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Dipole Strengths in the Chlorophylls¶†

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ABSTRACT

Measurements of dipole strengths of chlorophylls in solution are reviewed and correlated. The refractive index dependence is found to be expressible in a simple empirical fashion that does not rely on the concept of vacuum dipole strength. The index dependence in some respects contradicts the dependence expected on the basis of effective field theories.

INTRODUCTION

The chlorophylls (Chl) exhibit their longest-wavelength dipole-allowed transitions in the red and bacteriochlorophylls (Bchl) in the infrared (1). The Q_y excited states involved are of huge importance in the bioenergetics of photosynthesis, not particularly because of these molecules' optical absorption, which is also accomplished at shorter wavelengths, but because of their involvement in antenna transport of the absorbed excitation energy (2,3). Quantitative estimates of the rates of this transfer require either absolute *in situ* absorption and emission spectra or knowledge of the associated transition dipole strengths. The most prominent antenna Chl in plants, algae and cyanobacteria (4,5) are Chl *a* and Chl *b* and in the case of bacteria (6,7) are Bchl *a* and Bchl *c*. We have found the dipole strength literature pertaining to the Chl to be confusing and at times contradictory. In response to this, the present note applies the findings of Knox (8) to the four Chl mentioned above.

The dipole strength associated with a physically infinitesimal spectral bandwidth $d\nu$ at frequency ν is $\boldsymbol{\mu}(\nu)^2 d\nu = e^2 \mathbf{r}(\nu)^2 d\nu$, where e is the electron charge and $\boldsymbol{r}(\nu)^2$ is the density of squared electronic transition matrix elements of the displacement operator at that point of the spectrum (2,3,9,10). As discussed in Knox (8), this dipole strength density may be integrated over an arbitrary region of the spectrum and the result related to the absorption coefficient $\varepsilon(\nu)$:

$$D = 9.186 \times 10^{-3} n \int_{\Delta\nu} \frac{\varepsilon(\nu)}{\nu} d\nu \quad (\text{debye}^2). \qquad (1)$$

The numerical coefficient is $3000\hbar c \ln(10)/(4\pi^2 N_A)$, where N_A is Avogadro's constant. This coefficient's units are chosen to produce the conventional units of D when the absorption coefficient is expressed in liters per mol per centimeter. The refractive index n refers to the average index in a region of space around the chromophore of the order of magnitude of an optical wavelength (10). All dipole strengths in this note are given in debye^2 (1 debye $= 10^{-18}$esu cm $= 3.336 \times 10^{-30}$ C m). The integration variable in Eq. 1 may be any spectral variable, wavelength, wave number, energy or frequency.

All experimental data analyzed in this note were taken from the literature. Rather than attempt to locate all competent spectra on each Chl type, we have allowed the literature to make a selection for us, that is, we consider mostly those spectra that have been quoted fairly widely and used as a basis for computation of electronic properties that depend on dipole or oscillator strengths. Spectra for which the specific absorptivity was not directly determined were not included in the quantitative survey. In this process we may have overlooked cases that would significantly increase or decrease our level of confidence in our present results. Naturally, we will appreciate being advised of such cases in continuing this project.

DATA SELECTION AND METHOD OF CALCULATION

The absorption spectrum of Chl *a* at room temperature and in ethanol (11) is shown in Fig. 1. The broad bands at 660 and 615 nm are traditionally referred to as the '0–0' and '0–1' bands, respectively, the numbers denoting the vibronic levels of an unspecific vibrational mode or set of modes of the porphyrin ring of the Chl near 1100 cm^{-1}. The bands themselves are composed of numerous vibronic subbands and undoubtedly have some inhomogeneous broadening. There is some involvement of the Q_x'0–0' transition, with a moment perpendicular to that of Q_y'0–0', whose exact position is unclear in Chl *a,* either under the Q_y'0–2' band (12,13) or under the Q_y'0–1' band (14,15); the Q_x band is better displaced to the blue in the case of the Bchl. In any event, we do not address the issue of sorting out these transitions. We concentrate on producing the best possible numbers for the Q_y'0–0' transitions. Workers may then use these, along with the extended spectra, to estimate and calibrate strengths based on more extended regions of the spectrum.

As will be seen, much of the primary literature appeared 30 or 40 years ago and is therefore unavailable in electronic format. To standardize our procedure and simplify it for easy checking by other workers, we adopt a venerable approximate method (*e.g.* 16,17) of determining the area under the presumed Q_y'0–0' peak.

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Abbreviations: Bchl, bacteriochlorophyll; Chl, chlorophyll; PVP, poly (vinylpyridine).

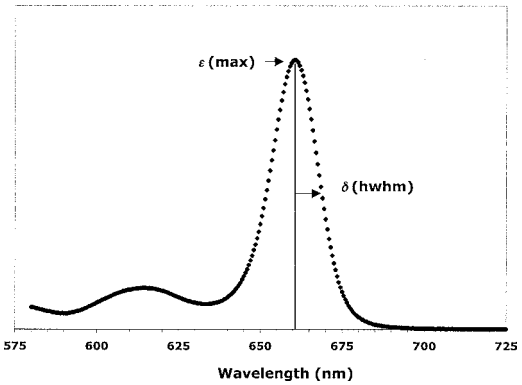

Figure 1. Absorption spectrum of Chl *a* in diethyl ether (data by M. F. J. Talbot, reported in Knox *et al*. [11]). The strength of the Q_y'0–0' line is operationally defined here to be proportional to the area of a Gaussian curve of half-width δ, measured on the long-wavelength side.

We associate the red edge of the main Q_y peak with a Gaussian curve of half-width δ because the red edge is the least likely to be contaminated by any other electronic transition. Thus, knowing δ and the peak value ε_{max}, we obtain the following approximate value by applying Eq. 1 in its wavelength form:

$$D \sim 9.19 \times 10^{-3} n(2.13\varepsilon_{max}\delta/\lambda_{max}) = 0.0196 n\varepsilon_{max}\delta/\lambda_{max}. \quad (2)$$

The units of δ are the same as those of λ_{max}, typically nanometers. The additional approximation of removing $1/\lambda$ from the integral has been made. The wavelength dependence of the index is ignored, and its value is generally the ''handbook'' value.

In our application of Eq. 2, we used the wavelength format to conform with the older literature. One might well argue that better approximations to the Q_y'0–0' integrated absorption could be made. Direct numerical integration is possible, but the choice of a cutoff point introduces arbitrariness. Another possibility is fitting the whole Q_y region with Gaussians or other absorption profiles (*e.g*. 16). This too has arbitrariness because the ''best fit'' either disregards principal vibronic components or requires arbitrary guidance. Our approximations are made without apology, because it would be folly to claim higher accuracy, for several reasons: some higher transitions may still contribute at the peak; reading half-widths directly from published spectra (which we have done, when the authors did not quote such values) is imprecise; and the Q_y'0–0' band is not a true Gaussian. We retain three or four figures for accuracy during the numerical determinations but claim nothing better than two figures in the results.

Our method is clear and unambiguous, limited only in its spectral scope. Many excitation transfer phenomena depend primarily on the '0–0' dipole strength, and when the strengths of other transitions are required, they may be estimated by scaling our results.

EMPIRICAL ANALYSIS OF CHL DIPOLE STRENGTHS

The principal results are shown in Figure 2 and Tables 1 and 2. Table 1 reports all extracted data (with some exceptions as noted below) along with linear-fitting parameters and recommended error designations. A complete summary of data (including names of solvents and spectral parameters) can be found in the Supplementary Material, which is located on the journal website (http://www.aspjournal.com). Table 2 reports ''recommended'' fits based on reduced data sets for which the statistical confidence (R^2) is somewhat improved over that in Table 1. The recommended sets are shown in Figure 2. In the following we explain the data selection.

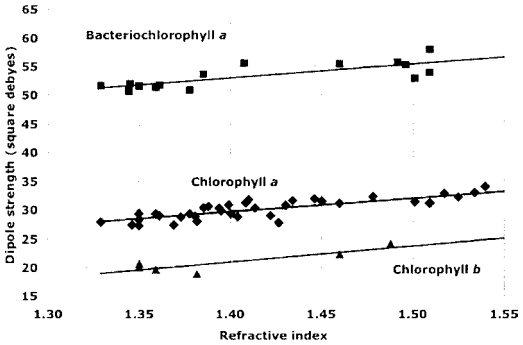

Figure 2. Q_y'0–0' dipole strengths in Bchl *a*, Chl *a* and Chl *b*. The selection of data points is explained in the text, and the equations for the linear fits are found in Table 2. Specific solvents associated with each index value may be found in the Supplementary Material.

Chlorophyll *a*

Since the extensive early work of Seely and Jensen (18), only a few quantitative determinations of *D* have appeared (13,15,19,20). However, Seely and Jensen's (18) work provided a large number of data points, and they were used in an earlier quantitative study emphasizing line shapes and decomposition into Gaussian components (16,17). We selected 43 out of 49 measurements for inclusion in the reduced Chl *a* data set. The strengths deduced from Lichtenthaler (20) were omitted because they were serious outliers (typically $D = 34$ debye^2 at $n = 1.35$). Similarly, some older outlying results were omitted (21,22). The strengths reported by Sauer and coworkers (13,19) were included as measured but recomputed with the present formalism and algorithms.

Bacteriochlorophyll *a*

Connolly *et al*. (23) studied Bchl *a* almost as extensively as Seely did Chl *a*. Other measurements (besides Connolly's) include three that are older (19,21,22) and one newer (24). The older ones are omitted from the recommended set because they are fairly serious outliers. Because Sauer's value of 37.6 in CCl_4 (19) has been widely quoted, we note that in the context of the present analysis it was increased to 50.1. The recommended linear fit predicts 54.1 for an index of 1.46. The value 50.1, if included in the recommended set, would alone reduce R^2 from 0.61 to 0.43. K. Sauer (personal communication) points out that there may have been inadvertent solvation of the Bchl *a* by traces of a component such as methanol or adventitious water.

A measurement by Scherz and Parson (25) of the Bchl *a* dipole strength is frequently quoted and well worth discussing. We have not used it in our recommended data set because we could not apply our algorithm to their data, but it presents an opportunity to illustrate our formalism. Scherz and Parson (25) divide their dipole strength integral for the entire Q_y band by a Lorentz correction factor (for acetone, with $n = 1.359$) to obtain a vacuum value $D_0(Q_y) = 41$ debye^2. Removing the Lorentz factor we find $D(Q_y) = 67.4$ debye^2. It has been our experience that the '0–0' band is 80% of the total; applying this rule of thumb we obtain

Table 1. Conservative mapping of dipole strengths of the chlorophylls as a function of n (refractive index of the solvent or mean environment). These expressions utilize the entire core data set. $0 \leq R^2 \leq 1$ is the residual sum of squares or statistical confidence index as defined in Excel™ spreadsheets

	$D(n)$ (debye^2)	Range (index)	R^2	Suggested error bar*	Notes
Chl *a*	$22.0 + 20.6(n - 1)$	1.33–1.64	0.432	−11%, +22%	7 Sources, 48 data points
Bchl *a*	$44.9 + 19.9(n - 1)$	1.33–1.52	0.131	−15%, +20%	5 Sources, 18 data points
Chl *b*	$11.8 + 22.5(n - 1)$	1.33–1.49	0.342	−12%, +15%	8 Sources, 11 data points
Bchl *c*	Mean 28.8 (see Notes)	1.33–1.51	—	SD = 7.6	Data too disparate for linear fit (Table 2)

* SD, standard deviation.

$D(Q_y\text{`}0-0\text{'}) = 53.9$ debye$^2$. Our recommended value, from Table 2, is $43.3 + 24.2(n-1) = 52.0$. The same measurement was done by Eichwurzel *et al.* (26) with the result $D_0(Q_y) = 46 \pm 7$ debye$^2$, from which we obtain $D(Q_y\text{`}0 - 0\text{'}) = 60.5 \pm 9$ debye^2. Our value agrees well with the Scherz–Parson result and is just within the Eichwurzel error limit.

Chlorophyll *b*

Only a few absolute measurements have been found for this less abundant light-harvesting pigment, which is known to be more difficult to purify. Data analyzed were those of Sauer *et al.* (19), Lichtenthaler (20), Holt and Jacobs (21), Smith and Benitez (22), Lhoste (27), Seely (28), Hägele *et al.* (29) and Cinque *et al.* (30). Analyses of the data of Harris and Zscheile (31) and Amster (32), which produced rather extreme outliers and very poor overall statistics, are included only in the Supplementary Material. All data were in simple solvents except Hagele's (polymethyl methacrylate). In the reduced data set, one major outlier ([27] 22 debye^2 at $n = 1.35$) was omitted as well as two of three of Seely's (28) data points in nitromethane-poly(vinylpyridine) (PVP) mixtures, the latter to avoid unduly weighting his results. Although the older data (21,22) were not as far outlying as the Chl *a* points of these authors, they were also omitted from the reduced set for consistency as well as the fact that one of them (22) was a chlorophyllide. The small and well-scattered data set produced no R^2 greater than 0.694 with any selection of data, and we have chosen to maximize both R^2 and the number of points retained. A clear message of this analysis is that it is important to the community to extend Chl *b* measurements to solvents with $n > 1.50$, especially to test our extrapolations for use in high-index protein environments.

Bacteriochlorophyll *c*

This interesting case (Fig. 3) is included in our study because of the status of Bchl *c* as a unique light-harvesting antenna pigment, one that self-organizes in great aggregates without the benefit of protein attachment (33). Interestingly, we found it difficult to reconcile recent extensive monomer data (15) with the slightly older data (34–37), and the problem appears to be related to the ready aggregation of the chromophores. All the spectra of Umetsu *et al.* (15) have the simple shape expected of monomers, whereas most spectra of Olson and colleagues (35,36) and other workers (34,37) cannot necessarily be considered monomeric at the lowest concentrations, as judged qualitatively from the Q_y band shapes. Correspondingly, Umetsu's dipole strengths are smaller compared with Olson's (both having been obtained after our convention, Eq. 2).

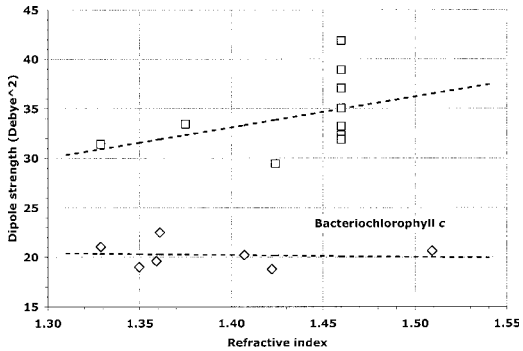

Figure 3. Q_y'0–0' dipole strengths in Bchl *c*. Diamonds are data points of Umetsu *et al.* (15), and squares are those of Olson and colleagues (35,36). The large difference between these data sets is possibly related to aggregation state. See text. See also the caption of Fig. 2.

DISCUSSION

A very interesting feature of the results may be seen in Figure 2 and in the second column of Tables 1 and 2. The coefficient of the linear term is nearly the same for every chromophore, spanning the range of 20–28. According to either of the effective field theories, this slope should scale with the overall strength of the transition.

Table 2. Recommended refractive index mappings of dipole strengths of the Chl. These expressions use selected data as described in the text and under Notes. The Bchl *c* case is recommended with the proviso that confirmatory data with unequivocal monomer spectra are desirable. $0 \leq R^2 \leq 1$ is the residual sum of squares or statistical confidence index as defined in Excel™ spreadsheets. The last two columns indicate values of vacuum dipole strengths that minimize the mean square deviation of the data set from theoretical curves based on cavity and Lorentz effective fields, respectively (8)

	D(n) (debye^2)	Range (index)	R^2	Suggested error bar*	Notes	D_0 (c)	D_0 (L)
Chl *a*	$20.2 + 23.6(n - 1)$	1.33–1.64	0.759	−9%, +8%	4 Sources, 43 data points	21.0	16.3
Bchl *a*	$43.3 + 24.2(n - 1)$	1.33–1.52	0.605	−5%, +4%	2 Sources, 15 data points	37.1	29.6
Chl *b*	$9.8 + 27.7(n - 1)$	1.33–1.49	0.755	−12%, +5%	5 Sources, 6 data points	14.7	12.0
Bchl *c*	Mean 20.3	1.32–1.51	—	SD = 1.3	Umetsu data only	NA	NA
Bchl *c*	Mean 34.3	1.32–1.46	—	SD = 3.7	Other data only	NA	NA

*SD, standard deviation; NA, not applicable.

There is no ready explanation for the failure of this to happen, short of abandoning these theories entirely for application to the three molecules under discussion. This is clearly an interesting subject for future investigation.

The suggested error bars in Tables 1 and 2 have very specific definitions. They are computed from the points in the respective data sets having the widest deviation from the linear fit. It is difficult to assess the effect of our approximations and assumptions in any other terms. In summary, the first major assumption is the use of the red-edge approximation to extract the '0–0' line shape. Second, is the fact that many linewidths and specific absorption maxima were taken directly from figures in published papers, of which some required magnification with consequent loss of accuracy. Third, no quantitative intrinsic error estimates were available in original papers. Fourth, the expression for the Gaussian integral (Eq. 2) assumes an invariant average wavelength in the denominator of the integrand. Finally, no correction has been made to produce the precise solvent refractive index at maximum absorption wavelengths nor has any variation across the absorption band been considered. We have taken the index as quoted by the authors except where obvious corrections were necessary, and the indexes are therefore generally sodium D-line values available in standard tables. As a result of these simplifications, we cannot expect our dipole strengths to be accurate to better than perhaps two significant figures (although the calculations have been carried out with more). Our object has been simply to juxtapose available data in a standard context, whose detail can be refined when necessary.

SUMMARY

In this article we collect and compare the observed values of dipole strength of the lowest vibronic transition of four Chl, with particular attention to their dependence on the refractive index of the solvent or other enveloping medium. The purpose is to provide an estimate for the value of a given strength in a medium for which an index can be estimated but for which a measurement is not available. Our finding is that a simple linear fit is adequate for the job and is superior in some respects to modeling the strengths on the basis of dielectric theory, as explained in Knox (8). Where necessary, literature values have been recomputed and corrected. A complete tabulation of the numerical values of the data on which the results are based may be found in the Supplementary Material.

Perhaps the most interesting result is finding similar slopes in the index dependence for three of the Chl, a fact that is difficult to understand on the basis of present effective field theories.

An important practical caution to the reader is that the strengths reported in this study are the '0–0' strengths. Care must therefore be taken when the remainder of the Q_y band strength (~20%) must be estimated and included. This applies particularly for estimating rates of fluorescence.

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