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Ab Initio Electron Propagator Calculations on the Ionization Energies of Free Base Porphine, Magnesium Porphyrin, and Zinc Porphyrin†

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Ab initio electron propagator methods are applied to the prediction, assignment, and interpretation of the valence photoelectron spectra of free base porphine and of magnesium and zinc porphyrins. Tests of various approximate self-energies, including the partial third (P3), the outer valence Green's function, and the nondiagonal, renormalized second-order (NR2) methods are performed. Basis set effects and reduced active orbital spaces are examined as well. The P3 method and the one-electron picture of ionization that accompanies it are validated for the first two cationic states and for states with σ holes that are localized in nitrogen, lone pair regions. In the remaining π-hole states, there is significant shake-up character and NR2 results provide useful diagnostics of correlation effects.

Introduction

Porphyrins and related macrocycles are crucial elements in many life processes.[1] Porphyrins and metalloporphyrins are present as central structural units in many substances involved in biochemical redox reactions.[2] The chemical reactivity of porphyrins in such events as electron transfer, oxygen transport, oxidation, and reduction is directly related to their ionization energies (IEs) and electron affinities, which in turn depend on the chemical environment about the porphyrin unit.

Recently, much interest has been displayed in the field of materials chemistry toward porphyrins and metalloporphyrins as nanometer-sized building blocks for films and other structures with useful optical and conductive properties, with C_{60}−zinc porphyrin (ZnP) diads and triads among the latest examples.[3−7] Therefore, understanding trends in electron binding energies of porphyrin units may be useful for the design of materials with optimal properties.

IEs of isolated molecules can be measured experimentally with gas phase, ultraviolet photoelectron spectroscopy. Reports of gas phase, ultraviolet photoelectron spectra (PES) of porphyrins are available only for free base porphine (H2P) and a number of heavily substituted (usually, octaethyl and tetraphenyl derivatives) porphyrins and metalloporphyrins.

In the PES of H2P, which first appeared in ref 8, there are four well-separated bands from 6 to 14 eV. The first appears as a sharp peak at 6.9 eV with an obvious, although not pronounced, shoulder at 7.1−7.2 eV. The second band consists of a plateau at 8−8.4 eV, followed by a peak at 9.1 eV with a high-energy shoulder. The third band is located between 10 and 11 eV and has significantly less intensity than the previous two. All of these bands were assigned to ionizations from π levels, and the rest of the spectrum was not assigned. No experimental spectra exist for either Mg or Zn unsubstituted porphyrins.

Most calculations on porphyrins have employed density functional methods.[9] Extensive literature exists on theoretical structures and on infrared and electronic spectra of porphyrins.[10−12] Ionization potentials of H2P, ZnP, and a number of substituted porphyrins have been calculated with various exchange correlation potentials as differences between a neutral ground state energy and cationic state energies.[9,10]

Several ab initio methods have been applied to porphyrins. An equation-of-motion coupled cluster method was applied to calculate both ionization and excitation spectra of H_2P.[13] A double-ζ basis set was used for C and N atoms, whereas the STO-3G basis was employed for hydrogens. IEs obtained from this study differed significantly from the observed spectrum by 0.3−0.7 eV.

A related ab initio approach, the symmetry-adapted cluster, configuration interaction method (SAC-CI) has been used in the investigation of H2P absorption spectra. Several positional isomers of H2P also were considered. To facilitate these calculations, a double-ζ basis set was employed and significant restrictions on the active orbital space were imposed.[14] In a related study with the SAC-CI method, excited states of ZnP and its dimers were examined with an active space of 282 MOs.[15]

A semiempirical version of the outer valence Green's function method of electron propagator theory (OVGF) has been used to calculate IEs of H2P and a number of substituted porphyrins.[16]

Ab initio electron propagator theory[17−19] offers another way of calculating electron binding energies of molecules that retains the conceptual economy of mean field theories while systematically describing correlation effects. In this approach, electron binding energies, ϵ, and Dyson orbitals (DOs), ϕ, are obtained as eigenvalues and eigenfunctions of a one-particle equation

$$[F + \Sigma(\epsilon_p)]\phi_p = \epsilon_p\phi_p \qquad (1)$$

where F is the usual Fock operator that contains the Coulomb exchange potential and $\Sigma(E)$ is the energy-dependent, nonlocal self-energy operator that accounts for final state orbital relaxation and electron correlation effects.

A relatively simple approximation of the self-energy operator known as partial third order (P3)[20] has been applied to the assignment of the lowest IEs of free base porphine and octamethyl porphyrin.[21] This method has proven to be useful in the assignment of the PES of organic molecules, especially

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polycyclic, aromatic structures with lone pairs on heteroatoms, where correlation effects determine the order of the cationic states. Alkyl substituents shift the porphyrin IEs to lower values, and these effects are related to the hyperconjugative interactions that are present in the DOs.

Methods that are capable of treating higher cationic states and that are sufficiently flexible to be applied to metalloporphyrins and other related species are sought in this work. Tests of several approximate self-energies and of measures for increasing the efficiency or feasibility of calculations are conducted. Approximate self-energies include the P3 method, the OVGF methods,[22] and the nondiagonal, renormalized second-order approximation (NR2).[23] Basis set comparisons and selection of active orbital spaces also are scrutinized. Computational results on H2P, Mg porphyrin (MgP), and Zn porphyrin reveal the capabilities and limitations of several approximations and therefore provide guidelines for subsequent research.

Electron Propagator Theory

To each IE or electron affinity, ϵ_p, there corresponds an eigenfunction, ϕ_p, known as a DO that describes the change in electronic structure that accompanies the addition or removal of an electron. For IEs of an N electron state, the DO reads

$$\phi_p(x_1) = \sqrt{N} \int \Psi_N(x_1, x_2, x_3, ..., x_N) \Psi^*_{p,N-1}(x_2, x_3, x_4, ..., x_N)\, dx_2\, dx_3\, dx_4 ... dx_N \quad (2)$$

where x_i is the space−spin coordinate vector for electron i, Ψ_N is the initial state, and $\Psi_{p,N-1}$ is the p-th ionized state. When the one-electron picture (which is exemplified by the frozen orbital approximation made in Koopmans's demonstration that IEs may be approximated by canonical Hartree−Fock orbital energies) is qualitatively valid, then the pole strength, P, defined by

$$P_p = \int |\phi_p(x)|^2\, dx \quad (3)$$

approaches unity. However, when p is the index of a correlation state, where shake-up character is large, then P_p has values that may be considerably closer to zero. For pole strengths that exceed 0.85, the one-electron picture is validated, but values below 0.80 are clear indications of strong shake-up character. Values between between 0.8 and 0.85 may be considered to be intermediate cases. When the self-energy operator is ignored in eq 1, IEs at the Koopmans's theorem (KT) level are produced, pole strengths equal unity, and no shake-up states are predicted. In correlated calculations, pole strengths may be obtained from the following expression

$$P_p = \left[1 - \frac{d\Sigma_{pp}(E)}{dE}\right]^{-1} \quad (4)$$

where the derivative is evaluated at $E = \epsilon_p$ and $\Sigma_{pp}(E)$ is a self-energy matrix element corresponding to the p-th DO normalized to unity.

Approximate solutions of eq 1 are defined partly by the orbital basis that is used to express the Fock operator, the self-energy operator, and the DOs. In addition, a computationally feasible approximation to the self-energy operator must be chosen. For the electron propagator methods that are employed here, a preliminary closed-shell Hartree−Fock calculation is performed. Matrix elements of the Fock and self-energy operators are expressed in the canonical Hartree−Fock basis.

The OVGF and P3 methods ignore nondiagonal self-energy matrix elements. In the diagonal self-energy approximation, each DO equals a canonical Hartree−Fock orbital times the square root of the pole strength. When pole strengths are below 0.8, the reliability of these methods becomes questionable.

OVGF formulas require evaluation of all of the third-order terms in the self-energy operator. Certain terms depend on two-electron integrals over four virtual orbitals and their computation determines the arithmetic bottlenecks and storage requirements of OVGF calculations. P3 calculations depend on the computation of fewer third-order terms and have arithmetic and storage requirements that are considerably reduced. In tests on small organic molecules, the mean absolute errors of P3 calculations are somewhat lower than their OVGF counterparts.[20,24]

The NR2 method generalizes the P3 approximation in several ways. It accounts for certain types of relaxation terms in the self-energy in all orders, and it does not make the diagonal self-energy approximation. In tests on shake-up states of small organic molecules, it has been found to produce accurate IEs and useful state assignments.[23,25]

Computational Methods

All calculations were performed with the Gaussian-03 suite of programs.[26] Geometry optimizations of free base porphine and the two metalloporphyrins of interest were performed with the B3LYP functional[27] and the 6-311G** basis set.[28] Harmonic frequency analysis revealed a D_{2h} minimum for the free base porphine and D_{4h} minima for the Mg and Zn porphyrins.

Ionization spectra of H2P and MgP were calculated with the 6-311G** basis. The 6-311+G** also was employed for H2P. For ZnP IEs, two basis sets were used as follows: 6-311G** (basis 1) and a more flexible basis on Zn described in detail in refs 29 and 30 (basis 2).

The number of basis functions was 516 and 612 for H2P, 530 for MgP, and 550 (basis 1) and 618 (basis 2) for ZnP. Routine execution of current programs with basis sets of this size would produce computational intermediates that are too large to be stored in external disk files. To overcome these impediments, reductions of the active orbital space used in electron propagator calculations have been considered. The dependence of the calculated IEs on the nature of the active space was studied for H2P.

In the case of MgP, the Mg 2s- and Mg 2p-like molecular orbital (MO) energies are close to the energies of the lowest, inner valence MOs of the system (−2.27 vs −1.27 au). Therefore, two propagator calculations were performed for MgP. In the first, the active space was restricted in the same manner as for H2P; that is, all core occupied MOs and the corresponding virtual MOs were dropped. In the second, four MOs corresponding to the 2s, 2p shell of Mg were retained. Calculations showed that incorporation of the Mg 2s and 2p MOs into the propagator calculations did not affect the IEs of MgP.

For ZnP, calculations with the smaller basis set required restrictions that are identical to those applied to H2P. The larger size of the second basis demanded more rigorous measures, and in this case, the virtual MOs with energies higher than 4.00 eV were dropped whereas all valence-occupied MOs were retained. Our P3 and OVGF codes are incorporated into the standard Gaussian-03 suite of programs. The NR2 codes are interfaced with Gaussian-03. In the NR2 calculations, all roots in the energy region from −15 to +1.0 eV were sought. Roots with pole strengths lower than 0.01 were discounted. Tables 1−4 contain IEs for free base porphine. Data on MgP are compiled in Tables 5 and 6. ZnP results are presented in Tables 7 and 8.

TABLE 1: Active Orbital Space Dependence of P3/6-311G Free Base Porphine IEs (eV)**

state	KT	P3[a]	P3[b]	P3[c]	P3[d]	P3[e]	P3[f]	P3[g]	P3[h]	exp. (8)
$^2B_{3u}$	6.68	6.96	6.96	6.90	6.77	6.69	7.00	6.98	6.86	6.9
^2A_u	6.14	7.02	7.02	6.99	6.87	6.78	6.98	6.94	6.90	7.1 sh
$^2B_{1g}$	9.13	8.30	8.30	8.23	8.10	8.03	8.35	8.30	8.24	8.0−8.4
$^2B_{3u}$	9.30	8.48	8.48	8.42	8.30	8.22	8.54	8.50	8.44	8.0−8.4
$^2B_{2g}$	10.05	9.10	9.09	9.07	8.98	8.92	9.12	9.10	9.05	∼9
$^2B_{2g}$	10.24	9.14	9.14	9.06	8.92	8.85	9.22	9.16	9.09	∼9
$^2B_{3u}$	10.27	9.20	9.20	9.13	9.00	8.92	9.28	9.22	9.16	∼9
$^2B_{1g}$	10.40	9.36	9.36	9.34	9.25	9.19	9.39	9.38	9.32	
^2A_g	11.49	9.58	9.58	9.47	9.30	9.21	9.67	9.58	9.48	
$^2B_{2u}$	11.56	9.61	9.70	9.51	9.33	9.25	9.61	9.61	9.50	
^2A_u	11.94	10.51	10.51	10.49	10.39	10.3	10.55	10.53	10.47	∼10.0−10.3

[a] Core occupied MOs (24) dropped. No virtual MOs dropped. [b] Core occupied MOs (24) dropped. Twenty-four upper virtual MOs dropped. [c] Core occupied MOs (24) dropped. Sixty-six upper virtual MOs dropped (energies higher than 3.86 au). [d] Core occupied MOs dropped. One hundred fifty upper virtual MOs dropped (energies higher than 2.75 au). [e] Core occupied MOs dropped. One hundred ninety upper virtual MOs dropped (energies higher than 2.33 au). [f] Thirty-five lowest occupied MOs (energies < −1 au) dropped. No virtual MOs dropped. [g] Thirty-five lowest occupied MOs dropped. Sixty-six upper virtual MOs dropped (energies higher than 3.86 au). [h] Thirty-five lowest occupied MOs dropped. One hundred six upper virtual MOs dropped (energies higher than 3.05 au).

TABLE 2: 6-311G Free Base Porphine IEs[a] (eV)**

			OVGF[b]			
state	KT	P3 (PS)	A (PS)	B (PS)	C (PS)	exp. (8)
$^2B_{3u}$	6.68	6.96 (0.85)	6.52 (0.88)	*6.66* (0.87)	6.76 (0.87)	6.9
^2A_u	6.14	7.02 (0.85)	6.32 (0.99)	6.61 (0.87)	*6.72* (0.87)	7.1 sh
$^2B_{1g}$	9.13	8.30 (0.80)	8.17 (0.82)	*8.37* (0.82)	8.43 (0.81)	∼8.0−8.4
$^2B_{3u}$	9.30	8.48 (0.81)	8.34 (0.83)	*8.54* (0.83)	8.60 (0.83)	∼8.0−8.4
$^2B_{2g}$	10.05	9.10 (0.68)	9.00 (0.71)	*9.08* (0.70)	9.19 (0.68)	∼9
$^2B_{2g}$	10.24	9.14 (0.82)	9.04 (0.82)	*9.22* (0.82)	9.28 (0.82)	∼9
$^2B_{3u}$	10.27	9.20 (0.81)	9.11 (0.82)	*9.30* (0.83)	9.35 (0.82)	∼9
$^2B_{1g}$	10.40	9.36 (0.67)	9.29 (0.70)	*9.36* (0.69)	9.48 (0.66)	
^2A_g	11.49	9.58 (0.87)	9.55 (0.84)	*9.83* (0.86)	9.75 (0.89)	
$^2B_{2u}$	11.56	9.61 (0.86)	9.59 (0.84)	*9.86* (0.86)	9.78 (0.88)	
^2A_u	11.94	10.51 (0.73)	10.46 (0.73)	*10.57* (0.74)	10.68 (0.72)	∼10.0−10.3

[a] Active space 468 MOs (corresponds to P3[b] in Table 1). [b] The value recommended by the selection procedure[31] is given in italics.

Results and Discussion

Free Base Porphine. *Active Orbital Space Restrictions.* Results of P3/6-311G** calculations with various restrictions on the size of the active orbital space are presented in Table 1. Koopmans's values of IEs (KT) and experimental peak values also are given. The columns labeled P3[a] and P3[b] pertain to minimal restrictions of the active space. All 24 occupied core MOs are excluded in both cases. In case *a*, all virtual MOs are included in the active orbital space, whereas the 24 highest virtual MOs are dropped in case *b*. These two orbital spaces generate the same IE values to within 0.01 eV with the exception of the $^2B_{2u}$, σ-hole state for which the IE increases slightly with the smaller virtual orbital set. Comparison with the next three columns shows that decreasing the space of active virtual MOs gradually diminishes the absolute values of IEs. Even with the smallest active space of 302 MOs, the first two IEs in column P3[e] remain within 0.2−0.3 eV of observed values.

More drastic reductions in the active orbital space may be necessary for the study of larger or less symmetric porphyrins. Columns P3[f] to P3[h] correspond to the cases where the 35 lowest occupied MOs with energies less than −1.00 au are dropped. All virtual MOs are retained in case *f*, 66 upper virtuals are dropped in case *g*, and 106 are dropped in case *h*. P3[a] and P3[f] results imply that little accuracy is lost because of the diminished space of occupied orbitals. Most of the IEs are increased slightly as a result of the latter active space reduction. However, the first two states become almost degenerate and their relative positions switch. A simultaneous cut in the virtual space in case *g* restores the IEs almost to their initial values and produces results that resemble those of case *b*. An additional reduction of the virtual space slightly lowers the IEs again in case *h*. One may conclude on the basis of this study that for molecules where restrictions of the active orbital space are unavoidable, balanced cuts of occupied and virtual subspaces are recommended, for the corresponding effects on the IEs tend to cancel.

Assignment of Ionized States. 6-311G** P3 and OVGF results for H2P are compiled in Table 2. All three OVGF approximations (A, B, and C) are shown. Data in italics pertain to the recommended values that emerge from the selection procedure discussed in ref 31. Table 3 contains IEs obtained with the same methods and the 6-311+G** basis.

P3 calculations with the 6-311G** (Table 2) and 6-311+G** (Table 3) basis sets provide excellent agreement with experimental data and a reasonable assignment of the first two π levels in the PES of free base porphine.[8] $^2B_{3u}$ and ^2A_u ionized states are predicted at 6.96 and 7.02 eV with the 6-311G** basis and at 7.00 and 7.06 eV with the 6-311+G** basis. A large correction to the Koopmans result is observed for the latter state. High pole strength values of ∼0.85 indicate the qualitative validity of the Koopmans description of the first two cationic states. Corresponding DOs are well-delocalized over the molecular framework. The largest amplitudes in the DO that pertain to the lowest IE occur on the meso carbons with only slight participation of pyrrolic nitrogens. This pattern suggests that meso substituents could have large effects on the energy of the $^2B_{3u}$ cationic state. In the case of the a_u DO that corresponds to the next cationic state, a pattern of π lobes with alternating phases on the pyrrolic α-carbon atoms is observed.

OVGF IE values deviate somewhat more from the experimental values with both basis sets. The order of the first two states holds with the recommended OVGF values, which are

TABLE 3: 6-311+G Free Base Porphine IEs[a] (eV)**

			OVGF[b]			
state	KT	P3	A	B	C	exp. (8)
$^2B_{3u}$	6.77	7.00	6.52	*6.66*	6.76	6.9
		0.85	0.88	0.87	0.87	
^2A_u	6.24	7.06	6.32	6.61	*6.72*	7.1 sh
		0.85	0.99	0.87	0.87	
$^2B_{1g}$	9.21	8.32	8.17	*8.37*	8.43	∼8.0−8.4
		0.81	0.82	0.82	0.82	
$^2B_{3u}$	9.37	8.51	8.34	*8.54*	8.60	∼8.0−8.4
		0.82	0.83	0.83	0.83	
$^2B_{2g}$	10.12	9.16	9.00	*9.08*	9.19	∼9
		0.68	0.71	0.70	0.68	
$^2B_{2g}$	10.31	9.13	9.04	*9.22*	9.28	∼9
		0.82	0.82	0.82	0.82	
$^2B_{3u}$	10.35	9.21	9.11	*9.29*	9.35	∼9
		0.82	0.82	0.83	0.82	
$^2B_{1g}$	10.47	9.42	9.29	*9.36*	9.48	
		0.68	0.70	0.69	0.67	
^2A_g	11.60	9.58	9.55	*9.83*	9.75	
		0.87	0.84	0.86	0.89	
$^2B_{2u}$	11.68	9.62	9.59	*9.86*	9.78	
		0.87	0.84	0.86	0.88	
^2A_u	12.02	10.57	10.46	*10.57*	10.68	
		0.73	0.73	0.73	0.72	

[a] Active space incorporates 491 MOs; all valence occupied MOs and virtual MOs with ϵ < 3.28 au are retained. [b] The value recommended by the selection procedure[31] is given in italics.

TABLE 4: NR2/6-311G Free Base Porphine IEs (eV)**

state	KT	P3[a]	PS	NR2[a]	PS	exp. (8)
$^2B_{3u}$	6.68	6.97	0.85	6.68	0.81	6.9
^2A_u	6.14	6.94	0.85	6.78	0.81	7.1
$^2B_{1g}$	9.13	8.30	0.81	8.10	0.40	∼8.0−8.4
				7.61	0.31	
				9.83	0.06	
				10.38	0.04	
				10.84	0.03	
$^2B_{3u}$	9.37	8.50	0.82	8.04	0.67	∼8.0−8.4
				9.86	0.08	
$^2B_{2g}$	10.05	9.10	0.68	8.72	0.49	
				8.46	0.10	
				8.86	0.04	
				10.61	0.16	
$^2B_{2g}$	10.24	9.16	0.82	8.86	0.58	
				7.58	0.06	
				8.46	0.05	
				8.72	0.08	
$^2B_{3u}$	10.27	9.22	0.82	8.76	0.67	
				10.66	0.04	
$^2B_{1g}$	10.40	9.38	0.67	8.91	0.43	
				8.10	0.02	
				10.55	0.22	
^2A_g	11.49	9.58	0.86	9.16	0.82	
$^2B_{2u}$	11.56	9.61	0.86	9.17	0.82	
^2A_u	11.94	10.53	0.73	9.88	0.45	
				10.00	0.06	

[a] Active orbital space includes all occupied MOs with $\epsilon > -1.00$ au and all virtual MOs with ϵ < 3.86 au.

italicized in the tables. For all cases except the ^2A_u state, the B approximation is selected.

Calculations in the NR2 approximation[23] confirm the Koopmans character of the first two cationic states (see Table 4). The pole strengths are smaller than those obtained with the P3 method. Although the absolute IE values are lower than the P3 results (which is normal for the basis set and the active orbital space used), the energy gap is consistent with the experimental and relative positions of the states. No shake-up states with significant pole strengths that borrow intensity from these two primary states are predicted.

A more nuanced interpretation is required for the experimental plateau at ∼8.4 eV. Table 4 shows lower pole strengths for the P3 predictions that pertain to the $^2B_{1g}$ and $^2B_{3u}$ final states. The corresponding IEs appear to be in excellent agreement with PES. However, the NR2 results show a high degree of intensity borrowing between states with similar b_{1g} and b_{3u} DOs. Similar results obtained for the subsequent $^2B_{2g}$, $^2B_{3u}$, and $^2B_{1g}$ states. There are two reasons to suspect that these correlation effects are exaggerated by the present NR2 calculations. First, a significant reduction of the active orbital space was necessary. Second, couplings between two-hole, one-particle operators are treated in first order only. However, the assumptions of the P3 method, especially the diagonal self-energy approximation, may not be valid in this energy range. Therefore, a definitive interpretation of the transitions that contribute to the second band in the PES must await the application of more advanced methodology.

The set of π-hole states is followed by two σ-hole states, ^2A_g and $^2B_{2u}$. Neither state has significant satellites, for the corresponding pole strengths are greater than 0.8 in NR2 calculations. The largest amplitudes in the corresponding DOs are associated with nitrogen-centered, lone pair lobes that have an in-phase (a_g) or an out-of-phase (b_{2u}) relationship. In both cases, there is extensive delocalization into the two nearest pyrrolic rings. The two states are almost degenerate, with the energy separation being no larger than 0.03 eV. The P3 method predicts both states at about 9.6 eV, whereas the OVGF method produces IEs at about 9.7−9.9 eV. These values are reasonably close to the experimental feature at ∼10 eV, but definitive assignment of the two states still must be regarded as tentative. The last ionized state described here is ^2A_u, which is predicted at 10.3−10.5 eV. This state also has pronounced shake-up character.

Mg Porphyrin. The 6-311G** IEs of MgP obtained with the P3 and OVGF methods are compiled in Table 5. Only core-occupied MOs and the corresponding virtual MOs were omitted from the active orbital space. This restriction is the same as in case *b* of H2P, and thus, the predicted IEs of the two species can be compared.

As was the case with H2P, the first eight ionized states have π holes. Of these, two pairs have E_g symmetry. The two lowest ionized states of MgP are predicted at 6.91 and 6.93 eV by P3 and are almost degenerate. OVGF values are smaller at 6.49 and 6.60 eV. Both IEs are predicted by all methods to be smaller than their H2P counterparts. The a_{1u} and a_{2u} DOs resemble the H2P a_u and b_{3u} DOs, respectively. Pole strengths for both IEs are over 0.85, and the ionizations may be treated as one-electron processes.

A set of three closely spaced states is predicted at ∼8.5 eV: a $^2B_{2u}$ state at 8.52 eV and a degenerate state ^2E_g at 8.55 eV. The latter has a pole strength of 0.80, which is low enough to reflect significant shake-up character.

The onset of σ states is predicted at about 10 eV by the P3 and OVGF methods. High pole strength values indicate the one-electron nature of these ionizations. The corresponding b_{1g} DO is spread over four nitrogen lone pair lobes in an alternating pattern of phases, and there is some delocalization into the pyrrolic rings. Another π-hole state, $^2B_{1u}$, follows, and its pole strength of 0.73 clearly marks it as having significant shake-up character. A second σ-hole state, a degenerate set with ^2E_u symmetry, is well-separated from the first one. IE values of 10.87 and 10.80 eV are predicted by P3 and OVGF. Pole strengths exceed 0.86 and indicate the one-electron nature of the ionization. Each e_u DO is an out-of-phase combination of the nitrogen lone pair lobes on two opposite nitrogens. The

TABLE 5: P3 and OVGF Mg Porphyrin IEs[a] (eV)

state	KT	P3 (PS)	OVGF[b] (PS)	state	KT	P3	OVGF[b]
$^2A_{1u}$	6.02	6.91 (0.85)	6.49 (0.87)	^2E_g	10.09	9.14 (0.68)	8.99 (0.71)
$^2A_{2u}$	6.63	6.93 (0.85)	6.60 (0.87)	$^2B_{1g}$	11.78	9.99 (0.87)	9.96 (0.87)
$^2B_{2u}$	9.38	8.52 (0.82)	8.41 (0.84)	$^2B_{1u}$	11.79	10.38 (0.73)	10.30 (0.74)
^2E_g	9.48	8.55 (0.81)	8.45 (0.82)	^2E_u	12.68	10.87 (0.87)	10.80 (0.86)
$^2A_{2u}$	9.84	8.90 (0.81)	8.82 (0.83)	$^2B_{2g}$	14.14	12.52 (0.87)	12.35 (0.87)

[a] Active orbital space includes all valence occupied MOs and all virtual MOs with $\epsilon < 24.8$ au. [b] Recommended by the selection procedure as in ref 31.

TABLE 6: NR2 and P3 Mg Porphyrin IEs[a] (eV)

state	KT	P3	PS	NR2	PS
$^2A_{1u}$	6.02	6.80	0.85	6.59	0.81
$^2A_{2u}$	6.63	6.80	0.85	6.53	0.81
$^2B_{2u}$	9.38	8.38	0.82	7.93	0.71
				10.08	0.11
^2E_g	9.48	8.42	0.81	8.14	0.48
				7.47	0.17
				8.36	0.12
				10.01	0.04
				10.21	0.03
$^2A_{2u}$	9.84	8.77	0.82	8.29	0.66
				10.24	0.09
^2E_g	10.09	9.06	0.69	8.64	0.48
				8.14	0.05
				10.21	0.08
$^2B_{1g}$	11.78	9.81	0.87	9.38	0.84
$^2B_{1u}$	11.79	10.29	0.74	9.65	0.52
^2E_u	12.68	10.71	0.87	10.25	0.82
$^2B_{2g}$	14.14	12.40	0.87	11.94	0.82

[a] Active orbital space, 367 MOs. Occupied MOs with $\epsilon < -1.09$ au dropped; virtual MOs with $\epsilon > 2.98$ au dropped.

TABLE 7: Zn Porphyrin IEs (eV)

	basis 1		basis 2	
state	KT	P3 (PS)	KT	P3 (PS)
$^2A_{1u}$	5.99	6.90 (0.85)	6.04	6.94 (0.85)
$^2A_{2u}$	6.64	6.93 (0.85)	6.79	7.02 (0.85)
$^2B_{2u}$	9.44	8.55 (0.82)	9.43	8.57 (0.82)
^2E_g	9.49	8.54 (0.81)	9.47	8.56 (0.81)
$^2A_{2u}$	9.85	8.88 (0.81)	9.92	8.97 (0.82)
^2E_g	10.10	9.14 (0.68)	10.13	9.19 (0.69)
$^2B_{1g}$	10.83	9.07 (0.88)	10.81	8.94 (0.88)
$^2B_{1u}$	11.82	10.40 (0.73)	11.84	10.44 (0.74)
^2E_u	12.85	11.07 (0.86)	12.88	11.09 (0.87)
$^2B_{2g}$	14.14	12.52 (0.87)	14.17	12.55 (0.87)
$^2A_{2g}$	14.18	12.40 (0.85)	14.20	12.43 (0.86)
$^2B_{2u}$	14.46	12.33 (0.72)	14.46	12.36 (0.72)
^2E_u	14.47	12.65 (0.85)	14.49	12.68 (0.85)
$^2A_{1g}$	14.57	12.64 (0.85)	14.56	12.61 (0.85)
$^2B_{1g}$	14.75	12.79 (0.85)	14.77	12.81 (0.85)

TABLE 8: 6-311G Zn Porphyrin IEs[a] (eV)**

state	KT	P3	PS	NR2	PS
$^2A_{1u}$	5.99	6.77	0.85	6.58	0.82
$^2A_{2u}$	6.64	6.82	0.85	6.56	0.82
$^2B_{2u}$	9.44	8.47	0.83	8.03	0.70
				10.13	0.11
^2E_g	9.49	8.44	0.81	8.18	0.49
				7.49	0.16
				8.41	0.12
				10.08	0.05
$^2A_{2u}$	9.85	8.82	0.82	8.35	0.66
				10.30	0.10
				11.13	0.02
^2E_g	10.10	9.10	0.69	8.70	0.47
				8.18	0.04
$^2B_{1g}$	10.83	8.86	0.88	8.40	0.85
$^2B_{1u}$	11.82	10.35	0.73	9.72	0.51
^2E_u	12.85	10.97	0.86	10.55	0.82
$^2B_{2g}$	14.14	12.50	0.87	12.06	0.82
$^2A_{2g}$	14.18	12.38	0.86	11.96	0.80

[a] Active space includes 356 MOs. Occupied MOs with $\epsilon < -1.063$ au and virtual MOs with $\epsilon < 2.973$ au are included.

delocalization patterns, including contributions from the pyrrolic ring carbons, coincide with those of the σN$_+$, a_g and σN$_-$, b_{2u} DOs of H2P.

The last ionized state under consideration has $^2B_{2g}$ symmetry. It is well-separated from the previous states and is expected at an energy of about 12.3–12.5 eV, based on P3 and OVGF results. The one-electron nature of the state is predicted by a pole strength value that is higher than 0.85. This is the first σ-hole state with no nitrogen lone pair character. The b_{2g} DO is delocalized over C–N, C–C, and *meso*-C–H σ bonding regions.

Table 6 displays P3 and NR2 results with a reduced active orbital space. This change lowers the P3 results with respect to the values of Table 5. NR2 IEs are lower than P3 results. For the first two IEs and for the σ-hole states, the pole strengths are above 0.8, but strong shake-up character is present in the remaining π-hole IEs.

Zn Porphyrin. P3 IEs of ZnP obtained with two basis sets are compiled in Table 7. Basis 2 has 68 more functions on Zn. There are almost no major differences between the IEs obtained with the two basis sets discussed above. One exception is the $^2B_{1g}$ state, for which the deviation is 0.13 eV. This discrepancy disappears when similar cuts in the active space are made for each basis. NR2 results that are produced with the smaller basis are presented in Table 8.

As in the molecules examined above, the two upper levels are nearly degenerate and the corresponding DOs bear a strong resemblance to their H2P and MgP antecedents. Pole strength values are high in both cases, and the one-electron ionization picture is confirmed for the $^2A_{1u}$ and $^2A_{2u}$ final states. The NR2 procedure finds slightly lower IEs with pole strengths above 0.8 for each state.

Starting with the third ionized state, the one-electron picture begins to lose its qualitative validity. Lower pole strengths found in P3 calculations for π-hole final states are juxtaposed with strong correlation effects in NR2 results for $^2B_{2u}$, ^2E_g, $^2A_{2u}$, and $^2B_{1u}$ states. For σ-hole final states such as $^2B_{1g}$, ^2E_u, and $^2B_{2g}$, the pole strengths are larger, even though the correlation corrections to KT IEs may exceed 1.5 eV.

The first σ-hole state, $^2B_{1g}$, appears at about 9 eV in P3 calculations. NR2 places this state at ~8.40 eV. This low value may be a consequence of the significant cut in the active orbital space. The NR2 pole strength indicates the one-electron nature of the ionization. For the corresponding b_{1g} DO, the chief contributions are made by nitrogen lone pair lobes with alternating phases, as was the case for MgP. Zn–N antibonding patterns that involve the Zn $d_{x^2-y^2}$ atomic orbital also are present. In MgP, the corresponding IE is predicted to be approximately 0.6 eV higher.

A set of degenerate e_u levels corresponding to out-of-phase combinations of opposite nitrogen lone pair lobes is placed at about 11 eV by P3. The one-electron picture holds for this state. Comparison with MgP does not show as large a shift as that, which was obtained in the b_{1g} case.

The other σ-hole states for which the one-electron picture holds have significantly higher IEs. This class includes $^2A_{2g}$, $^2B_{2g}$, another ^2E_u, and $^2A_{1g}$ states. The DO corresponding to the latter state shows a significant mixture of the Zn d_{z^2} orbital to the totally in-phase combination of the nitrogen lone pair lobes.

Conclusions

Computational studies of the IEs of H2P, MgP, and ZnP with ab initio electron propagator methods lead to the following conclusions. (i) In the valence PES of all three molecules, the one-electron picture of ionization holds only for the first two π-hole states and for σ-hole states whose DOs have large contributions from nitrogen lone pair lobes. Significant shake-up character may be attributed to the remaining π-hole states. (ii) Only one band of the H2P experimental PES can be unambiguously assigned to the ionization states mentioned above. The rest of the spectrum reflects a complex overlap of π shake-ups and σ one-electron ionizations. (iii) Balanced reductions of occupied and virtual active orbital spaces can lead to results that closely resemble those produced without omission of valence orbitals. (iv) Diffuse functions that are added in the 6-311+G** basis are not essential. (v) The P3 method provides accurate IEs for final states where the diagonal approximation is valid. (vi) The NR2 method is a useful diagnostic for π-hole states with appreciable shake-up character.

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