and J. Schnell, *ibid.*, **509**, 201 (1934).

(13) Due to the deprivation of the two additional hydrogen bonds in A, the exo interactions in B appear to be energetically less favorable than the endo interactions given in A. We note that under identical cooling conditions, the dimerization equilibrium constant is about two orders of magnitude more favorable for A than B (compare Figure 1b of this paper with Figure 9.19 of ref 2).

(14) The question of exagomous Chl a–protein binding in the reaction center aggregate has been discussed in F. K. Fong, translated into Japanese by Y. Inoue, *Protein, Nucleic Acid Enzyme*, **21** (9), 701 (1976).

(15) V. J. Koester and F. K. Fong, *J. Phys. Chem.*, **80,** 2310 (1976).

(16) K. D. Phillipson, V. L. Sato, and K. Sauer, *Biochemistry*, **11,** 459 (1972).

(17) Details of this analysis will be published elsewhere.

(18) R. E. Fenna and B. W. Mathews, *Nature* (*London*), **258,** 573 (1975).

(19) F. K. Fong, *J. Am. Chem. Soc.*, **98,** 7840 (1976).

(20) F. K. Fong, "The Primary Light Reaction in Photosynthesis: A Molecular Interpretation", Wiley-Interscience, New York, N.Y., in press.

F. K. Fong,* V. J. Koester, L. Galloway

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received May 24, 1976

Molecular Origin of Long-Wavelength Forms of Hydrated Chlorophyll a

Sir:

There has been a longstanding interest in the aggregation of hydrated Chl a.[1,2] Recent work has established that Chl a exists in three states of hydration.[2-9] Each of these three states gives rise to aggregate species that probably correspond to frequently encountered long-wavelength forms of in vivo and in vitro Chl a.[9b] It is believed[2-4,6-13] that the photoactive aggregate P700[14] (an in vivo Chl a complex that absorbs at 700 nm) in photosystem I is probably a C_2 symmetrical dimer of the monohydrate, (Chl a·H_2O)$_2$. On aggregation, the dihydrate yields the polymeric species (Chl a·$2H_2O$)$_n$ that has a red absorption maximum at 743 nm.[3,4,15] Much of the current work has been concerned with the in vitro preparation and characterization of 700 nm-absorbing Chl a aggregates.[3,9,10-13] Special attention has been focused on the specific roles of the C-9 keto[9,10-13] and C-10 carbomethoxy carbonyl[4,7-9] groups in bonding interactions in (Chl a·H_2O)$_2$ and on the photoactivity[16,17] of dimeric and polymeric hydrated Chl a.

One of the major unresolved problems is the question of the origin of absorption red shifts observed in Chl a aggregates. This question has been a subject of considerable speculation for some time[18] and has defied analysis on the basis of simple exciton theory.[19] The red shift in the A743 polymer (Chl a·$2H_2O$)$_n$ has been attributed[15] to transition dipole–transition dipole interactions according to the McRae and Kasha model.[20] However, the recently determined exciton splitting (~10^2 cm^{-1}) in the lowest excited singlet[9] of (Chl a·H_2O)$_2$ suggests that wavelength shifts due to transition dipole interactions are probably far too small to account for the sizable shift (~1500 cm^{-1}) found in A743. The attribution[12] of "environmental" red shifts to "π–π stacking" of neighboring chlorin planes in (Chl a·HOC_2H_5)$_2$ and (Chl a·$2H_2O$)$_n$ appears to be inconsistent with the appreciably smaller red shift (~288 cm^{-1}) observed in the anhydrous dimer Chl a$_2$[4,7] (with a red absorption maximum at 678 nm) in which π–π stacking occurs to a much larger extent than in the proposed structures for (Chl a·HOC_2H_5)$_2$ and (Chl a·$2H_2O$)$_n$. (Compare Figure 1 of ref 4 with Figure 3 of ref 12 and Figure 6 of ref 15.) The purpose of this communication is to present a systematic interpretation of exciton interactions in molecular aggregates in standard perturbation theory.[21] We delineate possible sources for the observed optical frequency shifts in Chl a aggregates, and identify the molecular interaction responsible for the optical frequency shifts characteristic of the various hydrated Chl a aggregates.

We consider a polymeric system consisting of N_0 identical monomeric units. The position vector $\mathbf{R}_n$ of unit n is given by integral multiples of the unit vector $\mathbf{a}$, i.e., $\mathbf{R}_n = n\mathbf{a}$. The total Hamiltonian may be written

$$\mathbf{H}_\mathrm{M} = \sum_{n=1}^{N_0} \mathbf{H}(n) + \frac{1}{2}\sum_{n,m}{}' \mathbf{V}(n,m) \qquad (1)$$

where $\mathbf{H}(n)$ is the Hamiltonian operator for the nth molecular unit, and $\mathbf{V}(n,m)$ is the pairwise interaction between the nth and mth units. In Chl a$_2$, (Chl a·H_2O)$_2$ and (Chl a·$2H_2O$)$_n$, the monomeric units are Chl a, Chl a·H_2O, and Chl a·$2H_2O$, respectively. In the following discussion monomeric units are referred to as "molecules", whereas the aggregate is designated as the "system". The molecular eigenstates and the eigenvalues of $\mathbf{H}(n)$ are given by $|\Phi_\lambda(n)\rangle$ and ϵ_λ, respectively. The eigenstates $|\Psi_\mathrm{k}\rangle$ and eigenvalues E_k of the system are determined by the Schrödinger equation

$$\mathbf{H}_\mathrm{M}|\Psi_\mathrm{k}\rangle = E_\mathrm{k}|\Psi_\mathrm{k}\rangle \qquad (2)$$

In zeroth-order approximation, the ground state of the system is given as the product state

$$|\Psi_0\rangle = \prod_n |\Phi_0(n)\rangle \qquad (3)$$

The ground state energy of the system is accordingly written

$$E_0 = N_0\epsilon_0 + \delta_0 \qquad (4)$$

where the energy of aggregation

$$\delta_0 = \frac{1}{2}\sum_{n,m}{}' \langle \Phi_0(n)\Phi_0(m)|V(n,m)|\Phi_0(n)\Phi_0(m)\rangle \qquad (5)$$

is the total of attractive interactions that stabilize the system in its ground state. A zeroth order excited state of the system may likewise be written

$$|X_\beta(n)\rangle = |\Phi_\beta(n)\rangle \prod_{m\neq n} |\Phi_0(m)\rangle \qquad (6)$$

in which the nth unit is prepared in the βth molecular state. Each excited eigenlevel of the aggregate is composed of N_0 components

$$|\Psi_{\beta\mathbf{k}_\nu}\rangle = N_0^{-1} \sum_{n=0}^{N_0-1} \exp[i\mathbf{k}_\nu \cdot \mathbf{R}_n]|X_\beta(n)\rangle \qquad (7)$$

where the wave vector is given by

$$\mathbf{k}_\nu = 2\pi\nu/N_0\hat{a} \qquad (8)$$

with

$$\nu = -(N_0 - 1)/2, -(N_0 - 1)/2 + 1, \ldots, (N_0 - 1)/2 \qquad (9)$$

and

$$\nu = -N_0/2 + 1, -N_0/2 + 2, \ldots, N_0/2 \qquad (10)$$

for systems with an odd and even number of molecules, respectively. On substitution of eq 7 in eq 2, we obtain the eigenvalues

$$E_{\beta\mathbf{k}_\nu} = \epsilon_\beta + (N_0 - 1)\epsilon_0 + \delta_\beta + M_\beta \cos(k_\nu a) \qquad (11)$$

where the aggregation energy of the excited-state system

$$\delta_\beta = \sum_m{}' \langle \Phi_0(m)\Phi_\beta(n)|\mathbf{V}(n,m)|\Phi_\beta(n)\Phi_0(m)\rangle$$

$$+ \frac{1}{2}\sum_{m,s\neq n}{}' \langle \Phi_0(m)\Phi_0(s)|\mathbf{V}(m,s)|\Phi_0(s)\Phi_0(m)\rangle \qquad (12)$$

differs from δ_0 in eq 5 in that the intermolecular interactions are of two types—those occurring between $(N_0 - 1)$ ground state molecules and those between these ground state molecules and the remaining excited molecule, and

$$M_\beta = \sum_{i=1,2,\ldots}{}' \langle \Phi_0(n)\Phi_\beta(n \pm i) \times |\mathrm{V}(n,n \pm i)| \Phi_\beta(n)\Phi_0(n \pm i)\rangle \quad (13)$$

is the energy shift due to various neighbor exciton interactions. In the case of (Chl a$\cdot$$H_2O$)$_2$, eq 13 may be explicitly rewritten in the point–dipole approximation[9]

$$M_\beta = \frac{e\mu^2}{R_{12}{}^3}\left[1 - \left(\frac{3R_\perp{}^2}{R_{12}{}^2} - 1\right)\sin^2\frac{\theta}{2}\right] \quad (14)$$

where μ, $R_\perp$, R_{12}, and θ are the monomeric transition dipole moment, the perpendicular distance between the two chlorin planes, the distance between, and the angle subtended by the transition dipoles, respectively.

The energies ϵ_0 and ϵ_β include all solvent interactions between the molecules and the surrounding medium. The difference between eq 11 and eq 4

$$\Delta E = \Delta\epsilon_{\beta 0} + \Delta\delta_{\beta 0} + M_\beta \cos(k_\nu a) \quad (15)$$

yields the energy gap between the ground state and the k_νth exciton component of the βth excited level. In eq 15 $\Delta\epsilon_{\beta 0} = \epsilon_\beta - \epsilon_0$ corresponds to the transition energy gap of the monomeric unit. The $\Delta\delta_{\beta 0} = \delta_\beta - \delta_0$ term signifies the difference between the aggregation energy of the excited state β and that of the ground state due to the change in *permanent* dipole moment in the excited molecule. For Chl a (and all polar molecules) the leading terms in eq 5 and eq 12 are of dipole–dipole origin.[22] For $(\mu_\beta - \mu_0) > 0$, we have $\Delta\delta_{\beta 0} < 0$ and a corresponding red shift in the aggregate absorption is obtained.

In a systematic analysis of exciton effects,[9] we find that $\Delta\delta_{\beta 0}$ is primarily responsible for the observed Chl a aggregation red shifts. The peak positions of monomeric hydrated Chl a, (Chl a$\cdot$2H_2O)$_2$, (Chl a$\cdot$$H_2O$)$_2$, and (Chl a$\cdot$2$H_2O$)$_n$ are respectively given 665 nm[3,9b] (A665), 695 nm[9b] (A695), 700 nm,[3,9b] and 743 nm[3,4] (A743) in 1:1 *n*-pentane:methylcyclohexane.[23] Assuming the red shift between A665 and A695, $\Delta\nu_{A695} = -649\ \mathrm{cm}^{-1}$, to be a unit of nearest neighbor dipole–dipole shift difference in (Chl a$\cdot$2H_2O)$_n$, the frequency shift for A743 can be computed according to the formula

$$\Delta\nu_{A743} = \Delta\delta_{S_1-S_0}(A743) = \sum_{i,1,2,\ldots} \frac{2\Delta\nu_{A695}}{i^3} = -1559\ \mathrm{cm}^{-1} \quad (16)$$

which gives 742 nm for the expected red-shifted (with respect to A665) absorption maximum position for (Chl a$\cdot$2H_2O)$_n$, in excellent agreement with experiment. In eq 16 the summation over i converges rapidly in view of the cube dependence on the separation distance in dipole–dipole interaction. The factor of 2 in eq 16 reflects the translation symmetry in (Chl a$\cdot$2H_2O)$_n$ as represented in Figure 6 of ref 15. The mth excited monomeric unit in (Chl a$\cdot$2H_2O)$_n$ sees pairs of identical interactions with units at $m \pm 1$, $m \pm 2$, $m \pm 3$, ...

We attribute the relatively large red shift in hydrated Chl a aggregates compared to that in Chl a$_2$ to hydrogen bonding of the water proton to a Chl a carbonyl. The presence of the proton enhances the excited-state electronic redistribution in favor of the electronegative end of the C=O bond. The close proximity of the peak positions in (Chl a$\cdot$$H_2O$)$_2$ and (pyroChl$\cdot$$H_2O$)$_2$[9,10] suggests that the same effect may be operative when either of the two ring V carbonyl groups is involved. Current frequency shift studies in this laboratory are concerned with the effect of π-conjugation involving the chlorin macrocycle and with the consequences of geometrical differences in the proposed structures for (Chl a$\cdot$$H_2O$)$_2$ and (pyroChl$\cdot$$H_2O$), as well as the inclusion of the relatively minor frequency shift due to exciton interaction in eq 13.

Acknowledgment. This research was supported by the National Science Foundation.

References and Notes

(1) For a comprehensive review of work prior to 1968, see, G. P. Gurinovich, A. N. Sevchenko, and K. N. Solovév, "Spectroscopy of Chlorophyll and Related Compounds", Chapter 9, available in a 1971 translation issued by the Division of Technical Information, U.S. Atomic Energy Commission, AEC-tr-7199.

(2) For a review of recent developments, see F. K. Fong, "Theory of Molecular Relaxation: Applications in Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1975, Chapter 9.

(3) F. K. Fong and V. J. Koester, *Biochim. Biophys. Acta,* **423,** 52 (1976); (b) V. J. Koester, L. Galloway, and F. K. Fong, *Naturwissenschaften*, **82,** 530 (1975); (c) V. J. Koester, J. S. Polles, J. G. Koren, L. Galloway, R. A. Andrews, and F. K. Fong, *J. Lumin.,* **12,** 781 (1976).

(4) F. K. Fong and V. J. Koester, *J. Am. Chem. Soc.*, **97,** 6888 (1975).

(5) N. Winograd, A. Shepard, D. H. Karweik, V. J. Koester, and F. K. Fong, *J. Am. Chem. Soc.,* **98,** 2369 (1976).

(6) (a) F. K. Fong, *J. Theoret. Biol.,* **46,** 407 (1974); (b) *Proc. Natl. Acad. Sci. U.S.A.,* **71,** 3692 (1974); (c) *Appl. Phys.*, **6** (2), 151 (1975).

(7) F. K. Fong, *J. Am. Chem. Soc.*, **97,** 6890 (1975).

(8) V. J. Koester and F. K. Fong, *J. Phys. Chem.*, **80,** 2310 (1976).

(9) (a) F. K. Fong, V. J. Koester, and j. S. Polles, *J. Am. Chem. Soc.*, **98,** 6406 (1976); (b) F. K. Fong, V. J. Koester, and L. Galloway, *J. Am. Chem. Soc.*, preceding paper in this issue.

(10) S. G. Boxer and G. L. Closs, *J. Am. Chem. Soc.,* **98,** 5406 (1976).

(11) The Closs model,[10] based on the self-aggregation of pyroChl a$\cdot$$H_2O$ (in which the C-10 carbomethoxy group is absent) through C-9 keto C=O$\cdots$H(H)O$\cdots$Mg bonds, differs somewhat from the Fong structure[6-9] in which the C_2 symmetry of (Chl a$\cdot$$H_2O$)$_2$ is derived from reciprocal C-10 carbonyl C=O$\cdots$H(H)O$\cdots$Mg interactions. For an optical spectroscopic analysis that differentiates these two models and for a comparison of the in vitro (Chl a$\cdot$$H_2O$)$_2$ optical spectrum with in vivo P700 spectroscopic measurements, see ref 9b.

(12) See, also, L. L. Shipman, T. M. Cotton, J. R. Norris, and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.,* **73,** 1791 (1976), for a variant model in which the water in (Chl a$\cdot$$H_2O$)$_2$ is replaced by C_2H_5OH.

(13) Following the procedure given in ref 3 for the preparation of (Chl a$\cdot$$H_2O$)$_2$, using C_2H_5OH instead of H_2O as the aggregation agent, J. J. Katz and coworkers[12] have prepared a 700-nm absorbing species that is most probably the dimer (Chl a$\cdot$$HOC_2H_5$)$_2$. The replacement of H_2O by C_2H_5OH precludes the involvement of the reciprocal C-10 carbonyl C=O$\cdots$H(H)O$\cdots$Mg interactions in (Chl a$\cdot$$H_2O$)$_2$ because of steric repulsion of the ethyl groups.[9b] The Katz variant structure is closely similar to the model given in ref 10.

(14) (a) B. Kok, *Biochim. Biophys. Acta*, **48,** 527 (1961); (b) B. Ke, *Arch. Biochem. Biophys.*, **152,** 70 (1972).

(15) H.-C. Chow, R. Serlin, and C. E. Strouse, *J. Am. Chem. Soc.*, **97,** 7230 (1975).

(16) (a) C. W. Tang and A. C. Albrecht, *J. Chem. Phys.*, **82,** 2139; **83,** 953 (1975); (b) C. W. Tang, F. Douglas, and A. C. Albrecht, *J. Phys. Chem.,* **79,** 2923 (1975); (c) C. W. Tang and A. C. Albrecht, *Mol. Cryst. Liq. Cryst.*, **25,** 53 (1974).

(17) (a) F. K. Fong and N. Winograd, *J. Am. Chem. Soc.*, **98,** 2287 (1976); (b) L. Fetterman, L. Galloway, N. Winograd, and F. K. Fong, *J. Am. Chem. Soc.*, **99,** 653 (1977).

(18) S. S. Brody and M. Brody, *Nature* (*London*), **189,** 547 (1961).

(19) See, for example, the recent exchange of comments between M. Gouterman and V. J. Koester, *J. Phys. Chem.*, **80,** 2312 (1976).

(20) E. G. McRae and M. Kasha, *J. Chem. Phys.,* **28,** 721 (1958).

(21) The formal derivation has been based in part on Chapter 8 of the Ph.D. Thesis by W. A. Wassam, Purdue University, 1974.

(22) For related discussions on solvent red shifts of π–π^* transitions and properties of excited states in polar molecules, see (a) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58,** 1002, 1006 (1954); (b) N. S. Bayliss, *J. Chem. Phys.*, **18,** 292 (1950); (c) E. Lippert, *Z. Elektrochem.*, **61,** 962 (1957); (d) E. G. McRae, *J. Phys. Chem.*, **61,** 562 (1957).

(23) It is of interest to note that most dimers of hydrated Chl a, regardless of the states of hydration and specific bonding interactions, including those in (pyroChl$\cdot$$H_2O$)$_2$[9b,10] and (Chl a$\cdot$$HOC_2H_5$)$_2$,[11] have absorption maxima close to 700 nm. See, however, ref 9b for a 716-nm absorbing polyhydrate species.

F. K. Fong,* W. A. Wassam
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 25, 1976

Tricoordinate Hypervalent Sulfur Compounds

Sir:

Molecular multicenter bonding which occurs when a given atom has more bonds than atomic orbitals as defined by the octet rule is termed hypervalent, and many examples are found