



## Vibrational energy levels

- The second-order vibrational perturbation theory (VPT2)**

- Expansion of the potential energy operator  $\hat{V}(q)$ :

$$\hat{V}(q) \approx \frac{1}{2} \sum_i \omega_i q_i^2 + \frac{1}{6} \sum_{ijk} k_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} k_{ijkl} q_i q_j q_k q_l$$

- Inclusion of a kinetic contribution arising from the vibrational angular momentum  $j_\alpha$ :

$$\sum_\alpha B_e^\alpha j_\alpha$$

- Improved accuracy at a reasonable computational cost**

- However, possible presence of singularities due to Fermi resonances
- (Type 1:  $\omega_i \approx 2\omega_j$ , Type 2:  $\omega_i \approx \omega_j + \omega_k$ ) Ex:  $\frac{k_{ijk}^2}{16(\omega_i - \omega_j - \omega_k)}$



## Treatment of singularities in energy levels calculations

- Identification of Fermi resonances**

- Near-null denominators  $\Rightarrow$  large contributions from resonant terms
- Evaluation criteria:
  - Threshold on  $\Delta\omega$ . However, the value of the numerator is ignored
  - Martin criteria: both numerator and denominator taken into account

$$\Delta_{ij} = \frac{k_{ij}^4}{256(\omega_i - 2\omega_j)^3} \quad \Delta_{jk} = \frac{k_{jk}^4}{64(\omega_i - \omega_j - \omega_k)^3}$$

- Singularity correction: DVPT2 and GVPT2<sup>1</sup>**

- Deperturbed VPT2: Near-resonant terms are removed
- Generalized VPT2:
  - Near-resonant terms are removed (same as DVPT2)
  - Removed terms are treated variationally
- However, both DVPT2 and GVPT2 results depend on the accuracy of the resonance criteria.

1. V. Barone, J. Chem. Phys. 122, 014108, 2005



## Treatment of singularities: “resonance-criteria free”

- Degeneracy-corrected PT2 (DCPT2)<sup>1</sup>**

- All terms are replaced by non-resonant terms, following the scheme:

$$\frac{S k^2}{2\epsilon} \rightarrow S(\sqrt{\epsilon^2 + k^2} - \epsilon) \quad \epsilon = \left| \frac{\Delta\omega}{2} \right|$$

**Pros:** No parameter used, calculations devoid of singularities

**Con:** Transformation is ill-suited for  $k \sim \epsilon \gg 1$

- HDCPT2: Hybrid VPT2-DCPT2<sup>2</sup>**

$$f_{\text{HDCPT2}} = \Lambda f_{\text{VPT2}} + (1 - \Lambda) f_{\text{DCPT2}}$$

$$\Lambda = \frac{\tanh \left( \alpha \left[ \sqrt{k^2 \epsilon^2} - \beta \right] \right) + 1}{2}$$

1. K.M. Kuhler, D.G. Truhlar, A.D. Isaacson, J. Chem. Phys. 104, 4664, 1996

2. J. Bloino, M. Biczysko, V. Barone, JCTC 8, 1015 (2012)



## Transition intensities

- Anharmonic vibrational IR, VCD and Raman spectra**

- IR: Molar extinction coefficient,  $\epsilon(\tilde{\nu}_0)$
- VCD: Difference in molar extinction coefficient,  $\Delta\epsilon(\tilde{\nu}_0)$
- Raman: Raman scattering  $\partial\sigma(\tilde{\nu}_0)/\partial\Omega$

$$\epsilon(\tilde{\nu}_0) = \frac{8\pi^3 N_A \tilde{\nu}_0}{3000 \ln(10) hc (4\pi e_0)} \sum_o \rho_o \sum_e D_{oe} \delta(\varepsilon_e - \varepsilon_o - \tilde{\nu}_0)$$

$$\Delta\epsilon(\tilde{\nu}_0) = \frac{32\pi^3 N_A \tilde{\nu}_0}{3000 hc^2 \ln(10)} \sum_o \rho_o \sum_e R_{oe} \delta(\varepsilon_e - \varepsilon_o - \tilde{\nu}_0)$$

$$\frac{\partial\sigma(\tilde{\nu}_0)}{\partial\Omega} = \frac{\hbar}{8\pi^2 c} \sum_o \rho_o \sum_e \frac{(\tilde{\nu}_0 - (\varepsilon_e - \varepsilon_o))^4 S_{oe}}{45(\varepsilon_e - \varepsilon_o) \left[ 1 - \exp(-\frac{hc(\varepsilon_e - \varepsilon_o)}{k_B T}) \right]} \delta(\varepsilon_e - \varepsilon_o - \tilde{\nu}_0)$$

$$\langle P | \chi_o \rangle \approx \frac{\langle \chi_o | P^e | \chi_e \rangle}{\sqrt{\langle \chi_o | \chi_o \rangle \langle \chi_e | \chi_e \rangle}} \quad \text{with} \quad P^e = \langle \phi_o | P^{\text{ele}} + P^{\text{nuc}} | \phi_o \rangle$$

- Both  $\chi$  and  $P^e$  must be treated anharmonically at the VPT2 level



## Vibrational spectroscopy

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## Transition intensities: transition dipole moment

- Generalized formulation for the transition dipole moment:

$$\mathbf{P} = \mathbf{P}^{(0)} + \lambda \mathbf{P}^{(1)} + \lambda^2 \mathbf{P}^{(2)}$$

$$\mathbf{P}^{(0)} = \mathbf{P}_0 + s_0 \sum_i \mathbf{P}_i (\mathbf{a}_i^\dagger + S \mathbf{a}_i)$$

$$\mathbf{P}^{(1)} = s_1 \sum_i \sum_j \mathbf{P}_{ij} \mathbf{q}_j (\mathbf{a}_i^\dagger + S \mathbf{a}_i)$$

$$\mathbf{P}^{(2)} = s_2 \sum_i \sum_j \sum_k \mathbf{P}_{ijk} \mathbf{q}_j \mathbf{q}_k (\mathbf{a}_i^\dagger + S \mathbf{a}_i)$$

- $s_0, s_1, s_2, P^0, P^1, P^{ij}, P^{ijk}$  and  $S$  are property-dependent

P	P <sub>0</sub>	P <sub>i</sub>	P <sub>ji</sub>	P <sub>ki</sub>	s <sub>0</sub>	s <sub>1</sub>	s <sub>2</sub>	S
$\mu$	$\mu_{\text{eq}}$	$\frac{\partial \mu}{\partial q_i}$	$\frac{\partial^2 \mu}{\partial q_i \partial q_j}$	$\frac{\partial^3 \mu}{\partial q_i \partial q_j \partial q_k}$	$1/\sqrt{2}$	$1/2\sqrt{2}$	$1/6\sqrt{2}$	+1
$m$	0	$\mathbf{A}_i$	$\frac{\partial \mathbf{A}_i}{\partial q_j}$	$\frac{\partial^2 \mathbf{A}_i}{\partial q_j \partial q_k}$	$i\hbar/\sqrt{2}$	$i\hbar/\sqrt{2}$	$i\hbar/2\sqrt{2}$	-1
$\alpha$	$\alpha_{\text{eq}}$	$\frac{\partial \alpha}{\partial q_i}$	$\frac{\partial^2 \alpha}{\partial q_i \partial q_j}$	$\frac{\partial^3 \alpha}{\partial q_i \partial q_j \partial q_k}$	$1/\sqrt{2}$	$1/2\sqrt{2}$	$1/6\sqrt{2}$	+1



## Vibrational spectroscopy

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## Transition intensities: transition dipole moment

- Development using the Rayleigh-Schrödinger perturbation theory

$$\begin{aligned} \langle \mathbf{P} \rangle_{o,e} &= \langle \mathbf{P} \rangle_{o,e}^{(0)} + \lambda \langle \mathbf{P} \rangle_{o,e}^{(1)} + \lambda^2 \langle \mathbf{P} \rangle_{o,e}^{(2)} \\ \langle \mathbf{P} \rangle_{o,e}^{(0)} &= \langle \chi_o^{(0)} | \mathbf{P}^{(0)} | \chi_e^{(0)} \rangle \\ \langle \mathbf{P} \rangle_{o,e}^{(1)} &= \langle \chi_o^{(0)} | \mathbf{P}^{(1)} | \chi_e^{(0)} \rangle + \langle \chi_e^{(1)} | \mathbf{P}^{(0)} | \chi_e^{(0)} \rangle + \langle \chi_o^{(0)} | \mathbf{P}^{(0)} | \chi_e^{(1)} \rangle \\ \langle \mathbf{P} \rangle_{o,e}^{(2)} &= \langle \chi_o^{(0)} | \mathbf{P}^{(2)} | \chi_e^{(0)} \rangle + \langle \chi_o^{(2)} | \mathbf{P}^{(0)} | \chi_e^{(0)} \rangle + \langle \chi_o^{(0)} | \mathbf{P}^{(0)} | \chi_e^{(2)} \rangle \\ &\quad + \langle \chi_o^{(1)} | \mathbf{P}^{(1)} | \chi_e^{(0)} \rangle + \langle \chi_o^{(0)} | \mathbf{P}^{(1)} | \chi_e^{(1)} \rangle + \langle \chi_o^{(1)} | \mathbf{P}^{(0)} | \chi_e^{(1)} \rangle \\ &\quad - \frac{\langle \chi_o^{(0)} | \mathbf{P}^{(0)} | \chi_e^{(0)} \rangle}{2} [\langle \chi_e^{(1)} | \chi_e^{(1)} \rangle + \langle \chi_o^{(1)} | \chi_o^{(1)} \rangle] \end{aligned}$$

- Large number of terms

- creation of dedicated, *ad hoc* tools to semi-automatize the treatment and reduce the risk of errors

- Integrals for fundamentals, overtones and combinations bands

- Extensible to other properties

- Fermi resonances can be present, as well as 1-1 resonances!

- Resonance terms removed: DVPT2

1. J. Bloino, V. Barone, J. Chem. Phys. 136, 124108 (2012)



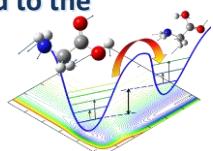
## VPT2 for thermodynamics

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## Thermodynamics beyond harmonic approximation

- Simple perturbation theory applied to the vibrational partition function

$$Q_{\text{vib}} = \frac{e^{-E_0/T}}{\prod_{i=1}^N \left( 1 - e^{-\hbar c_i v_i / T} \right)}$$



- $v_i$ : Wavenumber frequency of the  $i$ -th fundamental band,  
• devoid of singularity at the HDCPT2 level
- $E_0$ : Anharmonic ZPVE,

$$E(\mathbf{v}) = E_0 + \sum_i \omega_i v_i + \sum_{i \leq j} v_i v_j \chi_{ij}, \quad E_0 = \chi_0 + \sum_i \frac{\omega_i}{2} + \sum_{i \leq j} \frac{\chi_{ij}}{4}$$

- Extension to transition state:

- Reaction coordinate  $F$  treated separately from the remaining  $N_R$  modes,  $E_0 = E_0^{NR} + \chi_0^F$

1. J. Bloino, M. Biczysko, V. Barone, JCTC 8, 1015 (2012)



## Vibrational spectroscopy: PES and FF

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## VPT2 for medium-to-large systems

- PES

- polynomial of 4<sup>th</sup> order containing at most three independent normal coordinates

- Vibrational energy levels

$$E_v = \chi_0 + \sum_i a_i \left( v_i + \frac{1}{2} \right) + \sum_i \sum_{j \neq i} \chi_{ij} \left( v_i + \frac{1}{2} \right) \left( v_j + \frac{1}{2} \right)$$

- $\chi_{ij}$  set of anharmonic constants
- simple function of 3rd ( $K_{jk}$ ) and semidiagonal 4th ( $K_{ijj}$ ) energy derivatives with respect to normal modes

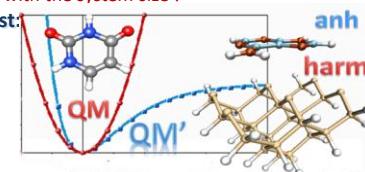
- Energy third and semi-diagonal fourth derivatives are computed numerically<sup>1</sup>

$$K_{ijk} = \frac{K_{jk}(\delta q_i) - K_{jk}(-\delta q_i)}{2\delta q_i} \quad K_{ijj} = \frac{K_{jk}(\delta q_i) + K_{jk}(-\delta q_i) - 2K_{jk}(0)}{\delta q_i^2}$$

- Computational cost grows quickly with the system size !

- Solutions to limit computation cost:

- Hybrid models
- Reduced-dimensionality



1. V. Barone, J. Chem. Phys. 122, 014108 (2005), V.B et al Chem. Phys. Lett., 496, 157-161 (2010)

2. V. B., M. B., J. B., M. Borkowska-Panek, I. Carnimeo, P. Panek, Int. J. Quantum. Chem. 112, 2185 (2012)



## Reduced dimensionality models<sup>1</sup>

- Displacement along selected vibrations**

- set of M normal modes for which anharmonic frequencies will be evaluated
- spectra range of interest, most intense (observed) vibrations, molecular probe etc..

- Anharmonic constants  $\chi_{ij}$**

- index **i** corresponds to an active mode
  - cubic force constants  $K_{ijk}$  where index i is present at least once (i.e.  $K_{ijk}, K_{ijl}, K_{ikl}, K_{ill}$ ) evaluated
  - along with all semi-diagonal quartic force constants  $K_{ijj}$

$$4\hbar c \sqrt{\lambda_i \lambda_j} \chi_{ij} = K_{lljj} - \frac{2K_{ijj}}{4\lambda_i + \lambda_j} - \frac{2K_{ijj}^2}{4\lambda_j - \lambda_i} - \frac{K_{iil}K_{ijj}}{\lambda_i} - \frac{K_{jjj}K_{ijj}}{\lambda_j} \\ + \sum_{\substack{k=1 \\ k \neq j, l}}^N \left[ \frac{2(\lambda_i + \lambda_j - \lambda_k)K_{ijk}^2}{\lambda_i^2 + \lambda_j^2 + \lambda_k^2 - 2(\lambda_i\lambda_j + \lambda_i\lambda_k + \lambda_j\lambda_k)} \right] \frac{K_{ilk}K_{ijk}}{\lambda_k} \quad \boxed{K_{ijk}}$$

- Difference wrt full treatment**

- some limited number cubic force constants (terms including only j and k indices) **not evaluated**
- non-resonant terms (treatment of Fermi resonances not affected)
- important **ONLY** if vibrations **j, k** and **i** are coupled
  - vibrations mainly localized on the same region of a molecular system (e.g. functional group) and with similar frequencies

- Practical recipe to select normal modes to be considered simultaneously**

- nature of the vibrations and energy range

- Reduced dimensionality schemes well-suited to study environment effects**

- adsorption, solute-solvent interactions

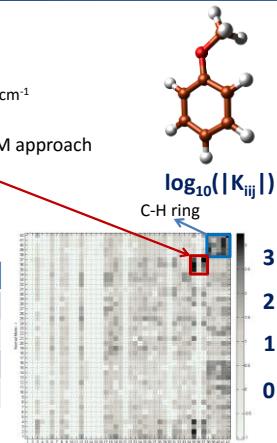
## Reduced GVPT2 scheme: validation

- IR spectra of anisole**

- Full dimensional (All Modes) GVPT2
  - good accuracy
  - MUE (mean unsigned error) wrt experiment 9 cm<sup>-1</sup>

- Reduced (N modes) approach**

- 27 over 42 modes can be computed with 1M approach
- coupled modes, eg. CH<sub>3</sub> stretchings
- graphical representation of couplings
  - absolute value of the cubic force constants  $K_{ijk}$



mode	Exp	1M	3M
$\nu_{\text{CH}_3}$ sym. stretch	2900	2856	2898
$\nu_{\text{CH}_3}$ asym. stretch	2942	2817	2924
$\nu_{\text{CH}_3}$ asym. stretch	3004	2964	2992
MUE (cm <sup>-1</sup> )	<b>56</b>	<b>11</b>	



## Semi-diagonal Quartic Force Field

- PES generation:**

- Energy third and semi-diagonal fourth derivatives are computed numerically

- Basic requirements**

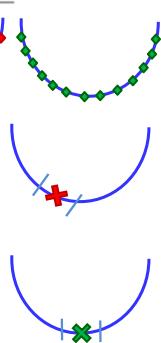
$$K_{ijk} = \frac{K_{jk}(\delta q_i) - K_{jk}(-\delta q_i)}{2\delta q_i}$$

- Tight optimization criteria

- Ultrafine Grid (DFT) + SCF tight

- Example: H<sub>2</sub>CO**

mode	Opt-tight Int-Uf		Opt Int		Opt-tight Int	
	Harm.	$\Delta\text{Anh}$	Harm.	$\Delta\text{Anh}$	Harm.	$\Delta\text{Anh}$
$v_1$	2881.6	-152.7	2881.8	-161.1	2881.0	-152.7
$v_2$	1816.0	-26.3	1816.2	-26.8	1816.0	-26.3
$v_3$	1532.4	-33.0	1532.5	-33.6	1532.5	-33.6
$v_4$	1200.1	-18.0	1200.3	-17.9	1200.3	-18.0
$v_5$	2937.5	<b>-125.3</b>	2937.7	<b>-261.3</b>	2936.8	<b>-124.9</b>
$v_6$	1266.6	-21.3	1266.7	-21.5	1266.7	-21.3



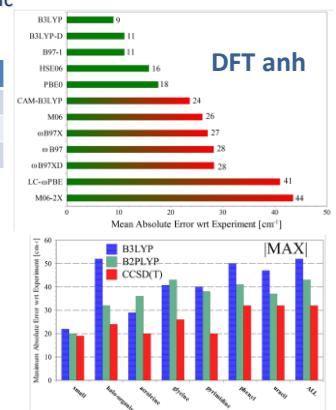
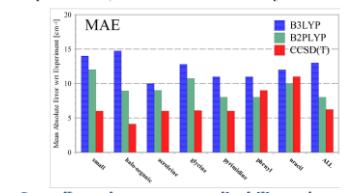
## Vibrational frequencies

- Harmonic frequencies and anharmonic contributions B3LYP vs CCSD(T)

B3LYP	harm	anh	hybrid
MIN	-25	-28	-26
MAX	+108	+142	+39
MUE	30	30	7

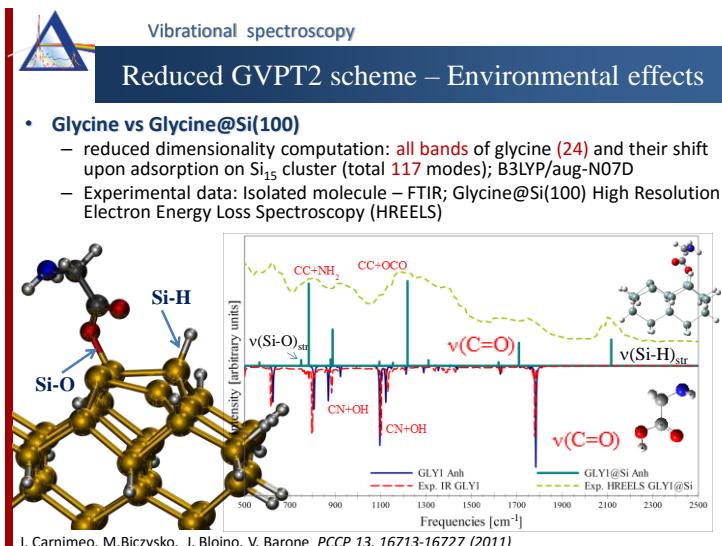
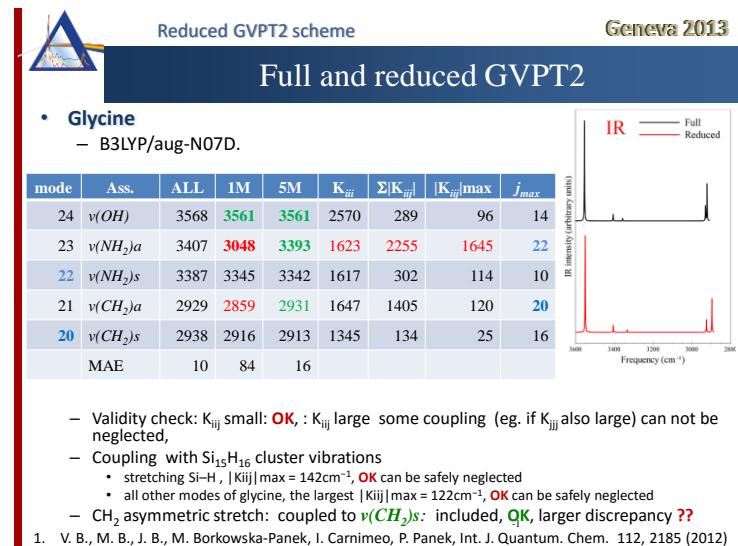
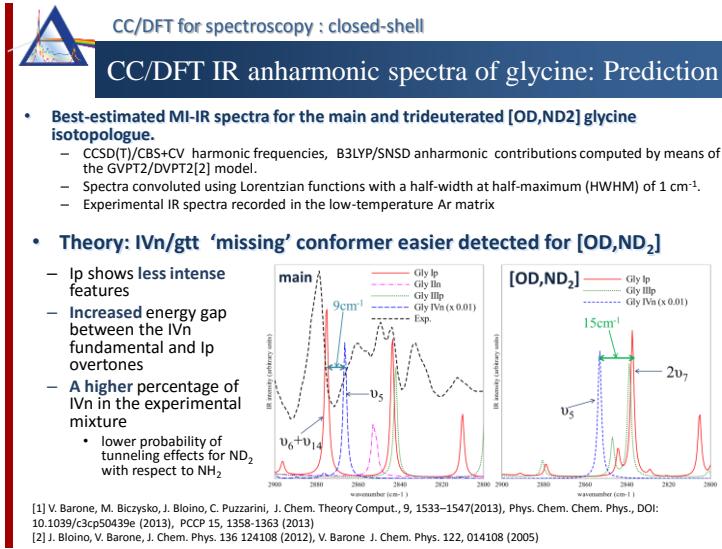
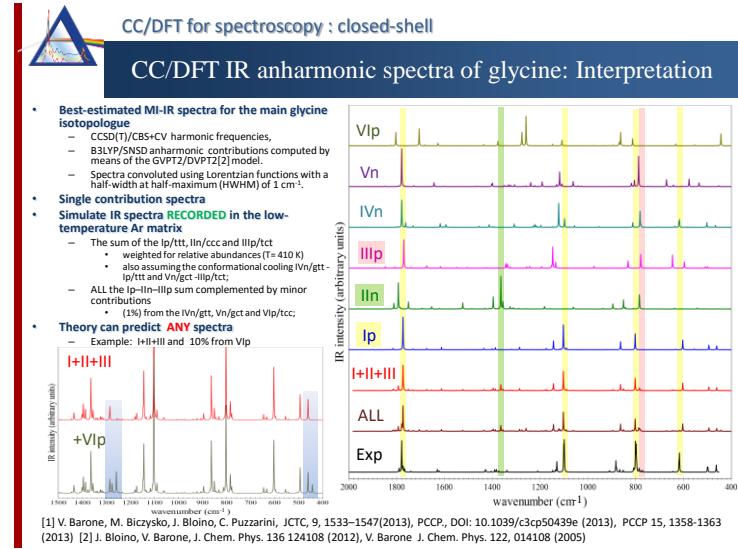
- DFT vs Experiment

- Hybrid CC/DFT models vs Experiment



Overall good accuracy + applicability to larger systems





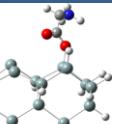
## Reduced GVPT2 scheme

L717

## Vibrational spectra of large systems

## • Glycine@Si(100)

- reduced dimensionality computation: all bands of glycine (24) and their shift upon adsorption on Si<sub>15</sub> cluster (total 117 modes); B3LYP/aug-N07D.



Label	Ass.	Exp.	$\nu$	$K_{ii}$	$\Sigma  K_{ij} $	$ K_{ij} _{\max}$	$j_{\max}$
117	$\nu(NH_2)a$	3460	3419	181	2392	1643	116
116	$\nu(NH_2)s$	3410	3379	1623	470	101	80
115	$\nu(CH_2)a$	3040 ? 2932	2932	1422	1381	934	114
114	$\nu(CH_2)s$	2940	2901	1620	774	398	115
112	$\nu(SiH)$	2115	2110	1124	894	142	107

- Validity check:  $K_{ij}$  small: **OK** ;  $K_{ij}$  large some coupling (eg. if  $K_{ij}$  also large) can not be neglected,
- Coupling with Si<sub>15</sub>H<sub>16</sub> cluster vibrations
  - stretching Si-H,  $|K_{ij}|_{\max} = 142\text{cm}^{-1}$ , **OK** can be safely neglected
  - all other modes of glycine, the largest  $|K_{ij}|_{\max} = 122\text{cm}^{-1}$ , **OK** can be safely neglected
- CH<sub>2</sub> asymmetric stretch: coupled to  $\nu(CH_2)s$ : included, **OK**, larger discrepancy ??

1. V. B., M. B., J. B., M. Borkowska-Panek, I. Carnimeo, P. Panek, Int. J. Quantum. Chem. 112, 2185 (2012)

## Reduced GVPT2 scheme

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## HREELS spectrum of glycine@Si

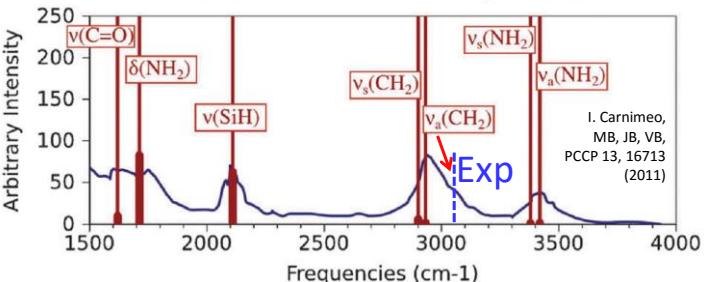
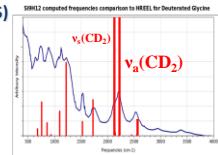
## • High Resolution Electron Energy Loss Spectroscopy (HREELS)

• Glycine@Si<sub>15</sub>H<sub>16</sub>

– Reduced dimensionality GVPT2 + B3LYP/aug-N07D

• CH<sub>2</sub> stretch

- band at 3040 cm<sup>-1</sup> still present at 400 C,
  - where glycine is considered completely desorbed
  - "Experimental" assignment based on harmonic frequencies
  - Reassignment confirmed by the good agreement with spectra of deuterated Glycine

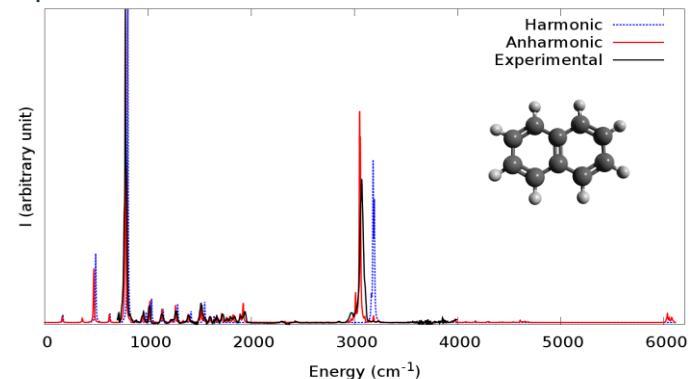


## Vibrational spectra: GVPT2/DVPT2

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## Harmonic vs Anharmonic IR spectra: naphthalene

Computational details: B3LYP/aug-N07D  
Experimental data: source: NIST Database

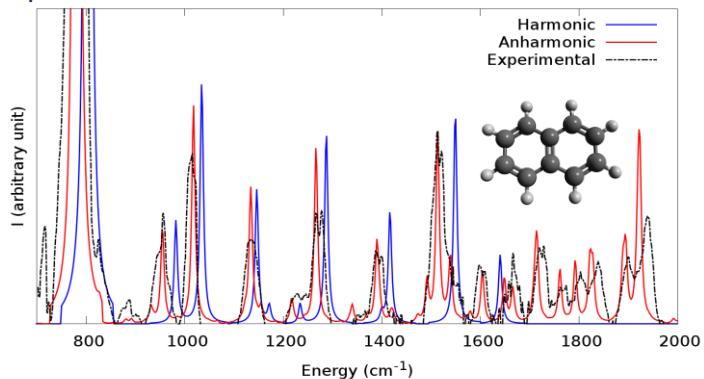


## Vibrational spectra: GVPT2/DVPT2

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## Harmonic vs Anharmonic IR spectra: naphthalene

Computational details: B3LYP/aug-N07D  
Experimental data: source: NIST Database





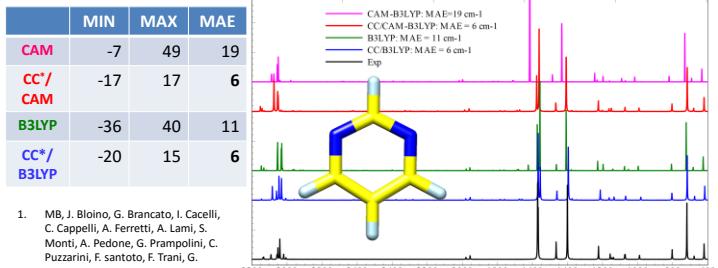
## DFT and Hybrid CC/DFT

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## IR anharmonic spectra : pyrimidine

## • Computed vs Experimental spectra

- Vibrational freq in  $\text{cm}^{-1}$ , Intensities in km/mol, GVPT2/DVPT2, DFT/aug-N07D
- Mean Absolute Error (MAE), and largest negative (MIN) and positive (MAX) deviations with respect to experiment (Ar Matrix, S. Breda *et al.* *J. Mol. Struct.* 786, 193 (2006))



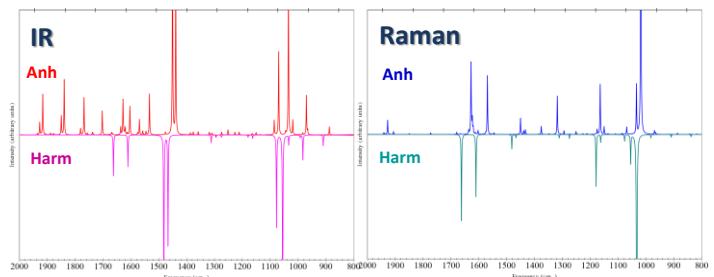
CC = CCSD(T)/VTZ + QZ(MP2/VQZ-MP2/VTZ) + CV(MP2/CVTZ) + aug(MP2/aVTZ-MP2/VTZ)

## CC/DFT for spectroscopy : open-shell

## IR and Raman spectra of phenyl radical

• IR and Raman harmonic and anharmonic spectra  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{D}_5$ 

- CCSD(T)/aug-cc-pVTZ harmonic frequencies,
- B3LYP/SNSD anharmonic contributions computed by the GVPT2/DVPT2[2] model.

[1] V. Barone, M. Biczysko, J. Bloino, F. Egidi, C. Puzzarini, *J. Chem. Phys.* 138, 234303 (2013)[2] J. Bloino, V. Barone, *J. Chem. Phys.* 136 124108 (2012), V. Barone *J. Chem. Phys.* 122, 014108 (2005)

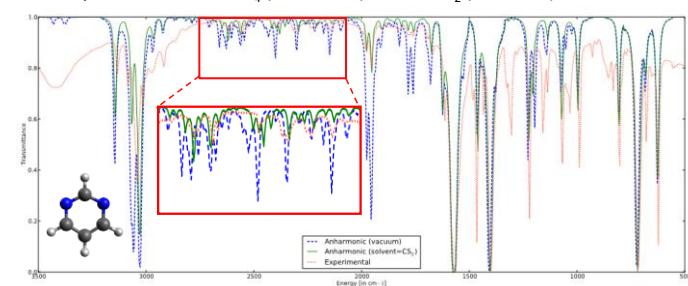
## Vibrational spectra: GVPT2/DVPT2

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## Solvent effects

• Non-equilibrium implicit solvent<sup>1</sup> : Case of pyrimidine

- Non-equilibrium approach simulates the slower reorganization of the solvent molecules with respect to the vibrations.
- Computation: B3LYP/aug-N07D, Broadening: Lorentzian, HWHM=4 $\text{cm}^{-1}$
- Experiment: 10% in  $\text{CCl}_4$  (3800-1370), 10% in  $\text{CS}_2$  (1370-450)



## CC/DFT for spectroscopy : open-shell

## IR spectra of phenyl radical

• CC/DFT IR of  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{D}_5$  [1]

- CCSD(T)/aug-cc-pVTZ harmonic frequencies +IR intensities,
- B3LYP/SNSD anharmonic contributions computed by the GVPT2/DVPT2 [2] model

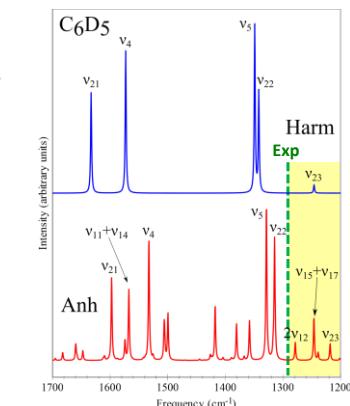
## • Overall accuracy

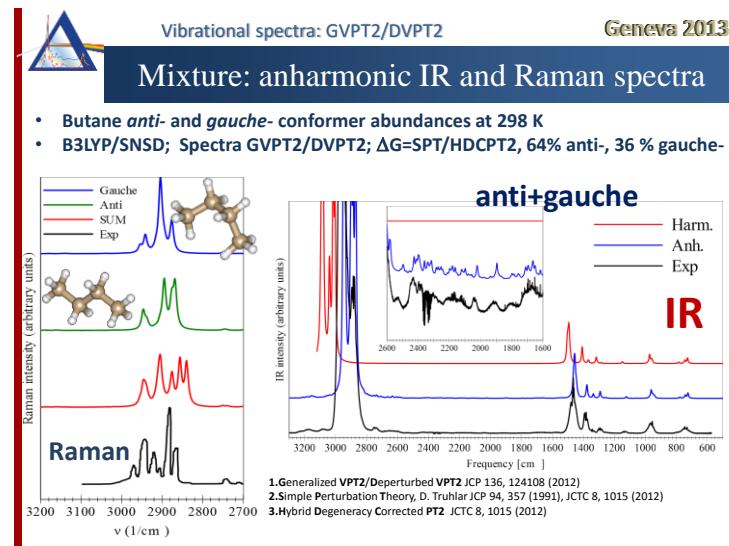
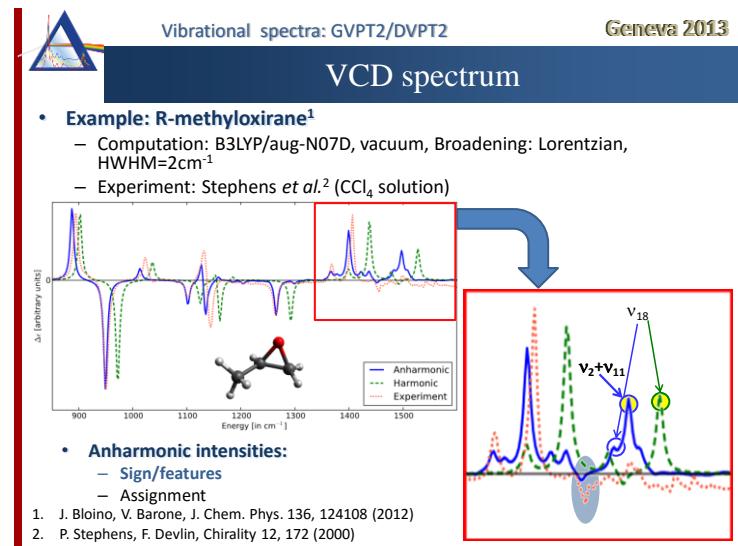
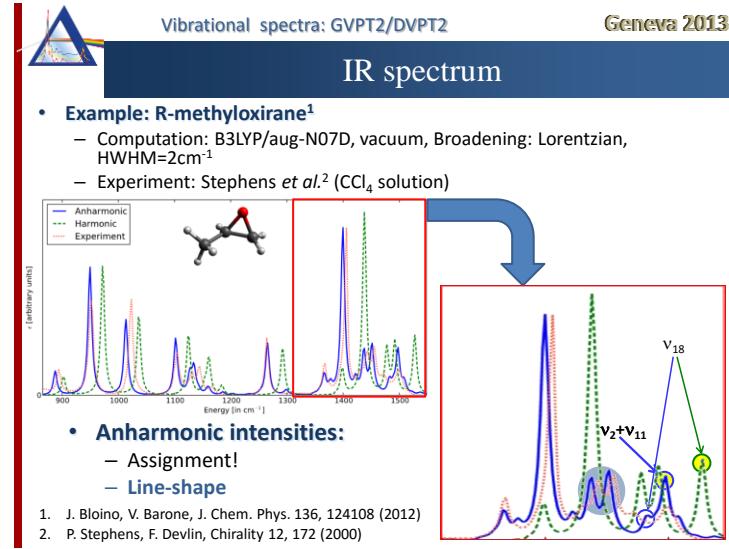
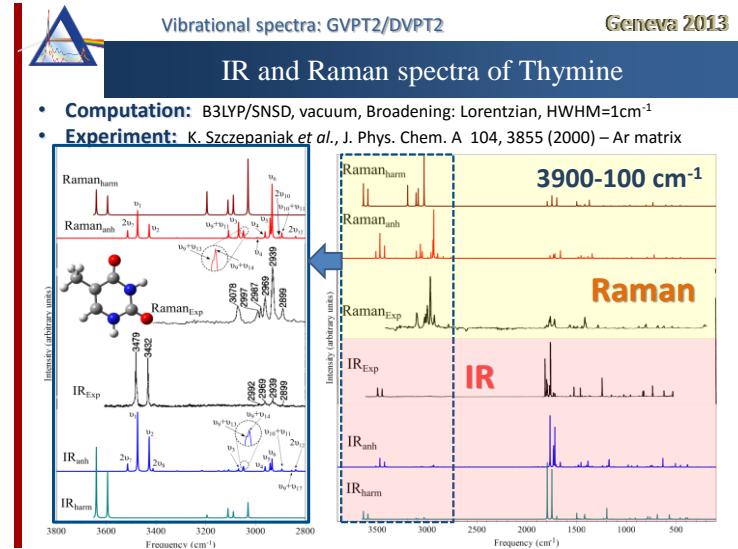
 $\text{C}_6\text{H}_5$ : |MAX|: 32  $\text{cm}^{-1}$  MAE: 8  $\text{cm}^{-1}$  for 24 normal modes $\text{C}_6\text{D}_5$ : |MAX|: 38  $\text{cm}^{-1}$  MAE: 11  $\text{cm}^{-1}$  for 16 normal modes• Exceptional cases (e.g  $v_{23}$  of  $\text{C}_6\text{D}_5$ )

- Less certain assignment

## • Reinvestigation?

- with the help of fully anharmonic IR and/or Raman spectra
- accounting for the species possibly present in the experimental mixture
- including a few sets of isotopically substituted precursors

[1] V. Barone, M. Biczysko, J. Bloino, F. Egidi, C. Puzzarini, *J. Chem. Phys.* 138, 234303 (2013)[2] J. Bloino, V. Barone, *J. Chem. Phys.* 136 124108 (2012), V. Barone *J. Chem. Phys.* 122, 014108 (2005)



- J. Bloino, V. Barone, J. Chem. Phys. 136, 124108 (2012)
- P. Stephens, F. Devlin, Chirality 12, 172 (2000)



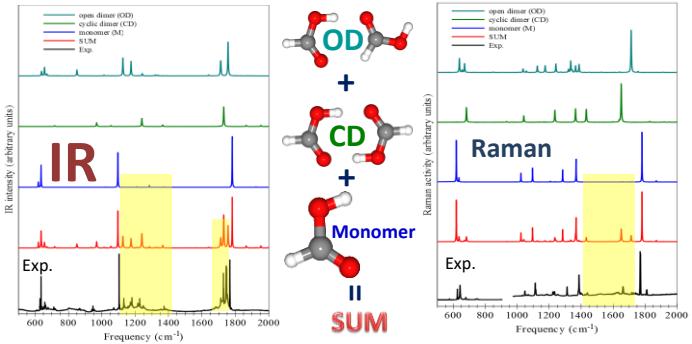
## Vibrational spectra: GVPT2/DVPT2

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## Mixture: Molecule+complexes

## Example: IR and Raman spectra of formic acid (+ dimers)

- Computation: B3LYP/aug-N07D, vacuum, Broadening: Lorentzian, HWHM=2cm<sup>-1</sup>
- Experiment: A. Olbert-Majkut et al., Chem. Phys. Lett. 468, 176 (2009) – Ar matrix

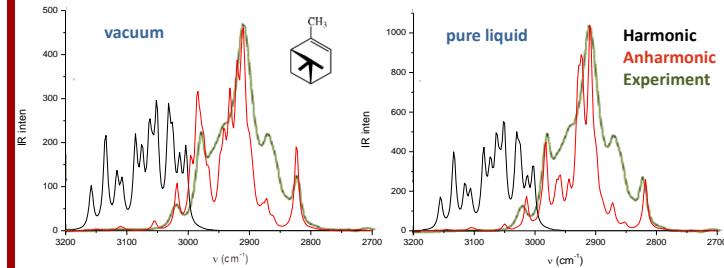


## Vibrational spectroscopy

## Solvent and anharmonic effects: IR

• Non-equilibrium implicit solvent<sup>1</sup> : Case of  $\alpha$ -pinene<sup>2</sup>

- Computation: PCM with vibrational nonequilibrium and local field effects, B3LYP/N07D
  - Non-equilibrium approach simulates the slower reorganization of the solvent molecules with respect to the vibrations.
- Experiment: L. Nafie and coworkers, *Vibr. Spectrosc.* 42, 254 (2006)



- C. Cappelli, F. Lipparini, J. Bloino, V. Barone, *J. Chem. Phys.* 135, 104505, 2011
- C. Cappelli, J. Bloino, F. Lipparini, V. Barone, *J. Phys. Chem. Lett.*, 3, 1766-1773, 2012

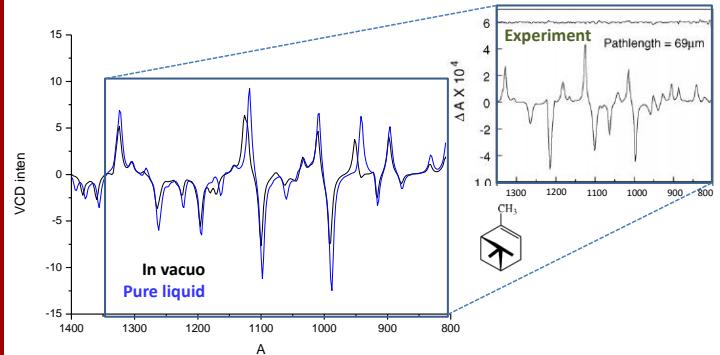


## Vibrational spectroscopy

## Solvent effects: VCD

• Anharmonic calculations: gas phase vs pure liquid for  $\alpha$ -pinene<sup>2</sup> (800-1350 cm<sup>-1</sup>)

- Computation: PCM with vibrational nonequilibrium<sup>1</sup> and local field effects, B3LYP/N07D
- Experiment: L. Nafie and coworkers, *Vibr. Spectrosc.* 42, 254 (2006)



- C. Cappelli, F. Lipparini, J. Bloino, V. Barone, *J. Chem. Phys.* 135, 104505, 2011
- C. Cappelli, J. Bloino, F. Lipparini, V. Barone, *J. Phys. Chem. Lett.*, 3, 1766-1773, 2012



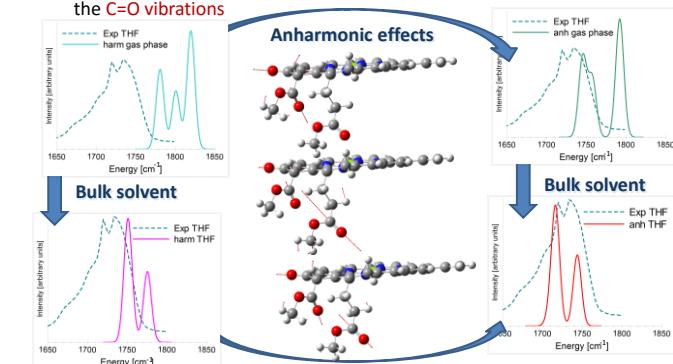
## Reduced GVPT2 scheme

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## Large molecular systems – spectra range

## • IR spectra of chlorophyll-a cation in tetrahydrofuran (THF) solution

- 186 normal modes
- Limited dimensionality anharmonic treatment : spectrum window related to the C=O vibrations





## Status of the Multi-purpose virtual spectrometer

- Computational Strategies for Spectroscopy
  - from Small Molecules to Nano Systems,
  - Edited by V. Barone,
  - John Wiley & Sons, Inc, Hoboken, New Jersey, 2012
- PCCP Cover Article
  - Barone et al. *Implementation and validation of a multi-purpose virtual spectrometer for large systems in complex environments*
  - PCCP Themed issue: Theoretical chemical physics of biological systems
  - Phys. Chem. Chem. Phys., 2012, 14, 12404–12422



<http://dreams.sns.it>

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C. Puzzarini (UniBo)

O. Crescenzi (UniNa)

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