Attosecond Coherent X-ray Stimulated Raman (CXRS) Spectroscopy

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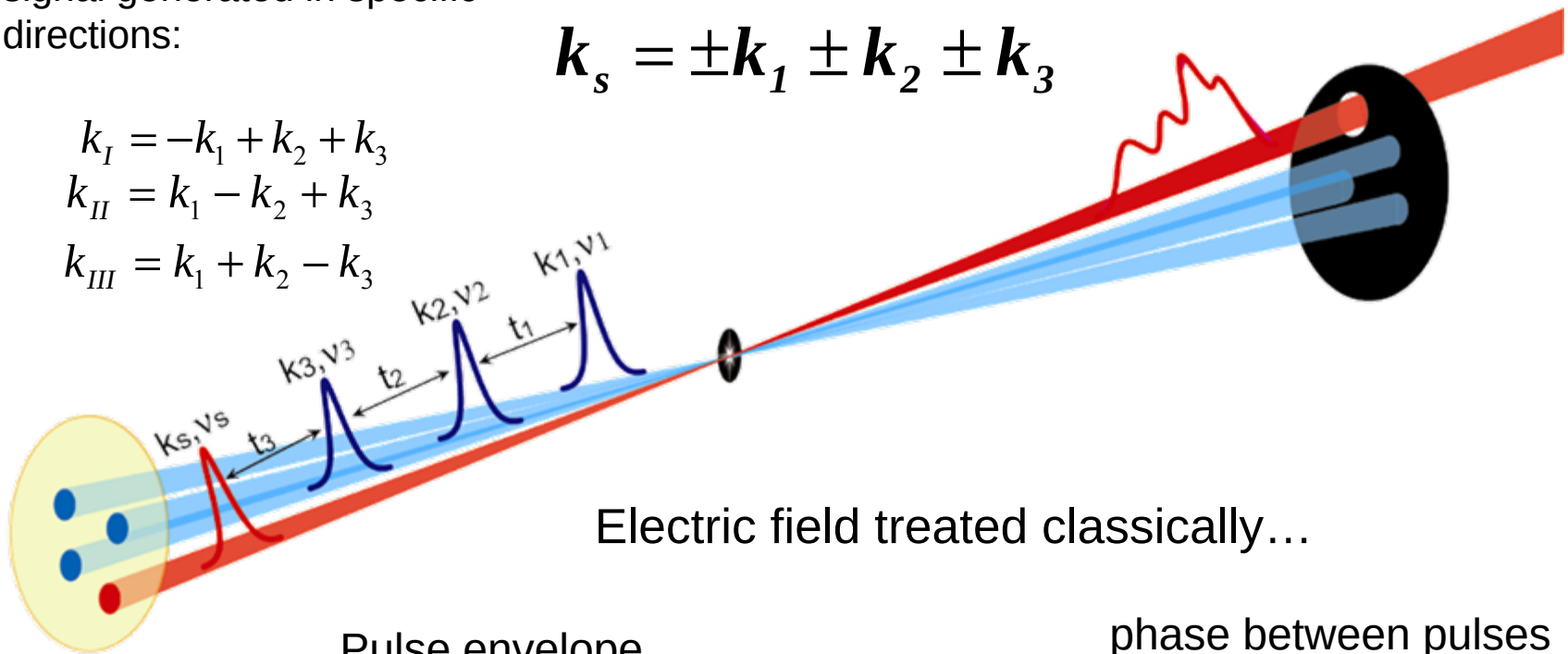
Heterodyne-Detected (Stimulated) Four Wave Mixing

signal generated in specific directions:

$$\boldsymbol{k}_s = \pm \boldsymbol{k}_1 \pm \boldsymbol{k}_2 \pm \boldsymbol{k}_3$$

$$k_I = -k_1 + k_2 + k_3$$
$$k_{II} = k_1 - k_2 + k_3$$
$$k_{III} = k_1 + k_2 - k_3$$



Electric field treated classically…

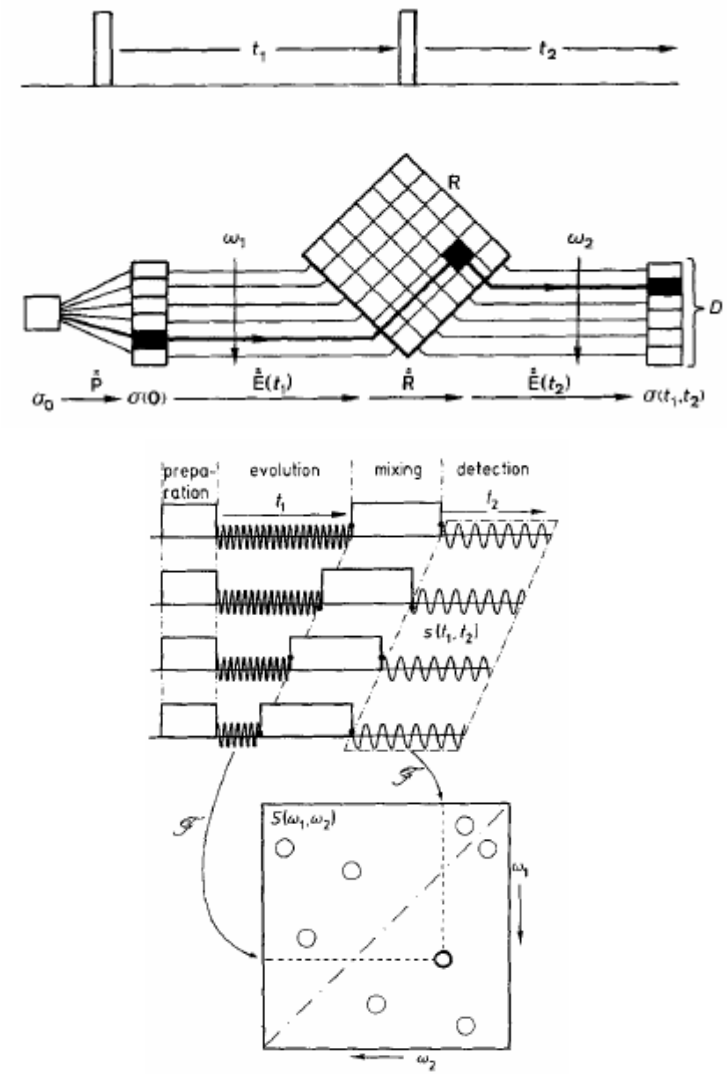
$$\boldsymbol{E}(\boldsymbol{r},\tau) = \sum_{j=1}^{4} \sum_{\nu} \overbrace{E_{j\nu}(\tau - \bar{\tau}_j)}^{\text{Pulse envelope}} \exp[ik_j r - i\bar{\omega}_j(\tau - \bar{\tau}_j) \overbrace{- i\varphi_{j\nu}(\tau - \bar{\tau}_j)}^{\text{phase between pulses}}] + c.c.,$$

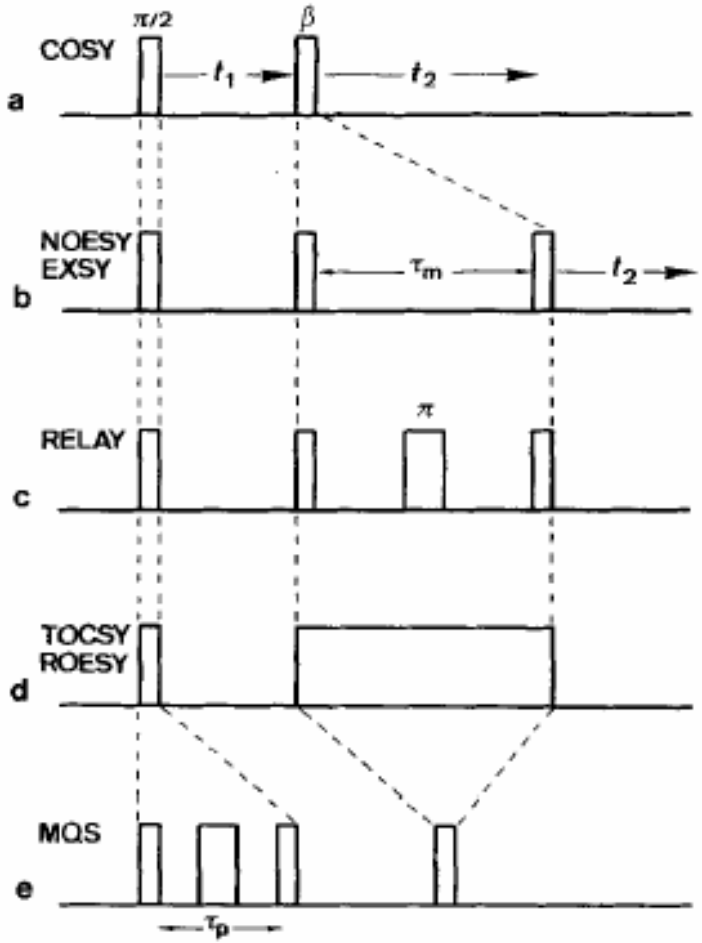
pulse #

polarization

…induces a polarization in the material

2D NMR Spectroscopy





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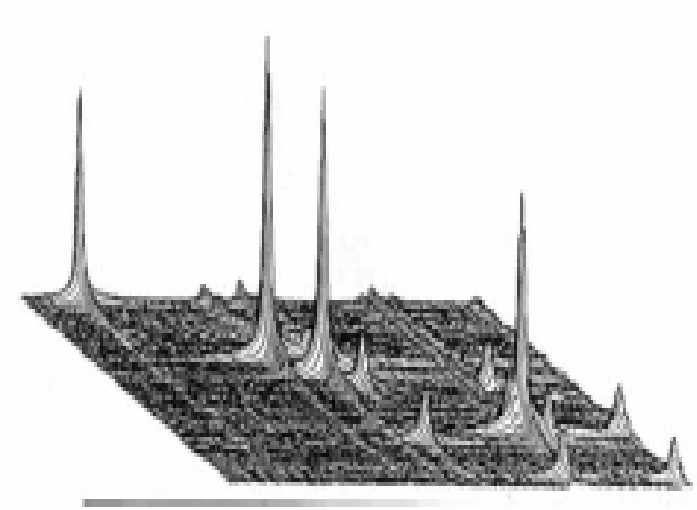
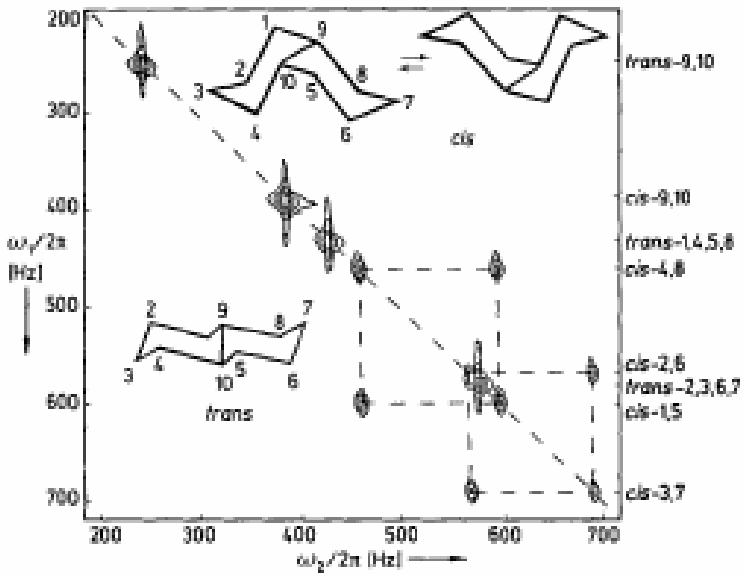
Nuclear Magnetic Resonance Fourier Transform Spectroscopy (Nobel Lecture)**

By Richard R. Ernst*





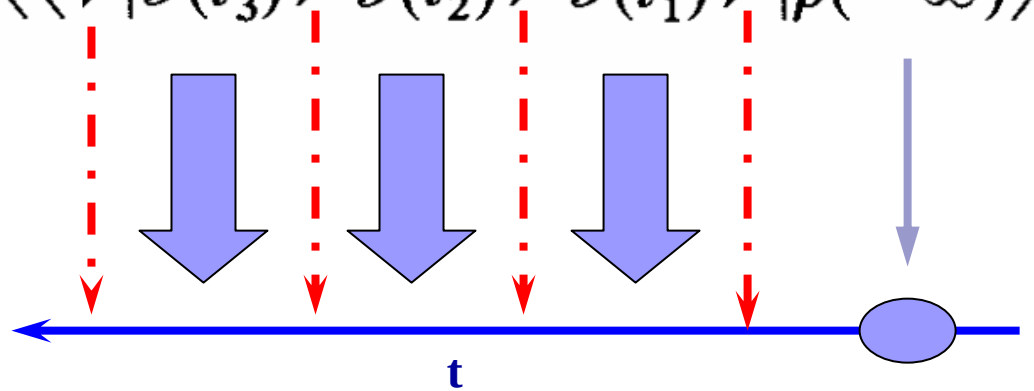
The Nonlinear Response Functions

$$P(\mathbf{r},t) = P^{(1)}(\mathbf{r},t) + P^{(2)}(\mathbf{r},t) + P^{(3)}(\mathbf{r},t) + \ldots$$

Nonlinear polarization $\quad P^{(n)}(\mathbf{r},t) \equiv \langle\langle V|\rho^{(n)}(t)\rangle\rangle \equiv Tr[V\rho^{(n)}(t)]$

$$\boxed{\begin{aligned} P^{(n)}(\mathbf{r},t) &= \int_0^\infty dt_n \int_0^\infty dt_{n-1} \ldots \int_0^\infty dt_1 S^{(n)}(t_n, t_{n-1}, \ldots, t_1) \\ &\times E(\mathbf{r}, t-t_n) E(\mathbf{r}, t-t_n-t_{n-1}) \ldots E(\mathbf{r}, t-t_n-t_{n-1}\ldots-t_1), \end{aligned}}$$

$$S^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \langle\langle V|\mathscr{G}(t_3)\mathscr{V}\mathscr{G}(t_2)\mathscr{V}\mathscr{G}(t_1)\mathscr{V}|\rho(-\infty)\rangle\rangle$$



Two-dimensional correlation plots

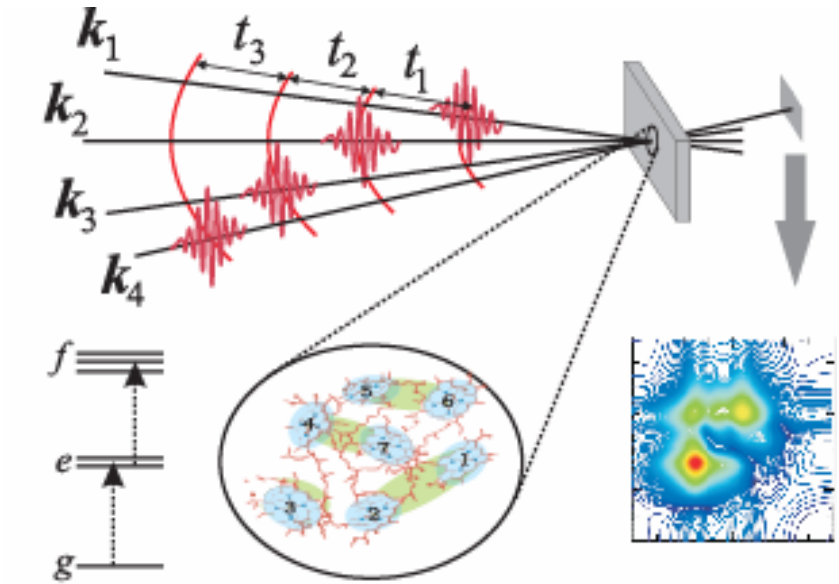
- Double Fourier transform:

$$S_I(\Omega_1, t_2, \Omega_3) = \int_0^\infty dt_3 \int_0^\infty dt_1 e^{i\Omega_1 t_1 + i\Omega_3 t_3} S(t_1, t_2, t_3)$$

$$S_{III}(t_1, \Omega_2, \Omega_3) = \int_0^\infty dt_3 \int_0^\infty dt_2 e^{i\Omega_2 t_2 + i\Omega_3 t_3} S(t_1, t_2, t_3)$$

- Particularly useful for displaying structural information, in analogy with 2D NMR
- Ultrafast (50 fs) time resolution
- Probe intra- and intermolecular interactions
- Spreading transitions in multiple dimensions
- Lineshapes give environment fluctuations

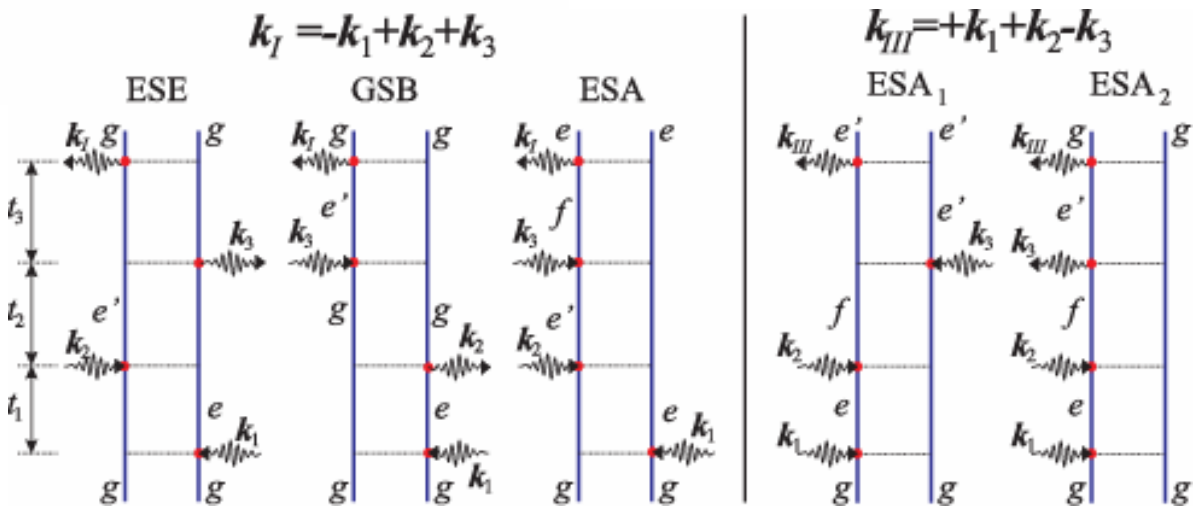
The scheme of the four-wave-mixing experiment



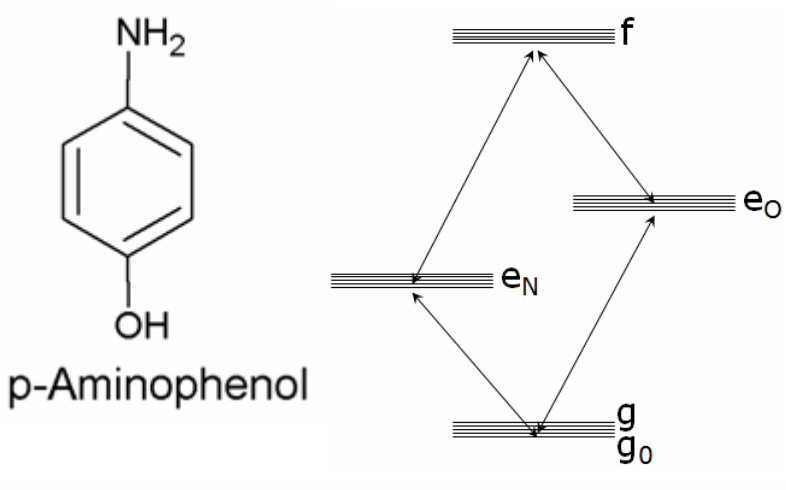
- The delay times between the pulses are the experiment parameters.
- Fourier transformations of signals with respect to time delays generate multidimensional spectrograms.

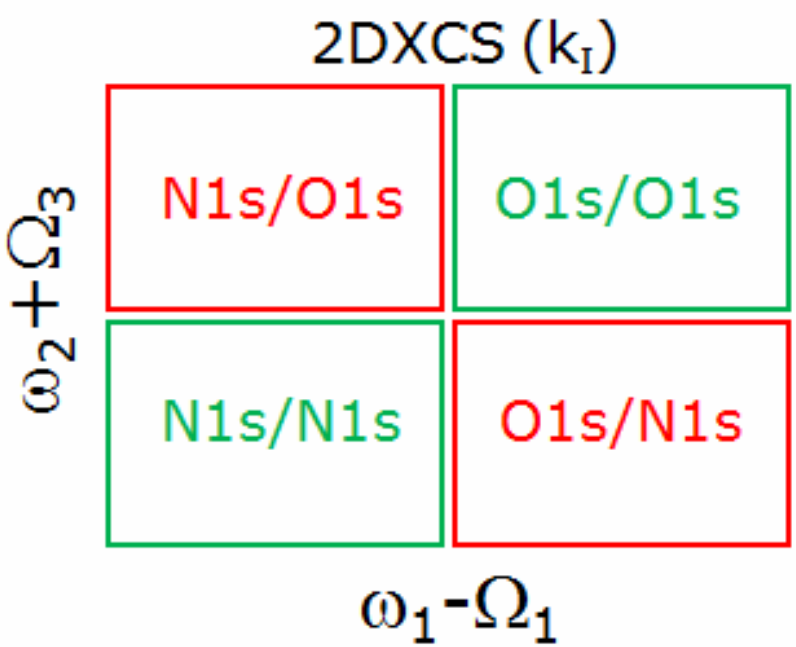
Generic three-band model

Feynman diagrams

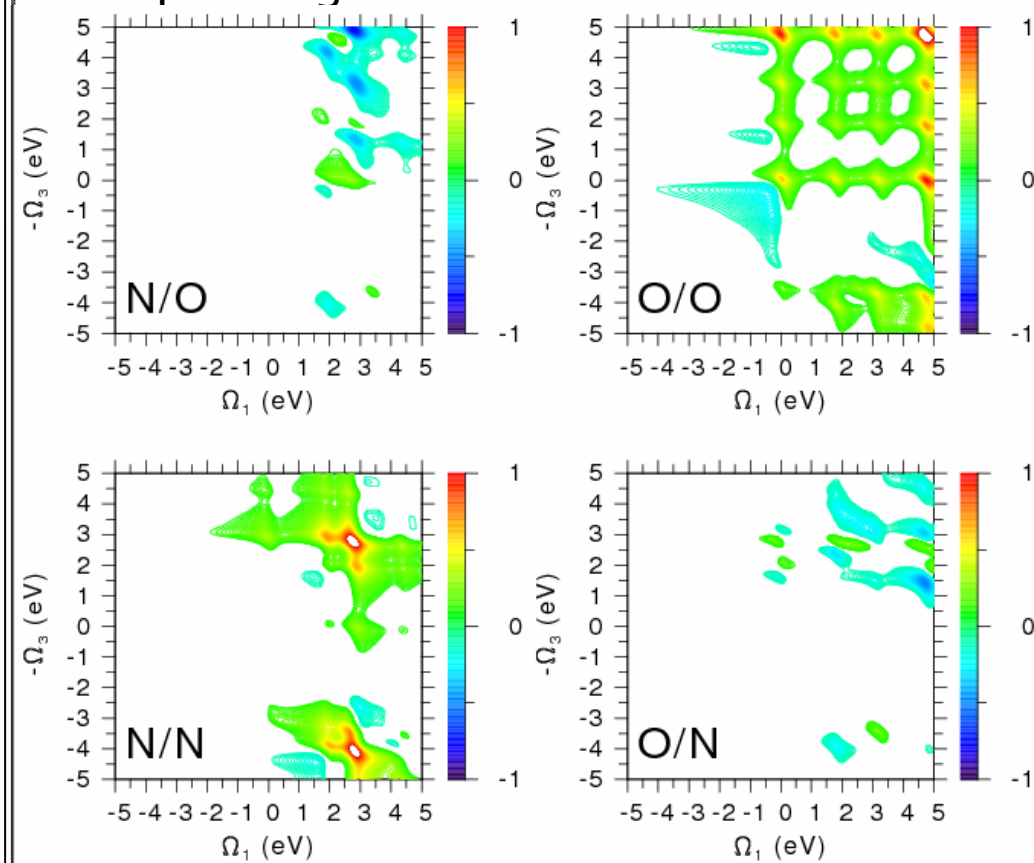


Simulated 2DXCS signal of para-aminophenol



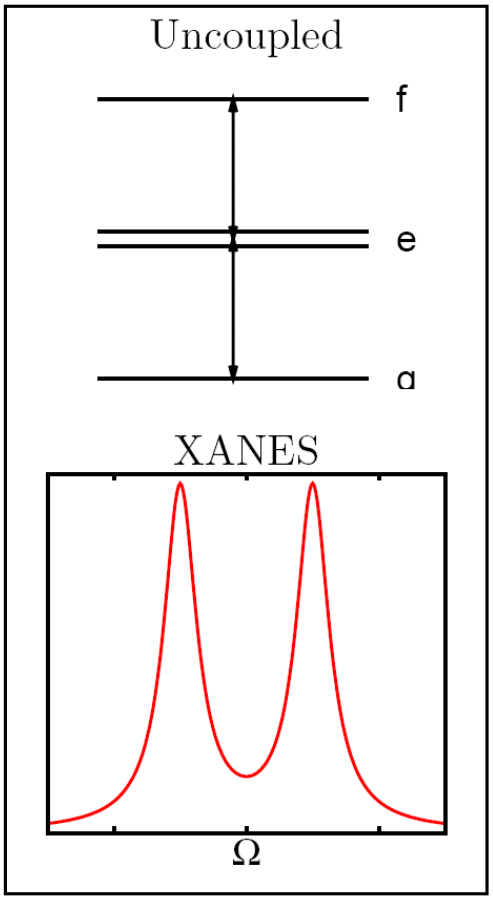


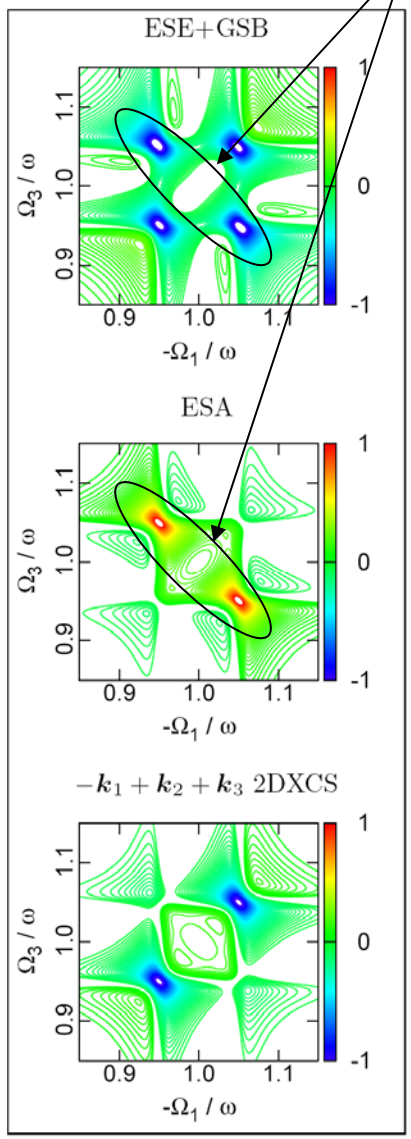
Simulation:
- Equivalent-core approx.
- B3LYP/6-311G** orbitals
- Bandwidth: 6 eV
- Dephasing: 0.3 eV

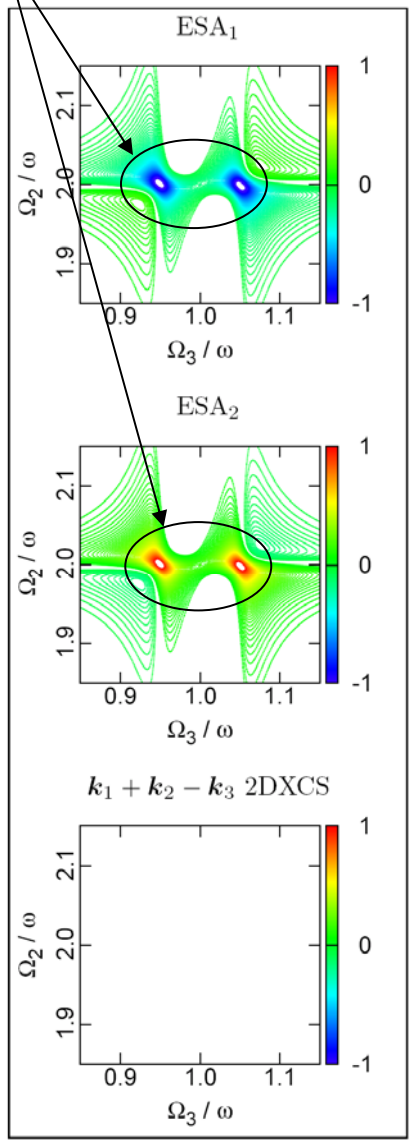


k_I and k_{III} of an uncoupled system

opposite signs



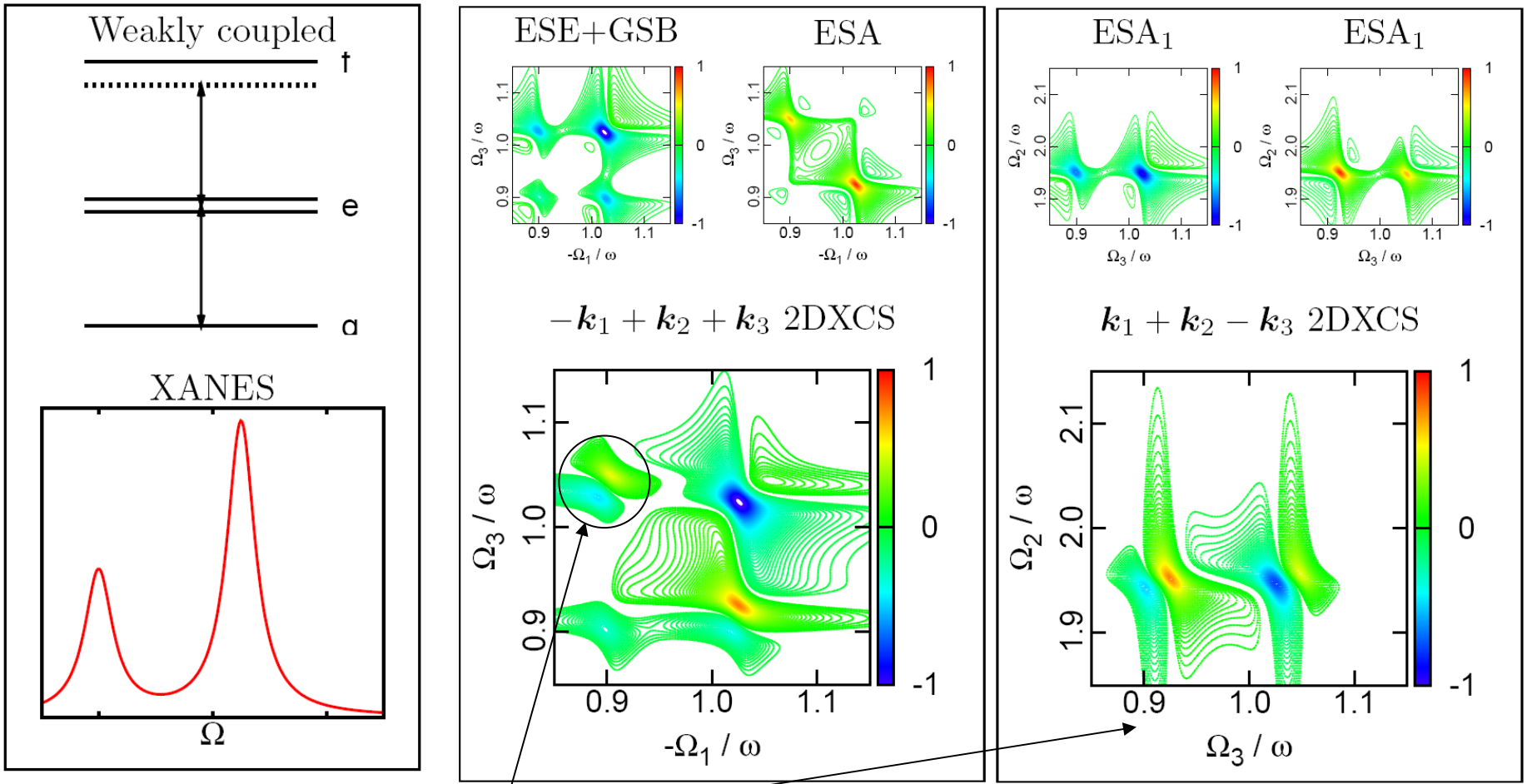




off diagonal peaks in photon echo cancel exactly

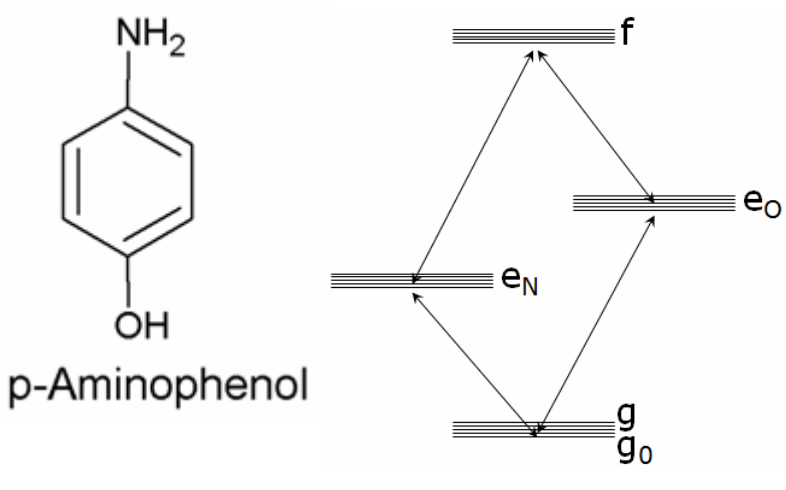
…as does the k_{III} signal.

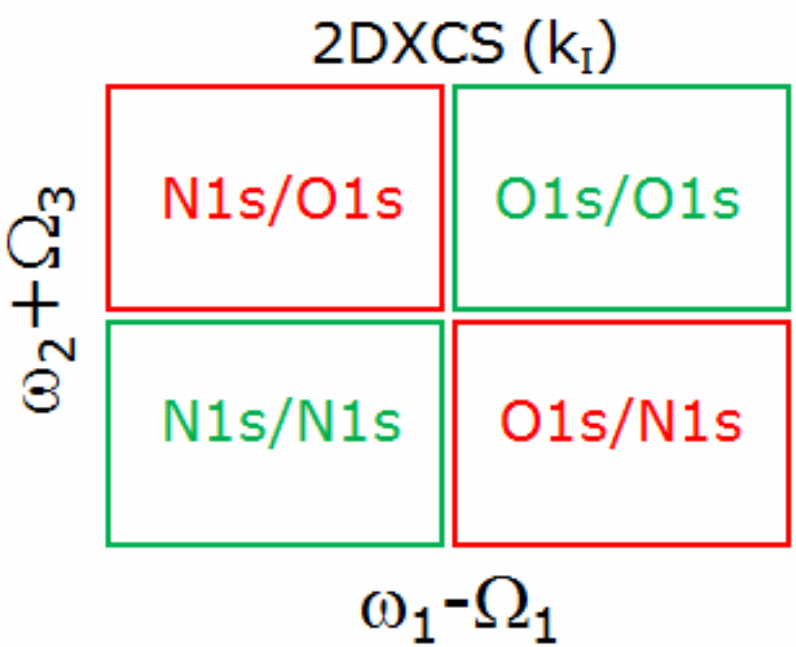
k_I and k_{III} of a coupled system



off-diagonal cross-peaks in k_I and a non-vanishing k_{III} signal are signatures of core-hole coupling

Simulated 2DXCS signal of para-aminophenol





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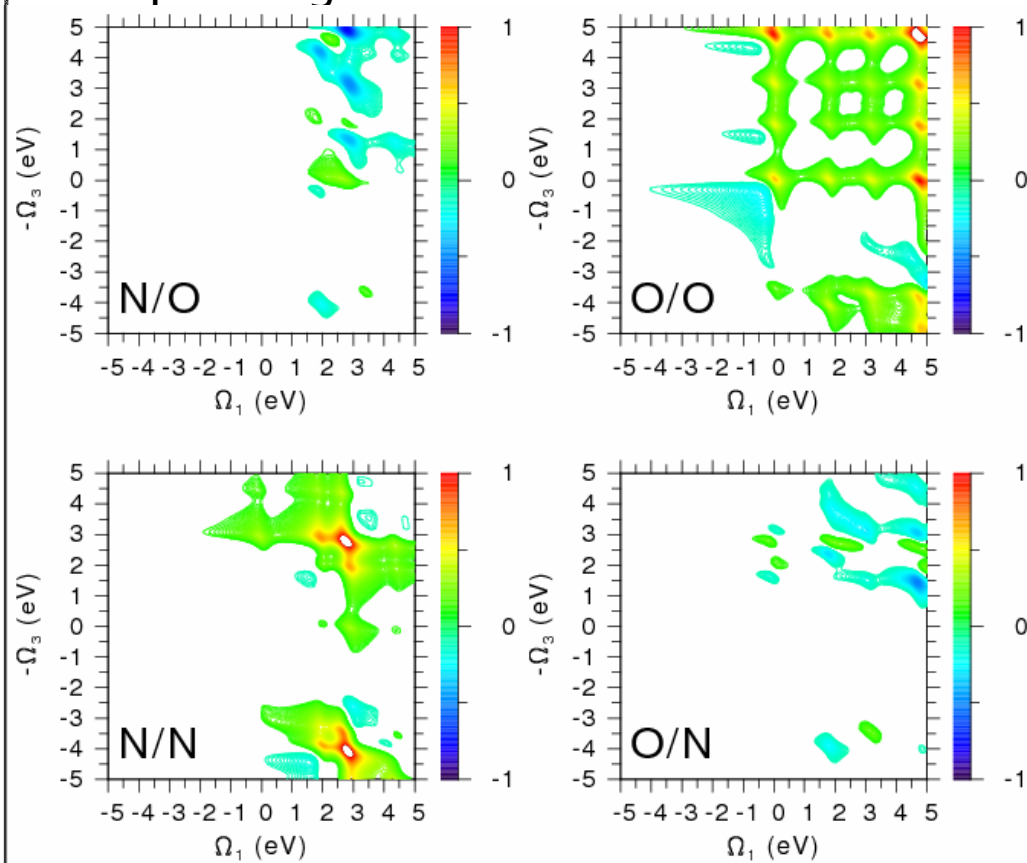
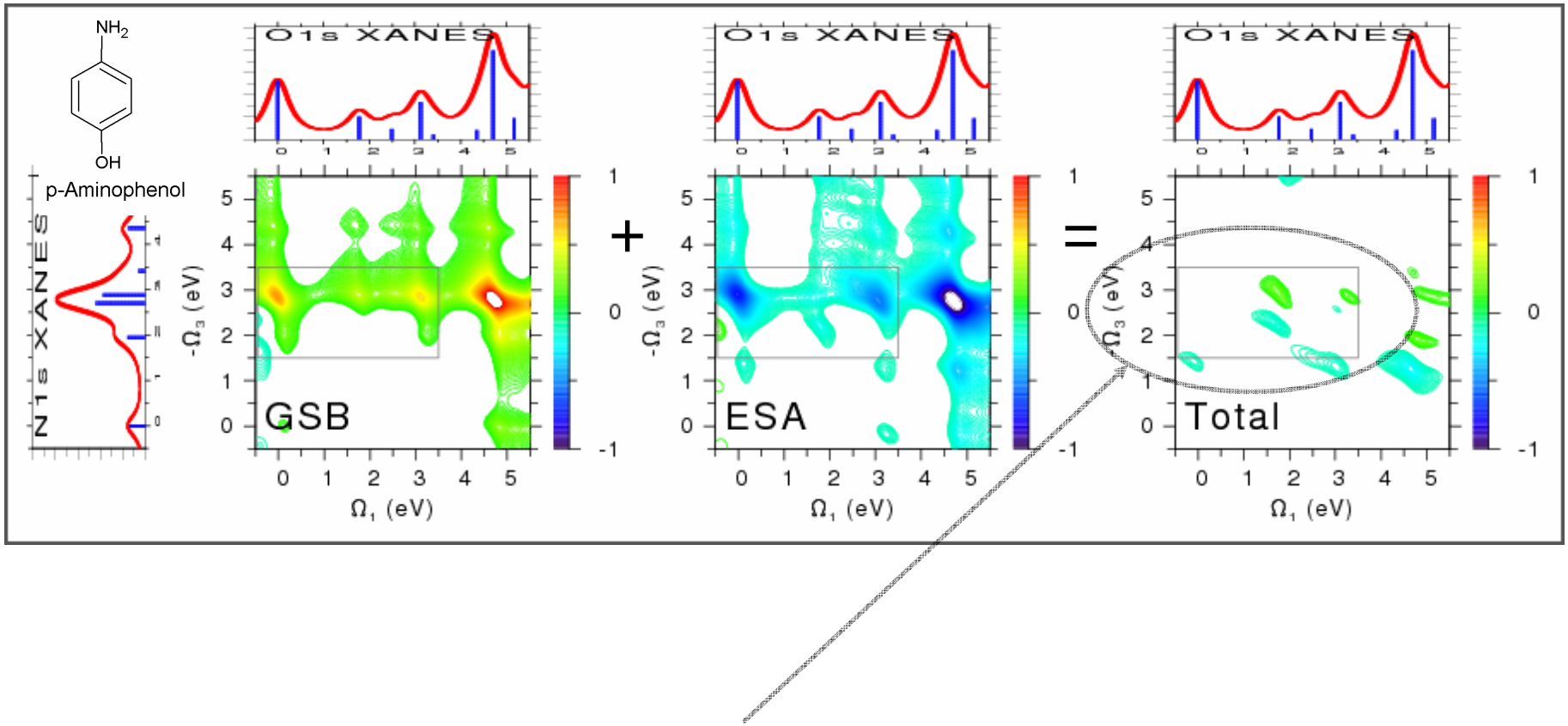
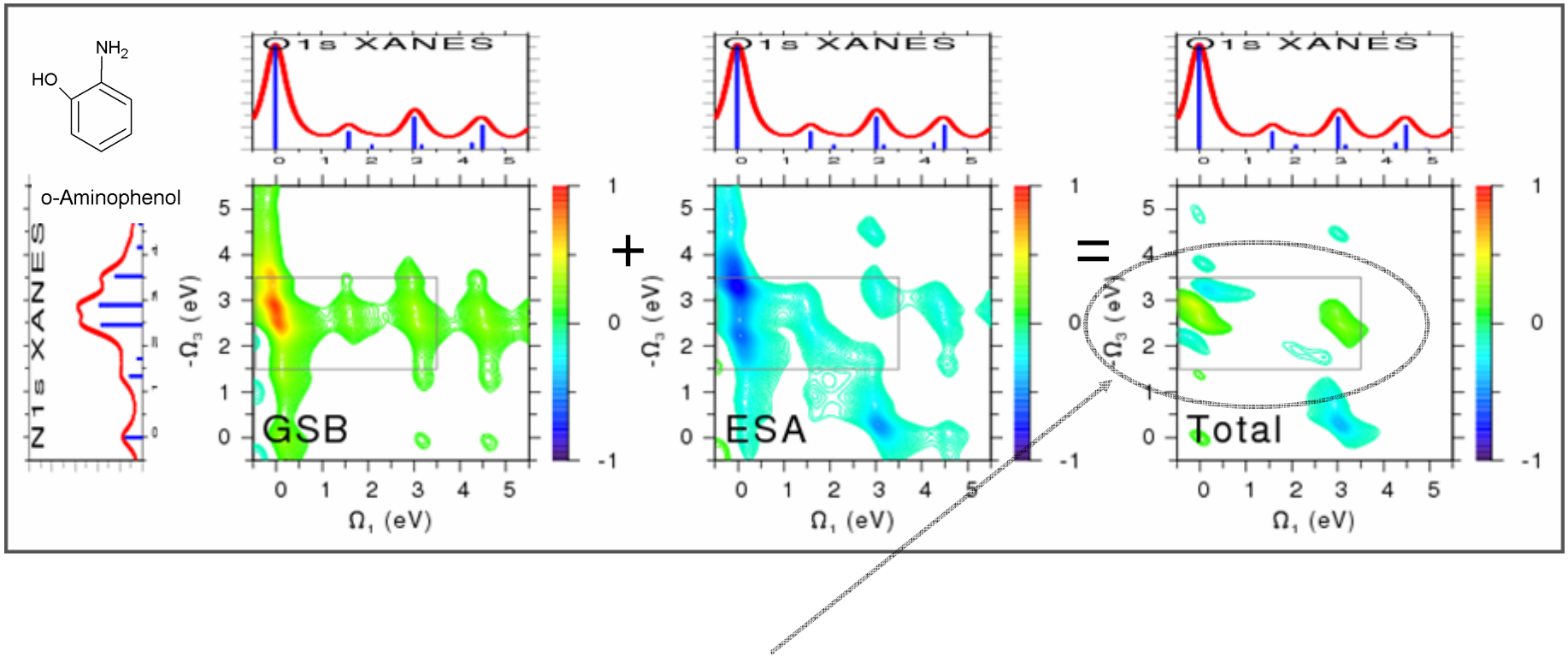


Simulated O1s/N1s 2DXCS cross peak of para-aminophenol



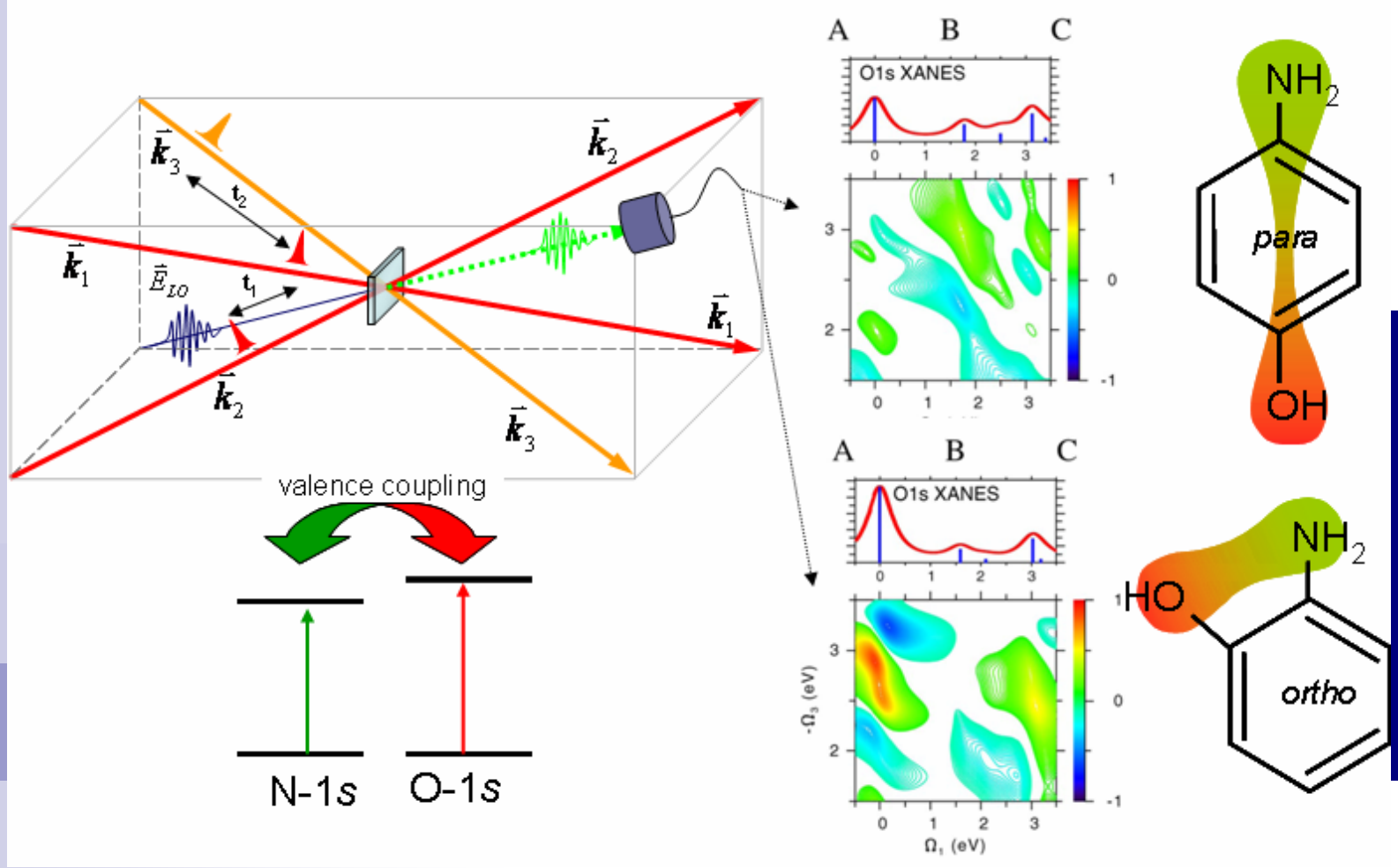
- In the para isomer, interactions between N1s and O1s core transitions are weak $\Rightarrow$ cross peaks are weak despite the strong GSB and ESA components

Simulated O1s/N1s 2DXCS cross peak of ortho-aminophenol

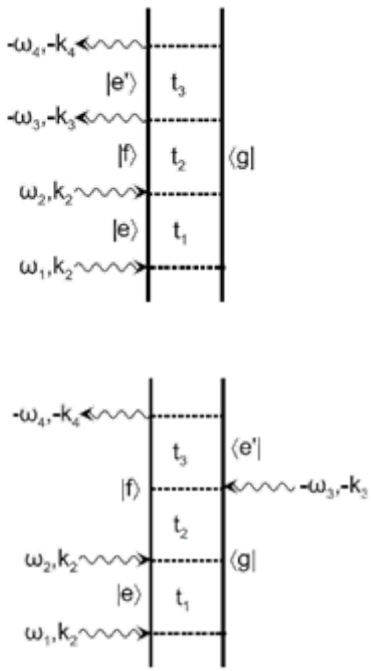


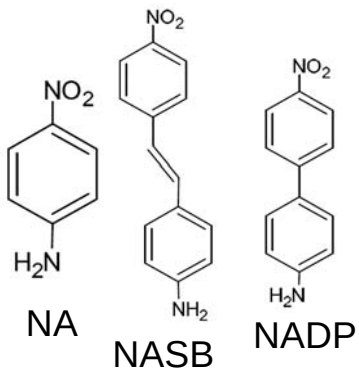
- In the ortho isomer, interactions between the N1s and O1s are stronger ⇒ different peak pattern with stronger cross peaks

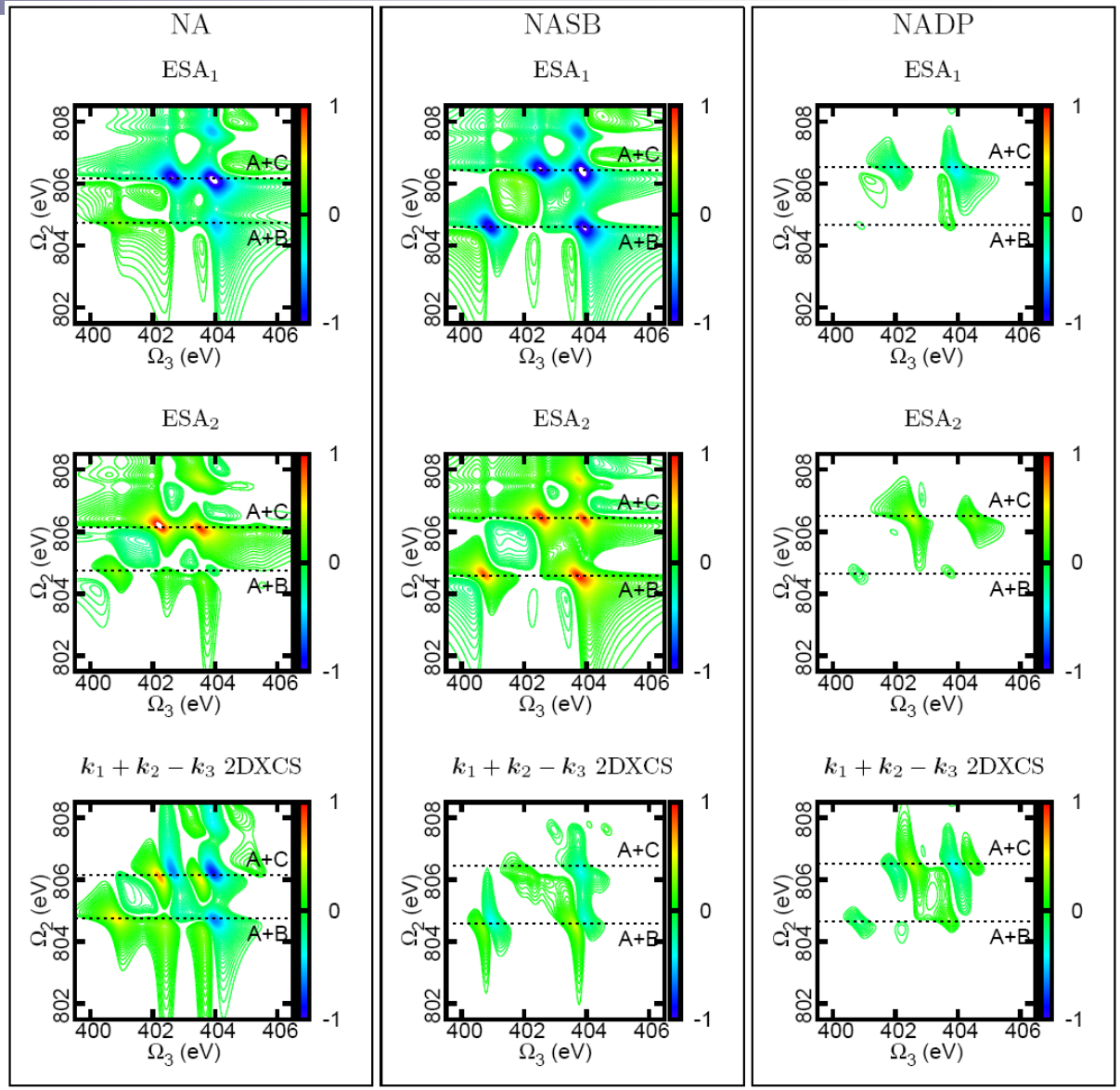
-Unlike XANES, 2DXCS cross peaks are sensitive to the relative position of the O and N atoms

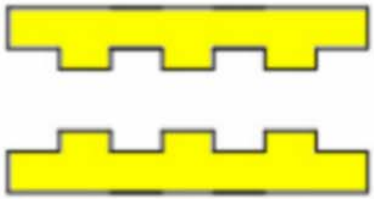


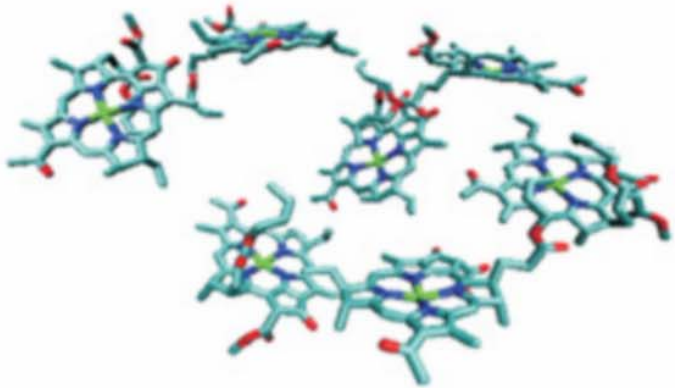
Left: Proposed four-wave mixing of ultrashort x-ray pulses resonant with the O-1*s* and N-1*s* levels; **Middle**: theoretically predicted two-dimensional spectra the lower of which exhibits the coupling of excitations on the oxygen with those of the nitrogen in para and ortho-aminophenol molecules at right [from S. Mukamel].

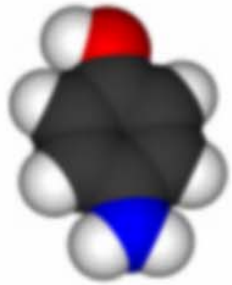

-ω4,-k4
|e'⟩
t3
-ω3,-k3
|f⟩
t2
⟨g|
ω2,k2
|e⟩
t1
ω1,k2
-ω4,-k4
t3
⟨e'|
|f⟩
-ω3,-k3
t2
ω2,k2
⟨g|
|e⟩
t1
ω1,k2

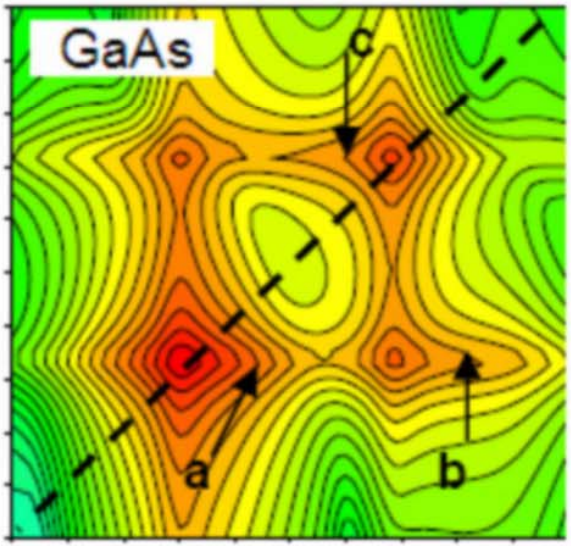

NO2
H2N
NO2
NH2
NO2
H2N
NA
NASB
NADP


NA
NASB
NADP
ESA1
ESA2
k1 + k2 − k3 2DXCS
A+C
A+B
Ω2 (eV)
Ω3 (eV)
802
804
806
808
400
402
404
406
1
0
-1

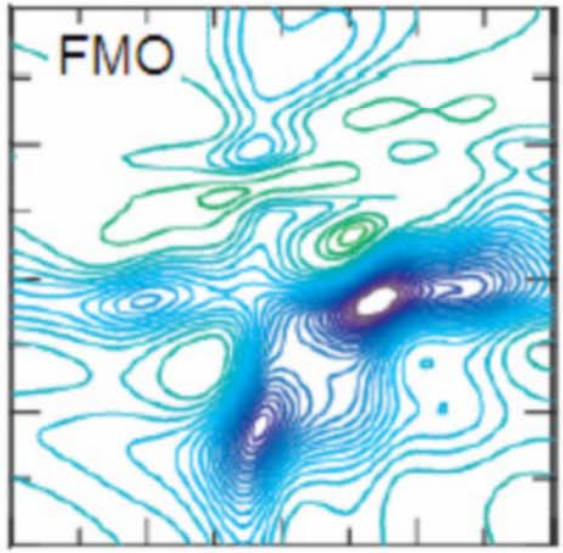




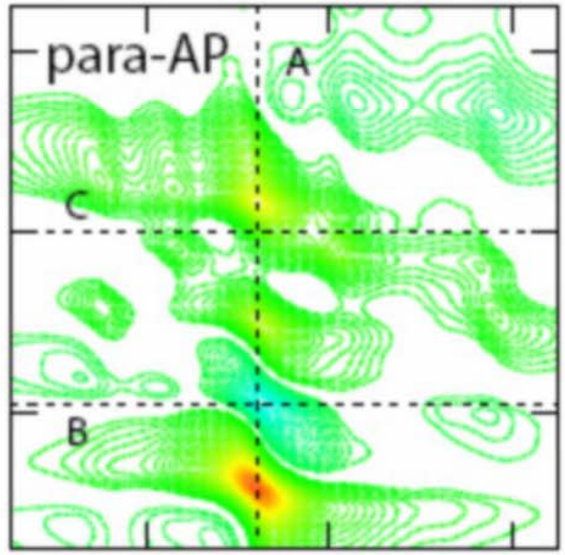




Wannier excitons
(meV)



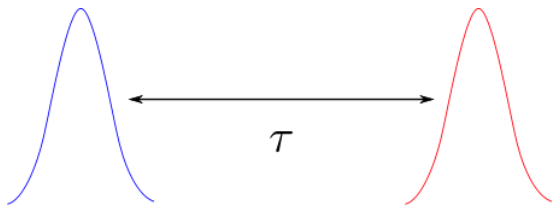
Frenkel excitons
(0.1 eV)

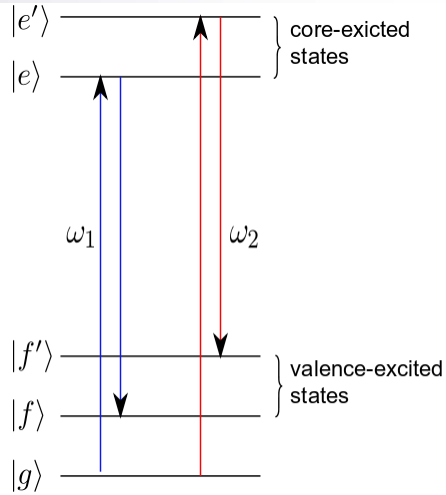


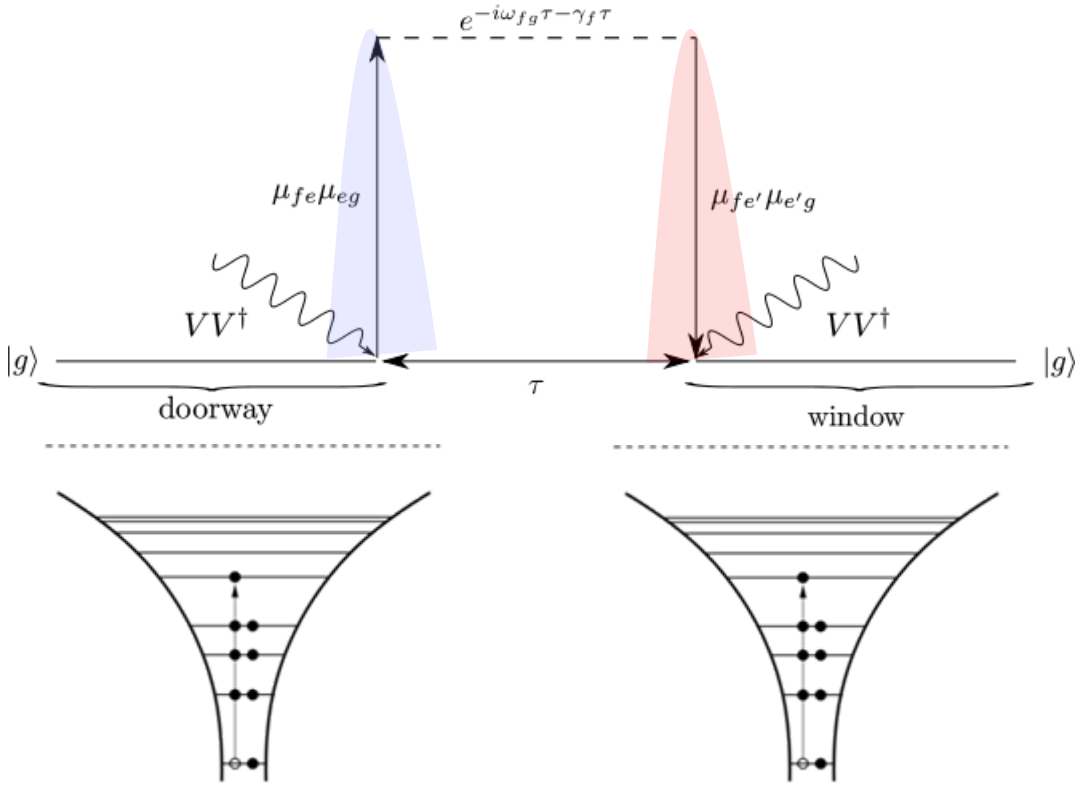
Core excitons
(eV)

Coherent X-ray Stimulated Raman Spectroscopy (CXRS)

- Two well-separated pulses with Gaussian envelopes
- Each pulse interacts with the molecule twice, to create a valence electronic wave packet. No phase control is needed.
- Delay time between pulses (fs~ps) is not limited by core-hole lifetime.



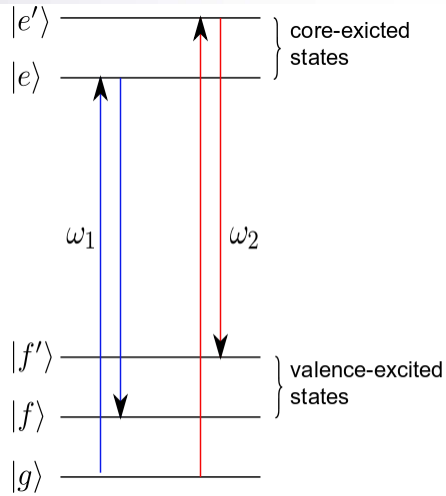




Schweigert, Mukamel; PRA, 76 0125041 (2007)

Harbola, Mukamel; PRB 79, 085108 (2009)

Hamiltonian



$$\hat{H}_{total} = \hat{H}_{mol} + \hat{H}_{int}$$

$$\hat{H}_{mol} = \sum_i \epsilon_i c_i^\dagger c_i + \frac{1}{2}\sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_l c_k$$

orbital energies

Coulomb scattering

$$V_{ijkl} = \int d\vec{r} \int d\vec{r}' \frac{\phi_i^*(\vec{r})\phi_j^*(\vec{r})\phi_k(\vec{r}')\phi_l(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

molecular orbitals

$c_i^\dagger,\ c_i$ ← Fermi operators

two X-ray pulses

$$\mathcal{E}\left(\vec{r},t\right) = \sum_{j=1,2} E_j\left(\vec{r},t\right) + E_j^*\left(\vec{r},t\right)$$

pulse duration

with gaussian pulse envelopes

central frequency

$$E_j(\vec{r},t) = \frac{1}{\sigma_j\sqrt{2\pi}} e^{-t^2/2\sigma_j^2} e^{i\vec{k}_j\cdot\vec{r} - i\omega_j t}$$

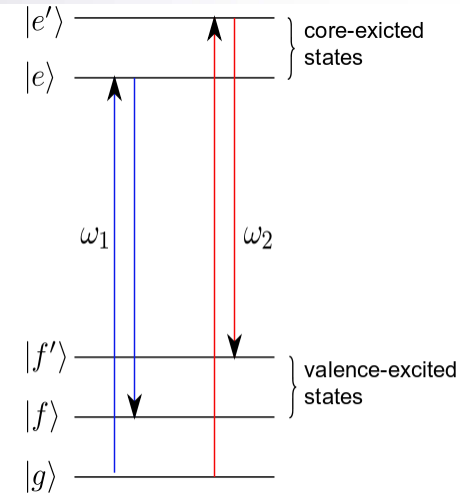
wave vector

in the frequency domain:

$$E(\vec{r},\omega) = \sum_{j=1,2} E_j^+(\vec{r},\omega) + E_j^-(\vec{r},\omega)$$

$$E_j^{\pm}(\vec{r},\omega) = \frac{\sigma_j}{\sqrt{2\pi}} e^{-(\omega\pm\omega_j)^2\sigma_j^2/2} e^{\pm i\vec{k}_j\cdot\vec{r}}$$

Closed-Time-Path Loop Diagrams



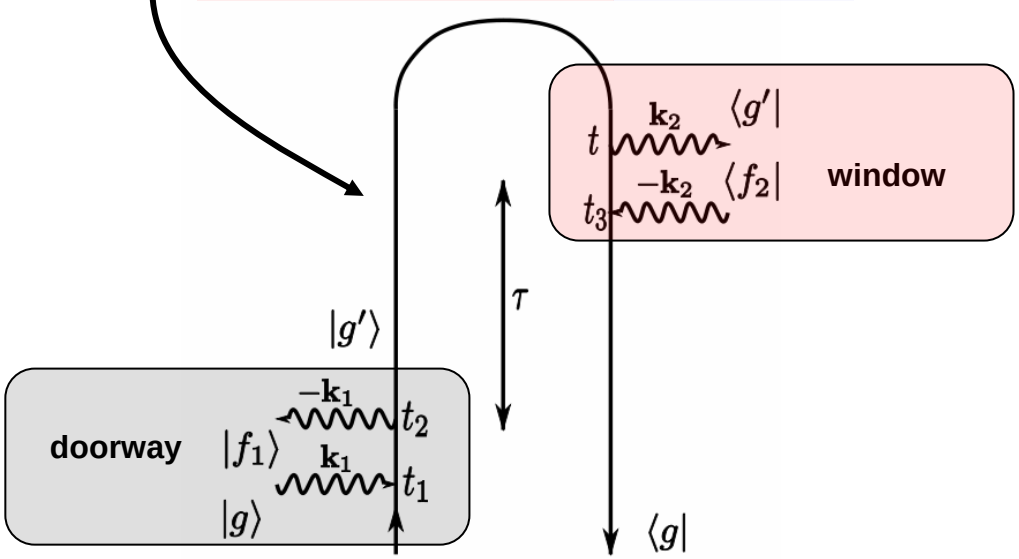
The stimulated Raman signal is a sum over two terms:

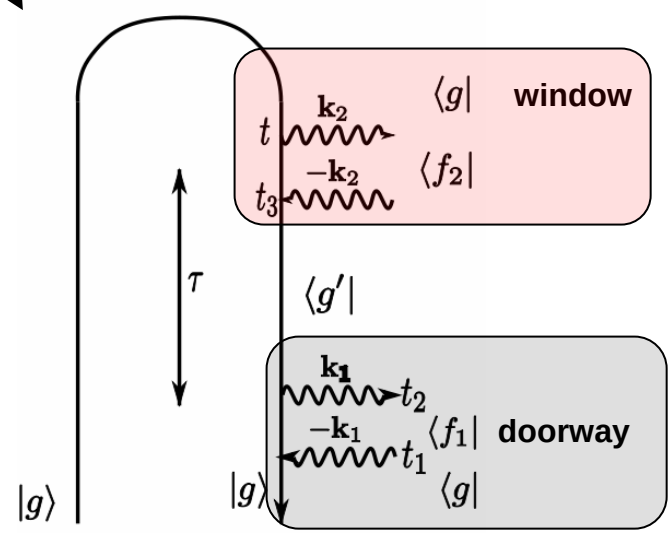
$$S_{SR}(\tau) = 2\mathrm{Re}\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt_3$$

$$\times \Big[\int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 \big\langle V(t_3)V^\dagger(t)V(t_2)V^\dagger(t_1)\big\rangle$$

$$+ \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \big\langle V(t_2)V^\dagger(t_1)V(t_3)V^\dagger(t)\big\rangle\Big]$$

$$E_2(t-\tau)E_2^*(t_3-\tau)E_1^*(t_2)E_1(t_1)$$





CXRS Signal: Doorway-Window Picture

A time-dependent overlap between valence electronic wavepackets

$$S_{SR}(\tau) = \mathrm{Re}\sum_f W_f^* D_f e^{-i\omega_{fg}\tau - \gamma_f \tau}$$
$$= \mathrm{Re}\,\langle W | D(\tau)\rangle$$

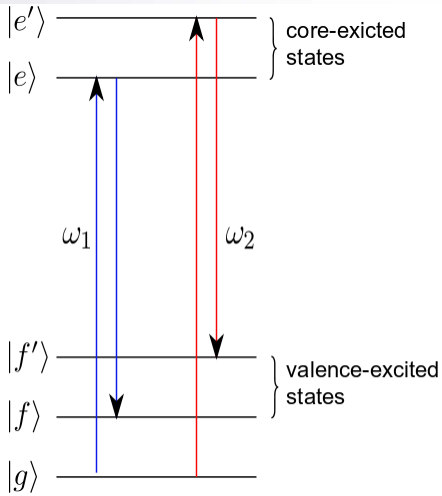
valence-excited state decay rate

$$|D(\tau)\rangle = \sum_f D_f e^{-i\omega_{fg}\tau - \gamma_f \tau} |f\rangle$$

doorway and window wave packets expanded in many-body valence-excited states

$$|W\rangle = \sum_f W_f |f\rangle$$

CXRS Signal: Doorway and Window Wave Packets



Two difficulties calculating the SOS expressions

$$D_f = \sum_e \mu_{fe}\mu_{eg} \int \frac{d\omega}{2\pi} \frac{E_1^*(\omega)E_1(\omega-\omega_{fg})}{\omega-\omega_{fg}-\omega_e+i\gamma_e}$$

(1) Matrix elements evaluated between states with different core occupations

$$W_f = \mathrm{Im}\sum_{e'} \mu_{fe'}\mu_{e'g} \int \frac{d\omega}{2\pi} \frac{E_2^*(\omega)E_2(\omega-\omega_{fg})}{\omega-\omega_{fg}-\omega_{e'}+i\gamma_{e'}}$$

(2) Integration over electric field envelopes performed analytically

Spntaneous Resonant inelastic x ray scattering Kramers-Heisenberg Expression

$$S_{\mathrm{RIXS}}(\omega_1,\omega_2) = \sum_{ac} |A_{ca}(\omega_1)|^2 \delta\left(\omega_1 - \omega_2 - \omega_{ca}\right)$$

$$A_{ca}(\omega_1) = \sum_{e} \frac{B_{ce} B_{ea}}{\omega_1 - \omega_{ea} + i\Gamma_{ea}}$$

- ω_1 and ω_2 are the incoming and outgoing modes
- a and c are valence N - electron ground and singly excited states
- B_{ea} and B_{ce} are matrix elements of dipole operator
- Γ is the inverse life - time of the excited state wave - packet

Computation of Core-Excited States

- Deep core electrons are weakly correlated with other electrons.

  Large energy separation between core orbital space and valence orbital space.

- Strong orbital relaxation upon core-electronic excitations.

  Koopmans' theorem does not apply.

Goals:

- Describe orbital relaxation.
- Describe different core-hole configurations: deep and shallow core-holes.
- Incorporate electron correlations, especially for shallow core-hole configurations.

Core-Excited States: Equivalent-Core Approximation (ECA)

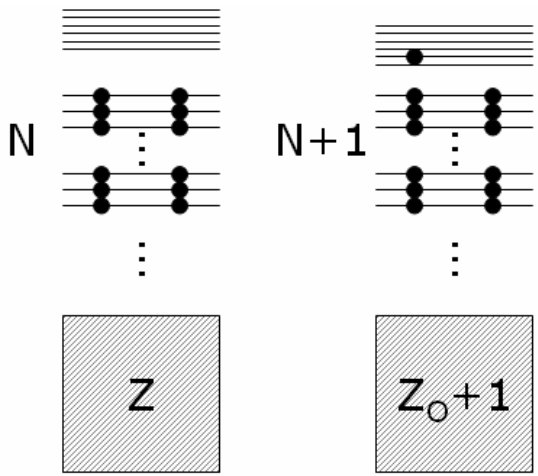
ECA(Z+1) approximation: Mimics the creation of the core hole by incrementing the nuclear charge and adding a valence electron

Advantages:

- Number of electrons and nuclear configuration are standard input in existing electronic structure packages.
- Explicit treatment of core-hole is avoided.
- Double-core excitations are treated similarly.

Limitations:

- Inherently incorrect spin symmetry — Modified ECA model by Cederbaum et al. JCP,116:8723 (2002)
- Does not hold for shallow core holes



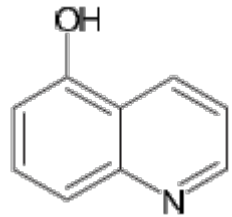
References:

W. H. E. Schwarz and R. Buenker, Chem. Phys., 12:153 (1976)

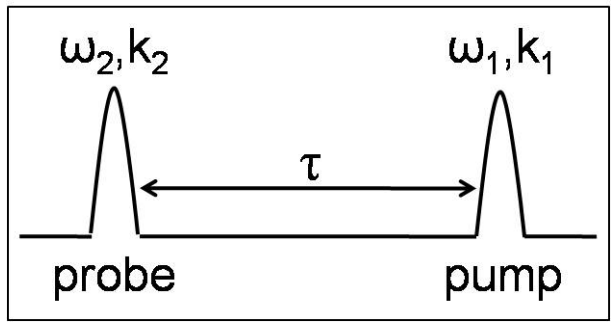
X-ray stimulated Raman spectroscopy of quinolinol (ECA)

All-x-ray resonant pump probe measurement

- pump prepares molecules either in ground/valence or core/core coherences
- core/core coherences decay rapidly ($T_e \approx 10$ fs) due to the Auger ionization
- only Raman-type, GSB terms contribute for $\tau > T_e$



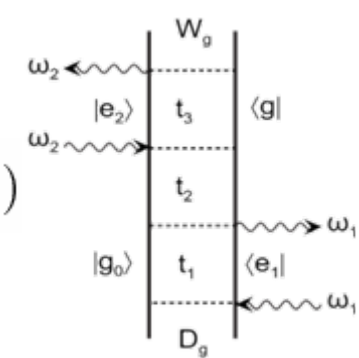
quinolinol



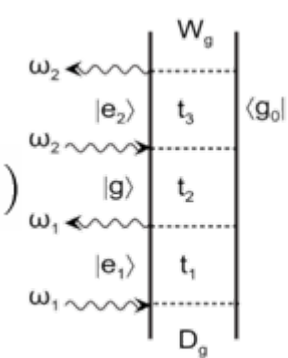
Stimulated Raman signal

$$S(\omega_1,\omega_2,\tau) = \mathrm{Im}\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \Big[R_I^{(3)}(t,\tau_3,\tau_2,\tau_1)\mathcal{E}_2^*(t-\tau)\mathcal{E}_2(\tau_3-\tau)\mathcal{E}_1(\tau_2)\mathcal{E}_1^*(\tau_1)e^{i\omega_2(t-\tau_3)-i\omega_1(\tau_2-\tau_1)} + R_{II}^{(3)}(t,\tau_3,\tau_2,\tau_1)\mathcal{E}_2^*(t-\tau)\mathcal{E}_2(\tau_3-\tau)\mathcal{E}_1^*(\tau_2)\mathcal{E}_1(\tau_1)e^{i\omega_2(t-\tau_3)+i\omega_1(\tau_2-\tau_1)}\Big]$$

$R_I^{(3)}(t,\tau_3,\tau_2,\tau_1)$



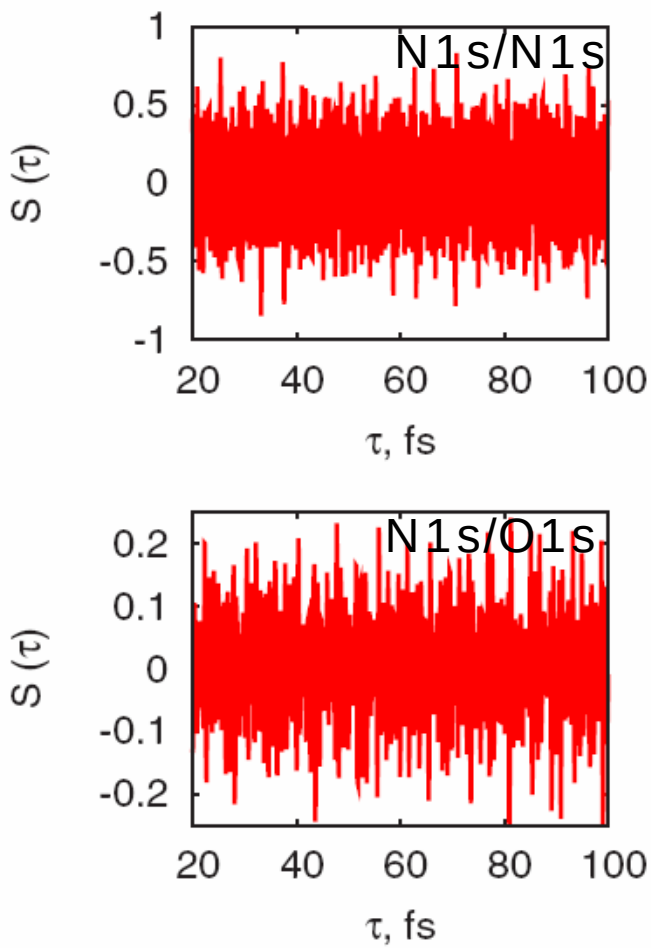
$R_{II}^{(3)}(t,\tau_3,\tau_2,\tau_1)$

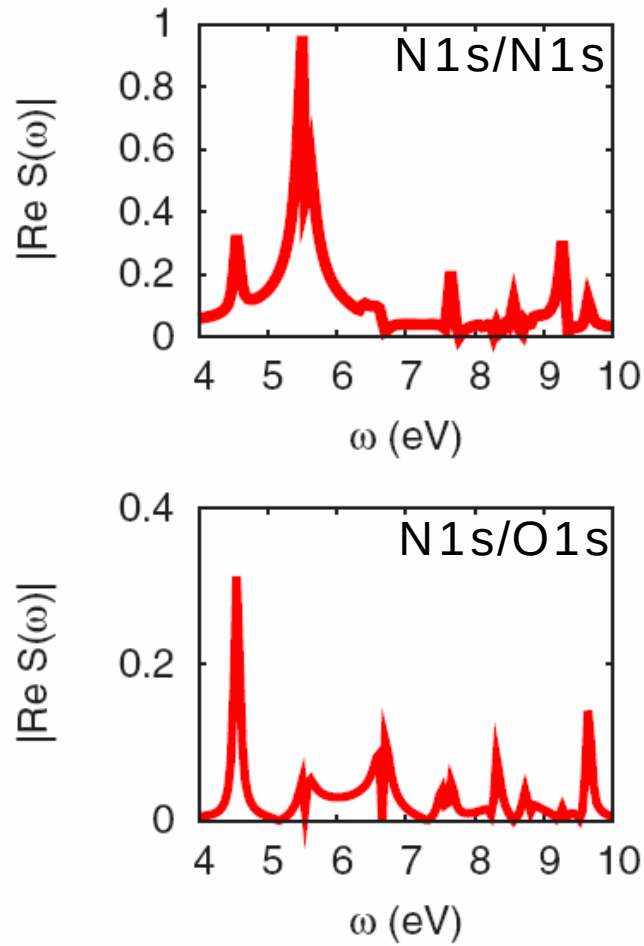


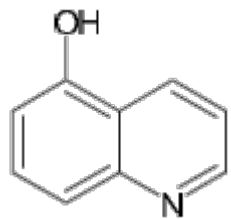
X-ray stimulated Raman spectroscopy of quinolinol

Stimulated Raman signal, $10 < \tau < 100$ fs

Real part of the Fourier transform w.r.t. τ







Core and valence transitions: Singly-substituted KS determinants in the equivalent-core approximation, B3LYP/6-311G**

-Peaks in the Fourier transform correspond to the energies of valence excited states contributing to the pump-induced wavepacket

Core-Excited States: Static-Exchange (STEX) Approximation

Step 1: Optimize ground state of the neutral molecule at Hartree-Fock (HF) level.

$|\Psi^N_{ref}\rangle_0$ with energy E^N_0

For valence-excited states using configuration interaction singles (CIS) wave function using HF orbitals. (Not a good approximation for core-excited states)

$$|\Psi^N_{i\to a}\rangle = \sum_{ia} C^a_i c^\dagger_a c_i |\Psi^N_{ref}\rangle_0$$

References:

H. Ågren, Theor. Chem. Acc, 97:14 (1997)

W. Hunt and W. Goddard, CPL, 3:414 (1969)

Step 2: Instead, for core-excited state, create ionized state with an electron ejected from a specific core orbital.

$$|\Psi^{N-1}_{n_\sigma}\rangle_0 = c_{n_\sigma} |\Psi^N_{ref}\rangle_0$$

core orbital

Core-Excited States: Static-Exchange (STEX) Approximation

Step 3: Optimize occupied orbitals of the target ionized state with occupation number fixed.

$$|\Psi_{n_\sigma}^{N-1}\rangle_0 \longrightarrow |\Psi_{n_\sigma}^{N-1}\rangle_{rel} \text{ with energy } E_n^{N-1}$$

Step 4: Optimize unoccupied orbitals by the static-exchange Hamiltonian holding occupied orbitals fixed.

$$\hat{F}_n^{STEX} = \hat{F} - \hat{J}_n + 2\hat{K}_n$$

$$\hat{F}_n^{STEX}\psi_a = \varepsilon_a \psi_a$$

excited orbital

Step 5: Add an electron to one of the optimized unoccupied orbitals, and construct the final core-excited state as an anti-symmetrized product of the target ionized state and the excited orbital.

$$|\Psi_{n\to a}^{N}\rangle_{rel} = \frac{1}{\sqrt{2}}\left(c_{a_\alpha}^\dagger |\Psi_{n_\alpha}^{N-1}\rangle_{rel} + c_{a_\beta}^\dagger |\Psi_{n_\beta}^{N-1}\rangle_{rel}\right)$$

Core-Excited States: Static-Exchange (STEX) Approximation

Step 6: Excitation energy of core-excited state :

$$E^N_{n\to a} = E^{N-1}_n + \varepsilon_a - E^N_0$$

ionized state energy

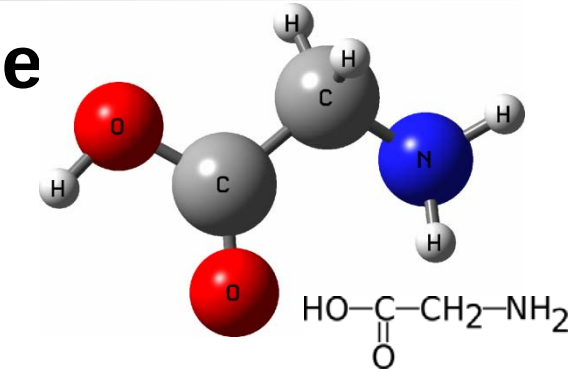
excited orbital energy

ground state energy

Advantages:

- Correct spin symmetry (singlet -> singlet)
- Occupied and unoccupied orbital relaxation
- Can describe different core-hole configurations
- Electron correlation effects can be incorporated by using more accurate wave functions (e.g. CISD …)

Application to Glycine



- Geometry optimized at B3LYP/6-311G** level.
- Energies and transition dipole moments calculated with 6-311G** basis set.
- Valence-excited states described at CIS level. In molecular orbital basis:

$$\begin{cases} |D(\tau)\rangle = \sum_f D_f e^{-i\omega_{fg}\tau - \gamma_f \tau}|f\rangle \\ |W\rangle = \sum_f W_f |f\rangle \end{cases} \Rightarrow$$

$$\begin{cases} |D(\tau)\rangle = \sum_{f,ia} e^{-i\omega_{fg}\tau - \gamma_f \tau} D_{f;ia} c_a^\dagger c_i |g\rangle \\ |W\rangle = \sum_{f,ia} W_{f;ia} c_a^\dagger c_i |g\rangle \end{cases}$$

$$|f\rangle = \sum_{ia} C_i^a c_a^\dagger c_i |g\rangle$$
$$D_{f;ia} = D_f \times C_i^a$$
$$W_{f;ia} = W_f \times C_i^a$$

Stohr, *NEXAFS Spectroscopy*

Linewidth:

$$\gamma_N = 0.085\text{eV}$$
$$\gamma_O = 0.10\text{eV}$$
$$\gamma_f = 0.05\text{eV}$$

Pulse duration:

$$\sigma_j = 77\text{as}(1/\sigma_j \simeq 10\text{eV})$$

Simulation time:

$$\tau = 145.1fs(6000a.u.)$$

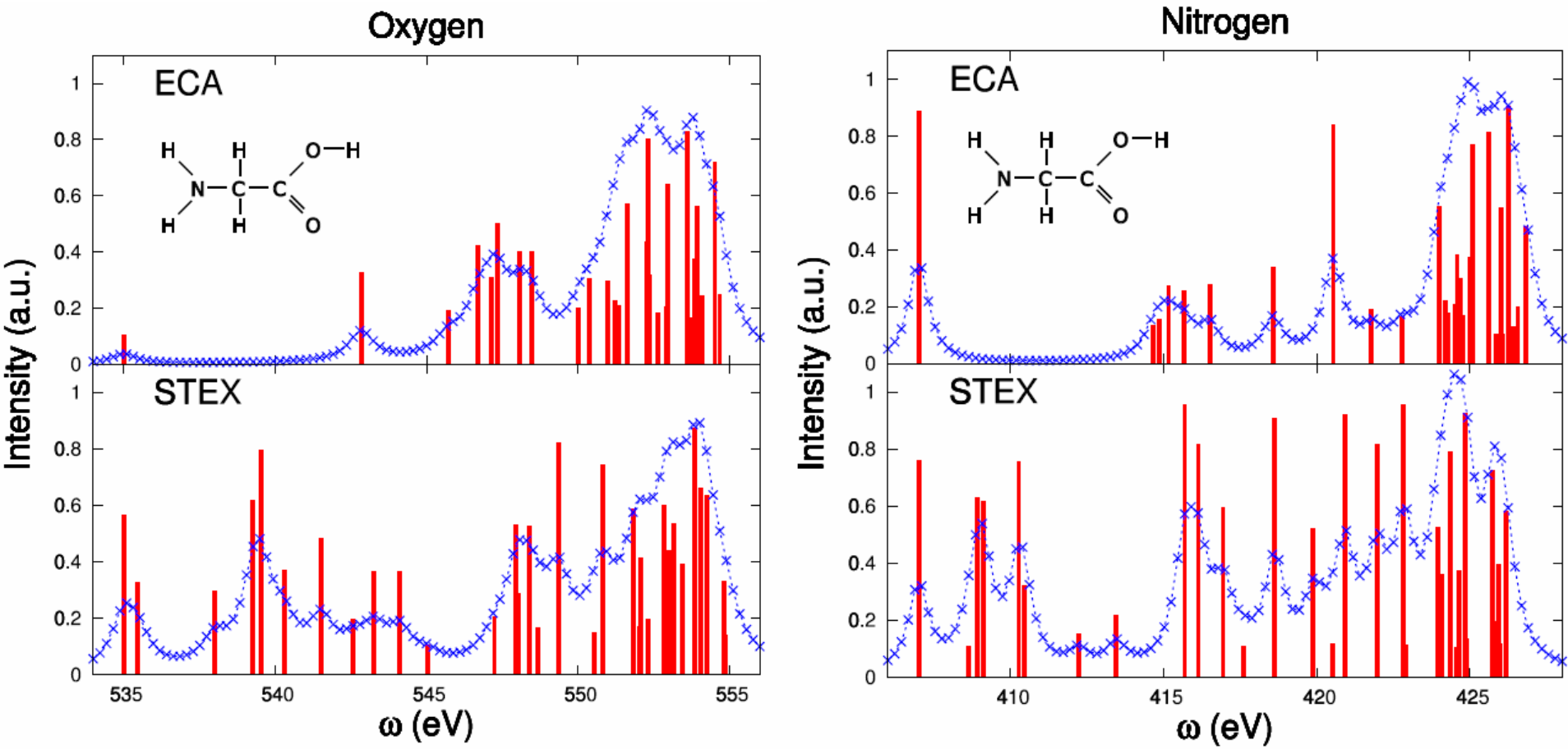
Time step:

$$24.19as(1a.u.)$$

XANES Spectra

STEX reports additional XANES peaks due to improved unoccupied orbitals.

$$S_{XANES}(\omega) = \frac{1}{\pi}\sum_f |\mu_{fg}| \frac{\gamma_f^2}{(\omega-\omega_{fg})^2+\gamma_f^2}$$



CXRS Signal

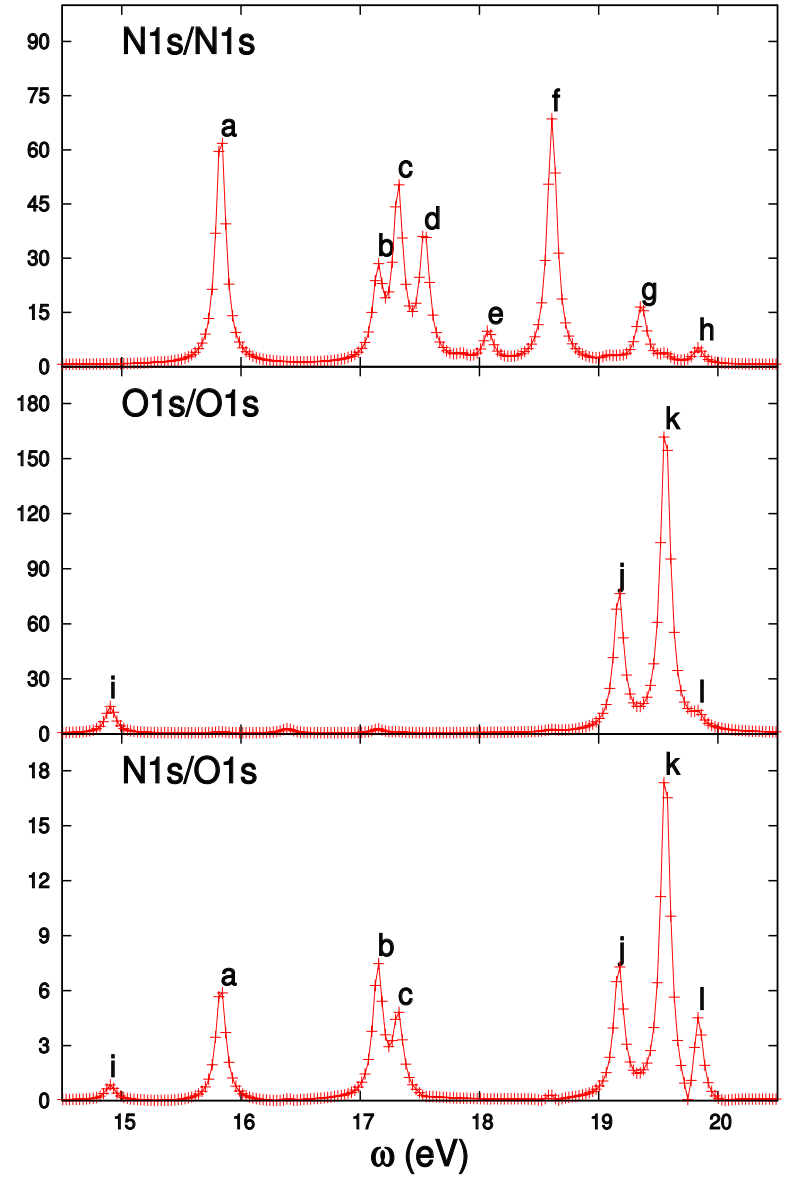
$$|D(\tau)\rangle = \sum_{f,ia} e^{-i\omega_{fg}\tau - \gamma_f \tau} D_{f;ia} c_a^\dagger c_i |g\rangle |W\rangle = \sum_{f,ia} W_{f;ia} c_a^\dagger c_i |g\rangle$$

N1s doorway at time t=0 (i, a: relaxed orbitals)

	$\omega_{fg}(eV)$	$D_{f;ia}$	i	a
a	15.83	0.49	HOMO	LUMO+2
b	17.15	0.29	HOMO-2	LUMO
c	17.32	0.42	HOMO-1	LUMO+1
d	17.54	0.36	HOMO-2	LUMO+1
e	18.07	0.17	HOMO-2	LUMO+2
f	18.61	0.49	HOMO-2	LUMO+3
g	19.36	0.24	HOMO-2	LUMO+4
h	19.84	0.12	HOMO-2	LUMO+5

O1s window

	$\omega_{fg}(eV)$	$W_{f;ia}$	i	a
i	14.90	0.23	HOMO	LUMO
j	19.17	0..53	HOMO-3	LUMO
k	19.56	0.79	HOMO-3	LUMO+1
l	19.84	−0.15	HOMO-2	LUMO+5



Visualization of Electron Dynamics

Molecular orbital representation is good for assigning CXRS peaks. But to visualize the wave packet evolution, it requires to monitor all the particle-hole pairs that contribute to the signal.

$$|D(\tau)\rangle = \sum_{f,ia} e^{-i\omega_{fg}\tau - \gamma_f \tau} D_{f;ia} c_a^\dagger c_i |g\rangle$$

$$|W\rangle = \sum_{f,ia} W_{f;ia} c_a^\dagger c_i |g\rangle$$

In fact, there are no dominant particle-hole pairs that contribute to the signal in the molecular orbital basis. To visualize the electron dynamics, we choose natural transition orbital representation, which provides a more compact representation.

References:

E. Schmidt, Math. Ann., 63:433 (1907)

A. T. Amos and G. G. Hall, Proc. R. Soc. Lond. A, 263:483 (1961)

R. L. Martin, JCP, 118:4775 (2003)

the window matrix and the signal are also expanded in terms of these orbitals

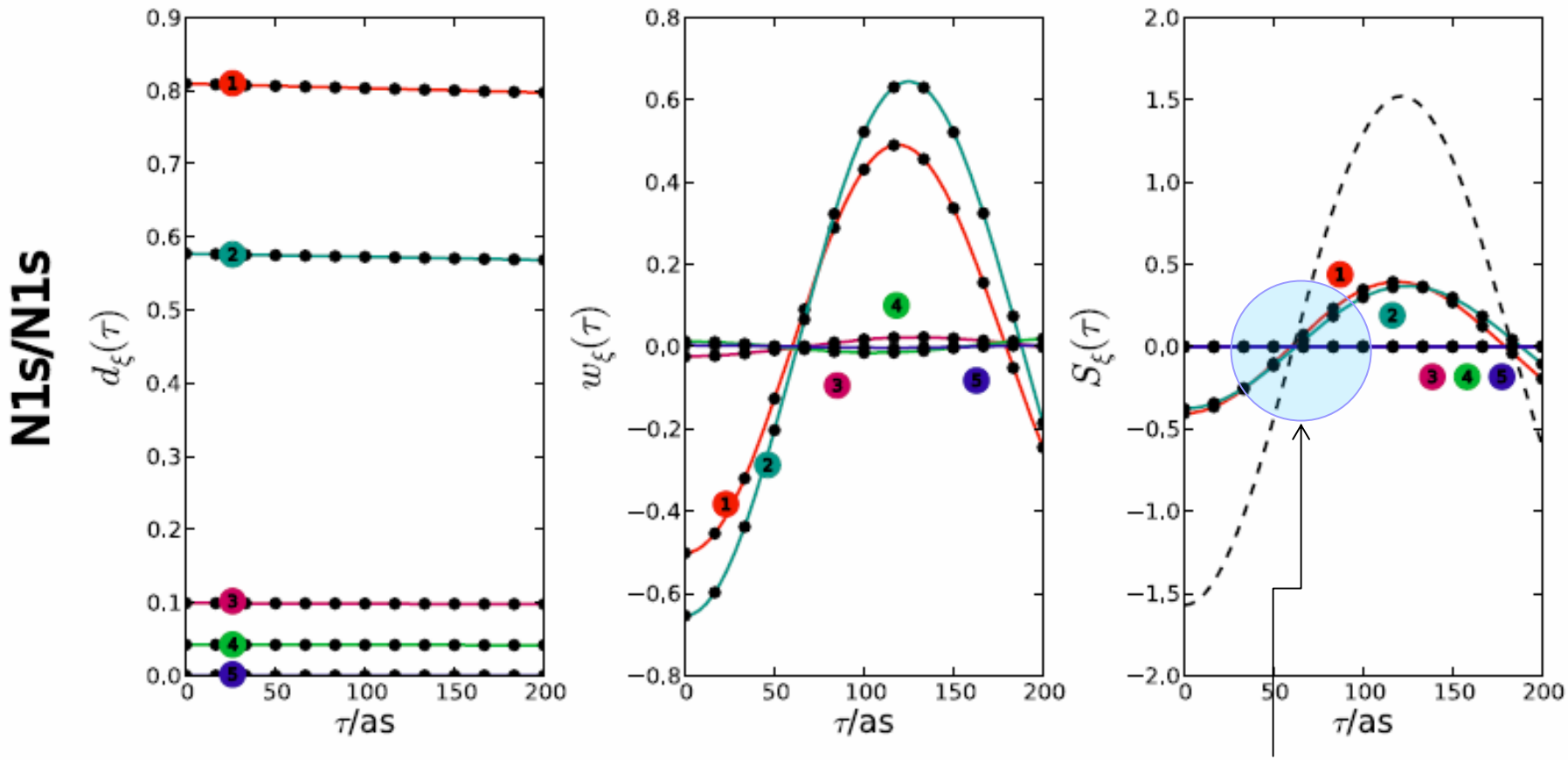
$$
\begin{aligned}
S(\tau) &= 2\mathrm{Re}\,\mathrm{Tr}\left[\mathbf{W}^{\mathbf{T}}\mathbf{D}(\tau)\right] \\
&= 2\mathrm{Re}\,\mathrm{Tr}\left[\mathbf{W}^{\mathbf{T}}\mathbf{X}^{p}(\tau)\mathbf{X}^{p\,\dagger}(\tau)\mathbf{D}\mathbf{X}^{h}(\tau)\mathbf{X}^{h\,\dagger}(\tau)\right] \\
&= 2\mathrm{Re}\sum_{\xi} w_{\xi}(\tau)d_{\xi}(\tau)
\end{aligned}
$$

where the time-dependent doorway and window natural orbital weights are defined as

$$
\begin{aligned}
w_{\xi}(\tau) &= \sum_{ai} \chi^{h}_{\xi i} W^{*}_{ia} e^{-\omega_{ai}\tau} \chi^{p}_{a\xi} \\
d_{\xi}(\tau) &= \sum_{ai} \chi^{p*}_{a\xi} D_{ai} \chi^{h*}_{\xi i} e^{-\Gamma_{ai}\tau}
\end{aligned}
$$

Signal is now expressed as a weighted sums of products, each representing the contribution of a single natural orbital

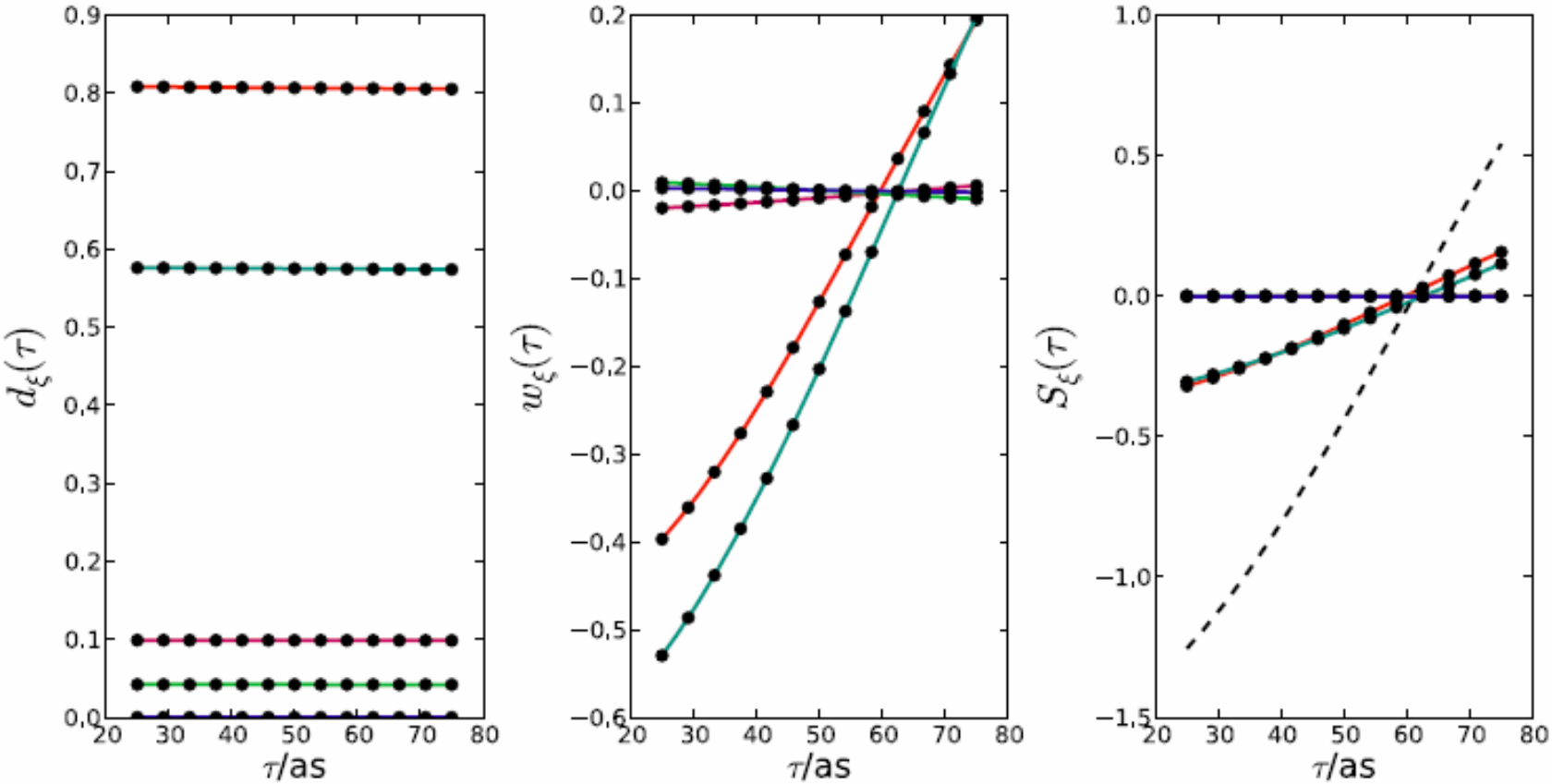
Signal decomposition by natural orbital pair



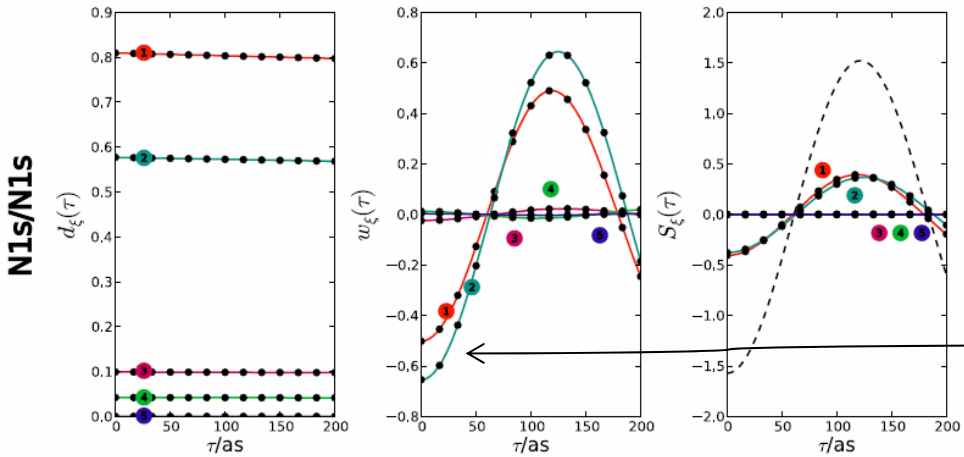
Pulse width: $\sigma_j = 77\mathrm{as}(1/\sigma_j \simeq 10\mathrm{eV})$

zooming in on the crossing…

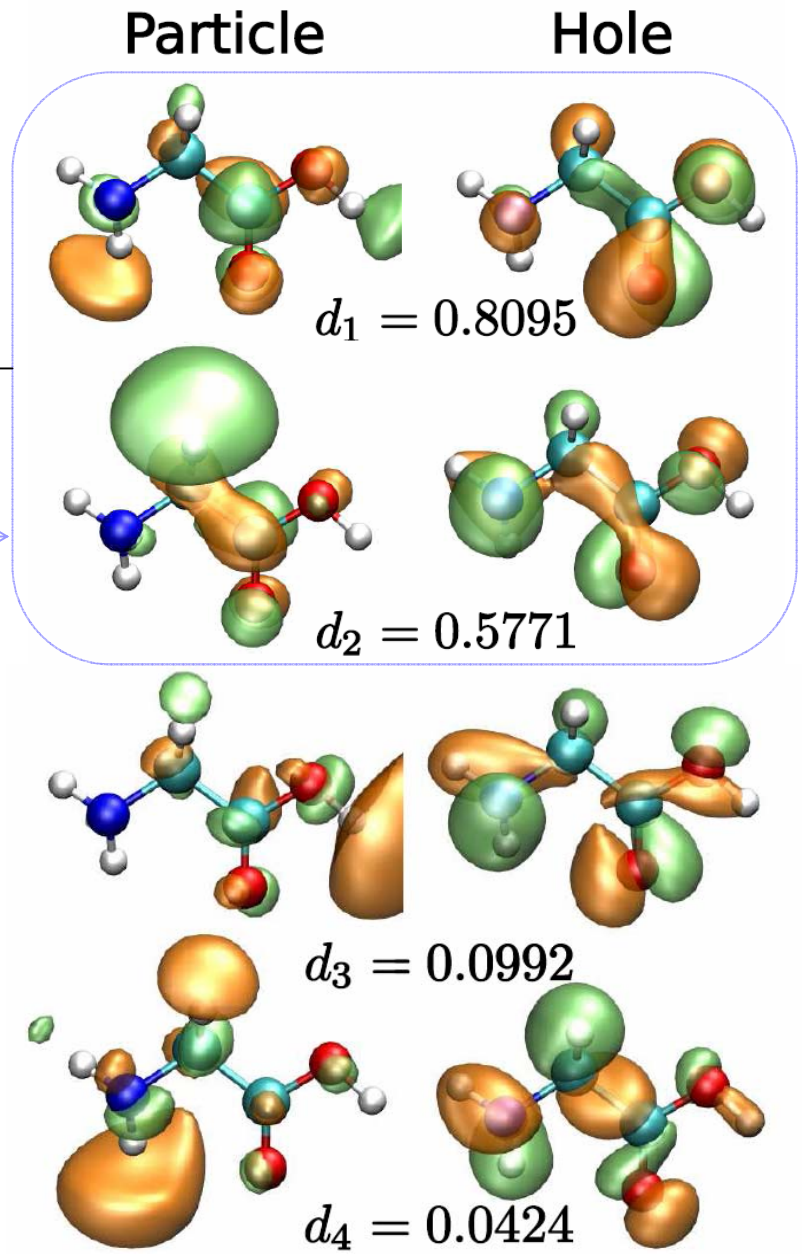
N1s/N1s



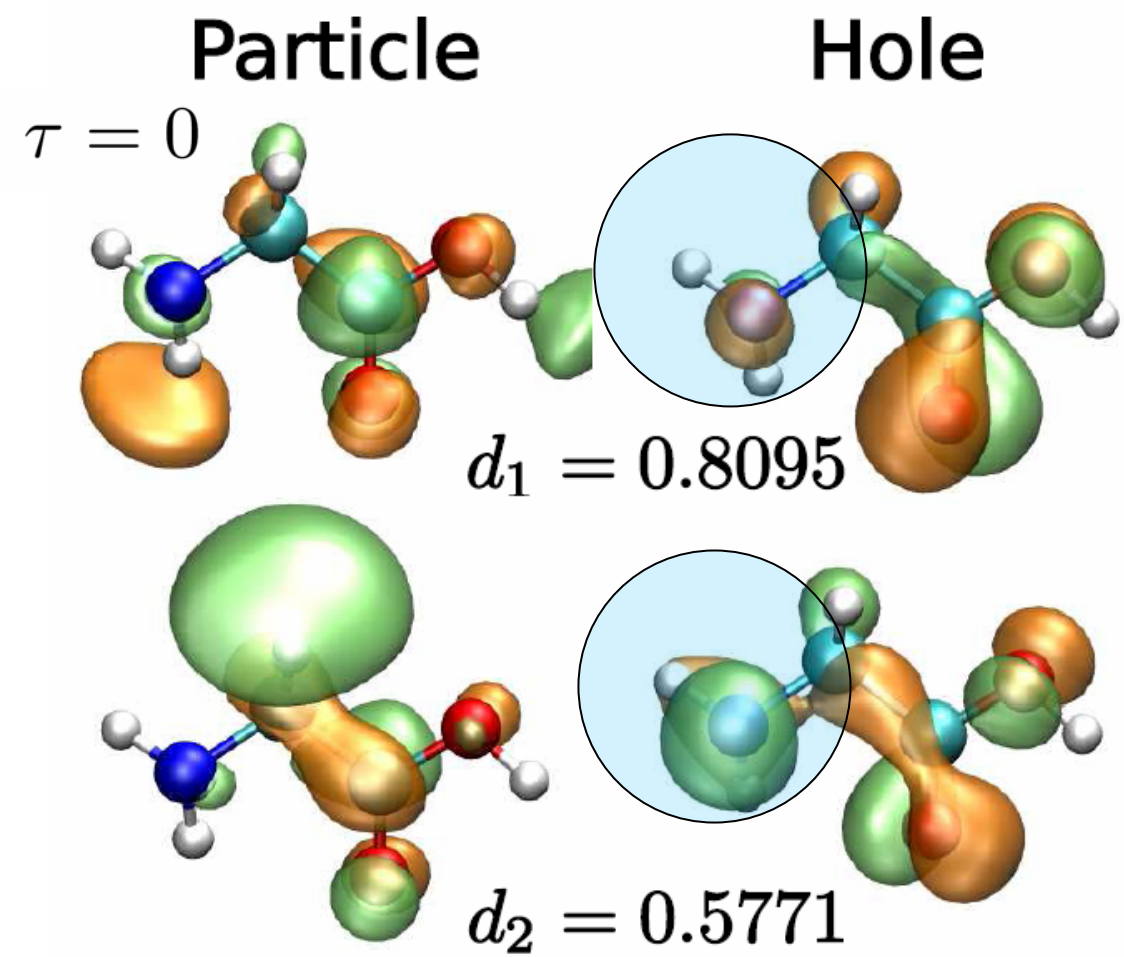
for this system, the dominant contribution comes from the natural orbitals with the strongest doorway weights



Natural Orbitals at $\tau = 0$



The strongest contribution is from the first two natural orbitals.



Selection rule: x-ray dipole is strong between s type core-orbitals, and valence orbitals with a strong projection onto the p-orbitals local to the resonant core.

both of the natural orbitals contributing strongly to the signal contain p-orbital character in their hole natural orbitals.

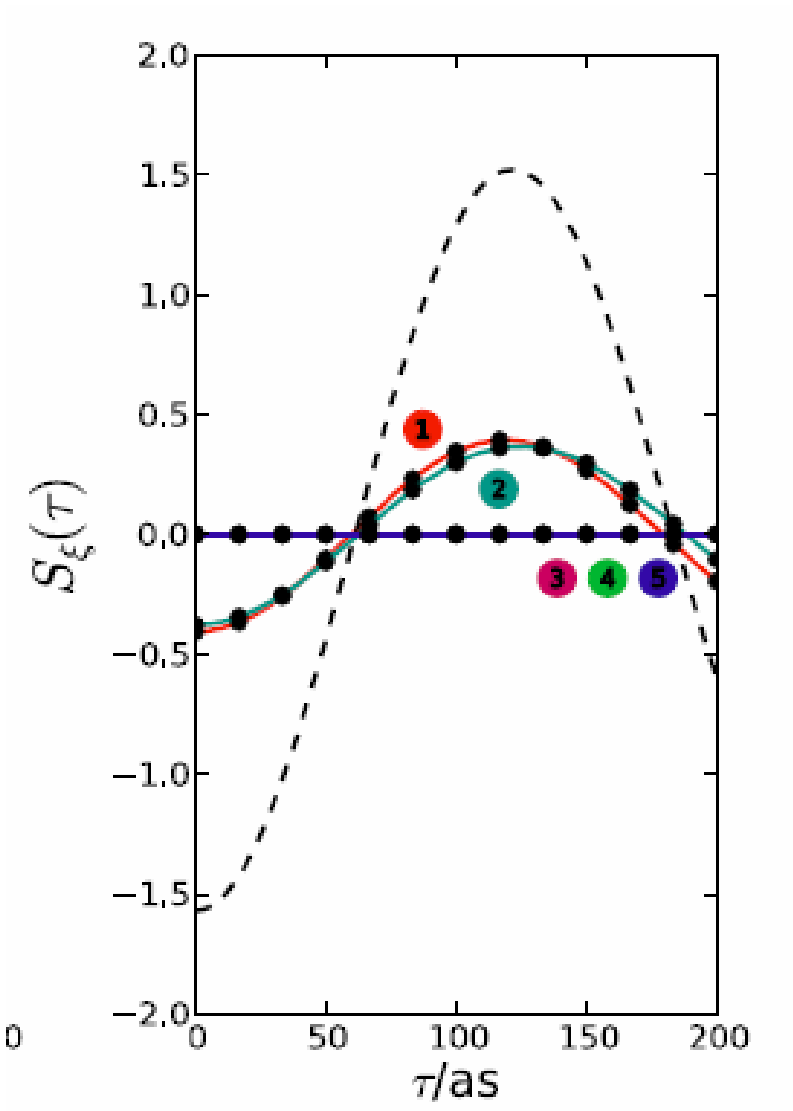
Spatial Representation of Natural Orbitals

The natural orbitals can be expanded in the atomic basis functions of the signal

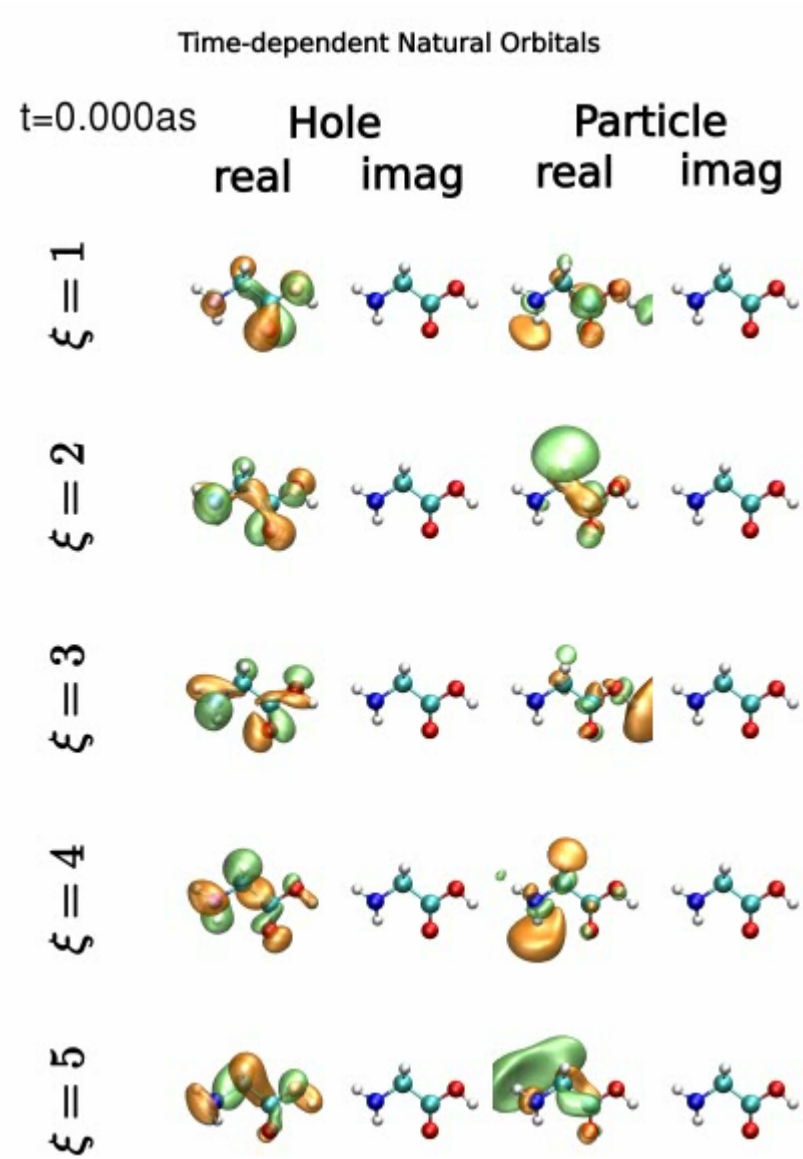
$$\phi^*_{p,\xi}(r,\tau) = \sum_{a\alpha} \chi^p_{a\xi} C_{a\alpha} \phi^*_\alpha(r) e^{-i\varepsilon_a \tau}$$

$$\phi_{h,\xi}(r,\tau) = \sum_{i\beta} \chi^h_{\xi i} C^*_{i\beta} \phi_\beta(r) e^{i\varepsilon_i \tau}$$

Time-dependent Natural Orbitals



Time: 0as – 200as

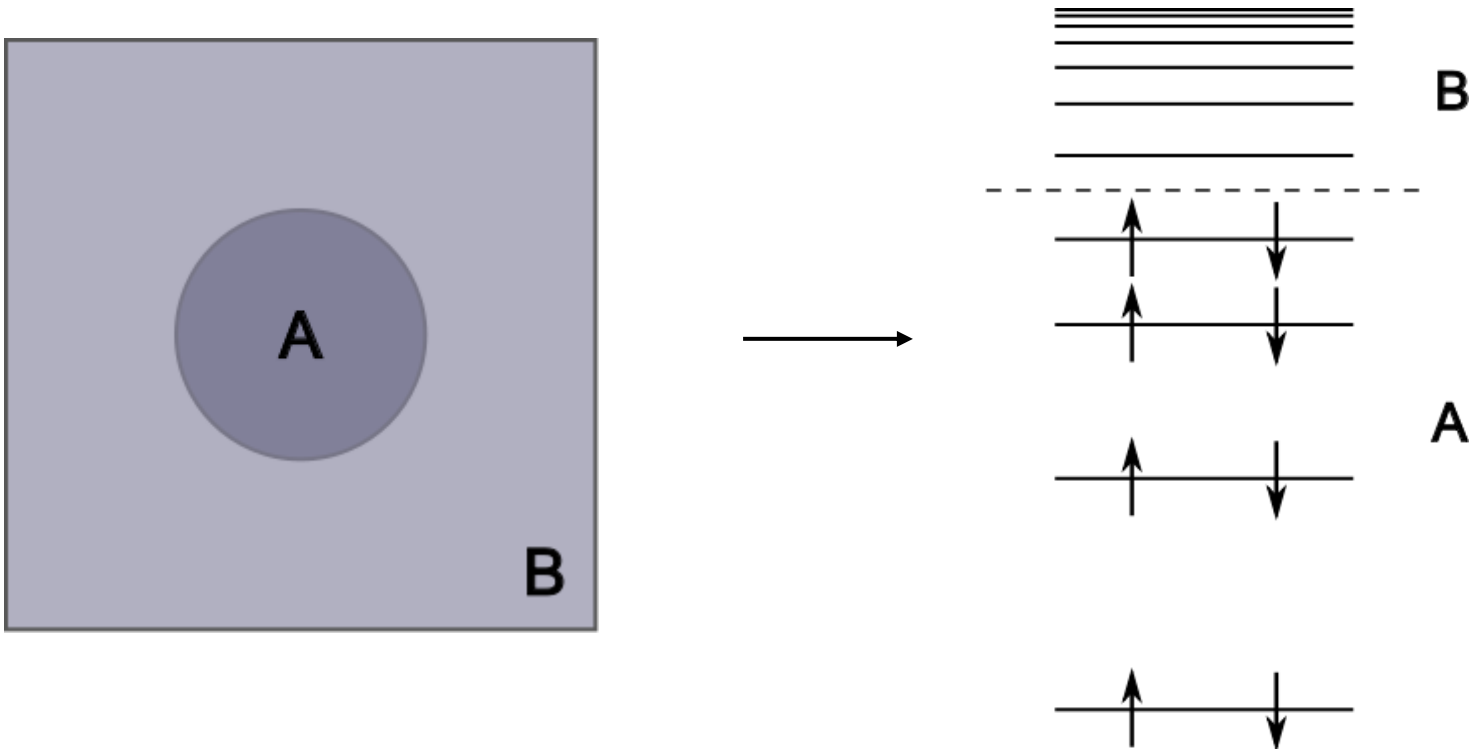


Manipulating Quantum Entanglement of Quasiparticles in Many-Electron Systems by Attosecond X-ray Pulses

Shaul Mukamel and Haitao Wang

Department of Chemistry, University of California, Irvine

Entanglement: concurrence



Concurrence

Reduced density matrix:

$$\sigma_e = \mathrm{Tr}_h \left|\psi\right\rangle\left\langle\psi\right| = S^\dagger S \qquad \sigma_h = \mathrm{Tr}_e \left|\psi\right\rangle\left\langle\psi\right| = S S^\dagger$$

Schmidt representation diagonalizes both σ_e and σ_h simultaneously, sharing d non-zero eigenvalues λ_ν with $\nu = 1, 2, \cdots, d$.

$$\left|\psi(t)\right\rangle = \sum_{\nu=1}^{d} \sqrt{\lambda_\nu(t)} c_\nu^\dagger d_\nu^\dagger \left|g\right\rangle$$

<u>Participation ratio</u> R^{-1} with $R = \mathrm{Tr}\sigma_e^2 = \sum_\nu \lambda_\nu^2$ measures the number of electron-hole pairs participating in the wave packet.

<u>Concurrence</u> $C = \sqrt{2(1-R)} = \sqrt{\sum_{\nu<\nu'} \lambda_\nu \lambda_{\nu'}}$ is another measure of entanglement commonly used in quantum information applications.

Simulation results: carbon monoxide (CO)

- Geometry optimized at B3LYP/6-311G** level.
- Excitation energies and transition dipole moments calculated with the minimal basis STO-3G basis set.
- Line-width: $\Gamma_f = 0.5eV$ and broadband width: $\sigma_1 = 20eV$

$\|g'\rangle$	$\omega_{g'g}$ (eV)	$\|D_{g'}\|^2$ (oxygen K-edge)	$\|D_{g'}\|^2$ (carbon K-edge)	$\|D_{g'}\|^2$ $(\sigma_1 \rightarrow \pi^*)$
4	10.69	0.03796	0.01182	0.00905
5	10.69	0.06269	0.01953	0.01495
8	19.56	0.06073	0.37849	0.44332
11	31.68	0.68598	0.58300	0.11670
14	36.50	0.15025	0.00051	0.38921
15	55.53	0.00240	0.00665	0.02677

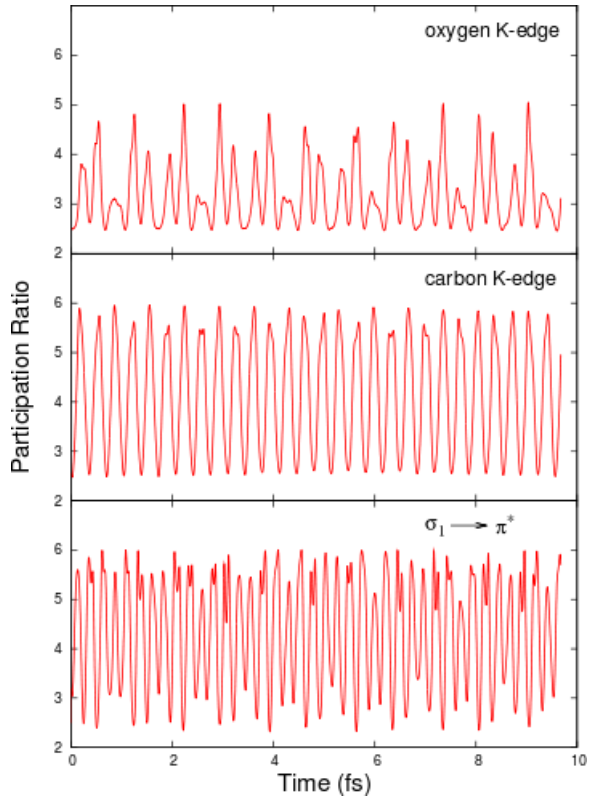
Table: The 6 major valence-excited state contributions to the valence wave packets prepared by the three core transitions used in the present simulations. The states are labeled in increasing order of energies (column 1).

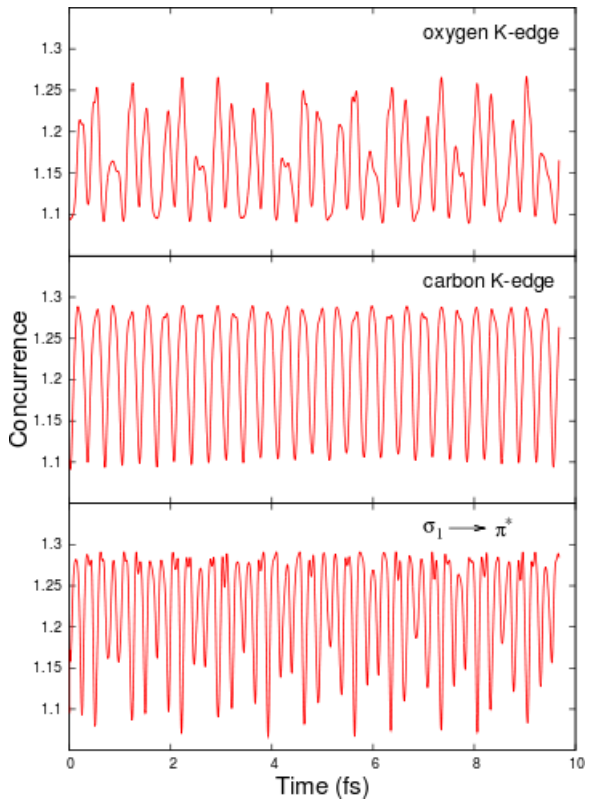
Simulation results: carbon monoxide (CO)

For a given d, the concurrence has a maximum value of $C_{max} = \sqrt{2(1-1/d)}$

$$2 < d < 6$$

$$C_{max} = \begin{cases} 1.00 & d = 2 \\ 1.29 & d = 6 \end{cases}$$



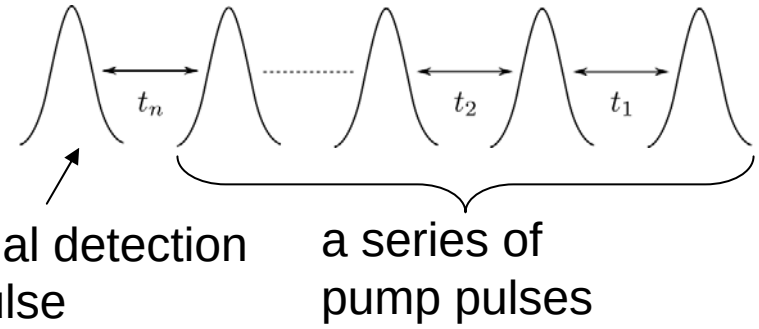


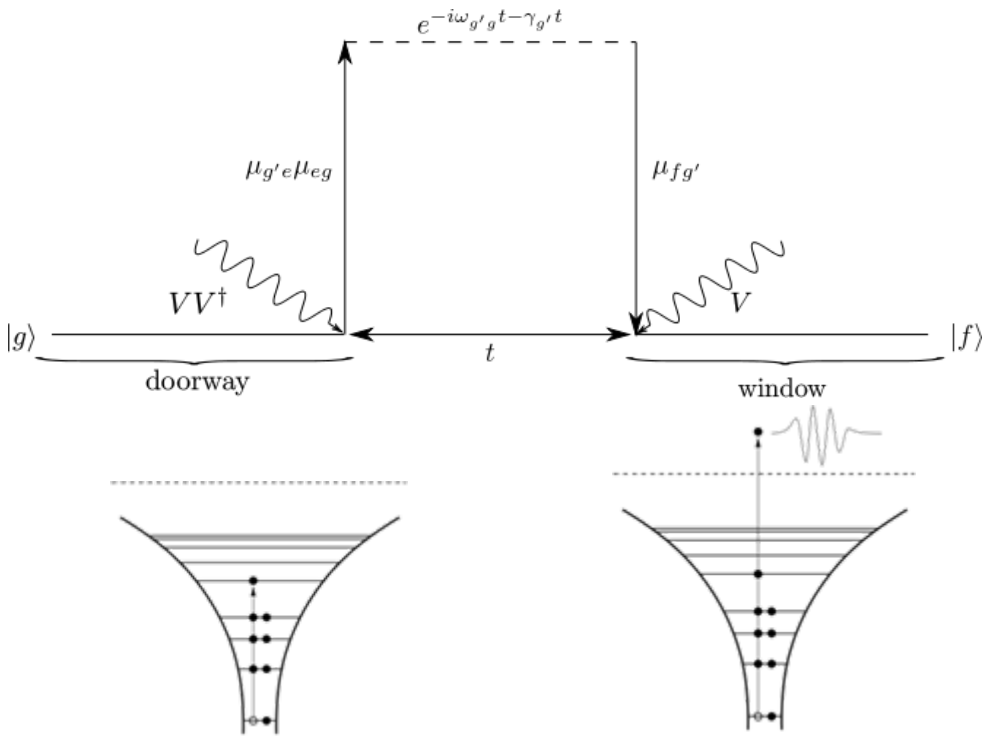
Multidimensional Attosecond Photoelectron Spectroscopy

Shaul Mukamel, Haitao Wang ,
Saar Rahav
University of California, Irvine

Multidimensional Attosecond Photoelectron Spectroscopy

- Well-separated pulses
- Detection pulse interacts with the molecule once, ionizes the molecule, and generates a photoelectron.
- The signal is the number of photoelectron with kinetic energy $\mathcal{E}_{\mathbf{k}}$.





Photoelectron Signal in Frequency Domain

The signal is a square modulus of transition amplitude evaluated at the transition frequency.

$$\tilde{S}(\varepsilon) = \hbar^{-2} \int d\omega \, |T_{fg}(\omega)|^2 \, \rho_f(\varepsilon) \delta\left(\omega - \omega_{f,g}\right)$$

$$= \hbar^{-2} \, |T_{fg}(\omega_{fg})|^2 \, \rho_f(\varepsilon)$$

where $\varepsilon_f^- + \varepsilon - \varepsilon_g = \hbar\omega_{fg}$ ← transition energy

internal energy of the ion state

kinetic energy of the photoelectron

internal energy of the neutral state

The transition amplitude can be expanded in powers of various pulses:

$$T_{fg}(\omega) = \int d\omega_1 E^d(\omega_1) \tilde{T}_{fg}^{(1)}(\omega_1) \delta\left(\omega - \omega_1\right)$$

$$+ (2\pi\hbar)^{-1} \int d\omega_1 d\omega_2 E^p(\omega_1) E^d(\omega_2) \tilde{T}_{fg}^{(2)}(\omega_2, \omega_1) \delta\left(\omega - \omega_1 - \omega_2\right)$$

$$+ (2\pi\hbar)^{-2} \int d\omega_1 d\omega_2 d\omega_3 E^p(\omega_1) E^p(\omega_2) E^d(\omega_3) \tilde{T}_{fg}^{(3)}(\omega_3, \omega_2, \omega_1) \delta\left(\omega - \omega_1 - \omega_2 - \omega_3\right) + \cdots$$