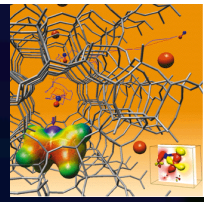
Università degli Studi di Padova

universa universis patavina libertas



"Modellistica per le Scienze Molecolari"

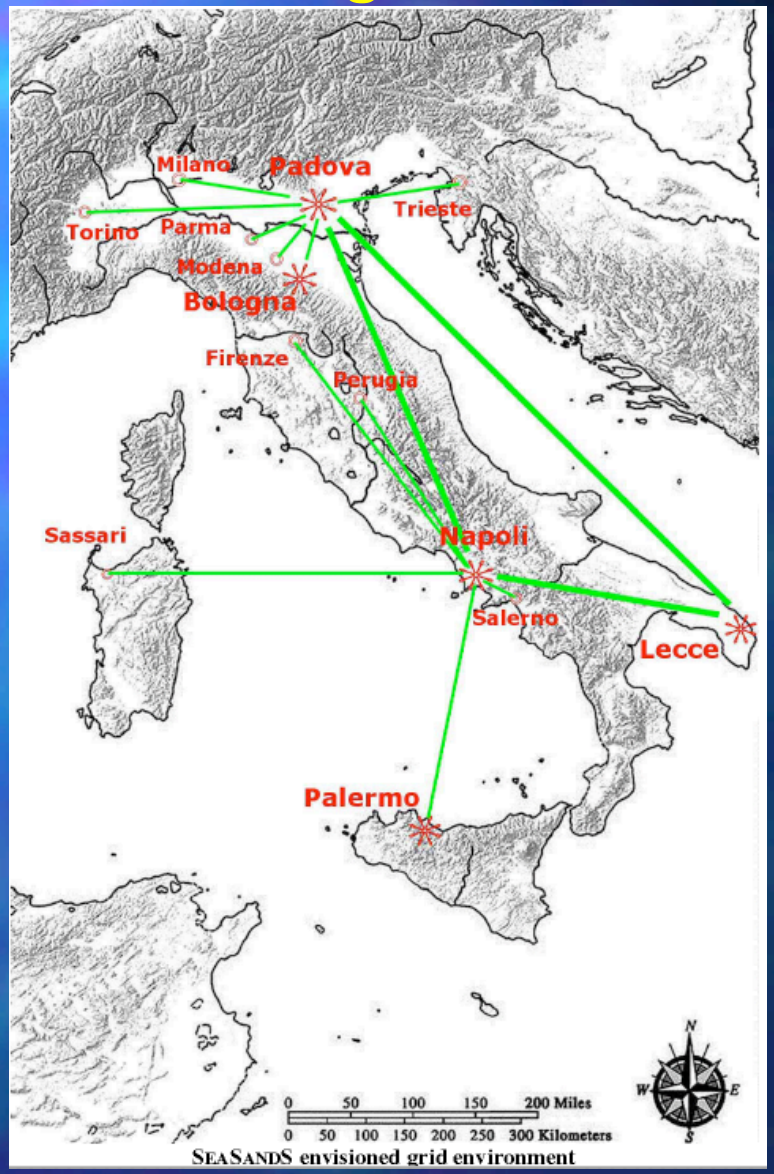
Maurizio Casarin - Dipartimento di Scienze Chimiche

"Il calcolo scientifico a Padova: condivisione di competenze e creazione di strutture integrate"

Padova - 19 Dicembre 2007
Palazzo del Bo - Archivio Antico

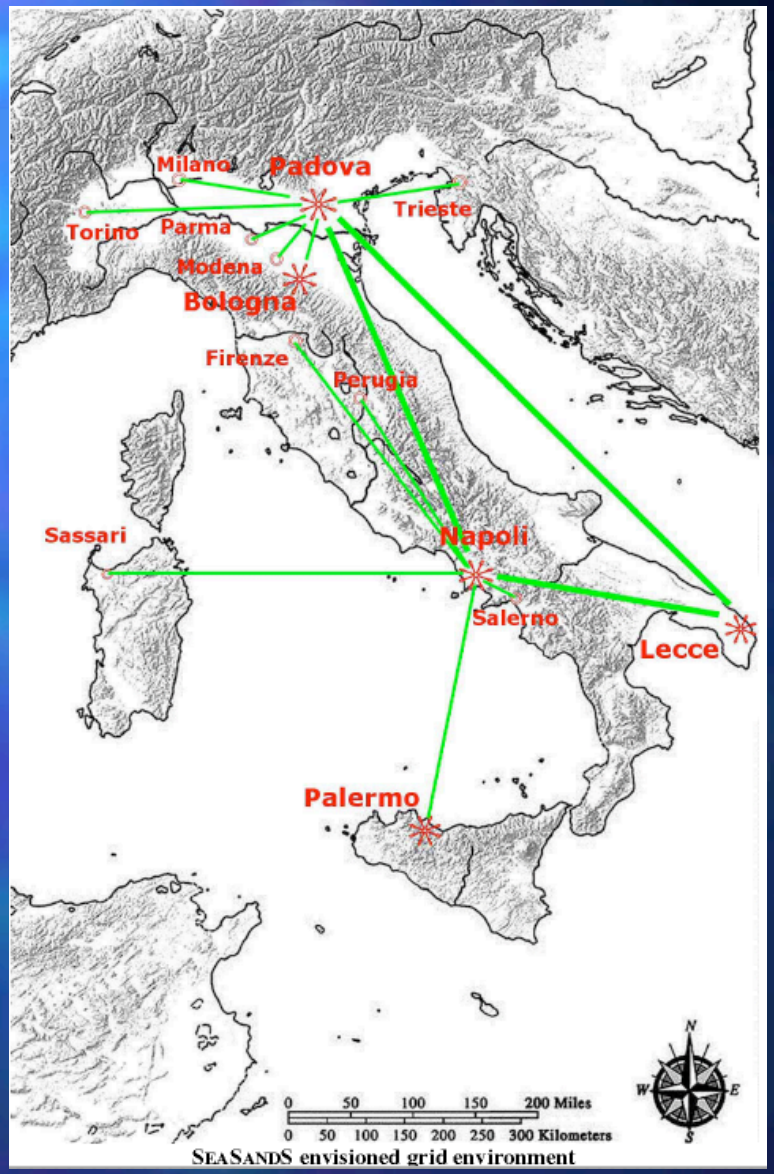
South European Association for the in Silico Approach to Nanomaterial Design and Structure

Università di Bologna
Università di Firenze
Università di Lecce
Università di Milano
Università di Modena
Università di Napoli
Università di Padova
Università di Palermo
Università di Pavia
Università del Piemonte Orientale
Università di Salerno
Università di Sassari
Università di Trieste

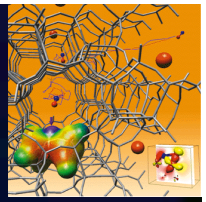


VILLAGE

VILLAGE:
Virtual Italian Laboratory for Large-scale Applications in a Geographically distribuited Environment.



SEASANDS envisioned grid environment



FROM SILICON TO RNA: THE COMING OF AGE OF AB *INITIO* MOLECULAR DYNAMICS

"First principle quantum mechanical calculations are by now considered a sort of new spectroscopy, being widely recognized that the chemical and structural information they provide is often more accessible and likewise reliable than that provided by conventional spectroscopies"

M. Parrinello, Solid State Commun. **1997,** *102*, 107

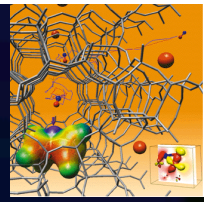
1 Covalency:

organic chemistry
- noble gas configuration;
- Lewis structures;
- qualitative valence bond theory.

inorganic chemistry
- crystal field;
- ligand field.

Molecular Orbital Theories

2 Molecular nanostructures as model systems and as building blocks for the bottom-up synthesis of functional nanomaterials



Surface-supported organic nanostructures of interest for:

- catalysis
- sensing devices
- molecular electronics
- non-linear optical properties
- molecular recognition
- model systems for the study of biological activity
- …

1 Covalency:

organic chemistry
- noble gas configuration;
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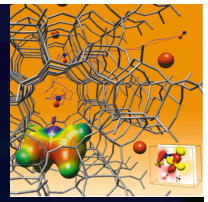
Molecular Orbital Theories



"Bonding is the degree of interaction between two atoms, which can be described by the amount of covalent mixing of their atomic orbitals."

Solomon et al.

Acc. Chem Res. 2000, *33*, 859

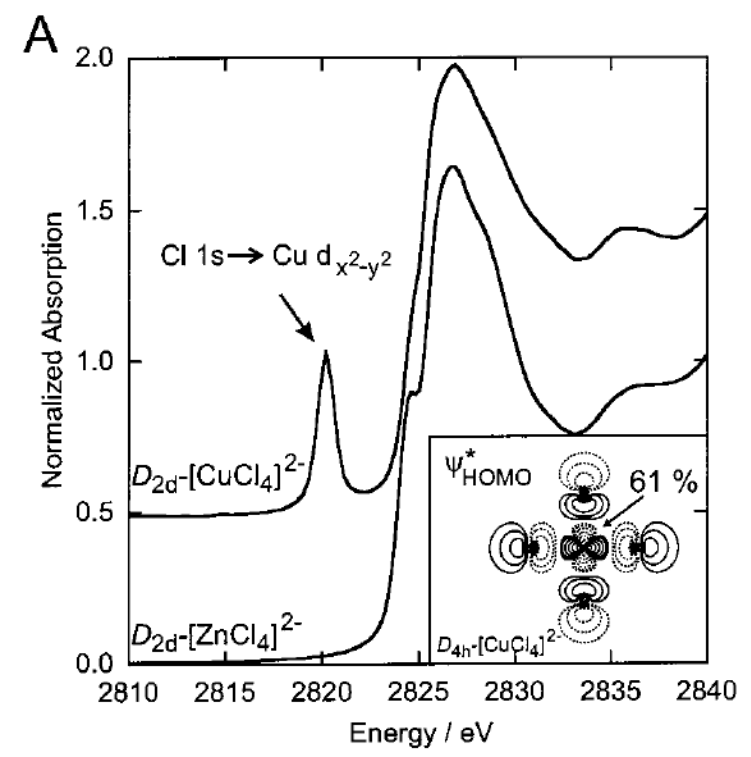
Covalency in a spectroscopic sense is related not only to metal-ligand orbital mixing ratios (the "symmetry-restricted covalency") but also to the distortions of the metal orbitals upon bond formation (the "central-field covalence")

XAS: X-ray absorption spectroscopy

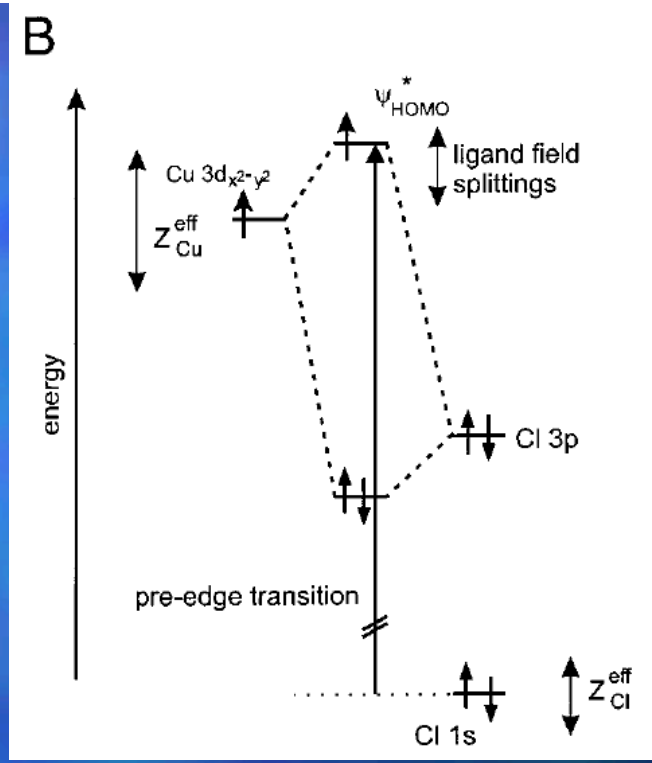
M K-edge: electric dipole forbidden (but quadrupole allowed) $1s^M \rightarrow nd^M$ transitions

M L-edge: electric dipole allowed $2p^M \rightarrow nd^M$ transitions

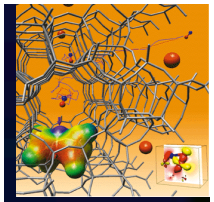
L K-edge: electric dipole allowed $1s^L \rightarrow np^L$ transitions



Cl K-edge XAS spectra of $[ZnCl_4]^{2-}$ and D_{2d}-$[CuCl_4]^{2-}$; inset shows the $d_{x^2-y^2}$ HOMO of D_{4h}-$[CuCl_4]^{2-}$.



Orbital energy diagram showing the ligand pre-edge transition.



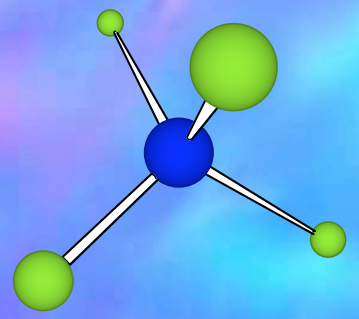
$$\psi^* = \sqrt{\left(1-\alpha^2\right)}\left|\text{Cu } 3d_{x^2-y^2}\right\rangle - \alpha\left|\text{Cl } 3p\right\rangle$$

Cl 1s → ψ^*

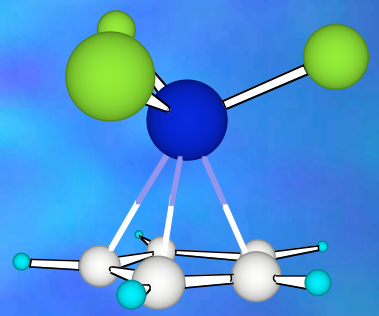
$$\text{Int}\left(\text{Cl 1s} \rightarrow \psi^*\right) = \text{const}\left|\left\langle \text{Cl 1s}\left|\vec{r}\right|\psi^*\right\rangle\right|^2 \approx \alpha^2 \text{const}\left|\left\langle \text{Cl 1s}\left|\vec{r}\right|\text{Cl 3p}\right\rangle\right|^2$$

Ligand K-edge spectroscopy is a direct probe of the covalency of a metal-ligand bond.

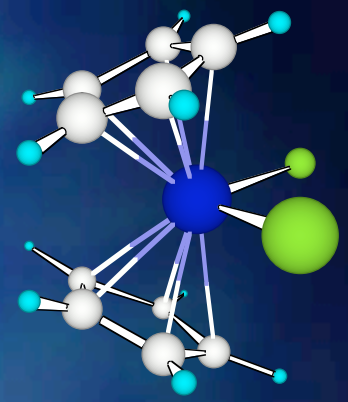
Application of SO-RTD-DFT to closed shell complexes



$TiCl_4$



$Ti(\eta^5\text{-}C_5H_5)Cl_3$



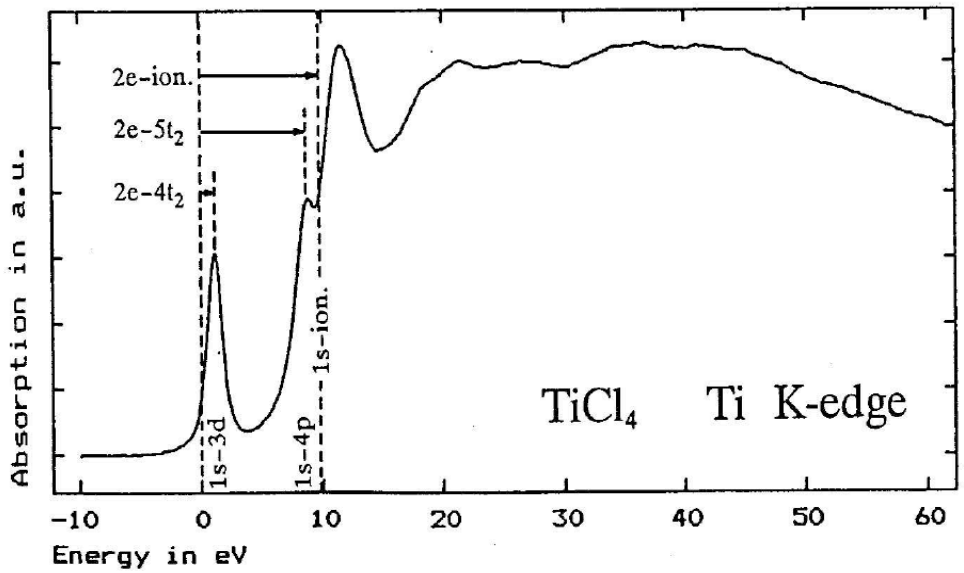
$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$

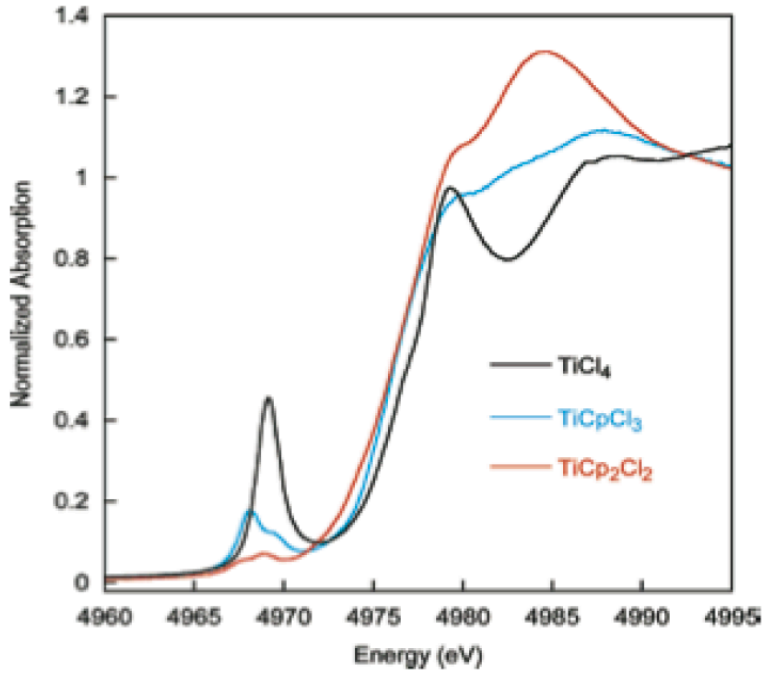
The interest for this complexes has to be ultimately traced back to two factors:

i) the catalytic activity of both mono- and bis - cyclopentadienyl titanium(IV) complexes;

ii) the possible use of titanocene dichloride and its water soluble derivatives as possible alternatives to t he widely used heavy metal based anticancer drugs.

Ti K-edge of $TiCl_4$, $TiCpCl_3$, $TiCp_2Cl_2$





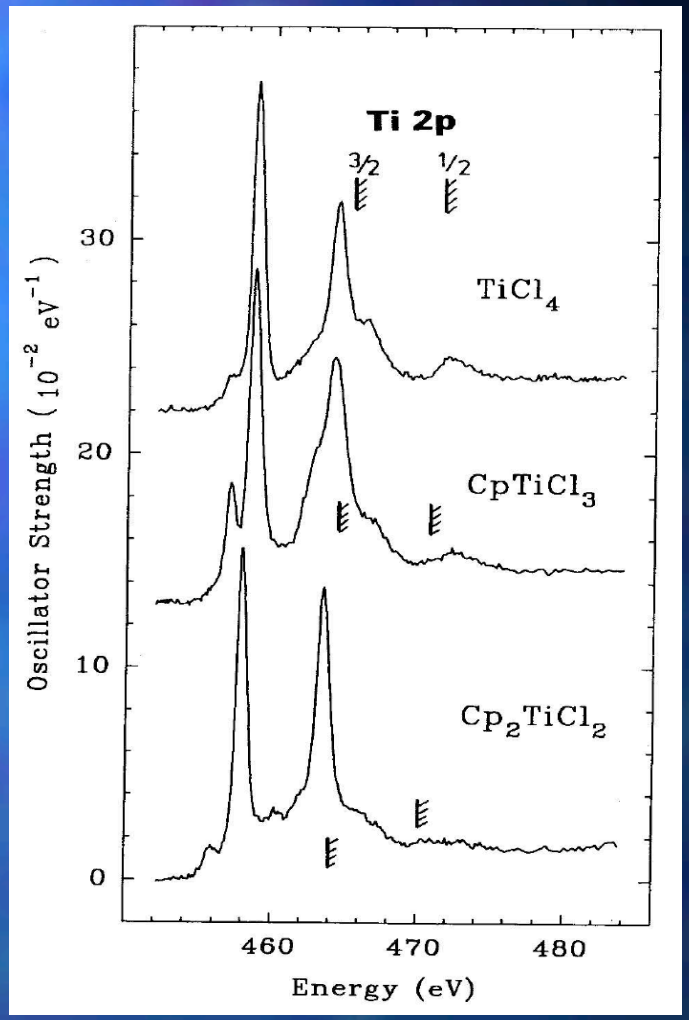
Kuetgens & Hormes

SIF Conference Proceedings **1990**, *25*, 59

DeBeer George *et al.*

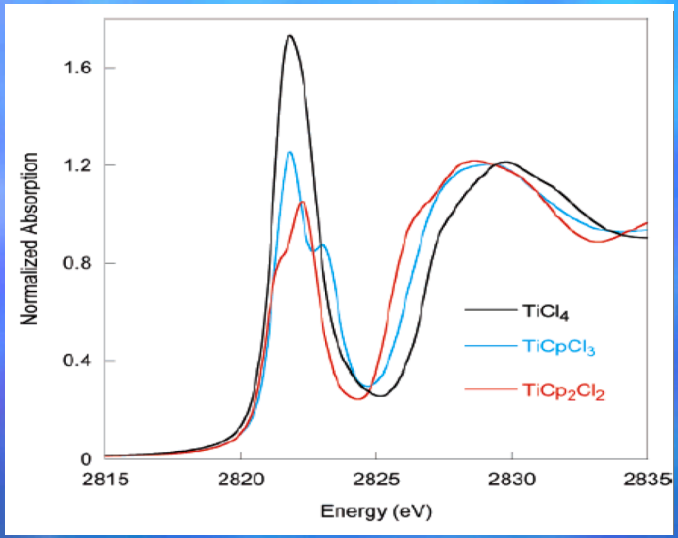
J. Am. Chem. Soc. **2005**, *217*, 667

Ti $L_{2,3}$-edge
$TiCl_4$, $TiCpCl_3$, $TiCp_2Cl_2$



Wen & Hitchcock
Can. J. Chem. **1993**, *71*, 1632

Cl K-edge
$TiCl_4$, $TiCpCl_3$, $TiCp_2Cl_2$



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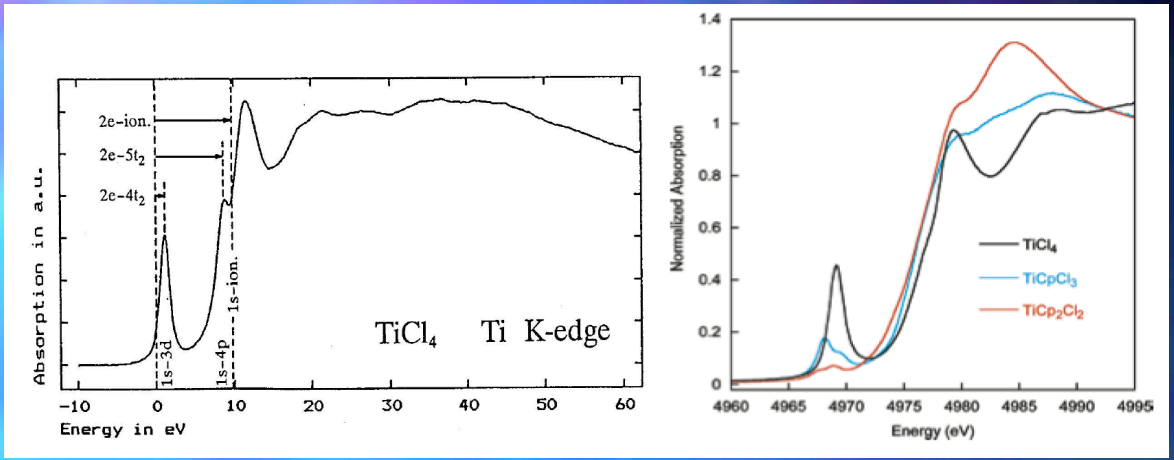
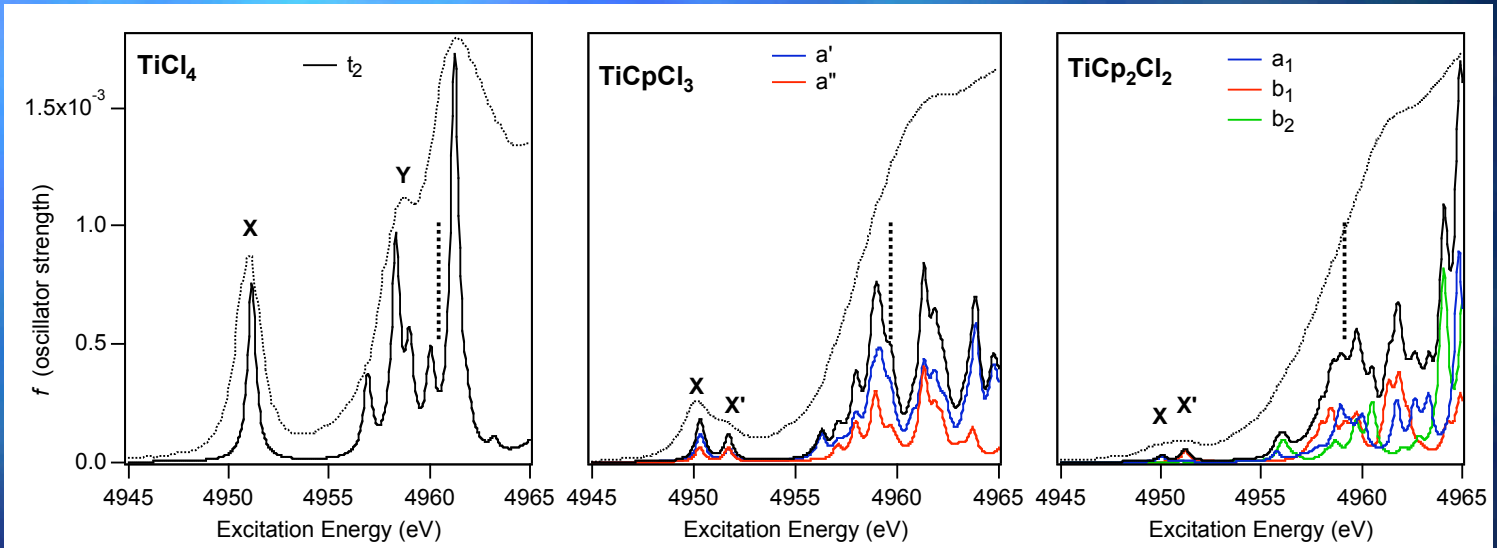
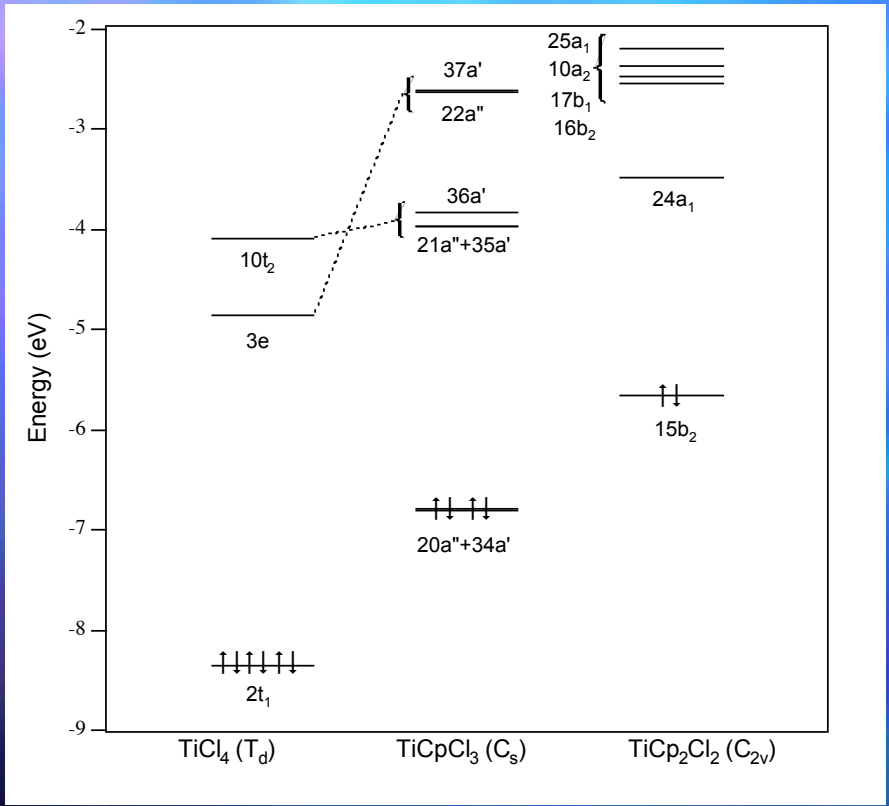
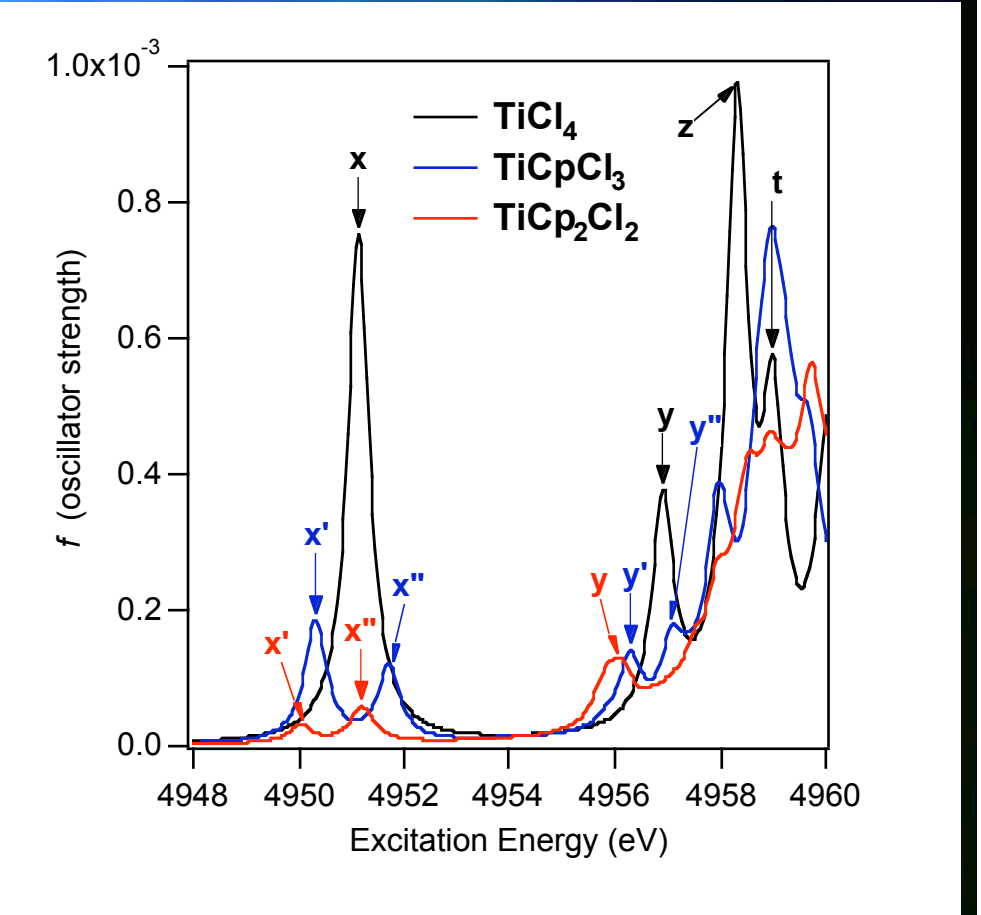
J. Am. Chem. Soc. **2005**, *217*, 667





Casarin et al. *J. Phys. Chem. A* **2007**, *111*, 24





Casarin et al. *J. Phys. Chem. A* **2007**, *111*, 24

Cl K-edge
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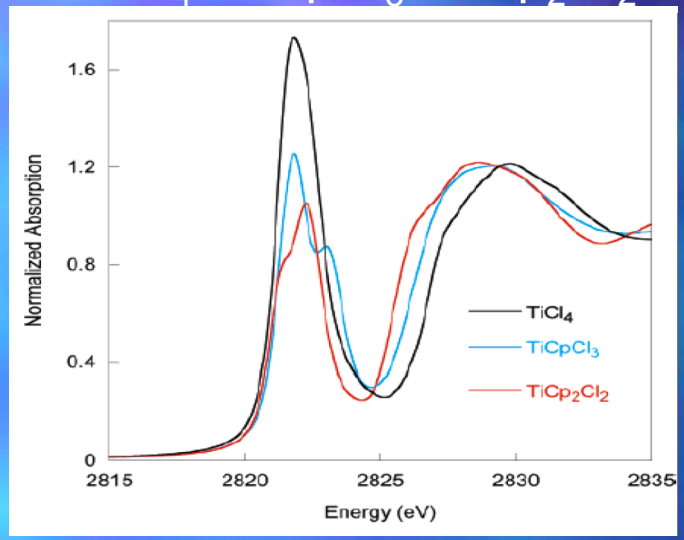
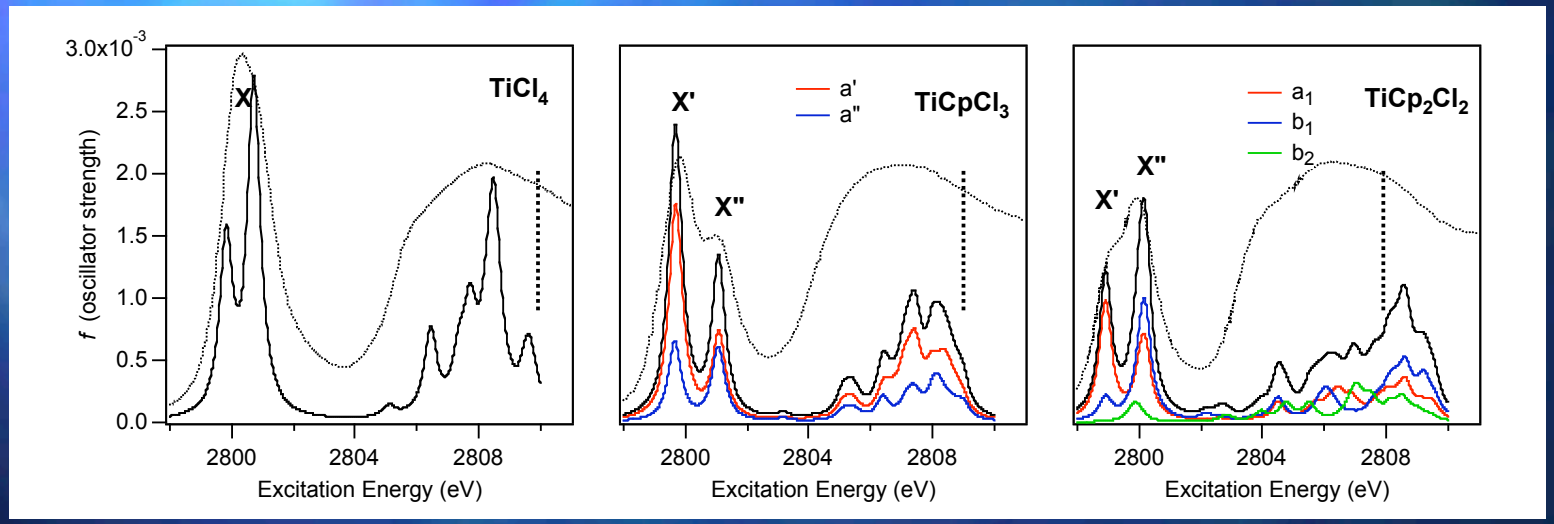


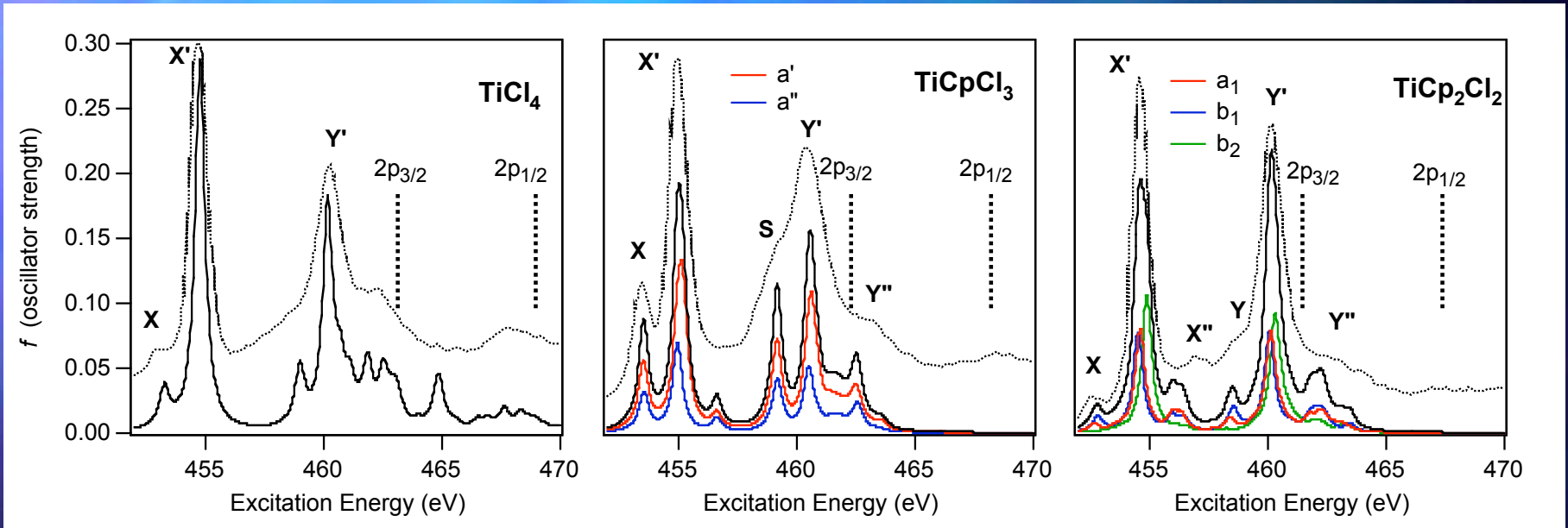
DeBeer George *et al.*

J. Am. Chem. Soc. **2005**, *217*, 667



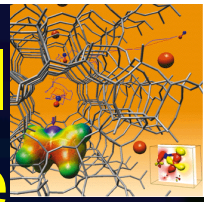
Casarin et al. *J. Phys. Chem. A* **2007,** *111*, 24

Ti $L_{2,3}$-edge



Casarin et al. *J. Phys. Chem. A* **2007**, *111*, 24

2 Molecular nanostructures as model systems and as building blocks for the bottom-up synthesis of functional nanomaterials



Surface-supported organic nanostructures of interest for:

- catalysis
- sensing devices
- molecular electronics
- non-linear optical properties
- molecular recognition
- model systems for the study of biological activity
- …

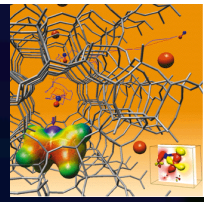
Factors affecting molecular self-assembly

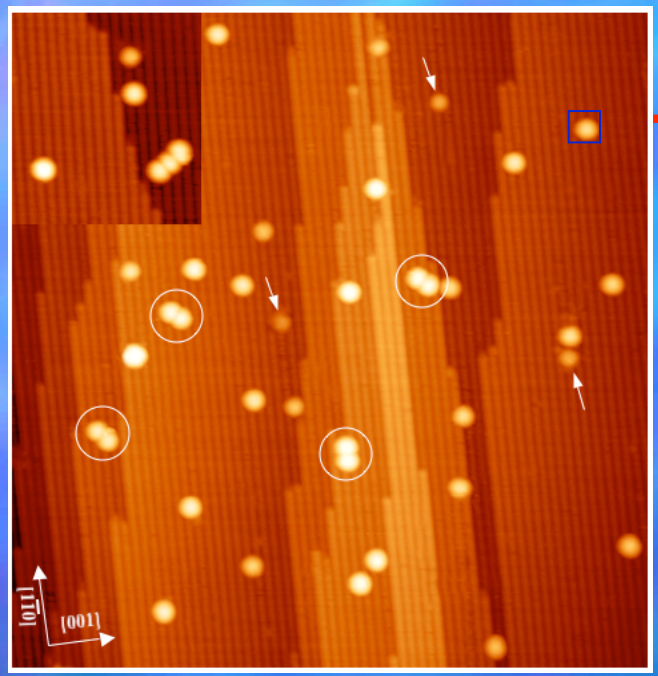
- substrate chemical composition, structure, symmetry and energetics
- vertical molecule-substrate vs lateral intermolecular interactions
- molecular functionalization
- chirality

Characterization tools

- SPM (STM)
- computational chemistry methods

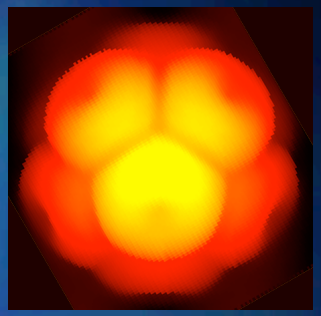
C_{60} on (1 × 2) Pt (110): room temperature deposition





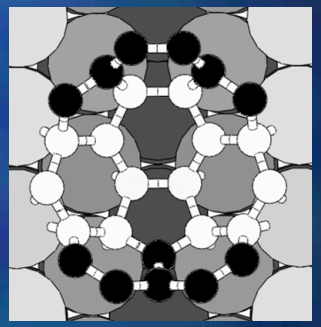
62 × 62 nm²
(inset: 16.5 × 19 nm²)

1.9 × 1.9 nm²



DFT simulation
Tersoff - Hamann

E_{ads}=3.81 eV!

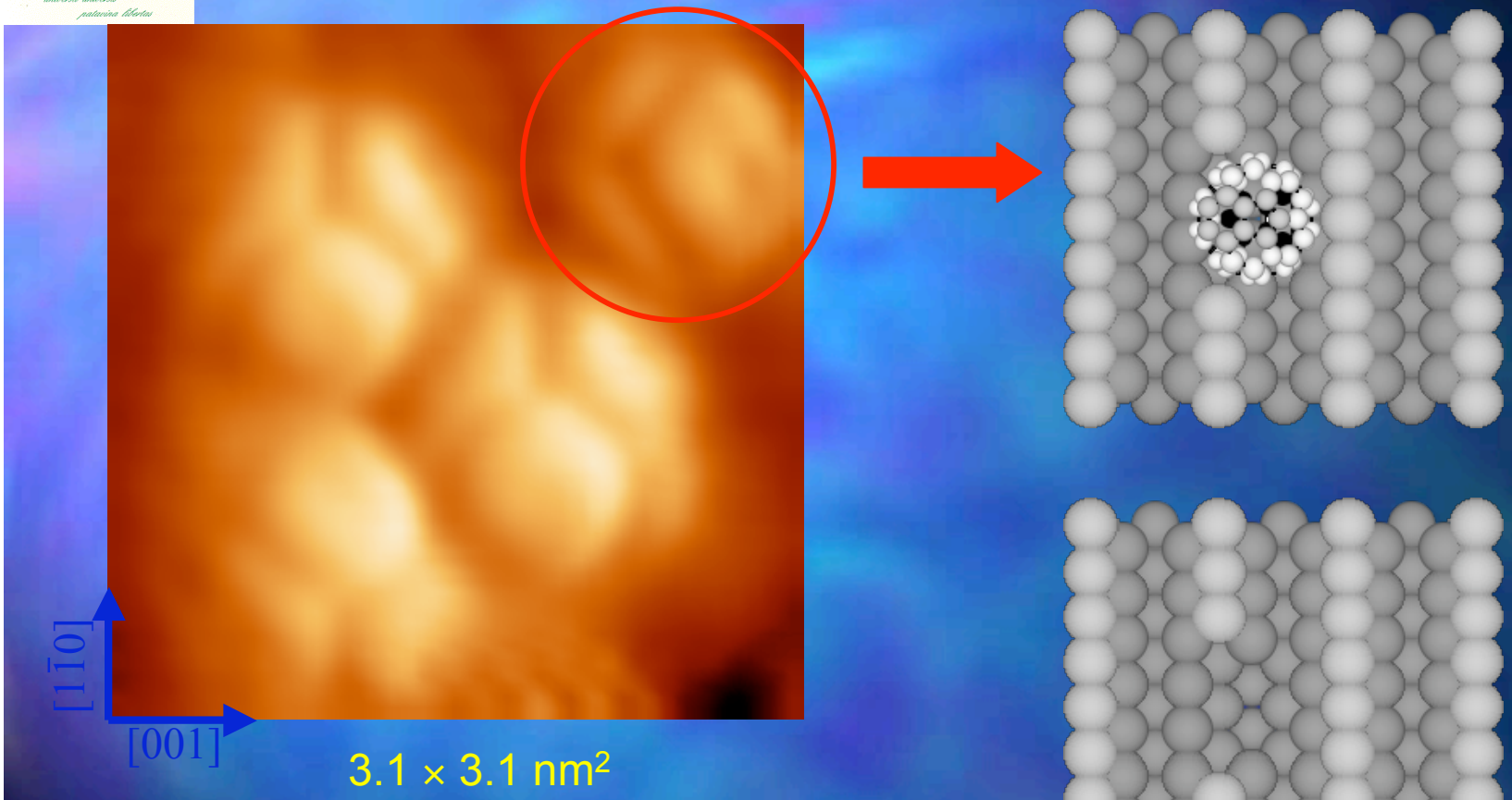


DFT model: “M1 site”

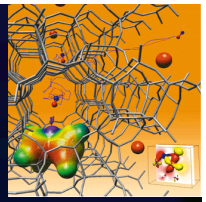
Covalent bonding

Casarin et al. *J. Phys. Chem. C* **2007**, *111*, 9365

C_{60} on (1 × 2) Pt (110): defect decoration



Casarin et al. *J. Phys. Chem. C* **2007**, *111*, 9365



"People want to change the natural into the useful unnatural"

Hoffmann, R.
in the Introduction to "*The new* chemistry"
Nina Hall ed.
Cambridge University Press, 2000

Thanks to

Correzzola Claudio

Forrer Daniel

Orzali Tommaso

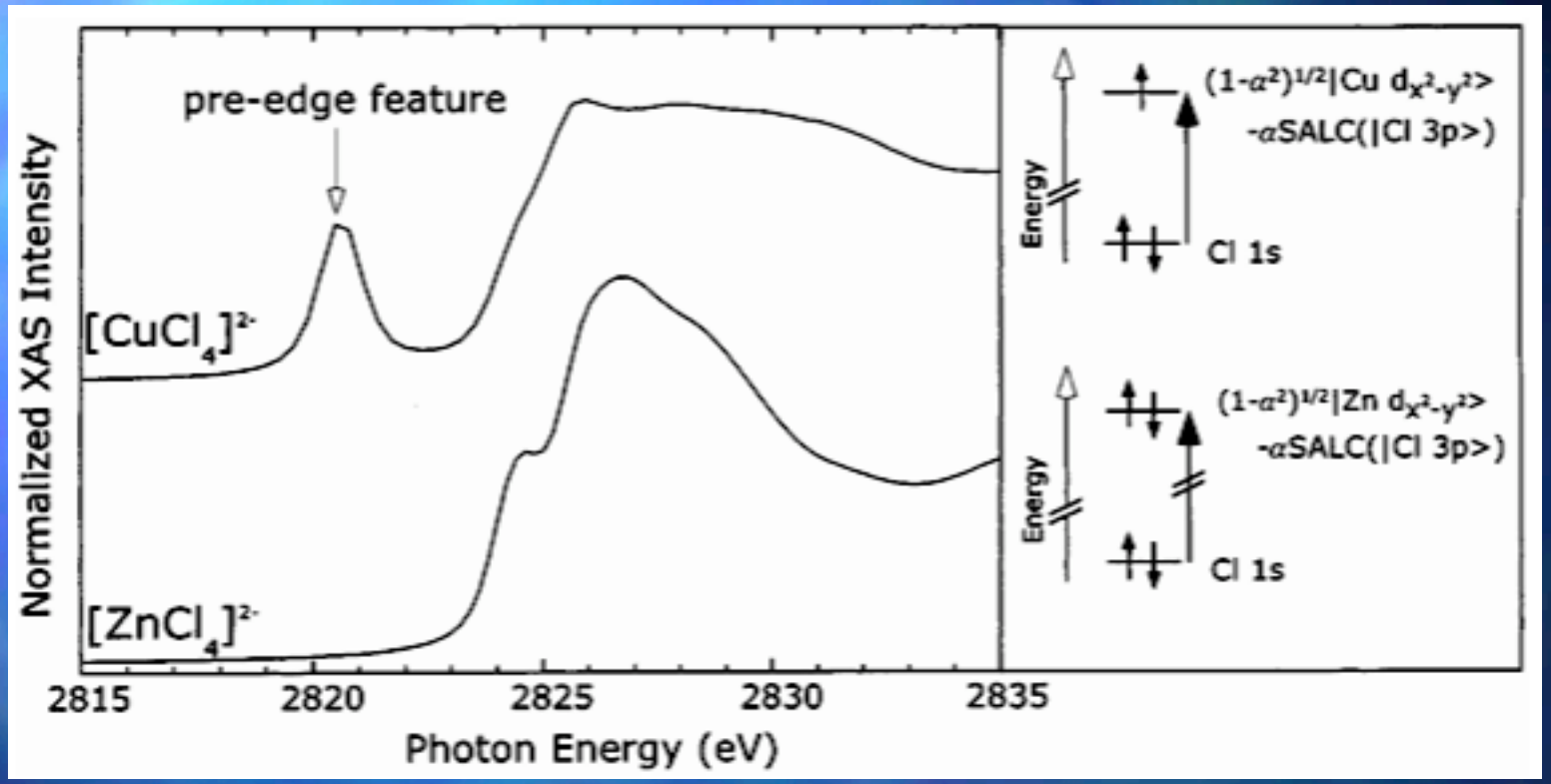
Sambi Mauro

Sedona Francesco

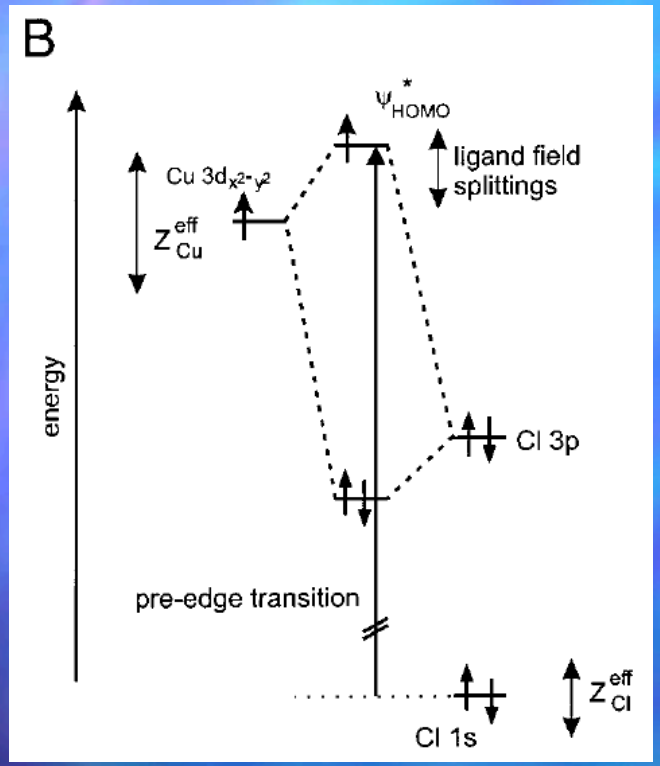
Tondello Eugenio

Vittadini Andrea

Ligand K-edge X-ray absorption spectroscopy (XAS) is a new experimental probe of the covalency of a metal-ligand bond.



The principal ligand K-edge XAS experiment and illustrative experimental data for $[CuCl_4]^{2-}$ and $[ZnCl_4]^{2-}$.



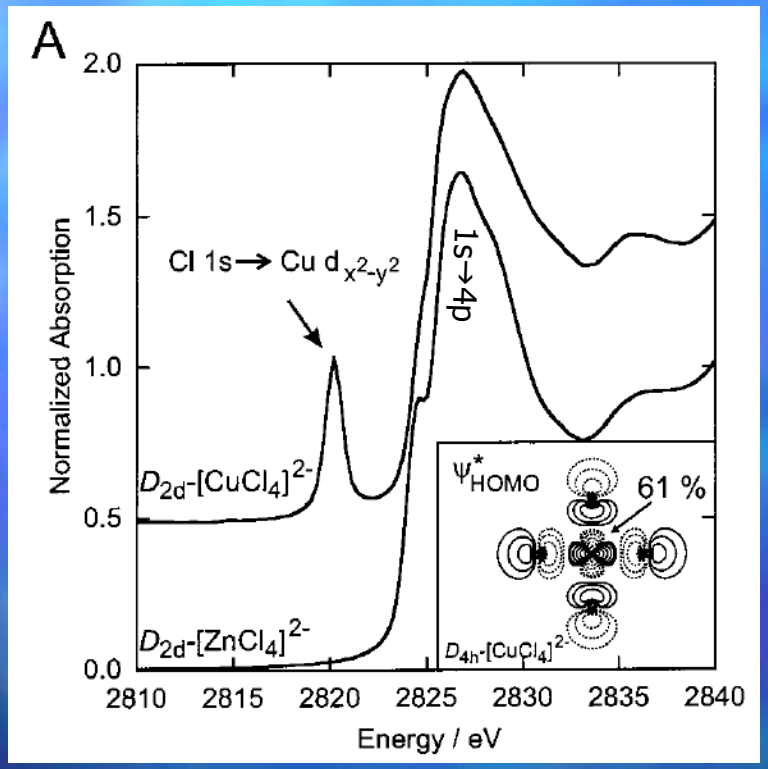
Orbital energy diagram showing the ligand pre-edge transition.

$$\psi^* = \sqrt{\left(1-\alpha^2\right)}\left|\text{Cu } 3d_{x^2-y^2}\right\rangle - \alpha\left|\text{Cl } 3p\right\rangle$$

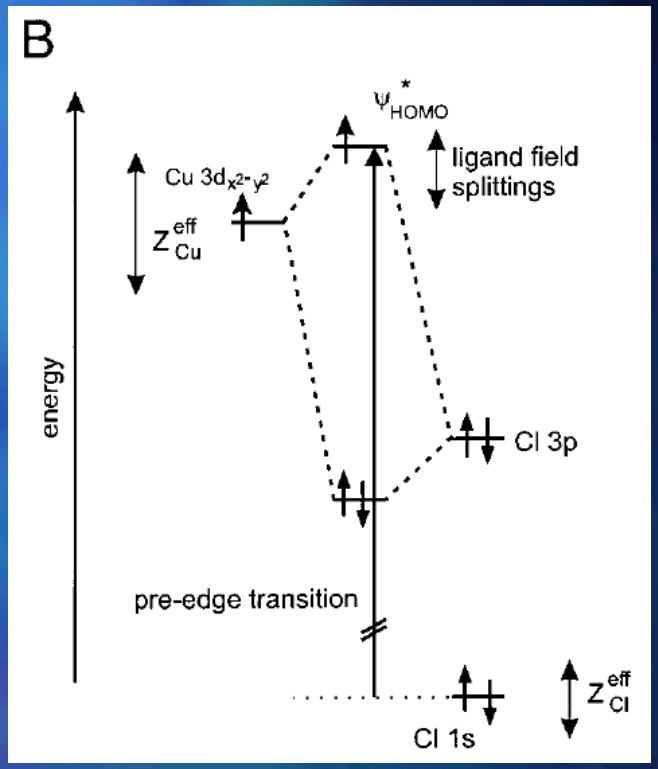
$$\text{Cl } 1s \rightarrow \psi^*$$

$$\text{Int}\left(\text{Cl } 1s \rightarrow \psi^*\right) = \text{const}\left|\left\langle \text{Cl } 1s\left|\vec{r}\right|\psi^*\right\rangle\right|^2 \approx \alpha^2 \text{const}\left|\left\langle \text{Cl } 1s\left|\vec{r}\right|\text{Cl } 3p\right\rangle\right|^2$$

Ligand K-edge spectroscopy is a direct probe of the covalency of a metal-ligand bond.



Cl K-edge XAS spectra of $[ZnCl_4]^{2-}$ and D_{2d}-$[CuCl_4]^{2-}$; inset shows the $d_{x^2-y^2}$ HOMO of D_{4h}-$[CuCl_4]^{2-}$.



Orbital energy diagram showing the ligand pre-edge transition.

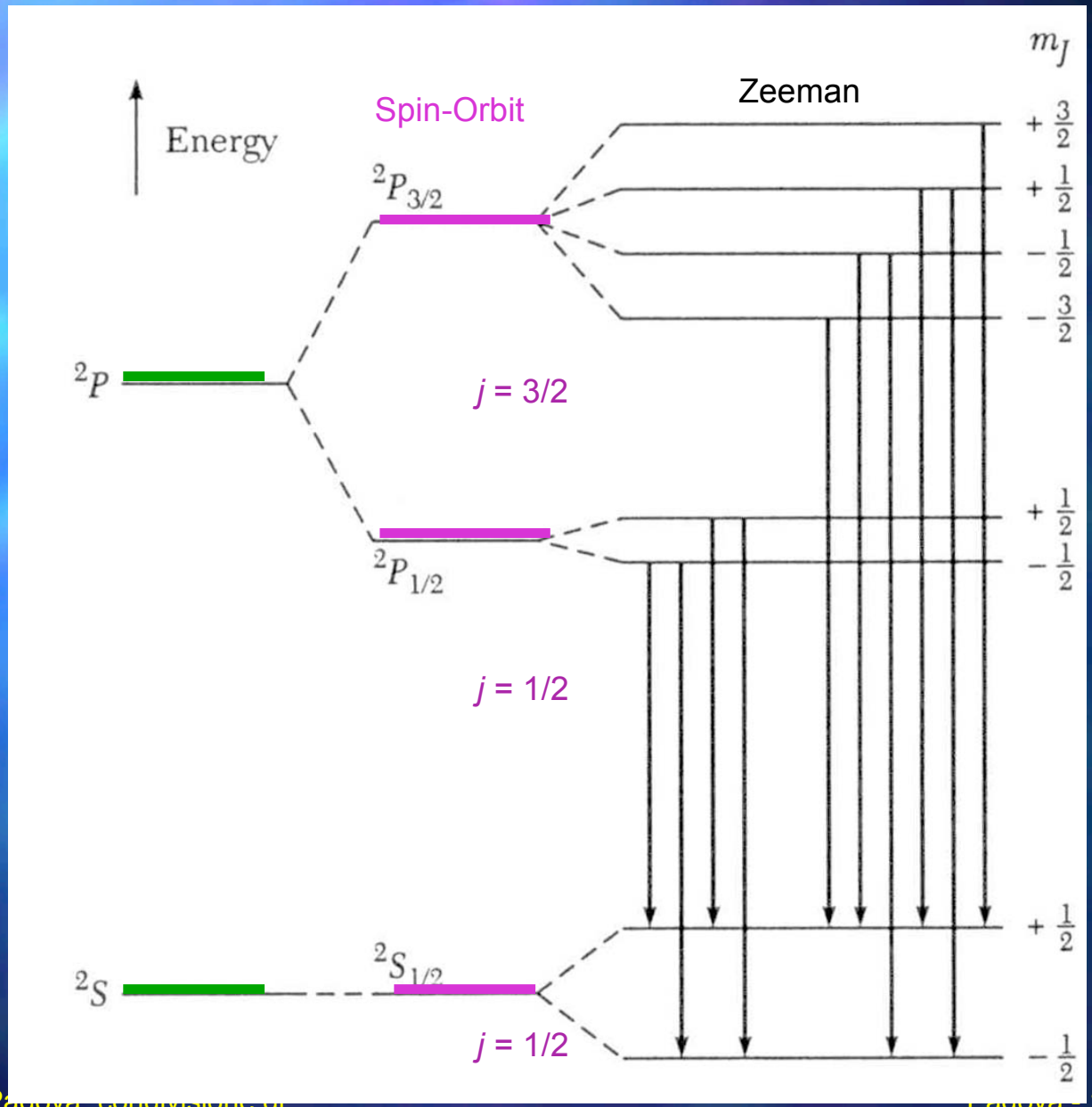
	Ligand K-edge L—M	Charge-Transfer L—M
Acceptor MO	 $(1-\alpha^2)^{1/2}\|M\ 3d\rangle-\alpha\|L\ np\rangle$	 $(1-\alpha^2)^{1/2}\|M\ 3d\rangle-\alpha\|L\ np\rangle$
Donor MO	 $\|L\ 1s\rangle$	 $\alpha\|M\ 3d\rangle+(1-\alpha^2)^{1/2}\|L\ np\rangle$
Transition Density		
Transition Dipole Moment	 $\alpha\langle 1s\|x\|np\rangle$	 $\alpha(1-\alpha^2)^{1/2}R$

Comparison of the electric dipole intensity mechanisms for ligand K-edge transitions and optical charge transfer transitions.

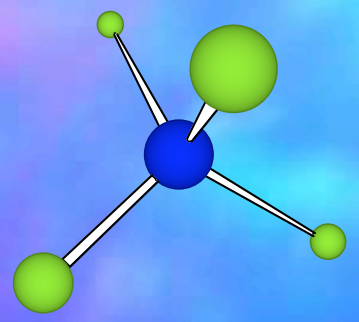
M K-edge: electric dipole forbidden (but quadrupole allowed) $1s^M \rightarrow nd^M$ transitions

M L-edge: electric dipole allowed $2p^M \rightarrow nd^M$ transitions

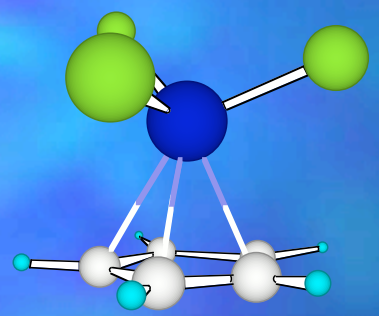
L K-edge: electric dipole allowed $1s^L \rightarrow np^L$ transitions


Energy
Spin-Orbit
Zeeman
m_J
$^2P_{3/2}$
^2P
j = 3/2
$^2P_{1/2}$
j = 1/2
$^2S_{1/2}$
^2S
j = 1/2
$+\frac{3}{2}$
$+\frac{1}{2}$
$-\frac{1}{2}$
$-\frac{3}{2}$
$+\frac{1}{2}$
$-\frac{1}{2}$
$+\frac{1}{2}$
$-\frac{1}{2}$
mj = 3/2
mj = 1/2
mj = –1/2
mj = –3/2
mj = 1/2
mj = –1/2
mj = 1/2
mj = –1/2
ℓ = 1 (p)
s = 1/2
ℓ = 0 (s)
s = 1/2

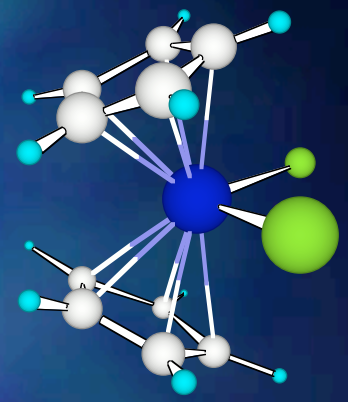
Application of SO-RTD-DFT to closed shell complexes



$TiCl_4$



$Ti(\eta^5\text{-}C_5H_5)Cl_3$

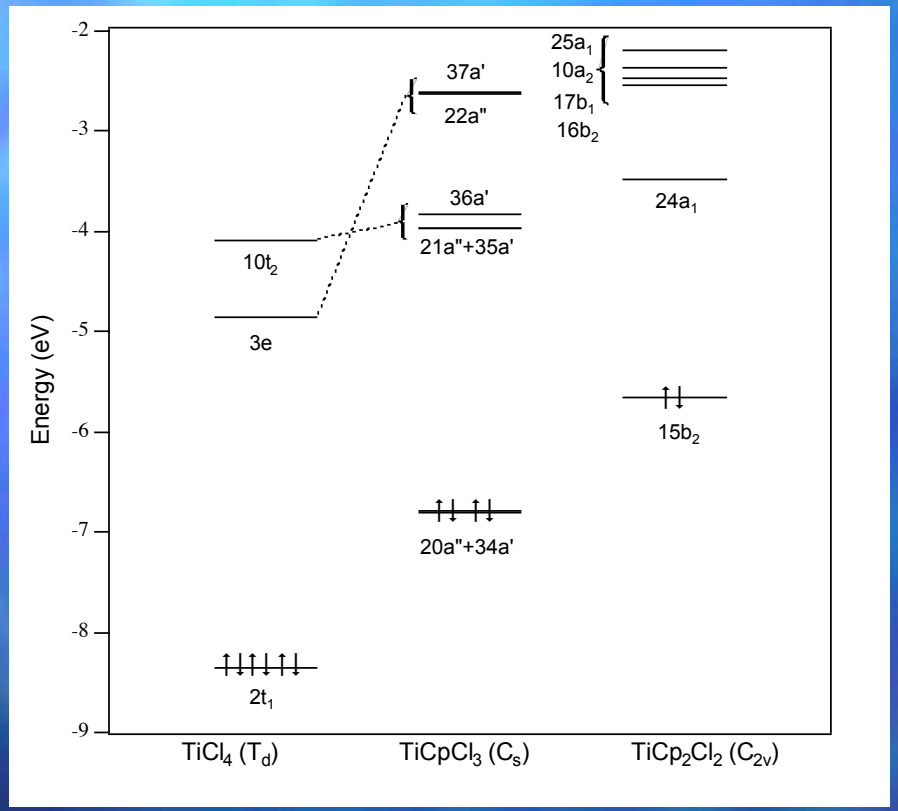


$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$

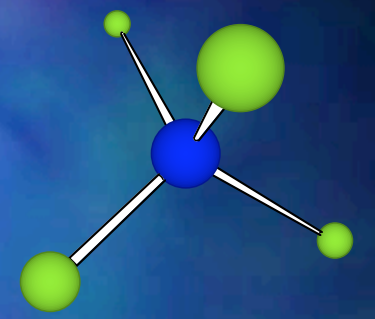
The interest for this complexes has to be ultimately traced back to two factors:

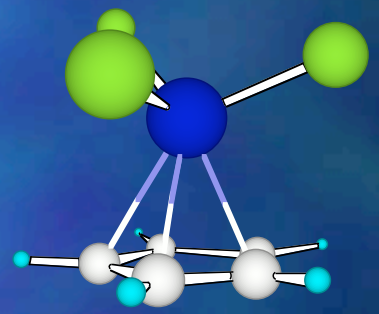
i) the catalytic activity of both mono- and bis-cyclopentadienyl titanium(IV) complexes;

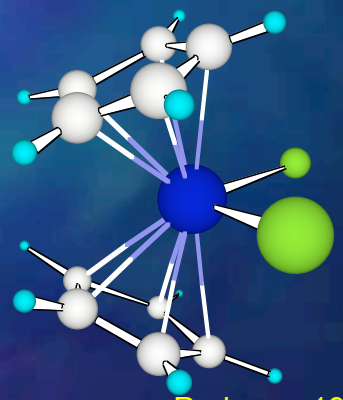
ii) the possible use of titanocene dichloride and its water soluble derivatives as possible alternatives to t he widely used heavy metal based anticancer drugs.

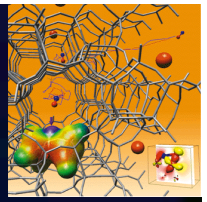


Correlation diagram of $TiCl_4$, $TiCpCl_3$, and $TiCp_2Cl_2$ frontier orbitals









The relativistic two-component *ZORA-TDDFT*

F. Wang et al.

J. Chem. Phys. **2005**, *122,* 204103

This method allows the calculation of excitation energies and intensities for closed shell molecules, including spin–orbit coupling and with full use of symmetry.

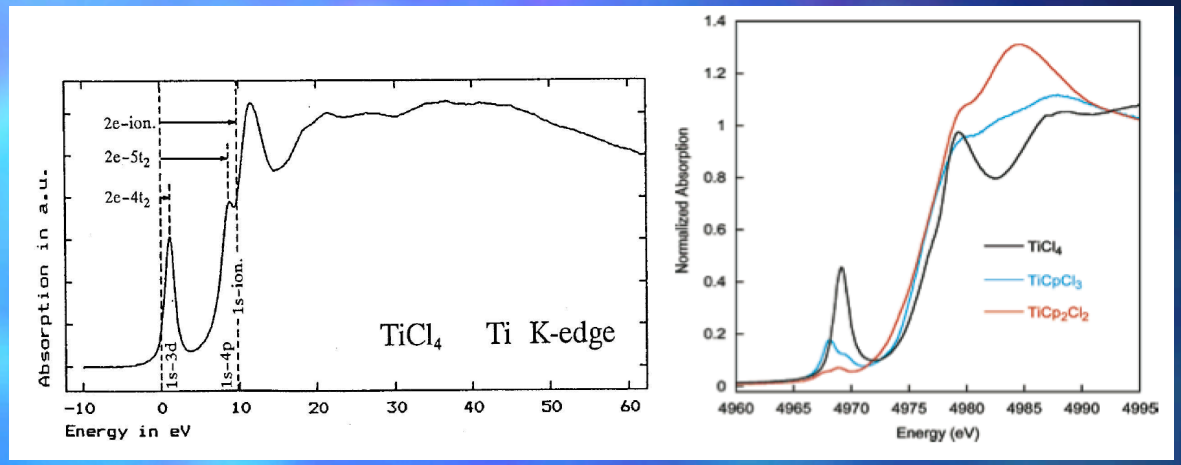
ZORA-TDDFT

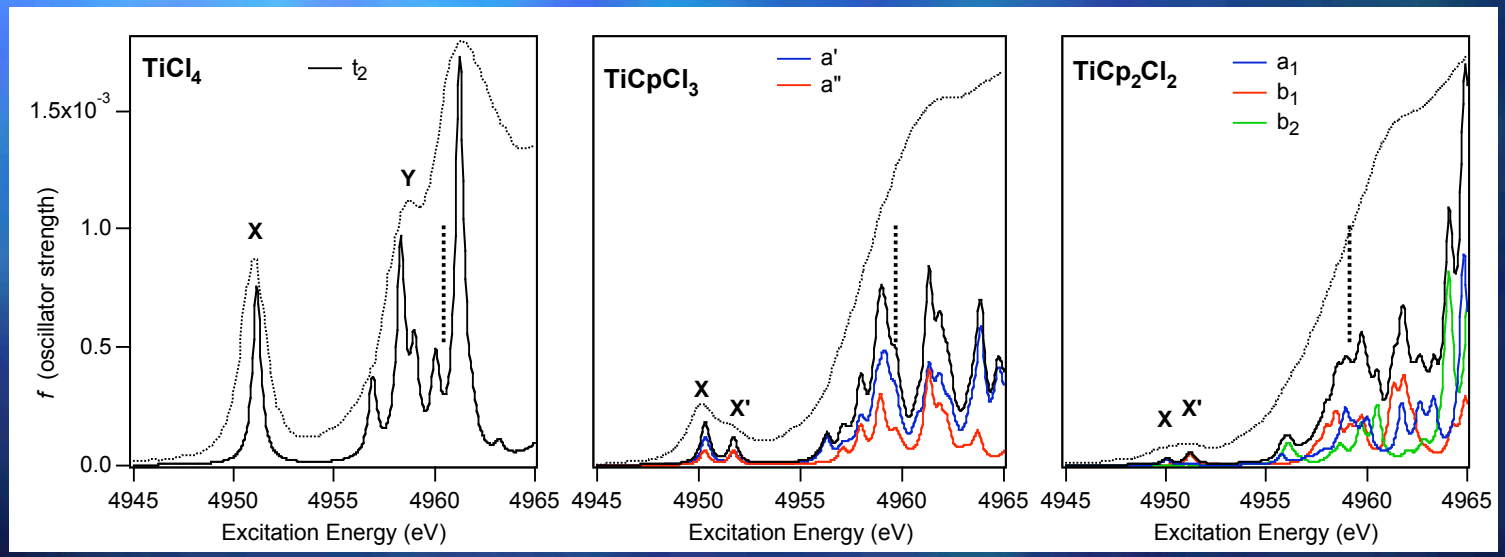
$$\Omega F_\ell = \omega_\ell^2 F_\ell$$

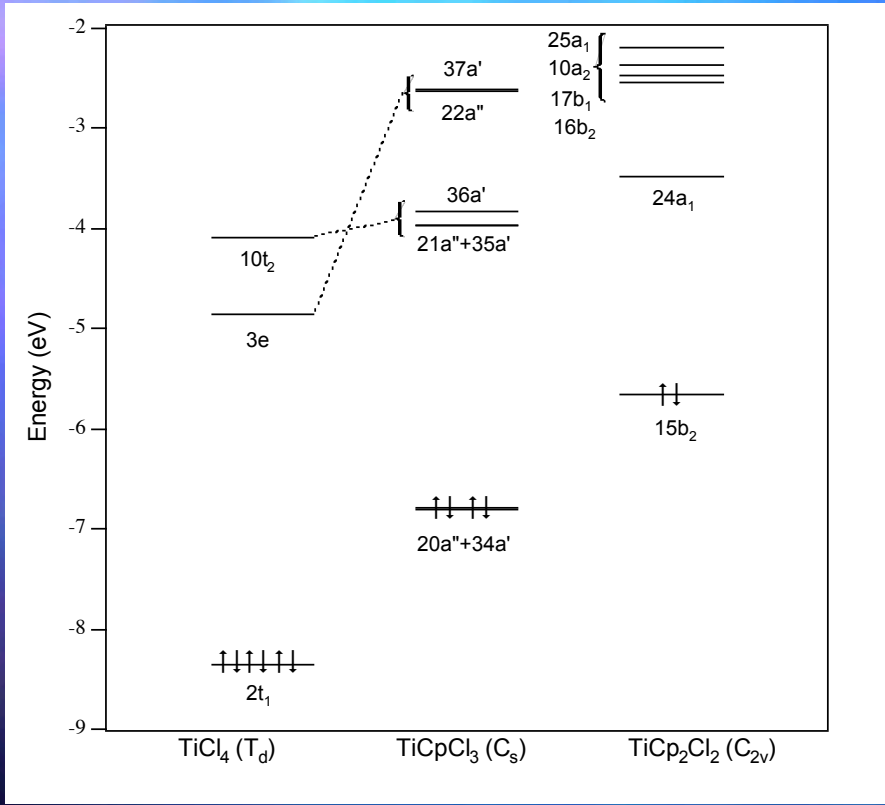
ω_ℓ^2 = corresponds to to square of the excitation energies

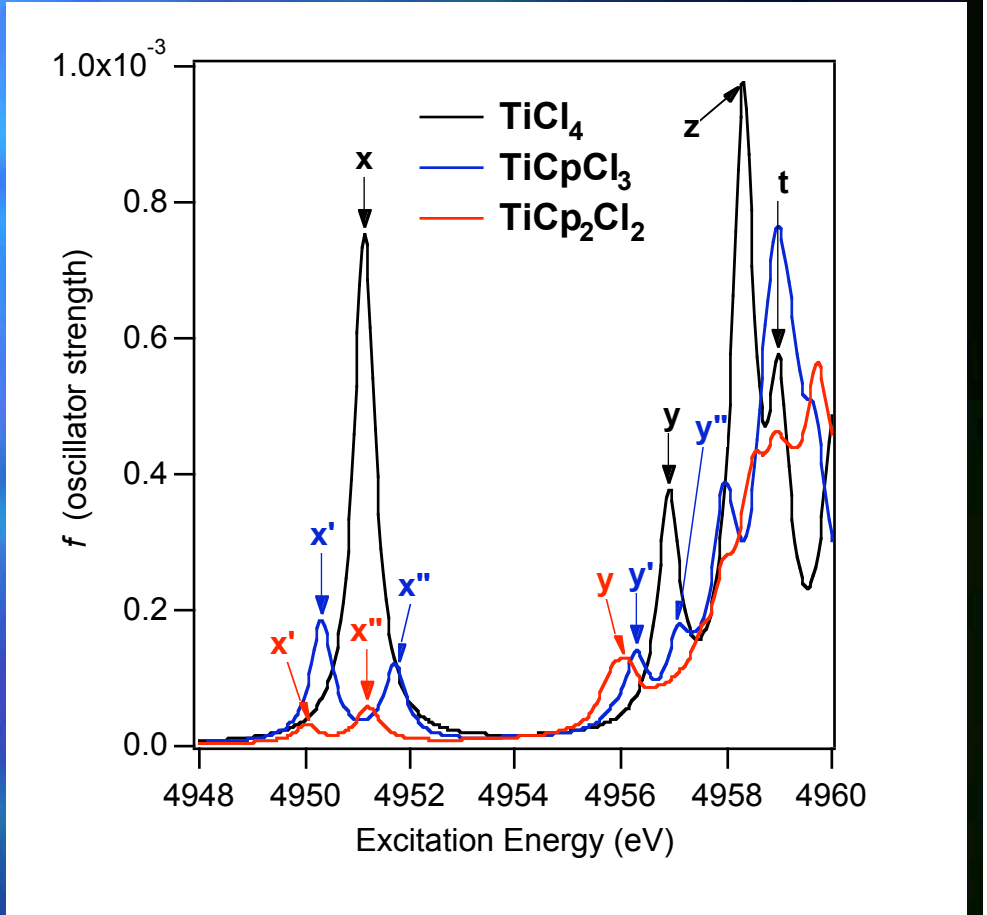
The oscillator strength f_ℓ can be exctracted from F_ℓ

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right)^2 + 2\sqrt{\left(\varepsilon_a - \varepsilon_i\right)}\frac{\partial F_{ia}}{\partial P_{jb}}\sqrt{\left(\varepsilon_b - \varepsilon_j\right)}$$

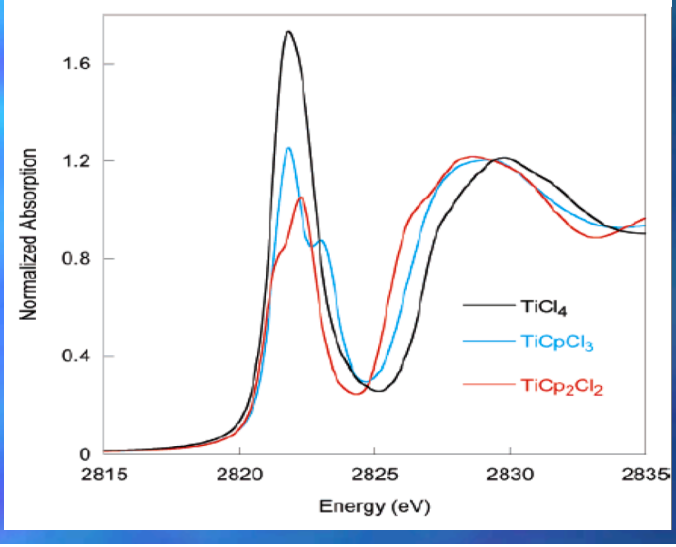
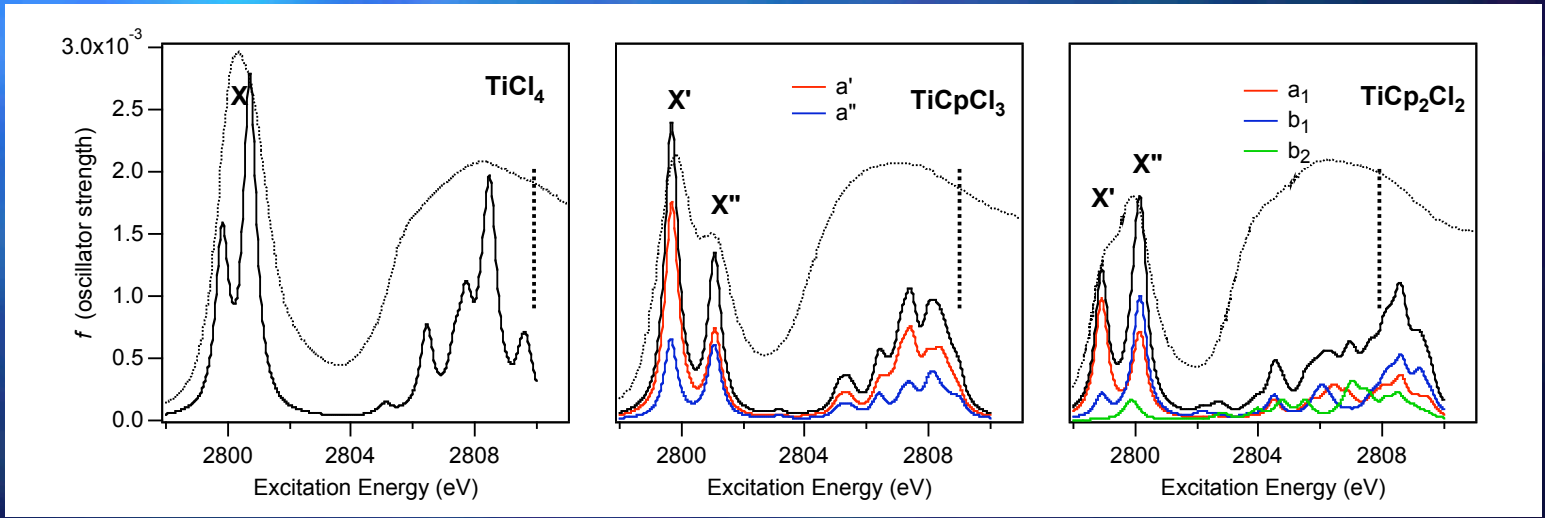

2e-ion.
2e-5t2
2e-4t2
1s-3d
1s-4p
1s-ion.
TiCl4 Ti K-edge
Absorption in a.u.
Energy in eV
Normalized Absorption
Energy (eV)
TiCl4
TiCpCl3
TiCp2Cl2


TiCl4
t2
X
Y
TiCpCl3
a'
a"
X
X'
TiCp2Cl2
a1
b1
b2
X
X'
f (oscillator strength)
Excitation Energy (eV)


Energy (eV)
-2
-3
-4
-5
-6
-7
-8
-9
2t1
3e
10t2
37a'
22a"
36a'
21a"+35a'
20a"+34a'
25a1
10a2
17b1
16b2
24a1
15b2
TiCl4 (Td)
TiCpCl3 (Cs)
TiCp2Cl2 (C2v)


1.0x10-3
0.8
0.6
0.4
0.2
0.0
f (oscillator strength)
TiCl4
TiCpCl3
TiCp2Cl2
x
x'
x"
y
y'
y"
z
t
4948
4950
4952
4954
4956
4958
4960
Excitation Energy (eV)

Cl K-edge
$TiCl_4$, $TiCpCl_3$, $TiCp_2Cl_2$

DeBeer George *et al.*

J. Am. Chem. Soc. **2005**, *217*, 667