Band structure information from soft x-ray spectroscopy

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Materials World Network

Spintronics group

- Ben Ruck, Joe Trodahl

Electronic structure group

- Walter Lambrecht

Novel Materials Lab

- Kevin Smith

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NML at BU

Kevin Smith

Louis Piper

Sang Wan Cho

Alex DeMasi

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NML at BU

- Novel materials
  - Nitrides: Rare-earth nitrides, III-V
  - Oxides: TCO, SOFC, low dimensional
  - Organics

- X-ray spectroscopy
  - Absorption (XAS)
  - Emission (XES)
  - Resonant emission (RXES, RIXS)
  - Photoemission (XPS)
  - Angle resolved photoemission (ARPES)

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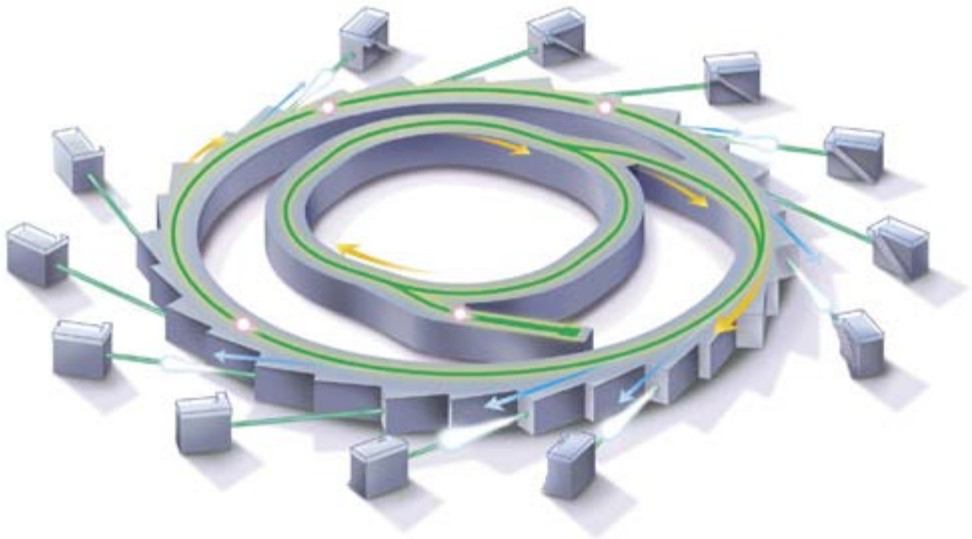
NML at BU

- Synchrotron based
  - National Synchrotron Light Source – X1B
  - Advanced Light Source – BL7, BL12
  - MAXlab – 5II



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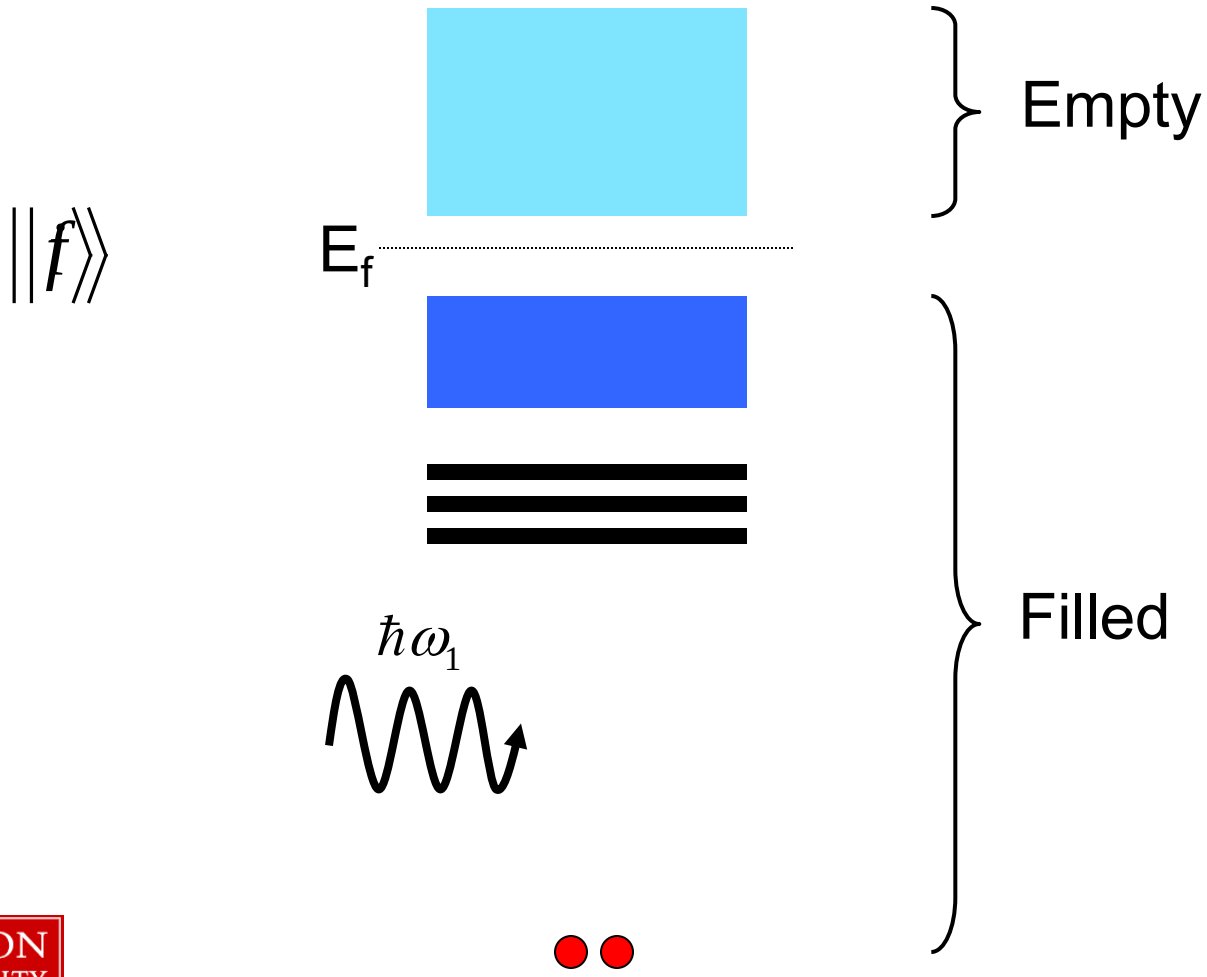
Spectroscopy

$$P_{i\to f} \propto \left|\left\langle f \left| T \right| i \right\rangle\right|^2 \rho_f(E)$$

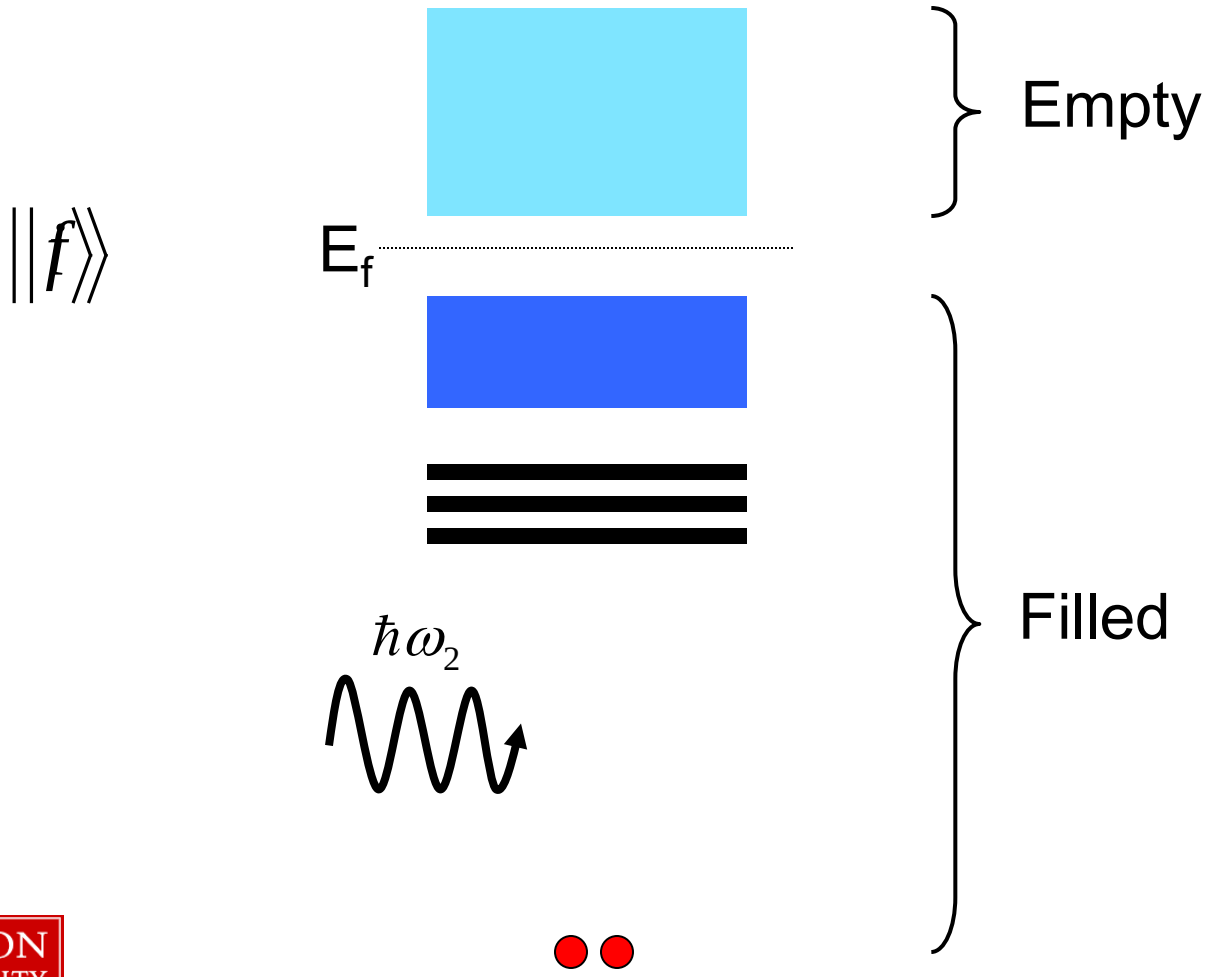
Spectroscopy

$$P_{i\to f} \propto \left|\left\langle f \left| \varepsilon \cdot r \right| i \right\rangle\right|^2 \rho_f(E)$$

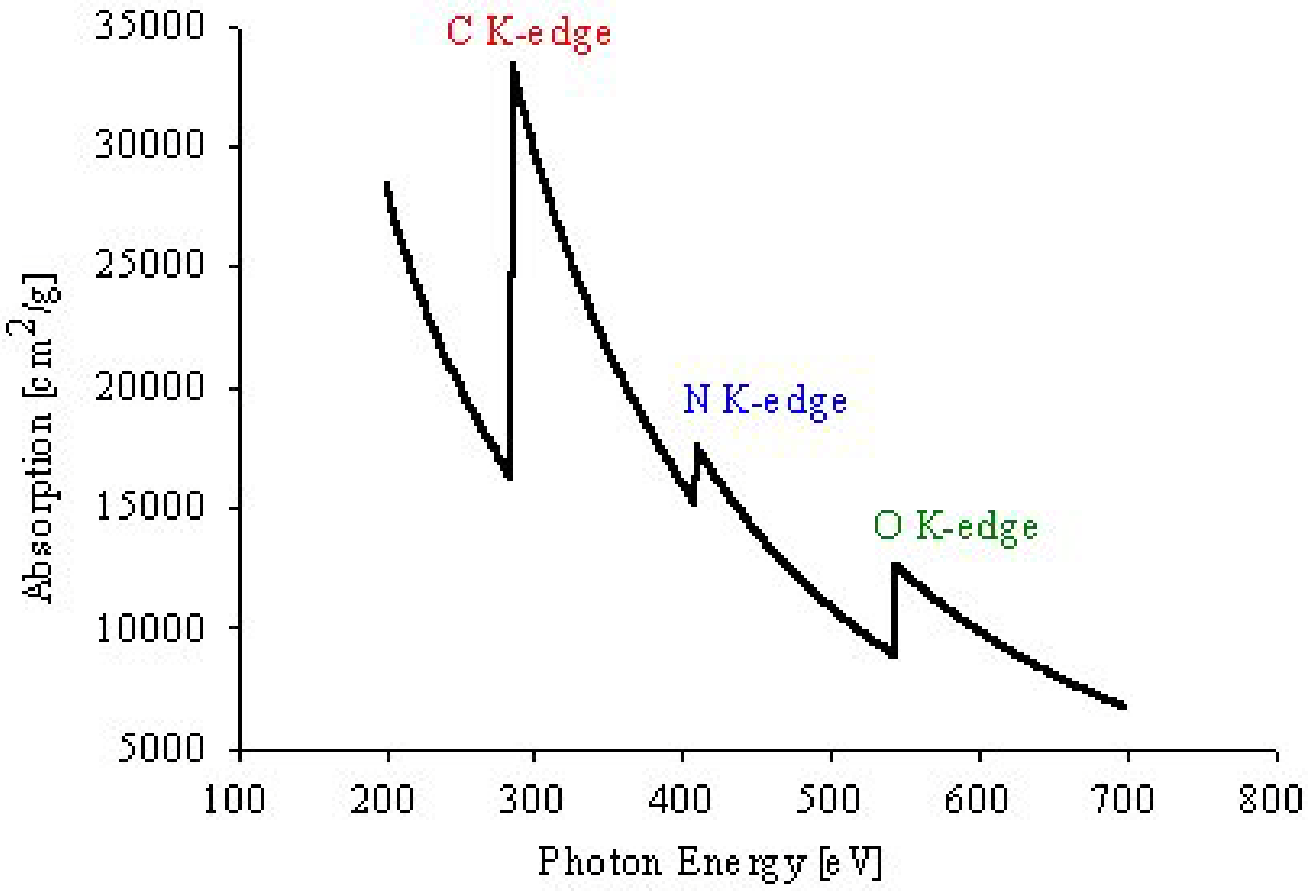
X-ray absorption (XAS)



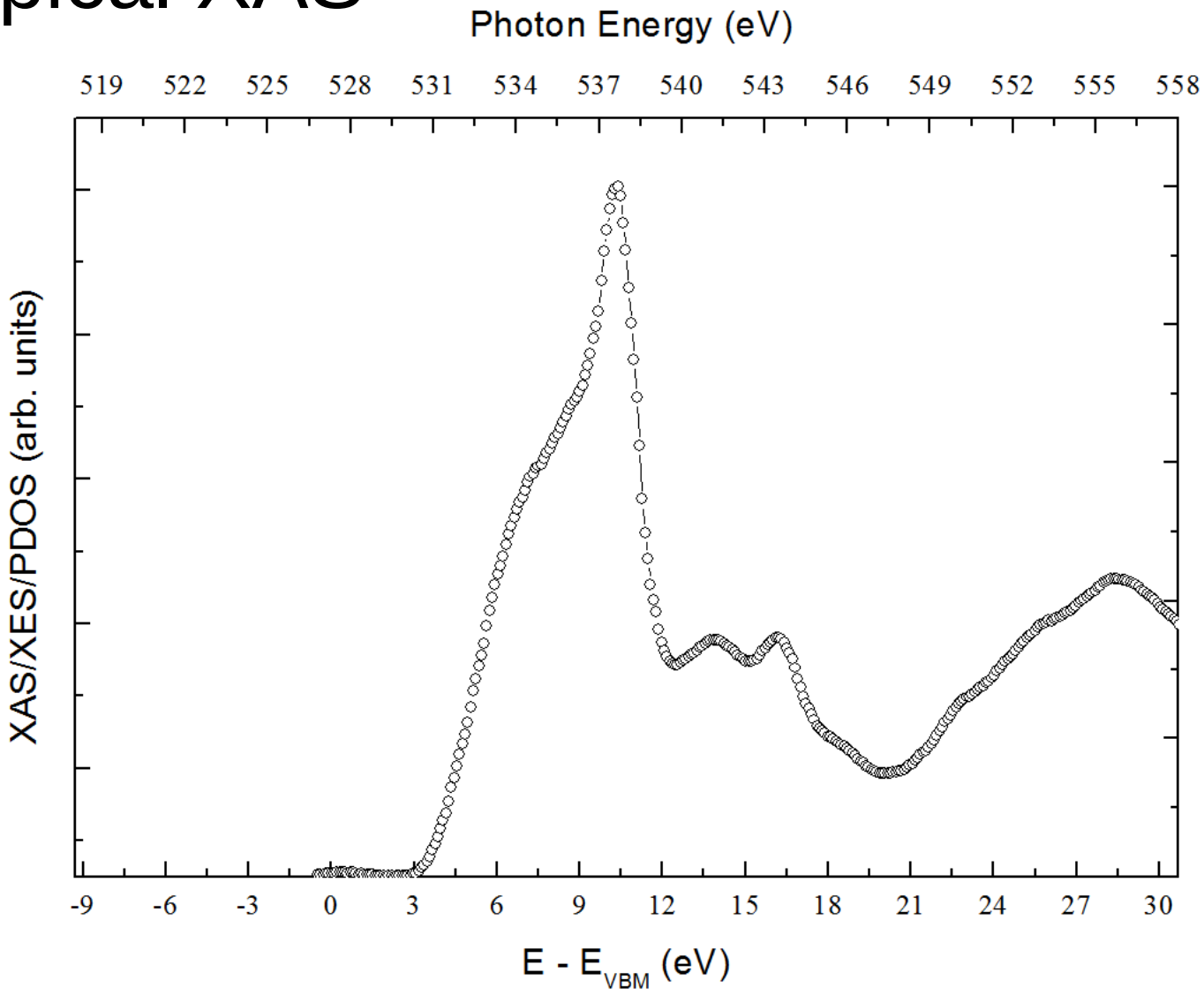
X-ray absorption (XAS)



Site selectivity

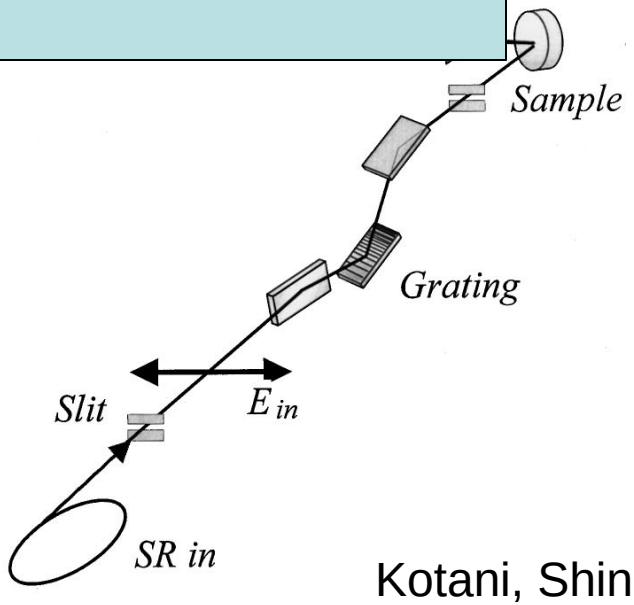


Typical XAS


Photon Energy (eV)
519 522 525 528 531 534 537 540 543 546 549 552 555 558
XAS/XES/PDOS (arb. units)
-9 -6 -3 0 3 6 9 12 15 18 21 24 27 30
E - E_VBM (eV)

XAS

Curtain!



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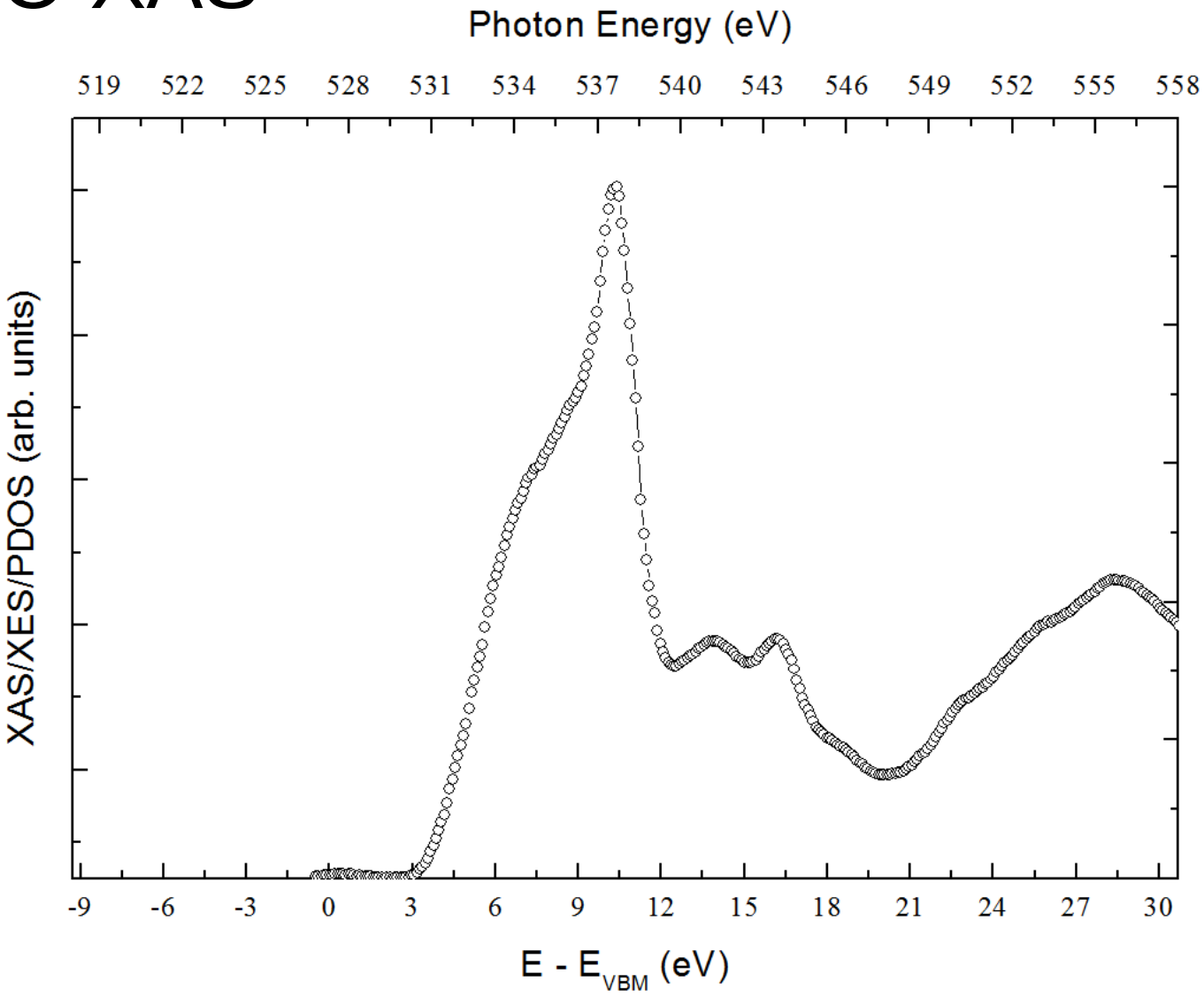
Rev. Mod. Phys. 73, 203 (2001)

ZnO XAS


Photon Energy (eV)
519
522
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XAS/XES/PDOS (arb. units)
-9
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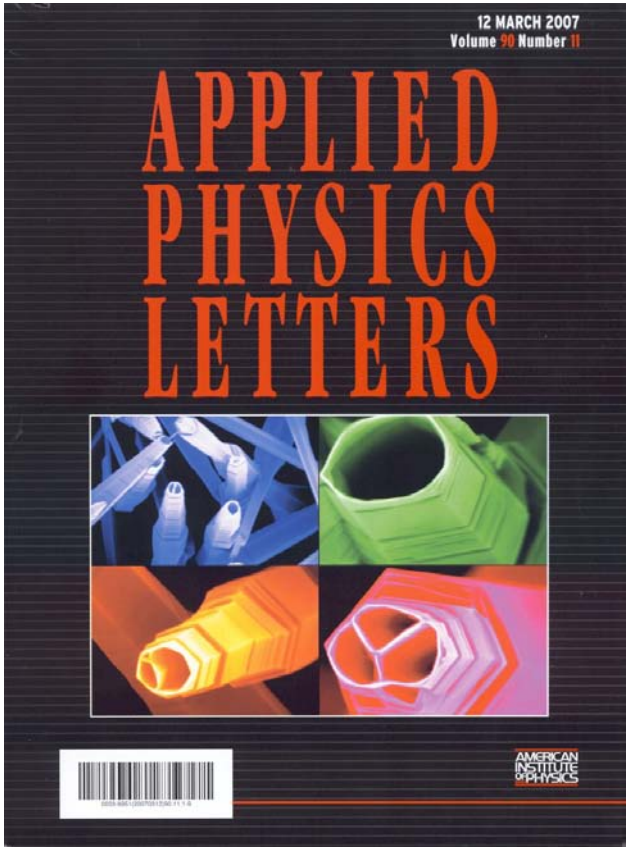
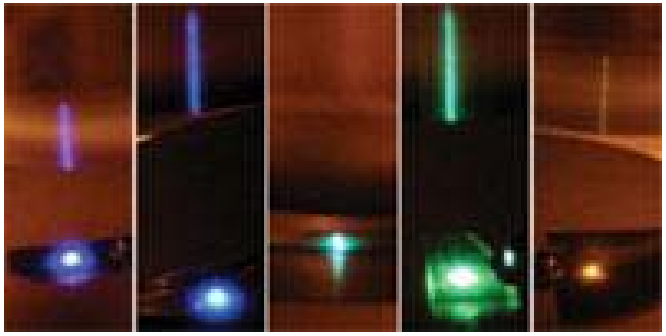
E - E_VBM (eV)

Zinc oxide

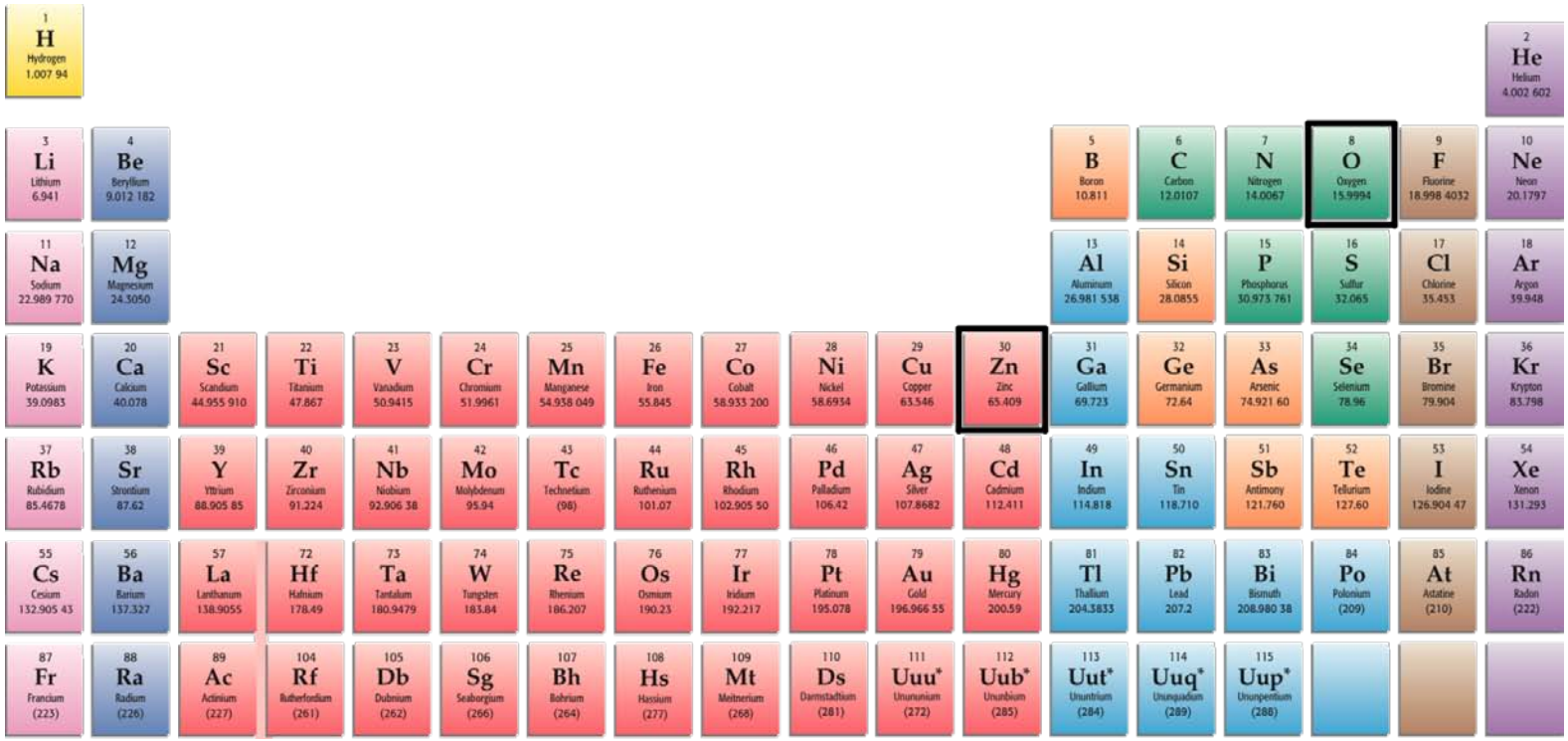

12 MARCH 2007
Volume 90 Number 11
APPLIED PHYSICS LETTERS
AMERICAN INSTITUTE OF PHYSICS




氧化鋅軟膏
Zinc Oxide Oint "W.P."
Zinc oxide oint

Zinc oxide

- Zn = $[Ar]3d^{10}4s^2$ O = $[He]2s^22p^4$



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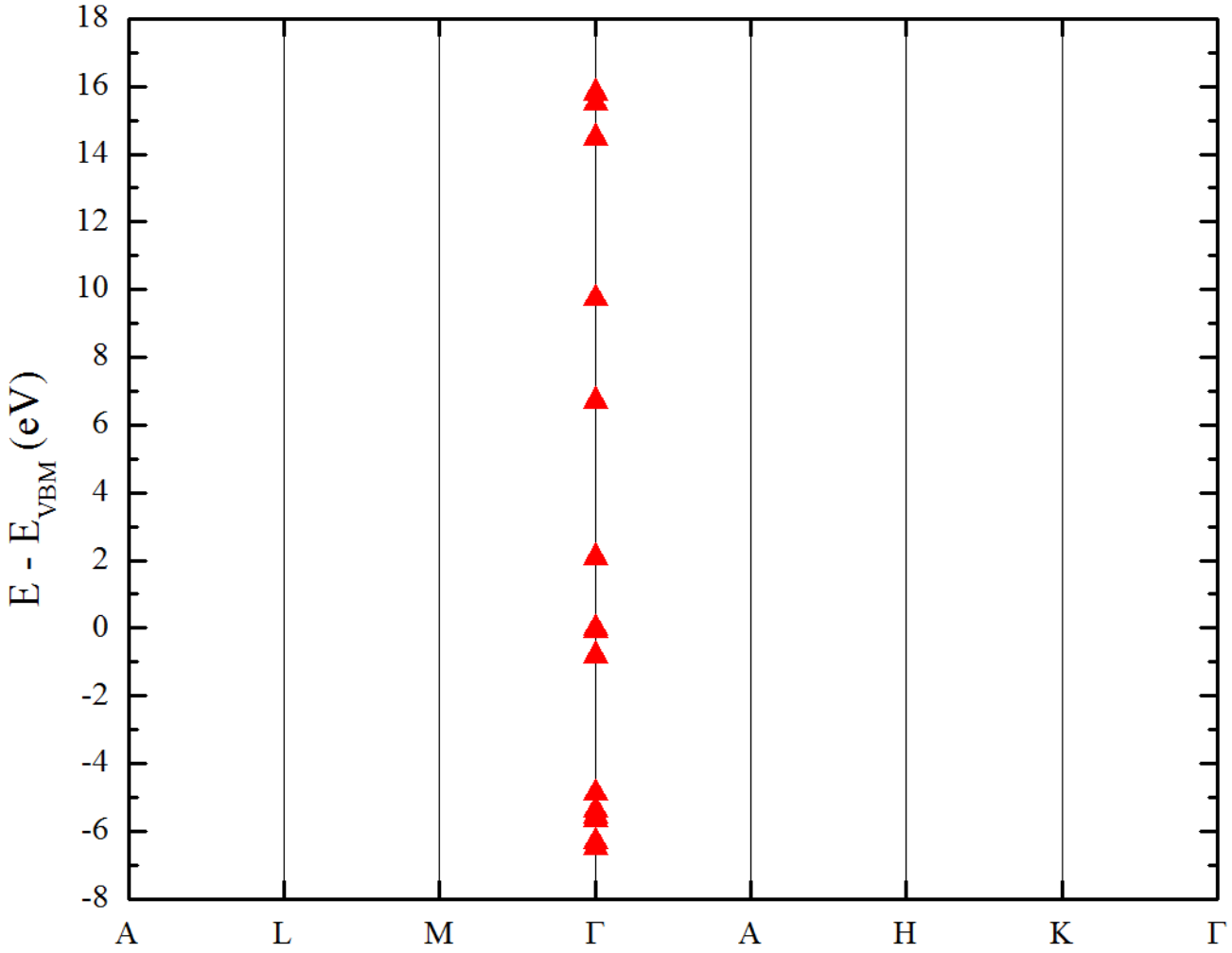
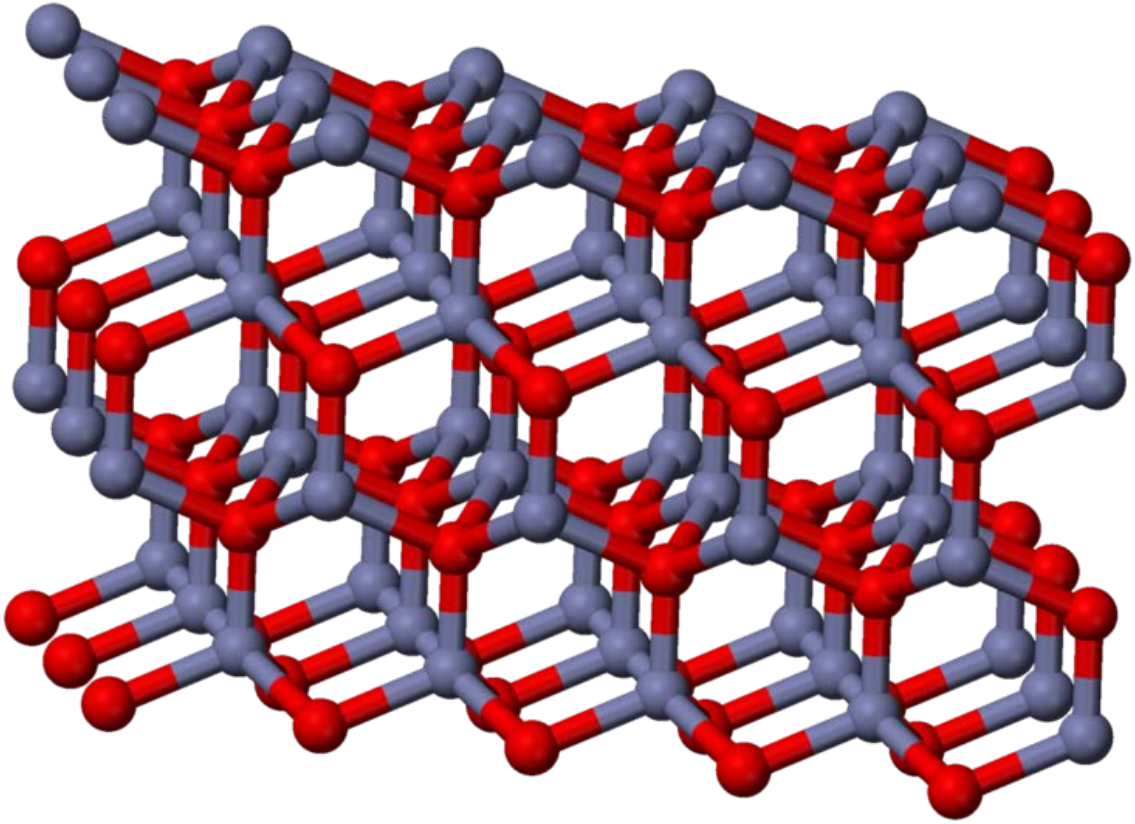
ZnO electronic structure

- Density functional theory
  - HSE03 XC functional
  - GW correction
- Essential for correctly locating the Zn 3d electrons, bandgap

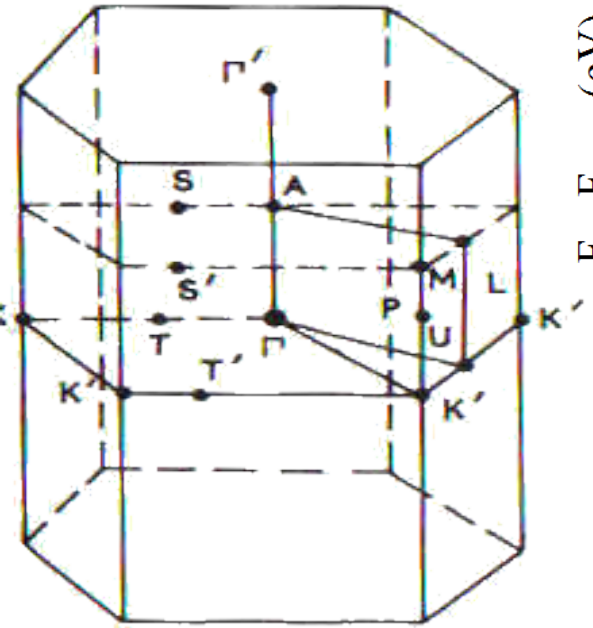
ZnO electronic structure

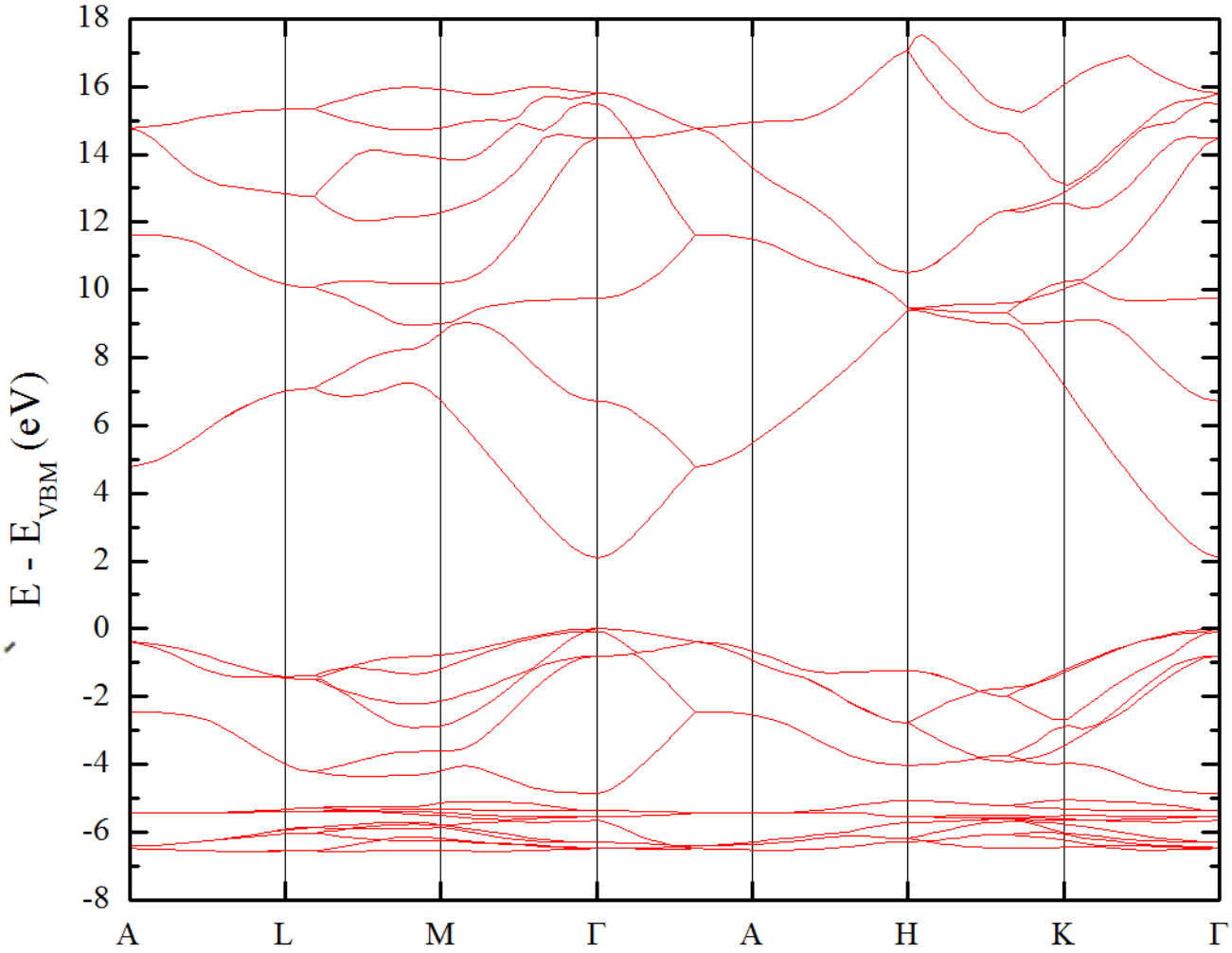


Zinc oxide



ZnO electronic structure



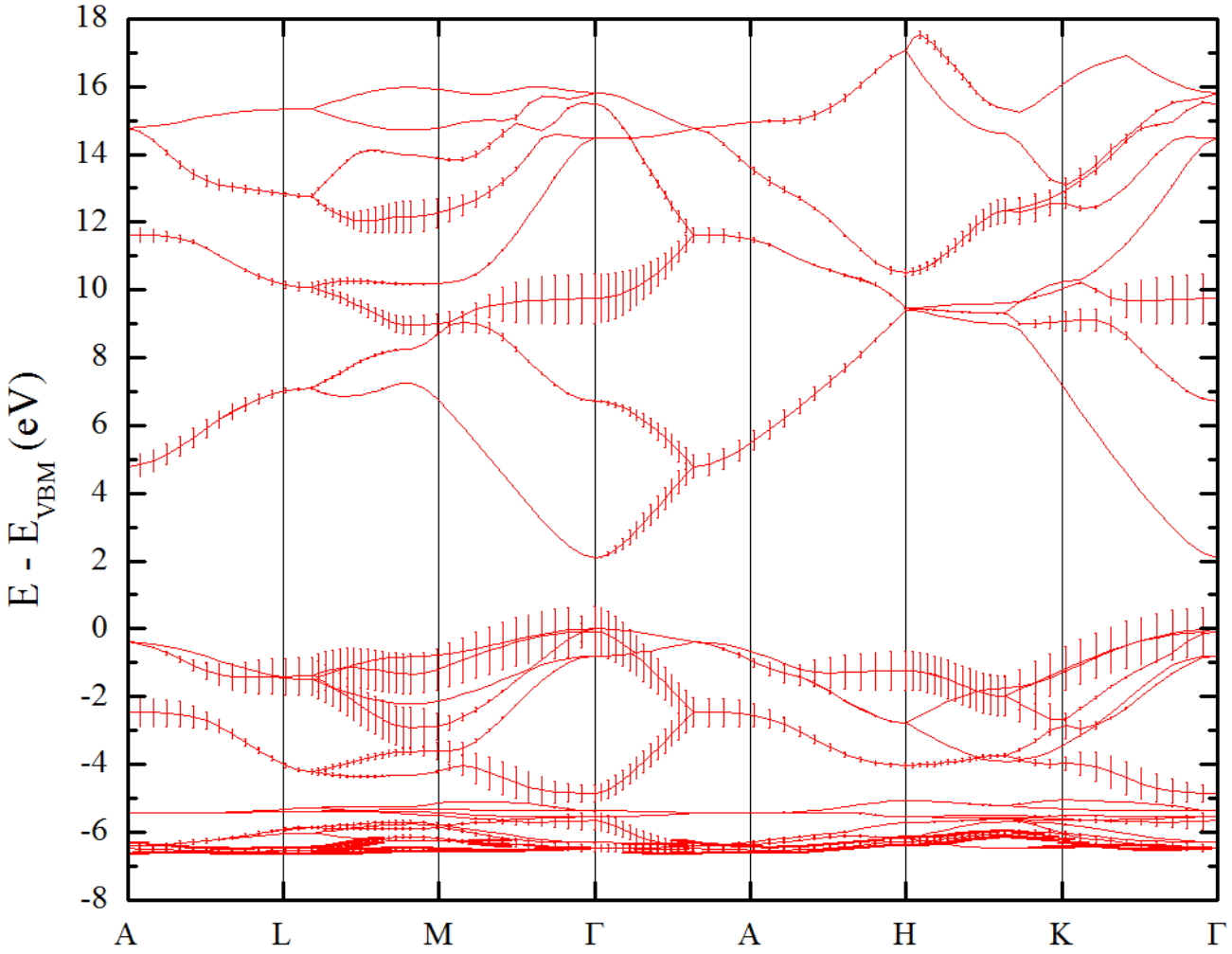


Dipole approximation

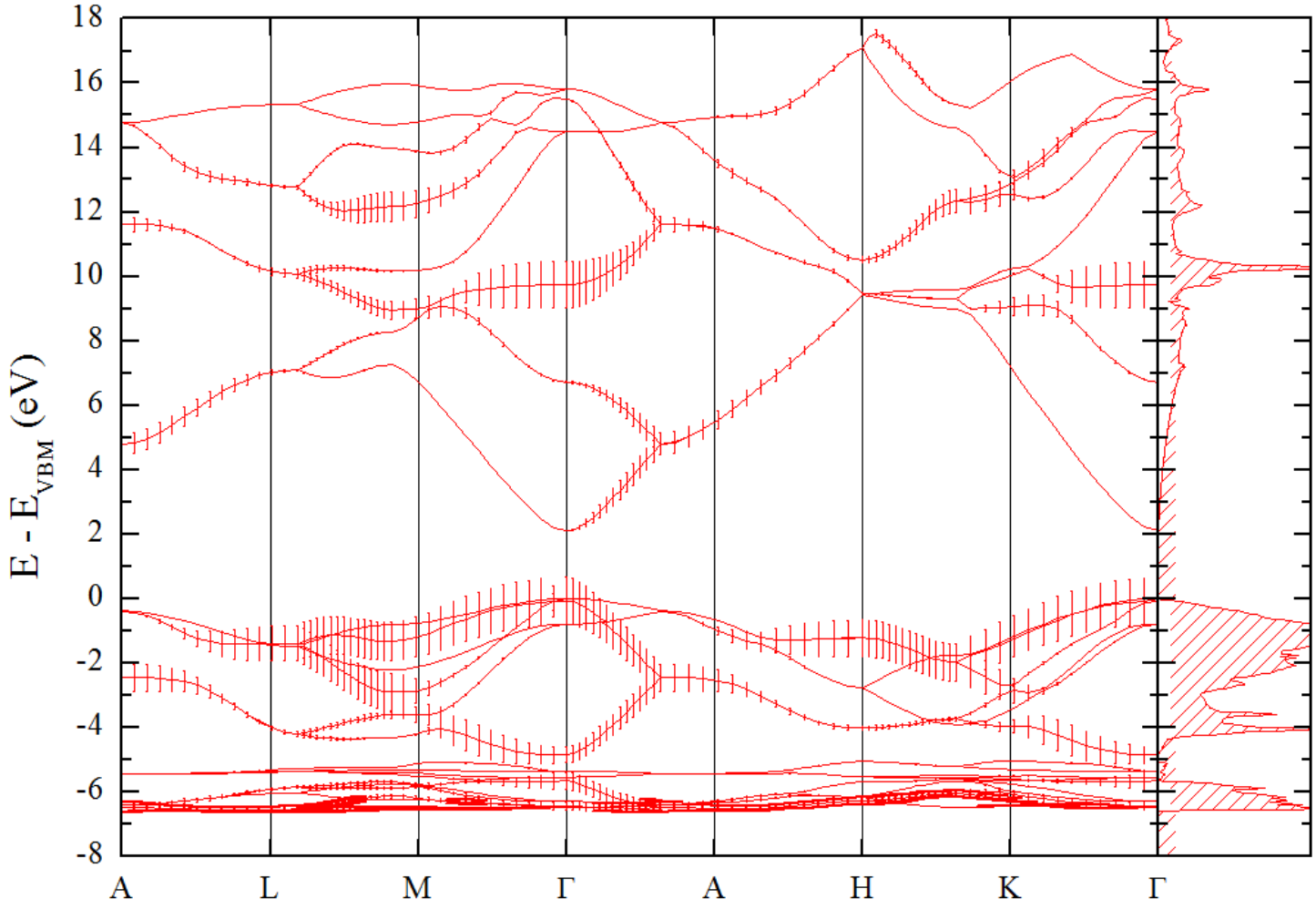
$$P_{i\to f} \propto \left|\left\langle f \left| \boldsymbol{\varepsilon}\cdot\mathbf{r} \right| i \right\rangle\right|^2 \rho_f(\hbar\omega - \Delta E)$$

- Orbital selection
- $\Delta l = \pm 1$
- s -> p

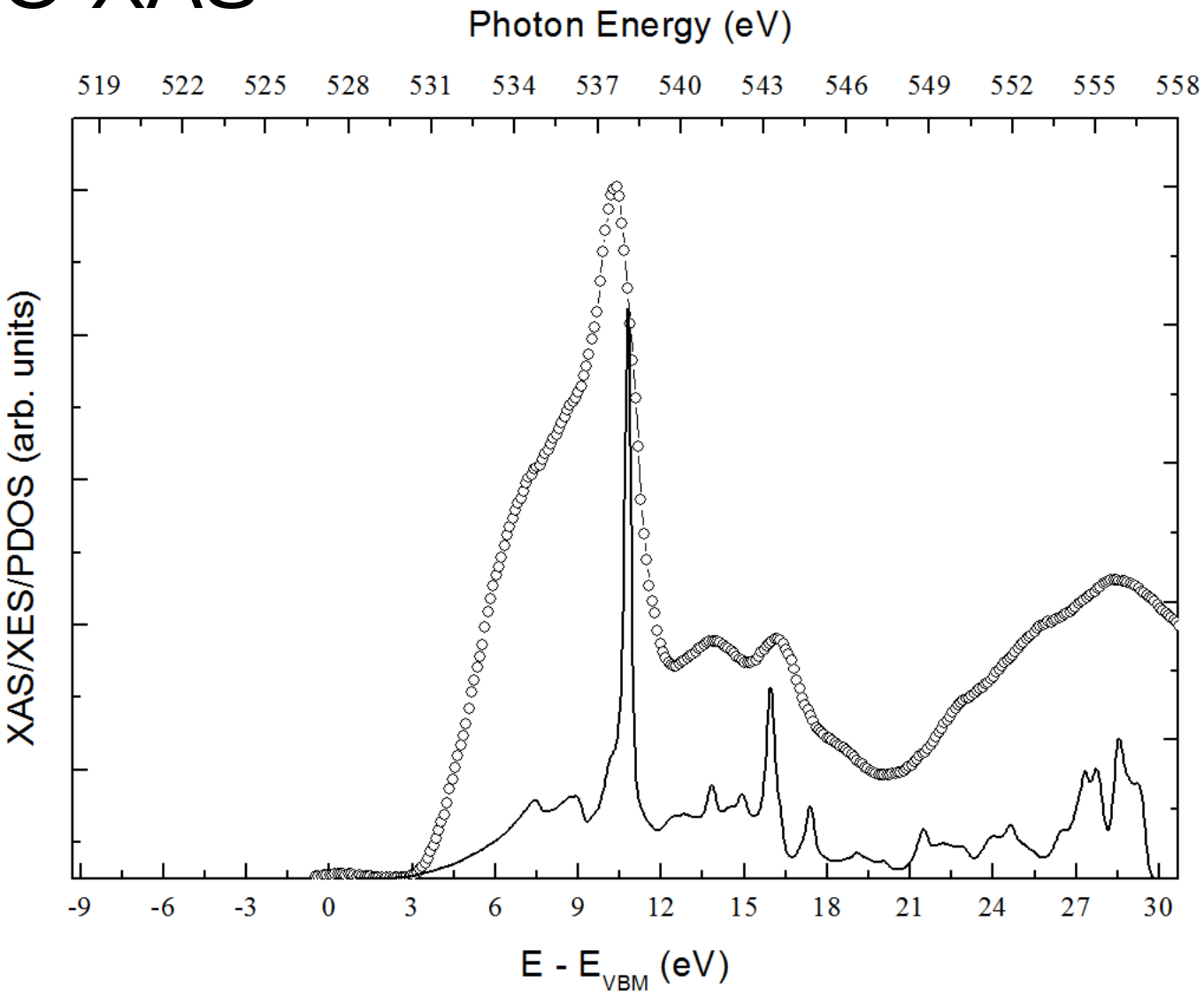
ZnO electronic structure



ZnO electronic structure



ZnO XAS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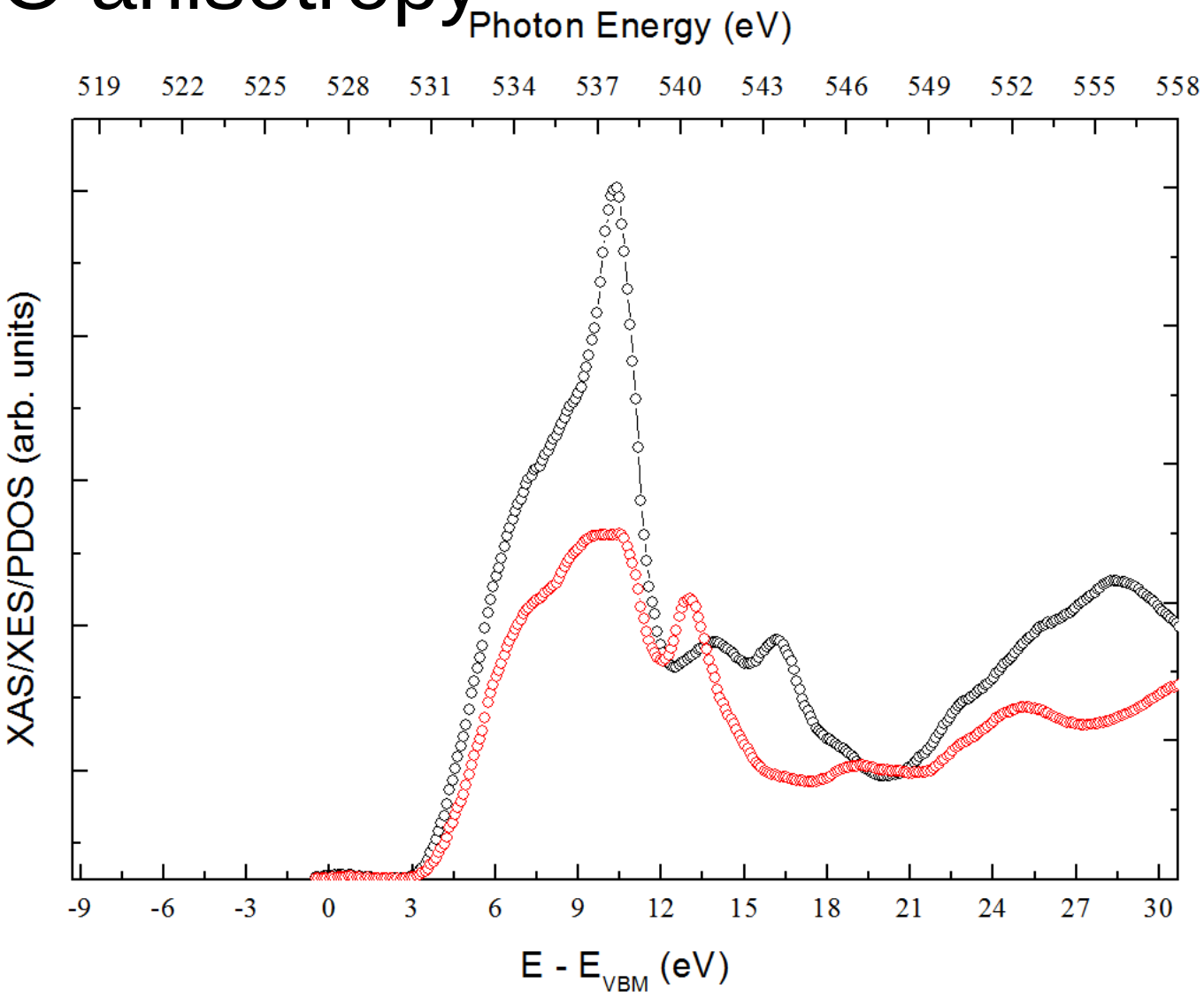
ZnO anisotropy



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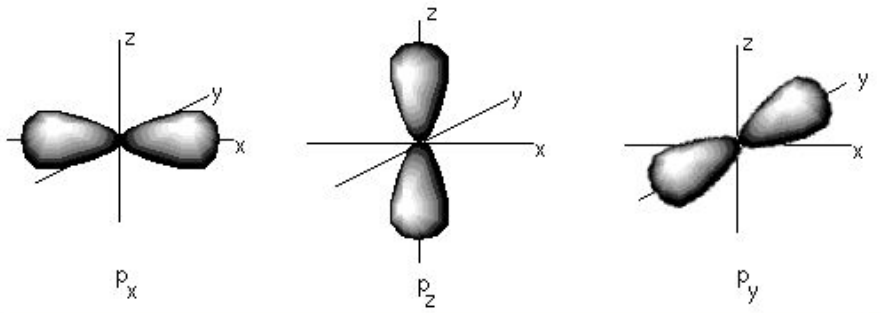
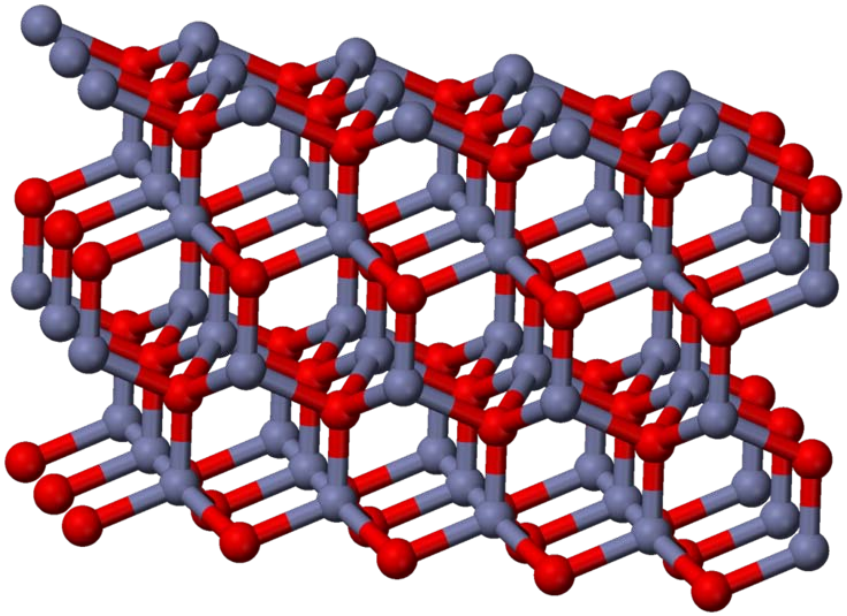


O p orbitals



ZnO crystal

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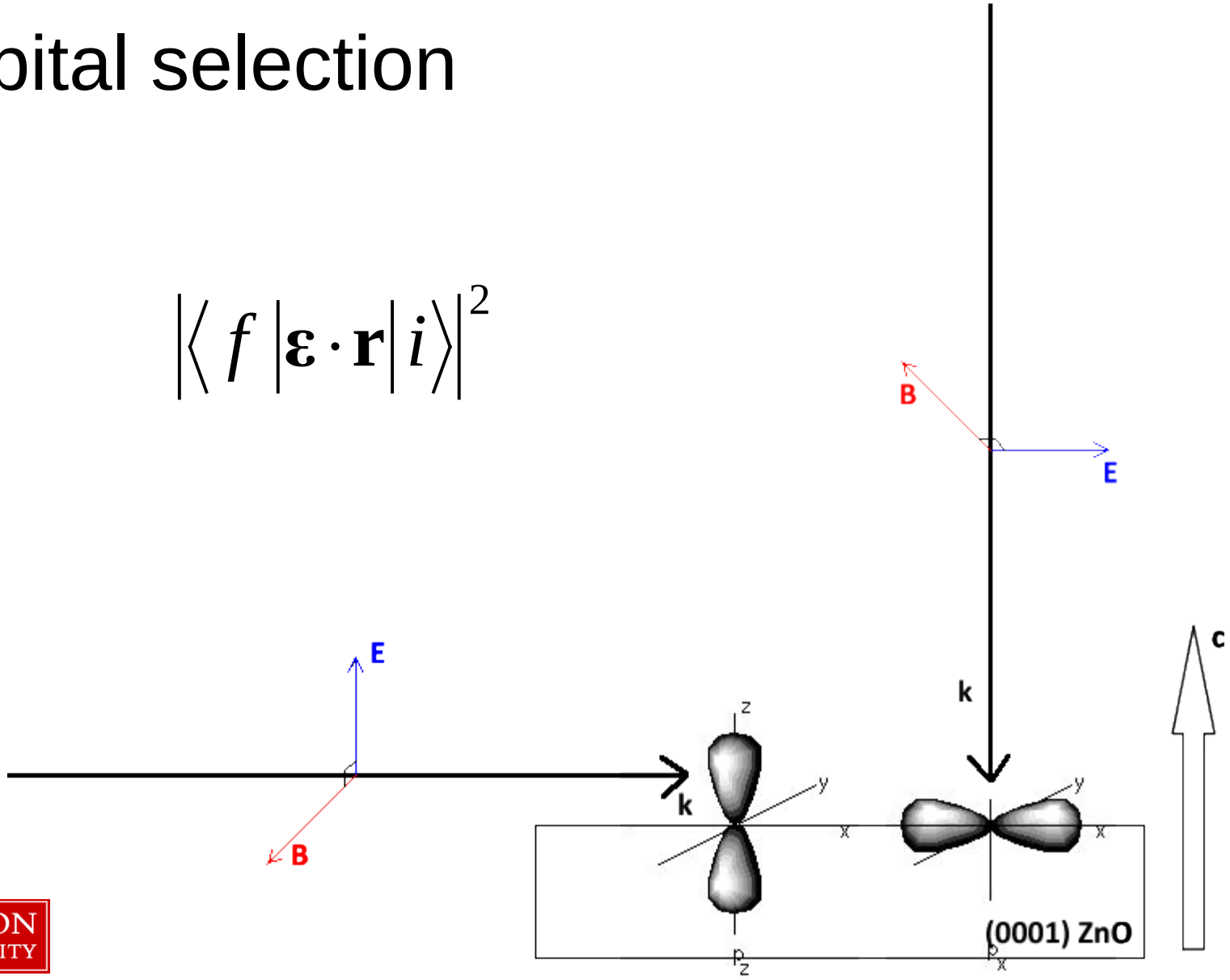
Orbital selection

$$\left| \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle \right|^2$$



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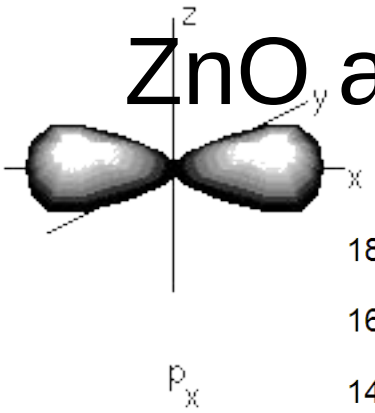
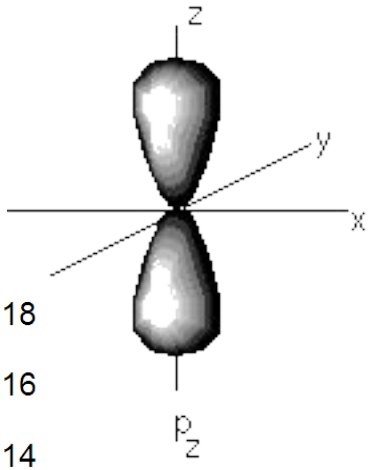
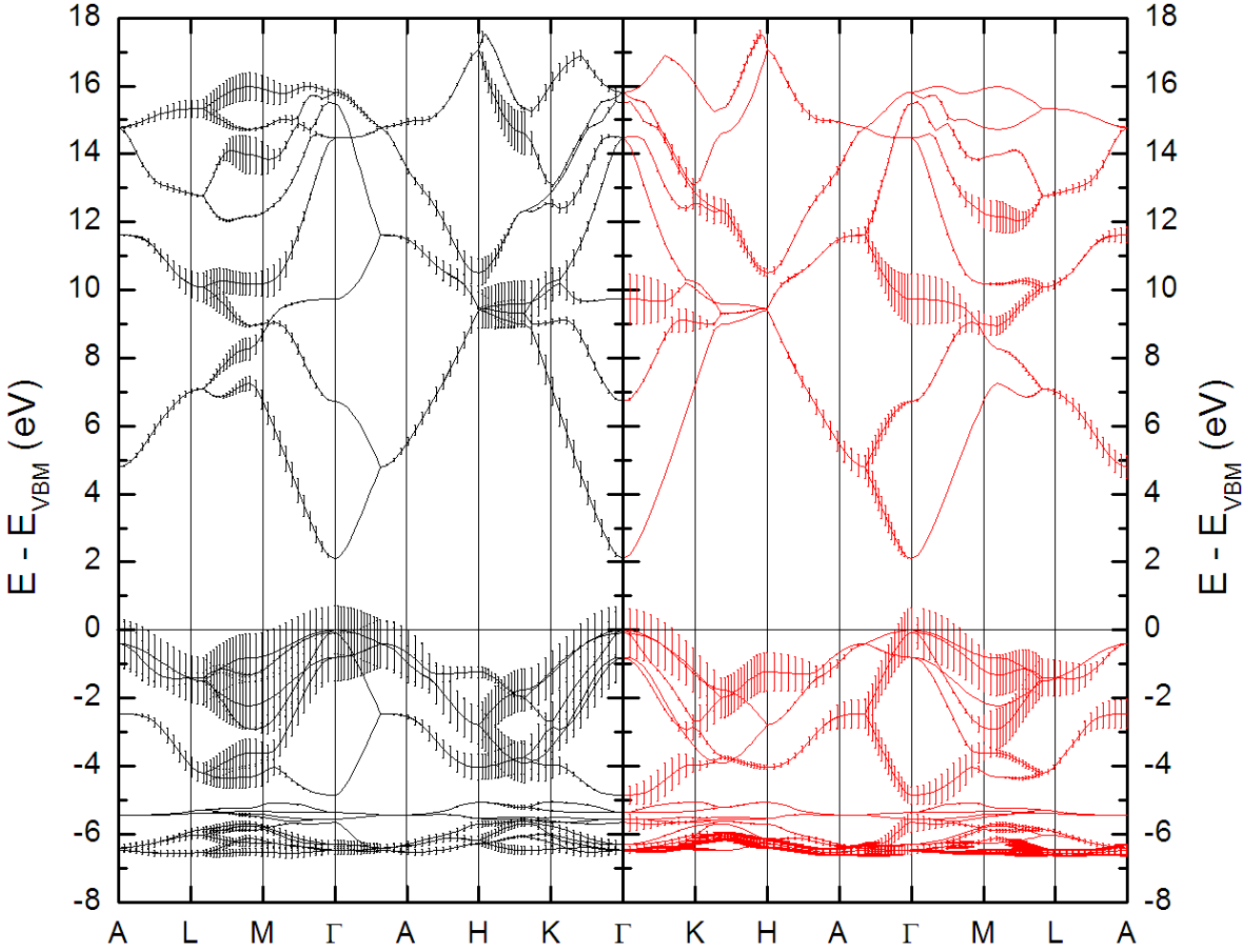
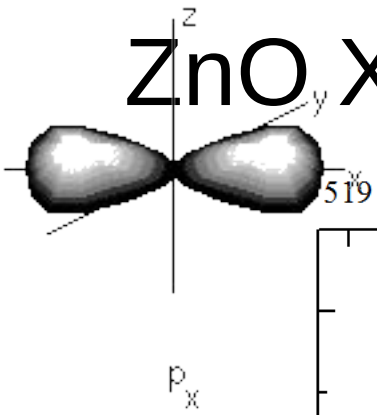
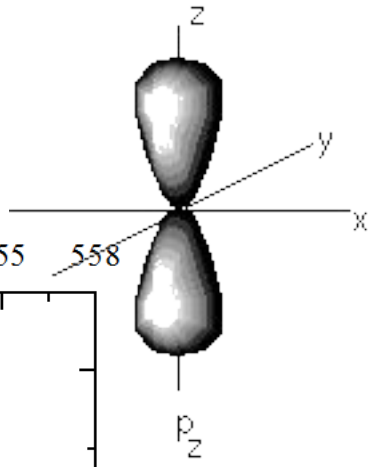






ZnO XAS


z
y
x
p_x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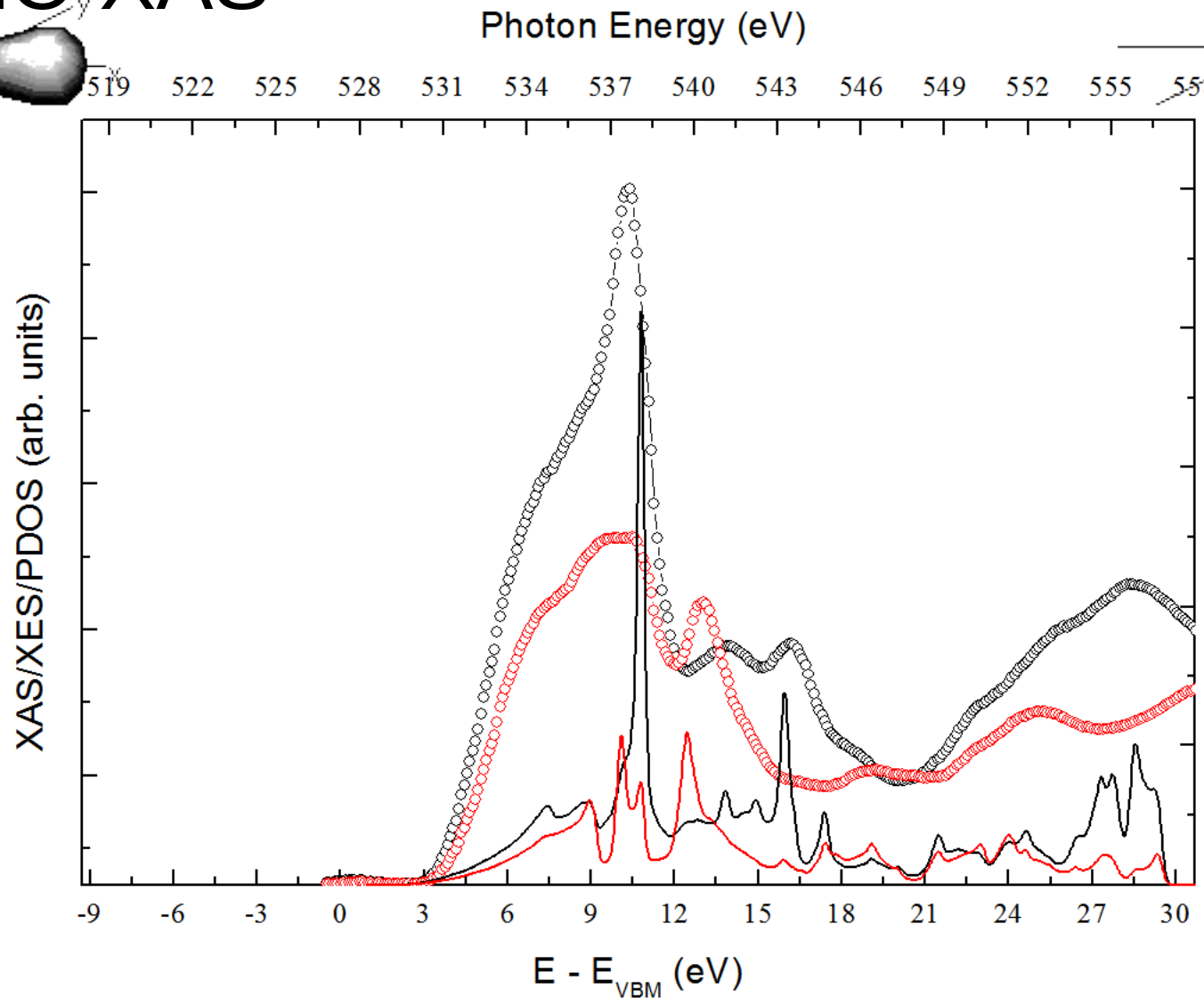
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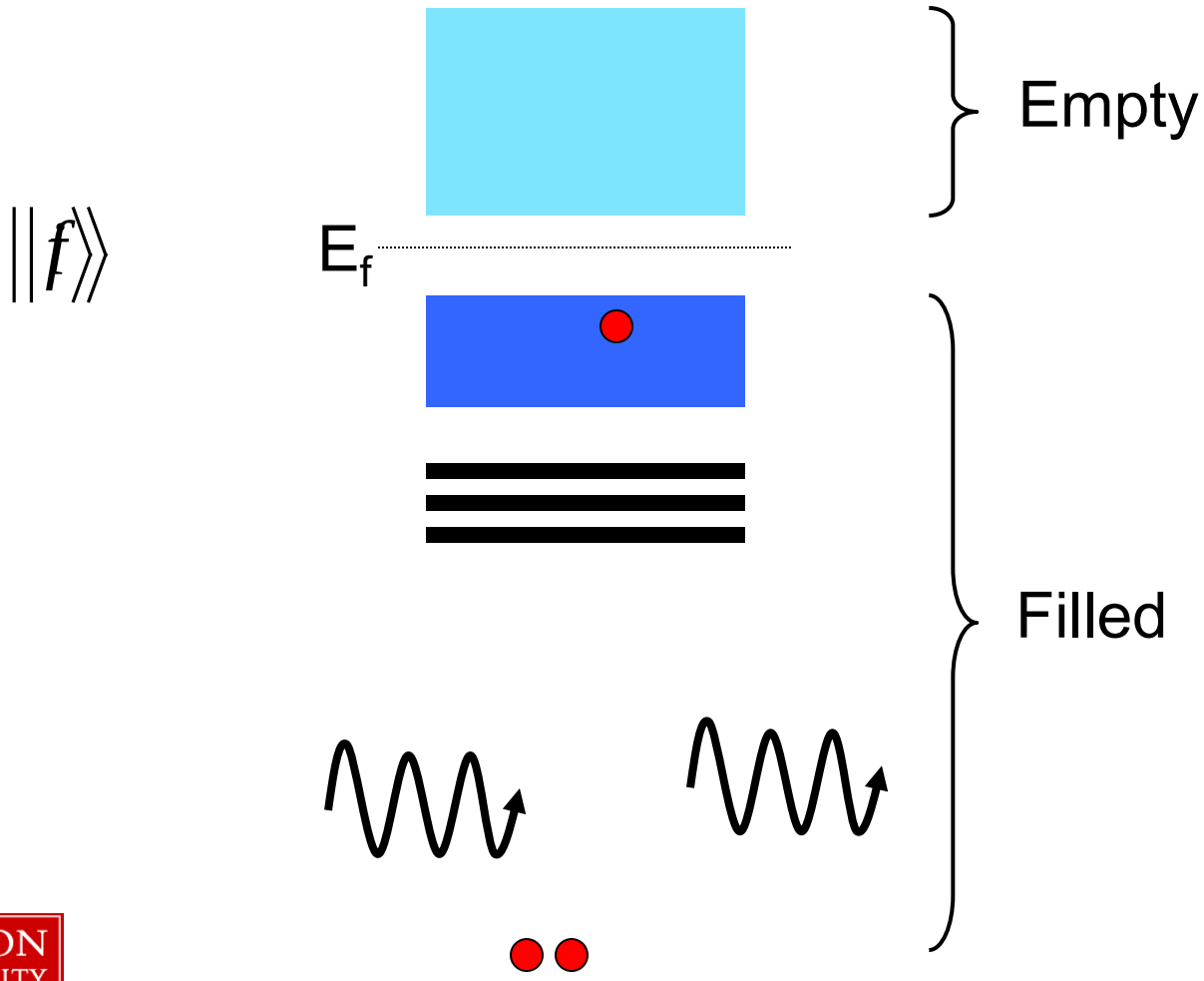
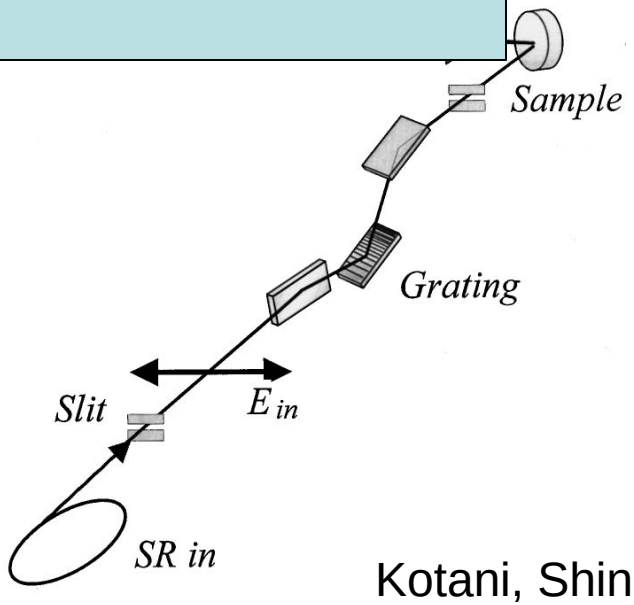
E - E_{VBM} (eV)

X-ray emission (XES)



XES

Curtain!



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Dipole approximation

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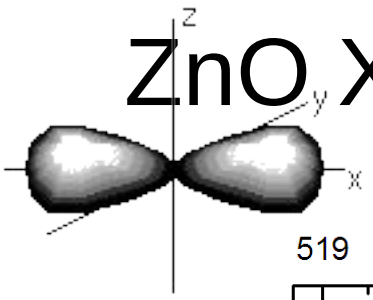
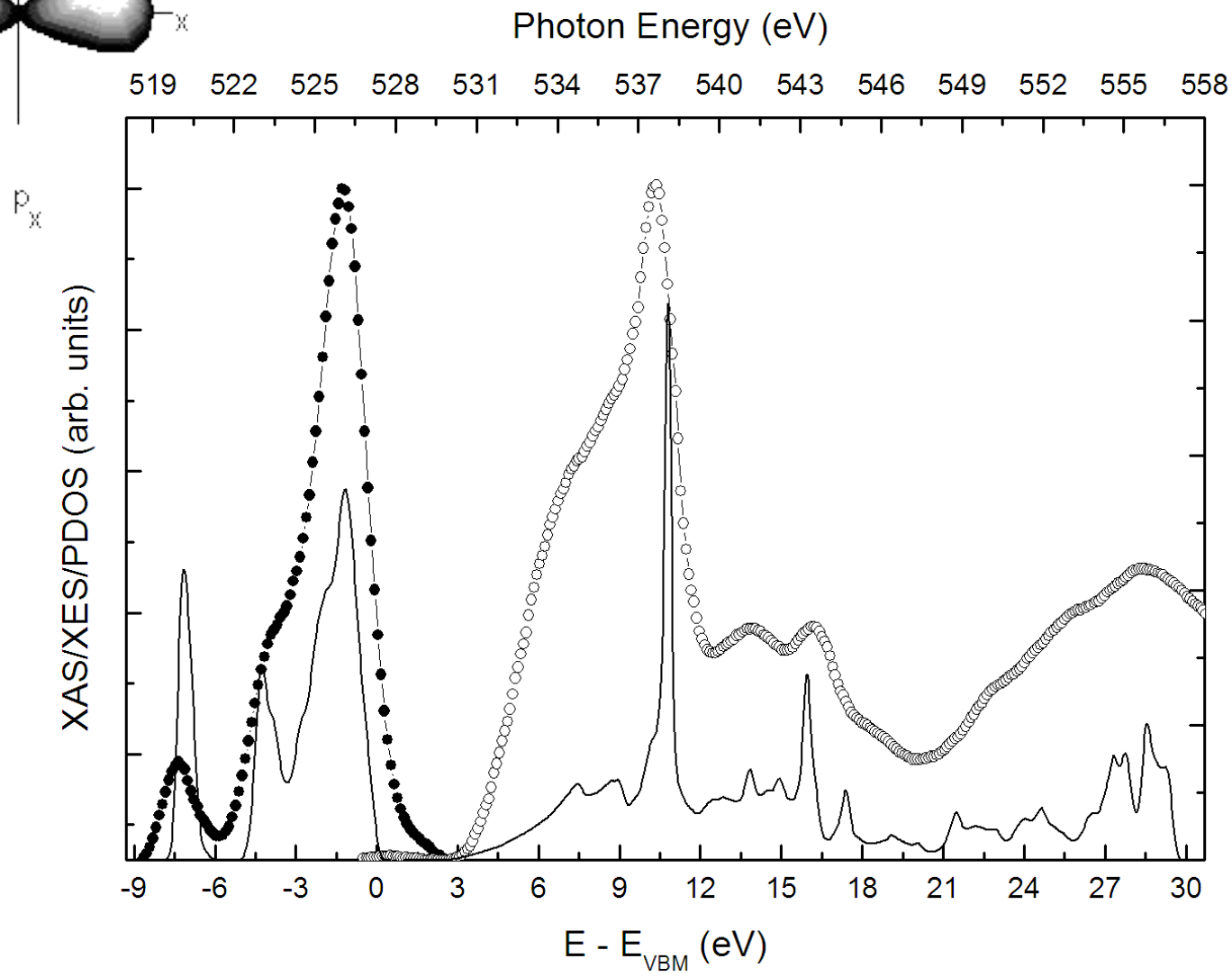
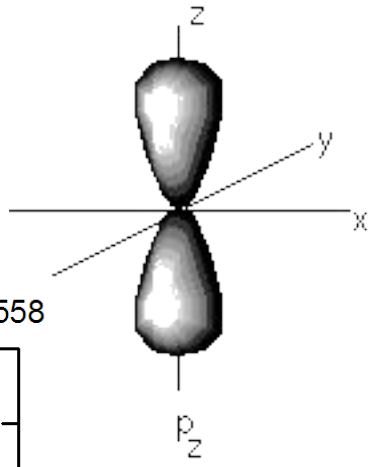
- Orbital selection
- $\Delta l = \pm 1$
- p -> s

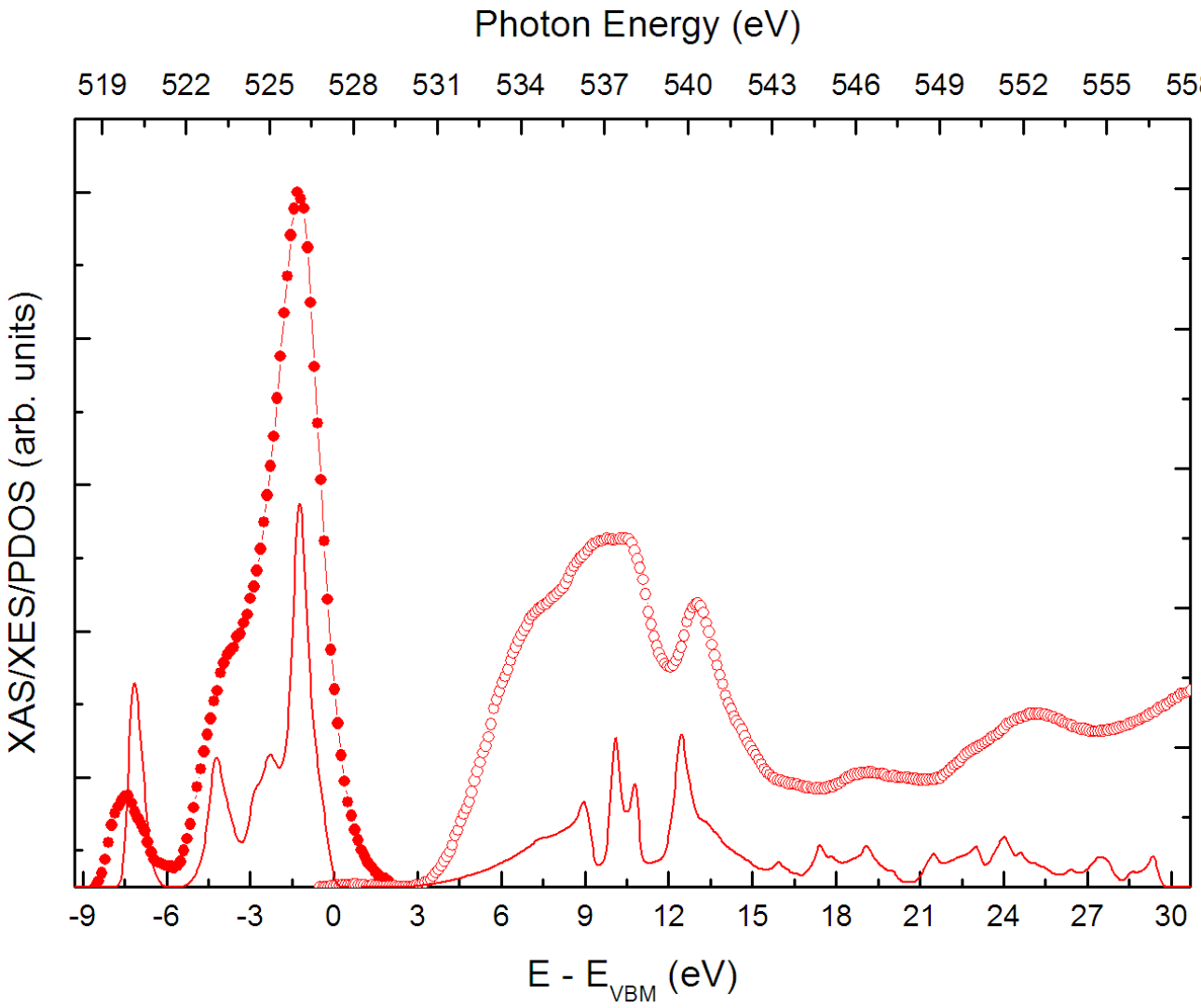
ZnO XAS and XES



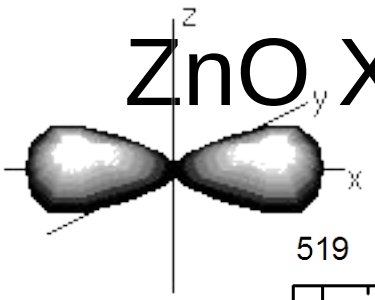


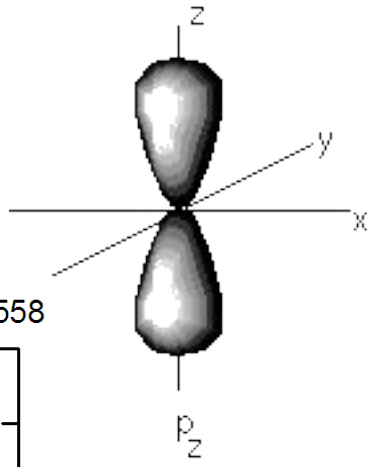
ZnO XAS and XES

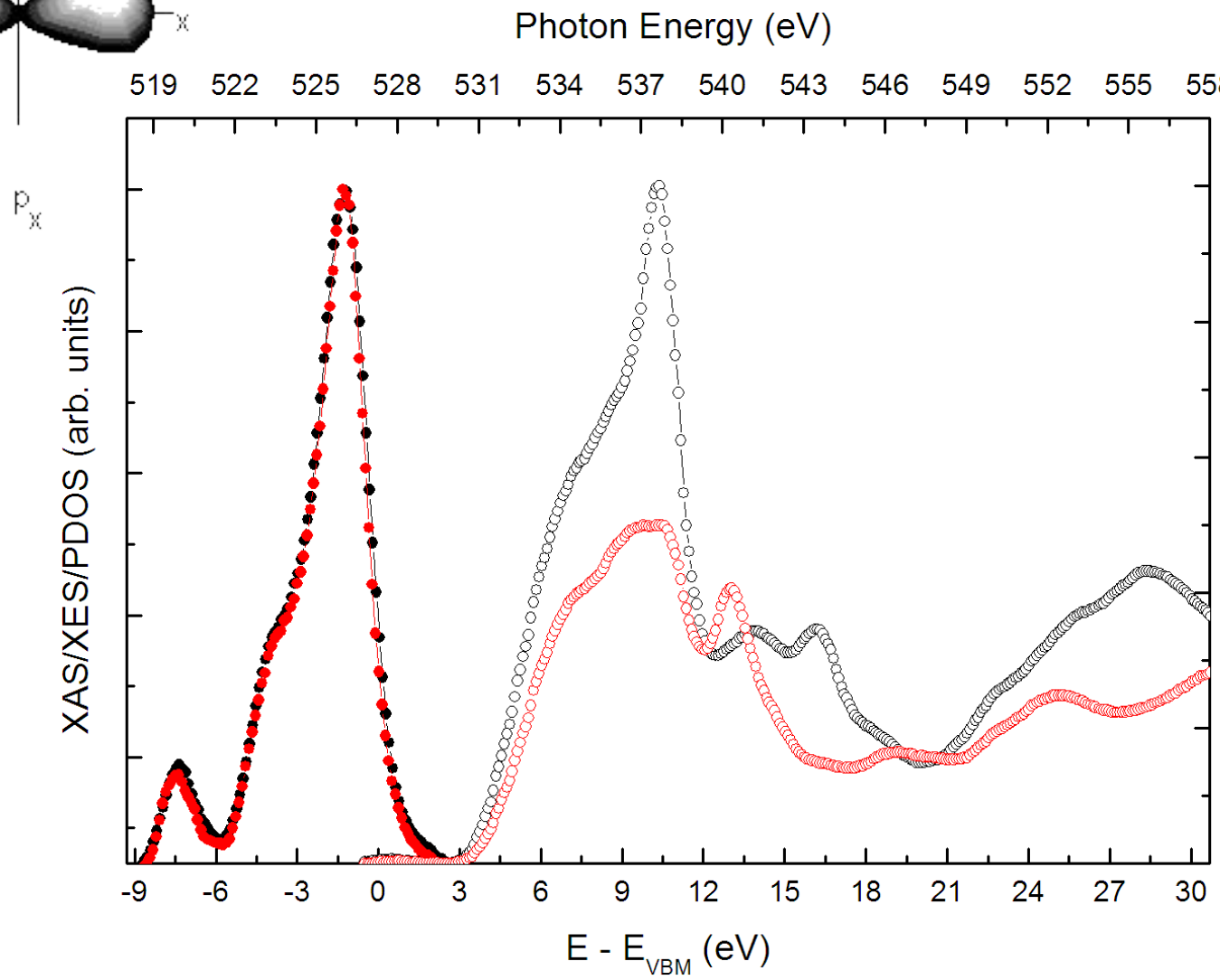




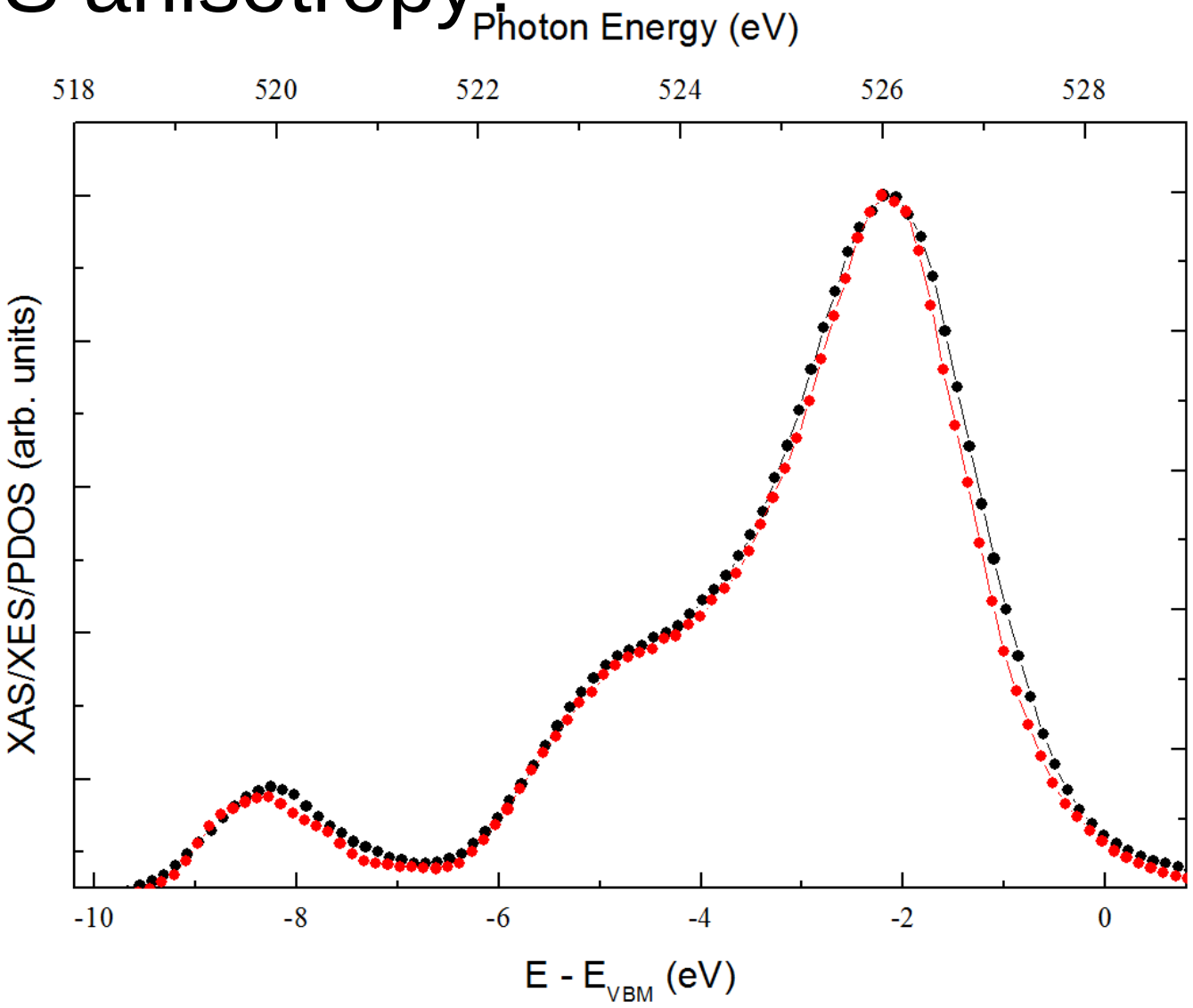
ZnO XAS and XES



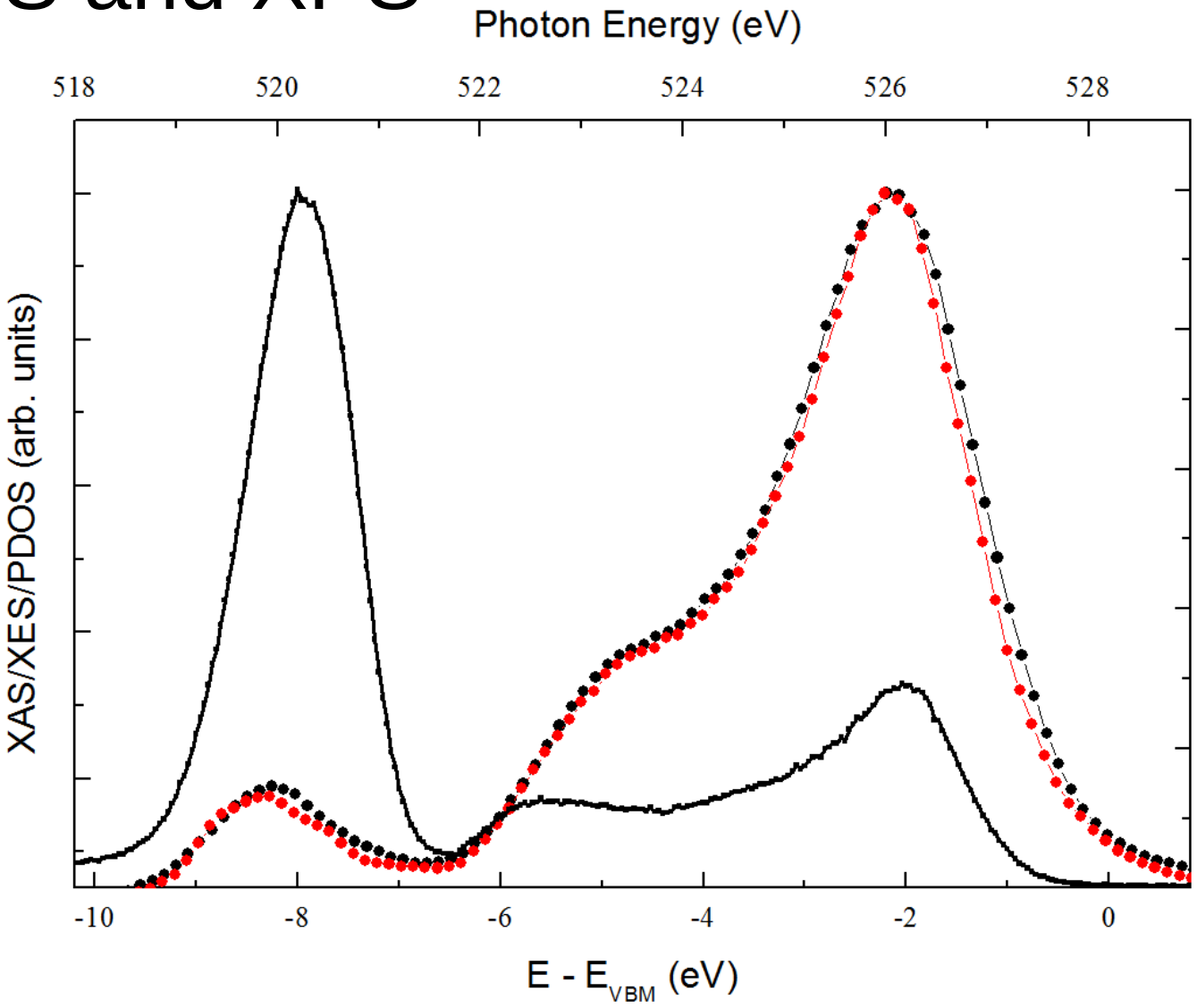




XES anisotropy?



XES and XPS


Photon Energy (eV)
518
520
522
524
526
528
XAS/XES/PDOS (arb. units)
-10
-8
-6
-4
-2
0
E - E_VBM (eV)

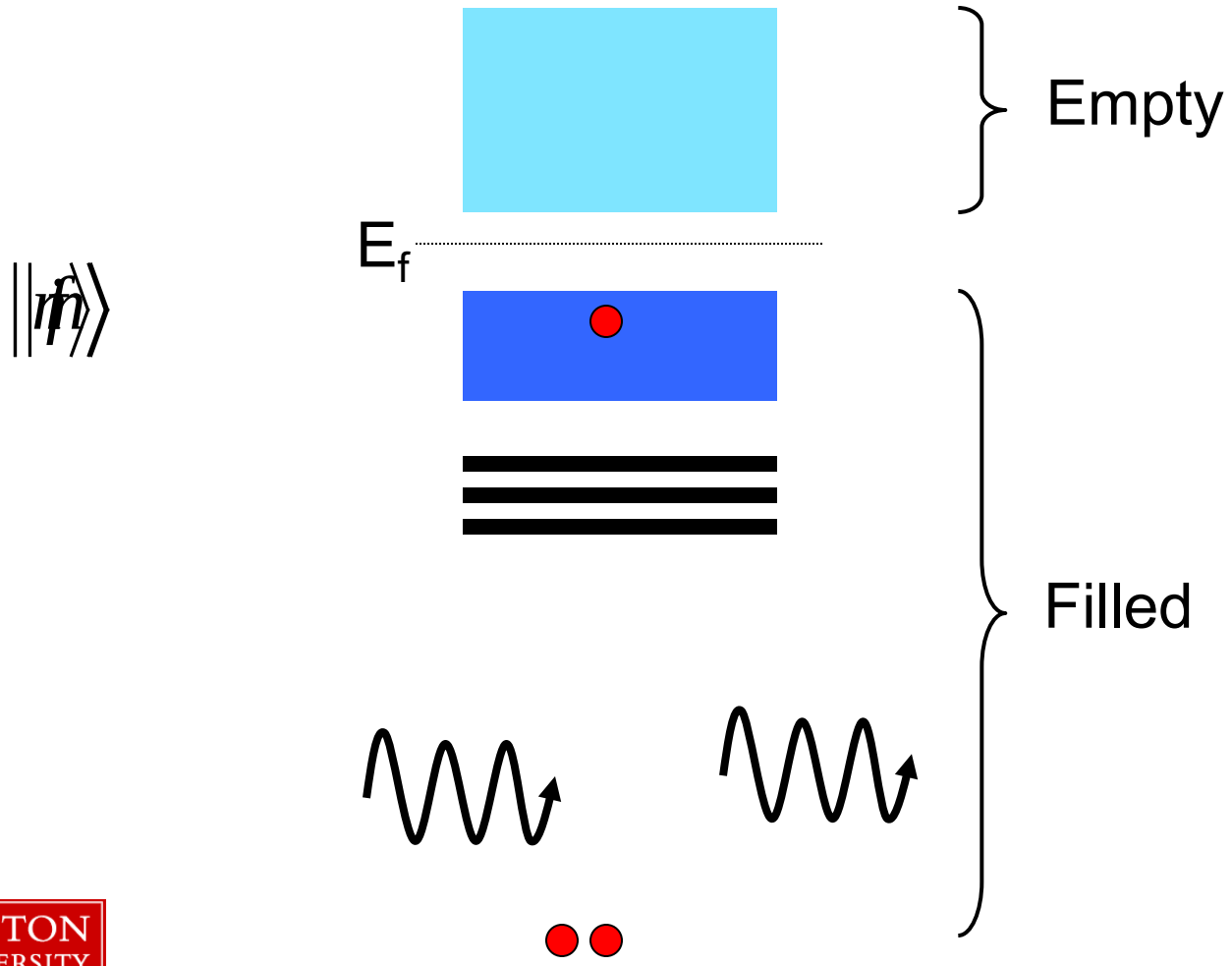
XAS and XES

- Optical processes (photon in/photon out)
  - Magnetic fields
  - Insulators
  - Dirty surfaces
  - Capping layers
- Advantages over photoemission in *some* domains

Selection rules

- Site selection
- Orbital selection
  - Dipole selection rule (conservation of angular momentum)
- Orbital selection 2
  - Linear polarization + crystalline anisotropy
- Dispersion?

Resonant x-ray emission (RXES)



RXES

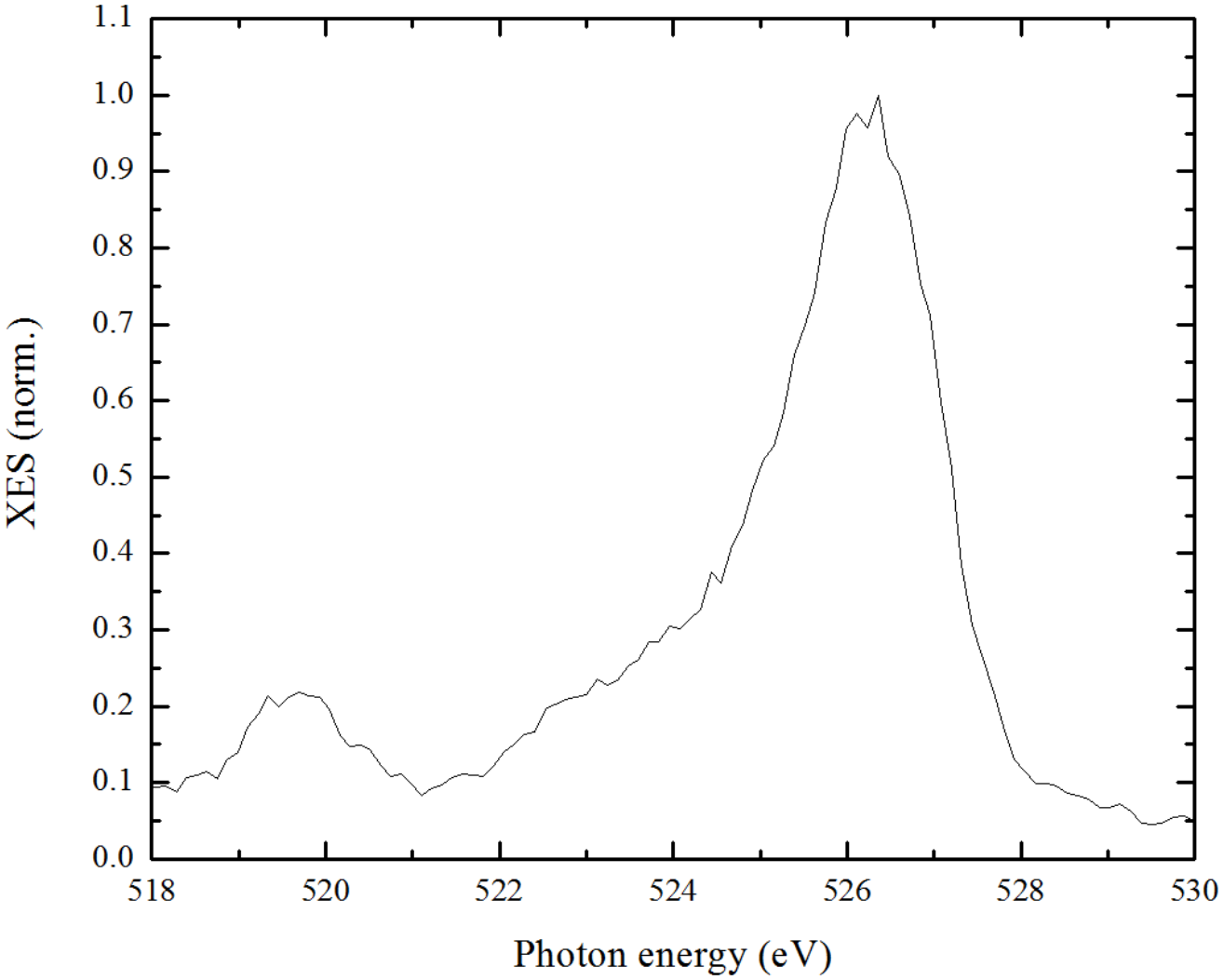
- Kramers-Heisenberg
- Coherent 2nd order process

$$F(\omega_{in},\omega_{out}) \propto \sum_f \left| \sum_i \frac{\langle f | \boldsymbol{\varepsilon}\cdot\mathbf{r} | m \rangle \langle m | \boldsymbol{\varepsilon}\cdot\mathbf{r} | i \rangle}{\hbar\omega_{in} - (E_m - E_i) - i\Gamma_i} \right|^2 \times \delta(\hbar\Delta\omega - (E_f - E_i))$$

  - XAS from |i> to |m>, followed by XES from |m> to |f>
- Selection rule: conservation of crystal momentum!

$$\delta(k_f - k_i)$$

RXES = coherent and incoherent XES



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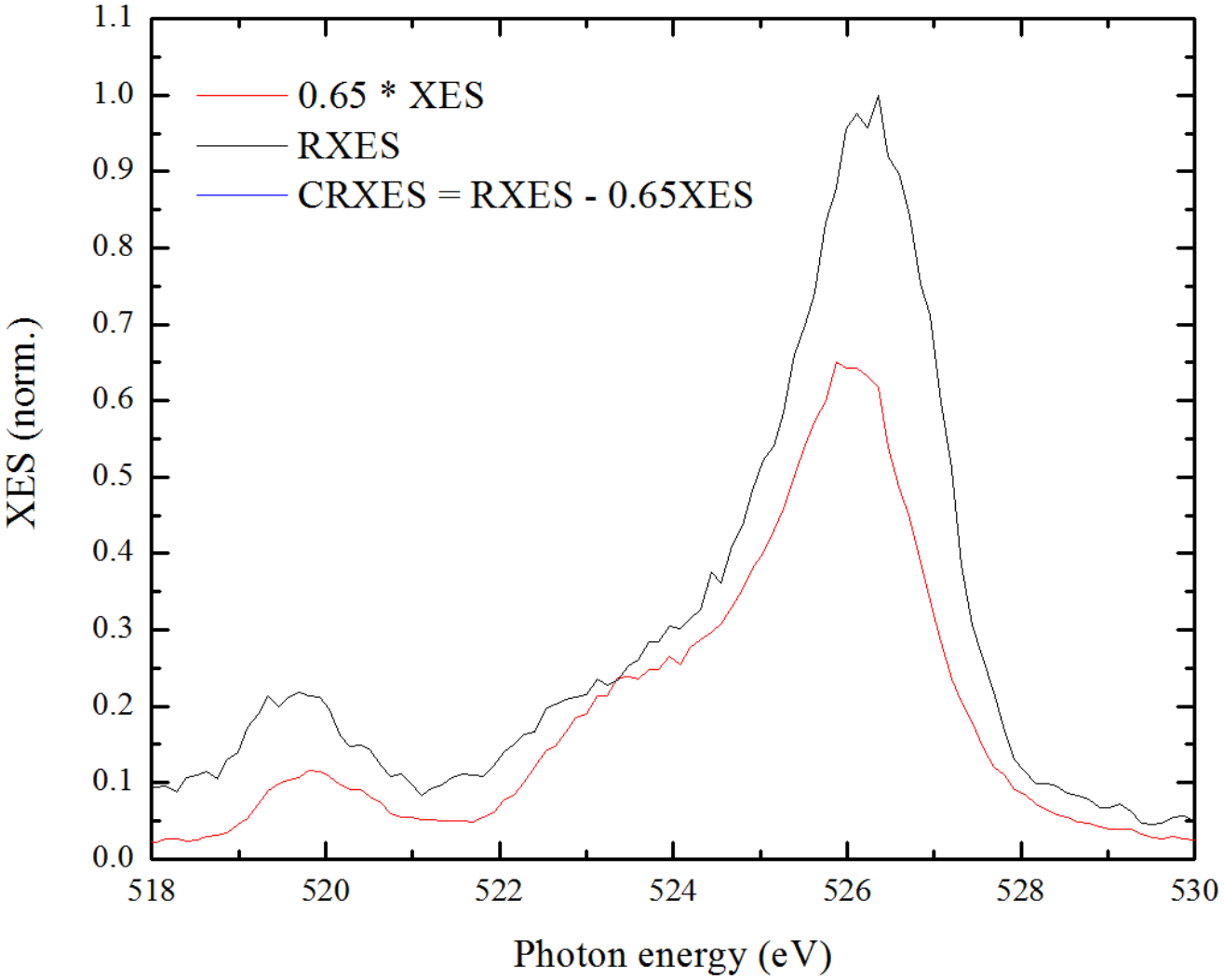
RXES



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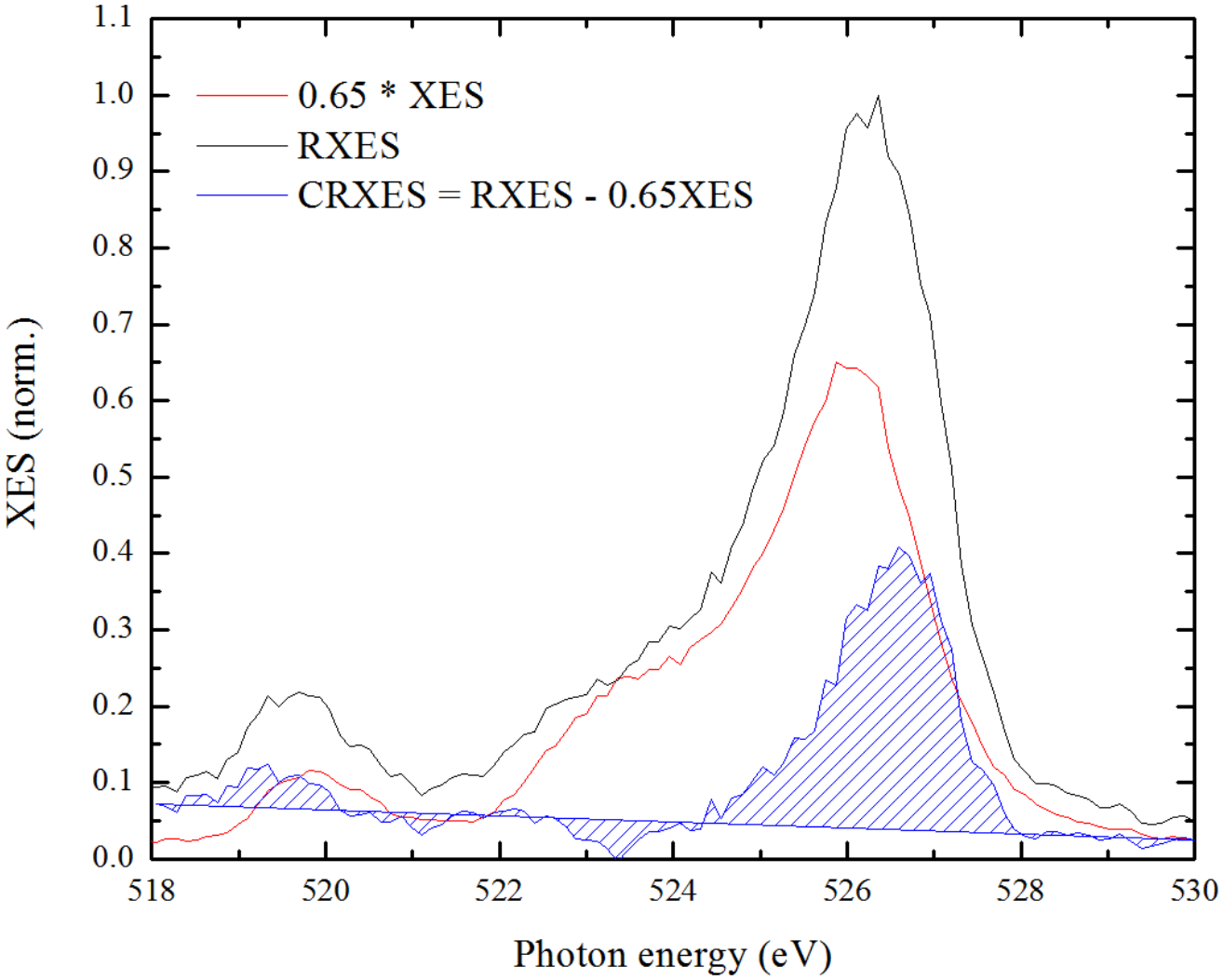

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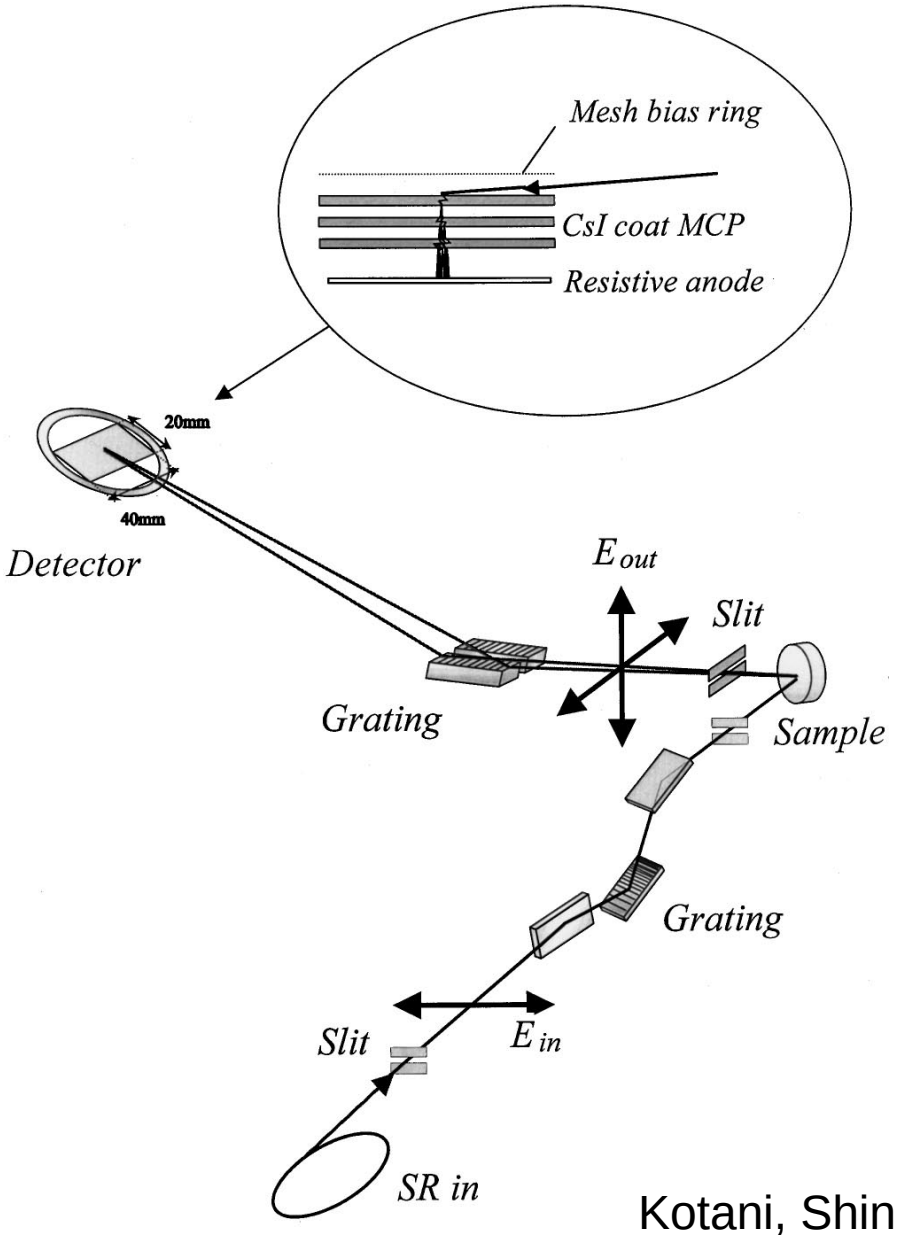
RXES



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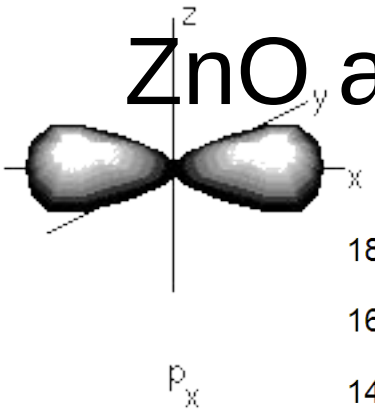
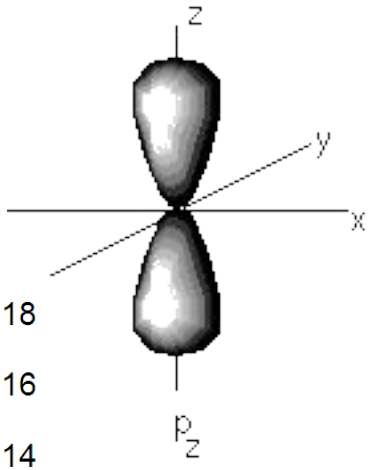
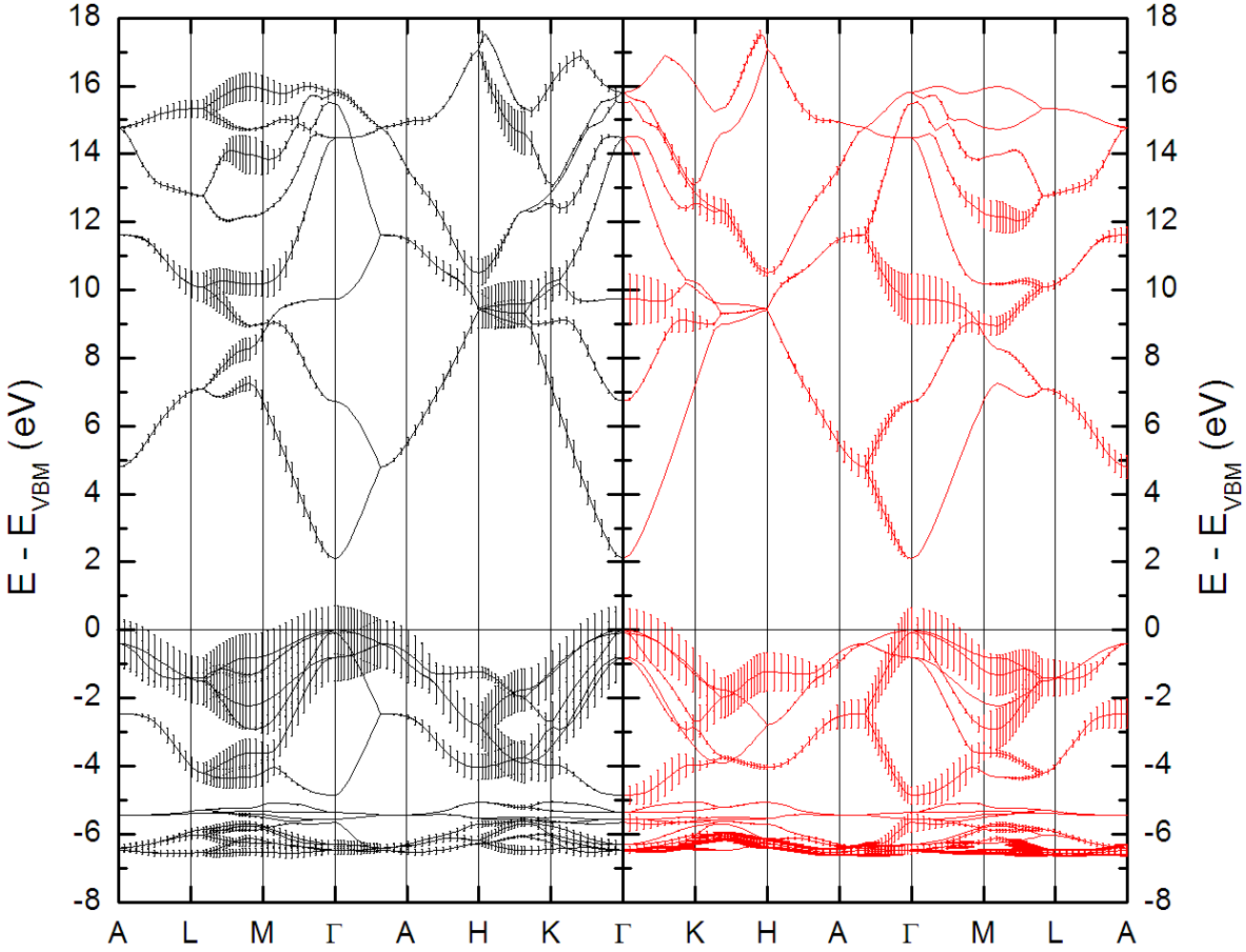
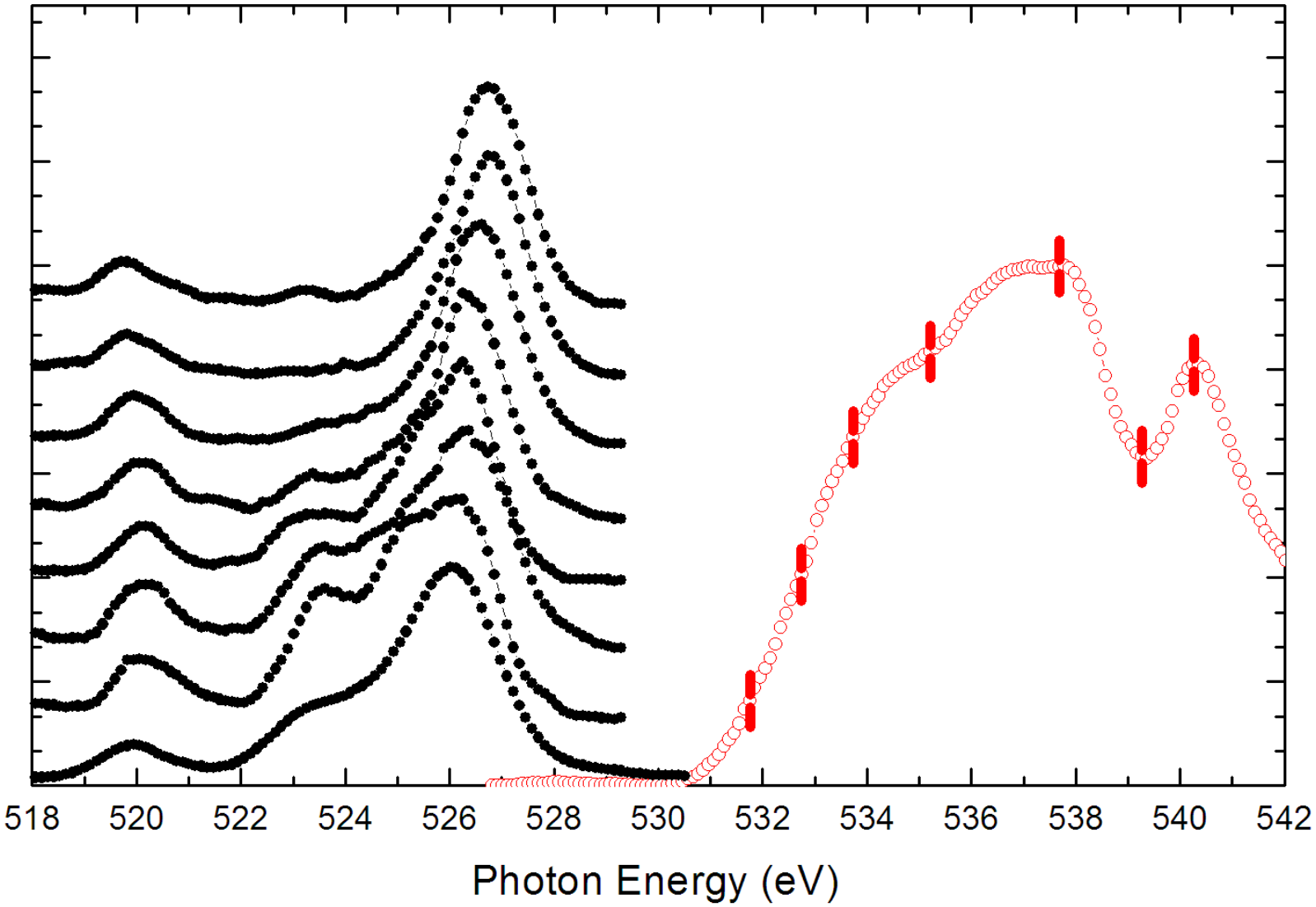
ZnO anisotropy







ZnO RXES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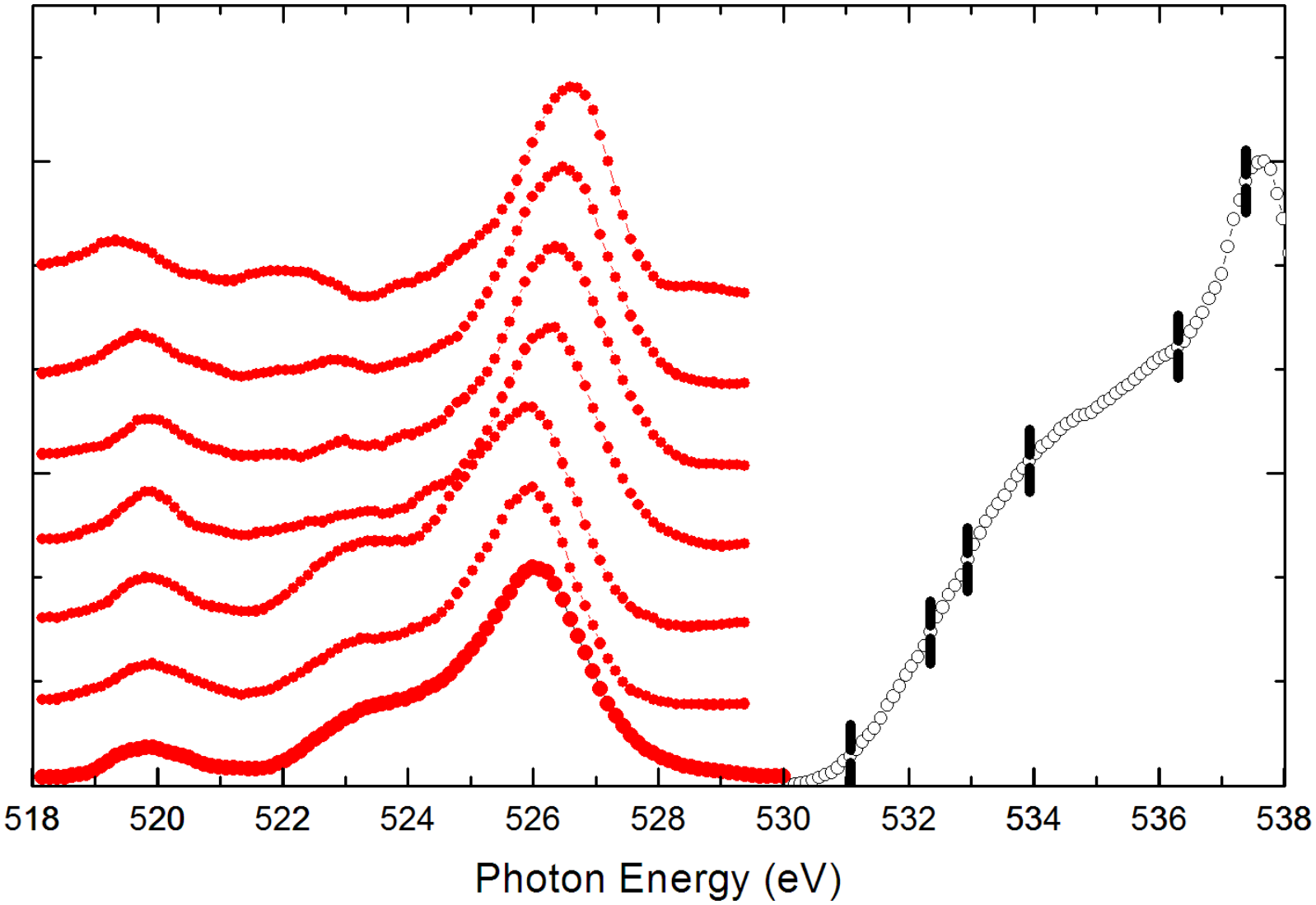
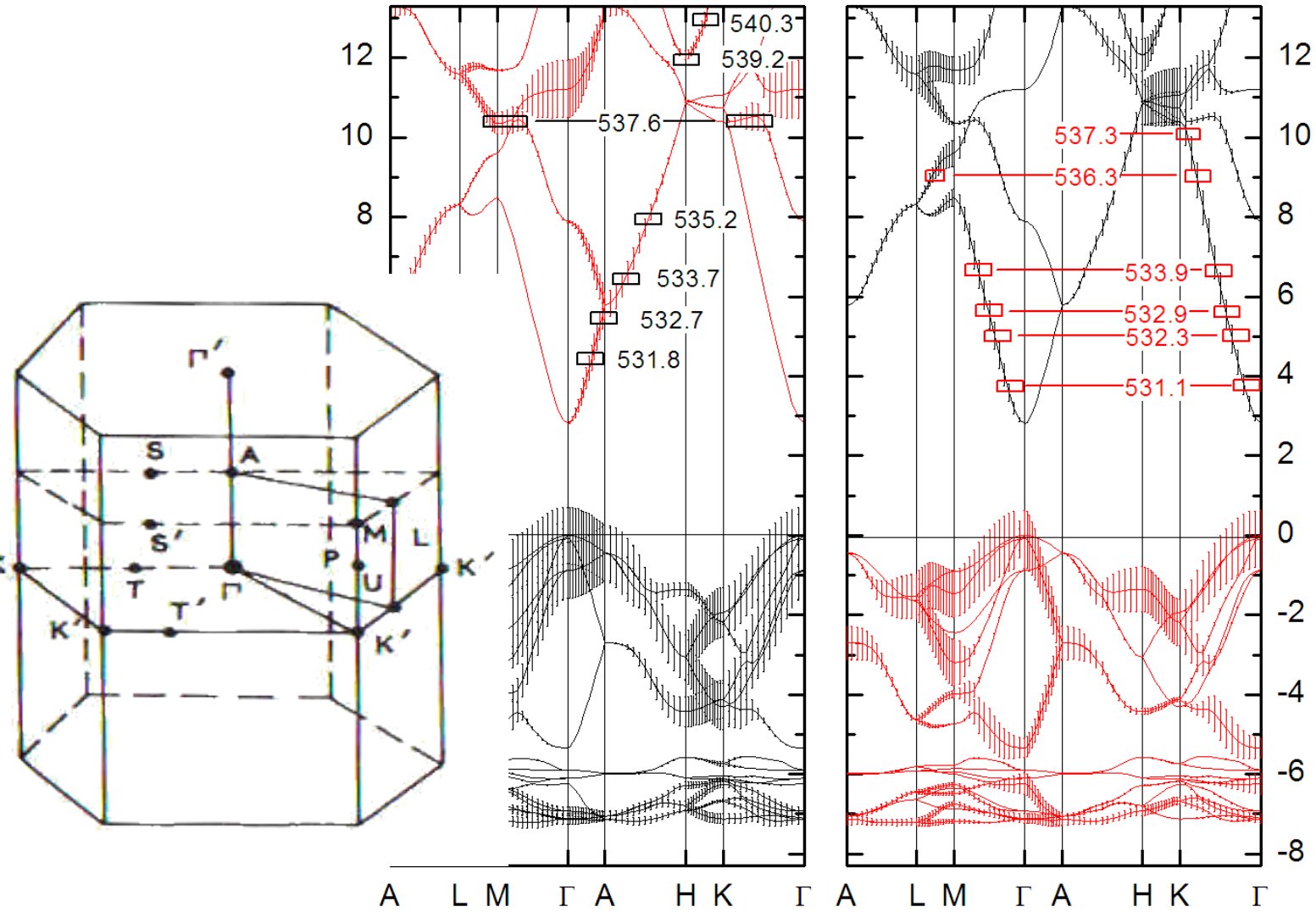
Photon Energy (eV)

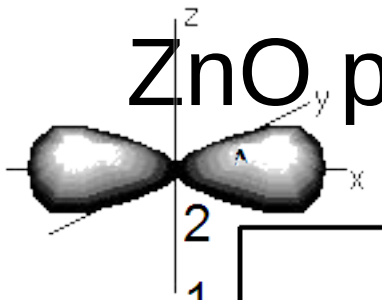
ZnO RXES

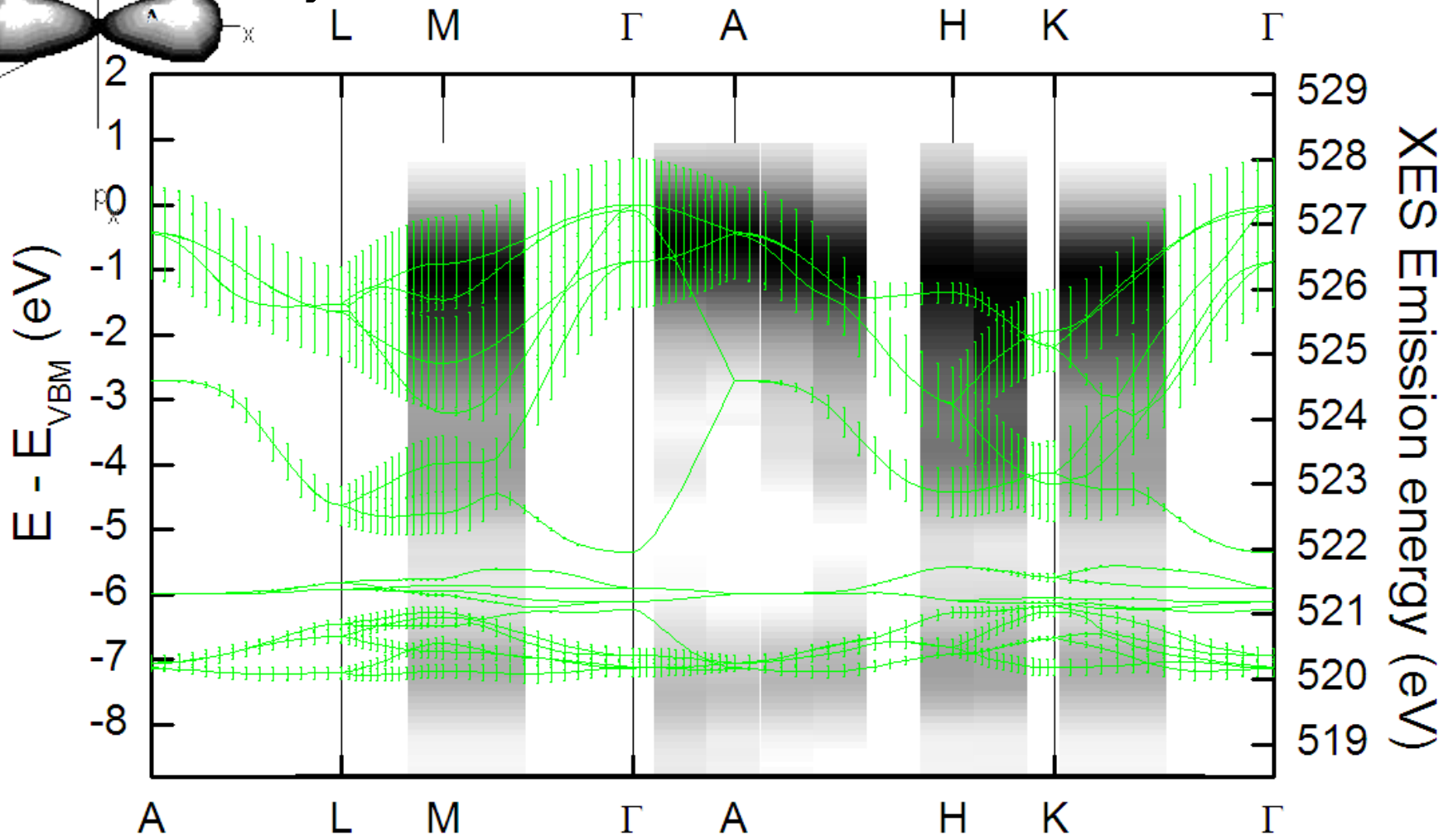


ZnO RXES

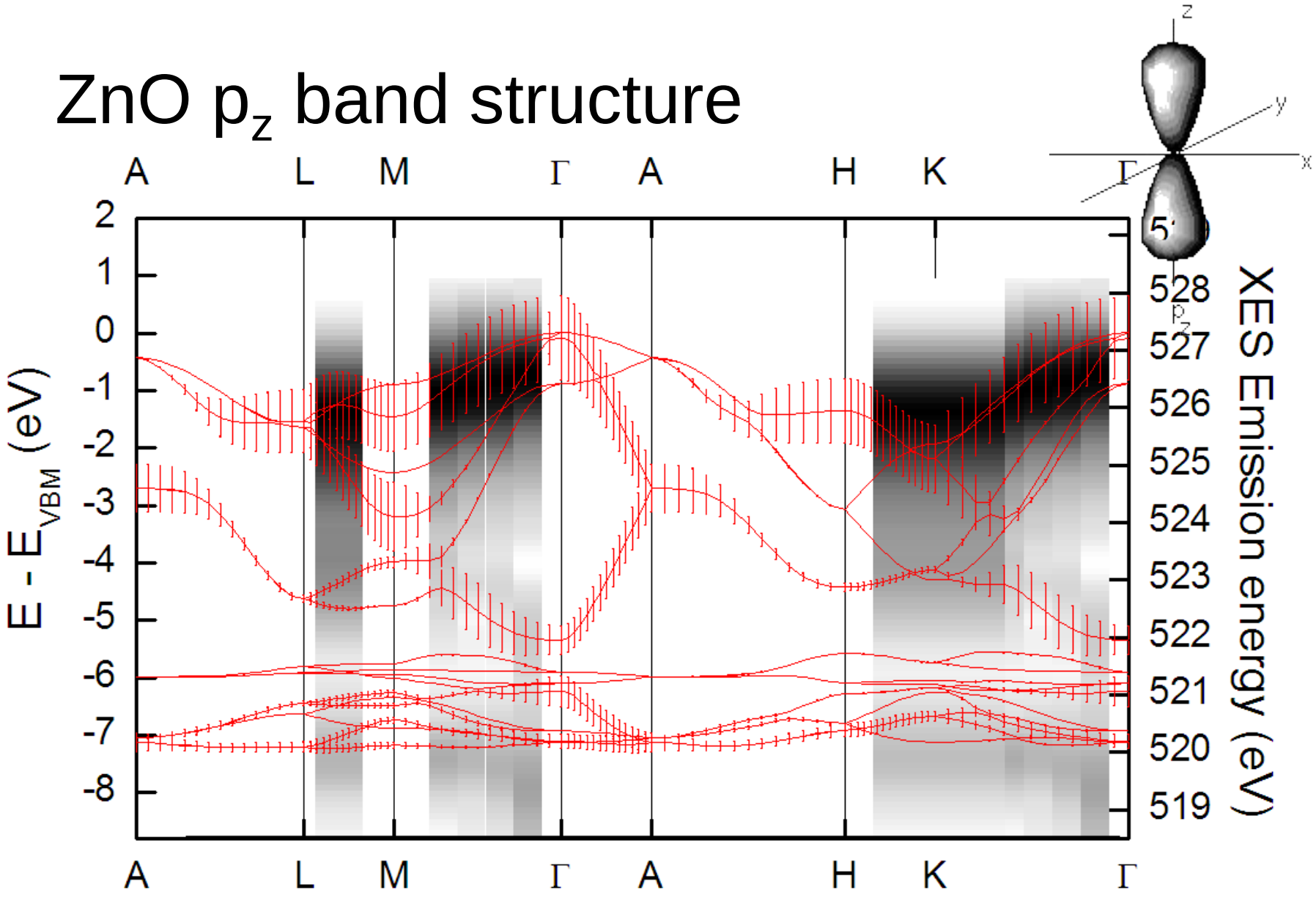

540.3
539.2
537.6
535.2
533.7
532.7
531.8
537.3
536.3
533.9
532.9
532.3
531.1
12
10
8
6
4
2
0
-2
-4
-6
-8
A L M Γ A H K Γ
A L M Γ A H K Γ
Γ′
S
A
S′
M
L
P
U
T
T′
Γ
K
K′
K′

ZnO p_{xy} band structure





ZnO p_z band structure



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- B. J. Ruck
  - Victoria University of Wellington
- L. F. J. Piper, A. DeMasi, K. E. Smith
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  - Friedrich-Schiller-Universitat
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Can we calculate the RXES?

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