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Comparative theoretical study of the electronic structures and electronic spectra of Fe^{2+} -, Fe^{3+} -porphyrin and free base porphyrin

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Abstract

The Intermediate Neglect of Differential Overlap quantum chemical procedure, with configuration interaction, as implemented in the ZINDO program, was employed for a theoretical calculation of Fe^{2+} -porphyrin, Fe^{3+} -porphyrin and free base porphyrin. The ground states for the first two species were found to be, at the HF level, a triplet and a quadruplet, respectively. The geometries, electronic charge distribution and energy levels, as well as theoretical UV/Vis spectra, for the three species are shown. The calculated wavelengths were in good agreement with the experimental values of the electronic spectra of Fe^{2+} -porphyrin, Fe^{3+} -porphyrin and free base porphyrin. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Porphyrin; Iron II; Iron III; ZINDO; Electronic spectra; Electronic structure

1. Introduction

One of the most important processes in living beings is the transport of oxygen by cells of the circulatory system and storage functions of cellular metabolism, for which hemoproteins have an essential role [1]. Hemoproteins include hemoglobin, cytochromes, catalase and peroxidase. The prosthetic group of hemoglobin is iron II porphyrin (Fe^{2+} -Porph), where oxygen is attached during transport. Also, porphyrins find application in medicine, as in photodynamic cancer therapy [2,3], skin diseases and viral and bacterial infections [4]. Also, the number of technological applications of synthetic porphyrins is

expanding, like Langmuir–Blodgett films [5], photo-reduction of gases [6], development of photochemical systems for solar energy conversion [7,8], and new materials as metal-porphyrin sponges [9]. Various oxo bridged metalloporphyrin dimers and trimers have been used and studied as a new class of compounds known as “molecular metals” [10–12].

Porphyrins possess a macrocyclic π system with a transition metal weakly attached [13]. They exhibit two characteristic electronic absorption bands, the Q band close to 600 nm and an intense ($\epsilon > 10^5$) band, called B or Soret, in the region of 380 nm. In free base porphyrin (Porph) there are two Q bands in 500–600 nm, actually both with a small vibrational component. The preferred geometry for Porph would be D_{2h} [14], with the H atoms linked to opposite nitrogen atoms (Fig. 1a). Other bands of higher energy are known as N, L and M [15,16]. When a metal atom is attached to the macrocycle, the symmetry rises to D_{4h} [17] (Fig. 1b); for such systems there appears

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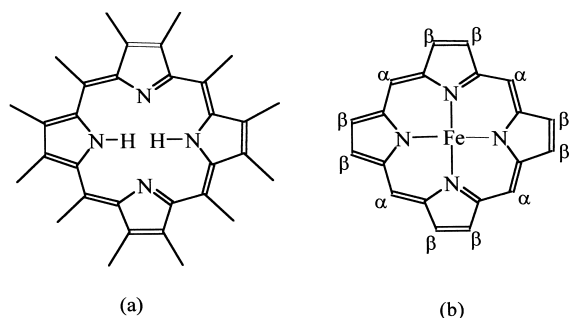


Fig. 1. Free base porphyrin (a) and iron porphyrin (b), with α and β positions indicated.

solely one Q band, while the B band remains the same or experiences minor red shifts. The kind of atomic metal has little influence on the absorption spectra, but does influence other chemical and structural properties [18].

The first theoretical studies on the electronic properties of porphyrins were attempted through the free electron model by Kuhn [19], Simpson [20] and Platt [21]. The first molecular orbital approach was the Hückel calculation by Longuet-Higgins et al. [22]. Later, Gouterman proposed the “four orbital model” for the spectra of porphyrins [23]. Many other calculations were to come, as the Pariser–Parr–Pople calculation of Gouterman et al. [24,25], followed by Extended Hückel [26], CNDO/2 [27] and ab initio calculations [28–30, X1]. We may add a few other calculations at various levels of sophistication [31–35]. Finally, we mention the studies of various authors introducing correlation at the semi-empirical level [36–41]. Recently the INDO/Configuration Interaction (CI) method was used by Li et al. in studies on the electronic spectra of tetraphenylporphyrine and its derivatives [42].

Multiconfigurational second-order perturbation (CASPT2) calculations have been performed to determine the main features of the electronic spectrum of the free base porphyrin by Merchan et al. [43] and most recently by Serrano-Andrés et al. [44]. Recent theoretical studies of the electronic ground state of iron (II) porphyrin has been investigated with multi-reference Møller–Plesset perturbation theory (MRMP), with complet active space self-consistent field (CASSCF) [45–48], in special in the work of Choe et al. [49,50].

Crescent attention has been given to Fe^{3+} -Porph, due to its importance in a large number of hemoproteins [51]. The configuration $3(d_{xz}-d_{yz})^3$ has been accepted for the ground state [52]. Guillemot and Simonneaux [53] believe in the unusual $3(d_{xy})^3(d_{xz}-d_{yz})^4$ configuration for the ground state and Goff and Shimomura [54], through NMR studies, claim a quadruplet ground state. The mayor role of Fe III is in aggregates, in which Fe II is inadequate to form extra axial bonds and maintain neutrality [55].

One of the more interesting features about porphyrinics compounds is how small variations on the basic structure of the tetrapyrrolic macrocycle, leads to wide diversity of biochemical functions. We have initiated the study of complexes of transition metals with macrocycles as phthalocianine, porphyrin, tetraazoporphyrin, both at the theoretical and the experimental levels, focussing various aspects, such as gas detecting properties [56], electronic spectra [57] and adduct formation [12]. At this time we wish to present a comparative theoretical study of Fe^{2+} -Porph and Fe^{3+} -Porph at the semi-empirical level, including correlation effects for the electronic spectra. The model utilized in the present work does not include axial ligands and equatorial substituents. The effects of the substitution of some groups like meso-tetrakis(*p*-sulfo-natophenyl) and meso-tetrakis(4-*N*-methyl-pyridiniumyl) is being discussed elsewhere [58].

2. Theoretical methodology

The calculations were performed at the Intermediate Neglect of Differential Overlap (INDO) [59,60] level by means of the ZINDO program. This program has shown useful for the calculations of properties of molecules containing first-row transition-metal complexes earlier [61–63].

The INDO approximation was introduced by Pople and collaborators [64–66] employing a parametrization for the first and second row atoms presented by Del Bene and Jaffé [67] for the calculation of molecular spectra.

Later, Bacon and Zerner [68–70] added parameters for the first row transition metals and the effect of electron correlation through CI. In this parametrization the main feature is the single ζ Slater type orbital

Table 1

Total charge, multiplicities, electronic configurations and SCF and CI total energies for Fe-porphirins in various states

Molecule	Total charge	Multiplicity	Electronic configuration	E_{HF} (eV)	E_{CI} (eV)
Fe ²⁺ -Porph	0	1	$3(d_z^2)^1 3(d_{x^2-y^2})^0 3(d_{xy})^1$ $3(d_{xz}-d_{yz})^4$	-4760.91	-4760.94
Fe ²⁺ -Porph	0	3	$3(d_z^2)^1 3(d_{x^2-y^2})^0 3(d_{xy})^1$ $3(d_{xz}-d_{yz})^4$	-4762.22	-4762.70
Fe ²⁺ -Porph	0	5	$3(d_z^2)^1 3(d_{x^2-y^2})^1 3(d_{xy})^1$ $3(d_{xz}-d_{yz})^3$	-4760.65	-4760.83
Fe ³⁺ -Porph	+1	2	$3(d_z^2)^0 3(d_{x^2-y^2})^0 3(d_{xy})^1$ $3(d_{xz}-d_{yz})^4$	-4773.85	-4773.85
Fe ³⁺ -Porph	+1	4	$3(d_z^2)^1 3(d_{x^2-y^2})^0 3(d_{xy})^1$ $3(d_{xz}-d_{yz})^3$	-4775.41	-4775.50

(STO) set with exponents calculated by Zerner [40]. The efficacy of CI for the porphyrinic systems in this study is clear in the calculation of one center exchange integrals necessary for the accurate separation of terms within a given configuration [71]. These integrals increase the interaction between states arising from $\pi \Rightarrow \pi^*$ and $\sigma \Rightarrow \sigma^*$ transitions and often reduce the calculated values of transition energies and oscillator strengths, thus providing reasonable absorption spectra for rather large molecules [72].

The ZINDO version utilized was the 3.5, using graphical interface software Cerius² 3.8, developed by Molecular Simulation Inc. The calculations were carried on a Silicon Graphics ORIGIN 2000 platform, with two R-10000 processors and graphical interface hardware Silicon Graphics O².

The particular Hamiltonian used in the geometry optimization routine was ZINDO/1 [64], with restrict open-shell Hartree–Fock approach (ROHF) for the molecule with doublet, triplet, quadruplet and quintuplet ground states. The restrict Hartree–Fock approach (RHF) was used for singlet ground states. The calculations routine for all molecules in this work, included geometry optimization by Broyden–Fletcher–Goldfarb–Shanno (BFGS) hessian update procedure with convergence criterion of 10^{-8} (normal convergence tolerance) in gradient components and 150 SCF cycles for each possible spin state. These parameters showed adequate for most ZINDO calculations.

Since the ZINDO program has not the D_{4h} group implemented, the actual calculations for the iron compounds were performed under D_{2h} symmetry. The porphyrin macrocycle is placed in the xy plane.

The oxidation states for iron were +2 and +3. Porph has closed shell singlet ground state with 114 electrons. Fe²⁺-Porph with 120 electrons, has two and four unpaired electrons in a triplet and quintuplet ground states, respectively. Fe³⁺-Porph, with 119 electrons, has one and three unpaired electrons in doublet and quadruplet ground states, respectively.

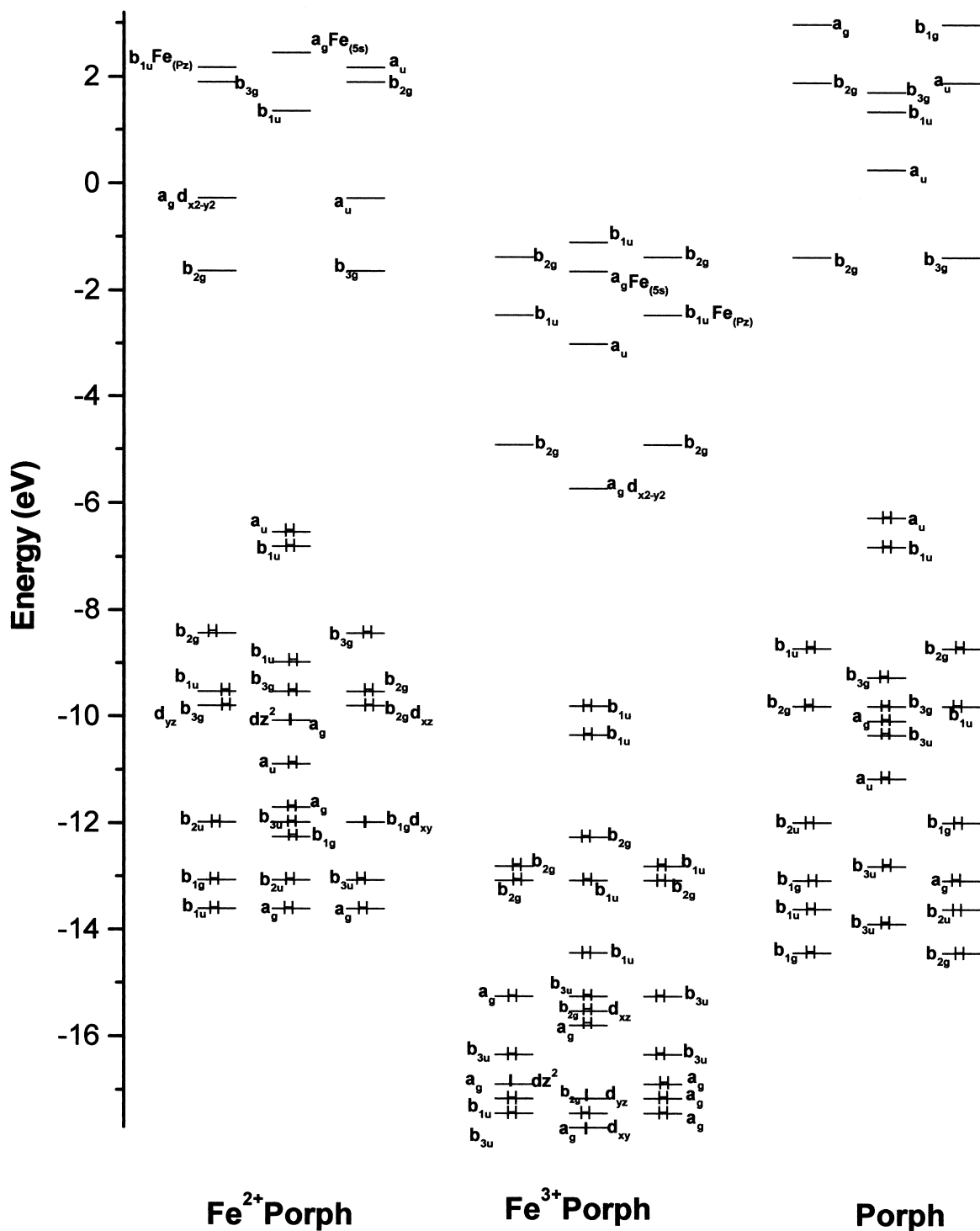
For the CI routine, the hamiltonian used was ZINDO/S [68], with the same multiplicities and approaches as in the optimization routine. Configuration interaction was limited to ten-occupied and ten-unoccupied orbitals. The CI method used for higher than singlet state multiplicities was the Rummel CI. Symmetry was included in CI and only single excitations were utilized. The theoretical spectra were plotted in a lorentzian fit, with width peak shape equal to 1000 cm^{-1} .

Only the states 1E_g , $^3A_{2g}$ and 5E_g for Fe²⁺-Porph were calculated, with occupation of d orbitals obtained directly from SCF-HF. Due the limitation of the ZINDO program, it was not possible to impose other reference states besides those calculated at the SCF-HF level. This same approach was adopted in the calculation of the multiplicities of Fe³⁺-Porph.

3. Results and discussion

3.1. Electronic structure

SCF (E_{HF}) and CI (E_{CI}) energy values are compared in Table 1. The ground state depression after CI is small and of the order of 10^{-2} cm^{-1} . However, qualitatively these little differences indicate the existence



of several spin states in close proximity, which is well known in the literature [13,15,17,40]. On the basis of the Hartree–Fock energies, the ground state for Fe^{2+} -Porph appears to be a triplet state, $^3\text{A}_{2g}$. By the same criterion, the ground state of Fe^{3+} -Porph is taken to be of quadruplet multiplicity.

The above result for Fe^{2+} -Porph is in agreement with the conclusions of Zerner et al. [13] who find the lower energy state to be $^3\text{A}_{2g}$ with configuration $3(d_z^2)^2 3(d_{xy})^2 3(d_{xz}-d_{yz})^2$. Hence, Zerner et al. suggest that the correct ground state is $^3\text{E}_g$, which has higher energy than the $^3\text{A}_{2g}$, but by only 240 cm^{-1} . NMR results obtained by Goff et al. [73] are in agreement with the $^3\text{A}_{2g}$ state found in this work. This result reach only the reference states found at the HF level, under the INDO approximation, thus do not exclude the possibility of the existence of other states with lower energy. Indeed, different ground states for Fe^{2+} -Porph have been found by experimental and theoretical chemists: $^3\text{A}_{2g}$ [73–75], $^3\text{E}_g$ [76–78], $^5\text{E}_g$ [79], $^5\text{A}_{1g}$ [80,81]. Some experimental studies indicate that the ground-spin multiplicity is a triplet state [73,75,81].

The almost negligible difference between the

Zerner's configuration and the one we have found is due to vibronic distortions in the D_{4h} symmetry, since it was used a lower symmetry. It is possible that the electronic configuration of the ground state is a mixture of Zerner's configuration and the reported in Table 4. For Fe^{3+} -Porph, the configuration found by us, $3(d_z^2)^2 3(d_{xy})^2 3(d_{xz}-d_{yz})^3$, $^4\text{A}_{2g}$, is in agreement with the considerations of Walker and Shimomura [44,45].

The energy level diagram for the Hartree–Fock calculation is shown in Fig. 2 for the three species under study. Only Porph has a closed shell configuration. All the last ten occupied orbitals have π bonding character, and the first ten unoccupied orbitals have π anti-bonding character. The Fe^{3+} -Porph levels are pushed down due to the +1.0 total charge.

Metal orbital contributions for Fe^{2+} -Porph appear in HOMO-2, -3, -8 and -9. In HOMO-2 and -3, with symmetries b_{3g} and b_{2g} , the d_{xz} and d_{yz} orbitals participate with coefficients 0.60. The same metallic orbitals have a weight of 0.78 in HOMO-8 and -9, also with symmetries b_{2g} and b_{3g} . In D_{4h} symmetry these orbitals originate the e_g degenerate orbitals. HOMO-10 is single occupied, a_g (a_{1g} in D_{4h} symmetry), being

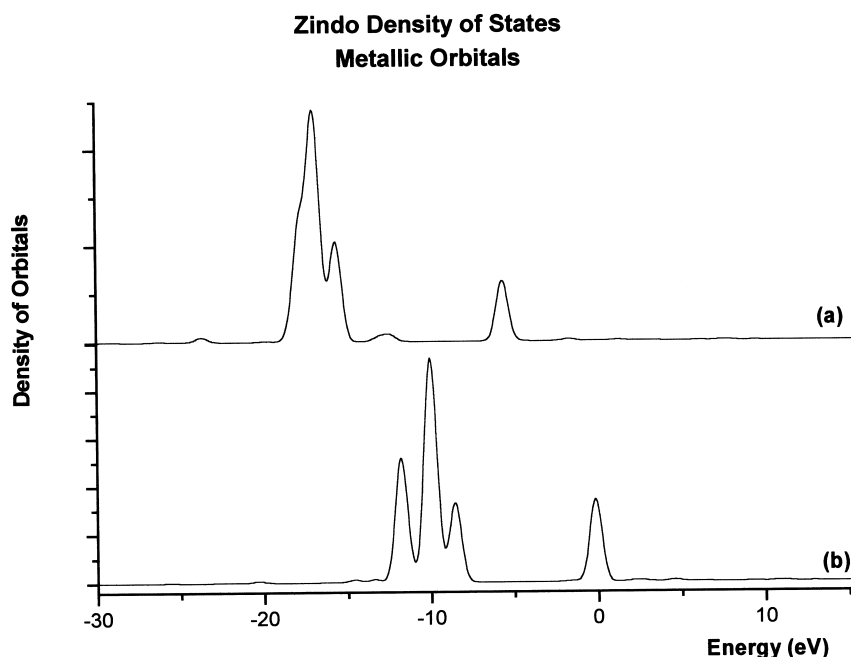


Fig. 3. Density of metallic d orbitals for (a) Fe^{3+} -Porph and (b) Fe^{2+} -Porph.

Table 2

Interatomic distances (Å) optimized by *zindo* program. M = H, Fe²⁺, Fe³⁺

Atoms pairs	Interatomic distances		
	Porph ^a	Fe ²⁺ -Porph	Fe ³⁺ -Porph
M-plane	0.00	0.00	0.00
M–N	1.06/1.06	2.09	2.01
N–C _{pirr}	1.37/1.38	1.38	1.39
C _β –C _β	1.35/1.37	1.37	1.36
C _{pirr} –C _α	1.38/1.39	1.43	1.40
C _{pirr} –C _β	1.42/1.44	1.44	1.44
C _β –H	1.09	1.09	1.09
C _α –H	1.10	1.12	1.10

^a The duplicate results for Porph are due to the existence of two H atoms instead of Fe.

almost pure d_z² (0.98). The other unpaired electron is in HOMO-13, b_{1g}, (a_{2g} in *D*_{4h} symmetry), a pure d_{xy} (0.99). The HOMO-1 has non-bonding character with contribution of carbons and nitrogenous atoms. Others occupied frontier orbitals, as HOMO, HOMO-4, -5, and -6, have a pronounced π bonding character. From LUMO to LUMO + 7, with exception of the LUMO + 2 that has metallic character, all have a pronounced π anti-bonding character. The LUMO + 2 is almost pure d_{x²-y²} (0.87), with weak contribution of the non-bonding nitrogen orbitals (ⁿ σ_s).

For Fe³⁺-Porph, the first unpaired electron is in HOMO-17, a_g, (a_{1g}, in *D*_{4h} symmetry), with pronounced weight of 0.96 from the d_z² orbital. The

Table 3

Net atomic charges for Porph, Fe²⁺-Porph and Fe³⁺-Porph. M = H, Fe²⁺, Fe³⁺

Atom	Net charges		
	Porph ^a	Fe ²⁺ -Porph	Fe ³⁺ -Porph
M	0.27/0.27	0.73	1.10
N	-0.44/-0.29	-0.43	-0.42
C _α	-0.04/-0.04	-0.06	-0.04
C _β	-0.07/-0.09	-0.07	-0.04
C _{pirr}	0.14/0.10	0.13	0.13
H _α	0.07	0.05	0.09
H _β	0.06	0.07	0.08

^a The duplicate results for Porph are due to the existence of two H atoms instead of Fe.

other two unpaired electrons are also located in pure metallic orbitals: one in HOMO-19 (0.92 d_{yz} and 0.30 d_{xz}) and the other in HOMO-24 (0.98 d_{xy}). All frontier orbitals from HOMO to HOMO-7 have π bonding character. The first virtual orbital is σ_{sp}^* with 0.74 from the metallic orbital d_{x²-y²}. This orbital, in symmetry *D*_{4h}, is pushed upwards after CI, being replaced by a π orbital. From LUMO + 1 to LUMO + 4, the orbitals have a pronounced π anti-bonding character. The LUMO + 5 is a predominantly metallic orbital, with the strong contribution (0.93) of the 4p_z.

The shapes of the HOMO and HOMO-1 in Fe²⁺-Porph are nearly the same as those of the corresponding orbitals in Porph, and the LUMO and LUMO + 1 turns out to be degenerate. The difference in mono-electronic energies HOMO–LUMO is slightly greater in Fe²⁺-Porph and Porph (4.9 eV) than in Fe³⁺-Porph (4.1 eV).

The density of d states in the frontier region is poor (Fig. 3). The greatest densities are localized between -15 and -20 eV for Fe³⁺-Porph, and -9.0 and -12 eV for Fe²⁺-Porph. Therefore, there is no significant metal contributions for the frontier region, which has mainly π character, except as already seen, the moderate contribution for LUMO + 2 in Fe²⁺-Porph and LUMO in Fe³⁺-Porph.

3.2. Geometry, charge distribution and bond indexes

Geometry optimization with the ZINDO program shows all three compounds under study to be planar (see Table 2). As Fe³⁺-Porph possesses a charge larger than Fe²⁺-Porph, the attraction for the N atom is enhanced, thus shortening the distance of 2.09–2.01 Å, which leads to a slight increase of the distance between the nitrogenous and the pyrrolic carbon atoms. Since ab initio and ZINDO do not properly converge in this situation, it is interesting the comparison between these approaches. In this case, for Fe²⁺-Porph neutralized with chlorine, Zwaans et al. [82] found a Fe–N distance of 2.049 Å in a ab initio calculation. Experimentally, for Fe²⁺-Porph stabilized with pyridine, Grinstaff et al. found a Fe–N value of 1.96 Å [83].

Calculated net charges, from Mulliken population analysis, are shown in Table 3, with distinct values for carbons α , β and pyrrolic. The duplicated values for Porph are originated by the presence of two H atoms

Table 4

Interatomic bond indexes for Porph, Fe^{2+} -Porph and Fe^{3+} -Porph.
 $M = \text{H}, \text{Fe}^{2+}, \text{Fe}^{3+}$

Linkage	Bond indexes		
	Porph ^a	Fe^{2+} -Porph	Fe^{3+} -Porph
M–N	0.88/0.88	0.71	0.82
N–C _{pirr}	1.25/1.17	1.22	1.18
C _β –C _β	1.70/1.40	1.64	1.62
C _{pirr} –C _α	1.42/1.19	1.35	1.38
C _{pirr} –C _β	1.13/1.39	1.19	1.20
C _β –H	0.97	0.97	0.97
C _α –H	0.98	0.98	0.98

^a The duplicate results for Porph are due to the existence of two H atoms instead of Fe.

in the center of the cycle. There is charge transfer from the two H_C to the two corresponding nitrogen atoms, which have their charges reduced to 0.27. Also, charge transfer is apparent for atoms close to the metal. It is perceptible the charge transfer from the macrocycle to the metal, specially to the nitrogenous, which change from $-0.44/-0.29$ (in Porph) to $-0.43/-0.42$, in Fe^{2+} -Porph and Fe^{3+} -Porph, respectively. The most distant atoms from the metallic center present only a light fluctuation in their charges. The total charges for Porph, Fe^{2+} -Porph and Fe^{3+} -Porph are 0.0, 0.0 and 1.0, respectively.

For bond indexes (Table 4) one finds similarity for the three structures. Values show the resonant

Table 5

Principal electronic transitions for Porph, Fe^{2+} -Porph and Fe^{3+} -Porph

Molecule	Principal electronic transitions			
	Origin	Character	Energy (cm ⁻¹)	Oscillator strengths
Porph	HOMO → LUMO	$\pi \rightarrow \pi^*$	13837.2	0.0242
	HOMO → LUMO + 1	$\pi \rightarrow \pi^*$	16 696.8	0.0294
	HOMO – 1 → LUMO	$\pi \rightarrow \pi^*$	27495.4	1.7263
	HOMO – 1 → LUMO + 1	$\pi \rightarrow \pi^*$	28565.8	2.4735
	HOMO – 3 → LUMO	$\pi \rightarrow \pi^*$	33598.5	1.6793
	HOMO – 3 → LUMO + 1	$\pi \rightarrow \pi^*$	35674.2	0.3972
	HOMO – 5 → LUMO	$\pi \rightarrow \pi^*$	38997.2	0.3663
	HOMO – 5 → LUMO + 1	$\pi \rightarrow \pi^*$	40818.6	0.3021
	HOMO → LUMO + 6	$\pi \rightarrow \pi^*$	44789.4	0.2594
	HOMO – 3 → LUMO + 3	$\pi \rightarrow \pi^*$	54588.5	0.1899
	HOMO – 6 → LUMO + 2	$\pi \rightarrow \pi^*$	57336.1	0.2834
	HOMO – 7 → LUMO + 2	$\pi \rightarrow \pi^*$	57634.9	0.3832
	HOMO – 6 → LUMO + 3	$\pi \rightarrow \pi^*$	58918.2	0.2007
	HOMO – 3 → LUMO + 6	$\pi \rightarrow \pi^*$	60388.8	0.3605
	HOMO – 7 → LUMO + 3	$\pi \rightarrow \pi^*$	62508.4	0.2267
	HOMO – 5 → LUMO + 5	$\pi \rightarrow \pi^*$	65654.0	0.2826
	HOMO – 3 → LUMO + 9	$\pi \rightarrow \pi^*$	70350.5	0.2345
Fe^{2+} -Porph	HOMO → LUMO	$\pi \rightarrow \pi^*$	15544.7	0.0282
	HOMO → LUMO + 1	$\pi \rightarrow \pi^*$	15572.2	0.0253
	HOMO – 1 → LUMO	$n_{(\text{C,N})} \rightarrow \pi^*$	28777.5	2.6524
	HOMO – 1 → LUMO + 1	$n_{(\text{C,N})} \rightarrow \pi^*$	28786.8	2.6434
	HOMO – 4 → LUMO + 2	$\pi \rightarrow d_{xy}^2 (^n\sigma_g)$	42185.8	0.0011
	HOMO – 10 → LUMO + 7	$d_z^2 \rightarrow \pi^*$	49566.6	0.0504
Fe^{3+} -Porph	HOMO → LUMO + 1	$\pi \rightarrow \pi^*$	15513.9	0.0255
	HOMO → LUMO + 2	$\pi \rightarrow \pi^*$	19436.2	0.0085
	HOMO – 1 → LUMO + 1	$\pi \rightarrow \pi^*$	28718.0	0.8451
	HOMO – 1 → LUMO + 2	$\pi \rightarrow \pi^*$	29208.3	1.2573
	HOMO – 2 → LUMO + 3	$\pi \rightarrow \pi^*$	52491.4	0.0568
	HOMO – 5 → LUMO + 3	$\pi \rightarrow \pi^*$	53122.3	0.0155
	HOMO – 7 → LUMO + 3	$\pi \rightarrow \pi^*$	55591.6	0.0060

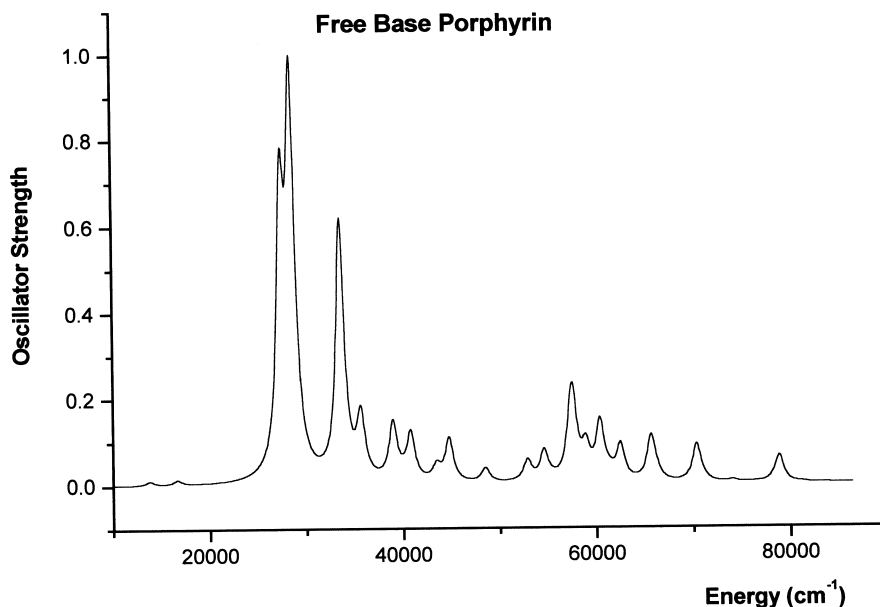


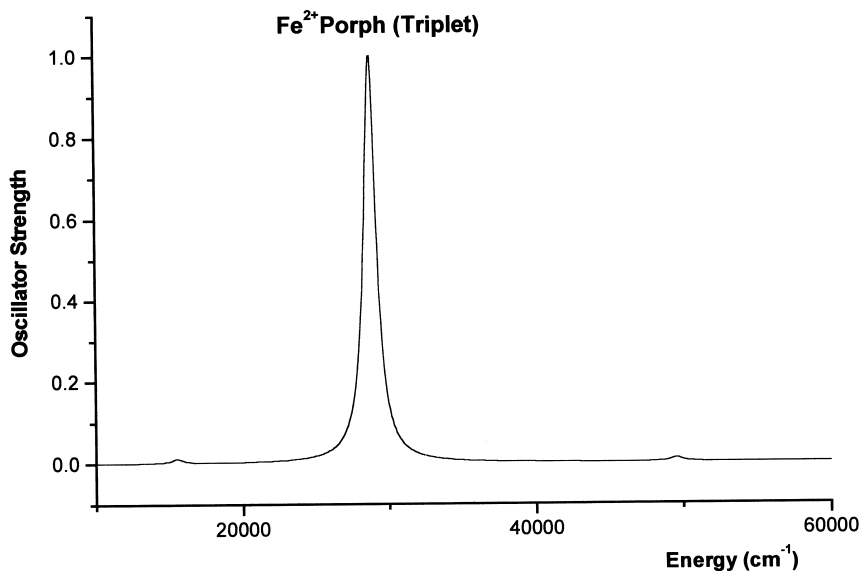
Fig. 4. Free base porphyrin UV/Vis-Zindo spectrum.

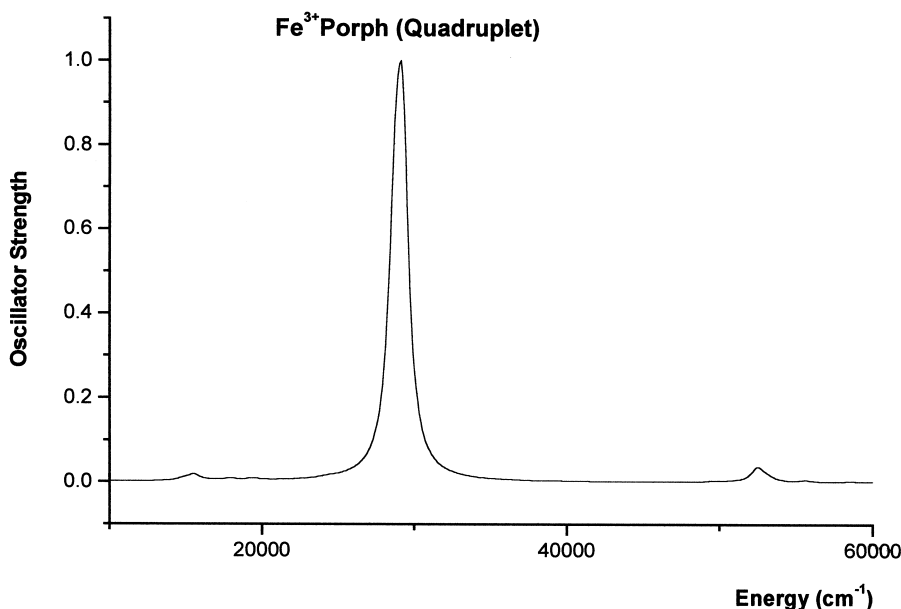
character of the macrocycle and the larger electron density is found between the β carbon atoms.

3.3. Electronic spectra

The principal electronic transitions for the three

species were calculated at the ZINDO/CI level and are shown in Table 5. The Porph structure presents high number of calculated electronic transitions. The transitions at 13 800 and 16 600 cm⁻¹ clearly Q bands. The two transitions around the 28 000 cm⁻¹ region, with high oscillator strength, are characteristic

Fig. 5. Fe²⁺Porph UV/Vis-Zindo spectrum.

Fig. 6. Fe^{3+} Porph UV/Vis-Zindo spectrum.

of the Soret band. In both electronic transition bands, the two last occupied and two first unoccupied frontier orbitals are the responsible for the transitions, and these are $\pi \rightarrow \pi^*$ transitions polarized in the macro-cycle plane. The calculated transition between 33 000 and 35 000 cm^{-1} are characteristic of the N band [15]. The transition at 44 790 cm^{-1} is characteristic of the M band and the intermediate transitions (38 000–40 000 cm^{-1}) are out of the energetic range of the M band, but are usually related to the L band [15,84]. Other higher energy bands were encountered and are plotted in the theoretical spectrum (Fig. 4).

For Fe^{2+} -Porph, transitions between HOMO-2/

HOMO-3 and LUMO were not observed (Fig. 5), due to the presence of the metal in these orbitals. The d orbitals only participate in more high energetic transitions than Q and B bands. Edwards et al. [13] found d–d transitions at lower energies than those of the Q and B bands, at values 19 200 cm^{-1} and other red shifted. Nevertheless, in this case the geometry used was D_{4h} and the Fe–N distance is 0.1 Å lower than the calculated in our work. For Fe^{3+} -Porph, the unique d frontier orbital (LUMO) does not participate in the transitions. Such as in the Fe^{2+} Porph, the presence of bands is smaller than the verified for Porph (Fig. 6).

Table 6

Transition energies for the Q and B bands for Porph, Fe^{2+} Porph and Fe^{3+} Porph

Molecule	Q Band (cm^{-1})		B Band (cm^{-1})	
	Experimental	Calculated	Experimental	Calculated
Porph	15 000/16 600 [83] ^a	13 800/16 700	24 800 [84]	28 500
Fe-Porph^{2+}	16 300 [88]	15 500	23 600 [88]	28 700
Fe-Porph^{3+}	15 800 [15] ^b	15 500	24 700 [83] ^b	29 200

^a Porph presents two characteristic Q bands.

^b The experimental results for Fe^{3+} -Porph are influenced by the presence of the oxy and halogen groups for Q and B bands, respectively.

Various experimental spectra are available, although the molecular structures studied are derivatives of Fe-porphyrin. Such molecules have counterions and substituents, which shift slightly the bands towards the red or the blue [15,40,82]. Among the main substituents one finds four phenyl groups in the β positions [53,84] or four methyl groups in the α positions [85]. As counterions, chlorine, bromine and pyridine are the most frequent [52].

The experimental values used for the comparison in Table 6 are close to the mean of most experimental values. The results obtained for the Q bands are very satisfactory.

As for the B bands, Zerner and collaborators [13,86,87] have discussed that INDO/CI, while giving an accurate value for the Q band, produces the Soret band some 4000–5000 cm^{-1} above the experimental value. In this sense, the values calculated for the Soret band in this work are reasonable. For both Fe^{2+} -Porph and Fe^{3+} -Porph the Q and B bands are of the $\pi \rightarrow \pi^*$ type and occur from HOMO and HOMO-1 to LUMO orbitals. This demonstrates that the presence of the metal atom affects weakly the electronic transition bands.

4. Conclusions

From our quantum mechanical INDO/CI comparative study, by means of the ZINDO program, for Porph, Fe^{2+} -Porph and Fe^{3+} -Porph, the following conclusions can be drawn.

The geometries, electronic structures and electronic spectra are adequately described through the INDO/CI calculation.

At the Hartree–Fock level of calculation, the predicted ground states for Fe^{2+} -Porph and Fe^{3+} -Porph are $^2\text{A}_{2g}$ and $^4\text{A}_{2g}$, respectively. Qualitatively, the CI calculation indicates several spin states close to the former, suggesting the possibility of state mixture.

The presence of the iron atom produces only minor modifications of the properties that were studied. The calculated electronic spectra for Fe^{2+} -Porph and Fe^{3+} -Porph are similar.

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