Abstract

Essentially all important industrial and biological reactions occur in solution, where the motions of the solvent affect the rate at which the reactions occur. While advanced spectroscopies have helped uncover underlying solvent motions, computer simulations, if accurate, promise to reveal many more details. We utilize a new mixed molecular dynamics and quantum mechanics method that closely connects simulation and experiment. We report the effects of simulation length, sampling rate, and different quantum mechanical models. We have observed differences in varying these parameters on linear absorption and nonlinear 3PEPS spectra and compare our results to experiment.

Introduction

Most chemical reactions take place in solution where solvent molecules surround solute. The effect of the solvent on the solute is to dramatically lower the energy of intermediates or transition states. The amount of energy lowering is highly dependent on the particular arrangement of solvent around the solute.

Studying Solvent Motion

Because changes in charge distribution in the solute cause the solvent to move and vice versa, techniques that study the distribution of electrons in the solute, such as linear and nonlinear spectroscopies, can be used to study the solvent motion. Such techniques depend on the fact that solvent motion changes the amount of energy required to excite a solute molecule electronically. Experimental techniques have been very successful in mapping optical information to the solvent response function, the overall effect of solvent on the solute as a function of time.

Simulations such as those employed here have predicted the spectra of large systems with remarkable accuracy considering the approximations used. However, there is still a considerable amount of uncertainty in how best construct such a simulation. We are currently performing a series of calculations to explore the following system parameters and their effects on the overall description of how the system responds to light:

- **Molecular dynamics (MD) trajectory length**: over how long a period of time must we simulate the motion of the system?
- **Quantum mechanical sampling rate**: how frequently must snapshots of the system be analyzed?
- **QM model chemistry**: how many basis set functions are needed to build an accurate description of the electronic distribution of the solute for each snapshot and how carefully must the solute wavefunction be constructed from the chosen basis set?
- **Methanol Solvent Shell Size**: how small of a solvent shell of methanol can be used under periodic boundary conditions so that the oxazine-4 molecules do not interact with each other?

We are able to simulate the motion of the solvent and solute and infer the optical response of the system from it. An example of this is described below using Figure 2.

1. The movement of the system is simulated with molecular dynamics (MD), a classical mechanics treatment of nuclei suitable for large numbers of solvent molecules. Many "snapshots" of the different system configurations are saved providing a sampling of the ground state potential surface.
2. The amount of energy required to excite the solute is calculated for each of the snapshots generated from MD. Quantum mechanics is required since we are interested in electronic changes. From the changes in this electronic energy gap over time (see Figure 4-c), one can obtain the optical response function of the system.

Methods

We are currently simulating the dye oxazine-4 (Ox4, below) dissolved in methanol. Experimental data for the response function of this system are available. We use the MD package AMBER 7 to simulate one Ox4 molecule dissolved in ~12,500 methanol molecules. Electrostatics are treated with particle-mesh Ewald (PME) under a truncated octahedral periodic boundary condition, which roughly mimics a spherical distribution of solvent.

![Figure 2](image_url)

**Figure 2**: Solvation Coordinate (Solvation Position)

We report the effects of simulation length, sampling rate, and quantum mechanics method that closely connects simulation and experiment.
Molecular Dynamics

MD provides the necessary time-ordered configurations of solute and solvent. The position of every atom in the system is saved every step. 1 ns of equilibration was performed, followed by 20 ps of production MD.

Quantum Mechanics

QM provides the excited state energy for each timestep, $U(t)$, necessary to map the optical response of the system. We are currently running quantum mechanics (Gaussian 98) at the National Center for Supercomputing Applications. The results presented here utilized over 20 years of CPU time, and thus maximizing throughput of QM calculations is critical.

Linking MD and QM

The following figure illustrates the process of our mixed MD-QM method.

![Figure 4](image)

Parts (a) and (b) depict the MD and QM, respectively, at two different moments. The MD snapshots show how the solvent and solute are arranged and the QM illustrates how the solvent field changes the electronic distribution of the solute. Thus, the motions of the system have a profound effect on the energy gap between the ground and excited states of the solute. The fluctuation of this gap over time shown in (c) defines the optical properties of the solute and is used to simulate spectroscopic observables such as the linear absorption spectrum shown in (d).

Results and Status

![Figure 5](image)  
![Figure 6](image)

Figures 5 and 6 respectively show the linear absorption and nonlinear 3PEPS spectra from the various QM model chemistries using a 1 fs QM sampling period from 20 ps of MD trajectory. All of the models roughly agree with experiment. The best fit to the experiment was the CIS/STO-3G, although this was probably fortuitous cancellation of QM overestimation by MD underestimation of solvent fluctuations. The ZINDO method was particularly encouraging because of its low computational cost and reasonable comparison to experiment in both the linear and nonlinear spectra. The TD-B3LYP method had similar results to the CIS method. The non-linear spectrum shows a rapid decay over the first 100 ps by all of the methods that do not correspond to the experiment.

Using the CIS/3-21G* model chemistry and 20 ps of MD trajectory, a variety of QM sampling periods were tested (Figures 7 and 8) in addition to a variety of trajectory lengths with a 1 fs step size (Figures 9 and 10). Sampling periods as large as 10 fs yield results that are essentially indistinguishable from the smaller sampling periods in the linear spectra (Fig. 7). Greater differences are seen in the nonlinear spectra though sampling periods up to 4 fs are still similar.

Future Research

Our future plans with this project with regard to MD can be divided into several components. The first of these is changing the size of the system used in the MD to a smaller size of around 30 Å. We are also interested in making the oxazine-4 static during the MD simulations in order to see its effects. In addition, we will be examining the method of QM/MM, where in each molecular dynamics calculation a quantum calculation will occur to recalculate the forces and force constants parameters that AMBER uses. Both of these future goals we hope will help fix the rapid decay in the non-linear spectra from Figure 6.

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References
