

Semiclassical Initial Value Representation Molecular Dynamics for Spectroscopy

Riccardo Conte, Chiara Aieta, Fabio Gabas, Gianluca Bertaina,
Marco Cazzaniga, Alessandro Rognoni, Michele Gandolfi,
Giacomo Botti, Giacomo Mandelli, Giovanni Di Liberto, Marco
Micciarelli, Davide Moscato, Cecilia Lanzi, Michele Ceotto

Dipartimento di Chimica, Università degli Studi di Milano (Italy)

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Goals

- To add quantum mechanical effects to nuclear dynamics
- No *ad hoc* assumptions
- No tunable parameters
- Precisions of the order of few wavenumbers for spectra calculations
- Fully ab initio: both potential and dynamics calculations
- Direct dynamics approach: “on-the-fly”
- Keep the quantum phase of the Feynman Path Integral: **realtime quantum dynamics**

SCIVR in one slide...

PI slicing: $\langle \mathbf{q} | e^{-i\hat{H}t/\hbar} | \mathbf{q}_0 \rangle = \lim_{N \rightarrow \infty} \left(\frac{m}{2\pi i \hbar \Delta t} \right)^{N/2} \int_{-\infty}^{+\infty} d\mathbf{q}_1 \dots \int_{-\infty}^{+\infty} d\mathbf{q}_{N-1} e^{iS_N(q)/\hbar}$

where $S_N(q) = \frac{Nm}{2t} \sum_{K=1}^N (q_K - q_{K-1})^2 - \frac{t}{N} \left[\sum_{K=1}^{N-1} V(q_K) + \frac{1}{2}(V(q_0) + V(q_N)) \right]$

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Stationary Phase Approximation: $\int_{-\infty}^{+\infty} dx e^{if(x)} \approx \sum_{\{x_j | df(x_j)/dx=0\}} \sqrt{\frac{2\pi i}{d^2 f(x_j)/dx^2}} e^{if(x_j)}$

van Vleck prop. $\langle \mathbf{q} | e^{-i\hat{H}t/\hbar} | \mathbf{q}_0 \rangle \approx \sum_{roots} \left[(2\pi i \hbar)^F \left| \frac{\partial \mathbf{q}}{\partial \mathbf{p}_0} \right| \right]^{-1/2} e^{\frac{i}{\hbar} S_t(\mathbf{q}, \mathbf{q}_0)} e^{-iv\pi/2}$

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IVR trick:
choose \mathbf{p}_0 such that $\mathbf{q} = \mathbf{q}_t$ $\sum_{roots} \rightarrow \int d\mathbf{p}_0 \left| \frac{\partial \mathbf{q}}{\partial \mathbf{p}_0} \right| \delta(\mathbf{q}_t - \mathbf{q})$

$$\langle \Psi | e^{-\frac{i}{\hbar} \hat{H}t} | \Psi \rangle = \int d\mathbf{q} \int d\mathbf{q}_0 \langle \Psi | \mathbf{q} \rangle \langle \mathbf{q} | e^{-\frac{i}{\hbar} \hat{H}t} | \mathbf{q}_0 \rangle \langle \mathbf{q}_0 | \Psi \rangle \approx$$

van Vleck SC IVR propagator $\approx \int d\mathbf{p}_0 \int d\mathbf{q}_0 \left[\frac{1}{(2\pi i \hbar)^F} \left| \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right| \right]^{1/2} e^{\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0)} e^{-iv\pi/2} \Psi^*(\mathbf{q}_t) \Psi(\mathbf{q}_0)$

... actually two...

$$\langle \Psi | e^{-\frac{i}{\hbar} \hat{H} t} | \Psi \rangle \approx \int d\mathbf{p}_0 \int d\mathbf{q}_0 \left[\frac{1}{(2\pi i \hbar)^F} \left| \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right| \right]^{1/2} e^{\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0)} e^{-i v \pi / 2} \Psi^*(\mathbf{q}_t) \Psi(\mathbf{q}_0)$$

Coherent States Representation $\langle \mathbf{x} | \mathbf{q}_t \rangle \rightarrow \langle \mathbf{x} | \mathbf{p}_t \mathbf{q}_t \rangle = \left(\frac{\det(\Gamma)}{\pi^F} \right)^{\frac{1}{4}} e^{-\frac{1}{2} (\mathbf{x} - \mathbf{q}_t)^T \Gamma (\mathbf{x} - \mathbf{q}_t) + \frac{i}{\hbar} \mathbf{p}_t^T (\mathbf{x} - \mathbf{q}_t)}$

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$$\langle \Psi | e^{-i \hat{H} t / \hbar} | \Psi \rangle \approx \left(\frac{1}{2\pi\hbar} \right)^F \int d\mathbf{p}_0 \int d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0)} \langle \Psi | \mathbf{p}_t \mathbf{q}_t \rangle \langle \mathbf{p}_0 \mathbf{q}_0 | \Psi \rangle$$

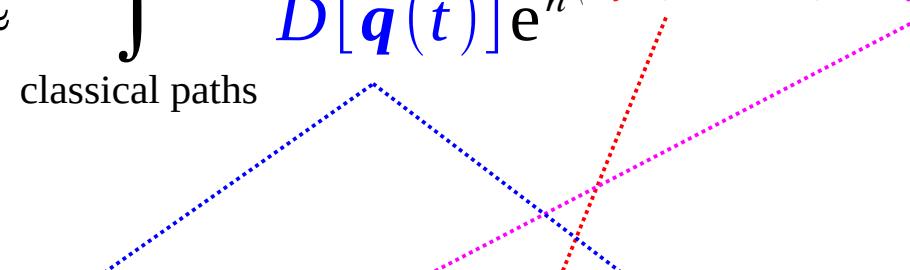
where $C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\det \left[\frac{1}{2} \left(\mathbf{M}_{\mathbf{qq}} + \Gamma^{-1} \mathbf{M}_{\mathbf{pp}} \Gamma + \frac{i}{\hbar} \Gamma^{-1} \mathbf{M}_{\mathbf{pq}} + \frac{\hbar}{i} \mathbf{M}_{\mathbf{qp}} \Gamma \right) \right]}$

and $\mathbf{M}(t) \equiv \begin{pmatrix} \mathbf{M}_{\mathbf{pp}} & \mathbf{M}_{\mathbf{pq}} \\ \mathbf{M}_{\mathbf{qp}} & \mathbf{M}_{\mathbf{qq}} \end{pmatrix} = \begin{pmatrix} \partial \mathbf{p}_t / \partial \mathbf{p}_0 & \partial \mathbf{p}_t / \partial \mathbf{q}_0 \\ \partial \mathbf{q}_t / \partial \mathbf{p}_0 & \partial \mathbf{q}_t / \partial \mathbf{q}_0 \end{pmatrix}$

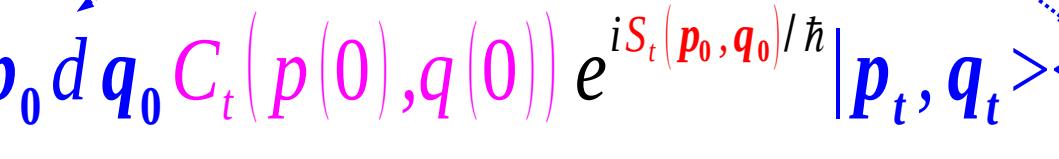
with equation of motion: $\frac{d}{dt} \mathbf{M}(t) = \begin{pmatrix} \mathbf{0} & -\mathbf{K}_t \\ \mathbf{m}^{-1} & \mathbf{0} \end{pmatrix} \mathbf{M}(t)$

in summary...

1. Semiclassical approximation to Feynman Path Integrals

$$e^{-i\hat{H}t/\hbar} \approx \int_{\text{classical paths}} D[\mathbf{q}(t)] e^{\frac{i}{\hbar} (S_t^{(0)}(\text{classical}) + \delta S_t^{(2)}(\text{classical}))}$$


2. The Herman-Kluk Propagator

$$e^{-i\hat{H}t/\hbar} = \frac{1}{(2\pi\hbar)^F} \iint d\mathbf{p}_0 d\mathbf{q}_0 C_t(p(0), q(0)) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t, \mathbf{q}_t\rangle \langle \mathbf{p}_0, \mathbf{q}_0|$$


3. Gaussian coherent states basis set

$$\langle \mathbf{q} | \mathbf{q}_{eq}, \mathbf{p}_{eq} \rangle = \prod_{i=1}^F \left(\frac{\gamma_i}{\pi} \right)^{F/4} e^{-\frac{\gamma_i}{2} (q_i - q_{eq,i})^2 + i p_{eq,i} (q_i - q_{eq,i})/\hbar}$$

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The Time Averaging Method

$$\langle A \rangle = \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{T} \int_0^T A(p_t, q_t) dt$$

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Time-averaged autocorrelation function

$$C_{pp}(t) = \langle p(t) p(0) \rangle = \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{T} \int_0^T dt_1 p(t + t_1) p(t_1)$$

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Time-averaged Power Spectrum

$$I(E) = \int_0^{+\infty} dt e^{iEt/\hbar} \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{T} \int_0^T dt_1 p(t + t_1) p(t_1)$$

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...changing variable... $\tau = t + t_1$

$$= \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{T} \int_0^{T \rightarrow +\infty} dt_1 \int_{t_1}^{+\infty} d\tau e^{iE(\tau - t_1)/\hbar} p(\tau) p(t_1)$$

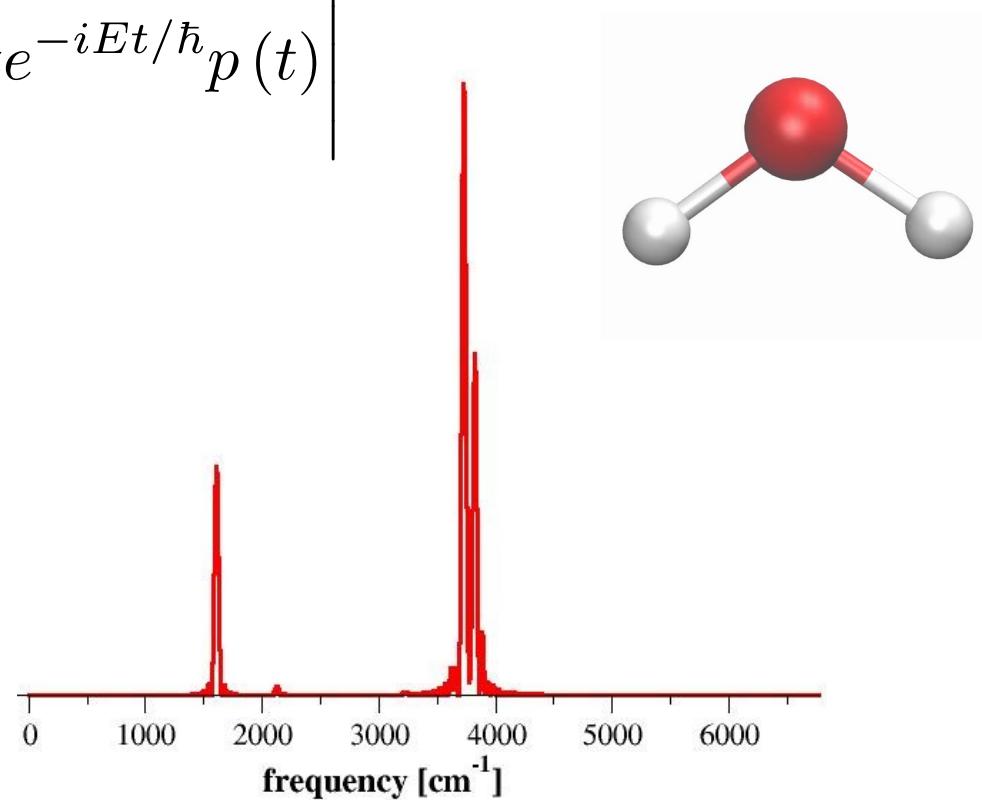
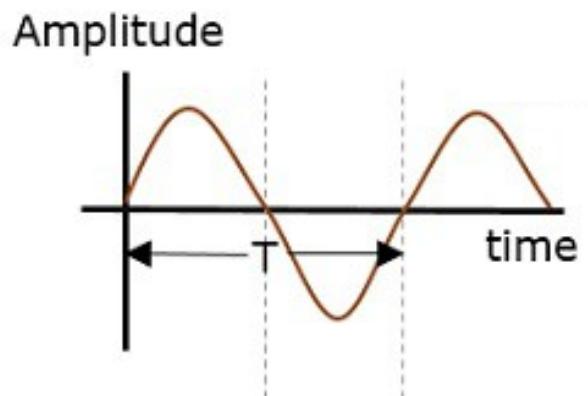
$$= \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{2T} \left| \int_0^T dt e^{-iEt/\hbar} p(t) \right|^2$$

Classical Molecular Dynamics for Spectra Calculations

$$I_{cl}(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle v(t) v(0) \rangle e^{i\omega t} dt =$$

$$= \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{2T} \left| \int_0^T dt e^{-iEt/\hbar} p(t) \right|^2$$

Time Domain
Representation



Only classical frequencies are obtained
No quantum overtones, combinations, ZPE, etc.

The TA SCIVR Method for Power Spectra

$$I(E) \equiv \langle \chi | \delta(\hat{H} - E) | \chi \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle e^{iEt/\hbar} dt$$

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where in SCIVR approximation

$$\langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle \approx \left(\frac{1}{2\pi\hbar} \right)^F \int \int d\mathbf{p}_0 d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0)} \langle \chi | \mathbf{p}_t \mathbf{q}_t \rangle \langle \mathbf{p}_0 \mathbf{q}_0 | \chi \rangle$$

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and by applying the time averaging filter

$$I(E) = \left(\frac{1}{2\pi\hbar} \right)^F \int \int d\mathbf{p}_0 d\mathbf{q}_0 \frac{1}{2\pi\hbar T} \left| \int_0^T e^{\frac{i}{\hbar} [S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi_t]} \langle \chi | \mathbf{p}_t \mathbf{q}_t \rangle dt \right|^2$$

where $\phi_t = \text{phase}[C_t(\mathbf{p}_0, \mathbf{q}_0)]$

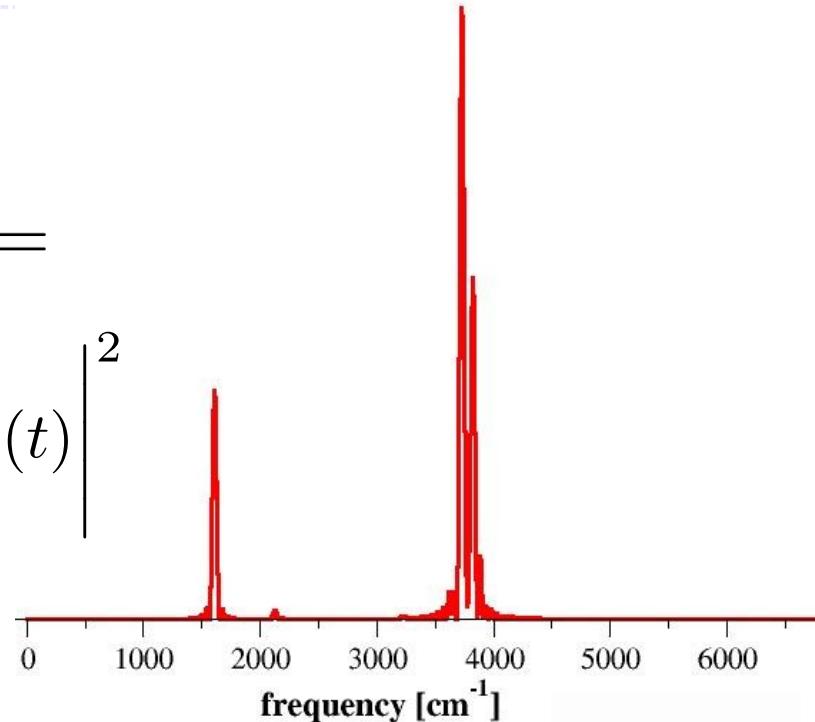
$$C_t(\mathbf{p}(0), \mathbf{q}(0)) = \sqrt{\det \left[\frac{1}{2} \left(\frac{\partial \mathbf{q}(t)}{\partial \mathbf{q}(0)} + \Gamma^{-1} \frac{\partial \mathbf{p}(t)}{\partial \mathbf{p}(0)} \Gamma + \frac{i}{\hbar} \Gamma^{-1} \frac{\partial \mathbf{p}(t)}{\partial \mathbf{q}(0)} + \frac{\hbar}{i} \frac{\partial \mathbf{q}(t)}{\partial \mathbf{p}(0)} \Gamma \right) \right]}$$

The TA SCIVR Method for Power Spectra

CLASSICAL

$$I_{cl}(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle v(t) v(0) \rangle e^{i\omega t} dt =$$

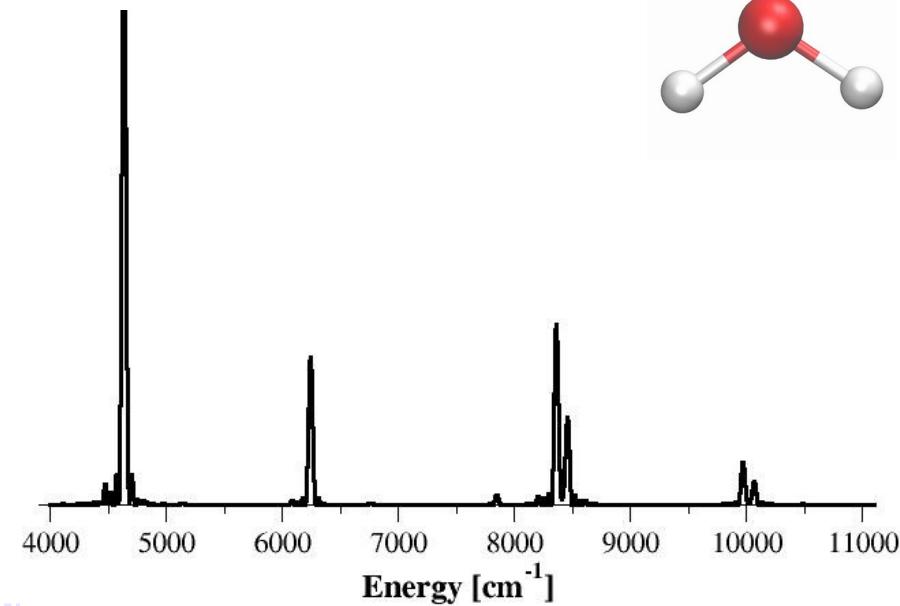
$$= \int \int dp_0 dq_0 \rho(p_0, q_0) \frac{1}{2T} \left| \int_0^T dt e^{-iEt/\hbar} p(t) \right|^2$$



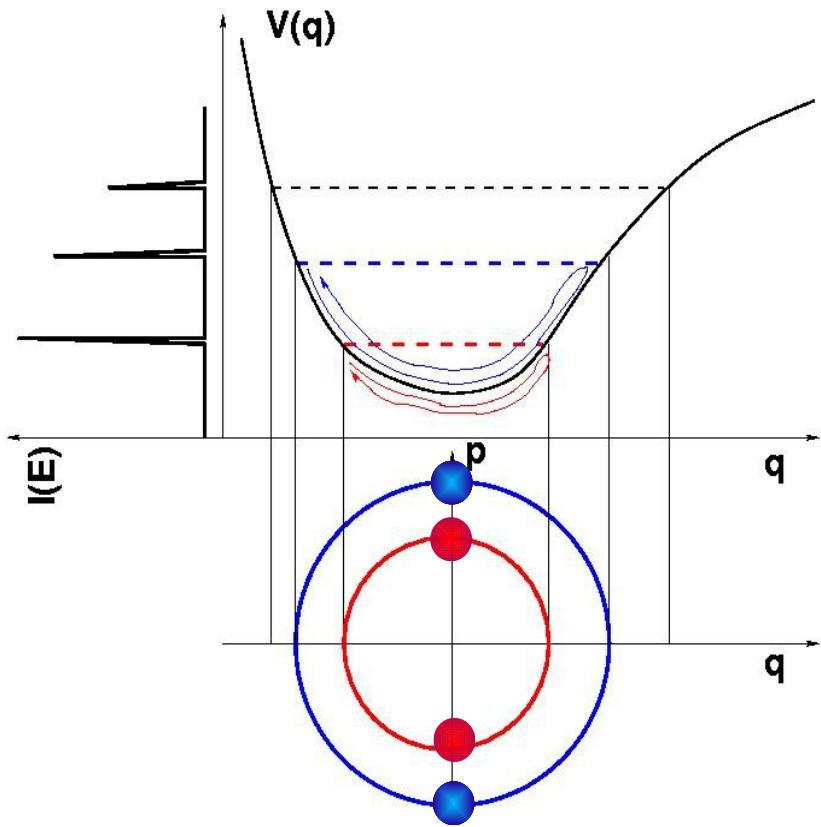
SEMICLASSICAL

$$I(E) = \left(\frac{1}{2\pi\hbar} \right)^F \int \int d\mathbf{p}_0 d\mathbf{q}_0 \frac{1}{2\pi\hbar T}$$

$$\times \left| \int_0^T e^{\frac{i}{\hbar} [S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi_t]} \langle \chi | \mathbf{p}_t \mathbf{q}_t \rangle dt \right|^2$$



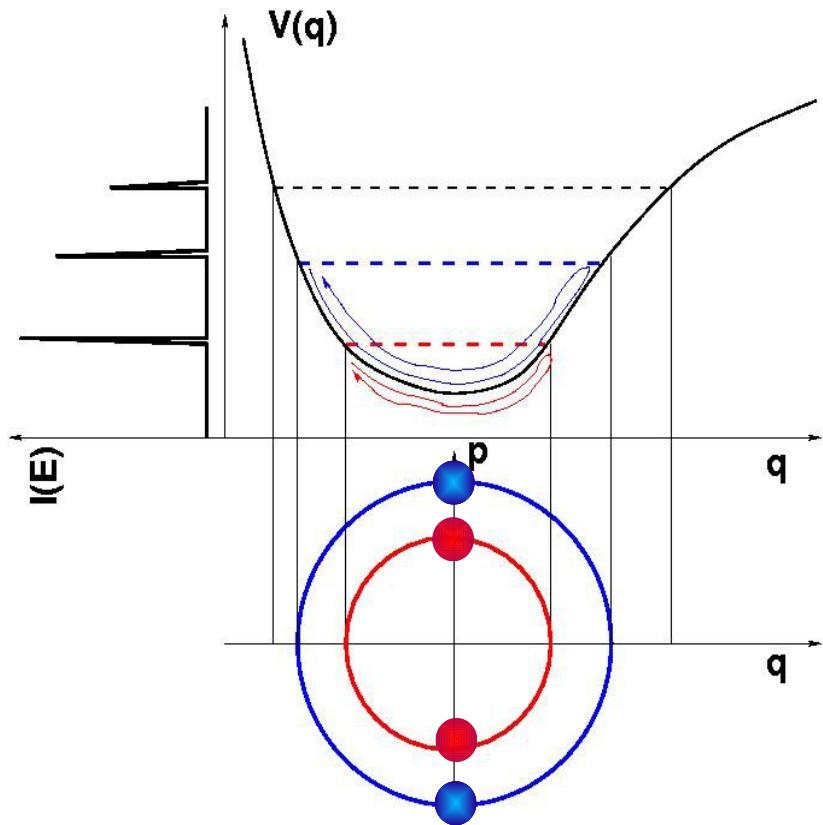
Multiple Coherent states TA-SCIVR: few on-the-fly trajectories



$$|\chi\rangle = \sum_{k=1}^{N_{states}} \prod_{j=1}^F \epsilon_k(j) |p_{eq,j}^k, q_{eq,j}^k\rangle$$

q_{eq} at equilibrium geometry
Harmonic sampling for p_{eq}

Multiple Coherent states TA-SCIVR: few on-the-fly trajectories

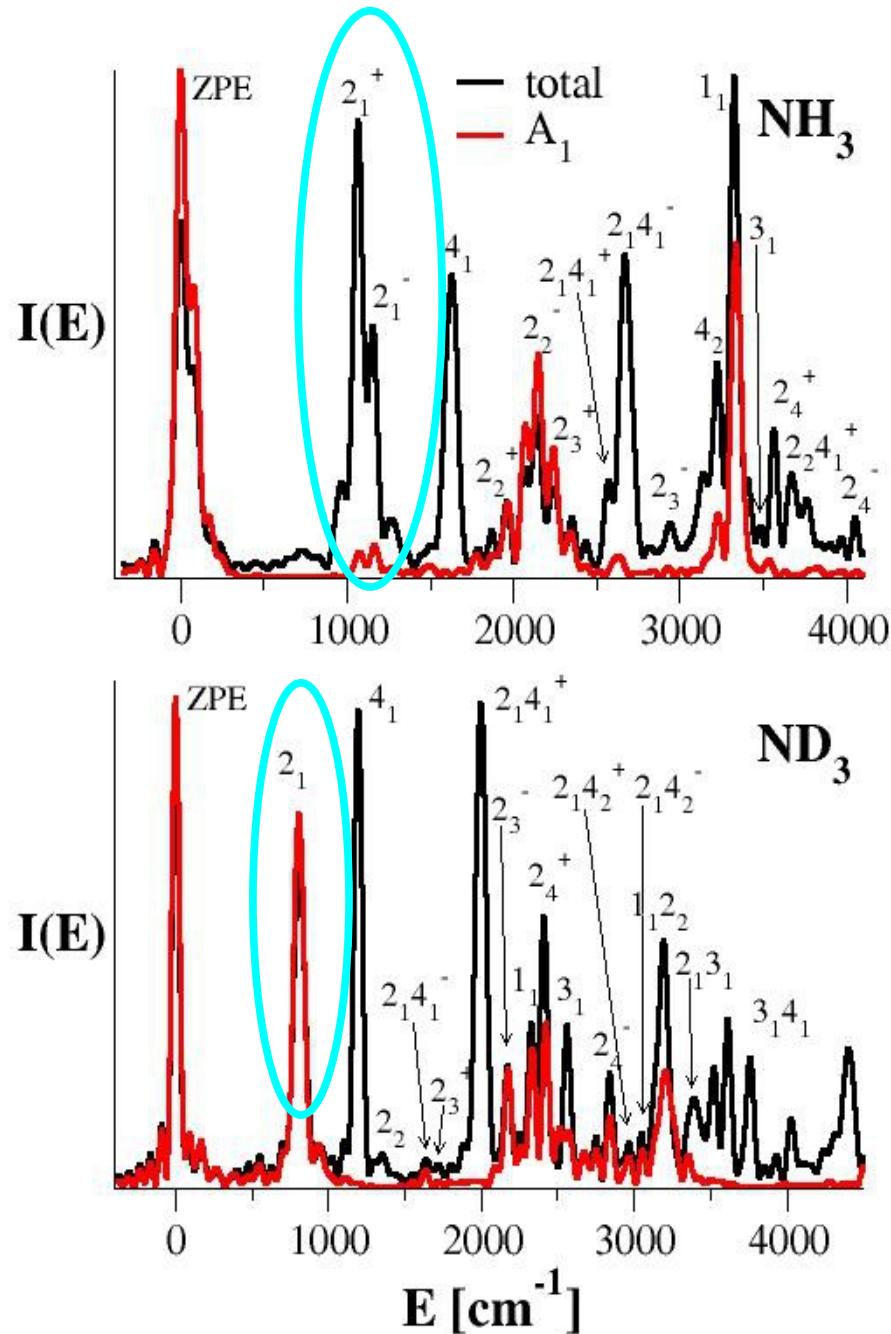


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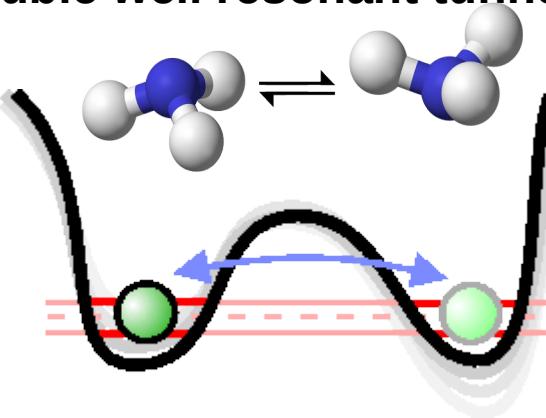
\mathbf{q}_{eq} at equilibrium geometry
Harmonic sampling for \mathbf{p}_{eq}

$$I_\chi(E) = \left(\frac{1}{2\pi\hbar} \right)^F \sum_{k=1}^{N_{traj}} \frac{1}{2\pi\hbar T} \left| \int_0^T dt \langle \chi | \mathbf{p}_t, \mathbf{q}_t \rangle e^{\{ \frac{i}{\hbar} [S_t + Et + \phi_t] \}} \right|^2$$

On-the-fly Ammonia Power spectrum



Double well resonant tunneling



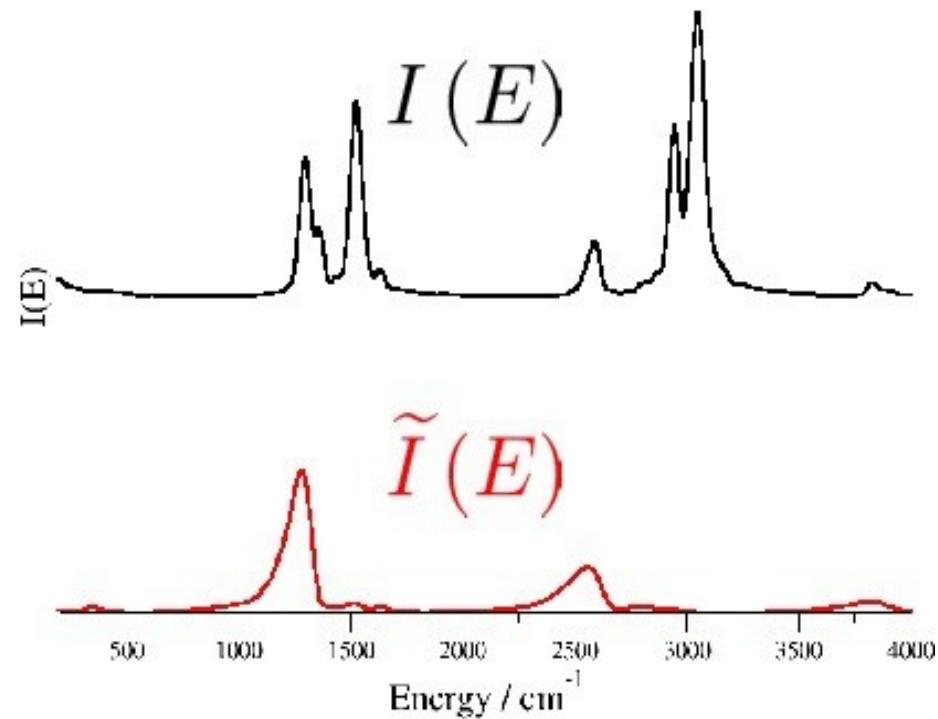
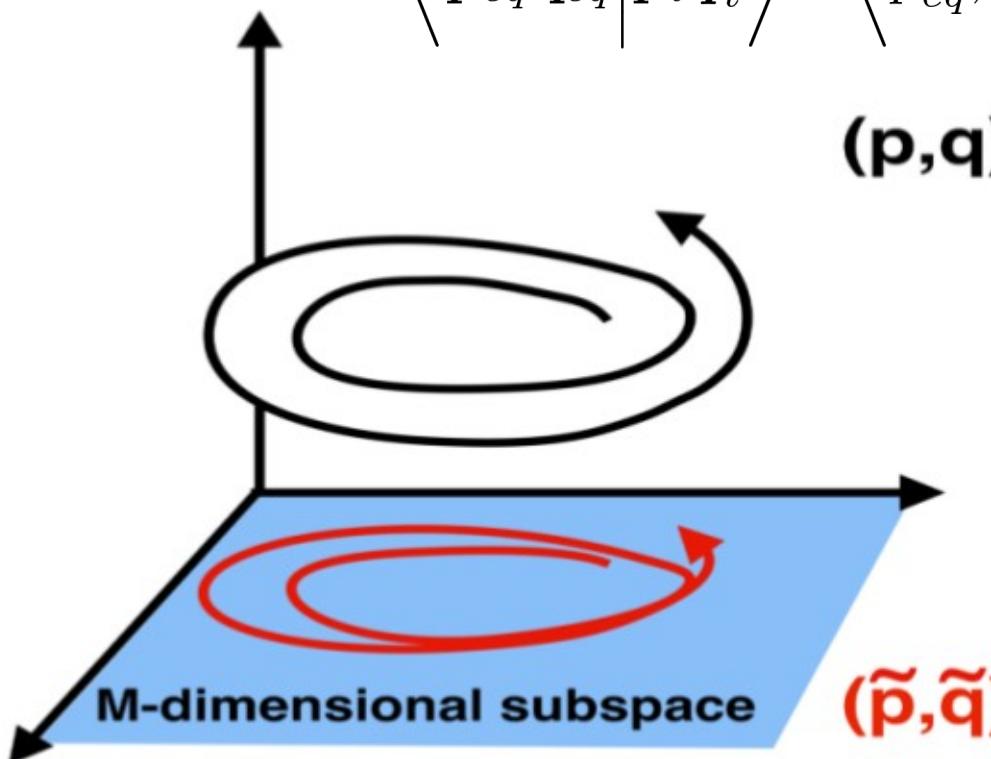
- A B3LYP/cc-pVDZ basis set was used (Qchem suite of codes)
- NH_3 ZPE = 7342 cm^{-1}
 ND_3 ZPE = 5370 cm^{-1}
- Tunneling splittings are greatly reduced after deuteration
- Vibrational spacing is greatly reduced after deuteration
- Mean Absolute Error (MAE= 38 cm^{-1}) respect to exact Hamiltonian Lanczos diagonalization

Divide-and-Conquer Semiclassical Dynamics: the idea

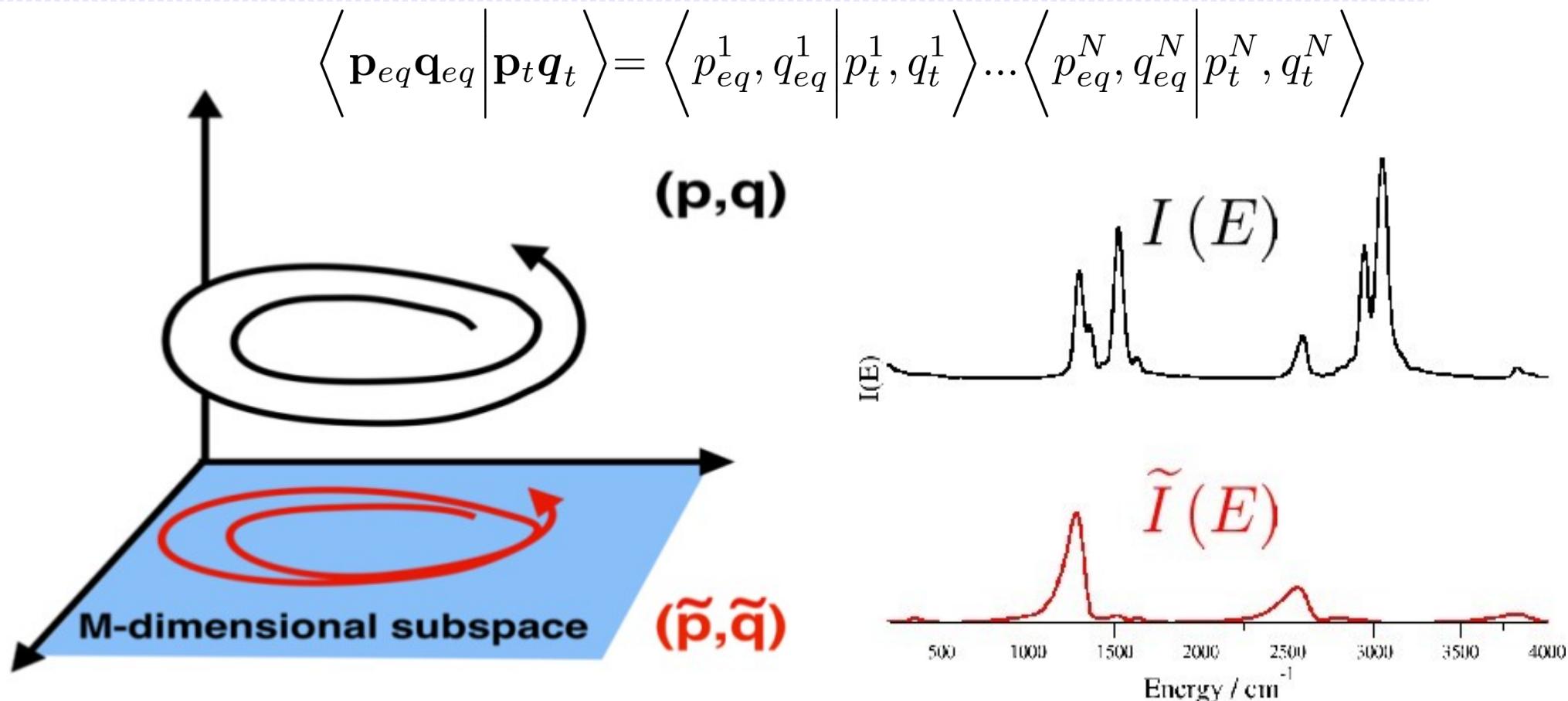
$$\left\langle \mathbf{p}_{eq} \mathbf{q}_{eq} \middle| \mathbf{p}_t \mathbf{q}_t \right\rangle = \left\langle p_{eq}^1, q_{eq}^1 \middle| p_t^1, q_t^1 \right\rangle \dots \left\langle p_{eq}^N, q_{eq}^N \middle| p_t^N, q_t^N \right\rangle$$

Divide-and-Conquer Semiclassical Dynamics: the idea

$$\left\langle \mathbf{p}_{eq} \mathbf{q}_{eq} \middle| \mathbf{p}_t \mathbf{q}_t \right\rangle = \left\langle p_{eq}^1, q_{eq}^1 \middle| p_t^1, q_t^1 \right\rangle \dots \left\langle p_{eq}^N, q_{eq}^N \middle| p_t^N, q_t^N \right\rangle$$



Divide-and-Conquer Semiclassical Dynamics: the idea

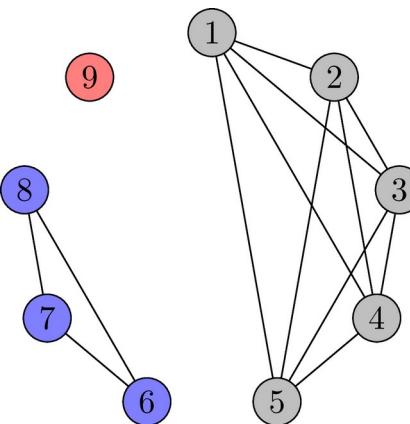


$$\tilde{I}(E) = \left(\frac{1}{2\pi\hbar} \right)^M \int \int d\tilde{\mathbf{p}}_0 d\tilde{\mathbf{q}}_0 \frac{1}{2\pi\hbar T} \left| \int_0^T e^{\frac{i}{\hbar} [\tilde{S}_t(\tilde{\mathbf{p}}_0, \tilde{\mathbf{q}}_0) + Et + \tilde{\phi}_t]} \langle \tilde{\chi} | \tilde{\mathbf{p}}_t \tilde{\mathbf{q}}_t \rangle dt \right|^2$$

The semiclassical partial spectra are obtained from subspace projected quantities, while the classical dynamics is full dimensional

Divide-and-Conquer Semiclassical Dynamics: Subspace partition

A Probability Graph-Evolutionary Algorithm PG-EA



$$\mathbf{C} = \begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

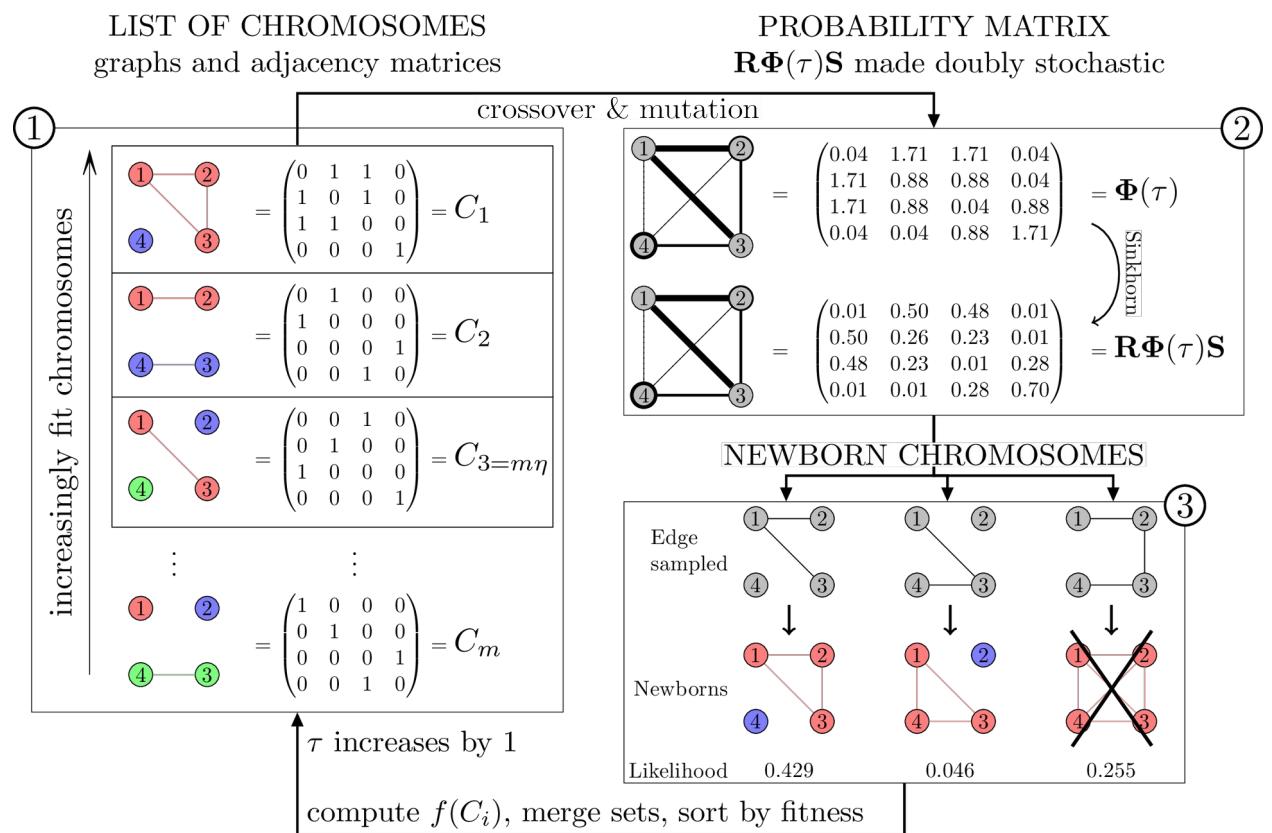
Graph representation of subspace subdivision between normal modes

Fitness function

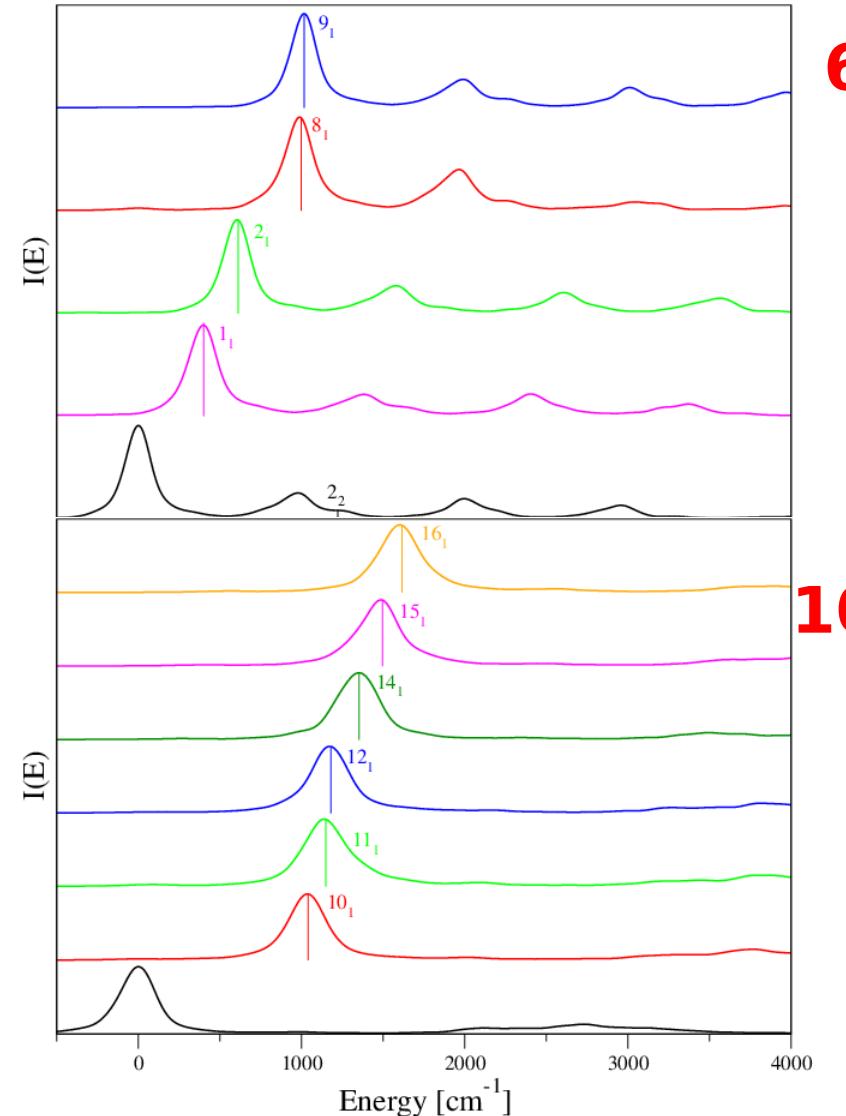
$$\prod_{i=1}^n \det \tilde{\mathbf{J}}_i \approx 1$$



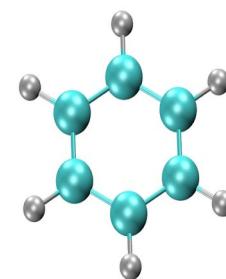
$$f(C) = \frac{1}{N} \sum_{\text{steps } s \in S}^N \sum \left| 1 - \left| \det(\tilde{J}_s) \right| \right|$$



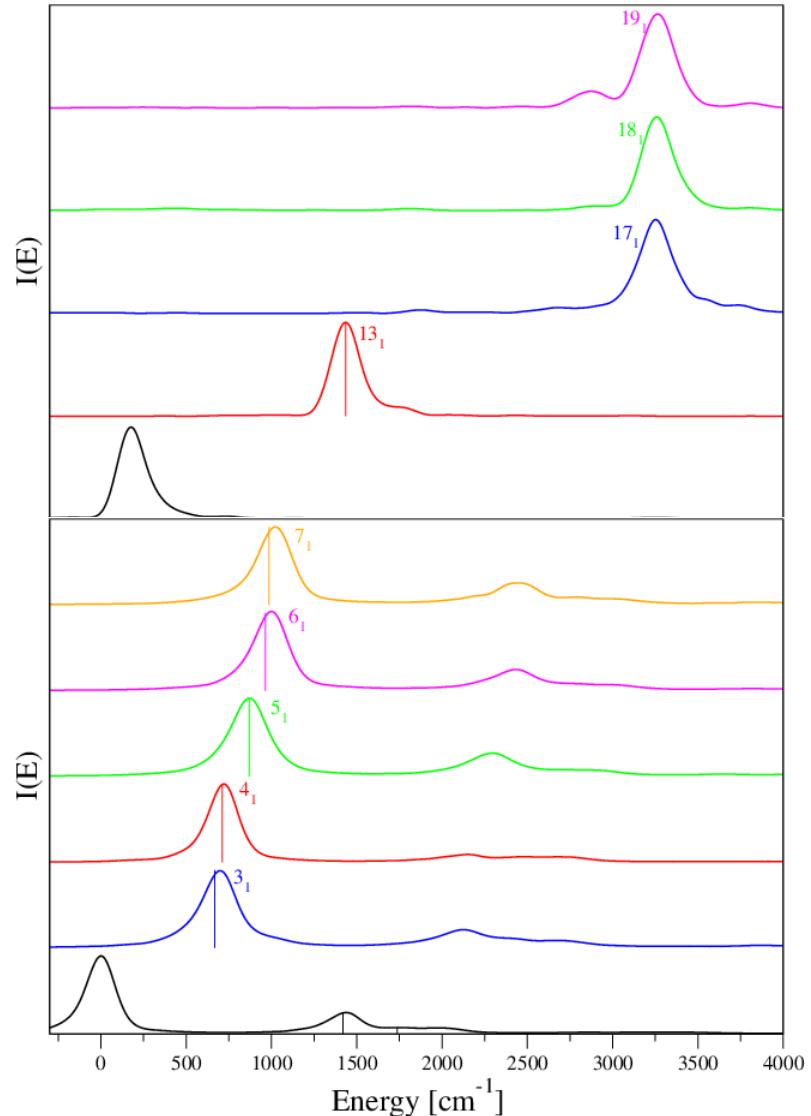
Divide-and-Conquer Semiclassical Dynamics: Benzene



6D



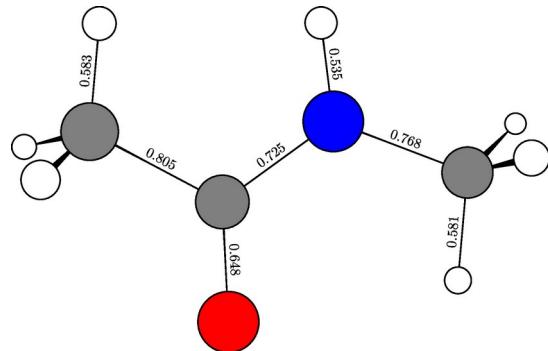
10D



7D

Vertical Lines are the exact values from T. Halverson and B. Poirier, J. Phys. Chem. A 119, 12417 (2015)
MAE from exact: 9 cm⁻¹

Divide-and-Conquer SC Dynamics: Trans-N-methylacetamide



Permutationally invariant B3LYP/cc-pVDZ full-PES

C. Qu and J. M. Bowman, J. Chem Phys. **150**, 141101 (2019)

Three subspaces obtained with the **Evolutionary Algorithm**:

A = (3, 5, 7, 10, 11, 12, 15, 21, 23, 26, 28, 30)

B = (4, 9, 14, 16, 17, 18, 19, 22, 24, 25, 27, 29)

C = (6, 8, 13, 20)

Amide II: NH bend

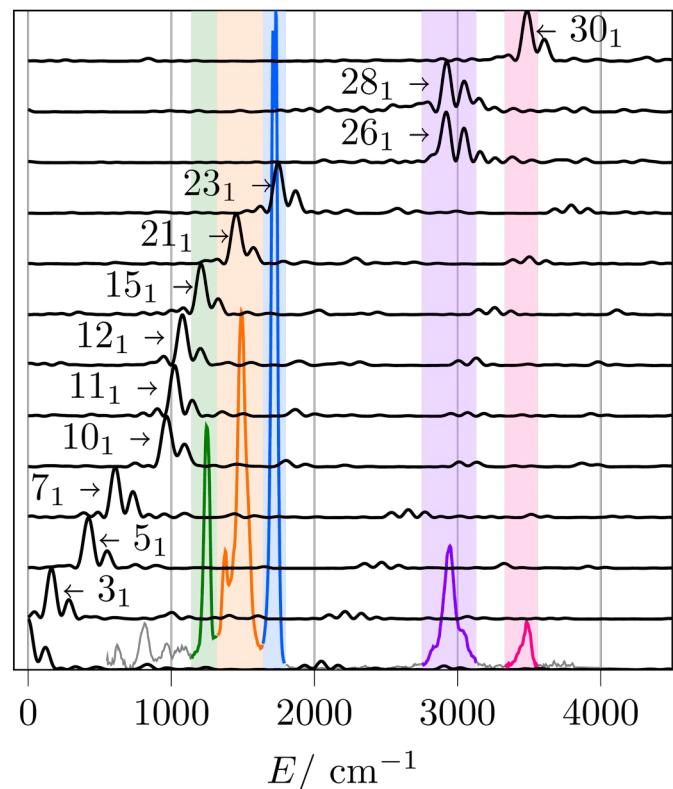
II: -CH₃ umbr, wag, bend; CN stretch

I: CO stretch

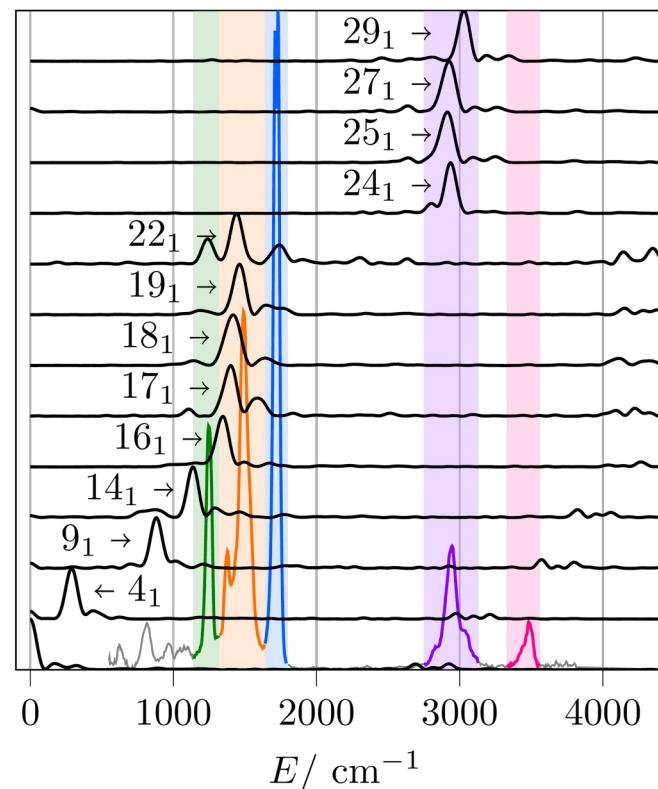
-CH₃ stretch

A: NH stretch

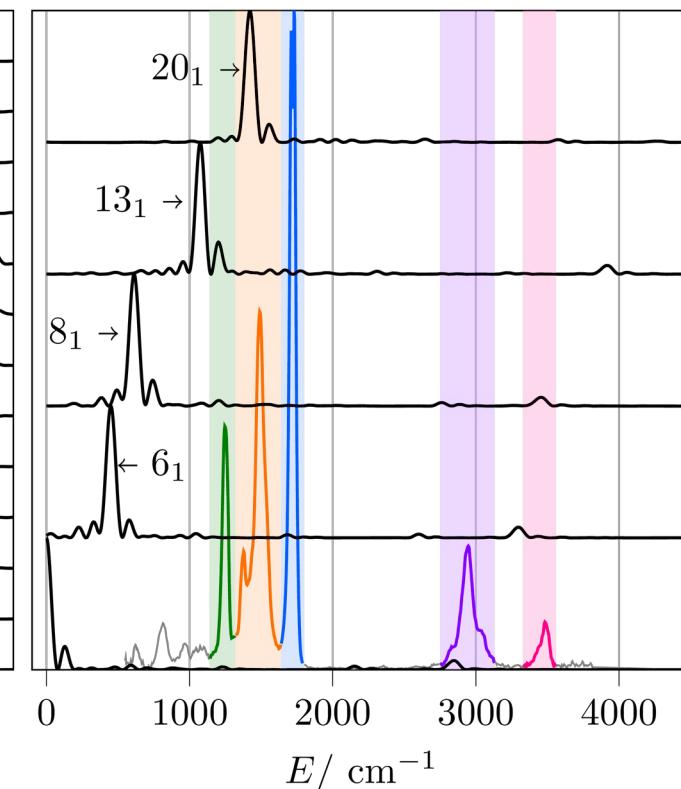
(a) PG-EA A



(b) PG-EA B

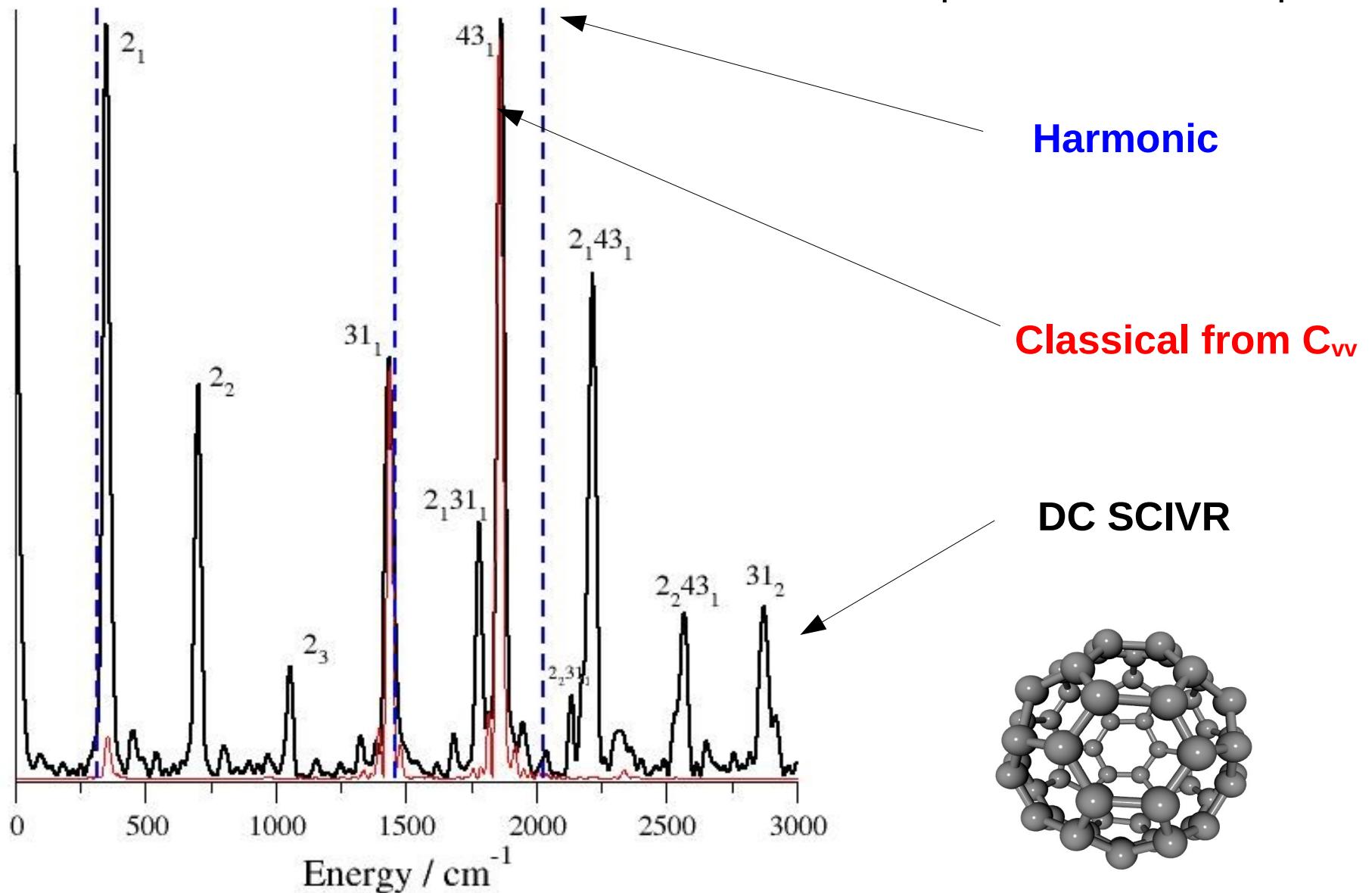


(c) PG-EA C

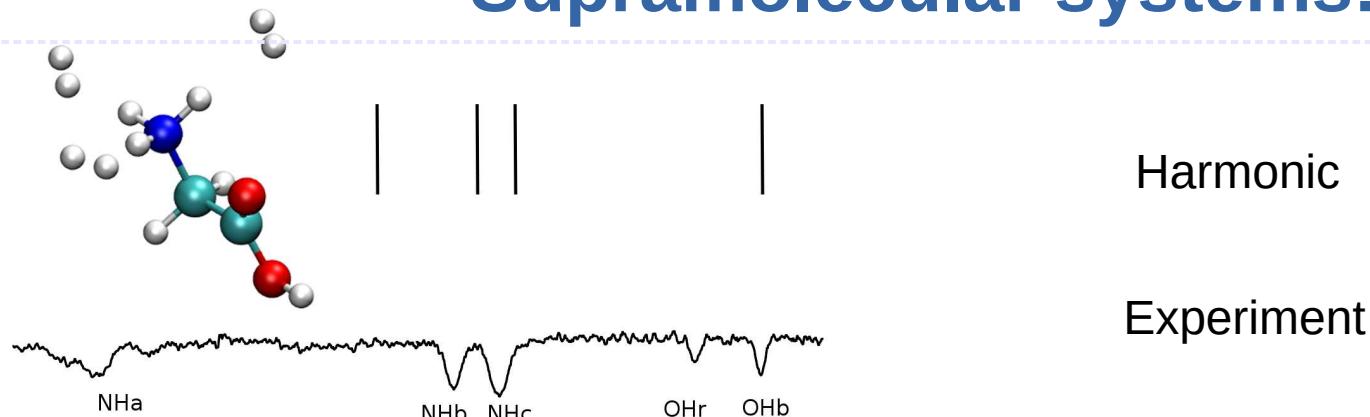


Divide-and-Conquer Semiclassical Dynamics: C₆₀ Fullerene

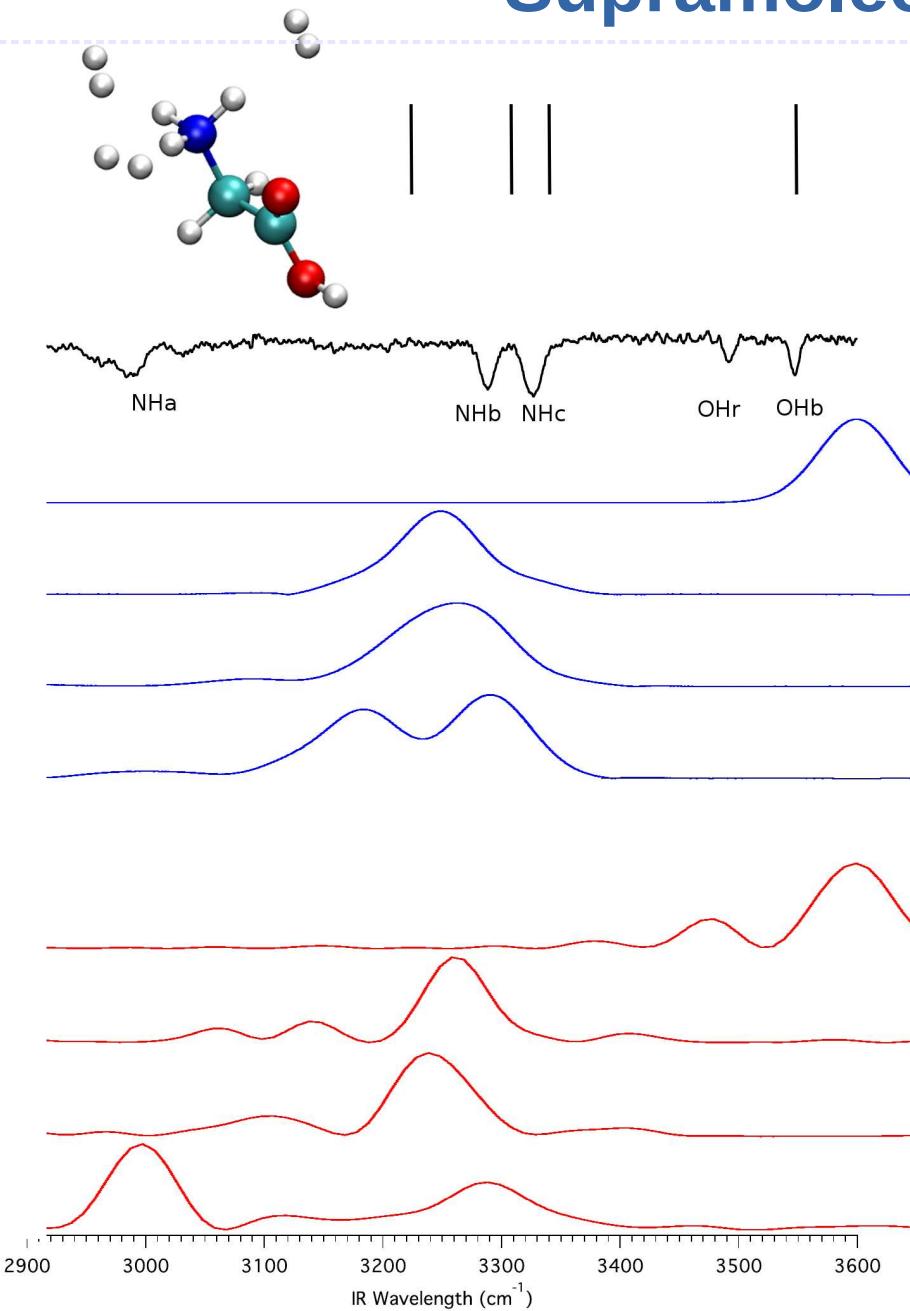
The spectrum of a subspace



Supramolecular systems: (GlyH + 3H₂)⁺



Supramolecular systems: (GlyH + 3H₂)⁺



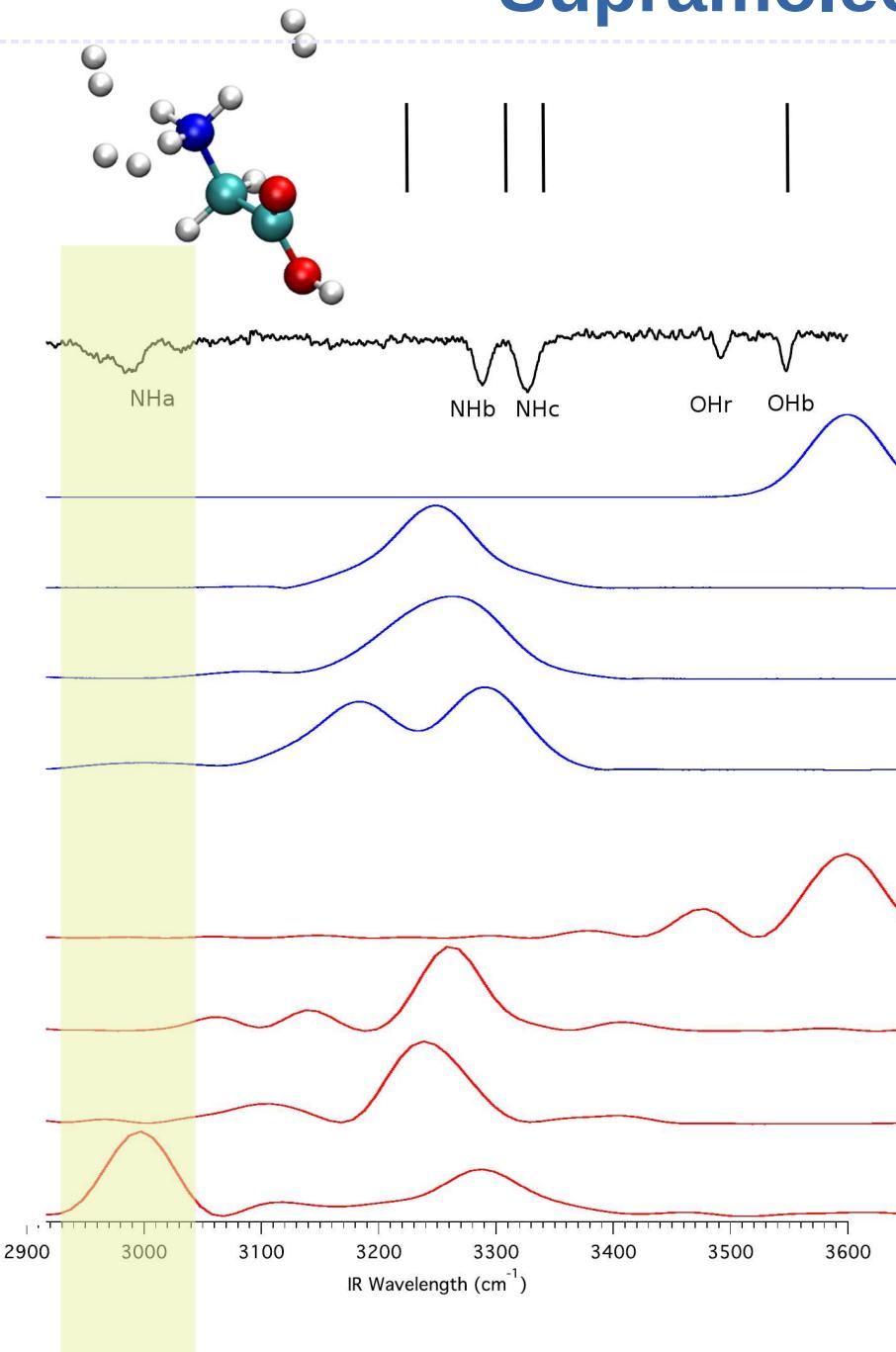
Harmonic

Experiment

Classical

Semiclassical:
Divide-and Conquer SCIVR

Supramolecular systems: (GlyH + 3H₂)⁺



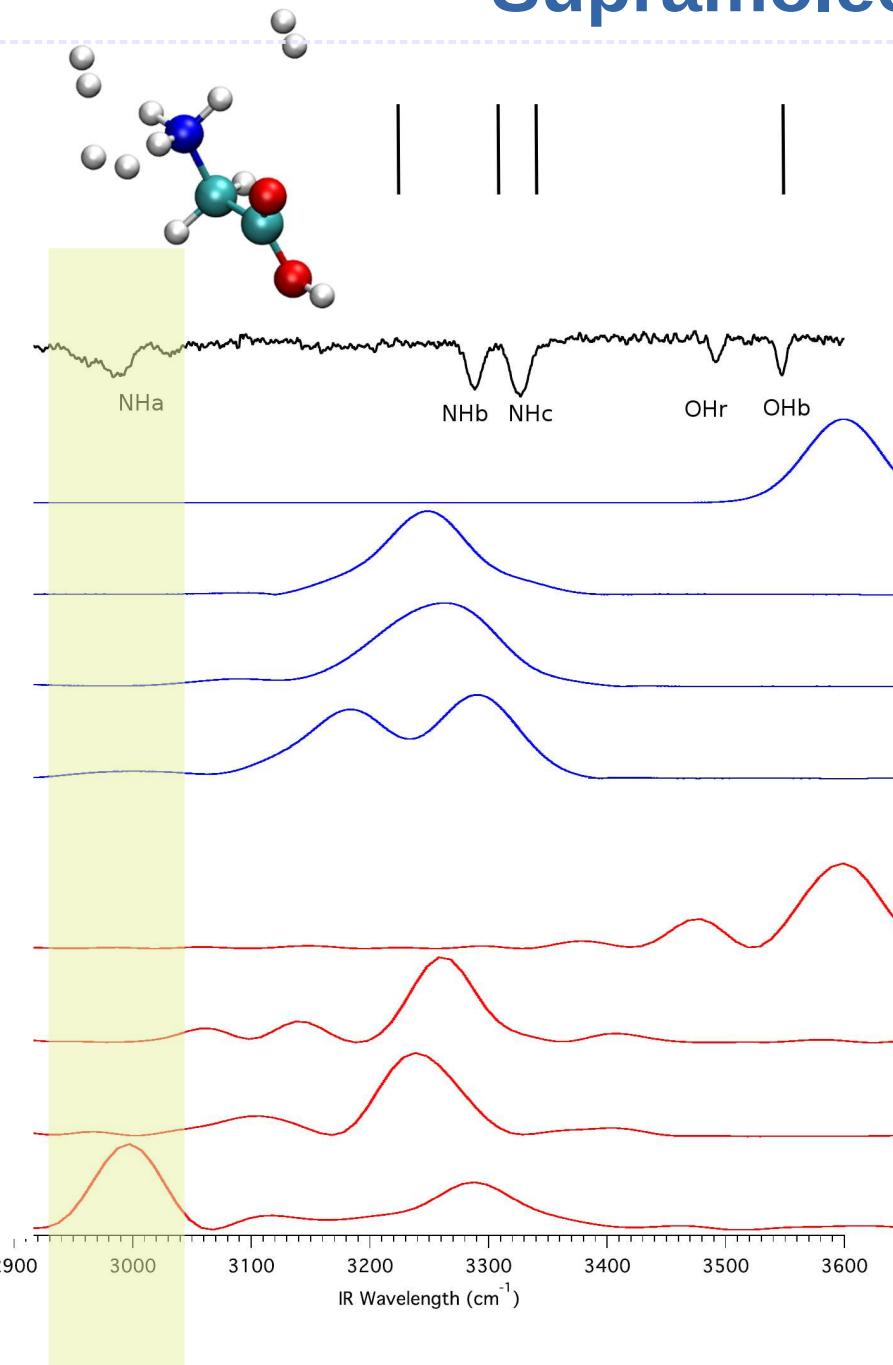
Harmonic

Experiment

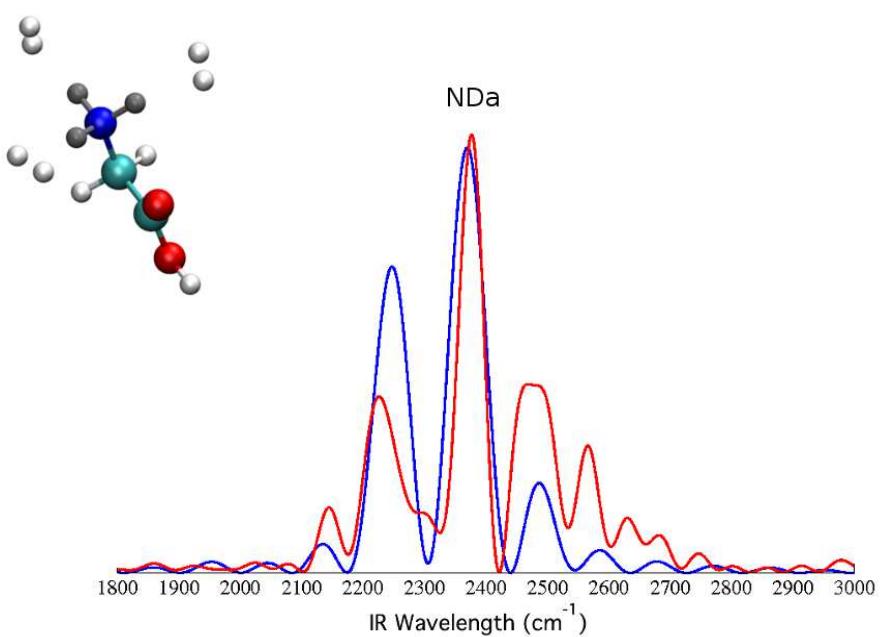
Classical

Semiclassical:
Divide-and Conquer SCIVR

Supramolecular systems: (GlyH + 3H₂)⁺

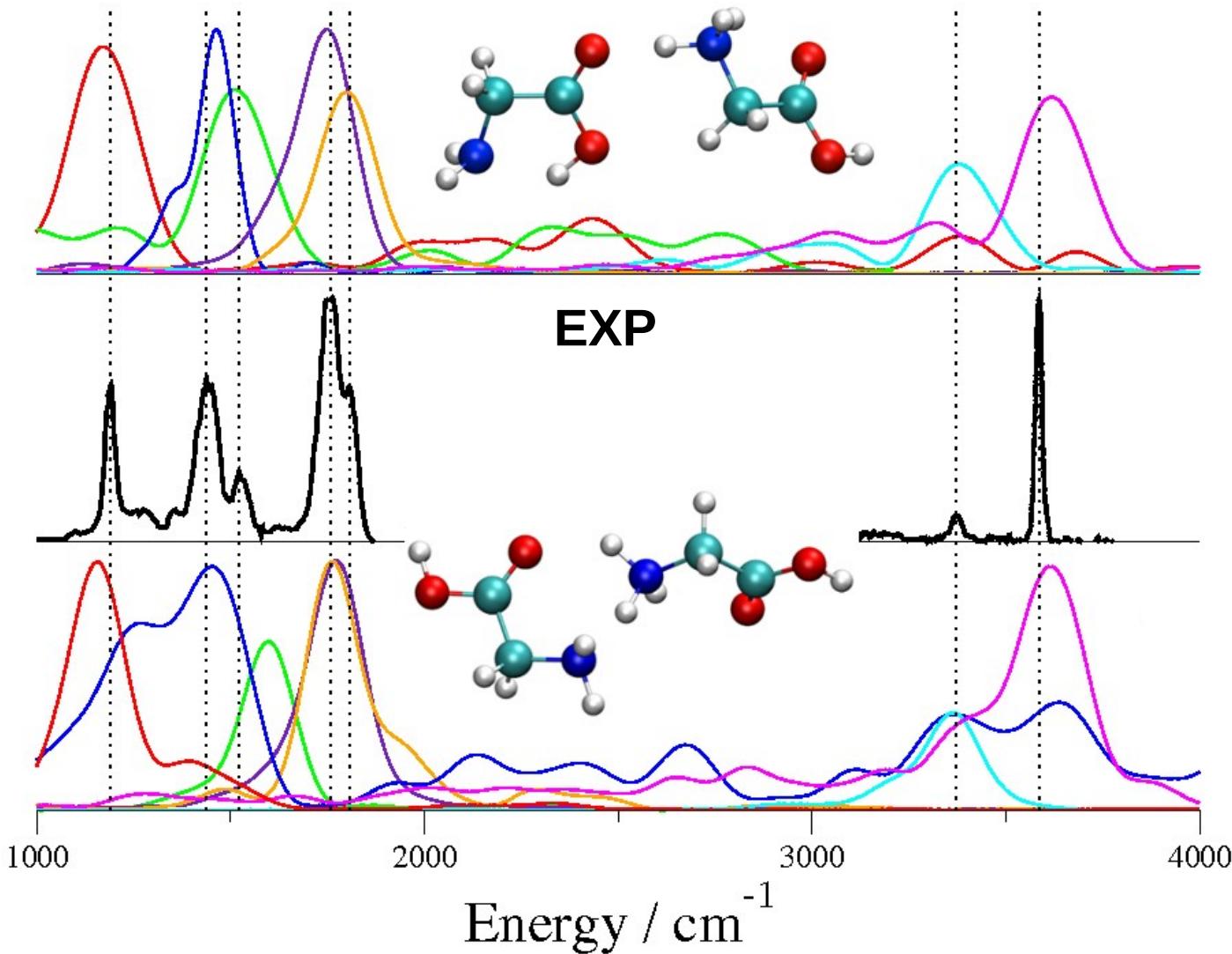


Classical vs semiclassical
after deuteration



Protonated Glycine dimer (Gly_2H^+)

DFT B3LYP/6311+G(d,p)

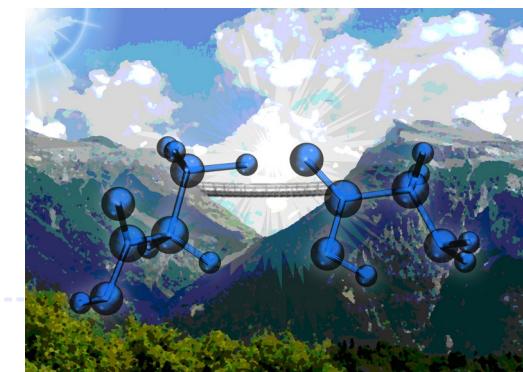


CS01

MAE 14 cm^{-1}

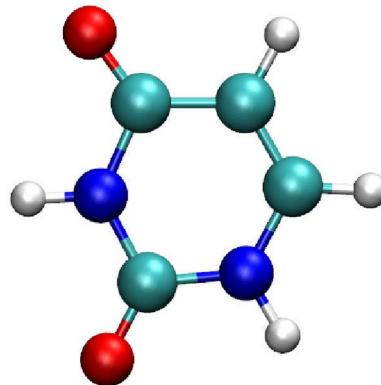
CS02

MAE 32 cm^{-1}

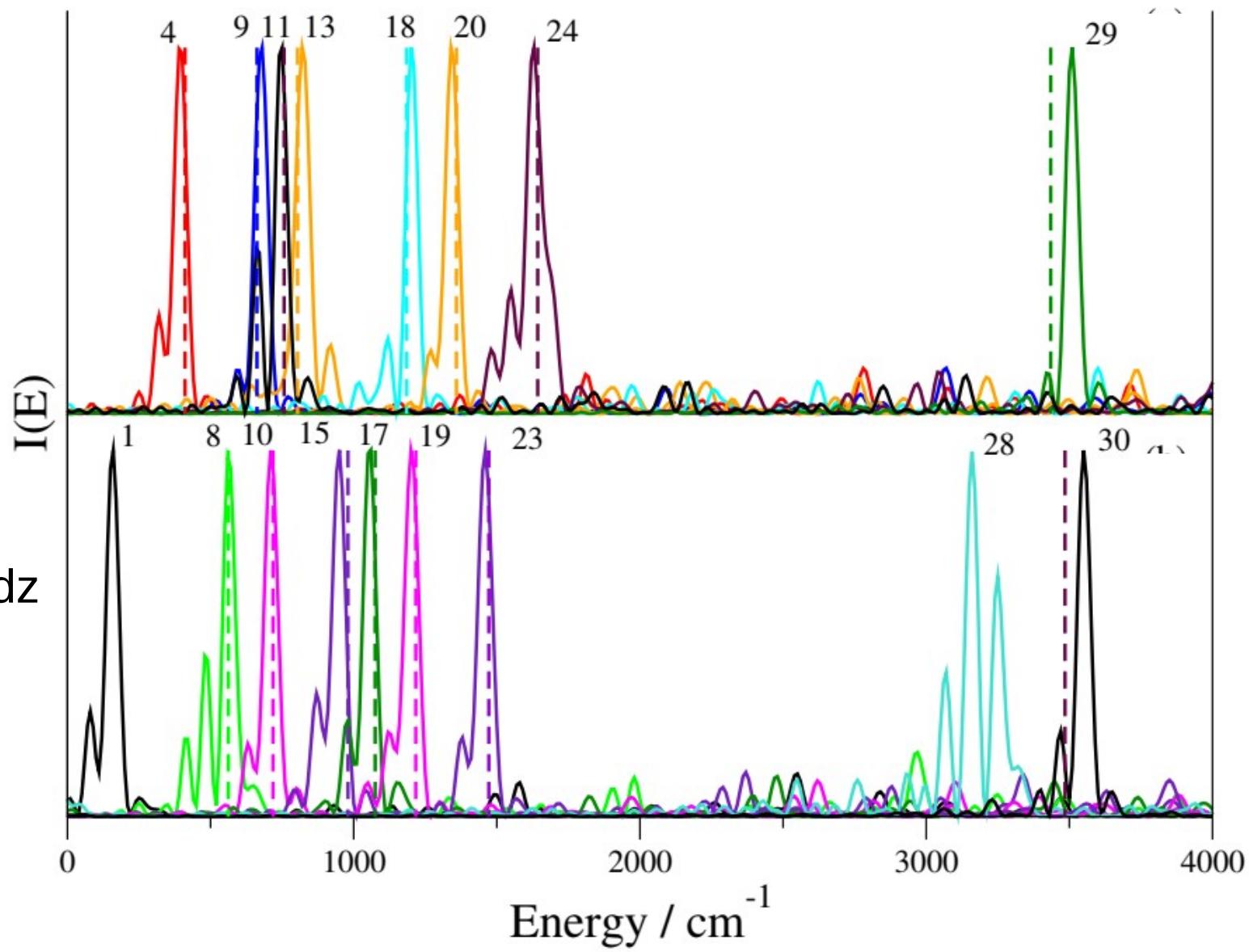


A vibrational spectroscopic view at nucleobases: Uracile

17D subspace



DFT
B3LYP/aug-cc-pvdz
time = 25000 a.u.

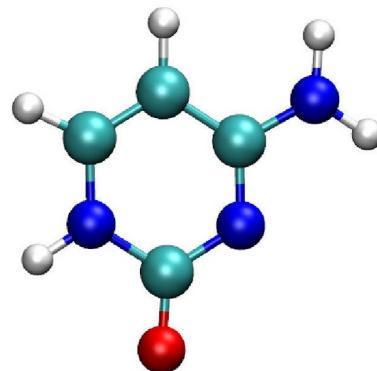


Mean Absolute Error (MAE) = 20 cm⁻¹

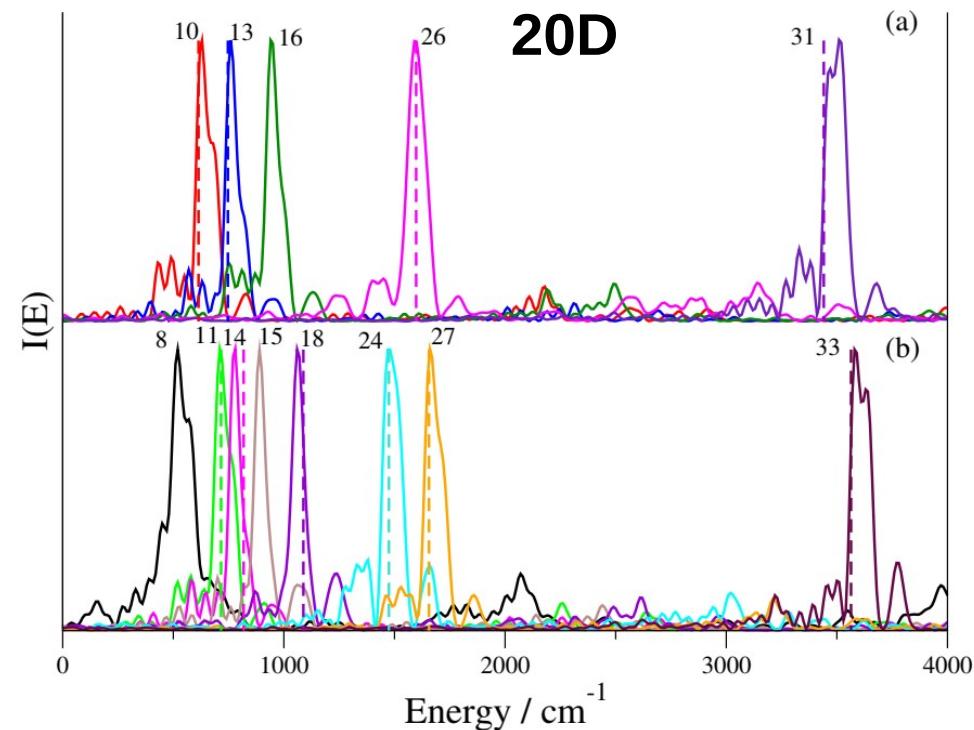
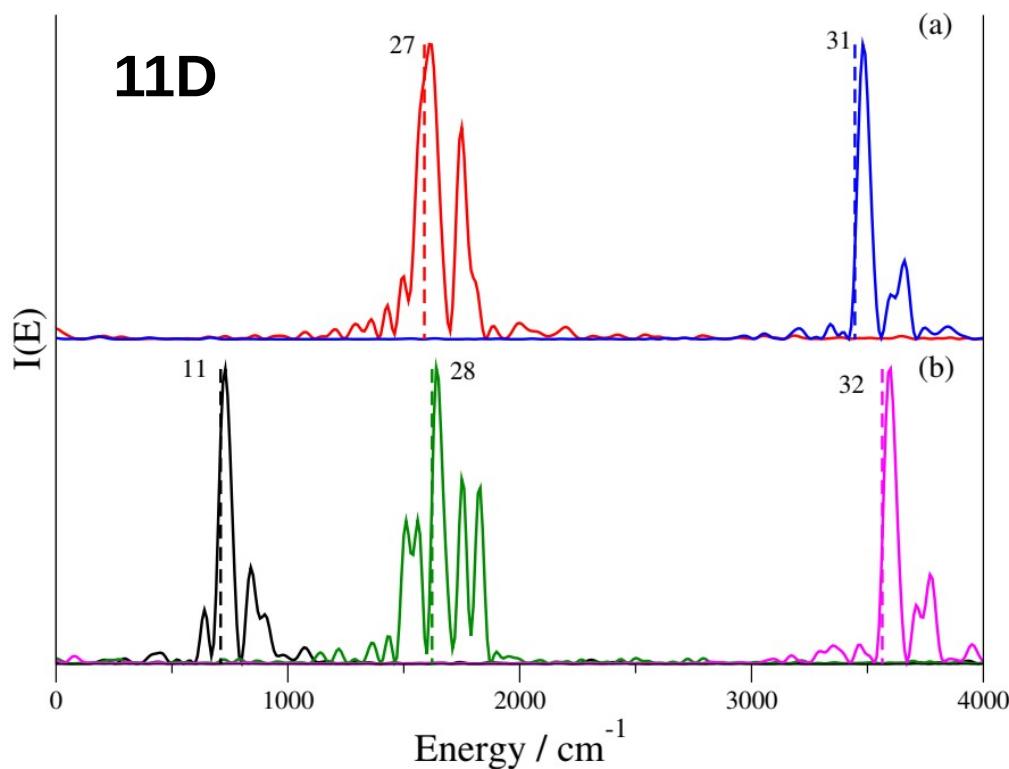
A vibrational spectroscopic view at nucleobases: Cytosine

Oxocytosine

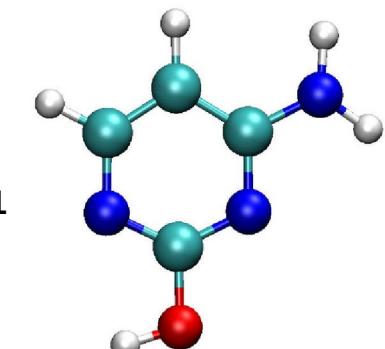
MAE = 13 cm⁻¹



11D



Hydroxycytosine

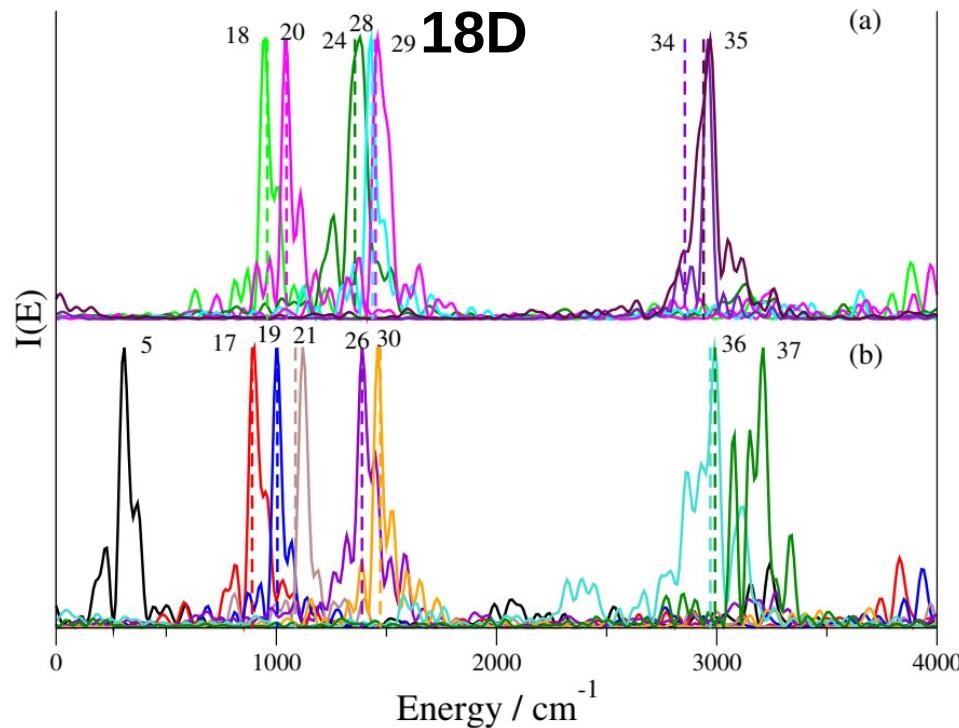
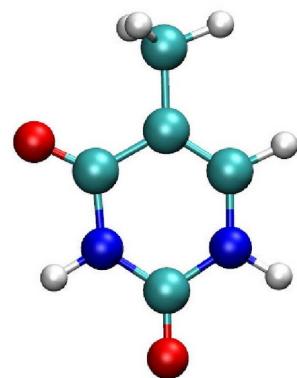
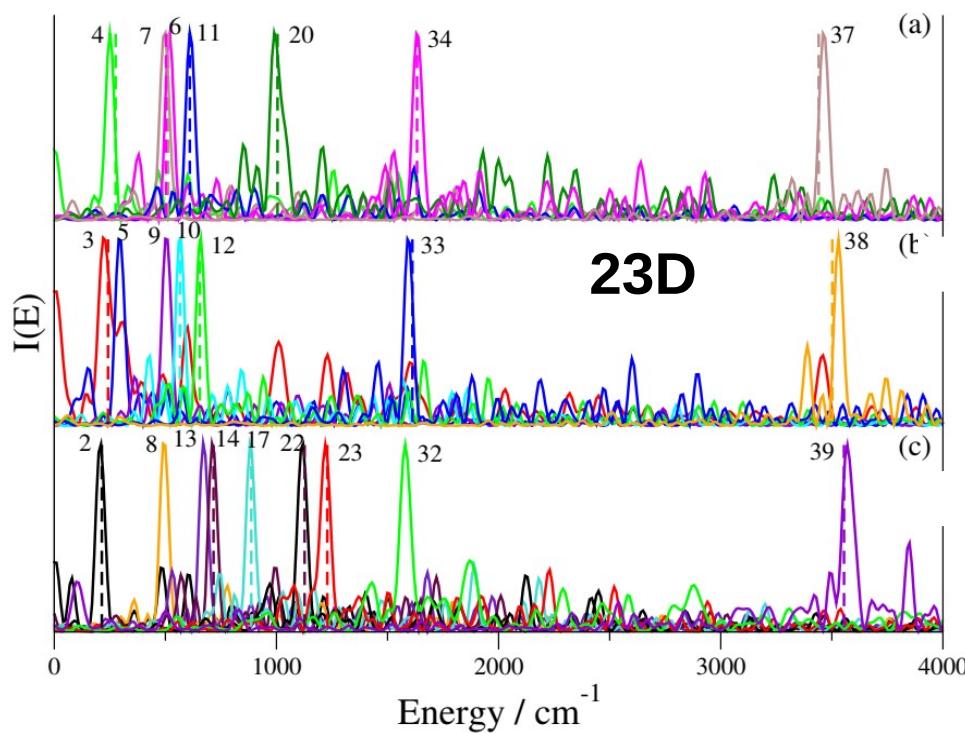


MAE = 16 cm⁻¹

A vibrational spectroscopic view at nucleobases: Thymine, Adenine

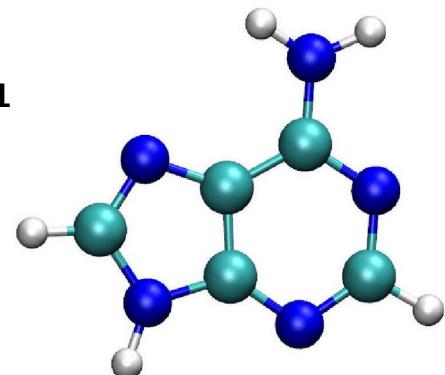
Thymine

MAE = 17 cm⁻¹



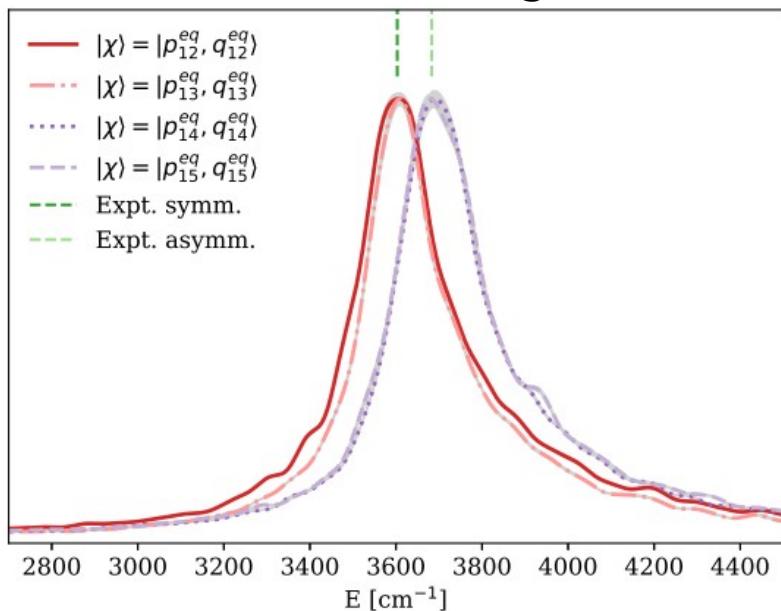
Adenine

MAE = 16 cm⁻¹

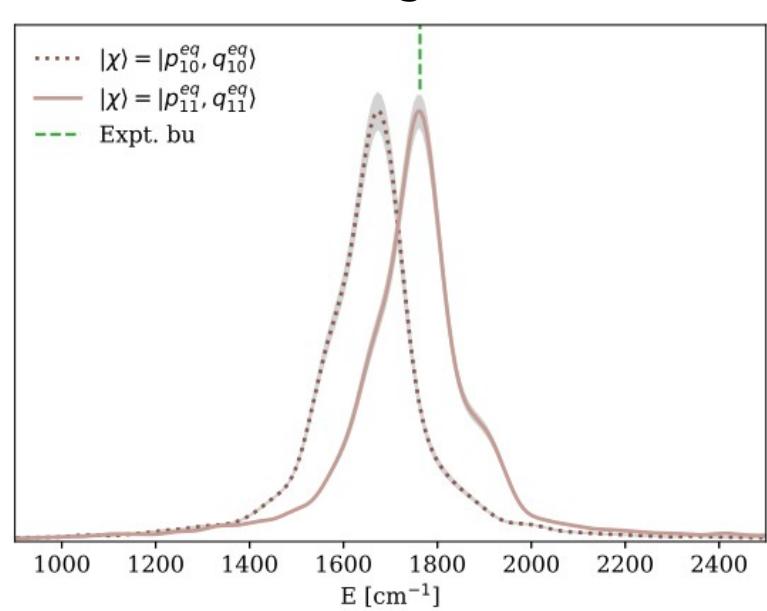


Semiclassical power spectra for floppy molecules: Zundel cation

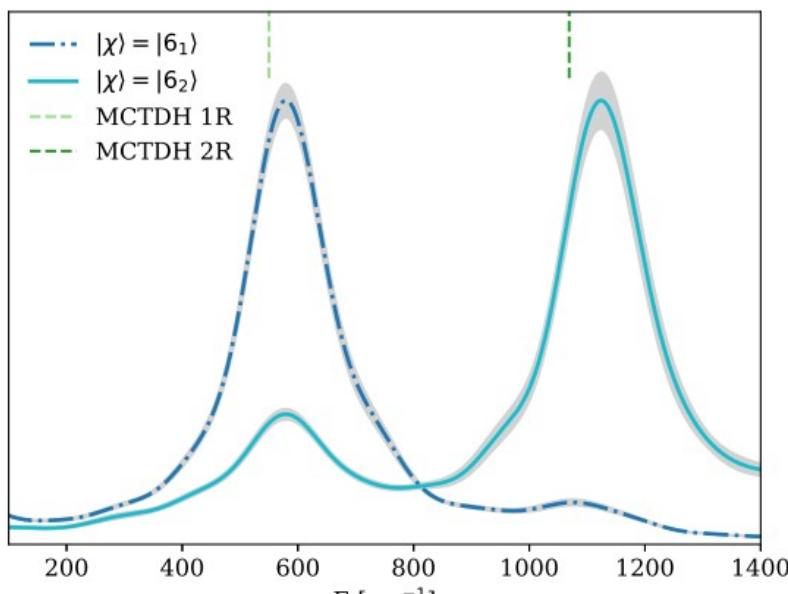
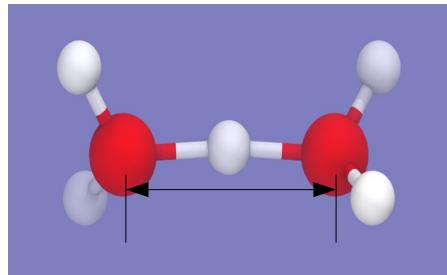
Stretchings



Bendings



O-O stretchings



Zundel cation: analyzing the proton transfer

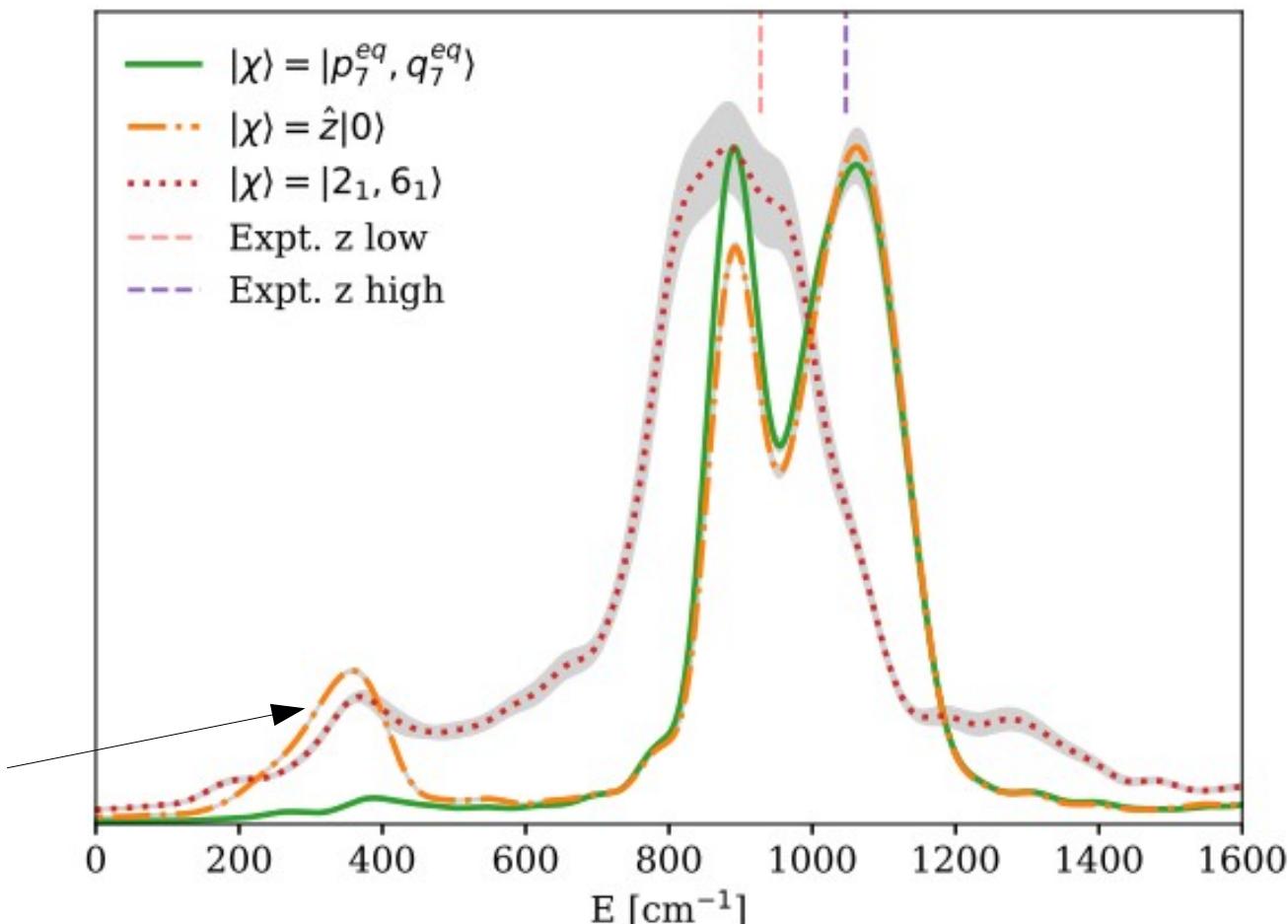
1. $|\chi\rangle \approx |q_7^{eq}, p_7^{eq}\rangle$

2. $|0\rangle \approx |q^{eq}, p^{eq} = 0\rangle$

$$\hat{z} = \sum_i L_{zi} \hat{Q}_i$$



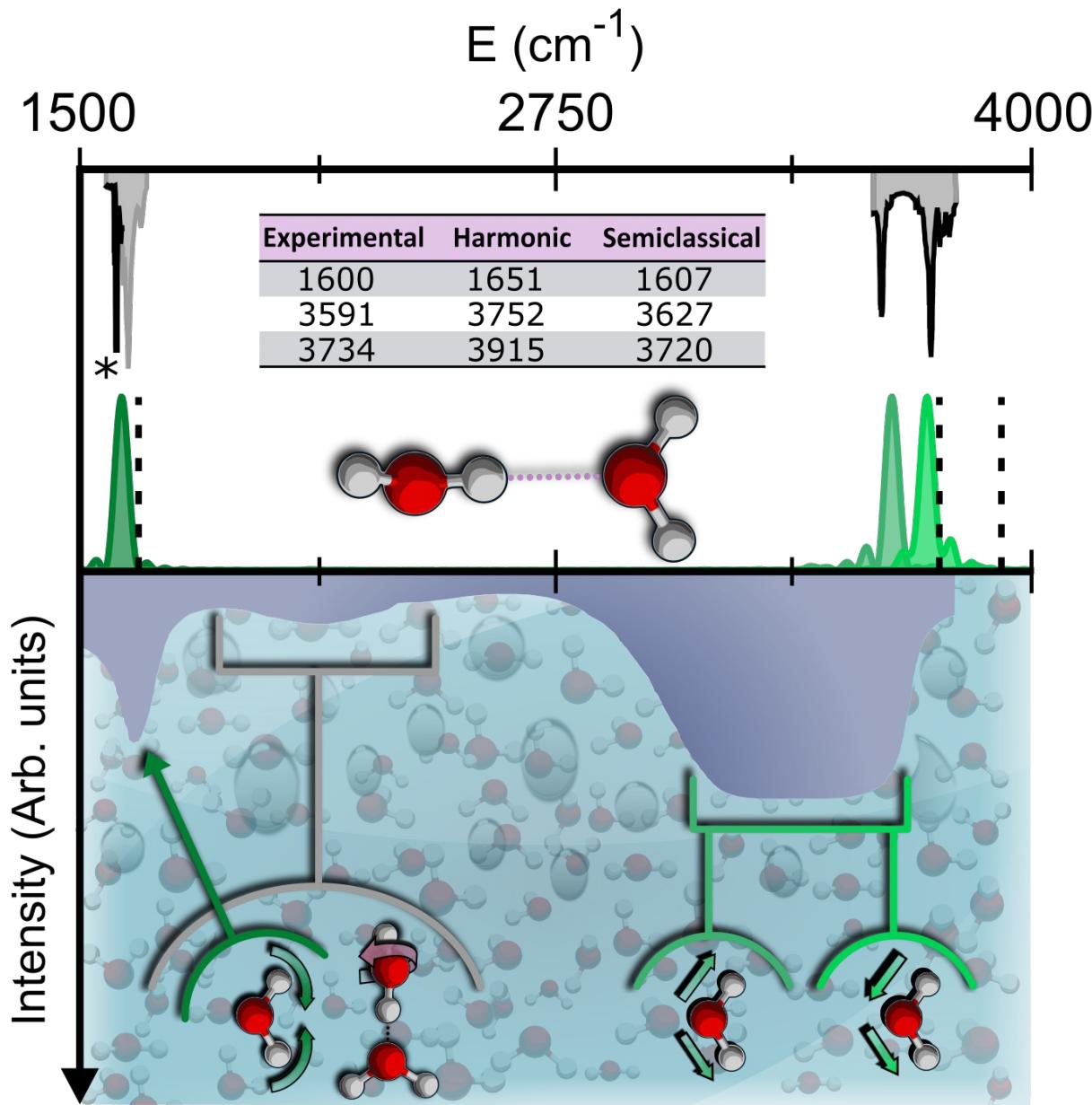
$$\langle 0 | \hat{z} \hat{z}(t) | 0 \rangle \approx \langle 0 | \hat{z} \mathcal{P}_{HK}(t) \hat{z} | 0 \rangle e^{\frac{i E_0 t}{\hbar}}$$



3. $\langle 2_1, 6_1 | \mathcal{P}_{HK}(t) | 2_1, 6_1 \rangle e^{\frac{i E_0 t}{\hbar}}$

Role of **wagging** + **OO stretching** in “Transfer low” peak. See [Vendrell, Gatti, and Meyer, JCP 127, 184303 (2007)]

How many water molecules are needed to solvate one?



Expt. Water Dimer

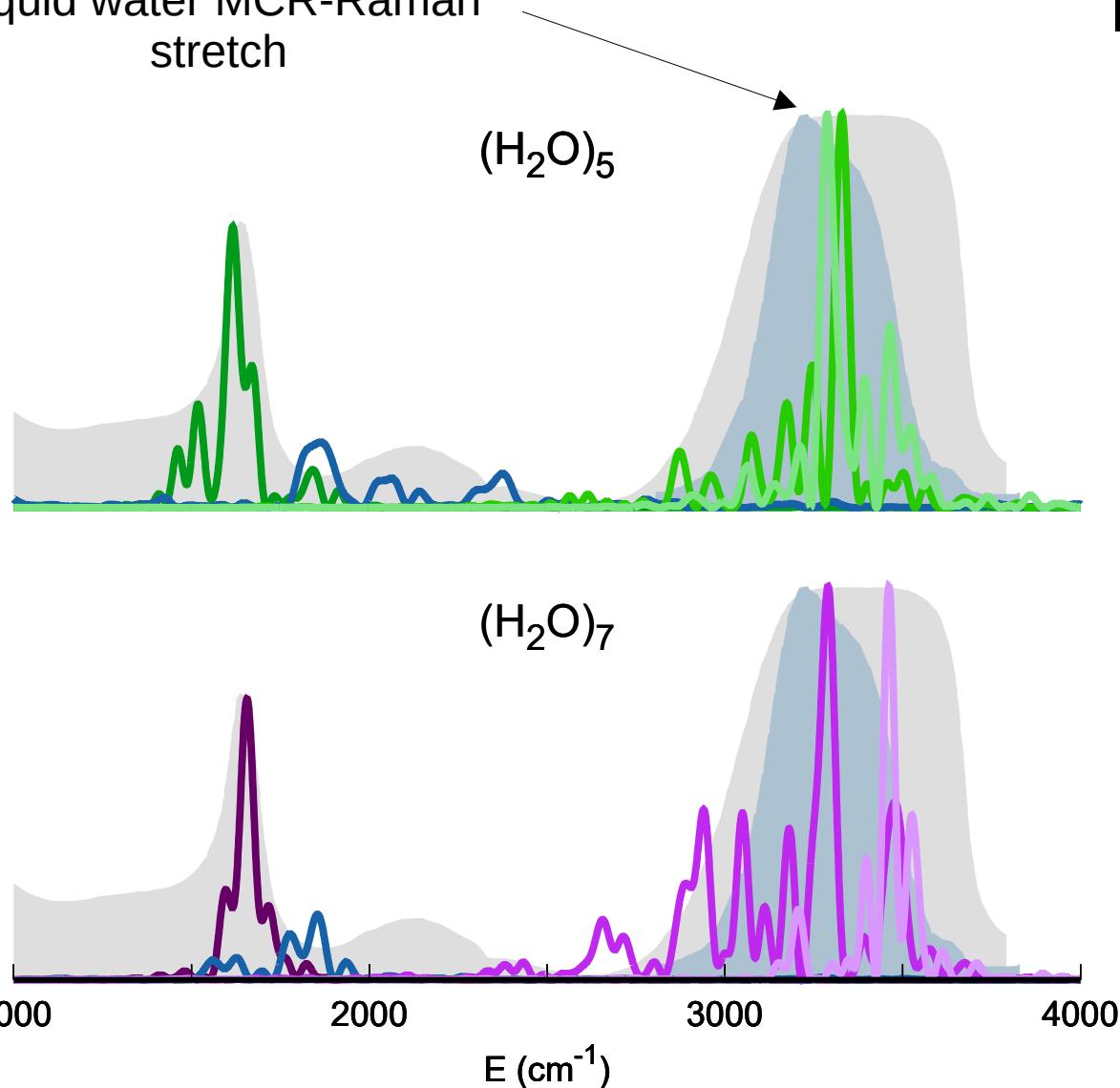
Semiclassical Theory
Water Dimer

Expt. Liquid Water

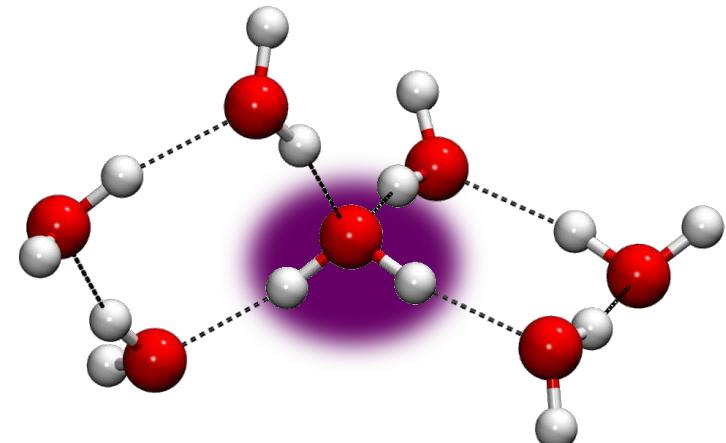
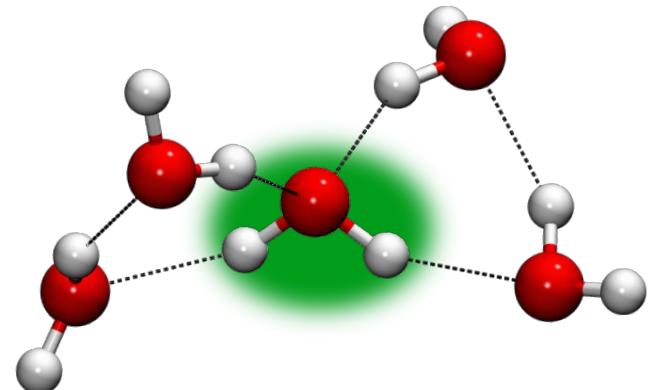
Liquid Water Modes

How many water molecules are needed to solvate one?

Liquid water MCR-Raman stretch

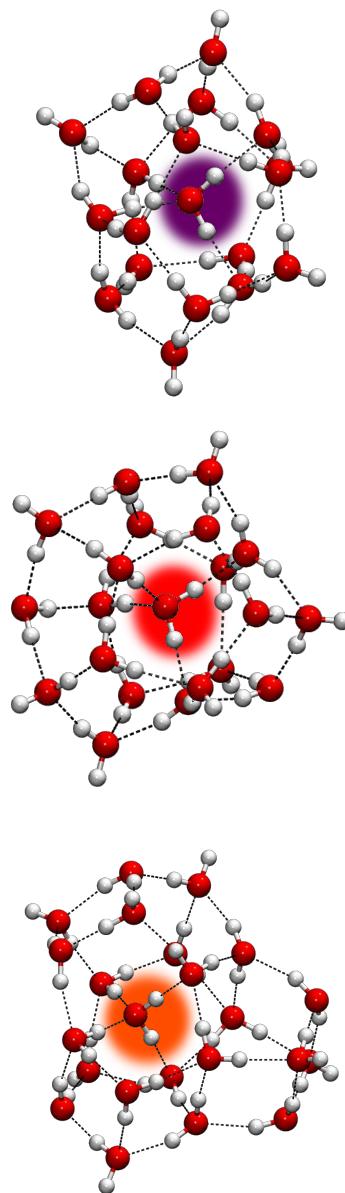
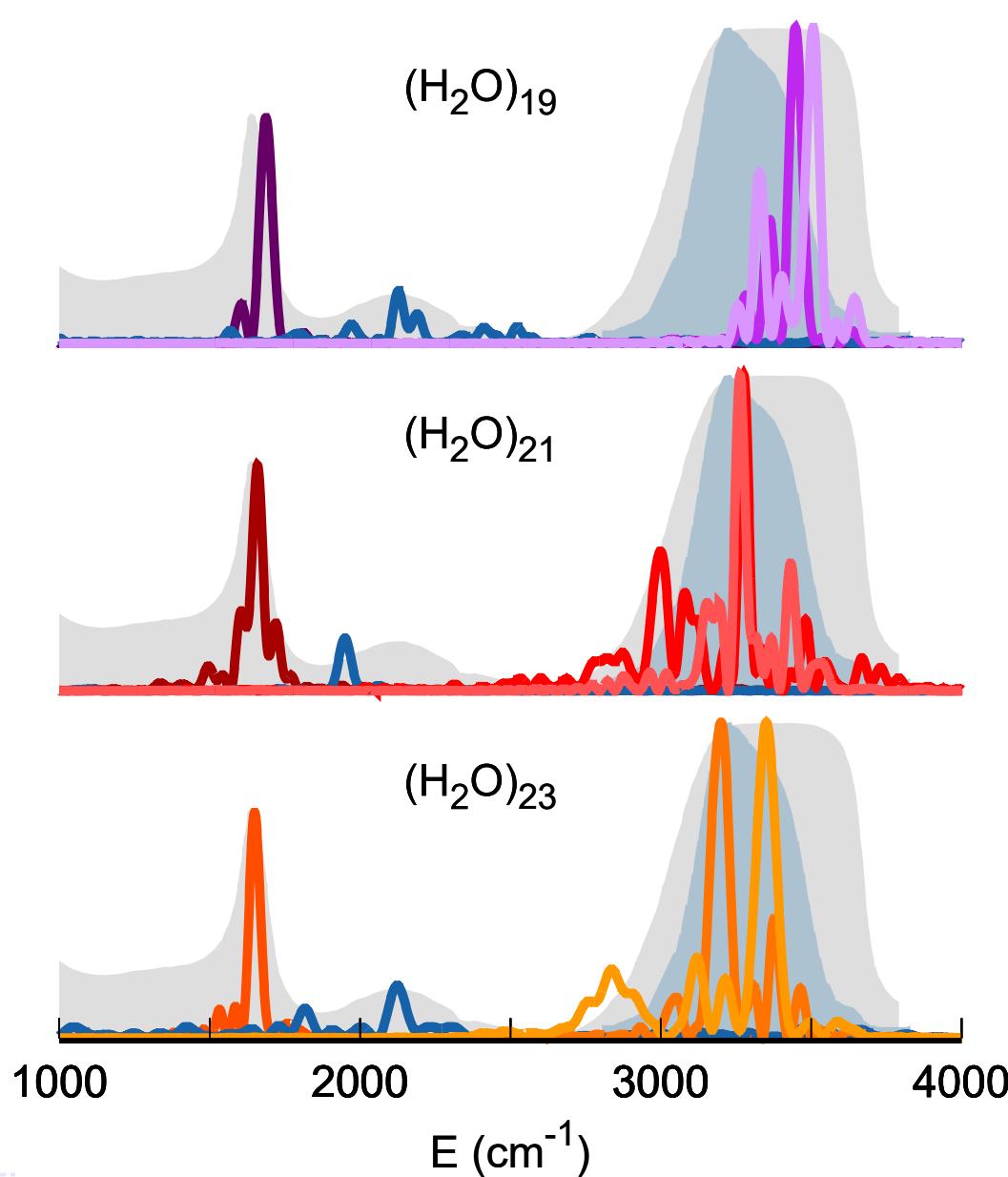


Is the tetrahedral conformation enough for solvation?



How many water molecules are needed to solvate one?

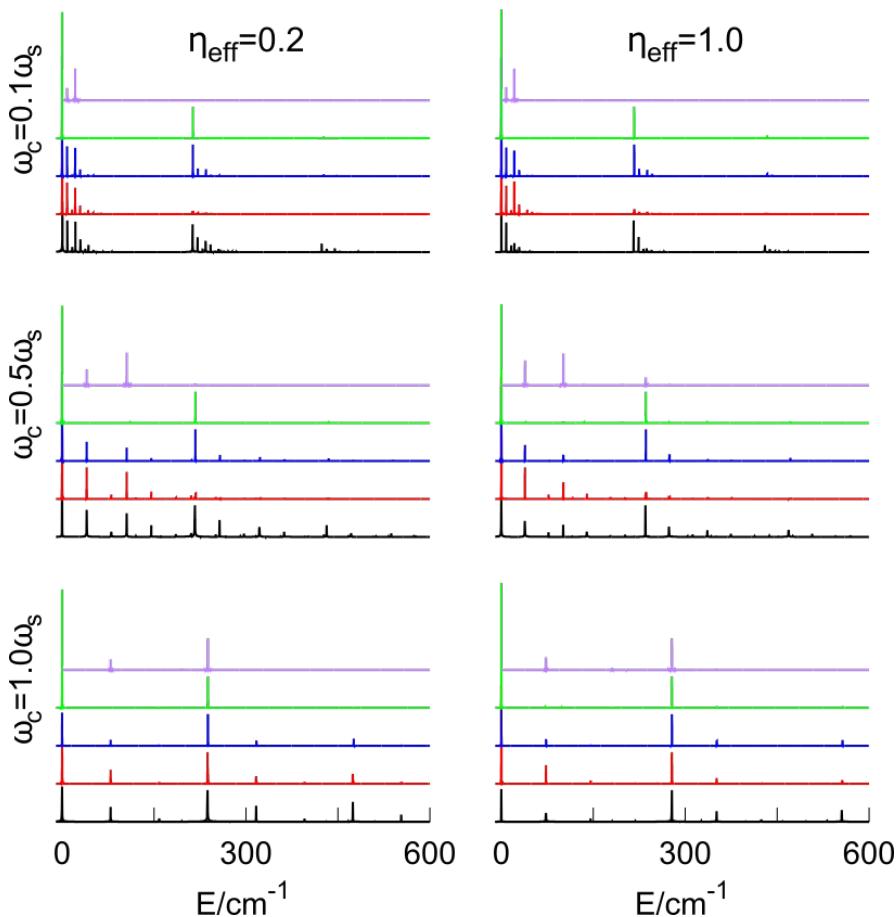
The answer is “at least 21”.



Ab initio vs model potential: the Caldeira-Leggett model

$$\mathcal{H} = \mathcal{H}_s + \sum_{i=1}^{F_b} \left\{ \frac{p_i^2}{2} + \frac{1}{2} \left[\omega_i y_i + \frac{c_i}{\omega_i} (s - s_{eq}) \right]^2 \right\}$$

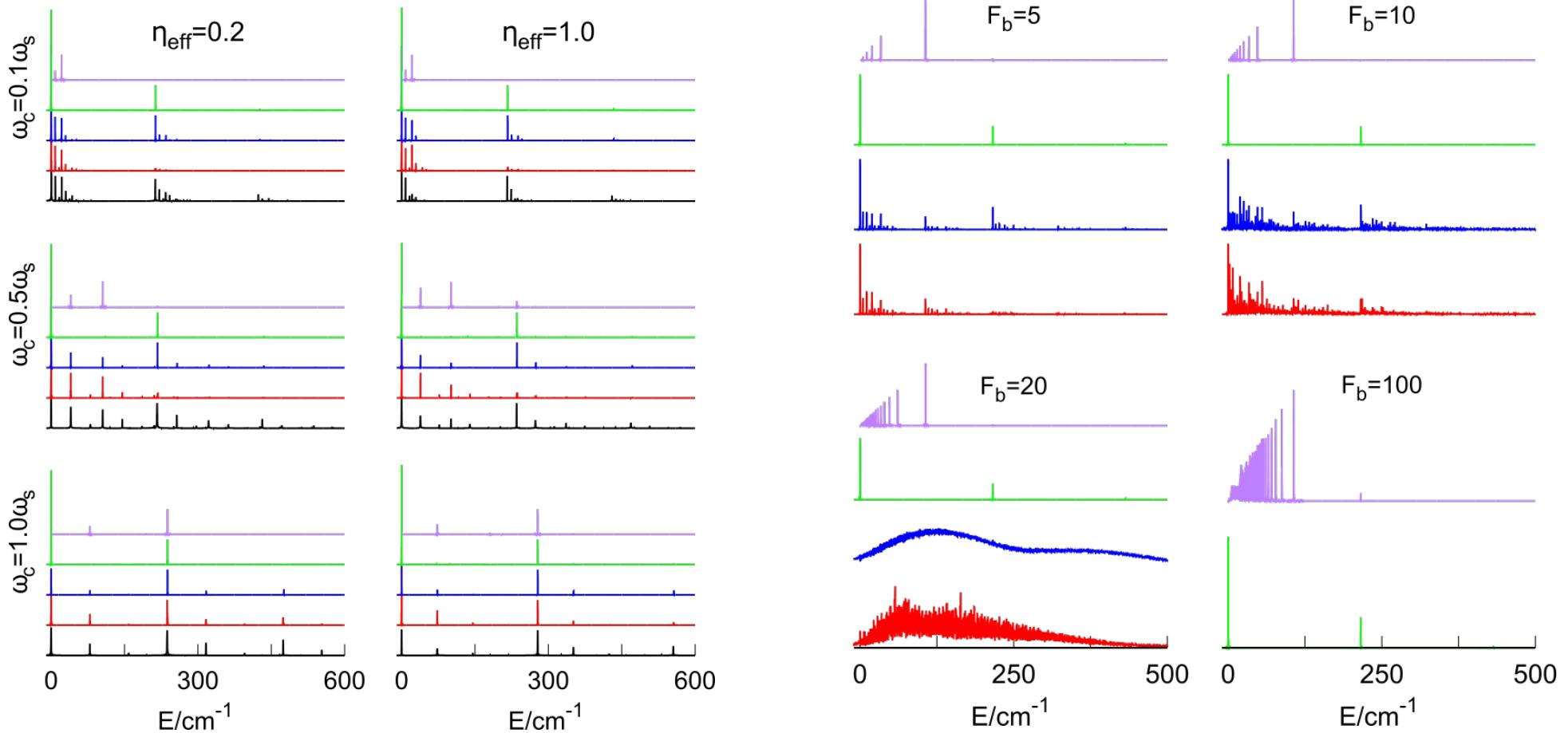
Bath quasiclassical	—
MC DC SCIVR	—
MC SCIVR	—
TA SCIVR 10^4 traj	—
QM	—



Ab initio vs model potential: the Caldeira-Leggett model

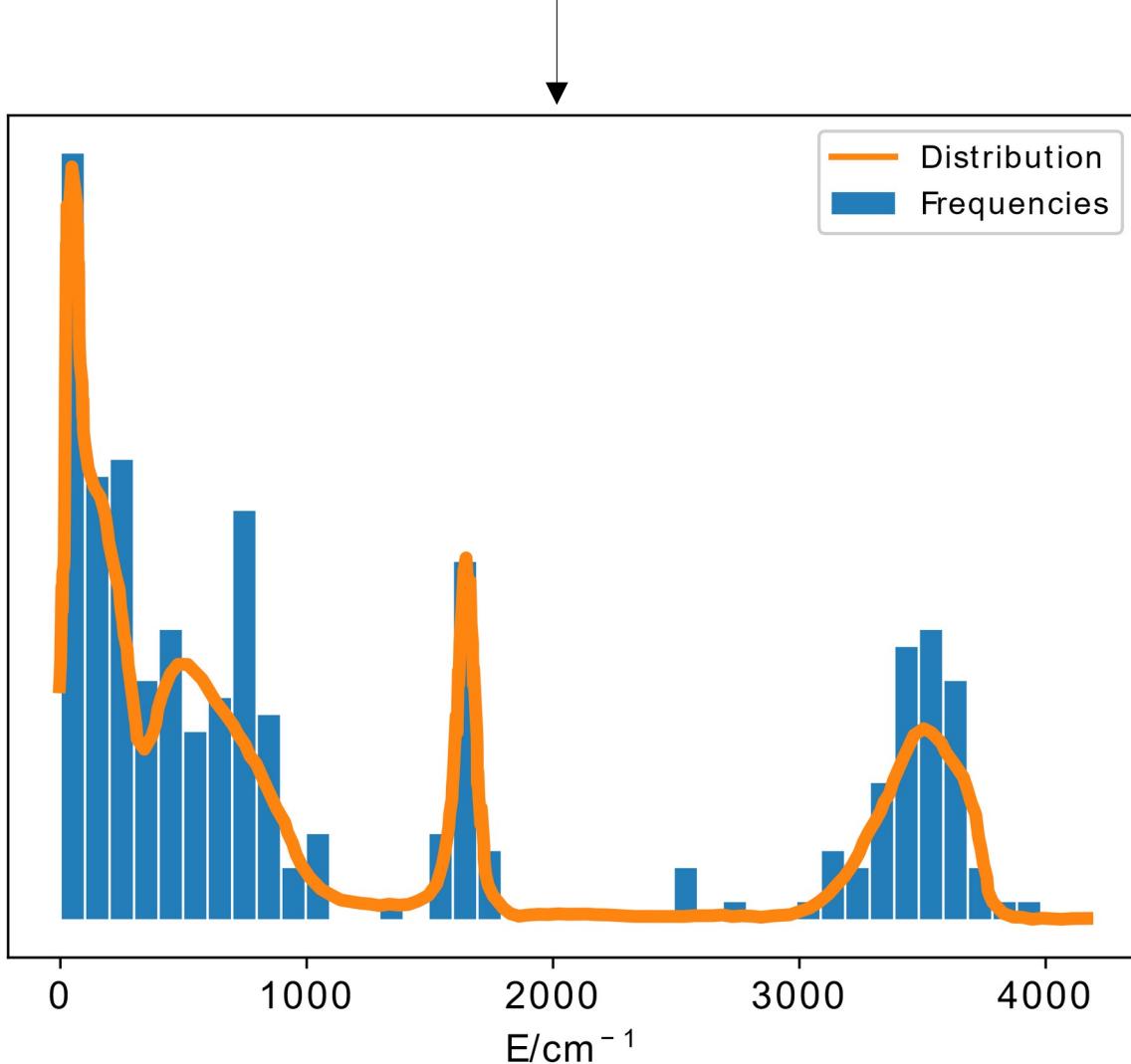
$$\mathcal{H} = \mathcal{H}_s + \sum_{i=1}^{F_b} \left\{ \frac{p_i^2}{2} + \frac{1}{2} \left[\omega_i y_i + \frac{c_i}{\omega_i} (s - s_{eq}) \right]^2 \right\}$$

Bath quasiclassical	—
MC DC SCIVR	—
MC SCIVR	—
TA SCIVR 10 ⁴ traj	—
QM	—

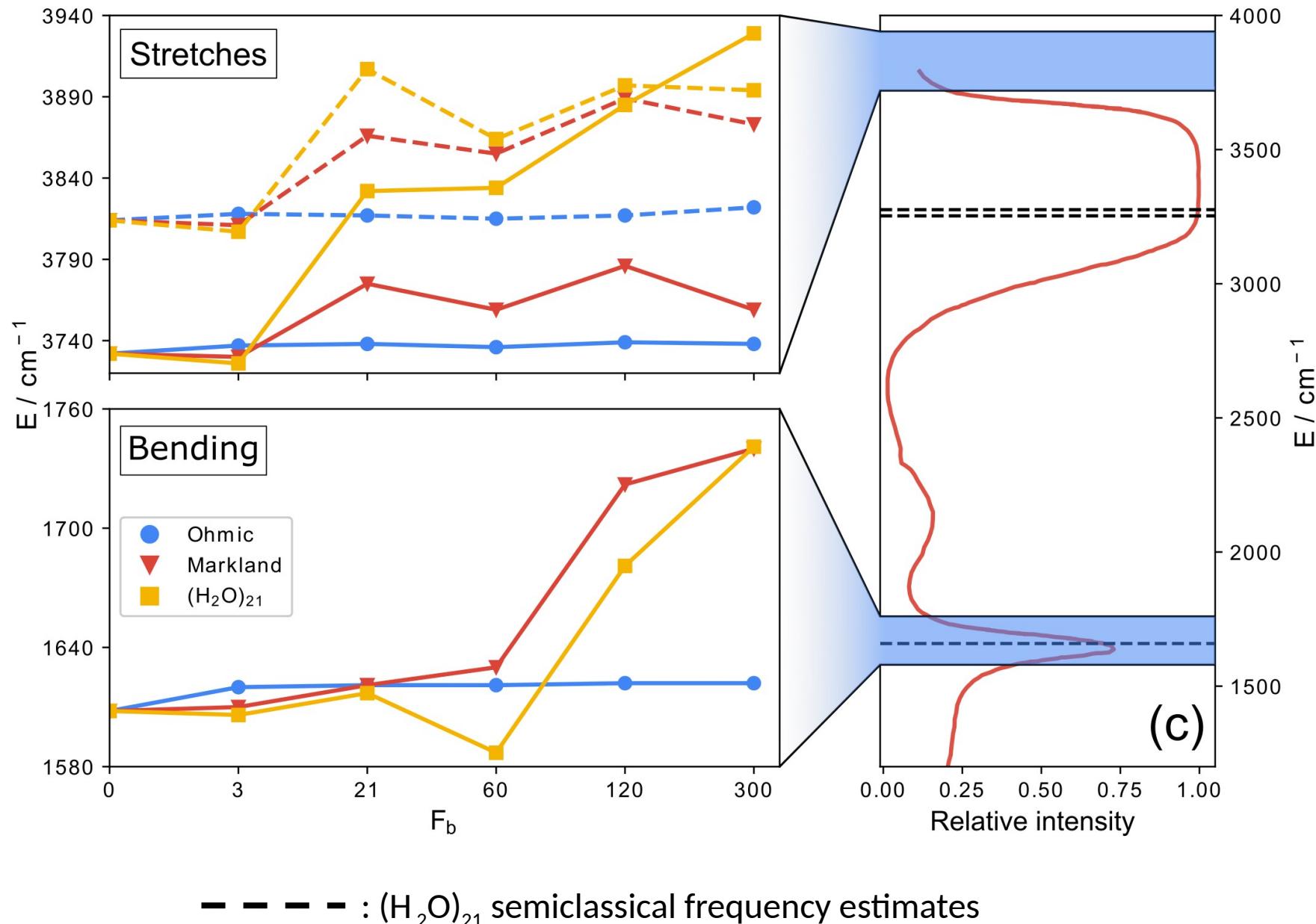


Ab initio vs model potential: the Caldeira-Leggett model

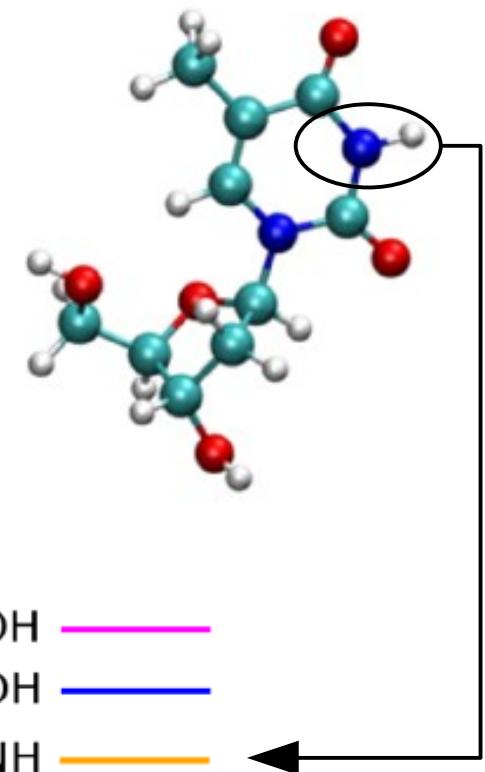
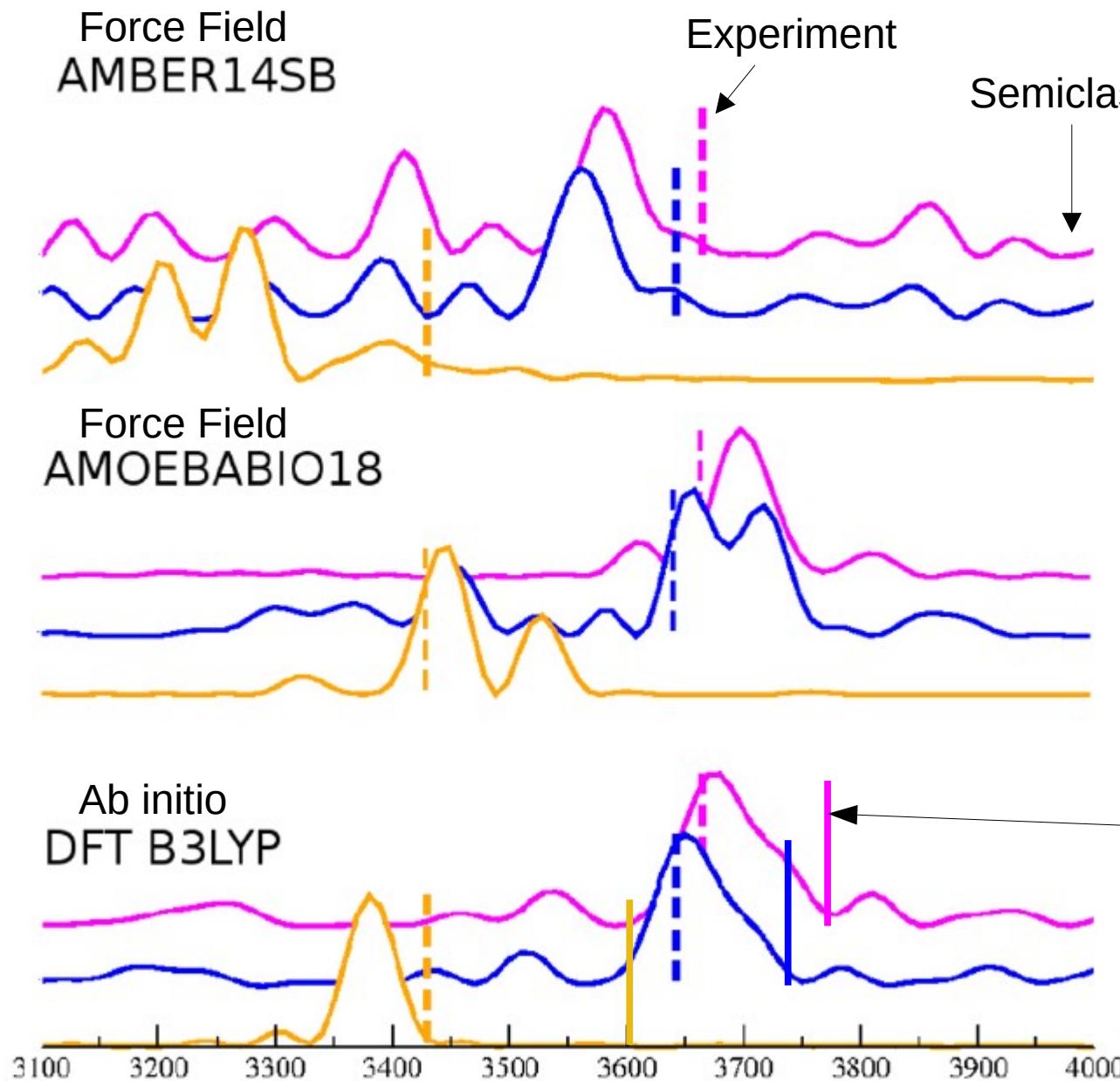
$$\mathcal{H} = \mathcal{H}_s + \sum_{i=1}^{F_b} \left\{ \frac{p_i^2}{2} + \frac{1}{2} \left[\omega_i y_i + \frac{c_i}{\omega_i} (s - s_{eq}) \right]^2 \right\}$$



Ab initio vs model potential: the Caldeira-Leggett model

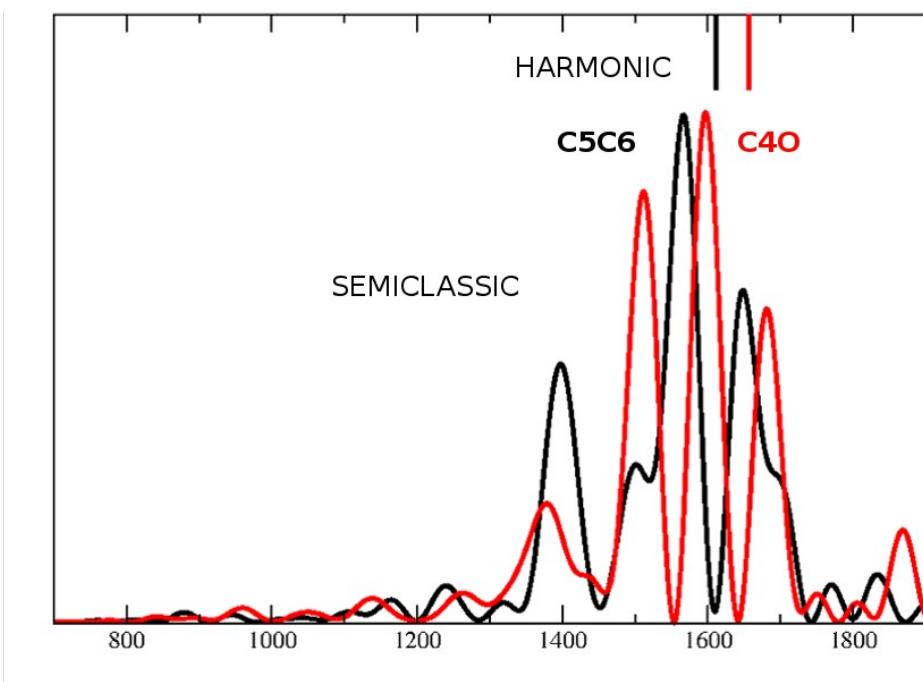
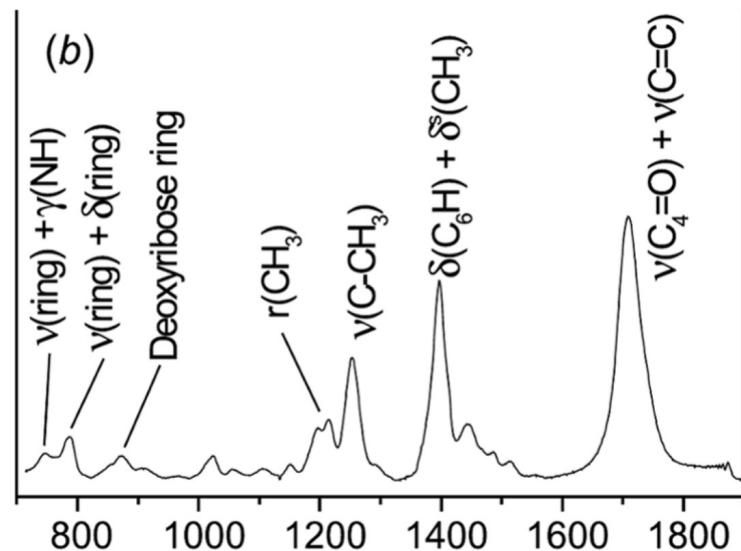


Thymidine in gas phase

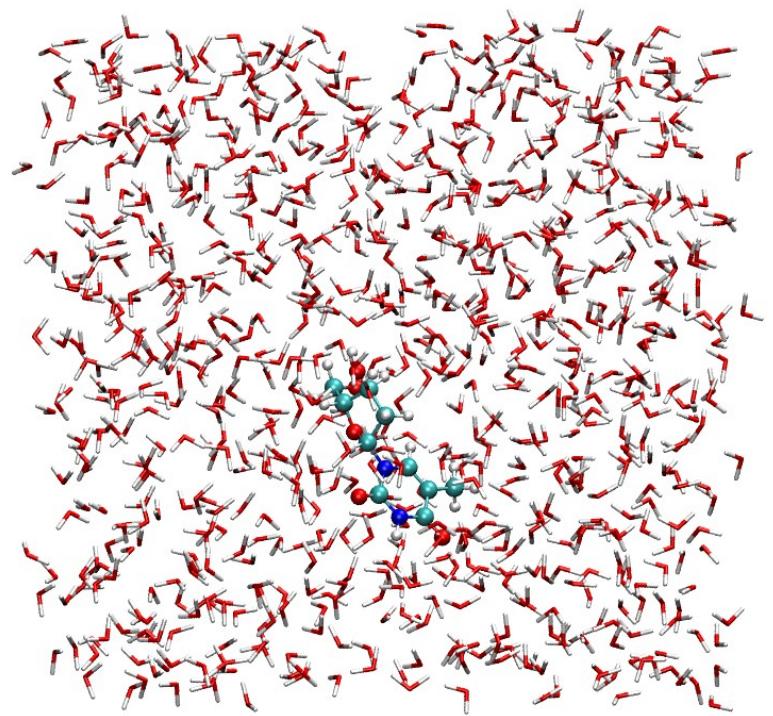


Thymidine in water condensed phase

Experiment

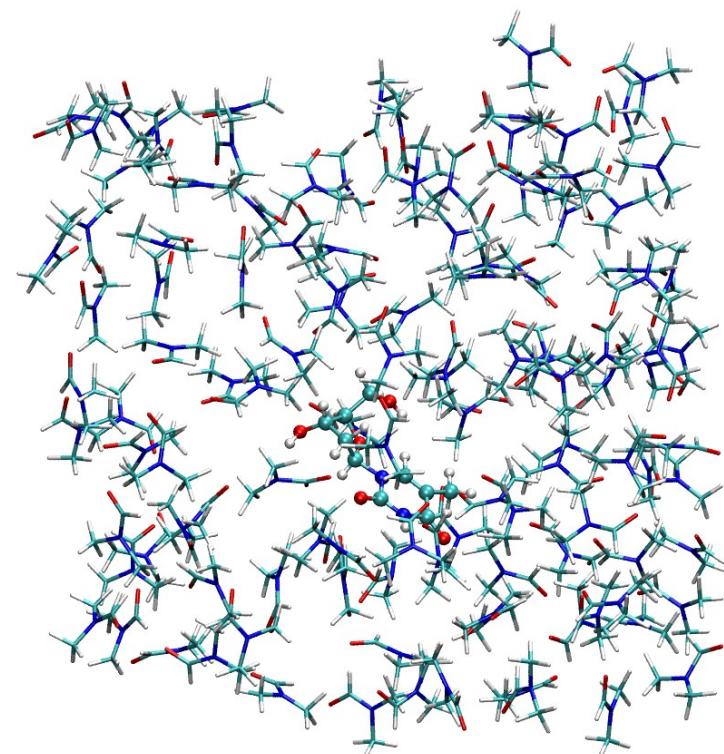
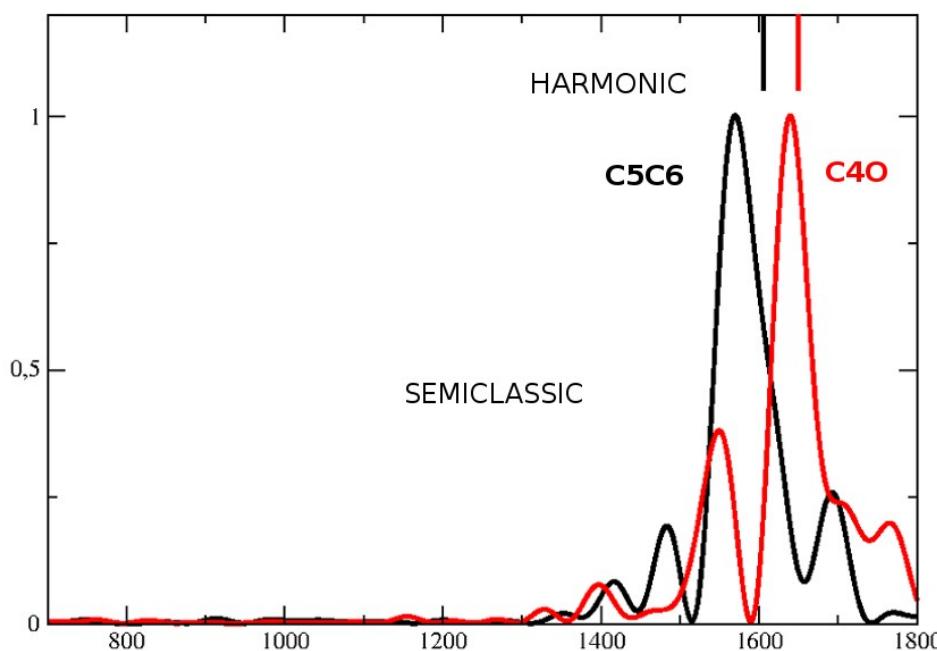
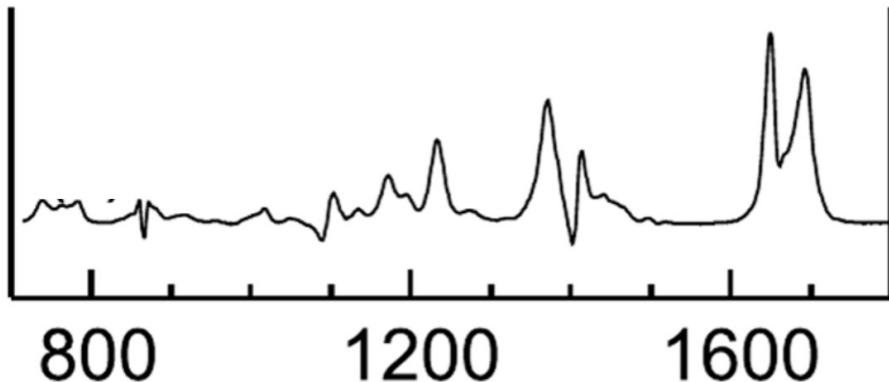


Condensed phase simulation water box



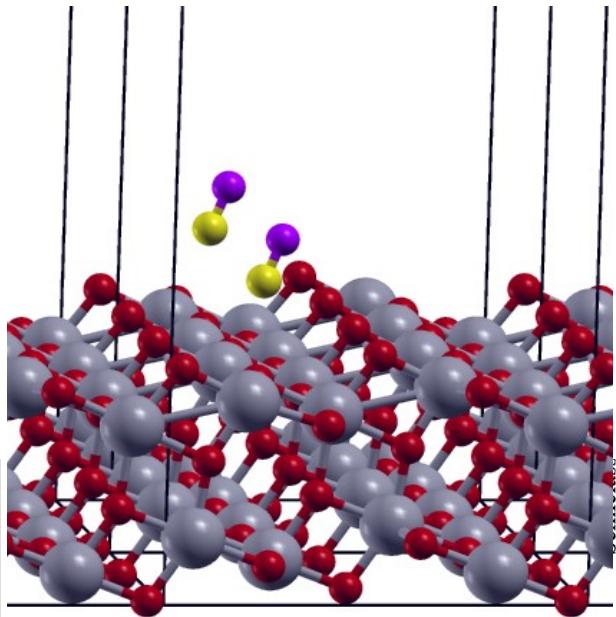
Thymidine in N,N-DMF condensed phase

Experiment

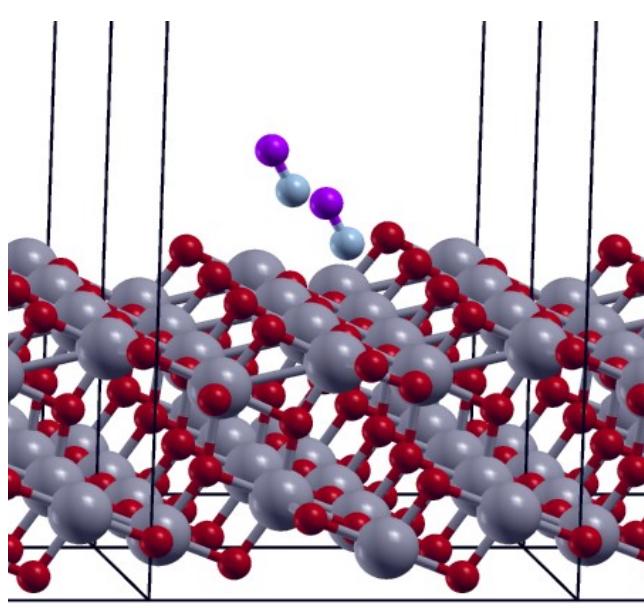


Molecular Adsorbates Vibrational Spectroscopy

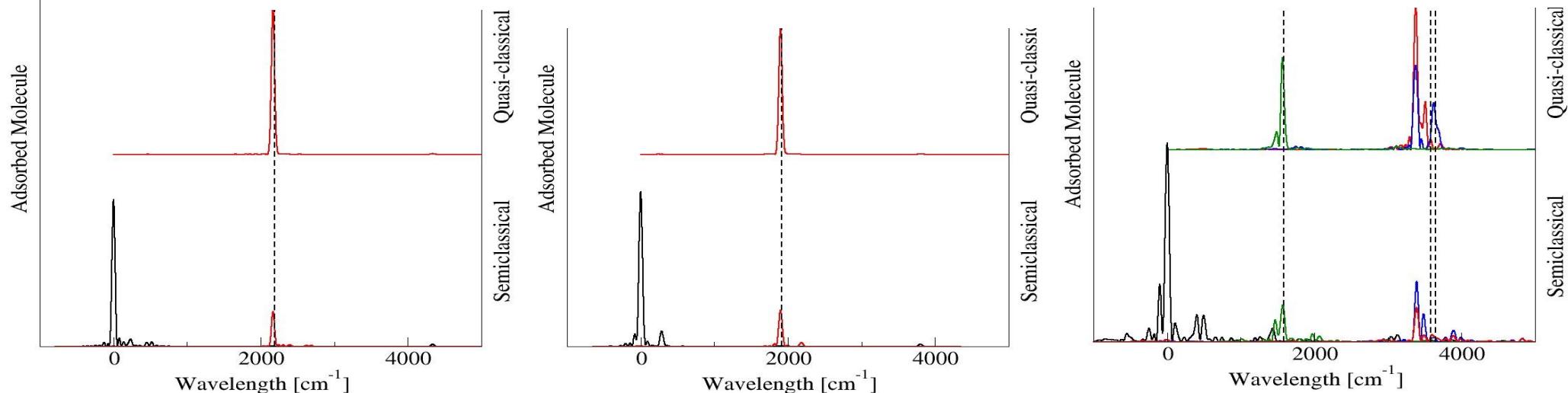
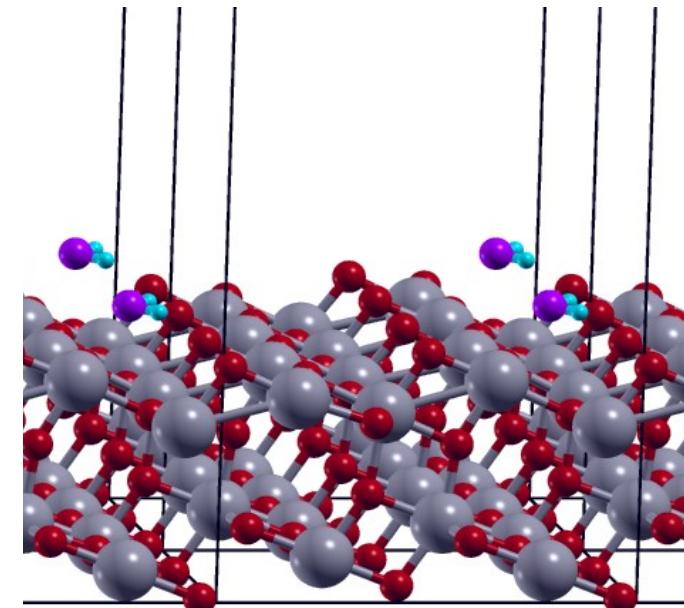
CO @ TiO₂



NO @ TiO₂



H₂O @ TiO₂

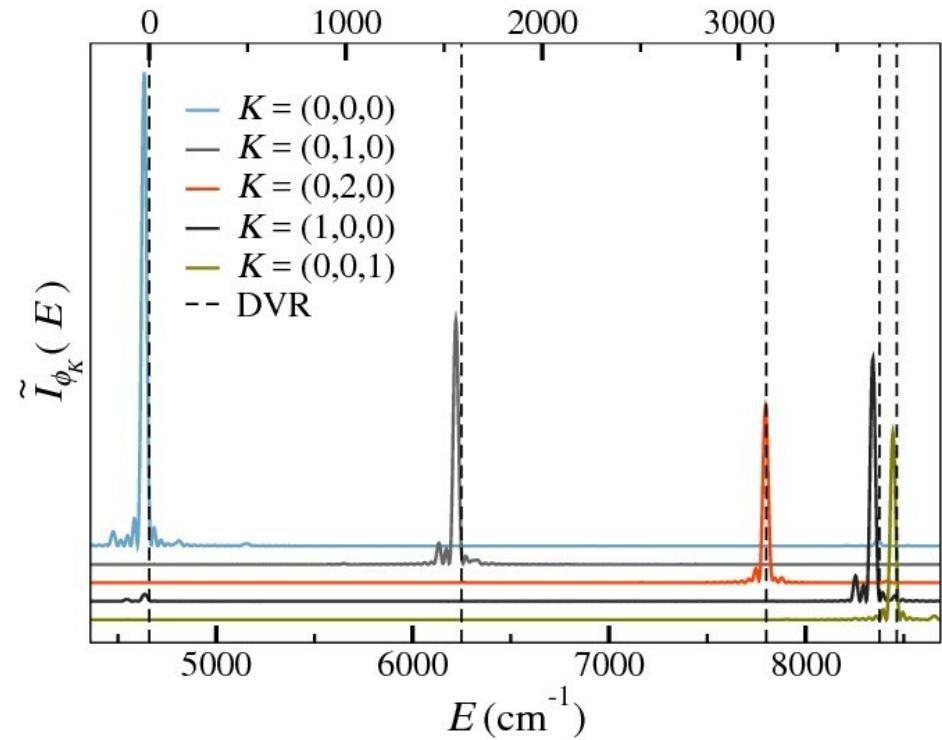


IR spectra: Eigenstates on Harmonic basis

$$\hat{H} |e_n\rangle = E_n |e_n\rangle$$

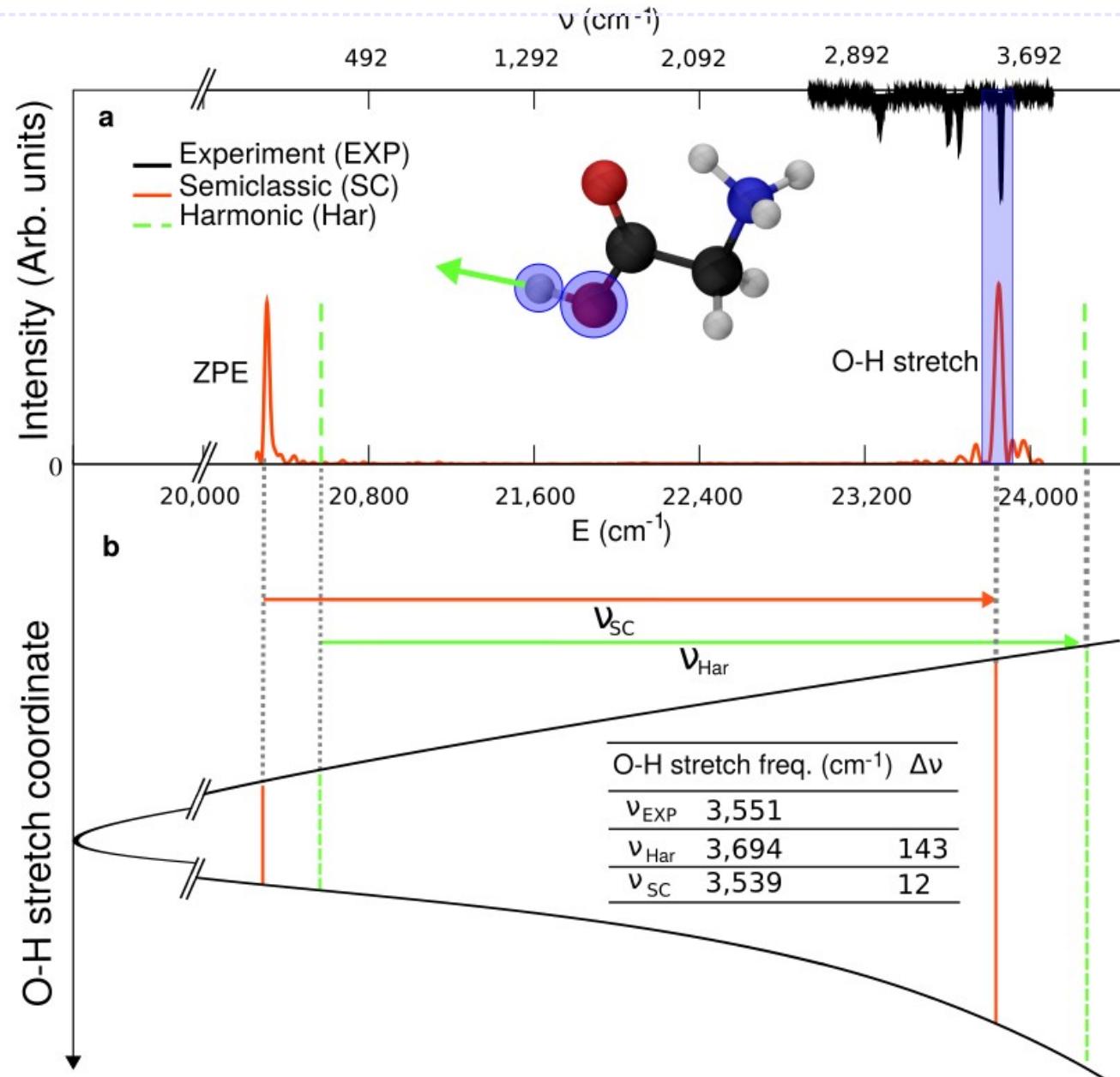
$$|e_n\rangle = \sum_{\mathbf{K}} C_{n,\mathbf{K}} |\phi_{\mathbf{K}}\rangle$$

$$\langle \mathbf{q} | \phi_{\mathbf{K}} \rangle = \prod_i \phi_{K_i}(q_i)$$



$$C_{n,\mathbf{K}} = \langle e_n | \phi_{\mathbf{K}} \rangle = \frac{\tilde{I}_{\mathbf{0K}}(E_n) - \tilde{I}_{\phi_{\mathbf{0}}}(E_n) - \tilde{I}_{\phi_{\mathbf{K}}}(E_n)}{2\sqrt{\tilde{I}_{\phi_{\mathbf{0}}}(E_n)}}$$

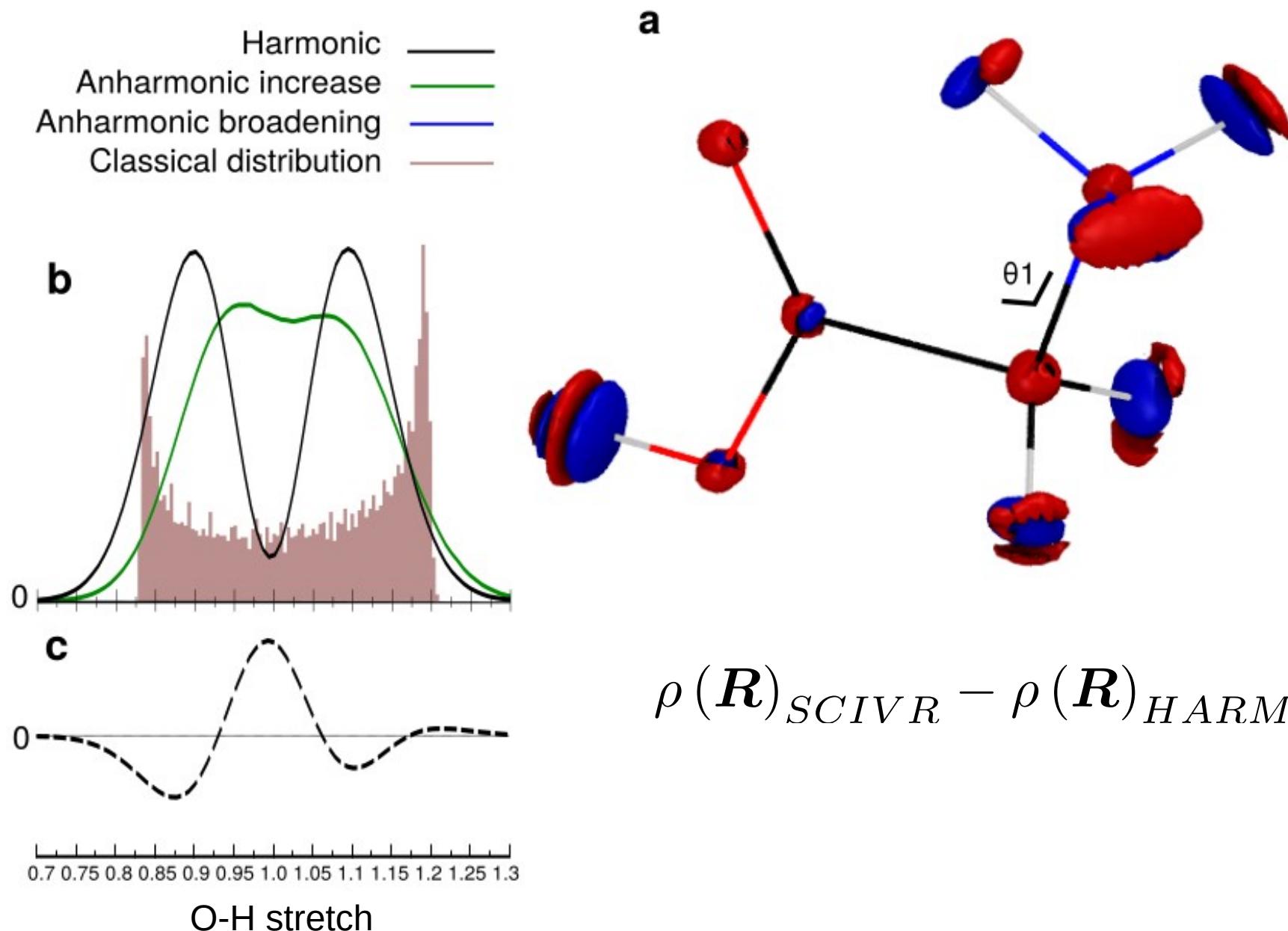
Protonated Glycine (GlyH⁺)



One-nucleous
marginal density

$$\rho_{n,\mathbf{R}_i}(\mathbf{R}) = \int d^{3N}Q |\langle Q | e_n \rangle|^2 \delta(Q^{RT}) \delta(R_i(Q) - R)$$

Protonated Glycine (GlyH⁺): OH stretch nuclear density



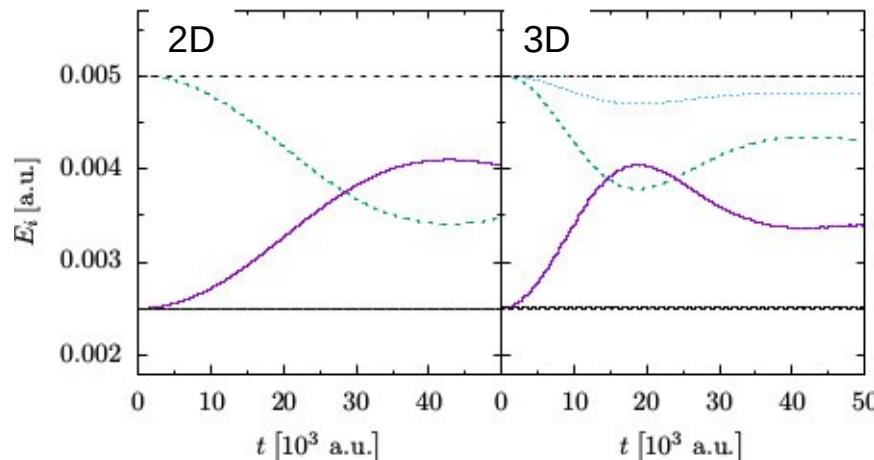
$$\rho(\mathbf{R})_{SCIVR} - \rho(\mathbf{R})_{HARM}$$

Semiclassical Zero Point Energy Leakage (ZPEL)?

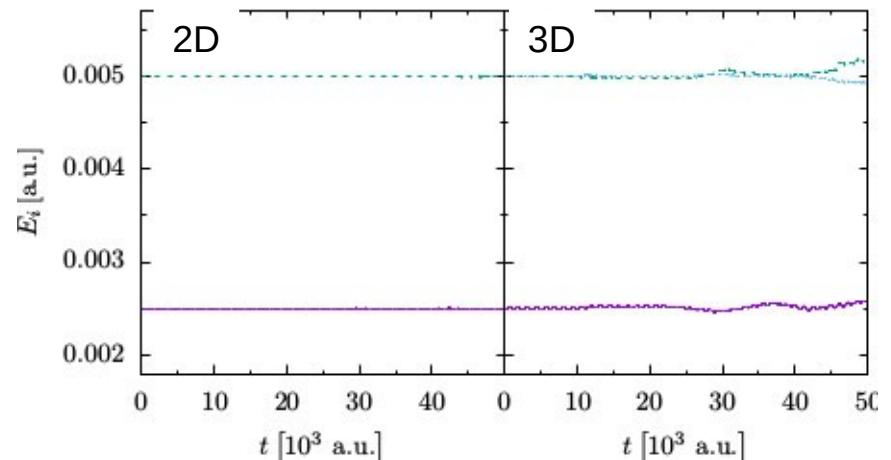
$$H = \sum_{i=1}^F \frac{p_i^2}{2} + \sum_{i=1}^F \frac{\omega_i^2 q_i^2}{2} + \sum_{i < j} C_{ij} (q_i - q_j)^3$$

$$E_i(t) = \frac{1}{2} \langle \hat{p}_{x,i}^2 \rangle(t) + \frac{\omega_i^2}{2} \langle \hat{x}_i^2 \rangle(t)$$

LSC-IVR

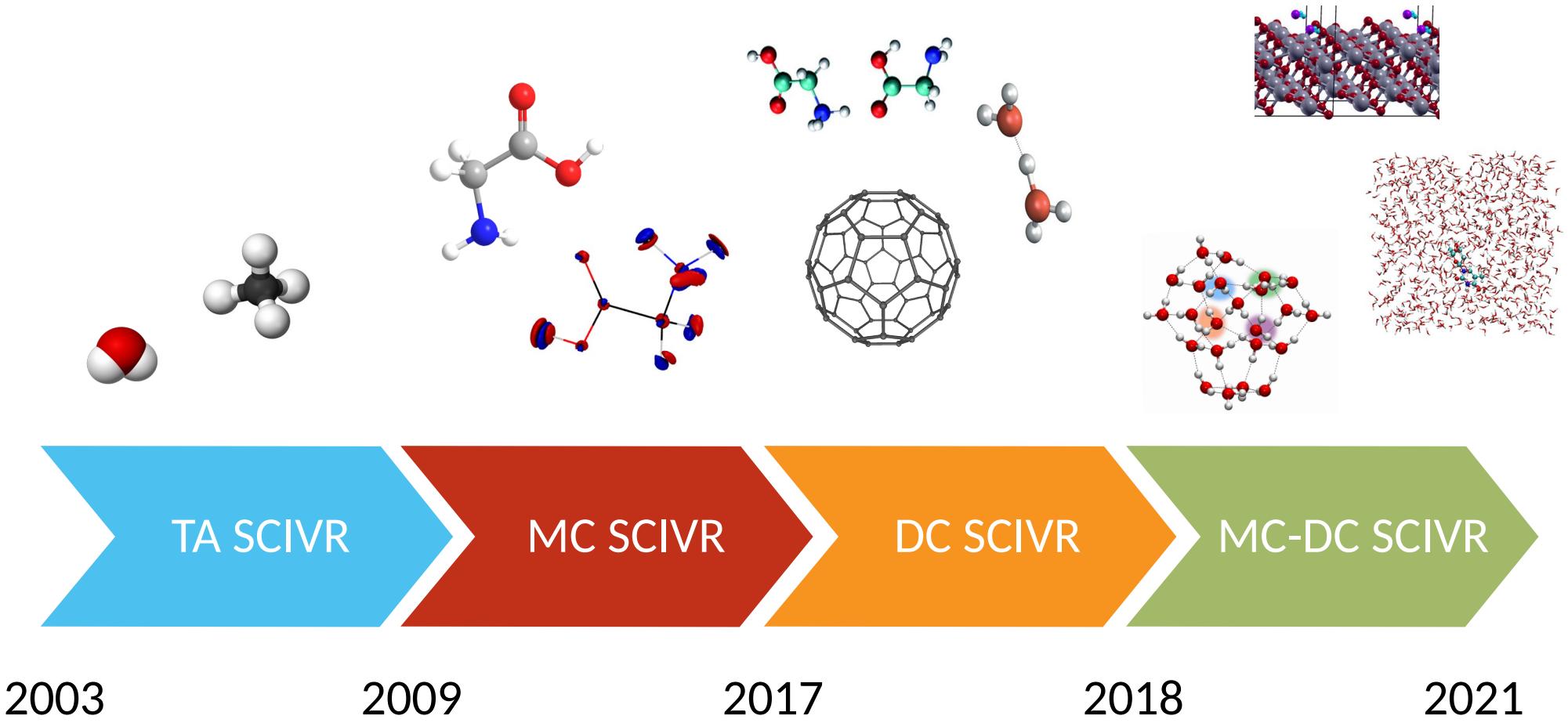


HK SC-IVR



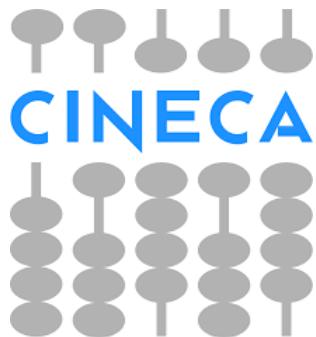
No ZPEL for SC-IVR

SCIVR for Spectroscopy: Conclusions



SC-IVR is a practical tool to add quantum mechanical effects to classical dynamics

Acknowledgments



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Established by the European Commission

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....and thank to you for your kind attention!