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Time-dependent DFT calculations of core electron shake-up states of metal-(free)-phthalocyanines

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Abstract

We have introduced a new approach for the calculation of the shake-up structures of molecular photoelectron spectra, based on the combination of time-dependent density functional theory (TD-DFT) and equivalent core hole (or $Z+1$) approximation. The method, suitable for large molecules, has been applied to compute the complex shake-up states associated with the carbon 1s X-ray photoelectron spectroscopy (XPS) of metal-free and nickel phthalocyanines (H_2Pc and NiPc, respectively). A similar satellite profile emerges for both molecules.

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The profiles of X-ray photoelectron spectra (XPS) of large molecular systems of biological and technological interest, are often characterized by the presence of a complex shake-up structure. An interplay of theoretical and experimental methods is generally required to fully understand the origin of the many satellite peaks. This is the case of the carbon 1s XPS of metal and metal-free phthalocyanines (Pc), where the interpretation of the spectra has been under debate for a long time (Niwa et al., 1974; Ottaviano et al., 1997; Peisert et al., 2002; Schwieger et al., 2002). The Pc are stable, conjugated aromatic macrocycles, with very interesting optical and electric properties, that provide a vast range of applications, from biomimetics (Grennberg et al., 1993) to organic semiconductors in solar cells (Thelakkat et al., 2002). Due to the low vapor pressure, they are easy to handle in vacuum, and have been the subject of many soft X-ray spectroscopies like XPS.

A large number of experimental and theoretical works have been dedicated to the shake-up phenomenon since its discovery, about 40 years ago, in the form of satellite features of generally low intensity, associated with the XPS experiments (Ågren and Carravetta, 1992). The shake-up is a multi-electron process related to the photoionization of a core electron. In a molecule, in the event of a core ionization, the correlation of the remaining electrons may provoke the excitation of valence electrons into unoccupied orbitals. These are the shake-up transitions, that appear in the photoelectron spectra at the higher binding energy side of the main photoelectron peaks. The calculation of the shake-up states of large molecules in general represents a challenging task for theoretical modellings.

Our approach is based on the combination of TD-DFT, for the calculation of the shake-up excitation energies, and on the equivalent core hole (or $Z+1$)

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approximation, for the description of the core ionized atom. The TD-DFT allows to calculate simultaneously all possible multiple valence excitations, and makes very convenient to handle large molecules from the point of view of the computational cost. We have applied this method to the calculation of the shake-up states associated to the C1s photoionization in Pc, and have started by analysing the H_2Pc (Brena et al., 2004). The interpretation of the shake-up structure of the H_2Pc and of other metal Pc like CuPc and PbPc has been controversial for a long time (Niwa et al., 1974; Peisert et al., 2002; Schwieger et al., 2002; Ottaviano et al., 1997), but no calculations had been performed about the shake-up states of the H_2Pc before. In this work we compare the results of the shake-up calculations for the H_2Pc to those of a metal Pc, the NiPc.

The H_2Pc and the NiPc studied in this work are both planar molecules, and are shown in Fig. 1. The central aza-nitrogens of the PC can either be bound to two hydrogens (metal free or H_2Pc) or to a metal (metal Pc). The carbon 1s shake-up structure of the H_2Pc and of metal-Pc is complicated by the simultaneous presence in the molecule of several non-equivalent carbon atoms, characterized by different chemical shifts and different shake-up structures. In the present study, we have considered eight non-equivalent carbons in H_2Pc and four in NiPc, as shown in Fig. 1, due to the different symmetries of the two molecules. The H_2Pc molecule has a C_2v symmetry, and the NiPc a C_4v symmetry. In the H_2Pc, the carbons C_1–C_6 are of benzene type, while C_7 and C_8 are of pyrrole type. In NiPc, C_1 is of pyrrole type, and C_2–C_4 are of benzene type. The pyrrole and benzene type carbons have a different chemical environment, since the pyrrole carbons are bound to two nitrogens and one carbon while the benzene carbons are bound only to carbons and hydrogens (or only to carbons). The experimental spectrum of the carbon 1s XPS of H_2Pc (Brena et al., 2004), as well as those of many metal Pc like, for instance CuPc (Niwa et al., 1974; Peisert et al., 2002; Schwieger et al., 2002), NiPc (Ottaviano et al., 1997) and PbPc (Papageorgiou et al., 2003), is characterized by three main features. This is

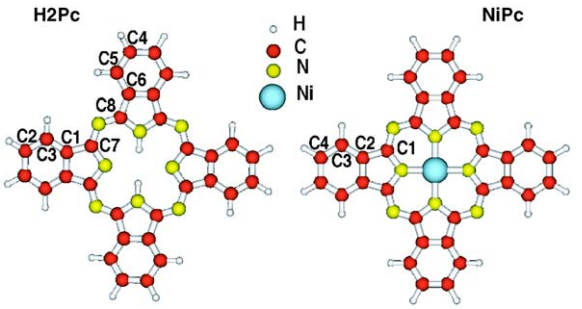

Fig. 1. Molecular structures of H_2Pc and NiPc. The non-equivalent carbon atoms in the two molecules are indicated.

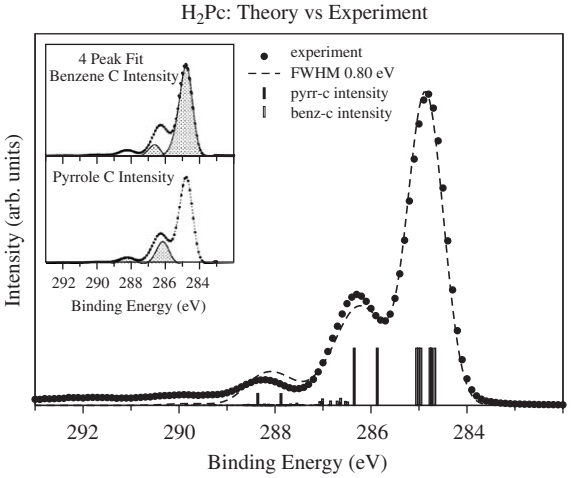

Fig. 2. The computed shake-up and C1s main lines of H_2Pc (bars) are convoluted by a Gaussian curve of 0.8 eV FWHM (solid line), and compared with the experiment (dots). In the insert, the proposed four peak fit is shown, and the total contribution to the benzene carbon and pyrrole carbon intensities are indicated by the areas under the experimental spectrum.

illustrated in Fig. 2 where the spectrum of a H_2Pc is shown. The three peaks are usually interpreted as the benzene and pyrrole carbon main lines, respectively, at 284.9 and 286.2 eV, and the shake-up associated to the pyrrole carbon, at 288.3 eV. A three peak fit of the H_2Pc experimental curve, guided by this assignment, leads however to a wrong intensity ratio between the benzene and pyrrole carbons with respect to the number of atoms of each type present in the molecule (the expected ratio pyrrole vs benzene carbon should ideally be 25%:75%). The intensity of the spectral features is estimated as the total area of all the peaks related to each of the two carbon types. It has been argued for H_2Pc, and at least, to our knowledge, for copper and lead Pc, that the intensity of the benzene carbon contribution is underestimated, because the related shake-up peak is hidden under the main pyrrole peak, and therefore not distinguishable in the experiment (Niwa et al., 1974; Peisert et al., 2002; Schwieger et al., 2002; Papageorgiou et al., 2003). By verifying this hypothesis, our calculations of the shake-up structure of H_2Pc have contributed to shed light onto this matter (Brena et al., 2004).

The TD-DFT implementation in the GAUSSIAN03 code has been used to compute the shake-up structures (Frisch et al., 2004). The intensity of the shake-up excitations was evaluated as the squared overlap between the initial-state and the final-state wave functions. The intensity of each shake-up peak is expressed in this work as the percentage of the intensity of the related main line. Benchmark calculations presented in a previous paper (Brena et al., 2005), have investigated the