Ground and excited states of carboxyheme: a SAC/SAC-CI study

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Abstract

The SAC (symmetry adapted cluster)/SAC-CI method is applied to calculations of the ground and excited states of carboxyheme ($FeC_{24}N_6OH_{16}$). The excited states are calculated up to 7.8 eV. The calculated excitation energies and oscillator strengths reproduce well the electronic spectrum. The Q bands are explained by the excitations within Gouterman's 4 orbitals. The B, N, L and M bands are explained by the excitations within '6 orbitals', in which the lower porphyrin π orbitals, $44a'$ and $45a'$, are added to the 4 orbitals. The B band shoulder in the higher energy side has a d, $\sigma-d^*$, σ^*, CO^* nature. The states higher than the M band are characterized by the $d-\pi^*$ and $\pi-d^*$ states; therefore, the intensities are predicted to be small.

1. Introduction

Hemoglobin and myoglobin play an important role in mammalian life through the transport and storage of oxygen. These physiological functions in the presence of significant concentrations of CO have been the focus of considerable research interest [1]. Although the bonding of an O_2 molecule to free porphyrin is further stabilized by a hydrogen bond between the terminal oxygen atom and the neighboring proteins [2], a poisoning molecule, CO, binds to free porphyrin much more strongly than O_2 molecule and gives carboxyheme: it is much more stable than oxyheme. Various investigations for carboxyheme have been carried out [3,7–9]. Carboxyheme has CO

at the distal site and imidazole at the proximal site as a residue of histidine in protein and is diamagnetic.

Recent experimental research of carboxyheme reports the crystal structure [4–6], electronic structure, and the nature of the Fe–C–O bonding using resonance Raman spectroscopy [10–12]. Theoretical studies on carboxyheme have been carried out by the semi-empirical [7,9], ab initio [6,8] and X α [7] methods. However, knowledge of the electronic structures of the ground and excited states of carboxyheme is still incomplete. A more elaborate study including a large amount of electron correlations is necessary for a sound and reliable understanding of the electronic structures of carboxyheme, especially in its excited states. We have recently studied the ground and excited states of free base porphin [13], Mg porphin [14], tetrazaporphin [15] and oxyheme [16] with considerable accuracy using SAC (symmetry adapted

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Table 1
Atomic coordinates of carboxyheme (Å)

Segment	Atom [a]	x	y	z	Segment	Atom [a]	x	y	z
porphine	N1	1.9537	0.0	0.0	imidazole	N1	0.0	0.0	−2.0654
	C2	4.1889	0.6915	0.0		C2	−1.2095	0.0	−2.7916
	C3	2.8060	1.1297	0.0		N3	−0.8706	0.0	−4.2036
	C4	2.4702	2.4702	0.0		C4	0.5376	0.0	−4.2391
	H5	5.0604	1.3294	0.0		C5	1.0562	0.0	−2.9478
	H6	3.2339	3.2339	0.0		H6	−2.2826	0.0	−2.6693
carbon-	C1	0.1850	0.0	1.7603		H7	−1.5281	0.0	−5.0604
monoxide [b]	O1	0.5020	0.0	2.8658		H8	1.0035	0.0	−5.2134
iron	Fe	0.0	0.0	0.0		H9	2.0637	0.0	−2.5587

[a] The numbering of atoms in each segment is given in Fig. 1.

[b] The lengths of Fe–C1, C1–O1, Fe–Npor and Fe–NIm are 1.77, 1.15, 1.95, 2.07 Å, respectively. The Fe–C1–O1 angle and the angle between Fe–C and heme normal are 170° and 6°, respectively.

cluster) [17] theory for the ground state and SAC-CI theory for the excited states [18]. We study here the ground and excited states of carboxyheme using the SAC/SAC-CI method. The present SAC-CI calculations of carboxyheme is so far the largest calculation in the size of the active orbitals. The accuracy and the effectiveness of the SAC/SAC-CI method is now well established [19] and the SAC/SAC-CI code [20,21] is available on request.

2. Computational details

Carboxyheme, $FeC_{24}N_6OH_{16}$, consists of 48 atoms and 236 electrons. The geometry of carboxyheme is shown in Table 1 and Fig. 1. We adopted X-ray crystallographic data for human carboxyhe-

moglobin [4] with small modifications; the porphyrin skeleton is modified to have D_{4h} symmetry, and the imidazole plane, one of the N_{por}–Fe–N_{por} axes and the C–O axis are put on the mirror plane as shown in Fig. 1. The entire molecular symmetry is C_s. Other geometrical parameters are taken from those used previously for oxyheme [16]. Note that the Fe–C1 bond is not on the normal line of the porphyrin ring; the angle from the normal line is 6°. Further, the CO bond is not on the line of the Fe–C1 bond: the Fe–C1–O1 angle is 170°. Such a bending structure of CO was supported by ab initio calculations [6].

The quality of the GTO basis functions used here is the same as those used previously for the calculations on porphyrins [13–16]. For the Fe atom, we use Huzinaga's $(5333/53/5)/[5332l/53/4l]$ set [22] plus p-type polarization function ($\alpha = 0.082$), for C, N, and O, the $(63/5)/[63/4l]$ set [22] plus p-type anion basis ($\alpha = 0.059$) for oxygen, and for H the
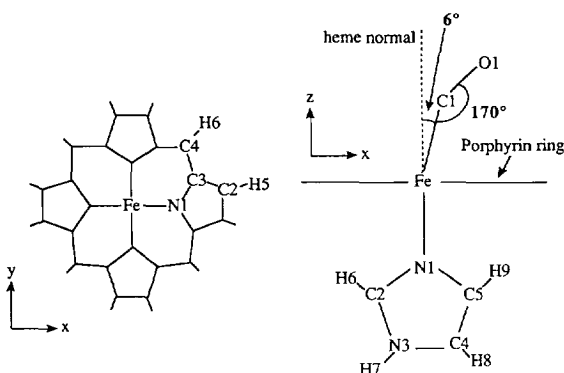

Fig. 1. Geometry of carboxyheme. The numbering of atoms corresponds to those shown in Table 1.

Table 2
Dimension of the linked term for the SAC/SAC-CI calculations of the singlet states of carboxyheme

State	Before selection	N [a]	After selection
SAC			
A′	34706619	1	16664
SAC-CI			
A′	34706619	5	92350
A″	34671690	5	120182

[a] N denotes the number of the excited configurations used as the reference configuration selection scheme.

(4)/[4] set [23]. The basis set for imidazole is minimal; for C and N, the (63/5)/[63/5] set [22] and for H the (4)/[4] set [23]. The total number of contracted GTOs is 278.

The SAC/SAC-CI calculations were carried out using SAC85 [20] and its modified version [21]. The HF molecular orbitals (MOs) were used as reference orbitals. A total of 229 MOs were used as active

MOs: all valence orbitals were included in the active space and only the 1s orbitals of C, N, and O atoms and the core orbitals (1s, 2s, 2p, 3s, and 3p) of Fe were treated as frozen cores. All the single excitations and the selected double excitations within this active space constitute the linked operators and their products the unlinked operators. The perturbative configuration selection procedure [13,24] was per-

Table 3
Orbital energies and characters of some HF orbitals of carboxyheme

MO No. [a]	Symmetry	Orbital energy (eV)	Nature [b]
occupied orbitals			
38	$26a'$	−17.219	$CO(\pi b^o) + Fe\ d_{xz}$
39	$13a''$	−17.099	$CO(\pi b^p) + Fe\ d_{yz} + Im\ \pi^p$
41	$14a''$	−16.912	$CO(\pi b^p) + Fe\ d_{yz} - Im\ \pi^p$
42	$28a'$	−16.883	$CO(\pi b^o) + Fe\ d_{xz} - Im\ \pi^o$
43	$29a'$	−16.692	$CO(\pi b^o) - Fe\ px - Im\ \pi^o\sigma$
50	$18a''$	−15.130	$CO(O1^c)p_y - Fe\ d_{yz} + Por(\pi) - Im(N3^c)py$
51	$33a'$	−15.097	$CO(O1^c)p_x - Fe\ d_{xz} + Por(\pi)$
54	$20a''$	−14.868	$Fe\ d_{xy} + Por(\sigma)$
61	$39a'$	−13.378	$Fe\ s + Fe\ d_{z^2} + CO(\sigma)Im(\sigma)$
62	$23a''$	−12.849	$CO\ (O1^c)p_y - Fe\ d_{yz} + Im\ \pi^p$
63	$40a'$	−12.464	$CO\ (O1^c)p_x - Fe\ d_{xz} + Por(\sigma)$
64	$24a''$	−12.362	$CO\ (O1^c)p_y - Fe\ d_{yz} + Im\ \pi^p + Por\ (\sigma)$
68	$26a''$	−12.076	$Fe\ d_{xy}$
69	$27a''$	−11.671	$Fe\ d_{yz} - Im\ \pi^p$
71	$43a'$	−10.170	$Por\ (\pi)$
72	$29a''$	−10.011	$Fe\ d_{yz} - Im\ \pi^p$
73	$44a'$	−9.412	$Por\ (\pi)$
74	$45a'$	−9.160	$Por\ (\pi)$
75	$46a'$	−8.963	$Por\ (\pi) - Fe\ d_{xz}$
76	$30a''$	−8.841	$Por\ (\pi) - Fe\ d_{yz}$
77	$47a'$	−6.578	$Por\ (\pi)\ (n\text{-HOMO};\ 4\ orbitals)$
78	$31a''$	−6.115	$Por\ (\pi)\ (HOMO;\ 4\ orbitals)$
unoccupied orbitals			
79	$32a''$	+0.298	$Por\ (\pi) - Fe\ d_{yz}\ (LUMO;\ 4\ orbitals)$
80	$48a'$	+0.327	$Por\ (\pi) - Fe\ d_{xz}\ (n\text{-LUMO};\ 4\ orbitals)$
81	$33a''$	+3.096	$Por\ (\pi)$
83	$49a'$	+3.893	$CO\ (\pi a^o) - CO(\sigma) - Fe\ d_{z^2} - Fe\ d_{x^2-y^2} - Por\ (\sigma)$
84	$35a''$	+4.490	$CO\ (\pi a^p) - Fe\ d_{yz}$
85	$50a'$	+4.491	$CO\ (\pi a^o) - Fe\ d_{xz} - Por\ (\sigma)$
87	$52a'$	+5.295	$CO\ (\pi a^o) - Fe\ d_{x^2-y^2}$
88	$36a''$	+5.341	$CO\ (\pi a^p) - Fe\ p_y - Por\ (\sigma)$
90	$53a'$	+5.701	$CO\ (\sigma) - Fe\ d_{z^2} - Fe\ d_{x^2-y^2} + Por(\sigma)$
91	$38a''$	+6.019	$CO\ (\pi a^p) - Por\ (\pi) - Im\ \pi^p$
101	$58a'$	+9.440	$CO\ (\sigma) + Fe\ d_{z^2} - Fe\ d_{x^2-y^2} - Por(\sigma)$

[a] The numbering of the HF molecular orbitals. The numbering starts from the lowest energy orbital into the active space.
[b] The plus (+) and minus (−) signs denote the bonding and antibonding interactions, respectively. The 'πb' and 'πa' denote the π-type bonding and antibonding orbitals localized at CO. The superscripts 'o' and 'p' denote that the orbitals are on and perpendicular to the mirror plane, respectively.
[c] O1 and N3 atoms are illustrated in Fig. 1.

formed with the energy threshold 1×10^{-5} au for the excitations within the π space and 2×10^{-5} au for the others for the ground state, and for the excited states with the threshold 5×10^{-7} au for the excitations within the π space and 1×10^{-6} au for the others. The resultant dimensions for the SAC/SAC-CI calculations are shown in Table 2.

3. Electronic structure of the ground state

First we analyze the HF orbitals for the ground state. The HF orbital energy and character are shown in Table 3. The numbering of MOs excludes core orbitals and starts from the lowest MO in the active space. $CO(\pi_b)$ and $CO(\pi_a)$ denote the π-type bonding and antibonding orbitals localized at carbon monoxide. The superscripts 'o' and 'p' as in $CO(\pi_b^o)$ and $CO(\pi_a^p)$ denote that the orbitals are on and perpendicular to the mirror plane, respectively. The π-type orbitals gather in the HOMO–LUMO regions. Particularly, the HOMO (31a'': 78), next-HOMO (47a': 77), LUMO (32a'': 79), and next-LUMO (48a': 80), called the 'four orbitals', are separated in energy from the other orbitals, implying the validity of Gouterman's four orbital model [25]: this was also observed in free base porphin [13] and Mg–porphin [14]. These four orbitals are mostly the porphin π-orbitals, though the Fe $d\pi$ orbitals mix with the unoccupied MOs. The mixing of the CO orbitals to the four orbitals is small. On the other hand, the PPP (Pariser–Parr–Pople) SDCI calculation [7] showed that the 4 orbitals model was destroyed by the appearance of the porphyrin π + Fe d_{xz} orbital in the next HOMO.

The orbital shapes of the 4 orbitals are shown in Fig. 2. These orbitals are porphyrin π-type, and the components of Fe d_{xz} and d_{yz} orbitals in the two LUMOs are small. In addition, the HOMO is an a_{1u} like orbital and is higher than the a_{2u} like next HOMO in agreement with the results of the NMR [26,27] and ESR [28,29] measurements of metallo-porphyrin without substituents on the meso position.

The interaction between Fe and CO is classified into σ and π types. The σ-type orbitals exist in the occupied and unoccupied spaces: MOs numbered 61, 83, 90, and 101. MO 61 has the nature of σ donation from CO and imidazole to Fe d_{z^2}. MO 101 con-
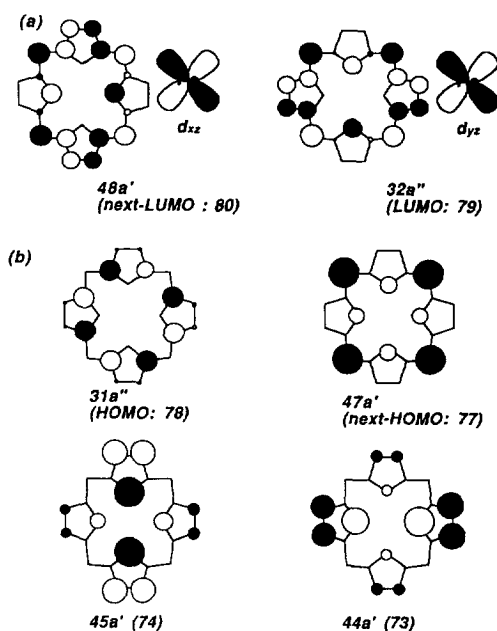

Fig. 2. The '6 orbitals' for carboxyheme: (a) the unoccupied MOs (48a' and 32a'') and (b) the occupied MOs (31a'', 47a', 45a', and 44a').

tributes to the excitations from Fe to CO in the VUV region, as described in the following section. Many π-type orbitals exist in the occupied and unoccupied spaces: MOs 38, 39, 41, 42, 84, and 85. In MOs 38, 39, 41, and 42, the Fe orbitals mix with the CO orbitals. In particular, MOs 39 and 42 extend further the imidazole orbitals. In addition, the MOs with the O1 π character localized on CO exist in 50, 51, 62, and 63, and they are delocalized over the entire molecule through Fe and porphyrin even to imidazole.

In carboxyheme, the orbitals of the CO ligand do not appear in the MOs in the HOMO–LUMO region. This is in marked contrast to oxyheme. In oxyheme, the oxygen (p)–Fe (d) π antibonding orbital represents the LUMO and the O_2 π orbital mixes with the HOMO [16]. The bond strength between Fe and the distal ligand, O_2, is small compared to carboxyheme. Oxyheme also differs from carboxyheme in the coupling with the imidazole π orbitals.

In the eigenvector of the SAC ground state, the HF configuration, which corresponds to the low-spin state of Fe(II), is dominant: the coefficients of the

excited configurations are less than 0.03. This result is consistent with the previous ab initio result [8]. Thus, the single reference theory can describe the ground state of the carboxyheme with sufficient accuracy. The correlation energy calculated by the SAC method is 11.6 eV.

4. Excited states

We calculated the excited states of carboxyheme in a wide energy range from the visible to UV, up to 7.8 eV, but the experimental spectrum [30] covers only up to 4.9 eV.

Fig. 3 shows the electronic absorption spectrum of carboxyheme observed for the horse carboxyhemoglobin [30] compared with the excitation spectrum calculated by SAC-CI theory in the UV and visible energy region, and Table 4 gives more detailed information on the excited states. The calculated spectrum well reproduces the experimental one in both the excitation energy and the oscillator strength. The average discrepancy from the observed peaks is 0.33 eV. Case et al. reported many years
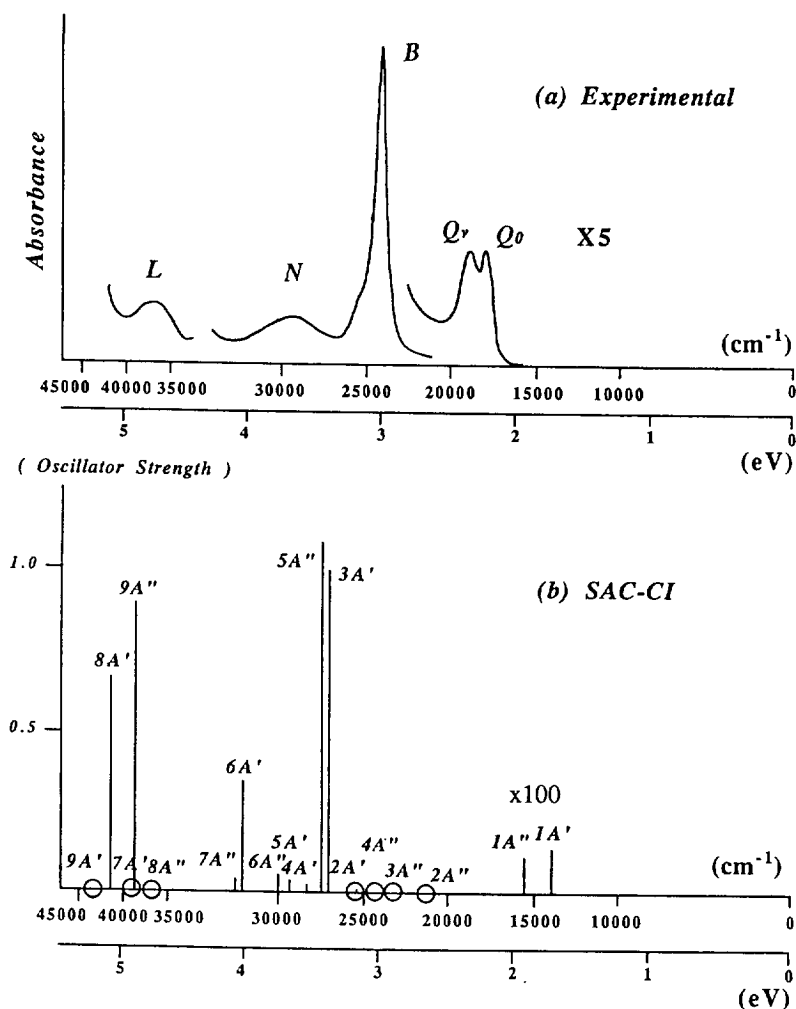

Fig. 3. Electronic absorption spectrum of carboxyheme. (a) Experimental spectrum of horse hemoglobin [30]. (b) SAC-CI theoretical spectrum. Open circles indicate singlet states with small oscillator strengths.

ago [7] a semi-empirical PPP-SDCI calculation for the excited states of carboxyheme. The average discrepancy from the observed peak was 0.40 eV even in their semi-empirical calculation. These results indicate that the accuracy of the SAC-CI method is superior to the PPP-SDCI method even for a molecule as large as carboxyheme. We note here that the characters of the excitations by the PPP-SDCI method are significantly different from the present ones, since the 4-orbital model is destroyed in the PPP-SDCI method [7].

The first and second absorption peaks called the Q_0 and Q_v bands are assigned to the 1A′ and 1A″ states, respectively. These Q bands are well described, as seen from Table 4, within the '4 orbitals'; two almost degenerate configurations mix strongly as in the free base porphin and Mg porphin. In oxyheme, however, the $Fe-O_2$ π antibonding orbital, which is LUMO, affects the nature of the Q bands [16]. Further, a weak band originating from the excitation within the O_2 ligand was observed in oxyheme in a lower energy region of the Q band [16].

A strong sharp absorption peak is observed in the 350–450 nm region of the experimental spectrum and is called the B (Soret) band. It is assigned to the

3A′ and 5A″ states calculated at 3.36 and 3.41 eV, respectively, with large oscillator strengths of 1.04 and 1.13, respectively. The 18-membered cyclic polyene model [31,32] of porphin has explained that the B band consists of the two degenerate states arising from Gouterman's 4 orbitals. In the present calculations, we see that other lower porphyrin π orbitals, 73 and 74, also mix with the B bands: a similar mixing of the lower MOs is also seen for all the porphyrins studied previously [13–16]. We therefore name these orbitals '6 orbitals', which are illustrated in Fig. 2.

The shoulder of the B band in the higher energy side is assigned to 4A′, 5A′, and 6A″ states; the 5A′ and 6A″ states have d,σ to d*,σ*,CO* nature (CO* is C–O π antibonding). These excited states have been associated with the photodissociation of CO in flash photolysis experiments [33–35]. Although the free base porphin has a similar B band shoulder, it has been assigned to the porphyrin $\pi-\pi^*$ (B_y) transition [13].

The next strong bands called N and L bands are assigned to 6A′ and 9A″ states, respectively. We see from Table 4 that the nature of these states is similar to that of the B band. The difference between the B band and the N, L bands lies only in the size of the

Table 4
Excited states of carboxyheme calculated by the SAC/SAC-CI method

SAC-CI						Exp	
state	main configuration ($|C| > 0.25$)	nature [a]	excitation energy (eV)	polarization	oscillator strength	excitation energy (eV)	
1A′	$-0.70(77-80) + 0.65(78-79)$	$\pi-\pi^*$	1.84	x	0.00139	2.18	Qo
1A″	$0.70(77-79) + 0.65(78-80)$	$\pi-\pi^*$	1.94	y	0.00110	2.30	Qv
2A″	$-0.86(75-79) - 0.27(63'-79)$	$\pi-\pi^*$	2.72	y	0.00144		
3A″	$0.55(76-80) + 0.47(68-102) + 0.42(68-108) + 0.23(68-115)$	$d,\pi,\sigma-d^*,\pi^*,\sigma^*$	2.96	y	0.00037		
4A″	$-0.68(76-80) + 0.40(68-102) + 0.36(68-108)$	$\pi-\pi^*$	3.00	y	0.00003		
2A′	$0.64(75-80) - 0.58(76-79)$	$\pi-\pi^*$	3.15	x	0.00742		
3A′	$0.65(78-79) + 0.51(77-80) - 0.34(74-80) + 0.26(73-80)$	$\pi-\pi^*$	3.36	x	1.04	2.96	B
5A″	$0.66(78-80) - 0.53(77-79) - 0.39(73-79)$	$\pi-\pi^*$	3.41	y	1.13	2.96	B
4A′	$0.64(76-79) + 0.59(75-80)$	$\pi-\pi^*$	3.52	x	0.0179		
5A′	$-0.46(63-101) + 0.28(63-113) - 0.27(75-101) -0.25(63-112)$	$d,\sigma-d^*,\sigma^*,CO^*$	3.63	x	0.0359		
6A′	$-0.85(74-80) - 0.35(77-80)$	$\pi-\pi^*$	3.98	x	0.350	3.60	N
7A″	$-0.86(74-79) - 0.35(73-79)$	$\pi-\pi^*$	4.06	y	0.0397		
8A″	$-0.72(68-101) + 0.34(68-113) - 0.29(68-105)$	$d,\sigma-d^*,\sigma^*,CO^*$	4.65	y	0.00043		
9A″	$-0.77(73-79) + 0.39(74-79) + 0.33(77-79)$	$\pi-\pi^*$	4.71	y	0.928	4.53	L

[a] 'σ' and 'π' denote the porphyrin σ and π MOs, respectively. 'd' denotes the Fe d orbital and 'CO*' the CO π antibonding orbital.

SAC-CI coefficients. In the B band, the SAC-CI coefficients within the 4 orbitals are larger than those for the excitations from the two lower porphyrin π MOs, 73 and 74 of the 6 orbitals to the LUMO and next-LUMO, while the N and L bands have the opposite nature with respect to the SAC-CI coefficient.

In conclusion, it is found that the large peaks in the VUV region except for the B band shoulder, can be explained by the excitations within the '6 orbitals', Gouterman's 4 orbitals plus the lower porphyrin π

MOs 73 and 74. On the other hand, in the PPP-SDCI calculation [7] the four orbitals model is already disintegrated in the Q band. Similarly the B, N, and L bands also has complex nature.

In our calculations, the excited states lying higher than 5 eV were also calculated, as shown in Table 5. The SAC-CI method is quite straightforward, so that there are no limitations for the number of states to be calculated. We predict the existence of a large peak due to the 8A′ state at around 5.1 eV in the region higher than the L band. It is called the M band in the

Table 5
Excited states of carboxyheme calculated by the SAC/SAC-CI method

State	Main configuration ($|C| > 0.25$)	Nature [a]	Excitation energy (eV)	Polarization	Oscillator strength
7A′	$-0.93(78-81)$	$\pi-\pi^*$	5.01	x	0.00549
8A′(M)	$0.91(73-80)$	$\pi-\pi^*$	5.12	x	0.655
10A″	$0.34(62-101) + 0.30(62-108)$ $+0.29(76-102) - 0.28(69-102)$	d,σ–d*,CO*	5.31	y	0.00004
11A″	$0.59(63-79) - 0.37(77-81)$ $-0.34(665-79) - 0.27(75-79)$	d,$\sigma-\pi-^*$	5.54	y	0.00066
9A′	$0.41(63-102) + 0.36(63-108)$ $-0.29(63-101) + 0.25(75-102)$	d,σ,π–d*,CO*	5.55	x,z	0.00063
12A″	$0.47(62-80) - 0.45(69-80)$ $-0.26(76-80)$	d,$\sigma-\pi^*$	5.63	y	0.00002
13A″	$0.81(77-81)$	$\pi-\pi^*$	5.88	y	0.00138
10A′	$0.47(62-79) - 0.45(69-79)$ $-0.35(76-79) - 0.30(63-80)$ $-0.27(64-79)$	d,$\sigma-\pi^*$	5.91	z	0.00020
11A′	$-0.56(63-80) - 0.39(71-80)$ $+0.33(75-80) + 0.28(70-79)$	d,$\pi-\pi^*$	6.00	x,z	0.00041
12A′	$0.61(71-80) - 0.50(70-79)$ $-0.29(63-80)$	$\pi-\pi^*$	6.11	x	0.00008
14A″	$-0.74(71-79) - 0.55(70-80)$	$\pi-\pi^*$	6.14	y	0.0
15A″	$-0.88(75-81)$	d,$\pi-\pi^*$	6.49	y	0.105
13A′	$0.91(76-81)$	d,$\pi-\pi^*$	6.63	x	0.0952
14A′	$-0.69(70-79) - 0.61(71-80)$	$\pi-\pi^*$	6.68	x	0.00041
16A″	$0.72(70-80) - 0.56(71-79)$	$\pi-\pi^*$	6.93	y	0.00001
15A′	$-0.76(77-85) - 0.54(77-83)$	π–d*,CO*	7.33	x,z	0.0283
17A″	$0.77(68-88) - 0.52(68-85)$	d–CO*	7.34	y	0.00047
18A″	$0.89(78-83) + 0.39(78-85)$	π–d*,CO*	7.36	y	0.0186
19A″	$-0.78(78-86) + 0.30(73-81)$ $-0.30(78-85) + 0.25(78-83)$	π–d*,π^*,CO*	7.46	y	0.00062
20A″	$0.72(70-80) - 0.56(71-79)$	$\pi-\pi^*$	7.47	y	0.0355
16A′	$0.86(77-86) - 0.34(77-83)$	π–d*,CO*	7.49	z	0.00331
17A′	$0.87(78-84) - 0.31(78-91)$ $+0.27(78-82)$	π–d*,σ^*,CO*, Im $\pi*$ [b]	7.61	x	0.0471
18A′	$-0.79(64-79) + 0.37(69-79)$	d,$\sigma\pi^*$	7.74	z	0.00198

[a] See the footnote of Table 4.
[b] 'Im π^*' denotes the imidazole π antibonding orbital.

free base porphin, for example. The main configuration of this peak is the excitation from 73 to 80 MO within the '6 orbitals'.

The nature of the excited state is very different for the states higher than 5.2 eV. The main configurations can not be written only by the six orbitals because they include excitations involving Fe d orbitals and CO π^* orbitals in addition to the porphyrin π, and π^* MOs. For this reason, the intensities of the transitions lying higher than 5.2 eV are in general small. We predict that no intense band exists in the region above the M band. An exception is the 15A″ state calculated at 6.49 eV.

5. Conclusions

The SAC/SAC-CI method is applied to calculations of the ground and excited states of the carboxyheme. We summarize the results as follows:

(1) The calculated results for the excitation energy and the oscillator strength reproduce well the experimental spectrum. The average discrepancy of the present SAC-CI results from the experimental peaks is 0.33 eV.

(2) The Q_0 and Q_v peaks are assigned to the 1A′ and 1A″ states, respectively. These bands consist of excitations within Gouteman's 4 orbitals.

(3) The B, N, L, and M bands are described by excitations within the '6 orbitals', two lower occupied MOs 73 and 74 being added to the 4 orbitals.

(4) The B band is assigned to the 3A′ and 5A″ states. In the B band, the excitations within the 4 orbitals are larger than those from the two lower porphyrin π orbitals, 73 and 74, of the 6 orbitals to the LUMO and next-LUMO. In the N and L bands, the weights of the excitations within the 4 orbitals are smaller than those of the other configurations in the 6-orbital model.

(5) The M band is assigned to the 8A′ state, which also has the porphyrin $\pi–\pi^*$ nature from the 73 to 80 MOs. In this case, the excitations within the 4 orbitals are minor.

(6) It is found that the B band shoulder in the higher energy side has the nature of the excitation from the d,σ orbital to the d*, σ^* and CO* orbital.

(7) In the region higher than 5.2 eV, the excited states have the nature of the transitions d–π^*, d–

CO*, etc. For this reason, no strong peaks are predicted in the region higher than the M band.

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