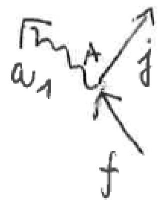
# FOTONSKO SIPANJE (POSKUSI PHOTON IN – PHOTON OUT)

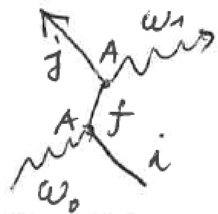


ABSORPCIJA FOTONA


EMISIJA FOTONA




SIPANJE FOTONA




$$H = \underbrace{\overset{\text{atom}}{H_1} + \overset{\text{polje}}{H_2}}_{H_0} + \overset{\text{sklopitev}}{\Delta H(t)}$$

$$\boxed{\Delta H = \vec{p}\cdot\vec{A} + \frac{A^2}{2}}$$

operator anihilacije fotona $\vec{k}$, polarizacije $p$

$$\vec{A}(\vec{r},t) = \frac{1}{\sqrt{V}} \sum_{\vec{k},pol} \sqrt{\frac{2\pi}{\omega_{\vec{k},pol}}} \left( \hat{a}_{\vec{k},p}\, \hat{\varepsilon}^{p}\, e^{i\vec{k}\cdot\vec{r} - i\omega t} + \hat{a}^{\dagger}_{\vec{k},p}\, \hat{\varepsilon}^{p*}\, e^{-i\vec{k}\cdot\vec{r} + i\omega t} \right)$$

operator kreacije fotona

ENERGIJA EMP V VOLUMNU V JE ENAKA ENERGIJI FOTONA $\omega_{\vec{k},pol}$

DRUGA KVANTIZACIJA: VEKTORSKI POTENCIAL V VOLUMNU V RAZVIJEMO V FOURIEROVO VRSTO IN ENERGIJO OSCILATORJEV OMEJIMO NA VEČKRATNIK $\omega$

- SKLOPITEV $\Delta H(t)$ POVZROČI PREHODE MED STANJI ATOM–EMP.
- VERJETNOST ZA PREHOD POIŠČEMO S TEORIJO ČASOVNO ODVISNE PERTURBACIJE, KER JE $\Delta H$ RELATIVNO MAJHEN.

$$\Psi(t) = \sum_{k} \underline{\underline{c_k(t)}}\, u_k\, e^{-iE_k t}, \qquad H_0 u_k = E_k u_k$$

ČASOVNO ODVISNI KOEFICIENTI RAZVOJA PO LASTNIH FUNKCIJAH $H_0$

STACIONARNA STANJA

$$\psi(0) = u_i \longrightarrow c_i(0)=1\ ,\ c_{k\neq i}(0)=0$$



1. RED:

$$c_j^{(1)} = \frac{1}{i}\int_0^t dt' \langle j|\Delta H|i\rangle e^{i(E_j-E_i)t'}$$

2. RED:

$$c_j^{(2)}(t) = \frac{1}{i^2}\sum_f \int_0^t dt'' \int_0^{t''} dt' \langle j|\Delta H(t'')|f\rangle e^{i(E_j-E_f)t''}\langle f|\Delta H(t')|i\rangle e^{i(E_f-E_i)t'}$$

VERJETNOST ZA PREHOD NA ČASOVNO ENOTO $|i\rangle \to |j\rangle$: $w_{ji} = \dfrac{|c_j(t)|^2}{t}$.

KER NAS TIPIČNO ZANIMA PREHOD V SKUPINO KONČNIH STANJ:

$$w_{ji} = \int \frac{|c_j|^2}{t}\rho(E_j)\,dE_j \qquad \ldots\ \rho(E_j)\ \text{gostota končnih stanj v energijskem prostoru.}$$

V 1. REDU JE TREBA IZRAČUNATI MATRIČNI ELEMENT:

$$\langle j|\Delta H|i\rangle = \langle \vec{k}_1, p_1; J|\Delta H|\vec{k}_0, p_0; I\rangle = \langle \vec{k}_1, p_1; J|\cancel{\vec{p}\cdot\vec{A}} + \frac{A^2}{2}|\vec{k}_0, p_0; I\rangle$$

atomsko stanje

SIPALNI PRISPEVEK $\vec{p}\cdot\vec{A}$ V PRVEM REDU JE NIČ, KER SPREMENI ŠT. FOTONOV ZA 1.

$$c_j^{(1)}(t) = \frac{2\pi}{iV\sqrt{\omega_0\omega_1}}\langle J|I\rangle \hat{\varepsilon}^{p_0}\cdot\hat{\varepsilon}^{p_1 *}\int_0^t e^{i(\omega_1+E_J-\omega_0-E_I)t'}dt'$$

$$c_j^{(2)}(t) = -\frac{2\pi}{iV\sqrt{\omega_0\omega_1}}\sum_F\left(\frac{\langle J|\vec{p}\cdot\hat{\varepsilon}^{p_1 *}|F\rangle\langle F|\vec{p}\cdot\hat{\varepsilon}^{p_0}|I\rangle}{E_F-E_I-\omega_0} + \frac{\langle J|\vec{p}\cdot\hat{\varepsilon}|F\rangle\langle F|\vec{p}\cdot\hat{\varepsilon}^{*}|I\rangle}{E_F-E_I+\omega_1}\right) * \int_0^t e^{i(\omega_1+E_J-\omega_0-E_I)t''}dt''$$

$$\frac{d\sigma}{d\Omega} = \alpha^4 \frac{\omega_1}{\omega_0} \left| \delta_{J1}\, \hat{\varepsilon}^0 \cdot \hat{\varepsilon}^{1*} - \sum_F \left( \frac{\langle J|\vec{p}\cdot\hat{\varepsilon}^{1*}|F\rangle\langle F|\vec{p}\cdot\hat{\varepsilon}^0|I\rangle}{E_F - E_I - \omega_0} + \frac{\langle J|\vec{p}\cdot\hat{\varepsilon}^0|F\rangle\langle F|\vec{p}\cdot\hat{\varepsilon}^{1*}|I\rangle}{E_F - E_I + \omega_1} \right) \right|^2$$

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**| KRAMERS – HEISENBERGOVA ENAČBA |**

$\omega_1 + E_J - \omega_0 - E_I = 0 \leftarrow$ pogoj

$$\alpha^4 \cdot r_B^2 = r_0^2 = (2.83 \cdot 10^{-15})^2 m^2 = 8 \cdot 10^{-30} m^2$$

$r_0 \leftarrow$ klasični radej elektrona

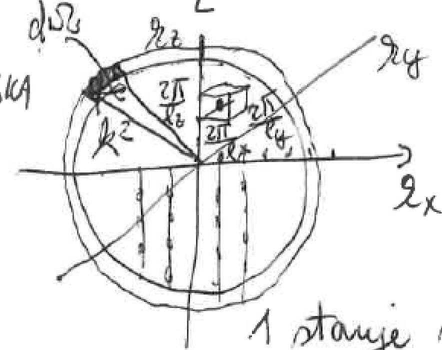
Bohrov radij $5.29 \cdot 10^{-11} m$

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 m c^2} \simeq 2.83 \cdot 10^{-15} m$$

– nekaj vmesnih korakov: $C = \int_0^t e^{i\overbrace{(\omega_1 + E_J - \omega_0 - E_I)}^{E} t'} dt' = \frac{i}{E}(1 - e^{iEt}) = \frac{i}{E}(1 - \cos Et - i \sin Et)$

- $CC^* = \frac{2(1-\cos Et)}{E^2} = \frac{4 \sin^2 \frac{Et}{2}}{E^2} = \frac{t^2 \sin^2 \frac{Et}{2}}{\left(\frac{Et}{2}\right)^2}$

- ENERGIJSKA GOSTOTA KONČNIH STANJ




$k_x = \frac{n_x 2\pi}{l_x} \quad n_x = 1, 2, \dots$

$k_y = n_y \frac{2\pi}{l_y} \quad n_y = 1, 2, \dots$

$k_z = n_z \frac{2\pi}{l_z} \quad n_z = 1, 2 \dots$

periodični robni pogoji v škatli

$V = l_x \cdot l_y \cdot l_z$

1 stanje v kocki z volumnom $\left(\frac{V}{(2\pi)^3}\right)^{-1}$

$dN = k^2 dk\, d\Omega \frac{V}{(2\pi)^3} \quad \omega = \frac{k}{\alpha}$

$\frac{dN}{d\Omega} = k^2 dk \frac{V}{(2\pi)^3} \quad d\omega = \frac{dk}{\alpha}$

$= \frac{\omega^2 V}{(2\pi)^3 \alpha^3} d\omega \leftarrow \rho(\omega)$

- PRESEK

$\frac{d\sigma}{d\Omega} = \frac{w_{ji}}{I} \leftarrow \left[\frac{1}{s}\right]$

tok vpadnih fotonov $\left[\frac{1}{m^2 s}\right]$ $\quad I = \frac{c}{V} = \frac{1}{\alpha V}$

④

■ KH. FORMULA DIVERGIRA ZA RESONANČNO SIPANJE $\omega_0 \approx E_F - E_I$

UPOŠTEVATI JE TREBA, DA VMESNO STANJE RAZPADA (ŽIVLJENSKI ČAS $\Gamma_F^{-1}$)

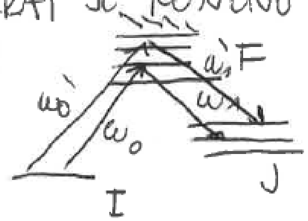
$$\dot{c}_f^{(1)} = \frac{1}{i}\langle f|\Delta H(t)|i\rangle e^{i(E_f-E_i)t} \underbrace{- \frac{\Gamma_f}{2} c_f(t)}_{} \quad \text{DODATNI ČLEN}$$

$\Downarrow$

$$\frac{d\sigma(\omega_0)}{d\Omega\, d\omega_1} = \alpha^4 \left(\frac{\omega_1}{\omega_0}\right) \left| \sum_F \frac{\langle J|\vec{p}\cdot\hat{\varepsilon}^{1*}|F\rangle\langle F|\vec{p}\cdot\hat{\varepsilon}^{0}|I\rangle}{E_F - E_I - \omega_0 - i\frac{\Gamma_F}{2}} \right|^2 \delta(\omega_1 + E_J - \omega_0 - E_I)$$

**RIXS** ← RESONANTNO SIPANJE RENTGENSKE SVETLOBE

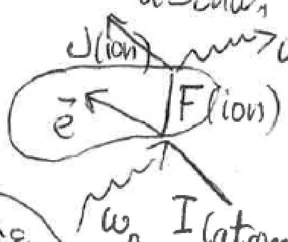
■ VELIKOKRAT JE KONČNO STANJE $|J\rangle$ DOSEGLJIVO SAMO PREKO ENEGA VMESNEGA STANJA!




$$Xe + \gamma(\omega_0) \to Xe\, 2p^{-1}5d \to Xe\, 3d^{-1}5d + \gamma(\omega_1)$$
$$+ \gamma(\omega_0') \to 2p^{-1}6d \to 3d^{-1}6d + \gamma(\omega_1')$$

$$\frac{d\sigma(\omega_0)}{d\Omega\, d\omega_1} = \alpha^4 \left(\frac{\omega_1}{\omega_0}\right) \frac{|\langle J|\vec{p}\cdot\hat{\varepsilon}^{1*}|F\rangle|^2 |\langle F|\vec{p}\cdot\hat{\varepsilon}^{0}|I\rangle|^2}{(E_F - E_I - \omega_0)^2 + \Gamma_F^2/4} \delta(\omega_1 + E_J - \omega_0 - E_I)$$

RESONANTNI PRISPEVEK RIXS

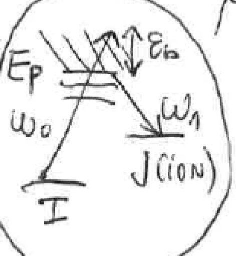



■ PRI ABSORPCIJI FOTONA LAHKO PRIDE DO IONIZACIJE ATOMA,

$|F\rangle = |e, \varepsilon_b\rangle \cdot |F(ion)\rangle$

KO JE $\omega_0 \gtrsim E_P$. EMISIJA TEDAJ POTEČE V IONU Z VRZELJO V NOTRANJI LUPINI

$$Xe + \gamma(\omega_0) \to Xe^+ 2p^{-1} + e(\varepsilon_b)$$
$$\hookrightarrow Xe^+ 3d^{-1} + \gamma(\omega_1)$$




$$\frac{d\sigma(\omega_0)}{d\Omega\, d\omega_1} = \alpha^4 \left(\frac{\omega_1}{\omega_0}\right) \sum_{j_B} \int \frac{|\langle J(ion)|\vec{p}\cdot\hat{\varepsilon}^{1*}|F(ion)\rangle|^2 |\langle F(ion)\, e\varepsilon_b j_b|\vec{p}\cdot\hat{\varepsilon}^{0}|I\rangle|^2}{(\underbrace{E_P + \varepsilon_b}_{E_F} - E_I - \omega_0)^2 + \Gamma_{F\,ion}^2/4} d\varepsilon_b$$
$$\times\, \delta(E_{J(ion)} - E_I + \varepsilon_b + \omega_1 - \omega_0)$$

KONTINUUMSKI PRISPEVEK RIXS

DEJSTVO, DA TUDI KONČNO STANJE $|J\rangle$ PO EMISIJI TUDI NAJVEČKRAT NI STABILNO, UPOŠTEVAMO TAKO, DA

$$\delta(\omega_1+E_J-\omega_0-E_I) \rightarrow \frac{\Gamma_J/2\pi}{(\omega_1+E_J-\omega_0-E_I)^2+\frac{\Gamma_J^2}{4}}$$

RIXS K-H FORMULA:

$\sum_i \vec{r}_i$

$$\frac{d^2\sigma(\omega_0)}{d\Omega_1\, d\omega_1} = \alpha^4\left(\frac{\omega_1}{\omega_0}\right)\Bigg[\boxed{\sum_J\sum_F \frac{(E_J-E_F)^2\,|\langle J|\vec{r}\cdot\hat{\varepsilon}^{1*}|F\rangle|^2\,(E_F-E_I)^2\,|\langle F|\vec{r}\,\hat{\varepsilon}^0|I\rangle|^2}{(E_F-E_I-\omega_0)^2+\Gamma_F^2/4}}$$

RESONANTNI RIXS

RAMANOV EFEKT

$$+\boxed{\sum_{jB}\int_0^\infty d\varepsilon_B\, \frac{(E_J(ion)-E_F(ion))^2\,|\langle J(ion)|\vec{r}\cdot\hat{\varepsilon}^{1*}|F(ion)\rangle|^2\,(E_F-E_I)^2\,|\langle F(ion)\,e\varepsilon_b j_b|\vec{r}\cdot\hat{\varepsilon}^0|I\rangle|^2}{(E_p+\varepsilon_b-E_I-\omega_0)^2+\Gamma_{F\,ion}^2/4}}\Bigg]$$

KONTINUUMSKI RIXS

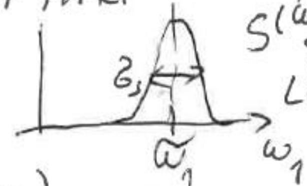
$$\times \frac{\Gamma_J/2\pi}{(\omega_1+E_J-\omega_0-E_I)^2+\frac{\Gamma_J^2}{4}} \qquad \times \frac{\Gamma_J(ion)/2\pi}{(E_J(ion)-E_I+\varepsilon_b+\omega_1-\omega_0)^2+\frac{\Gamma_J^2}{4}}$$

GLADEK, NI RESONANTNE STRUKTURE

MULTIPLIES RESONANT PART
CHANGING $\omega_0$ CAUSES CHANGE OF $\omega_1$ FOR THE SAME AMOUNT
RAMAN EFECT

ENTERS THE INTEGRAL IN NON RESONANT PART

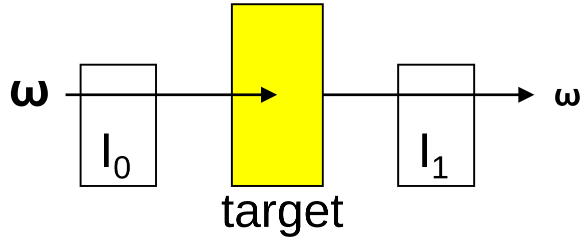
EKSPERIMENTALNA RAZŠIRITEV:


$$\frac{d^2\sigma(\omega_0)}{d\Omega_1\, d\omega_1} \rightarrow \frac{d^2\sigma(\tilde{\omega}_0)}{d\Omega_1\, d\tilde{\omega}_1} = \int d\omega_0\, \frac{dP(\tilde{\omega}_0;\omega_0)}{d\omega_0}\int d\omega_1\, \frac{dS(\tilde{\omega}_1;\omega_1)}{d\omega_1}\,\frac{\partial^2\sigma(\omega_0)}{d\Omega_1\, d\omega_1}$$

## Fotoabsorpcija:

$$A(\Gamma_0) + \omega(\sigma_p) \longrightarrow A^*(\Gamma_i)$$




Meritev prepuščenega fotonskega toka v odvisnosti od **$\omega$** podaja informacijo o fotoabsorpcijskem preseku tarče.Ker je življenski čas začetnega stanja 1/$\boldsymbol{\Gamma_0} \sim \infty$**,** so spektralne strukture razširjene kot $\boldsymbol{\sigma_p + \Gamma_i}$ , kjer je $\boldsymbol{\sigma_p}$ spektralna razširitev vpadne svetlobe in **1/$\boldsymbol{\Gamma_i}$** življenski čas vzbujenega stanja

## Neelastično sipanje fotonov:

N: Nonresonantno (fotoionizaciji sledi emisija):

- $A(\Gamma_0) + \omega(\sigma_p) \longrightarrow A^+(\Gamma_i) + e^-$ **(elektron ni detektiran)**

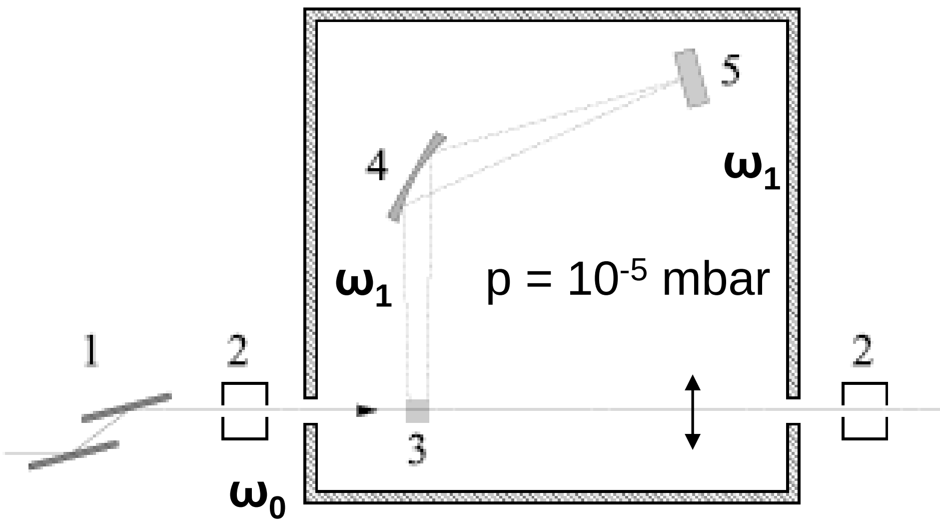
  $\hookrightarrow A'(\Gamma_f) + \omega'(\sigma_s)$

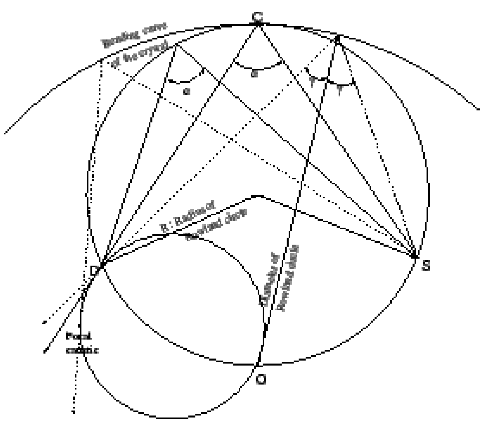
- R: Resonant (photon in – photon out):

$$A(\Gamma_0) + \omega(\sigma_p) \longrightarrow A^*(\Gamma_i) \longrightarrow A'(\Gamma_f) + \omega'(\sigma_s)$$

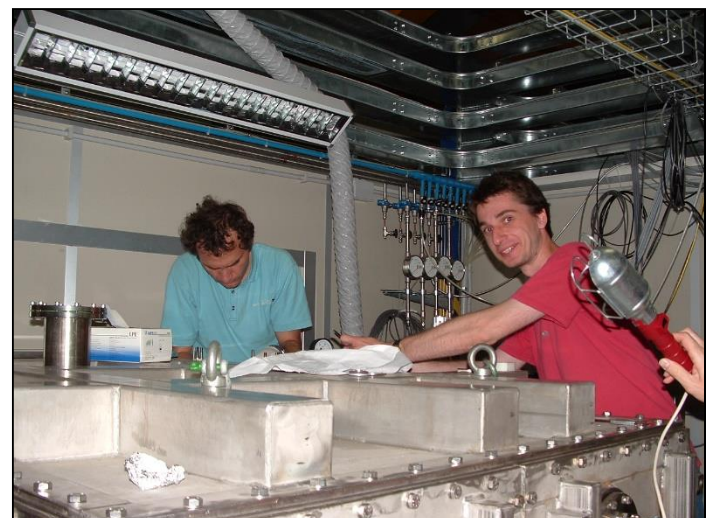
Merimo spekter izsevanih fotonov $\boldsymbol{\omega}_1$ pri dani energiji vpadnih fotonov $\boldsymbol{\omega_0}$**.** V **neresonantnem primeru** je razširitev spektralnih črt $\boldsymbol{\sigma_s + \Gamma_i + \Gamma_f}$, v **resonantnem** primeru pa $\boldsymbol{\Gamma \sim \sigma_p + \sigma_s + \Gamma_f}$ **.** Razširitev po vmesnem vzbujenem stanju odpade zaradi ohranitve energije in prav zato se tudi resonančne spektralne črte premikajo enako kot vpadna energija $\boldsymbol{\omega_0}$ (Cu – P. Eisenberger et al PRL 36, 1976).

# High resolution X - ray spectrometer @ JSI

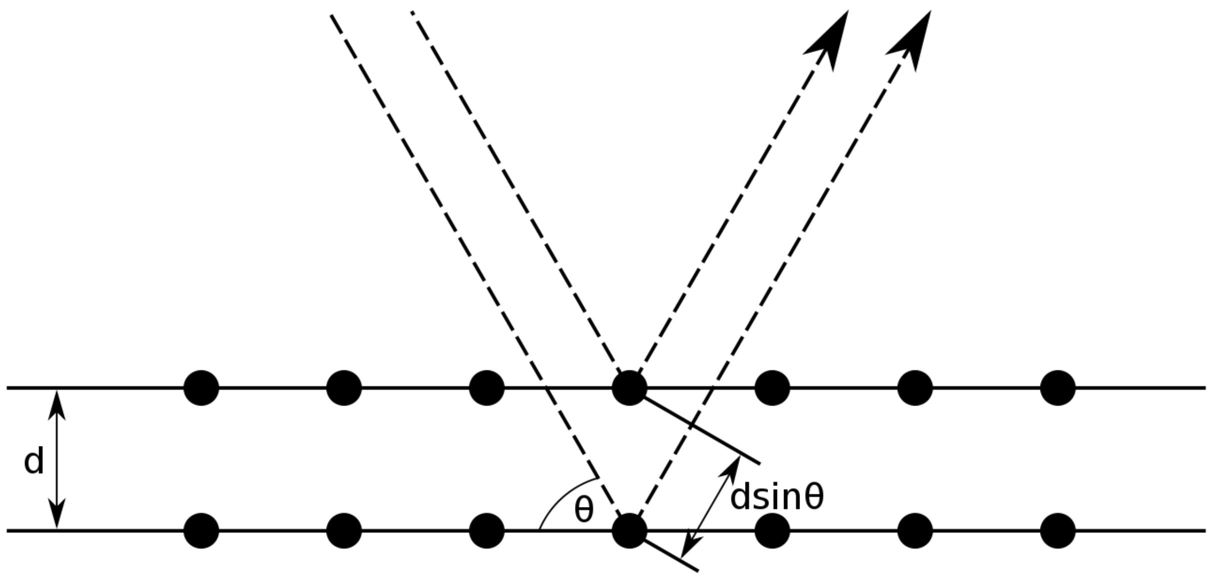


1 – beamline monochromator
2 – ionization cell
3 – gas cell
4 – curved crystal:
quartz (10-10) or Si(111)
Rowland radius = 500 mm
Johansson geometry
5 – CCD camera
770 x 1153 pixels
(22.5 x 22.5 μm$^2$)

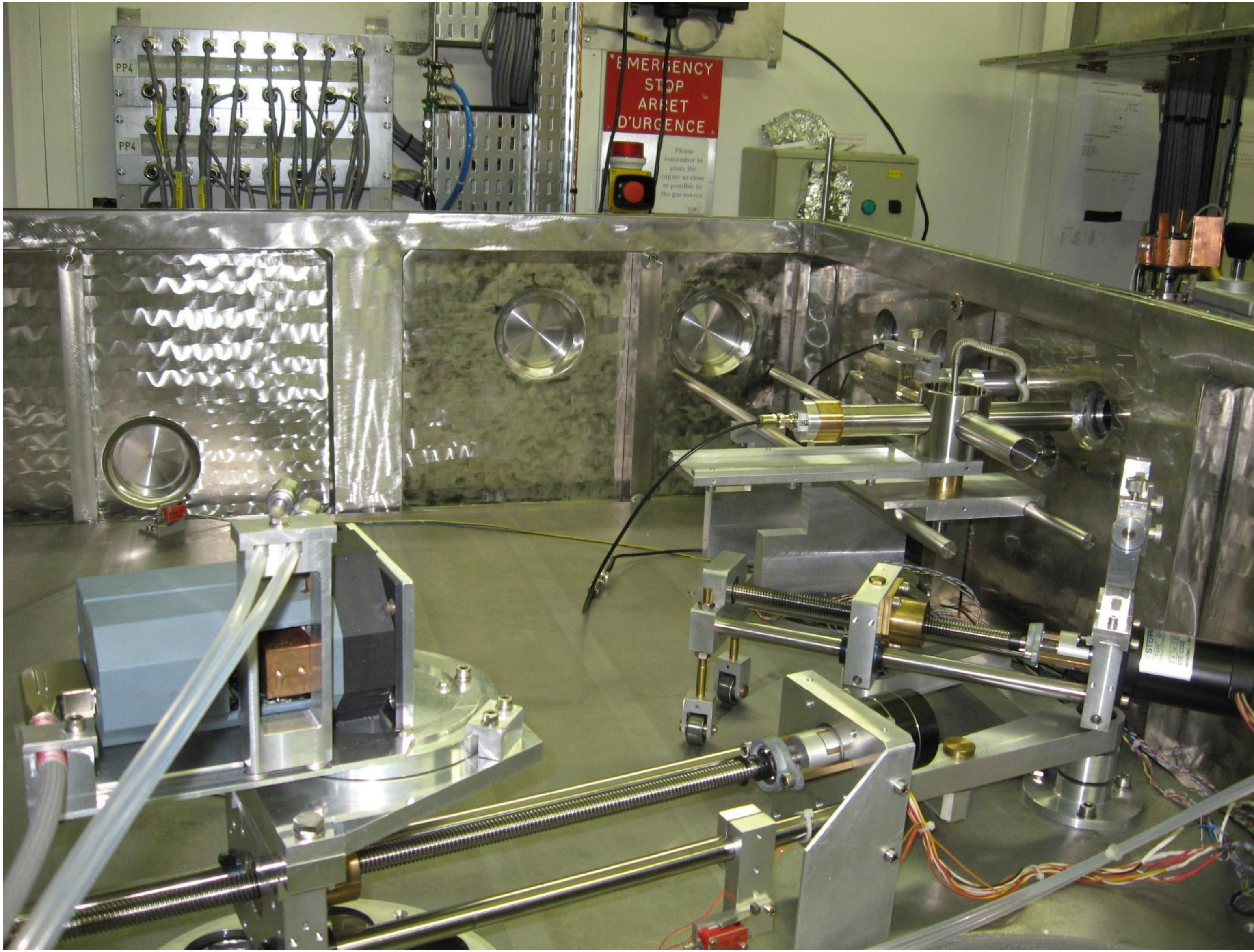


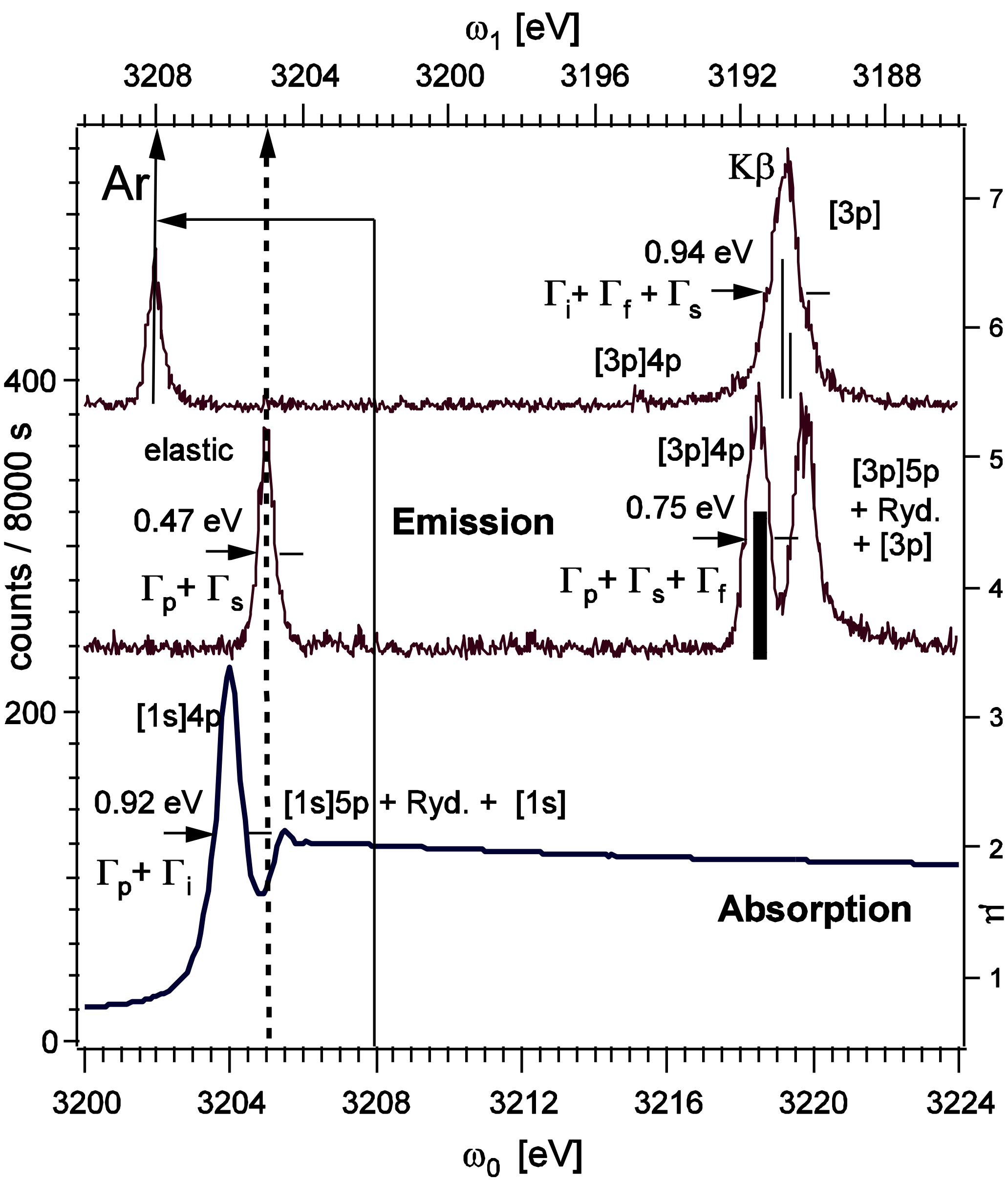
BM XAFS, Elettra, ≈ $10^{10}$ photons/s

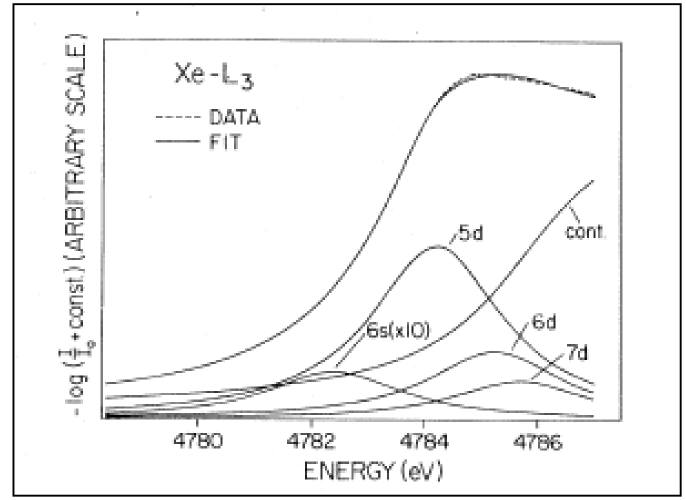



**Braggov pogoj**

$$\mathbf{2d\ Sin\ \theta = N\ \lambda}$$


PP4
PP4
EMERGENCY
STOP
ARRET
D'URGENCE
Please remember to place the captor as close as possible to the gas source



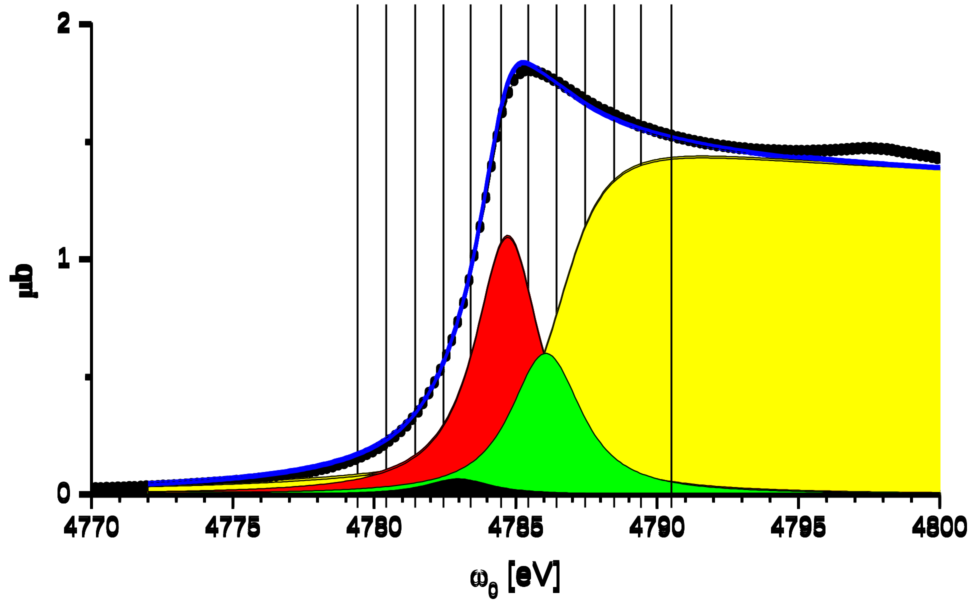




M. Breinig et al, PRA 22 1980

Scan over $L_3$ edge of Xe

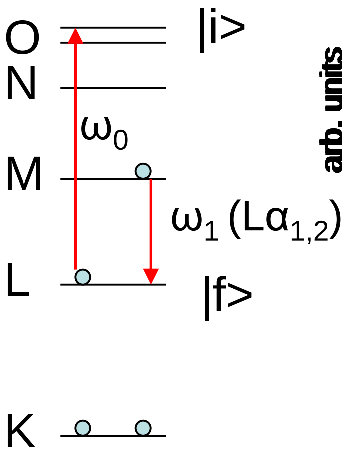
$$Xe+\omega_0 \rightarrow [2p_{3/2}]R$$
$$\downarrow$$
$$[3d_{5/2,3/2}]R+\omega_1$$

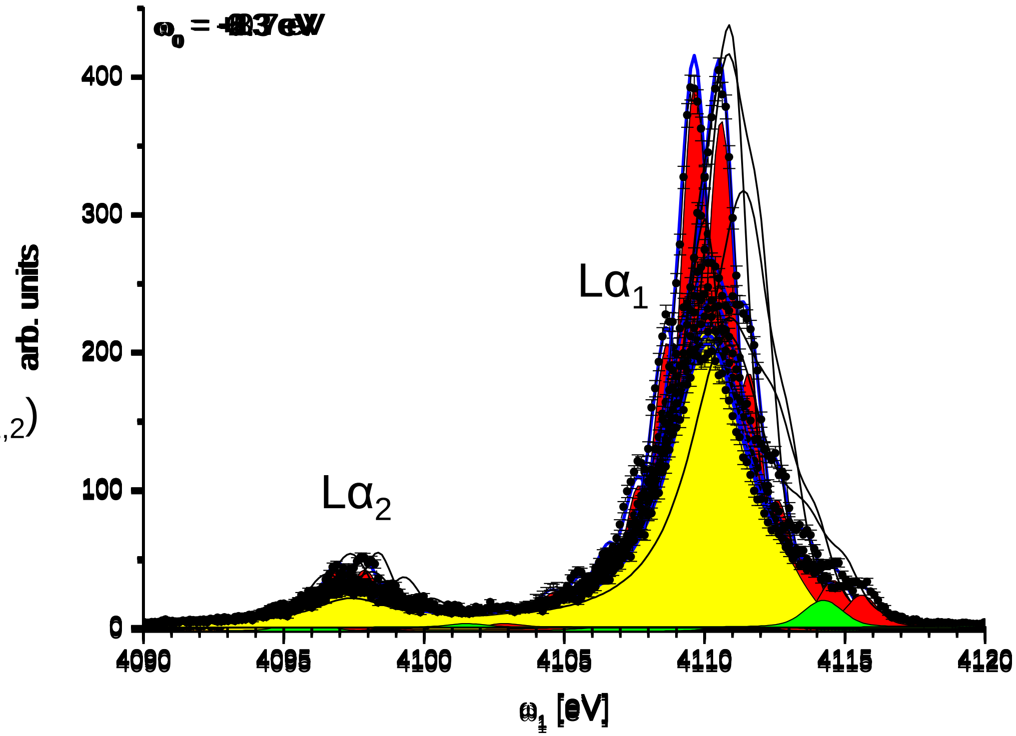
$\Gamma_i$ = 2.6 eV
$\Gamma_f$ = 0.5 eV
$2.35\sigma_p$ ~ 0.65 eV
$2.35\sigma_s$ ~ 0.73 eV




$\Gamma$ = 3.1 eV

- [2p]6s
- [2p]5d
- [2p]≥6d
- [2p]
- model




$\Gamma_{R/N}$ =1.0/3.3 eV

**PHOTON YIELD : resonant terms + nonresonant terms**

$$I(\omega_0,\omega_1)=\sum_{i,f} I_{if}(\omega_0,\omega_1)+\sum_{F} I_{IF}(\omega_0,\omega_1)$$

**Parametrization is based on the Kramers-Heisenberg formula:**

emission strength (dipole matrix elements <fIDIi>, <iIDIg>, angular factors)

instrumental widths

intermediate state energy

$$f_{0if}\iint d\omega d\omega'\Big[\frac{\omega}{\omega'}\exp[-\frac{(\omega-\omega_0)^2}{2\sigma_p^2}-\frac{(\omega'-\omega_1)^2}{2\sigma_s^2}]$$
$$\times[(E_i-E_0-\omega)^2+\Gamma_i^2/4]^{-1}$$
$$\times[(E_f-E_0-\omega+\omega')^2+\Gamma_f^2/4]^{-1}\Big].$$

intermediate state linewidth

final state energy

final state linewidth

emission strength density at threshold

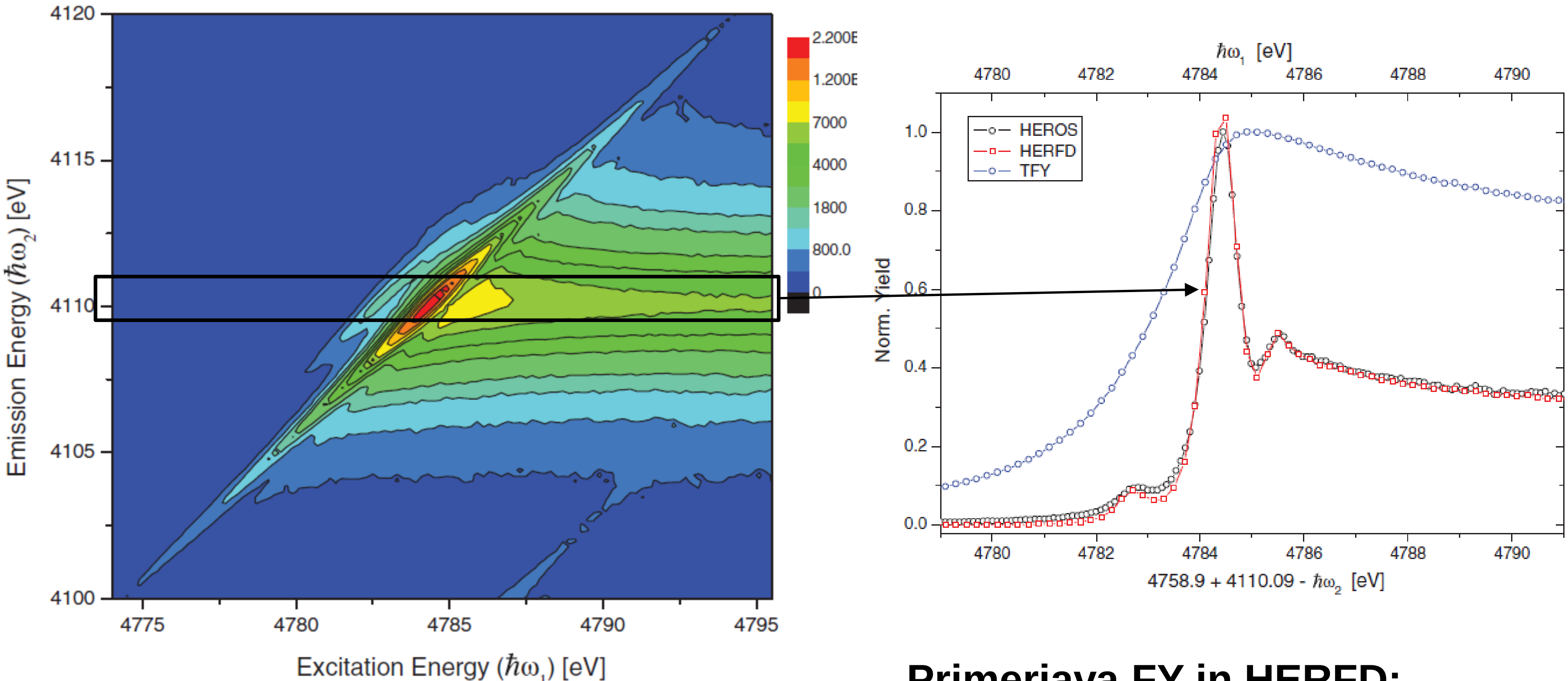
$$\left(\frac{\partial f}{\partial\epsilon}\right)_{0IF0}\iint d\omega d\omega'\left[\frac{\omega}{\omega'}\exp[-\frac{(\omega-\omega_0)^2}{2\sigma_p^2}-\frac{(\omega'-\omega_1)^2}{2\sigma_s^2}]\right.$$
$$\left.\times K(E_0,E_I,E_F,\omega,\omega')\right],$$

integration over the ejected electron energy

threshold energy

$$K=\int_0^{\epsilon_\infty}d\epsilon\Big[\left(\frac{1+a\epsilon}{1+b\epsilon}\right)[(E_I+\epsilon-E_0-\omega)^2+\Gamma_I^2/4]^{-1}$$
$$\times[(E_F-E_0+\epsilon+\omega'-\omega)^2+\Gamma_F^2/4]^{-1}\Big]$$

# Xe La RIXS




**Spektralni zemljevid $Y(\omega_0,\omega_1)$**

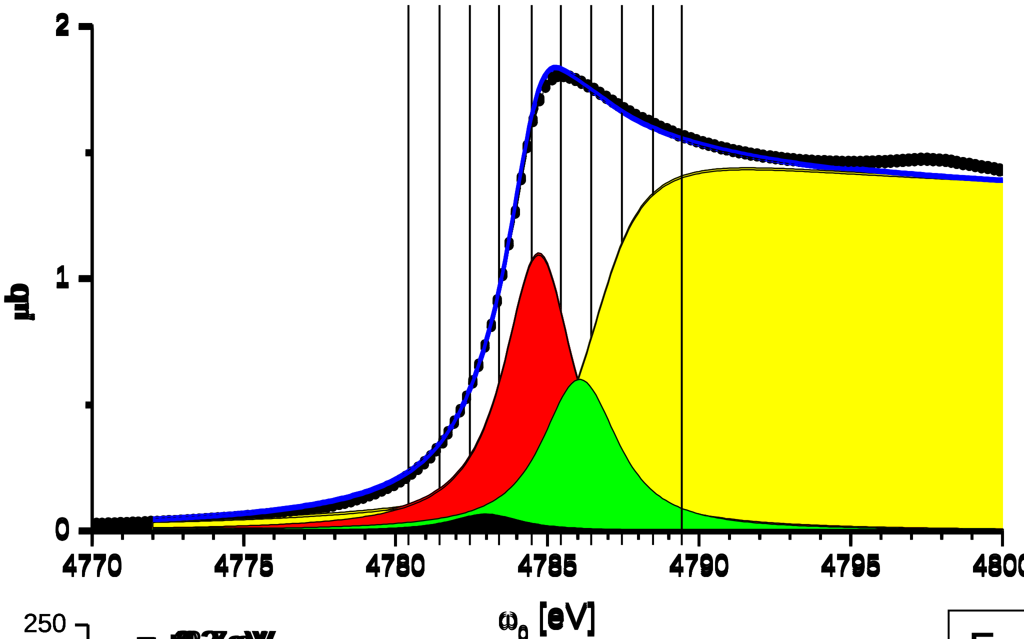
**Primerjava FY in HERFD: Izboljšana ločljivost na robu glede na absorpcijsko meritev**

Scan over $L_3$ edge of Xe

$Xe+\omega_0 \longrightarrow [2p_{3/2}]R$

$\downarrow$

$[4d_{5/2,3/2}]R+\omega_1$




$\Gamma_i = 2.6$ eV

$\Gamma_f = 0.1$ eV

$2.35\sigma_p \sim 0.65$ eV

$2.35\sigma_s \sim 0.67$ eV

$\Gamma \sim 2.8$ eV

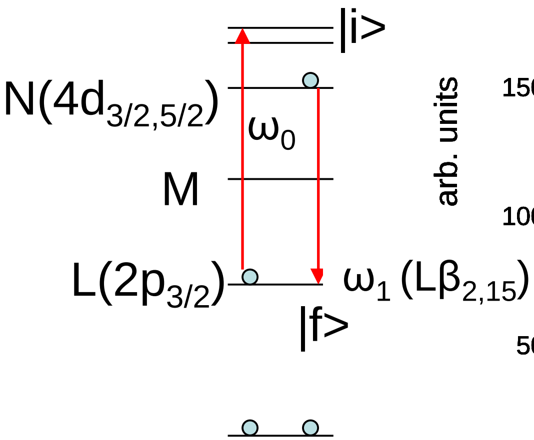
[2p]6s

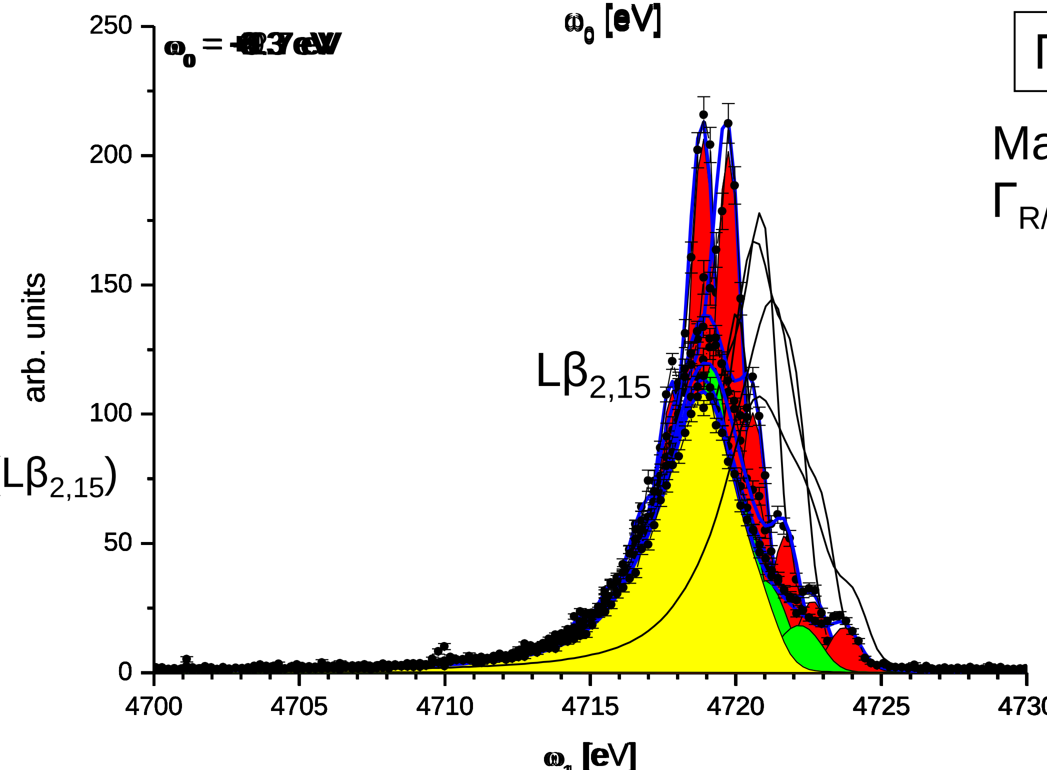
[2p]5d

[2p]≥6d

[2p]

model




$\Gamma_{R/N} \sim 0.94/3.0$ eV

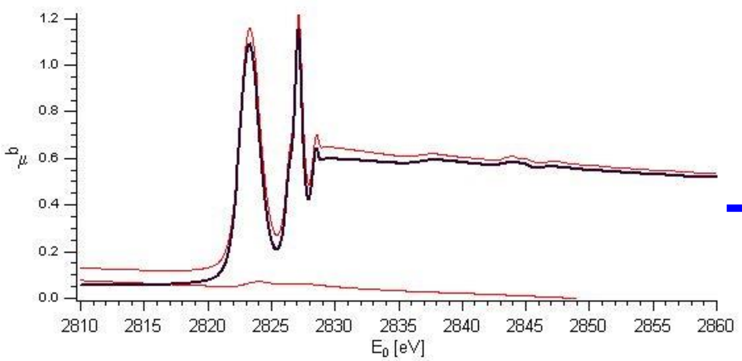
MacDonald et al, 1995

$\Gamma_{R/N} \sim 2.6/3.0$ eV

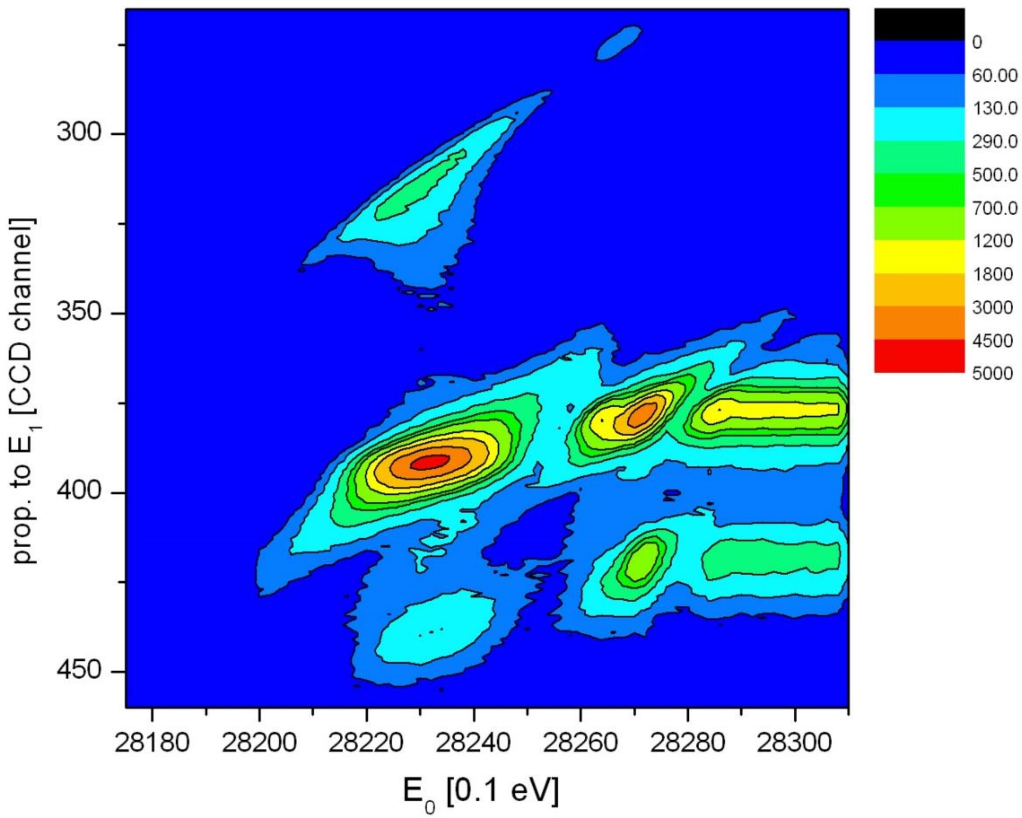
# HCl: Femtosecond nuclear motion probed by resonant X - ray scattering

Uses the concept of an effective duration time of the scattering process to extract temporal dynamics *a posteriori.*

**Abs. Cl K**




**RIXS Cl Kβ**



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# $Na_2MoO_4$

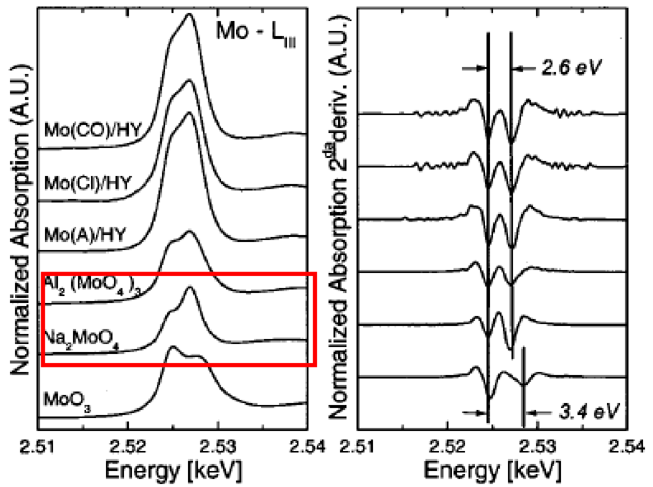
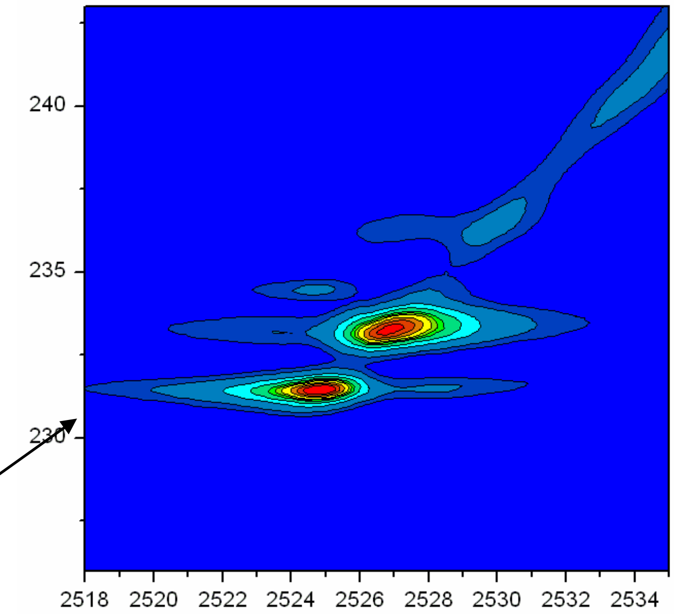
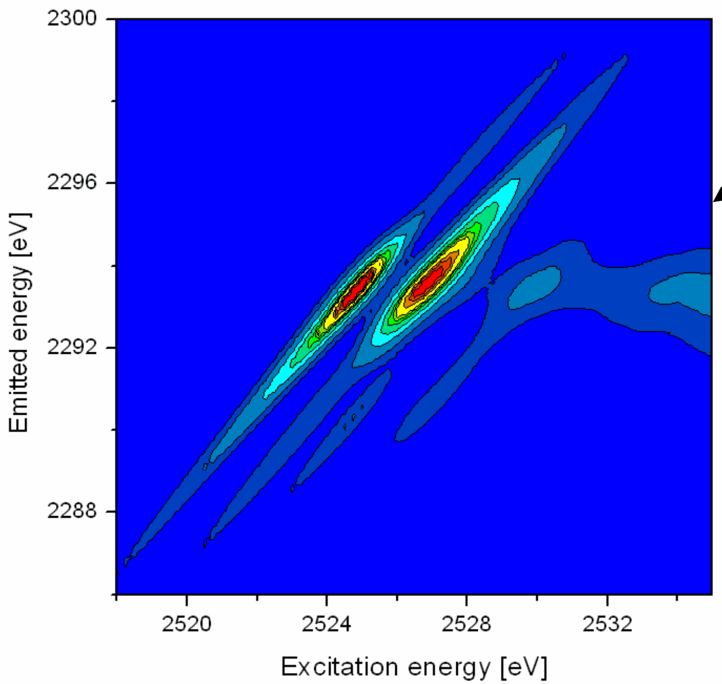



**Figure 2.** Mo $L_{III}$-edge XANES spectra (left) and second-derivative curves (right) for Mo/HY catalysts and reference compounds.

**XANES**




**RIXS:** Mo Lα line




**RIXS:** Mo Lβ lne