Oxidation of Carbon Nanotubes by Singlet O_2

Siu-Pang Chan,[1] Gang Chen,[1,2] X. G. Gong,[3,1,2] and Zhi-Feng Liu[1,*]
[1]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong, China*
[2]*Institute of Solid State Physics. Chinese Academy of Sciences, Hefei, Anhui, China*
[3]*Department of Physics, Fudan University, Shanghai, China*
(Received 19 August 2002; published 27 February 2003)

Chemisorption of singlet $^1\Delta_g$ O_2 on single-walled carbon nanotubes is reexamined by first principles calculations, and the reaction barrier is substantially lower than previously reported when the spin on O_2 is correctly treated. The process is initiated by the cycloaddition of a singlet O_2 on top of a C-C bond and ended with an epoxy structure with each of the two oxygen atoms occupying a bridge position. The overall process is exothermic, with an activation barrier as low as 0.61 eV for the (8, 0) tube. Our results raise the possibility that carbon nanotubes with small diameters could be degraded after exposure to air and sunlight, similar to the degradation of natural rubber and synthetic plastics.

DOI: 10.1103/PhysRevLett.90.086403 PACS numbers: 71.20.–b, 68.43.–h, 73.22.–f, 82.65.+r

The recent experimental finding [1,2] that the electronic properties of single-walled carbon nanotubes are sensitive to oxygen exposure is a mixed blessing for their potential applications. On the one hand, it is envisioned that such property changes could be used as the basis for chemical sensors [1,3]. However, sensitivity to the presence of O_2 could pose a problem for the stability of the devices made of carbon nanotubes upon air exposure [1]. Accordingly, a number of experimental and theoretical studies have been reported to understand the oxidation of carbon nanotubes.

Experimentally, it has been well established that both the electronic properties [1] and the thermoelectric power [2] could be effected. Nuclear magnetic resonance measurement also showed that the spin lattice relaxation rate for the carbon nanotubes changed significantly in the presence of oxygen [4]. Based on density functional theory (DFT) calculations, the triplet O_2 was found to physisorb on carbon nanotubes, as characterized by a shallow adsorption well ~0.25 eV and a fairly long C-O distance ~2.7 Å [5]. Physisorbed triplet O_2 affected the magnetic properties of carbon nanotubes significantly. The O_2 molecule was also found in tight-binding calculations to react readily with the edges and caps of carbon nanotubes, but not with the tube walls [6]. Nonetheless, there was experimental evidence that chemisorption may play a role, as in the thermoelectric power measurement, in which recovering oxygen free tubes could take up to 200 h [2].

The ground state for O_2 is a triplet $^3\Sigma_g^-$, with two spin parallel electrons each occupying one of the doubly degenerate $pp\pi^*$ orbitals. However, upon photoexcitation, especially in the presence of a photosensitizer, singlet oxygen could be produced in a small amount, in either the $^1\Delta_g$ or $^1\Sigma_g^+$ state, with an excitation energy of 0.98 and 1.63 eV, respectively [7]. The $^1\Sigma_g^+$ state decays readily into the $^1\Delta_g$ state [8], which, with a half-life around 5×10^{-2} sec at atmospheric pressure and a mean diffusion path of 114 ± 20 Å in thin film [9], is much more reactive than the triplet state and has attracted considerable attention due to its important biological and chemical effects [8,9]. In interesting relevance to the carbon nanotubes, singlet O_2 was found to react readily with conjugate carbon-carbon double bonds and was responsible for the degradation of natural rubber and synthetic polymers upon exposure to air and sunlight.

There are two very recent theoretical studies on the chemisorption of singlet O_2 on the walls of carbon nanotubes, and both found chemisorption unlikely [10,11]. The most sophisticated and detailed study on this process was reported by Sorescu *et al.*, using plane wave and pseudopotential based DFT methods to find both the energy difference and reaction barriers [10]. The chemisorption process was found to be endothermic, and, moreover, the activation barrier was over 30 kcal/mol, making it unlikely at room temperature.

In this Letter, we reexamine the interaction of a singlet $^1\Delta_g$ O_2 with carbon nanotubes by first principles calculations. Our conclusion is very different from previous results. When the electron spin is treated correctly, the chemisorption of singlet O_2 occurs readily on the walls of (8, 0) and (6, 6) tubes, and the final products are energetically more stable than the physisorbed triplet O_2.

Our calculations were performed within the framework of DFT with a plane wave basis set and pseudopotentials for the atomic core regions [12,13], as implemented in the Vienna *ab initio* simulation package (VASP) [14]. GGA (general gradient approximation) exchange-correlation functional [15] and Vanderbilt ultrasoft pseudopotentials [16] were used. The cutoff energy is 396 eV for the plane wave basis set. A supercell is used to model a carbon nanotube or a flat graphene sheet, with details given in Table I. We studied both the single-walled (8, 0) and (6, 6) tubes, for which the c parameter of the supercell is adjusted according to the periodicity along the tube direction, while the a and b parameters are enough so that

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TABLE I. Structure parameters and energies obtained from first principles calculations on the adsorption of O_2 on carbon nanotubes and a graphene sheet.

System (Å) (box size $a \times b \times c$, tube diameter)		Structure (Å) C—C:C—O:O—O	Energy (eV) Adsorb. energy E_{adS}[a]:E_{adT}[b]	Reaction barrier E_a	Band gap	$^3\Sigma_g^- \rightarrow {}^1\Delta_g$ gap for physisorbed O_2
O_2 on (8, 0) crossing	Cycloaddition	1.596:1.486:1.516	−0.09:0.83	0.61 (*1.15*)[c]	0.53	0.93 (0.39)[c]
(13 × 15 × 8.527, 6.35)	Epoxy	1.470:1.463:3.008	−1.26:−0.34	0.54	0.23	
O_2 on (8, 0) parallel	Cycloaddition	1.528:1.482:1.510	−0.48:0.46	0.75 (*1.30*)[c]	0.44	0.95 (0.40)[c]
O_2 on (8, 0) parallel[d]	Cycloaddition	1.528:1.483:1.510	···:0.44	(∼*1.5*)[c]	···	··· (0.43)[c]
O_2 on (6, 6)	Cycloaddition	1.552:1.494:1.513	0.23:1.05	0.87 (*1.35*)[c]	0	0.85 (0.37)[c]
(15 × 15 × 7.49, 8.11)	Epoxy	1.589:1.439:3.322	−0.99:−0.16	0.56	0	
O_2 on (8, 8)	Cycloaddition	1.551:1.495:1.511	0.38:1.32	···	0	0.96 (0.40)[c]
(20 × 20 × 7.49, 10.9)	Epoxy	1.559:1.447:3.227	−0.64:0.31	···	0	
O_2 on (10, 10)	Cycloaddition	1.551:1.499:1.511	0.59:1.44	···	0	0.86 (0.39)[c]
(20 × 20 × 7.49, 13.6)	Epoxy	1.545:1.452:3.154	−0.32:0.53	···	···	
O_2 on graphite	Cycloaddition	1.528:1.503:1.511	1.13:2.19	···	···	1.09 (0.43)[c]
(7.38 × 7.38 × 8.00, ∞)	Epoxy	1.484:1.466:2.567	0.57:1.63	···	···	
O_2 on graphite[d]	Cycloaddition	1.529:1.501:1.510	···:2.18	···	···	··· (∼ 0.4)[c]
(7.38 × 7.38 × 8.00, ∞)						
Free O_2 (10 × 10 × 10)	···	···:···:1.245	···	···	···	1.14 (0.44)[c]
Free O_2 experimental	···	···:···:1.207[e]	···	···	···	0.98[f]

[a]E_{adS}, adsorption energy relative to singlet O_2 physisorbed on nanotube; [b]E_{adT}, adsorption energy relative to a free triplet O_2 + bare nanotube; [c]Values obtained by spin-contaminated calculations are in parentheses; [d]Reference [10]; [e]Reference [8]; [f]Reference [7].

there is little interaction between a tube and its periodic images. The minimum energy reaction path is mapped out using the nudged elastic band method, developed by Jónsson and co-workers [17,18].

Direct addition of a singlet $^1\Delta_g$ O_2 on top of a C═C is known as cycloaddition, with the two C-O bonds formed and the bond between two oxygen atoms kept, as shown in Fig. 1. The ground state for the product is a singlet, and thus the reaction is spin forbidden for the triplet O_2. Since the setup of our calculations are almost the same as that in the work of Sorescu *et al.* [10], it is not surprising that the optimized structure parameters for the cycloaddition product on an (8, 0) tube and on a flat graphene are almost

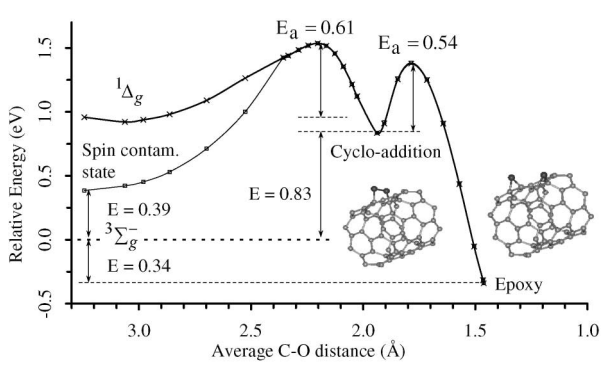

FIG. 1. Relative energy along the reaction path for the chemisorption of a singlet O_2 on an (8, 0) single-walled carbon nanotube, with average C-O distance taken as the reaction coordinate.

identical with their results, as shown in Table I. For the energy relative to a free triplet O_2 with either a bare (8, 0) tube or a bare graphene sheet, we also obtained values for the cycloaddition process that are within 0.02 eV of the previously reported results (Table I) [10].

However, significant differences are found for the activation barrier and for the excitation energy between triplet and singlet O_2. The activation barrier (Table I) for a singlet O_2 to react with an (8, 0) tube is only 0.61 eV, significantly lower than the value around 1.5 eV obtained before. Also, as shown in Table I, the energy to excite an O_2 molecule from the triplet $^3\Sigma_g^-$ to the singlet $^1\Delta_g$ ranges from 0.9 to 1.1 eV in our calculation, with the variation caused by the difference in the physisorption of the triplet and singlet O_2 on carbon nanotubes or on a flat graphene. These values are substantially higher than the value of 0.43 eV (9.92 kcal/mol) in the previous study [10]. In terms of methods, the only significant difference between the previous calculations of Sorescu *et al.* and that of ours is in the treatment for the singlet state. Although specific details were not provided in Ref. [10] for the calculation of singlet O_2, we believe that spin-polarized density functions were used, as that is the only way we could reproduce their result for the energy separation between triplet and singlet O_2. Within this scheme, two distinct density functions are used, one for spin up and one for spin down, subject to the constraint that the total number of spin-up electrons is the same as that for the spin-down electrons. In contrast, we treated the singlet O_2 in our calculations as a closed-shell system

within spin-restricted DFT. In other words, the density function for the spin-up electrons is exactly the same as that for the spin-down electrons. Although there is more freedom for varying the spin densities in a spin-polarized DFT calculation, thus producing lower total energy for singlet O_2, it unfortunately leads to a spin-contaminated state and the calculated reaction barriers and excitation energies are unreliable.

The highest occupied orbitals in an O_2 molecule are a pair of doubly degenerate π orbitals, occupied by only two electrons. There are three possible states, $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$, due to spin-orbit interactions. The wave function for the singlet $^1\Delta_g$ is represented by one determinant, either $|\pi_+\overline{\pi}_+|$ (D1) or $|\pi_-\overline{\pi}_-|$ (D2), as the two electrons with opposite spins occupy only one orbital. Similarly, for the ground state triplet $^3\Sigma_g^-$, there are two one-determinant components, $|\pi_+\pi_-|$ (T1) and $|\overline{\pi}_+\overline{\pi}_-|$ (T2), with each orbital occupied by one electron and with the two electrons having parallel spins. However, the third component for the triplet $^3\Sigma_g^-$ involves two determinants, $|\pi_+\overline{\pi}_-| + |\overline{\pi}_+\pi_-|$ (T3), and thus does not lend itself to a simple and straightforward orbital picture. In addition, the excited singlet $^1\Sigma_g^+$ state also involves two determinants, as $|\pi_+\overline{\pi}_-| - |\overline{\pi}_+\pi_-|$ (S1).

It is well known that spin-polarized DFT is well defined only for spin densities derived from a single-determinant wave function [19]. The configurations D1, D2, T1, and T2 are all based on a single determinant and can be adequately treated within DFT. For the triplet $^3\Sigma_g^-$ (T1 or T2), it requires a spin-polarized calculation, while for the singlet $^1\Delta_g$ (D1 or D2), it requires a spin-restricted (close-shell) calculation. Within GGA, we obtained an energy of 1.1 eV for the $^3\Sigma_g^-$ to $^1\Delta_g$ excitation, which is favorably compared to the experimental value of 0.98 eV [7], and also to the previously reported LDA (local density approximation) value about 1 eV [5].

On the other hand, great care must be taken when DFT is applied to the modeling of a multideterminant configuration, such as the $^1\Sigma_g^+$ S1 of O_2, by spin-polarized densities. The single-determinant configuration $|\pi_+\overline{\pi}_-|$ is neither S1 nor T3, but a mixture of the two [19]. Such mixing of configurations with different spin multiplicity is known as "spin contamination" and is an important consideration in the calculation of transition metal clusters [20]. As the two spin densities are varied independently, the extent of spin contamination is also varied depending on the internuclei distance and symmetry. For transition metal dimers, such as Cr_2 and Mo_2, the ground state is the singlet $^1\Sigma_g^+$, and spin contamination is found to be minor [21]. However, for O_2, the ground state is the triplet $^3\Sigma_g^-$, and $^1\Sigma_g^+$ is an excited state. In this case, spin contamination is a serious problem, as indicated by the calculated energy for the $^3\Sigma_g^-$ to $^1\Sigma_g^+$ excitation around 0.4 eV (Table I), which is substantially underestimated in comparison to the experimental value of 1.63 eV [7].

Actually, for the oxidation of carbon nanotubes, the calculation of the singlet $^1\Sigma_g^+$ state is unnecessary, as its lifetime is very short due to its rapid decay to the $^1\Delta_g$ state [8], and its role is basically limited to that as a source of $^1\Delta_g$ oxygen. More unfortunately, spin contamination significantly lowers its energy, which is even lower by 0.6 eV than that for the first excited $^1\Delta_g$ state. This problem seriously affects the calculation of the activation barrier for the cycloaddition of singlet O_2 onto a carbon nanotube.

As shown in Fig. 1, for O_2 in $^1\Delta_g$, the barrier is 0.61 eV. However, if spin-polarized DFT is used for the singlet O_2, the spin contamination lowers the energy of the physisorbed singlet O_2 by around 0.6 eV, and the resulting barrier is thus raised to $\sim$1.2 eV. It is also interesting to notice that around the transition structure the spin-restricted ($^1\Delta_g$) and spin-polarized (spin-contaminated) calculations converge to each other. This is due to the fact that the bonding interaction between the O_2 and the tube changes the electronic structure on O_2, which breaks the degeneracy between the two π components. The ground state thus become a single-determinant singlet state, wth the two valence electron now occupying the same orbital, which can be adequately modeled by both methods.

It should be pointed out that the reaction path shown in Fig. 1 is slightly different from that reported before. The O_2 bond crosses the tube direction in Fig. 1, while in previous work [10] the O_2 molecule was parallel to the tube axis. We also examined the barrier for the parallel configuration, and, as shown in Table I, the barrier is slightly higher at 0.75 eV for the $^1\Delta_g$ O_2 addition. When spin-polarized DFT is used, the barrier is again raised to 1.3 eV due to spin contamination, close to the value $\sim$1.5 eV obtained in previous calculations [10]. In light of these results, the conclusion regarding the chemisorption of singlet O_2 must be revised. Provided that there is singlet O_2 present by photoexcitation, the barrier for its addition to an (8, 0) is not very high and can be overcome in ambient conditions.

Relative to a triplet O_2 and a bare (8, 0) tube, the cycloaddition product is 0.83 eV less stable, and, as shown in Fig. 1, the barrier for desorption, the reversal process, is also quite low. However, the cycloaddition product could go through another step of reaction, with the O-O bond broken and the two oxygen atoms each taking an epoxy (bridge) position. For the (8, 0) tube, the barrier is only 0.54 eV, and this step is exothermic by 1.17 eV, making the epoxy structure 0.34 eV more stable than even the triplet O_2 plus a bare tube. More importantly, once such a structure is formed, the desorption barrier at 1.7 eV is quite high. The presence of such structures is most likely responsible for the experimental observation that it is difficult to completely cleanse the adsorbed O_2 [2].

Similar processes could take place on a (6, 6) tube, as shown in Table I, with a barrier of 0.87 eV for the cycloaddition step, and of 0.56 eV for breaking the O-O bond to form the epoxy structure. The overall process is slightly

exothermic by 0.16 eV, and the desorption barrier for the epoxy structure at 1.8 eV is again quite high.

The sensitivity of carbon nanotubes to O_2 exposure is an important issue, as it raises questions about the stability of devices built by such tubes. To put it in perspective, we should emphasize that the reaction depends on the presence of singlet O_2, which is produced in small quantities by the photoexcitation of triplet O_2 and catalyzed by photosensitizers [8], such as C_{60} and C_{70} [22]. Experimentally (10, 10) carbon nanotubes were found to be unable to photosensitize formation of singlet O_2 [23]. The experimentally found high oxygen sensitivity of carbon nanotubes [1] may be due to the presence of fullerene impurities as the photosensitizers, although the current knowledge on photophysical properties of carbon nanotubes is still quite limited. Even without the presence of photosensitizers, the (8, 0) and (6, 6) tubes may still be affected by O_2 chemisorption after an extended period of air exposure, similar to the aging of rubber or polymers, due to the reaction with singlet O_2.

It should also be noted that the barriers we obtained are only for (8, 0) and (6, 6) tubes, for which the tube diameter is less than 1 nm. Relative to the triplet O_2 and a bare tube, the energy of the epoxy structure increases from an exothermic -0.16 eV on (6, 6) to an endothermic 0.31 eV on (8, 8), 0.53 eV for (10, 10), and 1.63 eV on a flat graphene sheet. In other words, the chemisorption process becomes energetically less favorable as the tube diameter increases. As shown in Table I, the same trend is also observed for the cycloaddition step. As the diameter of a carbon nanotube increases, the curvature on the rolled graphene sheet decreases, and it becomes more similar to a flat graphene in terms of reactivity. As a result, the chemisorption of singlet O_2 becomes more difficult.

The effect of chemisorption on the conductivity of carbon nanotubes will depend on the epoxy structure, rather than on the cycloaddition structure which is only an intermediate. It is well known that an (8, 0) tube is a semiconductor, and at the GGA level we obtain an energy gap of 0.58 eV, in good agreement with the previous LDA result of 0.6 eV [5]. For the chemisorbed epoxy structure, the gap is decreased to 0.23 eV, implying an increase in conductivity and in agreement with experiments [1]. On the other hand, for the metallic (6, 6) tube, the epoxy structure remains metallic according to band structure calculations.

In conclusion. singlet O_2 produced by photoexcitation of triplet O_2 could react with (8, 0) and (6, 6) carbon nanotubes, through an intermediate cycloaddition step to an epoxy structure. The overall process is exothermic, while the activation barrier is accessible at room temperature. It would be interesting to investigate whether such reactions would result in a slow buildup of epoxy adsorbate when these tubes are exposed to air. However, as the tube diameter increases, the chemisorption process becomes more difficult.

The work reported was supported by an Earmarked Grant (Project No. CUHK 4252/01P) from the Research Grants Council of Hong Kong SAR Government. X. G. G. acknowledges support from the NNSF of China, from the Special Funds for Major State Basic Research of China, and from the Key Projects of the Chinese Academy of Sciences. We are grateful for the generous allocation of computer time for the clusters of AlphaStations at the Chemistry Department, and the Center for Scientific Modeling and Computation, as well as the high performance computing facilities at the Information Technology Service Center, all located at the Chinese University of Hong Kong.

*Corresponding author.

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