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SECOND SCHOOL ON THE USE OF SYNCHROTRON RADIATION IN SCIENCE AND TECHNOLOGY: *"JOHN FUGGLE MEMORIAL"*

25 October - 19 November 1993

Miramare - Trieste, Italy

Photon- Matter Interaction:

Absorption Cross Section

A. Fontaine
L.U.R.E.
Orsay, France

II PHOTON - MATTER INTERACTION: ABSORPTION CROSS SECTION

II.1 HAMILTONIAN (COULOMB GAUGE)

$\vec{\nabla}\cdot\vec{A} = 0$

CHARGED PARTICLES + PHOTON $(\vec{E}, \vec{B})$

$\vec{r}_\alpha$, q_α, m_α — $\vec{A}(\vec{r},t)$

$\vec{p}_\alpha \longrightarrow \frac{\hbar}{i}\vec{\nabla}_\alpha$ — Coulomb $\vec{A}_{//} = 0$

$\vec{A}_\perp(\vec{r},t)$

$$\mathcal{H} = \sum_\alpha \frac{1}{2m_\alpha}\left[\vec{p}_\alpha - q_\alpha \vec{A}(\vec{r}_\alpha)\right]^2 - \sum_\alpha \frac{g_\alpha q_\alpha}{m_\alpha}\vec{S}_\alpha\cdot\vec{B}(\vec{r}_\alpha) + \underbrace{V_{Coul}}_{③} + \underbrace{H_R}_{④}$$

① ②

① Kinetic energy

$$\dot{r}_\alpha = \frac{1}{i\hbar}[\vec{r}_\alpha, H] = \frac{\partial H}{\partial \vec{p}_\alpha} = \frac{1}{m_\alpha}\left[\vec{p}_\alpha - q_\alpha\vec{A}(\vec{r}_\alpha)\right]$$

② Magnetic term (Schrödinger non relativistic: spin = external degree of freedom)

RELATIV. DIRAC EQUATION $[H, \vec{J}] = 0$

③ Coulomb Energy of the system = Σ pair energies

④ Transverse field energy

$$H_R = \frac{\epsilon_0}{2}\int d^3r \left[E_\perp^2(\vec{r}) + c^2 B^2(\vec{r})\right]$$

Quantic $H_R = \sum_j \hbar\omega_j\left(a_j^+ a_j + \tfrac{1}{2}\right)$ a_j^+ a_j — j mode $\vec{k}_j$ $\vec{e}_j$ polar

II·1$_{(7)}$ ORDER of MAGNITUDE of the 3 TERMS

- $H_0 = H_P + H_R$

$$H_P = \sum \frac{p_x^2}{2m_x} + V_{Coulomb}$$

- PERTURBATION W

$$W = H_{I1} + H_{I2}^{S} + H_{I2}$$

$$-\sum_x \frac{q_x}{m_x} \vec{p}\cdot\vec{A} \qquad -\sum_x g_x \frac{q_x}{2m_x} \vec{S}_x \cdot \vec{B} \qquad + \sum_x \frac{q_x^2}{2m_x} \left[\vec{A}(\vec{r}_x)\right]^2$$

- H_0 well. defined eigenstates

H_P includes $V_{Coulomb}$ $\longrightarrow$ VALID for BOUND STATES ATOMS, MOLECULES, SOLID

- $\dfrac{H_{I2}}{H_{I1}} = \dfrac{q^2 A^2/m}{q\, A\, p/m} = \dfrac{q\, A\, p/m}{p^2/2m} \simeq \dfrac{H_{I1}}{H_P} \ll 1$

$$\frac{H_{I_1}^{S}}{H_{I_1}} = \frac{q/m\, \hbar k A}{q/m\, p\, A} \sim \frac{a_{0(1s)}}{\lambda} \ll 1$$

Essential for the following

- R_q — A^2 very weak linear regime $\neq$ laser. $+ \begin{cases} \text{spin } \hbar \\ \vec{B} = \vec{\nabla}_1 \vec{A} \\ \hat{B} = i\vec{k}\vec{A} \end{cases}$

$\Rightarrow$ left with $\sum_x -\frac{q_x}{m_x} \vec{p}\cdot\vec{A}$

#1 INTERACTION

$$\sum_\alpha -\frac{q_\alpha}{m_\alpha}\vec{p}_\alpha \cdot \vec{A}$$

$$\sum_\alpha -\frac{g_\alpha q_\alpha}{2m_\alpha}\vec{s}_\alpha \cdot \vec{B}$$

$$\sum_\alpha \frac{q_\alpha^2}{2m_\alpha}\left[\vec{A}(\vec{r}_\alpha)\right]^2$$

#2 TIME-DEPENDENCE OF THE INTERACTION IS HARMONIC

- $(\vec{r}, t)$ are separated.

ESSENTIAL TO ESTABLISH THE FERMI GOLDEN RULE

#3 THE FERMI GOLDEN RULE GIVES

A TIME-INDEPENDENT RATE OF TRANSITION

Linear regime

$|c_f(t)|^2$ *is weak.*

#4 FINAL STATES (Empty)

- *Tuning the* PHOTON ENERGY.
- *Contain A* CORE HOLE
- VALIDITY *of the* ONE ELECTRON PICTURE ?

#5 = ORDERS of MAGNITUDE of the 3 TERMS of the INTERACTION

II.3.g DIPOLE APPROXIMATION & SELECTION RULES

$$\Gamma_{if} = \frac{2\pi}{\hbar} \left[|\langle f | H_{INT} | i \rangle|^2 \right] \rho(E_f) \, \delta(E_f - E_i - \hbar\omega)$$

NOTE. $\frac{1}{\hbar}$ instead of $\frac{1}{\hbar^2}$ since $\rho(E_f)$ substitutes $\rho(\omega)$

$$H_{INT} \simeq H_{I_1} \simeq -\frac{q}{m} \vec{p} \cdot \vec{A}$$

- Semi classical approximation
  - $\vec{e}$ in matter — QUANTUM MECHANICS
  - Photon — CLASSICAL "

$$\vec{p} \cdot \vec{A} \Leftrightarrow q\vec{R} \cdot \vec{E} = qzE$$

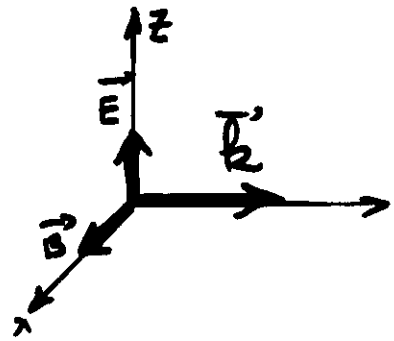
Cohen-Tann. p 1299 T.2.

Linear polarisation

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \vec{\nabla}\chi$$
$$U \rightarrow U' = U - \frac{\partial \chi}{\partial t}$$

$$H_1 = -\frac{q}{m} qz \left[E_0 e^{i(ky - \omega t)} + cc \right]$$

$$= -\frac{q^2}{m} z E_0 \left[e^{iky} e^{-i\omega t} + e^{-iky} e^{i\omega t} \right]$$



- Extension of the core level orbitals $< \lambda$ (photon) $\rightarrow ky < 1$ MULTIPOLAR DEVELOP.

$$e^{iky} = 1 + iky + \cdots$$

DIPOLAR — QUADRIPOLAR.

II.9.5 $E = E_0 \epsilon \, e^{-}$

DIPOLAR : $\vec{r} \cdot \vec{\epsilon}$

QUADRIPOLAR $(\vec{r} \cdot \vec{\epsilon})(\vec{k} \cdot \vec{r})$ — High Z ↓ Imp^t when there is nothing else

K-edge ENERGY		K (1s)	L_I (2s)	L_{II}, L_{III} (2p)	ENERGY
1.5	Al	0.012	0.004	0.001	
9	Cu	0.058	0.026	0.01	
25	Ag	0.152	0.073	0.03	
61	Yb	0.314	0.194	0.06	10, 8.9 keV
81	Au	0.397	0.270	0.084	14.4, 12.7

keV

Quad. / Dipolar

- Selection rules ⇒ dipole-allowed final states.

Matrix element $M = \langle f | z | i \rangle$

$z = R\cos\theta = \sqrt{\frac{4\pi}{3}} \, R \, Y_1^0(\theta,\varphi)$

$M = \int d\Omega \, Y_{l_f}^{m_f *}(\theta,\varphi) \, Y_1^0(\theta) \, Y_{l_i}^{m_i}(\theta,\varphi)$

$\neq 0$ IF

$l_f = l_i \pm 1$

$m_f = m_i + 1, 0, -1$

Remarks

- z is ODD $|i\rangle \not\perp |f\rangle$ different parity
- If $f(r)\,\vec{L}\cdot\vec{S}$ do exist $\vec{J} = \vec{L} + \vec{S}$

Stationnary states l, s, J, m_j

$\Delta J = 0, \pm 1$

$\Delta l = \pm 1$

$\Delta m_j = 0, \pm 1$

Spherical harmonics Composition

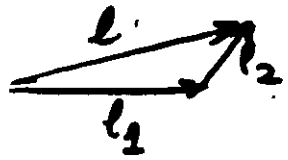
$$Y_{l_1}^{m_1}\, Y_{l_2}^{m_2} = \sum_{l=|l_1-l_2|}^{l=|l_1+l_2|} C_{l_1 m_1}^{l_2 m_2}\, Y_l^{m}$$

with $m = m_1 + m_2$ and $C \neq 0$ if

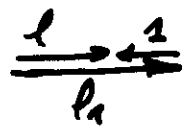
$$l = l_1+l_2,\ l_1+l_2-2,\ l_1+l_2-4,\ \ldots,\ |l_1-l_2|$$

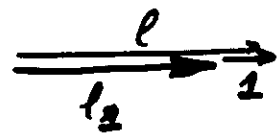
(l, integer)

* TRIANGLE RULE



PRESENT CASE $l_2 = 1$





Therefore M transforms into

$$M = \int d\Omega\ Y_{l_f}^{m_f *} \left[c_1\, Y_{l_i+1}^{m_i \pm 1} + c_2\, Y_{l_i-1}^{m_i \pm 1} \right]$$

$M = 0$ except if $l_f = l_i + 1$ OR $l_f = l_i - 1$

* NOTE #1

C α CLEBSCH-GORDAN COEFF.

development of $|J, M\rangle$ with the $|j_1, m_1, j_2 m_2\rangle$ basis

$$|J, M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \langle j_1, j_2; m_1, m_2 | J, M\rangle\ |j_1, j_2; m_1, m_2\rangle$$

E.9[3]

* NOTE #2

$\vec{R} \cdot \vec{\varepsilon} = z$ is only one simple CASE

$\vec{R} = R_x \vec{u}_x + R_y \vec{u}_y + R_z \vec{u}_z$

$R_x = R \sin\theta \cos\varphi$; $R_y = R \sin\theta \sin\varphi$; $R_z = R\cos\theta$

or

$R^{\pm} = R_x \pm i R_y = R \sin\theta \, e^{\pm i\varphi}$; $R_z = R\cos\theta$

$R_1 = -\frac{R}{\sqrt{2}} \sin\theta \, e^{i\varphi}$; $R_0 = R\cos\theta$, $R_{-1} = \frac{R}{\sqrt{2}} \sin\theta \, e^{-i\varphi}$

CIRCULAR POLARISATION

$\Delta\ell = \pm 1$
$\Delta j = \pm 1$
$\Delta s = 0$
→ $\Delta m = \pm 1$

LINEAR POLARISATION

$\Delta\ell = \pm 1$
$\Delta j = \pm 1$
$\Delta s = 0$
→ $\Delta m = 0$

II . 10₄ ABSORPTION COEFFICIENT μ and TRANSITION RATE given by the FERMI GOLDEN RULE (DIPOLAR APPROXIMATION)

$$\Gamma_{if} = \frac{2\pi}{\hbar \cdot 2^2} \left| \langle f | e z E_0 | i \rangle \right|^2 \rho(E_f)$$

$\cos \omega t = \frac{e^{i\omega t} + e^{-i\omega t}}{2}$ $\qquad E_f = E_i + \hbar\omega$

- Energy absorbed from the EM wave / volume unit / time unit

$$\frac{dU}{dt} = \hbar\omega \Gamma_{if} N_a$$

N_a number of atoms / volume unit

- Energy density of the E.M. wave

$$U = E_0^2 / 8\pi$$

- EM velocity : $c \longrightarrow dx = c\,dt$

$$\frac{dU}{dx} = (-) \frac{4\pi^2 \omega e^2}{c} N_a U \left| \langle f | z | i \rangle \right|^2 \rho(E_f)$$

$$\frac{dU}{dx} = -\mu U$$

$$\mu = \frac{4\pi^2 \omega e^2}{c} N_a \left| \langle f | z | i \rangle \right|^2 \rho(E_f)$$

II.M 5

SUMMARY

④ INTERACTION DIPOLAR ELECTRIC

and SOMETIMES QUADRIPOLAR

⑧ XAS Atom-selective
PDOS - selective

© XAS POLARISATION-DEPENDENT

Molecule on surface

MAGNETISM

Ⓓ STUCK with the ONE ELECTRON PICTURE

MANY BODY PROBLEMS NEED EXTRA INGREDIENT

& CORE HOLE
PHOTON ELECTRON in THE FINAL STATE

Ⓔ ∫ XAS / FERMI G.R. 4 TOOLS

a/ Atomic Selectivity
b/ PDOS Selectivity
c/ Symmetry-Sensitivity
d/ Core-hole-induced relaxation

Ⓕ INITIAL STATE (one elect. picture) is VERY SIMPLE

AT THE OPPOSITE of VISIBLE LIGHT ABSORPTION

The x-ray absorption cross-section

- Hamiltonian for the interaction of light with matter

$$\mathcal{H}=(1/2m)[-i\hbar\vec{\nabla}-q\vec{A}]^2+V(\vec{r})-(gq/2m)\vec{s}.\vec{B}+H_R$$

The non-linear term is negligible

$$\frac{H_{I2}}{H_{I1}}\sim\frac{|q^2A^2/2m|}{|\hbar q\vec{A}.\vec{\nabla}/m|}\sim 10^{-4}\sim\frac{qAp/m}{p^2/m}\simeq\frac{H_{I1}}{H_0}\simeq\frac{a^{eff}}{\lambda}$$

Vector potential of a plane wave

$$\vec{A}(\vec{r},t)=\mathrm{Re}\{A_0\,\hat{\varepsilon}\exp[i(\vec{k}.\vec{r}-\omega t)]\}$$

- **The Golden Rule**

$$\sigma=(2\pi/\hbar)\sum_f|\langle f|W|i\rangle|^2\delta(E_f-E_i-\hbar\omega)$$

Expansion up to the electric quadrupole term $\lambda \gg a_0^{eff}$

$$\exp[i(\vec{k}.\vec{r})]\simeq 1+i\vec{k}.\vec{r}$$

Absorption cross-section including electric dipole and quadrupole contributions

Dipolar

$$\sigma(\omega)=4\pi^2\alpha\hbar\omega\{\sum_f\underline{|\langle f|\hat{\varepsilon}.\vec{r}|i\rangle|^2}\delta(E_f-E_i-\hbar\omega)$$

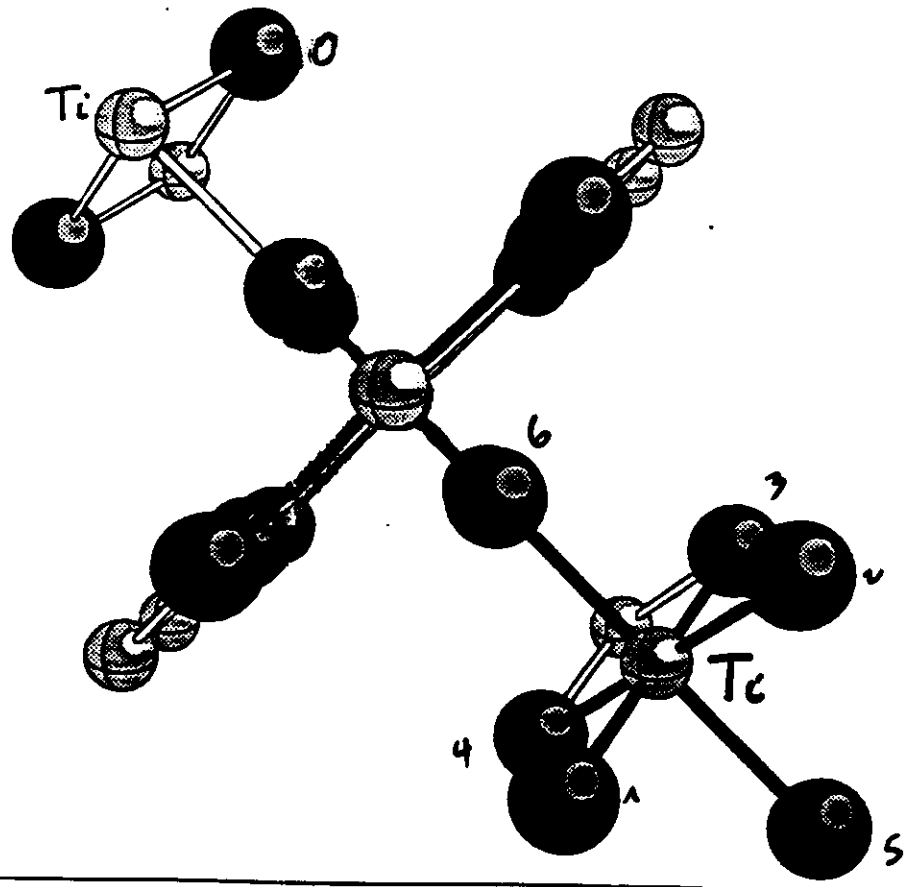
$$+\sum_f(1/4)\underline{|\langle f|\hat{\varepsilon}.\vec{r}\,\vec{k}.\vec{r}\,|i\rangle|^2}\}\delta(E_f-E_i-\hbar\omega)$$

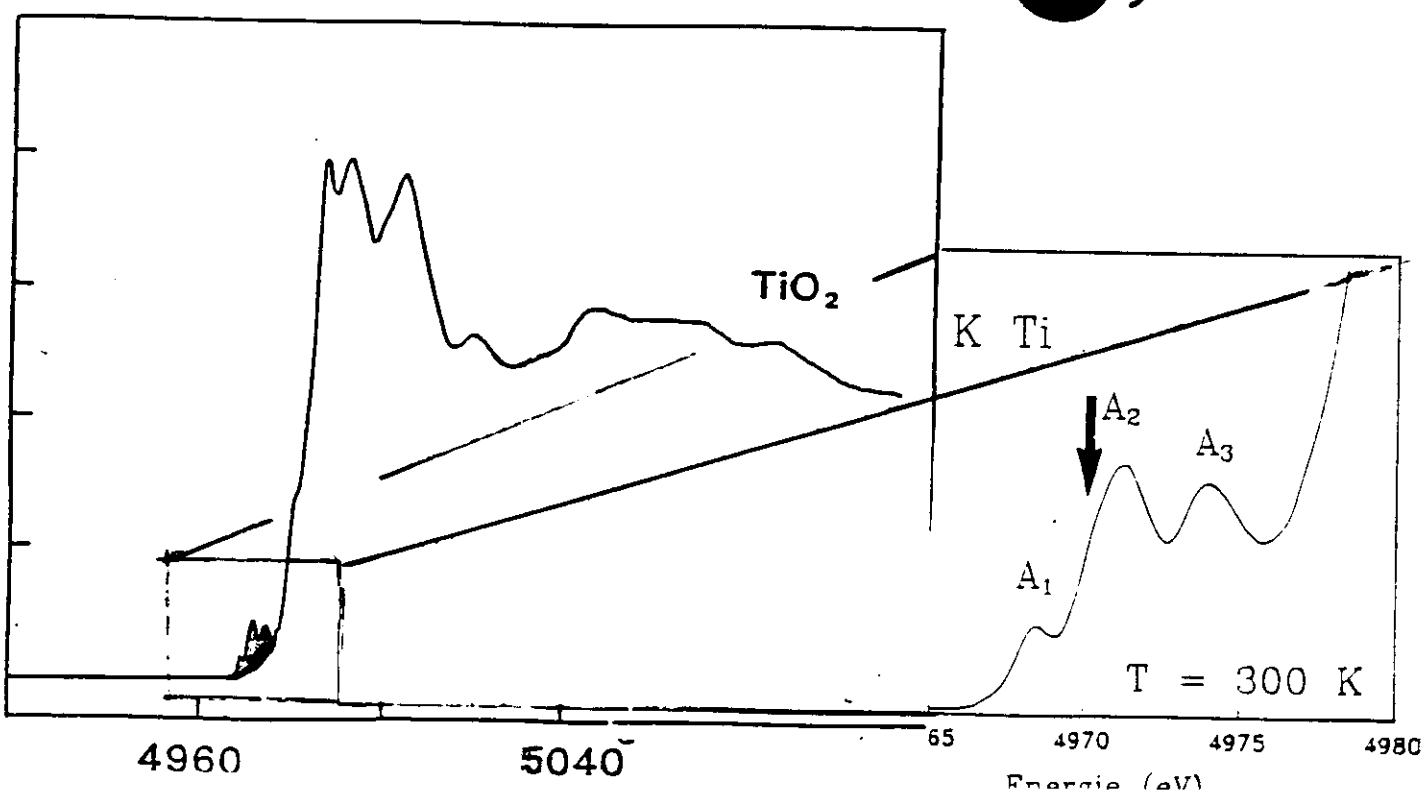
Quadrupolar < Dipolar

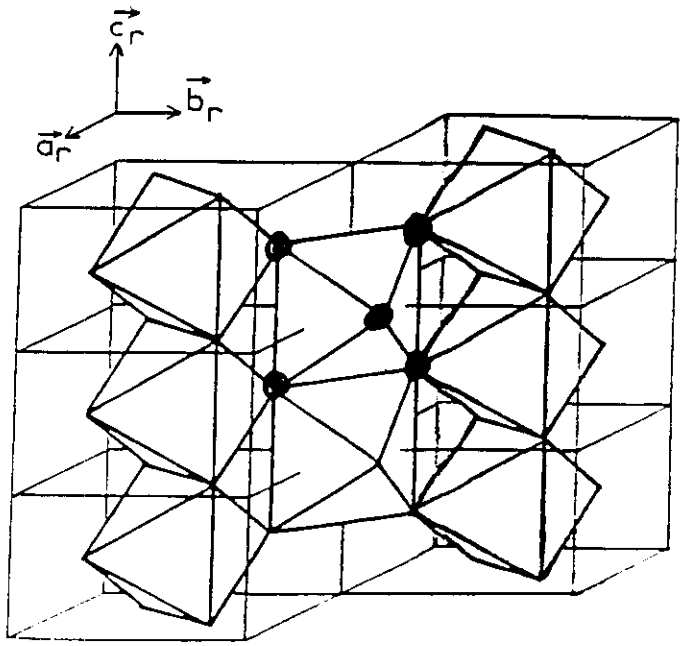
$\Delta\ell=\pm 2$. $\Delta\ell=\pm 1$

parity

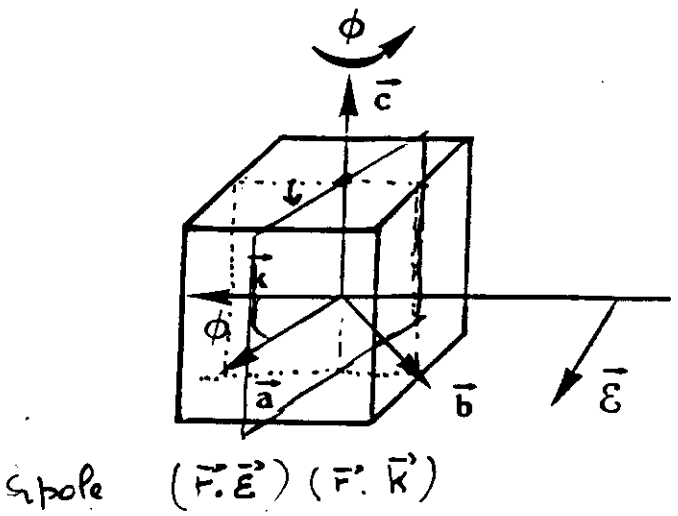
Quadrupole transitions : the mystery of the pre-edge peaks in TiO_2 K-absorption spectrum.

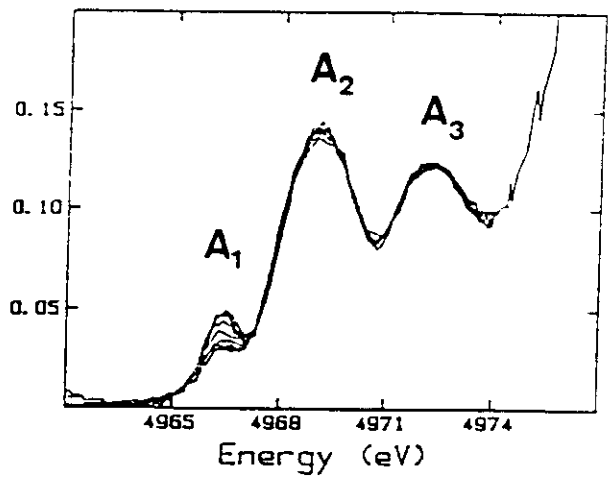






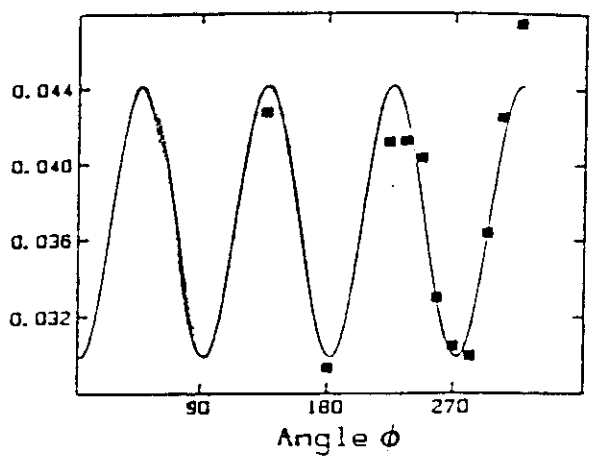
Apex
chain to chain
Side within chain





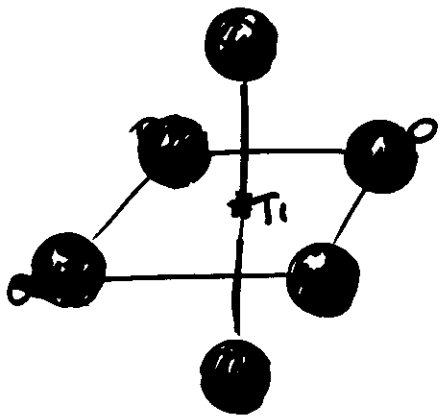
S pole $(\vec{F}.\vec{\varepsilon})(\vec{F}.\vec{k})$

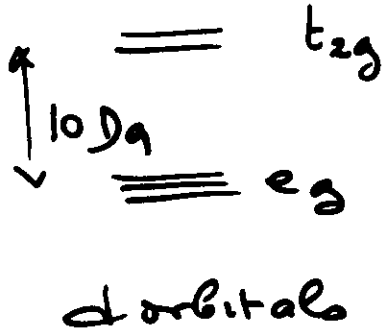
Figure 10: Spectres de TiO_2 pour différents angles (C. Brouder [29]).

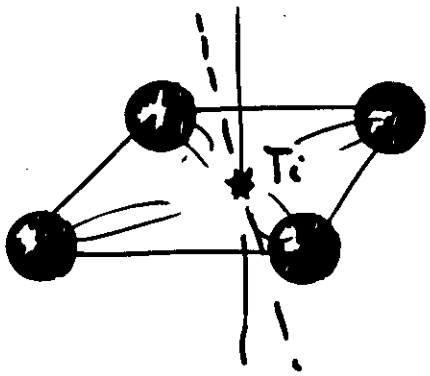


.12 Evidence of core-hole induced relaxation

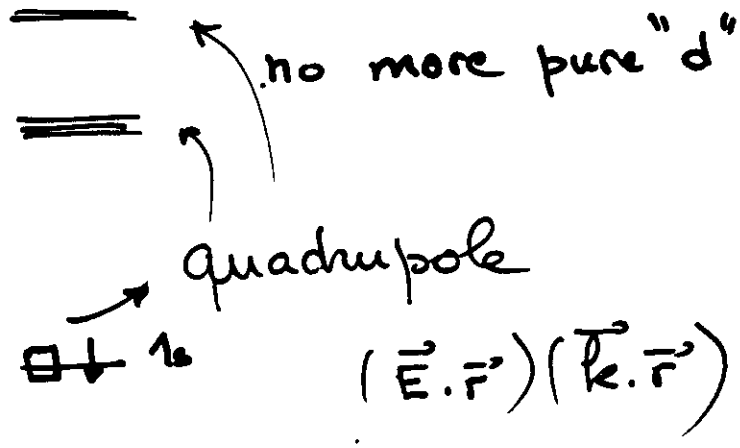
TiO_2 $\quad Ti^{IV}$ $\quad 3d^0$

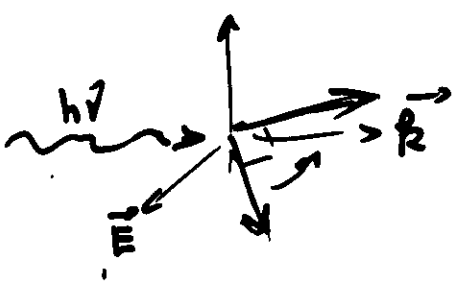


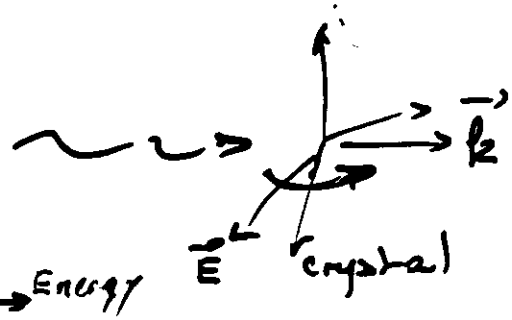




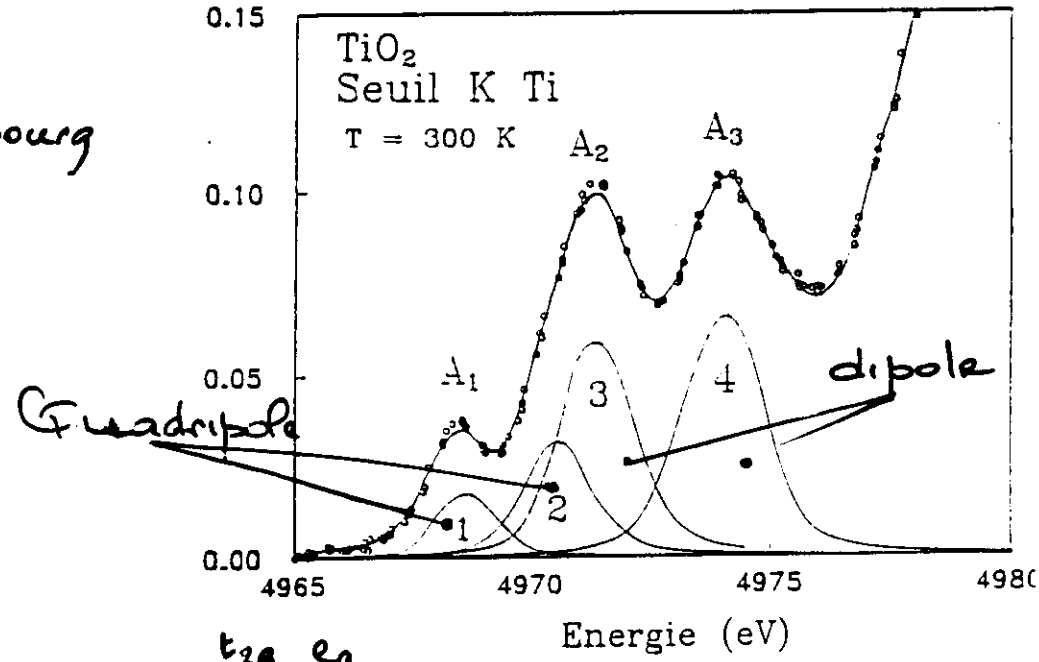
d & p orbitals hybridize

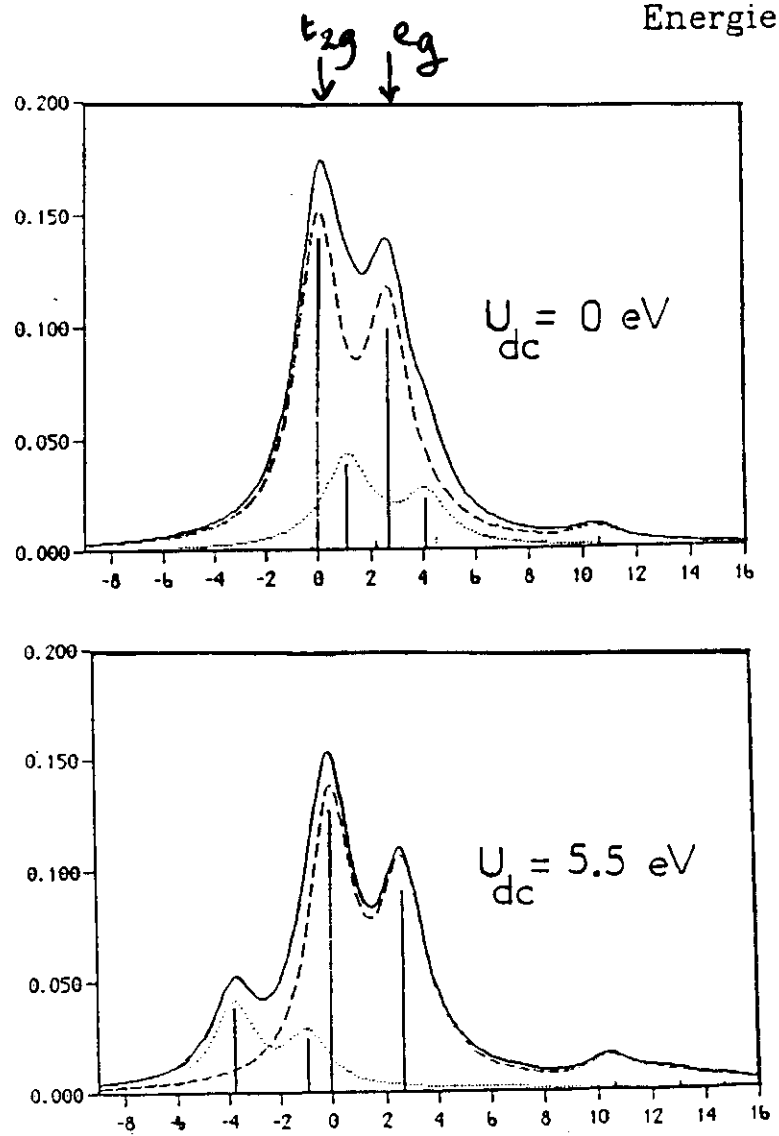






BIROUDER
BEAUREPAIRE
DURMEYER
KAPPLER
IPCM Strasbourg





KOTANI

Figure 13: Spectre d'absorption au seuil K du Ti calculé. Décomposition des transitions dipolaires (tirets) et quadrupolaires