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Ground and excited states of Mg porphin studied by the SAC/SAC-CI method

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Abstract

The SAC (symmetry adapted cluster)/SAC-CI method is applied to the ground and excited states of magnesium porphin (MgP). The π interaction between the Mg atom and the porphin ring is small and, therefore, the essential difference between MgP and free base porphin (FBP) lies in symmetry; the former is D_{4h} and the latter D_{2h}. The degenerate excited states in MgP split into two in FBP. The SAC-CI results for the excitation energy and the oscillator strength compare reasonably well with the experimental spectra for Mg etioporphyrin (MgEtio) and Mg tetraphenylporphin (MgTPP) and the natures of the excited states are clarified. Gouterman's four-orbital model holds well for the Q band, but the excitations from the $2a_{2u}$ MO below the four orbitals mix in the B band, as was found previously for FBP. The natures of the N bands are different between MgP and FBP.

1. Introduction

Photosynthesis is one of the more important biological reactions. In the X-ray crystallographical structure of the reaction center of *Rhodopseudomonus (Rps.) viridis* [1], Mg porphyrin takes a central part as a special pair and its important role in photosynthesis is more and more revealed by many studies. It is said that the excitations of the special pair initiates the charge separation in the photosynthesis, so that it is significant to study the electronic structures of the ground and excited states of Mg porphyrins.

Gouterman proposed that the lower excited states of porphyrins are well understood by the four-orbital model [2]. Many calculations on the excited states of porphyrins were reported using semi-empirical methods [2–5] and ab initio methods [2,6–13]. For free base porphin (FBP), accurate and reliable calculations for the ground and excited states were reported by Roos et al. with the CASPT2 method [10] and by Nakatsuji et al. with the SAC-CI method [11]. They revealed some important aspects of the electronic structures of FBP. More recently, we have also studied the ground and low-lying excited states of oxyheme [12] and tetrazaporphin [13] by the SAC-CI method.

We study here the ground and excited states of Mg porphin (MgP) using the SAC[14]/SAC-CI[15] method [16,17]. We use here the modified version

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[18] of the SAC85 program [19]. We note that the EOM-CC method [20,21] published from Bartlett's group is essentially the same as our SAC-CI method published much earlier. The SAC-CI theory is a wide and essentially exact concept [15,16] and includes not only excitations but also ionizations and electron attachments and, therefore, the SAC-CI method also involves the IP-EOMCC [22] and EA-EOMCC [23] method: such ideas have been published many years ago [16] and used for many years in various applications [17,24–26]. Our SAC-CI program can deal with the ground and excited states having spin multiplicities from singlet to septet [27].

2. Computational details

MgP, $MgC_{20}N_4H_{12}$ has D_{4h} symmetry and is considered as the complex of the Mg^{2+} ion coordinated at the center of the dianion porphin ring. For the nuclear coordinates of the porphin skeleton, those of the FBP by Sekino and Kobayashi [3] are adopted and the Mg atom is located at the inversion center of the D_{4h} symmetry.

The basis set is of double-ζ quality for the valence 2p orbitals of carbon and nitrogen. We used the (63/5)/[63/41] set of Huzinaga [28] for carbon and nitrogen, and Huzinaga's (4)/[4] set [29] for hydrogen. For the Mg atom, we used two different basis sets. In calculation (A) we used Huzinaga's (533/5)/[53111/41] set [28] plus two p-type polarization functions ($\alpha = 0.045$, 0.143), and in calculation (B) we used the (533/5)/[53111/311] set plus the same p-type functions and the d-type polarization functions ($\alpha = 1.01$). The total number of contracted GTOs is 221 for calculation (A) and 230 for calculation (B). The Hartree–Fock (HF) self-consistent field (SCF) orbitals were calculated by the HONDO program [30]: the number of occupied MOs is 86.

The electron correlations in the ground and excited states are taken into account by the SAC/SAC-CI method. In calculation (A), the higher 42 occupied orbitals and the lower 124 virtual orbitals, and in calculation (B), the higher 53 occupied orbitals and the lower 132 virtual orbitals are included in the active space: in calculation (B), only the inner core MOs are frozen. The total number of active orbitals is 166 in calculation (A) and 185 in calculation (B). The active space includes all π-type orbitals and a large number of σ-orbitals. All the single excitations and the selected double excitations are included in the linked term. The energy threshold in the configuration selection step is different for the $\pi-\pi^*$ excitations and the others. For the former, the energy thresholds 1.0×10^{-5} and 5.0×10^{-7} au are used for the ground and excited states, respectively, and for the latter, 2.0×10^{-5} and 1.0×10^{-6} au, respectively, are used [11,31]. Table 1 shows the dimensions of the linked terms before and after the selection.

3. Ground state electronic structure

The orbital energy and the nature of some higher occupied and lower unoccupied MOs are shown in Table 2. The π-type orbitals gather in the HOMO, LUMO regions. In particular, the HOMO, next-HOMO, and the LUMO which is degenerate are well separated from the other orbitals, implying the valid-

Table 1
Dimensions of the linked terms in the SAC/SAC-CI calculations of the singlet states of MgP

State	Calc. (A)			Calc. (B)		
	before selection	N [a]	after selection	before selection	N [a]	after selection
SAC						
^1A_g	1738599	1	10827	3185815	1	11755
SAC-CI						
$^1B_{1u}$ ($^1A_{1u}$)	1655788	1	12172	2935912	1	13152
$^1B_{2u}$ (^1E_u)	1735955	4	51654	3182250	4	60539
$^1B_{3u}$ (^1E_u)	1735955	4	51654	3182250	4	60539

[a] N is the number of states used in the configuration selection step.

Table 2
HF orbital energy and orbital character of MgP in calculation (B)

MO	Orbital energy (eV)	Character	Mg component [a]
higher occupied orbitals			
$4b_{1g}$	−14.897	σ	
$9e_u$	−14.628	σ	
$1b_{2u}$	−14.609	π	
$4a_{2g}$	−14.407	σ	
$6a_{1g}$	−14.401	n	3s
$5b_{2g}$	−14.380	σ	
$10e_u$	−12.791	n	
$1b_{1u}$	−12.058	π	
$5b_{1g}$	−11.807	n	
$2e_g$	−10.295	π	
$2a_{2u}$	−9.989	π	
$3e_g$	−9.622	π	
$2b_{2u}$	−9.501	π	
$3a_{2u}$ (next-HOMO)	−6.651	π	
$1a_{1u}$ (HOMO)	−6.368	π	
lower unoccupied orbitals			
$4e_g$ (LUMO)	0.153	π	
$7a_{1g}$	2.824	σ	3s
$2b_{1u}$	2.932	π	
$4a_{2u}$	3.405	π	pol. p_z
$11e_u$	5.169	σ	pol. p_x, p_y
$3b_{2u}$	5.319	π	
$5e_g$	5.721	π	d_{xz}, d_{yz}
$2a_{1u}$	6.311	π	
$2b_{1u}$	6.892	π	
$8a_{1g}$	7.370	σ	3s

[a] Mg AOs included.

ity of the four-orbital model of Gouterman [2]. These four orbitals and some lower orbitals which play an important role in the present study are illustrated in Fig. 1. All these orbitals are well localized on the porphin ring. Four occupied lone-pair (n) orbitals on the nitrogens lie below most of the π MOs and the σ-type orbitals are below these orbitals.

The Mg 3s orbital mixes in the lower three n orbitals, representing the coordination bonds between the Mg atom and the porphin ring. They lie on a rather lower side of the occupied MOs as shown in Table 2. In the unoccupied manifold, some MOs have the Mg component but they lie higher than the LUMO belonging to the four orbitals. Actually, the energy levels and the characters of the MOs of the Mg porphin are quite similar to those of FBP. The HOMO–LUMO energy gaps are also quite similar: 6.45 eV in FBP and 6.53 (calculation (A)) or 6.52 (calculation (B)) eV in MgP.

These facts indicate that the π interaction between the Mg atom and the porphin ring is small, implying a similarity in the nature of the excited states between FBP and MgP. However, a large difference that exists between them is the symmetry. Some orbitals and excited states are degenerate in MgP, but not in FBP. This causes a large difference in the excitation spectrum, as shown below.

The correlation energy for the ground state is calculated to be 9.67 (calculation (B)) or 8.70 (calculation (A)) eV by the SAC method. In the eigenvector for the ground state, the Hartree–Fock configuration is dominant. For example, the coefficients of the excited configurations involving the four orbitals are less than 0.05. Thus, the single reference theory can

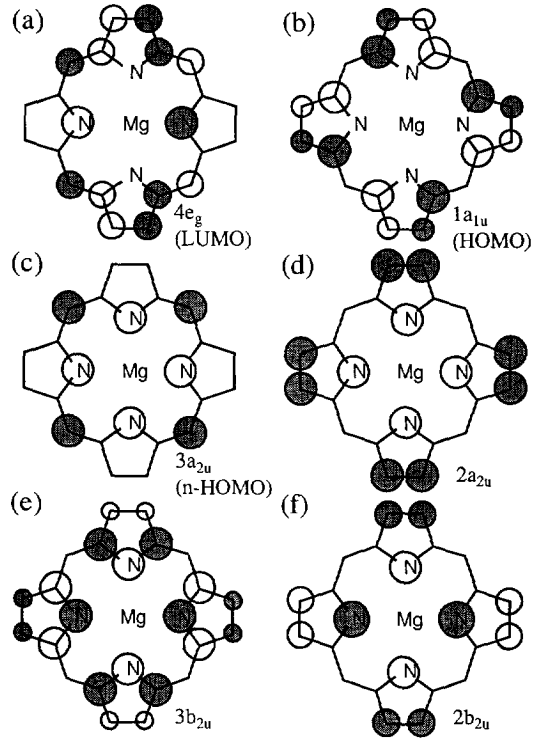

Fig. 1. Some molecular orbitals of MgP. (a) $4e_g$ (LUMO), (b) $1a_{1u}$ (HOMO), (c) $3a_{2u}$ (n-HOMO), (d) $2a_{2u}$, (e) $3b_{2u}$, (f) $2b_{2u}$.

describe the ground state of MgP with sufficient accuracy.

4. Excited states

The SAC-CI theoretical spectrum for MgP is compared in Fig. 2 with the experimental spectrum for Mg etioporphin (MgEtio) measured in the vapor phase by Edwards et al. [32]. Table 3 summarizes the SAC-CI results for the optically allowed states. The main configurations, characters, excitation energies and oscillator strengths are shown.

We have observed in the above section that the π interaction between the Mg atom and the porphin ring is small in the MgP and that the Mg orbitals do not lie in the HOMO–LUMO region nor mix with the four orbitals. This means that the nature of the lower excited states should be similar between FBP and MgP. However, a large difference lies in the symmetry; the former is D_{2h} but the latter D_{4h}. Therefore, the degenerate excitations in MgP should split into two in FBP. A comparison between the spectra of FBP and MgP should thus be quite useful for the assignment of the observed peaks. However, a point of difficulty is that there is no observed spectrum for MgP, though we have that for FBP. In Fig. 3 and Table 3, we compare the SAC-CI levels of the excited states of FBP and MgP with the experimentally observed levels for FBP, free base TPP (tetraphenylporphin), MgEtio, and MgTPP [32].

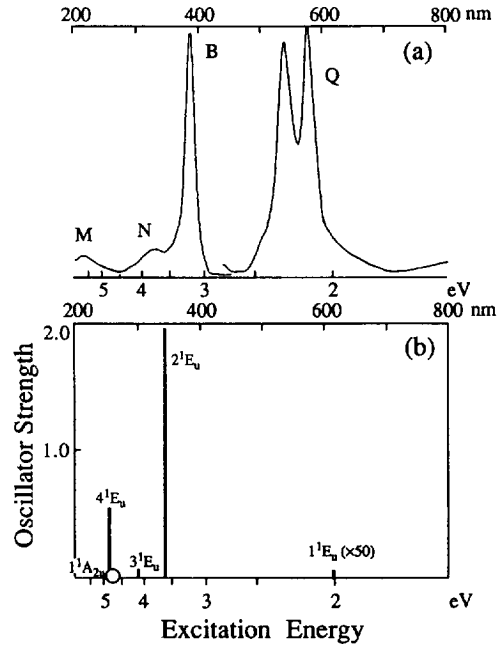

Fig. 2. (a) Vapor-phase experimental electronic spectrum of MgEtio [32] and (b) SAC-CI theoretical spectrum of MgP, where an open circle denotes the $1\,^1A_{2u}$ state.

Table 3
Ground and excited states of MgP

State	SAC-CI (B)				SAC-CI (A)		Exp. [a]			
	main configuration ($C > 0.3$)	character	excitation energy (eV)	oscillator strength	excitation energy (eV)	oscillator strength	excitation energy (eV)		intensity	
							MgEtio	MgTPP		
$X\,^1A_{1g}$	1.00(HF [b])	0.00 [c]	–	0.00 [d]	–					
$1\,^1E_u$	$0.68(1a_{1u} \rightarrow 4e_g)$ $-0.67(3a_{2u} \rightarrow 4e_g)$	π–π^*	2.01	1.52×10^{-3}	2.14	5.65×10^{-3}	2.14	2.07	Q	w
$2\,^1E_u$	$-0.67(1a_{1u} \rightarrow 4e_g)$ $-0.61(3a_{2u} \rightarrow 4e_g)$ $-0.27(2a_{2u} \rightarrow 4e_g)$	π–π^*	3.63	1.99	3.78	2.14	3.18	3.04	B	s
$3\,^1E_u$	$-0.90(2b_{2u} \rightarrow 4e_g)$	π–π^*	4.15	0.069	4.38	0.0723	3.82	3.96	N	m
$1\,^1A_{2u}$	$0.96(3a_{2u} \rightarrow 7a_{1g})$	π–Mg(3s)	4.75	4.46×10^{-3}	5.38	6.93×10^{-3}	4.7	5.16	L	w
$4\,^1E_u$	$-0.88(2a_{2u} \rightarrow 4e_g)$	π–π^*	4.89	0.590	5.12	0.566	5.23	6.20	M	ms

[a] Ref. [32].
[b] Hartree–Fock configuration.
[c] Correlation energy for the ground state is 9.67 eV.
[d] Correlation energy for the ground state is 8.70 eV.

The dotted lines in Fig. 3 connect states having a similar nature. In Fig. 2, the experimental spectrum is actually for MgEtio.

The Q band is composed of a weak peak observed at about 2.1 eV. By the SAC-CI calculations, the Q band is assigned to the degenerate $1\,^1E_u$ state calculated at 2.1 eV in calculation (A) and 2.0 eV in calculation (B). The intensity is small in accordance with the weakness of the observed peak. The main configuration of the $1\,^1E_u$ state is composed of the excitations within the four orbitals and the weight of the two main configurations, $1a_{1u} \rightarrow 4e_g$ and $3a_{2u} \rightarrow 4e_g$ are almost the same, causing quite a small intensity of the Q band [13]. This nature is essentially the same as that of FBP [11], though it splits into Q_x and Q_y peaks in FBP.

A strong sharp absorption peak is observed around 400 nm in the experimental spectrum. It is called the B (Soret) band. The B band is assigned to the degenerate $2\,^1E_u$ state calculated at 3.78 eV in calculation (A) and 3.63 eV in calculation (B). The peak in the experimental spectrum lies in the 3.0–3.5 eV region for MgEtio (see Fig. 2) and MgTPP. The main configuration of the $2\,^1E_u$ state includes not only the excitations within the four orbitals but also the excitation from the lower $2a_{2u}$ MO. This was also seen previously for FBP [11]. In FBP the mixing of the excitations from the $4b_{1u}$ MO, corresponding to the $2a_{2u}$ MO in this case, was large; the weight was 27% in the $2\,^1B_{3u}$ state. For MgP, the weight is smaller and only about 7%. Thus, the four-orbital model applies better to MgP than to FBP.

The N band is a weak peak observed in the 3.8–4.0 eV region for MgEtio and MgTPP. This band is assigned to the $3\,^1E_u$ state calculated at 4.4 eV in calculation (A) and 4.2 eV in calculation (B). The main configuration, $2b_{2u} \rightarrow 4e_g$ does not belong to the excitations within the four orbitals. The nature of this state is different from that of FBP. The N band of MgP corresponds to the L band of FBP, and the N band of FBP corresponds to one element of the degenerate B band of MgP, as clearly seen from Fig. 3. This difference in the electronic structure of the N band between FBP and MgP is supported by the difference in the intensity. In the observed spectra, the intensity of the N band is quite small for MgTPP and MgEtio in comparison with that of the B band, but for FBP and free base TPP, the intensity of the N band is comparable with that of the B band [32]. Our theoretical results agree with this observation. The calculated intensity of the N band of FBP is comparable with that of the B band since it originates from the same degenerate electronic state [11], but the calculated intensity of the N band of MgP is quite small in comparison with that of the B band. Furthermore, comparing the experimental energy levels of

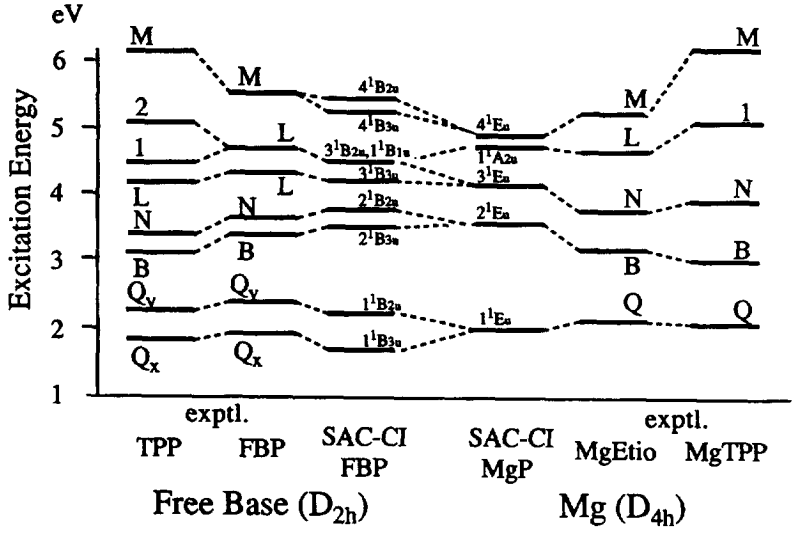

Fig. 3. Energy levels of the excited states of FBP and MgP calculated by the SAC-CI method compared with the experimentally observed energy levels for FBP, TPP, MgEtio, and MgTPP [32].

MgTPP directly with those of TPP as shown in Fig. 3, we notice that the N band of MgTPP is closer to the L band of TPP than to its N band.

The experimental spectra for MgEtio and MgTPP show considerably strong absorptions, called the M band, in the 5.8–6.2 eV region. This band may be assigned to the $4\,^1E_u$ state calculated at 5.1 eV in calculation (A) and 4.9 eV in calculation (B). The main configuration of this state is again out of the four-orbital model.

The $1\,^1A_{2u}$ state obtained in this calculation has only a weak intensity and we cannot see the band which corresponds to it in the experimental spectrum of MgEtio. However, in the experimental spectrum of MgTPP, we can see a weak '1' band in the corresponding energy region [32], so that the $1\,^1A_{2u}$ state might correspond to it. The calculated excitation energy of the $1\,^1A_{2u}$ state is 4.8 eV by calculation (B) and lies between the $3\,^1E_u$ and $4\,^1E_u$ state. This ordering is seen in the experimental spectrum of MgTPP. The result of calculation (A) does not reproduce this ordering. In the case of FBP, the $1\,^1B_{1u}$ state corresponds to this $1\,^1A_{1u}$ state of MgP. The $1\,^1B_{1u}$ state of FBP is due to the excitation from the lone pair orbital of nitrogen to the LUMO or next-LUMO, while the $1\,^1A_{1u}$ state of MgP is due to the excitation from the next-HOMO to the Mg 3s orbital. In calculation (B), we have given a wider freedom to the Mg basis set than in calculation (A), so the stability of about 0.6 eV for the $1\,^1A_{2u}$ state of MgP is reasonable.

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