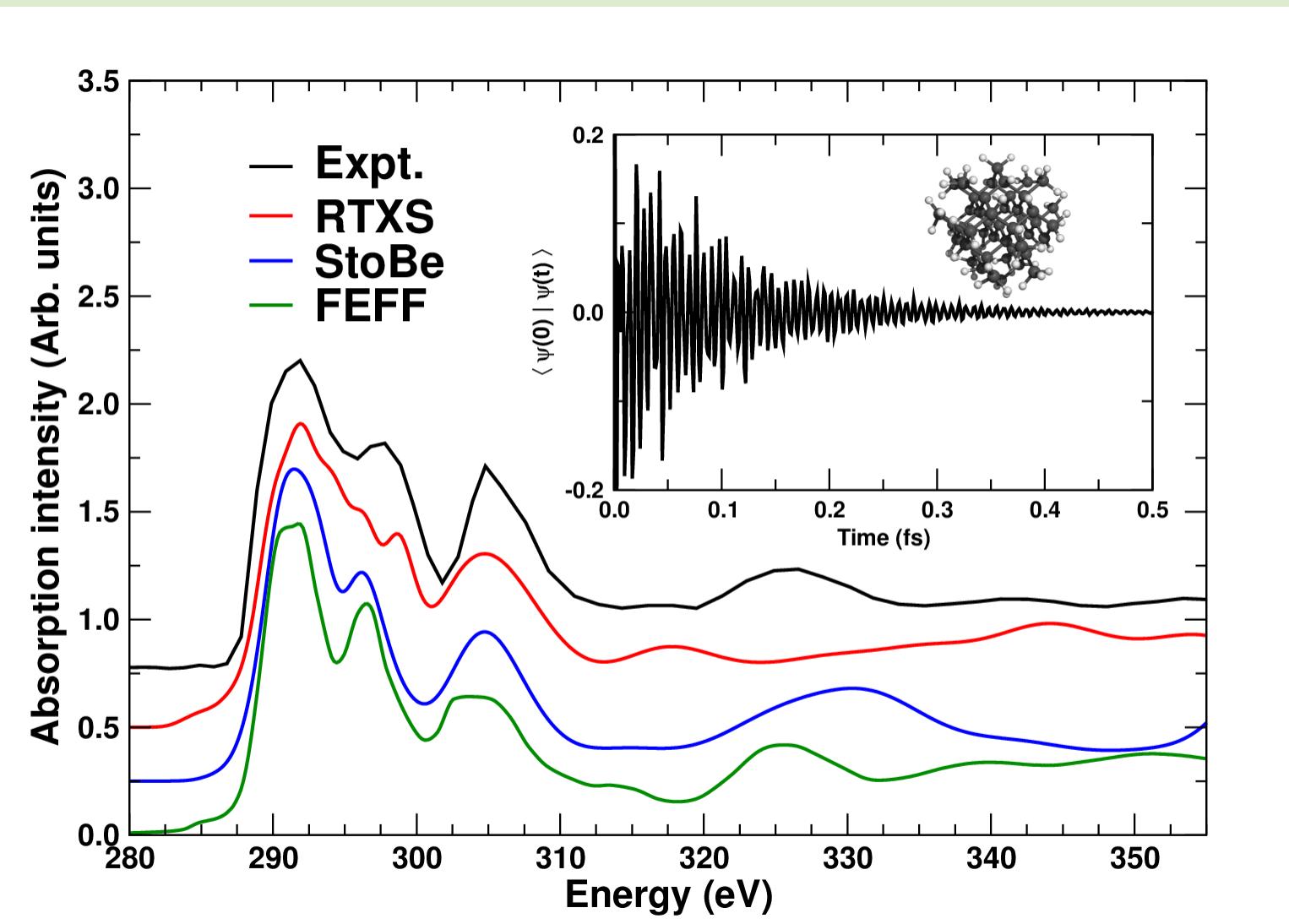


Expt: Skytt *et al.*, Phys. Rev. A 52, 3572 (1995)

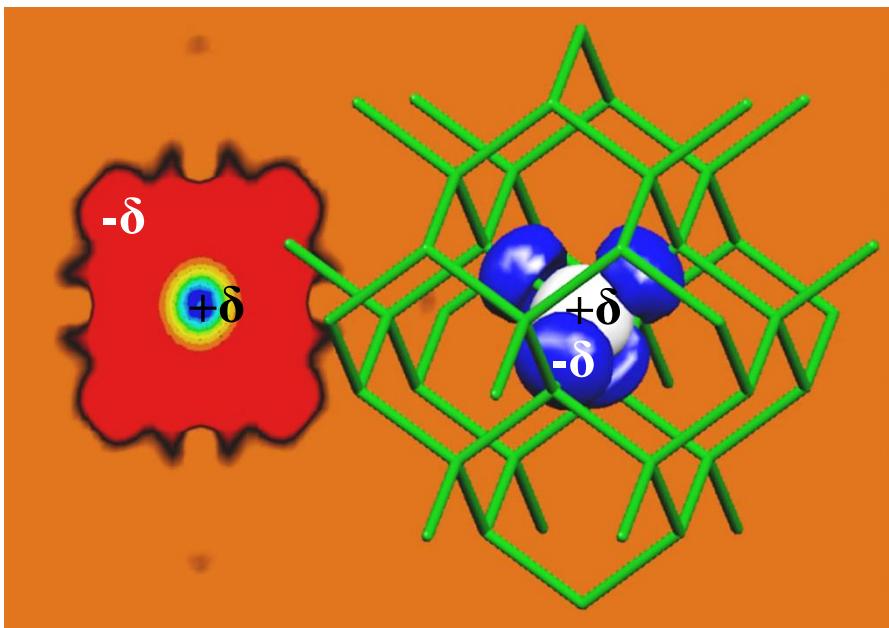
# C K $\alpha$ XES of Diamond ( $C_{47}H_{60}$ cluster)



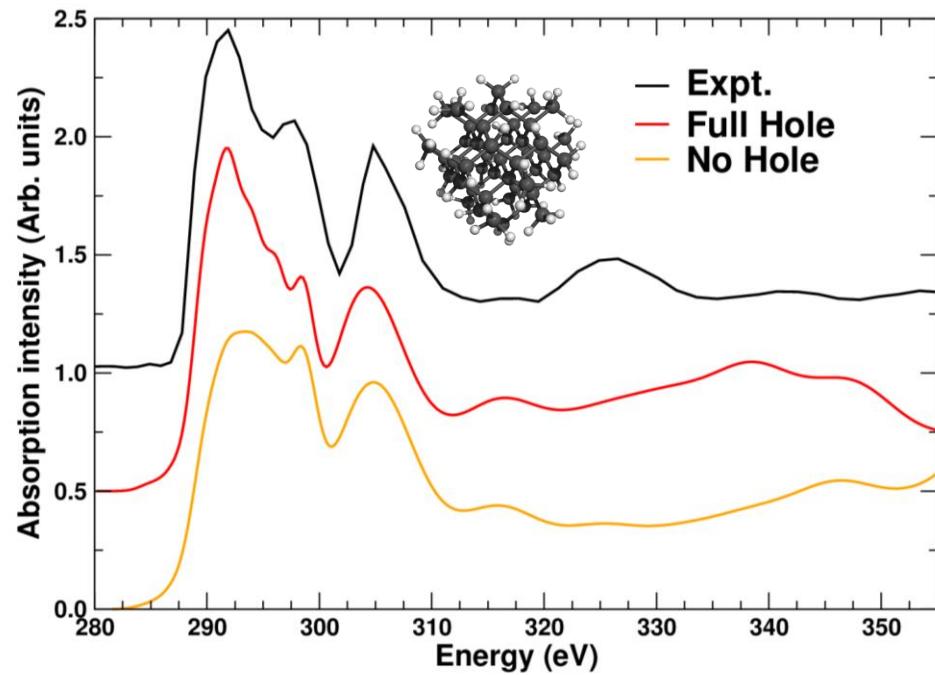
# C K-Edge XAS of Diamond ( $\text{C}_{47}\text{H}_{60}$ cluster)



# Core Hole Density Relaxation and XAS Effects in Diamond



Density Relaxation  
(Isosurface and Projection)



XAS

# **Current Developments**

**Other dynamical effects:**

**Core hole formation and screening**

**Photoelectron dynamics with valence relaxation**

## **Summary**

**New, real-time autocorrelation method for x-ray response:**

**Simulated XAS and XES in good agreement with other methods (FGR and RSGF) and experiment**

# Real-time core-hole spectral functions

# Why core-hole?

## Why real-time?

XPS satellites:

Signature of many-body corr. effects beyond GW/QP

Core XPS:

Reflects CH spectral function – excitation spectra<sup>1</sup>

X-ray spectra → atomic and electronic structure

XPS: DOS, chemical analysis

XAS, RIXS, etc: DOS, atomic structure

Dynamic theory ↔ Time-resolved experiment

<sup>1</sup>Guzzo *et al.*, Phys. Rev. Lett. 107, 166401 (2011)

# Real time approach (preliminary)

Core-hole Green's function: Cumulant form<sup>1,2</sup>

$$g(t) = e^{-i\epsilon_c t + C(t)}$$

Cumulant from linear response to transient potential<sup>2,3</sup>

$$\frac{dC(t)}{dt} = \int d^3r d^3r' v_c(\mathbf{r}) v_c(\mathbf{r}') \int d\omega \chi(\mathbf{r}, \mathbf{r}'; \omega) \frac{e^{i\omega t} - 1}{i\omega}$$

Response function from RT-TDDFT

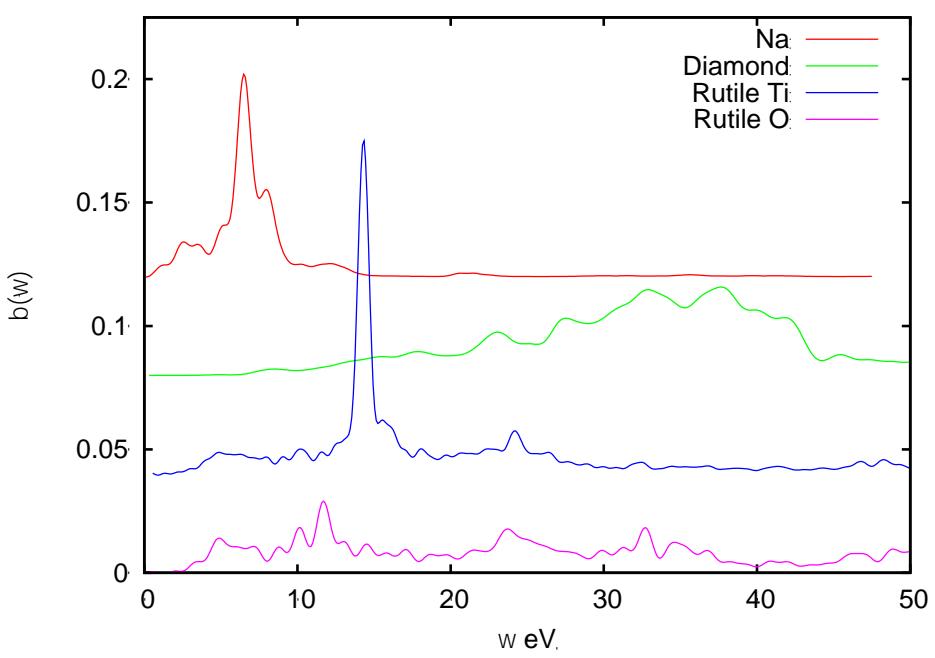
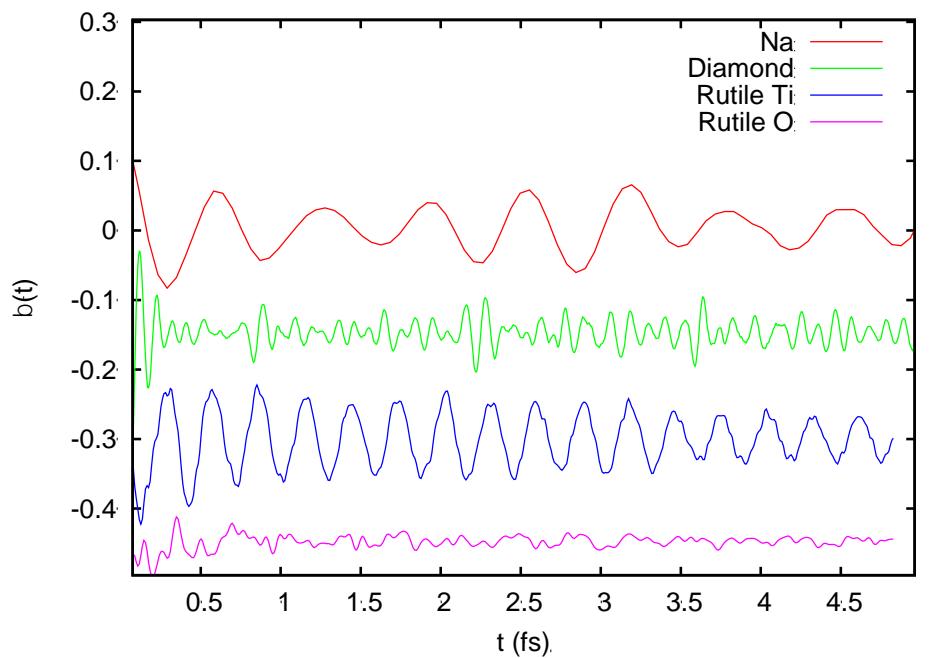
$$\delta\rho(\mathbf{r}, \omega) = \int d^3r' \chi(\mathbf{r}, \mathbf{r}'; \omega) v_c(\mathbf{r}') \Rightarrow$$
$$\frac{dC(t)}{dt} = \int d\omega \beta(\omega) \frac{e^{i\omega t} - 1}{i\omega}; \quad \beta(\omega) = \int d^3r v_c(\mathbf{r}) \delta\rho(\mathbf{r}, \omega)$$

<sup>1</sup>P. Nozières and C. T. de Dominicis, Phys. Rev. **178**, 1097 (1969).

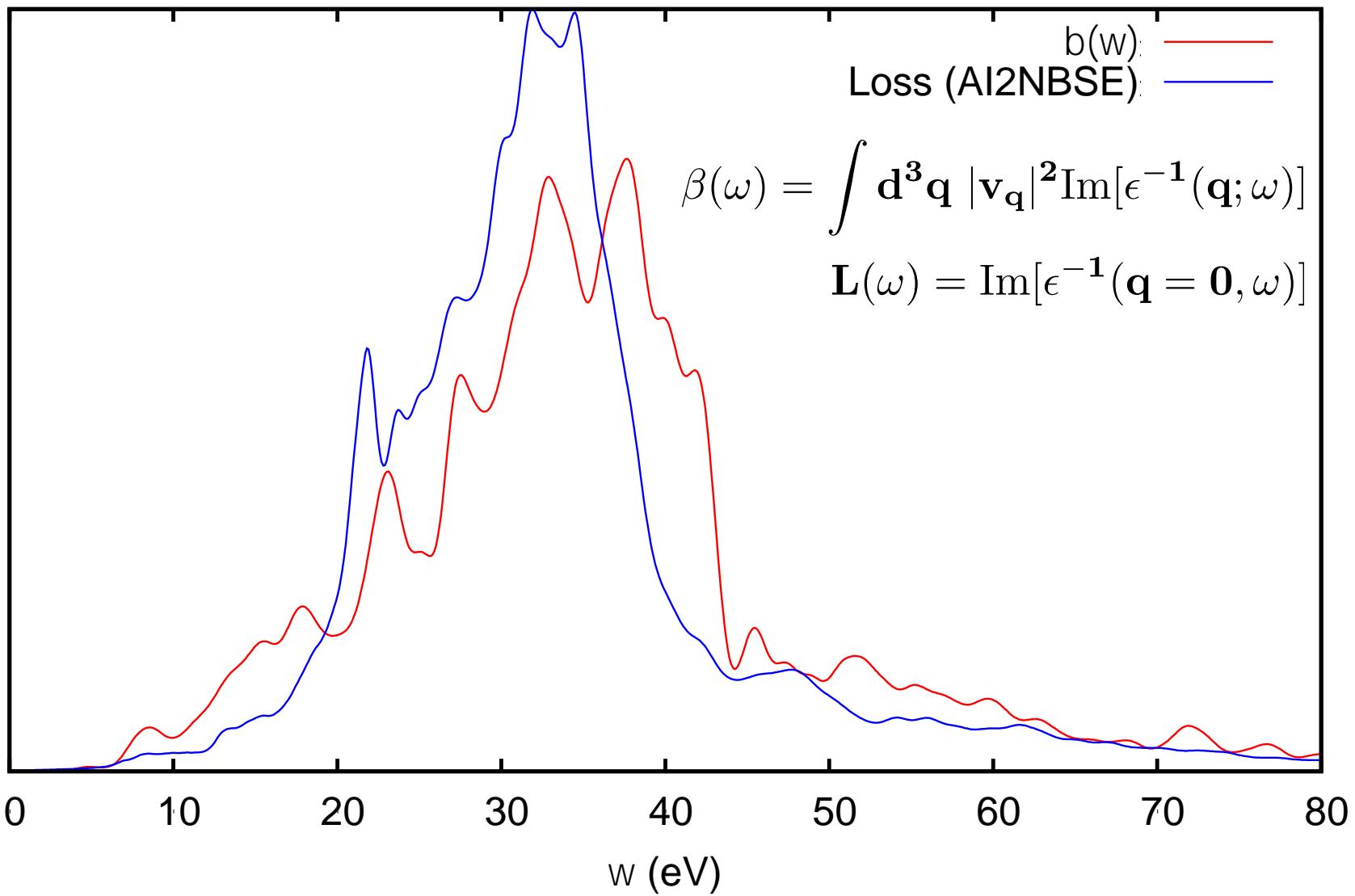
<sup>3</sup>Rehr et al., Preprint

<sup>2</sup>D. C. Langreth, Phys. Rev. B 1, 471–477 (1970)

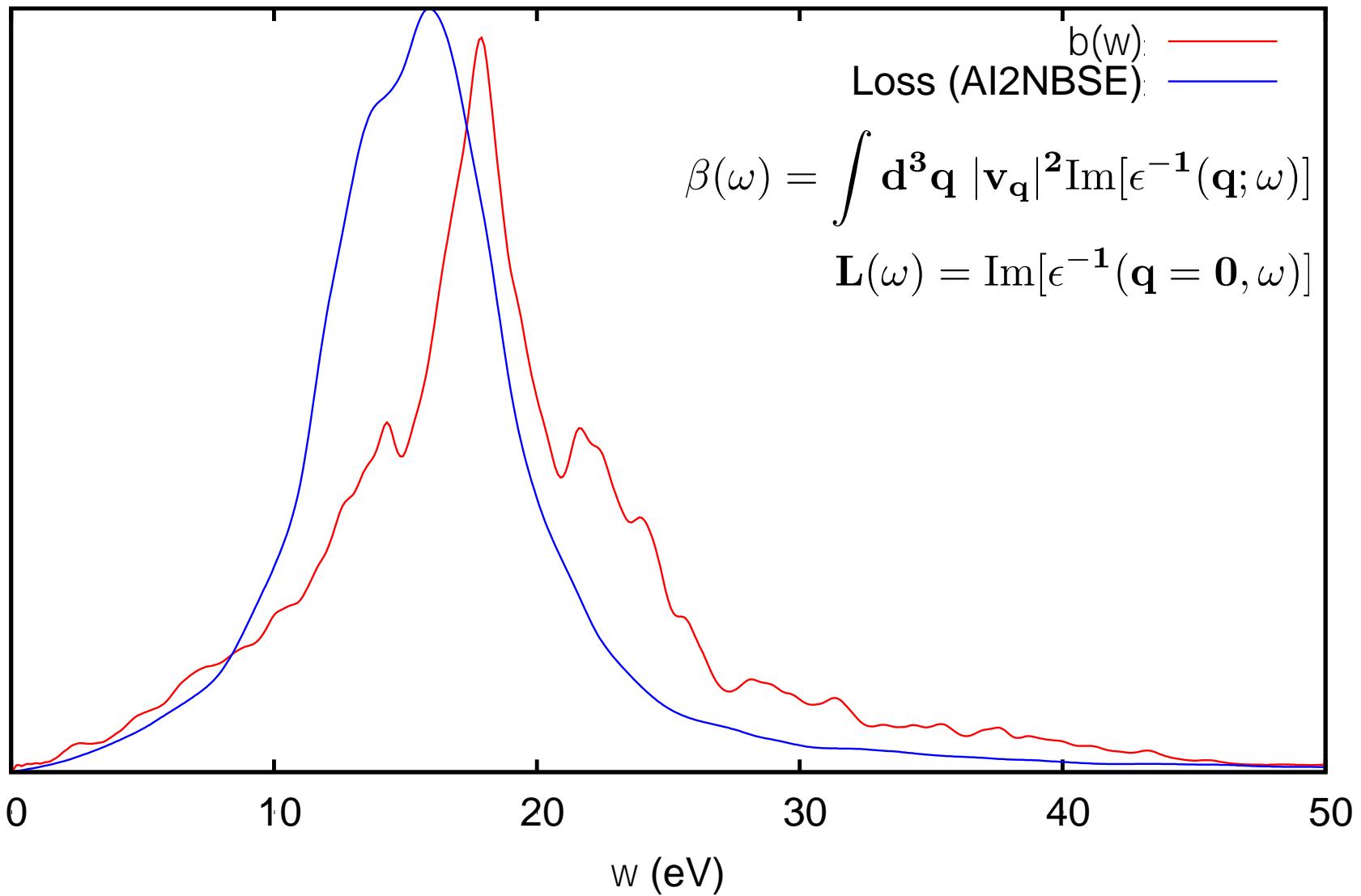
# Real time vs freq. response



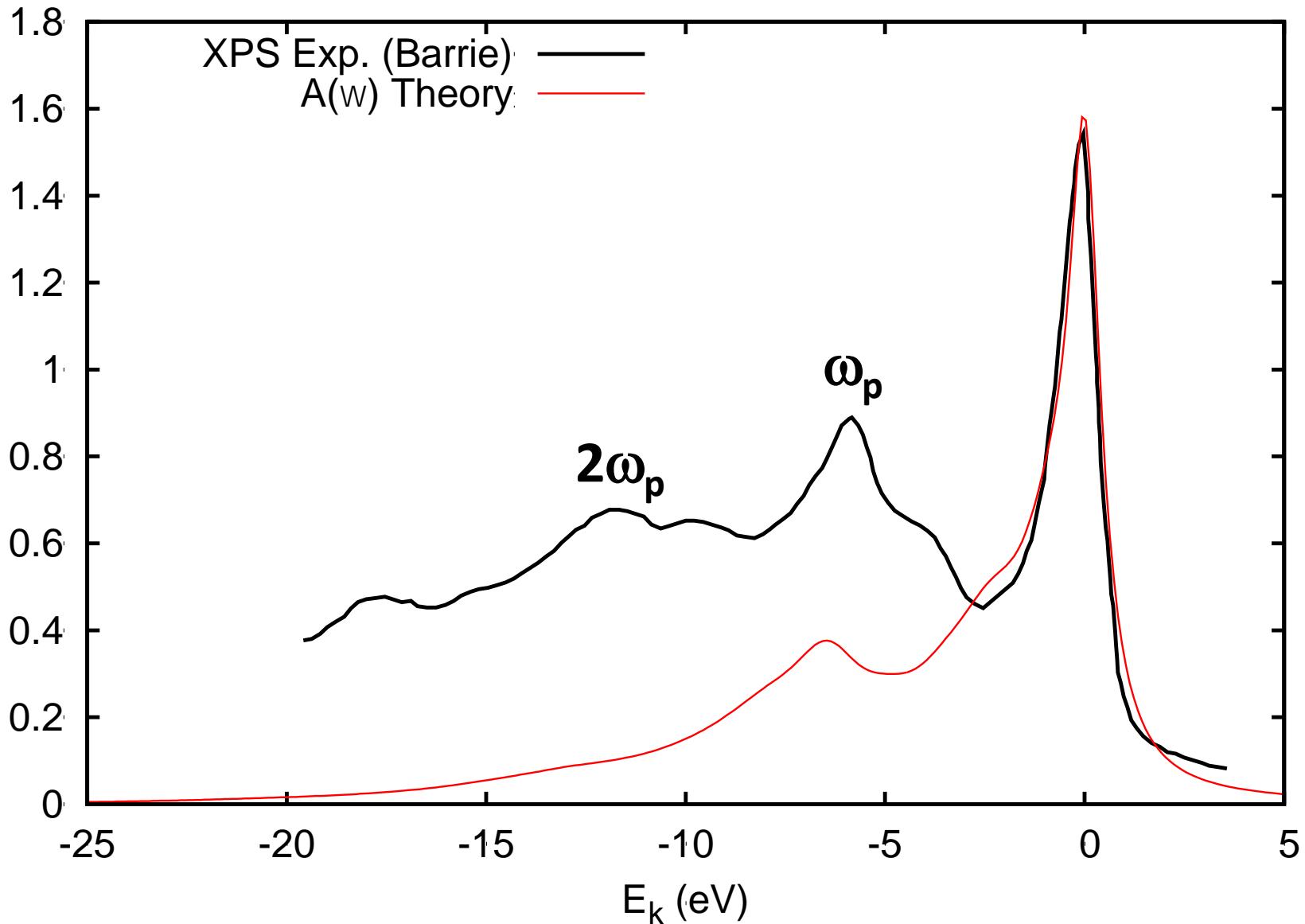
# Comparison to loss function: Diamond



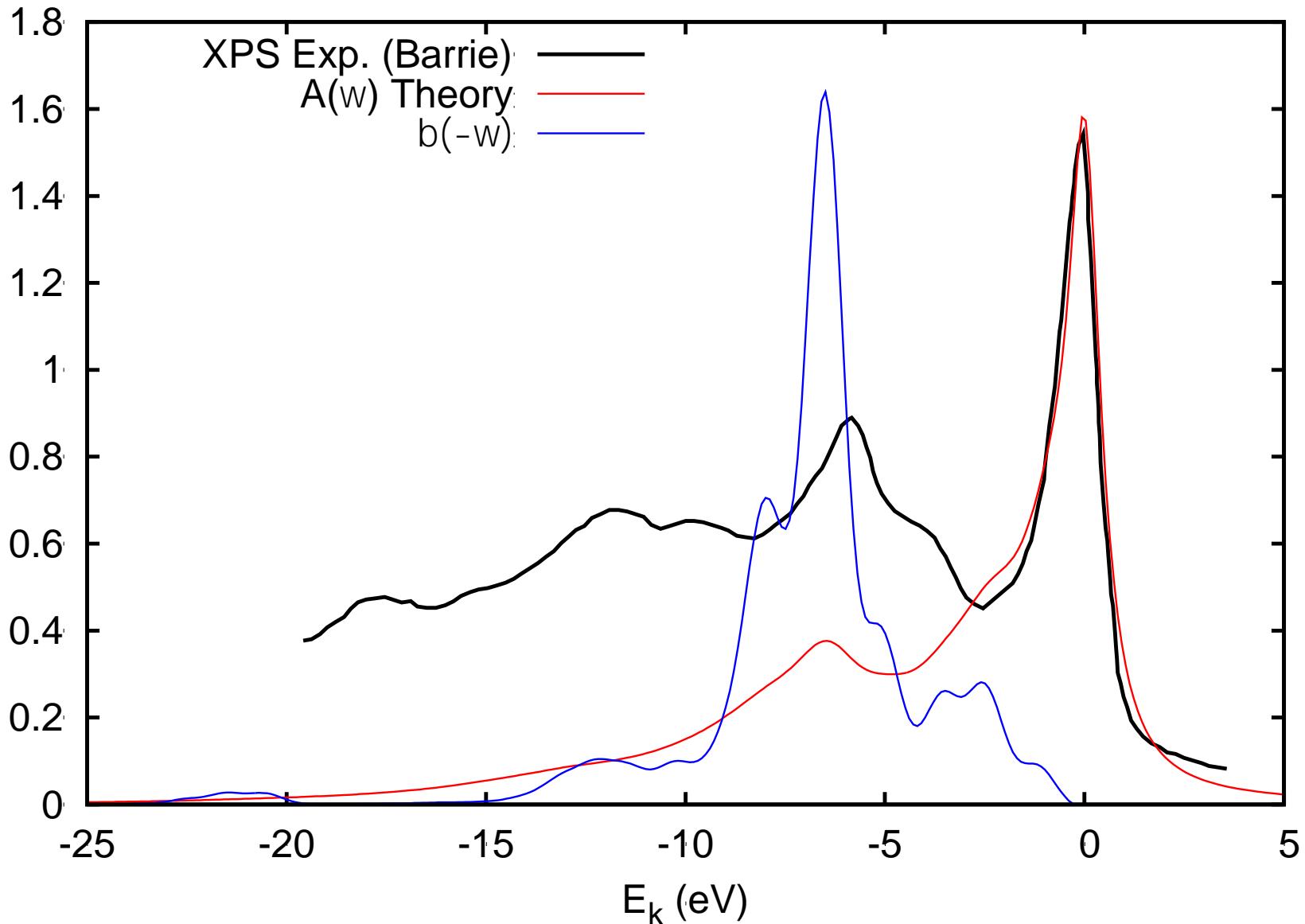
# Comparison to loss function: Silicon



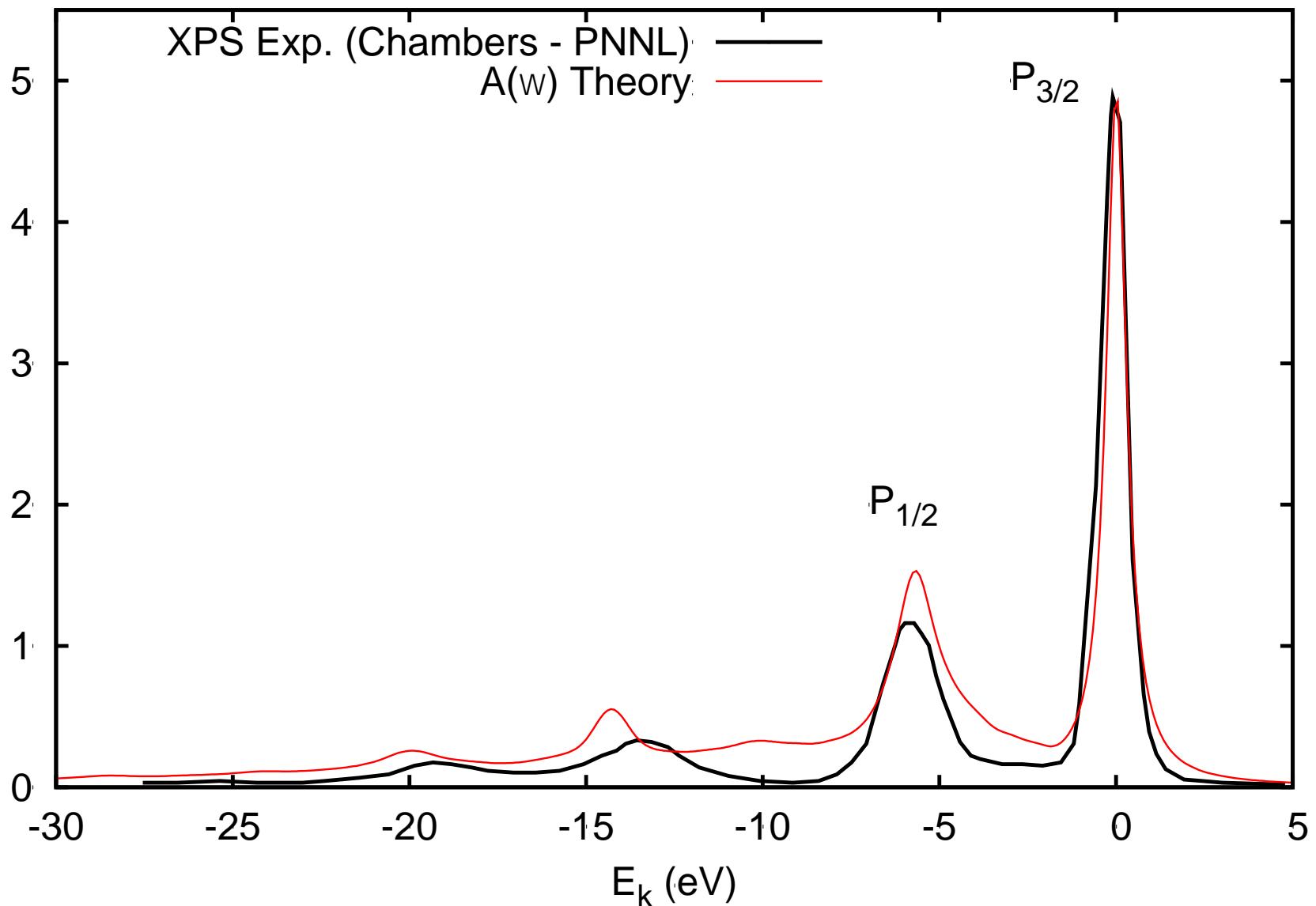
# XPS vs CH spectral function: Sodium



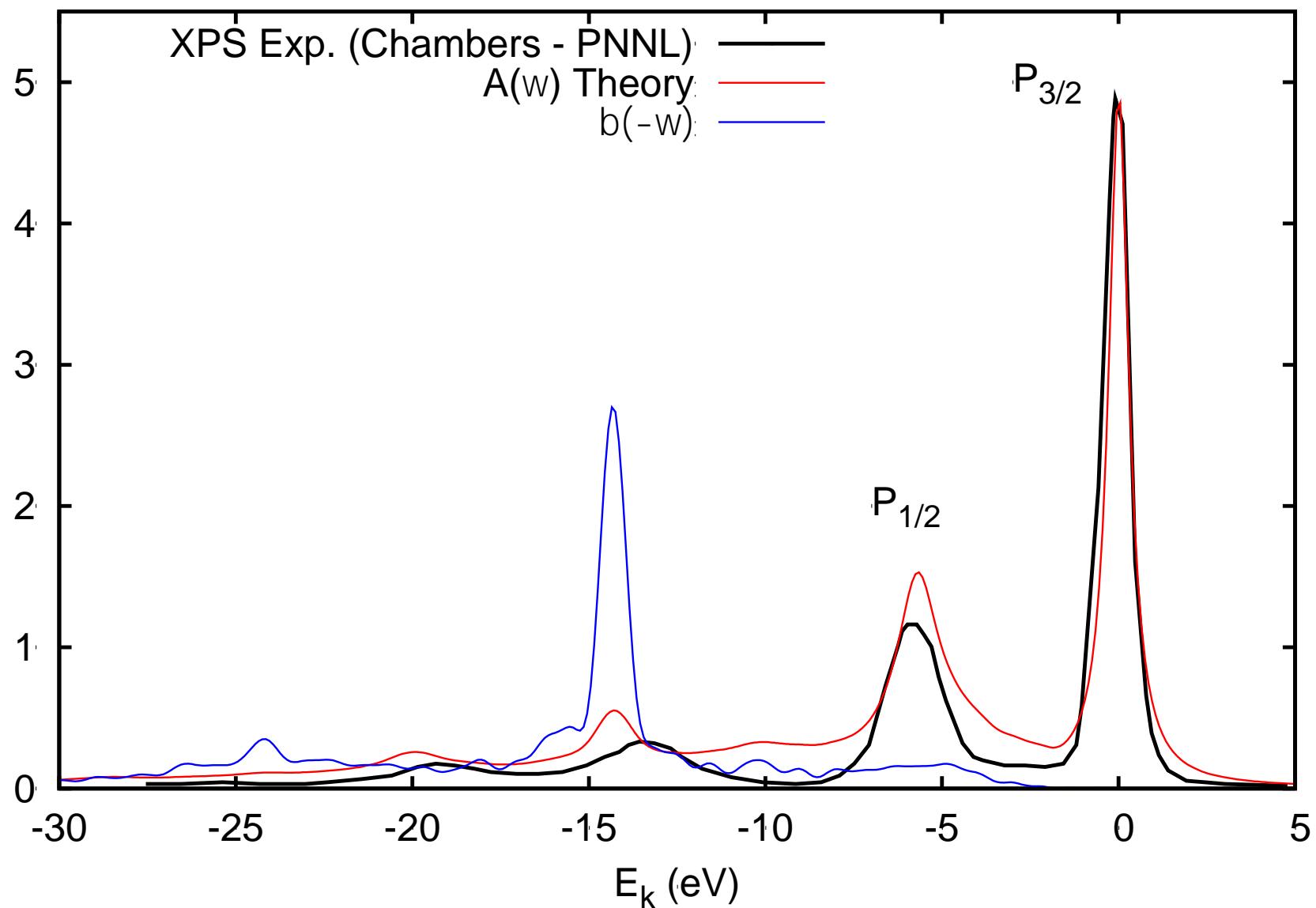
# XPS vs CH spectral function: Sodium



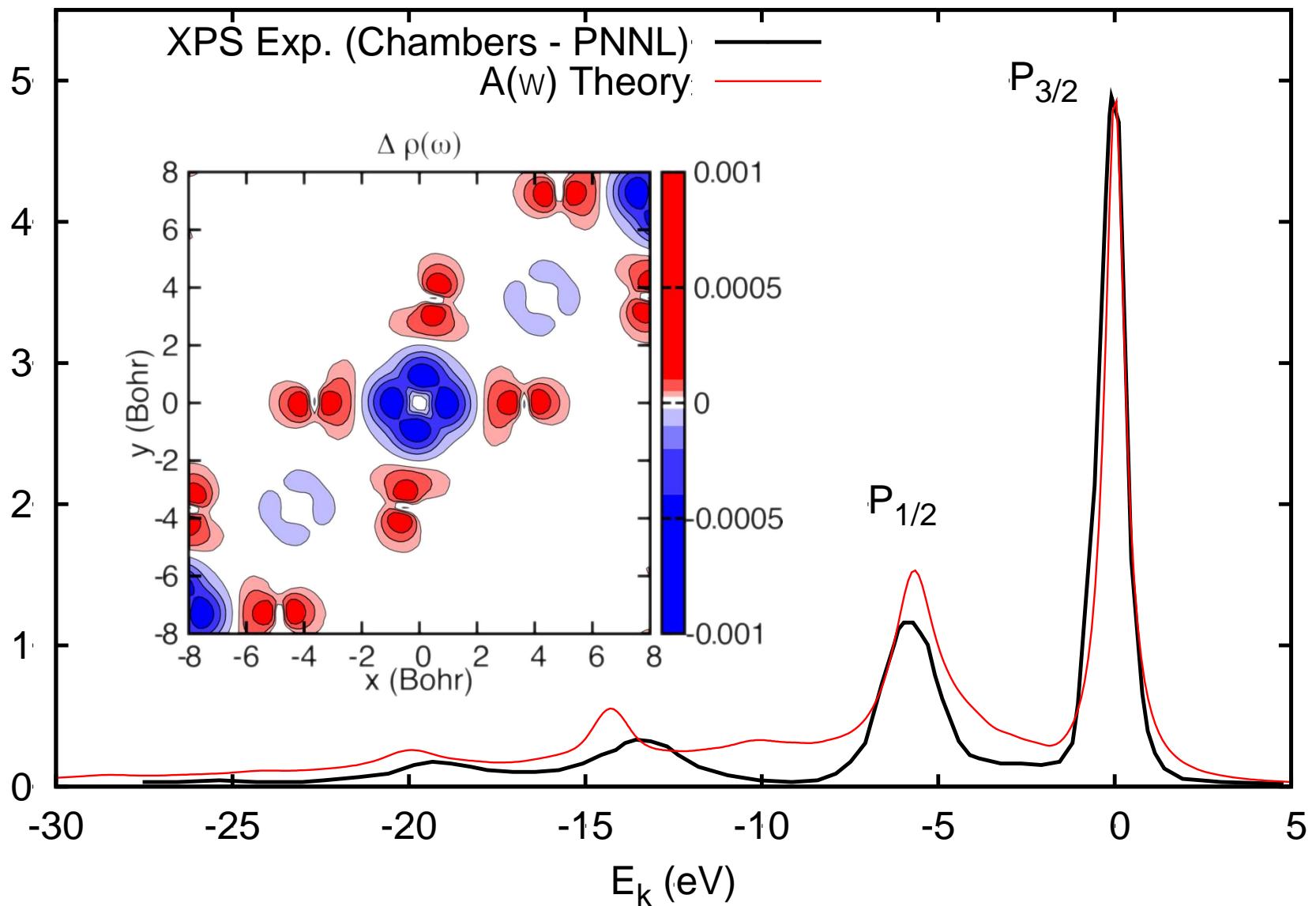
# XPS vs CH spectral function: Ti (Rutile)



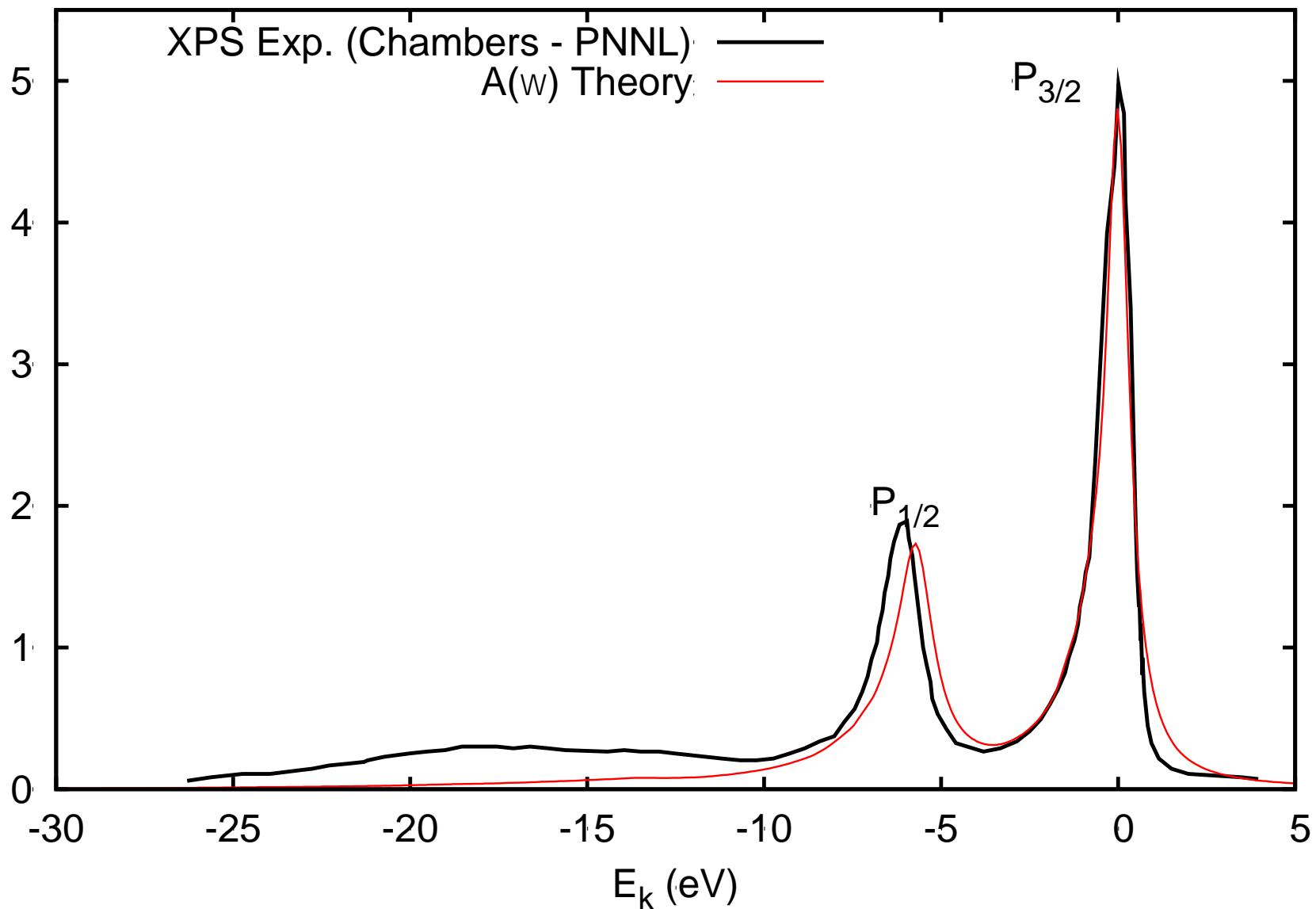
# XPS vs CH spectral function: Ti (Rutile)



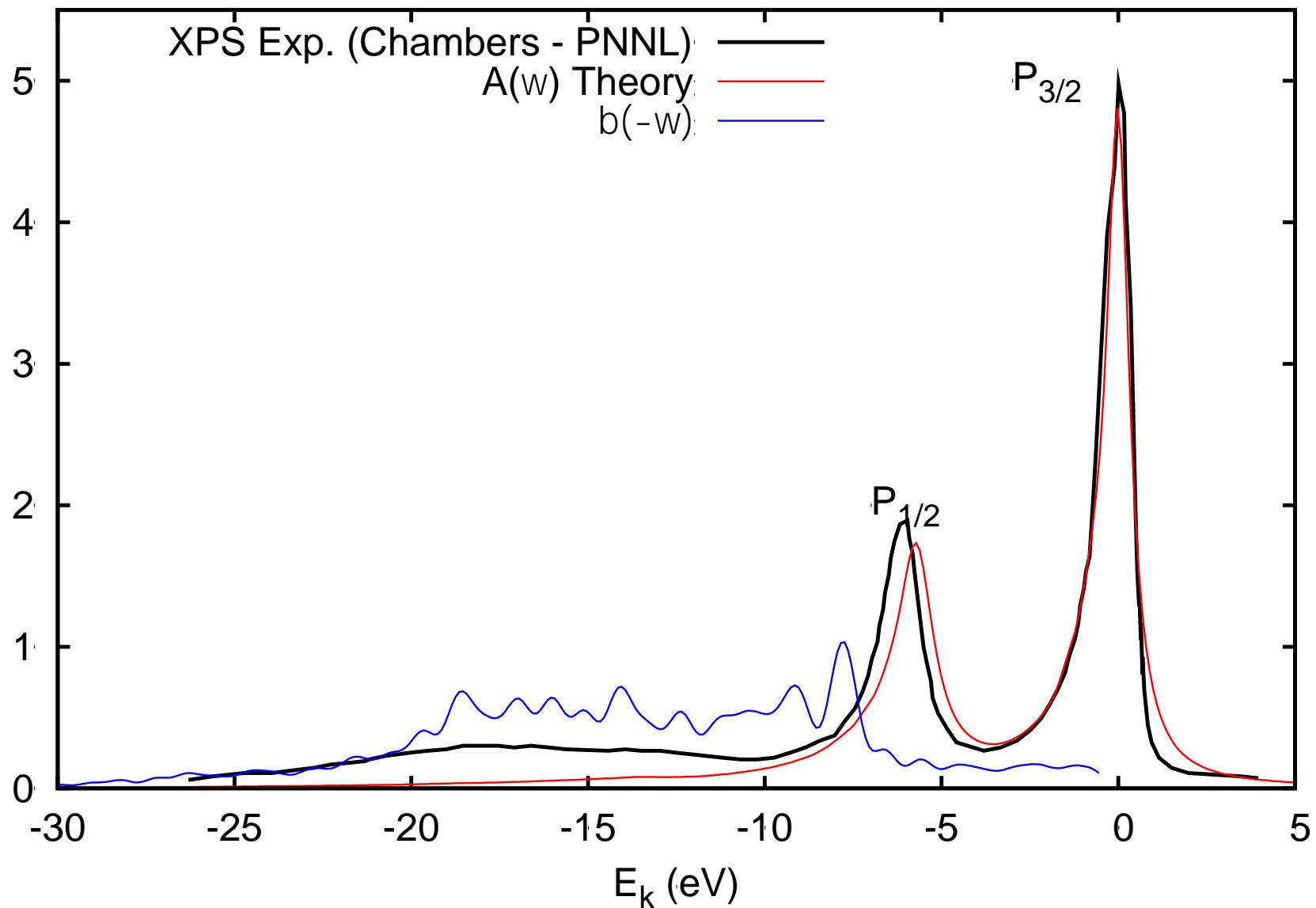
# XPS vs CH spectral function: Ti (Rutile)



# XPS vs CH spectral function: Ti (Metal)



# XPS vs CH spectral function: Ti (Metal)



# **Current Developments**

**Use PAW potential**

**Extrinsic effects**

## **Summary**

**Cumulant expansion:**

**Explains multiple plasmon satellites in XPS**

**Core response is local**

**Qualitative agreement with experiment**

# Conclusions

**RT-SIESTA: very versatile implementation of RT-TDDFT**

**Applicable to wide range of systems**

**Linear and nonlinear optical response**

**Core spectroscopies**

**Core-hole response and spectral function**

# Acknowledgements

T. Ahmed

A. Tsolakidis

G. F. Bertsch

K. Yabana

B. E. Eichinger

B. H. Robinson

C. Luscombe

A. Jen

