

Excited and ionized states of free base porphin studied by the symmetry adapted cluster-configuration interaction (SAC-CI) method

Hiroshi Nakatsuji,^{a)} Jun-ya Hasegawa, and Masahiko Hada

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-01, Japan

(Received 24 April 1995; accepted 23 October 1995)

The SAC(symmetry adapted cluster)/SAC-CI method is applied to the calculations of the ground, excited, and ionized states of the free base porphin. The electronic spectrum of porphin is well reproduced and new assignments for the *B* (Soret), *N*, *L*, and *M* bands are proposed. The present result shows that the four-orbital model is strongly perturbed for the *B* and *N* bands by the excitations from the lower $4b_{1u}$ MO and that the σ electron correlations are important for the description of the excited states. The absorption peaks in the ionization spectrum are assigned and the reorganization effect is found to be large especially for the n and σ electron ionizations.

© 1996 American Institute of Physics. [S0021-9606(96)00105-7]

I. INTRODUCTION

Porphyrins play a key role in some biological reactions like photosynthesis and oxygen absorption.¹ To clarify the electronic mechanisms of these reactions, the electronic structures of porphyrins have been actively investigated.^{2–19} The excited and ionized states of porphyrins observed in the vuv spectra²⁰ and the photoelectron spectra²¹ are also investigated by the semiempirical^{2–8} and *ab initio*^{9–13} methods. Among them, the CASPT2 study by Roos *et al.*¹³ would be the best calculation so far made.

In the electronic spectrum of free base porphin, shown in the upper side of Fig. 1, the peaks are named as *Q*, *B* (Soret), *N*, *L*, and *M* bands from low-energy peaks. The polarization studies^{22,23} showed that the two peaks of the *Q* band are polarized perpendicular to each other, and the same is true for the *B* and *N* bands.

Previous theoretical studies^{7–13} showed that the lower energy peak is polarized parallel to the inner H–H axis (Q_x) and the other one perpendicular (Q_y). Similar polarizations were also assumed for the *B* band: The lower and higher energy regions of the peak have the same polarizations as the Q_x and Q_y peaks, respectively.^{12,13} However, some ambiguity still remains in these studies, since in the past, porphin was a large molecule for accurate theories of quantum chemistry.

We study here the ground, excited, and ionized states of porphin, based on the SAC (symmetry adapted cluster) theory for the ground state²⁴ and the SAC-CI theory for the excited, ionized and electron attached states.²⁵ We use here the accelerated version²⁶ of the SAC85 program.²⁷ The SAC/SAC-CI method has been shown to be quite accurate and useful for studying molecular spectroscopy and (catalytic) surface reactions.²⁸ It has been applied successfully, for example, to five-membered ring compounds,²⁹ benzene,³⁰ pyridine,³¹ naphthalene,³² many metal complexes like tetraoxo complexes^{33–36} and halogen complexes,^{37–39} and the

models of surface reactions like Pd_nH_2 ($n=1-3$),⁴⁰ Ag_4O_2 ,⁴¹ etc. A review was published in Ref. 28. Recently, some accelerations of the program were done for the integral evaluation and diagonalization parts.²⁶ Preliminary results of the present calculations were presented at the Workshop held in Braunlage in the summer of 1994.⁴²

II. COMPUTATIONAL DETAILS

Free base porphin $\text{C}_{20}\text{N}_4\text{H}_{14}$ is assumed to have D_{2h} symmetry with D_{4h} skeleton. The atomic coordinate is taken from Sekino and Kobayashi.⁷

The basis set is of double- ζ quality for the valence $2p$ orbitals. We used Huzinaga's (63/5)/[$2s2p$] set⁴³ for carbon and nitrogen and (4)/[$1s$] set⁴⁴ for hydrogen. The total number of contracted GTO's is 206. The Hartree–Fock SCF orbitals, calculated by the HONDO program,⁴⁵ consists of 81 occupied and 125 unoccupied MO's.

In the SAC/SAC-CI calculations, the higher 42 occupied orbitals and the lower 114 unoccupied MO's are included in the active space. The total number of active orbitals is 156. The active space includes all the π -type orbitals, 13 occupied π and 35 unoccupied π^* orbitals, and a large number of σ orbitals are included. The frozen cores consist of $1s$ AO's and some lower combinations of $2s$ AO's of carbon and nitrogen and their antibonding counterparts at the top of the unoccupied space. From the previous calculations on benzene, etc.,^{5,12,13,30} the reorganization of the σ -electron space due to the π – π^* excitation is important especially for the *V* states.

All single excitations and the selected double excitations are included in the linked term. The selection scheme in the SAC-CI calculation is modified slightly from the original one⁴⁶ by adding the SE-CI coefficient C_i^a of the reference configuration Ψ_i^a to the second-order perturbation energy expression as

$$\frac{|C_i^a \langle \Psi_i^a | H | \Psi_{jk}^{bc} \rangle|^2}{\langle \Psi_i^a | H | \Psi_i^a \rangle - \langle \Psi_{jk}^{bc} | H | \Psi_{jk}^{bc} \rangle}.$$

^{a)}Also belongs to the Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto, 606, Japan.

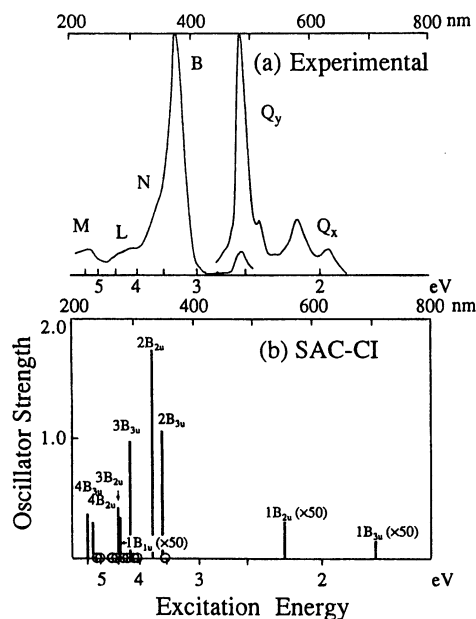


FIG. 1. Electronic spectrum of free base porphrin. (a) Gas-phase experimental spectrum due to Edwards *et al.* (Ref. 20) and (b) SAC-CI theoretical spectrum. The optically forbidden states are indicated by open circles.

In this scheme, the weight of the reference configuration is reflected in the selection scheme.

For the ground state, the energy thresholds of 1×10^{-5} and 2×10^{-5} hartree are used for the $\pi-\pi^*$ and the other excitations, respectively. For the singlet excited states, two calculations with different sets of energy thresholds are carried out. In calculation A, the energy threshold is 1×10^{-6} hartree. In calculation B, doubly excited configurations having coefficients larger than 0.05 in calculation A are added to the reference configurations for the selection and the energy threshold for the $\pi-\pi^*$ excitations is improved to 5×10^{-7} hartree. For the ionized states, the thresholds, 1×10^{-5} and 2×10^{-5} hartree are used for the ionizations from the π and the other orbitals, respectively. The numbers of the reference

TABLE II. Timing data for the SAC/SAC-CI calculations of porphrin.^a

Step	Timing
SCF	17 min.
Integral transformation	93 min.
SAC (for ground state)	84 min.
SAC-CI (per state)	
Singlet excited state	80 min.
Ionized state	2 min.

^aComputations are performed by the NEC SX-3 computer at the Computer Center of the Institute for Molecular Science.

states and of the resultant linked configurations are summarized in Table I. The unlinked terms of the SAC and SAC-CI calculations represent the higher-order effects and the transferable correlations, respectively. They are included by the standard procedure.^{28,46} Table II shows the timing data of the SAC/SAC-CI calculations of porphrin.

III. RESULTS AND DISCUSSIONS

A. Ground state

The energies and the natures of some higher occupied and lower unoccupied MOs are shown in Table III. The π -type orbitals gather in the HOMO, LUMO regions. In particular, the HOMO($2a_u$), next-HOMO($5b_{1u}$), the LUMO($4b_{2g}$), next-LUMO($4b_{3g}$), called "four orbitals," are well separated from the other orbitals, implying the validity of the four-orbital model of Gouterman.¹ Two lone pair orbitals on the nitrogens, $7b_{2u}$ and $8a_g$ MOs, lie in the deeper side of the occupied π orbitals. The σ -type orbitals are below of most occupied π orbitals.

In Fig. 2, the orbital shapes of the four orbitals and the lower occupied $4b_{1u}$ and $7b_{2u}$ (lone pair) MOs are shown. These orbitals are π -type except for the $7b_{2u}$ MO. The $5b_{1u}$ (n -HOMO) and $2a_u$ (HOMO) MOs have 20-membered π conjugation with 8 nodes and the $4b_{3g}$ (n -LUMO) and $4b_{2g}$ (LUMO) MOs have 18-membered π -conjugation with 10

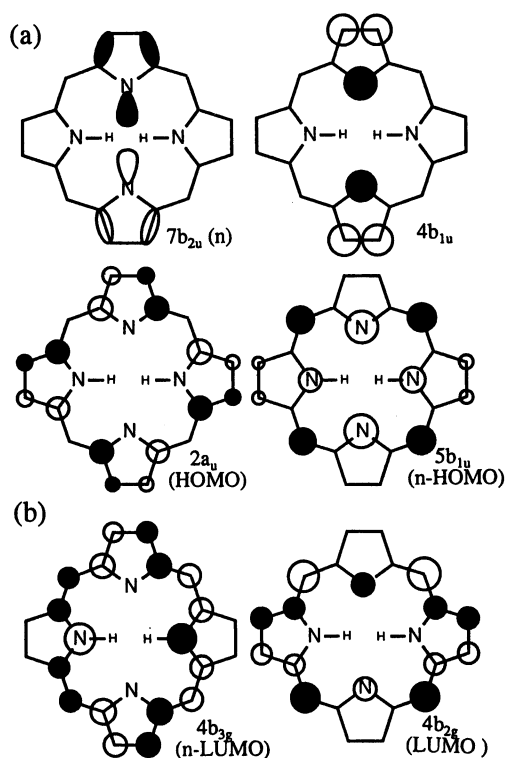
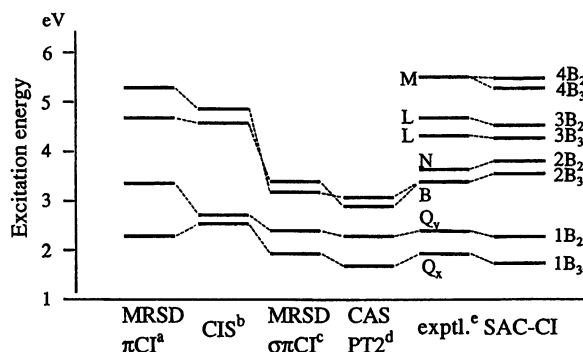
TABLE I. Dimensions of the SAC/SAC-CI calculations for the singlet and ionized states.

State	Singlet state						Ionized state		
	Before selection	Calc. A		Calc. B		After selection	Before selection	After selection	After selection
		$N(1)^a$	After selection	$N(1)^a$	$N(2)^a$				
SAC									
A_g	1 362 631	1	10 879						
SAC-CI									
A_g	1 362 631	3	42 176	3	9	46 199	25 560	8	6939
B_{1g}	1 360 246	3	51 051	3	12	54 848	25 523	7	5985
B_{2g}	1 308 922	1	20 723	1	2	21 230	22 979	3	3082
B_{3g}	1 308 922	1	20 882	1	2	21 441	22 979	3	2809
A_u	1 308 888	1	20 145	1	2	20 688	22 962	2	1755
B_{1u}	1 308 958	1	20 280	1	2	20 855	22 993	5	4215
B_{2u}	1 360 282	4	49 836	4	11	53 515	25 543	7	6301
B_{3u}	1 360 282	4	45 905	4	9	49 391	25 543	7	6478

^a $N(n)$ denotes the number of the n electron excited configurations used as the reference configurations in the configuration selection scheme.

TABLE III. HF orbital energy and orbital nature of porphrin.

MO	Orbital energy (eV)	Character
Higher occupied orbitals		
7a _g	-14.661	σ
6b _{2u}	-14.646	σ
7b _{3u}	-14.480	σ
7b _{1g}	-14.355	σ
1a _u	-12.216	π
7b _{2u}	-11.415	n
8a _g	-11.263	n
3b _{1u}	-10.679	π
2b _{2g}	-10.632	π
2b _{3g}	-10.590	π
3b _{2g}	-10.321	π
4b _{1u}	-9.327	π
3b _{3g}	-9.122	π
5b _{1u}	-6.686	π
2a _u	-6.521	π
Lower unoccupied orbitals		
4b _{2g}	-0.069	π
4b _{3g}	0.141	π
3a _u	2.842	π
6b _{1u}	5.064	π
5b _{2g}	5.698	π
5b _{3g}	5.702	π
4a _u	6.177	π
8b _{3u}	6.852	σ
8b _{2u}	7.437	σ
8b _{1g}	8.046	σ

FIG. 2. Illustration of the orbitals for (a) the occupied MOs (7b_{2u}, 4b_{1u}, 5b_{1u}, and 2a_u) and (b) the unoccupied MOs (4b_{2g} and 4b_{3g}).FIG. 3. *Ab initio* theoretical electronic spectra for free base porphrin. The dotted lines show the assignment of the experimental peaks by each method. (a) Reference 10. (b) Reference 11. (c) Reference 12. (d) Reference 13. (e) Reference 20.

nodes. The energy separations within these two pairs of MOs depend on whether the π conjugation involves the nitrogen atoms, since the lower D_{2h} symmetry exists only around these atoms.

The 4b_{1u} MO will be shown important later for it strongly perturbs the four-orbital model, and the 7b_{2u} nitrogen lone pair MO gives the lowest $n-\pi^*$ excitation. The MO shapes of Fig. 2 are useful when we investigate the substituent effects on the uv and ionization spectra.

The SAC correlation energy for the ground state is 10.0 eV. This is a reasonable value for our valence 2p double- ζ basis, since it is comparable with the correlation energy of 12.6 eV obtained by the MRSDCI calculation using split valence basis.¹² However, it is small in comparison with those obtained by the CASPT2¹³ and MP2¹⁴ calculations because of the smallness of the active space and the basis set used.

In the eigenvector for the ground state, the Hartree-Fock configuration is dominant. Though the four orbitals lie close to each other, the coefficients of the excited configurations involving these orbitals are less than 0.05. Then the single reference theory can describe the ground state of the free base porphrin with a sufficient accuracy.

B. Excited states

Ab initio calculations of the excited states of porphrin have appeared in recent years.¹⁰⁻¹³ Figure 3 shows the results together with the present ones (calculation B). The dotted lines show the assignments of the experimental peaks by each method. Only the lower four levels were calculated in the previous calculations.

Nagashima *et al.*¹⁰ performed MRSD π CI using the minimal basis set. The results were not satisfactory because of the crudeness of the basis set and the limitation of the active space within π orbitals. Foresman *et al.*¹¹ reported CIS calculations using 6-31G+ basis. Though the energies for the Q band were much improved, those for the Soret band were not improved: Higher excited configurations are necessarily included for an improvement. Yamamoto *et al.* carried out MRSD $\sigma\pi$ CI¹² using split valence basis and much

TABLE IV. Excited states of free base porphyrin calculated by the SAC-CI method.

State ^a	SAC-CI (B)			SAC-CI (A)		Exptl. ^b Excitation energy (eV)	Other <i>ab initio</i> theoretical excitation energy (eV)						
	Main configuration (<i>C</i> > 0.3)	Nature	Excitation energy (eV)	Polariz- ation	Oscillator strength (eV)		Excitation energy (eV)	Polariz- ation	MRSD π CI ^c	CIS ^d	MRSD $\sigma\pi$ CI ^e	CASPT2F ^f	
1B_{3u}	0.73 (5 <i>b</i> _{1u} →4 <i>b</i> _{3g})-0.61 (2 <i>a</i> _u →4 <i>b</i> _{3g})	$\pi-\pi^*$	1.75	<i>x</i>	1.13×10 ⁻³	1.80	<i>x</i>	1.98	<i>Q_x</i>	2.27	2.53	1.97	1.70
1B_{2u}	-0.70 (2 <i>a</i> _u →4 <i>b</i> _{2g})-0.66 (5 <i>b</i> _{1u} →4 <i>b</i> _{3g})	$\pi-\pi^*$	2.23	<i>y</i>	5.66×10 ⁻³	2.25	<i>y</i>	2.42	<i>Q_y</i>	3.42	2.66	2.40	2.26
1B_{1g}	0.93 (3 <i>b</i> _{3g} →4 <i>b</i> _{2g})	$\pi-\pi^*$	3.55		0.0	3.59							
2B_{3u}	-0.64 (2 <i>a</i> _u →4 <i>b</i> _{3g})+0.52 (4 <i>b</i> _{1u} →4 <i>b</i> _{2g})	$\pi-\pi^*$	3.56	<i>x</i>	1.03	3.59	<i>x</i>	3.33	<i>B</i>	4.72	4.6	3.41	2.91
2B_{2u}	-0.43 (5 <i>b</i> _{1u} →4 <i>b</i> _{2g})	$\pi-\pi^*$								5.29	4.8	3.24	3.04
2B_{1u}	0.66 (5 <i>b</i> _{1u} →4 <i>b</i> _{3g})-0.63 (2 <i>a</i> _u →4 <i>b</i> _{2g})	$\pi-\pi^*$	3.75	<i>y</i>	1.73	3.79	<i>y</i>	3.65	<i>N</i>				
1B_{2g}	-0.25 (4 <i>b</i> _{1u} →4 <i>b</i> _{3g})												
1B_{2g}	0.94 (8 <i>a</i> _g →4 <i>b</i> _{2g})	$n-\pi^*$	4.05		0.0	4.06							
1A_u	-0.93 (7 <i>b</i> _{2u} →4 <i>b</i> _{2g})	$n-\pi^*$	4.18		0.0	4.18							
3B_{3u}	0.76 (4 <i>b</i> _{1u} →4 <i>b</i> _{2g})+0.33 (2 <i>a</i> _u →4 <i>b</i> _{3g})	$\pi-\pi^*$	4.24	<i>x</i>	0.976	4.28	<i>x</i>	4.25	<i>L</i>				
2A_g	-0.40 (5 <i>b</i> _{1u} →4 <i>b</i> _{2g})												
2A_g	0.88 (3 <i>b</i> _{3g} →4 <i>b</i> _{3g})-0.32 (2 <i>a</i> _u →3 <i>a</i> _u)	$\pi-\pi^*$	4.25		0.0	4.29							
1B_{3g}	0.94 (8 <i>a</i> _g →4 <i>b</i> _{3g})	$n-\pi^*$	4.37		0.0	4.38							
1B_{1u}	0.93 (7 <i>b</i> _{2u} →4 <i>b</i> _{3g})	$n-\pi^*$	4.51	<i>z</i>	5.30×10 ⁻³	4.54	<i>z</i>		<i>L</i>				
3B_{2u}	0.89 (4 <i>b</i> _{1u} →4 <i>b</i> _{3g})	$\pi-\pi^*$	4.52	<i>y</i>	0.350	4.55	<i>y</i>	4.67	<i>L</i>				
2B_{1g}	0.91 (2 <i>a</i> _u →6 <i>b</i> _{1u})	$\pi-\pi^*$	4.62		0.0	4.63							
3A_g	-0.86 (2 <i>a</i> _u →3 <i>a</i> _u)-0.35 (3 <i>b</i> _{3g} →4 <i>b</i> _{3g})	$\pi-\pi^*$	4.74		0.0	4.78							
3B_{1g}	0.66 (2 <i>b</i> _{3g} →4 <i>b</i> _{2g})+0.65 (3 <i>b</i> _{2g} →4 <i>b</i> _{3g})	$\pi-\pi^*$	5.13		0.0	5.17							
4A_g	0.86 (3 <i>b</i> _{2g} →4 <i>b</i> _{2g})-0.31 (2 <i>b</i> _{3g} →4 <i>b</i> _{3g})	$\pi-\pi^*$	5.28		0.0	5.32							
4B_{2u}	0.90 (3 <i>b</i> _{1u} →4 <i>b</i> _{3g})	$\pi-\pi^*$	5.31	<i>y</i>	0.280	5.34	<i>y</i>		<i>M</i>				
4B_{3u}	-0.93 (3 <i>b</i> _{1u} →4 <i>b</i> _{2g})	$\pi-\pi^*$	5.45	<i>x</i>	0.351	5.48	<i>x</i>	5.50	<i>M</i>				

^aBold face letter is for the optically allowed state.^bReference 20.^cReference 10.^dReference 11.^eReference 12.^fReference 13.

improved the previous π -CI results.¹⁰ The peaks Q_x and Q_y for the Q band and the B band were calculated in good agreement with the experiment, though the polarizations of the two peaks corresponding to the B band may contradict with the experimental result.^{22,23} The CASPT2 result reported by Roos *et al.*¹³ showed a good agreement with experiment, though it tends to underestimate the excitation energy.

Our present result is also shown in Fig. 3. Different from the previous *ab initio* calculations, our SAC-CI calculation gives the excitation energies for all the states below 5.5 eV observed in the vuv spectrum. Our method is general and effective so that we can calculate all the excited states lying in the observed energy range. In Fig. 1, the SAC-CI theoretical spectrum is compared with the experimental one in a vapor phase measured by Edwards and his co-workers.²⁰ Table IV summarizes the details of the SAC-CI results not only for the optically allowed states, but also for the optically forbidden singlet states. The optically allowed eight π - π^* and one n - π^* excited states and the dipole-forbidden six π - π^* and three n - π^* states are calculated in the present SAC-CI study. Main configurations, natures, excitation energies and oscillator strengths are given together with the experimental and other *ab initio* theoretical results.

Referring to Figs. 1 and 3, we see that the present SAC-CI results reproduce well the experimental spectrum in both excitation energy and oscillator strength. The average discrepancy from the observed peaks are 0.13 and 0.14 eV by the present calculations A and B, respectively. We discuss each band subsequently below.

The Q band is composed of the two weak peaks Q_x and Q_y at 1.98 and 2.42 eV, respectively, and Q_y has a larger intensity than Q_x . By the SAC-CI calculations, Q_x and Q_y are assigned to the 1^1B_{3u} and 1^1B_{2u} states calculated at 1.8 and 2.2–2.3 eV, respectively. No other excited states including forbidden states are found in this area. The error in the excitation energy is within 0.2 eV. The present calculations reproduce the energy separation between Q_x and Q_y and the order of the oscillator strength in the experimental spectrum. Since the 1^1B_{3u} and 1^1B_{2u} states polarize in x and y directions, respectively, the present result is consistent with the experiment. The main configurations shown in Table IV are composed of the excitations within "4 orbitals": two configurations mix strongly and cause a quasidegenerate nature of these states.

A strong absorption band that consists of a sharp peak and a shoulder in the higher energy side is observed in the 310–400 nm region of the spectrum. The sharp peak and the shoulder are called B (Soret) and N bands, respectively. The 18 membered cyclic polyene model^{47,48} of porphyrin explained that the B band consists of the two degenerate states. In some previous theoretical studies including the *ab initio* ones^{10–13} and the semiempirical ones,^{7,8} the B band was assigned to the two nearly degenerate 2^1B_{3u} and 2^1B_{2u} states, following the Gouterman's four-orbital model, and the N band to another electronic state.

The present SAC/SAC-CI results indicate different assignment. The excitation energies of the 2^1B_{3u} and 2^1B_{2u}

states are calculated to be 3.59 and 3.79 eV, respectively, in the calculation A and 3.56 and 3.75 eV, respectively, in the calculation B and no other peaks are calculated in the 3–4 eV region. Then, we assign the 2^1B_{3u} and 2^1B_{2u} states to the B and N bands, respectively. In other words, the N band which is the shoulder of the B band in the experimental spectrum shown in Fig. 1 is actually B_y and the B band is B_x . The excitation energies for these states are overestimated by 0.26 and 0.14 eV, respectively, in the calculation A and 0.23 and 0.10 eV in the calculation B. The energy splitting between the B and N bands, which is 0.32 eV, is calculated to be 0.20 eV. If the conventional assignment is adopted in our present result, no assignment is possible for the N band. Namely, the present proposal for the B and N bands are based not only on the calculated excitation energies for the $2B_{2u}$ and $2B_{3u}$ states, but also on the comparison of the present results, as a whole, with the peaks in the experimental spectrum.

The polarization studies for the free base tetraphenylporphyrin^{22,23} showed that the sharp B band and the shoulder are polarized perpendicular to each other and that the B band and its shoulder have the same polarization as the Q_x and Q_y peaks, respectively. This is consistent with our assignment.

The symmetry lowering from D_{4h} metal porphyrins to its D_{2h} free base ones often cause a spectral broadening on the B band.²⁰ This is consistent with the present assignment, since the 2^1B_{2u} and 2^1B_{3u} states of the present molecule (D_{2h}) become degenerated in the D_{4h} symmetry. In the following, we use the traditional notations B and N , though they are actually B_x and B_y , respectively, for the free base porphyrin.

The main configurations of the 2^1B_{3u} and 2^1B_{2u} states include not only the excitations within the 4 orbitals, but also the excitations from the lower $4b_{1u}$ orbital (see Table III and Fig. 2). As shown in Table IV, the two transitions from the $4b_{1u}$ MO to the $4b_{2g}$ and $4b_{3g}$ MOs strongly mix into the configurations within the 4-orbital model in the calculated 2^1B_{3u} and 2^1B_{2u} states, respectively. Furthermore, the extent of mixing is quite different between the 2^1B_{3u} and 2^1B_{2u} states, so that these states are no longer degenerate. The natures of the B (2^1B_{3u}) and N (2^1B_{2u}) bands are different in this point from that of the Q band. In the CASPT2F calculation, the $4b_{1u}$ MO was not included in the active space of CASSCF, though as shown here it strongly perturbs the picture of the four-orbital model of the B band.

Referring to Fig. 1 and Table IV, we see that the calculated intensity is larger for the 2^1B_{2u} (N) states than for the 2^1B_{3u} (B) states. This may contradict with the observed spectrum shown in Fig. 1. However, we may interpret the observed spectrum as follows. The N band is a broad band, the B band is sharp, and the B band lies on the right-hand side top of the broad N band, so that the N band looks like a shoulder of the B band.

The present proposal for the assignment of the B and N bands needs to be examined by using more extended basis and for other related compounds, which are now under way.

The effects of the σ electron-correlation were found to

TABLE V. The number of configurations that have CI coefficients larger than 0.01.

State	$1B_{2u}$	$2B_{2u}$	$3B_{2u}$	$4B_{2u}$	$1B_{3u}$	$2B_{3u}$	$3B_{3u}$	$4B_{3u}$
$\pi-\pi^*$	15	22	15	20	18	19	15	18
Nature $\sigma-\pi^*$	0	0	0	0	0	0	0	0
$\sigma-\sigma^*$	0	8	1	1	0	4	3	0

be important for the description of the $\pi-\pi^*$ excitations of the π conjugated systems. This is now a well-known fact verified by the SAC-CI,²⁸⁻³² CASPT2,^{13,49-52} and other calculations⁵³⁻⁵⁶ in particular for larger π -electron molecules. In Table V, the number of the configurations whose CI coefficients are larger than 0.01 is shown for several states. The $\sigma-\sigma^*$ excitations mix with the $\pi-\pi^*$ excitations especially in the 2^1B_{3u} (B) and 2^1B_{2u} (N) states. The difference of these states from the Q band is clear also from this point.

For the L and M bands, no *ab initio* calculations have been reported except for the semiempirical treatments.^{7,8} The L bands at 4.25 and 4.67 eV are assigned to the 3^1B_{3u} and 3^1B_{2u} states, respectively, since these two states have relatively large intensities (for the 1^1B_{1u} state, see later). The errors of the SAC/SAC-CI excitation energies from the experiment are within 0.2 eV. Since the intensity of the 3^1B_{3u} state is larger than that of the 3^1B_{2u} state, the shape of the L band is unsymmetric with higher intensity in the lower energy side. The main configurations of the 3^1B_{3u} and 3^1B_{2u} states are the transitions from the $4b_{1u}$ MO to the $4b_{2g}$ and $4b_{3g}$ MOs, respectively. These are the mixing configurations to the four orbital model in the B and N states. The $\sigma-\sigma^*$ effect is relatively large in the 3^1B_{3u} states as shown in Table V.

It is interesting to note that we have obtained several $n-\pi^*$ type transitions for the porphin as shown in Table IV. Among these, the optically allowed one is the 1^1B_{1u} state calculated at 4.51 eV, but the calculated intensity is very small and is similar to those of the Q_x and Q_y peaks. In the experimental spectrum shown in Fig. 1, this peak may be concealed by the L band. Since the $7b_{2u}$ MO is the lone pair orbital on nitrogen, it will be blocked by forming metal porphyrins, so that this peak will disappear. We have obtained several other $n-\pi^*$ states, 1^1B_{2g} state at 4.05 eV, 1^1A_u state at 4.18 eV and 1^1B_{3g} state at 4.37 eV, though they are all optically forbidden at the D_{2h} symmetry. In the semiempirical calculation of Baker and Zerner,⁸ a $n-\pi^*$ excitation was calculated at 4.91 eV with the oscillator strength of 0.019.

In the absorption band lying in the energy region 4.0–4.7 eV, which is called L band in the spectrum shown in Fig. 1, it became clear that at least three optically allowed transitions exists, 3^1B_{3u} , 1^1B_{1u} ($n-\pi^*$), and 3^1B_{2u} states, and their polarization are all different, x , z , and y directions, respectively, though the intensity of the 1^1B_{1u} ($n-\pi^*$) state is small. Therefore, a detailed polarization study for the peaks in this energy region is very interesting and waited. We note that for free base tetraphenylporphyrin, three peaks, L , 1,

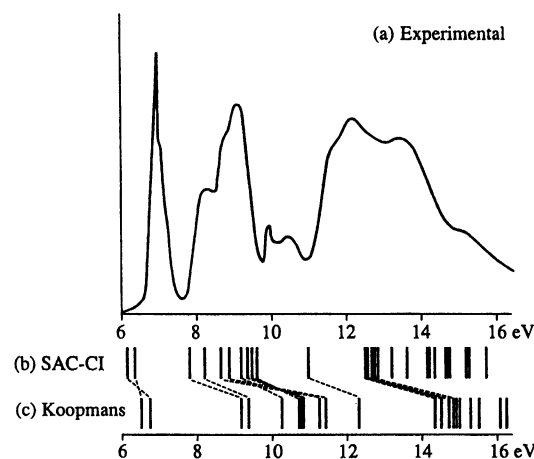


FIG. 4. Ionization spectrum of free base porphyrin. (a) Photoelectron spectrum (Ref. 21). (b) SAC-CI and (c) Koopmans ionization potentials. The dotted lines show the correspondences between the Koopmans IP's and the SAC-CI ones.

and 2 were reported in the energy region of the L band of the free base porphyrin.²⁰

The M band at around 5.5 eV in the experimental spectrum is composed of the two $\pi-\pi^*$ transitions due to the 4^1B_{2u} and 4^1B_{3u} states. They are the transitions from the $3b_{1u}$ MO to the $4b_{3g}$ and $4b_{2g}$ MOs, respectively. In comparison with the L band, the starting MO is lower but the ending MOs are the same. Note that the order of the polarizations is different: x and y in the increasing energy for the L band and y and x for the M band. Experimental examination of such polarization property is also interesting.

In the present SAC-CI calculations, two different thresholds are used in the perturbation selection procedure for examining the accuracy of the present result. In the calculation B , the better thresholds are used for the $\pi-\pi^*$ excitations and some doubly excited configurations, which might be important in the excited states, are used as reference configurations in the perturbation selection step. The calculation B is therefore more accurate than the calculation A . Comparing two sets of the results shown in Table IV, we find the two calculations to be quite similar: no special differences are observed between the calculations A and B . The calculation B gives about 0.03 eV lower energy than the calculation A . This result indicates that the principal correlations necessary for describing the excited states of porphyrin are already included in the calculation A , and that the present result should be already approximation invariant.

C. Ionized states

The photoelectron spectrum of the free base porphyrin in a vapor phase was observed by Dupuis *et al.*²¹ and is shown in Fig. 4. It is very characteristic that the first ionization potential of the free base porphyrin is as low as 6.9 eV. This low IP is believed to have some relation with the photosynthesis.

The SAC-CI ionization spectrum is compared with the Dupuis' experimental spectrum in Fig. 4. The dotted lines denote the correspondence between the SAC-CI result and

TABLE VI. Ionized states of free base porphin.

State	Main configuration ($C > 0.3$)	Expt. ^a (eV)	Present (eV)		Δ^c	Almlöf ^b (eV)		
			SAC-CI IP	Koopmans IP		Δ SCF IP	Orbital energy	Orbital reorganization energy
1^2B_{1u}	-0.97 ($5b_{1u}$): π	6.9	6.09	6.52	0.43	8.00	8.42	0.42
1^2A_u	0.98 ($2a_u$): π	7.2sh	6.35	6.69	0.34	8.39	8.78	0.39
1^2B_{3g}	-0.97 ($3b_{3g}$): π	8.4	7.98	9.12	1.14	10.41	11.02	0.61
2^2B_{1u}	0.97 ($4b_{1u}$): π		8.21	9.33	1.12	11.08	11.41	0.33
1^2A_g	-0.96 ($8a_g$): n	8.8sh	8.65	11.26	2.61	11.82	12.76	0.94
1^2B_{2u}	-0.96 ($7b_{2u}$): n		8.79	11.42	2.63	11.24	12.76	1.52
1^2B_{2g}	-0.69 ($3b_{2g}$): π	9.11	9.10	10.32	1.22	12.16	12.74	0.58
	-0.68 ($2b_{2g}$): π							
3^2B_{1u}	0.96 ($3b_{1u}$): π		9.34	10.68	1.34	12.44	12.75	0.31
2^2B_{2g}	0.69 ($2b_{2g}$): π		9.42	10.70	1.28	12.35	12.58	0.28
	-0.68 ($3b_{2g}$): π							
2^2B_{3g}	-0.97 ($2b_{3g}$): π		9.54	10.63	1.09	12.62	12.89	0.27
2^2A_u	-0.97 ($1a_u$): π		10.85	12.22	1.37			
1^2B_{1g}	-0.97 ($7b_{1g}$): σ		12.40	14.36	1.96			
1^2B_{3u}	0.95 ($7b_{3u}$): σ		12.43	14.48	2.05			
2^2B_{1g}	-0.94 ($6b_{1g}$): σ		12.67	14.63	1.96			

^aReference 21.^bReference 15.^c Δ is the difference between the Koopmans IP and the SAC-CI IP.

the Koopmans result. The reorganization effect is larger as the IP level is deeper. The observed spectrum can be assigned by the SAC-CI spectrum. Some of the lower ionized states calculated by the SAC-CI method are summarized in Table VI. For the first and second ionizations, both the Koopmans and SAC-CI IP's underestimate the observed values. The peaks at 6.9 and 7.2 eV are assigned to the ionizations from HOMO ($5b_{1u}$) and next HOMO ($2a_u$), respectively. Since our present basis set is $2p$ double- ζ quality and does not include polarization functions, the ionization potentials due to the HOMO and the next HOMO are not properly reproduced.

In the region deeper than 8 eV, the Koopmans method is not appropriate for the assignment. From the SAC-CI result shown in Fig. 4, the absorption band in 8.0–9.5 eV is found to be composed of the eight ionized states (six π ionized states and two σ ionized states). Two ionizations from the $2b_{3g}$ and $1a_u$ MOs are assigned to the peaks in the region 9.5–11.0 eV. The observed broad peak in 11–16.0 eV region involves the ionizations from the σ -type MOs. We also found many shake-up ionization peaks in this region. However, since the present SAC-CI calculations include only singles and doubles in the linked term, it is difficult to reproduce the shake-up ionizations with enough accuracy. The SAC-CI (general- R) method⁵⁷ can give more accurate descriptions of the shake-up processes.

In Table VI, Δ shows the difference between the Koopmans IP and the SAC-CI IP. It represents the reorganization and electron correlation effects. We see that the Δ values are grouped into four. The Δ values for the IP's from HOMO and next HOMO are about 0.4 eV, those for the π -type MOs are 1.1–1.4 eV, those for the σ -type MOs are about 2 eV, and those for the n -type MOs are 2.6 eV. This clearly shows the

relative importance of the reorganization and correlation effects in each type of the ionized states. Similar tendency was also found previously for the π -conjugated molecules like benzene³⁰ and pyridine.³¹

As shown in Fig. 4, the Koopmans ionization spectrum is much improved by using the SAC-CI method, since the electron correlation and the reorganization effects are important.

Almlöf performed in 1974 the Δ SCF calculations for the π - and n -type ionization potentials of the free base porphin.¹⁵ Table VI also shows his result. The difference between the Δ SCF IP and the orbital energy corresponds to the orbital reorganization energy after ionization. This reorganization energy is 0.3–0.6 eV for the π -type MOs and 0.9–1.5 eV for the n -type orbitals. In comparison with the present Δ values discussed above, these Almlöf's values are much smaller. This is because the present Δ values include not only the orbital reorganization, but also the electron correlation effects. It is interesting to note that for the first two IP's (1^2B_{1u} and 1^2A_u), the present difference value is so close to that of Almlöf.

Table VI gives the information on the main configurations. In most states the Koopmans configuration is the main configuration, but for the 1^2B_{2g} and 2^2B_{2g} states, the ionizations from the $3b_{2g}$ and $2b_{2g}$ MOs mix strongly.

IV. CONCLUSION

The SAC/SAC-CI method is applied to the calculations of the ground, excited and ionized states of the free base porphin. The theoretical result for the excitation energy and

the oscillator strength reproduce well the experimental spectrum. New assignments for the B , N , L , and M bands are proposed.

The B and N bands in the experimental spectrum shown in Fig. 1 are assigned to the 2^1B_{3u} and 2^1B_{2u} states, respectively, so that they actually correspond to the B_x and B_y states, respectively. This assignment does not contradict with the polarization experiments, the spectral intensity, and the spectral differences between the D_{2h} and D_{4h} porphyrins. Further examinations of this proposal are now in progress. The assignments of the Q_x and Q_y peaks are the same as the previous ones.

Though the Gouterman's four-orbital model holds well for the Q band, it breaks down for the B (and N) bands because the excitations from the lower $4b_{1u}$ orbital mix strongly to these bands. Further, the mixing is different for the B and N bands.

Since the SAC-CI method is general and effective, we need not to restrict our subject to the lower four levels. The L band lying in the 4.2–4.7 eV region is assigned to be composed of the 3^1B_{3u} , 1^1B_{1u} , and 3^1B_{2u} states. Their polarizations are x , z , and y , respectively and the intensity of the $n-\pi^*$ transition due to the 1^1B_{1u} state should be very small. The M band is assigned to the 4^1B_{2u} and 4^1B_{3u} states whose transitions have the polarizations in y and x directions, respectively.

We have also calculated several symmetry forbidden states as shown in Table IV. They involve $\pi-\pi^*$ and $n-\pi^*$ transitions.

The mixing of the $\sigma-\sigma^*$ excitations to the $\pi-\pi^*$ excitations is shown important particularly in the 2^1B_{3u} (B), 2^1B_{2u} (N), and 3^1B_{3u} (L) states.

The average discrepancies of the present SAC-CI results from the experimental peaks are 0.13 and 0.14 eV for the calculations A and B , respectively. Two calculations differ only about 0.01 eV, showing that the present result is already approximation invariant within the present basis set and the framework of the theory.

The SAC-CI ionization spectrum compares reasonably well with the Dupuis' photoelectron spectrum. The reorganization and electron correlation effects are large for the ionizations from the n and σ orbitals. The first two ionization potentials are calculated at 6.09 and 6.35 eV, which are smaller than the experimental values, 6.9 and 7.2 eV. This is probably due to the lack of the flexibility in the valence region and the polarization function in our basis set.

ACKNOWLEDGMENTS

The calculations were carried out with the SX-3 computer at the Institute for Molecular Science. The authors thank the IMS computer center for the grant of computing time. This study has been partially supported by the Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture.

- ¹M. Gouterman, *The Porphyrins*, edited by D. Dolphin (Academic, New York, 1977), Vol. 3.
- ²C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectrosc.* **16**, 415 (1965).
- ³M. Sundbom, *Acta Chim. Scand.* **22**, 1317 (1968).
- ⁴A. J. McHugh, M. Gouterman, and C. Weiss, *Theoret. Chim. Acta.* **24**, 346 (1972).
- ⁵H. Sekino and H. Kobayashi, *J. Chem. Phys.* **86**, 5045 (1987).
- ⁶W. D. Edwards, B. Weiner, and M. C. Zerner, *J. Am. Chem. Soc.* **108**, 2196 (1986).
- ⁷H. Sekino and H. Kobayashi, *J. Chem. Phys.* **75**, 3477 (1981).
- ⁸J. D. Baker and M. C. Zerner, *Chem. Phys. Lett.* **175**, 192 (1990).
- ⁹J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, *J. Mol. Spectrosc.* **71**, 64 (1978).
- ¹⁰U. Nagashima, T. Takada, and K. Ohno, *J. Chem. Phys.* **85**, 4524 (1986).
- ¹¹J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, *J. Phys. Chem.* **96**, 135 (1992).
- ¹²Y. Yamamoto, T. Noro, and K. Ohno, *Int. J. Quantum Chem.* **42**, 1563 (1992).
- ¹³M. Merchán, E. Ortí, and B. O. Roos, *Chem. Phys. Lett.* **226**, 27 (1994).
- ¹⁴J. Almlöf, T. H. Fischer, P. G. Gassman, A. Ghosh, and M. Häser, *J. Phys. Chem.* **97**, 10964 (1993).
- ¹⁵J. Almlöf, *Int. J. Quantum Chem.* **3**, 915 (1974).
- ¹⁶S. F. Suntum, D. A. Case, and M. Karplus, *J. Chem. Phys.* **79**, 7881 (1983).
- ¹⁷M. Merchán, E. Ortí, and B. O. Roos, *Chem. Phys. Lett.* **221**, 136 (1994).
- ¹⁸S. Yamamoto, and H. Kashiwagi, *Chem. Phys. Lett.* **205**, 306 (1993).
- ¹⁹S. Yamamoto, J. Teraoka, and H. Kashiwagi, *J. Chem. Phys.* **88**, 303 (1988).
- ²⁰L. Edwards and D. H. Dolphin, *J. Mol. Spectrosc.* **38**, 16 (1971).
- ²¹P. Dupuis, R. Roberge, and C. Sandorfy, *Chem. Phys. Lett.* **75**, 434 (1980).
- ²²J. W. Weigl, *J. Mol. Spectrosc.* **1**, 133 (1953).
- ²³B. G. Anex and R. S. Umans, *J. Am. Chem. Soc.* **86**, 5026 (1964).
- ²⁴H. Nakatsuji, K. Hirao, *J. Chem. Phys.* **68**, 2035 (1978).
- ²⁵H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); **67**, 329, 334 (1979).
- ²⁶H. Nakatsuji, M. Hada, H. Nakai, and J. Hasegawa (unpublished).
- ²⁷H. Nakatsuji, Program System for SAC and SAC-CI calculations, Program Library No. 146 (Y4/SAC), Data Processing Center of Kyoto University, 1985; Program Library SAC85, No. 1396, Computer Center of the Institute for Molecular Science, Okazaki, 1981.
- ²⁸H. Nakatsuji, *Acta. Chem. Hung.* **129**, 719 (1992).
- ²⁹H. Nakatsuji, O. Kitao, and T. Yonezawa, *J. Chem. Phys.* **83**, 723 (1985).
- ³⁰O. Kitao and H. Nakatsuji, *J. Chem. Phys.* **87**, 1169 (1987).
- ³¹O. Kitao and H. Nakatsuji, *J. Chem. Phys.* **88**, 4913 (1988).
- ³²H. Nakatsuji, M. Komori, and O. Kitao, *Chem. Phys. Lett.* **142**, 446 (1987).
- ³³H. Nakatsuji and S. Saito, *J. Chem. Phys.* **93**, 1865 (1990).
- ³⁴H. Nakatsuji and S. Saito, *Intern. J. Quantum Chem.* **39**, 93 (1991).
- ³⁵H. Nakai, Y. Ohmori, and H. Nakatsuji, *J. Chem. Phys.* **95**, 8287 (1991).
- ³⁶S. Jitsuhiro, H. Nakai, M. Hada, and H. Nakatsuji, *J. Chem. Phys.* **101**, 1029 (1994).
- ³⁷H. Nakatsuji, M. Ehara, M. H. Palmer, and M. F. Guest, *J. Chem. Phys.* **87**, 2561 (1992).
- ³⁸K. Yasuda and H. Nakatsuji, *J. Chem. Phys.* **99**, 1945 (1993).
- ³⁹H. Nakatsuji and M. Ehara, *J. Chem. Phys.* **101**, 7658 (1994).
- ⁴⁰H. Nakatsuji, M. Hada, and T. Yonezawa, *J. Am. Chem. Soc.* **109**, 1902 (1987).
- ⁴¹H. Nakatsuji and H. Nakai, *J. Chem. Phys.* **98**, 2423 (1992).
- ⁴²H. Nakatsuji, International workshop on electronic structure methods for truly large systems: moving the frontiers in quantum chemistry, Braunschweig, Germany, August 1–7, 1994.
- ⁴³S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Set for Molecular Calculations* (Elsevier, New York, 1984).
- ⁴⁴S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ⁴⁵M. Dupuis and A. Farazdel, *MOTEC91* (Center for Scientific and Engineering Computations, IBM Corporation, 1991).
- ⁴⁶H. Nakatsuji, *Chem. Phys.* **75**, 425 (1983).

- ⁴⁷H. Kuhn, J. Chem. Phys. **17**, 1198 (1949).
- ⁴⁸W. T. Simpson, J. Chem. Phys. **17**, 1218 (1949).
- ⁴⁹B. O. Roos, M. P. Fülscher, P. Malmqvist, M. Merchán, and L. Serrano-Andrés, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer, Dordrecht, 1994).
- ⁵⁰B. O. Roos, K. Andersson, and M. P. Fülscher, Chem. Phys. Lett. **192**, 5 (1992).
- ⁵¹L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, B. O. Roos, and M. P. Fülscher, J. Am. Chem. Soc. **115**, 6184 (1993).
- ⁵²M. P. Fülscher, K. Andersson, and B. O. Roos, J. Phys. Chem. **96**, 9204 (1992).
- ⁵³R. J. Cave, and E. R. Davidson, J. Phys. Chem. **91**, 4481 (1987).
- ⁵⁴J. M. O. Matos, B. O. Roos, and P. Malmqvist, J. Chem. Phys. **86**, 1458 (1987).
- ⁵⁵M. H. Palmer, and I. C. Walker, Chem. Phys. **133**, 113 (1989).
- ⁵⁶Y. Yamamoto, T. Noro, and K. Ohno, Intern. J. Quantum Chem. **51**, 27 (1994).
- ⁵⁷H. Nakatsuji, Chem. Phys. Lett. **177**, 331 (1991).