Structural Dynamics in Hydrogen-Bonded and Transition-Metal Systems

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& Center for Free Electron Laser Science

SwissFEL Photonics Pump Laser Workshop

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Courtesy: hammeskrause architekten

Chemical Dynamics in Solvated Systems

Elucidating chemical reaction pathways and intermediates in solution and at interfaces via time-resolved X-ray Absorption and Photoemission Spectroscopy

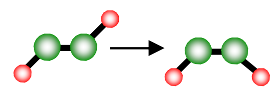
- energy levels & coupling constants
- charge distribution & bonding
- spin-state-dependent effects

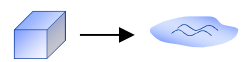
How fast is SwissFEL?

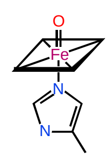
or what is the timing jitter…

- charge transfer
- electronic phase transitions
- correlated electron systems

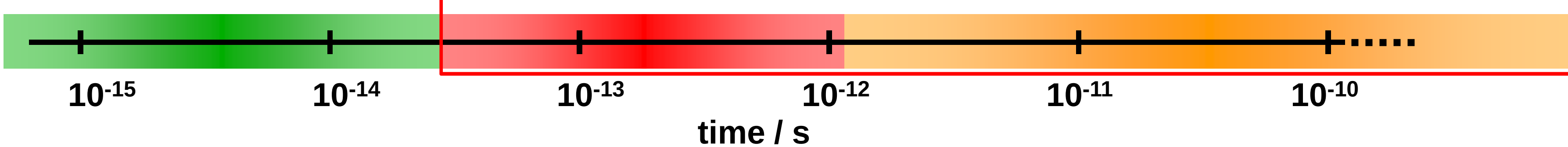
- ultrafast chemical reactions
- ultrafast phase transitions
- surface dynamics
- resonant energy transfer







- vibrational relaxation & VER
- vibrational energy redistribution
- molecular reorientation
- macromolecular reconfiguration



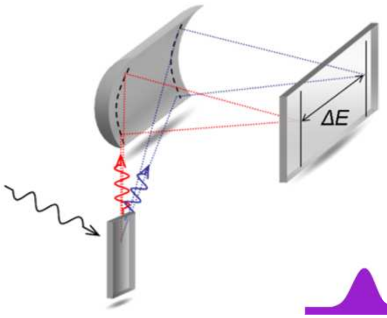
Transient X-ray Spectroscopic Methods

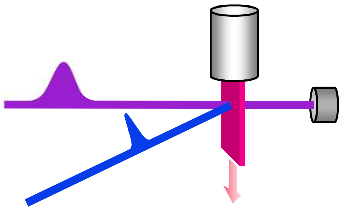
X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XES)

Resonant Inelastic X-ray Scattering (RIXS)

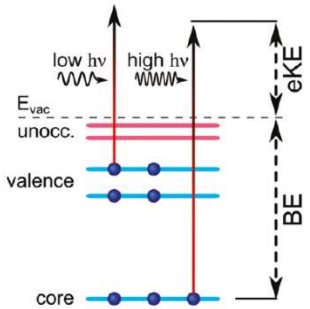
- Photon-only → no worries about space charge, sample charging, laser field streaking
- Moderate to no vacuum requirements

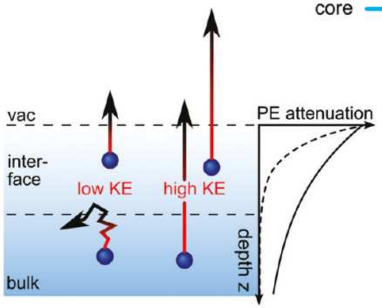




Photoemission Spectroscopy (PES)

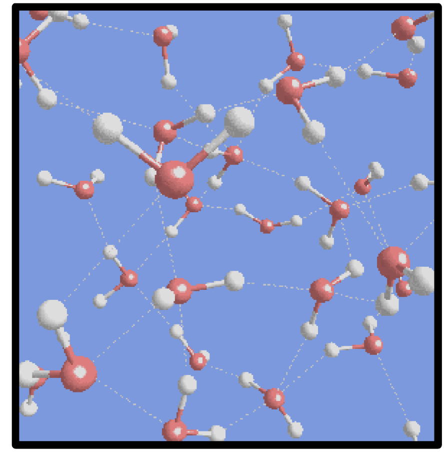
- Efficient & atom-specific probe for surface chemistry
- Depth-dependence of excess kinetic energy uniquely suite for interface chemistry
- Angle-resolved PES delivers new insights into anisotropic effects in chemical reactions



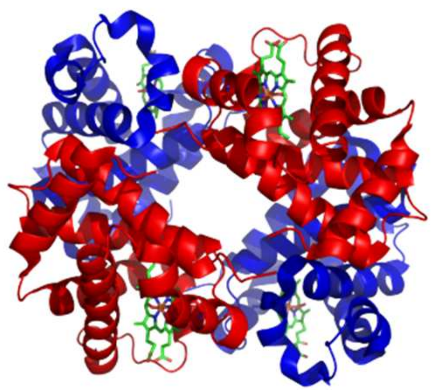


Research Objectives

➢ ***Hydrogen Bond Research***



➢ ***Solute Dynamics***



➢ ***Liquid-Phase Chemistry***

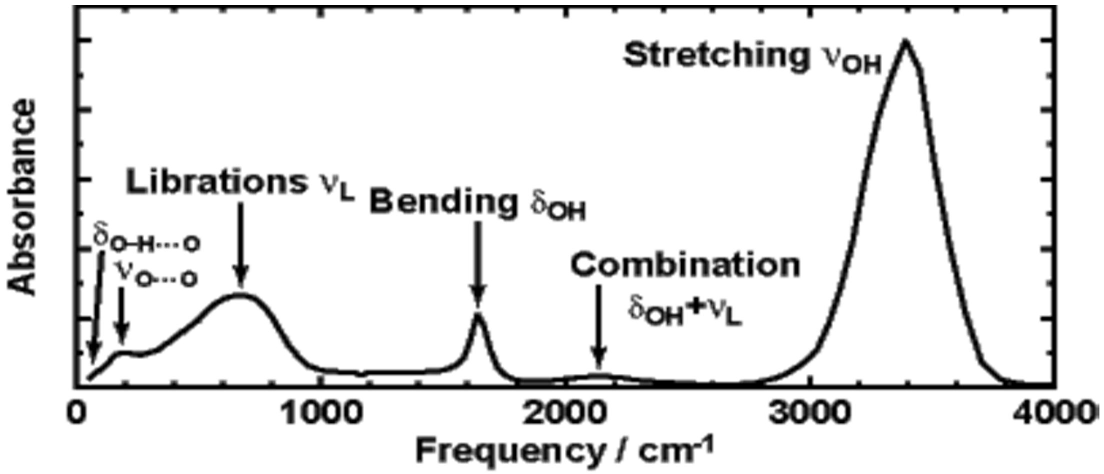
$$OClO(X^2B_1) + h\nu \rightarrow ClO(^2\Pi) + O(^3P_g)$$

$$OClO(X^2B_1) + h\nu \rightarrow Cl(^2P_u) + O_2(^3\Sigma_g^-)$$

$$OClO(X^2B_1) + h\nu \rightarrow Cl(^2P_u) + O_2(^1\Delta_g)$$

$$OClO(X^2B_1) + h\nu \rightarrow ClOO \rightarrow Cl(^2P_u) + O_2(^3\Sigma_g^-)$$

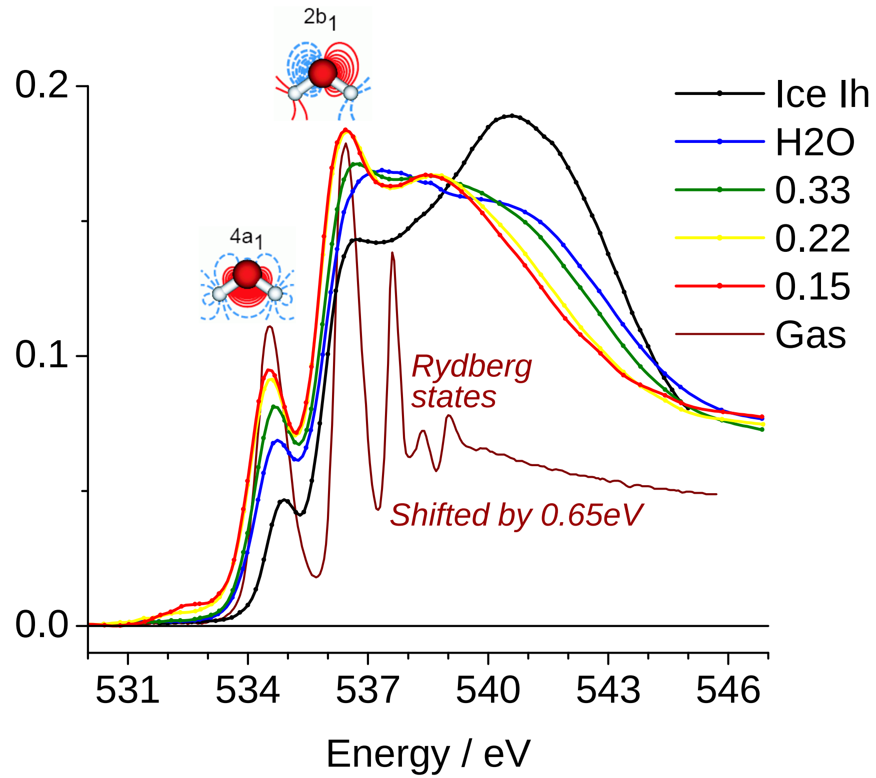
Infrared Spectroscopy of Water

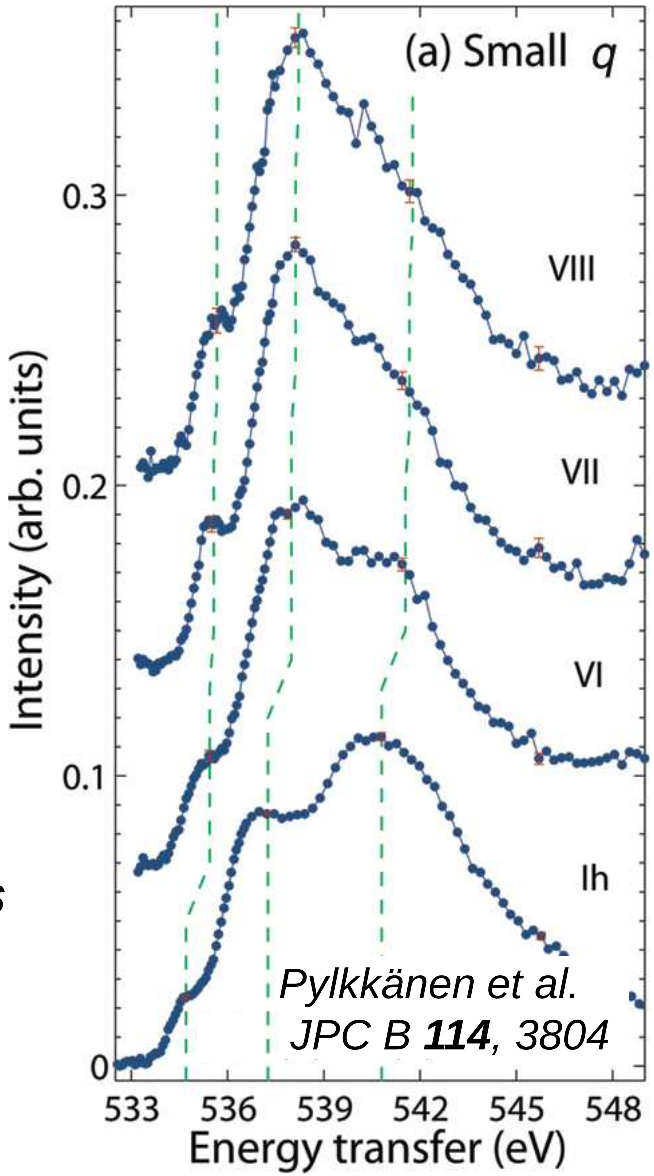


- *O-H stretching modes (3400cm^{-1})* — *~ 0.01ps*
- *O-H bending mode (1650cm^{-1})* — *~ 0.02ps*
- *Librations (300 to 1500 cm^{-1})* — *~ 0.03 to 0.2ps*
- *Slower intermolecular modes (< 300cm^{-1})* — *< 0.2ps*
- *Intermolecular coupling:*
  dephasing, spectral diffusion, H-bond cleavage — *~0.05 to several ps*

Microscopic dynamics of water over a wide range of timescales

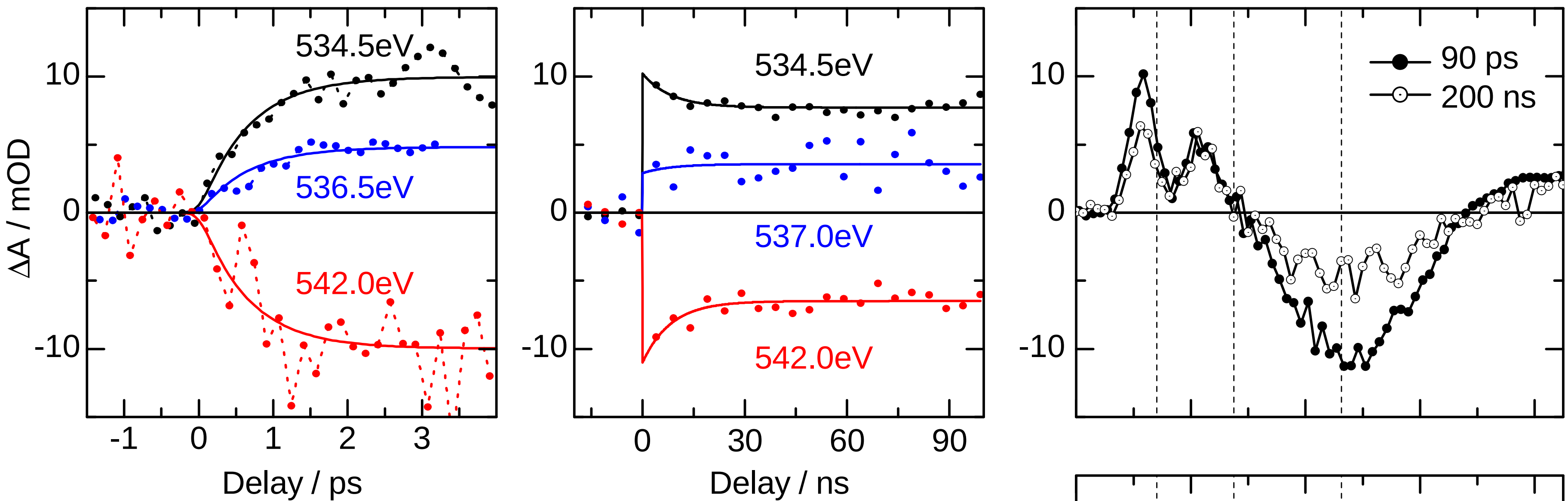
Spectral Features in Water and Phases of Ice

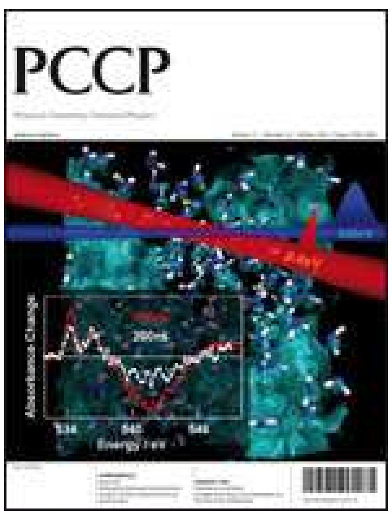




- ***Pre-edge height seems not to be unique to HB strength but the spectral position is***
- ***Time-resolved x-ray probe measurements reproduce the same spectral behavior***

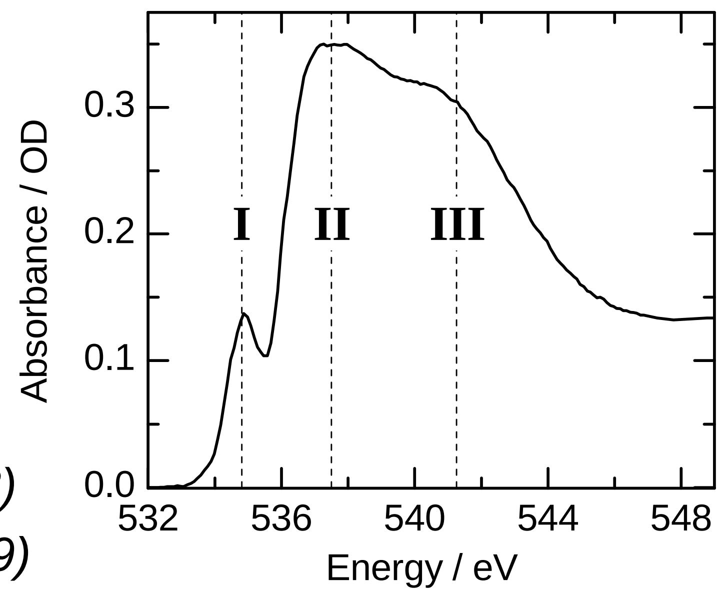
Ultrafast Soft X-ray Spectroscopy on H_2O



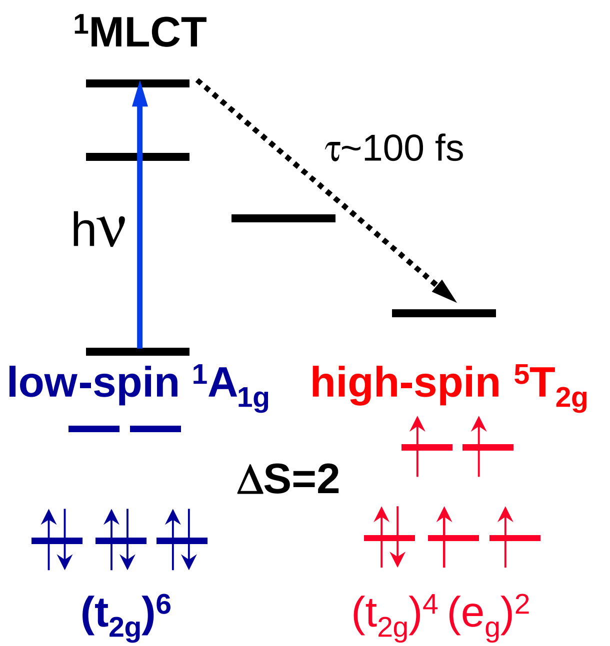


- ***Thermalization***
  → Isochoric Heating
- ***Adiabatic Expansion***
- ***Pressure Dependence?***

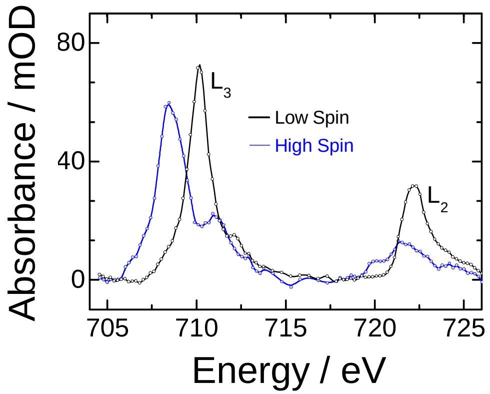
*Wernet et al., APA **92**, 511 ('08)*
*Huse et al. PCCP **11**, 3951 ('09)*
*Wen et al. JCP **131**, 234505 ('09)*



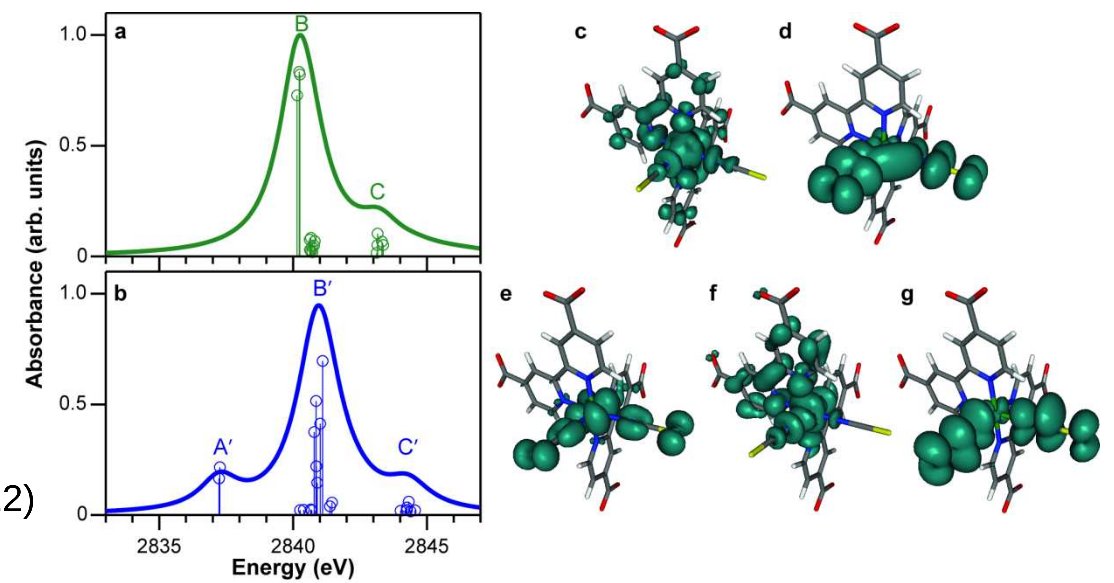
Transient Soft X-ray Spectroscopy of Solutes



Molecular Magnetism, Metal-Ligand Interactions



Artificial Photosynthetic Systems



Huse et al. *PCCP* **11**, 3951 (2009)

Wen et al. *JCP* **131**, 234505 (2009)

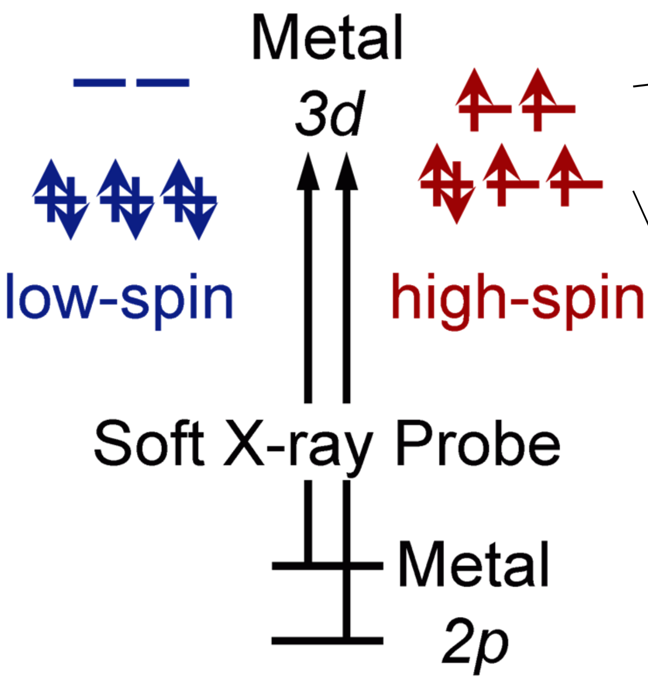
Huse et al. *JACS* **132**, 6809 (2010)

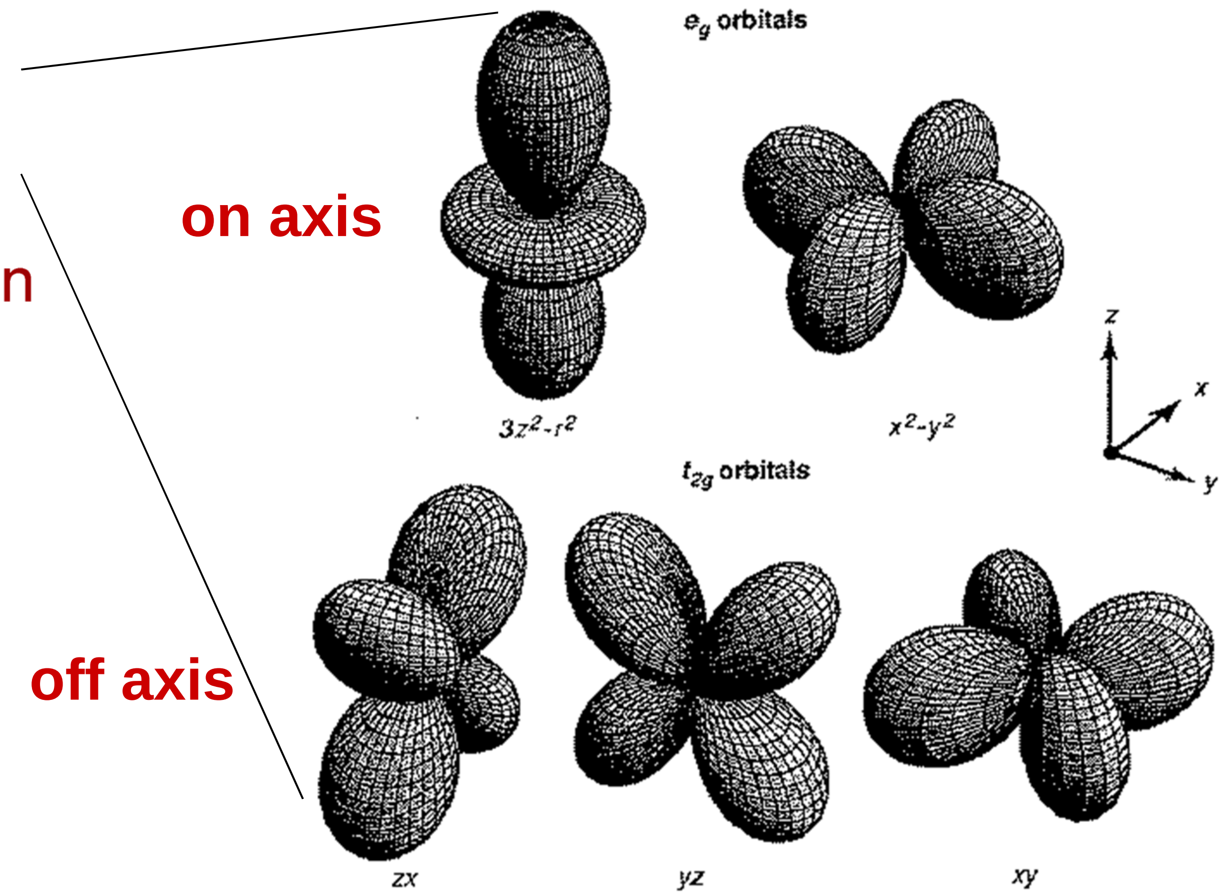
Huse et al. *JPCL* **2**, 880 (2011)

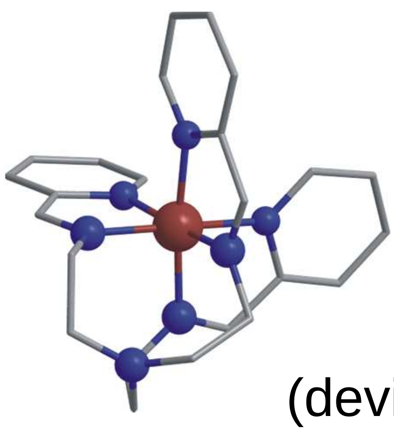
Van Kuiken et al. *JPCL* **3**, 1695 (2012)

Cho et al. *Faraday Discuss.* **157**, 463 (2012)

Probing the Metal *d*-Orbitals



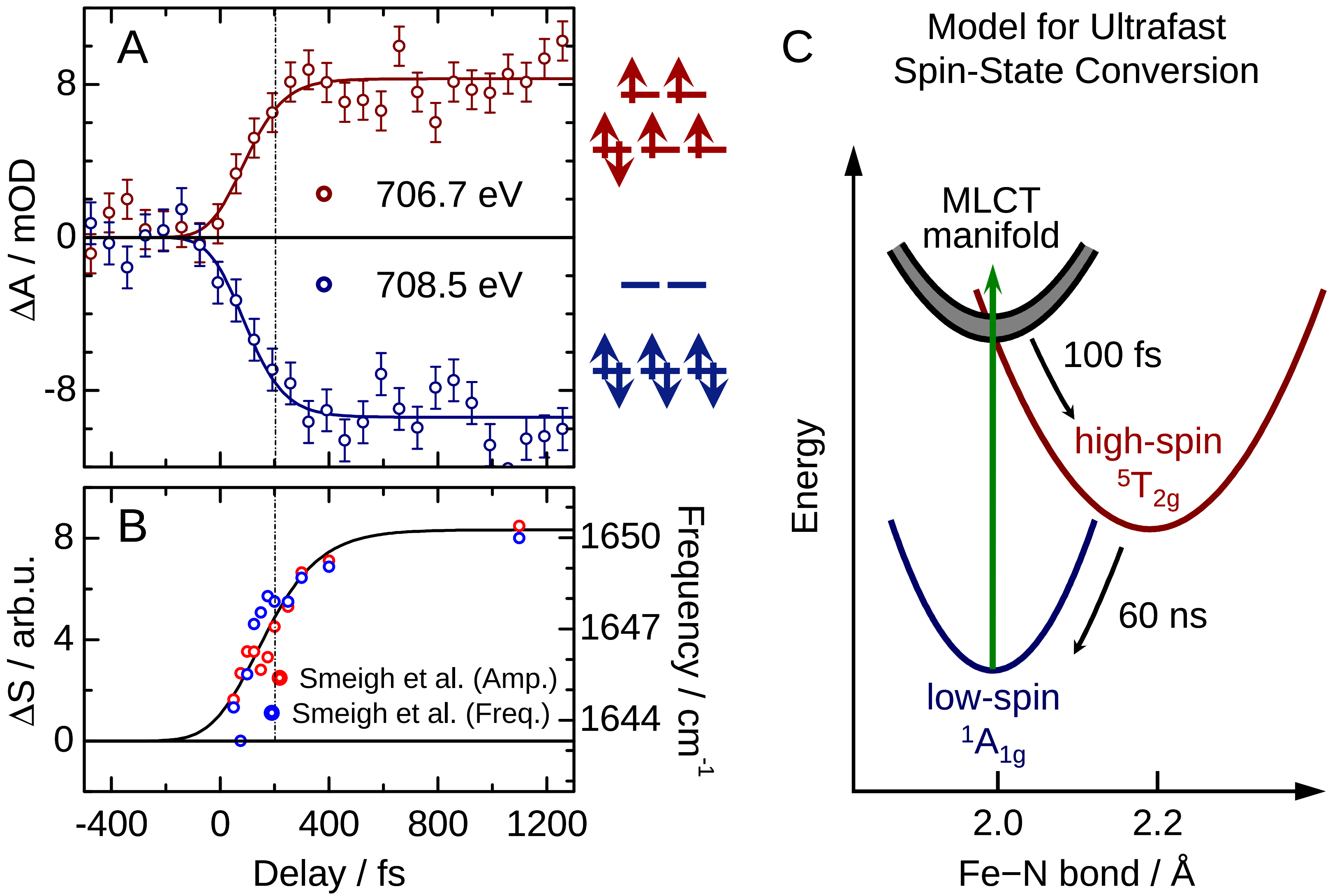




approximate symmetry is octahedral

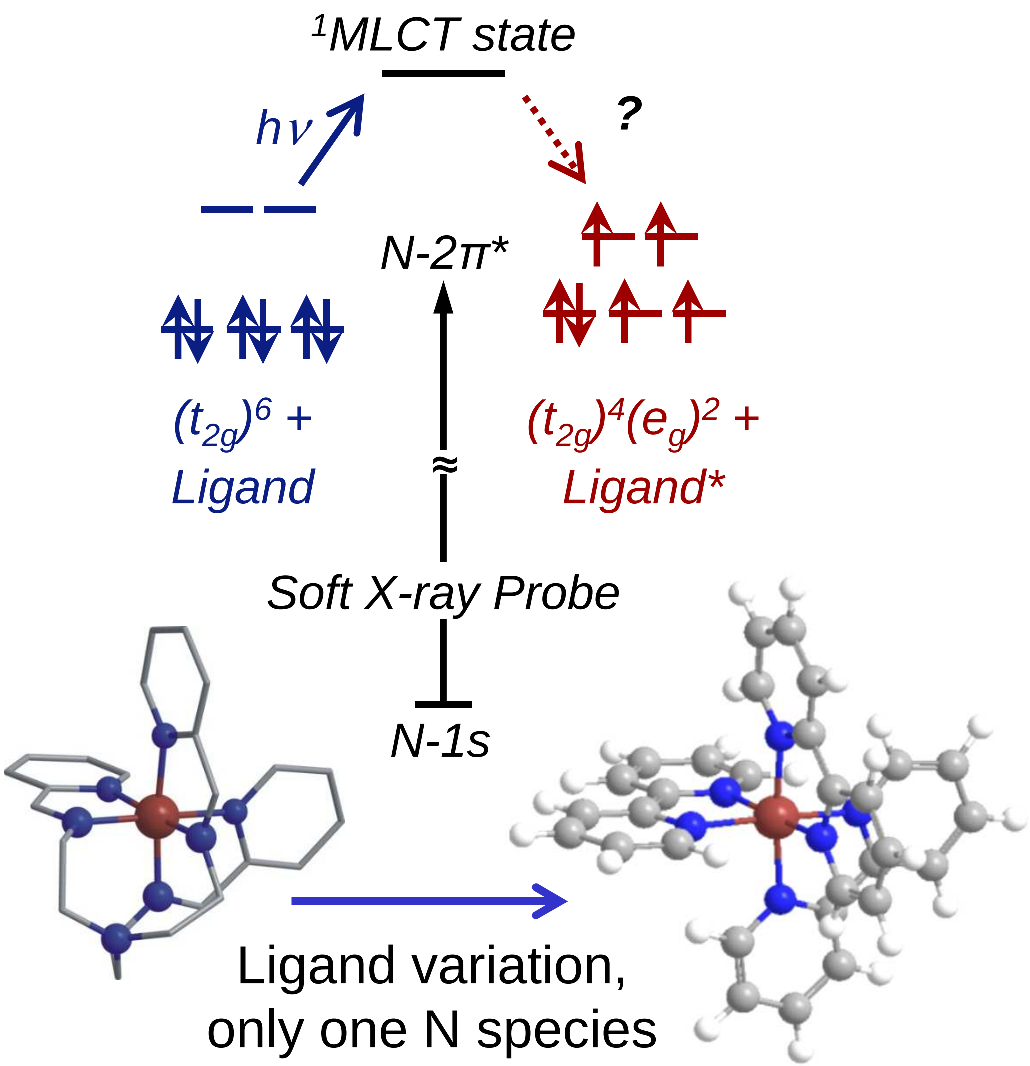
(deviations → Cho et al., *Faraday Discuss.* **157**, submitted)

Trading Spin for Orbital Angular Momentum



Huse et al. *JPCL* **2**, 880 (2011)

Probing the Ligand View at the Nitrogen K-edge

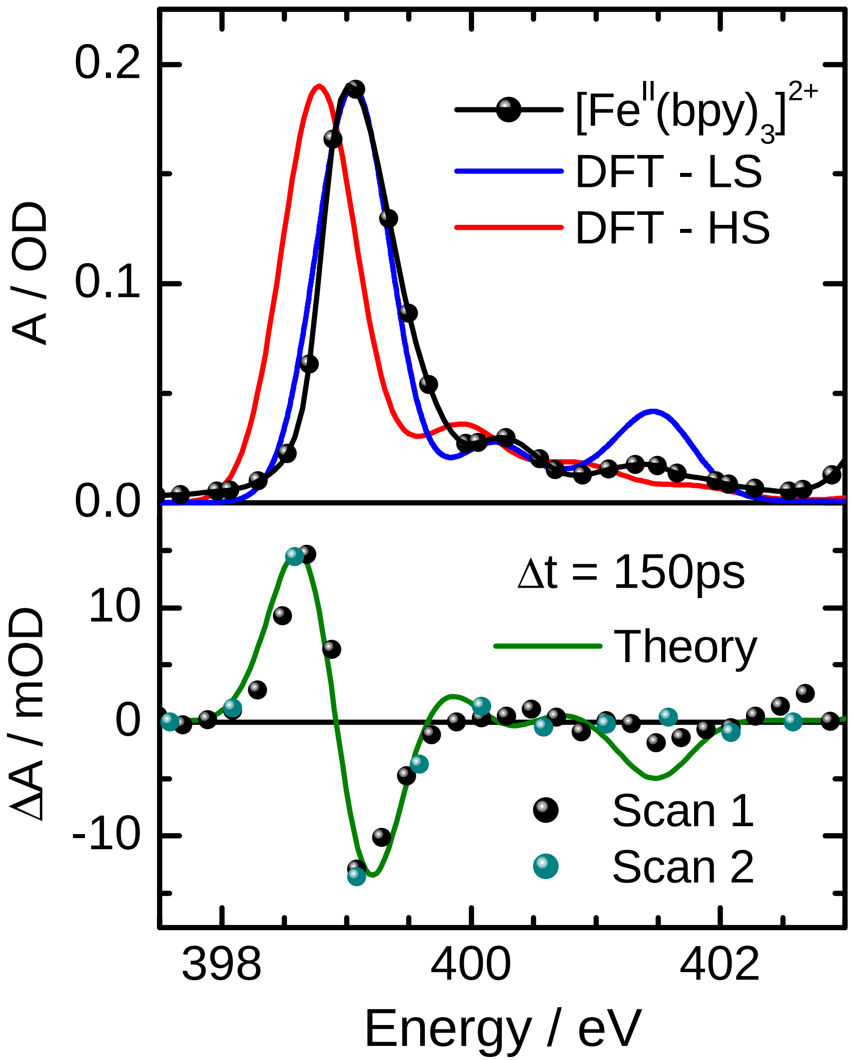


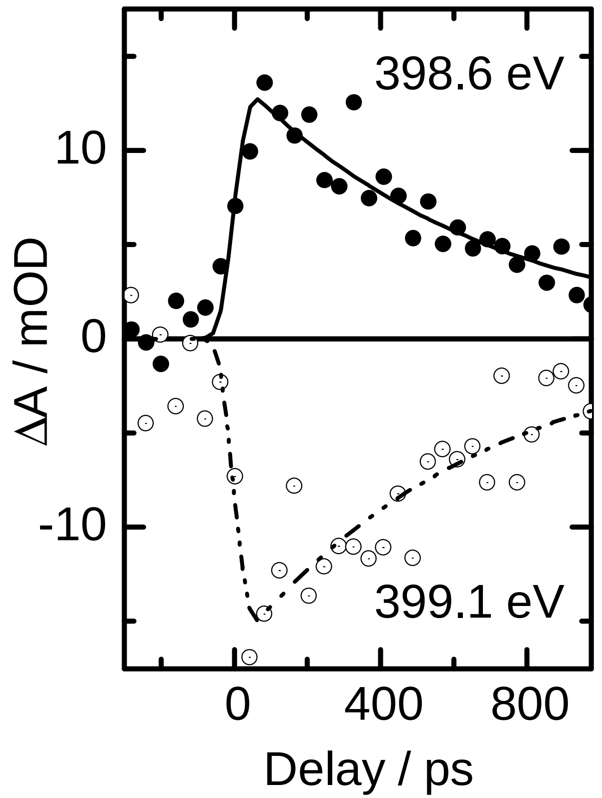
(cf. Cho et al., *Faraday Discuss.* **157**, submitted)

Advantages:

- Theory is quite matured
- No multiplet effects due to weaker spin orbit coupling
- Increased solvent transmission
- Complementary information on metal-ligand interactions
- Prospect of laser-based femtosecond X-ray spectroscopy and beyond

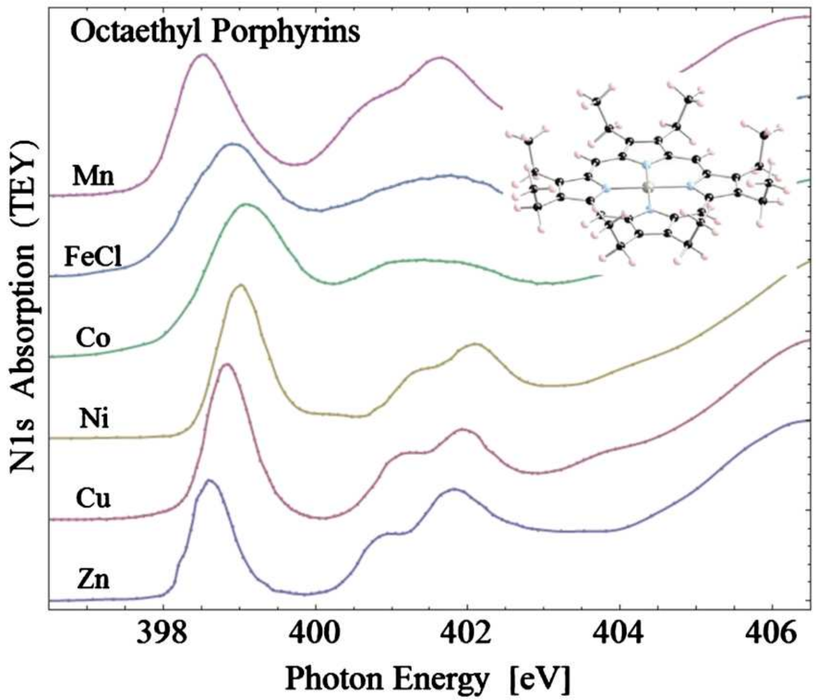
$Fe^{II}(bpy)_3$ in Water

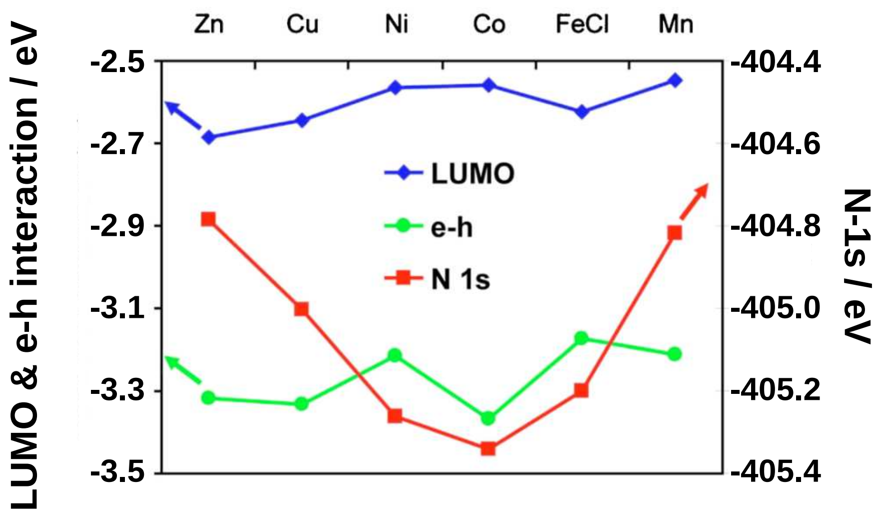


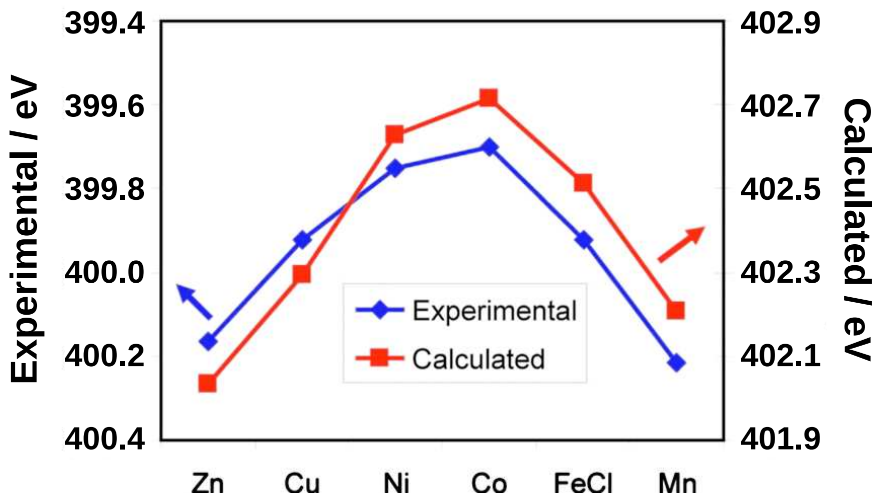


- **Ab inito DFT calculations, only energy axis has been shifted**
- **Bound-bound N-*1s* core-level transitions only (using ORCA)**

Core-Level Sensitivity to Valence Charge



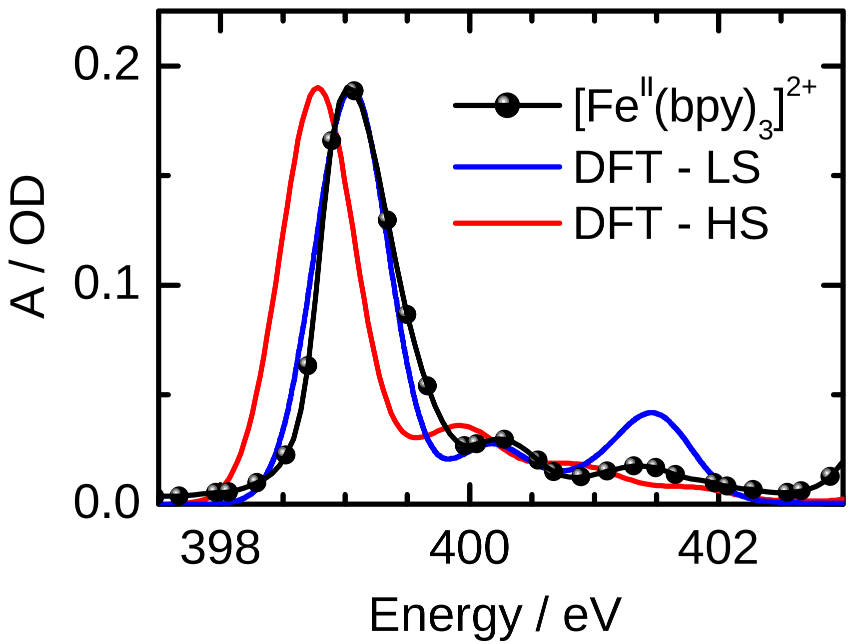


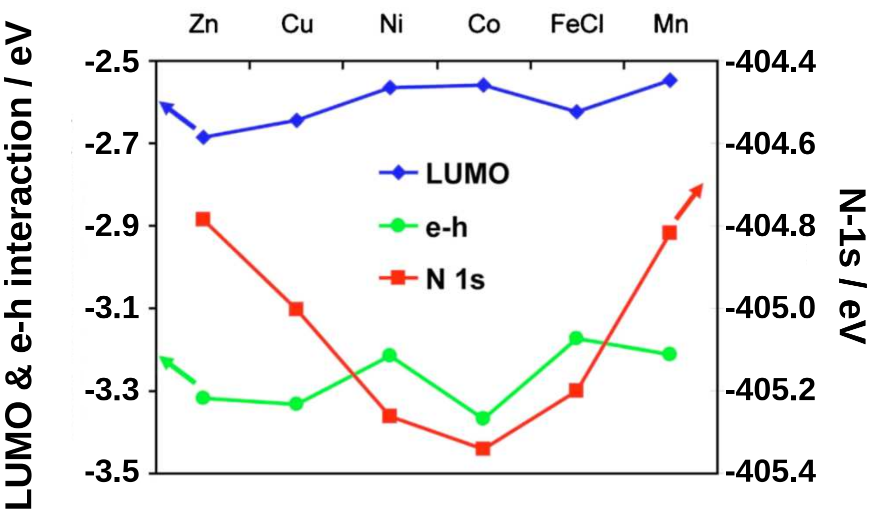


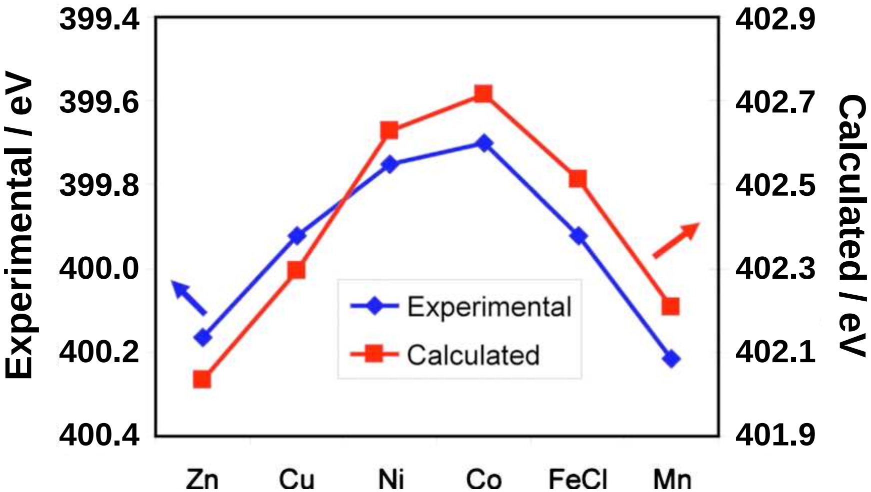
- Core-level transition shifts due to **core-level shift**
- Core-level energy highly sensitive to **amount of valence charge**

García-Lastra et al. *JCP* **133**, 151103

Core-Level Sensitivity to Valence Charge



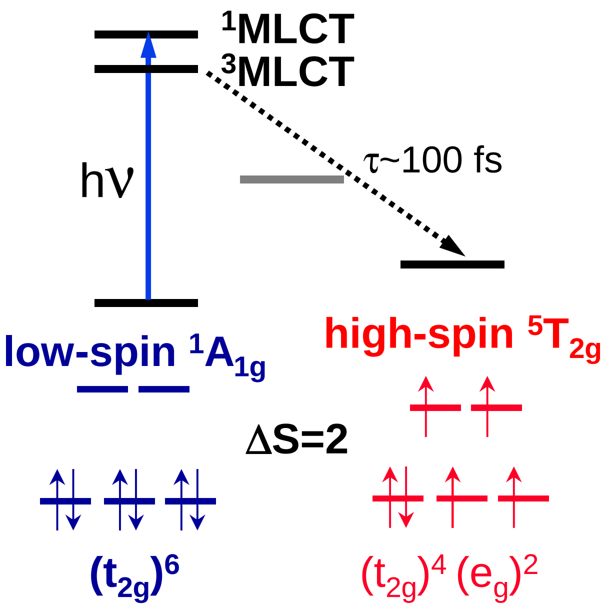


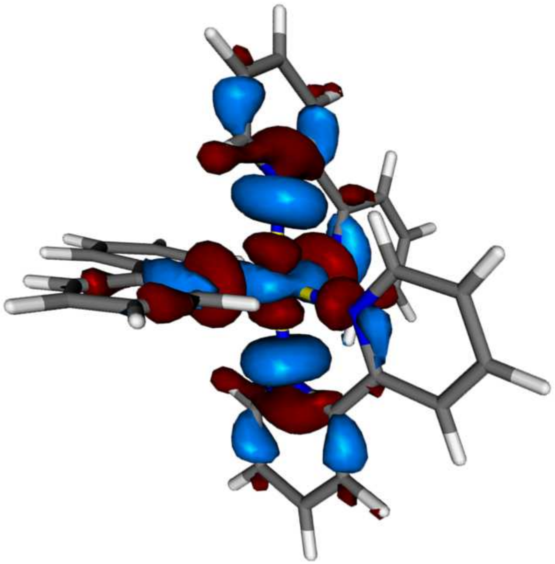


- 0.2eV **core-level shift** to higher energy → **more charge** on nitrogen
- Spectral gear box amplifies spectral shifts in addition to valence charge changes on target atom

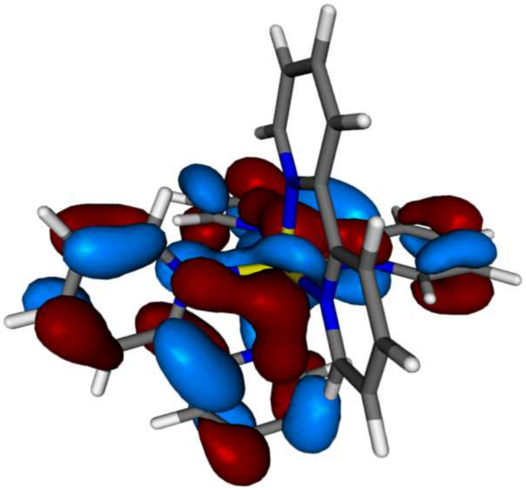
García-Lastra et al. *JCP* **133**, 151103

High-Spin Valence Charge Distribution



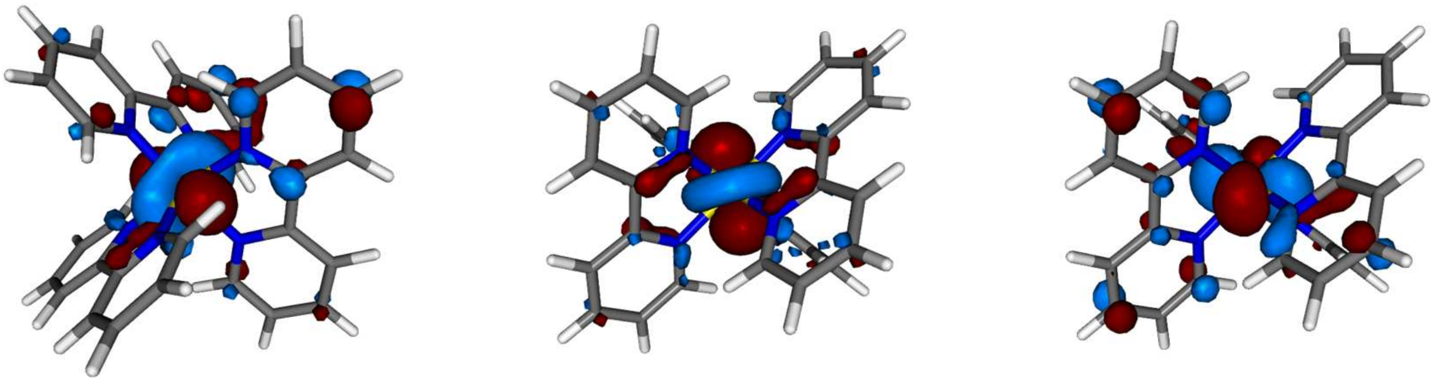


$^{5}T_2$ HOMO

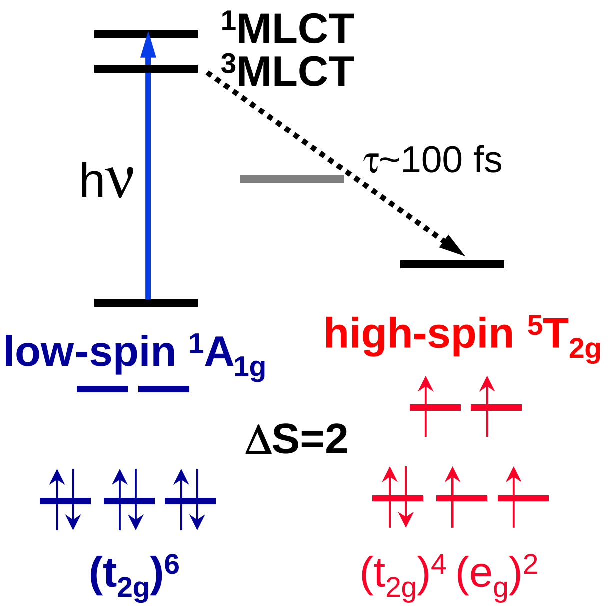


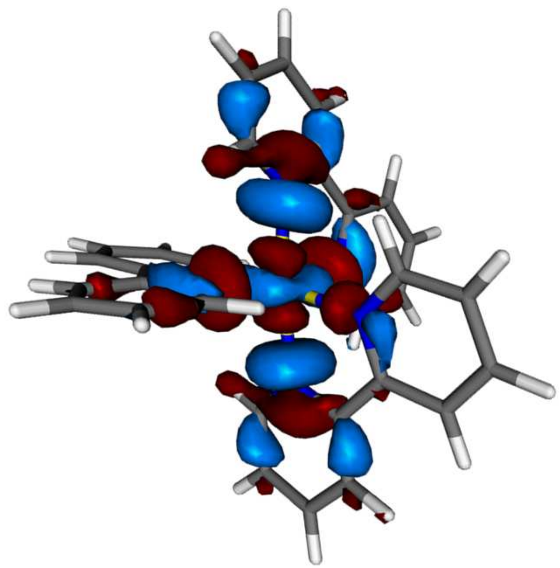
$^{5}T_2$ LUMO

Ground-state HOMOs

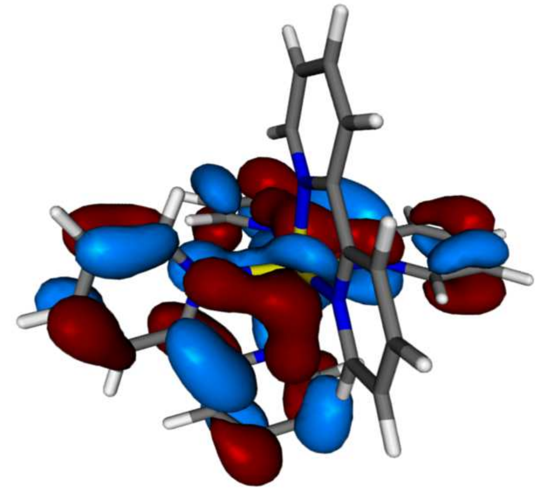


High-Spin Valence Charge Distribution





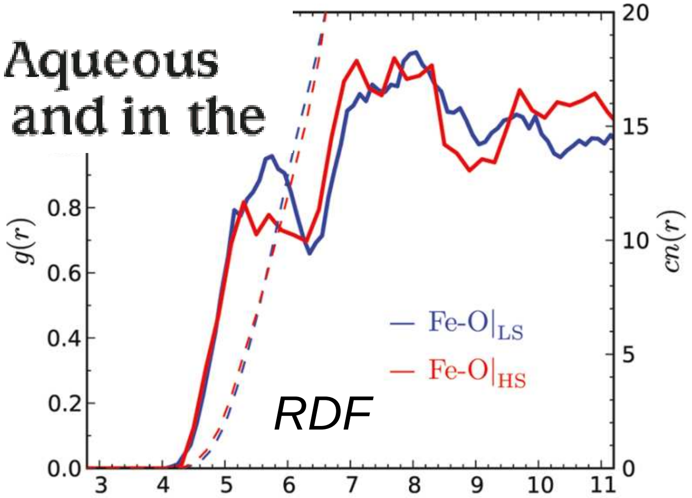
$^5T_2$ *HOMO*



$^5T_2$ *LUMO*

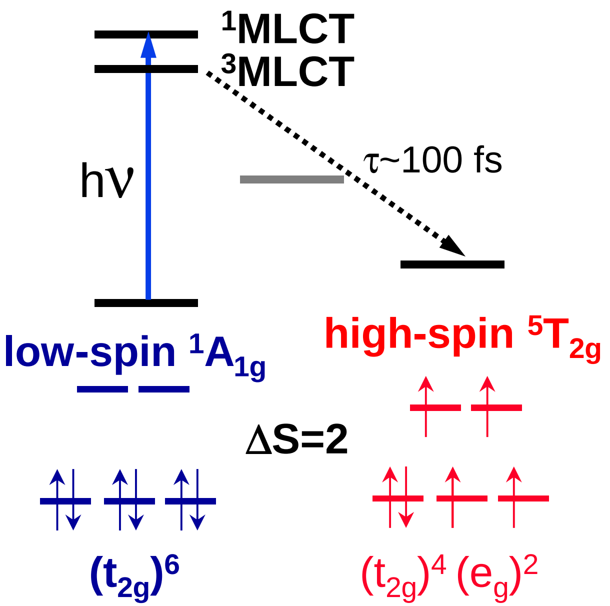
Ab Initio Molecular Dynamics Study of an Aqueous Solution of $[Fe(bpy)_3](Cl)_2$ in the Low-Spin and in the High-Spin States

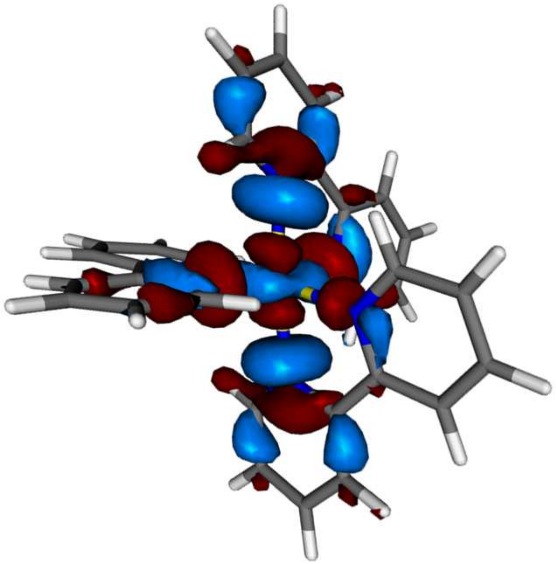
Latévi Max Lawson Daku* and Andreas Hauser *JPCL* **1**, 1830



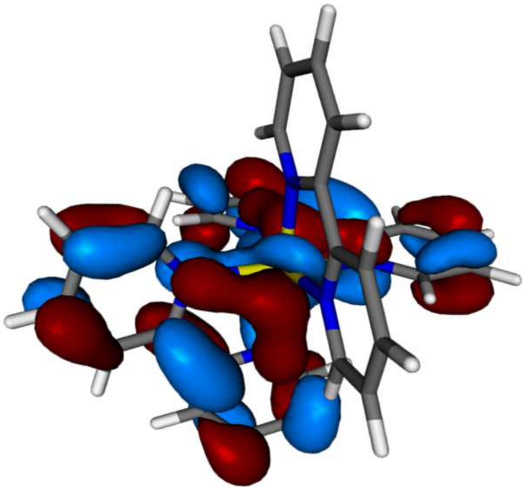
Increased mixing and delocalization of metal-ligand valence charge density promotes expelling solvent

High-Spin Valence Charge Distribution



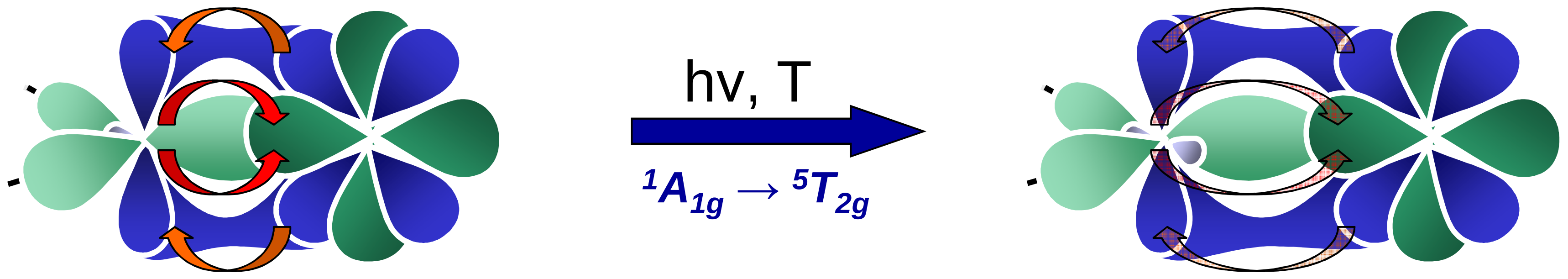


$^5T_2$ *HOMO*



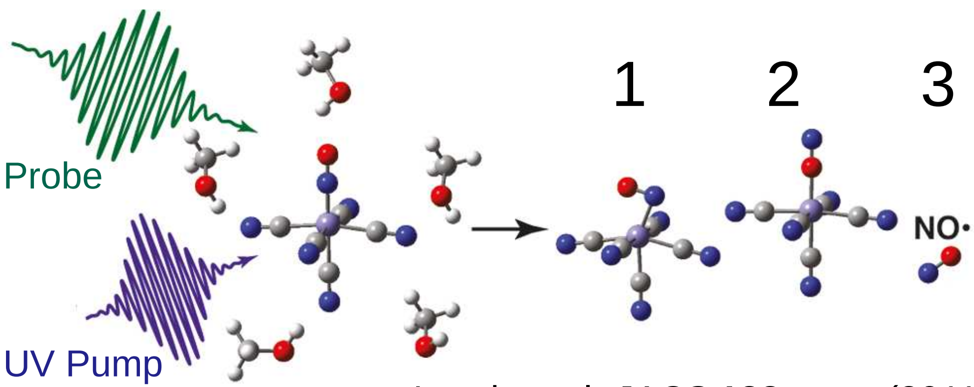
$^5T_2$ *LUMO*

Strong M-L orbital mixing → Structural change → **???**



Science Drivers – Hard X-rays

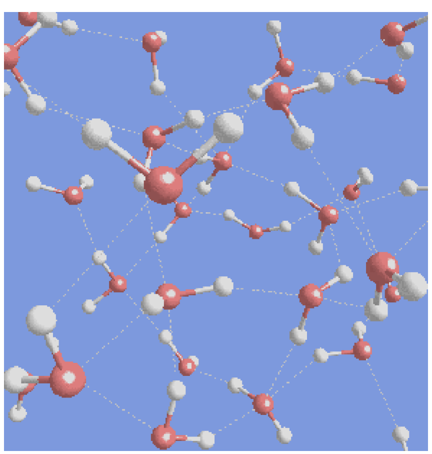
Reaction intermediates in (metal)organic chemistry



Lynch et al. *JACS* **133**, 5255 (2011)

- Unique characterization of transient valence charge density
- Atomic specificity
- Spin-sensitivity

Solute-Water Interactions



Enzymatic Activity and Cooperativity

UV-to-THz Tunability & CEP Control

Tunable laser system (highly robust and reliable)

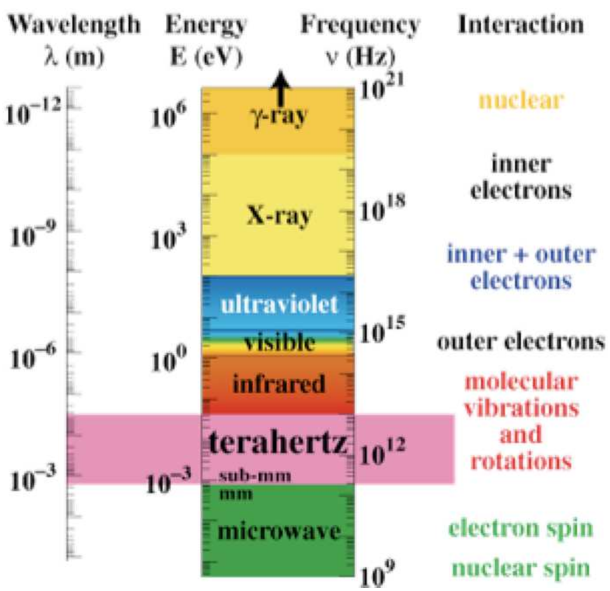
- Electronic excitation triggers over broad range with λ > 200nm ✓
- Mid-infrared generation for vibrational excitations with λ < 20um ✓
- Intense THz pulses reaching up to 15THz → needs insertion device ?

Carrier envelope stability (or better control) ?

- Coherent excitations at sub-cycle resolution
- Access to phase-sensitive phenomena
- Controlled excitations

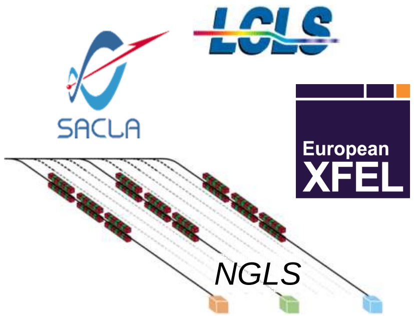
Laser pulse requirements

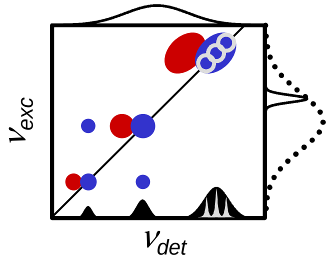
- 10fs (UV-Vis) to single-cylce (THz)
- 10s of uJ from UV to THz



Final Considerations & Summary

- ***Manpower and expertise will determine user involvement. Undogmatic approach desirable***
- ***Large tunability will ensure broad application spectrum***
- ***CEP control will drive new science, use of synergy effects to solve timing issues***
- ***X-ray science provides unique ways of studying matter beyond electronic excitations***
- ***What about 'Two-color' 2DFT spectroscopy?***





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Lindsey Jamula & Jim McCusker

Haidan Wen & Aaron Lindenberg
Dennis Nordlund & Anders Nilsson
Erzsi Szilagyi, Dan Daranciang & Tim Miller

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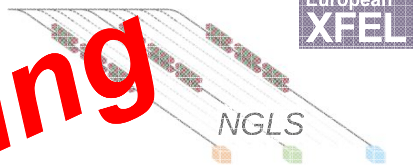

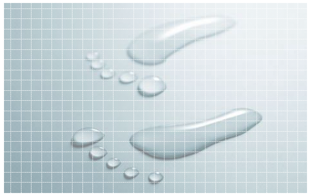

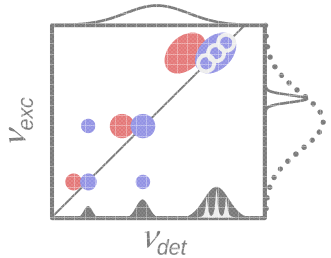

Thank you for listening

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