The response of single-walled carbon nanotubes to NO₂ and the search for a long-living adsorbed species

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Contact-passivated sensor devices allow one to measure the response of individual ultraclean single-walled carbon nanotubes to 1 ppm NO₂, and show that the activation energies for desorption from nanotubes of diameters in the 1.5–3.5 nm range are of the order of 1 eV. DFT calculations based on several exchange-correlation functionals are presented and critically examined. The nature of the molecular binding is thus clarified for NO₂, N₂O₄, and NO₃, and also the dependence on the size of the nanotube. The binding strength of physisorbed NO₃ is consistent with the experimental data on desorption. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4940422>]

Starting from the work of Kong *et al.*,¹ a wealth of papers have investigated the response of carbon nanotubes (CNTs) when exposed to gas molecules and established their potential as components of gas sensors of extraordinarily low power and unusually high sensitivity.^{2–8}

Special focus has been placed on nitrogen dioxide (NO₂), which is well-known as a highly toxic air pollutant. However, the sensing mechanism has not been established to satisfaction yet, and two important issues continue to be debated: (i) Regarding the adsorption itself, it is generally unclear to what extent metal contacts contribute to the observed change in conductivity after gas exposure. Some authors even argue that the metal contacts are the only responsive elements in the device, via changes in the metal work function.^{9–11} However, several studies^{1,12,13} have shared the view that adsorption takes place on the tube surface and involves charge transfer to the molecule, thus modifying the carrier transport in the channel (p-doping). Only very recently, by using devices based on ultraclean, suspended single-walled nanotubes (SWNTs) and with masked metal contacts, some of us have demonstrated that individual nanotubes can respond directly to NO₂ of 200–900 ppb concentration.¹⁴ (ii) Furthermore, it has been known from the earliest experiments that an important difference exists between the response time, which is of the order of seconds or minutes, and the recovery time, which has long been reported to be of the order of 10 h.^{1,2,15} Although NO₃¹⁶ was originally suggested as the species responsible for the long recovery time, most theoretical approaches^{13,17} supported the hypothesis that chemisorption states of one or more (co-adsorbed) molecules could form on the nanotube surface, with or without defects. Indeed, X-ray photoemission spectra (XPS) have identified nitrogen oxides of different

stoichiometry adsorbed on the surface of SWNTs. For example, for mixed metallic and semiconducting SWNTs exposed at 150–200 K, XPS revealed N(1s) core-level shifts of several oxides, with predominance of NO₃.¹⁰ More recently, XPS and absorption spectra¹⁸—taken at 100 K on ultraclean and metallicity-sorted SWNTs—were found to be consistent with NO₂—as predominant species—and NO, and only weak components of the spectra were attributed to their dimers and to NO₃. This work has also revealed that at 140 K thermal desorption started already after 2 min and recovery was fast for both semiconductor and metal SWNTs, although faster for the former. Electrical measurements on individual suspended and ultra-clean SWNTs with passivated contacts,¹⁹ however, appeared to confirm recovery times of the order of 10 h.¹⁴ Rough estimates for desorption barriers $E_{a,des}$ range then from 0.2–0.4 eV (Ref. 18) to 1–1.2 eV.^{14,15} In conclusion, dramatic discrepancies emerge from a simple survey of the experimental situation and seem to originate from several factors in principle, namely, not only metallicity sorting and cleanliness are relevant but also the presence of metal contacts and oxide substrates may influence the outcome of any measurement and the results could depend also on the (generally unknown) size and chirality of the nanotubes and on the NO₂ concentration. The latter ranges from 200–900 ppb (Ref. 14) to doses of 15 L (Ref. 15) or 70 L–260 L.¹⁸

From the theoretical side, severe difficulties are currently encountered in quantifying the strength of the interaction of NO₂ with a SWNT, which is believed to have primarily a physisorptive character. Calculations have so far applied density-functional-theory (DFT) in either the local-density approximation (without LDA^{13,16,20–22}) and with spin polarization LSDA^{13,16,18} or in the spin-polarized (S) gradient-corrected PBE^{23,24} functional.^{13,17} A summary is reported in Ref. 25. Here, we remark that LSDA values²⁶ for the binding energy (E_B)²⁷ on the (10,0)-CNT range from 0.147 eV (Ref. 13) to 0.5 eV,¹⁶ and that the PBE value reduces to 0.04 eV.¹³ Indeed, there are doubts about the

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adequacy of both L(S)DA and GGA functionals, because neither accounts for the long-range dispersion forces. On the other hand, higher-level quantum-chemical calculations of NO₂ adsorption^{28,29} have so far been performed only for very small fragments of CNTs that cannot be considered reliable models for the charge distribution on the surface of a nanotube and for the variations induced by molecular adsorption. The case of NO₃ was given less attention. PBE calculations for the (8,0)-CNT¹⁷ provide a comparison between NO₂ and NO₃: higher E_B was found for the latter (0.525 vs. 0.032 eV) and the absence of chemical bonding was claimed in both cases. On the contrary, chemisorption was predicted in case of coadsorption of two close-by molecules. In particular, the NO-NO₃ pair was found stable at close distances (~ 1.5 Å) from the (8,0)-CNT, and with E_B of 0.61 and 0.69 eV, depending on the GGA functional adopted. A further PBE study³⁰ suggested the existence of two relevant states for NO₃ on zig-zag CNTs ((8,0) and (13,0)), namely, beyond the equilibrium “physisorption state,” a metastable “chemisorption state” was identified on neutral CNT surfaces (0.23 and 0.64 eV higher, respectively) and the relative stability was suggested to be influenced by the charge state of the surface. On the other hand, the LSDA prediction (1.17 eV) for the (10,0)-CNT¹⁶ was interpreted as a sign of chemisorption.¹⁰

The recently demonstrated possibility of establishing the intrinsic response of individual SWNTs from a sensor device with passivated contacts—as mentioned above—allows in principle for a clean comparison between theory and experiment. Moreover, the nature of the binding of nitrogen oxides and the dependence on the size of the nanotubes must be clarified. This is the motivation of the work we present here. A series of DFT-based calculations were performed,^{25,31} in the frame of several exchange-correlation (xc) functionals, namely, gradient-corrected GGA functionals (PBE²³ and BLYP^{32,33}) including semi-empirical corrections for dispersion forces,³⁴ and the hybrid parameter-free PBE0 functional.³⁵ More sophisticated descriptions of the dispersion forces within DFT have been developed,^{36–41} but their use is still prohibitive for the model sizes we need to consider here. We also extend our measurements of Ref. 14, so as to identify the behavior of semiconducting SWNTs after exposure to 1 ppm NO₂, and obtain a more specific characterization of the desorption at ambient temperature.²⁵

We performed several experiments on three different devices—with SWNTs of diameters in the range 1.5–3.5 nm⁴²—exposed to 1 ppm NO₂ at ambient conditions. All devices were partially covered with Al₂O₃, namely, the gate electrode, metal leads, and bond pads were passivated. Figure 1 monitors the variation of the electrical signal during the whole exposure time and shows, in particular, the decay due to desorption at room temperature. We can safely attribute this response to the SWNTs that present the only relevant sensitive surface to NO₂. The usual procedure was applied to extract the desorption rate constant. First, by assuming that the sensor response is proportional to the change of the surface concentration of the NO_x species, one can estimate the surface residence time, namely, the time τ_{des} that the species spends on the nanotube surface before desorption. This turns out to be 3100 ± 100 s.⁴³ Then, by assuming that desorption is

FIG. 1. Response of a contact-passivated device to 1 ppm NO₂, under constant bias ($V_{sd} = 1$ V, $V_g = -10$ V). NO₂ is injected at t_1 and continuously flowing until t_2 . Inset: the desorption rate constant is estimated from an exponential fitting of the marked section (dotted line).

a first order process, one can express the desorption rate constant in an Arrhenius form and use it to fit the transient response (Figure 1). The estimate thus obtained for the desorption activation energy $E_{a,des}$ at room temperature is about 0.9 eV and is quite insensitive to the pre-exponential factor (in the range of 10^{12} – 10^{13} s^{−1}). The discrepancy from the values (0.2–0.4 eV) in Ref. 18 should be ascribed to the very different conditions of the experiment. Beyond the absence of contact passivation, the lower temperature and the exposure to the saturation dose of NO₂ are expected to influence the relative concentration of the NO_x species and their binding strength.

It is difficult to reconcile a desorption energy of the order of 1 eV with the expected weak binding of NO₂. The only comparable values were predicted by some of the LDA calculations.^{16,22,25} Here, we consider three molecules: NO₂, NO₃, and N₂O₄. The structural characteristics are reported in Ref. 25. N₂O₄ has not been treated earlier—if not marginally—in the study of CNT adsorption. However, it is of interest because at room temperature the dioxide gas phase consists of both monomers and dimers in equilibrium.⁴⁴ Symmetric N₂O₄ is the ground state isomer of NO₂ dimers⁴⁵ and has a relatively weak N-N covalent bond. The dissociation energy is strongly dependent on the DFT-functional:²⁵ it is higher in PBE relative to BLYP (0.88 vs. 0.61 eV) and is weakened from the partial introduction of exact exchange (0.64 eV (PBE0) and 0.45 eV (B3LYP)) that stabilizes the monomer radical. In all cases, the bond is sufficiently strong to prevent dissociation on the nanotube.

Figure 2 and Table I show our results for the equilibrium configurations of the three molecules adsorbed on the (10,0)-CNT. These structures are largely independent of the xc functional. For example, the minimum distances are in the range of 2.9–3.5 Å. In both NO₂ and N₂O₄, the nitrogen is the closest atom to the tube, with the closest oxygen 0.54–0.63 Å further away in the former and only 0.11–0.16 Å in the latter. In NO₃, on the other hand, one oxygen is at the same distance as the nitrogen. Changes in both the molecular and the nanotube structures are negligible.²⁵ The only structural data available from experiment refer to N₂O₄ on graphite⁴⁶ at high coverage (monolayer regime) and were found to be consistent with a configuration perpendicular to the surface. On the CNT, this structure is unstable—at least at very low coverage—and spontaneously transforms to the ground state with the N-N axis parallel to the tube axis (see Figure 2).

FIG. 2. NO_2 , N_2O_4 , and NO_3 (from left to right) adsorbed on the surface of a (10,0)-CNT: Equilibrium configurations (top view) and Electron-localization-function (ELF) (isosurface value = 0.8).

Independent of the xc functional, we find that a chemical bond never forms, as shown by the electron-localization-function (ELF)⁴⁷ in Figure 2. NO_2 and NO_3 are radicals and adsorption is accompanied by a small charge transfer from the tube. Estimates from Bader's analysis of the electron density⁴⁸ are 0.1e for NO_2 and 0.5–0.6e for NO_3 . The Kohn-Sham density of states mirrors the superposition of those of the separated systems and only over a small portion of the k-space, the lowest unoccupied state of the molecule is lower than the CNT-states near the top of the valence band. We have verified that this picture is the same in the xc functionals examined here and clarifies the small charge transfer but also shows the difficulty to accurately account for it.

Our results are fully consistent with physical adsorption. The origin of the binding is both in the attractive long-range part of the dispersion forces and in the interaction of the small charge localized on the molecule with the delocalized, highly polarizable density of the π electron states delocalized on the surface of the nanotube, as illustrated in Figure 3. The latter component dominates in NO_3 which is a stronger acceptor than NO_2 , and explains the higher binding energy. We remark that this same mechanism (called “polarization interaction”) was suggested to be predominant in the adsorption of DNA on a CNT surface.⁴⁹ The outcome of the PBE0 functional relative to PBE, namely, the decrease of E_B , can thus be associated to a decrease in polarization, which

TABLE I. (10,0)-CNT: NO_x . Binding energies E_B (eV) and minimum distances d (Å). The dimer does not bind to the nanotube in BLYP. Calculations use a 360-atoms-supercell and $k = 0$ in the Brillouin Zone.²⁵

	S-PBE		S-PBE-D2		S-PBE0		S-BLYP		S-BLYP-D2	
	E_B	d	E_B	d	E_B	d	E_B	d	E_B	d
NO_2	0.07	3.22	0.17	2.87	0.04	3.22	0.06	3.40	0.19	2.86
N_2O_4	0.08	3.54	0.28	3.14	0.05	3.27	—	—	0.32	3.12
NO_3	0.63	3.28	0.80	3.08	0.44	3.12	0.69	3.45	0.94	3.06

FIG. 3. (10,0)-CNT: NO_3 . Differential electron density. Isovalue = $0.0001(\text{a.u.})^{-3}$.

correlates with the increase in the CNT energy gap (see below), and to the partial cancellation of the self-interaction which is indeed more effective in NO_3 .

In the case of N_2O_4 , the Bader charge on the molecule is vanishingly small and is consistent with the weak PBE E_B value that essentially reflects the non-linear dependence of the correlation energy on the density. Adsorption must be associated with the van der Waals attraction, as from PBE-D2 and BLYP-D2 calculations. Indeed Grimme's correction to the GGA functionals has the expected effect in all cases, namely, it increases the binding energy and decreases the equilibrium distance.⁵⁰

Additional calculations were performed for NO_3 on the (8,4)-CNT—of diameter similar to that of the (10,0)-CNT—to investigate whether the dependence on the chirality would affect the conclusions drawn above. We found very similar results, namely, with the PBE-D2 functional, $d = 2.9$ Å and $E_B = 0.8$ eV. Regarding the identification of metastable “chemisorbed states” in the proximity of the tube in Ref. 30, we have verified that also for the (10,0) CNT an energy minimum exists (~ 0.5 eV higher than the ground state). This is very shallow as in the other cases.²⁵ Regarding co-adsorption of, e.g., the NO - NO_3 pair, our own calculations confirm the chemisorbed state in the proximity of the nanotube for the (8,0)-CNT, as predicted in Ref. 17, but such a configuration becomes unstable on passing to the (10,0)-CNT. We emphasize that the (8,0)-CNT—and others with diameters of ~ 0.7 nm or less—are peculiar cases, because of the especially enhanced curvature. Also, the energy gap does not follow the well-known trend with varying diameter.

We now turn to investigate the desorption process. In our calculations, the energy variation for large distances—beyond equilibrium—indicated a vanishing barrier for the desorption of either molecule. Therefore, within the approximations of our model, the activation energy for desorption ($E_{a,\text{des}}$) does not exceed the binding energy E_B , at least at low temperatures.

The size range investigated experimentally is larger than what we can afford with accurate *ab initio* calculations. Still, we can understand how the tube size affects the binding energies. We consider the trend on the zig-zag (n,0)-CNTs ($n \geq 9$), within PBE-D2, for both NO_2 and NO_3 . Figure 4(a) shows how the binding energy depends on the nanotube diameter. Both the minimum molecule-nanotube distance and the amount of charge transfer do not vary appreciably from $n = 10$. Therefore, the origin of the changes must be found in those of the intrinsic properties of the nanotubes. The

FIG. 4. (a) Dependence of the binding energy (see text) on the diameter for zig-zag-nanotubes and (b) on the energy gap. Open (filled) circles denote “metallic” (“semiconducting”) nanotubes. Note that some of the “metallic” CNTs have tiny gaps as also reported in Ref. 45. Calculations use 80-atoms-supercell and uniform k-mesh.²⁵ Dashed lines serve as a guide to the eye.

qualitative behavior is the same for both molecules, namely, two different curves can be distinguished: one showing an increase in the binding energy with the increasing diameter, the other nearly insensitive to it. The former corresponds to the “semiconducting” nanotubes ($n = 10, 11, 13, 14, 16, 17, 19$, and 20), and the latter to the “metallic” ones ($n = 9, 12, 15$, and 18). Indeed, the behavior in Figure 4(a) can be associated with the variation of the fundamental energy gap E_g , which is known to scale inversely with the diameter, as explicitly shown in Figure 4(b). We consider E_g as a measure of the electron polarization at the CNT surface, and thus of the polarization interaction. The latter—and consequently E_B —are higher for a metallic CNT at a given size, increase with the diameter for semiconducting CNTs and are almost independent from it for the metallic ones. This finding is in qualitative agreement with the experimental data for the desorption energy of Ref. 18 which is higher for metallic nanotubes. Consistent with our understanding of the binding mechanism, there is an important quantitative difference between the two molecules, with E_B varying by less than 0.1 eV for NO_2 for diameters from 0.8 to 1.6 nm. Therefore, not only the strength of the binding but also its variation with the tube size is more significant for NO_3 . We must realize, however, that not only the absolute values of the energy gaps⁵¹ but also the difference between two cases is underestimated in GGA. For example, on passing from the (10,0)- to the (16,0)-CNT, the energy gaps calculated with hybrid functionals differ by ≈ 0.3 – 0.4 eV, instead of 0.2 eV in GGA. This leads us to predict slightly stronger variations of the binding energy with increasing diameter than in Figure 4(b). Another source of binding enhancement with size can be expected from the variation of the attractive component of the van der Waals interaction (C_6 coefficient),⁴⁰ which is not

accounted for in Grimme’s approximation. On the other hand, an almost size-independent self-interaction correction must be considered (see Table I). In conclusion, the examination of our results leads us to suggest that physisorbed NO_3 could indeed reach a binding energy of ~ 1 eV on semiconducting nanotubes of $D \approx 2$ – 2.5 nm.

Our results are in apparent disagreement with predictions^{17,28} that the binding weakens for increasing size of the nanotube. The reason is however clear: those calculations referred to “chemisorbed states,” for which the bond strength depends on the degree of sp^2 – sp^3 rehybridization of the carbon atoms involved, and thus decreases with the decreasing curvature of the nanotube.³¹

In conclusion, the analysis of our experimental data on contact-passivated individual SWNTs with diameters in the range of 1.5–3.5 nm exposed to 1 ppm NO_2 leads us to establish that the long-living species on the surface of the nanotube have binding energies on the order of 1 eV. Our calculations show that, unless defects are present, it is not necessary to invoke chemisorption to account for it. Physisorbed NO_3 can indeed be expected to be such a long-living species, in contrast with both NO_2 and N_2O_4 which should desorb more easily. Moreover, our study has provided new insights into the nature of the binding of these three oxides, and on the variation of its strength with increasing diameter. We emphasize the electrostatic contribution to the adsorption mechanism, which in cases like NO_3 dominates and can be responsible for binding energies of the order of those of molecular chemisorption. For both NO_2 and NO_3 —although on a different scale—adsorption (desorption) energies must be expected to increase with size (decreasing gap) for semiconducting nanotubes and almost size independent for metallic nanotubes. This behavior is in contrast with the case of chemisorption and could be verified experimentally. Our results challenge the interpretation of the adsorption of these (and similar) molecules also on other carbon nanostructures. However, for a systematic quantitative study, the use of more sophisticated functionals is desirable.

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