

SAC-CI Study on the Excited and Ionized States of Free-Base Porphin: Rydberg Excited States and Effect of Polarization and Rydberg Functions

Y. Tokita,^{†,‡,§} J. Hasegawa,[†] and H. Nakatsuji^{*,†,‡,||}

Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, The Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto 606, Japan, Research Center, Denki Kagaku Kogyo Co., Ltd., 3-5-1 Asahimachi, Machida-shi Tokyo 194, Japan, and Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

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The ground, excited, and ionized states of free-base porphin (FBP) are reinvestigated by the SAC (symmetry-adapted cluster)/SAC-CI (configuration interaction) method. In particular, the Rydberg excited states, the valence–Rydberg mixing, and the effect of polarization d-functions are studied. The lowest Rydberg excited state would exist at around 5.5 eV with a weak intensity, but the valence–Rydberg mixing is small. The effects of both the Rydberg and polarization d-functions are relatively small for the excitation energies of the main peaks, whereas the polarization d-functions affect considerably the ionization spectrum.

I. Introduction

Porphyrins have important functions in biological systems.¹ To elucidate the mechanisms of these functions, the electronic structures of porphyrins have been actively investigated.^{2–25} The excited and ionized states of porphyrins observed in the VUV²⁶ and photoelectron spectra,²⁷ respectively, have been investigated by semiempirical^{2–8} and ab initio methods.^{9–13} In our laboratory, the ground, excited, and ionized states of many kinds of porphyrins have been investigated^{14–20} by the SAC (symmetry-adapted cluster)²⁸/SAC-CI (configuration interaction)^{29,30} method. Among these, free-base porphin (FBP) shown in Figure 1 is a key compound, and the result was as follows.¹⁴ (1) The ground state could be described by the single-reference (Hartree–Fock configuration) theory. (2) The excitation energy and oscillator strength reproduced well the experimental spectrum,²⁶ and new assignments for the B, N, L, and M bands were proposed. (3) Although Gouterman's four-orbital model¹ appeared to be valid for the Q bands, it broke down for the B and N bands because the excitations from the lower b_{1u} orbital mixed strongly with these bands. Further, the mixing was different for the B and N bands. (4) Mixing of σ – σ^* excitations with π – π^* excitations was shown to be important, particularly in the 2^1B_{3u} (B), 2^1B_{2u} (N), and 3^1B_{3u} (L) states. (5) The calculated ionization spectrum roughly explained the Dupuis photoelectron spectrum.²⁷ The effects of the reorganizations and electron correlations were large particularly for the ionizations from the n and σ orbitals.

These results as a whole reproduced well the electronic features of FBP. However, when we performed such calculations, the computational environment was not good: we had to use 2p double- ζ basis sets and a relatively small active space. Therefore, in this study we perform two higher-level calculations of FBP to elucidate the accuracy of the previous calculations.

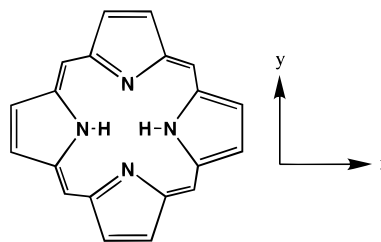


Figure 1. Structure of free-base porphin.

One calculation uses the valence double- ζ basis set plus Rydberg functions to clarify the Rydberg excited states and the effect of the Rydberg functions on the excited states. Since the peaks of the Rydberg excited states are generally weak,^{31–33} the assignment of the Rydberg excited states is difficult by experimental technique alone and theoretical information is necessary. Furthermore, if the valence–Rydberg mixing is large as in the excited states of ethylene,³¹ furan,³² benzene,³³ etc.,³⁴ good results cannot be expected by the calculations including valence basis sets alone, and a large basis set dependence may exist.^{31–33} The other calculations use the valence double- ζ basis set plus polarization d-functions to improve the description of the valence excited and ionized states.³³ Both calculations are carried out using a larger active space than that in the previous calculation. The details of the calculations are described in the next section. The accuracy and effectiveness of the SAC/SAC-CI method are now well established,^{35,36} even for a relatively large porphyrin group of molecules.

II. Methods

FBP $C_{20}N_4H_{14}$ is assumed to have D_{2h} symmetry with a D_{4h} skeleton (Figure 1). The atomic coordinates taken from Sekino and Kobayashi⁷ are the same as the previous one for comparison with our previous result. This molecule consists of 162 electrons and 38 atoms.

We performed two different calculations, A and B. In calculation A, the basis set is of double- ζ quality for the valence

* To whom correspondence should be addressed. Fax: 81-75-753-5910.

[†] Kyoto University.

[‡] The Institute for Fundamental Chemistry.

[§] Denki Kagaku Kogyo Co., Ltd.

^{||} The University of Tokyo.

TABLE 1: Dimensions of the Linked Terms for SAC/SAC-CI Calculations A, B, and C of the Singlet States, and for Calculations B and C of the Ionized States of Free-Base Porphin

state (r-nos.) ^a	singlet state						ionized state				
	B		calculations				B		C		
	before selection	after selection	before selection	after selection		before selection	after selection	before selection	after selection		
			valence	Rydberg							
SAC											
A _g (1)	17 879 553	84 928	4 410 565	11 478		1 362 631	10 879				
SAC-CI											
A _g (2,8)	17 879 553	158 339				1 362 631	46 199 ^b	132 208	65 380	25 560	6 939
B _{1g} (3,7)	17 871 092	239 449				1 360 246	54 848	132 105	62 359	25 523	5 985
B _{2g} (1,3)	16 052 930	119 097				1 308 922	21 230	102 610	28 938	22 979	3 082
B _{3g} (1,3)	16 052 830	120 767				1 308 922	21 441	102 586	27 971	22 979	2 809
A _u (1,2)	16 052 770	118 294				1 308 888	20 688	102 648	37 431	22 962	1 755
B _{1u} (1,5)	16 052 990	120 165				1 308 958	20 855	102 648	37 431	22 993	4 215
B _{2u} (4,7)	17 871 153	297 923	4 406 819	79 921 ^c	70 971 ^c	1 360 282	53 515	132 144	61 684	25 543	6 301
B _{3u} (4,7)	17 871 256	270 331	4 406 819	76 062 ^c	63 722 ^c	1 360 282	49 391	132 169	62 609	25 543	6 478

^a r-nos. denotes the number of one-electron excited configurations used as reference configurations in the configuration selection scheme in calculations B and C. Numbers on the left and right are the singlet and ionized reference numbers, respectively. ^b The reference number is three. ^c The reference number is five.

2s, 2p orbitals, and we added Rydberg s and p functions ($\alpha_s = 0.024$, $\alpha_p = 0.022$) on all of the N atoms. The Rydberg exponents are the mean values of the four carbons and one nitrogen consisting of the pyrrole unit. The purpose of adding the Rydberg functions are two-fold: one is to calculate Rydberg excited states of FBP, and the second is to examine the valence–Rydberg mixing, which can be eliminated only by adding proper Rydberg bases. The valence bases are Huzinaga’s (63/5)/[3s2p] set³⁷ for carbon and nitrogen and a (4)/[1s] set³⁸ for hydrogen. The total number of contracted GTOs is 246. The Hartree–Fock (HF) SCF orbitals used as the reference orbitals consist of 81 occupied and 165 unoccupied MOs. The SAC/SAC-CI calculations were carried out using SAC85³⁹ and its modified version,⁴⁰ within the 57 higher occupied MOs and the 144 lower unoccupied MOs included in the active space. The total number of active orbitals was 201: all of the valence and Rydberg orbitals were included in the active space, and only the 1s orbitals of C and N atoms were treated as frozen cores. All of the single excitations and selected double excitations within this active space constituted linked operators, and their products unlinked operators. The perturbative configuration selection procedure^{14,41} was performed with the energy thresholds of 1×10^{-5} au ($\pi-\pi^*$) and 2×10^{-5} au (others) for the ground state, and 5×10^{-7} au ($\pi-\pi^*$) and 1×10^{-6} au (others) for the excited states.

In calculation B, the basis set is double- ζ quality for the valence 2s, 2p orbitals, the same as in calculation A, plus polarization d-functions (C; $\alpha = 0.600$; N, $\alpha = 0.864$) on all of the C and N atoms, but does not include the Rydberg functions. The total number of contracted GTOs is 374. The HF SCF orbitals consist of 81 occupied and 293 unoccupied MOs. In the SAC/SAC-CI calculations, the 57 higher occupied MOs and the 289 lower unoccupied MOs, a total number of 346 MOs, were included in the active space: all of the valence orbitals were included in the active space, and only the 1s orbitals of C and N atoms were treated as frozen cores. The configuration selection^{14,41} was performed with an energy threshold of 5×10^{-6} au for the ground state, and with thresholds of 2×10^{-7} and 7×10^{-7} au for the excited and ionized states, respectively. We also performed SAC-CI calculations further including $\langle R(1)|H|R(1)S(1) \rangle$ and $\langle R(2)|H|R(1)S(1) \rangle$ unlinked terms to examine the effect of S(1) on the excitation energies, and this calculation is called calculation B2.

Note that S(1) is the SAC single-excitation operator and R(1) and R(2) are the SAC-CI single and double-excitation operators, respectively.

We compare the present results with the previous calculation,¹⁴ called here calculation C. The basis set there was double- ζ quality only for 2p AOs of carbon and nitrogen and no Rydberg and polarization functions were added. The total number of contracted GTOs was 206. The HF SCF orbitals consisted of 81 occupied and 125 unoccupied MOs, and among these 42 higher occupied and 114 lower unoccupied MOs were included in the active space of the SAC/SAC-CI calculations. The total number of active orbitals was 156, in comparison with 201 in calculation A and 346 in calculation B. The thresholds of the configuration selection were the same as in calculation A. We have performed two different calculations in which only the thresholds of the configuration selection were changed. One calculation C2 was performed with the energy thresholds of 1×10^{-5} au for the ground state and 5×10^{-7} au for the excited states. The other calculation C3 was performed with energy thresholds of 6×10^{-6} au for the ground state and 1×10^{-7} au for the excited states. The resultant dimensions for the SAC/SAC-CI calculations are shown in Tables 1 and 3.

III. Electronic Structure of the Ground State

We investigated the effects of Rydberg orbitals on the HF orbital energy by comparing calculations A and C¹⁴ shown in Table 2. Some important MOs are illustrated in Figure 2. In the case of pyrrole,³² the unoccupied valence π orbitals have some diffuse character: the second moments perpendicular to the molecular plane for unoccupied π_4^* and π_5^* orbitals were 16.06 and 10.77 a_0^2 , respectively, while those for occupied π_2 and π_3 are 2.28 and 2.51 a_0^2 , respectively.³² This is why it is believed that Rydberg–valence mixing³⁴ may occur in the π^* orbitals of FBP and that the energy and oscillator strength of the allowed $\pi-\pi^*$ excited states may be affected by changes in the nature of the valence π^* orbital. However, as shown in Table 2, the energy and the nature of the valence orbitals in calculation A are almost the same as those in calculation C, except for the orbitals with Rydberg nature. The second moments perpendicular to the molecular plane for the π orbitals, 56MO (next-HOMO), 57MO (HOMO), 58MO (LUMO), and 59MO (next-LUMO) are 4.829, 4.876, 5.086, and 5.120 a_0^2 ,

TABLE 2: Hartree–Fock Orbital Energy and Character of Free-Base Porphin in Calculations A, B, and C

MO no. ^a	symmetry	orbital energy (eV) calculations			character
		A	B	C	
Occupied Orbitals					
45	b _{3u}	-14.414	-13.149	-14.484	σ
46	b _{1g}	-14.325	-12.885	-14.355	σ
47	a _u	-12.147	-12.061	-12.216	π
48	b _{2u}	-11.386	-11.574	-11.415	n
49	a _g	-11.257	-11.476	-11.263	n
50	b _{1u}	-10.586	-10.592	-10.679	π
51	b _{2g}	-10.541	-10.555	-10.632	π
52	b _{3g}	-10.514	-10.459	-10.590	π
53	b _{2g}	-10.252	-10.187	-10.321	π
54	b _{1u}	-9.249	-9.250	-9.327	π
55	b _{3g}	-9.067	-9.082	-9.122	π
56	b _{1u}	-6.631	-6.827	-6.686	π
57	a _u	-6.485	-6.200	-6.521	π
Unoccupied Orbitals					
58	b _{2g}	-0.031	0.065	-0.069	π
59	b _{3g}	0.164	0.176	0.141	π
(60)	b _{3u}	1.589			σ,Ryd(3s,3p _x)
(61)	b _{2u}	1.675			σ,Ryd(3s,3p _y)
(62)	a _g	1.744			σ,Ryd(3s,3p _x ,3p _y)
(63)	a _g	2.001			σ,Ryd(3s,3p _y)
(64)	b _{1u}	2.185			π,Ryd(3p _x)
(65)	b _{2g}	2.553			π,Ryd(3p _y)
(66)	b _{1g}	2.621			σ,Ryd(3p _x)
(67)	b _{3g}	2.659			π,Ryd(3p _x)
60 (68)	a _u	2.844	3.014	2.842	π
(69)	b _{3u}	2.957			σ,Ryd(3s,3p _x)
(70)	b _{2u}	2.982			σ,Ryd(3s,3p _y)
(71)	b _{1u}	3.037			π,Ryd(3p _x)
(72)	b _{1g}	3.146			σ,Ryd(3p _x ,3p _y)
(73)	a _g	3.588			σ,Ryd(3p _x ,3p _y)
(74)	b _{3u}	3.904			σ,Ryd(3p _x)
(75)	b _{2u}	4.097			σ,Ryd(3p _y)
(76)	a _g	4.605			σ,Ryd(3p _x ,3p _y)
61 (77)	b _{1u}	5.116	5.002	5.002	π
62	a _g		5.485	6.917	σ
63 (79)	b _{3g}	5.719	5.756	5.702	π
64 (78)	b _{2g}	5.712	5.785	5.698	π
65	b _{3u}		5.809	6.852	σ
66	b _{2u}		5.915	7.437	σ
67 (80)	a _u	6.183	6.306	6.177	π

^a The numbering of the Hartree–Fock orbitals in calculation A including Rydberg orbitals is shown in the brackets.

TABLE 3: Excited ¹B_{3U} States of Free-Base Porphin by the SAC-CI Method Due to Different Configuration Selection Thresholds in Calculation C

calculation	dimensions		excitation energy (eV)		
	ground	excited	¹ B _{3u}	² B _{3u}	Δ (eV) ^a
C	10 879	49 391	1.75	3.56	1.81
C2	31 404	64 300	1.96	3.77	1.81
C3	60 988	149 638	1.94	3.78	1.84
exptl ^b			1.98	3.33	1.35

^a Δ is the difference in energy between the ²B_{3u} and ¹B_{3u} states.

^b Reference 27.

respectively, while those of the Rydberg 64, 65 and 67MOs are 79.868, 82.182 and 82.361 a₀², respectively. Thus, the Rydberg–valence mixing is not observed in the π* orbitals of FBP.

The HF orbital energy is significantly affected by the polarization functions as seen from calculations B and C shown in Table 2. The porphyrin σ-type orbitals vary greatly, while the π and n orbitals change only a little. This indicates that the polarization functions have a large reorganization effect on

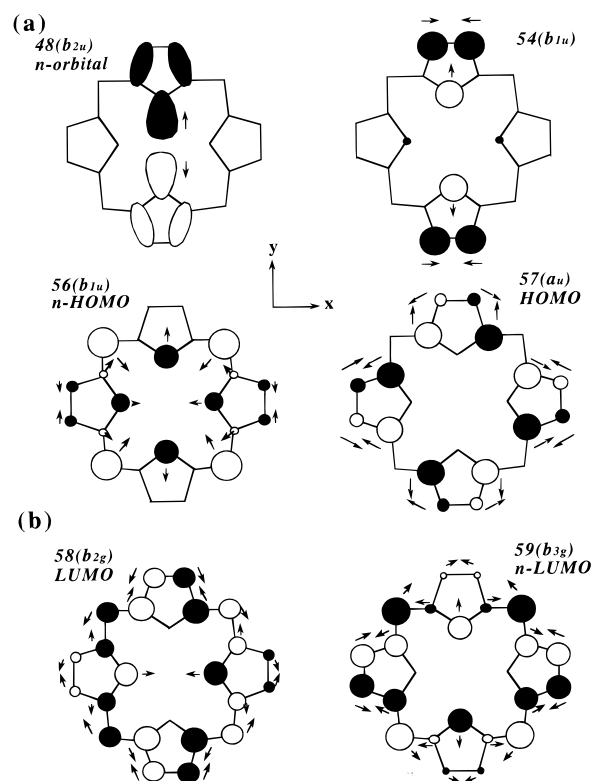


Figure 2. Orbitals for (a) the occupied MOs (48, 54, 56, 57) and (b) the unoccupied MOs (58, 59). The arrows show the polarization of π orbital due to the addition of polarization d-function.

the σ orbitals. The occupied and unoccupied σ-orbital energies are unstabilized and stabilized by about 1.2 eV, respectively. On the other hand, the π-orbital energies are slightly unstabilized by about 0.1 eV, except for 56MO (next-HOMO), which is stabilized by about 0.2 eV, and 57MO (HOMO), which is unstabilized by about 0.3 eV. The mechanism of the mixing of the polarization functions in the HF orbitals was studied earlier by Nakatsuji and Musher.⁴³ In the occupied orbitals, the effect of the polarization function is generally to unstabilize the orbital energy rather than stabilize,⁴³ though the total energy is of course stabilized by the addition of polarization functions.

The effects of the polarization d-functions on the π orbitals of FBP are illustrated in Figure 2. In the HOMO, the pπ AOs are polarized toward the pπ AOs of the adjacent atoms as shown by the arrows, by the addition of the polarization d-functions, so that neighboring π-electron repulsion increases and the MO energy is destabilized. The effect of the polarization d-functions on the other π MOs are exhibited similarly in Figure 2. The polarization functions tend to polarize the pπ functions in such a way to increase the positive (bonding) overlap between the adjacent AOs. On the other hand, in the next-HOMO, the neighboring atoms share little π-electron density, and therefore, the energy of this MO is only slightly affected by the polarization d-functions. Thus, the energy of the next-HOMO is slightly stabilized rather than unstabilized.⁴³ In the n orbital (48 (b_{2u})) the electron density of the lone-pair opposing nitrogens is reduced by the polarization function, so that this orbital is stabilized by about 0.2 eV.

The SAC correlation energies in calculations A and B for the ground state are 10.2 and 19.7 eV, respectively, in comparison with those of calculation C and the MRSDCI calculation,¹² which give correlation energies of 10.0¹⁴ and 12.6 eV,¹² respectively.

TABLE 4: Excited States of Free-Base Porphin Calculated by SAC-CI Calculation A^e

state	SAC-CI										exptl ^d
	calculation A					second moment ^b				calculation C	
	main configurations ^c (C > 0.30)	nature	excitation ^d energy (eV)	polarization	oscillator strength	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle R^2 \rangle$	excitation energy (eV)	
1 ¹ B _{3u}	0.72(56-58)-0.60(57-59)	$\pi-\pi^*$	1.70(-0.05)	x	1.91 × 10 ⁻³	-81.449	-91.754	-114.182	-287.386	1.75	1.98 Q _x
1 ¹ B _{2u}	-0.69(57-58)-0.66(56-59)	$\pi-\pi^*$	2.19(-0.04)	y	5.19 × 10 ⁻³	-79.664	-93.265	-114.182	-287.225	2.23	2.42 Q _y
2 ¹ B _{3u}	-0.65(57-59)+0.51(54-58)	$\pi-\pi^*$	3.43(-0.13)	x	1.10	-86.267	-87.470	-114.370	-288.107	3.56	3.33 B
	-0.44(56-58)										
2 ¹ B _{2u}	0.64(56-59)-0.63(57-58)	$\pi-\pi^*$	3.62(-0.13)	y	1.87	-84.065	-91.064	-114.449	-289.578	3.75	3.65 N
	-0.28(54-59)										
3 ¹ B _{3u}	0.76(54-58)+0.40(57-59)	$\pi-\pi^*$	4.08(-0.16)	x	1.09	-86.469	-80.783	-114.449	-289.578	4.24	4.25 L
	-0.32(56-58)										
3 ¹ B _{2u}	0.89(54-59)	$\pi-\pi^*$	4.36(-0.16)	y	0.437	-96.419	-70.339	-114.477	-281.235	4.52	4.67 L
4 ¹ B _{2u}	0.89(50-59)	$\pi-\pi^*$	5.15(-0.16)	y	0.290	-66.983	-97.943	-114.482	-279.408	5.31	M
4 ¹ B _{3u}	-0.91(50-58)	$\pi-\pi^*$	5.25(-0.20)	x	0.412	-56.633	-108.795	-114.492	-279.919	5.45	5.50 M
5 ¹ B _{3u}	0.96(56-65)	Ryd	5.51	x	9.21 × 10 ⁻³	-96.970	-81.145	-151.137	-329.251		
5 ¹ B _{2u}	0.96(56-67)	Ryd	5.55	y	3.82 × 10 ⁻³	-68.008	-110.211	-151.272	-329.490		
6 ¹ B _{2u}	-0.96(57-65)	Ryd	5.62	y	1.85 × 10 ⁻³	-96.071	-78.250	-151.090	-325.672		
6 ¹ B _{3u}	0.97(57-67)	Ryd	5.79	x	2.07 × 10 ⁻³	-67.543	-106.778	-151.351	-325.672		
7 ¹ B _{3u}	0.87(55-68)	$\pi-\pi^*$	6.56	x	0.297	-95.231	-84.745	-115.259	-295.275		
7 ¹ B _{2u}	-0.88(47-58)	$\pi-\pi^*$	6.71	y	2.66 × 10 ⁻²	-75.162	-97.782	-114.512	-287.456		
8 ¹ B _{2u}	0.68(57-65)-0.59(55-64)	Ryd	6.75	y	1.54 × 10 ⁻²	-89.911	-77.745	-151.299	-318.955		
8 ¹ B _{3u}	-0.75(57-67)-0.42(56-78)	$\pi-\pi^*$	6.82	x	2.01 × 10 ⁻⁴	-81.181	-92.985	-114.438	-288.605		
	+0.33(50-58)										
9 ¹ B _{2u}	0.90(56-79)	$\pi-\pi^*$	6.93	y	4.00 × 10 ⁻²	-100.377	-83.570	-115.280	-299.277		
9 ¹ B _{3u}	0.80(56-78)+0.42(47-59)	$\pi-\pi^*$	7.16	x	1.48 × 10 ⁻³	-75.765	-106.615	-114.821	-297.201		
10 ¹ B _{2u}	0.90(57-78)	$\pi-\pi^*$	7.21	y	9.05 × 10 ⁻²	-76.304	-102.332	-114.929	-293.565		
10 ¹ B _{3u}	-0.84(57-79)-0.40(50-58)	$\pi-\pi^*$	7.42	x	0.143	-92.987	-85.675	-114.868	-293.530		

^a Reference 27. ^b Sums of second moments of electron and nuclear charges. ^c Numbering of the orbitals is given in Table 2 and Figure 2. ^d Values in parentheses show the difference from the result of calculation C. ^e Only the symmetry-allowed states ¹B_{2u} and ¹B_{3u} were calculated

IV. Excited States

(a) Effect of Selection. We first performed large-dimension calculations C2 and C3 using the same basis sets as in calculation C.¹⁴ These calculations were carried out only for B_{3u} states with *x* polarization, and the results are shown in Table 3. We monitored the energy difference between ¹B_{3u}(Q_x band) and ²B_{3u}(B band), since the energies of these states were under- and overestimated, respectively, in calculation C. The excitation energy for the ¹B_{3u} state was certainly improved by about 0.2 eV, but the ²B_{3u} state is further overestimated by the same amount, the difference energy Δ being almost the same.

(b) Rydberg Excited States and the Effect of Rydberg Basis Set. We investigated the Rydberg excited states and the effect of Rydberg functions on the excitation energies of FBP. Table 4 gives detailed information about the excited states due to calculation A. We found that the Rydberg states appeared at 5.5–5.8 eV with small intensities, and therefore the assignment of the experimental peaks of FBP was the same as those with calculation C.¹⁴ The Rydberg orbitals shifts the Q bands by 0.05 eV to lower energy and other valence excited states (B–M bands) by 0.13–0.2 eV again to lower side: the Rydberg orbitals stabilize more the excited state than the ground state, as expected, and the effect increases as energy level of the excited state increases, again as expected. However, generally speaking, the Rydberg basis has only a secondary effect on the calculations of the valence excited states of FBP: the valence–Rydberg mixing is small as expected from the HF MOs.

The Rydberg states are distinguished from the valence states using the second moment: in Table 4, the second moments $\langle z^2 \rangle$ of the Rydberg states are about 150 *a*₀², while those of the typical valence states are 114 *a*₀². The oscillator strengths of these Rydberg states are 10⁻²–10⁻³, which are much smaller than those of the valence states except for the Q_x (¹B_{3u}) and Q_y (¹B_{2u}) states. The ⁸B_{2u} state has an oscillator strength of 1.54

× 10⁻². Thus, although the M band contains valence $\pi-\pi^*$ states (⁴B_{2u} and ⁴B_{3u}) and Rydberg states (⁵B_{3u}, ⁵B_{2u}, ⁶B_{2u}, and ⁶B_{3u}), the Rydberg states have almost no effect on the shape of the M band. Though several valence and Rydberg states were calculated at the energy region higher than that observed, i.e., 5.5 eV, only the ⁷B_{3u} and ¹⁰B_{3u} states have large oscillator strengths, 0.297 and 0.143, respectively, so that the existence of new bands is indicated at 6.6 and 7.4 eV.

(c) Effect of Polarization Function. In calculation B, we calculated the excited states of FBP over a wide energy range from visible light to UV up to 5.8 eV. The polarization of electron cloud was poorly described in calculation C, since it used only a 2p double- ζ basis set. On the other hand, calculation B uses a valence double- ζ basis set plus polarization d-functions, so that such polarization of electron cloud should be described much better, and this calculation may be expected to improve the excitation energies compared with calculation C.

In Figure 3, the SAC-CI B and C theoretical spectra are compared with the experimental spectrum in the vapor phase as measured by Edwards and Dolphin,²⁵ and Table 5 gives more detailed information on the excited states. The assignments of the main peaks having large oscillator strengths are the same as those due to calculation C. In addition, the energies and oscillator strengths of the excited states are similar to those with calculation C. However, the effects of the polarization d-functions are not monotonic to the excitation energies, unlike the effect of the Rydberg functions: some levels are shifted up but some levels are shifted down. The width is -0.22 to +0.19 eV as seen from the values in parentheses in Table 5. As seen from Figure 3, these shifts are generally small, so that the polarization function does not have a large effect on the excited states and that calculation C was almost valid for the excited states, though the dimensions calculated were small.

We see from Table 5 that the $\pi-\pi^*$ excited states are generally stabilized by the addition of the polarization functions,

TABLE 5: Excited States of Free-Base Porphin Calculated by SAC-CI Calculations B and B2

SAC-CI										
state ^a	calculation B					calculation C			calculation B2	exptl ^c
	main configurations ^b (C > 0.25)	nature	excitation ^d energy (eV)	polarization	oscillator strength	polarization	oscillator strength	excitation energy (eV)	excitation energy (eV)	excitation energy (eV)
1¹B_{3u}	0.71(56–58)–0.66(57–59)	$\pi-\pi^*$	1.77(0.02)	x	2.80×10^{-3}	x	1.13×10^{-3}	1.75	1.71	1.98 Q _x
1¹B_{2u}	–0.71(57–58)–0.66(56–59)	$\pi-\pi^*$	2.01(–0.22)	y	1.32×10^{-2}	y	5.66×10^{-3}	2.23	1.96	2.42 Q _y
1¹B_{1g}	–0.94(55–58)	$\pi-\pi^*$	3.45(–0.10)		0.0		0.0	3.55		
2¹B_{3u}	0.61(54–58)–0.58(57–59) –0.44(56–58)	$\pi-\pi^*$	3.47(–0.09)	x	0.772	x	1.03	3.56	3.44	3.33 B
2¹B_{2u}	0.67(56–59)–0.63(57–58) –0.28(54–59)	$\pi-\pi^*$	3.73(–0.02)	y	1.62	y	1.73	3.75	3.71	3.65 N
3¹B_{3u}	–0.71(54–58)–0.47(56–58) –0.40(57–59)	$\pi-\pi^*$	4.20(–0.04)	x	1.32	x	0.976	4.24	4.16	4.25 L
1¹B_{2g}	0.95(49–58)	$n-\pi^*$	4.22(0.17)		0.0		0.0	4.05		
2¹A_g	–0.94(55–59)	$\pi-\pi^*$	4.24(–0.05)		0.0		0.0	4.29		
1¹A_u	–0.94(48–58)	$n-\pi^*$	4.32(0.14)		0.0		0.0	4.18		
3¹B_{2u}	–0.89(54–59)+0.27(50–59)	$\pi-\pi^*$	4.38(–0.14)	y	0.339	y	0.350	4.52	4.35	4.67 L
1¹B_{3g}	0.95(49–59)	$n-\pi^*$	4.51(0.19)		0.0		0.0	4.37		
1¹B_{1u}	0.95(48–59)	$n-\pi^*$	4.63(0.12)	z	3.02×10^{-3}	z	5.30×10^{-3}	4.51		L
3¹A_g	0.94(57–60)	$\pi-\pi^*$	4.74(0.0)		0.0		0.0	4.74		
4¹B_{2u}	–0.89(50–59)	$\pi-\pi^*$	5.15(–0.16)	y	0.319	y	0.280	5.31	5.13	M
2¹B_{1g}	–0.72(53–59)+0.59(52–58) +0.25(51–59)	$\pi-\pi^*$	5.22		0.0		0.0			
4¹B_{3u}	–0.94(50–58)	$\pi-\pi^*$	5.44(–0.01)	x	0.295	x	0.351	5.45	5.39	5.50 M
3¹B_{1g}	–0.84(51–59)+0.43(52–58)	$\pi-\pi^*$	5.80		0.0		0.0			

^a Boldface letters show optically allowed states. ^b Numbering of the orbitals is given in Table 2 and Figure 2. ^c Reference 27. ^d Values in parentheses show the difference from the result of calculation C.

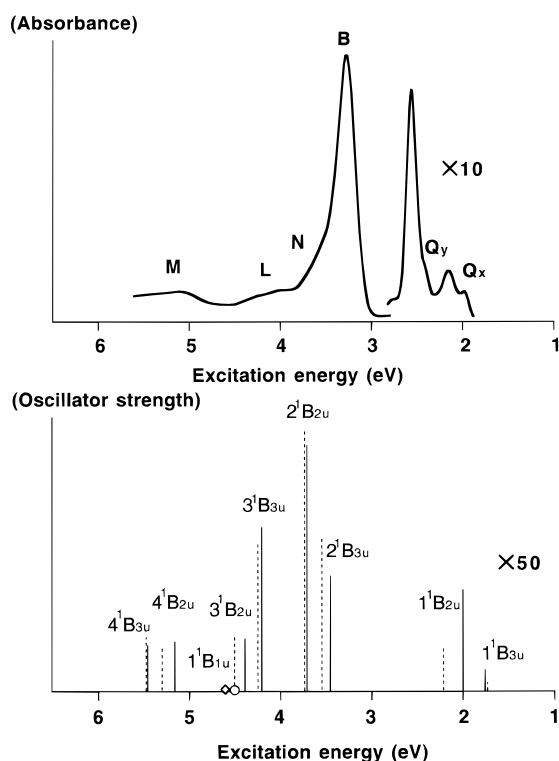


Figure 3. Electronic spectra of free-base porphin: (a) gas-phase experimental spectrum from Edwards and Dolphin and (b) SAC-CI theoretical spectra. The solid and dotted lines are the results of calculations B and C, respectively. The 1^1B_{1u} states of calculations B and C are indicated by the open diamond (\diamond) and circle (\circ), respectively.

except for the Q_x state, while the $n-\pi^*$ states are destabilized. The polarization d-functions have larger stabilization effects on the excited states than on the ground state. This is the same as the Rydberg functions studied above. On the other hand, the energies of the $n-\pi^*$ states are 0.12–0.19 eV higher than those

with calculation C. This is explained by the fact that the HF n orbitals are much stabilized by the polarization d-functions (Table 2).

In Figure 3, the 1^1B_{2u} (Q_y), 2^1B_{3u} (B), 3^1B_{2u} (L), and 4^1B_{2u} (M) states are more largely stabilized than the other states by the addition of the polarization d-functions. In case of 1^1B_{2u} state, it is expected that the excitation energy is affected by the energy change of the Gouterman 4 orbitals,¹ because the Q bands can be described well by the 4-orbital model.^{1,14} The orbital energy difference for the excitation from MO 57 to 58, which is one of the main configurations, decreases by 0.317 eV compared with that of calculation C, whereas the other counterpart, the excitation from MO 56 to 59, increases by 0.176 eV. Since the contributions of the both configurations to the excitation energy are almost equal (Table 5), 0.71 and 0.66, respectively, the 1^1B_{2u} state energy decreases. On the other hand, for the 1^1B_{3u} (Q_x) state the orbital energy differences between the MOs 56 and 58 and MOs 57 and 59 increase and decrease by 0.275 and 0.286 eV, respectively, compared with those of calculation C, and the coefficients of the former and latter configurations are comparable, 0.71 and 0.66, so that the effects are almost canceled out. Thus, the 1^1B_{3u} state energy scarcely changes.

The 2^1B_{3u} (B) state has three main configurations. Two of them are the same as the 1^1B_{3u} state; and the other is the configuration from MO 54 to 58, which is dominant in calculation B: the Gouterman 4-orbital model does not hold for the B state. As shown in the previous paper,¹⁴ the B state is a typical ionic state, so that reorganization of electron cloud following the excitation is important and therefore the polarization d-functions work to stabilize the B state.

The 3^1B_{2u} (L) and 4^1B_{2u} (M) states, both being y-polarized, have the main configurations from MO 54 to 59 and 50 to 59, respectively, and they are stabilized by 0.14 and 0.16 eV, respectively. On the other hand, the counterpart x-polarized states 3^1B_{3u} (L) and 4^1B_{3u} (M) states have main configurations from MO 54 to 58 and 50 to 58, respectively, and they are

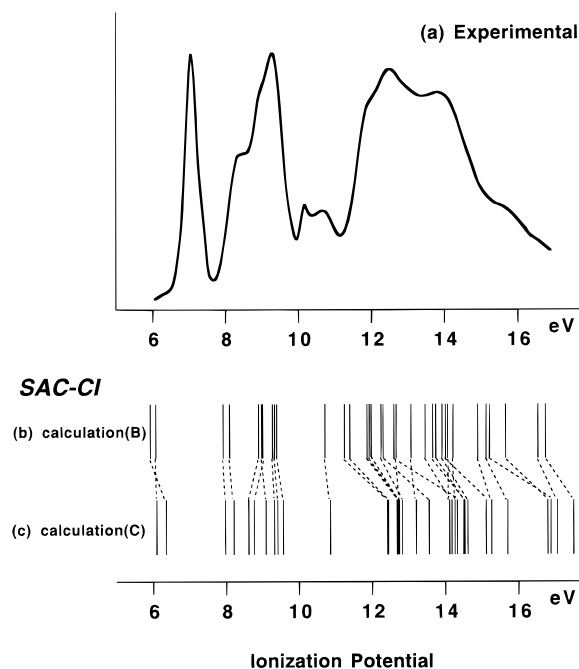


Figure 4. Ionization spectra of free-base porphyrin. (a) Photoelectron spectrum. (b) and (c) are the ionization potentials of SAC-CI calculations B and C, respectively. The dotted lines show correspondence between the ionization potentials of calculations B and C.

scarcely stabilized (0.04 and 0.01 eV, respectively). This is understood from the change in the orbital energy shown in Table 2. All the MOs involved are destabilized by the addition of the polarization d-functions except for the MO 59, and therefore, the excitations to MO 59 are stabilized relatively more largely than the excitations to MO 58.

We also performed calculations for the ${}^1B_{2u}$ and ${}^1B_{3u}$ states, adding the $\langle R(1)|H|R(1)S(1)\rangle$ and $\langle R(2)|H|R(1)S(1)\rangle$ terms in the unlinked term of SAC-CI in calculation B2. However, the effects of these unlinked terms on the excitation energies were small, as shown in Table 5.

V. Ionized States

The photoelectron spectrum of FBP was observed in the vapor phase by Dupuis et al.²⁷ and is shown in Figure 4. SAC-CI calculations B and C are compared with the experimental spectrum in Figure 4 and Table 6. The dimensions of calculation B are about 10 times larger than those of calculation C, as shown in Table 1. The polarization function has a large reorganization effect for the n and σ states, whereas this effect is small for the π states. In particular, the energies of the σ states are lowered by as large as 1 eV by the addition of the polarization functions. This result is similar to that in our previous investigation of benzene.³³

The first and second ionized states are exchanged from those of calculation C.¹⁴ This is caused by the fact that the HOMO energy is unstabilized and the next-HOMO energy is slightly stabilized due to the effect of the polarization d-function, as described in section III. Actually, only the energy of the 1A_u state (HOMO) decreases significantly, while that of the ${}^1B_{1u}$ state (next-HOMO) changes only slightly. In addition, the first and second ionized peaks observed at 6.9 and 7.2 eV are underestimated by calculation B at 5.96 and 6.08 eV, as with calculation C, despite the use of polarization d-functions. This could be due to the fixed D_{4h} structure or poor primitive basis sets.

TABLE 6: Ionized States of Free-Base Porphyrin by SAC-CI Calculations B and C

state	main configuration ^a (C > 0.3)	nature	exptl ^b (eV)	SAC-CI calculations (eV)		
				B	C	Δ^c
1A_u	-0.98(57)	π	6.9	5.96	6.35	-0.39
${}^1B_{1u}$	0.98(56)	π	7.2sh	6.08	6.09	-0.01
${}^1B_{3g}$	0.98(55)	π	8.4	7.91	7.98	-0.07
${}^2B_{1u}$	-0.97(54)	π		8.13	8.21	-0.08
1A_g	-0.97(49)	n	8.8sh	8.88	8.65	+0.23
${}^1B_{2g}$	0.77(53)+0.61(51)	π		8.97	9.10	-0.13
${}^1B_{2u}$	-0.97(48)	n	9.11	9.00	8.79	+0.21
${}^3B_{1u}$	0.97(50)	π		9.29	9.34	-0.05
${}^2B_{2g}$	0.77(51)+0.61(53)	π		9.33	9.42	-0.09
${}^2B_{3g}$	0.98(52)	π		9.37	9.54	-0.17
2A_u	0.98(47)	π	10.17	10.70	10.85	-0.15
${}^1B_{1g}$	-0.97(46)	σ	10.67	11.25	12.40	-1.15
${}^1B_{3u}$	-0.94(45)	σ		11.37	12.43	-1.06
${}^2B_{2u}$	-0.88(44)+0.39(39)	σ	11.83sh	11.85	12.77	-0.92
${}^2B_{1g}$	0.96(42)	σ		11.90	12.67	-0.77
${}^2B_{3u}$	-0.95(41)	σ		11.98	12.69	-0.71
2A_g	-0.96(38)	σ		12.27	12.83	-0.56
${}^3B_{2u}$	0.89(39)+0.40(44)	σ		12.30	13.54	-1.24
3A_g	0.95(43)	σ	12.5	12.57	14.34	-1.77
${}^4B_{1u}$	-0.97(40)	π		12.63	12.74	-0.11
${}^3B_{3g}$	-0.97(37)	π		13.06	13.19	-0.13
${}^3B_{1g}$	0.95(36)	σ		13.43	14.16	-0.73
${}^3B_{3u}$	-0.96(35)	σ		13.66	14.52	-0.86
${}^4B_{2u}$	-0.97(34)	σ	13.8	13.75	14.51	-0.76
${}^4B_{1g}$	-0.95(30)	σ		13.94	14.62	-0.68
4A_g	0.95(32)	σ		14.01	15.11	-1.10
${}^3B_{2g}$	0.97(33)	π		14.06	14.13	-0.07
${}^5B_{1u}$	-0.97(31)	π		14.18	14.25	-0.07
${}^4B_{3u}$	-0.97(29)	σ		14.88	15.27	-0.39
5A_g	-0.97(28)	σ		15.12	15.69	-0.57
${}^5B_{3u}$	0.96(27)	σ		15.21	16.89	-1.68
${}^5B_{2u}$	0.95(26)	σ	15.6	15.64	16.81	-1.17
6A_g	0.97(25)	σ		16.53	17.03	-0.50
${}^6B_{2u}$	0.95(24)	σ		16.71	17.49	-0.78
${}^5B_{1g}$	0.96(23)	σ		17.17	18.52	-1.35
${}^6B_{3u}$	0.97(22)	σ		17.78	18.72	-0.94
${}^6B_{1g}$	-0.96(21)	σ		18.01	19.49	-1.48
7A_g	0.95(20)	σ		18.29	19.40	-1.11
${}^7B_{2u}$	-0.97(19)	σ		18.77	19.73	-0.96
${}^7B_{3u}$	-0.97(18)	σ		19.38	20.00	-0.62
${}^7B_{1g}$	-0.96(17)	σ		19.53	20.87	-1.34
8A_g	0.96(16)	σ		19.72	20.52	-0.80

^a Numbering of the orbitals is given in Table 2 and Figure 2. ^b Reference 28. ^c Δ is the difference between SAC-CI calculations B and C.

The ionization energies of the 1A_g and ${}^1B_{2u}$ states with n nature increase and reflect the change in MO energies as described in section III. Furthermore, the peaks at 10~11 eV are reassigned. The energy of the ${}^2B_{3g}$ state, 9.54 eV in calculation C, which was assigned to the experimental lower peak at 10.17 eV,¹⁴ becomes even lower in calculation B, 9.37 eV, so that this state is reassigned to the higher side of the large peak at around 9 eV. The 2A_u state with π nature, 10.70 eV in calculation B, is then reassigned to the experimental lower peak, 10.17 eV. In addition, the energies of the higher states, ${}^1B_{1g}$ and ${}^1B_{3u}$ with σ nature, decrease about 1 eV compared to those with calculation C, so that these two states, 11.25 and 11.37 eV, are assigned to the experimental higher broad peak at 10.67 eV. This tendency is also seen with the other higher σ states: the reorganization occurs in the higher energy region. Overall, the description of the ionization spectrum is improved by an addition of the polarization functions.

We here performed SAC-CI SD-R calculations, in which only single and double-excitation operators were included in the SAC-CI linked operators. This level of calculation is known

good for the main peaks of the ionization spectra.⁴³ However, for shake-up peaks, which involve two- and even higher electron processes,^{35,44,45} SAC-CI calculations using general-R operators (SAC-CI general-R) should be performed,^{44,45} though at the present stage, the computer code we have now is not efficient enough for this type of calculation. This is an interesting calculation to be done in future.

VI. Conclusions

The ground, excited, and ionized states of FBP were recalculated by the SAC/SAC-CI method with adding Rydberg s and p functions on all of the nitrogen atoms (calculation A) and with adding polarization d-functions on all of the nitrogen and carbon atoms (calculation B). The lowest Rydberg excited state appeared at around 5.5–5.8 eV with a weak intensity, but the valence–Rydberg mixing was small. The effects of the polarization and Rydberg functions were relatively small for the excitation energies of the main peaks, whereas the polarization functions affected rather largely the ionization spectrum. Therefore, the previous calculation C with 2p double- ζ basis sets was valid for the excited states but not enough for the ionized states.

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