RELATIVE ENERGY DIAGRAM OF THE LOWEST UNOCCUPIED MOLECULAR ORBITALS OF OXO-, THIO- AND SELENO-VANADIUM (IV) PORPHYRINS, AS INFERRED FROM COMBINED XANES AND ESR DATA

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RELATIVE ENERGY DIAGRAM OF THE LOWEST UNOCCUPIED MOLECULAR ORBITALS
OF OXO-, THIO- AND SELENO-VANADIUM (IV) PORPHYRINS, AS INFERRED FROM
COMBINED XANES AND ESR DATA

M.F. RUIZ-LOPEZ*, D. RINALDI*, C. ESSELIN*,
J. GOULON***, J.L. PONCET*** and R. GUILARD***

*Laboratoire de Chimie Théorique, U.A. 510 CNRS, Université
de Nancy I, BP 239, F-54506 Vandoeuvre-les-Nancy Cedex,
France

**LURE, L.P. CNRS, MEN, CEA, Université de Paris-Sud,
Bâtiment 209D, F-91405 Orsay Cedex, France

***Laboratoire de Synthèse et Electrosynthèse, U.A. 33 CNRS,
Faculté des Sciences Gabriel, 6, Boulevard Gabriel,
F-21100 Dijon, France

Sommaire

Les spectres XANES des porphyrines d'oxo- thio- et seleno-vanadium (IV) ainsi que les mesures de RPE de ces composés ont été utilisés pour étudier le diagramme d'énergie des orbitales moléculaires à caractère 3d. Nous examinons la possibilité de déduire une valeur approchée de la constante de couplage spin-orbite à partir de ces données expérimentales et des résultats des calculs théoriques.

Abstract

The XANES spectra of oxo- thio- and seleno-vanadium (IV) porphyrins together with ESR measurements on these compounds have been used to study the energy diagram of the 3d-like molecular orbitals. Possibilities for extracting an approximate value of the spin-orbit coupling constant are discussed on the basis of experimental data and theoretical results.

Introduction

The Vanadium K-edge spectra of oxo- thio- and seleno-vanadyl porphyrins all exhibit a well resolved preedge white line, but quite significant shifts of the position of this pre-peak and of its intensity can be measured. Considering the symmetry of these systems (C_{4v} group) and consistent with a formal metal oxidation state IV, the preedge lines can be assigned to electronic transitions from the metal 1s core level to 3d-like molecular orbitals (M.O.) of symmetry a_1 and e . Thus, the observed shifts in XANES show that significant energy variations of the metal 3d levels exist within the present series of compounds.

Relative variations of 3d-like M.O. of symmetry b_1 and e have also been detected from careful ESR studies of these d^1 metalloporphyrins[1]. However, in this case the determination of the absolute energy shifts requires an estimation of the spin-orbit coupling constant ξ , which is usually interpolated using the metal net charge and atomic calculations of ξ .

Conversely, the observed shifts in XANES could be used to extract an approximate value of ξ to be used for analyzing ESR data, provides one is able to account for orbital relaxation effects after the creation of a deep core hole in XANES.

In this work, we try to correlate XANES and ESR data with the help of theoretical calculations using the unrestricted Hartree-Fock INDO/S method [2] and the $X\alpha$ scattered-wave approximation [3].

Experimental data

XANES spectra

The XANES spectra of 2,3,7,8,12,13,17,18 octaethylporphyrinato -oxo and -thio vanadium (IV) complexes OEP:V=X (X=O,S) are reproduced in figure 1a, the corresponding edge first derivatives being shown in figure 1b. These spectra were recorded at LURE on the EXAFS-II station operating in the conventional absorption mode. The spectra of the oxo- and seleno- derivatives are also compared in figures 1c/1d. Due to the strong absorbance of the selenovanadyl compound, these data were recorded in the X-ray fluorescence mode. The quality

Figure 1 : XANES spectra of the series OEP:V=X (X=O, S, Se)

Comparison of edge spectra : 1a) X=S v.s. X=O

1c) X=Se v.s. X=O

Comparison of the edge first derivatives : 1b) X=S v.s. X=O

1d) X=Se v.s. X=O

and the resolution of the later spectra were also improved by the use of an efficient two mirror harmonic rejector. It is clear from figures 1a (1c) that the prepeak of the thio- (seleno-) derivative is slightly shifted towards lower energies with respect to the prepeak of OEP:V=0 by $\Delta E = 1.0$ eV (1.2 ± 0.2 eV).

ESR measurements

The morphology of the ESR spectra of these compounds is characteristic of Vanadium (IV) complexes having a single 3d electron. Considering the symmetry of the systems, one concludes that the electronic ground state has a configuration $(b_2)^1$, b_2 being a M.O. with a strong contribution of the metal $d_{x^2-y^2}$ orbital. For these axially symmetrical compounds, the anisotropic g tensor is defined by its two components $g^{\parallel}$ and $g^{\perp}$, easily determined from powder EPR spectra. Due to spin-orbit coupling ξ , these factors become related to the energy differences of the M.O., $\Delta'' = \epsilon_{b_1} - \epsilon_{b_2}$ and $\Delta^{\perp} = \epsilon_e - \epsilon_{b_2}$, according to:

$$\Delta''/\alpha^2 = 2 \delta^2 \xi (g_e - g^{\parallel})$$

$$\Delta^{\perp}/\gamma^2 = 2 \delta^2 \xi (g_e - g^{\perp})$$

where α , γ and δ are the coefficients of the metal 3d orbitals in the M.O. of symmetry b_1 , e and b_2 respectively. The last one corresponds to the d_{xy} orbital so that one may consider $\delta \approx 1$. On the other hand, the spin-orbit coupling constant may be estimated to be $\xi = 170$ cm⁻¹ by assuming a V^{2+} charge [1]. These considerations lead to $\Delta''/\alpha^2 = 4.2, 4.4, 5.3$ eV and $\Delta^{\perp}/\gamma^2 = 2.4, 1.4, 0.7$ eV for OEP:VO, OEP:VS and OEP:VSe respectively. From previous EH calculations [4] one has $\alpha \approx 0.95$ and $\gamma \approx 0.91$ so that one estimates $\Delta''_{OEP-VO} - \Delta''_{OEP-VS} = 0.18$ eV and $\Delta^{\perp}_{OEP-VO} - \Delta^{\perp}_{OEP-VS} = 0.8$ eV. Making the hypothesis that the b_2 levels have almost the same energy in these compounds, the last value gives approximatively the shift between the e levels in OEP:VO and OEP:VS and can be compared with the observed shift in the prepeak of XANES spectra, which is 1eV. We notice, finally, that the variation of Δ'' , which depends on the metal-macrocycle interaction, is correlated with the metal to plane distance determined with EXAFS which decreases from OEP:VO to OEP:VSe [1].

Theoretical calculations

We have performed unrestricted Hartree-Fock INDO/S calculations for OEP:VO and OEP:VS in their electronic ground states. The 3d-like M.O. obtained are plotted in Figure 2. The energy of the singly occupied b_2 orbital is a spin-average of the calculated α and β levels, so that it approximatively follows Koopman's theorem [2]. From the figure, one sees that the b_1 and b_2 orbitals have almost the same energy in both compounds. On the contrary, the orbitals a_1 and e are more stabilised in the case of OEP:VS by 1.2eV and 0.8eV respectively. The value of the shift predicted by our theoretical calculations for the orbital e corresponds exactly to the observed shift in Δ . For the orbital b_2 our results do not predict a significant shift, and, in fact, the variation of Δ observed in ESR is rather small. One notices also that the position of the M.O. a_1 , which is not detected in ESR, is not far from that of the M.O. e , specially in the case of OEP:VS. This can explain why in XANES, where both $1s \rightarrow a_1$ and $1s \rightarrow e$ transitions are symmetry allowed, any splitting of the white line is observed.

It is interesting to compare now these results with the energy shifts observed in XANES. In order to determine the importance of the orbital relaxation after the creation of a core hole, we have performed X α -SW calculations for OEP:VO and OEP:VS systems. The energy separation between the e levels in the XANES' final state $(1s) \dots (b_2)^1 (e)^1$ is predicted to be 1eV, in perfect agreement with the observed shift (see Figure 1). The slightly greater value of this energy separation compared to that obtained in ESR is explained

Figure 2 : Unrestricted Hartree-Fock INDO/S molecular orbitals of OEP:V=O and OEP:V=S in the electronic ground state

by considering the orbital relaxation energies. Our results predict that the difference $\epsilon_a - \epsilon_{b_2}$ decreases in the XANES final state because a greater stabilisation of the e orbitals. However, the decrease is more important in the case of OEP:VS (0.5 eV) than in the case of OEP:VO (0.4 eV)

The self-consistency of the experimental measurements and the theoretical calculations presented in this work justify the assumptions made in the discussion. In particular, the choice of the spin-orbit coupling constant $\xi = 170 \text{ cm}^{-1}$ is consistent with the estimation made here for the XANES relaxation effects. More detailed calculations will be presented in a forthcoming paper (M.F. RUIZ-LOPEZ, R. NATOLI, J. GOULON, to be published).

Conclusion

The results presented in this paper show that combined XANES and ESR measurements allow to describe the 3d-like M.O. of this kind of paramagnetic system well. The orbital relaxation effects in XANES have to be taken into account if one wants to use the experimental data from both techniques to extract informations about spin-orbit coupling. While quantitative values for these relaxation effects cannot be obtained without sophisticated *ab initio* techniques, we have shown that reasonable results can be deduced with a semiempirical method as INDO/S, or with methods based on the X α approximation. A more general study of these effects is now in progress (M.F. RUIZ-LOPEZ, to be published).

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