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

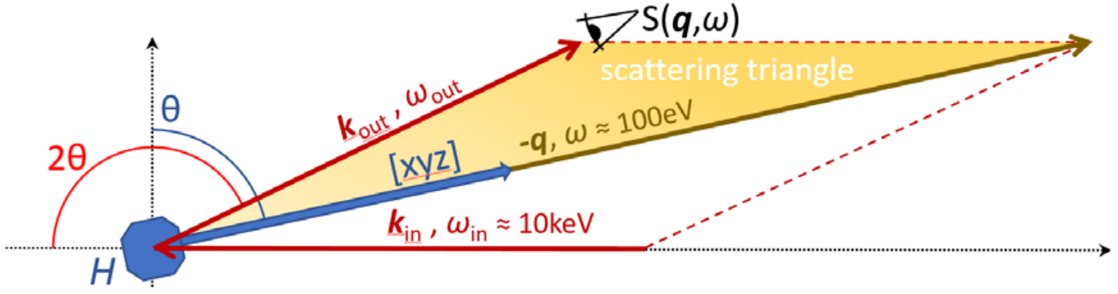
  G. Amoretti et al., PRB 40, 1856 (1989)

  R. Caciuffo et al., PRB 84, 104409 (2011)
- Calculations yield larger CF splittings than INS

  H.U. Rahman and W.A. Runciman, J. Phys. Chem Solids 27 1833 (1966)
- Higher multipoles in NIXS at the U $O_{4,5}$ edges ($5d \rightarrow 5f$) yield GS symmetry & give insight to the UO_2 CF scheme

Crystal field scheme of UO_2 measured with NIXS

What is the principle of NIXS?



$$\frac{d^2\sigma}{d\Omega\, d\hbar\omega} = \underbrace{\frac{\omega_{out}}{\omega_{in}}\left(\frac{e^{-2}}{2m_{e^-}}\right)^2 |\boldsymbol{\epsilon}^*_{out}\cdot\boldsymbol{\epsilon}_{in}|^2}_{\text{Thomson}} \underbrace{\sum_{|f\rangle}|\langle f|T|i\rangle|^2\, \delta(E_f - E_i - \hbar\omega)}_{S(\boldsymbol{q},\omega)}$$

$$H = \sum_{j=1}^{N} \frac{\boldsymbol{p}_j^2}{2m_{e^-}} + \underbrace{\frac{e^-}{m_{e^-}}\boldsymbol{p}_j\cdot\boldsymbol{A}}_{\text{resonant}} + \underbrace{\frac{e^{-2}}{2m_{e^-}}\boldsymbol{A}^2}_{\text{non resonant}} + \ldots$$

Double differential cross section

- ➢ Physics in S($\boldsymbol{q}$,ω)

Electron photon interaction

- ➢ Beyond weak field approximation

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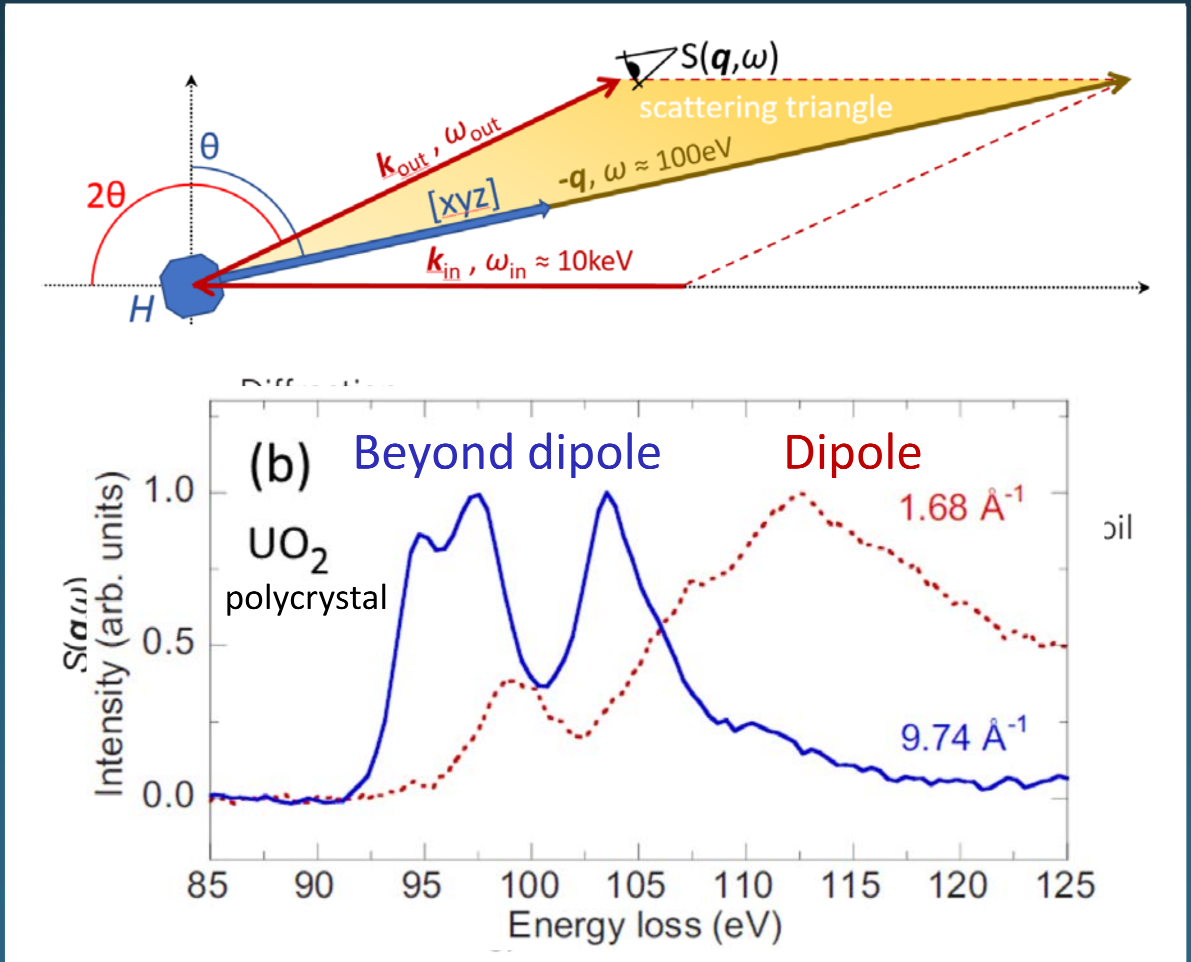
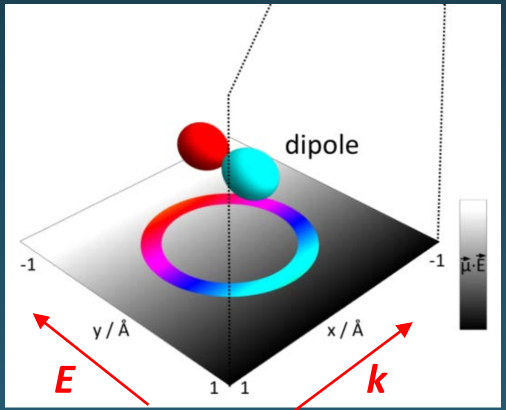


R. Caciuffo et al., PRB 81 195104 (2010); S. Huotari et al., Nature Materials 10 489 (2011)

Local projection of *T*:

Absorption/Emission: *p·A*

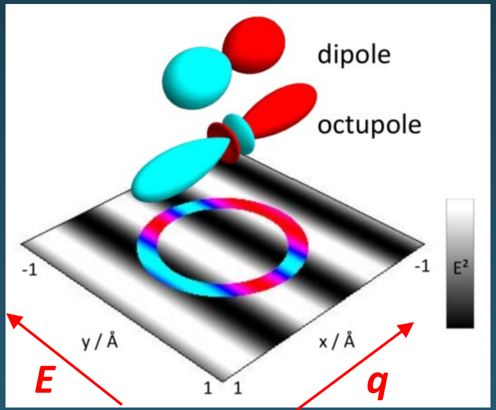
$$T = \boldsymbol{\mu} \cdot \boldsymbol{E}\, e^{i\boldsymbol{k}\boldsymbol{r}}$$



Dipole approximation: $e^{i\boldsymbol{k}\boldsymbol{r}} \approx 1$

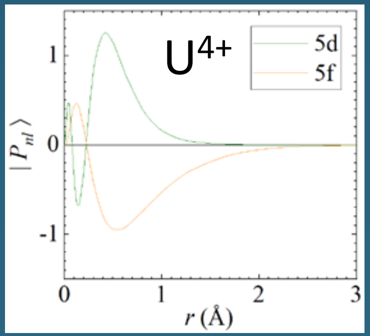
Non-resonant: A^2

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



Large $|\boldsymbol{q}|$: $\boldsymbol{q} \cdot \boldsymbol{r} > 1$

quantization axis changes from ***E*** to ***q***



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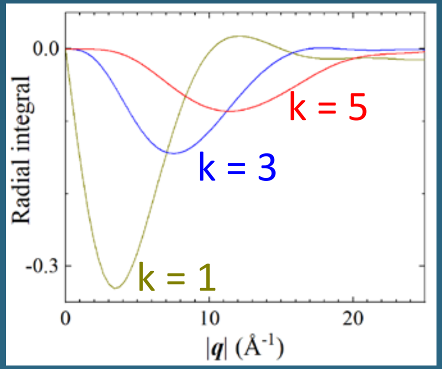

Triangular condition:
$|l_f - l_i| \le k \le l_f + l_i$

Parity rule:
$l_f + l_i + k$ = even

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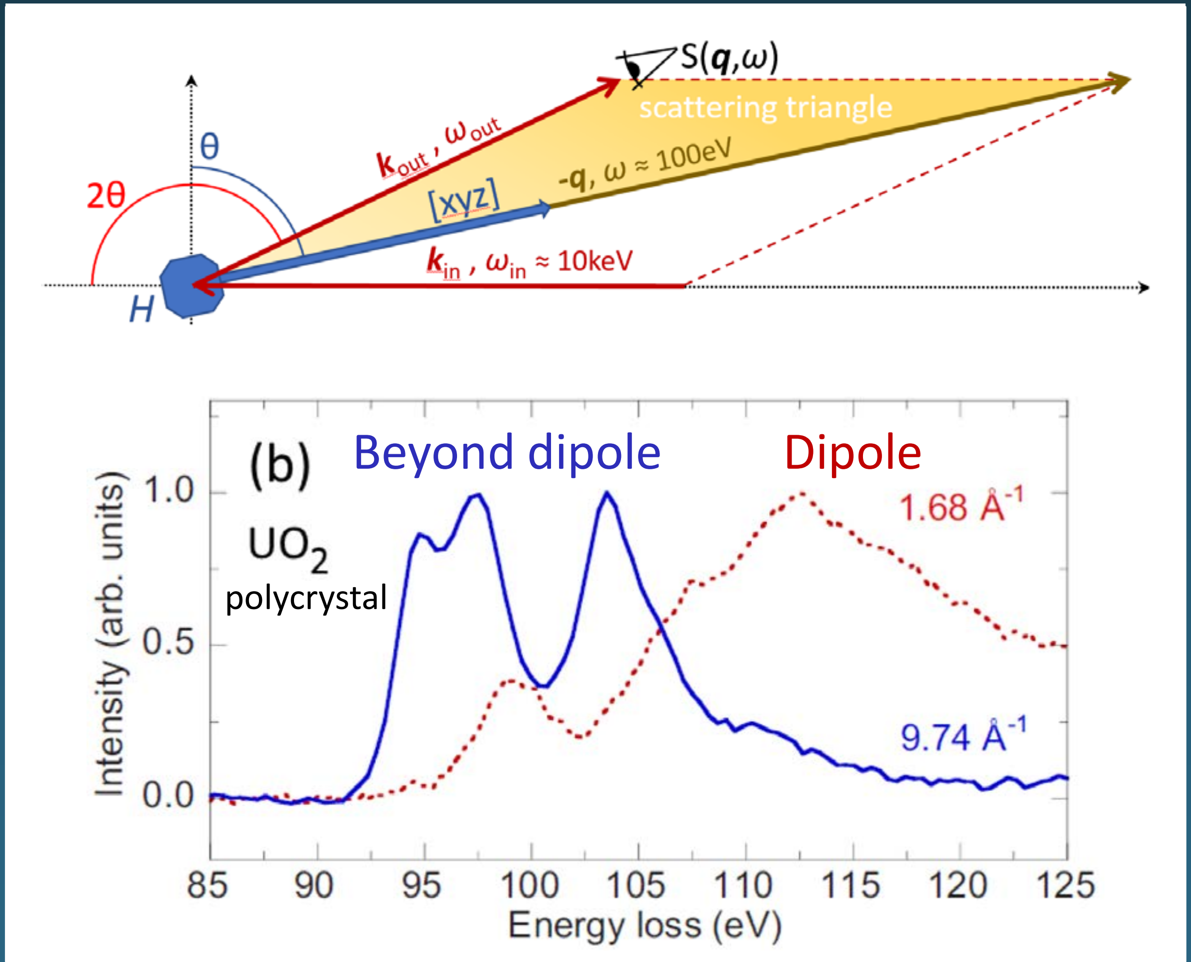

R. Caciuffo *et al.*, PRB **81** 195104 (2010)

Features of NIXS:

- Photon in - photon out with hard x-rays
  - + no UHV
  - + 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 4*f*: M. Sundermann *et. al.*, EPL **117** 17003 (2017)
M. Sundermann *et. al.*, PRL **120** 016402 (2018)

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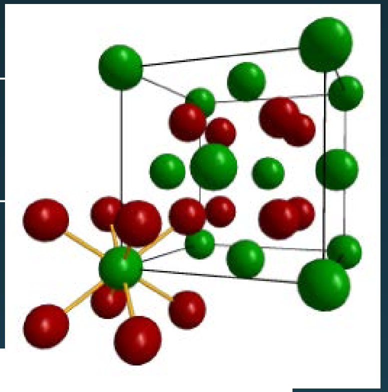
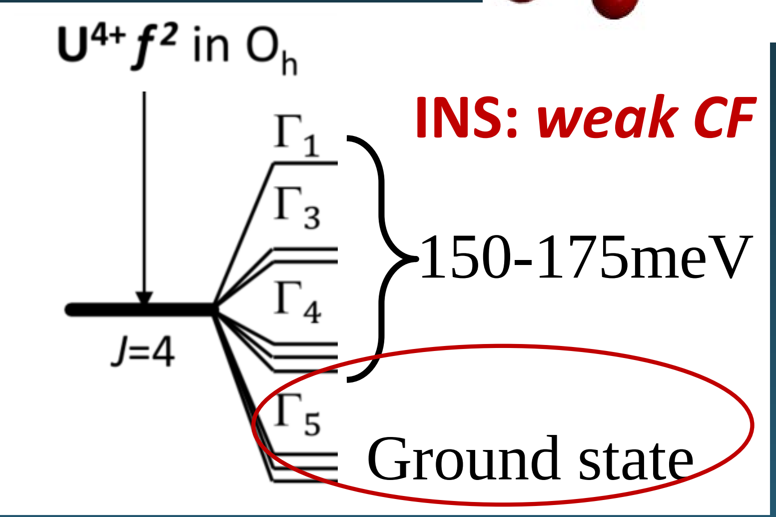


Discussion: INS (*weak CF*) ⇔ calculation (*strong CF*)

***Weak CF*: INS finds** V_4 = -123 meV V_6 = 26.5 meV

G. Amoretti *et al.*, PRB **40**, 1856 (1989)
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 meV V_6 = 25 meV

H.U. Rahman and W.A. Runciman, J. Phys. Chem Solids 27 1833 (1966)

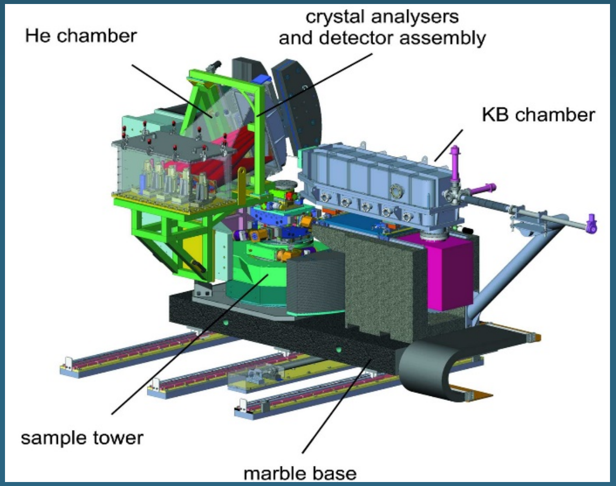
NIXS experiment: 5*d*→5*f*

ID20 - RIXS spectrometer (2013)

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

Single analyzer: Si(660) @ 2θ = 140°

- |q| ≈ 9.1Å^{-1} ΔE ≈ 0.65eV
- Experiment @ T = 300K since CF splittings are large



M. Moretti Sala *et al.*, J. Syn. Rad. **25** 580 (2018)

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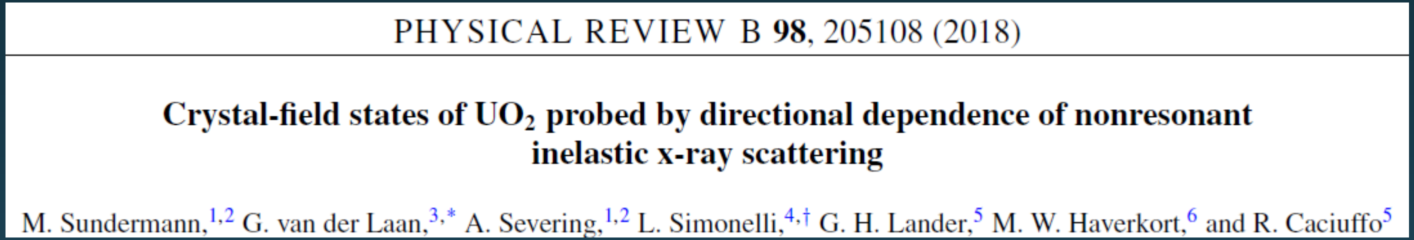
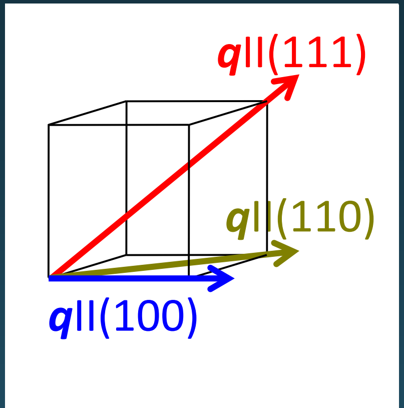
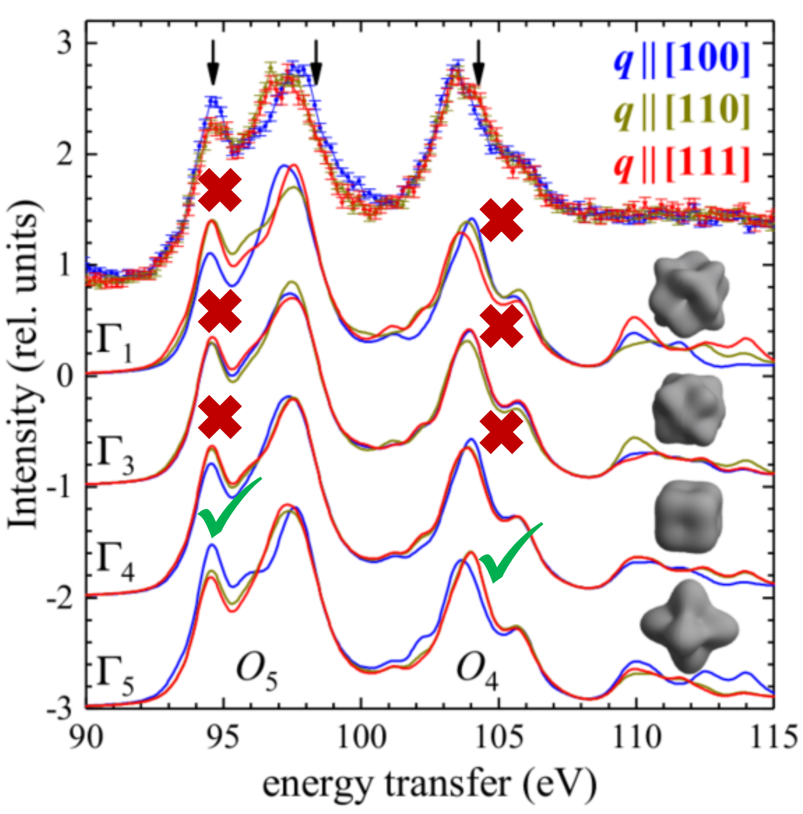


PHYSICAL REVIEW B **98**, 205108 (2018)

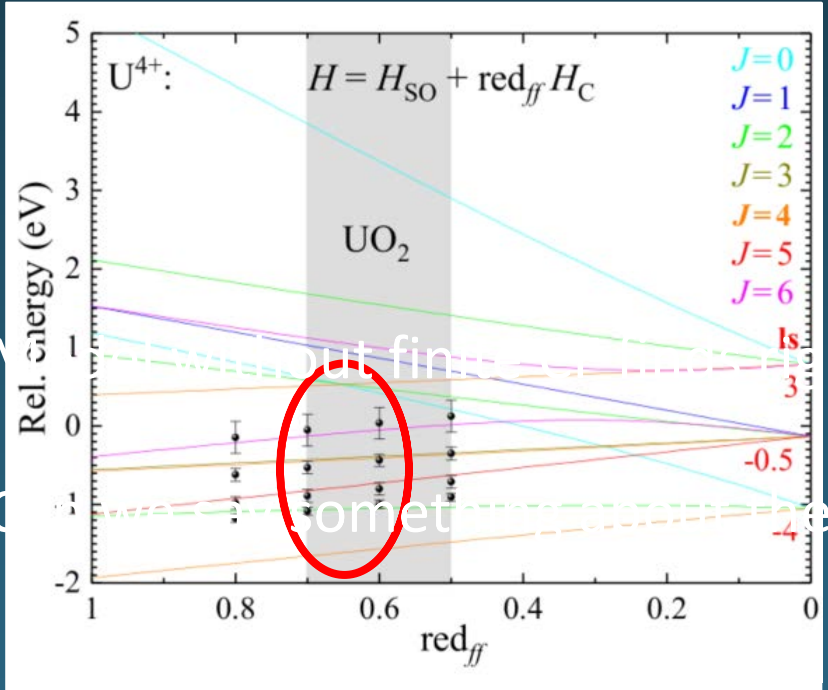
Crystal-field states of UO_2 probed by directional dependence of nonresonant inelastic x-ray scattering

M. Sundermann,[1,2] G. van der Laan,[3,*] A. Severing,[1,2] L. Simonelli,[4,†] G. H. Lander,[5] M. W. Haverkort,[6] and R. Caciuffo[5]





No free parameters left



GS multiplet = 86% $^3H_4$ + 13% $^1G_4$ + 1% $^3F_4$

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

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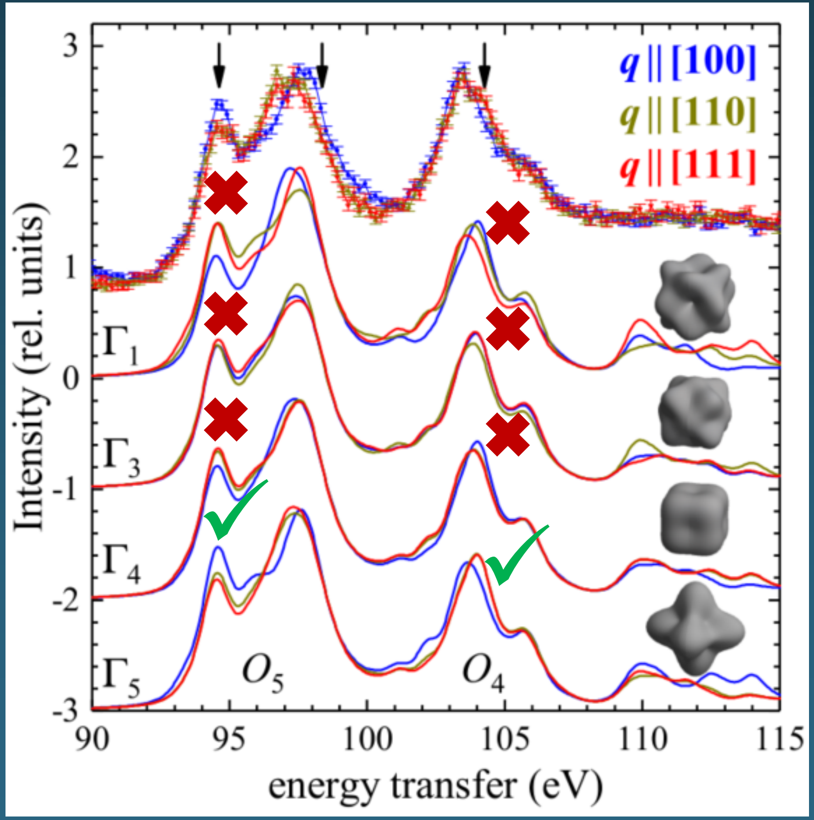

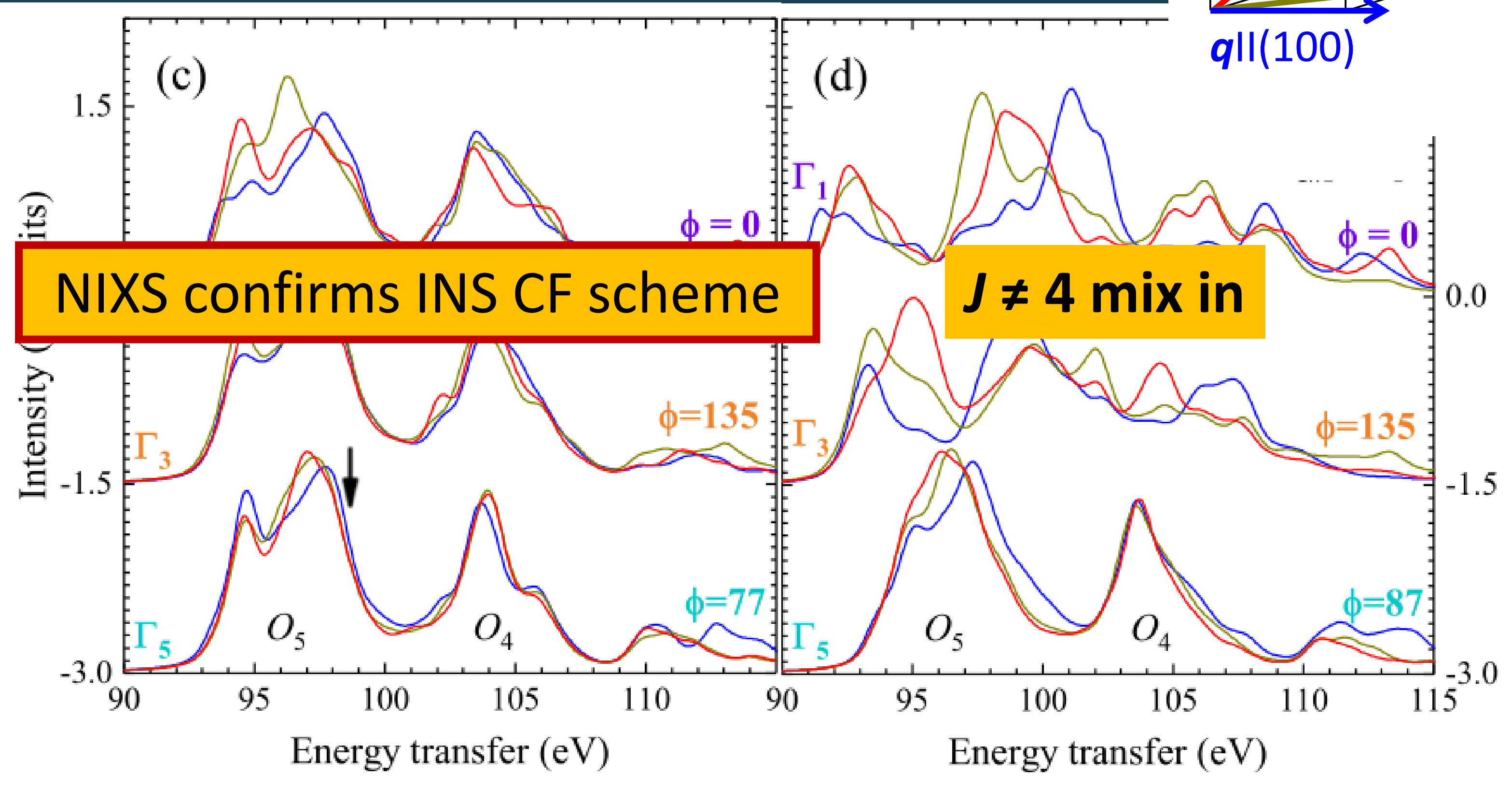

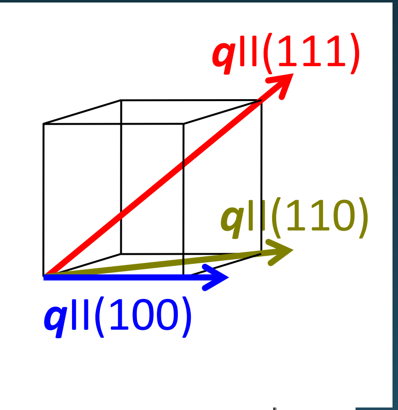

CF states without CF splitting

weak CF

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

Strong CF

Parameters based on:
H. Rahman and W. Runciman,
Phys. & Chem. of Solids **27** 1833 (1966)

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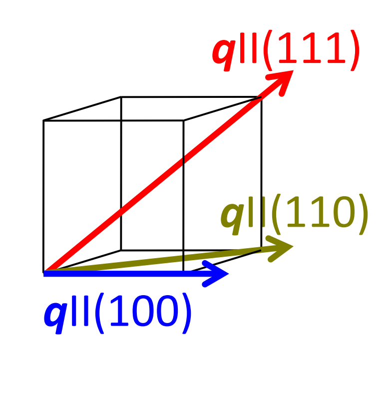
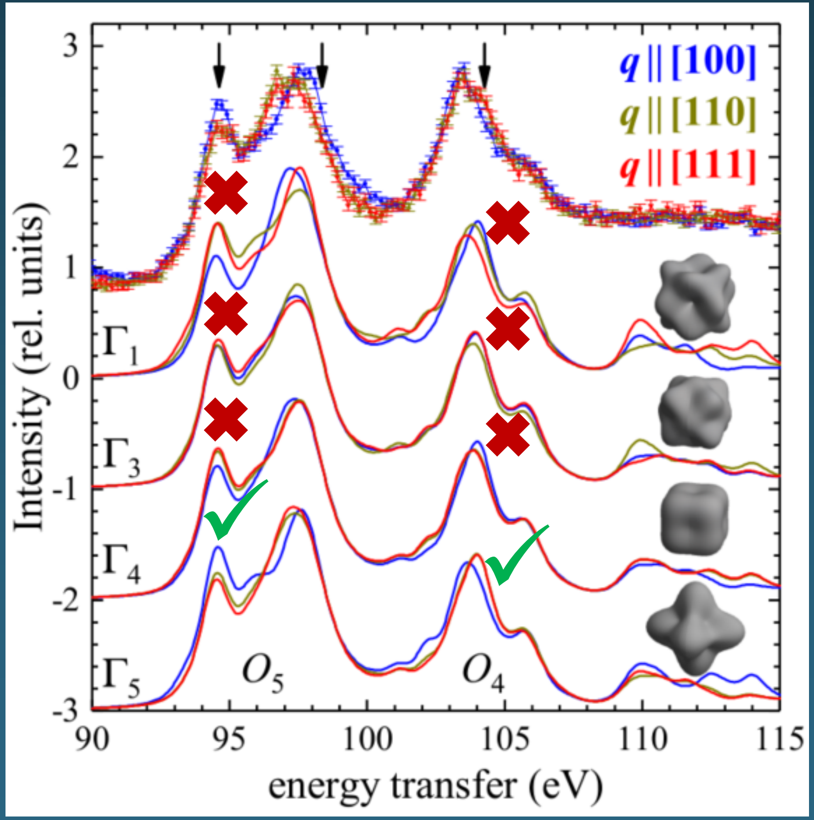
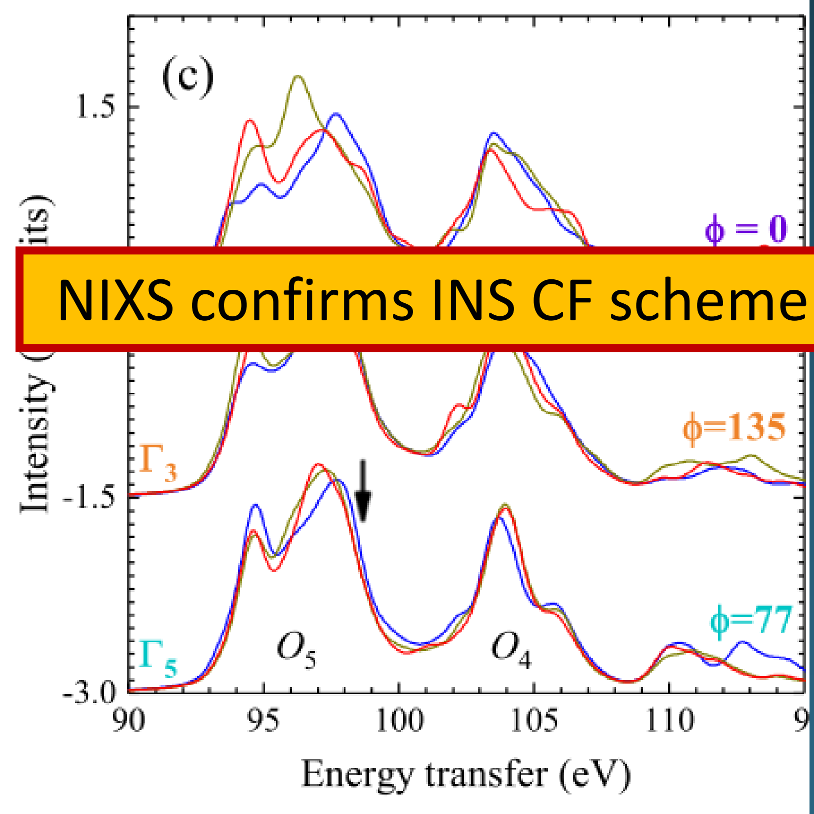




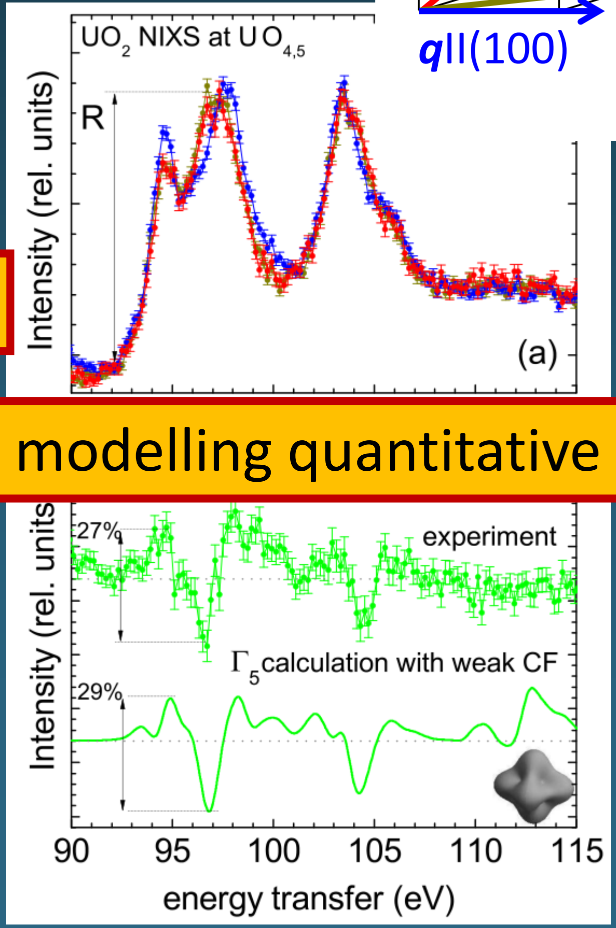
CF states without CF splitting



NIXS confirms INS CF scheme

weak CF

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



modelling quantitative

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- 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%)

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

- Method has previously been successfully applied to metallic 5*f* material
  see URu_2Si_2 in Sundermann *et al.* PNAS **113** 13989 (2016)

Thank you

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