

Atomic Oxygen Chemisorption on Carbon Nanotubes

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Introduction

The task of our research within the CabTuRes project is that of investigating, within a joint theoretical and experimental effort, the effects of functionalization on the electronic and mechanical properties of single-wall carbon nanotubes. So far we have considered two limiting cases: hydrogen and oxygen at low concentration. This poster focuses on our more recent results on oxygen chemisorption, and refers to our published results on hydrogen chemisorption for comparison.

Carbon Nanotubes (CNTs) show a high chemical sensitivity to atomic oxygen [1]. Despite a rich variety of experimental results, theoretical results are fragmentary and do not provide a coherent picture. Criticism on the model dependence of the calculations was raised in [2]. Here we present calculations based on large-scale density-functional theory (DFT) and STS experiments aimed at investigating the changes induced by oxygen chemisorption on the structural and electronic properties of two CNTs of different chiralities.

Methods

Theory: DFT calculations [3] were performed in the Perdew-Burke-Ernzerhof (PBE, [4]) approximation for the exchange-correlation (xc) functional, using norm-conserving (Martins-Troullier) pseudopotentials and valence electron wavefunctions were expanded in plane waves up to a 100 Ry cutoff. Our model systems contain up to 360 and 336 carbon atoms for the (10,0) and (8,4) CNTs respectively.

Experiment: The chemisorption sites are produced under ultra high vacuum conditions (i.e. at base pressures of better than 10^{-10} mbar). In this procedure SWNT are individually dispersed on a clean gold (111) surface. Then molecular hydrogen or oxygen is thermally cracked to atomic H or O respectively. The exposure of the SWNT to the atomic species leads to the formation of chemisorption sites, which can be detected as hillocks in scanning tunnelling microscopy images. The local density of electronic states (LDOS) can be measured by scanning tunnelling spectroscopy (STS) at low temperatures. By recording a series of STS spectra along the axis of the SWNT containing a chemisorption defect the electronic signature at the chemisorptions site can be characterized and compared to the pristine regions of the SWNT. In the case on H and O such defect sites are characterized by "impurity states" which are localized in energy and position.

Results

Structures and Energetics

E_b : binding energy w.r.t. to CNT + triplet O
 E_d : deformation energy of the tube induced by chemisorption
 E_c : energy gain due to clustering (referred to 1a)

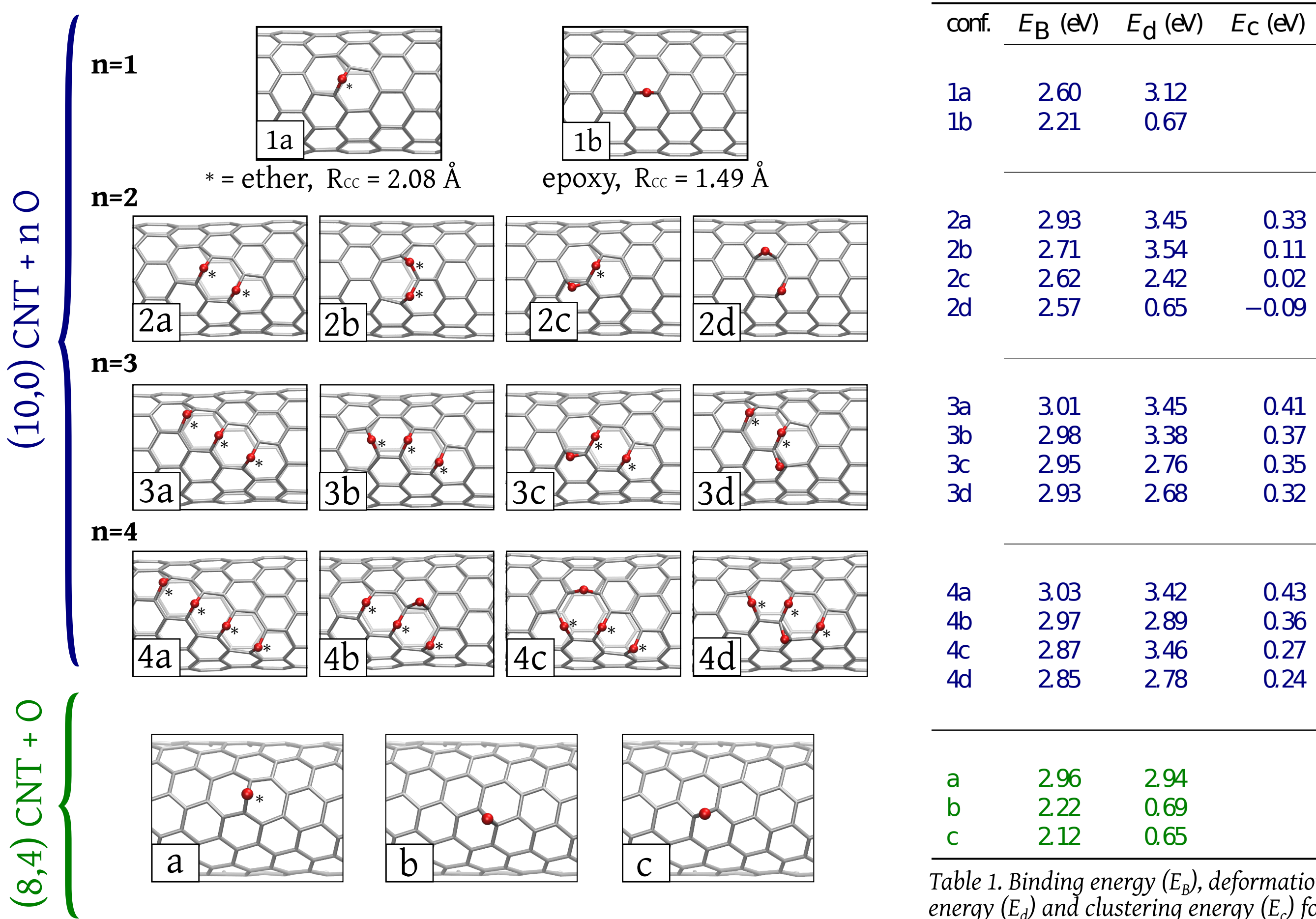


Table 1. Binding energy (E_b), deformation energy (E_d) and clustering energy (E_c) for the (10,0) and (8,4) CNT.

Ether (ET) vs. Epoxy (EP):

Strong Model Dependence from Tables 2 and 3

(10,0) - n=1 (PBE)

Our calculations:

Model I: PBC 360C (k=0); Model II: H-terminated - 360C + 40H; Model II': H-terminated - 240 C + 40H; Model III (Ref. [5]) PBC 40C (80 k points)

- Model II allows for more extended structural relaxation reducing edge stress: ether-epoxy energy difference decreases by 0.2 eV.
- Model II' shows convergence with respect to size.
- Ref. [5] uses a localized basis set. We have repeated these calculations within our computational scheme and obtained the same results.

(8,4) - n=1 (PBE)

Model A: PBC 336 C; Model B (Ref. [5]) PBC 112 C (30 k points)

N.B. in Ref. [6]: $\Delta E = 0.02$ eV for the (8,0) CNT (PW91; PBC 32 atoms; 12 k points)

Oxygen vs. Hydrogen [7]

- Oxygen induces much stronger changes on the CNT surface (deformation energies up to ~3 eV with ET groups)
- Both O and H atoms tend to cluster but energy gains are lower in the case of oxygen
- Hydrogen adsorbates with different structures exist with comparable binding energies from n = 3 on. Oxygen adsorbates show a clear preference for open ET structures.

	ΔE_{ab} (eV)	
Model I	0.39	
Model II	0.16	
Model II'	0.16	
Model III	0.02	

Table 2. Energy difference between ether and epoxy for different (10,0) CNT models. Ether is favored.

	ΔE_{ab} (eV)	ΔE_{ac} (eV)
Model A	0.74	0.84
Model B	0.85	0.90

Table 3. Energy difference between ether and epoxies on the (8,4) CNT.

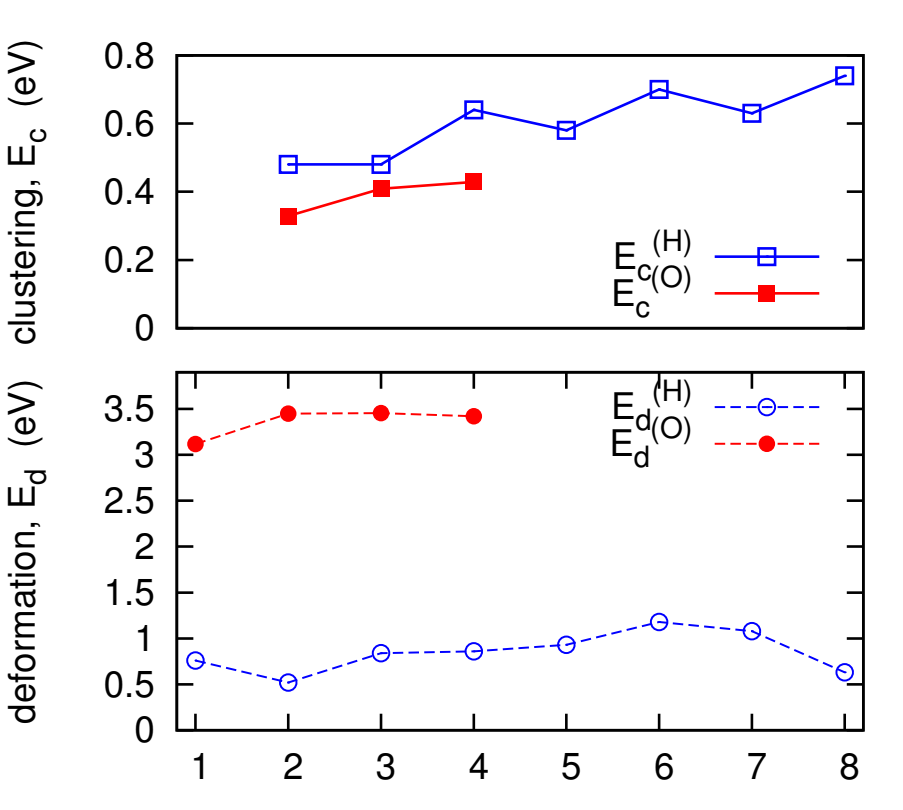


Fig. 1 - Clustering and deformation energies for the most stable oxygen CNT configurations compared to results on hydrogen chemisorption.

Electronic Density of States (DOS) : can we distinguish ETs and EPs?

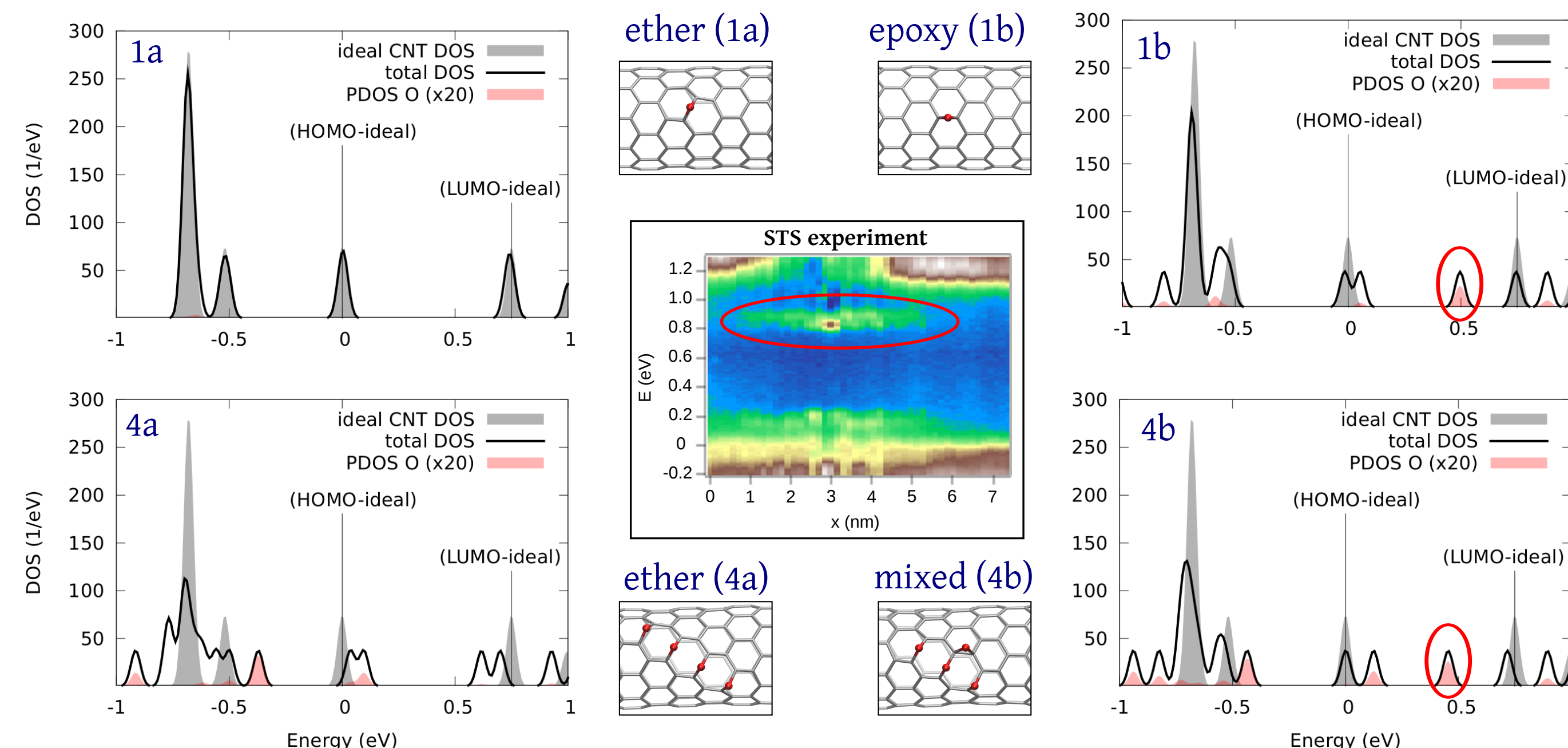


Fig. 2 - (10,0) CNT with oxygen: DOS and oxygen-projected DOS compared with the pristine CNT.

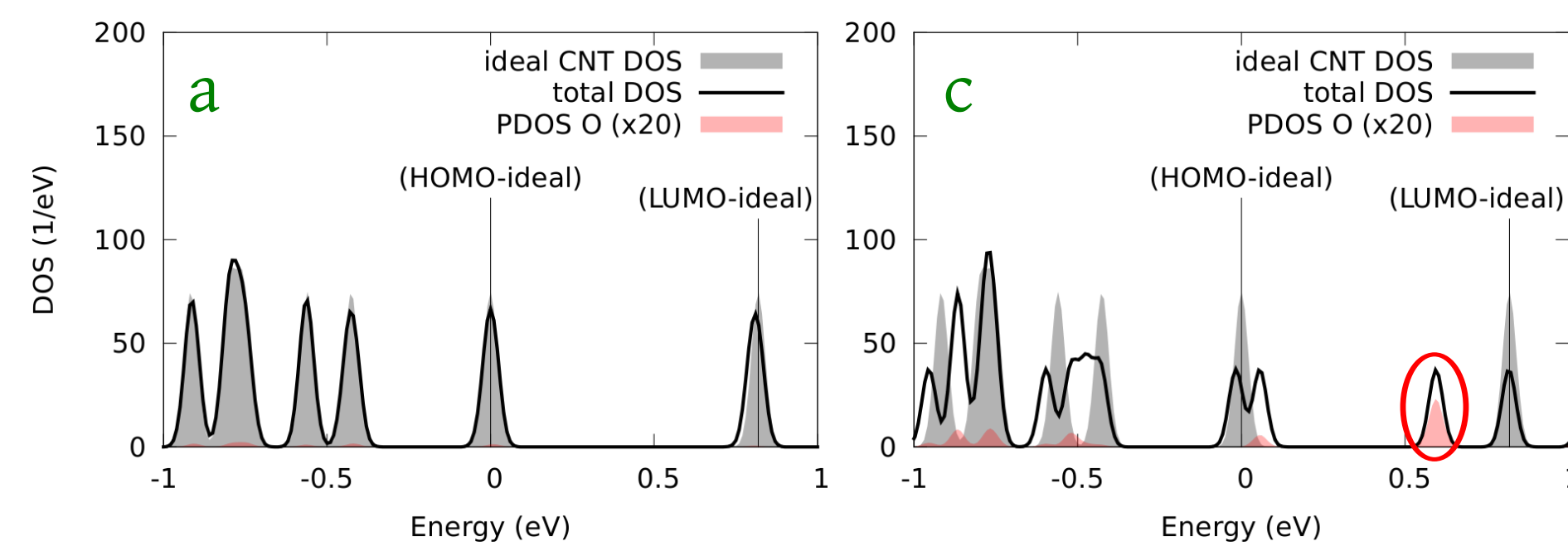


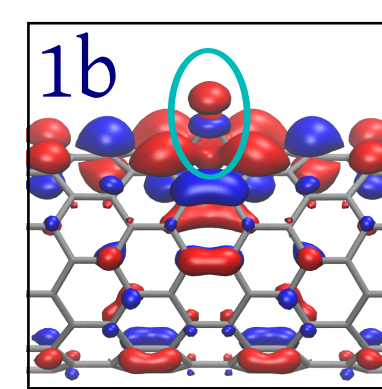
Fig. 2 - (8,4) CNT with oxygen: DOS and oxygen-projected DOS compared with the pristine CNT.

Figures 2 and 3 show

- No sign of ET at band edges: not visible in STS
- Midgap level: fingerprint of EP

The "impurity" state

Is the state in the gap localized on the defect?



The KS state corresponding to the midgap level corresponds to the combination of the oxygen lone-pair and CNT orbitals

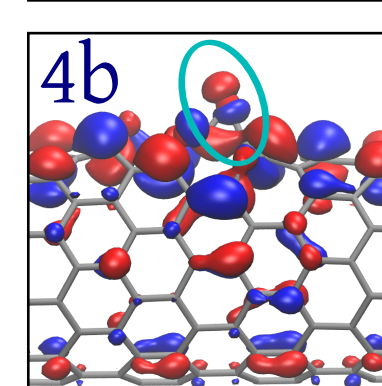
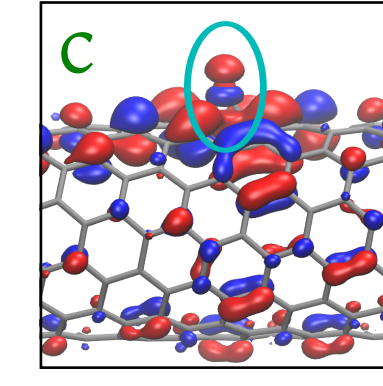


Fig. 4 - Wavefunctions of the impurity states marked in Fig. 2 and 3 for the (10,0) (left) and (8,4) CNT (right).



Why Epoxy?

Thermodynamically the ether is strongly favored: Why do experiments show epoxy?

(10,0) (model I):

Calculations using the nudged elastic band (NEB) method [8] indicate an energy barrier of approx. 1 eV for the oxygen transition from EP (1b) to ET (1a).

Kinetic Trapping

Conclusions

- DFT calculations show that on CNTs oxygen is preferentially chemisorbed in open (ET) configurations but 3-membered rings (EP) can be kinetically trapped on the surface.
- Only EPs generate midgap levels that can be detected with STS experiments.
- ETs tend to cluster as found in the case of H chemisorption [7].
- The O-binding pattern is different with the one calculated for graphene [9].

Warning: An accurate theoretical description of hydrogen and oxygen chemisorption is not trivial. First-principles simulations are mandatory for reliable predictions. One important requirement is the use of large-scale models that allow for an appropriate account of the (long-range) structural relaxation of the nanotube.

Next: We will complete the study of the migration and reaction dynamics of oxygen on the surface of the tube. Also vibrational spectra will be calculated to investigate to what extent they can distinguish the different structures of the oxygen adsorbates. The effects of chemisorption on mechanical properties will be examined also in conjunction of the on-going development of a novel reactive force-field.

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