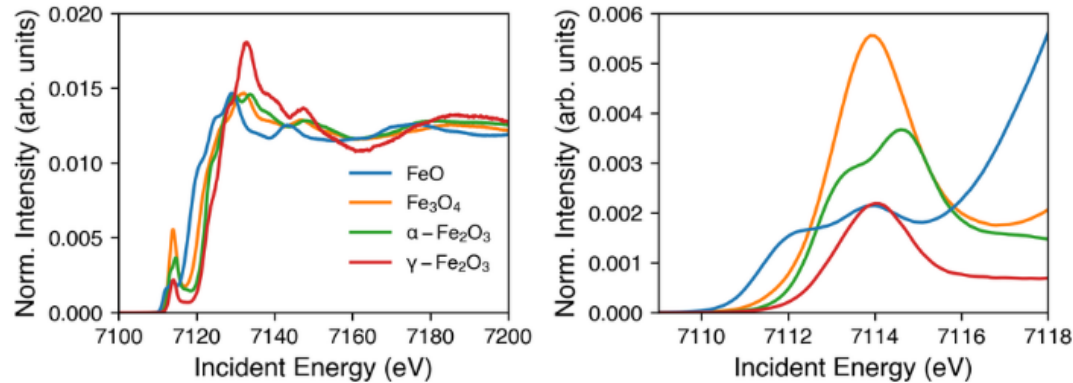




| The European Synchrotron

Experimental X-ray spectroscopy data are often evaluated by comparison to reference compounds.



Computational X-ray spectroscopy provides a deeper insight by *maximizing* the amount of information that can be extracted from the experimental data.

Specialized *ab initio* codes:

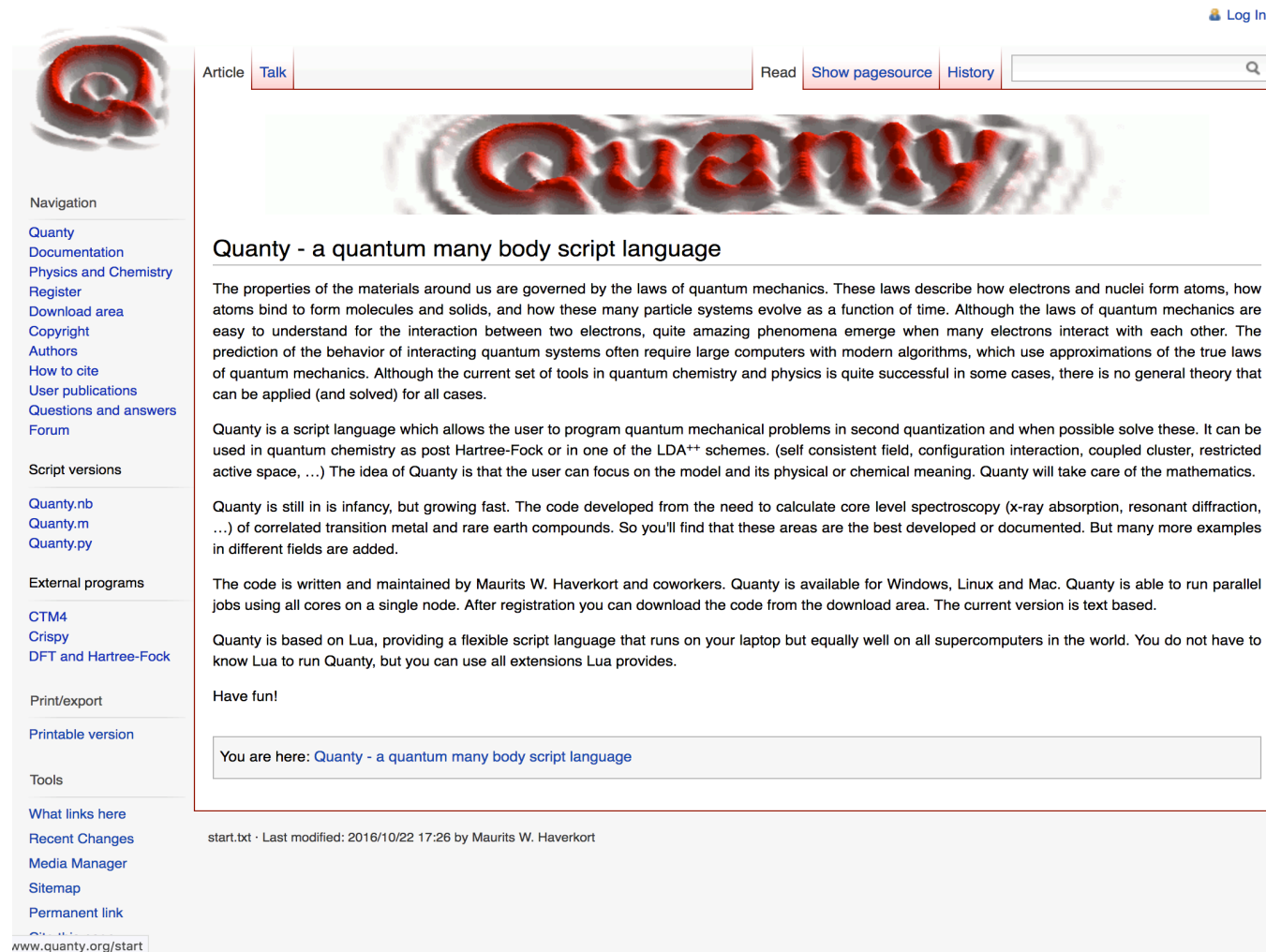
FEFF, FDMNES, OCEAN, ...

Generic *ab initio* codes:

ORCA, MOLCAS, ADF, Wien2k, VASP, Quantum ESPRESSO, ...

Semi-empirical multiplets codes:

Cowan's Codes (RCN), Quanty, Xclaim, XTLS, Hilbert++, ...



The screenshot shows the homepage of the Quanty website. At the top right, there is a 'Log In' button. Below it, there are navigation tabs for 'Article' and 'Talk', and a search bar with 'Show pagesource' and 'History' options. The main header features a large, stylized 'Quanty' logo in red and white. The main content area is titled 'Quanty - a quantum many body script language'. It contains three paragraphs of text describing the software's capabilities and development. A navigation sidebar on the left lists various links such as 'Quanty', 'Documentation', 'Physics and Chemistry', 'Register', 'Download area', 'Copyright', 'Authors', 'How to cite', 'User publications', 'Questions and answers', 'Forum', 'Script versions', 'External programs', 'Print/export', 'Tools', and 'What links here'. At the bottom of the page, there is a footer with the text 'start.txt · Last modified: 2016/10/22 17:26 by Maurits W. Haverkort'.

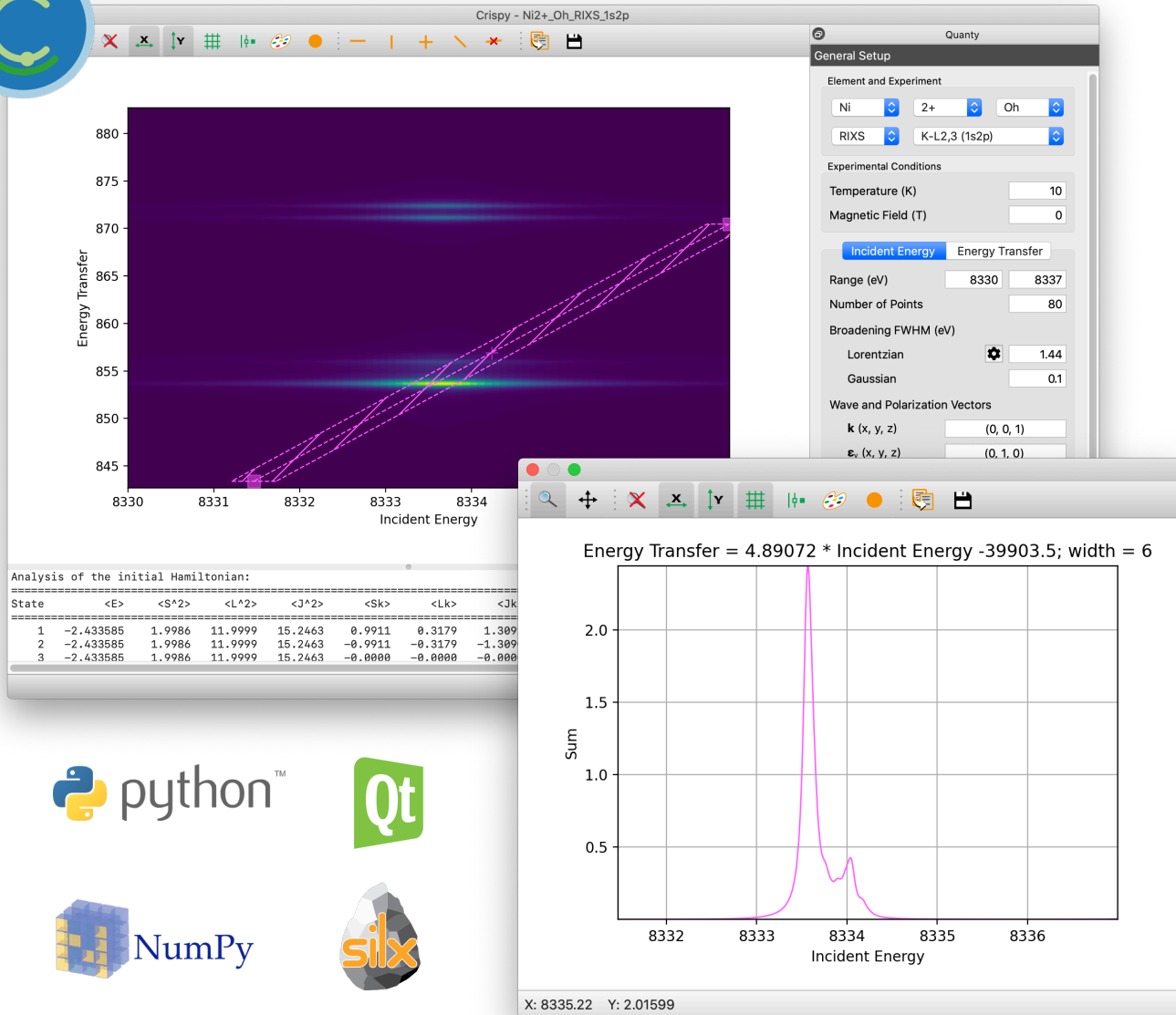
<http://quandy.org>

Developed by **Maurits Haverkort** at Heidelberg University.

Quanty is a powerful and versatile library, but...

- You will have to write code to perform calculations.
- The program is very forgiving, and it can take a long time to spot an error.

CRISPY: USER INTERFACE FOR MULTIPLIET CALCULATIONS



crispy + esrf

Calculations:

- transition metals, lanthanides, and actinides
- XAS, XMCD, X(M)LD, XES, XPS, and RIXS
- a large number of edges
- O_h , D_{4h} , C_{3v} , T_d , and D_{3h} symmetries

Additional features:

- logging console to display the progress
- dialog showing the details of a calculation
- interactive broadening using FFT
- save and load functionality
- easy-to-use installers for Windows and macOS
- Jupyter notebook interface



SEMI-EMPIRICAL MULTIPLETS: HAMILTONIAN

$$H = \underbrace{H_{kin} + H_{en} + H_{ee} + H_{so}}_{\text{Free ion (spherical)}} + \underbrace{H_{cf}}_{\text{Crystal Field}} + \underbrace{H_{hyb}}_{\text{Hybridization}} + \underbrace{H_{Zeeman}}_{\text{Magnetic Field}} + \underbrace{H_{ex}}_{\text{Exchange}}$$

$$H_{kin} = - \sum_i \frac{\hbar^2 \nabla_i^2}{2m}$$

Kinetic energy of the electrons

$$H_{en} = - \sum_i \sum_I \frac{Z_I e^2}{|r_i - R_I|}$$

Electron–nuclear interaction

$$H_{ee} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|r_i - r_j|}$$

Electron–electron interaction

$$H_{so} = \sum_i \xi(r_i) l_i \cdot s_i$$

Spin–orbit interaction

$$H_{cf} = \sum_{k=0}^{\infty} \sum_{m=-k}^k r^k A_{k,m} C_{k,m}(\theta, \phi)$$

Crystal field potential

Electronic repulsions: direct and exchange integrals

The Slater radial integrals are reduced from their Hartree–Fock values using empirical reduction factors.

$$0.7 \leq \kappa \leq 0.9 \quad \text{ionic character}$$

$$0.5 \leq \kappa \leq 0.6 \quad \text{covalent character}$$

Spin-orbit coupling constants

They are usually close to the Hartree–Fock atomic values.

Crystal field parameters

Initial values are usually taken from EPR, optical absorption, or ab initio calculations

10Dq for octahedral symmetry (O_h)

Dq, Ds, Dt with a tetragonal distortion (D_{4h})

Ligand field (charge transfer, hybridization) parameters

Many ad hoc parameters: $\Delta, U_{dd}, U_{pd}, V(e_g), V(t_{2g})$

- 1) Calculating the $L_{2,3}$ XAS spectrum of NiO.
- 2) Following spin transitions in iron compounds.
- 3) Application of the XMCD sum-rules.
- 4) Crystal field and covalency effects in uranates.

Always press Return (Enter) after changing a value in any of the input boxes.

Experimental Conditions

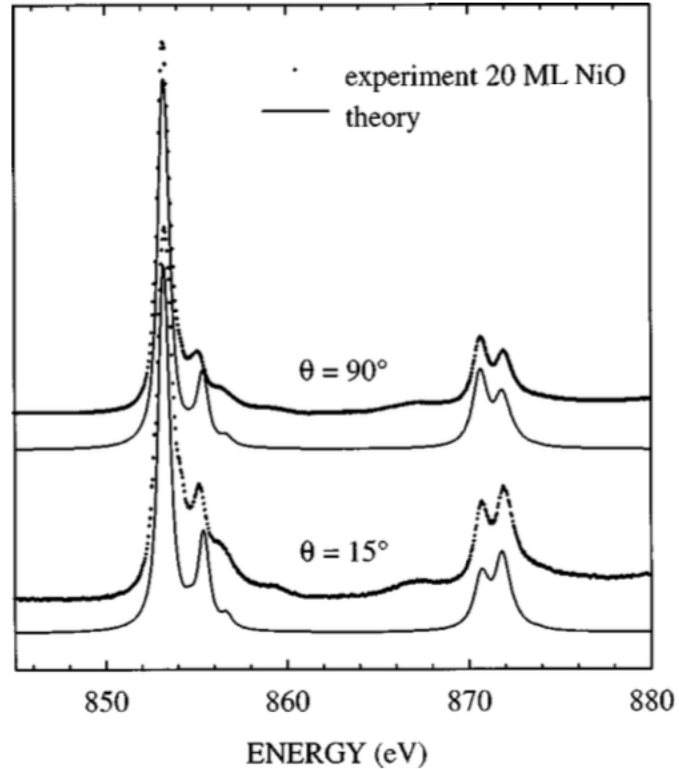
Temperature (K)

Any modification to the combo boxes will reset all parameters to default values.

Element and Experiment

Fe
3+
C3v
XAS
L2,3 (2p)

Calculating the $L_{2,3}$ XAS Spectrum of NiO



Experimental details:

- 20 monolayer NiO(100) thin film
- temperature ($T = 298$ K)
- $\theta = 90^\circ$ normal incidence

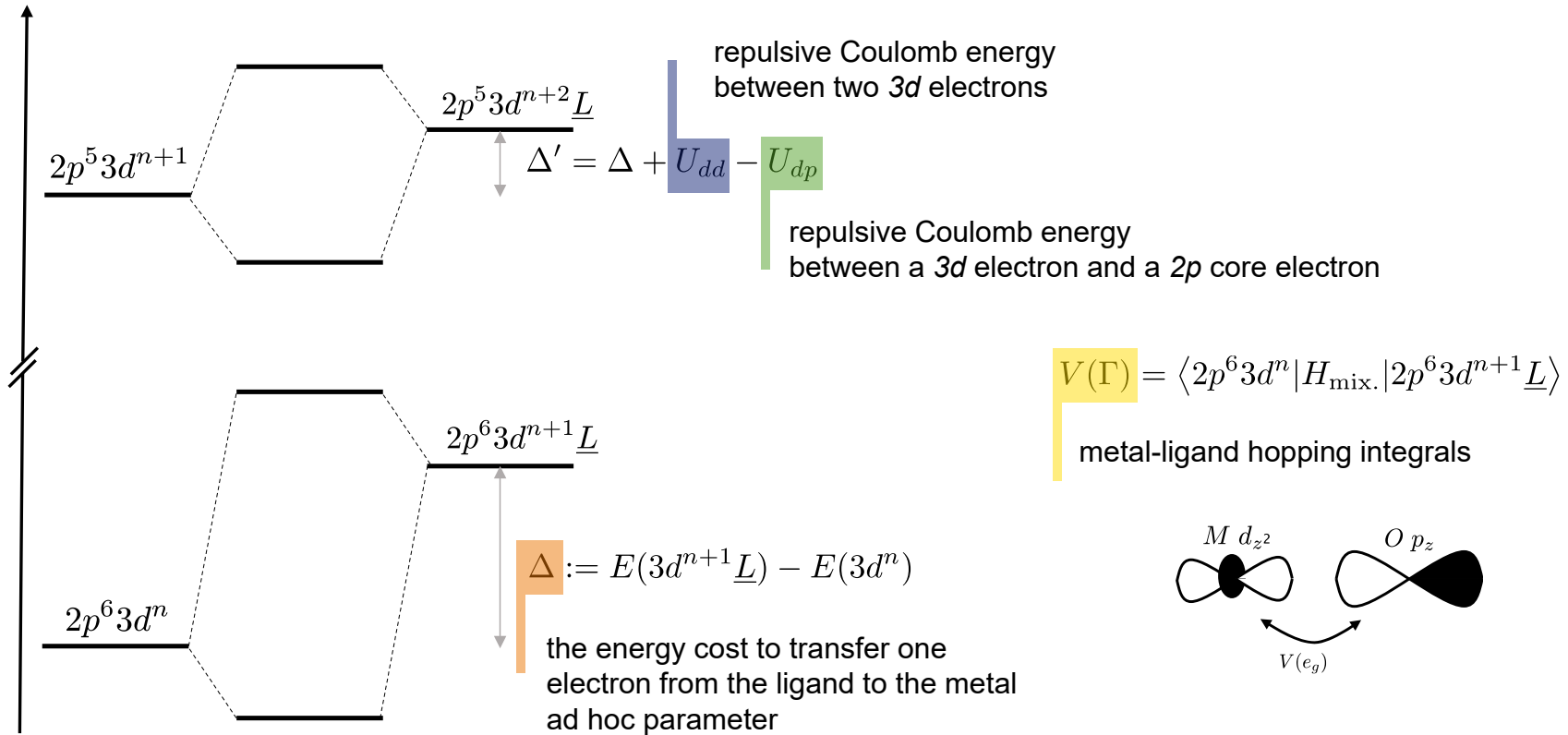
Measured spectrum:

<http://bit.ly/multiplets>

Alders et al., Phys. Rev. B, 1998, 57 (18), 11623–11631

- 1) Calculate the spectrum using the default parameters but increase the Gaussian broadening to 0.4. Identify the L_2 and L_3 edges in the calculated spectrum.
- 2) Run a calculation with the scaling of the 2p spin orbit coupling constant, $\zeta(2p)$, set to 0.5. After the calculation finishes, set this value back to 1.0, and run a second calculation with the 3d spin orbit coupling, $\zeta(3d)$ set to 0.5. Which interaction affects the most the energy separation between the L_2 and L_3 edges?
- 3) Change the default scaling of the Slater integrals (κ) to 0.6, 0.4, and 0.2 and rerun the calculation. Overlay the four spectra to see the evolution of the main peak and its high energy shoulder when the scaling parameter is decreased.

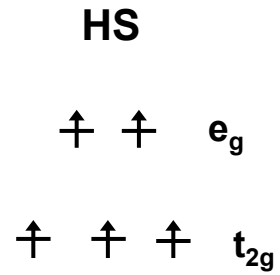
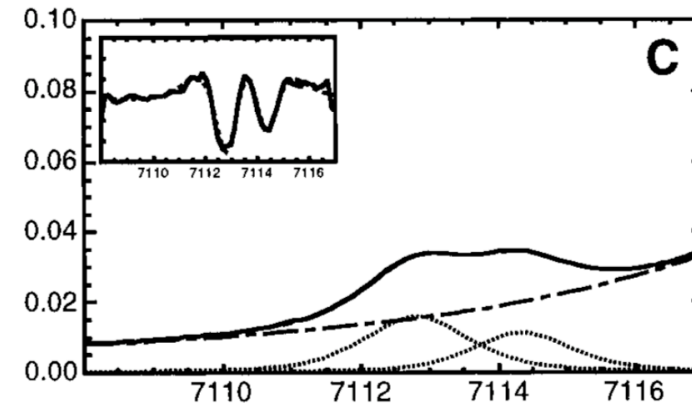
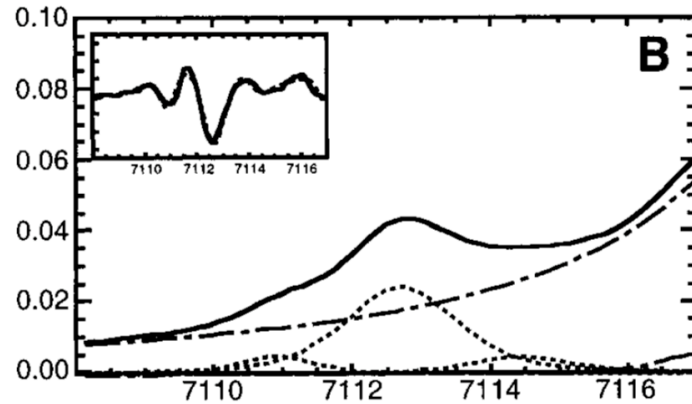
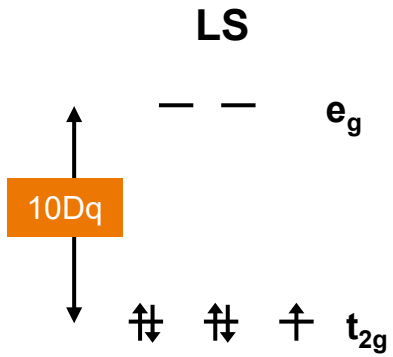
Proper treatment of hybridization requires more than one electronic configuration.



- 1) Load the experimental spectrum (Tools → Load experimental data) from the NiO folder.
- 2) Run a calculation using the following parameters:
 - $\kappa = 0.9$, $U(3d,3d) = 7.5$ eV, $U(2p,3d) = 8.5$ eV (*Atomic*)
 - $10Dq(3d) = 0.7$ eV (*Crystal Field*)
 - $\Delta(3d,Ld) = 4.3$ eV, $Veg(3d,Ld) = 2.0$ eV, $Vt2g(3d,Ld) = 1.0$ eV, $10Dq(Ld) = 1.4$ eV (*3d-Ligands Hybridization (LMCT)*)
- 3) Repeat the above calculation while varying Δ between 0.0 and 10.0 eV. Notice the changes in the number of the metal 3d and the ligand electrons ($\langle N_{3d} \rangle$ and $\langle N_{Ld} \rangle$ in the logging window). What happens if Δ is negative?
- 4) Try to get a better agreement with the experimental spectrum by varying the crystal field parameters, $10Dq(3d)$ and $10Dq(Ld)$, and the hopping integrals, $Veg(3d,Ld)$ and $Vt2g(3d,Ld)$.

Following Spin Transitions in Iron Compounds

FOLLOWING SPIN TRANSITION IN IRON(III) COMPOUNDS



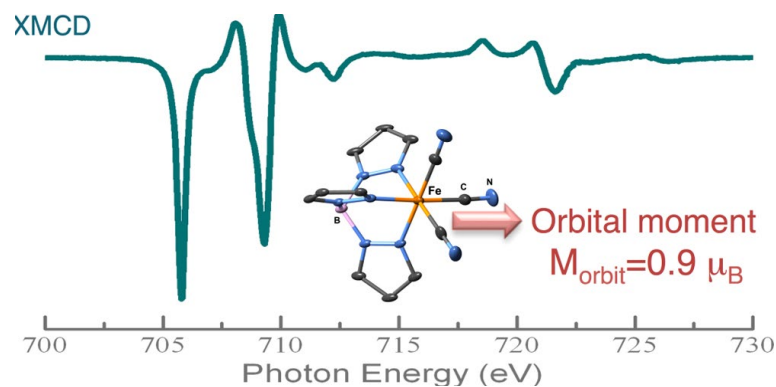
Westre et al., J. Am. Chem. Soc., 1997, 119 (27), 6297–6314.

- 1) Write down the electronic configuration of Fe³⁺. Show that there are two ways to fill the 3d orbitals, leading to a high spin ($S = 5/2$) and a low spin ground state ($S = 1/2$).
- 2) Run two K pre-edge calculations for Fe³⁺ in an octahedral crystal field, one with $10Dq$ set to 2.0 eV and 3.3 eV.
- 3) Change the $10Dq$ value from 2.6 to 3.6 eV in steps of 0.1 eV. At what value do you observe the spin transition?

Application of the XMCD Sum-Rules

Large Orbital Magnetic Moment Measured in the $[\text{TpFe}^{\text{II}}(\text{CN})_3]^-$ Precursor of Photomagnetic Molecular Prussian Blue Analogues

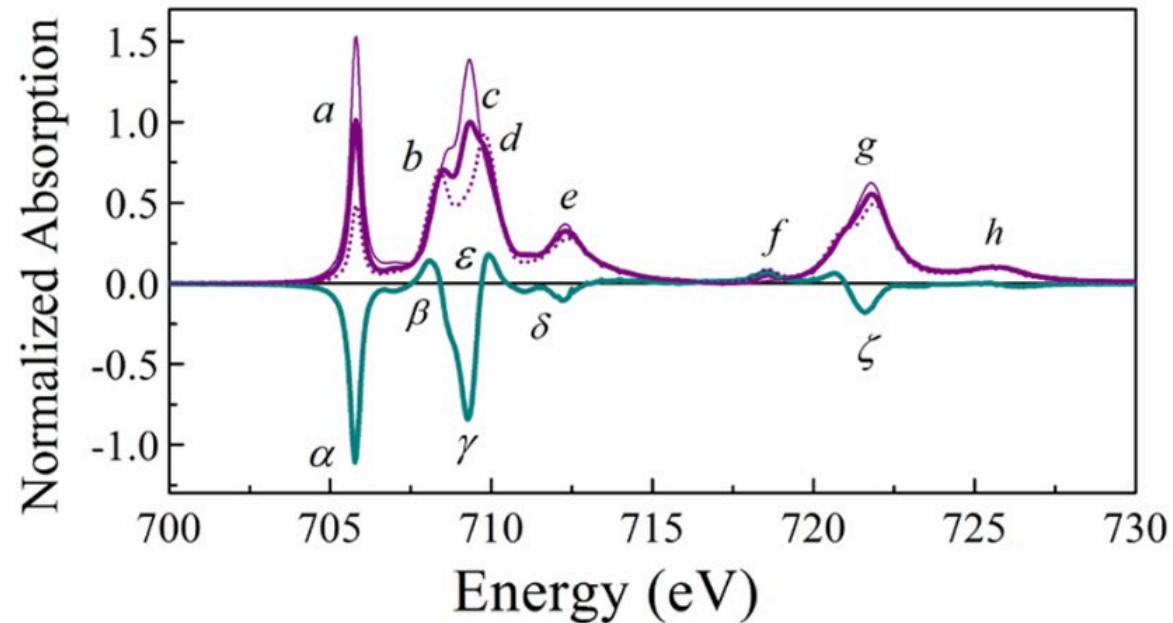
Sadaf Fatima Jafri,[†] Evangelia S. Koumoussi,^{‡,§,||} Philippe Saintcavit,^{†,⊥} Amélie Juhin,[†] Vivien Schuler,[†] Oana Bunău,[†] Dmitri Mitcov,^{§,||} Pierre Dechambenoit,^{§,||} Corine Mathonière,^{¶,‡} Rodolphe Clérac,^{§,||} Edwige Otero,[⊥] Philippe Ohresser,[⊥] Christophe Cartier dit Moulin,^{#,@} and Marie-Anne Arrio^{*,†}



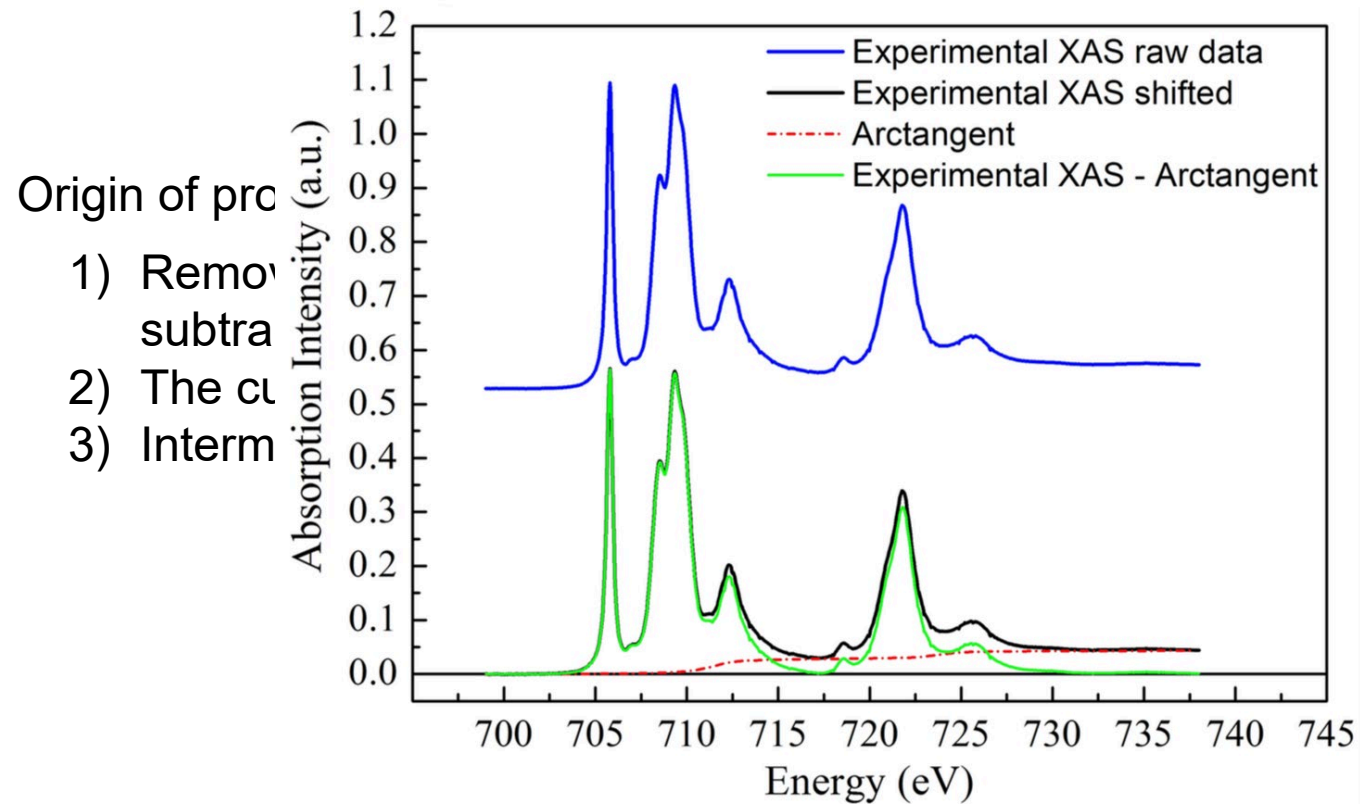
Jafri et al., *Inorg. Chem.*, 2016, 55 (14), 6980–6987

$$\mathbf{B} \parallel \hat{z} \quad m_{\text{orbit}} = -\langle L_z \rangle / \mu_B \quad m_{\text{spin}} = -g_0 \langle S_z \rangle / \mu_B = -2 \langle S_z \rangle / \mu_B$$

$$\langle L_z \rangle = \frac{4}{3} \frac{\int_{L_3+L_2} (\sigma^- - \sigma^+)}{\int_{L_3+L_2} (\sigma^- + \sigma^+)} \cdot n_h \quad \langle S_z \rangle + \frac{7}{2} \langle T_z \rangle = \frac{3 \int_{L_3} (\sigma^- - \sigma^+) - 2 \int_{L_3+L_2} (\sigma^- - \sigma^+)}{\int_{L_3+L_2} (\sigma^- + \sigma^+)} \cdot n_h$$

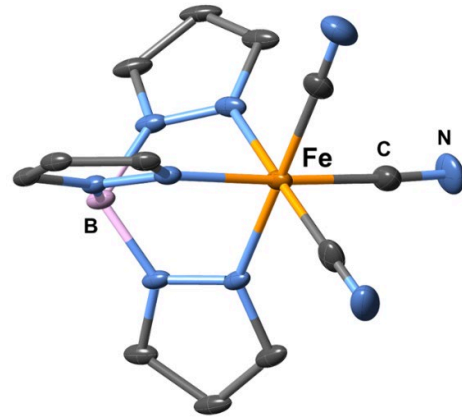


The sum rules can provide very useful information on the magnetic electronic structure by separating the orbit and spin parts of the magnetization.



Origin of pro
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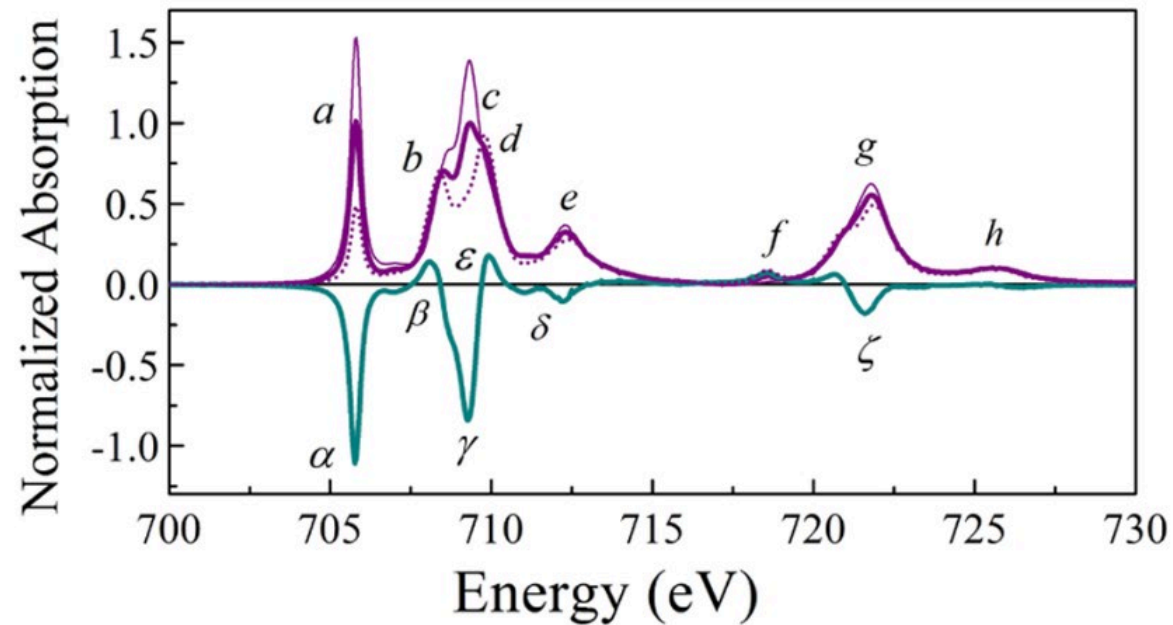
ne by
 spectrum.



Experimental details:

- the metal atom in FeTp is Fe^{3+}
- temperature ($T = 2 \text{ K}$)
- magnetic field ($B = 6.5 \text{ T}$)

Measured spectra: <http://bit.ly/multiplets>



- 1) Calculate the spectrum using the following parameters:
 - Lorentzian FWHM: 0.5 for L_3 and 1.0 for L_2
 - Gaussian FWHM: 0.24
 - scale factors: $F_k = G_k = 0.7$, $\zeta = 1.0$

- 2) After the first calculation, open the “Details” dialog and normalize the spectrum to the maximum.

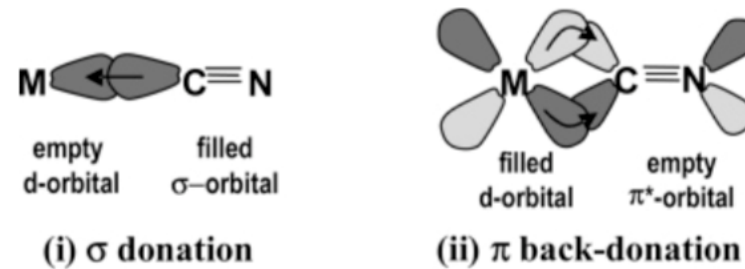
- 3) Increase the $10Dq$ value in steps of 0.5. Note the effect on the calculated spectrum. Are there any feature that start to appear in the spectrum for larger $10Dq$? Follow the changes in the expectation value of the $\langle S_z \rangle$ operator.

- 4) Note the expectation values of the spin (S), orbital (L), and magnetic dipole (T) operators for $10Dq = 2.8$ eV. How do they compare with the calculations from the original publication?

	$\langle S_z \rangle$	$\langle L_z \rangle$	$\langle T_z \rangle$
Jafri <i>et al.</i>	-0.1786	-0.8521	-0.0523

1) Add the metal-ligand hybridization charge transfer (MLCT) term with the following parameters:

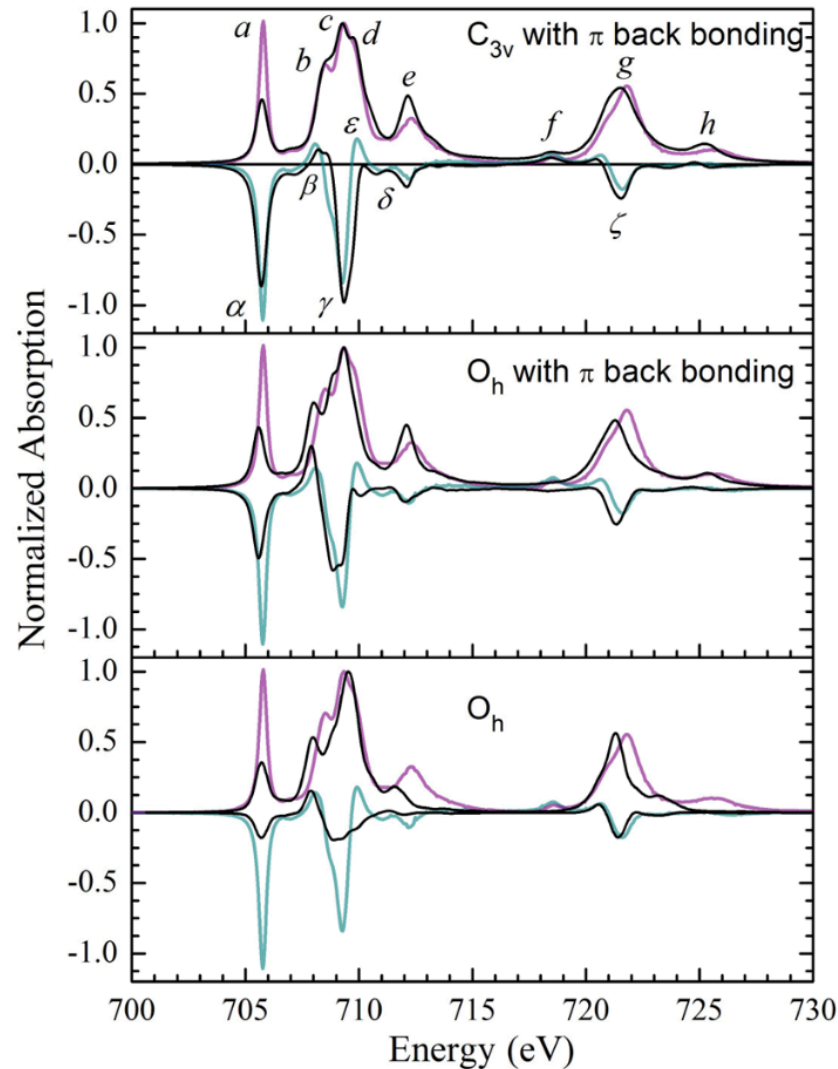
$$\Delta_i = 3.0, \Delta_f = 3.4, V(e_g) = -0.8, V(t_{2g}) = 1.8.$$



Hocking et al., J. Am. Chem. Soc., 2006, 128 (32), 10442–10451

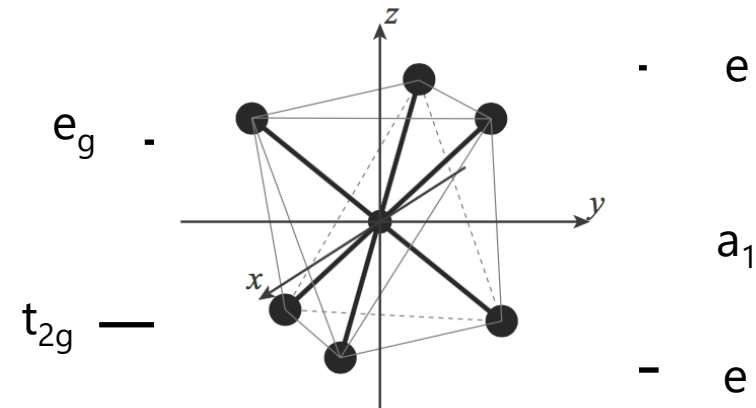
2) Note the additional features appearing in the spectrum and the changes in the expectation values; compare them with the ones from the original publication.

	$\langle S_z \rangle$	$\langle L_z \rangle$	$\langle T_z \rangle$
Jafri <i>et al.</i>	-0.1704	-0.7754	-0.0594



1) Change the symmetry to C_{3v} and rerun the calculation using the following parameters for the crystal field:

- $Dq = 0.28$ eV ($\equiv 10Dq = 2.8$ eV)
- $D\sigma = 0.07$ eV
- $D\tau = 0.12$ eV



2) Did you manage to reproduce the feature ***f***?

Crystal field and covalency effects in uranates

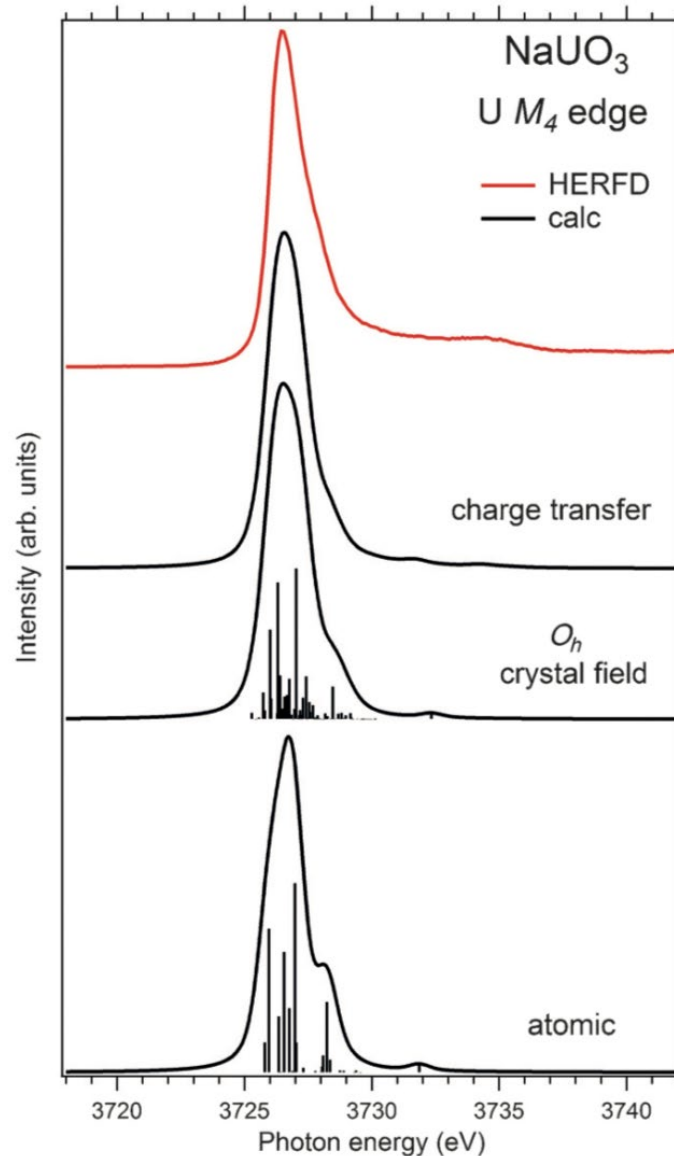
■ X-ray Absorption Spectroscopy

Crystal-Field and Covalency Effects in Uranates: An X-ray Spectroscopic Study

Sergei M. Butorin,^{*,[a]} Kristina O. Kvashnina,^[b, f] Anna L. Smith,^[c] Karin Popa,^[d] and
Philippe M. Martin^[e]

Abstract: The electronic structure of U^V- and U^{VI}-containing uranates NaUO₃ and Pb₃UO₆ was studied by using an advanced technique, namely X-ray absorption spectroscopy (XAS) in high-energy-resolution fluorescence-detection (HERFD) mode. Due to a significant reduction in core-hole lifetime broadening, the crystal-field splittings of the 5f shell were probed directly in HERFD-XAS spectra collected at the U3d edge, which is not possible by using conventional XAS. In addition, the charge-transfer satellites that result from U5f–O2p hybridization were clearly resolved. The crystal-

field parameters, 5f occupancy, and degree of covalency of the chemical bonding in these uranates were estimated by using the Anderson impurity model by calculating the U3d HERFD-XAS, conventional XAS, core-to-core (U4f–3d transitions) resonant inelastic X-ray scattering (RIXS), and U4f X-ray photoelectron spectra. The crystal field was found to be strong in these systems and the 5f occupancy was determined to be 1.32 and 0.84 electrons in the ground state for NaUO₃ and Pb₃UO₆, respectively, which indicates a significant covalent character for these compounds.



1) Calculate the *atomic* M₄ spectrum for U⁵⁺ using the following parameters:

- scale factors: $F_k = G_k = 0.7$
- Lorentzian FWHM: 0.35 eV
- Gaussian FWHM: 0.8 eV

2) Add a *crystal field* contribution with the Wybourne's parameters:

- $B_{40} = 2.03$ eV
- $B_{60} = 0.17$ eV

3) Finally, add the *hybridization* term with the ligands (LMCT):

- $\Delta = 4.0$ eV,
- $U(5f,5f) = 3.5$ eV
- $U(3d,5f) = 6.0$ eV
- $V_i = 1.2$ eV, and $V_f = 0.9$ eV