

Coupled-cluster calculations of the electronic excitation spectrum of free base porphrin in a polarized basis

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Similarity transformed equation-of-motion coupled-cluster calculations on the excited states of free base porphrin are reported. These are the first calculations to use polarization functions for all of the excited states, and the polarization functions are found to be very important for accurately describing the optically allowed states. These calculations strongly support the traditional interpretation of the electronic spectrum of free base porphrin. © 1998 American Institute of Physics. [S0021-9606(98)01816-9]

I. INTRODUCTION

Because of their importance in such biological processes as photosynthesis, electron transfer, and oxygen absorption and transport, the porphyrins have been extensively studied.¹ As the base molecule for the porphyrins, the electronic spectrum of free base porphrin has received much attention, both with semiempirical (see, for example, Ref. 2) and *ab initio* methods.³⁻⁸ The interesting part of the spectrum (see Fig. 1) consists of, in order, two visible peaks known as the Q bands, a very intense peak known as the B (or Soret) band, a shoulder on the B band, called the N band, and two other small peaks, the L and M bands.

The traditional interpretation of the spectrum is that, with the molecule in the *xy* plane and with the two internal hydrogens along the *x* axis, the lowest-energy band, the Q_x band, comes from exciting to the 1^1B_{3u} state. The Q_y band then comes from the 1^1B_{2u} , with the B band assigned to the 2^1B_{3u} and 2^1B_{2u} states.³ Nakatsuji *et al.*,⁷ based on their SAC-CI (symmetry adapted cluster-configuration interaction) calculations,⁹ reassigned the spectrum. They agreed with the assignments of the Q bands, but they claimed that the B band should be assigned to only the 2^1B_{3u} state, with the N band being the 2^1B_{2u} state.

However, their results have three significant weaknesses. The first is the method used. In principle SAC-CI energies (but not oscillator strengths) could be equivalent to EOM-CCSD (equation-of-motion coupled-cluster singles and doubles)¹⁰ and coupled-cluster singles and doubles linear response¹¹ energies. In practice, though, some nonlinear terms in the underlying ground state coupled-cluster result are always omitted. Also, in these calculations many double excitations were omitted, based on a perturbation selection.⁷ For complex organic molecules, even the untruncated EOM-CCSD may not be sufficient. In a study of benzene and the azabenzenes, EOM-CCSD had an average error of 0.32 eV for the $\pi \rightarrow \pi^*$ states.¹² SAC-CI should do no better than this, unless it has some fortuitous error cancellations.

The second criticism is the basis set used. Nakatsuji *et al.*⁷ discuss the importance of σ rearrangement to the excitation energies, yet their basis set only had $2s$ -type and $2p$ -type functions on the carbons and nitrogens, giving it no

flexibility to describe the $2s$ orbitals. They also dropped some of the occupied and virtual orbitals corresponding to the $2s$ orbitals, along with all of the $1s$ orbitals on the carbons and nitrogens. The result is that the basis set had limited flexibility, no polarization functions, and no diffuse functions. The lack of diffuse and polarization functions corresponds to the conventional viewpoint that, for at least the lowest states of free base porphrin, polarization and diffuse functions are not needed.⁶

Finally, there is a problem with the oscillator strengths. The N band appears as a shoulder to the B band, but Nakatsuji *et al.*⁷ calculate the excitation to the 2^1B_{2u} state to have an oscillator strength 68% larger than the excitation to the 2^1B_{3u} state. They argue that the N band is actually quite broad, with the B band being a narrow peak on top of it. But if that is true, then the splitting between the vertical excitation energies for the B and N bands would be less than the 0.32 eV reported.¹³ To answer some of these questions, a series of STEOM-CCSD (similarity transformed equation-of-motion coupled-cluster singles and doubles)¹⁴ excited state calculations have been performed.

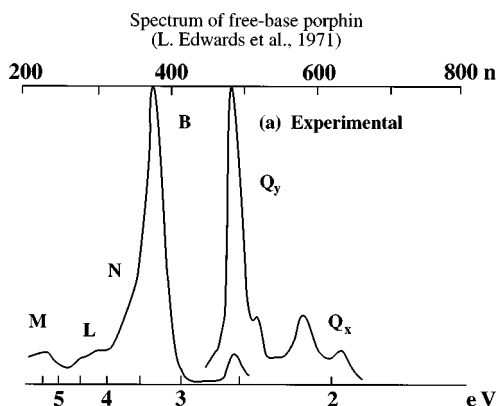


FIG. 1. The electronic absorption spectrum of free base porphrin, with the relevant bands labeled [from Edwards *et al.* (Ref. 13) and Nakatsuji *et al.* (Ref. 7)].

TABLE I. Ionization potentials (in eV) for free base porphyrin.

	SAC-CI ^a	STEOM-CC ^b	“D _{4h} ”			“Opt”		Expt. ^c
			DZ	Diffuse	Polarized	DZ	Diffuse	
1 ² A _u (π)	6.35	6.34	6.65	6.63	6.66	6.71	6.69	6.9
1 ² B _{1u} (π)	6.09	6.16	6.46	6.43	6.68	6.48	6.46	7.2
1 ² B _{3g} (π)	7.98	7.84	8.11	8.09	8.19	8.29	8.27	8.4
2 ² B _{1u} (π)	8.21	8.11	8.38	8.36	8.43	8.53	8.51	8.8
1 ² A _g (n)	8.65	8.50	8.78	8.76	9.18	8.96	8.94	9.1
1 ² B _{2g} (π)	9.10	8.79	9.08	9.06	9.20	9.01	8.99	
1 ² B _{2u} (n)	8.79	8.57	8.84	8.82	9.23	8.99	8.96	
3 ² B _{1u} (π)	9.34	9.10	9.37	9.36	9.47	9.22	9.20	
2 ² B _{2g} (π)	9.42	9.22	9.50	9.47	9.55	9.43	9.41	
2 ² B _{3g} (π)	9.54	9.31	9.59	9.57	9.64	9.66	9.63	
2 ² A _u (π)	10.85	10.43	10.71	10.69	10.72	10.76	10.74	

^aReference 7.^bReference 8.^cReference 26.

II. COMPUTATIONAL DETAILS

A. STEOM-CC

In a STEOM-CCSD^{14, 15} calculation (i.e., a STEOM-CC calculation¹⁴ based on a CCSD¹⁶ ground state), two similarity transformations are applied to the second quantized Hamiltonian, such that the one- and two-body terms in the Hamiltonian that increase the excitation level are set to zero. This effectively blocks the Hamiltonian matrix by the excitation level, so that the single excitations can be accurately calculated with a diagonalization over just the singles-singles block. The higher excitation parts of the excited state wave function are then implicitly included through the similarity transformations. In this way, STEOM-CC has the same conceptual appeal as monoexcited CI, but now in a fully correlated structure. The STEOM-CCSD method has been implemented into ACES II.¹⁷

The first similarity transformation, the same as in EOM-CCSD,¹⁰ involves the T amplitudes from a ground state CCSD¹⁶ calculation. The new Hamiltonian is then

$$\bar{H} = e^{-T} H e^T. \quad (1)$$

The next step is to solve for a set of states with one electron removed and one electron added by means of the IP-EOM-CCSD (ionization potential EOM-CCSD)¹⁸ and the EA-EOM-CCSD (electron attachment EOM-CCSD)¹⁹ methods. These involve diagonalizing \bar{H} over the space of $1h - 2h1p$ and $1p - 2p1h$ determinants, respectively. These eigenvectors are used to determine the S coefficients in the second similarity transformation,

$$G = \{e^S\}^{-1} \bar{H} \{e^S\}. \quad (2)$$

The final double similarity transformed Hamiltonian G is then diagonalized over the space of single excitations. For a detailed description of the method, see Ref. 15.

In the current implementation the final wave function in terms of G has only single excitations, limiting the method to only singly excited states, but in terms of the normal Hamiltonian, the wave function actually includes all possible excited determinants (with only the singles having optimized coefficients). Specifically, the wave function contains double

excitations in the form of S_2R and T_1R , and triple excitations in the form of S_2^2R , T_2R , and T_1S_2R . Here, R is the STEOM-CC single excitation eigenvector.

Since the higher excitations and the differential correlation between the ground and excited states are described via the S operator, it is critical that the excitation be described within the set of active orbitals chosen for the IP-EOM-CC and EA-EOM-CC calculations and included in S . In the calculations presented here, the active components of the excitations are almost always above 99% and in all singlets are above 98%. In test calculations the energy seems to be converged to within 0.05 eV when the active component is 98%.¹⁴

B. Basis set and geometry

The basis set used for the calculations presented here come from the large ANO basis set of Widmark, Malmqvist, and Roos.^{20,21} This is a very large, generally contracted basis set. It has $14s9p4d3f$ primitives for carbon and nitrogen and $8s4p3d$ primitives for hydrogen. From this set, the first $3s$ and $2p$ contractions were used for C and N and the first s contraction was selected for H. This basis set, consisting of 230 functions, was the same as used by Merchán *et al.*⁶ It is the same number of contracted functions as that used by Nooijen and Bartlett,⁸ but their basis set had a much smaller set of primitives. This set is also significantly larger than the one used by Nakatsuji *et al.*⁷

This basis set was then extended in two different ways. First, to gauge the effect of polarization functions on the excitation energies, the first d contraction from the ANO set was added on the carbon and nitrogen atoms, while the sec-

TABLE II. Electron affinities (in eV) for free base porphyrin.

	IP-EOM-CC ^a	“D _{4h} ”			“Opt”	
		DZ	Diffuse	Polarized	DZ	Diffuse
1 ² B _{2g}	0.50	0.83	0.81	1.07	0.80	0.78
1 ² B _{3g}	0.37	0.70	0.67	0.99	0.78	0.76

^aReference 8.

TABLE III. Singlet excited states of free base porphyrin through 5.33 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D _{4h} "			"Opt"	
	DZ	Diffuse	Polarized	DZ	Diffuse
¹ B _{3u} (V)	1.70 (—)	1.70 (—)	1.75 (0.0007)	1.71 (0.0003)	1.71 (0.0004)
¹ B _{2u} (V)	2.59 (0.018)	2.59 (0.017)	2.40 (0.013)	2.65 (0.007)	2.65 (0.006)
¹ B _{1g} (V)	3.57	3.56	3.44	3.77	3.78
¹ B _{3u} (V)	3.64 (0.982)	3.63 (0.981)	3.47 (0.693)	3.71 (1.21)	3.71 (1.23)
¹ B _{2u} (V)	3.74 (1.36)	3.74 (1.37)	3.62 (1.20)	3.78 (1.46)	3.77 (1.48)
¹ A _g (V)	4.04	4.04	3.95	4.09	4.10
¹ B _{2g} (V)	4.05	4.05	4.21	4.25	4.25
¹ A _u (V)	4.09	4.09	4.24	4.26	4.26
¹ B _{3u} (V)	4.22 (0.721)	4.22 (0.741)	4.06 (0.931)	4.34 (0.494)	4.35 (0.501)
¹ B _{3g} (V)	4.43	4.41	4.51	4.55	4.54
¹ B _{1g} (V)	4.44	4.44	4.53	4.41	4.41
¹ B _{1u} (V)	4.50 (0.004)	4.48 (0.003)	4.56 (0.002)	4.59 (0.004)	4.58 (0.005)
¹ B _{1u} (R)	7.18 (0.008)	4.51 (0.006)	5.48 (0.013)	7.23 (0.006)	4.54 (0.004)
¹ B _{2u} (V)	4.63 (0.441)	4.63 (0.444)	4.35 (0.422)	4.65 (0.239)	4.66 (0.241)
¹ A _g (V)	4.67	4.66	4.46	4.72	4.72
¹ A _u (R)	7.33	4.72	5.52	7.40	4.78
¹ B _{2g} (R)	6.63	4.74	5.89	6.63	4.78
¹ B _{1g} (V)	4.79	4.78	4.66	4.67	4.67
¹ B _{3g} (R)	6.78	4.82	6.04	6.80	4.84
¹ A _g (R)		4.89			4.94
¹ B _{3g} (R)	6.83	4.94	5.91	6.87	5.01
¹ A _g (V)	5.00	4.99	4.87	5.01	5.02
¹ B _{2g} (R)	6.97	5.01	6.08	7.03	5.06
¹ A _u (R)	7.14	5.07	6.62	7.14	5.09
¹ B _{1g} (R)		5.13			5.19
¹ B _{1u} (R)		5.14 (0.0006)	6.89 (0.000 003)	7.93 (0.002)	5.17 (0.0005)
¹ B _{1u} (R)		5.20 (0.001)			5.22 (0.0008)
¹ B _{2u} (V)	5.22 (0.172)	5.22 (0.182)	5.00 (0.153)	5.06 (0.290)	5.07 (0.312)
¹ B _{3u} (R)		5.23 (0.007)			5.28 (0.010)
¹ A _g (V)	5.28	5.25	5.12	5.26	5.27
¹ B _{1g} (V)	5.26	5.26	5.04	5.25	5.25
¹ B _{1u} (R)		5.28 (0.000 008)		7.37 (0.000 02)	5.33 (0.000 02)
¹ B _{2u} (R)		5.31 (—)		6.65 (0.075)	5.32 (0.002)
¹ A _u (R)	8.19	5.33	6.78	8.22	5.40
¹ B _{3u} (V)	5.33 (0.400)	5.33 (0.387)	5.17 (0.272)	5.22 (0.471)	5.23 (0.476)

ond *s* function was added to the hydrogens. This gave a [3*s*2*p*1*d*] set on C and N and a [2*s*] set on H, with a total of 364 contracted functions. In other calculations, to gauge the effect of diffuse functions on the excited states, a set of 2*s* and 2*p* uncontracted functions were added to the center of the molecule and to the geometrical center of each ring. The diffuse exponents were taken from Ref. 22, and have been used for naphthalene²² and biphenyl,²³ where they were placed at the center of the molecule. Since two functions of

each type were used, the exact exponent chosen should not matter significantly. In all calculations the first 24 occupied orbitals, corresponding to the 1*s* orbitals on carbon and nitrogen, were left uncorrelated.

Two different geometries were used in this study. The first is an idealized x-ray structure,²⁴ where the molecule, without the two internal hydrogens, is constrained to be *D*_{4h} symmetry. The internal hydrogens make it *D*_{2h}. It was used in several of the previous studies^{7, 8} and will be referred to as

TABLE IV. Singlet excited states of free base porphyrin from 5.39 to 6.23 eV. Energies are in eV. Oscillator strengths are given in parentheses below the excitation energies.

	"D _{4h} "			"Opt"	
	DZ	Diffuse	Polarized	DZ	Diffuse
¹ A _u (R)		5.39			5.45
¹ B _{2u} (R)		5.45			5.52
		(0.002)			(0.001)
¹ B _{2g} (R)	7.84	5.46	7.43	7.90	5.48
¹ B _{3g} (R)		5.47		7.91	5.50
¹ B _{3u} (R)		5.50			5.55
		(—)			(—)
¹ B _{1u} (R)		5.51			5.54
		(0.001)			(0.001)
¹ B _{2g} (R)		5.53			5.55
¹ B _{3g} (R)		5.56			5.58
¹ A _g (R)		5.57			5.60
¹ A _g (R)		5.61			5.64
¹ B _{3g} (R)		5.65	7.50		5.71
¹ B _{2g} (R)		5.66			5.68
¹ B _{2g} (R)		5.66			5.72
¹ B _{3g} (R)		5.68			5.70
¹ A _g (R)		5.69			5.72
¹ A _g (R)		5.71			5.77
¹ B _{3g} (R)		5.72			5.78
¹ B _{1u} (R)		5.72			5.74
		(0.000 04)			(0.000 07)
¹ A _g (R)	5.71	5.72	5.51	5.68	5.68
¹ A _u (R)		5.73			5.75
¹ B _{1u} (R)		5.75			5.78
		(0.001)			(0.0007)
¹ B _{2g} (R)		5.75			5.81
¹ B _{3u} (R)		5.76			5.80
		(0.002)			(0.0005)
¹ B _{1g} (R)		5.78			5.84
¹ B _{2u} (R)		5.80			5.82
		(0.002)			(0.002)
¹ B _{1g} (R)		5.80			5.85
¹ A _u (R)		5.82			5.84
¹ B _{3g} (R)		5.85			5.92
¹ B _{2g} (R)		5.87			5.93
¹ B _{1g} (R)	5.88	5.88	5.59	5.88	5.90
¹ B _{2g} (R)		5.90			5.92
¹ B _{1g} (R)		5.90			5.96
¹ B _{3g} (R)		5.91			5.93
¹ B _{3g} (R)		5.91			5.95
¹ B _{2g} (R)		5.92			5.94
¹ A _u (R)		5.92			5.99
¹ B _{1u} (R)		5.93			5.99
		(0.000 05)			(0.000 002)
¹ A _u (R)		5.94			6.00
¹ A _g (R)		5.95			5.98
¹ B _{2u} (R)		5.97			6.03
		(0.001)			(0.0008)
¹ B _{3g} (R)	7.89	5.99	6.73		6.10
¹ B _{3u} (R)		5.99			6.05
		(—)			(—)
¹ B _{1u} (R)	7.94	6.00	6.70		6.07
	(0.091)	(0.006)	(0.021)		(0.001)
¹ A _g (R)		6.01			6.03
¹ B _{1u} (R)	7.81	6.01	6.72		6.39
	(0.003)	(0.006)	(0.020)		(0.006)
¹ B _{1u} (R)		6.04			6.06
		(0.001)			(0.005)
¹ B _{2g} (R)		6.05			6.08
¹ B _{3g} (R)		6.08			
¹ B _{3g} (R)					6.11
¹ B _{1u} (R)					6.15
					(0.018)
¹ B _{3g} (R)		6.09			6.16
¹ B _{2g} (R)		6.10			6.16
¹ B _{1u} (R)		6.10			6.12
		(0.0003)			(0.005)
¹ B _{2g} (R)		6.13			6.19
¹ A _u (R)		6.14			6.17
¹ B _{1g} (R)		6.17			6.24
¹ B _{1u} (R)		6.19			6.21
		(0.022)			(0.023)
¹ A _g (R)		6.19			6.28
¹ B _{1g} (R)		6.20			6.25
¹ B _{3u} (V)	6.20	6.20	6.07		6.33
	(0.166)	(0.160)	(0.182)		(0.110)
¹ A _u (R)		6.23			6.29

“ D_{4h} .” With the $[3s2p/1s]$ basis set, this geometry had a SCF energy of $-982.955\,034$ Hartrees and a CCSD energy of $-985.154\,443$ Hartrees. The $[3s2p1d/2s]$ basis set gave a SCF energy of $-983.416\,854$ Hartrees and a CCSD energy of $-986.676\,253$ Hartrees. The basis with the diffuse functions gave a SCF energy of $-982.967\,070$ Hartrees and a CCSD energy of $-985.182\,042$ Hartrees.

The other geometry is a B3PW91/6-31G* optimized geometry,²⁵ which will be referred to as “Opt.” It also has D_{2h} symmetry. This geometry gave a SCF energy of $-982.964\,858$ Hartrees and a CCSD energy of $-985.163\,441$ Hartrees with the $[3s2p/1s]$ basis set. The diffuse basis gave a SCF energy of $-982.977\,085$ Hartrees and a CCSD energy of $-985.191\,231$ Hartrees. The $[3s2p1d/2s]$ basis gave a SCF energy of $-983.430\,681$ Hartrees and a CCSD energy of $-986.688\,179$ Hartrees, putting this geometry 7.5 kcal/mol below the “ D_{4h} ” geometry.

III. RESULTS

A. Ionized and electron attached states

In all of the current calculations, the occupied part of the active space consisted of 11 orbitals. Therefore, 11 IP-EOM-CCSD states were calculated. In Table I the current results, with the three basis sets, are compared with the SAC-CI results,⁷ with the previous STEOM-CC results,⁸ and with experiment.²⁶ Because of the low resolution of the experimental spectrum, it is very difficult to relate the measured peaks to the calculated states. Therefore, the assignments given should be considered very tentative.

While adding the diffuse functions does little to change the ionization potentials, every other time that the basis set was enlarged, from the previous STEOM-CC results,⁸ to the DZ (the $[3s2p/1s]$ basis) results, to the polarized (the $[3s2p1d/2s]$ basis) results, the electron became more bound. Adding the polarization functions had the most dramatic effect. It caused the first two states to switch and the sixth and seventh states to switch. However, the differences are close to an order of magnitude smaller than the errors in the calculations, so nothing can be said definitively. Going from the “ D_{4h} ” geometry to the “Opt” geometry had effects of less than 0.2 eV. The “Opt” geometry typically had larger IPs.

Twenty-three virtual orbitals ($4a_g$, $2b_{1g}$, $3b_{2g}$, $3b_{3g}$, $3a_u$, $2b_{1u}$, $3b_{2u}$, and $3b_{3u}$) were included in the active space for the DZ and the polarized basis sets. For the diffuse basis set several more orbitals had to be included. The diffuse basis added 40 Rydberg orbitals, and most of them had orbital eigenvalues very close to zero. Therefore, to include all of the equivalent orbitals that were included for the DZ basis, the active space needed to consist of 59 virtual orbitals. But that many orbitals caused convergence problems. The final set included in the active space consisted of 51 virtual orbitals ($10a_g$, $4b_{1g}$, $5b_{2g}$, $5b_{3g}$, $3a_u$, $8b_{1u}$, $5b_{2u}$, and $5b_{3u}$). If an IP-EOM-CC or an EA-EOM-CC eigenvector is less than 70% singles, the code automatically excludes it from the second similarity transformation. For the diffuse basis, one of the B_{3g} states was excluded, leaving 50 states for the similarity transformation.

TABLE V. Triplet excited states of free base porphyrin through 4.92 eV. Energies are in eV.

	“ D_{4h} ”			“Opt”	
	DZ	Diffuse	Polarized	DZ	Diffuse
$^3B_{2u}(V)$	1.19	1.19	1.26	1.15	1.15
$^3B_{3u}(V)$	1.82	1.83	1.80	1.87	1.88
$^3B_{2u}(V)$	2.02	2.02	1.85	2.07	2.07
$^3B_{3u}(V)$	2.29	2.28	1.98	2.31	2.31
$^3B_{1g}(V)$	2.96	2.97	2.87	3.09	3.10
$^3B_{3u}(V)$	3.10	3.11	2.98	3.21	3.21
$^3A_g(V)$	3.49	3.48	3.33	3.61	3.61
$^3B_{1g}(V)$	3.50	3.50	3.45	3.47	3.47
$^3A_g(V)$	3.81	3.81	3.64	3.82	3.82
$^3B_{1g}(V)$	4.02	4.02	3.93	3.83	3.84
$^3B_{2g}(V)$	4.04	4.04	4.19	4.24	4.24
$^3B_{2u}(V)$	4.08	4.08	3.85	3.90	3.90
$^3A_u(V)$	4.10	4.10	4.23	4.27	4.27
$^3B_{3g}(V)$	4.15	4.14	4.29	4.27	4.26
$^3B_{1u}(V)$	4.20	4.18	4.33	4.28	4.27
$^3B_{2u}(V)$	4.23	4.24	4.07	4.29	4.31
$^3A_g(V)$	4.48	4.47	4.31	4.47	4.47
$^3B_{1u}(R)$	7.17	4.50	5.43	7.22	4.52
$^3A_u(R)$	7.29	4.71	5.49	7.36	4.77
$^3B_{2g}(R)$	6.57	4.73	5.85	6.58	4.77
$^3B_{1g}(V)$	4.76	4.74	4.57	4.82	4.82
$^3B_{3g}(R)$	6.71	4.81	5.98	6.72	4.83
$^3A_g(R)$		4.90			4.94
$^3B_{3u}(V)$	4.92	4.92	4.74	4.83	4.83

In each of the calculations two positive electron affinities were predicted. They are listed in Table II. The other electron attached states, even though they do not correspond to stable states, are still essential for the calculation of the excited states. They go into the second similarity transformation and help describe the differential correlation between the ground and excited states.

B. Excited states

The singlet excited states of free base porphyrin are listed in Tables III and IV, and the triplet excited states are in Tables V and VI. The important states will be discussed later, but some general comments can be made. The first is that the Rydberg states start about 4.5 eV, which is right in the region of most interest. It has been hypothesized that if the Rydberg states of the related chlorophylls were low enough, they could participate in photosynthesis.²⁶ The second is that the addition of the diffuse functions never changes the energy of the valence states by more than 0.02 eV. This has several consequences. It implies that the DZ basis set has diffuse enough tails that the diffuse functions are not needed to describe the valence region. It also means that there is essentially no mixing between Rydberg and valence excited states. Finally, it suggests that adding diffuse functions to the polarized basis would not significantly change the energetics. Adding diffuse functions might, however, have an effect on the oscillator strengths. Those tend to change a little with the addition of the diffuse functions.

In general, going from the “ D_{4h} ” geometry to the “Opt” geometry has little effect on the spectrum. The excitation energy typically increases by about 0.1 eV. The im-

TABLE VI. Triplet excited states of free base porphyrin from 4.93 to 6.11 eV. Energies are in eV.

	"D _{4h} "			"Opt"	
	DZ	Diffuse	Polarized	DZ	Diffuse
³ B _{3g} (R)	6.80	4.93	5.89	6.84	5.01
³ A _g (V)	4.98	4.97	4.76	4.97	4.97
³ B _{2g} (R)	6.50	5.01	6.05	7.00	5.06
³ A _u (R)	7.02	5.06	6.53	7.02	5.08
³ B _{1g} (R)		5.10			5.18
³ B _{1u} (R)		5.13	6.87	7.79	5.17
³ B _{1u} (R)		5.20			5.22
³ B _{1g} (V)	5.24	5.24			5.23
³ B _{3u} (R)		5.24	5.27		5.28
³ B _{1u} (R)	7.34	5.28	6.70	7.37	5.33
³ B _{2u} (R)		5.30			5.32
³ A _u (R)		5.32	6.76	8.19	5.39
³ B _{2u} (R)		5.39	5.28		5.50
³ A _u (R)		5.39			5.45
³ B _{2g} (R)	7.74	5.45		7.80	5.48
³ B _{3g} (R)		5.47			5.49
³ B _{3u} (R)		5.49			5.55
³ B _{3u} (R)	5.51	5.51		5.57	5.63
³ B _{1u} (R)		5.51			5.53
³ B _{2g} (R)		5.52			5.55
³ B _{3g} (R)		5.55			5.57
³ B _{2u} (R)	5.52	5.56		5.59	5.66
³ A _g (R/V)		5.56	5.26	5.59	5.57
³ A _g (R)		5.57			5.60
³ A _g (R)		5.64			5.66
³ B _{3g} (R)		5.65		8.09	5.71
³ B _{2g} (R)		5.66			5.68
³ B _{2g} (R)		5.66			5.72
³ B _{2g} (R)		5.68			5.70
³ A _g (R)		5.70			5.72
³ A _u (R)		5.71			5.77
³ B _{3g} (R)		5.71			5.78
³ B _{1u} (R)		5.71			5.74
³ A _u (R)		5.72			5.75
³ B _{2g} (R)		5.75			5.80
³ B _{1u} (R)		5.75			5.78
³ B _{3u} (R)		5.77			5.80
³ B _{1g} (R)		5.77			5.84
³ B _{2u} (R)		5.80			5.82
³ B _{1g} (R)		5.80			5.87
³ A _u (R)		5.82			5.84
³ B _{3g} (R)		5.85			5.92
³ B _{2g} (R)		5.87			5.93
³ B _{1g} (R)		5.88			5.95
³ B _{3g} (R)		5.89			6.07
³ B _{2g} (R)		5.89	6.64		5.92
³ B _{3g} (R)		5.91			5.93
³ B _{2g} (R)		5.92			5.94
³ A _u (R)		5.92			5.98
³ B _{1u} (R)		5.93			5.99
³ A _u (R)		5.94			6.00
³ B _{1u} (R)	7.75	5.96	6.63		6.09
³ B _{1g} (R)		5.96			6.06
³ B _{2u} (R)		5.96			6.03
³ B _{3g} (R)		5.96			5.94
³ A _g (R)		5.97			5.99
³ B _{3u} (R)	5.97	5.97	5.77	6.05	6.07
³ B _{3u} (R)		6.00			6.04
³ A _g (R)		6.00			6.03
³ B _{1u} (R)		6.01			6.06
³ B _{1u} (R)		6.04			6.06
³ B _{2g} (R)		6.05			6.08
³ B _{3g} (R)		6.08			6.11
³ B _{3g} (R)		6.09			6.15
³ B _{2g} (R)		6.10			6.16
³ B _{1u} (R)		6.10			6.13
³ B _{3g} (R)		6.11			6.31

portant exceptions are the ¹B_{2u} state, which drops from 5.22 to 5.07 eV, and the ¹B_{3u} state, which drops from 5.33 to 5.23 eV.

A note should be made about the oscillator strengths. The oscillator strengths are calculated as

$$f = \frac{2}{3} \omega_x \langle \tilde{\Psi}_g | \mu | \Psi_x \rangle \langle \tilde{\Psi}_x | \mu | \Psi_g \rangle, \quad (3)$$

where ω is the excitation energy. The right-hand ground state is the coupled-cluster wave function, the left-hand ground state is the lambda solution from coupled-cluster theory,²⁷ and the right-hand excited state is the STEOM-CC state. Currently, several approximations are introduced when calculating the left-hand excited state.¹⁴ These sometimes can cause numerical problems with the properties calculated. When the oscillator strength is listed as (—), it means that the approximations are too severe, and the calculated oscillator strength is unreliable. Since the energies are calculated with the right-hand excited state wave function, they are still correct. For the polarized basis results, another approximation is made. Because the cost of calculating the ground state lambda vector is prohibitive for that large a basis set, the left-hand ground state is estimated with the same approximations as the excited state left-hand wave function. In a test calculation with the DZ basis, this makes a difference in the oscillator strengths of less than 20% in every case. Even for the properly calculated oscillator strengths, errors of 20% or more are possible.

The "D_{4h}" geometry, polarized basis results for the singlet valence states from Tables III and IV are listed in Table VII, along with CASPT2,⁶ SAC-CI,⁷ previous STEOM-CC,⁸ and EOM-CCSD results. The EOM-CCSD calculation is at the "D_{4h}" geometry with the DZ basis. The valence states are numbered for convenience, but these numbers are only accurate through ³B_{1g}. After that the Rydberg states should enter into the numbering.

The energy of the first triplet state has been measured in frozen solvent at 77 K.²⁸ The phosphorescence peak is at 1.58 eV, well above our polarized basis result of 1.26 eV. The CASPT2 result is between the two at 1.37 eV.⁶

IV. DISCUSSION

The recent controversy over the assignment of the spectrum centers around how to assign the N band. The argument of Nakatsuji *et al.*,⁷ essentially, is that they calculated no other optically allowed states in the 3–4 eV range, and, therefore, by default, the N band must be ²B_{2u}. Table VII shows the poor quality of their results. Had they used a decent basis set and had they not made the approximations that are always used in their SAC-CI calculations,⁷ their calculated energies would have approached the EOM-CCSD excitation energies, meaning that they all would have increased. At that point, it becomes impossible to draw any meaningful conclusions about the assignment of the spectrum.

The CASPT2⁶ results for the B band are too low. This could have been caused by the size of their active space. It has been shown several times^{29,5,7,8} that for the ²B_{3u} and ²B_{2u} states, Gouterman's four orbital model^{30–32} is not suf-

TABLE VII. Singlet valence excited states for free base porphyrin. Energies are in eV. Oscillator strengths given in parentheses below the excitation energies.

	CASPT2 ^a	SAC-CI ^b	EOM-CCSD	STEOM-CC ^c	“ D_{4h} ” polarized	Expt ^d
1 $^1B_{3u}$	1.70 (0.001)	1.75 (0.0001)	2.15 (0.0007)	1.72 (—)	1.75 (0.0007)	1.98 Q _x (0.01)
1 $^1B_{2u}$	2.26 (0.016)	2.23 (0.0006)	2.76 (0.007)	2.61 (0.016)	2.40 (0.013)	2.42 Q _x (0.06)
1 $^1B_{1g}$		3.55		3.63	3.44	
2 $^1B_{3u}$	2.91 (1.66)	3.56 (1.03)	3.89 (1.00)	3.66 (1.03)	3.47 (0.693)	3.33B (1.15)
2 $^1B_{2u}$	3.04 (1.54)	3.75 (1.73)	4.05 (1.56)	3.77 (1.42)	3.62 (1.20)	
2 1A_g		4.25		4.08	3.95	
3 $^1B_{3u}$		4.24 (0.976)	4.51 (0.812)	4.28 (0.71)	4.06 (0.931)	3.65N (<0.1)
1 $^1B_{2g}$		4.05		4.08	4.21	
1 1A_u		4.18		4.14	4.24	
3 $^1B_{2u}$		4.52 (0.350)	4.83 (0.313)	4.67 (0.44)	4.35 (0.422)	4.25L (~0.1)
1 $^1B_{3g}$		4.37		4.45	4.51	
2 $^1B_{1g}$		4.62		4.50	4.53	
1 $^1B_{1u}$		4.51 (0.005)	4.82 (0.004)	4.54 (0.004)	4.56 (0.002)	
3 1A_g		4.74		4.72	4.46	
3 $^1B_{1g}$		5.13		4.82	4.66	
4 1A_g		5.28		5.06	4.87	
4 $^1B_{2u}$		5.31 (0.280)		5.26 (0.20)	5.00 (0.153)	4.67L (~0.1)
4 $^1B_{1g}$				5.32	5.12	
5 1A_g				5.31	5.04	
4 $^1B_{3u}$		5.45 (0.351)		5.38 (0.41)	5.17 (0.272)	5.50M (~0.3)
5 $^1B_{3u}$				6.26 (0.19)	6.07 (0.182)	
5 $^1B_{2u}$				6.57 (0.002)	6.21 (0.004)	

^aReference 6.^bReference 7.^cReference 8.^dReference 13.

ficient; the $4b_{1u}$ orbital must also be included. Merchant *et al.*⁶ did not include it in their active space. More CASPT2 calculations, with a larger active space and with d functions, would be very informative.

The CASPT2 results for the B band are actually in very good agreement with the RPA results of Baker and Zerner² using the INDO/S Hamiltonian. The excitation energies are 2.91 and 3.04 eV for the CASPT2 versus 2.99 and 3.03 eV for the INDO/S. The INDO/S results are also low for the Q bands at 1.46 and 1.97 eV.

The Q_x and Q_y bands belong to the 1^1B_{3u} and 1^1B_{2u} states. Our results show fortuitously good agreement with the Q_y band. For the Q_x band all of the methods predict too low an excitation energy. A fluorescence spectrum of free base porphyrin taken in a supersonic jet expansion³³ placed the 0–0 transition for the Q_x band at 2.0234 eV and the 0–0 transition for the Q_y band at 2.4653 eV, slightly higher than the vertical excitation energies reported by Edwards *et al.*¹³ The addition of polarization functions increased the Q_x excitation energy by 0.05 eV, so the use of much larger basis sets may

further increase the calculated excitation energy, moving it toward the experimental number.

The current results strongly support the original assignment for the B band being both the 2^1B_{3u} and 2^1B_{2u} states. The N band is then assigned to the 3^1B_{3u} state. If the assignments of Nakatsuji *et al.* were correct, it would mean that the polarized basis STEOM-CC energies would have to be 0.19 eV too low for the first L peak and 0.32 eV too low for the second L peak. Instead, this assignment puts 2^1B_{3u} 0.14 eV above the B peak and 2^1B_{2u} 0.29 eV above the B peak. The 3^1B_{3u} state is 0.41 eV above the N peak. Although the 0.41 eV error is uncomfortably large, we feel it is much more likely that the STEOM-CC is overestimating the excitation energies than that it is consistently underestimating them. Also, the calculated energies of all of these states dropped substantially when the polarizations functions were added. Larger basis set calculations should further decrease these gaps.

The intensities still present a problem. The experimental oscillator strength of the N band is less than 0.1, and the

TABLE VIII. User CPU time needed for the steps in the STEOM-CCSD calculation with the polarized basis.

Step	User CPU time in seconds
Integrals	29 229
Property integrals	136
SCF	166
Integral transformation	2491
Integral reordering	2744
CCSD	56 405
Forming \bar{h}	3937
11 IP-EOM-CCSD states	243
23 EA-EOM-CCSD states	9873
Forming G	789
84 STEOM-CC states	3016

calculated oscillator strength is 0.93. Edwards *et al.*¹³ mention that the shape of the B and N bands would be consistent with the two states of the B bands being split by 1500 cm^{-1} and an intense N band donating intensity into the B band. Our calculations give a splitting of 1200 cm^{-1} between the 2^1B_{3u} and 2^1B_{2u} states. Thus, these calculations agree with the possible interpretation given by Edwards *et al.*¹³ Our splitting is larger than the B band splitting of 240 cm^{-1} measured in a low-temperature crystal spectrum,³⁴ but the assignment of the 240 cm^{-1} splitting to the energy difference between the two electronic states has been disputed.³⁵

These assignments then leave the two peaks of the L band assigned to the 3^1B_{2u} and 4^1B_{2u} states. The diffuse basis energy for the 3^1B_{2u} state agrees well with the first L peak, but the 4^1B_{2u} state is 0.33 eV higher than the second L peak. This difference should also be reduced with larger basis sets. The experimental oscillator strength for the two states combined is about 0.1. The calculated oscillator strengths are well above that. The 1^1B_{1u} state sits under the L peak, but its intensity is so small that it is not visible.

The one remaining problem with this assignment is the M peak. The calculated excitation energy for the 4^1B_{3u} state is 5.17 eV , 0.33 eV lower than the M band maximum. The intensities match well, though, and there is no other assignment that makes sense. To say that 4^1B_{3u} is part of the L band would require that the excitation energy drop by 0.5 eV , and it would cause problems assigning the other states. Still, it is not clear why the calculated excitation energy would be so low.

Finally, a point should be made about the cost of these calculations. For the polarized basis calculation there are 57 occupied and 283 virtual functions. This gave 2479 T_1 and 34 170 895 T_2 amplitudes. The time taken for each step on a Cray C90 is listed in Table VIII. It took only 36 s per excited state to calculate the energies and properties. Most of that time was used calculating the properties. The energies took 1.4 s each. This is a very important advantage of the STEOM-CC method. The total time for the calculation is effectively independent of the number of excited states calculated. That makes it possible to study entire spectra instead of just a few selected states.

V. CONCLUSIONS

STEOM-CCSD¹⁴ calculations on free base porphyrin using a $[3s2p1d/2s]$ basis set are presented. These are the first reported calculations on excited states above the lowest that use polarization functions. For the important optically allowed excited states, the polarization functions have a significant effect. These calculations support the traditional interpretation of the spectrum, in that the intense B band is assigned to both the 2^1B_{3u} and 2^1B_{2u} states. The errors in excitation energies for some of the higher lying excited states are still quite large, however. This suggests that even bigger basis sets are needed to truly converge the excitation energies.

This study is possible only because the second similarity transformation in STEOM-CCSD means that the excited states can be represented in terms of single excitations with respect to a highly modified Hamiltonian. Thus, it is possible to efficiently calculate many excited states at once.

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