

Dramatic Reduction of IR Vibrational Cross Sections of Molecules Encapsulated in Carbon Nanotubes

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1. Introduction: Molecular Encapsulation in Carbon Nanotubes (CNTs)

- Applications: molecular carrier, sensor, nanoreactor, ... (Figure 1)
- Characterization methods: TEM, IR, Raman, NMR
- Encapsulation can be easily confirmed by shift in IR or Raman spectra of the encapsulated molecule. However, the signal intensity is considerably decreased.
- The polarization of π -electrons of CNTs can screen electric fields and act as a Faraday cage. This effect has been known for molecules adsorbed on metallic surfaces.¹

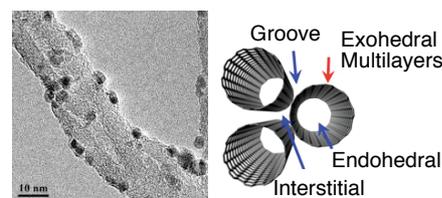


Figure 1. Rh catalyst encapsulated in CNTs and possible incorporation sites of SWCNTs.

Screening Effect of IR Absorption of Molecules Adsorbed on the Surface of a Conductor

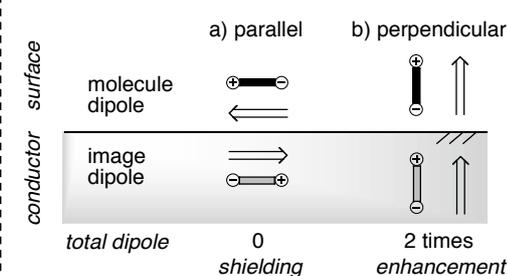
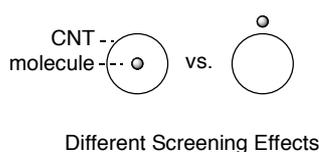


Figure 2. Changes during the vibration of a dipole near the surface of a conductor.

- IR absorption occurs when the vibration or rotation of the molecule causes a change in the dipole moment.
- Dipoles parallel or perpendicular to the surface of a conductor produces virtual-image dipoles (Figure 2).
- The image dipole change can cancel or strengthen the dipole change originating in the vibrating molecule (= screening effect).



Different Screening Effects

This Work: theoretical studies of the screening effect of the different incorporation sites of SWCNTs and determination of the main incorporation site by comparison with experimental data

2. Previous Work: Acetone Adsorption to Single-Walled Carbon Nanotubes (SWCNTs)²

- Adsorption of acetone molecules to SWCNTs can be applied as a chemical sensor.
- Adsorption was measured by temperature programmed desorption MS (TPD-MS) (Figure 3).

=> Adsorption energy can be measured by the intensity of the mass signal of acetone after increase of the temperature of the sample (2 K s^{-1}).

- Two peaks were obtained in the TPD-MS spectrum of acetone-SWCNTs complex (Figure 4a). These peaks could be assigned by comparison with reference samples (carbon black).

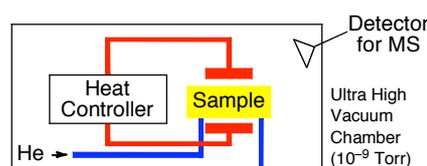


Figure 3. Schematic image of TPD-MS measurement.

1. Weakly adsorbed acetone (140 K, w): exohedral and multilayer sites
2. Strongly adsorbed acetone (300 K, s): groove, interstitial and endohedral sites

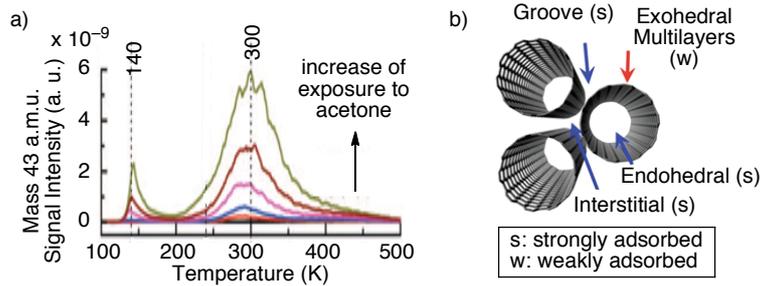


Figure 4. (a) Encapsulation sites of a bundle of SWCNTs. (b) Desorption of acetone from purified SWCNTs annealed at 900 K and exposed to 1 to 100 langmuirs* of acetone. * Langmuir = unit of exposure to a surface; 1 langmuir = 10^{-6} Torr exposure during one second.

3. This Work: Redution of IR Signal of Encapsulated Molecules in SWCNTs

3.1. Experimental Studies: Relation between Desorption Energy and IR Absorption

- *TPD analysis* (Figure 5a):

- intensity ratio of weakly adsorbed acetone (w) and strongly adsorbed acetone (s) = 1:9.

- *IR analysis* (Figure 5b)

- 90% decrease of IR intensity after flash heating to 200 K
- 10% decrease would be the expected value (TPD-MS)

=> strongly adsorbed molecules suffer much stronger screening

- *Generality:*

- same result was obtained lower quality CNTs (non-purified and multi-walled CNTs)

- diethyl ether and heptane showed the same behavior

=> all IR modes are screened to a similar degree

=> orientation of the molecule does not play a crucial role for screening effect

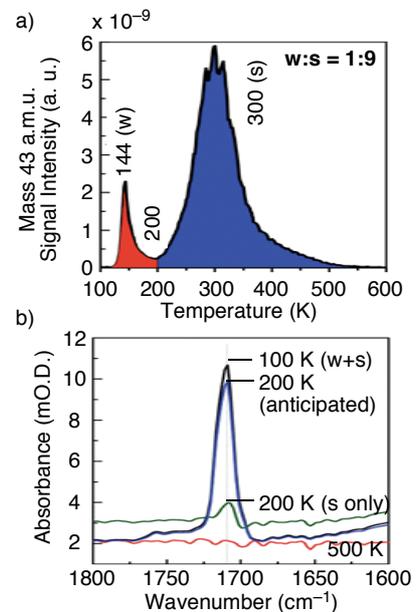


Figure 5. (a) TPD-MS spectrum of acetone desorption from purified SWCNTs after 100 langmuir dose. (b) IR cross-section of the $\nu(\text{C}=\text{O})$ mode of acetone before and after flash heating. s = strongly; w = weakly.

3.2. Theoretical Studies

3.2.1. Considerations for Calculations

- Self-consistent-charge density-functional tight-binding (SCC-DFTB-D) method was used.

- Two types of semiconducting chiral SWCNTs were considered

- 1) model S: small diameter of 7.7 Å; chiral indice (6,5)

- 2) model L: large diameter of 14.0 Å, chiral indice (11,9)

- Calculated values:

- Δq (induced Mulliken charges): charge fluctuations upon formation of acetone-SWCNTs complex

=> intensity of screening effect

- δq (dynamic charge fluctuations): variation of atomic partial charges during the C=O bond stretch
=> change in the intensity of screening effect during C=O bond stretch

• Dipole moment (μ) and IR spectrum (A) can be calculated from Δq and δq (Equations 1 and 2).

$$\mu_j = \sum_A q_A X_{Aj} \quad (\text{Equation 1}), \quad A_i = K \left(\frac{v_i}{\omega_i} \right) \left[\left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \right] \quad (\text{Equation 2})$$

3.2.2. Calculation Studies (1): Endohedral and Exohedral Sites

- Endohedrally adsorbed acetone: IR activity is strongly suppressed (Table 1a, Figure 6a1)
- Exohedrally adsorbed acetone: IR intensity depends on acetone alignment to CNTs wall
 - PP position (planar parallel): small suppression of IR intensity (Table 1b, Figure 6a2)
 - UP position (perpendicular): increase of IR intensity (Table 1c, Figure 6a3)

screening effect: endohedral >> exohedral

Table 1. Schematic images of charge fluctuation after complex formation. Maximum value for charge fluctuation after complex formation and variation of atomic charges during C=O bond stretch. * Dipole values are given relative to gas phase acetone dipole moment set to unit.

	a) endo_S	b) exo_S_PP	c) exo_S_UP
Δq	0.027	0.015	0.006
δq	0.002	0.005	0.006
μ (dipole)*	0.006	0.651	1.312

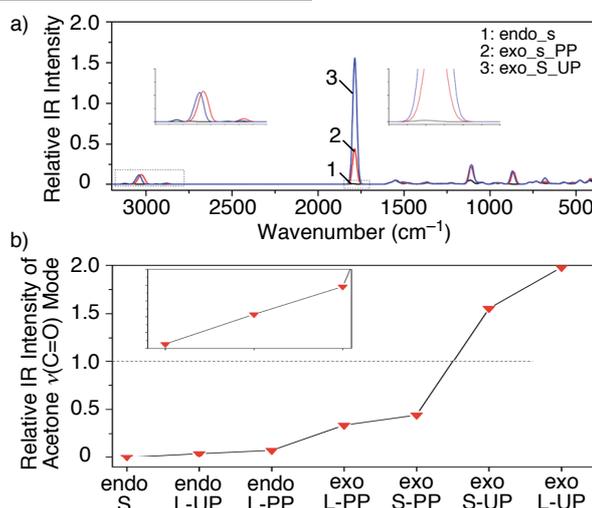


Figure 6. (a) Theoretical IR spectra of endo_S, exo_S_PP, and exo_S_UP. (b) Theoretical IR intensities of acetone $\nu(\text{C}=\text{O})$ at 1796 cm^{-1} in different acetone-SWCNTs complexes. IR intensities are given relative to gas phase acetone $\nu(\text{C}=\text{O})$ band scaled to unity.

• Size of SWCNT affects the efficiency of shielding (Figures 6b and 7)

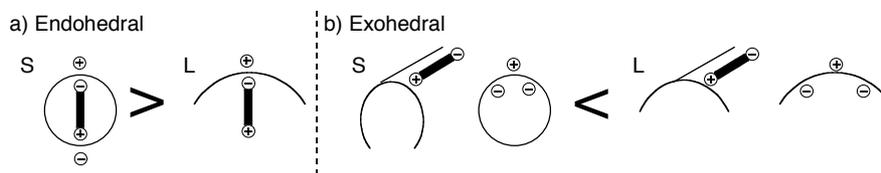


Figure 7. Effect of curvature of SWCNTs in the screening effect.

3.2.3. Calculation Studies (2): Groove and Interstitial Sites

- Δq and δq of groove and interstitial adsorptions are of the same order as in the case of single-tube exohedral complexes (Table 2).
- Groove sites: IR signal reduction/enhancement depends on the orientation of the C=O bond (similar to exohedral adsorption site) (Table 2a, b and Figure 8a1, 2).

- Interstitial sites: competition between the IR signal enhancement and reduction due to simultaneous UP and PP orientations => reduction of IR signal (Table 2c, Figure 8a3).

Table 2. Schematic images of charge fluctuation after complex formation. Maximum value for charge fluctuation after complex formation and variation of atomic charges during C=O bond stretch. * Dipole values are given relative to gas phase acetone dipole moment set to unit.

	a) groove_SS_PP	b) groove_SS_UP	c) interstitial_SSS
Δq	0.022	0.006	0.011
δq	0.002	0.001	0.002
μ (dipole)*	0.726	1.198	0.767

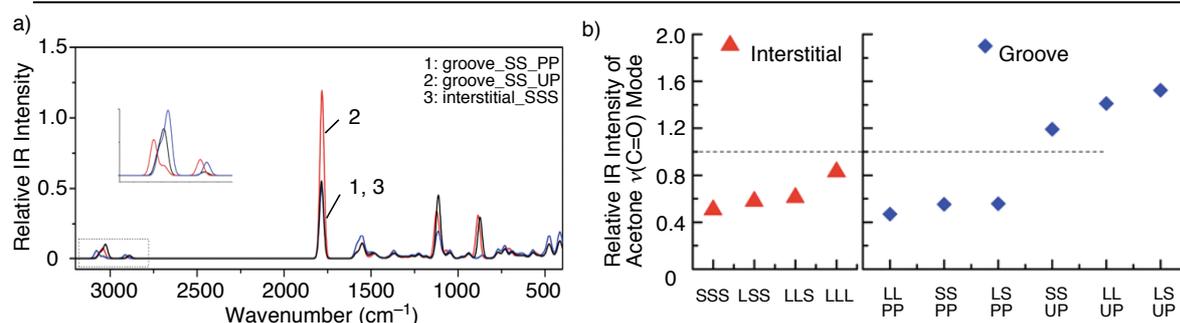
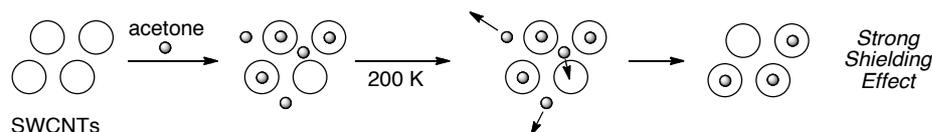


Figure 8. (a) Theoretical IR spectra of groove_ss_PP, groove_ss_UP, and interstitial_sss. (b) Theoretical IR intensities of acetone $\nu(\text{C}=\text{O})$ at 1796 cm^{-1} in different acetone-SWCNTs complexes. IR intensities are given relative to gas phase acetone $\nu(\text{C}=\text{O})$ band scaled to unity.

4. Discussion

- Experiment: 90% decrease in IR signal after heating to 200 K
- Theory: reduction of the intensity of $\nu(\text{C}=\text{O})$ vibration mode of acetone
(endohedral site = 90% decrease) vs. (exohedral, groove, interstitial sites = max. of 50% decrease)
=> *strongly adsorbed acetone molecules are located mainly in endohedral sites* (Scheme 1)

Scheme 1. Adsorption of acetone in SWCNTs and desorption after heating to 200 K.



- This result is consistent with the uniform screening of all vibrational modes of acetone.

5. Conclusion

- Intensity of screening effect was determined to different adsorption sites of SWCNTs.

endohedral >> exohedral (PP), groove (PP), interstitial >> exohedral (UP), groove (UP)

- Intensity of screening effect was used to determine the main incorporation site of encapsulated molecules.

References

1. Pearce, H. A.; Sheppard, N. *Surf. Sci.* **1976**, *59*, 205.
2. Kazachkin, D.; Nishimura, Y.; Irle, S.; Morokuma, K.; Vidic, R. D.; Borguet, E. *Langmuir* **2008**, *24*, 7848.