Quantum Chemistry approaches to correlations & spectroscopies (1,2)

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MAX-PLANCK-INSTITUT FÜR
CHEMISCHE ENERGIEKONVERSION

Molecular Theory and Spectroscopy
Prof. Dr. Frank Neese

- Advanced Experimental
  and Theoretical Spectroscopy group

Heterogeneous Reactions
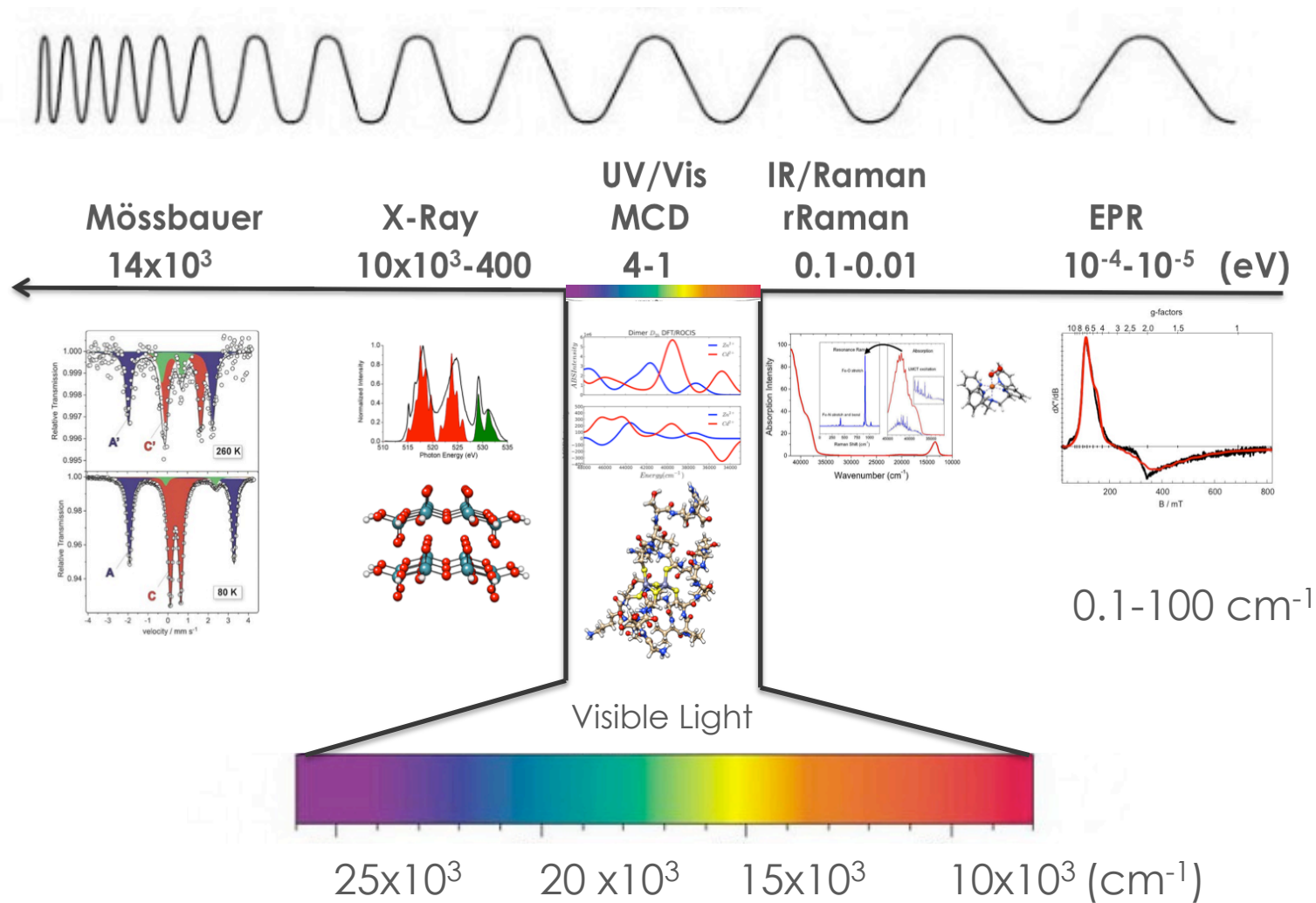Prof. Dr. Robert Schlögl

X-Ray spectroscopy
Prof. Dr. Serena DeBeer

Department of Molecular Theory and Spectroscopy

The spectroscopic energy scale

Mössbauer	X-Ray	UV/Vis MCD	IR/Raman rRaman	EPR
14×10^3	$10 \times 10^3 - 400$	$4-1$	$0.1-0.01$	$10^{-4} - 10^{-5}$ (eV)

$0.1-100$ cm^{-1}

Visible Light

25×10^3 20×10^3 15×10^3 10×10^3 (cm^{-1})

Theoretical Methodologies to X-RAY Spectroscopies

States vs Orbitals

States versus Orbitals

It is essential to understand that **Orbitals** are **NOT** observables

What is observed in Spectroscopy are the many electron states

In the simplest MO picture **STATES** are constructed as follows:

- Specify how electrons are distributed over the availiable MOs:
  Spatial configuration vector **n**=(n_1,n_2,n_3)
- Couple the unpaired electrons to the desired **total spin S.**
  There are several ways to do that, a given spin coupling is
  denoted as $S_K M$)
- Determine the spatial symmetry of the state by taking the
  direct product of all single occupied MOs (Irreps denoted as
  ΓM_Γ)

Note: Total Spin $\hat{S} = \sum_i \hat{s}_i$

Projection $\hat{S}_z = \sum_i \hat{s}_{zi}$

} „Constants of Motion"

Relationships $\left[\hat{S}_p, \hat{s}_{jq}\right] = i\hbar\varepsilon_{pqr}\hat{s}_{jr}$

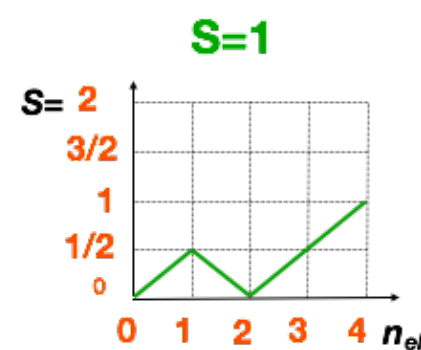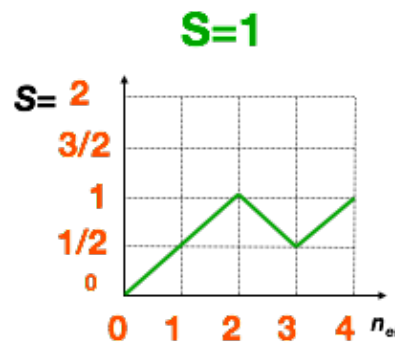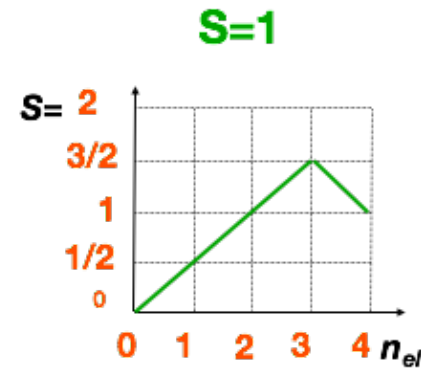*Deep connection; basis for the application of the Wigner-Eckart theorem to the total spin problem*
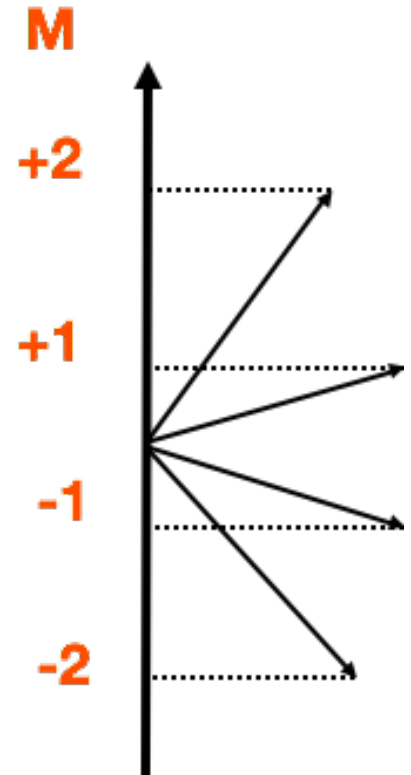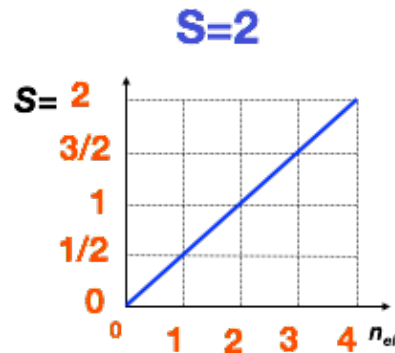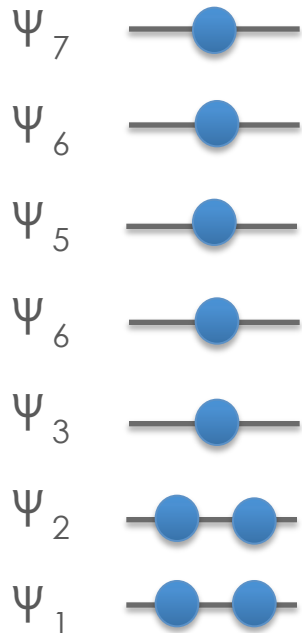
What does it mean Really?

- Now we have found out that for three electrons in three orbitals we have two eigenfunctions with S=1/2.

- Typical situation: excited state of a radical

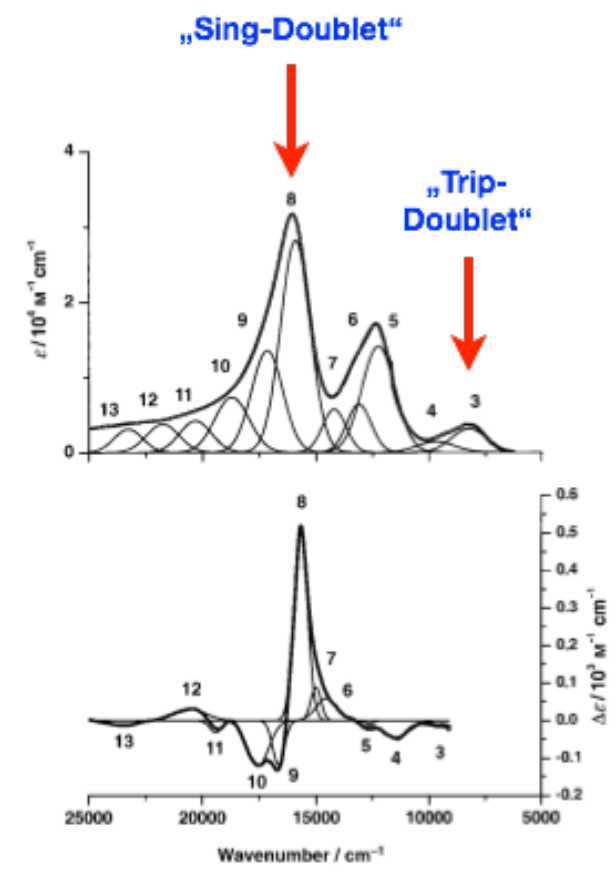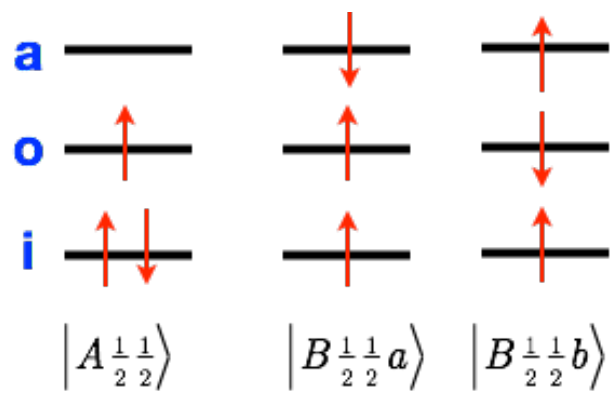$$\left| A \tfrac{1}{2}\tfrac{1}{2} \right\rangle = \left| \psi_i^\beta \psi_i^\beta \psi_o^\alpha \right|$$

$$\left| B \tfrac{1}{2}\tfrac{1}{2} a \right\rangle = \sqrt{\tfrac{1}{2}} \left(\left| \psi_i^\alpha \psi_a^\beta \psi_o^\alpha \right| - \left| \psi_i^\beta \psi_a^\alpha \psi_o^\alpha \right| \right)$$

$$\left| B \tfrac{1}{2}\tfrac{1}{2} b \right\rangle = \sqrt{\tfrac{1}{6}} \left(2\left| \psi_i^\alpha \psi_o^\alpha \psi_o^\beta \right| - \left| \psi_i^\beta \psi_a^\alpha \psi_o^\alpha \right| - \left| \psi_i^\alpha \psi_a^\beta \psi_o^\alpha \right| \right)$$

Ground State

„Sing-Doublet"

„Trip-Doublet"

Bill. E. et al. (**2004**) *Chem. Eur. J.,* <u>11, 204</u>

The Multiplet Problem

- What we have just realized is a general phenomenon: **More than one states can arise from a given orbital configuration.** These are called **MULTIPLETS**
- They are difficult to treat if one starts from a single reference determinant since many of the multiplet components look like higher excitations on a spin-orbit level
- Typical examples:

  Russel-Saunders terms in atoms and ions:
  e.g. d^7: $^4F + {}^4P + {}^2G + {}^2P + {}^2H + {}^2D + {}^2F$

  d-d excited states of transition metal complexes
  e.g. $(t_{2g})^2(e_g)^0$: $^3T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}$

  core excited states of transition metal complexes
  e.g. $(2p)^5(3d)^m$, $m=0\text{-}10$
  Others:

  Exchange couplings in oligomeric transition metal cluster

  Metal Radicals

Optical Spectroscopy

Molecules exist in states!

Application of any kind of perturbing field with Hamiltonian H1(ω) will **induce** transition between the **different states** of the systems

$\left| KS'''M'''\Gamma''' \right\rangle$

$\left| JS''M''\Gamma'' \right\rangle$

$\left| IS'M'\Gamma' \right\rangle$

$\left| 0SM\Gamma \right\rangle$

Energy

Intensity

Transition Probability
(„Fermi's Golden Rule")

$$ I \propto \left| \left\langle \Psi_{initial} \mid H_1 \mid \Psi_{final} \right\rangle \right|^2 $$
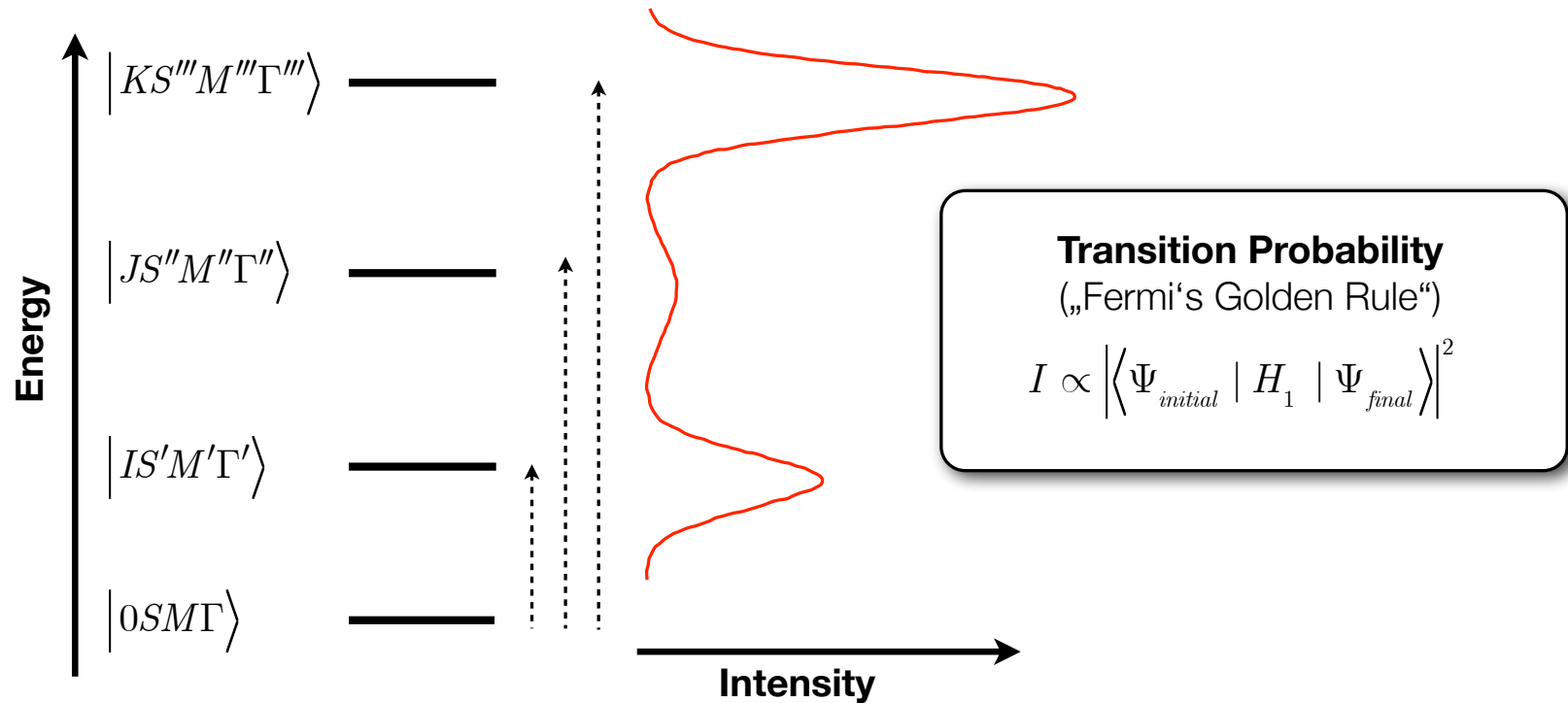
Optical excitations and beyond

Total Spin S'

$\downarrow$

2S'+1 Components
Ms=S',S'-1,...,-S'

valence

core

Electronically
Excited State
Multiplet

Total Spin S

$\downarrow$

2S+1 Components
Ms=S,S-1,...,-S

valence

core

Electronic
Ground State
Multiplet

$|+1/2\rangle$

$g^{es} \beta$ B

Δ E=~0-10 cm^{-1}
**Excited State
SH:g^{es}, D^{es}...**

$|-1/2\rangle$

Δ E=1-8000 eV

$|+1/2\rangle$

$g^{gs} \beta$ B

Δ E=~0-10 cm^{-1}
**Ground State
SH:g^{gs}, D^{gs}...**

EPR

$|-1/2\rangle$

Electronic Transitions
Probed by **ABS, MCD**, **XAS, XMCD**...

Magnetic Field
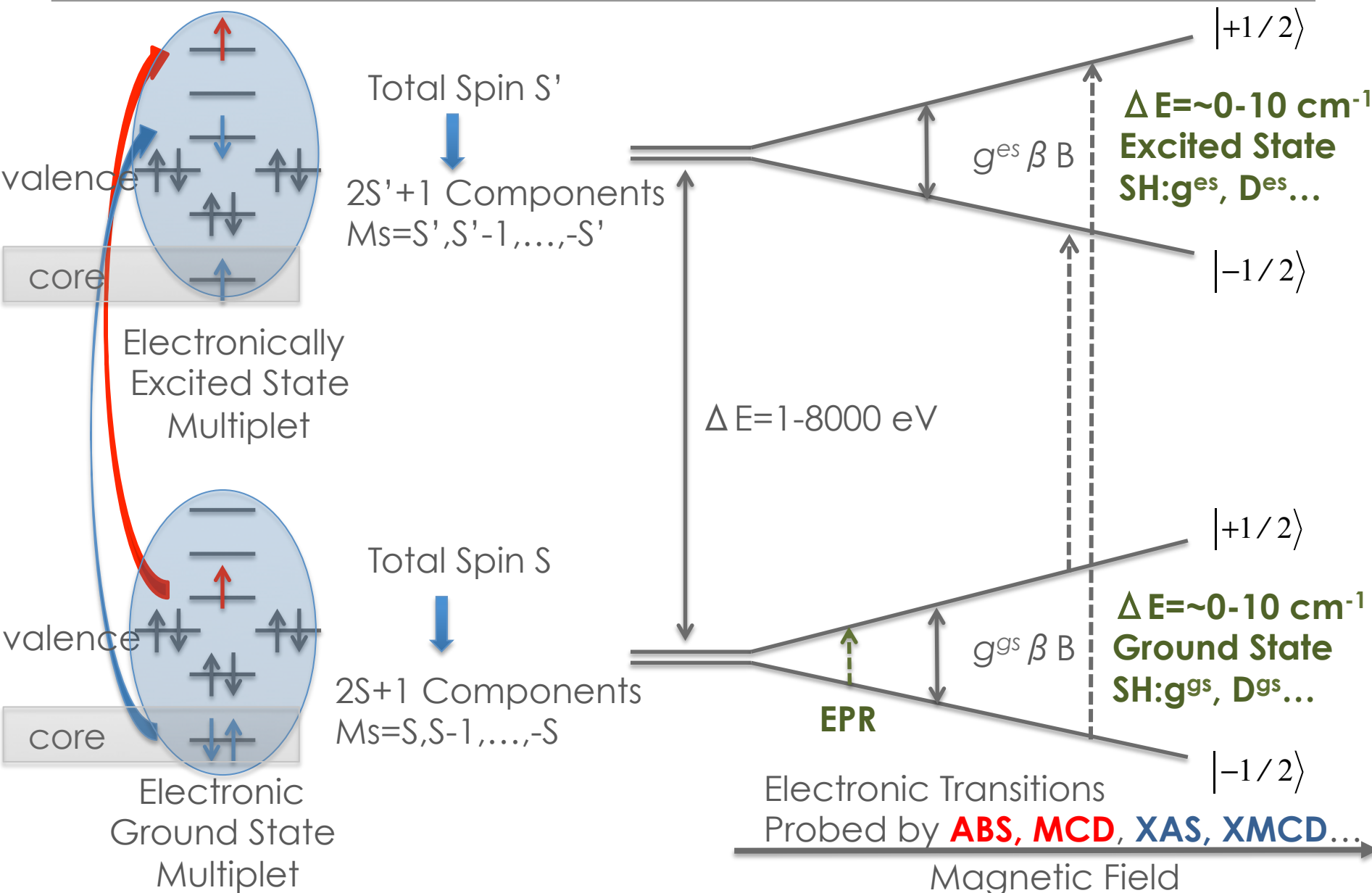
Type of Excitations in Transition Metals
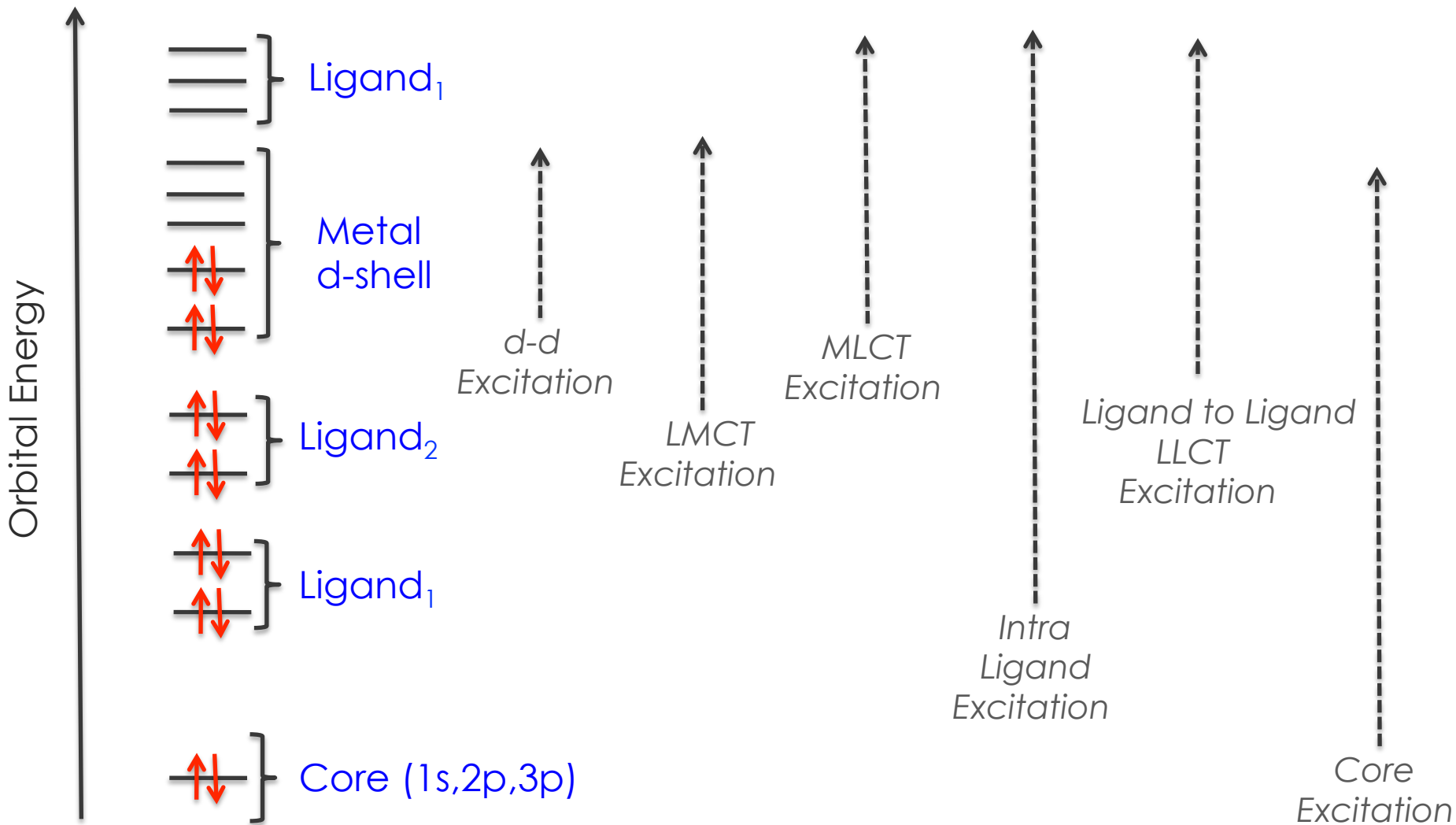
- Many if not most organic and main group compounds exist in states that are well described by a single closed-shell determinant of the HF type:

- However, the fun starts if this is not the case, e.g. in:
  Short lived radicalic reaction intermediates
  Stable radicals as in spin labels
  Diradicals
  Radical Pairs
  Triplet states (carbenes, excited states)
  Transition metal complexes
  Oligonuclear transition metal clusters
  Metal radical assemblies
  ...
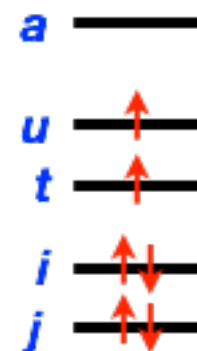
  These molecules are much more difficult to describe accurately with quantum chemical methods

- The easiest open-shell situation is met when there are no degenerate orbitals and **n electrons occupy n orbitals**, all with spin-up (**HIGH-SPIN-STATE S=n/2**)

- These '**Principle component**' (**$M=S$**) can be described by a single determinant:

$$\left| ...\psi_i \, ...\psi_j \, ...\psi_t \, \psi_u ... \right|$$
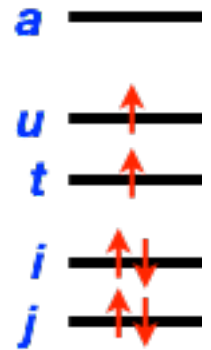
- It is now up to us how to distribute the electrons in groups. One way of doing this is to divide the electrons in spin-up and spin-down groups and optimize a determinant of the **unrestricted Hartree-Fock (UHF)** type ($n_\alpha - n_\beta = n$):

$$\left| \Psi_{UHF}^{SS} \right\rangle = \left| ...\psi_i^\alpha ...\psi_j^\alpha ...\psi_{n_\alpha}^\alpha ...\overline{\psi}_i^\beta ...\overline{\psi}_j^\beta ...\overline{\psi}_{n_\beta}^\beta \right|$$

the spatial orbitals ψ_i^α and ψ_i^β may look totally different.

- The other choice is to group electrons into 'closed-shell' and 'open-shell' electrons and optimize a determinant of the **restricted open-shell Hartree-Fock (ROHF)** type:

the overbar means a spin-down spin-function, non of them is spin-up

$$\left| \Psi_{ROHF}^{SS} \right\rangle = \left| ...\psi_i \, \overline{\psi}_i \, ...\psi_j \, \overline{\psi}_j \, ...\psi_t \, \psi_u ... \right|$$

Methods for excited and open shell states

- ROHF is a ‚cleaner' technique than UHF:
  It can describe more complicated open-shell situations properly that require more than one-determinant:
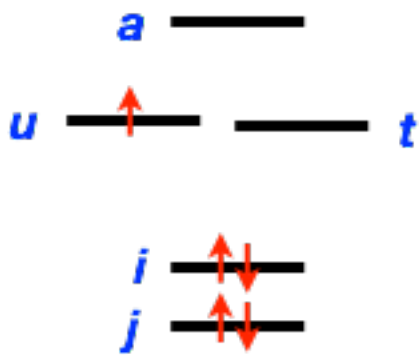
Degenerate states
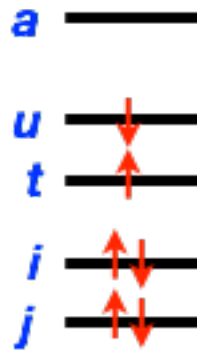
Open-Shell Singlets
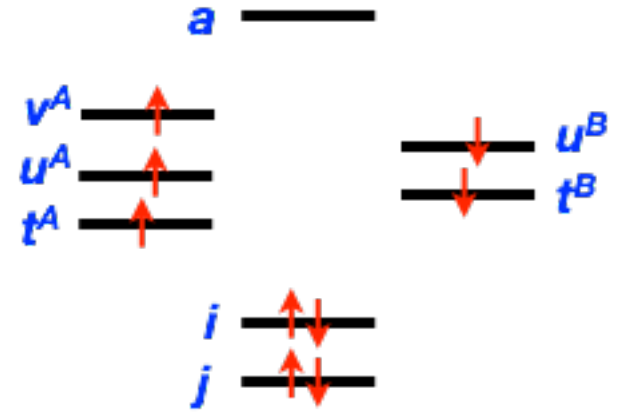
Antiferromagnetic Coupling

Complete Active Space Self Consistent Field (CASSCF)

Configuration State Function Space

Virtual
a,b,c,d
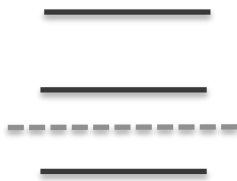
Active
p,q,r,s

Inactive
I,j,k,l

$$\left| \Psi_I^{SM(0)} \right\rangle = \sum_{K \in CAS} d_{KI} \left| \Phi_K^{SM;CAS} \right\rangle$$
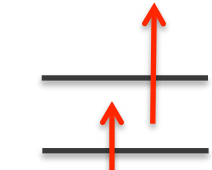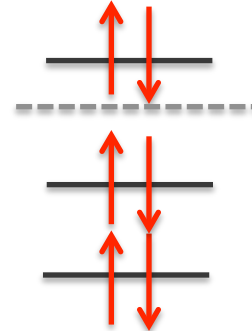
- Single-Double excitations within the active space
  - Active space ~14 electrons
  - Static correlation
  - SOC is included

- Perturbative treatment of Dynamic correlation through the NEVPT2 scheme

➢ Optical spectroscopy
➢ Magnetic properties
- Core el. Spectroscopies?

Multi Reference Configuration interaction (MRCI)

CASSCF calculations often provide a good qualitative starting point for the description of the states of interest.

But in order to cover dynamic correlation there are many more excitations that we can make on top of the CAS
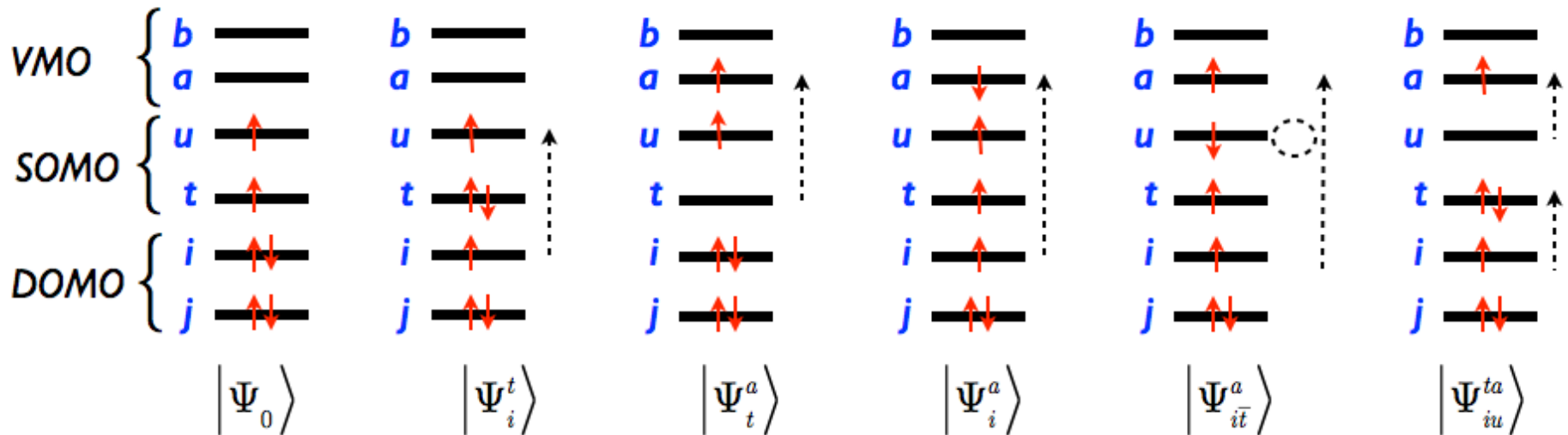
Variational optimization of the coefficients of the CSFs gives MRCI

Configuration Interaction

In the concept of CI we write for the state I:

$$\left| \Psi_I^{SM} \right\rangle = \sum_K C_{KI} \left| \Phi_K^{SM} \right\rangle \qquad\qquad \left| \Phi_K^{SM} \right\rangle \quad \text{One of the \color{red}{excited} CSFs}$$

- The simplest method of this type only includes the **single orbital replacements** (CI with single excitations, **CIS**)
- On starts by defining a single HF determinant:

$$\left| \Psi_I \right\rangle = \sum_{ia} C_a^i \left| \Phi_i^a \right\rangle$$

- And solve the eigenvalue problem explicitly:

$$\mathbf{HC} = E\mathbf{C} \qquad\qquad H_{ia,jb} = \left\langle \Phi_i^a \mid H \mid \Phi_j^b \right\rangle = \delta_{ia,jb}(\varepsilon_a - \varepsilon_i) + \underbrace{\left\langle ib \,\|\, aj \right\rangle}_{(ia|jb)-(ij|ab)}$$

- For transition metal complexes, the HF method is very bad, because there is a lot of dynamic correlation missing.

- While many excited states are dominated by single excitations, a fair number of them requires either addition spin-flips to complete actual multiplet states or involve double excitations

- CIS or excited states is even worse than HF for the ground state - on top of all HF failures the use of frozen orbitals and the lack of differential dynamic correlation between ground and excited states make the method unbalanced and grossly inaccurate (1-6 eV errors)

- Need a theoretical methods that are more „democratic" with respect to the treatment of ground- and excited states

- For the valence region this is provided by Multireference Configuration Interaction (**MR-CI**), Difference-Dedicated CI (**DDCI**) and Spectroscopy Oriented Configuration Interaction (**SORCI**)

Multireference Configuration Interaction

- Now we need to cover differential dynamic correlation by performing excitations relative to at least the important CSFs of the CAS

$$\left| \Psi_I^{SM;MRCI} \right\rangle = \sum_{K \in CAS} C_{KI} \left| \Phi_K^{SM} \right\rangle \quad + \quad \sum_{K \notin CAS} C_{KI} \left| \Phi_K^{SM} \right\rangle$$
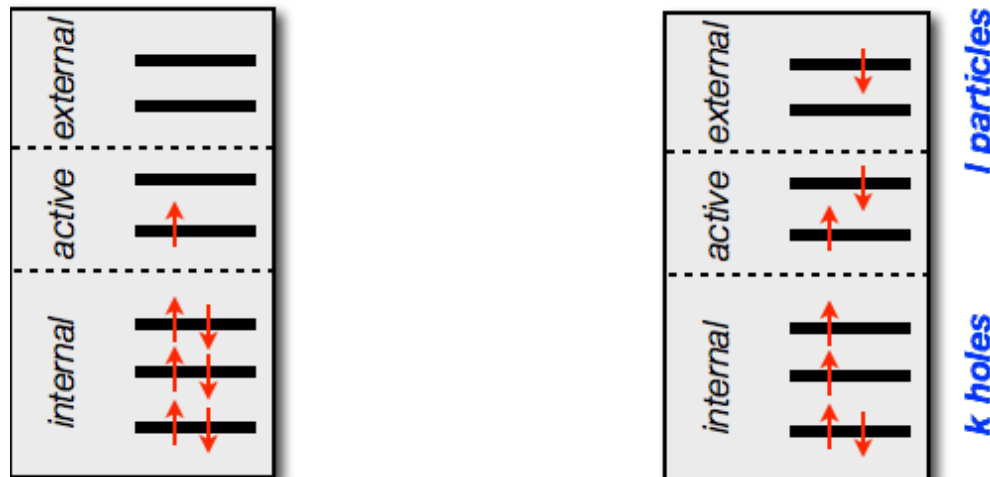
- Fortunately from the HUGE number of **(k-holes,l-particle)** CSFs, only a small fraction contributes to the differential dynamic correlation energy !!!
(idea of **DDCI** (Malrieu) and **SORCI** (Neese))

- Still these methods although nicely accurate are also computationally very expensive for medium sized molecules and impossible for large ones

Time-Dependent DFT

- In Density Functional Theory, we only have theorems for the ground state - excited states are not covered. **There is no CI in DFT, there is no CAS in DFT!**

- Instead one takes an indirect route to excitation energies and properties

- Let us study the response of the ground state energy with respect to an oscillating electric field (**F**), the induced dipole moment() is the polarizability of the system:

$$E(\omega) = E_0 + \vec{\mu}(\omega)\vec{F}(\omega) + \vec{F}^+(\omega)\vec{\vec{\alpha}}(\omega)\vec{F}(\omega) + ...$$

- As a consequence of the perturbation the Kohn-Sham orbitals themselves also become time dependent. The *Ansatz* is:

$$\psi_j(\mathbf{x},\omega) \rightarrow \psi_j(\mathbf{x},0) + \frac{1}{2}\sum_b \left\{ X_{bj}e^{-i\omega t} + Y_{bj}^* e^{+i\omega t} \right\}$$

- We now search for those frequencies where $\alpha(\omega)$ becomes infinite (**poles**). This must then be a valid excitation energy of the system! It is possible to show that the coefficients **X** and **Y** satisfy a non-standard eigenvalue problem:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

With:

$$A_{bj,ck} = \delta_{bj,ck}(\varepsilon_b - \varepsilon_j) + \langle kj \mid cb \rangle + \langle kj \mid f_{xc} \mid cb \rangle - c_{HF} \langle jc \mid kb \rangle$$

$$B_{bj,ck} = \langle kj \mid cb \rangle + \langle kj \mid f_{xc} \mid cb \rangle - c_{HF} \langle jk \mid cb \rangle$$

- These are the **TD-DFT equations**. If the B-matrix is neglected, one obtains the **Tamm-Dancoff approximation**. It looks like CIS with HF exchange replaced by the exchange correlation kernel.

$$\mathbf{AX} = \omega \mathbf{X}$$
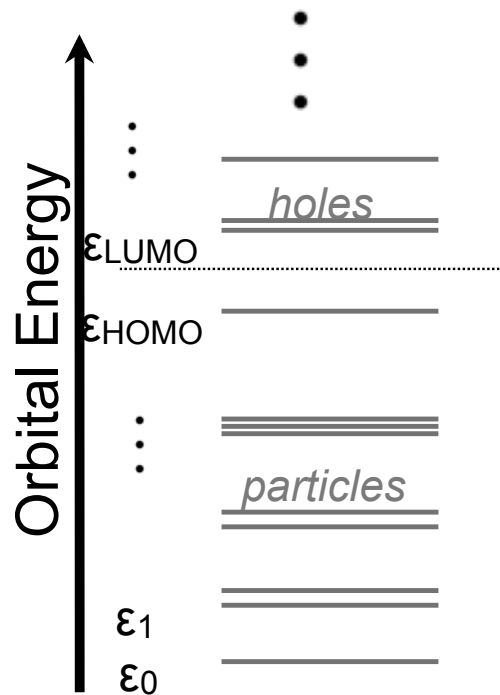
- Single electron excitations
- ➢ Works for Absorption spectra

But:

- No double excitations
- No spin-flip excitations

➢ Works for core electron K-edge

But:

- Cannot treat the multiplet structure
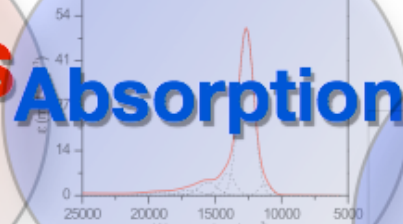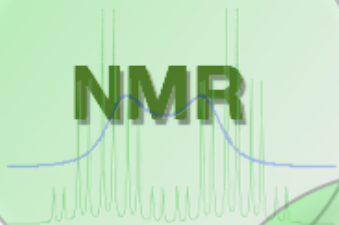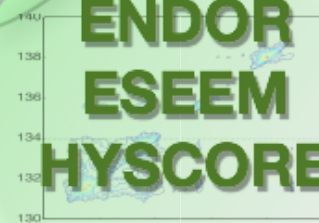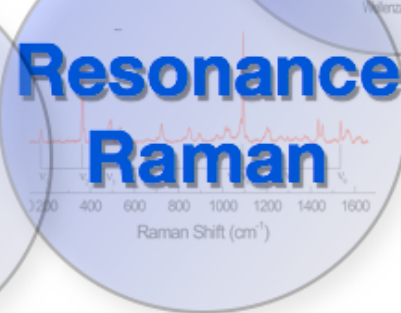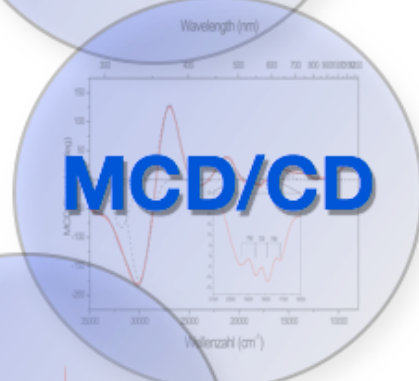
XAS spectroscopy (metal L- and K-edges)
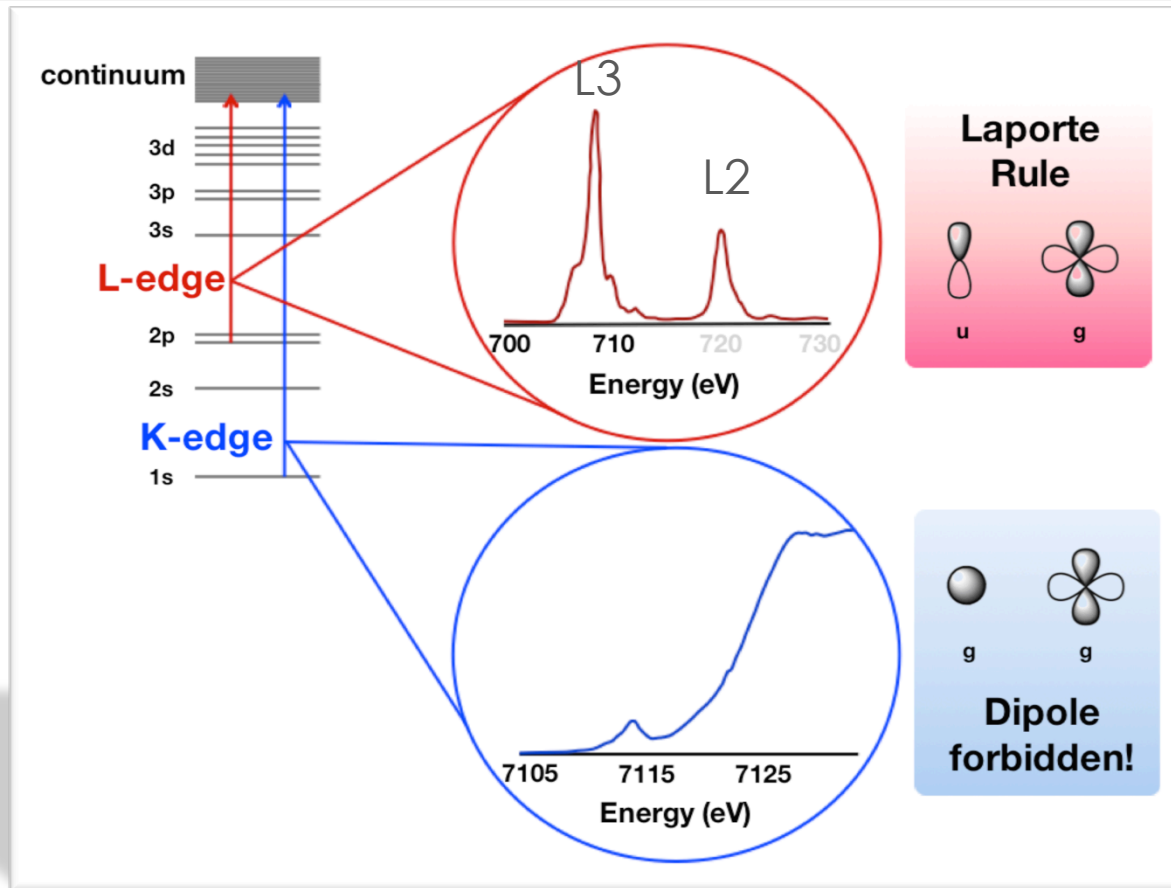
- **K-edge:** (1s→valence) →dipole forbidden transitions

- **L$_{2,3}$-edges:** (2p→valence) →dipole allowed transitions

- **L$_{2,3}$-edges** are more intense and more structured than **K-edges**

Metal L-edge spectroscopy at work…

- Metal L-edge spectroscopy is used to understand

Functionality
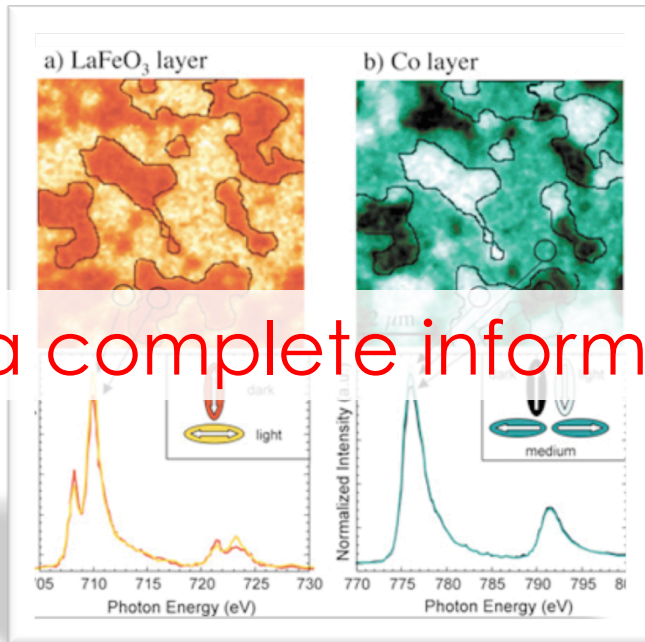
Reactivity of materials

a complete information content is needed
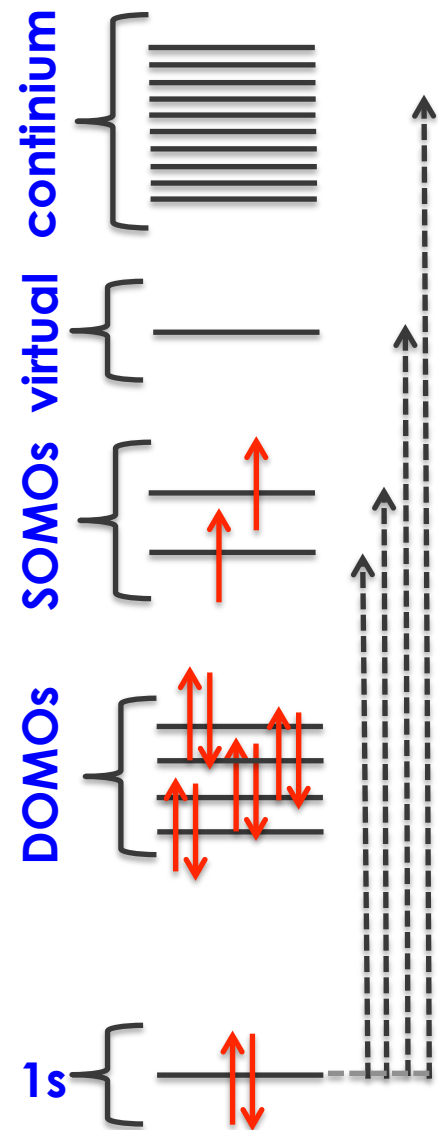
- Localize 1s-orbitals

- Include the 1s-Virtual in the TD-DFT equations

- Calculate dipole and quadrupole contributions to the transition moments

- Use large basis sets on the XAS absorber atom

- Treat relativistic effects

- Compensate negative total charges through COSMO

DeBee S. George, Petrenko T., Neese F., ICA, **2007**

DeBeer S. George, Petrenko T, Neese F., J. Phys. Chem. A, **2008**, 112, 12936

Prediction of metal and ligand K- edges
is accessible via TD-DFT methodologies .

DeBee S. George, Petrenko T., Neese F., ICA, **2007**

DeBeer S. George, Petrenko T, Neese F., J. Phys. Chem. A, **2008**, 112, 12936

Iron K-edge X-Ray Emission Spectroscopy

XES Valence to core region as a unique probe
of valence orbital composition

N. Lee, T. Petrenko, U. Bergmann, F. Neese, S. DeBeer, J. Am. Chem. Soc., 2010, 132, 9715-9727.

p/h is not always good for metal L-edges
even for 'simple' cases: V_2O_5 ($2p^5 3d^1$)

Ligand Field Multiplet
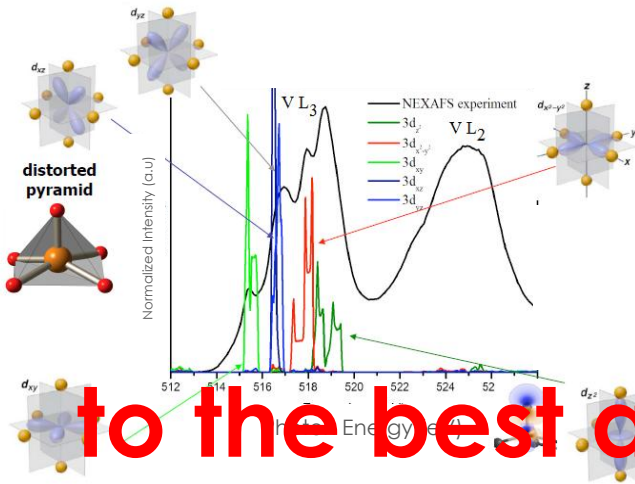
Charge Transfer Multiplet
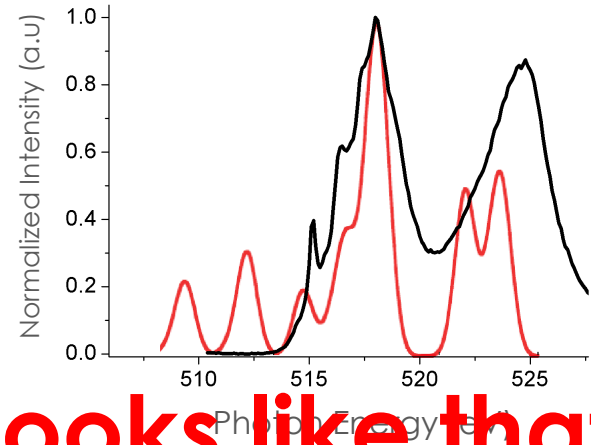
TD-DFT

TD-DFT+SOC

to the best attempt looks like that!

Existing approaches
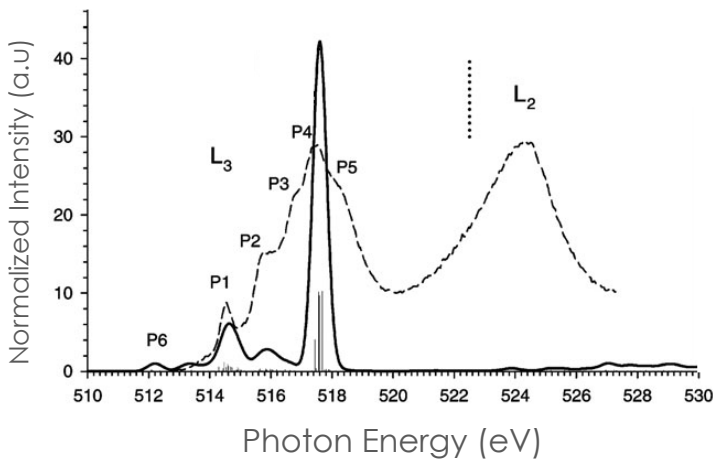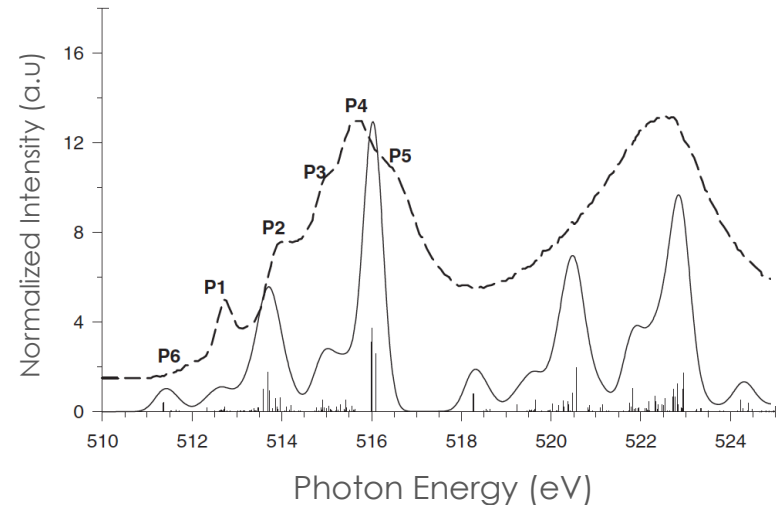
A) Particle Hole Pair Methods:

Response theory with particle/hole pairs
- Can do a good job on the electronic structure
- Contain no adjustable parameters
- but
- Do not correctly span the space of the final states
- They have problems to predict the number and relative intensities of spectral features correctly

B) Multiplets

- Correct physics!
- Requires *many* parameters, in particular for states outside the $|p^5d^{n+1}>$ manifold. The parameters may not be easy to predict from first principles.
- Progress has been made in this respect

Why is it so difficult?

Particle hole spectrum

Orbital Energy

holes

ε_{LUMO}

ε_{HOMO}

particles

ε_1

ε_0
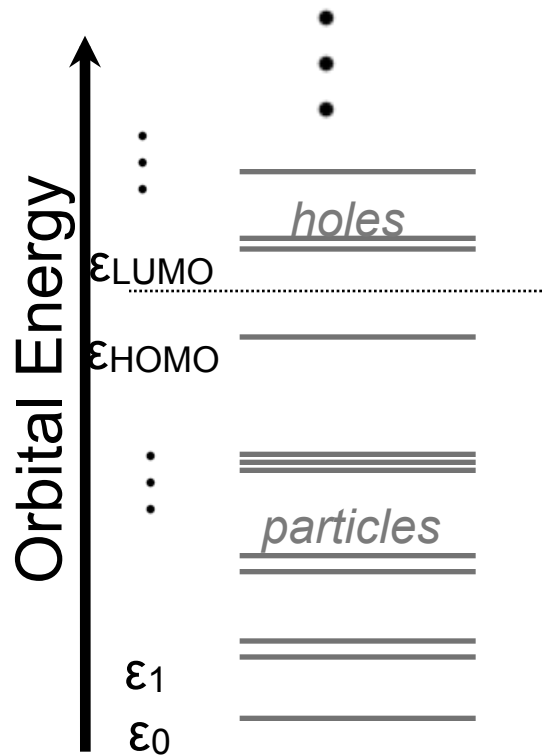
Many particle spectrum (observable)

Energy

$E_{2(core)}$
$E_{1(core)}$

$E_{n(val)}$

E_2
E_1

E_0
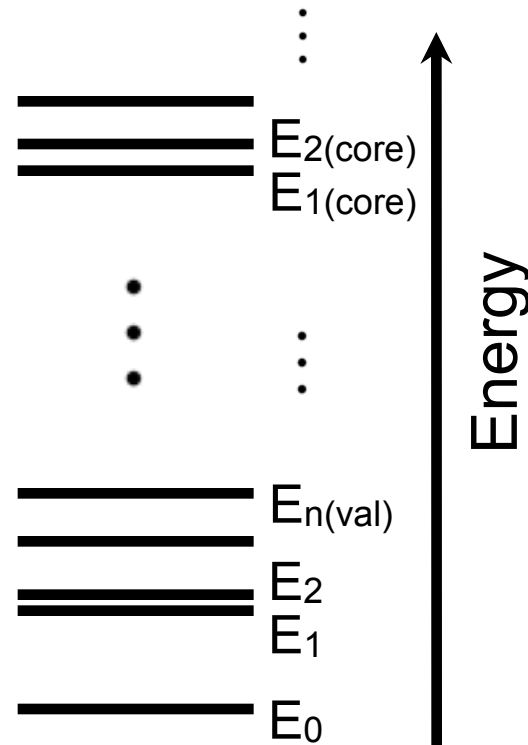
- In some cases the spectrum of orbital energy differences **might look** similar with the of the many particle spectrum
- e.g. for K-edges

In general, they have **nothing** in common!

L-edge excitations lead to final states with a **(n-1)p core hole**, e.g.:

X-Ray

nd

$(n$-1)p
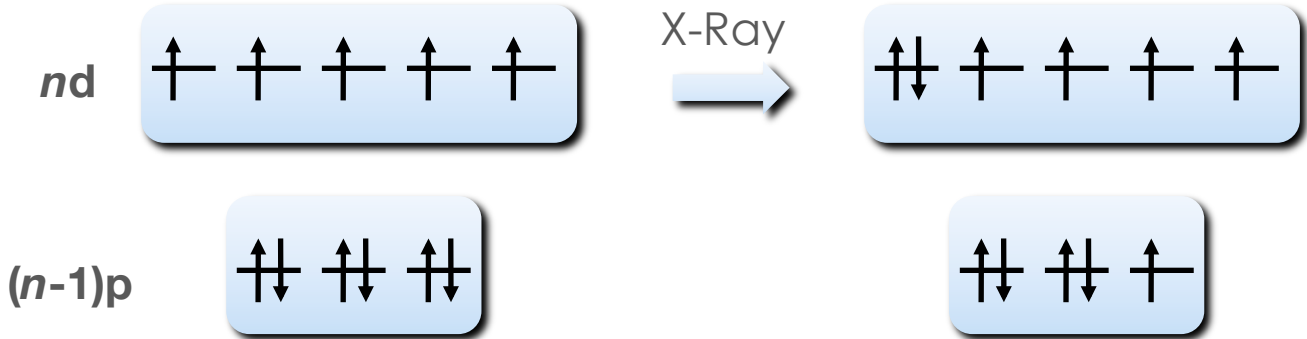
Electronic State: $^1A \otimes {}^6A$

$^2P_J \otimes {}^5D$

6 x 25 $^6\Gamma, {}^4\Gamma, {}^2\Gamma$ = 550 CSFs (**1512** STATES)

only **15** particle/hole pairs

The p/h space spans **only** a small part of the final state manifold!

An example: The Mn^{2+} Ion (^{6}S, high-spin d^5)

Many particle spectrum
(RAS-CI)
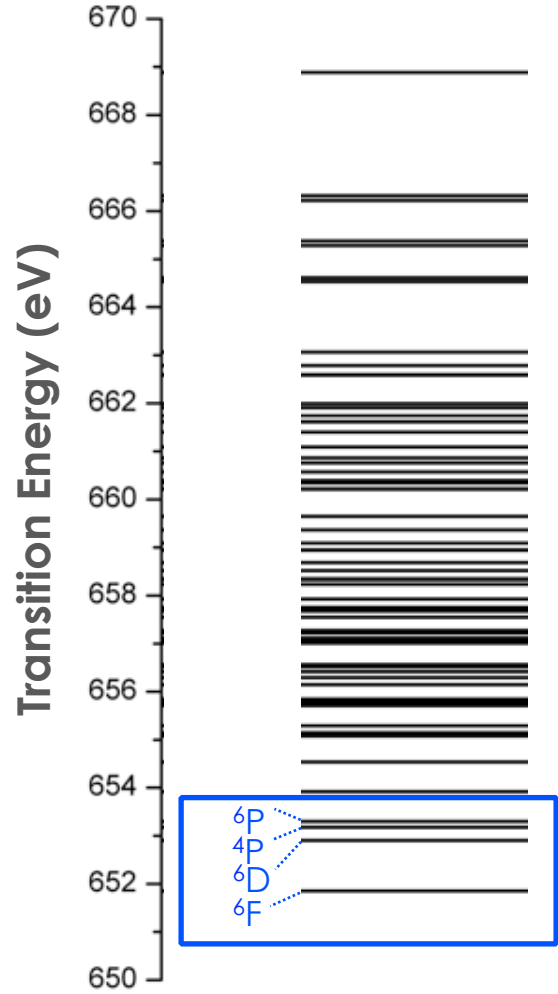
p/h spectrum
(BP86 TD-DFT +30 eV)

**all multiplets arising
from spin-flips are missing!**

qualitatively correct

Spin-Orbit Coupling

- The 2p^5 corehole has a very strong „in state" spin-orbit coupling that „scrambles" the multiplets

- Each Multiplet $^{2S+1}\Gamma$ has 2S+1 „Magnetic sublevels" M_S=S,S-1,....,-S
  Typical single p/h treatments can only hope to approximate *one* of the M_S levels but completely miss all others!

- The SOC operator is a two-electron operator
  It mixes all M_S levels of all multiplets!
  All M_S levels must be included in the treatment
  Most single determinantal based methods, even four component, fail to do so because they are missing determinants

$$\left\langle \Psi_I^{SM} \left| \sum_i h_i^{SOC} s_i^{(m)} \right| \Psi_J^{S'M'} \right\rangle = \underbrace{\begin{pmatrix} S' & 1 & S \\ M' & m & M \end{pmatrix}}_{Clebsch-Gordon\,Coefficient} \underbrace{\left\langle \Psi_I^S \left\| \sum_i h_i^{SOC} \right\| \Psi_J^{S'} \right\rangle}_{\mathrm{Re}\,duced\,Matrix\,Element\,Y_{IJ}^{SS'}}$$

For atoms this is well understood:

✓ **LS (Russel-Saunders) coupling:**
- ▸ First couple orbital-**l**(i) and spin **s**(i)- to total **L** and total **S**
- ▸ Then coupling total **L** and total **S** to total **J**

✓ **jj coupling:**
- ▸ First couple orbital-**l**(i) and spin **s**(i)- to individual electron **j**(i)
- ▸ couple individual **j**(i) to total **J**

✓ When carried through exactly, both treatments arrive at the same answers. (Arguably LS is more transparent)

✓ For molecules, the jj-coupling approach appears to be prevalent (2-component, 4-component) but it is rarely carried through to an extent that the results approaches the relativistic many particle spectrum. (Requires highly excited determinants and lots of CI!)

✓ We prefer LS coupling (does not need highly excited configuration state functions and very little CI) → readily arrive at a spectrum that resembles the many particle relativistic spectrum much more closely

It is **needed** to develop a method:

- Predictive
- Direct
- Physically proper
- Complete final state manifold
- Will be able to operate on large systems

In principle:

- Construction of many particle wavefunctions
  including relativity is well understood
  e.g. Multireference Configuration Interaction

However

This is presently possible for only very small systems (MRCI)
or relative small transition metal complexes (CASSCF, RASSCF)

Core excitation problem of CO_2
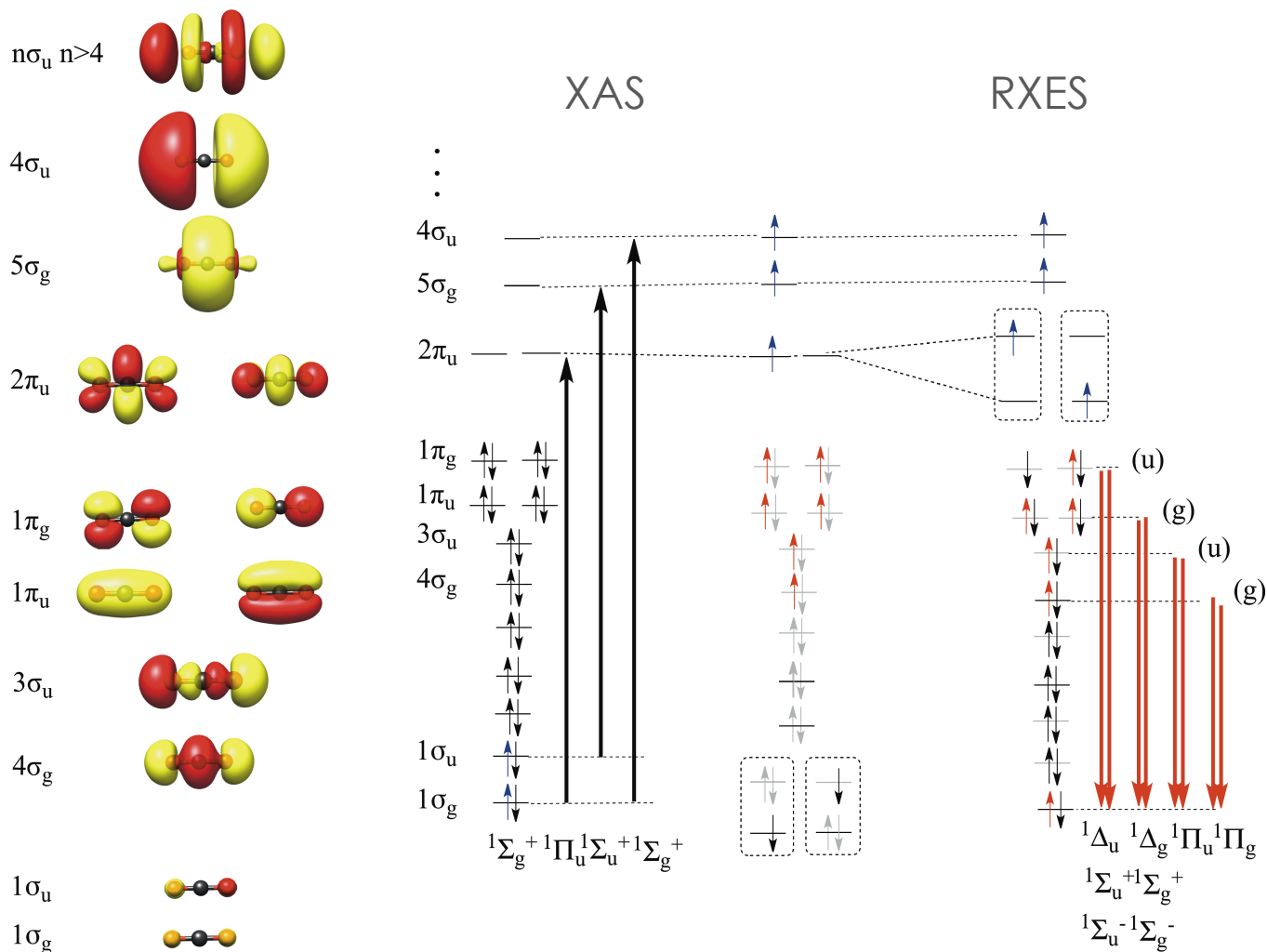
MRCI treatment of XAS and RXES spectra of CO_2

Maganas D, DeBeer S, Schlögl R. Neese F *et al*. JCP C, 2014
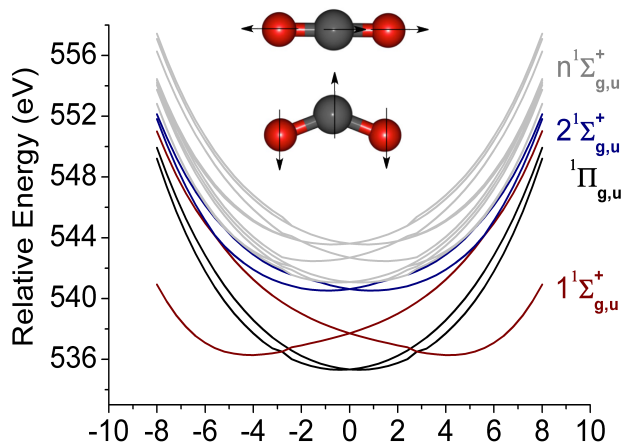
Complicated multireference problem
- Vibrational structure
- Vibronic coupling

All is fine but we need to simplify for larger systems

O K-edge XAS
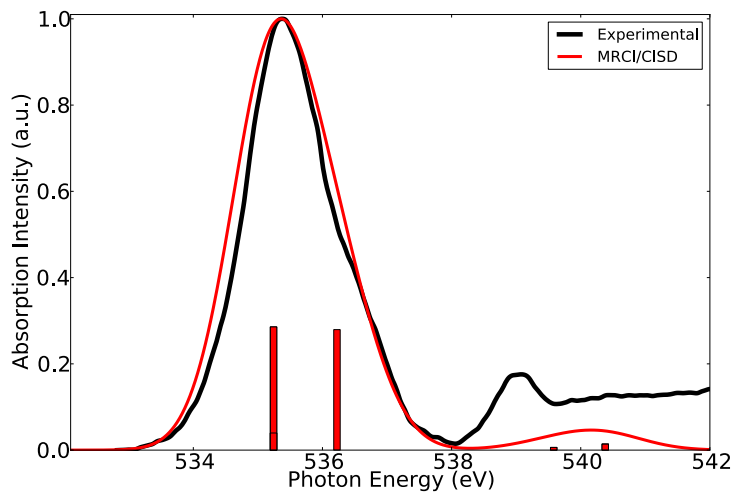
Resonance Emission
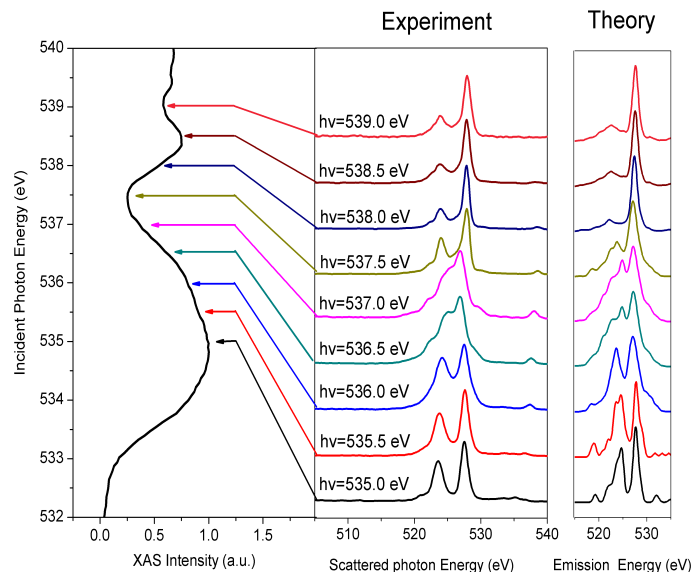
✓ Physical model space spin adapted single excitations from a high spin reference:

$$\left|\Phi_0\right\rangle \equiv \left|0\right\rangle \quad \left|\Phi_i^t\right\rangle = E_i^t\left|0\right\rangle \quad \left|\Phi_t^a\right\rangle = E_t^a\left|0\right\rangle \quad \left|\Phi_i^a\right\rangle = \frac{1}{\sqrt{2}}E_i^a\left|0\right\rangle \quad \left|\Phi_{wi}^{at}\right\rangle = E_w^a E_i^t\left|0\right\rangle \quad \left|\Phi_{ti}^{at}\right\rangle = E_t^a E_i^t\left|0\right\rangle$$
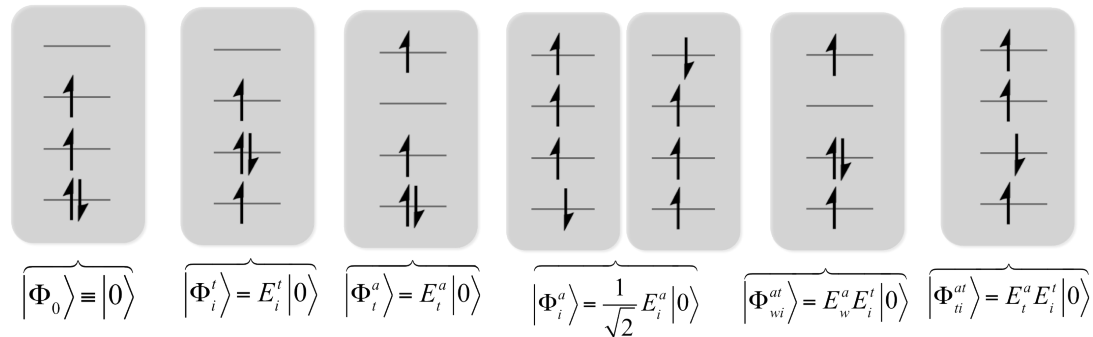
✓ Multiplet configuration interaction through the full hamiltonian

✓ Electron-electron screening is introduced via only 3 parameters to gain efficiency:

$$H_{ia,ia}^{DFT/ROCIS} = F_{aa}^{C(KS)} - F_{ii}^{C(KS)} - c_1\left(ii\mid aa\right) + 2c_2\left(ia\mid ia\right) \quad \text{(diagonal)}$$

$$H_{ia,jb}^{DFT/ROCIS} = c_3\left\{\delta_{ij}F_{ab}^{C(KS)} - \delta_{ab}F_{ji}^{C(KS)} - \left(ij\mid ab\right) + 2\left(ia\mid jb\right)\right\} \quad \text{(off-diagonal)}$$

✓ Relativistic effects (spin orbit coupling) are explicitly treated via 2-particle spin-orbit operators (**not** parametric!)

$$\left\langle \Psi_I^{SM}\left|\hat{H}_{BO} + \hat{H}_{SOC}\right|\Psi_J^{S'M'}\right\rangle = \delta_{IJ}\delta_{SS'}\delta_{MM'}E_I^{(S)} + \left\langle \Psi_I^{SM}\left|\hat{H}_{SOC}\right|\Psi_J^{S'M'}\right\rangle$$

Applications
Calculation Protocols for
X-Ray spectroscopies

TD-DFT protocol for K-edges

- Localize 1s-orbitals

- Include the 1s-Virtual in the TD-DFT equations

- Calculate dipole and quadrupole contributions to the transition moments

- Use large basis sets on the XAS absorber atom

- Treat relativistic effects

- Compensate negative total charges through COSMO

continium

virtual

SOMOs

DOMOs

1s

DeBee S. George, Petrenko T., Neese F., ICA, **2007**

DeBeer S. George, Petrenko T, Neese F., J. Phys. Chem. A, **2008**, 112, 12936

Prediction of Metal and Ligand K- edges
 is accessible via TD-DFT methodologies .

DeBee S. George, Petrenko T., Neese F., ICA, **2007**

DeBeer S. George, Petrenko T, Neese F., J. Phys. Chem. A, **2008**, 112, 12936

The same holds for Metal K-edges

- agreement between theory and experiment is good after constant shift of the excitation energy and inclusion of quadrupole intensity

$$\sigma\left(\omega_{em}\right) = \frac{4\pi}{3}\omega_{em}\sum_{i_\sigma j_\sigma}\sum_{\alpha=x,y,z}\frac{\left|\left\langle i_\sigma\left|m_\alpha\right|j_\sigma\right\rangle\right|^2\Gamma}{\left(\omega_{FI}-\omega_{em}\right)^2+\frac{1}{4}\Gamma^2} = \frac{4\pi}{3}\omega_{em}\sum_{i_\sigma j_\sigma}\sum_{\alpha=x,y,z}\left|\left\langle i_\sigma\left|m_\alpha\right|j_\sigma\right\rangle\right|^2 f\left(\omega_{em},\omega_{ij},\Gamma\right)$$

- Emission energies are calculated as ΔE berween one-electrom Kohn-Sham orbitals
- Transitions require metal character in molecular orbitals involved in the emission process
- Intensity is governed by the electric dipole operator (m_a)

N. Lee, T. Petrenko, U. Bergmann, F. Neese, S. DeBeer, J. Am. Chem. Soc., 2010, 132, 9715-9727.
Lancaster, K.M.; Finkelstein, K.D.; DeBeer, S. Inorg. Chem. 2011, 50, 6767-6774.
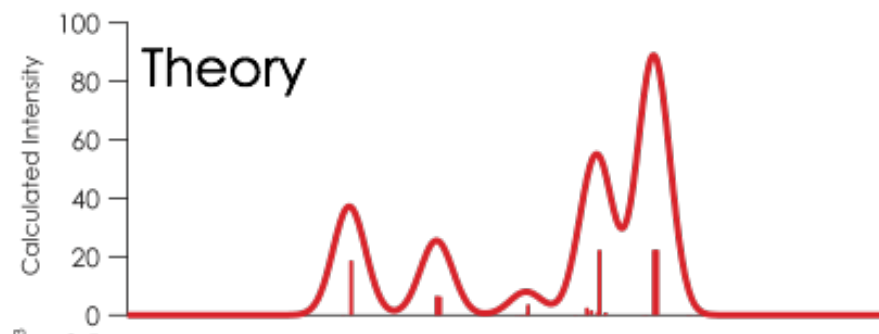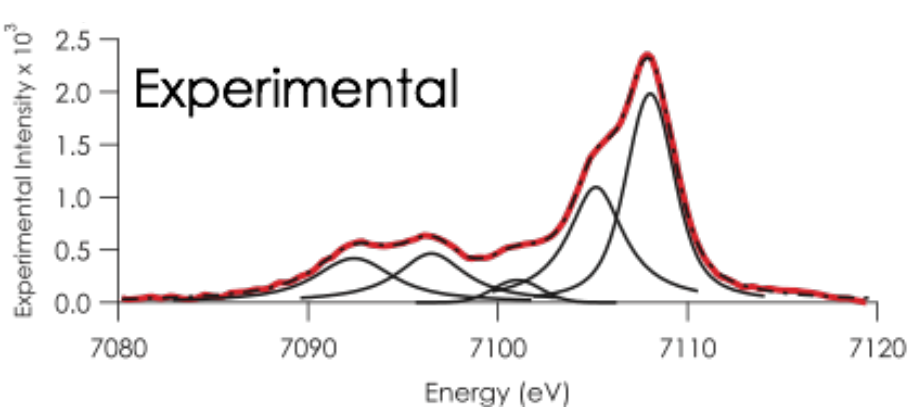
Can we use wavefunction based methodologies CI or CAS and describe the core electron excitation processes explicitly? ✓ Yes
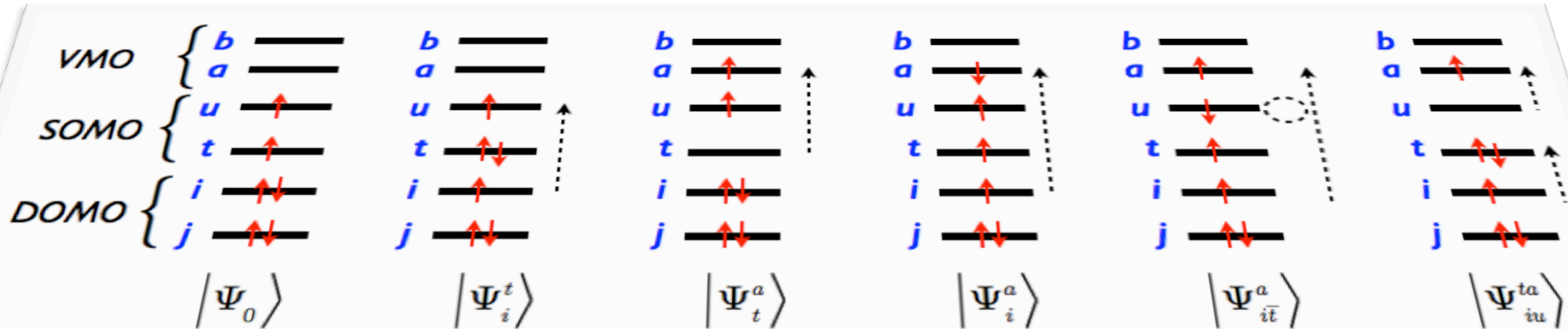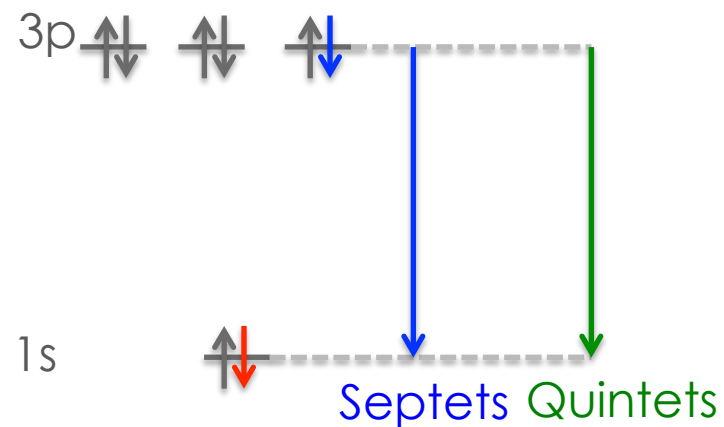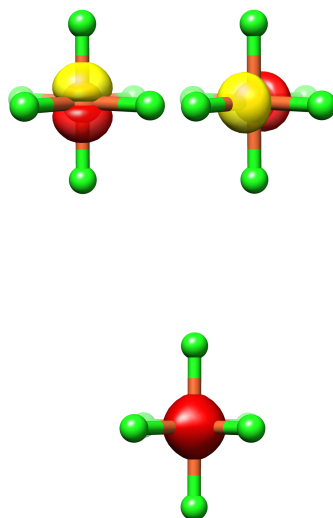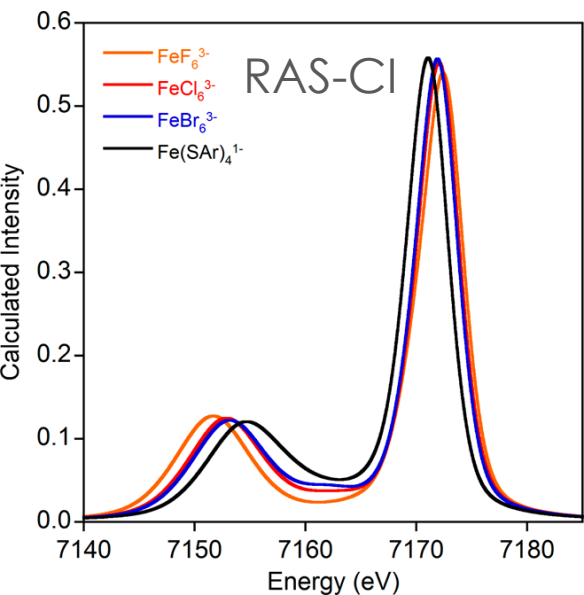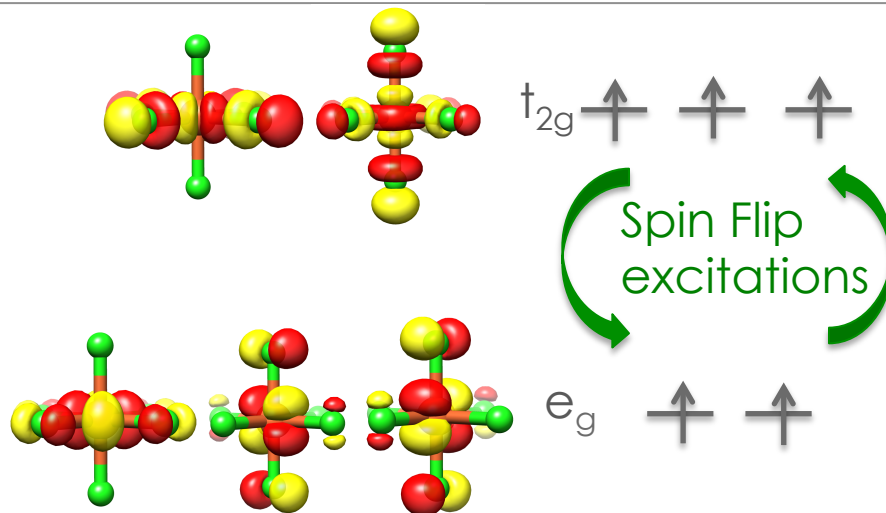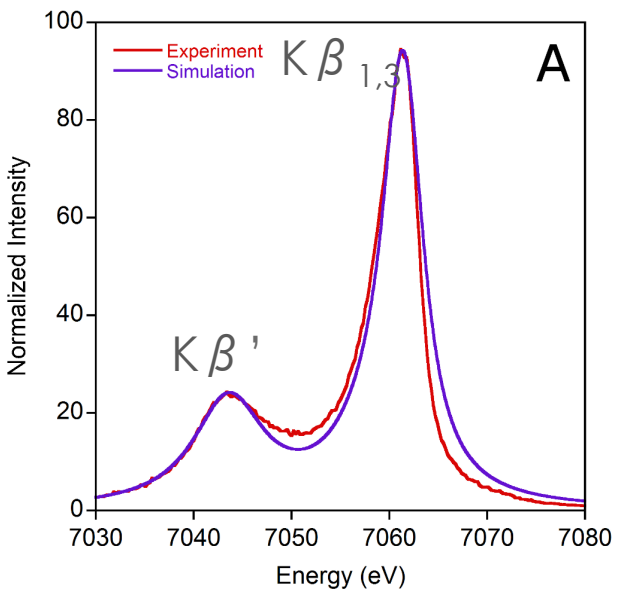
The RASCI protocol for XES

Rotate $1s^2$, $3p^6$ MOs

continium
virtual
SOMOs
DOMOs
3p
1s

RAS3:Nothing

RAS2:Full CI

RAS1:1p exc
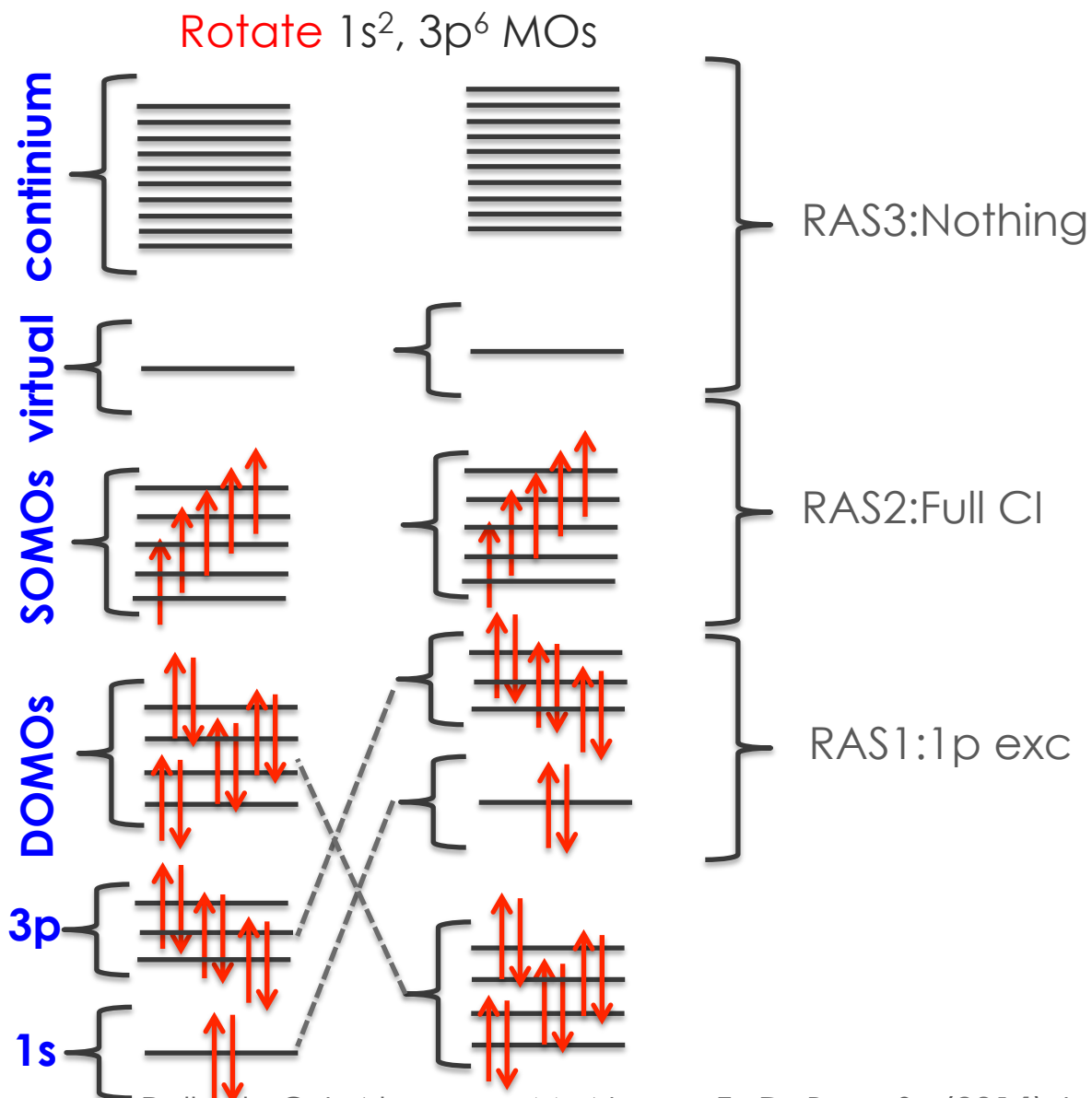
- **Generate** a CAS or QRO orbitals for the Valence states

- **Rotate** $1s^2$, $3p^6$ MOs bellow the $3d^5$ ones

- **Perform** the RAS-CI SOC of the ionized complex $[FeCl6]^{3-,}$ including 2S+1=7,5 multiplicities

- **Compensate** negative total charges through COSMO

Pollock, C.J.,Atanasov, M., Neese, F., DeBeer, S., (**2014**) J. Am. Chem. Soc.;, 136, 9453-9463.

RAS-CI vs Multiplets

Multiplets

Fe^{3+}

RAS-CI
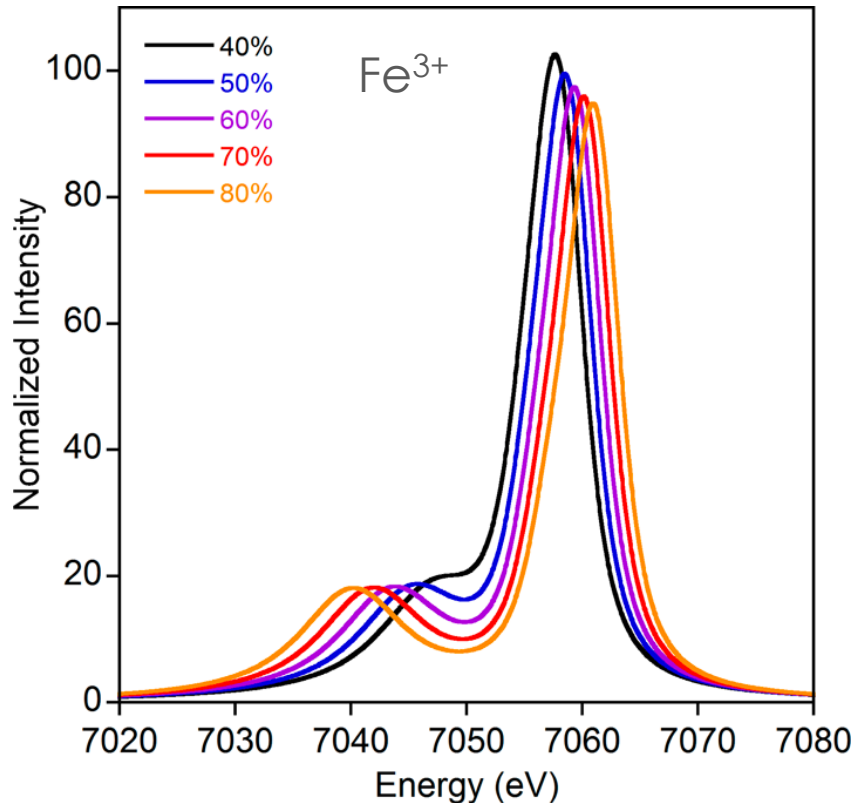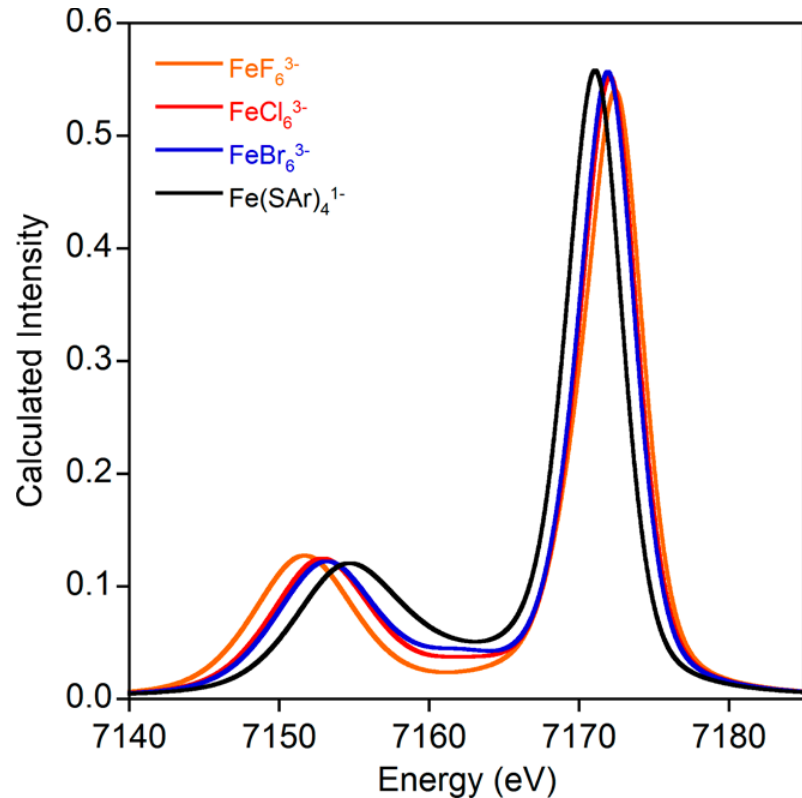
$$I_{K_\beta} \sim \left(3p \,|\, 3d\right) * (1-a)^2 Fe_{3d}$$

- Intensity mechanism: reduction of the p– d exchange
  as modulated by metal– ligand covalency

Core excitation problem of CO_2
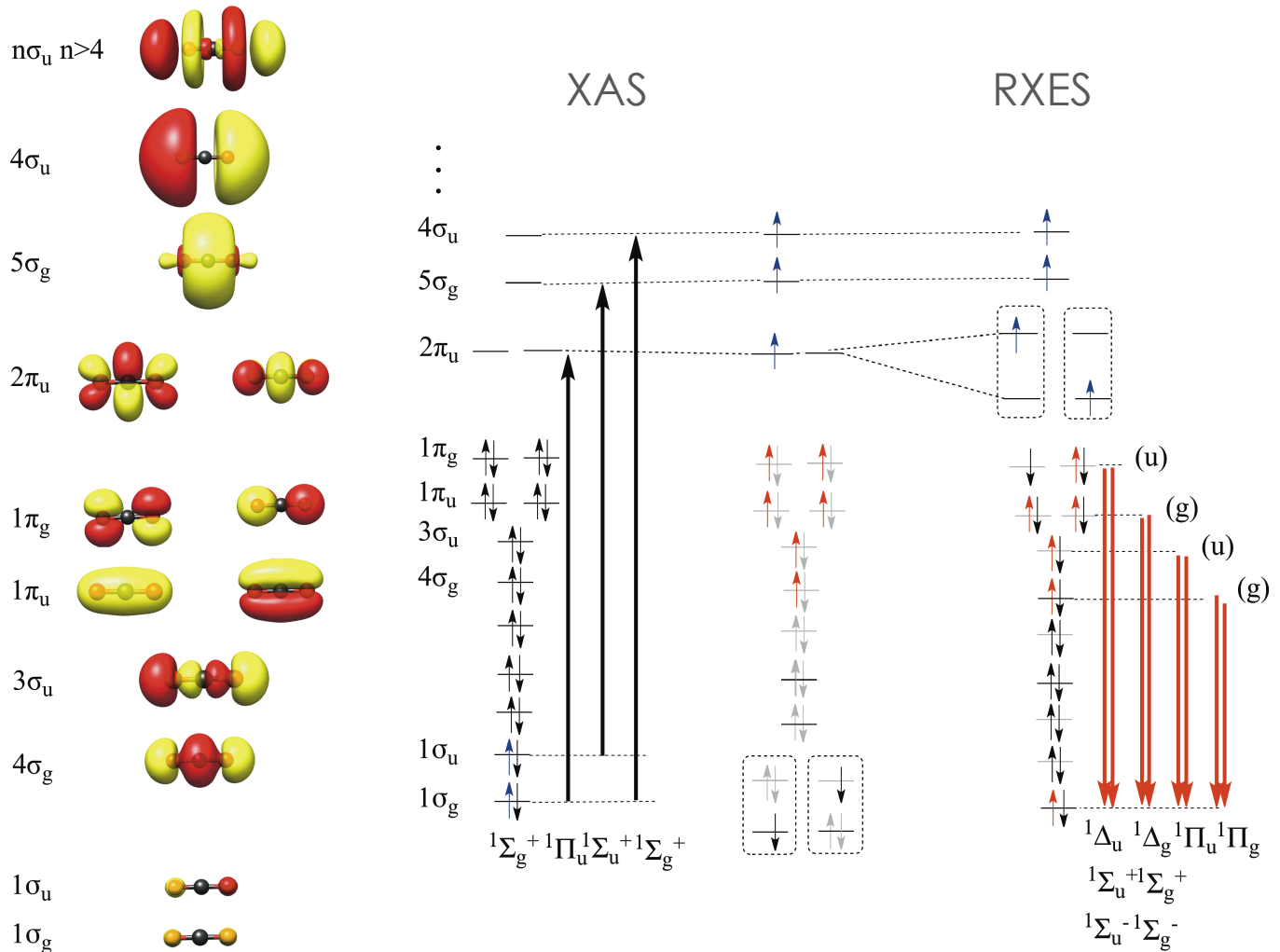
MRCI treatment of XAS and RXES spectra of CO_2

Maganas D, DeBeer S, Schlögl R. Neese F *et al*. JCP C, 2014
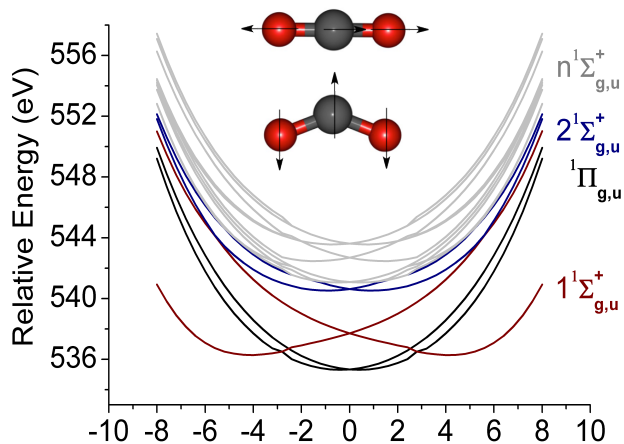
Complicated multireference problem
- Vibrational structure
- Vibronic coupling

All is fine but we need to simplify for larger systems

O K-edge XAS
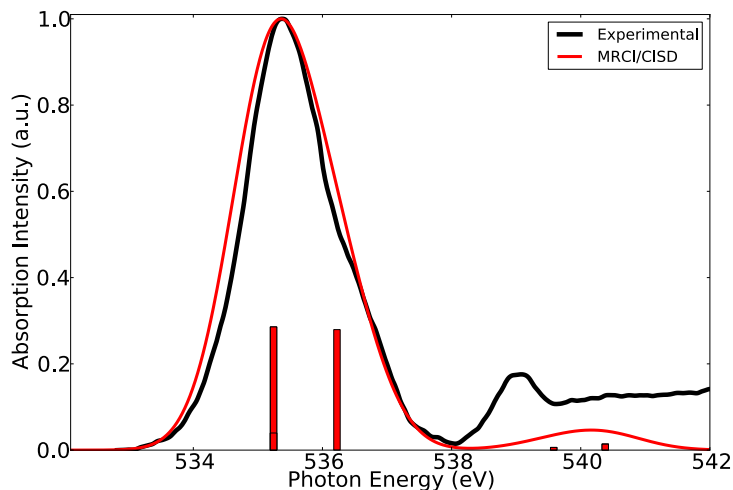
Resonance Emission
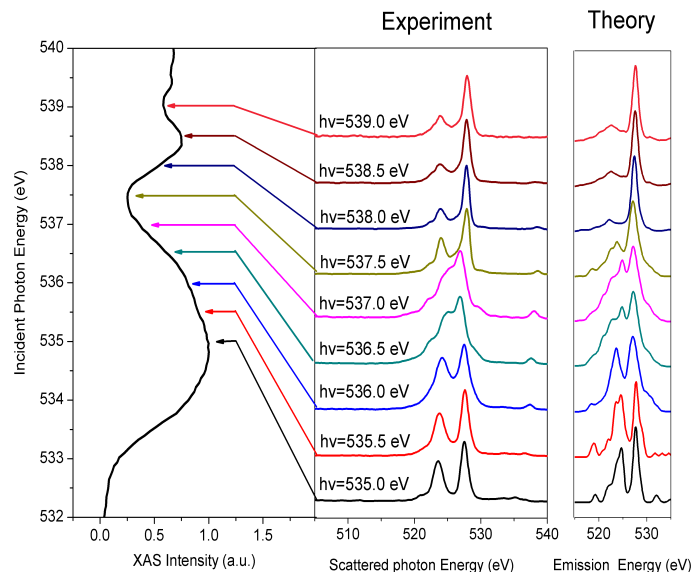
It is an implementation:

- Efficient
- Can do 100s of states

100s of atoms → It is applicable to large systems
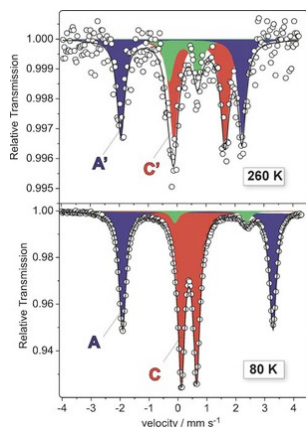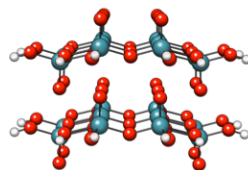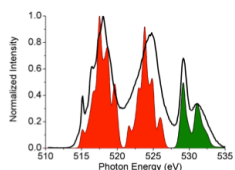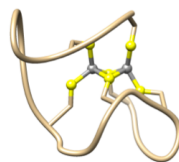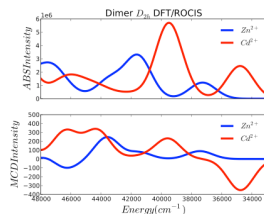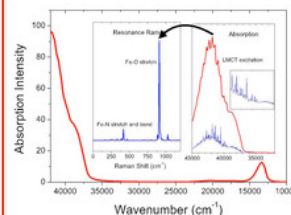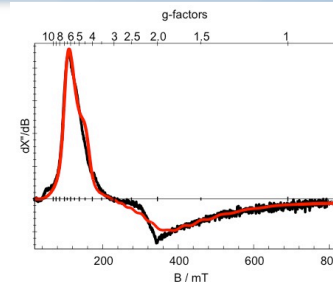
Roemelt, M. Neese F., *J Phys. Chem. A.* **2013**, *117*, 3069

Roemelt, M., Maganas D., DeBeer S, Neese F., *J. Chem. Phys.* **2013**, *138*, 204101.

Validation: Mononuclear complexes

V^V

V^{IV}

V^{III}

L3 L2

(1) d^0:$[V^{(V)}O(O_2)_2C_5H_4NCOO)]^{2-}$

(2) d^0:$V^{(V)}O(O_2)_2C_2H_4]^{2-}$
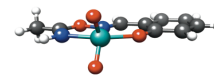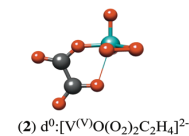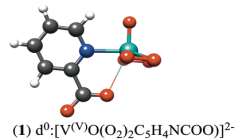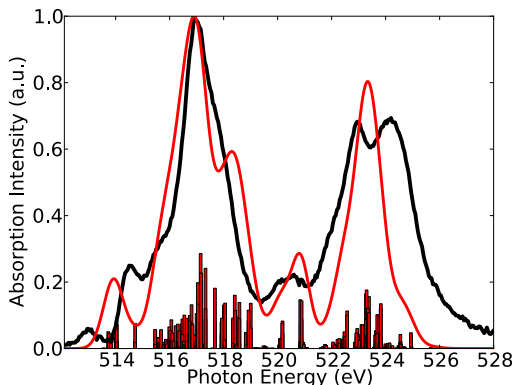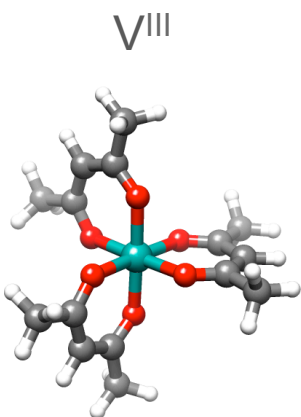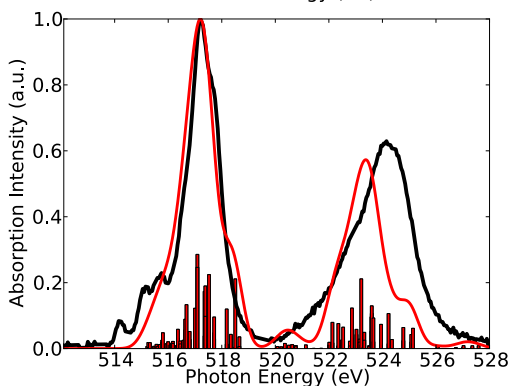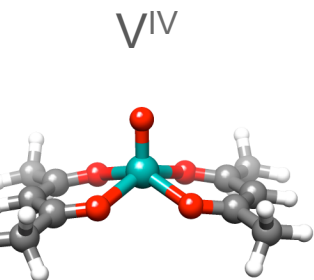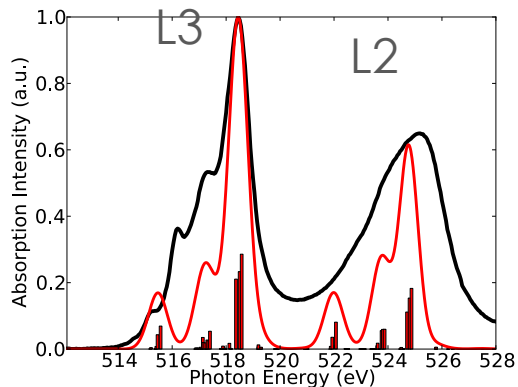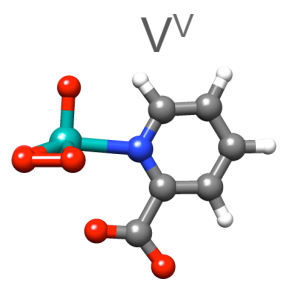
d^0:$V^{(V)}O_2{}^{R,R'}L_1$
(3) R:Me, R' :Ph
(4) R:H, R' :Me
(5) R:H, R' :Ph
(6) R:H, R' :PhNO$_2$

(7) d^1:$V^{(IV)}O(acac)_2$

(8) d^1:$V^{(IV)}O(acac)_2Py$

(9) d^1:$V^{(IV)}O(TPP)$
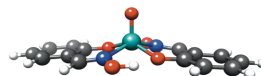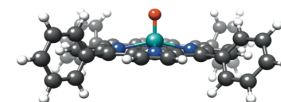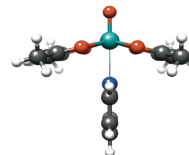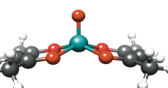
d^1:$V^{(IV)}O(H^RL_2)$
(10) R: Me
(11) R: Et
(12) R: Cl

(13) d^1:$V^{(IV)}O(salen)$

(14) d^1:$V^{(IV)}(MeO)[L_3]$
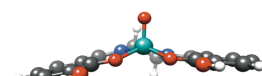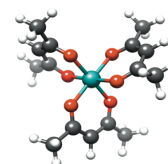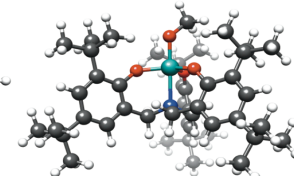
(15) d^2:$V^{(III)}(acac)_3$

(16) d^2:$V^{(III)}(MeOH)[L_3]$

Roemelt, M., Maganas D., DeBeer S, Neese F. *J. Chem. Phys.* **2013**, *138*, 204101.

Maganas D., Roemelt M., Weyhermuller T., Blume R., Haevecker M., Knop A., DeBeer,S., Schlögl R., Neese F. 16, 264 *PCCP* **2014**

The Multiplet structure

V^V, d^0

C_{3v}

S=1,3

$M_s = \left|0\right\rangle, \left|\pm 1\right\rangle$

MOrbitals

Maganas D., Roemelt M.,Weyhermuller T., Blume, R., Haevecker, M., Knop-Gericke, A.; DeBeer, S., Schlögl, R., Neese, F. 16, 264 *PCCP* **2014**

The Multiplet structure

Maganas D., Roemelt M., Weyhermuller T., Blume, R., Haevecker, M., Knop-Gericke, A.; DeBeer, S., Schlögl, R., Neese, F. 16, 264 *PCCP* **2014**

V^V

C_{3v}

- Good agreement
- Rather simple multiplet structure

$3d_{z2}$

$3d_{xy/x2-y2}$

$3d_{xz/yz}$

$2p_{x/y}$

$2p_z$

$^{1,3}A_1 \quad ^{1,3}A_1 \quad ^{1,3}E \qquad ^{1,3}E \quad ^{1,3}E \quad ^{1,3}A_1$
$^{1,3}A_2 \quad ^{1,3}A_2$
$^{1,3}E \quad ^{1,3}E$

$^1A_1$

Maganas D., Roemelt M.,Weyhermuller T., Blume, R., Haevecker, M., Knop-Gericke, A.; DeBeer, S., Schlögl, R., Neese, F. 16, 264 *PCCP* **2014**
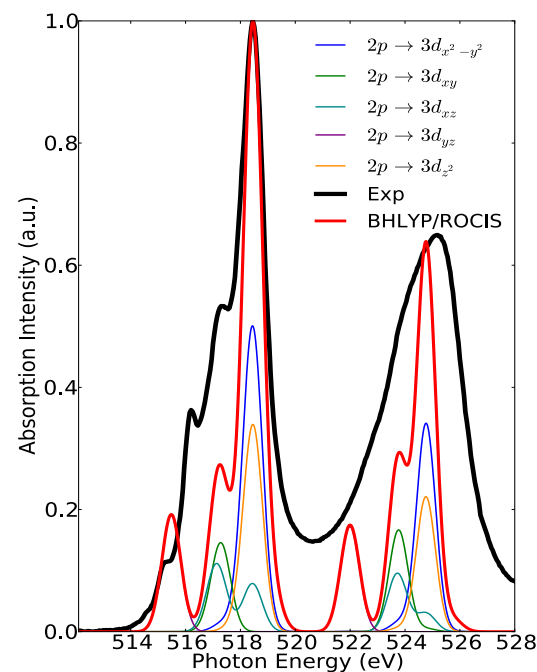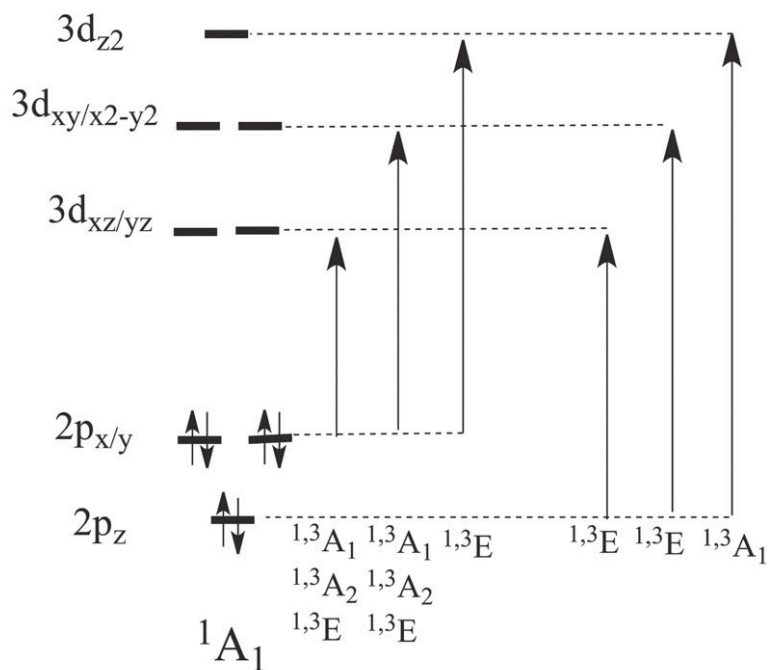
p/h vs many particle spectrum

V^{IV}

C_{4v}
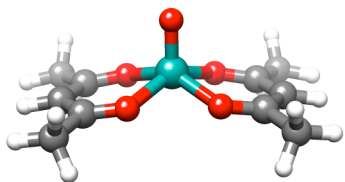
- **Relatively good** agreement
- Quite complicated multiplet structure

Maganas D., Roemelt M., Weyhermuller T., Blume, R., Haevecker, M., Knop-Gericke, A.; DeBeer, S., Schlögl, R., Neese, F. 16, 264 *PCCP* **2014**
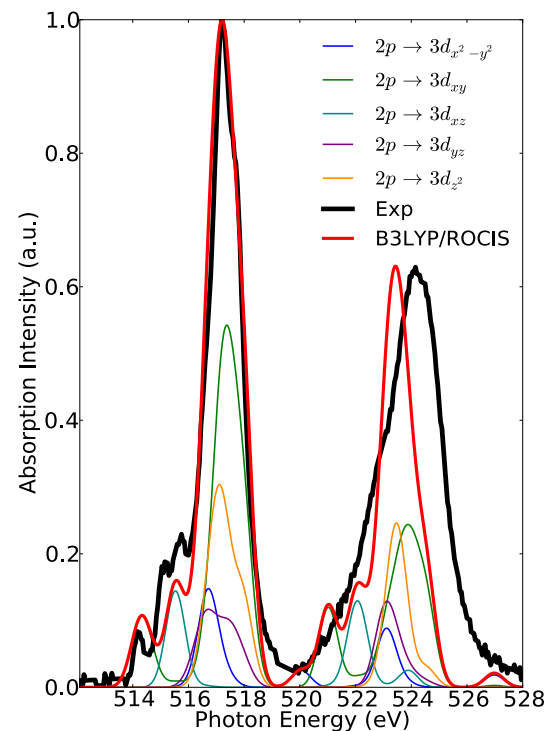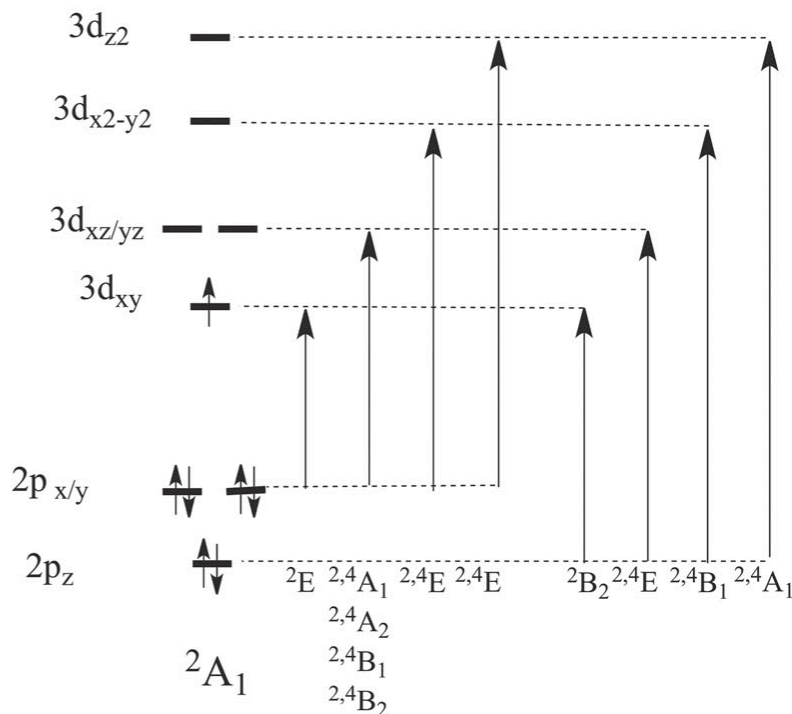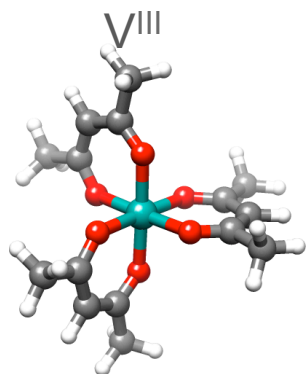
- **Bad** agreement!
- Very complicated multiplet structure

Maganas D., Roemelt M., Weyhermuller T., Blume, R., Haevecker, M., Knop-Gericke, A.; DeBeer, S., Schlögl, R., Neese, F. 16, 264 *PCCP* **2014**
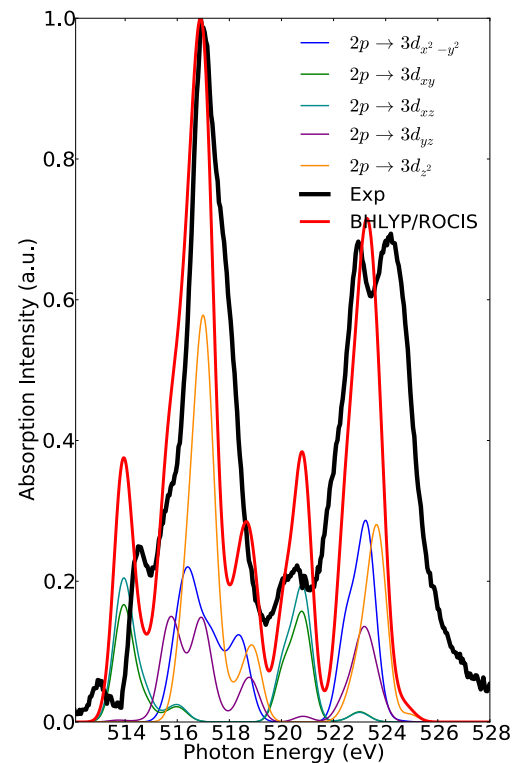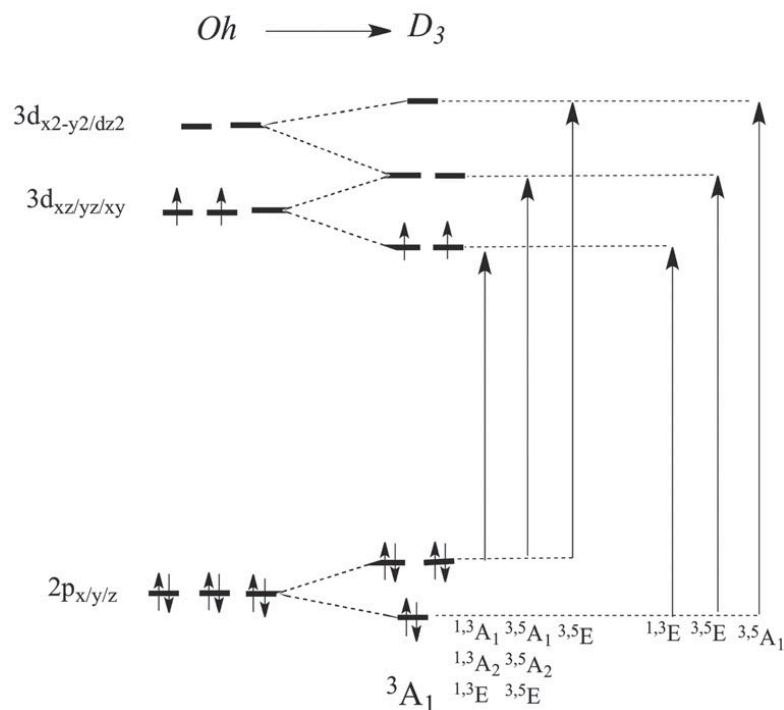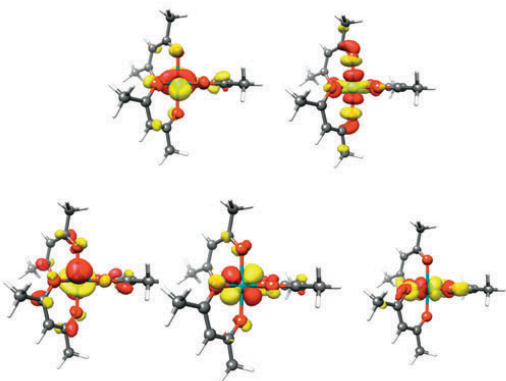
Calculated absolute transition energies carry errors that arise from:

- Shortcomings of the density functionals in the core region
- Limitations of the one-particle basis set
- Shortcomings in the accurate modeling of spin-free relativistic effects.

✓ These errors are usually highly systematic and for a given basis set and density functional be taken into account by introducing an element–dependent shift.

✓ Simple linear regression is sufficient to establish predictive accuracy in the calculated transition energies

B3LYP/def2-TZVP
$R^2 = 0.90$

$${}^{B3LYP}_{def2\text{-}TZVP(\text{-}f)}\Delta E_v = 13.3 eV$$

BHLYP/def2-TVP
$R^2 = 0.90$

$${}^{BHLYP}_{def2\text{-}TZVP(\text{-}f)}\Delta E_v = -3.2 eV$$

Experiment

19.9 eV
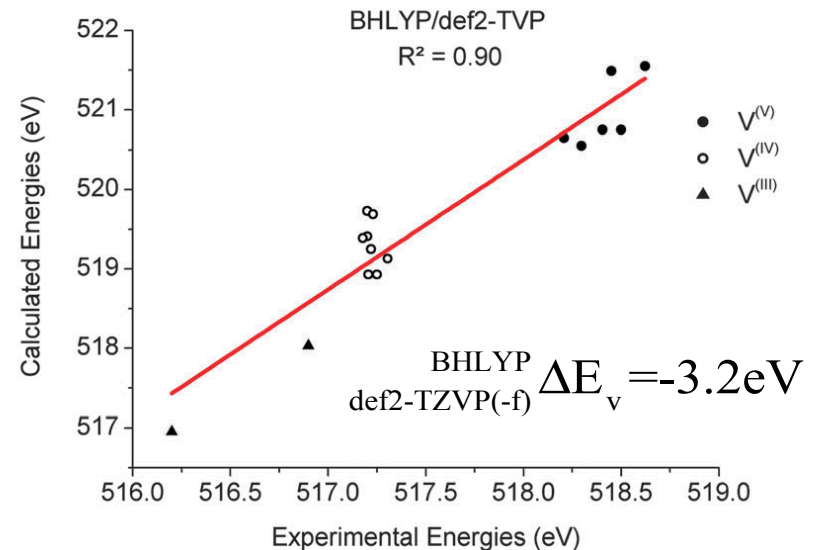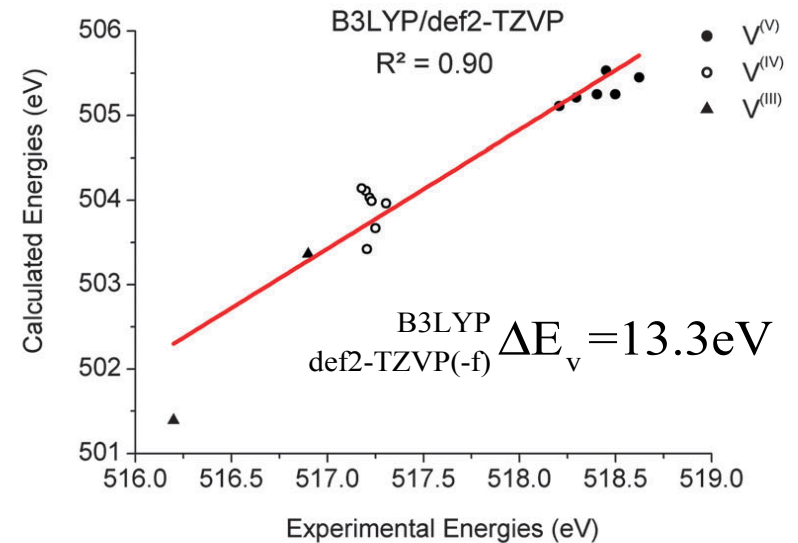
3-4% underestimation of L2 position relative to L3 spectrum position what is the origin?

$$\left|\phi_{MO}\right\rangle = (1-a)^2 Cu_{3d} + aCl_{2p}$$

LUMO

ROCIS

19.0 eV

— D$_{2d}$
— D$_{4h}$

DFT/ROCIS

18.9 eV

Energy [eV]
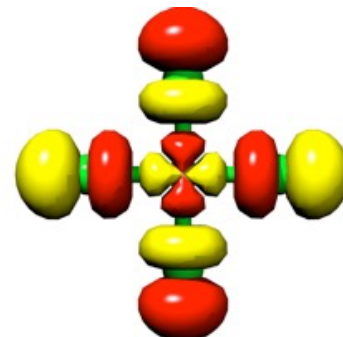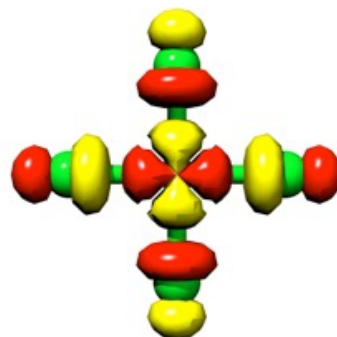
UHF	B3LYP
100% HF-X	20% HF-X
86% Cu	54% Cu

„Experimental" estimate ~61%

Roemelt, M., Maganas D., DeBeer S, Neese F., *J. Chem. Phys.* **2013**, *138*, 204101.
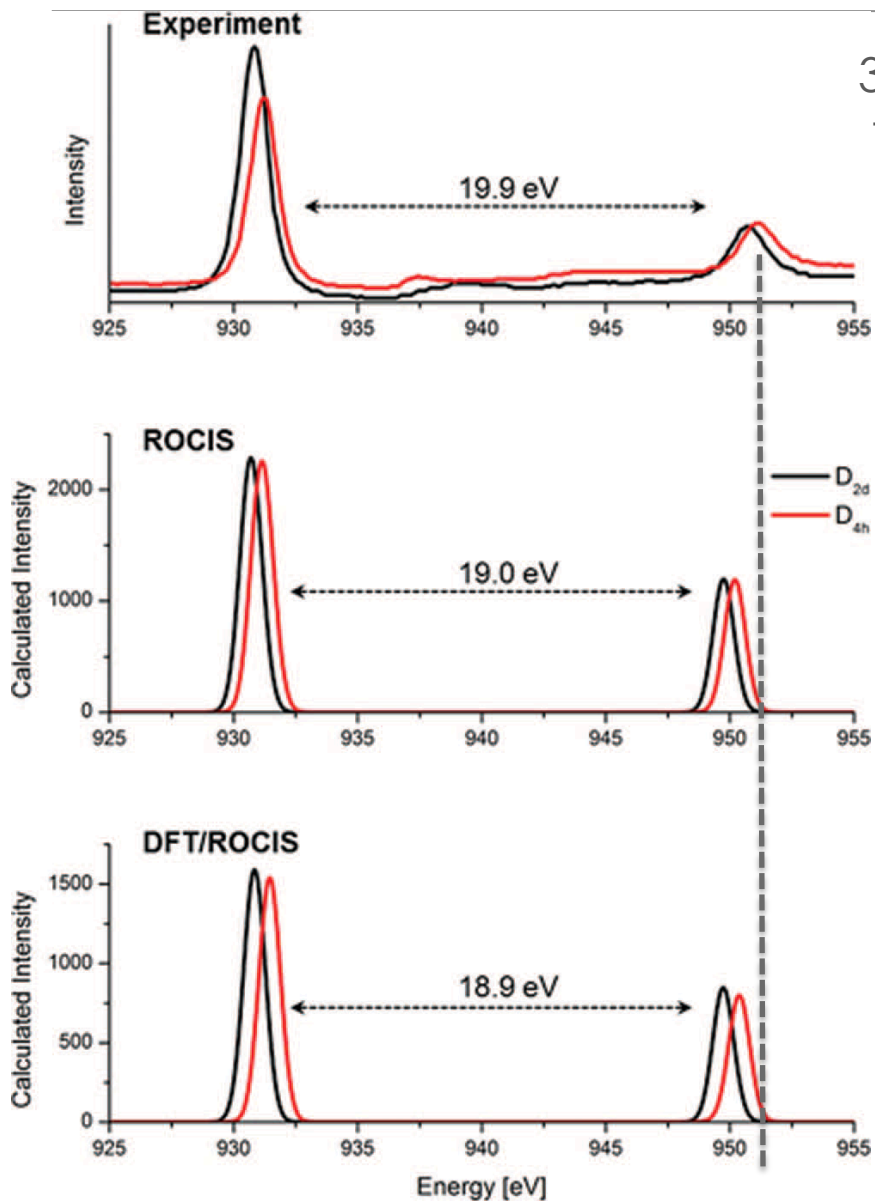
Effect of Relativity treatment

D_{2d} $[CuCl_4]^{2-}$

No Relativistics

18.9 eV

DKH

20.0 eV

DKH + Picture Change

19.1 eV
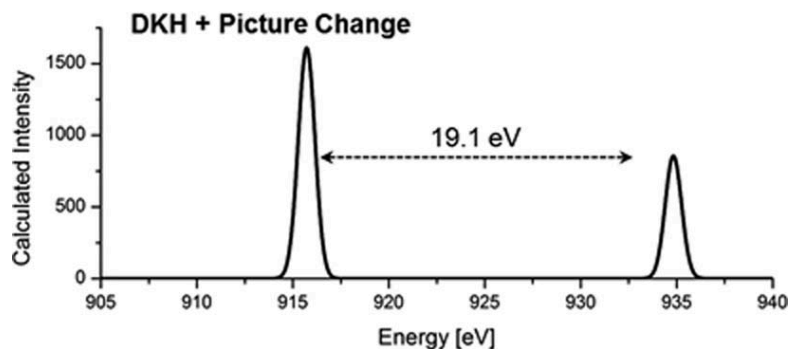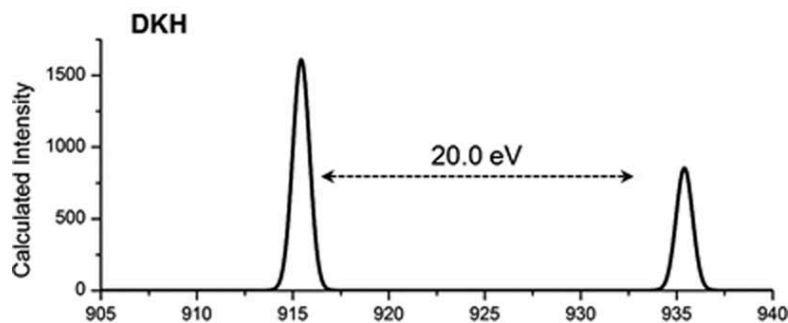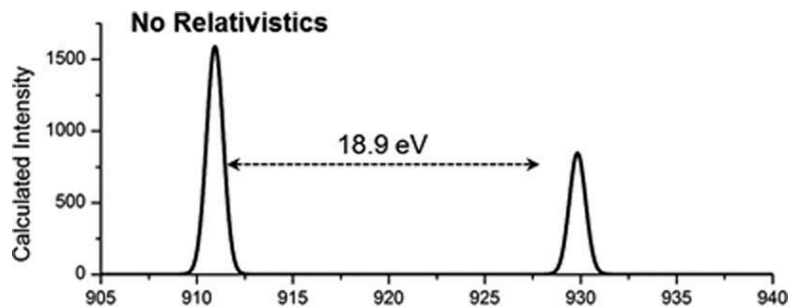
Relativistic effects influence
the calculated transition energies

But not the spectral shape

$[FeCl_4]^{2-}$

No Relativsitic Correction
ZORA
DKH

Roemelt, M., Maganas D., DeBeer S, Neese F., *J. Chem. Phys.* **2013**, *138*, 204101.
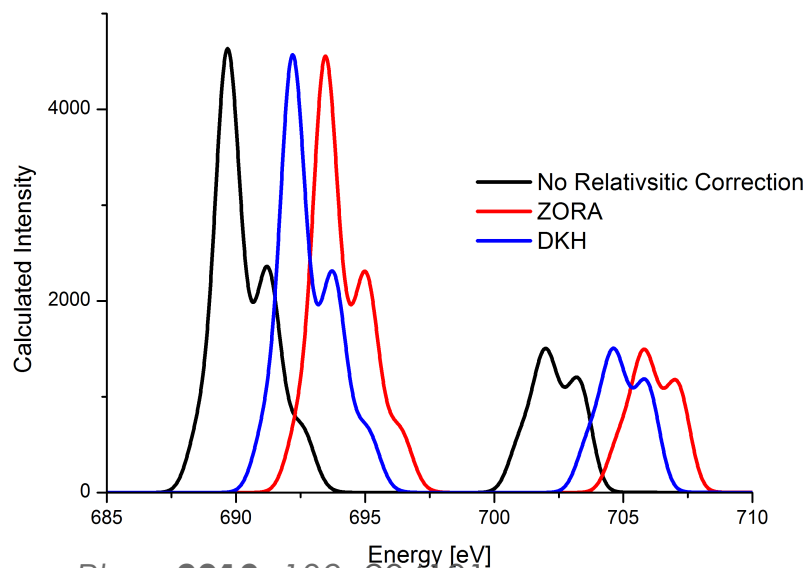
[FeCl$_4$]$^{-1}$: comparison to experiment

(a) [FeCl$_4$]$^{2-}$ — Experiment / ROCIS
(b) [FeCl$_4$]$^{2-}$ — Experiment / DFT/ROCIS
(c) [FeCl$_6$]$^{4-}$ — Experiment / ROCIS
(d) [FeCl$_6$]$^{4-}$ — Experiment / DFT/ROCIS
(e) [FeCl$_6$]$^{3-}$ — Experiment / ROCIS
(f) [FeCl$_6$]$^{3-}$ — Experiment / DFT/ROCIS
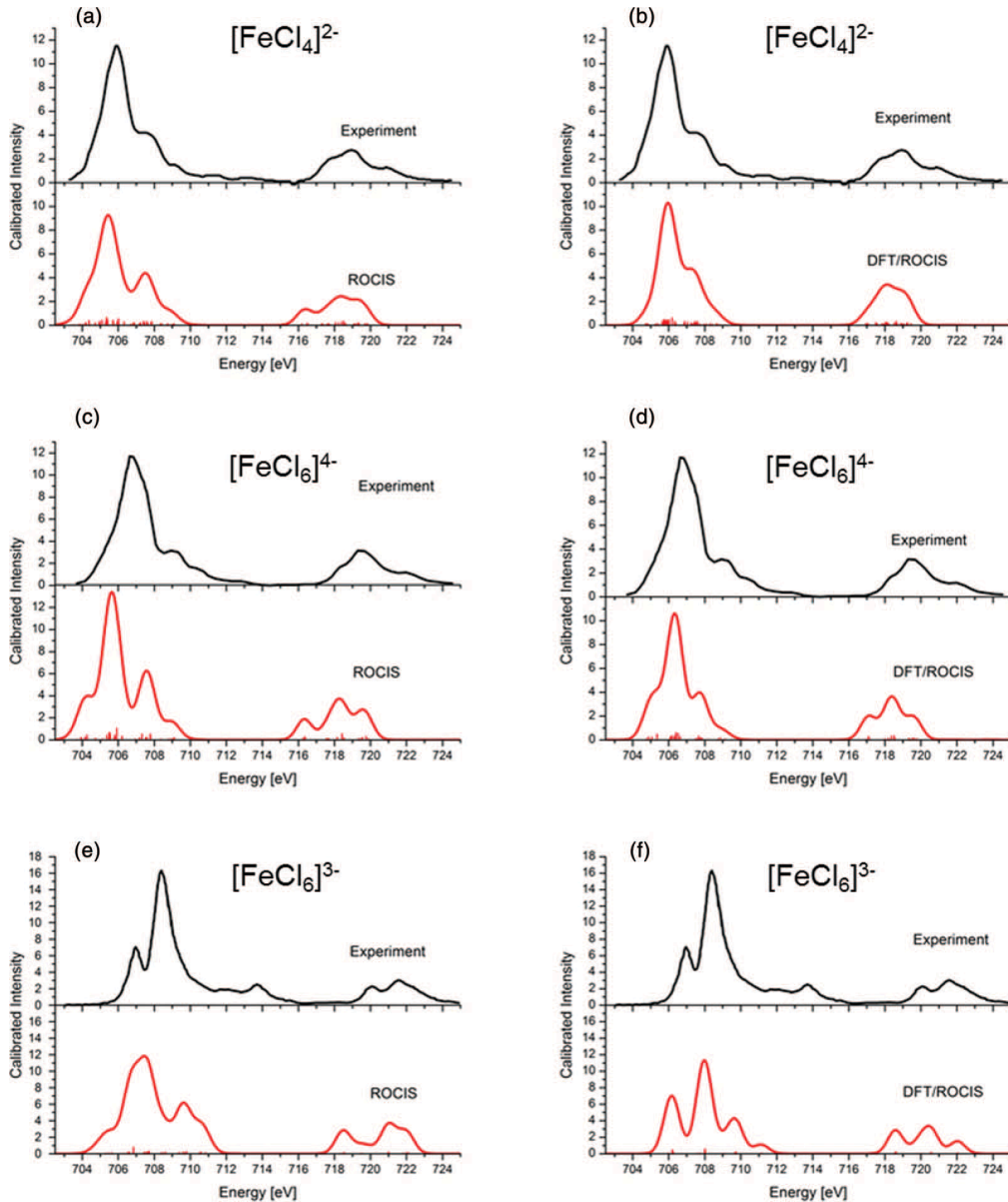
- In general ROCIS and DFT/ROCIS perform similarly for iron chlorides

- Covalency modifies the LF splittings inside the L3 features

- The missing or incorrect intensity features originate to the missing double excitations from the DFT/ROCIS Ansatz

Correct
Incorrect
Missing

exp
calc

Roemelt, M., Maganas D., DeBeer S, Neese F., *J. Chem. Phys.* **2013**, *138*, 204101.
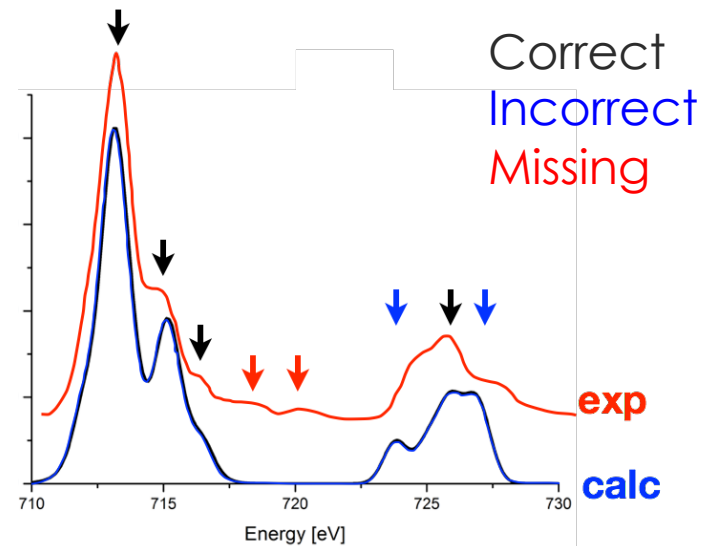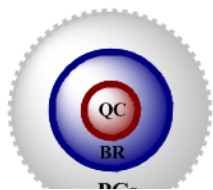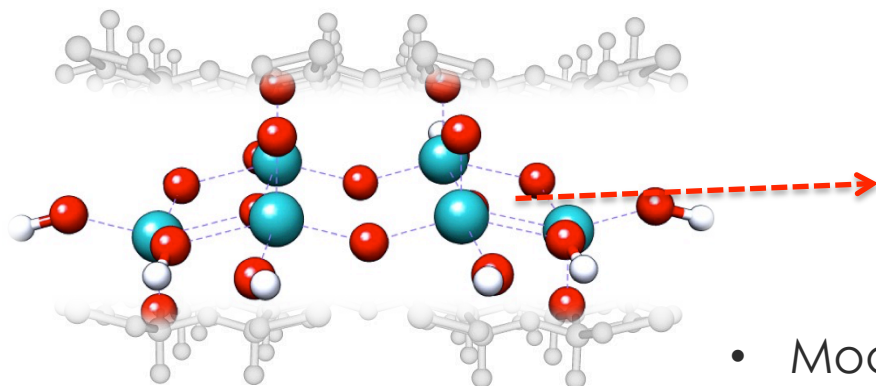
- Model is extracted from the sold crystallographic shell
- Embedded in a point charge field
- **Don't** always use formal charges!
- Use capped ECPs to prevent charge flow
- Compensate for negative charges

V$_2$O$_5$

LFM
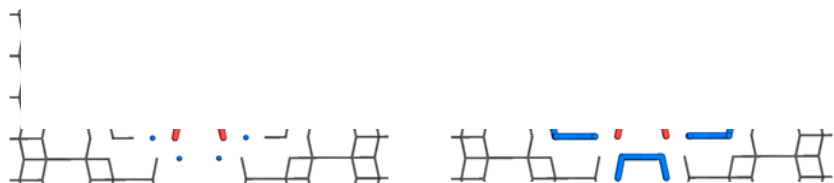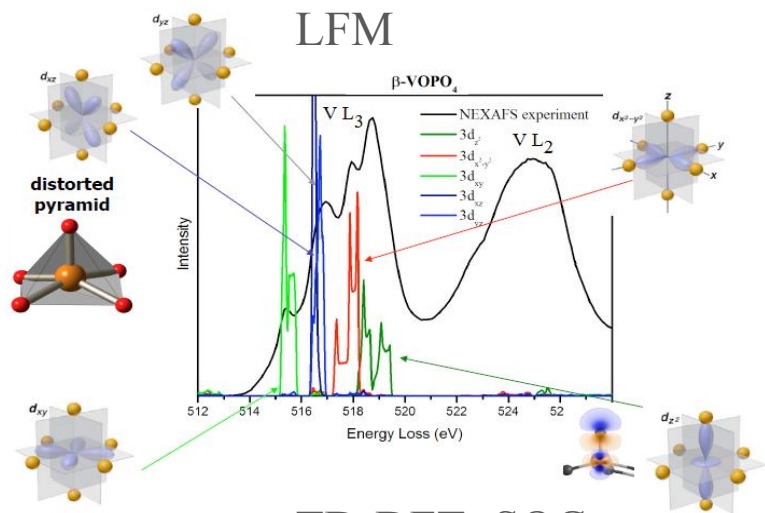
TD-DFT+SOC
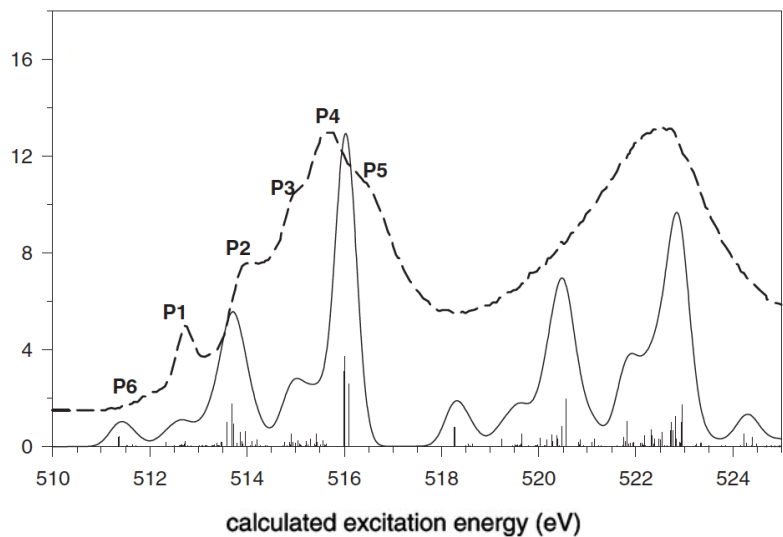
De Francesco, R.; Stener, Fronzoni, G. et.al.
Phys. Chem. Chem. Phys., **2006**, 8, 4300
J. Phys. Chem., **2012**, 137, 224308
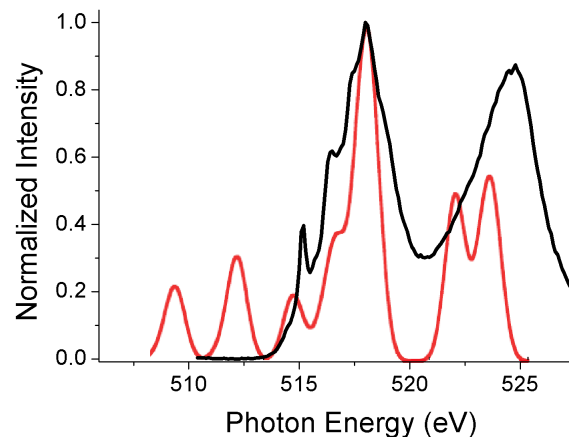
M.G. Brik K. Ogasawara H., Ikeno, and I. Tanaka *Eur. Phys. J.* B **2006,** 51**,** 345
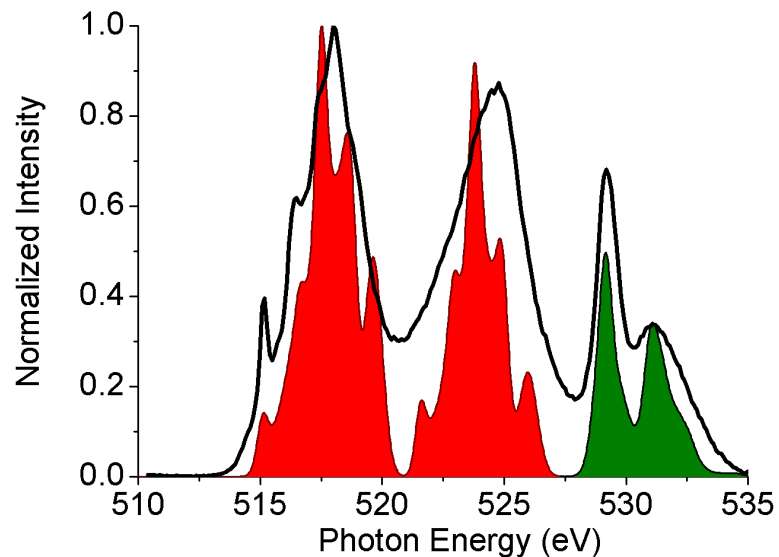
Maganas, D, Roemelt M, Schlögl, R., Neese F. et. al.
PCCP **2013**, 15, 7260
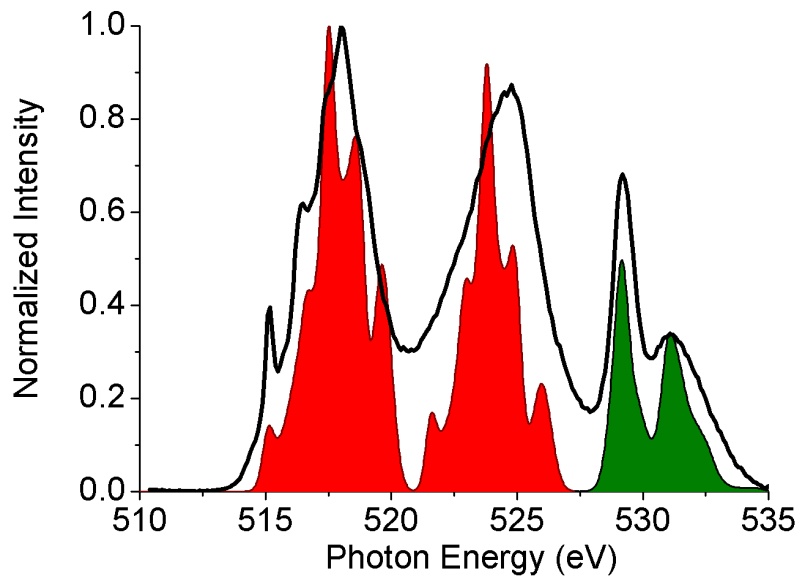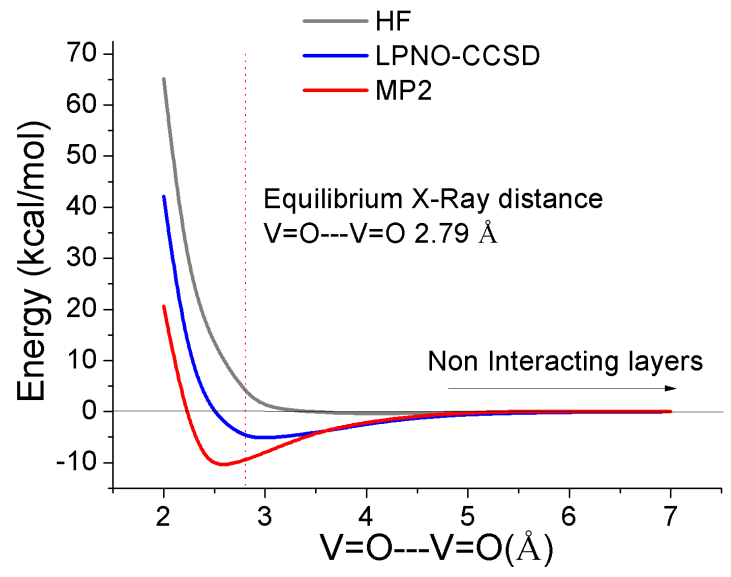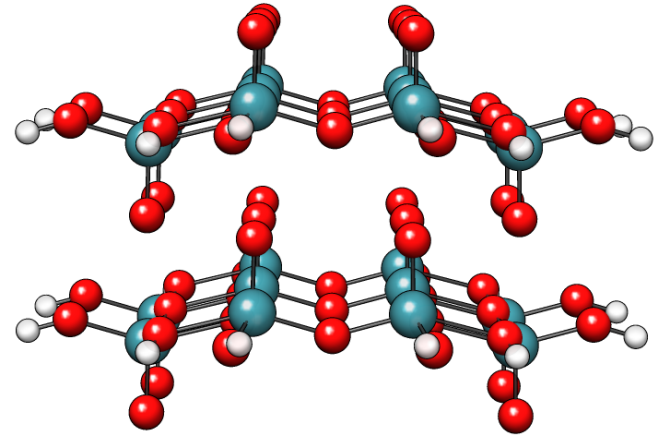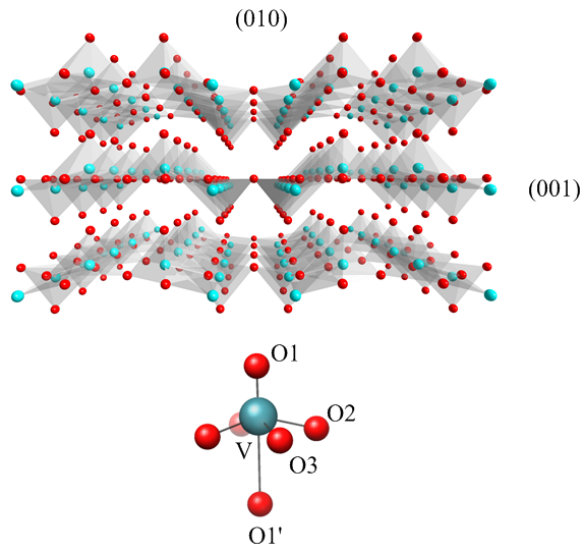
Open shell oxides

L-edge

M-edge

$[Fe_4O_{20}]^{-28}$

$[Fe_6O_{38}]^{-36}$
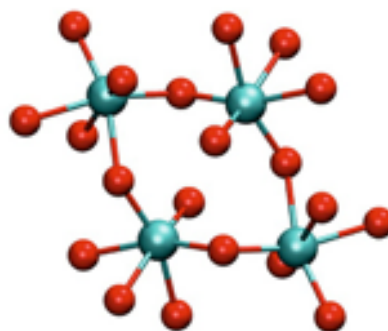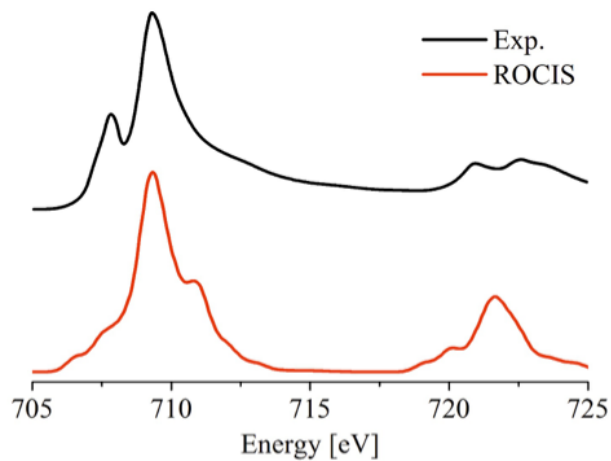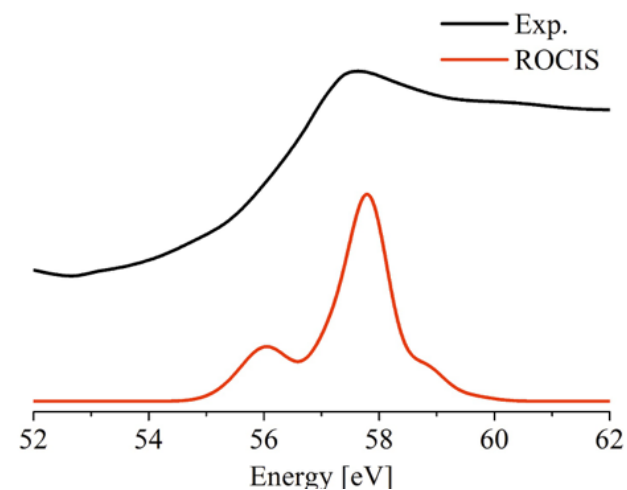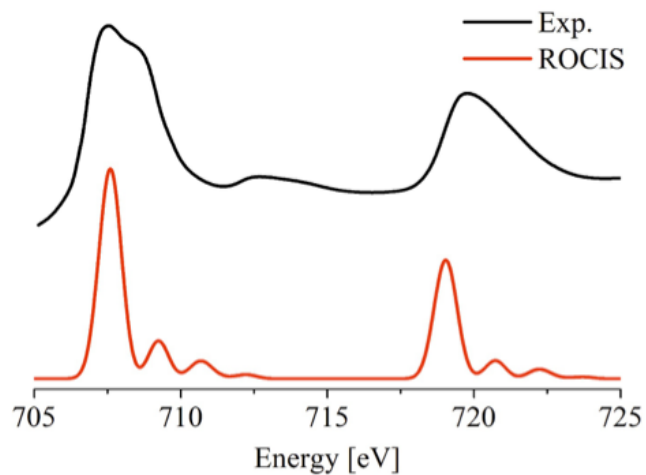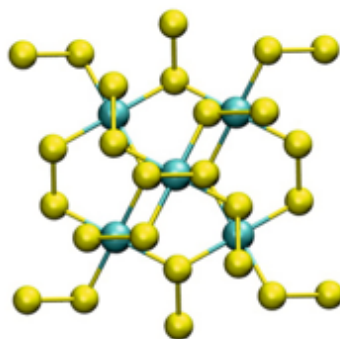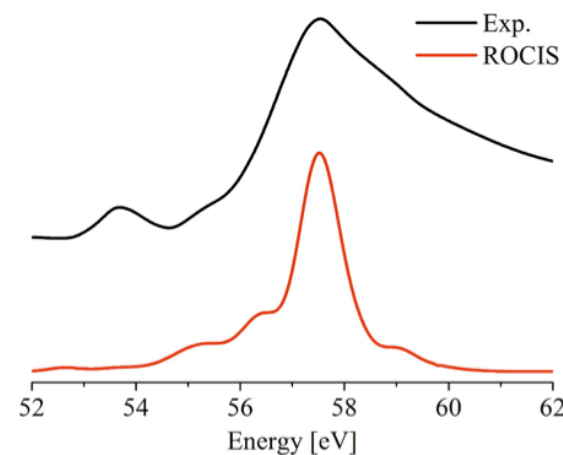
Not only that: CaF$_2$ and TiO$_2$
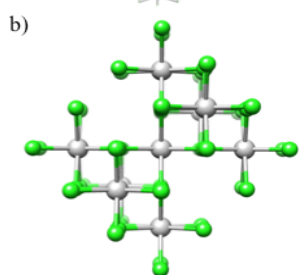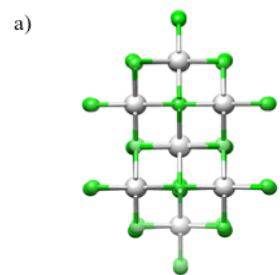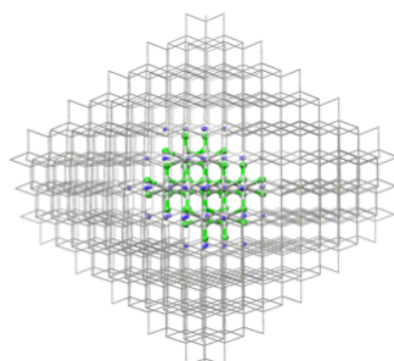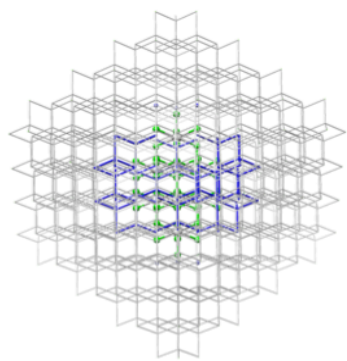
CaF$_2$
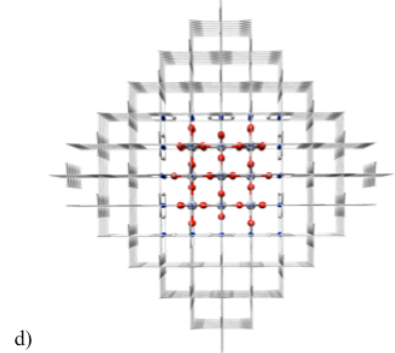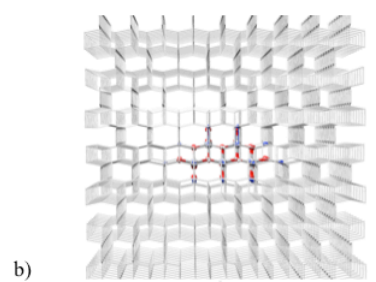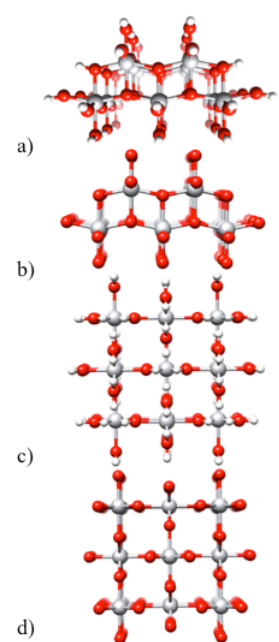
TiO$_2$-rutile

TiO$_2$-anatase

Maganas D., DeBeer S., and Neese F., Inorganic Chemistry Forum **2014,** 53, 6374
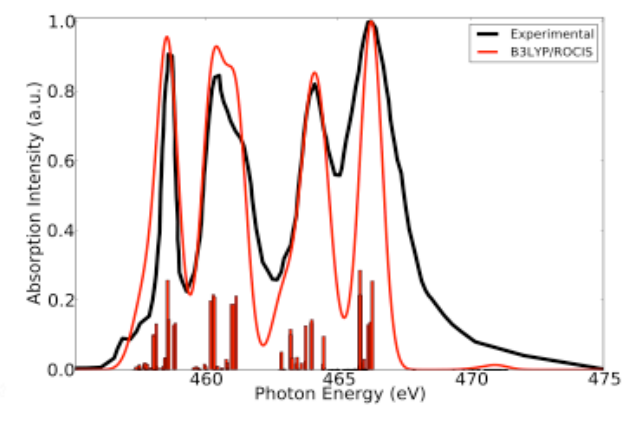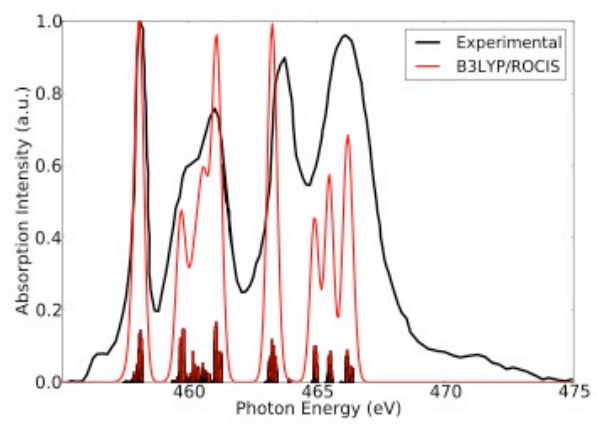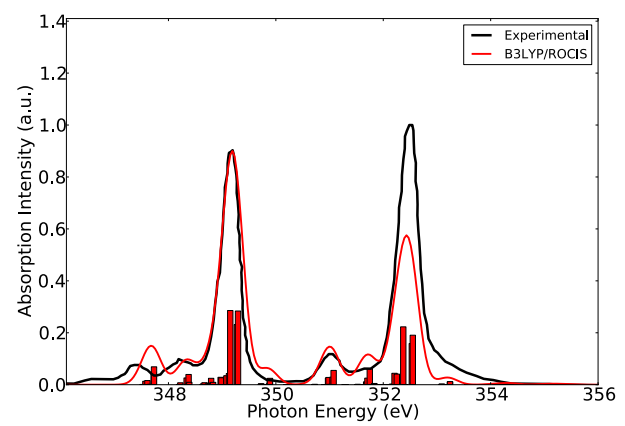
Mixed Valence Oxides

L-edge

$[Co_9O_{20}]^{-36}$

M-edge
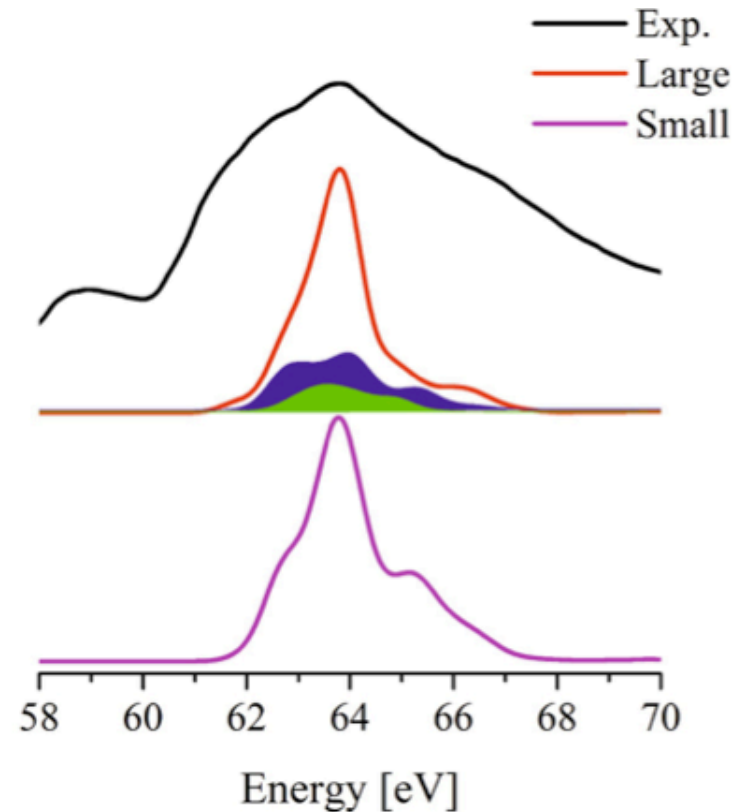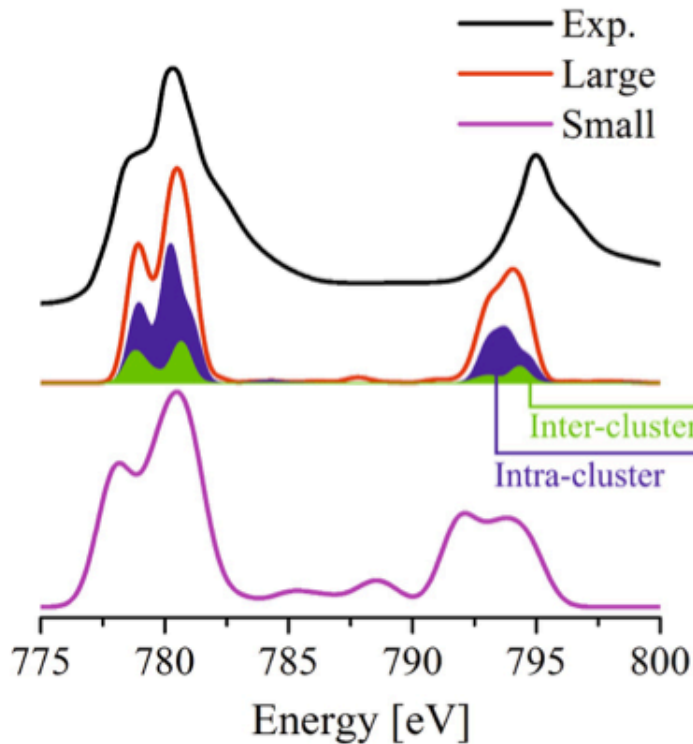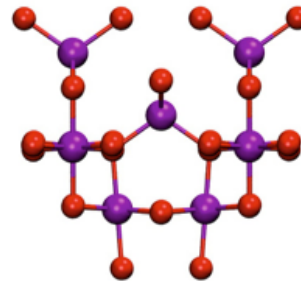
Reactivity group
Annete Trunschke

Catalysis

- **Combination of spectroscopic techniques for both Experiment and Theory is needed**

- State of the art XAS and Raman experimental techniques
- Well established and fully implemented calculation protocols are used:
  Raman/rRaman (**independent mode displaced harmonic oscillator model**)
  NEXAFS (**DFT/ROCIS**)

Petrenko T., Neese F, J., Chem. Phys. **2012** 137, 234107.
Roemelt M., Neese, F., *J Phys. Chem. A.* **2013**, *117*, 3069.
Roemelt M., Maganas D., DeBeer S. and Neese F., J. Chem. Phys. **2013** 138, 204101.

Bridging Molecular and Heterogeneous Catalysis

Homogeneous Catalysis

Heterogeneous Catalysis

Dimitrios Maganas, Annette Trunschke, Robert Schlögl, Frank Neese Faraday Discussions 2016
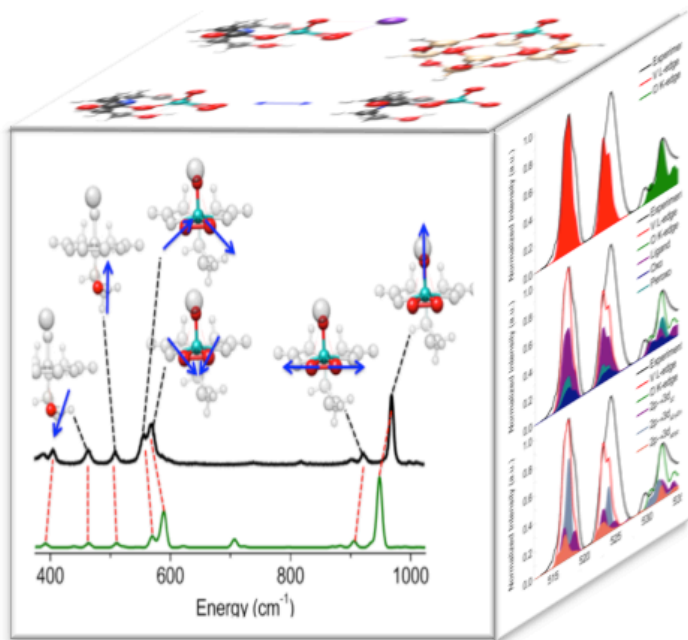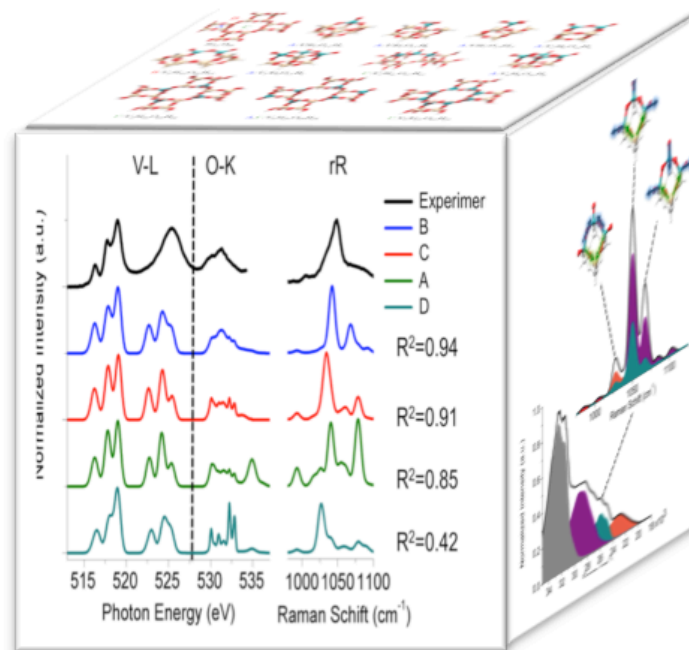
Oxo-Peroxo Vanadium Catalysts
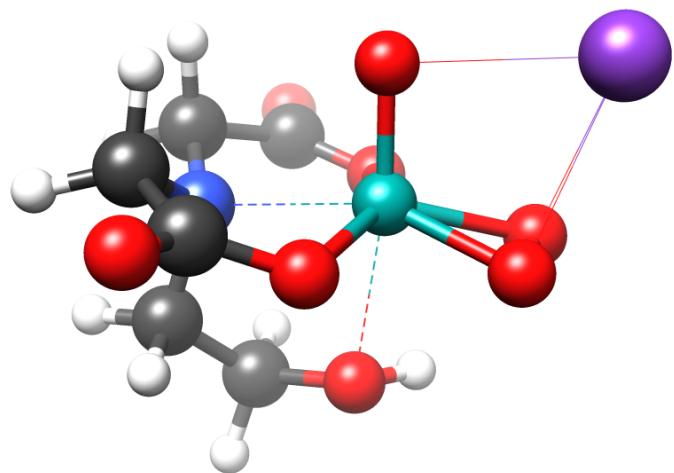
- Catalyze oxydation reactions (alcohols)
- Increased functionality due to different Oxygen groups (oxo, peroxoxo,
➢ It is needed to correlate:
   Oxygen type to particular reaction step

Trunschke A., Haevecker M., Hermann K, Schlögl R., et.al. J. Phys. Chem. C, **2014**, 118, 24611

Silica Supported Catalysts
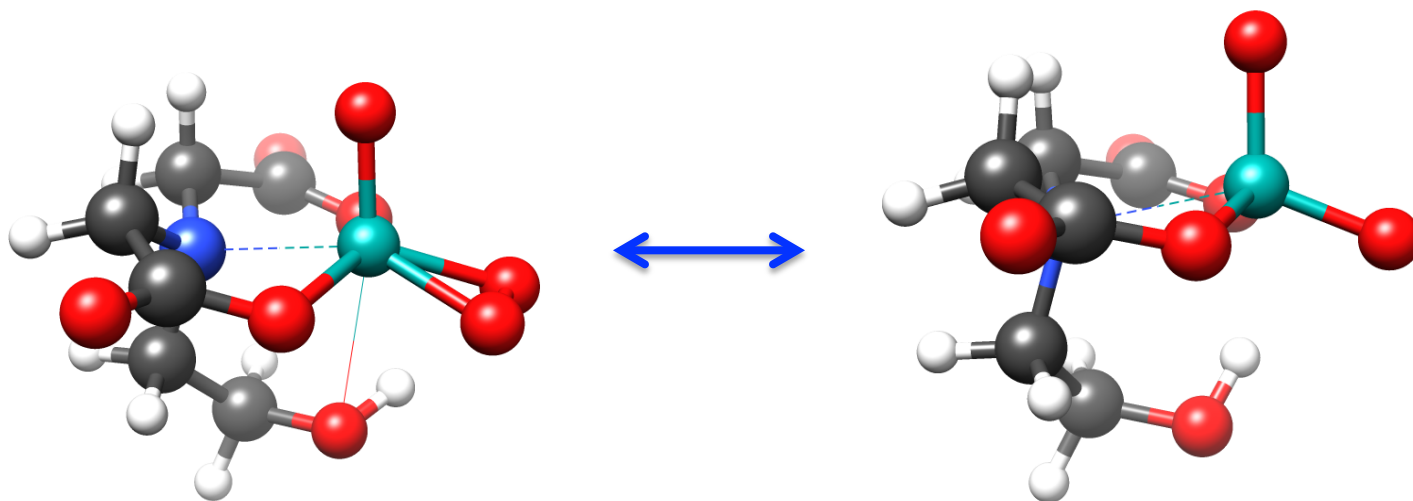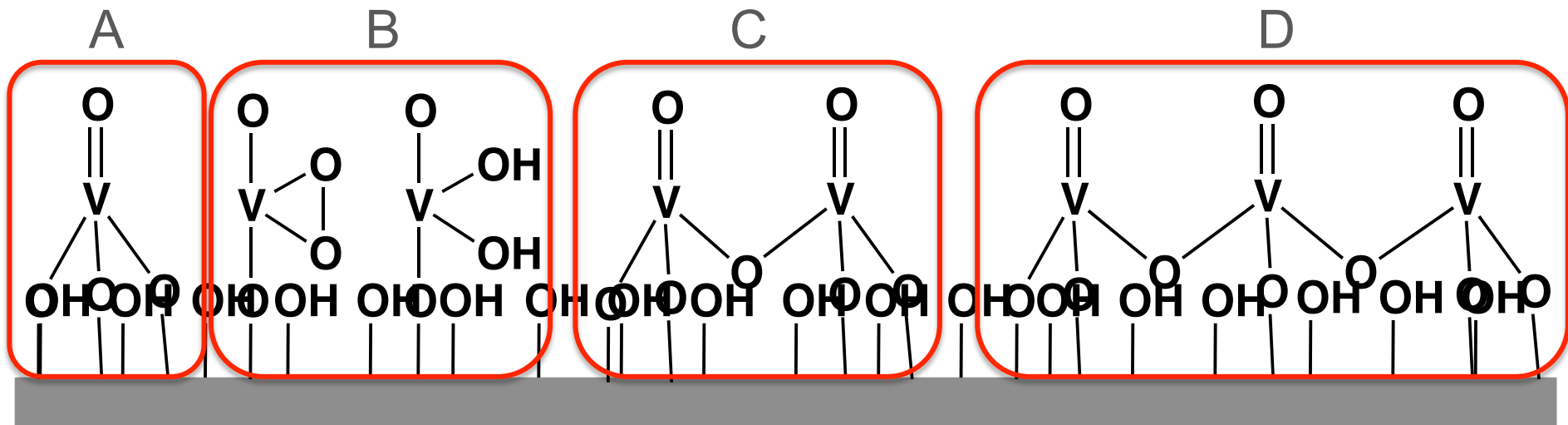
A: Vanadyl type

B: Umbrella type

C: Dimer

D: Oligomer

V/SiO$_2$: Monolayer-type vanadia catalysts:

- Have been proven to be more active than crystalline V$_2$O$_5$ nanoparticles on specific oxidation reactions
- The structure of the catalytic center remains elusive

Trunschke A., Haevecker M., Schlögl R., et.al, Catal. Sci. Technol. 7, **2012**, 2

$Si_{32}O_{80}$

B

$V_2Si_6O_{14}H_6$

$V_2Si_{12}O_{23}H_{12}$

A

C

$V_4Si_4O_{16}H_4$

V_4Si_{28}

$Si_{32}O_{80}$

$V_8Si_{24}O_{80}H_{28}$
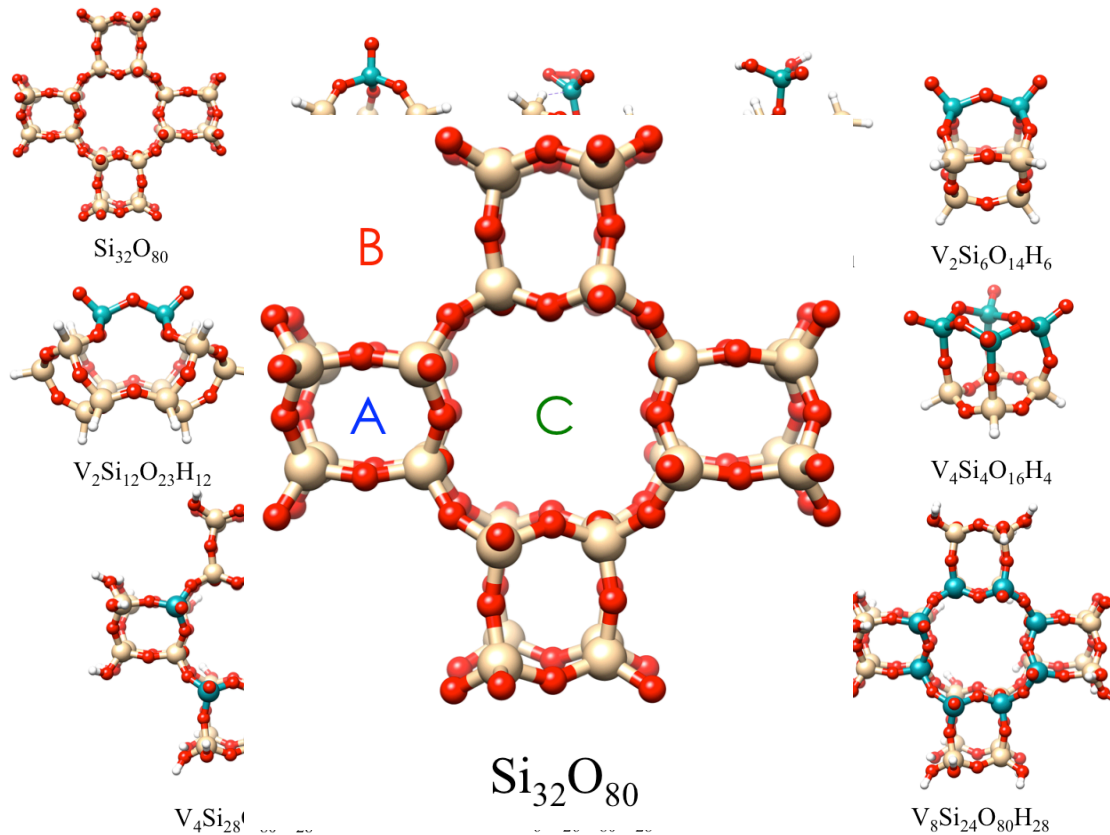
Optical & Raman Spectroscopy
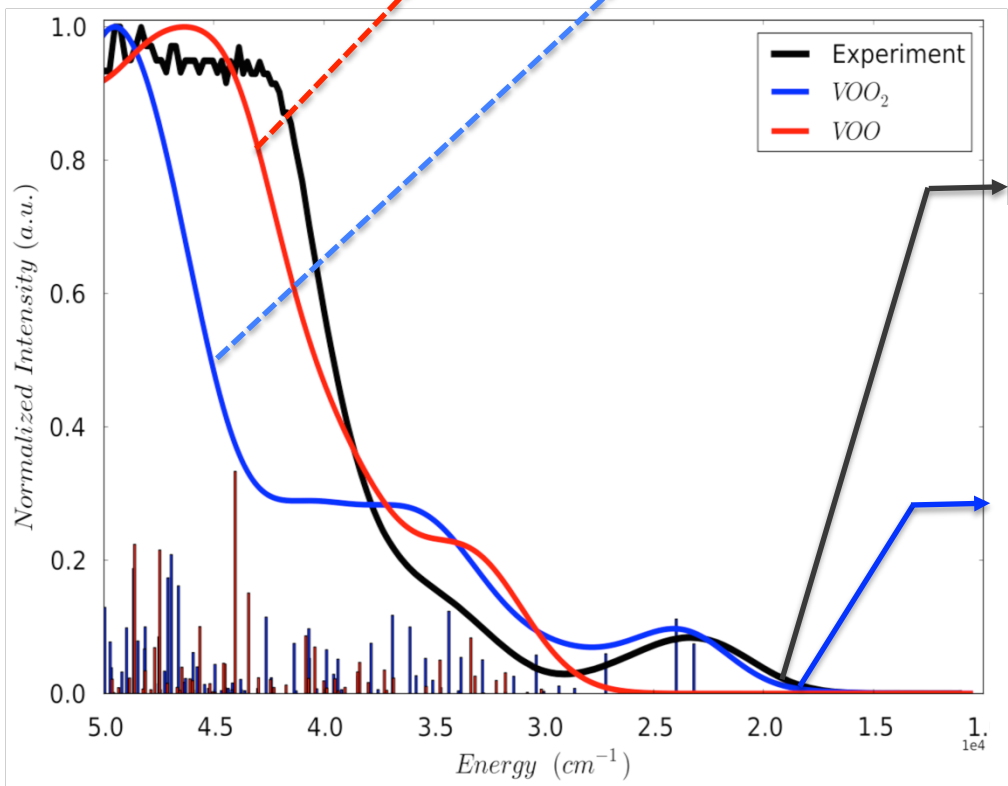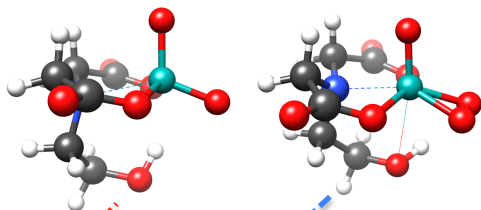
Trunschke A., Haevecker M., Hermann K, Schlögl R., et.al. J. Phys. Chem. C, **2014**, 118, 24611

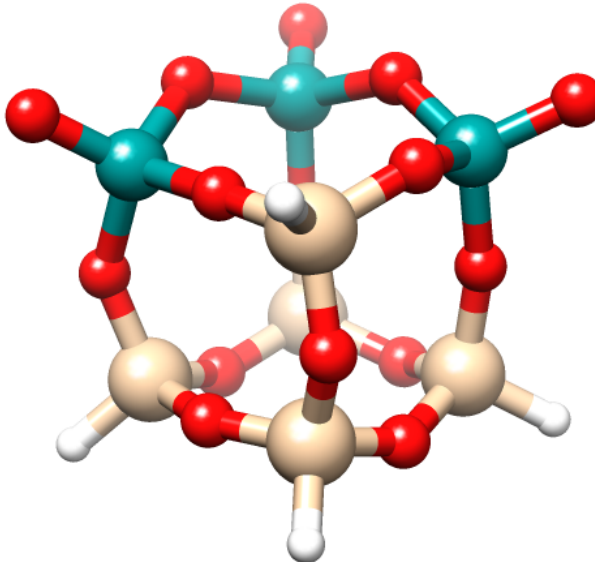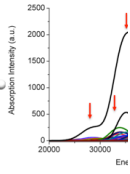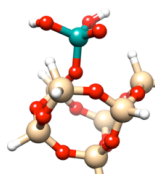Petrenko T., Neese F, J., Chem. Phys. **2012** 137, 234107.

Energy (cm^{-1})
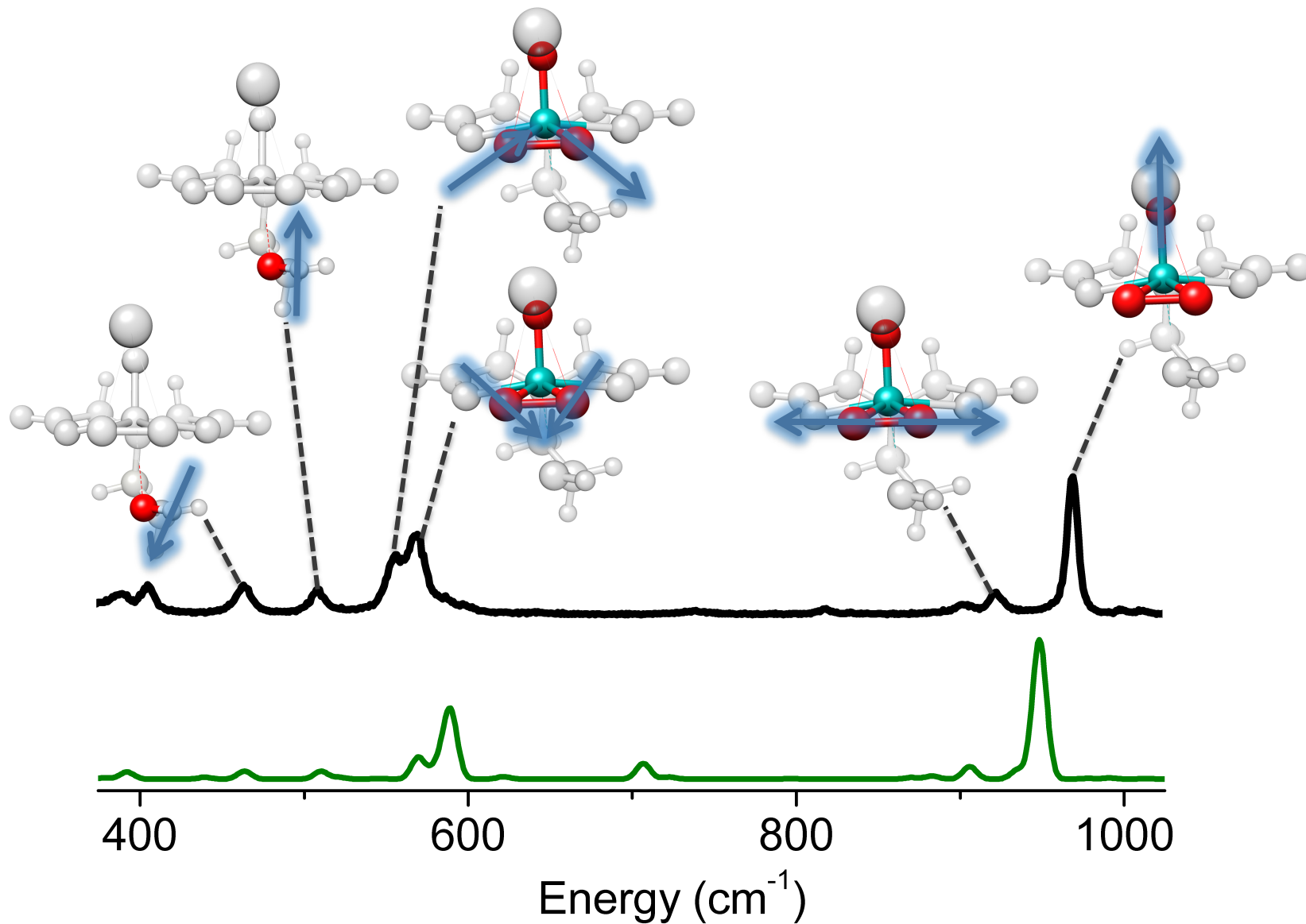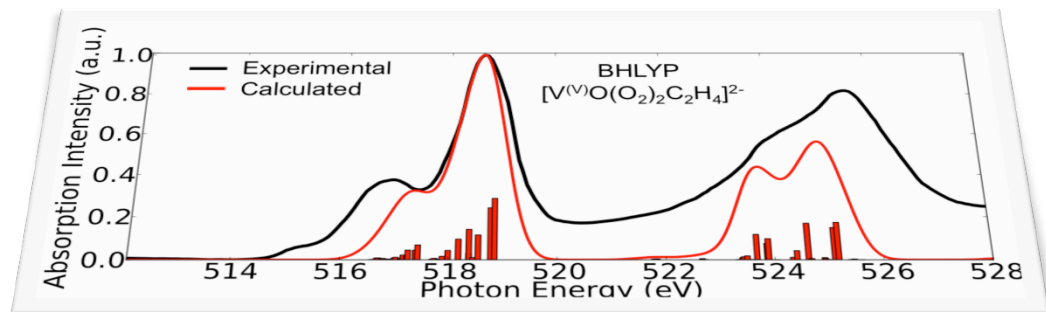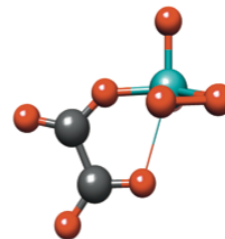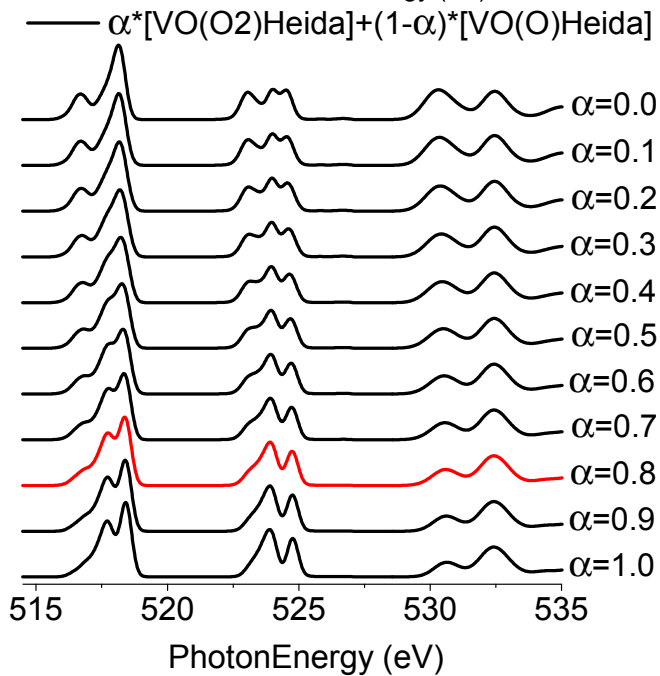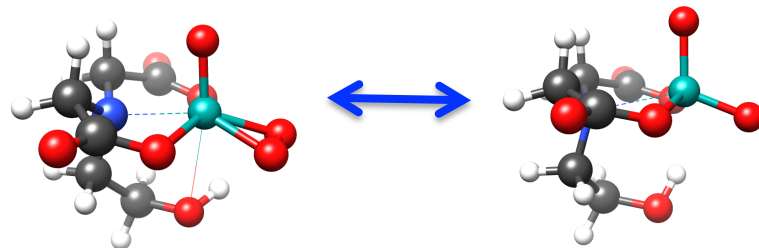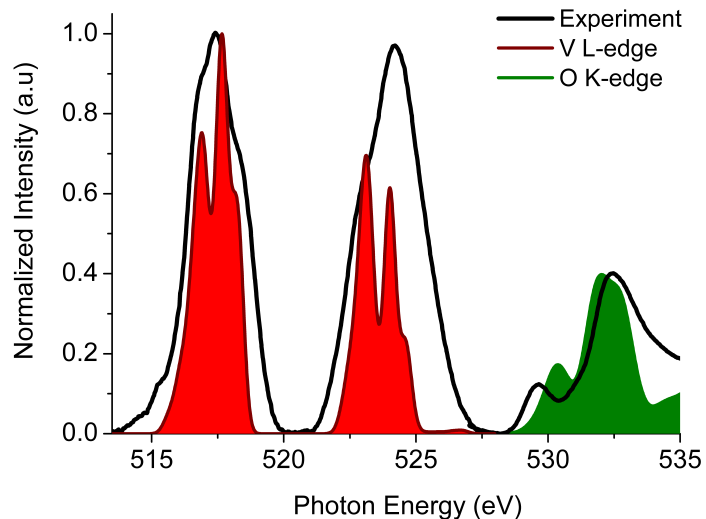
Simultaneous analysis

Models   UV

V/CeO$_2$ STM

0.7 V atoms nm^{-2}

Sauer I., et al. Angewante Chemie **2012** 42, 8006
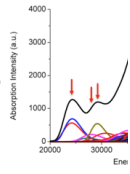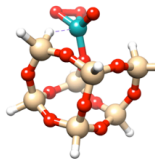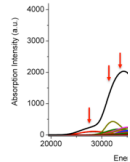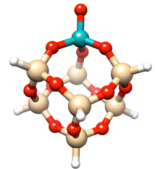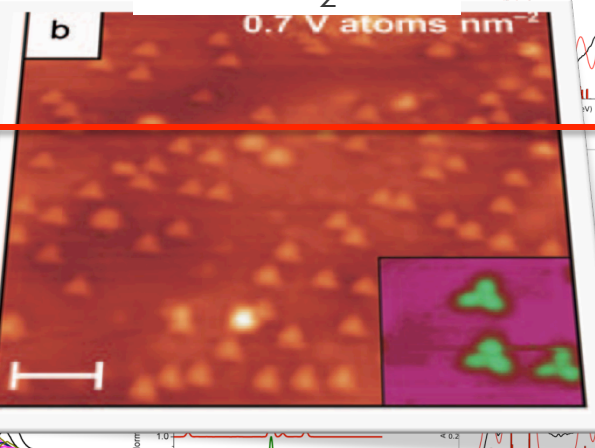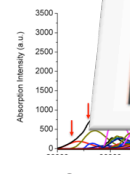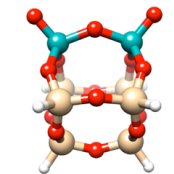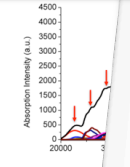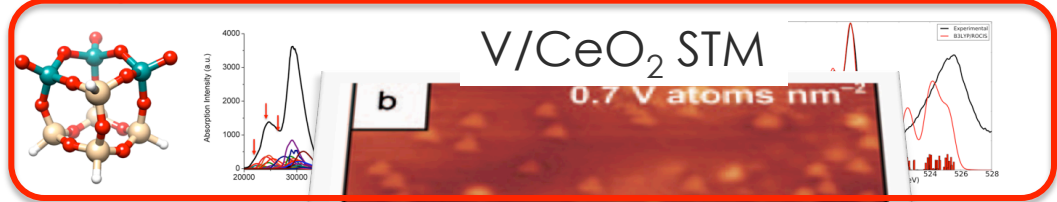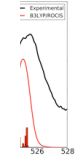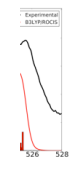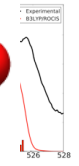
Weighted fit to both three experiments
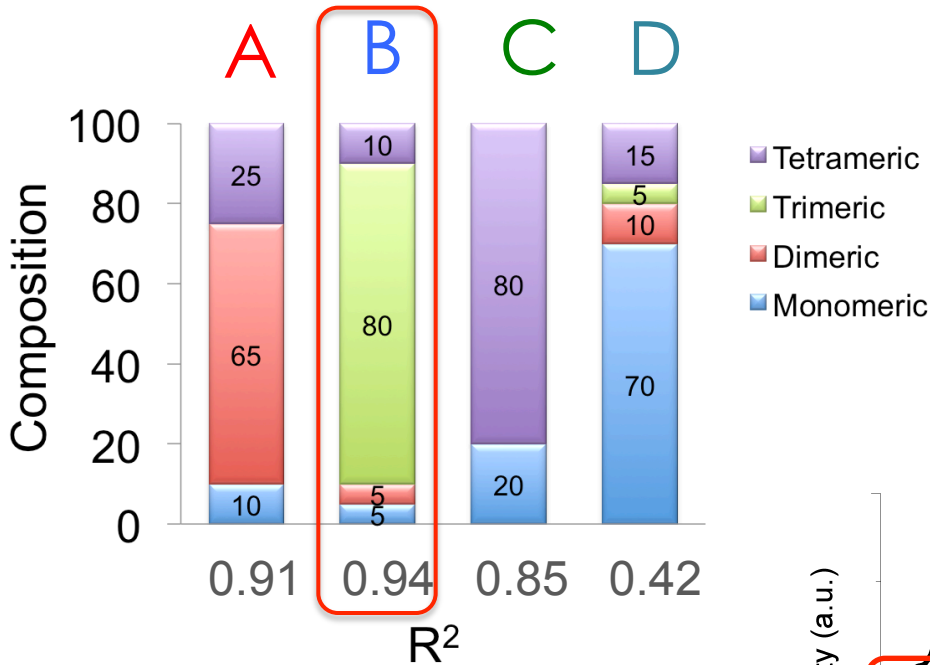
Of course the catalytic center
Is sensitive to many things
(Environment of the support,
reaction conditions, …)

Evidence:
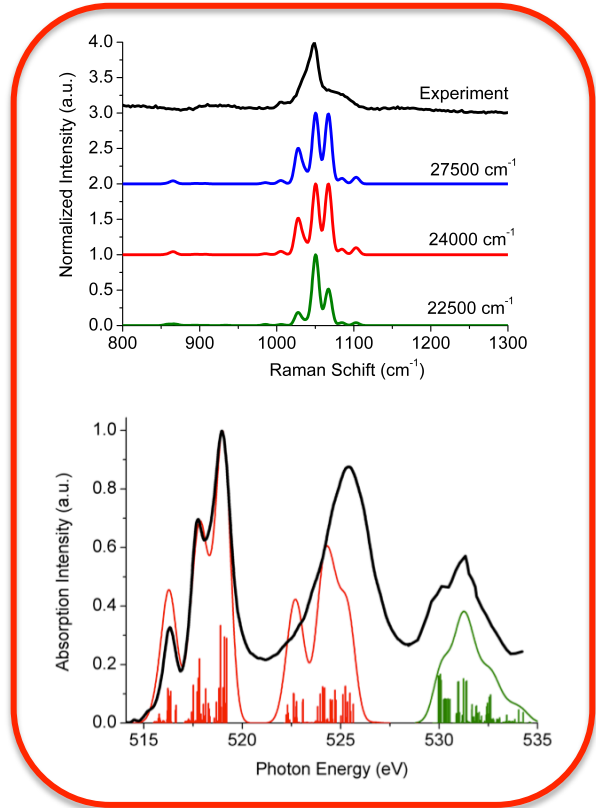Spectroscopic response
to structural correlation

Just like in molecular systems!

Dimitrios Maganas, Annette Trunschke, Robert Schlögl, Frank Neese Faraday Discussions 2016
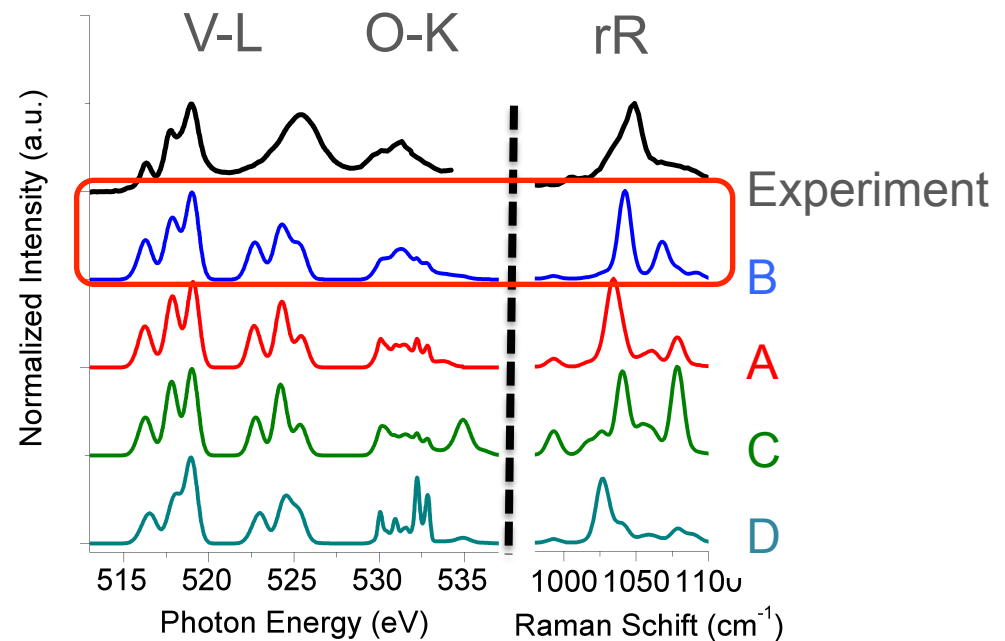
- Results of predictive accuracy can be obtained for both molecular and heterogeneous catalytic systems

  By employing unified experimental and theoretical protocols

Thank you for your attention!

The Orca Computational Package

Semiempirical

INDO/S,MNDO,AM1,PM3,NDDO/1

Density Functional

LDA, GGA, Hybrid Functionals
Double hybrid functionals,
RI-Approx., Newton-Raphson
RKS,UKS,ROKS

Hartree-Fock

RHF,UHF,ROHF,CASSCF
Direct, Semidirect, Conventional,
RI-Approx., Newton-Raphson

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http://www.cec.mpg.de/
downloads.

Excited States

TD-DFT/CIS+gradients
MR-CI/DDCI/SORCI

Electron Correlation

MP2/RI-MP2
CCSD(T),QCISD(T),CEPA,CPF
(all with and without RI, Local)
MR-MP2, MR-MP3, MR-MP4(SD)
MR-CI, MR-ACPF, MR-AQCC

Molecular Properties

Analytical Gradients(HF,DFT,MP2) + Geometries + Trans.
States
Polarizabilities, Magnetizabilities (Coupled-Perturbed HF/
KS)
COSMO Solvation Model Throughout
IR, Raman and Resonance Spectra (Numerical
Frequencies)
EPR-Parameters (g,A,D,J,Q)
Mössbauer-Parameters (δ,ΔE_Q)
X-ray absorption-emission spectroscopy
ABS,CD,MCD Spectra
Population Analysis, NBOs, Localization, Multipole
Moments,...

Relativistic Methods

1st-5th Order Douglas-Kroll-Hess
Zero'th Order Regular Approximation (ZORA)
Infinite Order Regular Approximation (IORA)
Picture Change Effects, All electron basis sets,
(Effective core potentials)