Simulation of accurate vibrationally resolved electronic spectra: the integrated time-dependent/time-independent approach

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SCUOLA NORMALE SUPERIORE

DREAMS

National Research Council of Italy

Outline

Computational spectroscopy: challenges and perspectives

Challenges

- Accurate results, comparable to experiment
- Good reproduction of experimental conditions
- Efficient to work on medium-size systems

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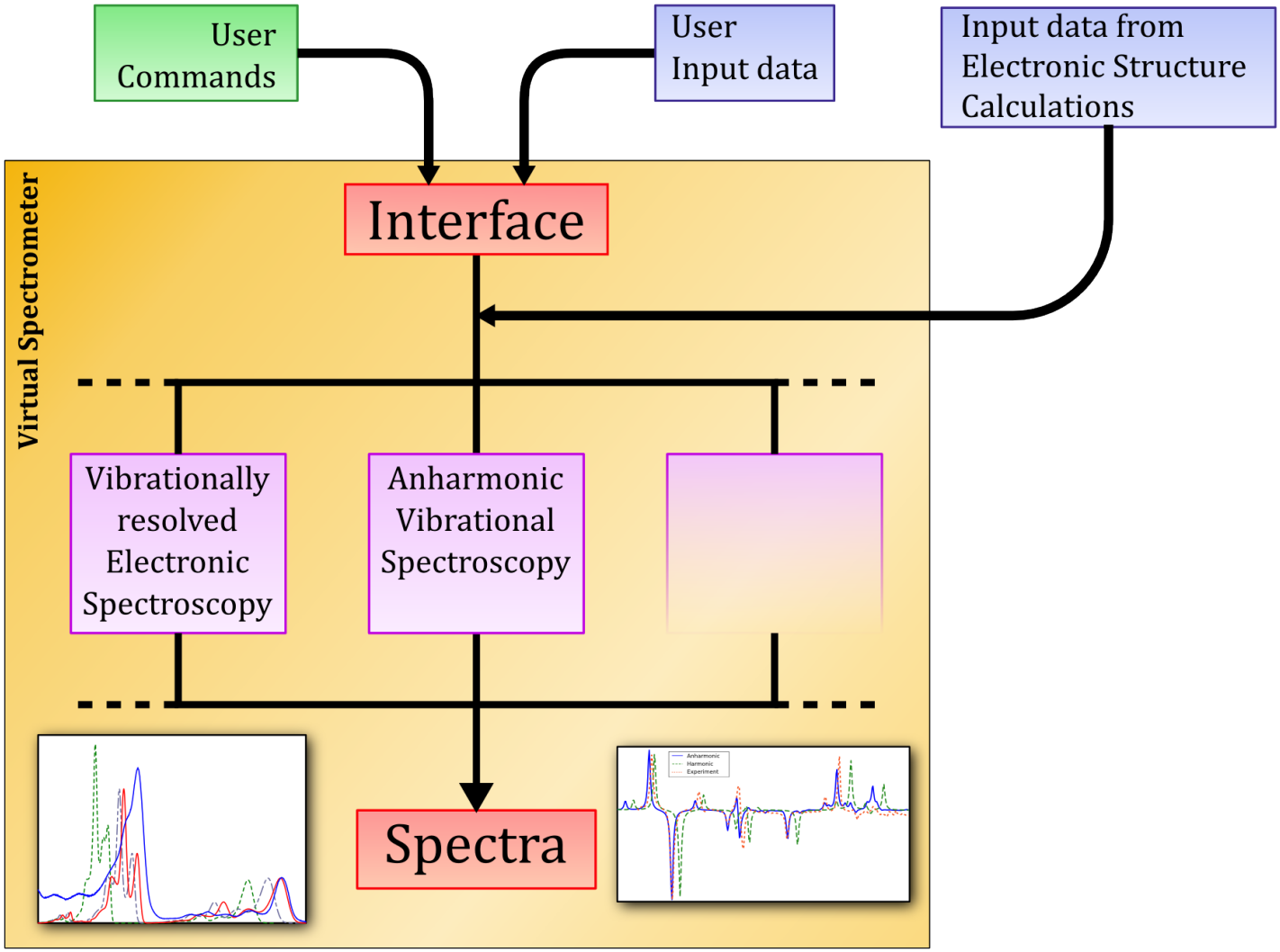
- Cost-efficient model, able to work on medium- to large-size systems
- Usable as a black-box procedure

Virtual spectrometer[1]



[1] VB, AB, MB, JB, C. Cappelli and F. Lipparini, PCCP, 2012, 14, 12404

A generalized formulation

A general formulation of vibronic spectroscopy

- **one-photon absorption** and **one-photon emission**
- **electronic circular dichroism** and **circularly polarized luminescence**

Generalized sum-over-states formula

$$I = \alpha\omega^{\beta} \sum_{i,f} \rho_{\gamma} \mathbf{d}_{A,if} \cdot \mathbf{d}^{*}_{B,if} \delta\left(\omega_{if} - \omega\right)$$

OPA	$I = \epsilon$	$\alpha = \frac{10\pi N_a}{3\epsilon_0 \ln(10)\hbar c}$	$\beta = 1$	$\gamma = i$	$\mathbf{d}_{A,if} = \mathbf{d}_{B,if} = \boldsymbol{\mu}_{if}$
OPE	$I = \frac{I_{em}}{N_i}$	$\alpha = \frac{2}{3\epsilon_0 c^3}$	$\beta = 4$	$\gamma = f$	$\boldsymbol{d}_{A,if} = \mathbf{d}_{B,if} = \boldsymbol{\mu}_{if}$
ECD	$I = \Delta\epsilon$	$\alpha = \frac{40\pi N_a}{3\epsilon_0 \ln(10)\hbar c^2}$	$\beta = 1$	$\gamma = i$	$\mathbf{d}_{A,if} = \boldsymbol{\mu}_{if}$ $\mathbf{d}_{B,if} = \Im(\mathbf{m}_{if})$
CPL	$I = \frac{\Delta I_{em}}{N}$	$\alpha = \frac{8N_a}{3\epsilon_0 c^4}$	$\beta = 4$	$\gamma = i$	$\mathbf{d}_{A,if} = \boldsymbol{\mu}_{if}$ $\mathbf{d}_{B,if} = \Im(\mathbf{m}_{if})$

Resonance-Raman spectroscopy

Basic features

- **Raman effect**: **inelastic** diffusion of light $\longrightarrow$ frequency scattered light $\neq$ incident light (ω_{inc})
- **Resonance-Raman**: incident light corresponds to an electronic transition
- scattered intensity $\longleftrightarrow$ polarizability tensor $\boldsymbol{\alpha}^{if}$

Kramers-Heisenberg-Dirac formula

$$\alpha^{if}_{\rho\sigma} = \frac{1}{\hbar}\sum_{m\neq i,f}\frac{\langle\Psi_f|\boldsymbol{\mu}(\rho)|\Psi_m\rangle\langle\Psi_m|\boldsymbol{\mu}(\sigma)|\Psi_i\rangle}{\omega_{im}+\omega_{\text{inc}}+i\gamma_m}+\frac{1}{\hbar}\sum_{m\neq i,f}\frac{\overbrace{\langle\Psi_f|\boldsymbol{\mu}(\rho)|\Psi_m\rangle}^{\mathbf{d}_{A,if}(\rho)}\overbrace{\langle\Psi_m|\boldsymbol{\mu}(\sigma)|\Psi_i\rangle}^{\mathbf{d}^*_{B,if}(\sigma)}}{\omega_{im}-\omega_{\text{inc}}-i\gamma_m}$$

- γ_m damping factor, related to the lifetime of the excited state. Extracted from the OPA spectrum
- ω_I: set with respect to the theoretical value to be meaningful

Definition of the main approximations

Goal: calculation of $\mathbf{d}_{X,if} = \langle \overline{\Psi} | \mathbf{d}_X | \overline{\overline{\Psi}} \rangle$

- Born-Oppenheimer approximation, Eckart conditions, harmonic oscillator model for both the PES $\longrightarrow \langle \overline{\Psi} | \mathbf{d} | \overline{\overline{\Psi}} \rangle = \langle \overline{\chi} | \mathbf{d}^e_{if} | \overline{\overline{\chi}} \rangle$
- **Duschinsky transformation** between the two sets of normal modes.

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

  - **J**: **Duschinsky matrix**
  - **K**: **shift vector**

- zeroth (**Franck-Condon**) and first-order (**Herzberg-Teller**) Taylor expansion of the transition dipole moment

$$\mathbf{d}^e_{if}(\mathbf{Q}) \approx \mathbf{d}^e_{if}(\mathbf{Q}_{eq}) + \sum_{k=1}^{N} \left(\frac{\partial \mathbf{d}^e_{if}}{\partial Q_k} \right)_{eq} Q_k$$

The TD/TI approach

- **TI**: sum over all the final states must be explicitly calculated. Each transition is treated independently.
- **TD**: initial state wavepacket propagated over the excited-state PES. Spectrum calculated numerically as a Fourier-transform of the dipole moment autocorrelation function.

Time-dependent

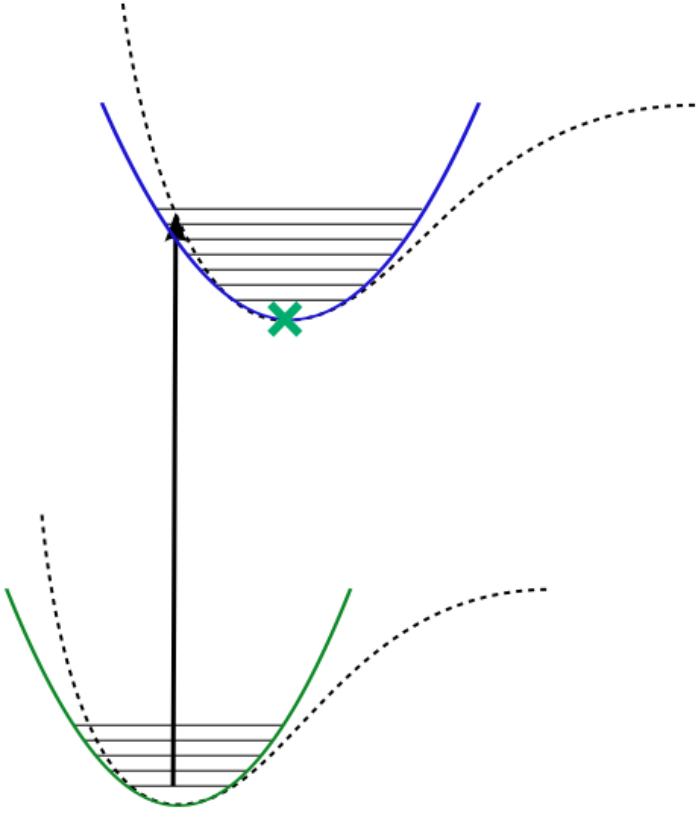
- automatic inclusion of all the final states
- computational cost independent of the temperature

Time-independent

- possibility of band-assignment
- numerical stability

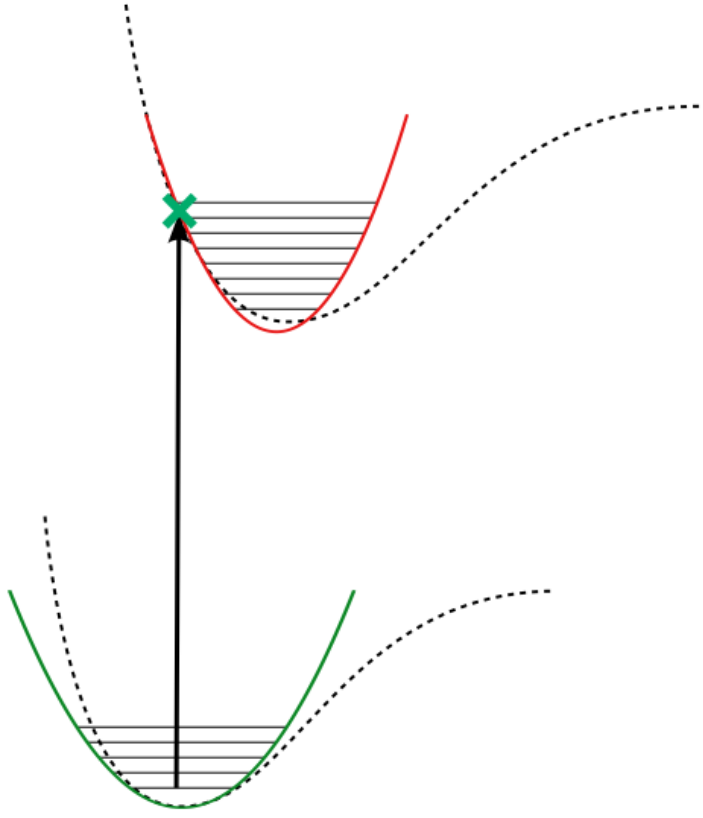
Requirements for vibronic calculations

Adiabatic Hessian



- **IS**: eq. geom, Hessian (ω)
- **FS**: eq. geom, Hessian (ω)

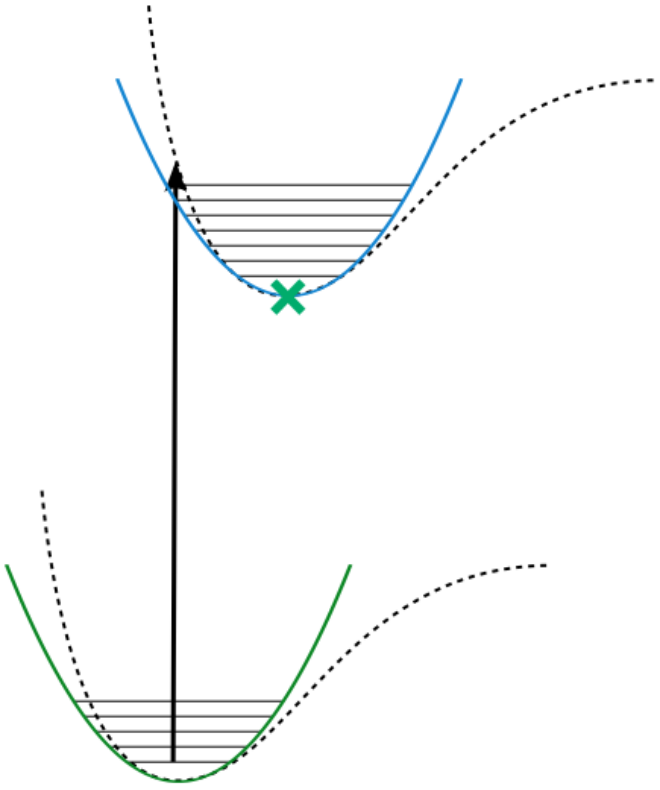
Vertical Hessian



- **IS**: eq. geom, Hessian (ω)
- **FS**: gradient, Hessian

Requirements for vibronic calculations

Adiabatic Shift



- **IS**: eq. geom, Hessian (ω)
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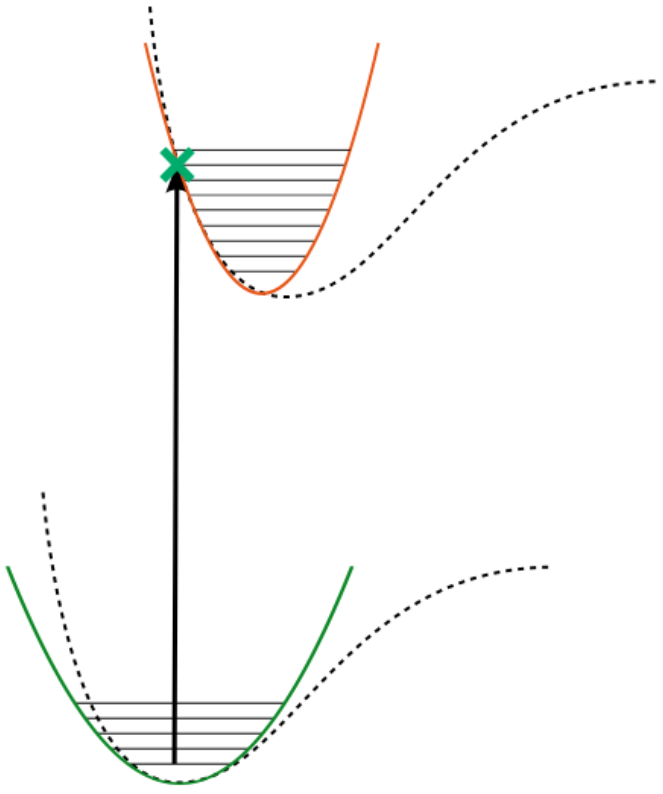
Vertical Gradient



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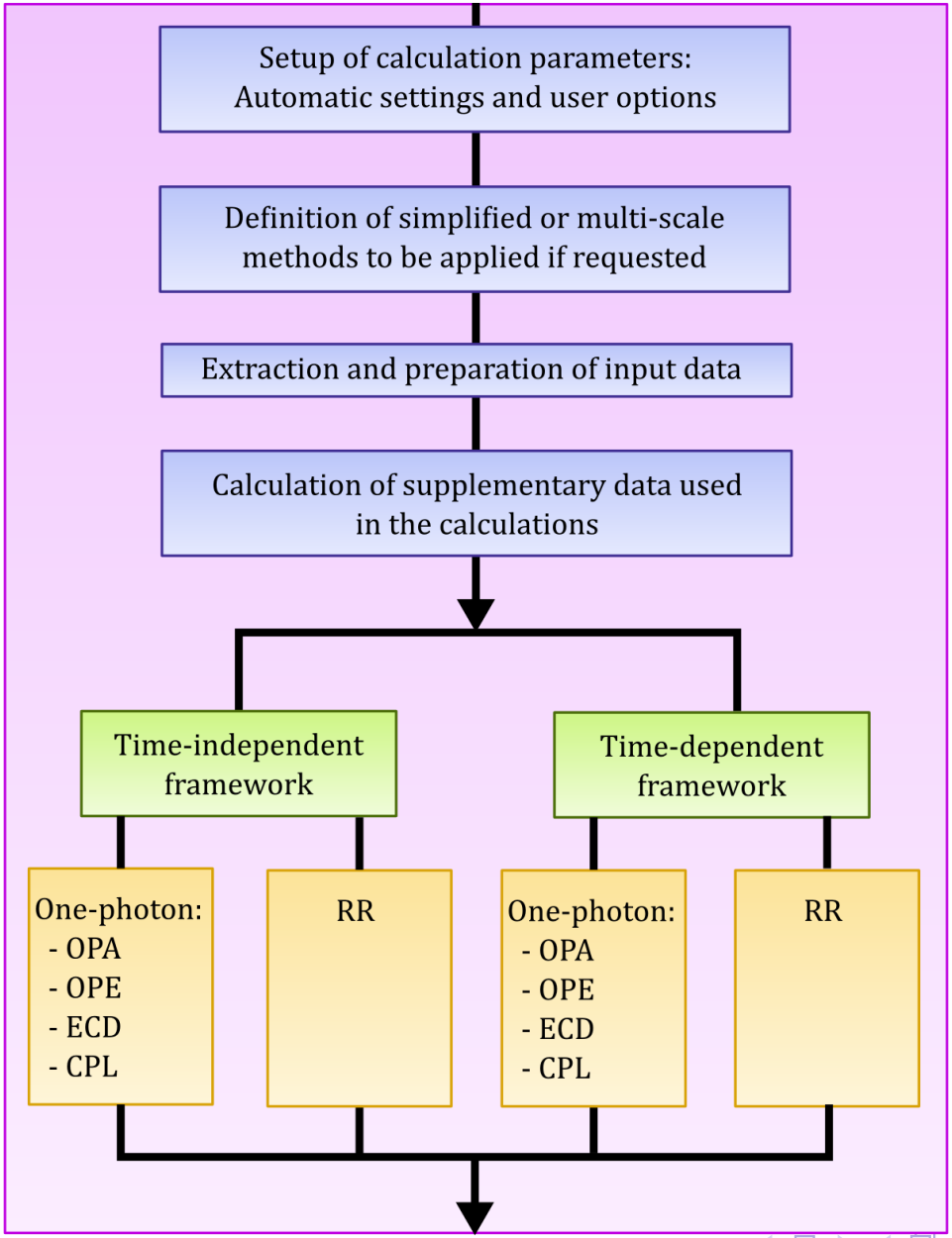
The implemented procedure (vibronic module)

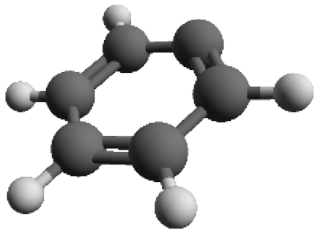


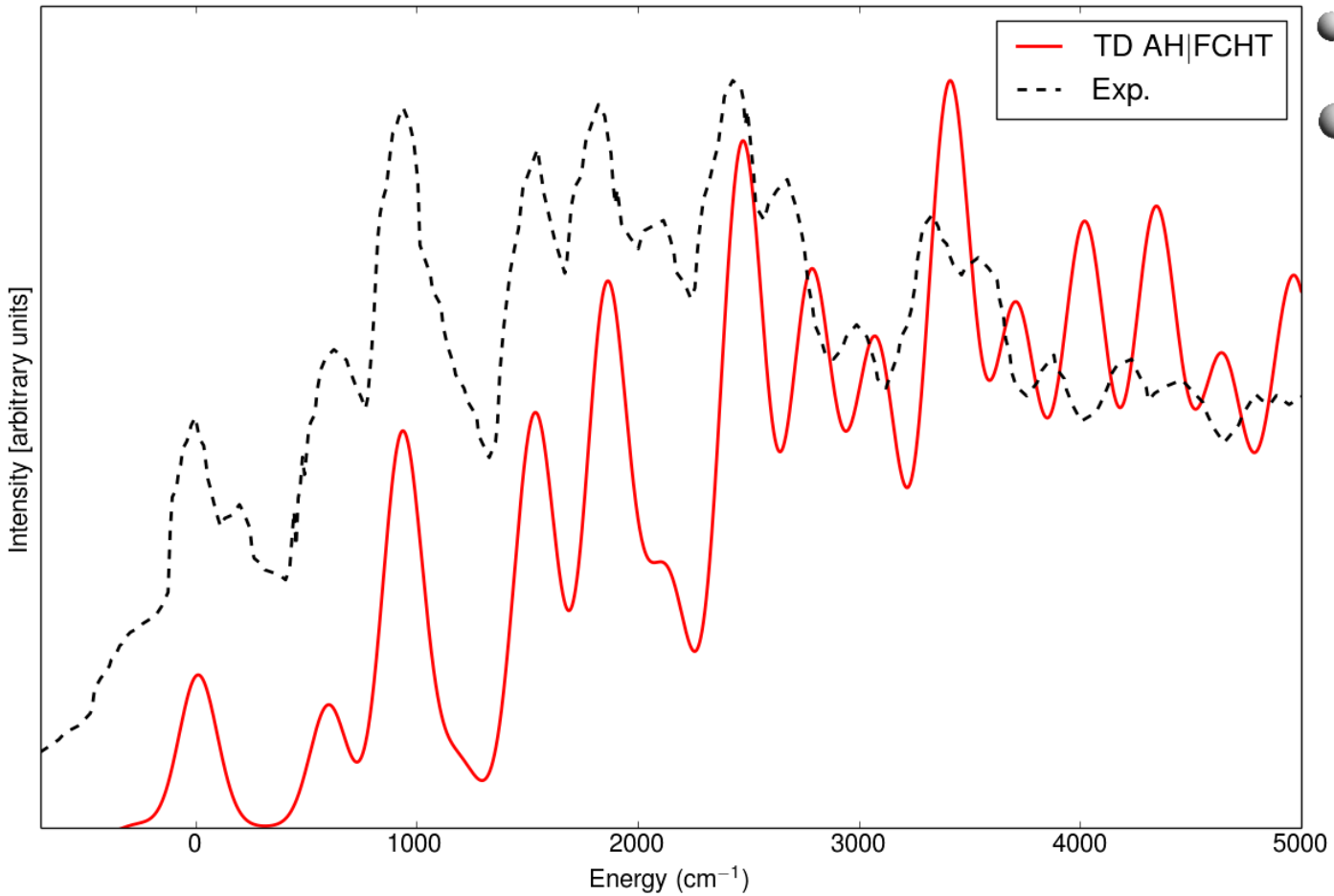
OPA spectrum of phenyl radical: $A^2B_1 \longleftarrow \widetilde{X}^2A_1$

Method: DFT/TD-DFT, B3LYP/SNSD

Parameters: T=10^{-9} s, 2^{24} step, AH|FCHT, Gau. HWHM=100 cm^{-1}

Experimental: J.G. Radziszewski, Chem. Phys. Lett., 1999, 301, 565





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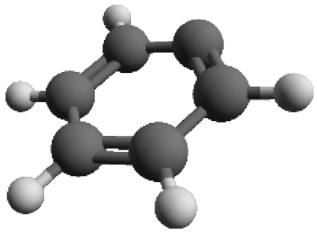

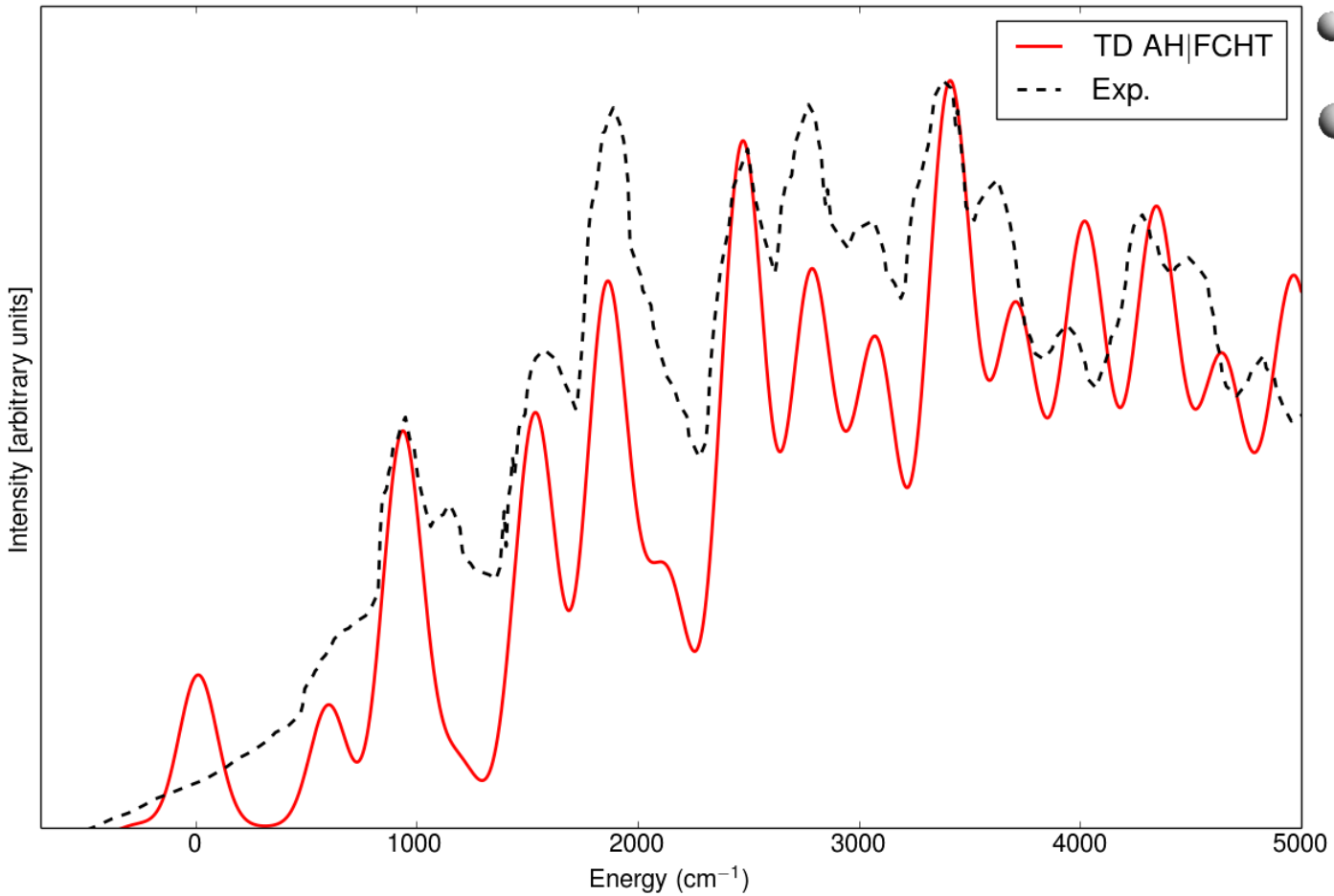

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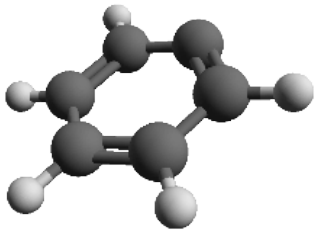

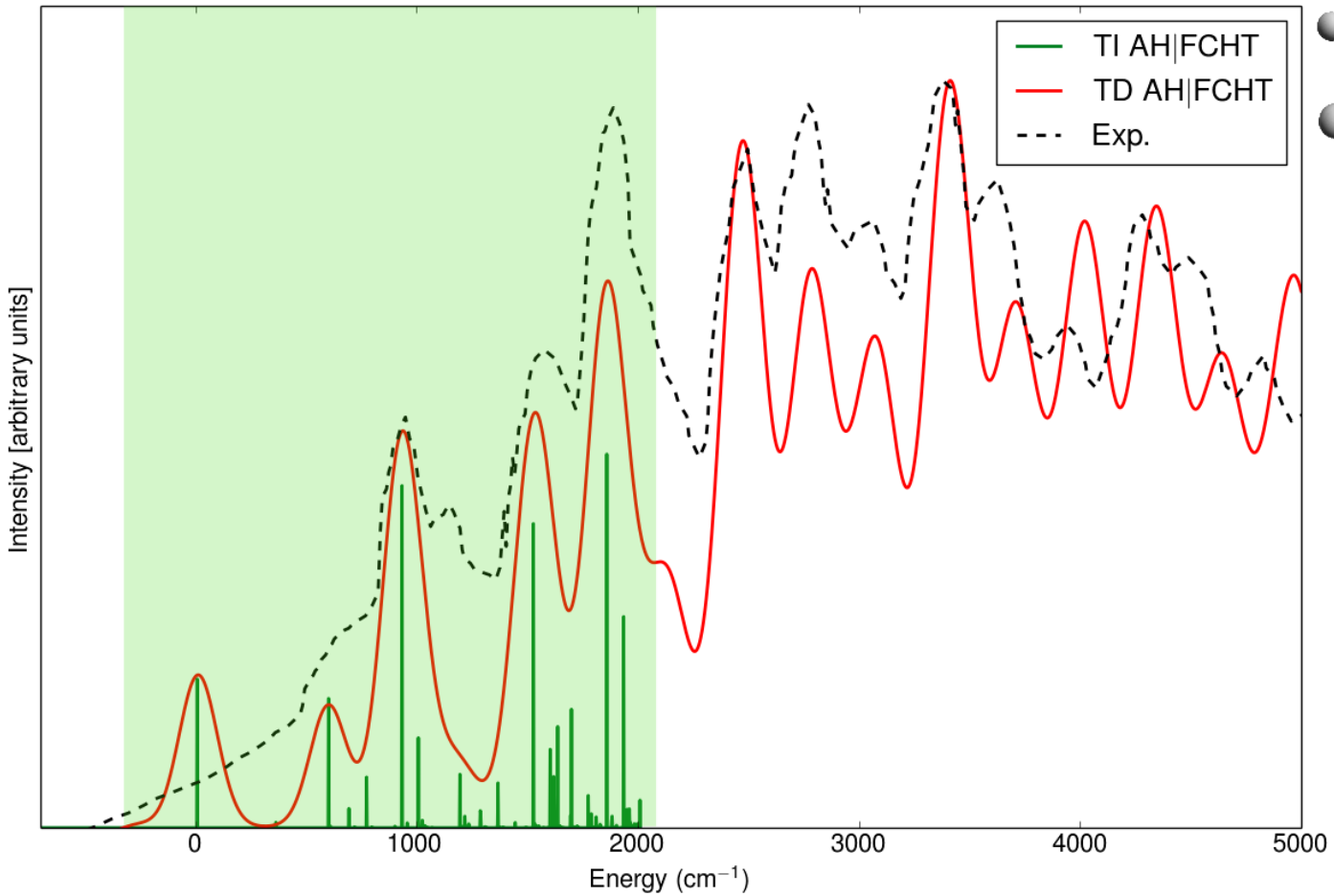

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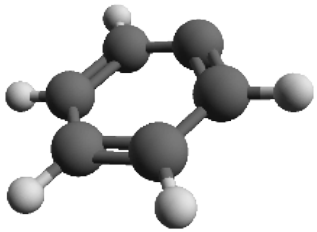
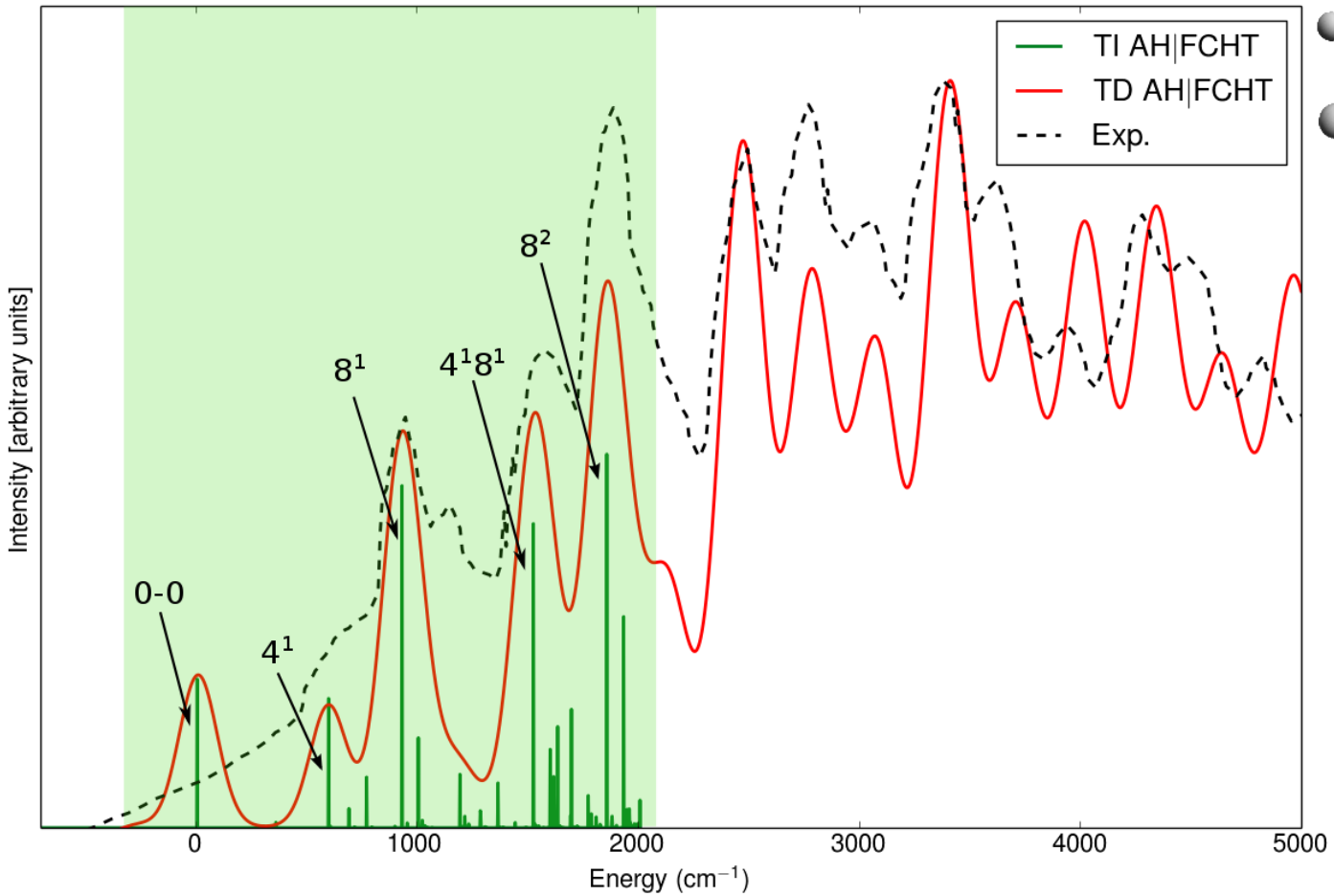
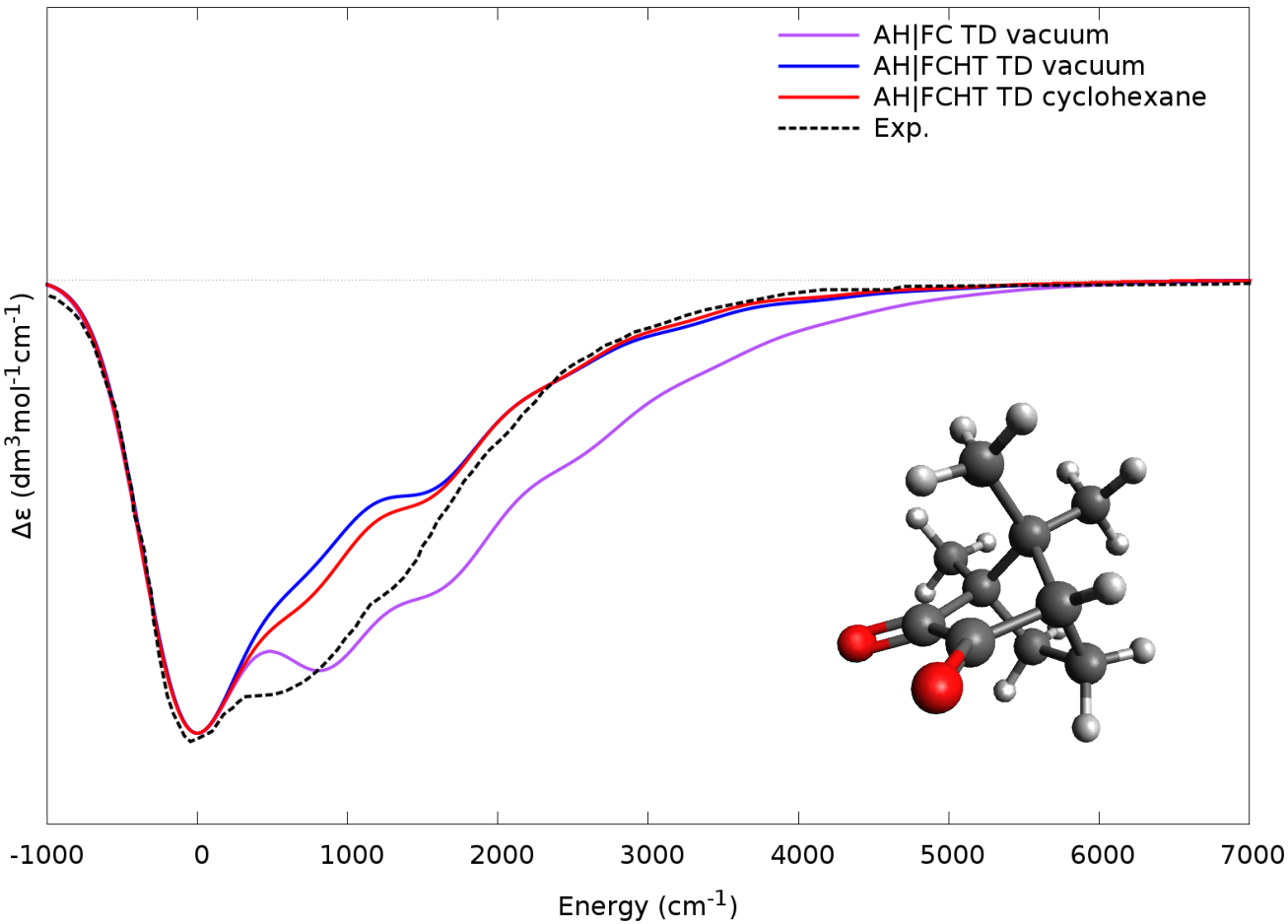




ECD spectrum of (1R)-camphorquinone: $S_1 \longleftarrow S_0$

Method: DFT/TD-DFT, B3LYP/SNSD, IEF-PCM

Experimental: G. Longhi *et al.*, Chirality, 2013, 25, 589



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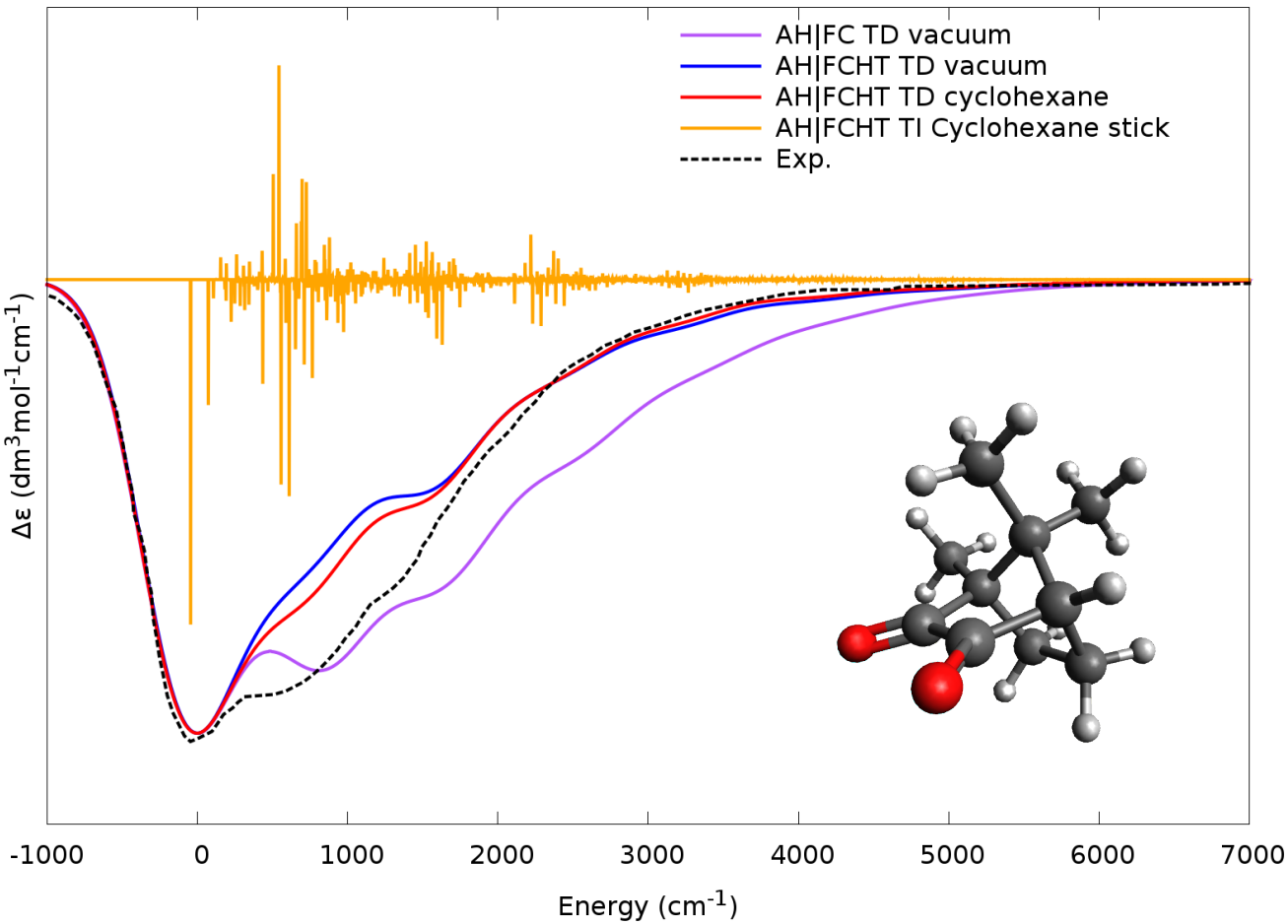

OPA spectrum of coumarin: $S_1 \longleftarrow S_0$

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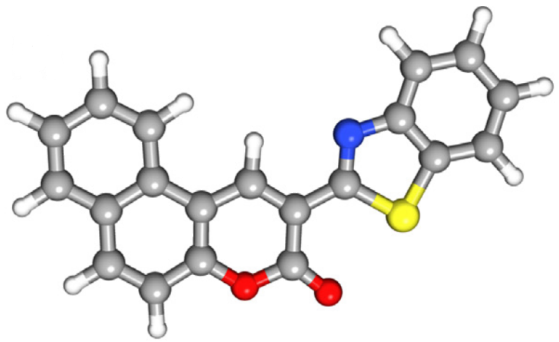
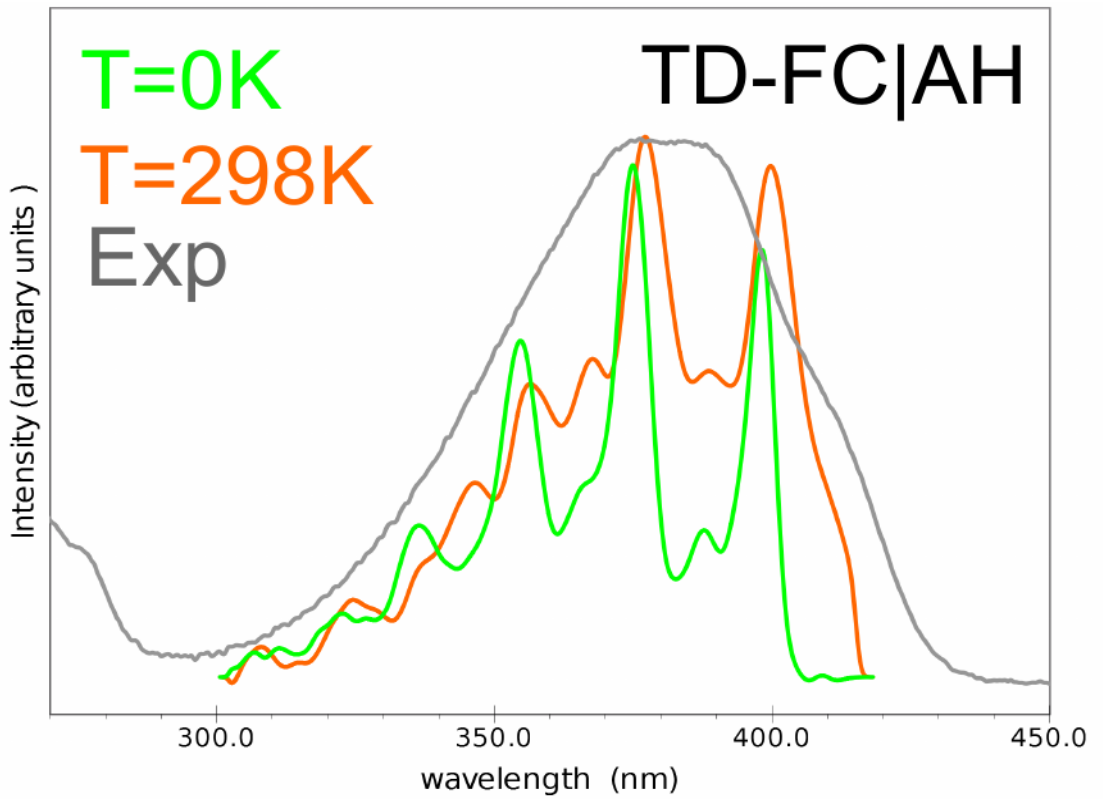
Experimental: G. Signore *et al.*, JACS, 2010, 132, 1276





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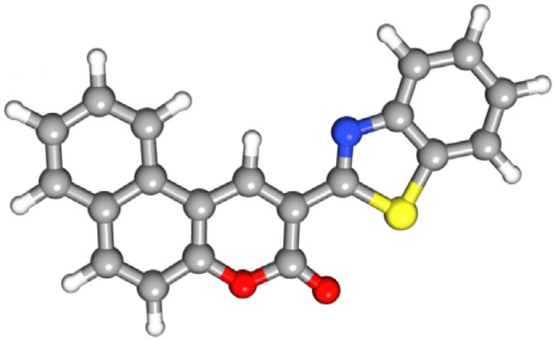
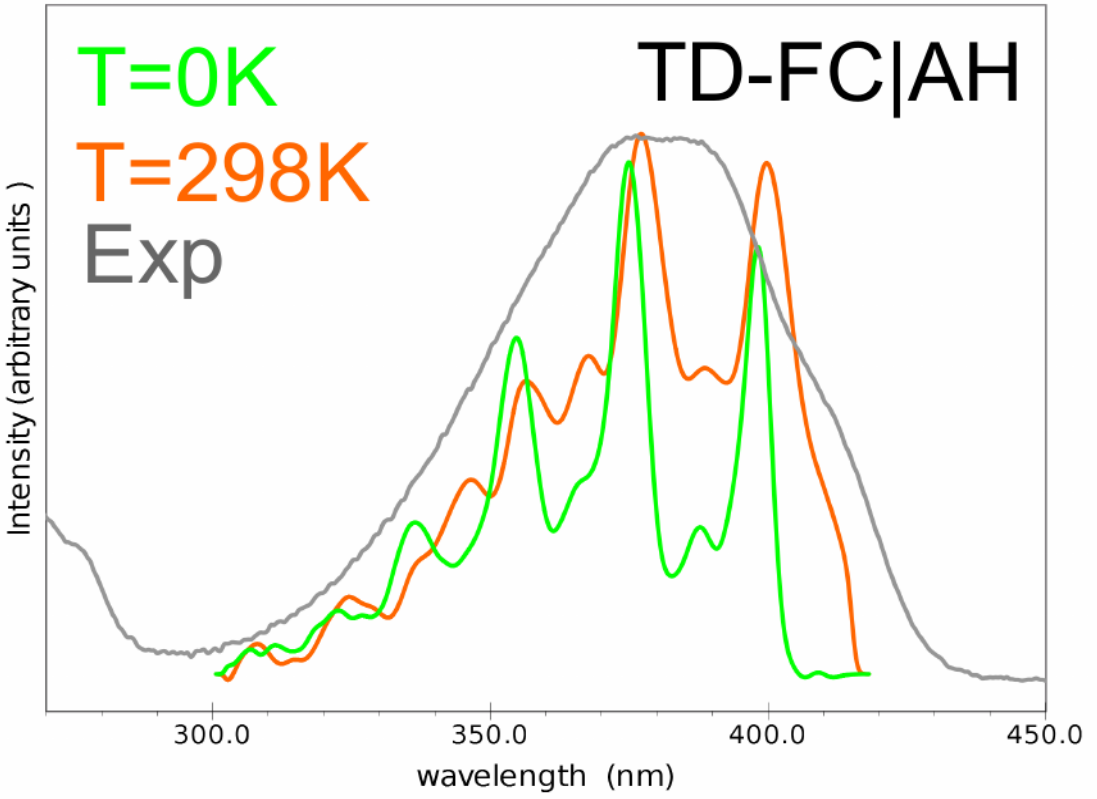




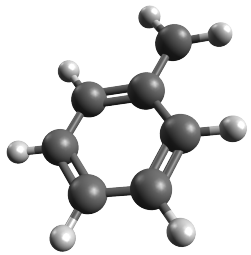
Vibronic effects important even for low-resolution spectra

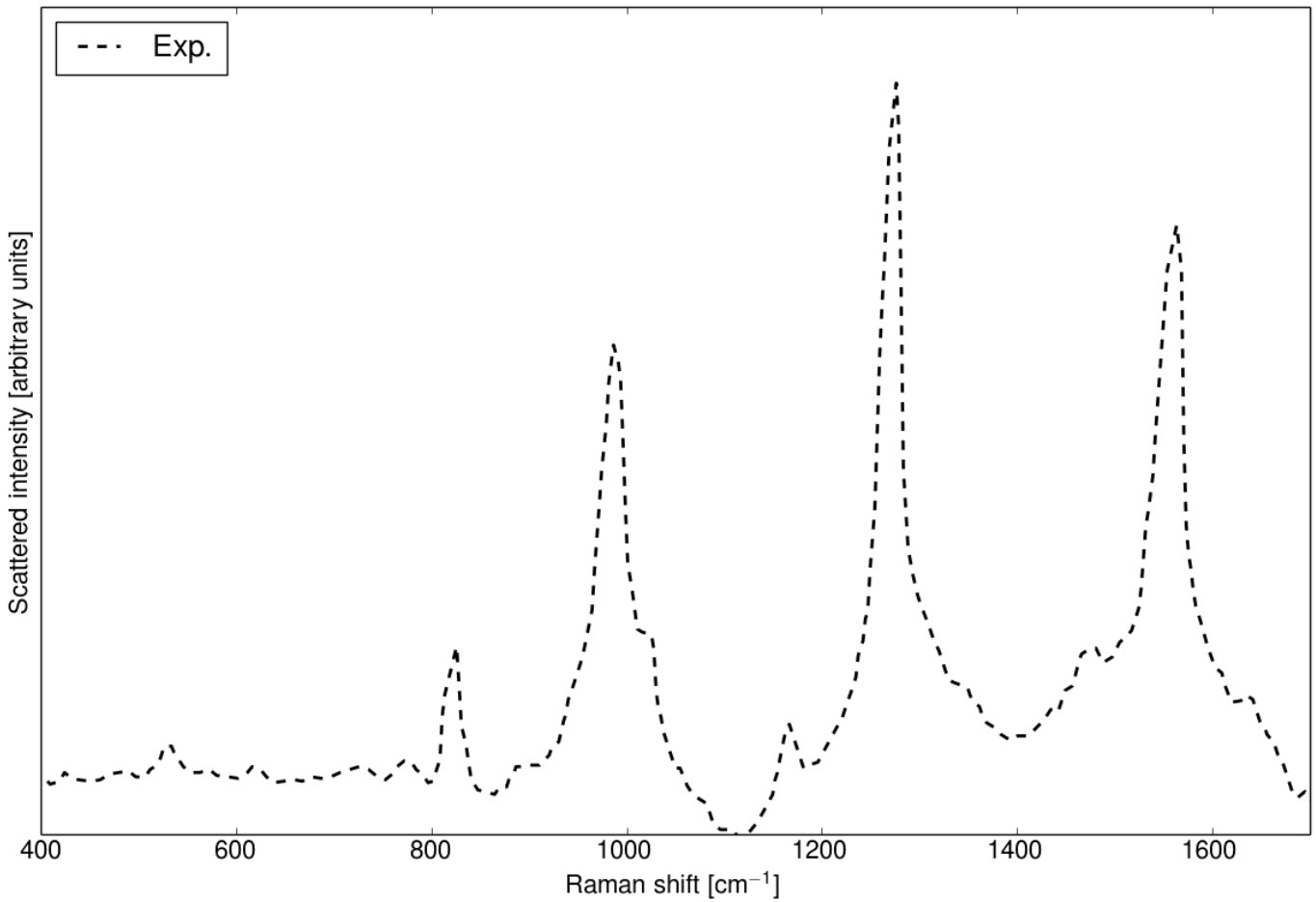
RR spectrum of benzyl radical

Method: DFT/TD-DFT, B3LYP/cc-pVTZ

Parameters: T=10^{-12} s, 2^{12} steps, Lor. HWHM=20 cm^{-1}, $\omega_{inc} = 320nm$ (D_3)

Experimental: F. Langkilde *et al.*, JCP, 1994, 100, 3503





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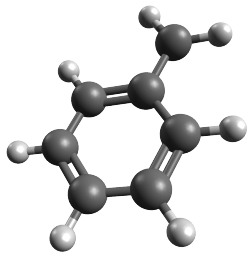

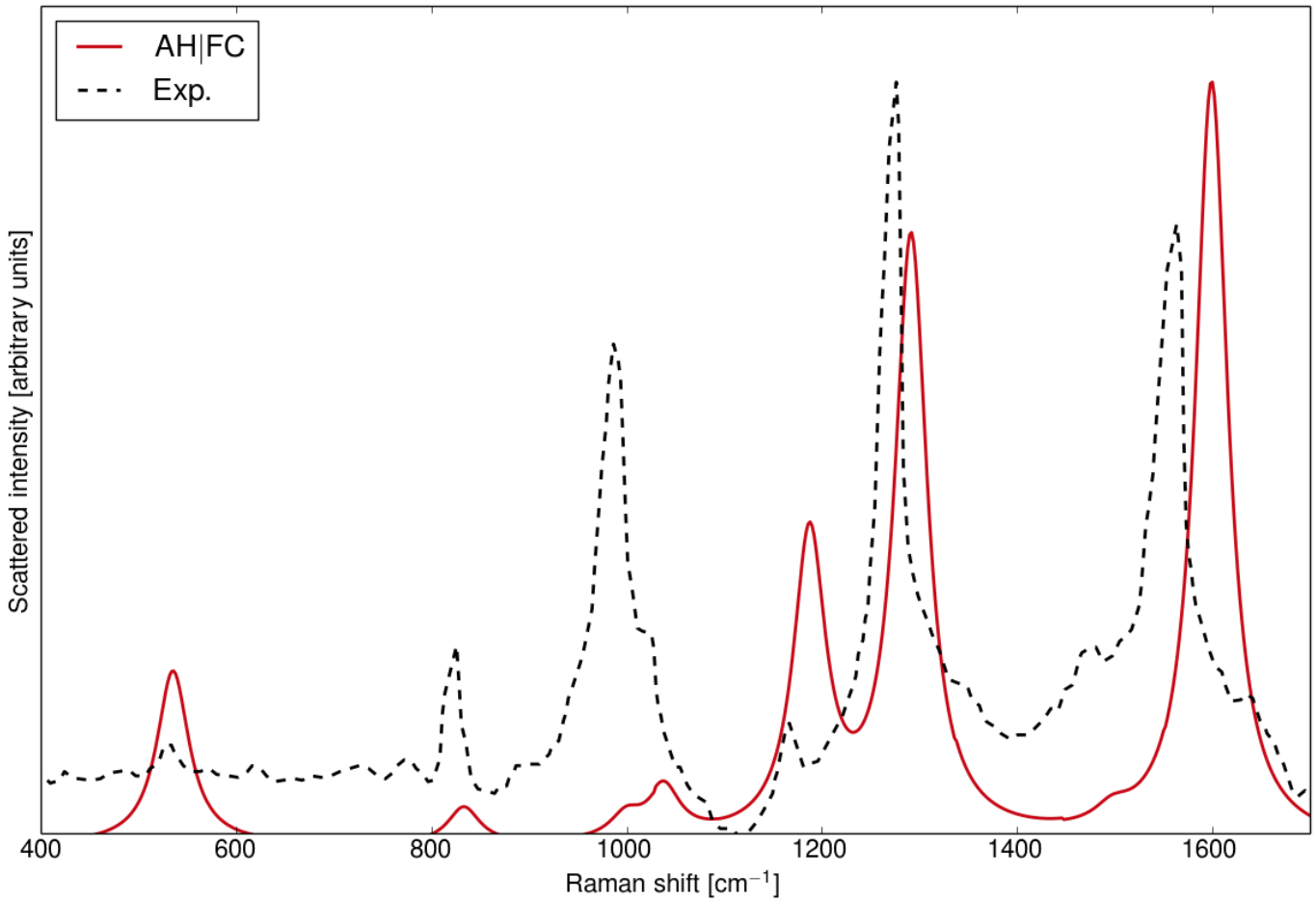

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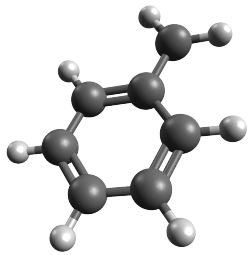

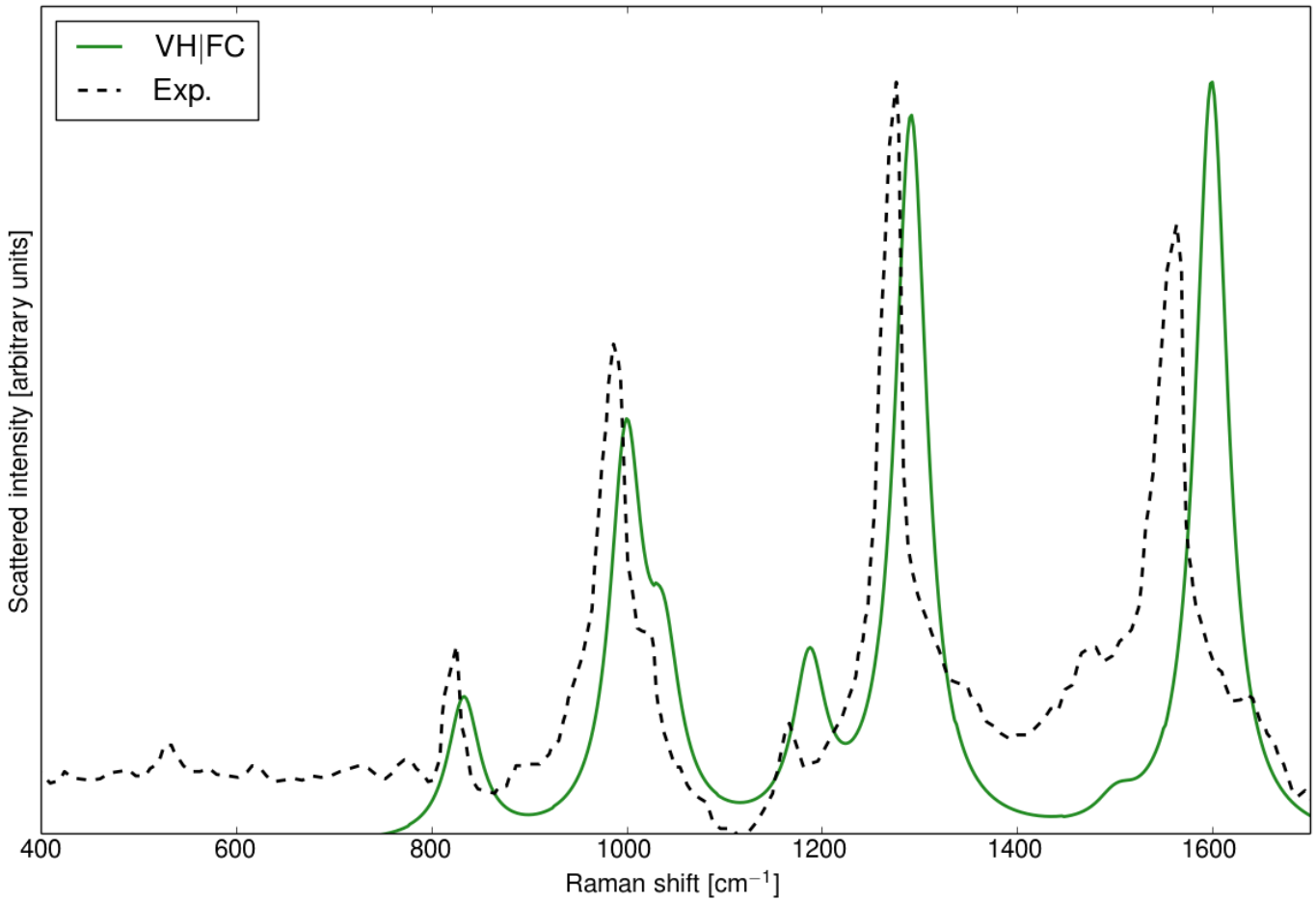

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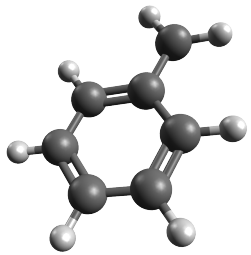

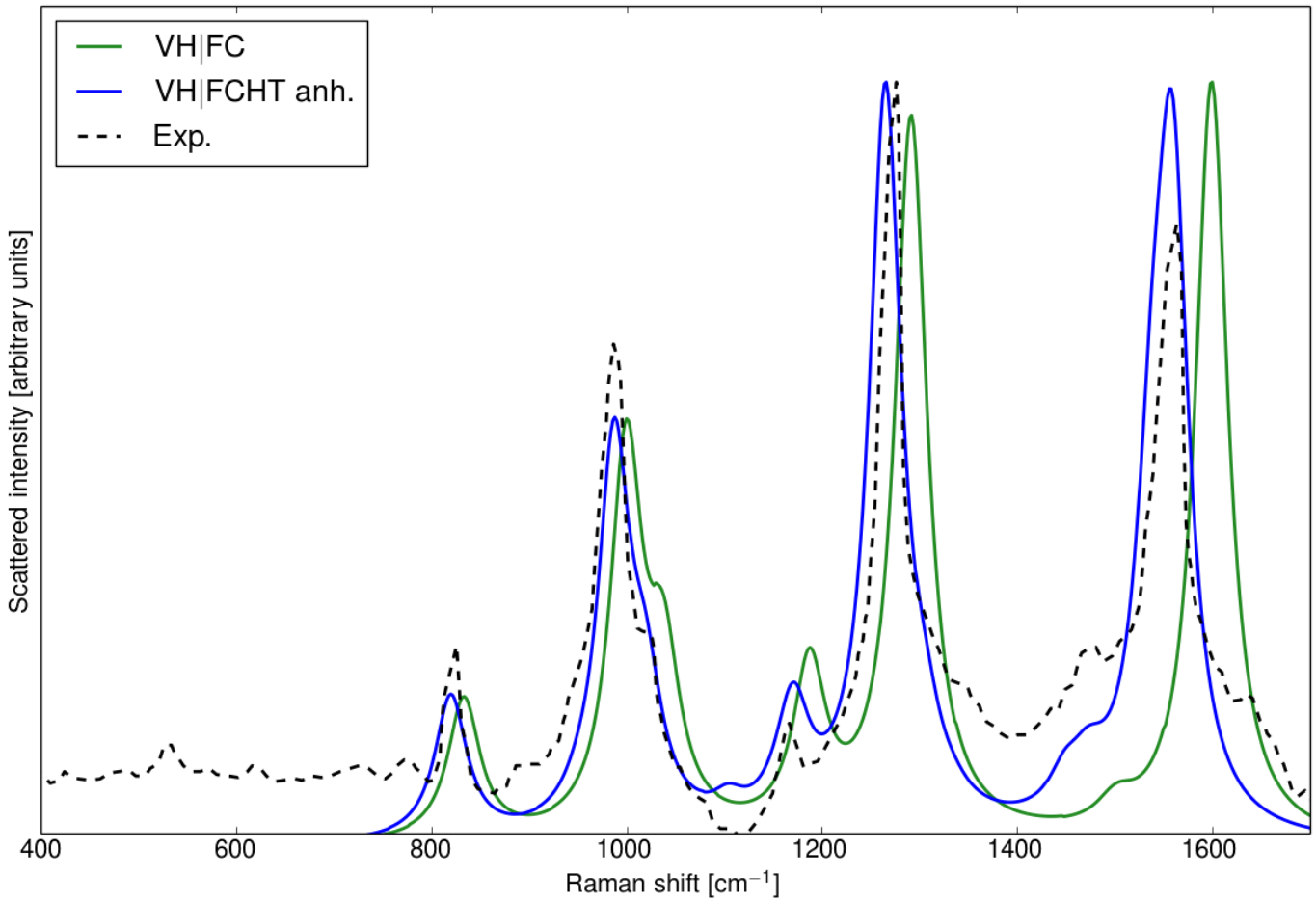

Conclusions and perspectives

Conlusions

- integrated TD/TI procedure to support extensive analysis of experimental spectra of medium-to- large molecular systems
- use of accurate models with extension of multiple effects (vibration, solvent, anharmonicity, temperature...) necessary for accurate simulation
- model designed in a general way to facilitate future extensions
- all models available within a single, easy-to-use and reliable procedure.

Future works

- extension of the framework to internal coordinate system
- application of the procedure to inorganic molecules
- practical applications to virtual screening to select efficient cromophores for technological purposes (solar cells)

Thank you for your attention

General formulation for OP:

- VB, AB, JB, Chirality, 2014, DOI: 10.1002/chir.22325
- JB, MB, F. Santoro, VB, JCTC, 2010, 6, 1256

Resonance Raman:

- VB, AB, JB, J. Chem. Phys., 2014, submitted
- F. Egidi, JB, C. Cappelli, VB, JCTC, 2014, 10, 346

TD framework:

- VB, AB, JB, J. Chem. Phys., 2014, submitted
- AB, JB, VB, JCTC, 2013, 9, 4097

Examples:

- Coumarin: VB, MB, JB, Luciano Carta, Alfonso Pedone, Comp. and Theo. Chem., 2014, 1037, 35
- Phenyl radical: MB, JB, VB, Chem. Phys. Lett, 2009, 471, 143