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IDEA *In-Silico Developments for Emerging Applications* Laboratory
Scuola Normale Superiore, Pisa, Università Federico II di Napoli, *Italy*

Vibrationally-resolved electronic spectra in Gaussian 09

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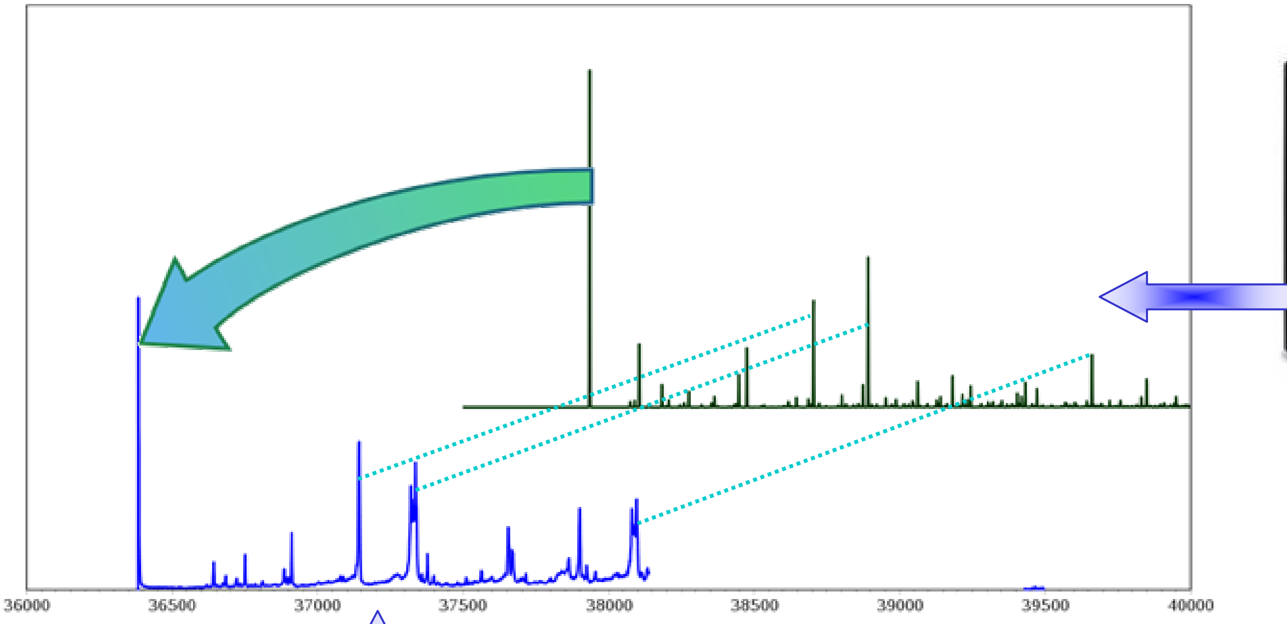
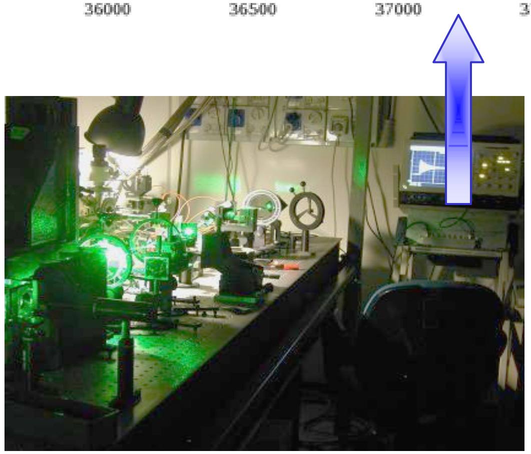
Scope: automatic vis-à-vis comparison





- direct comparison with experiment
- accuracy → interpretation
- easy-to-use procedure

Time independend and time dependent approaches

The time independent approach:

- Search for stationary points: minima (determination of structure), saddle points (determination of energy barriers and reactivity),
- Normal modes (internal motions, accurate determination of spectroscopic parameters)

The time dependent approach:

- Sampling of the energy surface: collection of trajectories (Molecular Dynamics approach).
- The energy (and the properties) are determined ‘on the fly’ during the integration on time of the Newton-like equations or by a previous calculation of grids on the energy surface.

Time-independent approach to compute vibrationally resolved electronic spectra

1. Theoretical framework – short overview.
2. Effective scheme to choose the most probable transitions: *FCClasses*.
3. Implementation in G09 – technical details.
4. Applications: accuracy and interpretation.

Calculation of the one photon absorbtion (OPA) or emission (OPE) spectra

- **Absorption stick spectrum**

$$\sigma(\omega) = \frac{4\pi^2\omega}{3c} \sum_i \rho_i \sum_f |\langle \Psi_i | \vec{\mu}_e \vec{e} | \Psi_f \rangle|^2 \, \delta(E_f - E_i + \hbar\omega)$$

ω is the incident energy

Ψ_i, Ψ_f are the wavefunction of the initial and final state, respectively

$\langle \Psi_i | \vec{\mu}_e \vec{e} | \Psi_f \rangle$ is the transition dipole moment integral

ρ_i is the Boltzmann population of the initial state *i*

$\vec{\mu}_e \vec{e}$ is the electric dipole moment

- Emission: the dependence on ω^3;
- 0 K: Only excitations from zero-vibrational level considered.
- Intensity proportional to integral: $|\langle \Psi_i | \vec{\mu}_e \vec{e} | \Psi_f \rangle|^2$

A general method to compute vibrationally resolved electronic spectra [1].

- Born-Oppenheimer approximation
- Eckart conditions (minimize the coupling between the rotations and vibrations)
- Harmonic oscillator

In general case of two interacting transition dipole moments the intensity of a spectrum line is determined by:

$$\langle \varphi_i | \mathbf{d}_A | \varphi_f \rangle \langle \varphi_f | \mathbf{d}_B | \varphi_i \rangle$$

where φ_i and φ_f are the vibrational wave functions of the initial and final states, respectively

- **O**ne-photon absorption (OPA) or emission (OPE) $\mathbf{d}_A = \mathbf{d}_B = \boldsymbol{\mu}_{if}$

electronic transition dipole moment

- Electronic circular dichroism (ECD) $\mathbf{d}_A = \boldsymbol{\mu}_{if}$ and $\mathbf{d}_B = \Im(\mathbf{m}_{if})$

magnetic transition dipole moment

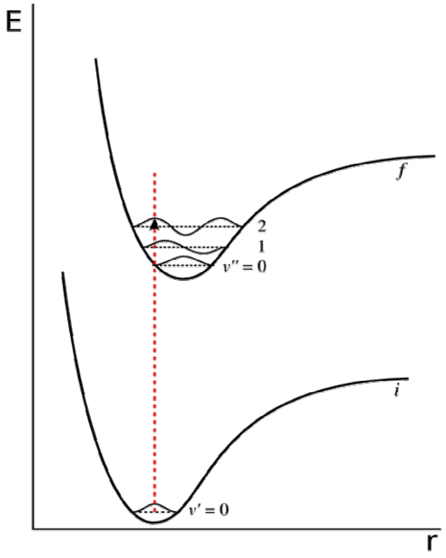
However,

There is **no** general **analytic solution** for m_{if} and μ_{if} !

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

Approximation of the transition dipole moments

The Franck-Condon principle



- Electron jump takes place in such a short time that nuclei are nearly unaltered by the molecular vibrations
- Franck-Condon: d_A and d_B are constant during the transition
- Herzberg-Teller: d_A and d_B vary linearly with the normal coordinates
- Taylor expansion of d_A and d_B about the equilibrium geometry of the final state

- Computation of the overlap integrals between initial and final vibrational states requires the use of a common coordinates set.
- Duschinsky transformation: normal coordinates of the initial state (Q') as linear transformation of the normal coordinates of the final state (Q'').

mixing between normal modes

$$Q'_i = \sum_{j=1}^{N} J_{ij} Q''_j + K_i$$

shift vector

Selection of transitions to be computed

❑ Using recursion fotmulae it is in principle possible to evaluate the transition dipole moment integrals $\langle \varphi_i | \mathbf{d}_A | \varphi_f \rangle$ and $\langle \varphi_i | \mathbf{d}_B | \varphi_f \rangle$ 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

FCClasses an *a priori* scheme to select the most intense transitions [1,2].

Principle

- Transitions are separated in classes depending on the number of simultaneously excited modes of the final state

- Cheap transitions for ***classes*** 1 and 2 are calculated up to a set, safe limit and their values stored

- Information from ***classes*** **1** (effect of the **shift** in equilibrium positions and frequencies on the vibrational progression of each mode) and **2** (effect of the **Duschinsky mixing**) are used to evaluate ***a priori*** the transitions to compute for each ***class*** starting from the third one.

- The calculations depend on the **number of integrals** ($N_I^{\max}$) to compute **NOT** on the **dimensionality** of the system

1. F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone, J. Chem. Phys. 126, 084509 (2007)
2. F. Santoro, A. Lami, R. Improta, J. Bloino, V. Barone, J. Chem. Phys. 128, 224311 (2008)

A priori scheme to select the most intense transitions:reliability [1,2].

A *black-box* procedure

- Very fast evaluation procedure
- The few required parameters can be set automatically

BUT - need to check the reliability!

◆ The total intensity calculated **after each class** is checked with the total intensity **expected** using analytic sum rules:

$$I^{\text{tot}} = \left|\mu_{if}(\mathrm{Q}_0'')\right|^2 \sum_{v'} \rho' \langle\, v' \mid v' \,\rangle = \left|\mu_{if}(\mathrm{Q}_0'')\right|^2$$

FC case

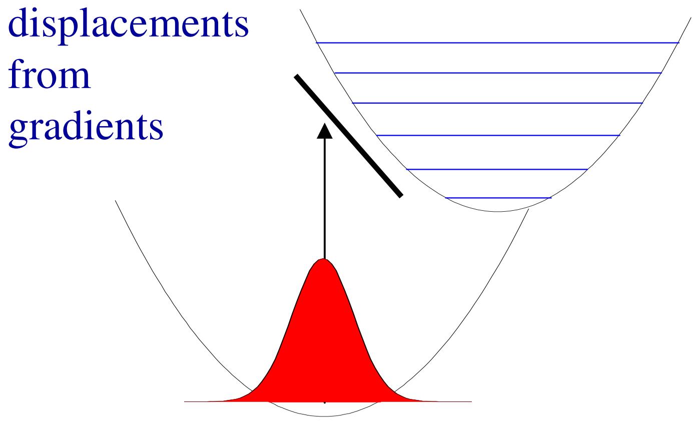
$$\boxed{spectrum \quad progression = \frac{\left|\left\langle 0' \middle| \mu_{if} \middle| v'' \right\rangle\right|^2}{I^{tot}}}$$

0K

1. F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone, J. Chem. Phys. 126, 084509 (2007)
2. F. Santoro, A. Lami, R. Improta, J. Bloino, V. Barone, J. Chem. Phys. 128, 224311 (2008)

Simulation of electronic spectra: Approximations

Simplest zero-order harmonic approx. – PES in **S_0** and **S_1** do not differ – geometries, normal modes and freq. identical – **most** of the vibrational bands are **missing.**



+ S_1 gradients at S_0 geometry

Gradient FC approach (GFC) *aka* LCM (linear coupling model) – **translation** vector (K') between S_1 and S_0 PES

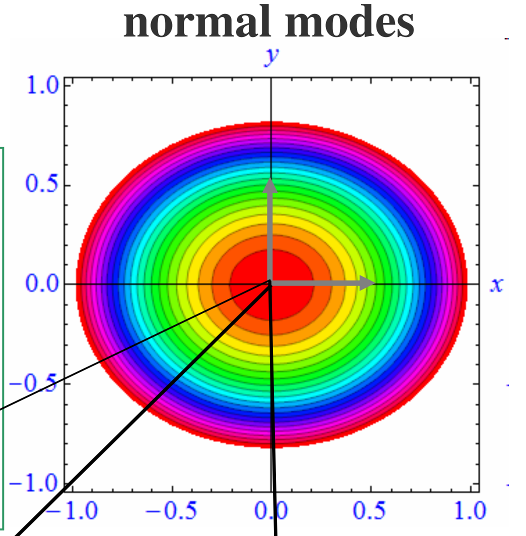
+ S_1 Hessian at S_0 geometry

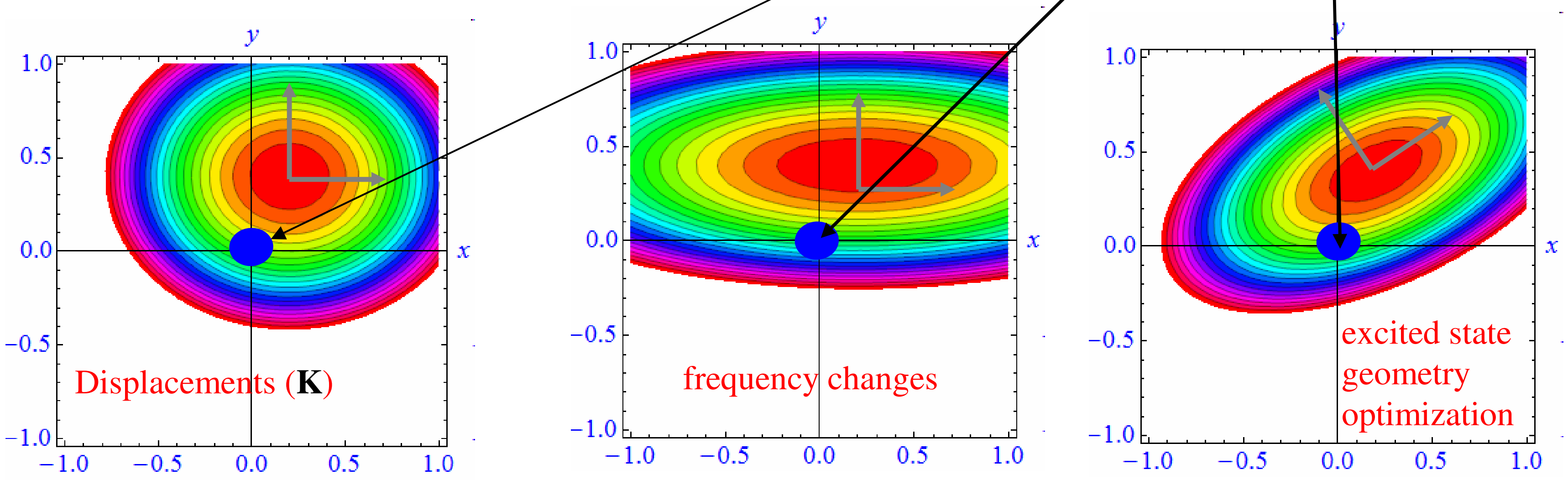
Harmonic Vertical Hessian Franck-Condon approach (**HFC**): well suited for a proper description of low-resolution features and the region the region of maximum band.

Simulation of electronic spectra: Harmonic Adiabatic FC Model

+ S_1 Hessian at S_1 geometry

Harmonic Adiabatic Franck-Condon (**AFC**) approach: excited states geometry optimisation and frequency calculations. **S_1: TD numerical** Hessian from **analytical gradients**[1]. Better description and assignment of high resolution spectra.





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1. Scalmani, G.; Frisch, M.J.; Mennucci, B; Tomasi, J.; Cammi, R; Barone, V.; J. Chem. Phys. 124 (2006) 094107.

Harmonic Adiabatic FC: Duschinsky rotation

the normal modes in $\mathbf{S_0}$ and $\mathbf{S_1}$ are in general not coincident ($\mathbf{J} \neq \mathbf{I}$)

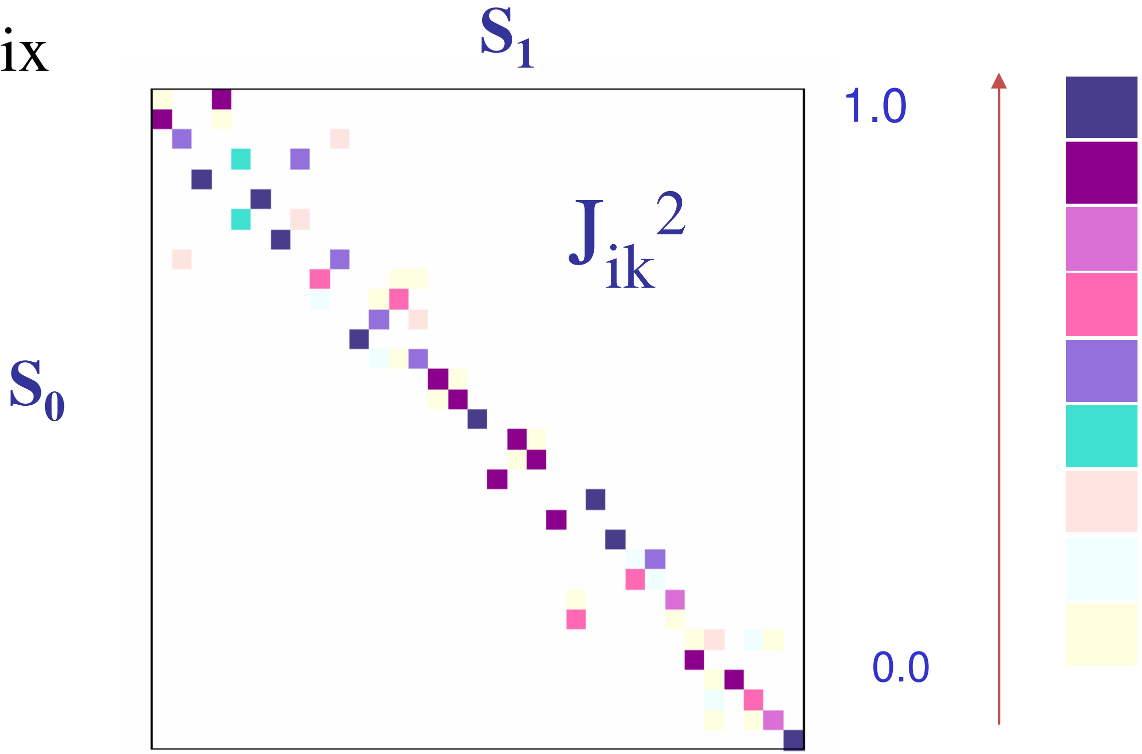
$Q''_i \neq Q'_i$ – Duschinsky rotation.

Q''_i as a linear combination of the S_0 ones:

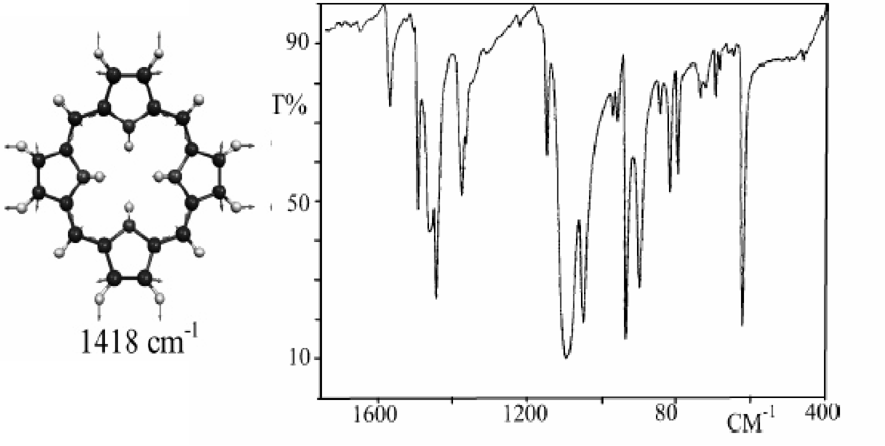
$\mathbf{Q''=JQ'+K}$;

J - Duschinsky matrix

K - shift vector.



Beyond harmonic approximation



Vibrational Spectrum

EXPERIMENT

THEORY

Vibrational Hamiltonian

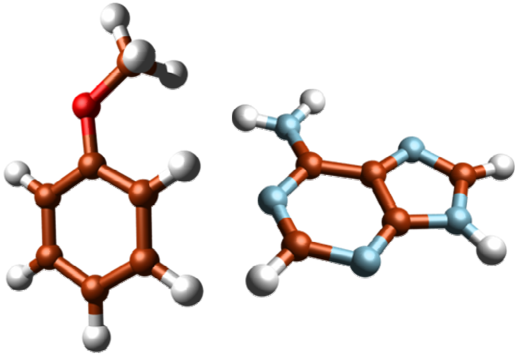
$$\mathbf{H}_{vib} = \underbrace{\frac{1}{2}\sum_r \omega_r (\mathbf{p}_r^2 + \mathbf{q}_r^2)}_{\text{Harmonic oscillator}} + \underbrace{\frac{1}{6}\sum_{rst} \phi_{rst}\, \mathbf{q}_r \mathbf{q}_s \mathbf{q}_t + \frac{1}{24}\sum_{rstu} \phi_{rstu}\, \mathbf{q}_r \mathbf{q}_s \mathbf{q}_t \mathbf{q}_u}_{\text{Anharmonic contributions}} + \ldots$$

Perturbative anharmonic corrections in the ground state [1], anisole[3], adenine [4,5]

PT2 computations

$$E_n = \xi_0 + \sum_i \omega_i \left(n_i + \frac{1}{2} \right) + \sum_i \sum_{j<i} \xi_{ij} \left(n_i + \frac{1}{2} \right) \left(n_j + \frac{1}{2} \right)$$

- ω's the harmonic wave-numbers,
- ξ's simple function of **3rd** (F_{ijk}) and semidiagonal **4th** (F_{iijj})energy derivatives with respect to normal modes **Q**
- **F_{ijk}** and **F_{iijj}** evaluated from **numerical** differentiation of **analytical Hessian**
- Proper treatment of **Fermi** resonances based on effective selection criterium [2]
- **Good** agreement with experimental data.



Comp vs. Exp.	anisole	adenine
Max. (-) Dev. [cm⁻¹]	-39	-22
Max. (+) Dev.[cm⁻¹]	27	19
MUE[cm⁻¹]	9	6

Anisole: B3LYP/6-311+G(d,p)
Adenine: B3LYP/6-311++G(2df,2pd)

1. V. Barone, J. Chem. Phys. 122, 014108 (2005)
2. A.D. Boese, J. Martin, J. Phys. Chem. A 108 (2004) 3085
3. J. Bloino, M. Biczysko, O. Crescenzi, V. Barone J. Chem.Phys. 128, 244105 (2008).
4. W. Zierkiewicz, L. Komorowski, D. Michalska, J.Cěrny, P. Hobza, J. Phys. Chem. B 112 (2008) 16734;
5. M. Biczysko, P. Panek, V. Barone, Chem. Phys. Lett. 475, 105 (2009).

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

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:

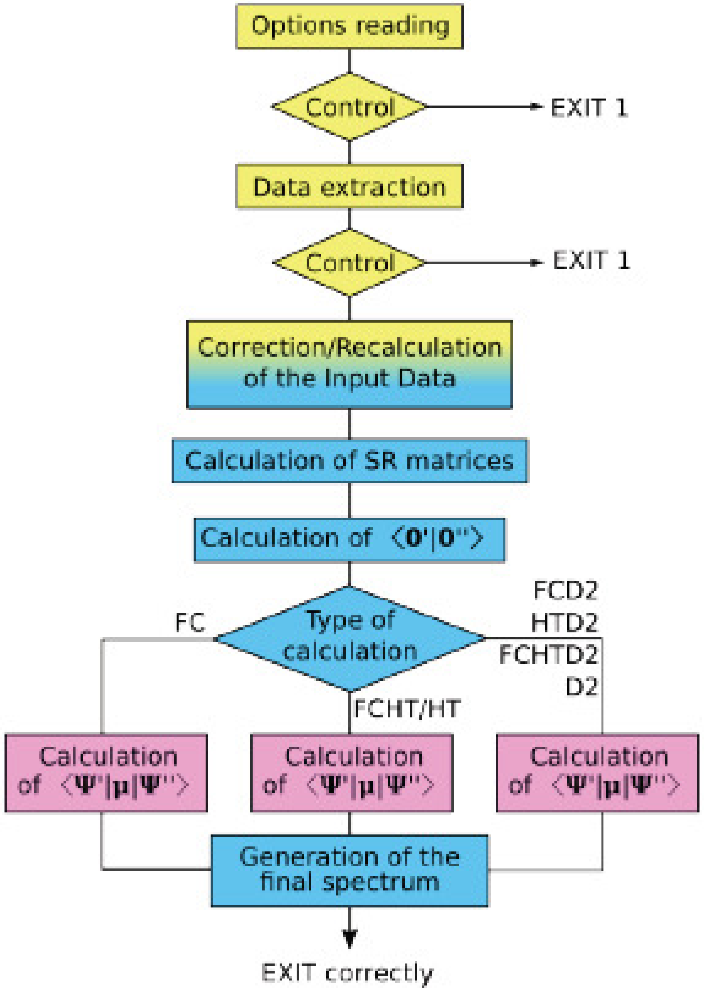
$$\alpha''(i) = \sum_{k}^{N} J_{ik}^{2}\alpha'(k) \qquad \upsilon''(i)=\alpha''(i)\omega''(i)$$

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

Implementation in Gaussian09

1. Fully integrated procedure: an overview.
2. Simple test case: input and output description.
3. Options to fine-tune spectra computations.

Franck: a fully integrated procedure


Options reading
Control
EXIT 1
Data extraction
Control
EXIT 1
Correction/Recalculation of the Input Data
Calculation of SR matrices
Calculation of ⟨0'|0''⟩
FC
Type of calculation
FCD2
HTD2
FCHTD2
D2
FCHT/HT
Calculation of ⟨Ψ'|μ|Ψ''⟩
Calculation of ⟨Ψ'|μ|Ψ''⟩
Calculation of ⟨Ψ'|μ|Ψ''⟩
Generation of the final spectrum
EXIT correctly

- Implementation as an easy-to-use procedure integrated in a quantum mechanical computational package, GAUSSIAN
- Direct access to precise data on the properties of electronic states inside the computational package GAUSSIAN
- Efficient and versatile procedure to compute vibrationally resolved electronic spectra
- Few required settings from the user but many possibilities to fine-tune the calculations
- Clear output with description of the most intense transitions

Simple test case: $^2A_2 \leftarrow\ ^2B_1$ absorption spectrum of phenoxyl radical

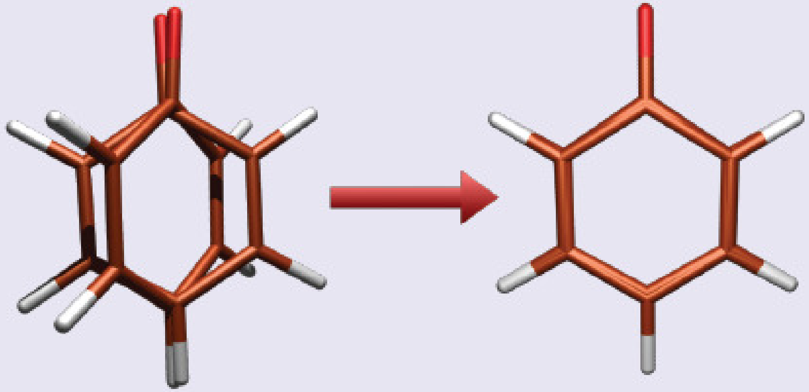
Procedure

Calculation is done at DFT level for the initial state and TD-DFT for the final state (B3LYP/TZVP)

1. optimization of the structure of the initial state
2. optimization of the structure of the final state
3. calculation of the frequencies of the initial state
4. calculation of the frequencies of the final state and calculation of the spectrum

An automatic black-box procedure

- Extraction of the data for the initial state from the checkpoint file (*phenoxyl_S0.chk*)
- Extraction of the data for the final state from the actual calculation
- Superposition of the structures



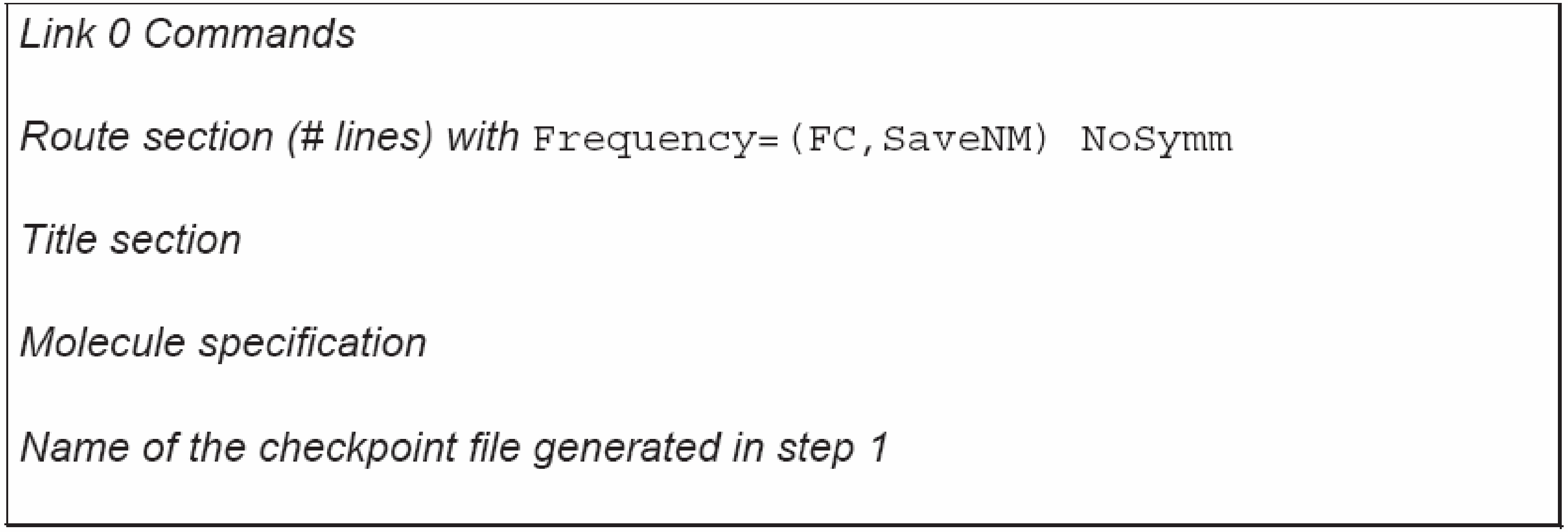
- Recalculation of the frequencies and vibrational normal modes
- Calculation of the FC spectrum

Gaussian input for 2-step procedure

2-step procedure:

1. Calculation of the frequencies for the final state
2. Calculation of the frequencies for the initial state followed by the generation of the spectrum.

In the input file for the second step, the keyword **`FC,FCH`** or **`HT`** is given for **`Frequency`**



Link 0 Commands

Route section (# lines) with `Frequency=(FC,SaveNM) NoSymm`

Title section

Molecule specification

Name of the checkpoint file generated in step 1

`SaveNM:` not generally mandatory (save the frequencies and normal modes in the checkpoint file).

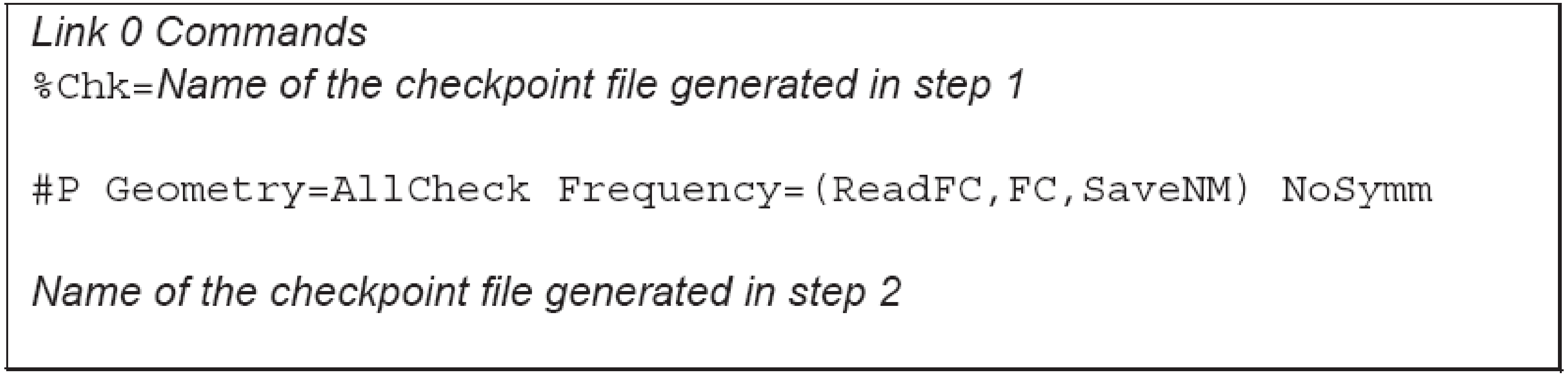
But necessary for QM/MM calculations or when dealing with frozen atoms .

Gaussian input for 3-step procedure

2-step procedure requires the computation of frequencies each time a spectrum must be generated thus is not well suited when diverse parameters must be tried.
A second way of using GAUSSIAN is through a **3-steps procedure** where the last step is broken down in two separate steps as follows:

3-step procedure:

1. Calculation of the frequencies for the **initial** state.
2. Calculation of the frequencies for the **final** state.
3. Generation of the spectrum, input file:



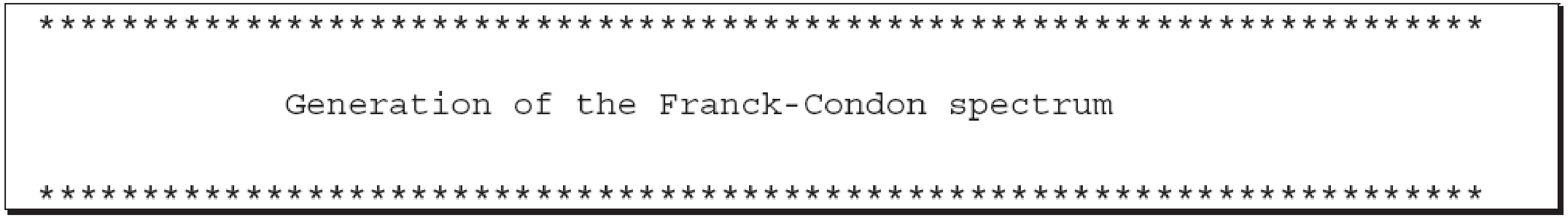
```
Link 0 Commands
%Chk=Name of the checkpoint file generated in step 1

#P Geometry=AllCheck Frequency=(ReadFC,FC,SaveNM) NoSymm

Name of the checkpoint file generated in step 2
```

Steps 1-2 can be done simultaneously.

Simple test case: OPA spectrum of phenoxyl radical

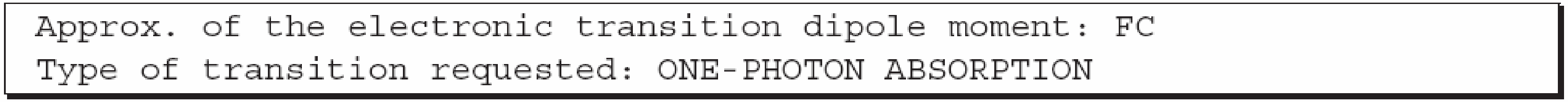
Gaussian output: generation of the spectrum

Starts:



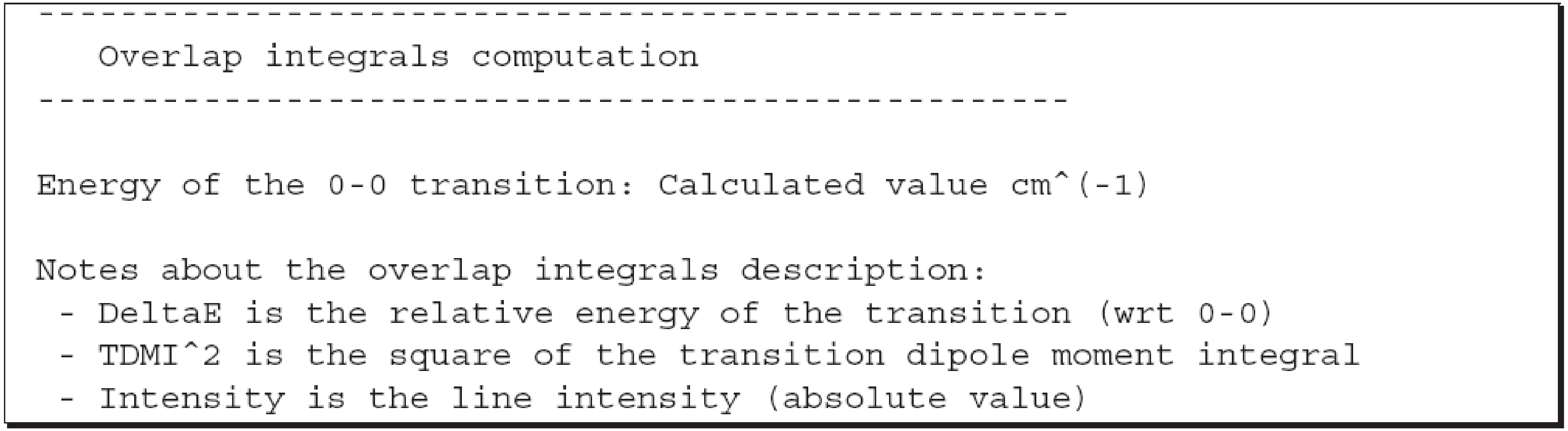
```
 ******************************************************************

            Generation of the Franck-Condon spectrum

 ******************************************************************
```

Type of : approximation of the electronic transition dipole moment **(FC)** and transition **(OPA)**



```
 Approx. of the electronic transition dipole moment: FC
 Type of transition requested: ONE-PHOTON ABSORPTION
```

The actual calculation:



```
 --------------------------------------------------
    Overlap integrals computation
 --------------------------------------------------


 Energy of the 0-0 transition: Calculated value cm^(-1)

 Notes about the overlap integrals description:
  - DeltaE is the relative energy of the transition (wrt 0-0)
  - TDMI^2 is the square of the transition dipole moment integral
  - Intensity is the line intensity (absolute value)
```

Gaussian output: generation of the spectrum

The **most intense** transitions (`PrtInt=`) are printed by incrementing *class*:

mode^quanta

```
Initial State: <0|
Final State: |x^x,x^x>
  DeltaE =      x.xxxx | TDMI^2 = x.xxxxExxx, Intensity = x.xxxxExxx
  ........................................
```

After each class **the convergence** of the spectrum is printed:

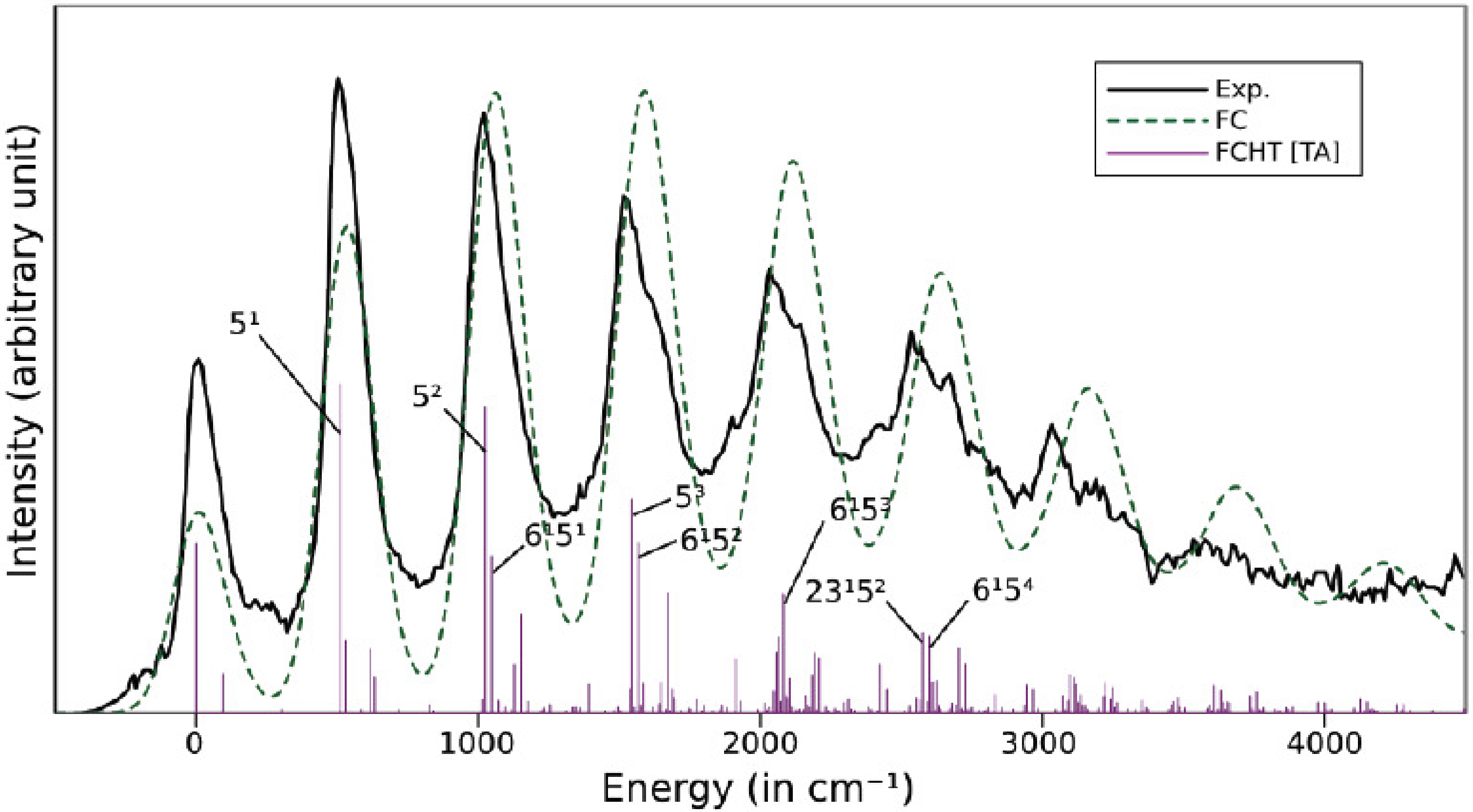
```
++ Spectrum progression:  xx.xx%
```

Finally, **the spectrum** generated by **GAUSSIAN:**

```
+-------------------+
|  Final Spectrum   |
+-------------------+

 Axis X = Energy (in cm^-1)
 Axis Y = Intensity (in arbitrary units)

 ------------------------------------------------------------
       xxxxx.xxxx        x.xxxxxxDxxx
```

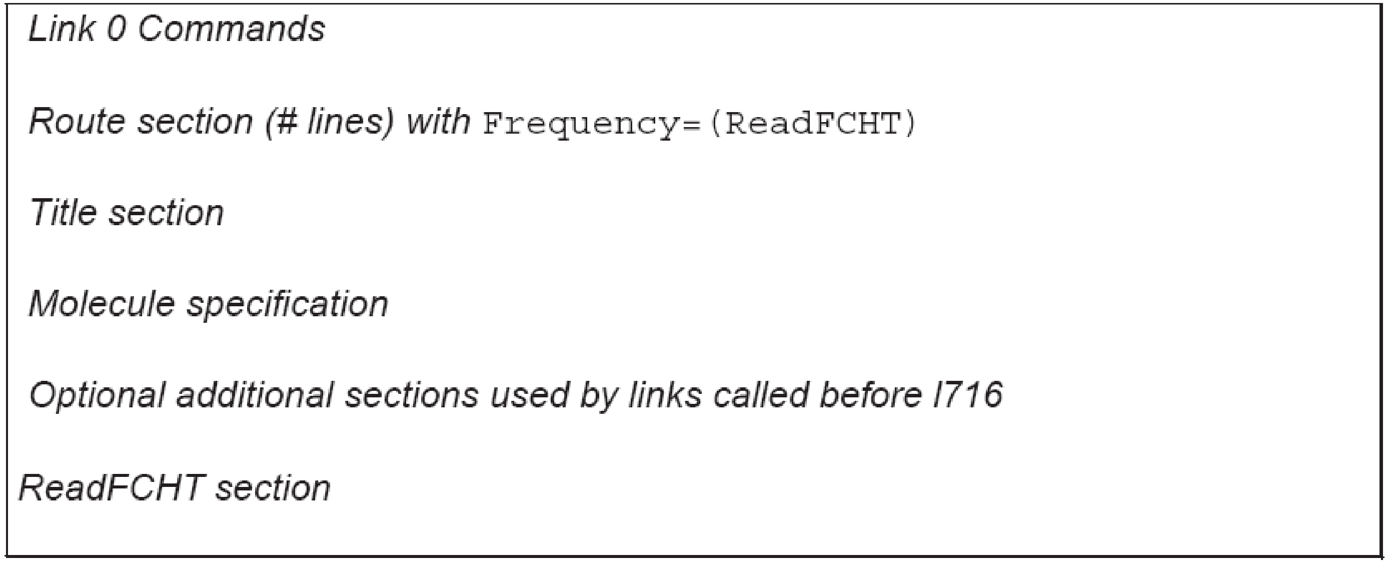
Gaussian output: generation of the spectrum

- ❑ Stick spectrum
- ❑ Convoluted spectrum
- ❑ Assignment of vibronic transitions



Gaussian input: ReadFCHT section

Input:



Link 0 Commands

Route section (# lines) with `Frequency=(ReadFCHT)`

Title section

Molecule specification

Optional additional sections used by links called before l716

ReadFCHT section

- General parameters of the calculations: **`FC/FCHT/HT, ABS/EMI`**
- Sources of input data: **`Calc/Chk/Out, NState`**
- User-given input data or modification: **`InpDEner, SclVec, JDusch/JIdent`**
- Parameterization of the GAUSSIAN output: **`PrtMat, AllSpectra, PrtInt`**
- Setting of the spectrum layout: **`SpecMin, SpecMax, NoRelI00, SpecRes, SpecHWHM`**

Options ruling spectrum accuracy:

- **`MaxOvr(MaxC1):`** Sets the maximum quantum number that has to be considered for each mode of C_1 (C_1^{max}), default=20;

- **`MaxCmb(MaxC2):`** Sets the maximum quantum number to consider for each mode involved in the combination bands in C_2 (C_2^{max}) default=13;

- **`MaxInt:`** Sets the maximum number of integrals (N_I^{max}, expressed in million) to compute for each class above C_2, default=100 (10^8 integrals).

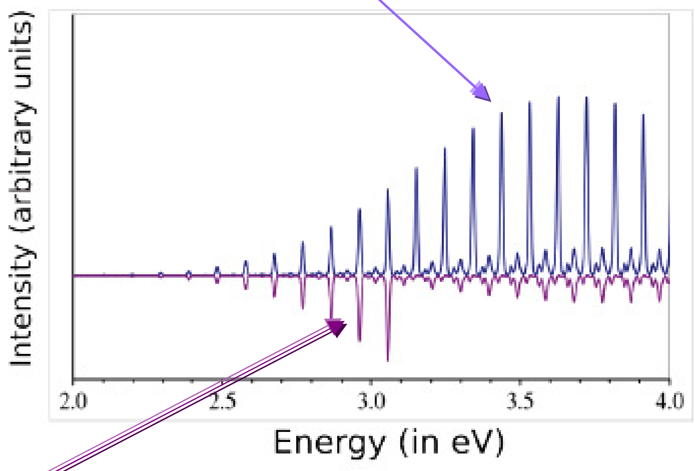
- **`MaxBands:`** Sets the maximum class to consider. Calculations can end before if there are not enough excited modes or DELTASP is also defined and the condition imposed by the latter is met before; default=7;

- **`DeltaSP:`** Sets a condition on the spectrum convergence. If the spectrum progression with respect to the total intensity between two consecutive classes is below DeltaSP (in absolute value), then the calculations end, default= 0.0.

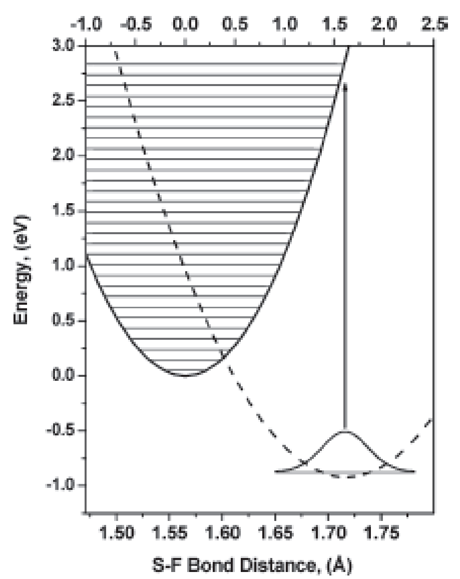
Parameterizing the prescreening method: Photodetachment spectrum of SF_6^-:

- ❑ The default settings are insufficient to correctly reproduce the photodetachment spectrum of SF_6^-

```
%Chk=SF6_neutral_freq.chk
#P Geom=AllCheck Freq=(ReadFC,FC,SaveNM,ReadFCHT) NoSymm

 PRTMAT=12 MAXC1=100 MAXBANDS=4 SPECHWHM=0.5

SF6_anion_freq.chk
```



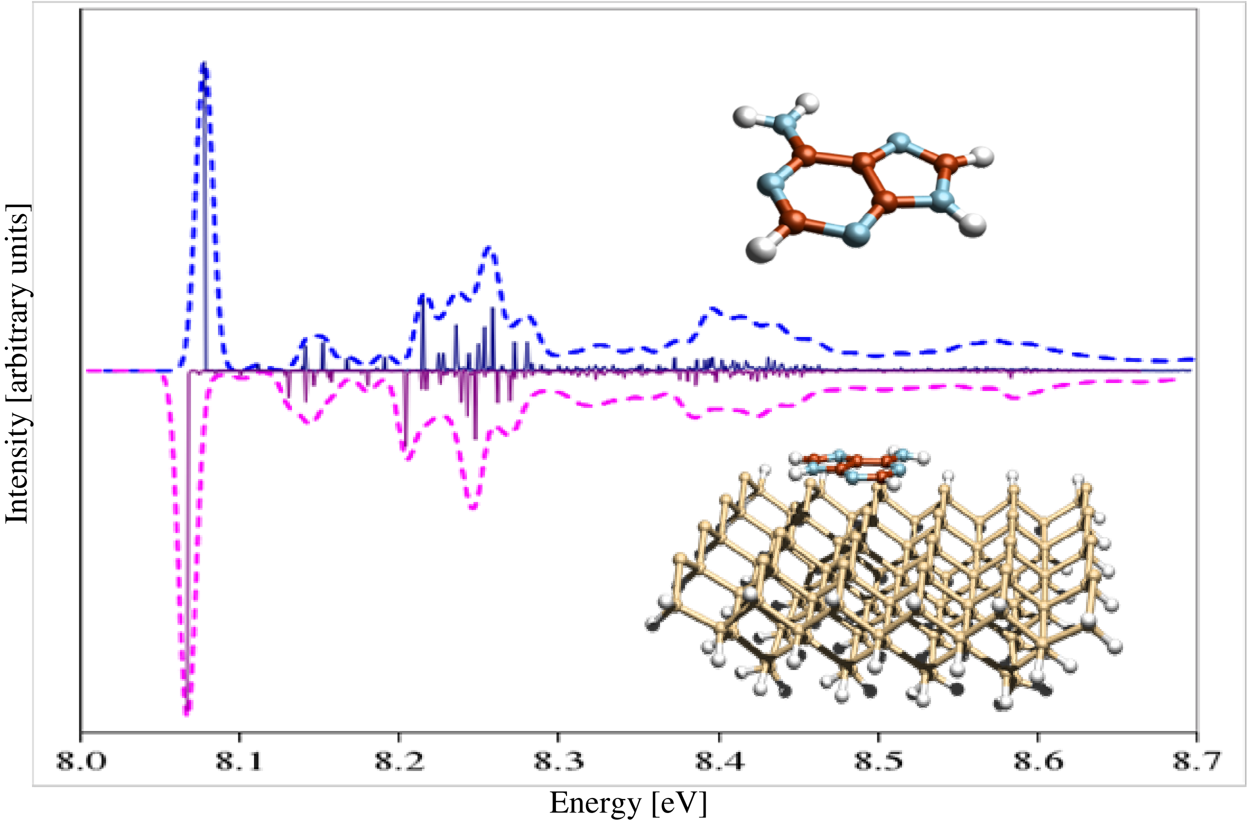
MAXC1=20



Illustrative examples

1. Efficiency of *a priori* selection scheme
2. Spectrum convergence
3. Full vs. reduced dimensionality vibrational treatment
4. Accuracy and interpretation
5. Environmental effects by discrete or continuum models
6. DFT for spectroscopy and non-covalent interactions.

Photoelectron Spectrum of Adenine and Adenine@Si(100) [1].



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

.... FWHM=200 cm^{-1}
—— FWHM=2 cm^{-1}

1. **V. Barone**, *et al* J. Chem. Theory Comp. 5, 540 (2009)

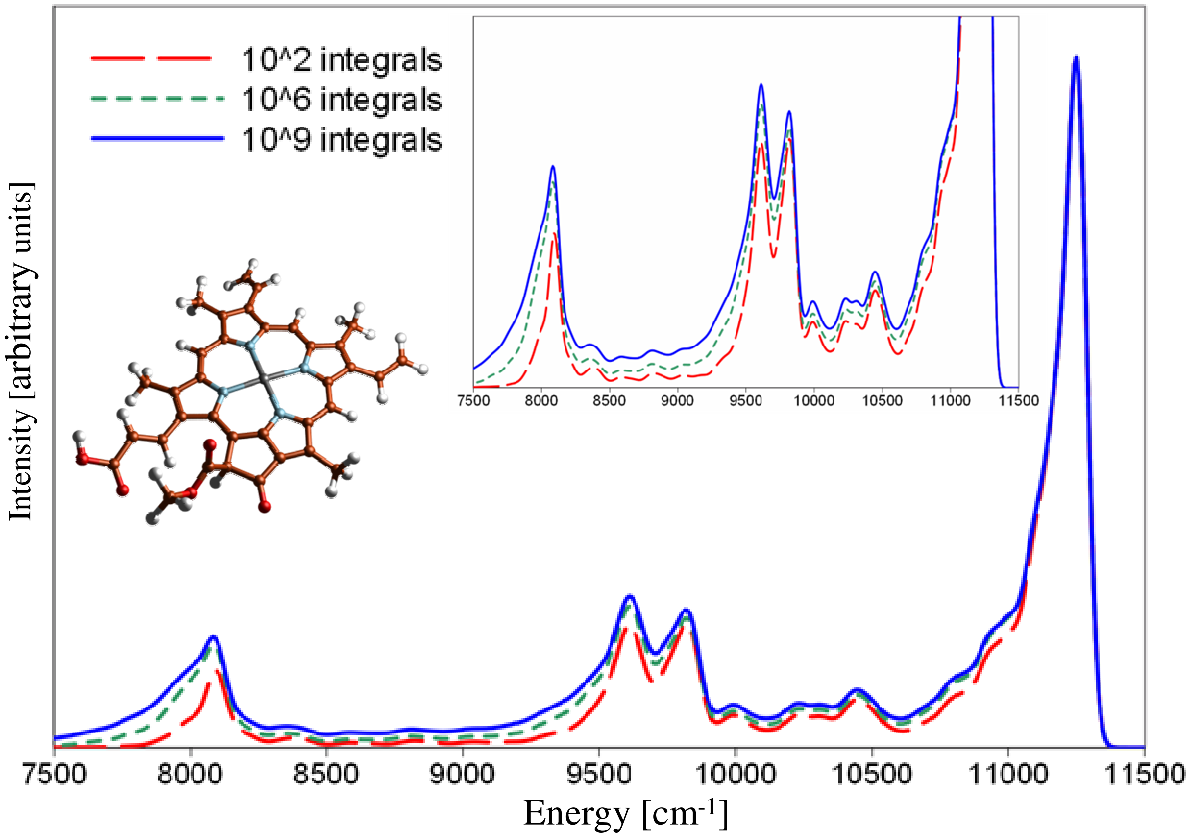
A priori scheme - almost **all** spectrum intensity (about 98%) for an isolated molecule or a macrosystem at an equivalent computational cost (localized transition).

Computational cost related to the number of integrals **not** the system size.

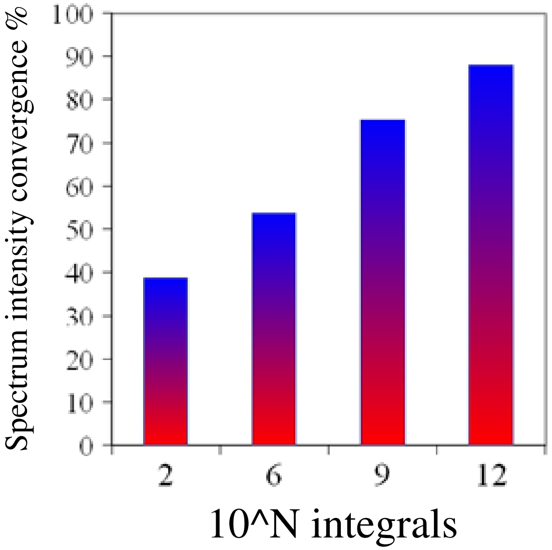
Spectrum **changes** upon adsorption - insights into the nature of adsorbate-surface interactions

Spectrum convergence, intensity vs. line-shape

Phosphorescence Spectrum of Chlorophyll *c2* [1].



Chlorophyl c2:
213 normal modes
S_0, T_1: B3LYP/6-31+G(d,p)

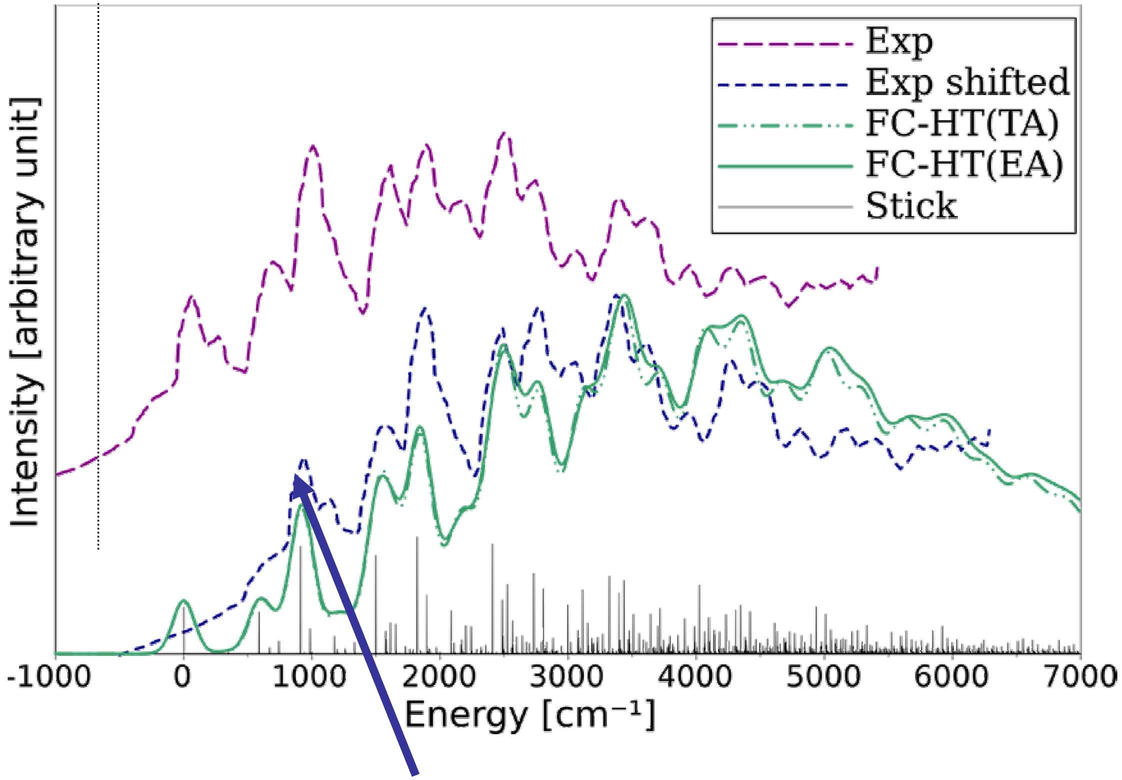


Spectrum quality **~** intensity convergence **~** number of integrals **~** computational cost.
Line shape - information about most important transitions, converges much **faster** than spectrum intensity: 10^2 integrals ≈ 40%, 10^9 ≈ 80% , 10^12 ≈ 90 %.
Main spectrum features **well reproduced** by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

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

Full-dimensional vibronic treatment

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



S_0-B3LYP/N07D +
PT2 anharmonicity

S_1-TD-B3LYP/N07D+
(TA) (EA) correction scheme

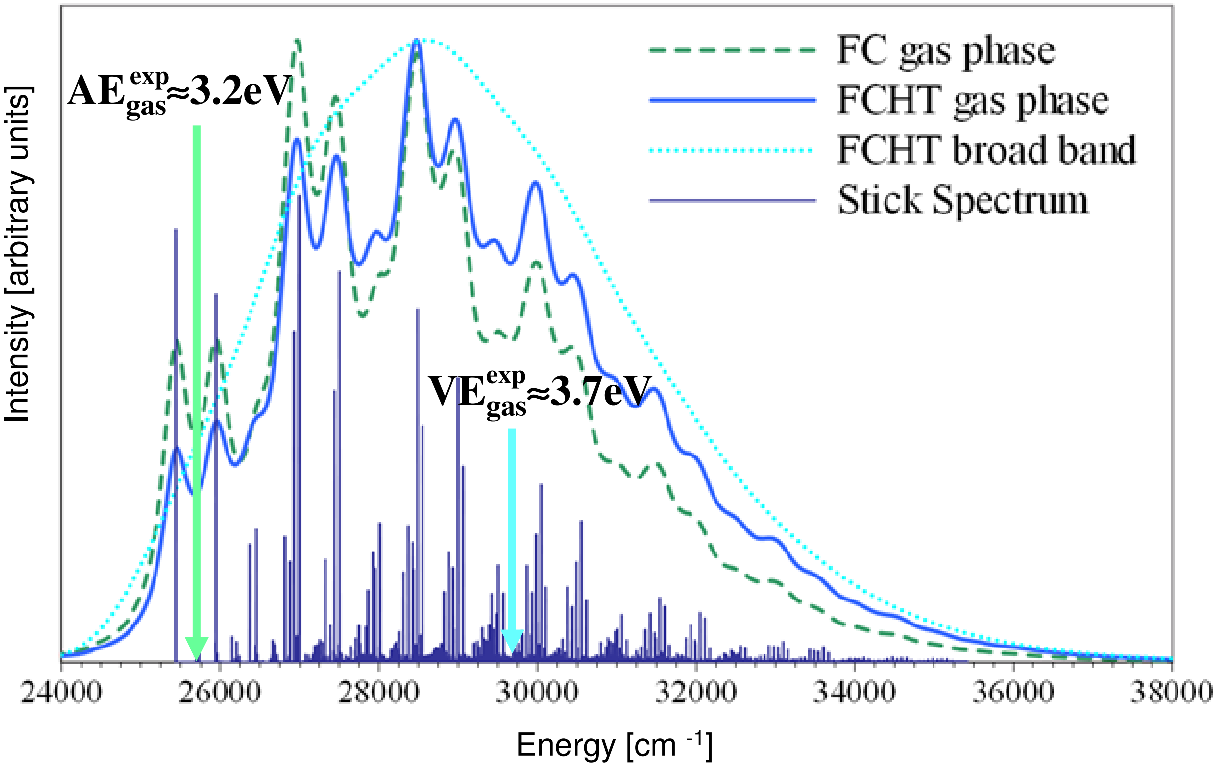
1. M. Biczysko, J. Bloino, V. Barone
Chem. Phys. Lett. 471, 143 (2009)
2. G.S. Kim, A. Mebel, S. Lin
Chem. Phys. Lett. 361, 421 (2009)

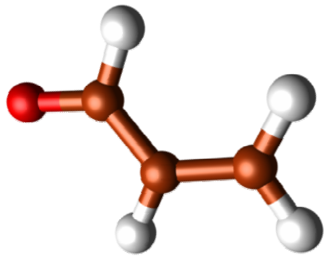
Good agreement with **shifted** experimental spectra:
transition assign as 0–0 progression to the excited vibrational state of A^2B_1**?**

Limited dimensionality simulations [2] – spectrum almost **featureless:**
Full dimensional vibronic models – **reproduce** the spectrum shape
Full-D **prior** to analyze the possible role of **nonadiabatic effects.**

FC vs FCHT approximation

UV Spectrum of Acrolein in the Gas Phase [1].



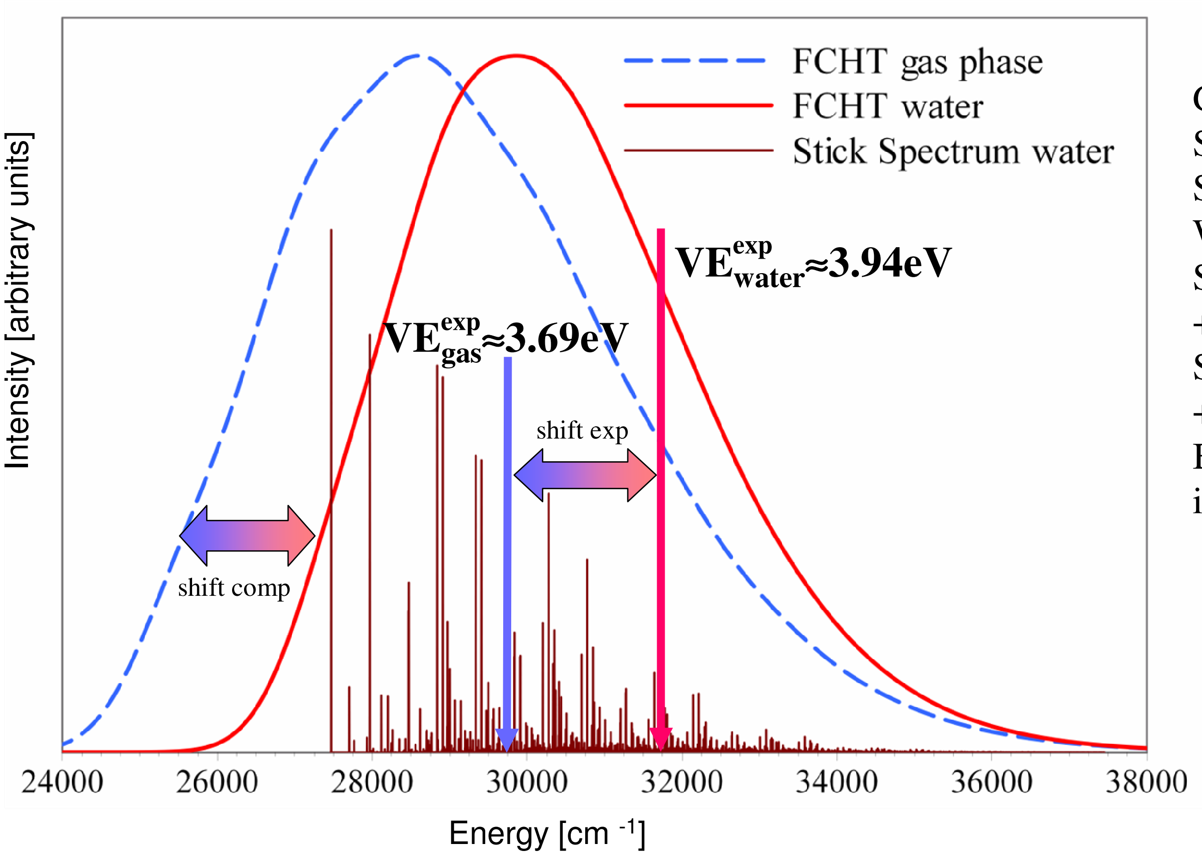


Gas phase:
S_0-B3LYP/6-311++G(2d,2p)
S_1-TD-B3LYP/6-311++G(2d,2p)
FWHM=400 cm^{-1},
homogoneous (Lorenzian) broadening
Broad band:
FWHM=1500 cm^{-1}
inhomogenous (Gaussian) broadening

Origin and band **maximum** of n→π* electronic transition **agree well** with experiment [2]. **Weakly allowed** n→π* transition, **FCHT** (with homogenous broadening) better reproduce vibrational structure of gas phase experimental spectrum [2].

1. V. Barone, *et al*. J. Chem. Theory Comp. 5, 540 (2009) 2. K. Aidas, *et al.* J. Chem. Phys. 128, 194503 (2008)

Vibrationally resolved electronic spectra:
UV Spectrum of Acrolein in the Gas Phase and Aqueous Solution [1].

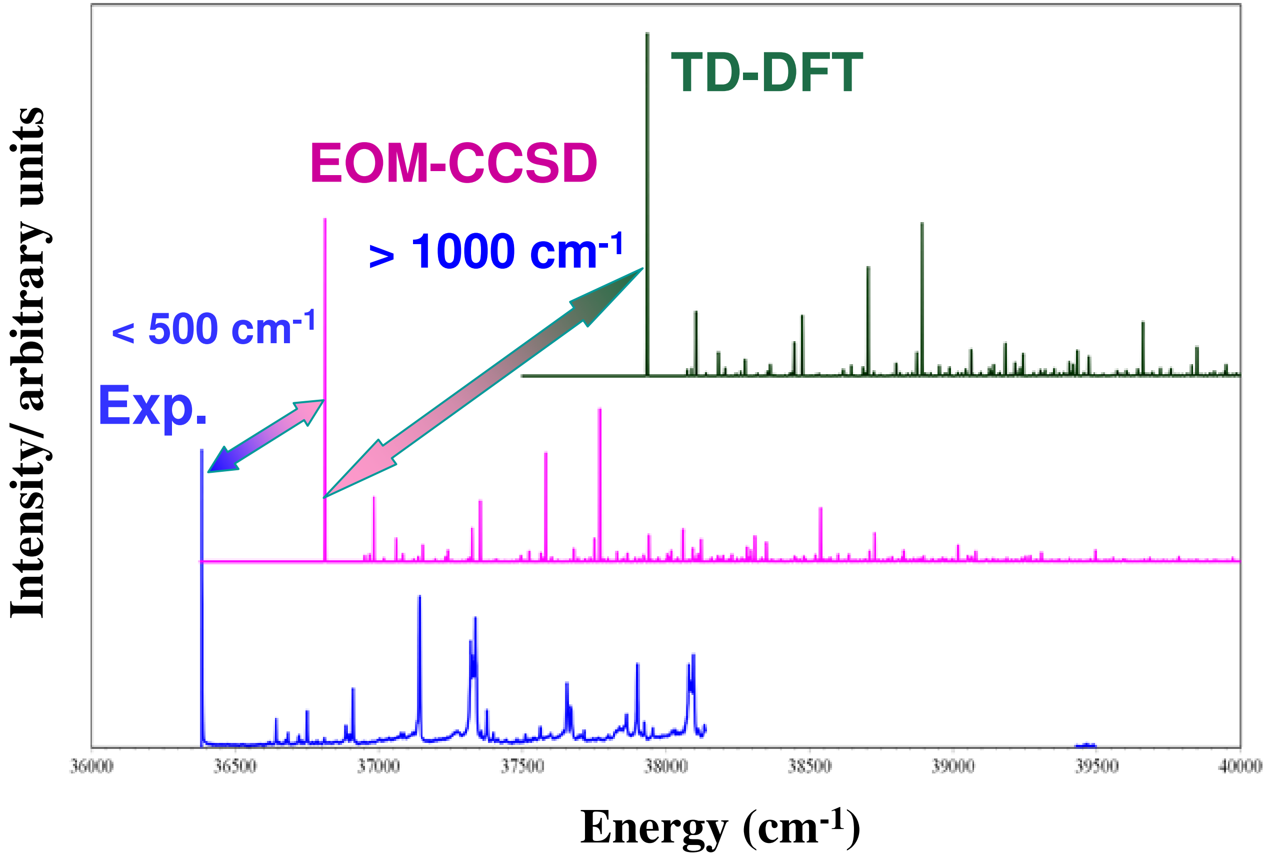


Gas phase:
S_0-B3LYP/6-311++G(2d,2p)
S_1-TD-B3LYP/6-311++G(2d,2p)
Water:
S_0-B3LYP/6-311++G(2d,2p)
+CPCM
S_1-TD-B3LYP/6-311++G(2d,2p)
+CPCM
Both: FWHM=1500 cm^{-1}
inhomogenous (Gaussian) broadening

Straightforward simulation **o**f both the gas phase and aqueous solution absorption spectra. **Solvent** spectra – observed featureless **broad** band [2], **simulation**: detailed description of underlying **vibrationa**l contributions. **Solvent shift** well reproduced by DFT/CPCM.

1. **V. Barone**, *et al*. J. Chem. Theory Comp. 5, 540 (2009) 2. K. Aidas, *et al.* J. Chem. Phys. 128, 194503 (2008)

Refinement: absolute and relative energies: $S_1 \leftarrow S_0$ electronic transition of anisole [1].



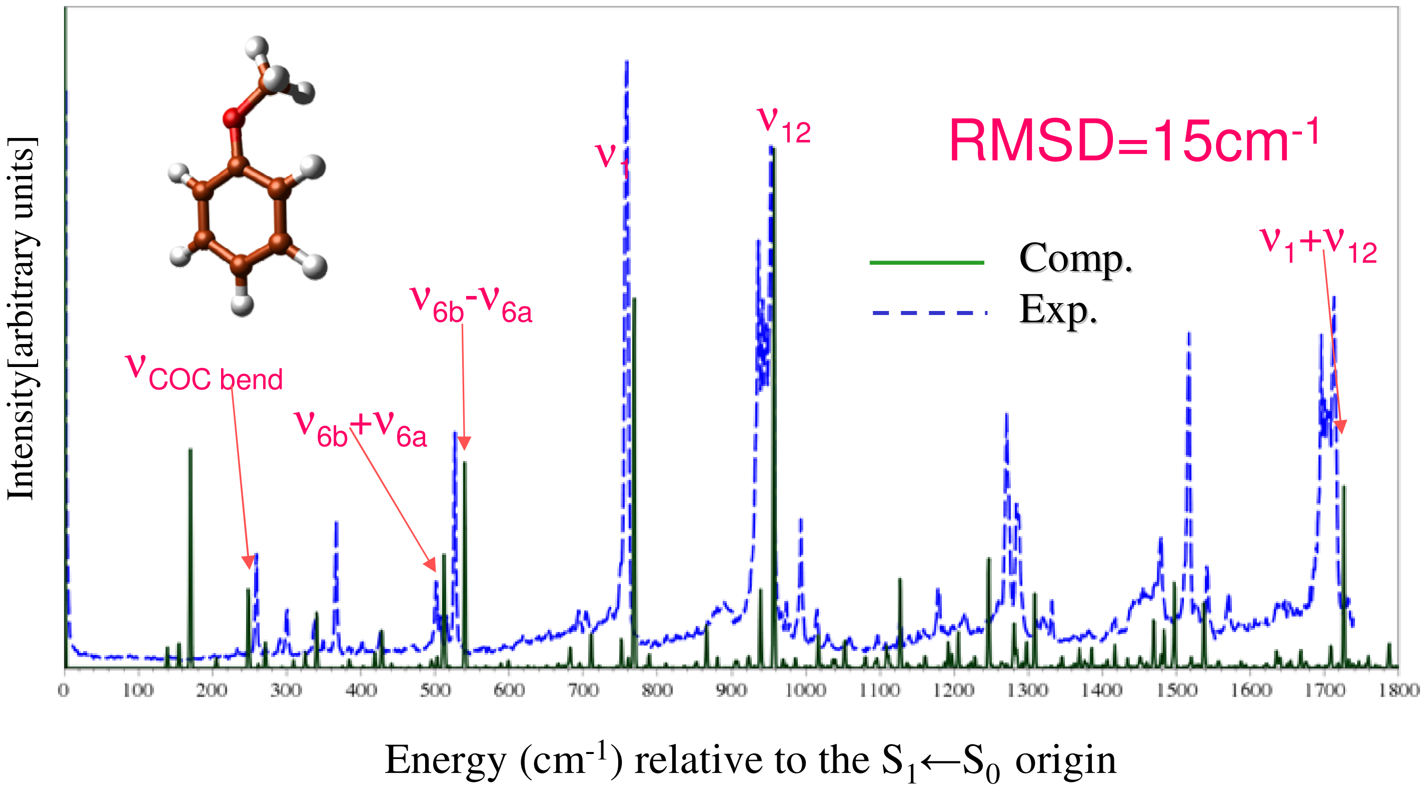
S_0:
CCSD/aug-cc-pVDZ//
B3LYP//6-311+G(d,p);

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

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} → necessary to compare spectra **shifted** to the **0-0** origin.

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

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



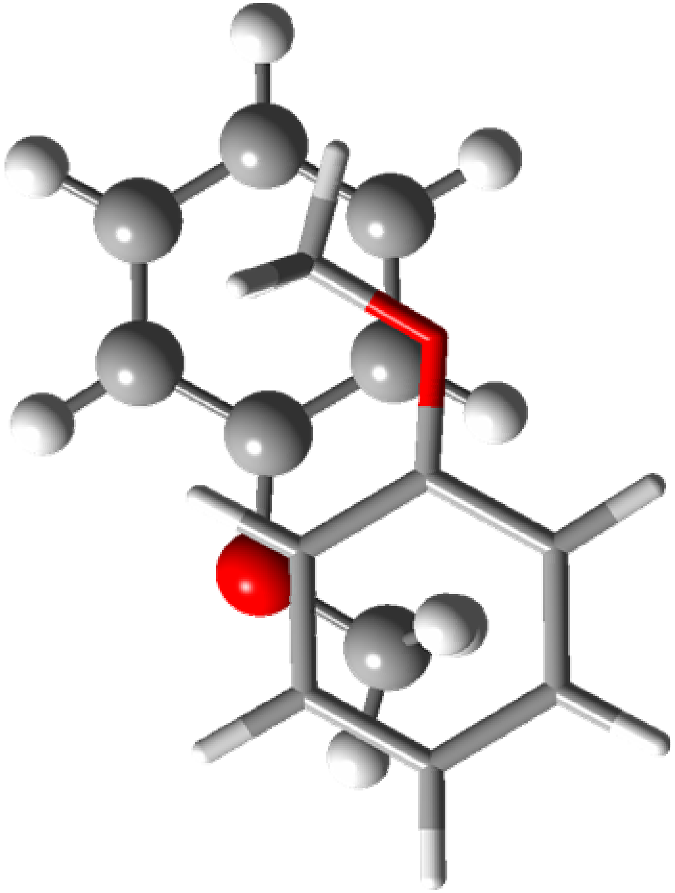
S_0: B3LYP/6-311+G(d,p) Perturbative (PT2) anharmonic corrections [2],
S_1:TD-B3LYP/6-311+G(d,p) Anharmonic corrections derived from ground state data[1].

A **very good agreement** between computed and experimental 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 (2005) 014108

Systems with non-covalent interactions: Accuracy

$S_1 \leftarrow S_0$ electronic transition of anisole dimer [1,2]: structure of the complex

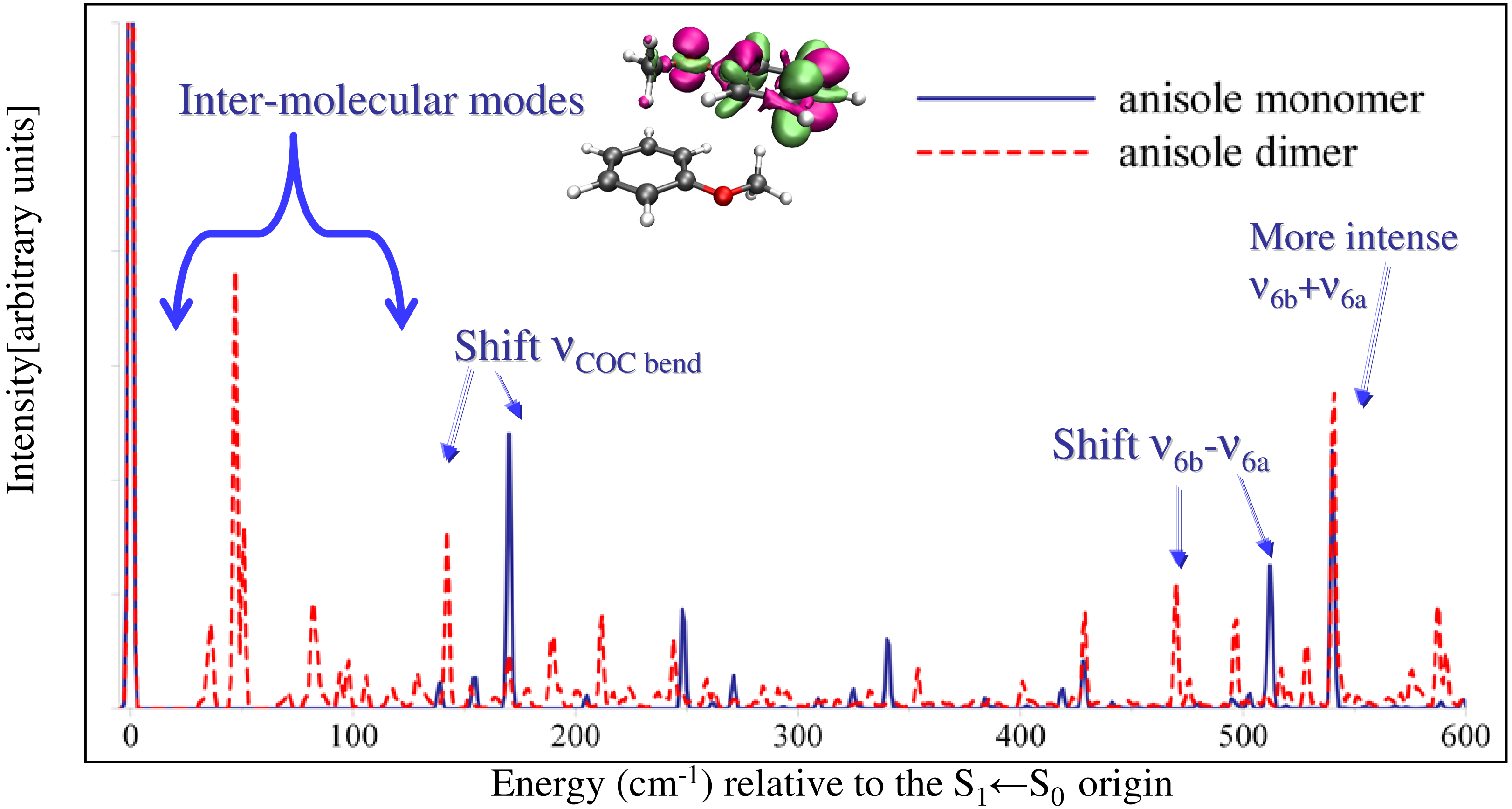


Rotational constants in the ground and first excited electronic state

	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**

1. M. Pasquini, ..., M. Becucci, M. Biczysko, J. Bloino, V. Barone submitted J. Phys. Chem. A;
2. N. Schiccheri, ..., M. Becucci, M. Biczysko, J. Bloino, V. Barone in preparation

$S_1 \leftarrow S_0$ electronic transition of anisole dimer [1,2]: Dimer *vs.* monomer OPA spectra

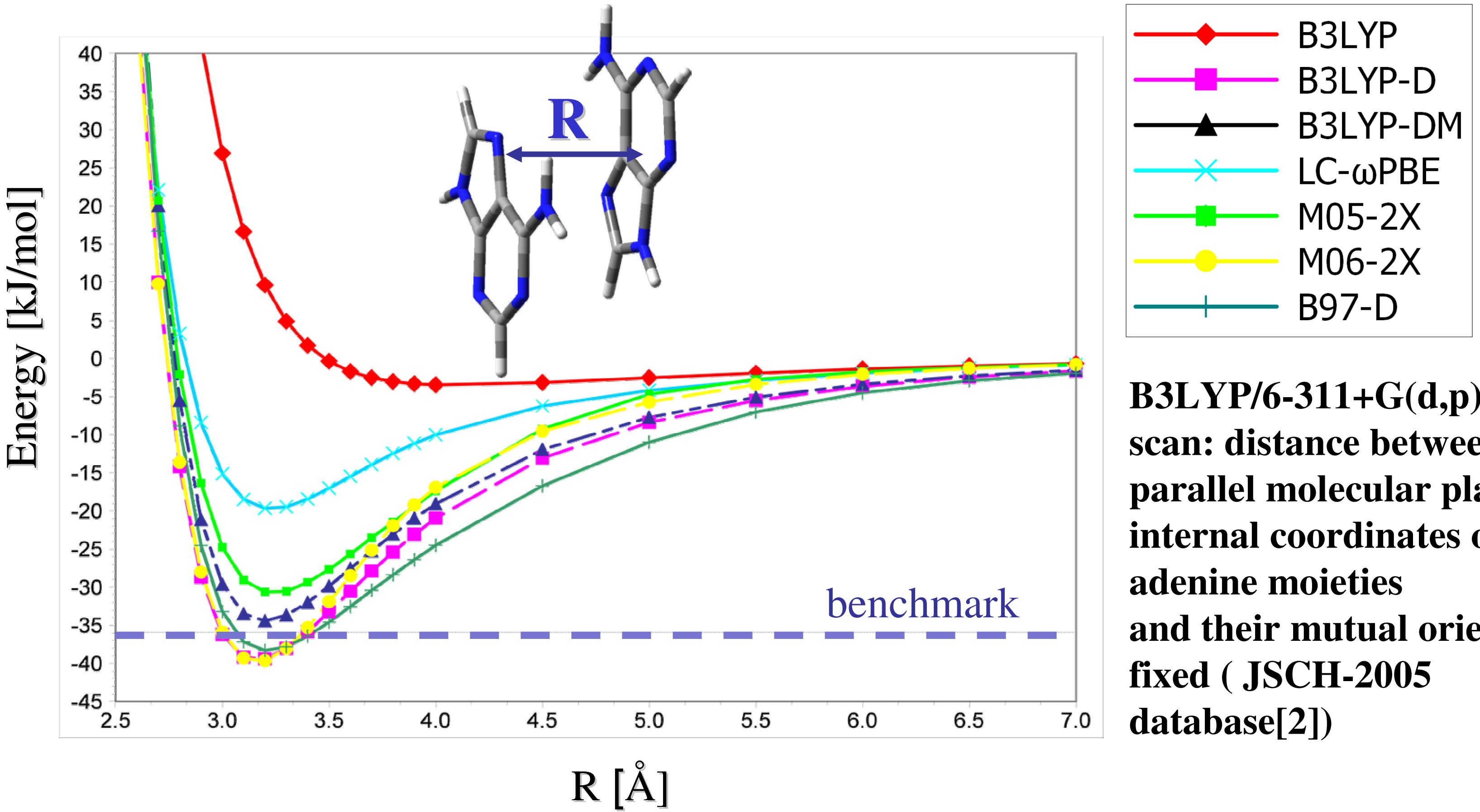


Structures: S_0: M05-2X/6-31+G(d,p), S_1: TD-M05-2X/6-31+G(d,p)
Anharmonic corrections: ground state (PT2) B3LYP-D/6-31+G(d,p) + 'mode-specifig scaling factors' scheme for excited state

1. M. Pasquini, ..., M. Becucci, M. Biczysko, J. Bloino, V. Barone submitted J. Phys. Chem. A;
2. N. Schiccheri, ..., M. Becucci, M. Biczysko, J. Bloino, V. Barone in preparation

Systems with non-covalent interactions

Performance of long-range/dispersion corrected DFT functionals [1]: PES of adenine dimer.

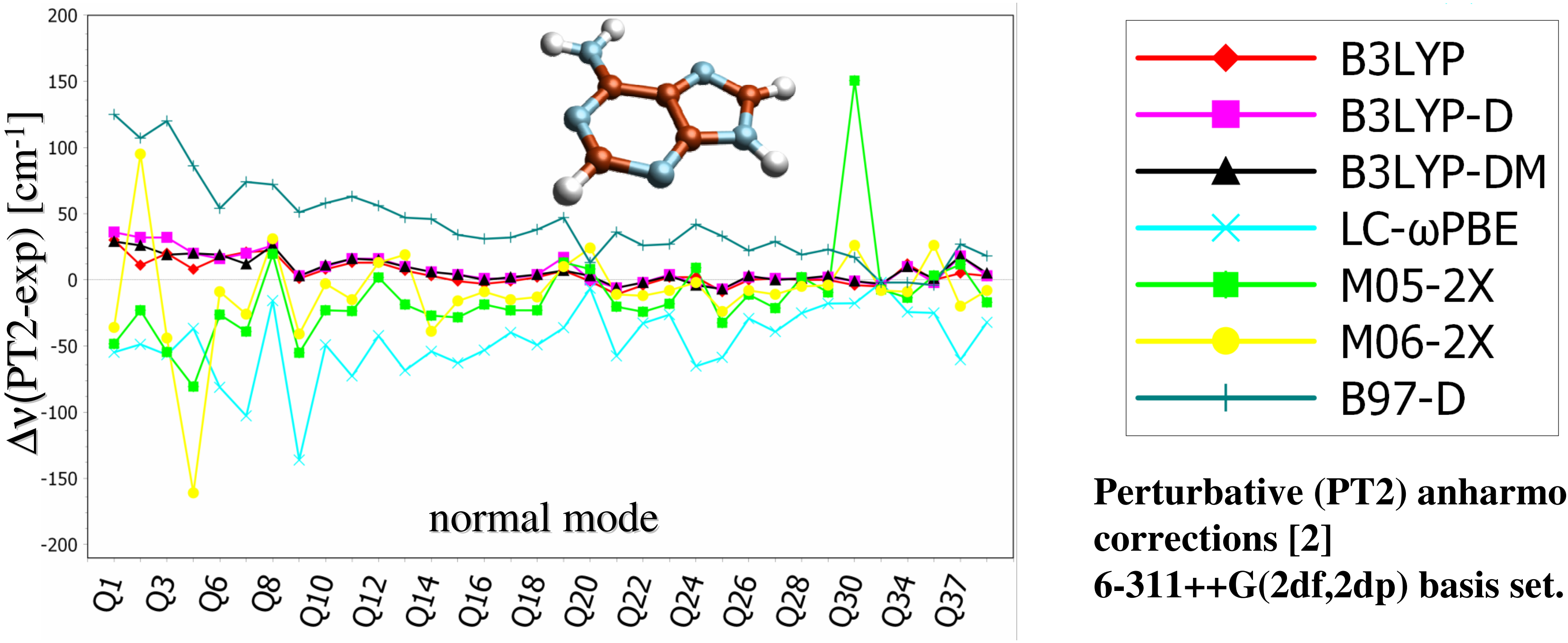


B3LYP/6-311+G(d,p) scan: distance between parallel molecular planes, internal coordinates of adenine moieties and their mutual orientation fixed (JSCH-2005 database[2])

DFT-D models and the **M06-2X** functional: a binding energy in **good agreement** with the benchmark data [2]; Standard **B3LYP** → **NOT** suitable for the studies of molecular complexes bound by dispersion/stacking interactions,

1. M. Biczysko et al. Chem. Phys. Lett. 475, 105 (2009) **2**. P. Jurečka, et al. Phys. Chem. Chem. Phys. 8 (2006) 1985

Performance of long-range/dispersion corrected DFT functionals [1]: Anharmonic frequencies



Perturbative (PT2) anharmonic corrections [2]
6-311++G(2df,2dp) basis set.

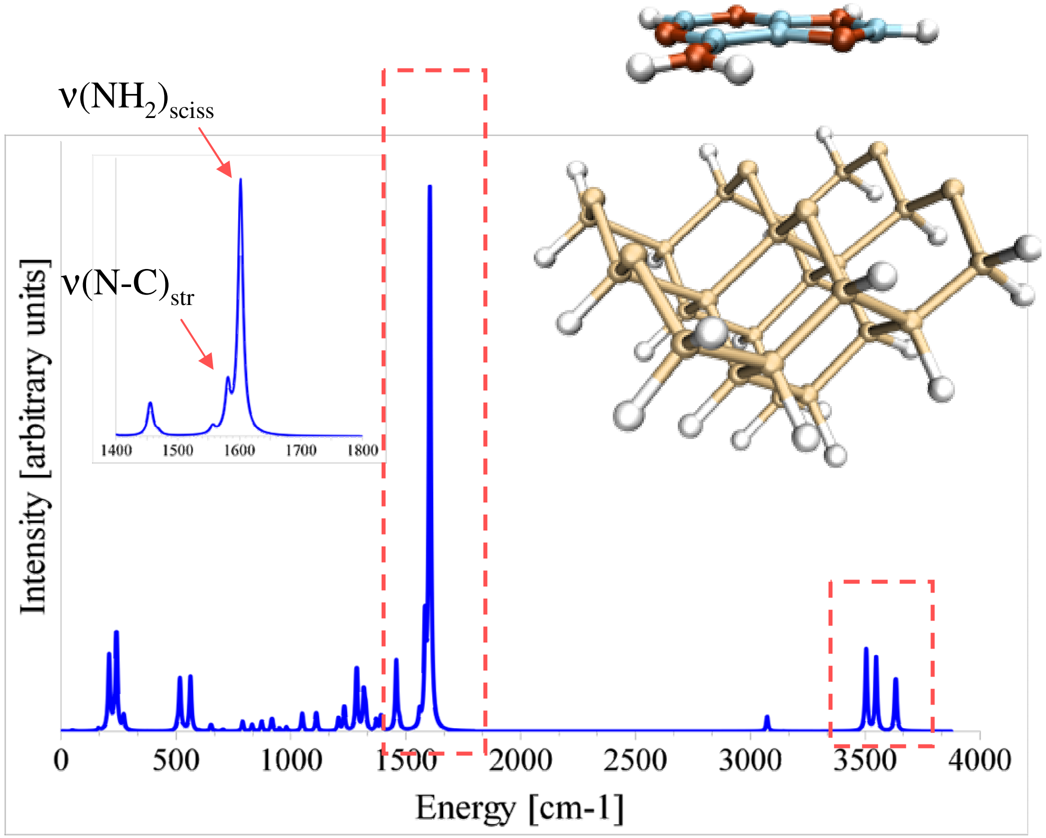
cm^{-1}	B3LYP	B3LYP-D	B3LYP-DM	LC-ωPBE0	M05-2X	M06-2X	B97-D
Max. (-) Dev.	-22	-26	-26	-10	-147	-88	-108
Max. (+) Dev.	19	19	17	137	76	157	10
MUE	6	9	8	48	29	28	41

From **DFT** approaches which correctly describe **dispersion** interaction in adenine dimer only **B3LYP-D/DM** yield anharmonic frequencies with **agreement** to experimental data.

1. M. Biczysko, P. Panek, V. Barone Chem. Phys. Lett. 475, 105 (2009)

Anharmonic corrections

Perturbative anharmonic corrections in ground state[1]:
adenine [2,3], adenine@Si.



Reduced anharmonicity:
Adenine@Si(100): ONIOM B3LYP/6-311++G(2df,2pd) +UFF,
5 of 195 normal modes

mode	adenine	adenine@Si$_{28}$	shift
$\nu(NH_2)_{asym}$	**3539**	**3541**	**+2**
$\nu(N\text{-}H)_{str}$	**3497**	**3491**	**-6**
$\nu(NH_2)_{sym}$	**3432**	**3441**	**+9**
$\nu(NH_2)_{sciss}$	**1616**	**1636**	**+20**
$\nu(N\text{-}C)_{str}$	**1591**	**1597**	**+6**

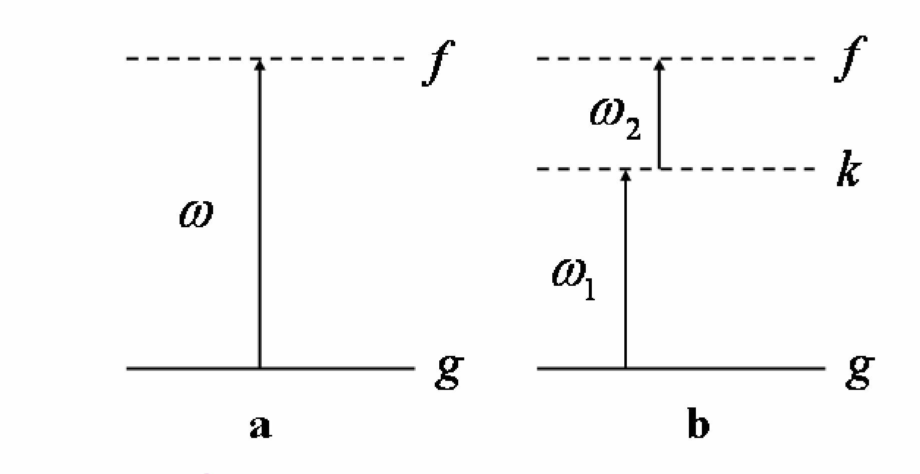
Possibility of reduced dimensionality computation: **5 most intense** bands of adenine and their shift upon absorbtion on Si$_{28}$ cluster.

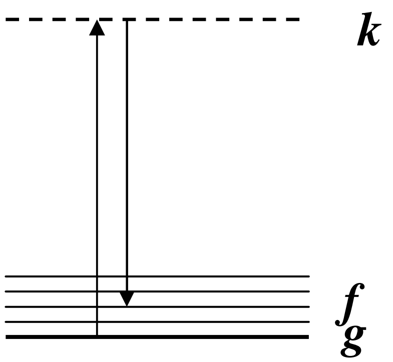
1. V. Barone J. Chem. Phys. 122 (2005). 014108,
2. W. Zierkiewicz, L. Komorowski, D. Michalska, J.Cěrny, P. Hobza, J. Phys. Chem. B 112 (2008) 16734
3. M. Biczysko, P. Panek, V. Barone, Chem. Phys. Lett. 475, 105 (2009)

Computational spectroscopy with G09

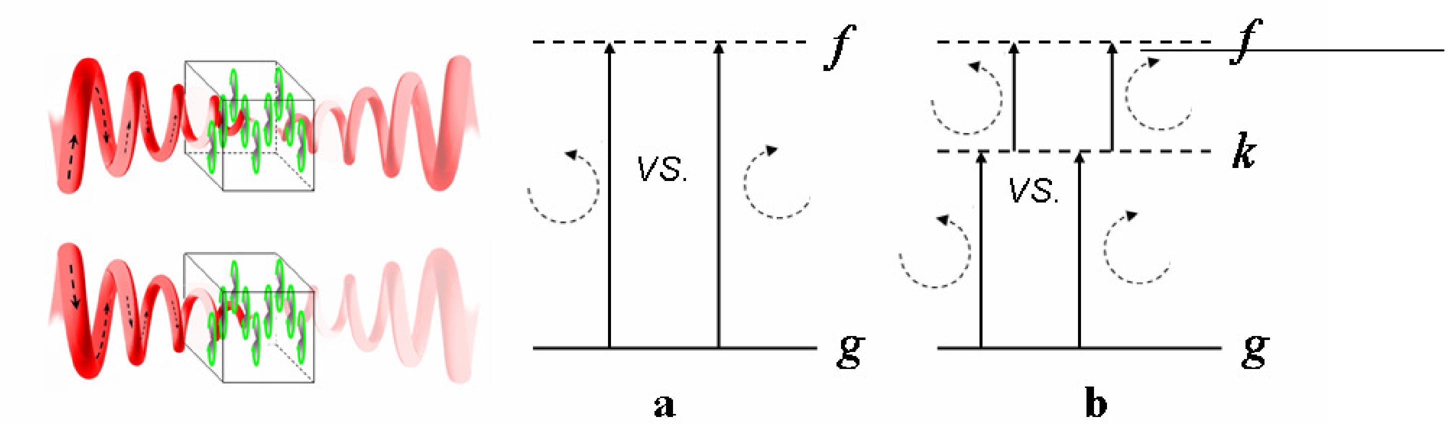
- ☐ A fully **integrated** method in a well-known, general-purpose quantum mechanical computational package, GAUSSIAN: highly **accurate** calculations from internal data, possibility to combine with **all tools** available within package
- ☐**Easy-to-use** with high possibilities of **adjustments** for special cases
- ☐**Fast** and reliable results for medium-to-large systems
- ☐Integrated **analysis** of the most important transition lines
- ☐Scalable to the study of **large systems**.

Circular dichroism, Multi-photon Spectroscopy + Temperature effects


f
ω
g
a
f
ω_2
k
ω_1
g
b



OPA **TPA** **RR**


f
vs.
g
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ECD **TPCD**

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