Origin of the Large N 1s Binding Energy in X-ray Photoelectron Spectra of Calcined Carbonaceous Materials

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Abstract: Theoretical models and ab initio Hartree−Fock wave functions are used to investigate the N 1s core level binding energies of N-containing calcined carbonaceous materials. Comparison of calculated and experimental values for a series of test molecules reveals that the N 1s core level shift from one compound to another is mainly originated by initial state effects. This permits a systematic study of different situations and allows establishment that three different types of nonoxidized N atoms can be present in these materials. These are “pyridinic”, “pyrrolic”, and “graphitic” nitrogen with binding energies of ≈399.0, ≈400.3, and ≈401−403 eV, respectively. This assignment is in very good agreement with a recent experimental X-ray photoelectron spectra on petroleum cokes and demonstrates, for the first time, that it is possible for N to exhibit rather large core level 1s energies without requiring the presence of any charge transfer from *N*-oxide groups. Theoretical reasons for such a behavior are also given.

I. Introduction

Carbonaceous materials are obtained in large quantities in the oil refining processes after removing volatile material from petroleum. These carbonaceous materials are most often known as petroleum cokes and are commonly used as fuel in other industries (i.e., thermal power stations, portland factories, etc.). The presence of heteroatoms, mainly N, O, and S, in these materials involves a decrease of their quality. From the technological point of view, they affect the graphitization process, mechanical properties, etc. Moreover, the use of these cokes as fuel is limited by their N and S content because of the large contaminant behavior of these elements. In fact, combustion of cokes having high N or S concentration will result in undesired large emissions of SO_2 and NO_x. To avoid a decrease on the fuel quality of these cokes and, also, to reduce their contaminant behavior, it is necessary to treat the cokes in such a way that the undesired heteroatoms are removed.

As a first step toward the design of desulfuration and denitrogenation processes, a precise knowledge of the chemical structures of N and S in these materials seems unavoidable. A suitable experimental technique which may help to establish these structural features at an atomic level is X-ray photoelectron spectroscopy (XPS). Core level binding energies (BE’s) determined from XP spectra are quite regularly used to study gas phase atoms and molecules as well as to study condensed phase systems.[1] The XPS spectra may be used either to identify the atomic and molecular composition of the sample being examined or to obtain information about the chemical bonding and related properties of an atom in a given system. In particular, the shifts of the BE’s of an atom from the atom in one molecule to the atom in a different molecule are used to characterize differences in the bonding of a given chemical element in the two different molecules. Hence, these shifts are referred to as chemical shifts. Another type of chemical shifts arise when the same atom is in different, inequivalent positions in the same molecule;[2] in this case, the XPS chemical shifts may indicate the chemical differences of the various inequivalent sites.

In a recent study of petroleum fuel cokes treated by heating them to a high temperature, i.e. calcined at different temperatures ranging from 480 to 2800 °C,[3] XPS has been used to try to elucidate the chemical nature of the structures in which these heteroatoms are included in cokes. In that study the authors show that the N 1s band exhibits, in general, three different components. In the low-temperature ($\leq$700 °C) samples, only two components were observed and directly assigned to “pyridinic” (398.6 eV) and “pyrrolic” (400.3 eV) N types. Here, we must point out that the terms pyridinic and pyrrolic are used in a rather broad sense; the first one is used to refer to N atoms which contribute to the π system with one p-electron, whereas the second refers to N atoms with two p-electrons on the π system although not necessarily in a five-member ring as in pyrrole. At higher temperatures, the BE’s shift to higher values (399.5 and 401.4 eV, respectively) and the third component develops. This last component appears at a rather high BE (402.7 eV), and comparison with experimental BE’s of reference compounds shows that it is close to that expected for *N*-oxide functional groups. However, after a careful experimental analysis, Jiménez-Mateos and Fierro concluded that this functional group or similar oxidized species were present on the samples.[3] Indeed, a very strong argument in this line is given by the poor thermal stability of oxidized N groups: this third component is clearly patent at higher temperatures ($>$700 °C), and hence, it is unlikely that oxidized N groups can be found after calcination. Then, the origin of this high-BE component is unclear, but it was tentatively assigned to

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(1) Siegbahn, K.; Nordling, C.; Fahlman, A.; Norderg, R.; Hamrin, K.; Johansson, G.; Bergmark, T.; Karlson, S. E.; Lindgren, I.; Lindberg, B. *ESCA-Atomic, Molecular, and Solid State State Structure Studied by Means of Electron Spectroscopy*; Almqvit and Wiksell: Uppsala, Sweden, 1967.

(2) Bagus, P. S.; Coolbaugh, D.; Kowalczyk, S. P.; Pacchioni, G.; Parmigiani, F. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *51*, 69.

(3) Jiménez-Mateos, J. M.; Fierro, J. L. G. *Surf. Interface Anal.* **1996**, *24*, 223.

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"graphitic" N (N atoms replacing C atoms in graphene layers) considering also an earlier X-ray diffraction study.[4] In this way, similar hypothesis have been proposed by other authors in other carbonaceous material,[5,6] although the theoretical or experimental supports given in these works are not conclusive.

Before any further comment, we must point out that the experimental BE's in carbonaceous materials are not usually absolute measures, that is to say, they are not referred to vacuum but to the C 1s peak arbitrarily placed at 284.5−285.0 eV. Moreover, the fact that 285 eV is used for C 1s means that the BE is measured with respect to the Fermi level of graphitic carbon. Hence, the experimental BEs are in fact chemical shifts although referred to a reference atom. Both, chemical shifts and absolute BE values can be accurately obtained by means of ab initio Hartree−Fock calculations.[7−9] Also, a theoretical approach permits simulation of situations with N atoms substituting C atoms in different position of graphene layers. This can be hardly carried out experimentally, but it is feasible using different physical models.

Then, the purpose of the present work is 2-fold: on the one hand, we will show that the interpretation for the high-BE component of the N 1s peak in terms of "graphitic" N[3,6] is supported by accurate ab initio model calculations of the core level ionization potentials and of the core level shifts. On the other hand we will show, for the first time, that rather high N 1s binding energies in N-containing compounds may be observed without *N*-oxide functional groups in the sample. This is an important conclusion, of general validity, not previously recognized in the XPS literature.

This paper is organized as follows: In section II we briefly describe the theoretical ab initio framework used in the present study. Section III presents results for some test molecules with well-characterized XPS for the N 1s peak; comparison between experimental values and theoretical calculated results provide a convenient strategy to design models. These models are then used to simulate graphene layers as those appearing in carbonaceous materials (considering mainly the previous work on petroleum cokes[3]). The corresponding theoretical results for the N 1s BE's for these models of carbonaceous materials are presented in section IV. Finally, section V presents our general conclusions.

II. Theoretical Approach

Before entering into the details of the electronic structure calculations, we must recall that the total BE's contain two different contributions usually referred to as initial and final state effects.[7] The initial state effects reflect the environment due the charge distribution in the initial, unionized state while the final state effects include the relaxation of the passive orbitals caused by the core-hole created in the ionization. In order for the chemical shifts of the BE's to actually provide information about chemical differences, it is necessary that the shifts be dominated by initial state effects. It has been shown,[2,7] that the relaxation energy arising from final state effects depends most strongly on the number of atoms in a molecule but only weakly on the location of the ionized atom. Thus, the chemical shifts of inequivalent atoms in a molecule do indeed reflect their different chemical bonding. Further, the final state relaxation energy may not vary extremely rapidly with the number of atoms in a molecule. Thus, it may be that chemical shifts of atoms in molecules of different but similar size may also reflect the chemical environment and we shall investigate whether this is the case for the systems investigated in this paper.

The calculations we report are based in Hartree−Fock self-consistent field (SCF) wave functions. These ab initio SCF wave functions are specially well suited to study core level energies because they permit division of the contributions to the BE's into initial state and final state terms.[7] Also, we must recall that the mean field approximation inherent to the SCF approach is a very good approximation to the calculation of core level ionization energies. This is because the core level energy is essentially a measure of the electric field at the nucleus of the atom to be ionized, and this is very well described at the Hartree−Fock level of theory.

The initial state terms reflect only the chemical environment of the atom that will be ionized. This BE is given by Koopmans' theorem (KT).[10] For the KT-BE all canonical orbitals are frozen as they are for the initial state of the molecule.[11] Both initial and final state effects are taken into account if the SCF wave function for the state with the core hole is computed. The BE in this case is given by the difference of the energies of the initial and final, core ionized states; this is described as a ΔSCF-BE. The difference between the KT-BE and the ΔSCF-BE is called the relaxation energy (E_R). While E_R is large, if it is approximately constant, then the shift in the KT-BE's does largely account for the observed shift. We must point out that for transition metal containing molecules and in chemisorption systems final effects may be very important to determine the BE shifts.[12−14] However, we shall show that for the systems under consideration the shift is largely accounted for by initial state effects.

For the test molecules described in the next section, the N 1s BE has been computed at three different molecular geometries. The first one is the ab initio Hartree−Fock SCF geometry optimized when the orbitals of C, N, and H are described by a standard triple-ζ plus polarization basis set, obtained from by the appropriate contraction of the Dunning primitive set.[15] These SCF-optimized geometries may have some differences from the experimental gas phase ones. However, they are not expected to lead to significant changes in the core level BE's because previous calculations have shown that small changes in bond distances only lead to very small changes in the core level BE's.[8,9] In the following, we will describe this set of calculations as TZP/TZP to indicate that the SCF wave function is computed with a TZP basis set at a geometry optimized also using the TZP basis set. These TZP/TZP calculations are used as a reference because for the very large graphene models a slightly different approach has to be employed. For this reason

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(4) Jiménez-Mateos, J. M.; Romero, E.; Gómez de Salazar, C. *Carbon* **1993**, *31*, 1159.

(5) Strelko, V. V.; Lavrinenko-Ometsinkaya, Y. D. *J. Mol. Struct. (THEOCHEM)* **1989**, *188*, 13.

(6) Pels, J. R. Ph.D. Thesis University of Delf, The Netherlands, 1985, Chapter 7, pp 199−256.

(7) Bagus, P. S.; Brundle, C. R.; Pacchioni, G.; Parmigiani, F. *Surf. Sci. Rep.* **1993**, *19*, 265.

(8) Nelin, C. J.; Bagus, P. S. in *Festkpörperprobleme (Advances in Solid State Physics)*; Grosse, P., Ed.; Vieweg: Braunscheig, Germany, 1985; Vol. 25, p 135.

(9) Bagus, P. S.; Brundle, C. R.; Illas, F.; Parmigiani, F.; Polzonetti, G. *Phys. Rev. B* **1991**, *44*, 9025.

(10) Koopmans, T. *Physica* **1934**, *1*, 104.

(11) Nesbet, R. K. *Adv. Chem. Phys.* **1965**, *9*, 321.

(12) Bagus, P. S., Pacchioni, G., Parmigiani, F., Eds. *Core Level Spectroscopies for Magnetic Phenomen: Theory and Experiment*; NATO ASI Series; Plenum Press, 1995; Vol. 345.

(13) Martensson, N.; Nilson, A. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 1.

(14) Tillborg, H.; Nilsson, A.; Martensson, N. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *62*, 73.

(15) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

we have carried out a second set of calculations where the basis set of N is the same as in the previous set but C and H atoms are described with a 6-31G basis set.[16] This second suite of calculations is referred to as mix/mix to indicate that both the SCF wave function and molecular geometry have been obtained by employing the mixed basis set just described. Finally, the third set of calculations explore the effect on the BE's of using a more approximate geometry. In this case the ab initio SCF wave function is computed using also the mixed basis set but the molecular geometry is that obtained with the semiempirical AM1 method.[17] We will refer to this third group of calculations as mix/AM1. In the next section we will show that, as far as BE's are concerned, the mix/AM1 approach is accurate enough. Therefore, this will be the one used to carry out the SCF calculations on the graphene layer models.

Because the main interest of the present work is the study of core level shift it is important to show that initial state KT-BE's are able to explain the main trends. To further support this idea, we draw on the work of Bagus, Illas, Casanovas, and Jiménez-Mateos[18] where ΔSCF calculations were performed for pyridine and pyrrole. These more complex ΔSCF calculations were carried out using the (9s5p/4s3p) Van Duijneveldt sets for C and N[19] whereas the basis for hydrogen is a (4s1p/2s1p) with the 4s primitive taken also from ref 19 and $\alpha_p = 1.0$. We must also point out that the N 1s core level BE shifts have been computed with respect to the C 1s placed arbitrarily at 285 eV. Notice that in all the molecules considered there are many possible carbon atoms with different C 1s levels (although the range of C 1s KT energies is of only ≈1 eV). Therefore, we have taken the calculated KT value of the C 1s as the average of all C 1s levels and placed it equal to 285 eV. This has been done to follow the previous experimental work[3] where this choice was made to avoid charge effects on the sample and to avoid reference to vacuum or to the graphitic carbon Fermi level. Here, we must remark that the experimental spectra for the C 1s are characteristic of graphitic carbon and because of the high asymmetry of the main graphitic peak a separation of these peak in components was not performed in ref 3. Therefore, we will refer all the calculated values to a single C 1s peak centered at 285 eV. Finally, it is important to stress that secondary peaks, generally referred to as satellites, shake-up or shake-down, usually appear in photoemission spectra of transition metal compounds or even of small molecules.[12,20] However, in the XPS spectra of the petroleum fuel cokes considered in the present work, no satellites other than the plasmon peak due to the $\pi \rightarrow \pi^*$ shake-up transition characteristic of graphitic carbon C(1) peak (cf. ref 3 and references therein) were observed. In particular, no satellite structure was observed for the N 1s peak. This fact justifies the study of the N 1s BE shifts using the theoretical framework described above. In particular, the fact that no satellites need to be considered permits reliance on Hartree−Fock wave functions.

All calculations except the ΔSCF ones have been carried out using the HONDO[21] program, whereas ΔSCF calculations were carried out using the Molecule-Alchemy[22] suite of programs.

Table 1. Experimental and Calculated Values for the N 1s Binding Energy of Test Molecules Referred to the C 1s Taken as 285 eV[a]

		computational approach		
molecule	exptl[b]	TZP/TZP	mix/mix	mix/AM1
pyridine	398.9	402.17 (3.27)	402.14 (3.24)	402.07 (3.17)
pyrrole	400.4	404.09 (3.69)	404.07 (3.67)	403.92 (3.52)
pyridine *N*-oxide	403.2	405.93 (2.73)	405.84 (2.64)	406.50 (3.30)
pyridinium	401.2	404.49 (3.29)	404.47 (3.27)	404.10 (2.9)

[a] Values in parentheses are the absolute differences between calculated and experimental results. The meaning of TZP/TZP, mix/mix, and mix/AM1 is given in section II. All values are in eV. [b] From refs 3 and 6.

III. Core Level Binding Energies of Test Molecules

The purpose of this section is to check different computational approaches that can be used to describe the core level BE of N-containing compounds related to carbonaceous materials and petroleum cokes among them. In the recent experimental work by Jiménez-Mateos and Fierro,[3] the first and second N 1s components were straightforwardly assigned to "pyridinic" and "pyrrolic" N-types, respectively, in the spectra of the samples calcined at low temperatures. At higher temperatures, the BE's of these components shift to higher values by ≈1 eV and a third component is clearly observed. The assignment was now not so straightforward. It is thought that the first and second components should correspond to somehow modified pyridinic and pyrrolic structures and the third component was tentatively assigned to graphitic N, although it appeared in the region corresponding to oxidized N groups. Obviously, the logical choice to start with corresponds to the isolated pyridine, pyrrole, and pyridine *N*-oxide. In addition we will also include the pyridinium ion because this is a charged molecule and will permit us to check if the difference between the N 1s and the C 1s is affected or not by the charge of the molecule.

In Table 1, we report a summary of results for all the molecules described above and compare them with the results available in the literature. The calculated values always appear to be larger than the experimental ones although the difference between calculated and experimental values is almost constant. Moreover, the calculated values are almost unaffected by the computational approach used. For a given molecule, all the ab initio SCF results differ by less than 0.3 eV in the worse case. Considering that the N 1s−C 1s shift is of ≈100 eV the deviation is small. Notice that for these test molecules both the N 1s and C 1s have been explicitly calculated and that the N 1s−C 1s difference is not affected by any arbitrary setting. This fact provides a first strong argument to support the idea of using the mix/AM1 approach to study the core level BE's of the graphene layers simulating petroleum cokes. A second important point concerns the relative N 1s−C 1s shift between the different test molecules. The ab initio SCF calculations nicely follow the trend observed between the different molecules. This provide a second strong argument to use SCF wave functions to study the N 1s XPS spectra of N-containing petroleum cokes.

The fact that the ab initio SCF calculated values for the N 1s−C 1s shift follows the experimental trend indicates that the origin of the N 1s shift between the different molecules is, in fact, an initial state effect. We must recall that up to now all the reported values correspond to the use of the Koopmans' theorem. Now, we will further proove that the above-commented N 1s shifts are governed by initial state effect. The KT values for the N 1s−C 1s shift are 117.23 and 118.97 eV for pyridine and pyrrole, respectively, the difference between

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(16) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Steward, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(18) Bagus, P. S.; Illas, F.; Casanovas, J.; Jiménez-Mateos, J. M. *J. Electron Spectrosc. Relat. Phenom.*, in press.

(19) van Duijneveldt, F. B. IBM Research Report No. RJ 1971, unpublished.

(20) Cederbaum, L. S.; Domcke, W.; Schirner, J.; Von Niessen, W. *Phys. Scripta* **1980**, *21*, 481.

(21) Dupuis, M.; Johnston, F.; Márquez, A. *HONDO 8.5 from CHEM-Station*; IBM Corporation: Kingston, NY, 1994.

(22) *Molecule-Alchemy*. Almlof, J.; Bagus, P. S.

Table 2. Results for the N(1s) BE's in Pyridine and Pyrrole[a]

	pyridine	pyrrole	Δ
exptl	404.94[b]	406.15[c]	1.21
ΔSCF	405.09	406.26	1.17
KT	423.91	424.80	0.89

[a] Values are given for experiment, ΔSCF, and frozen KT. The chemical shift, Δ, is defined as Δ = BE(pyrrole) − BE(pyridine). All values are in eV. [b] See ref 19. [c] See ref 20.

them being 1.64 eV. The experimental values are 113.8 and 115.4 eV or a difference of 1.6 eV.[23,24] Hence, the experimental difference is well reproduced by the calculated KT values although the total calculated value for the N 1s−C 1s shift is too large by ≈3.2 eV. If our interpretation for the N 1s BE difference between pyridine and pyrrole in terms of initial and final state effects is correct, the origin of this ≈3.2 eV difference between calculated and experimental N 1s−C 1s shift must lie in the different relaxation energy of the C 1s and N 1s holes and can be checked by ΔSCF calculations for the C 1s and N 1s holes for pyridine and pyrrole. The calculated ΔSCF values for N 1s−C 1s are 113.39 and 115.40 eV; the agreement with experiment is now almost perfect and shows that the ≈3.2 eV energy difference commented above is indeed due to the different relaxation energy of the C 1s and N 1s core-holes. Still, the coincidence between theoretical and experimental values can be fortuitous because the C 1s BE is arbitrarily taken as 285 eV. To avoid this arbitrariness, we notice that, while absolute values of the N 1s in carbonaceous materials cannot be measured because of the unknown value of the work function of a given material, it is well possible to measure absolute values of the N 1s in the gas phase for pyridine and pyrrole.[23,24] The accuracy of our computed SCF results for the BE's and for the shifts, Δ, between pyridine and pyrrole can be found by comparing the results given in Table 2. The calculated ΔSCF BE's are surprisingly accurate. They are within 0.15 eV of the experimental values; indeed this is within the experimental uncertainty. The experimental difference between the absolute gas phase binding energy or ionization potential values for the N 1s in pyrrole and pyridine is 1.21 eV; the ΔSCF shift is 1.17 eV. These values are essentially the same and show that, for the present purposes, the ΔSCF description is more than adequate. We turn now to consider the initial state effects as by given the KT-BE obtained from the SCF wave functions. The relaxation energies are quite large, ≈18.5 eV; thus, the KT-BE's are quite larger than the experimental values. However, the relaxation energy (E_R) for pyridine is only 0.28 eV larger than that of pyrrole; thus, the extra carbon atom in pyridine does not add significantly to E_R. This means that the KT-BE shift is $\Delta = 0.9$ eV, reasonably close to the experimental and ΔSCF values of 1.2 eV. Indeed, the chemical shift between the N 1s in pyridine and pyrrole is dominated by the initial state effects.

The fact that the initial state effects dominate allows us to examine the KT-BE's for the different models used to the simulate graphene layers. Moreover, given the closeness between the TZP/TZP, mix/mix, and mix/AM1 values, the later approach has been chosen to study the XPS spectra of carbonaceous materials models. Accordingly, all the ab initio SCF calculations have been carried out at the geometry obtained with the AM1 method. Geometry optimization was considered for all the N-substituted molecular models of carbon cokes.

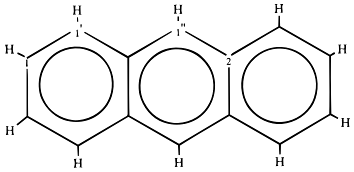

Figure 1. Schematic representation of the anthracene model. Different positions are indicated for which substitution of a C atom or of a CH group by a N atom has been considered.

IV. Core Level Binding Energies of Petroleum Coke Models

Petroleum cokes, as other carbonaceous materials, exhibit structural features which largely resemble graphitic layers. In the present work, these graphitic layers have been modeled by a series of systems constituted by several six-membered carbon rings. We have considered models having 3−10 six-membered rings, and when possible, different structures with the same number of carbon rings are considered. The geometry of this graphitic layers without any N atoms has been optimized using the AM1 semiempirical method. After geometrical optimization, the inclusion of N atoms in these models has been considered in two different ways. First, a given C atom has been substituted by a N atom. In the second case, a CH group has been substituted by a N atom; clearly this second possibility cannot always be considered.

We must point out that depending on the C or CH group substituted by a N atom the resulting structure may be either a closed shell system or a radical. Notice that electronic paramagnetic resonance and magnetic measurements carried out for different carbonaceous materials indicate the existence of unpaired electrons [see for example refs 25 and 26]. Therefore, both kinds of electronic structure have been considered. For the closed shell systems, restricted Hartree−Fock (RHF) wave functions are obtained whereas the unrestricted Hartree−Fock (UHF) formalism has been used to describe the electronic structure of radicals. In this later case, the N 1s BE has been taken as an average of the spin α and β components. It is worth bringing up that for open-shell systems there are two different final states depending on the spin coupling between the unpaired core electron and the valence open-shell electrons. As a result of this spin coupling, a multiplet structure appears in the XPS spectra [see ref 2 and references therein]. In particular, this multiplet splitting leads to a broadening of the XPS peaks that may be as large as 1 eV. In the case of using an UHF wave function, the splitting can be estimated already by considering initial state effects only and the difference between the α and β core energies.[27] Finally, it is important to notice that when the SCF wave function for the unionized neutral molecule has open shells the Koopmans theorem BE must be defined from the proper average of the different coupling states.[28,29]

Now let us start the description of the results for the simplest case where three carbon rings, as in anthracene, are considered (Figure 1). In this case we will consider four different positions designed as 1, 1′, 1″, and 2 as shown in Figure 1. In this case substitution of a C atom by a N one always leads to radical structures whereas substitution of CH by N leads to a closed

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[23] Brown, R. S.; Tse, A. *Can. J. Chem.* **1980**, *58*, 694.

[24] Chambers, S. A.; Thomas, T. D. *J. Chem. Phys.* **1977**, *67*, 2596.

[25] Fischback, D. B. The kinetics and mechanism of graphitization. Walker, P. L., Jr., Ed.; In *Chemistry and Physics of Carbon*; Marcel Dekker Inc.: New York, 1971; Vol. 7, p 1.

[26] Pacault, A. The kinetics of graphitization. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker Inc.: New York, 1971; Vol. 7, p 107.

[27] Bagus, P. S.; Bennett, B. I. *Int. J. Quantum Chem.***1975**, *9*, 143.

[28] Hermann, K.; Bagus, P. S. *Phys. Rev.* **1976**, *16*, 4195.

[29] Cox, P. A. *Mol. Phys.* **1972**, *30*, 389; *J. Chem. Phys.* **1984**, *80*, 4378.

Table 3. Theoretical Values for the N 1s Binding Energy of Petroleum Coke Models in Which Either a C Atom or a CH Group Has Been Substituted by a N Atom[a]

model	site	C substituted	C-H substituted
anthracene (Figure 1)	1	400.7*	398.9
	1′	399.9*	398.9
	1″	399.9*	398.8
	2	402.6*	
perinaphtalene (Figure 2)	1	400.4	398.9*
	1′	400.2	399.2*
	2	400.5*	
	3	401.9	
coronene (Figure 3)	1	400.2*	399.0
	2	401.2*	
	3	402.7*	
graphitic (Figure 4)	1	400.1	399.2*
	1′	400.6	399.0*
	2	402.2	
	3	401.2	

[a] The N 1s BE's are referred to the C 1s taken as 285 eV. Reported theoretical values correspond to the calculated initial state ones corrected by substracting 3.2 eV to account for differential final state effect between C 1s and N 1s core-holes (see discussion in section IV). All values are in eV. Radical structures are marked with an *.

shell electronic structure. In Table 3 we report calculated values for the N 1s BE corresponding to each of the situations above described. In order to allow a more direct comparison with experiment the values reported in Table 3 are the KT calculated ones but "corrected" by substracting 3.2 eV. This is somehow empirical although results on the previous section have univocally shown that the origin of the 3.2 eV average difference between calculated and experimental values is the different relaxation energy of a C 1s core-hole as compared to a N 1s core-hole. Also, we would like to remark that our calculated values have uncertainties of about ±0.3 eV. Again, notice that both, calculated and experimental, values are indeed referred to C 1s taken as 285 eV.

Results for anthracene in Table 3 already contain what will be a quite general characteristic. The N 1s BE values calculated for structures C-substituted in the 1, 1′, and 1″ are close to that typically assigned to pyrrole N-type (400.3 eV[3]) and significantly different from the N 1s BE values for the CH substituted cases which are coincident for the experimental BE values for pyridinic N-type (398.6 eV[3]). In the first case, however, there is a significant scattering of the values (≈0.8 eV) which suggests broadened peaks. This is indeed the case as shown in ref 3. Nevertheless, the first case can be considered as the N(2) component in ref 3, and the second one can correspond to the N(1) component of the experimental spectra. Here, we must remember that "pyridinic" is used to refer to N atoms which contribute to the π system with one p-electron whereas "pyrrolic" refers to N atoms with two p-electrons on the π system. Finally, the N 1s BE for position 2 is rather high, ≈3.6 eV higher than N(1) and 2.6 eV higher than N(2). This third value can be tentatively related to the N(3) component (402.7) described in ref 3. The above discussion is based on a single simple model, and agreement with experiment may be fortuitous. The analysis of the results for the largest models will show that this is not the case.

Our second model also contains three six-membered rings but in this case arranged in a nonlinear way (Figure 2). The resulting model is similar to the perinaphtalene radical, and four different positions namely 1, 1′, 2, and 3 have been considered. As in the previous model, substitution of a C atom in position 1 or 1′ results in a BE that is characteristic of "pyrrolic" N or of the N(2) component of the experimental spectra. Also, substitution of a CH group in 1 or 1′ by a N atom lead to "pyridinic" N as in the previous case. However, this perinaphtalenic model contains a third new position for which the N 1s BE (401.9 eV) is intermediate between the experimental values for N(2) components in samples calcinated above 700 °C (401.4 ± 0.4 eV) and the N(3) component (402.7 ± 0.6 eV). With respect to position 2, the difference between the two models is surely due to the fact that, once C is substituted by N, the anthracene model corresponds to a radical while it is a two unpaired electron system for the perinaphtalene model.

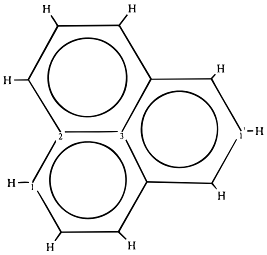

Figure 2. Schematic representation of the perinaphtalene model. Different positions are indicated for which substitution of a C atom or of a CH group by a N atom has been considered.

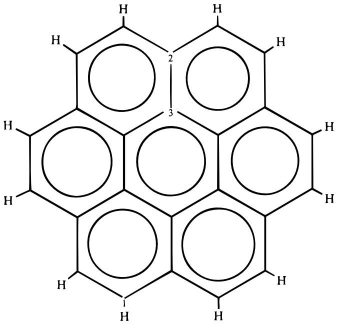

Figure 3. Schematic representation of the coronene model. Different positions are indicated for which substitution of a C atom or of a CH group by a N atom has been considered.

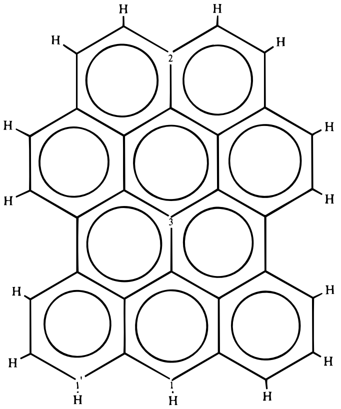

Figure 4. Schematic representation of the graphitic model. Different positions are indicated for which substitution of a C atom or of a CH group by a N atom has been considered.

Our next two models represent an attempt to simulate graphitic structures where moderately internal carbon atoms can be substituted by N. Hence, our third model contains seven six-member rings as in coronene (Figure 3), and our largest model is formed of 10 carbon rings and will be referred to as a "graphitic" model (Figure 4). In the case of the coronene model we consider positions 1, 2, and 3; substitution of a C in any of these position by a N leads to a radical, but substitution of the CH group of position 1 by a N atom preserves the closed shell structure of the model. Likewise, the isolated graphitic structure is a radical and substitution of C by N in 1, 1′, 2, and 3 leads to a closed shell system whereas substitution of CH by

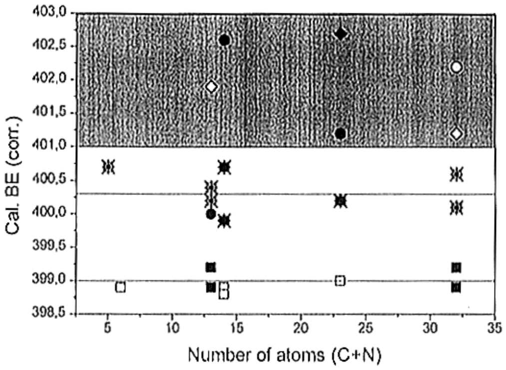

Figure 5. Plot of the calculated BE's vs the total number of atoms (C + N) in the graphene layer. N's in positions 1, 1′, and 1″ are symbolized by squares (□), position 2 by circles (○), and position 3 by diamonds (◇). Open symbols are for closed shell system, whereas solid symbols stand for radical structures. Points marked with a star (*) correspond to N substituing a CH group. Note how the calculated values are distributed around 399.0 and 400.3 eV or in the sahdowed zone between 401 and 403 eV (see text).

N in 1 and 1′ leads to a radical electronic structure with one unpaired electron.

For these larger models, results in Table 3 show the same behavior already commented for the smaller models. Substitution of either C or CH by N in positions 1 and 1' leads to N 1s BE's which correspond to pyrrolic and pyridinic N as in the previous cases. Also, substitution of C by N in positions 2 and 3 always leads to higher values of the N 1s BE. These higher values of N 1s BE are in agreement with the N(2) component at high temperature and with the N(3) component of the experimental spectra reported in ref 3.

V. Conclusions

From the results discussed in the previous section (cf. Table 3), three different zones can be defined in the general N 1s spectrum of carbonized carbonaceous materials (petroleum cokes among them), as it is shown schematically in Figure 5. The calculated BE's are distributed around 399.0 eV, 400.3 eV, and a broad zone between 401.0 and 403.0 eV. This result is in perfect agreement with previous experimental works.[3,6] In the three cases, the structures are of N atoms bonded only to C (and sometimes also to H), either in radicals or in closed shell structures, without considering oxidized N groups to justify the high-BE components. The zone at 399.0 eV is characterized by a N just on the edge of the graphene layer, only bonded to two C atoms, whereas the zone at 400.3 eV corresponds to N atoms on the edge as well but bonded to two C atoms and an H atom. Finally, the high-BE zone is originated by N atoms in inner positions ("graphitic" nitrogen). The radical nature of the final structure seems not to affect the BE values. Also, it is interesting to remark that, although these three zones can be defined from the theoretical results, there is a noticeable scattering of the values, which is very large in the high-BE zone. As it has been pointed out before, this effect would be observed in the experimental spectra as a broadening of the peaks. This effect may preclude the resolution of the spectra in the different components. Again, this effect is also experimentally observed.[3]

The analysis of the N 1s core level BE of several test molecules has established that the different value of this observable in different N-containing heterocycles is largely due to initial state effects. Moreover, detailed Hartree−Fock, KT, and ΔSCF calculations of the core level shift between N 1s and C 1s evidenced that this quantity is unquestionably well reproduced by KT values. Comparison between KT and experimental values for the N 1s−C 1s shift reveals a ≈3.2 eV average discrepancy between theory and experiment. However, final state ΔSCF calculations show that this difference may be explained by the different relaxation energy of the C 1s and N 1s core-holes.

Calculated values for a series of models simulating carbonaceous materials with N atoms inserted in different positions demonstrate that there are three different regions of the N 1s spectra. Two of these regions are the pyridinic (≈399.0 eV) and pyrrolic (≈400.3 eV) ones which correspond to well-known defined peaks in N-containing carbonaceous materials [see for example ref 6] and to the N1 and N2 XPS peaks reported in ref 3 for petroleum fuel cokes. The third region, appearing at higher BE's (401.0−403.0 eV), corresponds to highly coordinated N atoms substituting inner C atoms on the graphene layers. This assignment was already tentatively suggested by experimental studies[3,4,6] and is corroborated by the present model calculations.

Finally, a general and important conclusion of the present work is to univocally prove that high values of the N 1s can be found without the presence of *N*-oxide groups. The presence of these functional groups to interpret N 1s BE's between 401.0 and 403.0 eV (measured with respect to C 1s taken as 285 eV) is suggested simply because it is most common to consider the chemical shifts as arising from charge transfer to or from the ionized atom plus an electrostatic potential due to the effective charges of the surrounding atoms.[1,23] However, there is evidence, especially for condensed phase systems, that other effects may make an important contribution to core level chemical shifts.[7] In fact, in a very recent work, it has been demonstrated that the N 1s difference between pyridine and pyrrole is due to hybridization and not to any charge transfer.[18] Results on the present work reinforce this new idea that shifts in core level BE's cannot be related in a meaningful way to the effective charge of the ionized atom unless other effects, including the consequences of hybridization, are taken into account.

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