PHYSICAL REVIEW B **70**, 195214 (2004)

Equivalent core-hole time-dependent density functional theory calculations of carbon 1*s* shake-up states of phthalocyanine

Barbara Brena, Yi Luo,* and Mats Nyberg
Theoretical Chemistry, Royal Institute of Technology, SCFAB, SE-10691, Stockholm, Sweden

Stéphane Carniato
Laboratoire de Chimie Physique, Matière et Rayonnement, UMR 7614, Université Pierre et Marie Curie, 11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

Katharina Nilson, Ylvi Alfredsson, John Åhlund, Nils Mårtensson, Hans Siegbahn, and Carla Puglia[†]
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

(Received 7 July 2004; published 22 November 2004)

The shake-up transition energies of the carbon 1*s* photoelectron spectrum of metal-free phthalocyanine (H_2Pc) have been calculated by means of time-dependent density functional theory, for which an equivalent core approximation is adopted. Model calculations for the C 1*s* shake-up states of benzene are in excellent agreement with the latest experimental results. The complex C 1*s* shake-up structures associated with the aromatic and pyrrole carbons in the phthalocyanine are computed, as well as their ionization potentials. They allow us to determine the origin of the anomalous intensity ratio between the pyrrole and benzene carbons in a high resolution C 1*s* photoelectron spectrum measured for a H_2Pc film, as due to a benzene-related shake-up contribution, hidden under the pyrrole main intensity feature.

DOI: 10.1103/PhysRevB.70.195214 PACS number(s): 71.15.Mb, 79.60.Fr

The phthalocyanine molecules have been the object of several investigations, due to their many possible applications in optical and electronic devices,[1,2] and to their thermal and chemical stability. Their structural similarity to the active sites of chlorofyll and hemoglobin, makes phthalocyanines very interesting for biomimetic applications as catalysts for oxidation reactions in heterogeneous catalysis.[3–6]

The phthalocyanines are planar organic molecules that consist of a porphyrinlike ring surrounded by four benzene rings, with either a metal atom (metal phthalocyanine) or two hydrogen atoms in the center (metal-free phthalocyanine or H_2Pc, as shown in Fig. 1). The phthalocyanines have been extensively studied by x-ray spectroscopic techniques that provide detailed information about their electronic structure.[7–13]

In this work we report a joint experimental and theoretical investigation of the shake-up satellite structures associated with the excitation of the carbon 1*s* in the metal-free phthalocyanine. The carbon 1*s* shake-up structure of the Pc molecules has been under debate for decades.[7,10,12,13] We have obtained a high resolution x-ray photoelectron spectrum of the C 1*s* of a phthalocyanine film deposited in situ on a conducting glass substrate. The main lines of the spectrum have been calculated using the Δ Kohn-Sham approach and their shake-up satellites are obtained using the time-dependent density functional theory (TDDFT)[14–16] for a description of the valence electron excitations, while the core-hole is represented by the equivalent core approximation.

The photoelectron spectra are formed by the main lines, which are associated with the photoionization of the core electrons, in the present case to the 1*s* core orbital of the chemically inequivalent carbons in the molecule, and by a number of satellite structures of different origin. When a core electron is photoemitted, several processes take place in the system due to the correlation and the relaxation of the remaining electrons. Among these processes, there is the excitation of valence electrons into unoccupied states, experimentally observable as satellite lines, lying at higher binding energies than the main peaks. The computations performed up to now in the calculation of the shake-up energy positions are based on *ab initio* configuration interaction (CI),[17] on the Hartree-Fock static exchange technique (HF-STEX),[18] and, in the majority, on semiempirical techniques. For instance, in the study of the shake-up structure associated with the C 1*s* spectra in aromatic rings like benzene, several works are based on the INDO/CI (Intermediate Neglect of Differential Overlap, including CI) (Refs. 19 and 20) and CNDO/S (Complete Neglect of Differential Overlap, including single CI) (Ref. 21) methods. In general, the calculated results have successfully helped to interpret the experimental spectra. However, there are no calculations on the C 1*s* shake-up satellites of H_2Pc reported so far.

In this work, we have introduced a new computational scheme to calculate the shake-up structures of H_2Pc. The method is a combination of equivalent core hole approximation and time-dependent density functional theory (ECH-TDDFT). A detailed description of this method will be published elsewhere.[22] The use of TDDFT allows one to incorporate electron correlation effects easily, to determine all possible multiple excitations automatically, and to compute large systems at a reasonable computational cost. Moreover, with this technique, the involvement of both σ and π orbitals are always fully considered. A large number of singlet and triplet states are calculated simultaneously. However, it should be noted that at this stage the spin-orbital coupling is neglected, as is the coupling between singlet and

1098-0121/2004/70(19)/195214(6)/$22.50 ©2004 The American Physical Society

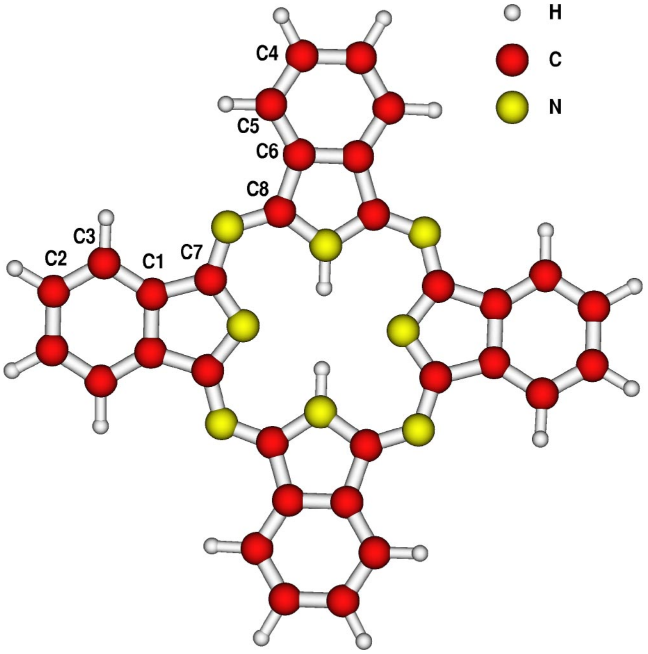

FIG. 1. (Color online) The molecular structure of the H_2Pc molecule. The carbon atoms labeled from 1 to 6 are benzene-type while 7 and 8 are pyrrole-type.

triplet states. The intensity of the shake-up peaks has been calculated for the singlet-type transitions as the squared overlap between the initial-state and the final-state wave functions. The hybrid density functional B3LYP has been used throughout all the computations. The 6-31++G basis set for the core ionized atom and 6-31G for the other atoms, as implemented in the GAUSSIAN 98 package,[23] have been used for all the shake-up calculations of the Pc molecule. The igloo-iii triple ζ basis of Kutzelnigg, Fleischer, and Schindler[24] has been used in the calculations for the benzene molecule.

The ionization potentials (IP) of the eight inequivalent carbons of the phthalocyanine (six of the benzene-type and two of the pyrrole-type)—that correspond to the main lines of the x-ray photoelectron spectrum—were computed with the gradient-corrected DFT code DEMON[25] as the energy difference between the ground state and the core hole state (the Δ Kohn-Sham approach). We have used the PD86 correlation and exchange functional by Perdew and Wang,[26] and the igloo-iii triple ζ basis set, to describe the core-excited atoms, and double ζ bases sets and effective core potentials (ECP) for the remaining atoms. With the same program the H_2Pc molecule has been geometry-optimized. The obtained geometry is slightly distorted from a perfectly D_{2h} symmetric structure. The theoretical method for the calculations of the shake-up energy positions was first tested on the C 1*s* shake-up satellites of the benzene molecule, for which both experimental data and theoretical calculations obtained with different techniques are available in the literature.[27,28] Our theoretical results reproduce with a good accuracy most of the main shake-up features resolved in the experimental studies. A sequence of 9 main shake-up satellites was identified in an Al $K\alpha$ excited C 1*s* spectra for energies up to 19 eV from the main C 1*s* line.[28] A more recent experiment probed different excitation energies (298 and 309 eV) resolving a few extra smaller features in the energy range of 7 eV from the main line, at 3.9, 4.2, and 6.2 eV, that appear as shoulders of other well-defined structures.[27] The resulting

TABLE I. The experimental and theoretical energy and intensity of the main C 1*s* shake-up features of the benzene.

Benzene					
Experiment[a] Energy[b] eV	Intensity[c] %	This work Energy[d] eV	Intensity[c] %	S/T[e]	Assignment
3.9±0.1		3.73		T	
4.2±0.1		4.33		T	
4.8±0.1		4.53		T	
5.2±0.1					
5.8±0.1	2.21	5.95	2.87	S	$2b_1(\pi)\rightarrow 3b_1(\pi^*)$
6.2±0.1		6.57		T	
		6.57		T	
		6.80		T	
7.15±0.05	5.52	7.12	4.89	S	$1a_2(\pi)\rightarrow 2a_2(\pi^*)$
8.4±0.1	4.47	9.15	6.61	S	$1b_1(\pi)\rightarrow 3b_1(\pi^*)$
9.8±0.2	2.01				

[a] Data taken from Ref. 27.
[b] Shake-up energy positions as the energy difference from the experimental main line.
[c] In percent of the main peak's intensity.
[d] Shake-up energy positions as the energy difference from the IP.
[e] Triplet (T) or singlet (S) character.

peaks are reported in Table I for energies up to 9.8 eV from the main line, together with our theoretical results. For the excited states of singlet-type, we report also the calculated intensity and indicate the assignment of the electrons subject to the transitions. The first three transitions are of triplet type, and they have a complex structure, involving several electronic excitations. In these transitions, σ-type orbitals are involved together with π-type orbitals. The computed shake-up energy positions account very well for the most prominent features in this energy window. The ECH-TDDFT approach is thus expected to describe C 1*s* shake-up states of similar systems, such as H_2Pc, with good accuracy.

Previous experimental works have studied the x-ray photoelectron spectrum of the C 1*s* core level in phthalocyanines and in molecules with related structures, like naphthalocyanine and, in some of these studies, the role of eventual shake-up satellites associated with the benzene carbons has been discussed.[7,10,12,13] In fact, the proposed assignments of the experimental peaks to the different types of carbon atoms in the molecule, does not lead to an intensity ratio corresponding to the number of carbons belonging to each type.[10] To illustrate this problem, we refer to the C 1*s* x-ray photoelectron spectroscopy (XPS) experiment of H_2Pc deposited on a conducting glass substrate, shown in Fig. 2. The experimental data, taken with an overall resolution of 0.4 eV, were obtained with a Scienta ESCA 300 spectrometer (described elsewhere[29]). The latter is an ultrahigh vacuum (UHV) system which allows molecular film preparation *in situ* and uses monochromatized Al $K\alpha$ radiation as an excitation source. The H_2Pc was purchased from Aldrich (98% dye content) and sublimated onto the substrate in the UHV chamber. A more detailed description of the experiment can be found in Ref. 30. This C 1*s* XP spectrum, similarly to the cited studies of metal Pc,[12,13] is characterized by three major features: one main high intensity peak centered at 284.9 eV, attributed to the 24 benzene carbons, a second, less intense peak at 286.2 eV, attributed to the remaining 8 pyrrole carbons, and a third, low intensity structure at about 288.3 eV, which is usually interpreted as a shake-up transition associated with the photoionization of the pyrrole carbons (see Fig. 2).[10–13] However, following these assignments, the resulting intensity ratio of the peaks does not agree with the 1:3 value expected from the pyrrole/benzene carbon ratio for H_2Pc, as shown in the upper part of Fig. 2 by a three-peak fit of the experimental C 1*s* XP spectrum. Before performing the fitting procedure, a Shirley background was subtracted from the experimental data. The energy difference in the calculated IP of the carbons of the same type (see Tables II and III) are not resolved in the experimental XP spectra. Therefore, for the six benzene carbons, one peak centered at the mean value 284.8 eV was used, and for the two pyrrole carbons a feature was placed at 286.3 eV. These two curves were simulated by Voigt functions, which account for the asymmetry due to the molecular vibrations. The peak at 288.3 eV, assumed to be a shake-up related to the pyrrole carbons, was simulated by a gaussian curve centered at 288.3 eV. Smaller features were added on higher binding energies to fit the background structures, not shown in Fig. 2. From this fitting procedure, the total intensity associated with the two peaks related to the pyrrole carbons—the main peak and shake-up—sum to 33% of the total intensity, instead of the expected 25%. In previous studies, it has been argued that a fourth peak, due to the shake-up structure of the benzene carbons, might lie below the higher-intensity pyrrole peak.[7,8,12] This would give an intensity contribution related to the benzene carbons hidden under the higher binding energy peak and usually included in the pyrrole intensity. According to this consideration, in the case of CuPc,[12,13], a four-peak curve fitting has been proposed, where the fourth peak would represent the shake-up satellite intensity associated with the benzene carbons. In this way, a significant improvement in the agreement between the molecular stoichiometry and the experimental intensity ratio has been obtained.

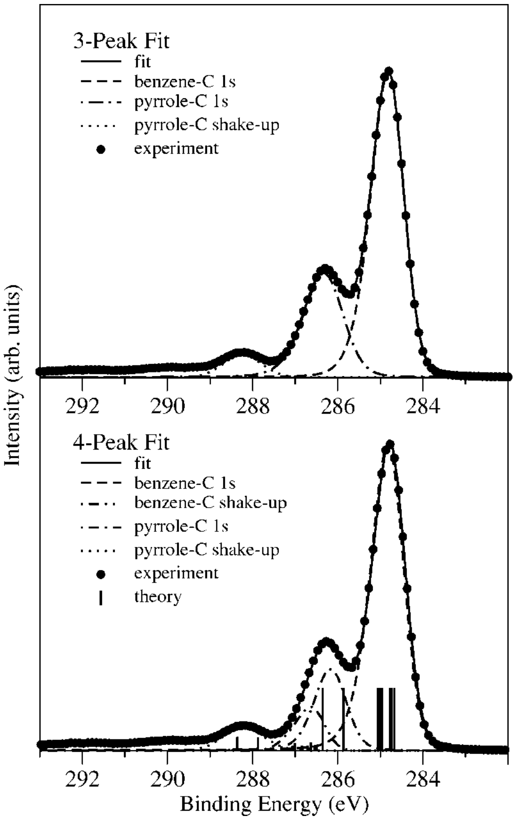

FIG. 2. Three-peak fit (upper part of the figure) and four-peak fit (lower part of the figure) of the experimental C 1*s* XPS curve of H_2Pc. The different curves employed in the fitting procedure to simulate the main lines and the shake-up features are illustrated, along with the total fit and the experimental data (dotted line). The theoretical values (bar graph) are compared to the peak positions of the four-peak fit.

We have applied the ECH-TDDFT method to the H_2Pc molecule, and the energies and intensities we have obtained for the shake-up lines, related to the eight inequivalent C atoms in the H_2Pc, are reported in Tables II and III. The carbon atoms labeled from 1 to 6 are the benzene-like carbons, while the carbons 7 and 8 are pyrrole-like (see Fig. 1). The tables report also the IP calculated for each of the 8 carbons considered. The calculated IP are referred to the vacuum level, and, in the comparison with the experiment, they have been shifted by −5.1 eV in order to be aligned to

TABLE II. Theoretical shake-up energies and intensities for the benzene-type C 1*s* in H_2Pc.

Benzene C in H_2Pc									
C Atom	IP eV	Energy[a] eV	Intensity[b] %	T/S[c]	C Atom	IP eV	Energy[a] eV	Intensity[b] %	T/S[c]
C1	289.77	0.99		T	C4	290.06	0.93		T
		1.53		T			1.28		T
		1.96	12.1	S			1.74	7.2	S
		2.37	0.6	S			2.06	5.8	S
		2.96	0.9	S			2.51	0.5	S
C2	289.84	0.96		T			2.82	0.6	S
		1.51		T			3.11	0.6	S
		1.91	4.1	S			3.33	1.5	S
		2.13	0.8	S			3.44	0.6	S
		2.38	0.9	S			3.50	1.3	S
		2.80	3.7	S	C5	290.11	0.96		T
		2.94	3.3	S			1.27		T
		2.96	0.6	S			1.48	5.9	S
		3.04	0.9	S			2.06	6.4	S
		3.09	0.9	S			2.83	0.7	S
		3.14	1.2	S			3.13	1.9	S
		3.48	2.1	S			3.32	0.9	S
		3.54	1.0	S	C6	290.15	1.04		T
		3.82	1.7	S			1.29		T
		3.85	1.1	S			1.96	11.2	S
C3	289.87	1.05		T			3.32	0.6	S
		1.43		T			3.41	0.6	S
		1.76	6.8	S					
		2.07	7.4	S					
		2.87	1.1	S					
		3.16	1.3	S					
		3.32	0.6	S					
		3.69	0.6	S					

[a] Shake-up energy position as the energy difference from the IP.

[b] In percent of the main peak's intensity.

[c] Triplet (T) or singlet (S) character.

the experimental data. The shift takes into account the different binding energy scales used for gas phase spectra (in this case the theoretical simulation) and the photoemission experimental results for the solid film. The IP of the benzene carbons are lower, ranging from 289.77 and 290.15 eV and the IP of the pyrrole carbons are 290.97 and 291.45 eV—values referred to the vacuum level. The carbon shake-up lines reported in Tables II and III for energies up to about 4 eV from the main peak, present a similar shake-up structure for all the carbon atoms, with two triplet states followed by a singlet state between about 1.6–2.0 eV. The considerable number of higher energy triplet transitions were not reported in the tables. In the case of the benzene carbons, the first singlet shake-up features fall very close in energy to the pyrrole main lines, and consequently have to be included, in a correct fitting, as a separate peak in the pyrrole carbon binding energy region. This result represents the first theoretical support to the procedure taken in a recent work[12,13] to fit the experimental data by introducing a fourth peak. This peak represents the benzene shake-up intensity contribution, hidden under the spectral intensity related to the pyrrole carbon.

A four-peak fitting of the experimental spectrum is illustrated in the lower part of Fig. 2. It must be observed that, in the case of aromatic molecules, the shake-up structure is rather complex, as can be seen in Tables I–III; nevertheless it may be convenient in a fitting procedure to approximate the shake-up energies with a reduced number of peaks, by including only the transitions that give the most intense contributions. In the four-peak fitting procedure, two peaks have been used for the aromatic carbons (at 284.82 and 286.60 eV) and two for the pyrrole carbons (at about 286.17 and 288.20 eV), representing the main line and the shake-up contribution for each type of carbon, respectively. To be

TABLE III. Theoretical shake-up energies and intensities for the pyrrole-type C 1*s* in H_2Pc.

Pyrrole C in H_2Pc				
C Atom	IP eV	Energy[a] eV	Intensity[b] %	T/S[c]
C7	290.97	1.16		T
		1.67		T
		2.01	20.3	S
		3.97	1.3	S
C8	291.45	1.17		T
		1.56		T
		2.01	20.7	S
		3.88	1.0	S

[a] Shake-up energy positions as the energy difference from the IP.

[b] In percent of the main peak's intensity.

[c] Triplet (T) or singlet (S) character.

noted that the energy position and the intensity of the four peaks used in the fitting procedure (Fig. 2, lower panel) take into account the theoretical results, shown by bars in the same figure for comparison. The introduction of the fourth peak at 286.6 eV leads to an intensity ratio of 24% for the pyrrole carbon with respect to the benzene carbons, in much better agreement with the molecular stoichiometry of 25%. In Fig. 3 are shown three simulations of the experimental spectrum obtained by convoluting all the calculated shake-up features of the singlet-type (for which the intensity has been computed) and the main line peaks with Gaussian curves of full width at half maximum (FWHM) 0.7, 0.8, and 0.9 eV, respectively, obtaining a good agreement between theoretical curves and experimental spectrum.

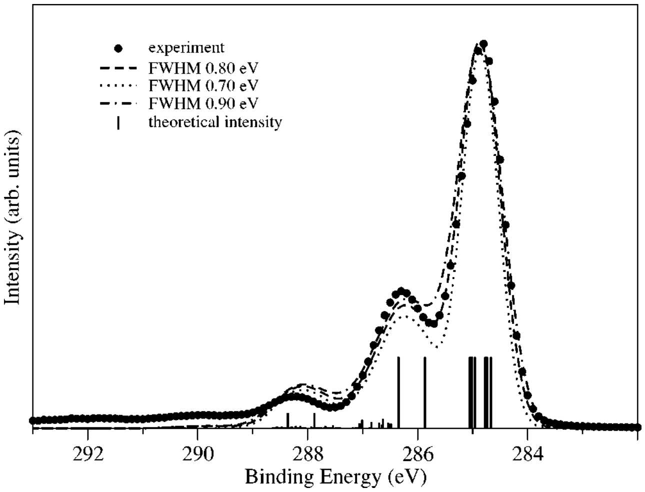

FIG. 3. Simulation of the experimental C 1*s* XP spectrum by convoluting the calculated intensities of the main lines and the shake-up features with gaussian curves of different FWHM (0.70, 0.80, and 0.90 eV, as indicated in the figure). The calculated intensities (bar graph) and the experimental curve (dotted line) are also shown.

In summary, we have introduced a new computational scheme to calculate the shake-up structures of photoelectron spectra, by combining the equivalent core approximation and the time dependent density functional theory. The use of TD-DFT allows to easily incorporate the electron correlation effects, to determine all possible multiple excitations, and to compute large systems at a reasonable computational cost. A detailed description of the C 1*s* shake-up profile of H_2Pc is reported and an excellent agreement between the theoretical simulation and experimental data has been obtained. The application of the method has permitted to determine the origin of the anomalous intensity ratio between the pyrrole and benzene carbons in the high resolution XPS spectra, as caused by previous failure to appreciate the important benzene shake-up contribution.

This work was supported by the Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF), and the Göran Gustafsson Foundation. We acknowledge Professors P. A. Brühwiler and U. Gelius for valuable discussions.

---

*Author to whom correspondence should be addressed. Electronic address: luo@theochem.kth.se

†Electronic address: carla.puglia@fysik.uu.se

[1] G. Gu, G. Parthasarathy, and S.R. Forrest, Appl. Phys. Lett. **74**, 305 (1999).

[2] S. Riad, Thin Solid Films **370**, 253 (2000).

[3] H. Grennberg, S. Faizon, and J.-E. Bäckvall, Angew. Chem., Int. Ed. Engl. **32**, 263 (1993).

[4] H. Grennberg and J.-E. Bäckvall, Acta Chem. Scand. **47**, 506 (1993).

[5] J. Wöltinger, J.-E. Bäckvall, and A. Szigmund, Chem.-Eur. J. **5**, 1460 (1999).

[6] F. Bedioui, Coord. Chem. Rev. **144**, 39 (1995).

[7] Y. Niwa, H. Kobayashi, and T. Tsuchiya, J. Chem. Phys. **60**, 799 (1974).

[8] A. Gosh, J. Fitzgerald, P.G. Gassman, and J. Almlöf, Inorg. Chem. **33**, 6057 (1994).

[9] G. Dufour, C. Poncey, F. Rochet, H. Roulet, M. Sacchi, M. De Santis, and M. De Crescenzi, Surf. Sci. **319**, 251 (1994).

[10] L. Ottaviano, S. Di Nardo, L. Lozzi, M. Passacantando, P. Picozzi, and S. Santucci, Surf. Sci. **373**, 318 (1997).

[11] L. Ottaviano, L. Lozzi, F. Ramondo, P. Picozzi, and S. Santucci, J. Electron Spectrosc. Relat. Phenom. **105**, 145 (1999).

[12] H. Peisert, M. Knupfer, and J. Fink, Surf. Sci. **515**, 491 (2002).

[13] T. Schwieger, H. Peisert, M.S. Golden, M. Knupfer, and J. Fink, Phys. Rev. B **66**, 155207 (2002).

[14] R.E. Stratman and G. Scuseria, J. Chem. Phys. **109**, 8218 (1998).

[15] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. **256**, 454 (1996).

[16] M.E. Casida, C. Jamorski, K.C. Casida, and D.R. Salahub, J.

Chem. Phys. **108**, 4439 (1998).
[17] G. De Alti, P. Decleva, and A. Lisini, Chem. Phys. **90**, 231 (1984).
[18] L. Yang and H. Ågren, Chem. Phys. **222**, 139 (1998).
[19] S. Lunell, M.P. Keane, and S. Svensson, Chem. Phys. **90**, 4341 (1989).
[20] B. Sjögren, J. Chem. Phys. **96**,8338 (1992).
[21] R.W. Bigelow and H.J. Freund, J. Chem. Phys. **77**, 5552 (1982).
[22] B. Brena, S. Carniato, and Y. Luo (unpublished).
[23] M. J. Frisch *et al.*, GAUSSIAN 98, Revision A.11 (Gaussian, Inc., Pittsburgh, Pennsylvania, 2001).
[24] W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR Basic Principles and Progress* (Springer Verlag, Heidelberg, 1990), Vol. 23.
[25] M. E. Casida *et al.*, DEMON-KS, Version 4.0 (DEMON Software, 1997).
[26] J.P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[27] E.E. Rennie, B. Kempgens, H.M. Köppe, U. Hergenhahn, J. Feldhaus, B.S. Itchkawitz, A.L.D. Kilcoyne, A. Kivimäki, K. Maier, M.N. Piancastelli, M. Polcik, A. Rüdel, and A.M. Bradshaw, J. Chem. Phys. **113**, 7362 (2000).
[28] D. Nordfors, A. Nilsson, N. Mårtensson, S. Svensson, and U. Gelius, J. Chem. Phys. **88**, 2630 (1988).
[29] U. Gelius, B. Wannberg, P. Baltzer, H. Fellner-Feldregg, G. Carlsson, C.-J. Johansson, J. Larsson, P. Münger, and G. Vegerfors, J. Electron Spectrosc. Relat. Phenom. **52**, 747 (1990).
[30] Y. Alfredsson, B. Brena, K. Nilson, J. Åhlund, M. Nyberg, A. Sandell, C. Puglia, and H. Siegbahn (unpublished).