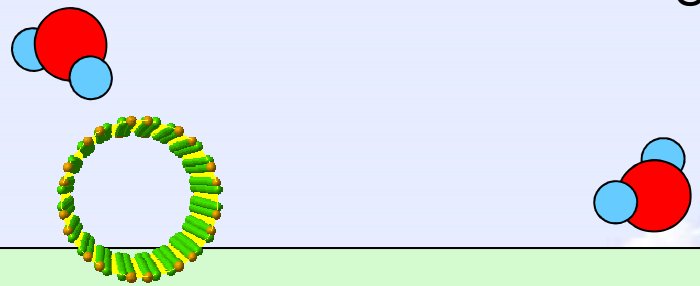
Workshop on Molecular Thermal Engineering
Univ. of Tokyo
2013. 07. 05



Interaction between Single-walled Carbon Nanotubes and Water Molecules

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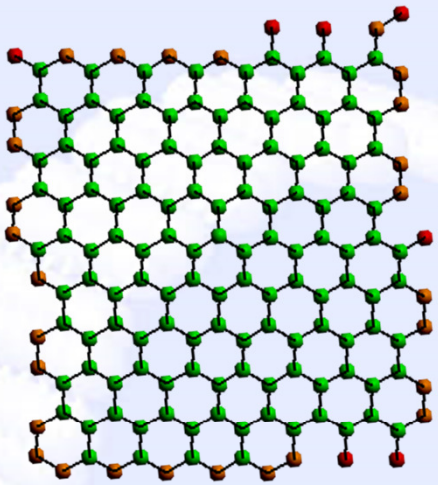
Outline

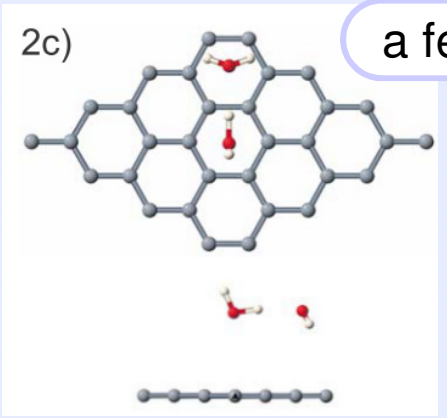
1. Background
2. Objective
3. Methods (experiment and simulation)
4. Results & Discussion
   4.1 Spectroscopy (PL & Raman)
   4.2 MD Simulations
5. Conclusions

SWNT & Water Molecules



- large aspect ratio
- large specific surface
- one atomic layer

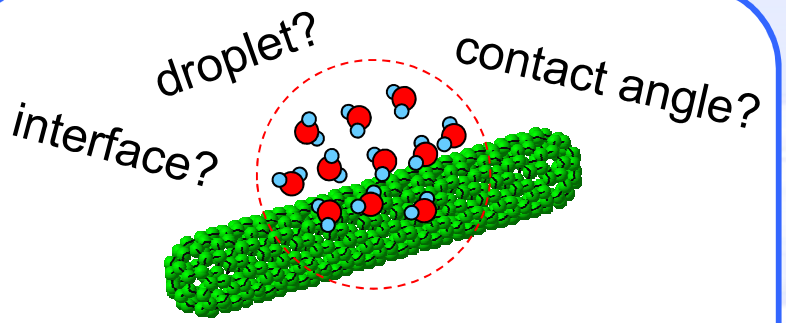
single-walled carbon nanotube (SWNT)



a few molecules

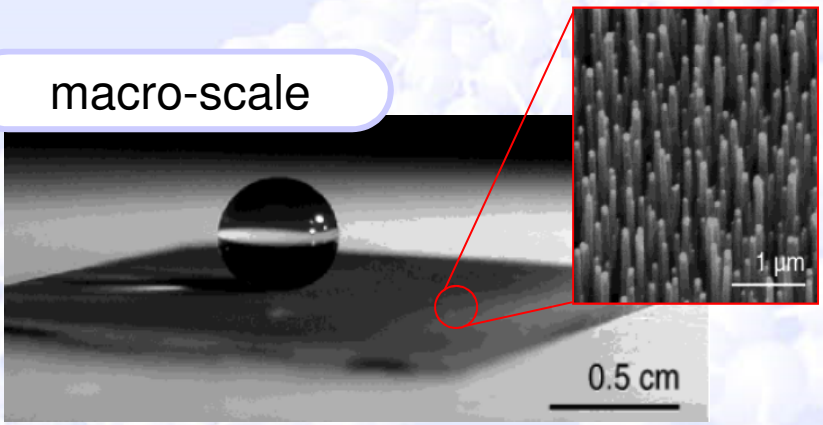
Adsorption energy per molecules:
1 - 2 kJ/mol
(DFT cal.) [1]

Interaction between a few water molecules and graphene.



hydrophobicity (wettablity) of SWNTs in **nano**-scale

macro-scale



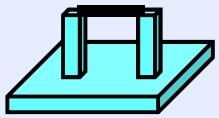
Water drop on CNT carpet. [2]
high contact angle -> “hydrophobic”

[1] O. Leenaerts, et al., *Phys. Rev. B* **79** (2009) 235440.
[2] K. K. S. Lau, et al., *Nano Lett.*, **3** (2003) 1701.

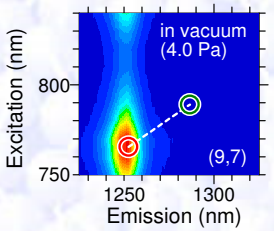
Objective

Investigation of the interaction between an **SWNT** and **water molecules**

by using

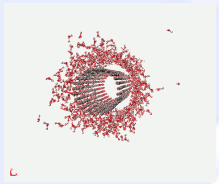


suspended SWNTs [1],



photoluminescence (PL) spectroscopy,

Raman scattering spectroscopy,



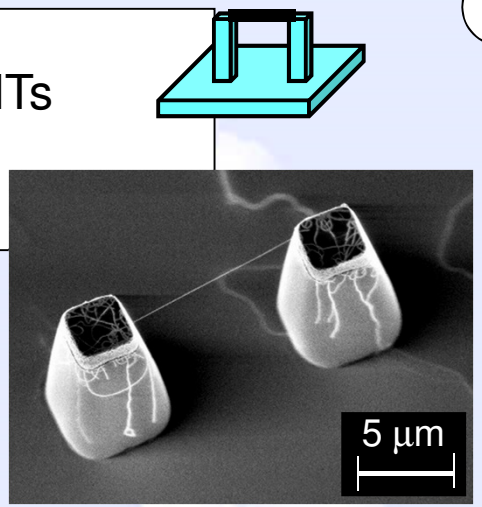
and **molecular dynamics** (MD) simulation

[1] Y. Homma, S. Chiashi, Y. Kobayashi, *Rep. Prog. Phys*, **72** (2009) 066502.

Methods (Experiments & Simulation)

SWNT sample

- suspended SWNTs
  length: 7 μm,
  diameter: 1 nm



SEM image of suspended SWNT.

MD simulation

- NTV emsemble
(SCIGRESS ver. 2.3, Fujitsu Ltd.)
- H_2O: SPC/E force field
- SWNT: Tersoff
- carbon-H_2O: Universal force field [1]

[1] A. K. Rappe, et al., *JACS* **114** (1992)10024.

PL

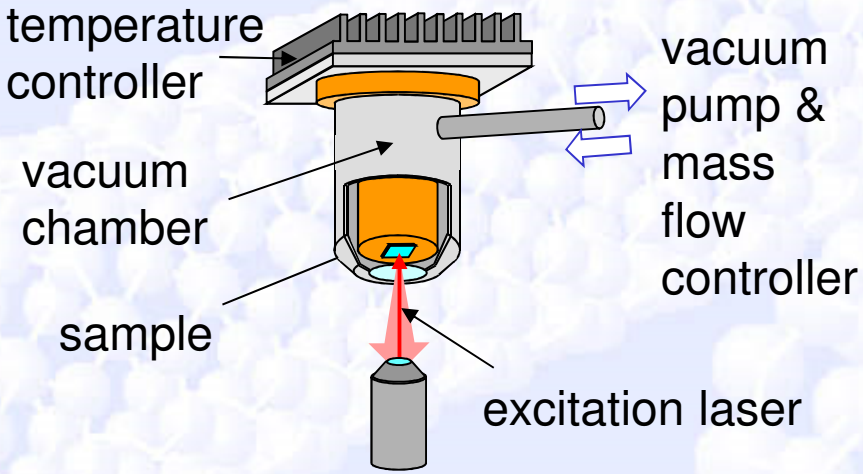
- excitation: 690-830 nm
- emission: 1000-1600 nm

Raman

- excitation: 785 nm

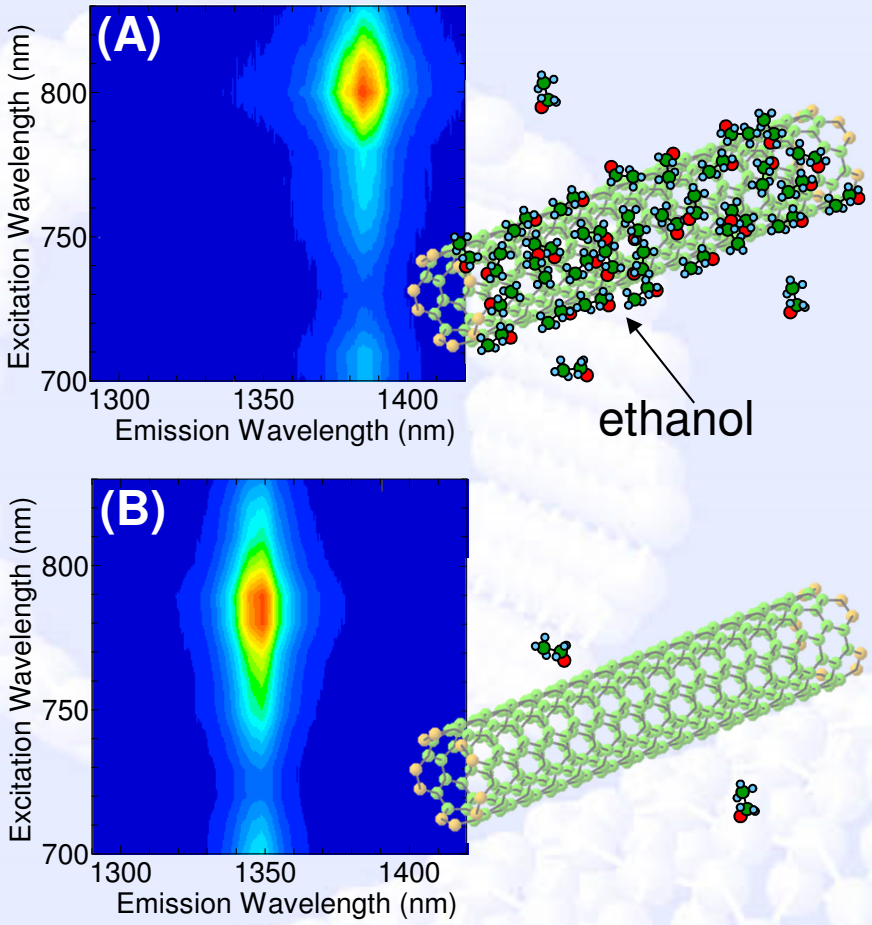
Conditions

- temperature: -15 to 80 °C
- gas atmosphere: water

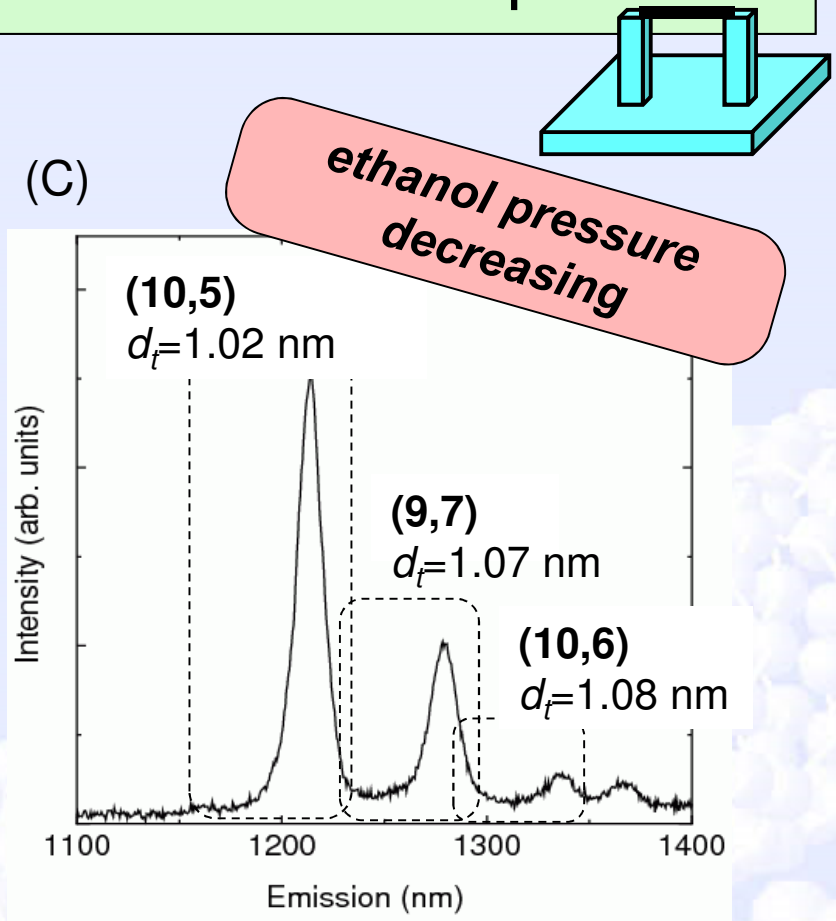


Schematic illustration of the environmental PL & Raman scattering measurement system.

Ethanol Gas Pressure Dependence of PL Spectra



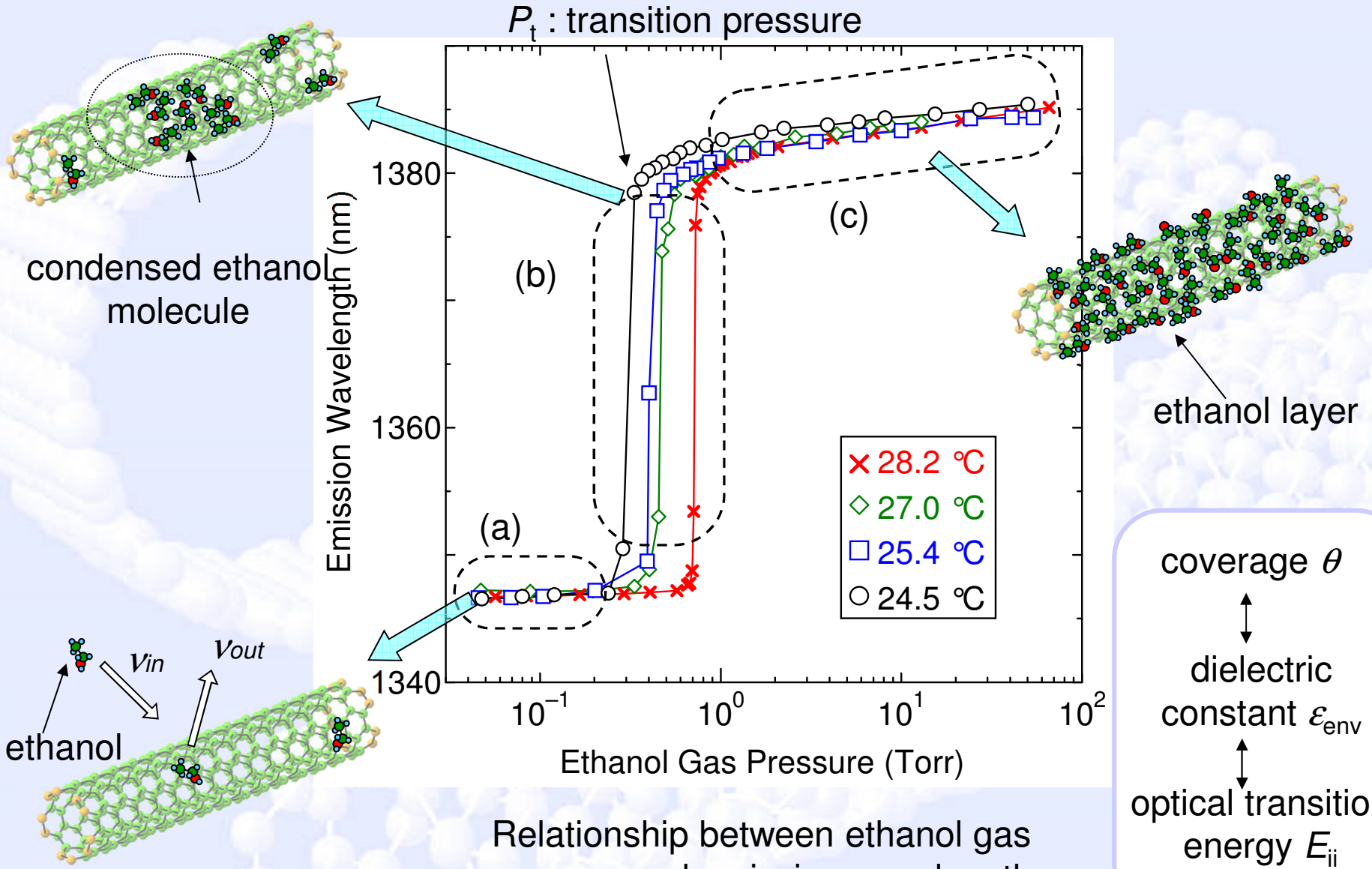
PL mapping of (9,8) SWNT (A) in ethanol gas atmosphere and (B) in vacuum.



PL spectra measured with decreasing ethanol gas pressure.

S. Chiashi, S. Watanabe, T. Hanashima, Y. Homma, *Nano Letters* **8**(2008) 3097.

Adsorption and Desorption of Ethanol Molecules



coverage θ

↕

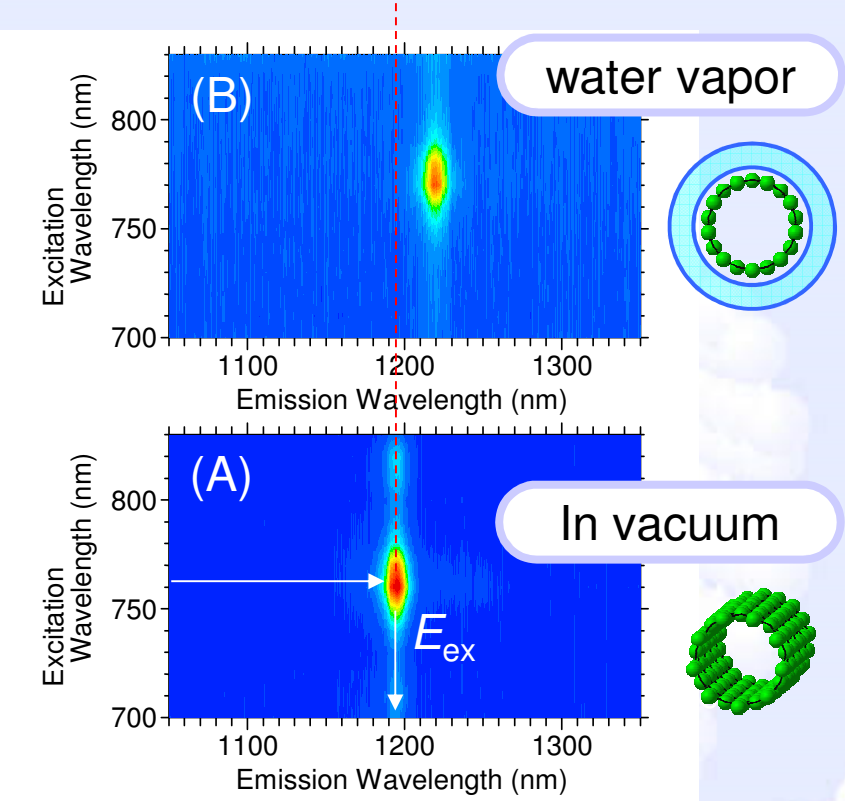
dielectric constant ε_{env}

↕

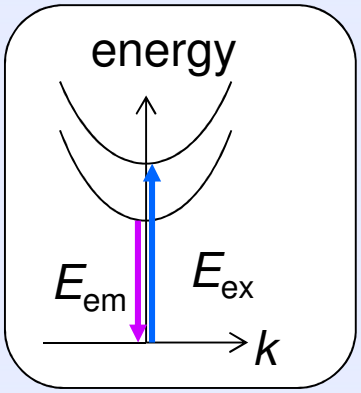
optical transition energy E_{ii}

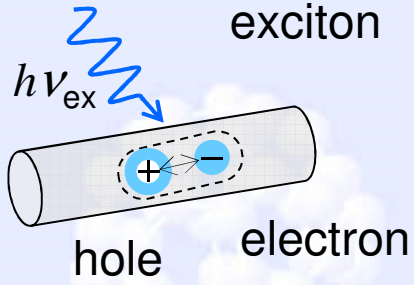
Relationship between ethanol gas pressure and emission wavelength.

PL maps in Vacuum & Water Vapor



PL maps from suspended SWNT measured in (A) vacuum and (B) water vapor.





Coulomb interaction between electron and hole

$$F = \frac{q_1 q_2}{4\pi} \frac{1}{\varepsilon} \frac{\hat{r}}{r^2}$$

(binding energy of the exciton: ~100 meV)

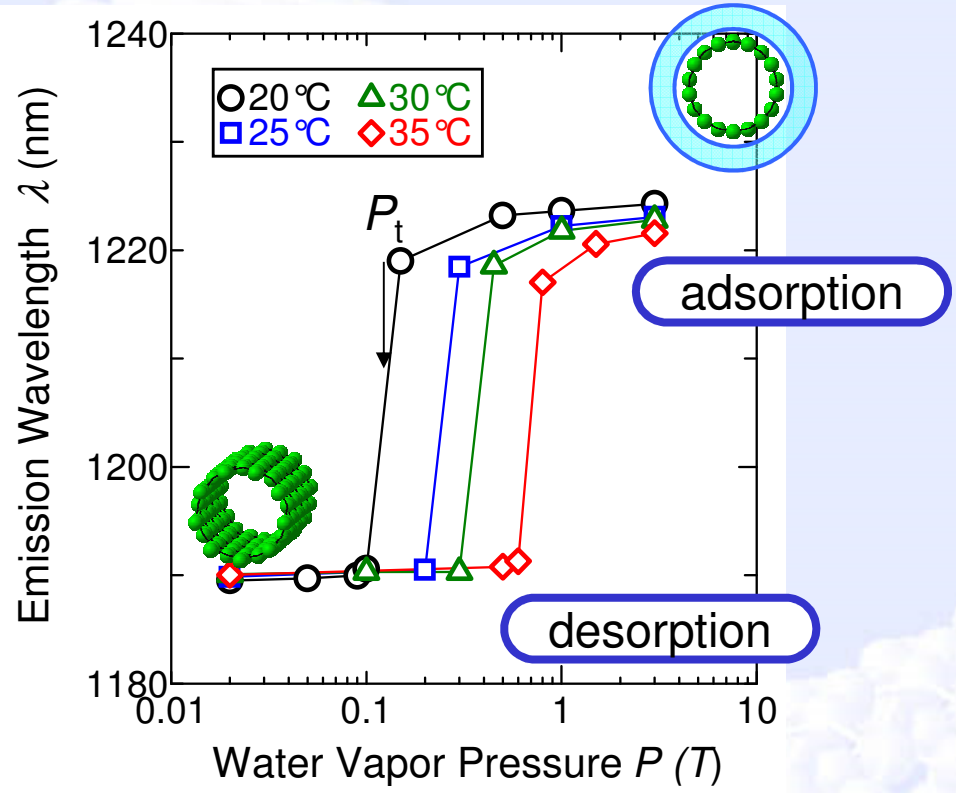
ε : dielectric constant (electron polarization)
"*environmental effect*" (ε_{env})

PL spectroscopy molecular adsorption effect on PL spectra [1]
-> water molecules adsorb on SWNT surface

[1] S. Chiashi, Homma, et al., *Nano Lett.* **8** (2008) 3097.

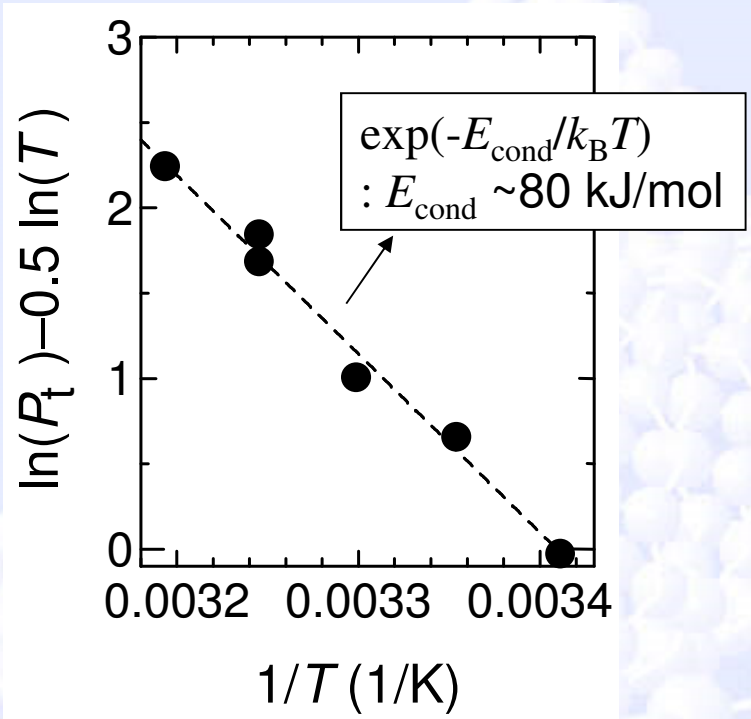
Temp. & Pressure Dependence

P_t: transition pressure



Temperature (T) and water vapor pressure (P) dependence of emission wavelength.

(heat of evaporation of bulk water: 44 kJ/mol at 25 °C)



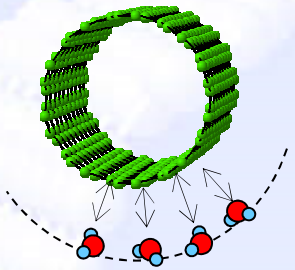
Temperature dependence of the transition pressure (P_t).

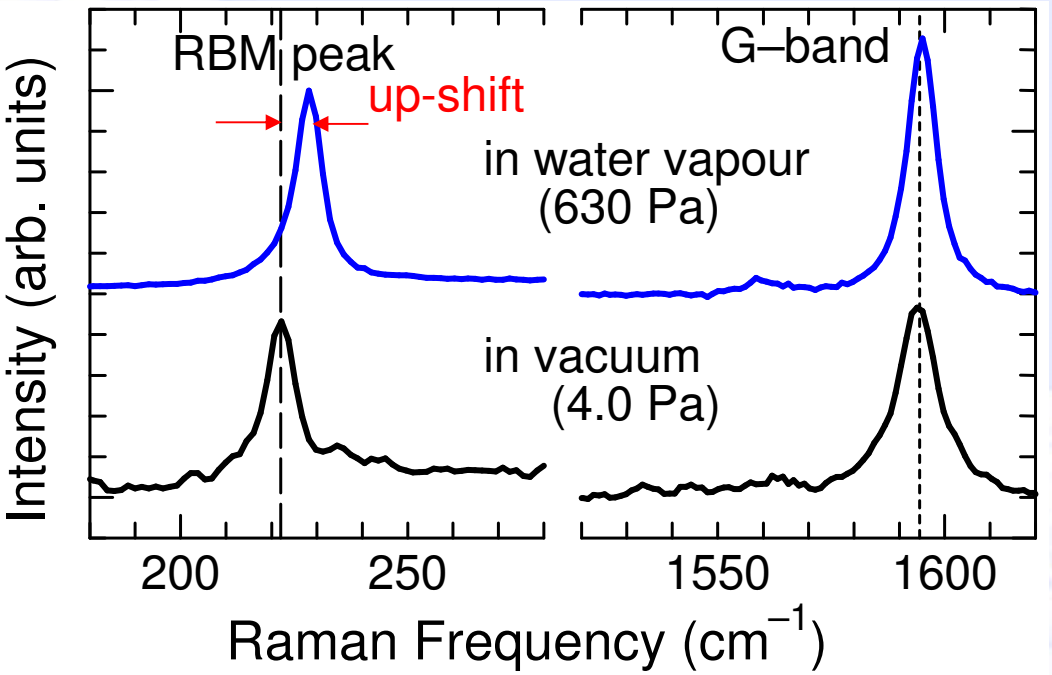
water molecules show a transition phenomenon on SWNT surface

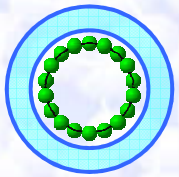
(extremely large condensation energy)

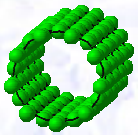
Raman Scattering Spectroscopy

RBM: radial breathing mode







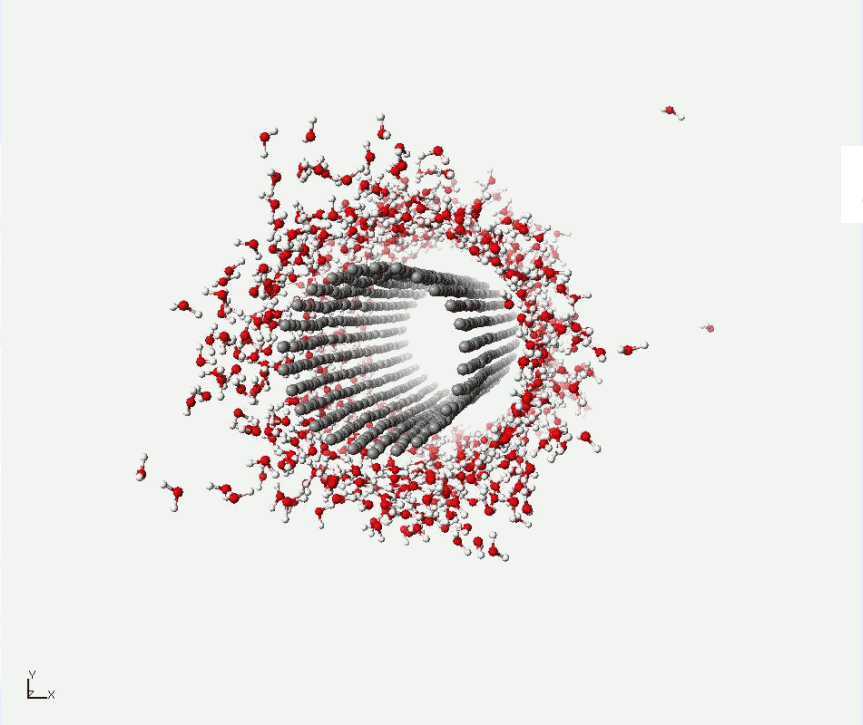


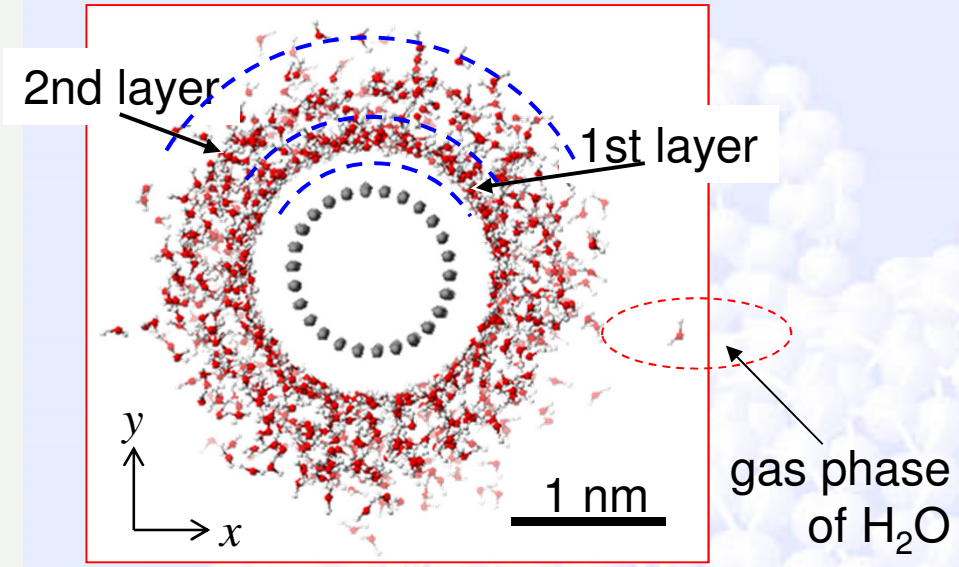
Raman scattering spectra from SWNT measured in vacuum and water vapor.

water molecules mechanically affect the vibration property of SWNTs

the up-shift of RBM peak indicates that water molecules uniformly adsorb on the SWNT surface

Adsorption Layer (MD Simulation)





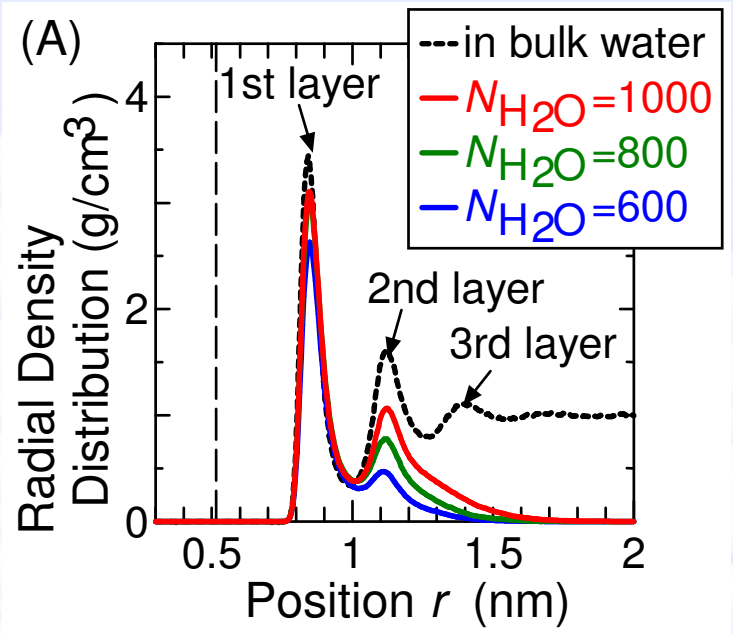
Snapshot of MD simulation of water molecules on an SWNT (13,0) at 25 °C.

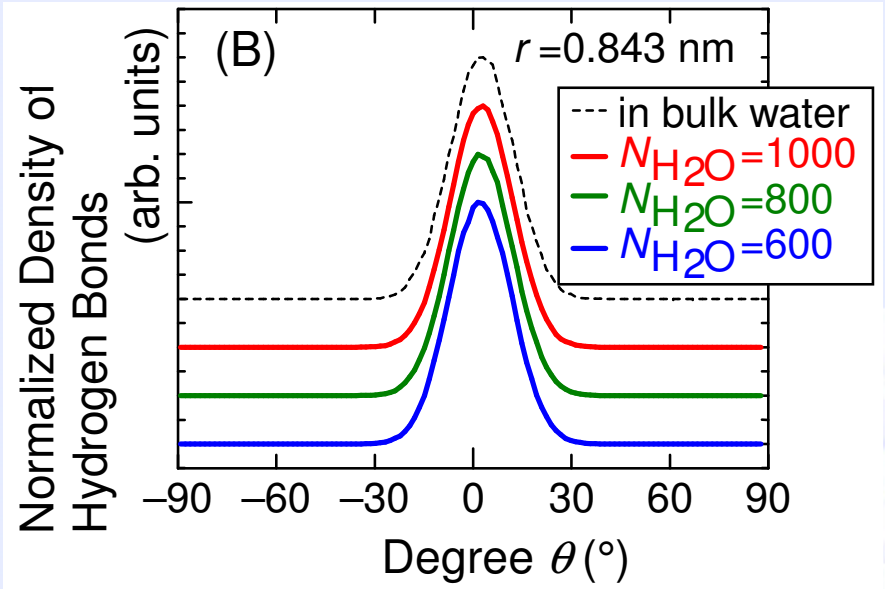
water molecules form adsorption layer on SWNT,

which is hydrophobic!

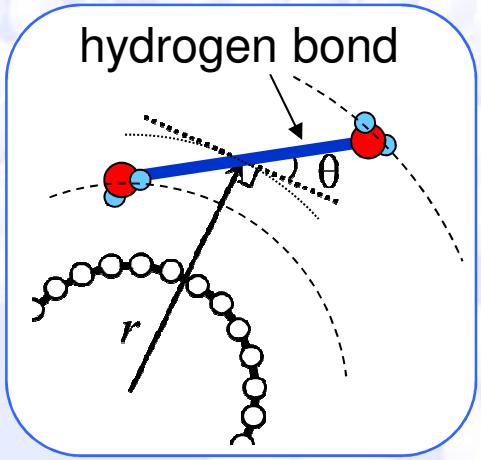
(uniform and thermally stable adsorption layer)

Structure of the Adsorption Layer (MD Simulation)





(A) Radial distribution functions of water molecules around SWNT in a water vapor. (B) Angle distribution between hydrogen bonds in the 1st layer and the tangential plane of the tube surface.



Water molecules form adsorption layer with lateral hydrogen bonding.

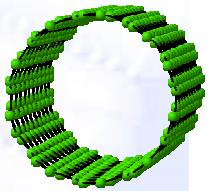
the origin of the stability, large condensation energy?

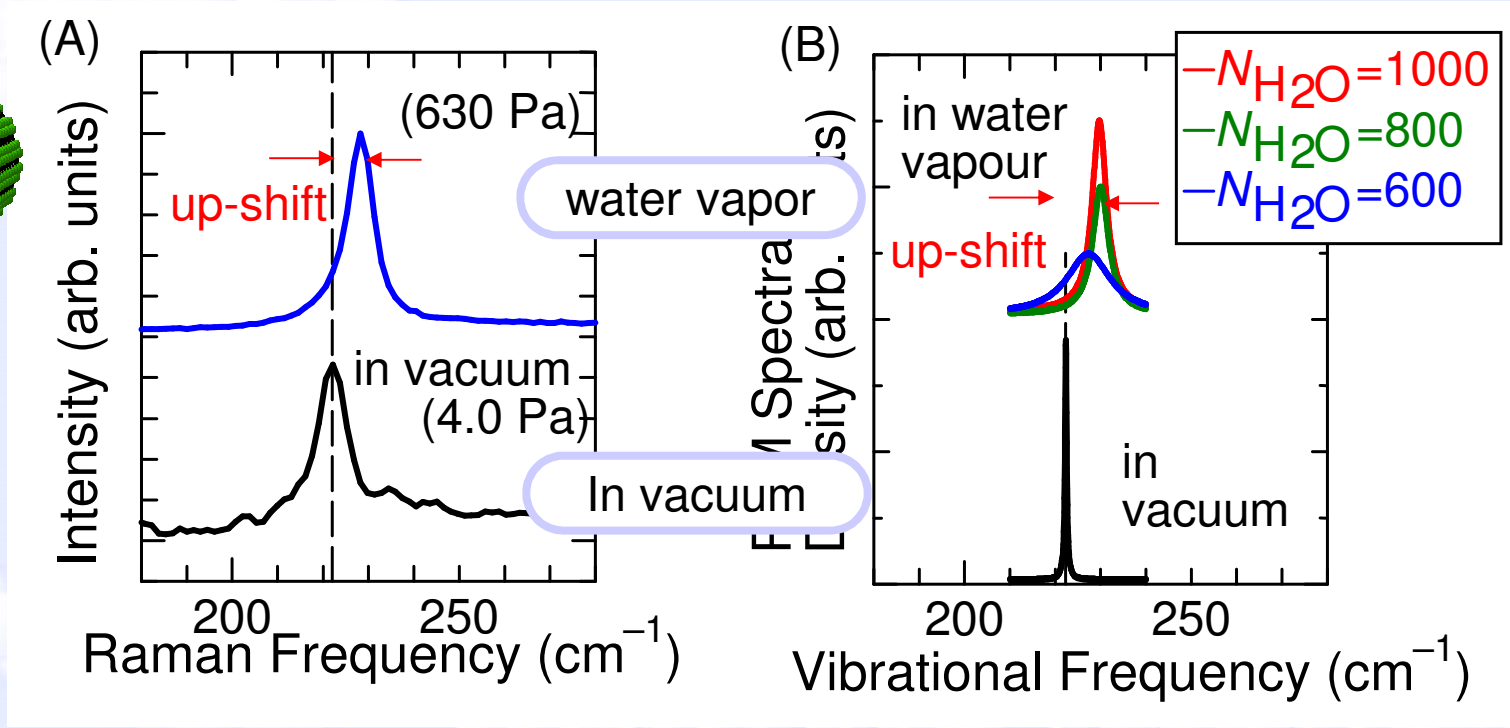
Comparison between Exp. & Sim.

RBM peak

Experiment

MD simulation





(A) Experimentally measured RBM peak and
(B) calculated radial breathing mode frequency.

quantitative agreement between **experimental** and **simulation** results

Conclusions

1. PL and Raman scattering spectroscopy indicate that water molecules adsorb on SWNT surface.[1]
2. MD simulation clearly elucidate the structure of the adsorption layer.[1]
3. Although the interaction between SWNT surface and water molecules is week, water molecule form stable and uniform adsorption layer on SWNT surface. [1]

[1]Y. Homma, S. Chiashi, T. Yamamoto, et al., *Phys. Rev. Lett.*, **110** (2013) 157402.