

# Carbonyl group generation on single-wall carbon nanotubes with nitric acid: A theoretical description



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## ABSTRACT

The initial steps of single-wall carbon nanotube (SWNT) oxidation in nitric acid were studied using a (6,6) supercell with a mono-vacancy defect and employing spin-polarised density functional theory. According to our results, the geometric changes that occur during the process are significantly localised around the vacancy. The carbonyl group generation does not change the metallic nature of the nanosystem. Vibrational thermal corrections calculated using full and partial Hessian vibrational analysis indicated a small contribution to the reaction energy. An overall favourable oxidation pathway is proposed and includes an initial  $\text{NO}_2^+$  exothermic electrophilic attack followed by an endothermic oxaziridine formation.

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## 1. Introduction

Due to the chemical inertia of pristine (as-synthesised) carbon nanotubes (CNTs), activation steps are necessary prior to chemical modification [1]. In this sense, oxidative processes should be highlighted as a procedure for purification, removing amorphous carbon and catalyst particles, and surface activation [2]. According to some studies, oxidation occurs preferably at the positions of greatest stress [3–6]. Furthermore, cuts may be made on the tube surface, resulting in open-ended structures or holes in the tube walls [7].

Studies of CNT oxidation may result in many benefits, including (i) improvement in purification processes, (ii) an increase in solubility, (iii) higher chemical reactivity, (iv) new strategies for chemical functionalisation and (v) insights into reaction mechanisms for carbon-based compounds. The interaction of oxidising reagents with CNTs, similar to the oxidation of alkenes, may result in the formation of C–OH, C=O, C–O–C, and O=C–OH functional groups [8,9]. The presence of these groups is often verified by infrared [10] and XPS [11] spectroscopies. A large number of commonly used oxidising agents and their structural consequences have been addressed in the literature. The most common oxidants include air [6],  $\text{O}_2$  [12–15],  $\text{O}_3$  [16–18], HCl [19],  $\text{HNO}_3$  [6,9,20–21], and  $\text{H}_2\text{SO}_4/\text{HNO}_3$  [22]. Each oxidant has intrinsic characteristics and promotes distinct structural changes, which are not completely understood at the molecular level, although these processes date back to the mid-1990s [23]. Nonetheless, the products of these reactions are

commonly used as reagents for further chemical processing, for example, for the insertion of amines on the surface of the nanotubes [24]. Among the main oxidising species, the most important are  $\text{HNO}_3$  (generally preferred due to its minimal damage on the CNT structures) and  $\text{H}_2\text{SO}_4/\text{HNO}_3$  (this mixture is often more destructive) for liquid phase processes. These species provide purification of as-grown CNTs as well as surface functionalisation with oxygen-containing groups [8,22].

The experimental procedures used to obtain oxidised single-wall carbon nanotube (SWNT) in aqueous solution may involve heating to reflux [21], sonication [25], sonication followed by reflux [26], and hydrothermal autoclaving [8]. For nitric acid, the main products are oxygenated functional groups whose chemical identities and quantities depend on the reaction conditions [21]. According to Gerber et al. [21], for multi-wall carbon nanotube (MWNT) in reflux with an aqueous nitric acid solution (65% v/v) at 393 K, the oxidation reaction starts with the formation of carbonyl groups, which reach a maximum concentration after 1 h. After this, lactones, anhydrides, and carboxylic functional groups are generated. The phenol formation follows a parallel reaction process. Moreover, according to the authors, after four hours, the concentration of surface groups remains nearly constant. After 2 h of reaction, the functional groups are present in the following order: phenol > carbonyl > carboxylic > anhydride > lactone. Despite its chemical importance, the carboxylic group is not dominant. According to Romanos et al. [8], for SWNTs that are hydrothermally treated with an aqueous nitric acid solution (1.25% v/v) in an autoclave at 473 K, a similar order is observed, namely, phenol > carboxylic > lactone > anhydride > carbonyl. For both SWNTs and MWNTs, the phenol group is present in the greatest concentration.

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According to published studies [22,27,28], for both  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4/\text{HNO}_3$  reagents, the  $\text{NO}_2^+$  species acts as the oxidising agent. Cabria et al. [29], using a density functional theory (DFT) solid state approach, observed that  $\text{NO}_2^+$  ion binds strongly to a perfect armchair (4,4) SWNT through a charge transfer mechanism, producing significant structural deformities in the vicinity of the adsorbed nitronium ion. The role of the counterion was also investigated ( $\text{BF}_4^-$ , for a nitronium tetrafluoroborate salt as the oxidising reagent). According to the authors, the anion does not play a primary role in the oxidation of SWNTs. Gerber et al. [21], using nanoflakes with a mono-vacancy defect (usually labelled v1) as a model to mimic CNTs, proposed a possible role of the  $\text{NO}_3^-$  species (through a nucleophilic attack) in oxidation reactions, thus broadening the range of possibilities for the respective mechanism. That particular vacancy defect has been widely studied in recent years, mainly due to its influence on chemical [30,31] and physical properties [32,33]. In addition, Kim et al. [34] showed that the nitronium hexafluoroantimonate salt (NHFA) can be used as a strong p-type dopant on SWNTs due to a charge transfer process from the SWNT to the  $\text{NO}_2^+$  ion. Therefore, these oxidation processes may be useful in the technological applications of CNTs.

Given the importance of the oxidation processes of CNTs, in the present letter, the first step for carbonyl group formation was studied. The system chosen was an armchair (6,6) supercell (labelled a(6,6) hereafter) with a mono-vacancy defect. The computational methodology employed was the periodic boundary conditions (PBC) as implemented in the Quantum ESPRESSO (QE) package [35]. The oxidising agent used was the nitronium ion ( $\text{NO}_2^+$ ) resulting from an acid–base  $\text{HNO}_3$  dissociation. Structural, electronic, vibrational, and thermodynamic properties were calculated and discussed.

## 2. Calculation methodology

All *ab initio* calculations were performed using the Quantum ESPRESSO distribution [35] using spin-polarised DFT with a plane-wave basis set to represent the one-electron wave functions of the Kohn–Sham equations. The Vanderbilt ultrasoft pseudopotentials [36] were used to describe the core electrons, and the

**Table 1**  
Structural and electronic parameters used in the quantum calculations.

General informations about the nanosystem	
Chirality	Armchair (6,6)
Nominal diameter	8.14 Å
Defect	Reconstructed mono-vacancy
Minimum formula	$\text{C}_{71}^{\text{a}}(\text{C}_{71}\text{H}_2\text{O}_6\text{N}_2)^{\text{b}}$
<i>Structural parameters used</i>	
$a = b, c$	18.00 Å, 7.39 Å
$\alpha = \beta = \gamma$	90.0°
<i>Self-consistency fied (SCF), ionic and cell convergence thresholds</i>	
SCF	1.0 $\mu\text{Ry}$
Forces for ionic minimization	1.0 mRy $a_0^{-1}$
Pressures for cell optimization	0.5 kbar
Total energy	0.1 mRy $\text{atom}^{-1}$
<i>Cutoff energies and k-point mesh</i>	
Plane-wave cutoff kinetic energy	25 <sup>c</sup> (40) <sup>d</sup> Ry
Charge-density cutoff energy	200 <sup>c</sup> (320) <sup>d</sup> Ry
k-Point mesh ( $k_x \times k_y \times k_z$ ) <sup>e</sup>	1 × 1 × 8

<sup>a</sup> The isolated and reactive systems, respectively.

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<sup>c</sup> Preprocessing (e.g. structural optimizations) and post-processing (e.g. phonon calculations at gamma point) jobs, respectively.

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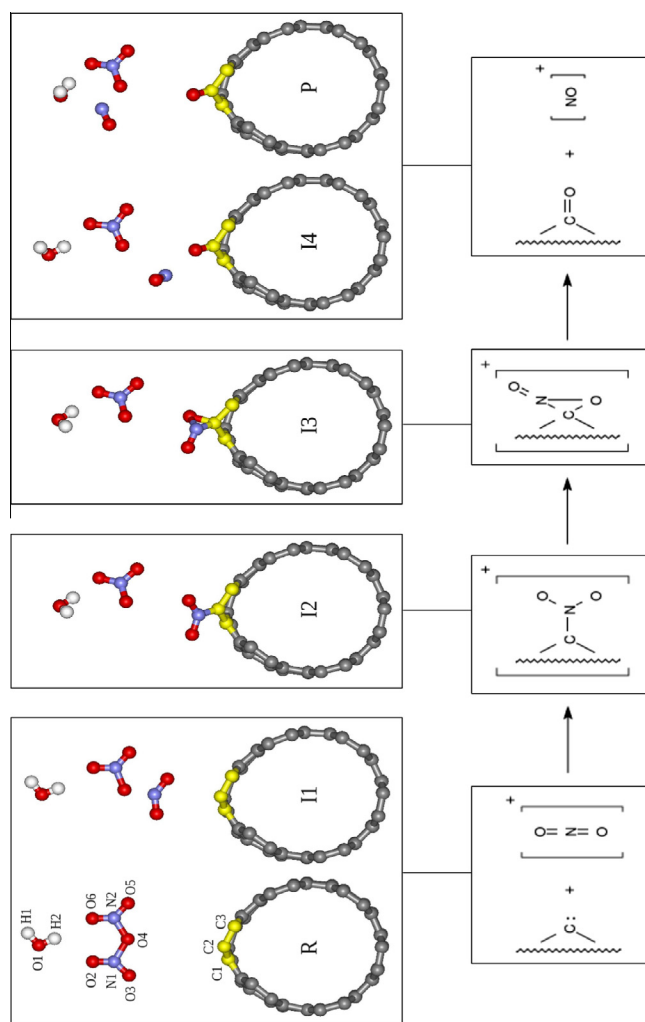
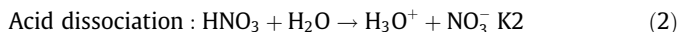
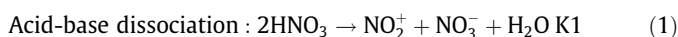
<sup>e</sup> Determined by the Monkhorst–Pack procedure.

PW91 generalised gradient approximation functional [37] was used to describe the exchange–correlation potential for the valence electrons. The additional technical details are summarised in Table 1.

## 3. Results and discussion

### 3.1. The SWNT + $\text{HNO}_3$ reaction model

For the CNT model, a supercell of an armchair (6,6) containing 71 carbon atoms was used. It included a reconstructed vacancy defect (v1) [38] to represent the topological defect, usually produced as-synthesised [3]. A greater supercell would be more representative of the ‘real’ system but would require too much computational power. Considering the oxidising environment, the first step is to define which species are available in the aqueous nitric acid solution. Initially, the following main processes can be considered Eqs. (1) and (2):



**Figure 1.** A schematic representation of the proposed chemical process (a transverse section of the structures are depicted). Only the highlighted carbon atoms (yellow colour) were included in the partial Hessian vibrational analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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