Electronic Structure and Chemical Reactivity of Carbon Nanotubes: A Chemist's View

Ernesto Joselevich*[a]

A qualitative description of the electronic structure of single-wall carbon nanotubes from a chemical perspective is presented using real-space orbital representations and traditional concepts of aromaticity, orbital symmetry and frontier orbitals. This unusual view of carbon nanotubes allows us to merge the solid-state physics description of band structures with the molecular orbitals framework of reaction mechanisms used in organic chemistry and to predict intriguing chemical selectivity based on electronic structure.

Introduction

One of the difficulties in rationalizing the *chemical* properties of single-wall carbon nanotubes in terms of their electronic structure is that the latter is usually described in the framework of solid-state physics,[1] by using band structure representations in reciprocal space. Although extremely useful for the description of *physical* properties, these diagrams cannot be easily used to visualize the molecular orbitals involved in the mechanism of a chemical reaction, as usually done in advanced organic chemistry.[2] Moreover, the solid-state physics perspective does not exploit a few concepts of chemistry that have been extremely useful in describing the chemical stability and reactivity of many molecules, such as aromaticity,[3] orbital symmetry and Woodward–Hoffmann rules,[4,5] and frontier orbitals.[6] This Concept proposes a qualitative description of the electronic structure of carbon nanotubes from a chemical perspective and predicts interesting chemical selectivity based on electronic structure.

Our discussion is meant to be accessible to any chemist, even if not familiar with solid-state physics. In such a case, one can safely skim through the reciprocal-space representations and continue with the real-space molecular orbitals.

Motivation, Experimental Observations, and Theoretical Models

Single-wall carbon nanotubes have unique mechanical and electronic properties, which make them promising building blocks for molecular electronics.[7] A major critical issue toward their widespread application in nanotechnology is the control of their electronic properties, which can be metallic or semiconducting in their pristine form, depending on their diameter and chirality.[8–12] Since all preparative methods yield mixtures of "metallic" and semiconducting nanotubes, of different diameters and chiralities, extensive research has been devoted to the modification of electronic structure and the separation between the different electronic types by both physical and chemical processes.[13–17] The latter requires finding a suitable chemical process that is selective for metallic versus semiconducting carbon nanotubes. Understanding the interplay between electronic structure and chemical reactivity is thus critical.

A few recent reports describe some degree of metallic/semiconducting selectivity toward the noncovalent adsorption of surfactants and single-stranded DNA.[16,17] The effect of electronic structure on a covalent functionalization of single-walled carbon nanotubes was recently reported by Strano et al.[18] The nanotubes reacted with diazonium reagents, which led to addition of aryl groups to the nanotube side-wall. The reaction was highly selective for metallic nanotubes, leaving the semiconducting ones nearly intact, and the reactivity of the metallic nanotubes was inversely related to their diameter.

Previous observations and discussions on the chemical reactivity of carbon nanotubes had attributed a major role to curvature-induced local strain, which arises from pyramidalization of the sp^2-hybridized carbon atoms and misalignment of π-orbitals.[19,20] The diameter selectivity found by Strano et al. can be correctly predicted by this formalism. However, the metallic/semiconducting selectivity underscores the role of the electronic band structure in determining the chemical reactivity of the single-wall carbon nanotubes. To account for this selectivity, a reaction mechanism was proposed whereby the diazonium reagent forms a charge-transfer complex at the nanotube surface. Electron donation stabilizes the transition state that leads to the decomposition of the diazonium functionality and the covalent attachment of the aryl group to the nanotube. The extent of electron donation correlates with the density of states at the Fermi level, which is larger for metallic nanotubes.

The strength of the pyramidalization picture is that it presents a chemical view of the electronic structure of carbon nanotubes, which fits into the molecular orbitals description of organic reaction mechanisms. However, it only regards the *localized* electronic structure of carbon nanotubes, without including in the same molecular orbitals picture the rich and

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[a] *Dr. E. Joselevich*
Department of Materials and Interfaces
Weizmann Institute of Science, Rehovot 76100 (Israel)
Fax: (+972) 8-9342350
E-mail: ernesto.joselevich@weizmann.ac.il

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unique *delocalized* electronic band structure of carbon nanotubes.

The present view, on the contrary, focuses mainly on the relationship between the band structure and chemical properties of single-wall carbon nanotubes. For simplicity, we will ignore curvature effects and the localized electronic structure, even though they are important too, and analyze the π system, adopting the assumptions of the Hückel model. Our chemist's view of the band structure of single-wall carbon nanotubes follows several ideas from Roald Hoffmann's description of bonding in extended structures.[21–23]

We shall start by using the solid-state physics picture to show the effect of dimensionality on the electronic structure of various conjugated systems and compare the electronic structures of carbon nanotubes with those of well-known organic molecules. Then, we will use a real-space molecular-orbitals representation to explain, in a chemical language, why and when carbon nanotubes are metallic or semiconducting. Finally, we shall combine these ideas in a frontier orbital perspective that could explain some of the recent experimental findings and predict other possible electronic-structure selective chemical processes.

Aromaticity, HOMO, and LUMO

The concepts of aromaticity, highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) are of fundamental importance in understanding the chemical stability and reactivity of many organic molecules. Carbon nanotubes can be regarded as quasi-1D cylindrical aromatic macromolecules.[19] Indeed, both metallic and semiconducting carbon nanotubes have positive resonance energies, although "metallic" nanotubes are slightly less aromatic than semiconducting ones.[24] This aromaticity confers onto both types of nanotubes a relatively similar *thermodynamic* stability. However, the *kinetic* stability (i.e. the opposite of chemical reactivity) of polycyclic aromatic systems is usually more related to their HOMO–LUMO energy gap[25] than to their resonance energy.

The effect of geometric structure of carbon nanotubes on their electronic structure and chemical reactivity can be intuitively appreciated by an illustrative analogy between the imaginary process of rolling up a polyacetylene to form annulenes[21–23] and the roll-up of graphene to form single-walled carbon nanotubes.[26] This will lead us to the interesting conclusion that semiconducting nanotubes are analogous to [4*n*+2]annulenes, which are usually considered *aromatic* by the Hückel rule, whereas metallic nanotubes are analogous to [4*n*]annulenes, which are often considered *antiaromatic* by the Hückel rule, even though only small ones, such as cyclobutadiene, have negative resonance energies.[27]

Figure 1 represents four kinds of π-conjugated systems of different dimensionalities. Polyacetylene (a) is a 1D system, which can be rolled up to form a series of annulenes (b), each being a quasi-0D system. Graphene (c) is a 2D system, which can be rolled up to from a series of single-walled carbon nanotubes, each being a quasi-1D system.

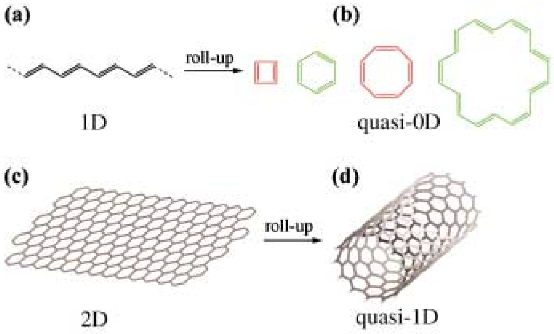

Figure 1. *Four π-conjugated systems of different dimensionalities: (a) polyacetylene; (b) annulenes (cyclobutadiene, benzene, cyclooctatetraene, [18]annulene, etc.); (c) graphene; (d) single-walled carbon nanotubes. Classical aromatic and antiaromatic structures are painted green and red, respectively.*

Figure 2a shows the band structure of an idealized (undistorted) polyacetylene, using a Hückel model. It is a metal because it has a quasi-continuum of allowed states crossing the Fermi level (in reality, this structure is unstable, and undergoes a Peierls distortion that opens a gap at the Fermi level, so that polyacetylene is actually semiconducting). Figure 2d shows the corresponding density of states of the undistorted polyacetylene. Rolling up the polyacetylene chain to form an annulene imposes on the system a periodic boundary condition, $C_h k = 2\pi q$, where C_h is the circumference of the annulene, k is the 1D wavevector, and q is an integer number. This condition leads to a quantization of k, which can only adopt discrete values, represented by the yellow lines in Figure 2b–c. The al-

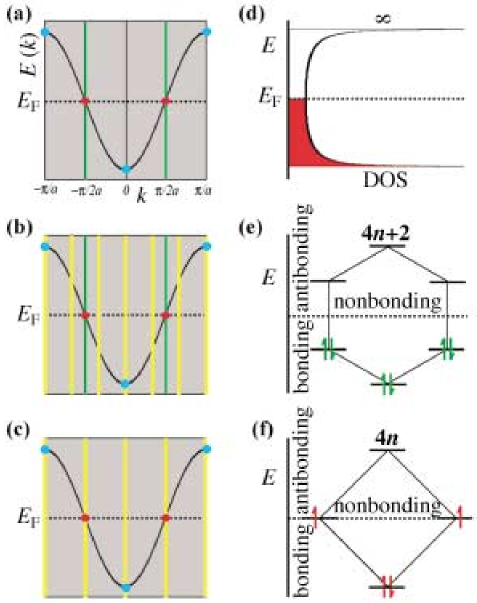

Figure 2. *Band structures (left) and electronic densities of states (right) of: (a, d) polyacetylene; (b, e) [4n+2]annulenes (e.g., benzene); (c, f) [4n]annulenes (e.g., cyclobutadiene). Blue dots denote energy maxima and minima; red dots indicate Fermi level. The yellow lines indicate the allowed wave vectors after roll-up of the polyacetylene chain.*

lowed k values are separated by the inverse of the annulene radius. If the number of carbon atoms is $4n$ (Figure 2c), where $n=q$, then the nonbonding orbitals remaining from the Fermi level are allowed. But if the number of carbon atoms is $4n+2$ (Figure 2b), then the nonbonding orbitals are not allowed. The corresponding energy diagrams are shown in Figure 2e and 2f.

Figure 3 is analogous to Figure 2, but with one additional dimension. Figure 3a shows the band structure of graphene,[28] calculated by the tight-binding method,[29] which is analogous to the Hückel method. Figure 3d displays the corresponding density of states. Rolling up the graphene sheet to form a nanotube imposes on the system a periodic boundary, given by $\mathbf{C_h}.\mathbf{k}=2\pi q$, where $\mathbf{C_h}$ is the roll-up vector (see below, Figure 5), which becomes the circumference of the nanotube, and q is an integer number. This condition leads to a quantization of $\mathbf{k}$, which forms a series of subbands, represented by the yellow lines in Figure 3b and 3c. The allowed subbands are separated by the inverse of the nanotube radius. If the (n,m) crystallographic indices of the nanotubes are such that $n-m=3q$, then the electronic states at the Fermi level are allowed and the nanotubes are metallic, but if $n-m=3q\pm1$, then there is a gap of forbidden states at the Fermi level, and the nanotube is semiconducting. The corresponding densities of state are shown in Figures 3e and 3f. The density of states of graphene, Figure 3d, is relatively dull because there are no energy minima or maxima inside each band, except for the saddle points **M**, which give rise to one spike on each band. However, Figures 3b and 3c show that in the nanotubes there is at least one point of energy minimum along each subband. Around each of these points there are many states with similar energy; therefore, the density of states goes to infinity. This gives rise to the spikes, called van Hove singularities, in the density of states (Figures 3e and 3f). Effectively, the HOMO and LUMO of semiconducting carbon nanotubes correspond to the first van Hove singularities in the valence and conduction bands, respectively, whereas the HOMO and LUMO of metallic nanotubes correspond to the Fermi leveland have a zero HOMO–LUMO gap.

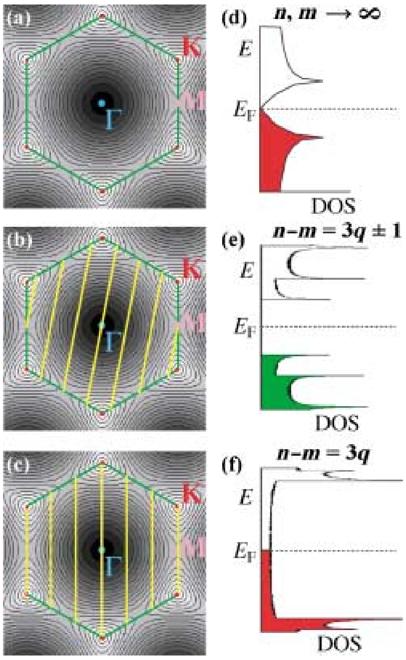

Figure 3. *Band structures (left) and electronic densities of states (right) of: (a, d) graphene; (b, e) semiconducting single-wall carbon nanotubes (e.g., (n,m) = (4,3)); (c, f) metallic single-wall carbon nanotubes (e.g., (n,m) = (3,3)). Darker color indicates further energy from the Fermi level in the* k_x,k_y *plane. Blue dots denote energy maxima and minima (**Γ** point), red dots indicate Fermi level (**K** point), pink dots indicate saddle points (**M** point). The yellow lines indicate the allowed wave vectors after roll-up of the graphene sheet.*

We know from organic chemistry and the so-called Hückel rule that $[4n+2]$annulenes, such as benzene, are very stable (i.e., "aromatic") because they have completely filled low-lying bonding orbitals and empty high-lying antibonding orbitals (Figure 2f). In addition to a large resonance energy, these systems have a large HOMO–LUMO gap, which means that adding or extracting an electron or disturbing the conjugation has a relatively high energetic cost. $[4n]$annulenes, on the other hand, have a pair of half-filled, degenerate, nonbonding orbitals (Figure 2e), which means that electrons can be added or extracted at relatively low cost, and the system is actually stabilized by a Jahn–Teller distortion that lowers the symmetry and breaks the orbital degeneracy. Even though $[4n]$annulenes larger than cyclobutadiene have positive resonance energies,[27] their idealized, undistorted structures have a zero HOMO–LUMO gap or, in any case, a smaller one than that of $[4n+2]$annulenes. Likewise (Figures 3e and 3f), carbon nanotubes, although with one additional dimension, can either have a full valence band (bonding) and an empty conduction band (antibonding) with a significant gap in between, or have electronic states at the Fermi level (nonbonding) with a zero gap. The additional dimension results in: i) a Hückel rule determined by two numbers (n,m), instead of one $(4n+2)$; ii) continuous bands with van Hove singularities in the density of states, instead of discrete levels; and iii) a very rigid lattice instead of a flexible one. The π system in metallic nanotubes, like in $[4n]$annulenes, should be stabilized by a distortion, in this case a Peierls distortion; however, this is inappreciable due to the extreme rigidity of the lattice, which includes also σ bonds.

Thus, the traditional concepts of aromaticity and HOMO–LUMO gap could be used to explain the different reactivity of metallic and semiconducting nanotubes in processes that are thermodynamically or kinetically controlled by noncovalent π interactions, such as those proceeding via charge-transfer complexes (as in the mechanism proposed by Strano et al.[18]), π stacking, coordination with transition metals, etc. According to organic-chemistry textbooks, one of the chemical properties that characterize aromatic molecules, versus nonaromatic or antiaromatic ones, is a lower tendency to undergo reactions of addition.[2,3] Coincidentally or not, metallic carbon nanotubes are more reactive to addition than semiconducting ones,[18] as should be expected from species being less aromatic or having a smaller HOMO–LUMO gap.

Orbital Symmetry and Woodward–Hoffmann Rules

Why and when carbon nanotubes are metallic or semiconducting, which was shown previously in reciprocal space, can also be represented in real space by applying common constructions and concepts used in organic chemistry. A chemical reaction involving the closure of a conjugated system is called an electrocyclic reaction. Thus, the virtual process of rolling up a graphene sheet to form a nanotube could be regarded, from a chemical point of view, as a ″virtual electrocyclic reaction“. Woodward–Hoffman rules are commonly used to describe the stereochemistry of real electrocyclic reactions based on the principle of orbital symmetry conservation.[4,5] Analogously, we can apply this rule to the graphene roll-up process. To do this with molecules one usually looks at the symmetry of the relevant orbital, that is, the HOMO if it is a thermal process or the LUMO if it is a photochemical process.

Figure 4 shows linear combinations of atomic orbitals (LCAO) representations of a few molecular orbitals of graphene, corresponding to the **Γ**, **M**, and **K** points of the band structure diagram shown in Figure 3 a.[30] These localized representations can be generated as linear combinations of degenerate Bloch functions. In fact, there are an infinite number of such valid combinations, but the ones shown here are convenient because they have real solutions and not complex ones. The LCAO coefficients are obtained by summing up simple sine or cosine functions of the position with the directions and periodicities that correspond to the different **Γ**, **M**, or **K** wave vectors in the first Brilloiun zone (Figure 3). Note how the degree of bonding varies from the most bonding at the bottom to the most antibonding at the top. The two degenerate orbitals in the middle are nonbonding and correspond to the Fermi level. These are the orbitals whose symmetry will determine the properties of the nanotube.

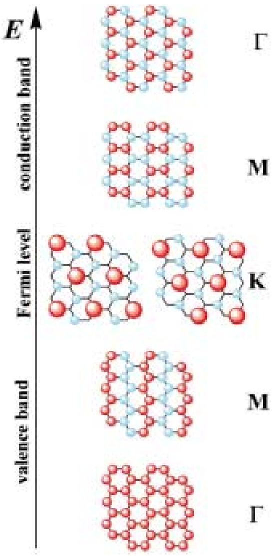

*Figure 4. Real-space LCAO representations of molecular orbitals in graphene corresponding to the same **Γ**, **K**, and **M** points indicated in Figure 3. These are top views of the p_z orbitals contributing to the molecular orbitals, where the red and blue circles correspond to positive and negative LCAO coefficients, respectively. In the Fermi level nonbonding orbitals (**K**), the red and blue circles represent LCAO coefficients +1 and $-^1/_2$, respectively.*

If the graphene sheet is rolled up to form a nanotube in a way that overlaps carbons with similar LCAO coefficients (Figure 5 a—red with red, blue with blue), then the periodicity of the orbital will be conserved in the nanotube, there will be allowed states at the Fermi level, and the nanotube will be metallic. On the other hand, if the graphene sheet is rolled up to form a nanotube in a way that overlaps carbon atoms with different LCAO coefficients (Figure 5 b), then the orbital symmetry conservation rule will not allow this orbital to exist in the nanotube, there will be a gap at the Fermi level, and the nanotube will be semiconducting. Since the LCAO coefficients repeat themselves every three translations by any of the lattice basis vectors, a nanotube is metallic when the difference between the indices *n* and *m* is a multiple of three, and otherwise it is semiconducting. The advantage of this new real-space representation of the electronic structure of carbon nanotubes, besides its illustrative or didactic value, is that it fits in the same framework of organic chemistry that is used to describe the reactions that the nanotubes undergo.

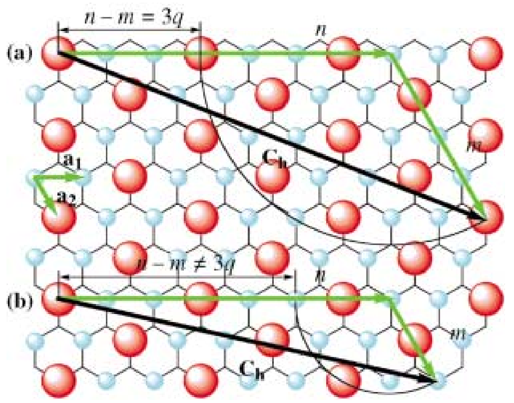

Figure 5. Roll-up of a nonbonding orbital of graphene corresponding to the Fermi level. Black arrows represent the roll-up vector $\mathbf{C_h}$ that connects two carbon atoms in the graphene sheet that become equivalent in the nanotube. The roll-up vector can be represented as a linear combination of the lattice vectors $\mathbf{a_1}$ and $\mathbf{a_2}$, with coefficients n and m, that is, $\mathbf{C_h}=\mathrm{n}\mathbf{a_1}+\mathrm{m}\mathbf{a_2}$. The green arrows indicate the components $\mathrm{n}\mathbf{a}_1$ and $\mathrm{m}\mathbf{a}_2$. (a) When roll-up connects carbons with equal LCAO coefficient (red to red), the nanotube is “metallic”. (b) When roll-up connects carbons with different LCAO coefficients (red to blue), the nanotube is semiconducting.

Beyond the virtual process of roll-up, orbital symmetry may play as important a role in real chemical processes involving carbon nanotubes as it does in real pericyclic reactions. The solid-state physics rule of crystal momentum conservation is very important in determining the transport properties and spectroscopy of carbon nanotubes.[1,7,10] The orbital symmetry conservation rule is the molecular equivalent to the crystal momentum conservation rule in the solid state. If this rule governs physical processes, it is likely to govern chemical processes too. In this context, it has been noted that the interaction of carbon nanotubes with metals, which is an important factor determining the nanotube–electrode contact resistance, is related to the matching between the Fermi wavevectors of the nanotubes and the metal.[31] Likewise, for a molecule to interact with a nanotube, there must be a good matching between the shapes of the frontier orbitals of the molecule and of the nanotubes, as we shall see below.

A Frontier Orbital Picture of Carbon-Nanotube Chemistry

A more comprehensive picture that could be useful to describe this π chemistry of carbon nanotubes is Roald Hoffmann's frontier orbital perspective of chemisorption.[21–23] Molecule–surface orbital interactions are classified according to the total number of electrons in the two orbitals involved, as shown in Figure 6a. These include not only the usual HOMO–LUMO (1) and LUMO–HOMO (2) two-electron interactions that normally dominate the overall interaction between two molecules, but also interactions between occupied orbitals (four-electron) (3) or between empty orbitals (zero-electron) (4), which are usually repulsive but become attractive after charge transfer to or from the surface, respectively, depending on the relative position of the Fermi level with respect to the mixed molecule–surface orbitals, as shown in Figures 6b and 6c. In addition, there is another interaction (5) associated with the reorganization of the electronic structure of the surface as a result of the interaction with the molecule. Interactions (3) and (4), since they become attractive only via charge transfer, can make a large difference between metallic and semiconducting nanotubes. Interaction (3), for instance, when applied to carbon nanotubes can be represented as in Figure 7. In this case, the metallic nanotube can establish attractive interactions with the molecule that the semiconducting nanotube cannot. The frontier orbitals of semiconducting nanotubes can be related to the first van Hove singularities in the valence and conduction bands, whereas those of metallic nanotubes correspond to the orbitals near the Fermi level that can establish the strongest interaction with the molecule. Nanotube orbitals can be represented in the LCAO format in real space by combining Bloch functions[32] as in Figure 4. For the frontier orbitals of the molecule and the nanotube to interact, according to perturbation theory, they need a small difference in energy and a good match between their shapes (i.e., nodal properties).

Figure 7 could well describe the experimental results reported by Strano et al.,[18] in which the mixed molecule–nanotube orbitals represent those of the charge-transfer complex. In addition, interaction (5) could also be stronger with metallic nanotubes, due to their Peierls instability, if the interaction with the molecules opens a gap at the Fermi level and stabilizes the system. The overall interaction with the nanotube also has an important effect on the molecule. As in heterogeneous catalysis, chemisorption weakens the inner bonds inside the molecule and activates it toward chemical reaction. This could be the reason that diazonium decomposes and reacts faster with the metallic carbon nanotubes. Although most criteria point to a higher reactivity for metallic nanotubes in general, since specific orbital overlap could play a role, the possibility that certain molecules actually interact better with semiconducting nanotubes than with metallic ones may not be discarded.

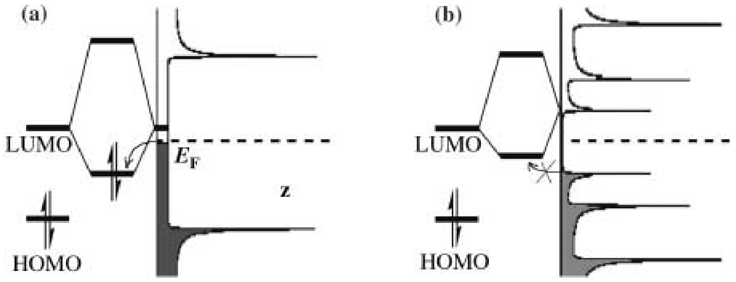

Figure 7. Frontier-orbital picture representation of zero-electron interactions between a molecule and a "metallic" (a) or a semiconducting (b) single-wall carbon nanotube. The molecule frontier orbitals are designated as HOMO and LUMO, and the nanotube orbitals are represented by the density of states plots. The interaction with the "metallic" nanotube becomes attractive due to charge transfer, but is not effective with the semiconducting nanotube.

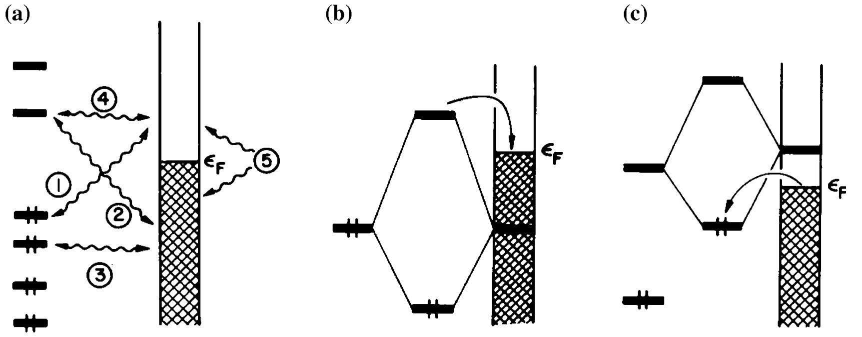

Figure 6. Frontier-orbital picture of chemisorption, from reference [21]. (a) Classification of molecule–surface two-orbital interactions. (b) Four-electron interaction of type (3), which becomes attractive after charge transfer to the surface. (c) Zero-electron interaction of type (4), which becomes attractive after charge transfer from the surface.

Concluding Remarks

We have shown how a few traditional concepts of molecular orbitals, commonly used to describe the stability and reactivity of many organic molecules, can be merged with the solid-state physics description of carbon nanotubes to describe the nanotubes' chemical reactivity. The delocalized electronic structure (π band structure) of carbon nanotubes can have chemical effects as important as the localized electronic structure (sp^2 pyramidalization). As in many instances in organic chemistry, these two effects could be separated into resonance and steric effects, respectively.

We hope that this chemist's view, in spite of its (so far) qualitative approach, may provoke new thoughts in the perspective of chemists, physicists, and theoreticians exploring the chemistry of carbon nanotubes.

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