

## A Density Functional Normal Mode Calculation of a Bacteriochlorophyll *a* Derivative

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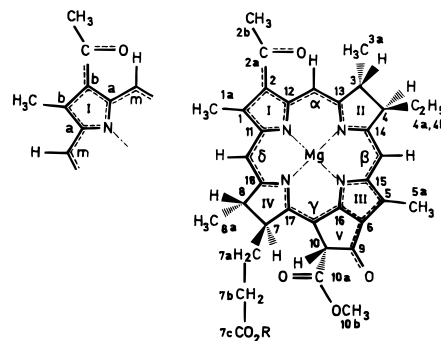
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Chlorophylls play a fundamental role in procaryotic and eucaryotic photosynthesis. Because of the specific adaptation of their electronic spectra to collection of light from near UV to near-IR, they constitute excellent resonance Raman (RR) probes of the structural organization of their underlying protein environment. The local and detailed information provided by RR spectroscopy of photosynthetic membrane proteins is remarkably complementary to that provided by X-ray crystallography.<sup>1</sup> The interpretation of changes in the RR spectra of the bacteriochlorophylls in terms of changes of their structure and local environment requires detailed knowledge of the vibrational origins of the observed Raman bands.

In the past, empirical and semiempirical approaches have been used to obtain a normal mode description of bacteriochlorophylls. One of the results of these approaches is the remarkably different behavior of the ring stretches associated with the methine bridges in porphyrins and bacteriochlorophylls.<sup>2</sup> In this contribution we present the first high quality DFT ab initio calculation of the vibrational structure of a bacteriochlorophyll derivative and discuss the assignment of the in-plane frequencies detectable by RR spectroscopy.

We have performed ab initio calculations on an isolated methyl bacteriochlorophyll (MeBChl) *a* molecule (Scheme 1). Our computations are based on the density functional theory (DFT)<sup>3</sup> in the local density plus gradient corrections approximation.<sup>4</sup> We use ab initio norm-conserving pseudopotentials<sup>5</sup> and expand single-electron orbitals on a basis of plane waves with a cut-off of 70 Ry in a supercell of 18 Å. Electronic and nuclear optimizations were performed as described in previous publications.<sup>6–8</sup> For the initial structure of our calculations we chose the optimized coordinates obtained in a previous work<sup>8</sup> for methyl bacteriochlorophyll *a* where the two central hydrogens were replaced by a magnesium. Vibrational modes were computed by diago-

**Scheme 1.** Chemical Structure of Methyl Bacteriochlorophyll *a*, with R = CH<sub>3</sub><sup>a</sup>



<sup>a</sup> On the right: numbering of carbon atoms according to the Fischer system. On the left: generic labeling of meso and pyrrolic carbon atoms.

nalizing a finite difference approximation for the dynamical matrix. The computed normal modes were transformed into a set of non-redundant internal coordinates,<sup>9</sup> and the assignment was carried out based on the M-matrix method.<sup>10</sup>

Given the symmetry of the electronic excitations involved, the (RR) spectra of chlorophylls are expected to consist of mostly in-plane vibrations.<sup>11</sup> Thus, those DFT ab initio modes having a prevalent in-plane character can be directly compared with experimental RR assignment (Table 1). To relate calculated with observed frequencies, we used not only a proximity criterion, but also calculated <sup>14</sup>N → <sup>15</sup>N and <sup>24</sup>Mg → <sup>26</sup>Mg isotopic shifts, for which experimental data are available.

The carbonyl stretching modes are computed in the range 1648–1732 cm<sup>-1</sup>, in agreement with experimental assignments.<sup>1,11</sup> Our calculation predicts that modes  $\nu 9$  and  $\nu 10a$  are intimately coupled in both of two modes at 1718 and 1732 cm<sup>-1</sup>. Such a high mixing of these coordinates is not observed in the experimental bands at 1735 and 1695 cm<sup>-1</sup>, although it might partially account for the 1735 cm<sup>-1</sup> mode activity in (pre)resonant Raman spectra. In agreement with experimental assignment the  $\nu 2a$  stretch is the least energetic of the C=O stretching modes. At variance with previous semi-empirical calculations,<sup>12,15</sup> but in agreement with experimental data on <sup>15</sup>N isotopic shifts, all three computed carbonyl stretching modes involve quite small amounts of  $\nu CC$  and  $\nu CN$  coordinates. The in-plane bending of the 9 keto C=O computed at 492 cm<sup>-1</sup> mixes with  $\nu MgN$ , as empirically proposed for a 445 cm<sup>-1</sup> RR band (see below).<sup>11</sup>

Vibrations involving  $C_a C_m$ ,  $C_b C_b$ , and CN stretchings are computed in the 1634–1447 cm<sup>-1</sup> range. In agreement with experimental data,<sup>14</sup> and at variance with semi-empirical calculations,<sup>12,13</sup> no such mode is computed at any frequency higher than 1634 cm<sup>-1</sup>. Modes predominantly involving the  $\nu C_a C_m$  coordinates occur at the highest frequencies (1634–1571 cm<sup>-1</sup>) of this range, followed at lower frequencies by those involving  $\nu C_b C_b$  (1545–1498 cm<sup>-1</sup>). The present calculation provides a good agreement with the observed frequencies (generally better than 10 cm<sup>-1</sup>, except for the nitrogen-sensitive mode at 1420–1429

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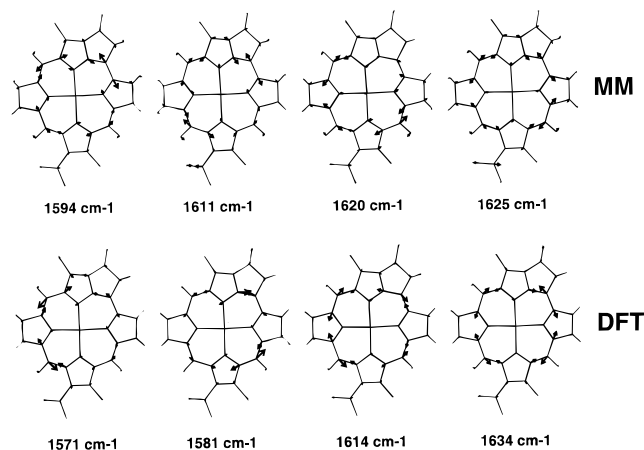
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**Table 1.** Comparison of the DFT-Computed Frequencies and Isotopic Shifts of the In-Plane Modes of Methyl-Bacteriochlorophyll *a* (this work) with Experimental Data from Ref 13 (unless Otherwise Stated)<sup>a</sup>

DFT	<sup>15</sup> N sensitivity		<sup>26</sup> Mg sensitivity		obsd	M-matrix assignment
	calcd	expt	calcd	expt		
1732					1735 <sup>b</sup>	$\nu_9$ C=O $\nu_{10a}$ C=O
1718					1695	$\nu_{10a}$ C=O $\nu_9$ C=O
1648					1660	$\nu_{2a}$ C=O
1634						as $\nu_{C_aC_m}(\alpha\beta\gamma\delta)$
1614					1605	as $\nu_{C_aC_m}(\alpha\beta\gamma\delta)$
1581	(1)				1577	as $\nu_{C_aC_m}(\gamma\delta)$
1571						as $\nu_{C_aC_m}(\alpha\beta)$
1545	(1)	(2)			1537	$\nu_{C_bC_b}$ s $\nu_{C_aC_m}(\gamma)$ $\nu_{CN}(\text{III})$
1513	(3)	(3)			1525	$\nu_{C_bC_b}$ s $\nu_{C_aC_m}(\gamma)$ $\nu_{CN}(\text{III})$
1498	(1)	(1)			1500	$\nu_{C_bC_b}$
1463	(2)	(1)			1470	s $\nu_{C_aC_m}(\alpha)$ $\nu_{CN}(\text{II})$
1458	(2)				1447	CH <sub>3</sub> bend. s $\nu_{C_aC_m}(\delta)$ $\nu_{CN}(\text{IV})$
1447	(4)	(3)			1420	CH <sub>3</sub> bend. s $\nu_{C_aC_m}(\beta)$ $\nu_{CN}(\text{II})$
1422	(1)					CH <sub>3</sub> bend. $\nu_{C_6C_{16}}$
1391	(3)	(3)			1395	$\nu_{CN}(\text{I})$ $\delta C_mH(\alpha)$
1383	(3)	(2)			1382	$\nu_{CN}(\text{I})$ $\delta C_mH(\delta)$ CH <sub>3</sub> bend.
1371	(2)	(3)			1345	$\delta C_mH(\delta)$ CH <sub>3</sub> bend.
1349	(3)	(7)			1363	$\nu_{CN}(\text{III})$ $\delta C_mH(\beta)$ CH <sub>3</sub> bend.
1344	(3)					$\delta$ defs.
1299	(6)	(9)			1257	$\nu_{CN}(\text{IV})$ $\nu_{C_7C_{17}}$
1245	(3)	(4)			1248	$\delta$ defs.
1182	(6)	(7)			1165	$\delta C_mH(\beta)$
1174	(1)					$\delta$ defs.
1139	(4)	(12)			1144	CH <sub>3</sub> bend. $\nu_{CN}(\text{III})$ $\nu_{C_5C_{5a}}$
1127	(10)	(9)			1120	$\nu_{CN}(\text{I})$
1114	(7)	(6)			1068	$\delta(\text{IV})$ CH <sub>3</sub> bend. CH <sub>2</sub> bend.
1099		(3) <sup>c</sup>			1030	$\nu_{C_4C_{4a}}$ $\nu_{C_3C_4}$
1099						CH <sub>3</sub> bend. $\nu_{C_7C_8}$
942	(2)	(5)			972	$\delta$ defs.
922	(3)	(5)			950	$\nu_{C_3C_4}$ CH <sub>3</sub> bend.
912	(5)					s $\delta\text{NCC}_m(\delta)$
899	(3)	(2)			895	s $\delta\text{NCC}_m(\beta)$
889	(5)					$\nu_{C_7C_{17}}$ $\nu_{C_7C_8}$
874	(5)	(3–5)			850	$\delta$ defs.
868	(2)					$\nu_{C_8C_{18}}$ CH <sub>2</sub> bend.
780	(4)	(9)			797	$\delta(\text{IV})$ $\delta(\text{III})$ $\gamma$ defs.
774	(5)	(4)			765	$\delta(\text{III})$
733	(4)	(5)			735	s $\delta\text{NC}_aC_m(\alpha)$
717	(4)	(3)	[1]		696	$\delta$ defs.
704	(4)	(9)			685	$\delta(\text{I})$
686	(4)					$\delta(\text{IV})$
604					627	$\delta_{2a}$ C=O $\gamma_{2a}$ C=O $\delta(\text{I})$
602	(1)					$\nu_{C_9C_{10}}$ $\delta(\text{II})$
593						$\nu_{C_{7b}C_{7c}}$ $\delta_{7c}$ C=O $\gamma_{7c}$ C=O
580	(3)				590	$\delta_{2a}$ C=O $\delta\text{CC}_1C_{1a}$
551	(5)	(10)			568	$\delta(\text{III})$ as $\delta\text{NCC}$
492	(1)	(9)	[5]	[7] <sup>d</sup>	445	$\nu_{MgN}$ $\delta_{9}$ C=O
477	(2)		[2]			$\delta$ defs.
443	(1)		[7]			$\tau_{C_8C_{8a}}$ $\nu_{MgN}$
388	(2)	(5)	[4]	[4]	360	$\delta\text{CNMg}$
321	(2)	(10)	[8]	[7]	300	$\delta\text{CNMg}$ $\tau_{C_7aC_{7b}}$
317	(3)		[4]			$\tau_{C_{4a}C_{4b}}$
262	(2)	(4)			257	$\delta_{2a}$ C=O as $\delta\text{NCC}$ $\delta\text{CCC}$
250	(2)		[1]			$\delta\text{CCC}$
234	(2)				233	$\delta$ defs.
195	(1)		[5]			$\gamma_{MgN}$ $\tau_{C_{7b}-C_{7c}}$ CH <sub>2</sub> bend.
190	(2)		[15]	[7] <sup>d</sup>	198	$\gamma_{MgN}$ $\tau(\text{II})$
174	(2)		[3]			$\gamma_{MgN}$ $\gamma_9$ C=O

<sup>a</sup> In the table,  $\nu$  labels stretching,  $\delta$  in-plane bendings,  $\gamma$  out-of-plane bendings,  $\tau$  torsions. Moreover, s stands for symmetric and as for antisymmetric. Finally, isotope sensitivities are relative isotope shifts ( $10^3 \times \Delta\nu/\nu$ ). <sup>b</sup> From Mattioli T. A.; Hoffmann, A.; Robert, B.; Schrader B.; Lutz M. *Biochemistry* **1991**, *30*, 4648. <sup>c</sup> From Noguchi, T.; Furukawa Y.; Tasumi, M. *Spectrochim. Acta* **1991**, *47A*, 1431. <sup>d</sup> From ref 18.

$\text{cm}^{-1}$  computed at 1447  $\text{cm}^{-1}$ ). It also provides <sup>15</sup>N-induced shifts which are in remarkably good agreement with experiment (Table 1). We note that the 1634, 1614, 1581, and 1571  $\text{cm}^{-1}$  modes mostly consist of antisymmetric combinations of  $\nu_{C_aC_m}$  coordi-

**Figure 1.** Antisymmetric  $\nu_{C_aC_m}$  ring modes as computed by density functional theory (DFT) and by molecular mechanics (MM).

nates. Additionally, symmetric combinations of the same coordinates sizably contribute to modes at 1545, 1513, 1463, 1458, and 1447  $\text{cm}^{-1}$ , together with larger contributions from  $\nu_{C_bC_b}$  and CH<sub>3</sub> bends. These results are in contrast with those of earlier semiempirical calculations,<sup>12</sup> which predicted localized  $C_aC_m$  stretching modes in (bacterio)phosphoride-type macrocycles. Indeed, we find that the symmetry of the  $\nu_{C_aC_m}$  coordinates which is observed for porphyrins<sup>2</sup> is maintained in our bacteriochlorophyll structure (Figure 1). An explanation for this effect is that the force constants of the  $C_aC_m$  bonds adjacent to saturated rings (II and IV) are stronger than those of bonds adjacent to aromatic rings (I and III). Empirical force fields taking this distinction into account predict delocalization of  $\nu_{C_aC_m}$  as well, as shown in Figure 1.<sup>15</sup>

Below 1447  $\text{cm}^{-1}$  down to 1114  $\text{cm}^{-1}$  our calculation provides a series of modes involving high contributions from  $\nu_{CN}$ . The experimental <sup>15</sup>N-induced shifts generally are quite correctly predicted, except for the 1139 (calcd)/1144 (exp) mode.

Frequencies computed at 1391, 1383, 1371, 1349, and 1182  $\text{cm}^{-1}$  have contributions from  $\delta C_mH$  bending. On the basis of isotope shift we tend to assign the mode at 1371  $\text{cm}^{-1}$  to the band observed at 1345  $\text{cm}^{-1}$  and assigned empirically to  $\delta C_mH$ .<sup>11</sup>

Our calculation provides two modes significantly involving the  $\nu_{MgN}$  coordinate, at 492 and 443  $\text{cm}^{-1}$ . One of these should correlate with a 445  $\text{cm}^{-1}$  Raman band, which exhibits a  $7.0 \times 10^{-3}$  relative shift upon <sup>26</sup>Mg substitution.<sup>16</sup> The proposed 492/445  $\text{cm}^{-1}$  correlation takes empirical assignment of the latter band to  $\delta C=O$  into account.<sup>11</sup> The modes calculated at 388 and 321  $\text{cm}^{-1}$  and involving the  $\delta\text{CNMg}$  coordinates can be related with two <sup>26</sup>Mg-sensitive RR bands at the same frequencies. A  $\approx 195$   $\text{cm}^{-1}$  mode has also been reported as <sup>26</sup>Mg-sensitive.<sup>11,17</sup> It may well correlate with modes calculated at 195 and 190  $\text{cm}^{-1}$  and involving MgN out-of-plane deformation.

To conclude, the set of assignments of RR-active modes of bacteriochlorophyll *a* provided by the present calculation appears altogether to offer a good agreement with available experimental data. It hence should provide a reliable interpretative frame for further analysis of Raman vibrational data on photosynthetic bacterial proteins.

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