Theory of Photophysical Properties of Symmetric Chlorophyll Hydrated Dimers

Karl F. Freed

Contribution from The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received October 5, 1979*

Abstract: A quantum-mechanical description is presented of the radiative and nonradiative decay characteristics of the lowest singlet states in symmetric chlorophyll hydrated dimers. The zeroth-order representation in terms of symmetric and antisymmetric "exciton-like" states is shown to imply that both states can decay by internal conversion to the ground state of the hydrated dimer. The symmetric state has allowed radiative decay to the ground state, while the antisymmetric state is found to be vibronically induced by an antisymmetric dimer vibration, thereby yielding a considerably slower radiative decay process than from the symmetric dimer state. Within the "exciton-like" model raditionless transitions between the symmetric and antisymmetric states are strictly forbidden. They are shown, however, to be induced by interchlorophyll interactions through an asymmetric vibration. For small energy splittings between the symmetric and antisymmetric dimer excited singlet states, the activation energy for the radiationless transition requires the activation of this antisymmetric vibration, producing much higher activation energies than would naively be expected. Solvent effects can enhance the preexponential factor for the symmetric ↔ antisymmetric state radiationless transition, but they do not affect the promoting mode constraints on the activation energy. The theoretical predictions are in accord with recent picosecond studies of the fluorescence from folded symmetrical chlorophyll hydrated dimers by Pellin, Wasielewski, and Kaufmann. It should be emphasized that the general theory also applies to other symmetric dimers.

I. Introduction

Research on the mechanism of the primary processes of photosynthesis has focused attention on the study of the photophysical and photochemical properties of symmetric chlorophyll hydrated dimers. Various dimers having their absorption maxima at 700 nm have been studied because this is also the absorption maximum of the P 700 reaction center of photosystem I in green plants.

Fong and co-workers,[1] Boxer and Closs,[2] and Katz and coworkers[3] have prepared symmetric chlorophyll hydrated dimers with different structures. The theoretical discussion of this paper considers the experimental data on the Boxer–Closs structure, but the predictions should apply also on the Fong-type dimer. Luminescence experiments on the Fong-type dimer will be of interest in further testing and refining the theory presented herein. Boxer and Closs have prepared covalently linked dimers of both Chl *a* and pyrochlorophyll *a* (PChl *a*) to mimic the properties of reaction center I in photosynthetic systems. These dimers have the two chlorophylls joined at their propionic acid side chains by means of an ethylene glycol diester linkage. The chlorophyll dimers fold into a C_2 symmetric conformation when the solutions of these linked dimers in dry nonnucleophilic solvents are treated with an excess of a hydrogen-bonding nucleophile. The folding causes a shift in the absorption maximum of the longest wavelength band from 663 nm in the monomer to 680 nm in the dry, unfolded state, and then to 694 nm in the folded dimer, making the study of these dimers of interest as model compounds for the study of chlorophyll dimers with two hydrogen bonding linking partners.

Pellin, Wasielewski, and Kaufmann[4] have studied the picosecond fluorescence dynamics of the PChl *a* folded dimer as a function of temperature and solvent. For methylene chloride as a solvent the fluorescence lifetime is found to be independent of temperature to within 25% below 200 K and then to decrease sharply as the temperature is increased further. The fluorescence lifetime changes by a factor of greater than 40 in going from 200 K to room temperature. On the other hand, the fluorescence quantum yield remains constant to within a factor of 2 in the range of 200–290 K when the fluorescence lifetime is varying markedly.[4] The chlorophyll dimer transient excited state absorption spectrum displays two temperature dependences and a time dependence which follows the fluorescence lifetime.[4] In carbon tetrachloride the fluorescence dynamics of the system is markedly different.[4] At 298 K the fluorescence quantum yield is ten times the value observed at the same temperature in methylene chloride, while the fluorescence lifetime corresponds to the low-temperature value observed in methylene chloride. The transient optical density change is similar to that observed in the low-temperature experiments in methylene chloride. The experiments have carefully measured the time dependence of the transient optical density changes, observing a lack of dependence on concentration, polarization, intensity, and path length.[4]

The experimental results have been interpreted[4] in terms of a kinetic model involving two singlet states of the folded chlorophyll dimer, both of which may decay through internal conversion to the ground state. The state found in carbon tetrachloride solvents and in cold methylene chloride is termed S_1 by Pellin et al. S_1 is taken to decay by internal conversion to the ground state and by nonradiative transfer to the other state, S_2. (S_1 and S_2 should not be confused with the first two excited singlet electronic states in the chlorophyll monomer.) The state present in methylene chloride at room temperatures is denoted as S_2. S_2 may fluoresce, undergo internal conversion to the ground state, and, also in principle, undergo back radiationless transitions to S_1. The relative populations of S_1 and S_2 are kinetically determined rather than thermodynamically determined because the $S_1 \leftrightarrow S_2$ transfer rates are extremely small under certain conditions.[4]

In this paper we demonstrate how the general observed kinetic scheme can be explained in terms of a quantum-mechanical description of the states S_1 and S_2 and their radiative and nonradiative decay properties. First we introduce a simple zeroth-order product function representation of the dimer electronic states, where S_1 and S_2 are taken respectively to be the antisymmetric and symmetric linear combinations

$$\psi_{\pm} = (2)^{-1/2}(\phi_\alpha{}^*\phi_\beta \pm \phi_\alpha\phi_\beta{}^*) \tag{1.1}$$

$$|S_1\rangle \equiv \psi_-, \ |S_2\rangle \equiv \psi_+ \tag{1.1a}$$

where ϕ_α and $\phi_\alpha{}^*$ denote respectively the electronic wave functions for the ground and excited states of the chlorophyll moiety α (etc., for β) along with one of the hydrogen-bonding nucleophiles. This simple model is shown in the next section to provide the following selection rules: Internal conversion

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from S_1 and/or from S_2 to the ground state, $\psi_0 = \phi_\alpha\phi_\beta$, is symmetry allowed, although vibrational considerations make the S_1 decay slower than that for S_2. The $S_1 \leftrightarrow S_2$ internal conversion is symmetry forbidden *even* through the participation of an antisymmetric vibration. The S_2 fluorescence is allowed, while the S_1 fluorescence is symmetry forbidden. Thus, the gross kinetic scheme, postulated by Pellin et al.,[4] is shown here to emerge as a set of symmetry selection rules within the simple quantum-mechanical model. Interactions between the two moieties of the folded chlorophyll dimer are then demonstrated to enable the occurrence of a weak $S_1 \leftrightarrow S_2$ internal conversion process. This internal conversion transfer is shown to have a high activation energy, much larger than the small energy spacing between the minima of the symmetric and antisymmetric excited dimer states. It is then argued that the polar methylene chloride solvent can either enhance the charge-transfer interaction or it may be weakly bound to the excited or unexcited chlorophyll unit, thereby partially destroying the C_2 symmetry and making the two solvated configurations $(\phi_\alpha\phi_\beta{}^*)_{\rm solv}$ and $(\phi_\alpha{}^*\phi_\beta)_{\rm solv}$ of different energies in which the methylene chloride preferentially binds to one side of the dimer. This partial symmetry destruction, therefore, enables the $S_1 \leftrightarrow S_2$ internal conversion to be partially allowed.

II. Quantum Model

The zeroth-order description of the symmetric chlorophyll hydrated dimer (using the term hydrated to represent any of the utilized hydrogen-bonding nucleophiles) excited singlet state electronic wave functions is given schematically in (1.1). To pursue the quantum-mechanical analysis, it is necessary to more precisely define the model wave functions. Let $\phi_\alpha(q_\alpha,Q_\alpha)$ denote the electronic wave function for the ground electron state of one of the chlorophyll units *and* one of its hydrogen-bonded water molecules, while $\phi_\alpha{}^*(q_\alpha,Q_\alpha)$ is the corresponding first electronically excited singlet state. q_α represents the electronic coordinates on unit α, while Q_α designates the collective set of vibrational coordinates of the single chlorophyll-water pair. The vibrational wave functions of this chlorophyll-water pair are written as $\chi_{\alpha j}(Q_\alpha)$ and $\chi_{\alpha j}{}^*(Q_\alpha)$, with j the vibrational quantum numbers.

The states of the chlorophyll dihydrate dimer are expressed in zeroth order by using product wave functions for each of the units, α and β, as

$$|S_1\rangle = (1/\sqrt{2})\,[\phi_\alpha{}^*(q_\alpha,Q_\alpha)\phi_\beta(q_\beta,Q_\beta) \\ -\phi_\alpha(q_\alpha,Q_\alpha)\phi_\beta{}^*(q_\beta,Q_\beta)]\chi_{\alpha\beta}{}^-(Q_\alpha,Q_\beta,Q_{\alpha\beta}) \quad (2.1)$$

$$|S_2\rangle = (1/\sqrt{2})\,[\phi_\alpha{}^*(q_\alpha,Q_\alpha)\phi_\beta(q_\beta,Q_\beta) \\ +\phi_\alpha(q_\alpha,Q_\alpha)\phi_\beta{}^*(q_\beta,Q_\beta)]\chi_{\alpha\beta}{}^+(Q_\alpha,Q_\beta,Q_{\alpha\beta}) \quad (2.2)$$

Here the electronic symmetry states appear as in (1.1), and $\chi_{\alpha\beta}{}^+$ are the vibrational wave functions which depend on the unit nuclear coordinates, Q_α and Q_β, as well as the interunit vibrational coordinates $Q_{\alpha\beta}$ involving the relative vibrations between the two Chl $a\cdot H_2O$ units. Note that the zeroth-order model (2.1) and (2.2) ignores electron exchange and Coulomb interactions between the α and β units. Our general symmetry selection rules are unchanged by the portion of the Coulomb and exchange interactions which are symmetric with respect to interchange of α and β, while the role of the antisymmetric component is discussed in subsection C below. The ground singlet state of the hydrated dimer as the zeroth-order wave function

$$|0\rangle = \phi_\alpha(q_\alpha,Q_\alpha)\phi_\beta(q_\beta,Q_\beta)\chi_{\alpha\beta}{}^0(Q_\alpha,Q_\beta,Q_{\alpha\beta}) \quad (2.3)$$

where the vibrational quantum numbers are omitted for simplicity throughout.

A. Radiative Decay Rates. Simple symmetry considerations lead to the expectation that the $|S_2\rangle \rightarrow |0\rangle$ radiative transition is symmetry allowed, while the $|S_1\rangle \rightarrow |0\rangle$ one is forbidden. A calculation of the relevant matrix elements indicates the nature of the symmetry-breaking terms which could induce very weak $|S_1\rangle \rightarrow |0\rangle$ radiative transitions.

Consider first the $|S_2\rangle \rightarrow |0\rangle$ radiative transition. If the dipole operator is written as $\boldsymbol{\mu}$, the relevant dipole matrix element is

$$\langle S_2|\boldsymbol{\mu}|0\rangle = (2)^{-1/2}\langle(\phi_\alpha{}^*\phi_\beta + \phi_\alpha\phi_\beta{}^*)\chi_{\alpha\beta}{}^+|\boldsymbol{\mu}|\phi_\alpha\phi_\beta\chi_{\alpha\beta}{}^0\rangle \quad (2.4)$$

We first perform an integration over the electronic coordinates, using the orthogonality of the electronic functions on an individual unit:

$$\int dq_\alpha\phi_\alpha{}^*(q_\alpha,Q_\alpha)\phi_\alpha(q_\alpha,Q_\alpha) = 0 \\ \int dq_\alpha\phi_\alpha(q_\alpha,Q_\alpha)\phi_\alpha(q_\alpha,Q_\alpha) = 1, \text{ etc., for } \beta \quad (2.5)$$

where the electronic functions have been taken to be real for notational simplicity. The first, $\phi_\alpha{}^*\phi_\beta$, factor in (2.4) yields the electronic matrix element

$$\int dq_\alpha \int dq_\beta\phi_\alpha{}^*(q_\alpha,Q_\alpha)\phi_\beta(q_\beta,Q_\beta)\boldsymbol{\mu}\phi_\alpha(q_\alpha,Q_\alpha) \\ \times \phi_\beta(q_\beta,Q_\beta) = \int dq_\alpha\, \phi_\alpha{}^*(q_\alpha,Q_\alpha)\boldsymbol{\mu}\phi_\alpha(q_\alpha,Q_\alpha) \\ \equiv \boldsymbol{\mu}(Q_\alpha) \quad (2.6)$$

$\boldsymbol{\mu}(Q_\alpha)$ is just the electronic dipole transition matrix element for a single hydrogen-bonded chlorophyll-water unit—a function of Q_α. Thus, (2.4) reduces to

$$\langle S_2|\boldsymbol{\mu}|0\rangle = (2)^{-1/2}\int dQ\chi_{\alpha\beta}{}^+(Q_\alpha,Q_\beta,Q_{\alpha\beta}) \\ \times [\boldsymbol{\mu}(Q_\alpha) + \boldsymbol{\mu}(Q_\beta)]\chi_{\alpha\beta}{}^0(Q_\alpha,Q_\beta,Q_{\alpha\beta}) \quad (2.7)$$

where we introduce the notation $\int dQ \equiv \int dQ_\alpha \int dQ_\beta \int dQ_{\alpha\beta}$.

The electric dipole transition is allowed in the chlorophyll monomer as well as in the chlorophyll-water unit. Hence, the dipole moment function, $\boldsymbol{\mu}(Q_\alpha)$, may be expanded in a Taylor series about the S_2 equilibrium positions $Q_{\alpha,j}{}^0$ for the jth modes of α:

$$\boldsymbol{\mu}(Q_\alpha) = \boldsymbol{\mu}(Q_\alpha{}^0) + \sum_j \left(\frac{\partial\boldsymbol{\mu}(Q_\alpha)}{\partial Q_{\alpha,j}}\right)_{Q_\alpha{}^0}(Q_{\alpha,j} - Q_{\alpha,j}{}^0) + \ldots \quad (2.8)$$

The leading term in (2.8) is taken to provide the dominant contribution for optically allowed transitions, so (2.7) becomes

$$\langle S_2|\boldsymbol{\mu}|0\rangle = (2)^{1/2}\boldsymbol{\mu}(Q^0)\int dQ\chi_{\alpha\beta}{}^+(Q)\chi_{\alpha\beta}{}^0(Q) \quad (2.9)$$

where the symmetry-induced equality, $\boldsymbol{\mu}(Q_\alpha{}^0) = \boldsymbol{\mu}(Q_\beta{}^0)$, has been used. Since the purely radiative decay rate is proportional to $|\langle S_2|\boldsymbol{\mu}|0\rangle|^2$, the folded dimer radiative decay rate has its electronic factor, $2|\boldsymbol{\mu}(Q^0)|^2$, twice that of the individual unit, $|\boldsymbol{\mu}(Q^0)|^2$, but there is some possible difference between the folded dimer Franck–Condon factor, $|\int dQ\chi_{\alpha\beta}{}^+\chi_{\alpha\beta}{}^0|^2$, and that, $|\int dQ_\alpha\chi_\alpha{}^*(Q_\alpha)\chi_\alpha{}^0(Q_\alpha)|^2$, for a single unit.

For the $|S_1\rangle \rightarrow 0\rangle$ radiative decay rate, the above analysis simply yields

$$\langle S_1|\boldsymbol{\mu}|0\rangle = (2)^{-1/2}\int dQ\chi_{\alpha\beta}{}^-(Q)[\boldsymbol{\mu}(Q_\alpha) \\ - \boldsymbol{\mu}(Q_\beta)[\chi_{\alpha\beta}{}^0(Q) \quad (2.10)$$

When (2.8) is substituted into (2.10), the terms in $\boldsymbol{\mu}(Q_\alpha{}^0) - \boldsymbol{\mu}(Q_\beta{}^0)$ cancel, leaving only the vibronically induced portion:

$$\langle S_1|\boldsymbol{\mu}|0\rangle = (2)^{-1/2}\sum_j \left(\frac{\partial\boldsymbol{\mu}}{\partial Q_{\alpha,j}}\right)_{Q_j{}^0}\int dQ\chi_{\alpha\beta}{}^-[(Q_{\alpha,j} - Q_{\alpha,j}{}^0) \\ - (Q_{\beta,j} - Q_{\beta,j}{}^0)]\chi_{\alpha\beta} \quad (2.11)$$

Consequently, the $|S_1\rangle \rightarrow |0\rangle$ radiative decay is induced by an (or some) antisymmetric vibration(s) of the form $Q_{\alpha,j}$ −

$Q_{\beta,j}$. Hence the $|S_1\rangle \rightarrow |0\rangle$ purely radiative decay rate should be smaller than the $|S_2\rangle \rightarrow |0\rangle$ purely radiative decay rate by orders of magnitude. Note that the interunit vibrations, $Q_{\alpha\beta}$, involve the relative motions of the two units, i.e., the hydrogen-bond linkages between the two units. These interunit vibrations are symmetric with respect to interchange of α and β, so these vibrations cannot vibronically induce the radiative $|S_1\rangle \rightarrow |0\rangle$ transition.

B. The Nonradiative Decay Rates. The general theory of nonradiative decay[5-7] processes provides the expression for nonradiative decay rates:

$$k_{i\rightarrow f} = (2\pi/\hbar) \sum_{mn} p_{im} |T_{im,fn}|^2 \rho_{fn}(E_{im})$$

where i and f designate the initial and final electronic states and m and n are their respective vibrational levels. $T_{im,fn}$ is the coupling matrix element inducing the transition, while $\rho_{fn}(E_{im})$ is the density of final $|fn\rangle$ at the energy, E_{im}, of the initial state $|im\rangle$. p_{im} denotes the relative population of the state $|im\rangle$ which can be taken to be a Boltzmann distribution for time scales such that the initial electronic state is thermally equilibrated. In "noninert" condensed media the solvent shell must be incorporated in the description of the initial and final states, so $|im\rangle$ and $|fn\rangle$ contain wave functions for the extended supermolecule containing the solvent molecules.[8]

As in (2.6) it is convenient to first evaluate the electronic matrix element

$$T_{i\rightarrow f}(Q) = \int dq \phi_i(q,Q) T(q,Q) \phi_f(q,Q)$$

The electronic matrix elements for internal conversion[5-8] involve the operator $\partial/\partial Q_k$ with Q_k the kth vibrational coordinate which we have implicitly taken to be either the interunit vibrations $Q_{\alpha\beta}$ or the symmetric or antisymmetric combinations $Q_{\alpha,j} \pm Q_{\beta,j}$. The electronic matrix element for the $|S_2\rangle \rightarrow |0\rangle$ internal conversion is, in principle, nonzero for symmetric modes and interunit modes. Since it is unlikely that the interunit hydrogen bonding symmetric vibrations more efficiently induce the radiationless transition than the chlorophyll vibrations that are active in inducing the transition in the monomer, we may consider only the former mode(s) j which induce internal conversion in the separate chlorophyll–water unit. The $|S_2\rangle \rightarrow |0\rangle$ internal conversion electronic transition moment is then

$$T_{S_2\rightarrow 0} = (2)^{-1/2} \int (\phi_\alpha^* \phi_\beta + \phi_\alpha \phi_\beta^*) \left(\frac{\partial}{\partial Q_{\alpha,j}} + \frac{\partial}{\partial Q_{\beta,j}}\right) \times \phi_\alpha \phi_\beta \, dq_\alpha \, dq_\beta \quad (2.12)$$

Using (2.5) and the fact that $\partial/\partial Q_{\alpha,j} \int dq_\alpha \, \phi_\alpha \phi_\alpha = \partial/\partial Q_{\alpha,j} \times (1) = 0$ etc., (2.12) is seen to reduce to

$$T_{S_2\rightarrow 0} = (2)^{1/2} \int \phi_\alpha^* \frac{\partial}{\partial Q_{\alpha,j}} \phi_\alpha \, dq_\alpha \quad (2.13)$$

Again invoking a Condon approximation (evaluating $T_{S_2\rightarrow 0}$ at Q^0), implies that the electronic contribution to the internal conversion $|T_{S_2\rightarrow 0}|^2$ is twice that, $|\int \phi_\alpha^* (\partial/\partial Q_{\alpha,j}) \phi_\alpha \, dq_\alpha|^2$, for an individual unit. The Franck–Condon factors are again different in both cases, and, if there were more than one promoting mode, the factor of 2 change in the electronic factor would persist only if the promoting modes were unchanged in the $\phi_\alpha^* \rightarrow \phi_\alpha$ transition.[5-8]

The $|S_1\rangle \rightarrow |0\rangle$ internal conversion process can be induced by an antisymmetric vibration, $Q_{\alpha,j} - Q_{\beta,j}$, where j is (are) the same mode(s) that participates in the $|S_2\rangle \rightarrow |0\rangle$ decay. This follows from the electronic matrix element

$$\begin{aligned} T_{S_1\rightarrow 0} &= (2)^{-1/2} \int (\phi_\alpha^* \phi_\beta - \phi_\alpha \phi_\beta^*) \\ &\quad \times \left(\frac{\partial}{\partial Q_{\alpha,j}} - \frac{\partial}{\partial Q_{\beta,j}}\right) \phi_\alpha \phi_\beta \, dq_\alpha \, dq_\beta \\ &= (2)^{1/2} \int \phi_\alpha^* \frac{\partial}{\partial Q_{\alpha,j}} \phi_\alpha \, dq_\alpha = T_{S_2\rightarrow 0} \quad (2.14) \end{aligned}$$

The vibrational matrix elements associated with the $|S_1\rangle \rightarrow |0\rangle$ and $|S_2\rangle \rightarrow |0\rangle$ transitions may differ considerably. If we evaluate (2.14) again at the equilibrium configuration as in (2.8), the relevant vibrational matrix element for $|S_1\rangle \rightarrow |0\rangle$ is

$$\int dQ \chi_{\alpha\beta}{}^0(Q) \left(\frac{\partial}{\partial Q_{\alpha,j}} - \frac{\partial}{\partial Q_{\beta,j}}\right) \chi_{\alpha,\beta}{}^-(Q) \quad (2.14a)$$

with plus signs for the $|S_2\rangle \rightarrow |0\rangle$ transition. For the very crude model of the vibrational wave functions involving products of individual unit wave functions and interunit wave functions, i.e., $\chi_{\alpha\beta}{}^0 \doteq \chi_\alpha{}^0 \chi_\beta{}^0 \chi_{\alpha+\beta}{}^0$ and $\chi_{\alpha\beta}{}^- \doteq \chi_\alpha{}^- \chi_\beta{}^- \chi_{\alpha+\beta}{}^-$, (2.14a) vanishes while the corresponding equation for the $|S_2\rangle \rightarrow |0\rangle$ transition does not. Despite the fact that the vibrational wave functions depart considerably from this simple model, it illustrates how the $|S_1\rangle \rightarrow |0\rangle$ internal conversion rate can be much smaller than that for $|S_2\rangle \rightarrow 0$ as observed by Pellin et al.

By symmetry an antisymmetric vibration should be sought to induce the $|S_2\rangle \rightarrow |S_1\rangle$ internal conversion. (Note that the $\partial^2/\partial Q^2$ part of the internal conversion coupling operator T cannot induce this transition because this operator is symmetric in α and β.) Hence, evaluating the electronic matrix element with an antisymmetric vibration, $i-$, yields

$$\begin{aligned} T_{S_2\rightarrow S_1} &= \frac{1}{2} \int dq_\alpha \int dq_\beta (\phi_\alpha^* \phi_\beta + \phi_\alpha \phi_\beta^*) \\ &\quad \times \left(\frac{\partial}{\partial Q_{\alpha,i}} - \frac{\partial}{\partial Q_{\beta,i}}\right) (\phi_\alpha^* \phi_\beta - \phi_\alpha \phi_\beta^*) = 0 \quad (2.15) \end{aligned}$$

because the eight individual terms coming from the products in (2.15) are of the form $(\int dq_\alpha \phi_\alpha^* (\partial/\partial Q_{\alpha,i}) \phi_\alpha^*)(\int dq_\beta \phi_\beta \cdot \phi_\beta)$ which vanish because of the normalization of ϕ_α^* (hence $(\partial/\partial Q_{\alpha,i}) \int dq_\alpha \, \phi_\alpha^* \phi_\alpha \equiv (\partial/\partial Q_{\alpha,i}) 1 = 0$), or they are of the form $(\int dq_\alpha \phi_\alpha^* (\partial/\partial Q_{\alpha,i}) \phi_\alpha)(\int dq_\beta \; \phi_\beta \phi_\beta^*)$, which again vanish because of the orthogonality of ϕ_β and ϕ_β^* (etc., for terms with $\alpha \leftrightarrow \beta$). Hence, the $|S_2\rangle \leftrightarrow |S_1\rangle$ internal conversion process cannot be induced, even by antisymmetric vibrations when the zeroth-order dimer model states (2.1) and (2.2) are considered.

C. Charge-Transfer and Exchange Interactions. The above model, given by (2.1)–(2.3), does not include the effects of interunit interactions and interactions with the solvent. We consider these effects sequentially.

Interunit (and solvent) interactions could perhaps affect the $|S_1\rangle \rightarrow |0\rangle$ radiative decay rate, but this effect is probably of comparable magnitude to that produced by the vibronic inducement described in subsection A. Thus, the only interesting possible ramifications of the interunit interaction are associated with the symmetry-forbidden $|S_2\rangle \leftrightarrow |S_1\rangle$ internal conversion process, so this is discussed here.

The interunit interaction is written as $V(q,Q)$, and this interaction introduces changes in the electronic wave functions of (1.1). Specifically, using first-order perturbation theory, the perturbed folded dimer electronic wave functions become

$$\begin{aligned} \psi_+{}^{(1)} &= (2)^{-1/2} (\phi_\alpha^* \phi_\beta \pm \phi_\beta \phi_\alpha^*) \\ &\quad + \sum_{\lambda \neq \pm} \frac{\psi_\lambda{}^{(0)} (q,Q) \int dq' \, \psi_\lambda{}^{(0)}(q',Q) V(q',Q)}{E_\pm{}^{(0)}(Q) - E_\lambda(Q)} \\ &\quad \times [\phi_\alpha^*(q_\alpha',Q_\alpha) \phi_\beta(q_\beta',Q_\beta) \\ &\quad \pm \phi_\alpha(q_\alpha',Q_\alpha) \phi_\beta^*(q_\beta',Q_\beta)] \quad (2.16) \end{aligned}$$

where $E_\pm{}^{(0)}(Q)$ denotes the potential-energy surfaces arising from the functions, $\psi^{(0)} = (2)^{-1/2} (\phi_\alpha^* \phi_\beta \pm \phi_\alpha \phi_\beta^*)$, and $\psi_\lambda{}^{(0)}(q,Q)$ denote the remaining complete set of zeroth-order folded dimer states with potential-energy surfaces $E_\lambda(Q)$. The $\psi_\lambda{}^{(0)}(q,Q)$ may involve states which are approximately represented in terms of products of individual unit states, as is $\psi_\pm{}^{(0)}$, or they may involve charge-transfer states which cannot be expressed in such a fashion but require ionic states of the units. It is perhaps customary[9] to see the last term in (2.16) be written in terms of charge-transfer states $(2)^{-1/2}(\phi_\alpha{}^+\phi_\beta{}^- \pm \phi_\alpha{}^-\phi_\beta{}^+)$. This is useful in situations where the dominant physical effects are associated with the mixing in of particular charge-transfer states or the emergence of charge-transfer bands. Here we are concerned with symmetry-breaking contributions which need not arise from the dominant charge-transfer configuration, so the more general form (2.16) is used.

The contributions, $\psi_\lambda{}^{(0)}$, of interest in promoting the $|S_1\rangle \leftrightarrow |S_2\rangle$ internal conversion are antisymmetric ones for the $\psi_+{}^{(1)}$ state and symmetric ones for the $\psi_-{}^{(1)}$ state. Let us consider one such contribution to the $\psi_+{}^{(1)}$ state and utilize the popular Taylor series expension of $V(q,Q)$ analogous to that in (2.8). The leading contribution is then of the form

$$\psi_{\lambda^-}{}^{(0)}(q,Q)\int \mathrm{d}q'\ \psi_{\lambda^-}{}^{(0)}(q',Q)\sum_j \left(\frac{\partial V(q',Q)}{\partial Q_{\alpha,j}}\right)_{Q_0} \times [(Q_{\alpha,j} - Q_{\alpha,j}) - (Q_{\beta,j} - Q_{\beta,j}{}^0)]\,(2)^{-1/2} \times \frac{[\phi_\alpha{}^*(q_\alpha{}',Q_\alpha)\phi_\beta(q_\beta{}',Q_\beta) + \phi_\alpha(q_\alpha{}',Q_\alpha)\phi_\beta{}^*(q_\beta{}',Q_\beta)]}{E_+{}^{(0)}(Q) - E_{\lambda^-}(Q)} \tag{2.17}$$

where λ^- implies an antisymmetric state, e.g., of the charge-transfer form $(2)^{-1/2}(\phi_\alpha{}^+\phi_\beta{}^- - \phi_\alpha{}^-\phi_\beta{}^+)$ with $\phi_\alpha{}^\pm$ a positive or negative ion state of unit α, etc. Thus the electronic matrix element for $S_2 \leftrightarrow S_1$ internal conversion is "borrowed" from the $\lambda^- \rightarrow S_1$ internal conversion electronic matrix element:

$$T_{\lambda^-\rightarrow S_1} = \int \mathrm{d}q(2)^{-1/2}(\phi_\alpha{}^*\phi_\beta - \phi_\beta{}^*\phi_\alpha) \times \left(\frac{\partial}{\partial Q_{\alpha,l}} + \frac{\partial}{\partial Q_{\beta,l}}\right)\psi_{\lambda^-}{}^{(0)} \tag{2.18}$$

where the promoting mode(s), l_+, must now be totally symmetric (or possibly, but less likely, involve the interunit vibrations $Q_{\alpha\beta}$).

Equations 2.17 and 2.18 can be combined together to provide the electronic matrix element for the $S_2 \leftrightarrow S_1$ internal conversion, but the full cumbersome final expression is not relevant. If the individual electronic matrix elements $\int \mathrm{d}q\psi_{\lambda^-}{}^{(0)}(\partial V/\partial Q_{\alpha,j})\psi_+{}^{(0)}$ and $\int \mathrm{d}q\psi_{\lambda^-}{}^{(0)}((\partial/\partial Q_{\alpha,l}) + (\partial/\partial Q_{\beta,l}))\psi_{\lambda^-}{}^{(0)}$ and the $E_+{}^{(0)}(Q) - E_{\lambda^-}(Q)$ are evaluated in lowest order at Q^0, then the nonradiative decay rate for the $S_1 \rightarrow S_2$ internal conversion is of the form

$$k_{S_1\rightarrow S_2} = \frac{2\pi}{\hbar}|\beta_{\mathrm{el}}|^2 \sum_{S_1,S_2} p_{S_1}\left|\int \chi_{\alpha\beta}{}^-\left[(Q_{\alpha,j} - Q_{\beta,j})\left(\frac{\partial}{\partial Q_{\alpha,l}} + \frac{\partial}{\partial Q_{\beta,l}}\right)\right]\chi_{\alpha\beta}{}^+\,\mathrm{d}Q\right|^2 \delta(E_{S_1} - E_{S_2}) \tag{2.19}$$

where the sum runs over all vibronic states of S_1 and S_2, p_{S_1} is the Boltzmann factor for the initial S_1 vibronic states, one contribution j and l have been taken for notational simplicity, $Q_{\alpha,j}{}^0 = Q_{\beta,j}{}^0 \equiv 0$, the δ function provides the energy-conservation condition (the density of states factor), and $|\beta_{\mathrm{el}}|^2$ involves all the electronic matrix elements.

At low temperatures the folded dimers in S_1 are in the lowest vibrational state with some population in vibrational states with very low frequencies. In the limit of 0 K it might be assumed that the $S_1 \rightarrow S_2$ transition would proceed slowly with no activation energy if S_1 were higher in energy than S_2 (or the $S_2 \rightarrow S_1$ transition if the opposite were true), while the $S_2 \rightarrow S_1$ transition would be thermally activated with activation energy equal to the spacing between the zero-point levels of S_2 and S_1, the S_2-S_1 energy gap ΔE_{12} (etc., if S_2 is higher). However, the presence of the $Q_{\alpha,j} - Q_{\beta,j} \equiv Q_{j-}$ and $\partial/\partial Q_{\alpha,l} + \partial/\partial Q_{\beta,l} \equiv \partial/\partial Q_{l+}$ factors in the integrand in (2.19) lead to selection rules on the $j-$ and $l+$ vibrations which can substantially alter these expectations. To simplify the discussion of this point, the vibrational matrix element in (2.19) is taken to factor into a product of a part for the $j-$ vibration, $|\langle v_{j-}{}^{(1)}|Q_{j-}|v_{j-}{}^{(2)}\rangle|^2$, a part from the $l+$ vibration, $|\langle v_{l+}{}^{(1)}|\partial/\partial Q_{l+}|v_{l+}{}^{(2)}\rangle|^2$, and the Franck–Condon factor for the remaining vibrations of the symmetric chlorophyll hydrated dimer. Here, $v_{j-}{}^{(1)}$ and $v_{l+}{}^{(1)}$ denote respectively the vibrational quantum numbers of vibrations $j-$ and $l+$ in S_1, while $v_{j-}{}^{(2)}$ and $v_{l+}{}^{(2)}$ are the corresponding quantum numbers of these vibrations in S_2. Note that the contribution from the initial S_1 state $|v_{j-}{}^{(1)}v_{l+}{}^{(1)}\ldots\rangle$ enters in (2.19) with the appropriate Boltzmann factor, p_{S_1}, for the usual thermalized S_1 state conditions.

The harmonic oscillator selection rules imply that $v_{j-}{}^{(2)}$ differ from $v_{j-}{}^{(1)}$ by an odd number of quanta (provided, of course, that $v_{j-}{}^{(2)}$ and $v_{j-}(l)$ are both nonnegative). It is, however, most likely that the vibration $j-$ be essentially identical in S_1 and S_2 because of the strong electronic similarity of the two states. In this case the selection rule becomes $|v_{j-}{}^{(2)} - v_{j-}{}^{(1)}| = 1$. Thus, if we begin with $v_{j-}{}^{(1)} = 0$, this condition requires that $v_{j-}{}^{(2)} = 1$. However, if the vibrational quantum of energy, $\hbar\omega_{j-}{}^{(2)}$, is greater than the electronic energy, ΔE_{12}, that is converted to S_2 vibrational energy, there is insufficient energy to permit the $v_{j-}{}^{(1)} = 0$ term to contribute. The $S_1 \rightarrow S_2$ transition must be thermally activated! The contribution to (2.19) from $v_{j-}{}^{(1)} = 1$ enters with activation energy $\hbar\omega_{j-}$. The selection rule that $v_{j-}{}^{(2)} = 0$ can now be safely satisfied with the energy $\Delta E_{12} + \hbar\omega_{j-}$ going into vibrational energy in modes other than $j-$ in S_2. In principle, we may begin in S_1 in a state with $v_{j-}{}^{(1)} = 0$ and the vibrational energy $\hbar\omega_{j-} - \Delta E_{12}$ in certain other vibrational modes, so the final state in S_2 is $v_{j-}{}^{(2)} = 1$ and the remaining vibrations are unexcited. Thus, the minimum $S_1 \rightarrow S_2$ activation energy is $\hbar\omega_{j-} - \Delta E_{12}$. Likewise, for the $S_2 \rightarrow S_1$ transition similar arguments produce the minimum activation energy $\hbar\omega_{j-}$ when due regard is taken for the $Q_{\alpha,j} - Q_{\beta,j}$ factor in (2.19). This feature also follows naturally from detailed balance arguments and the $S_1 \rightarrow S_2$ activation energy. If changes in frequency in $j-$ are permitted between S_1 and S_2, then transitions containing $|v_{j-}{}^{(1)} - v_{j-}{}^{(2)}| = 3, 5, \ldots,$ may also enter into (2.19). However, all such processes require higher activation energies.

So far, we have ignored any selection rules imposed by the $\partial\partial Q_{l+}$ term in (2.19). This factor is more complicated, and two cases emerge. If this vibration has a moderate shift in frequency and/or equilibrium position between S_1 and S_2, the matrix element $|\langle v_{l+}{}^{(1)} = 0|\partial/\partial Q_{l+}|v_{l+}{}^{(2)} = 0\rangle|^2$ is appreciable, and the above discussion on the minimum activation energies for the $S_1 \rightarrow S_2$ transitions remain unchanged. However, because of the strong electronic structure similarity of S_1 and S_2, these changes may be negligible. Then the selection rule from the $l+$ part of the matrix element in (2.19) becomes $|v_{l+}{}^{(1)} - v_{l+}{}^{(2)}| = 1$. It is, thus, of the same form as the selection rule imposed by vibration $j-$. Pursuing the above line of reasoning implies that the minimum activation energies for the $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_1$ transitions are respectively $\hbar\omega_{j-} + \hbar\omega_{l+} - \Delta E_{12}$ and $\hbar\omega_{j-} + \hbar\omega_{l+}$. The energy-level scheme and activation energies are summarized in Figure 1. We believe this case with $\hbar\omega_{l+}$ in the activation energy to be the more likely, but experimental studies are required to establish this matter.

Note that the case of $\Delta E_{12} < \hbar\omega_{j-} + \hbar\omega_{l+}$ is considered as the $S_1 \leftrightarrow S_2$ splitting is taken to be smaller than the sum of the two promoting mode energy quanta. (See the experimental reasons in section III.) For situations where $\Delta E_{12} > \hbar\omega_{j-} + \hbar\omega_{l+}$ (or $\Delta E_{12} > \hbar\omega_{j-}$ with moderate changes in $l+$ between S_1 and S_2), the selection rules on $j-$ and the energy conservation constant may be satisfied for the vibrationless level in S_1. Hence, for these other cases $S_1 \rightarrow S_2$ transition is nonac-

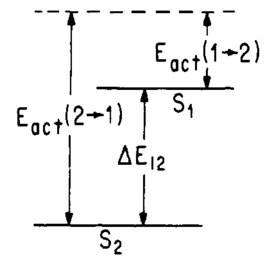

Figure 1. Schematic representation of the energy levels and activation energies for the case in which the antisymmetric state S_1 is the higher state. (If S_2 is higher, as in the Fong dimer, the indexes 1 and 2 are simply interchanged.) The separation between the zero-point levels is ΔE_{12} and is assumed to be smaller than the required promoting mode energies. If the symmetric promoting mode for the internal conversion remains the same in S_1 and S_2 or changes very slightly, then the activation energy is $E_{act}(2 \to 1) = \hbar\omega_{j-} + \hbar\omega_{l+}$, where $\hbar\omega_{l+}$ is the symmetric promoting mode quantum of energy, and $\hbar\omega_{j-}$ is the quantum for the asymmetric vibration responsible for the vibronic symmetry breaking. $E_{act}(2 \to 1)$ arises because the coupling operator in vibrational integral (2.19) requires that one quantum of each mode be excited in S_2 to enable the transition to S_1. The similar condition implies that $E_{act}(1 \to 2) = E_{act}(2 \to 1) - \Delta E_{12}$. If the vibrational mode $l+$ changed considerably in going between S_1 and S_2 (believed to be unlikely for the hydrated chlorophyll dimer), then $E_{act}(2 \to 1)$ becomes only $\hbar\omega_{j-}$ and $E_{act}(1 \to 2)$ reduces to $\hbar\omega_{j-} - \Delta E_{12}$. When ΔE_{12} is larger than $\hbar\omega_{j} - + \hbar\omega_{l+}$ (for $l+$ unchanged in the $S_1 \leftrightarrow S_2$ transition) or than $\hbar\omega_{j-}$ (if $l+$ suffers a large change), then the $S_1 \to S_2$ transition converts a sufficient amount of electronic energy, ΔE_{12}, into vibrational energy in S_1 to produce states in S_1 with the required excitations in the promoting mode(s). Hence, $E_{act}(1 \to 2) = 0$ and $E_{act}(2 \to 1) = \Delta E_{12}$, as naively would have been presupposed.

tivated, while the $S_2 \to S_1$ transition has the activation energy ΔE_{12}.

The nature of the promoting mode $Q_{\alpha,l} + Q_{\beta,l}$ is not simply deduced from theoretical arguments as the promoting mode has not been unambiguously determined for the radiationless decay of even the simple isolated gas-phase benzene molecule. Likewise, it appears difficult to specify the antisymmetric vibronic mixing mode $Q_{\alpha,j} - Q_{\beta,j}$. More work on this question might be illuminating. However, it is clear that these modes can produce a rather high activation energy against even the downward (in energy) internal conversion at room temperature.

D. Solvent Effects. The above discussion in A–C rigorously pertains to the isolated folded dimer molecules, and solvent effects must be considered in order to explain the experimental data of Pellin et al.[4] The $\phi_\alpha \to \phi_\alpha^*$ excitation in a unit is assumed to produce a nonnegligible change in the dipole moment of the moiety. This plausible assumption has been invoked by Fong to explain the red shifts in the longest wavelngth absorptions for various states of cholorphyll aggregation.[10] The interactions of the ground, ϕ_α, and excited, ϕ_α^*, units with nonpolar solvents is expected to be rather similar. Thus, in the CCl_4 experiments of Pellin et al. the $S_2 \leftrightarrow S_1$ interconversion is blocked or very weak because of high activation barriers and/or very slow pre-Arrhenius factors due to weak mixings into (2.17) of states, $\psi_\lambda{}^{-(0)}$, which can induce the nonradiative decay. Hence, the behavior observed in CCl_4 should be expected to occur also for other inert nonpolar solvents. Inert implies the absence of chemical (e.g., even exciplex) interactions of the solvent with ϕ_α^* (or ϕ_α).

In polar solvents the molecule–solvent interactions, e.g., the ϕ_α^*-solvent interactions, can provide the couplings, V in (2.17), to enhance the nonradiative decay rate. This is analogous to the external heavy atom effect in increasing intersystem crossing and phosphorescence rates. Alternatively, the solvent may differentially align (or bind) to ϕ_α^* and ϕ_α, making the $(\phi_\alpha^*\phi_\beta)_{\text{solvated}}$ symmetry inequivalent (e.g., having different energies) from $(\phi_\alpha\phi_\beta^*)_{\text{solvated}}$ and thereby enabling an allowed transition between the perturbed S_1 and S_2 states. When the second-order quantum-mechanical rate expression is written in terms of the zeroth-order $\psi_\pm{}^{(0)}$ levels, these two mechanisms appear identically as a solvent-induced enhancement of the Arrhenius preexponential factor—the activation energy should be unchanged apart from possible solvent shifts in ΔE_{12} which should be small because of the similar electronic structure of S_1 and S_2. Hence, the CH_2Cl_2-induced enhancement of $S_1 \leftrightarrow S_2$ interconversion in the folded chlorophyll dimer should persist in other chemically inert polar solvents, while the experimentally observed luminescence behavior in CCl_4 should be found in other nonpolar solvents which do not chemically interact with the chlorophyll hydrated dimer. Because of the experimental difficulty in finding the requisite "chemically inert" polar solvents, it may be useful to employ nonpolar solvents which can have exciplex-type interactions with electronically excited chlorophyll but not with ground-state chlorophyll. This would also serve to introduce the symmetry-breaking couplings as in (2.17).

III. Discussion

The radiative and nonradiative decay characteristics of the excited singlet electronic states of symmetric chlorophyll hydrated dimers have been considered by using the simple zeroth-order description of these dimer states in terms of the symmetric and antisymmetric "exciton" states and by a consideration of symmetry-breaking "charge-transfer" and solvent-induced interactions. The zeroth-order model implies that the symmetric component, $|S_2\rangle$, has allowed radiative and nonradiative decay to the ground electronic state, $|0\rangle$, of the dimer. The $|S_2\rangle \to |0\rangle$ nonradiative decay is induced by a symmetric vibration (composed of a symmetric combination of individual unit vibrations) which is presumably derived from the inducing mode(s) for internal conversion in the individual chlorophyll units. The antisymmetric component, $|S_1\rangle$, has an allowed $|S_1\rangle \to |0\rangle$ internal conversion which is promoted by an asymmetric vibration that is expected to be the antisymmetric counterpart of the vibration(s) producing the $|S_2\rangle \to |0\rangle$ internal conversion. However, the vibrational matrix element for the $|S_1\rangle \to |0\rangle$ internal conversion can be much smaller than that for the $|S_2\rangle \to |0\rangle$ decay leading to a slower internal conversion process in the antisymmetric dimer state $|S_1\rangle$. The $|S_1\rangle \to |0\rangle$ radiative decay is only vibronically induced by an antisymmetric vibration(s) of the dimer, so this pure radiative decay rate should be orders of magnitude less than the $|S_2\rangle \to |0\rangle$ decay rate such that on the picosecond time sale $|S_1\rangle$ may appear to be nonradiative or only weakly radiative.

Naively, the $|S_1\rangle \leftrightarrow |S_2\rangle$ transition would be expected to thermalize these two electronic manifolds for temperatures such that the thermal energy, k_BT, is comparable to the electronic energy separation, ΔE_{12}. However, within the simple "exciton state" dimer model this $|S_1\rangle \leftrightarrow |S_2\rangle$ interconversion is strictly forbidden. The introduction of interunit charge transfer and exchange interactions can provide a weak $|S_1\rangle \leftrightarrow |S_2\rangle$ internal conversion, but with an activation energy for the upward transition that is equal to a quantum of the antisymmetric vibration, $\hbar\omega_{j-}$, which induces the symmetry-breaking charge-transfer or exchange interaction. For $\hbar\omega_{j-} > \Delta E_{12}$ even the back radiationless transition (downhill in energy) has an activation energy $\hbar\omega_{j-} - \Delta E_{12}$. If the symmetric vibration, inducing the $|S_1\rangle \leftrightarrow |S_2\rangle$ transition in the weakly symmetry broken dimer, is unchanged between these two electronically similar states, as is quite plausible, then the activation energies for the $|S_1\rangle \leftrightarrow |S_2\rangle$ transitions (both directions) require additionally a quantum, $\hbar\omega_{l+}$, of this symmetric inducing vibration in order that the radiationless transition occur. Thus, the theory clearly predicts that $|S_1\rangle$ and $|S_2\rangle$ are not in thermal communication at low temperatures because of the higher activation energies than naively expected on the basis of the energy separation, ΔE_{12}, between the two electronic states and because of the low preexponential Arrhenius factors.

The experiments of Pellin et al. give evidence that the splitting ΔE_{12} is smaller than the required promoting mode(s) energies as follows. The angle between the transition moments on the monomers is 180° in the Boxer-Closs dimer. The simple dipole-dipole approximation implies that the symmetric $|S_2\rangle$ state is the lower in energy. The experiments observe thermal activation of the short-lived $|S_2\rangle$ state in methylene chloride. The nonradiative decay rate gives an activation energy of 3.6 kcal/mol, and the radiative decay rate yields 4.1 kcal/mol. This corresponds to the experimental observation of an activated population of the *lower of the two* excitonic components, so the promoting mode(s) energy requirements are obtained as about 4 kcal/mol + ΔE_{12}.

It is interesting to note that the angle between the monomer transition moments in the Fong dimer is 60°. Here the long-lived antisymmetric excitonic component $|S_1\rangle$ is the lower in energy. The overall dipole-dipole interaction is reduced in the Fong dimer by a factor of 4 from the Boxer-Closs dimer by angular factors, but the inverse sixth power of the intermonomer distance variation of the dipole-dipole approximation splitting cannot simply be evaluated because the origin of the "point transition dipoles" in the monomers is uncertain. The Boxer-Closs dimer has a smaller interplanar separation than the Fong dimer. The chlorophyll planes are displaced laterally with respect to each other in the former case but not in the latter, so the interplane spacing is not necessarily the relevant quantity. (Also higher multipole contributions may be nonnegligible.) It will be of interest to consider similar experiments on the Fong dimer because of the shift in relative energies of S_1 and S_2 as well as the change magnitude of ΔE_{12}.

Polar solvents are seen to provide an additional contribution to the $|S_1\rangle \leftrightarrow |S_2\rangle$ internal conversion rates, but the chemically inert solvent does not affect the activation energies as solvent is assumed not to introduce inducing modes for the nonradiative transition. Similar effects may be produced by nonpolar solvents which have exciplex interactions with only the electronically excited chlorophyll unit.

The theoretical predictions of the model are in excellent accord with the kinetics obtained in the experiments of Pellin et al.[4] on the radiative and nonradiative properties of the singlet states of folded chlorophyll hydrated dimer. Checks with other solvents will be of interest. Similarly, the theoretical predictions should apply to the Fong symmetrical chlorophyll hydrated dimer.[1] The dihydrated dimer in vivo has C_s symmetry, so a theoretical description of its properties must be considered separately, and this should be an interesting project. In vitro the dihydrate of chlorophyll exists only as a polymer with translational symmetry[11] producing a band of "exciton" states whose properties should likewise be amenable to theoretical description.

The Boxer-Closs and the Fong dimers dissociate in the triplet state.[12] It is possible to apply the theory to the triplets in the event that bound dimers can be prepared. Here, however, there are the three additional triplet sublevels to be considered. If the analogous triplet splitting, ΔE_{12}, becomes very small, on the order of a wavenumber, then small spin interactions might be able to induce the $|T_1\rangle \leftrightarrow |T_2\rangle$ nonradiative decay, and this point should be considered further.

It should be emphasized that the majority of the theoretical discussion in this paper applies equally well to symmetrical dimers other than chlorophyll hydrated dimers as only certain specific facets of the chlorophyll case have been introduced such as allowed $\phi_\alpha \rightarrow \phi_\alpha{}^*$ radiative transitions in the monomer. By introducing any required particular differences, the theory can be adapted to other symmetrical dimer systems, and, in particular, the study of symmetric paracyclophanes would be of interest. For unsymmetrical dimers the symmetry constraints are partially lifted, and additional theoretical analysis is warranted.

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