# Inelastic x-ray scattering: recent applications

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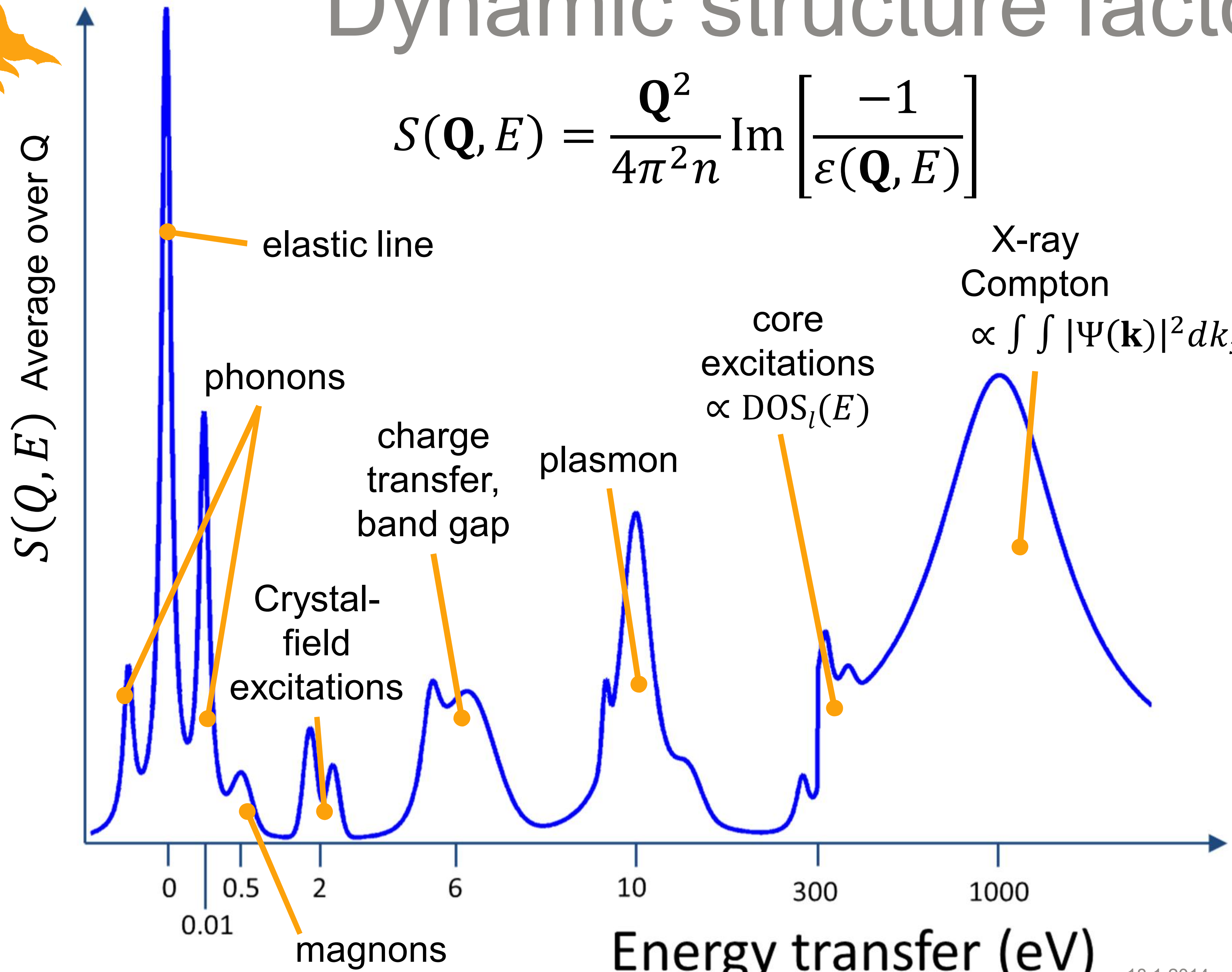
**Benasque TDDFT workshop January 2014**

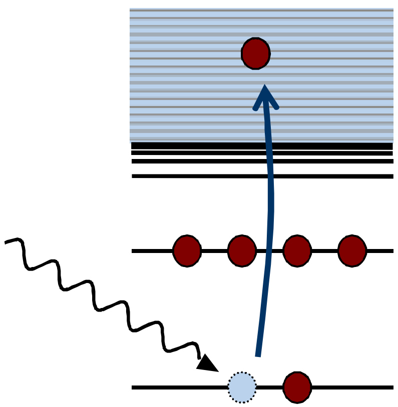
# Dynamic structure factor

$$S(\mathbf{Q}, E) = \frac{\mathbf{Q}^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q}, E)}\right]$$

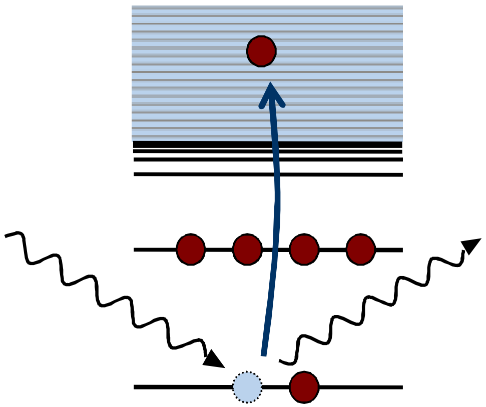


# (Nonresonant) Inelastic X-ray Scattering

Absorption

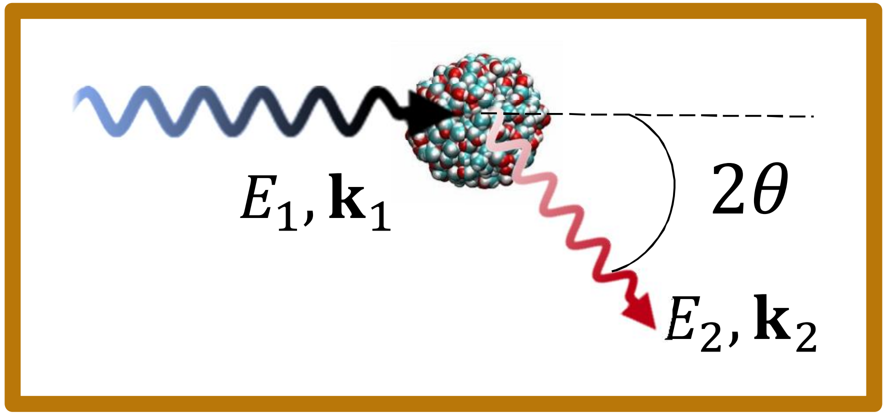


nonresonant IXS



Variables:

$$E = E_1 - E_2$$
$$\hbar\mathbf{Q} = \hbar\mathbf{k}_1 - \hbar\mathbf{k}_2$$
$$Q = 4\pi\sin(2\theta/2)/\lambda$$

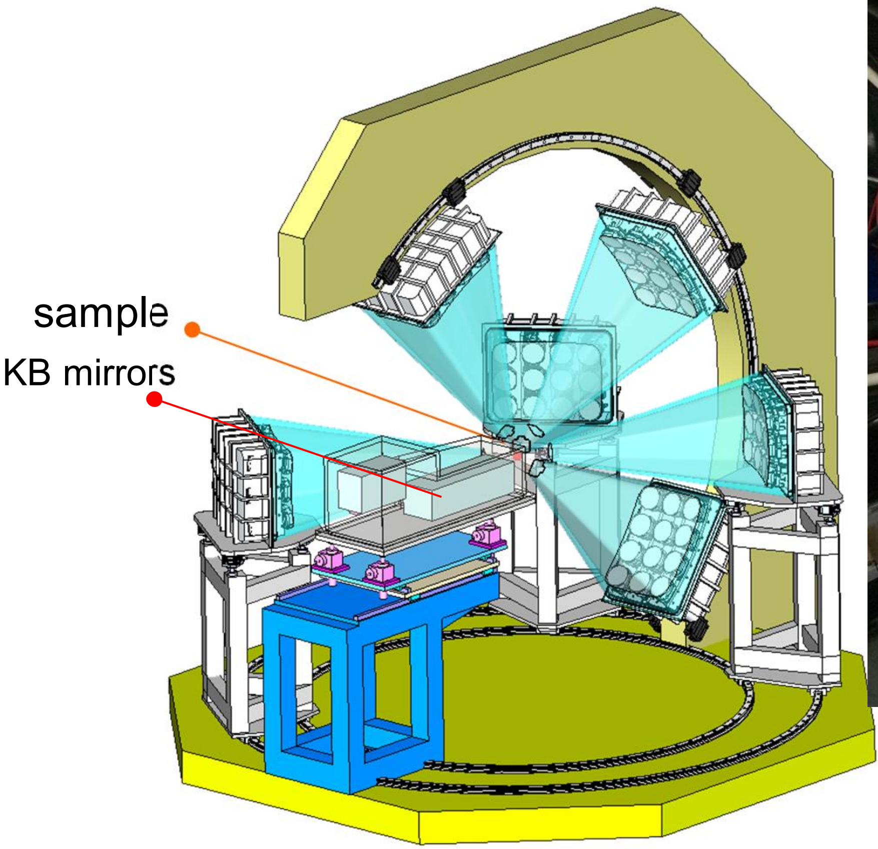


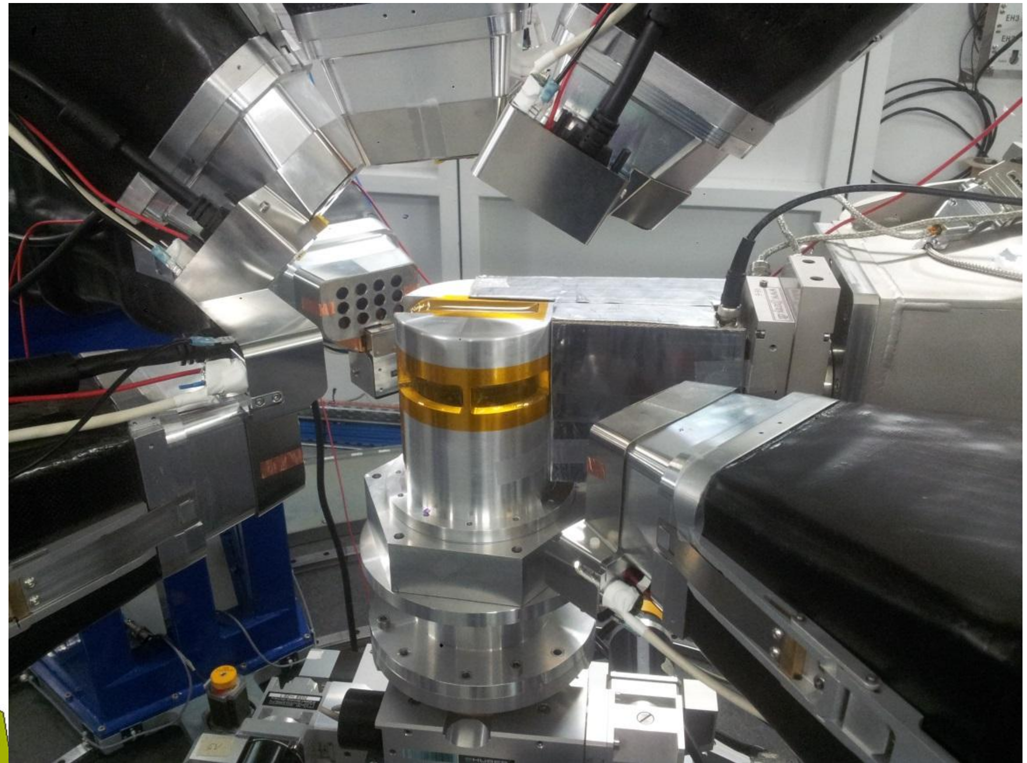

Measured quantity:
the dynamic structure factor

$$S(\mathbf{Q},E) \propto \sum_f |\langle f|\exp(i\mathbf{Q}\cdot\mathbf{r})|i\rangle|^2$$

$$e^{i\mathbf{Q}\cdot\mathbf{r}} = 1 + i\mathbf{Q}\cdot\mathbf{r} - (\mathbf{Q}\cdot\mathbf{r})^2/2 + \cdots$$

# ID20@ESRF, Grenoble, France

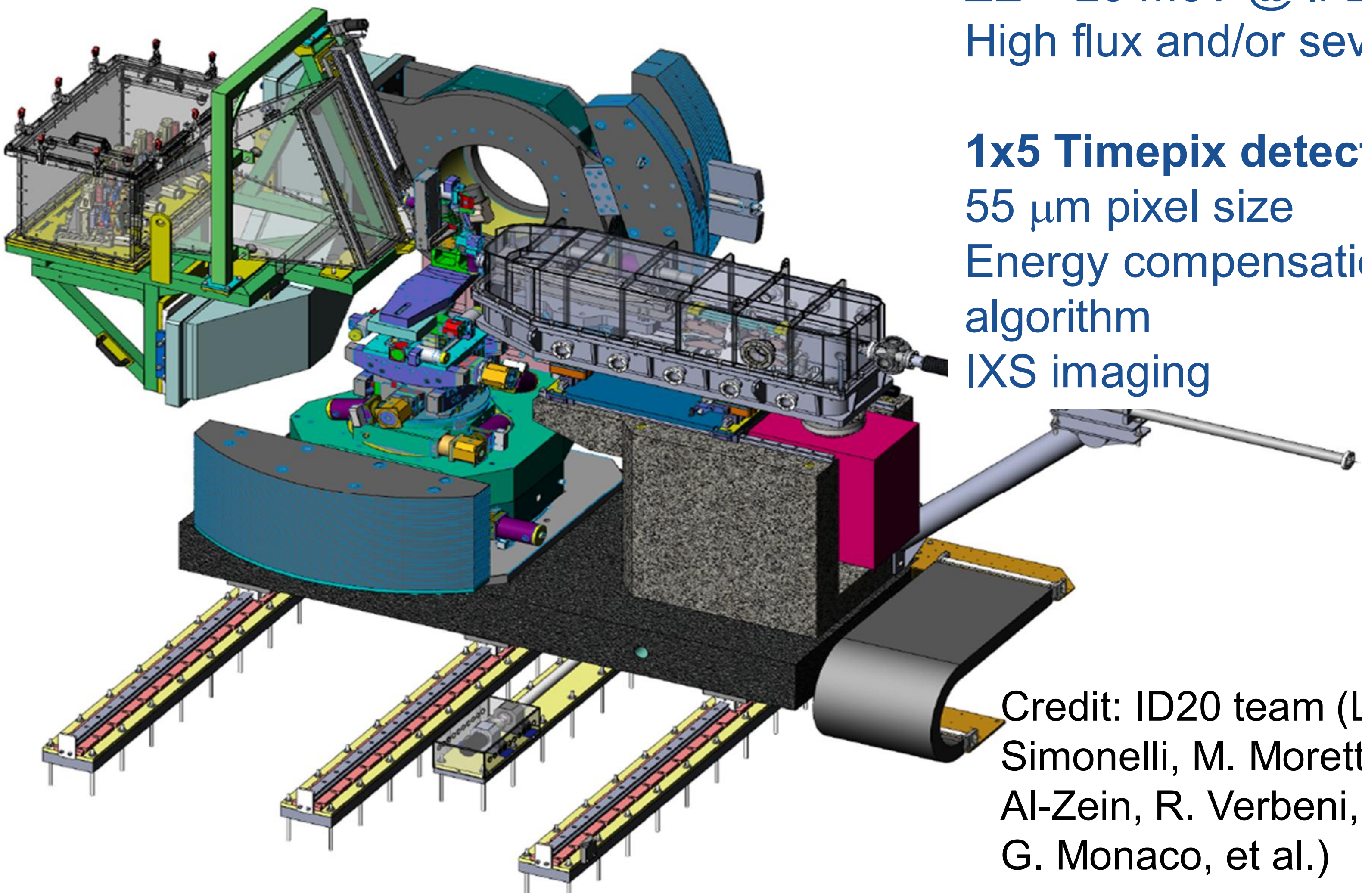


ID20 team and coworkers (Laura Simonelli, M. Moretti Sala, Ali Al-Zein, R. Verbeni, M. Krisch, P. Glatzel, G. Monaco, et al.)

72 analyser crystals (=grating monochromators)
3 horizontal and vertical modules of 12 analysers each

# ID20 @ ESRF: Resonant IXS



**5 bent or diced analysers**
$\Delta$E ~ 25 meV @ Ir $L_3$
High flux and/or several **q**'s

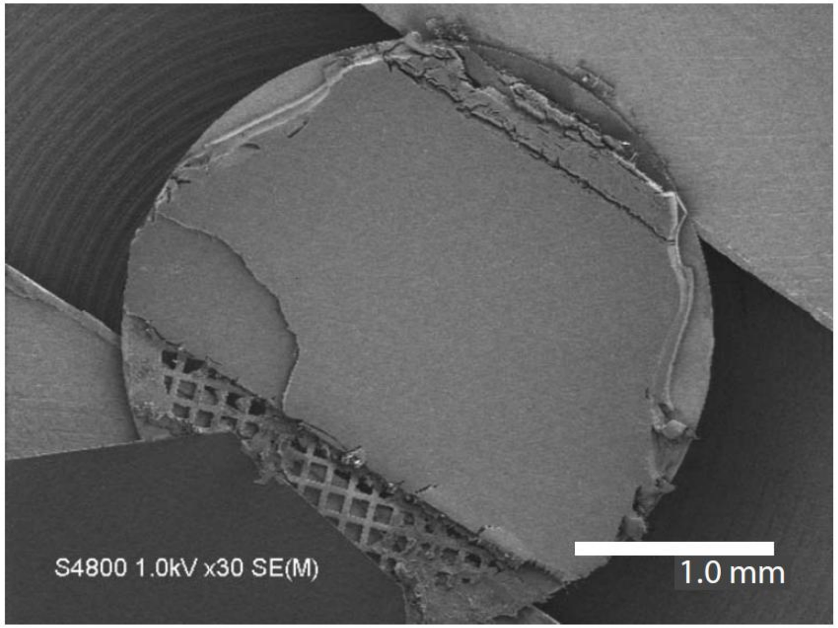
**1x5 Timepix detectors**
55 $\mu$m pixel size
Energy compensation algorithm
IXS imaging

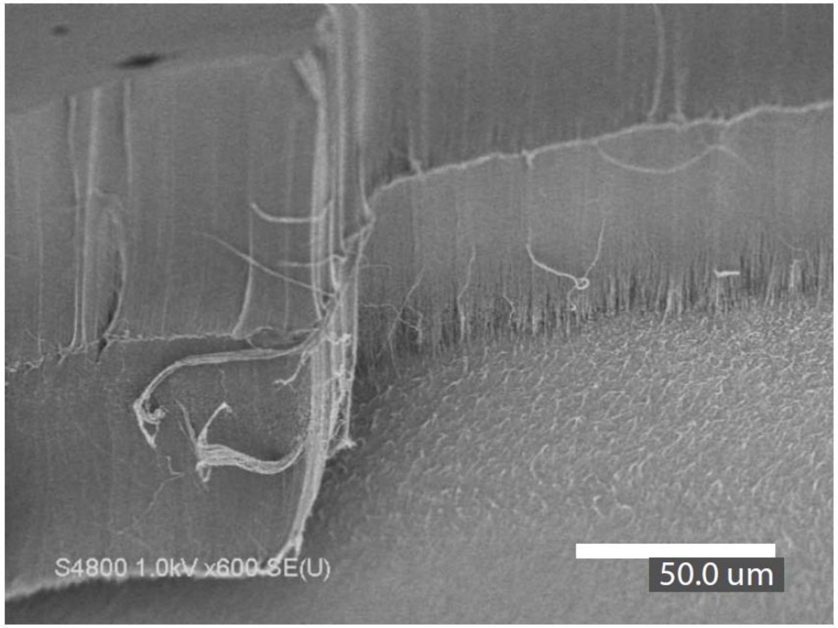
Credit: ID20 team (Laura Simonelli, M. Moretti Sala, Ali Al-Zein, R. Verbeni, M. Krisch, G. Monaco, et al.)

# Outline

| | |
|---|---|
| Part 1 | Carbon nanotubes and graphite |
| Part 2 | Optical excitations in $CO_2$ |
| Part 3 | $d \rightarrow d$ excitations in CuO |
| Part 4 | Momentum distribution |

# Aligned carbon nanotube forest




IXS: Intensity $\propto S(\mathbf{Q},E) = \frac{\mathbf{Q}^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q},E)}\right]$

- weak interaction with sample, difficult to focalize beam on individual nanoparticle

EELS (e.g. in an electron microscope): Intensity $\propto S(\mathbf{Q},E)/Q^4$

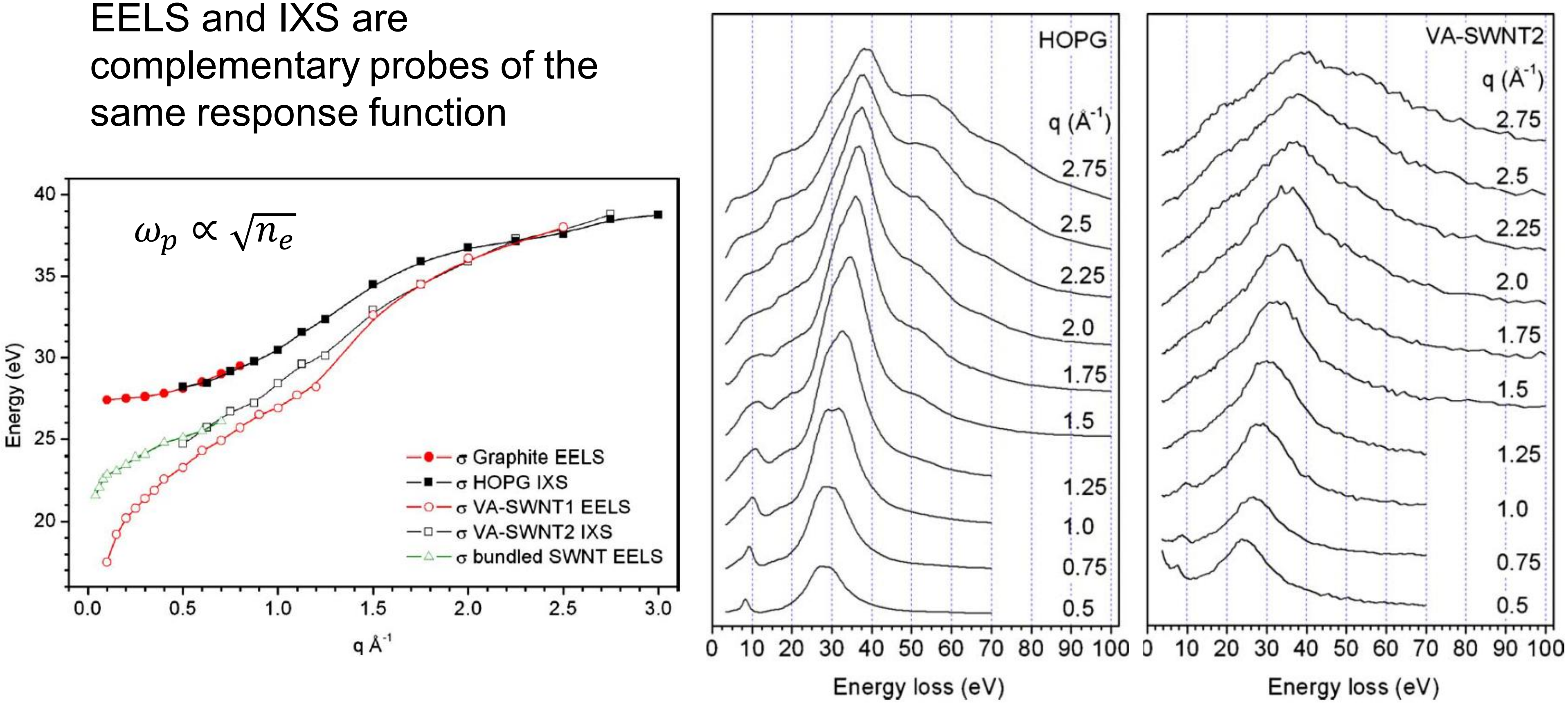
- large interaction, possible to focus electron beam on very small spot

C. Kramberger et al., PRB 81, 205410 (2010)

# IXS spectra from HOPG/SWNT

EELS and IXS are complementary probes of the same response function

Bulk plasmon in graphite and carbon nanotubes



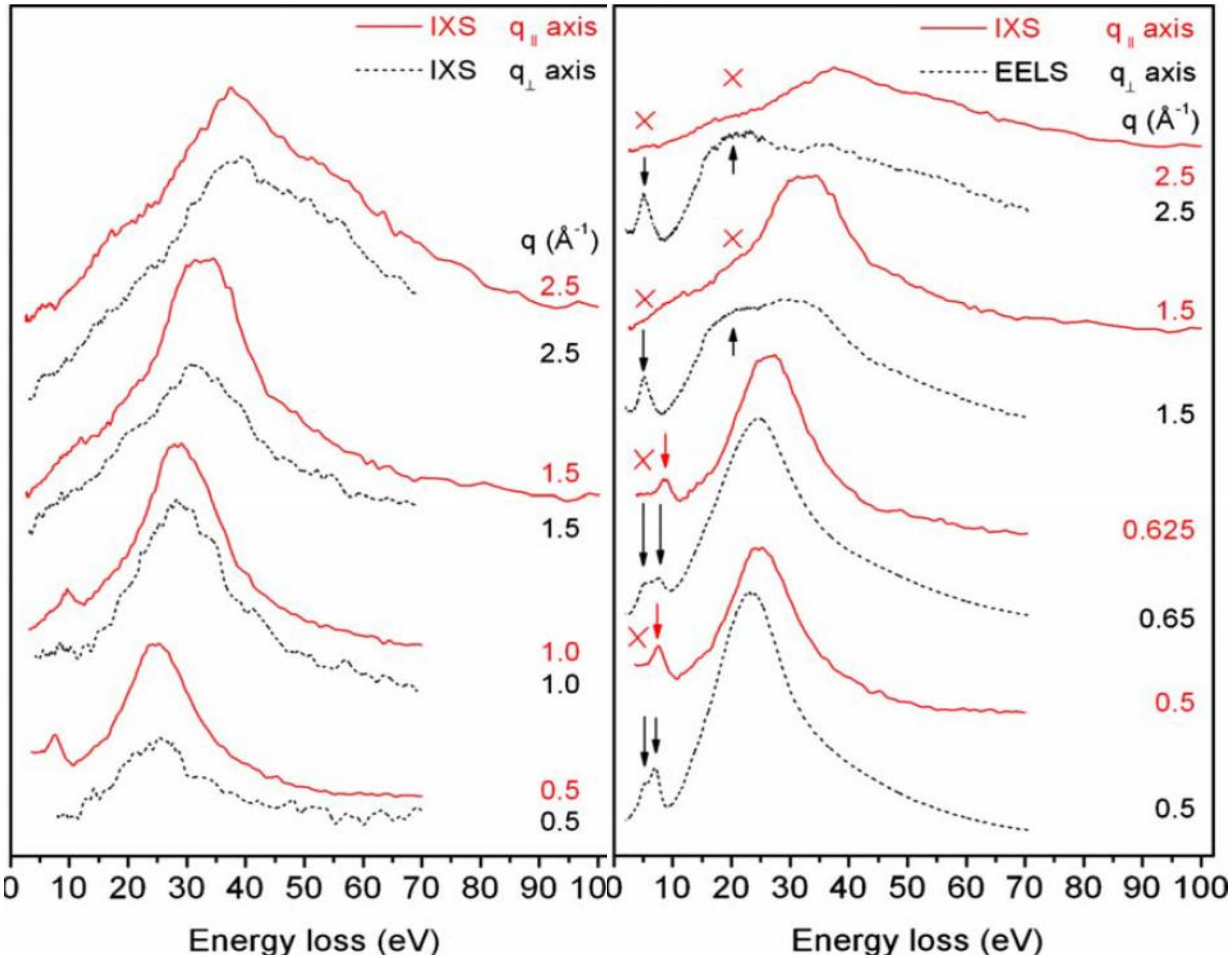

C. Kramberger et al., PRB 81, 205410 (2010)

# IXS compared to EELS

Vertically aligned single walled carbon nanotubes

q parallel to tube axis (along $sp^2$)

q perpendicular to tube axis (out-of-plane)




EELS measurements also in
C. Kramberger et al. PRL 100, 196803 (2008)

C. Kramberger et al., PRB 81, 205410 (2010)
Phys. Status Solidi C **7**, 2789 (2010)

# Outline

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Part 2 Optical excitations in $CO_2$

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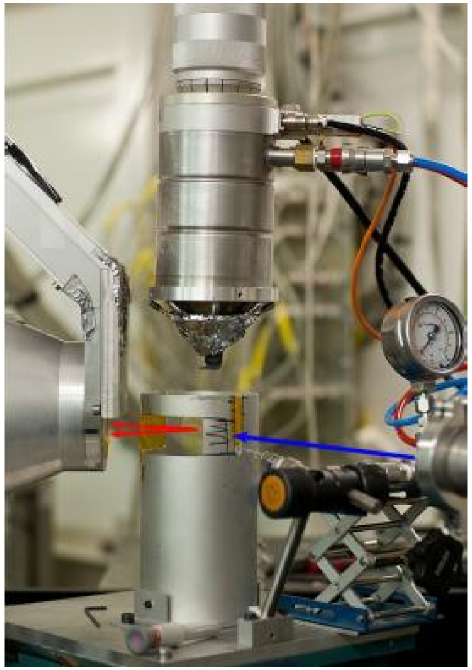
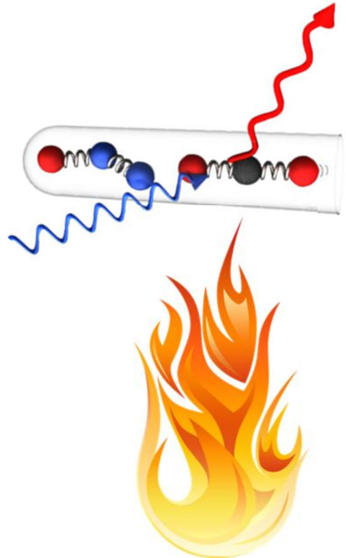
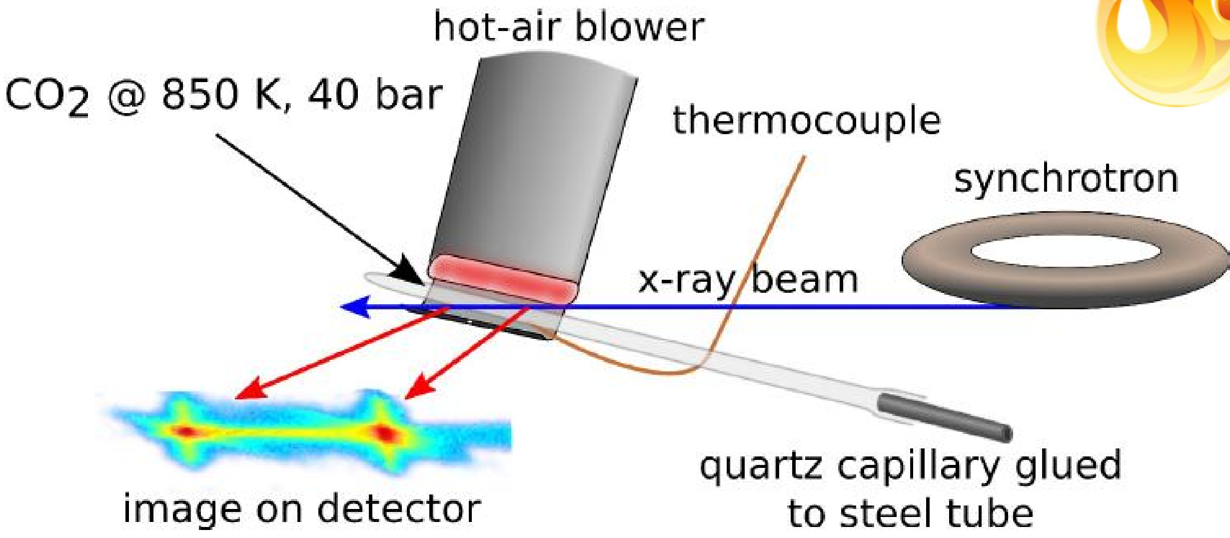
# Optical excitations in $CO_2$

- high pressure, high temperature
- access UV-excitations with IXS
- new information on non-dipolar transitions
- also inner core shell excitations studied



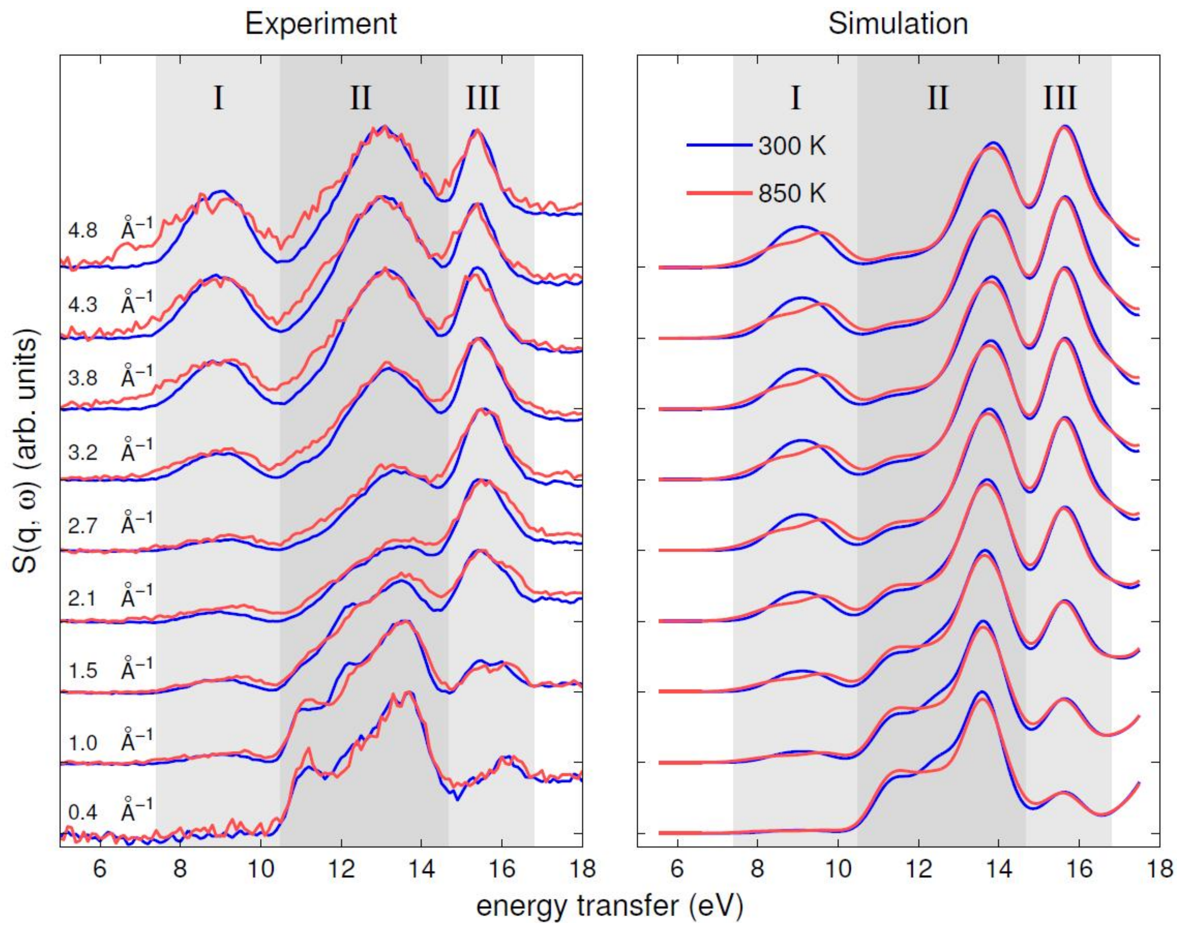


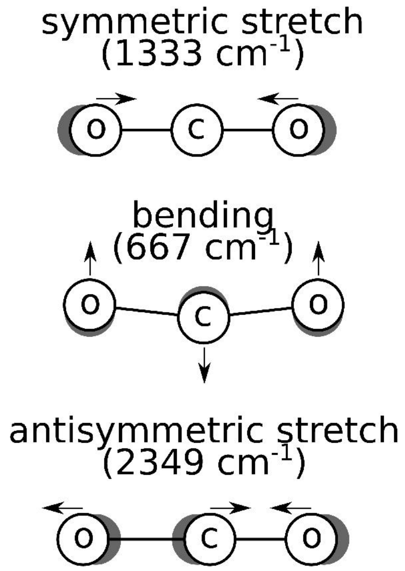



J. Inkinen et al., PCCP 15, 9231 (2013)
A. Sakko et al., PCCP 13, 11678 (2011)

# Optical excitations in $CO_2$

$$\frac{d\sigma(\mathbf{q},\omega)}{d\Omega dE} = (\mathbf{e}_2^* \cdot \mathbf{e}_1)\frac{\omega_2}{\omega_1}\delta(E_f - E_i - E)\rho(i,\nu_i) \sum_{i,f,\nu_i,\nu_f} \left| \langle \nu_f | \nu_i \rangle \sum_j \langle \psi_f | e^{i\mathbf{q}\cdot\mathbf{r}_j} | \psi_i \rangle \right|^2$$



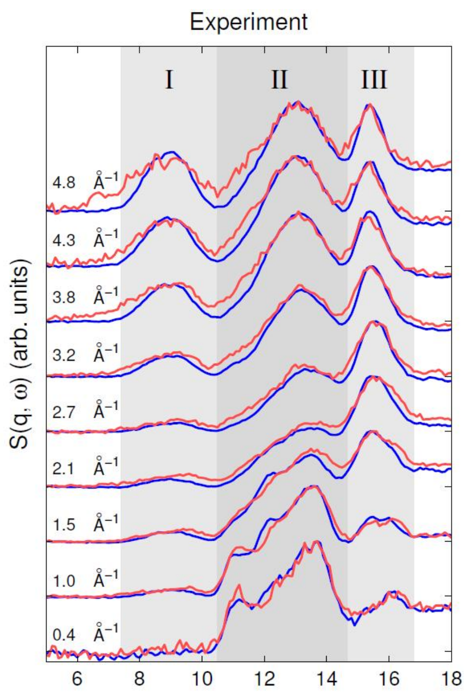

- Coupled cluster method
- MOLPRO code
- aug-cc-pVQZ basis set

J. Inkinen et al. in preparation

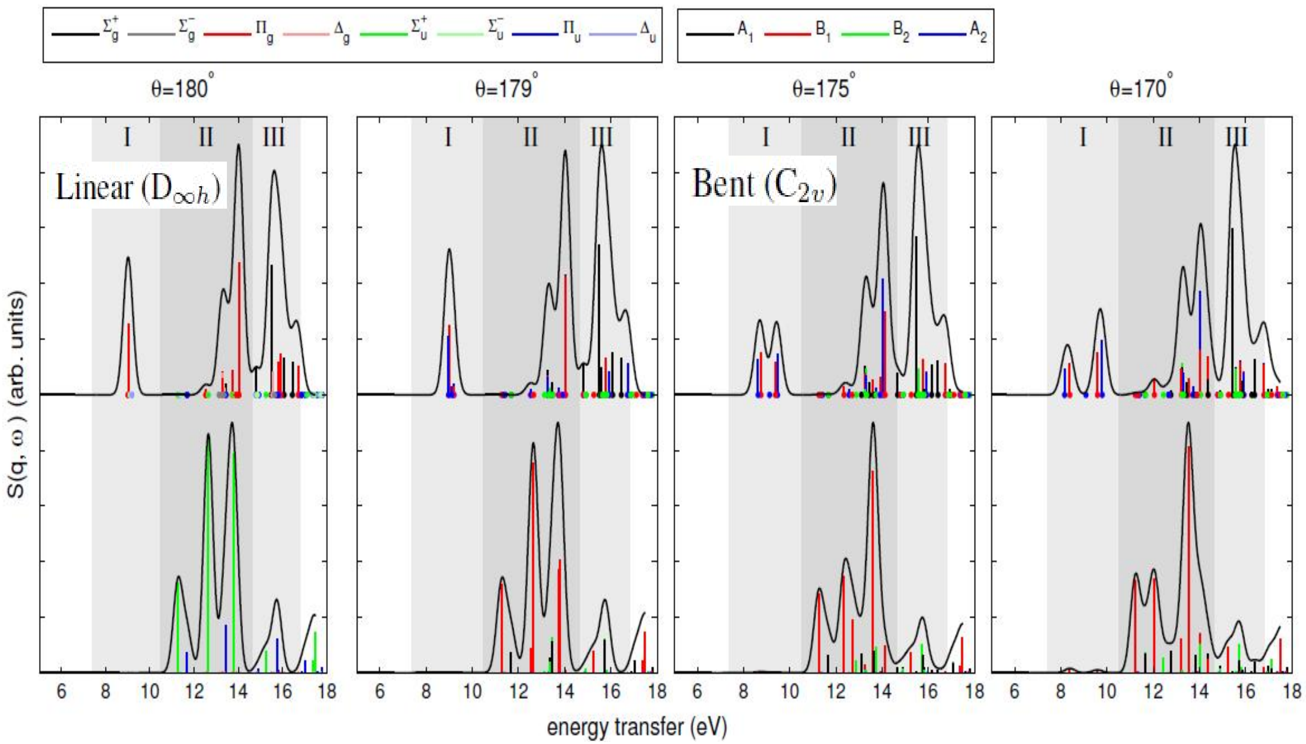
# Optical excitations in $CO_2$

- simulation by Johannes Niskanen, Univ. Helsinki
- dipolar and quadrupolar transitions
- EOM-CCSD

$$\langle \psi_f(\theta)|e^{i\mathbf{q}\cdot\mathbf{r}}|\psi_i(\theta)\rangle$$
$$\approx \langle \psi_f(\theta)|1 + i\mathbf{q}\cdot\mathbf{r} - 1/2(\mathbf{q}\cdot\mathbf{r})^2|\psi_i(\theta)\rangle$$
$$= i\sum_k q_k \langle \psi_f(\theta)|r_k|\psi_i(\theta)\rangle - 1/2\sum_{k,l} q_k q_l \langle \psi_f(\theta)|r_k r_l|\psi_i(\theta)\rangle$$

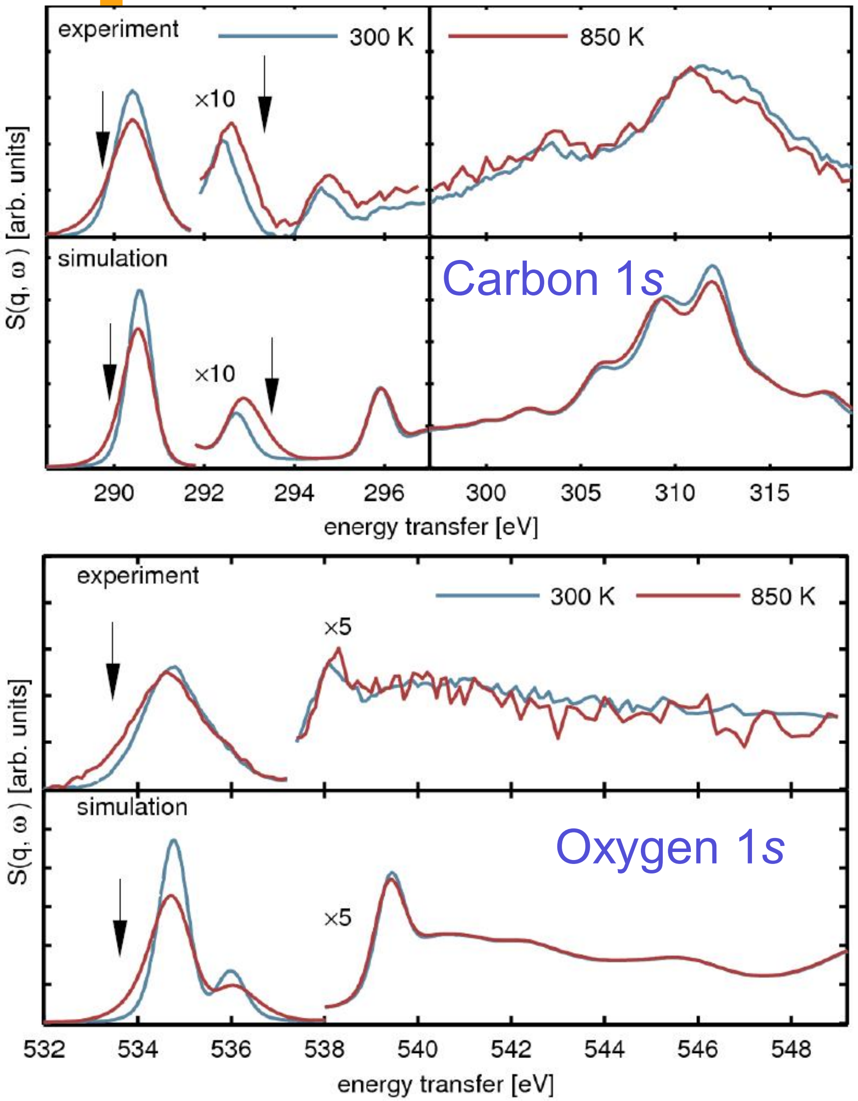


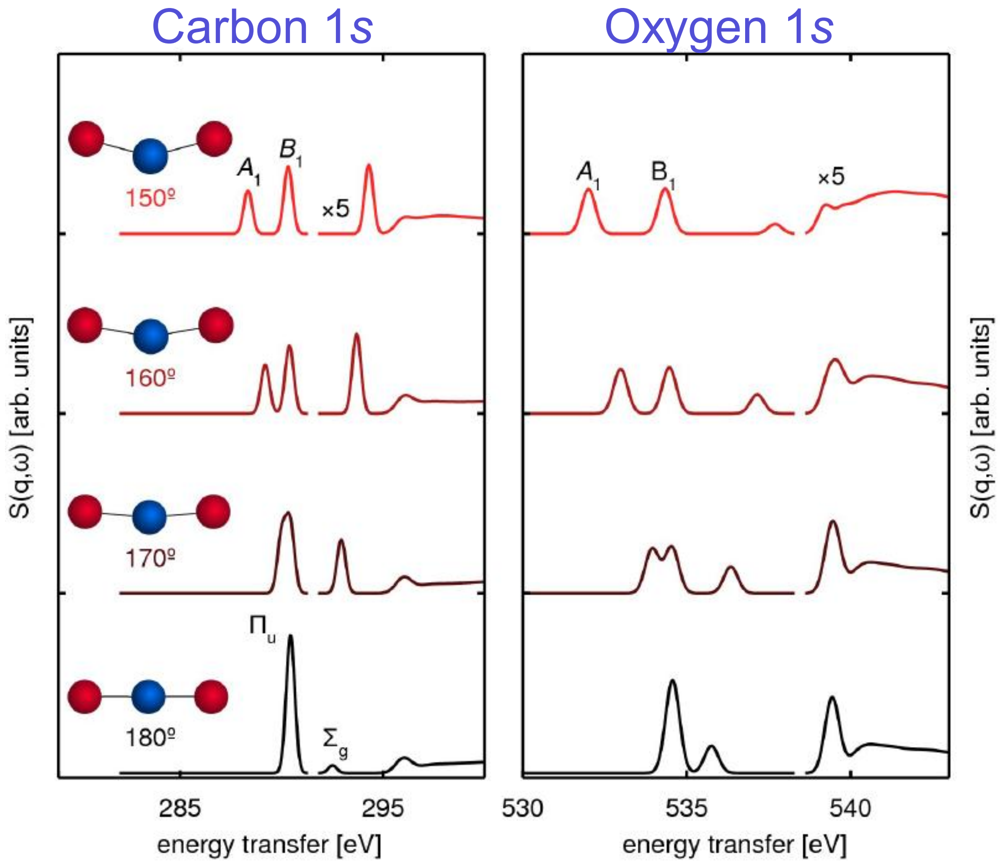

energy transfer (eV)




J. Inkinen et al. in preparation

# Also inner core level excitations




J. Inkinen et al., PCCP 15, 9231 (2013)
A. Sakko et al., PCCP 13, 11678 (2011)
Calculations done using DFT
(ERKALE code developed in Helsinki by S. Lehtola et al., http://**erkale**.google**code**.com)

# Outline

Part 1 Carbon nanotubes and graphite

Part 2 Optical excitations in $CO_2$

**Part 3 $d \to d$ excitations in CuO**

Part 4 Momentum distribution

# Cupric oxide

Nature Materials 2008 **LETTERS**

## Cupric oxide as an induced-multiferroic with high-$T_C$

T. KIMURA[1]*, Y. SEKIO[1], H. NAKAMURA[1], T. SIEGRIST[2] AND A. P. RAMIREZ[2]
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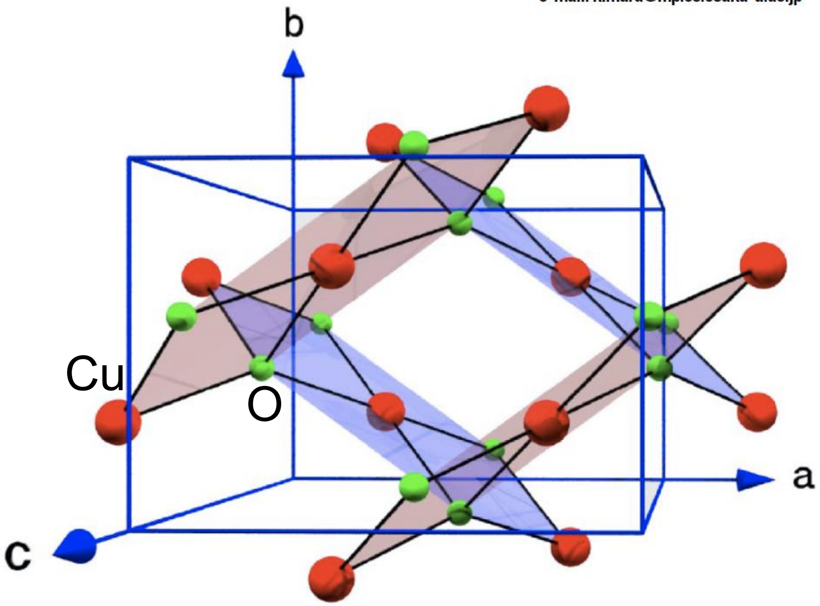
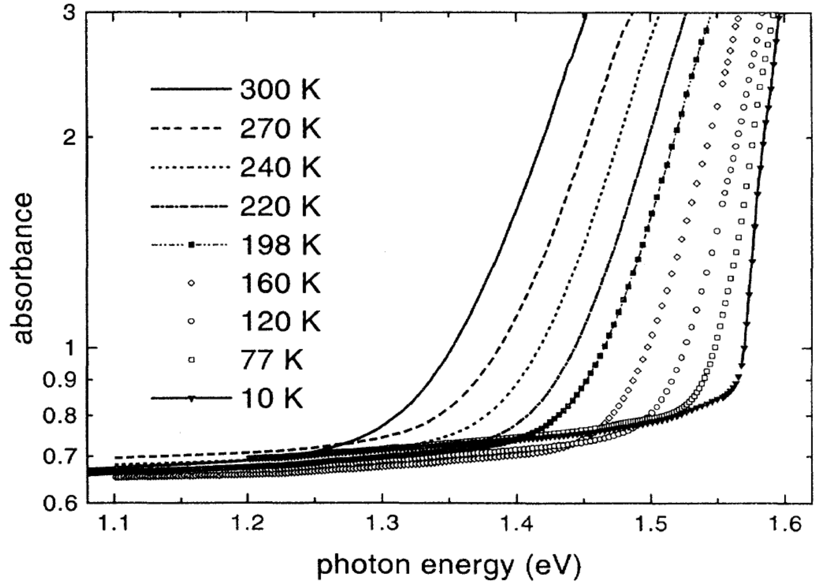



G. Döring et al. PRB 2004

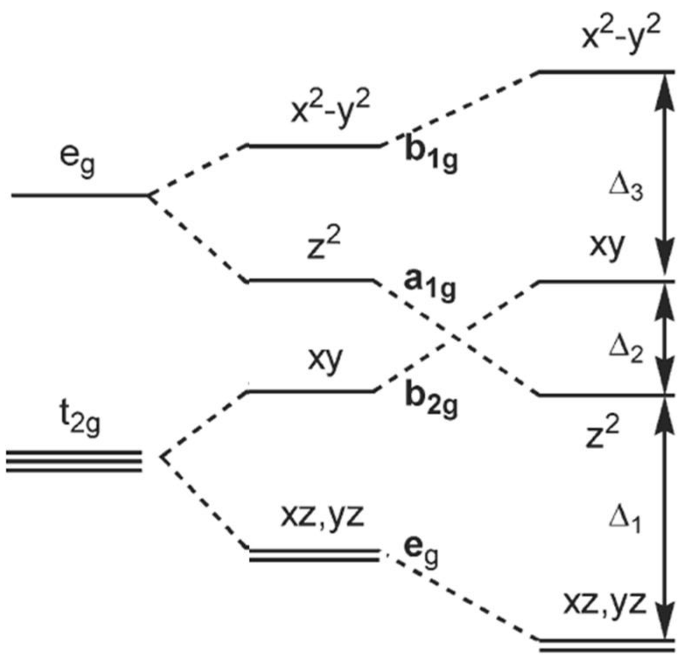
Band gap in CuO as a function of T

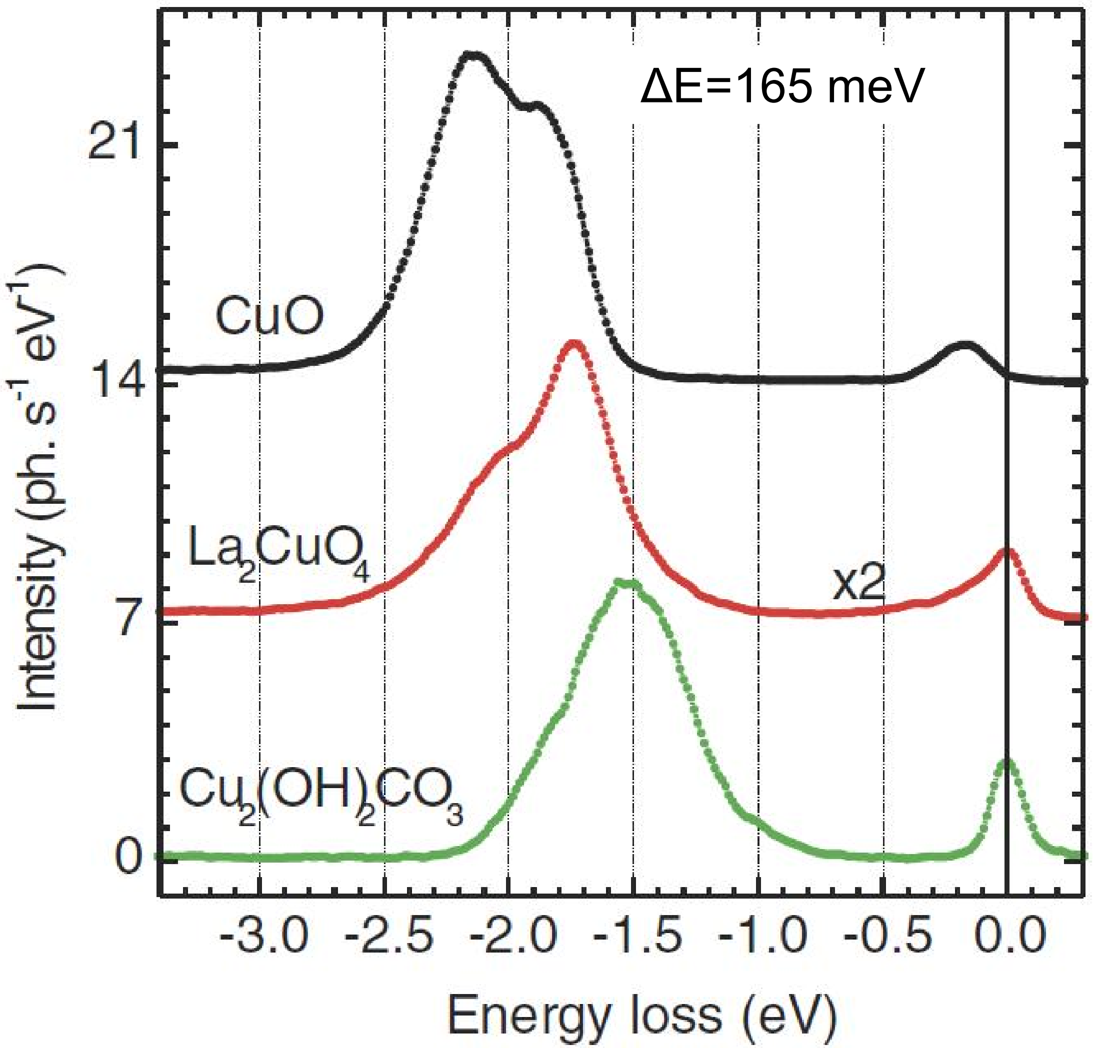



Marabelli et al. PRB 1995

# Cupric oxide

crystal field
excitations

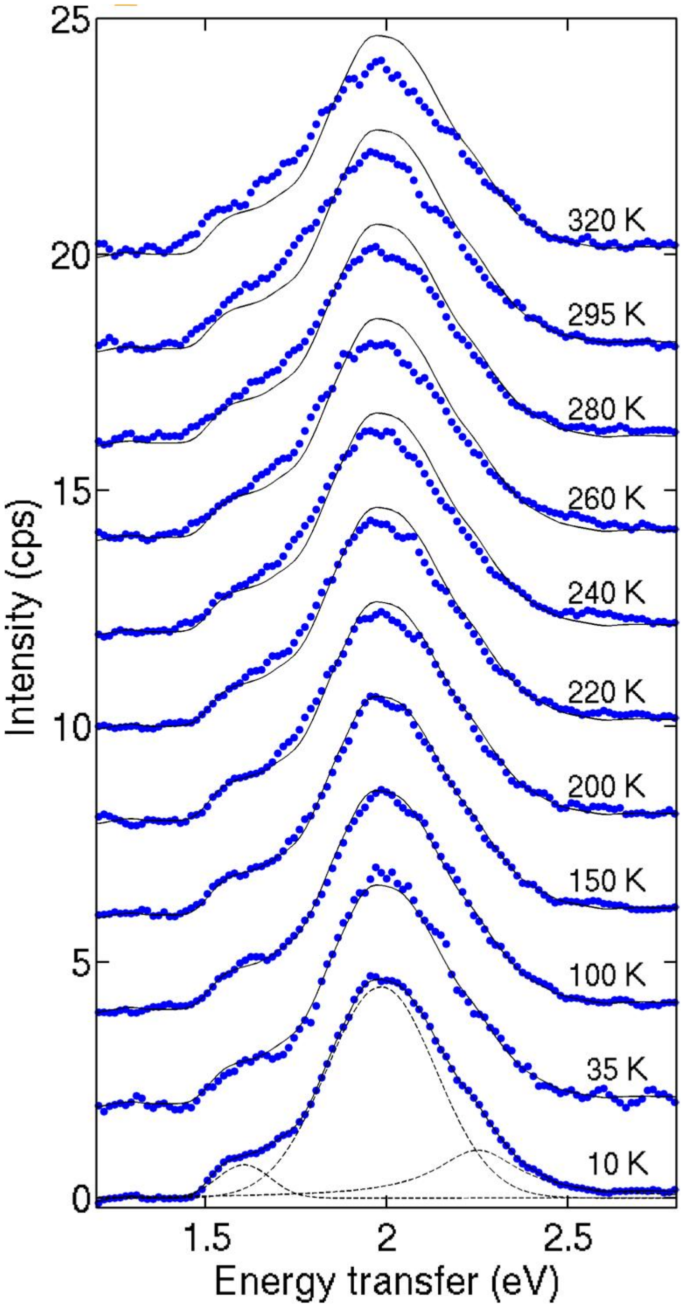


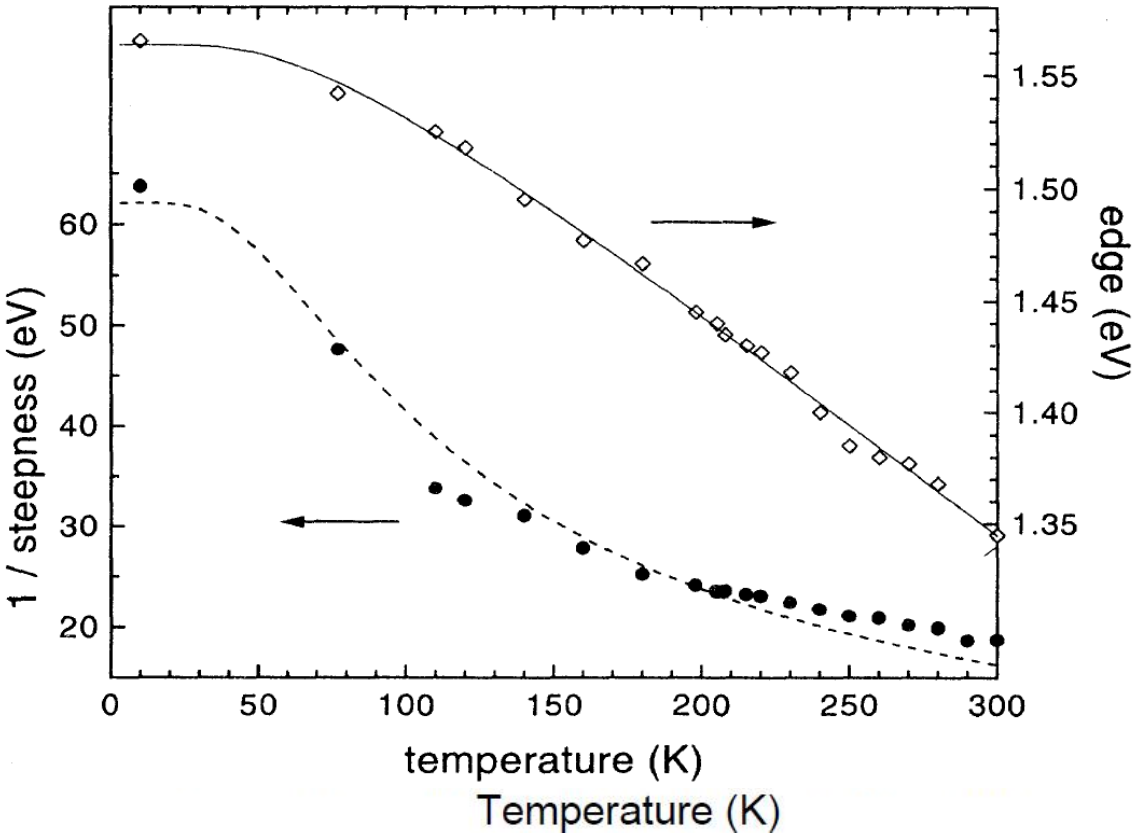

G. Ghiringhelli et al. PRL 2009

# Cupric oxide

## crystal field excitations



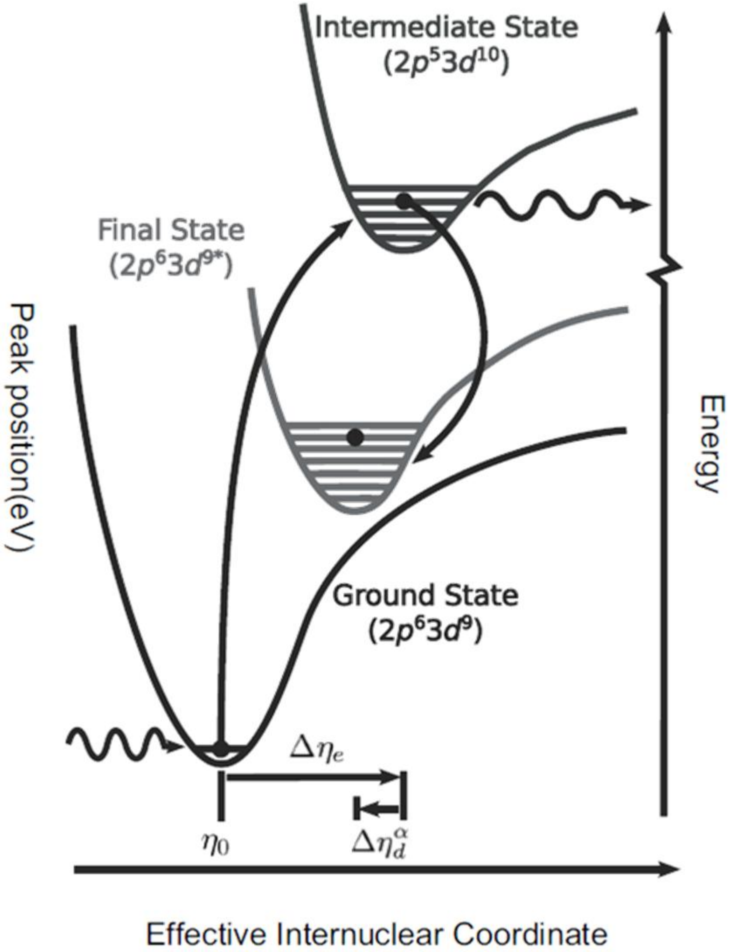

Marabelli et al. PRB 1995: band gap



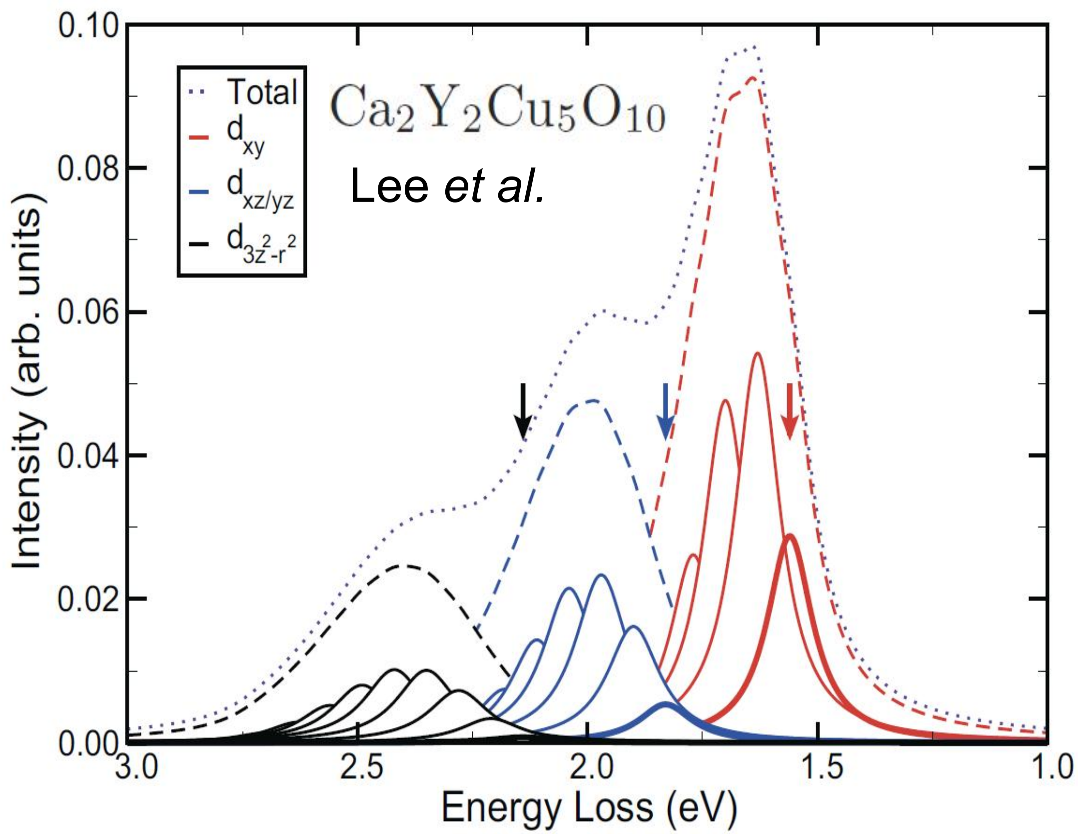

S. Huotari et al., submitted, in arXiv

# Franck-Condon treatment

## …more advanced




J. J. Lee *et al.*, arXiv: 1312.2639v1 [cond-mat.str-el]



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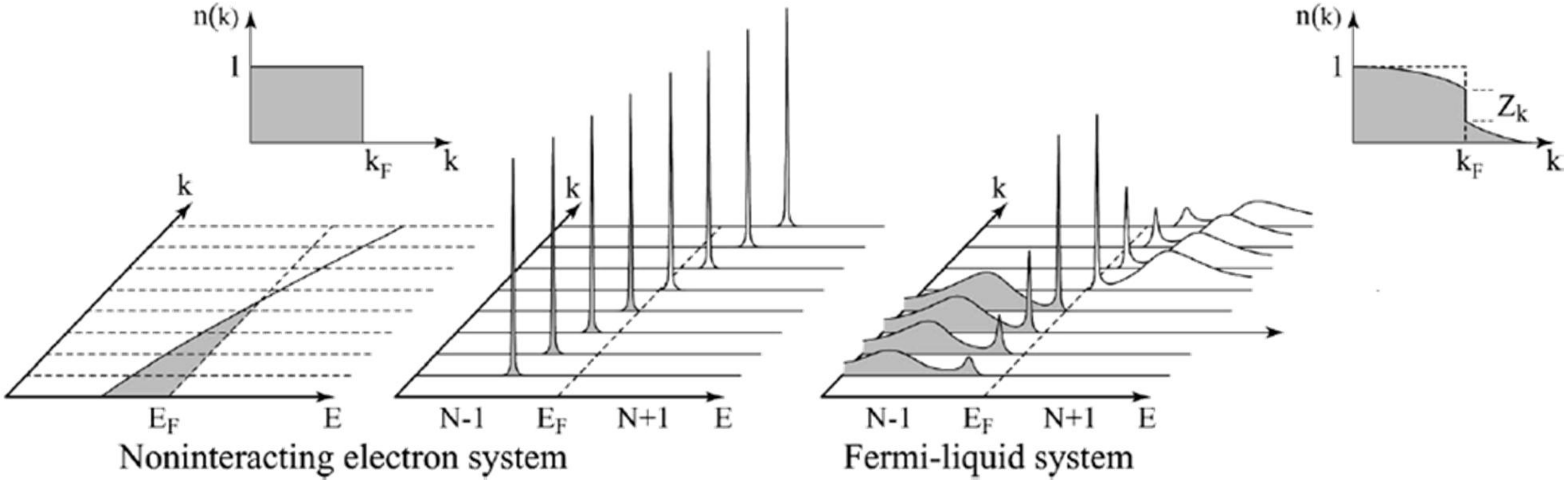
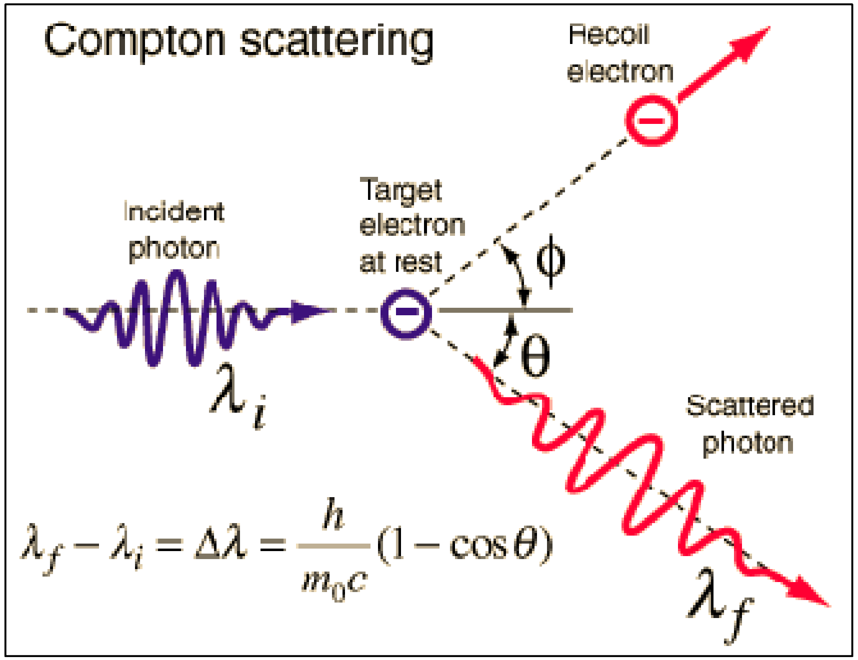
# Quasiparticle renormalisation



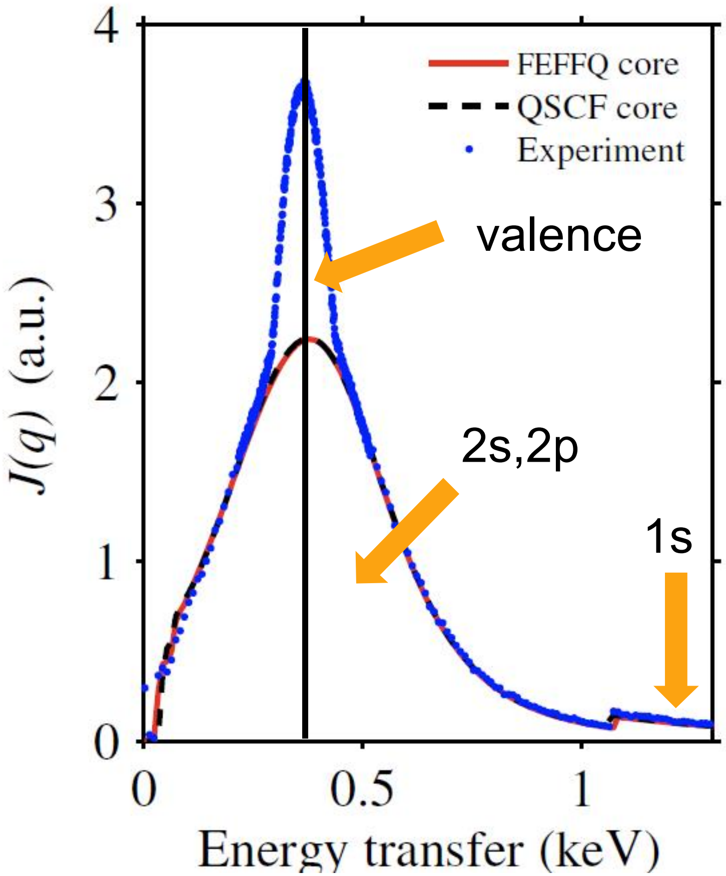

$$\mathrm{PES} \propto \sum_{f,i} \left| M^{\mathbf{p}}_{f,i} \right|^2 A(\mathbf{p}, E)\, \delta(E_K + E_m^{N-1} - E_i^N - \omega_1)$$

A. Damascelli et al.,
Rev. Mod. Phys 75, 473 (2003)

# Compton spectroscopy




http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/compton.html



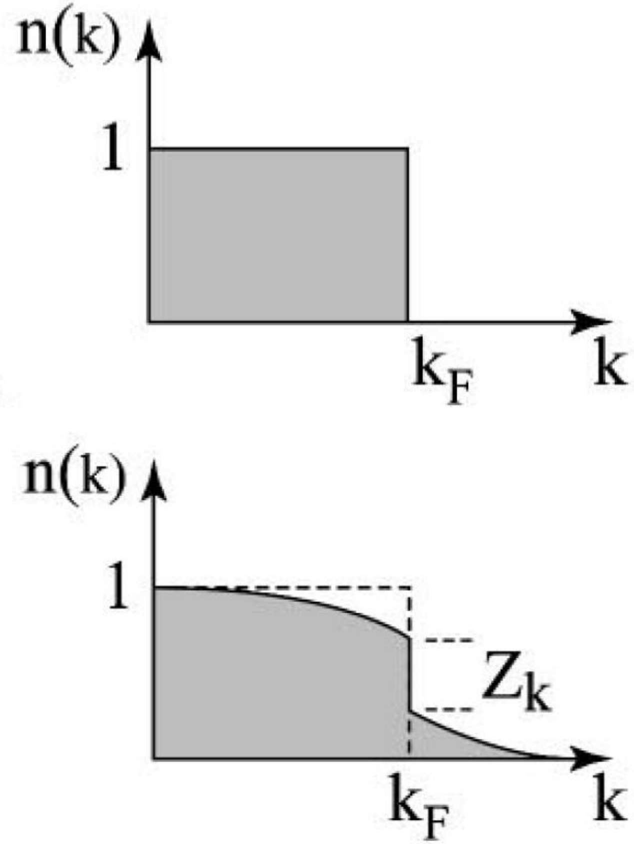

Compton profile $J(q)$

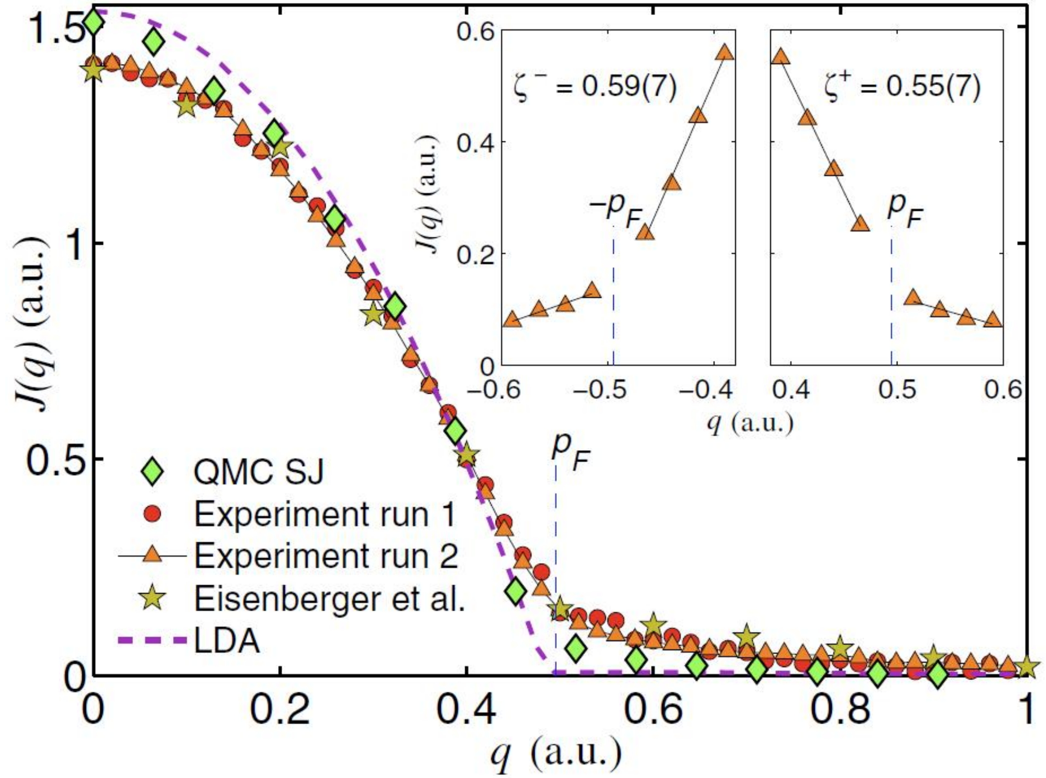
$$J(q) = \frac{3}{8\pi p_F^3}\int_{4\pi} d\Omega \int_{|q|}^{\infty} pn(\mathbf{p})dp$$

S. Huotari et al.,
PRL 105, 086403 (2010)

# Compton spectroscopy

Independent electrons:
$J(q) \propto (p_F^2 - q^2)$ for $|q| < p_F$

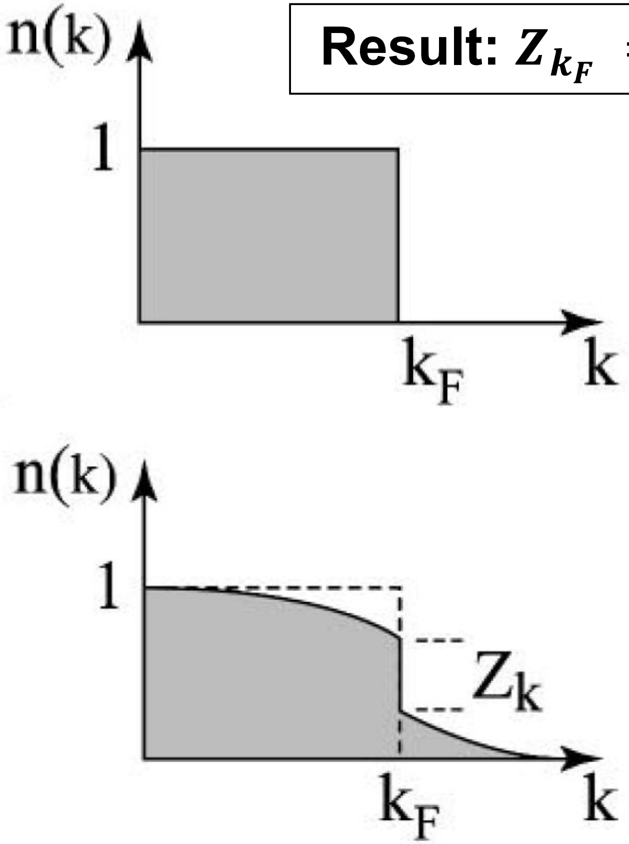



A. Damascelli et al.,
Rev. Mod. Phys 75, 473 (2003)

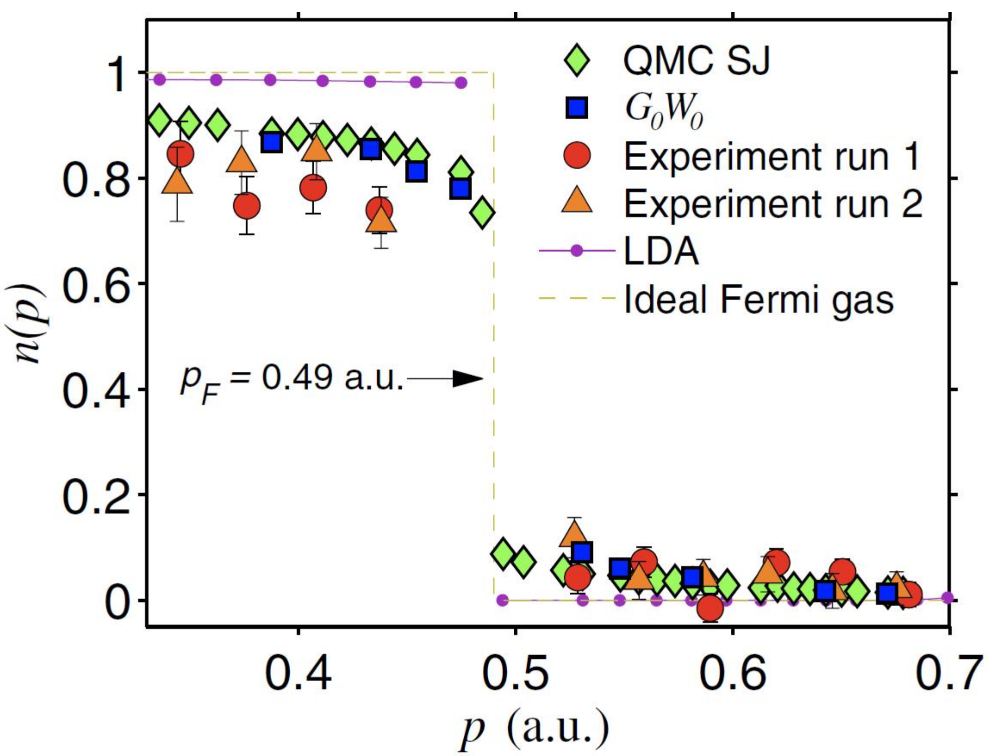
S. Huotari et al.,
PRL 105, 086403 (2010)

# Momentum density of the electron gas




**Result: $Z_{k_F} = 0.58 \pm 0.07$ for Na**

$$n(p) = -\frac{2p_F^3}{3p}\frac{dJ(q)}{dq}\bigg|_{q=p}$$




S. Huotari et al.,
PRL 105, 086403 (2010)

# Helsinki Electronic Structure and IXS group

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  R. Verbeni, P. Glatzel et al.

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