

Band structure information from soft x-ray spectroscopy

Andrew Preston

andrew@preston.co.nz

Materials World Network



Spintronics group

- Ben Ruck, Joe Trodahl



Electronic structure group

- Walter Lambrecht



Novel Materials Lab

- Kevin Smith

NML at BU



Kevin Smith



Louis Piper



Sang Wan
Cho



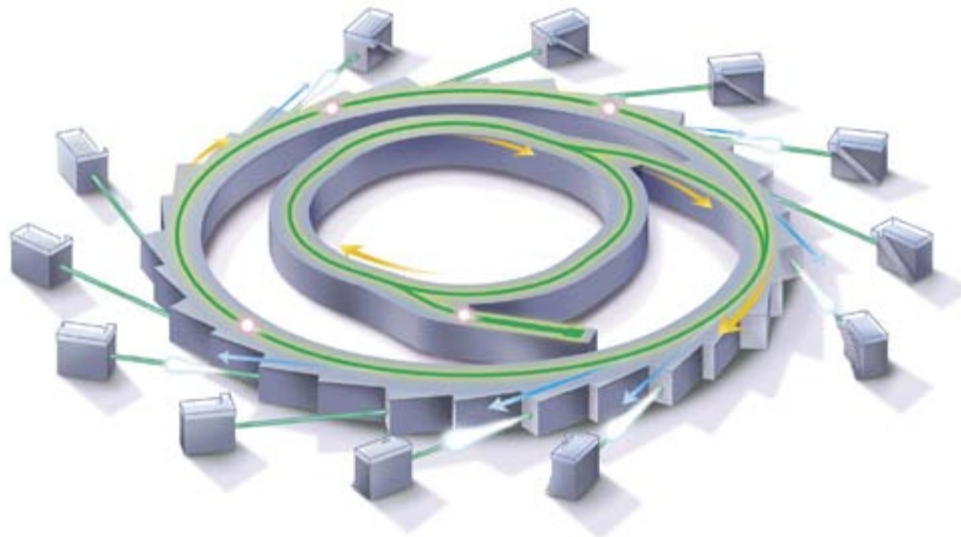
Alex DeMasi

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)

NML at BU

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



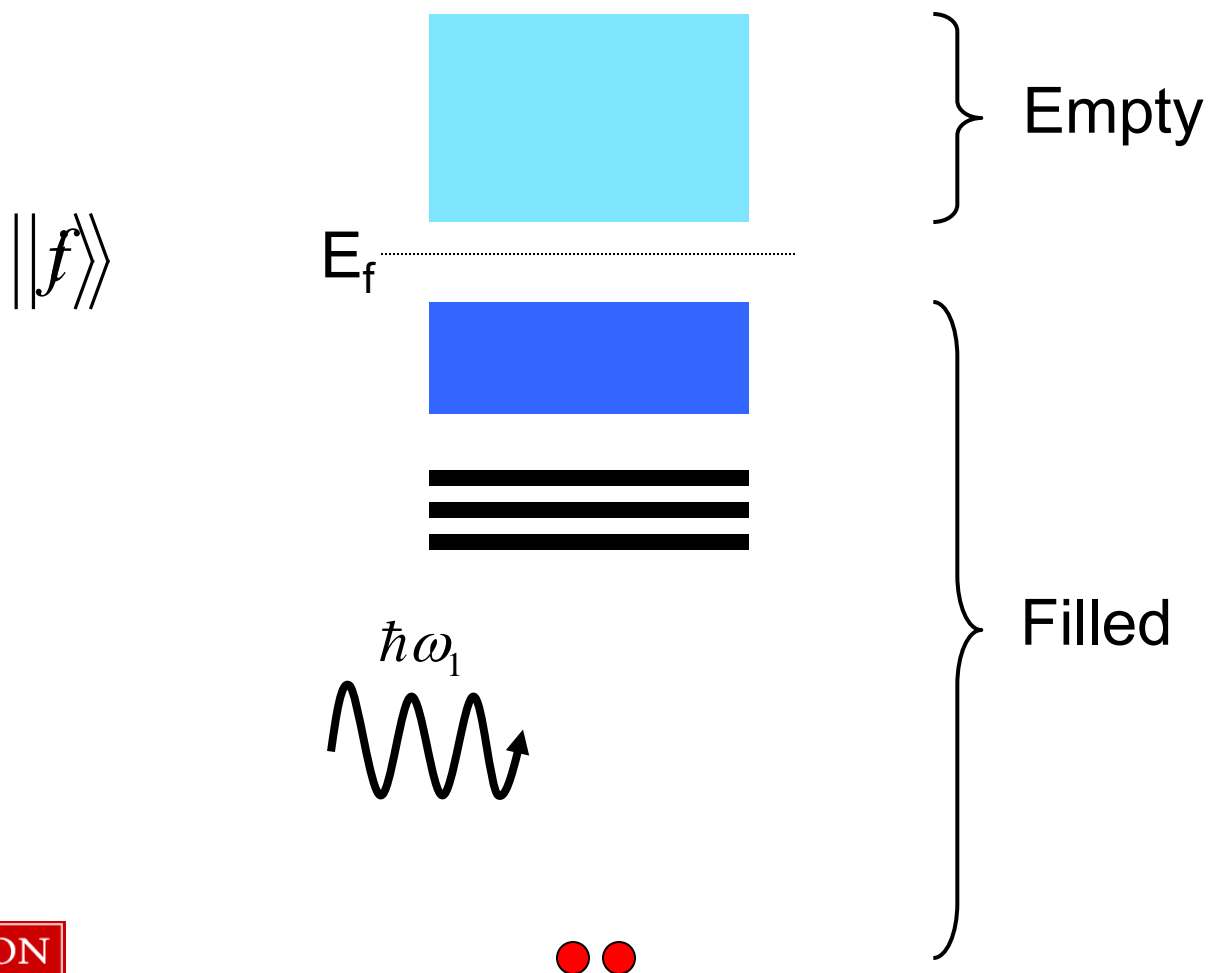
Spectroscopy

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

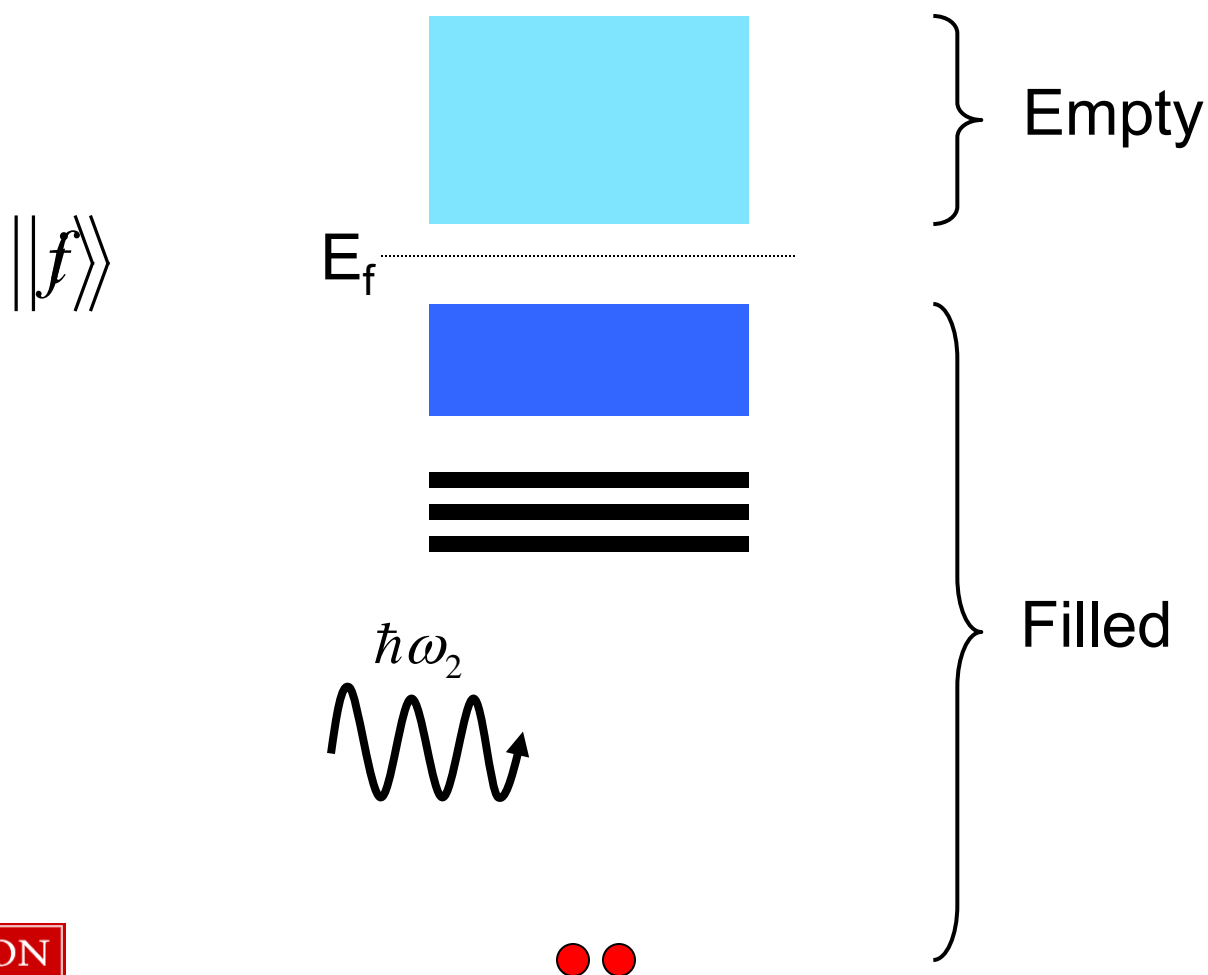
Spectroscopy

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

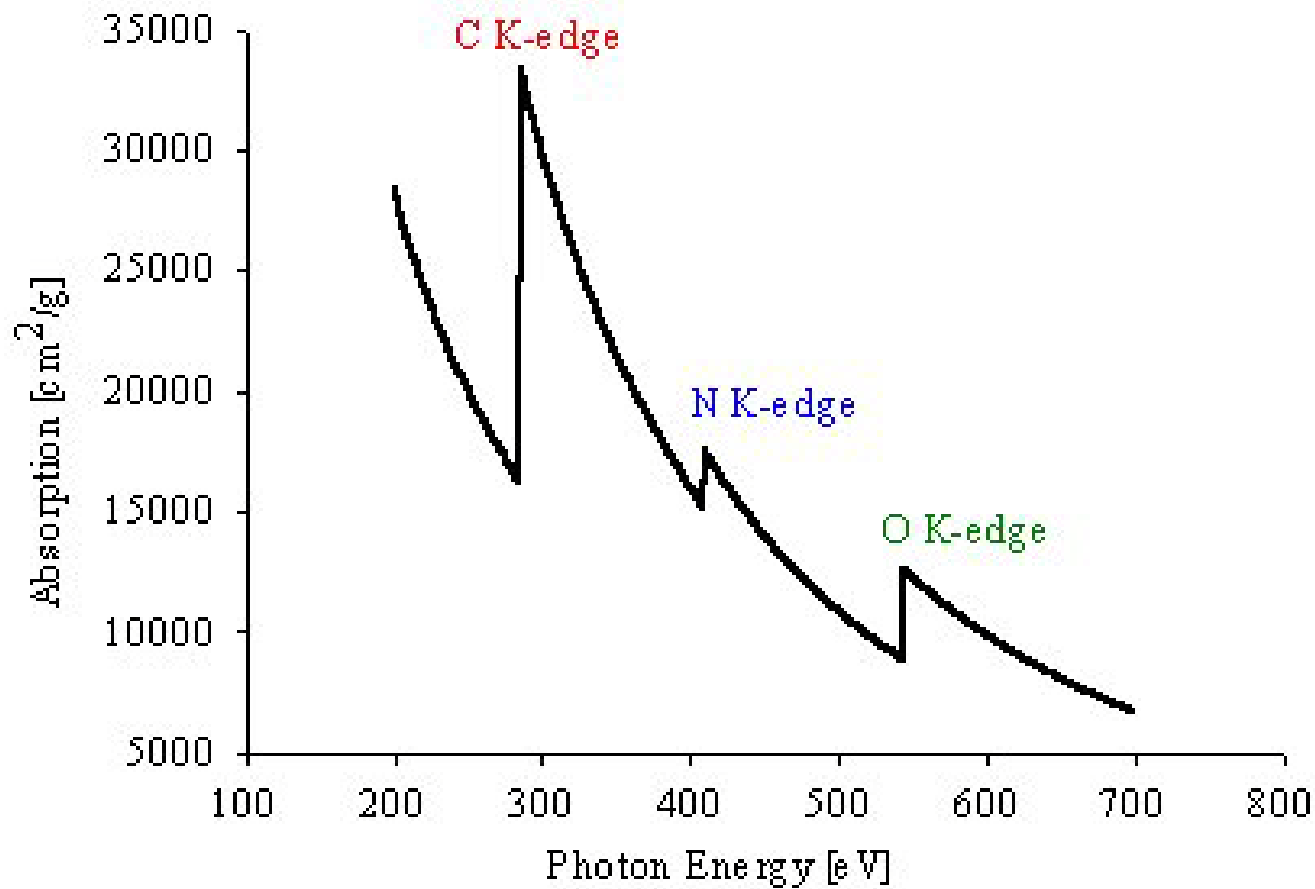
X-ray absorption (XAS)



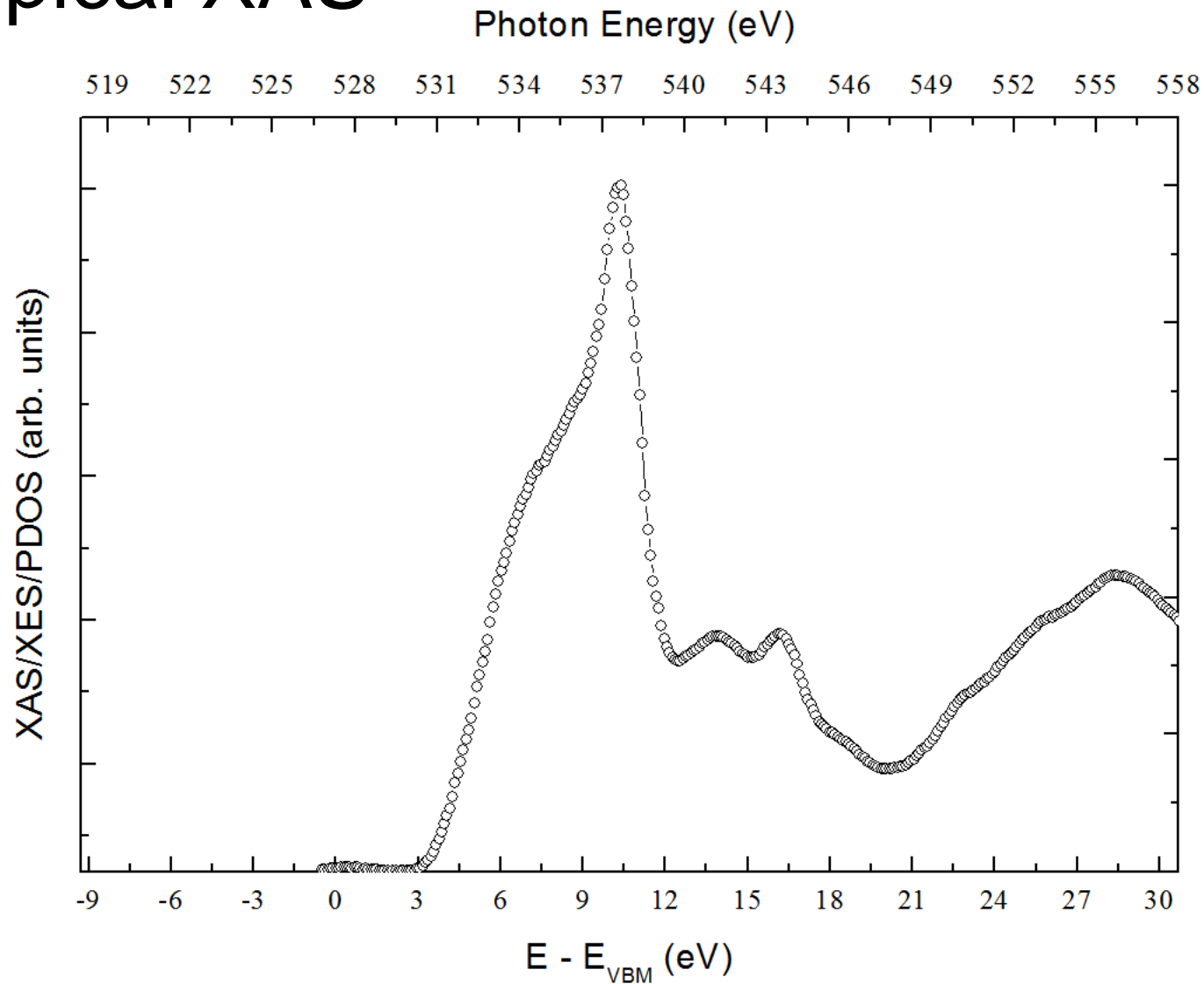
X-ray absorption (XAS)



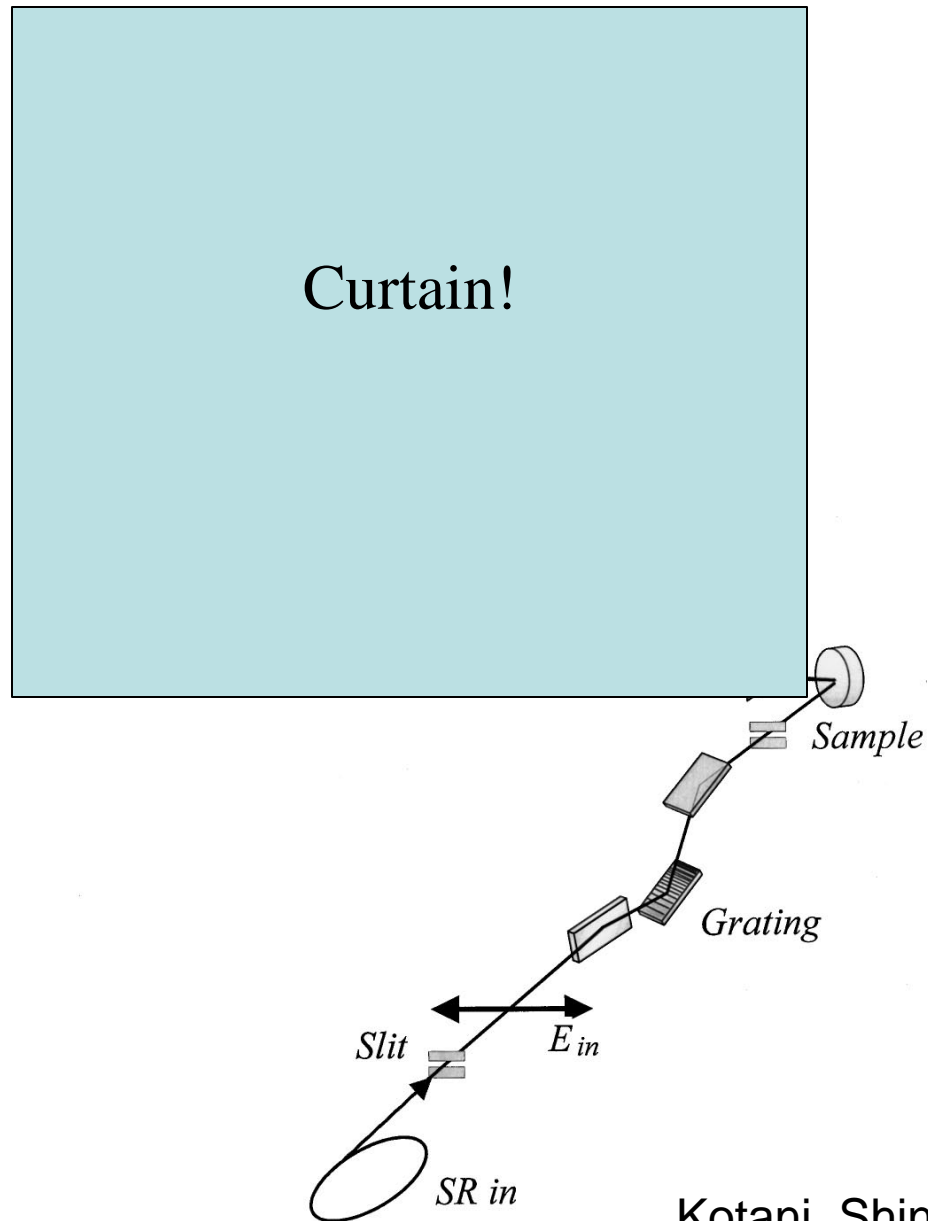
Site selectivity



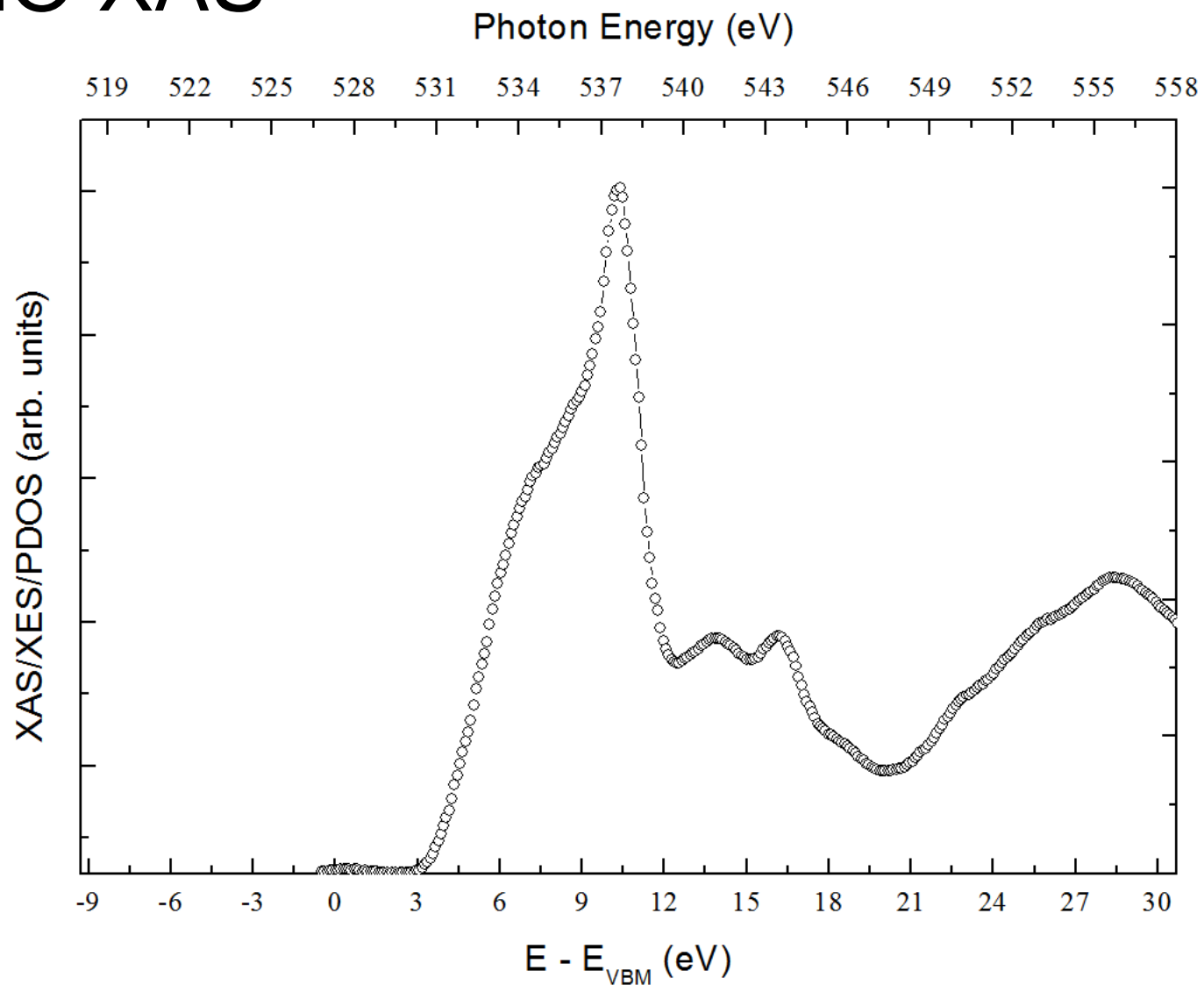
Typical XAS



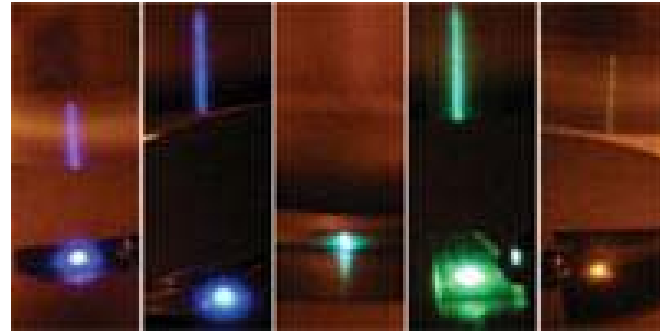
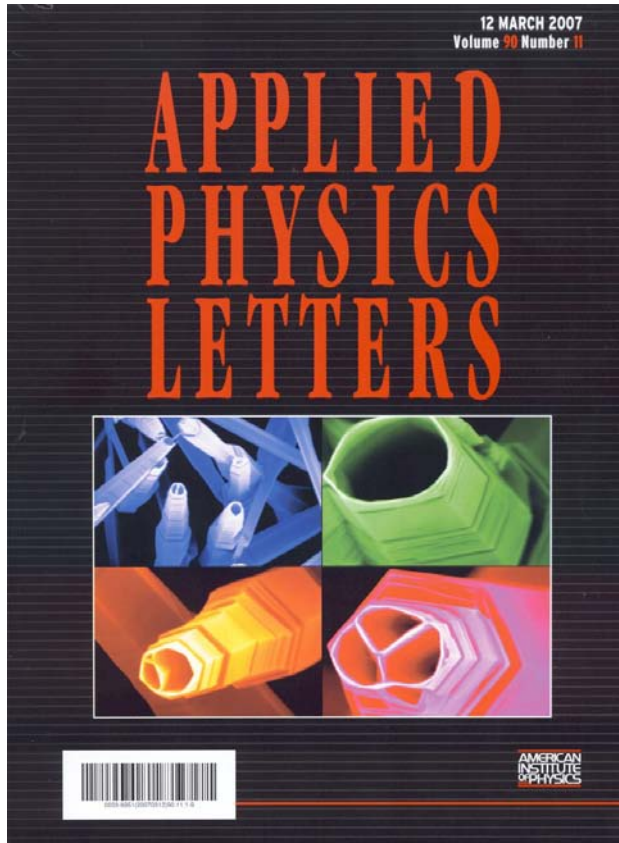
XAS



ZnO XAS



Zinc oxide



Zinc oxide

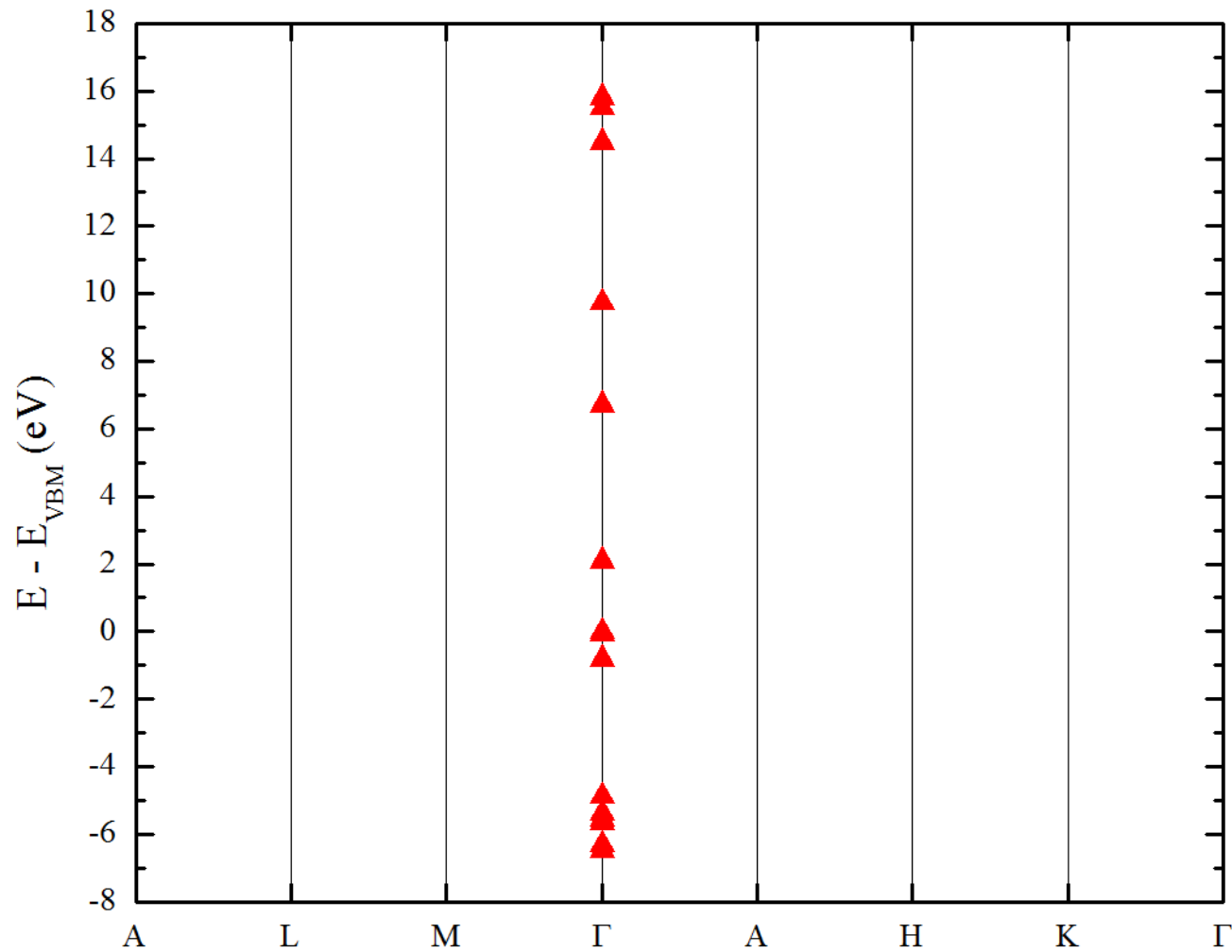


1 H Hydrogen 1.007 94																	2 He Helium 4.002 602
3 Li Lithium 6.941	4 Be Beryllium 9.012 182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.998 4032	10 Ne Neon 20.1797
11 Na Sodium 22.989 770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981 538	14 Si Silicon 28.0855	15 P Phosphorus 30.973 761	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955 910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938 049	26 Fe Iron 55.845	27 Co Cobalt 58.933 200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.921 60	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.905 85	40 Zr Zirconium 91.224	41 Nb Niobium 92.906 38	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905 50	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904 47	54 Xe Xenon 131.293
55 Cs Cesium 132.905 43	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.966 55	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.980 38	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (281)	111 Uuu* Ununium (272)	112 Uub* Unbium (285)	113 Uut* Ununtrium (284)	114 Uuq* Ununquadium (289)	115 Uup* Ununpentium (288)			

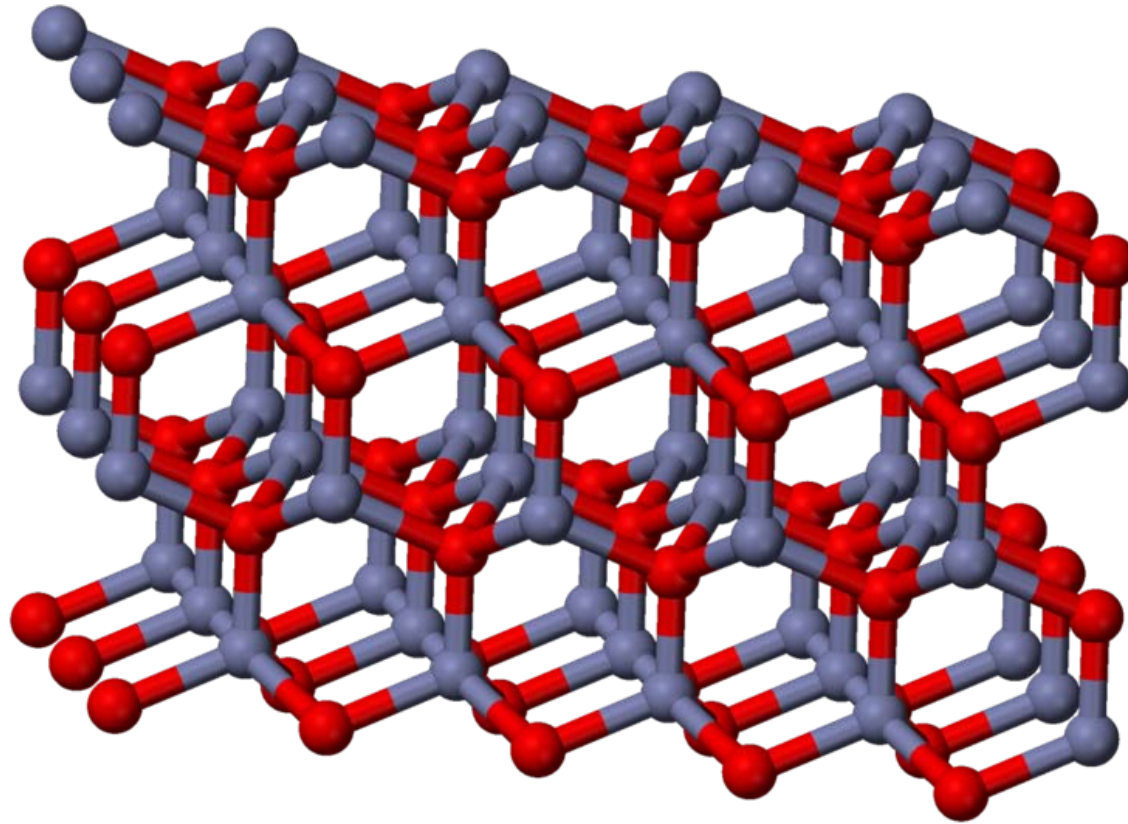
ZnO electronic structure

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

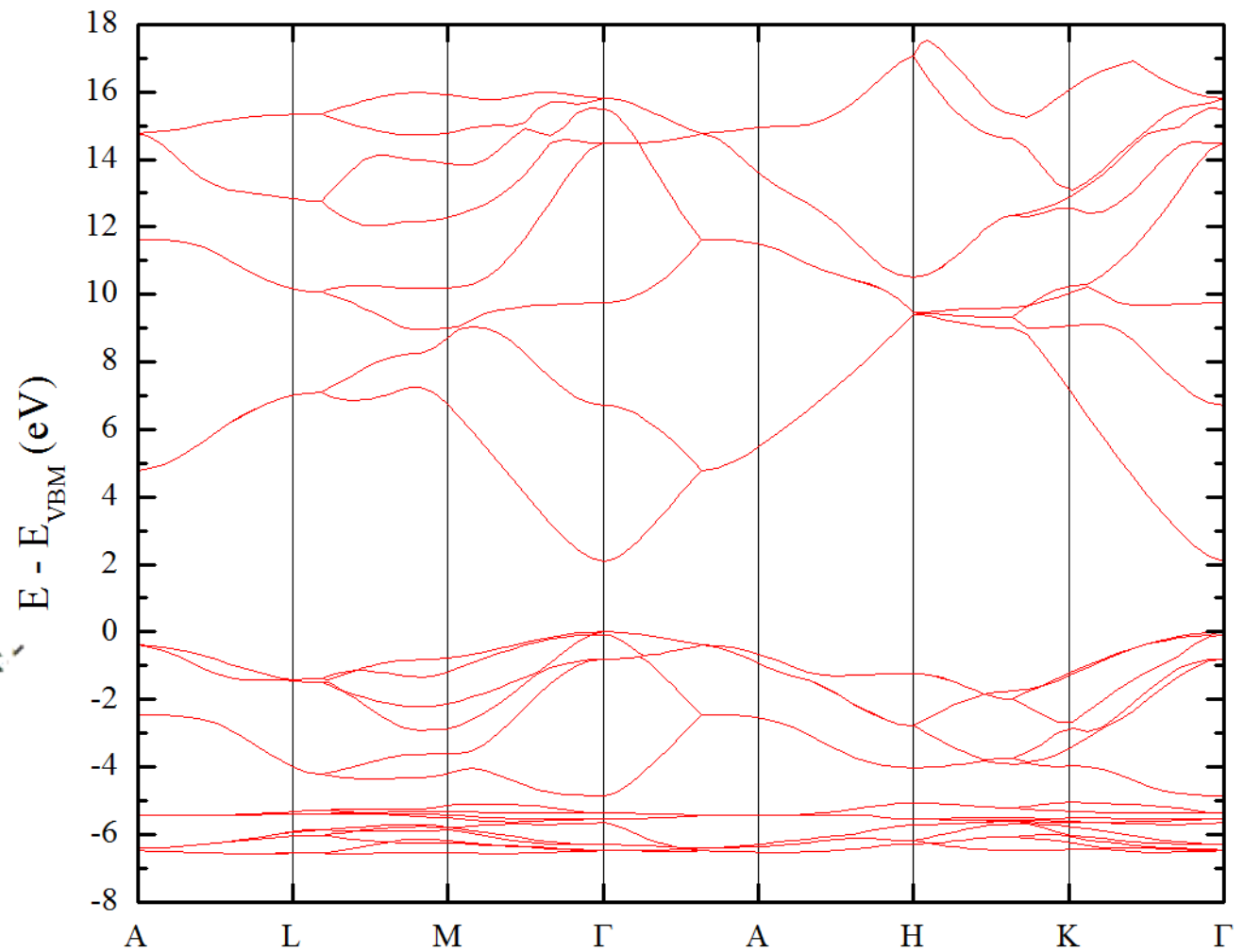
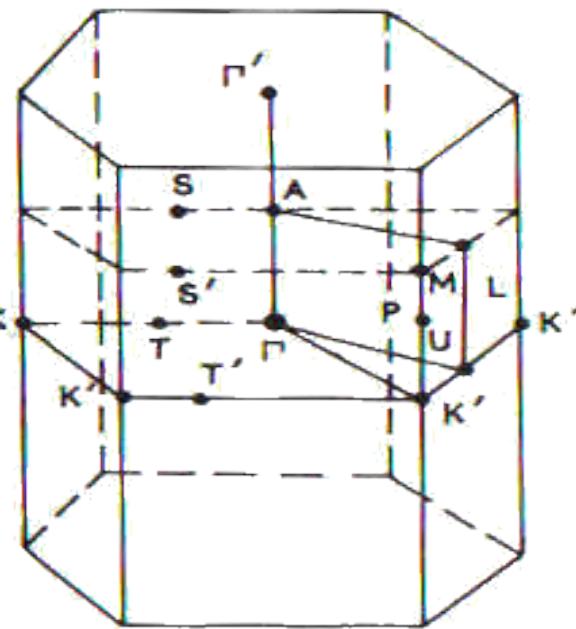
ZnO electronic structure



Zinc oxide



ZnO electronic structure

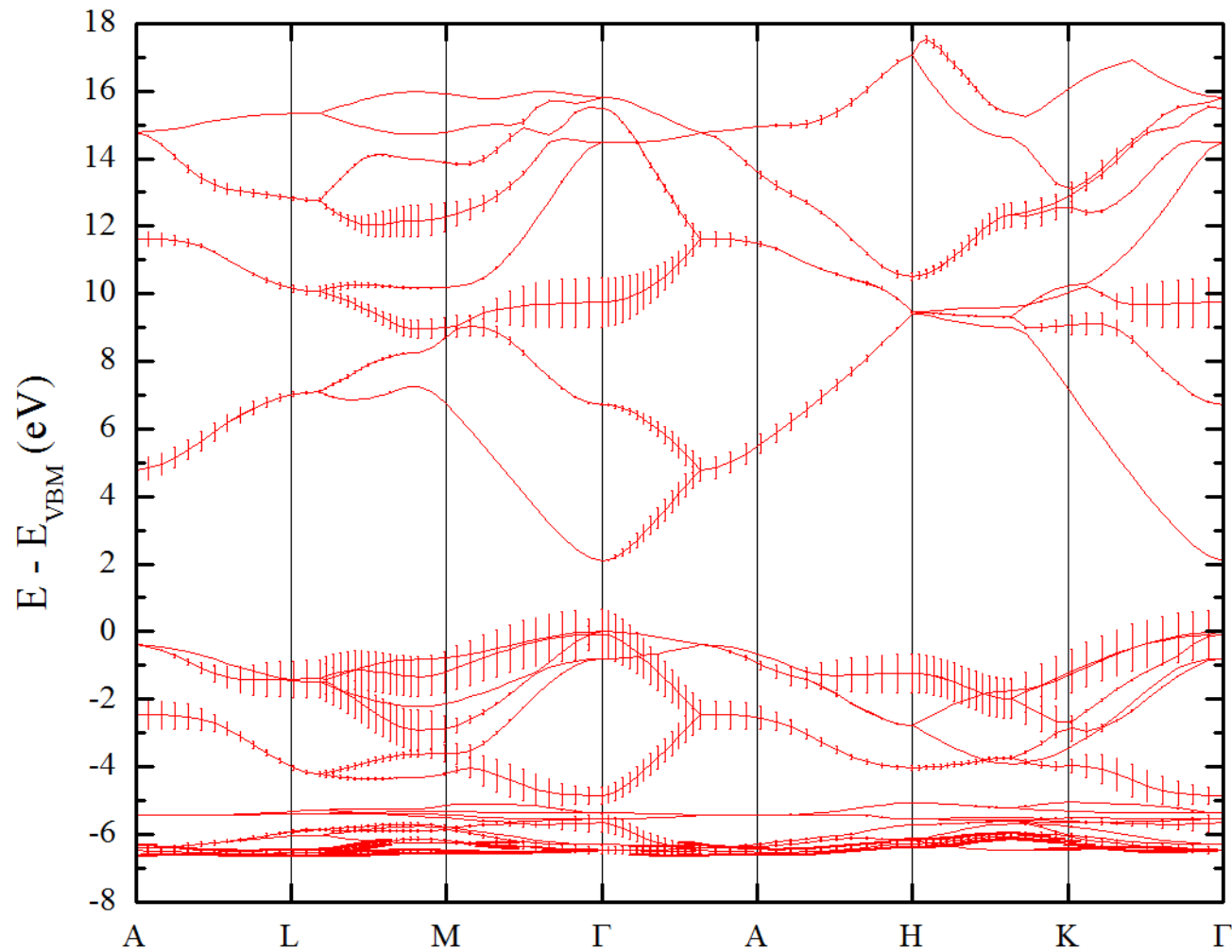


Dipole approximation

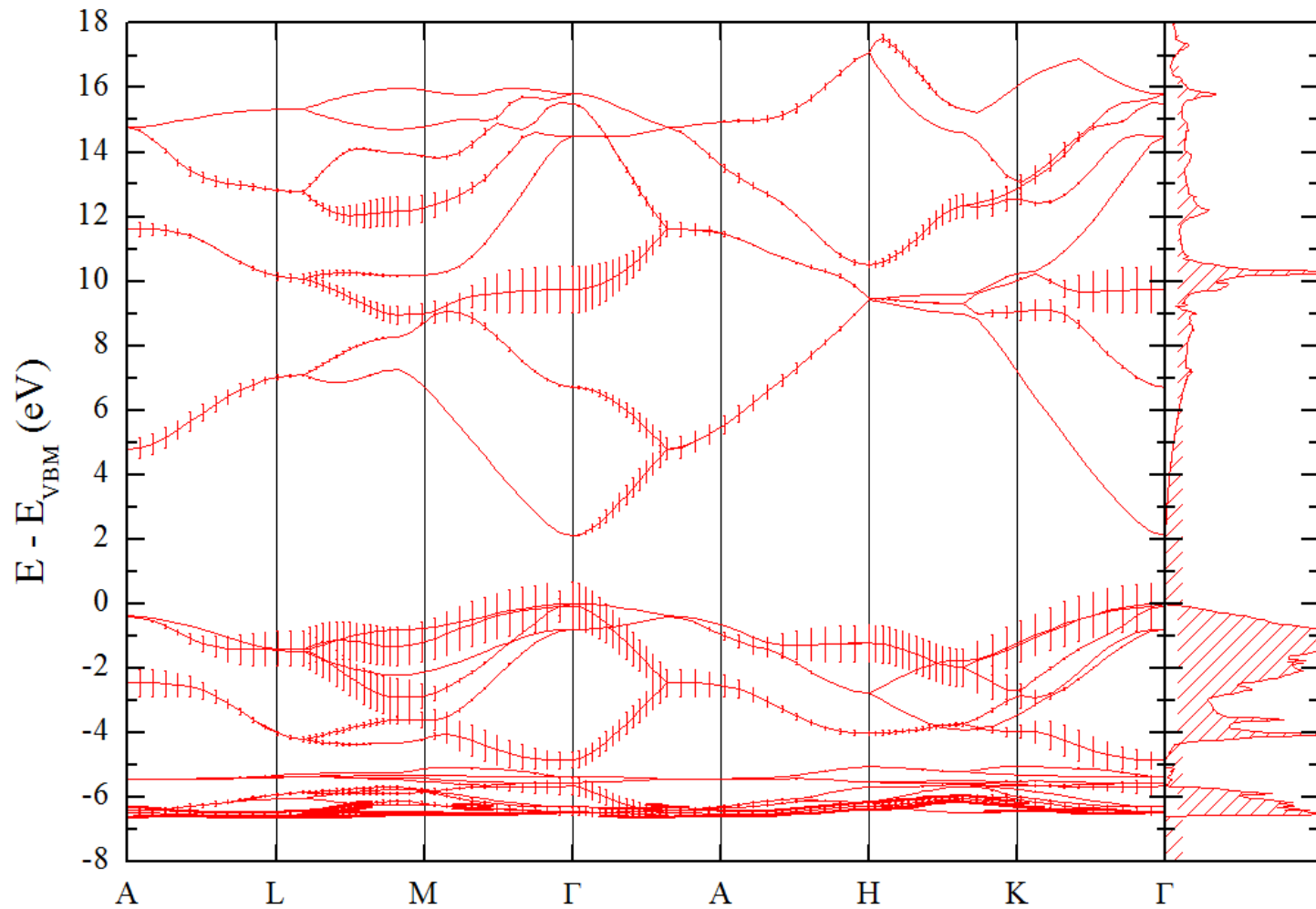
$$P_{i \rightarrow f} \propto \left| \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle \right|^2 \rho_f (\hbar\omega - \Delta E)$$

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

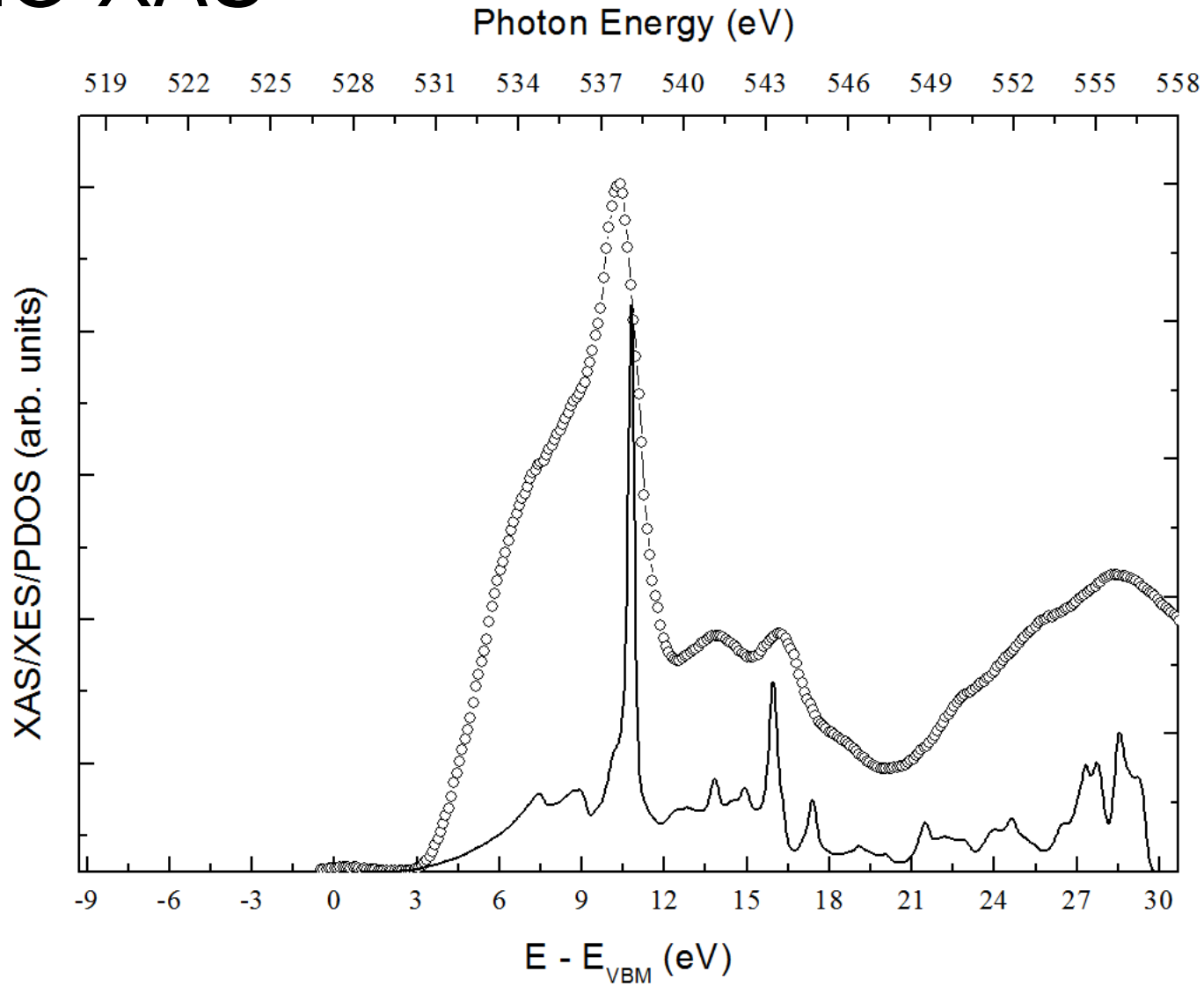
ZnO electronic structure



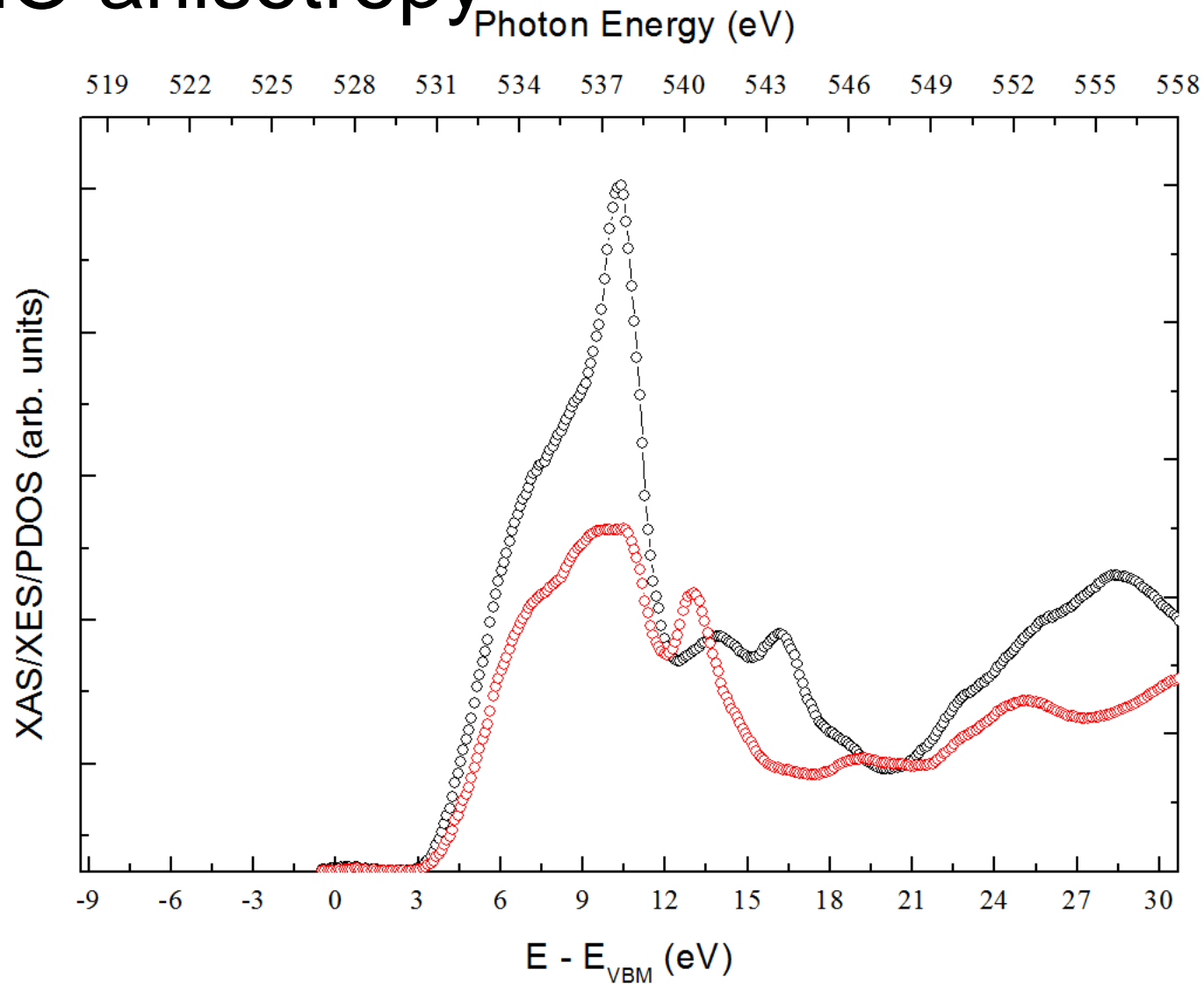
ZnO electronic structure



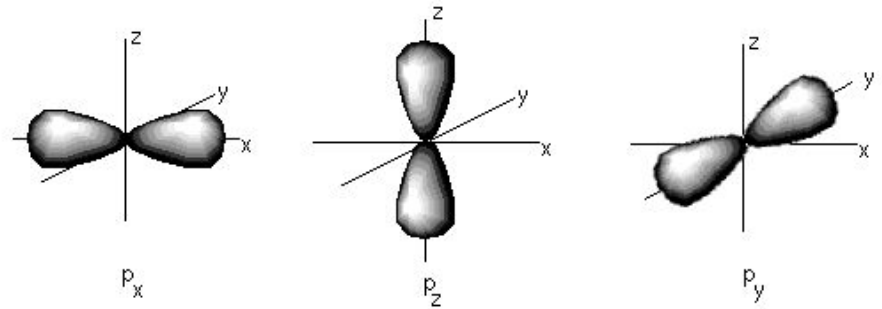
ZnO XAS



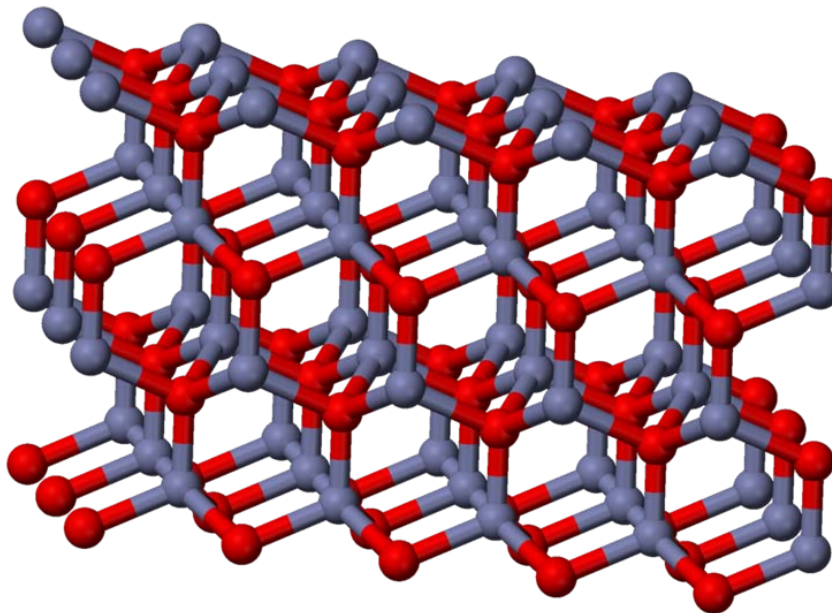
ZnO anisotropy



ZnO anisotropy



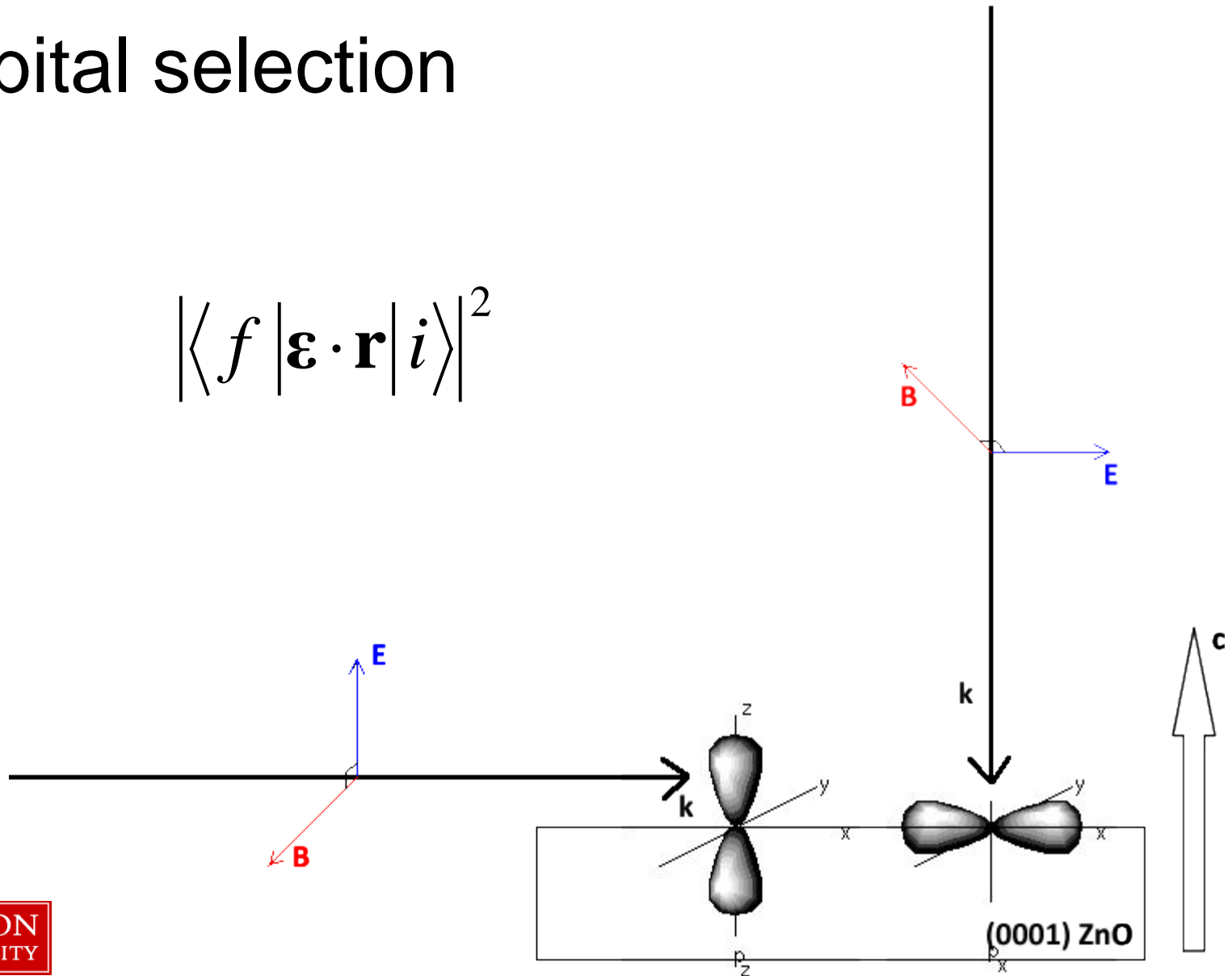
O p orbitals



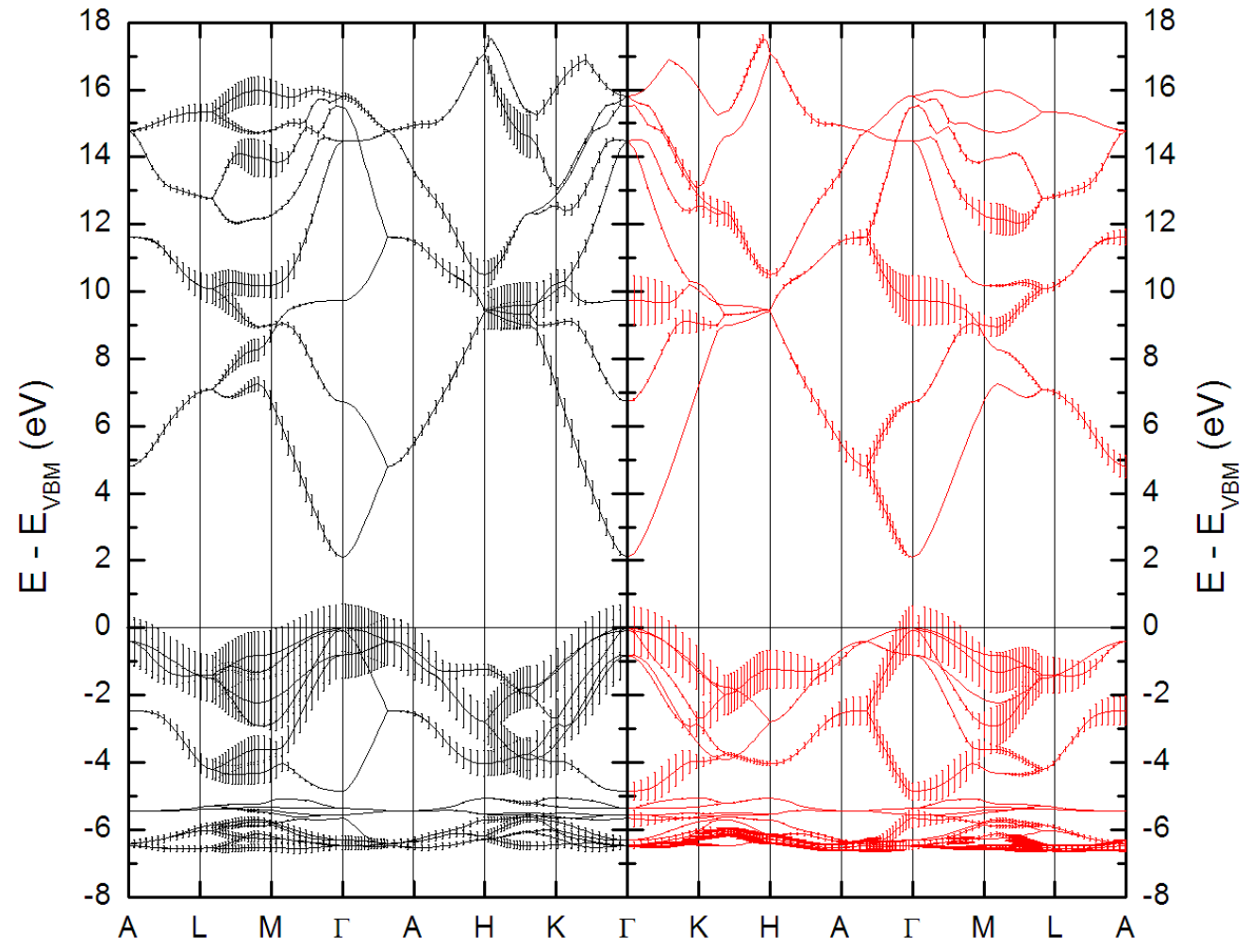
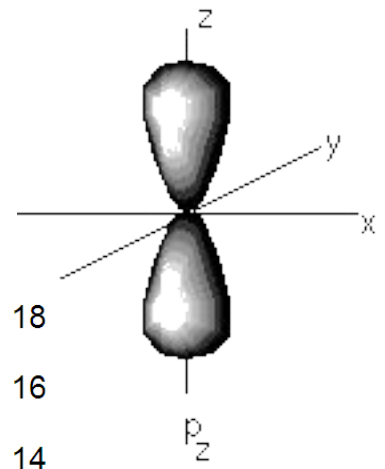
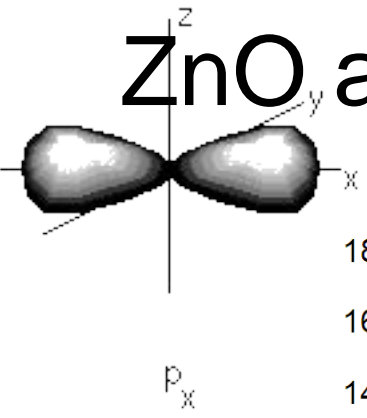
ZnO crystal

Orbital selection

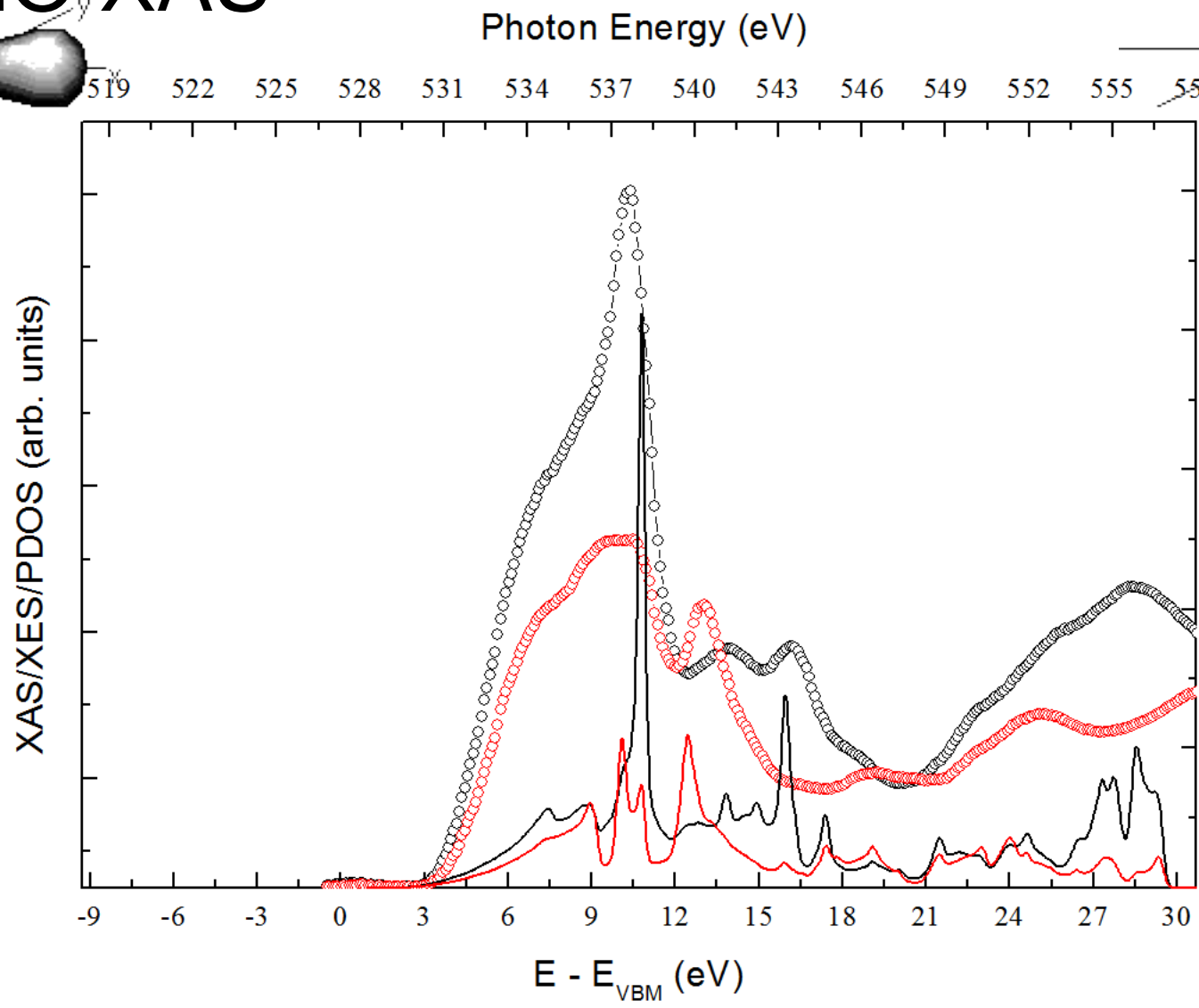
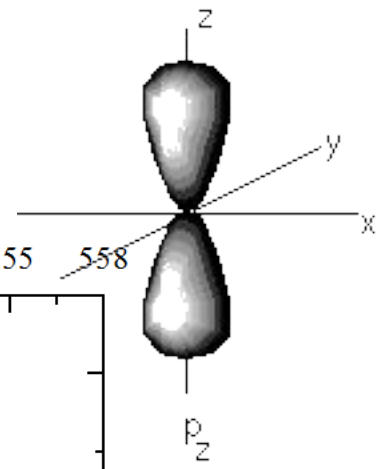
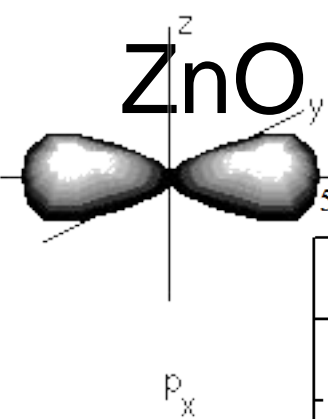
$$|\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle|^2$$



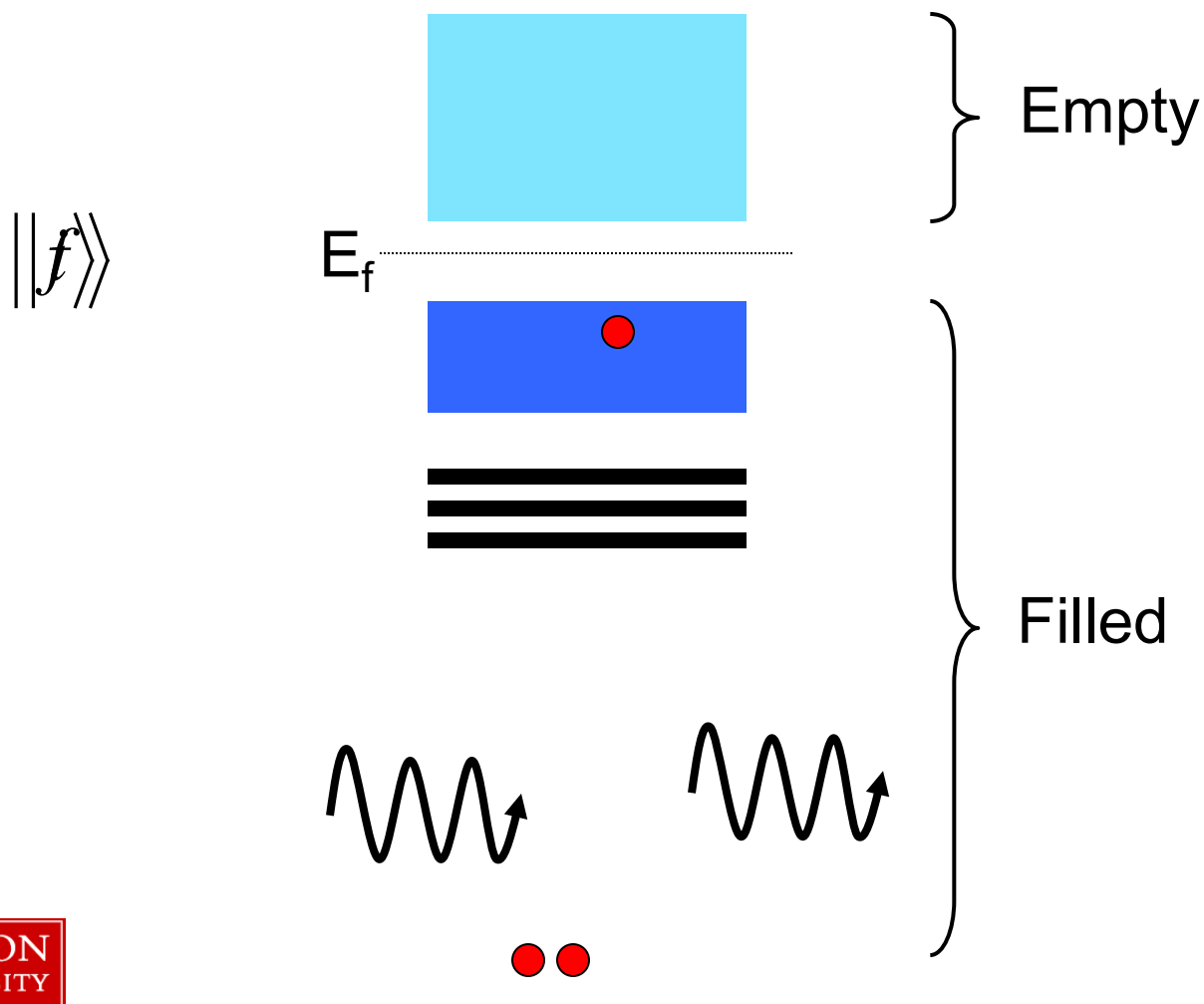
ZnO anisotropy



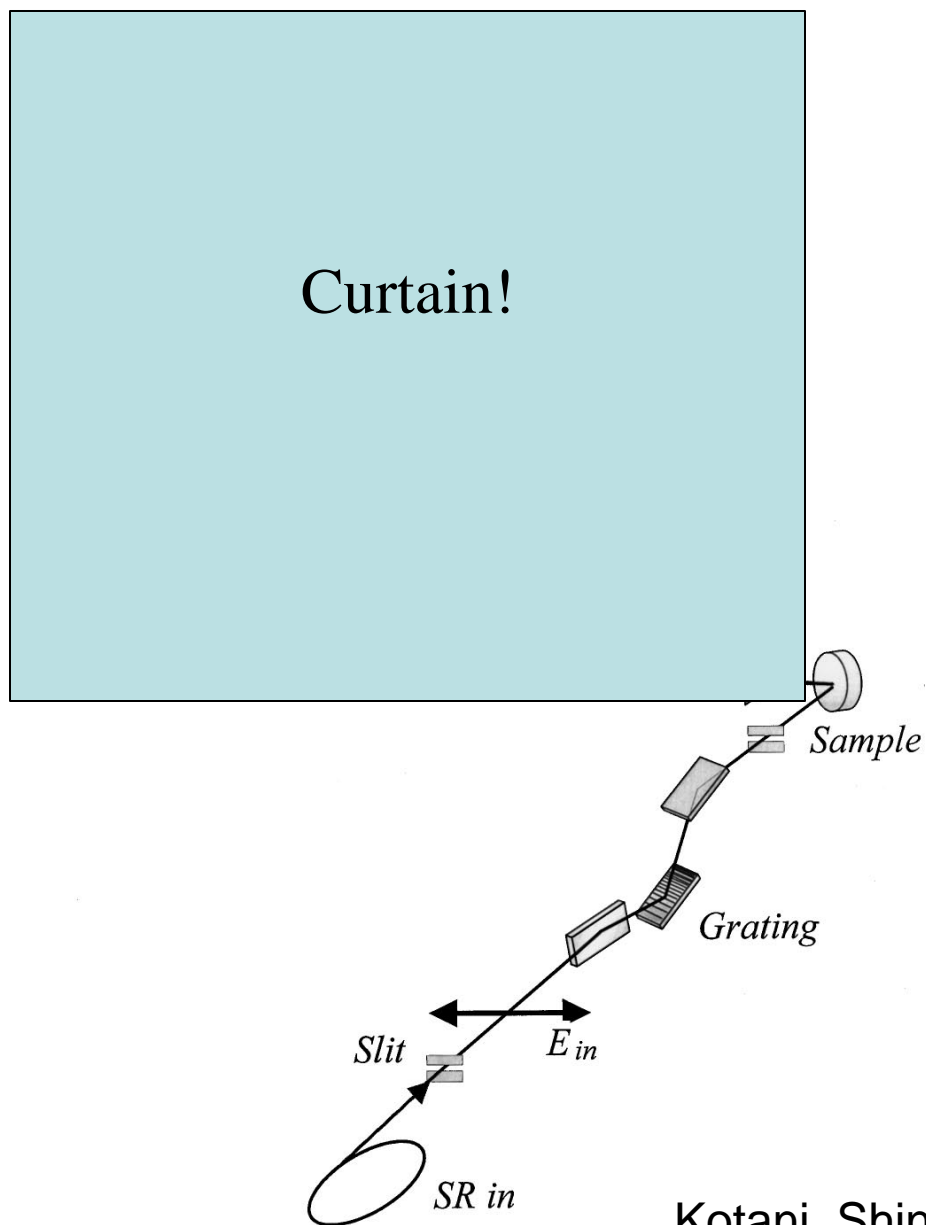
ZnO XAS



X-ray emission (XES)



XES

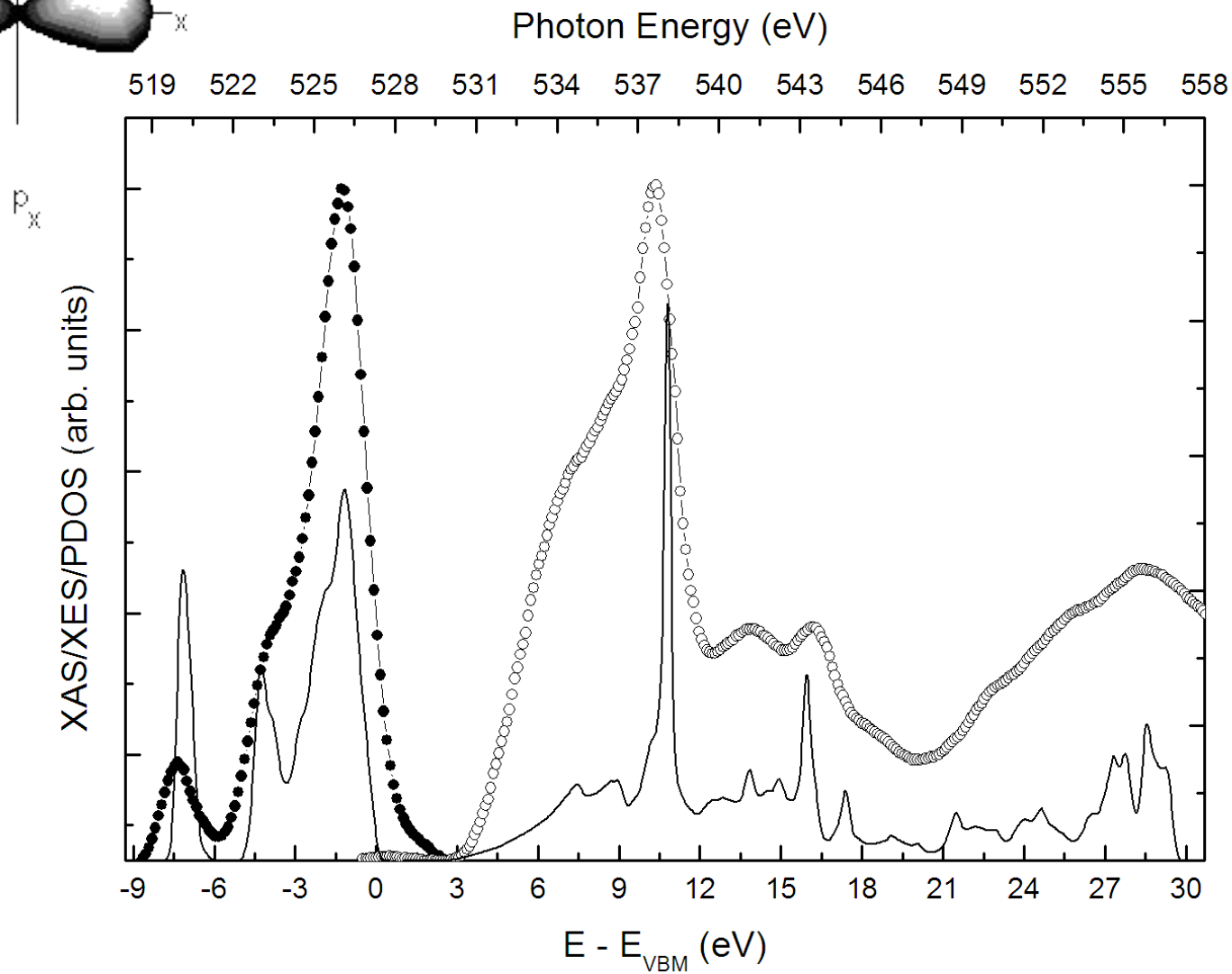
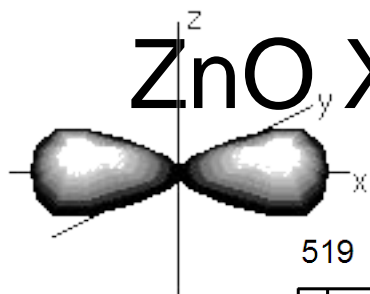


Dipole approximation

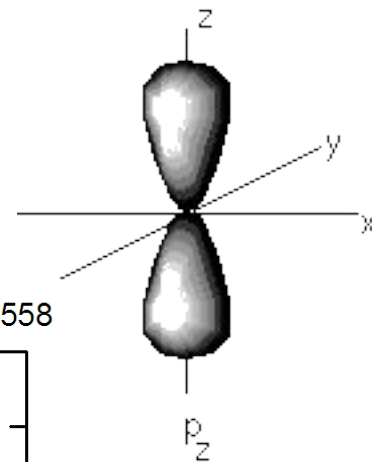
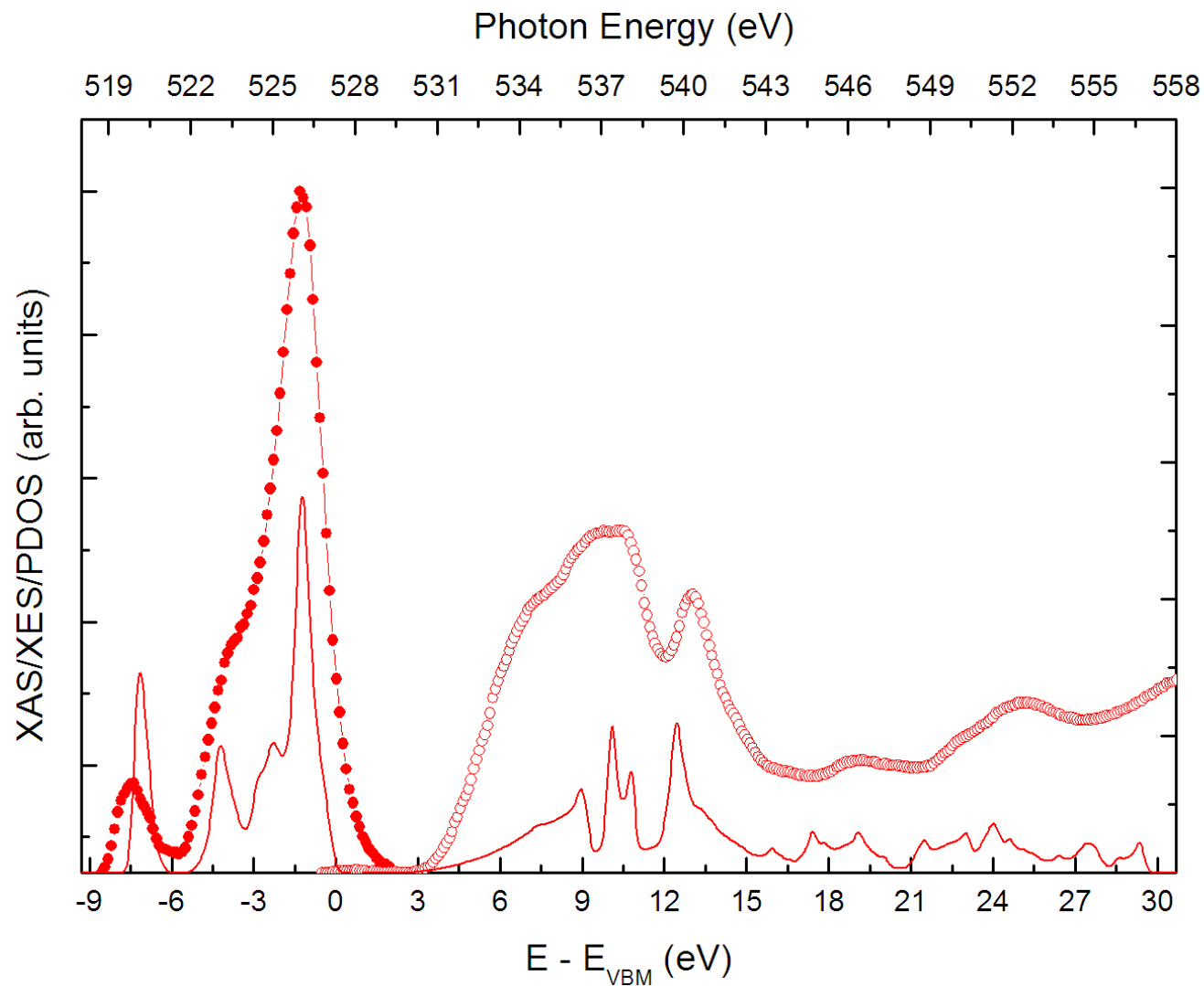
$$P_{i \rightarrow f} \propto \left| \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle \right|^2 \rho_f (\hbar\omega - \Delta E)$$

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

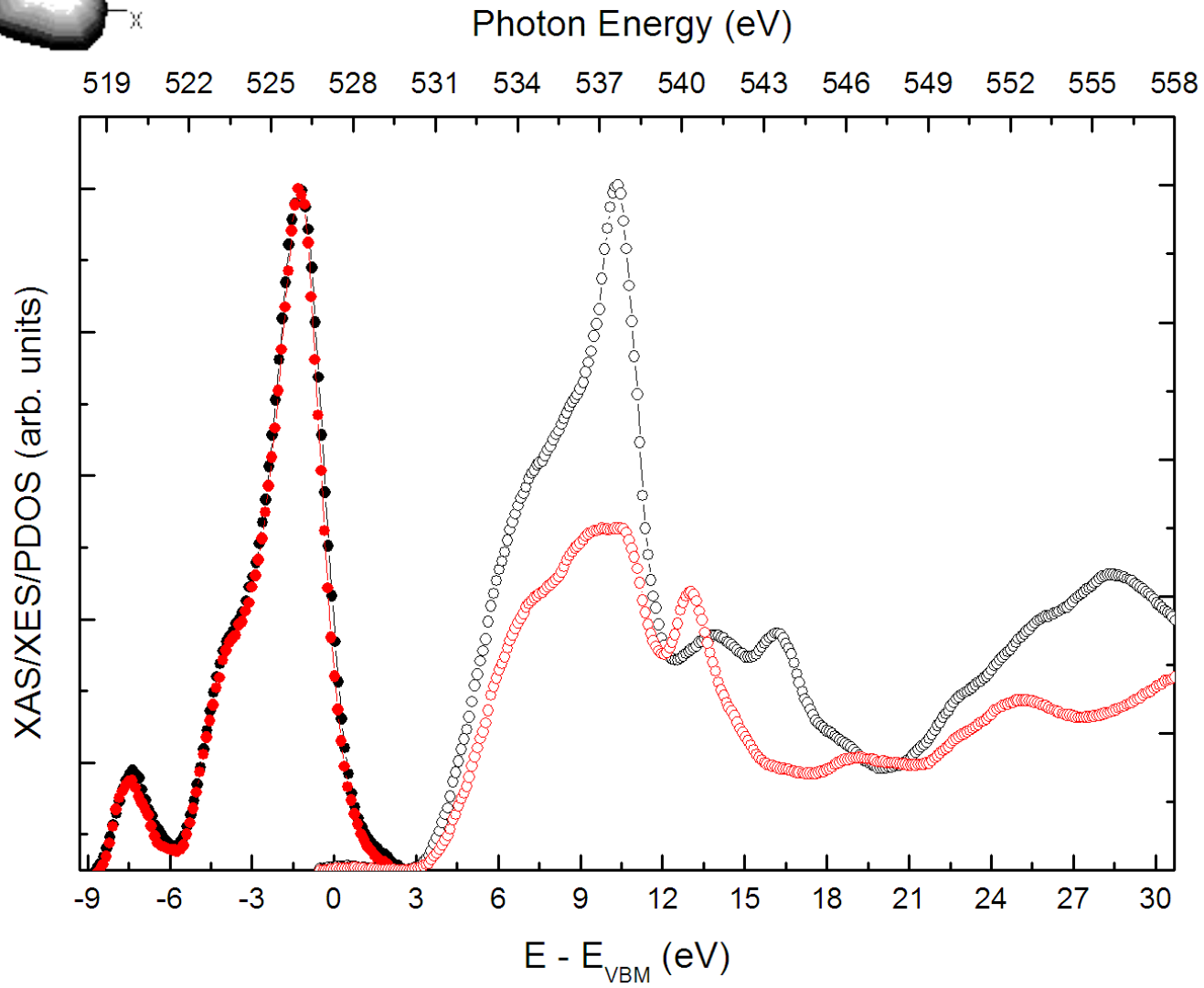
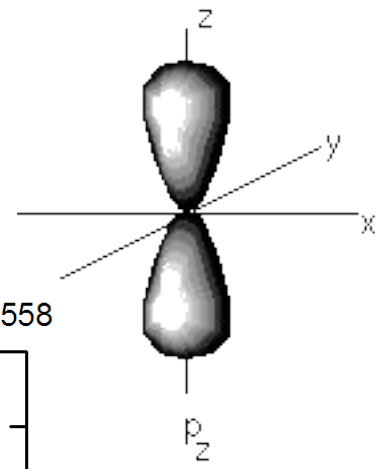
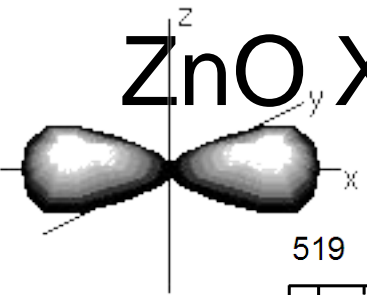
ZnO XAS and XES



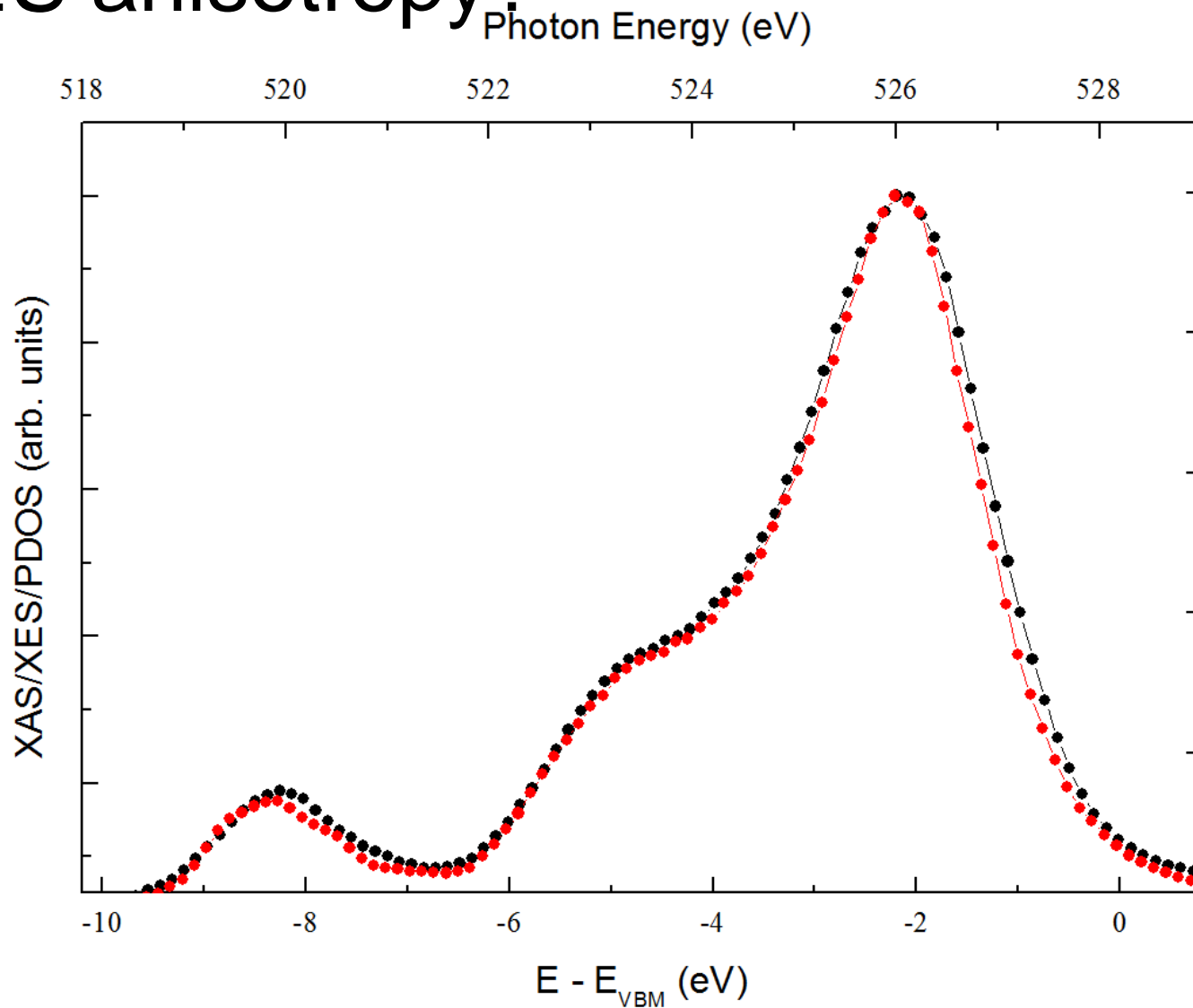
ZnO XAS and XES



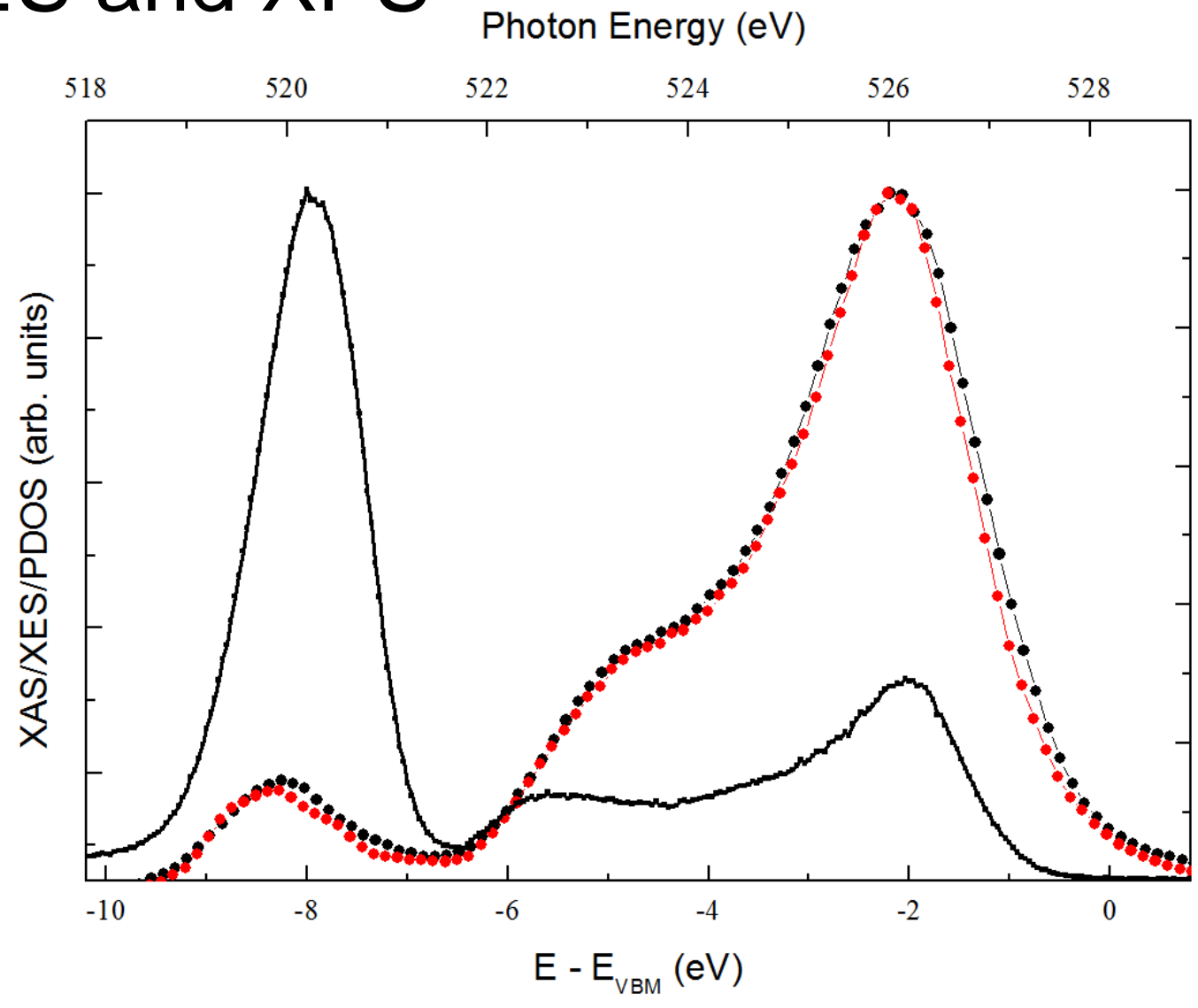
ZnO XAS and XES



XES anisotropy?



XES and XPS



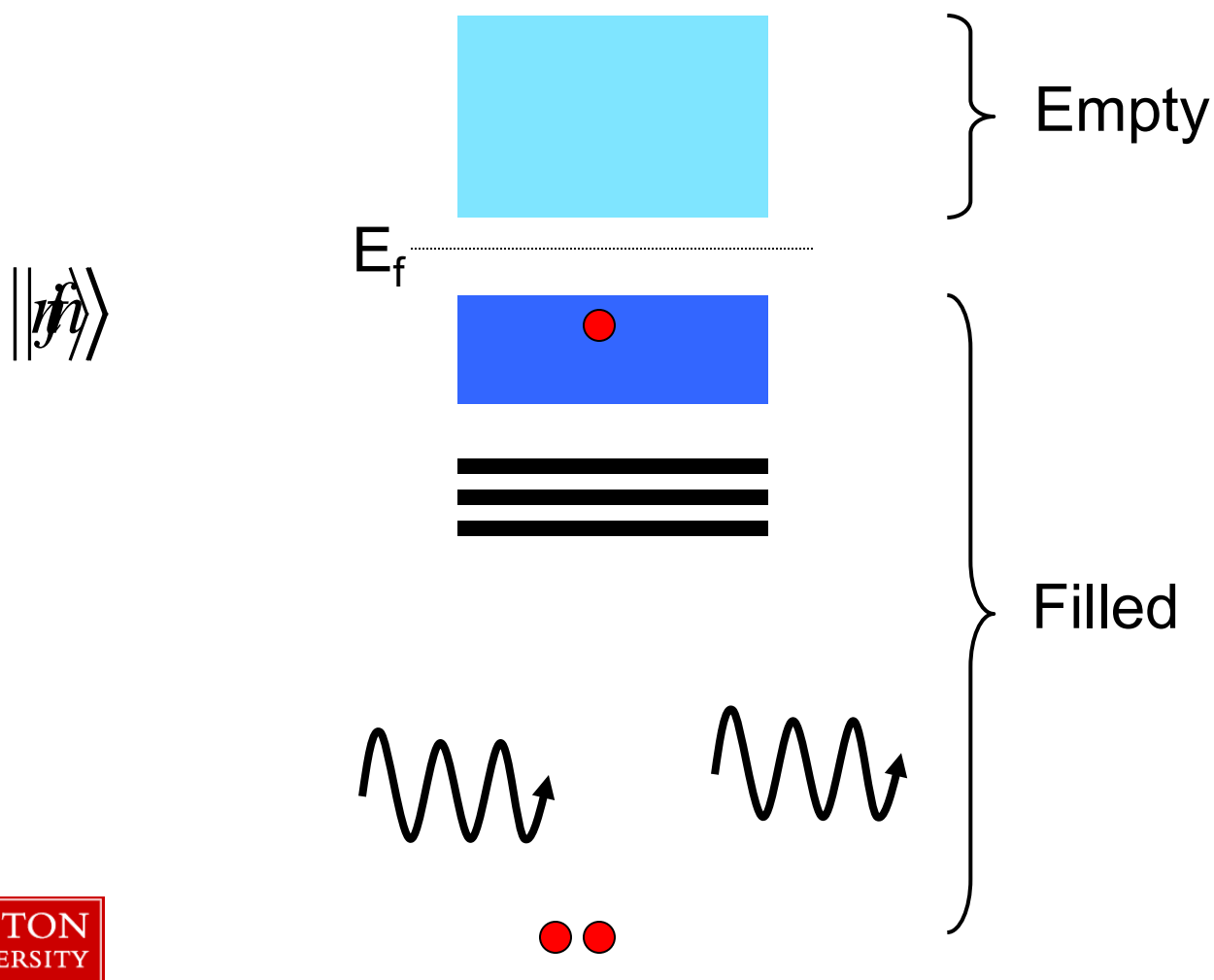
XAS and XES

- 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

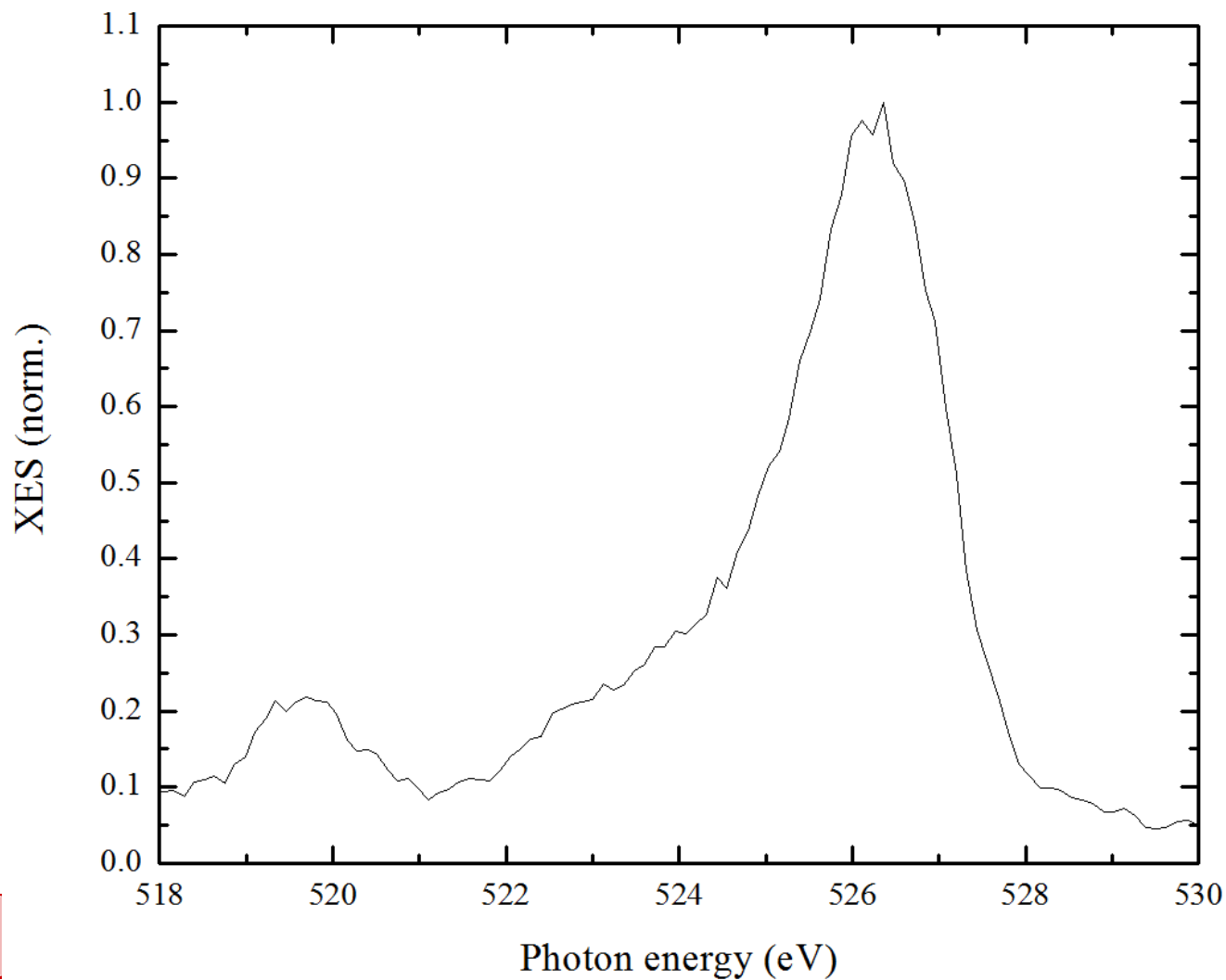
- Kramers-Heisenberg
- Coherent 2nd order process

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

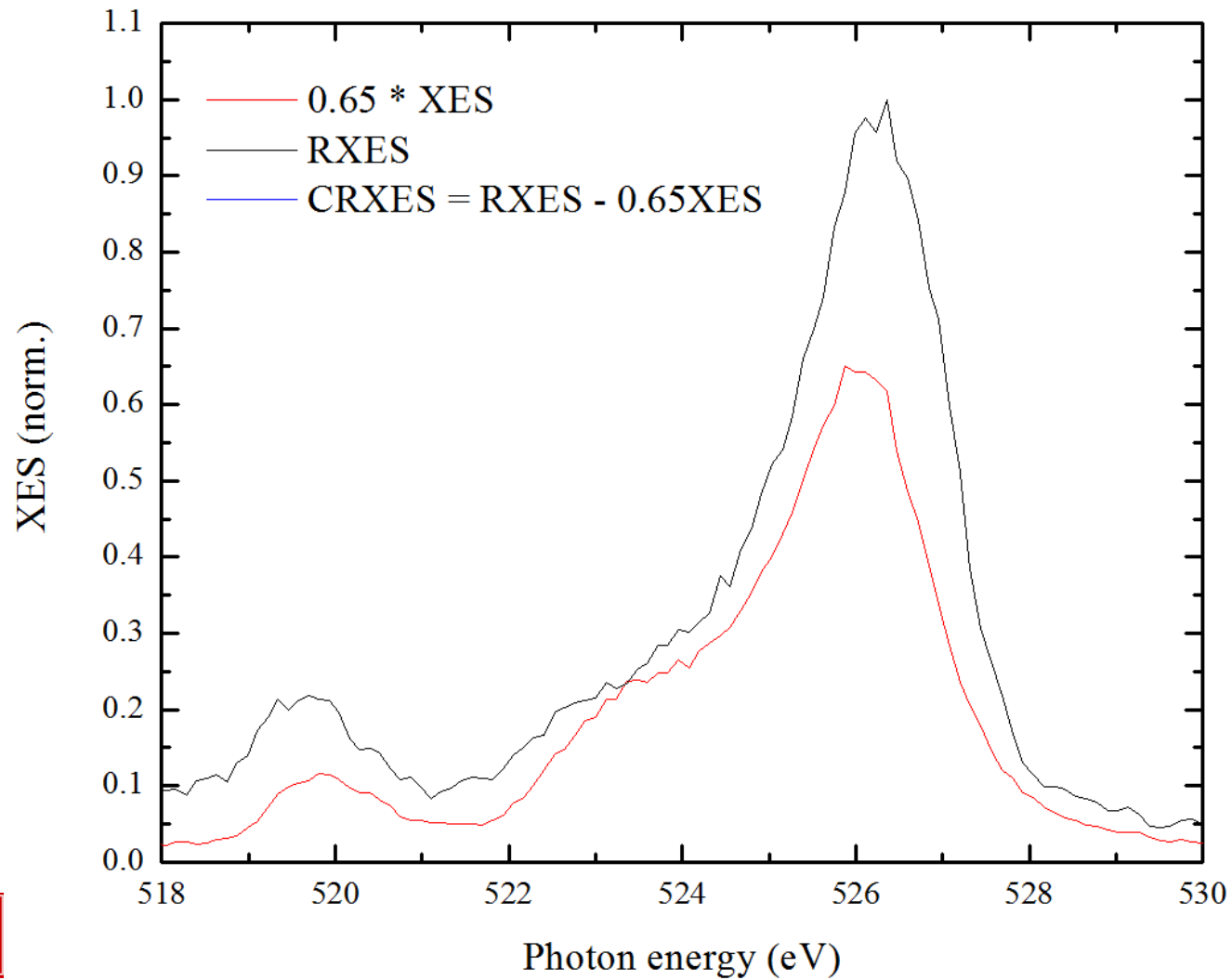
- XAS from $|i\rangle$ to $|m\rangle$, followed by XES from $|m\rangle$ to $|f\rangle$
- Selection rule: conservation of crystal momentum!

$$\delta(k_f - k_i)$$

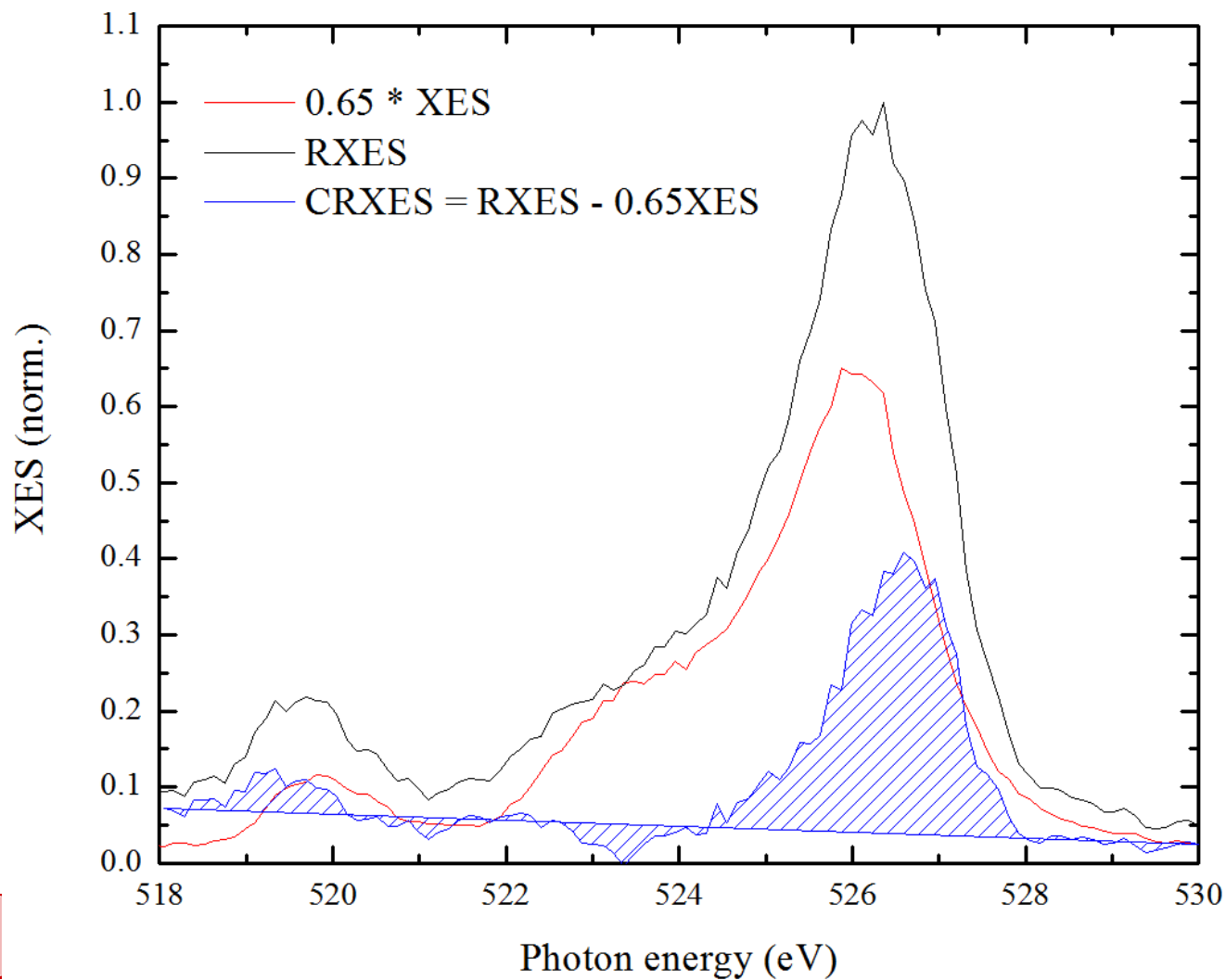
RXES = coherent and incoherent XES



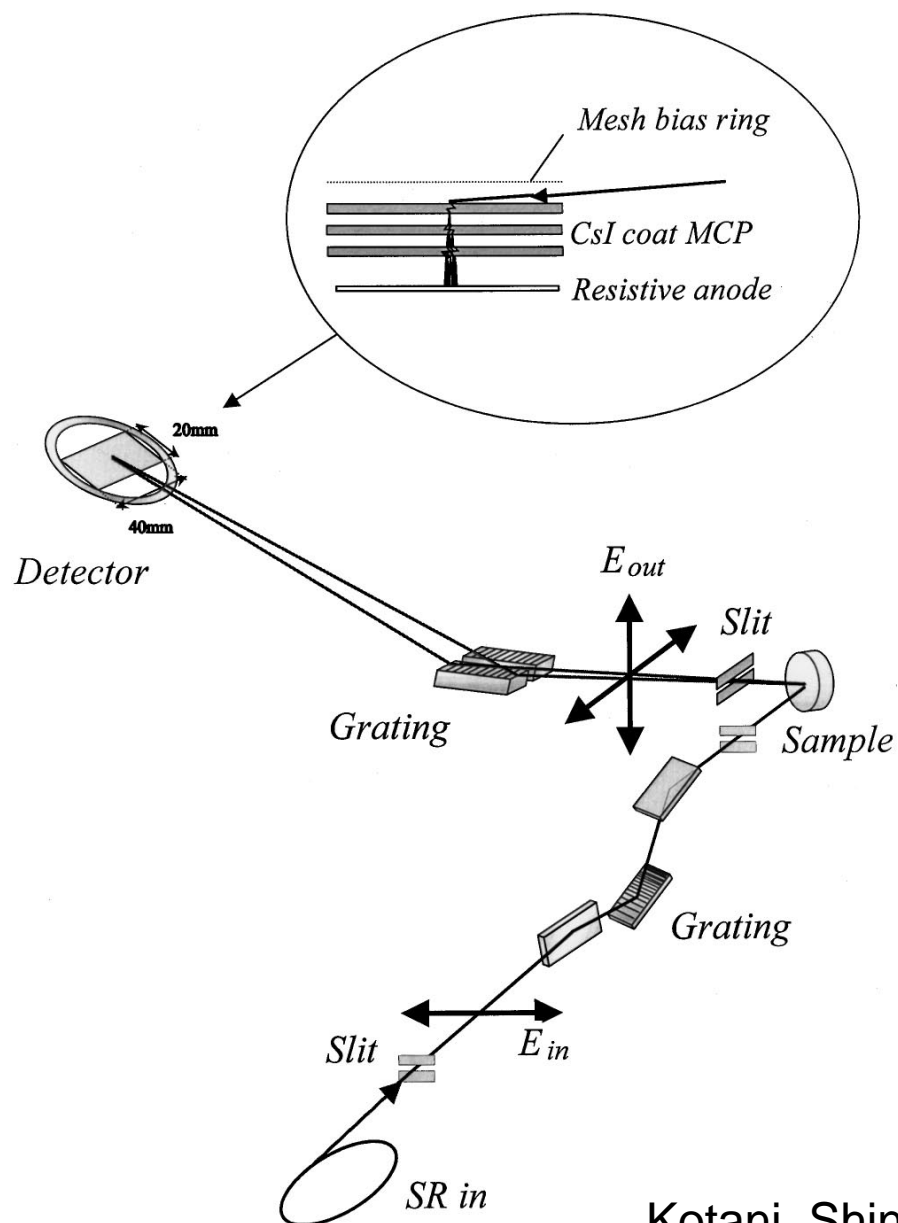
RXES



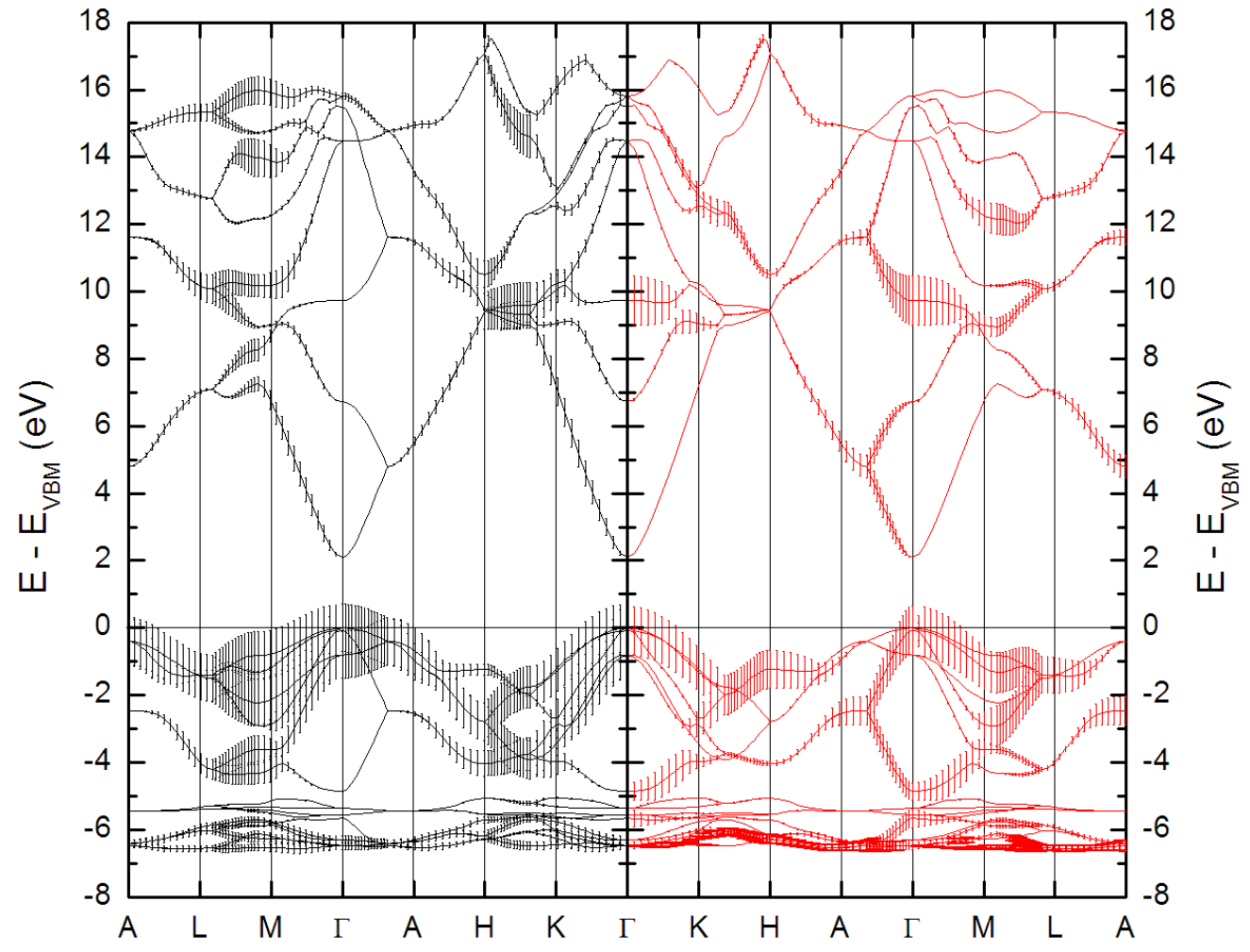
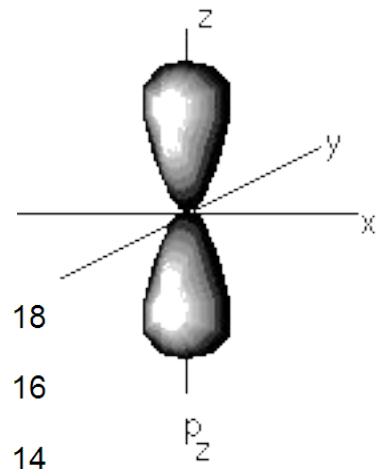
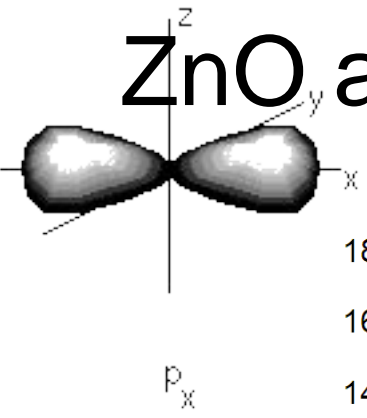
RXES



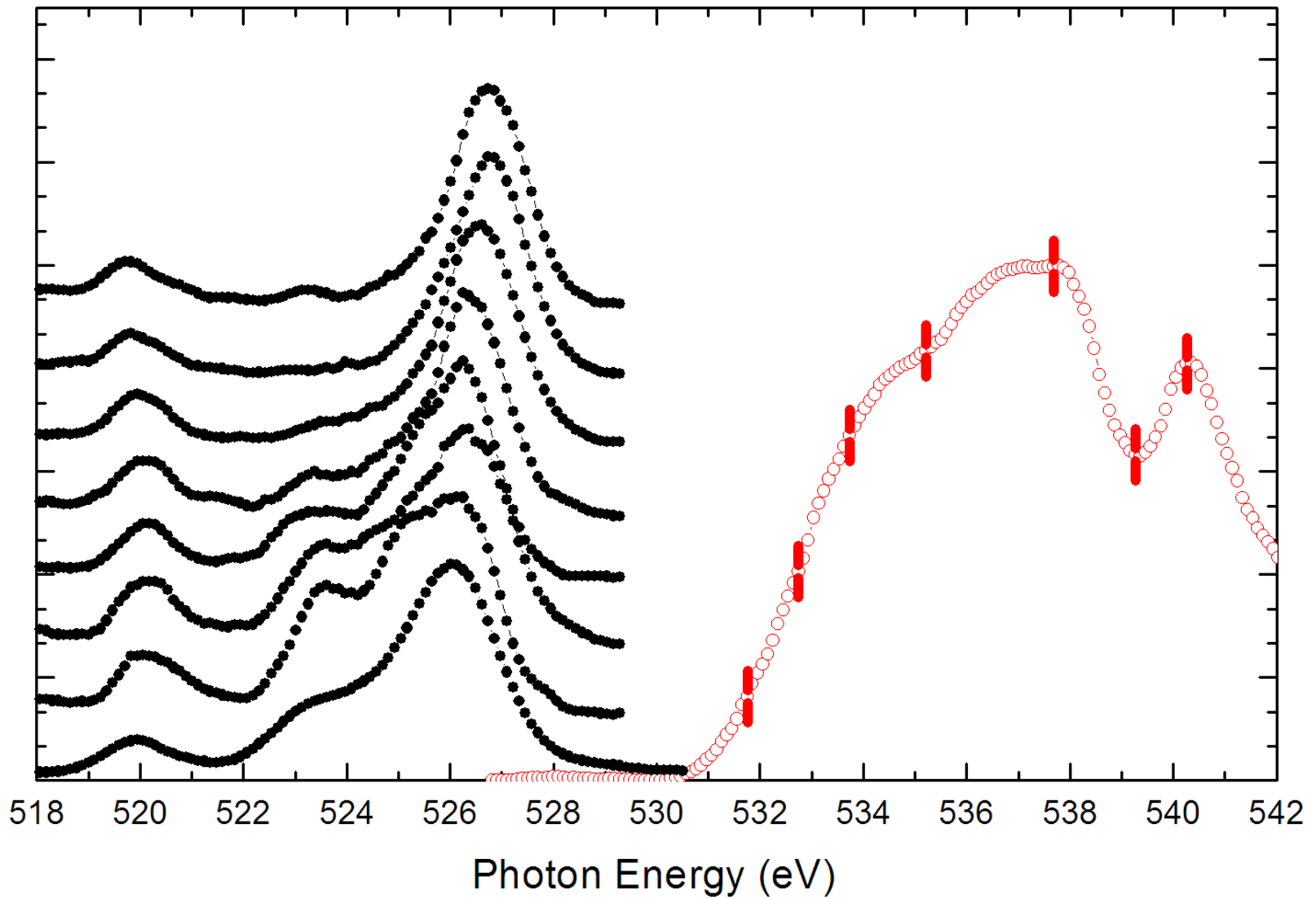
RXES



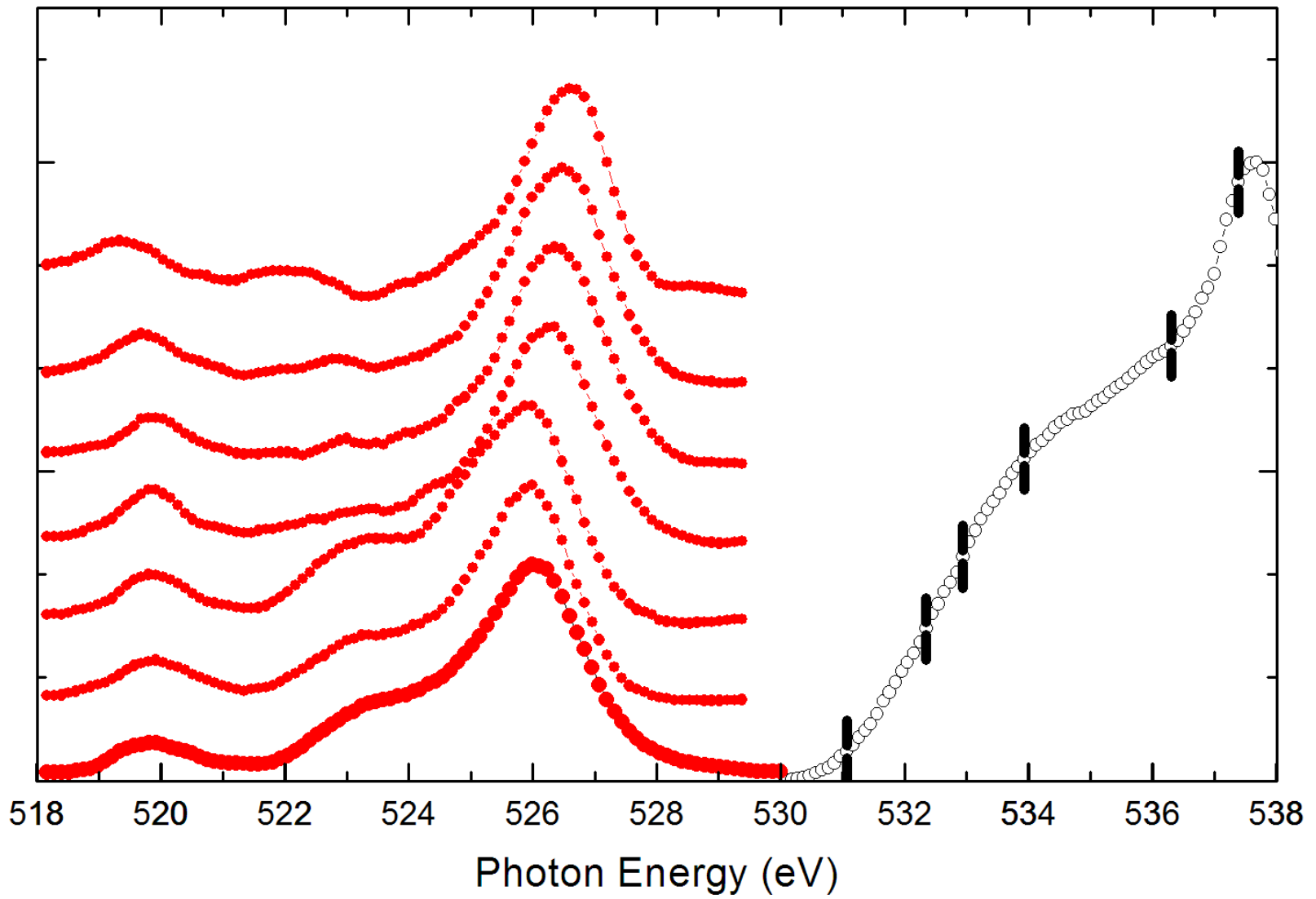
ZnO anisotropy

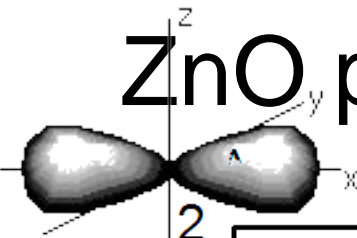


ZnO RXES

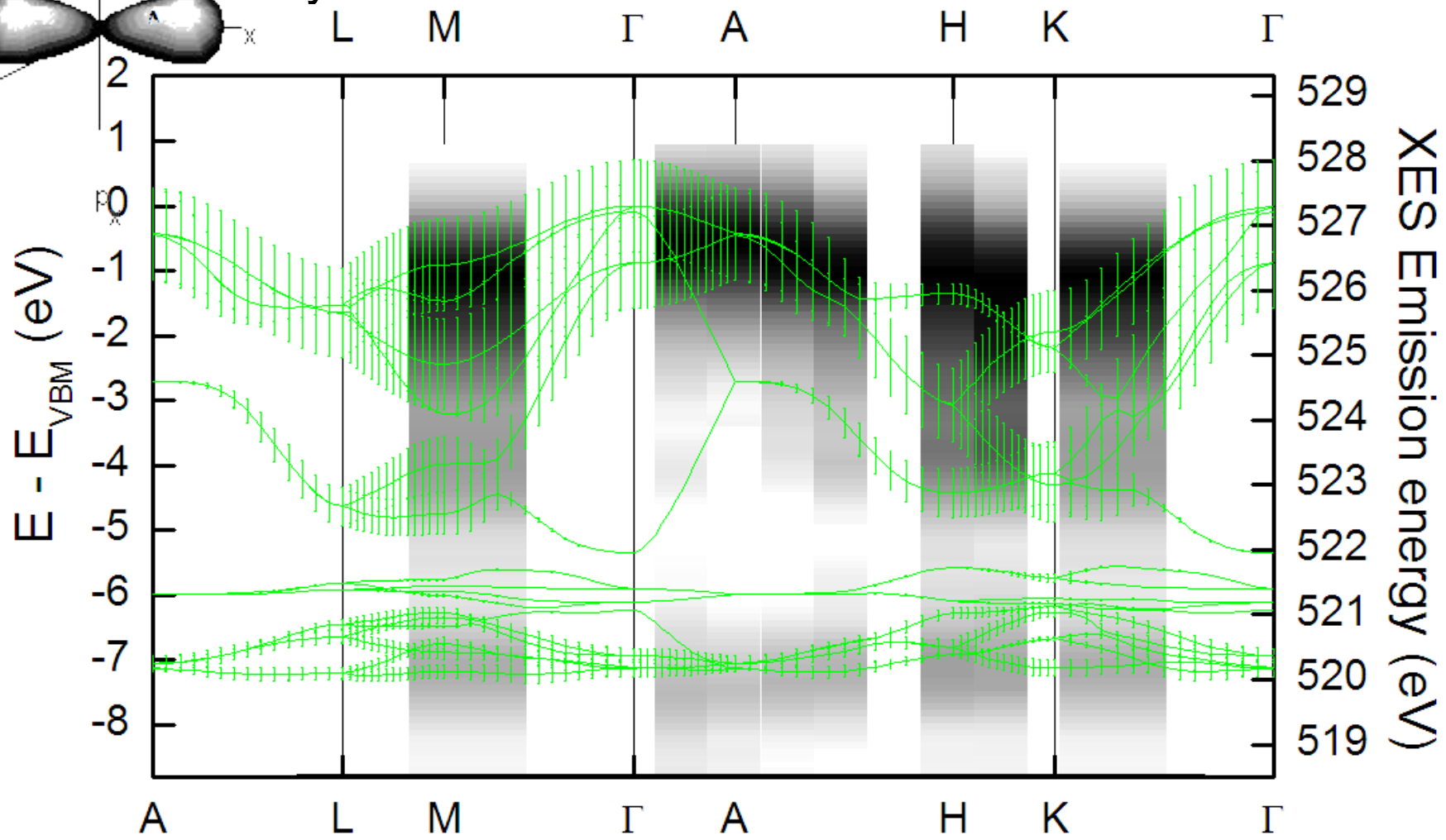


ZnO RXES

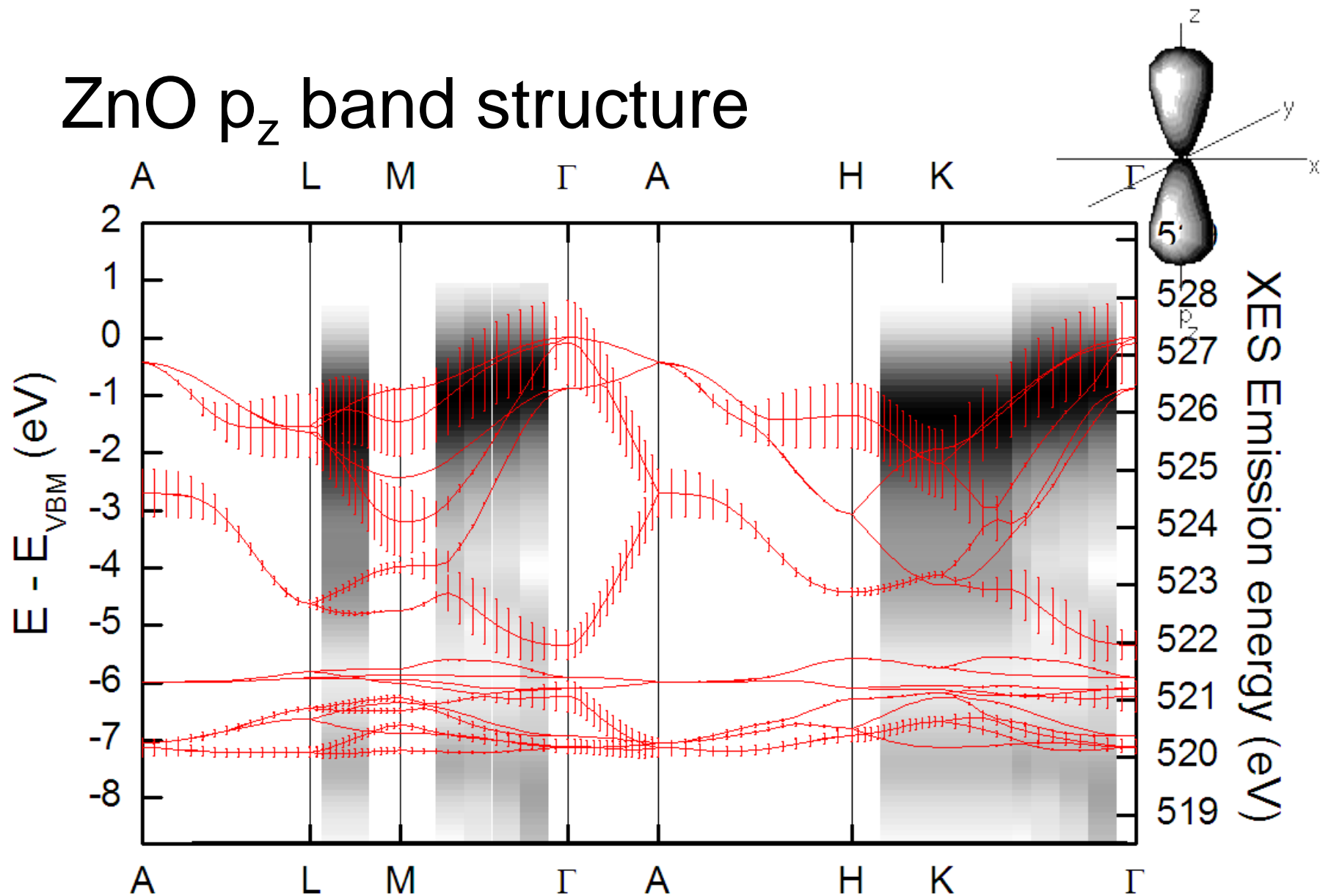




ZnO p_{xy} band structure



ZnO p_z band structure



Phys. Rev. B 78, 155114 (2008)

- XAS, XES, and RXES to measure orbital resolved electronic structure and band dispersion
- B. J. Ruck
 - Victoria University of Wellington
- L. F. J. Piper, A. DeMasi, K. E. Smith
 - Boston University
- A. Schleife, F. Fuchs, F. Bechstedt
 - Friedrich-Schiller-Universität
- J. Chai, S. M. Durbin
 - Canterbury University

Can we calculate the RXES?

andrew@preston.co.nz