Bethe-Salpeter Equation Calculations of Resonant Inelastic X-ray Scattering

---

John Vinson
exciting NEWS 2021

National Institute of
Standards and Technology
U.S. Department of Commerce

Disclaimers

- Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

- These opinions, recommendations, findings, and conclusions do not necessarily reflect the views or policies of NIST or the United States Government.

OCEAN

- www.ocean-code.com
  - BSE code for optical/UV and x-ray absorption, emission, and scattering
  - PRB **83**, 11506 (2011); Comp. Phys. Comm. **197**, 109 (2015); arXiv/2005.07834
  - Keith Gilmore, Josh Kas, Yufeng Liang, Das Pemmaraju, David Prendergast, John Rehr, Eric Shirley, Fernando Vila, and John Vinson
- External pseudopotential DFT foundation
  - ABINIT or QuantumESPRESSO
- Should be equivalent to exciting

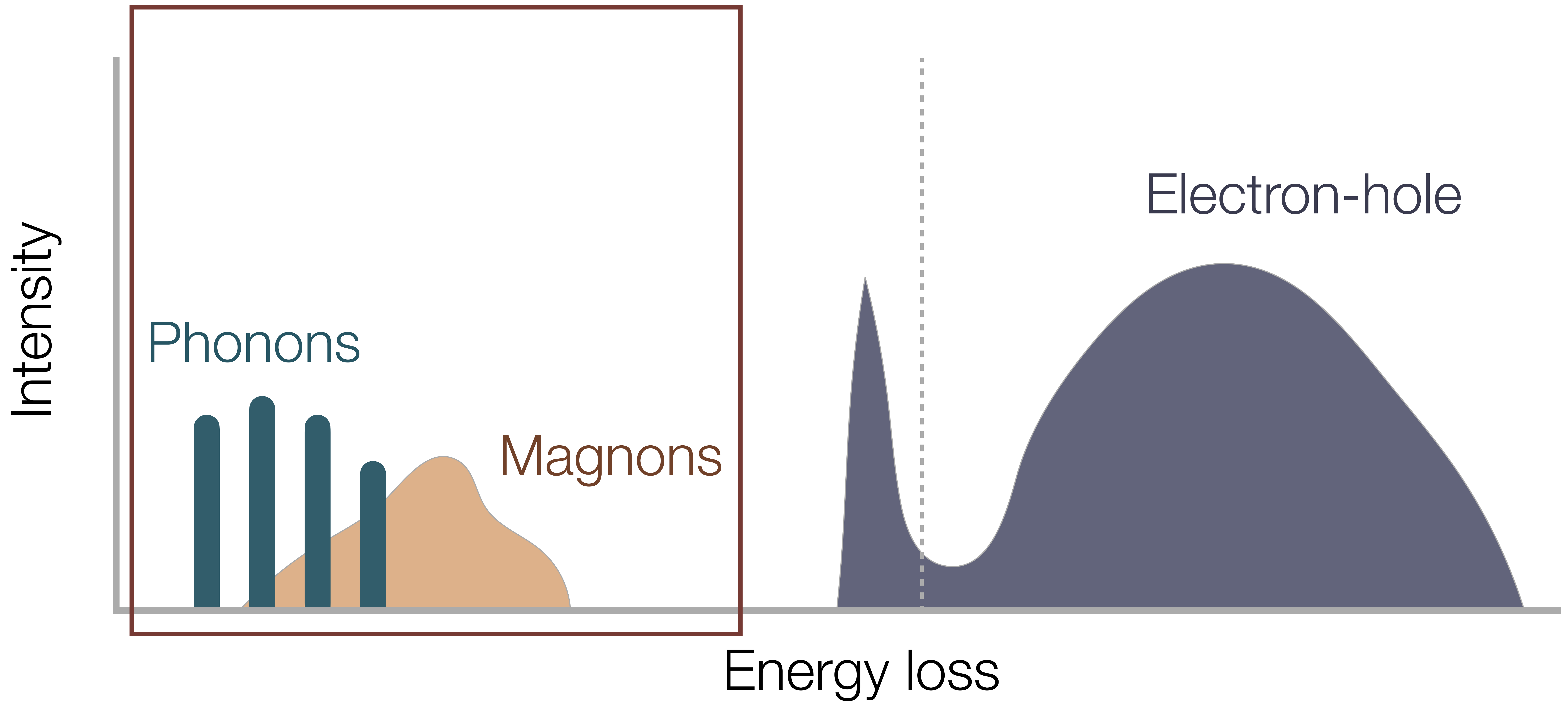
Outline

- What is RIXS?
- How do we calculate it?
- Examples
- Missing pieces and future work

Resonant Inelastic X-ray Scattering

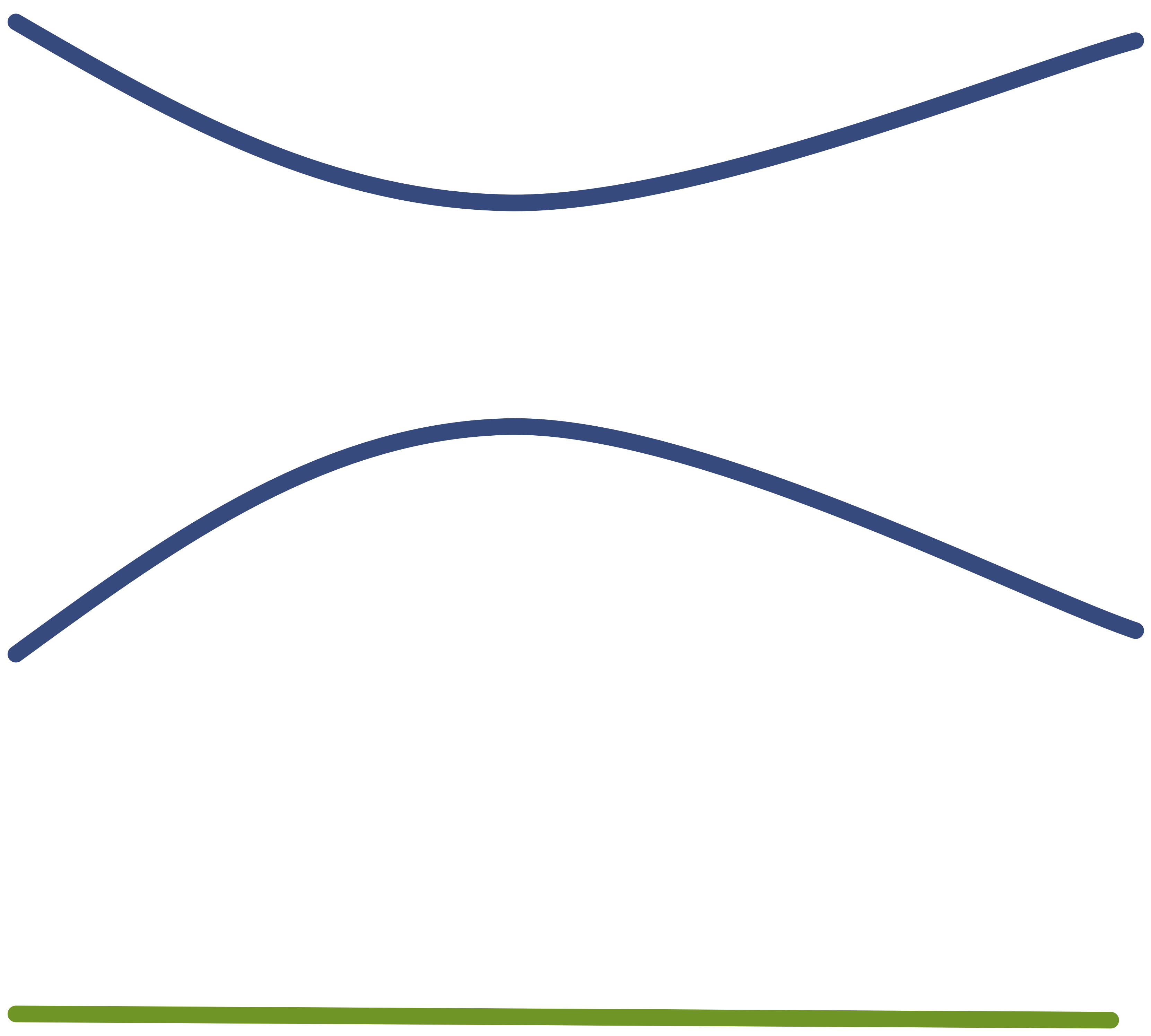
- X-ray — 100 eV to 100 keV
- Scattering — X-ray in — X-ray out
- Resonant — Tuned near a core level
- Inelastic — Energy losses & changes in momentum

RIXS Excitations



Ament *et al.*, Rev. Mod. Phys. **83**, 705 (2011)

Indirect Resonant Inelastic X-ray Scattering

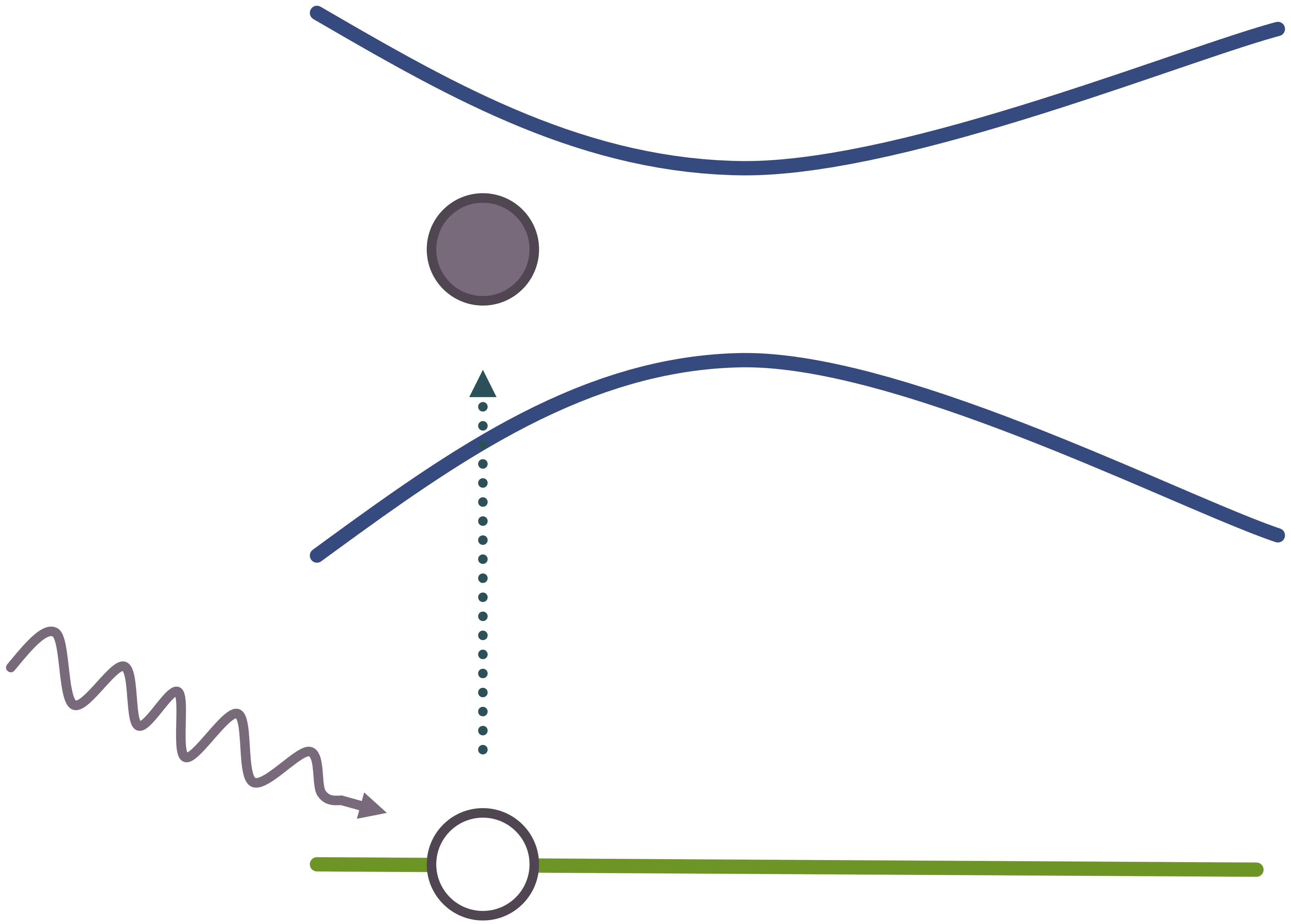


Conduction band

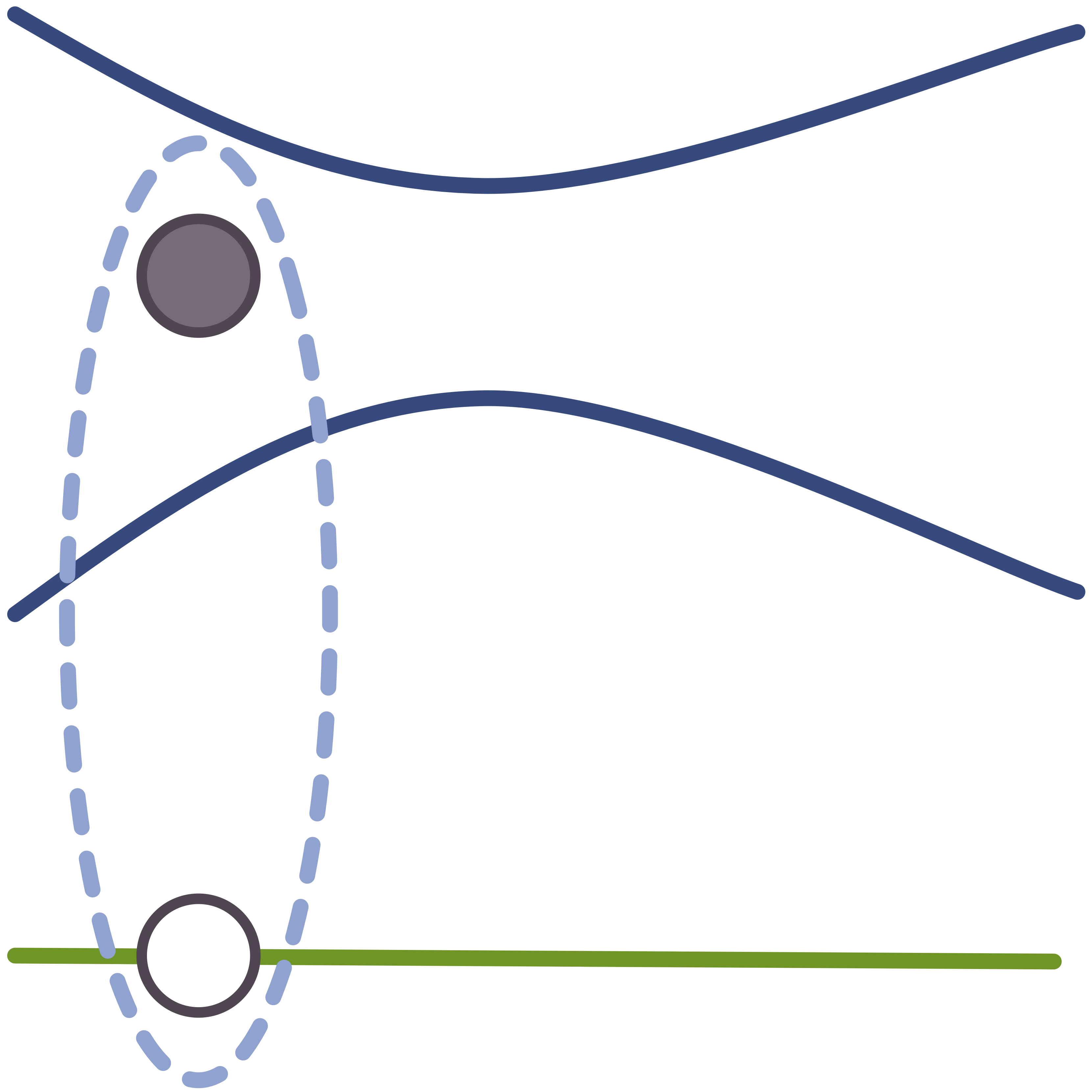
Valence band

Deep core

Indirect Resonant Inelastic X-ray Scattering

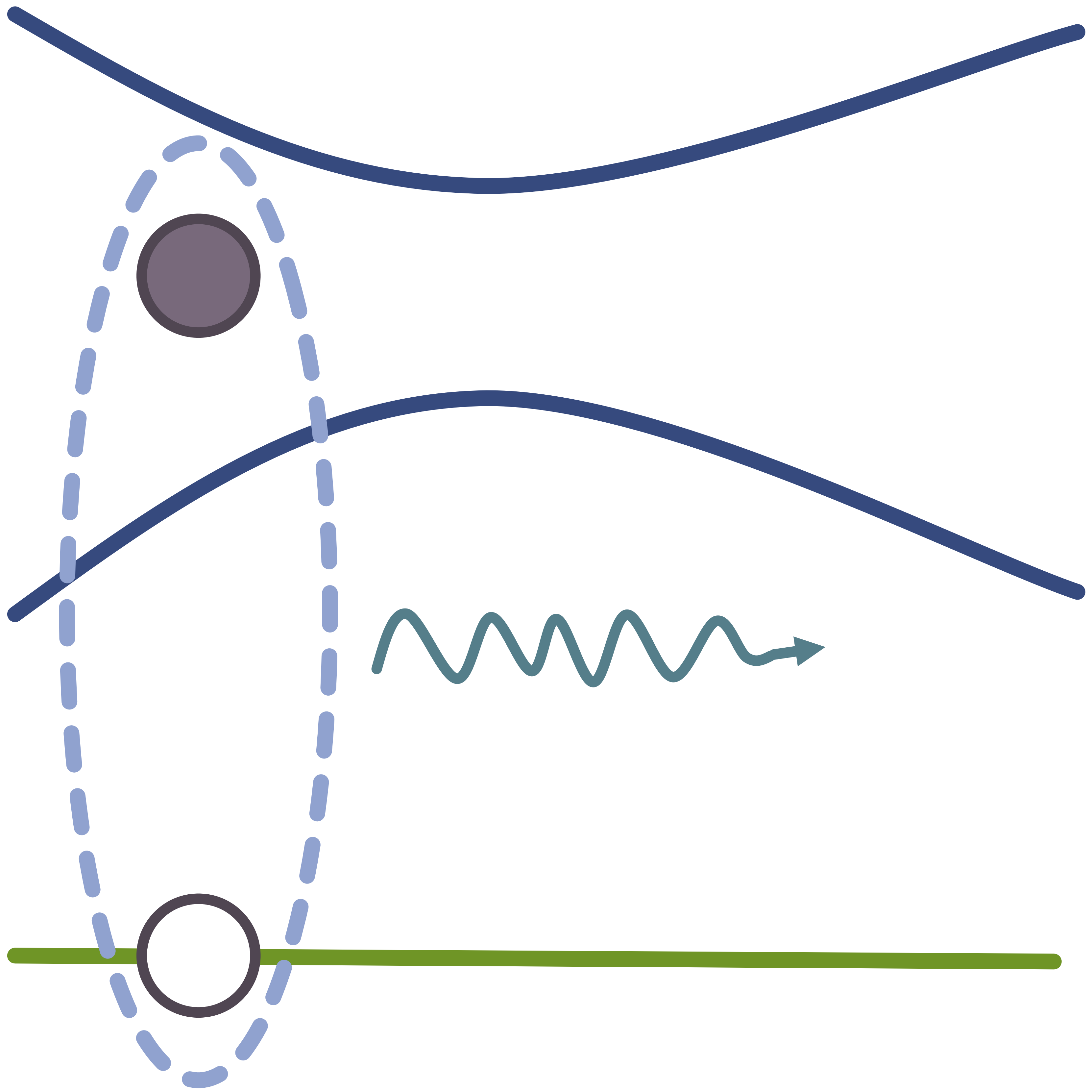


Indirect Resonant Inelastic X-ray Scattering



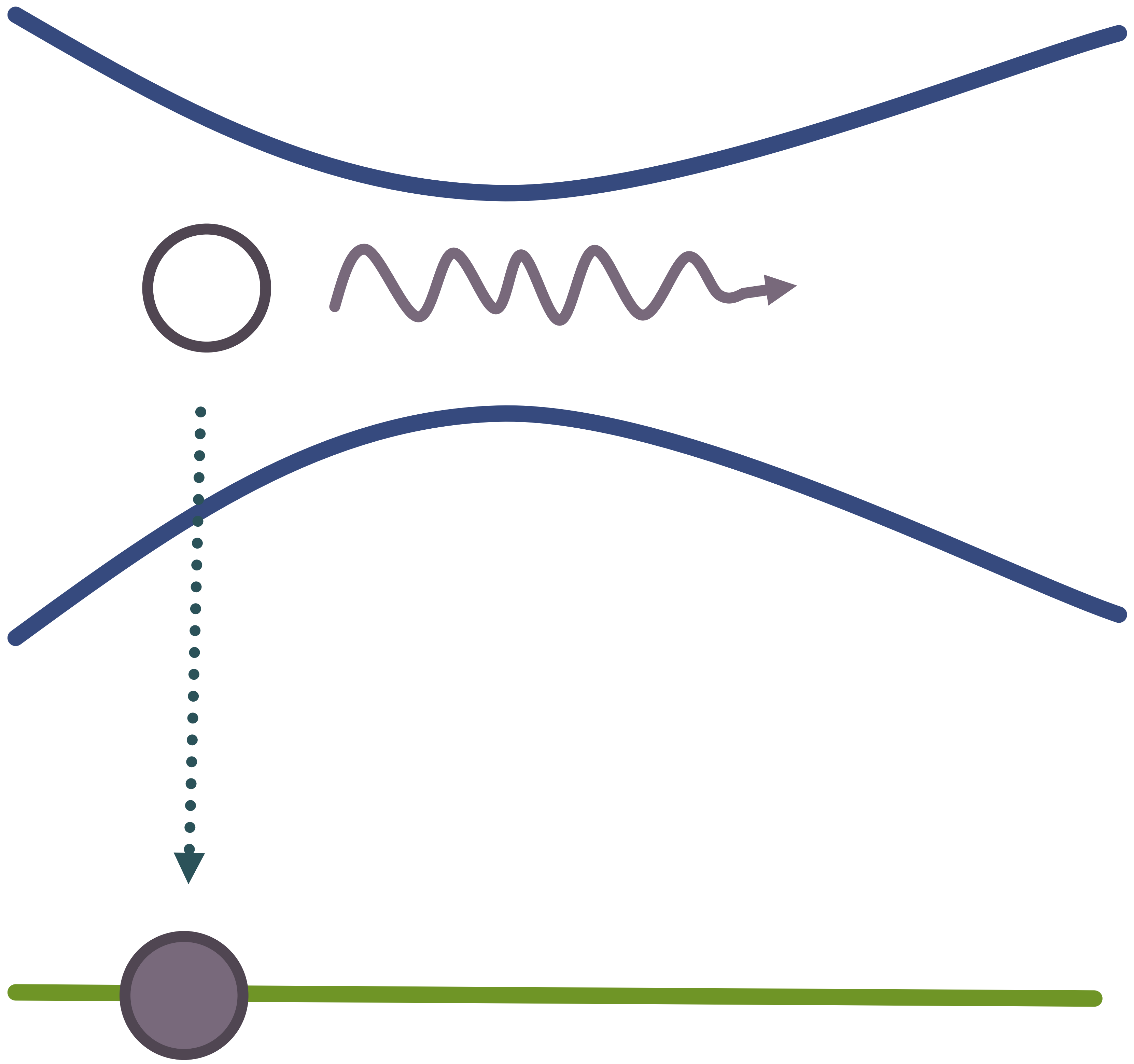
- Excitation into short-lived virtual state

Indirect Resonant Inelastic X-ray Scattering



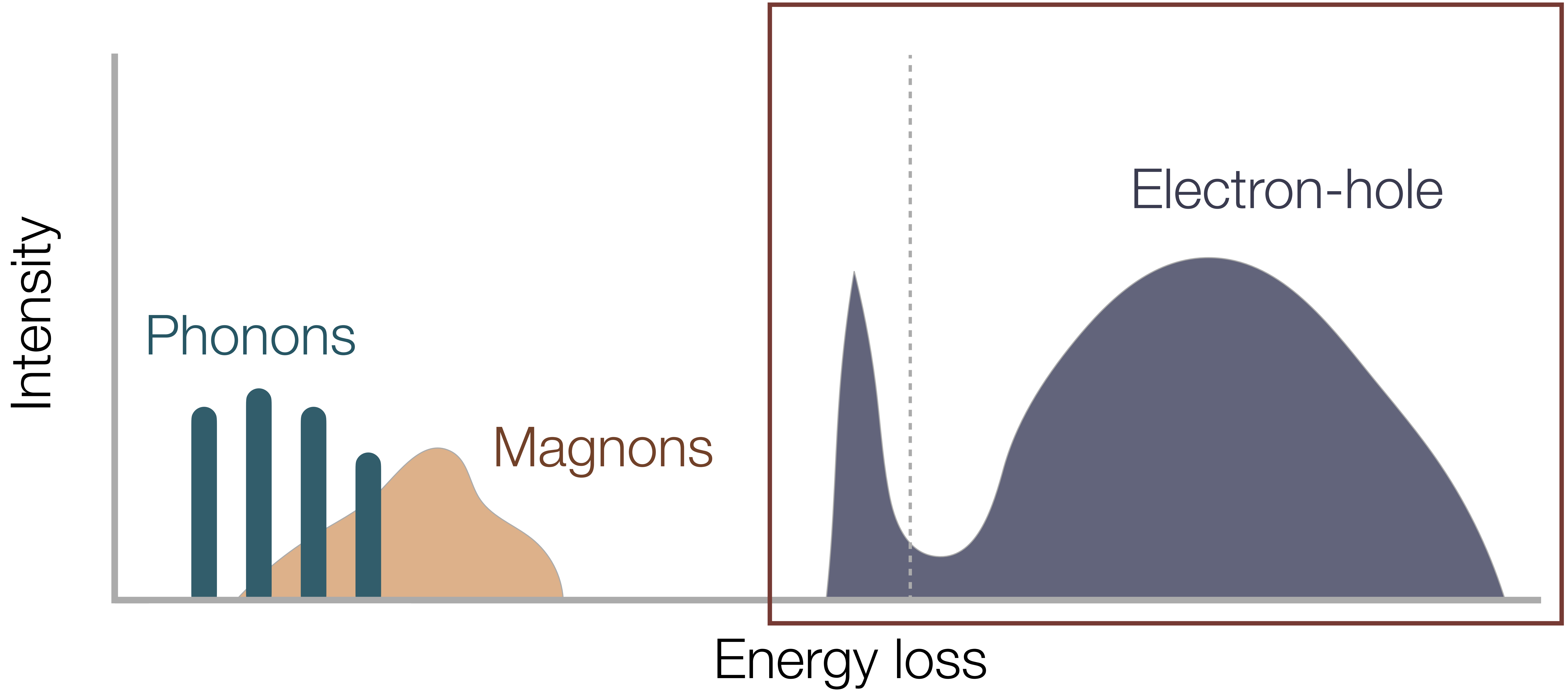
- Excitation into short-lived virtual state
- Exciton can create low-energy excitations
  - Phonons
  - Magnons

Indirect Resonant Inelastic X-ray Scattering



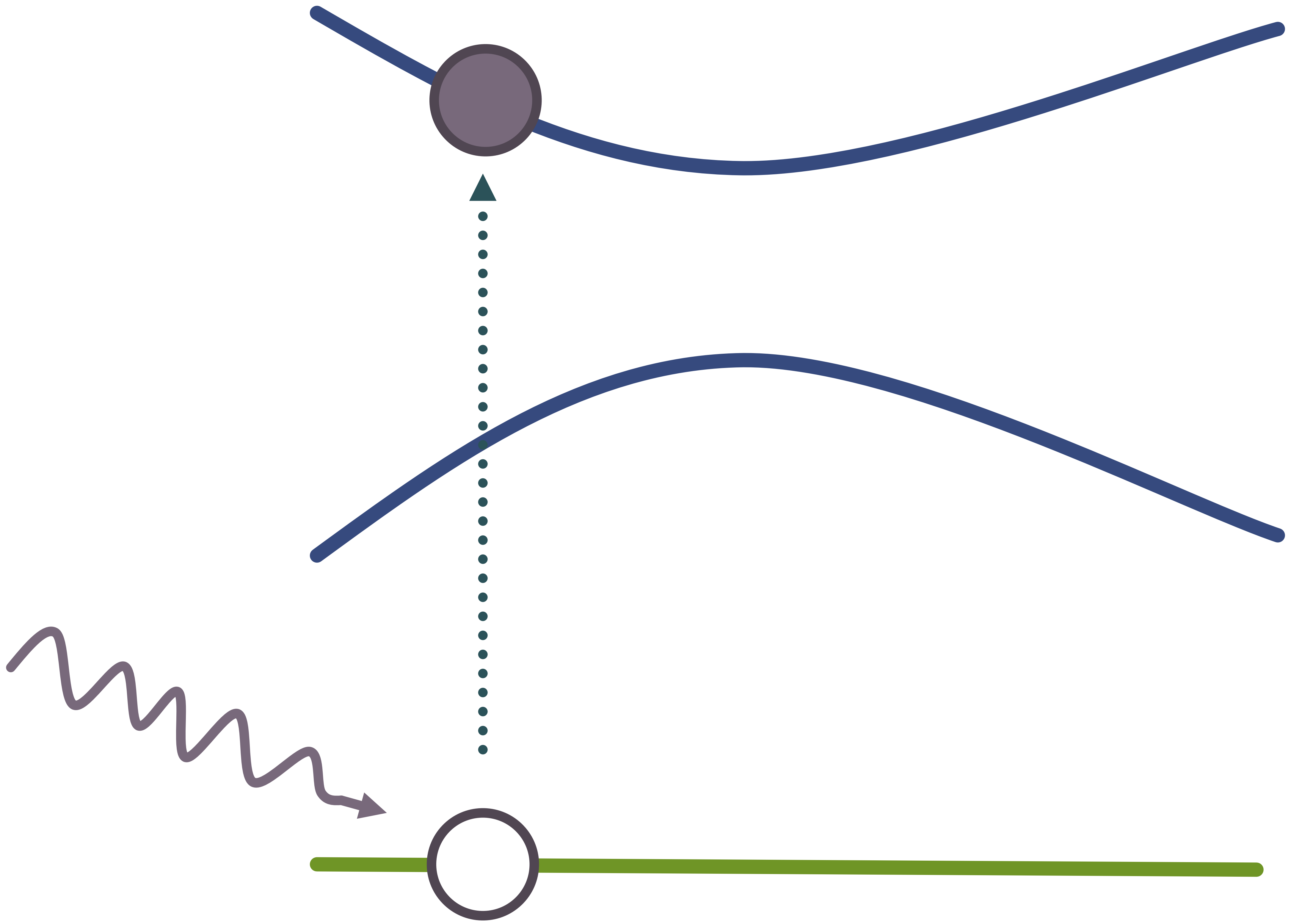
- Excitation into short-lived virtual state
- Exciton can create low-energy excitations
- Measure out-going x-ray
- Energy losses & momentum change due to intermediate-state scattering

RIXS Excitations

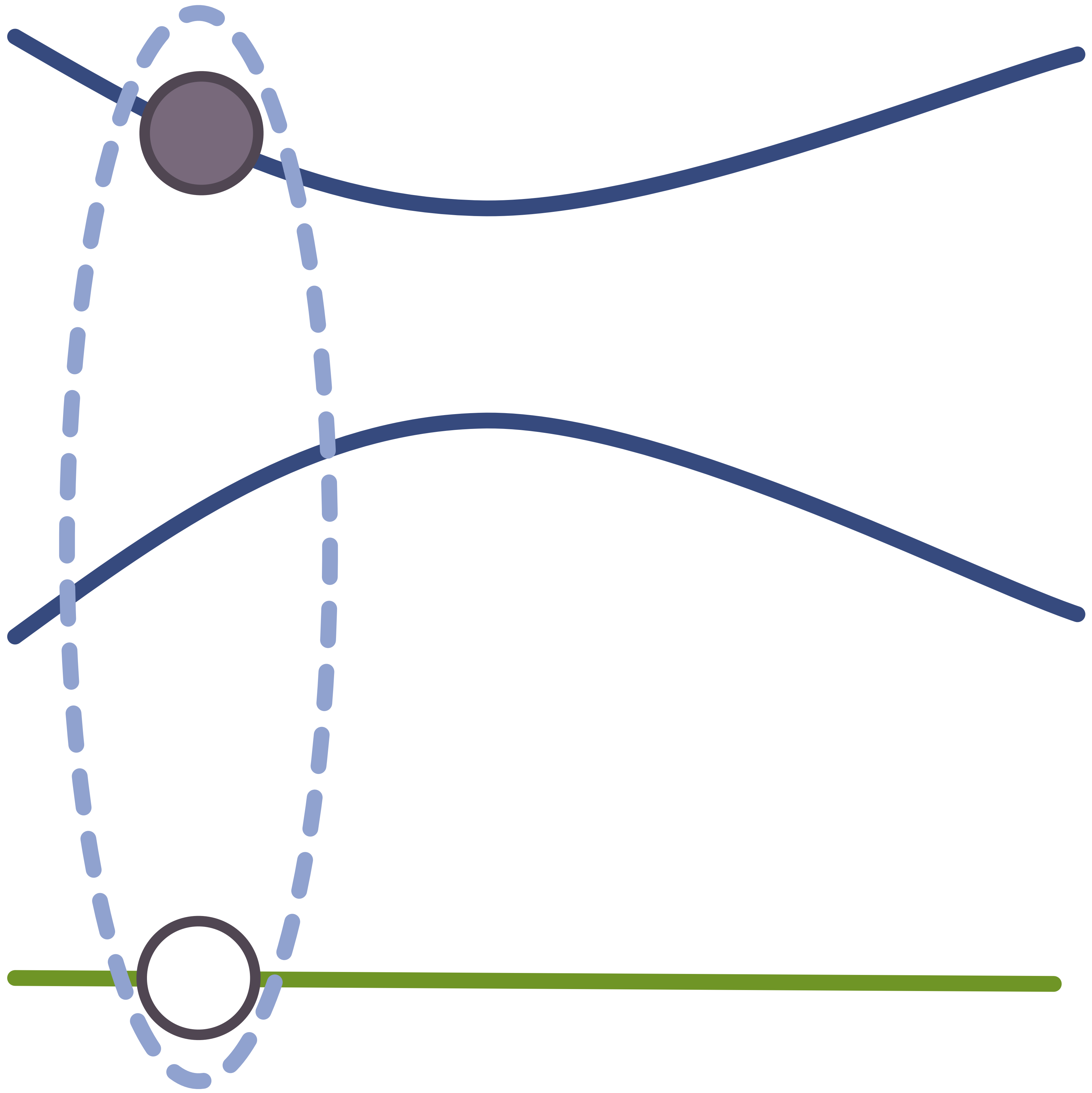


Ament *et al.*, Rev. Mod. Phys. **83**, 705 (2011)

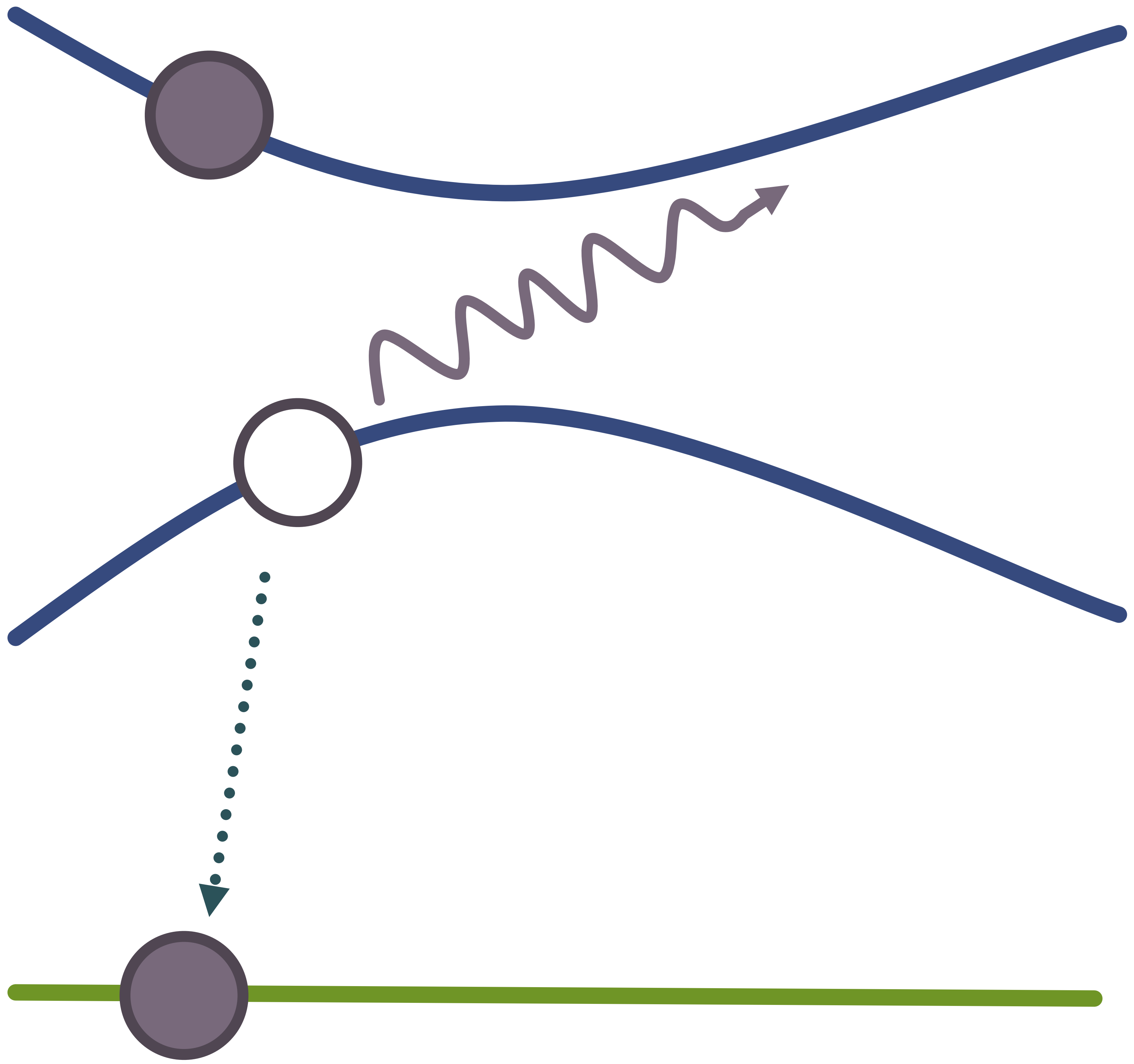
Direct Resonant Inelastic X-ray Scattering



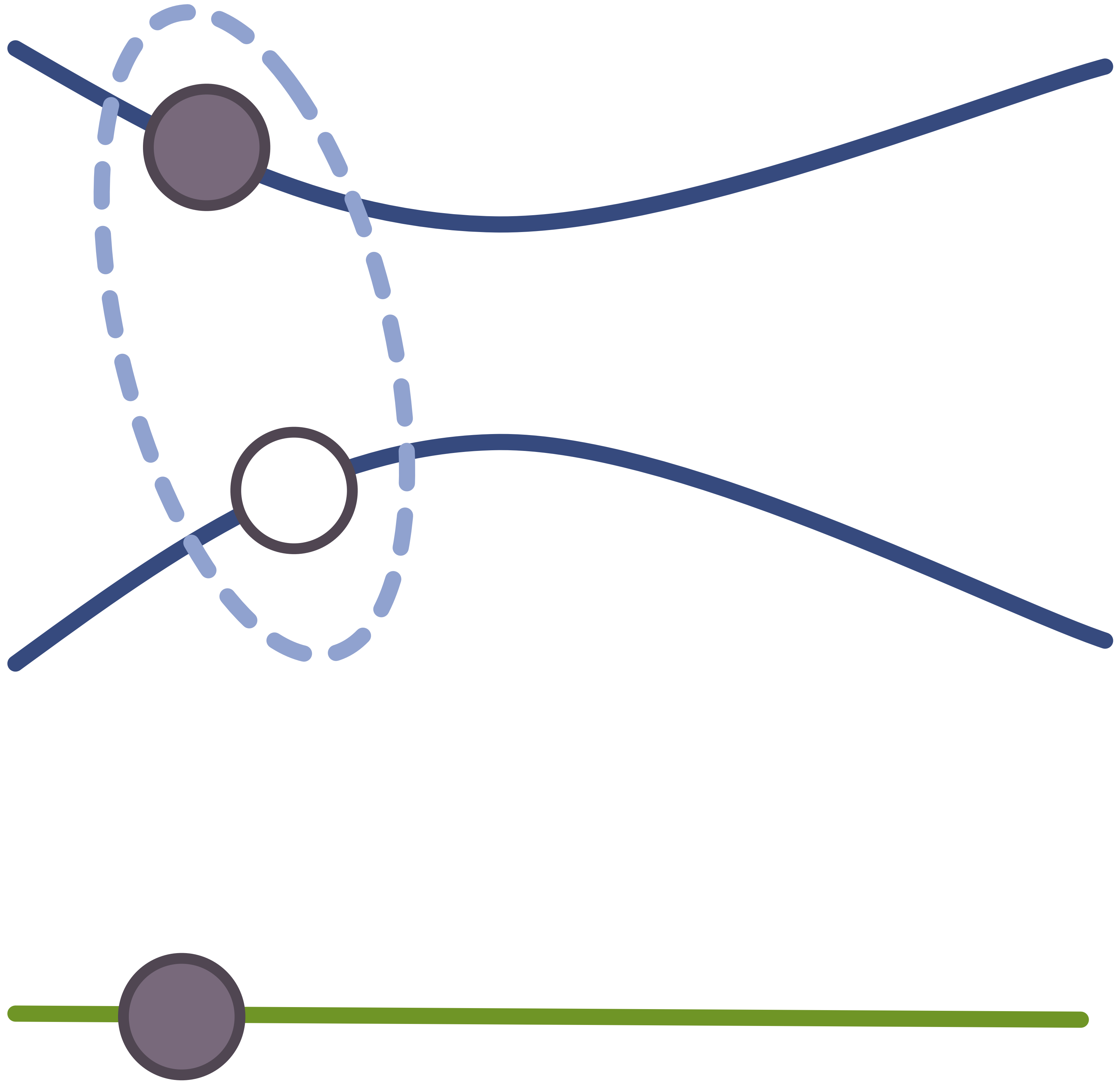
Direct Resonant Inelastic X-ray Scattering



Direct Resonant Inelastic X-ray Scattering

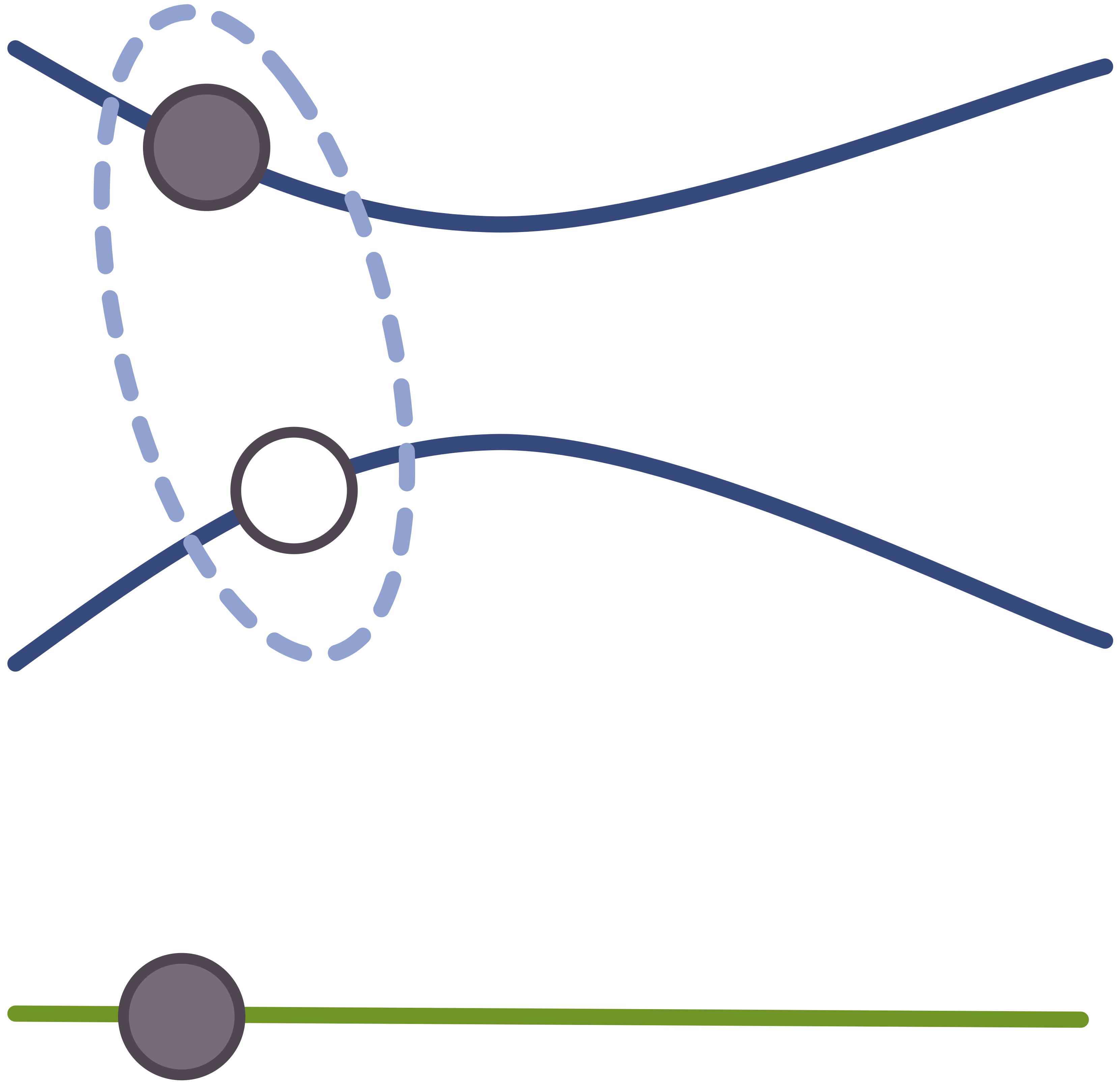


Direct Resonant Inelastic X-ray Scattering



- Measure out-going x-ray
- Energy losses due to band structure & exciton binding
- Transitions constrained
  - X-ray (dipole) selection
  - Nearly zero momentum transfer

Direct Resonant Inelastic X-ray Scattering



- Measure out-going x-ray
- Energy losses due to band structure & exciton binding
- Transitions constrained
- Measure valence and conduction bands

Photon interactions

p . A

Absorption

Photon interactions

p . A

Absorption

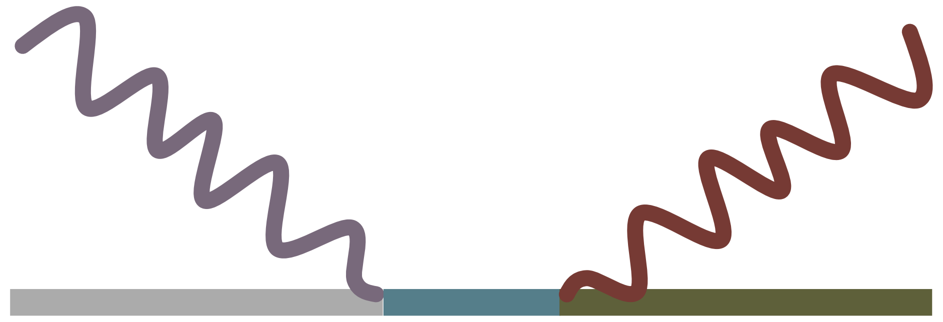
$$\sum_F \left| \langle F | \hat{d}_1 | \Phi_0 \rangle \right|^2 \delta(\omega_1 - \varepsilon_F)$$

Photon interactions

p . A

Absorption

$$\sum_F \left|\langle F|\hat{d}_1|\Phi_0\rangle\right|^2 \delta(\omega_1 - \varepsilon_F)$$



(p . A) G (p . A)

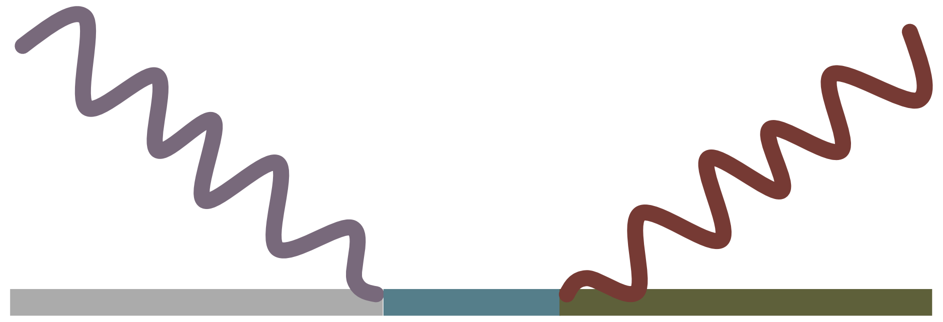
RIXS

Photon interactions

p . A

Absorption

$$\sum_F \left|\langle F|\hat{d}_1|\Phi_0\rangle\right|^2 \delta(\omega_1 - \varepsilon_F)$$



(p . A) G (p . A)

RIXS

$$\sum_F \left|\langle F|\hat{d}_2^\dagger G(\omega)\hat{d}_1|\Phi_0\rangle\right|^2 \delta(\omega_1 - \omega_2 - \varepsilon_F)$$

Review: Calculating Absorption

- $\sum_{F} \left| \langle F | \hat{d}_1 | \Phi_0 \rangle \right|^2 \delta(\omega_1 - \varepsilon_F)$
- d_1 excites single electron
- *F* two-particle excitation (electron + hole)
- Hole and electron states from DFT

Calculating RIXS

- $$\sum_F \left| \langle F | \hat{d}_2^\dagger G(\omega) \hat{d}_1 | \Phi_0 \rangle \right|^2 \delta(\omega_1 - \omega_2 - \varepsilon_F)$$
- Same approximations
- Now d_2 fills core hole, creates valence hole

Change of perspective, sum over final states

$$\sum_F \left| \langle F | \hat{d}_1 | \Phi_0 \rangle \right|^2 \boxed{\delta(\omega_1 - \varepsilon_F)}$$

$$\downarrow$$

$$\pi\delta(\omega_1 - \varepsilon_F) \rightarrow \frac{\eta}{(\omega_1 - \varepsilon_F)^2 + \eta^2} = \mathrm{Im}\left[\frac{1}{\omega_1 - \varepsilon_F - i\eta}\right]$$

$$\sum_F \left| \langle F | \hat{d}_1 | \Phi_0 \rangle \right|^2 \delta(\omega_1 - \varepsilon_F) \propto \mathrm{Im}\left[\sum_F \langle \Phi_0 | \hat{d}_1^\dagger \frac{|F\rangle\langle F|}{\omega_1 - \varepsilon_F - i\eta} \hat{d}_1 | \Phi_0 \rangle\right]$$

$$\propto \mathrm{Im}\left[\langle \Phi_0 | \hat{d}_1^\dagger G(\omega_1) \hat{d}_1 | \Phi_0 \rangle\right]$$

$$G(\omega_1) = \sum_F \frac{|F\rangle\langle F|}{\omega_1 - \varepsilon_F - i\eta} = \frac{1}{\omega_1 - H}$$

Change of perspective, sum over final states

$$\sum_F \left| \langle F|\hat{d}_2^\dagger G(\omega)\hat{d}_1|\Phi_0\rangle \right|^2 \delta(\omega_1 - \omega_2 - \varepsilon_F)$$

$$\propto \sum_F \left| \boxed{\sum_M} \langle F|\hat{d}_2^\dagger \frac{|M\rangle\langle M|}{\boxed{\omega_1 - \varepsilon_M - i\eta}} \hat{d}_1|\Phi_0\rangle \right|^2 \delta(\omega_1 - \omega_2 - \varepsilon_F)$$

- Excitation to M resonant with incoming x-ray
- Interference between states M

$$\propto \sum_{MM'F} \mathrm{Im}\left[\langle\Phi_0|\hat{d}_1^\dagger \frac{|M\rangle\langle M|}{\omega_1 - \varepsilon_M - i\eta} \hat{d}_2 \frac{|F\rangle\langle F|}{\omega_1 - \omega_2 - \varepsilon_F - i\gamma} \hat{d}_2^\dagger \frac{|M'\rangle\langle M'|}{\omega_1 - \varepsilon_M - i\eta} \hat{d}_1|\Phi_0\rangle \right]$$

Calculating RIXS with OCEAN

- $\langle \Phi_0 | \hat{d}_1^\dagger \frac{1}{\omega_1 - H^{core}} \hat{d}_2 \frac{1}{\omega_1 - \omega_2 - H^{val}} \hat{d}_2^\dagger \frac{1}{\omega_1 - H^{core}} \hat{d}_1 | \Phi_0 \rangle$

$$x(\omega_1) = \frac{1}{\omega_1 - H^{core}} \hat{d}_1 | \Phi_0 \rangle$$

- Skip matrix diagonalize/inversion

- Use GMRES to solve for $x(\omega_1)$ at a given energy: A x = b
  - $\boxed{(\omega_1 - H^{core})}\boxed{x(\omega_1)} = \boxed{\hat{d}_1 | \Phi_0 \rangle}$
  - Y. Saad and M. Schultz SIAM J. Sci. Stat. Comput. 7, 856 (1986)

Calculating RIXS with OCEAN

- $\langle\Phi_0|\hat{d}_1^\dagger \, \frac{1}{\omega_1 - H^{core}} \, \hat{d}_2 \, \frac{1}{\omega_1 - \omega_2 - H^{val}} \, \hat{d}_2^\dagger \, \frac{1}{\omega_1 - H^{core}} \, \hat{d}_1|\Phi_0\rangle$
  - Use GMRES to solve for $x(\omega_1)$ at a given energy
    - NB! RIXS is coherent. Sum over all absorbing atoms
    - $x(\omega_1) = \frac{1}{\omega_1 - H^{core}}\hat{d}_1|\Phi_0\rangle$
- $\langle x(\omega_1)|\hat{d}_2 \frac{1}{\omega_1 - \omega_2 - H^{val}} \hat{d}_2^\dagger|x(\omega_1)\rangle$
- Now it looks like optical/UV absorption: $\langle\Phi_0|\hat{d}_1^\dagger G(\omega_1)\hat{d}_1|\Phi_0\rangle$

Calculating RIXS with OCEAN

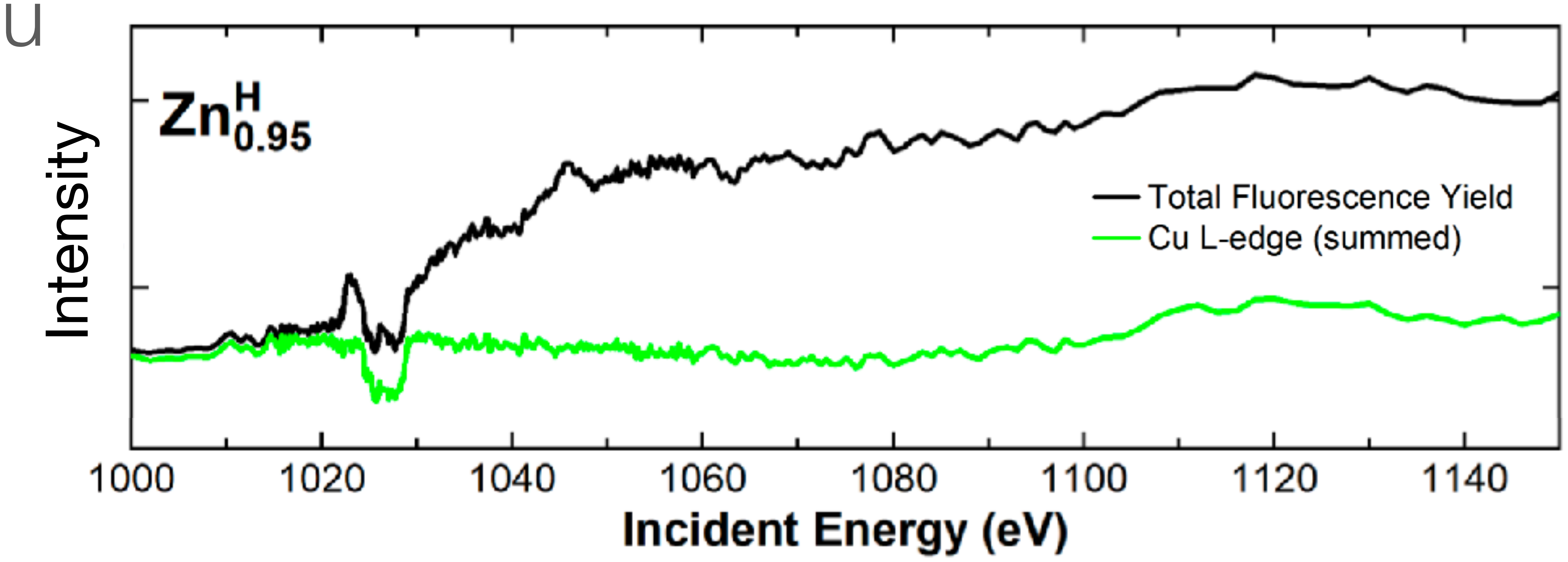
- Calculate XAS excitons $x(\omega_1)$
  - A. A few selected features
  - B. Many closely spaced, i.e., RIXS plane
- For each ω_1 calculate emission using Lanczos/Haydock
  - $\langle x(\omega_1)|\hat{d}_2 \frac{1}{\omega_1 - \omega_2 - H^{val}} \hat{d}_2^\dagger |x(\omega_1)\rangle$
  - Function of energy loss: $\omega_1 - \omega_2$
- exciting also calculates RIXS, just different method

Outline

- What is RIXS? How do we calculate it?
- Examples
    - **Zn dopants Cu-rich minerals**
    - Fingerprints of oxygen oxidation
    - Phonon disorder
    - Many-body self-energy corrections
- Missing pieces and future work

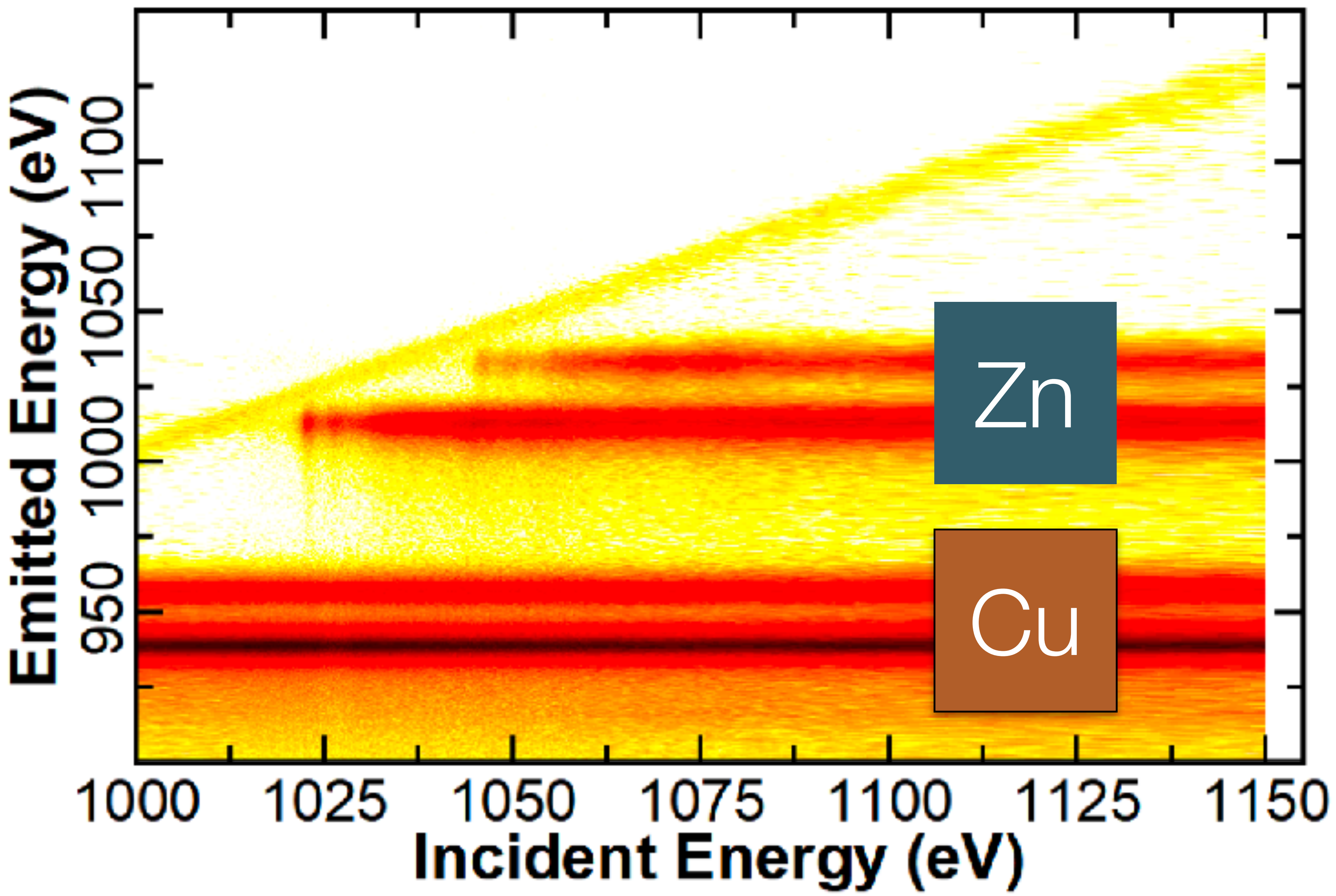
Zn dopants in Quantum Spin Liquid candidates

- Rebecca Smaha, *et al.*, PR Materials **4**, 124406 (2020)
- Zn-Barlowite $Cu_3Zn_xCu_{1-x}(OH)_6FBr$ x=0.95
- Herbertsmithite $Cu_3Zn(OH)_6Cl_2$
- Interested in Zn, but too much Cu for Zn L-edge XAS



Zn dopants in Quantum Spin Liquid candidates

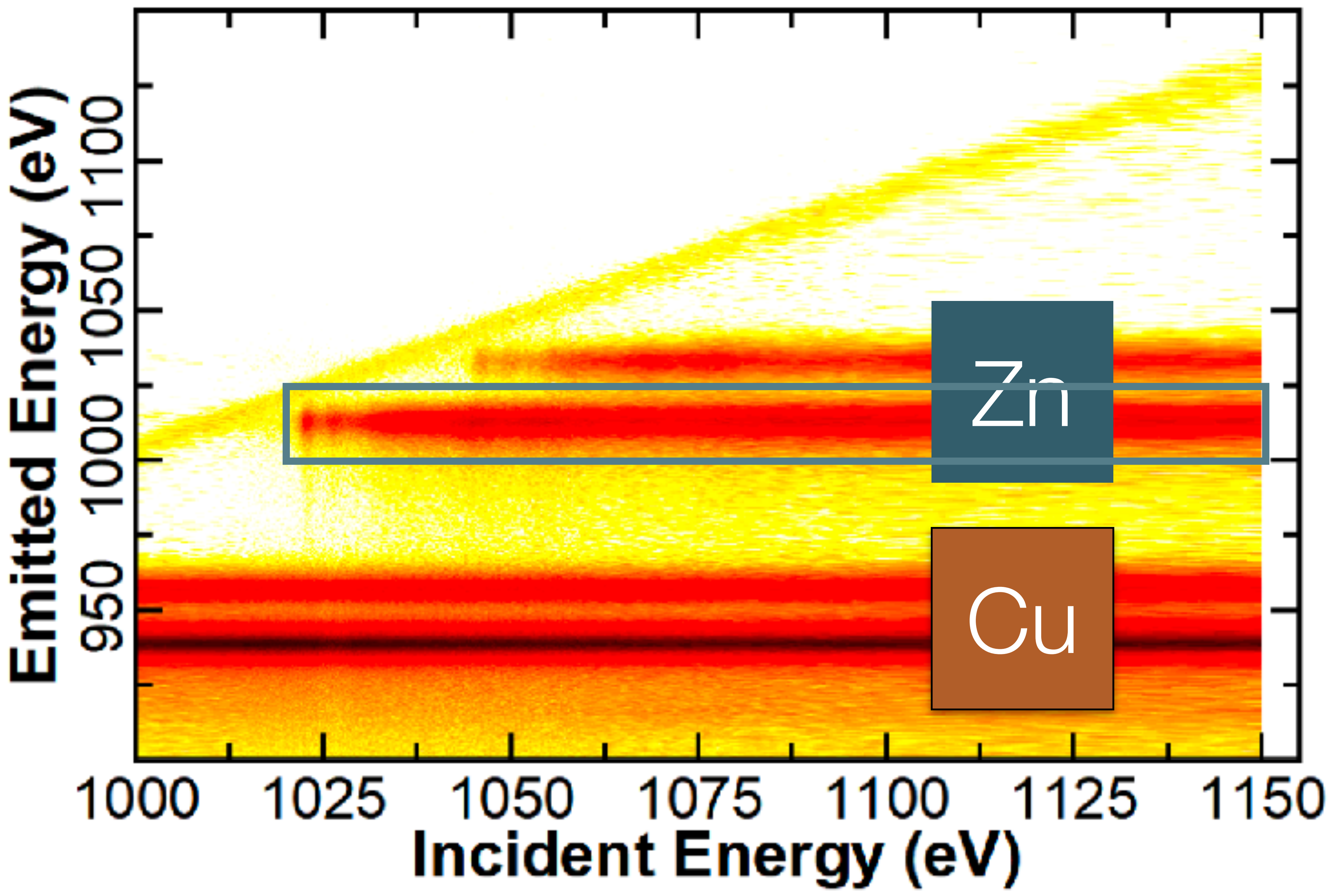
- Turn to RIXS
- Used Transition Edge Sensors
  - Huge energy acceptance (100s of eV)
  - Moderate energy resolution (1-2 eV)
  - Rev. Sci. Instrum. **90**, 113101 (2019)



PR Materials **4**, 124406 (2020)

Zn dopants in Quantum Spin Liquid candidates

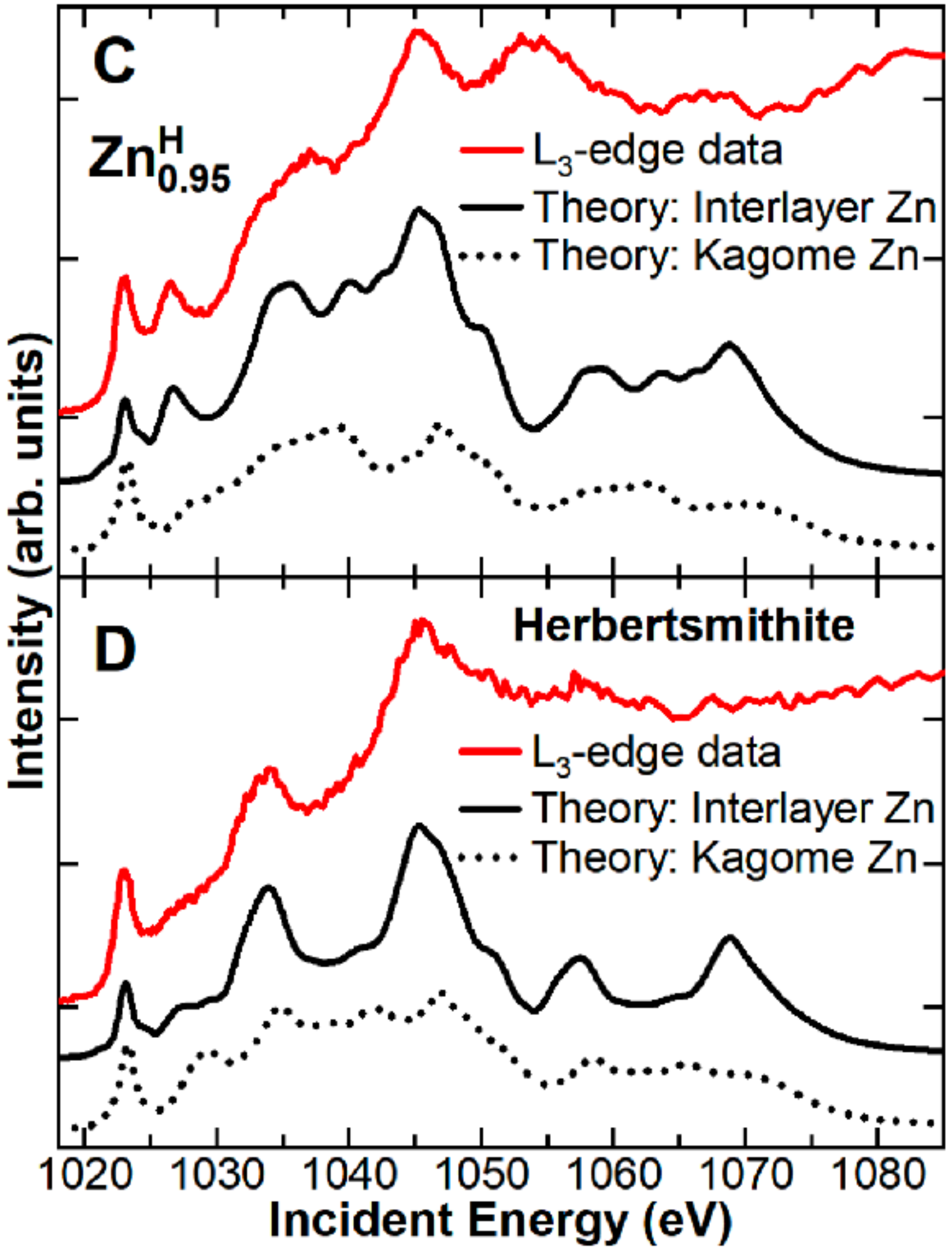
- Turn to RIXS
- Used Transition Edge Sensors
- Sum emission from specific element / edge
  - Result is proportional to absorption only at Zn L_3



PR Materials 4, 124406 (2020)

Zn dopants in Quantum Spin Liquid candidates

- Turn to RIXS
- Used Transition Edge Sensors
- Sum emission from specific element / edge
- Compare to standard XAS calculations
  - Check possible structures
  - Zn is sitting on interlayer sites



PR Materials 4, 124406 (2020)

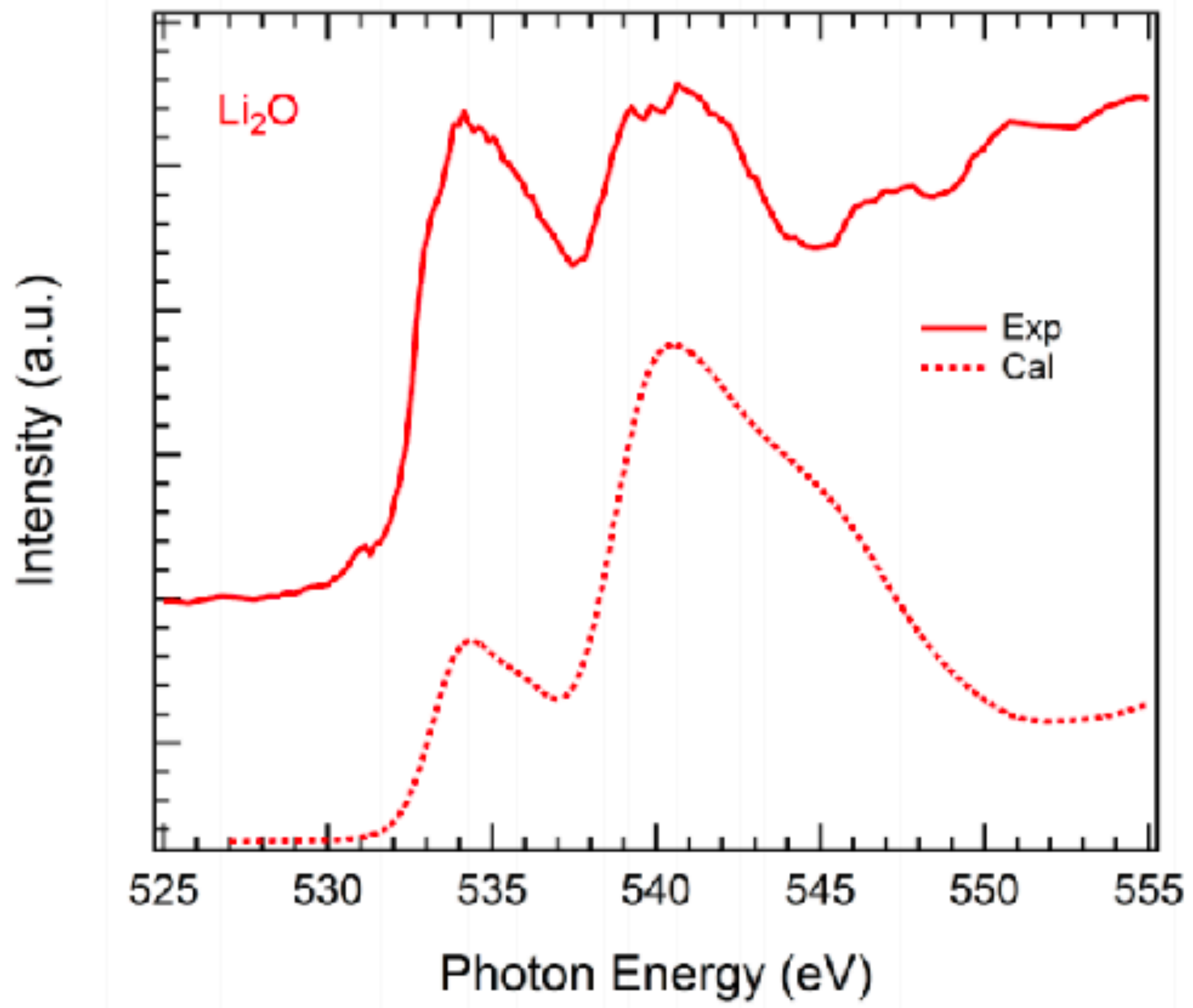
Outline

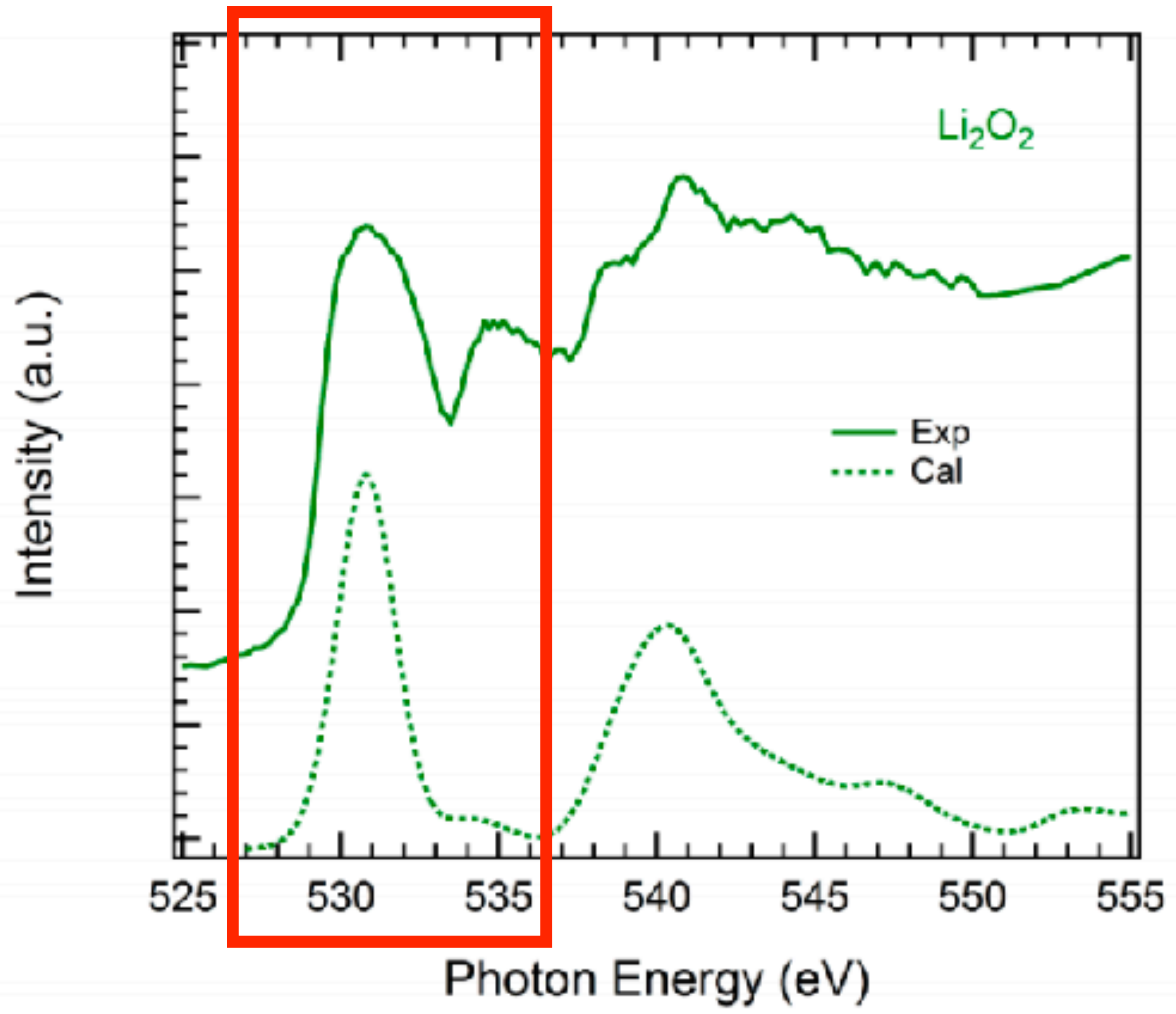
- What is RIXS? How do we calculate it?
- Examples
  - Zn dopants Cu-rich minerals
  - **Fingerprints of oxygen oxidation**
  - Phonon disorder
  - Many-body self-energy corrections
- Missing pieces and future work

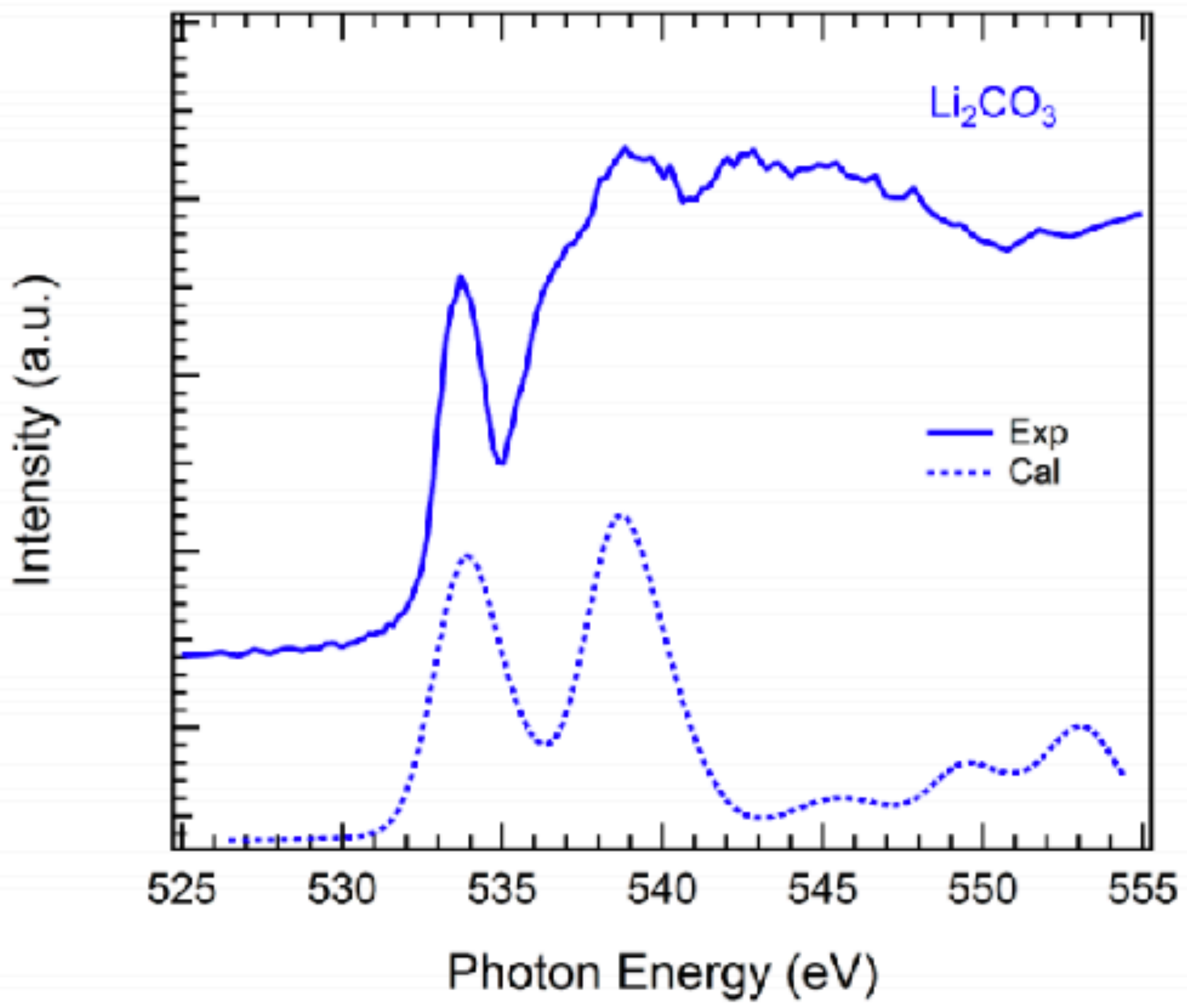
Lithium peroxide Li_2O_2

- Zengqing Zhuo & C. Das Pemmaraju
  - J. Phys. Chem. Lett. **9**, 6378–6384 (2018)
- Battery design
  - Store/use maximum charge
  - Repeatedly & safely
- Does the oxygen sub-lattice participate in redox?
  - How can we tell?

X-ray absorption



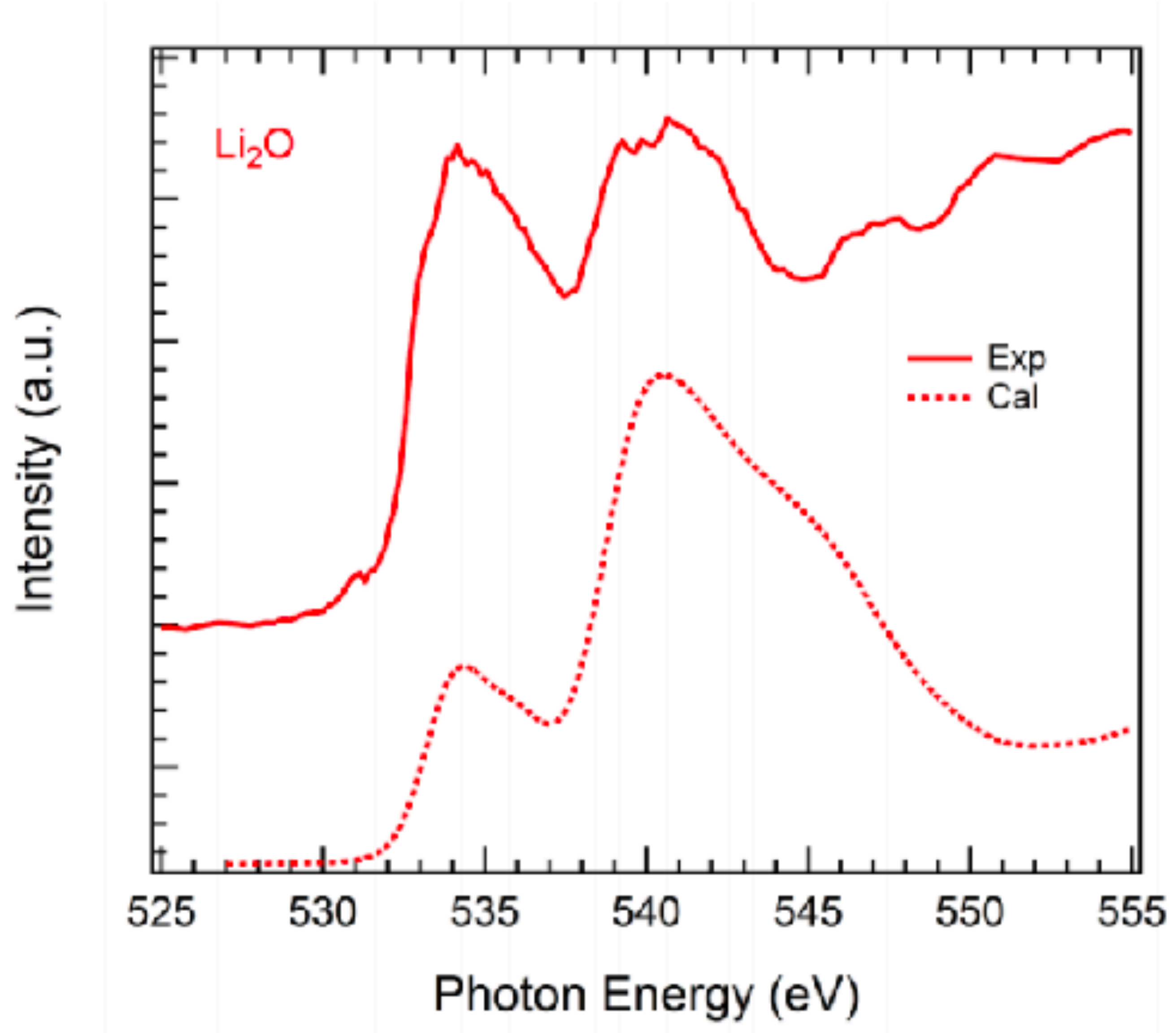


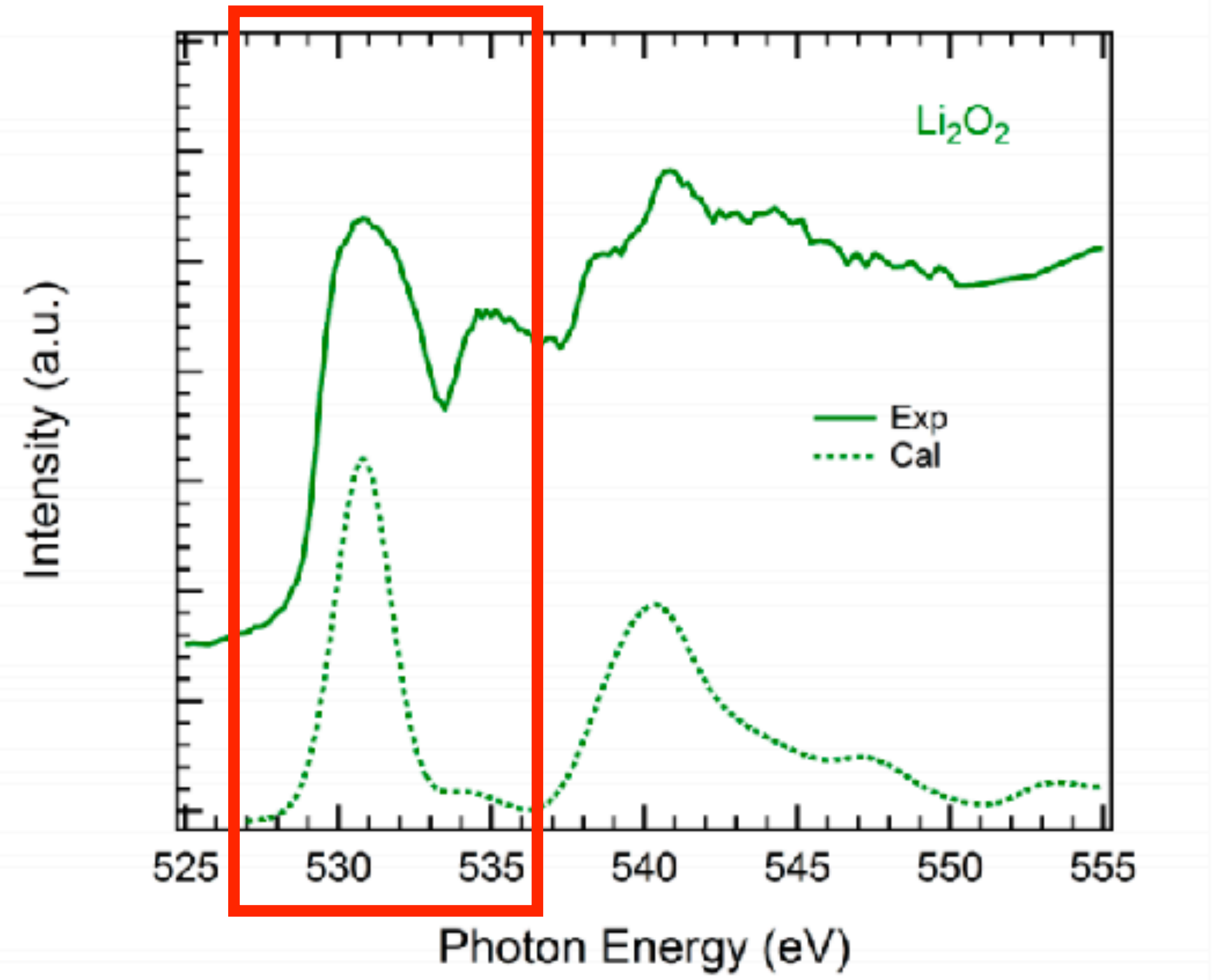


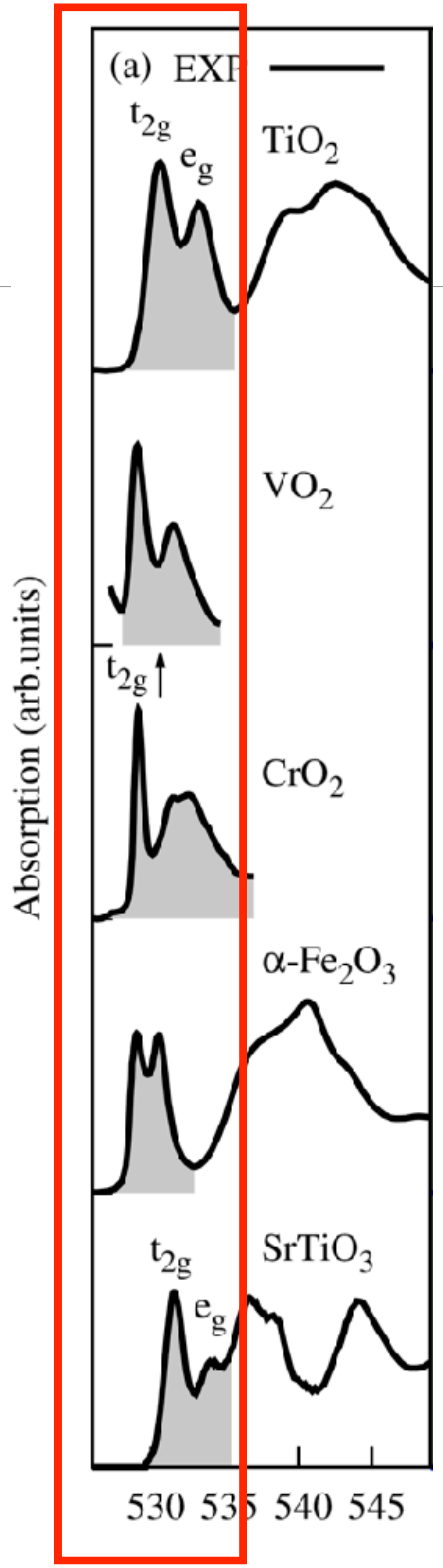
- Clear red-shift, sign of oxidation

J. Phys. Chem. Lett. **9**, 6378–6384 (2018)

X-ray absorption







- Clear red-shift, sign of oxidation
- Also sign of hybridization with metal 3*d*
  - Figure in Y. Li *et al.*, PRL 118, 096402 (2017);
    See also, de Groot *et al.*, PRB 40, 5715 (1989)

Lithium peroxide Li_2O_2

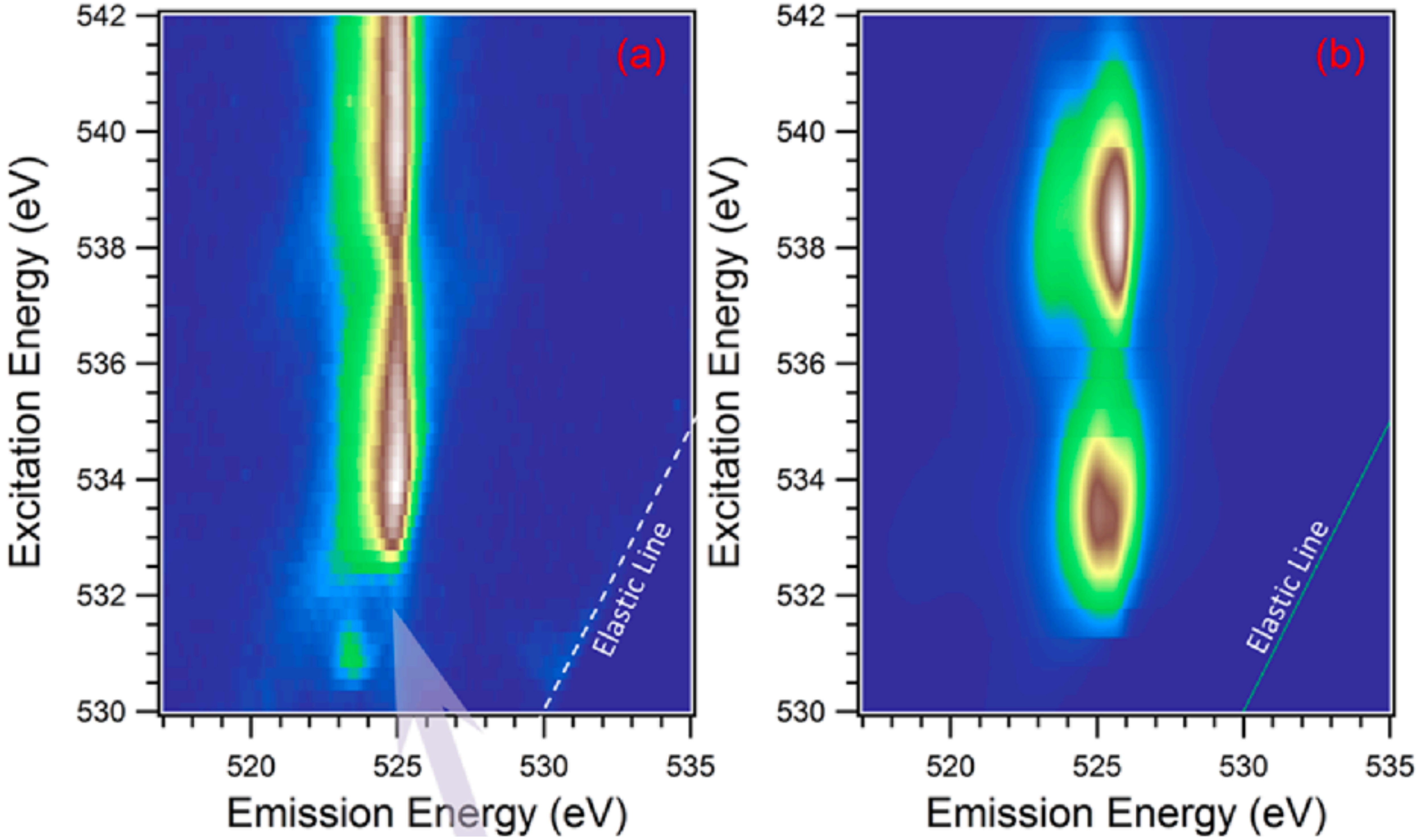
- O K-edge RIXS of Li_2O, Li_2CO_3, and Li_2O_2
  - 2*p* hole – n*p* electron
- Divalent oxygen has a closed shell
  - Lowest absorption into 3*p*-like states

Lithium peroxide Li_2O_2

- O K-edge RIXS of Li_2O, Li_2CO_3, and Li_2O_2
  - 2*p* hole – n*p* electron
- Divalent oxygen has a closed shell
- In peroxide the 2*p* isn’t filled
  - 2*p* hole – 2*p* electron
  - Conjecture: more localized – stronger exciton binding

Li_2O RIXS

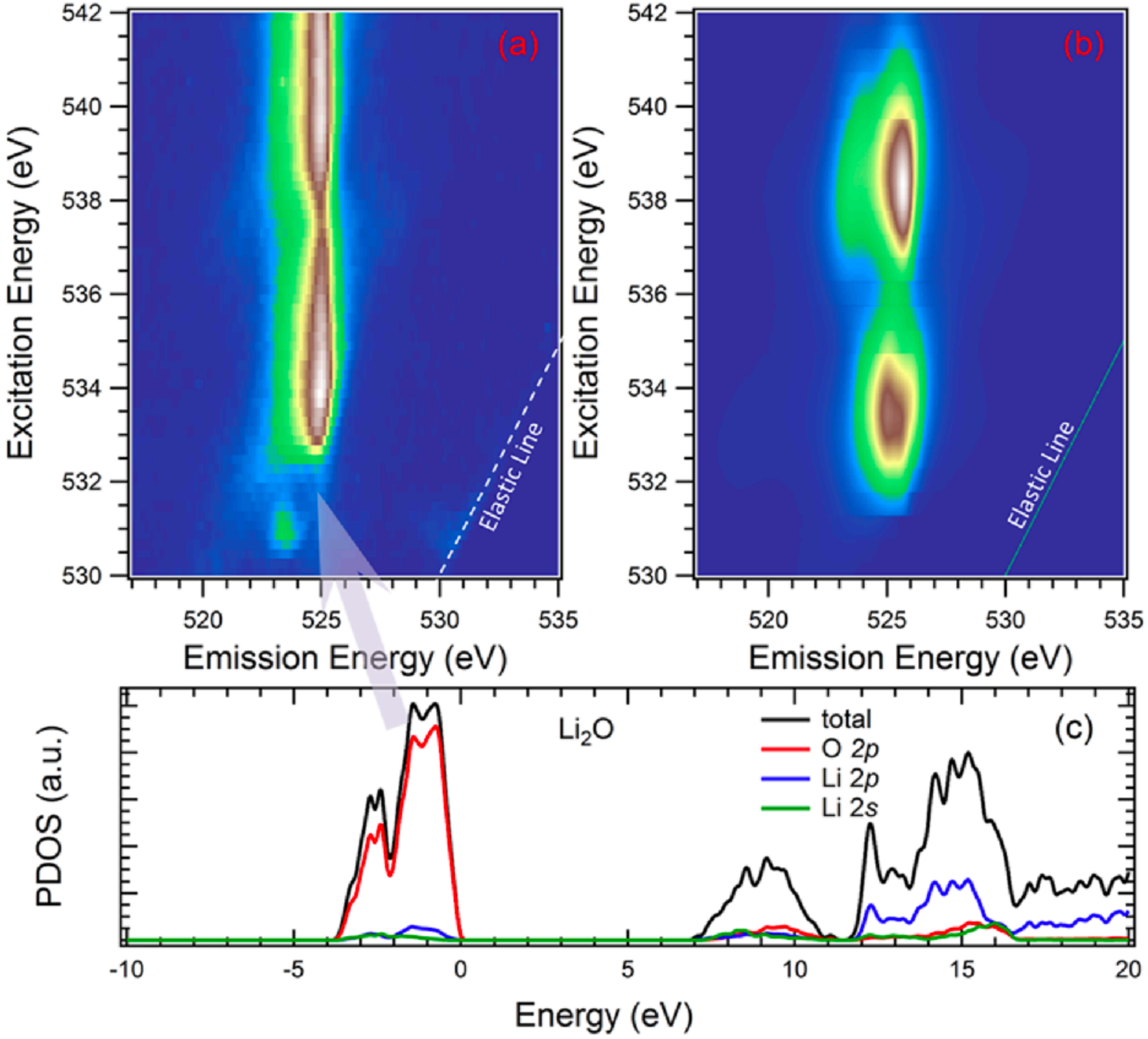
- Single emission feature



J. Phys. Chem. Lett. **9**, 6378–6384 (2018)

Li_2O RIXS

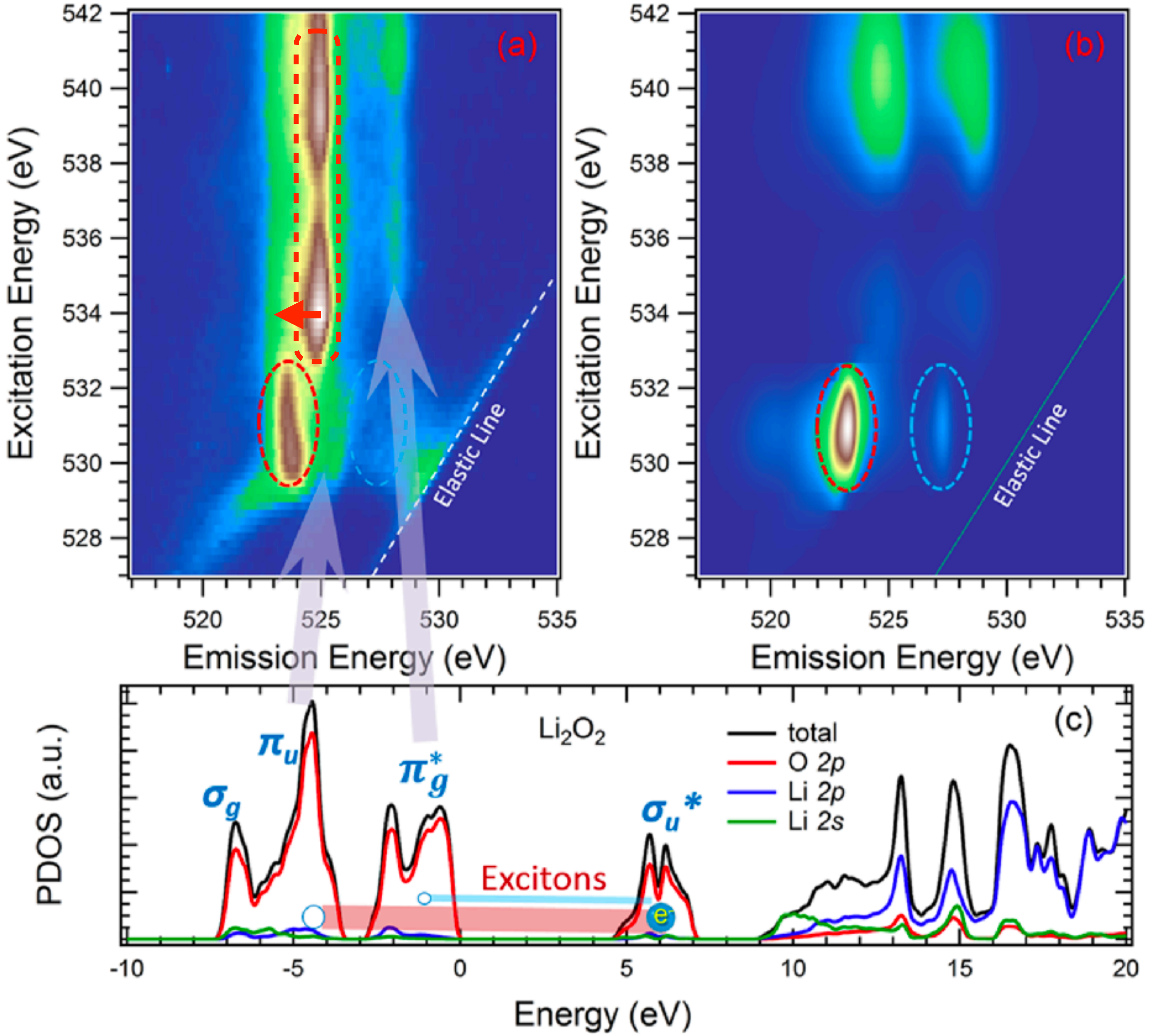
- Single emission feature



J. Phys. Chem. Lett. **9**, 6378–6384 (2018)

Li_2O_2 RIXS

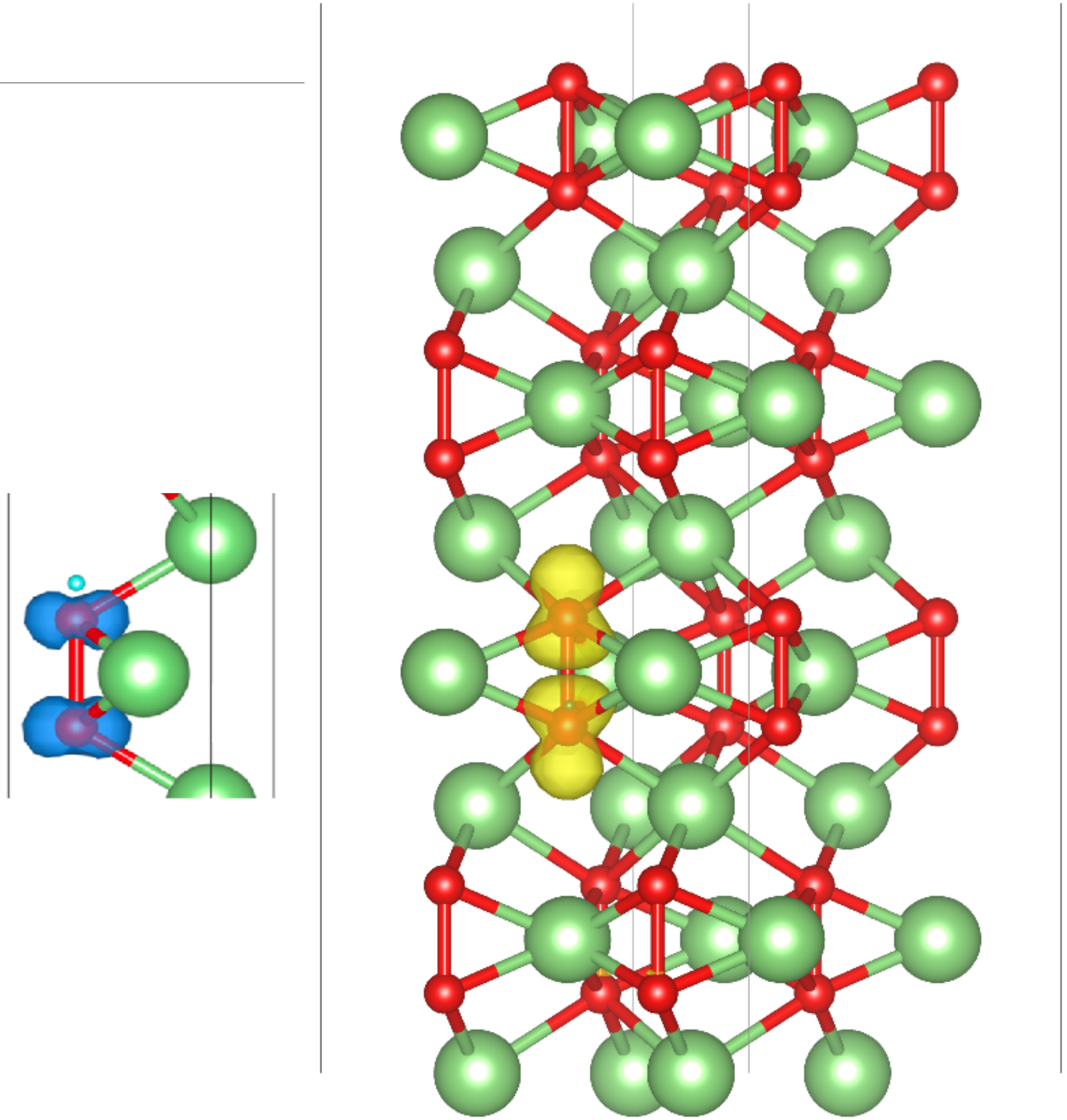
- Double emission feature
- Strong binding at threshold
  - Shift of emission features



J. Phys. Chem. Lett. **9**, 6378–6384 (2018)

Li_2O_2 RIXS

- With computational spectroscopy we can plot out the exciton
    - Electron in yellow
    - Hole in blue
- Highly-localized exciton

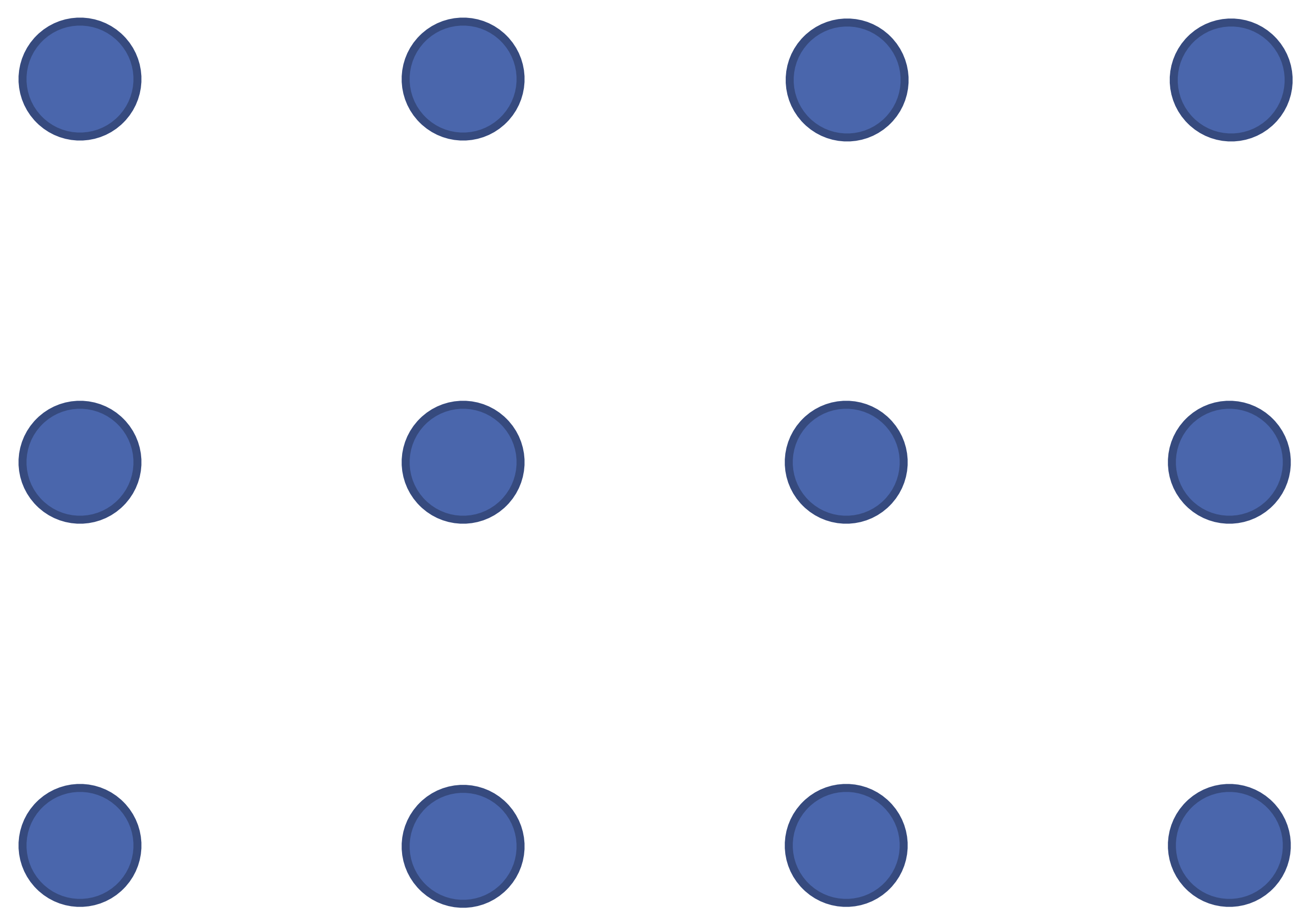


Outline

- What is RIXS? How do we calculate it?
- **Examples**
  - Zn dopants Cu-rich minerals
  - Fingerprints of oxygen oxidation
  - **Phonon disorder**
  - Many-body self-energy corrections
- Missing pieces and future work

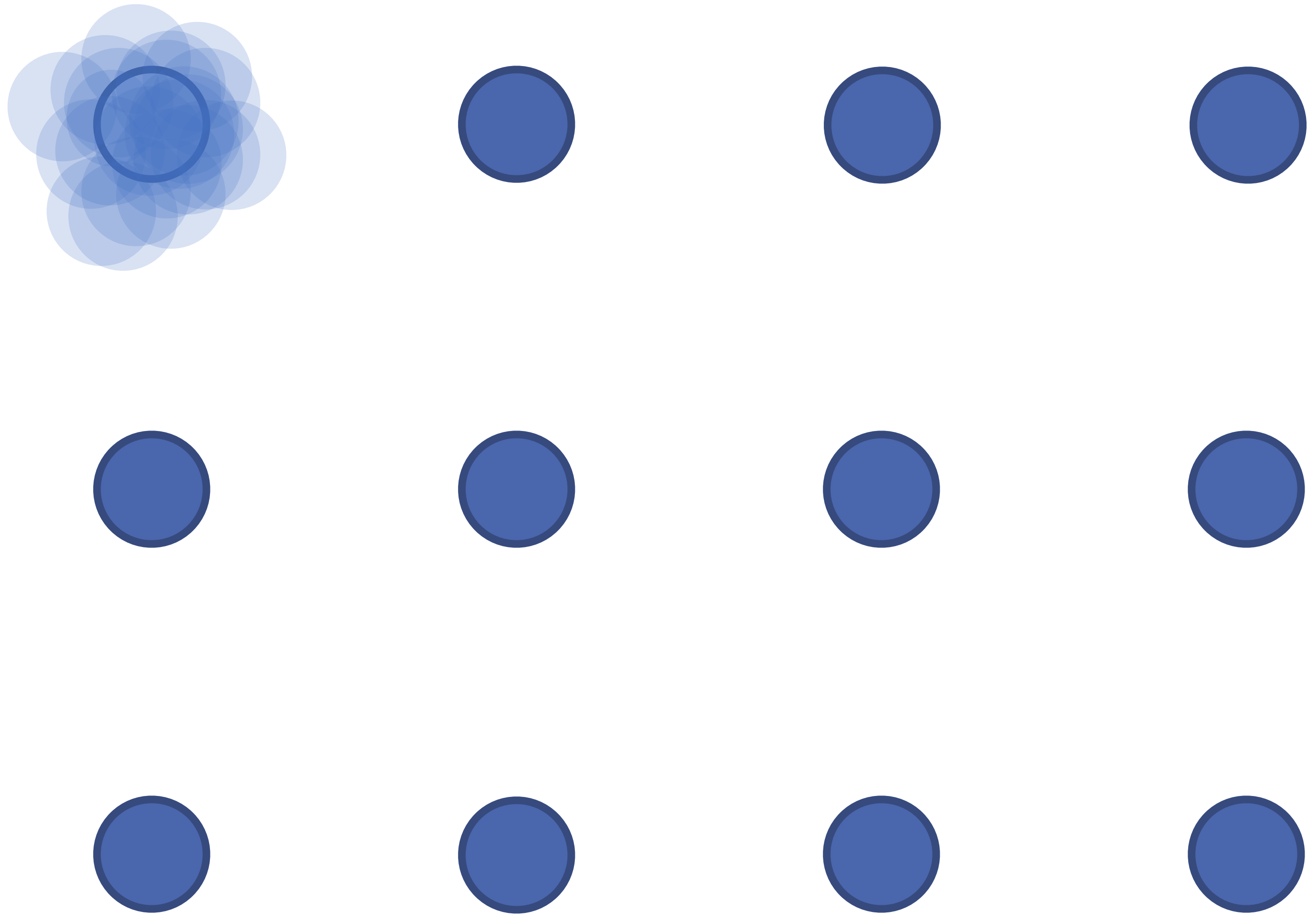
Phonon disorder

- What structure do we simulate?
- What structure is measured?



Phonon disorder

- What structure do we simulate?
- What structure is measured?
  - Atoms always vibrating



- Can lead to new features
  - Ch. Brouder *et al.*, PRB **81**, 115125 (2010)
  - T. Pascal *et al.*, J. Chem. Phys. **140**, 034107 (2014)

Phonon disorder approximations

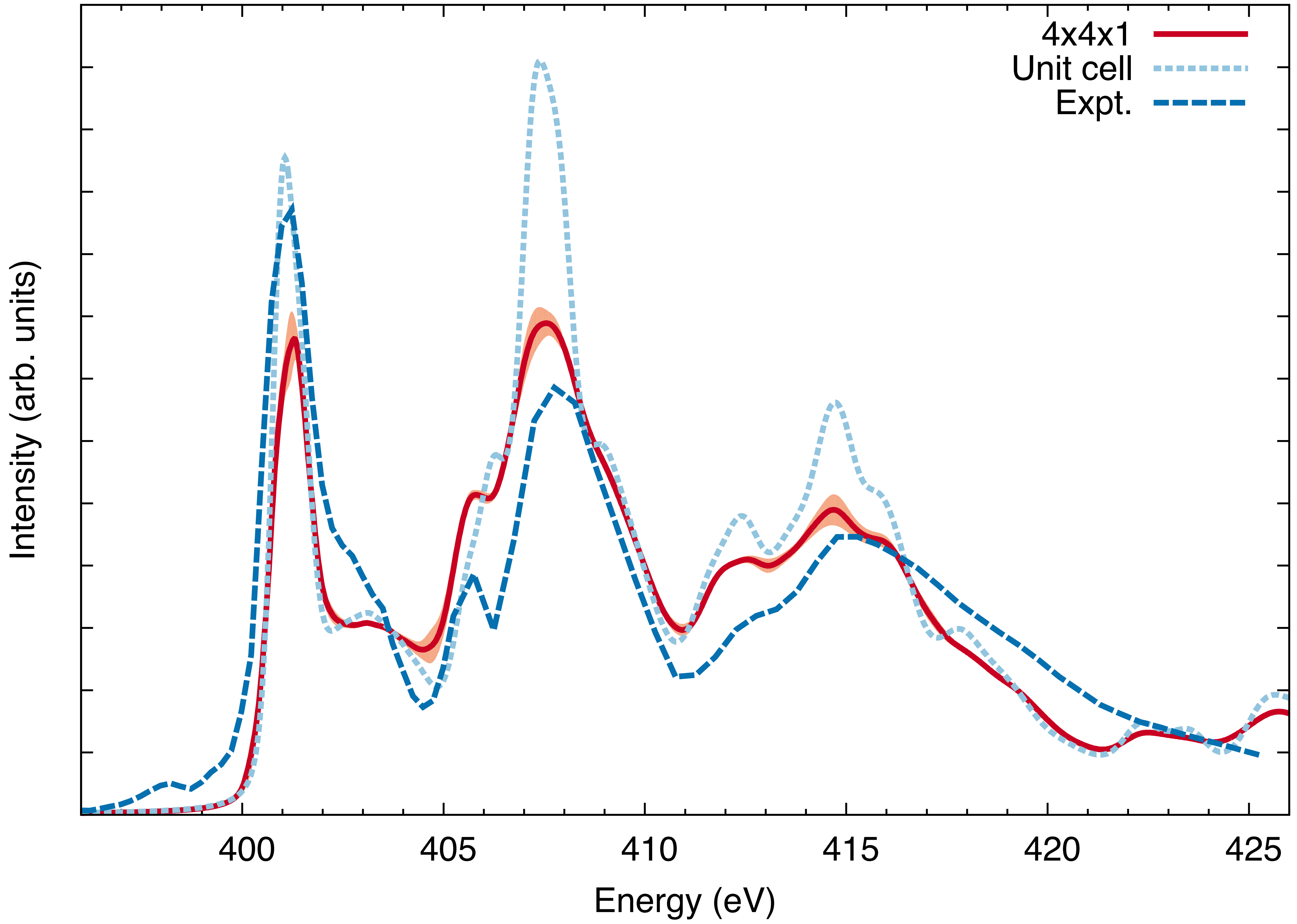
- ~~Perfect infinite crystal~~ Disordered structure
- Ions fixed
  - X-ray timescale too short
  - Vibrational energy too small
    - Ch. Brouder et al., PRB **81**, 115125 (2010)

Phonon disorder approximations

- Average over an ensemble of structures
  - Similar to amorphous or liquid systems
  - Might need supercell
- Many options for generating structures
  - Molecular dynamics — *e.g.*, J. Chem. Phys. **140**, 034107 (2014)
  - Thermal parameters — *e.g.*, PRB **81**, 115125 (2010)
  - Phonon modes — *e.g.,* PRB **92**, 144310 (2015); PRB **90**, 205207 (2014)

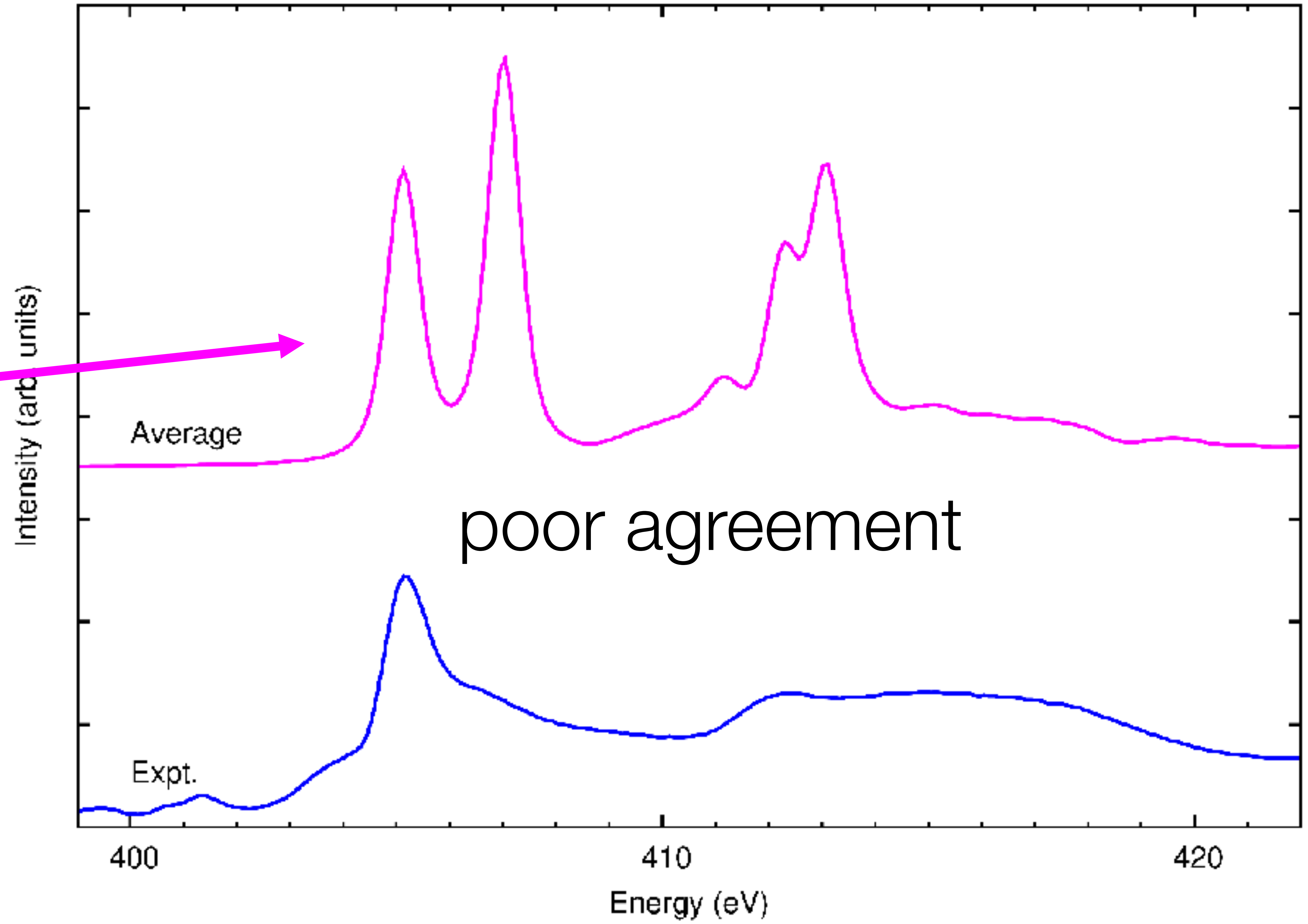
Effect of disorder

- N K-edge XAS of hBN
  - Vinson and Jach *et al.*, PRB **96**, 205116 (2017)
- Some change in peak intensities



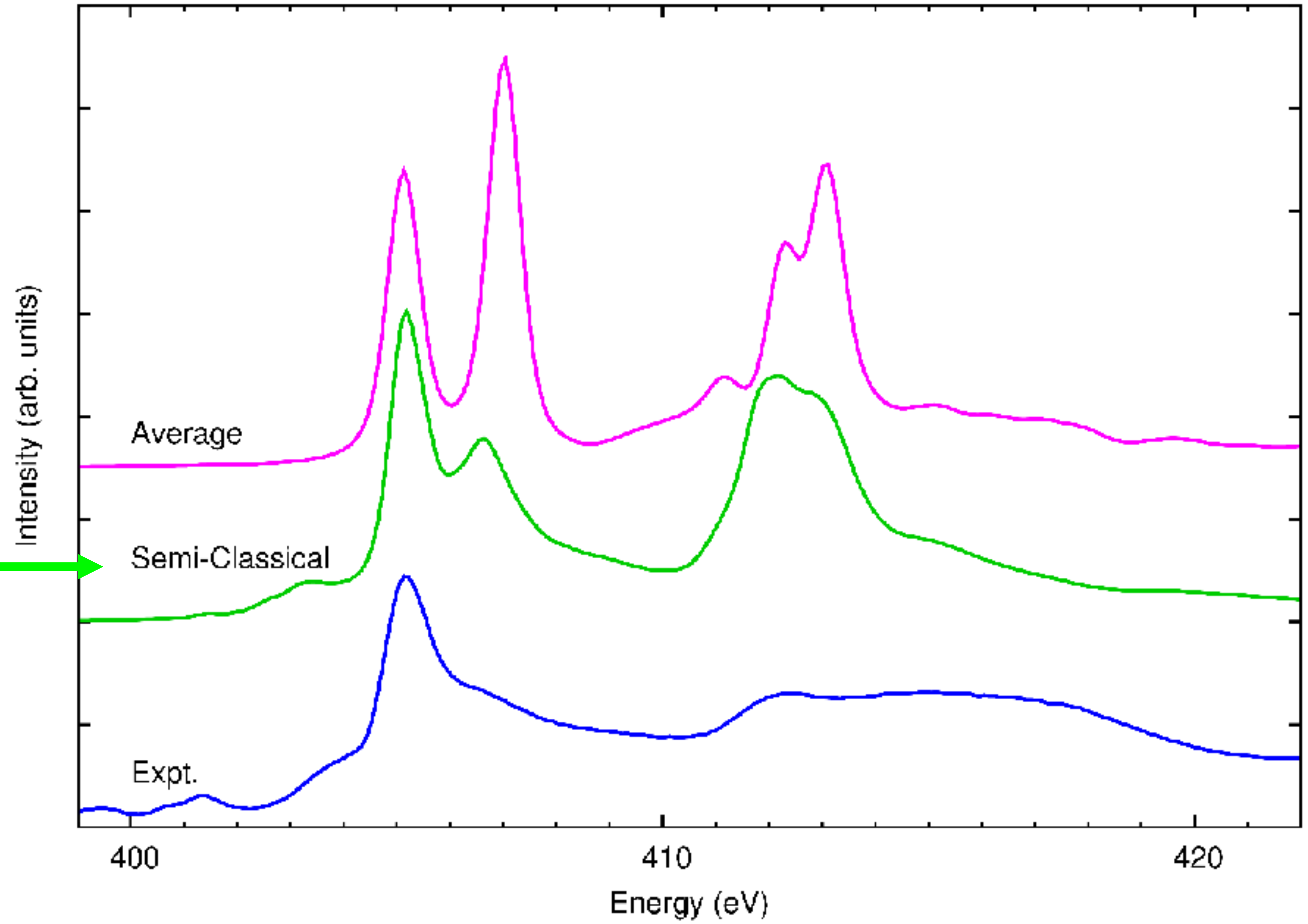
Effect of disorder

- N K-edge XAS of NH_4NO_3
  - Vinson and Jach *et al.*, PRB **90**, 205207 (2014)
- Perfect crystal atomic positions



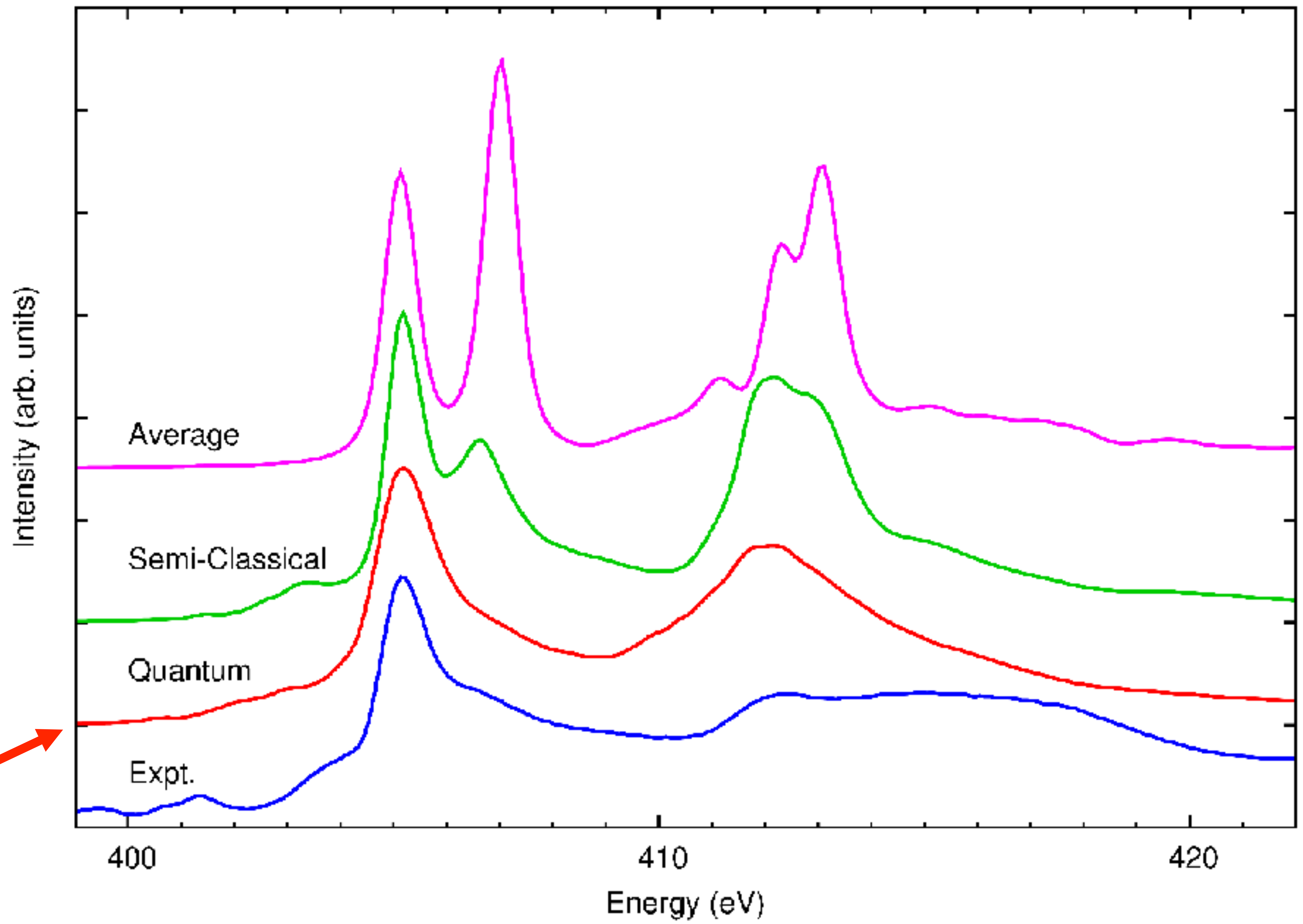
Effect of disorder

- N K-edge XAS of NH_4NO_3
  - Vinson and Jach *et al.*, PRB **90**, 205207 (2014)
- Perfect crystal atomic positions
- Semi-classical – Phonon occupation is $n(\omega; T)$



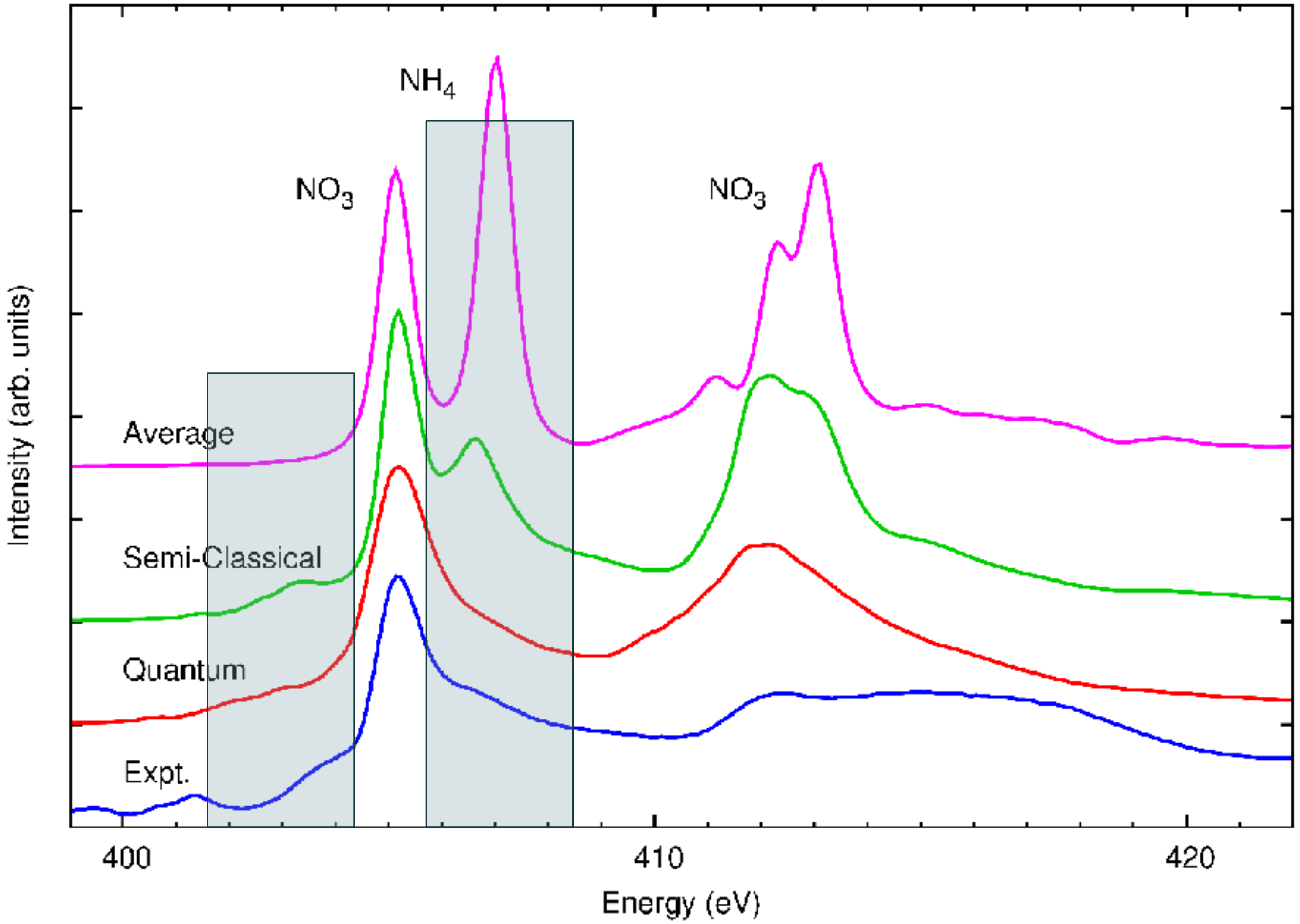
Effect of disorder

- N K-edge XAS of NH_4NO_3
  - Vinson and Jach *et al.*, PRB **90**, 205207 (2014)
- Perfect crystal atomic positions
- Semi-classical – Phonon occupation is $n(\omega;T)$
- Quantum – Phonon occupation is ½ $+n(\omega;T)$



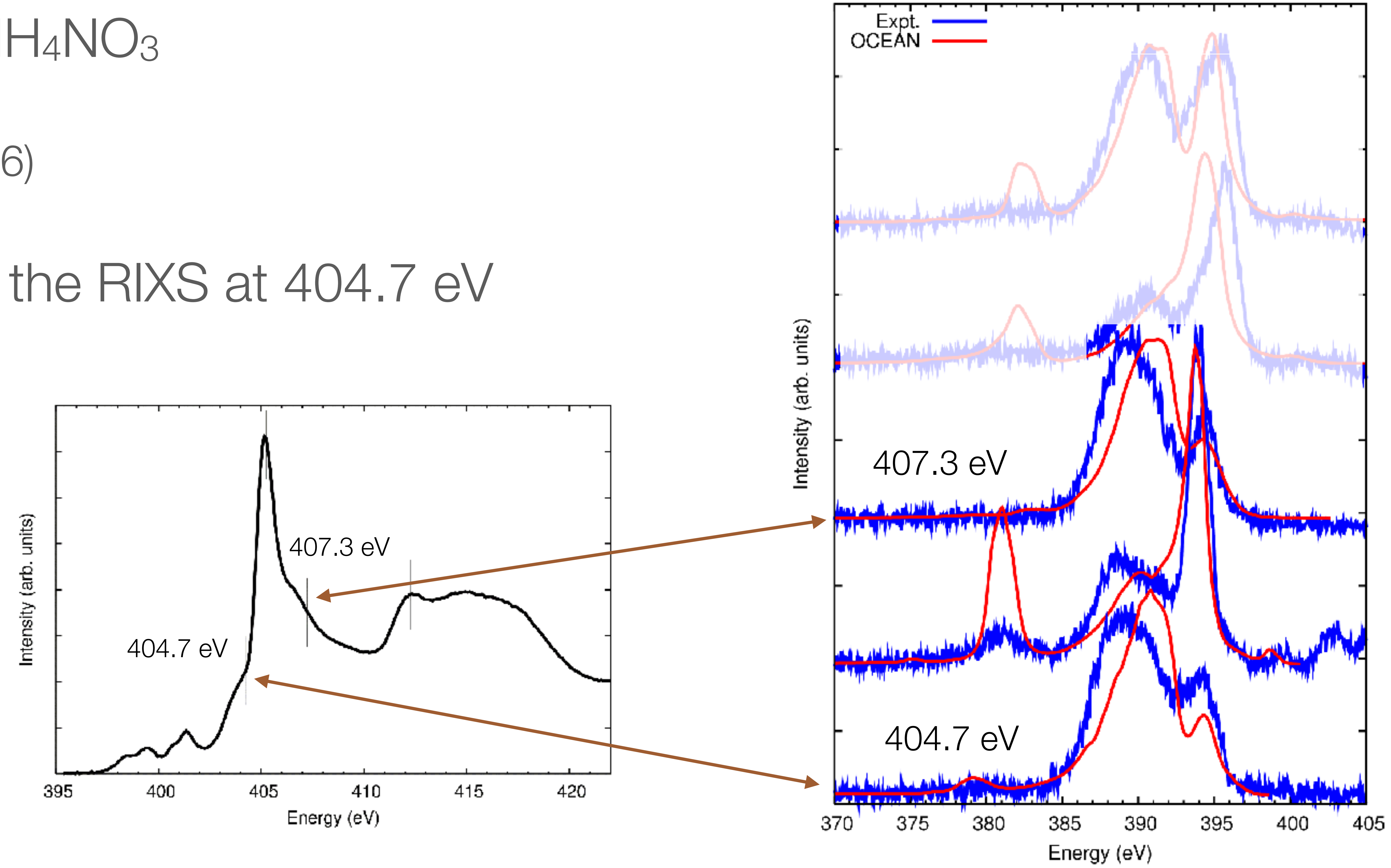
Effect of disorder

- N K-edge XAS of NH_4NO_3
  - Vinson and Jach *et al.*, PRB **90**, 205207 (2014)
- Perfect crystal atomic positions
- Semi-classical – Phonon occupation is $n(\omega; T)$
- Quantum – Phonon occupation is ½ $+n(\omega; T)$



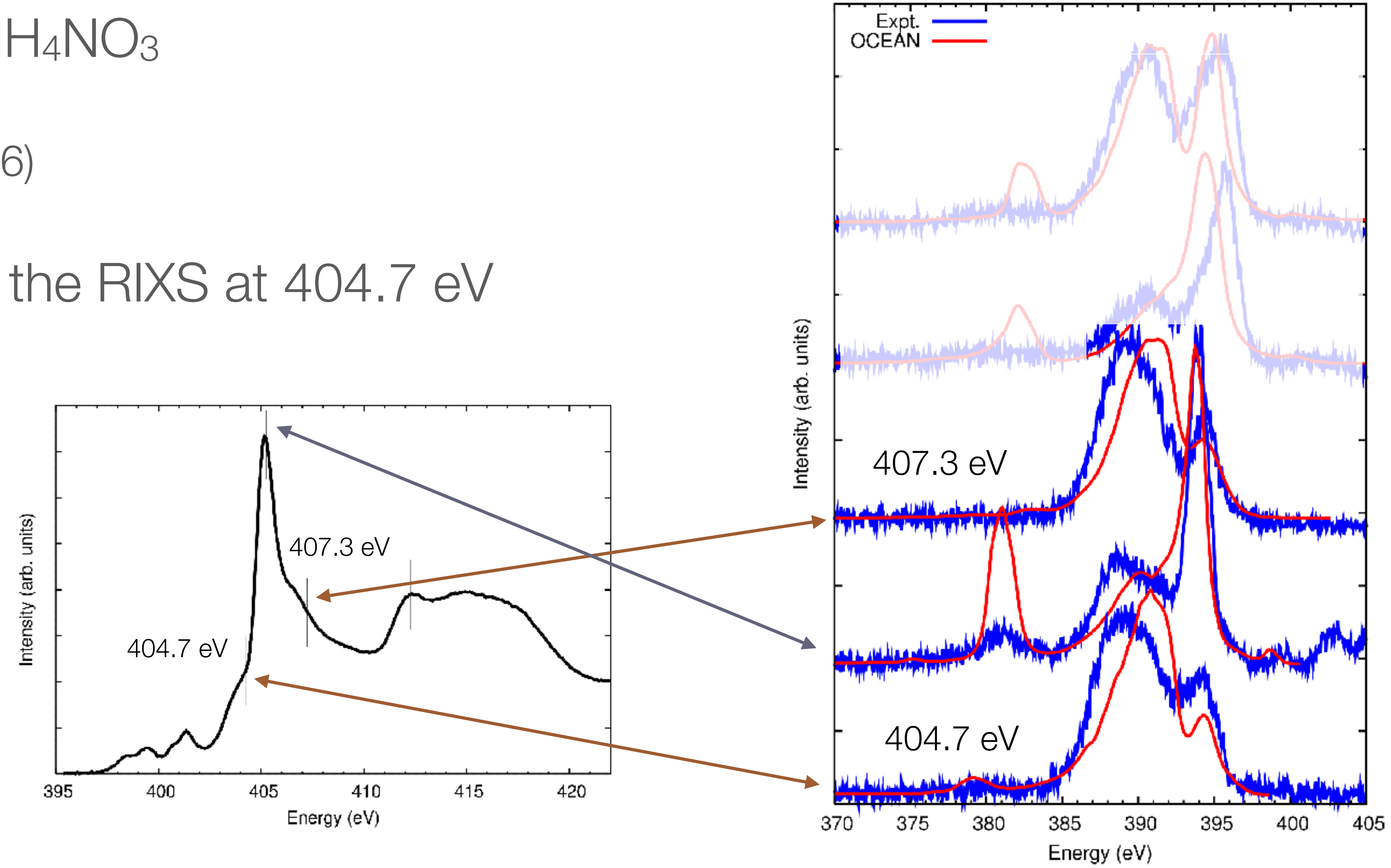
Effect of disorder

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)
- Clear sign of NH_4 in the RIXS at 404.7 eV



Effect of disorder

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)
- Clear sign of NH_4 in the RIXS at 404.7 eV
- Distinct from NO_3 at 405.e eV



Outline

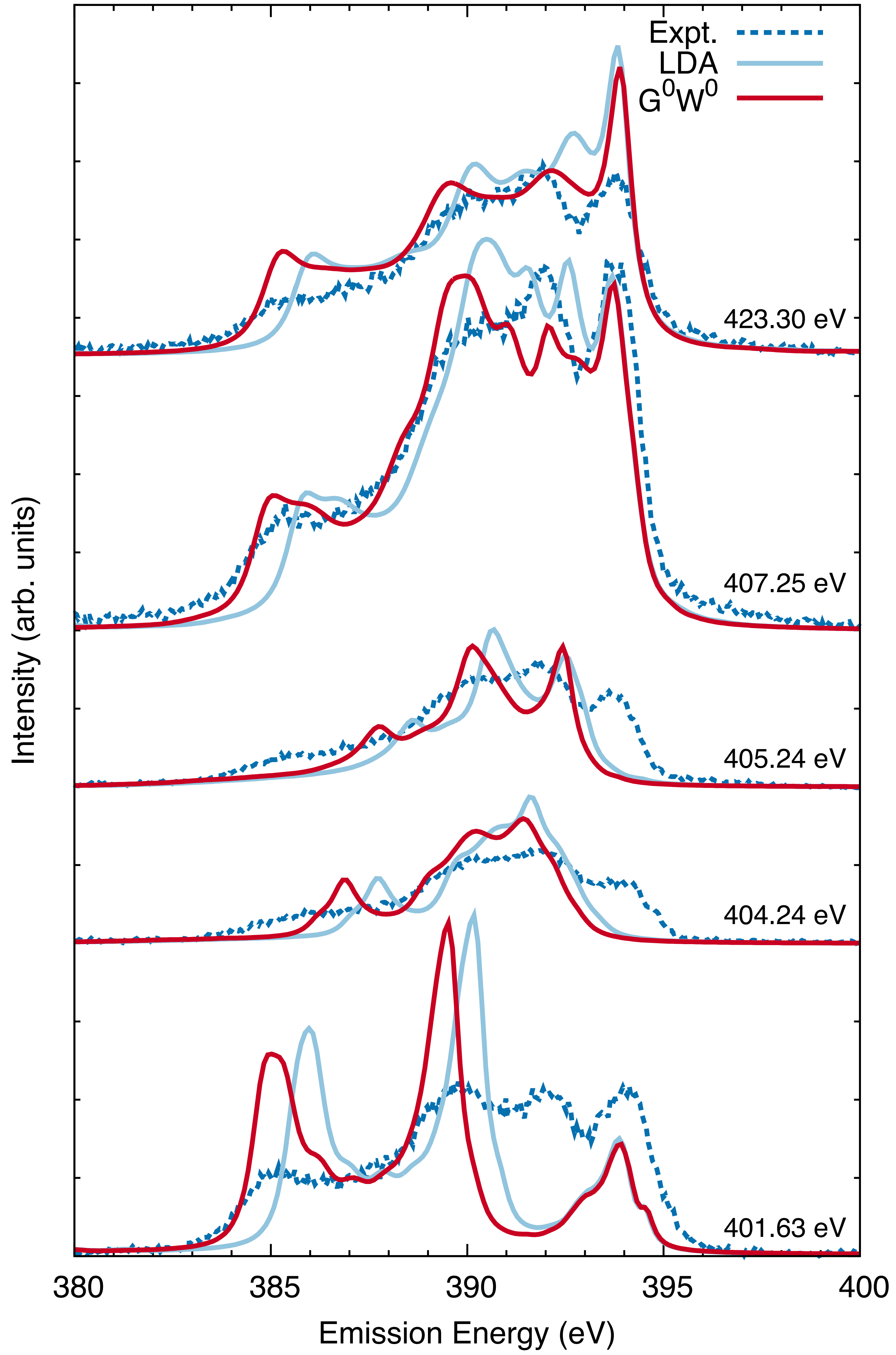
- What is RIXS? How do we calculate it?
- **Examples**
    - Zn dopants Cu-rich minerals
    - Fingerprints of oxygen oxidation
    - Phonon disorder
    - **Many-body self-energy corrections**
- Missing pieces and future work

Many-body self-energy effects

- Solving BSE using DFT basis
  - ψ & ε come from LDA, GGA, etc
  - Bands gaps and band widths too small
- Turn to *GW* self-energy corrections
  - Lowest order; change energies ε only

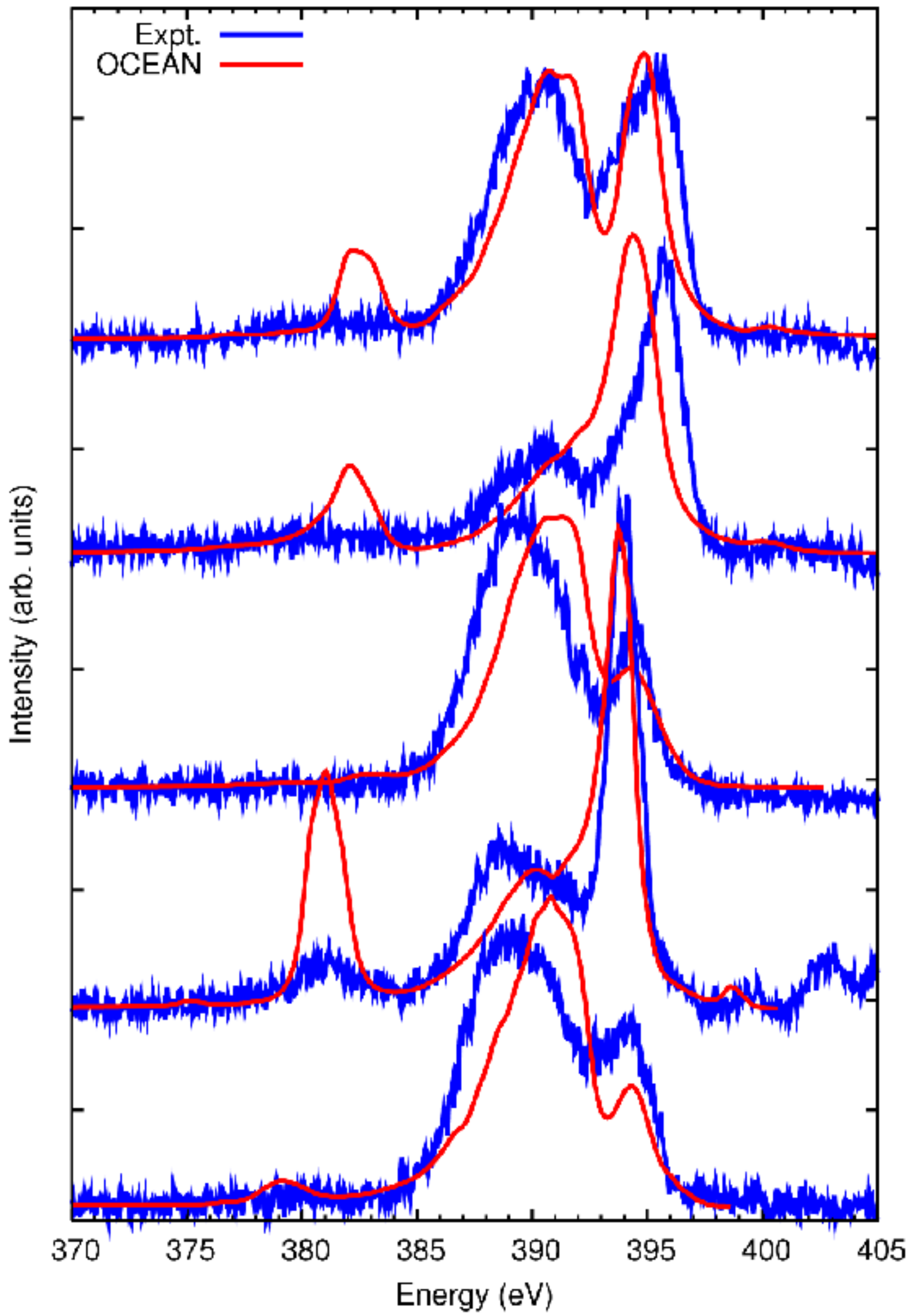
Many-body self-energy effects

- N K-edge RIXS of hBN
  - PRB **96**, 205116 (2017)
- *G^0W^0* improves valence band width



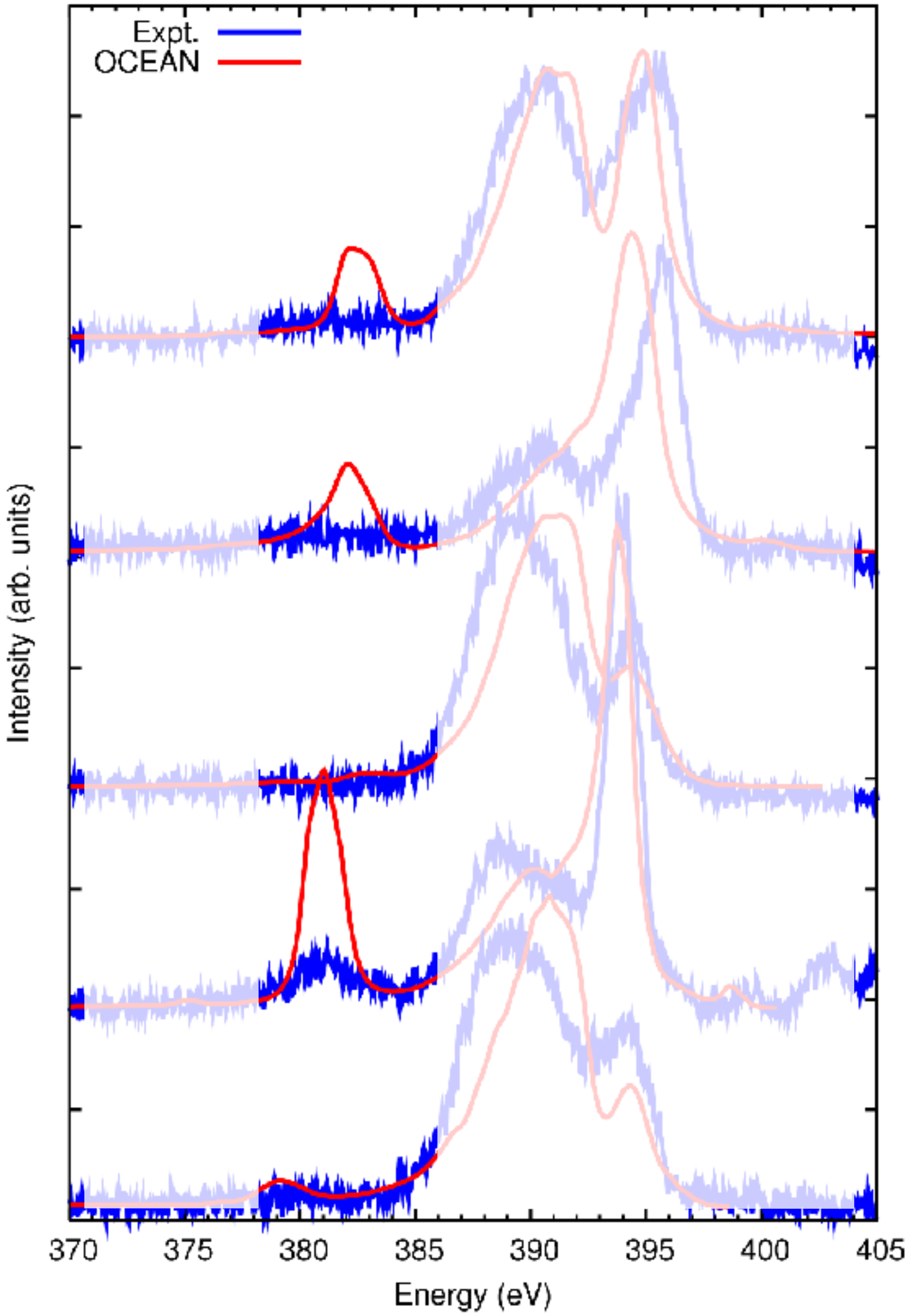
Many-body self-energy effects

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)



Many-body self-energy effects

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)
- Clear disagreement around 380 eV

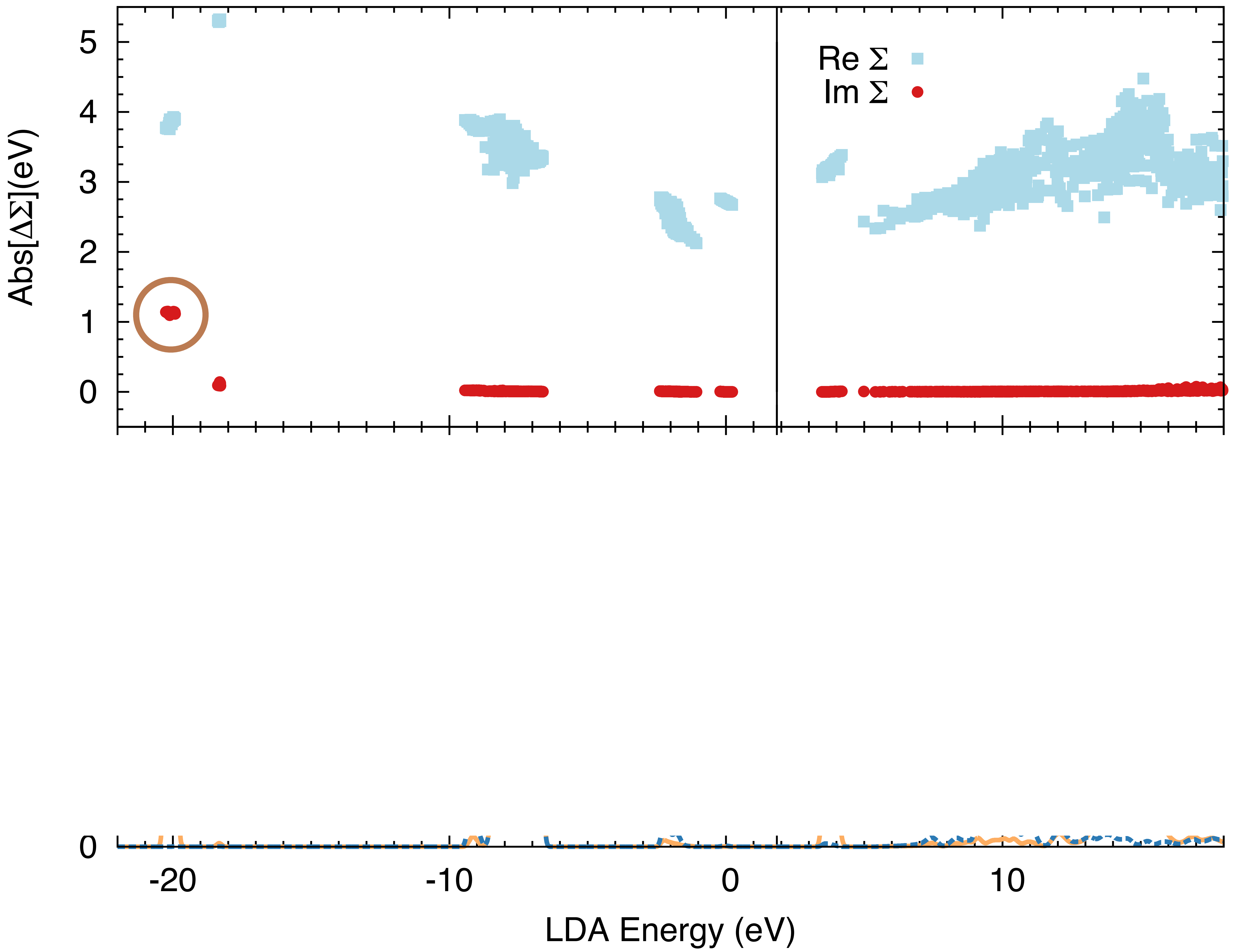


Many-body self-energy effects

- Final state in RIXS calculations is valence hole and conduction electron
  - Not the ground state
  - Quasi-particles have finite lifetimes
- Complex-valued self-energy corrections from *GW*

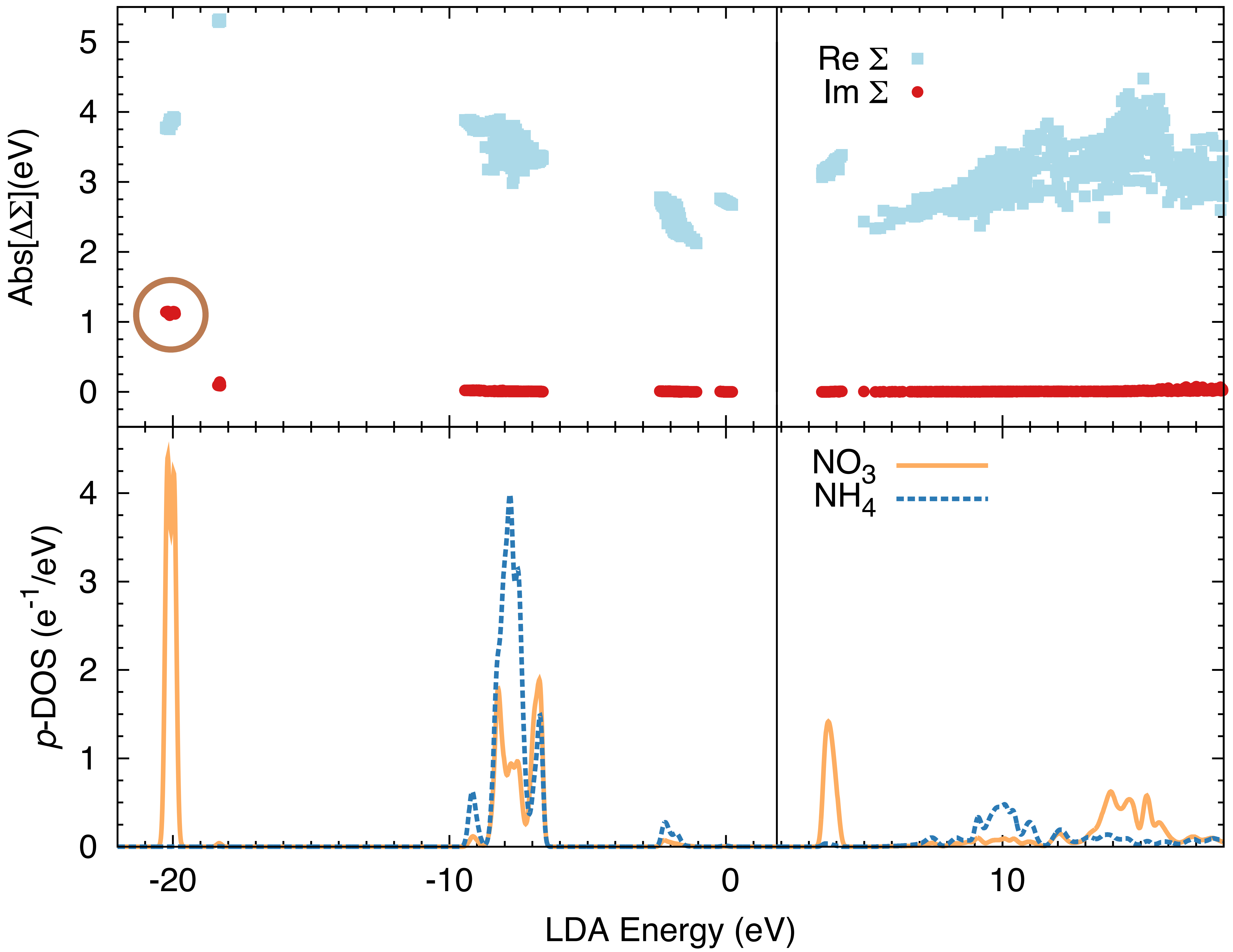
Many-body self-energy effects

- NH_4NO_3 *GW* calculations
- Most states have a small imaginary component



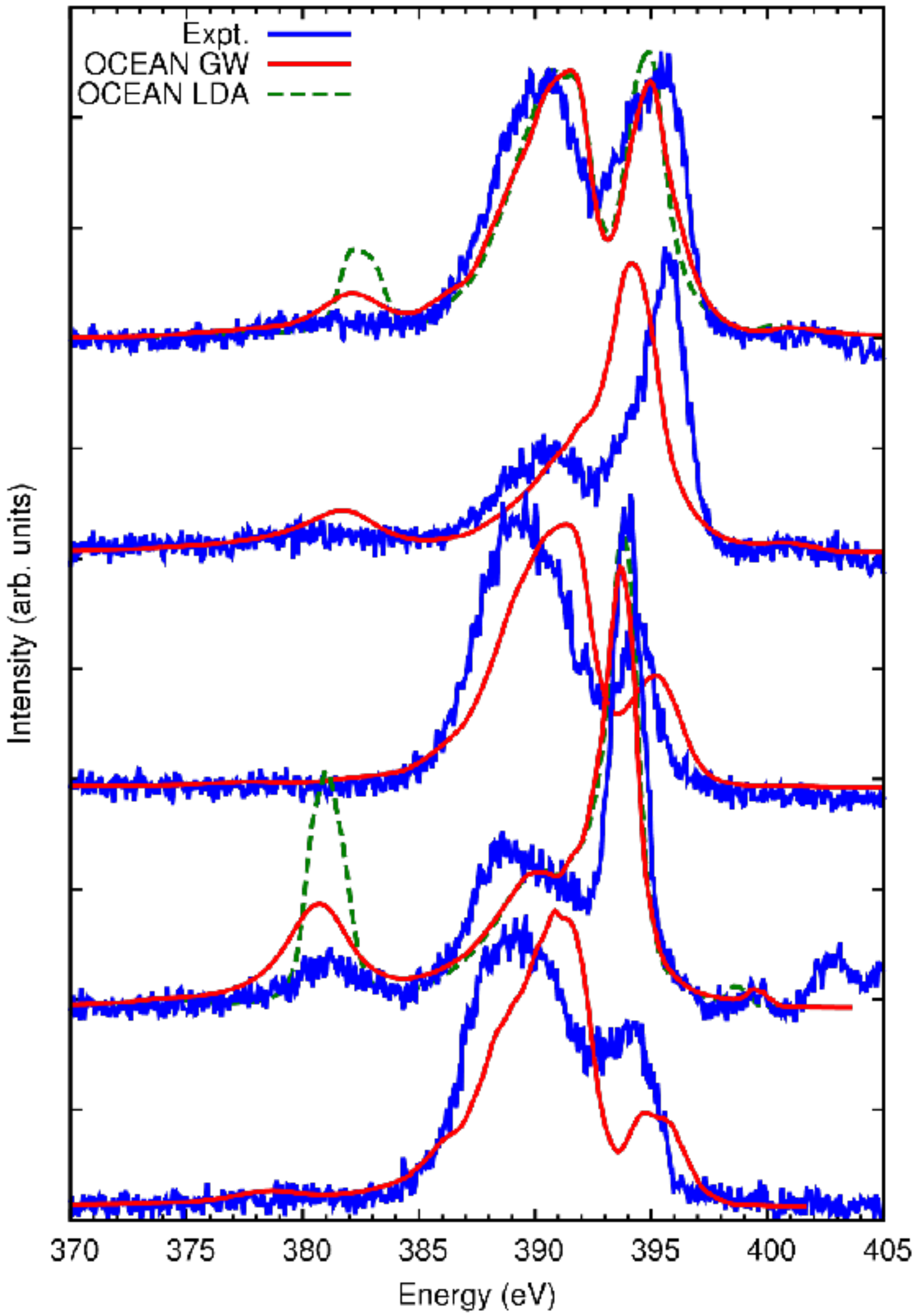
Many-body self-energy effects

- NH_4NO_3 GW calculations
- Most states have a small imaginary component
- Except *p*-type states on the NO_3 nitrogen, NOσ bond



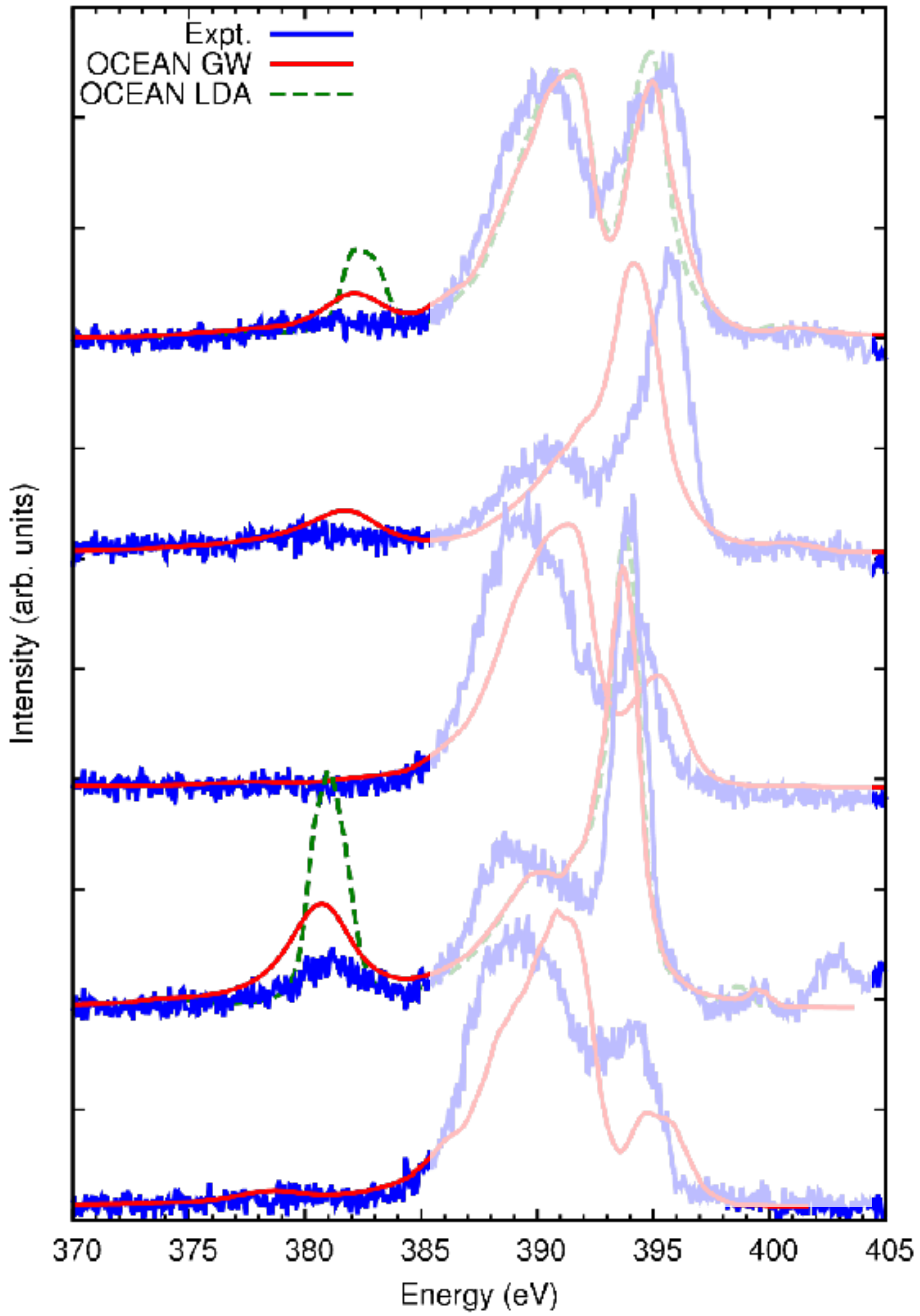
Many-body self-energy effects

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)



Many-body self-energy effects

- N K-edge RIXS of NH_4NO_3
  - PRB **94**, 035163 (2016)
- Similar results seen for $LiNO_3$
  - PRB **100**, 085143 (2019)



Outline

- What is RIXS?
- How do we calculate it?
- Examples
- **Missing pieces and future work**

Missing piece and future work

- Atoms aren’t frozen during x-ray excitations
  - React to the exciton density
  - Well known in molecules, hard with many phonons and electrons
  - Embedded molecules, i.e., water or aqueous systems
    - M. Odelius *et al.*, PRL **94**, 227401 (2005)
  - Model electron systems/model phonons
    - T. P. Devereaux *et al.*, PRX **6**, 041019 (2016); Geondzhian & Gilmore, PRB **101**, 214307 (2020)

Missing piece and future work

- Atoms aren’t frozen during x-ray excitations
- Beyond G^0W^0 @ LDA/PBE
  - Better starting wave functions
    - Exact exchange J. Chem. Phys. **153**, 204106 (2020)
  - Cumulant approach
    - Tzavala *et al.*, PR Research **2**, 033147 (2020)
  - Lifetime of e-h pair ≠ e + h

Missing piece and future work

- Atoms aren’t frozen during x-ray excitations
- Beyond G^0W^0 @ LDA/PBE
- Cross-code comparison efforts
    - On-going collaboration — Brookhaven, HU Berlin, NIST
    - Improved defaults and automation

end