Proc. Natl. Acad. Sci. USA
Vol. 75, No. 10, pp. 4920–4924, October 1978
Biophysics

Bacteriochlorophyll electronic transition moment directions in bacteriochlorophyll *a*–protein

(circular dichroism/cryogenic spectroscopy/excitons/molecular orbital theory/photosynthesis)

ROBERT M. PEARLSTEIN* AND RICHARD P. HEMENGER†

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Communicated by William Arnold, July 17, 1978

ABSTRACT **The low-temperature 800-nm band absorption and circular dichroism spectra of the bacteriochlorophyll (Bchl) *a*-protein from *Prosthecochloris aestuarii* strain 2K are analyzed theoretically. These spectra show considerable structure that is attributed primarily to resonance (exciton) interactions among the lowest singlet transitions of the Bchl *a* molecules contained in each protein. We calculate these spectra from the known arrangement of the Bchl molecules in the protein. With the conventional assignment of the lowest singlet transition of Bchl *a* as Q_y (*y*-polarized), agreement of calculated spectra with experiment is poor. All of our attempts, based on this conventional assignment, to improve the theoretical fits to absorption and circular dichroism spectra simultaneously are unsuccessful. However, by making the simple but unconventional assumption that the lowest singlet transition in each of the Bchl *a* molecules in each protein is *x*-polarized rather than *y*-polarized, we find good agreement between calculated and observed spectra. If these results are not fortuitous, they indicate that there is a systematic error in the protein structural model, that the conventional assignments of Bchl *a* transitions are incorrect, or that the protein environment provides a sufficiently strong perturbation to rotate the lowest singlet transition moment direction by ~90°, presumably by changing the order of certain of the Bchl *a* orbitals.**

The bacteriochlorophyll (Bchl) *a*–protein complex (1) from the green sulfur bacterium *Prosthecochloris aestuarii* strain 2K (2) is the only structure from a photosynthetic organism whose three-dimensional arrangement of chlorphylls is known (3–5). Although the isolated protein is photochemically inert, it forms a part of photochemically active reaction center complexes derived from the same and related organisms (6–8).

Philipson and Sauer (9) were the first to analyze absorption and circular dichroism (CD) spectra of the Bchl *a*–protein in terms of resonance interactions (exciton interactions) among the electronic transitions of the Bchl molecules in the protein. They studied the two longest wavelength bands of the protein spectrum, near 600 and 800 nm, respectively. It was assumed that each of these two bands is associated with one of the two longest wavelength transitions, labeled Q_x and Q_y, of the Bchl *a* molecule. Philipson and Sauer interpreted structure in each of the bands in the protein spectra as resulting primarily from interactions among the transition dipole moments of the Bchl molecules in each protein. This exciton interpretation was supported by four arguments: (*i*) Each of the two bands in the protein spectra displays an essentially conservative (zero integral) CD spectrum whose individual features indicate very large rotational strengths; these CD properties are characteristic of exciton interactions (10, 11). (*ii*) Low-temperature absorption bands are observed to split into sub-bands having unequal dipole strengths; these are more readily explained by exciton effects than, for example, by multiple environments in the protein. (*iii*) The widths of the resolved spectral peaks are much narrower than the widths of Bchl *a* transitions in organic solvents. [Some narrowing is expected as a result of excitonic delocalization of the electronic state energy over several Bchl molecules. In fact, the degree of exciton narrowing of spectral features due to resonance interactions can now be calculated explicitly for strong interactions and used in the analysis of spectra (ref. 12; see also *Results*)]. (*iv*) Working at a time before the structure of the Bchl *a*-protein was known, Philipson and Sauer also correctly estimated the Bchl–Bchl nearest neighbor distance of 12 Å on the assumption that the overall widths of the protein absorption bands are due primarily to exciton interactions. On the basis of the known structure, one may now turn this around to say that observed and calculated exciton bandwidths agree (~450 cm^{-1} for the 800-nm band). Recently reported high-resolution absorption spectra of the Bchl *a*-protein at 5 K (13) further strengthen Philipson and Sauer's second argument.

In spite of the general acceptance of the exciton picture for the Bchl *a*-protein (4, 9, 14), the detailed features of its low-temperature absorption and CD spectra, particularly the longest wavelength band (near 800 nm), have not been explained in terms of its known structure. The Bchl *a*-protein is a trimer of three identical subunits (3, 4). Each subunit consists of a folded 39,000 dalton polypeptide chain that wholly encloses seven molecules of Bchl *a*. The porphyrin rings of the seven Bchls are roughly coplanar, but there is no other obvious intrasubunit symmetry. According to molecular orbital theory (15), the dipole moment of the electronic transition from the ground state to the lowest excited singlet state of Bchl *a* is directed along an axis connecting the nitrogens of the two unreduced pyrrole rings (I and III). This is called the *y* axis of Bchl *a*; the transition is called the Q_y. Similarly, the *x* axis is defined by the line joining the nitrogens of pyrrole rings II and IV. It is presumably the Q_y transition moments that interact to produce the characteristic exciton features in the 800-nm region of the Bchl *a*-protein's optical spectra. Yet, when these Q_y moment vectors are taken from the Bchl coordinates (5) in the Bchl *a*-protein and used to calculate optical spectra, agreement with experiment is poor (4). The observed bathochromic (toward longer wavelength) shift of the longest wavelength absorption band of Bchl *a* on going from ether solution to the Bchl *a*-protein is underestimated by a factor of 4. In addition, many details of the calculated spectra are also wrong, such as the relative magnitudes and positions of peaks and even some of the signs of CD features (see *Results*).

In this paper we examine a number of possible explanations,

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "*advertisement*" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

Abbreviations: Bchl, bacteriochlorophyll; CD, circular dichroism; DGS, degenerate ground state.

* Present address: Chemistry Department, Battelle Columbus Laboratories, 505 King Avenue, Columbus, OH 43201.
† Present address: New England College of Optometry, 424 Beacon Street, Boston, MA 02115.

consistent with the exciton interpretation, of the anomalies in the calculated 800-nm band optical spectra of the Bchl *a*–protein.‡ Although we cannot reject most of the putative explanations outright, with one exception we find no way to explain the major difficulties in fitting the absorption and CD spectra simultaneously based on any of them. The excepted explanation is very simple on the one hand and quite unconventional on the other. It is that each of the Bchl *a* transitions that interact to form the 800-nm band of the protein lies along a direction identified from the Bchl *a*–protein structural model (5) as the *x* axis in each Bchl *a* molecule rather than the conventionally assumed *y* axis. If this explanation is correct, it implies either that there is a systematic error in the Bchl *a*–protein structural model or that the usual assignments of Bchl *a* transitions are wrong, at least for the Bchl *a* in the protein.

THEORETICAL METHODS

Exciton Interaction Energies. The resonant intermolecular, or exciton, interaction energies were calculated in one of three ways, the point dipole method (16), the extended dipole method, or the point monopole expansion of Weiss (15) as programmed by Philipson (17). In the extended dipole method, each moment is represented as a pair of charges of opposite signs placed a finite distance apart; the interaction energy is then the sum of the coulomb energies of the four pairs of charges. The separation of the two charges that constitute the extended dipole is determined from monopole calculations (18). The extended dipole method is a significant improvement over the point dipole and is much simpler than the monopole expansion for calculations. For this reason the extended dipole method was used in most of the calculations whose results are presented here.

Optical Spectra of Molecular Aggregates in the Exciton Limit (Matrix Method). The essential feature of the matrix method (19) of calculating aggregate optical spectra is its simplicity. The calculation has two parts. In the first part, one finds the eigenvalues and eigenvectors of the *J* matrix, a real symmetric $M \times M$ matrix in which M is the number of interacting molecular electronic excited states. The off-diagonal elements of this matrix are simply the intermolecular resonance energies and the diagonal terms are the individual transition energies in the absence of resonance interactions. In the second part of the calculation, the eigenvectors of this matrix are used along with the molecular electric transition dipoles to calculate an absorption intensity and a rotational strength for each of the M eigenvalues. The results of these calculations are a representation of aggregate optical absorption and CD spectra in the form of line spectra. In order to give these line spectra the appearance of actual spectra, it is usual to superimpose a smooth function on each line. The widths of these functions, usually gaussians, are then adjusted to fit experimental spectra.

The main deficiency of the matrix method is that it takes no account of band shapes of molecular transitions. In some cases this may lead to substantial error (11, 20). Furthermore, in fitting line spectra to experiment, additional parameters that have no obvious physical interpretation are introduced (19).

Optical Spectra of Molecular Aggregates from Degenerate-Ground-State (DGS) Theory. This method (11, 12, 20) of calculating optical spectra is a generalization of the matrix method and, to a large extent, overcomes the latter's deficiencies but at the expense of computing time. Computation of spectra by using the DGS theory requires the evaluation of an $(M - 1)$-fold integral with a fairly complicated integrand. By using a Monte Carlo method we have been able to calculate spectra for the case of interest here, $M = 7$, within reasonable computer times. The input to the DGS calculation consists of the *J* matrix, the molecular electronic transition dipoles, and the optical absorption spectra associated with each of these uncoupled molecular transitions. The calculation then yields aggregate optical spectra that are continuous functions of energy and that are to be compared directly to experimental spectra. Information regarding band shapes of individual molecular transitions is incorporated into these spectra in an essentially correct way. This assertion is based on a number of observations, the most important of which are that the DGS theory gives correct results for both weak and strong coupling, that it satisfies a series of exact moment relations for arbitrary coupling strengths, and that it gives absorption spectra in excellent agreement with those from an exact calculation for a dimer whose monomers have a single vibrational progression (12, 20). One property of the DGS theory that is especially interesting in the present context is its ability to give correctly the narrowing of spectral features that results from resonance interactions. Specifically, it has been shown that, for M identical molecular transitions interacting strongly, the ratio of the widths of features in the absorption spectrum to the width of the uncoupled transitions may be as small as $M^{-1/2}$ (12).

Computer Search Methods. In some of our studies, it was necessary to search the values of unknown parameters by computer. This was always done in two phases: a search that involved only line spectra, and a subsequent corroborative run with a program based on the DGS theory. For example, if parameters searched were the seven uncoupled Bchl singlet energies, the values found as the result of a search would be input to the DGS program as the seven diagonal values of the *J* matrix. The searches themselves were done with a program that simultaneously varies any number of parameters.

RESULTS

Table 1 lists the Q_y exciton interaction energies for all pairs of Bchls in one subunit. Effects of intersubunit Bchl–Bchl exciton interactions, although not entirely negligible, are minor and are not considered here (see below). Fig. 1 *left* shows the line absorption spectrum calculated from the Q_y exciton interaction energies in Table 1 by the matrix method. In this calculation the assumption is made that the unperturbed energy of the lowest excited singlet level of each Bchl molecule in a subunit is 12987 cm^{-1} above the ground state, corresponding to the 770-nm absorption peak ascribed to that level of Bchl *a* in ether solution (9). Comparison of the line absorption spectrum with the experimental spectrum (13) also shown in Fig. 1 *left* shows that this exciton calculation gives approximately the right bandwidth. It also gives a bathochromic shift relative to the absorption of Bchl *a* in ether. However, the shift is too small by about a factor of 4.

If one arbitrarily shifts the line spectrum and superimposes symmetric gaussians, other difficulties with this theoretical fit become evident (Fig. 1 *right*). Use of the DGS theory rather than the matrix method does not noticeably improve the fit (Fig. 2 *upper*). Similar discrepancies occur in attempts to fit the 800-nm band CD spectrum (Fig. 2 *lower*). The two negative CD peaks of large magnitude (9, 14) have been particularly difficult to fit.

We can summarize the theoretical difficulties as follows. First, the experimental spectra display a fairly large batho-

‡ We do not consider the 600-nm band here because it is much weaker and the corresponding resonance interactions are therefore much smaller. In consequence, there is less information regarding exciton effects to be gleaned from these spectra. In addition, because the interactions are smaller, some of the theoretical and experimental uncertainties become relatively more important, which further increases the difficulty of interpretation.

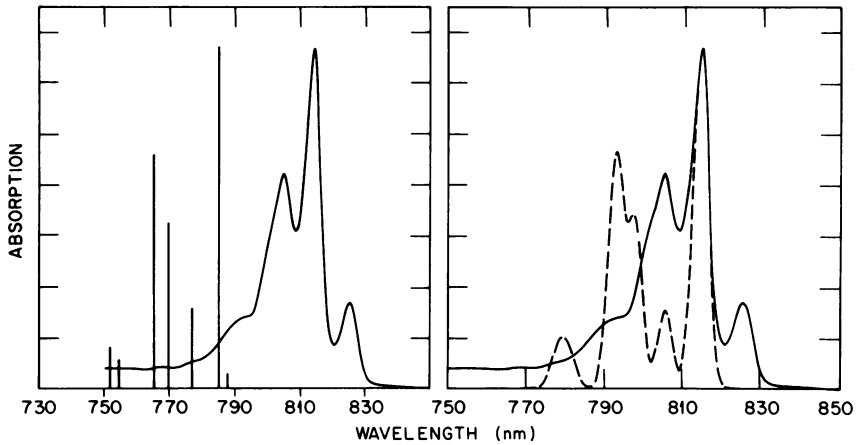

FIG. 1. (*Left*) Theoretical Q_y line absorption spectrum and 5 K experimental absorption spectrum (solid curve) of Bchl *a*-protein. (*Right*) Shifted theoretical Q_y line absorption spectrum with superimposed gaussians (dashed curve) to improve fit to the same data. Values of *ad hoc* parameters: overall bathochromic shift, 29 nm (454 cm^{-1}); symmetric gaussian full-width-at-half-maximum, 72 cm^{-1}. In both parts, theoretical ordinate normalization is arbitrarily chosen to match maximal peak height with that of experiment.

chromic shift relative to our calculated spectra (Fig. 1 *left*). Second, the widths of individual features in the experimental spectra are very narrow. According to DGS theory, which correctly accounts for exciton narrowing of linewidths (12), only part of this narrowing can be accounted for by exciton effects. For example, a Bchl *a* monomer absorption spectrum assumed to have a full-width of 170 cm^{-1} gives the best fit to the protein absorption spectra shown in Figs. 2 and 3, whose individual features are no more than 70 cm^{-1} wide (at 5 K). In solution, on the other hand, the full-width of the Bchl *a* 770-nm band is ~700 cm^{-1} (9). Third, and most important, there is very poor agreement between the relative positions and intensities of exciton features in our calculated spectra and those in the experimental spectra. In an attempt to account for these discrepancies we have considered a number of possible explanations.

Mistaken Chemical Identity. If the pigment in the protein were not in fact Bchl *a*, one might be able to account for some of these discrepancies. However, the identity of the pigment as Bchl *a* has been confirmed both *in situ* by the structural model of Fenna and Matthews (3–5) and as extracted pigment by absorption spectroscopy (21).

Table 1. Resonance (exciton) interaction energies (cm^{-1}) for 800-nm band*

Bchl†	1	2	3	4	5	6	7
1	—	−252.9	12.7	−11.9	12.8	−30.1	−9.2
		(138.1)	(−9.0)	(−1.4)	(38.0)	(−69.6)	(29.3)
2		—	66.0	17.6	4.3	27.9	9.2
			(−107.3)	(32.8)	(−10.6)	(15.2)	(−52.2)
3			—	−127.1	−3.3	−20.8	9.6
				(−48.8)	(−2.6)	(−12.6)	(27.5)
4				—	−165.9	−34.8	−125.5
					(140.8)	(19.8)	(−18.2)
5					—	133.4	−0.7
						(−111.6)	(27.3)
6						—	91.9
							(144.2)
7							—

* Numbers not in parentheses are calculated by the point monopole method for *y*-polarized Bchl *a* transitions having an assumed squared dipole strength of 52 D^2. Numbers in parentheses are calculated by the extended dipole method (separation of charges taken to be 5.9 Å) for *x*-polarized Bchl *a* transitions having an assumed squared dipole strength of 46 D^2. The interaction energy matrix is symmetric. See text for discussion of diagonal values.

† Numbering scheme for Bchls is that of Fenna and Matthews (3).

Differential Environmental Shifts. One approach to the problem of improving the theoretical fits is based on the assumption that most of the bathochromic shift of the Bchl *a* absorption in the protein is due to the difference in local environments between ether solution and the interior of the protein, even though the large magnitude of this shift is quite outside the range of observed shifts of the chlorophyll Q_y transition energies in various polar and nonpolar solvents (22)§. If this hypothesis is correct, it is possible that there is a distinct shift for each Bchl rather than the same shift for all and that such differential shifts might also account for the other fitting difficulties. This leads to the idea of a computer search of the values of seven shifts and possibly other parameters as well. We undertook many such searches in which the values of up to 14 parameters were varied (see *Theoretical Methods*), both singly and in various combinations.

Our findings from all these searches are that, although good fits can be obtained to the absorption spectrum, no set of parametric values that produces such a fit simultaneously yields a good fit to the CD spectrum. In fact, we observed *no* good fit to CD, irrespective of the goodness of fit to absorption. Furthermore, we noticed some indication of anticorrelation: any parametric set we found that gives the two longest wavelength absorption peaks (at ~815 and ~825 nm) in roughly the right ratio also gives a longest wavelength CD peak of the wrong sign. Although one cannot conclude from our results that no set of parameters can be found that produces a simultaneous fit to the Q_y absorption and CD spectra of the Bchl *a*-protein, we were persuaded to look elsewhere for an explanation of the spectral fitting difficulties.

Transition Dipole Moment Directions. According to molecular orbital theory, the lowest electronic singlet transition of Bchl *a* is *y*-polarized. Theoretical predictions of absolute transition polarizations in porphyrins have seldom been tested experimentally (23, 24), and certainly not for Bchl *a* in the protein. On the other hand, the prediction (15) that the two lowest electronic transitions have mutually perpendicular polarizations in the porphyrin ring plane has been experimentally verified for Bchl *a* in solution (25). Thus, we decided to consider the possibility that, although the theoretical symmetry argument (that the transitions are either *x*- or *y*-polarized) appears

§ We note the contrasting behaviors of the ~600-nm and ~770-nm bands of Bchl *a* in organic solvents: the former can vary over a range of 30 nm or more depending on the relative polarity of the solvent, whereas the latter is constant to within ~5 nm.

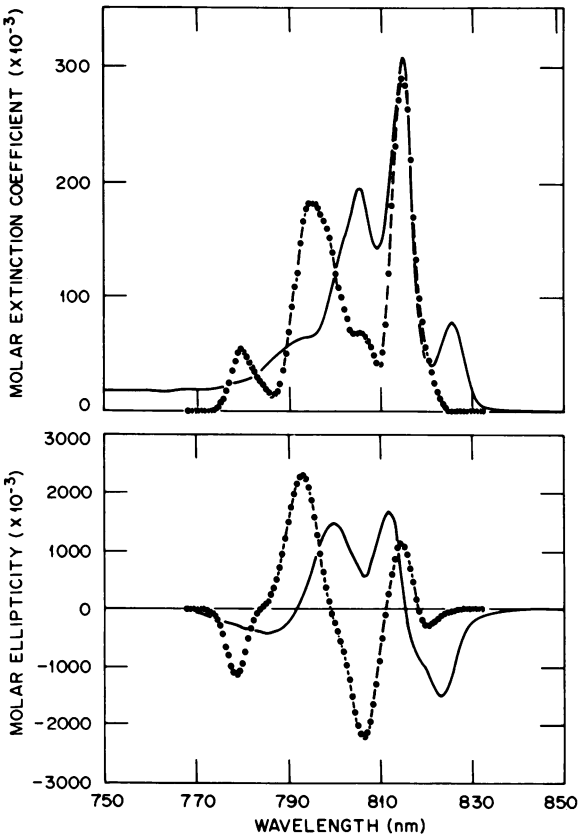

FIG. 2. (*Upper*) DGS theory Q_y absorption spectrum (points) with two *ad hoc* parameters, superimposed on 5 K experimental data (solid curve). Both theory and experiment are plotted as molar extinction coefficients. The theoretical extinction was calculated from the same value of squared transition dipole strength, 52 D^2, that was used to calculate the exciton interaction energies in Table 1. Experimental extinction was determined from the absolute extinction at 300 K and the extinction relative to that at 5 K. The uncoupled Bchl absorption is taken to be a symmetric gaussian of full-width-at-half-maximum equal to 167 cm^{-1}, and the overall bathochromic shift from the peak position of Bchl *a* in ether (770 nm) is 28.6 nm (465 cm^{-1}). (*Lower*) DGS theory Q_y CD spectrum (points), with two *ad hoc* parameters, superimposed on 77 K experimental data (solid curve). Both theory and experiment are plotted as molar ellipticities. The theoretical ellipticity was calculated for a squared transition dipole strength of 52 D^2. Experimental ellipticities were determined from the data of Philipson and Sauer (9). The overall bathochromic shift is taken as in *Upper*; the full-width is increased by 20%, to 200 cm^{-1}, as partial compensation for the higher temperature.

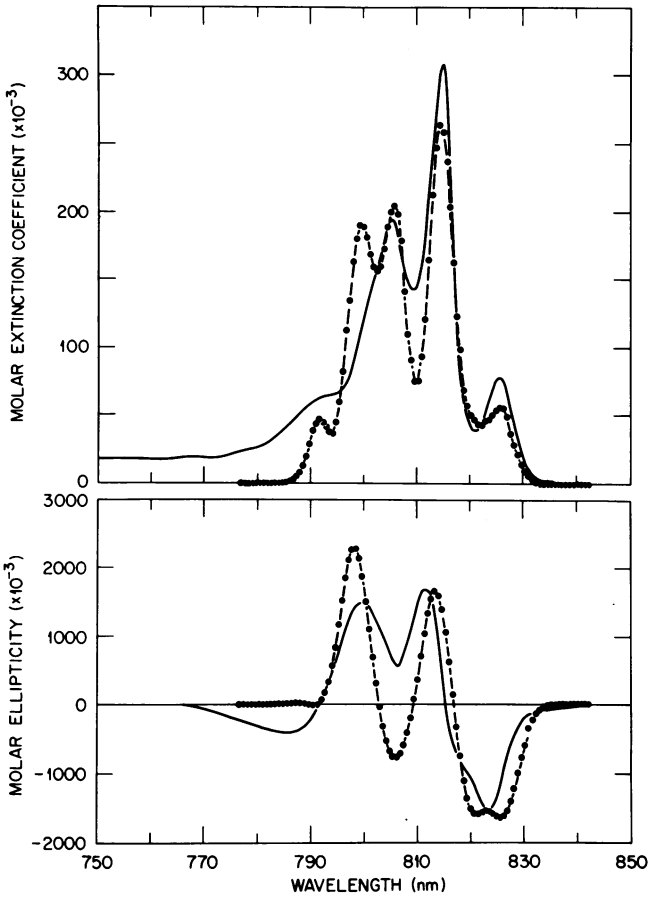

FIG. 3. (*Upper*) DGS theory absorption spectrum for the 800-nm band transition assumed to be *x*-polarized in each Bchl *a* molecule (points), with two *ad hoc* parameters, superimposed on 5 K experimental data (solid curve). Conditions otherwise similar to those in Fig. 2 *upper*: bathochromic shift, 37.6 nm (605 cm^{-1}); uncoupled Bchl *a* absorption full-width, 170 cm^{-1}; squared transition dipole strength, 52 D^2 (extinction) or 46 D^2 (exciton interaction energies). (*Lower*) DGS theory 800-nm band, *x*-polarized CD spectrum (points), with two *ad hoc* parameters, superimposed on 77 K experimental data (solid curve). Conditions otherwise the same as in Fig. 2 *lower*, except that the bathochromic shift is taken to be 37.6 nm (605 cm^{-1}) and the squared transition dipole strength used in the calculation of exciton interaction energies is taken to be 46 D^2.

to be correct, perhaps the absolute polarization prediction is not. Is it possible that in the Bchl *a*-protein the moments of the lowest energy singlet electronic transition are *x*-polarized in each molecule of Bchl *a*? In the *Discussion* we present several alternative means by which an apparent transition moment rotation might arise, including one that, although unlikely, is consistent with the absolute prediction as well. Here we consider only the consequences of such a rotation for the theoretical 800-nm band absorption and CD spectra.

These consequences are demonstrated by the comparative results shown in Figs. 2 and 3. In Fig. 2 the transition moments are all taken along the Bchl *y* axes as in Fig. 1, and in Fig. 3 the moments are all along the Bchl *x* axes. The DGS fits shown in Fig. 3 bear much closer resemblances to the corresponding experimental spectra. The greatly improved simultaneous fits to the absorption and CD spectra that result from taking the 800-nm band transition to be *x*-polarized can already be discerned in outline from shifted line spectra, although we do not show these here.

Other Explanations. We mention here a number of other possible effects that we have considered. In our judgment, none of these effects is important enough to explain any of the gross spectral fitting difficulties, although some of them may affect finer details of fitting: (*i*) exciton interactions of Bchl molecules in separate subunits (4); (*ii*) interactions involving higher electronic excited states; (*iii*) point monopole corrections to the extended transition dipoles; (*iv*) residual errors in the Bchl *a* atomic coordinates reported by Fenna *et al.* (5); (*v*) conformational change induced by cryogenic solvents or low temperatures (13); (*vi*) higher-order corrections to the approximations used in DGS theory (11); (*vii*) inhomogeneous broadening of spectra due to a statistical distribution of protein conformational variants; (*viii*) effects of higher vibronic sublevels of the lowest electronic excited singlet state; (*ix*) dielectric effects (e.g., "solvent" shifts); and (*x*) Bchl–Bchl charge transfer.

DISCUSSION

By assuming that the lowest singlet electronic transition of Bchl *a* in the Bchl *a*-protein is *x*- rather than *y*-polarized, we have

obtained a reasonably good simultaneous fit to the 800-nm band low-temperature absorption and CD spectra of the protein. We can think of three possible explanations for this finding: that the transition is actually y-polarized and the apparent simultaneous fit with x-polarization is fortuitous; that there is a systematic error in the structural model of Fenna and Matthews; or that the lowest singlet transition of Bchl a in the Bchl a–protein is Q_x rather than Q_y.

The kind of error required in the protein structural model to account for our result is difficult to imagine. It would be necessary, for example, to suppose that in the protein (but not in solution) pyrrole rings I and III rather than II and IV are reduced, in effect rotating the "Bchl a" x-axis by 90°. However, this would change the relative order of the alternating single and double bonds in the "Bchl a" conjugated macrocycle and consequently the orientations of the various side groups. It seems quite unlikely that such an altered structure could be reconciled with the Fenna–Matthews electron density map.

Can it be that the 800-nm band transition of the Bchl a in the protein is Q_x? One possibility is that the prediction of molecular orbital theory that the lowest singlet transition in Bchl a is y-polarized (little tested experimentally) is simply incorrect for Bchl a under any circumstances. We believe this to be unlikely (15). We must then consider the possibility that the theoretical prediction is incorrect specifically for Bchl a in the Bchl a–protein. In order for this to be true, some standard assumption of molecular orbital theory that holds for Bchl a in organic solvents must be violated as a result of the interaction between the protein and the Bchl. There is, however, no precedent for such a perturbation of chlorophyll orbitals, so that at present this alternative, too, must be viewed as unlikely.

The experimental results we have analyzed in this study are not the only independent ones possible to obtain. It would be valuable to measure, for example, the absorption spectrum of linearly polarized light in the 800-nm band of the Bchl a–protein oriented in such a way that the axis of orientation is clearly identified (26). This linear dichroism spectrum can be calculated in the same theoretical framework as were the theoretical absorption and CD spectra shown in Fig. 3. Because ordinary absorption, CD, and linear dichroism are theoretically three linearly independent functions of the transition dipole moment, linear dichroism would provide an independent corroboration of transition moment rotation.

We thank S. R. Blum and J. A. Carney for expert programming assistance, B. W. Matthews for providing the bacteriochlorophyll atomic coordinates in convenient form, and R. E. Fenna, C. Weiss, Jr., and W. B. Whitten for several valuable discussions. We are especially grateful to R. E. Fenna for sending us the results of his unpublished exciton calculations. This research was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

1. Olson, J. M. (1978) in *The Photosynthetic Bacteria*, eds. Clayton, R. K. & Sistrom, W. R. (Plenum, New York), pp. 161–197.
2. Olson, J. M. (1978) *Int. J. Syst. Bacteriol.* **28**, 128–129.
3. Fenna, R. E. & Matthews, B. W. (1975) *Nature (London)* **258**, 573–577.
4. Fenna, R. E. & Matthews, B. W. (1977) *Brookhaven Symp. Biol.* **28**, 170–182.
5. Fenna, R. E., ten Eyck, L. F. & Matthews, B. W. (1977) *Biochem. Biophys. Res. Commun.* **75**, 751–755.
6. Fowler, C. F., Gray, B. H., Nugent, N. A. & Fuller, R. C. (1973) *Biochim. Biophys. Acta* **292**, 692–699.
7. Olson, J. M., Giddings, T. H., Jr. & Shaw, E. K. (1976) *Biochim. Biophys. Acta* **449**, 197–208.
8. Pearlstein, R. M., Whitten, W. B. & Olson, J. M. (1978) *Biophys. J.* **21**, 9a (abstr.).
9. Philipson, K. D. & Sauer, K. (1972) *Biochemistry* **11**, 1880–1885.
10. Tinoco, I., Jr. & Cantor, C. R. (1970) in *Methods of Biochemical Analysis*, ed. Glick, D. (Wiley-Interscience, New York), Vol. 18, pp. 81–203.
11. Hemenger, R. P. (1978) *J. Chem. Phys.* **68**, 1722–1728.
12. Hemenger, R. P. (1977) *J. Chem. Phys.* **67**, 262–264.
13. Whitten, W. B., Nairn, J. A. & Pearlstein, R. M. (1978) *Biochim. Biophys. Acta* **503**, 251–262.
14. Olson, J. M., Ke, B. & Thompson, K. H. (1976) *Biochim. Biophys. Acta* **430**, 524–537.
15. Weiss, C., Jr. (1972) *J. Mol. Spectrosc.* **44**, 37–80.
16. DeVoe, H. (1965) *J. Chem. Phys.* **43**, 3199–3208.
17. Philipson, K. D. (1972) Dissertation (University of California, Berkeley, CA).
18. Chang, J. C. (1977) *J. Chem. Phys.* **67**, 3901–3909.
19. Bayley, P. M. (1973) *Prog. Biophys.* **27**, 3–76.
20. Hemenger, R. P. (1977) *J. Chem. Phys.* **66**, 1795–1801.
21. Olson, J. M. (1966) in *The Chlorophylls*, eds. Vernon, L. P. & Seely, G. R. (Academic, New York), pp. 413–425.
22. Seely, G. R. & Jensen, R. G. (1965) *Spectrochim. Acta* **21**, 1835–1845.
23. Goedheer, J. C. (1957) Dissertation (University of Utrecht, Netherlands).
24. Anex, B. G. & Umans, R. S. (1964) *J. Am. Chem. Soc.* **86**, 5026–5027.
25. Goedheer, J. C. (1966) in *The Chlorophylls*, eds. Vernon, L. P. & Seely, G. R. (Academic, New York), pp. 147–184.
26. Whitten, W. B., Pearlstein, R. M., Phares, E. F. & Geacintov, N. E. (1978) *Biochim. Biophys. Acta*, in press.