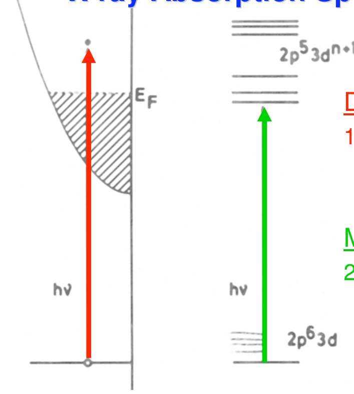
X-ray absorption

Excitation of core electrons to empty states.

Spectrum given by the **Fermi Golden Rule**

$$I_{XAS} \sim \Sigma_f \left| \left\langle \Phi_f \left| \hat{e} \cdot r \right| \Phi_i \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray Absorption Spectroscopy



DFT:
1s edges

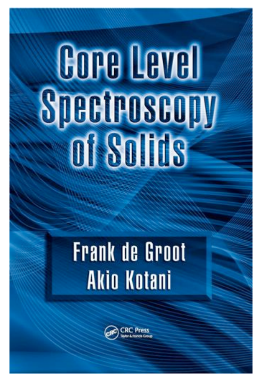
Multiplets:
2p, 3s, 3p edges

Charge Transfer Multiplet program

Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

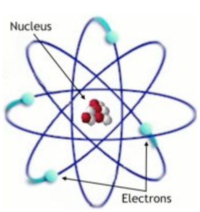
ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS



Atomic Multiplet Theory

HΨ=EΨ

$$H = \sum_N \frac{p_i^2}{2m} + \sum_N \frac{-Ze^2}{r_i} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

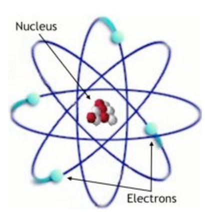


- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

Atomic Multiplet Theory

HΨ=EΨ

$$H = \sum_N \cancel{\frac{p_i^2}{2m}} + \sum_N \cancel{\frac{-Ze^2}{r_i}} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$



- Kinetic Energy
- Nuclear Energy
- Electron-electron interaction
- Spin-orbit coupling

Atomic Multiplet Theory

$$H = \sum_N \cancel{\frac{p_i^2}{2m}} + \sum_N \cancel{\frac{-Ze^2}{r_i}} + \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

$$H'_{ee} = H_{ee} - \langle H_{ee} \rangle = \sum_{pairs} \frac{e^2}{r_{ij}} - \left\langle \sum_{pairs} \frac{e^2}{r_{ij}} \right\rangle$$

Atomic Multiplet Theory

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Electron Correlation of Valence States

$$\frac{e^2}{r_{12}} \equiv \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = 4\pi e^2 \sum_{k=0}^{\infty} \frac{1}{2k+1} \frac{r_<^k}{r_>^{k+1}} \mathbf{Y}_1^{(k)} \cdot \mathbf{Y}_2^{(k)}.$$

$$E_C = \left\langle l_1 l_2 LS \left| \frac{e^2}{r_{12}} \right| l_1 l_2 LS \right\rangle = \sum_k (f_k F^k \pm g_k G^k)$$

Weissbluth, Atoms & Molecules, chapter 21

Atomic Multiplet Theory

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k$$

Electron Correlation of Valence States

$$H_{ATOM} = \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Valence Spin-orbit coupling

Atomic Multiplet Theory

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

Core Valence Overlap

$$H_{ATOM} = \sum_{pairs} \frac{e^2}{r_{ij}} + \sum_N \zeta(r_i)\, l_i \cdot s_i$$

Core Spin-orbit coupling

Multiplet Effects

1s	2s	2p	3s	3p
0.07	**5**	**8**	**13**	**17**
	Core Valence Overlap			
0	**0**	**17**	**0**	**2**
	Core Spin-orbit coupling			

Term Symbols (LS)

${}^{2S+1}L$

L Azimuthal quantum number

$L = |l_1 - l_2|, |l_1 - l_2 + 1|, \ldots l_1 + l_2$ 3d: $l=2$ 3d^2: $L=0,1,2,3,4$

S Spin quantum number

$S = |s_1 - s_2|, |s_1 - s_2 + 1|, \ldots s_1 + s_2$ 3d: $s=1/2$ 3d^2: $S=0,1$

m_L magnetic quantum number

$m_L = -L, L+1, \ldots L$ 3d: $m_l = 2,1,0,-1,-2$

m_S spin magnetic quantum number

$m_S = -S, S+1, \ldots, S$ 3d: $m_s = 1/2, -1/2$ (↑,↓)

Term Symbols (LSJ)

$^{2S+1}L_J$

J Spin quantum number

J= |L-S|, |L-S+1|, …, L+S   3d: j=3/2,5/2 $3d^2$: j=0,1,2,3,4

m_J total magnetic quantum number

m_J=-J, J+1, …J

$3d_{5/2}$: m_j=5/2,3/2,1/2,-1/2,-3/2,-5/2

Term Symbols

- **Term symbols of a $1s^1 2s^1$ configuration**
- $1s^1$ → $^2S_{1/2}$ (S=1/2, L=0, J=1/2)
- $2s^1$ → $^2S_{1/2}$ (S=1/2, L=0, J=1/2)
- $1s^1\ 2s^1$ → S_{TOT} = 0 or 1
  → L_{TOT} = 0
  → $^1S_0$ + $^3S_1$
  [Σ(2J+1)=1+3=4]

Term Symbols

- **Term symbols of a $1s^1 2p^1$ configuration**
- $1s^1$ → $^2S_{1/2}$ (S=1/2, L=0, J=1/2)
- $2p^1$ → $^2P_{1/2}$, $^2P_{3/2}$ (S=1/2, L=1, J=1/2,3/2)
- $1s^1\ 2p^1$ → S_{TOT} = 0 or 1
  → L_{TOT} = 1
  → $^1P_1$ + $^3P_0$, $^3P_1$, $^3P_2$
  [Σ(2J+1)=3+1+3+5=12]

Term Symbols

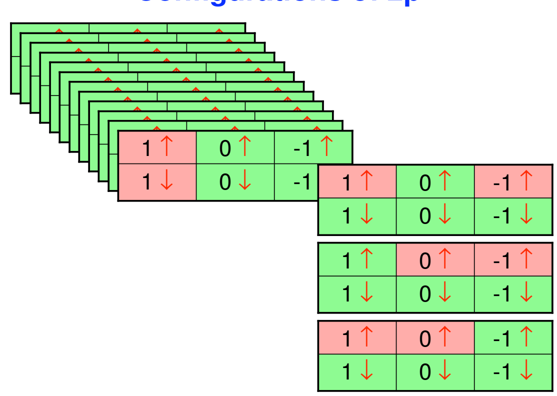
- **Term symbols of a $2p^1 3d^1$ configuration**
- $2p^1$ → $^2P_{1/2}$, $^2P_{3/2}$ (S=1/2, L=1, J=1/2,3/2)
- $3d^1$ → $^2D_{3/2}$, $^2D_{5/2}$ (S=1/2, L=2, J=3/2,5/2)
- $2p^1 3d^1$ → S_{TOT} = 0 or 1
  → L_{TOT} = 1 or 2 or 3
  → $^1P_1$ + $^3P_0$, $^3P_1$, $^3P_2$
  → $^1D_2$ + $^3D_1$, $^3D_2$, $^3D_3$
  → $^1F_3$ + $^3F_2$, $^3F_3$, $^3F_4$

[Σ(2J+1)=3+1+3+5+5+3+5+7+7+5+7+9=60]

Term Symbols

- **Term symbols of a $2p^2$ configuration**

Configurations of $2p^2$



Term Symbols of $2p^2$

	$M_S=1$	$M_S=0$	$M_S=-1$
$M_L=2$	0	1	0
$M_L=1$	1	2	1
$M_L=0$	1	3	1
$M_L=-1$	1	2	1
$M_L=-2$	0	1	0

LS term symbols: ^1S, ^1D, ^3P

LSJ term symbols:

$\boxed{^1S_0\ \ ^1D_2\ \ ^3P_0\ \ ^3P_1\ \ ^3P_2}$

Term Symbols

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

$M_L=4$
$M_S=0$
$M_J=4$

2 ↑	1 ↑	0 ↑	-1 ↑	-2 ↑
2 ↓	1 ↓	0 ↓	-1 ↓	-2 ↓

$M_L=3$
$M_S=1$
$M_J=4$

Term Symbols

$2p^2$-configuration: $^1S_0$, $^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$,

$3d^2$-configuration: $^1S_0$, $^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$, $^1G_4$, $^3F_2$, $^3F_3$, $^3F_4$

Matrix Elements

$$\left\langle {}^{2S+1}L_J \,|\, \tfrac{e^2}{r_{12}} | {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

$1s^1\ 2s^1$

$$\langle {}^1S | \frac{e^2}{\mathbf{r}_{12}} | {}^1S \rangle = F^0(1s2s) + G^0(1s2s),$$

$$\langle {}^3S | \frac{e^2}{\mathbf{r}_{12}} | {}^3S \rangle = F^0(1s2s) - G^0(1s2s).$$

Matrix Elements

$$\left\langle {}^{2S+1}L_J \,|\, \tfrac{e^2}{r_{12}} | {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

general

$$f_k = (2l_1+1)(2l_2+1)(-1)^L \begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix},$$

$$g_k = (2l_1+1)(2l_2+1)(-1)^S \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix}.$$

Matrix Elements

$$f_k = (2l_1+1)(2l_2+1)(-1)^L \begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix},$$

$$g_k = (2l_1+1)(2l_2+1)(-1)^S \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix}.$$

^1S of $2p^2$ **$l_1=1$ $l_2=1$ $k=2$ $L=0$**

$$f_2({}^1S) = (3)(3) \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 2 \end{Bmatrix} = 9 \cdot \frac{2}{15} \cdot \frac{1}{3} = \frac{2}{5}.$$

Matrix Elements

$$f_k = (2l_1+1)(2l_2+1)(-1)^L \begin{pmatrix} l_1 & k & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2 & l_1 & k \end{Bmatrix},$$

$$g_k = (2l_1+1)(2l_2+1)(-1)^S \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix}.$$

$3d^2$ $l_1=2$ $l_2=2$ $k=\{2,4\}$ $L=\{0,1,2,3,4\}$

$$f_k = \frac{10}{7} - 1^L \begin{Bmatrix} 2 & 2 & L \\ 2 & 2 & k \end{Bmatrix}.$$

Matrix Elements

	f_2		f_4		Energy
^1S	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 0 \\ 2 & 2 & 2 \end{Bmatrix}$	2/7	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 0 \\ 2 & 2 & 4 \end{Bmatrix}$	2/7	$0.46F^2$
^3P	$-\frac{10}{7}\begin{Bmatrix} 2 & 2 & 1 \\ 2 & 2 & 2 \end{Bmatrix}$	3/21	$-\frac{10}{7}\begin{Bmatrix} 2 & 2 & 1 \\ 2 & 2 & 4 \end{Bmatrix}$	−4/21	$0.02F^2$
^1D	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 2 \\ 2 & 2 & 2 \end{Bmatrix}$	−3/49	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 2 \\ 2 & 2 & 4 \end{Bmatrix}$	4/49	$-0.01F^2$
^3F	$-\frac{10}{7}\begin{Bmatrix} 2 & 2 & 3 \\ 2 & 2 & 2 \end{Bmatrix}$	−8/49	$-\frac{10}{7}\begin{Bmatrix} 2 & 2 & 3 \\ 2 & 2 & 4 \end{Bmatrix}$	−1/49	$-0.18F^2$
^1G	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 4 \\ 2 & 2 & 2 \end{Bmatrix}$	4/49	$\frac{10}{7}\begin{Bmatrix} 2 & 2 & 4 \\ 2 & 2 & 4 \end{Bmatrix}$	1/441	$0.08F^2$

$$\boxed{F^4 = 0.62F^2}$$

Matrix Elements

$3d^2$ $l_{min}=2 > k_{max}=4$ f_0, f_2, f_4, no exchange

$$\left\langle {}^{2S+1}L_J \left| \frac{e^2}{r_{12}} \right| {}^{2S+1}L_J \right\rangle = \sum_k f_k F^k + \sum_k g_k G^k$$

Calculate energy levels due to e/r integrals

(45x45 matrix blocked into irred. Representations)

		Relative Energy	Relative Energy
^1S	$F^0 + 2/7\ F^2 + 2/7\ F^4$	$0.46F^2$	4.6 eV
^3P	$F^0 + 3/21\ F^2 - 4/21\ F^4$	$0.02F^2$	0.2 eV
^1D	$F^0 - 3/49\ F^2 + 4/49\ F^4$	$-0.01F^2$	-0.1 eV
^3F	$F^0 - 8/49\ F^2 - 1/49\ F^4$	$-0.18F^2$	-1.8 eV
^1G	$F^0 + 4/49\ F^2 + 1/441\ F^4$	$0.08F^2$	0.8 eV

Matrix Elements of 3 electron states

$$|d^n[LS]\rangle = \sum_{L_1S_1} C^{LS}_{L_1S_1}\, |d^{n-1}[L_1S_1]d'\rangle.$$

$$|d^3[{}^4P]\rangle = -\sqrt{\frac{8}{15}}\, |d^2[{}^3P]d'\rangle - \sqrt{\frac{7}{15}}\, |d^2[{}^3F]d'\rangle,$$

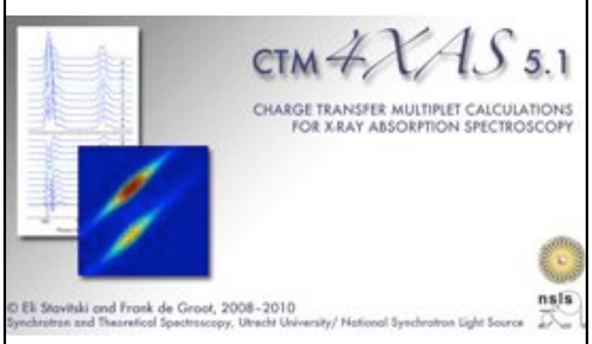
Term Symbols and XAS

- Ti^{IV} ion in TiO_2:
- Ground state: $3d^0$
- Final state: $2p^5 3d^1$
- Dipole transition: p-symmetry

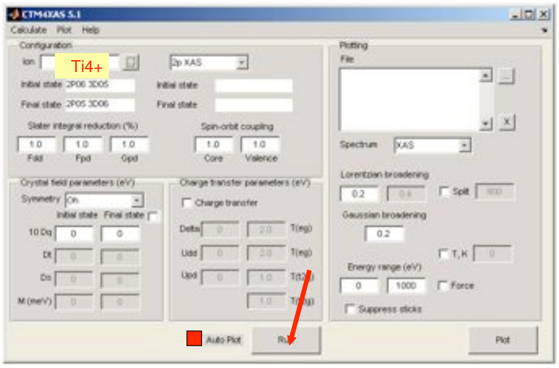
- $3d^0$-configuration: ^1S j=0
- $2p^1 3d^9$-configuration: $^2P \otimes {}^2D = {}^{1,3}PDF$ j'=0,1,2,3,4
- p-transition: ^1P $\Delta j=+1,0,-1$

- ground state symmetry: ^1S $^1S_0$
- transition: $^1S \otimes {}^1P = {}^1P$
- possible final states: ^1P $^1P_1, {}^3P_1, {}^3D_1,$

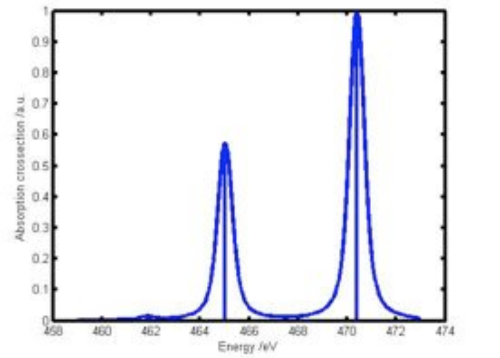
The CTM4XAS program



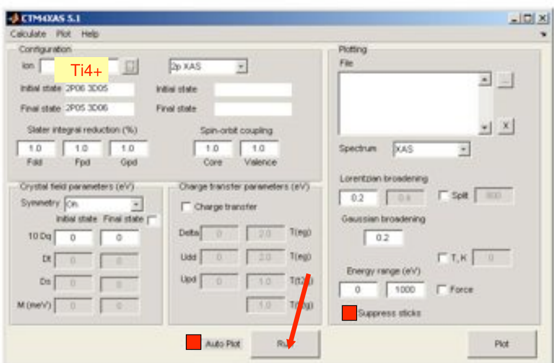
The CTM4XAS program



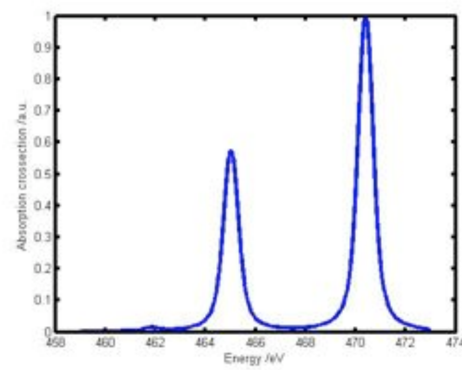
2p XAS of TiO_2



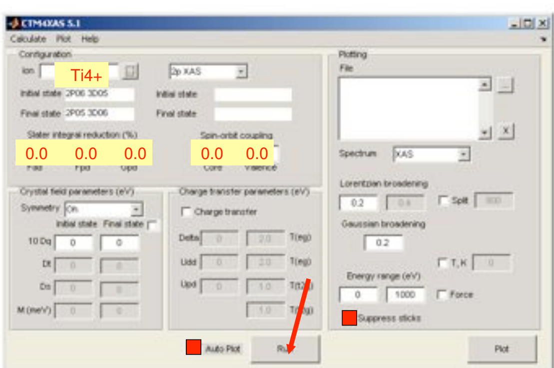
The CTM4XAS program



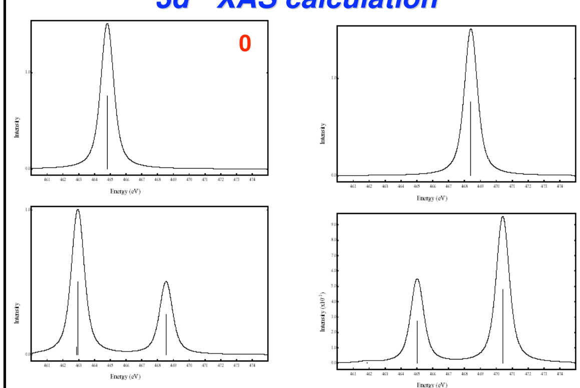
2p XAS of TiO_2



The CTM4XAS program



$3d^0$ XAS calculation



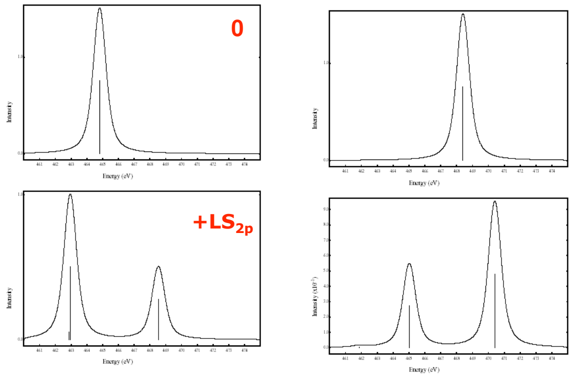
2p XAS of TiO_2

als3ti4a.org **(all zero)**

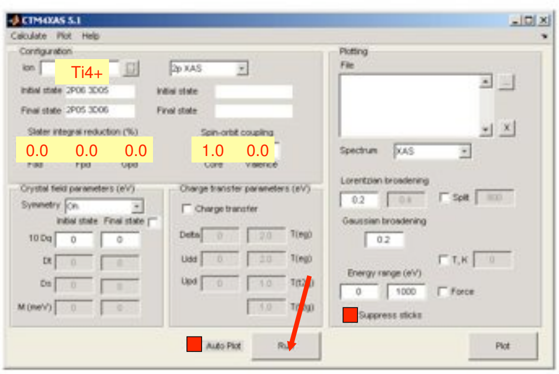
```
1 ENERGY MATRIX   (    LS COUPLING)        J= 1.0

                          1         1         1
                   (2P) 3D   (2P) 3P   (2P) 1P   (
                          1         2         3
  1 (2P) 3D  1    464.811     0.000     0.000
  1 (2P) 3P  2      0.000   464.811     0.000
  1 (2P) 1P  3      0.000     0.000   464.811
```

```
 EIGENVECTORS    (    LS COUPLING)


       1           P05 3D    P05 3D    P05 3D
                   (2P) 3D   (2P) 3P   (2P) 1P   (
  1 (2P) 3D  1    1.00000   0.00000   0.00000
  1 (2P) 3P  2    0.00000   1.00000   0.00000
  1 (2P) 1P  3    0.00000   0.00000   1.00000
```

$3d^0$ XAS calculation



The CTM4XAS program



2p XAS of TiO_2

als3ti4b.org **(+LS_{2p})**

```
1 ENERGY MATRIX   (    LS COUPLING)        J= 1.0

                   (2P) 3D   (2P) 3P   (2P) 1P   (
                          1         2         3
  1 (2P) 3D  1    465.755     1.635     2.312
  1 (2P) 3P  2      1.635   463.867     1.335
  1 (2P) 1P  3      2.312     1.335   464.811
```

```
0  EIGENVALUES       (J= 1.0)
                   462.923   462.923   468.587
```

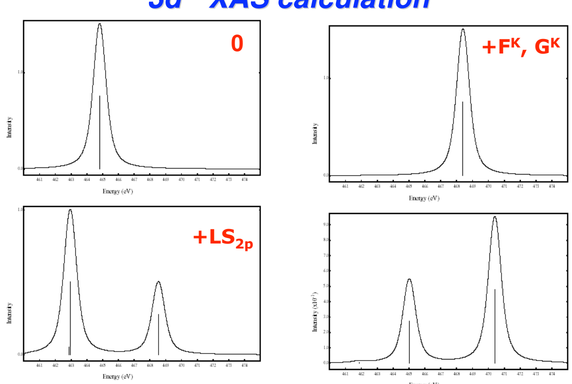
$\Delta E=5.664 = 3/2*LS_{2p}$

```
 EIGENVECTORS    (    LS COUPLING)
       1           P05 3D    P05 3D    P05 3D
                   (2P) 1P   (2P) 3P   (2P) 3D   (
  1 (2P) 3D  1   -0.67098   0.22312  -0.70711
  1 (2P) 3P  2    0.12977  -0.90360  -0.40826
  1 (2P) 1P  3    0.73003   0.36569  -0.57734
```

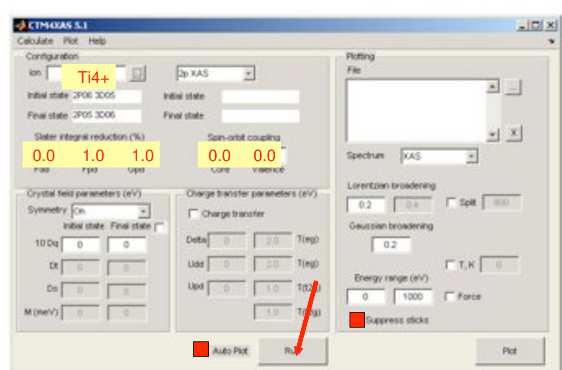
$0.73003^2+0.36569^2=0.6666$

$-0.57734^2=0.3333$

$3d^0$ XAS calculation



The CTM4XAS program

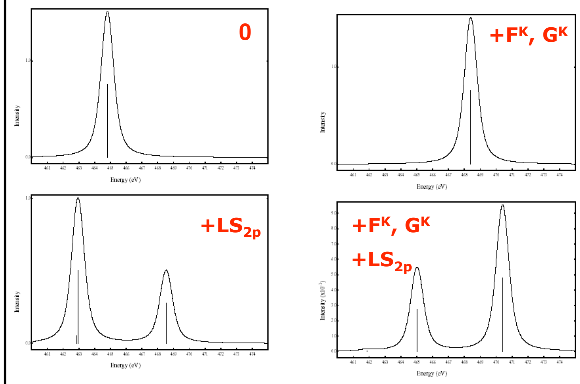


2p XAS of TiO_2

als3ti4c.org **($+F^K$, G^K)**

```
1 ENERGY MATRIX    (     LS COUPLING)        J= 1.0

                  (2P) 3D   (2P) 3P   (2P) 1P   (
                     1         2         3
  1 (2P) 3D  1    465.482    0.000     0.000
  1 (2P) 3P  2      0.000  463.466     0.000
  1 (2P) 1P  3      0.000    0.000   468.402

0   EIGENVALUES       (J= 1.0)
                  463.466   465.482   468.402

 EIGENVECTORS     (    LS COUPLING)
       1          P05 3D    P05 3D    P05 3D
                  (2P) 3P   (2P) 3D   (2P) 1P   (
  1 (2P) 3D  1    0.00000   1.00000   0.00000
  1 (2P) 3P  2    1.00000   0.00000   0.00000
  1 (2P) 1P  3    0.00000   0.00000   1.00000
```

$3d^0$ XAS calculation



2p XAS of TiO_2

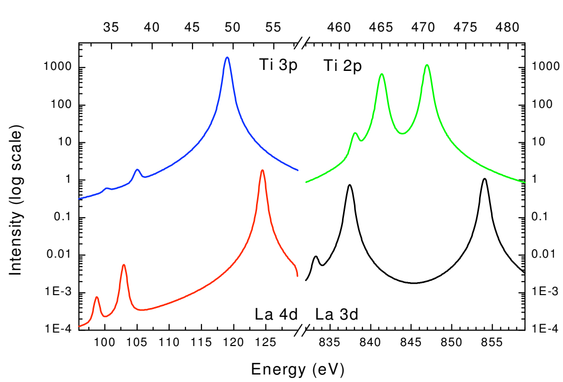
als3ti4d.org **($+LS_{2p}$ $+F^K$, G^K)**

```
1 ENERGY MATRIX    (     LS COUPLING)        J= 1.0

                  (2P) 3D   (2P) 3P   (2P) 1P   (
                     1         2         3
  1 (2P) 3D  1    466.426    1.635     2.312
  1 (2P) 3P  2      1.635  462.522     1.335
  1 (2P) 1P  3      2.312    1.335   468.402

0   EIGENVALUES       (J= 1.0)
                  461.886   465.019   470.446

 EIGENVECTORS     (    LS COUPLING)
       1          P05 3D    P05 3D    P05 3D
                  (2P) 3P   (2P) 3D   (2P) 1P   (
  1 (2P) 3D  1    0.29681  -0.77568   0.55698
  1 (2P) 3P  2   -0.95074  -0.18539   0.24845
  1 (2P) 1P  3    0.08946   0.60328   0.79250
```

$3d^0$ XAS calculation

Edge	Ti 2p	Ti 3p	La 3d	La 4d
Average Energy (eV)	464.00	37.00	841.00	103.00
Core spin-orbit (eV)	3.78	0.43	6.80	1.12
F^2 Slater-Condon (eV)	5.04	8.91	5.65	10.45
Intensities:				
Pre-peak	0.01	10^{-4}	0.01	10^{-3}
$p_{3/2}$ or $d_{5/2}$	0.72	10^{-3}	0.80	0.01
$p_{1/2}$ or $d_{3/2}$	1.26	1.99	1.19	1.99

$3d^0$ XAS calculation



Term Symbols and XAS

Ti^{IV} ion in TiO_2:
Ground state: $3d^0$
Final state: $2p^5 3d^1$
Dipole transition: p-symmetry

$3d^0$-configuration: ^1S — $j=0$
$2p^1 3d^9$-configuration: $^2P \otimes {}^2D = {}^{1,3}PDF$ — $j'=0,1,2,3,4$
p-transition: ^1P — $\Delta j=+1,0,-1$

ground state symmetry: ^1S — $^1S_0$
transition: $^1S \otimes {}^1P = {}^1P$
possible final states: ^1P — $^1P_1, {}^3P_1, {}^3D_1$,

$3d^N$ XAS calculation

Transition	Ground	Transitions	Term Symbols
$3d^0 \rightarrow 2p^5 3d^1$	$^1S_0$	3	12
$3d^1 \rightarrow 2p^5 3d^2$	$^2D_{3/2}$	29	45
$3d^2 \rightarrow 2p^5 3d^3$	$^3F_2$	68	110
$3d^3 \rightarrow 2p^5 3d^4$	$^4F_{3/2}$	95	180
$3d^4 \rightarrow 2p^5 3d^5$	$^5D_0$	32	205
$3d^5 \rightarrow 2p^5 3d^6$	$^6S_{5/2}$	110	180
$3d^6 \rightarrow 2p^5 3d^7$	$^5D_4$	68	110
$3d^7 \rightarrow 2p^5 3d^8$	$^4F_{9/2}$	16	45
$3d^8 \rightarrow 2p^5 3d^9$	$^3F_4$	4	12
$3d^9 \rightarrow 2p^5 3d^{10}$	$^2D_{5/2}$	1	2

Hunds rules

- Term symbols with **maximum spin** S are lowest in energy,
- Among these terms:

  Term symbols with **maximum L** are lowest in energy
- In the presence of spin-orbit coupling, the lowest term has
- J = |L-S| if the shell is less than half full
- **J = L+S** if the shell is more than half full

$3d^1$ has $^2D_{3/2}$ ground state $3d^2$ has $^3F_2$ ground state
$3d^9$ has $^2D_{5/2}$ ground state $3d^8$ has $^3F_4$ ground state

Give the Hund's rule ground states for $3d^1$ to $3d^9$

Term Symbols and XAS

Ti^{IV} ion in TiO_2:
Ground state: $3d^0$
Final state: $2p^5 3d^1$
Dipole transition: p-symmetry

$3d^0$-configuration: ^1S j=0
$2p^1 3d^9$-configuration: $^2P \otimes {}^2D = {}^{1,3}PDF$ j'=0,1,2,3,4
p-transition: ^1P Δj=+1,0,-1

ground state symmetry: ^1S $^1S_0$
transition: $^1S \otimes {}^1P = {}^1P$
two possible final states: ^1P $^1P_1$, $^3P_1$, $^3D_1$,

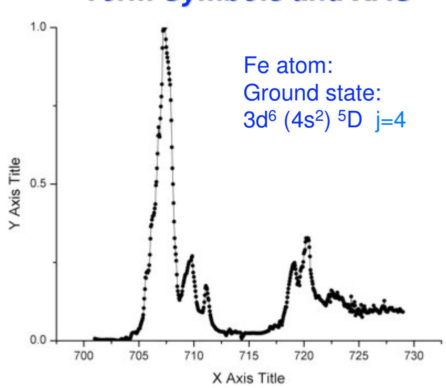
Term Symbols and XAS

Fe atom:
Ground state: $3d^6$ $(4s^2)$
Final state: $2p^5 3d^7$
Dipole transition: p-symmetry

$3d^6$-configuration: ^5D, etc. j=4
$2p^5 3d^7$-configuration: 110 states j'= 3,4, 5
p-transition: ^1P Δj=+1,0,-1

ground state symmetry: ^5D $^5D_4$
transition: $^5D \otimes {}^1P = {}^5PDF$
possible final states: 68 states

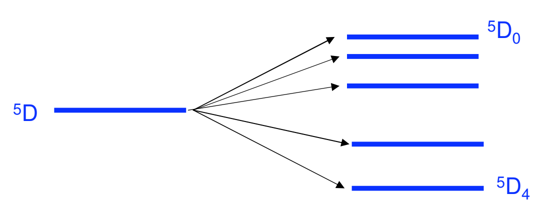
Term Symbols and XAS



Fe atom:
Ground state:
$3d^6$ $(4s^2)$ ^5D j=4

Term Symbols and XAS

Fe atom:
Ground state: $3d^6$ $(4s^2)$ ^5D j=4



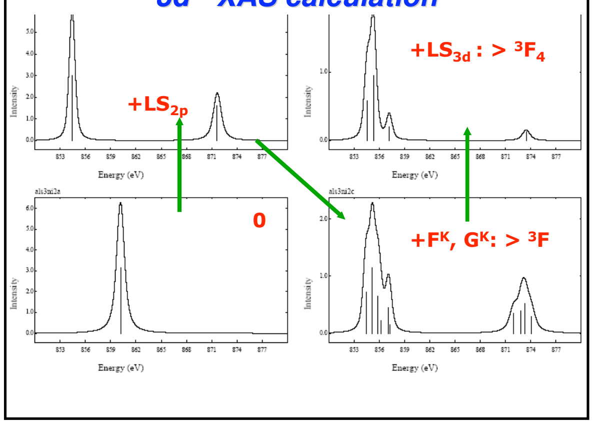
Term Symbols and XAS

Ni^{II} ion in NiO:
Ground state: $3d^8$
Final state: $2p^5 3d^9$
Dipole transition: p-symmetry

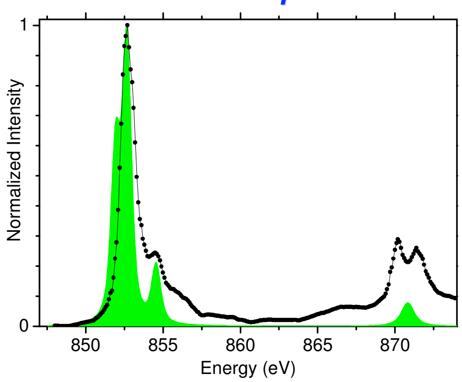
$3d^8$-configuration:	^1S, ^1D, ^3P, ^1G, ^3F	j=4
$2p^5 3d^9$-configuration:	$^2P \otimes {}^2D = {}^{1,3}PDF$	j'=0,1,2,3,4
p-transition:	^1P	Δj=+1,0,-1

ground state symmetry:	^3F	$^3F_4$
transition:	$^3F \otimes {}^1P = {}^3DFG$	
two possible final states:	^3D, ^3F	$^3D_3$, $^3F_3$, $^3F_4$, $^1F_3$

$3d^8$ XAS calculation



Atomic multiplets



Charge Transfer Multiplet program

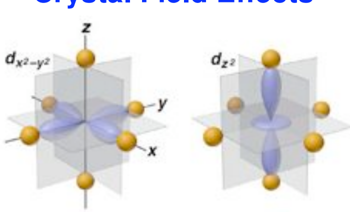
Used for the analysis of XAS, EELS,

Photoemission, Auger, XES,

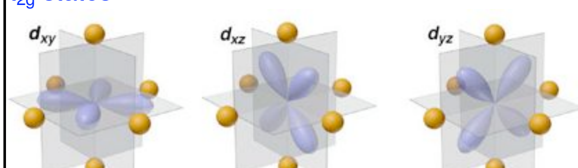
ATOMIC PHYSICS
⇓
GROUP THEORY
⇓
MODEL HAMILTONIANS

Crystal Field Effects

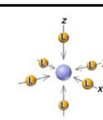
e_g states

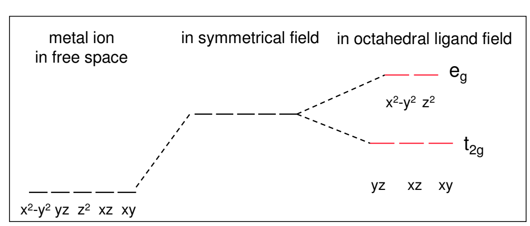


t_{2g} states

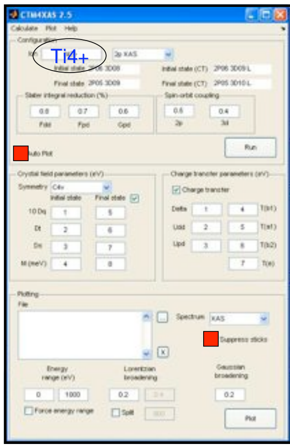


Octahedral crystal field splitting

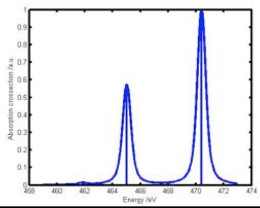




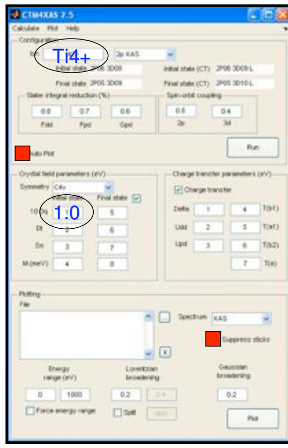
2p XAS of TiO_2



Put Ti4+ in Ion
Set Autoplot ON
Press Run

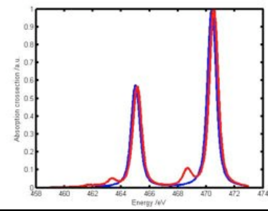


2p XAS of TiO_2

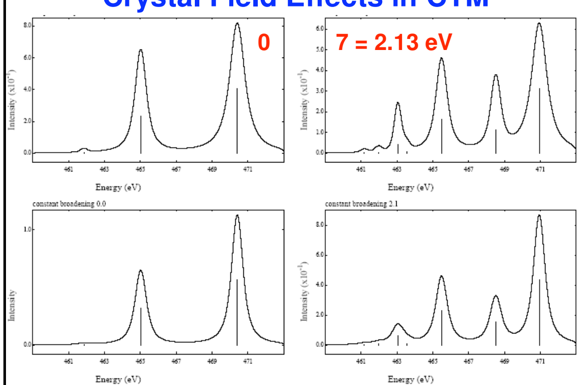


Crystal field effect:

+ 1 for 10Dq



Crystal Field Effects in CTM



Crystal Field Effects

SO_3			O_h (Mulliken)
S	0		A_1
P	1		T_1
D	2		$E+T_2$
F	3		$A_2+T_1+T_2$
G	4		$A_1+E+T_1+T_2$

2p XAS of TiO_2 (atomic multiplets)

Ti^{IV} ion in TiO_2:

$3d^0$-configuration:	^1S	j=0
$2p^13d^9$-configuration:	$^2P \otimes ^2D$ = ^{1,3}PDF	j'=0,1,2,3,4
p-transition:	^1P	Δj=+1,0,-1

Write out all term symbols:

	$^1P_1$	$^1D_2$	$^1F_3$	
$^3P_0$	$^3P_1$	$^3P_2$		
	$^3D_1$	$^3D_2$	$^3D_3$	
		$^3F_2$	$^3F_3$	$^3F_4$
1	3	4	3	1

Crystal Field Effect on XAS

J in SO_3	Deg.			
0	1			
1	3			
2	4			
3	3			
4	1			
Σ	12			

$<^1S_0|\text{dipole}|^1P_1>$ goes to $<A_1|T_1|T_1>$

Crystal Field Effects

SO_3			O_h (Mulliken)
S	0		A_1
P	1		T_1
D	2		$E+T_2$
F	3		$A_2+T_1+T_2$
G	4		$A_1+E+T_1+T_2$

Crystal Field Effect on XAS

J in SO_3	Deg.	Branchings		
0	1	A_1		
1	3	$3\times T_1$		
2	4	$4\times E$, $4\times T_2$		
3	3	$3\times A_2$, $3\times T_1$, $3\times T_2$		
4	1	A_1, E, T_1, T_2		
Σ	12			

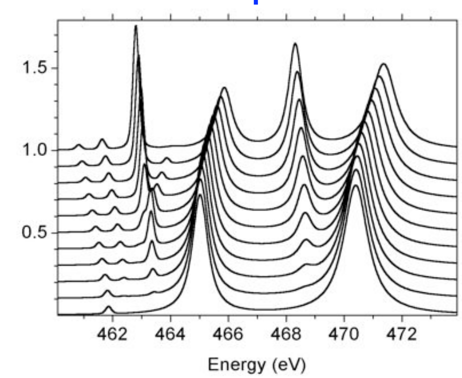
$\langle {}^1S_0|\text{dipole}|{}^1P_1\rangle$ goes to $\langle A_1|T_1|T_1\rangle$

Crystal Field Effect on XAS

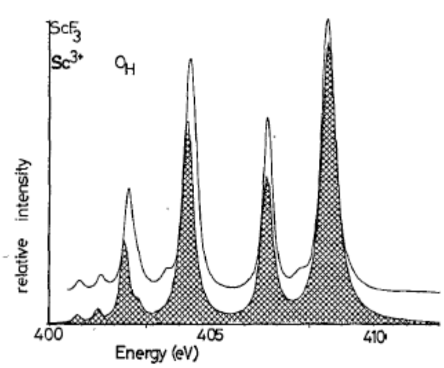
J in SO_3	Deg.	Branchings	Γ in O_h	Deg.
0	1	A_1	A_1	2
1	3	$3\times T_1$	A_2	3
2	4	$4\times E$, $4\times T_2$	T_1	7
3	3	$3\times A_2$, $3\times T_1$, $3\times T_2$	T_2	8
4	1	A_1, E, T_1, T_2	E	5
Σ	12			25

$\langle {}^1S_0|\text{dipole}|{}^1P_1\rangle$ goes to $\langle A_1|T_1|T_1\rangle$

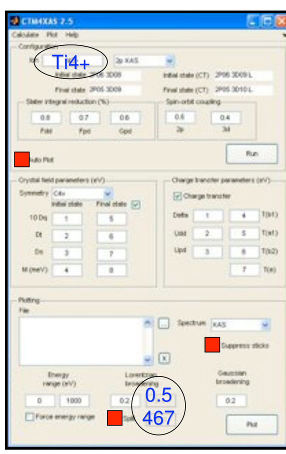
Effect of 10Dq on XAS:3d^0



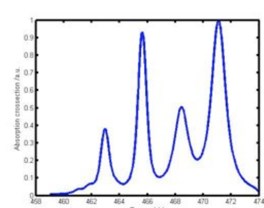
Comparison with Experiment



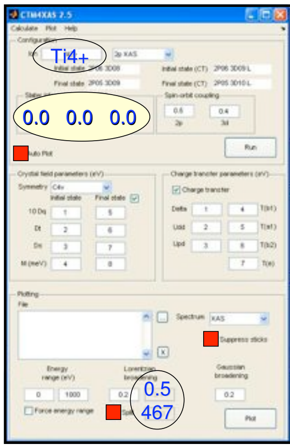
2p XAS of TiO_2



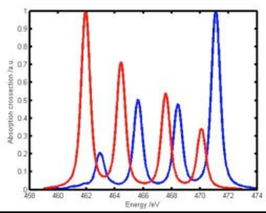
Crystal field effect:
+ 2.5 for 10Dq
+ Split ON
+ 0.5 Lorentzian L2
+ 467 split energy



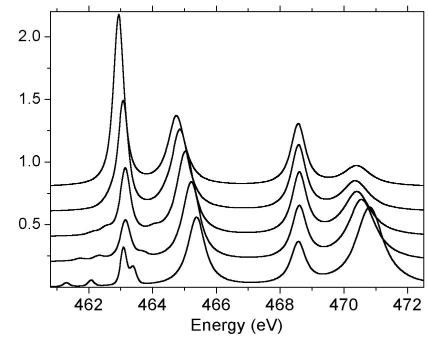
2p XAS of TiO_2



+
Set Expert options ON
Add 1 1 1 for Fdd, etc.



Turning multiplet effects off



Partly filled 3d-shells

Hunds rules

- Term symbols with **maximum spin** S are lowest in energy,
- Among these terms:

  Term symbols with **maximum L** are lowest in energy
- In the presence of spin-orbit coupling, the lowest term has
- J = |L-S| if the shell is less than half full
- **J = L+S** if the shell is more than half full

$3d^1$ has $^2D_{3/2}$ ground state
$3d^9$ has $^2D_{5/2}$ ground state

$3d^2$ has $^3F_2$ ground state
$3d^8$ has $^3F_4$ ground state

Crystal Field Effects on $3d^8$ states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {^1T_2}$	
^3F	-1.8 eV	$\mathbf{^3A_2} + {^3T_1} + {^3T_2}$	
^1G	0.8 eV	$^1A_1 + {^1T_1} + {^1T_2} + {^1E}$	

Crystal Field Effects

SO_3		O_h (Butler)	O_h (Mulliken)
S	0	0	A_1
P	1	1	T_1
D	2	2 + ^1	$E+T_2$
F	3	^0+ 1 +^1	$A_2+T_1+T_2$
G	4	0 + 1 + 2 + ^1	$A_1+E+T_1+T_2$

Crystal Field Effects on 3d^8 states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	$A_1 \otimes A_1 = A_1$
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	$\mathbf{^3A_2} + {}^3T_1 + {}^3T_2$	$T_1 \otimes T_2 = T_1 + T_2 + E + A_2$
^1G	0.8 eV	$^1A_1 + {}^1T_1 + {}^1T_2 + {}^1E$	

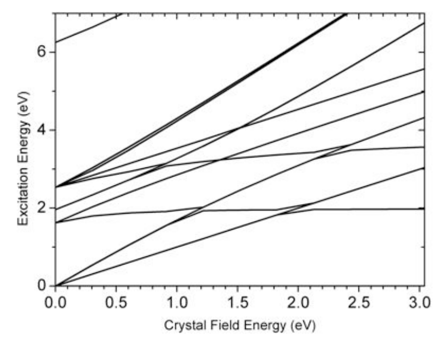
The multiplication table of O_h symmetry

O	**A_1**	**A_2**	**T_1**	**T_2**	**E**
A_1	**A_1**	**A_2**	**T_1**	**T_2**	**E**
A_2	**A_2**	**A_1**	**T_2**	**T_1**	**E**
T_1	**T_1**	**T_2**	**$T_1 + T_2 + E + A_1$**	**$T_1 + T_2 + E + A_2$**	**T_1+T_2**
T_2	**T_2**	**T_1**	**$T_1 + T_2 + E + A_2$**	**$T_1 + T_2 + E + A_1$**	**T_1+T_2**
E	**E**	**E**	**T_1+T_2**	**T_1+T_2**	**A_1+A_2+E**

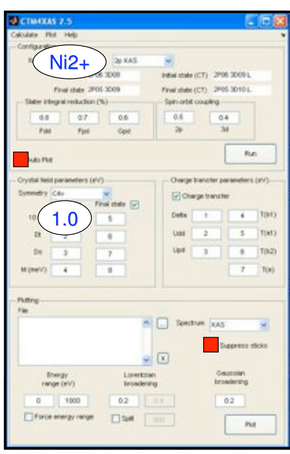
Crystal Field Effects on 3d^8 states

	Energy	Symmetries O_h	Total symmetry
^1S	4.6 eV	$^1A_1$	$^{A1}A_1 = A_1$
^3P	0.2 eV	$^3T_1$	
^1D	-0.1 eV	$^1E + {}^1T_2$	
^3F	-1.8 eV	$\mathbf{^3A_2} + {}^3T_1 + {}^3T_2$	$(T_2)+(A_1+E_1+T_1+T_2)+(A_2+E+T_1+T_2)$
^1G	0.8 eV	$^1A_1 + {}^1T_1 + {}^1T_2 + {}^1E$	

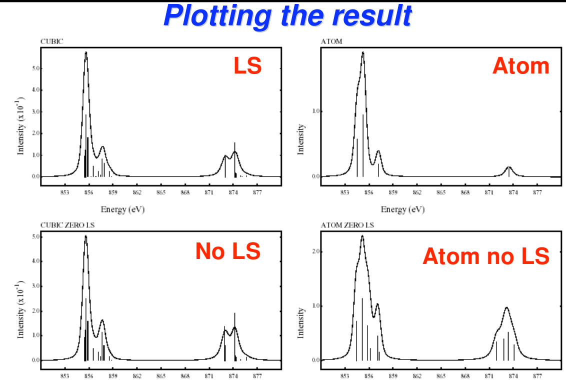
Crystal Field Effects: Tanabe-Sugano



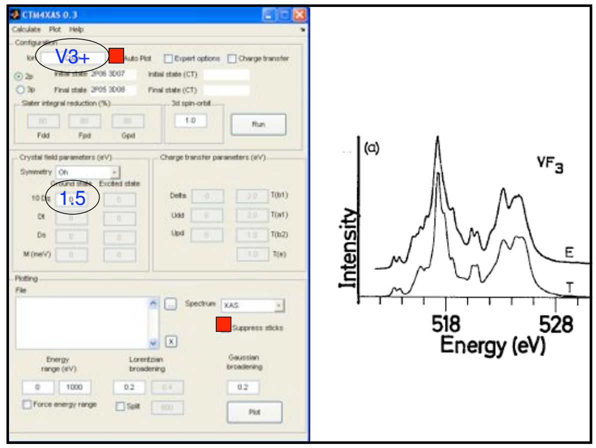
Tanabe-Sugano



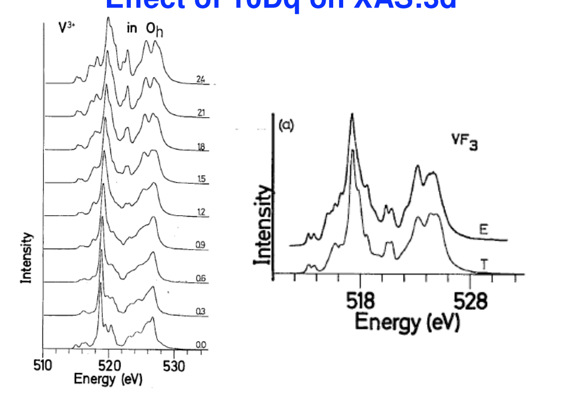
Plotting the result



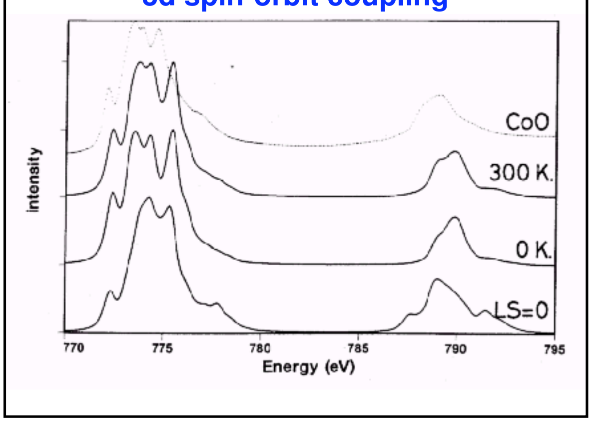
Conf.	SO3	Oh	Spin in Oh	Deg.	Overall Symmetry in Oh
$3d^0$	$^1S_0$	$^1A_1$	A_1	1	A_1
$3d^1$	$^2D_{3/2}$	$^2T_2$	U_1	2	$U_2 + G$
$3d^2$	$^3F_2$	$^3T_1$	T_1	4	$E+T_1+T_2+A_1$
$3d^3$	$^4F_{3/2}$	$^4A2$	G	1	G
$3d^4$	$^5D_0$	^5E $3T_1$	$E + T_2$ T_1	5 4	$A_1+A_2+E+T_1+T_2$ $E+T_1+T_2+A_1$
$3d^5$	$^6S_{5/2}$	$^6A_1$ $2T_2$	$G+U_2$ U_1	2 2	$G+U_2$ $G+U_2$
$3d^6$	$^5D_2$	$^5T_2$ $1A_1$	$E+T_2$ A_1	6 1	$A_1+E+T_1+T_1+T_2+T_2$ A_1
$3d^7$	$^4F_{9/2}$	$^4T_1$ 2E	G U_1	4 1	$U_1+U_2+G + G$ G
$3d^8$	$^3F_4$	**$^3A_2$**	T_1	1	**T_2**
$3d^9$	$^2D_{5/2}$	^2E	U_1	1	G

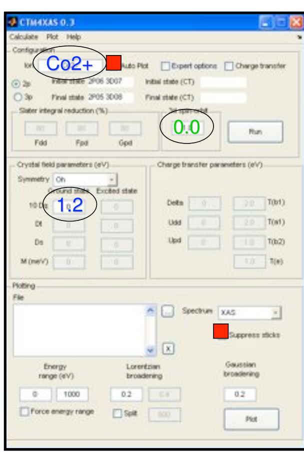


Effect of 10Dq on XAS:3d^N



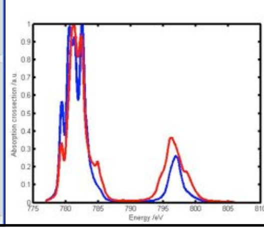
3d spin-orbit coupling



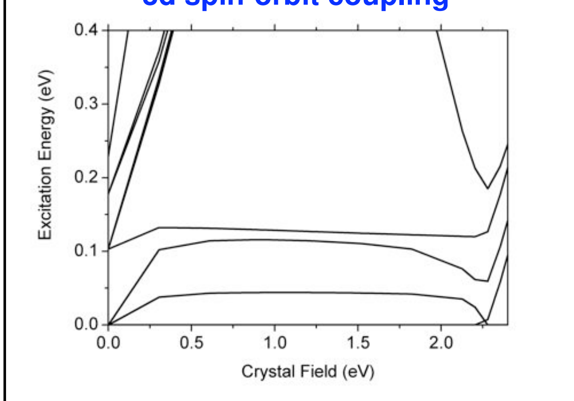


2p XAS of CoO

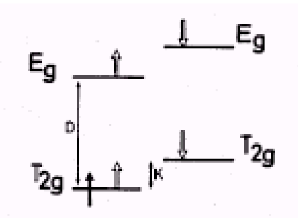
+ with and without 3d spin-orbit (1.0 and 0.0)



3d spin-orbit coupling



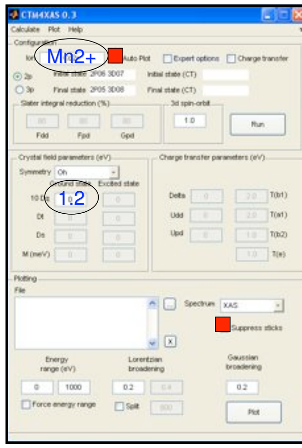
High-spin or Low-spin



10Dq > 3J
(d^4 and d^5)

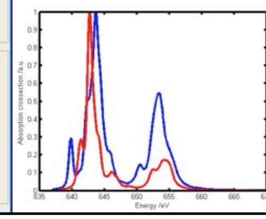
10Dq > 2J
(d^6 and d^7)

2p XAS of Mn2+



High-spin: 10Dq = 1.2

Low-spin: 10Dq = 3.0



2p XAS of Mn2+