Challenges with Young Colleagues for Structural Adsorption Science

Structural Adsorption Science on Molecules and Ions in Nanopore Spaces

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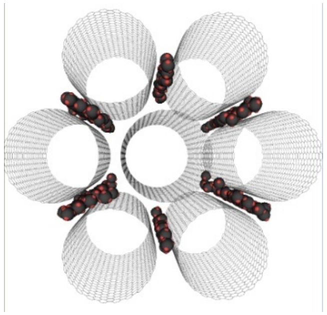
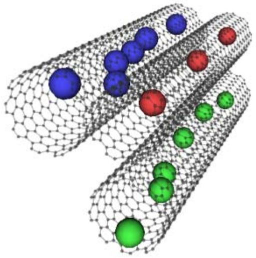
SAASAA at San Luis, Argentina
18-22 February, 2013





An Essentially Important Role of Young researchers (Students) in Structural Adsorption Science

Chiba University, Japan: 24 years

Structural adsorption science

Project in Shinshu University :3 years

Application of nanospaces
to sustainable materials science

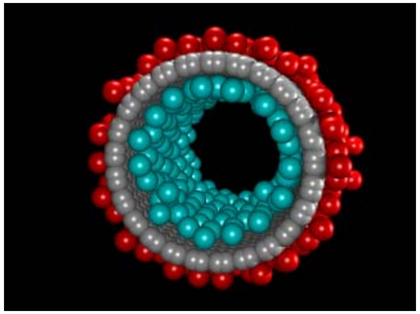
Nanospace Molecular Science (Structural adsorption science) to Nanospace Sustainalble Science

Guide for my Presentation

Why I start to study "Nanospace molecular science"

or "Structural adsorption nanoscience" ?

Nanospace concept



Challenges with young colleagues

in Adsorption Areas

Past

Recent

Application to

sustainable materials

science

Sea-front
Chiba University for 39 years

to Mountain area
Shinshu University

Nagano

Shinshu

In Mountains

Tsunami

Tokyo

Chiba

Narita
Airport

Mt. Fuji

Why I Start Adsorption Studies on Nanopores?

What is the most promising area for me in Chiba

in *1985*

Intensive interests

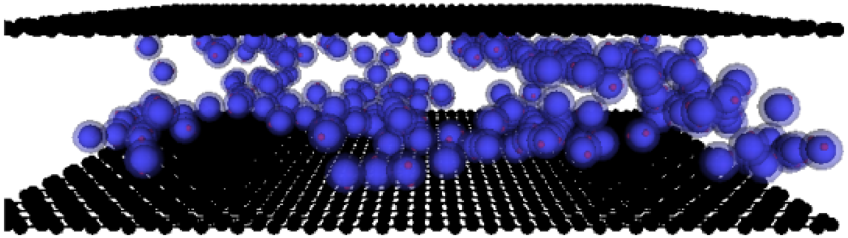
in Solid state physics and Molecular science

Surface Science is the most attractive for me

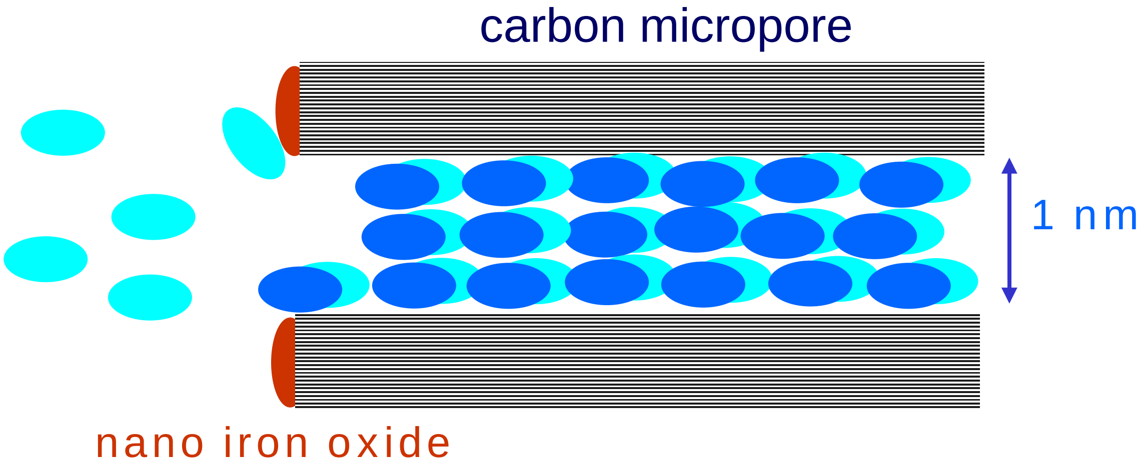
----- Real research situation gave a new direction

to avoid a hopeless competition

“Studies on hidden surfaces and molecular systems confined in nanoscale pores”



Research Seed for Future Adsorption Studies



Supercritical NO transforms into vapor with dimerization $(NO)_2$

NO adsorption amount > 30 % of adsorbent weight

Carbon (1986) *J. Chem. Phys*. (1987)

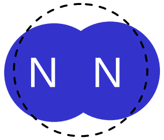
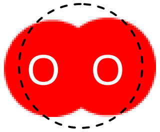
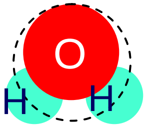
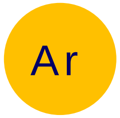
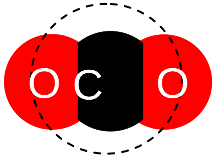
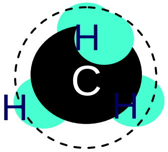
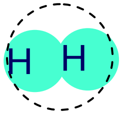
Big questions

What is "Micropore filling of supercritical gas" ?

➡ **Studies on Adsorption**

How can we understand "micropore structure in disordered solid " ? ➡ **Studies on Carbon**

Molecules in Atmosphere *“Treasure of Human”*

	content/vol. %	structure	size
N_2	78		0.36 nm
O_2	21		0.34 nm
H_2O	< 4		0.32 nm
Ar	0. 9		0.33 nm
CO_2	0. 036		0.38 nm
CH_4	0. 00017		0.37 nm
H_2	0. 00005		0.29 nm

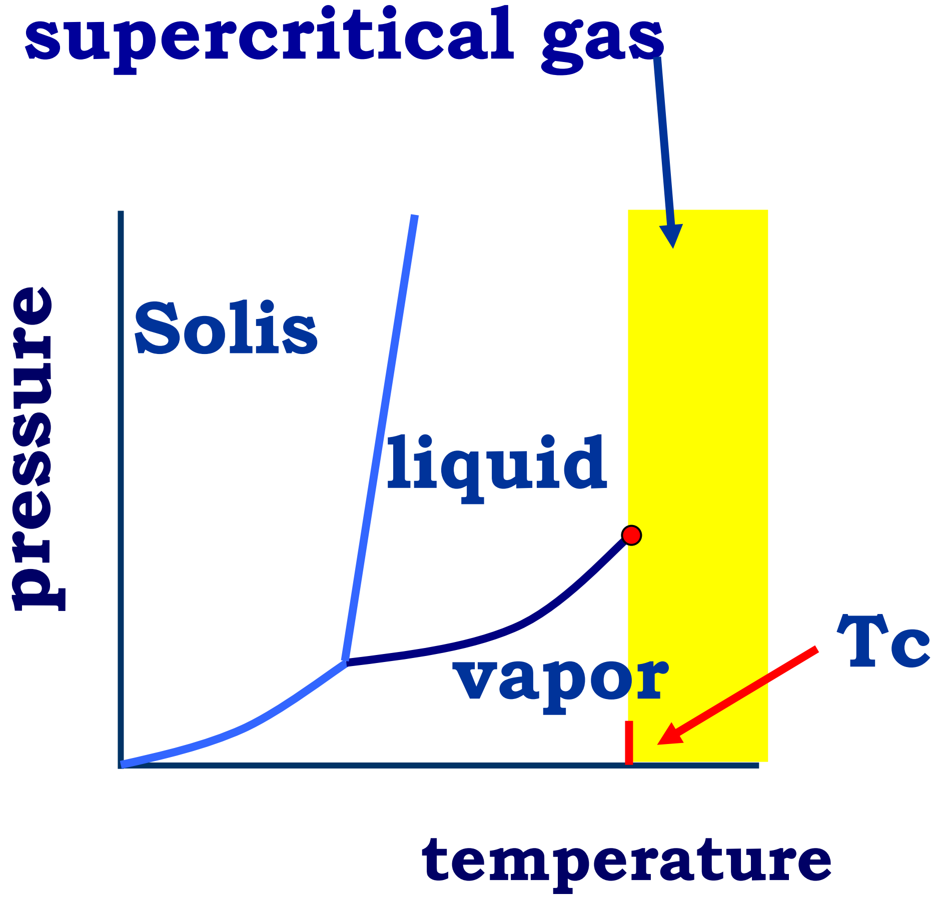
http://image.search.yahoo.co.jp/

Properties of Important Gases

Molecule	T_b	T_c	P_c	σ_{ff}	ε_{ff}/k_B	Multipole moment	Magnetism
	K	K	MPa	nm	K		
H_2	20.3	33.0	1.29	0.292	38.0	*quadrupole* $+2.1 \times 10^{-40}$	*diamag*
O_2	90.2	154.6	5.04	0.338	126.3	*quadrupole* -1.33×10^{-40}	*paramag*
N_2	77.3	126.2	3.39	0.363	104.2	*quadrupole* -4.90×10^{-40}	*diamag*
NO	121.4	180	6.48	0.347	119	*dipole* 0.158×10^{-30}	*paramag*
CO	81.6	132.9	3.50	0.359	110	*dipole* 0.112×10^{-30}	*diamag*
CO_2	194.7	304.2	7.48	0.376	245.3	*quadrupole* -14.9×10^{-40}	*diamag*
CH_4	111.6	190.5	4.60	0.372	161.3	*octapole*	*diamag*

Here T_b, T_c, and P_c are the boiling temperature, critical temperature, and critical pressure. The units of *dipole* and *qu*adrupole moments are Cm and Cm^2, respectively. Although NO and CO have the quadrupole moment in addition to the dipole moment, their quadrupole moments are omitted. "*diamag*" and "*paramag*" denote diamagnetism and paramagnetism.

Supercritical Gases and Vapors



No saturated vapor pressure P_0 for supercritical gases

Critical temp.

H_2 33 K

CH_4 196 K

Four categories of gas-solid interaction

Storage-related concepts

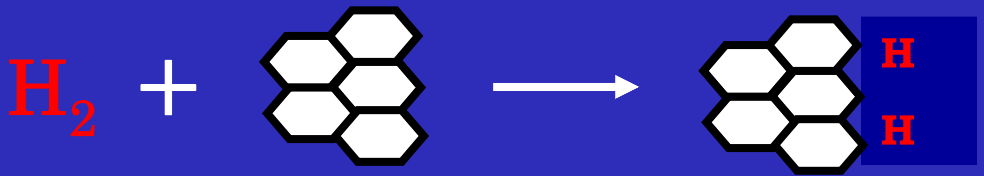
	Structural change	
	molecule	solid (not surface)
Physical adsorption	**none**	**none**
Chemisorption	change	none
Absorption	none	change
Occlusion*	change	change

*(narrow concept of storage)

- Kaneko's classification

Chemisorption, Occlusion, Absorption

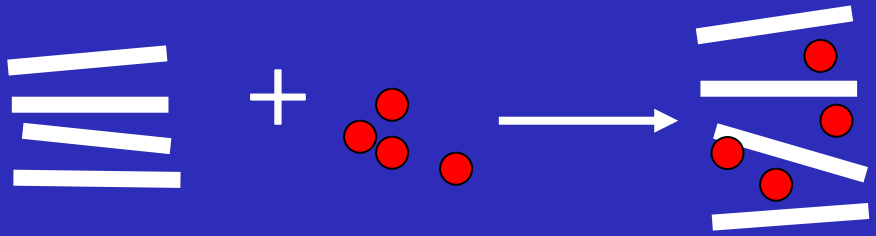
Chemisorption



Occlusion

$$Pd + H_2 \longrightarrow Pd_xH_y$$

Absorption



Surrounding Situation around 1990

Development of new activated carbons by Industries

Activated carbon fiber (ACF) around 1985

Competitive development by Osaka gas, Toyobo, Kurare, Toho rayon,--

Superhigh surface area carbon **Kansai Kokes 1989**

Entering the stage of well-defined porous solids

Mesoporous Silicas

C. Kato:K. Kuroda 1990, K.Kuroda; S. Inagaki 1993

C. T. Kresge et al (Mobil) USA 1992

Carbon nanotube CNT S. Iijima 1991 : MWCNT, 1993:SWCNT (discovery)

M. Endo 1976 (synthesized)

(Porous Coordination Polymer (PCP) or Metal organic framework (MOF))

(S. Kitagawa 1997 K. Seki (gate adsorption K. Kaneko 2001)

New Attempts in Adsorption Studies around 1990

Theoretical studies

Analysis with statistical mechanics

[Barrer Takaishi Ruthven ----]

Molecular simulation, molecular dynamics, theory

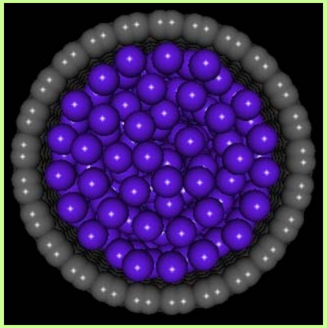
W. Steele	Adsorption on surfaces
G. Zgrablich	Adsorption on surfaces
D. Nicholson	Adsorption in pores
K. E. Gubbins	Adsorption in pores
N. Seaton, N. Quirk	Pore size distribution
P. Monson	
A. Neimark	
D. D. Do	

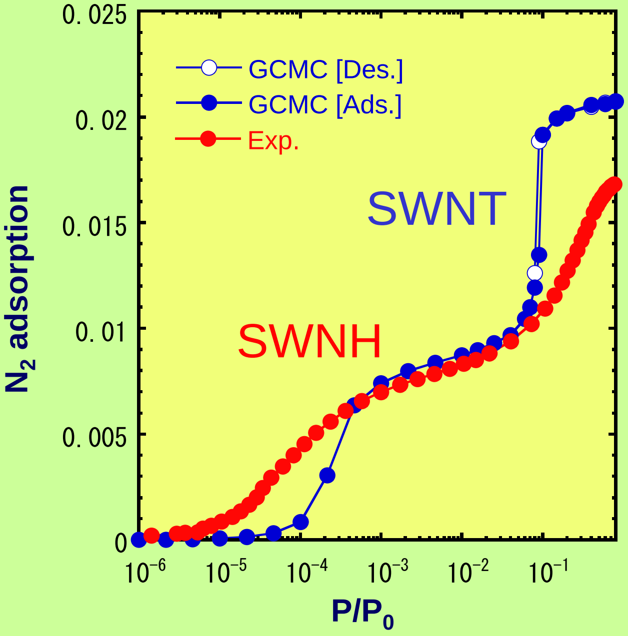
Collaboration has promoted our studies

Fractal analysis D. Avnir P. Pfeifer

Bridging between Molecular Simulation and Experimental Studies

Molecular simulation





Experimental approaches

High resolution isotherm
Ultra-low pressure isotherm
Wide-temp. range isotherm

Structural analyses

in situ X-ray diffraction
in situ SAXS
in situ IR spectr.
(in situ Raman sp.)
XAFS

Nanoporous solids
Carbon

By H. Tanaka

Talentful Student-Depending Research

A pioneering subject for a hopeful student

for utilization of nanopore spaces for molecules and ions

Designing a new experimental method

Construction and Set-up of the new experimental method

Strengthening theoretical or analytical method

"International-level Specialist"

then addition of other skills and interests

Mainly PhD students

had developed new methods, new analysis, and ------

They are talentful and challenging instructors for me

Nanospace Molecular Science

(Current Target: Nanospace Materials Engineering)

Being Different from Surface Science

Confinement effect without specific interaction with surface

How can we confine molecules in nanoscale spaces ?

1. **Nanopores of real walls**

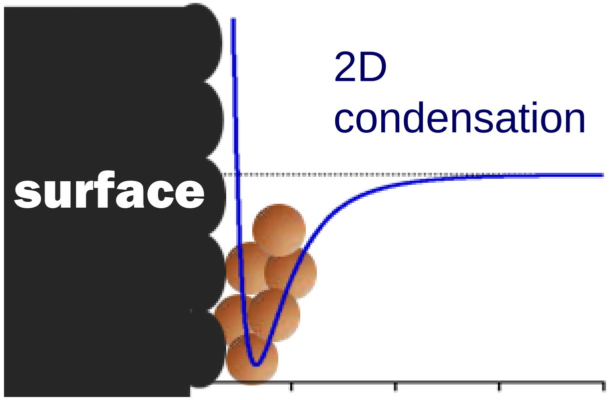
    Interaction potential wells

2. **Potential well without any real pore**

    Nano-range area at solid surface

    Potential well

    by external electromagnetic potential



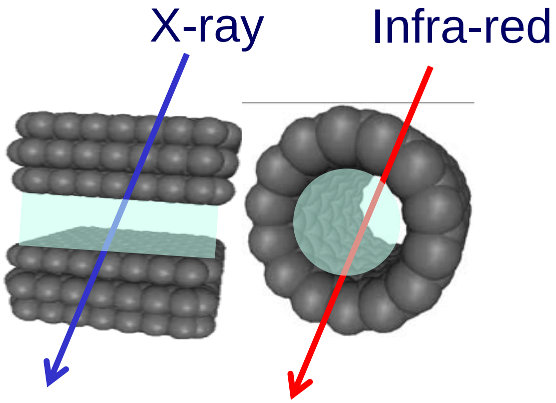
Better porous system

Carbon sp^2 π-conjugated flat wall without specific site

Neutral surfaces (or pore walls)

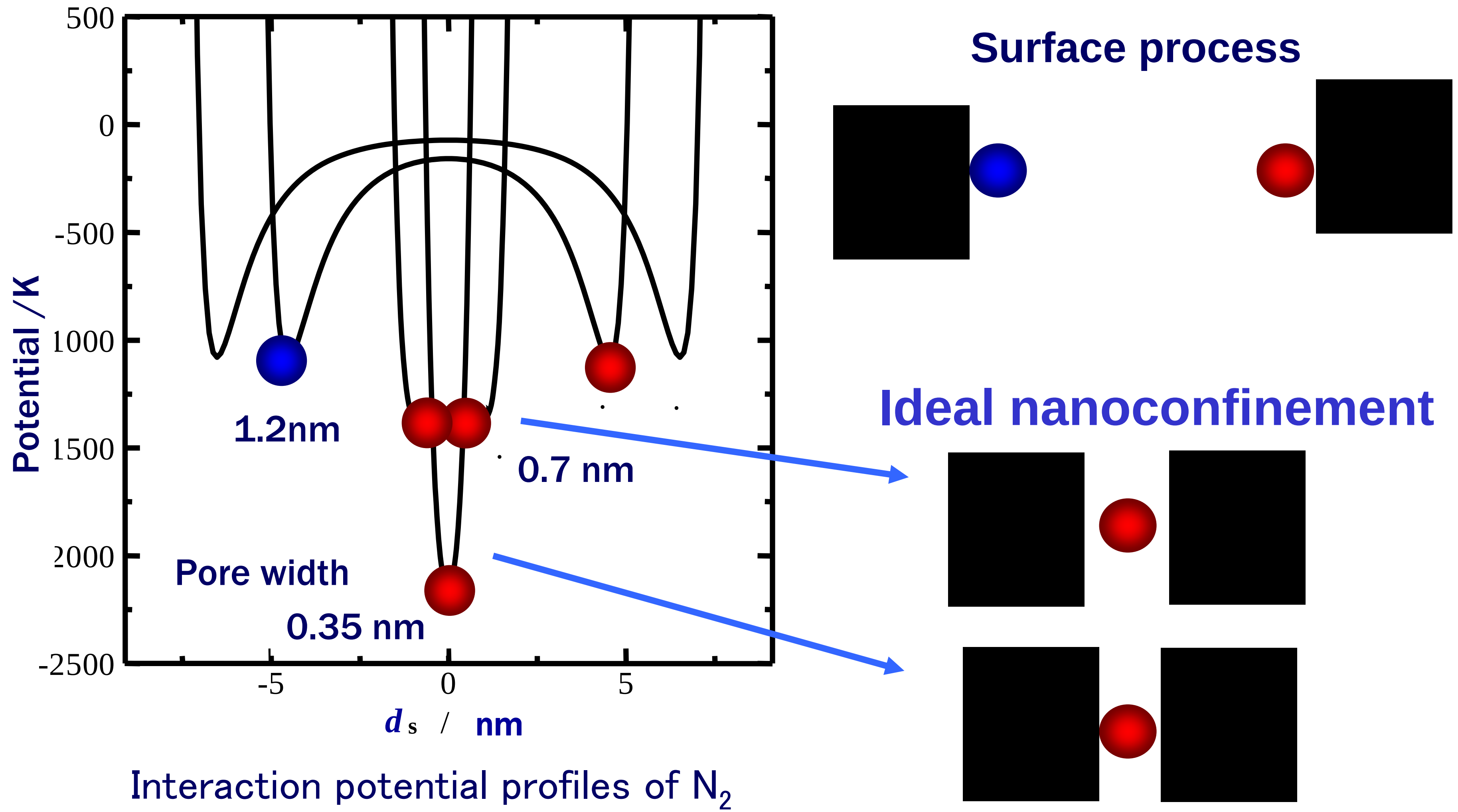
X-ray: Applicable

Spectroscopy: Applicable to single wall nanocarbon



Nanoconfinement:

Ideal Nanoconfinement and Surface Process



Surface process

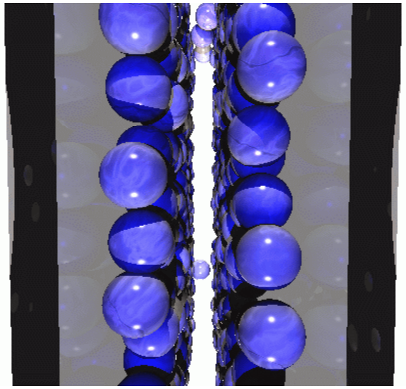
Ideal nanoconfinement

Interaction potential profiles of N_2

in a graphite slit pore

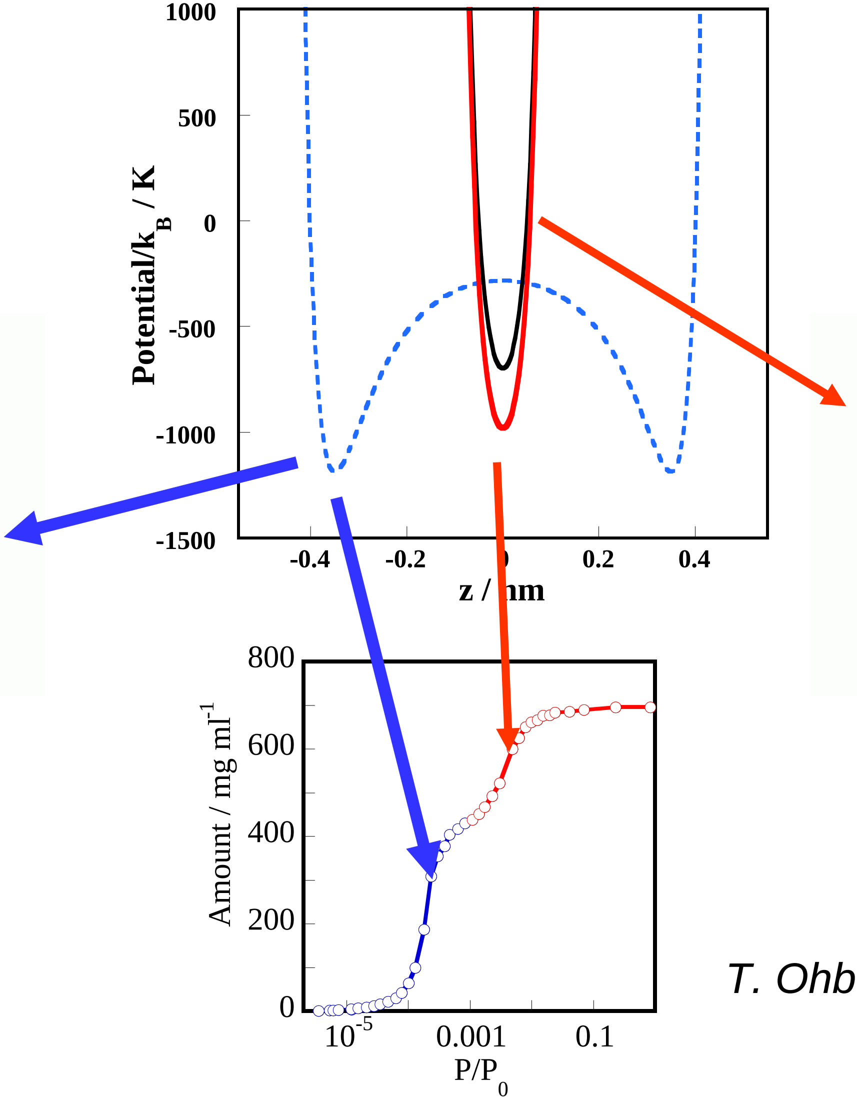
Nanoconfinement after Monolayer Completion

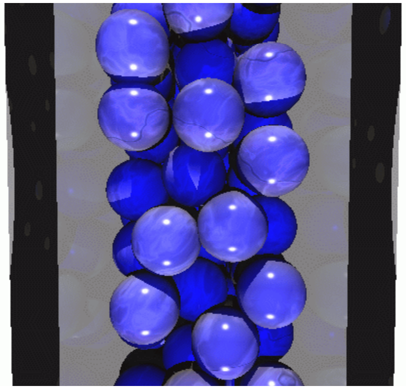
N_2 adsorption in graphite slit pore



Monolayer-covered

pore walls





Enhanced pore filling in the residual space

T. Ohba et al., Chem. Phys. Lett., **326**, 158 (2000)

Experimental Progresses in Adsorption Studies around 1990

Comparison plot analysis K. S. W. Sing

Calorimetric measurement J. Rouquerol

CO_2 adsorption F. Rodriguez-Reinoso

Topics

Adsorption on mesoporous silica (MCM, FSM)

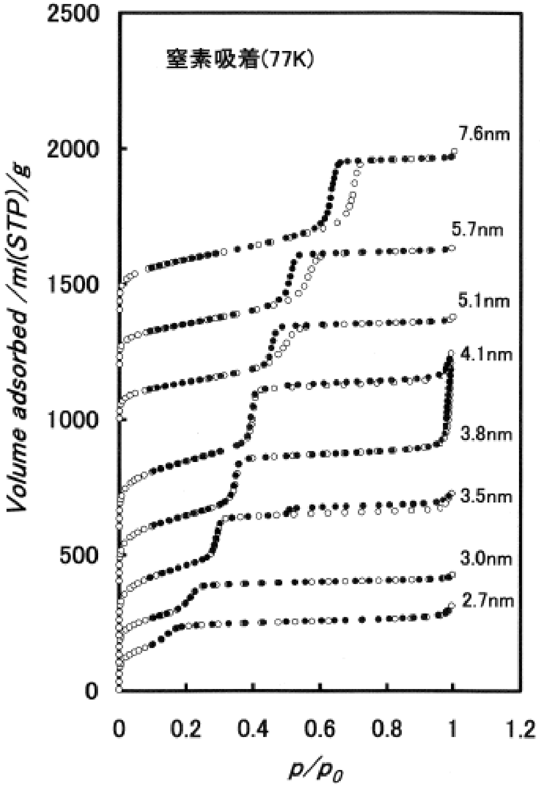
Adsorption hysteresis:

Dependence on temp. and pore width

K. Kaneko et al: Surface roughness model

Prediction of Hysteresis Disappearance in the Adsorption Isotherm of N_2 on Regular Mesoporous Silica

Langmuir, **14**, 3079(1998).



by Prof. Morishige

Main contributors in Nanospace Molecular Science

Materials

Oxide N. Uekawa*

ACF A. Matsumoto* J. Imai* Z. Wang* M. Ruike* M. Aoshima*

Carbon aerogel Y. Hanzawa*

SWCNH SWCNT K. Murata, E. Bekyarova* C. Yang S. Gotvacz* T. Fujimori* S. Utsumi*

T. Itoh* B. Wang F.Khoerunnisa

Cu-MOF Gate adsorption Li Di, H. Noguchi A. Kondo*

Mesoporous zeolite Y. Tao* (Graphene related materials M. Asai)

Method

T. Suzuki *

High resolution adsorption isotherms $P/P_0 = 10^{-6}, 10^{-9}$ K. Kakei, M. Sunaga. N. Setoyama

He adsorption at 4.2 K H. Kuwabara, N. Setoyama

in situ structural studies XRD SAXS (water adsorption) T. Iiyama* T. Ohba* A. Tanaka

Molecular simulation aided-SAXS T. Ohba*

Low temperature adsorption from 4 K to 300 K H. Tanaka* D. Noguchi

Low temperature IR H. Tanaka*, Raman: SERS T. Fujimori*

Detailed high pressure adsorption analysis K. Murata, J. Miyawaki*, J. Miyamoto*

EXAFS Y. Hattori*, T. Ohkubo*

Low temperature magnetic susceptibility C. Ishii, H. Kanoh*

HR-TEM K. Urita* ***[black: Master, blue:PhD, * Univ. or AIST]***

Molecular simulation

T. Suzuki*, M. Aoshima*, H.Tanaka*, T. Ohba* P. Kowalczyk*

Adsorption Related Researches

1. **Origin of superhigh surface area and SPE method**
2. **Evaluation of subnanometer pores**
3. **Adsorption mechanism of supercritical gases**
4. **Soft nature of nanoporous solids: Gate adsorption**
5. **Unusual intermolecular structures in nanopores**
6. **Superhigh pressure compression effect**
7. **Quantum molecular sieving effect**
8. **Water adsorption mechanism in hydrophobic pores**
9. **Structural understanding of ions in pores**
10. **Adsorption anomaly in carbon edge surfaces**

Origin of superhigh surface area and SPE method

Superhigh surface area > 2630 m^2/g (graphene)

4000 m^2/g can be correctly evaluated

by **subtracting pore effect (SPE) method**

BET gives an overestimated surface area by ∼ 50%

SPE surface area

Removal of excess adsorption by enhanced interaction potential of micropores

with high resolution α_s plot analysis

Stacked Carbon Hexagon Model

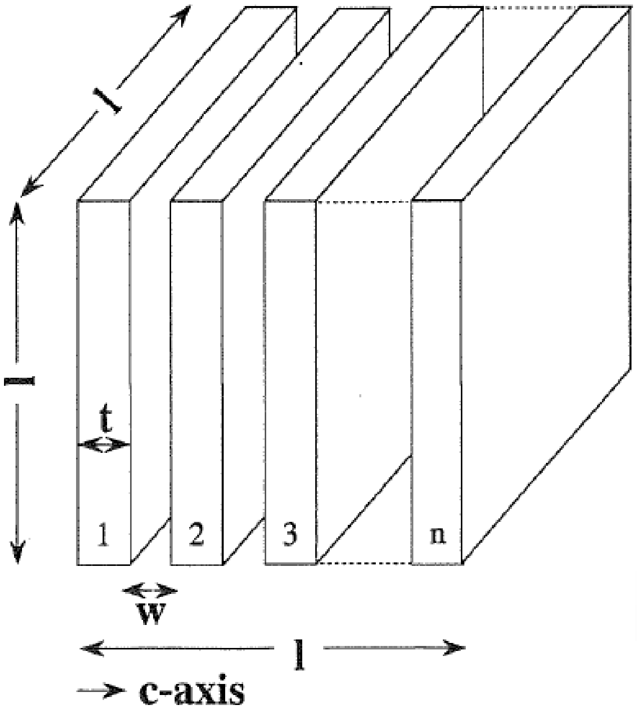


Fig. 1. The graphitic crystallite assembly model.

ORIGIN OF SUPERHIGH SURFACE AREA AND
MICROCRYSTALLINE GRAPHITIC
STRUCTURES OF ACTIVATED
CARBONS

Carbon, 1992, 30, 1075-1088

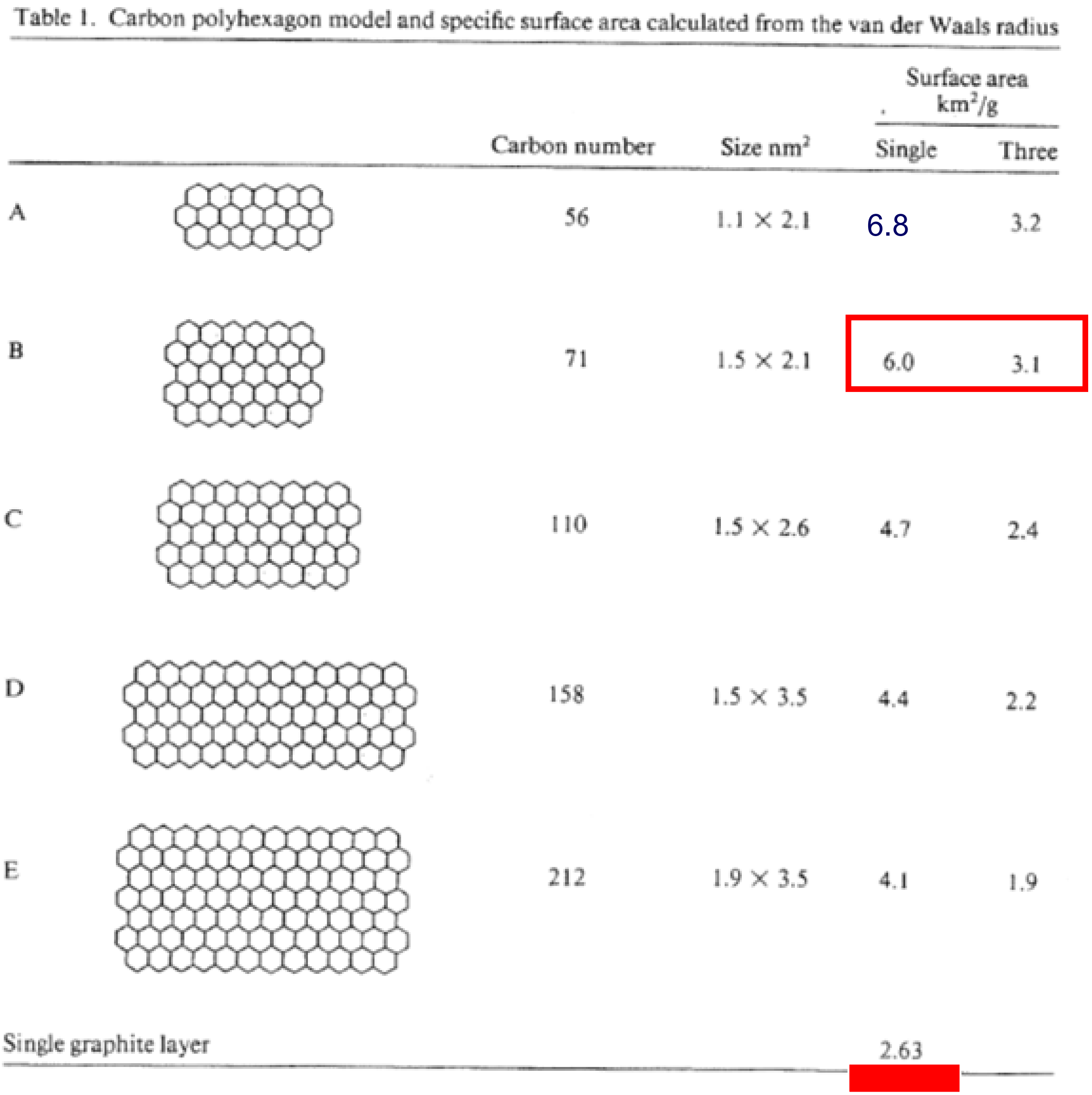
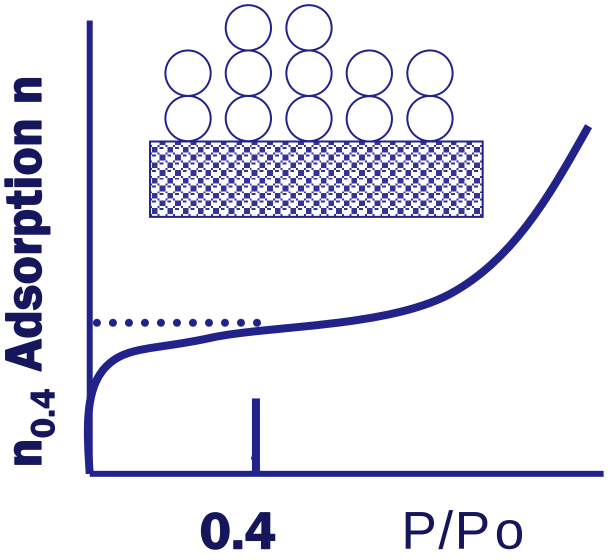
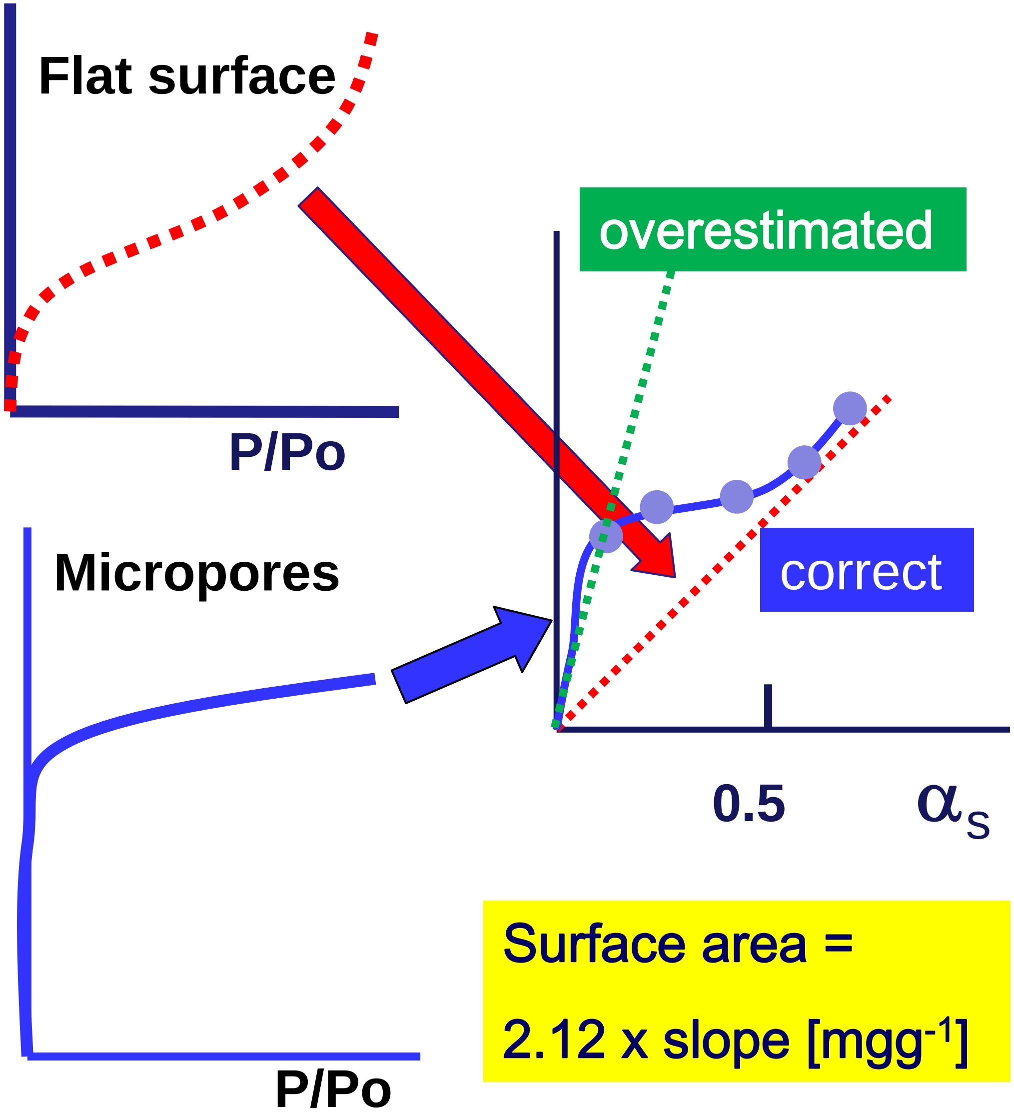


Table 1. Carbon polyhexagon model and specific surface area calculated from the van der Waals radius

		Carbon number	Size nm^2	Surface area km^2/g Single	Surface area km^2/g Three
A		56	1.1 × 2.1	6.8	3.2
B		71	1.5 × 2.1	6.0	3.1
C		110	1.5 × 2.6	4.7	2.4
D		158	1.5 × 3.5	4.4	2.2
E		212	1.9 × 3.5	4.1	1.9
Single graphite layer				2.63	

High Resolution Comparison (α_s) Plot Analysis





K.S.W. Sing's definition

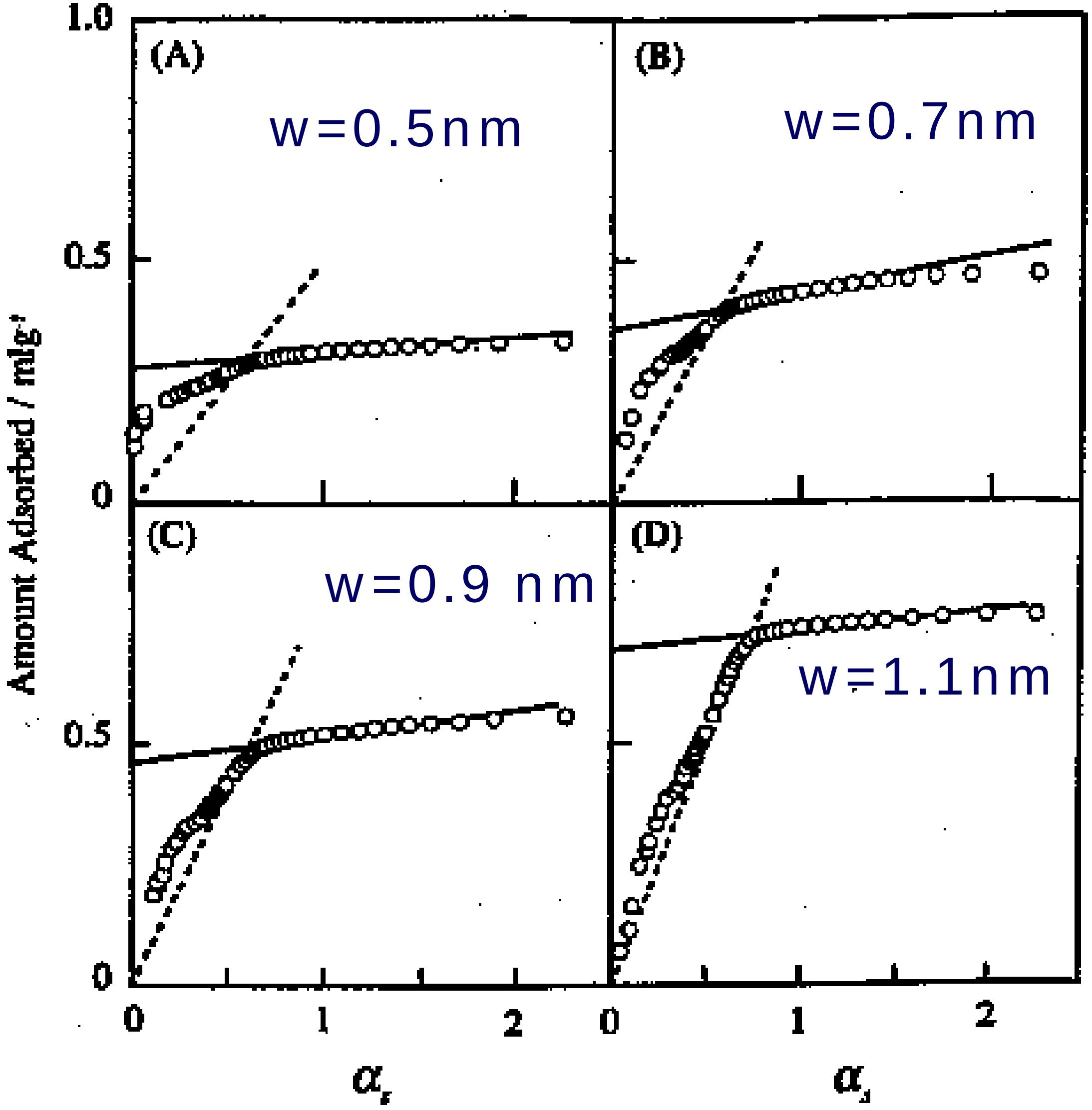
α_s = 1 at P/Po=0.4

$\alpha_s = n/\, n_{0.4}$

Surface area =

2.12 x slope [mgg^{-1}]

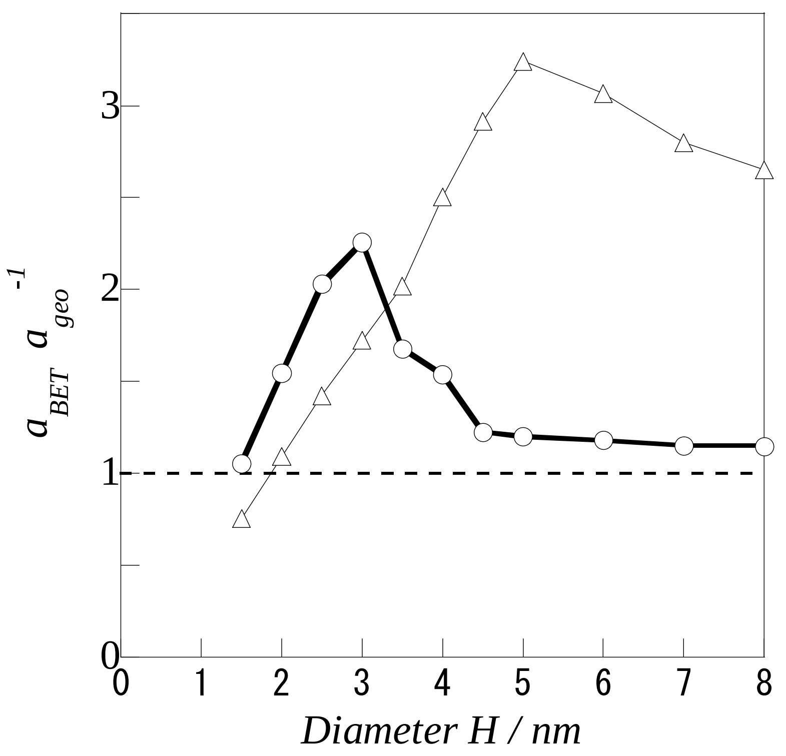
α_s Plot Shape and Pore Width of Slit-Pore



N. Setoyama et al

Carbon, **36**, 1459-1467 (1998).

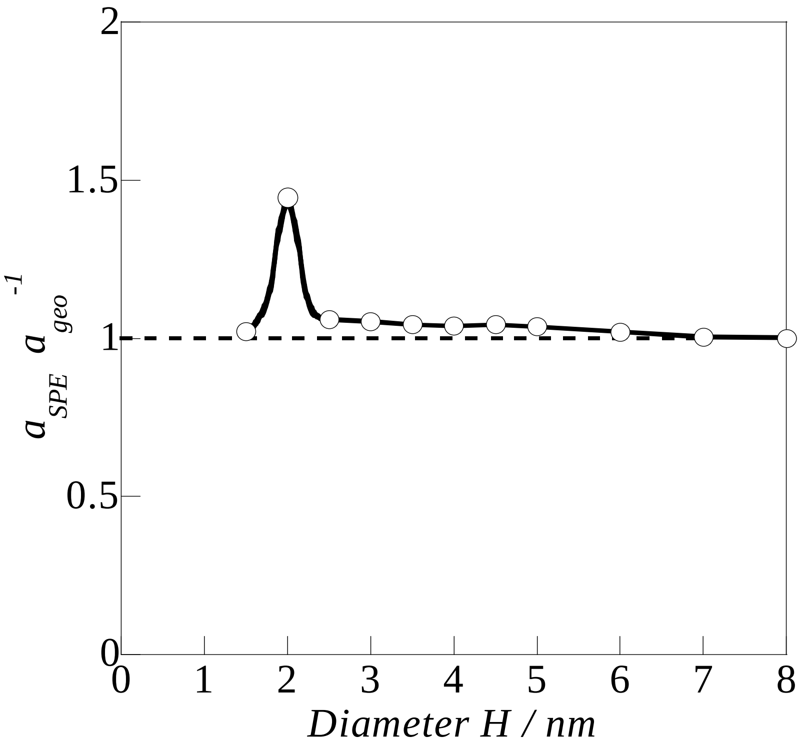
Inapplicability of BET and Effectiveness of SPE for Internal Surface Area of SWCNT



Ratio of a_{BET} to a_{geo} wiith width H for the internal surface area.

a_{BET} from P/P_0 = 0-0.05: ○

and P/P_0 = 0.05-0.35: △.

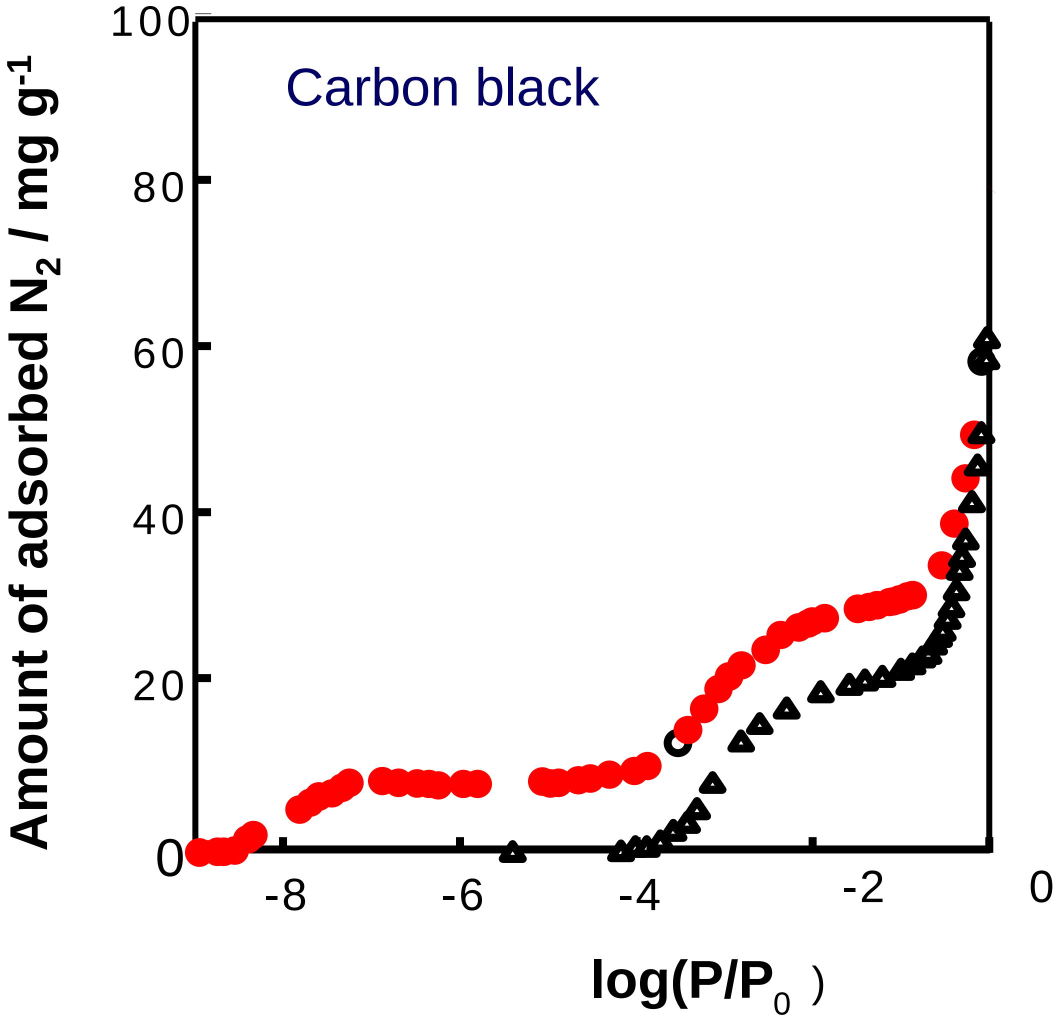


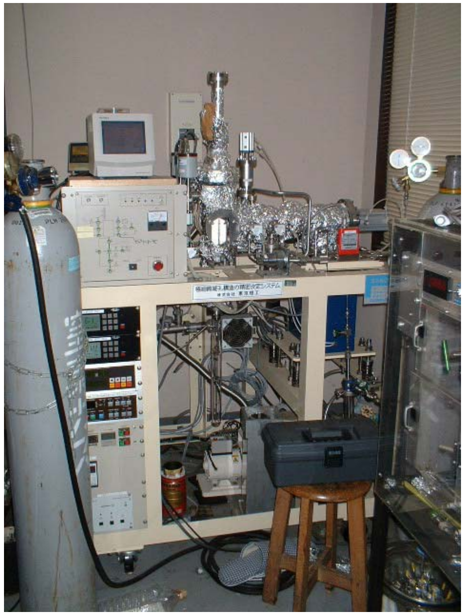
Change in the a_{SPE} *vs.* a_{geo} ratio with physical width from α_S plot

T. Ohba; K. Kaneko, *J. Phys. Chem*. B **106**, 7171-7176 (2002).

Evaluation of Subnanometer Pores

Superwide-pressure range adsorption isotherm $P/P_o = 10^{-9} \sim 1$





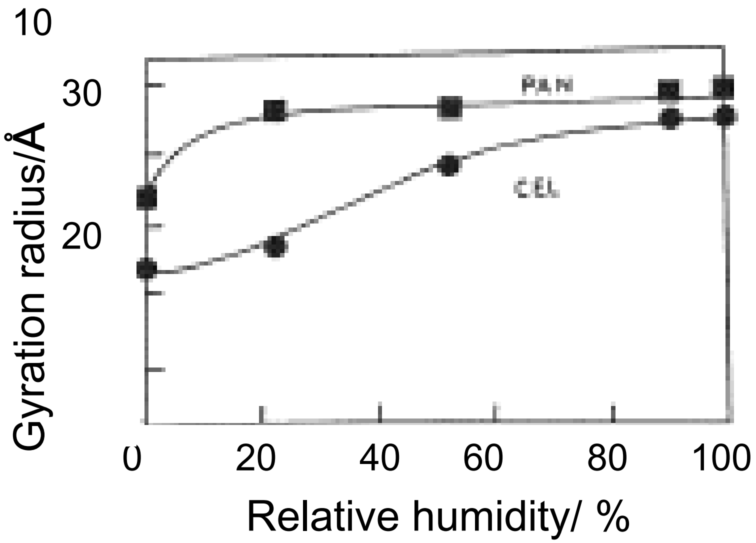
Ultrahigh vacuum system

M. Sunaga,et, *J. Phys. Chem. B*, *2004*, ***108, 1065.***

Soft Nature of Nanoporous Solids: Gate adsorption

Nanoporous Solids sensitive
to nano-range environments

Swelling of micropores and shrinkage of nanographitic walls of ACF



Gyration radius vs. RH relation
from in situ SAXS

$$ln\ I(s) = -s^2Rg^2/3 + \text{const.}$$

T. Suzuki, K.Kaneko, Carbon, 26,743 (1989).
K. Fujiwara et al. J. C. S. Faraday, 87, 2763 (1991)

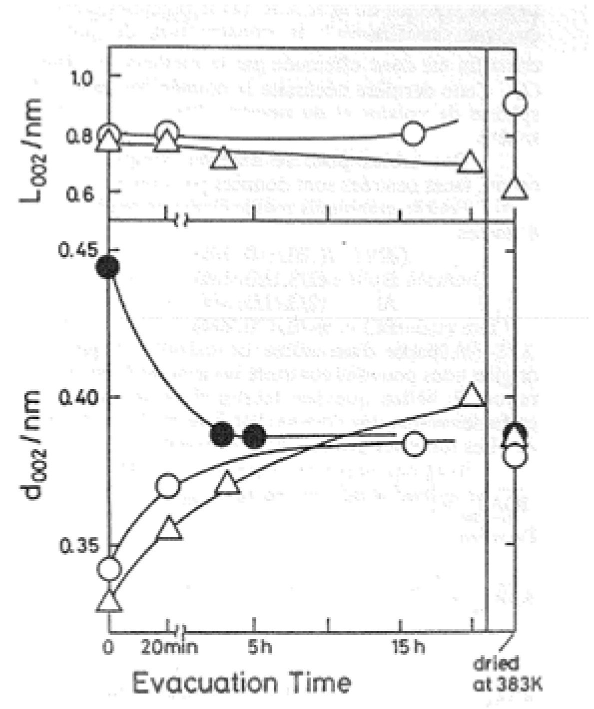


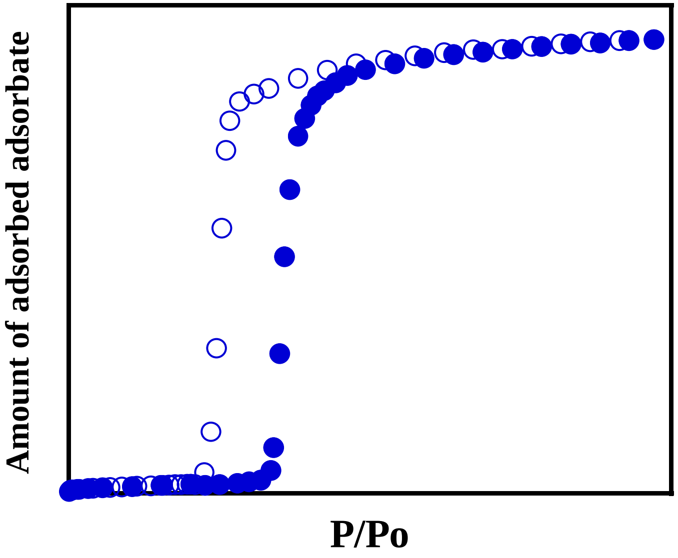
Fig. 3. The interlayer spacing d_{002} and crystallite size L_{002} from the (002) peak as a function of evacuation time: Water-adsorbed ACF (O), benzene-adsorbed ACF (●), and water-adsorbed α-ACF (Δ).

T. Suzuki and K. Kaneko,
J. Colloid Interface Sci., **138**, 590 (1990).

Finding of Gate Adsorption in Cu-MOF

Lattice structural change associated with gas adsorption in inorganic-organic hybrid microcrystals: Gate Adsorption S. Ohnisi, T. Ohkubo, L.Di, K. Kaneko

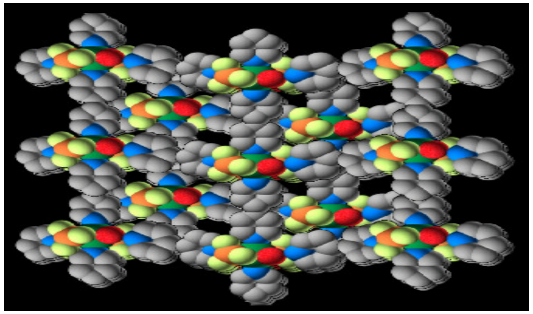
FOURTH INTERNATIONAL SYMPOSIUM on EFFECTS OF SURFACE HETEROGENEITY IN ADSORPTION AND CATALYSIS ON SOLIDS ISSHAC IV
POLAND, 27-31 August, 2001



Adsoption isotherm of CO_2 at 273 K

D.Li;K.Kaneko, *Chem. Phys. Lett.*, 335, 50, (2001)

[Cu(bpy)(BF$_4$)$_2$(H$_2$O)(bpy)$_n$]



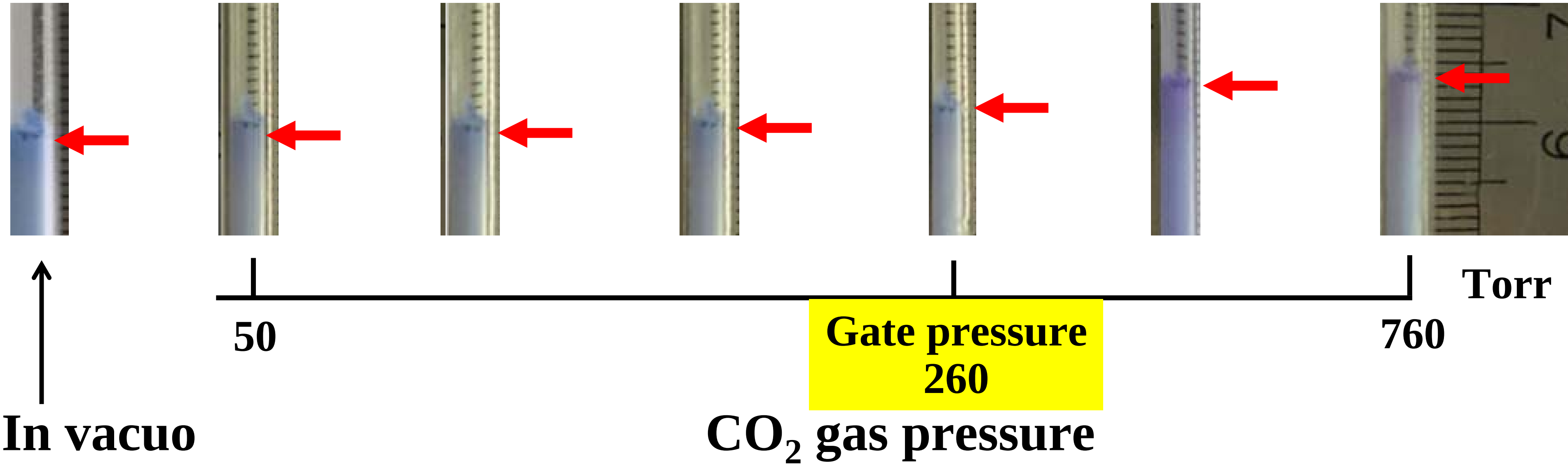
Force constant of the gate valve spring

$$\frac{1}{2}\Delta k q^2 = k_B T \ln\left(\frac{P_{ad.gate}}{P_{des.gate}}\right)$$

$1.4 \times 10 \sim 6 \times 10^2$ N m^{-1}

***Appl. Surf. Sci*. 196, 81 (2002)**

Apparent Volume Change of LPC : *$[Cu(bpy)(BF_4)_2(H_2O)(bpy)_n]$* on CO_2 Gas Adsorption



In vacuo

50

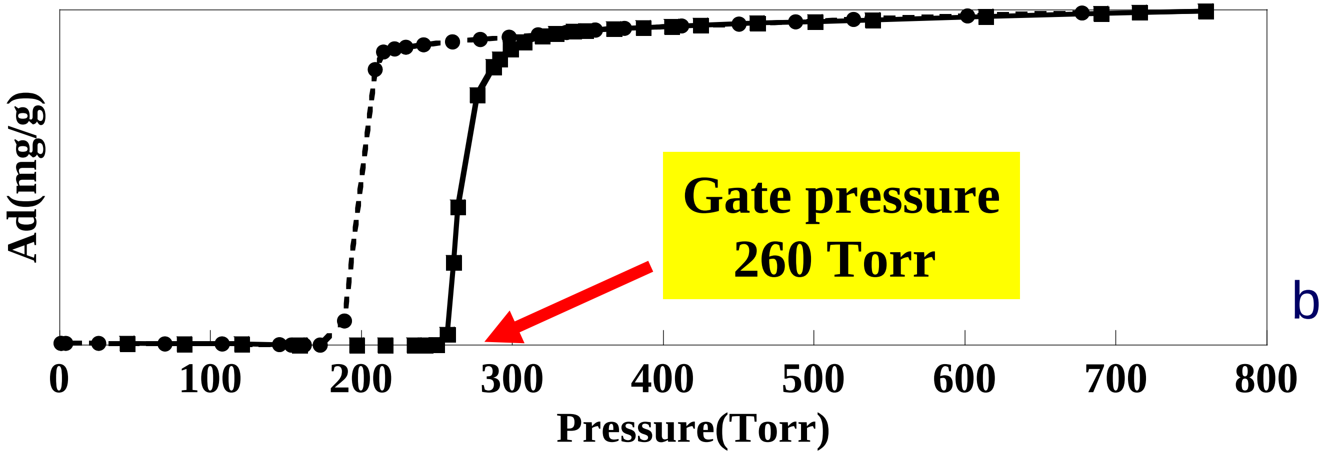
Gate pressure
260

760

Torr

CO_2 gas pressure

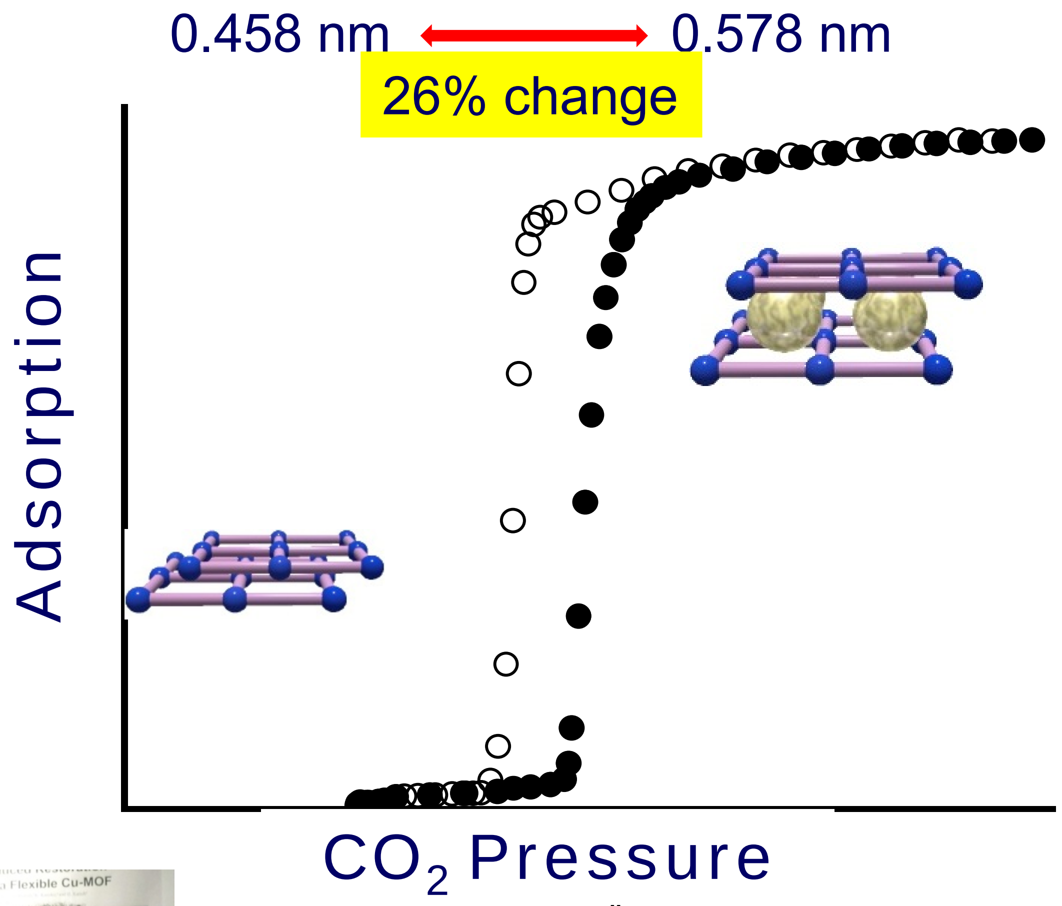
CO_2 adsorption isotherm

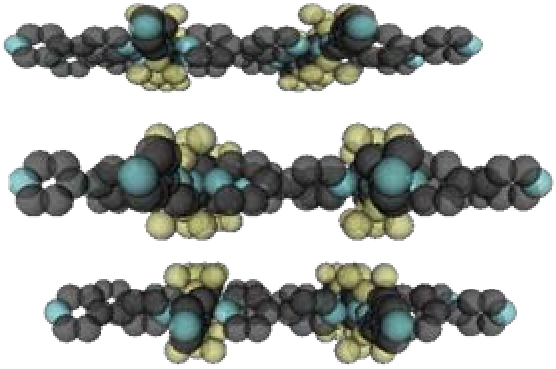


Gate pressure
260 Torr

by A. Kondo

Cu-complex crystals: Aspiring CO_2





Reversible Clathrate Formation with CO_2

A.Kondo, H. Kanoh, K. Kaneko et al, *Nano Lett*, 6, 2581-2584 (2006).

Tokyo University of Agriculture and Technology

Morphological Defect-Associated Structure Change with Surface Enhanced Raman Scattering (SERS)

Preceding researches **Intensity enhancement was reported**

M.Dresselhaus et al. Phys.Rev. (2000), J. Azoulay et al, CPL (2000)

Y. Fang et al, J.Colloid Interface Sci. (2006)

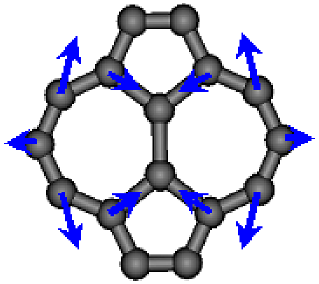
No application to study defective structure analysis

Morphological defects

Stone–Thrower-Wales defect, 7-member ring, 5-member ring

Fujimori et al, *J.Phys.Chem*.C (2008)

Fujimori, Radovic, et al, *Carbon*, (2012) Invited to special issue dedicated to Dr. P. Thrower



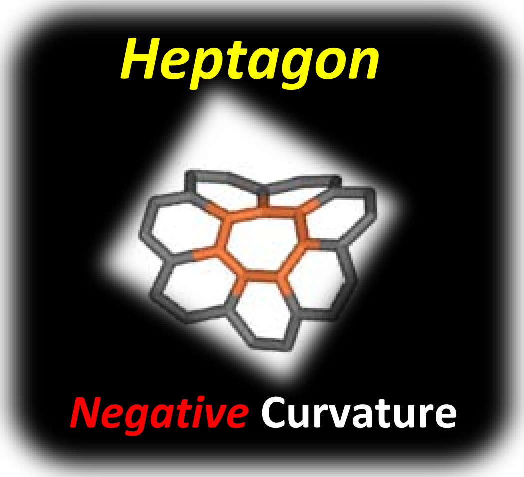
Topological Defects in Carbon

by T. Fujimori

Shinshu U.

Pentagon

Positive **Curvature**

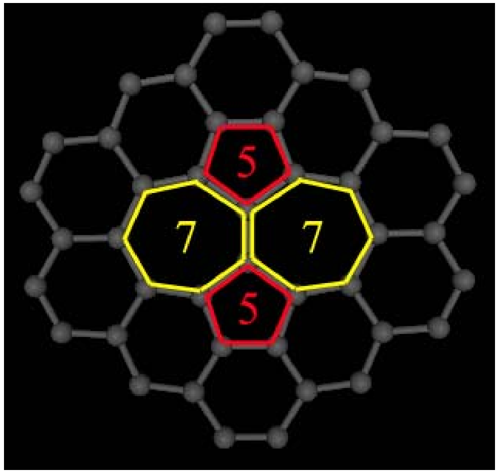


Heptagon

Negative **Curvature**

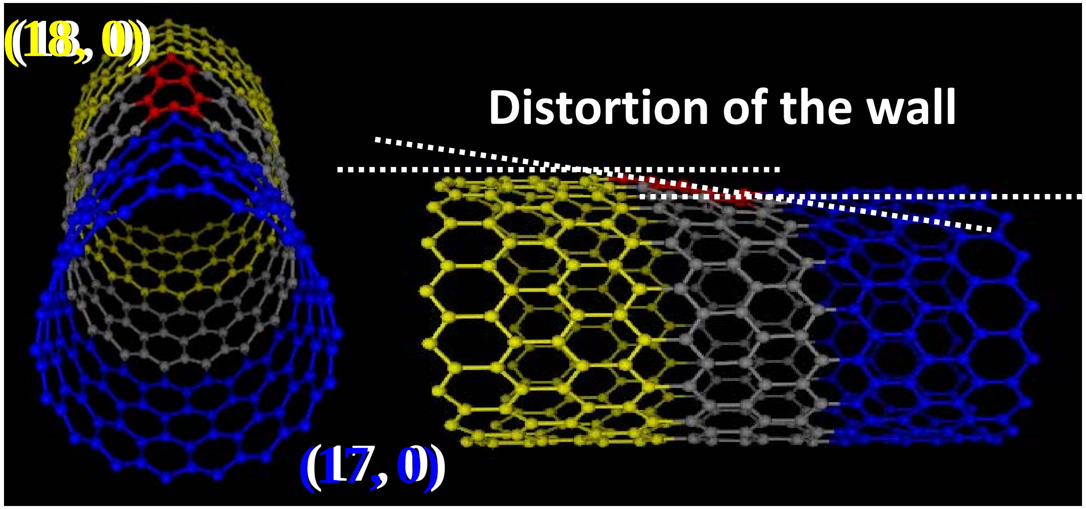
Stone-Thrower-Wales Defect

(cancelled the curvature: plane)

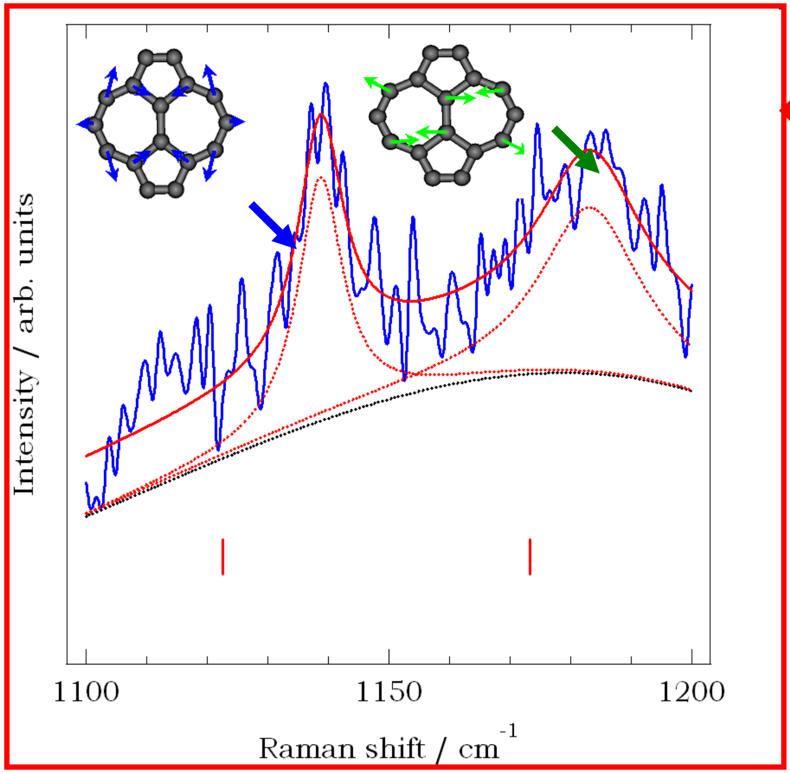


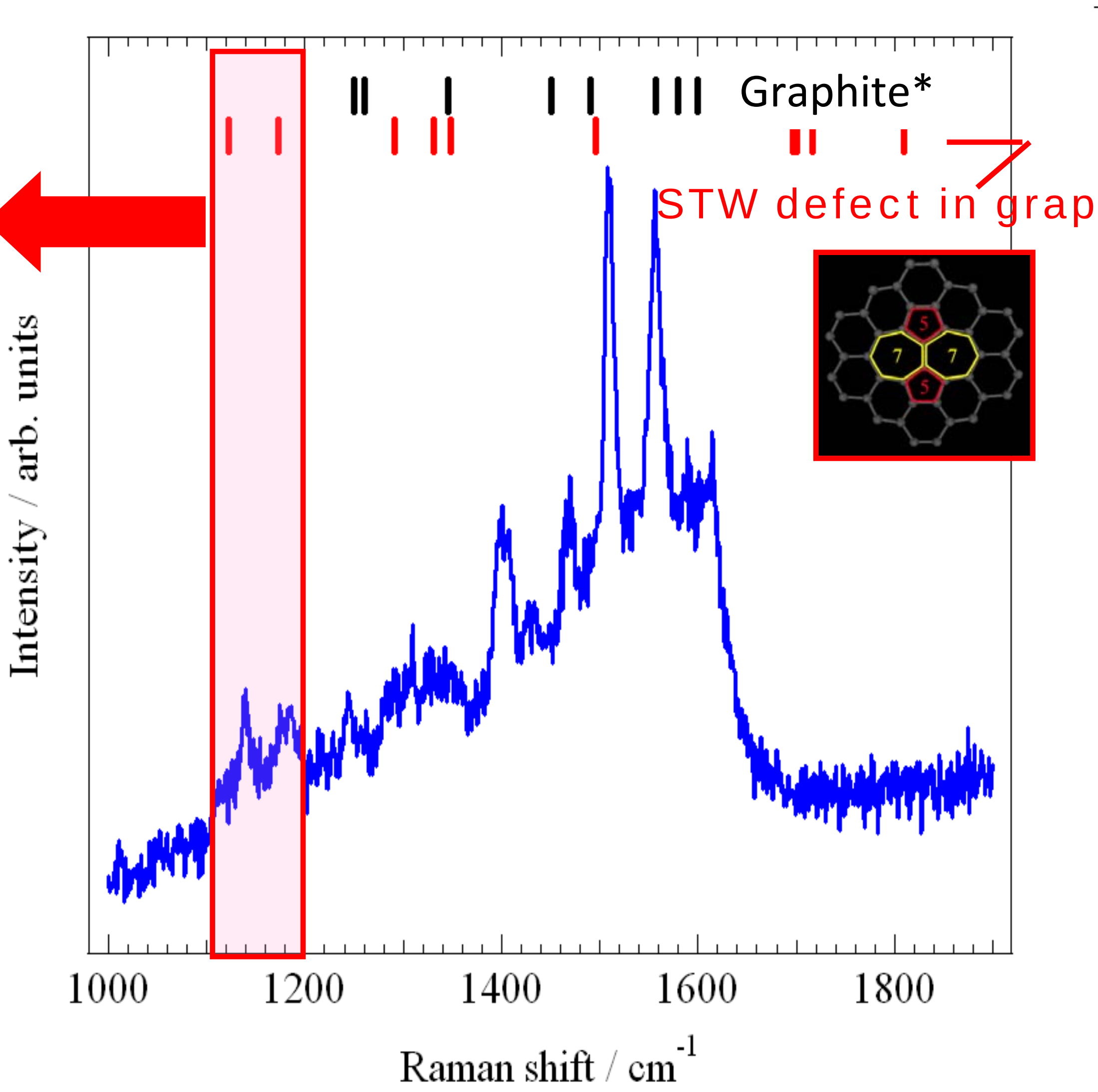
One 5-7 pair

(inducing further curvature in the wall)



Evidence of STW defects by SERS





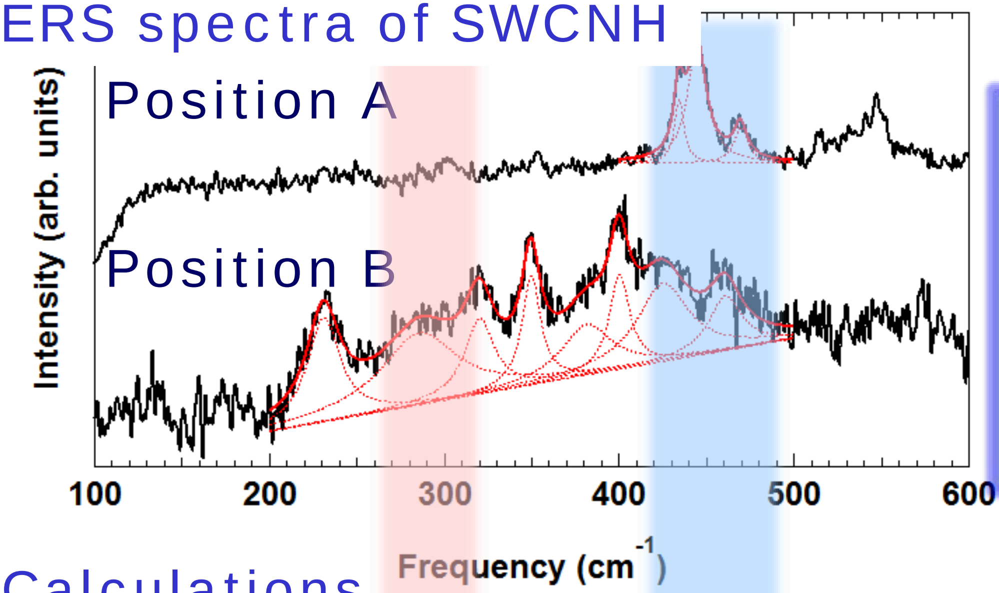
T. Fujimori et al,
J. Amer. Chem. Soc., 132, 6764 (2010)

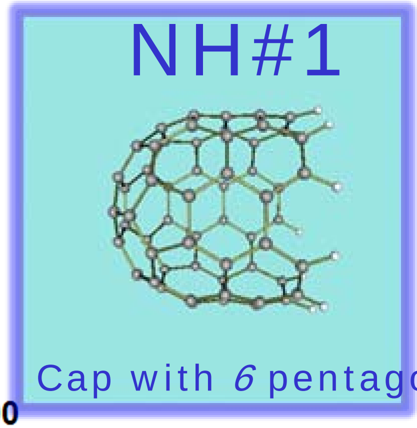
* R. Saito et al., *Physica B* 2002, *323*, 100.
** G. Wu et al., *Phys. Rev. B* 2006, *73*, 245414.

Localized Vibrations on 0-Dimentional Defect

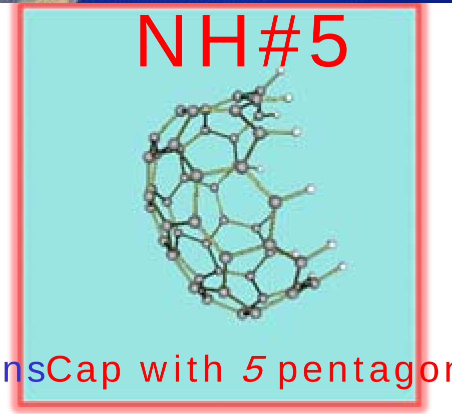
T. Fujimori, D.Tomanek,et al,. J.Chem. Phys. (2012)

SERS spectra of SWCNH



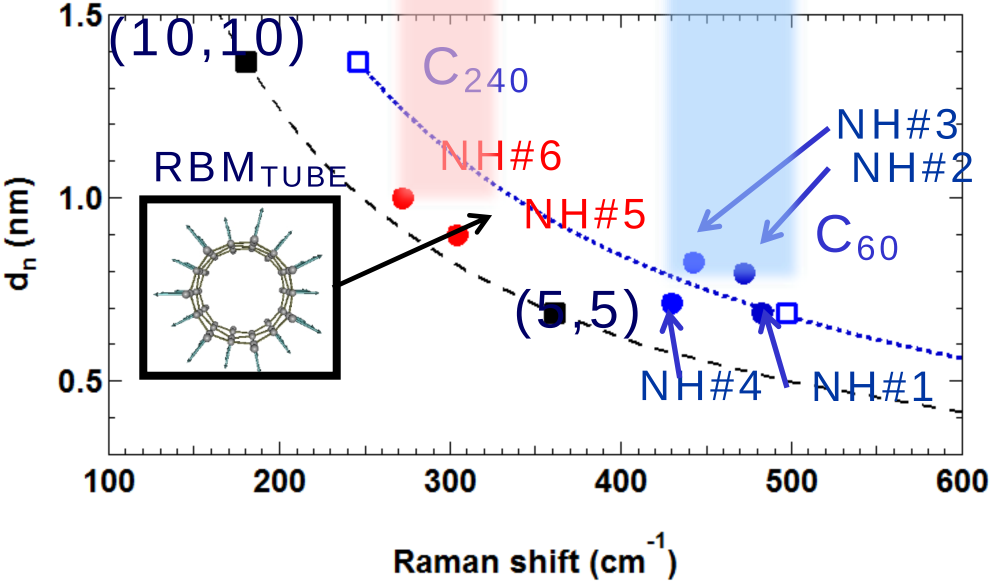


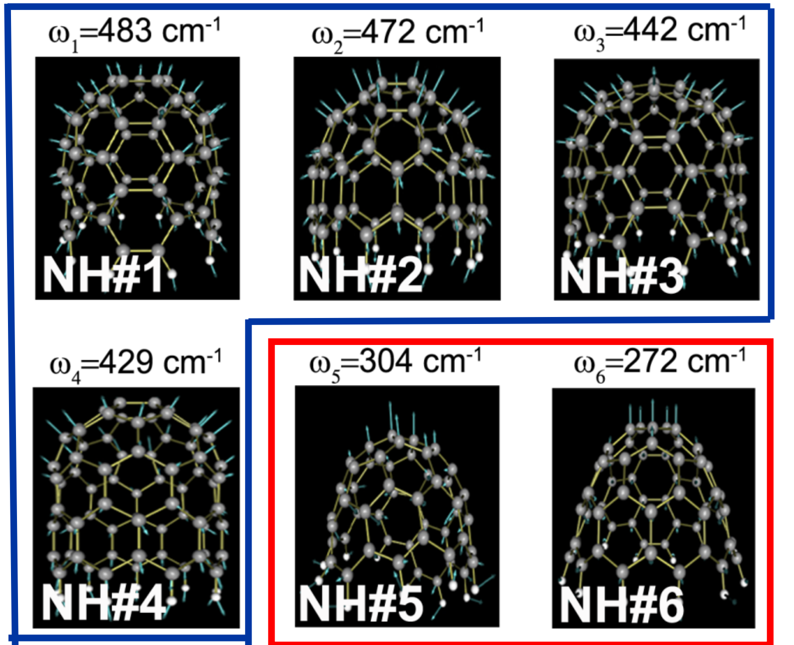
Cap with *6* pentagons



Cap with *5* pentagor

Calculations





Unusual intermolecular structures in nanopores

In Slit Pore Spaces

NO at 303 K: Highly concentrated $(NO)_2$

Kaneko et al, J. Chem. Phys., **87**, 776 (1987).

H_2O at 303 K : Quasi solid from X-ray diffraction

T. Iiyama et al, J. Phys. Chem., **99**, 10075 (1995).

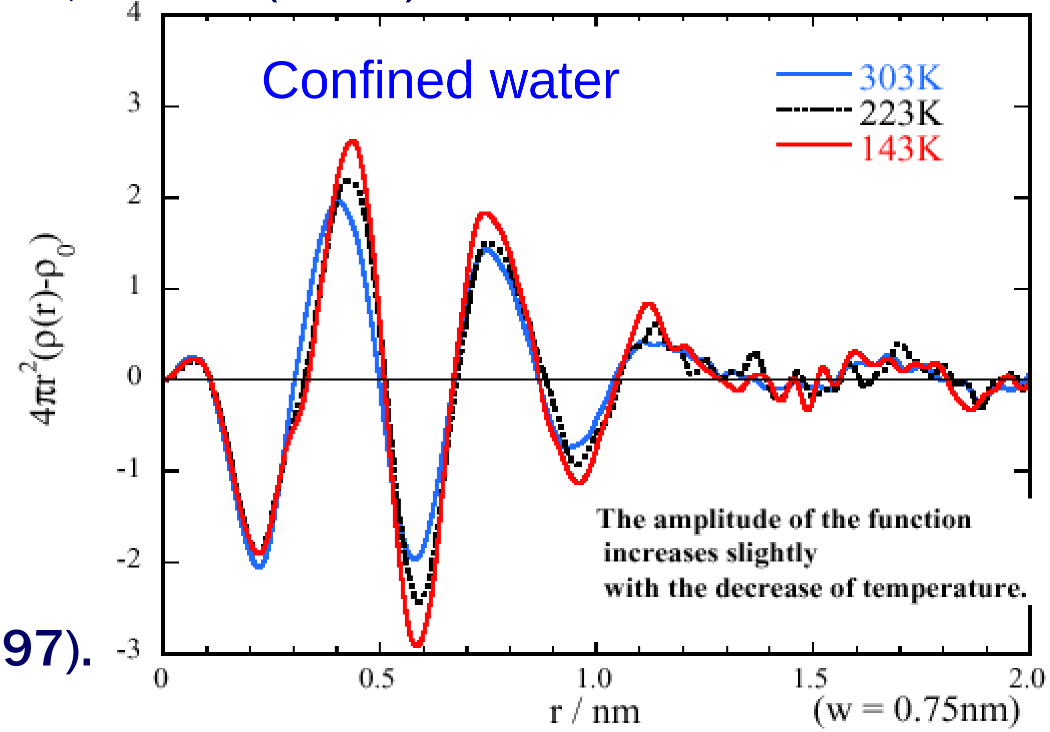
T. Iiyama
Shinshu
Univ.
Fac. of Sci.

CCl_4 at 303 K: Plastic

crystal form below 250 K

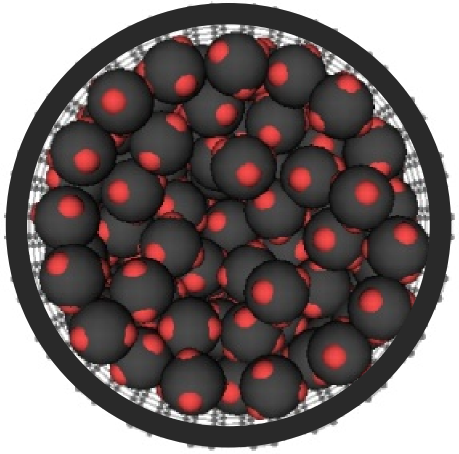
T. Iiyama et al.

J. Phys. Chem. B, **101**, 3037 (1997).

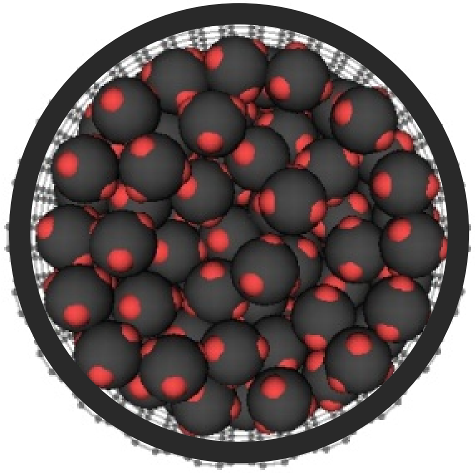

Confined water

The amplitude of the function increases slightly with the decrease of temperature.

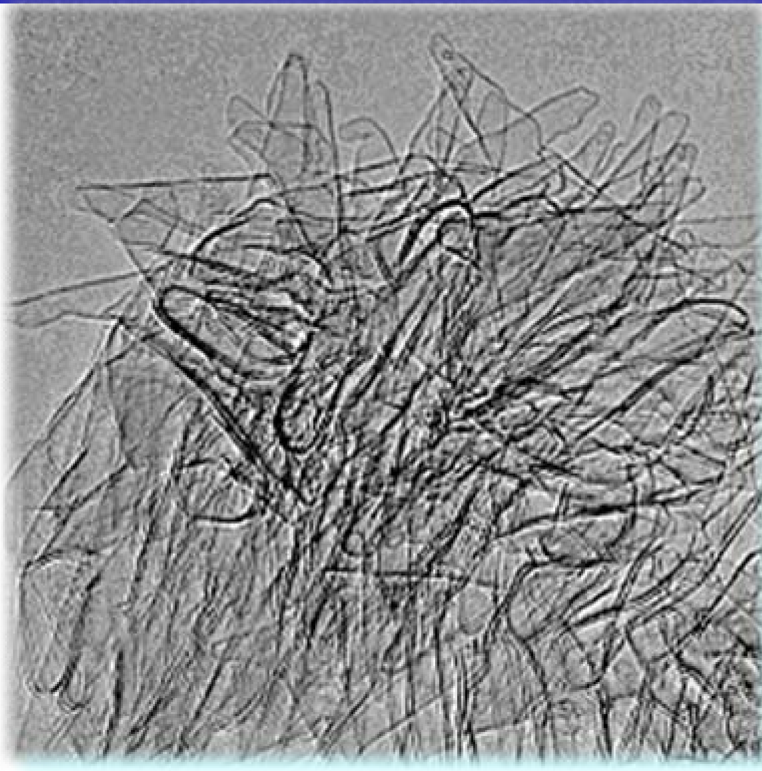
Evidence for Suppressed Rotational Motion of CH_4 Molecules in Single-Walled Tube Spaces



111 K



130 K



Single wall carbon nanohorn

S.Hashimoto (Master grad.)et al.

J. Amer. Chem. Soc. **133**, 2022 (2011).

How can we understand compressed states ?

How can we understand “motional states” of molecules confined in nano-scale pores experimentally?

Molecular–level understanding

Can we apply spectroscopy ?

Single wall carbon-----light penetrable

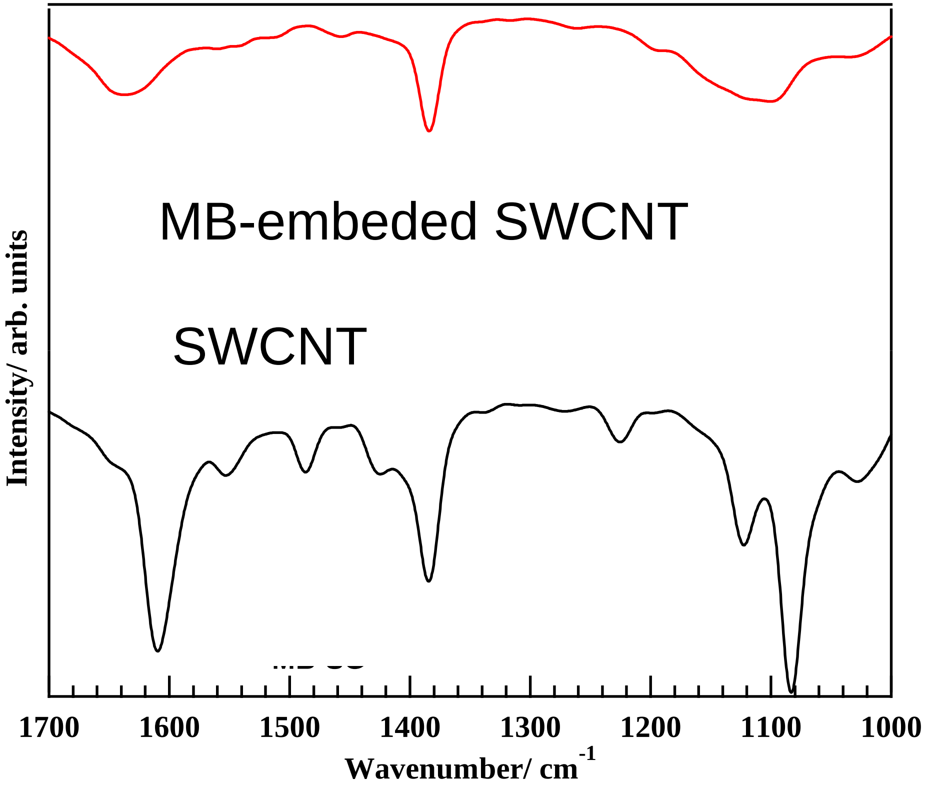
In situ FT-IR measurement of CH_4 on SWCNH

SWCNH : Single wall carbon nanohorn

(Bulk b.p. of CH_4 : 111.5 K)

IR Can Transmit Single Wall Carbon

FT-IR Spectra of SWCNT



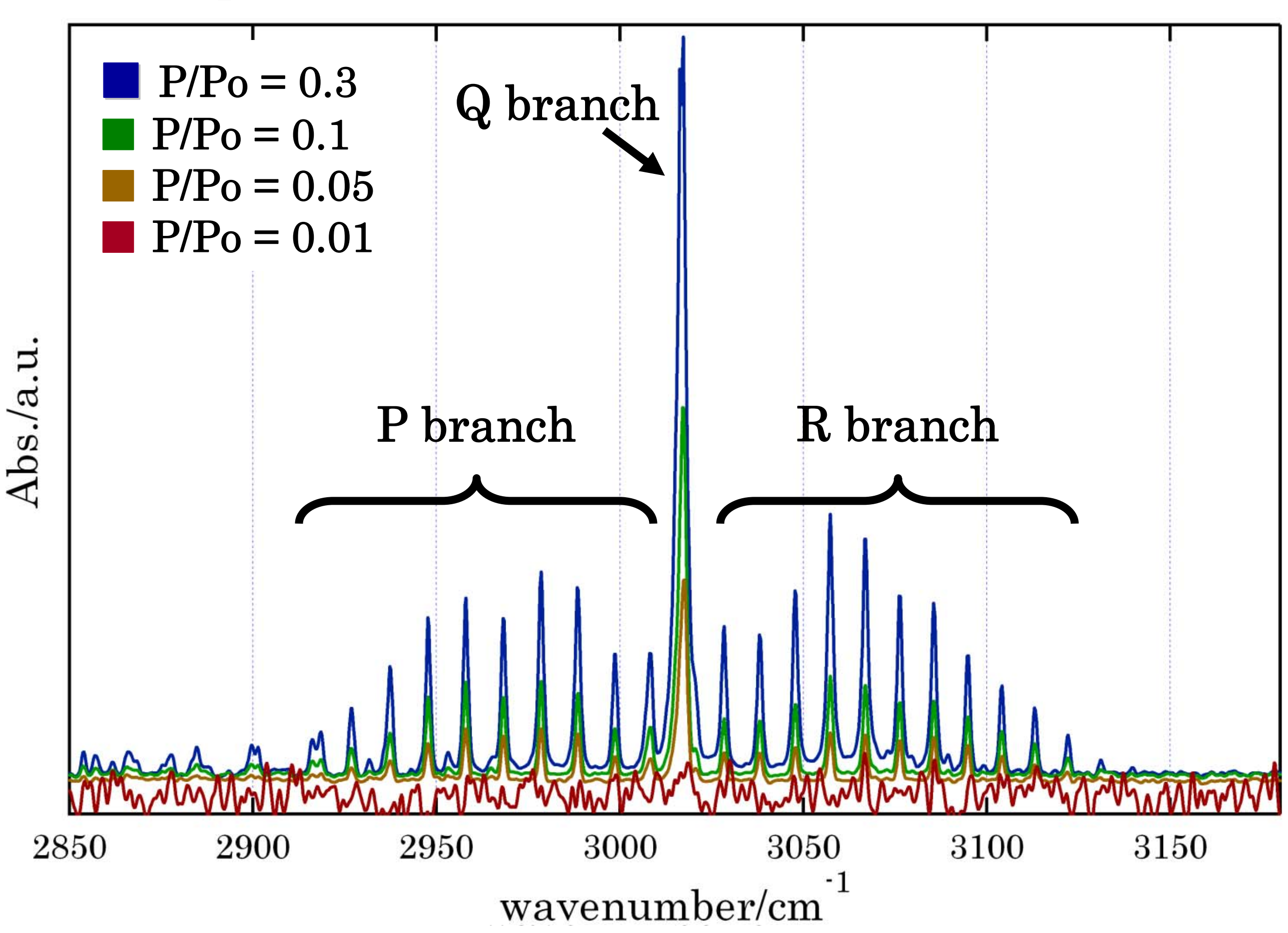
Fitri Khoerunnisa et al,

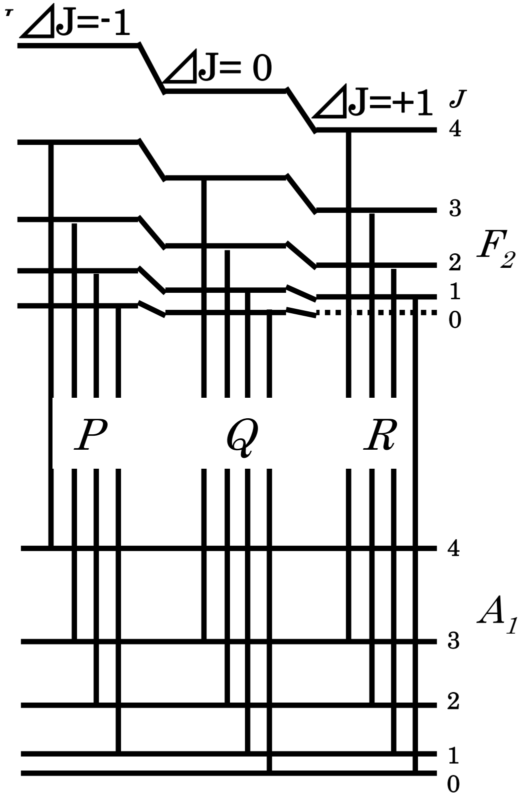
J. Phys. Chem. C (2012)

Vibration modes	Wavelength/ cm^{-1}	
	SWNT	MB-SWNT
C-O-C	1082 1122	1104 1200
C-O	1226	1270
C-H stretching of alkanes	1385	1384
C-H bending/scissoring	1489	1462
C=C (benzene ring)	1553	1539
C=O of quinone	1610	1637
C-H_of methyl	2860	2853
C-H of methyl	2924	2925
O-H stretching/NH of amine	3387	3450

Pressure dependence of ν_3 band at 111 K

After adsorption



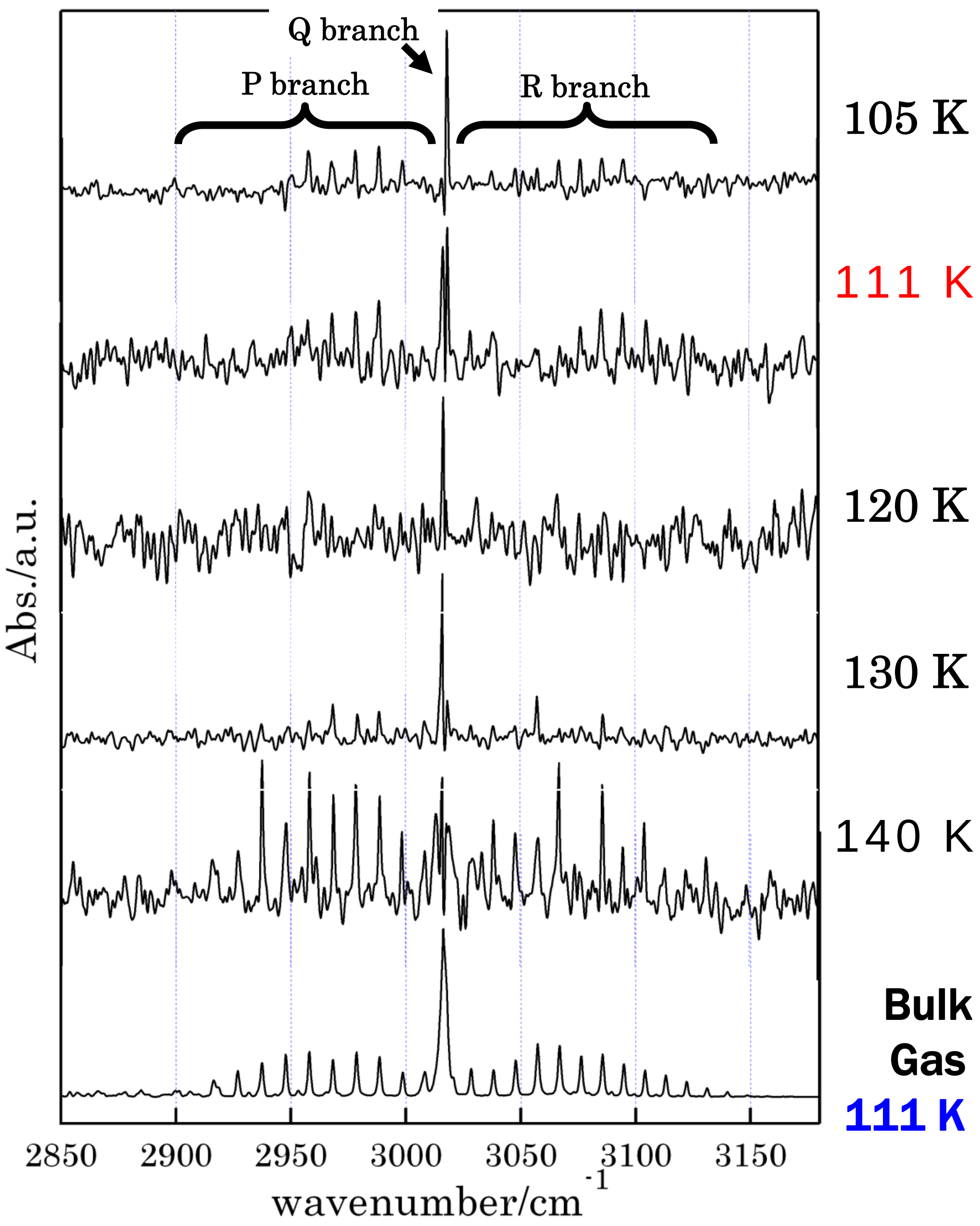


Rotational energy levels of methane

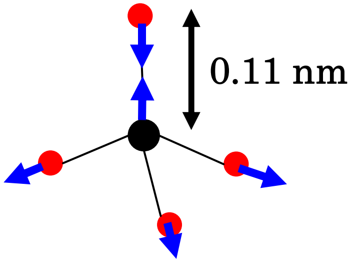
F_2 : Excited state

A_1 : Ground state

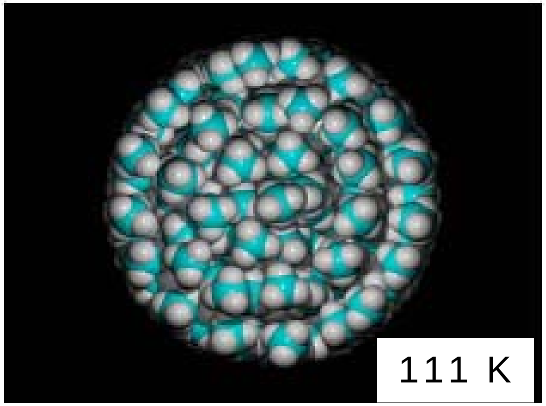
Difference spectra (ν_3 band)

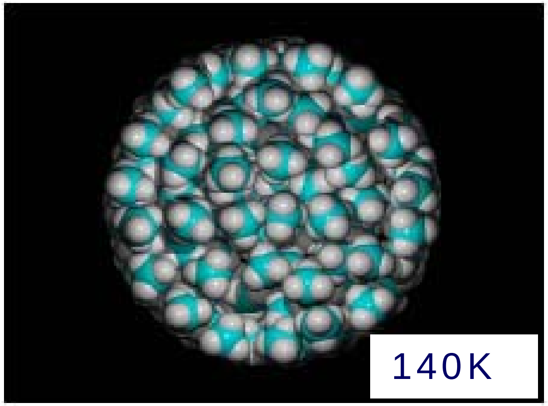


P/Po = 0.05



Asymmetric stretching vibration mode





Elevation of “boiling temperature” in nanospaces

- Boiling point of bulk CH_4

→ 111.5 K

- Confined CH_4

For asymmetric stretching vibration

→ 133 ~ 135 K

For bending vibration

→ 120 K

Superhigh Pressure Compression Effect

Formation of quasi-condensed NO under 20 MPa is evidenced in slit-shaped nanospaces of ACF

High pressure (>200 atm) gas phase reaction occurs below 0.1 MPa tm

K. Kaneko, et al, *J. Chem. Phys.*, **87**, 776 (1987).

J. Imai et al, *J. Phys. Chem*. **95**,9955 (1991) $3(NO)_2 = 2N_2O + (NO_2)_2$ 20MPa

Y. Nishi et al, *J. Phys. Chem. B*, **101**, 1938 (1997).

N_2 formation from NO at ambient temperature

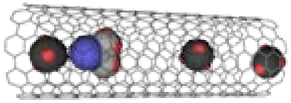
Other group

K. Hashimoto, A.Fujishima et al, *J.Electrochem. Soc*. **147**, 3393 (2000). Exp. Study

Electrochemical reduction of CO_2 to CO (methanol etc) under 10MPa

K.E.Gubbins et al, *J.Chem.Phys*. **125**, 084711(2006). Theoretical study

Superhigh pressure effect – GPa Pressure in tube space



High Pressure Science and Technology

Superhigh pressure

Pressure at the bottom of ocean 1,100 atm
(110 MPa)

Ammonia Synthesis

200-1,000 atm (20 – 100 MPa)
(700 – 900 K)

Haber-Bosch 1918 Nobel Prize in Chemistry

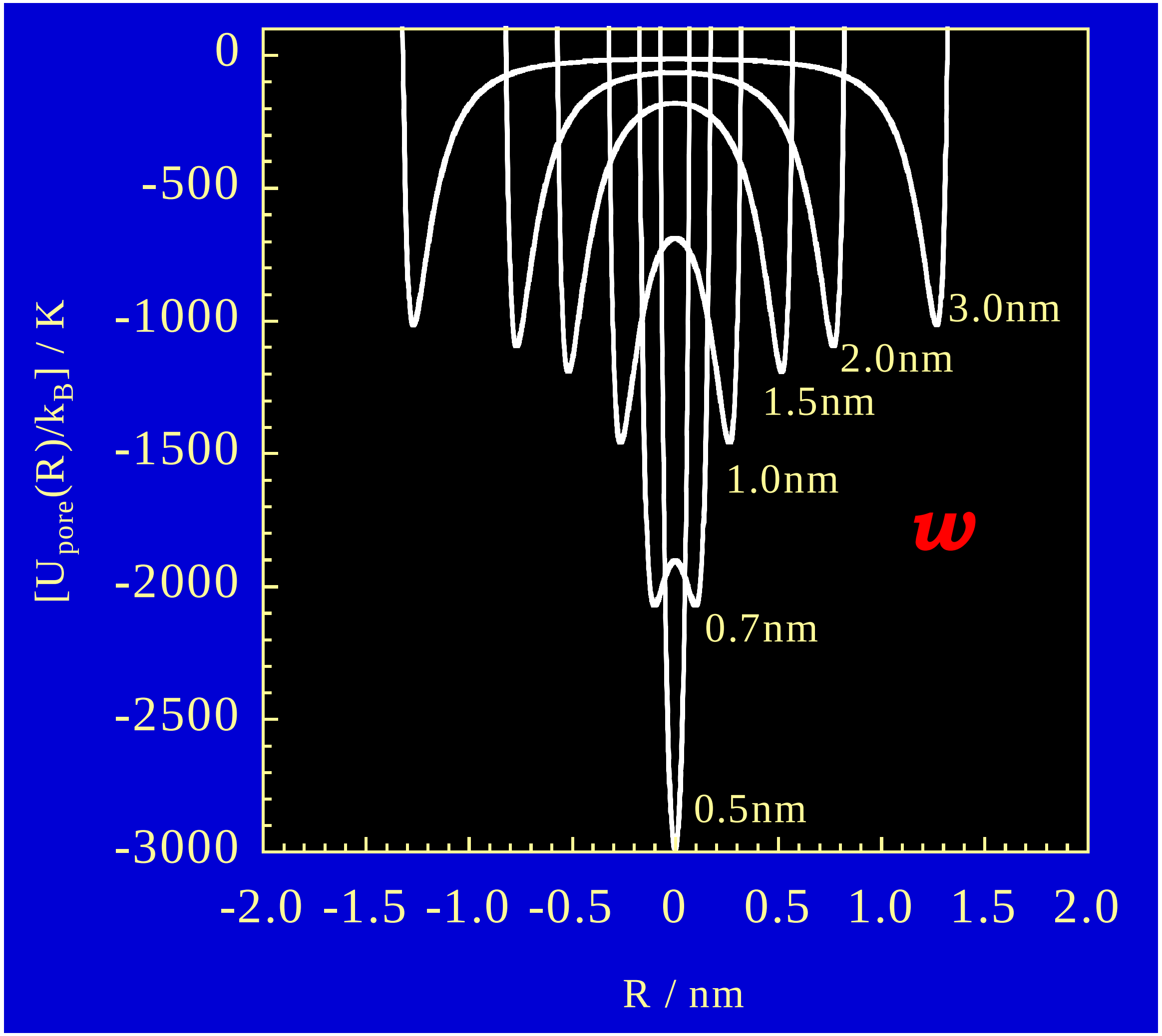
Development of superhigh pressure systems

10,000 atm (10GPa)

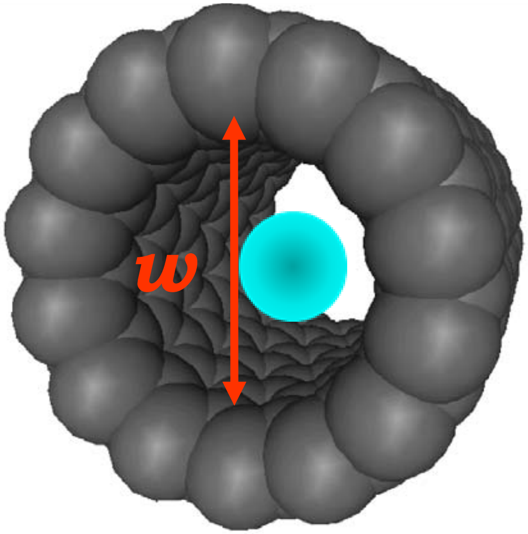
Bridgman 1946 Nobel Prize in Physics

Very Deep Interaction Potential Well

N_2-SWCNT interaction



SWCNT



Cylindrical pore

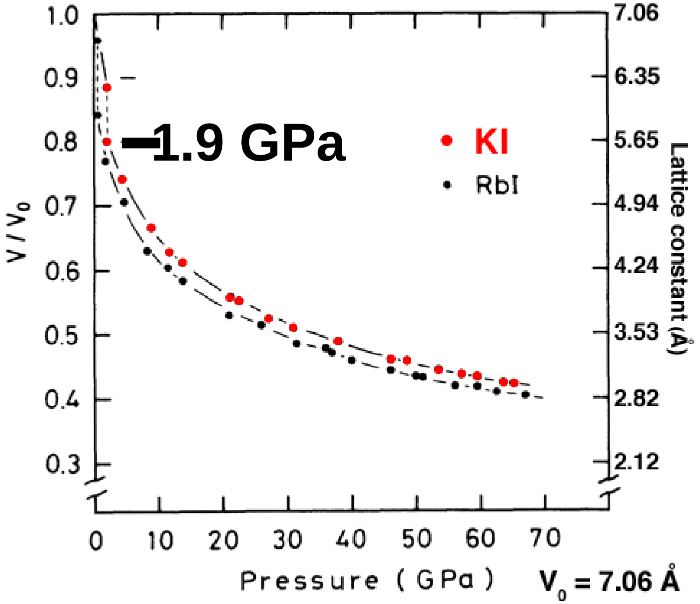
A More Predominant

High pressure effect ?

Remarkable Stabilization of High Pressure Solid Phase

KI

Hygroscopic material

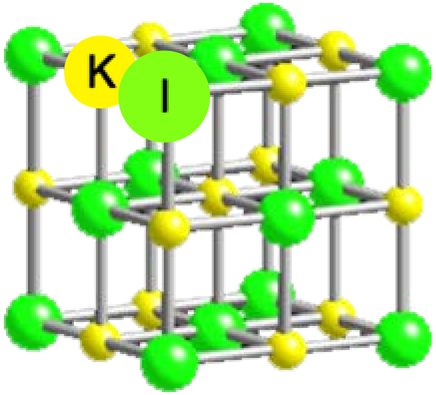


$V_0 = 7.06$ Å

K. Asaumi et al, PRB (1983)

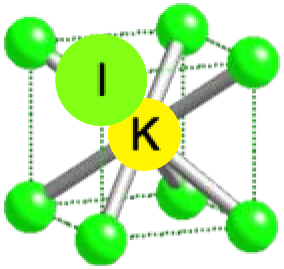
K. Urita,

Nagasaki Univ.



B1 [$Fm\bar{3}m$]

a = 7.06 Å



B2 [$Pm\bar{3}m$]

a ≤ 5.65 Å

How about KI assemblies in carbon nanospaces ?

Single Walled Carbon Nanohorn SWCNH

Advantage of SWCNH

Laser ablation of graphite in Ar

at room temp.

No catalyst High purity

Production rate – 10 g/h

Material-Yield ~ 90%

Close SWCNH

(as-received)

Open SWCNH (ox-SWCNH)

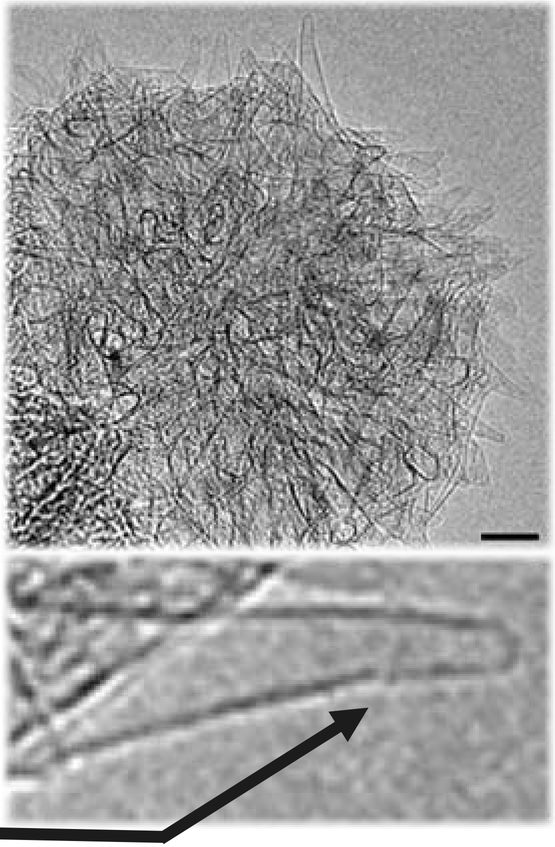
Oxidation of SWNH

at 693 K in O_2

Nanowindow

P.J.F.Harris et al (1994) product by arc-evaporation of microporous carbon

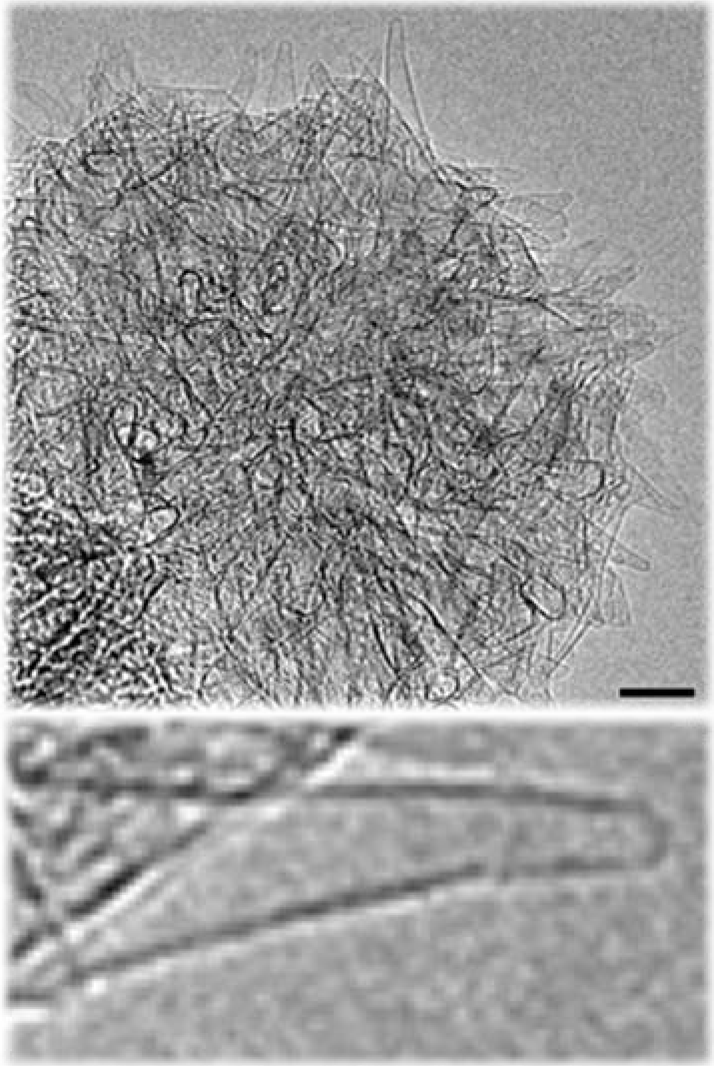
S.Iijima et al (1999) Pure form production with laser ablation of graphite



TEM images

JEOL-2010
Gun: LaB$_6$
V$_{acc}$: 200 kV

Before doping **SWCNH**

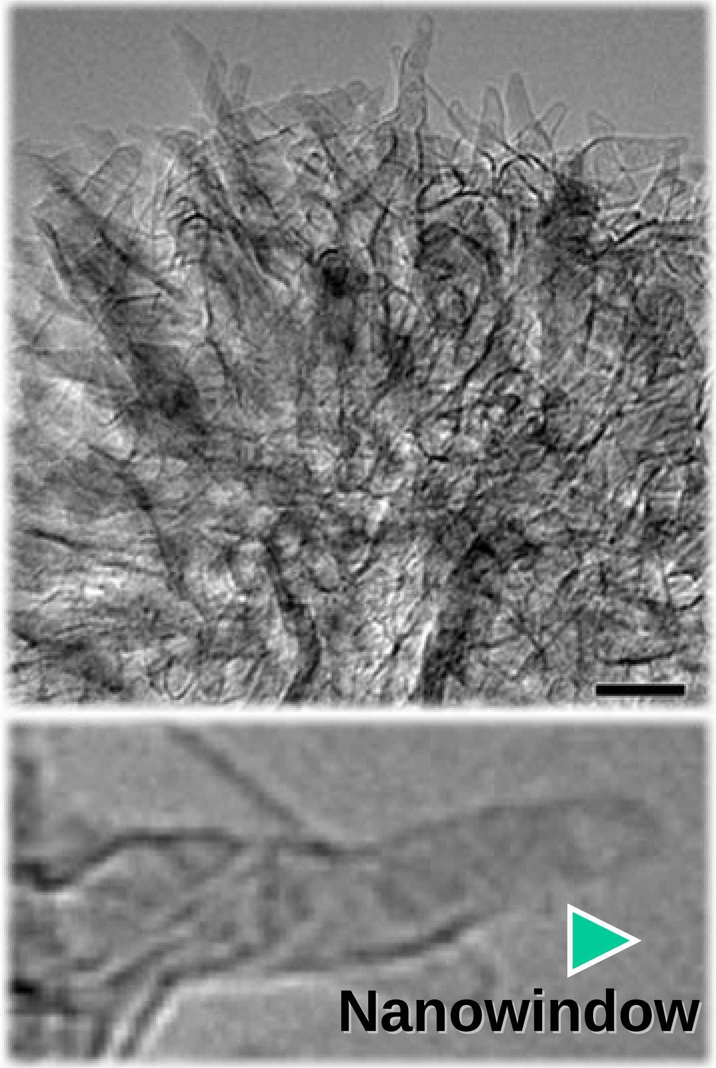


Doping

1073K

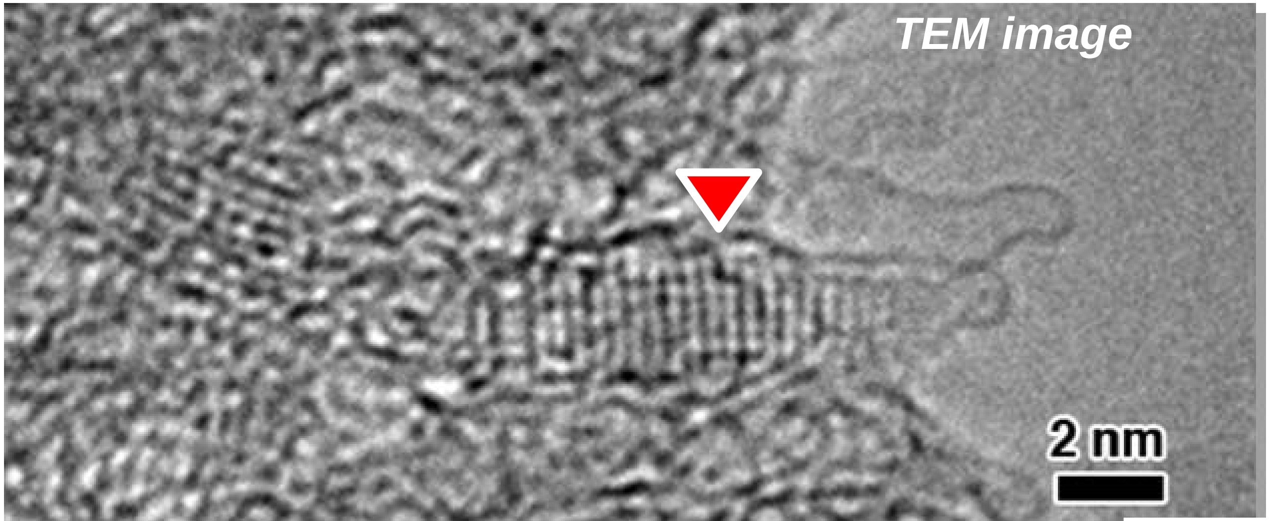
8h

After KI doping **oxSWCNH/KI**



Bar: 10 nm

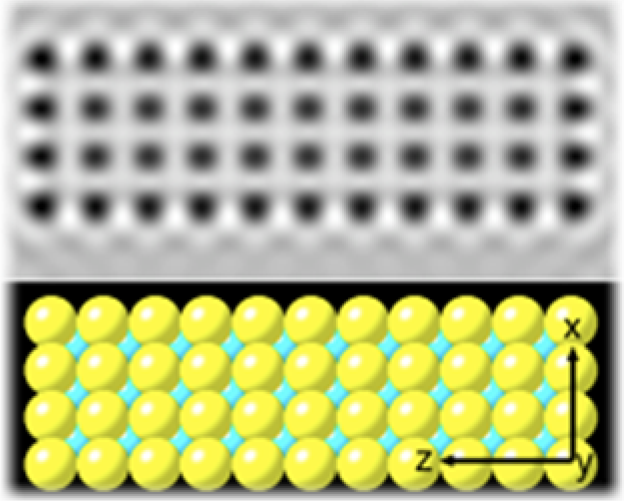
Crystal Structure Determination from TEM Image



Crystal growth: horn axis

Black dot: iodine atom

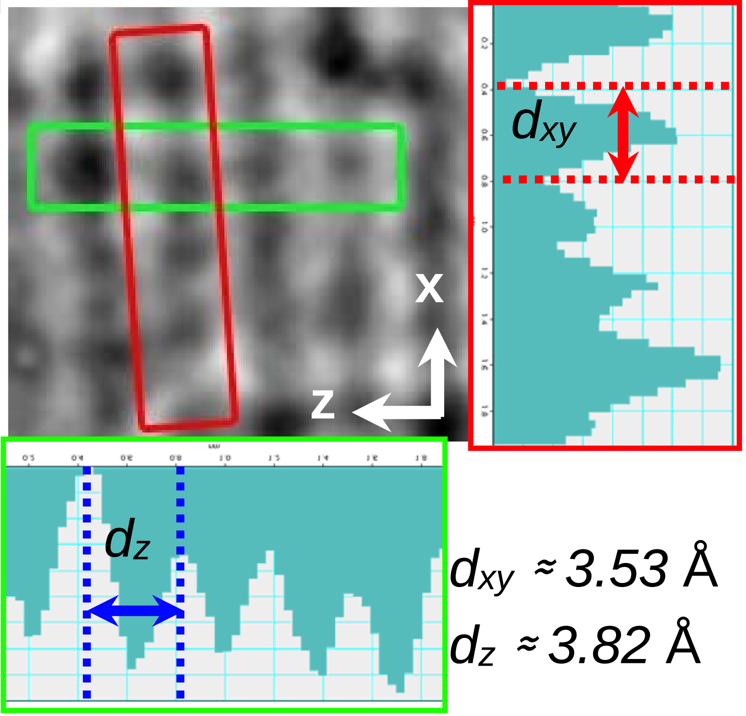
Simulated image (B2)



>1.9GPa

a, b ≈ 3.53 Å

c ≈ 3.82 Å

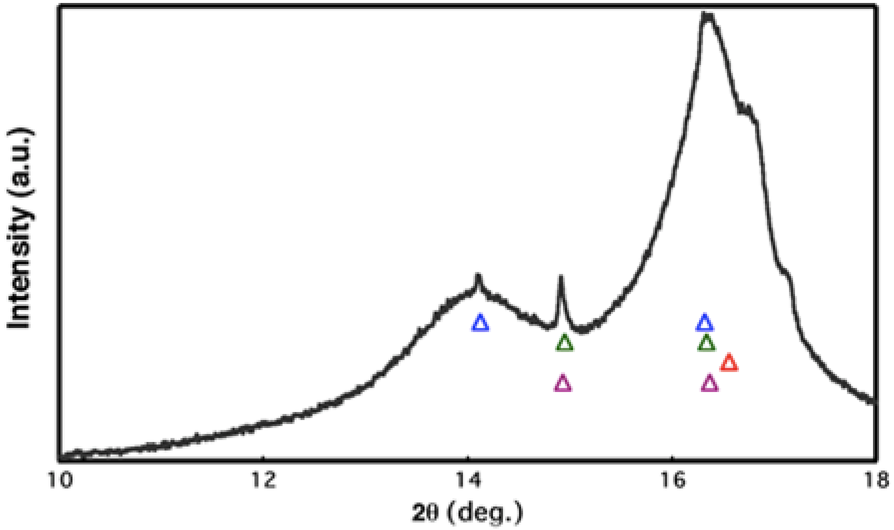


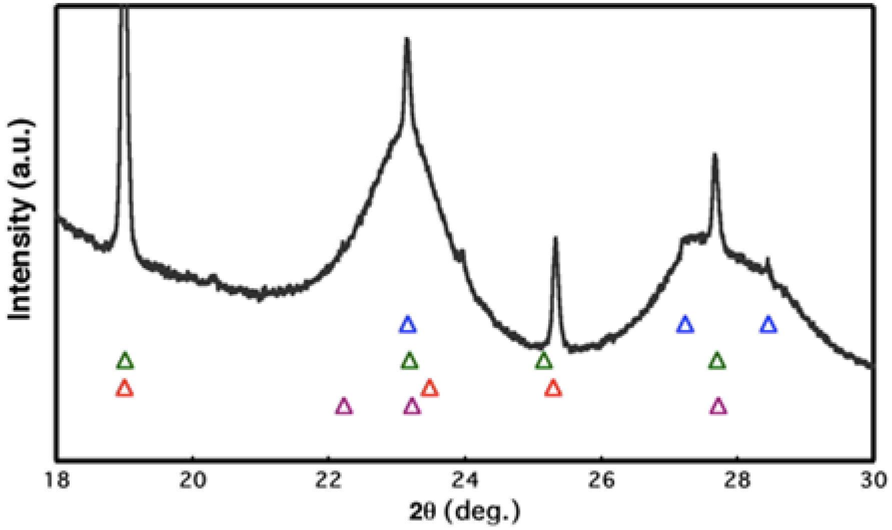
d_{xy} ≈ 3.53 Å

d_z ≈ 3.82 Å

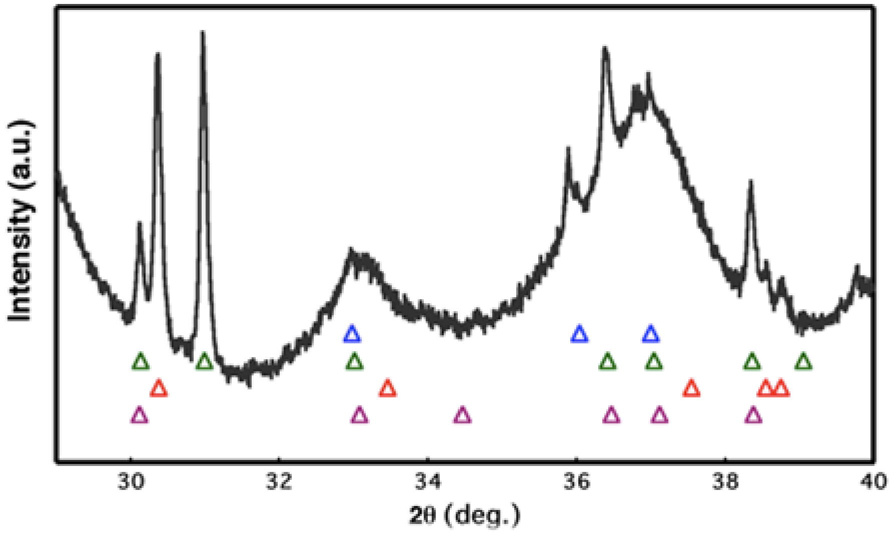
Synchrotron XRD KI/SWCNH

λ = 1.003 Å
(SPring-8)



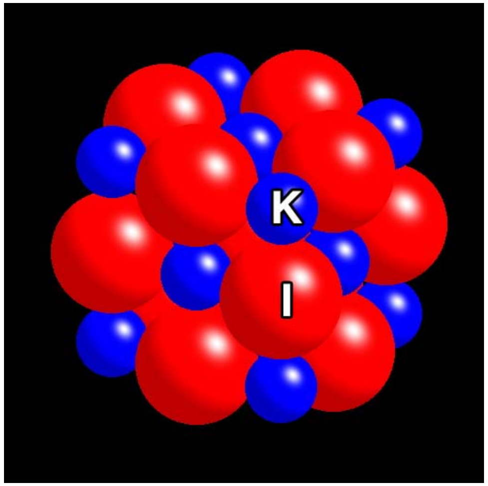


△B1 (a = b = c = 7.061 Å)
△B1 (a = b = 7.061 Å, c = 6.078 Å)
△B2 (a = b = 3.485 Å, c = 3.040 Å)
△B2 (a = b = 3.530 Å, c = 3.863 Å)



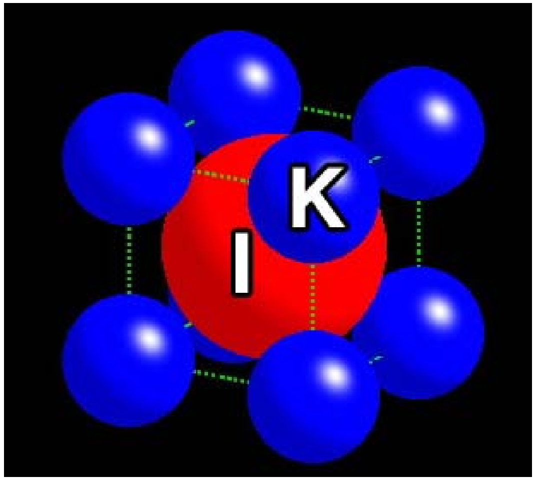
Distorted high pressure phase

Super high pressure phase is stabilized in nanospaces

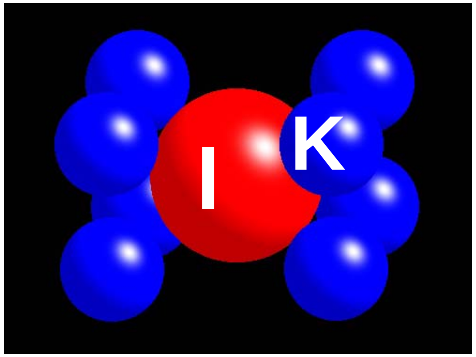


B1 NaCl type

>1.9 GPa



B2 CsCl type



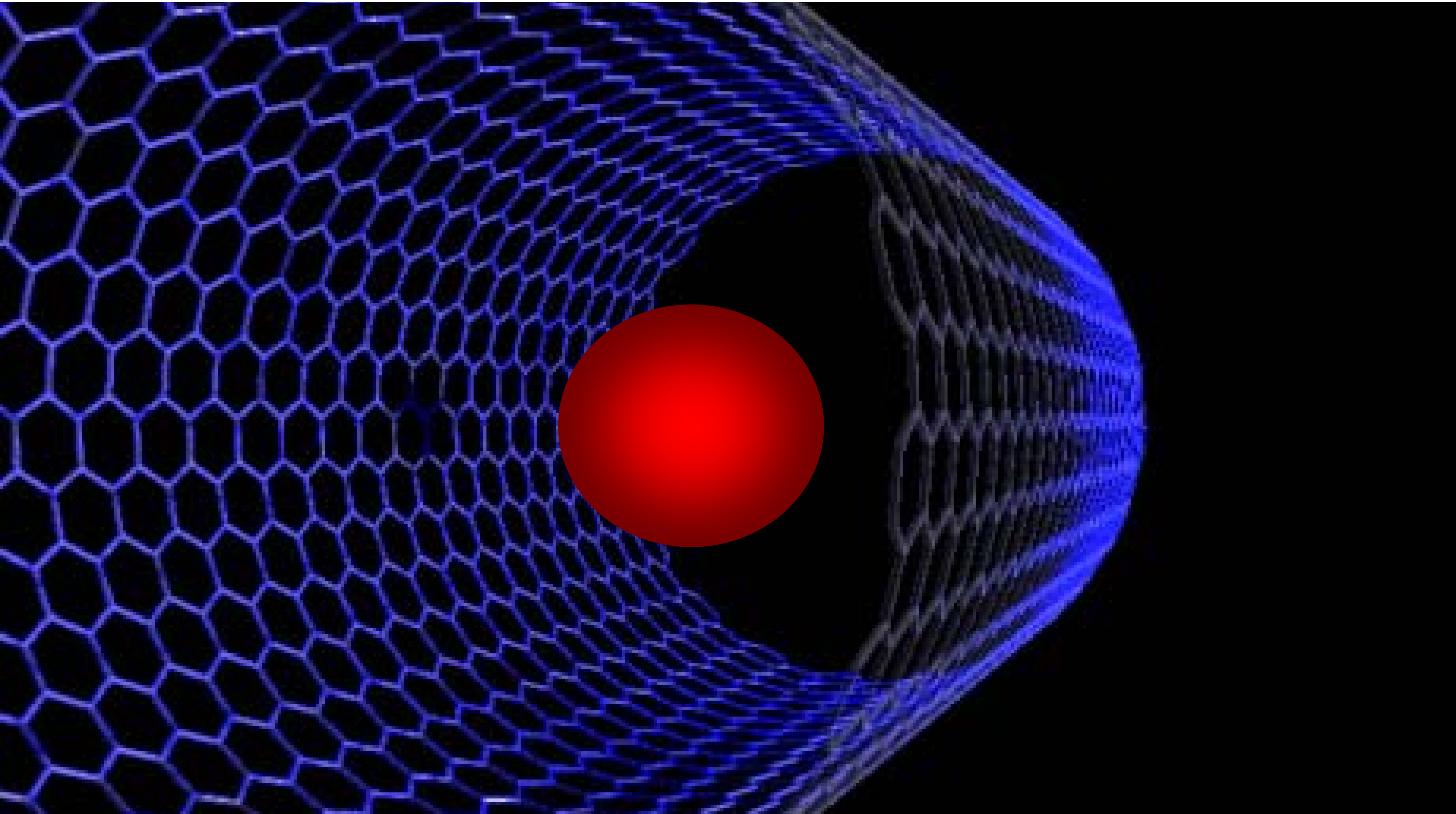
Tetragonal

The structure of high-pressure phase can be formed in nanospaces below 0.1 Mpa.

Urita et al, *J. Amer.Chem. Soc.*133, 10344 (2011)

Quantum Molecular Sieving Effect

Uncertainty in Position of Light Molecules



Quantum Molecular Sieving Effect

H_2 and D_2 on SWCNH, ACF, MOF, SWCNT

Published

The followings will be presented on Saturday

by T. Fujimori

$^{12}CH_4$ and $^{12}CD_4$ ($^{12}CH_4$ and $^{13}CH_4$)

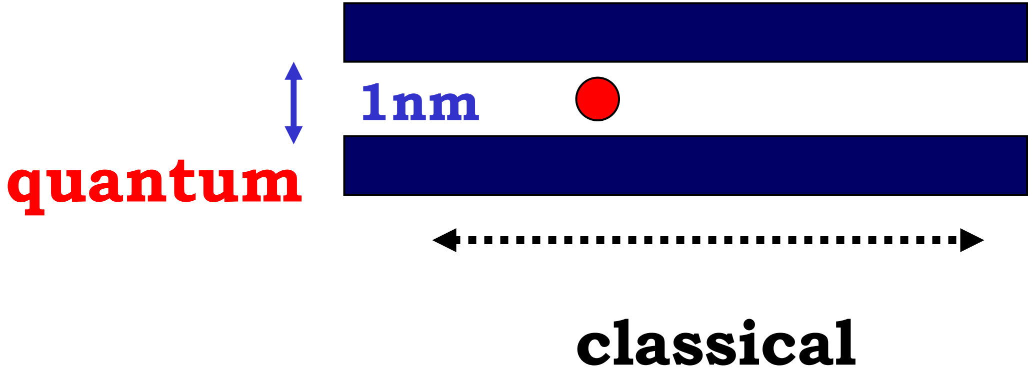
New, unpublished

Application potential

to radioactive ^{14}C separation

Quantum Nature of He in Nanopores at 4.2K ?

1994 Kaneko et al



(COPS Characterization of

Porous Solids

(J. Rouquerol))

He adsorption on ACF, Slit pore

$$E_n = n_s^2 h^2 / [8m(w - \sigma)^2]$$

Possibility in size uncertainty

real size > classical size

Active Theoretical and Simulation Studies on Physical Adsorption on SWCNT

J.J.M. Beenakker (1995)

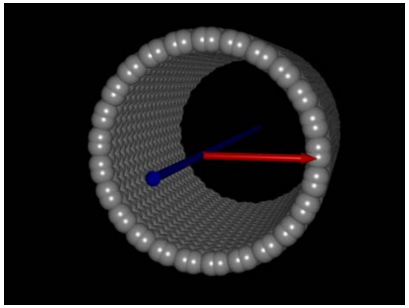
Single-walled carbon nanotubes (SWCNT) and its bundles, *"Quantum sieving"*, *A simple model*

G.W.Stan and M.W.Cole (1998) Quantum effect

K.Jonhson et al (Phys. Rev. Lett. 1999)

Pioneering contributions

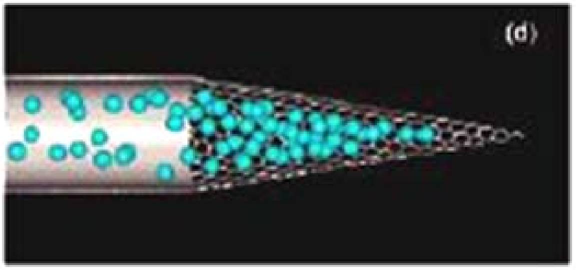
Prediction of a significant quantum effect in H_2 adsorption on SWCNT with Path Integral



No sufficient experimental studies

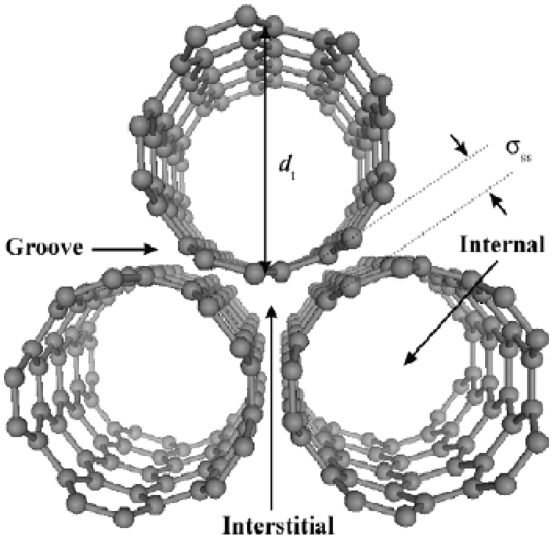
Preceding Studies on Quantum Molecular Sieving

SWCNH 1)



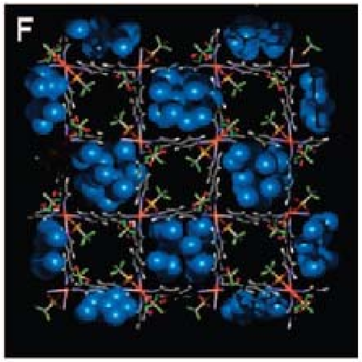
ACF 2)

SWCNT 5)

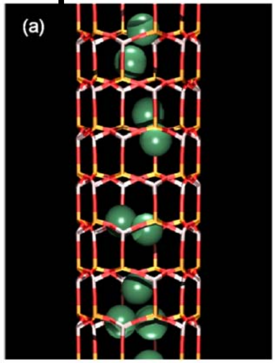


H. Tanaka
Kyoto Univ.

CuBOTf 3)



AlPO$_4$-5 4)



1) H. Tanaka, H. Kanoh, M. Yudasaka, S. Iijima, K. Kaneko, *J. Am. Chem. Soc*. **2005**, *127*, 7511.
2) Y. Hattori, H. Tanaka, F. Okino, H. Touhara, Y. Nakahigashi, S. Utsumi, H. Kanoh, K. Kaneko, *J. Phys. Chem B*. **2006**, *110*, 9764.
3) D. Noguchi, H. Tanaka, A. Kondo, H. Kajiro, H. Noguchi, T. Ohba, H. Kanoh, K. Kaneko, *J. Am. Chem. Soc*. **2008**, *130*, 6367.
4) H. Tanaka, D. Noguchi, A. Yuzawa, T. Kodaira, H. Kanoh, K. Kaneko, *J. Low Temp Phys*. **2009**, *157*, 352.
5) D. Noguchi, H. Tanaka, T. Fujimori, H. Kagita, Y. Hattori, H. Honda, K. Urita, S. Utsumi, Z. Wang, T. Ohba, H. Kanoh, K, Hata, K. Kaneko, *J. Phys. Cond. Mater*. **2010**, *22*, 334207.

Quantum Effects on Adsorption

◆Classical fluid

Lennard-Jones Potential

$$V_{LJ} = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right]$$

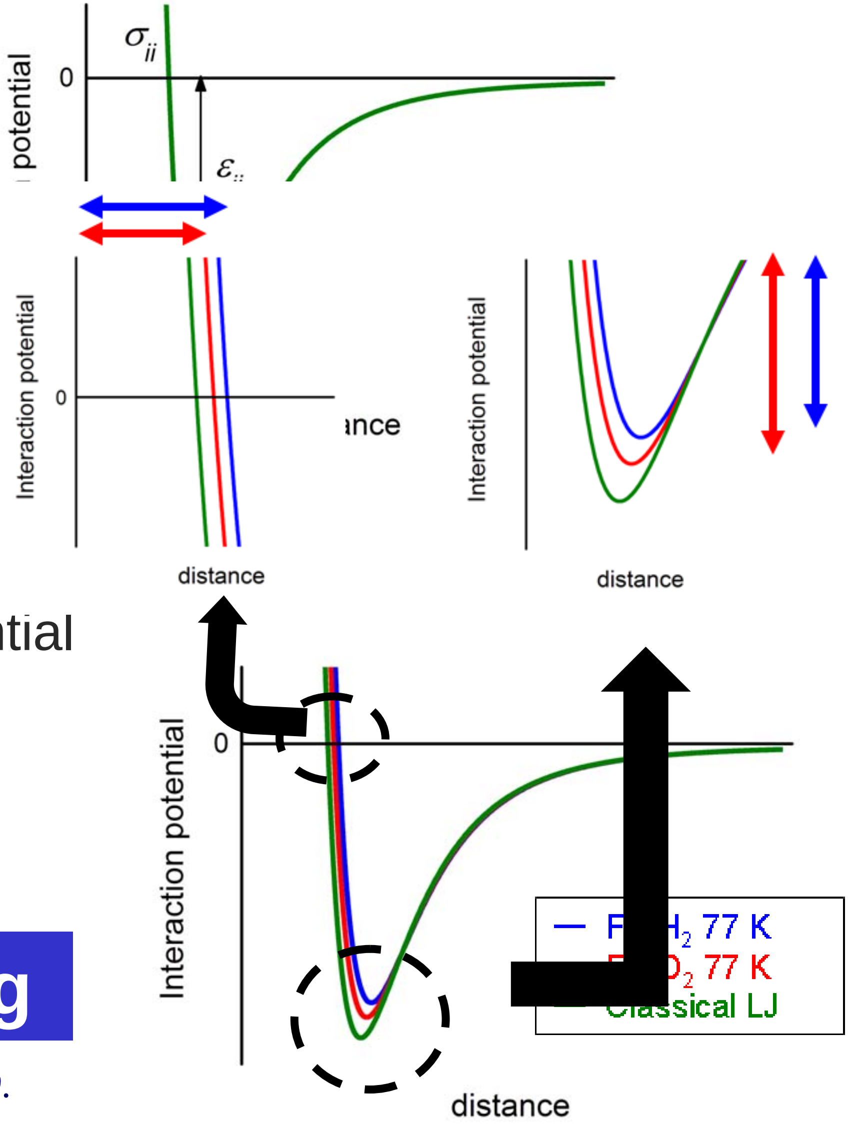
◆Quantum fluid

Quadratic Feynman-Hibbs effective potential

$$V_{FH} = V_{LJ} + \frac{\hbar^2}{12\boxed{m}k_B\boxed{T}}\left[V_{LJ}'' + \frac{2}{r}V_{LJ}'\right]$$

Isotope separation based on quantum

Quantum molecular sieving



J. J. M. Beenakker, *et al. Chem. Phys. Lett.* **1995**, *232*, *379*.

Q. Wang, S. R. Challa, D. S. Sholl, J. K. Johnson, *Phys. Rev. Lett.* **1999**, *82*, 956.

Adsorption Study on Quantum Fluids

Low Temperature Adsorption Measurement

Thermal transpiration effect was corrected

T. Takaishi, Y. Sensui, Trans. Faraday Soc. 53 (1963) 2503

Quantum Molecular Simulation

Feynman-Hibbs (FH) **effective potential V_{FH}**

$$V_{FH}(r)=\left(\frac{6\mu kT}{\pi\hbar^2}\right)^{2/3}\int d\mathbf{u}V_{LJ}(|r+\mathbf{u}|)\exp\left(-\frac{6\mu kT}{\hbar^2}u^2\right)$$

Taylor expanding about $\mathbf{u}=0$:

$$V_{FH}(r)=V_{LJ}(r)+\frac{\hbar^2}{24\mu kT}\left(V''_{LJ}(r)+\frac{2}{r}V'_{LJ}(r)\right)$$

V_{LJ}; Lennard-Jones pair potential

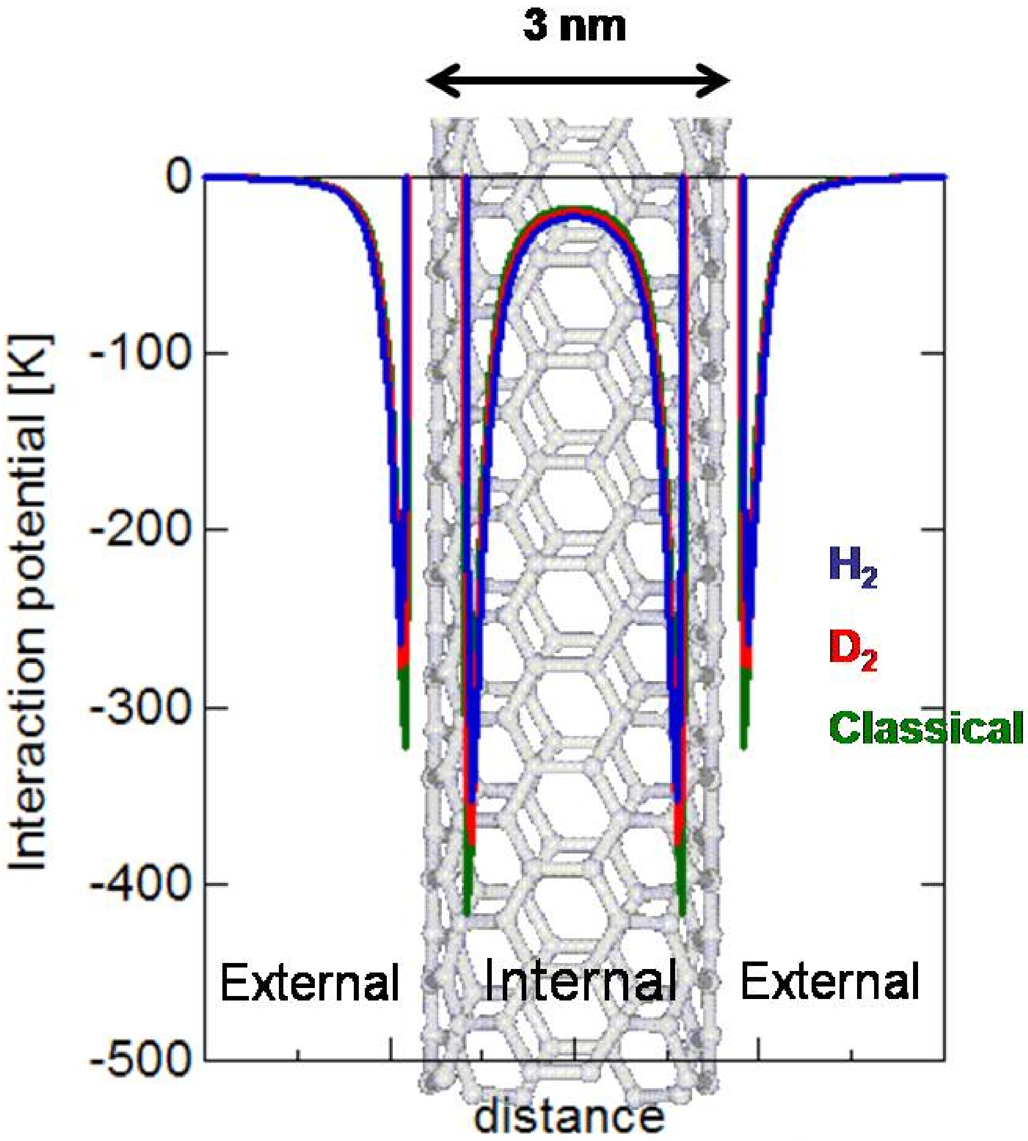
μ; Reduced mass of a quantum molecule (= $M/2$)

T; Temperature

Path integral formalism was used for limited case

Interaction Potential Profiles of H_2 and D_2 with SWCNT at 20 K

Classical: Identical Quantum: Different, H_2 D_2



Extent of Quantum Fluctuation

de Broglie Wave Length (nm)

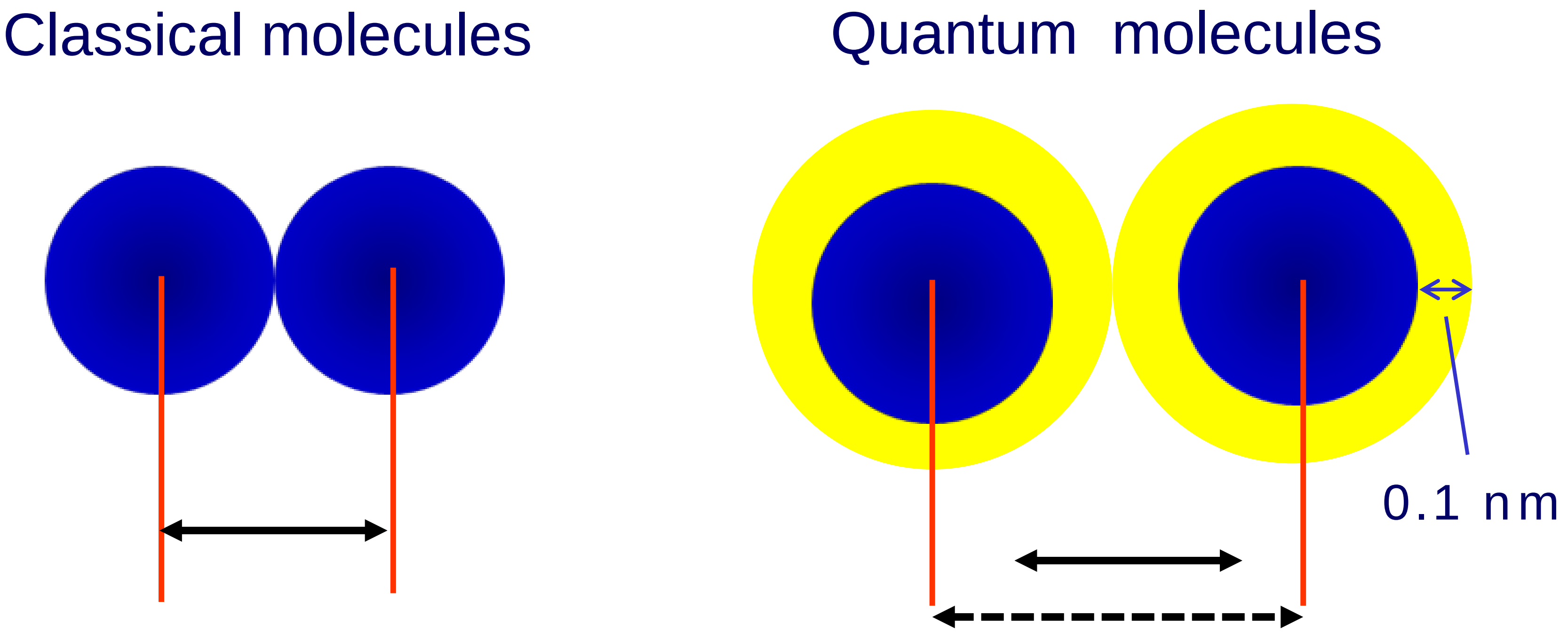
$$\lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2}$$

	20K	77K	300K
H_2	0.3	0.14	0.07
$D_2(He^4)$	0.17	0.11	0.05
Ne	0.06(27K)	0.05	0.02
N_2	—	0.04	0.017

Ne (AW: 20) at 27K

H. Tanaka, M. El-Merraoui, T. Kodaira, K. Kaneko, *Chem. Phys. Lett*., 2002, *351,* 417.

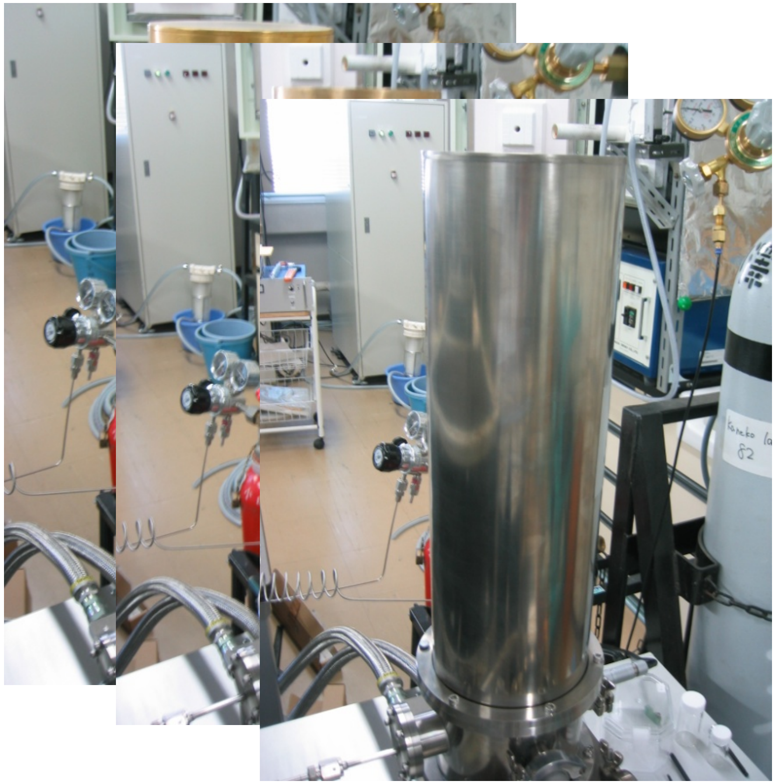
Inter-quantum Molecular Interaction



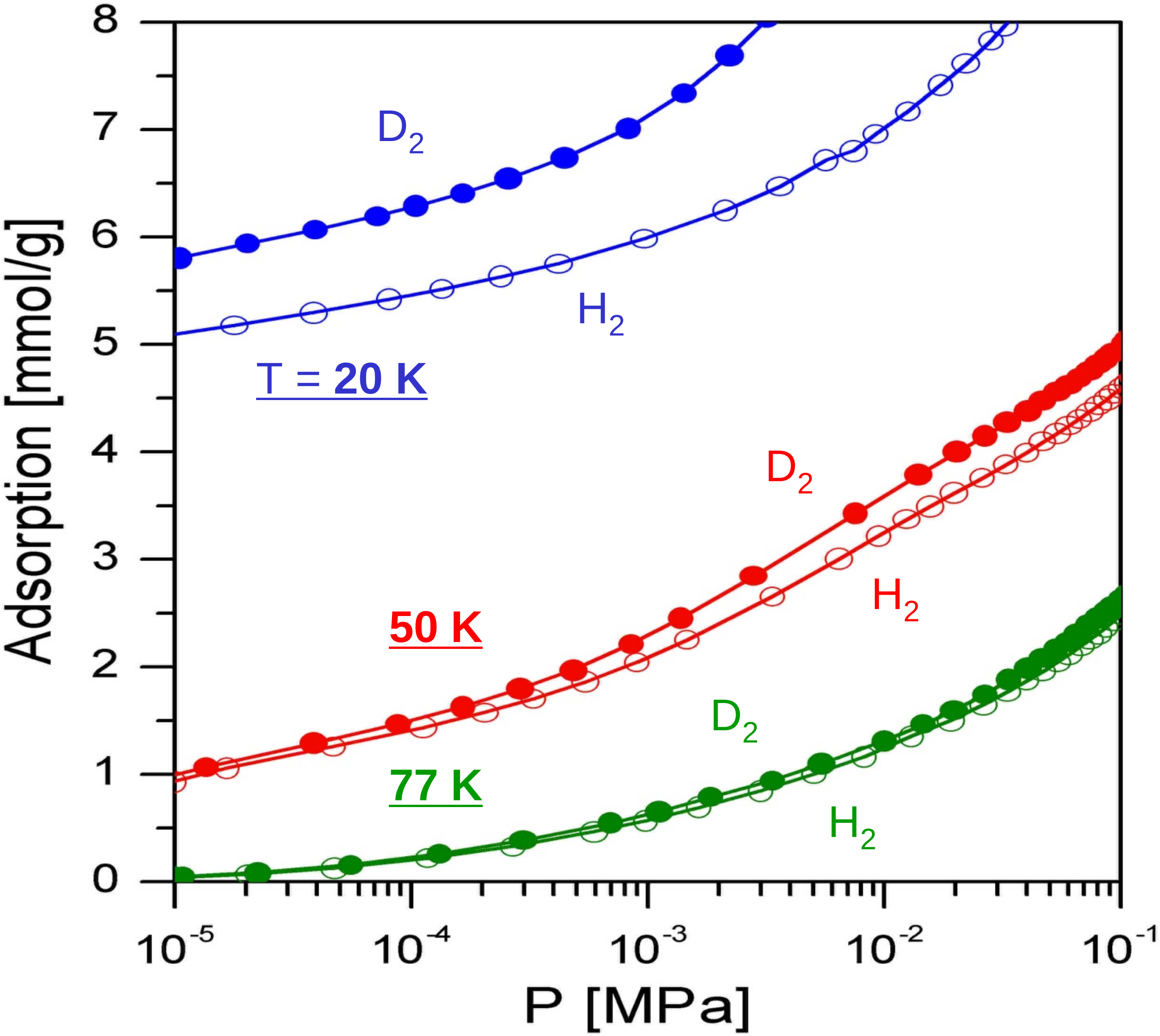
Fluctuation increases size,

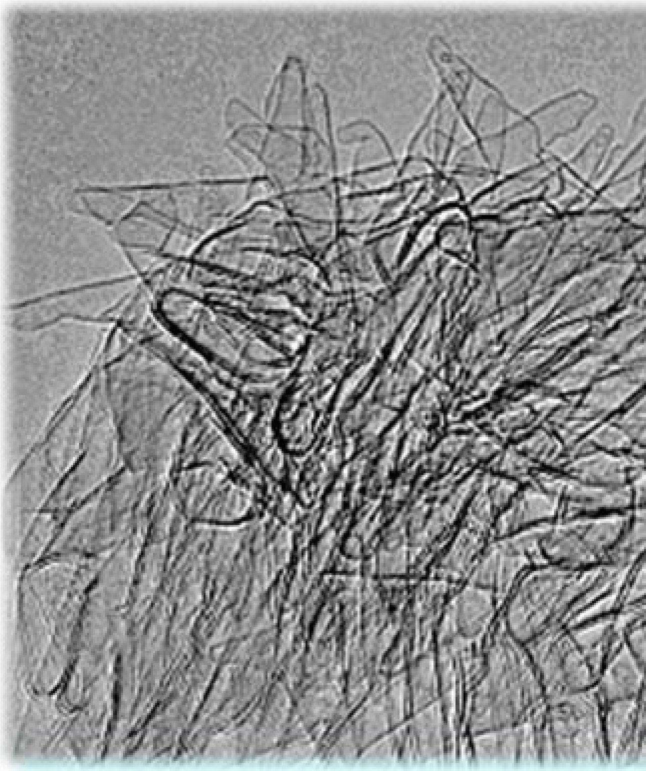
weakening interaction

Volumetric Adsorption System from 4 K



Temperature Dependence of Adsorption Isotherms of H_2 and D_2 in Interstitial Pores of SWCNH

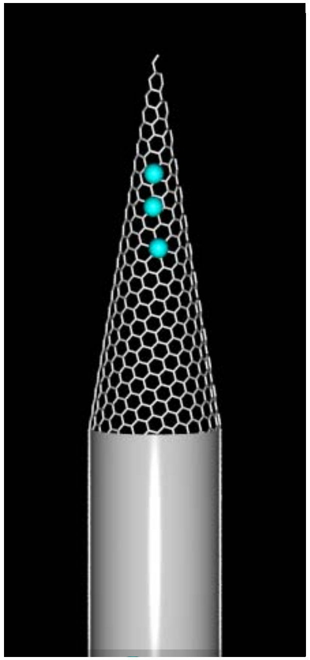




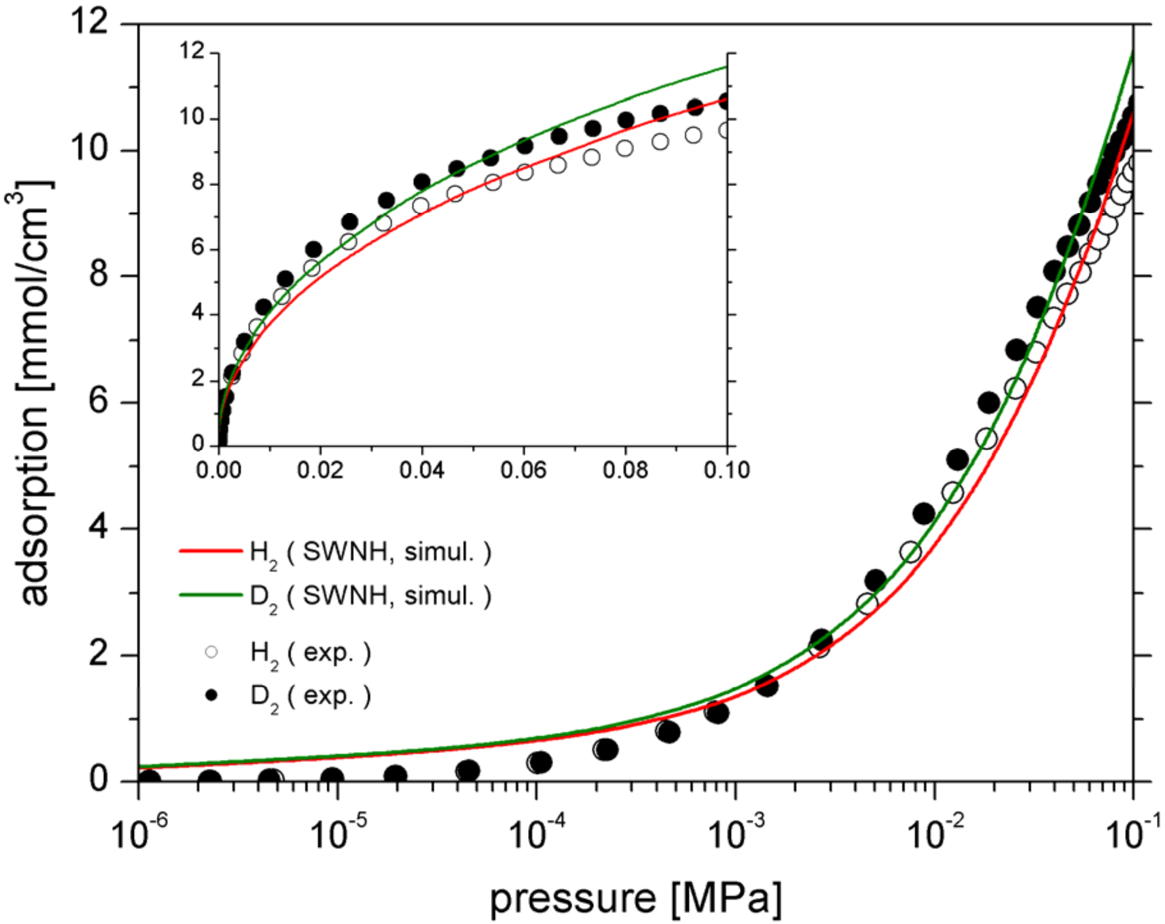
Single wall carbon Nanohorn SWCNH

Comparison of H_2 and D_2 Adsorption Isotherms only in Internal Tube Spaces from Simulation and Experiment at 77 K

Adsorbed density – liquid density at 20 K

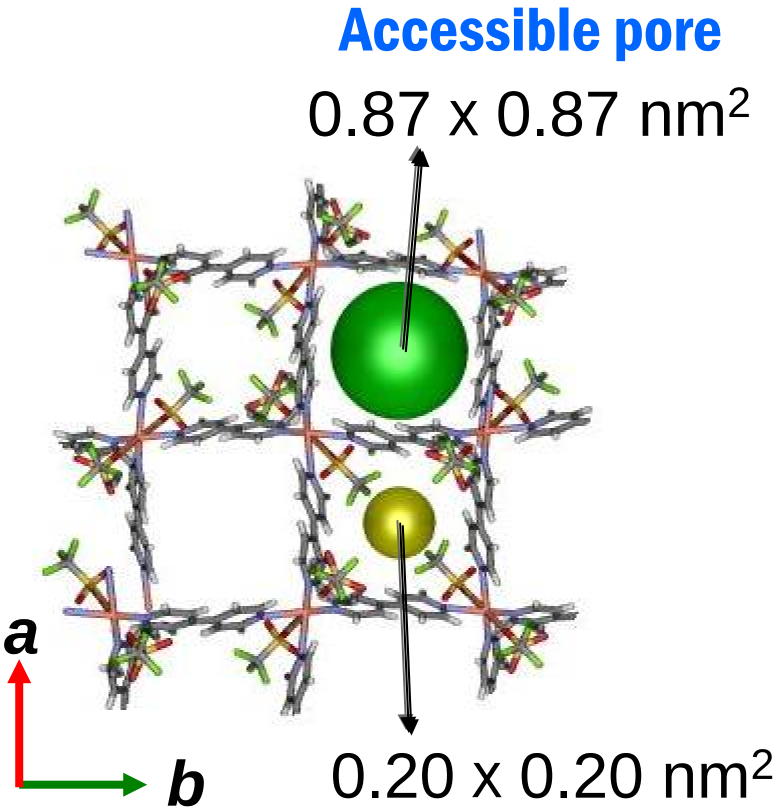


0.0001 MPa



H. Tanaka, H. Kanoh, M. Yudasaka, S. Iijima, K. Kaneko, *J. Am. Chem. Soc.* **2005**, *127*, 7511.

Quantum Sieving Effect of Three-Dimensional Cu-Organic Framework for H_2 and D_2



$[Cu(4,4'\text{-bipyridine})_2(CF_3SO_3)_2]_n$

Measurement of H_2 and D_2 isotherms

at 77 K and 40 K

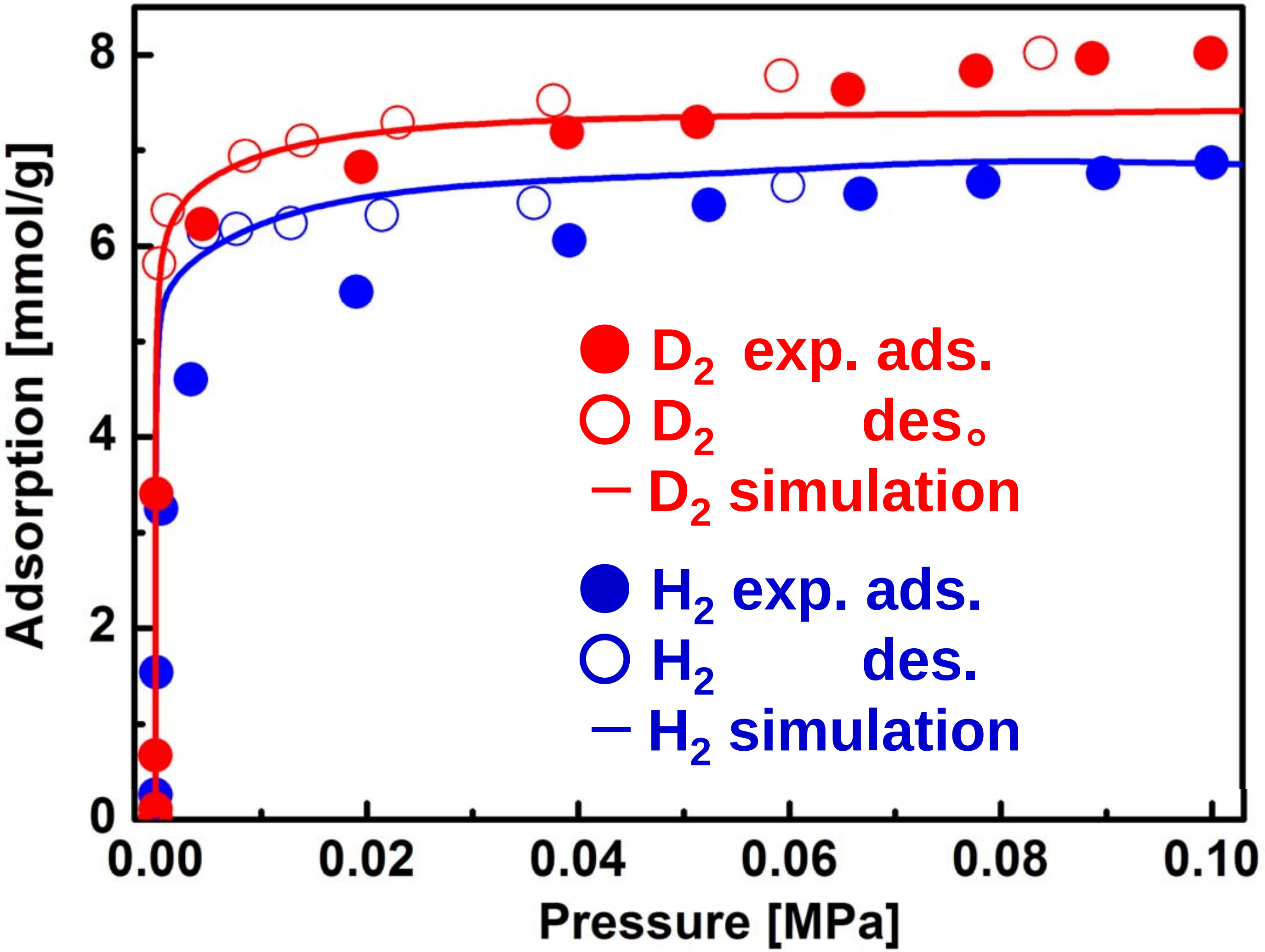
Quantum molecular simulation

of H_2 and D_2 adsorption

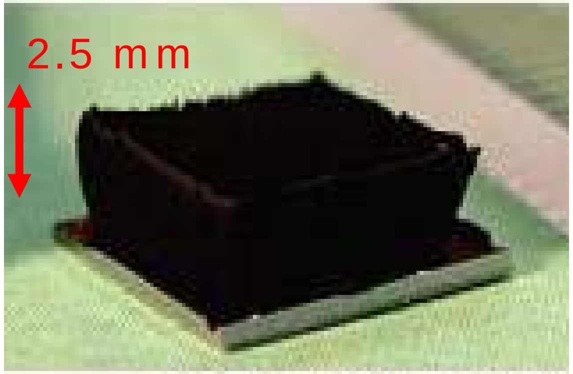
at 77 K and 40 K

D. Noguchi et al.
J. Am. Chem. Soc. **2008**, *130*, 6367.

Adsorption isotherms of H_2 and D_2 at 40 K



Adsorptpion of H_2 and D_2 on Porosity-Controlled SWCNT

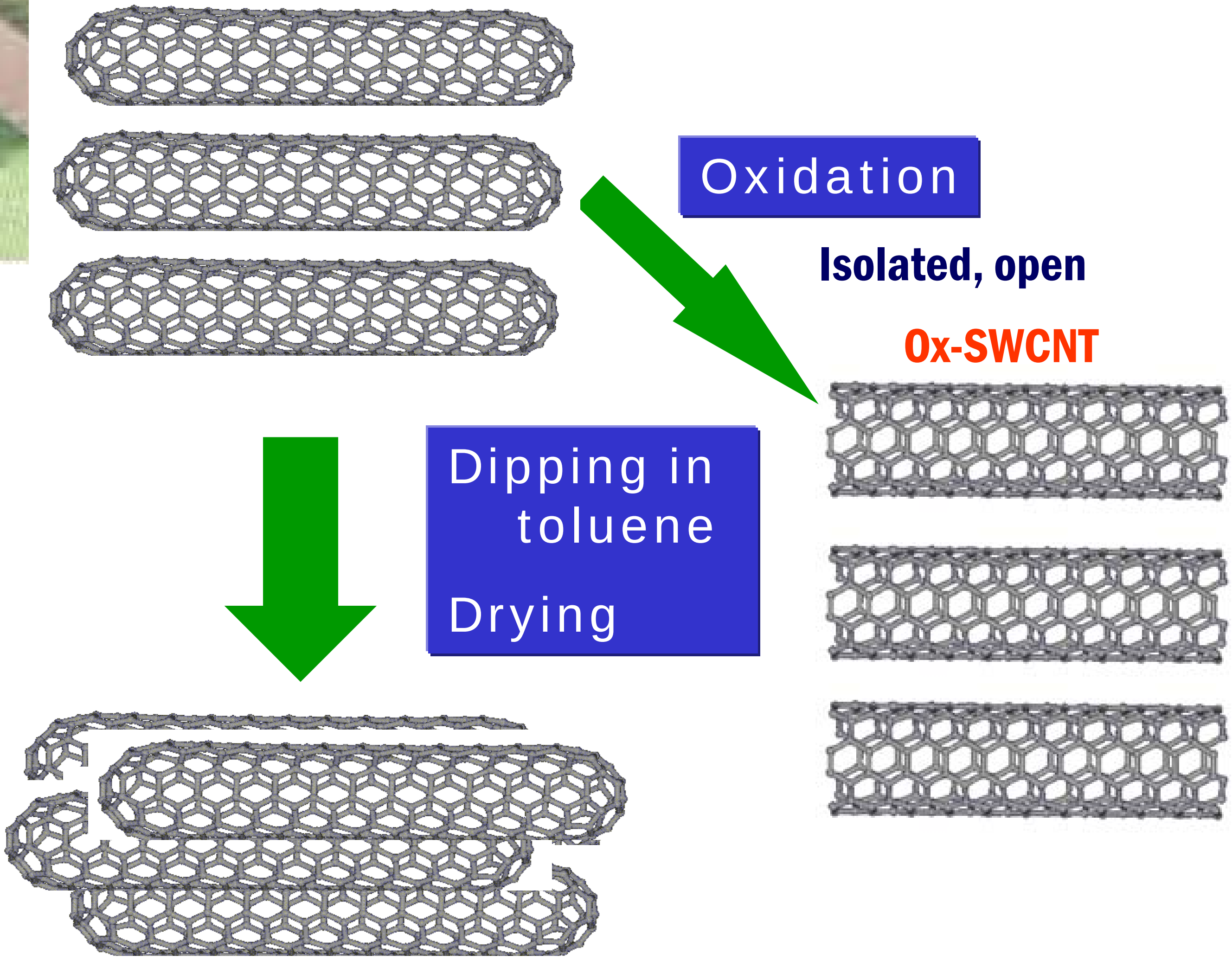


CVD

High purity ＞ 99.98 %

Tube diameter : 1 ~ 3 nm

K. Hata, *et al. Science* 2004, *306*, 1362.



Isolated, closed SWCNT

Oxidation

Isolated, open

Ox-SWCNT

Dipping in toluene

Drying

Bundle

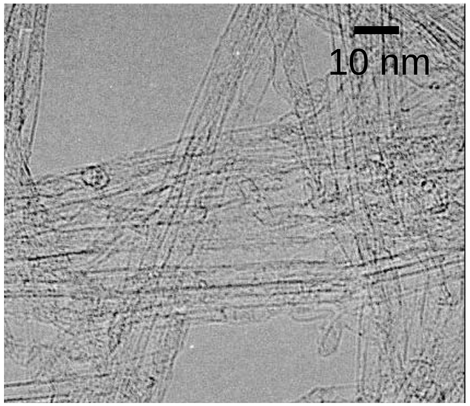
Bund-SWCNT

Kagita, Yamamoto et al, Adsorption (2011) Special Issue for Prof. R. Reinoso-Reinoso In press

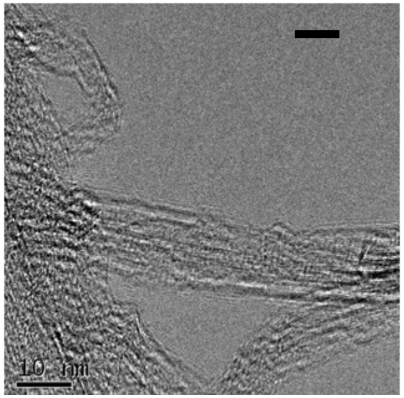
Pore Parameters and TEM Images of SWCNT Samples

	Surface area / $m^2\ g^{-1}$	**Nanopore volume / $cm^3\ g^{-1}$**
SWCNT	**1040**	**–**
ox-SWCNT	**1900**	**0.80**
Bund-SWCNT	**590**	**0.27**

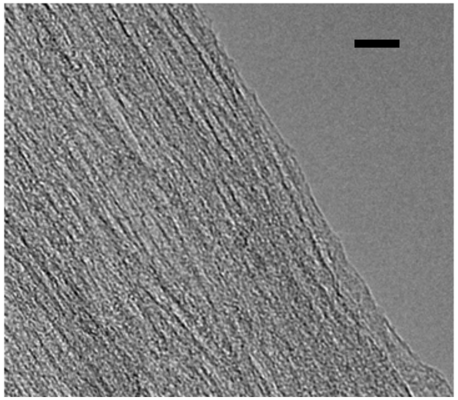
SWCNT



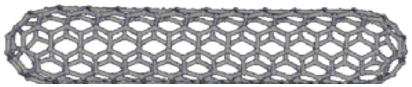
ox-SWCNT



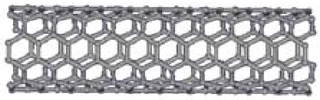
Bund-SWCNT



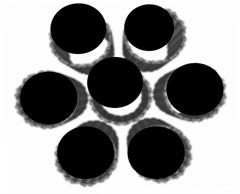
H_2 and D_2 adsorption isotherms on three samples at 20, 40, 77 K



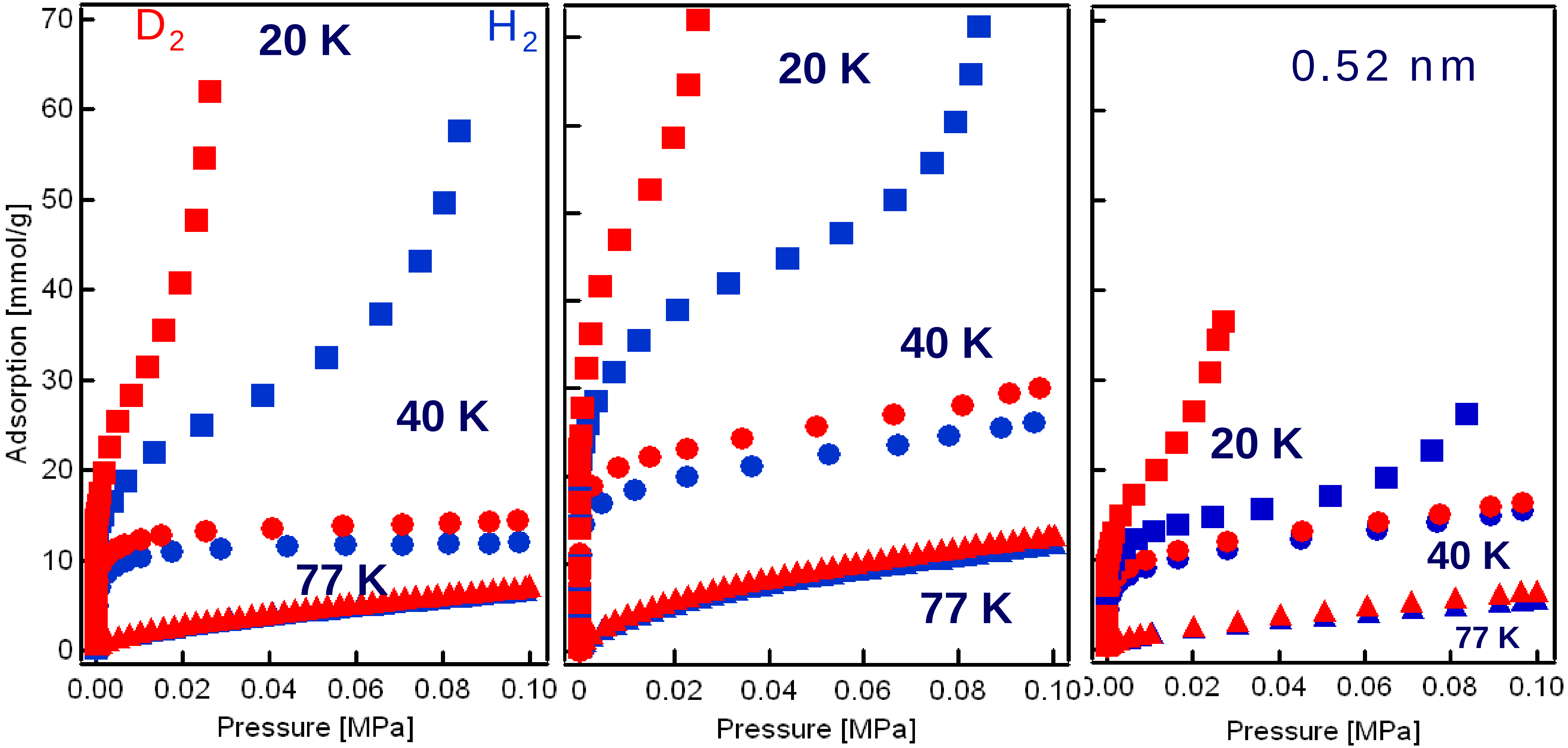
SWCNT



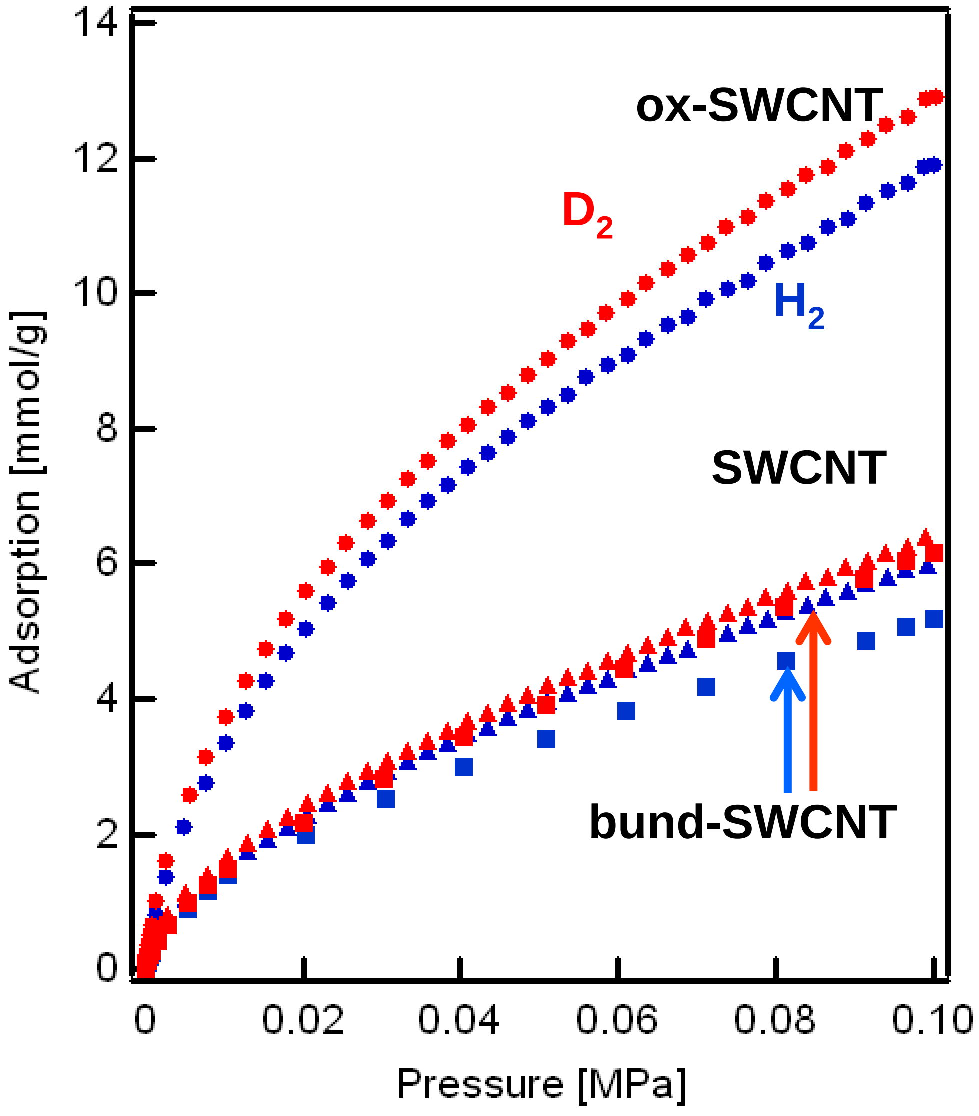
ox-SWCNT

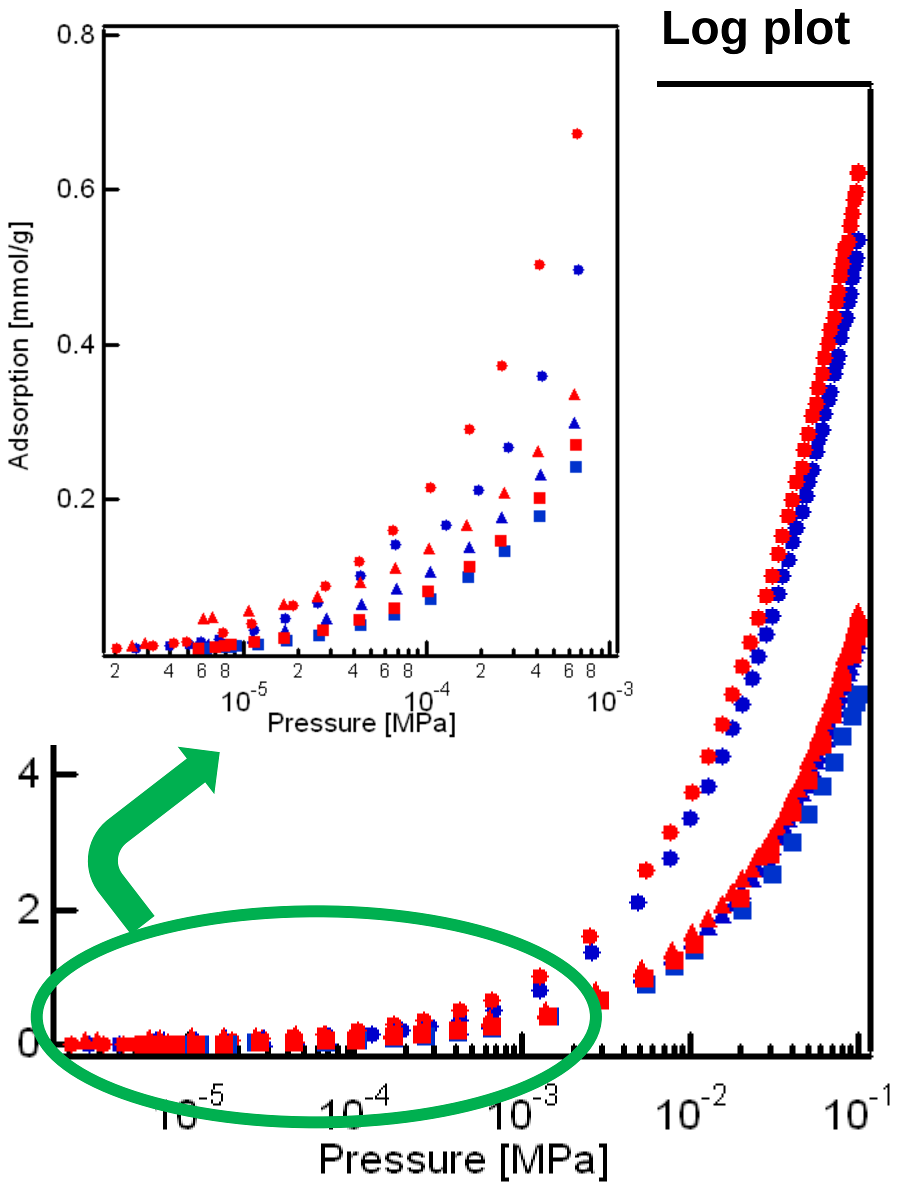


bund-SWCNT

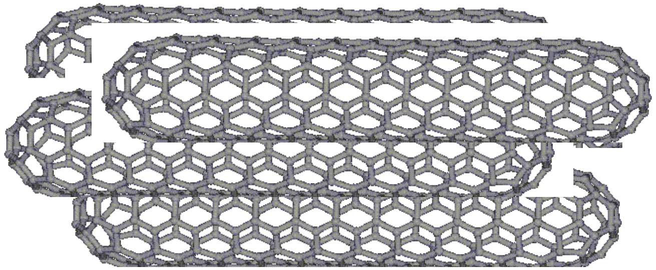


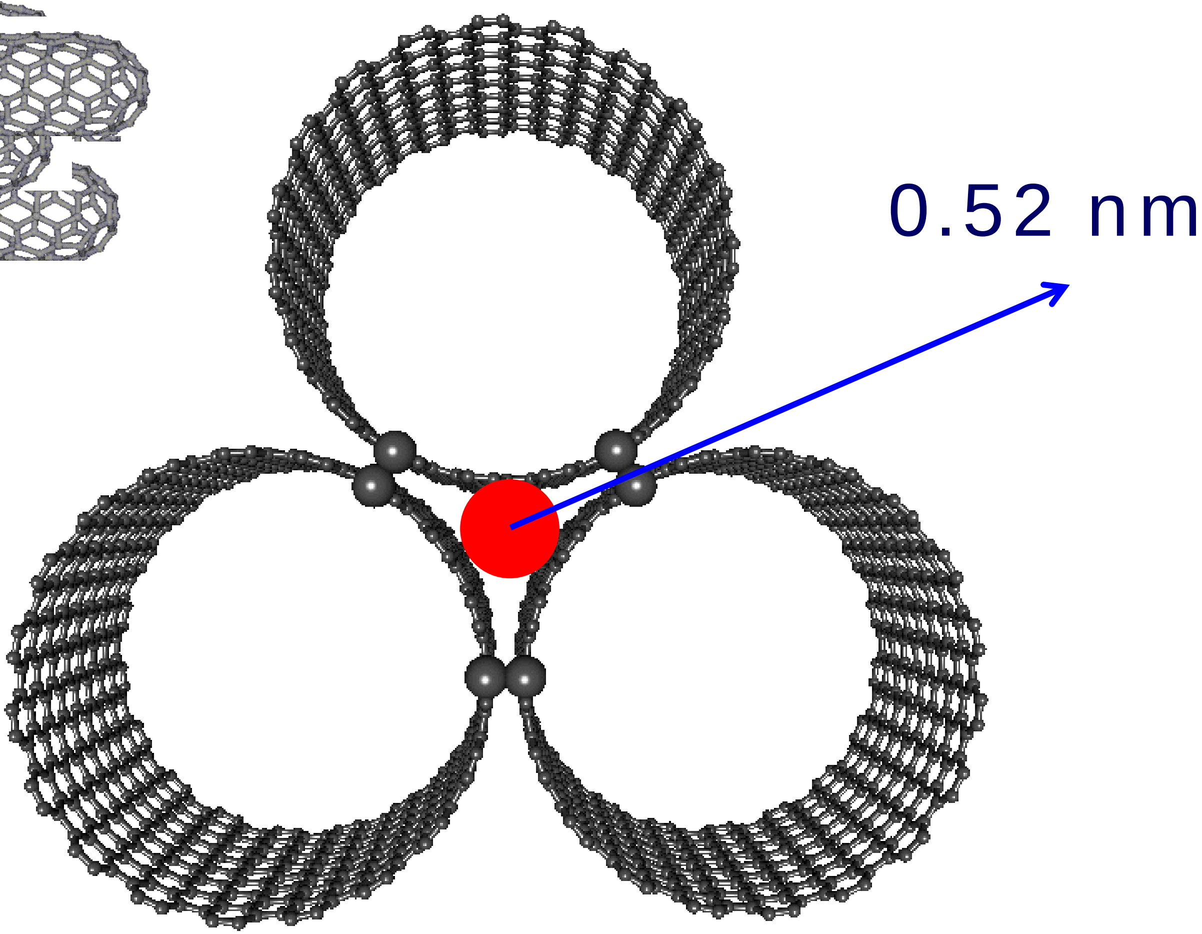
H_2 and D_2 adsorption isotherms at 77 K





Interstitial Pores of Bund-SWCNT





Dynamic Adsorption with H_2/D_2 mixture at 77 K

Importance of kinetic effect:

Kumar A V A and Bhatia S K 2005 *Phys. Rev. Lett.* **95** 245901

Kumar, A. V. et al (2006) *J. Phys. Chem. B*, *110* 33: 16666.

Theoretical and Neutron scattering studies

Mixed gas adsorption at low temp

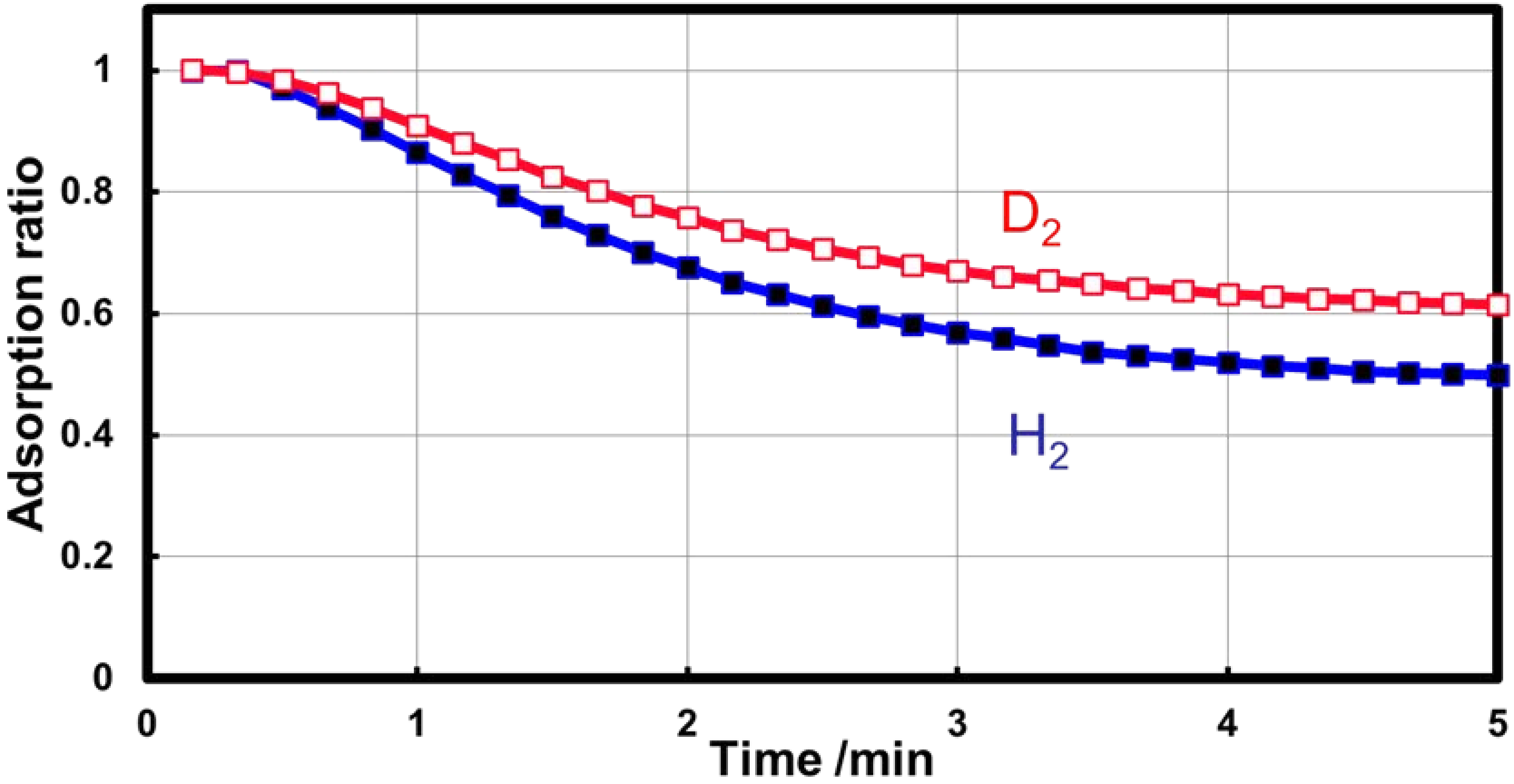
70 K --- 300 K

Gas: Detected

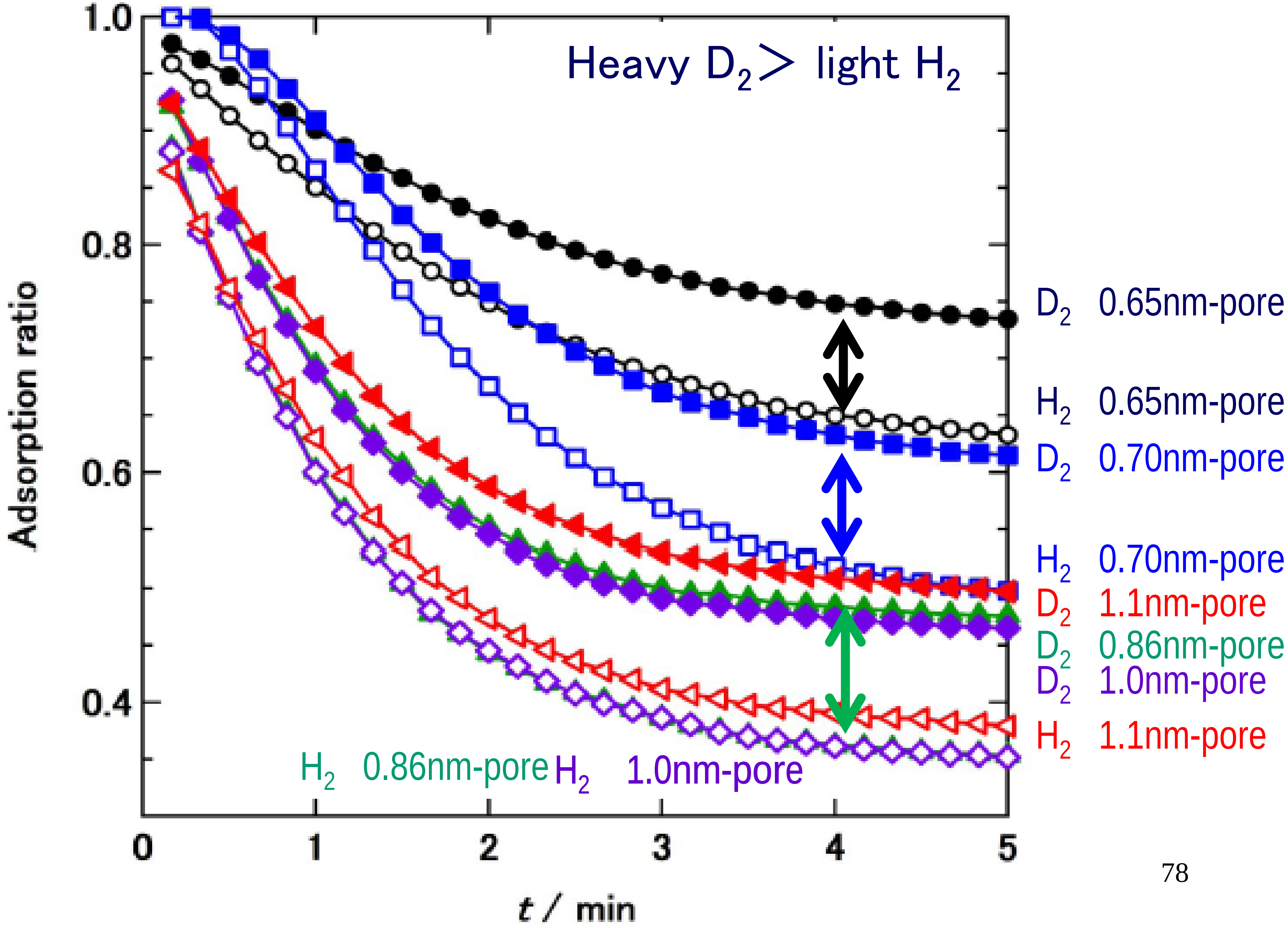
by a mass filter

Quantum Sieving Effet for H_2-D_2 at 77K

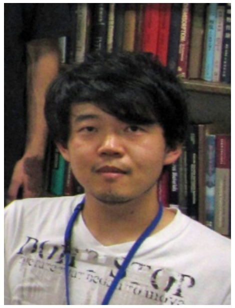
ACF 0.7 nm



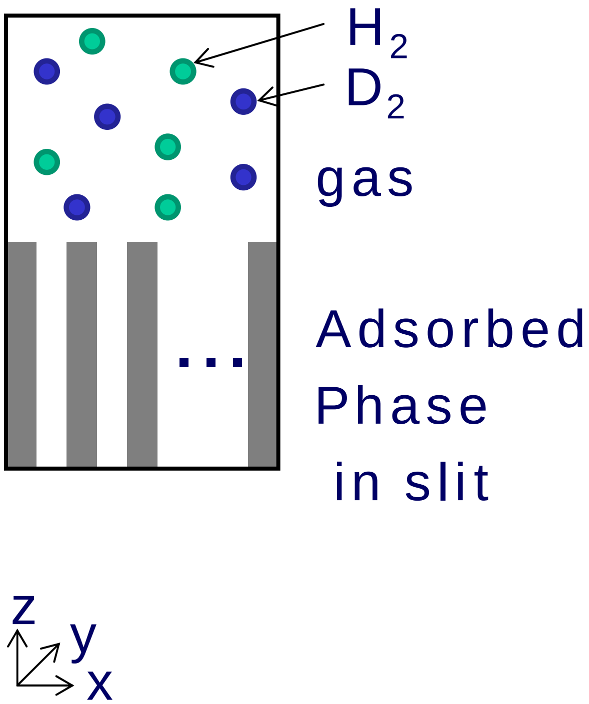
Selective Adsorptivity of ACF of Different Pore Width



Quantum Molecular Dynamics Approach to D_2/H_2 Selectivity



D. Minami



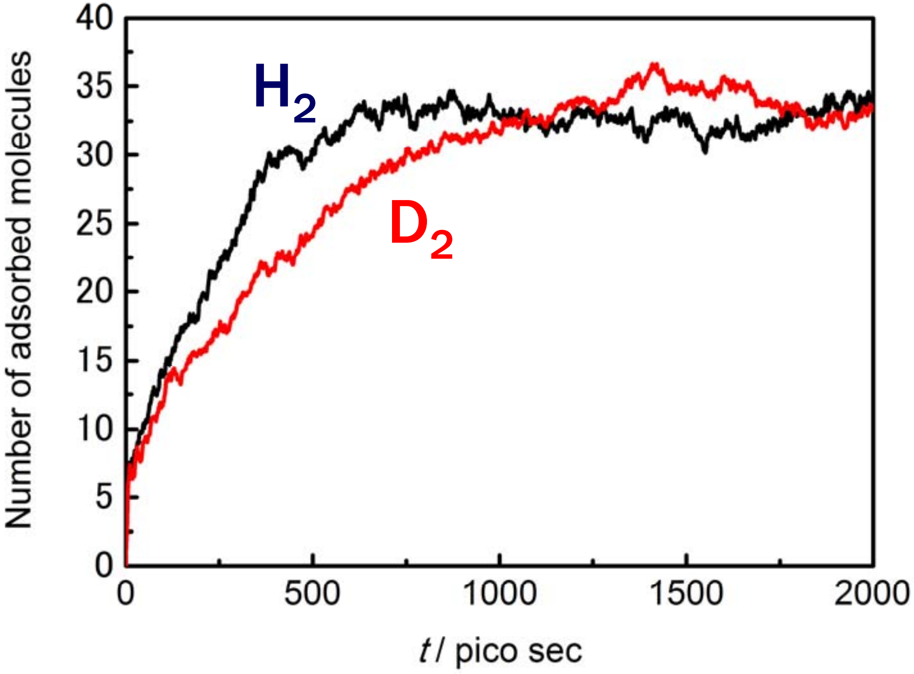
Simulation

- Time step : 0.1 fs
- Number of H_2 (D_2) : 65 (65)
- Model of methane : One center model
- Model of slit pore : Atomistic model
- Temperature : 77 K
- Periodic boundary conditions were applied in the x and y directions.
- Periodic shell boundary condition was applied in the z directions opposite side of graphite.
- The interaction was calculated by **Quadratic Feynman-Hibbs effective potential model.**

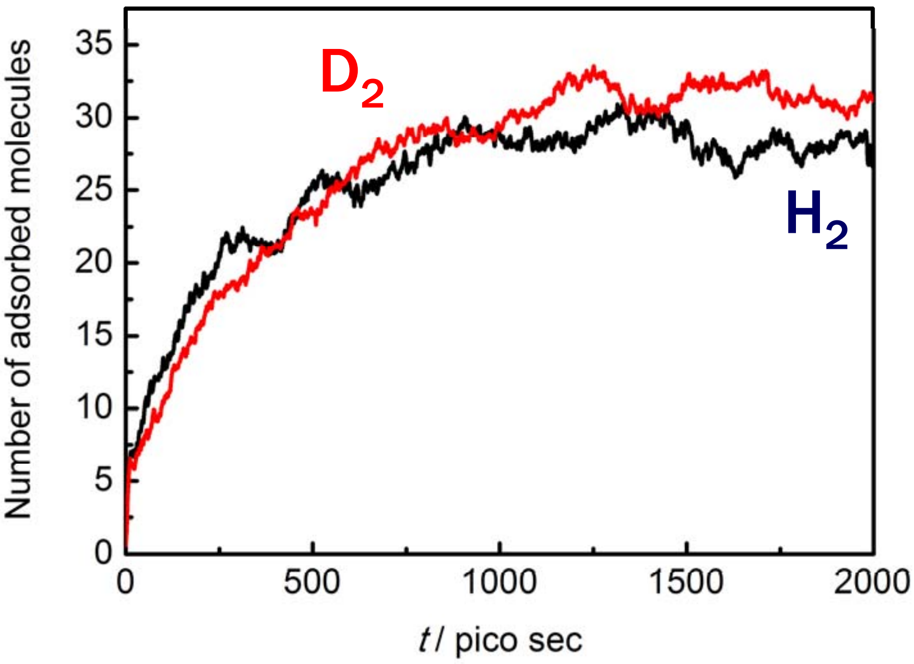
$$V_{FH} = V_{LJ} + \frac{\hbar^2}{12mk_BT}\left[V_{LJ}'' + \frac{2}{r}V_{LJ}'\right]$$

Increase of Adsorbed Molecular Number with Time

w = 1.0 nm



Classical LJ potential



Quantum FH potential

Selectivity for D_2 and H_2 for D_2 / H_2 Mixed Gas at 77 K

$$S(D_2/H_2) = \frac{[D_{2,ad}]/[H_{2,ad}]}{[D_{2,gas}]/[H_{2,gas}]}$$

at 1 minute

Material	Before Ad.(μmol)		After Ad. (μmol)		$S(D_2/H_2)$
	H_2	D_2	H_2	D_2	
ACF A20	5.02	4.99	1.83	1.38	1.5
ACF A15	5.08	5.04	2.12	1.64	1.5
ACF A10	5.01	4.99	2.08	1.60	1.5
ACF A7	5.05	5.00	1.29	0.92	1.5
ACF A5	5.23	5.16	0.82	0.54	1.6
MSC 5A	5.05	4.99	2.70	2.14	1.5
MSC 3A	8.62	8.66	8.25	7.75	2.7
Zeolite 4A	5.07	5.01	1.44	0.91	1.8
Zeolite 5A	5.18	5.28	1.32	0.81	1.9
Zeolite 13X	5.05	5.00	2.41	1.58	2.0

Niimura et al, *J. Amer. Chem. Soc.* (2012)

Quantum Molecular Sieving Effect Can Provide a Highly Efficient Isotope Separation even for Methane Isotopes

$^{12}CH_4/^{12}CD_4$

$^{13}CH_4/^{12}CH_4$

$^{14}CH_4/^{12}CH_4$

Quantum Fluctuation of Methane Isotopes

Molecular weight

CH_4 : 16 **CD_4 : 20**

de Broglie wave length

$$\lambda_D = \frac{h}{(2\pi m k_B T)^{1/2}}$$

(nm)

	20 K	77 K	112 K
H_2	0.27	0.14	0.117
D_2	0.17	0.11	0.083
$^{12}CH_4$		**0.050**	**0.041**
$^{12}CD_4$		**0.044_5**	**0.037**
$^{14}CH_4$		**0.047**	**0.039**
$^{13}CH_4$		**0.048**	**0.040**

0.005

0.002

0.004

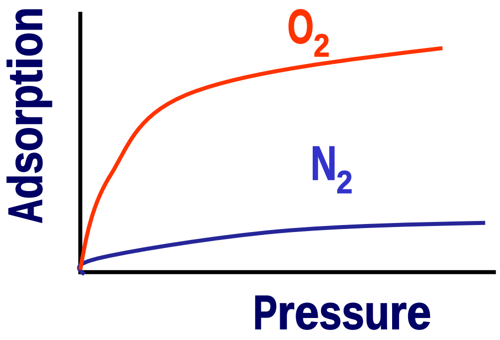
0.001

Difference

1-5 pm

Comparison with Classical Size Difference between N_2 and O_2

Classical molecular size



MSC

N_2 0.36 nm (0.42x 0.30 nm)

O_2 0.34 nm (0.38x 0.28 nm)

Difference (0.36nm – 0.34nm)

0.02 nm ***(20 pm)***

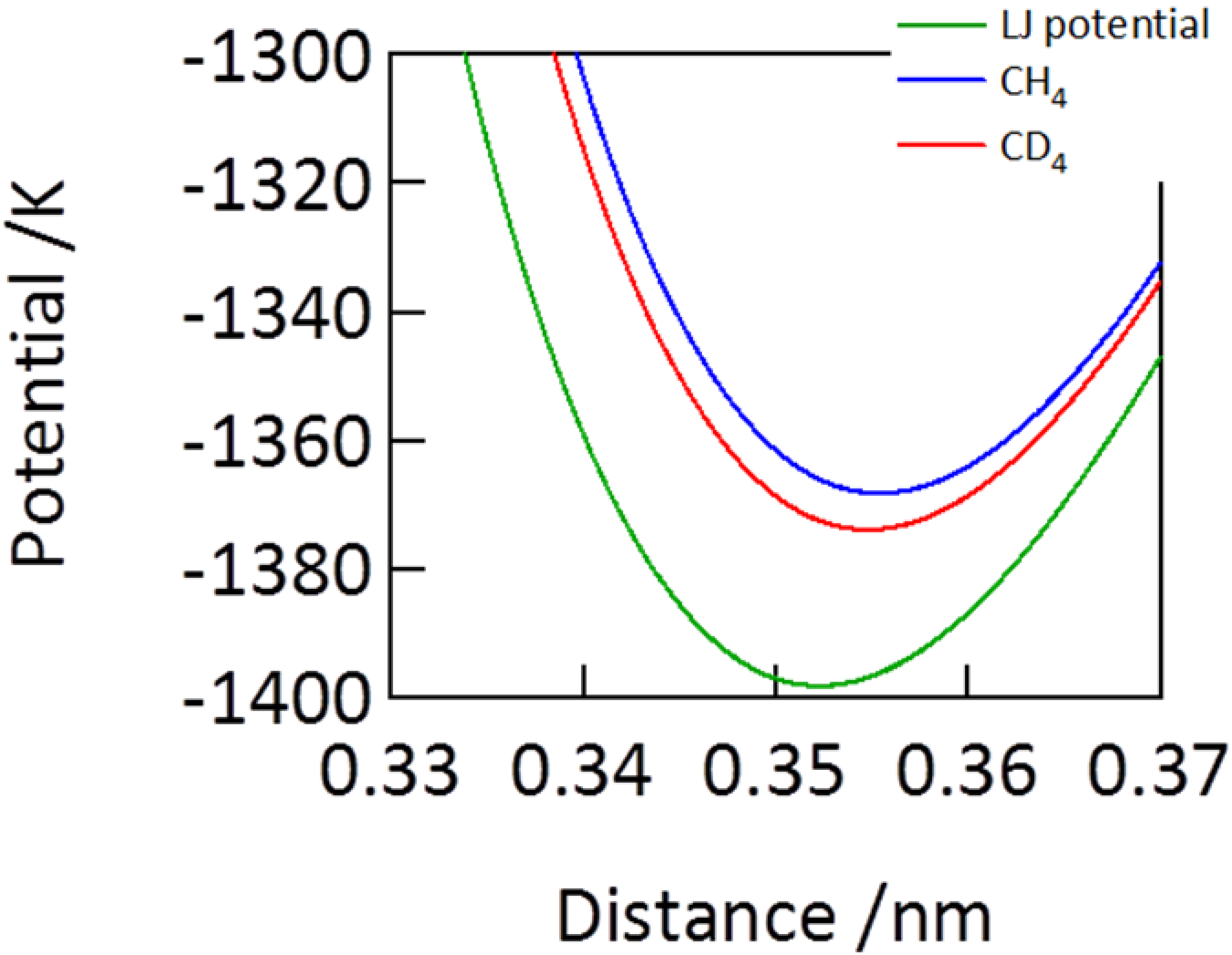
Present air separation technology

with molecular sieves

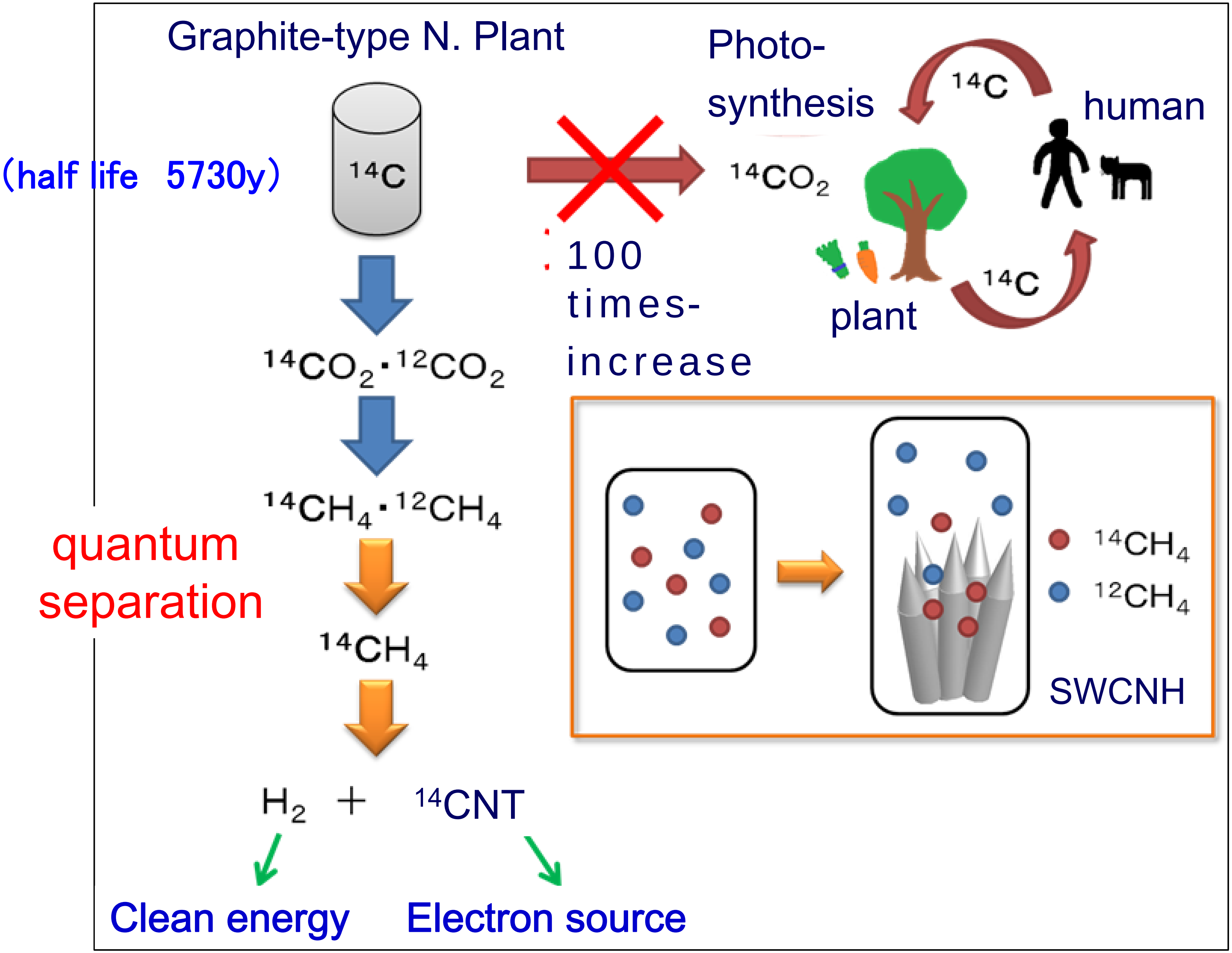
stems from this difference

Can we detect a Smaller Difference (0.004nm) in micropores?

Intermolecular Interaction of CH_4 and CD_4



Separation of ^{14}C and ^{14}CNT Production



Graphite-type N. Plant

（half life 5730y）

^{14}C

$^{14}CO_2 \cdot {}^{12}CO_2$

$^{14}CH_4 \cdot {}^{12}CH_4$

quantum separation

$^{14}CH_4$

H_2 ＋ ^{14}CNT

Clean energy

Electron source

100 times-increase

$^{14}CO_2$

Photo-synthesis

^{14}C

human

plant

^{14}C

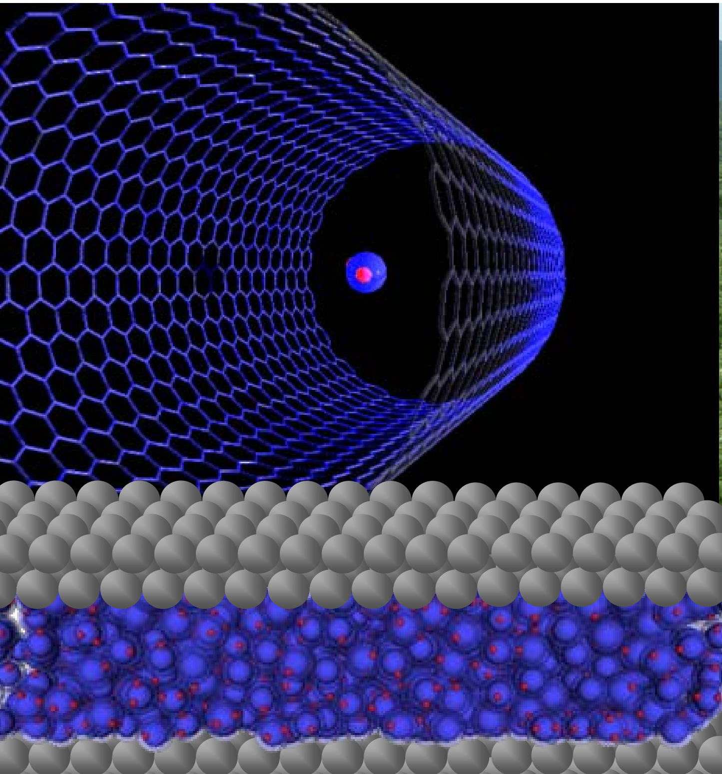
● $^{14}CH_4$

● $^{12}CH_4$

SWCNH

Water Adsorption on Nanoporous Carbon

Hydrophobicity to Hydrophilicity Transformation in Nanoporous Solids



Water

Water　Importance

Life　Society　Industry　Earth - - - -

Control of hydrophobicity and hydrophilicity of carbon materials

Understanding of water channel in our body: Model system

Composite production with polymers, - - - -

Stability in water-rich environments

Dispersion control in water or organic solvents

Adsorption performance

Gas adsorption　Water purification

Membrane performance

Heat pump

\- - - - -

Active Studies

K.S.W.Sing et al. Carbon(1995)Low burn-off AC no hysteresis
H.F.Stoeckli et al. Application of DA eq. to water isotherm
K.E.Gubbins et al. GCMC molecular simulation
Bridging of water molecules, Site density (1996)
M.-C.Bellissent-Funel et al. (1996) XRD and ND of wetted AC
F. Rodoriguez-Reinoso et al (1997) Heat of wetting
R. K. Harris et al (1998) NMR
J. Dore Neutron technique
L. Radvic et al. Adsorption
M. Thomas et al. Adsorption
I.Salame and J.T.Bandosz, (2000) Adsorption
N.Seaton et al (2002) GCMC simulation Hysteresis
A. M. Slasli et al. *Carbon*, 41 (2003).
Moula, Do, Kaneko Chem. Phys. Carbon Review (2003)
A.Striolo, K. E. Gubbins, P.T. Cummings---- (2003) (2004)(2005)
J.-C. Liu and P. A. Monson *Ind. Eng. Chem. Res.* 2006
Krisztina László et al. *Adsorption* (2008) SAXS
Wongkoblap and D.D. Do *Mol. Phy.* (2008) Simulation
D.D. Do, S. Junpirom, H.D. Do *Carbon*, (2009) Simulation
A. Storiolo, Adsorption Sci. Tech. (2011) Simulation
T. Iiyama and R. Futamura, PCCP (2012) Low temp X-ray diffraction
M. Tohmmes,---

Our studies on water adsorption in nanoporous carbons

1988 Structural change of ACF: XRD
1989 Swelling of ACF with SAXS
1990 Isotherm shape and surface modification
1995 Solid like-ordered structures by In situ by T. Iiyama
Adsorption on Fluorinated-ACF
Mixed adsorption of water and NO : Clathrate formation
1997 Temp. dep. of confined water with XRD
No adsorption in mesopores by Y. Hanzawa
1999 in situ XRD Ethanol, Methanol by T.Ohkubo
2000 In situ SAXS Hysteresis by T.Iiyama
Direct calorimetry (since 1994) by T. Kimura
2001 Methane hydrate with J. Miyawaki
2002 Water adsorption on SWNH assemblies by E. Beckyarova
2004 Heat of adsorption in ACF *J Phys Chem B*. by. T.Ohba
Potential calculation is slit-pore *J Amer Chem Soc* by. T.Ohba
2005 in situ SAXS and GCMC in ACF *Nano Lett, Euro J Chem* by. T.Ohba
2007 Surface oxygen effect *J.Phys.Chem.C* by. T.Ohba
2007 Cluster-associated filling of water molecules *Mol. Phy*. by T.Ohba
2009 Hydrophilicity control *J. Amer. Chem. Soc*. by Y.Tao
Equilibration time dependence on hysteresis, *Carbon*, by M. Nakamura
Neutron studies on water on SWCNH with J. Dore and M.-C.Bellissent-Funel
2010 DWCNT, *J. Amer. Chem. Soc.* Y. Tao,
2011 Adsorption hysteresis mechanism, *Langmuir*, by T. Ohba
2012 Structure in SWCNT spaces, *RSC Adv.*, by T. Ohba
Penetration mechanism of water molecules, *J. Phys. Chem.* by T. Ohba

“Hydrophobic-Hydrophilic Transformation” in Solid Surfaces

General concept of hydrophobic interaction

A. Ben-Naim recommends that the hydrophobic interaction can be expressed in terms of the potential of mean force between two non-polar solute in water

in Molecular theory of water and aqueous solution, (2009)

Empirical insights of hydrophobicity of material surfaces

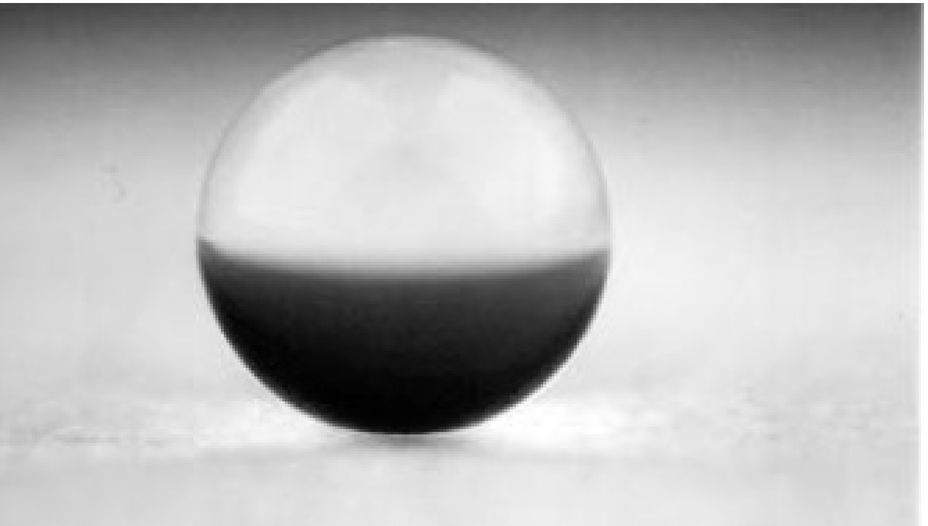
Surface chemistry surface OH

Surface roughness

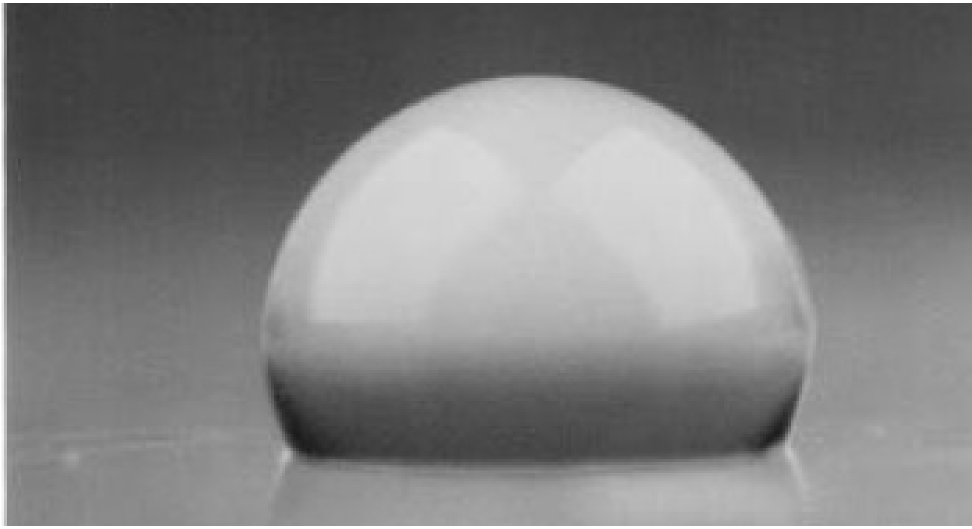
A Water Droplet on Hydrophobic Surface

Surface: Alkylketene Dimer

Rough Surface



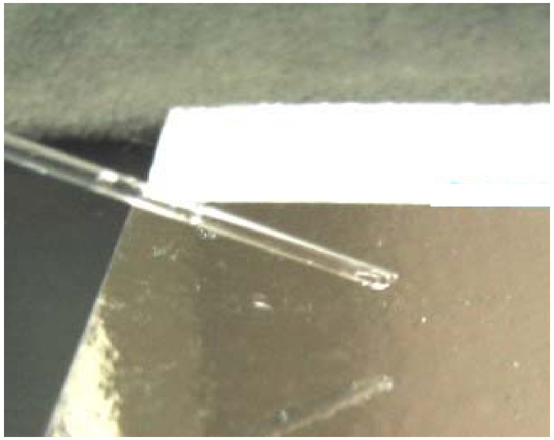
Smooth Surface



Importance of surface roughness

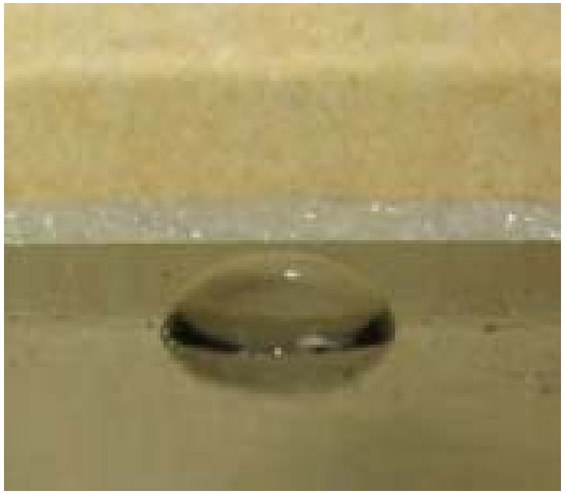
S. Shibuichi, K. Tsujii et al., *J. Phys. Chem.*, 100, 19512 (1996).

Wetting of H_2O and Cyclohexane to HOPG



Highly Oriented Pyrolytic Graphite (HOPG)

Just after contact



H_2O

less-wetted

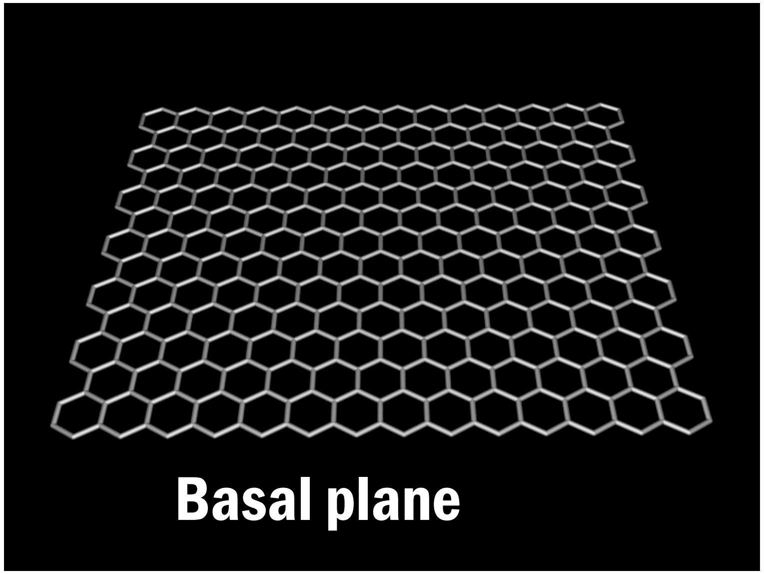
Cyclohexane

wetted

Very weak water-graphite interaction

Heat of wetting: 50 mJ/m² **116**

Carbon Surface (Basal Plane) Shows Hydrophobicity



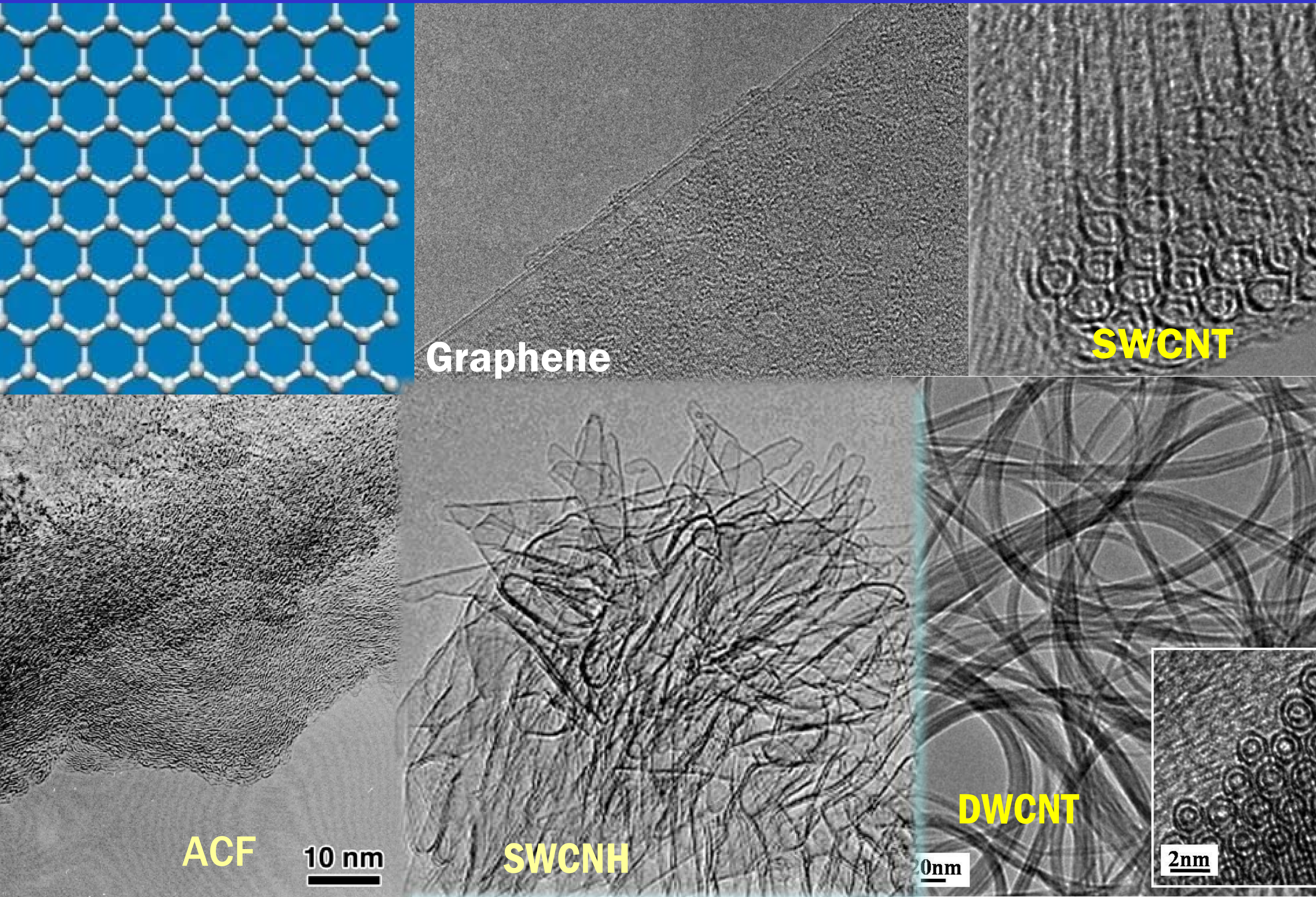
Contact angle:

86° (F. M.Fowkes: JACS (1940)) 42±7° (M. E.Schrader: JPC, 1980)

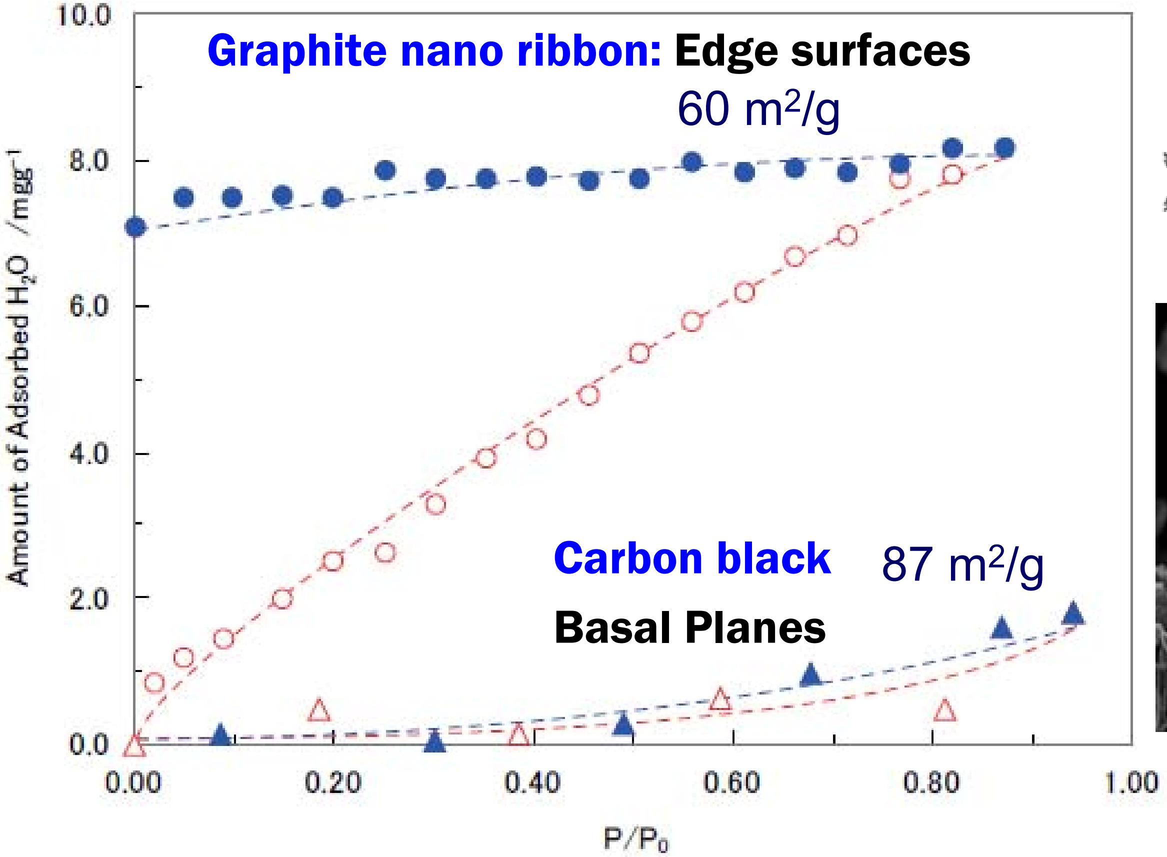
Molecular simulation dynamics by T. Werder et al, JPCB (2003)

Contact angle depends on the interaction potential

Hydrophobicity from graphene-structure



Edge-rich carbon shows “Hydrophilicity”

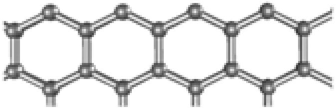


Graphite nano ribbon: **Edge surfaces**

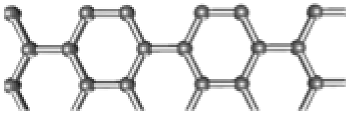
60 m^2/g

Carbon black 87 m^2/g

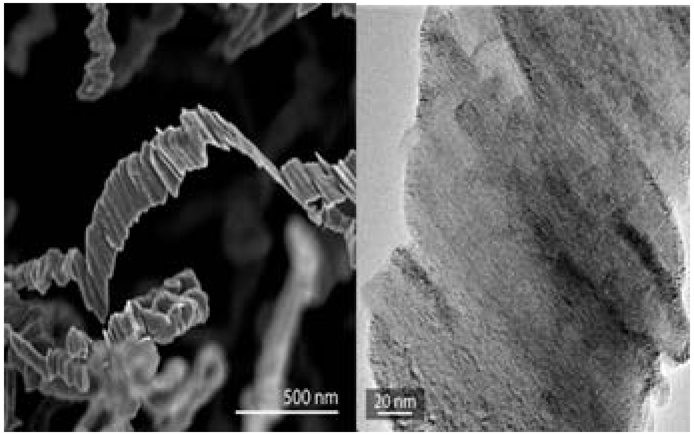
Basal Planes



zig-zag



arm chair



By M. Terrones et al

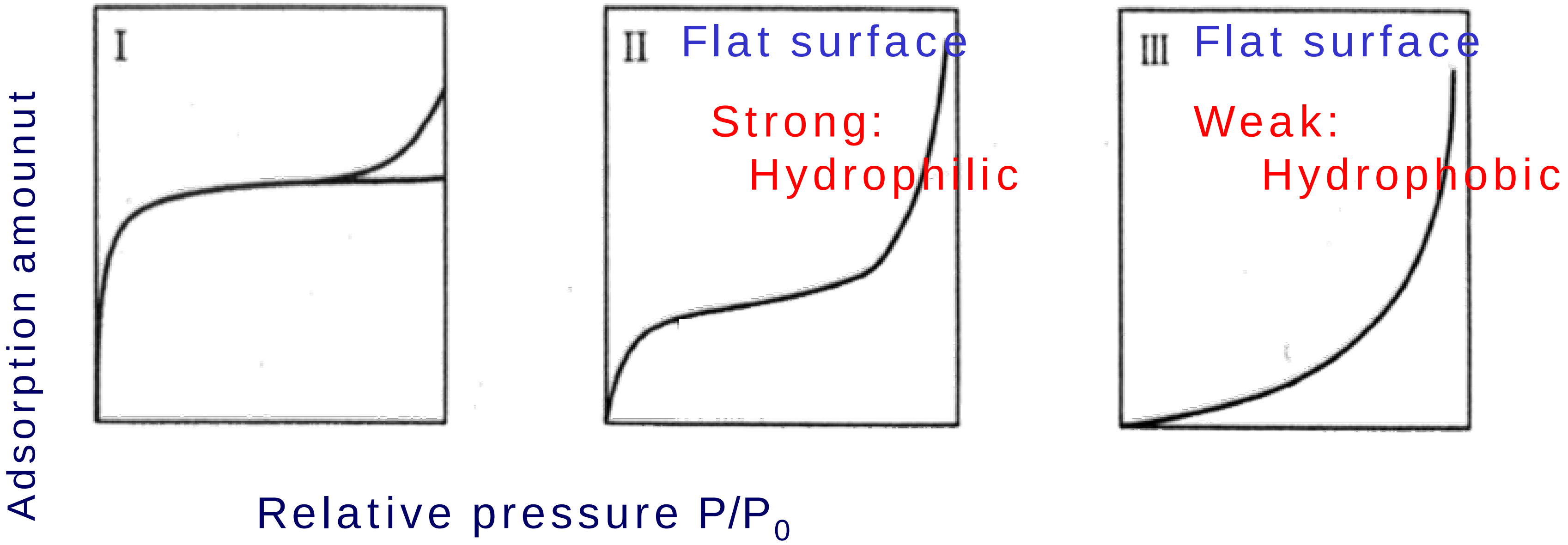
Irreversible Adsorptivity of Graphite Nanoribbon

Asai, Kaneko et al, J. Amer. Chem. Soc. 133, 14880 (2011)

How to evaluate “Molecular Affinity” ?

Adsorption isotherms of vapors

Equilibrium adsorption amount is measured at each equilibrium pressure



II Flat surface

Strong: Hydrophilic

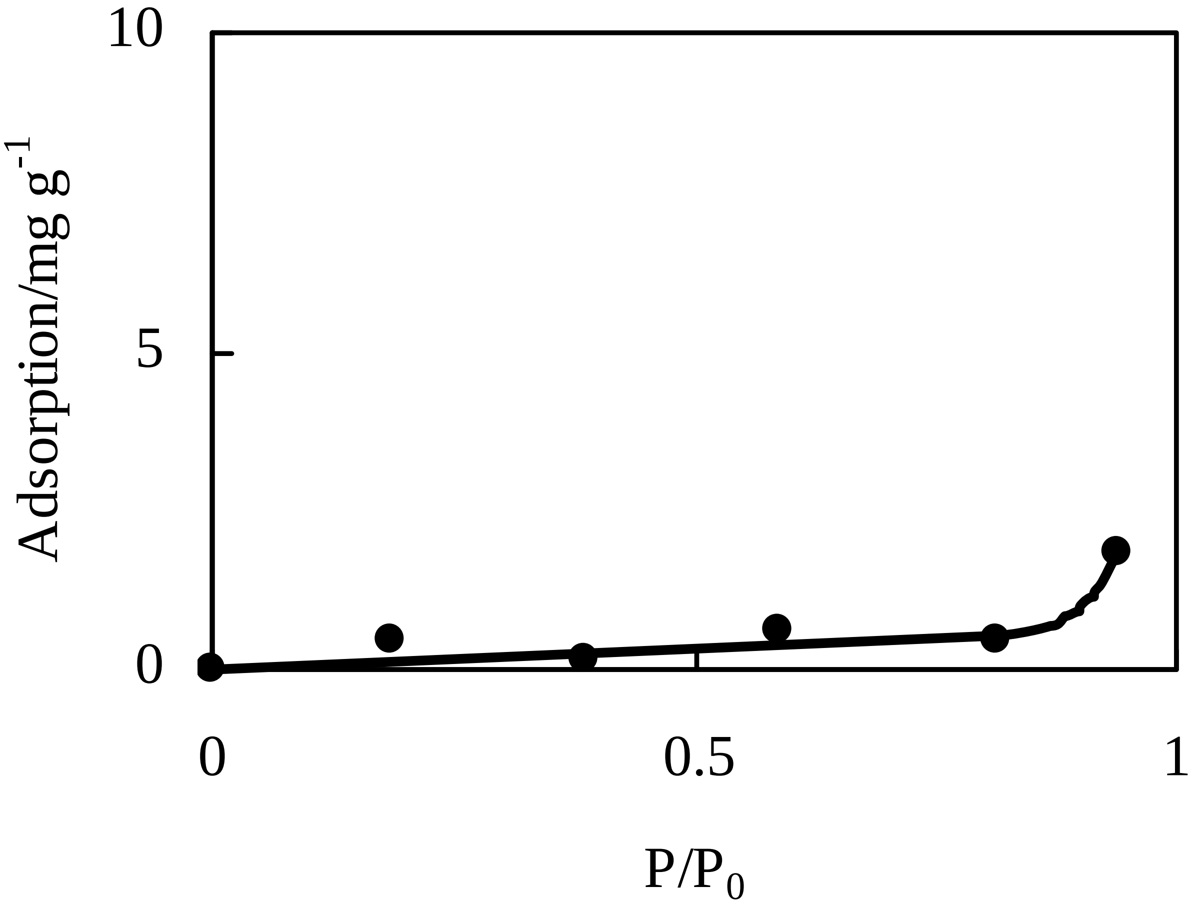
III Flat surface

Weak: Hydrophobic

P_0: Saturated vapor pressure

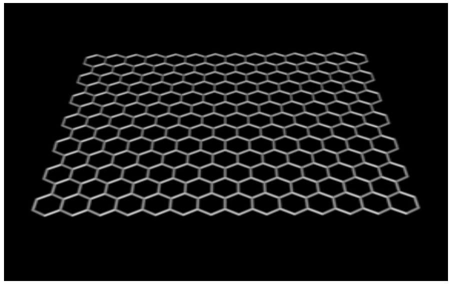
ater Vapor Adsorption Isotherm
f Nonporous Carbon Black

at 303 K



Flat surface

Very weak



No predominant adsorption

Nanoporous Carbons

Activated carbon

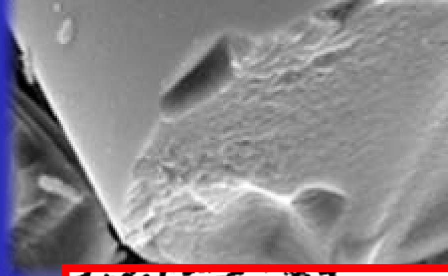
Activated carbon fiber ACF

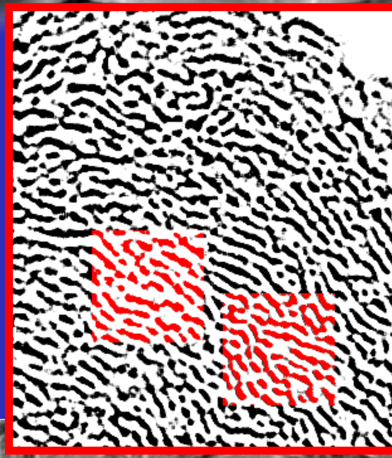
Carbide derived carbon CDC

Nanocarbons

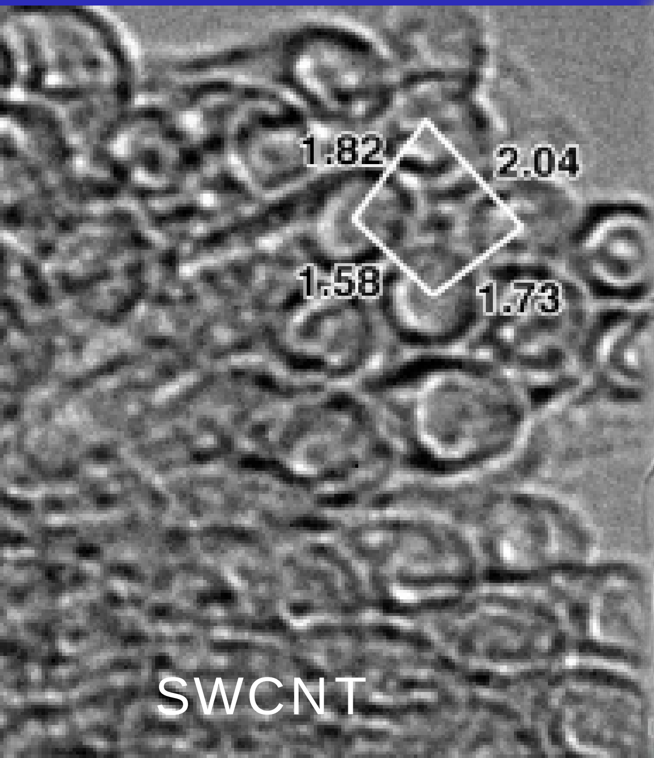
SWCNT DWCNT

MWCNT SWCNH

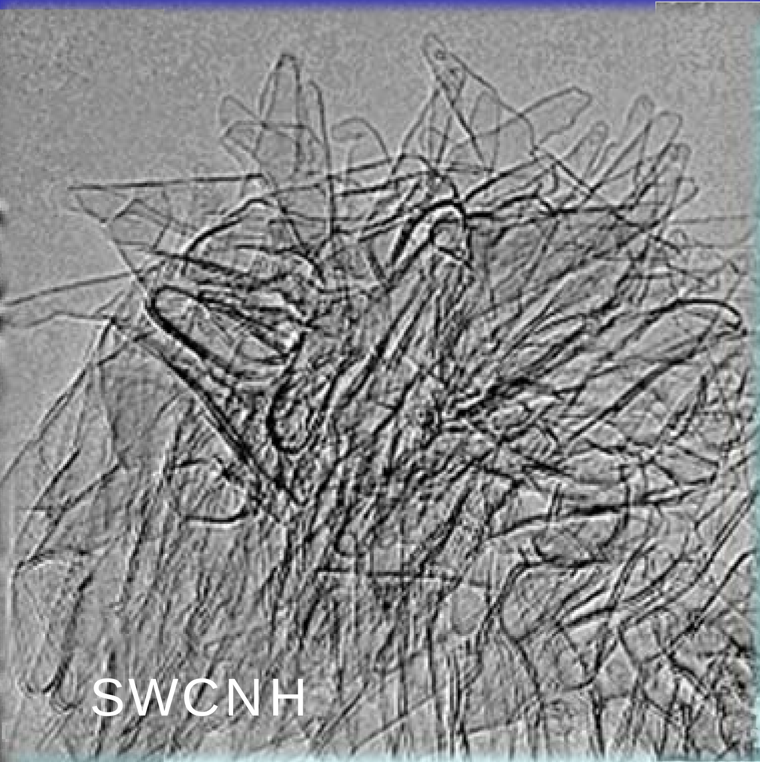




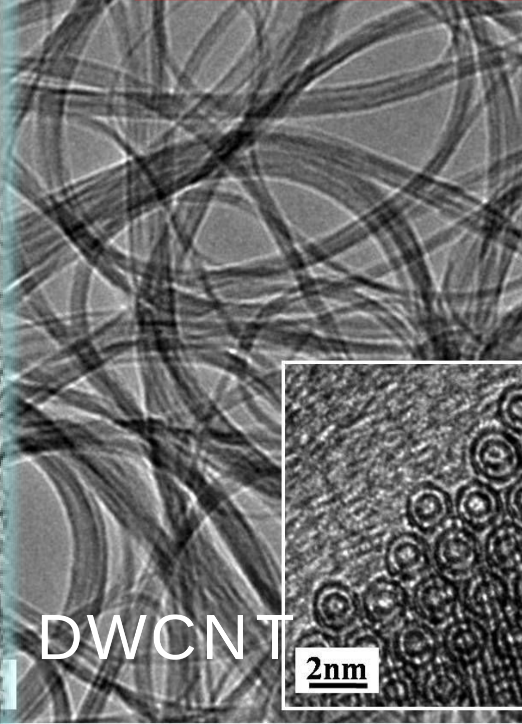
ACF



SWCNT



SWCNH



DWCNT

Are There Any Anomalies in Water Adsorption in Carbon Nanopores?

Formation of solid-like structure :

With X-ray diffraction (1995)

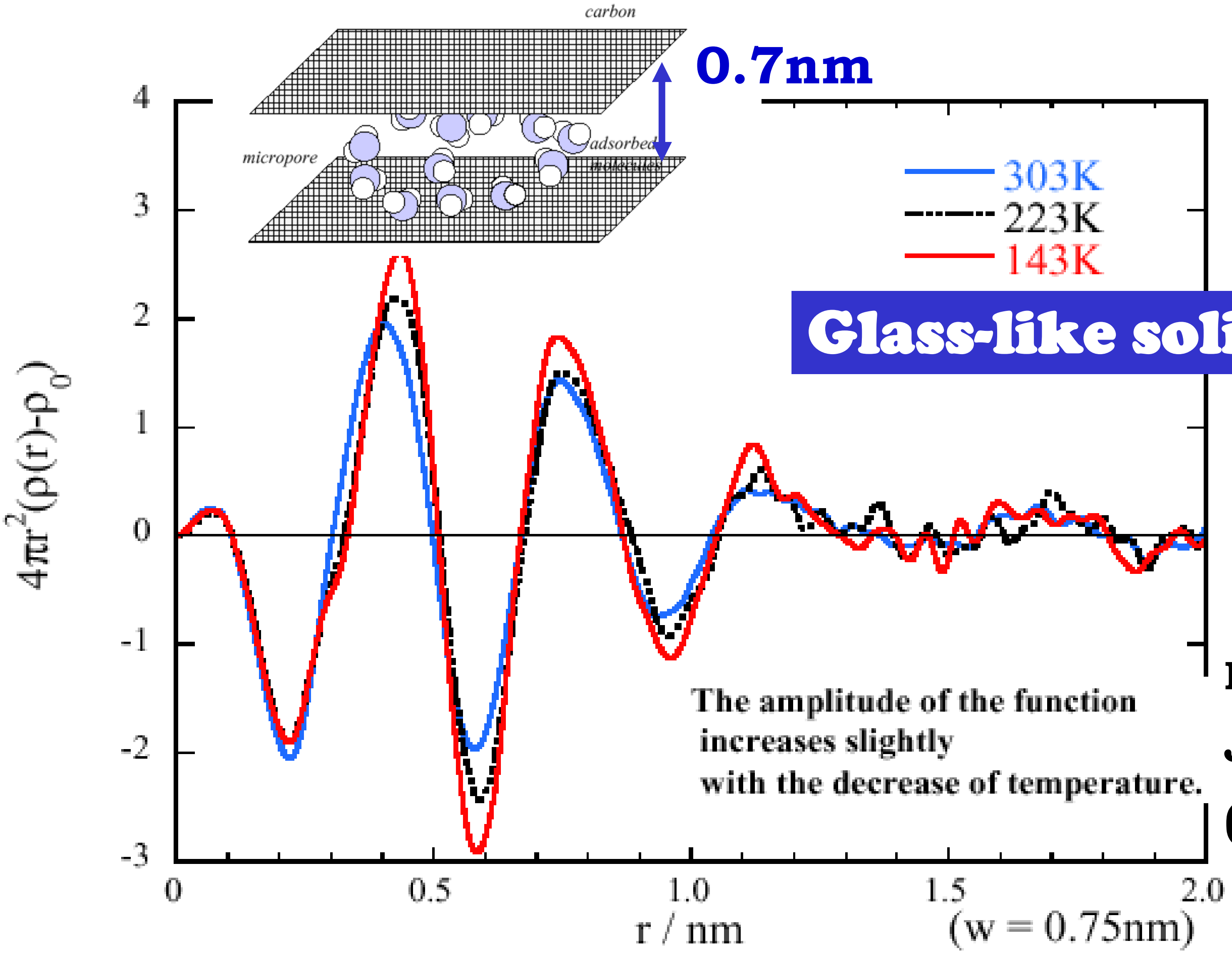
Water adsorption can change the carbon structure(1989,1990)

Adsorption mechanism of water is completely different from that of other vapors

Hydrophobicity to hydrophilicity transformation

Apparent hydrophilicity depends on the pore width

Water in Hydrophobic Nanopores



Glass-like solid ?

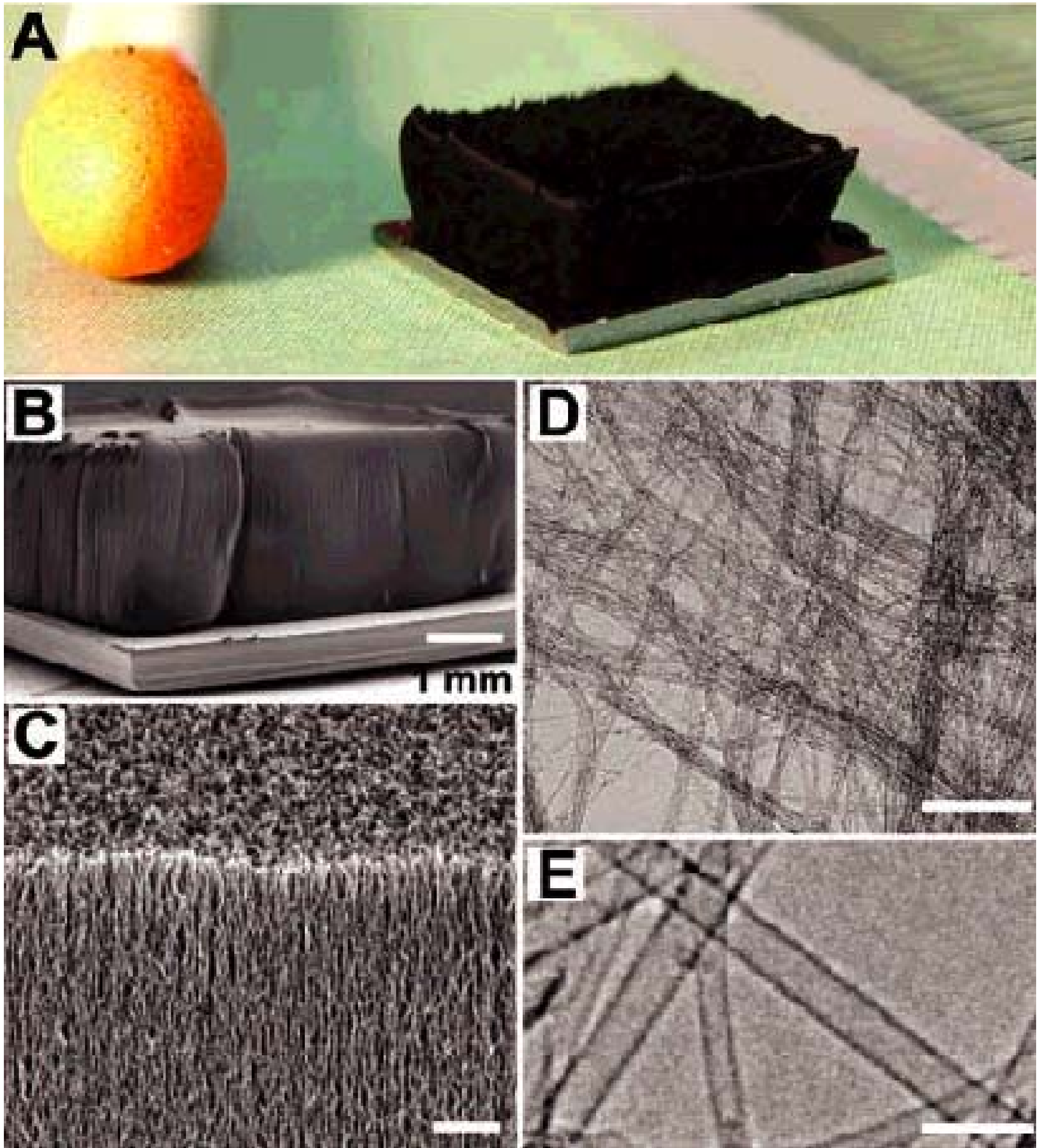
The amplitude of the function increases slightly with the decrease of temperature.

Iiyama et al

J Phys Chem

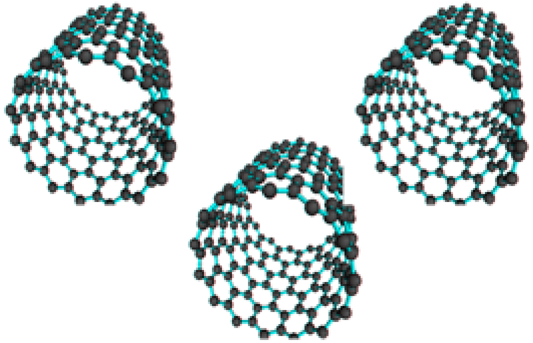
(1995)

Structure of Water Adsorbed in Highly Pure SWCNT



CVD
method

Isolated SWNTs



Dr. K. Hata produced this SWCNT. K. Hata et al., *Science*, 306, 1362 (2004)

Structure Analysis of Water in SWCNT at 303 K

SWCNT

✓ **Pretreatment**

(< 0.1 Pa, 2 h)

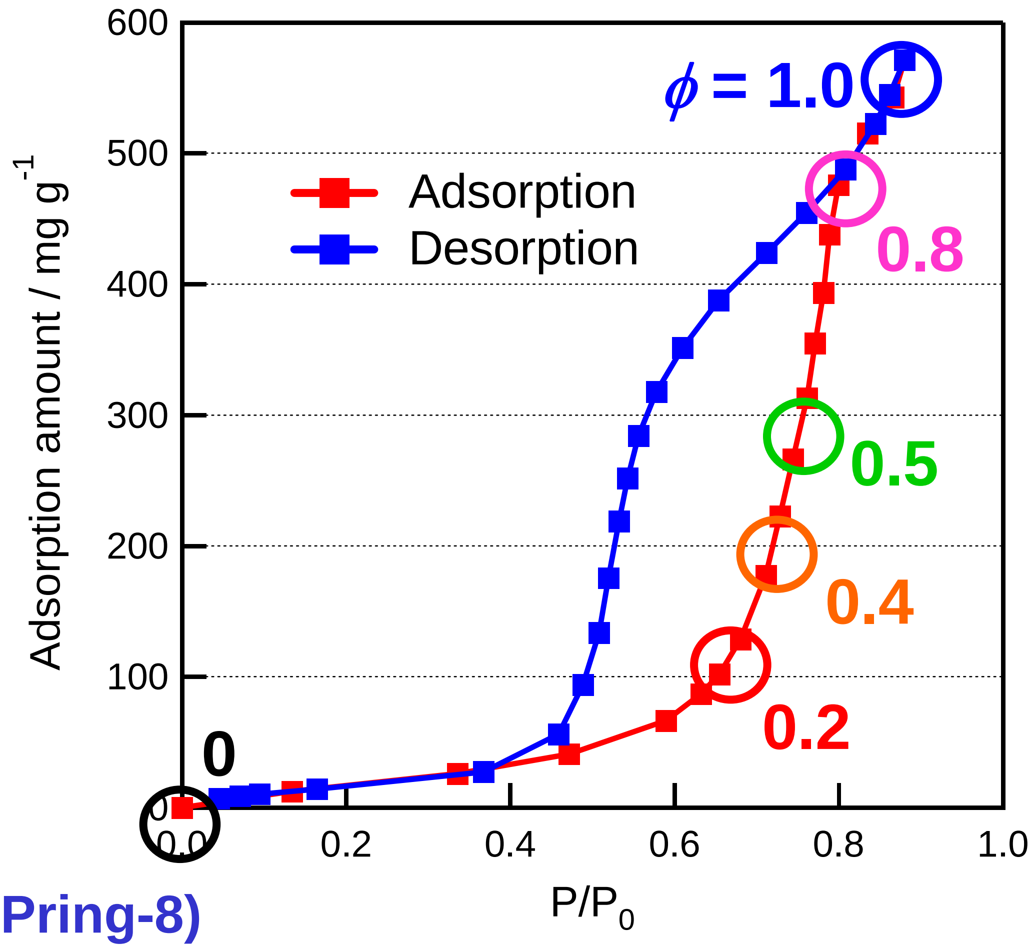
✓ **Water adsorbed at 303 K**

Fractional filling ϕ

0, 0.2, 0.4, 0.5, 0.8, 1.0

(Equilibrium time : 3 h)

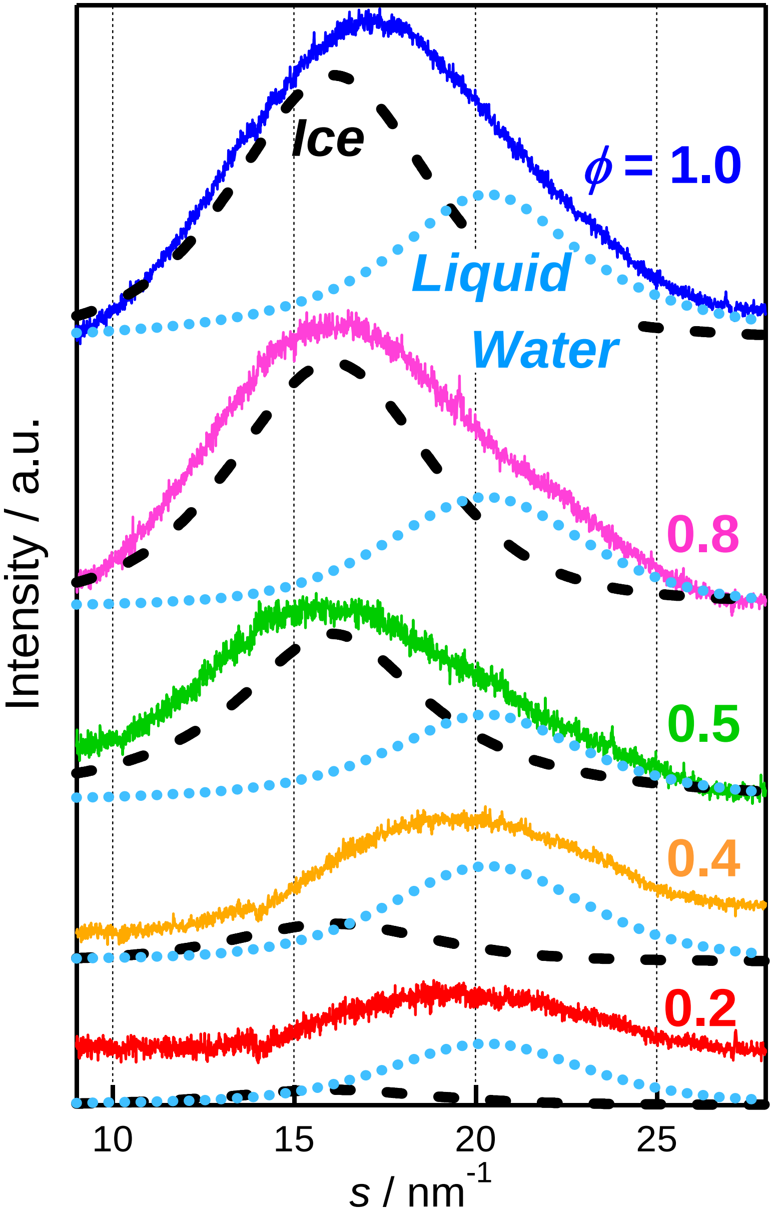
Water adsorption isotherm at 303 K

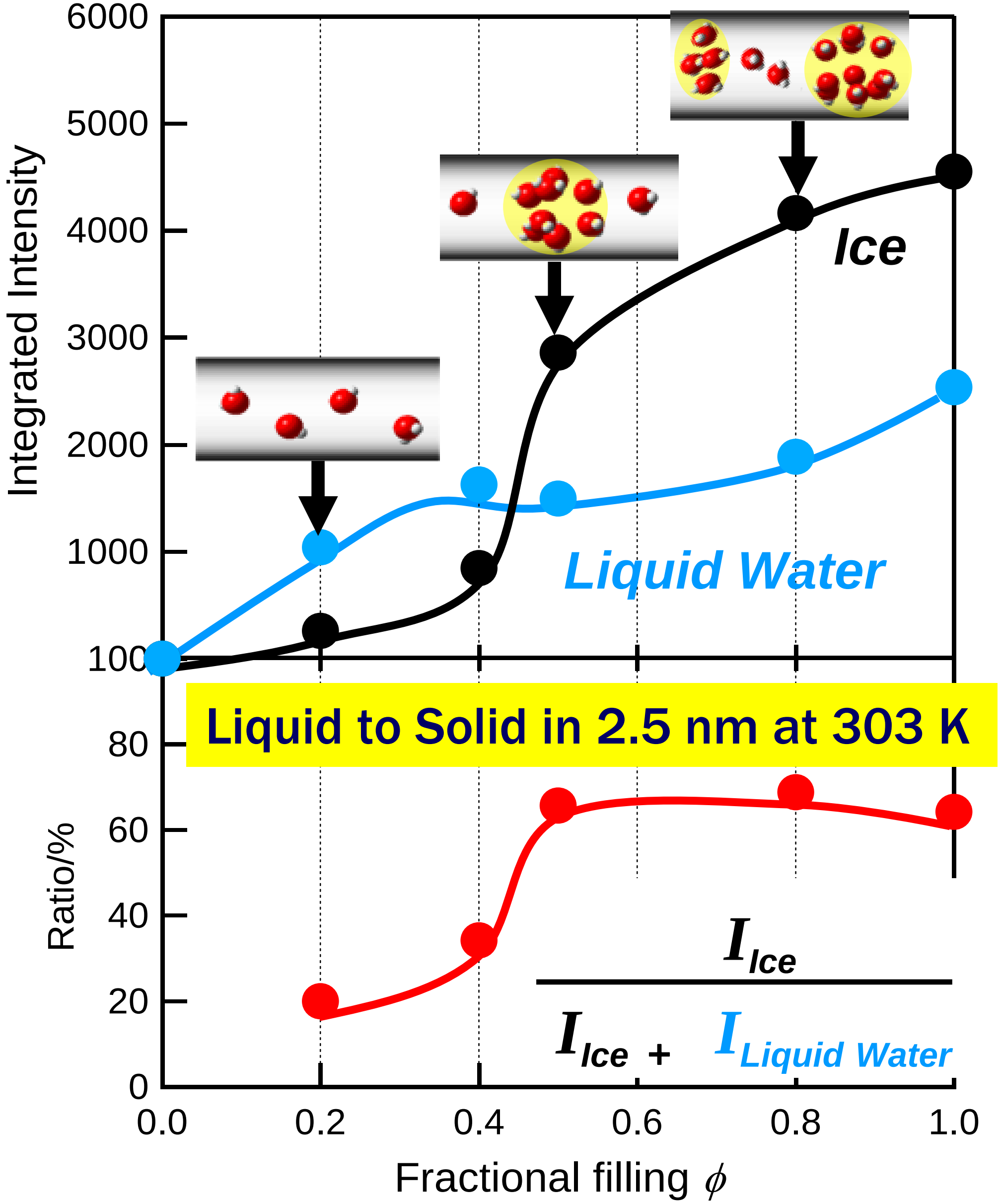


Synchrotron X-ray diffraction (SPring-8)

T. Ohba, *et al.*, *RSC Adv.*, 2012.

Crystallization of Water in Tube Spaces

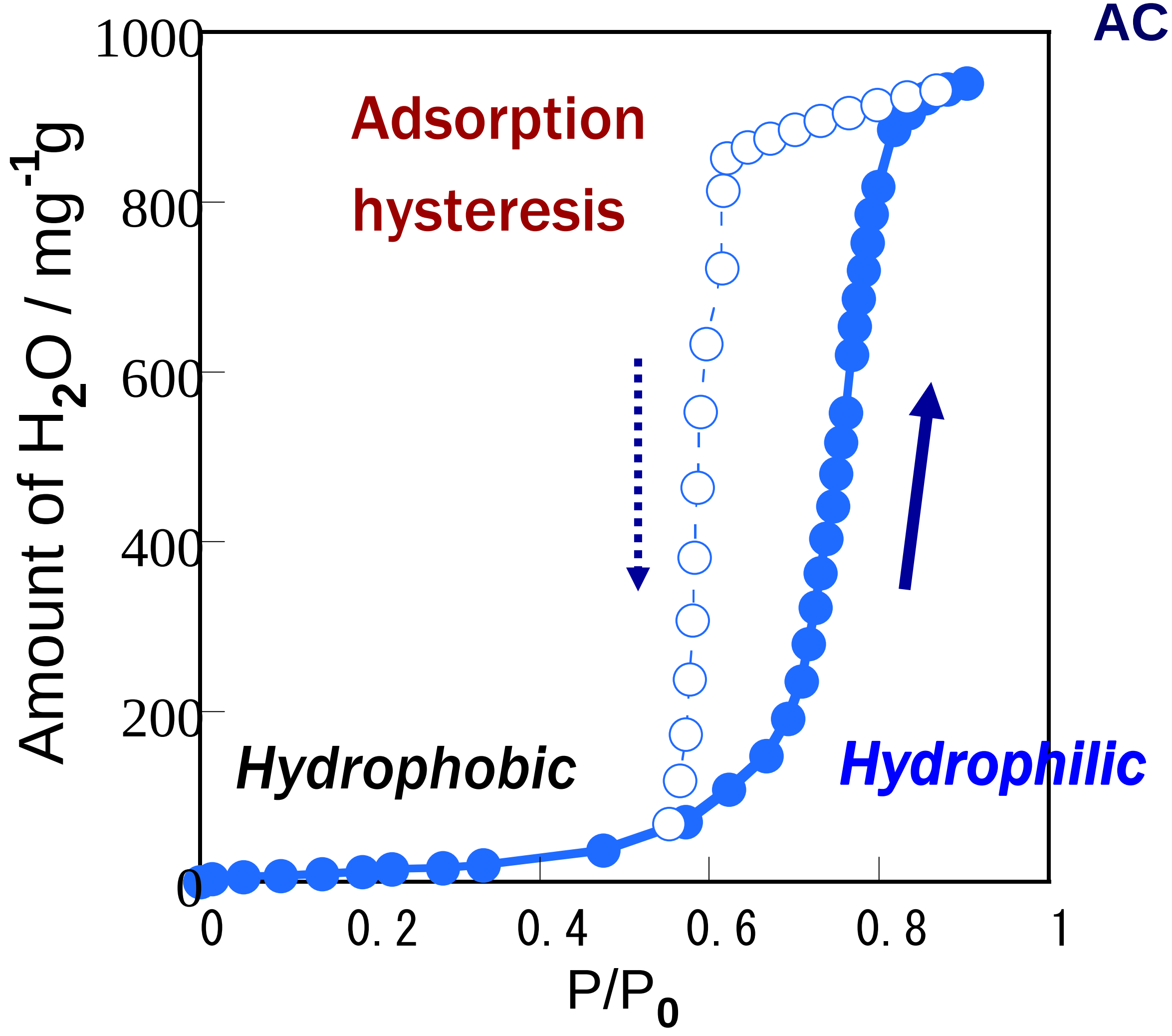




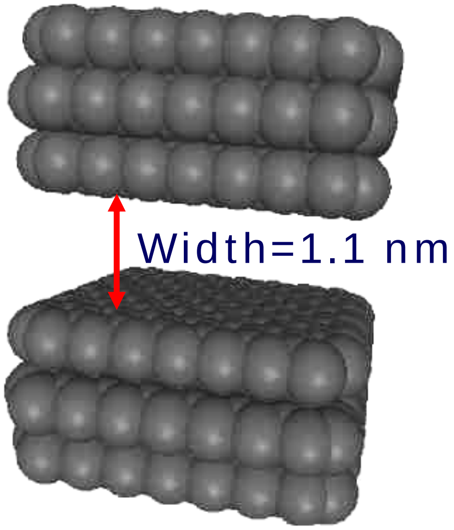
Liquid to Solid in 2.5 nm at 303 K

T.Ohba, *et al.*, *RSC Adv.*, 2012.

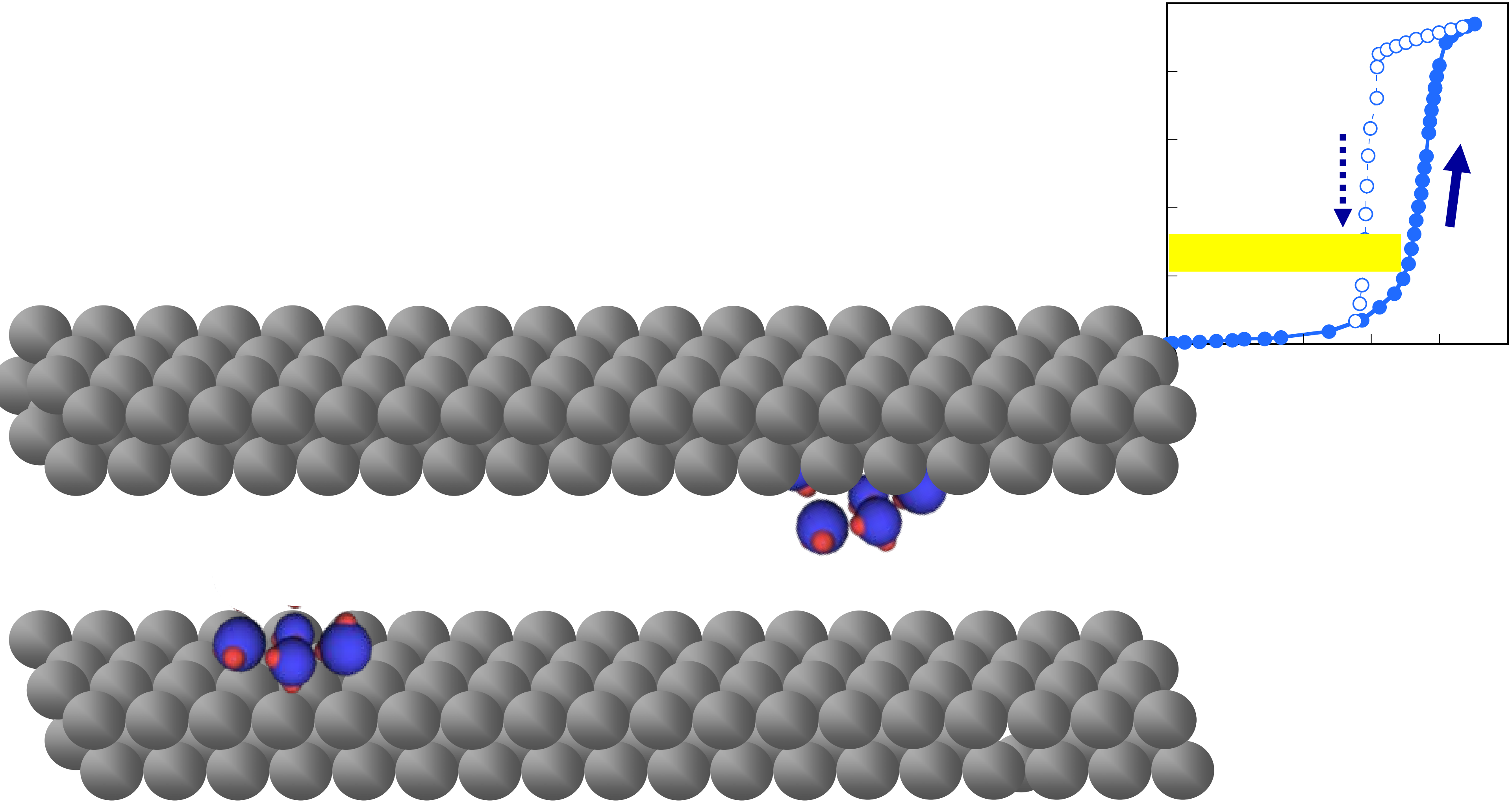
Hydrophobic-Hydrophilic Transformation
Predominant filling starts above $P/P_0=0.6$



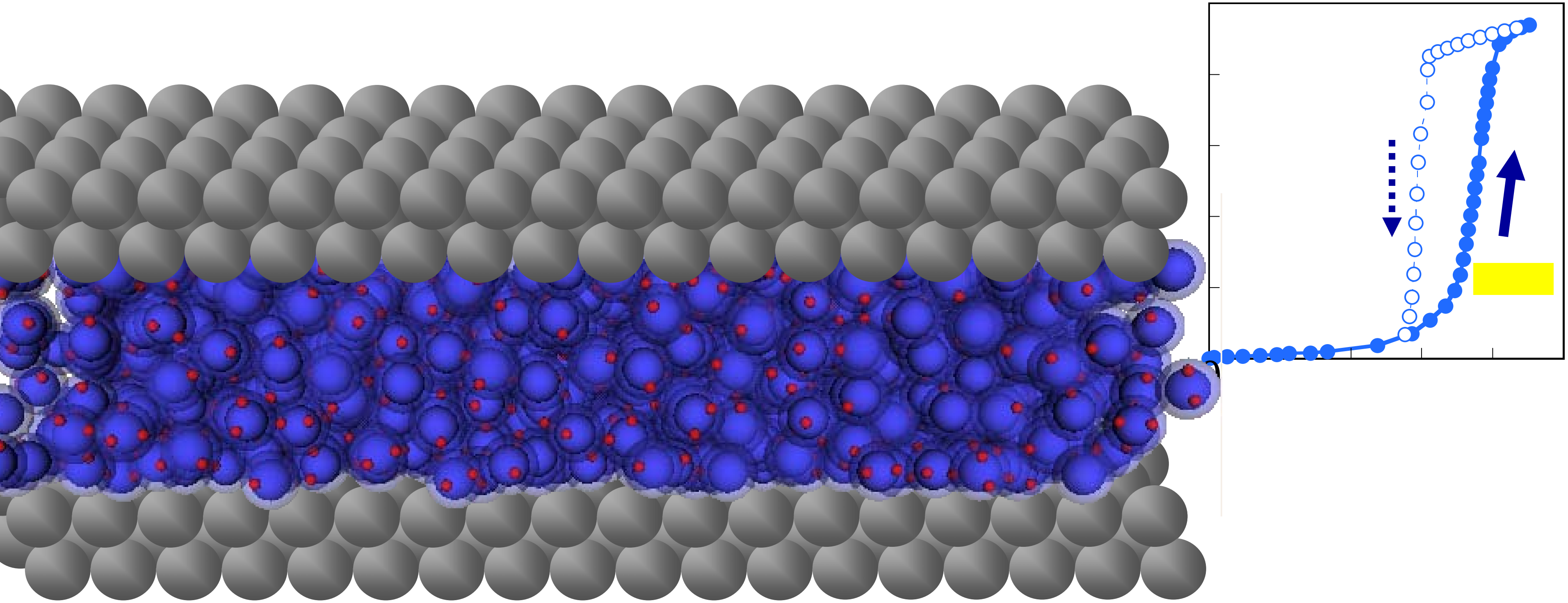
ACF : Slit pores



Hydrophobic Nature below Threshold Pressure



Hydrophilic Nature above Threshold Pressure



Question by

McBain et al. J. Am. Chem. Soc. 55,2294 (1933)

A very long research target

1 nm Order Pores induce “Hydrophobic-Hydrophilic Transformation”

How can we understand

this behavior of water vapor ?

Another group pointed out this importance

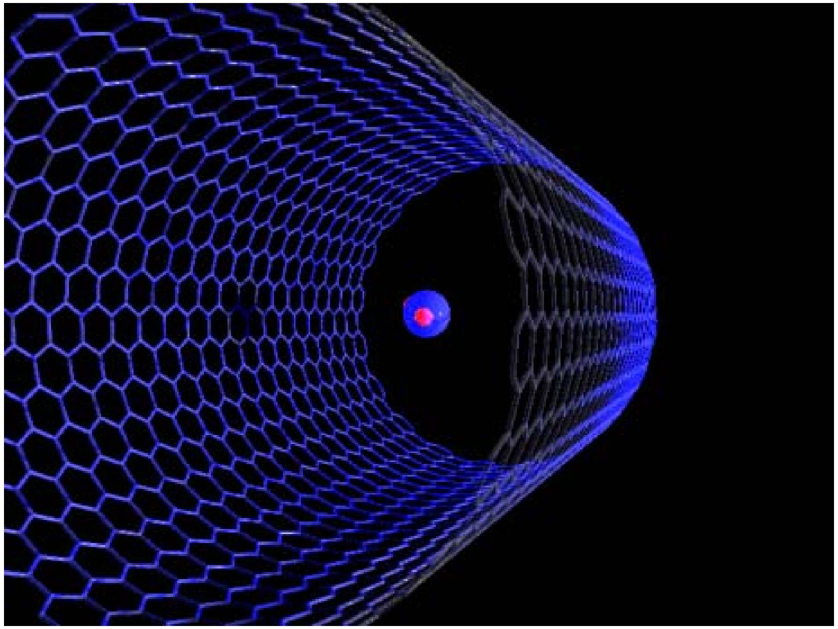
in carbon nanotubes

Wang, H.-J.; Xi, X.-K.; Kleinhammes, A.; Wu, Y.

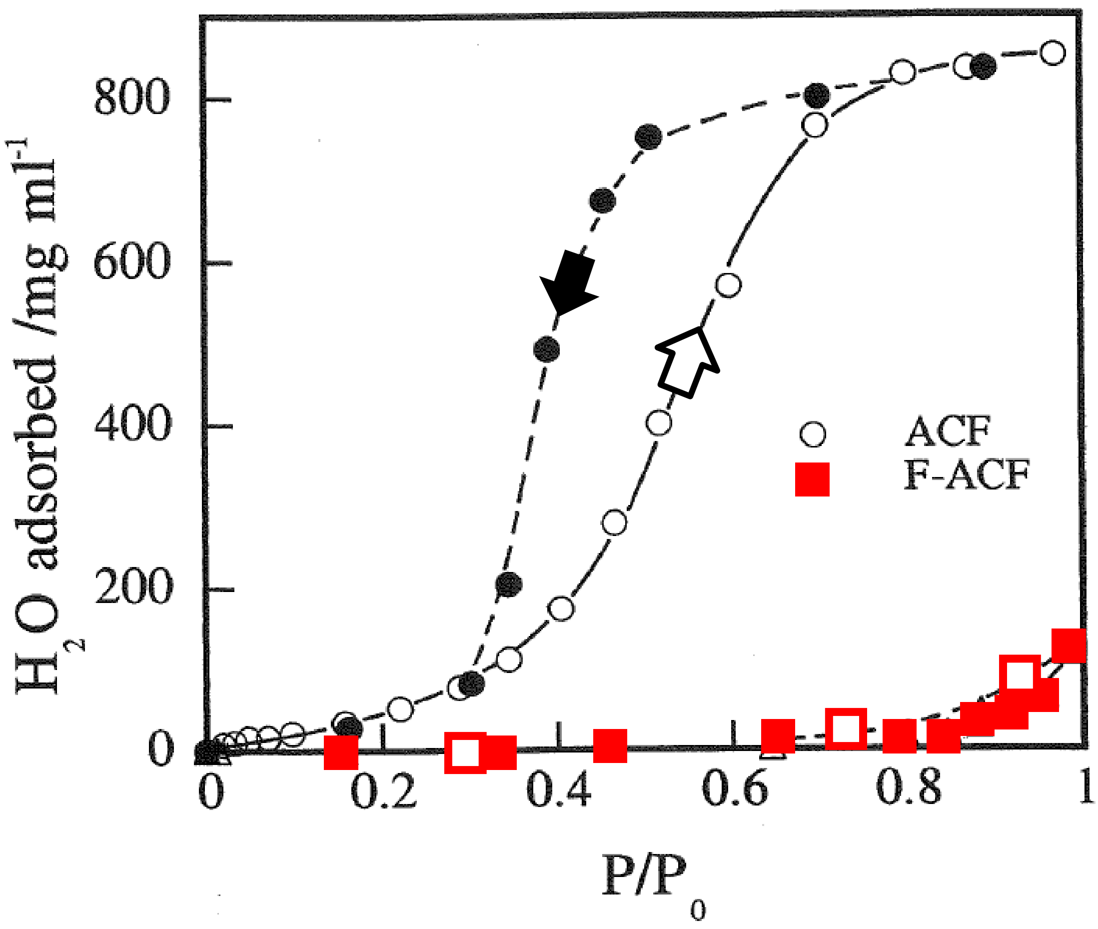
Science **2008**, *322*, 80–83.

Important Factors of Hydrophobic-Hydrophilic Transformation

Our research results will be shown

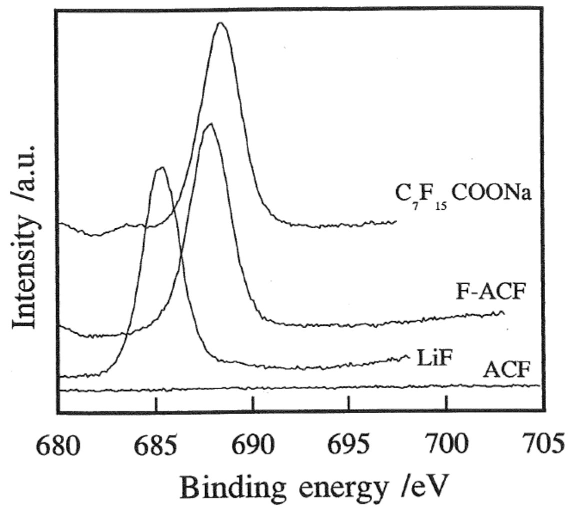


Effect of Fluorination on Water Adsorption Isotherms



F-ACF is fluorinated.

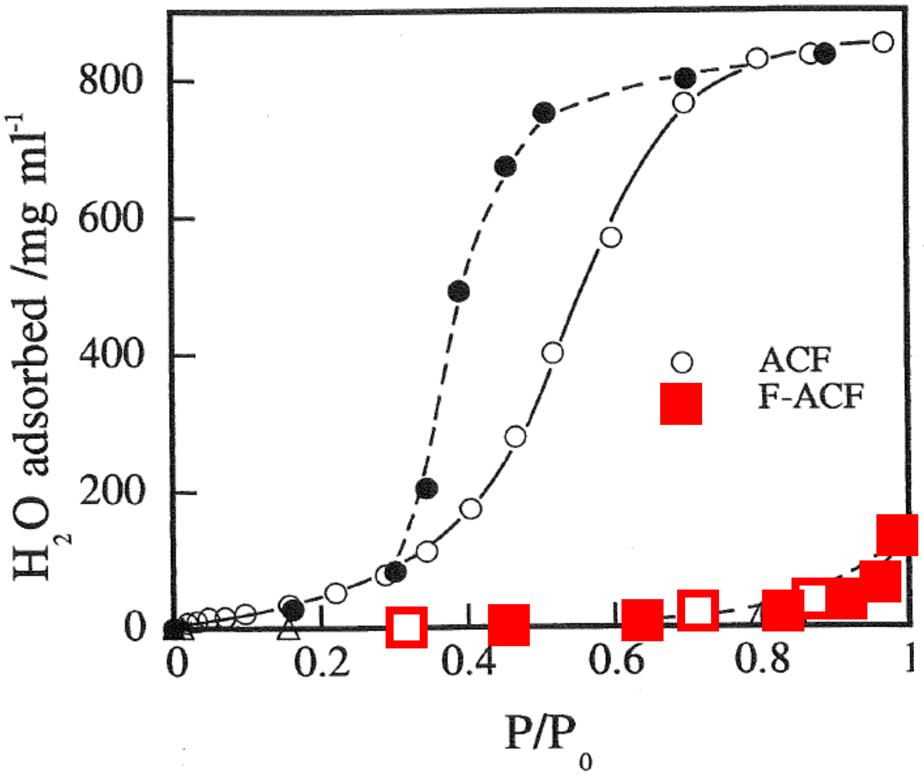
Covalent C-F bonded ACF



1s XPS

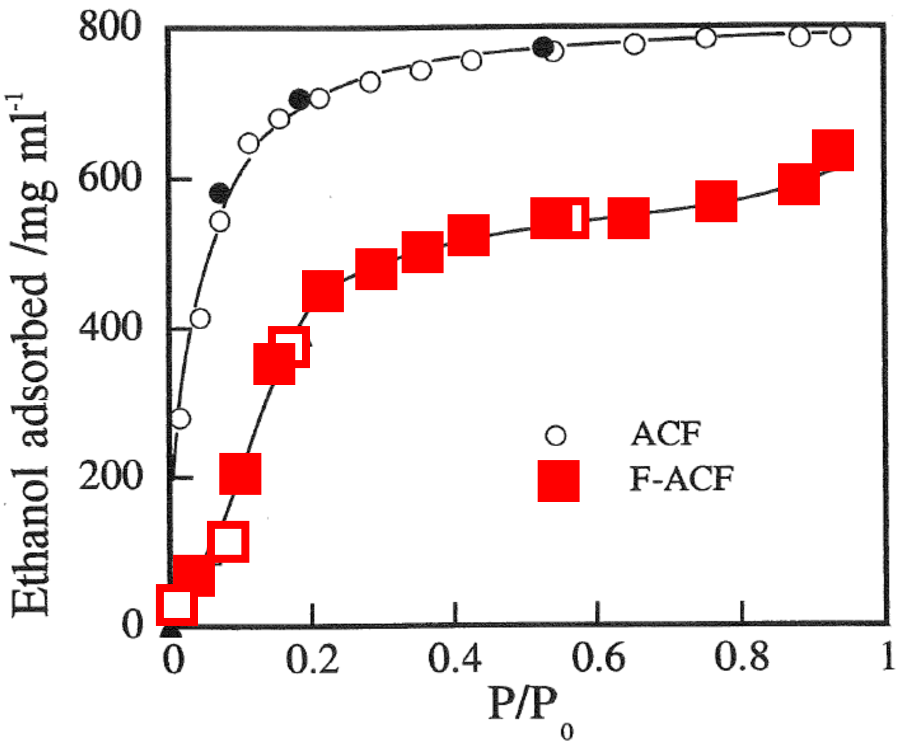
Adsorption Isotherms of Water and Ethanol on Fluorinated ACF

Water



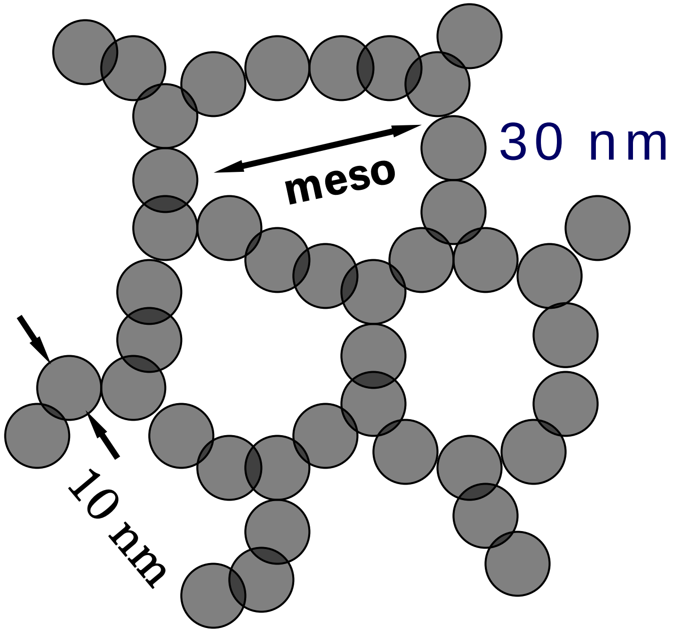
Typical hydrophobicity

Ethanol

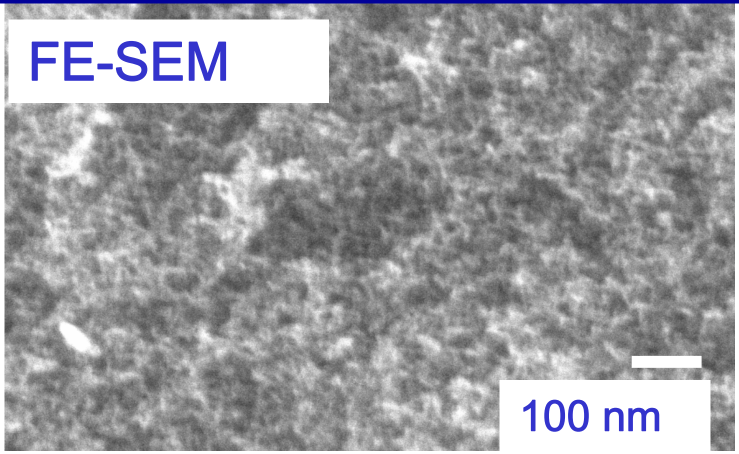


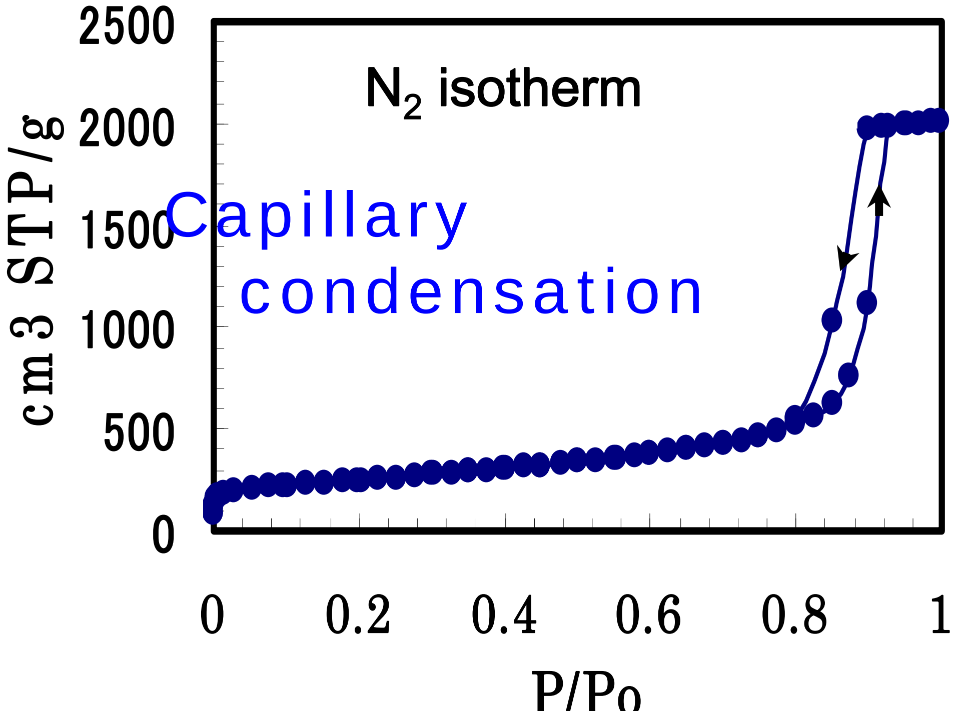
G. X. Li et al., *Langmuir*, **11**, 716 (1995).

Carbon Aerogel – Typical Mesoporous Carbon



Carbon aerogel model





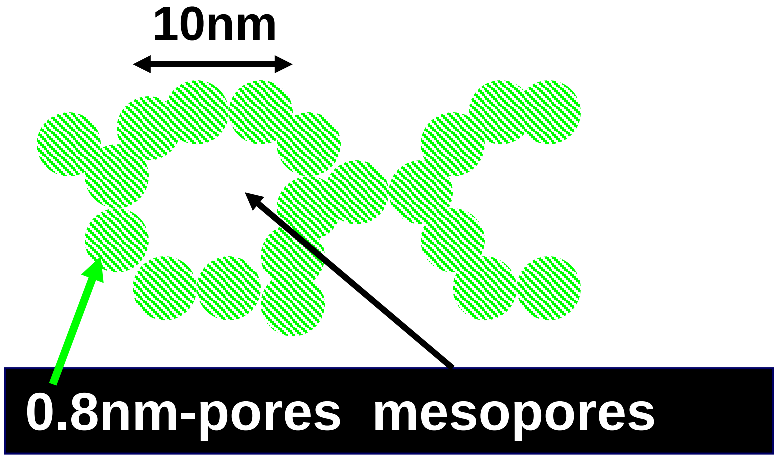
Addition of 0.8nm-pores with CO_2 activation

Y.Hanzawa et al (1997)

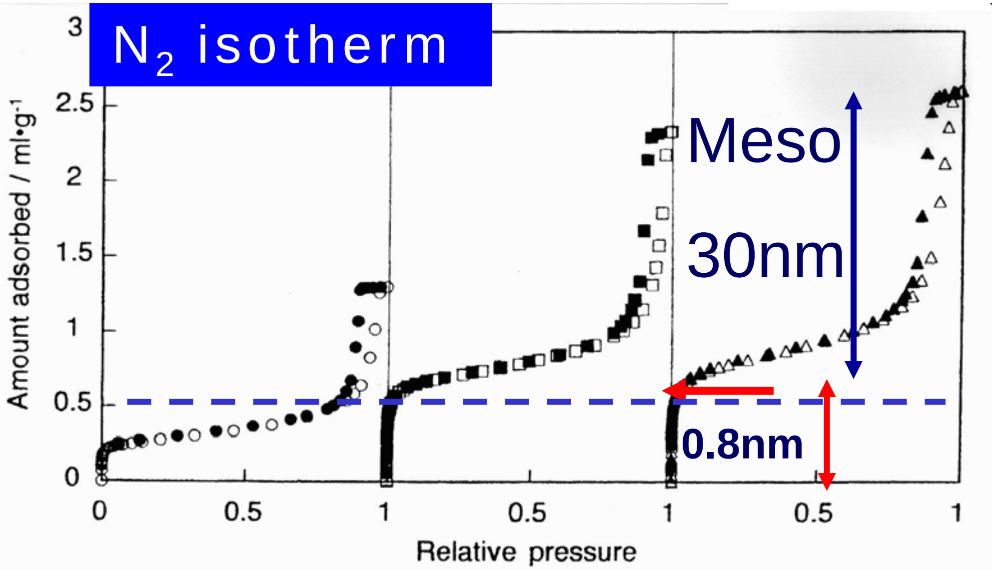
Adsorption Isotherms of N_2 at 77 K and Water at 303 K
n 0.8 nm-pores-added Carbon Aerogel

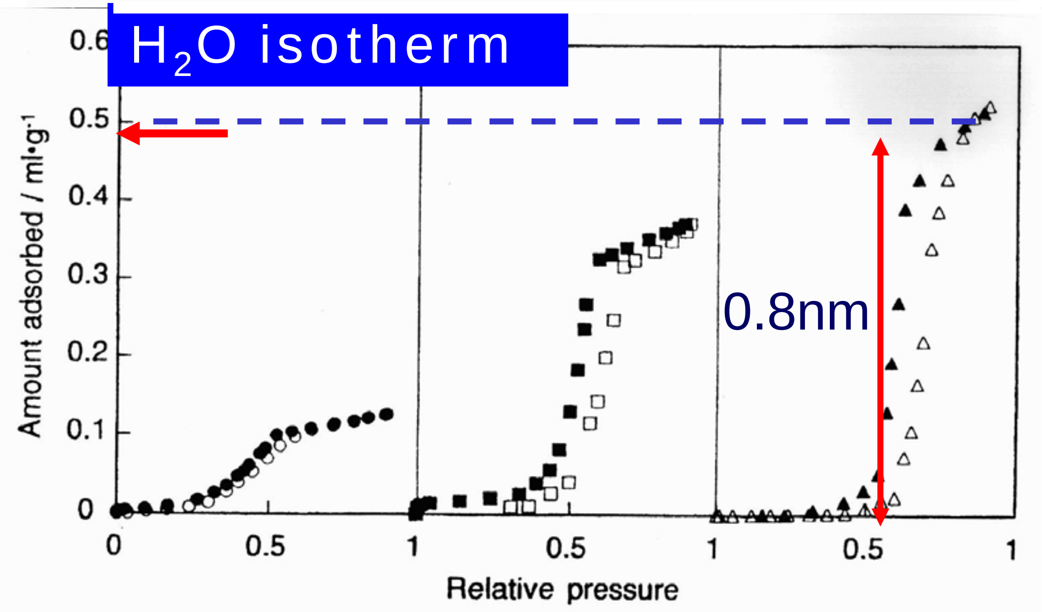
Water adsorption amount at 303 K corresponds to nanopore volume

w = 0.8 nm



Y.Hanzawa et al, Langmuir (1997)





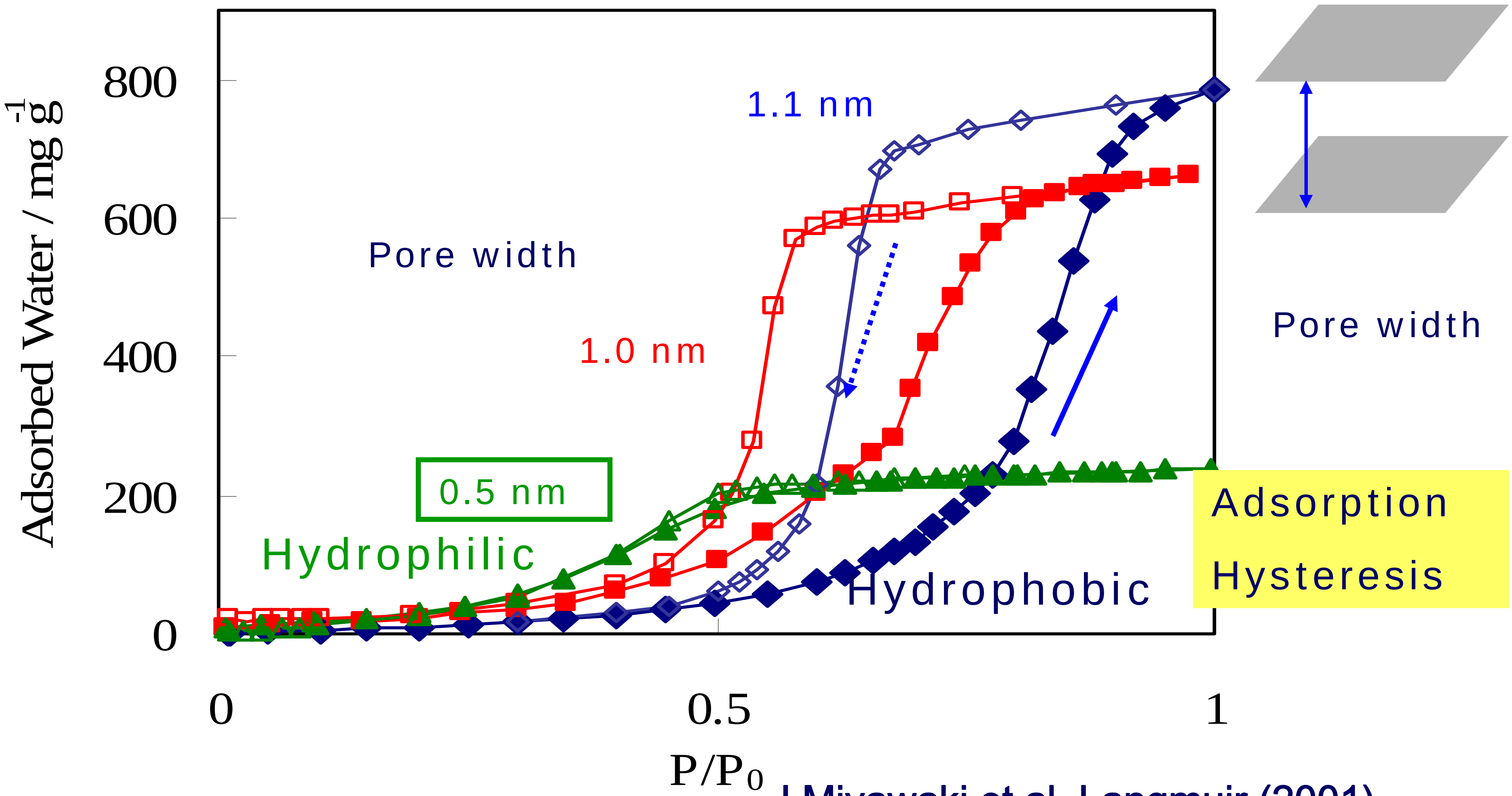
How Can We Understand Adsorption Hysteresis ?

Which is the most stable state

in “adsorption” and “desorption” ?

Water filling and hysteresis depend on pore width

at 303 K

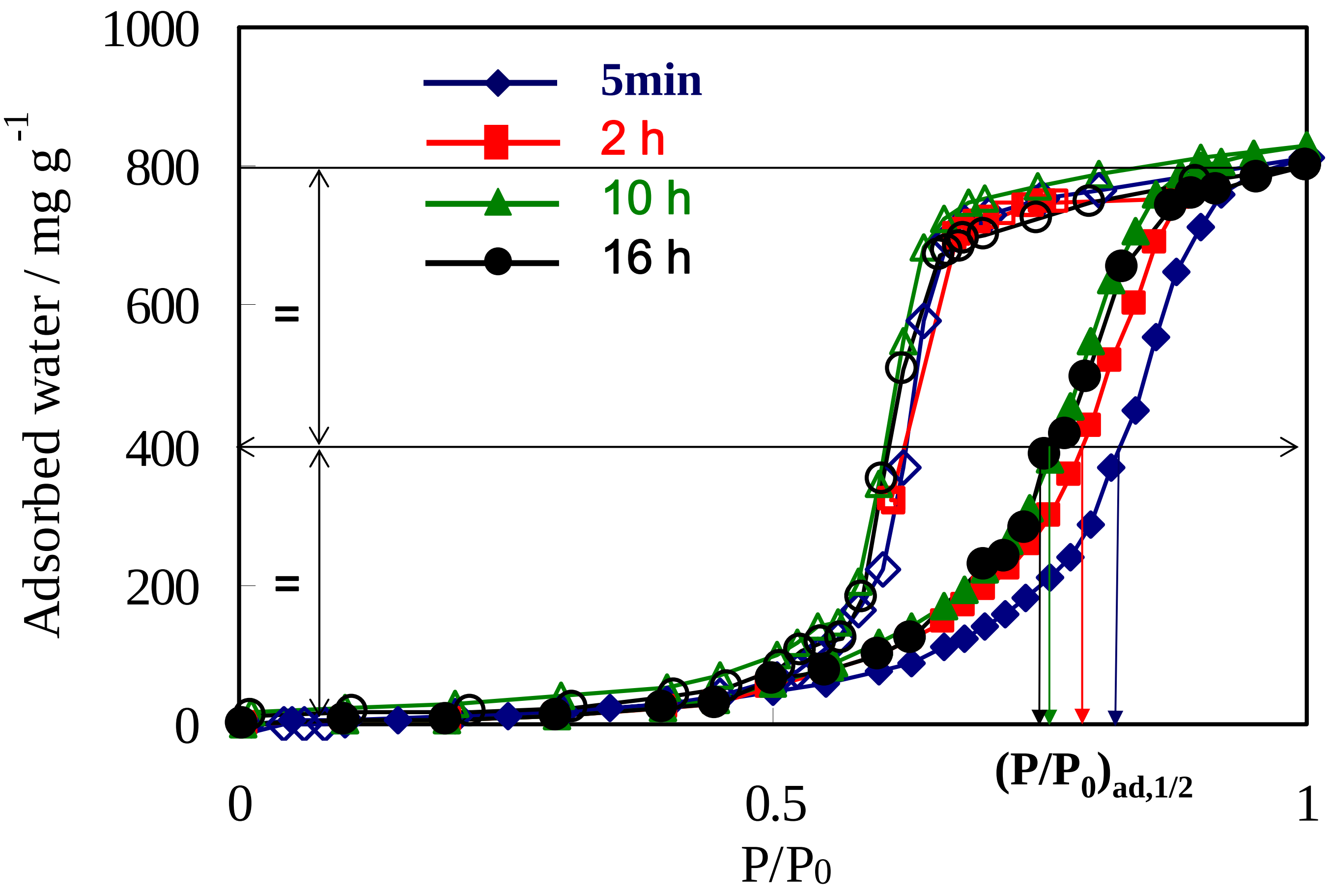


J.Miyawaki et al, Langmuir (2001)

Dependence of Adsorption Hysteresis on “Equilibration” Time at 303 K

ACF

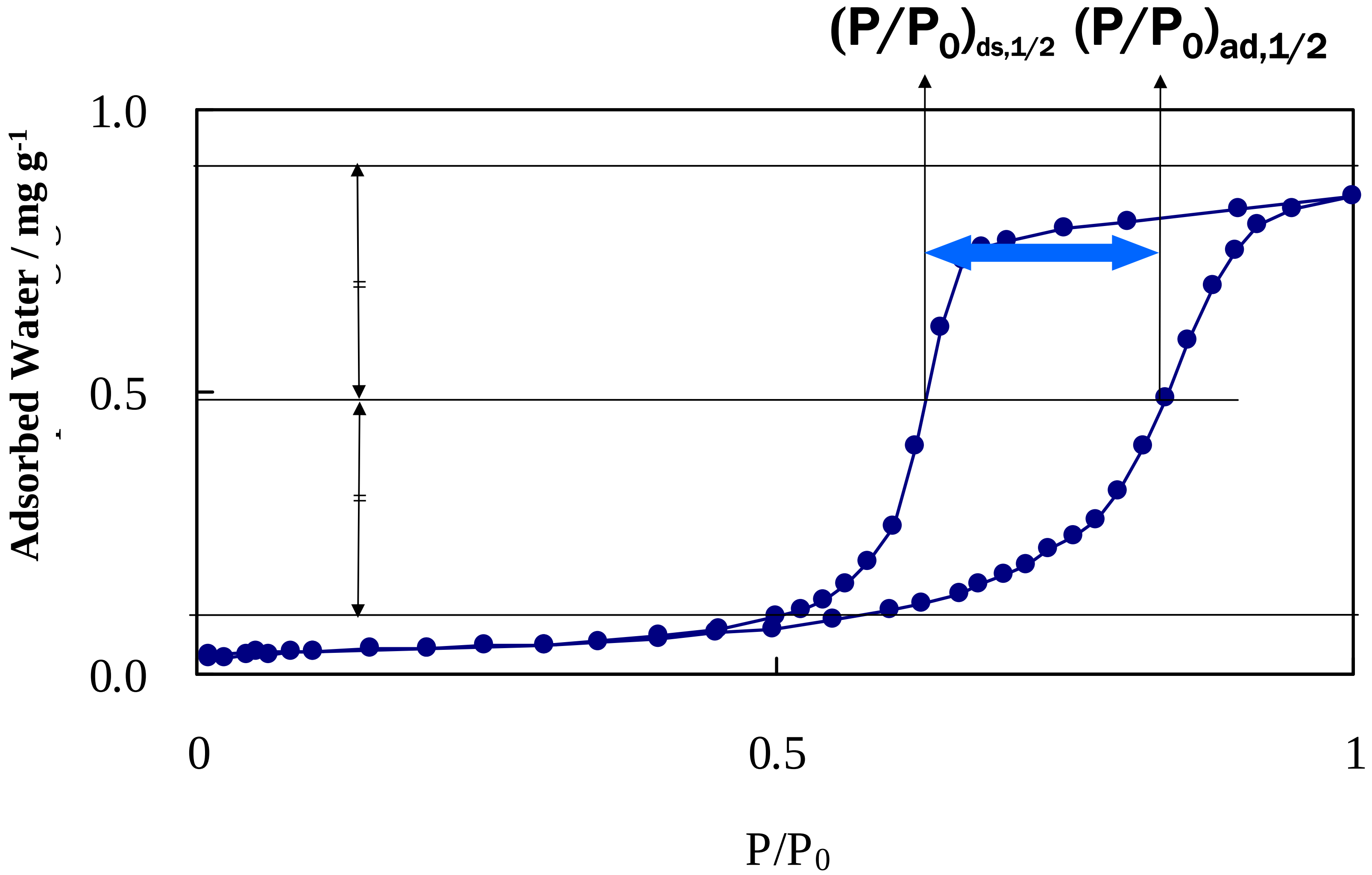
1.1 nm



Solid symbol; adsorption, Open symbol; desorption

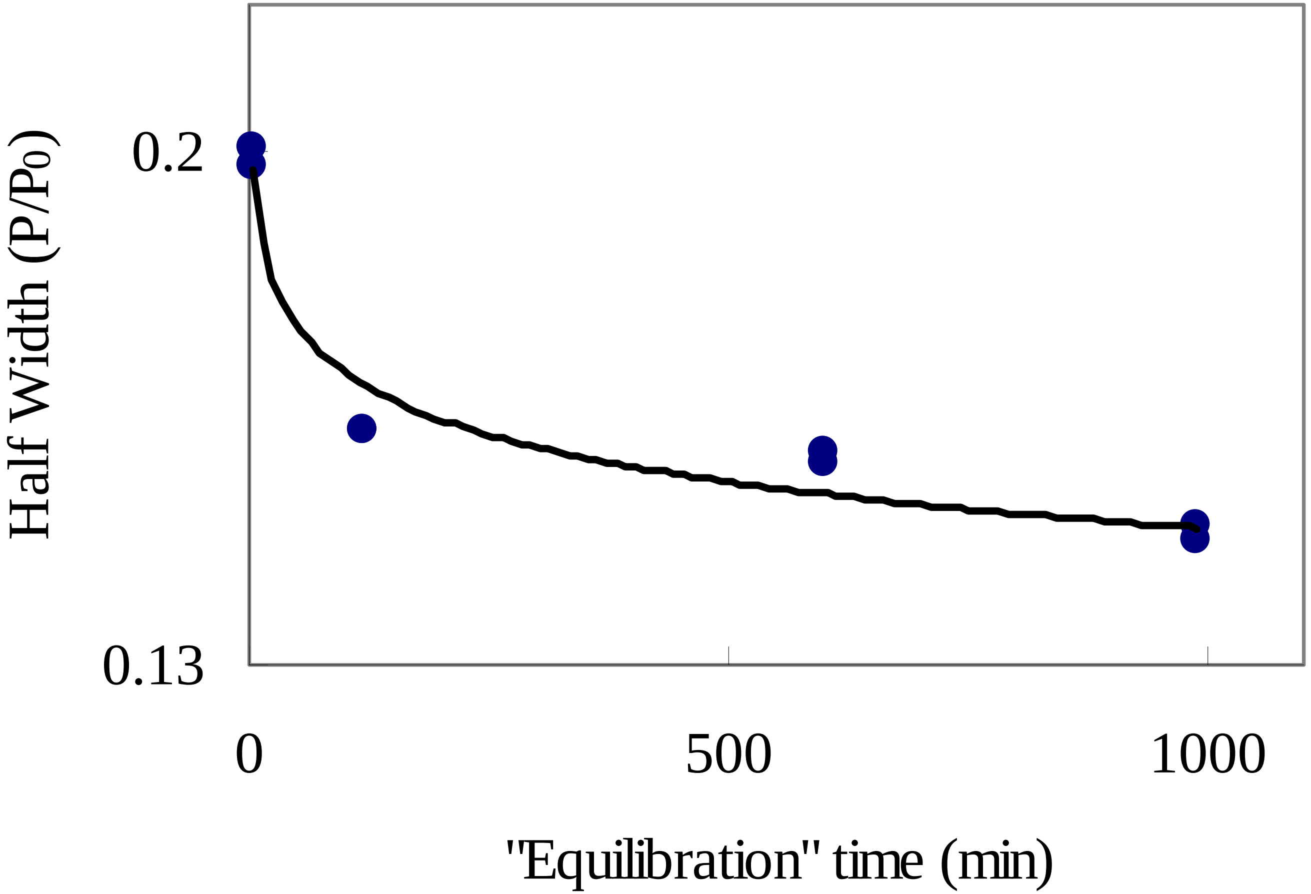
Half-Width of Adsorption Hysteresis Loop

The pressures defining the half width

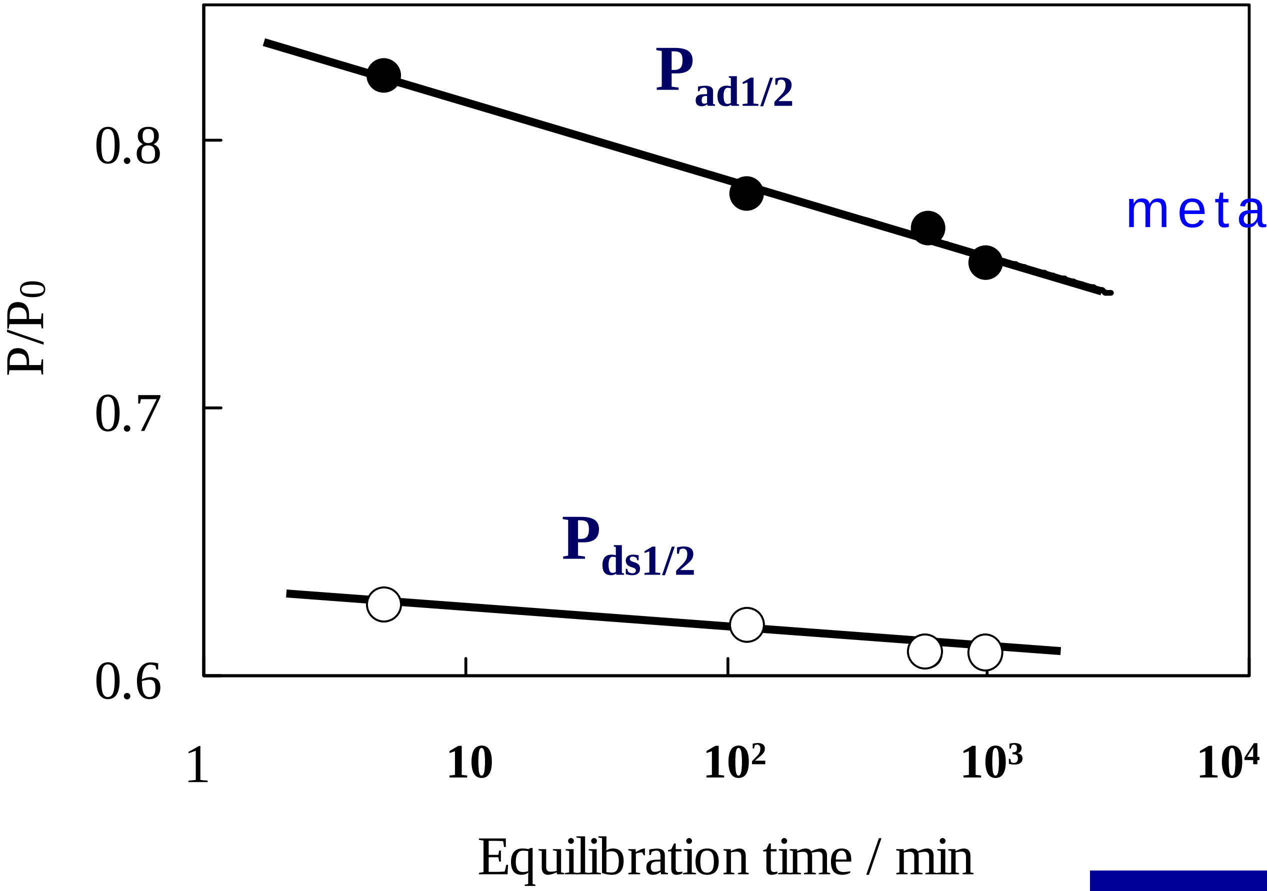


$(P/P_0)_{ds,1/2}$ $(P/P_0)_{ad,1/2}$

Relationship between Half-width of hysteresis loop and equilibration time



$P_{ad1/2}$ and $P_{ds1/2}$ against equilibration time at 303K



metastable

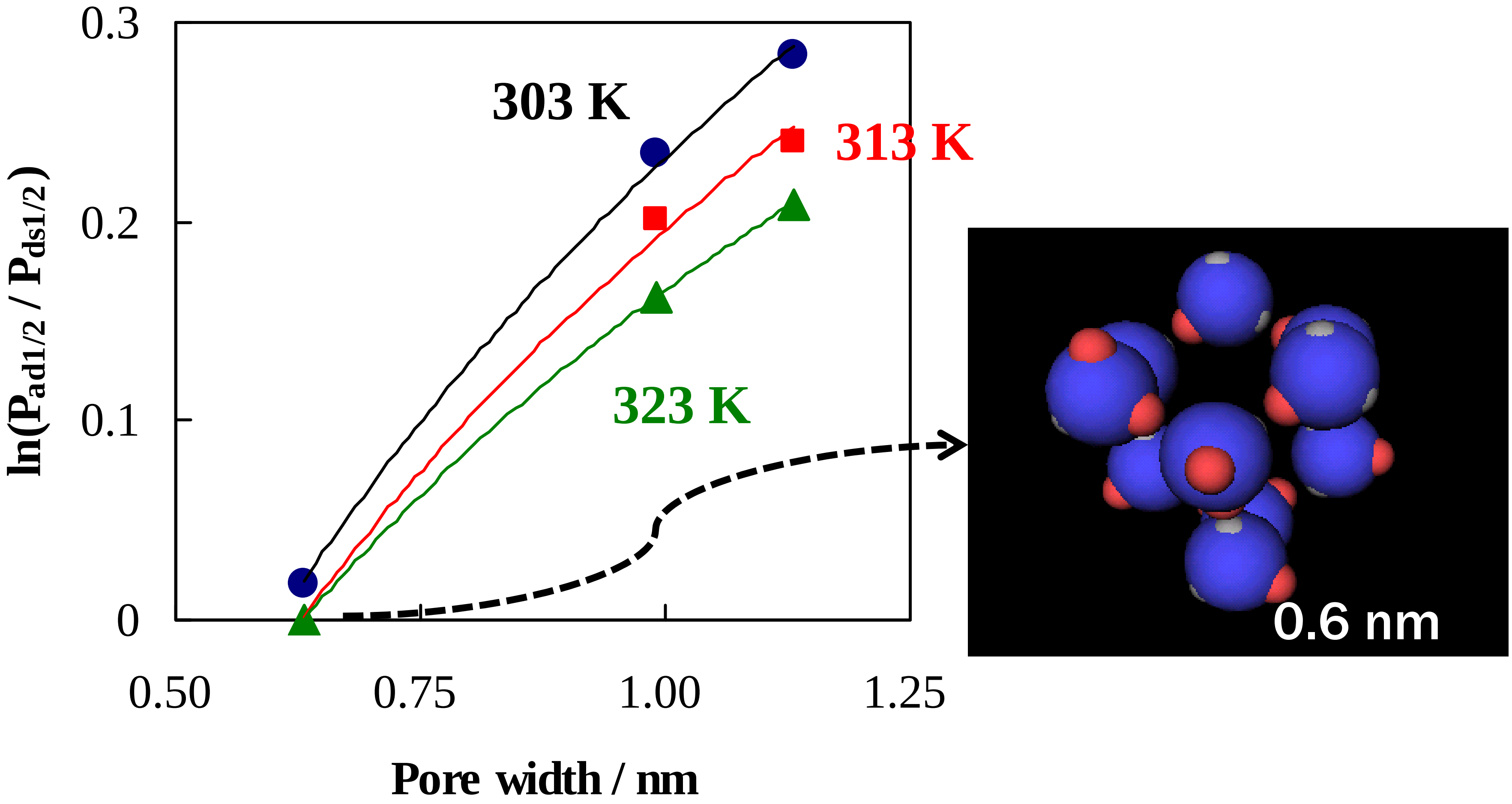
(more) Stable

Time dependence

from non-equilibrium measurement

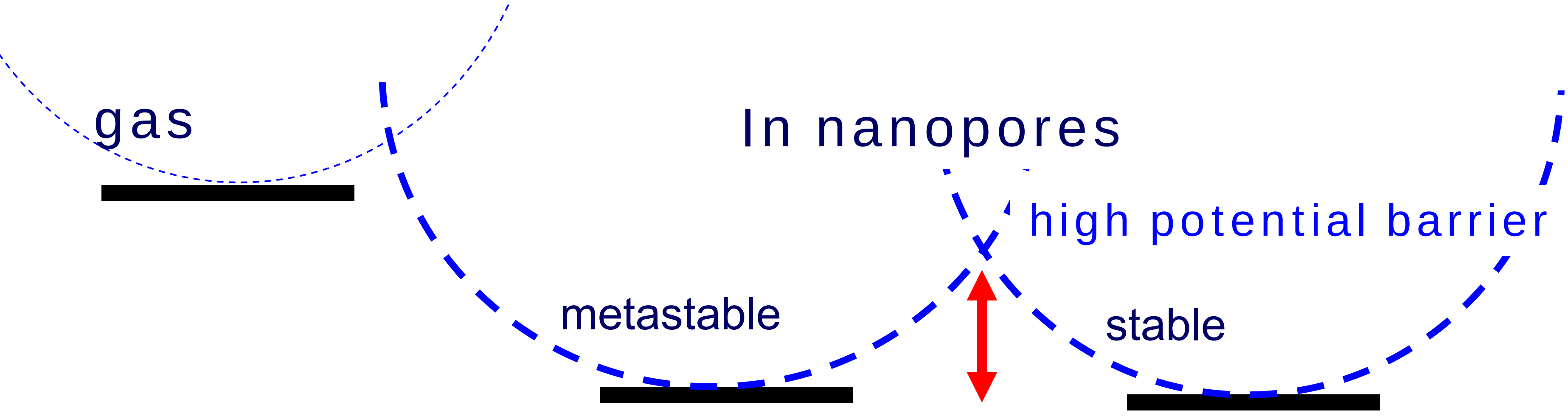
> 2000 years

Critical Pore Width for Hysteresis from $(P/P_0)_{ds,1/2} = (P/P_0)_{ad,1/2}$



M. Nakamura et al , *Carbon*, **48**, 305 (2010)

Extremely Stable Metastable-State



gas

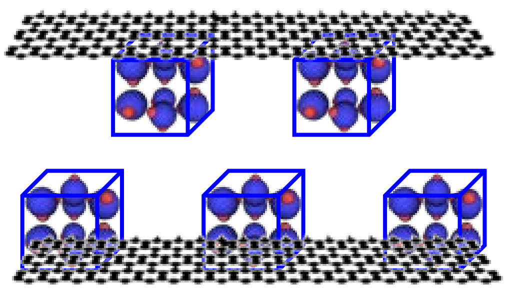
In nanopores

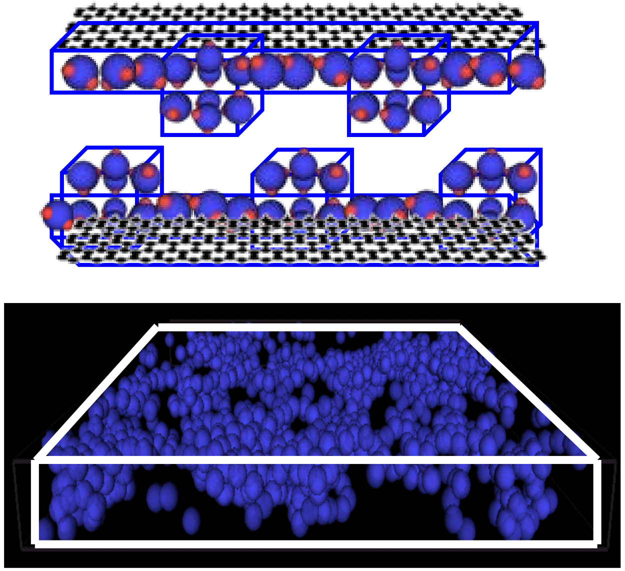
high potential barrier

metastable

stable

Filling =0.4





Effect of Surface Functional Groups on Water Adsorption

ACF

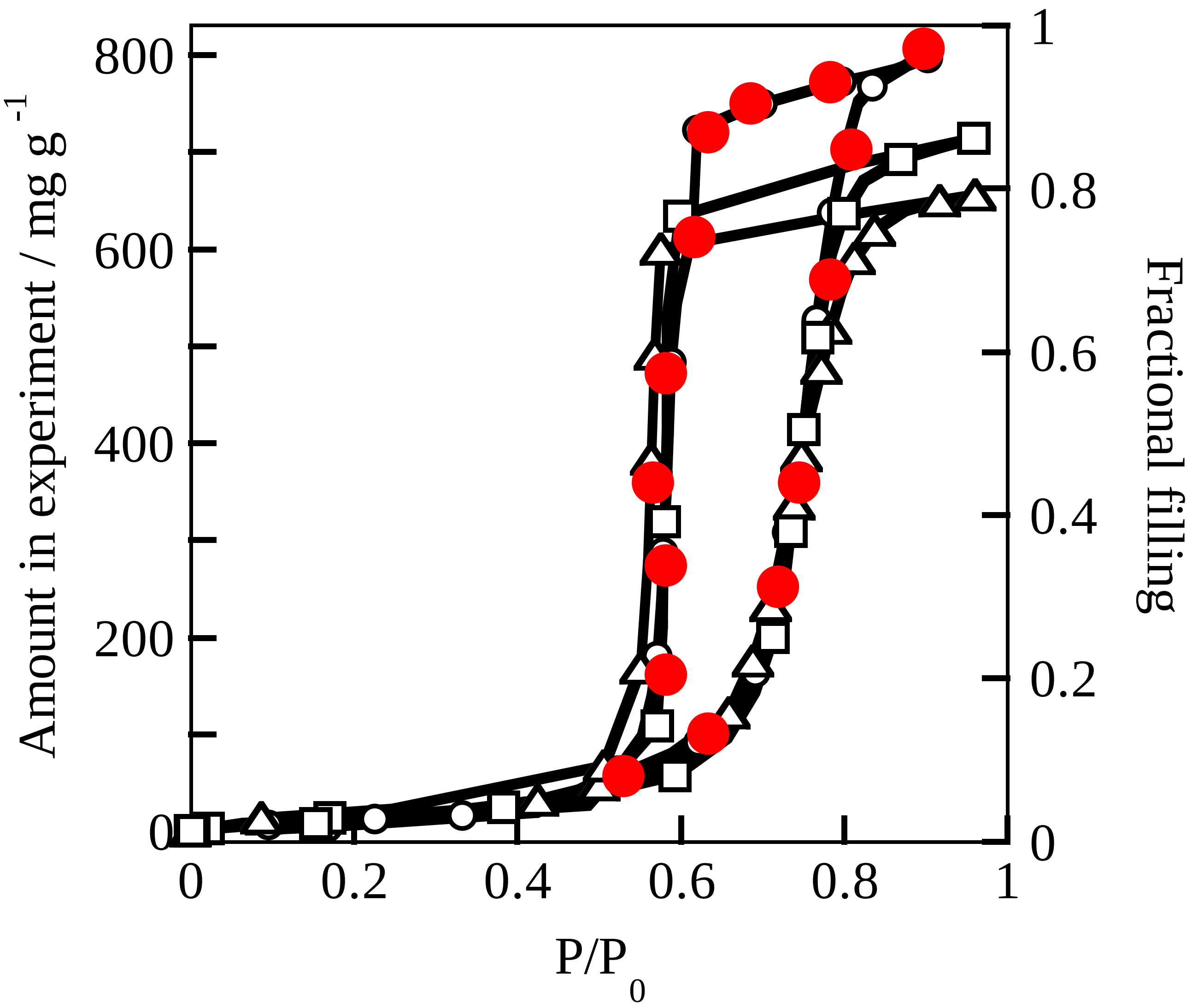
ACF treated in Ar

ACF reduced in H_2

O/C determined by XPS

T. Ohba, K. Kaneko, *J. Phys.Chem.C*. **111**, 6207-6214 (2007).

Adsorption Isotherms of Surface Modified ACF



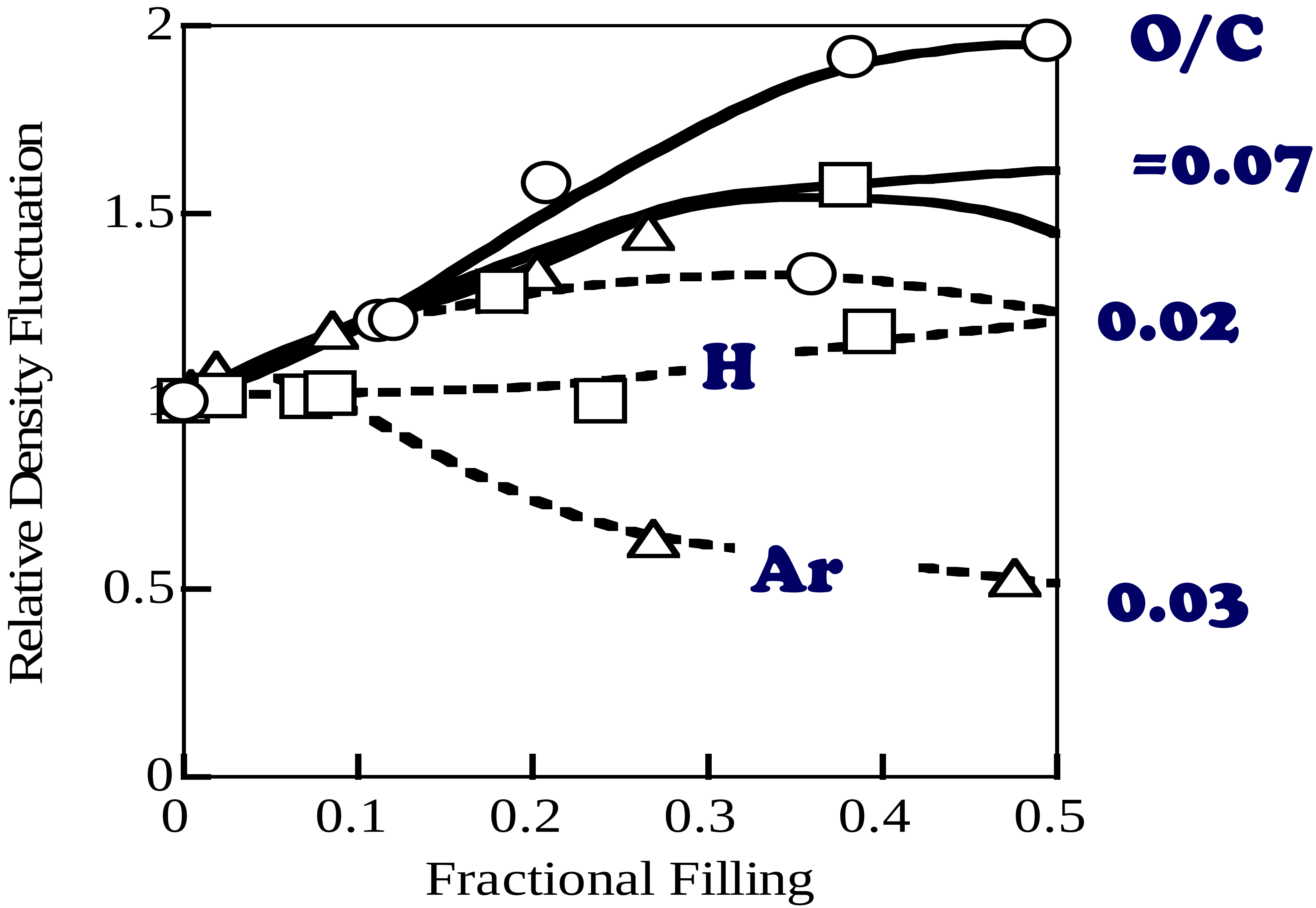
H-ACF: O/C = 0.02

ACF: O/C = 0.07

Ar-ACF: O/C = 0.07

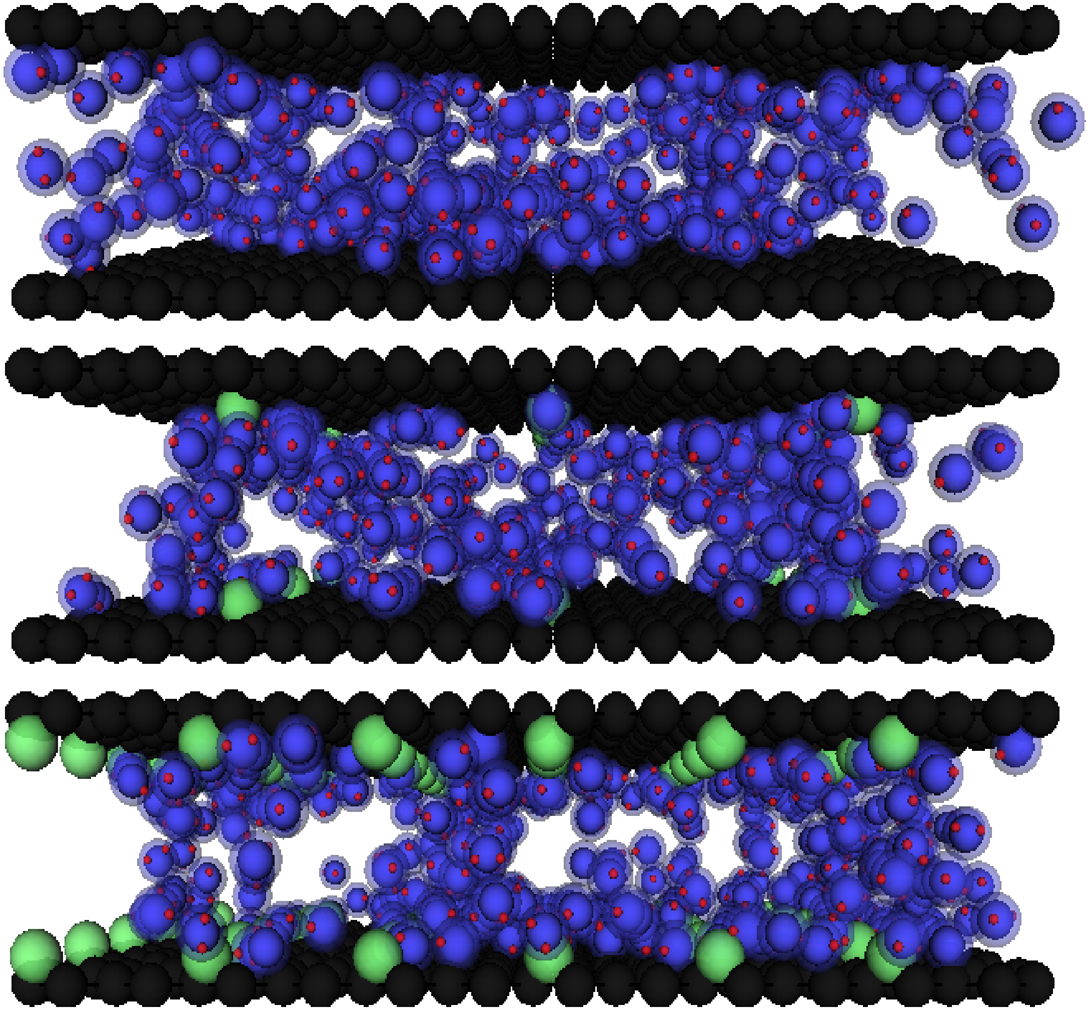
ensity fluctuation with adsorption

n ACF with surface oxygen



Snapshots of adsorbed water molecules

filling=0.4



O/C

=0.02

H-ACF

Surface oxygen

=0.03

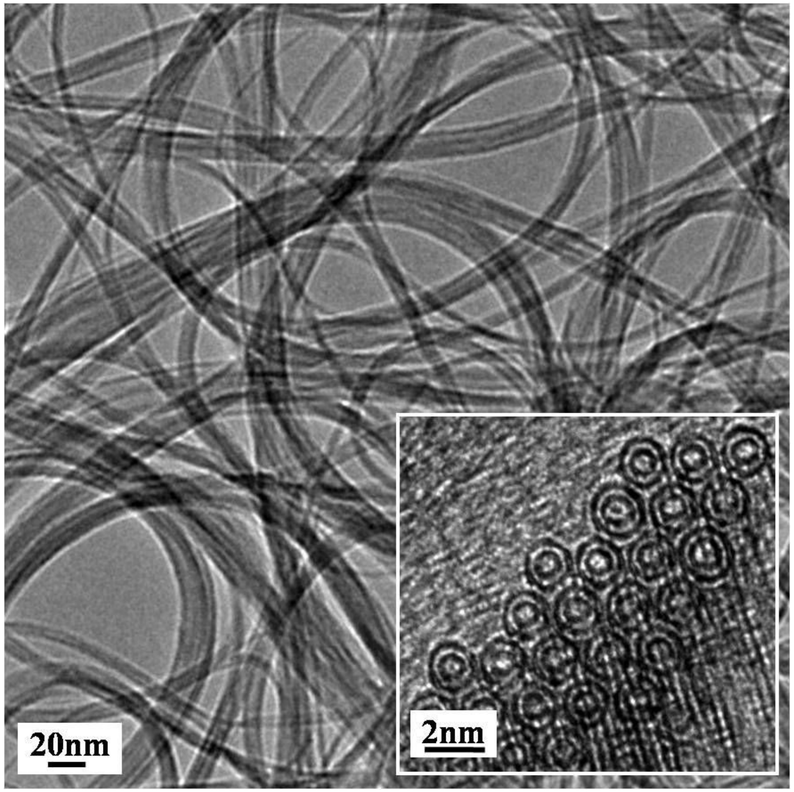
Ar-ACF

=0.07

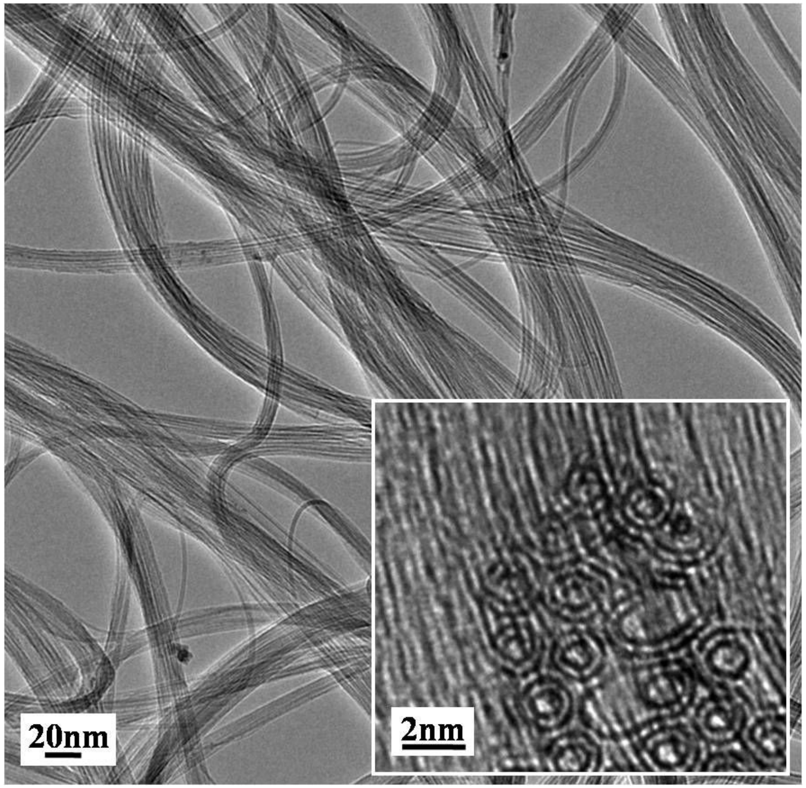
ACF

Highly Pure Double Wall Carbon Nanotube

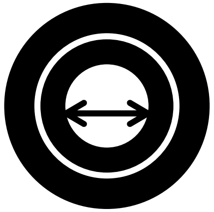
Merged tubes having larger tube spaces



Before heating



After heating at 2273 K in Ar

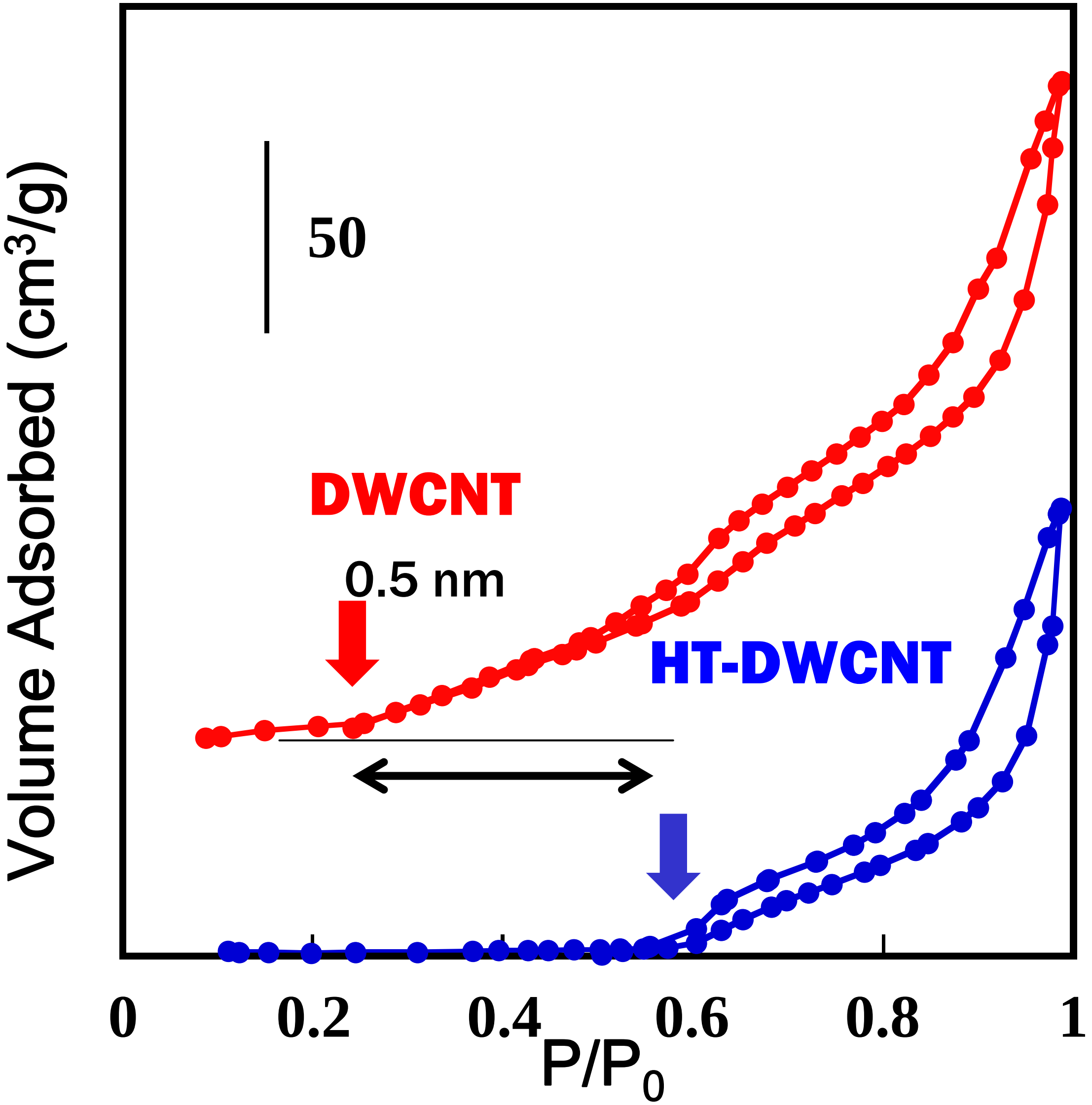


0.51 nm

0.5 ~ >1.5nm

Y.Tao et al, *J.Amer.Chem.Soc.* **132**, 1214 (2010)

Water adsorption isotherms at 308 K for DWCNTs and HT-DWCNTs



Y.Tao et al,

J.Amer.Chem.Soc. **132**, 1214 (2010)

Important Factors of “Hydrophobic-Hydrophilic Transformation”

Threshold pressure becomes lower
(Apparent hydrophilicity becomes more predominant)

with decreasing pore width

with fluorination (surface chemistry)

Apparent hydrophilicty needs presence of micropores
(< 2 nm scale)
1 D-hydrogen bonding network must be formed

GCMC-aided In situ Small Angle X-ray Scattering

Distribution of molecules in nanospaces

⇕

Snapshot from GCMC simulation

T. Ohba

Chiba Univ.

Ohba, T.; Kaneko, K. *J. Phys. Chem*. C 2007, 111, 6207–6214.

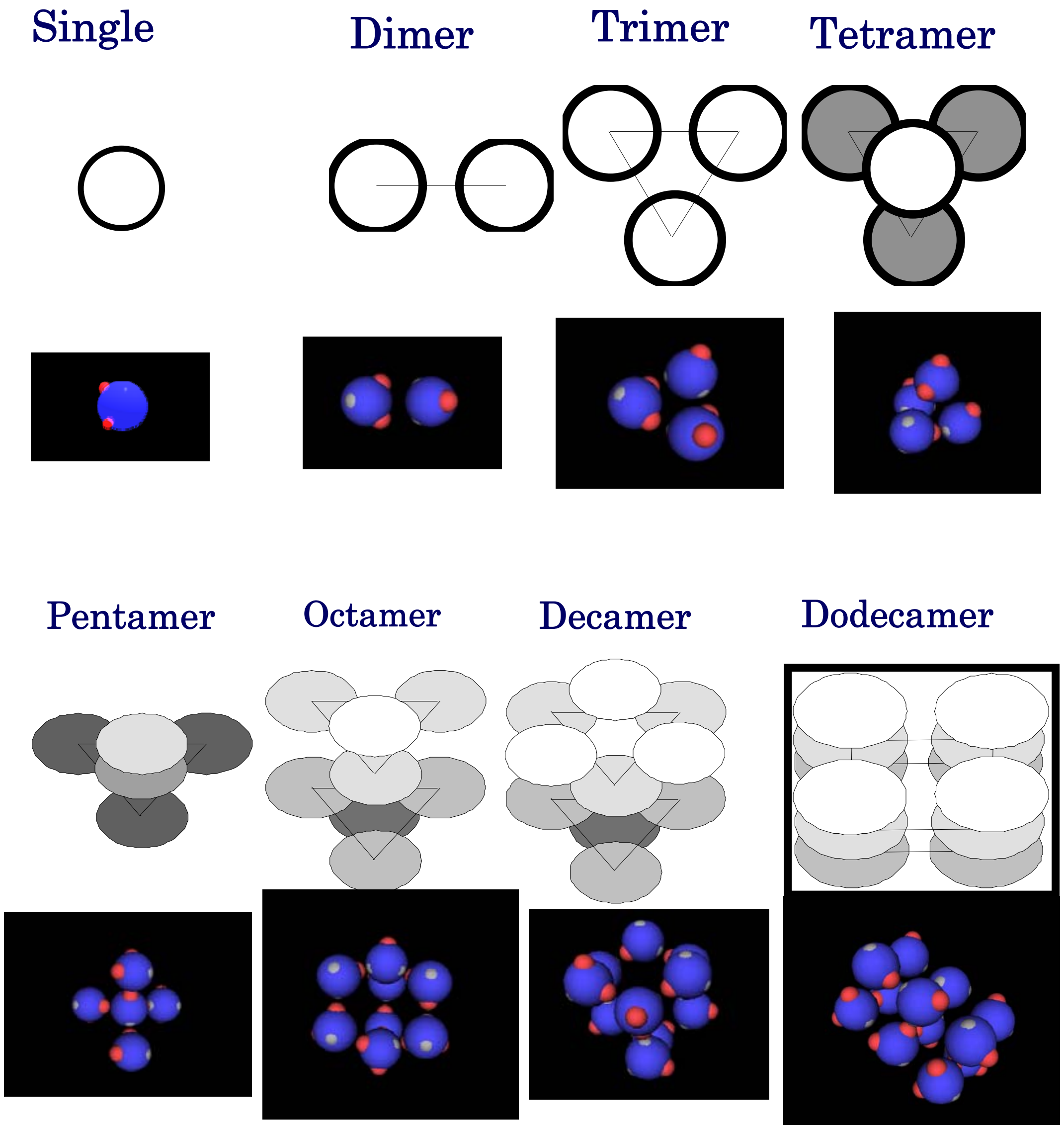
Ohba, T.; Kaneko, K. *Mol. Phys*. 2007, 105, 139–145.

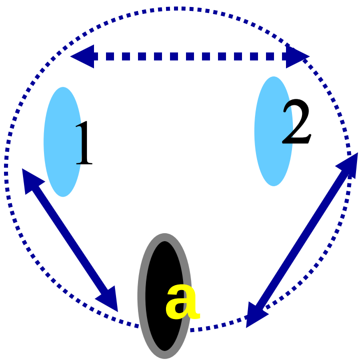
Ohba, T.; Kanoh, H.; Kaneko, K. *Nano Lett*. 2005, 5, 227–230.

“Kinetically Forbidden Transformations of Water Molecular Assemblies in Hydrophobic Micropores”

Ohba T. Kaneko, K. *Langmuir* 2011, 27, 7609–7613

Symmetrical Cluster Models





(Interaction from other molecules)

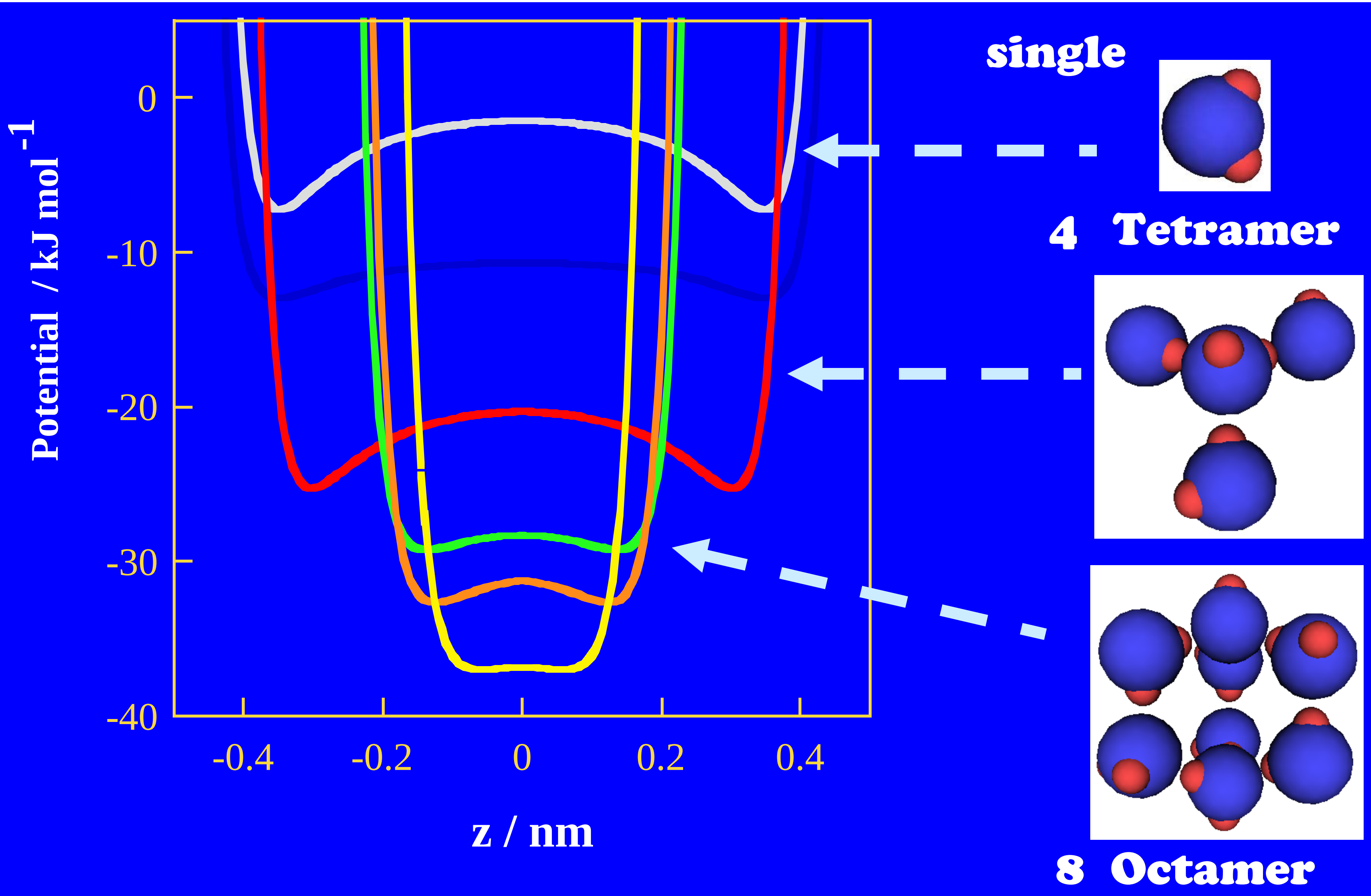
+ (surface-molecule interaction) =

Total Potential

For Slit-pore model
T. Ohba et al
J Amer Chem Soc (2004)

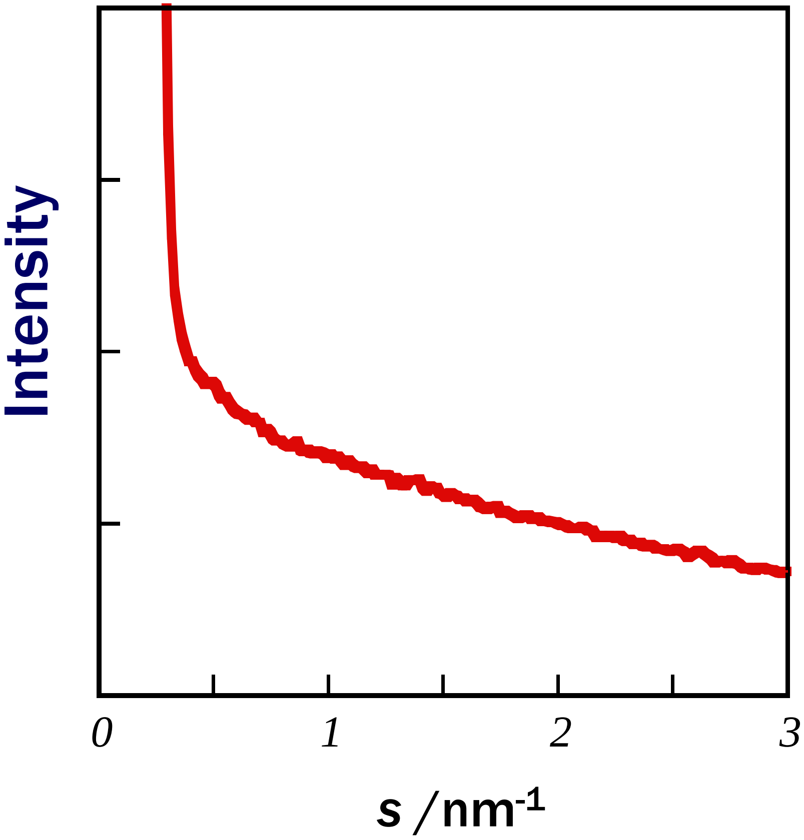
Total Potential Profiles for a Molecule in Cluster

T. Ohba and K. Kaneko, J. Amer. Chem. Soc.（2004）



Cluster Size and Adsorbed State of Water

Density Fluctuation from SAXS



SAXS profile

in situ conditions

Ornstein-Zernike Plot

$$\frac{1}{I(s)} = \frac{1}{I(0)} + \frac{\xi^2}{I(0)} s^2$$

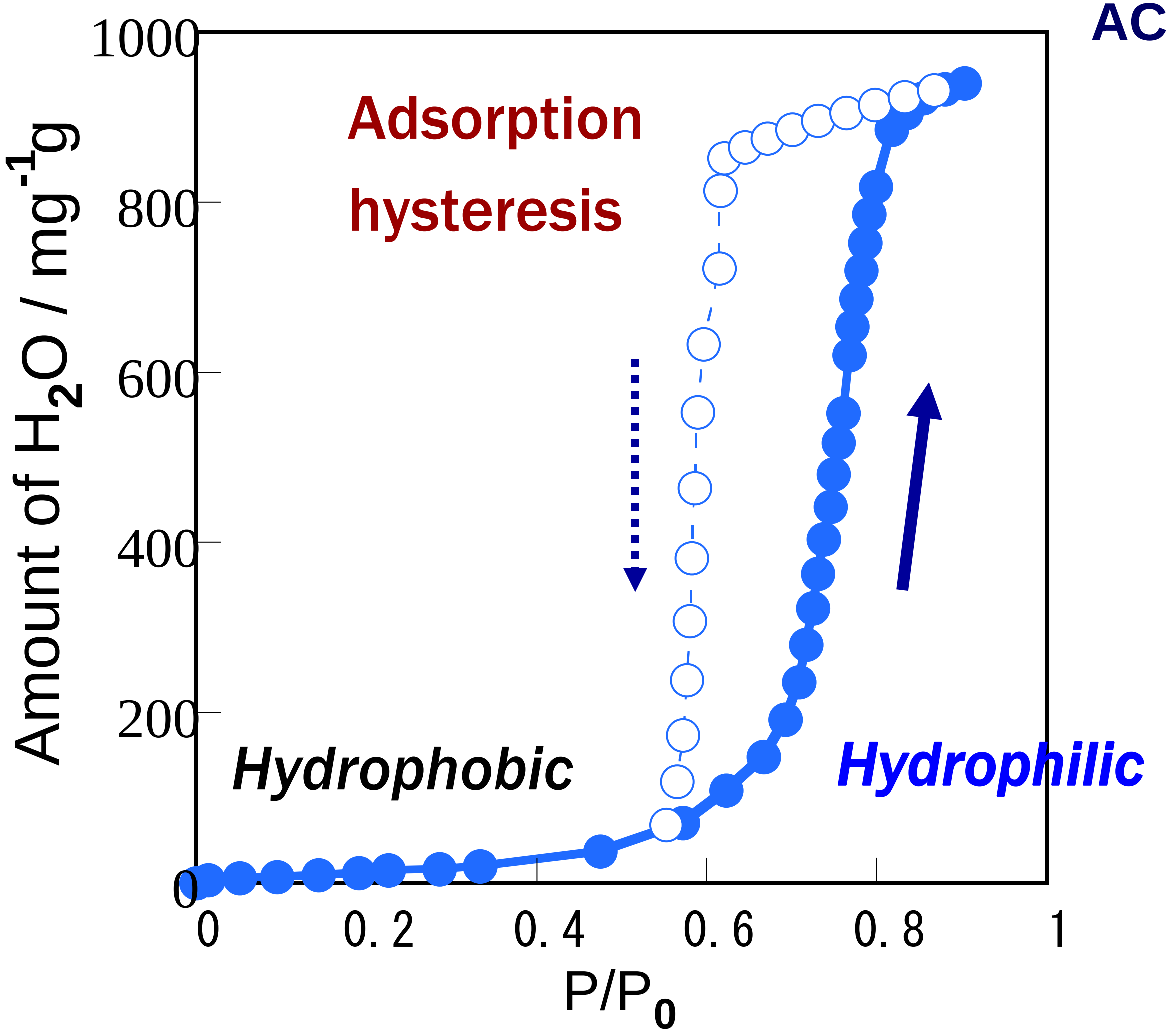
s :Scattering parameter

ξ : Correlation Length

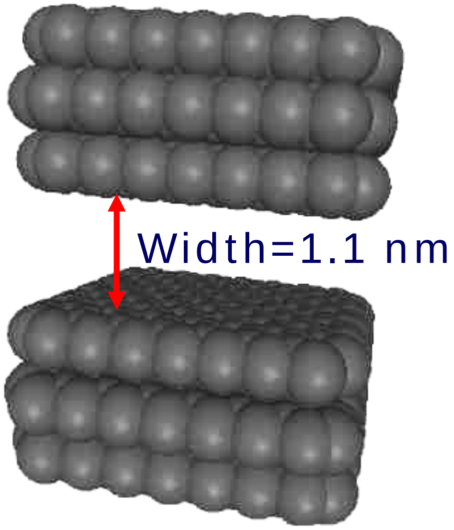
$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \frac{I(0)}{NZ^2}$$

Density Fluctuation

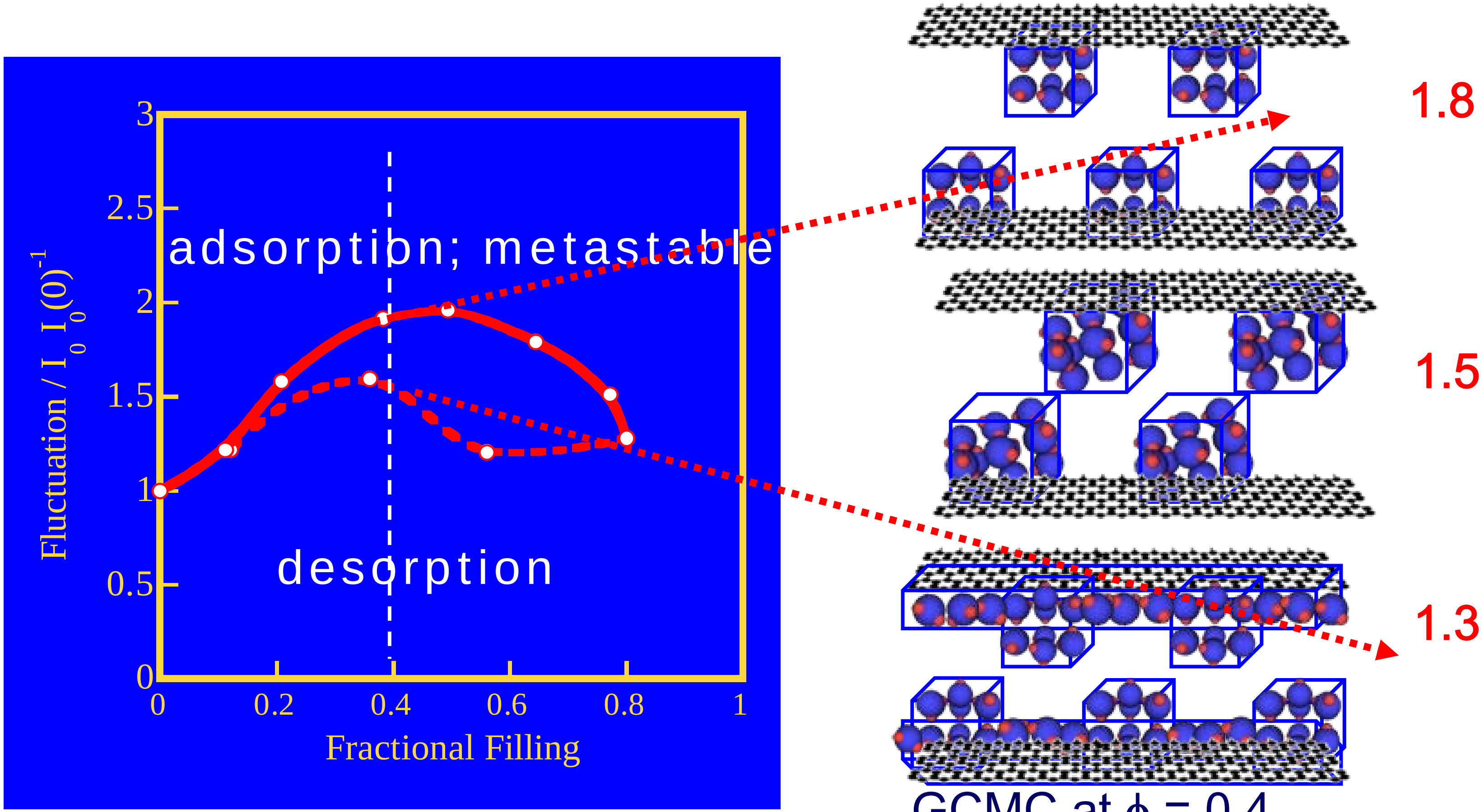
Application of Ornstein-Zernike Analysis to SAXS Data



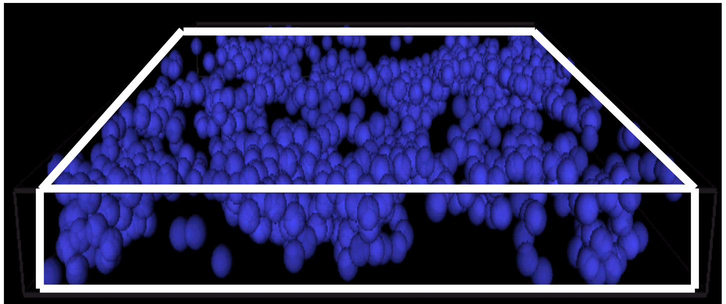
ACF : Slit pores



Metastable Structure in 1.1 nm Pores



GCMC at ϕ = 0.4



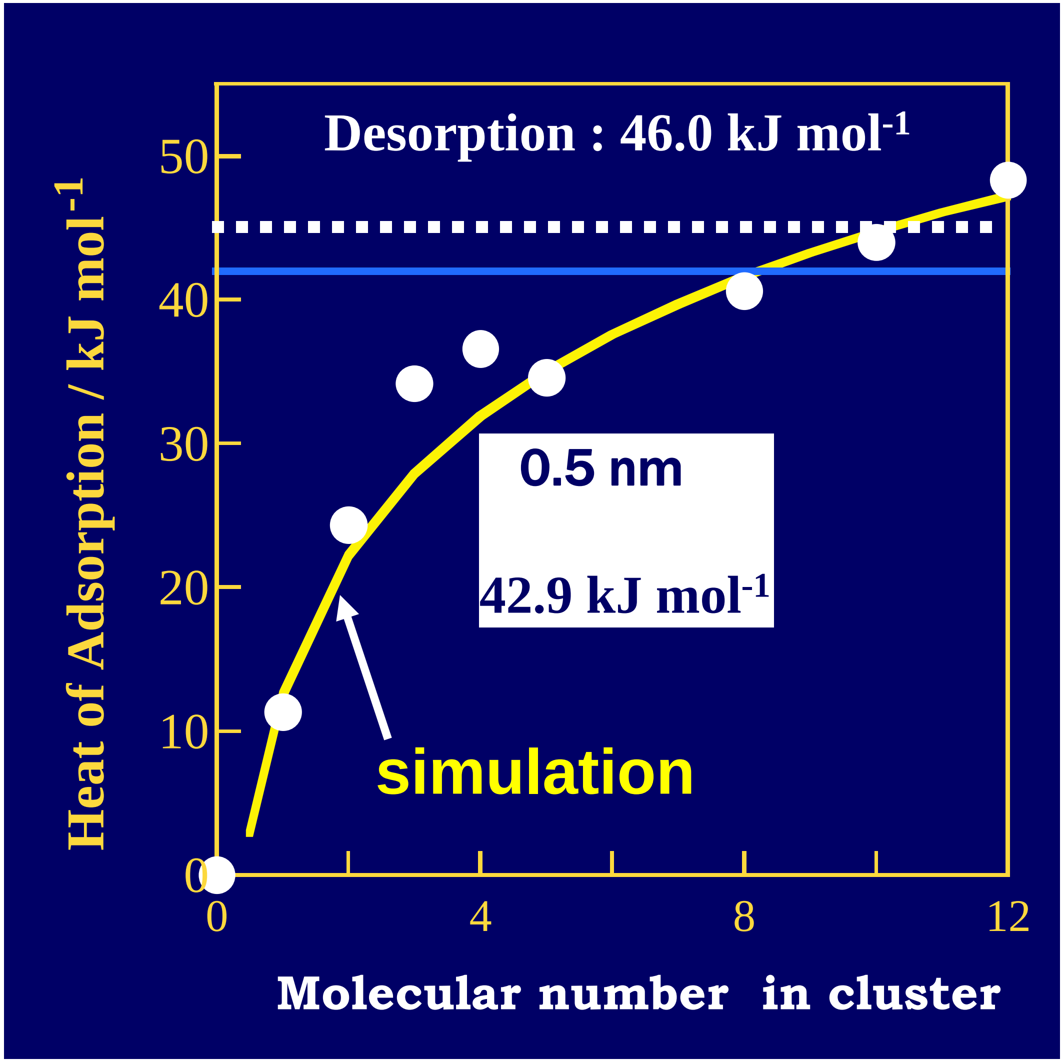
T. Ohba et al. *Nano Lett.* (2004).

Chem. Eur. J. (2004).

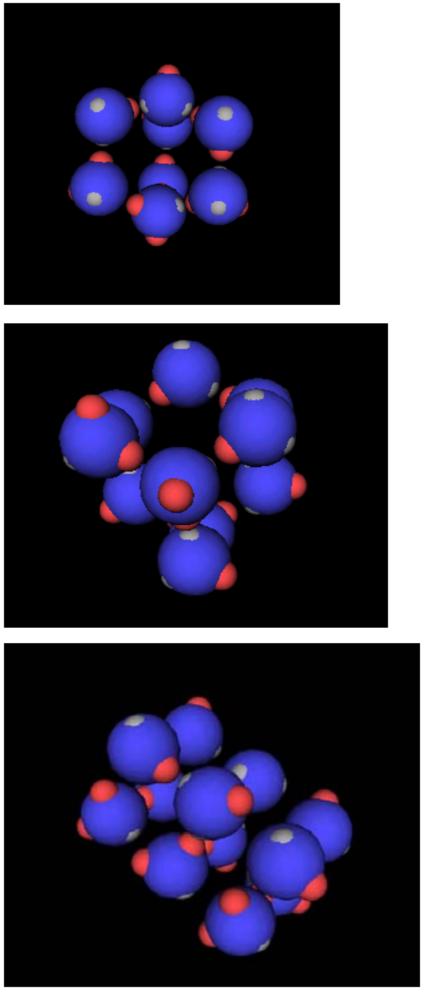
Mol. Phys. (2007).

Heat of Adsorption

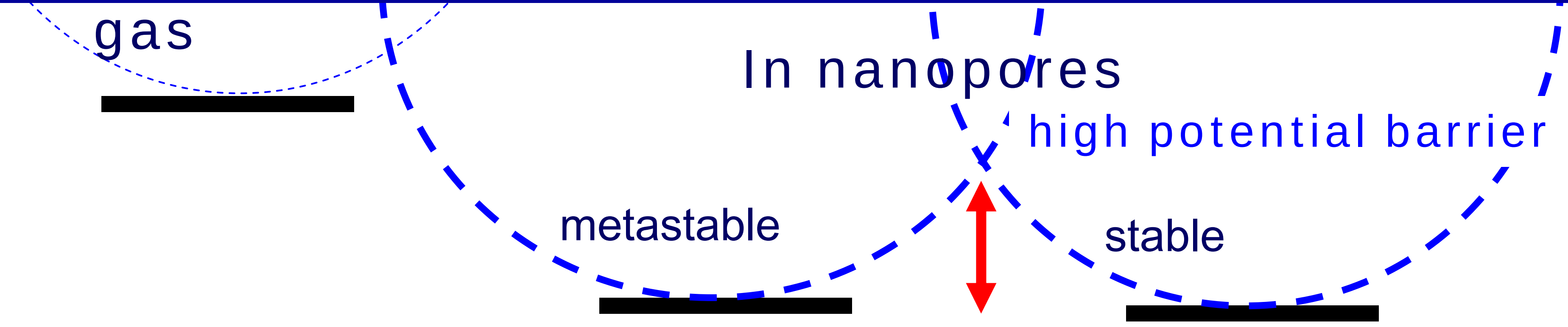
Change of q_{st} with Cluster Size from Simulation



Unit cluster size: 8---10



Present understanding



gas

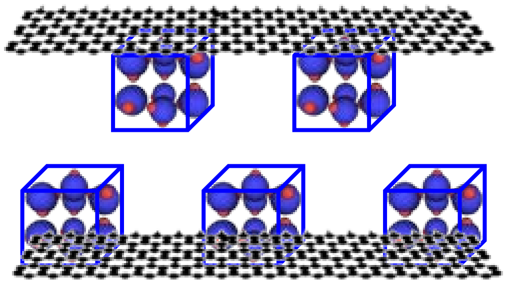
In nanopores

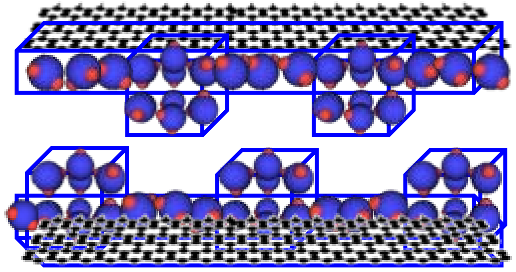
high potential barrier

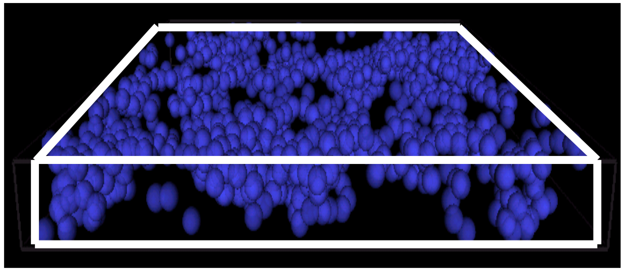
metastable

stable

Filling =0.4

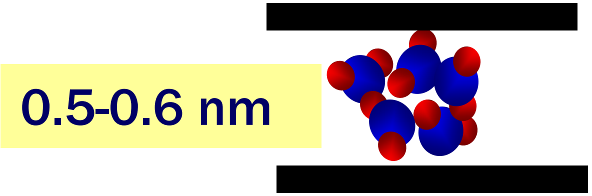


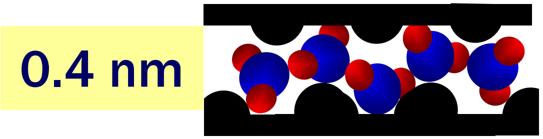




Conclusion: How Can We Understand "Hydrophobic-Hydrophilic Transformation" ?

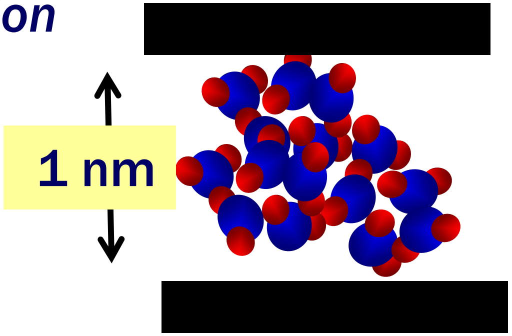
If solid can offer the stable field to water molecular clusters or low-dimensional network, "hydrophobic solid" can accept water molecules, inducing apparent hydrophilicity.





When solid can supply 1-2 nm scale pores which guarantee the growth of smaller clusters, adsorption begins suddenly at the relative pressure where the grown cluster size agrees with the pore size

Induction of hyrophobic-hydrophlic transformation



Water is really adaptable to the surrounding.

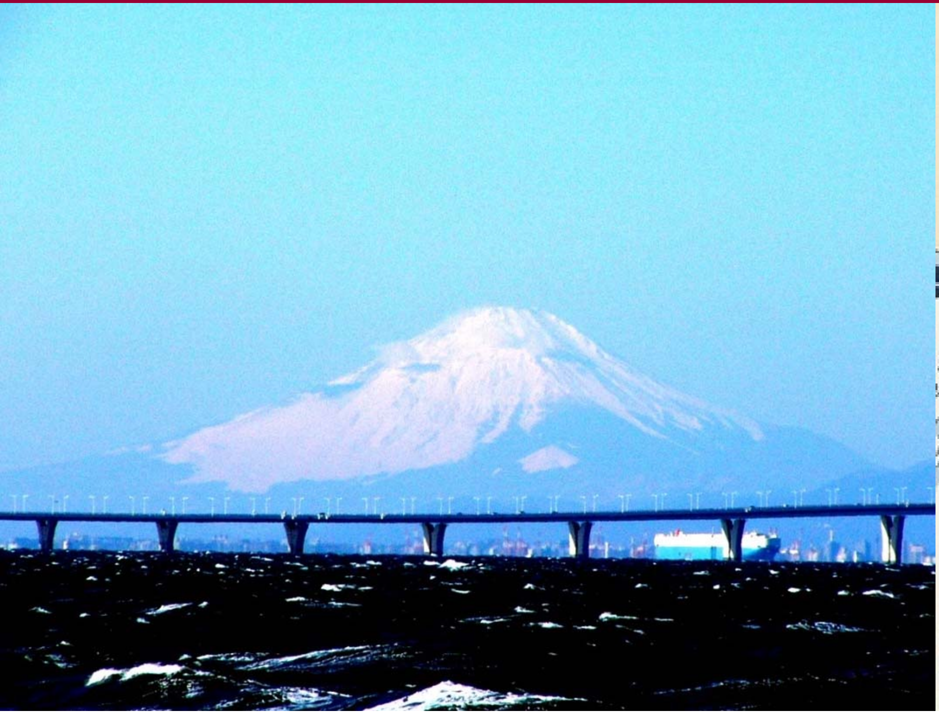
As to "Adsorption Hysteresis"

T. Ohba, K. Kaneko, *Langmuir*, 27, 7609 (2011)

K. Kaneko. *Chem. Lett.*41,466 (2012): Highlight review

Water confined in carbon pores

How mysterious and attractive



Mt. Fuji and Waves

Hokusai

Adsorption from Solution

Very important area

- **Preservation of beautiful earth**
- **Water resources**
- **Ocean resource engineering**

No predominant progress

- **in understanding**
- **without structural science aspects**

Ocean Resources

Resources : *Extremely diluted*

Li Batteries

D Nuclear fusion

Precious metals

Fuels Methane hydrate

Concentration of Elements in Ocean (Nozaki, 1996)

	(ng/kg)		(ng/kg)		(ng/kg)		(ng/kg)
Cl	19,350,000,000	U	3,200	Re	7.8	Sn	0.5
Na	10,780,000,000	V	2,000	He	7.6	Ho	0.36
Mg	1,280,000,000	As	1,200	Ti	6.5	Lu	0.23
S	898,000,000	Ni	480	La	5.6	Be	0.21
Ca	412,000,000	Zn	350	Ge	5.5	Tm	0.2
K	399,000,000	Kr	310	Nb	<5	Eu	0.17
Br	67,000,000	Cs	306	Hf	3.4	Tb	0.17
C	27,000,000	Cr	212	Nd	3.3	Hg	0.14
N	8,720,000	Sb	200	Pb	2.7	Rh	0.08
Sr	7,800,000	Ne	160	Ta	<2.5	Te	0.07
B	4,500,000	Se	155	Ag	2.0	Pd	0.06
O	2,800,000	Cu	150	Co	1.2	Pt	0.05
Si	2,800,000	Cd	70	Ga	1.2	Bi	0.03
F	1,300,000	Xe	66	Er			
Ar	620,000	Fe	30	Yb			
Li	180,000	Al	30	Dy			
Rb	120,000	Mn	20	Gd			
P	62,000	Y	17	Pr			
I	58,000	Zr	15	Ce			
Ba	15,000	Tl	13	Sc			
Mo	10,000	W	10	Sm	0.57		

Li

in ocean 2.3 x 10^{11} t

mineral resources

1.4 x 10^{7} t

M. Takahasi (Kouchi Univl) https://ir.kochi-u.ac.jp/dspace/bitstream/10126/325/1/3-1.pdf

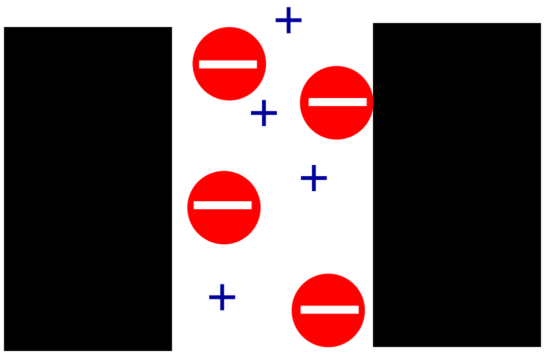
Supercapacitors: Clean Energy Technology

Ions in carbon nanospaces

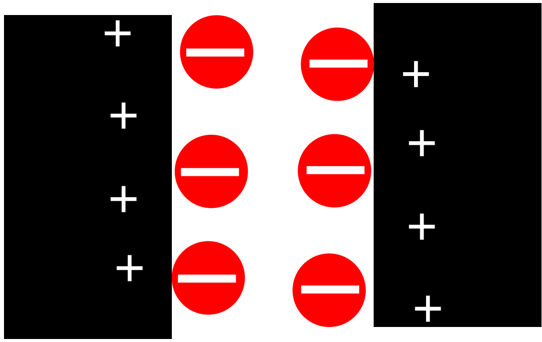
High surface area carbon: Electrode

Electrical double layer in nanospace ?

Ionic diffusion in nanospace ?



Without electric potential



\+ Potential

Being associated with supercapacitors

clean energy devices

Characteristics of Nanoporous Solids

	zeolite	carbon	MOF	silica
Electrical conductivity	×	○	×	×
Thermal conductivity	×	○	×	×
Thermal stability	○	○	△	○
Anti-oxidation property	○	×	×	○
Hydrophobicity	○	○	×	×
Ion exchangeability	○	×	×	×
Pore structure	Micro pore	Micro- and mesopore	micropore	mesopore
Uniform porosity	○	△	○	○
Tunability of pore size	○	△	○	○
high surface area (>1000 m^2 g^{-1})	×	○	○	○

Structural Understanding of Ions in Pores

"Compressed State " of Solution In Slit-Pores of ACF

Dehydration of simple metal cations
by nanoconfinement

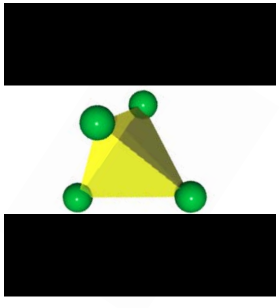
Rb^+ Cs^+ Sr^{2+} Ca^{2+} EXAFS

Simulation

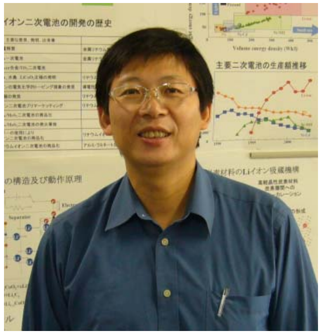
T. Ohkubo
Okayama Univ.

Dehydration and Symmetry Change
of transition metal ions

Cu^{2+} Co^{2+} Fe^{3+} EXAFS XANES



(mesoporous zeolite)



Y. Tao Fujian Inst. of Research
on the Structure of Matter, China

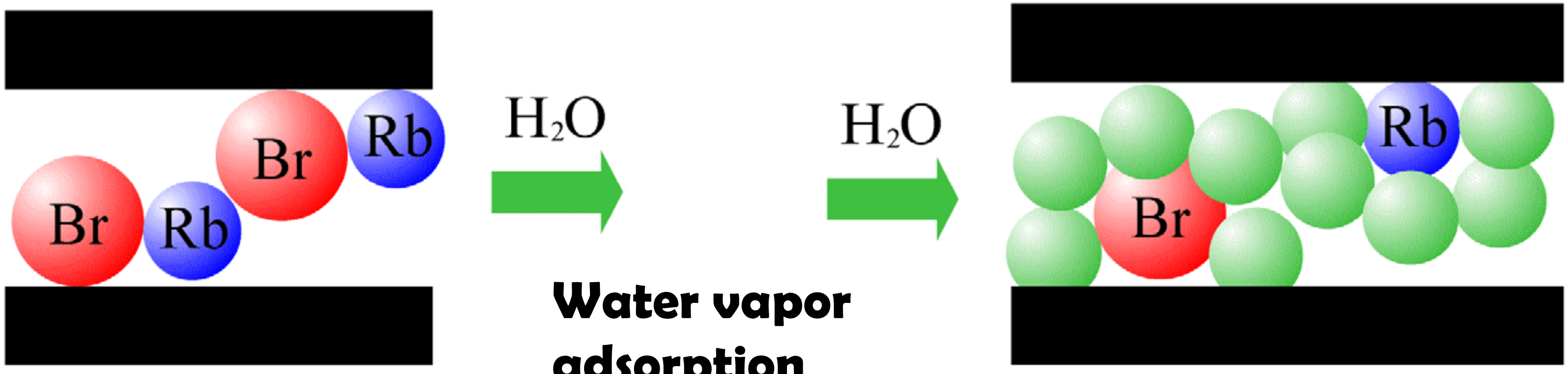
Hydration Structure around a Rb ion

Nanosolution of RbBr in carbon slit nanospaces of ACF

(ACF: 0.7 nm 1.1 nm)

Rb^+(0.149 nm), Br^- (0.195nm)

Hydration number around a target ion with EXAFS

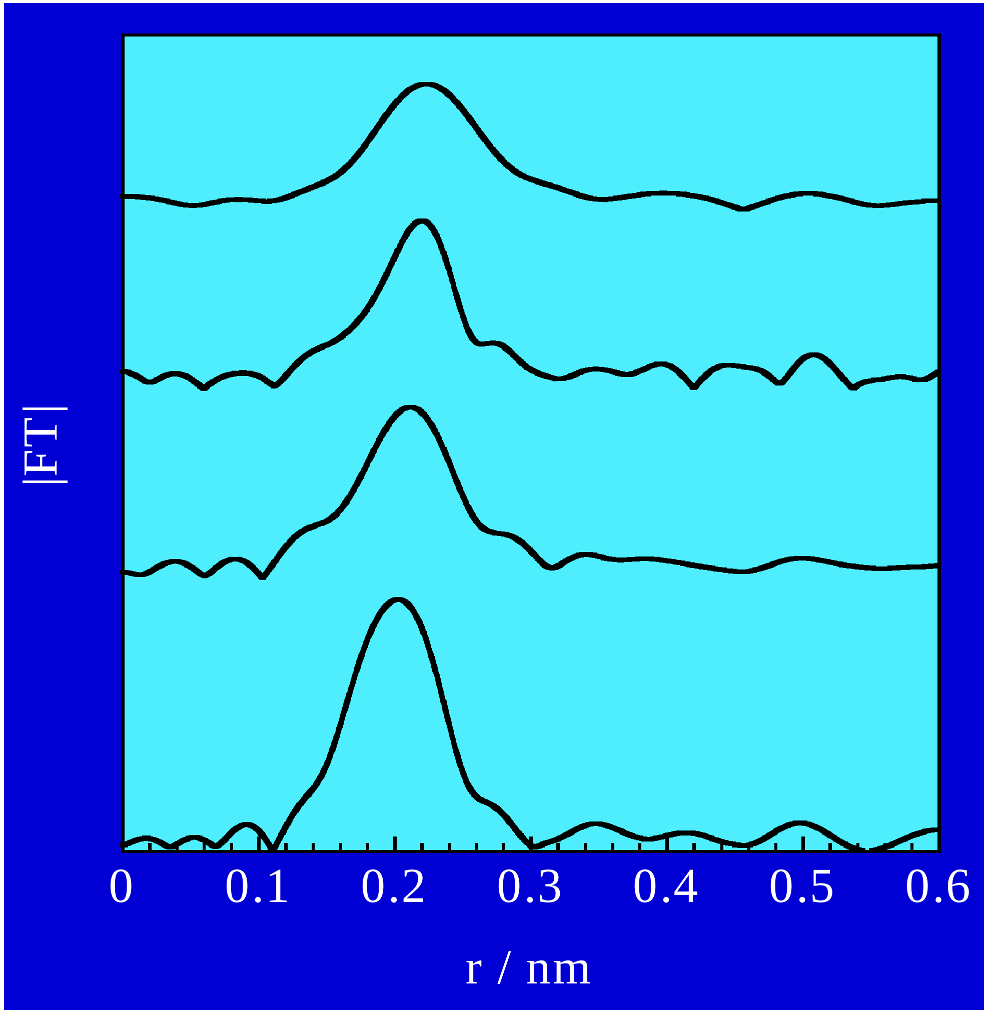


Water vapor adsorption

T.Ohkubo et al. ***J. Am. Chem. Soc.*** **(2002).** ***J. Phys. Chem.*****(2003)**

Radial Structure Function of EXAFS

RSFs of nanosolution around a Rb ion



Bulk RbBr solution (1M)

Nanosol-0.1M

1.1nm slit

Nanosol-1M

concentration

Nanosol-1M

0.7nm slit

Local structure around a Rb ion

Partial Dehydration

Sample	r(Rb-O)/nm	N(Rb-O)	DW factor/10^{-5} nm^2
Nanosol-1M **1.1nm**	0.284	5.3	32.2
Nanosol-0.1M	0.289	4.1	33.3
Nanosol-1M **0.7nm**	0.285	3.9	14.2
Bulk solution (1M)	0.291	6.0	42.6

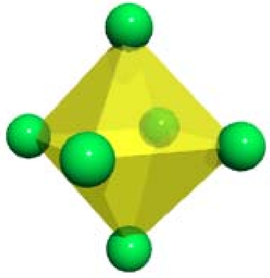
Decrease in H_2O-Rb distance

Dehydration

Ordered water structure

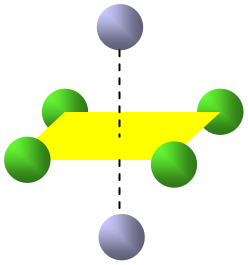
Transition Metal Ions

Transition metal ions under ligand field of a specific symmetry



O_h

Fe ions



D_{4h}

Cu ions

The coordination bond is stronger than an electrostatic hydration

Transition Metal Ions

Local structural parameters of transition metal ions (Fe^{3+}, Co^{2+}, and Cu^{2+}) confined in carbon nanospaces

	Coordination distance (nm)	Coordination number	Debye-Waller factor (nm^2)
Co^{2+} nanosol.	0.206	4.6	0.005
Bulk sol.	0.207	6	0.039
Fe^{3+} nanosol.	0.196	3.1	0.0068
Bulk sol.	0.202	6	0.048
Cu^{2+} nanosol.	0.191	3.2	0.0027
Bulk sol.	0.197	4	0.059

Slight decrease in H_2O-M distance

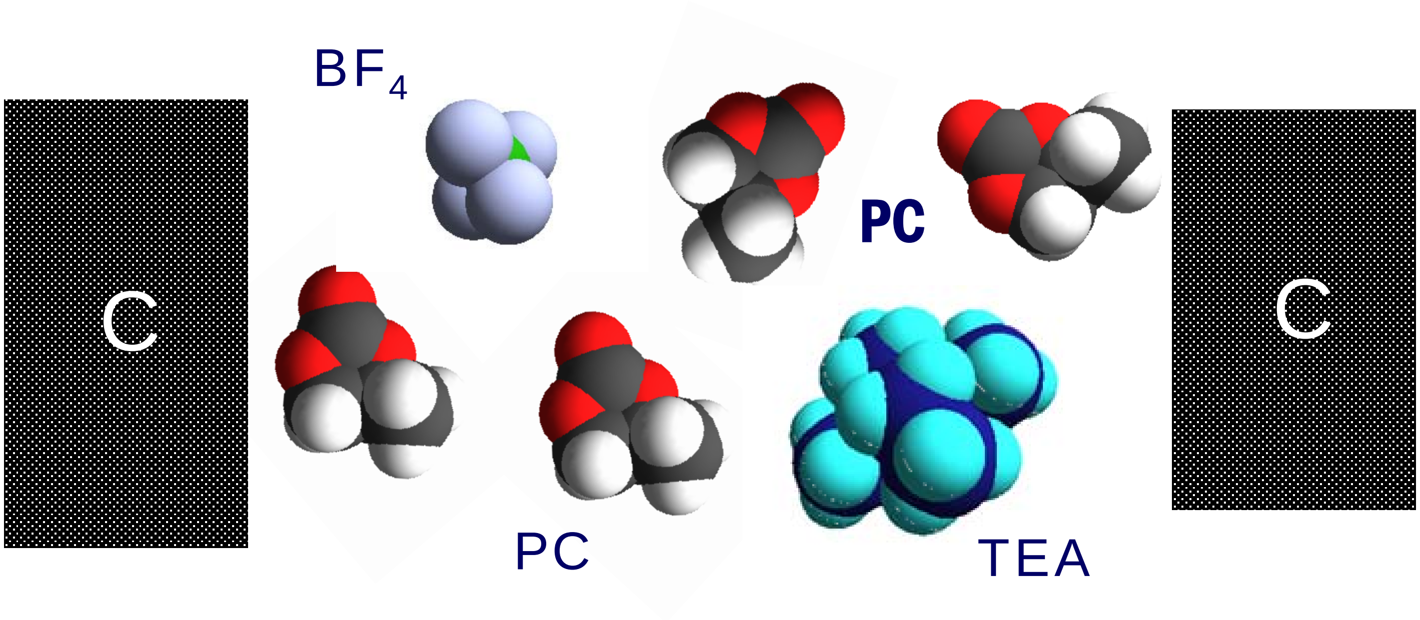
Dehydration

Ordered water structure

In 1.1 nm slit-pores Tao, unpublished

Structure of Organic Electrolyte Solution in Carbon Slit Nanopores

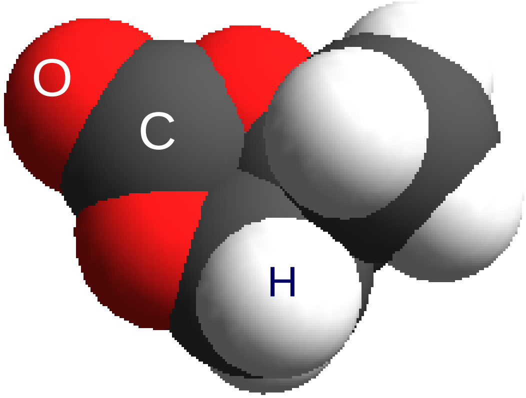
In Pore

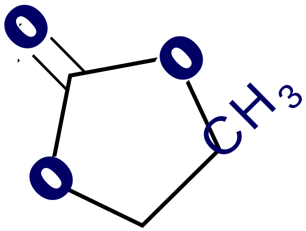


1 nm order

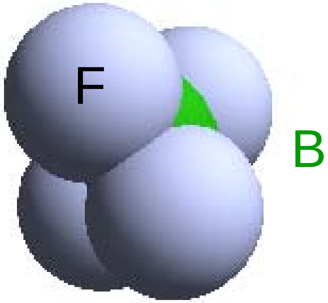
A. Tanaka, T. Iiyama, T. Fujimori, et al, *J. Amer. Chem. Soc.* **132**, 2112（2010）

Tetraethyl Ammonium$^+$ (TEA$^+$) BF$_4^-$ PC Solution

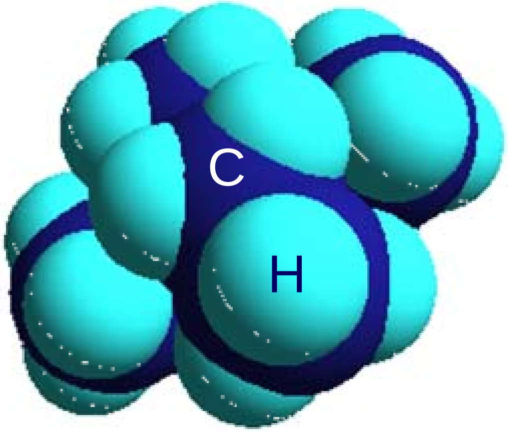




Propylene carbonate（PC）



BF$_4^-$

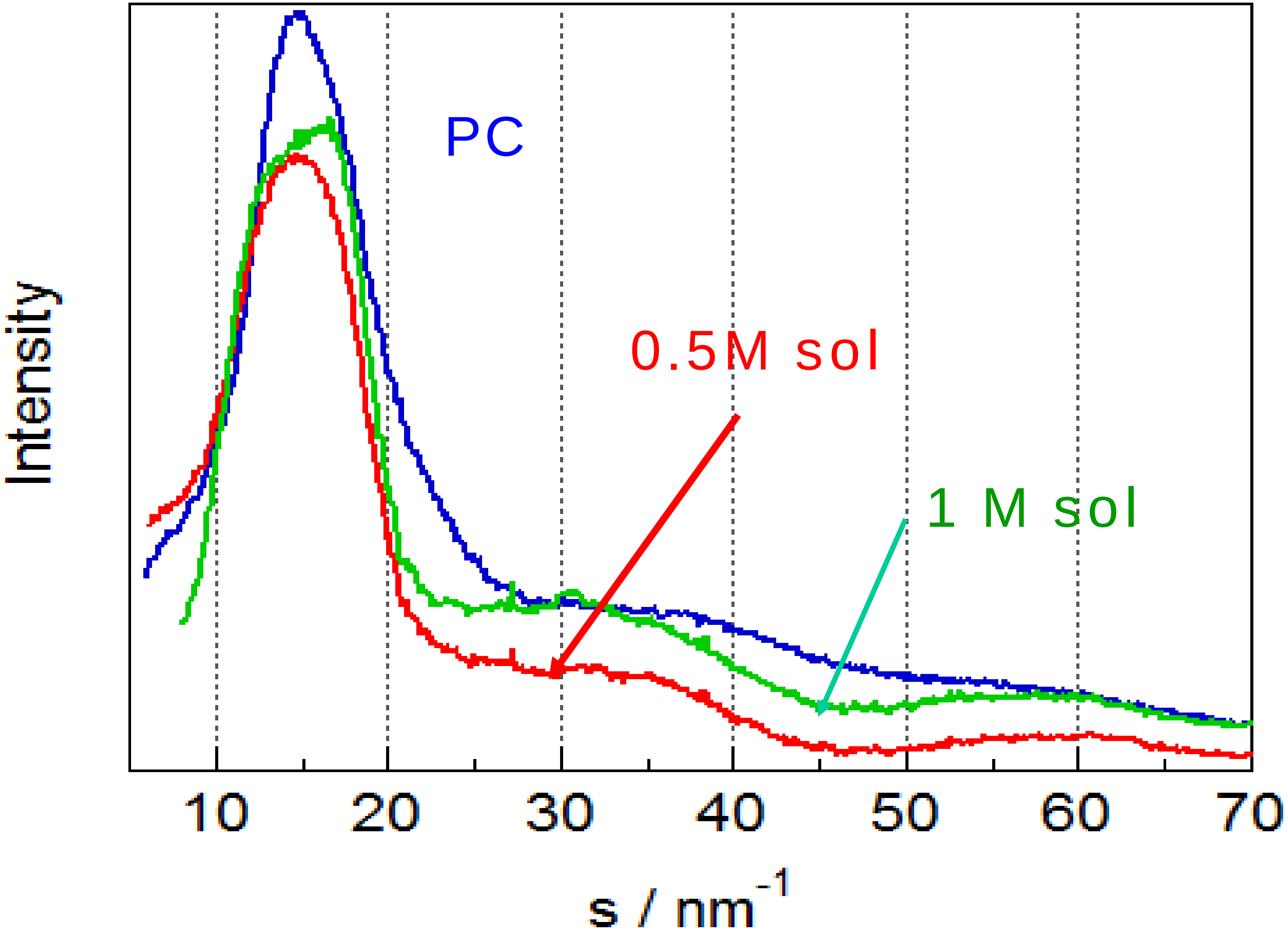


N: Inside

Tetraethyl ammonium（TEA$^+$）

XRD Patterns of Confined Solution

Synchrotron XRD



Correction Procedures for X-Ray Intensity

k **Unit conversion factor**

n_{sld} **Number of atoms in a solid of unit volume**

PGA **Correction factors of polarization, X-ray irradiating volume (geometrical), and X-ray absorption, respectively**

OK

I_{saxs} **Using Debye-Buche equation**

$$I^{s}_{sc} + I^{a}_{sc}$$

Scattering from admolecules

Scattering intensity of a porous solid in vacuo gives both terms

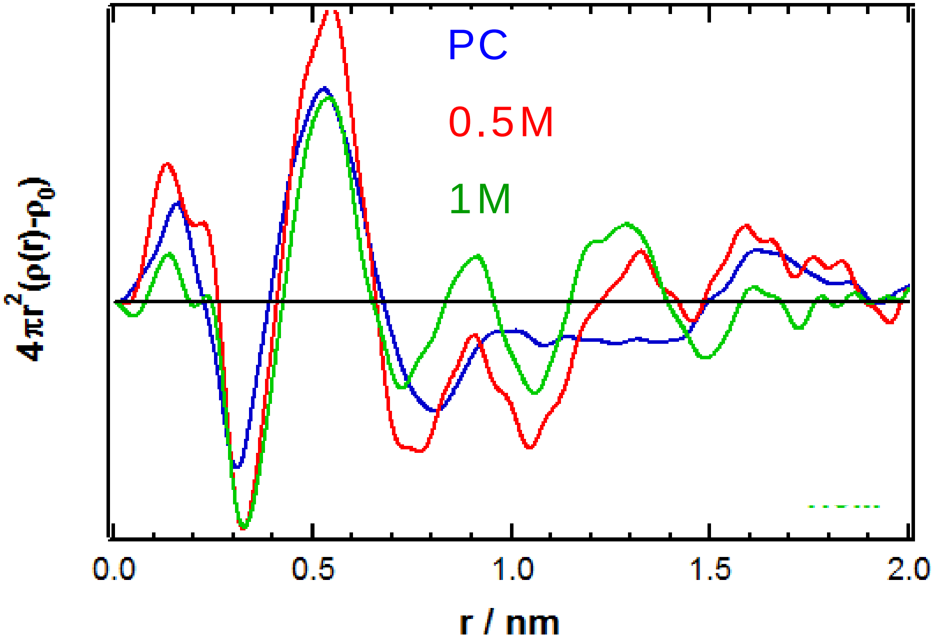
$$\underset{\text{Solid-solid}}{I^{s-s}_{if}} + \underbrace{\underset{\text{admol-admol}}{I^{a-a}_{if}} + \underset{\text{solid-mol}}{I^{s-a}_{if}}}$$

Evaluated by the simulated molecular configuration of admolecules in the model

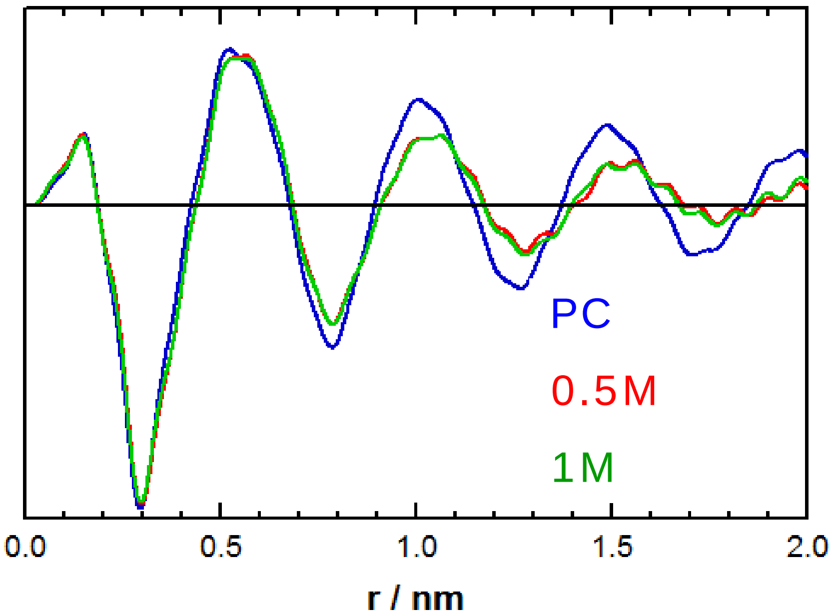
Iteration

Radial Distribution Functions of Confined and Bulk solutions

Confined solution

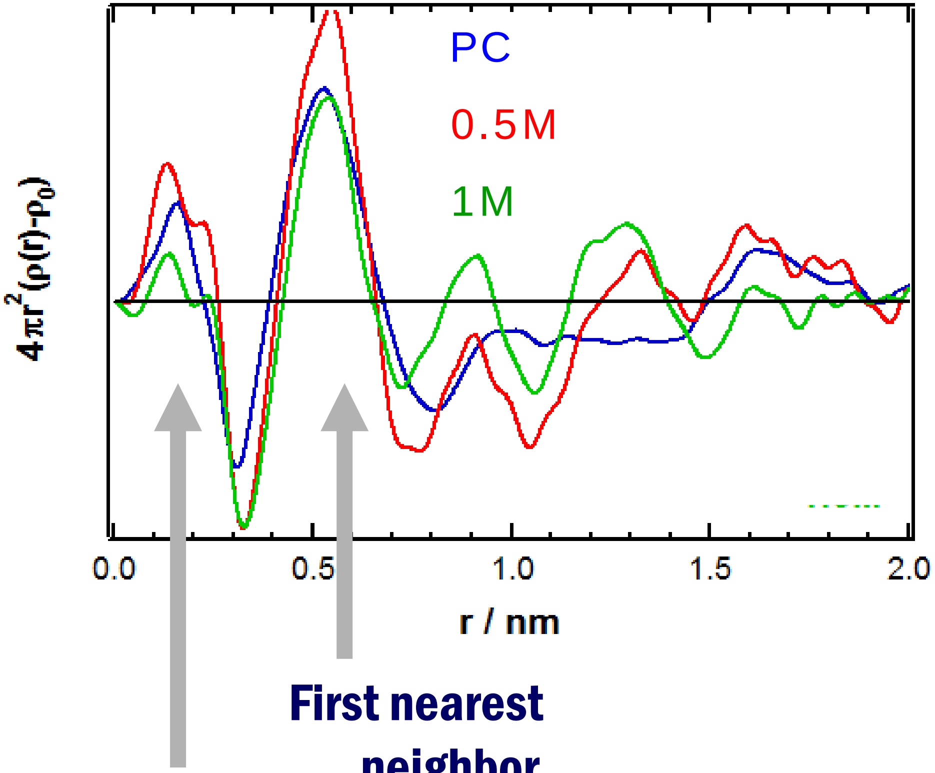


Bulk solution



Radial Distribution Functions of Confined and Bulk solution

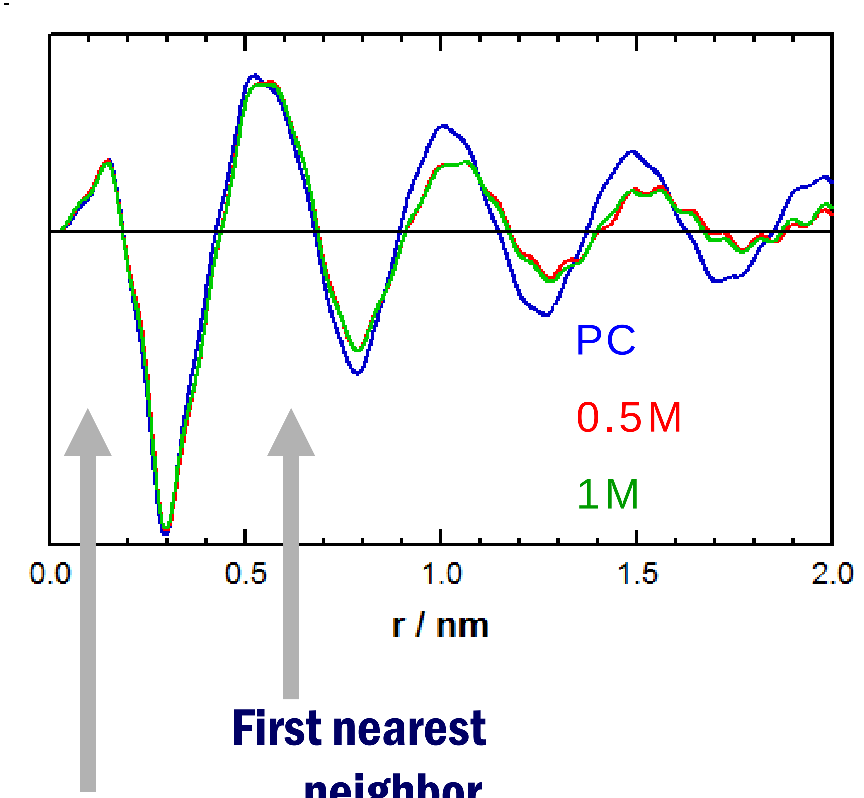
Confined solution



First nearest neighbor

Intra-molecule

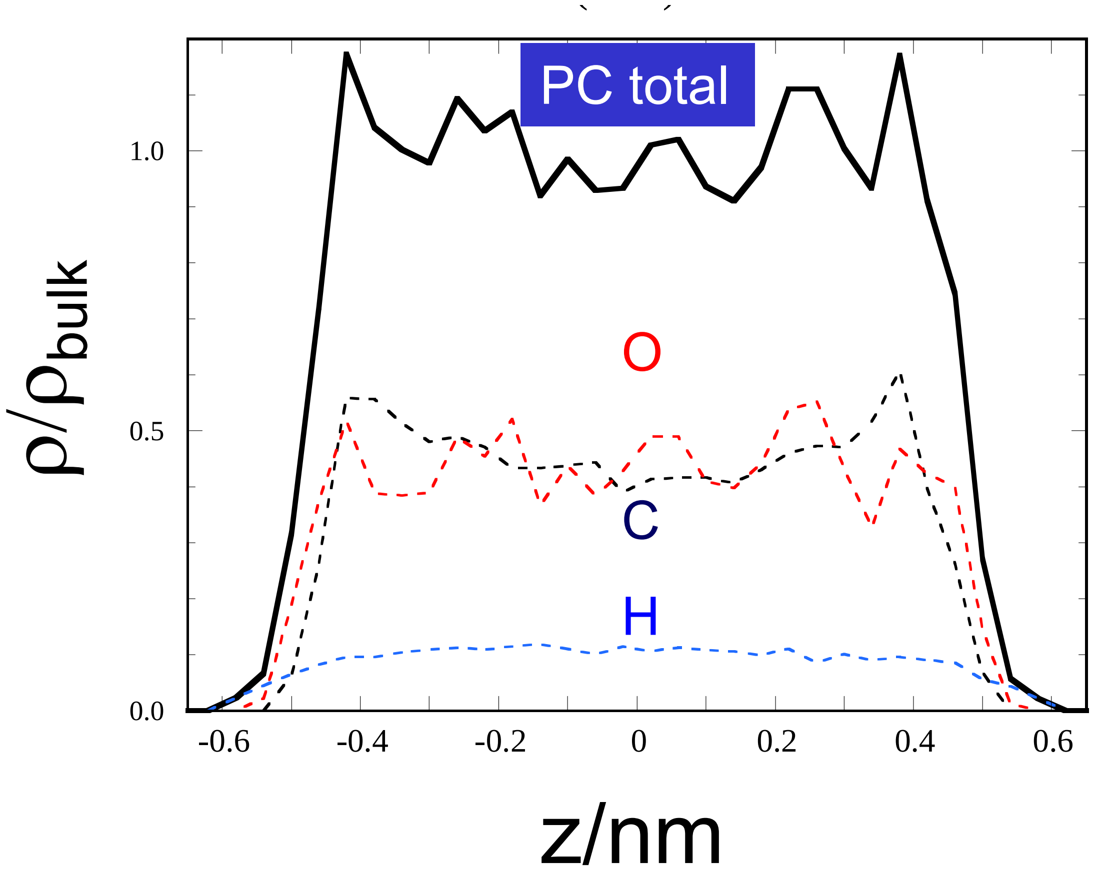
Bulk liquid

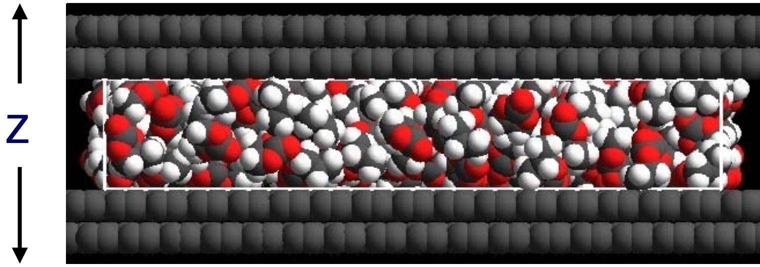


First nearest neighbor

Intra-molecule

Vertical Distribution of PC Molecules in Slit Pore



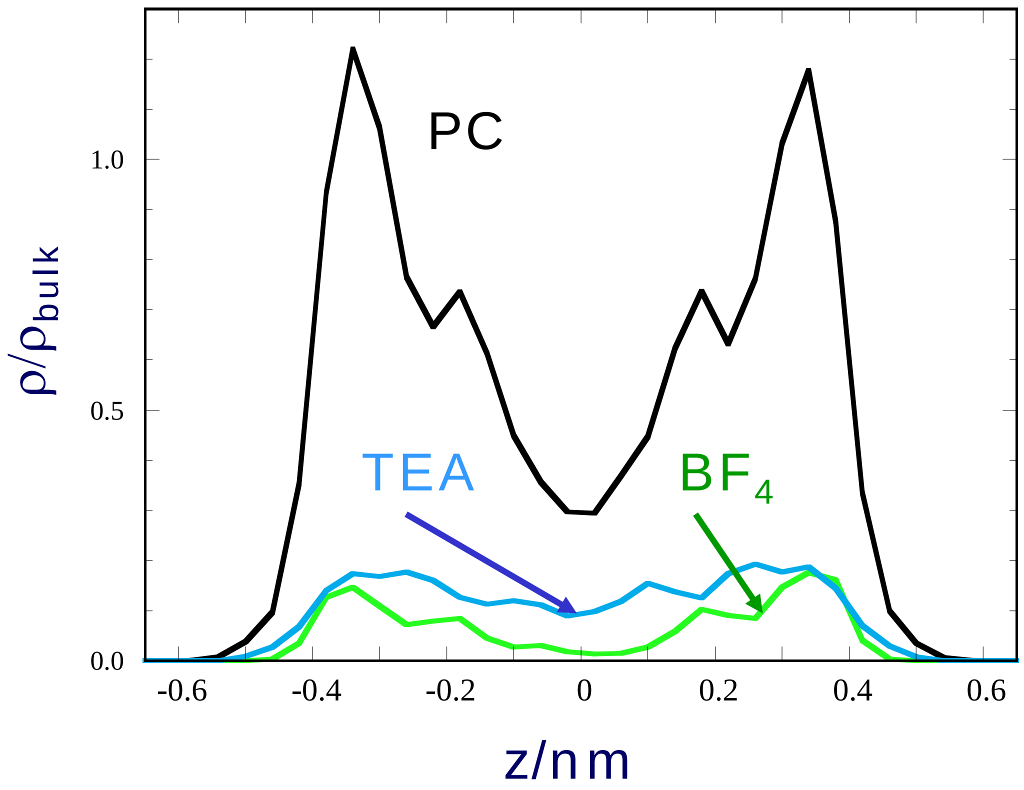


Uniform distribution

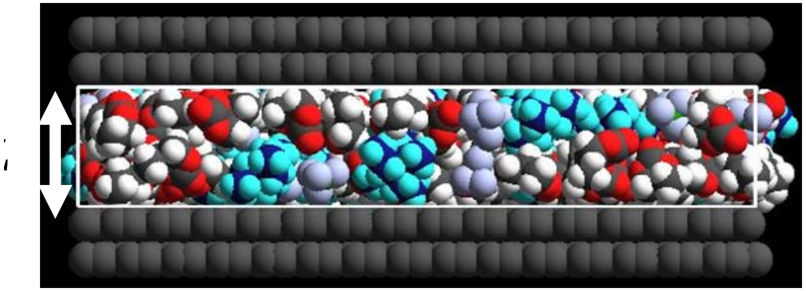
along the perpendicular

direction

Vertical Distribution of PC Molecules in Slit Pore in the Presence of Salt

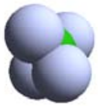


Side view

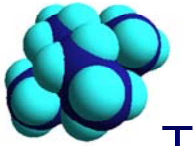


PC molecules are more distributed near the pore walls

: PC



: BF_4

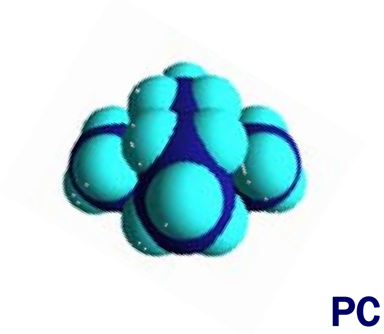


: Et_4N

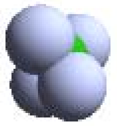
TEA

How about Structure in Molecular Size-Pore ?

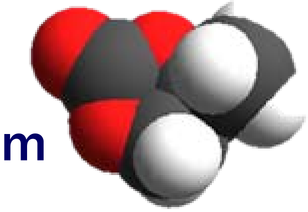
$(CH_3CH_2)_4N^+$
0.67 nm



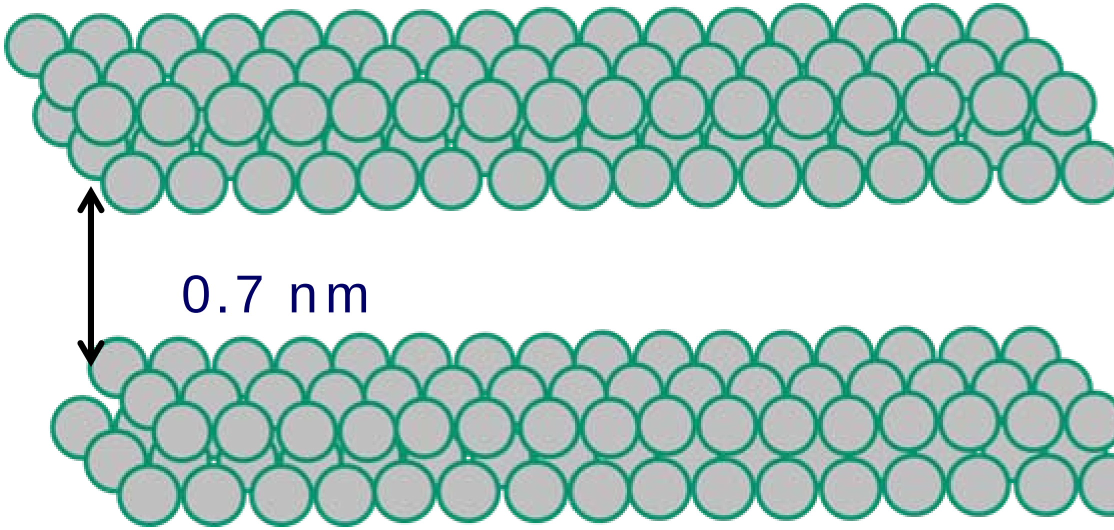
BF_4^-
0.48 nm



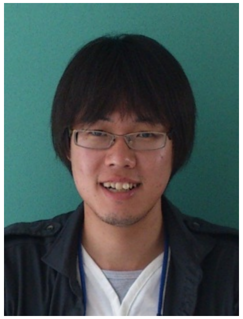
PC



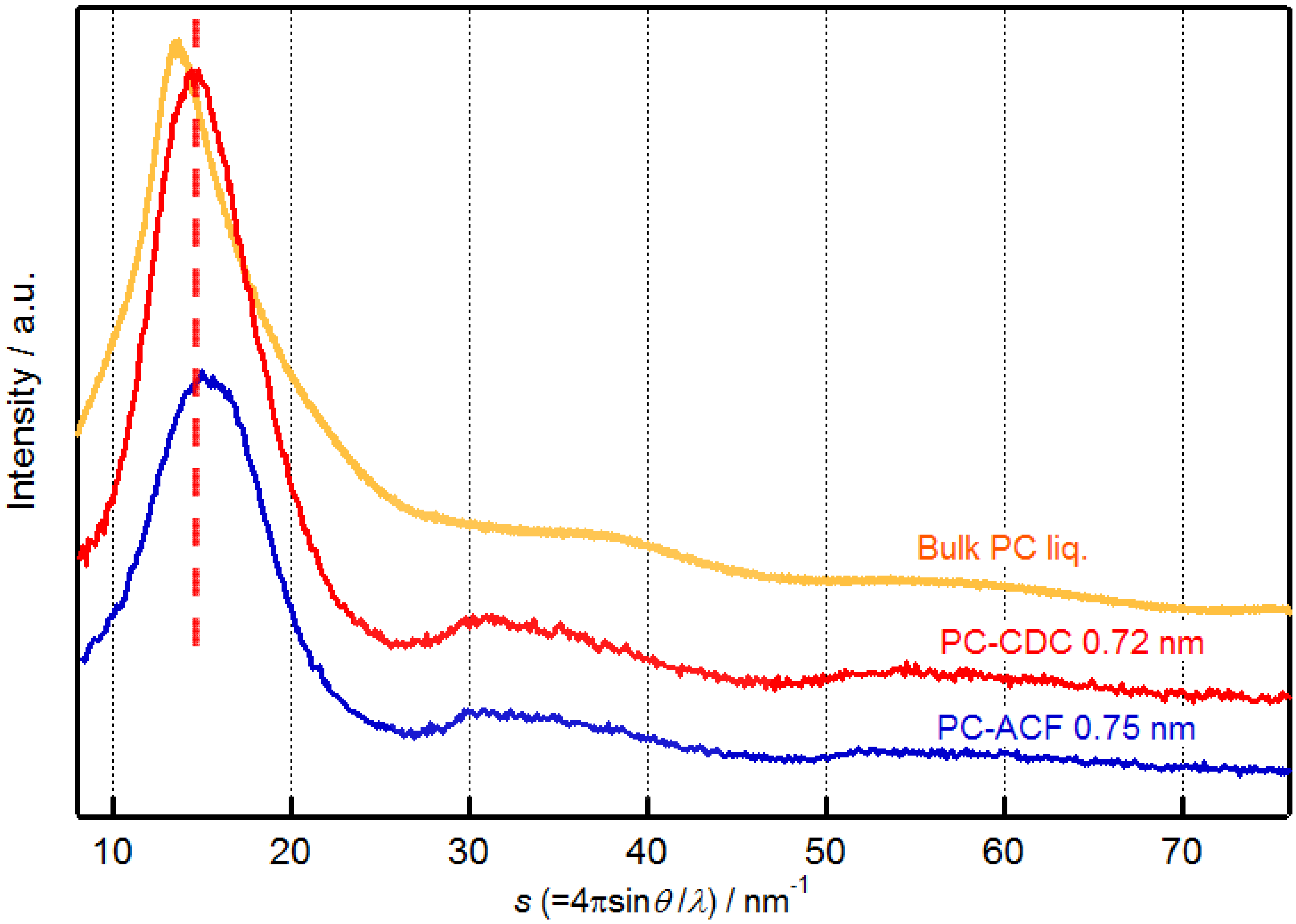
0.6 – 0.8 nm



Fukano, Fujimori, Futamura
Simon, Gogotsi, et al, J. Phys. Chem. C
in revision

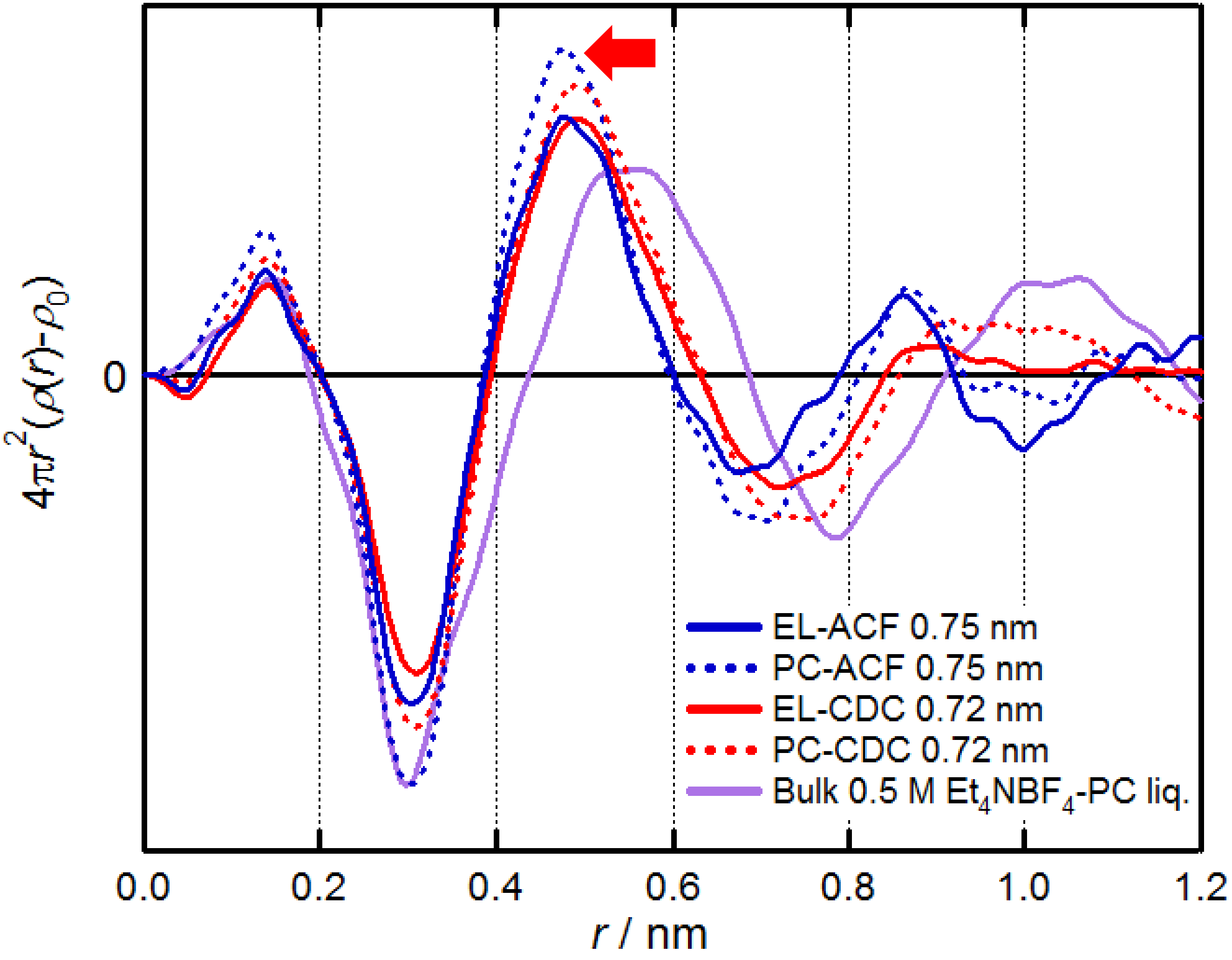


Corrected XRD Patterns of PC in Nanopores



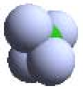
→ Structural change of PC confined in ultramicropores

ERDFs of Ionic Solution in Pores (0.7 nm)

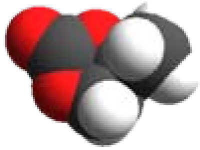


$(CH_3CH_2)_4N^+$
0.67 nm

BF_4^-
0.48 nm



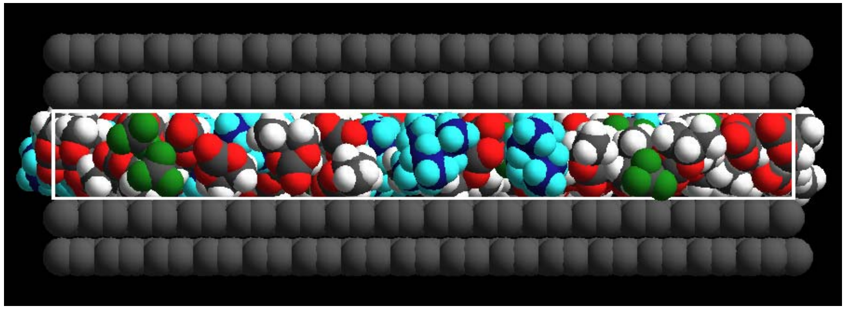
PC



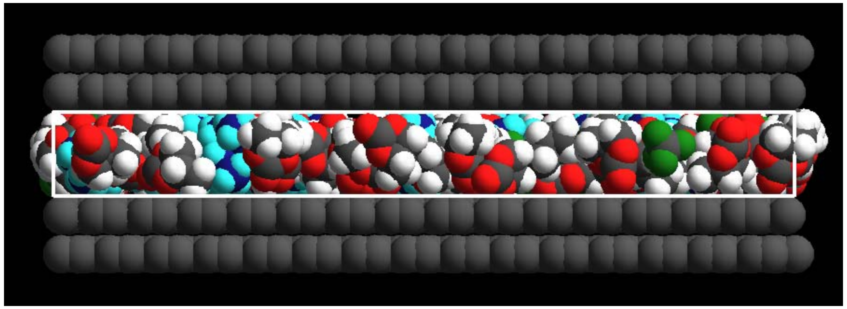
0.6～0.8 nm

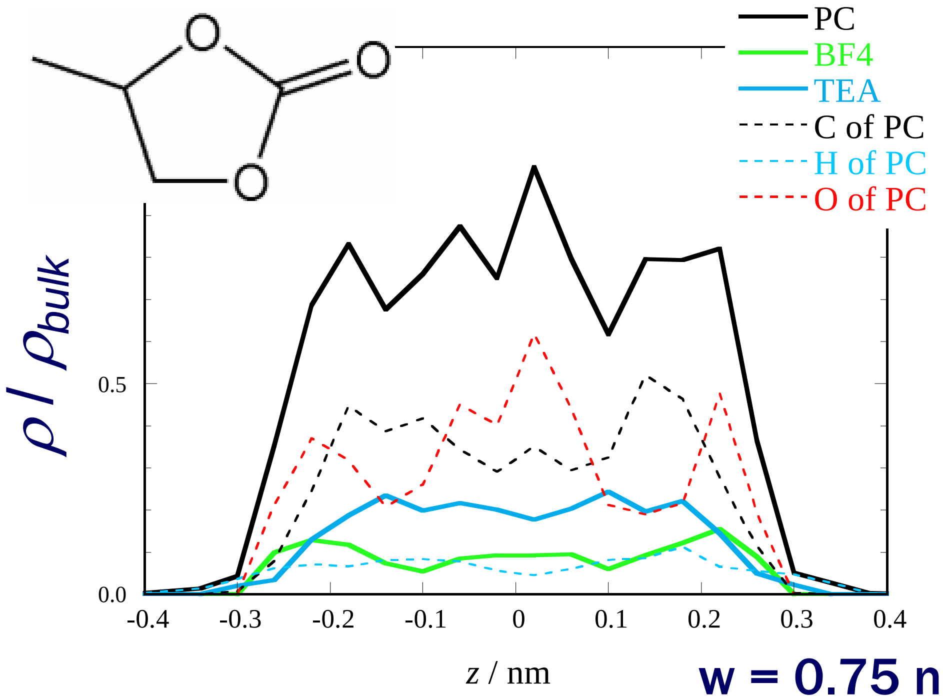
Structure of Electrolyte Solution Confined in Small Micropores by RMC Simulation

EL-ACF 0.75 nm

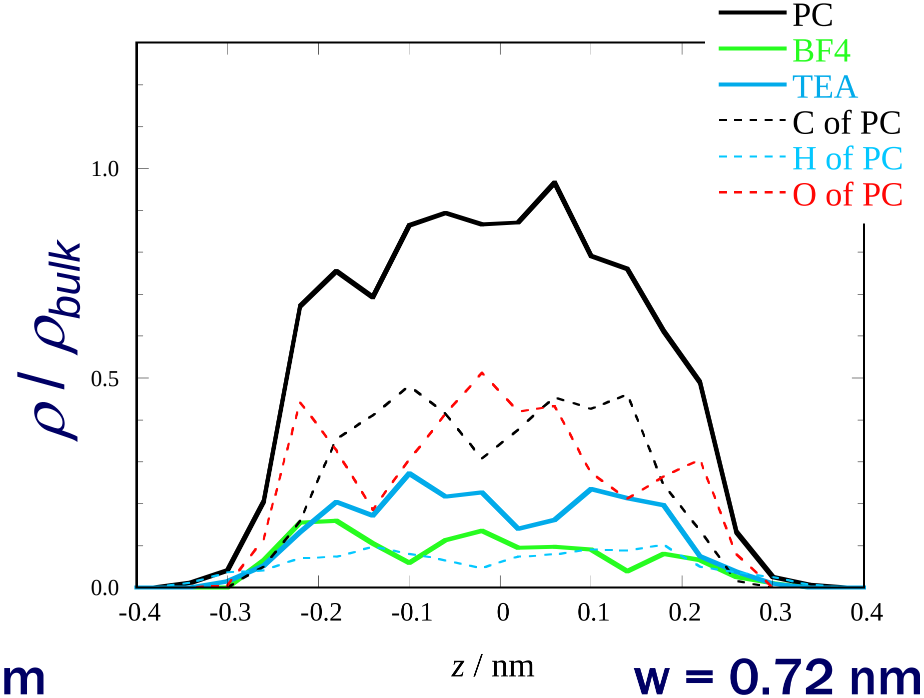


EL-CDC 0.72 nm





w = 0.75 nm



w = 0.72 nm

Distribution of PC molecules and electrolytes along the pore width

Future Challenges

Clean Energy

- CH_4 storage
- H_2 storage
- Supercapacitor
- (electricity storage)
- Air separation O_2, N_2
- Methane hydrate
- CO_2 separation
- Heat pump
- Nuclear fusion D_2

Adsorption

NanoScience

Resources

- Li ions
- Novel metals

Food Water

Medical Tech.

water channel

Environment Control

- Air
- Water
- Natural environ.

Acknowledgements

All Senior and Graduate Students of Molecular Chemistry
Chiba University

All Postdocrtal fellows at Chiba University
and Shinshu University

All colleagues at Chiba University
Prof. H. Kanoh (Chiba U) Dr. H. Tanaka(Kyoto U) Dr. T. Ohba (Chiba U)
Prof.S. Ozeki (Shinshu U, Sci.) Assoc. Prof. T. Suzuki(Shinshu U, Eng.)

Collaborators in Japan
Prof. S. Iijima, Dr. M. Yudasaka, Dr. K. Hata
Prof. M. Endo, His colleagues

Overseas Collaborators
Prof. F. Rodriguez-Reinoso, Prof. K. E. Gubbins, Dr. L. Abrams,
Prof. W.A. Steele, Prof. P. Simon, Prof. L. Radovic
Dr. D. Nicholson, Prof. D. Tomanek others

Supports by Industry Osaka gas, Fuji-chemical, ------

Adsorption should
be in full bloom
for world in future