ALS Workshop (Oct 20-22, 2005)

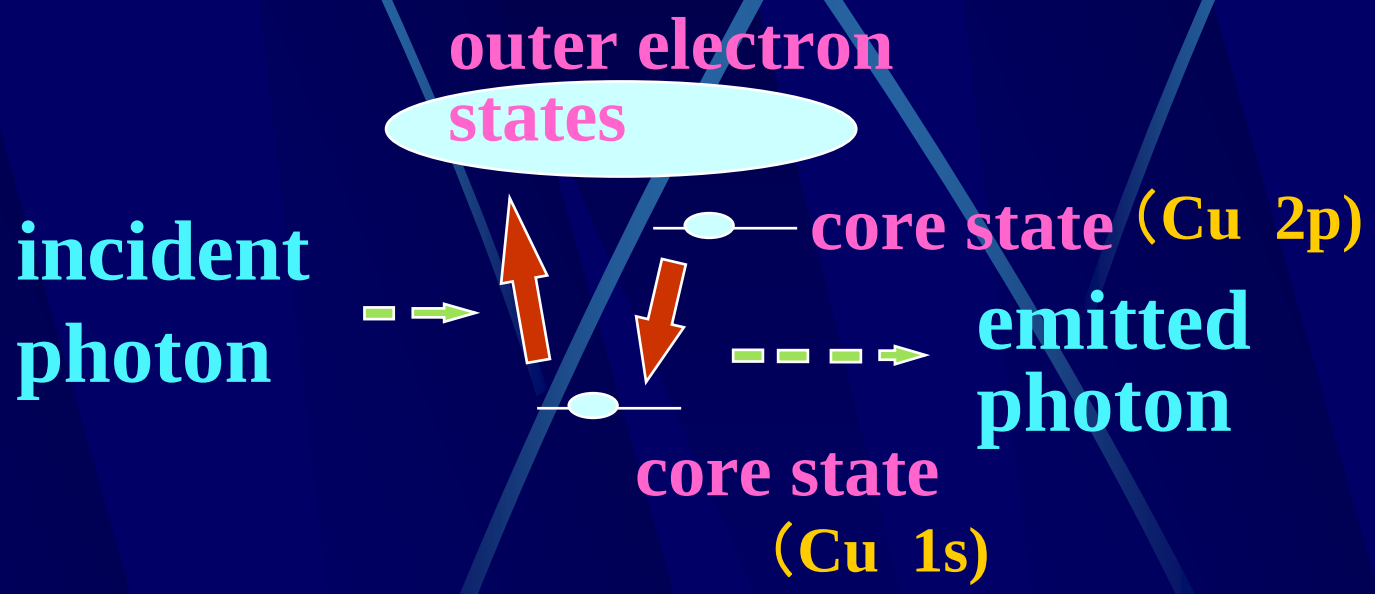
Theoretical and Experimental Investigations of Cu Kα Resonant X-ray Emission Spectra for La_2CuO_4

---- An Ultra-fine Probe for the Pre-edge Structure of Cu 1s Electron Excitation ----

RIKEN/Spring-8 and PF/KEK
A. Kotani

Resonant X-Ray Emission Spectroscopy (RXES)

Cu Kα RXES



Coherent second order optical formula:

$$F(\Omega,\omega)=\sum_f\left|\sum_m\frac{\langle f|T_2|m\rangle\langle m|T_1|g\rangle}{E_g+\Omega-E_m+i\Gamma_m}\right|^2\delta(E_g+\Omega-E_f-\omega),$$

Topics

1. LαRXES of Rare-Earth Systems

   A powerful tool to detect hidden structures in XAS

   (A) Excitation spectrum of RXES for Dy compounds:

   K. Hamalainen et al. (1991)

   (B) LαRXES for Gd:

   M.H. Krisch et al. (1995)

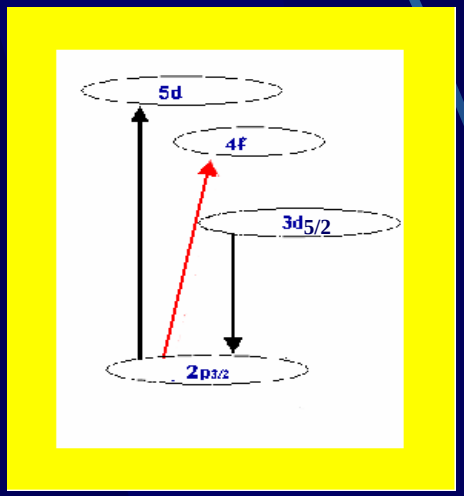
2. Cu KαRXES of La_2CuO_4

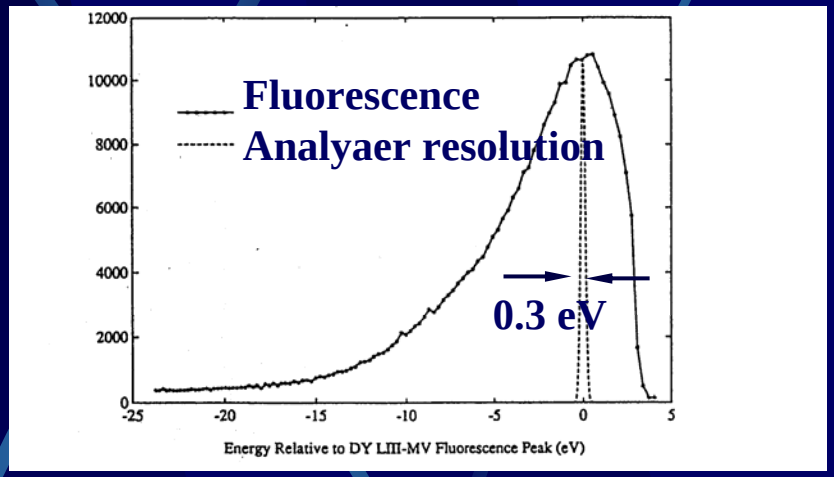
   An ultra-fine probe for the pre-edge structure of Cu 1s XAS

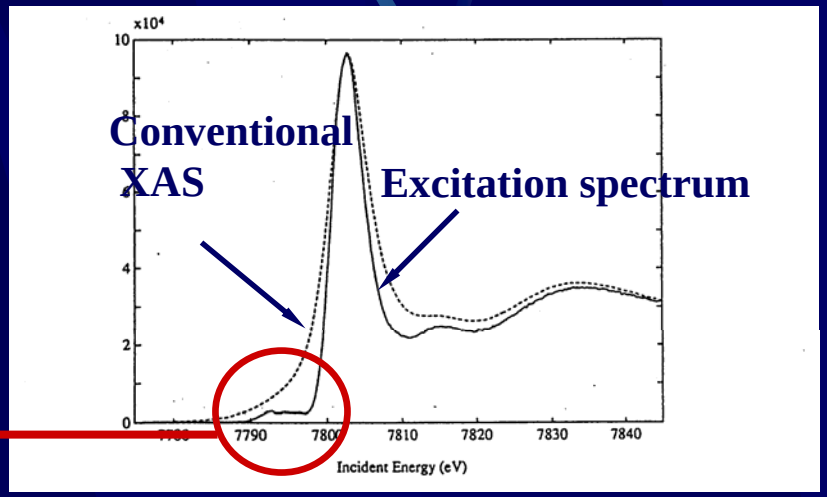
   A. Shukla et. al. (2005) preprint

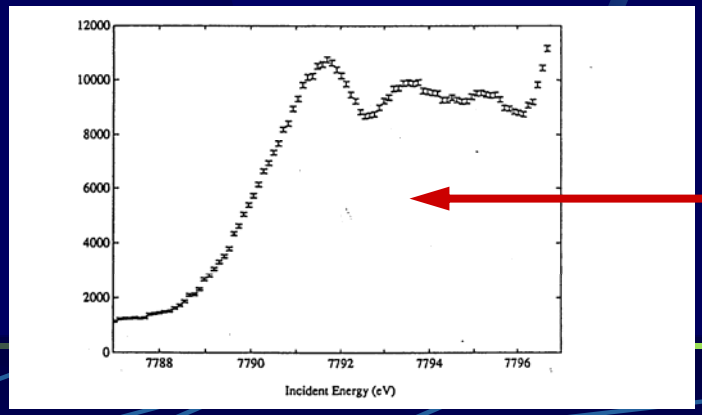
Electric quadrupole excitation

Excitation spectrum for LαRXES of $Dy(NO_3)_3$



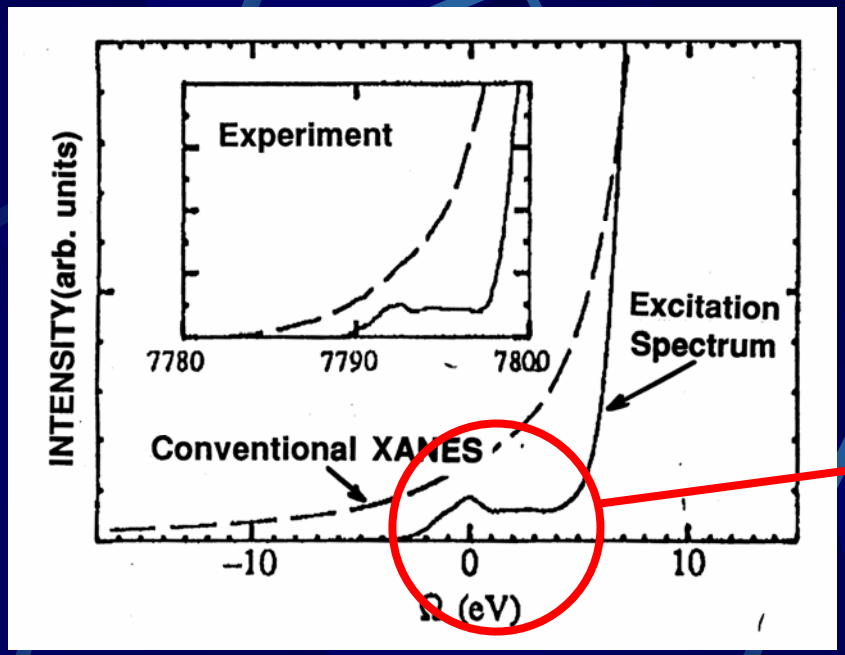


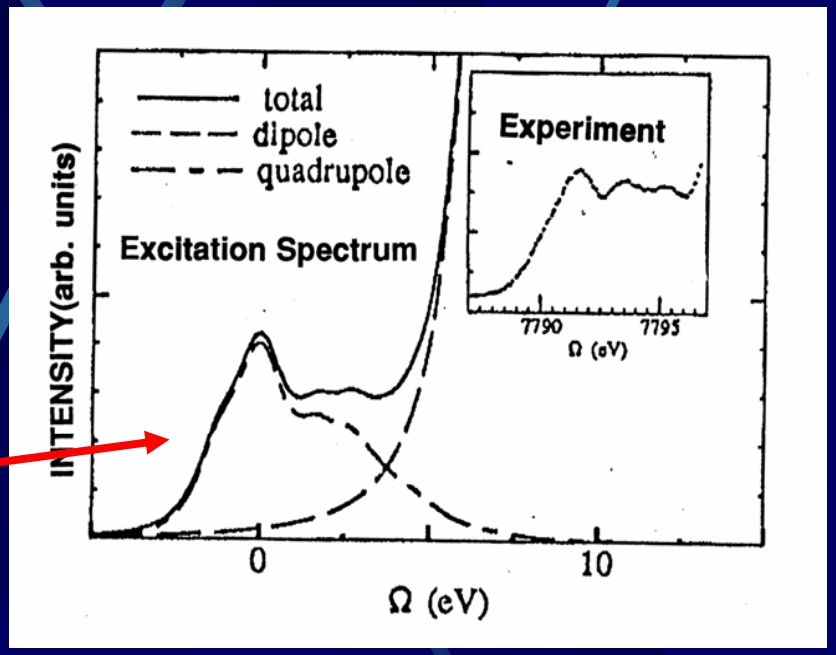




K. Hamalainen et al.
Phys. Rev. Lett. 67, 2850 (1991)

Theory and Experiment





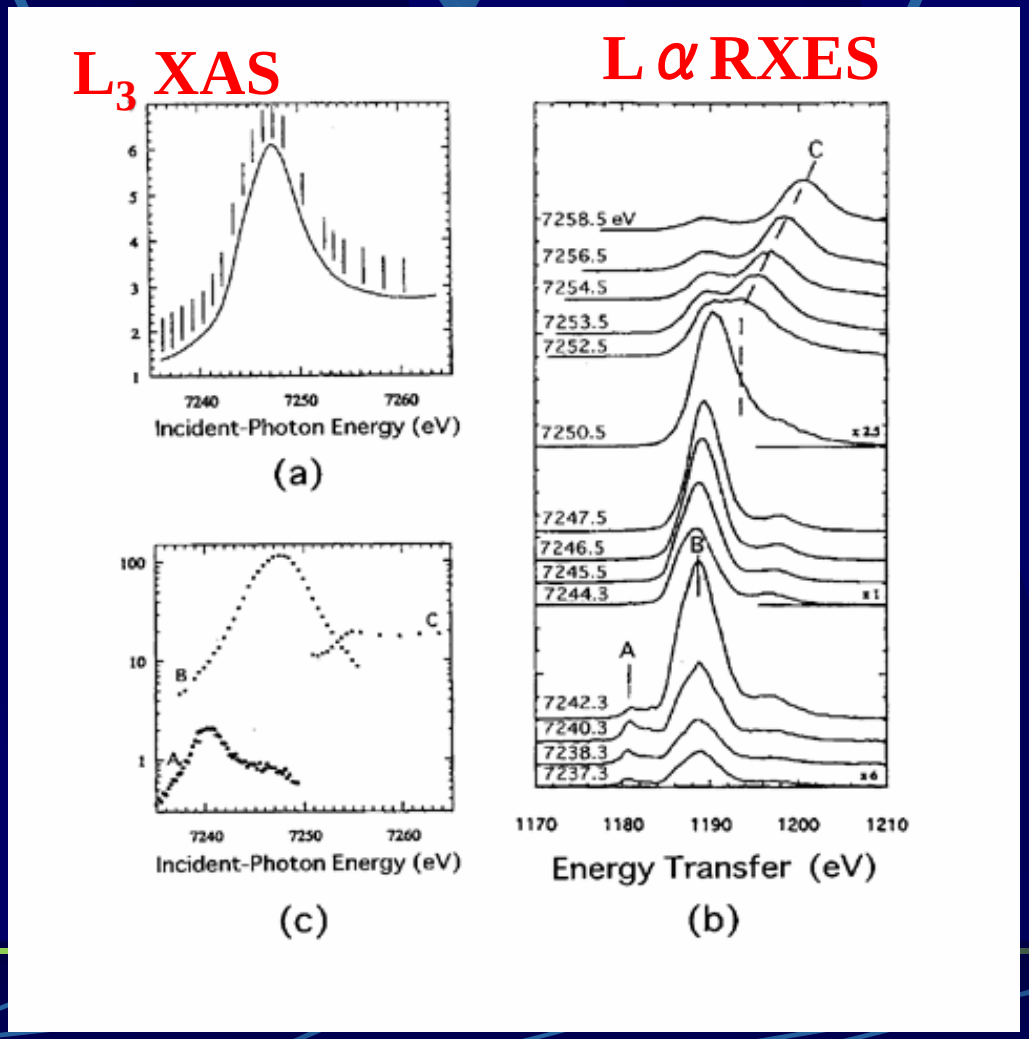
$$S(\Omega,\omega)=\sum_j\left|\sum_i\frac{<j|T_2^\dagger|i><i|T_1|g>}{E_g+\Omega-E_i-i\Gamma_L}\right|^2\frac{\Gamma_M/\pi}{(E_j+\omega-E_g-\Omega)^2+\Gamma_M^2}$$

Γ_L = 2.1 eV

Γ_M = 0.7 eV

S. Tanaka, K. Okada and A.Kotani : J. Phys.Soc. Jpn. 63, 2780 (1994)

Another example for LαRXES of Gd



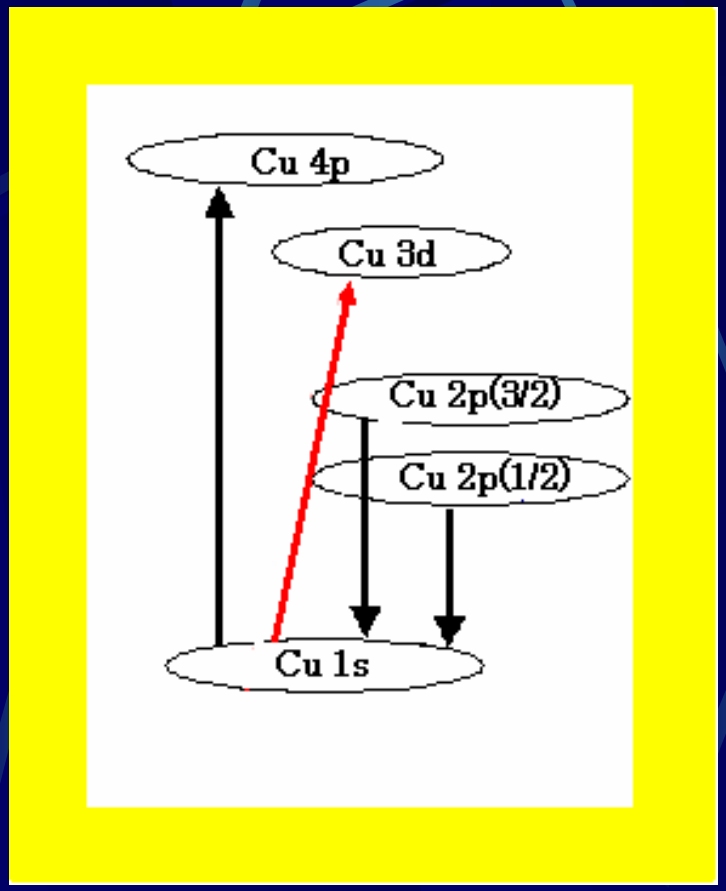
M.H. Krisch et al. (1995)

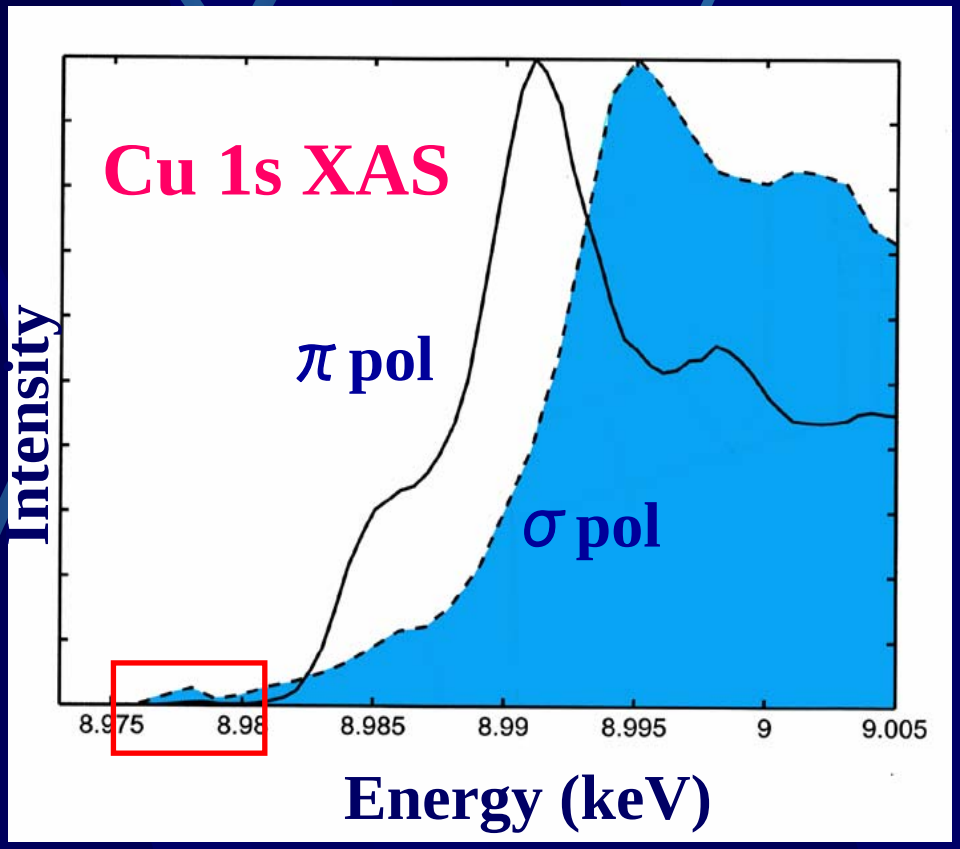
Cu Kα RXES in La_2CuO_4

Experiment : A. Shukla et al.
Theory: M. Calandra,
M. Taguchi and Kotani

preprint (cond-mat/0506650)

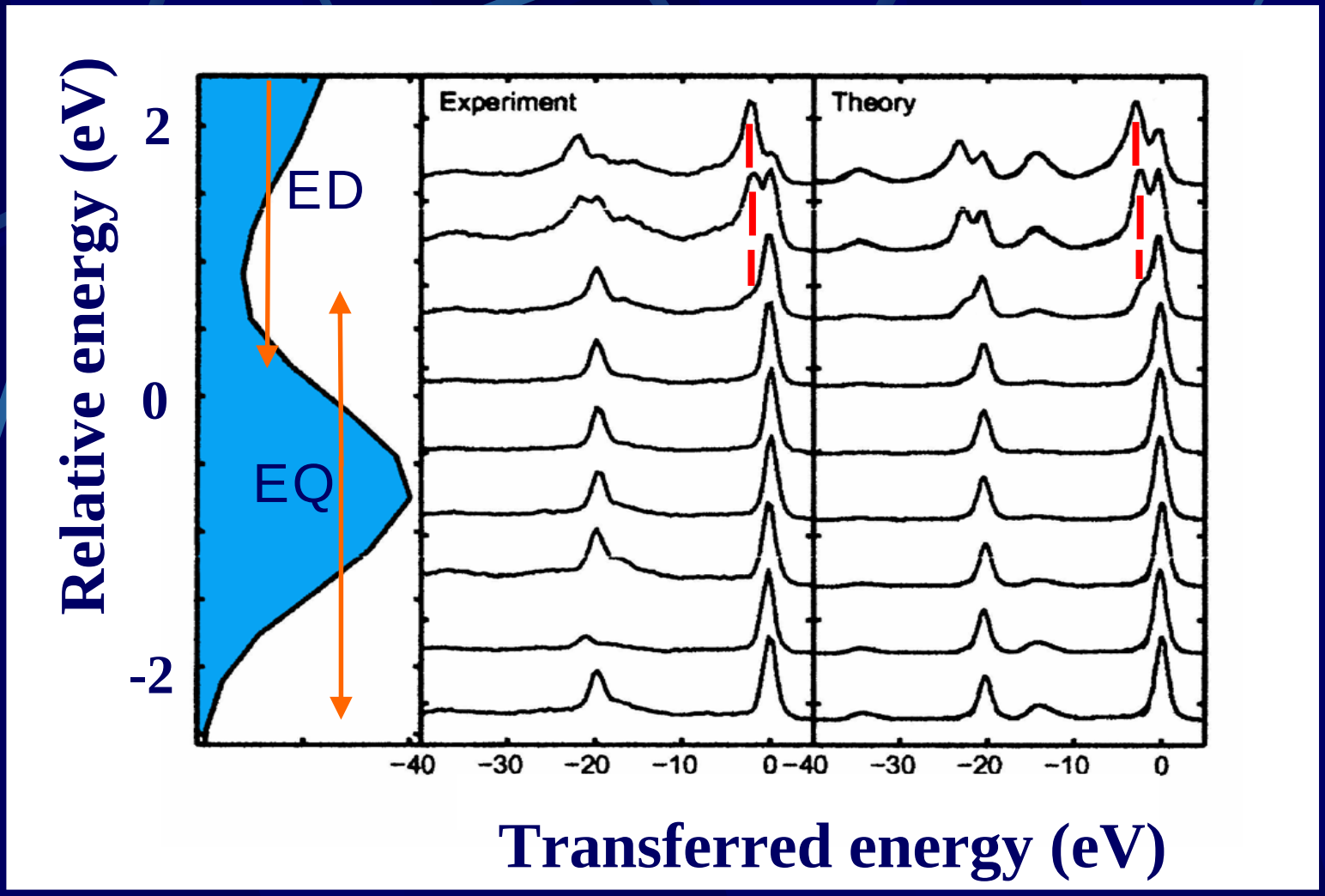
Cu Kα RXES in La_2CuO_4





Shukla et al. (2005)

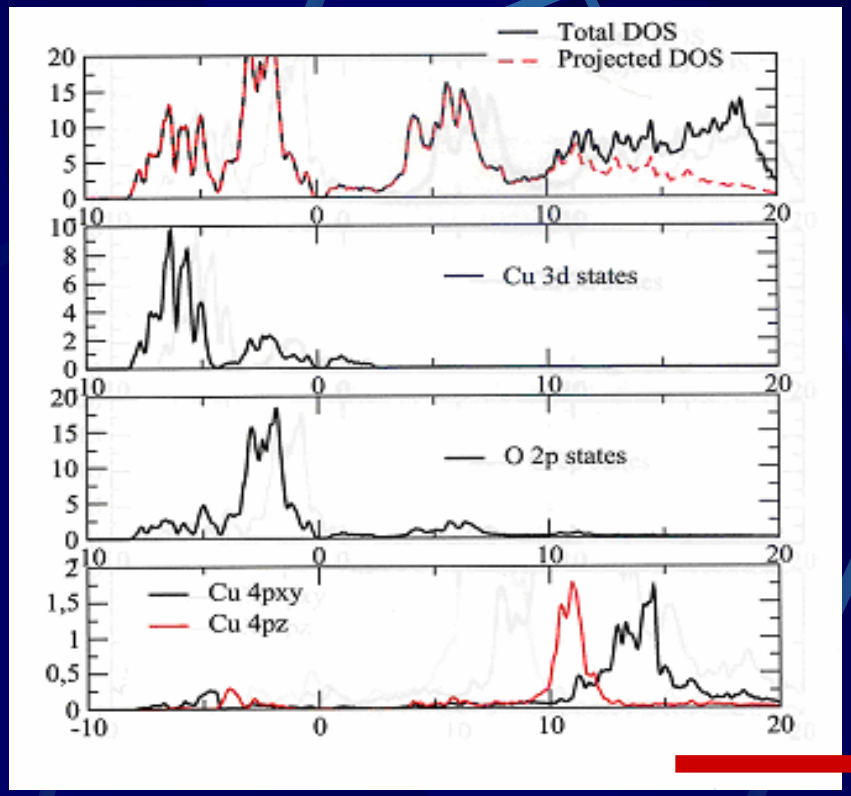
K α RXES for σ polarization



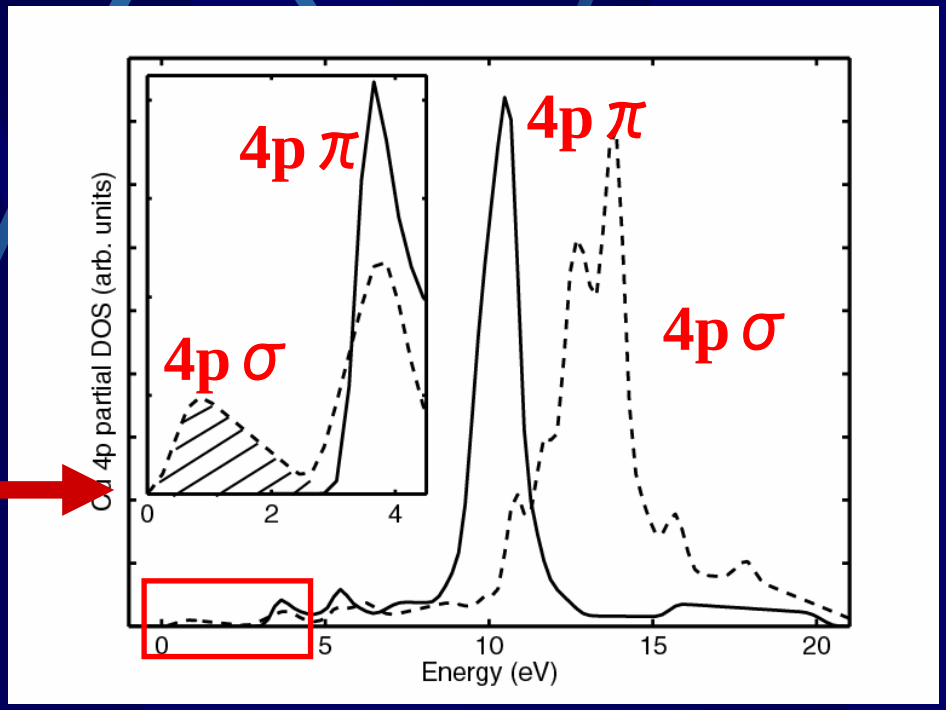
Exp. : Shukla et al.

Theory: Calandra, Taguchi and Kotani

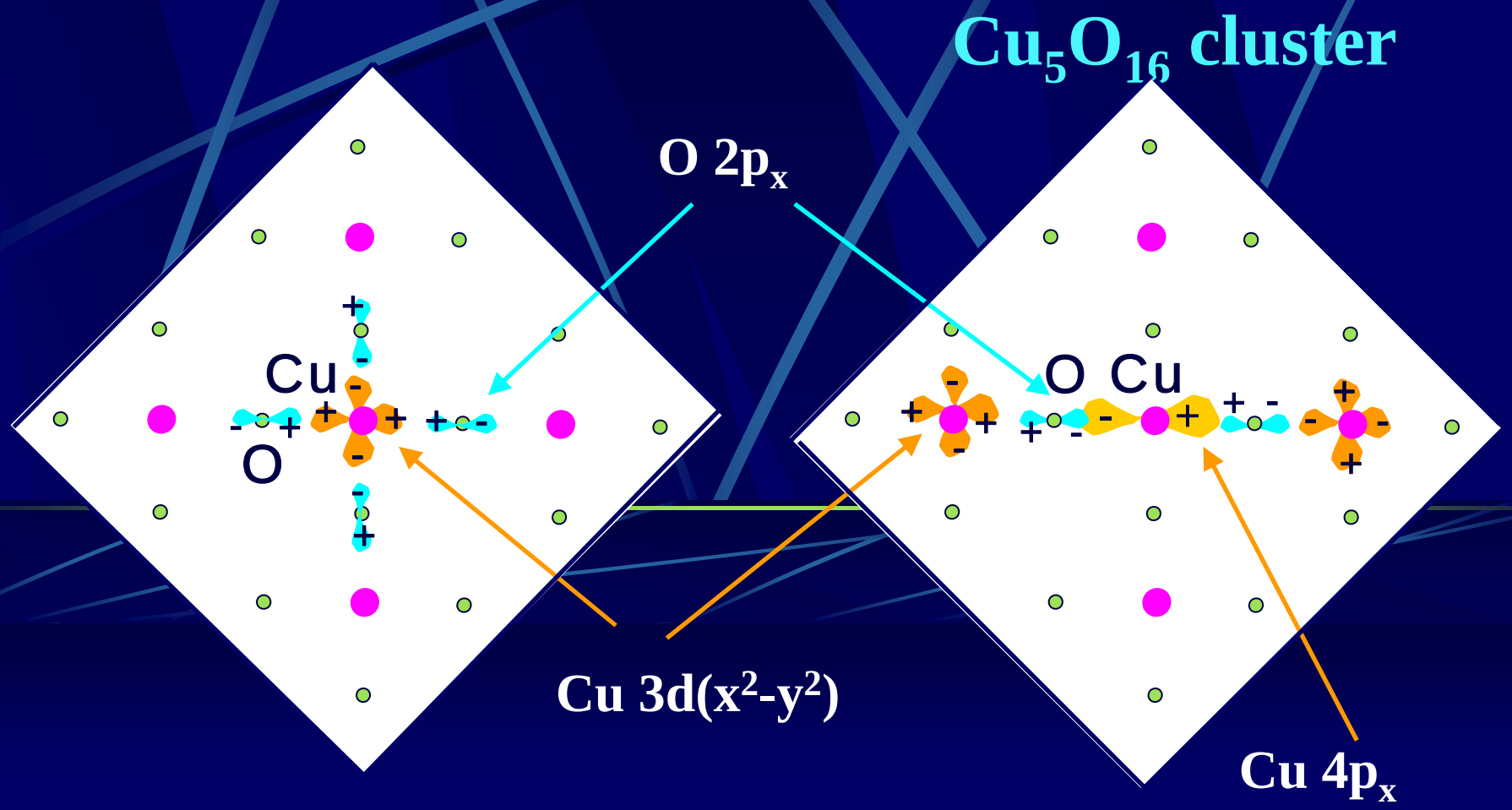
Theoretical Analysis



***ab initio* calculation by M. Calandra**



EQ and ED exitations



EQ
(on-site 3d)

ED
(off-site 3d)

Calculation of Cu Kα RXES in La_2CuO_4

Single impurity Anderson model incorporated with Cu 4p band

$$H = \sum_{\Gamma,\sigma} \varepsilon_{d\Gamma} a_{d\Gamma\sigma}{}^{+} a_{d\Gamma\sigma} + \sum_{4p,k,\sigma} \varepsilon_{4pk} a_{4pk\sigma}{}^{+} a_{4p\Gamma k\sigma} + \sum_{\mu=1s,2p} \varepsilon_{\mu} a_{\mu}{}^{+} a_{\mu} + \sum_{\Gamma,k,\sigma} \varepsilon_{\Gamma k} a_{\Gamma k\sigma}{}^{+} a_{\Gamma k\sigma}$$

$$+ \sum_{\Gamma,k,\sigma} V(\Gamma k)(a_{d\Gamma\sigma}{}^{+} a_{d\Gamma\sigma} + h.c.) + U_{dd} \sum_{(\Gamma,\sigma)\neq(\Gamma',\sigma')} a_{d\Gamma\sigma}{}^{+} a_{d\Gamma\sigma} a_{d\Gamma'\sigma'}{}^{+} a_{d\Gamma'\sigma'}$$

$$- U_{dc} \sum_{\Gamma,\sigma,\mu} a_{d\Gamma\sigma}{}^{+} a_{d\Gamma\sigma} (1 - a_{p\mu}{}^{+} a_{p\mu}) + (\textit{multiplet coupling interaction})$$

Calculation of Cu Kα RXES by single impurity Anderson model

EQ excitation (1s -> 3d)

$$S(\Omega,\omega)=\sum_f\left|\sum_m\frac{\langle f|T_D|m\rangle\langle m|T_D|i\rangle}{E_i+\Omega-E_m-i\Gamma_{1s}}\right|^2\frac{\Gamma_{2p}/\pi}{\left(E_i+\Omega-E_f-\omega\right)^2+\Gamma_{2p}^2}$$

E_i, E_m, E_f = Energy of initial $|i\rangle$, intermediate $|m\rangle$ or final $|f\rangle$ states

Ω, ω = Incident and scattered X-ray energies

Γ_{1s}, Γ_{2p} = 1s core hole and 2p core hole linewidths

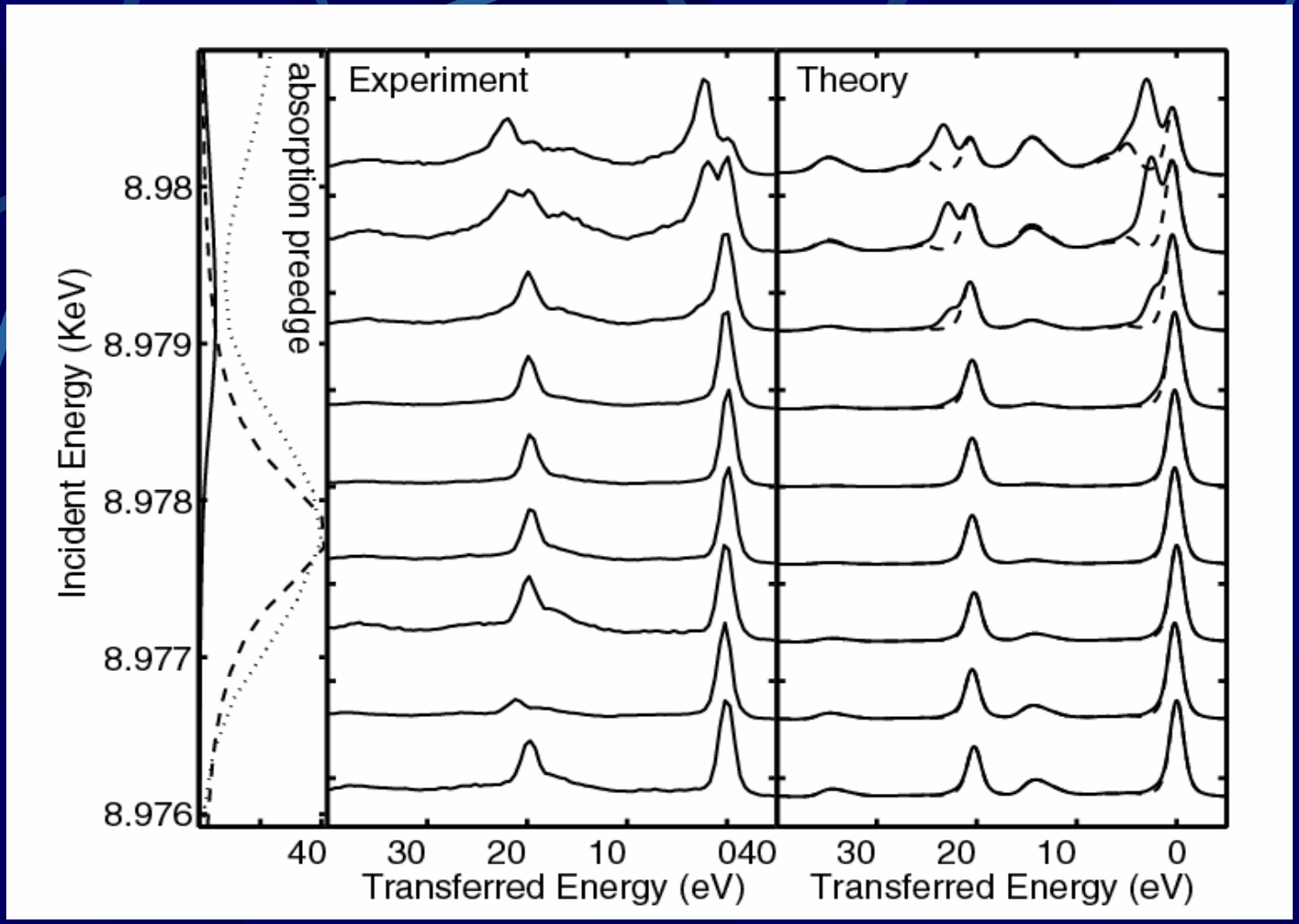
ED excitation (1s -> 4p)

$$S(\Omega,\omega)=\int d\varepsilon\,\rho(\varepsilon)\sum_f\left|\sum_m\frac{\langle f|T_D|mk\rangle\langle mk|T_D|i\rangle}{E_i+\Omega-E_m-\varepsilon-i\Gamma_{1s}}\right|^2\frac{\Gamma_{2p}/\pi}{\left(E_i+\Omega-E_f-\varepsilon-\omega\right)^2+\Gamma_{2p}^2}$$

4p dos

4p band energies

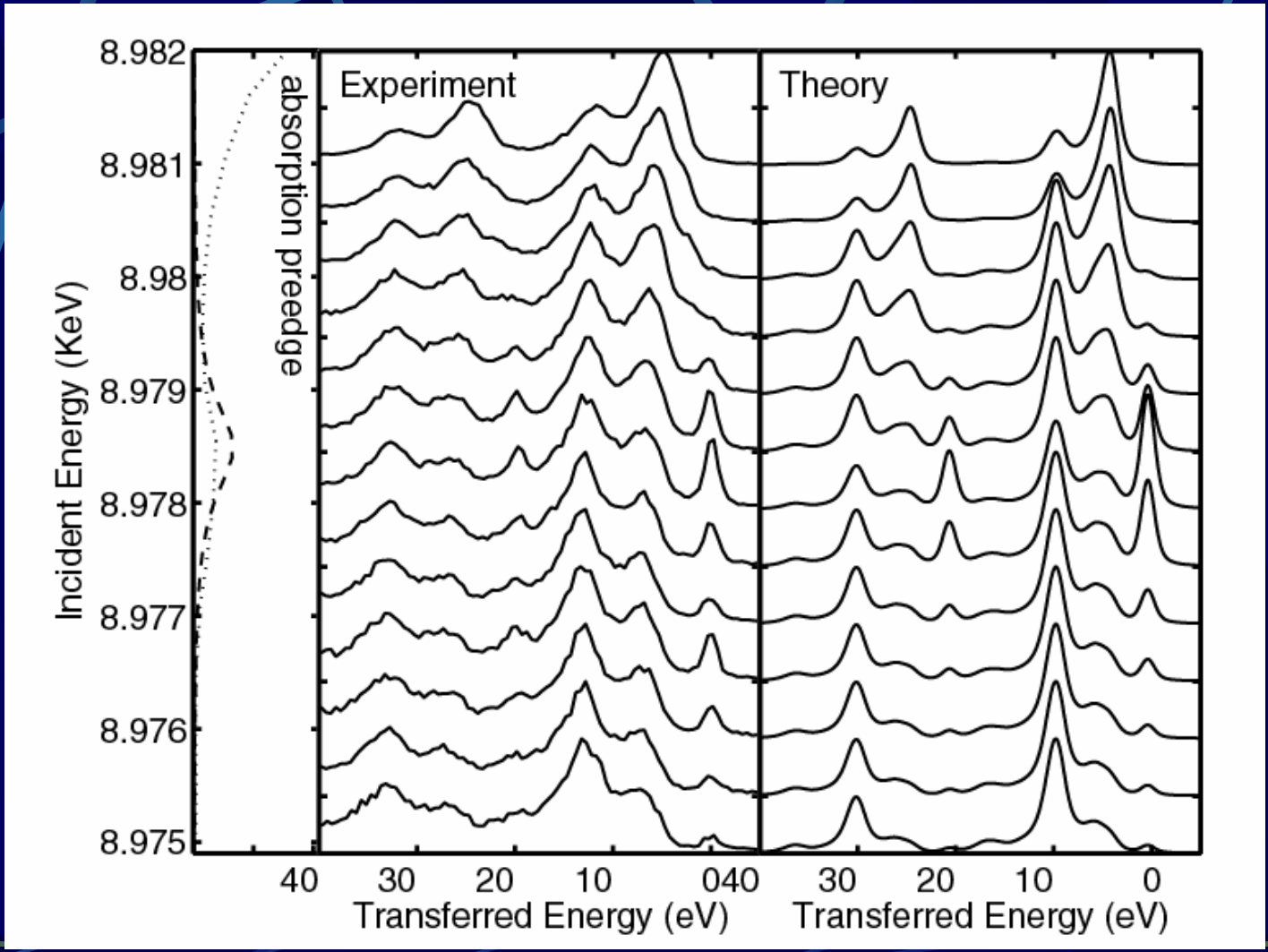
K α RXES for σ polarization



Exp. : Shukla et al.

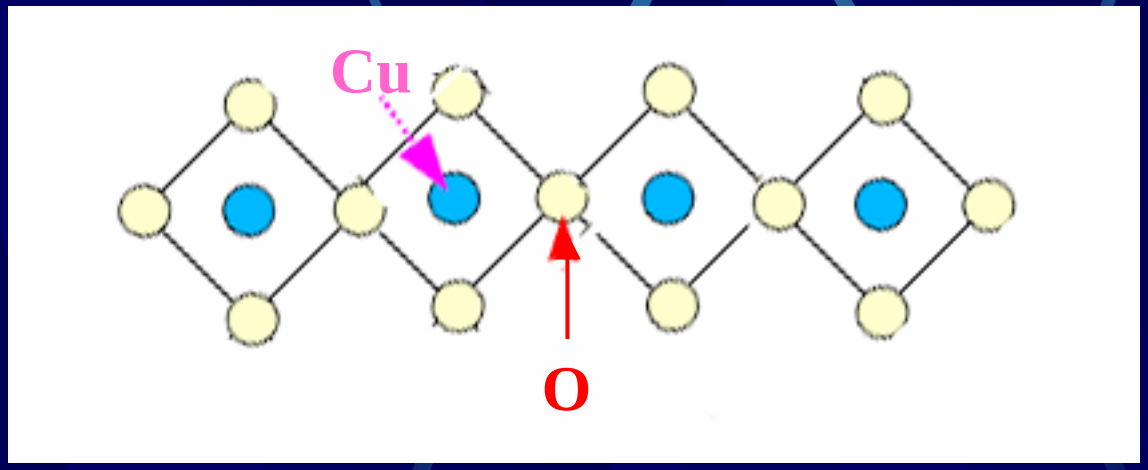
Theory: Calandra, Taguchi and Kotani

K α RXES for π polarization



Multi-Cu site cluster model calculation

Cu_4O_{12} cluster with periodic boundary condition

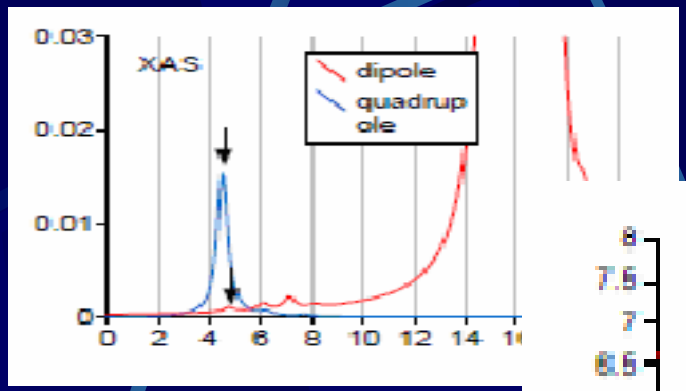


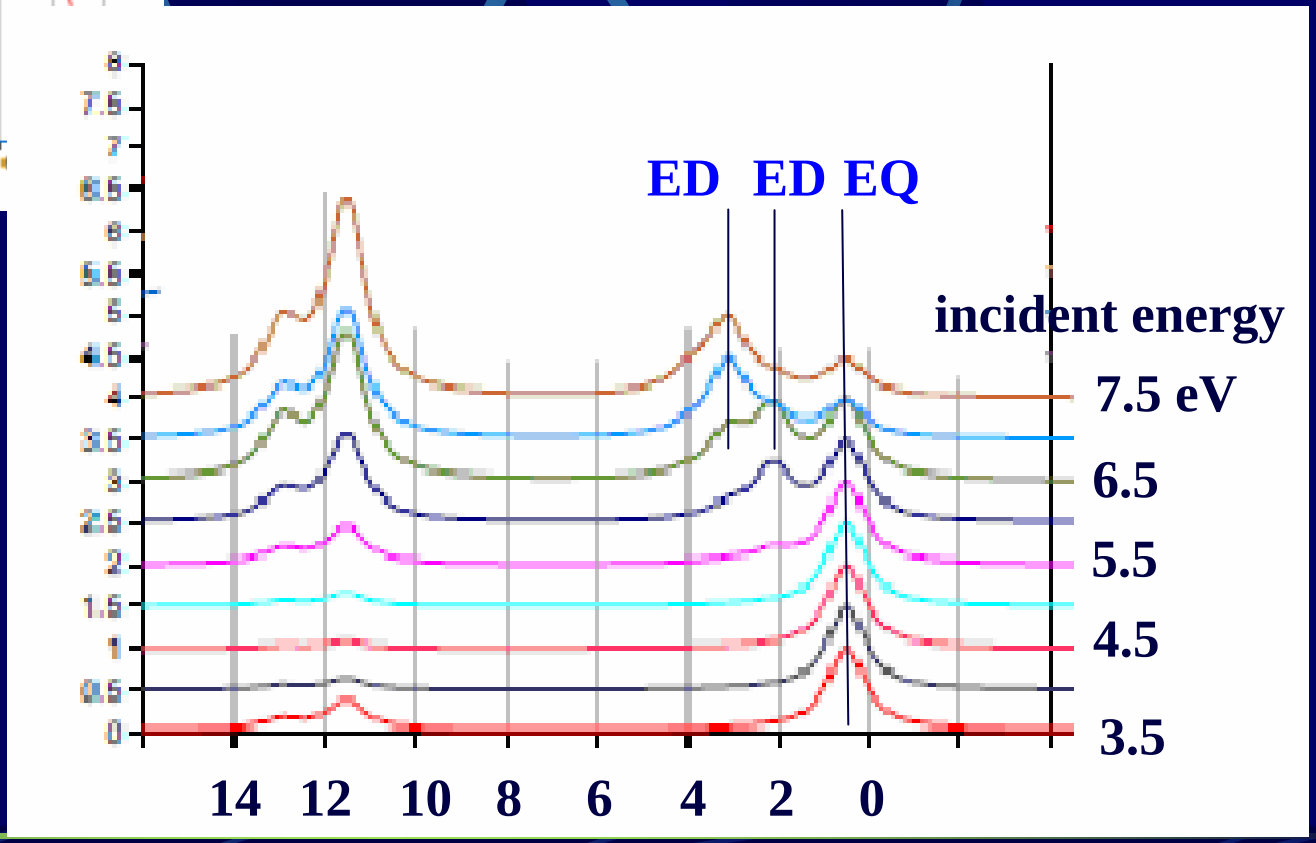
Parameter values

Δ =2.5 eV, U_{dc} = 7 eV, U_{dd} = 8 eV,

(pdσ)=1.5 eV, (ppσ)=0.5 eV

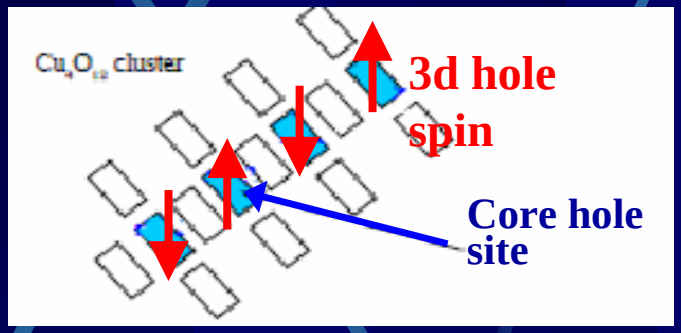
Calculated XAS and RXES





Lowest states of EQ and ED excitations

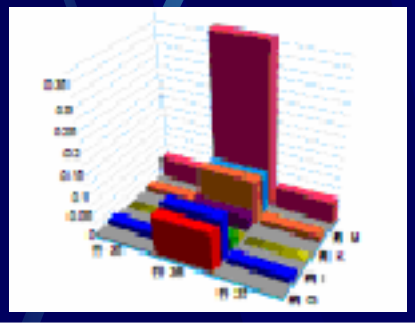
Ground state



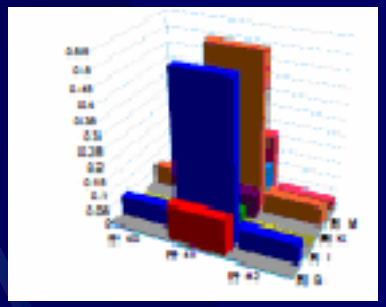
EQ

(up spin electron excitation)

Up spin (hole)



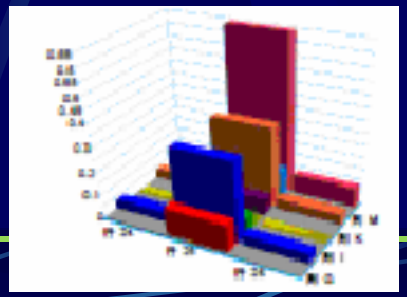
Down spin (hole)



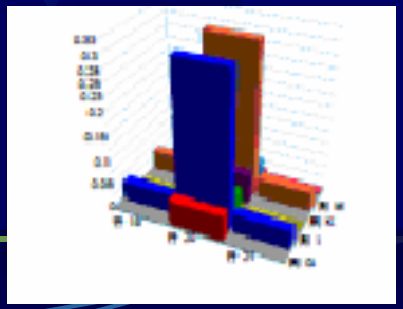
ED

(down spin electron excitation)

Up spin (hole)



Down spin (hole)



Conclusion

(1) Kα RXES of transition metal compounds and Lα RXES of rare earth compounds can be a ultra-fine probe for the pre-edge structures of XAS ---- a new frontier of RXES study

(2) Importance of collaborations of theory and experiment

(3) Combination of *ab initio* energy band calculation and impurity Anderson model ---- a new powerful method of theoretical calculations of RXES

Collaborators

K. Okada, M. Taguchi, A. Shukla,
M. Calandra, G. Vanko, and
S.-W. Cheong