

Theoretical study of high-valent vanadium oxo-porphyrins as a dopant of crude oil

Roberto Salcedo^{1,*}, L.M.R. Martínez, J.M. Martínez-Magadán

Programa de Simulación Molecular, Instituto Mexicano del Petroleo, Eje Central Norte Lázaro, Cárdenas 152, San Bartolo Atepehuacan, 07730 Del. Gustavo A. Madero, México DF, Mexico

Received 17 October 2000; accepted 1 November 2000

Abstract

The role played by the vanadyl porphyrinate as a dopant for zeolites in the refinement process of crude oil is analysed using DFT calculations. The pair formed by the vanadium atom and its bonded oxygen atoms seems to be the responsible items in the dopant reaction. However, the present paper shows the participation of the vanadium atom as being the most important. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vanadyl porphyrinate; Dopant; Zeolites

1. Introduction

Crude oil refinement has several steps in which there are some difficulties depending on the nature of the crude that is processed. Fluid catalytic cracking process is one of the most important steps [1]. This operation is carried out in the presence of a heterogeneous catalyst supported in zeolites. The presence of vanadyl porphyrinate in some crude oils promotes the inhibition of acid zeolite used as catalyst. However, this inhibition is not a consequence of blocking the acid sites of the zeolite but the destruction of the catalyst. This process has been studied, and this destruction occurs at crystallographic level, as has been suggested in Ref. [2]. Therefore the vanadyl complex reacting directly with the zeolite might be expected.

Nickel (II) and oxo-vanadium (IV) complexes of deoxyphylloerythroetioporphyrin (IV) (DPEP) (see Fig. 1) dominate petroleum, oil shales and sedimentary bitumen [3–5]. The concentration of such metals varies for different types of oil [6]. In general it is believed that 10% of the total metal in a crude oil is found in the form of porphyrin complexes [7].

Bonding of oxo-vanadium (IV) porphyrins to zeolites can occur via the oxygen atom of the vanadyl group as has been suggested in Ref. [8]. This phenomenon can happen because there are some trends to easily form a hydrogen bond [8] coming from a zeolite acid site with the oxygen of vanadyl since the vanadium atom seems to be unreachable for other chemical species (see Fig. 2).

This last proposition would be consistent with the mechanism that suggests an attack on the acid sites of the zeolite catalyst that have been shown to be of fundamental importance in the catalytic process. However, our results suggest a different mechanism for the attack indicating that there is a reaction between the zeolite and the vanadium atom itself.

* Corresponding author. Tel.: +52-53-33-8113.

E-mail address: salcedo@servidor.unam.mx (R. Salcedo).

¹ On sabbatical leave from the Instituto de Investigaciones en Materiales, UNAM.

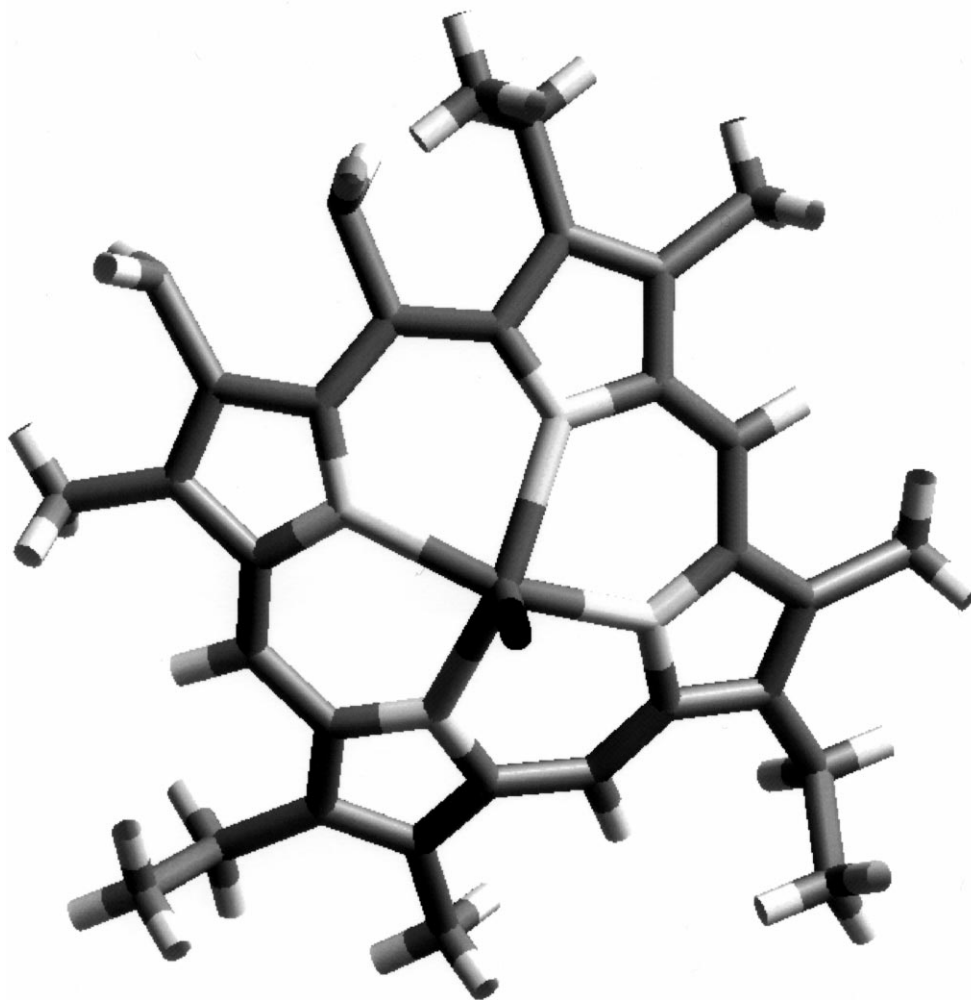


Fig. 1. Deoxophylloerythroetioporphyrin (IV) (DPEP) structure.

Thus the objective of this paper is to present our proposition for this phenomenon based on theoretical calculations of the possible dopant items.

2. Methodology

Unrestricted calculations were performed for all molecules through the DFT scheme, as implemented in the NWChem package 3.3.1 version [9,10]. In this study an all-electron approach has been combined for all atoms except V, where a LAN2DZ pseudopotential was improved. The complex structures are first optimised

using the BLYP functional. After that, stable complexes geometries are obtained within the ACM functional approach. In both steps, DZVP basis sets were used.

We get an average of 0.765 for the expectation value of S^2 against the exact value of 0.75, for all calculations. Therefore, the spin contamination is acceptable and does not affect the discussed results and conclusions, especially in the α - and β -frontier molecular orbital contributions.

The molecular orbital schemes were obtained taking advantage of the visualisation facilities of the DMol code included in the MSI-CERIUS2 software [11].

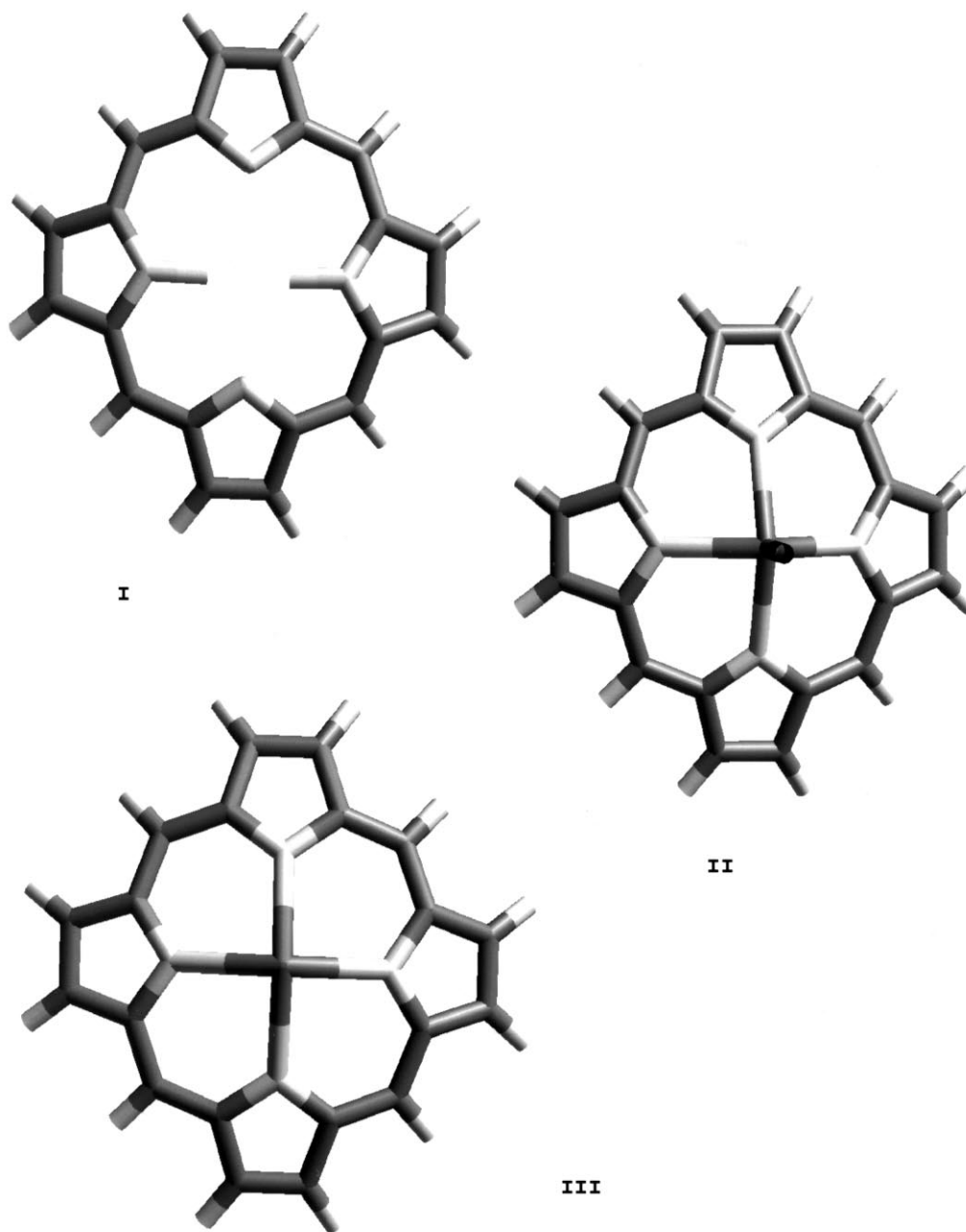


Fig. 2. Molecules under study.

3. Results and discussion

The calculations were carried out on the following three molecules: the porphyrin ring alone (I); the

vanadyl porphyrinate without substituents (II); and the planar vanadium porphyrin (III) without the oxygen atom (see Fig. 2).

Patchkovskii and Ziegler [13] previously calculated

one of the compounds under our study (i.e. compound II); they carried out a very elegant study about the EPR tensors generated by d^1 metal porphyrins and included the vanadium complex. Some of our results are in good agreement with those obtained by these authors.

The molecules analysed are shown in Fig. 2, and some important results are summarised in Table 1. As can be seen, critical measurements agree with that of the correspondent X-ray analysis [8]. Obtaining a similar V–O distance compared with experimental results was not a problem in the molecules that present this bond. The V–O distance obtained is 1.599 Å, which matches very well with the value reported by Drew and co-workers [8]. In the optimised structures all the complexes present a dome shape which arises from the position out of the plane that takes the vanadium atom. This result is also in good agreement with the results obtained by X-ray analysis [8].

Porphyrinate rings present a great affinity for the VO group [14]. This can be seen in the great stability obtained for the complex (molecule II); in fact, a calculation of the hypothetical compound (III) formed by the porphyrin ring and an isolated vanadium atom was performed in order to make a comparison and look for additional reasons for the observed stability. Considering the additional energy of the oxygen atom in one case (porphyrinate case) there is a big difference of 2.372998 eV between both structures favouring the vanadyl porphyrinate. It is expected that the simple complex of porphyrin and vanadium, being so reactive, would capture any oxygen atom near it, although the vanadyl group can be formed before any other coordination.

Nevertheless the feature that has great relevance in this study is that the complex yielded is an open shell species, due to the electronic configuration reached by the V(IV) ion (which has only one electron in its valence shell). The corresponding molecular orbital shapes for the fragments are shown in Fig. 3. The frontier molecu-

Table 1
Relevant results of the molecules under study

Molecule	Energy (eV)	$\epsilon_{\text{HOMO (SOMO)}}$	ϵ_{LUMO}	$\Delta\epsilon$
I	-26935.127	-5.5305	-2.605	-2.925
II	-31259.616	-5.8641	-2.6995	-3.1646
III	-29190.755	-5.375	-2.4697	-2.905

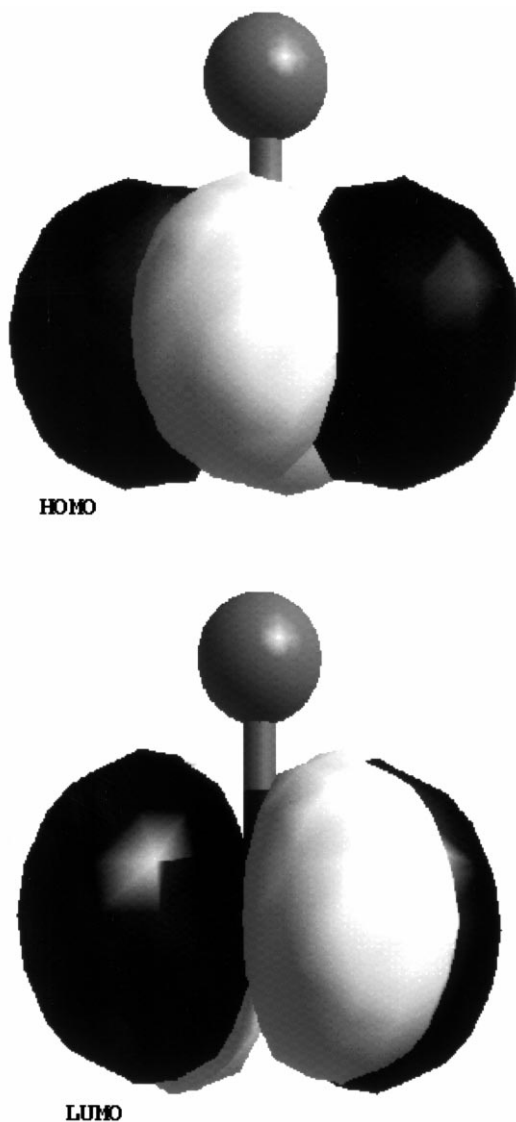


Fig. 3. Frontier orbitals of the vanadyl fragment.

lar orbitals of the vanadyl (V=O) fragment are very interesting because all the electronic probability is concentrated on the vanadium atom in both cases, (i.e. single occupied molecular orbital (SOMO) and lowest unoccupied molecular orbital (LUMO)) with an atomic orbital d_{xy} mainly contributing for SOMO and $d_{x^2-y^2}$ for LUMO. This behaviour means that the fragment is able to receive electrons via the LUMO (with low energy) and keeps the SOMO free with an unpaired electron for a nucleophilic reaction.

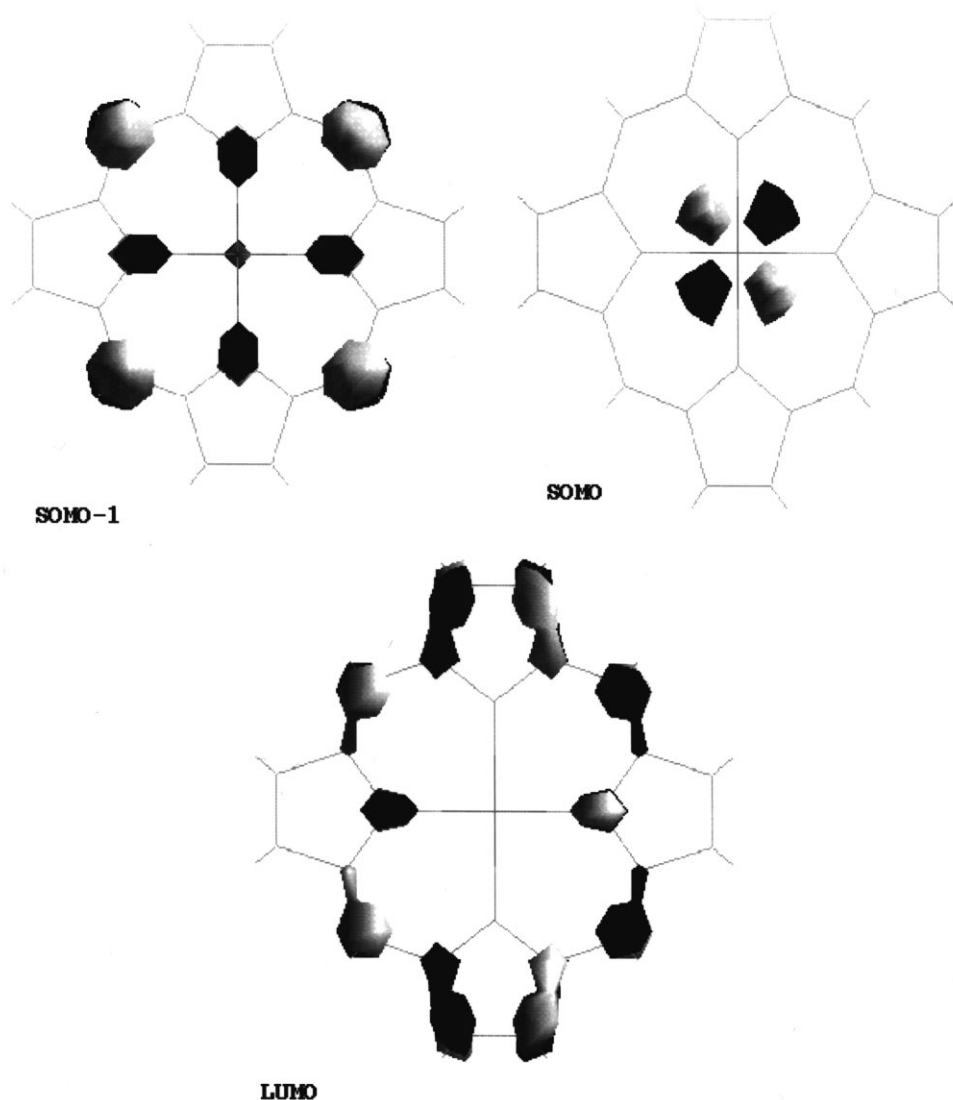


Fig. 4. Frontier orbitals of vanadyl porphyrinate.

With respect to the porphyrinate fragment, which belongs to the D_{2h} point group, these results agree with one recently published study [15], which was carried out by a semi-empiric method. The HOMO is in the b_{1u} irreducible representation and it is the expected donating orbital which can establish the interaction with the vanadium atom (or many other metallic ions) in order to form the coordination complex via the nitrogen atoms set of the inner aromatic ring. The LUMO belongs to the b_{2g} irreducible representation

and is concentrated in the outside double bond framework of the electronic delocalisation.

The relevant molecular orbitals for vanadyl porphyrinate are shown in Fig. 4. The molecule belongs to the C_{4v} point group. The most relevant feature here is the nature of the frontier orbitals. The b_1 LUMO and the β contribution to the b_2 SOMO (that is empty) in molecule II as well as in molecule III, have important contributions that arise from the atomic orbitals of vanadium (d_{xy}), whereas the a_1

SOMO-1 and the α contribution to SOMO (that posses one unpaired electron) arise mainly from the p_z orbitals of the porphyrin aromatic rings.

Thus, the attack of one of these molecules over other species should be directed through the vanadium atom and an important fact that *the corresponding reaction should follow a free radical pathway is suggested.*

It has been implied that the vanadium atom in these molecules is in a position that precludes a possible reaction [8], (i.e. in the geometrical centre of the square pyramid). However, there are other reports in which the authors claim the metal atom should be reactive [12]. The best support for this proposal is the broad existence of six co-ordinated octahedral species of vanadium [9,10,12].

The activity of zeolites as a catalyst has been studied from a theoretical point of view [16,17]. Some interesting results obtained from these studies are with respect to the frontier orbitals of a zeolite model. The important feature that concerns our study is the one that describes the shape and localisation of these orbitals.

There are different types of zeolite molecule that have catalytic activity. The work cited takes the compound HZSM-5 as a model. This catalyst has a simple unity formed by a 10-member ring in which each site of Si and Al is a tetrahedral atom bonded by oxygen atoms and saturated with hydrogen atoms.

The HOMO of that model is localised on the tetrahedral centre of the aluminium atom bonded to four oxygen atoms, whereas the LUMO is mainly on the hydrogen atom of the acid site. A low energy value of 3.52 eV separates these orbitals. The vanadyl porphyrinate complex would attack some of these two orbitals; the attack of an unpaired electron (coming from SOMO of vanadyl porphyrinate) on the HOMO of the catalyst precludes the rupture of one Al–O bond yielding the formation of a free radical in some of the oxygen atoms with the concomitant electronic rearrangement. This process can promote a chain reaction.

This last suggestion is very important in the oil processing fluid catalytic cracking process mentioned in Section 1, because from the point of view of this molecular orbital description, the destruction of the crystal structure of the catalyst *should be a free radical attack on the oxygen atoms of the zeolite.*

It should be noted that the compound found mainly in the crude oil is the vanadyl (DPEP) and not the vanadyl porphyrinate studied here, and the difference between compounds II and III is the lateral aliphatic chains found as substituents on the porphyrinate pyrrolic rings. The presence of these chains has no influence on the reactive behaviour of the compound III; it works in a similar way with II as a free radical reactive species.

4. Conclusions

The behaviour of some vanadyl porphyrinate complexes as dopants on some oil process was studied in a theoretical fashion. The dopant phenomenon arises because of the intrinsic nature of the frontier orbitals in all of these compounds. All of them are open shell species; therefore, the last SOMO is able to participate in reactions with atoms belonging to dangling bonds in other compounds as well as the zeolite itself and the silica or alumina that is normally used as support in oil cracking equipment. Thus we propose this reaction should be a free radical process that involves the oxygen atoms of the zeolite catalyst or their support. Then we propose an explanation to the phenomenon that implies the deactivation of the catalyst in such a process, because the reaction with the vanadyl porphyrinate involves the destruction of the crystalline structure of the zeolite.

References

- [1] P.H. Schipper, F.G. Dwyer, P.T. Sparrel, S. Mizrahi, J.A. Herbst, ACS Symposium Series, 194th Meeting, chap. 5, 1987, p. 64.
- [2] W.P. Hettinger Jr., Catal. Today 53 (1999) 367.
- [3] G.W. Hodgson, B.L. Baker, E. Peake, in: B. Nagy, U. Columbo (Eds.), Geochemistry of Porphyrins, Elsevier, Amsterdam, 1967.
- [4] E.W. Baker, S.E. Palmer, in: D. Dolphin (Ed.), The Porphyrins I, Academic Press, New York, 1978, p. 486.
- [5] A. Treibs, Angew. Chem. 49 (1936) 682.
- [6] M.L. Chicarelli, C.B. Eckardt, C.R. Owen, J.R. Maxwell, G. Eglinton, R.C. Hutton, A.N. Eaton, Org. Geochem. 15 (1990) 267.
- [7] H.N. Dunning, J.W. Moore, H. Bieber, R.B. Williams, J. Chem. Eng. Data 5 (1960) 546.
- [8] M.G.B. Drew, P.C.H. Mitchell, C.E. Scott, Inorg. Chim. Acta 82 (1984) 63.
- [9] J. Anshell, E. Apra, D.E. Bernholdt, P. Borowski, E. Bylaska,

- T. Clarck, D. Clerc, H. Dachselt, W. de Jong, M. Deegan, M. Dupuis, K. Dyllal, D. Elwood, G. Fann, H. Fruchtl, E. Glendenning, M. Gutowski, R.J. Harrison, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kendall, R. Kobayashi, R.A. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, J.A. Nichols, J. Nieplocha, A. Rendall, M. Rosing, G. Sandrone, M. Stave, T. Straasma, H. Taylor, G. Thomas, J. van Lenthe, T. Windus, K. Wolinski, A.T. Wong, Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 3.3.1, Pacific Northwest National Laboratory, Richland, Washington, 99352-0999, USA, 1999.
- [10] D.E. Bernholdt, E. Apra, H.A. Fruchtl, M.F. Guest, R.J. Harrison, R.A. Kendall, R.A. Kutteh, X. Long, J.B. Nicholas, J.A. Nichols, H.L. Taylor, A.T. Wong, G.I. Fann, R.J. Littlefield, J. Nieplocha, *Int. J. Quantum Chem. Symp.* 29 (1995) 475.
- [11] CERIUStm 4.2, Molecular Simulations, Inc. CA San Diego, 2000.
- [12] R. Cantú, J.R. Stencel, R.S. Czernuszewicz, P.R. Jaffé, T.D. Lash, *Environ. Sci. Technol.* 34 (2000) 192.
- [13] S. Patchkovskii, T. Ziegler, *J. Am. Chem. Soc.* 122 (2000) 3506.
- [14] M. Krauss, H. Basch, *J. Am. Chem. Soc.* 114 (1992) 3630.
- [15] R. Shediach, M.H.B. Gray, T. Uyeda, R.C. Johnson, J.T. Hupp, P.J. Angiolillo, M.J. Therien, *J. Am. Chem. Soc.* 122 (2000) 7017.
- [16] J.M. Martínez-Magadán, A. Cuan, M. Castro, *Int. J. Quantum Chem.* 75 (1999) 725.
- [17] I.P. Zaragoza, J.M. Martínez-Magadán, R. Santamaria, D. Dixon, M. Castro, *Int. J. Quantum Chem.* 80 (2000) 125.