How Solvent Controls Electronic Energy Transfer and Light Harvesting

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Received: April 1, 2007; In Final Form: May 21, 2007

The way that solvent (or host medium) modifies the rate of electronic energy transfer (EET) has eluded researchers for decades. By applying quantum chemical methods that account for the way solvent (in general any host medium including liquid, solid, or protein, etc.) responds to the interaction between transition densities, we quantify the solvent screening. We find that it attains a striking exponential attenuation at separations less than about 20 Å, thus interpolating between the limits of no apparent screening and a significant attenuation of the EET rate. That observation reveals a previously unidentified contribution to the distance dependence of the EET rate.

After photoexcitation, energy absorbed by a molecule can be transferred efficiently over a distance of up to several tens of angstroms to another molecule by the process of electronic energy transfer (EET).[1] The rate, or efficiency, of EET depends sensitively on the separation and geometric orientation of the donor and acceptor molecules. In other words, EET can be directed by the nanoscale organization of molecules; conversely, it can be used as a molecular-scale probe of such structures. By understanding the factors controlling EET, it has been possible to explore and design natural and artificial antennae for the capture and energy conversion of light,[2–5] to demonstrate amplification of fluorescence-based sensors,[6] to optimize organic light-emitting diodes,[7] and to measure structure in biology, even in living and moving systems.[8,9]

Recent work has examined molecular assemblies with well-defined structures, enabling the testing and elucidation of questions about the efficiency of EET and its relationship to the organization of molecules.[10–14] Single molecule studies have helped researchers to test theories by seeing within the ensemble distribution.[12,14] A recently demonstrated two-dimensional electronic spectroscopy has helped to reveal EET pathways in multichromophoric systems.[13] The partnership of these kinds of powerful experimental tools with theoretical models, enabling dynamics and spectroscopy to be correlated with the structural relationships among light absorbing molecules, will allow us to address detailed questions about how excitation energy moves in space, time, and energy.

While theories for predicting the rate of EET are well-developed, the precise effect of the solvent environment (or more generally, the host medium) surrounding the donor and acceptor

molecules is poorly understood. For example, typically, a simple screening model is used, originally proposed by Förster.[15] That model predicts a substantial reduction in the EET rate (by a factor of ∼4), regardless of how the donor and acceptor are oriented and positioned. However, chemical intuition would suggest a distance-dependent screening, like the empirical screening of electrostatic interactions used to model nucleic acids and proteins.[16] It would be expected that when two chromophores are close enough, the solvent should be excluded from the intermolecular region, thus probably leading to a reduction of the screening. However, to what extent is the screening reduced? The importance of this issue has already been raised in the literature,[17–20] but until now, quantum mechanical models for the description of the solvent effect in EET have been chiefly limited in three ways: (i) the chromophores have been assumed to be located inside *spherical* cavities in the surrounding medium; (ii) the *change* in the properties of the chromophores upon solvation have either been neglected or considered in a simplistic way; and (iii) the influence of solvent response on the *interaction* between transition densities has been neglected.

We developed a quantum mechanical model that overcomes these approximations,[21,22] and here, we have applied it to examine many pairs of molecules (chlorophylls, carotenoids, and bilins) taken from structural models of photosynthetic proteins, Figure 1. We find that the solvent screening attains a striking exponential attenuation at separations less than about 20 Å, thus interpolating between the limits of no apparent solvent screening and a significant attenuation of the EET rate. That observation reveals a previously unidentified contribution to the distance dependence of the EET rate. By examining many different donor–acceptor pairs, we obtain a simple empirical expression that can be used in theories for EET rates. Our findings thus have significant consequences for the quantitative description of nanoscale excitons, modeling EET dynamics, and application of fluorescence tools in structural biology.

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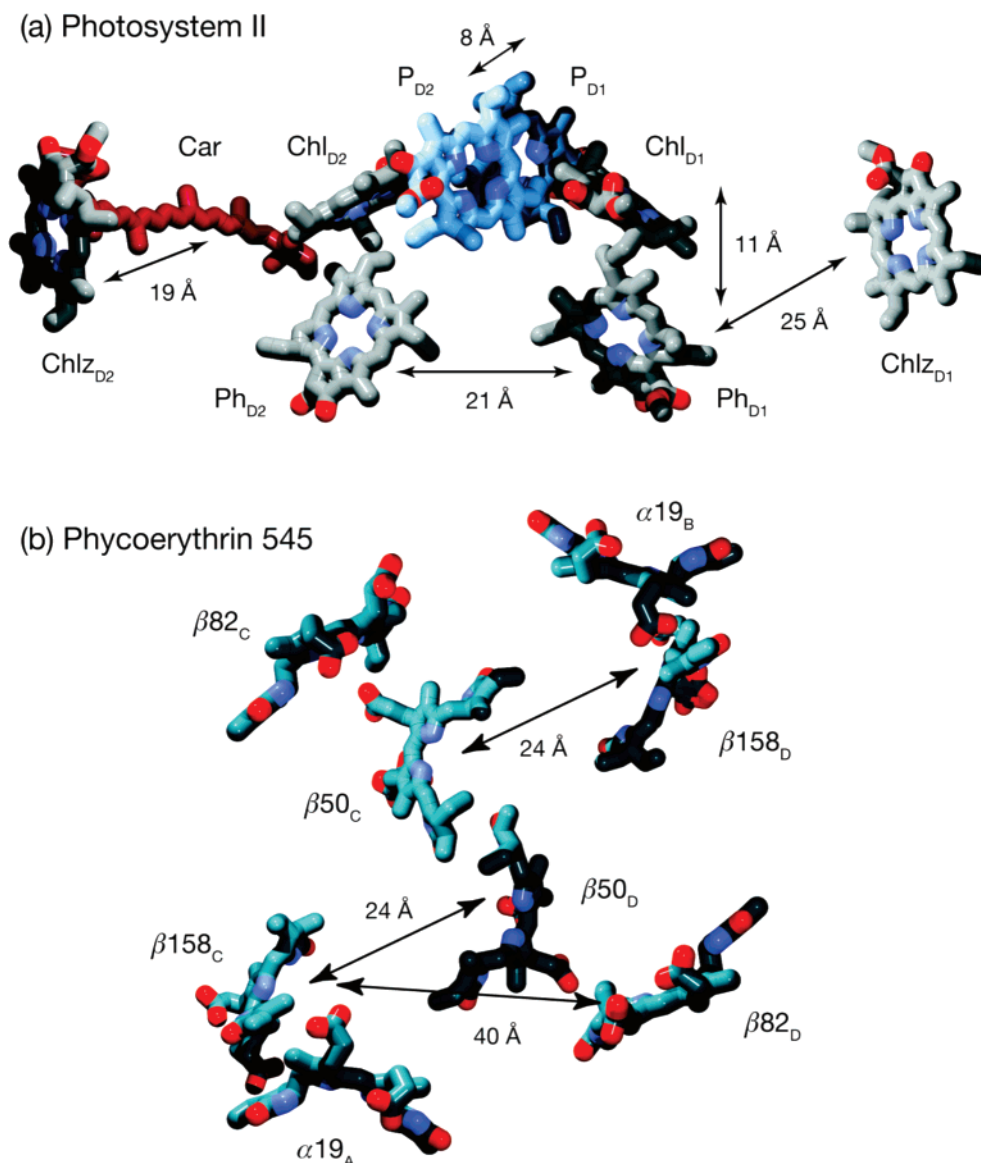
Figure 1. Light-absorbing molecules (chromophores) in photosynthetic proteins are arranged in close proximity to each other. The electronic interactions among these molecules determine the nature of excited states (nanoscale excitons) and the dynamics of energy transfer and relaxation. We have calculated electronic couplings between pairs of molecules in four different photosynthetic proteins. The structural models are shown of photosystem II (PSII) from the cyanobacteria *T. elongatus* and the phycoerythrin 545 (PE545) light-harvesting antenna from the cryptophyte algae *Rhodomonas CS24*. Typical interchromophore (center-to-center) separations are indicated.

Predicting the dynamics of EET requires four ingredients: spectral factors for the donor and acceptor molecules,[15] electronic coupling between them,[23] identification of possible coherence effects,[24] and account of the solvent as a dielectric medium.[17,21,25−27] For example, in the Förster (weak coupling) formula for predicting the rate of EET from a donor molecule D to an acceptor molecule A,

$$k = \frac{2\pi}{\hbar}|sV_s|^2 J \qquad (1)$$

where J is the spectral overlap factor,[1] the electronic coupling between donor and acceptor is V_s, and s is the solvent screening. It is the factor V_s, an interaction between the donor and the acceptor transition densities, that gives the EET rate its characteristic $1/R^6$ distance dependence according to the dipole−dipole approximation, where R is the interchromophore separation.

The subject of the present work is s, which is a factor explicitly due to the solvent medium that screens the direct coupling V_s. In Förster theory, $s^2 = 1/n^4$, where n^2 is the square of the solvent refractive index (the optical dielectric constant, ϵ_{opt}). One can therefore see its significance, since it reduces the predicted EET rate by a factor of ∼4 when the solvent (environment) refractive index is 1.4. However, despite over half a century of scrutiny, the solvent effect remains to be elucidated for realistic systems. It therefore represents an important obstacle to be addressed if we hope to model the results of experimental studies. Here, we examine this missing ingredient, solvent polarization (screening), which can now be investigated owing to the development of realistic models for the quantum mechanical description of solutes including a self-consistent treatment of how wave functions are modified by the solvent.[28] A recent evolution in this field has enabled us to calculate the effect of a solvent medium on electronic inter-actions in the excited state.[21,22]

The methodology we have used to include environment effects is the polarizable continuum model (PCM).[28] In such a model, the molecular system under scrutiny (here, the donor−

acceptor pair) is described as a quantum mechanical charge distribution within a molecular cavity of realistic shape while the environment is described as a structureless polarizable continuum, characterized by its dielectric constants. Our methodology captures the key features of the problem, such as an accurate calculation of electronic excited states, the shape of molecules, and the response of the surrounding medium to charge and, importantly, to transition densities. The protein medium, intrinsic water, and surrounding medium was collectively modeled as a dielectric continuum with a relative static dielectric constant of 15 and optical dielectric constant of 2.[29] While this is a complex host environment, the essential features are captured in the polarizability. When the medium is present, two contributions to the electronic coupling are calculated (see Supporting Information): the direct coupling, implicitly modified by the medium (V_s in eq 1) and a contribution to the coupling involving the explicit solvent effect ($V_{explicit}$). Conceptually, the oscillating transition density of the donor drives a response in the polarizable medium, which, in turn, affects the oscillation of the acceptor (and vice versa). This response of the medium to an electronic transition is here calculated introducing an apparent charge density on a cavity enclosing the molecule (this is the solvent reaction field, Φ_{RF}). Within this framework, the *s* factor defined in eq 1 becomes $s = V_{tot}/V_s = (V_s + V_{explicit})/V_s$. Because the solvent screening is thus defined as a ratio, the results are not strongly dependent on the quantum chemical approach used to calculate the excited-state wave functions.

Photosynthetic antenna proteins have turned out to be excellent model systems for the study of EET because they have well-known structures with an organization of chromophores on the nanoscale.[10] We have calculated electronic couplings between more than 100 pairs of molecules in four different photosynthetic proteins (Figure 1). Despite the range of sizes, shapes, and orientations of the donor and acceptor molecules, a trend is evident in the solvent screening quantified by *s*. By fitting the results of our calculations, Figure 2, we obtain the functional form:

$$s = A \exp(-\beta R) + s_0 \qquad (2)$$

The donor−acceptor separation enters this expression via the exponentially decaying contribution. The pre-exponential function is $A = 2.68$, indicating that $s = 1$ at a separation $R = 6.6$ Å, and $\beta = 0.27$ is the attenuation factor at close interchromophore separations. It is reasonable that at ∼6.6 Å the screening is negligible, since at that separation the molecules share a cavity in the medium; hence, there is little or no intervening solvent. At large distances, *s* reaches an asymptotic value ($s_0 = 0.54$). This result is intermediate within the limiting cases of screening between (infinitely thin) point dipoles, $s_0 \approx 1/n^2 = 0.5$ (commonly used in applications of Förster theory) and the prediction of Onsager theory, where the two dipoles are assumed to be contained in spherical cavities, $s_0 \approx 3/(2n^2+1) = 0.6$. It makes sense that real molecules fall somewhere between these limits, as dictated by their shapes.

We further examined the effect of changing both the static and the dynamic dielectric properties of the medium. We found that by decreasing the static dielectric constant ϵ_{static} from 15 to 2 the overall effect on the factor *s* is negligible. The reason is that only the optical dielectric effect directly influences the screening, because the Coulombic interaction between transition densities occurs at optical frequencies. However, an indirect effect on the coupling is possible if the static dielectric properties of the medium change the molecule's transition density. Thus
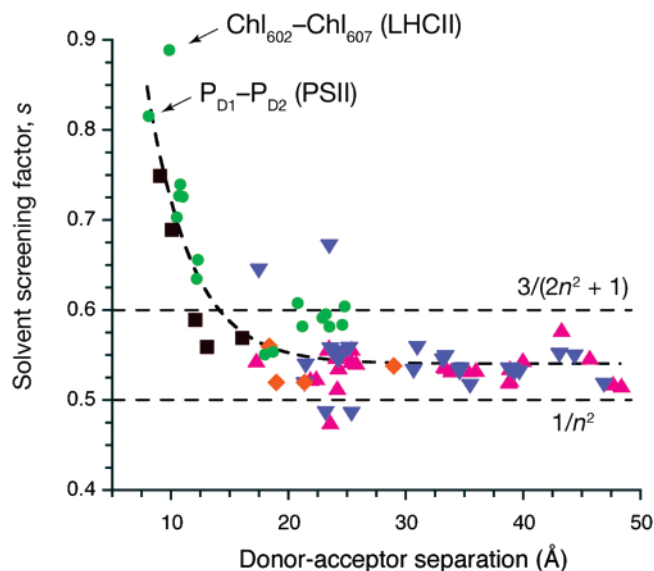

Figure 2. Solvent screening of electronic couplings. The correspondence between data point and structure is pink triangles = PE545, blue inverted triangles = PC645, green circles = PSII or LHCII, except orange diamonds = data involving the carotenoid in PSII, and brown squares = the $P_{D1}-P_{D2}$ dimer structure systematically separated along the center-to-center vector. The protein medium is modeled as a dielectric continuum with a relative static dielectric constant of $\epsilon_{stat} = 15$ and optical dielectric constant of $n^2 = 2$. Calculated values for the solvent screening factor $s = V_{tot}/V_s$ for various chromophore pairs. The Förster value, $1/n^2$, is indicated by the lower horizontal line, and the Onsager value, $3/(2n^2 + 1)$, is the upper line. The dashed curve is a fit through the data points by eq 2.

the optical dielectric properties of the medium determine the screening. We find that an increase of n^2 from 2 to 10 affects the asymptotic value of *s* but not its functional form. Once again the $s_0 = 0.12$ is found to be in between the Forster $1/n^2 = 0.10$ and the Onsager $3/(2n^2 + 1) = 0.14$ predictions. We thus find that both A and β are influenced by the optical dielectric constant of the medium. The values we report from analysis of Figure 2 are representative of typical condensed phase environments, including common solvents, water, and proteins.

To analyze the functional form of the solvent screening, we consider results for a chlorophyll dimer of LHCII as function of a systematic increase in the chlorophyll-a center-to-center separation, Figure 3. To allow a direct comparison with the Förster theory, we introduce here a simplified description in terms of the dipole approximation for the electronic coupling. It is clearly seen that the typical $1/R^3$ distance dependence is obscured by the intrinsic distance dependence we observe for the solvent screening. The qualitative form of the distance dependence is affected significantly by *s*, and the magnitude of the electronic coupling is modified by over a factor of 2 when the Förster expression $V_{dip-dip}/n^2$ is changed to the more realistic $sV_{dip-dip}$. The use of the screening function *s* therefore makes a significant correction to calculated EET rates which has particular importance for the quantitative application and testing of EET models such as those actively pursued in the study of photosynthetic light harvesting systems and conjugated polymers.[2,7,10,11,30]

Why does *s* depend on *R*, and also on the shape of the donor and acceptor molecules via the corresponding cavities formed when they are immersed in the dielectric medium? The calculated electronic coupling V_{tot} is reduced relative to the direct interaction between transition densities V_s by the additional coupling of the transition densities through the apparent surface charges that represent the effect of medium polarization, $V_{explicit}$.

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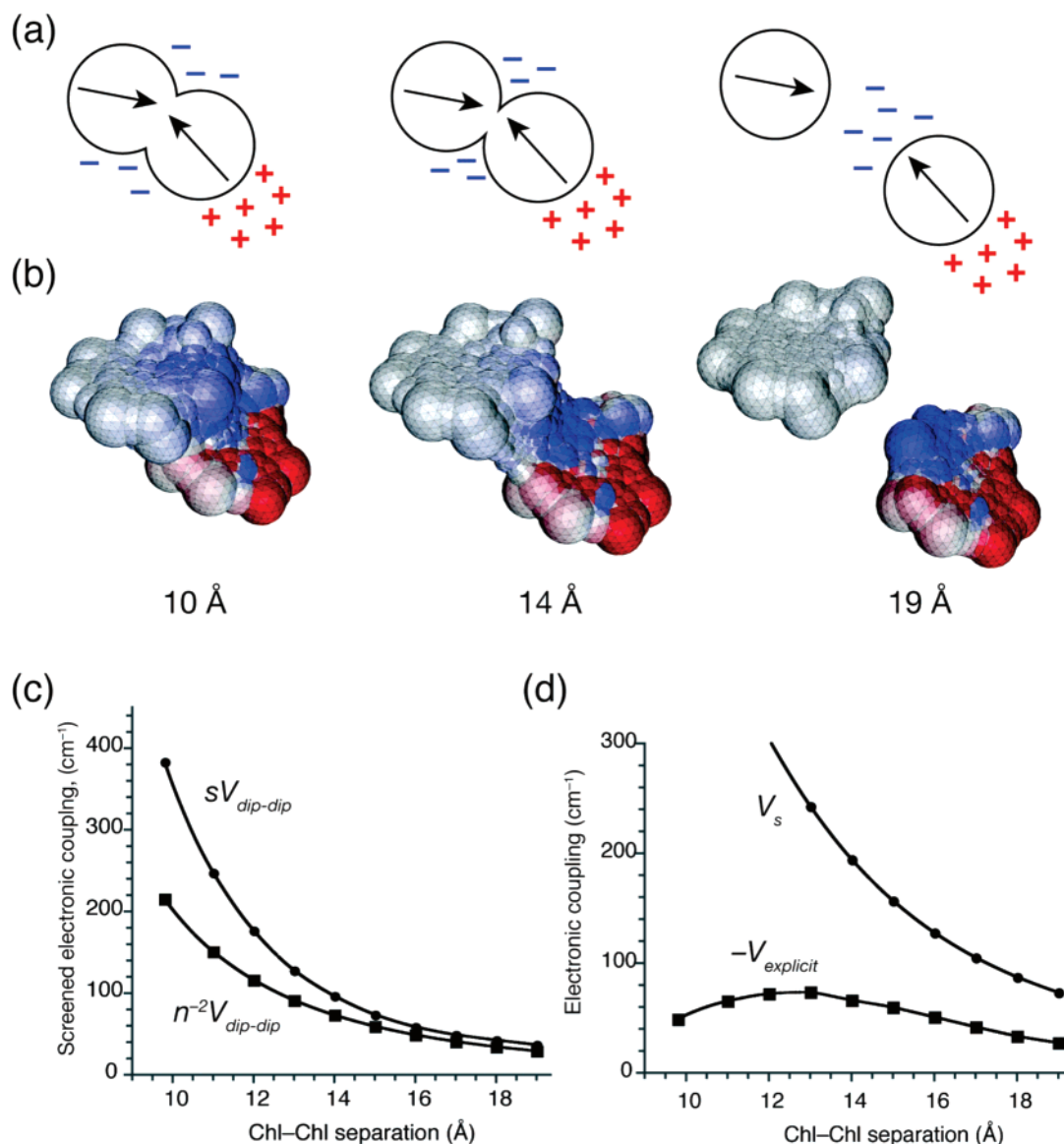
Figure 3. (a) Schematic depiction of the interaction between two transition dipoles (arrows) immersed within cavities in a polarizable medium. The effective charges representing the response of the medium to one transition dipole are drawn. As the cavities converge, the effective charges remain held away from the transition dipoles. (b) On the basis of the quantum mechanical calculations, the dependence of s on separation between the Chl_{602}–Chl_{607} molecules in the dimer structure from LHCII is explained by the formation of a common cavity, physically representing exclusion of solvent from the intermolecular region. The result is represented by a progressive spread of the effective surface charges over the acceptor microenvironment, as shown for three Chl–Chl separations. (c) The spread of the surface charges over the cavities is found to change the magnitude and functional form of the electronic coupling. The dipole–dipole coupling (screened by n^2), $V_{dip-dip}/n^2$ (squares), is compared to $sV_{dip-dip}$. The difference corresponds to a factor of at least 2 in the calculated rate of EET. (d) The origin of the distance dependence of s is seen by inspecting the ratio of the direct electronic coupling V_s to the explicit solvent contribution, $V_{explicit}$. As the intermolecular separation decreases, $V_{explicit}$ assumes diminishing significance and thus $s = V_s/V_{tot} \rightarrow 1$ because the total coupling $V_{tot} \approx V_s$.

In the case of large donor–acceptor distances, the apparent surface charges representing the medium polarization on one cavity are not influenced by the presence of the second cavity, Figure 3. The effect of the solvent is therefore independent of the separation ($s = s_0$). In this range, in addition, the location of the solvent between the chromophores leads to a reduction of the total coupling, as $V_{explicit}$ necessarily counteracts the direct V_s interaction.

As the molecules approach each other, the screening is partially reduced ($s > s_0$). Interestingly, this trend starts to show up as the chromophores begin to share a common cavity. In this process, the solvent apparent charges induced by the donor are progressively spread over the acceptor microenvironment, thus leading to a gradual decrease of the screening. When the two molecules are sufficiently close, the apparent surface

charges are spread over one large cavity enclosing the dimer, and their screening effect is significantly diluted. In this case, s approaches unity. Hence, while V_s increases as the molecules approach one another, $|V_{explicit}|$ at first increases, then decreases, Figure 3. At sufficiently close separations, we find that $V_s \gg |V_{explicit}|$, at which point the coupling is effectively unscreened.

The empirical form for the screening, obtained here using a quantum-mechanical description of the EET coupling, will be useful for improving estimates of electronic coupling by taking into account the distance-dependent screening which has been averaged over shapes and orientations of the donor and acceptor. Hence, accurate and detailed analyses of complex light-harvesting systems or fluorescence resonance energy transfer (FRET) data will be possible without having to calculate explicitly the medium effect. Considering the wider implications

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of our results, it is seen that as molecules approach one another solvent is excluded from the intermolecular region and screening effects are diminished significantly. Evidently, nature employs such as a strategy to increase light harvesting efficiencies, since solvent-suppression of EET is lessened at typical interchromophore distances of 8−12 Å found in many antenna complexes. Similarly, this must be a requirement for building wire-like linkages for directing EET between molecules, and it has implications for the consequences of chain packing in conjugated polymer films.

Supporting Information Available: Detailed methods and tables of calculated electronic couplings. This material is available free of charge via the Internet at http://pubs.acs.org.

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