

Valence ionization potentials and cation radicals of prototype porphyrins. The remarkable performance of nonlocal density functional theory

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Abstract. Nonlocal density functional theory (NLDFT) has been used to calculate the lower ionized states of the free-base forms of porphin, bacteriochlorin, and porphyrine and also zinc porphin. For porphin, the calculated vertical ionization potentials (IPs) quantitatively reproduce the low-energy end of the experimental gas-phase ultraviolet photoelectron spectrum, which suggests that NLDFT could be an exceptionally useful tool for studying IPs and cation radical states of a variety of porphyrinic materials.

Key words: Nonlocal density functional theory – Porphyrins – Photoelectron spectra – Ionization potentials

1 Introduction

Cation radicals of porphyrin-type molecules are of great importance in a number of biochemical and chemical processes [1]. For instance, ionized states of hydro-porphyrins are involved in the chemistry of the photosynthetic reaction centre [5]. The compound I reactive intermediates of a variety of heme oxygenases and peroxidases also contain porphyrin cation radicals [3]. A number of totally synthetic porphyrinoid cation radicals have been characterized [1]. In spite of extensive studies, many important aspects of these species remain insufficiently clear, which explains the continued rapid pace of significant discoveries in this area.

The two highest occupied molecular orbitals (HOMOs), which are a_{1u} and a_{2u} in a D_{4h} metalloporphyrin, of many porphyrin-type molecules are near-degenerate and well-separated energetically from other molecular orbitals (MOs) [4]. Accordingly, porphyrin cation radicals are typically either of the A_{1u} or A_{2u} type. Qualitative

diagrams of these a_{1u} and a_{2u} , MOs which also provide a qualitative representation of the unpaired spin distributions in the corresponding cation radicals, are given in Fig. 1. Much interest has focused on the question of what factors determine the A_{1u} or A_{2u} nature of the cation radicals. At present, there is some consensus that tetraphenylporphyrin (TPP)-type and octaethylporphyrin (OEP)-type cation radicals have A_{2u} and A_{1u} ground states, respectively [1].

For many other substitution patterns, the cation radical ground states are unknown or controversial. For instance, even for porphin (PH_2 , Fig. 2), the ground state of the cation radical is unknown. In principle, quantum chemical methods are useful for solving this problem. If the energies of both the lowest A_{2u} - and A_{1u} -type cationic states of different types of porphyrins can be reliably obtained, one should be able to achieve an understanding of the factors governing the ground states of porphyrin cation radicals. This is a rather tall order: we are seeking a theoretical method that can reliably determine the absolute and relative energies of two cation radical states which may differ in energy by only a couple of tenths of an eV. We have now identified nonlocal density functional theory (NLDFT) as a technique that possibly meets this demand and thereby fulfils a long-awaited need in the chemistry of porphyrin cation radicals.

The performance of NLDFT is validated by comparing calculated ionization potentials (IPs) with the experimental ultraviolet photoelectron spectrum (UPS) of PH_2 [5]. Methodological issues such as basis set effects, the performance of spin-restricted versus spin-unrestricted calculations, and the role of nonlocal or gradient corrections have been clarified. We have also made a preliminary exploration of the energy differences between vertical versus geometry-relaxed ionized states. Developing a good feel for this issue can provide a firm theoretical basis for using photoelectron spectroscopy (PES), which typically measures vertical IPs, for predicting porphyrin cation radical ground states. The quantitative agreement between calculated and UPS IPs of PH_2 has led us to predict the low-energy part of the valence photoelectron spectra of three other porphyrin-

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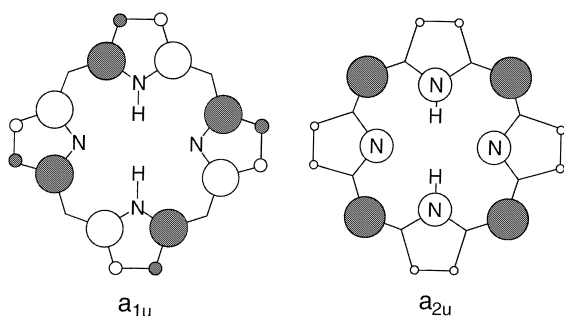


Fig. 1. Schematic diagram of the two highest occupied molecular orbitals (HOMOs) of a typical porphyrin

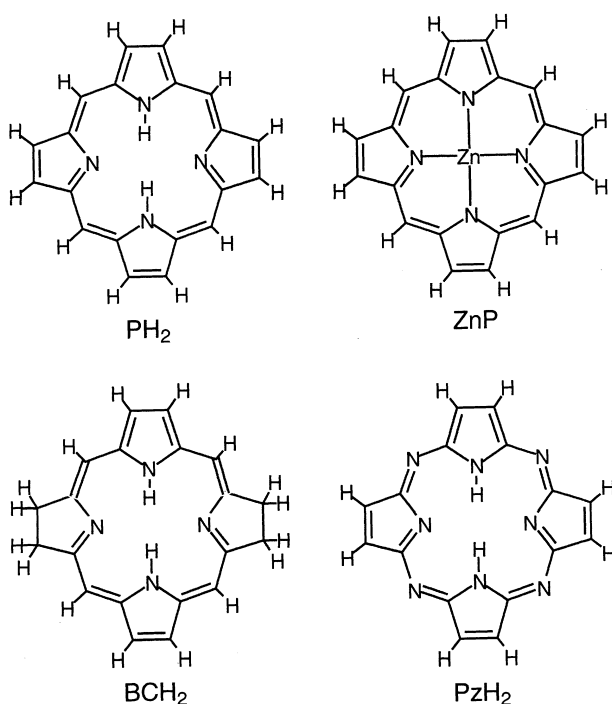


Fig. 2. Molecules studied in this work

type molecules with a high degree of confidence. The additional molecules studied were zinc porphyrin (ZnP), free-base bacteriochlorin (BCH₂), and free-base porphrazine (PzH₂) (Fig. 2). The calculated results on these molecules should provide accurate measures of the electronic effects of certain standard structural perturbations on the porphyrin macrocycle.

2 Methods

All new calculations reported in this paper have used density functional theory (DFT) as implemented in the Amsterdam density functional (ADF) program system [6]. Both local density functional (LDF) and NLDFT calculations have used the local exchange-correlation functional of Vosko, Wilk, and Nusair (VWN) [7]. In addition, the NLDFT calculations have used the Perdew-Wang 91 (PW91) [8] or Becke-Perdew

(BP) [9, 10] nonlocal corrections. Slater-type triple- ζ plus polarization (TZP) or triple- ζ plus double polarization (TZDP) basis sets and a fine mesh for numerical calculations of the matrix elements have been employed [6]. All IPs (except some previously [11] obtained by Hartree-Fock Koopmans' theorem (HF-KT) results quoted in Table 1) have been calculated in a Δ SCF manner, i.e. the IP equals the energy of the ionized state minus the energy of the neutral state. For any IP calculation, *both* the neutral and the ionized states are studied by either spin-restricted or spin-unrestricted calculations. Restricted and unrestricted calculations are indicated by appending R and U, respectively, to the abbreviation of the theoretical method in question.

Standard symbols for the irreducible representations of the molecular point groups have been used. The porphyrin molecules are assumed to be in the xy plane with the x and y axes defined by straight lines joining opposite nitrogens. For the free bases, the N—H...H—N axis was chosen as the y axis [11].

3 Results and discussion

3.1 Methodological issues

The different entries in Table 1 present our findings on various methodological aspects of calculations of IPs.

All the DFT Δ SCF (entries E–L) results agree remarkably well with one another. For instance, across all the different basis sets and exchange-correlation functionals used, the lowest vertical IP of PH₂ varies within 6.89–7.26 eV, i.e. a range of only 0.37 eV. The DFT results, as a whole, are quite different from *ab initio* HF [12, 13] (entries A–C) or SAC-CI [14] (entry D) results reported elsewhere. We will see in Sect. 3.2 that the DFT [15] results are the more quantitatively correct ones.

Among the DFT results, note that entries E and F are similar to each other and entries G–L are similar among themselves. This makes sense since E and F are LDF results, while the entries from G onwards include nonlocal corrections. Relative to the LDF results, nonlocal corrections have a distinct influence and appear to systematically lower the calculated IPs by about 0.2 eV.

How important is the choice of the exchange-correlation functional? Among the LDF results E and F in Table 1, note that the von-Barth-Hedin (vBH) [16] and VWN functionals give similar results that differ at most by 0.10 eV. Entries H and K, which are obtained with the PW91 and BP nonlocal corrections, respectively, agree to an even more impressive degree. The maximum difference between the PW91 (H) and BP (K) results is as little as 0.02 eV. Of the two local functionals used in the LDF calculations, the LDF-VWN results are closer to the nonlocal results and, thus, may be regarded as marginally better than the vBH results.

The maximum difference between the RNLDFT entries H and I, which differ only in their basis set, is only 0.01 eV. Accordingly, a double- or triple- ζ basis set and a single set of polarization functions appears to be adequate for accurate calculations of IPs [17].

Table 1. Vertical ionization potentials (eV) of free-base porphyrin obtained by different methods

Method	Ionized state			
	${}^2B_{1u}$	2A_u	${}^2B_{2g}$	${}^2B_{3g}$
A RHF-KT/DZ/unoptimized ^a	6.44	6.23	8.89	10.16
B RHF-ASCF/DZ//unoptimized ^b	6.00	5.80	–	–
C RHF-KT/TZDP//unoptimized ^a	6.77	6.15	9.04	10.16
D SAC-CI/DZ-minimal//unoptimized ^c	6.09	6.35	7.98	9.10
E ULDF-vBH/DZP//unoptimized ^b	7.26	7.37	8.24	8.90
F RLDF-VWN/TZP//RLDF-VWN/TZP ^d	7.18	7.36	8.14	8.82
G RLDF-VWN/TZP//RNLDFT-VWN-PW91/TZDP ^d	7.17	7.36	8.11	8.80
H RNLDFT-VWN-PW91/TZP//RNLDFT-VWN-PW91/TZP ^d	6.99	7.17	7.93	8.64
I RNLDFT-VWN-PW91/TZDP//RNLDFT-VWN-PW91/TZDP ^d	7.00	7.17	7.94	8.65
J UNLDFT-VWN-PW91/TZDP//RNLDFT-VWN-PW91/TZDP ^d	6.89	7.09	7.82	8.55
K RNLDFT-VWN-BP/TZP//RNLDFT-VWN-PW91/TZDP ^d	7.01	7.18	7.95	8.66
L RNLDFT-VWN-BP/TZP//RNLDFT-VWN-BP/TZP ^d	7.01	7.18	7.94	8.65

^a Ref. [12]^b Ref. [15]^c Ref. [14]^d This work

Comparing entries I and J, the spin-restricted and unrestricted results are again in excellent agreement with a maximum difference of 0.12 eV. Not surprisingly, the unrestricted calculations give somewhat lower energies for the open-shell cation radical states relative to the closed-shell unionized states than the restricted calculations.

The almost exact agreement between entries K and L and between entries F and G is an illustration of the fact that small differences in geometry that might result from optimizations at different levels of theory do not significantly affect Δ SCF IPs. Both LDF and NLDFT calculations seem equally acceptable for geometry optimizations for this purpose. It is worth noting, however, that ab initio HF theory is generally unsuitable for optimizations of porphyrin-type molecule [18].

3.2 The photoelectron spectrum of porphyrin

Figure 3 presents an edited version of a published gas-phase He I UPS of PH₂ [5]. The RNLDFT-VWN-PW91/TZDP IPs are essentially in quantitative agreement with features observed in the UPS. This emboldens us to interpret the UPS in greater detail than we previously did on the basis of LDF theory [17].

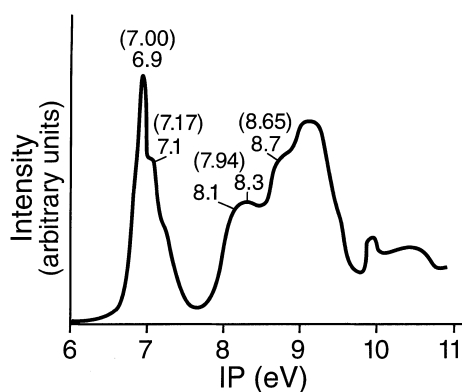


Fig. 3. Ultraviolet photoelectron spectrum (UPS) of PH₂ reproduced after stylistic modification [5]. Experimental and calculated (entry I, Table 1) features (eV) are shown outside and within parentheses, respectively

All the NLDFT calculations reproduce the approximately 0.2 eV gap between the two lowest one-electron IPs in the UPS (Fig. 3), in addition to their absolute values. Given this remarkable agreement between theory and experiment, the lowest one-electron IP of PH₂ is assigned, for the first time, to the ${}^2B_{1u}$ - or “ 2A_u -type” ionized state. The second lowest ionized state of PH₂ is then assigned to a 2A_u - or A_{1u} -type state. In retrospect, our previous LDF calculations have also reproduced the “correct” ordering of the ${}^2B_{1u}$ and 2A_u states of the PH₂ cation [17]. However, since the absolute values of the LDF IPs were in error by ~ 0.2 – 0.3 eV compared to the UPS peaks, we previously [15] refrained from making a definitive assignment of the ground state of [PH₂]⁺ on the basis of the LDF results alone.

The calculated lowest ${}^2B_{2g}$ state at 7.93 eV at the RNLDFT-VWN-PW91/TZDP level is in reasonable agreement with a feature that peaks at 8.3 eV in the experimental UPS (Fig. 3). The discrepancy of about 0.37 eV between 7.93 eV and 8.3 eV should not be regarded as nonquantitative performance of NLDFT. Instead, we believe that this experimental feature is a composite peak, i.e. corresponds to multiple ionized states. The HF orbital energy spectrum [11] as well as SAC-CI calculations by Nakatsuji et al. [14], suggest that there should be a second low-lying ${}^2B_{1u}$ state in this region of the spectrum. Unfortunately, we cannot use DFT to verify this explicitly for PH₂ since DFT applies to only the lowest state for each symmetry species. However, we will see that our DFT calculations on ZnP (Sect. 3.4) shed additional light on this point and lend support to our proposal that the UPS feature peaking at 8.3 eV has a composite character.

The calculated lowest ${}^2B_{2g}$ state at 8.65 eV (at the same level of theory as above) is again in essentially quantitative agreement with an experimental feature at 8.7 eV. Thus, we have reproduced four of the lowest one-electron IPs of PH₂ with essentially quantitative accuracy. This amazingly good performance of NLDFT may be contrasted with errors of about 0.8 eV in recently published SAC-CI values of the two lowest one-electron IPs of PH₂ [14].

Finally, it must be realized that the considerable insights offered by DFT calculations into the ionized states of PH₂ are partly a consequence of the high symmetry of

the molecule. For molecules of lower symmetry, fewer one-electron IPs can be obtained in this manner owing to the fewer different symmetry species of the point group in question. Nevertheless, DFT provides an excellent and general method for accurate calculations of the lowest IPs of a wide variety of molecules.

3.3 Geometry optimization studies of porphyrin ionized states

The ground state of a porphyrin cation radical is typically determined by actual isolation of the radical, a process often done electrochemically, followed by the appropriate spectroscopic measurements. Obviously, this approach does not shed any light on the energy of the A_{1u} -type state relative to the ground A_{2u} -type state. PES is potentially much more informative allowing a determination of multiple ionized states of molecules. However, PES features are typically vertical IPs and indicate nothing about the stability of the geometry-relaxed states. This raises the question of whether PES is really useful for predicting the ground states of porphyrin cation radicals.

The above issue is conveniently addressed by calculating by how much the energy of a “vertically ionized” porphyrin (i.e. a porphyrin cation whose geometry is kept the same as that of neutral porphyrin) is lowered on geometry relaxation or optimization. At the RNLDF-T-VWN-PW91/TZDP level, the energies of the “vertically ionized” lowest ${}^2B_{1u}$, 2A_u , ${}^2B_{2g}$ and ${}^2B_{3g}$ states (i.e. the vertical IPs) are 6.9993, 7.1727, 7.9396 and 8.6495 eV, respectively, relative to optimized, unionized PH_2 as zero-level. At the same level of theory, the optimized cationic ${}^2B_{1u}$, 2A_u , ${}^2B_{2g}$ and ${}^2B_{3g}$ states are 6.9846, 7.1299, 7.8476 and 8.5994 eV, respectively, relative to the same zero-level. In other words, the nuclear relaxation energies of the four vertically ionized states are 0.0147, 0.0428, 0.0920 and 0.0501 eV, respectively. There are no a priori reasons to doubt that nuclear relaxation energies of similar magnitudes should hold for other porphyrinic systems as well. Accordingly, we can conclude that although PES generally provides vertical IPs, it also provides a good estimate of the energy difference between the geometry-relaxed A_{1u} - and A_{2u} -type cation radicals of typical porphyrins for which these two states differ in energy by at least a couple of tenths of an eV. For porphyrins, where the two lowest cationic states differ in energy by as little as <0.05 eV or so, PES may be unreliable for determining the relative stability of the geometry-relaxed cationic states. This is an important insight since it shows that PES can play a much more important role than it has so far in our efforts to develop a detailed picture of the factors determining the ground states of porphyrin cation radicals.

The RNLDF-T-VWN-PW91/TZDP optimized structures of the neutral and the two lowest cationic states of PH_2 are shown in Fig. 4. The geometry of neutral PH_2 will not be commented upon here in any detail. Its

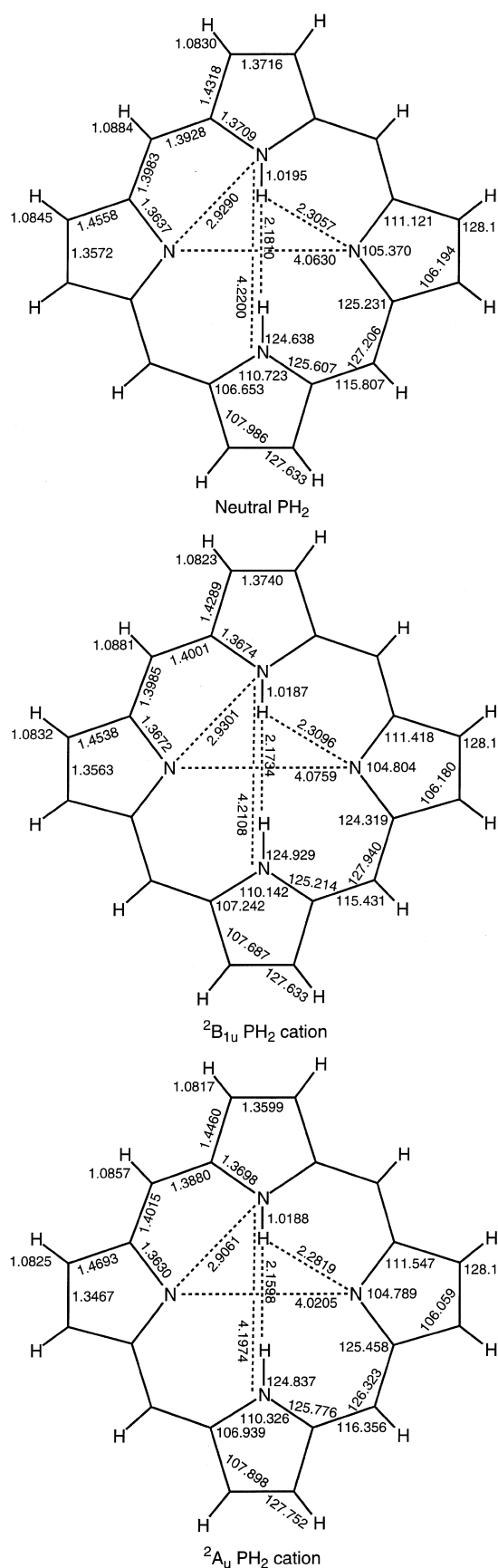


Fig. 4. RNLDF-T-VWN-PW91/TZDP optimized geometries (Å, degrees) of neutral and the two lowest cationic states of PH_2

Table 2. Selected bond lengths (Å) in neutral and cation radical states of PH₂. The entries symbolized Δ refer to changes in bond length relative to neutral PH₂ as zero-level

Bond	[PH ₂] ⁰	² B _{1u} [PH ₂] ⁺ (Δ)	² A _u [PH ₂] ⁺ (Δ)
In or adjacent to the <i>N</i> -protonated pyrrole ring			
C _β —C _β	1.3716	1.3740 (+0.0024)	1.3599 (−0.0117)
C _α —C _β	1.4318	1.4289 (−0.0029)	1.4460 (+0.0142)
C _α —C _{meso}	1.3928	1.4001 (+0.0073)	1.3880 (−0.0048)
C _α —N	1.3709	1.3674 (−0.0035)	1.3698 (−0.0011)
In or adjacent to the <i>N</i> -unprotonated pyrrole ring			
C _β —C _β	1.3572	1.3563 (−0.0009)	1.3467 (−0.0105)
C _α —C _β	1.4558	1.4538 (−0.0020)	1.4693 (+0.0135)
C _α —C _{meso}	1.3983	1.3985 (+0.0002)	1.4015 (+0.0032)
C _α —N	1.3637	1.3672 (+0.0035)	1.3630 (−0.0007)

qualitative features are in agreement with previous LDF and MP2 optimizations and with experimental values [18]. It is worth pointing out that the structure reported here is the most accurate optimized geometry of PH₂ reported so far. Differences in selected bond lengths between the structures in Fig. 4 are also listed in Table 2. These differences range from a few ten-thousandths to over a hundredth of an angstrom. Some of these changes can be qualitatively correlated with the nodal structure of the open-shell MO (Fig. 1). For instance, the C_β—C_β interactions in the b_{1u} (“a_{2u}”) and a_u (“a_{1u}”) HOMOs of PH₂ are bonding and antibonding, respectively. This correlates with the elongation and contraction of the C_β—C_β bonds in the ²B_{1u} and ²A_u states of the PH₂ cation relative to the bond lengths in neutral PH₂. Similarly, the significant elongation of the C_α—C_β bonds in the ²A_u state of [PH₂]⁺ reflects the C_α—C_β bonding interactions in the a_u MO.

The high-level optimizations reported here provide a unique qualitative view of the structural changes accompanying ionization of the porphyrin macrocycle. These changes are so small that they are completely overshadowed by solid-state intermolecular interactions in crystallographic studies. Fortunately, these subtle structural effects can be qualitatively correlated with vibrational spectroscopy results [20]. For instance, the C_β—C_β stretching mode ν₂ of CuOEP (~1592 cm⁻¹) upshifts by ~21 cm⁻¹ on conversion to its A_{1u}-type cation radical [20]. This is consistent with the shortening of the C_β—C_β bond in an A_{1u}-type cation radical. Again, the C_α—C_{meso} stretching mode ν₃₉ of CuTPP (~1520 cm⁻¹) downshifts by ~14 cm⁻¹ on conversion to its A_{2u}-type cation radical [20] which is consistent with our prediction of an increased C_α—C_{meso} distance in the ²B_{1u} state of the PH₂ cation. In this connection, it is worth noting that the lengths of adjacent C_α—C_{meso} bonds in the ²A_u state differ by 0.0135 Å, which is considerably more than the analogous values of 0.0055 Å and 0.0016 Å for neutral PH₂ and the ²B_{1u} state of [PH₂]⁺, respectively. Other structure-frequency correlations are of course possible, but these are complicated by the more complex internal-coordinate composition of the relevant vibrational modes. Finally, it is important to keep in mind that these structure-frequency correlations are only qualitative. Different elec-

tronic states of [PH₂]⁺ are only very approximate models of [CuOEP]⁺ and [CuTPP]⁺.

3.4 Zinc porphyrin

One reason why the computed NLDFT IPs of ZnP are of interest is that they allow us to determine the effects of metal-complexation on the porphyrin IPs. For both PH₂ and ZnP, the lowest ionized state is the A_{2u} type. For this lowest IP, zinc complexation results in an increase in the IP by 0.05 eV. In contrast, zinc complexation lowers the second IP, which corresponds to the A_{1u}-type ionized states, by 0.07 eV.

It is intriguing to try to correlate these trends with electrochemical redox potential data on porphyrins [21, 22]. For OEP derivatives, which oxidize to the A_{1u}-type cation radicals, the oxidation potential of the free base (0.81 V) is higher than the potentials for NiOEP (0.73 V), CuOEP (0.79 V), and ZnOEP (0.63 V) [20]. These electrochemical data seem to agree qualitatively with our calculated downshifting of the second one-electron IP of PH₂ on zinc complexation.

The situation with TPP derivatives is apparently more complex. The one-electron oxidation potential of the free base (0.95 V) is higher than that of CuTPP (0.90 V) or ZnTPP (0.71 V) [21]. This is apparently inconsistent with our finding that zinc complexation slightly elevates the IP corresponding to the A_{2u}-type ionized state. Fortunately, one can be fairly confident that this does not represent a failure of our calculations.

Metalloporphyrins in solution typically carry axial ligands, which we have not included in our calculation on ZnP. Moreover, we have not taken into account any solvent effects. However, some experimental support for our calculation may be derived from the fact that NiTPP, unlike CuTPP or ZnTPP, has a higher oxidation potential (1.01–1.05 V [22] or 1.10 V [21], depending on the reference) than TPPH₂. In view of a well-known valence tautomerism between Ni(II)(TPP⁺) and Ni(III)TPP species [23, 24] it should be pointed out that the oxidation potentials quoted here for NiTPP refer to macrocycle-centred oxidation. The d⁸ Ni(II) ion in a strong square planar ligand field may have a low axial ligand affinity in the dichloromethane solutions employed in the electrochemical measurements. Accordingly, one may speculate that the oxidation potential data on NiTPP may be the most suitable for comparison with our calculated data on axially unligated ZnP.

The situation with porphyrin derivatives is similar to that with TPP derivatives. The oxidation potential of PH₂ (0.91 V) is lower than the that of NiP (0.97 V) but higher than that of CuP (0.93 V) or ZnP (0.72 V).

Overall, it is possible to interpret the database of electrochemical oxidation potentials of free-base and metalloporphyrins to support our calculated differences between PH₂ and ZnP. However, this interpretation remains speculative mainly because we have not modelled the solvation or axial ligation of the complexed metal in our calculations.

As mentioned before, the DFT IPs of ZnP are also of interest because they allow a more detailed under-

Table 3. Vertical restricted nonlocal density functional theory-Vosko, Wilk and Nusair-Perdew-Wang 91/Slater-type triple-zeta plus polarization (RNLDFT-VWN-PW91/TZP) valence IPs (eV) of PH₂, ZnP, BCH₂ and PzH₂

PH ₂	ZnP	BCH ₂	PzH ₂
6.99(² B _{1u})	7.04(² A _{2u})	6.22(² A _u)	7.83(² A _u)
7.17(² A _u)	7.10(² A _{1u})	6.79(² B _{1u})	8.38(² B _{1u})
7.93(² B _{2g})	7.99(² E _g)	7.97(² B _{2g})	8.60(² B _{2g})
8.64(² B _{3g})	7.96(² B _{2u})	8.70(² B _{3g})	9.28(² B _{3g})
	10.09(² B _{1u})		

standing of the gas-phase UPS of PH₂. Because of the higher symmetry of ZnP, we have been able to compute five π -ionized states of ZnP corresponding to each of the five π -type symmetry species of the D_{4h} point group compared to only four for the D_{2h} -symmetric free bases that we have studied here. The D_{4h} π -type irreps shown in Table 3, $A_{2u}, A_{1u}, E_g, B_{2u}, B_{1u}$, on subduction to D_{2h} , reduce into $B_{1u}, A_u, B_{2g} + B_{3g}, B_{1u}$ and A_u , respectively. Table 3 shows that the three lowest one-electron IPs of PH₂, corresponding to ²B_{1u}, ²A_u, and ²B_{2g} (D_{2h} notation) ionized states, are very close to three of the lowest IPs of ZnP, corresponding to the ²A_{2u}, ²A_{1u}, and ²E_g (D_{4h} notation) ionized states. This correspondence is exactly that expected from descent of symmetry from D_{4h} to D_{2h} . The close similarity of the IPs of the two molecules is understandable since in both cases these ionizations take place from the porphyrin π -system. The IP at 7.96 eV corresponding to a ²B_{2u} (D_{4h} notation) ionized state of ZnP lends credence to our proposal that PH₂ too should have an IP at approximately 8 eV that corresponds to a ²B_{1u} (D_{2h} notation) ionized state. In other words, there is now good, albeit somewhat indirect, evidence that the UPS feature (Fig. 3) peaking at 8.3 eV for PH₂ corresponds to multiple ionized states.

3.5 Free-base bacteriochlorin

The IPs of free-base BCH₂ have been studied with ab initio and LDF calculations and, accordingly, here we will only underscore the special features of the NLDFT results. Compared to the RNLDFT-VWN-PW91/TZP values of the three lowest IPs of BCH₂ (Table 3) the corresponding LDF/DZP [25] values of 6.42, 6.99 and 8.14 eV are about 0.2 eV higher. This trend is exactly parallel to what we found for PH₂ (see Sect. 3.1) and it reflects the effect of the nonlocal corrections. Note that the two lowest IPs of BCH₂ are not near-degenerate as in the case of PH₂, with the lowest ionized state clearly and undoubtedly of the A_{1u} type. Note also that the lowest IP of BCH₂ is as much as 0.77 eV [25] lower than that of PH₂, while some of the other IPs of the two molecules, for analogous ionized states, are much closer.

3.6 Free-base porphyrazine

As for the other molecules, nonlocal corrections also lower the absolute values of IPs of PzH₂ by about 0.2 eV

relative to the LDF/DZP results [26]. The present NLDFT results show that the lowest IP of PzH₂, which again clearly corresponds to a ²A_u ionized state, exceeds that of PH₂ by 0.83 eV, a margin that is greater than previously suspected [26]. Overall, in many respects such as the spacing between different IPs of a particular molecule or differences in IPs among different molecules, NLDFT results are very close to LDF results [15, 25, 26].

The NLDFT results confirm a somewhat counter-intuitive feature of the IPs of PzH₂ that was first noted from a comparison of HF-KT and LDF results [26]. The two lowest HF-KT/DZP IPs of PH₂ are 6.05 and 6.69 eV, corresponding to ²A_u and ²B_{1u} ionized states, respectively (note the reversal of these states relative to DFT results) [25]. At the same level of theory, the two lowest IPs of PzH₂ are 6.25 and 9.03 eV, corresponding to ²A_u and ²B_{1u} ionized states [26]. In other words, both these IPs are upshifted compared to PH₂, which is not surprising, but the IP corresponding to the ²B_{1u} ionized state is upshifted dramatically more than the other IP. This is intuitively understandable, since aza-substitution of *meso* positions, where the b_{1u} HOMO has large amplitudes, is expected to strongly stabilize this MO. In contrast, the two lowest LDF/DZP IPs of PzH₂ (8.02 and 8.57 eV) were found to differ by only 0.55 eV. From a qualitative consideration of the shapes of the a_u and b_{1u} HOMOs, this gap seemed to be unexpectedly small and we had expressed a desire to confirm this by more advanced methods than LDF theory [26]. Now RNLDFT-VWN-PW91/TZP calculations show that these two IPs (7.83 and 8.38 eV) are indeed rather close, in agreement with the somewhat counter-intuitive LDF predictions. Moreover, the second one-electron IP of PzH₂ (8.38 eV) is actually closer to the third one-electron IP (8.60 eV) corresponding to a ²B_{2g} ionized state than to the lowest IP (7.82 eV). Accordingly, the IPs of PzH₂ follow a pattern that is rather different from one expected from Gouterman's four-orbital model [4] for porphyrin electronic spectra which stipulates that the two HOMOs of porphyrins are near-degenerate as are the two LUMOs (the LUMOs may be exactly degenerate) and these MOs are well-separated energetically from all other MOs.

4 Conclusions

1. NLDFT Δ SCF calculations have reproduced the low-energy part of the gas-phase UPS of free base porphyrin with quantitative accuracy. Four of the lowest IPs of PH₂ have been calculated to within about 0.1 eV of their experimental values.

2. Just as LDF Δ SCF IPs represent a dramatic improvement over IPs calculated at the HF level, the NLDFT results too represent a distinct improvement over LDF results. The NLDFT valence IPs are lower than the LDF values by 0.2–0.3 eV.

3. Regarding convergence with respect to basis set improvement, the DFT IPs are almost converged with double- ζ or triple- ζ basis sets augmented with a single set of polarization functions. Differences between IPs cal-

culated with spin-restricted and spin-unrestricted DFT calculations are only about 0.1 eV.

4. Geometry relaxation energies of vertical valence-ionized porphyrins are about <0.05 eV. This result establishes that PES, which typically yields vertical IPs, can also provide valuable information on the relative stabilities of geometry-relaxed A_{1u} - and A_{2u} -type porphyrin cation radicals.

5. Large differences are predicted between analogous IPs of PH_2 on the one hand and BCH_2 and PzH_2 on the other. It will be interesting to see whether PES can quantitatively reproduce the results for these compounds as well.

6. The results obtained here have important implications for many fundamental aspects of porphyrin chemistry. The remarkable performance of NLDFT for PH_2 suggests that a straightforward extension of this study should provide a detailed picture of the effects of various substitutions and structural perturbations on the relative stabilities of A_{1u} - and A_{2u} -type porphyrin cation radicals. This is indeed a long-awaited development in the chemistry of porphyrins.

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