Anharmonic vibrational spectroscopy

**Objective**
- An easy-to-use and reliable tool to compute spectroscopic data beyond the harmonic level,
- In particular:
  - Vibrational averages of a wide range of properties
  - Vibrational energy level (transition energies)
  - Transition integrals (band intensities)

**Requirements**
- Cost-effective
- Usable as a black-box procedure
- Able to account for environmental effects (solvent)
- Scalable (memory, computational time) to sizeable molecular systems

**Vibrational Spectrum**

- **Selection rules + intensity:** observed transitions
  - Transforming to the molecule fixed axis frame
    - Transition dipole moment integral:
      \[ \int \psi_i^\dagger \mu \psi_f d\tau_{il} d\tau_{fl} \]
  - Dipole moment
    - Expanded as a Taylor series in the vibrational coordinate
  - Non-zero transition probability
    - Some terms non-zero
    - Permanent dipole moment
    - Dipole moment vary during vibrations
  - Selection rules
    - \( \mu_e \) independent of \( q \) \( \Rightarrow \) do not influence selection rules
    - Main selection rule dependent on linear term
    - Secondary selection rule - quadratic term, etc

- **Fundamental bands**
  - \( \Delta v = 0 \)
  - Most transitions from \( \Delta v = 0 \)
  - \( \Delta v = 1 \) 
  - \( \Delta v = 2 \)
  - Overtones

**Beyond harmonic oscillator**

- **Reality: anharmonic potential**
  - Good approximation: Morse potential
  - \( \beta \): molecule dependent (curvature)
- **Vibrations**
  - Small displacements from \( R_e \)
  - Taylor expansion

- **Solving Schrödinger equation for Morse oscillator**
  - Energy in cm\(^{-1}\)
  \[ E_{vib}^{\text{anh}} = \left( v + \frac{1}{2} \right) \omega_{\text{vib}} \left( v + \frac{1}{2} \right) \omega_{\text{vib}} \chi_e \]

**Theoretical background**

- Transforming to the molecule fixed axis frame
- Dipole moment
  - Expanded as a Taylor series in the vibrational coordinate
- Non-zero transition probability
  - Some terms non-zero
- Selection rules
  - \( \mu_e \) independent of \( q \) \( \Rightarrow \) do not influence selection rules
  - Main selection rule dependent on linear term
  - Secondary selection rule - quadratic term, etc
Vibrational Spectra

• Harmonic wavenumber
• Anharmonic constant
• Anharmonic:
  - Bands shifted
  - More complex spectra

\[ E_{\text{vib}} = \left( \nu + \frac{1}{2} \right) \omega_e \]

\[ E_{\text{vib}} = \left( \nu + \frac{1}{2} \right) \omega_e \]

\[ \omega_e, \omega_a \]

\[ \chi_e, \chi_a \]

\[ \omega_e(1-2\chi_e) \]

\[ \omega_a(1-2\chi_a) \]

\[ \omega_e(2\chi_e) \]

\[ \omega_a(2\chi_a) \]

Anharmonic contributions

Vibrational spectroscopy

• Beyond harmonic approximation:
  - Vibrations with similar frequency can interact
  - Fermi resonance
    - Named after Enrico Fermi, who explained this phenomenon
    - Accidentally energies of the transitions have almost the same energy
    - Quantum mixing
    - Modification of the energies and intensities of absorption bands

Example: CO

- Vibrations: wavefunctions mix
- Intensity gain, \( \nu_1 \) observed

\[ \nu_1 (667 \text{ cm}^{-1}) \]

\[ \nu_2 (1388 \text{ cm}^{-1}) \]

2D vibrational wavefunctions

Anharmonic effects: resonances
Vibrational spectroscopy

Vibrational energy levels

- The second-order vibrational perturbation theory (VPT2)
  - Expansion of the potential energy operator $\hat{V}(q)$:
    $$\hat{V}(q) \approx \frac{1}{2} \sum_{i} \omega_{i} q_{i}^{2} + \frac{1}{6} \sum_{i,j} k_{ij} q_{i} q_{j} + \frac{1}{24} \sum_{i,j,k} k_{ijk} q_{i} q_{j} q_{k}$$
  - Inclusion of a kinetic contribution arising from the vibrational angular momentum $j_{\alpha}$:
    $$\sum_{\alpha} \beta_{\alpha} j_{\alpha}$$

- 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: $\frac{k_{ij}^{2}}{16(\omega_{i} - \omega_{j} - \omega_{k})}$

Vibrational spectroscopy

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
      $$\Delta \omega = \frac{k_{ij}^{4}}{256(\omega_{i} - 2 \omega_{j})^{3}}$$
  - Singularity correction: DVPT2 and GVPT2
    - 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.

Treatment of singularities: “resonance-criteria free”

- Degeneracy-corrected PT2 (DCPT2)
  - All terms are replaced by non-resonant terms, following the scheme:
    $$\frac{\delta}{2 \epsilon} \rightarrow S(\sqrt{\epsilon^{2} + k^{2} - \epsilon}) \epsilon = \frac{\Delta \omega}{2}$$
  - Pros: No parameter used, calculations devoid of singularities
  - Cons: Transformation is ill-suited for $k \sim \epsilon \gg 1$

- HDCPT2: Hybrid VPT2-DCPT2
  $$H_{DCPT2} = \Lambda \hat{V}_{PT2} + (1 - \Lambda) \hat{V}_{DCPT2}$$
  $$\Lambda = \frac{\tanh \left( \alpha \sqrt{k^{2} - \beta} \right) + 1}{2}$$

Anharmonic vibrational IR, VCD and Raman spectra

- IR: Molar extinction coefficient, $\chi(\tilde{\nu}_{0})$
- VCD: Difference in molar extinction coefficient, $\Delta \chi(\tilde{\nu}_{0})$
- Raman: Scattering $\partial r(\tilde{\nu}_{0})/\partial \Omega$

$$\chi(\tilde{\nu}_{0}) = \frac{8 \epsilon^{2} \chi(\tilde{\nu}_{0})}{3000(\chi(\tilde{\nu}_{0}) + \alpha / 24 \sum_{i} \chi(\tilde{\nu}_{0} - \epsilon_{i} - \tilde{\nu}_{0})}$$

$$\Delta \chi(\tilde{\nu}_{0}) = \frac{8 \epsilon^{2} \chi(\tilde{\nu}_{0})}{3000(\chi(\tilde{\nu}_{0}) + \alpha / 24 \sum_{i} \chi(\tilde{\nu}_{0} - \epsilon_{i} - \tilde{\nu}_{0})}$$

$$\partial r(\tilde{\nu}_{0}) = \frac{8 \epsilon^{2} \chi(\tilde{\nu}_{0})}{3000(\chi(\tilde{\nu}_{0}) + \alpha / 24 \sum_{i} \chi(\tilde{\nu}_{0} - \epsilon_{i} - \tilde{\nu}_{0})}$$

$$(\tilde{\nu}_{0}, \epsilon) \approx \frac{\chi_{\tilde{\nu}_{0}}}{\chi_{\tilde{\nu}_{0}} - 1 \chi_{\tilde{\nu}_{0}}}$$

- Both $\chi$ and $P_{\epsilon}$ must be treated anharmonically at the VPT2 level

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

Vibrational spectroscopy

Transition intensities

- Anharmonic vibrational IR, VCD and Raman spectra
  - IR: Molar extinction coefficient, $\chi(\tilde{\nu}_{0})$
  - VCD: Difference in molar extinction coefficient, $\Delta \chi(\tilde{\nu}_{0})$
  - Raman: Scattering $\partial r(\tilde{\nu}_{0})/\partial \Omega$
**Transition intensities: transition dipole moment**

- Generalized formulation for the transition dipole moment:

\[
P^{(n)} = P_0 + P_1 + \sum_{i} P_i + \sum_{ij} P_{ij} + \sum_{ijk} P_{ijk}
\]

- \( S_0, S_1, S_2, P_0, P_1, P_{ij}, P_{ijk} \) and \( S \) are property-dependent.

**Vibrational spectroscopy**

- Development using the Rayleigh-Schrödinger perturbation theory

\[
P^{(n)} = \left( P_0^{(n)} + \lambda P_1^{(n)} + \lambda^2 P_2^{(n)} \right)
\]

**VPT2 for medium-to-large systems**

- PES: polynomial of 4th order containing at most three independent normal coordinates
- Vibrational energy levels
  - \( K_{ij} \): set of anharmonic constants
  - \( E_0 \): simple function of 3rd \((K_{ij})\) and semi-diagonal 4th \((K_{ij})\) energy derivatives with respect to normal modes
- Energy third and semi-diagonal fourth derivatives are computed numerically

\[
K_{ij} = K_{ij}(v_0) - K_{ij}(v_0 - 1) + K_{ij}(v_0 - 1) - 2K_{ij}(0)
\]

- Computational cost grows quickly with the system size!

**Solutions to limit computation cost**

- Hybrid models
- Reduced-dimensionality

**Thermodynamics beyond harmonic approximation**

- Simple perturbation theory applied to the vibrational partition function

\[
Q_{ib} = \frac{1}{\prod_{i=1}^{N} (1 - e^{-\beta \chi_i})}
\]

- \( \nu_i \): Wavenumber frequency of the \( i \)-th fundamental band,
- \( \nu_i \): Anharmonic ZPVE,
- \( E_0 \): Energy third and semi-diagonal fourth derivatives are computed numerically

**VPT2 for small systems**

- PES: polynomial of 4th order containing at most three independent normal coordinates
- Vibrational energy levels
  - \( K_{ij} \): set of anharmonic constants
  - \( E_0 \): simple function of 3rd \((K_{ij})\) and semi-diagonal 4th \((K_{ij})\) energy derivatives with respect to normal modes
- Energy third and semi-diagonal fourth derivatives are computed numerically

\[
K_{ij} = K_{ij}(v_0) - K_{ij}(v_0 - 1) + K_{ij}(v_0 - 1) - 2K_{ij}(0)
\]

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**Solutions to limit computation cost**

- Hybrid models
- Reduced-dimensionality

---

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

• 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 $K_{ij}$
  - index $i$ corresponds to an active mode
  - cubic force constants $K_{ij}$ where index $i$ is present at least once (i.e. $K_{ii}$, $K_{ij}$, $K_{ij}$, $K_{ik}$)
  - along with all semi-diagonal quartic force constants $K_{ij}^{(2)}$
  - All $K_{ij}$ and $K_{ij}^{(2)}$ can be computed with 1M approach

• Difference wrt full treatment
  - some limited number cubic force constants (terms including only $i$ and $j$ 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$^{-1}$

• Reduced (N modes) approach
  - 27 over 42 modes can be computed with 1M approach
  - coupled modes, eg. CH$_3$ stretchings
  - graphical representation of couplings
    - absolute value of the cubic force constants $K_{ij}$

PES generation:

• Semi-diagonal Quartic Force Field
  - Energy third and semi-diagonal fourth derivatives are computed numerically

Basic requirements
  - Tight optimization criteria
    - Ultrafine Grid (DFT) + SCF tight

Example: H$_3$CO

<table>
<thead>
<tr>
<th>mode</th>
<th>Opt=tight Int=Uf</th>
<th>Opt Int</th>
<th>Opt=tight Int</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>2881.6 -152.7</td>
<td>2881.8 -161.1</td>
<td>2881.0 -152.7</td>
</tr>
<tr>
<td>$v_2$</td>
<td>1816.0 -26.3</td>
<td>1816.2 -26.8</td>
<td>1816.0 -26.3</td>
</tr>
<tr>
<td>$v_3$</td>
<td>1532.4 -33.0</td>
<td>1532.5 -33.6</td>
<td>1532.5 -33.6</td>
</tr>
<tr>
<td>$v_4$</td>
<td>1200.1 -18.0</td>
<td>1200.3 -17.9</td>
<td>1200.3 -18.0</td>
</tr>
<tr>
<td>$v_5$</td>
<td>2937.5 -125.3</td>
<td>2937.7 -261.3</td>
<td>2936.8 -124.9</td>
</tr>
<tr>
<td>$v_6$</td>
<td>1266.6 -21.3</td>
<td>1266.7 -21.5</td>
<td>1266.7 -21.3</td>
</tr>
</tbody>
</table>

Vibrational frequencies

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

<table>
<thead>
<tr>
<th>B3LYP</th>
<th>harm</th>
<th>anh</th>
<th>hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>MN</td>
<td>25</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>MAX</td>
<td>+108</td>
<td>+142</td>
<td>+39</td>
</tr>
<tr>
<td>MUE</td>
<td>30</td>
<td>30</td>
<td>7</td>
</tr>
</tbody>
</table>

• DFT vs Experiment
  - Hybrid CC/DFT models vs Experiment

Overall good accuracy + applicability to larger systems
**Vibrational spectroscopy**

**Geneva 2013**

- **Example: glycine**
  - Vibration energies in vacuum (in cm⁻¹)
  - Computational model: B3LYP/aug-107D

<table>
<thead>
<tr>
<th>mode</th>
<th>Harm.</th>
<th>GV</th>
<th>VPT2</th>
<th>DCP</th>
<th>HDC</th>
<th>Exp.</th>
<th>Assign.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν1</td>
<td>3750</td>
<td>3568</td>
<td>3568</td>
<td>3565</td>
<td>3566</td>
<td>3585</td>
<td>OH str.</td>
</tr>
<tr>
<td>ν2</td>
<td>3582</td>
<td>3407</td>
<td>3407</td>
<td>3404</td>
<td>3403</td>
<td>3410</td>
<td>NH2 (A) str.</td>
</tr>
<tr>
<td>ν3</td>
<td>3509</td>
<td>3387</td>
<td>3353</td>
<td>3304</td>
<td>3350</td>
<td>-</td>
<td>NH2 (S) str.</td>
</tr>
<tr>
<td>ν4</td>
<td>3079</td>
<td>2929</td>
<td>2929</td>
<td>2926</td>
<td>2926</td>
<td>2925</td>
<td>CH3 (A) str.</td>
</tr>
<tr>
<td>ν5</td>
<td>3044</td>
<td>2938</td>
<td>2933</td>
<td>2911</td>
<td>2910</td>
<td>2918</td>
<td>CH3 (S) str.</td>
</tr>
</tbody>
</table>

- Mean Unsigned Error (MUE) and largest absolute error ([MAX]) are calculated with respect to VPT2 for ALL normal modes.
- DCP: problems for strong couplings between low- and high-frequency vibrations occur (k-large and ε-large), also toluene CH2.

**Building blocks of biomolecules: closed-shell**

- **Can integrated CC and CC/DFT schemes shed light on the observation of elusive glycine conformers?**

- **Accurate**
  - structure (Rₐ)
  - thermodynamic (∆H, ∆G)
  - spectroscopic parameters
  - Bₚ, DₚK, IR, Raman...

**CC/DFT for spectroscopy and thermodynamics**

- Glycine conformers: IIlp and Iln [1]
- CC/DFT conformational energies wrt most stable IP, T=410 K
  - CCSD(T)/CBS+CV conformational energies, harmonic frequencies, B3LYP/SMD anharmonic contributions computed by means of the HDCPT2[2] model, in conjunction with simple perturbation theory (SPT)[3].

<table>
<thead>
<tr>
<th>Iln mol⁻¹</th>
<th>IIlp</th>
<th>ZPVE</th>
<th>RRHO*</th>
<th>HRAD** SPT Exp.</th>
<th>RRHO*</th>
<th>HRAD** SPT Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.81</td>
<td>4.74</td>
<td>7.48</td>
<td>7.94</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Accurate computations of entropy contributions require the proper treatment of low-frequency torsional motions and anharmonic effects.

**CC/DFT for spectroscopy: closed-shell**

- IR Vibrational frequencies and IR intensities of Ip/tt conformer [1]
  - CCSD(T)/CBS+CV harmonic frequencies.

<table>
<thead>
<tr>
<th>mode</th>
<th>B3LYP</th>
<th>B3LYP-D3</th>
<th>M05-2X</th>
<th>CC/B3LYP</th>
<th>Exp.</th>
<th>Assign.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν1</td>
<td>3582</td>
<td>3582</td>
<td>3582</td>
<td>3582</td>
<td>3582</td>
<td>sc*</td>
</tr>
<tr>
<td>ν2</td>
<td>3533</td>
<td>3535</td>
<td>3535</td>
<td>3535</td>
<td>3535</td>
<td>anh</td>
</tr>
<tr>
<td>ν3</td>
<td>3470</td>
<td>3473</td>
<td>3473</td>
<td>3473</td>
<td>3473</td>
<td>sc**</td>
</tr>
<tr>
<td>ν4</td>
<td>2925</td>
<td>2925</td>
<td>2925</td>
<td>2925</td>
<td>2925</td>
<td>anh</td>
</tr>
</tbody>
</table>

- Mean absolute error (MAE) and largest absolute error ([MAX]) with respect to experiment or CC results.

**CC/DFT for spectroscopy: closed-shell**

- MAX and MAE calculated for ALL normal modes
  - Mean absolute error (MAE) and largest absolute error ([MAX]) with respect to experiment or CC results.


**Best-estimated MI-IR spectra for the main and trideuterated [OD,ND2] glycine isotopologue.**
- CC/DFT(D/C)/CI harmonic frequencies, B3LYP/SNSD anharmonic contributions computed by means of the GPAW/GVPT2[2] model.
- Spectra convoluted using Lorentzian functions with a half-width at half maximum (HWHM) of 1 cm⁻¹.

**Experimental IR spectra recorded in the low-temperature Ar matrix.**

**Theory:** IVn/gtt 'missing' conformer easier detected for [OD,ND2] .
- Ip shows less intense features.
- Increased energy gap between the IVn fundamental and Ip overtones.
- A higher percentage of IVn in the experimental mixture.

**Experimental data:** Isolated molecule B3LYP/aug-cc-pVTZ. Simulate also CCSD(T)/CH

**Experimental data:** Isolated molecule B3LYP/aug-cc-pVTZ. Simulate also CCSD(T)/CCH

**Vibrational spectroscopy**

**Reduced GVPT2 scheme**

**Glycine vs Glycine@Si(100)**
- Reduced dimensionality computation: all bands of glycine [24] and their shift upon adsorption on Si12 cluster (total 117 modes); B3LYP/aug-CC
- Experimental data: Isolated molecule – FTIR; Glycine@Si(100) High Resolution Electron Energy Loss Spectroscopy (HREELS)

**Experimental data:** Isolated molecule B3LYP/aug-cc-pVTZ. Simulate also CCSD(T)/CCH

**B3LYP/SNSD harmonic frequencies, B3LYP/aug-cc-pVTZ anharmonic contributions computed by means of the GPAW/GVPT2[2] model.**

**Spectra convoluted using Lorentzian functions with a half-width at half maximum (HWHM) of 1 cm⁻¹.**
Vibrational spectra of large systems

- Glycine@Si(100)
  - Reduced dimensionality computation: all bands of glycine (24) and their shift upon adsorption on Si$_{15}$ cluster (total 117 modes); B3LYP/aug-N07D.

| Label | Asm | Exp | $\nu$ | $K_{ij}$ | $\Sigma |K_{ij}|$ | $|K_{ij}|_{max}$ | $\lambda$ |
|-------|-----|-----|------|---------|-----------|----------------|------|
| 117   | v(NH)$_{as}$ | 3460 | 3419  | 181     | 2392      | 1643           | 116  |
| 116   | v(NH)$_{as}$ | 3410 | 3379  | 1623    | 470       | 101            | 80   |
| 115   | v(CH)$_{as}$ | 3040 | 2932  | 1422    | 1381      | 934            | 114  |
| 114   | v(CH)$_{as}$ | 2940 | 2901  | 1620    | 774       | 398            | 115  |
| 112   | v(SiH)      | 2115 | 2110  | 1124    | 884       | 142            | 107  |

Validity check: $K_{ij}$ small: OK; $K_{ij}$ large: some coupling (e.g., if $K_{ij}$ also large) can not be neglected.

- Coupling with Si$_{15}$H$_{16}$ cluster vibrations
  - Stretching Si-H: $|K_{ij}|_{max} = 142$ cm$^{-1}$, OK can be safely neglected.
  - All other modes of glycine, the largest $|K_{ij}|_{max} = 122$ cm$^{-1}$, OK can be safely neglected.
  - CH$_2$ asymmetric stretch: coupled to $v(CH)_2$: included, OK, larger discrepancy ??

**Computed vs Experimental spectra**
- Vibrational freq in 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))

![Graph showing computed vs experimental spectra](image)

**Mean Absolute Error (MAE), and largest negative (MIN) and positive (MAX) deviations with respect to experiment**

<table>
<thead>
<tr>
<th></th>
<th>MIN</th>
<th>MAX</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAM</td>
<td>-7</td>
<td>49</td>
<td>19</td>
</tr>
<tr>
<td>CC'</td>
<td>-17</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>BSVP</td>
<td>-36</td>
<td>40</td>
<td>11</td>
</tr>
<tr>
<td>CC'</td>
<td>-20</td>
<td>15</td>
<td>6</td>
</tr>
</tbody>
</table>


**Non-equilibrium implicit solvent**
- 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=4cm$^{-1}$

**Experiment**: 10% in CCl$_4$ (3800-1370), 10% in CS$_2$ (1370-450)

**CC/DFT for spectroscopy: open-shell**

**IR and Raman harmonic and anharmonic spectra C$_6$H$_5$ and C$_6$D$_5$$^1$$^2$$^3$
- CCSD(T)/aug-cc-pVTZ harmonic frequencies,

**IR and Raman harmonic**

![Graph showing IR and Raman harmonic spectra of phenyl radical](image)

**Exceptional cases (e.g. $v_{23}$ of C$_6$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

**CC/DFT for spectroscopy: open-shell**

**IR spectra of phenyl radical**

![Graph showing IR spectra of phenyl radical](image)

**CC/DFT for spectroscopy: open-shell**

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**IR and Raman harmonic and anharmonic spectra C$_6$H$_5$ and C$_6$D$_5$$^1$$^2$$^3$
- CCSD(T)/aug-cc-pVTZ harmonic frequencies +IR intensities,

**Overall accuracy**
- C$_6$H$_5$: (MAX): 32 cm$^{-1}$ MAE: 8 cm$^{-1}$ for 24 normal modes
- C$_6$D$_5$: (MAX): 38 cm$^{-1}$ MAE: 11 cm$^{-1}$ for 16 normal modes

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**CC/DFT for spectroscopy: open-shell**

**IR spectra of phenyl radical**

![Graph showing IR spectra of phenyl radical](image)

**CC/DFT for spectroscopy: open-shell**

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**IR spectra of phenyl radical**

![Graph showing IR spectra of phenyl radical](image)
Vibrational spectra: GVPT2/DVPT2

IR and Raman spectra of Thymine

- Computation: B3LYP/SNSD, vacuum, Broadening: Lorentzian, HWHM=1cm⁻¹

Example: R-methyloxirane

- Computation: B3LYP/aug-N07D, vacuum, Broadening: Lorentzian, HWHM=2cm⁻¹
- Experiment: Stephens et al.² (CCl₄ solution)

Anharmonic intensities:
- Assignment!
- Line-shape


Butane anti- and gauche- conformer abundances at 298 K
- B3LYP/SNSD; Spectra GVPT2/DVPT2; ΔG=SPT/HDCPT2, 64% anti-, 36% gauche-

VCD spectrum

Example: R-methyloxirane

- Computation: B3LYP/aug-N07D, vacuum, Broadening: Lorentzian, HWHM=2cm⁻¹
- Experiment: Stephens et al.² (CCl₄ solution)

Anharmonic intensities:
- Sign/features
- Assignment

Mixture: anharmonic IR and Raman spectra

Geneva 2013
Mixture: Molecule+complexes

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

- Computation: B3LYP/aug-cc-pVDZ, vacuum, Broadening: Lorentzian, HWHM=2 cm⁻¹

Vibrational spectra: GVPT2/DVPT2

Solvent and anharmonic effects: IR

- Non-equilibrium implicit solvent¹: Case of α-pinene²
  - Computation: PCM with vibrational nonequilibrium and local field effects, B3LYP/aug-cc-pVDZ


Vibrational spectroscopy

Solvent effects: VCD

- Anharmonic calculations: gas phase vs pure liquid for α-pinene² (800-1350 cm⁻¹)
  - Computation: PCM with vibrational nonequilibrium and local field effects, B3LYP/aug-cc-pVTZ

Reduced GVPT2 scheme

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,

- **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

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