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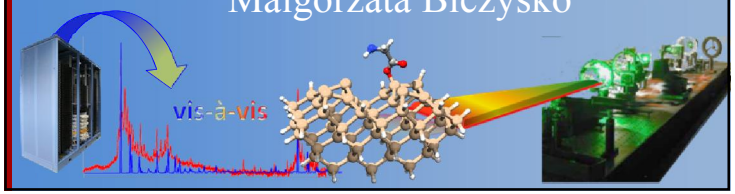
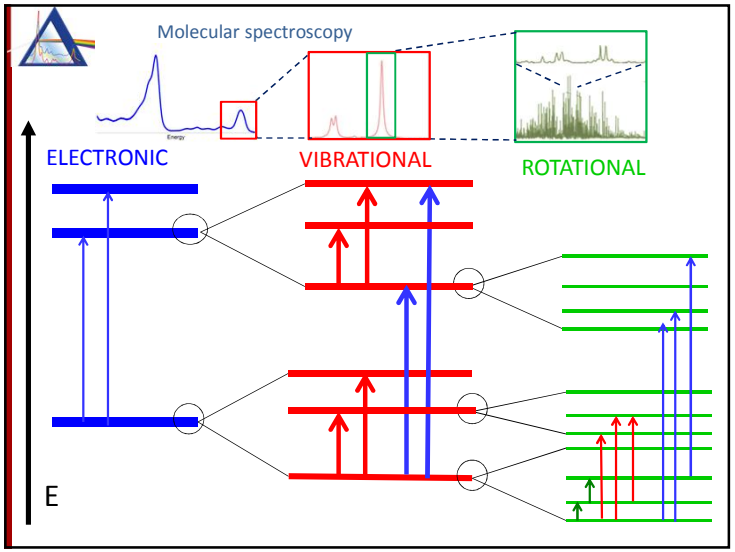
DREAMS Laboratory Scuola Normale Superiore, Pisa

SCUOLA NORMALE SUPERIORE PISA

Simulation of electronic and vibrational spectra line-shapes

Malgorzata Biczysko

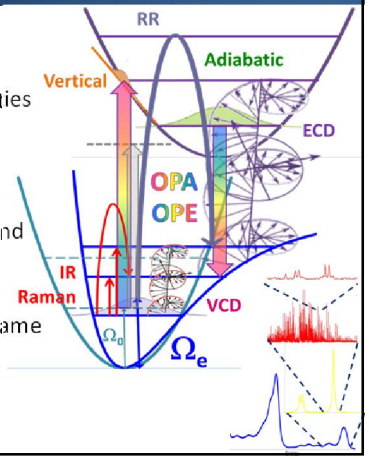




Experimental and computational spectroscopy

Unified and general theoretical model

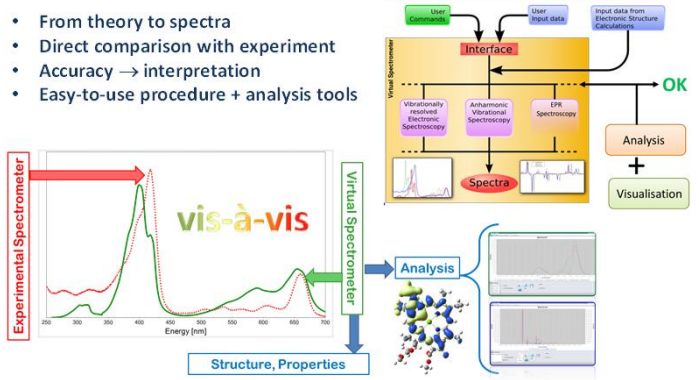
- **From 1 vibrational level to transitions between 2 PES**
  - Vibrational averaged properties
  - Vibrational spectroscopies
  - Vibronic transitions
- **Focus on nuclear part**
  - Beyond vertical transitions and harmonic approximation
- **General model**
  - Many spectroscopies – the same tool
  - Easy extensions – common kernels



Experimental and computational spectroscopy

Virtual spectrometer = vis-à-vis comparison

- From theory to spectra
- Direct comparison with experiment
- Accuracy → interpretation
- Easy-to-use procedure + analysis tools



1. V. Barone, J. Bloino, M. Biczysko, F. Santoro, *J. Chem. Theory Comput.*, 5, 540 **2009**; *JCTC*, 6, 1256 **2010**
2. VB, A. Baiardi, MB, J. Bloino, C. Cappelli , F. Lipparini , *Phys. Chem. Chem. Phys*, DOI: 10.1039/C2CP41006K, **2012**

Experimental and computational spectroscopy

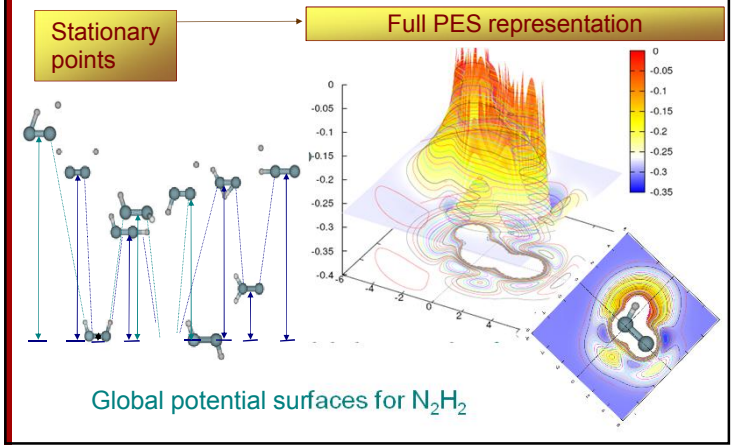
Overview

- **Vibronic spectroscopy**
  - General formulation for one-photon processes
  - The electronic transition integral
  - Calculation of the band-shape
  - Approximation schemes
- **Anharmonic vibrational spectroscopy**
  - Vibrational energy levels
  - Transition intensities
  - Vibrational averages of arbitrary properties
  - Medium-to-large systems

Theoretical models: PES

Global Potential Energy Surfaces

Stationary points → Full PES representation



Global potential surfaces for N_2H_2

Theoretical models: PES

PES representation

- **Numerical grid representation**
  - Assuming 10 points/coordinate

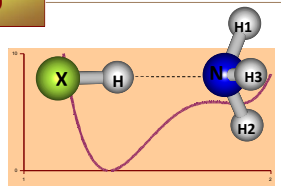
Number of atoms	Dimension	Grid
3	3	10^3=1000
4	6	10^6=1'000'000 !
n	3n-6	$10^{(3n-6)}$! !

- **Analytic function**
  - Eg. 6-D global PES for water dimer (X. Huang et al. *J. Phys. Chem A.* 2005, 110, 445)
  - fifteen variables of the fit, the polynomial to seventh order
  - in total there are 5227 terms in the expression for the PES

Theoretical models: PES

LOCAL Potential Energy Surfaces

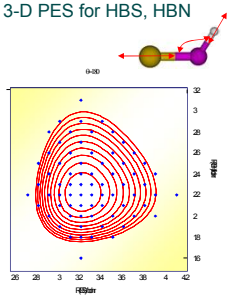
1-D → dimension → Full-D

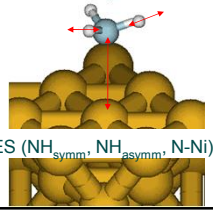


1-D PES for proton motion in $XH\text{-}NH_3$

Full 3-D PES for HBS, HBN

...



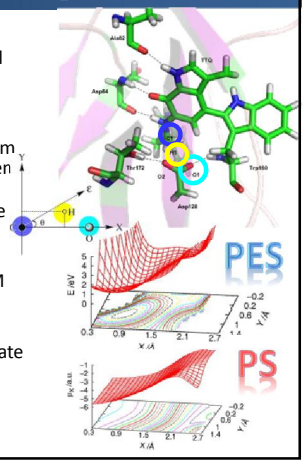


3-D PES (NH_{symm}, NH_{asymm}, N-Ni) for NH_3@Ni(111)

Theoretical models: PES + PS

Spectroscopy: PES + Property Surface

- **PES: dynamics, structures**
  - In principle can be studied by fully classical methodologies (Force Fields) + molecular mechanics or classical dynamics
- **PES + PS : spectroscopic properties**
  - Interaction with light – intrinsically quantum effect, electronic structure need to be taken into account
  - 'spectroscopically relavant part' need to be computed at QM level
- **Large systems**
  - QM/QM' (QM': semiempirical) or QM/MM
- **Example**
  - Design of laser pulses for mode specific vibrational excitation in an enzyme–substrate complex
  - QM/MM PES and dipole moment PS
  - Chemical Physics Letters 491 (2010) 230–236

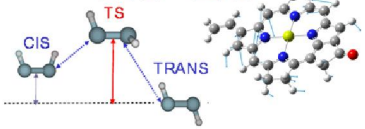


Theoretical models

Sampling of PES and PS

Time-independent

$\hat{H}\Psi=E\Psi$



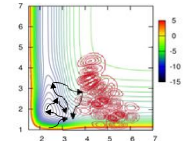
Eigenvalues, eigenfunctions

Search for stationary points: **minima** (determination of structure and properties), saddle points (determination of energy barriers and reactivity)

PES and PS described derivatives wrt nuclear coordinates (eg. Normal modes)

Time-dependent

$i\hbar\sigma/\delta t\Psi=\hat{H}\Psi$



wavepackets propagation

time-dependent correlation functions

Sampling of the energy surface: collection of trajectories (Classical or Quantum Molecular Dynamics approach)

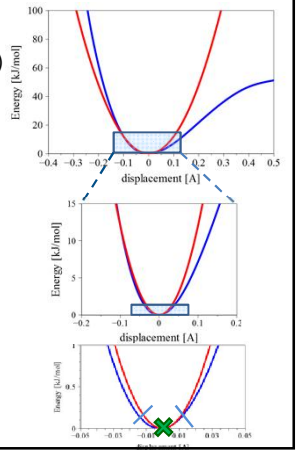
PES and PD are determined 'on the fly'

Or a priori from grid calculation

Theoretical models: PES

Time-independent + feasible approaches

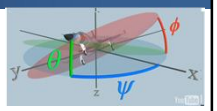
- **Born-Oppenheimer approximation**
  - One excited electronic state at a time (independent excited states = no coupling)
- **Harmonic description of PES as a 1st order approximation**
  - Semi-rigid molecular systems
  - PES close to the local minimum
  - Analytical (GS harm) or numerical (ES harm, GS anh)
  - Anharmonic corrections via perturbation theory
- **Normal modes representation**
  - Based on Cartesian coordinates
- **Eckart conditions**
  - Separate translation from rotation/vibration
  - Minimize interaction between rotational and vibrational motions



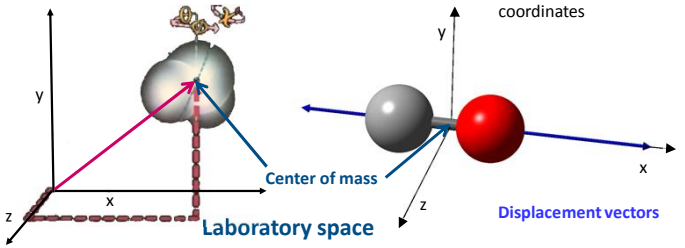
Theoretical models: PES

Coordinate system

- **Vibration described with respect to the center of mass**
  - Periodic, concerted displacement of nuclei
  - center of mass unaltered in laboratory space
- **N-atomic molecule: 3N coordinates**
  - x,y,z for each atom
- **Body-fixed coordinate system**
  - Origin (center of mass) wrt Laboratory space : 3 coordinates (translation)
  - Space orientation: 3 rotational coordinates
- **3N-6 vibrational coordinates (linear molecules 3N-5)**

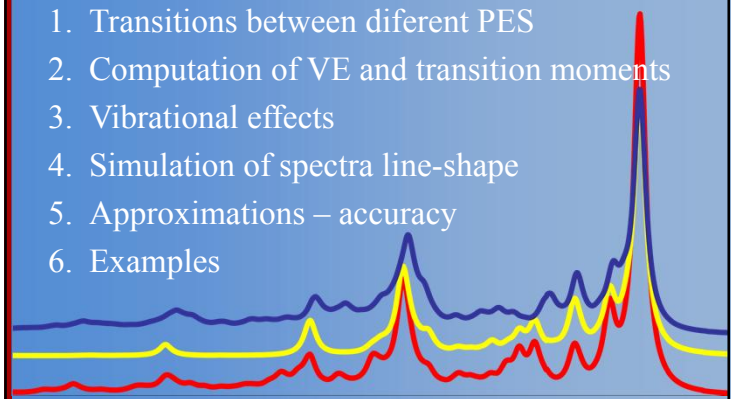


θ, φ, χ - Eulerian angles → Rotational coordinates



Electronic spectroscopy

1. Transitions between diferent PES
2. Computation of VE and transition moments
3. Vibrational effects
4. Simulation of spectra line-shape
5. Approximations – accuracy
6. Examples



Vibronic spectra: Theoretical framework

One-photon processes

- **General sum-over-states formula to compute spectrum band shape**

One-Photon Absorption: Molar absorption coefficient,

$$\epsilon(\omega) = \frac{10\pi N_A \omega}{3\epsilon_0 \ln(10)\hbar c} \sum_{m,n} \rho_m \left[\langle \Psi_m | \boldsymbol{\mu} | \Psi_n \rangle \cdot \{ \langle \Psi_m | \boldsymbol{\mu} | \Psi_n \rangle \}^* \right] \delta(\omega_{mn} - \omega)$$

One-Photon Emission: Energy emitted by one mole per second,

$$I_{em}/N_n = \frac{2\omega^4}{3\epsilon_0 c^3} \sum_{m,n} \rho_n \left[\langle \Psi_m | \boldsymbol{\mu} | \Psi_n \rangle \cdot \{ \langle \Psi_m | \boldsymbol{\mu} | \Psi_n \rangle \}^* \right] \delta(\omega_{mn} - \omega)$$

Electronic Circular Dichroism: Difference of molar extinction coefficients,

$$\Delta\epsilon(\omega) = \frac{40 N_A \pi \omega}{3 \ln(10)\hbar c^2} \sum_{m,n} \rho_m \left[\langle \Psi_m | \boldsymbol{\mu} | \Psi_n \rangle \cdot \{ \Im \langle \Psi_m | \boldsymbol{m} | \Psi_n \rangle \}^* \right] \delta(\omega_{mn} - \omega)$$

power of incident energy; lower state; higher state

$$I = \omega^\beta \sum_m \sum_n \rho_\gamma \left[\langle \Psi_m | \boldsymbol{d}^A | \Psi_n \rangle \cdot \{ \langle \Psi_m | \boldsymbol{d}^B | \Psi_n \rangle \}^* \right] \delta(\omega_{mn} - \omega)$$

constant; Boltzman population; Need to compute: $\langle \Psi_m | \boldsymbol{d}^X | \Psi_n \rangle$; distribution function

Vibronic spectroscopy: Theoretical framework

Equivalency table for the properties

OPA: Molar absorption coefficient ($I = \epsilon$)				
$\alpha = \frac{10\pi N_A}{3\epsilon_0 \ln(10)\hbar c}$	$\beta = 1$	$\gamma = m$	$\boldsymbol{d}_{Amn} = \boldsymbol{d}_{Bmn} = \boldsymbol{\mu}_{mn}$	
OPE: Energy emitted by one mole per second ($I = I_{em}/N_n$)				
$\alpha = \frac{2}{3\epsilon_0 c^3}$	$\beta = 4$	$\gamma = n$	$\boldsymbol{d}_{Amn} = \boldsymbol{d}_{Bmn} = \boldsymbol{\mu}_{mn}$	
ECD: Difference of molar absorption coefficient ($I = \Delta\epsilon$)				
$\alpha = \frac{40\pi N_A}{3\epsilon_0 \ln(10)\hbar c}$	$\beta = 1$	$\gamma = m$	$\boldsymbol{d}_{Amn} = \boldsymbol{\mu}_{mn}$	$\boldsymbol{d}_{Bmn} = \Im(\boldsymbol{m}_{mn})$
CPL: Difference of energy emitted by one mole per second ($I = \Delta I_{em}/N_n$)				
$\alpha = \frac{8}{3\epsilon_0 c^4}$	$\beta = 4$	$\gamma = n$	$\boldsymbol{d}_{Amn} = \boldsymbol{\mu}_{mn}$	$\boldsymbol{d}_{Bmn} = \Im(\boldsymbol{m}_{mn})$

1. J. Bloino, M. Biczysko, F. Santoro, V. Barone, JCTC, 6, 1256 (2010)

Vibronic spectra: Theoretical framework

The electronic transition integral

Approximations (electronic / nuclear)

- Born-Oppenheimer approximation ($|\Psi\rangle = |\phi\chi\rangle$)
- Eckart conditions ($|\chi\rangle \approx |\chi^t\chi^r\chi^v\rangle$)
- Harmonic oscillator ($|\chi^v\rangle = |v_1 \ldots v_N\rangle$)

– Only the vibrational wave function must be considered
– New transition dipole moment integral:

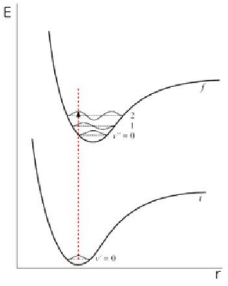
$$\langle \Psi_m | \boldsymbol{d}^X | \Psi_n \rangle \approx \langle \chi^v_{r(\underline{m})} | \boldsymbol{d}^X_{e,mn} | \chi^v_{s(\underline{n})} \rangle$$

- $r(\underline{m})$: vibrational state r associated to electronic state $\underline{m}$
- $\chi^v_{r(\underline{m})}$: vibrational wf of the lower electronic state
- $\chi^v_{s(\underline{n})}$: vibrational wf of the upper electronic state
- $\boldsymbol{d}^X_{e,mn}$: transition dipole moment $\boldsymbol{d}^X_{e,mn} = \langle \phi_{\underline{m}} | \boldsymbol{d}^X | \phi_{\underline{n}} \rangle$

Vibronic spectra: Theoretical framework

The transition dipole moment

- **There is no general analytical solution for $d^e_{x\,mn}$**
- **Approximation based on the Franck-Condon principle**



- Short-time electron jump → nuclei are nearly unaltered by the molecular vibrations
- Franck-Condon: $d^e_{x\,mn}$ is **constant** during the transition
- Herzberg-Teller: $d^e_{x\,mn}$ **varies linearly** with the normal coordinates
- Taylor expansion of $d^e_{x\,mn}$ about the equilibrium geometry of one electronic state

Vibronic spectra: Theoretical framework

Mathematical formalism of FC approximation

Transition dipole moment integral

$$\langle \Psi_m \mid d^x(\alpha) \mid \Psi_n \rangle$$

$$\downarrow$$

$$\underbrace{d^x_{e,mn}(\alpha, \boldsymbol{Q}_0)\langle \chi^v_{r(m)} \mid \chi^v_{s(n)} \rangle}_{\text{Franck-Condon}} + \underbrace{\sum_{i=1}^{N} \left(\frac{\partial d^x_{e,mn}(\alpha)}{\partial Q_i} \right)_0 \langle \chi^v_{r(m)} \mid Q_i \mid \chi^v_{s(n)} \rangle + \cdots}_{\text{Herzberg-Teller}}$$

- The problem is reduced to calculating overlap integrals between the vibrational wave functions
- But $\chi^v_{r(m)}$ and $\chi^v_{s(n)}$ are expressed with respect to different basis sets, **Q'** and **Q''**, respectively!

Vibronic spectra: Theoretical framework

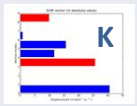
Transformation between the sets of coordinates

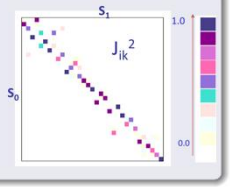
- The normal modes in S_0 and S_1 do not coincide (J≠I)

The Duschinsky approximation

Linear transformation between the normal modes

$$\mathbf{Q}' = \mathbf{J}\mathbf{Q}'' + \mathbf{K}$$





- **J**: Duschinsky Matrix
- **K**: Shift Vector

- Good approximation if no large distortion during the transition
- Other approaches
  - Curvilinear transformation [Lucas, N., J. Phys. B, 6, 155 (1973)]
  - Cartesian coordinates

Vibronic spectra: Theoretical framework

General case: calculation of $\langle \chi^v_{r(m)} \mid \chi^v_{s(n)} \rangle$

- **Presence of Hermite polynomials H_v : complex analytic formulae**

- **Analytic formulae**
  - One equation per overlap integral
    - *ad hoc* expressions for each overlap integral
    - **But** all necessary transitions must be predicted before actual calculations
  - General loops for a given number of excited modes
    - More general-purpose than per-integral equations
    - **But** loop nesting depends on highest number of excited modes supported
  - Complexity of expressions grows quickly with number of quanta

- **Recursive approach**
  - Only $\langle 0' \mid 0'' \rangle$ must be known exactly
  - Two formulae are needed to compute any Franck-Condon integral
  - **But** storage required to avoid redundant calculations

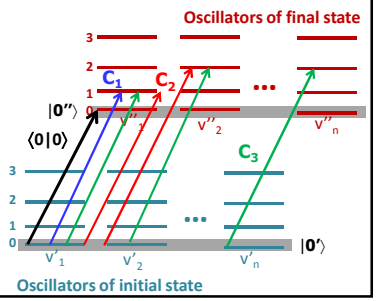
Vibronic spectra: Theoretical framework

Calculation of $\langle \chi^{v}_{r(m)} \mid \chi^{v}_{s(n)} \rangle$: Treatment by *classes*

- **Definition (class)**
  - *A class* represents the number of simultaneously excited modes in a state
  - Ex.: $|10_i\rangle$ in class 1, $|2_i\,;4_j\,;8_k\rangle$ in class 3

C_1 and C_2 intensities, computationally cheap

- **Recursion and analytic formulae**
  - For classes 1 and 2, per-integral analytic formulae are used when available, recursion formulae otherwise
  - For classes 3 and higher, recursion formulae are used



Theoretical framework

I718

To deal with infinity: selection of transitions

- **Recursive formulae**
  - possible to evaluate the transition dipole moment integrals by evaluating the overlap integrals between the vibrational initial and final states (FC integrals)
- **In principle,**
  - there is an infinite number of transitions to evaluate
  - But, most transitions have a low-to-negligible probability

Possible solutions

Using the spectrum bounds: only the transitions with the corresponding energy are taken into account.

⚠ Computational costs grow steeply with the upper bound energy !

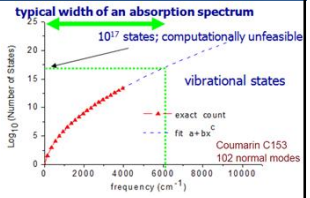
Using the transition probabilities: only those above a given threshold are taken into account.
This can be evaluated *a priori*, avoiding unnecessary calculations.

⚠ An efficient and consistent method to assess the likelihood of a transition is necessary

Vibronic spectroscopy: sum-over-states

A priori selection of transitions

- **Screening is used to select relevant transitions among an infinite number of combinations**



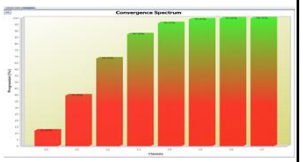
- ***a priori* screening**
  - avoids unnecessary calculations but transition integrals must be estimated
- **approach has been designed to be interfaced with various schemes**
- **current default prescreening: *FCClasses*[1]**
  - Transitions from classes 1 and 2 calculated up to a chosen limit and used to collect data:
  - For each class starting from 3, the highest number of quanta for each mode is calculated to stay below predefined number of integrals
- **The calculations depend on the number of integrals ($N_I^{\max}$) to compute NOT on the dimensionality of the system**

1. F. Santoro *et al.*, J. Chem. Phys. 126, 169903 (2007) and 128, 224311 (2008)

Vibronic spectroscopy: theoretical fremework

Sum rules and prescreening accuracy

- **Setting**
  - The selection of transitions to compute induces an approximation to the generated spectrum
  - The extent of the approximation for a priori schemes is generally not known
  - It is possible to know analytically the total intensity using sum rules



The analytic intensity

- **0K**

$$spectrum\ \ progression = \frac{\left|\langle 0'|\mu_{if}|v''\rangle\right|^2}{I^{tot}}$$

Checked after each class!

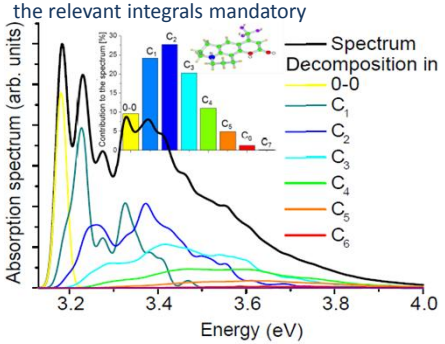
- For FC:

$$I_{\text{tot}} = \sum_{\alpha=x,y,z} d^{e}_{A\,mn}(\alpha, \mathbf{Q}'_0) \times d^{e}_{B\,mn}{}^{*}(\alpha, \mathbf{Q}'_0)$$

Validation: *a priori* selection scheme

Absorption spectrum of Coumarin 153

- Convergence of the spectrum calculation with respect to the *classes*; **99%** of the complete spectrum with ≈10^8 transitions considered
- Total number of transitions within 6000 cm^{-1} ≈ 10^{17}, scheme to choose the relevant integrals mandatory



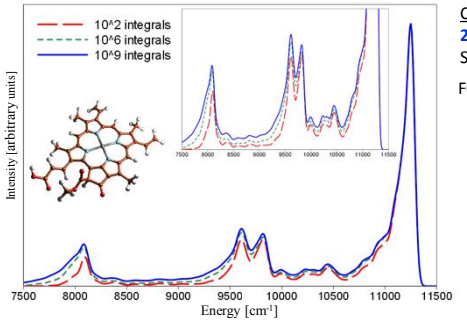
Coumarin *153*:
36 atoms
102 normal modes
FC|AH , Gaussian ,
FWHM=250 cm^{-1}.

- The contribution to the intensity decreases steeply with the order of the class,
- Contributions of the classes become flatter with the increase of the order of the class,

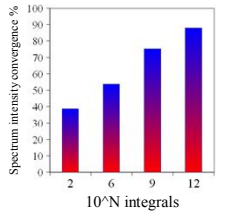
F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone *J Chem. Phys.* 126, 084509 (2007)

Validation: *a priori* selection scheme

Phosphorescence spectrum of Chlorophyll *c2*



Chlorophyll *c2*:
213 normal modes
S_0, T_1: B3LYP/6-31+G(d,p)
FC|AH , Gaussian broadening

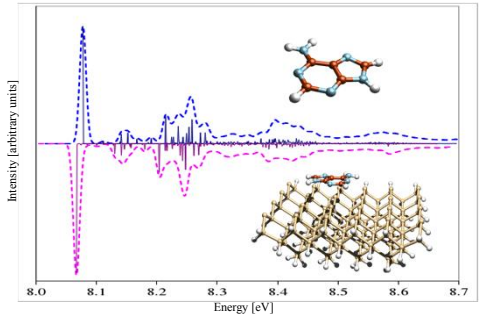


- Spectrum quality ~ intensity convergence ~ number of integrals ~ computational cost.
- **Line shape** - information about most important transitions, converges much **faster** than spectrum intensity: 10^2 integrals ≈ 40%, 10^9 ≈ 80% , 10^{12} ≈ 90 %.
- **Main** spectrum features **well reproduced** by cheap computation with **only 10^2** integrals.

V. Barone, J. Bloino, M. Biczysko, F. Santoro, *J. Chem. Theory Comput.*, 5, 540 (2009)

Validation: *a priori* selection scheme

Photoelectron spectrum of Adenine and Adenine@Si(100)



Adenine:
39 normal modes
B3LYP/6-31+G(d,p)
Adenine@Si(100):
> **600** normal modes
ONIOM:
QM: Adenine: B3LYP/6-31+G(d,p)
MM: Si_{119}: UFF force field

FC|AH
Gaussian broadening
FWHM = 200 cm^{-1}
FWHM = 2 cm^{-1}

A priori scheme - almost **all** spectrum intensity (about 98%) for an isolated molecule or a macrosystem at an equivalent computational cost (localized transition).
Computational cost related to the number of integrals **not** the system size.
Spectrum **changes** upon adsorption - insights into the nature of adsorbate-surface interactions

V. Barone, J. Bloino, M. Biczysko, F. Santoro, *J. Chem. Theory Comput.*, 5, 540 (2009)

Beyond harmonic approximation

Anharmonic corrections in excited states

S_0: possibilities

1. Anharmonic calculations **feasible** even for medium size systems
2. Accurate experimental data available.
3. Appropriate scaling factors **well** established

S_1: problems

1. Direct PT2 or VSCF calculations **not** feasible for larger systems
2. PT2 – **lack** of TD-DFT analytical Hessians
3. Appropriate scaling factors **not** well established

Solution for excited states:

make use of the data available for the ground electronic state

Beyond harmonic approximation

A scheme to evaluate anharmonic corrections in excited states [1].

- For each normal mode Q_i in S_0: mode specific scaling factor $\alpha(i)$

$$\alpha(i) = \upsilon(i)/\omega(i)$$

$\omega(i)$ harmonic frequencies,
$\upsilon(i)$: theoretical/calculated (TA) or experimental (EA) anharmonic frequencies

- Anharmonicity ~ PES, **if** $PES(S_0) = PES(S_1) \Rightarrow$ **one-to-one** relation between the normal modes $Q(i)$ and $Q'(i)$ of the ground and excited states $\Rightarrow \alpha(i)=\alpha'(i)$

- Excited state normal modes expressed as a function of ground state ones: $Q''=JQ'+K'$; J - Duschinsky matrix , K' - shift vector.

- Make use of TA or EA anharmonic frequencies for the ground state, to derive effective 'mode specific' scaling factors $\alpha'(i)$ for excited state:

$$\alpha''(i) = \sum_{k}^{N} J_{ik}^2 \alpha'(k) \qquad \upsilon''(i)=\alpha''(i)\omega''(i)$$

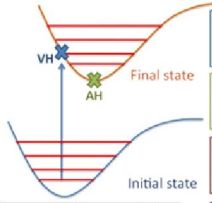
1. J. Bloino, M. Biczysko, O. Crescenzi, V. Barone J. Chem. Phys. 128, 244105 (2008)

Calculation of the band-shape

- **General sequence**
  1. Extraction of input data and possible conversions
  2. Superposition of the structures (minimization of rotation and translation)
  3. Calculation of **J** and **K**
  4. Calculation of Sharp and Rosenstock's matrices
  5. Calculation of $\langle 0'|0'' \rangle$
  6. Calculation of transition intensities
  7. Printing of the final spectrum

Input data: frequencies and normal modes

- **Models to describe PES**
  - Most accurate: Adiabatic Hessian
    - highly resolved spectra
  - Low resolution: Vertical Gradient
    - overal band shape
- **Nesessary computations**



VH: harmonic Hessian in the final state studied at **equilibrium geometry of the initial state**

AH: harmonic Hessian in the final state studied at **equilibrium geometry of the final state**

AS: same as AH but the Hessian in the final state is considered to be **the same as in the initial state's**

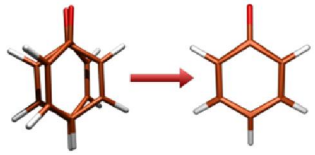
VG: same as VH but the Hessian in the final state is considered to be **the same as in the initial state's.**

computation	VH	VH|FCHT	AH	AH|FCHT	AS	VG
Initial state						
Cartesian coordinates of the atoms (equilibrium structure)	X	X	X	X	X	X
Energy at the minimum of the PES (equilibrium geometry)	X	X	X	X	X	X
Frequencies	X	X	X	X	X	X
Normal modes, expressed by the atomic displacements	X	X	X	X	X	X
Final state						
Cartesian coordinates of the atom at the minimum of the PES (equilibrium structure)			X	X	X	
Energy at the equilibrium geometry of the initial state	X	X				X
Energy at the minimum of the PES (equilibrium geometry)			X	X	X	
Forces at the equilibrium geometry of the initial state	X	X				X
Frequencies at the equilibrium structure of the final state			X	X		
Frequencies at the equilibrium structure of the initial state	X	X				
Normal modes, expressed by the atomic displacements	X	X	X	X		
General						
Atomic masses	X	X	X	X	X	X
Transition dipole moments	X	X	X	X	X	X
Derivatives of the transition dipole moments		X		X		

Computational cost:
QM input data required for simulation of vibrationally resolved electronic spectra

Superposition of the PES

- **Superposition of structures to minimize rotation and translation between sets of normal coordinates Q' and Q''**

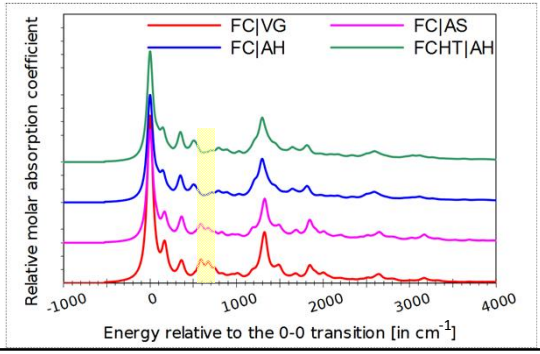


- **Procedure**
  - Use quaternions to minimize $\sum_{i=1}^{N_A} M_{ii} \sum_{j=1}^{3} X_{ref}(i,j) \times X_{new}(i,j)$
  - If residual total angular moment after 30 attempts, try using rotation angles
  - If failure after 100 attempts, stop.

Validation: PES approximations

Adiabatic vs. vertical models: lineshape

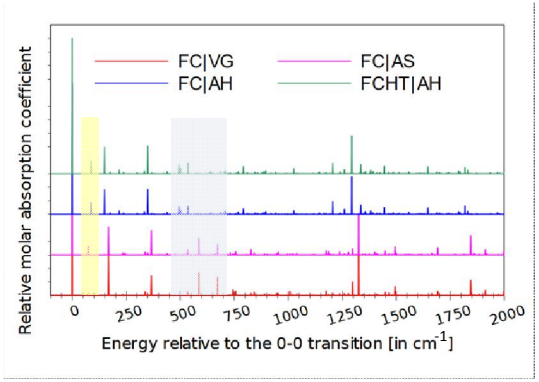
- **$S_2 \leftarrow S_0$ OPA spectrum of (R)-(+)-3 methylcyclopentanone (R3MCP)**
- Spectra simulated through Franck Condon approaches: Vertical Gradient **(FC|VG),** Adiabatic Shift **(FC|AS),** Adiabatic Hessian **(FC|AH)** and with the Franck-Condon Herzberg Teller **(FCHT|AH)** one, Lorentzian, HWHM of 80 cm^{-1}



Validation: PES approximations Porto 2010

Adiabatic vs. vertical models: stick spectrum

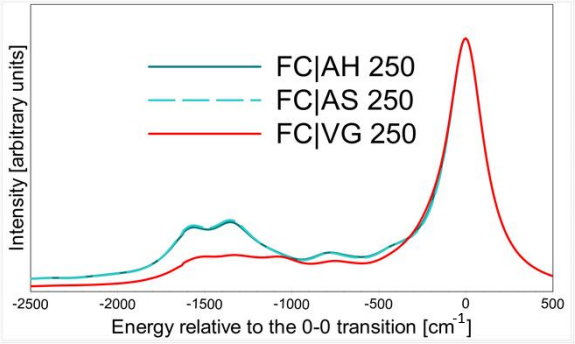
- **$S_2 \leftarrow S_0$ OPA spectrum of (R)-(+)-3 methylcyclopentanone (R3MCP)**
- **Stick spectra showing all vibronic transitions.**



Validation: PES approximations Porto 2010

Adiabatic vs. vertical models: lineshape

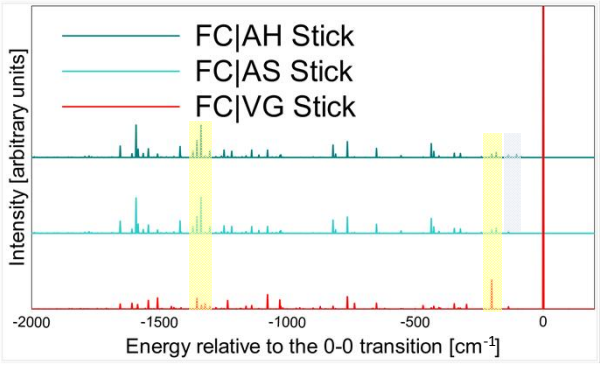
- **Phosphorescence spectrum of chlorophyll-a1**
- **Spectra simulated through Adiabatic Hessian, Adiabatic Shift and Vertical Gradient approaches within Franck-Condon framework, Lorentzian, HWHM of 250 cm^{-1}**



Validation: PES approximations Porto 2010

Adiabatic vs. vertical models: stick spectrum

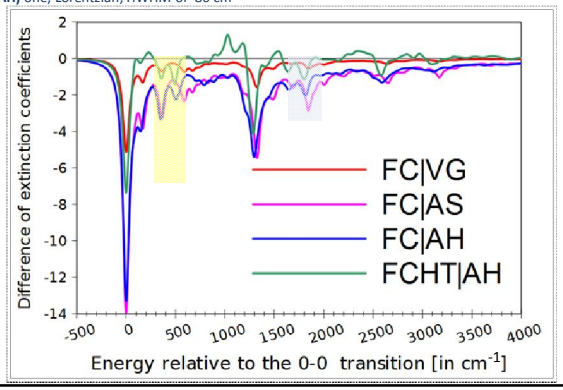
- **Phosphorescence spectrum of chlorophyll-a1**
- **Stick spectra showing all vibronic transitions simulated through Adiabatic Hessian, Adiabatic Shift and Vertical Gradient approaches within Franck-Condon framework**



Validation: ECD spectrum — Porto 2010

FC|VG to FCHT|AH models: ECD lineshape

- **$S_2 \leftarrow S_0$ ECD spectrum of (R)-(+)-3 methylcyclopentanone (R3MCP)**
- Electronic Circular Dichroism (ECD) spectra simulated through Franck Condon approaches: Vertical Gradient **(FC|VG),** Adiabatic Shift **(FC|AS),** Adiabatic Hessian **(FC|AH)** and with the Franck-Condon Herzberg Teller **(FCHT|AH)** one, Lorentzian, HWHM of 80 cm^{-1}

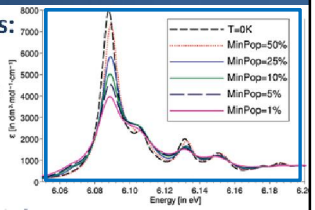


Vibronic spectroscopy — Porto 2012

Temperature effects

- **Selection criteria of initial states:**
  - Temperature (default: 298.15K)
  - Minimum population with respect to the ground state (default: 10%):

$$\rho_v / \rho_0 \leq \text{MinPop}$$

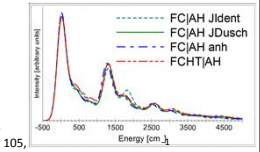


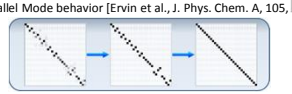
- ***Classes* are also used in the initial state**
  - starting from the lower to the higher
- **The number of initial states to treat is voluntarily set low by default**
  - to prevent unpractical computational times
  - more states can be selected with the simulation parameters
  - counting the number of states to handle prior to computation

Vibronic spectra: mode mixing — L718

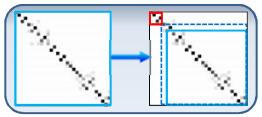
Approximation schemes: Duschinsky matrix

- **Use the real Duschinsky matrix (Jdusch)**
  - default for Vertical FC and Adiabatic FC
- **Replace the Duschinsky matrix with the identity matrix (Jident)**
  - default for Vertical Gradient and Adiabatic Shift
- **Reorder the Duschinsky matrix (Jdiag)**
  - Highest element of each row is set to 1.0 and the others to 0.0.
    - Simulate the Parallel Mode behavior [Ervin et al., J. Phys. Chem. A, 105, 10822 (2001)]





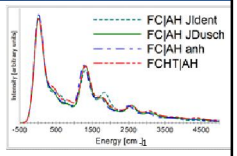
- **Reduced dimensionality (Jreduced)**
  - A list of the normal modes **to remove** is expected.
  - Threshold for the block construction (**BlockThresh**, default: 0.9)
  - Max. ratio allowed between the number of modes selected by block construction procedure and the initial number of modes (**BlockTol**, default: 1.6)

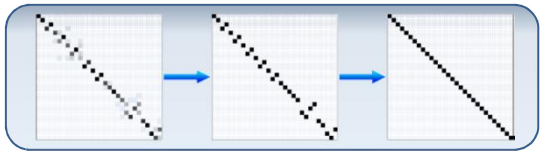


Vibronic spectroscopy

Approximation schemes: Duschinsky matrix

- **Modification of the Duschinsky matrix**
- **Use the real Duschinsky matrix (Jdusch)**
  - default for Vertical FC and Adiabatic FC
- **Replace the Duschinsky matrix with the identity matrix (Jident)**
  - default for Vertical Gradient and Adiabatic Shift
- **Reorder the Duschinsky matrix (Jdiag)**
  - Highest element of each row is set to 1.0 and the others to 0.0.

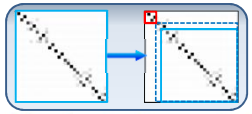




Vibronic spectroscopy

Reduced-dimensionality schemes

- **Activate the reduced dimensionality (Jreduced)**
  - A list of the normal modes **to remove** is expected.
  - Threshold for the block construction (**BlockThresh**, default: 0.9)
  - Max. ratio allowed between the number of modes selected by block construction procedure and the initial number of modes (**BlockTol**, default: 1.6)
- **Procedure:**



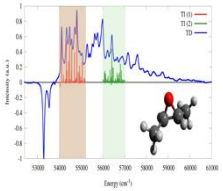
1. Read the N' modes of the reference state given in input (set $\mathcal{S}_{\text{ref}}$)
2. Copy the reference set $\mathcal{S}_{\text{ref}}$ as $\mathcal{S}_0$
3. For each mode i of $\mathcal{S}_0$, order the N values $J_{ik}{}^2$ in decreasing order
4. The first n modes k verifying the condition $\sum_{i=1}^{n} J_{ik}{}^2 \geq \texttt{BlockThresh}$ are selected in the set $\mathcal{S}_1$
5. Do steps 3 and 4 with each mode of $\mathcal{S}_1$
6. Do steps 3 to 5 until no new mode is selected in $\mathcal{S}_0$ and $\mathcal{S}_1$
7. Check if $\text{Dim}(\mathcal{S}_0)/\text{Dim}(\mathcal{S}_{\text{ref}}) < \texttt{BlockTol}$

Vibronic spectroscopy: integrated approach

Path integral vs Sum over states

- **Path integral vs Sum over states**

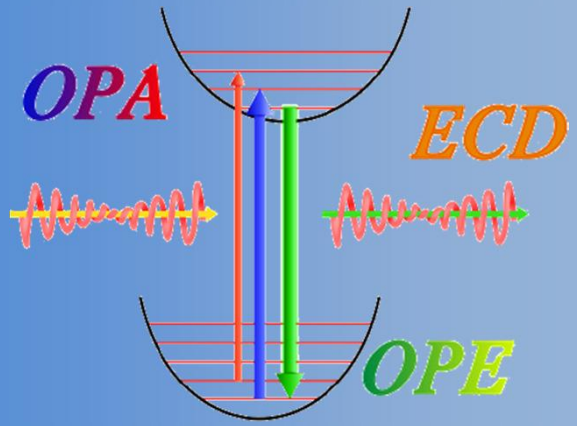
- **Sum over states (TI)**
  - Each transition treated individually
  - The band shape obtained by summing all transitions
  - Band assignment possible
  - "Infinite" sums



- **Path integral (TD)**
  - Assimilable to short-term approximation of the propagation of wave packets on the excited state surface of the molecule
  - Automatic inclusion of all vibrational states (including initial state)
  - Band assignment impossible

- **Integrated approach: combine advantages of both models**

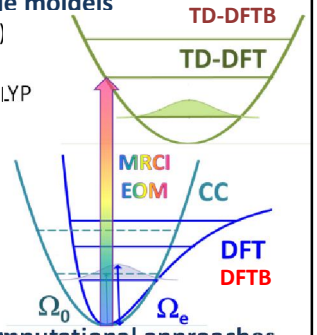
Electronic spectra



Integrated QM approach

Computational Strategy: QM

- **Validation of low-cost yet reliable moldels**
  - Eg. DFT/N07D (B3LYP, CAM-B3LYP)
- **Hybrid QM/QM' approaches**
  - Eg. CC/DFT, MRCI/DFT, B2PLYP/B3LYP
- **Higher level**
  - Properties at 'bottom of the well'
  - Harmonic frequencies
  - Vertical electronic transitions
- **Lower level**
  - Anharmonic corrections
  - Excited states PES



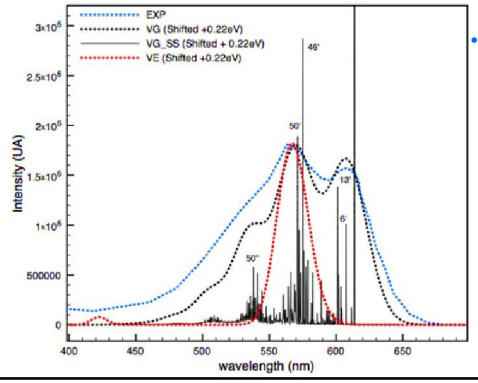
- **Reliable + feasible integrated computational approaches**

1. V. Barone, J. Bloino, M. Biczysko Phys. Chem. Chem. Phys., 12, 1092-1101 (2010)
2. C. Puzzarini, M.Biczysko, V. Barone, *J. Chem. Theory Comput.*, 6, 828 (2010)
3. MB, P. Panek, G. Scalmani, J. Bloino, V. Barone, , *J. Chem. Theory Comput* 6, 2115-2125 (2010)

Electronic spectra

From vertical transitions to band shape

- **Vertical transition:** intensity = μ_e
- **Vibronic transitions:** Intensity depend also on the vibrational overlaps



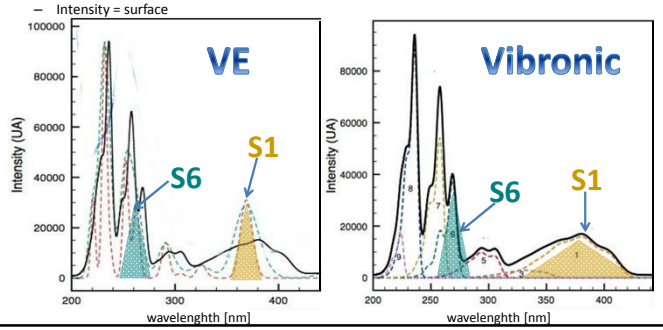
- **Experimental and theoretical electronic spectra of di-anionic alizarin.**
  - spectra computed at the **VG|FC** and **VE** levels, and red-shifted by 0.22 eV.
  - Both theoretical spectra have been convoluted with a HWHM of 500 cm^{-1}

Electronic spectra

Vertical vs vibronic

- **Relative intensity of electronic transitions**
- **VE**
  - states with similar oscillator strength – similar band
  - Intensity = hight
- **Vibronic**
  - Line-shape determined by vibrational pattern
  - Intensity = surface

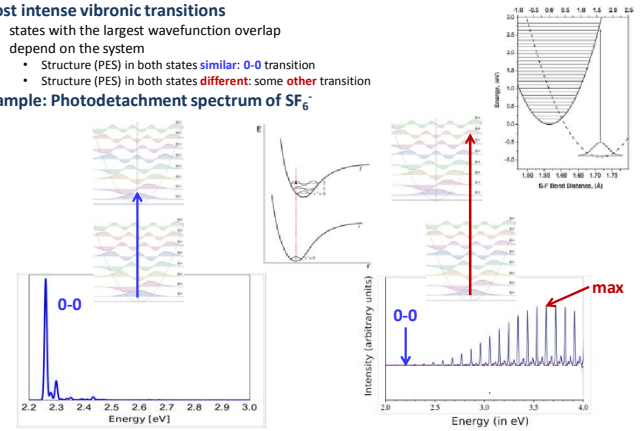
State	λ (nm)	f
S1	263	0.17
S6	369	0.20



Electronic Spectrum

Vibronic transitions : λmax

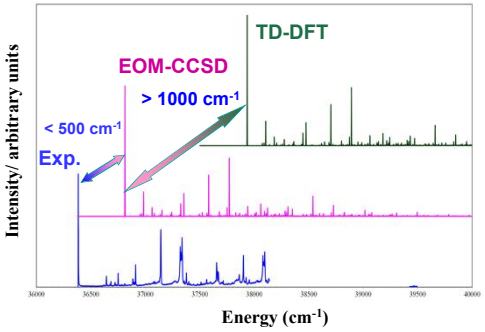
- **Most intense vibronic transitions**
  - states with the largest wavefunction overlap
  - depend on the system
    - Structure (PES) in both states **similar**: **0-0** transition
    - Structure (PES) in both states **different**: some **other** transition
- **Example: Photodetachment spectrum of SF_6^-**



Vibronic spectroscopy: Accuracy

Absolute and relative energy scale: $S_1 \leftarrow S_0$ electronic transition of anisole [1]

- **Refinement of the electronic transition origin by coupled cluster computation.**
- **To achieve fit between spectra, electronic transition would need to be computed with the accuracy of ≈10 cm^{-1}**
  - so still necessary to compare spectra shifted to the 0-0 origin.



S_0: **CCSD/aug-cc-pVDZ// B3LYP//6-311+G(d,p);**

S_1: **EOM-CCSD /aug-cc-pVDZ// TD-B3LYP/6-311+G(d,p)**

FC|AH FWHM=2cm^{-1}

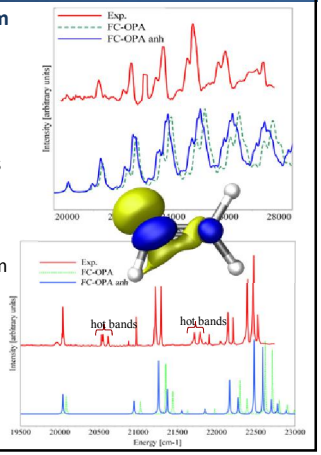
1. J. Bloino, M. Biczysko, O. Crescenzi, V. Barone *J. Chem. Phys.* 128, 244105 (2008)

Accuracy

I718

The $\tilde{A}^2A'' \leftarrow \tilde{X}^2A_1$ electronic transition of vinyl radical

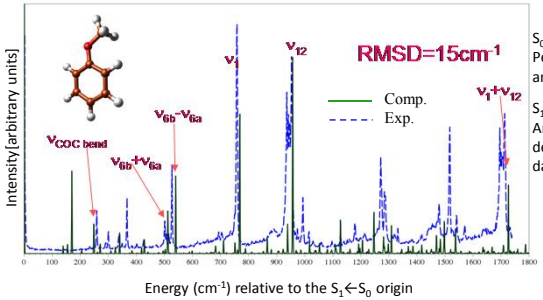
- **One Photon Absorption (OPA) spectrum**
  - simulated with FC|AH approach
  - TD-B3LYP/B3LYP//N07D
  - anharmonic corrections
- **Low resolution spectrum in UV-vis region:**
  - simulated spectra (width 8000 cm^{-1}) has been **shifted** by ≈ **500 cm^{-1}** to match experimentally observed electronic transition origin
  - spectrum convoluted with Lorentzian function with full width at half maximum (FWHM) of **150 cm^{-1}**
- **High resolution spectrum from molecular beam:**
  - spectrum (width 3500 cm^{-1}) convoluted with Lorentzian function with FWHM of **10 cm^{-1}**



V. Barone, J. Bloino, M. Biczysko
Phys. Chem. Chem. Phys., 12, 1092 (2010)

Vibronic spectroscopy: Accuracy

Anharmonic corrections in ground and excited state: the $S_1 \leftarrow S_0$ electronic transition of Anisole[1]

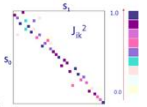


S_0: B3LYP/6-311+G(d,p) Perturbative (GVPT2) anharmonic corrections [2]

S_1:TD-B3LYP/6-311+G(d,p) Anharmonic corrections derived from ground state data[1]

$$\upsilon''(i)=\alpha''(i)\omega''(i)$$

$$\alpha''(i)=\sum_{k}^{N} J_{ik}^2 \alpha'(k)$$



A **very good agreement** between computed and experimental [3] REMPI spectrum has only been possible when the frequencies have been corrected for **anharmonicity**.

[1] J. Bloino, M.Biczysko, O. Crescenzi, V. Barone, *J. Chem. Phys.*, 128, 244105 (2008)
[2] V. Barone, *J. Chem. Phys.*, 122 014108 (2005);
[3] L. J. H. Hoffmann, S. Marquardt, A. S. Gemechu, and H. Baumgärtel, *PCCP* 8, 2360 (2006)

Electronic spectroscopies

Anharmonic frequencies in excited states

- **The photoionisation spectrum of furan**
  - B3LYP/SNSD
  - Frequencies directly computed (VPT2) and extrapolated (VPT2+FC)

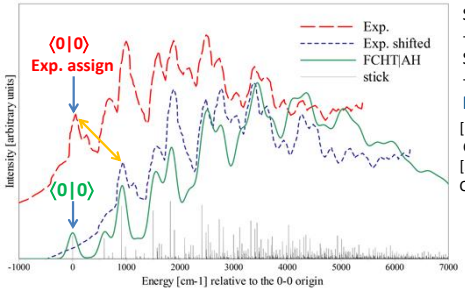
	Initial State		Final State			
Mode	harm	anh VPT2	harm	anh VPT2	anh VPT2+FC	Δ
ν_1	614	603	486	476	477	1
ν_2	620	608	500	491	491	-1
ν_3	729	715	768	750	754	3
ν_4	755	742	792	779	779	0
ν_5	843	829	854	838	840	3
ν_6	873	862	881	867	869	2
ν_7	896	874	907	885	886	0
ν_8	899	877	977	951	953	2
ν_9	1018	994	1011	987	988	1
ν_{10}	1065	1037	1041	1019	1014	-5
ν_{11}	1086	1065	1063	1041	1042	1
ν_{12}	1165	1142	1116	1094	1095	1
ν_{13}	1189	1166	1166	1141	1142	2
ν_{14}	1285	1259	1296	1269	1270	0
ν_{15}	1410	1379	1403	1379	1372	-7
ν_{16}	1512	1478	1452	1405	1420	15
ν_{17}	1597	1557	1515	1473	1477	4
ν_{18}	3247	3121	3247	3119	3121	2
ν_{19}	3258	3131	3256	3127	3129	2
ν_{20}	3285	3157	3259	3130	3132	2

|MAX|: 15 cm^{-1}
MAE: 2.7 cm^{-1}

Mean absolute error (MAE) and largest absolute error (|MAX|)

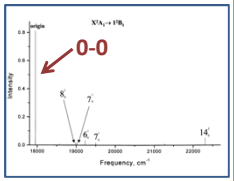
Interpretation of experimental spectra

The $A^2B_1 \leftarrow X^2A_1$ electronic transition of phenyl radical [1]



S_0: B3LYP/N07D
+ PT2 anharmonicity
S_1: TD-B3LYP/N07D
+ anharmonic corrections
FCHT|AH FWHM=200 cm^{-1}

[1] M. Biczysko, J. Bloino, V. Barone Chem. Phys. Lett. 471, 143 (2009)
[2] G.S. Kim, A. Mebel, S. Lin Chem. Phys. Lett. 361, 421 (2009)



Good agreement with the **shifted** experimental spectra:

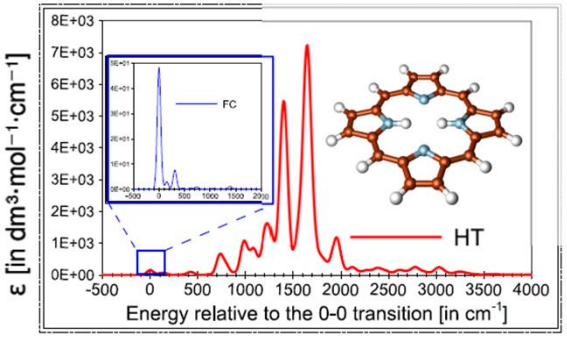
- Reassignment of 0-0 transition, the transition assigned experimentally as 0–0, a progression to the excited vibrational state of A^2B_1?

Limited dimensionality simulations [2]: spectrum almost **featureless**
Full dimensional vibronic models: **reproduce** the spectrum shape

Vibronic spectroscopy: transition dipole moment approximations

Beyond Franck-Condon approximation

- **Absorption spectra of the $S_1 \leftarrow S_0$ electronic transition of porphyrin computed with FC|AH and HT|AH approaches,**

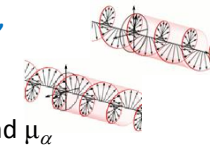


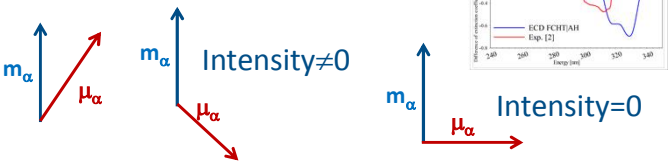
[1] F. Santoro, A. Lami, R. Improta, J. Bloino, V. Barone, *J. Chem. Phys.* 2008, 128, 224311.

Electronic Spectroscopies

Electronic Circular Dichroism

- **Two different transition dipole moments (d_z)**
  - **electronic** transition dipole moment μ_α,
  - **magnetic** transition dipole moment m_α
- **Intensity (Rotatory strength)**
  - proportional to the product of m_α and μ_α
  - depend on their mutual orientation
    - Sign change (also vibrationally induced)

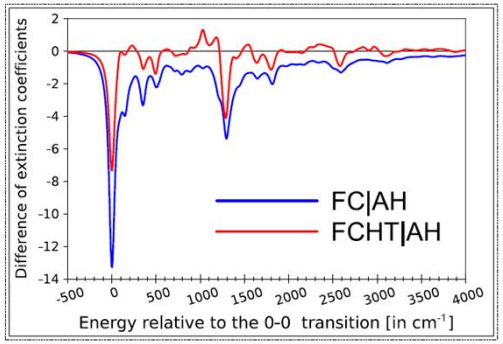




Electronic circular dichroism spectra

Beyond Franck-Condon approximation

- **ECD spectra of the $S_2 \leftarrow S_0$ electronic transition of ax-R3MCP computed with FC|AH and FCHT|AH approaches**
  - (R)-(+)-3 Methylcyclopentanone

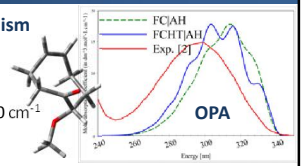


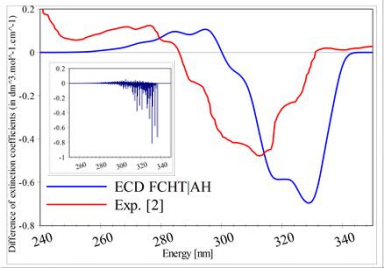
N. Lin, F. Santoro, X. Zhao, A. Rizzo, V. Barone, *J. Phys. Chem. A* 2008, 112, 12401; F. Santoro, V. Barone, *Int. J. Quantum Chem.* 2010, 110, 476

Vibronic spectroscopy: Interpretation

Beyond Franck-Condon approximation

- **$S_1 \leftarrow S_0$ absorption and electronic circular dichroism**
  - (Z)-8-Methoxy-4-cyclooctenone (MCO)
  - ECD: **several** bands of opposite sign
  - OPA: the **single** broad band
  - S_0: B3LYP/N07D; S_1: TD-B3LYP/N07D, FWHM=500 cm^{-1}





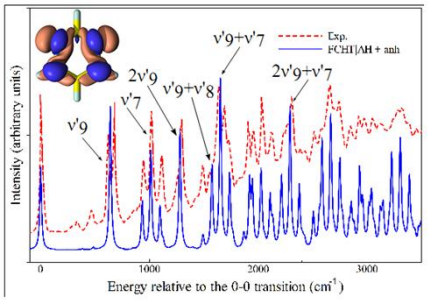
ECD spectrum:

- **Simple** simulation based on **vertical R** [2]: more than **three** conformers necessary for **qualitative** reproduction of the experimental spectra.
- **Vibronic** simulation + **Herzberg-Teller** effects: just **one** conformer **reproduce** the spectrum shape.

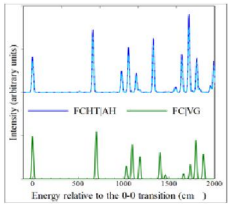
[1] J. Bloino, M. Biczysko, F. Santoro, V. Barone, J. Chem. Theory Comput. 6, 1256 (2010)
[2] T. Tanaka, M. Oelgemoller, F. Fukui, F. Aoki, T. Mori, T. Ohno, Y. Inoue, Chirality 19, 415 (2007)

The $S_1 \leftarrow S_0$ electronic transition

- **Computed [1] vs experimental [2] spectra:**
  - **FCHT|AH** spectrum, Gaussian broadening with HWHM of 1 cm^{-1}
  - TD-CAM-B3LYP/aug-N07D + anh CC/B3LYP + anh S_0/S_1
  - assignment of vibronic bands
  - Electron density difference: **gain**/**loose** of electron density upon transition



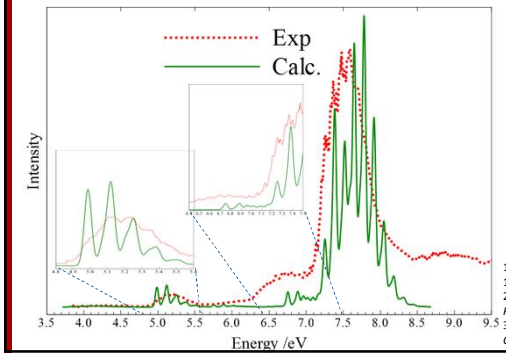
FCHT|AH and **FC|VG**



1. M. Biczysko et al. *Theor. Chem. Acc.*, 131, 1201 (2012)
2. S. F. Ferreira et al. *Phys. Chem. Chem. Phys.* 12, 6717 (2010)

Absorption spectrum in the 3.5-9.5 eV energy range

- **Computed [1] vs experimental [2] spectra:**
  - **FC|VG** level, Gaussian broadening with HWHM of 0.025 eV
  - Several (S_1 -S_{12}) excited electronic states
  - the hybrid CIPSI[3]/DFT (TD-CAM-B3LYP/aug-N07D) approach



VE (eV)

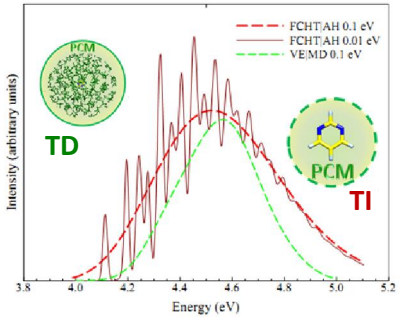
	CAM	CIPSI	Exp.[2]
S_1	4.58	4.19	4.18
S_2	4.94	4.59	4-5
S_3	5.85	5.16	5.22
S_4	6.03	5.68	
S_5	6.33	5.99	~6
S_6	6.71	7.02	6.69
S_{11}	7.63	7.79	7.48
S_{12}	7.84	8.13	

1. M. Biczysko et al. *Theor. Chem. Acc.*, 131, 1201 (2012)
2. S. F. Ferreira et al. *Phys. Chem. Chem. Phys.* 12, 6717 (2010)
3. CIPSI: R. Cimiraglia, M. Persico, J. *Comput. Chem.* 8 , 39 (1987)

TI and TD models

- **MD vs FC|AH UV spectra: Pyrimidine in CCl_4**
  - PCM (TI), explicit and implicit solvent (TD)

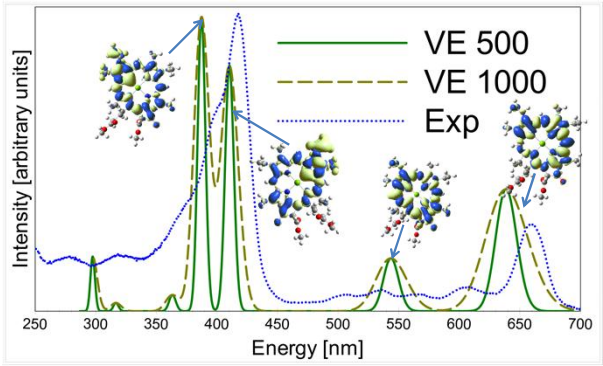
- **Both approaches agree on**
  - maxima positions
  - the width of the low-resolution spectra.
- **Different effects influencing and electronic band shape:**
  - TD: conformational flexibility
  - TI: analysis of individual vibronic contributions.



M. Biczysko , J. Bloino, G. Brancato, I. Cacelli, C. Cappelli, A. Ferretti, A. Lami, S. Monti, A. Pedone, G. Prampolini, C. Puzzarini, F. Santoro, F. Trani, G. Villani, *Theor. Chem. Acc.*, 131, 1201 (2012)

VE: Neglecting vibrational effects

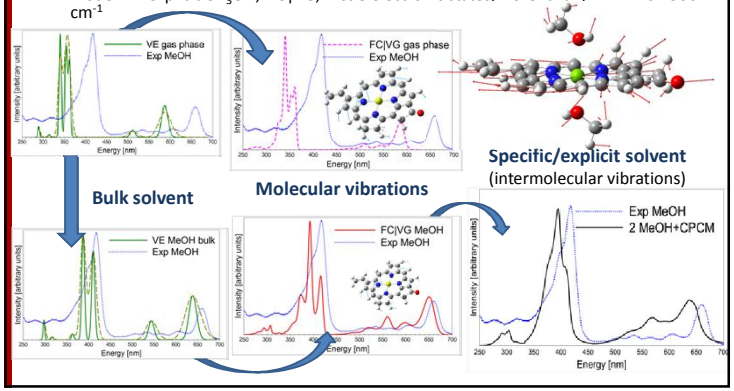
- **Spectrum obtained from vertical electronic energies (VE) by convolution with Lorentzian function with Full-Width at Half-Maximum (FWHM) of 500 (1000) cm^{-1}**
- **TD-CAMB3LYP/aug-N07D, methanol solution described as continuum CPCM model**



UV-vis spectrum of chlorophyll-a1

Vibrational and bulk + explicit solvent effect

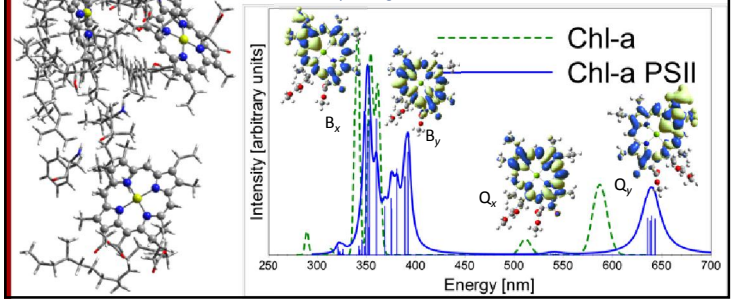
- **Contributions of various effects on the overall phenomena**
  - Final spectrum of simulated with the methanol solution described as continuum CPCM model + 2 explicit CH_3OH, FC|VG, first 8 electronic states, Lorentzian, FWHM of 500 cm^{-1}



UV-vis OPA spectrum of chlorophyll-a

Single molecule vs PSII

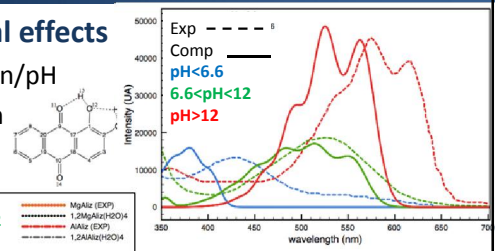
- **Chlorophyll-a in Photosystem II (PSII) environment**
  - **Not equivalent** Chlorphyll-*a* molecules (4 different considered)
  - Energy shifts, different transition intensities→ **complex spectra**
- Spectra obtained from vertical electronic energies (VE)
  - TD-CAMB3LYP/AN07D, convolution with Lorentzian function , FWHM of 500 cm^{-1}
  - QM:MM, PDB crystallografic structure for PSII

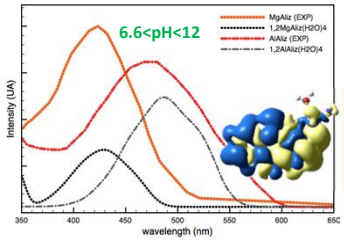


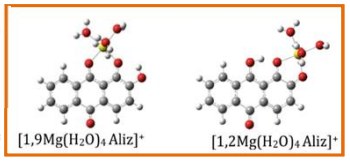
Uv-vis: Color changes

Alizarin and alizarin-Mg/Al complexes

- **Environmental effects**
  - Deprotonation/pH
  - Complexation





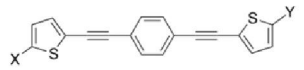


Test case: In silico design of new materials

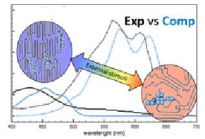
FIRB 2012

In silico design of new chromophores

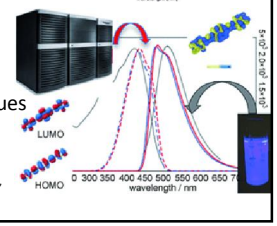
- **Thiophene-based π-conjugated chromophores**
  - Goal: tune the mechanochromic performances in smart polymer materials,



- **Virtual screening to select a derivative with optimal spectral features**
  - large Stokes shift and luminescent response



- **Effective two step procedure**
  - Step 1: low-cost Vertical Energy (VE) computations for large set of novel chromophore candidates
  - Step 2: more refined ab initio spectra simulations for restricted set of homologues

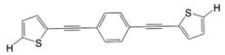


- **Best candidate chromophore selected and synthesized**

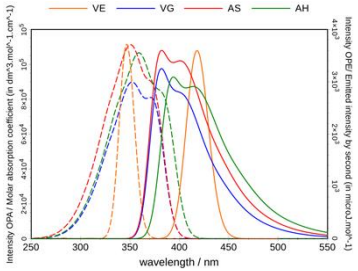
1. G. Prampolini, F. Bellina, M. B., C. Cappelli, L. Carta, M. Lessi, A. Pucci, G. Ruggeri, V. Barone, Chemistry - A European Journal, 19, 1996-2004 (2013)

Preliminary validation

- **Theoretical models validated for the simplest homologue of the series**
  - (X = Y = H)

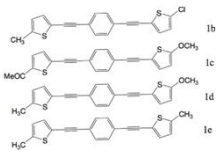


- **VG wrt AS**
  - very similar line-shapes, but slightly shifted positions (10nm) for both absorption and emission
  - predicted Stokes Shift remains almost unaltered
  - The Duschinsky effects do not play significant role and can be safely neglected
  - **good agreement**
- **VE wrt VG/AS**
  - loss of information concerning the band shape, but
  - the maximum absorption wavelength is well reproduced
  - a larger error is found for emission
  - **sufficient for preliminary screening**



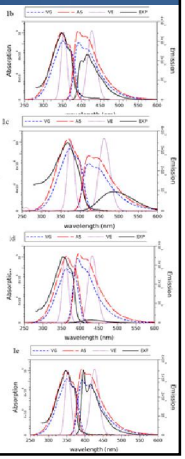
Validation: Comparison to Experiment

- **Futher validation**
  - bis-ethynylbenzeners spectra are recorded and calulated in THF
- **Experimental trend (1b ≈ 1e < 1d < 1c) correctly reproduced**



	Assorbimento (λ_{max})				Emissione (λ_{max})			
	VE	VG	AS	Exp	VE	VG	AS	Exp
1b	354	350	350	348	427	392	395	400
1c	376	374	373	368	462	420	424	bb[a]
1d	359	362	364	352	433	395	398	bb[b]
1e	353	350	349	348	426	392	395	395

[a]Broad band (bb) from 420 to 570nm.
[b]Broad band from 395 to 460nm.



- **VG and AS**
  - Good position and line-shape (absorption and emission)
  - Improvement whit respect VE most significant for emission
- **Computational model OK**
  - TD-CAM-B3LYP/SNSD/CPCM

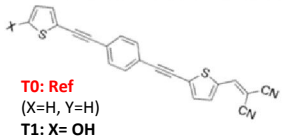
Step 1: Vertical Energy Computations

- **All X/Y pairs shift toward larger values both in absorption and emission,**
  - absence of a clear trend
  - rule out the possibility of a simple rationalization of the results, based only on "push/pull" effects,
  - important role of in silico screening in the molecular design
- **Restricted set of homologues selected**
  - based on VE results
  - considered for AS calculations in 2nd step
- **Y = CH=C(CN)2**
- **the largest Stokes shift**

X	Y	Absorption (nm)	Emission (nm)	Stokes Shift (nm)
H	H	347	418	71
	CHO	377	463	86
	CH=($C_6H_4O_2$)	434	534	100
OH	CH=C(CN)$_2$	426	527	101
	CH=C(CN)(COOH)	418	520	102
	COOH	370	454	84
	CHO	370	461	91
	CH=($C_6H_4O_2$)	433	529	96
SH	CH=C(CN)$_2$	419	520	101
	CH=C(CN)(COOH)	412	516	104
	COOH	364	454	90
	CHO	388	491	103
	CH=($C_6H_4O_2$)	442	562	120
NH_2	CH=C(CN)$_2$	436	567	131
	CH=C(CN)(COOH)	428	558	130
	COOH	382	479	97

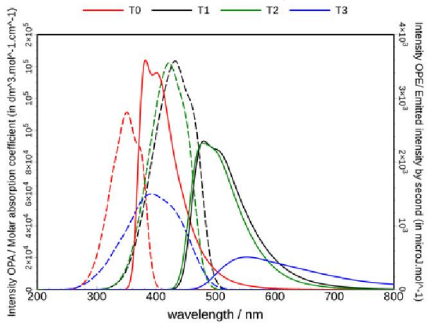
Step 2: Spectra simulation

- **Absorption and emission spectra are simulated at AS level**
- **AS computations 'added value'**
  - VE: T3 - larger Stokes shift, all similar transition dipole moments (VE)
  - direct simulation of spectra - T3 lower emission intensity



T0: Ref
(X=H, Y=H)
T1: X= OH
T2: X= SH
T3: X= NH_2

- **T1 and T2 more suitable**

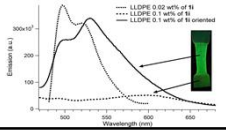


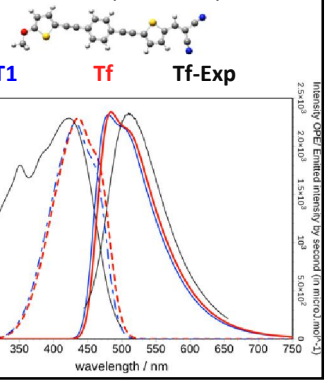
In silico design of new chromophores

FIRB 2012

Result: '*in silico*' designed chromophore

- **Final choice of chromophore to be prepared: Tf**
  - Similar to T1 (X=OH/OMe), added to set for practical/synthesis reason
- **'A posteriori' experimental characterisation**
  - very good agreement
  - desired optical properties
  - also desired mechanochromic properties
    - Once dispersed in polymer: Andrea Pucci

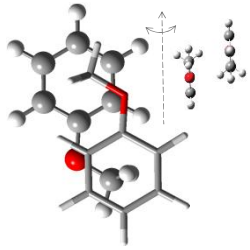




Systems with non-covalent interactions

Anisole dimer: structure of the complex

- **Determination of the ground and excited state stacking equilibrium structures of the anisole dimer**
  - Rotational constants in the ground and first excited electronic state

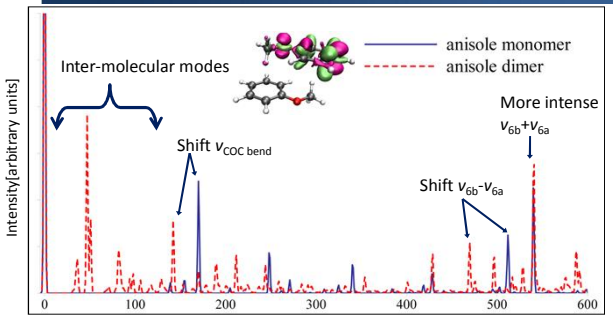


	B3LYP	B3LYP-D	LC–ωPBE	M05-2X	Exp.
			S_0		
A (cm^{-1})	0.8228	0.8865	0.8770	0.8570	**0.8407**
B (cm^{-1})	0.2955	0.3972	0.3931	0.3894	**0.3902**
C (cm^{-1})	0.2530	0.3364	0.3306	0.3257	**0.3255**
RMSD %	16.2	3.5	2.2	0.7	
			S_1		
A (cm^{-1})		0.7236	0.8775	0.8568	**0.8339**
B (cm^{-1})		0.5942	0.4000	0.4004	**0.3965**
C (cm^{-1})		0.4337	0.3391	0.3376	**0.3328**
RMSD %		31.1	2.7	1.7	
S_1<-S_0 transition (eV)		4.18	5.08	5.00	**4.48**

G. Pietraperzia, M. Pasquini, N. Schiccheri, G. Piani, M. Becucci, E. Castellucci, M. Biczysko, J. Bloino, V. Barone, *J. Phys. Chem. A*, 113, 14343 (2009)
N. Schiccheri, M. Pasquini, G. Piani, G. Pietraperzia, M. Becucci, M. B., J. Bloino, V. Barone, PCCP 12, 13547 (2010)

Systems with non-covalent interactions

$S_1 \leftarrow S_0$ electronic transition of the Anisole dimer

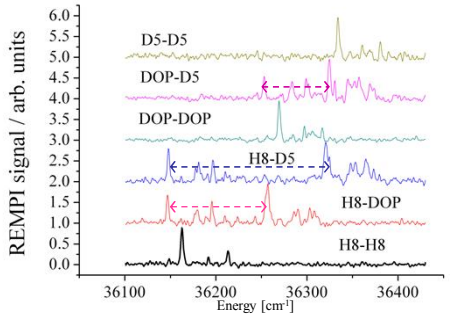


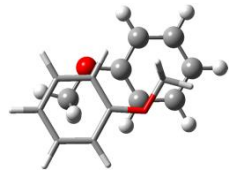
Structures: M05-2X/6-31+G(d,p)
Anharmonic corrections: ground state (PT2) B3LYP-D/6-31+G(d,p) + "mode-specifig scaling factors" scheme for excited state

G. Pietraperzia, M. Pasquini, N. Schiccheri, G. Piani, M. Becucci, E. Castellucci, M. Biczysko, J. Bloino, V. Barone, *J. Phys. Chem. A*, 113, 14343 (2009)
N. Schiccheri, M. Pasquini, G. Piani, G. Pietraperzia, M. Becucci, M. B., J. Bloino, V. Barone, PCCP 12, 13547 (2010)

Interpretation of experimental spectra

$S_1 \leftarrow S_0$ electronic transition of anisole dimer





Anisole monomers isotopic substitution:
H8 (all 1H), D5 (D on aromatic ring), DOP (D orto,para)

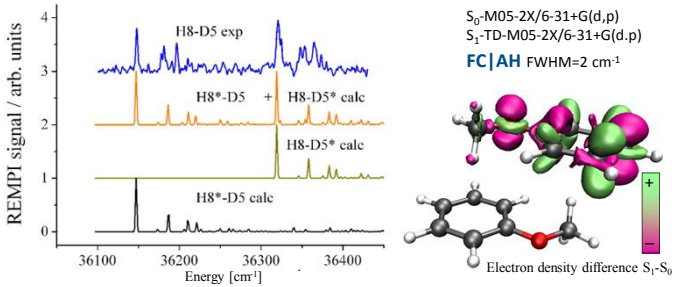
- **Experimental REMPI** (resonance enhanced multiphoton ionization) spectra:
  - **Single** band origin for homo-dimers (H8-H8, DOP-DOP, D5-D5)
  - **Two** band origins for hetero-dimers (H8-DOP, H8-D5, DOP-D5)

1. G. Pietraperzia, M. Pasquini, N. Schiccheri, G. Piani, M. Becucci, E. Castellucci, M. B., J. Bloino, V. Barone *J. Phys. Chem. A*, 113, 14343 (2009)
2. N. Schiccheri, M. Pasquini, G. Piani, G. Pietraperzia, M. Becucci, M. B., J. Bloino, V. Barone, PCCP, 12, 13547-13554 (2010)

Electronic absorption spectra of anisole dimer

Localized/delocalized excitation in complexes?

- **Anisole moieties in dimer NOT equivalent: Two bands origins – difference in ZPVE energy.**
  - simulated spectra as a sum of single contributions with isotopic substitution on 'excited'(*) or 'spectator' monomer.
- **Electronic excitation localized (97%) on one of the monomers.**

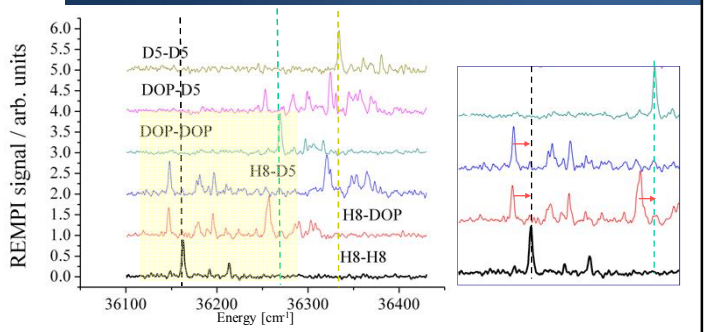


S_0-M05-2X/6-31+G(d,p)
S_1-TD-M05-2X/6-31+G(d.p)
FC|AH FWHM=2 cm^{-1}

1. G. Pietraperzia, M. Pasquini, N. Schiccheri, G. Piani, M. Becucci, E. Castellucci, M. Biczysko, J. Bloino, V. Barone *J. Phys. Chem. A*, 113, 14343 (2009)
2. N. Schiccheri, M. Pasquini, G. Piani, G. Pietraperzia, M. Becucci, M. B., J. Bloino, V. Barone, PCCP, 12, 13547-13554 (2010)

S_1←S_0 electronic transition of anisole dimer

Nature of intermolecular interaction: continued



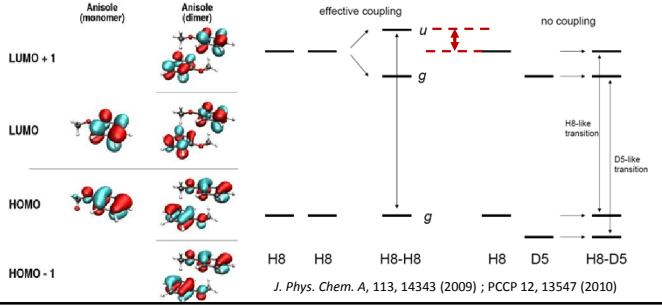
Experimental REMPI spectra:
Blue shift (≈ 15 cm^{-1}) of 0-0 transition origin in hetero-dimers, with respect to corresponding homo-dimers, marks of **delocalized** character of interaction **?**

J. Phys. Chem. A, 113, 14343 (2009) ; PCCP 12, 13547-13554 (2010)

S_1←S_0 electronic transition of anisole dimer

Excitonic splitting

- **Symmetric systems:**
  - **Excitonic coupling** affects only the electronic part of the wavefunction which is the same even for isotopically different clusters
  - **ZPVE deviation** between different isotopomers shifts the vibronic energy levels of monomers: **no coupling**
  - The isotopic substitution of a single unit in the complex removes the equivalence of both moieties, leading to the observed **excitonic splitting**

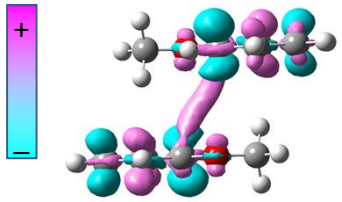


J. Phys. Chem. A, 113, 14343 (2009) ; PCCP 12, 13547 (2010)

S_1←S_0 electronic transition of anisole dimer

Vertical transition: delocalized character

- **Fully symmetric structure of anisole dimer in ground state**
  - Vertical excitation energy: two close lying electronic states, related to HOMO-LUMO transition in monomer
  - S_1 forbidden transition, S_2 – oscillator strength double with respect to monomer
  - Computed exciton shift ~ experimentally observed blue shift
- **Difference in electron density S_2-S_1**



state	E_{vert} (eV)	*f*
monomer		
S_1	5.33	0.0390
dimer		
S_1	5.28	0.0000
S_2	5.29	0.0756

Simulation of exciton shift

$$E_{exc} = \frac{E^D_{vert}(S_1) - E^D_{vert}(S_2)}{2} = -39\text{cm}^{-1}$$

J. Phys. Chem. A, 113, 14343 (2009) ; PCCP 12, 13547-13554 (2010)