



UNIVERSITÀ DEGLI STUDI DI MILANO

Quantum Vibrational Spectroscopy of Biomolecular Systems through Divide-and-Conquer Semiclassical Dynamics

Riccardo Conte and Michele Ceotto

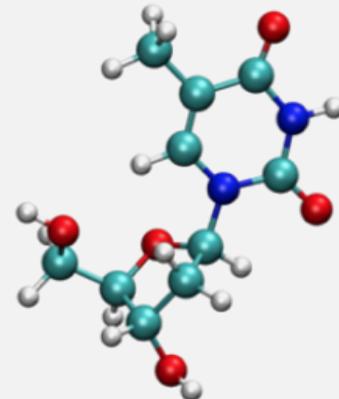
VISTA Meeting Feb. 17th, 2021

Vibrational spectroscopy of large dimensional systems

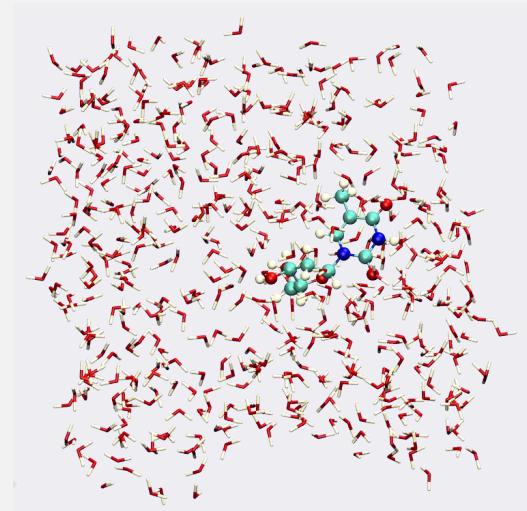
Examples of target systems

Isolated molecules with at least 10 atoms

- Glycine
- Thymidine



Solvated systems



Research goals

- Can a quantum description with spectroscopic accuracy be achieved for such kind of systems?
- Can we neglect quantum effects in dealing with these systems?
- How important is an accurate description of the potential energy surface (PES) of these systems?

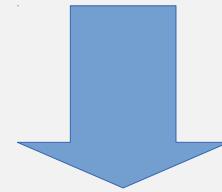
Semiclassical Power Spectra

Quantum vibrational spectral density as Fourier-transform of the survival amplitude of an arbitrary reference state $|\Psi\rangle = \sum_j c_j |E_j\rangle$

$$I(E) = \text{Re} \left[\frac{1}{\pi\hbar} \int_0^\infty dt e^{iEt/\hbar} \langle \Psi | e^{-i\hat{H}t/\hbar} | \Psi \rangle \right] = \sum_j |c_j|^2 \delta(E - E_j)$$



Semiclassical Approximation to the Quantum Propagator



Kaledin and Miller's time averaged Semiclassical Initial Value Representation (TA SCIVR)

$$I(E) = \frac{(2\pi\hbar)^{-N_{vib}}}{2\pi\hbar T} \int \int d\mathbf{p}_0 d\mathbf{q}_0 \left| \int_0^T dt \langle \Psi | \mathbf{p}_t, \mathbf{q}_t \rangle e^{(i/\hbar)(S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi_t(\mathbf{p}_0, \mathbf{q}_0))} \right|^2$$



Semiclassical Power Spectra

Kaledin and Miller's TA SCIVR

$$I(E) = \frac{(2\pi\hbar)^{-N_{vib}}}{2\pi\hbar T} \int \int d\mathbf{p}_0 d\mathbf{q}_0 \left| \int_0^T dt \langle \Psi | \mathbf{p}_t, \mathbf{q}_t \rangle e^{(i/\hbar)(S_t(\mathbf{p}_0, \mathbf{q}_0) + Et + \phi_t(\mathbf{p}_0, \mathbf{q}_0))} \right|^2$$

Coherent States

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

Phase ϕ_t of the Herman-Kluk prefactor

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

$$\mathbf{M}(t) \equiv \begin{pmatrix} \mathbf{M}_{\mathbf{pp}} & \mathbf{M}_{\mathbf{pq}} \\ \mathbf{M}_{\mathbf{qp}} & \mathbf{M}_{\mathbf{qq}} \end{pmatrix} = \begin{pmatrix} \partial \mathbf{p}_t / \partial \mathbf{p}_0 & \partial \mathbf{p}_t / \partial \mathbf{q}_0 \\ \partial \mathbf{q}_t / \partial \mathbf{p}_0 & \partial \mathbf{q}_t / \partial \mathbf{q}_0 \end{pmatrix} \quad \phi_t = \text{phase}[C_t(\mathbf{p}_0, \mathbf{q}_0)]$$

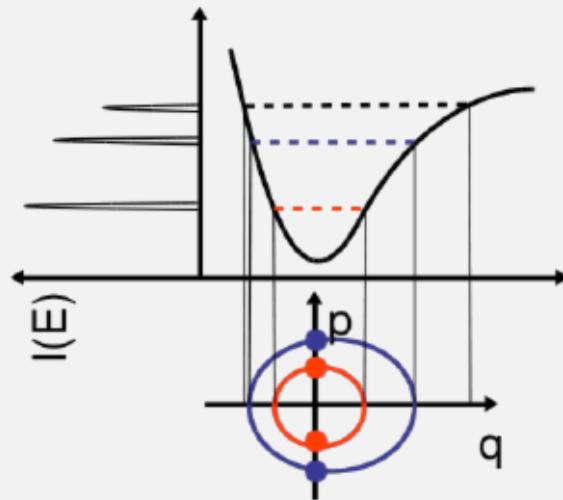
- For time-evolution of \mathbf{M} the instantaneous Hessian matrix of the potential is needed



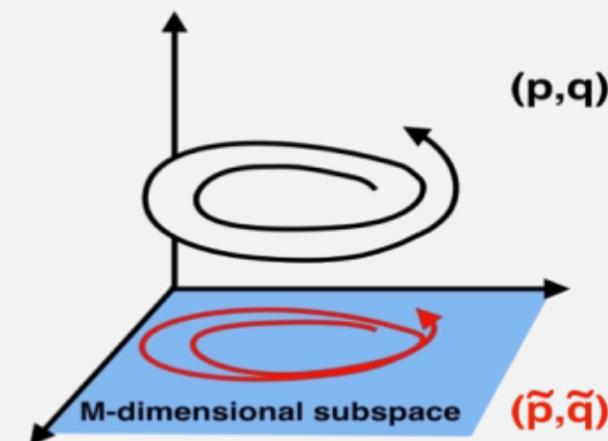
Semiclassical Power Spectra

How to simulate the quantum (semiclassical) vibrational spectroscopy of large dimensional systems?

1. Single trajectory simulations



2. Sensible spectroscopic signal



3. Reliable Potential Energy Surface (PES) description

3a. *Ab initio* “On-the-fly” MD

3b. Analytical PES

3c. Force Fields

3d. Coupling models (Caldeira-Leggett)

Multiple Coherent States Semiclassical Initial Value Representation (MC SCIVR)

Is it possible to get reliable results with single-trajectory propagation?

De Leon and Heller [*J. Chem. Phys.* **78**, 4005 (1983)]:

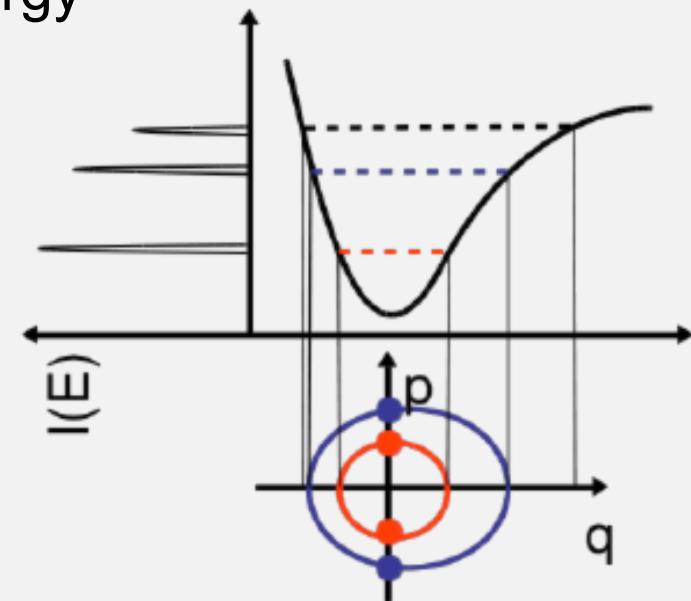
Accurate Semiclassical Eigenvalues and Eigefunctions from a Single Trajectory with “Correct” Energy

1) Classical Trajectories with Tailored Energy

q_{eq} at Equilibrium Geometry
Harmonic Sampling for p_{eq}

2) Tailored Choice of Reference State

$$|\Psi\rangle = \sum_{i=1}^{N_{st}} \prod_{j=i}^{N_{vib}} \varepsilon_i(j) |p_{eq,j}^{(i)}, q_{eq,j}^{(i)}\rangle$$

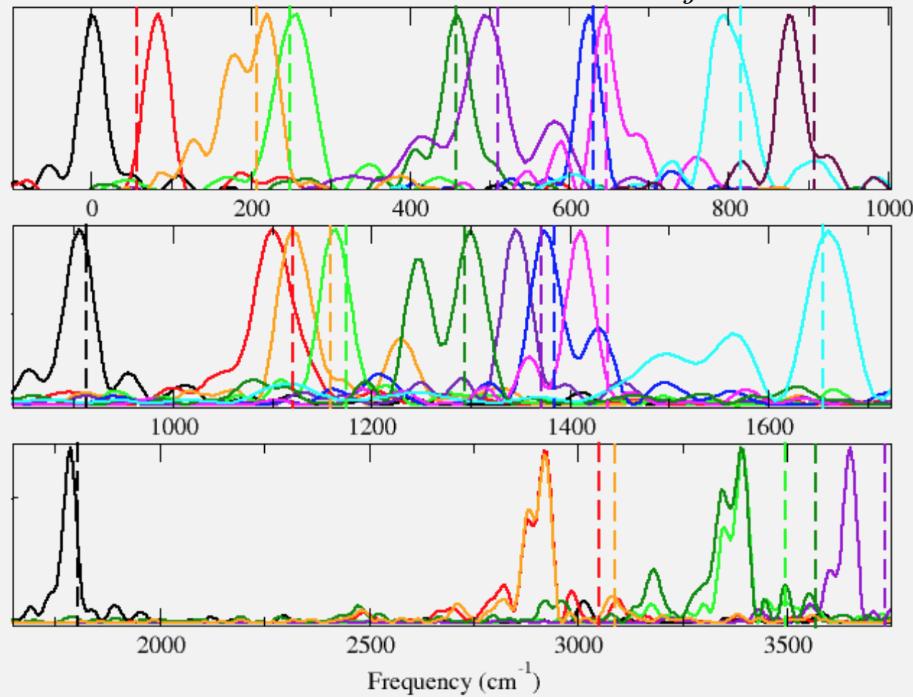
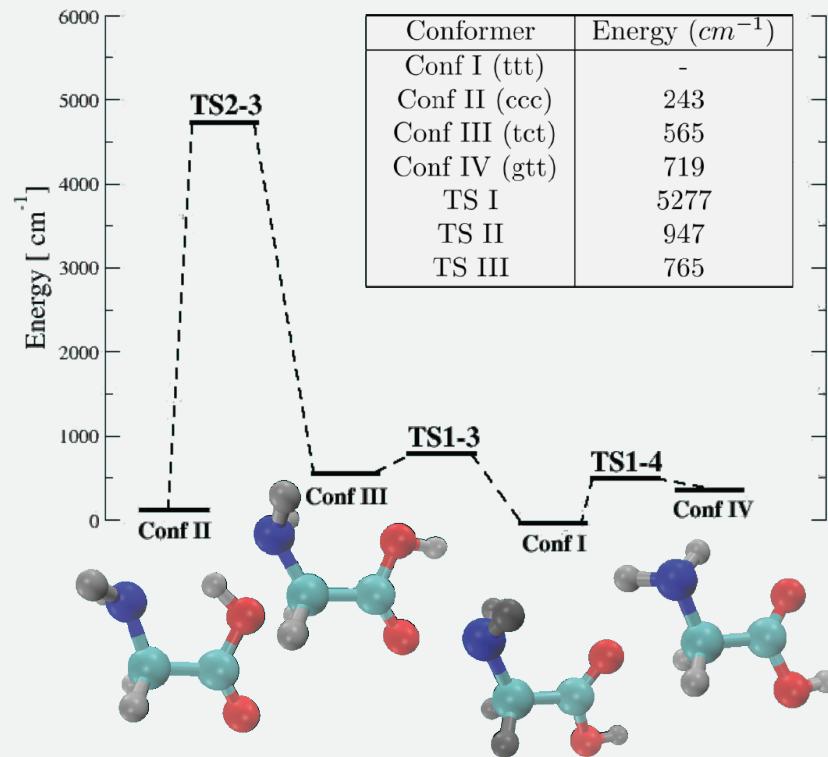


- M. Ceotto, S. Atahan, G. F. Tantardini, and A. Aspuru-Guzik *J. Chem. Phys.* **130**, 234113 (2009).
M. Ceotto, S. Valleau, G.F. Tantardini, and A. Aspuru-Guzik *J. Chem. Phys.* **134**, 234103 (2011).
R. Conte, A. Aspuru-Guzik, and M. Ceotto *J. Phys. Chem. Lett.* **4**, 3407 (2013).



An application in full dimensionality: Glycine (24 degrees of freedom)

Ab initio “on-the-fly” calculation of the PES (DFT/B3LYP/aug-cc-pVDZ)



MAE approximately 25 cm^{-1}

Construction of a permutationally-invariant polynomial surface at same level of theory has permitted identification of 8 conformers and several saddle points. An SCIVR calculation of the Zero point energy is within 5 cm^{-1} of the DMC value.

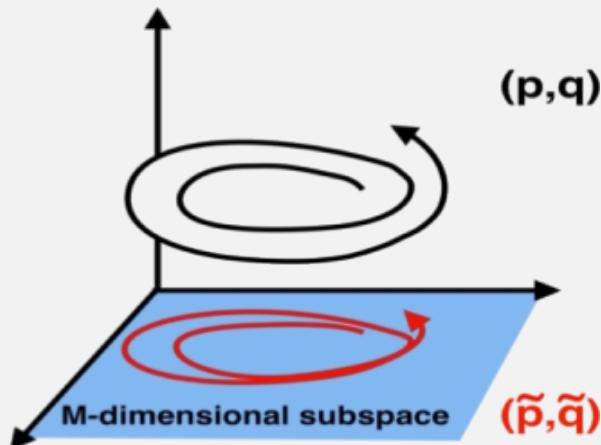
F. Gabas, R. Conte, and M. Ceotto *J. Chem. Theory Comput.* **13**, 2378 (2017).

R. Conte, P.L. Houston, C. Qu, J. Li, and J.M. Bowman *J. Chem. Phys.* **153**, 244301 (2020).



Divide-and-Conquer Semiclassical Initial Value Representation (DC SCIVR)

$$\langle \mathbf{p}_{eq}, \mathbf{q}_{eq} | \mathbf{p}_t, \mathbf{q}_t \rangle = \langle p_{eq}^{(1)}, q_{eq}^{(1)} | p_t^{(1)}, q_t^{(1)} \rangle \dots \langle p_{eq}^{(N_{vib})}, q_{eq}^{(N_{vib})} | p_t^{(N_{vib})}, q_t^{(N_{vib})} \rangle$$



Divide-and-Conquer SCIVR

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

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

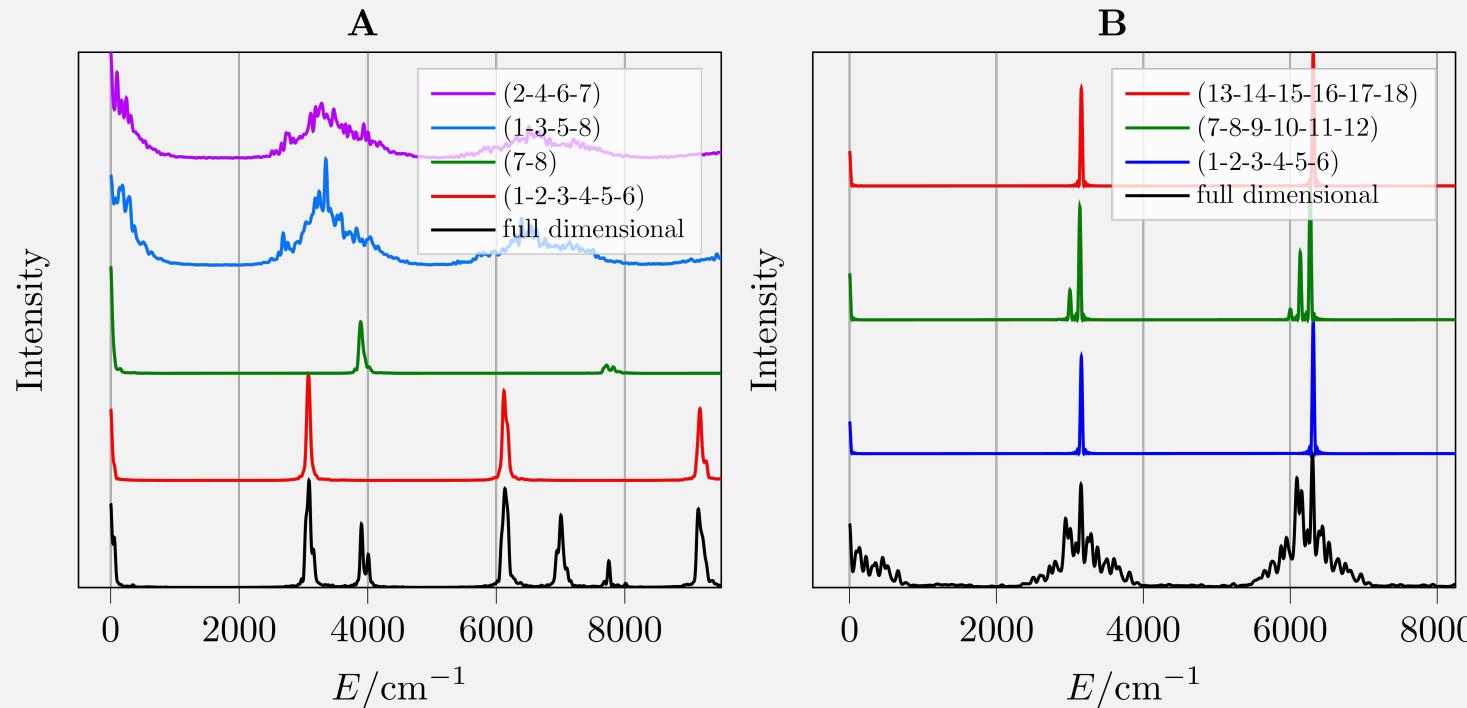
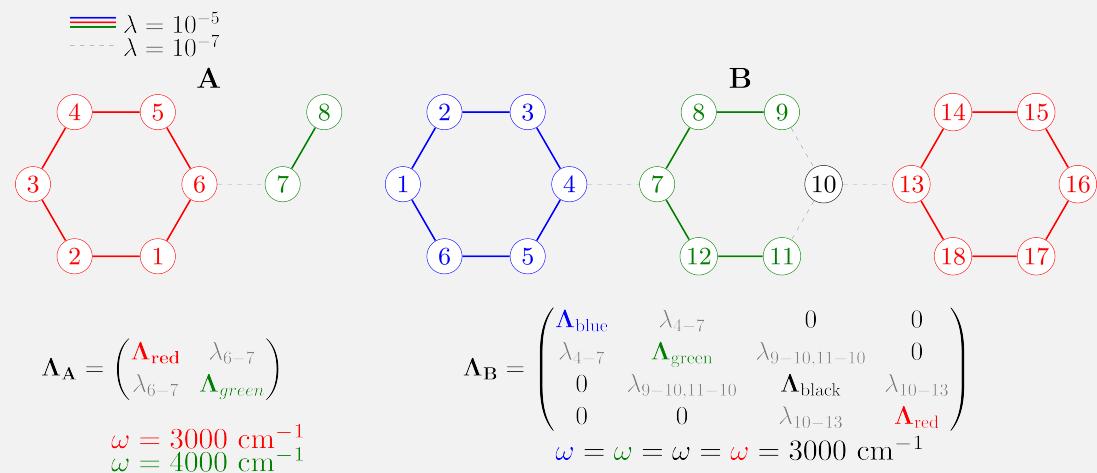
- How should subspaces be chosen?



Divide-and-Conquer Semiclassical Initial Value Representation (DC SCIVR)

The importance of subspace choice

$$V = \sum_{i=1}^F V_{Morse}(q_i) + \sum_{i=1}^F \sum_{j>i}^F \lambda_{ij}(q_i - q_{eq,i})(q_j - q_{eq,j})$$



Divide-and-Conquer Semiclassical Initial Value Representation (DC SCIVR)

How to determine the partition of the degrees of freedom into subspaces?

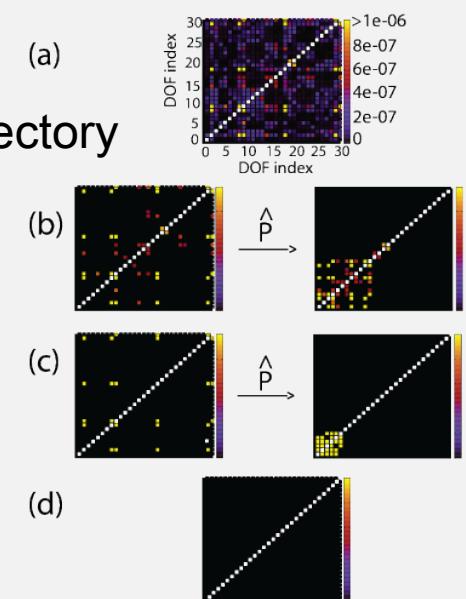
1. The Hessian method (fast, but threshold-dependent)

1A. Evaluation of the average of Hessian elements over a test trajectory

$$\tilde{H}_{ij} = \frac{1}{N_{steps}} \sum_{k=1}^{N_{steps}} H_{ij}$$

1B. Set-up of the coarse grained threshold $|\tilde{H}_{ij}| \geq \varepsilon$

1C. Arrange the Hessian in sub-blocks



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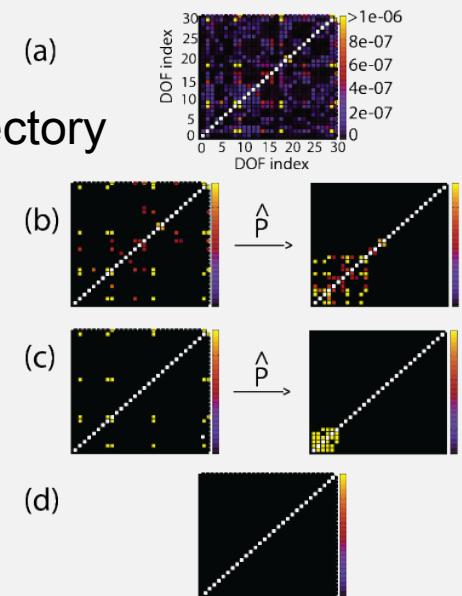
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2. Evolutionary Algorithm (no threshold dependency)

Fitness function derived from basic property of Jacobian matrix

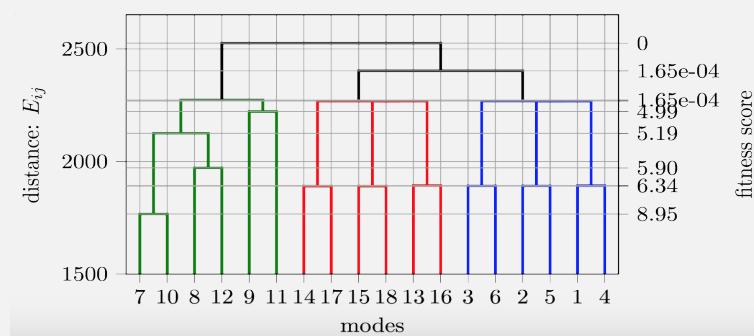
$$\mathbf{J}(t) = \begin{pmatrix} \partial \mathbf{q}_t / \partial \mathbf{q}_0 & \partial \mathbf{q}_t / \partial \mathbf{p}_0 \\ \partial \mathbf{p}_t / \partial \mathbf{q}_0 & \partial \mathbf{p}_t / \partial \mathbf{p}_0 \end{pmatrix}$$

Separable Systems

$$\prod_{i=1}^{N_{sub}} \det(\tilde{\mathcal{J}}_i(t)) = 1$$

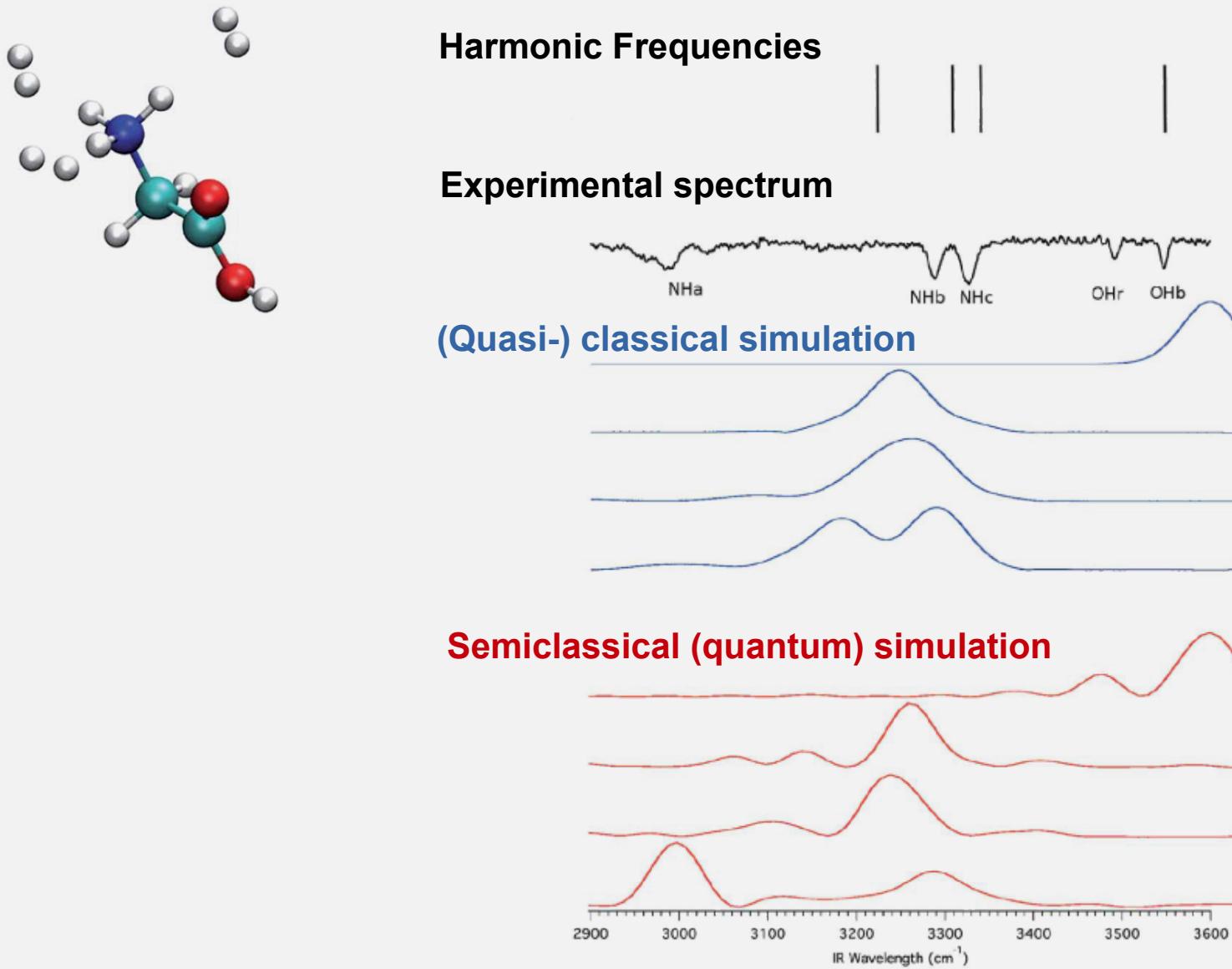
Non-Separable Systems

$$\prod_{i=1}^{N_{sub}} \det(\tilde{\mathcal{J}}_i(t)) \neq 1$$



Is it important to describe quantum effects in large systems?

1. Characterization of intramolecular hydrogen bonds

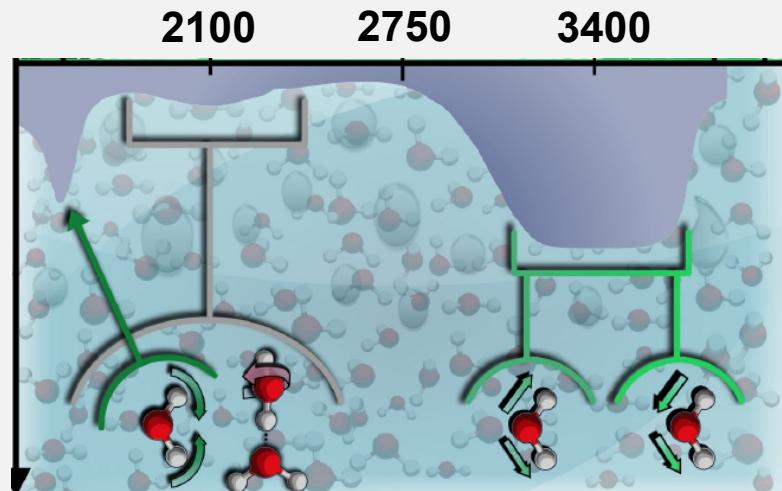


Is it important to describe quantum effects in large systems?

2. Description of hydrogen bonded supramolecular systems

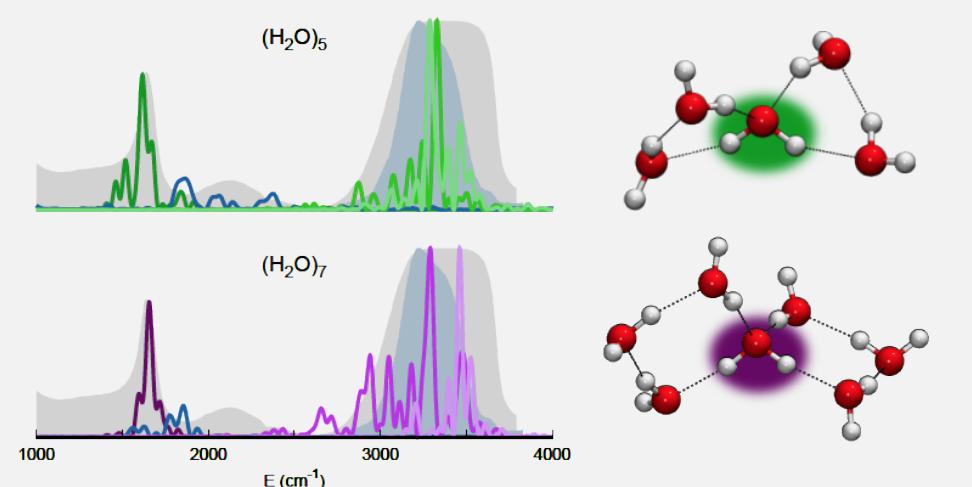
- How many water molecules are needed to solvate one?

Experimental spectrum of bulk liquid water.

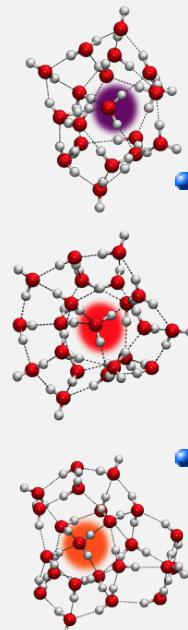
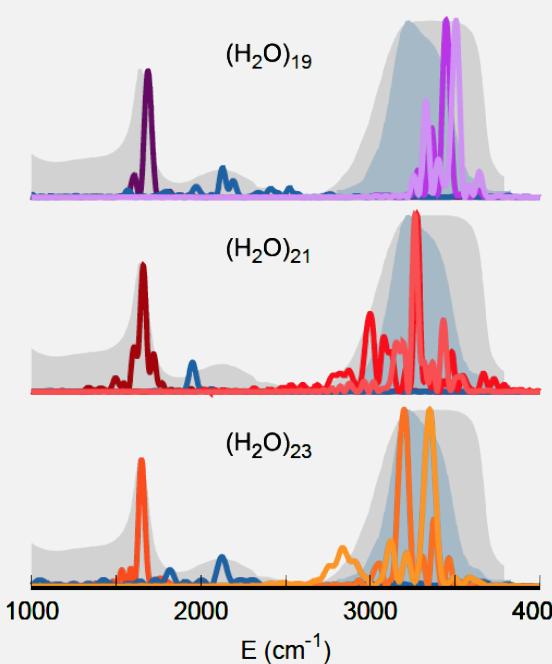


- 3 main spectral features:
Bending, Combination Band, Stretching
- Is tetrahedral coordination sufficient? The case of the pentamer and heptamer clusters

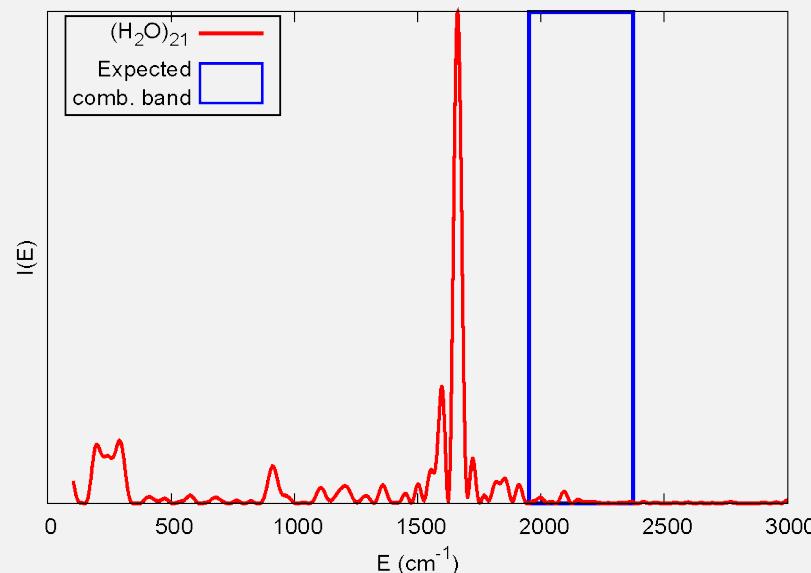
- Combination band does not match



Is it important to describe quantum effects in large systems?



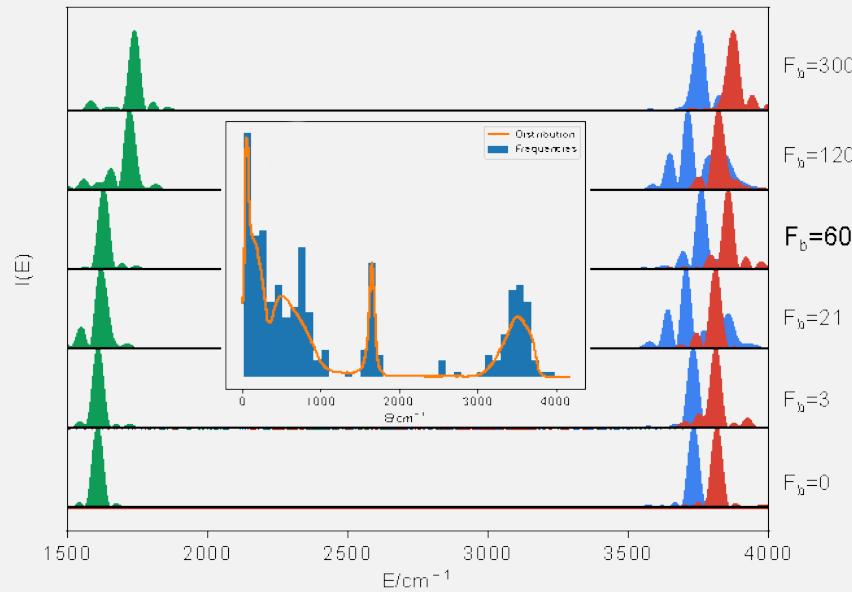
- $(\text{H}_2\text{O})_{21}$ is the smallest cluster to have the central monomer displaying all main spectroscopic features of the bulk.
- Key role played by the combination band, which needs a **quantum simulation** to be detected.
- Signal for the combination band is missing in a (quasi-) classical simulation.



The need for an accurate PES description

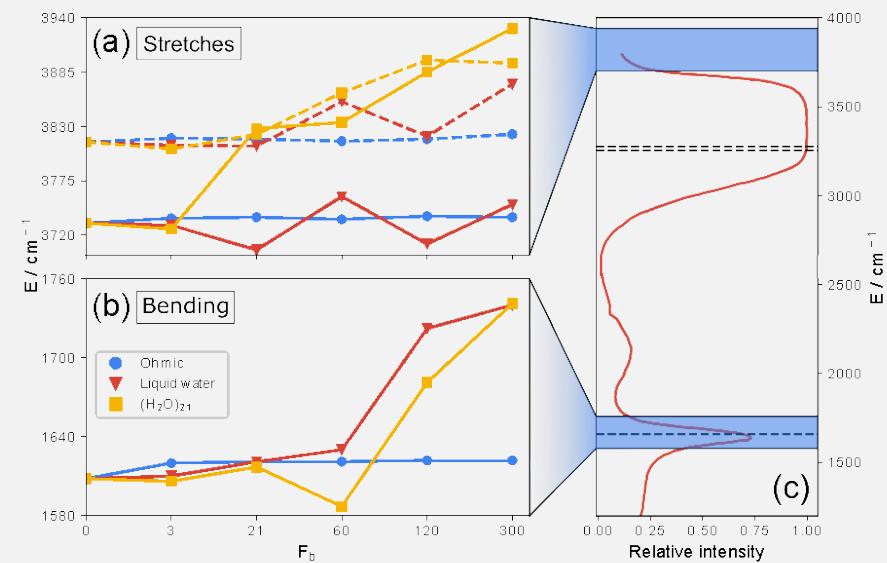
- Can we regain the same features of water solvation with a Caldeira-Leggett model?

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



- Red shift of stretches is totally lost!

- Bath frequencies extracted from spectral density of liquid water

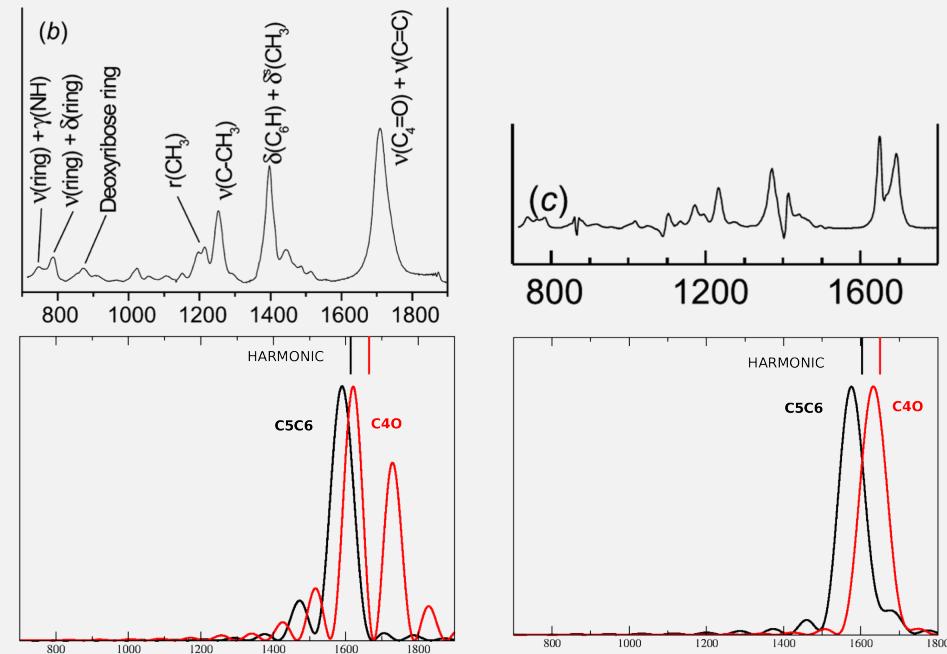
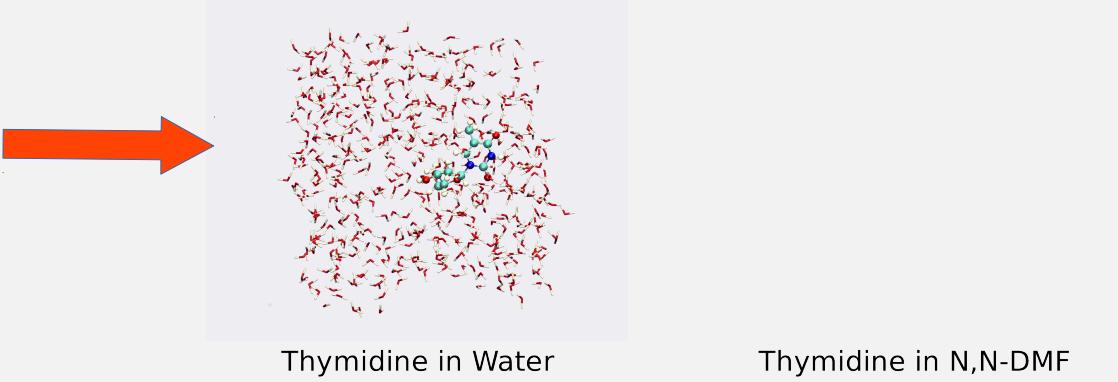
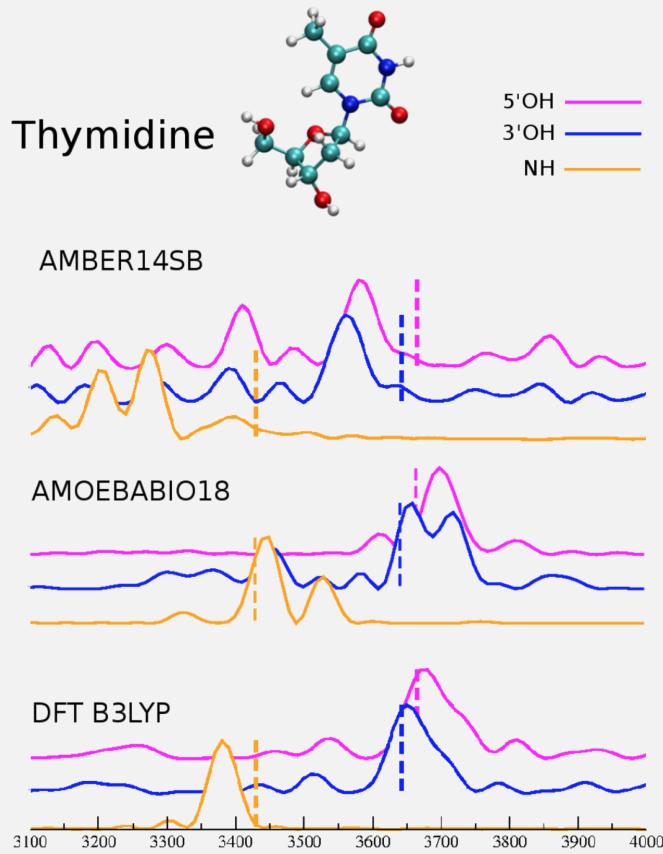


O. Marsalek and T. E. Markland, *J. Phys. Chem. Lett.* **8**, 1545 (2017).

A. Rognoni, R. Conte, and M. Ceotto *J. Chem. Phys.* accepted article (2021).

The need for an accurate PES description

- What about the force fields commonly adopted in the study of biological systems?



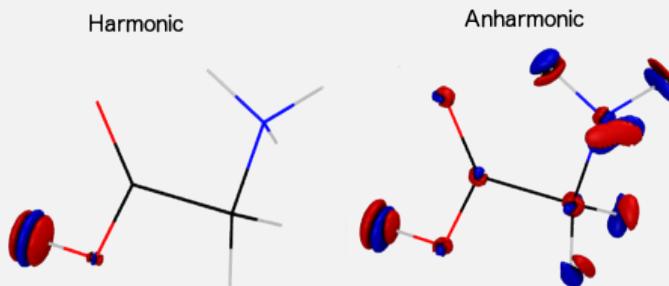
- A polarizable force field is needed



Further research in the semiclassical dynamics field

1

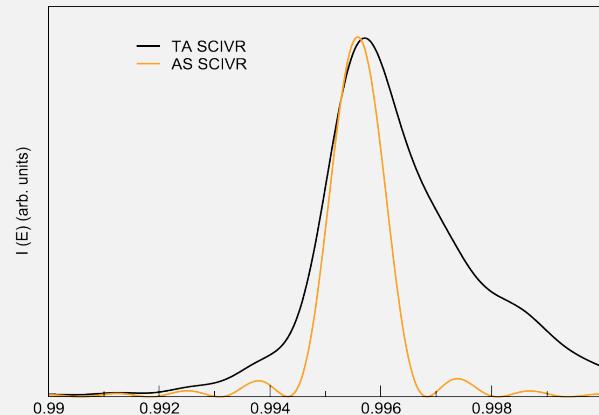
Nuclear densities and eigenfunctions



C. Aieta, M. Micciarelli, G. Bertaina, and M. Ceotto
Nat. Commun. **11**, 4348 (2020).

2

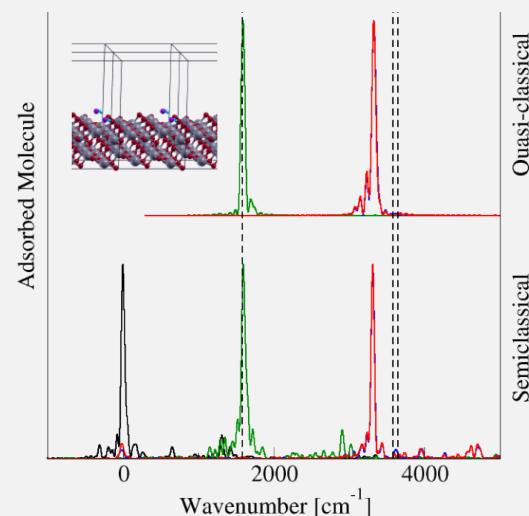
Enhanced precision (AS SCIVR)



R. Conte, L. Parma, C. Aieta, A. Rognoni, M. Ceotto
J. Chem. Phys. **151**, 214107 (2019).

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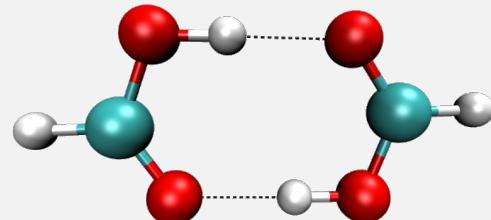
Spectroscopy of adsorbed molecules



M.Cazzaniga, M. Micciarelli, F. Moriggi, F. Gabas,
M. Ceotto *J. Chem. Phys.* **152**, 104104 (2020).

3

Multiple hydrogen bonded systems



A. Rognoni, R. Conte, M. Ceotto, *in preparation*.



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Prof. P. L. Houston, Cornell University, USA

Dr. C. Qu, University of Maryland, USA

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FRAMEWORK PER L'ATTRAZIONE E IL RAFFORZAMENTO
DELLE ECCELLENZE PER LA RICERCA IN ITALIA

Grant "QURE" from the Italian Ministry of University (MUR)



Divide-and-Conquer Semiclassical Initial Value Representation (DC SCIVR)

Calculation of projected action

$$\tilde{S}_t = \int_0^t (\tilde{T} - \tilde{V}) dt'$$

The projected potential should depend on M variables and $N_{\text{vib}} - M$ parameters.

Straightforward projection

$$\tilde{V} = V(\mathbf{q}_M; \mathbf{q}_{N_{\text{vib}} - M}^{eq})$$

Not suitable

Introduction of an appropriate **external field**

$$\tilde{V} = V(\mathbf{q}_M; \mathbf{q}_{N_{\text{vib}} - M}^{eq}) + \lambda(t)$$

$$\tilde{V} = V(\mathbf{q}_M(t); \mathbf{q}_{N_{\text{vib}} - M}(t)) - V(\mathbf{q}_M^{eq}; \mathbf{q}_{N_{\text{vib}} - M}(t))$$

