

A Study on Orientation and Absorption Spectrum of Interfacial Molecules by Using Continuum Model

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Abstract: In this work, a numerical procedure based on the continuum model is developed and applied to the solvation energy for ground state and the spectral shift against the position and the orientation of the interfacial molecule. The interface is described as a sharp boundary separating two bulk media. The polarizable continuum model (PCM) allows us to account for both electrostatic and nonelectrostatic solute–solvent interactions when we calculate the solvation energy. In this work we extend PCM to the interfacial system and the information about the position and orientation of the interfacial molecule can be obtained. Based on the developed expression of the electrostatic free energy of a nonequilibrium state, the numerical procedure has been implemented and used to deal with a series of test molecules. The time-dependent density functional theory (TDDFT) associated with PCM is used for the electron structure and the spectroscopy calculations of the test molecules in homogeneous solvents. With the charge distribution of the ground and excited states, the position- and orientation-dependencies of the solvation energy and the spectrum have been investigated for the interfacial systems, taking the electrostatic interaction, the cavitation energy, and the dispersion–repulsion interaction into account. The cavitation energy is paid particular attention, since the interface portion cut off by the occupation of the interfacial molecule contributes an extra part to the stabilization for the interfacial system. The embedding depth, the favorable orientational angle, and the spectral shift for the interfacial molecule have been investigated in detail. From the solvation energy calculations, an explanation has been given on why the interfacial molecule, even if symmetrical in structure, tends to take a tilting manner, rather than perpendicular to the interface.

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Key words: interfacial molecule; spectrum; continuum model; solvent effect

Introduction

The chemical processes occurring at interfaces between two immiscible liquids are well known to play an important role in many fields such as catalysis chemistry and biochemistry.¹ Various analytical techniques have been applied to reveal the characteristics of liquid/liquid interface. Linear and nonlinear laser spectroscopy by time-resolved total internal reflection fluorescence,^{2–5} sum frequency generation,^{6–9} and second harmonic generation (SHG)^{10–18} spectroscopy have been intensively used to draw information on liquid/liquid interfaces at the microscopic level. In the recent years, Wang and Eisenthal reported the average polarity model for the liquid interfaces from their experimental observations with SHG¹⁴. Later on, Steel and Walker used a series of so-called molecule ruler to measure the interfacial width^{11,12,15} and Ishizaka and Kitamura studied the interfacial solvent relaxation behaviors using molecule probes.⁵

On the other hand, many theoretical studies of physical and chemical processes occurring at interfaces were carried out. In this aspect, some authors used molecular dynamic simulation (MD)^{19–25} and a two-sphere model²⁶ to study the molecular behaviors at the interface and gained some instructional results. Recently, some authors used PCM approach to study solvation energy,²⁷ excited energy²⁸ at the interface and the rate constant in heterogeneous dielectric environments.²⁹

If the molecule–interface interaction is stable, the average effect will play an important role, and the interfacial dielectric

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property can address the average effect very well. On the other hand, the experimental technique of interfacial spectroscopy has been providing important information of the liquid interfaces as mentioned above, so it is important to study the relationship between the spectroscopy and the dielectric property at interface. For the homogeneous solvent, continuum model serves the purpose of studying the solvent effects and it has been widely used to deal with the molecular structures and reactions in condensed phase in the last decades.^{30–33} At the same time, There was some development to deal with interfacial processes within the framework of continuum model,^{19,27,28,34} and some useful arithmetic has been provided, such as integral equation formulation PCM (IEF-PCM) for interface case. In this article, we develop a numerical approach based on continuum model to study the behaviors of the interfacial systems, based on our new derivations of nonequilibrium solvation.

Several typical molecules that were used to study interfacial properties by Steel and Wang are chosen in this study.^{11,14,15} Various interfaces, e.g., air/water, cyclohexane/water, and heptane/water have been taken into account. A common conclusion drawn from the experiments and MD studies is that the stabilized interfacial molecule adopts the tilting manner at the interface, so we need to see insight into the mechanism. The goal of the present article is to investigate the most possible orientational angle of the molecule tilting at the interface, the embedding depth of the ground state molecule and the spectroscopic properties of the interfacial systems. From the solvation energy calculation of the ground state, the most possible location and orientation of the molecule can be predicated. One of the most important points in this report is that there are two competing factors that influence the orientational angle of the molecule at the interface: the molecular polarity and the cavitation energy. Intuitively, the molecular dipole tends to stand at the interface perpendicularly, with the hydrophilic group pointing to the more polar medium. However, a number of experimental observations revealed the tilting orientation of the interfacial molecules, hence some explanations should be given for this behavior. The present study shows the first time that the tilting manner of the molecule can reduce the cavitation energy, and thus brings the system a lower total energy and stabilizes the system. In bulk solution, as many authors indicate, the solute is subject to isotropic forces and the continuum model can describe the solute behavior validly.¹² However, at an interface, short-range interactions between a solute and its surroundings can lead to dramatic changes in solute properties. A more precise demonstration for those forces is very complicated; hence the present study is aimed at the qualitative and semi quantitative conclusions.

Theory

Continuum Model for Interfacial System

Adopting the numerical solution of the Poisson equation for a solute molecule embedded in an arbitrary cavity, the complete implementations of PCM are in such as Gaussian and Gamess packages.^{35–37} Variables of the PCM on the homogeneous bulk solvent have been elaborated in many literatures.^{28,35–37} With PCM, the bulk of the solvent is described as a polarizable con-

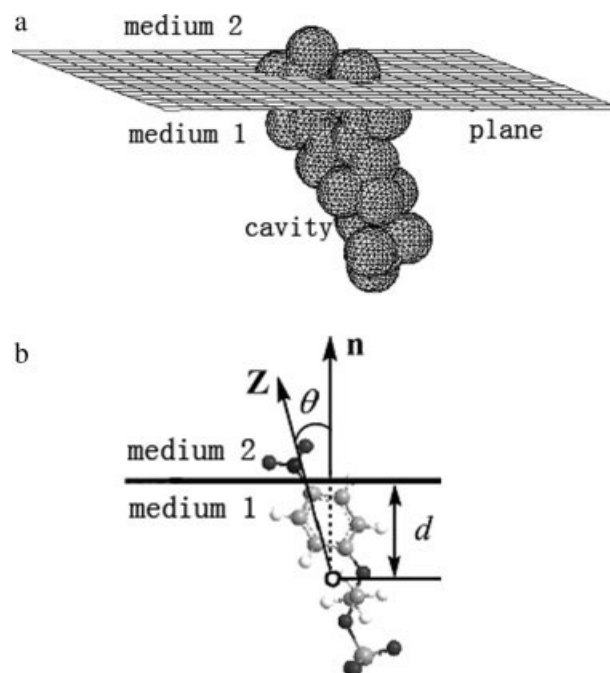


Figure 1. Schematic depiction of molecular ruler surfactant at interface (a) and the orientation of the inertial principle axis Z and the embedding depth d of the molecular mass center into the water phase (b).

tinuum characterized by its dielectric constant and by other macroscopic quantities. Here we only give the key formulations and show our extension to the interfacial system. Because several experiments and theoretical studies suggested that liquid/liquid interfaces are molecularly sharp,^{21,38,39} we suppose the liquid/liquid interface a simple ideal plane. We construct the interfacial cavity in the following way. The solute inserts a cavity formed by interlocking spheres and the cavity crosses the planar interface. The cavity surface and the plane are then partitioned into small elements called tesserae (see Fig. 1). In ref. 28, some authors presented the procedure with IEF-PCM. Such a method is based on the Green's function, and the interface between the two dielectrics is embedded into the Green's function. Here we adopt the D-PCM (D refers to dielectric) method for convenience.

PCM allows one to compute the solvation energy of the system as a sum of distinct contributions³⁰

$$G = G_{\text{el}} + G_{\text{cav}} + G_{\text{dis}} + G_{\text{rep}} \quad (1)$$

where G_{el} is the electrostatic interaction energy. G_{cav} denotes the surface work spent to create the cavity in the continuous medium, called the cavitation energy, which is given by

$$G_{\text{cav}} = \sum_j^{\text{spheres}} \left(\frac{A_j^{S1}}{4\pi l_j^2} G_j^{S1} + \frac{A_j^{S2}}{4\pi l_j^2} G_j^{S2} \right) - A^{\text{plane}} \gamma_{S1/S2} \quad (2)$$

In eq. (2), j runs over the spheres forming the cavity, l_j is the radius of sphere j with an area A_j^{S1} exposed to the solvent 1, A_j^{S2}

has the similar meaning but for solvent 2. G_j^{S1} and G_j^{S2} in eq. (2) is the parameterized cavitation energy for a sphere of radius l_j in solvents 1 and 2 respectively.⁴⁰ Unlike the usual PCM approach, special attention should be paid to another quantity, A^{plane} , which is the area of the interface portion cut off by the occupation of the molecule into the media (see Fig. 1). Here $\gamma_{S1/S2}$ denotes the interface tension between solvents 1 and 2. The last term in eq. (2) indicates a decrease of the free energy and it gives rise to the stabilization of a molecule at the interface. In the usual case, a tilting conformation of the molecule at the interface will produce a larger value of A^{plane} than the perpendicular manner. From this viewpoint, the most favorable orientation of the interfacial molecule is to lie at the interface, reaching a largest value of this term. G_{dis} and G_{rep} in eq. (1) are solute–solvent dispersion–repulsion interactions respectively, and their classical approximations are proposed as^{41–43}

$$G_{\text{dis(rep)}} = \sum_a^{\text{solute atoms}} \sum_s^{\text{solvent atoms}} K_{as} \left[-\frac{A}{z^6} + C \exp(-\alpha z) \right] \quad (3)$$

where

$$z = R_{as}/R_{as}^0$$

$A = 0.214$, $C = 47,000$ ($G_{\text{dis(rep)}}$ is in kcal/mol), R_{as} is the distance between a and s atoms. K_{as} , R_{as}^0 depends on a set of atom–atom parameters such as those proposed by Caillet and Claverie on the basis of crystallographic data.⁴³

The electrostatic contribution G_{el} plays the central role and needs more attention. The total electrostatic free energy is given by

$$G_{\text{el}} = \frac{1}{2} \int \rho \Phi dV = \frac{1}{2} \int \rho \psi dV + \frac{1}{2} \int \rho \varphi dV \quad (4)$$

where ρ is the solute (free) charge distribution, Φ the total electrostatic potential, ψ the potential due to solute charge in vacuum, and φ the polarization potential. In the present work, the solute charge distribution is assumed fixed for a specific state, without considering the influence from the polarization of the solvent. Under this approximation, $1/2 \int \rho \psi dV$ remains a constant when we change the orientational angle and the position of the interfacial molecule. In fact, this quantity is involved in the quantum mechanical calculation. Most conveniently, the polarization potential φ is represented in terms of polarization charges placed at the centers $\mathbf{r}'$ of the surface tesseraes,³⁰

$$\varphi(\mathbf{r}) = \sum_i^{\text{tesseraes number}} \frac{q(i)}{|\mathbf{r} - \mathbf{r}'|} \quad (5)$$

Polarization charge $q(i)$ depends on the solute charge distribution, the dielectric constant, and the cavity shape. Unlike the homogeneous medium, the polarization charge spreads on the tesseraes of both the cavity surface and the planar interface. Within the PCM framework, there are many mathematical approaches used to determine the polarization charges, but we take the following form^{44,45}

$$\mathbf{D} \mathbf{q} = \mathbf{b} \quad (6)$$

where the column vector $\mathbf{q}$ collects the polarization charges, but $\mathbf{b}$ collects the normal components of the solute electric field at the tesseraes. The square matrix $\mathbf{D}$ is related to cavity geometry and to the solvent dielectric constants. When we tend to the interfacial situation, we have

$$D_{ii} = \frac{2\pi}{a_i} \left(\frac{\varepsilon_{II} + \varepsilon_I}{\varepsilon_{II} - \varepsilon_I} + \sqrt{\frac{a_i}{4\pi l_i^2}} \right)$$

for the tesseraes on the cavity surface and

$$D_{ii} = \frac{2\pi \varepsilon_{II} + \varepsilon_I}{a_i \varepsilon_{II} - \varepsilon_I}$$

for the tesseraes on the interface plane. In practice, the outer part of the infinite interface is truncated to make the tesseraes on the interface limited. The off diagonal element of the D matrix is given by

$$D_{ij} = \frac{(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{n}_i}{|\mathbf{r}_i - \mathbf{r}_j|^3} \quad (i \neq j) \quad (7)$$

Besides, the element of b is of the following form,

$$b_i = - \sum_k Q(k) \frac{(\mathbf{r}_i - \mathbf{R}_k) \cdot \mathbf{n}_i}{|\mathbf{r}_i - \mathbf{R}_k|^3} \quad (8)$$

In the above equations, a_i is the area of tesserae i , l_i the radius of spherical cap of tesserae i , $\mathbf{n}_i$ the outer normal of the tesserae i , ε_I and ε_{II} the dielectric constants of the media inside and outside of tesserae i respectively, judged by $\mathbf{n}_i$, and $Q(k)$ the net charge of atom k at position $\mathbf{R}_k$.

The cavity construction for the interfacial system in this work needs to be stated. As shown in Figure 1, the surface on which the polarization charges spread includes two parts, interlocking spheres and a planar interface. For the former, the well-known GENERating POLyhedra (GEPOL) procedure⁴⁶ has been used with the van der Waals radii being scaled by a factor of 1.2. Each sphere is divided into 240 tesseraes in order to guarantee the computation precision. For the partition of the planar interface, we take a square region of 135.17×135.7 a.u.² into account. This region is further divided into two subregions. In the inner subregion, 45×45 a.u.², is divided into 30×30 equal square grids with an area of 1.5×1.5 a.u.² for one grid, which is 4 times bigger than the area of cavity tessera. The screen effect and the fast attenuation of the electric field outside the cavity allow us to take such bigger area for remaining appropriate weight of elements in D matrix. Considering that the outer part is less important in evaluating the solvent effect, the outer subregion is separated in such a way that every ring contains 29×4 adjoining squares. Up to 16 rings, the border length of the total plane is 135.17 a.u. The cavity diameter of the test molecules selected in this work are found less than 24 a.u., so the plane defined in this work is 135.17×135.17 a.u.². In order to guarantee the convergence of the electrostatic free energy, we inspect the dependence of the free energy on the cut off radius c . Figure 2 shows the numerical results of DEPNA system with

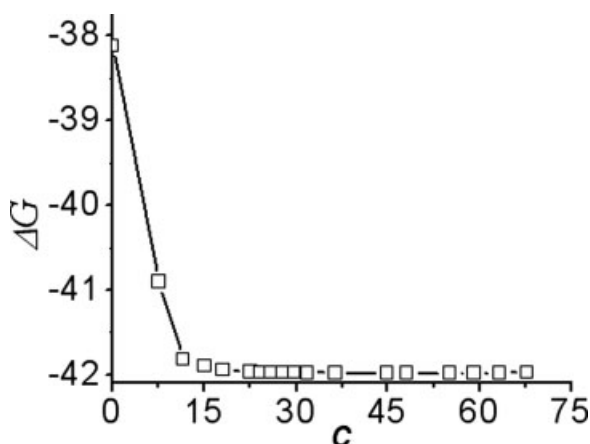


Figure 2. Contribution of electrostatic free energy caused by the existence of air/water interface for DEPNA system. c is the cut off radius in a.u. $\theta = 0^\circ$ and $d = 0$. $c = 0$ indicates the neglect of the interface contribution.

a perpendicular pattern. It is found that the electrostatic free energy keeps almost unchanged when the cut off radius goes beyond 20 a.u.

It is obvious that when the interlocking sphere cavity intersects the plane, some tesseraes at the joint will be severed, but the tesseraes are still taken as unbroken and no further treatment is performed here. Calculated result shows the construction of the cavity and the plane can provide an enough computation precision.

Nonequilibrium Solvation and Spectral Shift of Absorption

When a vertical excitation of the molecule occurs, the solute electronic transition is much faster than the reorientational motion of the solvent molecules. To consider such a retardation of polarization, two components of the polarization are considered: the fast one and the slow one. The fast component of the solvent polarization is able to adjust and match excitation of the solute, whereas the slow component of the polarization related to the orientational motion of the solvent molecules remains fixed as in the ground state. To describe this nonequilibrium phenomenon within the framework of continuum model, the polarization charge $q^e(i)$ corresponding to the excited state is split into two distinct parts,^{44,45}

$$q^e(i) = q_{\text{slow}}^e(i) + q_{\text{fast}}^e(i) \quad (9)$$

where $q_{\text{slow}}^e(i)$ is the slow component of the polarization charge at ground state, i.e.,

$$q_{\text{slow}}^e(i) = q^g(i) - q_{\text{fast}}^g(i) \quad (10)$$

Here q^g denotes the total polarization charge of the ground state and it can be gained using the procedure mentioned above, by setting ε_I and ε_{II} the static dielectric constants of the inner and outer medium and $\{Q(k)\}$ the solute charges of the ground state.

In the parallel way, q_{fast}^g can be obtained by setting ε_I and ε_{II} the corresponding optical dielectric constants. In eq. (9), q_{fast}^e represents the fast component of polarization charge at excited state. It is gained by using the solute charges $\{Q^e(k)\}$ instead.

For the ground state, the total free energy is written as follow³⁰

$$G^g = \frac{1}{2} \sum_i^{\text{tesseraes}} \sum_k^{\text{atoms}} Q^g(k) \frac{q^g(i)}{|\mathbf{r}_i - \mathbf{r}_k|} + G_{\text{el}}^{g0} + G_{\text{cav}} + G_{\text{dis}} + G_{\text{rep}} \quad (11)$$

G_{el}^{g0} is the self-energy of the solute charges at ground state in vacuum, and hence the solvation energy of the ground state can be defined as

$$\Delta G^g = G^g - G_{\text{el}}^{g0} \quad (12)$$

At the excited state, the electrostatic free energy, G_{el}^e , is related to the so-called nonequilibrium solvation. In a series of our previous papers, an expression for this quantity was derived to the following form,^{44,45,47,48}

$$G_{\text{el}}^e = \frac{1}{2} \int \rho^e \Phi^{\text{e,non}} dV = \frac{1}{2} \int \rho^e \varphi^{\text{e,non}} dV + \frac{1}{2} \int \rho^e \psi^e dV \quad (13)$$

Like the ground state case, we call the last term in eq. (13) the self-energy of the solute charges at the excited state in vacuum and denote it G_{el}^{e0} . The other parameters appearing in eq. (13) have the similar meanings as eq. (4). Discretization of the first integral of the right hand side of eq. (13) can be made, and the electrostatic free energy at the excited state is thus given by^{44,45}

$$G_{\text{el}}^e = \frac{1}{2} \sum_i^{\text{tesseraes}} \sum_k^{\text{atoms}} Q^e(k) \frac{q^e(i) - q_{\text{fast}}^g(i) + q_{\text{fast}}^e(i)}{|\mathbf{r}_i - \mathbf{r}_k|} + G_{\text{el}}^{e0} \quad (14)$$

When the cavitation energy and the solute-solvent dispersion-repulsion energies are supposed to unchanged during the excitation, the maximum band of the absorption of a molecule can be written as

$$h\nu_{\text{ab}} = G^e - G^g = h\nu_{\text{ab}}^0 + \Delta h\nu_{\text{ab}} \quad (15)$$

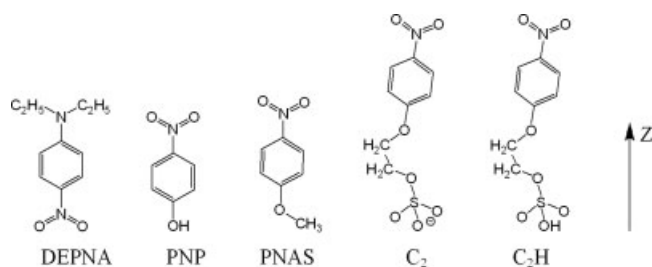
with

$$h\nu_{\text{ab}}^0 = G_{\text{el}}^{e0} - G_{\text{el}}^{g0}$$

and

$$\Delta h\nu_{\text{ab}} = \frac{1}{2} \sum_i^{\text{tesseraes}} \sum_k^{\text{atoms}} \left[Q^e(k) \frac{q^e(i) - q_{\text{fast}}^g(i) + q_{\text{fast}}^e(i)}{|\mathbf{r}_i - \mathbf{r}_k|} - Q^g(k) \frac{q^g(i)}{|\mathbf{r}_i - \mathbf{r}_k|} \right] \quad (16)$$

where $h\nu_{\text{ab}}^0$ represents the absorption of a molecule in vacuum, and $h\nu_{\text{ab}}$ measures the spectral shift. In the following sections, some details on program implementation will be described, and then this procedure will be applied to the several test molecules,



Scheme 1.

N,N-diethyl-*p*-nitroaniline (DEPNA), *p*-nitrophenol (PNP), *p*-nitroanisole (PNAS), C_2 (a surfactant anion containing 2 methylene groups), and C_2H (a hydrogen is attached to the unsaturated oxygen atom connecting sulfur atom in C_2 anion) (Scheme 1). All the five test molecules have the same chromophore. We take the inertial principle axis Z for each molecule for the convenience of discussion. We define the direction of Z pointing from the hydrophilic group to the hydrophobic one (from the bottom to the top in Scheme 1).

Results and Discussions

Time-dependent density functional theory (TDDFT) in Gaussian03⁴⁹ was used for the calculation in homogeneous solvent. Using the B3LYP functional with the 6-31+G* basis sets, the geometry optimizations of the five molecules, DEPNA, PNP, PNAS, C_2 , and C_2H , as shown in Scheme 1, have been performed in vacuum. With the optimal geometries, electronic structures of those species have been calculated in homogeneous solvents, water, cyclohexane, and heptane. PCM is adopted for the solvent effect. The results are collected in Table 1.

Here we illustrate the way through which we perform the calculation for the interfacial molecule. The charge distributions of ground and excited states of the test molecules in water, cyclohexane, and heptane have been determined with the B3LYP functional and 6-31+G* basis sets. The used static and optical dielectric constants are also listed in Table 2.

We choose the proper excited state to calculate the interfacial properties considering two reasons, one is the oscillator strength for the transition and the other is the orbital transition character consistent with the fact that the change of electronic structure occurs at PNAS-based chromophore.¹¹ The selected transitions with large oscillator strength are given in Table 1. It is seen that the transitions are assigned $S_0 \rightarrow S_1$ or $S_0 \rightarrow S_2$ except C_2 in vacuum. If the oscillator strength of transition $S_0 \rightarrow S_1$ is negligibly small, we choose the transition $S_0 \rightarrow S_2$ for our study (see Table 1). But we can see the oscillator strength and excited energies of C_2 in vacuum is very disordered, so we choose the bulk cyclohexane result of C_2 for the further calculation. For comparison, we take the result of bulk cyclohexane for C_2H also. The frontier molecular orbitals included in the transitions are presented in Figure 3.

From eq. (2), we can see G_{cav} is the sum over all the atoms. This energy is proportional to the areas of the boundary. For the first term of eq. (2), we only need to get the areas embedding in

the media for each sphere, thus the G_{cav} in the cavity part will be gained. On the other hand, the second term, $-A^{\text{plane}}\gamma_{S1/S2}$ in eq. (2), is contributed from the planar interface. Here A^{plane} is simply the area cut off by the interlocking spheres. The interface tension $\gamma_{S1/S2}$ is expressed as

$$\gamma_{S1/S2} = |\gamma_{S1} - \gamma_{S2}| \quad (17)$$

Here γ_{S1} and γ_{S2} are the surface tensions of the bulk solvents 1 and 2 respectively. The values of them are collected in Table 2.⁵⁰

Equation (3) is a discrete expression for $G_{\text{dis(rep)}}$, the sum is over all the atoms of the solute and solvent molecules. The solvent molecules are put on the grid points of the lattice and encircle the solute molecule. The radii of the locking spheres are adjusted to fit the bulk results given by Gaussian03. For all the calculation, we take the cutoff radii⁴² (the dispersion–repulsion energy induced by the further solvent molecules is neglected) being larger than 20 a.u.

The solute charge distributions for ground and excited states are the key quantities in calculating the electrostatic free energy of the ground state and the spectral shift of absorption. TDDFT has the advantage in the excitation energy calculations for a sole molecule, but there is still no reliable method associated with TDDFT for the calculation of charge distribution of an excited state. In order to obtain this quantity, the one-particle density calculation has been executed at present (keyword = RhoCI in gaussian03),^{49,51} RhoCI is a method used to get the first order density for TDDFT, so the charge distribution gained in this way is rather rough. Of course, CIS is another option, but the excited energy and charge distribution given by CIS is found very bad for our following work. A self-consistent reaction field (SCRf) program for the present interfacial systems is not available yet; therefore, we take the vacuum or bulk results calculated by Gaussian03 as the input in our procedure. From Table 1, we can see that the properties of the excited states in vacuum and in different bulks are similar for DEPNA, PNP, PNAS and C_2H , but C_2 is an exception. On the other hand, the experiment gives the similar spectral results because all of the molecules have the same chromophore except DEPNA. So we take the vacuum results for DEPNA, PNP and PNAS, whereas the charge distributions in bulk cyclohexane for C_2H and C_2 considering that C_2H is a substitute of C_2 (see Table 1).

In the above, we have investigated the properties of excited states of the test molecules in different bulk solvents using Gaussian03. Now we extend our calculation to the interfacial cases. The initial position of the molecule at interface is set such that the Z coincides with the normal of interface ($\theta = 0$, see Scheme 1) and the mass center of the molecule is located at the interface ($d = 0$). From our calculation, it is seen that the axis Z roughly superposes with the molecular dipole moment, depending on the molecular shape. Beside the position of mass center and the orientation angle, the rotation of the molecule around Z possibly applies influence to the results, but it is expected comparatively less important, and thus such a rotation is not included in the present discussions. For the fixed values of d and θ , we can calculate the solvation energy and the spectral shift of absorption $\Delta h\nu_{\text{ab}}$ [see eq. (16)] by performing the

Table 1. Dipoles of Ground and Excited States and Absorbance of Species.

	D_g/Debye^a	Trans ^b	f^c	λ/nm		$\Delta h\nu/\text{kcal mol}$		D_e^d
				Calcd ^e	Expt ^f	Calcd ^g	Expt ^h	
DEPNA								
Vacuum	8.78	S ₁ ⁱ	0.43	355	329	0.0	0.0	22.17
Water	12.23	S ₁	0.56	410	429	−10.8	−20.5	25.63
cyclohexane	10.04	S ₁	0.54	383		−5.9		23.86
Heptane	9.96	S ₁	0.53	381	359	−5.5	−6.7	23.77
PNP								
Vacuum	5.59	S ₁	0.00	330				
		S ₂ ⁱ	0.27	294		0.0		16.67
Water	7.50	S ₁	0.35	327	318	−5.3		18.63
Cyclohexane	6.32	S ₁	0.00	325				
		S ₂	0.35	311		−0.8		17.54
Heptane	6.26	S ₁	0.00	325				
		S ₂	0.34	310		−0.5		17.48
PNAS								
Vacuum	6.43	S ₁	0.00	331				
		S ₂ ⁱ	0.30	302		0.0		18.22
Water	8.38	S ₁	0.38	337	318 ± 2	−9.5		20.36
Cyclohexane	7.20	S ₁	0.00	325				
		S ₂	0.38	321	295 ± 2	−5.5		19.16
Heptane	7.15	S ₁	0.00	326				
		S ₂	0.37	319		−5.0		19.11
C ₂								
Vacuum	9.67	S ₁	0.00	451				
		S ₂ –S ₄	<0.08					
		S ₅	0.20	325				
Water	12.44	S ₁	0.42	350				18.31
Cyclohexane	10.77	S ₁	0.00	367				
		S ₂ ⁱ	0.31	355				18.45
Heptane	10.70	S ₁	0.00	371				
		S ₂	0.29	356				18.81
C ₂ H								
Vacuum	9.47	S ₁	0.00	331				
		S ₂	0.32	300		0.0		21.31
Water	12.48	S ₁	0.39	335	318 ± 2	−11.0		24.29
Cyclohexane	10.59	S ₁	0.00	326				
		S ₂ ⁱ	0.39	317	295 ± 2	−5.2		22.30
Heptane	10.51	S ₁	0.01	326				
		S ₂	0.38	316		−4.9		22.34

^aDipole moment of the ground state. The direction is from the NO₂ group to the substituent group linked to the benzene ring.

^bAll the transitions are from S_0 . The transition is mainly from HOMO to LUMO for all species, except C₂. The transition for C₂ is mainly from HOMO to LUMO in water, and from HOMO-1 to LUMO in cyclohexane and heptane. Please see Fig. 3 for the frontier molecular orbitals.

^cOscillator strength calculated for the specified transition.

^dDipole moment of specified excited state. The direction is from the NO₂ group to the substituent group linked to the benzene ring.

^eAbsorption wavelengths calculated.

^fExperimental absorption, from refs. 11 and 14.

^gBulk Spectral shift calculated by Gaussian03,⁴⁹ minus sign indicates the red shift.

^hExperimental spectral shift.

ⁱState whose charge distribution is chosen as $\{Q^e(k)\}$, without distinguishing the solvents, but the solute charge for the ground state is given by Mulliken population analysis for the individual solvent.

single point calculations. Separate codes have been developed for the calculations of the interfacial systems based on the formulations mentioned above. After the TDDFT calculations asso-

ciated with PCM in homogeneous solvent by means of gaussian03, the charge distribution of the molecules are brought to the calculation for the interfacial behaviors.

Table 2. Static and Optical Dielectric Constants and Surface Tension.^a

	ϵ_s	ϵ_{op}	γ (dyn/cm)
Water	78.36	1.78	72.88
Air	1.00	1.00	0.00
Cyclohexane	2.05	2.03	26.78
Heptane	1.92	1.92	20.06

^aData are taken from ref 50 at temperature of 20°C.

According to our procedure developed in this work, the position and orientation dependencies of the solvation energy of the ground state and the spectral shift of the absorption of DEPNA at air/water interface, in the region of $\theta = 0$ – 90° , are shown in Figures 4a and 4b. There is an obvious low-lying domain in the solvation energy surface, and the lowest point is located at the point of $d = -2$ a.u. and $\theta = 80^\circ$, but the energy minimum is very shallow, being only about 3.3 kcal/mol (see Fig. 5). When the cavitation energy and the solute–solvent dispersion–repulsion interactions are ignored, no energy minimum is found. This implies that the molecule will tend to move towards the water phase with a large value of d . This seems just the similar conclusion drawn by Benjamin using the spherical cavities, considering only the electrostatic contribution.²⁶ This reminds us that the surface energy possibly plays an important role in stabilizing the interfacial molecule. Figures 4c and 4d extend the calculations of the solvation energy and spectral shift to the region of 90 – 180° . The change of spectral shift is almost monotone against d and the limit of this quantity is -23 kcal/mol in bulk water, being higher than the value of -10 kcal/mol by TDDFT in bulk water (see Table 1), but closer to the experimental estimation of -20 kcal/mol.¹⁴ A possible explanation for the difference between our result and the one by TDDFT is that the Mulliken population analysis overestimates the dipole moment variation from ground state to the excited one and hence leads to a larger spectral shift. However, it seems to us that some errors in our treatment cancel out and finally we gain the value closer to the experimental measurement. A negative value of this quantity here indicates a red shift with respect to the vacuum absorption.

The absorption peak and the average orientational angle can be estimated in the following way,^{24,26}

$$\Delta h\nu_{ab,max} = \langle \Delta h\nu_{ab}(\mathbf{r}) \rangle = \frac{\int \Delta h\nu_{ab}(\mathbf{r}) \exp[-\beta \Delta G^s(\mathbf{r})] d\mathbf{r}}{\int \exp[-\beta \Delta G^s(\mathbf{r})] d\mathbf{r}} \quad (18)$$

$$\theta_{av} = \langle \theta(\mathbf{r}) \rangle = \frac{\int \theta(\mathbf{r}) \exp[-\beta \Delta G^s(\mathbf{r})] d\mathbf{r}}{\int \exp[-\beta \Delta G^s(\mathbf{r})] d\mathbf{r}} \quad (19)$$

Here, we take the spectral shift in vacuum the zero. $\beta = 1/k_B T$, with k_B being the Boltzmann's constant at room temperature. Thus, for DEPNA, the calculated result for $\Delta h\nu_{ab,max}$ is -11.9 kcal/mol. And it is consistent with the experimental result, -10 kcal/mol.¹⁴ It needs to say, because the spectral shift depends on the position and orientation of interfacial molecule strongly, all of the components of the solvation energy displayed in eq. (1) are important.

Using eq. (19), we gain an average orientational angle of about 68° , being in comparative agreement with the experimental fitting of 55° ⁵² and the value of 73° from molecular dynamics.²¹ In our previous paper,⁴⁸ linear interpolation is used to estimate the spectral shift for the interfacial molecule on the basis that the absorptions in both bulk media are known as the experimental values. In that paper, a single sphere description gave an estimation of orientational angle of $\sim 25^\circ$ for the DEPNA molecule at the air/water interface when the spherical center is assumed at the interface. In our previous work,⁴⁸ a value of $\sim 40^\circ$ was thought rational, but the later measurement seems support a larger value. For comparison, we give the spectral shift against the orientational angle in Figure 6. When the mass center of DEPNA is set at the interface, the single sphere model⁴⁸ and the present numerical treatment ($d = 0$) present some different features for the orientation dependency of the spectral shifts of absorption, as shown in Figure 6. A possible explanation is the neglect of the cavitation energy and the use of a spherical cavity. However, both models give qualitatively reasonable descriptions for the interfacial phenomena.

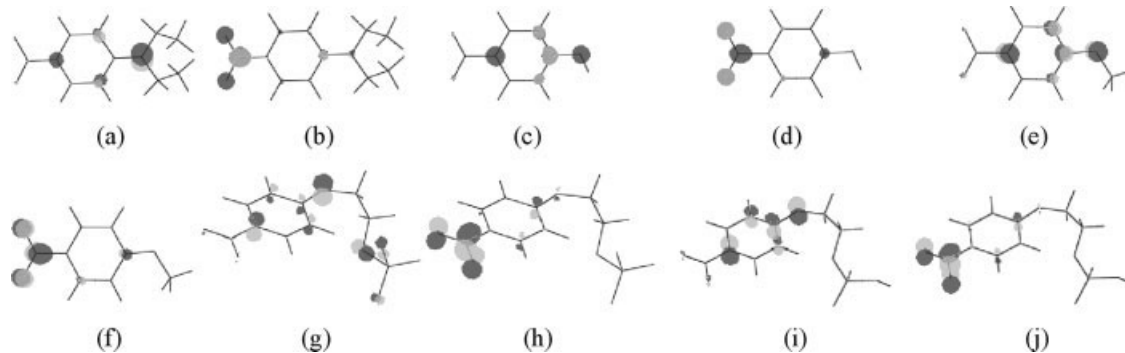


Figure 3. Frontier orbitals. HOMO (a) and LUMO (b) of DEPNA, HOMO (c) and LUMO (d) of PNP, HOMO (e) and LUMO (f) of PNAS, HOMO (g) and LUMO (h) of C₂, and HOMO (i) and LUMO (j) of C₂H.

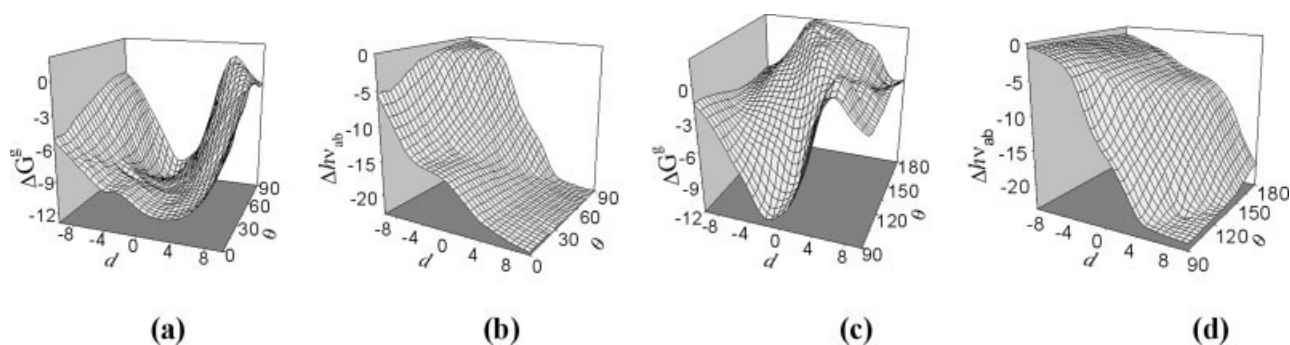


Figure 4. The d and θ -dependencies of solvation energy of ground state (a) and spectral shift of absorption (b) of DEPNA at air/water interface in the region of $\theta = 0^\circ \sim 90^\circ$. (c) and (d) extend the calculation to the region of $\theta = 90^\circ \sim 180^\circ$. ΔG^s is in kcal/mol, d in a.u., and θ in degree.

An analytical model, e.g., two-sphere or single-sphere model, cannot take the change of $A^{\text{plane}}_{\gamma_{S1/S2}}$ into account. This term has been given in eq. (2) and it contributes an extra part to the stability of the molecule at the interface, owing to the elimination of the interface portion within the cavity. In ref. 27, a study on phase transfer energy (solvation energy) using PCM has been reported. The neglect of the term of $A^{\text{plane}}_{\gamma_{S1/S2}}$ also predicts a global minimum of solvation energy at the perpendicular orientation. This indicates the significance of taking the term of $A^{\text{plane}}_{\gamma_{S1/S2}}$ into account. Now we survey the stability by considering the solvation energy with and without the contribution from the quantity $A^{\text{plane}}_{\gamma_{S1/S2}}$. We have calculated preponderant orientation angle and embedding depth for interfacial molecule by using the procedure developed here. We consider different cases: (a) calculating the solvation energy contributed by only the electrostatic free energy, G_{el} in eq. (1), (b) including all the contributions of the solvation energy, except the term $A^{\text{plane}}_{\gamma_{S1/S2}}$, and (c) complete inclusion of all the contributions. The solvation energies for these three cases of DEPNA at air/water interface are given in Figure 7. It is seen that if we only consider the electrostatic interaction only, the solvation energy monotonously

decreases along the increasing of the embedding depth of the molecule into the water phase (curve A in Fig. 7a). This indicates the molecule intends to entirely embed into the water side. On the other hand, from Figure 7b, we can see that the solvation energy monotonously increases with the increasing of the orientation angle. The energy minimum is close to $\theta = 0$, but the solvation energy is not sensitive to θ in the range of $\theta = 0 \sim 60^\circ$ (see curve D in Fig. 7b). We further take the electrostatic, cavitation and dispersion–repulsion contributions into account, but exclude the contribution of energy raised by cutting off a part of the interface plane [the last term at the right hand side of eq. (2)]. In this case, a minimum of the solvation energy appears at certain embedding depth (curve line B in Fig. 7a).

This means that the molecule can stand at the interface. However, at a fixed value of d , the solvation energy still monotonously increases along the increasing of the orientation angle (see curve E in Fig. 7b). This means the interfacial molecule will swing around $\theta = 0$, differing from the experimental obser-

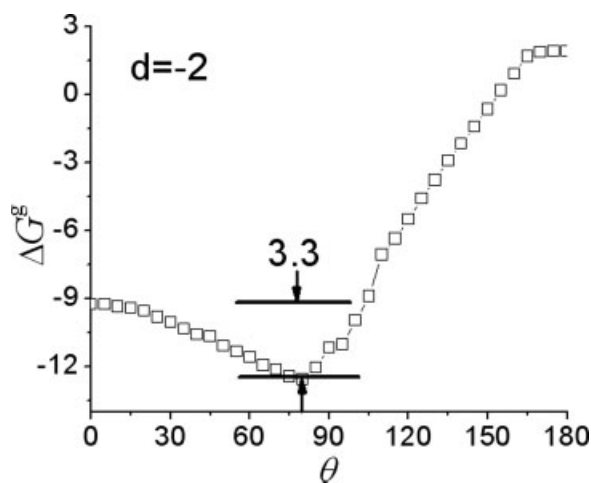


Figure 5. The θ -dependency of solvation energy at $d = -2$ a.u.

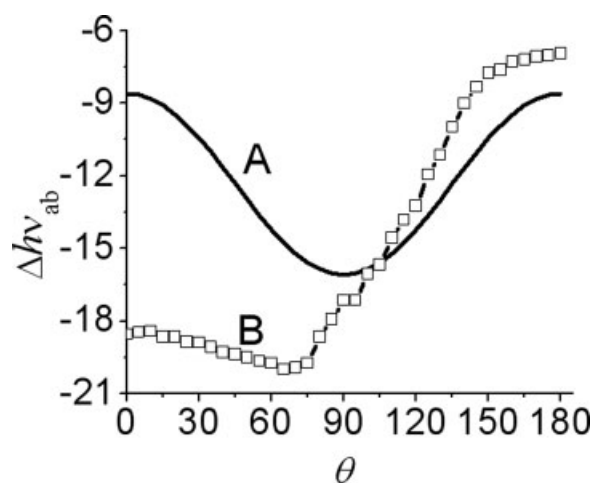


Figure 6. The change of spectral shift of absorption against the orientational angle at air/water interface with the single sphere model⁴⁸ (solid line) and the present numerical treatment with the mass center at the position of $d = 0$ a.u. (open square).

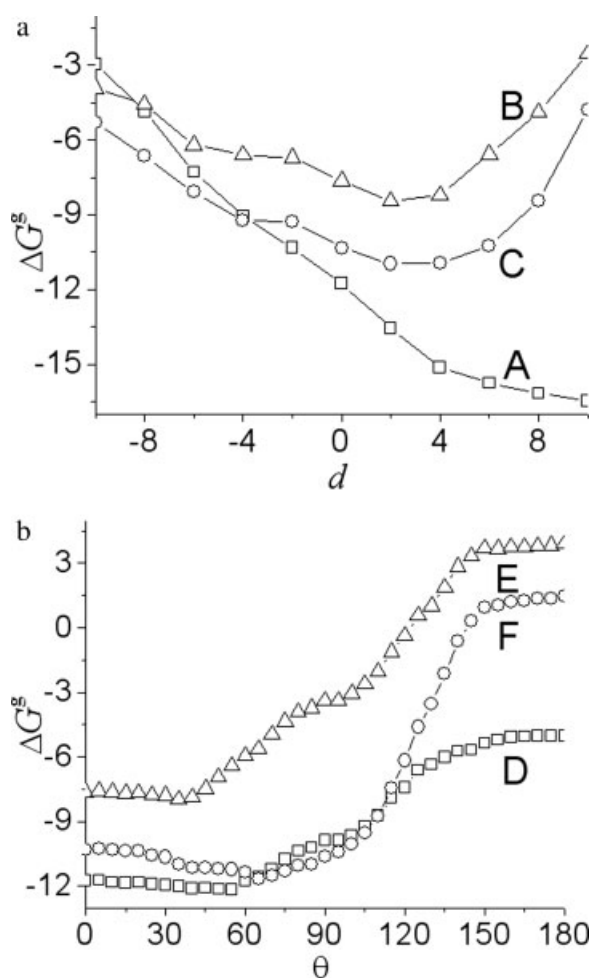


Figure 7. The d -dependency of solvation energy at $\theta = 0$ (a) and the θ -dependency of solvation energy at $d = 0$. (b) Open squares consider only the electrostatic contribution. Open triangles consider the contributions of electrostatic interaction, the cavitation energy, and the dispersion–repulsion interactions, without involving the surface energy term $A^{\text{plane}}_{\gamma_{S1/S2}}$. Open circles take all the terms in eq. (1) into account.

ations.¹⁴ Finally, we take the contribution from the elimination of the interface portion, $A^{\text{plane}}_{\gamma_{S1/S2}}$, into account as well. Curves C and F in Figure 7 show the calculated results of the solvation energy. The minimum appears at the point corresponding to some values of d and θ . From the analysis made here, we see that the contribution of solvation energy by cutting off the interface portion is very important in determining the depth and orientation angle. This analysis gives a reasonable explanation on why the interfacial molecules usually take the tilting conformation at the interface, rather than being perpendicular to it, just as those observed in experiments.

Similar calculations have been carried out for the other interfacial systems. The solvation energies and the spectral shifts are collected in Figure 8. In Figures 8a and 8b, the solvation energy and the spectral shift are evaluated for PNP at heptane/water

interface. Our calculation shows that the air/water and cyclohexane/water cases (not showed here) exhibit features similar to the heptane/water case. We take heptane as an example to perform the calculations because its data of cavitation energy and solute–solvent dispersion–repulsion interactions can be obtained by using Gaussian03, but its experimental result is not available. Because octane and heptane have similar structures and dielectric properties, we take the experimental results at water/octane interface to compare with the calculated results at heptane/water interface. When the mass center of PNP is set at the heptane/water interface ($d = 0$), the energy minimum appears at $\theta = 80^\circ$, and the corresponding spectral shift is -15.6 kcal/mol. This value is approximately the average of the calculated bulk limits, -17.3 kcal/mol in water and -13.5 kcal/mol in heptane. This feature is qualitatively consistent with the experimental observation for PNP at octane/water interface. From the present calculation, the spectral shift difference in bulk water and in bulk heptane is 3.8 kcal/mol. Although no experimental data of heptane available for the direct comparison, we can find an analogous molecule, octane, for this purpose. The spectral shift difference in bulk water and in bulk octane was reported 8.0 kcal/mol.¹¹ It is seen that the present calculation underestimates the transition energy difference in the bulk solvent cases. Furthermore, we investigate the solvent effects of PNP at different interfaces. For the air/water and cyclohexane/water interfaces, the energy minima of the ground states locate at $\theta = 80^\circ$ and $\theta = 85^\circ$ respectively, provided that we set $d = 0$. The values are close to the heptane/water interface. The spectral shift in bulk cyclohexane is calculated -14.3 kcal/mol, whereas the spectral shift for the cyclohexane/water interface is -16.1 kcal/mol. this value exhibits the average feature also. It should be emphasized that there are still some influencing factors not included in our present calculation, such as the exclusion of the short range interaction and the neglect of the mutual polarization between the solute charge and the polarization charge. We remind here that we use the vacuum charge distribution of the solute for the calculation in solution, but in the actual case, the solute charge will adjust itself to match the solvent polarization, as reported in ref. 28. Besides, the parameters used in the calculation of cavitation energy and solute–solvent dispersion–repulsion interactions have not been optimized for interfacial case. These reasons might cause further errors to the results. How to improve the procedure is still under consideration. A feasible approach to solving this problem, as mentioned by Benjamin in the analytical and the MD treatments, is to use the bulk results to fit these parameters before the calculation for interfacial system.^{21,23,26}

If the H of the hydroxyl of PNP is substituted by a methyl group, PNAS is formed. For this molecule, the solvation energy of the ground state is quite different from that of PNP (see Figs. 8a and 8c), but the spectral shift does not change too much (see Figs. 8b and 8d). Comparison shows that the hydrophilicity of methyl ether and that of hydroxyl are quite different, while the charge distributions of PNP and PNAS are very close. We only give the calculated results of PNAS at cyclohexane/water in Figures 8c and 8d due to the same reason as PNP. In the interface case, we have failed to find a minimum on the energy surface (Fig. 8c). For PNAS, the calculated bulk limits of the spectral shifts are -19.5 kcal/mol in water, -16.4 kcal/mol in cyclo-

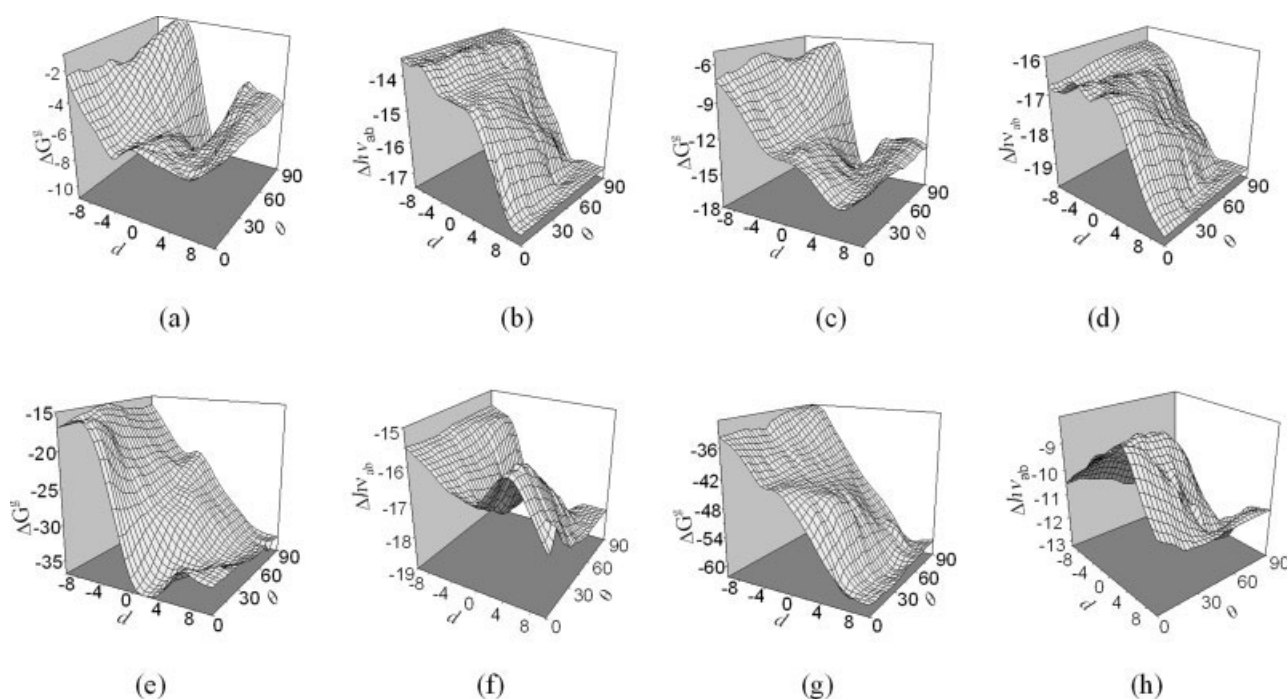


Figure 8. Solvation energy of the ground state (ΔG^0) and spectral shift $\Delta h\nu_{ab}$ for the absorption from the ground state to the specified excited state. (a) and (b) are for PNP at the heptane/water interface, (c) and (d) for PNAS at cyclohexane/water interface, (e) and (f) for C_2H at cyclohexane/water interface, and (g) and (h) are for C_2 cyclohexane/water interface.

hexane and -15.3 kcal/mol in heptane. As can be seen in Figure 8d, there is a large domain where the spectral shift close to the bulk limit of cyclohexane. This feature appears in the case of heptane/water also. This is interesting because experiment observations revealed that the interfacial spectral shift takes the average value of the bulk limits when the organic phase is cyclohydrocarbon but it approaches the organic phase limit in the cases of linear-hydrocarbon.¹¹

The solvation energies and spectral shifts of C_2H and C_2 at cyclohexane/water interface are given in Figures 8e–8h. In the paper by Steel and Walker,¹¹ the notation C_2 indicates that two methylene groups separate the sulfate headgroup from the PNAS-based chromophore, and the PNAS-based chromophore is set in the organic solvent. Therefore, we choose the charge distribution of excited state in cyclohexane to perform the interfacial property calculation for both. From Figs. 8e and 8g, no energy minimum is found. It is because that the electrostatic contribution plays the dominant role comparing in eq. (1). For both C_2H and C_2 , the electrostatic interaction is quite big (see Fig. 8e for C_2H and Fig. 7g for C_2). It is clear that the large electrostatic contribution of C_2 is due to the ionic structure which offers an extra Born term to the solvation energy. Furthermore, the “tail” of both C_2 and C_2H which serves as the hydrophilic group, containing several oxygen atoms in each. This group produces strong interaction with the polar solvent. The steep decline of the solvation energy with the increasing d indicates the tendency of whole molecule entering the water phase. In such cases, unlike the other three molecules, the cavitation

energy plays a relatively trivial role comparing with the strong electrostatic interaction. The spectral shifts for C_2H and C_2 (Figs. 8f and 8h) become complicated and are apparently different from the other three molecules. A striking feature that stands out in Figures 8f and 8h, especially in Figure 8h, is that the spectral shift may be larger than, less than or between the bulk limits in water and in cyclohexane, depending on the position of the molecule. This feature also appears in the cases of air/water and heptane/water. This indicates that the spectral shift of absorption remarkably depends on the orientation and the embedding depth. It looks strange that the interfacial spectral shift is lower than the bulk limit in the organic phase for some specific choices of position and orientation of C_2H and C_2 . This phenomenon may be due to the lack of symmetry for C_2H and C_2 comparing with the other molecules. Another reason may be the organic phase has higher optical dielectric constant than water phase, although it has a lower static dielectric constant. Furthermore in our rough arithmetic, the auto-polarization effect of solute is neglected, and it may magnify the peculiar effect also. Cyclohexane and heptane have the very close static and optical dielectric constants (see Table 2), so the d - and θ -dependencies for the cyclohexane/water and heptane/water cases are almost the same. But, according to the experimental observation of C_2 at cyclohexane/water interface,¹¹ the absorption spectrum mediates between the values of the two bulk limits. Furthermore, when this molecule locates at m-cyclohexane/water interface, the spectral shift value is close to the limit of organic phase. However, at the octane/water interface, the resonance-

Table 3. Absorption Peak, Orientation, and Embedding Depth of Species.

	Energy minimum		$\Delta\Delta h\nu_{ab}$ (kcal/mol)			$\theta_{av}/^\circ$	
	$d/a.u.$	$\theta/^\circ$	Calcd ^a	Calcd ^b	Expt ^c	Calcd ^d	Expt ^e
DEPNA							
Air/water	−2	80	11.2	9.5	10.5	68	55 ^f
Cyclohexane/water	2	70	0.2	0.7		65	
Heptane/water	2	85	1.1	1.2		71	
Air				23.1	20.5		
Cylohexane				4.5			
Heptane				5.7	10.0		
PNP							
Air/water	0	80	7.7	8.5		77	
Cyclohexane/water	0	85	1.1	1.1		78	
Heptane/water	0	80	1.7	1.6		80	
Air				17.3			
Cylohexane				2.9			
Heptane				3.8			
PNAS							
Air/water				7.8		86	
Cyclohexane/water				1.0	2.1	77	
Heptane/water				1.5		72	
Air				19.5			
Cyclohexane				3.1	6.8		
Heptane				4.2			
C₂H							
Cyclohexane/water				1.3	5.7	47	53 ^g
Cyclohexane				3.4	7.0		

^aSpectral shift at the energy minimum.^bAbsorption peak calculated with eq. (18).^cExperimental absorption.^dAverage orientation angle calculated by eq. (19).^eAverage orientation angle from experiment.^fFrom ref. 52.^gFrom ref. 11.

enhanced SHG spectrum goes beyond the organic limit.¹¹ Our calculation presents this extraordinary feature if we have a look at Figure 8h. In the range around $d = 0$, we can find a large domain where the spectral shift is even less than the organic limit. This reminds us if we can adopt some measure to make the molecule stabilized at the position around of $d = 0$, the absorption spectrum wavelength will be longer than those in the organic phase. In experiment, polarization-dependent SHG measurements have been used to determine the average orientation of the molecule relative to the interfacial normal, and the average orientation of chromophore of C₂ is reported 47° off the interfacial normal of water/cyclohexane interface.¹¹ We need to note that the direction of Z defined in this work and that of the chromophore by other authors are different for this system, and the corresponding value of θ is 53° using our definition. We take the calculated results and use eq. (19), the orientational angle is predicted to 47° for C₂H at the interface of cyclohexane/water.

The absorption peak, embedding depth, and orientational angles for DEPNA, PNP, PNAS, and C₂H are collected in Table 3. We can see that the positions of the energy minimum for DEPNA are close at different interface, and PNP exhibit the

same feature. This might be the reason of the average polarity model¹⁴: the molecule has similar preponderant positions at the different interface and the spectral shift only depends on the polarity of both phases. For the other systems, PNAS and C₂H, no energy minimum is found from the present calculations, and we only list the average value calculated by eqs. (18) and (19). It is difficult to compare the difference between calculated absorption peak and the experimental results, because no experimental spectrum in vacuum is available for most of the species. However, we have the spectral shift data in bulk water for all the species, hence we turn to define the spectral shift with respect to the bulk water as follows,

$$\Delta\Delta h\nu_{ab} = h\nu_{ab} - h\nu_{ab}^w = \Delta h\nu_{ab} - \Delta h\nu_{ab}^w \quad (20)$$

where $h\nu_{ab}^w$ and $\Delta h\nu_{ab}^w$ are the bulk limits of absorption and spectral shift in water respectively. In this sense, $\Delta\Delta h\nu_{ab}$ will be positive and exhibits a “blue shift”. The amount of this quantity is listed in Table 3. The calculated values of absorption peak have qualitative significance when compared with the experimental results. There are many reasons that cause these errors for the estimations of spectral shift, such as the charge distributions and the parameters of solvation model.

Conclusion Remarks

In the recent work, a continuum model is developed to investigate the interfacial behaviors of five test molecules. One of the crucial points is that we take the newly developed expression for the nonequilibrium free energy in the numerical solution. Based on the formulation of solvation energy for a molecule at the interface, a separate numerical program is coded. In virtue of the charge distribution calculation, the solvation energy of an interfacial molecule can be evaluated. The electronic properties including the transition energies, the oscillator strengths of the transition from the ground state, the charge distributions for both the ground state and the specific excited state, the solvation energy associated with a specified bulk solvent, have been calculated using Gaussian03. Extending the formulations of the nonequilibrium solvation to the interfacial system, the arithmetic for the computation has been developed. With the charge distributions for the specific state, ground or excited, our program predicts the solvation energies and the spectral shifts for the interfacial molecular systems. The five species, DEPNA, PNP, PNAS, C₂, and C₂H, have the same chromophore, but maximum absorption are found in the range of 327–410 nm. Compared with the calculated results in vacuum, DEPNA exhibits a larger red shift than PNP, since the excitation causes a larger change of the dipole moment of DEPNA.

With the TDDFT/PCM charge distributions of the ground state, the solvation energy calculation at the interface shows there are energy minima for DEPNA and PNP, but such a feature has not been found for the other interfacial systems. Considering the spectral shift at the interface, we see that DEPNA, PNP, and PNAS have the same trend, since they have the similar molecule shape and the electronic structures. On the other

hand, C_2 and C_2H exhibit quite different behaviors. The differences may be due to the effect of the longer substituent group. In addition, C_2 has strong ionic effect and its orbital structure is different from the others. Calculations show that the solvation energy and the spectral shift strongly depend on the embedding depth and the orientational angle for an interfacial molecule. By defining a quantity $\Delta\Delta h_{v,ab}$ to evaluate the spectral shift with respect to the water limit, the results collected in Table 3 indicate the underestimation of $\Delta\Delta h_{v,ab}$ for almost all cases. When we compute the properties of the excited state using TDDFT, the method of one-particle density using CI wavefunction (keyword = RhoCI) has been adopted to do the population analysis. We recall that the method of RhoCI only get the first order density for the excited state calculated by TDDFT. In many cases, this method can overestimate the magnitude of the charge distribution or the dipole moment.⁵³ Therefore, such the overestimation of the charge distribution will drive the interfacial absorption to the water limit, and thus, the value of $\Delta\Delta h_{v,ab}$ is underestimated. If we take the absorption in vacuum as the criterion, the overestimated charge distribution will predict an excessive red shift.

We can see that all of the components of solvation energy, including electrostatic energy, cavitation energy, and dispersion-repulsion energy are important for estimating the maximum interfacial spectral shift, because the interfacial spectral shift is sensitive for position and orientation. Especially, a significant finding in this article is that the cavitation energy of the molecule plays an important rule for the orientation of the interfacial molecule. DEPNA is taken as an example to discuss this issue. As shown in Figure 7, the inclusion of the cavitation energy will cause the molecule to depart from its perpendicular orientation, but take a tilting manner. From Figure 4 it is seen the orientational angle distributes in a large range. The interface energy portion $A^{\text{plane}}_{\gamma_{S1}/S2}$ will give rise to the stability of the interfacial system. The larger the orientational angle, the larger interfacial area (A^{plane}) is eliminated by the molecule occupation at the interface. In this sense, the molecule intends to lie on the interface. But on the other hand the electrostatic free energy will drive the molecule to the perpendicular manner in dilute solution. So these two factors reach a balance at a proper orientational angle.

We have not optimized the parameters of general PCM, such as the charge distribution of solute, the radii of interlocking spheres and the constants using in eqs. (2) and (3). In fact, some influencing factors have been ignored in this article. As have known, there are many issues need to be further discussed, for example the hydrogen bonding may affect the interfacial molecular position strongly, the anisotropic environment may modulate the molecular shape and its electronic structure, the actual interface may be molecularly rough and with definite width,^{5,11} and the high surface concentration and strong coupling may not be negligible. Nevertheless, the present theoretical model and the numerical treatment draw the valuable information for the interfacial systems.

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