



From anharmonicity to Nuclear Quantum Effects in medium and large sized molecular systems

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The nuclear vibrational motion in molecular systems and its spectroscopic representation can be accounted for at different levels of accuracy. The most simple and intuitive one is the diagonalization of the mass-scaled Hessian matrix at the equilibrium geometry. This approach does not take into account the anharmonic part of the Potential Energy Surface (PES), which strongly deviates from the harmonic approximation, especially for floppy systems. One way to overcome this issue is to run Molecular Dynamics (MD) simulations and calculate the power spectrum as the Fourier-Transform (FT) of the classical velocity autocorrelation function (Cvv). [1] However, in this case the result depends on the choice of the employed trajectories and it does not include nuclear quantum effects. In this work, [2] we examine different choices of initial conditions and how these choices reflect on the computation and the result of the classical spectrum. Furthermore, we show how the inclusion of Nuclear Quantum Effects (NQE) [3] to the computation of the vibrational eigenvalues contribute to the final results. To obtain these results we implemented the Divide and Conquer Semiclassical Initial Value Representation [4,5] (DC SCIVR) which made possible to calculate the quantum mechanical spectrum of an explicitly solvated supramolecular system featuring more than 30000 degrees of freedom. [6]

The vibrational power spectra

Classical spectrum:

$$I_j(\omega) = \iint d\mathbf{p}_0 d\mathbf{q}_0 \frac{\rho(\mathbf{p}_0, \mathbf{q}_0)}{2T} \left| \int_0^T p_j(t) e^{i\omega t} dt \right|^2$$

↑ Requires only classical trajectories

↑ Anharmonicities can be included

↓ No Nuclear quantum effects

Time Averaged Semiclassical Initial Value Representation:

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

↑ Requires classical trajectories

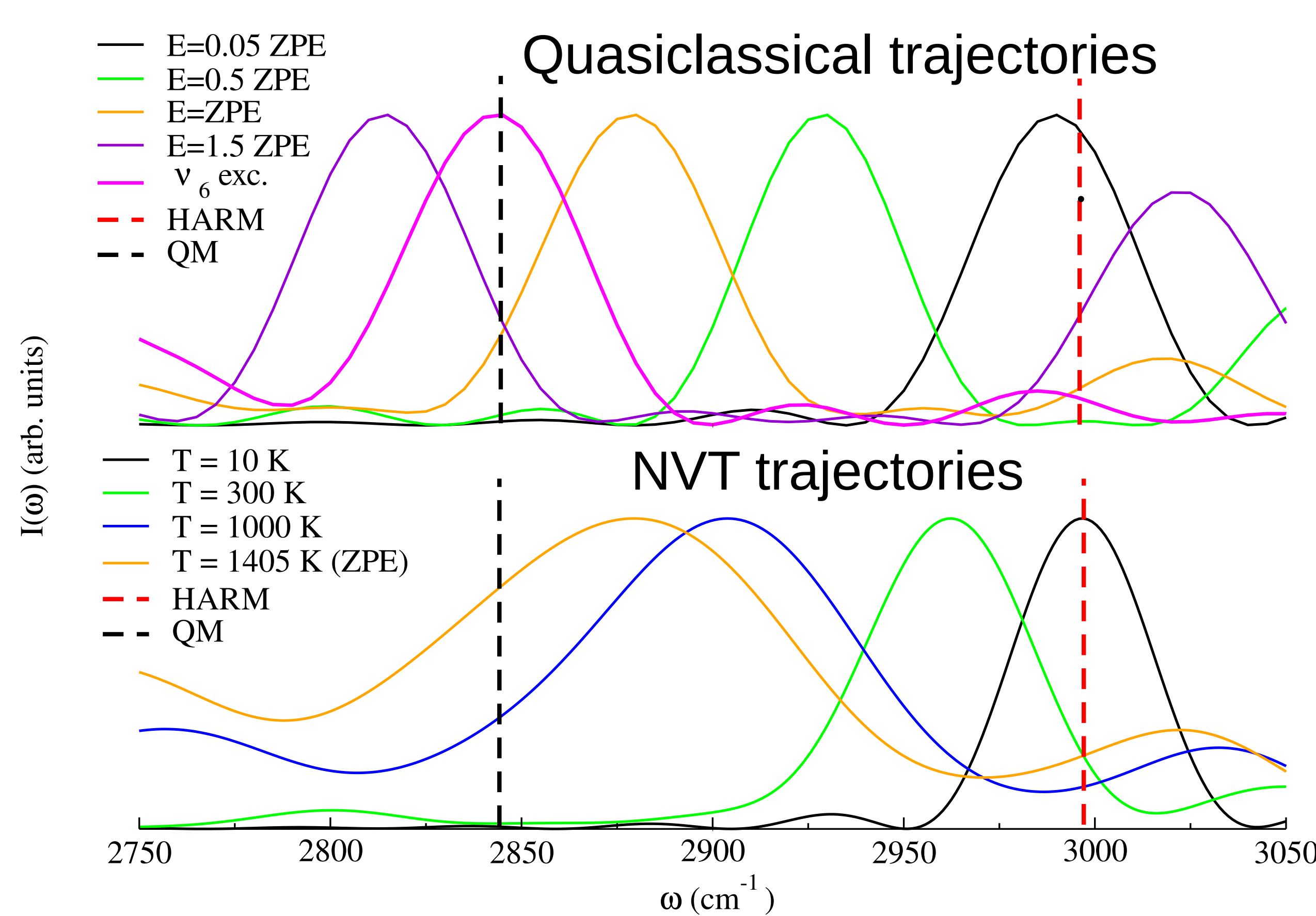
↑ Anharmonicities are included

↑ Nuclear quantum effects are included

↓ Computationally intensive

Classical Molecular Dynamics

In order to calculate the classical spectrum, one or more trajectories must be calculated. It is intuitive that since experiments are conducted at a finite and precise temperature, trajectory initial condition must be chosen through a thermal sampling. Since experimental spectra are often recorded at cryogenic or at room temperature, in such cases the computed trajectories would run at an energy which is very much below the vibrational Zero Point Energy (ZPE). This would cause the computed spectrum to be mostly harmonic since the trajectories would not be energetic enough to catch the anharmonicities of the PES.

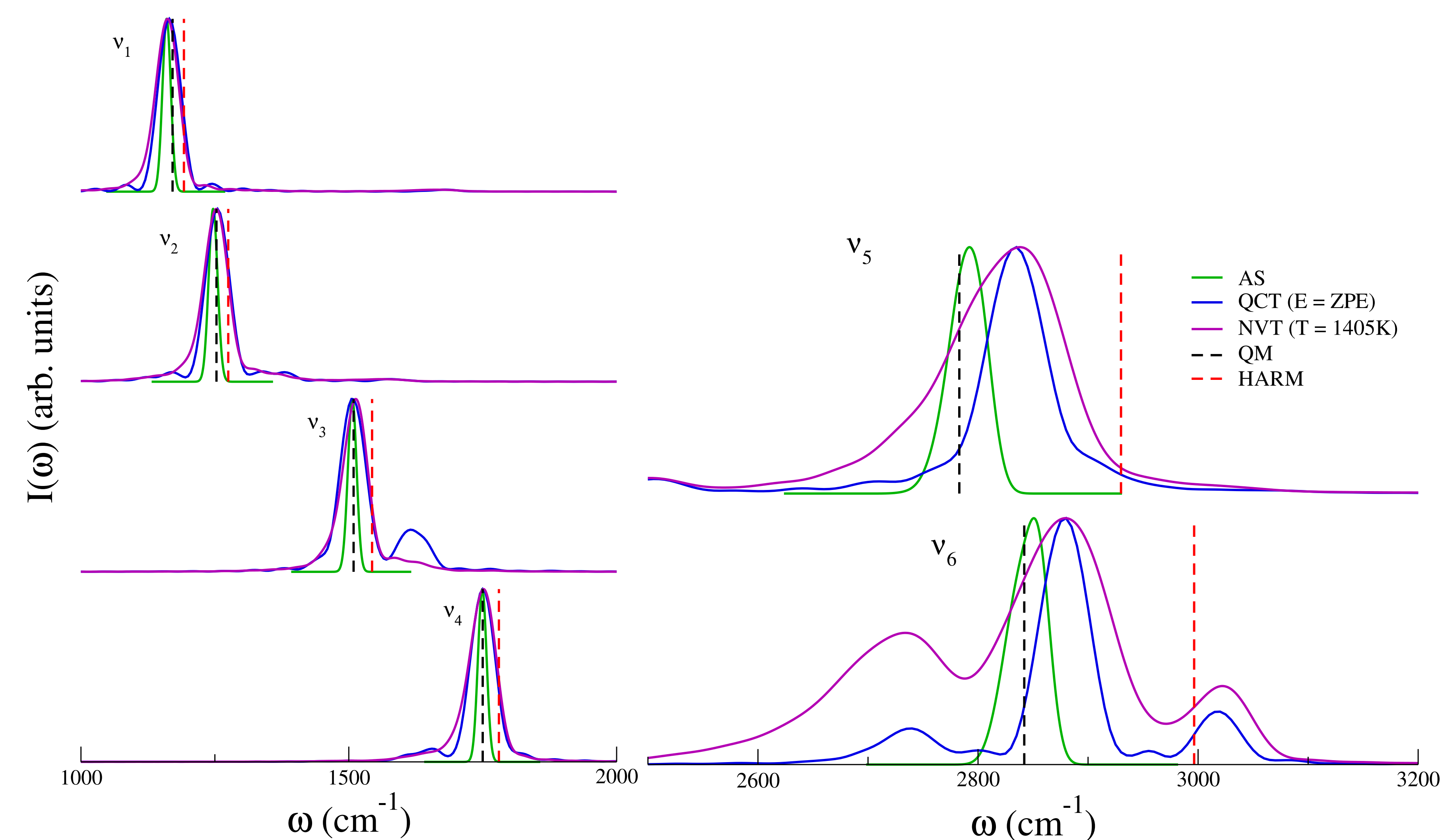


- 1000 short NVE trajectories per normal mode
- Initial positions are the equilibrium configuration
- Initial momenta are sampled from a gaussian distribution and rescaled in order to set the initial kinetic energy equal to the harmonic ZPE

- 1000 trajectories per normal mode
- For every trajectory an NVT MD simulation is run till thermalization is reached
- The initial conditions taken from the NVT run are used to initiate the production simulation which is a short NVE dynamics

The SCIVR method allows to add Nuclear Quantum effects to classical MD by considering second order deviations from the classical paths. One of the recently developed variants of the semiclassical methods is the Adiabatic Switching SCIVR (AS SCIVR). [7,8] This method based on the adiabatic theorem, switches on slowly the actual molecular Hamiltonian to generate a distribution of trajectories with energies near the anharmonic ZPE.

SemiClassical Molecular Dynamics



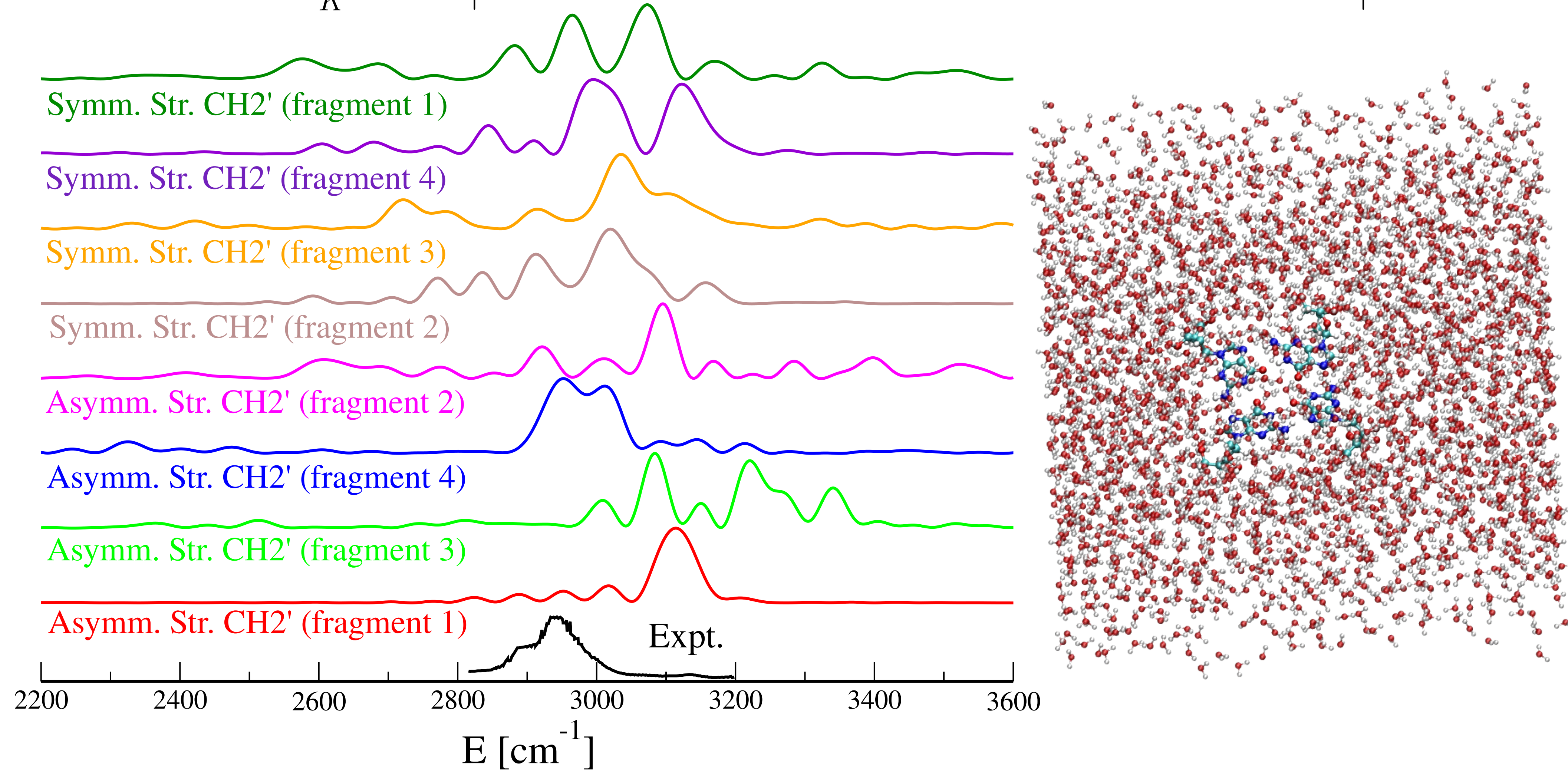
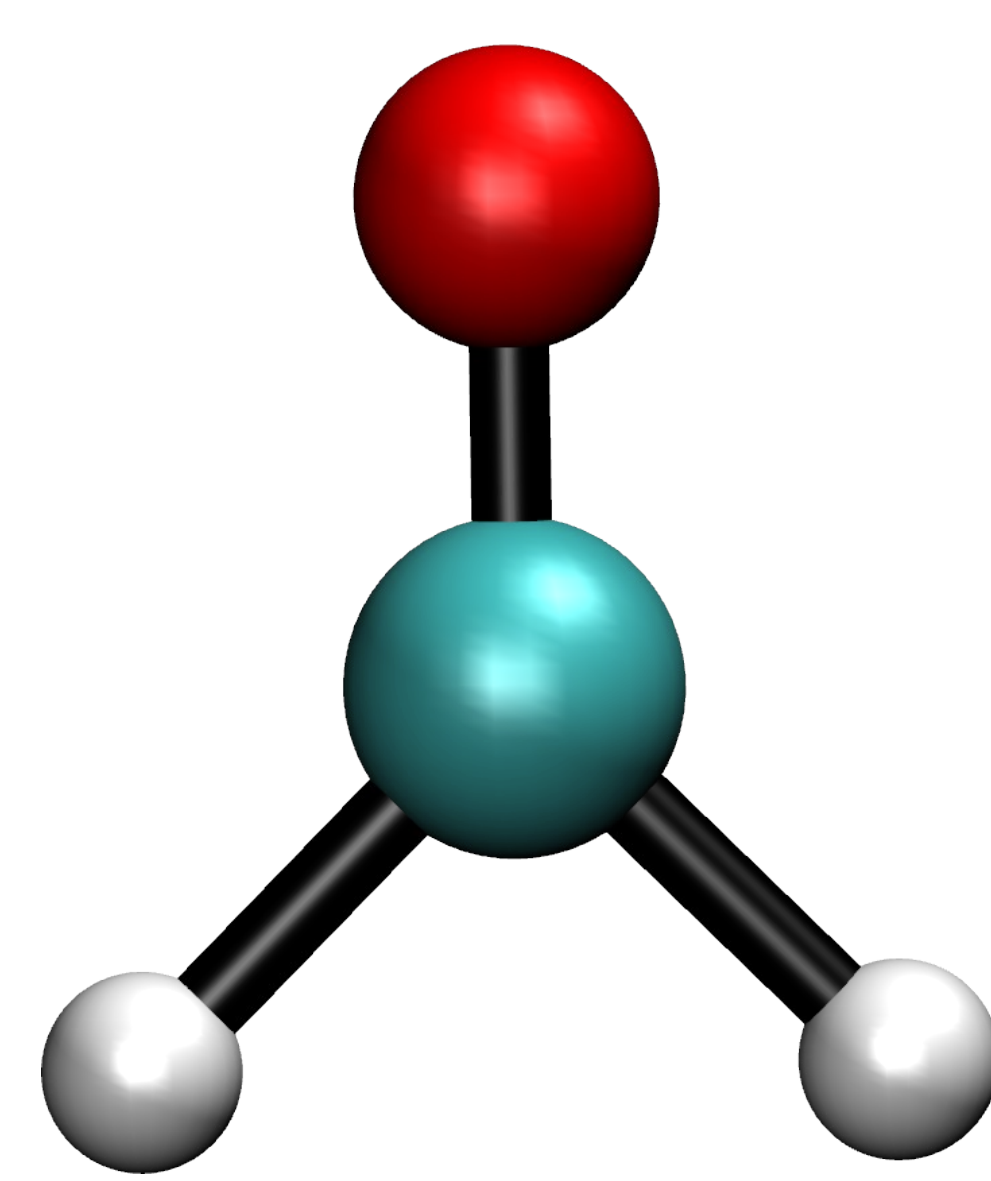
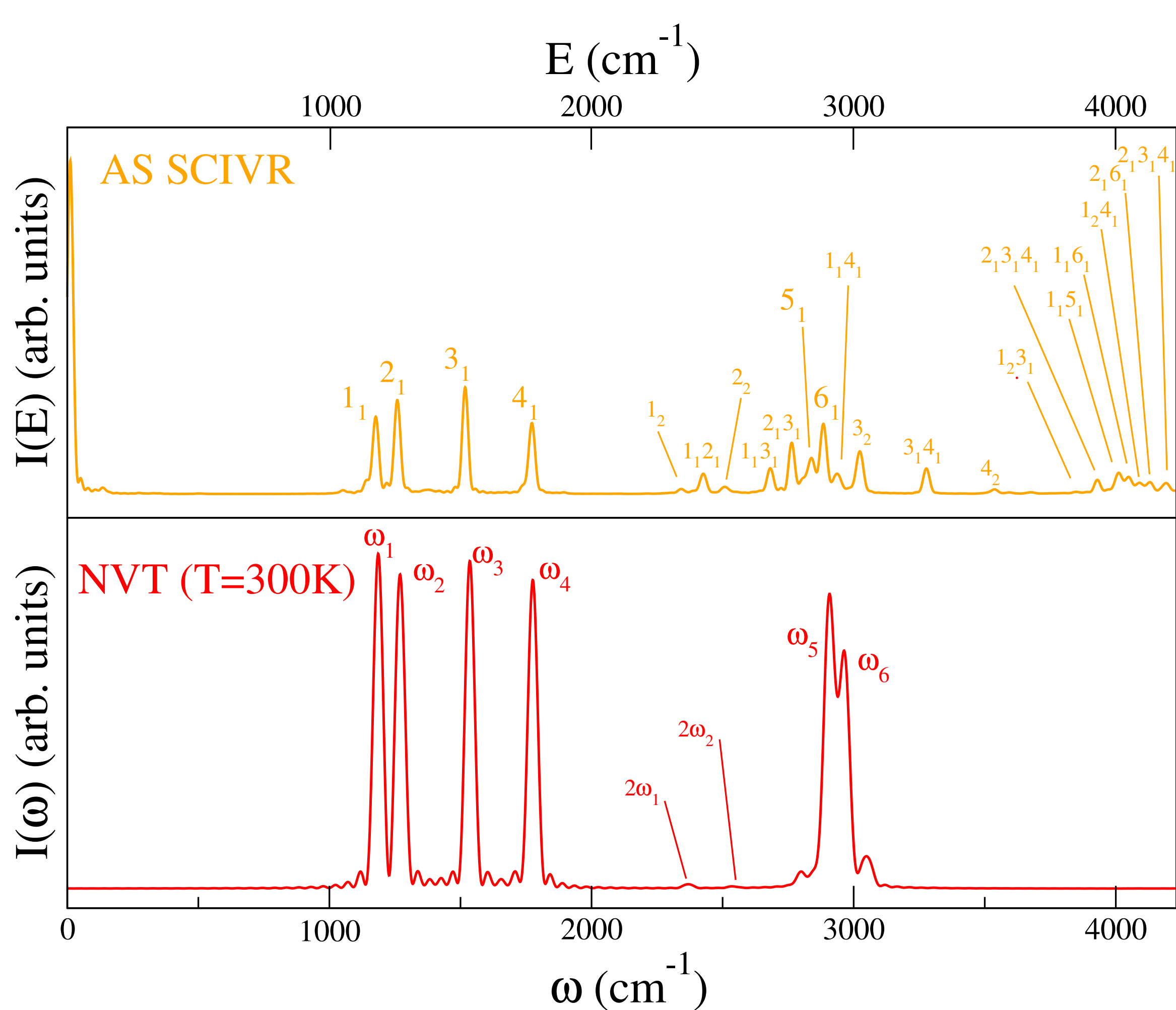
- 20000 trajectories
- For every trajectory a previous evolution using the switching Hamiltonian H_{AS} is run to generate the initial conditions of the production run
- The production run are short NVE trajectories used to compute the quantities needed for the TA-SCIVR method

$$H_{AS}(t) = H_0 + f(t)(H - H_0)$$

$$f(t) = \frac{t}{T_{AS}} - \frac{1}{2\pi} \sin\left(\frac{2\pi t}{T_{AS}}\right)$$

A more Challenging case

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



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