Exploring quasi-relativistic DFT approaches in the simulation of resonant inelastic x-ray scattering maps

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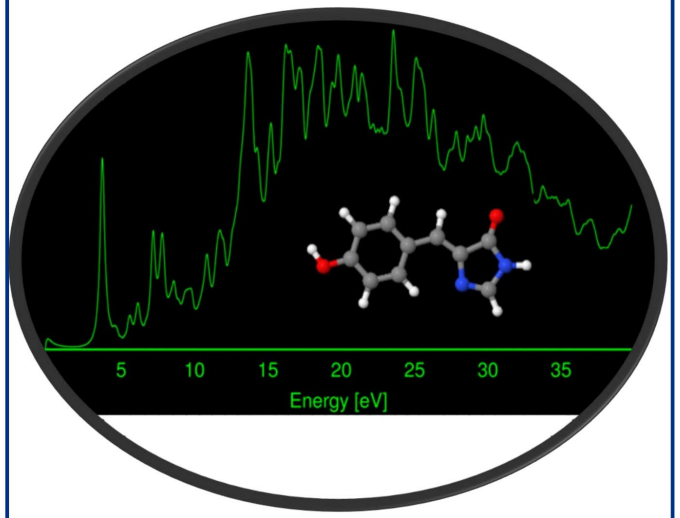
Department of Chemistry
The University of Memphis

Research in the Nascimento group

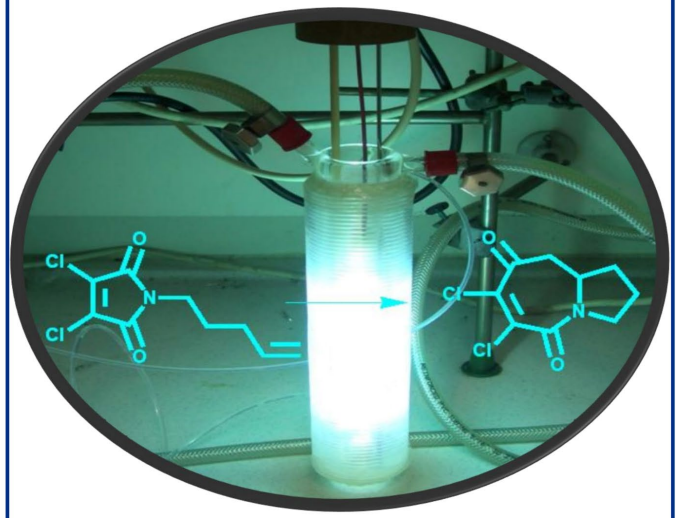
Spectroscopy



Can we characterize and tune the ability of a molecule to absorb, emit, or scatter light?

DRN and DePrince *JCTC* 2016, **12**, 12, 5834-584.

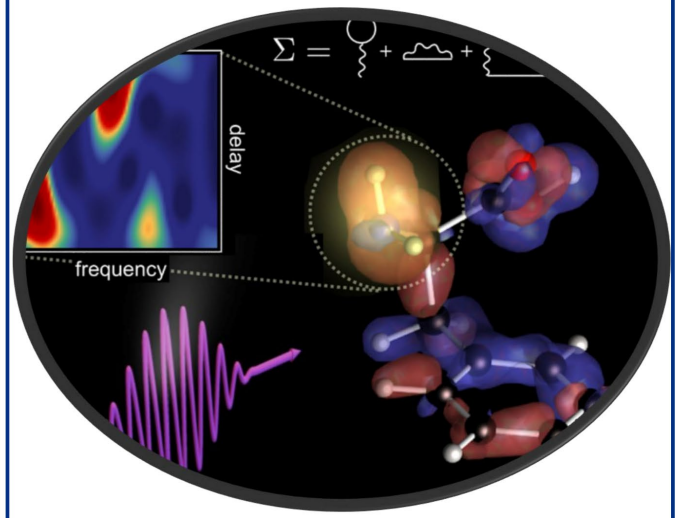
Photochemistry



How can we use light to promote or inhibit (control) specific chemical reactions?

https://chemicalengineeringmatters.wordpress.com

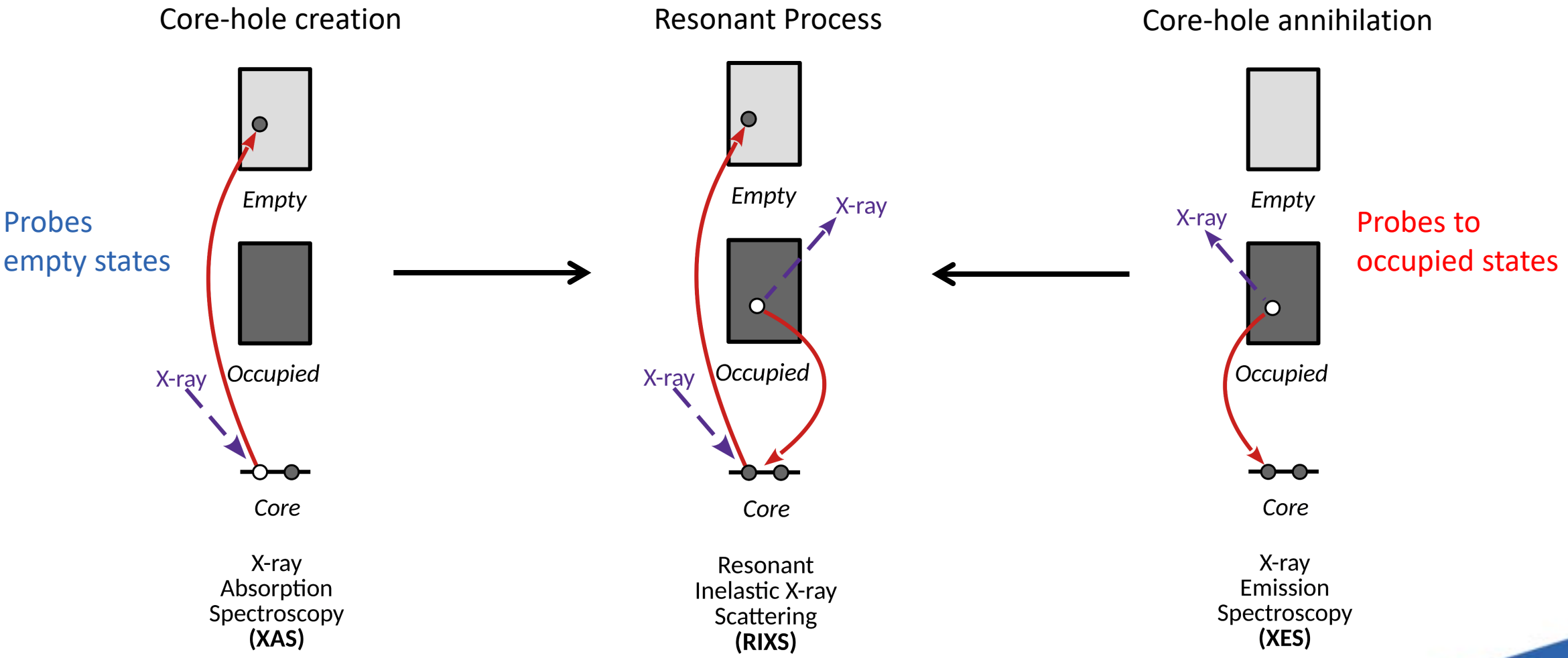
Electron Dynamics



Can we engineer laser pulses to probe and control electron flow in a molecule?

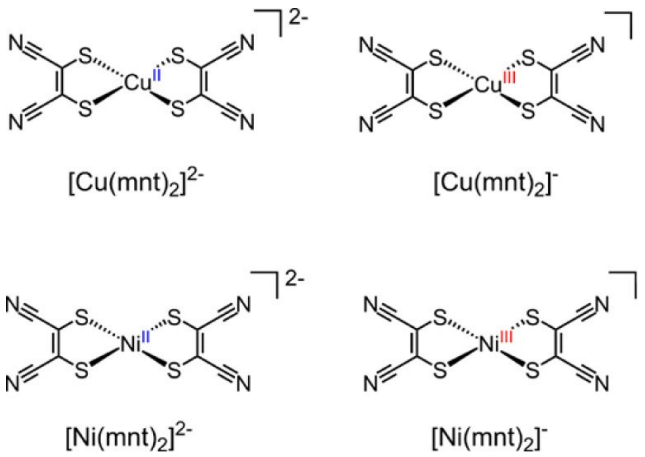
Perfetto *et al. JPCL* 2018, **9**, 6, 1353-1358

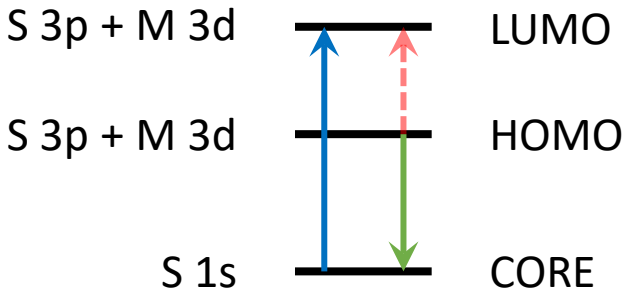
Radiative Core-Level Processes

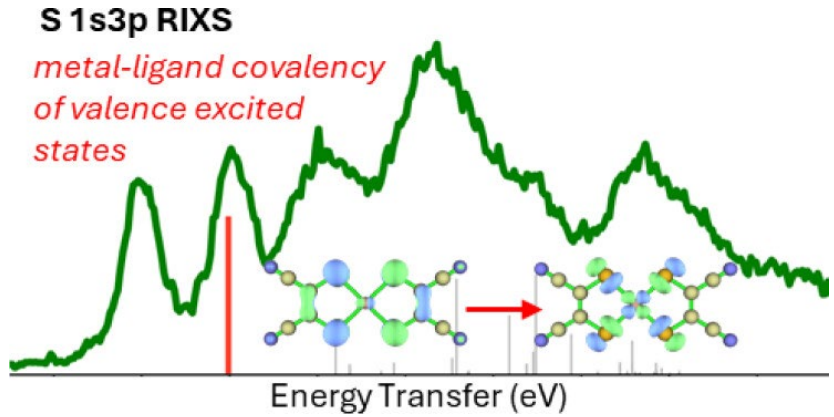


Resonant Inelastic X-ray Scattering (RIXS)

Probing the nature of the frontier orbitals in TM complexes:







Metal Dithiolenes

- Non-innocent ligand
- Frontier orbitals have dominant S 3p orbital character.

Important RIXS Characteristics:

- Atomic specificity
- Sensitivity to the local environment
- Resolution does not depend on core-hole lifetime

Larsen *et al. J. Am. Chem. Soc.* 2024, **146**, 41, 28561-28571

The RIXS cross-section: Kramers-Heisenberg formula

For randomly oriented molecules and a minimal elastic scattering angle:

$$S(\omega, \omega - \omega') = \frac{\omega'}{\omega} \sum_{fn} \sum_{\xi\xi'} \frac{1}{30} \left\| \left[4 \left(S_{fn}^{\xi\xi'} \right)^2 - S_{fn}^{\xi\xi} S_{fn}^{\xi'\xi'} - S_{fn}^{\xi\xi'} S_{fn}^{\xi'\xi} \right] \right\| \Delta(\omega, \omega - \omega')$$

Line Shape

Amplitudes: $S_{fn}^{\xi\xi'} = \langle f | \hat{\mu}_{\xi} | n \rangle \langle n | \hat{\mu}_{\xi'} | 0 \rangle$

Challenge: To efficiently compute excited-state transition moments for large excited-state manifolds (500+ states), incorporating scalar-relativistic and spin-orbit effects.

Proposed Solution: Begin with linear-response time-dependent density-functional theory (TDDFT) and build complexity as needed and in the simplest way possible.

Part 1: Excited-state transition dipole moments

Assume that excited-state wavefunctions can be constructed with TDDFT/TDA solution vectors:

$$|n\rangle \approx \sum_{ia} X_{ia}^{n} \hat{a}_a^{\dagger} \hat{a}_i |0\rangle \quad \text{with} \quad AX = \omega X \quad \text{and} \quad A_{iajb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (ia|bj) - \alpha(ij|ba) + f_{iabj}^{xc}$$

then

$$\langle n|\hat{\mu}_{\xi'}|0\rangle \approx \sum_{ia} X_{ia}^{n} \mu_{ia}^{\xi'} \quad \text{and} \quad \langle f|\hat{\mu}_{\xi'}|n\rangle \approx \sum_{ia} X_{ia}^{f} \left(\sum_{b} \mu_{ab}^{\xi'} X_{ib}^{n} - \sum_{j} X_{ja}^{n} \mu_{ji}^{\xi'} \right)$$

Unrelaxed second-order transition densities

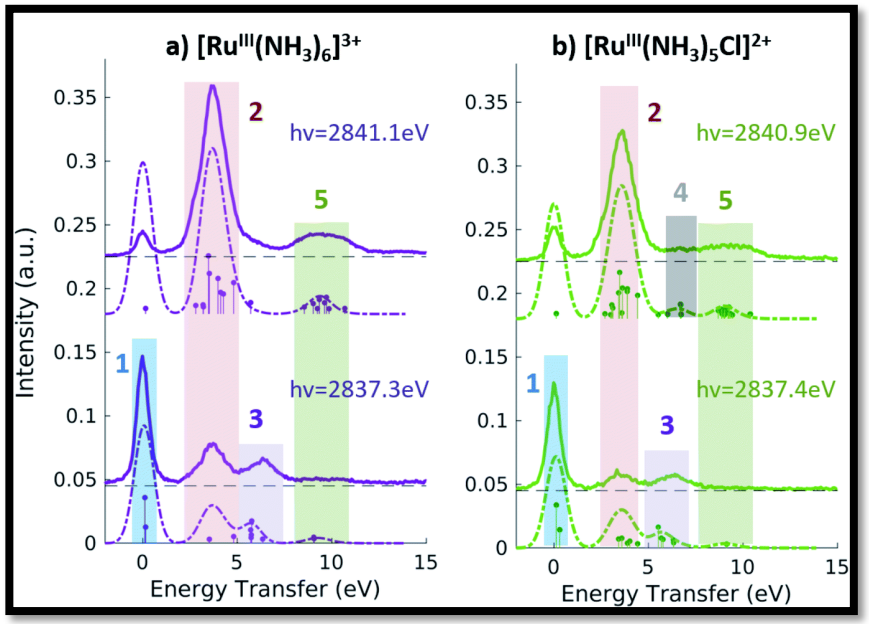
Using the core-valence separation (CVS) technique, all we need is to perform two separate TDDFT/TDA calculations. One for each excited-state manifold.

DRN *et al. JCTC* 2021, **17**, 5, 3031–3038

Part 1: Excited-state transition dipole moments

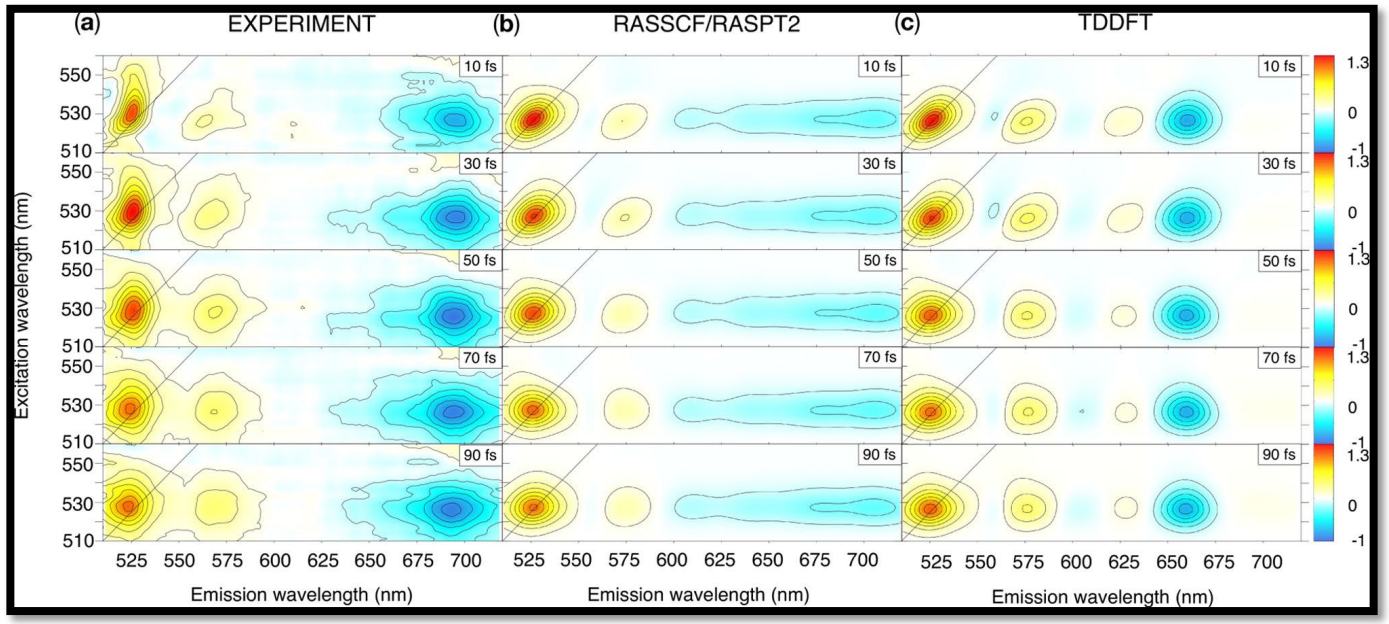
Successful examples:

2p4d RIXS of Ru Complexes



Biasin *et al. Chem. Sci.* 2021, **12**, 3713-3725

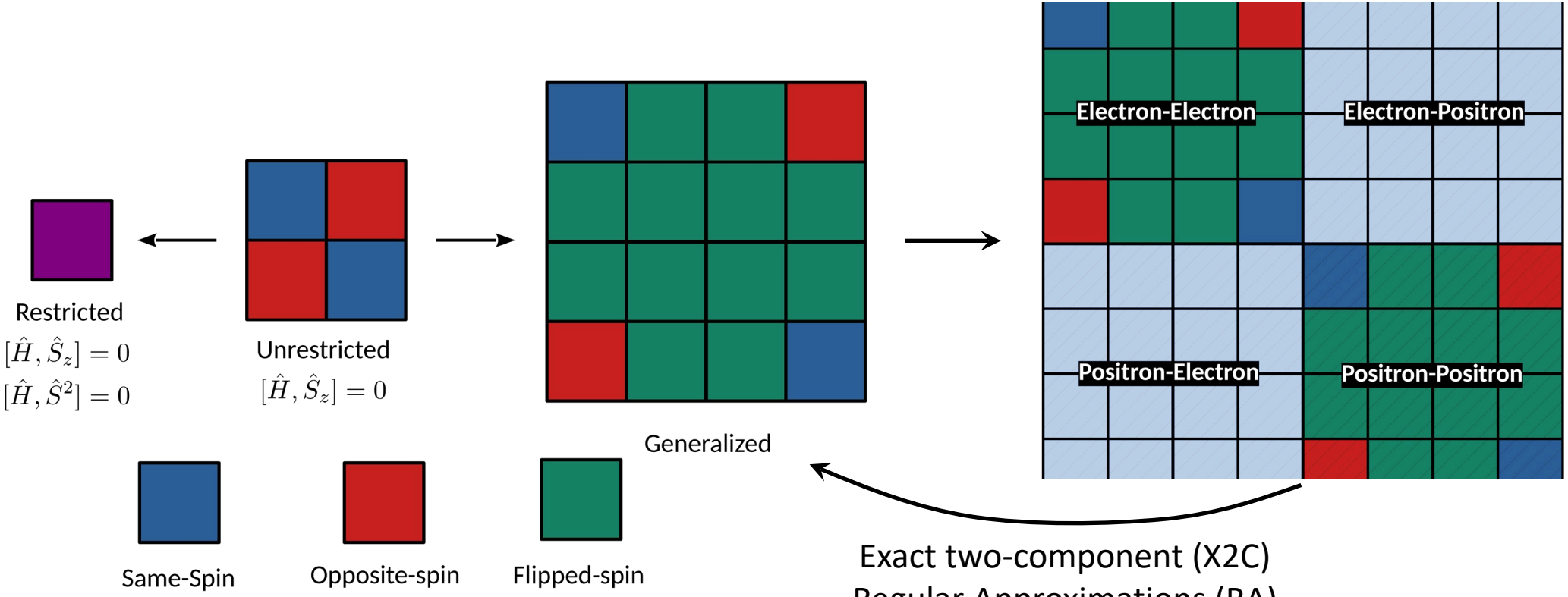
2DES maps of Perylene Bisimide



Segatta *et al. J. Chem. Theory Comput.* 2021, **17**, 11, 7134-7145

Part 2: Incorporating relativistic effects

Reference: Kohn-Sham (KS) → Dirac-Kohn-Sham (DKS)



Part 2: Incorporating relativistic effects

The Zeroth-Order Regular Approximation (ZORA):

Reference: Kohn-Sham (KS) → ZORA-Kohn-Sham (ZKS)

$$\hat{h}_{ZKS} = \frac{\boldsymbol{p}^2}{2} + \boldsymbol{p}\left(\frac{\kappa - 1}{2}\right)\boldsymbol{p} + \frac{\kappa^2}{4c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla} v^{KS} \times \boldsymbol{p}) + v^{KS}, \qquad \kappa = \left(1 - \frac{v^{KS}}{2c^2}\right)^{-1}$$

Kinetic Energy

Scalar Correction

Spin-Orbit

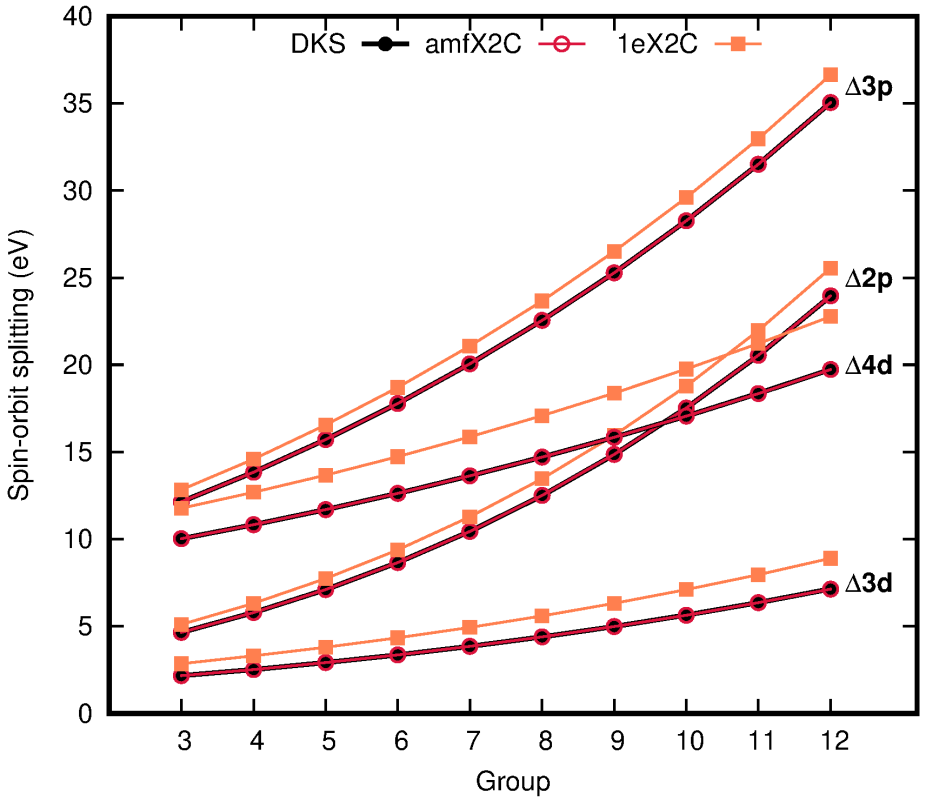
Following van Wüllen and coworkers, *J. Chem. Phys.* 1998, **109**, 2:

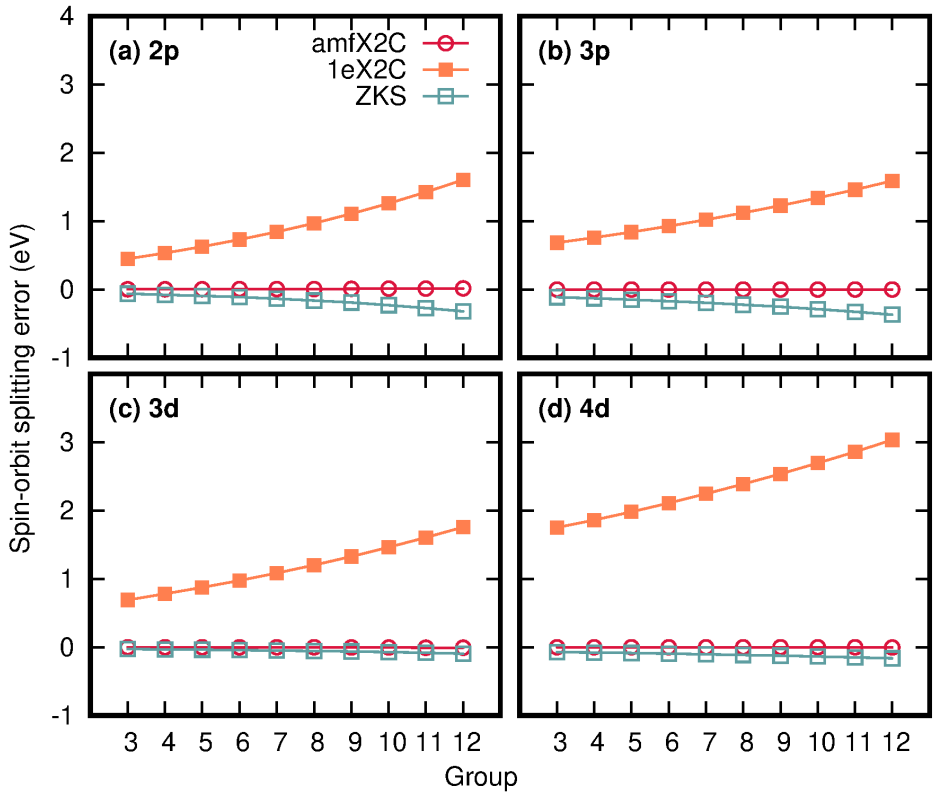
$$\hat{h}_{ZKS} = \frac{\boldsymbol{p}^2}{2} + \boldsymbol{p}\left(\frac{\tilde{\kappa} - 1}{2}\right)\boldsymbol{p} + \frac{\tilde{\kappa}^2}{4c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\tilde{v} \times \boldsymbol{p}) + v^{KS}, \qquad \tilde{\kappa} = \left(1 - \frac{\tilde{v}}{2c^2}\right)^{-1}$$

$\tilde{v}$ is an atom-centered spherical potential built from a model density that reproduces the DKS density.

Part 2: Incorporating relativistic effects

Reproducing SO splittings for d^0 TM cations: ZKS Spinors





Sarah Pak
(PhD 2025)

Pak et al. *JCP*, 2025, **163**, 094110

SO splittings obtained with different Hamiltonians for a set of d^0 transition metal cations. First row: 2p, Second row: 3p and 3d, Third row: 4d. Calculations performed with the PBE0 functional and Dyall DZP basis.

Part 2: Incorporating relativistic effects

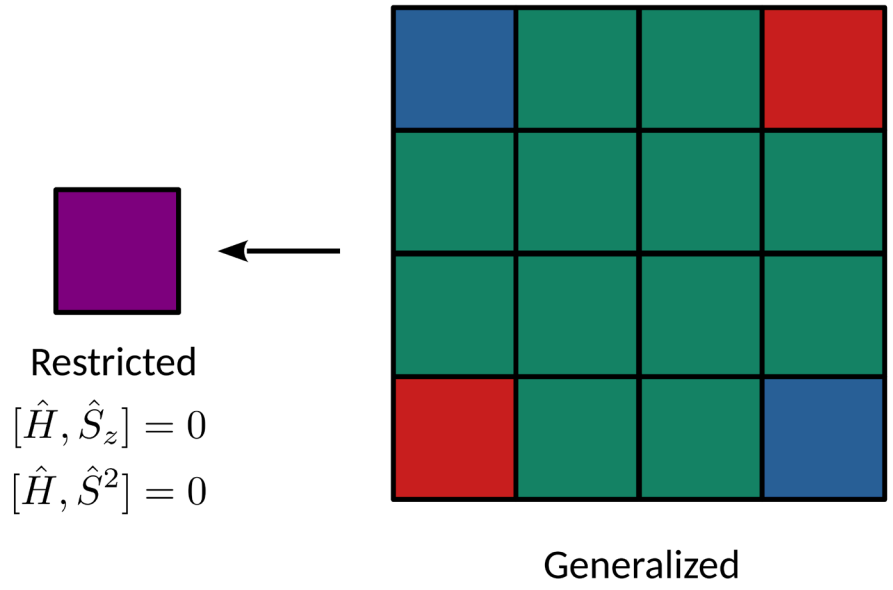
State-Interaction (SI) Approach:

$$\hat{h}_{ZKS} = \hat{h}_{SR} + \hat{h}_{SO}$$

$$\hat{h}_{SR} = \frac{\boldsymbol{p}^2}{2} + \boldsymbol{p}\left(\frac{\tilde{\kappa} - 1}{2}\right)\boldsymbol{p} + v^{KS}$$

$$\hat{h}_{SO} = \frac{\tilde{\kappa}^2}{4c^2}\boldsymbol{\sigma} \cdot (\boldsymbol{\nabla}\tilde{v} \times \boldsymbol{p})$$

Solve $A_{SR}X_{SR} = \omega_{SR}X_{SR}$ for the desired manifolds



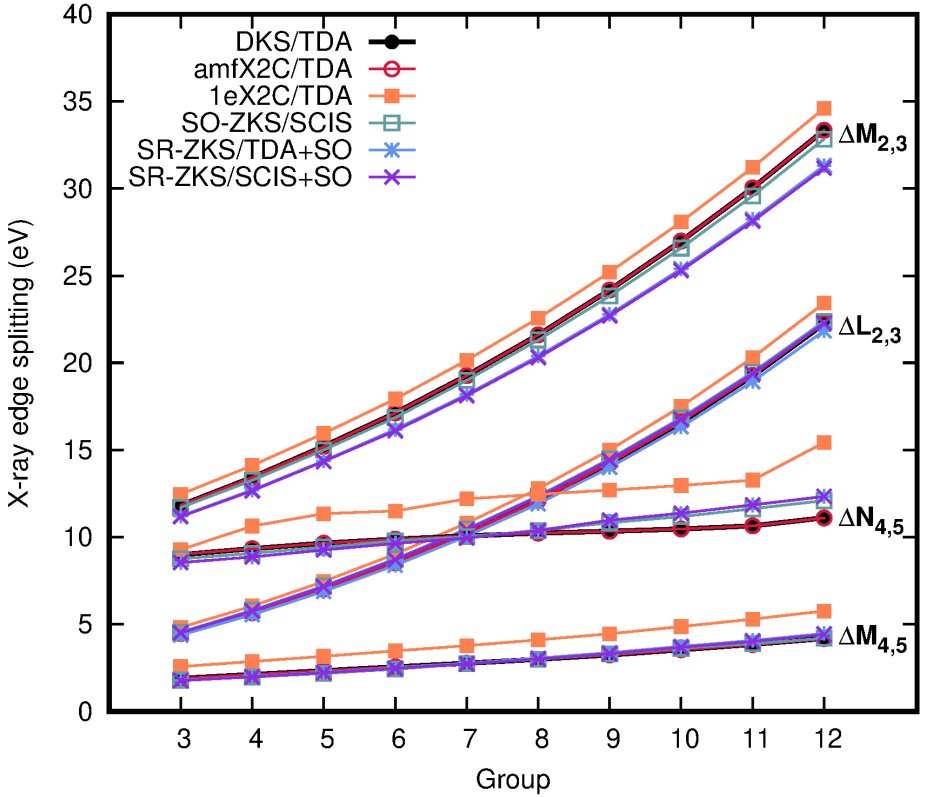
Then, project $\hat{h}_{SO}$ onto a selected states (usually a fraction of the full manifold):

$$\boxed{\left(X_{SR}^T \hat{h}_{SO} X_{SR} + \omega_{SR}\Delta\right)Z_{SO} = \Xi_{SO}Z_{SO}}$$

Pak *et al. JCP*, 2025, **163**, 094110; Franco de Carvalho *et al. JCP*, 2014, **140**, 144103; Roemelt *et al. JCP,* 2013, **138**, 204101.

Part 2: Incorporating relativistic effects

SO splitting of excitation energies:



1) DKS → TDA (very expensive, 128 RKS)

2) amfX2C-KS → TDA (expensive, 32 RKS)

3) 1eX2C-KS → TDA (expensive, 32 RKS)

4) Full ZKS → Scaled CIS (expensive, 32 RKS)

5) SR-ZKS → TDA → SI-SOC (cheap, 1 RKS)

6) SR-ZKS → Scaled CIS → SI-SOC (cheaper)

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Pak et al. *JCP*, 2025, **163**, 094110

Soft x-ray edge splittings obtained with different Hamiltonians for a set of d^0 transition metal cations. First row: $\mathrm{L}_{2,3}(2\mathrm{p} \rightarrow 3\mathrm{d})$, Second row: $\mathrm{M}_{2,3}(3\mathrm{p} \rightarrow 4\mathrm{d})$, and $\mathrm{M}_{4,5}(3\mathrm{d} \rightarrow 5\mathrm{p})$, Third row: $\mathrm{N}_{4,5}(4\mathrm{d} \rightarrow 6\mathrm{p})$.

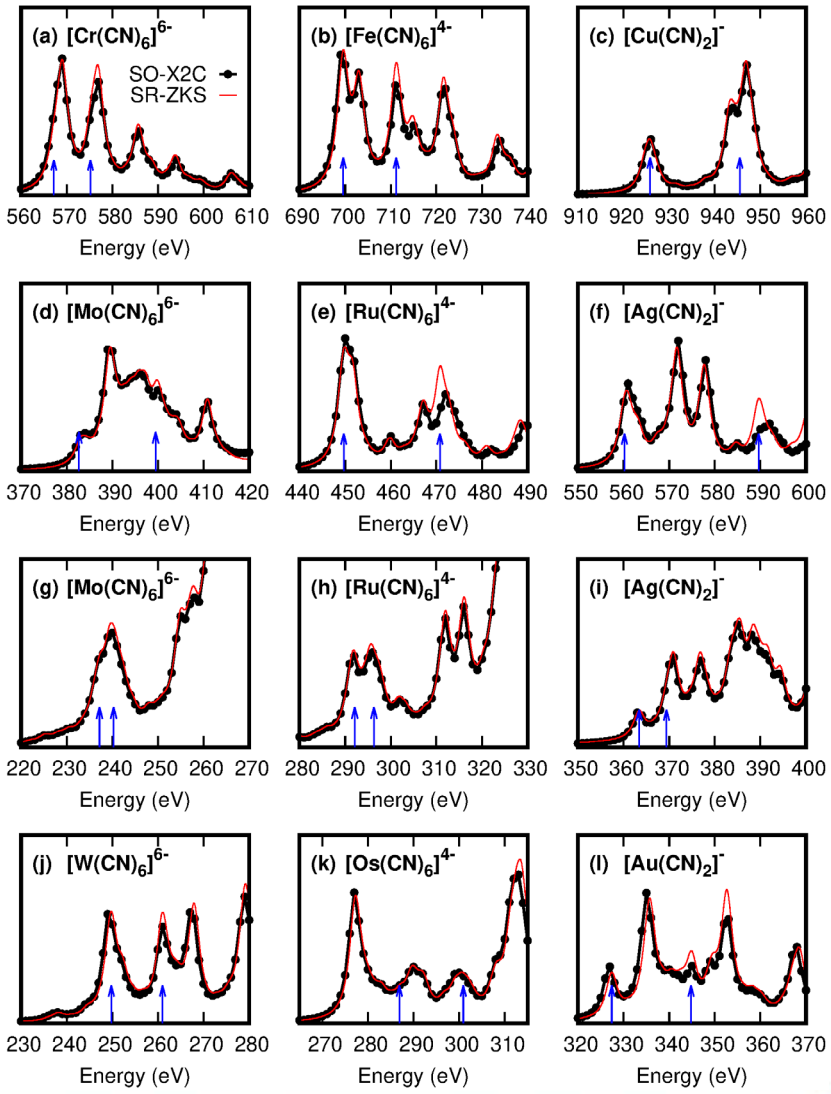
Part 2: Incorporating relativistic effects

Cyanometallates XAS:

XAS of cyanometallates calculated with the SR-ZKS/SCIS+SO (SR-ZKS) and mmfX2C/DR-TDDFT (SO-X2C) methods.

Functional: PBE0
Basis Set: Dyall DZP
Broadening: 1.5 eV.

First row: $L_{2,3}$ edge
Second row: $M_{2,3}$ and $M_{4,5}$ edges
Third row: $N_{4,5}$ edge



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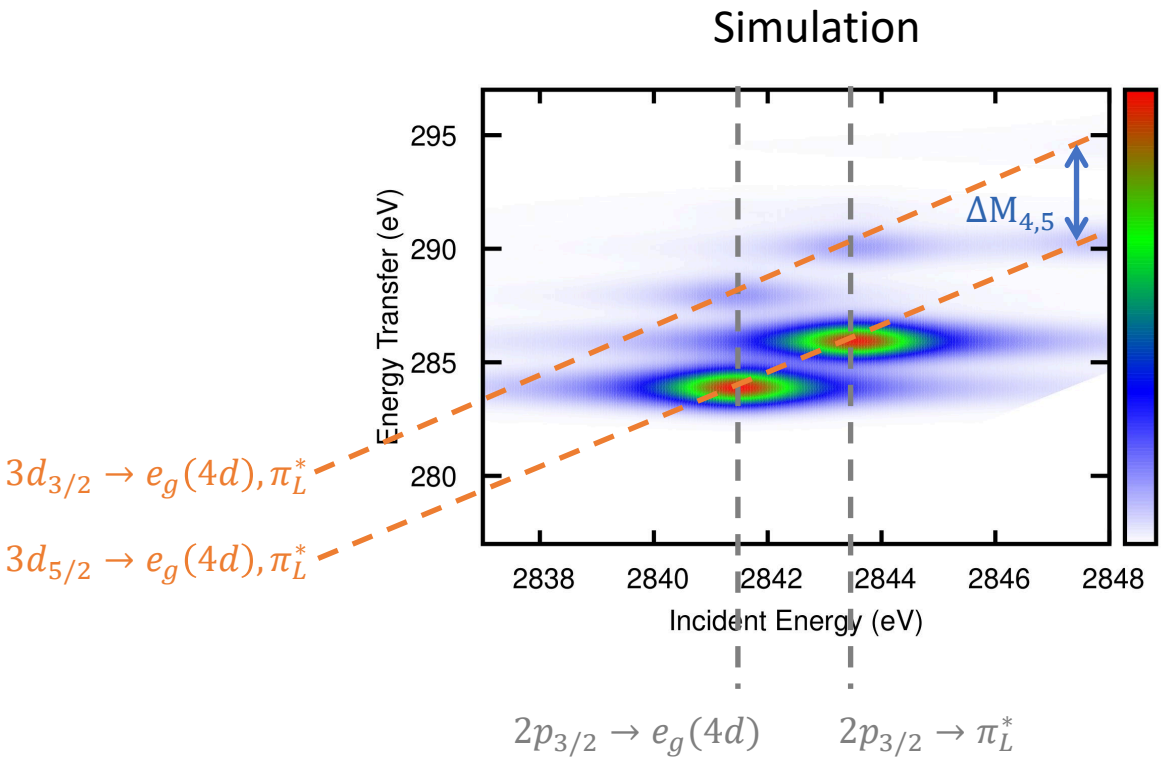
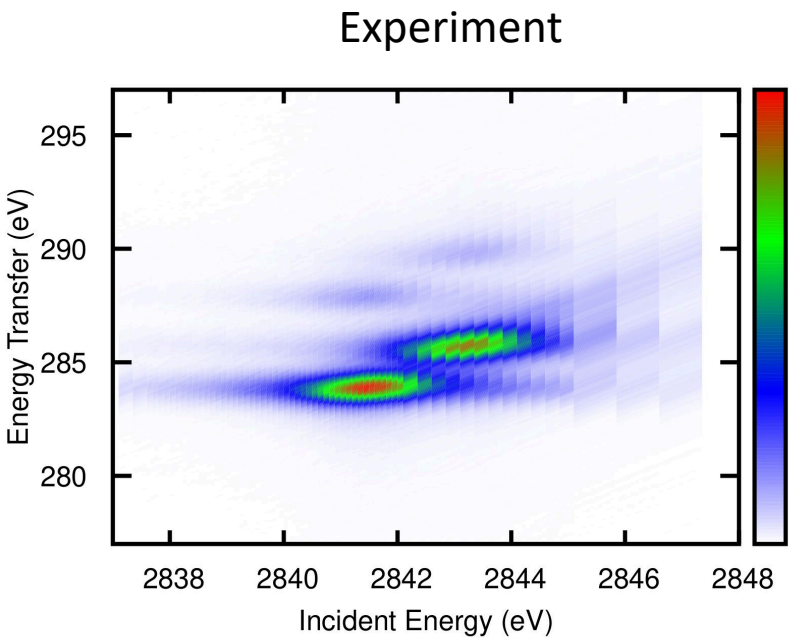
Pak et al. *JCP*, 2025, **163**, 094110

Application: 2p3d RIXS of $[Ru(CN)_6]^{4-}$





Muhammed Dada
(3rd-year PhD)

300 roots SR-ZKS/TDA+SO, B3LYP, Sapporo-DKH3-TZP-2012 (Ru) + 6-311G** (C,N,H). Shift (+40.5 eV, +7.1 eV).
Experimental data from: Khalil Group (University of Washington)

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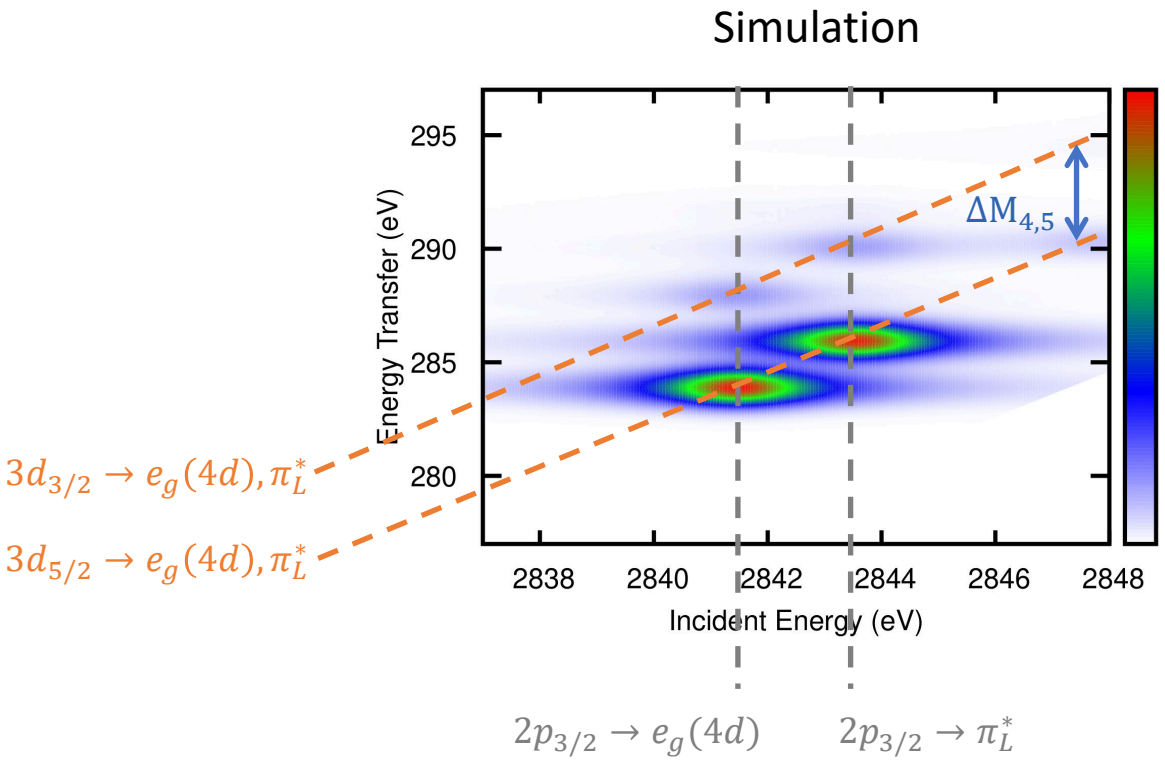

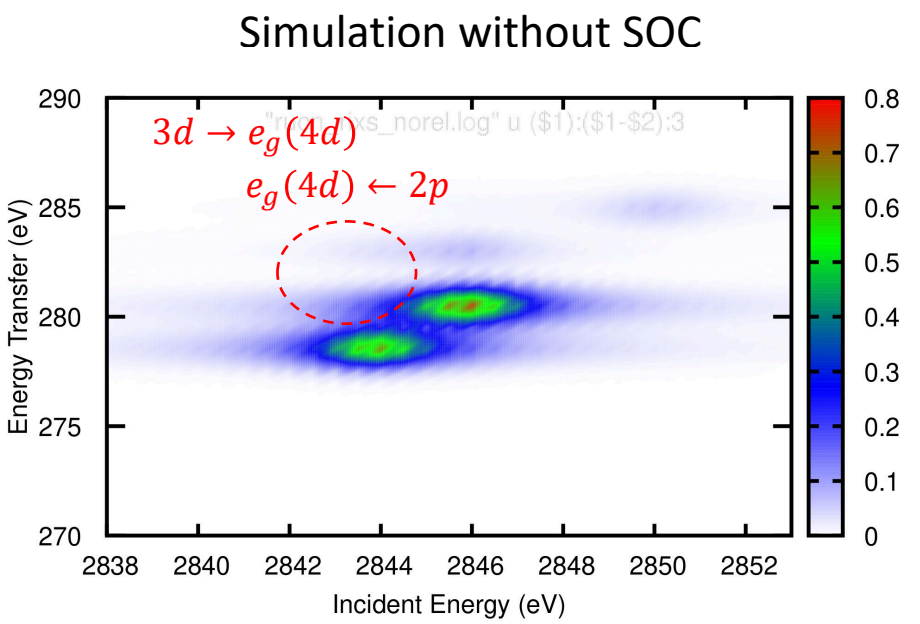

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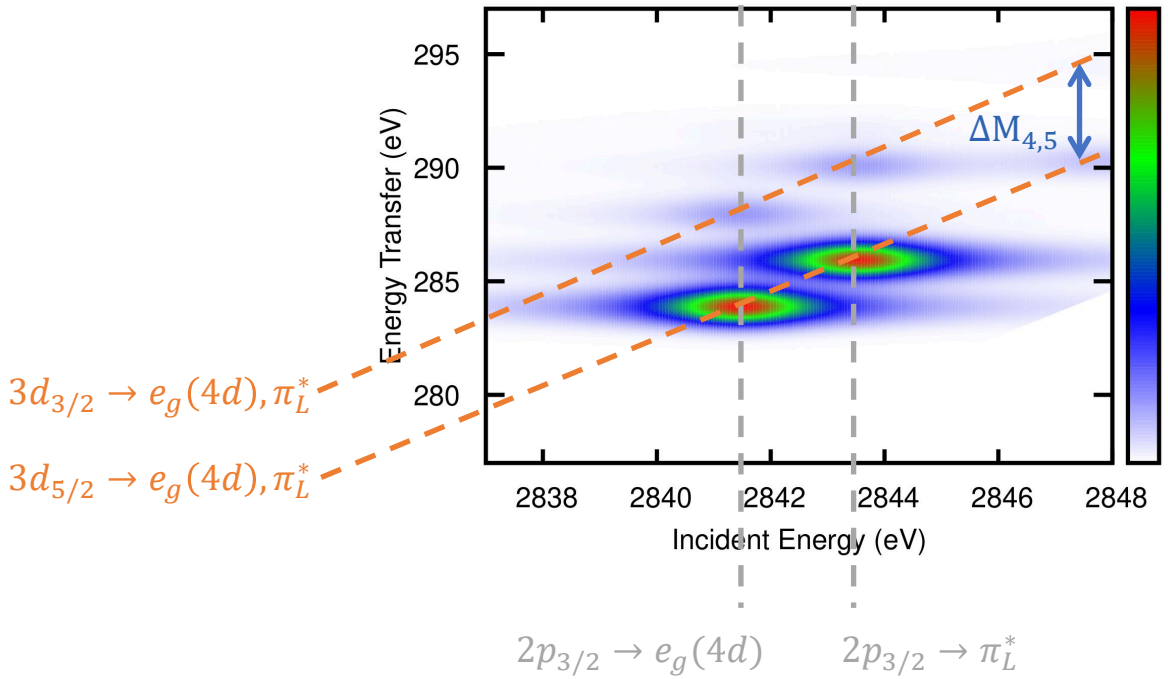
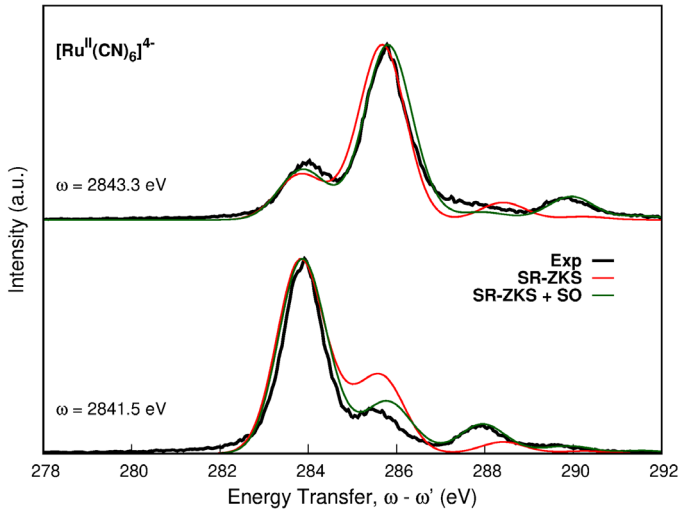
Simulation



Constant Energy Cut



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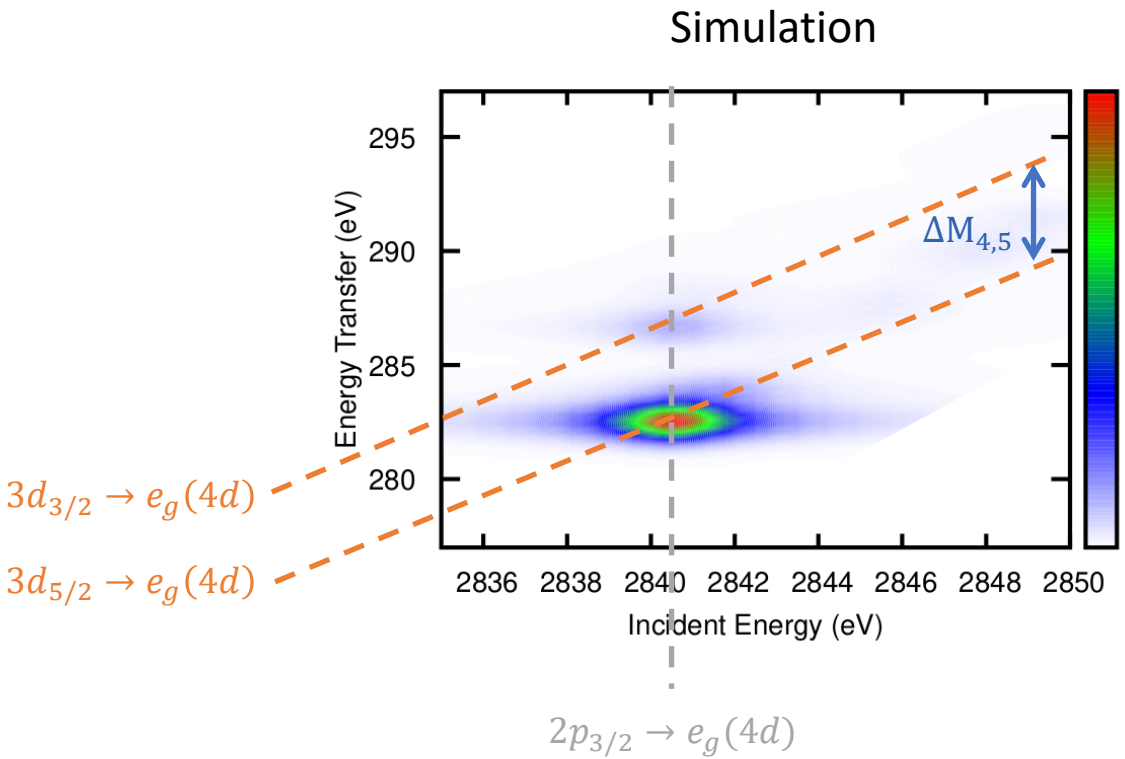

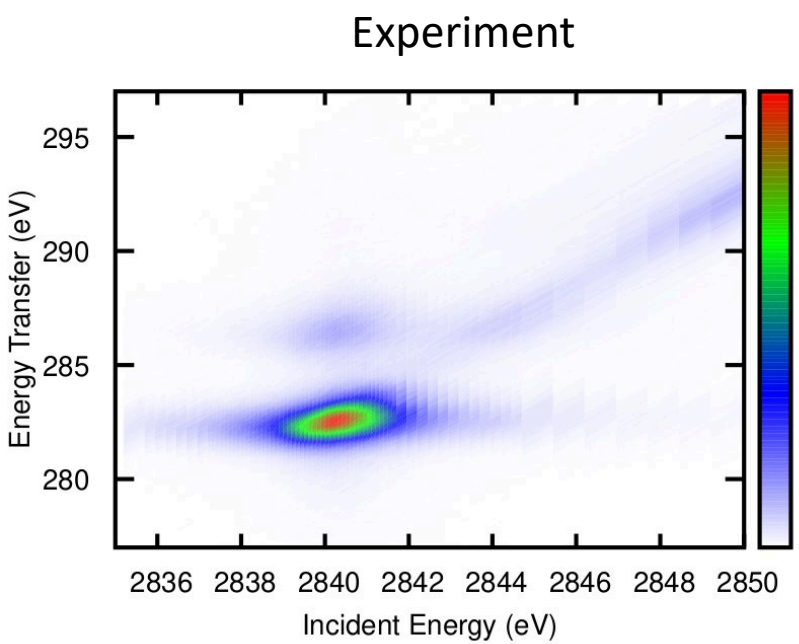

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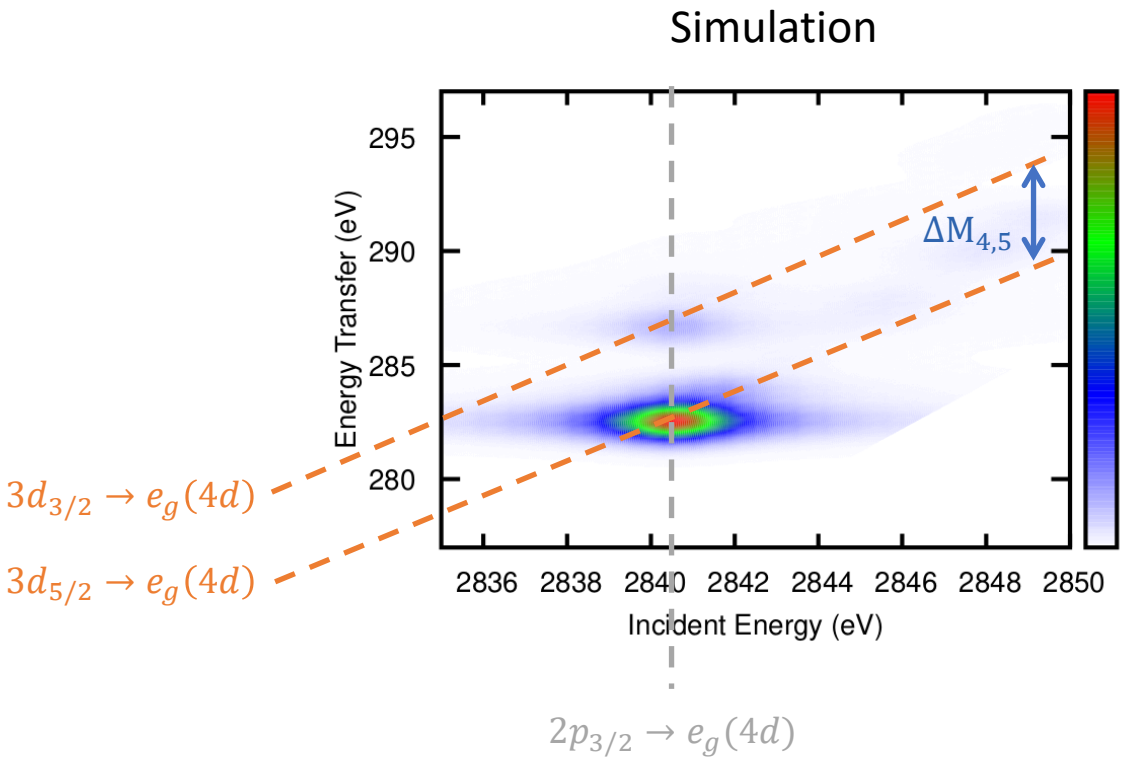

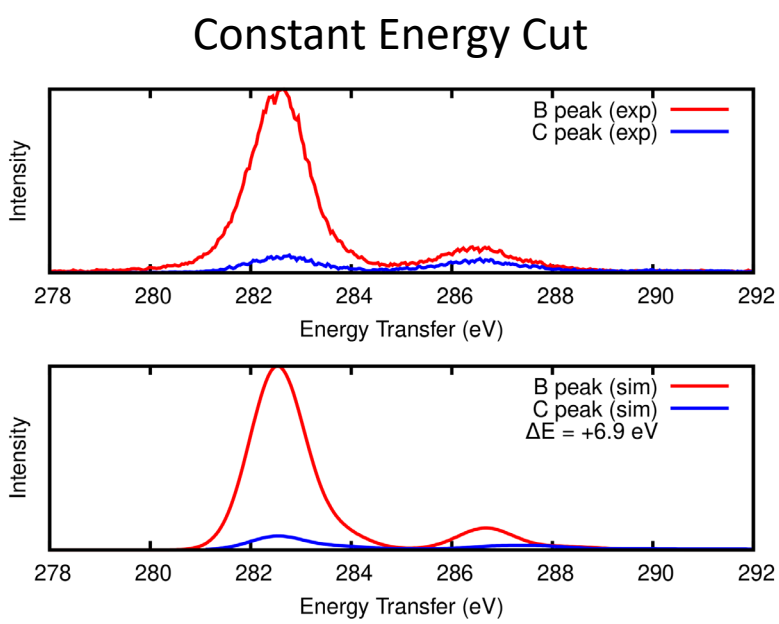

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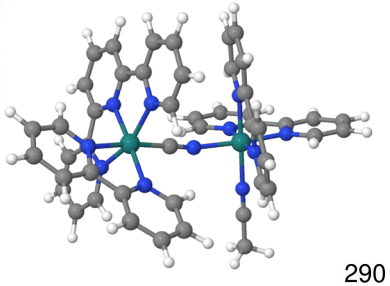

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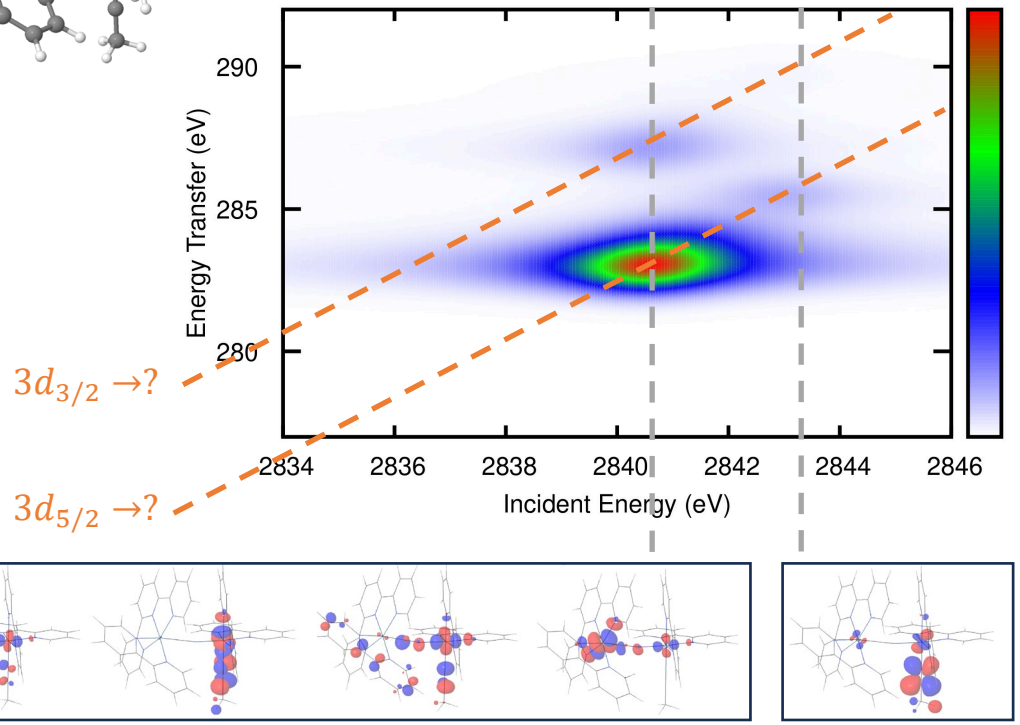
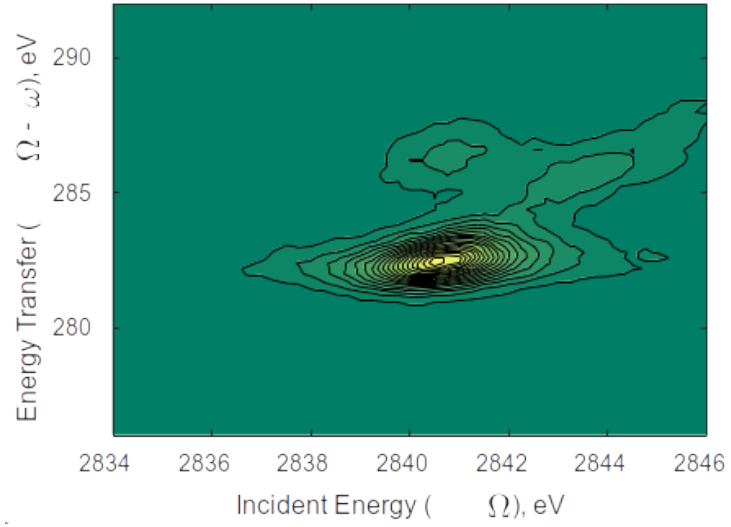


RuDimerACN, Ground State



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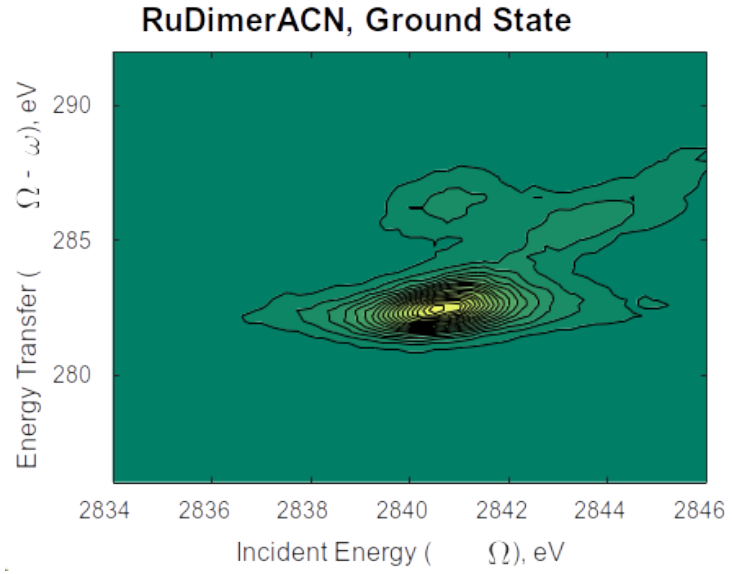
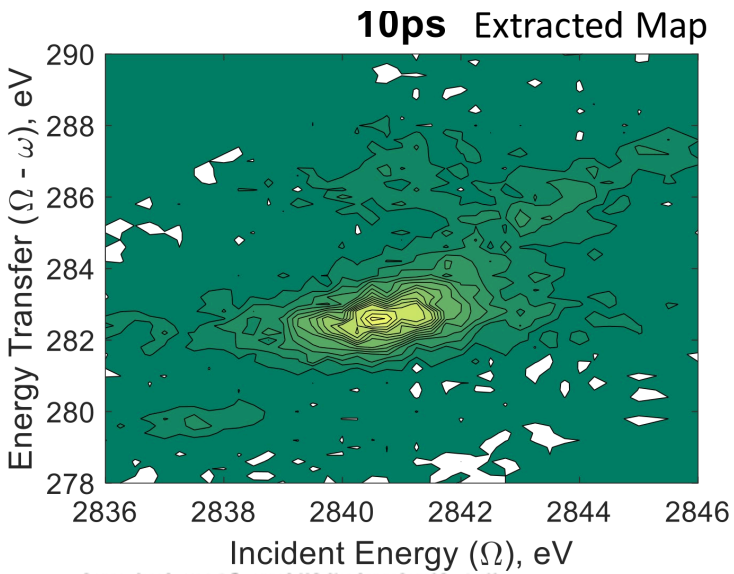
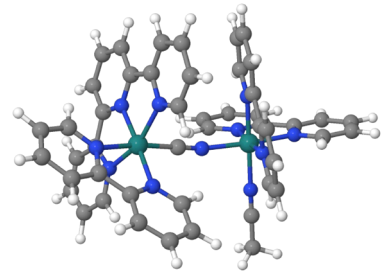
UV Pump/X-ray Probe



UV

$S_0 \rightarrow S_1 \rightarrow T_1$





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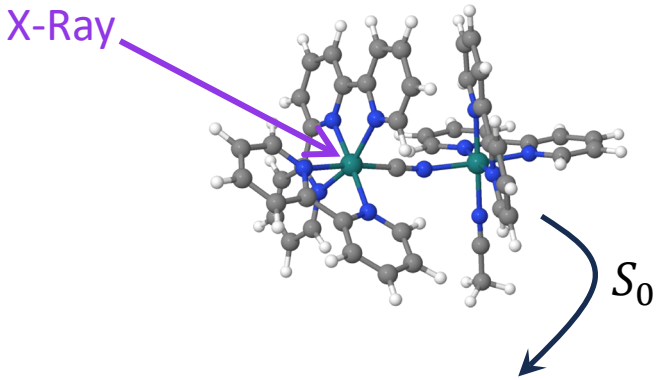

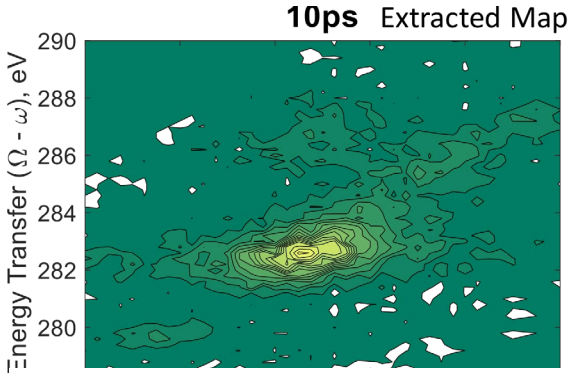

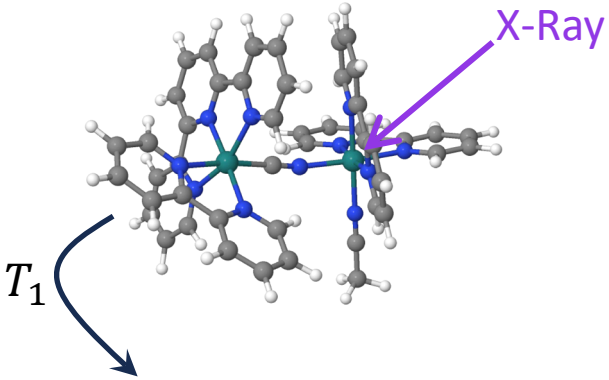

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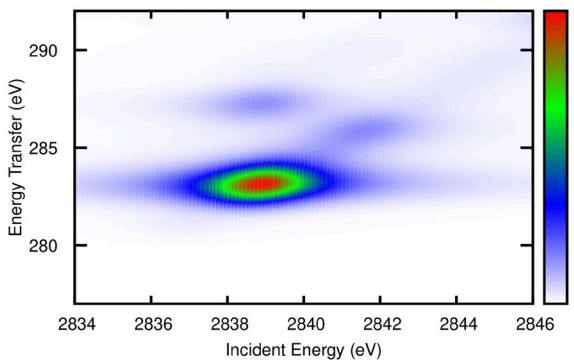

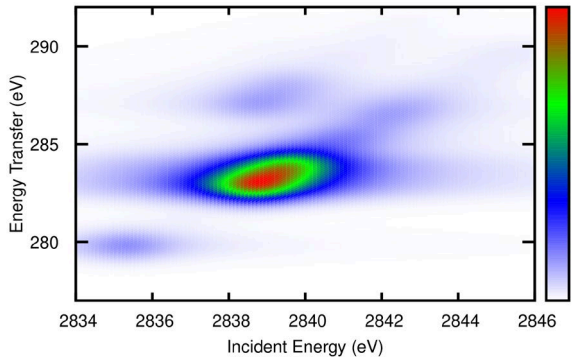

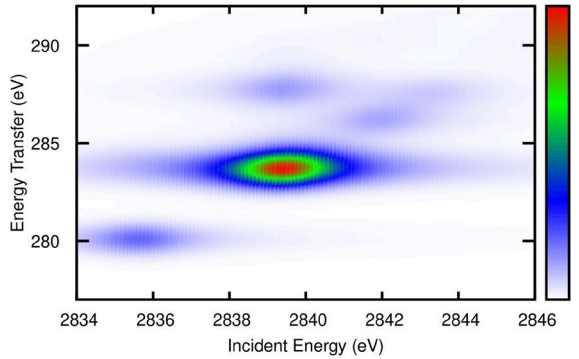

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Concluding Remarks

We developed a cost-effective protocol to simulate RIXS maps of transition metal complexes. The protocol is built on 3 key ideas:

- Excited-state transition moments can be calculated using linear-response TDDFT amplitudes, thus neglecting second-order relaxation effects;
- The exchange-correlation kernel doesn't significantly affect the quality of the simulated spectra, and thus, can be neglected;
- Excited-state spin-orbit couplings can be incorporated for a subset of excited states using an effective ZORA potential and the state-interaction approach;

Experimental RIXS maps are well reproduced by the simulations, and ground-state molecular orbitals can be used to gain qualitative understanding of possible RIXS pathways.

Acknowledgments

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Thank you!