# Communication: Systematic shifts of the lowest unoccupied molecular orbital peak in x-ray absorption for a series of 3d metal porphyrins

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Porphyrins are widely used as dye molecules in solar cells. Knowing the energies of their frontier orbitals is crucial for optimizing the energy level structure of solar cells. We use near edge x-ray absorption fine structure (NEXAFS) spectroscopy to obtain the energy of the lowest unoccupied molecular orbital (LUMO) with respect to the $N_{1s}$ core level of the molecule. A systematic energy shift of the $N_{1s}$ to LUMO transition is found along a series of 3d metal octaethylporphyrins and explained by density functional theory. It is mainly due to a shift of the $N_{1s}$ level rather than a shift of the LUMO or a change in the electron-hole interaction of the core exciton. © *2010 American Institute of Physics*. [doi:10.1063/1.3497188]

Metalloporphyrins form an important class of conjugated chromophores in which a central 3d metal atom is surrounded by ligands with nitrogen atoms as nearest neighbors.[1] They play a major role in many biological processes such as oxygen binding (hemoglobin) and photosynthesis (chlorophyll). Furthermore, there is a growing interest in developing dye-sensitized photovoltaic devices using porphyrins due to their relative low cost and tunable properties.[2–6] The idea is to reproduce the light-harvesting and charge transfer properties of biomolecules in simpler organic molecules. The frontier orbitals of the porphyrins (particularly their energies and wave functions) are critical for an optimum efficiency of the photochemical reactions.

The lowest unoccupied orbital (LUMO) is accessible experimentally by near edge x-ray absorption fine structure (NEXAFS) spectroscopy, which detects optical transitions from a core level to unoccupied valence orbitals. In an organic solar cell the LUMO influences the band gap that determines the optical absorption of the dye molecule. It also affects the energy drop from the LUMO of the dye to the LUMO of the acceptor, which is critical for separating the electron-hole pair created by the absorption process. In this work we present NEXAFS spectroscopy results for the transition from the N 1s core level ($N_{1s}$) to the LUMO for a series of metal octaethylporphyrins (OEPs), namely, MnOEP, FeClOEP, CoOEP, NiOEP, CuOEP, and ZnOEP.[7] A systematic shift of the transition energy is observed when varying the central metal atom [see Fig. 1(a)]. Our aim is to understand the origin of this shift by density functional theory (DFT) and to extract the position of the LUMO. This requires the calculation of the energy of the transition from the

$N_{1s}$ level to the LUMO through a methodology that takes into account the core electron-hole interaction. As a by-product, we obtain the wave functions of the frontier orbitals. These provide a deeper understanding of the chemical bonding that helps in designing new molecules with optimized energy levels.

Metal OEPs were purchased from Sigma-Aldrich and purified by selective sublimation during the deposition process in ultrahigh vacuum. This method produced well-ordered thin film samples as judged from the strong polarization-dependence of the NEXAFS spectra[8] and the narrow line width (substantially less than for powder samples). Specifically, a tantalum Knudsen cell containing the metal OEP was heated to ∼275 °C for ∼30 s with closed shutters to block out the volatile impurities. The metal OEP then was deposited for 60–90 s onto a Si(111) wafer passivated by its native oxide. For the MnOEP sample we started with MnClOEP and sublimated it at ∼455 °C where Cl is desorbed. The change in oxidation state from $Mn^{3+}$ to $Mn^{2+}$ was confirmed by the change in multiplet structure at the Mn 2p edge [see Fig. 5a in Ref. 8]. The films were thick enough to be visible, and the resulting spectra were independent of film thickness after normalizing the overall intensity.

Total electron yield (TEY) measurements were taken at the VLS-PGM beamline at the Synchrotron Radiation Center (SRC) in Madison. The data were first normalized to the incoming photon spectrum using the TEY spectrum of a gold mesh in the beamline. Then a linear background from the C 1s and valence absorption was subtracted. Lastly, a constant factor equalized the height of the jump from the pre-edge at 397 eV to the post-edge continuum above 415 eV, thereby normalizing the spectra to the number of N atoms sampled. The photon energy for each sample was calibrated using a

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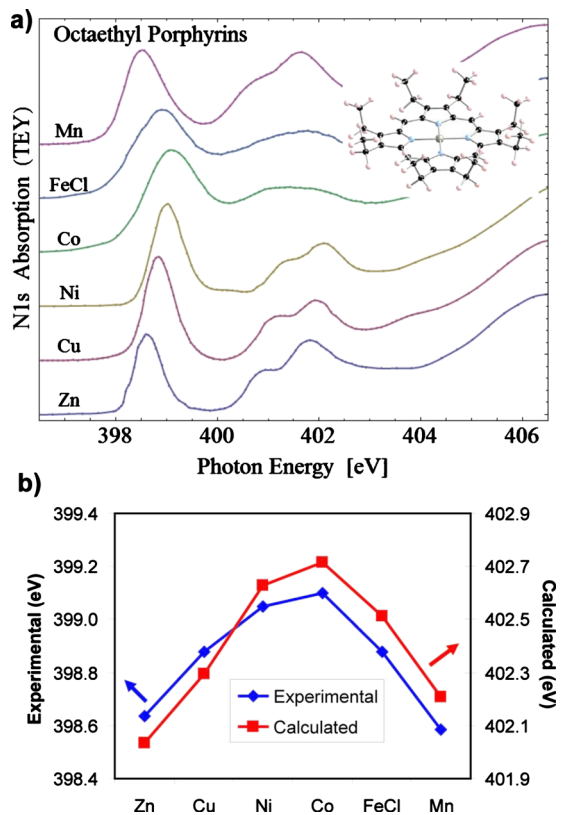
FIG. 1. (a) NEXAFS spectra for a series of 3d metal OEPs sorted by their atomic number Z. The lowest energy peaks correspond to the $N_{1s}$ to LUMO transition. The structure of an OEP is shown in the inset. (b) Comparison between experimental (left axis) and calculated (right axis) values for the maximum of the $N_{1s}$ to LUMO transition peak of the series of OEPs. Notice that the axis is shifted 3.5 eV between calculated and experimental values. The systematic shift of the LUMO peak with the atomic number Z is reproduced by the calculation.

constant wavelength shift determined by the first 2p-to-3d peak at 458.2 eV of $TiO_2$ rutile powder. The absolute accuracy of the photon energies is about ±0.1 eV, and the relative accuracy within a spectrum about ±0.05 eV.

DFT calculations were carried out by means of the Amsterdam density functional (ADF) code.[9] All atoms were described through basis sets of TZP quality (triple-$\zeta$ Slater-Type orbitals plus one polarization function) given in the program database, including all the core electrons in the calculation (i.e., with no frozen core approximation). The exchange-correlation energy was computed according to the local density approximation (LDA) by means of the Vosko–Wilk–Nussair[10] functional. The results were checked using the generalized gradient approximation by means of the Perdew–Burke–Ernzerhof (PBE) (Ref. 11) functional and a hybrid functional (PBE0).[12] The first step of the calculations consists of obtaining the structures of the different OEPs in their ground state. In a second step the $N_{1s}$ to LUMO transition was calculated using the ΔSCF method.[13] ΔSCF method uses to show energies shifted with respect to the experimental NEXAFS ones. We performed the calculations for isolated molecules, neglecting the weak van der Waals interactions between the molecules in a crystal.

In the geometry optimizations, we have imposed a $C_{4v}$ symmetry with all the ethyl groups above the molecule [see

inset Fig. 1(a)]. It has been previously shown that the outlying groups (and their arrangement) do not influence the electronic structure of the inner orbitals (3d metal, N and first C) in porphyrins,[14] which are relevant for the present study. In all degenerate ground states (the E states for Mn, FeCl, and Co), we took into account the Jahn–Teller (JT) effect and the symmetry of the system was reduced from $C_{4v}$ to $C_{2v}$ (this implies that two of the N atoms are slightly closer to the metal than the other two). We found very small JT distortions (less than 2 pm of deviation from the $C_{4v}$ symmetry). In those systems with an open shell configuration, we performed spin-polarized calculations for the geometry optimizations. By contrast, the ΔSCF calculations were non spin-polarized for all systems.

From previous work,[14,15] it is clear that the ground states for ZnOEP, CuOEP, NiOEP, and FeClOEP are $^1A_1[(b_2)^2(e)^4(a_1)^2(b_1)^2]$, $^2B_1[(b_2)^2(e)^4(a_1)^2(b_1)^1]$, $^1A_1[(b_2)^2(e)^4(a_1)^2(b_1)^0]$, and $^2E[(b_2)^2(e)^3(a_1)^0(b_1)^0]$, respectively (see Fig. 2). In the case of CoOEP,[14] there are two possible ground states: $^2A_1[(b_2)^2(e)^4(a_1)^1(b_1)^0]$ and $^2E[(b_2)^2(e)^3(a_1)^2(b_1)^0]$. Finally, there are three possible ground states for MnOEP:[15] $^6A_1[(b_2)^1(e)^2(a_1)^1(b_1)^1]$, $^4A_2[(b_2)^2(e)^2(a_1)^1(b_1)^0]$, and $^4E[(b_2)^1(e)^3(a_1)^1(b_1)^0]$. In the case of CoOEP we found the two states almost degenerate ($^2A_1$ is more stable than $^2E$ by 0.03 eV), in good agreement with the results of Liao *et al.*[14] On the other hand, the $N_{1s}{\rightarrow}$LUMO transition energy is almost independent of the considered ground state for CoOEP (less than 0.01 eV of difference). Thus, in the following we will only consider the $^2A_1$ state for CoOEP. We found that the ground state of the MnOEP *in vacuo* (gas phase) is the $^4E$ (it is 0.21 and 0.86 eV more stable than $^4A_2$ and $^6A_1$ states, respectively). This is again in good agreement with the results by Liao *et al.*[15] for other Mn porphyrins. However, in a crystal structure the ground state should be most likely the $^6A_1$ one for the following three reasons, namely: (i) Liao *et al.* predicted for other Mn porphyrins that the $^6A_1$ state becomes the most stable when the molecules are not *in vacuo*, but forming a crystal structure.[15] (ii) A magnetic susceptibility indicative of a high spin configuration has been measured for manganese tetraphenylporphyrin in solid samples.[16,17] (iii) There is a noticeable difference in the calculated $N_{1s}$ to LUMO transition energy for the three states (402.66 eV for $^4E$, 402.54 eV for $^4A_2$, and 402.21 eV for $^6A_1$). The only one that follows the experimental trend is the $^6A_1$ one [see Fig. 1(b)].

Figure 1(b) summarizes the results obtained for the $N_{1s}$ to LUMO transition in the different OEPs. The trend in the experimental results, i.e., the variation of the peak position along the series is well reproduced by the calculations despite the average shift of 3.5 eV between the calculated and the experimental values. The same variation is observed using PBE and PBE0 functionals. The only difference between the results of LDA and PBE and PBE0 is a constant shift with respect to the experiment, which is smaller in case of LDA. This shift could be due to screening by neighbor molecules in the crystal, which is not considered in the calculations. These shifts between experimental and theoretical results are also typical of time-dependent DFT (TDDFT)
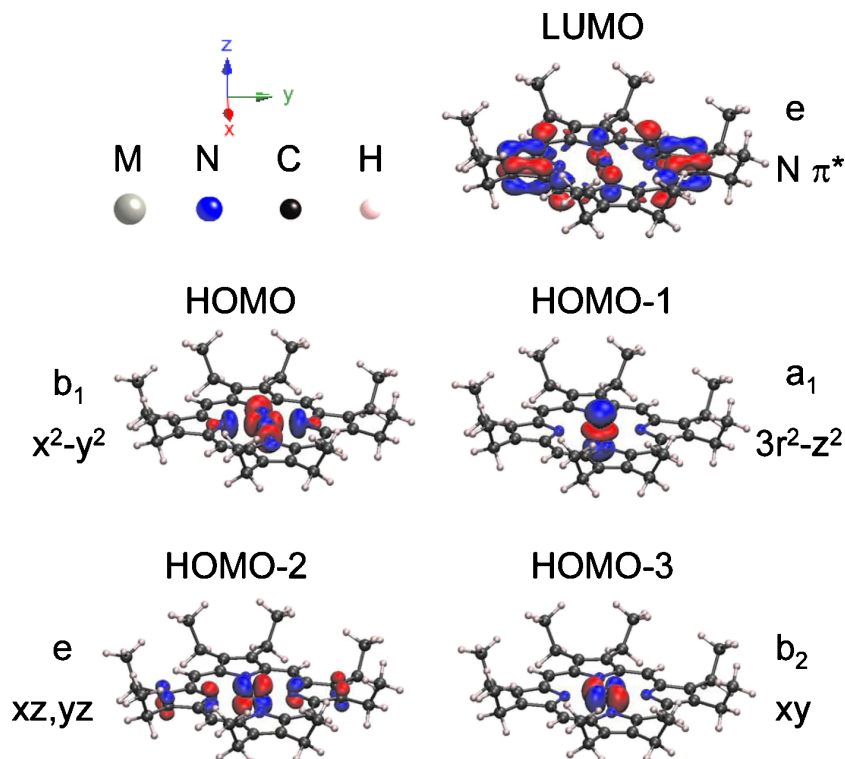
FIG. 2. Frontier orbitals of the OEPs. The orbitals are labeled according to the $C_{4v}$ symmetry group. The order of the orbitals from HOMO to HOMO-3 corresponds to MnOEP. This order varies depending on the considered OEP (Ref. 7). The LUMO is mainly determined by the $\pi^*$ orbitals of the aromatic rings, while the HOMOs are dominated by the 3d orbitals of the metal.

calculations.[18–20] In the case of NEXAFS transitions from the $N_{1s}$ level, it has been shown recently that the magnitude of this shift can be minimized (down to less than 0.6 eV) by using TDDFT calculations[20] with the BHandH-LYP hybrid functional.[21]

Since DFT is able to reproduce the experimental trends for the variation in the position of the $N_{1s}$ to LUMO transition peak, we feel confident to answer our original question: what is the origin of the variation? In order to do that, we have performed DFT calculations using the transition state (TS) theory proposed by Slater.[22] The TS theory states that the energy of an electronic transition from orbital A (the orbital $N_{1s}$ in our case) to orbital B (the LUMO in our case) can be approximated as the difference of energies of the orbitals A and B when orbital A is populated with 1.5 electrons and orbital B with 0.5 electrons in a non spin-polarized calculation.[22,23] We have checked that the difference for the $N_{1s}$ to LUMO transition using the $\Delta$SCF methodology and the TS is always smaller than 0.1 eV. Although TS is less rigorous than $\Delta$SCF methodology, it presents a big advantage: it is possible to follow the variation in the position of the $N_{1s}$ and LUMO energies independently. Therefore we can determine with the TS calculations what orbital is responsible for the variation of the $N_{1s}$ to LUMO transition peak.

Figure 3(a) shows the calculated variation of the positions of the LUMO and the $N_{1s}$ orbital along the OEP series. The LUMO varies along the series by about 0.1 eV, whereas the $N_{1s}$ core level varies by more than 0.5 eV. Thus it is clear that the $N_{1s}$ level is responsible for the variation of the LUMO peak in NEXAFS. The $N_{1s}$ level is shifted by the charge localized at the N atom. A more negative charge destabilizes the $N_{1s}$ level. This explanation is supported by the correlation between the position of the $N_{1s}$ level and the calculated charge at the N atom according to Bader's criterion,[24] as shown in Fig. 3(b).

While the LUMO changes little with the metal atom, the highest occupied molecular orbital (HOMO) shifts significantly (not shown). This is because the occupied frontier orbitals of the OEP have a strong d metal character (see Fig. 2). Depending on the occupancy of these d levels in each OEP, the nature of the HOMO and its energy varies considerably. This is in agreement with the calculations of Liao *et al.*[14,15] Thus, it is possible to tailor the HOMO and the HOMO-LUMO gap of the dye by varying the metal atom.

Finally, we analyze the variation of the core electron-hole interaction along the 3d metal OEP series. The core electron-hole interaction energy is defined as the difference between the photoemission gap (i.e., the difference between the energy corresponding to remove an electron from the $N_{1s}$ level and the electron affinity of the LUMO level) and the optical gap observed in NEXAFS (studied here by $\Delta$SCF). We find the core electron-hole interaction to be very large for all the OEPs studied [above 3 eV, see Fig. 3(a)]. However, it varies along the series by only 0.2 eV and is not correlated with the position of the absorption peaks [see Fig. 3(a)].

These results show that there is a synergy between NEXAFS experiments and DFT calculations. The capability of first-principles calculations to reproduce the experimental energy shifts validates the theoretical approach, and the individual energy levels can only be extracted from the data by
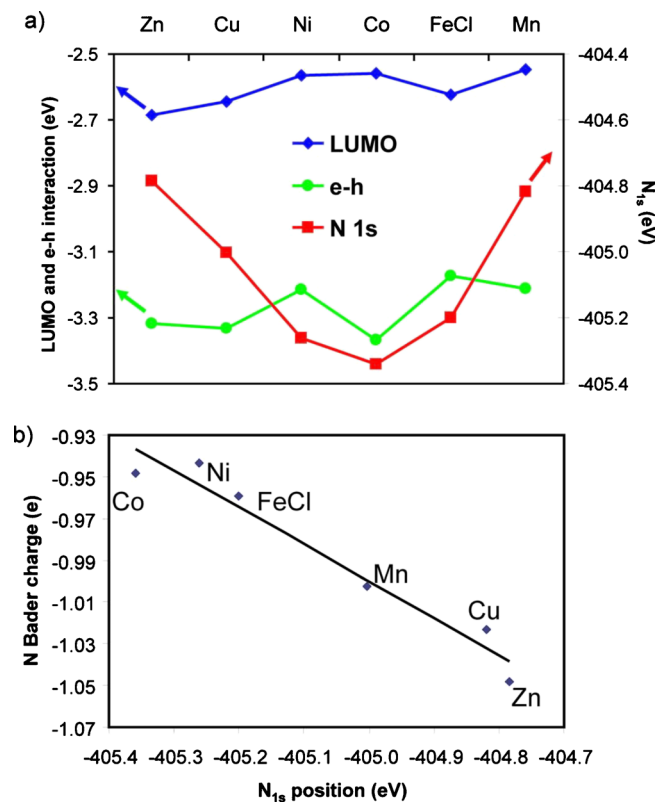
FIG. 3. (a) Plot of the three energies contributing to the $N_{1s}$ to LUMO transition observed in NEXAFS, i.e., the LUMO (blue diamonds, left axis), the $N_{1s}$ core level (red squares, right axis), and the core electron-hole interaction (with negative sign, green circles, left axis). These energies are plotted for a series of 3d metal OEPs, sorted by their atomic number Z. They are obtained by a LDA calculation for the optimized geometry with 1.5$e$ in the $N_{1s}$ core level and 0.5 e in the LUMO [following the transition state model proposed by Slater (Ref. 23)]. The $N_{1s}$ core level shift dominates the shift of the $N_{1s}$ to LUMO transition. (b) Bader charge on the nitrogen atoms vs the position of the $N_{1s}$ level for the series of 3d metal OEPs. A turnaround of the charge transfer near the middle of the series scrambles the sequence of atomic numbers in this plot. The different charges on the N atoms along the OEP series cause a shift of the $N_{1s}$ core levels and thus explain the shift of the $N_{1s}$ to LUMO transitions in NEXAFS (see Fig. 1).

using the calculation. Furthermore, the wave functions of the relevant orbitals can be calculated. Their localization on the metal atom versus the surrounding ring of N atoms determines how one needs to modify a porphyrin molecule to control its HOMO and LUMO, respectively.

In summary, we use a combination of NEXAFS spectroscopy with DFT calculations to show that the position of the LUMO level in OEPs (the nitrogen $\pi^*$ orbital[7]) is nearly independent of the central 3d metal ion of the porphyrin. The observed energy shift of the $N_{1s}$ to LUMO transition along the OEPs series is due to a shift of the $N_{1s}$ level, not the LUMO. It is caused by a variation of the charge localized on the N atoms. We also show that even though the core electron-hole interaction in this transition is very strong ($>3$ eV), it does not vary with the metal. Such a combination of experiment with theory is able to extract energy level shifts from NEXAFS data that cannot be obtained from the experimental results alone. This is crucial information for optimizing the energy level structure of solar cells by tailoring the dye molecules.

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