Real-time time-correlation approach for x-ray absorption and emission

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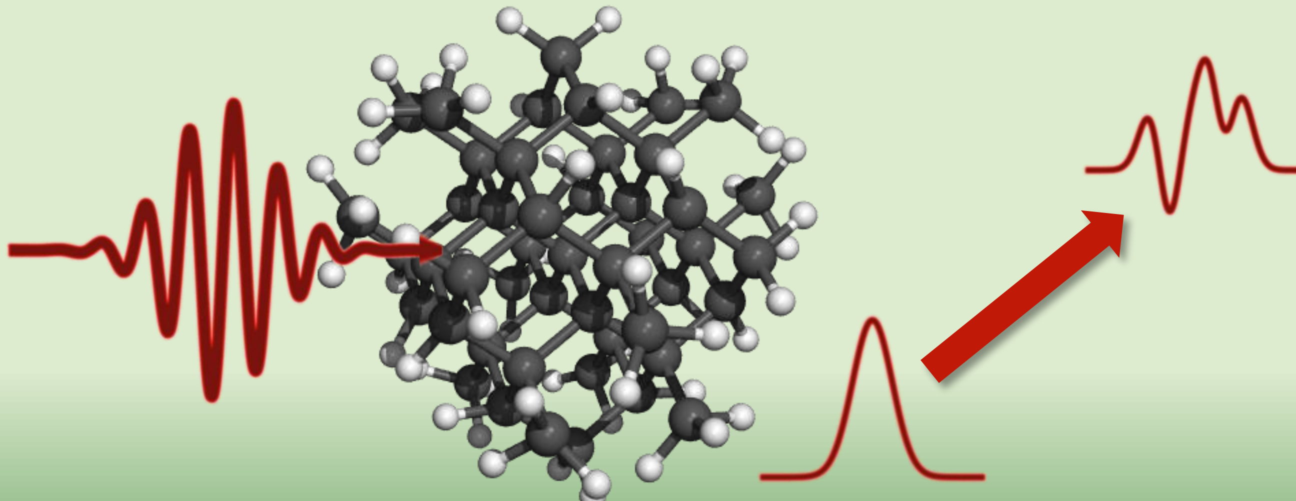

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Why Use a Time-Dependent Approach?

XAS 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

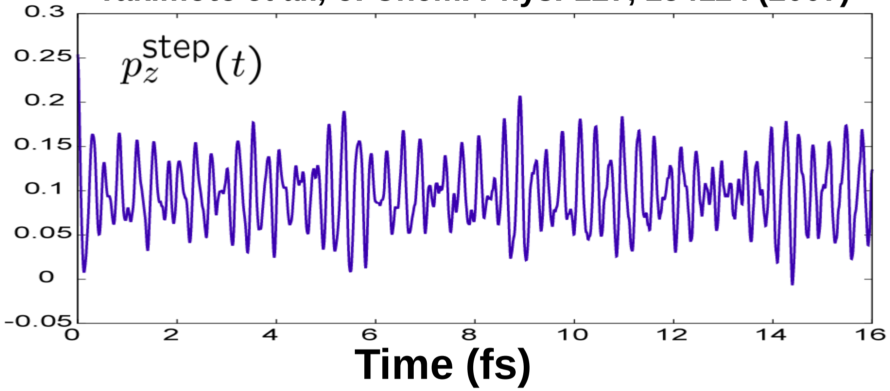
Goal:

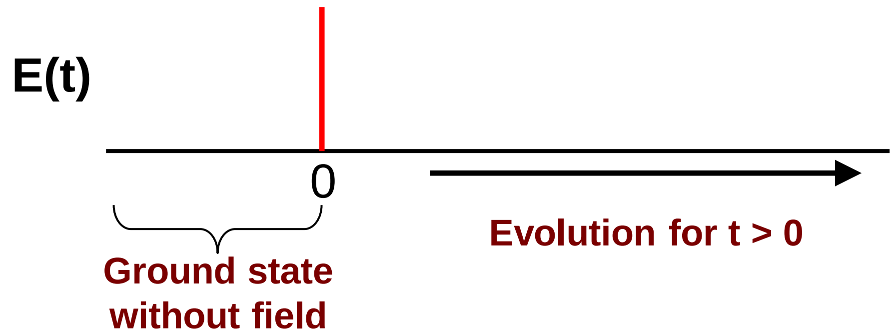
Time-dependent x-ray response, including core hole dynamics

TD Methods: Two Useful Examples

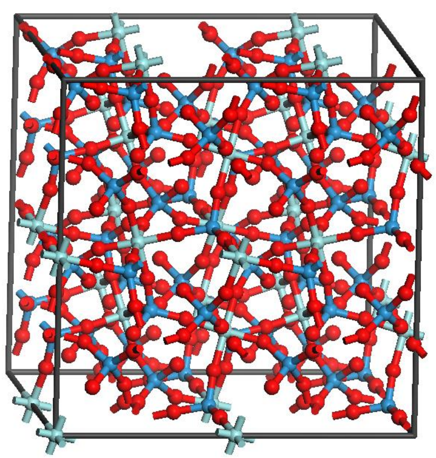
Real-Time TDDFT for NLO response

Takimoto *et al.*, J. Chem. Phys. 127, 154114 (2007)



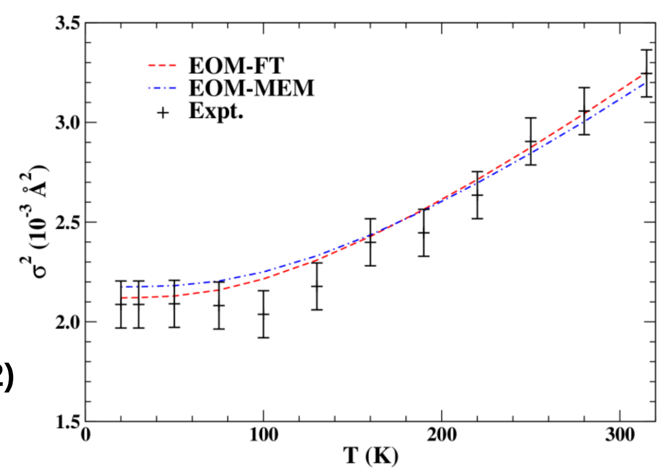


Real-Time DW factors



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

Vila *et al.*, Phys. Rev. B 85, 024303 (2012)



TD Methods: Two Useful Examples

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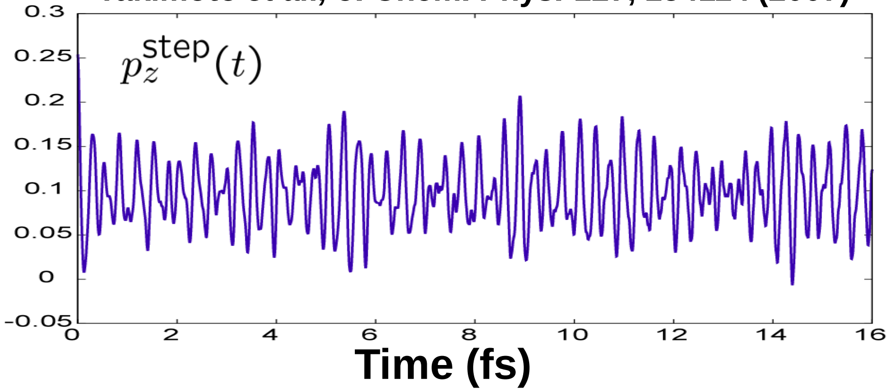

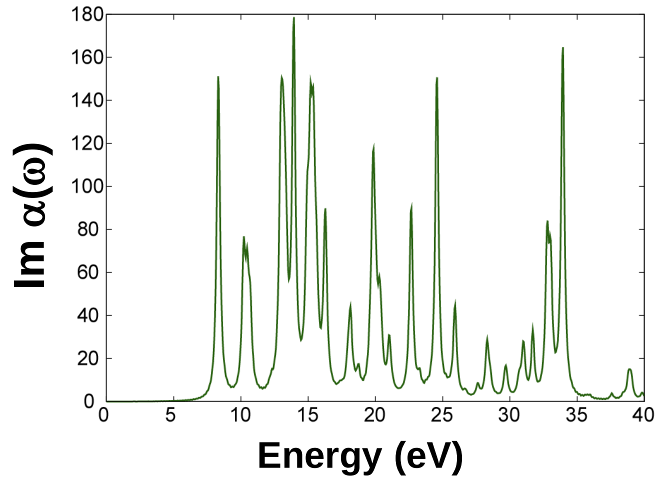

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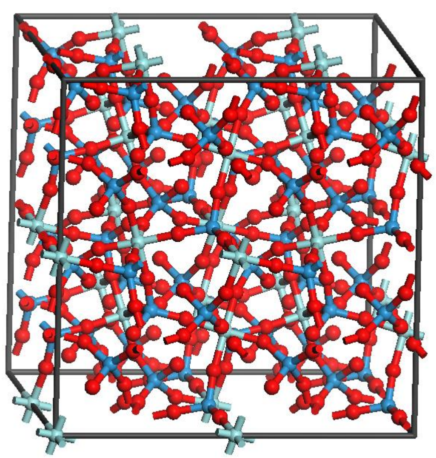

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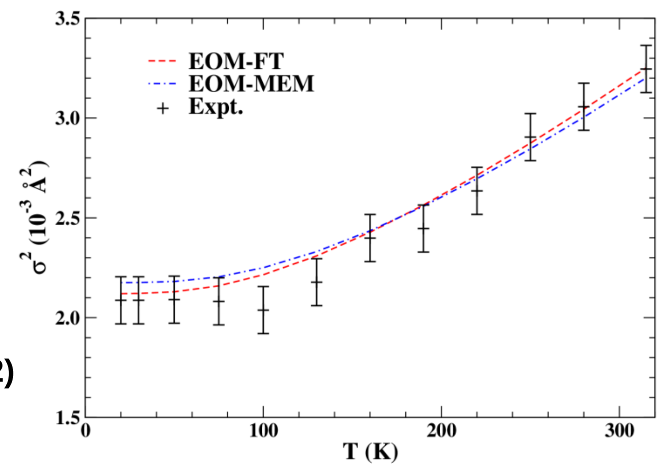
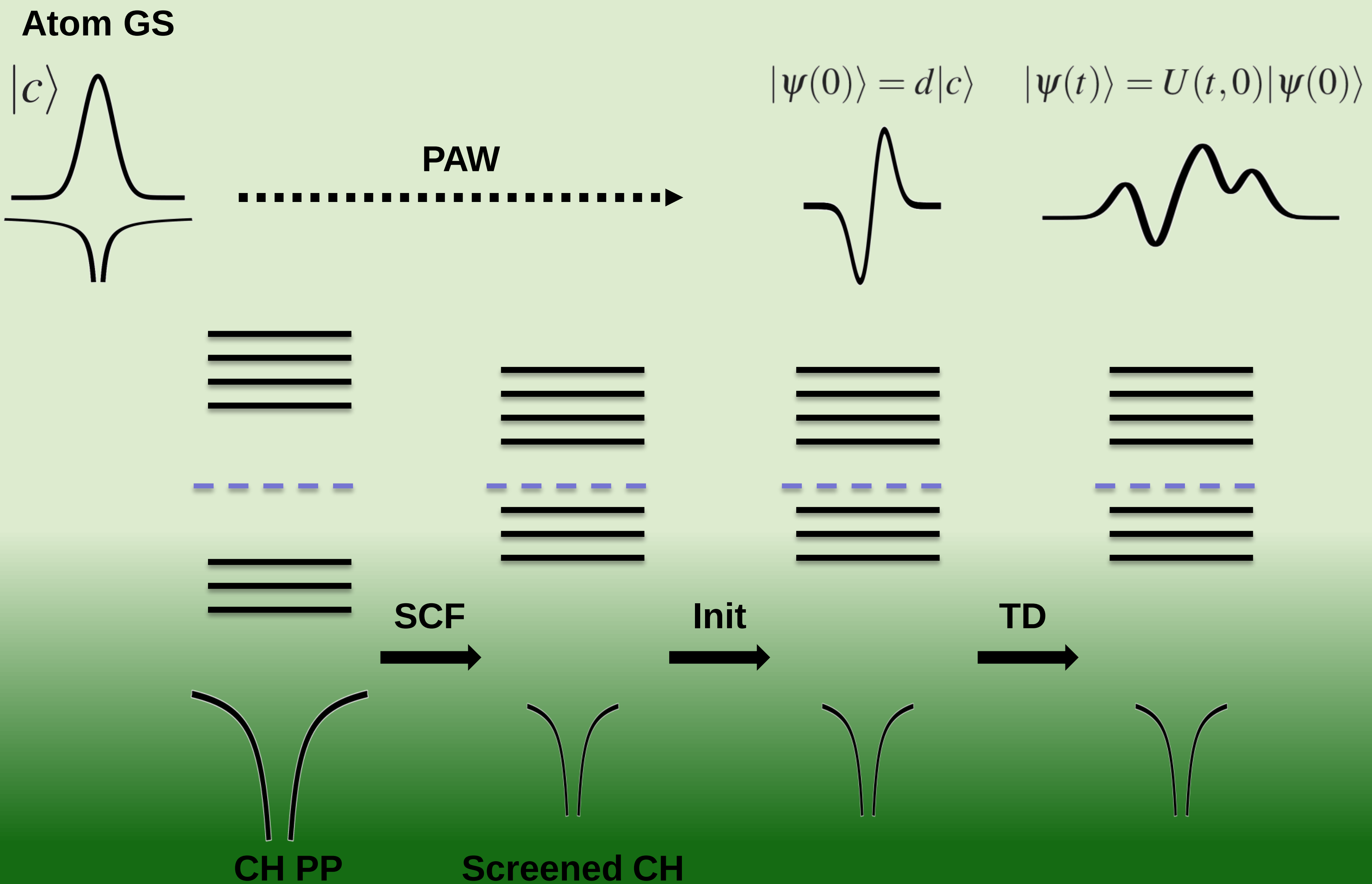


Real-Time X-Ray Spectroscopy (RTXS)



RTXS Equations

XAS Absorption (FGR, 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

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

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

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

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

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

Crank-Nicolson

$$\bar{t} = t + \Delta/2$$

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

Computational Details

Implemented on UW RT extension of SIESTA with:

Real-time propagation

PAW for dipole matrix elements (based on UW OCEAN)

Present implementation:

Quasi-monochromatic source with finite lifetime

SIESTA details:

TZDP basis

Norm conserving PP

150 Ryd grid cutoff

Experimental structures

TD:

Simulation time ~1-5 fs with 0.01 fs steps

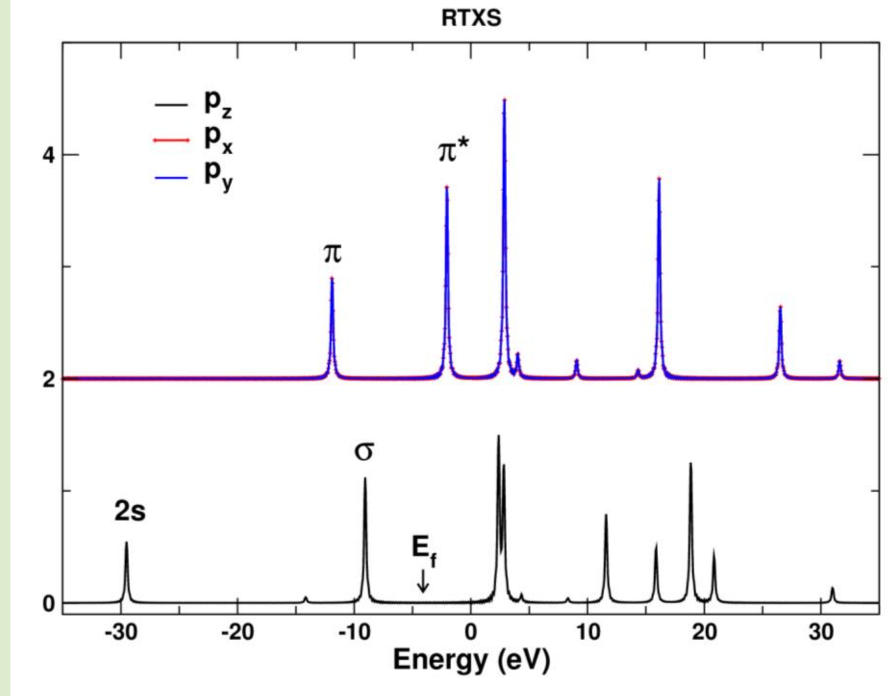
Broadening and E_c shift to match experiment

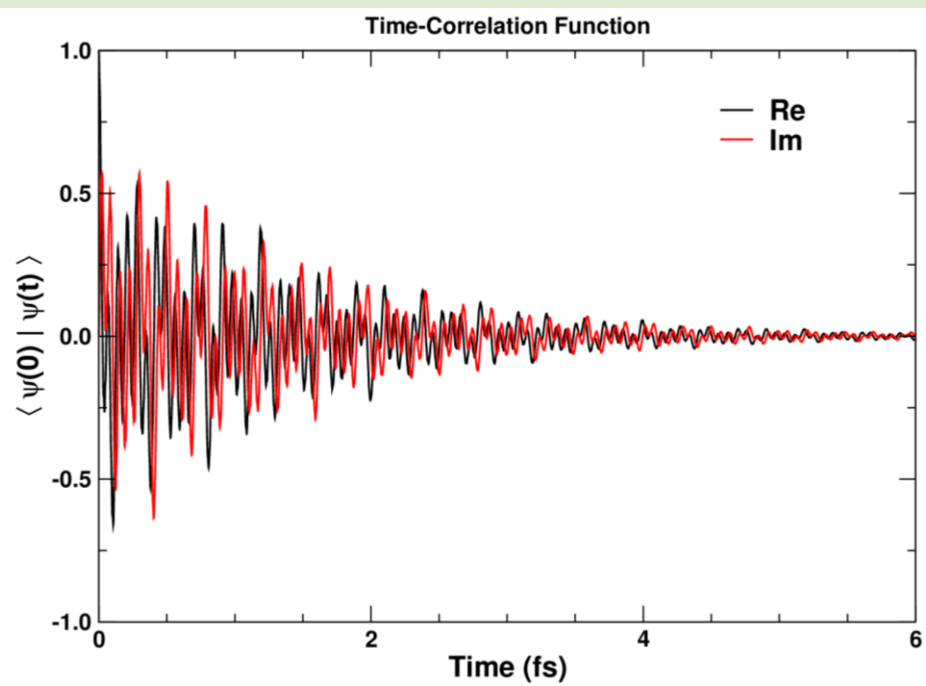
Comparisons with:

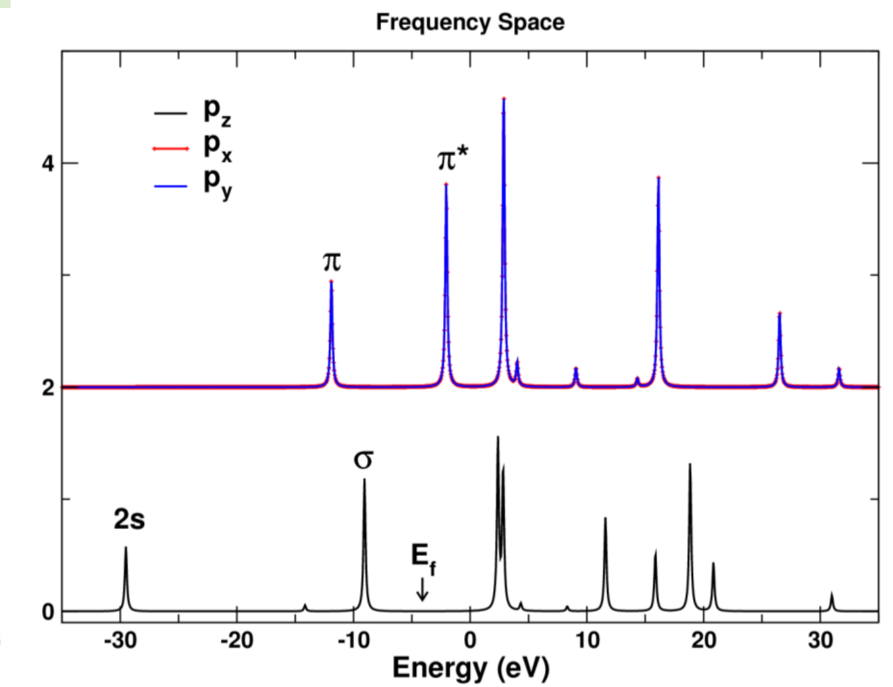
StoBe (GTO-based FGR, TST core hole approximation)

FEFF (Real Space Multiple Scattering, FSR)

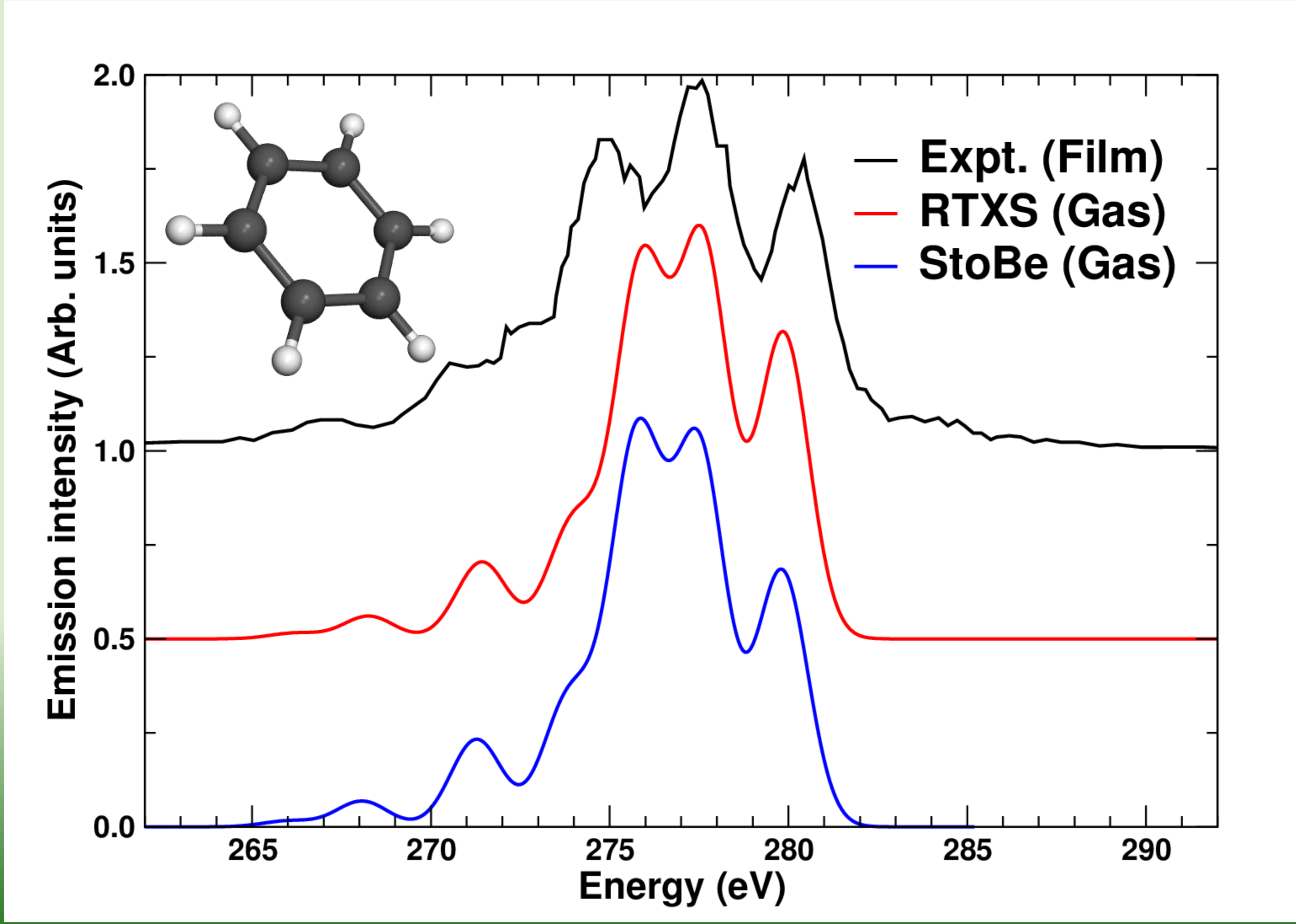
Autocorrelation Function and C pDOS for CO





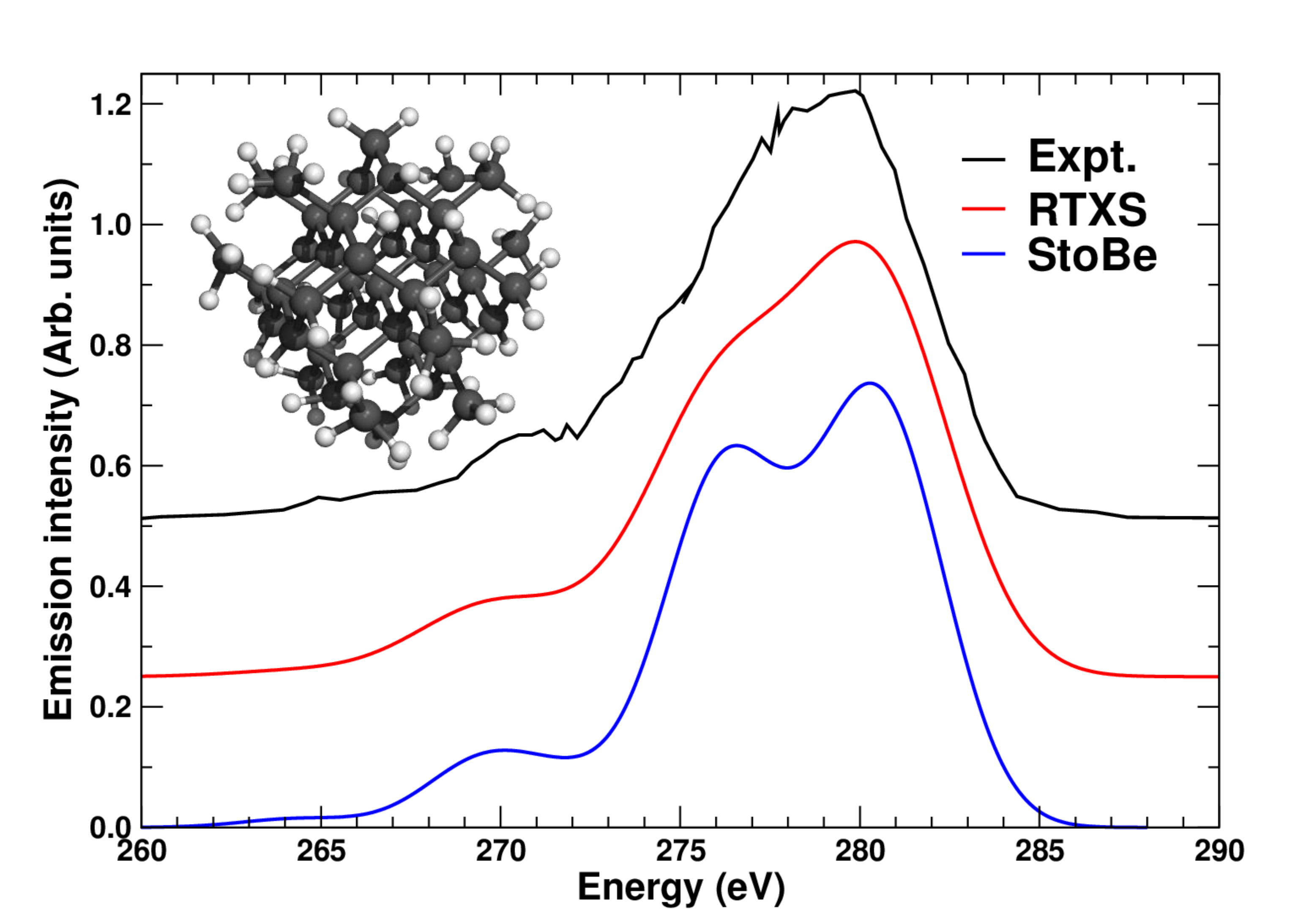


C Kα XES of C_6H_6



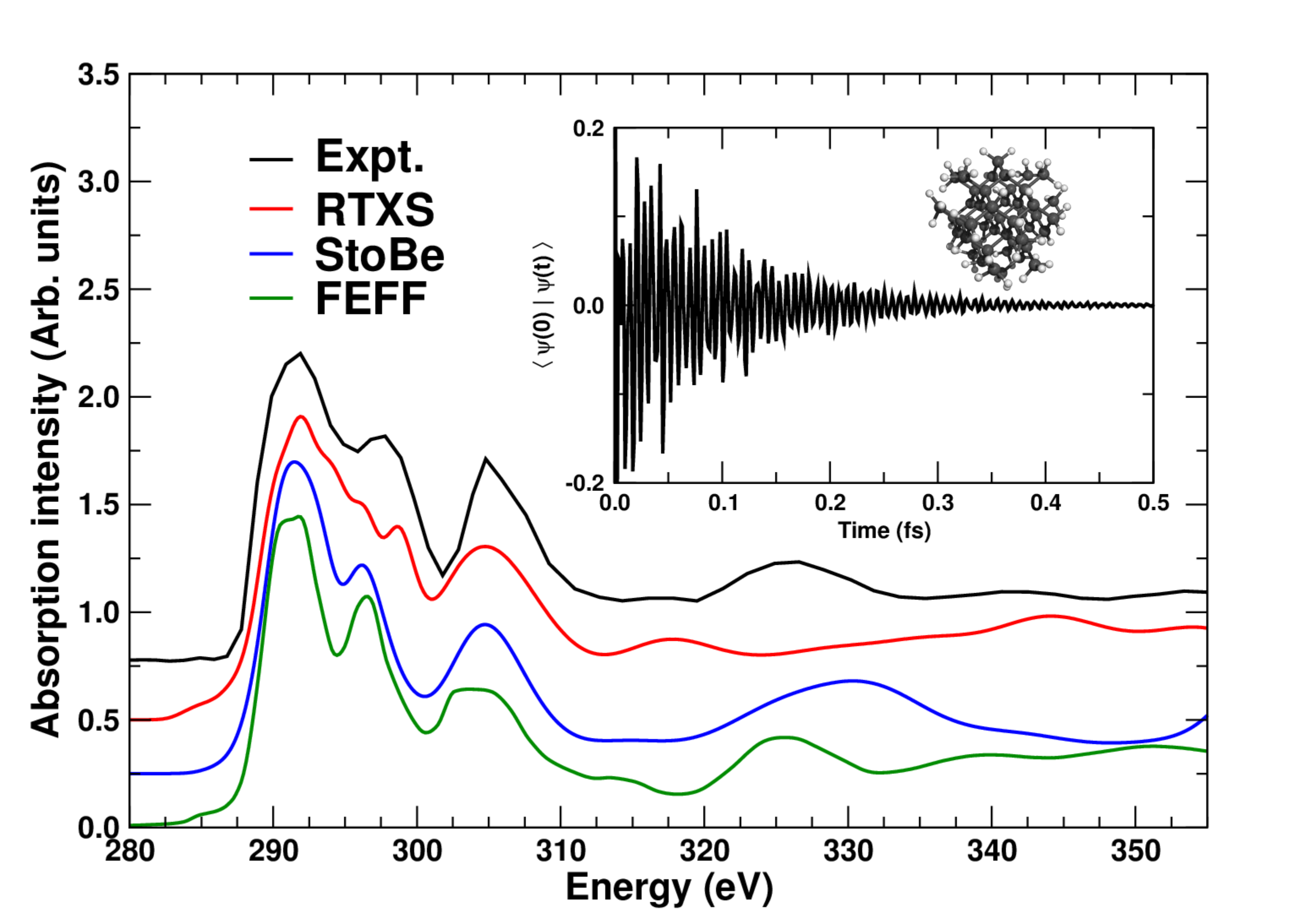
Expt: Skytt *et al.*, Phys. Rev. A 52, 3572 (1995)

C Kα XES of Diamond ($C_{47}H_{60}$ cluster)



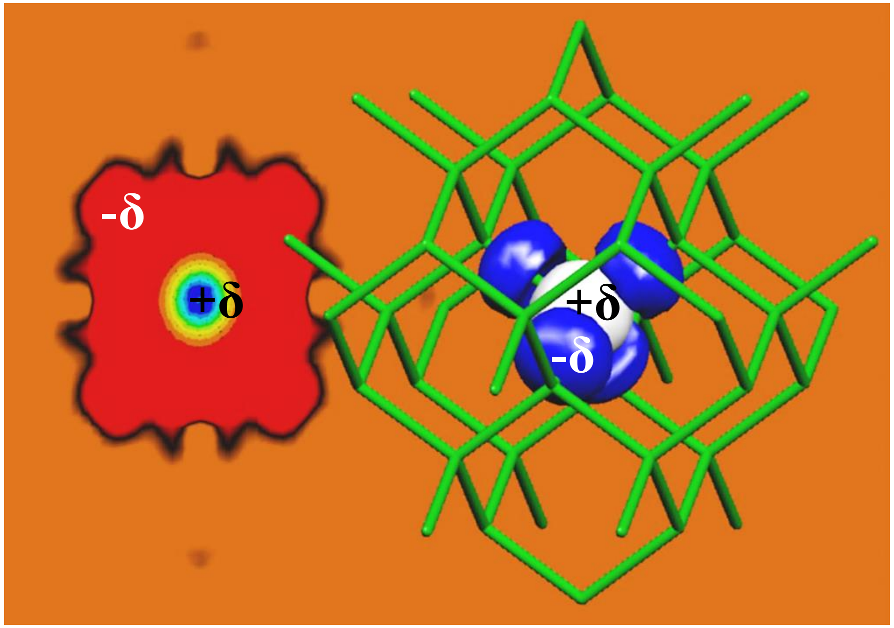
Expt: Ma *et al.*, Phys. Rev. Lett. 69, 2598 (1992)

C K-Edge XAS of Diamond ($C_{47}H_{60}$ cluster)

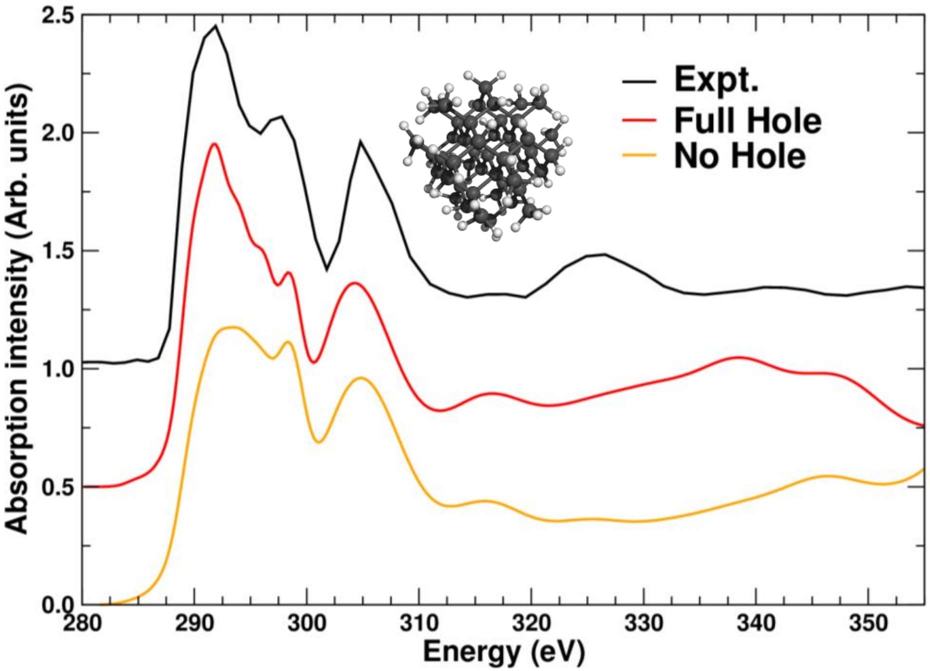


Expt: Fister *et al.*, Phys. Rev. B 75, 174106 (2007)

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

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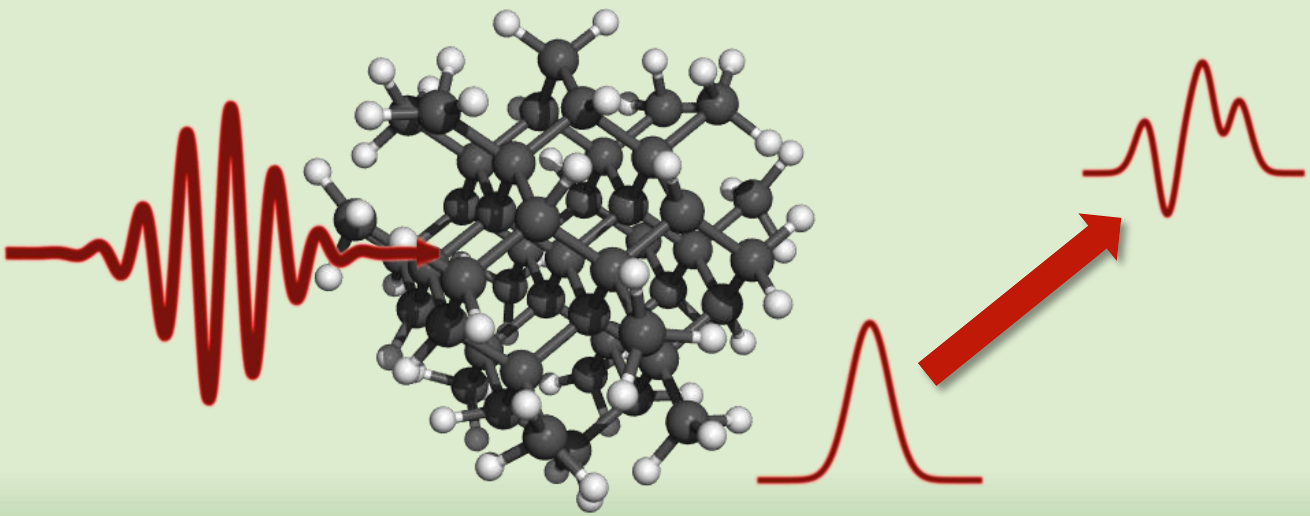

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