Crystal field scheme of UO$_2$ measured with NIXS

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Motivation:

- 5$f$-electrons have a large orbital degree of freedom
  - Special bonding character and new phases
- It is crucial to know which 5$f$-states are active in the GS
- Standard techniques as e.g. INS are hampered by the strong 5$f$-hybridization
- UO$_2$ is one of the few actinide oxides where INS could measure the CF excitations
  
  G. Amoretti et al., PRB 40, 1856 (1989)
  R. Caciuffo et al., PRB 84, 104409 (2011)
- Calculations yield larger CF splittings than INS
  
- Higher multipoles in NIXS at the U$_4$O$_{4,5}$ edges (5$d$ $\rightarrow$ 5$f$) yield GS symmetry
  & give insight to the UO$_2$ CF scheme
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What is the principle of NIXS?

- **Double differential cross section**
  - Physics in $S(q, \omega)$

- **Electron photon interaction**
  - Beyond weak field approximation

\[
\frac{d^2\sigma}{d\Omega \cdot dh}\omega = \frac{\omega_{\text{out}}}{\omega_{\text{in}}} \left( \frac{e^2}{2m_e} \right)^2 |\epsilon_{\text{out}}^* \cdot \epsilon_{\text{in}}|^2 \sum_{|l|} |(f | T | i)\rangle|^2 \delta(E_f - E_i - \hbar \omega)
\]

\[
H = \sum_{j=1}^{N} \frac{p_j^2}{2m_e} + \frac{e}{m_e} p_j \cdot A + \frac{e^2}{2m_e} A^2 + \ldots
\]

- **Thomson**
  - Resonant
  - Non-resonant
What is the principle of NIXS?

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Local projection of $T$:

Absorption/Emission: $p \cdot A$

$$T = \mu \cdot E \ e^{i k r}$$

Non-resonant: $A^2$

$$T = E \cdot E' \ e^{i(k-k')r}$$

Dipole approximation: $e^{ikr} \approx 1$

Large $|q|$: $q \cdot r > 1$

quantization axis changes from $E$ to $q$

Triangular condition: $|l_f - l_i| \leq k \leq l_f + l_i$

Parity rule: $l_f + l_i + k = \text{even}$
What is the principle of NIXS?

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Features of NIXS:
- Photon in - photon out + no UHV with hard x-rays + bulk sensitive (>1µm) + no cleaving
- Non-resonant - low cross-section + "no" self-absorption + no intermediate state
- XAS final state + Element specific + directional dependence
- Large $|q|$ + Beyond dipole + more excitonic → atomic multiplet calculation + not dipole limited → >2 fold rotational symmetry (e.g. cubic)

see also cubic 4f: M. Sundermann et. al., EPL 117 17003 (2017) M. Sundermann et. al., PRL 120 016402 (2018)
**Discussion:** \( \text{INS (weak CF)} \Leftrightarrow \text{calculation (strong CF)} \)

**Weak CF:** INS finds \( V_4 = -123 \text{ meV} \quad V_6 = 26.5 \text{ meV} \)

- R. Caciuffo et al., PRB 84, 104409 (2011)
- P. Santini et al., Rev. Mod. Phys. 81, 807 (2009)

**Strong CF:** calculation finds \( V_4 = -410 \text{ meV} \quad V_6 = 25 \text{ meV} \)


**NIXS experiment: 5d\( \to \)5f**

**ID20 - RIXS spectrometer** (2013)

- G. van der Laan, L. Simonelli, G. H. Lander, R. Caciuffo

  *Single analyzer: Si(660) @ 2\( \theta \) = 140°*

  - \(|q| \approx 9.1 \text{Å}^{-1} \quad \Delta E \approx 0.65 \text{eV} \)
  - Experiment @ T = 300K since CF splittings are large

**INS: weak CF**

\( |q| \approx 9.1 \text{Å}^{-1} \quad \Delta E \approx 0.65 \text{eV} \)

\( 150-175 \text{meV} \)

**Ground state**

150-175meV

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Full multiplet calculation:

Atomic Coulomb interaction:

5f - 5f & 5d

40% reduction

GS multiplet = 86% $^3$H$_4$ + 13% $^1$G$_4$ + 1% $^3$F$_4$

RIXS parameters taken from:
Butorin et al., Anal. Chem. 85 11196 (2013)

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No free parameters left

Can we say something about the size of the CF splittings?
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Crystal-field states of $\text{UO}_2$ probed by directional dependence of nonresonant inelastic x-ray scattering

$V_4 = -125 \text{ meV} \sin(\phi)$

$V_6 = 125 \text{ meV} \cos(\phi)$

$V_4 = -122 \text{ meV}$ $V_6 = 28 \text{ meV}$

Strong CF parameters based on:


Weak CF parameters based on:


NIXS confirms INS CF scheme

J ≠ 4 mix in

Parameters based on:

Crystal field scheme of UO₂ measured with NIXS

Crystal-field states of UO₂ probed by directional dependence of nonresonant inelastic x-ray scattering

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Parameters based on:
G. Amoretti et al., PRB 40, 1856 (1989)

NIXS confirms INS CF scheme
modelling quantitative
Crystal field scheme of UO$_2$ measured with NIXS

- NIXS confirms the CF scheme of UO$_2$ from INS
- Presence of distinct O$_4$ and O$_5$ edges indicates a GS with pure $J=4$ (>90%)

- **5f CF ground state can be determined by NIXS (higher multipoles)**

- Method has previously been successfully applied to metallic 5f material see URu$_2$Si$_2$ in Sundermann *et al.* PNAS **113** 13989 (2016)

Thank you
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