

Mixed Quantum/Classical Molecular Dynamics for Simulating Vibrational Spectroscopy of Peridinin in Solution

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Light-harvesting (LH) complexes are used by photosynthetic organisms to increase the overall efficiency of photosynthesis. This is accomplished by harvesting light energy and funneling it to the reaction center, where it is converted into electrochemical potential. Dinoflagellates, unicellular algae constituting one of the most important classes of phytoplankton, use a water-soluble LH complex called peridinin-chlorophyll-a-protein (PCP) with a 4:1 peridinin/chlorophyll ratio. The presence of peridinin molecules in the PCPs enables the organism to collect light in the visible spectral region where chlorophyll poorly absorbs. The peridinins of PCPs are also able to play a photoprotective role by efficient quenching of the chlorophyll triplet states, which may occasionally be populated, thus preventing the formation of the highly toxic singlet oxygen.

Infrared spectroscopy, and in particular time-resolved IR difference spectroscopy is a well-established technique which has been successfully used to investigate photophysical phenomena and photochemical reactions taking place in photosynthetic reaction center and LH complexes. This technique allows reaction-induced changes in both the protein and the cofactors to be monitored. In both static and time-resolved IR band assignment remains a difficult task. Vibrational frequencies can be obtained from theoretical calculations performed at molecular level such that the band assignment can be subsequently performed.

In studying IR signal a key signature is provided by the carbonyl function of the lactone ring. In particular the effect of different protein environments of the four peridinins present in PCP complex, was evocated to understand IR spectroscopy [1].

Based on this motivation, a set of IR and Resonance Raman experiments is going to be performed by Dr. A.Mezzetti of the University of Lille (France) to understand environmental effects on vibrational properties of peridinin. At this end three prototypical solvents were used in simulations: 1) an apolar/aprotic solvent, like cyclohexane; 2) a polar/aprotic solvent, like deuterated acetonitrile; 3) a polar/protic solvent like ethanol.

Ab-initio molecular dynamics should help for the band assignment that is a particularly important task to rationalize all those experiments. At this end we set-up a mixed Quantum Mechanics / Molecular Mechanics (QM/MM) approach where the peridinin is treated at DFT level, employing the PBE functional, while the different solvents at a classical level. This is achieved by using the CPMD package coupled with Gromos96. [3]

We have performed simulations in different solvents and vibrational spectra of key functions show the effect of different solute-solvent interactions at a microscopic level.

For each system we have performed QM/MM simulations using Born-Oppenheimer dynamics for the QM subsystem and classical MD with Amber force field for the MM subsystem. Newton's equation of motions were numerically integrated using a time step of 0.36 fs. For each run, after an equilibration time, we have accumulated the following trajectories : 12 ps

for cyclohexane, 15 ps for methanol and 13 ps of deuterated acetonitrile. The QM/MM partition scheme uses two simulation boxes: a “quantum box” where plane waves, expanded with a cut-off of 70 Ry (corresponding to a total number of 215049 plane waves) were used to represent electronic wavefunction and a classical box for the classical systems where periodic boundary conditions were enforced. For each system we used a rectangular QM box defined on the shape of peridinin – that has a long chain (see figure 1) – with the dimensions: 16.93 Å, 13.38 Å and 28.45 Å. The dimension of the classical boxes depends on the system, since for each system we have a different number of solvent molecules. For cyclohexane we have a 41.02x42.35x47.05 Å³ box where we placed 440 solvent molecules, for a total (QM+MM) system of 7959 atoms. For deuterated acetonitrile we have a 58.83x56.87x71.47 Å³ box where we placed 1749 solvent molecules for a total system of 10533 atoms. Finally, for methanol we have a 61.01x58.15x73.27 Å³ box where we placed 3742 solvent molecules for a total system of 22491 atoms. Box dimensions were obtained after NPT classical simulations with position restraints on the solute, providing these equilibrated box dimension for standard thermodynamic conditions of temperature and pressure.

Calculations were performed on CINECA and CINES supercomputing centers using 64 processors. Our scaling testes on CINES (Jade) have reported that the maximum in performances (i.e. the lowest (CPU time)/(number of CPUs) per time step ratio) is obtained for 192 processors (24 nodes, 8 core per node), but due to the difficulties to quickly enter such large queue, the 64 processor configuration was our final choice.

Simulations were first equilibrated in the NVT ensemble using standard Nosé-Hoover thermostat, at T=300 K, and then accumulation runs were done in the NVE ensemble where the temperatures of the total, the QM and the MM systems were checked to be stable around their target value.

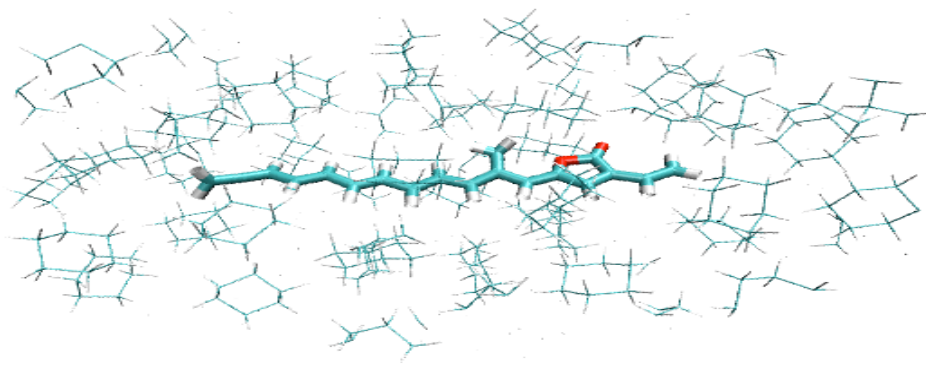


Figure 1. Peridinin model system (in sticks) with surroundings cyclohexane molecules.

For all 3 simulations we obtained velocity-velocity and dipole-dipole correlation functions. By Fourier transforming these functions, we also calculated the vibrational density of states (VDOS) and Infrared (IR) spectra. For this latter, the IR intensity, $I(\omega)$, is related to Fourier transform of the dipole-dipole correlation by the equation:

$$(1) I(\omega) = \frac{2\pi\beta\omega^2}{3cV} \int_{-\infty}^{\infty} dt \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle \exp[i\omega t]$$

where $\beta = (kT)^{-1}$, c is the in vacuum speed of light and V is the volume and $\mathbf{M}(t)$ is the molecular dipole calculated for the solute for each simulation step.

At variance with our calculations, the vibrational spectroscopy experiments performed by A. Mezzetti at University of Lille were resonance Raman. To obtain Raman spectra from experiments we should perform FT of the polarizability correlation function. Calculating polarizability for all the simulation steps will require an enormous amount of calculations – dipoles are obtained on-the-fly whereas polarizabilities are not – but information on vibrational motions are also present in the VDOS such that we can use VDOS information and compare those information with Raman spectroscopy data.

In Figure 2 we show VDOS obtained from simulations in the three solvents and we show also the Resonance Raman spectra, obtained for deuterated acetonitrile and methanol. Note that theoretical signals are not rescaled but are the pure signals obtained from simulations. Since simulations are performed at finite temperature, anharmonicity is directly taken into account. A shift in frequencies with respect observed experimental peaks is always present in this kind of calculations, due to the functional employed. As shown in figure 2 there is a good agreement between experiments and simulations.

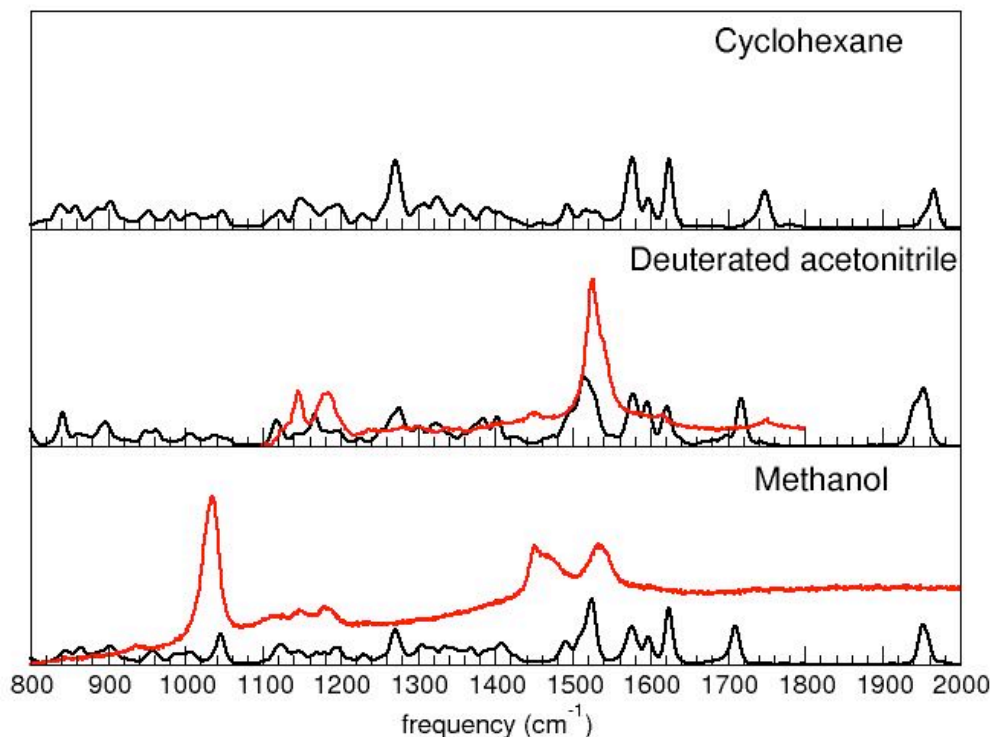


Figure 2: VDOS of peridinin model system obtained in three solvents. In red we show the resonance Raman spectra of peridinin.

In Figure 3 we show the three VDOS obtained from simulations to show better the solvation effects on vibrational bands. Peridinin is characterized by the presence of a carbonyl group in the lacton ring. The position of this band is largely influenced by the solvent, being at 1748, 1717 and 1710 cm^{-1} for cyclohexane, acetonitrile and methanol solvents respectively. A progressive red shift is obtained modifying the solvent from cyclohexane to acetonitrile and to methanol. This is quite expected since non-polar, non-protic solvents – like cyclohexane – slightly interact with the C=O group. On the other hand a polar solvent interacts with the polar C=O group and thus, weakening the bond, the band is red shifted. This effect is obtained for acetonitrile – a polar solvent – and largely for methanol, where an H-bond enhances this effect.

The high frequency band, corresponding to C=C=C vibration has a similar red shift trend. In this case the group cannot be involved in H-bond as C=O and this is reflected by the absence of differences in acetonitrile and methanol peak positions. Finally, the spectrum is characterized by a region between 1500 and 1620 cm^{-1} where are located the chain vibrational modes. These bands are Raman active and, looking in details, we noticed that the 10 cm^{-1} shift found in experiments between methanol and acetonitrile (in this case the acetonitrile solvent red shifts this band with respect methanol) is found also in the low frequency band obtained from simulations.

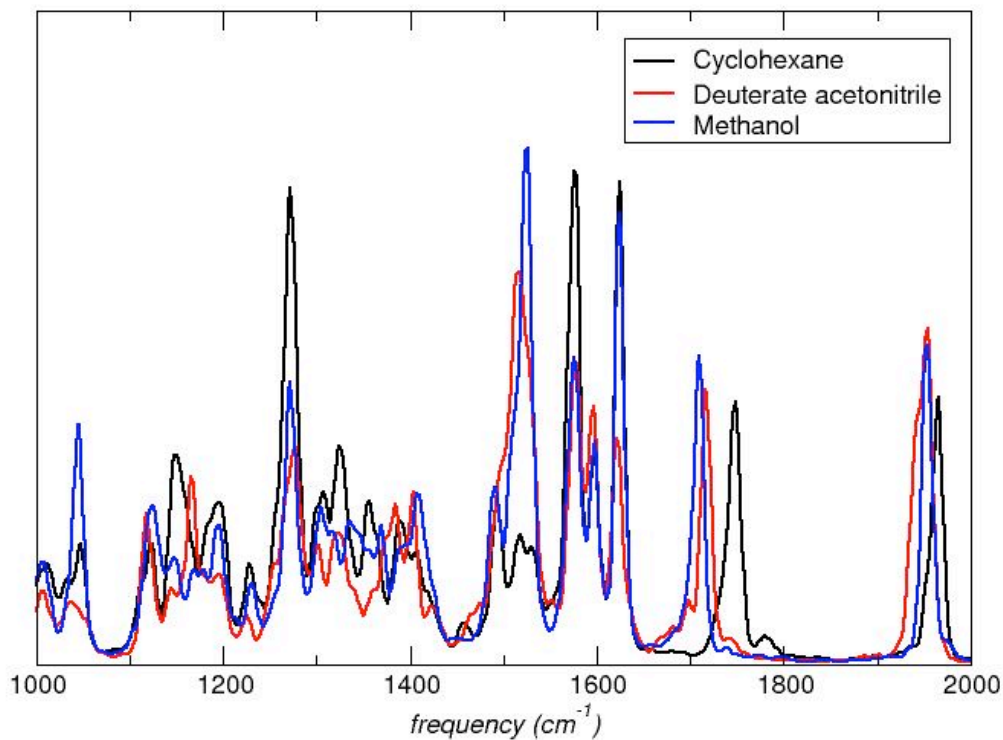


Figure 3. VDOS of peridinin model system in the three solvents studied. Zoom of the 1000-2000 cm^{-1} region.

More analysis are currently performed to clarify many details and in particular on the assignment of vibrational bands to the molecular normal modes, using the method developed recently by Martinez et al.[2].

References.

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