Infrared Spectroscopy of Carbon Materials: A Quantum Chemical Study of Model Compounds

E. Fuente,[†] J. A. Menéndez,[†] M. A. Díez,[†] D. Suárez,[‡] and M. A. Montes-Morán*,[†]

Instituto Nacional del Carbón (INCAR), CSIC, Francisco Pintado Fe, 26, Apartado 73, 33080 Oviedo (Spain), and Departamento de Química Física y Analítica, Universidad de Oviedo, Julián Clavería, 8, 33006 Oviedo (Spain)

Received: November 18, 2002; In Final Form: March 26, 2003

The present work reports a theoretical study of the infrared spectra of chemical structures that are suitable to the description of the surface chemistry of carbon materials. Prior to any consideration, the computational approach was tested and adapted by comparing the predicted IR spectra to those obtained experimentally for various reference compounds. Several models were considered, subsequently accounting for the most relevant functional groups that have been postulated to decorate the edges of graphene layers on carbon materials (i.e., anhydrides, carboxyls, lactones, phenolic, quinones, and pyrones). For each of the previous functional groups, different structures involving a different number of fused rings were considered. This strategy allowed us to establish the effect of conjugation on the shift of the IR frequencies corresponding to a given functional group. Cooperative effects between different functional groups (phenol−carboxyl, phenol−lactone, and so on) were another aspect that revealed itself to be an interesting issue when assigning frequencies in the IR spectra of highly oxidized carbon materials. Thus, it was found that the frequencies of the C═O bonds present in acid functional groups were systematically lowered when phenolic groups were close enough to establish hydrogen bonds. Special attention was also paid to the elucidation of the origin of the 1600-cm^{-1} band of carbons. It was found that, in the case of acid carbons, this band can be assigned to C═C stretching of carbon rings decorated mainly with phenolic groups. Cyclic ethers in basic carbons would also promote absorption in the 1600-cm^{-1} region of the IR spectrum. Finally, the predicted assignments are employed to interpret the IR spectra obtained experimentally for several activated carbons.

Introduction

Oxygen is the second most frequent element present in the surface of carbon materials. Thus, carbon surface oxides play a transcendental role in most of the applications of carbon materials.[1] Knowledge of the chemical properties of carbon surfaces as well as their microstructure is imperative in adsorption processes,[2] fabrication of composites,[3] prostheses implants, and many other different fields.[1,4] Oxygen atoms combine normally to carbon atoms, forming a wide spectrum of organic functionalities from carboxylic acids to ketones and ethers. These functionalities have been traditionally split into two families attending to their acidic or basic character in aqueous solution (Scheme 1).[1] On one hand, carboxyl, anhydrides, lactones, phenol, and lactol groups account for the acidic character of carbon materials. On the other hand, cyclic ketones and pyrone-like groups are likely the basic oxygen-containing functionalities, although other models (e.g., chromenes and cyclic ethers) have been proposed to explain carbon basicity.

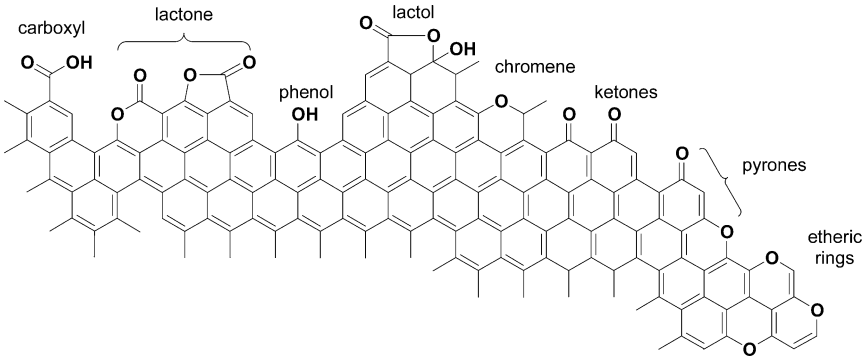
Surface chemistry on carbon materials is an area in which information at the molecular level is difficult to obtain. Consequently, all techniques that can provide direct information about the surface oxides are of primary importance in predicting the state and applications of carbon materials.[1] In this respect, infrared (IR) spectroscopy has been widely used to characterize the surface groups in coals,[5] carbon blacks,[6] chars,[7,8] carbon films,[9] and activated carbons.[10−13] However, IR spectra of carbon materials are difficult to obtain because of problems in sample preparation, poor transmission, uneven light scattering related to large particle size, and so forth.[14] Moreover, the electronic structure of carbon materials results in a complete absorption band through the visible region to the infrared. Fortunately, some of these problems can be overcome by improving sample preparation (e.g., carbon films) as well as by using the most recently developed IR techniques such as diffuse reflectance Fourier transform IR spectroscopy.[15−17]

Besides technical difficulties in obtaining IR spectra of carbon materials, their interpretation is often an additional problem because not all of the observed absorption bands may be assigned unequivocally to specific molecular motions of functional groups, most likely owing to the overlap of several bands. In other cases, it is not uncommon that some band assignments differ substantially among the recent IR studies on carbon materials. This is the case for the so-called "quinone band" that has been assigned to the 1660−1670[18] or 1550−1680 cm^{-1} interval.[17] Another controversial assignment corresponds to the band at 1600 cm^{-1}, which is a prominent feature in the IR spectra of active carbons, chars, coals, and so forth.[5−13] The 1600-cm^{-1} band has been attributed to either oxygen surface compounds or ring vibrations of the basal plane. Intriguingly, the presence and intensity of this band are strictly related to the concentration of surface oxides, but IR studies using ^{18}O-labeled carbon do not support an assignment to carbonyl-type

* Corresponding author. E-mail: miguel@incar.csic.es. Tel: +34 985 11 90 90. Fax: +34 985 29 76 62.
[†] CSIC.
[‡] Universidad de Oviedo.

10.1021/jp027482g CCC: $25.00 © 2003 American Chemical Society
Published on Web 06/10/2003

SCHEME 1



species. Thus, a widely accepted hypothesis assigns the 1600-cm^{-1} band to the C═C stretching modes of polyaromatic systems,[14] whose IR intensity would be reinforced by chemisorbed oxygen, most likely by increasing the extinction coefficient because of an increase in the dipole moment associated with these ring vibrations. However, the relationship between the nature of carbon surface oxides and the intensity of the 1600-cm^{-1} band is largely unknown.

Clearly, a more detailed assignment of the IR absorption bands of carbon materials may significantly increase our understanding of the carbon structure at the molecular level. In this work, we employed quantum chemical methods to calculate vibrational frequencies of a large set of polyaromatic model compounds to assign the vibrational motions in the 1400−1900 cm^{-1} range. We comparatively analyzed the calculated spectra of polyaromatic model compounds substituted with different oxygen functionalities (carboxyl, ketone, lactone, pyrones). Thus, we obtained valuable insight into the actual effect of conjugation on the shift of the carbonyl frequencies, the changes in the IR intensities of the C═C vibrations induced by oxygen functionalities at the edges of carbon surfaces, the cooperative effects among the functional groups in determining the location and intensity of IR bands, and so forth. From these results, we proposed some band assignments that can be helpful in the interpretation of experimental IR spectra.

Methods

All of the calculations were performed using the Gaussian 98 suite of programs.[18] The level of theory used in this work combines a density functional theory (DFT) method—the B3LYP hybrid functional corresponding to Becke's three-parameter exchange functional with the Lee−Yang−Parr gradient-corrected correlation functional[19]—with the 6-31G* basis set that is double-ζ augmented with one set of polarization functions on heavy atoms.[20] Some test calculations were made with a triple-ζ basis set including diffuse functions and more polarization functions: 6-311+G(2pd,2p).

All of the model compounds studied in this work were fully optimized in the gas phase at the B3LYP/6-31G* level. Following geometry optimizations, harmonic vibrational frequencies and dipole moment derivatives were calculated analytically. The infrared intensities were calculated from the dipole moment derivatives in the double-harmonic approximation, that is, ignoring cubic and higher force constants and omitting second and higher dipole moment derivatives.[21]

According to previous computational experience, vibrational frequencies computed at the B3LYP/6-31G* level tend to be ca. 1−4% too high because of the harmonic oscillator approximation and the incomplete treatment of electron correlation effects. Thus, many studies are done in which the B3LYP/6-31G* frequencies are multiplied by a correction factor of 0.9614 to obtain better estimates of the experimental results.[22] In this work, however, we used a different correction factor that was obtained from a least-squares fit to experimental frequencies of 1,9-anthraquinone, 1-naphthalenecarboxylic acid, and 1-8-naphthalic anhydride (see below). It has been reported that theoretical IR intensities converge toward experimental values with increasing correlation, although a large fraction of the difference between the calculated and observed intensities can be attributed to the double-harmonic approximation and to the experimental uncertainties. In general, MP2 or B3LYP methods combined with a basis set of double-ζ quality yield predict IR intensities that are qualitatively acceptable.[23] Larger basis sets (e.g., 6-311+G(3df,2p)) and more elaborate *N*-electron treatments (e.g., CCSD) are expected to give quantitative agreement with experimentally measured intensities.[24]

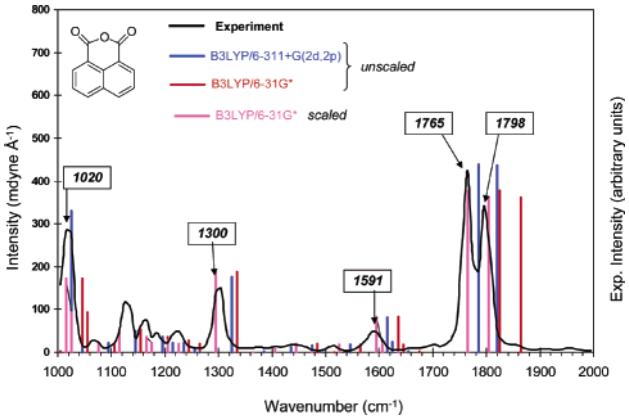


Figure 1. IR spectra of the 1,8-naphthalic anhydride. Comparison between experiment and theoretical predictions.

Results and Discussion

Assessment of the Computational Approach. We chose 1,8-naphthalic anhydride as an appropriate reference compound to illustrate the reliability of the computational methods in predicting the IR spectra of large polyaromatic systems. This tricyclic compound possess C═O, C−O, and C═C bonds whose stretching and bending motions are combined through the normal modes of the molecule. Figure 1 shows the computed spectrum of 1,8-naphthalic anhydride within the 1000−2000 cm^{-1} interval at the B3LYP/6-31G* and B3LYP/6-311+G(2d,-2p) levels of theory (stick spectra). The experimental FTIR spectrum in the gas phase is also plotted (thick line).[25]

We see in Figure 1 that the theoretical calculations reproduce fairly well the experimental spectrum of 1,8-naphthalic anhydride, whose most important peaks are located at 1798, 1765 (C═O), 1591 (C═C), and 1020−1300 cm^{-1} (C−O−C). As

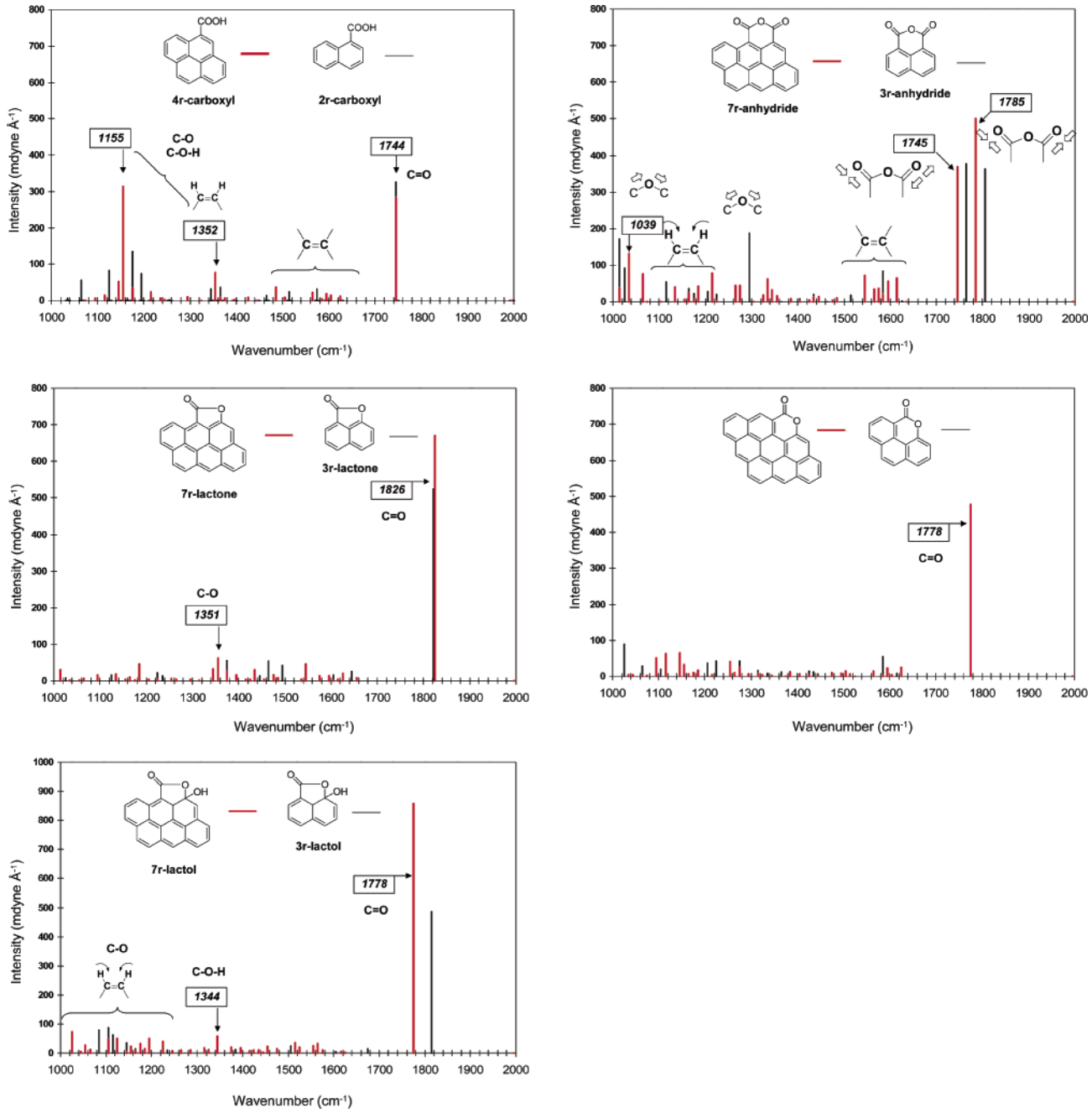


Figure 2. IR spectra of structures resembling acidic-type functional groups on carbon materials.

expected, all of the calculated wavenumbers are shifted upward (ca. 30−50 cm^{-1}, 2−3%) with respect to experimental wavenumbers because of the approximations in the computational approach. The relative intensities of the IR bands are correctly predicted, although in a semiquantitative manner. When comparing between the B3LYP/6-31G* and B3LYP/6-311+G(2d,-2p) results, it is clear that the larger basis set significantly improves the agreement between theory and experiment in terms of both the locations of the absorption bands and their relative intensities.

Unfortunately, the use of the B3LYP/6-311+G(2d,2p) level of theory was not amenable to large polyaromatic systems with 4−9 condensed rings because of computational shortcomings. Therefore, we decided to obtain a correction factor to make the B3LYP/6-31G* frequencies closer to the experimental values. To this end, we also computed the IR spectra of 1,9-anthraquinone and 1-naphthalenecarboxylic acid. These molecules, together with 1-8-naphthalic anhydride, can be considered to be small model compounds of oxidized carbon surfaces whose IR spectra are well known experimentally. The wavenumbers obtained theoretically ($\bar{\nu}_{theor}$) corresponding to the most important IR peaks of these systems were paired with the corresponding experimental values ($\bar{\nu}_{exp}$). Subsequently, the set of ($\bar{\nu}_{exp}$, $f\cdot\bar{\nu}_{theor}$) pairs were subject to a least-squares fit that gave an f value of 0.9687, the root-mean-squared deviation between the $f\cdot\bar{\nu}_{theor}$ and $\bar{\nu}_{exp}$ values being 13 cm^{-1}. This correction factor was used for the rest of the model compounds.

IR Spectra of Carboxyl, Lactone, and Anhydride Functional Groups. Figure 2 displays the theoretical spectra of polyaromatic systems bearing carboxyl, anhydride, lactone, and lactol functionalities, which are usually classified as acidic groups on carbon surfaces. For each functionality, two model compounds with a different number of carbon rings were examined. The wavenumbers signaling the most important peaks and some band assignments are also indicated in Figure 2.

The IR intensity of the C═O stretching motions results in

intense absorption peaks between 1744 and 1826 cm^{-1} for the model compounds shown in Figure 2. The relative ordering of the vibrational C═O frequencies in wavenumbers (cm^{-1}) is five-membered ring lactone (~1830) > anhydride (1810−1740) ≈ six-membered ring lactone (1790) > lactol (~1780) > carboxyl (~1750). Interestingly, the C═O stretching vibrations of the carboxyl and lactone models are not influenced by the size of the graphene platelet (Figure 2). In contrast, the corresponding wavenumbers of the lactol and anhydride models are clearly lowered (20−30 cm^{-1}) by increasing the number of carbon rings. These observations suggest that C═O vibrations of anhydride groups on carbon materials could result in a broad IR band (1740−1810 cm^{-1}) whereas the peaks due to "isolated" carboxyl and lactone groups should be sharper, more intense, and less sensitive to conjugation.

All of the model compounds in Figure 2 exhibit some IR intensity in the 1550−1600 cm^{-1} region, which is usually ascribed to vibrating C═C bonds in the aromatic rings. In effect, the animation of the harmonic oscillations confirmed that the corresponding normal modes consist of C═C stretching motions throughout the carbon skeleton. As expected, the size of the graphene platelet in the models determines the number of peaks appearing in this region. However, the relative intensity of these bands with respect to that of the carbonyl peaks is quite low, except for those of the anhydride models. This is not unexpected because the anhydride ring fused with other carbon rings favors electronic conjugation, which in turn affects the vibrations of both the carbonyl groups and carbon rings.

Other peaks appearing in the spectra shown in Figure 2 correspond to different motions of the oxygenated groups (C−O stretching, C−O−H bending, C−O−C symmetric and asymmetric stretching). Most of these bands, which are particularly active in the carboxyl and anhydride models (Figure 2), lie in the 1000−1400 cm^{-1} region. From the normal-modes analyses, we observed that these motions are accompanied by H−C═C or C═C−C bending motions. In fact, the number of peaks and their relative intensity are modulated by the number of carbon rings present in the model compounds. Therefore, we expect that acid carbon surfaces may present broad overlapping bands in this IR region, which would be difficult to assign.

IR Spectra of Phenolic Groups. Figure 3 shows the computed spectra for several polyaromatic systems whose edges are decorated with hydroxyl groups. First, we considered model compounds having two hydroxyl groups attached to separate carbon rings. The resultant IR spectra present many peaks with low intensity distributed from 1100 to 1650 cm^{-1}. Most of the peaks reflect some IR intensity of normal modes consisting of ring vibrations (~1600 cm^{-1}) and H−C═C bending motions (~1300 cm^{-1}) with simultaneous deformation of the C−O−H moieties.

The calculated spectra of **4r-phenol** and **9r-phenol** models suggest that isolated phenolic rings on carbon surfaces would not exhibit a particular imprint in the 1000−2000 cm^{-1} region. However, for oxygen-rich carbon materials, it may be reasonable that hydroxyl groups terminate the zigzag edges as in the 8r-phenol structure (see Figure 3). It is interesting that zigzag borders decorated with hydroxyl groups can be favored by the small size of the hydroxyl groups (preventing steric clashes) and the formation of intramolecular hydrogen bonds between vicinal hydroxyls. Most interestingly, we found that the zigzag arrangement of hydroxyl groups presents important cooperative effects so that IR peaks corresponding to ring vibrations and hydroxyl deformations are predicted to be quite intense (see Figure 3). The most intense peak (1590 cm^{-1}) is assigned to

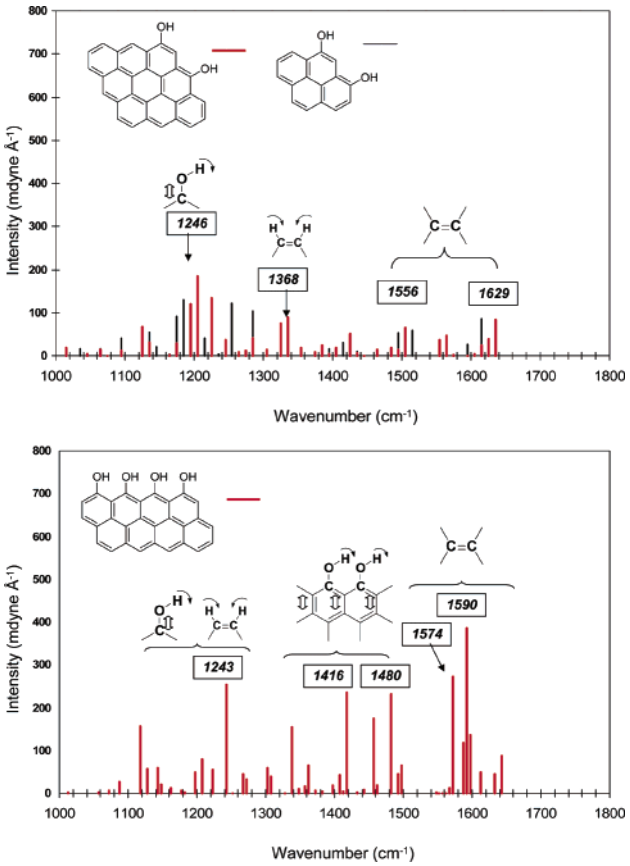


Figure 3. IR spectra of structures resembling phenolic groups on carbon materials.

carbon ring vibrations. Thus, the existence of the 1600-cm^{-1} band in carbon materials with acid character could be mainly due to the existence of phenol groups, given that the rest of the acid functionalities promote much less IR absorption in this region (Figures 2 and 3).

IR Spectra of Acidic Carbon Oxides Combined with Phenolic Groups. It is commonly thought that the edges of carbon surfaces treated with oxidizing agents (e.g., HNO_3, H_2O_2) are decorated with combinations of acid groups. Besides vicinal hydroxyl−hydroxyl contacts, other plausible combinations are carboxyl−hydroxyl, lactone−hydroxyl, and anhydride−hydroxyl pairs. We note again that these structures would be favored by the small size and hydrogen-bonding ability of the hydroxyl groups. It is well known that if carboxyl groups form hydrogen bonds with other polar groups or water molecules then the vibrational frequency of the C═O bond can decrease considerably. Thus, to take this effect into account in our calculations, we considered a series of polyaromatic systems combining phenol groups with carboxyl, anhydride, and lactone groups. The calculated IR spectra are shown in Figure 4.

The presence of close H-bond interactions between the C═O bond and hydroxyl groups exerts a large influence on their IR properties. For carboxyl−hydroxyl model **4A**, in which both the carboxyl and hydroxyl groups are coplanar with the polyaromatic system, the C═O frequency appears at 1655 cm^{-1}. This value is ~90 cm^{-1} lower than that of the carboxyl-only models as a consequence of the stronger polarization of the carbonyl bond in the $-C^{\delta+}=O^{\delta-}\cdots^{\delta+}H-O$ interaction. Moreover, the corresponding normal mode reveals that the C═O vibration is accompanied by an important C−O−H bending motion. The carboxyl group in model system **4B**, which is hydrogen bonded to two vicinal hydroxyl groups, lies nearly

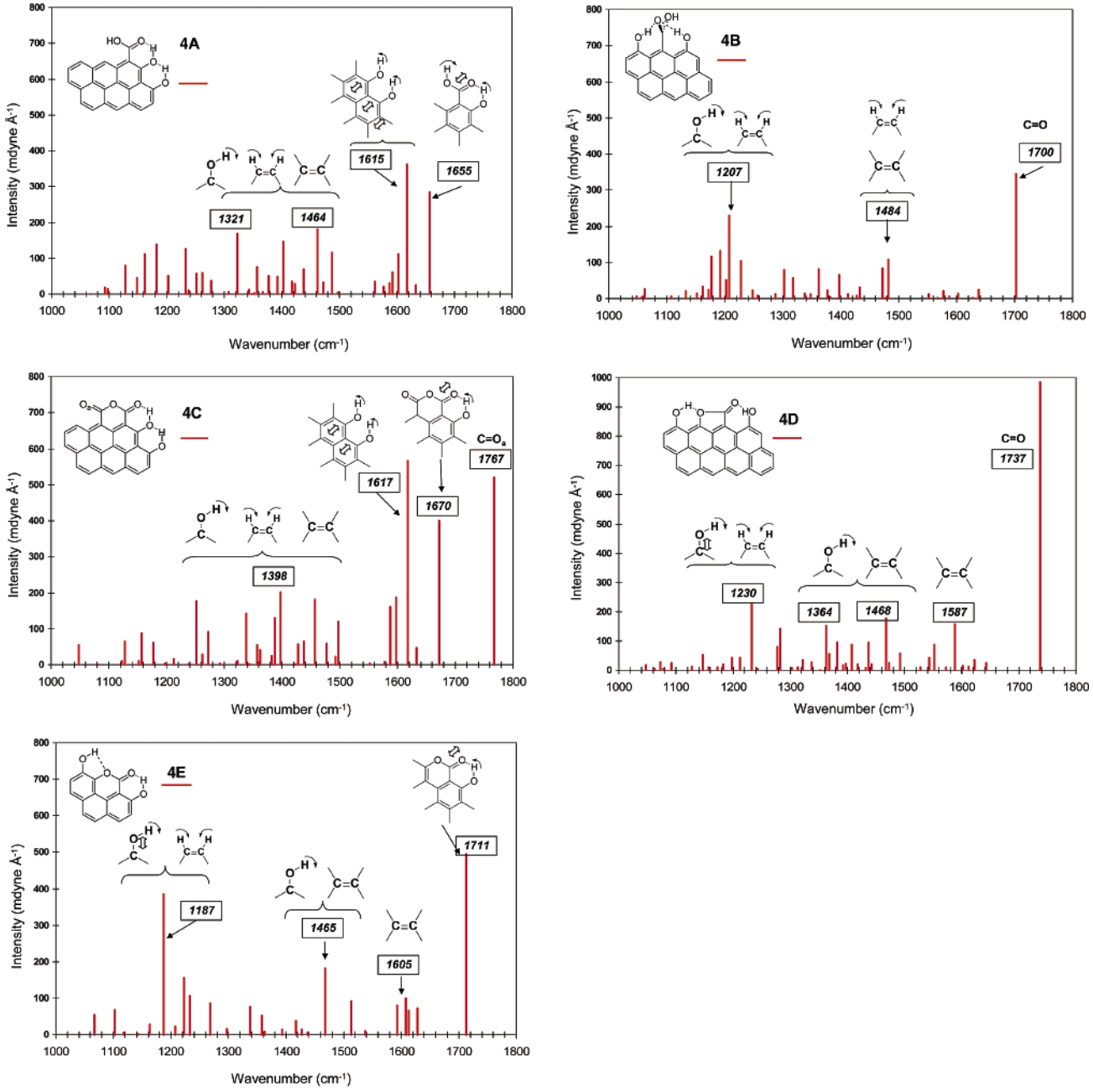


Figure 4. Cooperative effect between different acidic groups. Effect of hydrogen bonding on the frequencies of the normal modes.

perpendicular to the aromatic system. In this case, however, the C═O···H−O contacts have a weaker effect by lowering the C═O frequency by about 40 cm^{-1}. However, the anhydride−carboxyl (**4C**), the five-membered ring lactone−hydroxyl (**4D**), and the six-membered ring lactone−hydroxyl (**4E**) models result in low vibrational C═O wavenumbers of 1670−1767, 1737, and 1711 cm^{-1}, respectively (Figure 4). We note that, in the case of the anhydride−hydroxyl model, only the C═O bond that is hydrogen bonded to the vicinal OH group is affected. However, the IR intensity induced by the hydroxyl groups also responds to the presence of the carboxyl and anhydride groups. For example, the band at 1600 cm^{-1} ascribed to C═C vibrations with a simultaneous C−OH deformation is shifted upward by about 140 cm^{-1} with respect to the hydroxyl-only model (Figures 3 and 4). In the lactone−hydroxyl models, the peaks around 1600 cm^{-1} are not intense because the hydroxyl groups are not vicinal. It may also be worth noting that one carbonyl group and two vicinal hydroxyl groups are grossly similar in terms of their IR intensities.

In Figure 4, we see that the relative ordering of the vibrational C═O wavenumbers in the presence of hydrogen bond contacts is similar to that of the same groups in Figure 2, that is, five-membered ring lactone (∼1737) > six-membered ring lactone (1711) > anhydride (1770−1670) > carboxyl (∼1700−1660 cm^{-1}). However, it is also clear that the $-C^{\delta+}=O^{\delta-}\cdots{}^{\delta+}H-O$ interactions have a strong influence on the IR absorption of the C═O bonds. In fact, the polyaromatic systems in Figures 2 and 4 represent two extreme situations: "isolated" and "strongly H-bonded". In an actual carbon material, many intermediate situations could be possible depending on the amount of surface oxides and adsorbed water, the abundance of interlayer H-bond contacts, the exact positioning of the acidic groups, and so forth. A priori, the C═O bond of the carboxyl or carbonyl groups attached to carbon surfaces could give IR absorption in a very

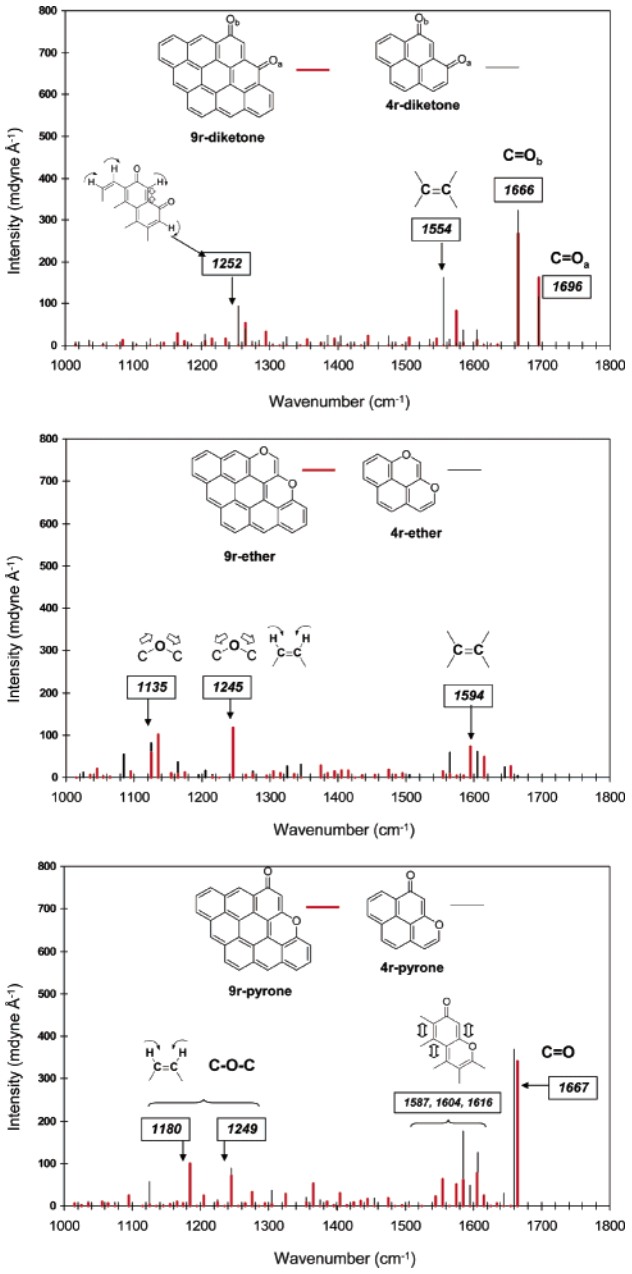
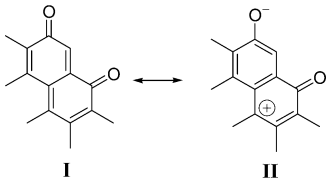


Figure 5. IR spectra of structures resembling basic-type functional groups on carbon materials.

broad range: 1650−1850 cm^{-1}. In the case of *heavily* oxidized carbons with high oxygen content, this interval should be smaller, 1650−1750 cm^{-1}, because the majority of the carbonyl groups would presumably be hydrogen bonded. In this subinterval, carboxyl groups would be characterized by strong absorption at low wavenumbers (∼1660) whereas lactone heterocycles would appear above ∼1710 cm^{-1}, although some overlap between lactone and carboxyl bands could be possible. The vibrational C═O wavenumbers of anhydrides would be dispersed throughout the whole interval.

IR Spectra of Basic Surface Oxides. The nature and relative abundance of surface oxides on carbon surfaces with basic character are still unanswered questions. As mentioned in the Introduction, it is thought that basic oxides may correspond to cyclic ketones (quinone groups) characterized by endocyclic carbonyl groups.[1,26] Other authors have pointed out that pyrones, which formally result from the combination of carbonyl and ether oxygen atoms located in different rings, can play an important role as basic sites.[27] Very recently, we have proposed

SCHEME 2



that a mixture of carbonyl (O) and cyclic ether (sp^3 O) groups populating the edges of basic carbon surfaces (i.e., pyrones) would be favored thermodynamically.[28]

As the first step in our study of the IR spectra of basic oxides, we considered diketone, pyrone, and cyclic ether structures in which the two O atoms are situated in adjacent carbon rings (Figure 5). In the calculated IR spectra for the diketone structures, there are two peaks corresponding to carbonyl vibrations that appear at low wavenumbers, 1666 and 1696 cm^{-1}. Similarly, the pyrone structures show a sharp peak at 1665 cm^{-1} that is ascribed to C═O stretching. The lowering of the C═O frequency with respect to that of the "isolated" acid groups (>1740 cm^{-1}) is well understood in terms of electronic conjugation between the endocyclic carbonyl groups and the adjacent C═C bonds, which can be represented by resonant phenolic forms (Scheme 2).

We see in Figure 5 that carbon rings in the basic model compounds are second to carbonyl groups in IR intensity. Thus, the intensity of the ring vibrational peaks within the 1550−1659 cm^{-1} region is ∼$^1/_5$ or $^1/_2$ times that of the carbonyl groups (Figure 5). These results suggest that either carbonyl groups or sp^3 O atoms linked to sp^2 C atoms can promote the IR absorption by skeletal vibrations of the carbon rings as phenol groups do. Animation of the corresponding normal modes confirms that conjugated C═C bonds vibrate throughout the carbon skeleton, although the C═O and C−O bonds are not involved.

The most intense C═C peaks in the diketone structures are located at 1554 and 1572 cm^{-1} for the medium and large models, respectively. These numbers are shifted downward with respect to the characteristic C−C frequency of aromatic compounds (1590−1600 cm^{-1}), which can be rationalized in terms of resonant structure II in Scheme 2 in which a positive charge is delocalized throughout the π system. However, the presence of sp^3 O atoms in the −C═C−O−C═C− moiety decreases the extent of C═C conjugation with respect to that of the diketone compounds. Consequently, the active C═C normal modes of the pyrone-like compounds tend to peak at higher wavenumbers (1587−1616 cm^{-1}), as observed computationally.

To characterize the nature of the 1600-cm^{-1} band further, we also computed the IR spectra of model systems **9r-ether** and **4r-ether**, which contain two etheric rings (Figure 5). Besides several peaks due to ring vibrations (∼1590 cm^{-1}), **9r-ether** and **4r-ether** present well-defined peaks corresponding to deformations of the C−O−C moieties concomitant with H−C═C bending motions. When we compare between ether and pyrone spectra, we find that the absence of the endocyclic carbonyl groups affects the location and intensity of the C═C peaks only moderately, thus emphasizing the role played by the sp^3 O atoms in increasing the IR absorption around 1600 cm^{-1}.

Besides considering polyaromatic compounds with two heterocycles (i.e., ketone or ether rings), it is clear that other possible combinations of etheric and/or ketone rings can exist on the surface of carbon materials with basic character. We considered three limiting situations: a polyaromatic system with

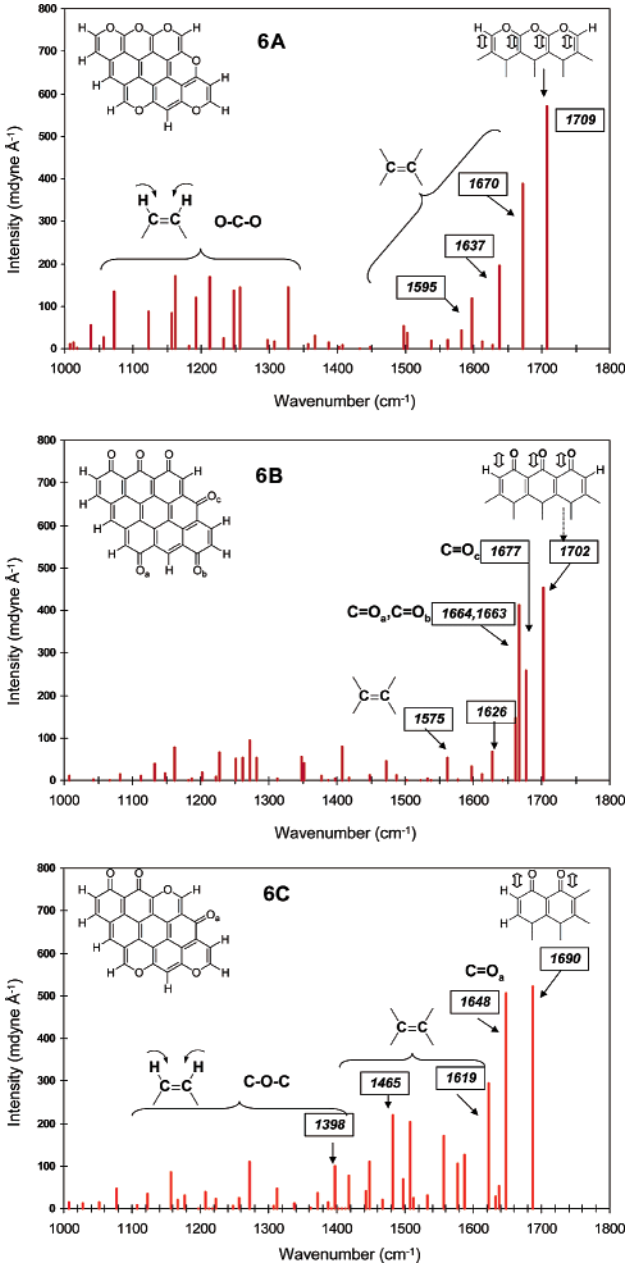
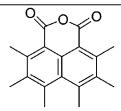
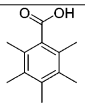
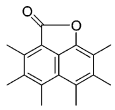


Figure 6. IR spectra of structures with different sp^3 O/sp^2 O rates decorating the graphene edges.

only ether rings (**A** in Figure 6), an analogous carbon skeleton in which carbonyl groups replace the sp^3 O atoms (**B** in Figure 6), and a mixed system (**C** in Figure 6) in which both ketone and ether rings coexist. The most realistic system should correspond to **6C**, given that mixing carbonyl and ether groups is thermodynamically favorable.[28] We note, however, that an exhaustive treatment of other realistic systems involving more carbon rings or with different sp^3 O/sp^2 O rates would be computationally costly.

The IR spectrum of model **6A** (all sp^3 O) shows two well-defined regions that reflect the IR intensity of the carbon skeleton ($\tilde{\nu}$ > 1595 cm^{-1}) and that of the H−C═C bending/C−O−C stretching motions ($\tilde{\nu}$ < 1350 cm^{-1}). The most striking observation is that C═C vibrations give rise to a series of peaks located at high wavenumbers between 1595 and 1709 cm^{-1}. The most intense peak is the one located at the highest wavenumber (1709 cm^{-1}), which is due to the symmetric stretching of C═C bonds linked to the three O atoms at the zigzag edge (Figure 6). These results reveal that the disruption of aromatic conjugation by the ether rings combined with the polarization of the C═C bonds attached directly to the sp^3 O atoms can promote strong IR absorption around 1700 cm^{-1} that could overlap with typical carbonyl bands.

TABLE 1: Structure of Simple Carbon Surface Oxides and Their Corresponding IR Assignments in the 1400−1900 cm^{-1} Region According to B3LYP/6-31G* Calculations on Polyaromatic Systems

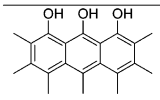
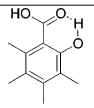
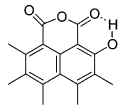
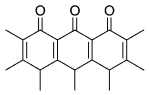
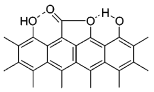
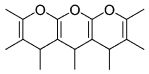
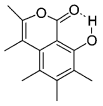
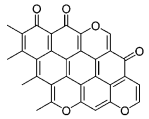
Structure	Assignment regions (cm^{-1})	Structure	Assignment region (cm^{-1})
 anhydride	1740-1760 (C=O, symmetric) 1780-1810 (C=O, antisymmetric)	 carboxyl	1740-1750 (C=O)
 5-membered ring lactone	~1820 (C=O)	cyclic ketones	1650-1700 (C=O) 1550-1600 (C rings)
5-membered ring lactone	~1790 (C=O)	cyclic ethers	1580-1620 (C rings)

The spectrum of model **6B**, which has six carbonyl groups, is dominated by the intense peaks corresponding to C═O vibrations. Quite remarkably, the rest of peaks in the spectrum including those due to ring vibrations are much less intense. As in the case of the bicyclic ketone and pyrone, the carbonyl peaks appear at relatively low wavenumbers between 1658 and 1701 cm^{-1}. The peak at 1701 cm^{-1} implies a symmetric stretching motion of the three C═O bonds placed consecutively at the zigzag edge whereas the peak at 1658 cm^{-1} results from the two cyclic ketone rings separated by an aromatic carbon ring (Figure 6). On the basis of these results, we predict that C═O absorption by a ketone-rich carbon surface would result in a broad band around 1700 cm^{-1} whose shape would depend on the exact distribution of carbonyl groups.

The spectrum of model **6C**, in which three ether rings and three ketone rings coexist, is quite complex. Two peaks, 1690 and 1648 cm^{-1}, can be assigned to the carbonyl groups (Figure 5). However, there is a peak due to carbon ring vibrations that is only 30 cm^{-1} below the C═O 1648-cm^{-1} signal. In fact, many peaks due to carbon ring vibrations are distributed along a wide interval from 1460 to 1629 cm^{-1}, thus reflecting the influence of two opposite effects—the C═C−C═O conjugation and the disruption of −C═C−C═C− conjugation by the sp^3 O atoms. On the basis of these computational results and the assumption that surfaces of basic carbon materials exhibit many possible combinations of pyrone-like structures, the IR spectra of basic carbons should exhibit two close, broad bands in the 1400−1750 cm^{-1} region. Some overlapping between carbon ring bands and carbonyl bands could be possible.

Infrared Assignments for the Principal Functional Groups on Carbon Surfaces. Tables 1 and 2 summarize the assignments for "simple" and "complex" carbon surface oxides, respectively. It is worth noting again that all data in Tables 1 and 2 were generated in a consistent manner by considering a large set of polyaromatic systems that are mainly relevant to the actual structure of carbon surfaces. We focus on the IR intensity in 1400−1900 cm^{-1} region, which results mainly from absorption involving carbonyl vibrations and carbon ring vibrations

TABLE 2: Structure of Complex Carbon Surface Oxides and Their Corresponding IR Assignments in the 1400−1900 cm^{-1} Region According to B3LYP/6-31G* Calculations on Polyaromatic Systems

Structure	Assignment regions (cm^{-1})	Structure	Assignment region (cm^{-1})
 zigzag phenol groups	~1590 (C rings) 1420-1480 (C-O-H and C=C deformation)	 carboxyl	~1660 (C=O)
 anhydride	1670-1770 (C=O)	 cyclic ketones (zigzag)	1690-1710 (C=O)
 5-membered ring lactone	~1740 (C=O)	 cyclic ethers (zigzag)	1600-1700 (C=C and C rings)
 6-membered ring lactone	~1710 (C=O)	 ketone and ether rings (pyrones)	1660-1700 (C=O) 1450-1640 (C rings)

throughout the polyaromatic systems. Assignments below 1400 cm^{-1} are rather problematic because motions of the H−C═C, C−O−C, and C−O−H moieties result in many peaks that are widely distributed along the 1000−1400 cm^{-1} region.

In Table 1, we propose IR assignments for "simple" carbon surface oxides (i.e., non-hydrogen-bonded to polar groups), which could be relevant to dry carbon surfaces with very low oxygen content. In general, the carbonyl groups of the different surface oxides have well-defined assignment regions that do not overlap with each other. These results also show that endocylic carbonyl groups in six-membered rings (e.g., anhydrides, cyclic ketones) as well as sp^3 O atoms inserted into carbon rings can promote IR absorption because of carbon ring vibrations. However, the utility of the data in Table 1 will not be large because IR spectra of carbon with low oxygen content are very difficult to obtain because of current experimental limitations.

In Table 2, we summarize the IR assignments obtained from complex surface oxides in which two functionalities are combined (e.g., acid and hydroxyl, cyclic ketone and ether, etc.). The polyaromatic systems bearing these groups are mainly relevant to oxygen-rich carbon surfaces. With respect to the spectral features of the isolated surface oxides, the spectra of the complex ones turn out to be mainly determined by hydrogen bonding and cooperative effects. This results in a large dispersion of the vibrational C═O wavenumbers. Either acidic or basic groups give C═O absorption in the 1660−1700 cm^{-1} region, except lactones, which appear at wavenumbers >1740 cm^{-1}. For the basic groups, the spectral features of the carbonyl groups in cyclic ketones and the C═C bonds of the aromatic rings are interrelated. Most interestingly, the IR intensity of the carbon rings is greatly reinforced by vicinal hydroxyl groups (phenols) and fused cyclic ethers, thus becoming comparable to that of the carbonyl groups. This observation should help to dispel the rather enigmatic character of the 1600-cm^{-1} band typical of carbon materials.

TABLE 3: Previous Tentative Assignments in the 1400−1900 cm^{-1} Region as Collected in Fanning et al.[17]

group or functionality	assignment regions (cm^{-1})
carboxylic acids	1665−1760
lactones	1675−1790
anhydrides	1740−1880
aromatic C═C stretching	1585−1600
quinones	1550−1680

Let us comparatively discuss the theoretical proposals and previous IR assignments that were collected by Fanning et al. on the basis of IR bands of small model compounds and expectations of the types of functional groups present on carbon materials.[17] For carboxyl groups, the lowest and highest theoretical C═O wavenumbers are in satisfactory agreement with previous tentative IR assignments (1665−1760 cm^{-1}). However, assignments of anhydride and lactone groups in Tables 1 and 2 differ from those adopted experimentally. These discrepancies could be explained in part by the different nature of the model compounds on which they are based. (Some previous IR assignments considered typical small organic compounds as reference systems.) For the aromatic C═C stretching, as mentioned in Table 3, our calculations reproduce the assignment region quite well and, most importantly, give new and valuable insight into the origin of this band. Thus, the 1600-cm^{-1} band is mainly linked to the presence of vicinal hydroxyl groups on acidic carbon surfaces and to pyrone groups in basic carbons. However, polycyclic conjugated ketones such as those in Figure 5 could be IR-active in the 1660−1700 cm^{-1} region whereas quinones, as mentioned in Table 3, are ascribed to a much wider region, 1550−1680 cm^{-1}.

The case of phenolic groups is particularly interesting. It is well known that these groups give IR bands in the 1000−1200 cm^{-1} region that are due to C−O stretching and C−O−H bending motions. Interestingly, our calculations show that strong cooperative effects can influence the IR intensity of hydroxyl groups terminating the zigzag edges of carbon materials. Besides promoting the IR absorption by carbon ring vibrations around 1600 cm^{-1}, we found that C−O−H deformation with simultaneous carbon ring vibrations also results in strong IR absorption in the 1420−1480 cm^{-1} region. In some experimental reports, a band at 1460 cm^{-1} that is typical of oxidized carbons has been attributed to O−H deformation in carboxyl groups. The same experimental spectra also show a pronounced band around 1600 cm^{-1}. According to our findings, both bands in oxidized carbons can be ascribed to the presence of phenolic groups.

Interpretation of Experimental IR Spectra On the Basis of the Theoretical Assignments. To find out if our theoretical results are consistent with the basic spectral features of carbon materials in the 1400−1900 cm^{-1} region, we analyzed the IR spectra of a series of activated carbons previously investigated by Moreno-Castilla et al.[13] These authors further characterized the activated carbons by other techniques such as temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), measurements of the pH at the point of zero charge (pH_{PZC}), and so forth. Figure 7 reproduces the FTIR spectra for one basic activated carbon (BV29) and three acidic carbons that were derived from BV29 after aqueous oxidation with H_2O_2 (BV29H), HNO_3 (BV29N), and $(NH_4)S_2O_8$ (BV29S). The total oxygen content ($[O]_T$) and the pH_{PZC} values for the different activated carbons are also indicated in Figure 7.

Sample BV29 contains only basic sites on its surface. Its oxygen content is low—only 0.9 wt %. Accordingly, the intensity

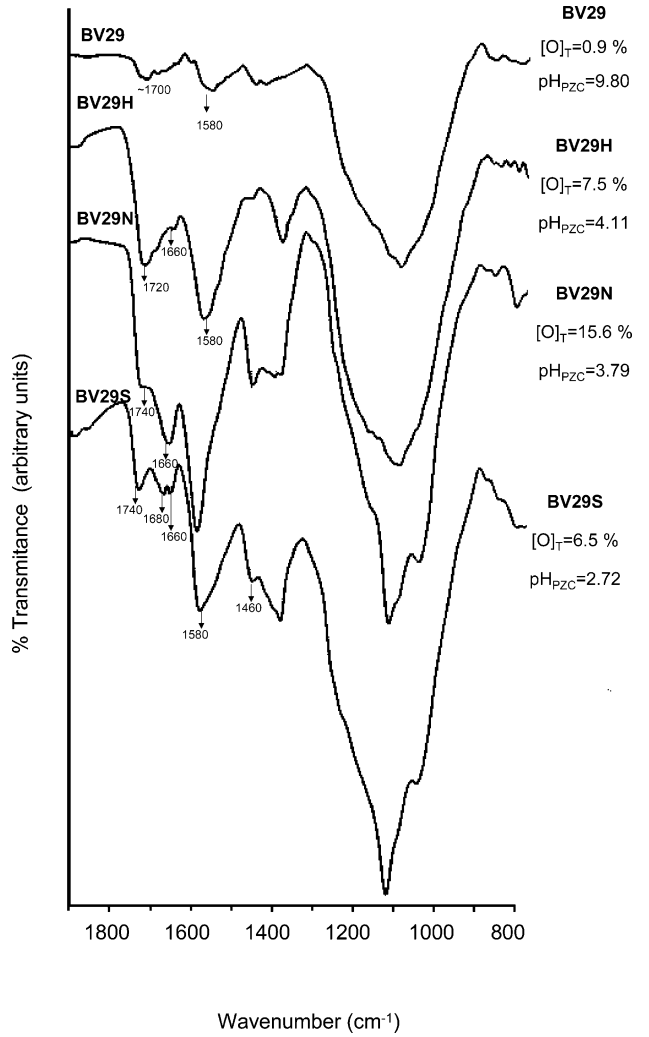


Figure 7. FTIR spectra of several activated carbons (reproduced partially from ref 13).

of the IR absorption bands in the 1400−1900 cm^{-1} region is low. Nevertheless, two broad bands of similar intensity centered at 1700 and 1580 cm^{-1} are clearly present. On the basis of our theoretical results, this spectrum should be assigned to polyaromatic systems in which both cyclic ketone and cyclic ether rings coexist on the carbon surface (model **C** of Figure 6). On one hand, the possible arrangements of cyclic ketone rings would result in C═O wavenumbers starting at 1660 cm^{-1} up to 1710 cm^{-1} or higher. On the other hand, the carbon ring vibrations become IR-active because of the presence of cyclic ether rings, thus explaining the IR absorption around 1600 cm^{-1}. It must be noted, however, that in this relatively complex picture simple functional groups cannot be distinguished, except perhaps pyrone-like structures of varying topology. We also note that this assignment is consistent with the notable basic strength of pyrones[28] and the observed basic character of the BV29 carbon in aqueous solution (pH_{PZC} = 9.80).

The total oxygen content of the active carbons rises to 6.5−15% upon oxidation treatment with different reagents. As expected, the oxidized samples show more pronounced bands than the original basic carbon. The bands corresponding to the carbonyl groups now show well-defined peaks and shoulders within the 1660−1740 cm^{-1} interval. Moreno-Castilla et al. assigned these peaks to lactone groups or nonaromatic carboxyls (1740−1720 cm^{-1}), aromatic carboxyls (1680−1700 cm^{-1}), and conjugated ketones (1660 cm^{-1}).[13] Therefore, we concur with former suggestions that lactone and carboxyl groups are responsible for these peaks. However, we interpret these peaks and shoulders in terms of binary functionalities, that is, carboxyl and phenol groups and lactone and phenol groups.

On the basis of the calculated spectra for the polyaromatic systems in Figure 4, carboxyl groups that are hydrogen bonded with vicinal hydroxyls would be identified by vibrational C═O wavenumbers as low as 1660 cm^{-1} whereas the carbonyl group of lactones interacting with hydroxyls would absorb above 1710 cm^{-1}. From these band assignments and the shape of the IR bands in Figure 7, it is clear that all of the oxidized carbons present both lactones and carboxyls that are bound to other polar groups (probably hydroxyl groups) via hydrogen bond contacts. Some qualitative preferences in the nature of the carbonyl groups can be outlined. Thus, sample BV29H, which has a maximum C═O absorption at 1720 cm^{-1} and a less intense peak at 1660 cm^{-1}, seems richer in lactone groups than in carboxyls after treatment with a mild oxidizing agent (i.e., H_2O_2). The IR spectrum of sample BV29N has only a well-defined C═O peak at 1660 cm^{-1} that can be assigned to carboxyl groups, that is, treatment with a strong oxidizing acid (HNO_3) leads preferentially to carboxyl groups. (This is not unexpected because the hydrolysis of ester and anhydride functionalities would be catalyzed by excess protons.) For the BV29S carbon, the triplet of IR peaks at 1740, 1680, and 1660 cm^{-1} with similar intensity suggests that oxidation with $(NH_4)S_2O_8$ equally favors the appearance of anhydride and carboxyl groups.

The band at about 1580 cm^{-1} appears in the originally basic sample and in the oxidized carbons. For the oxidized samples, this band is even more intense than the carbonyl band. In their study, Moreno-Castilla et al. point out that the 1580-cm^{-1} band does not admit an unequivocal interpretation, although they favor the hypothesis that C═C stretching that is highly conjugated to carbonyl groups explains it.[13] Here, we ascribe this band in the acidic carbons to the presence of vicinal hydroxyl groups, which in turn efficiently induce the IR absorption by carbon ring vibrations. Moreover, we found that this cooperative effect induces IR intensity not only at ∼1600 cm^{-1} but also in the 1380−1480 cm^{-1} region (Figure 4). In effect, the three oxidized carbons show absorption peaks in this region (Figure 7).

In summary, our interpretation of the IR spectra of activated carbons in the 1400−1900 cm^{-1} region puts emphasis on the role played by cooperative effects and the close contacts between acidic groups via hydrogen bonds. Although the IR bands of these carbon materials cannot be assigned to simple motions of individual functional groups, some useful structure−activity relationships such as the close link between carbon ring vibrations and phenol groups and the presence of pyrone-like structures in basic carbons emerge from our calculations.

Acknowledgment. This work was supported by the PRI (Asturias, Spain), project PB-EXP01-04. We are grateful to the CSIC (Spain) for a generous allocation of computer time in the CTI, CESGA, and CIEMAT.

Supporting Information Available: XYZ files containing the B3LYP/6-31G* optimized geometries and selected normal-mode displacements for the most important structures considered in this work. Normal-mode motions can be visualized using Chemscape Chime software (http://www.mdli.com/support/chime). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) León y León, C. A.; Radovic, L. R. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1994; Vol. 24, p 213.

(2) Radovic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla, J. In *Chemistry and Physics of Carbon*; Radovic, L. R., Ed.; Marcel Dekker: New York, 2001; Vol. 27, p 227.

(3) (a) Donnet, J.-B.; Wang, T. K.; Peng, J. C. M.; Rebouillat, S. *Carbon Fibers*; Marcel Dekker: New York, 1998. (b) Peebles, L. H. *Carbon Fibers*; CRC Press: Boca Raton, FL, 1995.

(4) Radovic, L. R.; Rodríguez-Reinoso F. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1997; Vol. 25, p 243.

(5) (a) de la Puente, G.; Iglesias, M. J.; Fuente, E.; Pis, J. J. *J. Anal. Appl. Pyrolysis* **1998**, *47*, 33. (b) Iglesias, M. J.; de la Puente, G.; Fuente, E.; Pis, J. J. *Vib. Spectrosc.* **1998**, *17*, 41.

(6) Rositani, F.; Antonucci, P. L.; Minutoli, M.; Giordano, N.; Villari, A. *Carbon* **1987**, *25*, 325.

(7) Starsinic, M.; Taylor, R. L.; Walter, P. L., Jr.; Painter, P. C. *Carbon* **1983**, *21*, 69.

(8) Zhuang, Q.-L.; Kyotani, T.; Tomita, A. *Energy Fuels* **1994**, *8*, 714.

(9) (a) Zawadzki, J. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1989; Vol. 21, p 147. (b) *Carbon* **1978**, *16*, 491. (c) *Carbon* **1981**, *19*, 19.

(10) Ishizaki, C.; Marti, I. *Carbon* **1981**, *19*, 409.

(11) Biniak, S.; Szymanski, G.; Siedlewski, J.; Swiatkowski, A. *Carbon* **1997**, *35*, 1799.

(12) Dandekar, A.; Baker, R. T. K.; Vannice, M. A. *Carbon* **1998**, *36*, 1821.

(13) Moreno-Castilla, C.; López-Ramón, N. V.; Carrasco-Marín, F. *Carbon* **2000**, *38*, 1995.

(14) Socrates, G. *Infrared Characteristic Group Frequencies*, 2nd ed.; Wiley & Sons: Chichester, England, 1994.

(15) Yang, C. Q.; Simms, J. R. *Fuel* **1995**, *74*, 543.

(16) Sellitti, C.; Koening, J. L.; Ishida, H. *Carbon* **1990**, *28*, 221.

(17) Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Becke, A. D. *Exchange-Correlation Approximation in Density-Functional Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.

(20) Herhe, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(21) McHale, J. L. *Molecular Spectroscopy*; Prentince-Hall: New York, 1998.

(22) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(23) Halls, M. D.; Schlegel, H. B. *J. Chem. Phys.* **1998**, *109*, 10587.

(24) Schaeffer, H. F.; Thomas, J. R.; Yamaguchi, Y.; DeLeeuw, B. J.; Vacek, G. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 3.

(25) *NIST Standard Reference Database*, release 69; http://webbook.nist.gov/chemistry, 2001.

(26) Contescu, A.; Vass, M.; Contescu, C.; Putyera, K.; Schwarz, J. A. *Carbon* **1998**, *36*, 247.

(27) (a) Boehm, H. P. *Carbon* **2002**, *40*, 145. (b) *Carbon* **1994**, *32*, 759. (c) Voll, M.; Boehm, H. P. *Carbon* **1971**, *9*, 481.

(28) Fuente, E.; Menéndez, J. A.; Suárez, D.; Montes-Morán, M. A. *Langmuir* **2003**, *19*, 3505.