27 April 2007　研究室セミナー

Ru(0001)表面およびCO/Ru(0001)表面における ナノクリスタル氷の成長ダイナミクス

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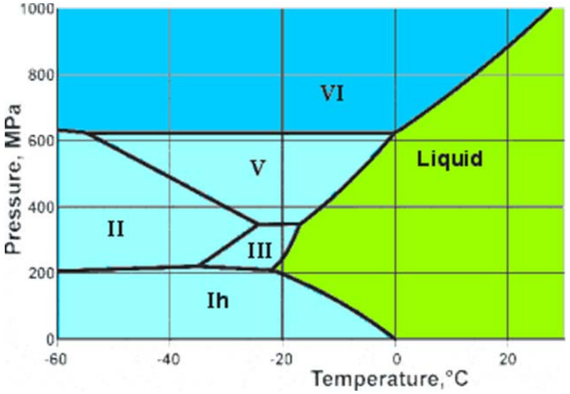
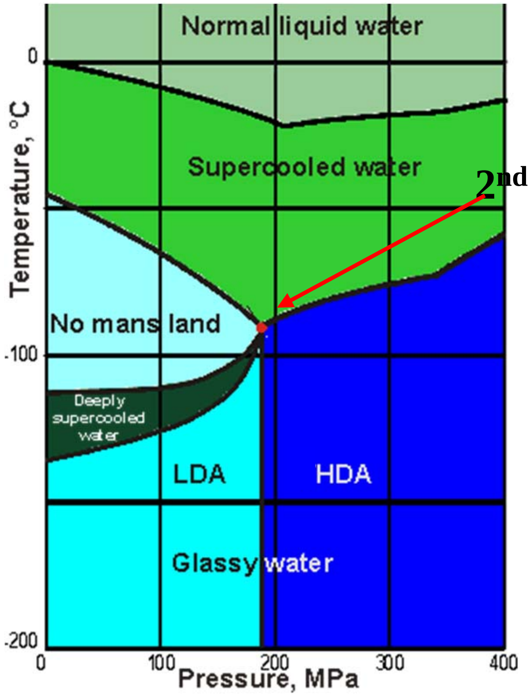
加藤浩之　（独立行政法人理化学研究所 川合表面化学研究室 先任研究員）
Mischa Bonn（オランダ国ライデン大学教授、FOMディレクター）

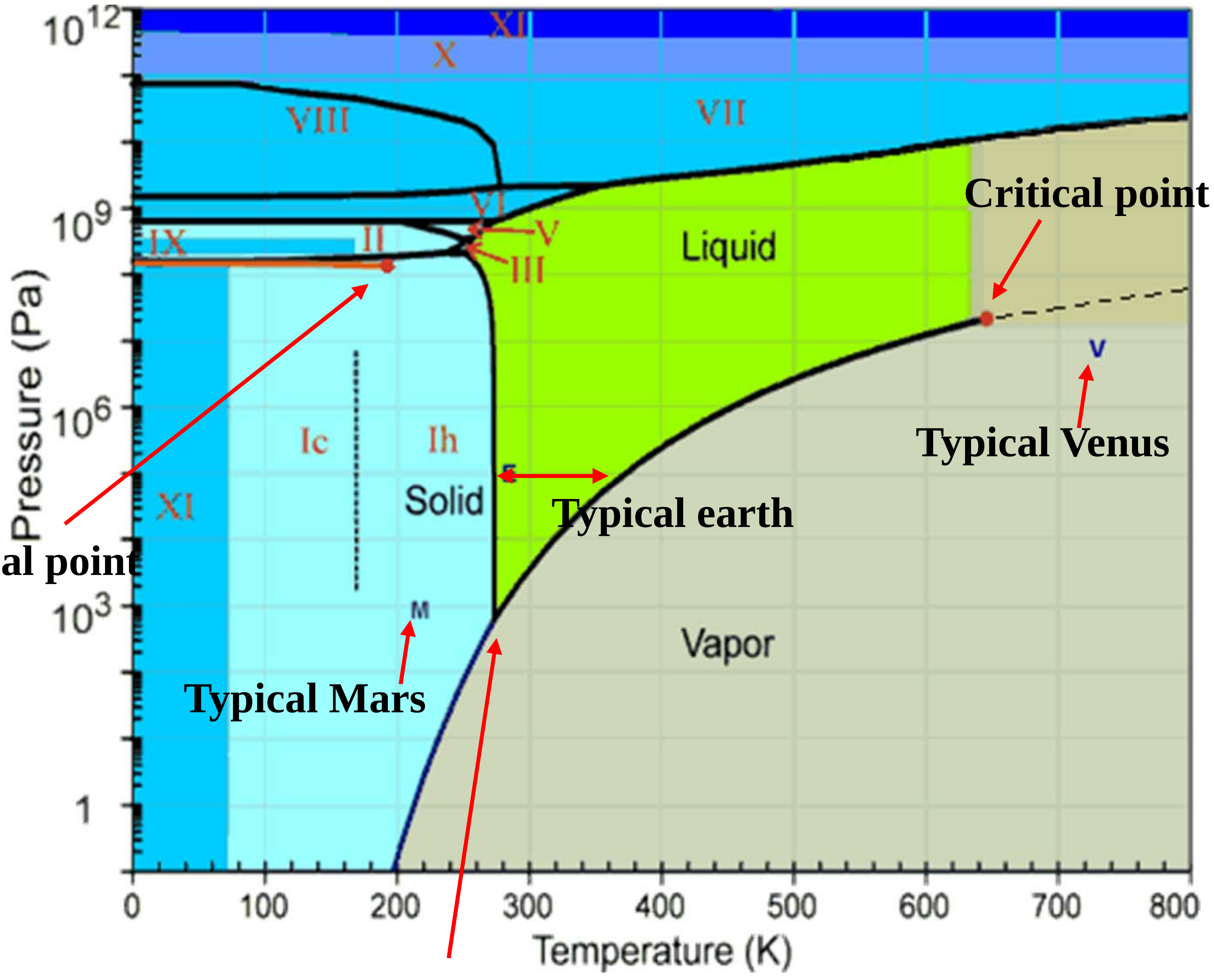
T. Kondo, et al., Surf. Sci. 600 (2006) 3570-3574.
T. Kondo, et al., Chem. Phys. Lett. 448 (2007) 121-126.
T. Kondo, et al., J. Chem. Phys. 126 (2007) 181103, 1-5.
T. Kondo, et al., J. Chem. Phys. 127 (2007) 094703, 1-14.

研究背景

Phase diagram of water







Critical point

Typical Venus

Typical earth

2nd Critical point

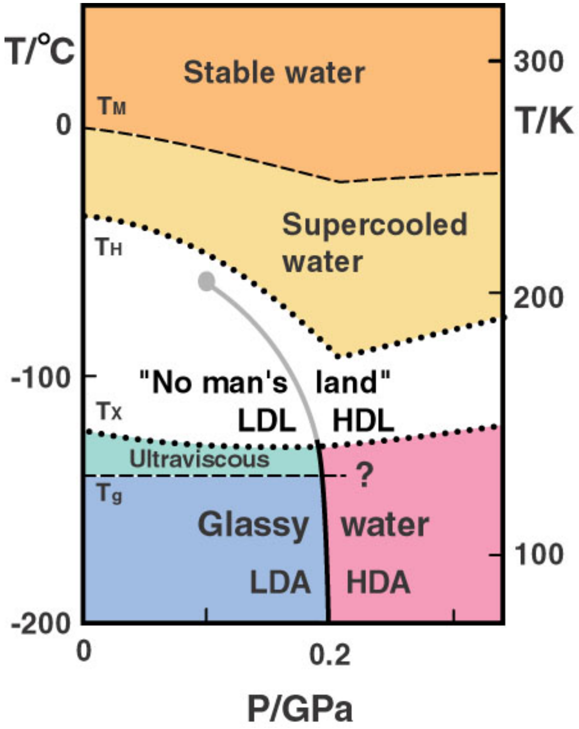
Typical Mars

triple point: 273.16 K, 610.6 Pa

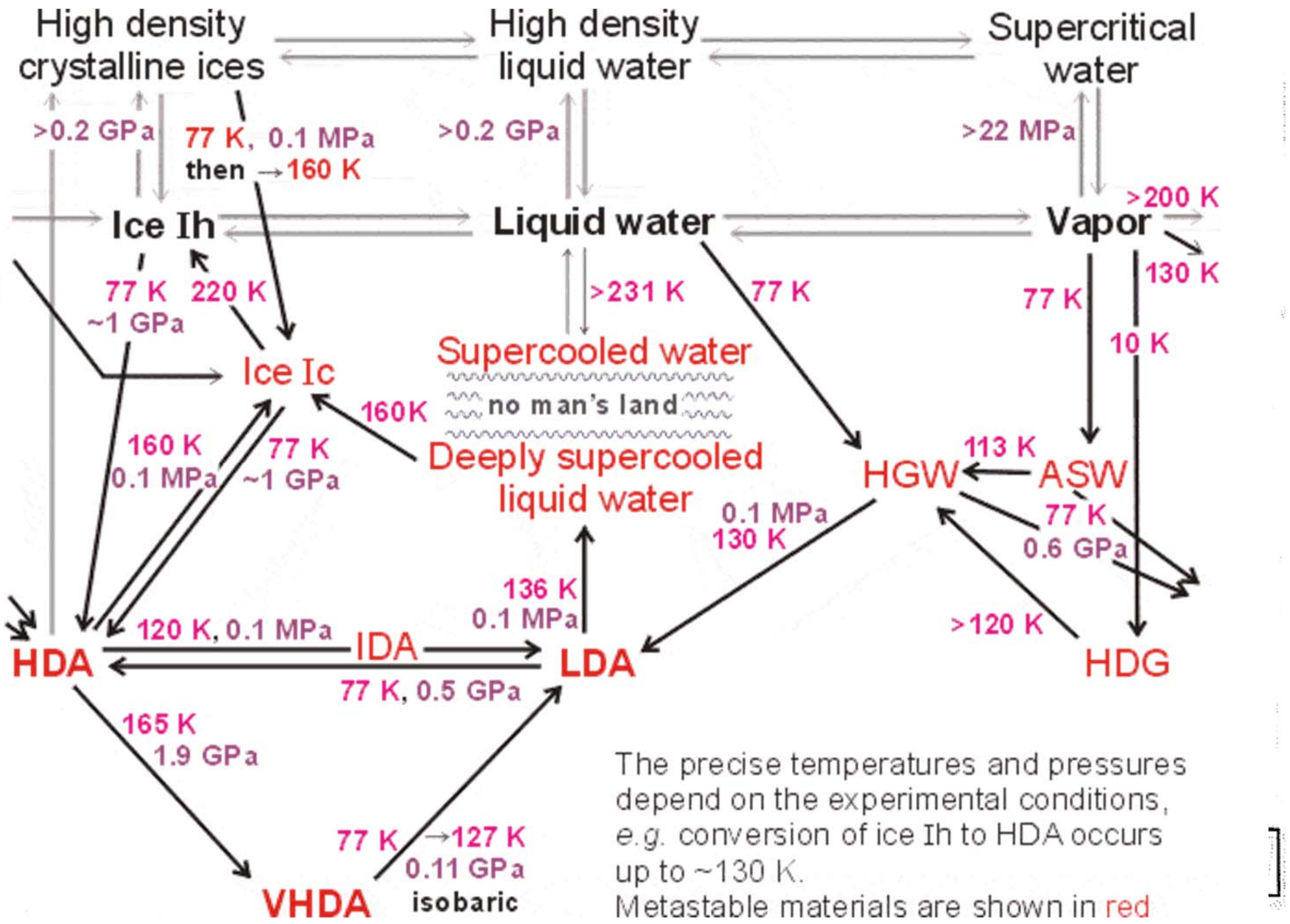
M.Chaplin, “*Water structure and behavior*”
http://www.lsbu.ac.uk/water/

研究背景

Metastable phase: Supercooled-water and glassy-water



O. Mishima, Nature 396 (1998) 329
O. Mishima, 高圧力の科学と技術, 13 (2003) 165.



The precise temperatures and pressures depend on the experimental conditions, *e.g.* conversion of ice Ih to HDA occurs up to ~130 K.
Metastable materials are shown in red

M.Chaplin,*"Water structure and behavior"*

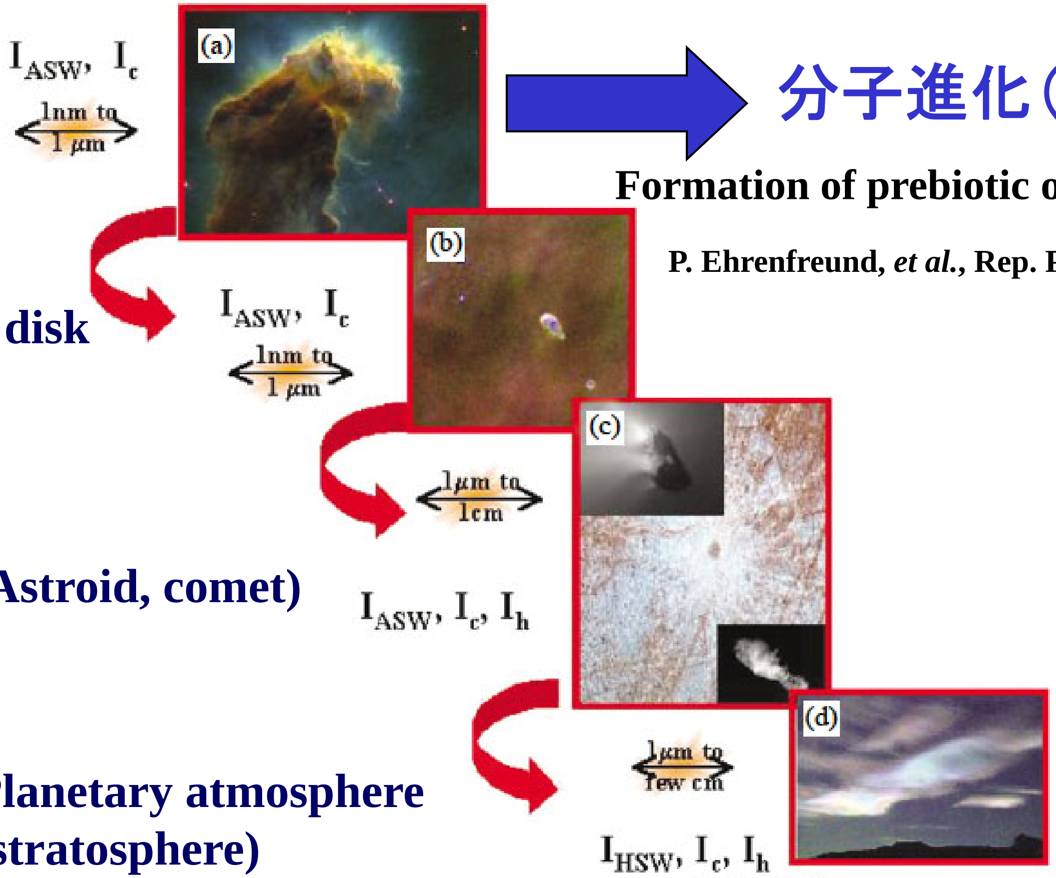
HGW : hyperquenched glassy water (if rapidly cooled)

I. Kohl, et al., Phys. Chem. Chem. Phys. 7 (2005) 3210.
V. Velikov, *et al*., Science 294 (2001) 2335.

研究背景

Both amorphous solid water(ASW) and crystalline ice (CI) are observed.

P. Ehrenfreund et al. / Planetary and Space Science 51 (2003) 473–494



Interstellar medium
(Cosmic dust clouds)

分子進化（生命の起源）

Formation of prebiotic organic molecule

P. Ehrenfreund, *et al.*, Rep. Prog. Phys. 65 (2002) 1427.

Proto planetary disk

Planetesim (Astroid, comet)

Planetary atmosphere
(stratosphere)

基礎科学的に氷表面での化学反応を明らかにする：**Well-defined**な氷表面の作成が必要

アモルファス氷の結晶化や氷表面のモフォロジーの理解が重要！

Background

アモルファス氷の結晶化

Vapor

Dosing on solid at <~120K, by <2nm/s

ASW : amorphous solid water

C. A. Angell, Ann. Rev. Phys. Chem. 55 (2004) 559.
T. Loerting, *et al*. J. Phys.: Cond. Matt. 18 (2006) R919.

ex) LDA (10~130K, UHV)

Heat

?

Supercooled water

P. G. Debenedetti, Nature, 410 (2001) 259.
P. G. Debenedetti, J. Phys.: Cond. Matt. 15 (2003) R1669.

Heat

Crystalline ice: I_c (cubic) **$0.93\ g\ cm^{-3}$**

Heat

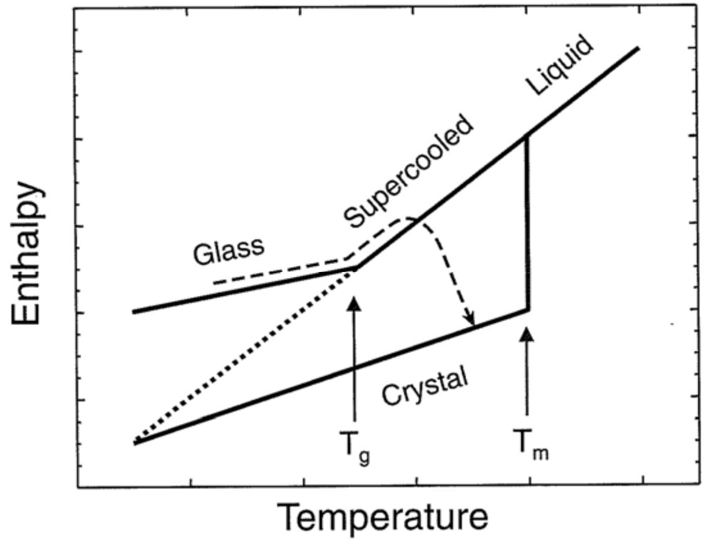
Crystalline ice: I_h (hexagonal)

LDA : low density amorphous ice
($0.94\ g\ cm^{-3}$)
O. Mishima, *et al*. Nature 396 (1998) 329.

HDG : high density glassy water
($1.1\ g\ cm^{-3}$)
A. H. Narten, *et al*., J. Chem. Phys. 64 (1976) 1106.
M. E. Palumbo, J. Phys.: Conf. Ser. 6 (2005) 211.

HDA : high density amorphous ice
($1.17\ g\ cm^{-3}$ at 0.1 Mpa, many dangling bonds)
O. Mishima, *et al*. Nature 396 (1998) 329.

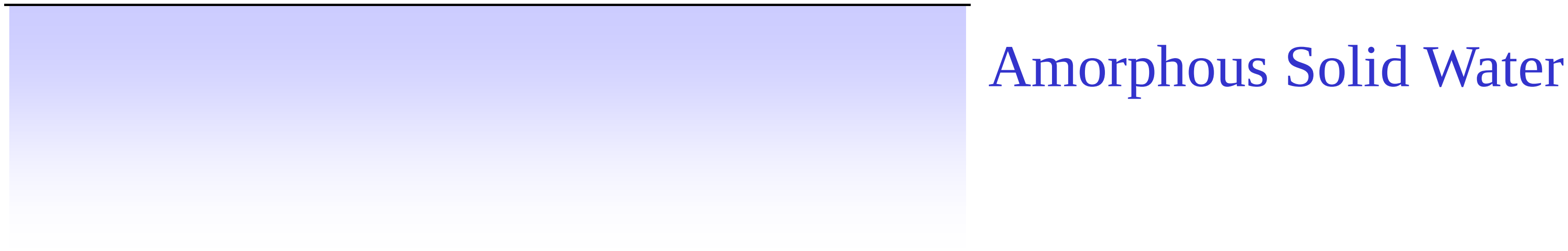
VHDA : very high density amorphous ice
($1.26\ g\ cm^{-3}$ at 0.1 Mpa, many dangling bonds)
T. Loerting, *et al*. Phys. Chem. Chem. Phys. 3 (2001) 5355.



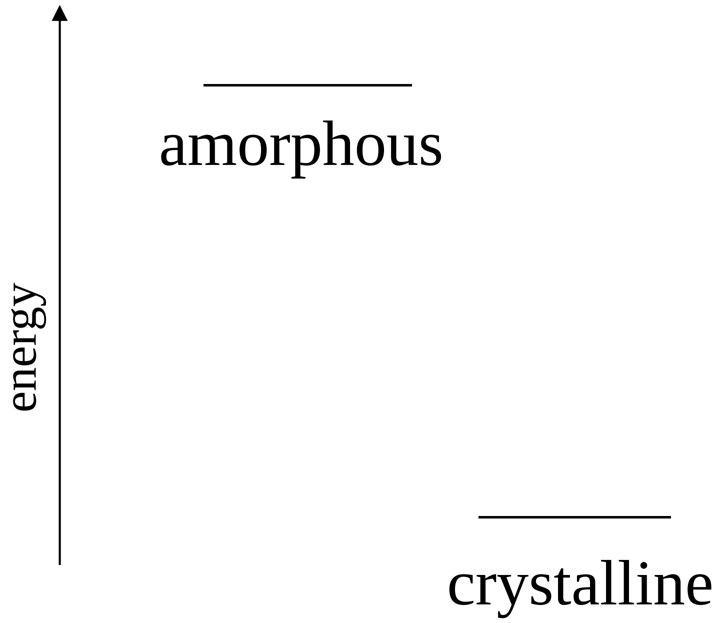
R. S. Smith, *et al*。*"water in confining geometries"* (2003) Edited by V.Buch, Springer

研究背景　　結晶化のメカニズム

結晶化はどこから起こるのか(表面？バルク？界面)?



Amorphous Solid Water



energy

amorphous

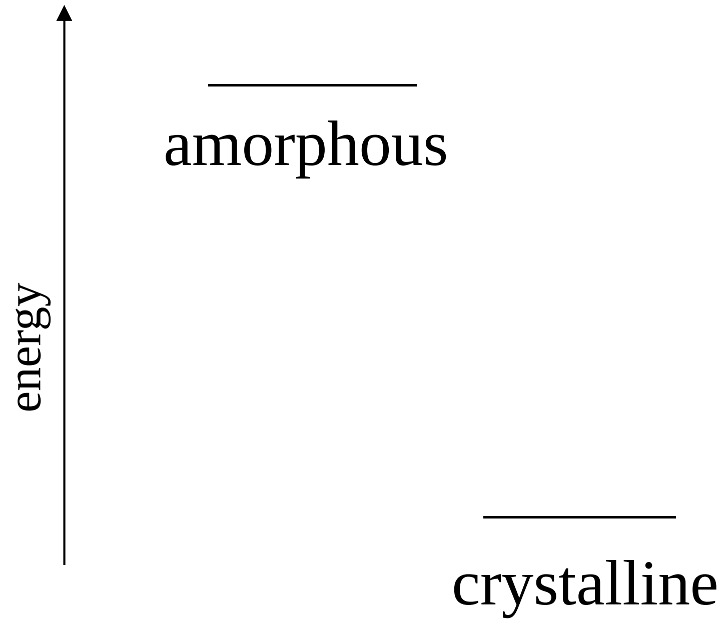
crystalline

結晶化のメカニズム

結晶化はどこから起こるのか（表面？バルク？界面）?

Amorphous Solid Water

ρ : the material density
μ : the chemical potential
γ: the surface tension between the phase



Classical nucleation theory

Change in free energy when a nucleus forms:

$$\Delta G(r) = \frac{4}{3}\pi r^3 \rho(\mu_{cryst} - \mu_{amorph}) + 4\pi r^2 \gamma$$

Bulk term negative

Surface term positive

Barrier at: $\frac{\partial \Delta G(r)}{\partial r} = 0$; Barrier height: $\Delta G(r^*)$

Nucleus size at maximum: $r^* = -\frac{2\gamma}{\rho(\mu_{cryst} - \mu_{amorph})}$

e.g. : Backus *et al.*, J. Chem. Phys. **121,** 1038 (2004)

研究背景

結晶化のメカニズム

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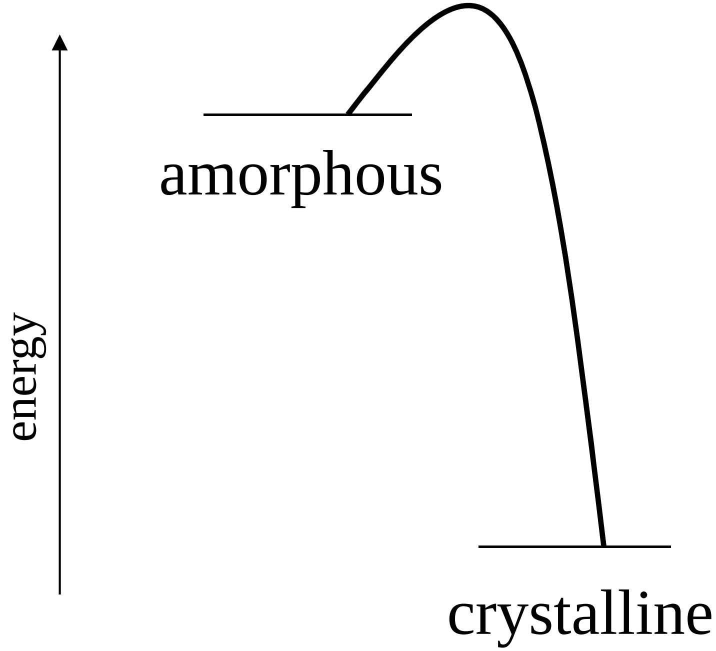

Classical nucleation theory

Change in free energy when a nucleus forms:

$$\Delta G(r) = \frac{4}{3}\pi r^3 \rho(\mu_{cryst} - \mu_{amorph}) + 4\pi r^2 \gamma_{CI/ASW}$$

Bulk term
negative

Surface term
positive

Barrier at: $\frac{\partial \Delta G(r)}{\partial r} = 0$; Barrier height: $\Delta G(r^*)$

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研究背景　　結晶化のメカニズム

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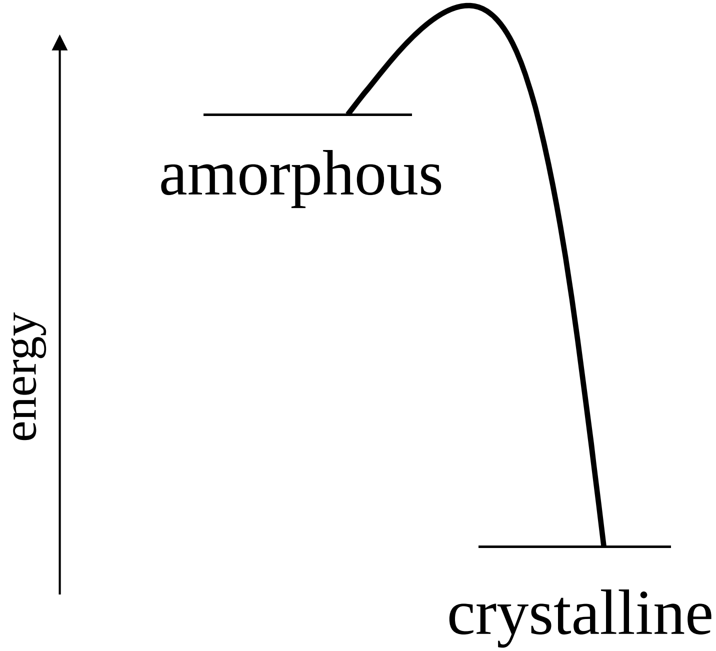

Classical nucleation theory

Change in free energy when a nucleus forms:

$$\Delta G(r) = \frac{1}{2}\left(\frac{4}{3}\pi r^3 \rho(\mu_{cryst} - \mu_{amorph}) + 4\pi r^2 \gamma_{CI/ASW} \right)$$

Bulk term
negative

Surface term
positive

e.g. : Backus *et al.*, J. Chem. Phys. **121,** 1038 (2004)

研究背景　　結晶化のメカニズム

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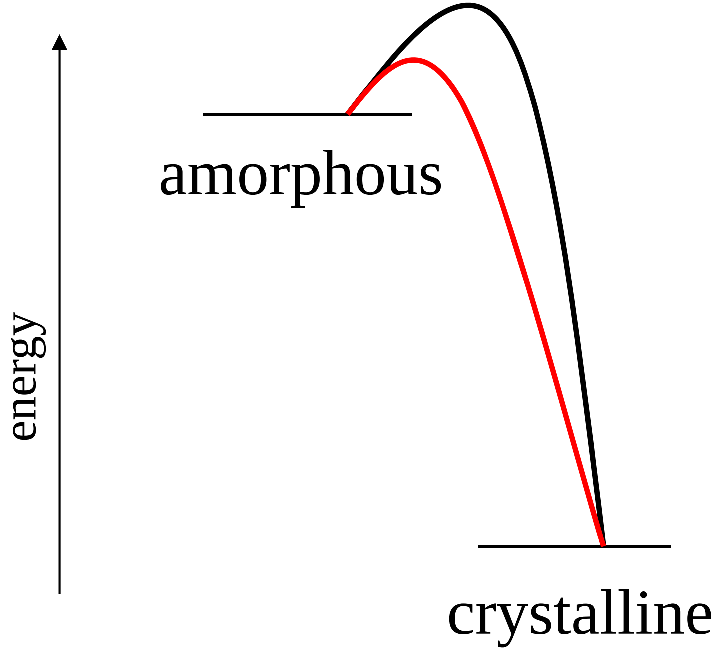

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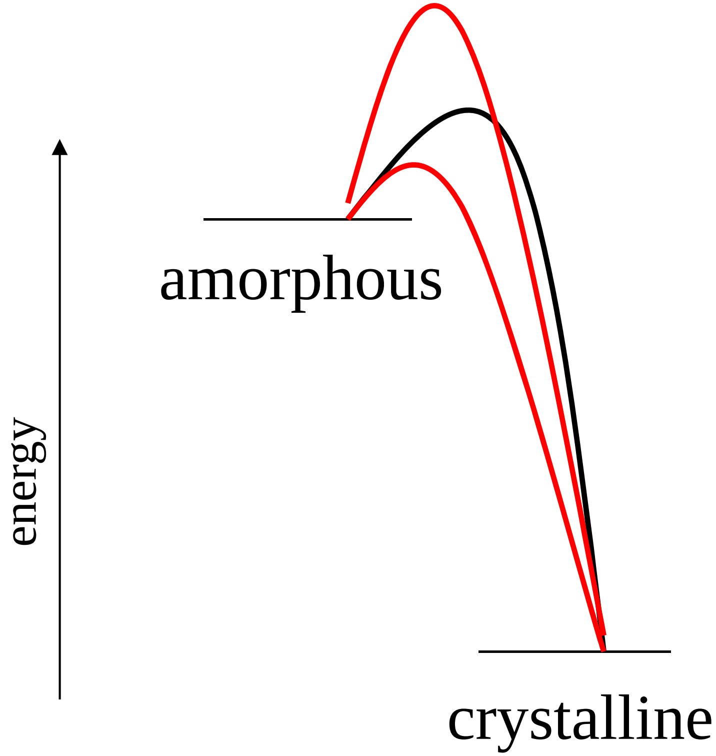


Classical nucleation theory

Change in free energy when a nucleus forms:

$$\Delta G(r) = \frac{1}{2}\left(\frac{4}{3}\pi r^3 \rho(\mu_{cryst} - \mu_{amorph}) + 4\pi r^2 \gamma_{CI/ASW}\right) + \pi r^2 (\gamma_{CI/air} - \gamma_{ASW/air}{}^{''}) + f(r)$$

Bulk term negative

Surface terms

Line tension

Additional terms affect for positive/negative??

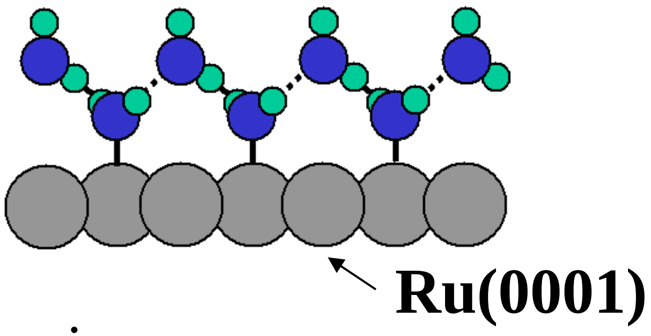
バルク、表面のどちらからもありうる

e.g. : Backus *et al.*, J. Chem. Phys. **121,** 1038 (2004)

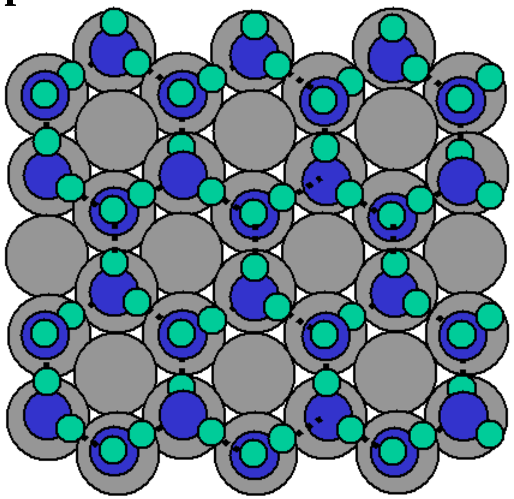
研究背景　　結晶化のメカニズム

結晶化はどこから起こるのか(表面？バルク？界面)?

Side-view　$(\sqrt{3}\times\sqrt{3})R30^{\circ}$



Top-view



D. L. Doering *et al.*,Surf. Sci. **123,** 305 (1982).

氷の結晶をそのまま乗せた構造

Modified Bernal-Fowler-Pauling rules に従う:

(1) water is bound to the surface through oxygen lone pair orbital
(2) tetrahedral bonding configuration is maintained for water
(3) O has two H attached at 0.96 Å with an H-O-H bond angle of 105°
(4) there is one hydrogen atom on each O-O axis

D. L. Doering *et al.*,Surf. Sci. **123,** 305 (1982).

Ru(0001) でのエピタキシャル成長の期待

D. L. Doering *et al.*,Surf. Sci. **123,** 305 (1982).

P. A. Thiel *et al.*, Surf. Sci. Rep. **7,** 211 (1987).

M. A. Henderson, Surf. Sci. Rep. **46,** 1 (2002).

下地が及ぼす"template effect"の期待

Z. Dohnálek, et al, J. Chem. Phys. **110,** 5489 (1999).

Z. Dohnálek, et al., J. Chem. Phys. **112,** 5932 (2000).

界面からの成長も十分に考えられる

研究背景　　結晶化のメカニズム

結晶化はどこから起こるのか（表面？バルク？界面）?

Crystalization initiates from Interface and/or bulk of ASW

B. Rowland *et al.*, J. Chem. Phys. **102** (1995) 8328.
V. Buch *et al.*, J. Phys. Chem. **100** (1996) 3732.
P. Löfgren *et al.*, Surf. Sci. **367** (1996) L19.
Z. Dohnálek *et al.*, J. Chem. Phys. **112** (2000) 5932.
P. Löfgren *et al.*, Langmuir **19** (2003) 265.

Different case

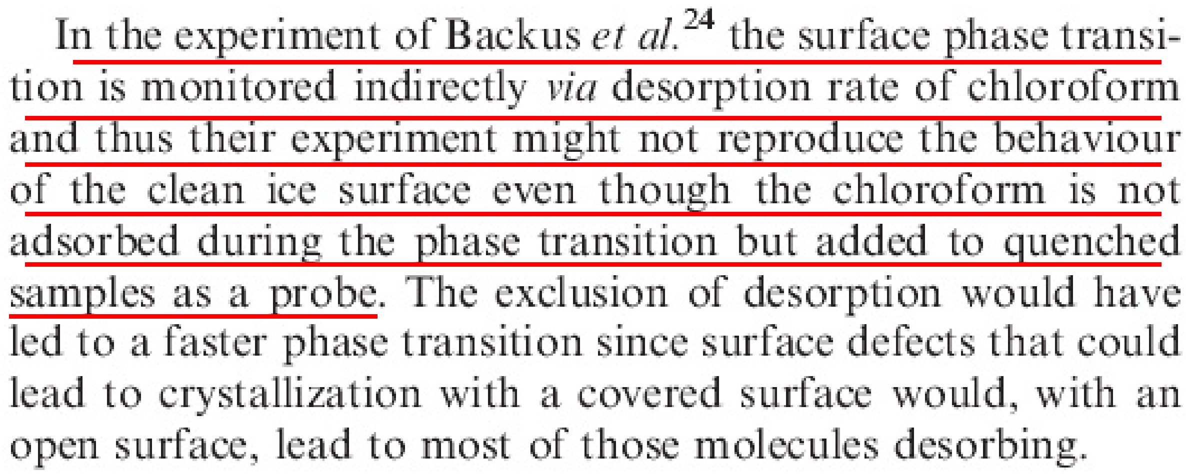
Crystalization initiate

E. H. G. Back

Denied by

Crystalization initiat

P. Ahlström, P. Lö

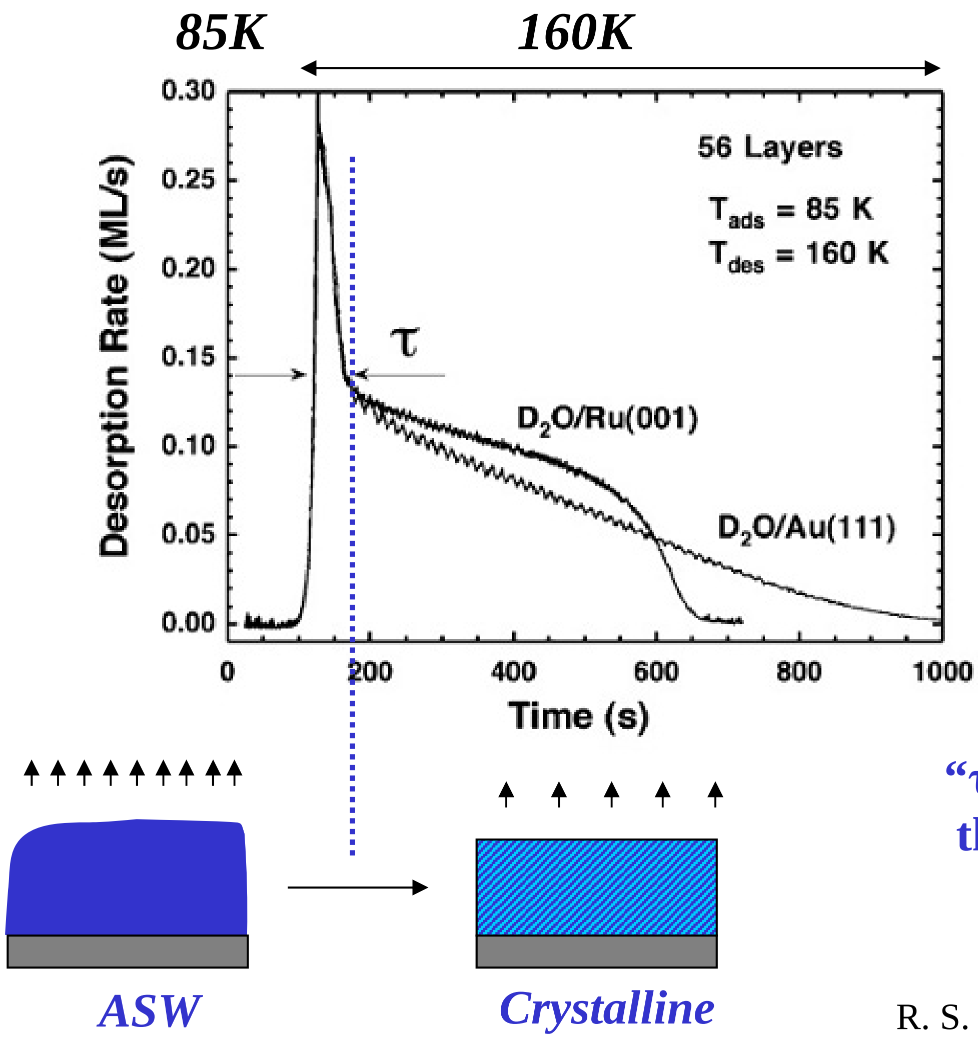


In the experiment of Backus *et al.*[24] the surface phase transition is monitored indirectly *via* desorption rate of chloroform and thus their experiment might not reproduce the behaviour of the clean ice surface even though the chloroform is not adsorbed during the phase transition but added to quenched samples as a probe. The exclusion of desorption would have led to a faster phase transition since surface defects that could lead to crystallization with a covered surface would, with an open surface, lead to most of those molecules desorbing.

本研究により詳細が明らかになった。

研究背景: どうやって結晶化したことを判断するのか？

等温脱離種計測 (ITPD)
(Isothermal temperature-programmed desorption, ITPD)

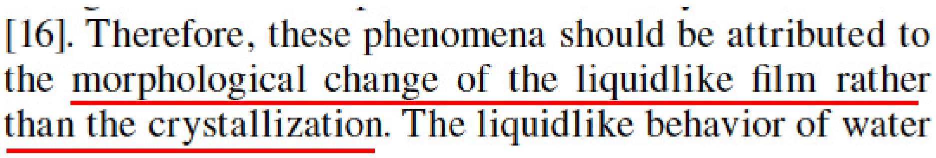


"τ" has been used to analyze the crystallization kinetics!

R. S. Smith *et al*. Surf. Sci, **367** (1996) L13.

最近になり…
異なるITPDの解釈が提案されている…

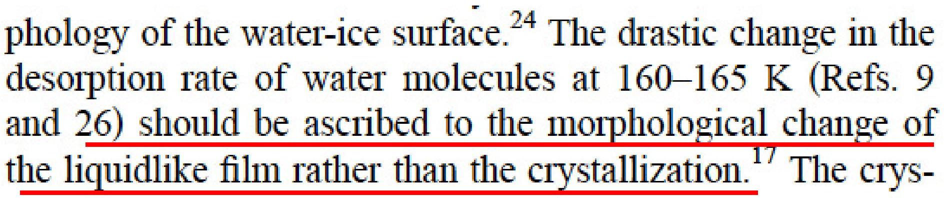
脱離率の違いは結晶化を示してはいない ???



[16]. Therefore, these phenomena should be attributed to the morphological change of the liquidlike film rather than the crystallization. The liquidlike behavior of water

モフォロジーの変化

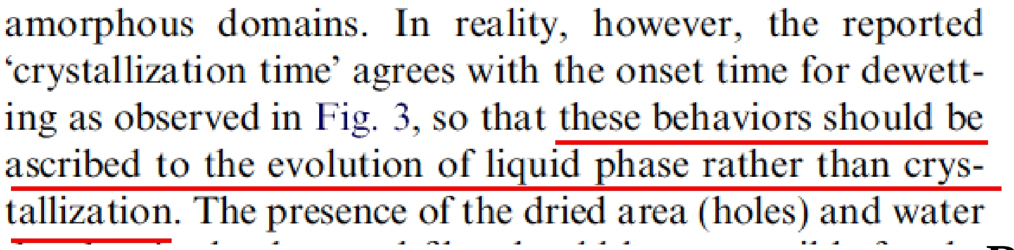
R. Souda, Phys. Rev. Lett. 93 (2004) 235502.



phology of the water-ice surface.[24] The drastic change in the desorption rate of water molecules at 160–165 K (Refs. 9 and 26) should be ascribed to the morphological change of the liquidlike film rather than the crystallization.[17] The crys-

モフォロジーの変化

R. Souda, J. Phys. Chem. 122 (2005) 134711.



amorphous domains. In reality, however, the reported ‘crystallization time’ agrees with the onset time for dewetting as observed in Fig. 3, so that these behaviors should be ascribed to the evolution of liquid phase rather than crystallization. The presence of the dried area (holes) and water

液体状態の相変化

R. Souda, Chem. Phys. Lett. 415 (2005) 146.

The morphological change of the ASW film should be induced by the long-range translational diffusion of the water molecules. This behavior is expected for the fluidized film, but the molecular diffusion is prerequisite for crystallization as well. The crystallization of water has been discussed extensively in the studies of temperature-programmed and isothermal
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モフォロジーの変化

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研究動機（1）

どちらのITPD解釈が正しいのかを
明らかにするためには

(1) <u>結晶性とモフォロジー両方のモニターが必要 !!!</u>

(2) <u>非破壊に計測することが重要 !!!</u>

181103.

ASV
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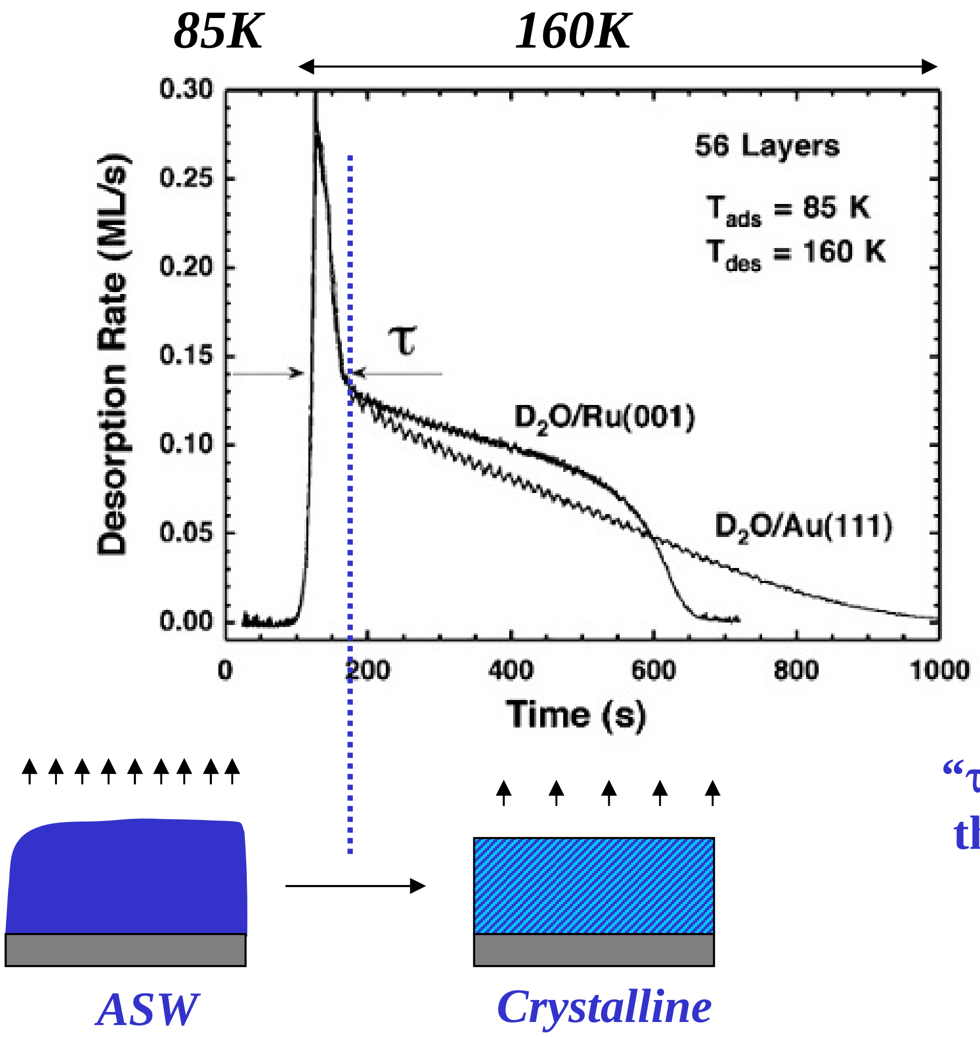
hum
co-v
crystallization. They also found that CCl_4 molecules embedded in the thick ASW films desorb explosively at around 160–165 K (Ref. 17) and explained this phenomenon by crystallization. In reality, however, the desorption rate of molecules should be dependent on many other factors, such as glass-liquid (or liquid-liquid) transition and the morphology change of the film.

ガラス—液体 (or 液体—液体) 相変化と
モフォロジーの変化

研究背景：ITPDによるモフォロジーの解釈

等温脱離種計測 (ITPD)

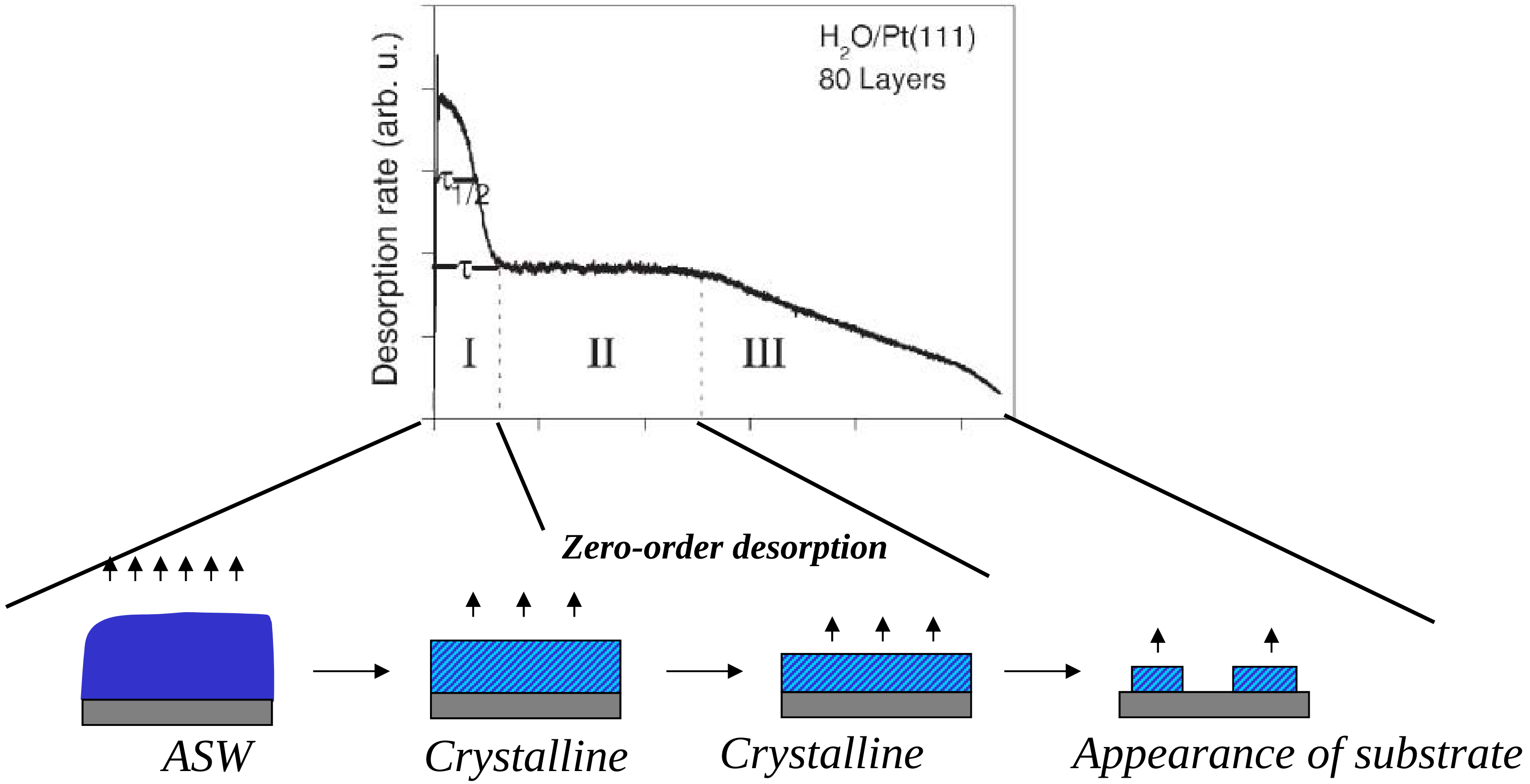


"τ" has been used to analyze the crystallization kinetics!

R. S. Smith *et al*. Surf. Sci, **367** (1996) L13.

研究背景　ITPDによるモフォロジーの解釈

下地表面の“濡れ性”によって解釈されてきた



Zero-order desorption

ASW

Crystalline

Crystalline

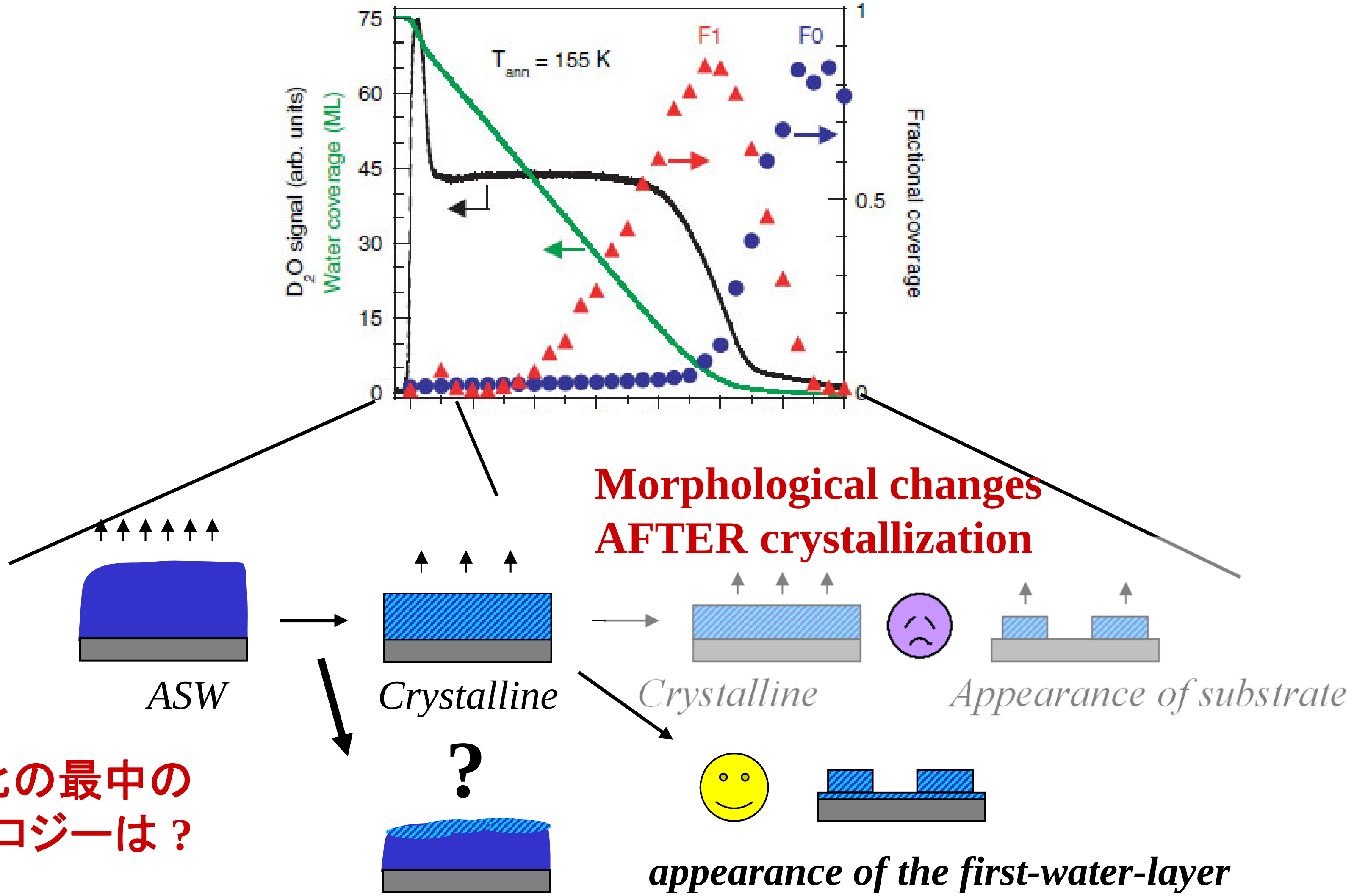
Appearance of substrate

Morphological change

P. Löfgren *et al*., Langmuir **19** (2003) 265.

P.Ahlstrom *et al*., Phys.Chem.Chem.Phys. **6** (2004) 1890.

研究動機(2)
結晶化の最中および結晶化後のモフォロジー



Morphological changes AFTER crystallization

ASW

Crystalline

Crystalline

Appearance of substrate

?

appearance of the first-water-layer

結晶化の最中の
モフォロジーは？

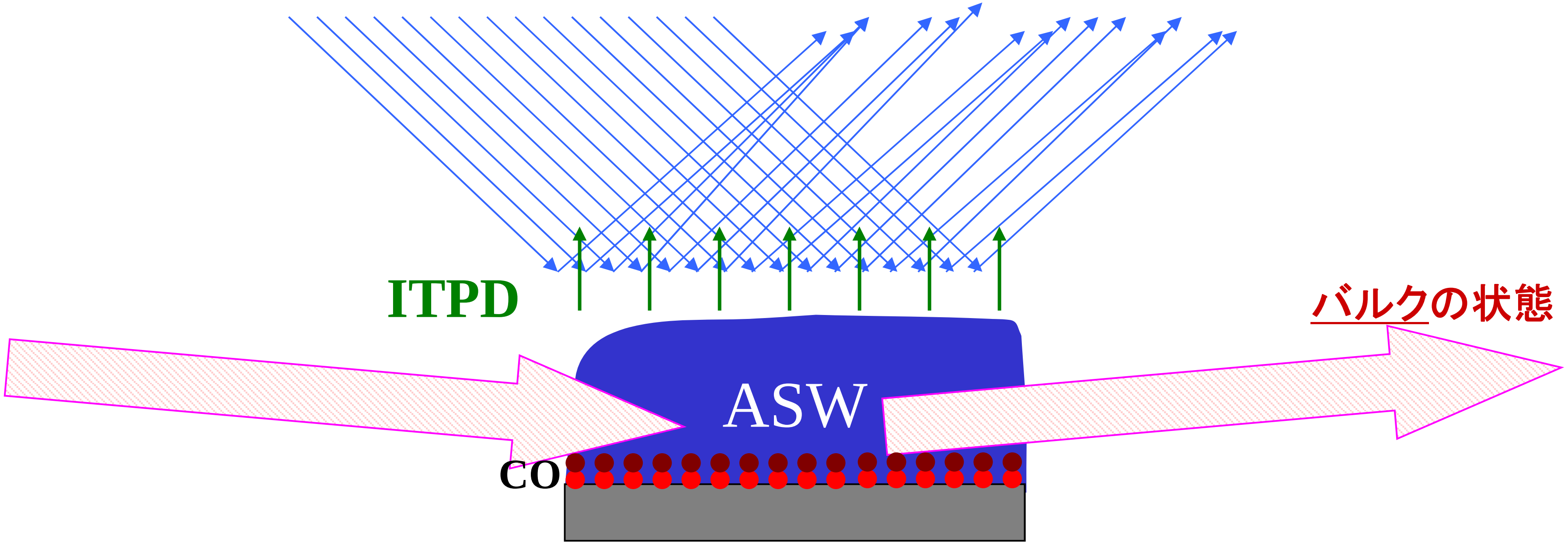
Bulk state (surely crystallize??)
Morphology ??

G. Kimmel *et al*., Phys. Rev. Lett. **95** (2005) 166102.
(also by G. Zimbitas *et al*., J. Chem. Phys. **123** (2005) 174701.)

研究目的

Ru(0001)のアモルファス氷（ASW）の結晶化過程を明らかにすること (**いつ**, **どこから**, **and どのように ?**)

Combination of ITPD, HAS and IRAS



ヘリウム原子線散乱 (HAS)　表面の結晶性とモフォロジー

ITPD

バルクの状態

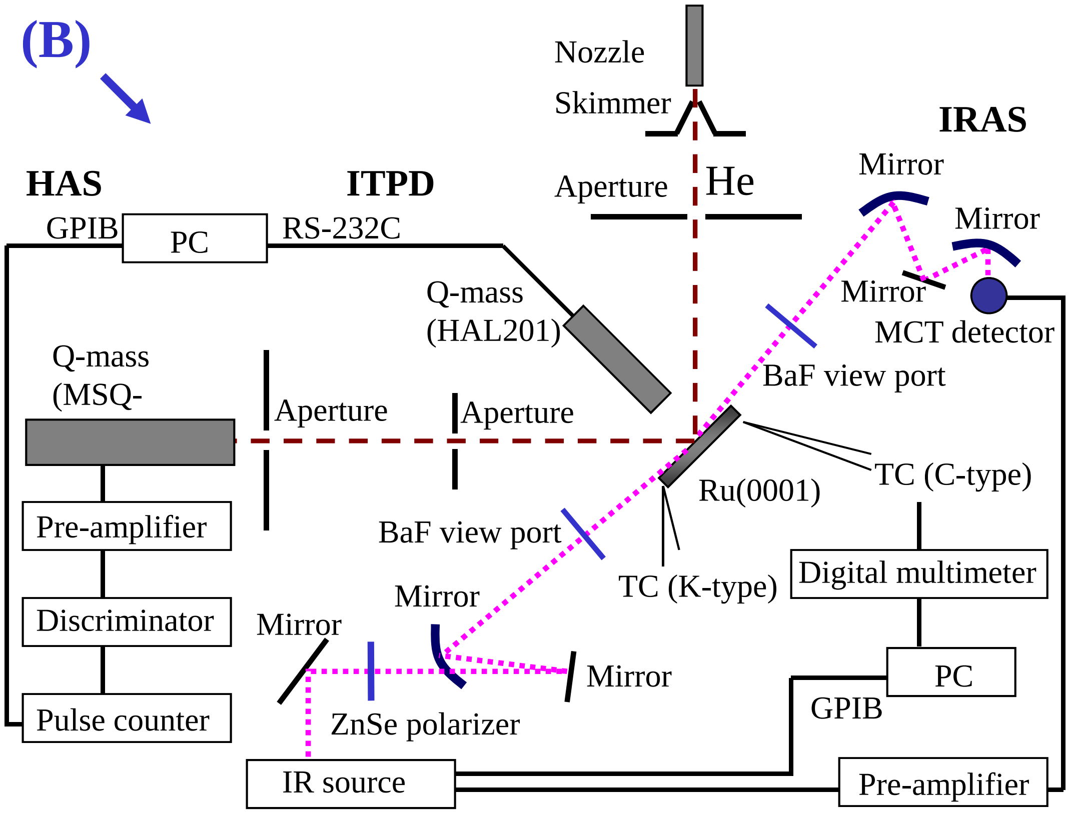
COの伸縮振動のエネルギー → 界面の状態

反射赤外吸収分光法 (IRAS)

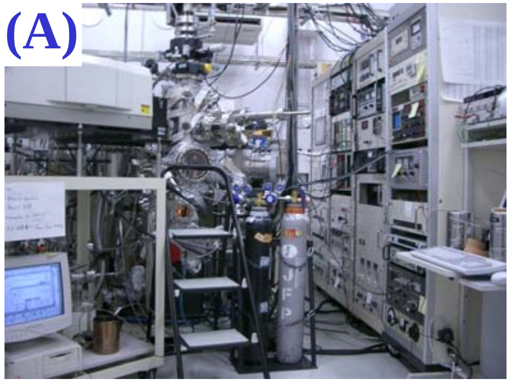
非破壊・無擾乱に同時計測！　！

実験装置

(B)

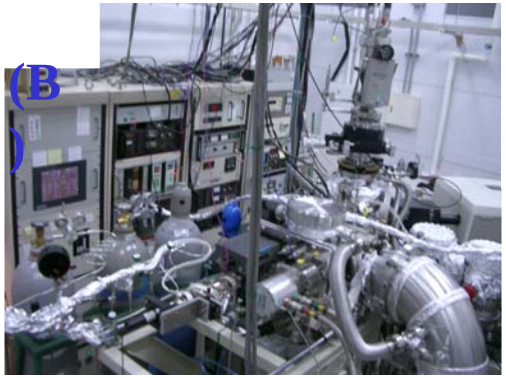


(A)



(B

)



1 Source chamber : < 3×10^{-7} Torr

2 Chopper chamber : < 2×10^{-8} Torr

3 Scattering chamber : < 1×10^{-10} Torr

4 Second chopper chamber: < 1×10^{-10} Torr

5 Detector chamber : < 9×10^{-11} Torr

T. Kondo, *et al*. Eur. Phys. J D **38** (2006) 129.

Clean Ru(0001) surface

清浄化

Ar ion bombardment (0.5keV, 20min.)

Annealing (1000K a few min.)

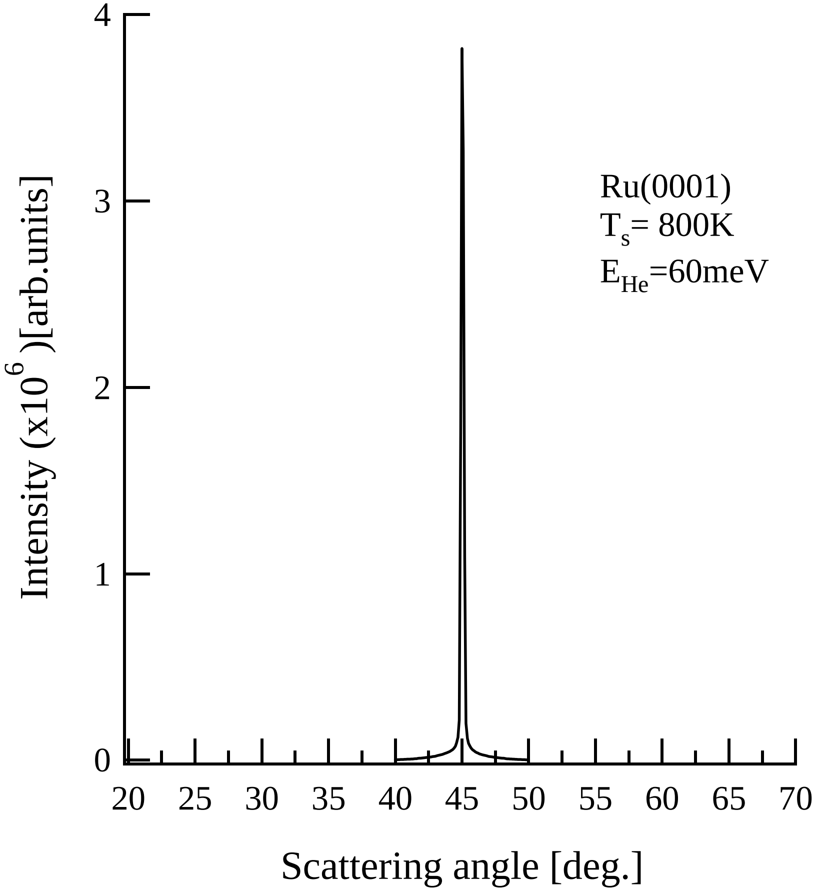
O_2 treatment (RT)

Flashing (up to 1560K)

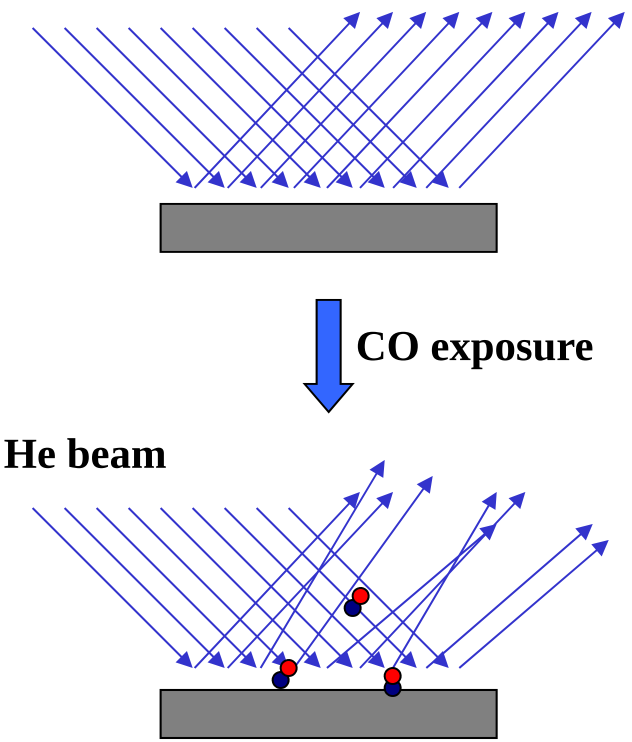
清浄性の確認

Low Energy Electron Diffraction

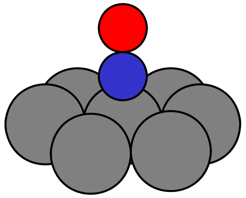
He atom scattering

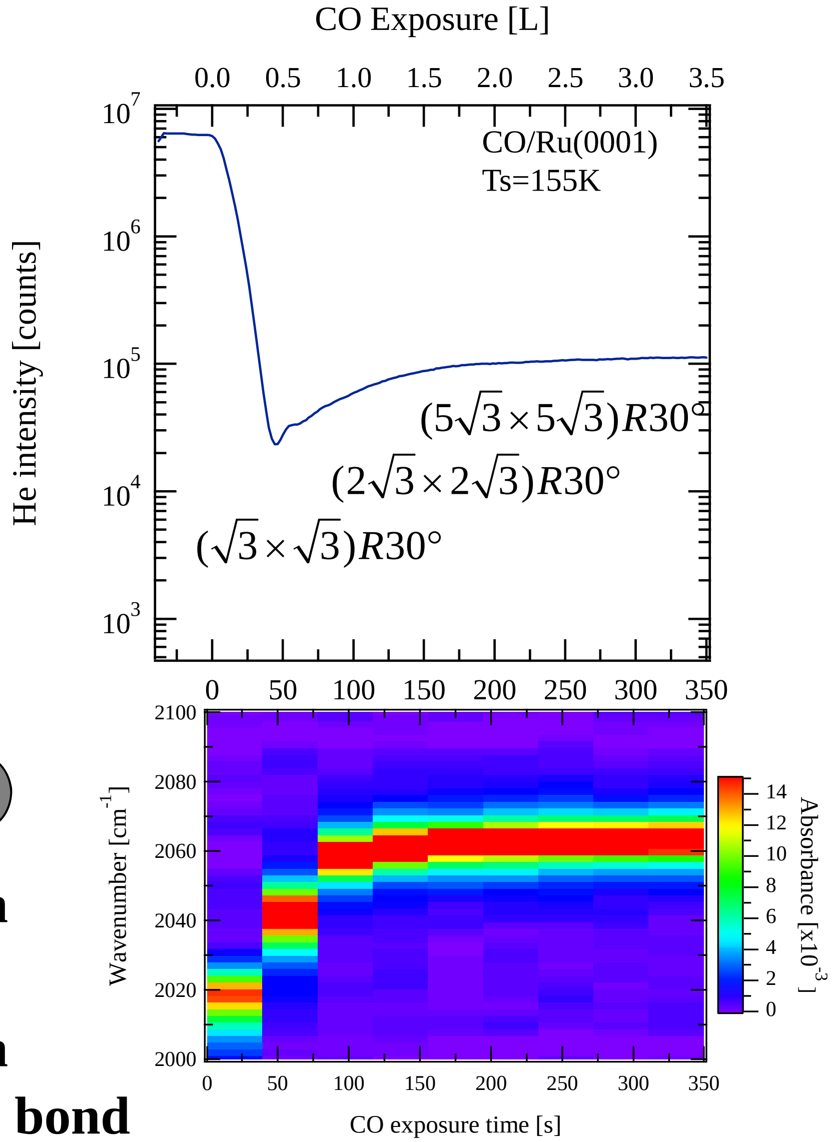


Adsorption of CO on Ru(0001)



on-top





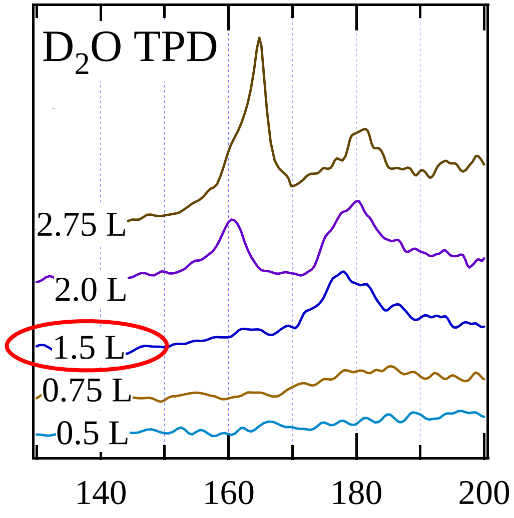
θ_{CO}< 0.33 **Lateral dipole interaction**

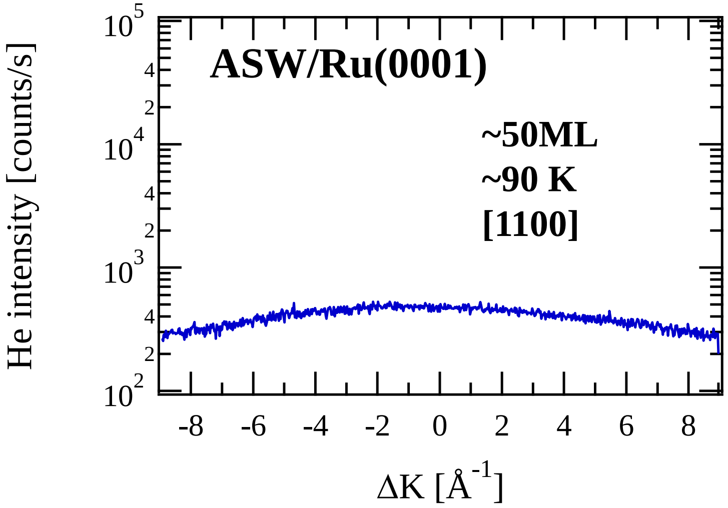
θ_{CO}> 0.33 { **Lateral dipole interaction**
Weakening of the Ru-CO bond

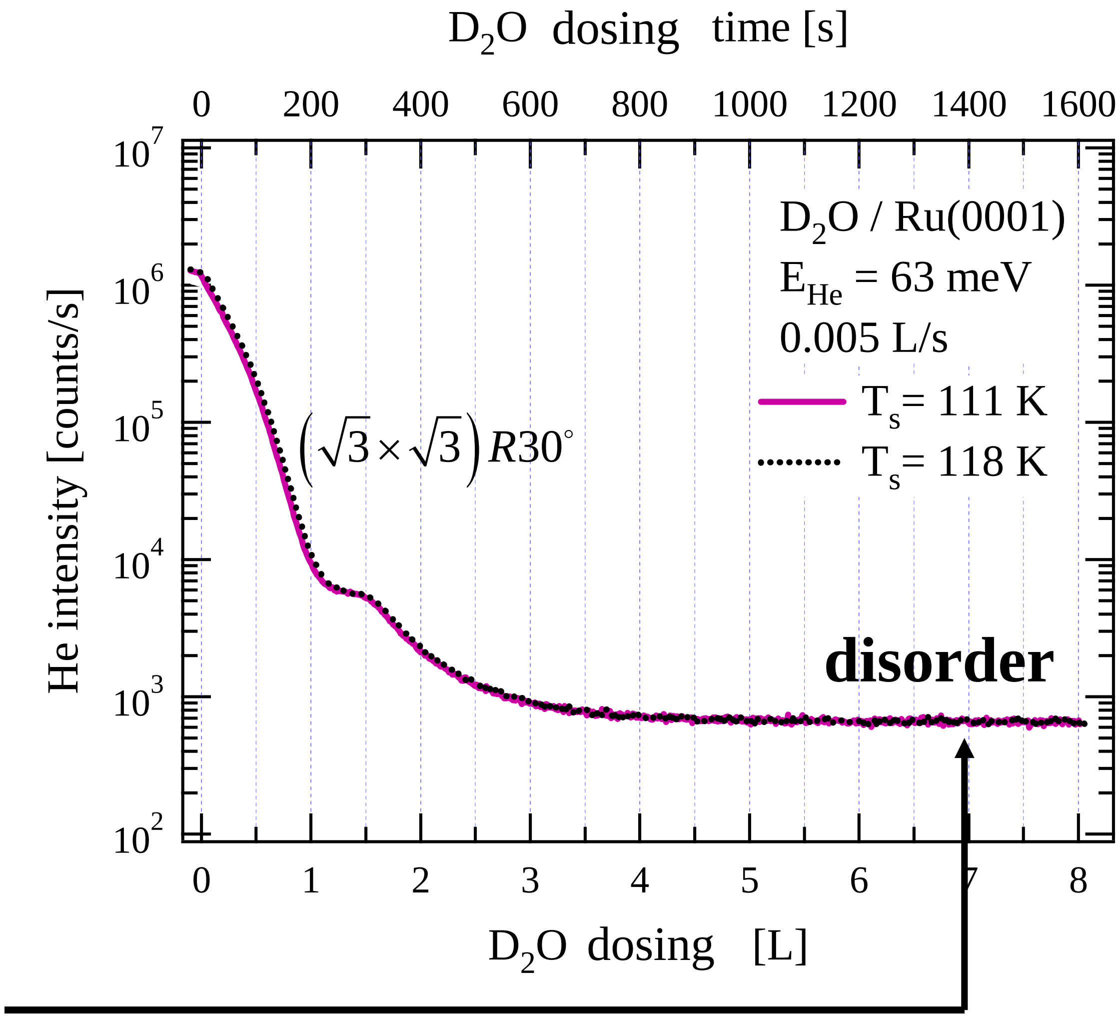
(S. H. Payne, et al., Surf. Sci. **594**, 240 (2005). and references therein)

Preparation of D_2O/Ru(0001)

He散乱で観るRu(0001)表面へのD_2O吸着

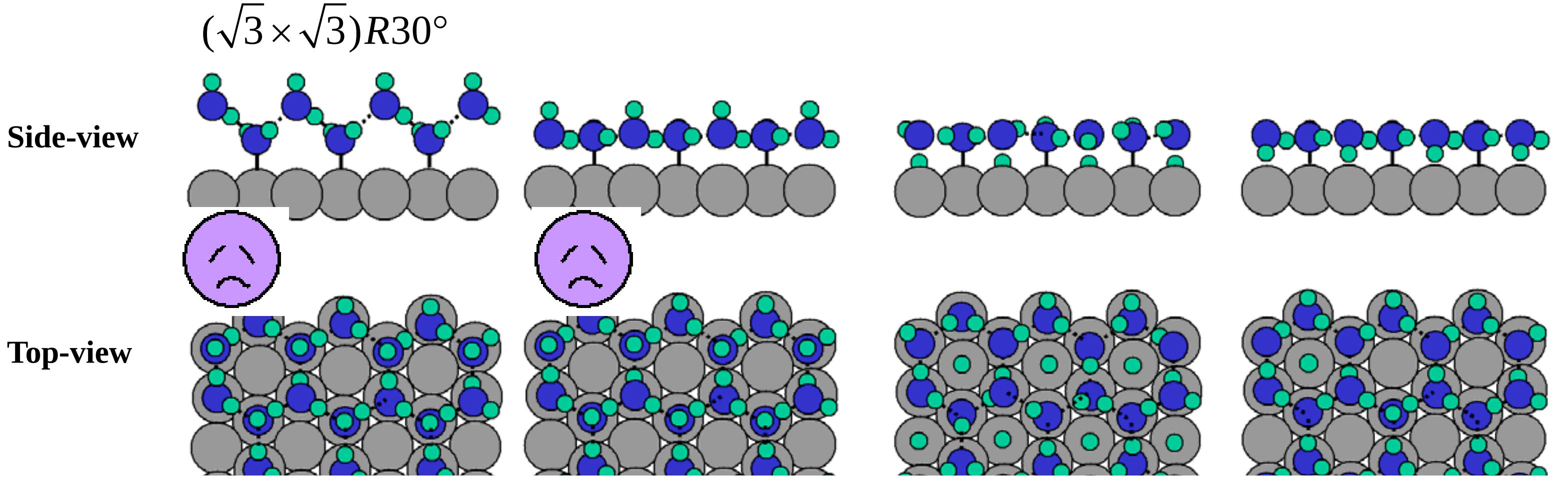


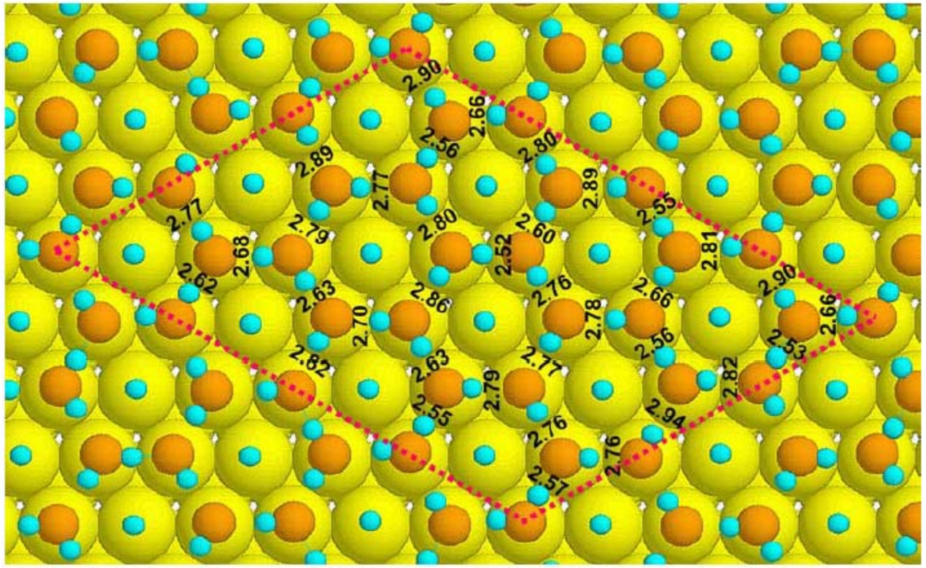




T. Kondo, *et al.*, Surf. Sci. **600** (2006) 3570

これまでに提案されてきた Ru(0001) における水分子吸着形態





Many possibilities

H-side ?
dissociated ?
Space for H

Fig. 2. A DFT-optimized 1/2-dissociated, periodic water adlayer (top view) on a 5-layer Ru(0 0 0 1) slab, with computed O–O separations given in Å. Large, medium and small spheres represent Ru, O and D atoms. The $4\sqrt{3}\times 3\sqrt{3}$ unit cell (dashed parallelogram) accommodates 24 water molecules in a low symmetry, fully H-bonded network.

P. J. Feibelman, Chem. Phys. Lett. **389** (2004) 92.

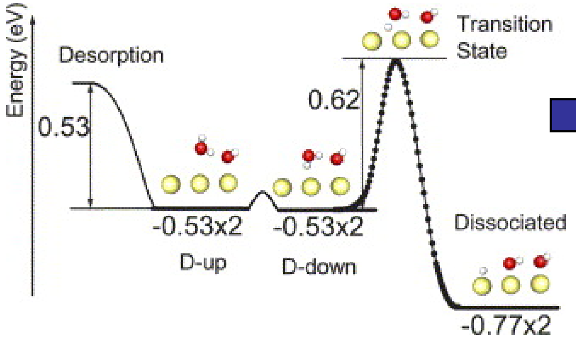
これまでに提案されてきた Ru(0001) における水分子吸着形態

Most stable structure is “dissociated phase” but essentially water is intact on Ru

Exceptionally high dissociation probability by the electron or x-ray

(N. S. Faradzhev, et al., Surf. Sci. **415** (2005) 165. and references therein)

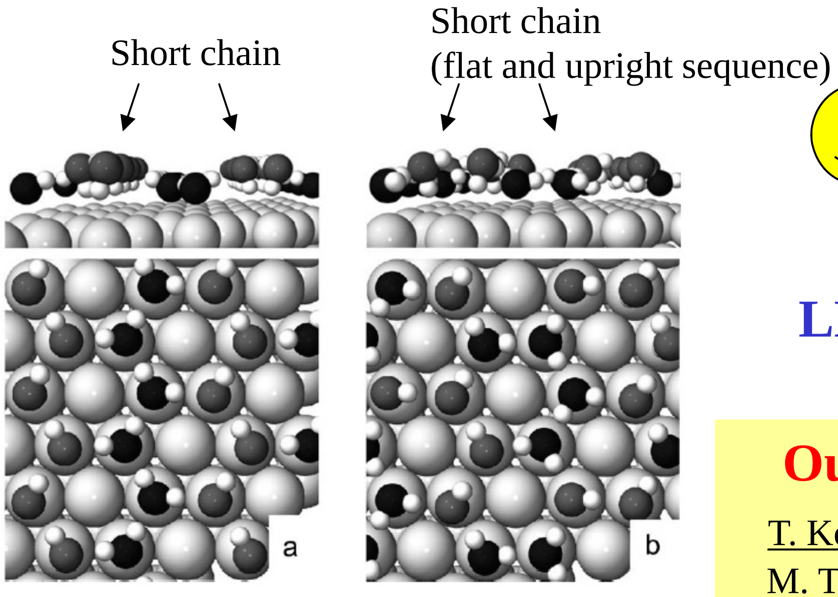
For satisfying the experimentally observed work function and SFG



H-up and H-down mixing structure

Proposed by DFT

S. Meng, Chem. Phys. Lett. **402** (2005) 384.



Chain structure models are proposed !

LEED, IRAS, DFT, work function

S. Haq, et al. Phys. Rev. B **73** (2006) 115414.

Our HAS, IRAS and TPD supports this view

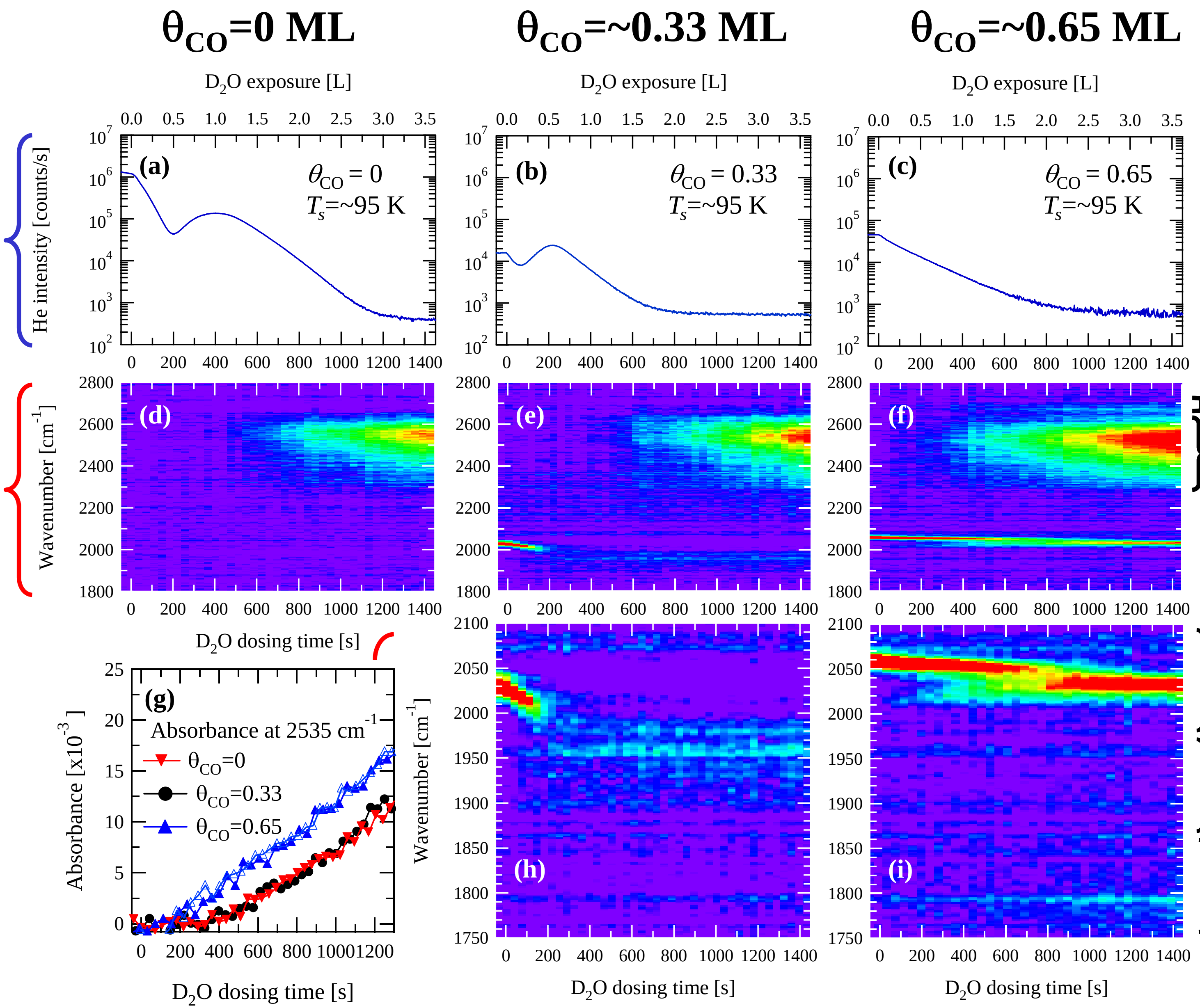
T. Kondo, *et al*., Surf. Sci. **600** (2006) 3570

M. Thiam, T. Kondo, *et al*., J. Phys. Chem B **109** (2005) 16024.

Preparation of D_2O/CO/Ru(0001)

HAS

IRAS (ν_{OD})



Free-OD

水素結合OD

CO at

on-top

bridge

hollow

Assignment was based on

H. Ibach and D. L. Mills, “*Electron energy loss spectroscopy and surface vibrations*”, (Academic Press, New York, 1982).

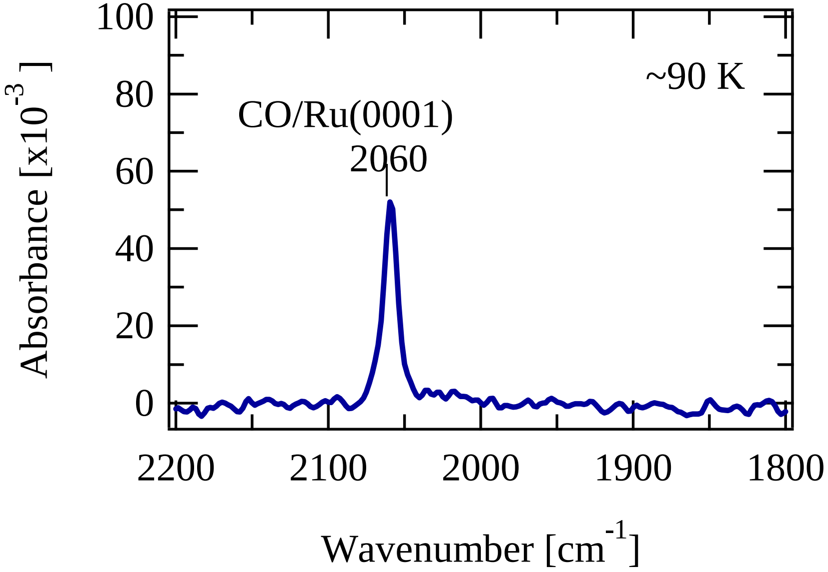
COの被覆率によってRu(0001)での D_2Oとの相互作用が大きく異なる！

θ_{CO}=~0.65 ML: $\left(5\sqrt{3}\times5\sqrt{3}\right)R30^{\circ}$-CO/Ru(0001)

Preparation

Exposing the Ru(0001) surface
to ~20 L CO at ~120 K

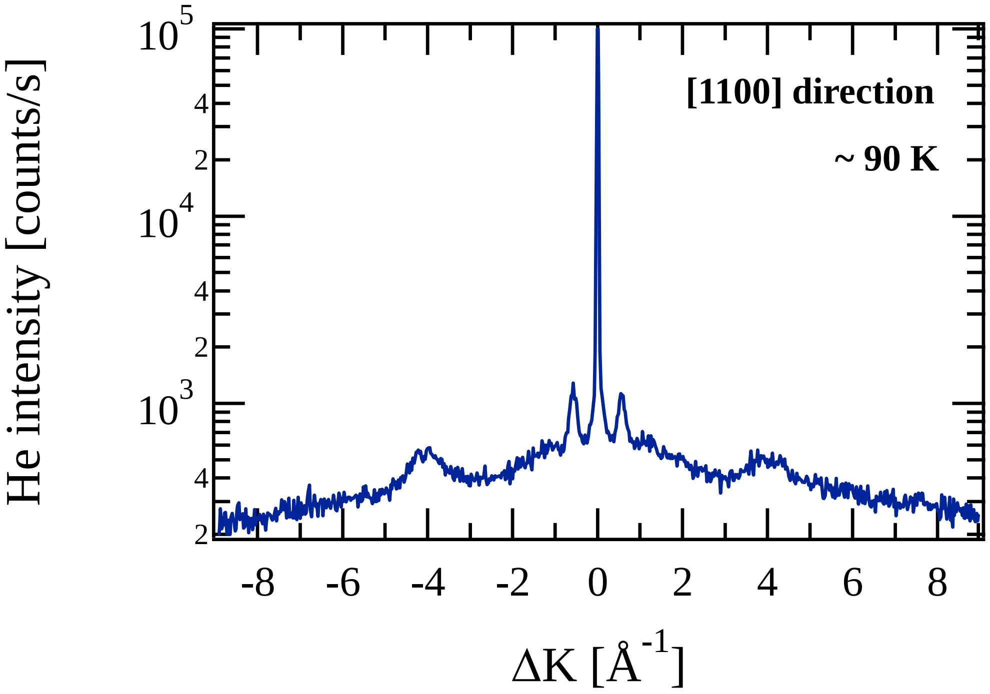
IRAS



Accords with the literature:
H. Pfnür, *et al.*,Surf. Sci. **93**, 431 (1980)

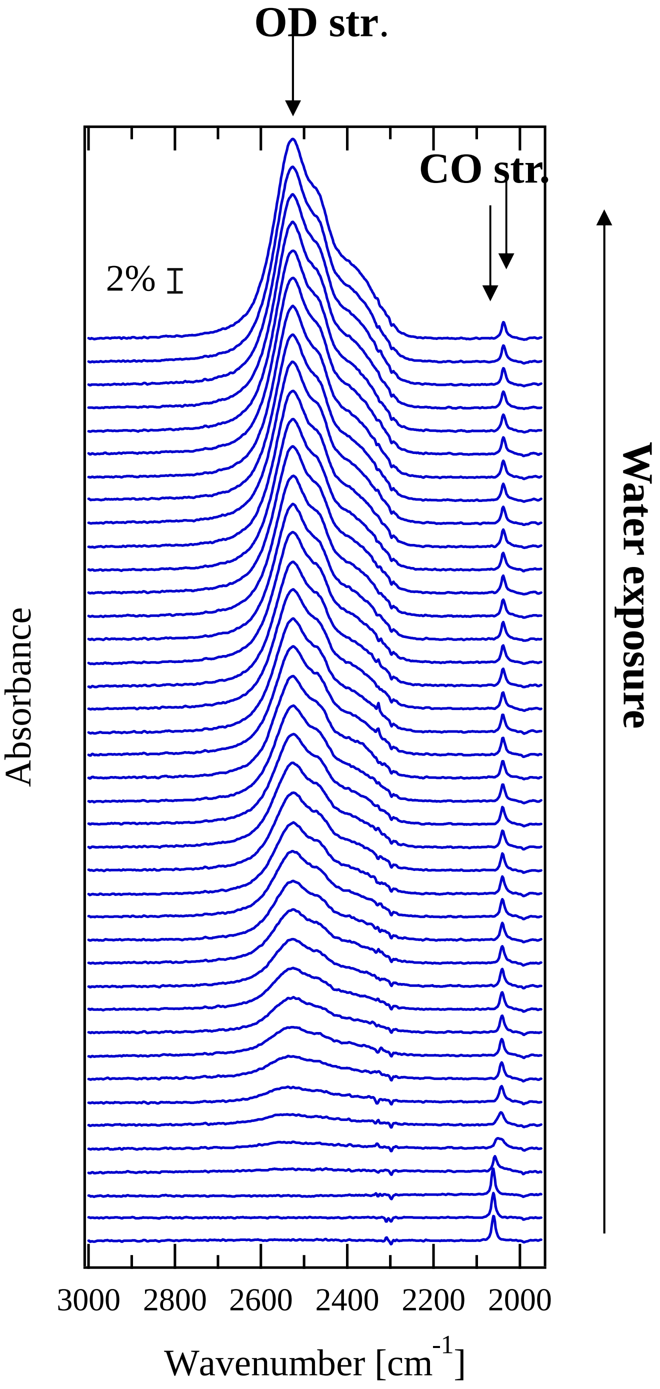
Helium diffraction

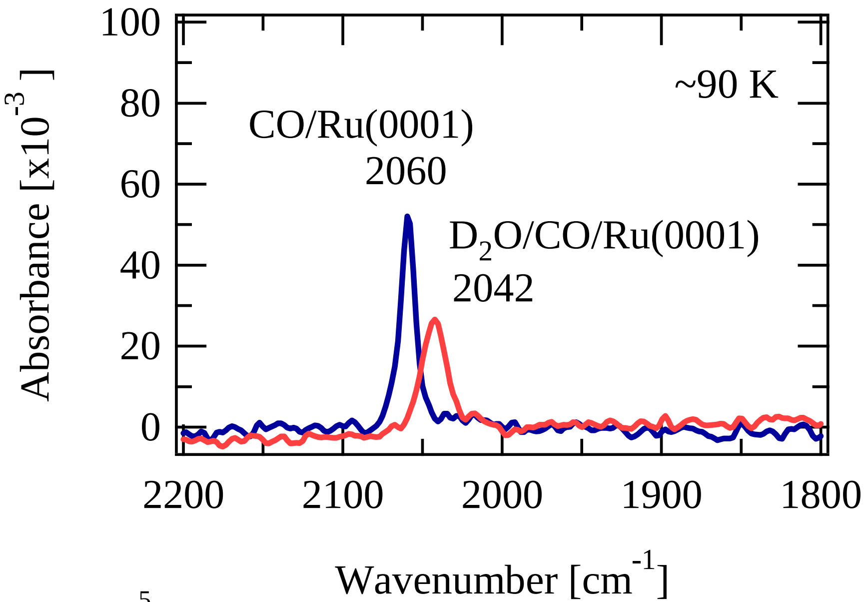
$\left(5\sqrt{3}\times5\sqrt{3}\right)R30^{\circ}$-CO/Ru(0001)

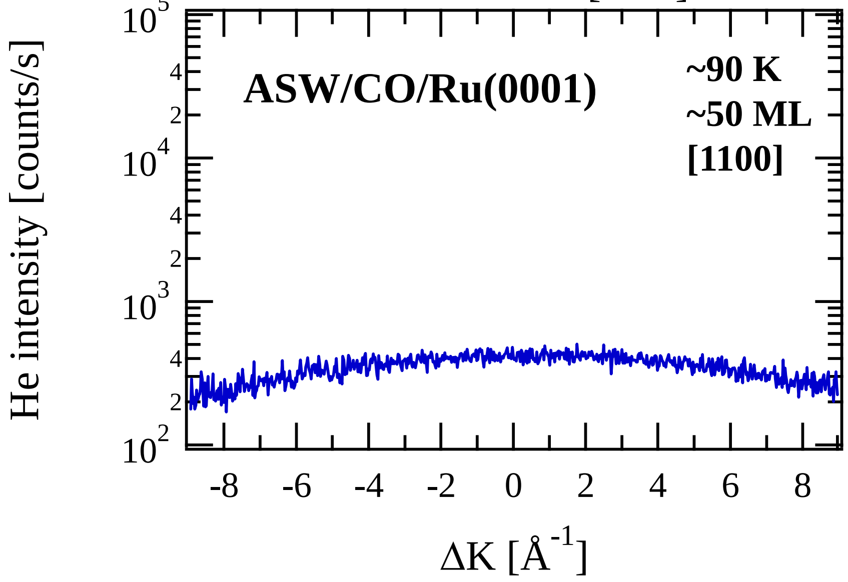


Accords with the literature:
J. Braun, *et al.*, J. Chem. Phys. 106, 8262 (1997).

$D_2O/(5\sqrt{3}\times5\sqrt{3})R30^\circ$-CO/Ru(0001)







50 ML

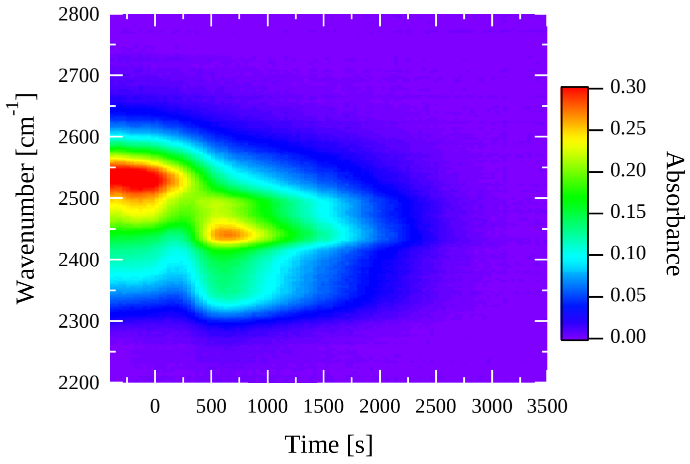
disorder

Crystallization of ASW(D_2O) on Ru(0001)

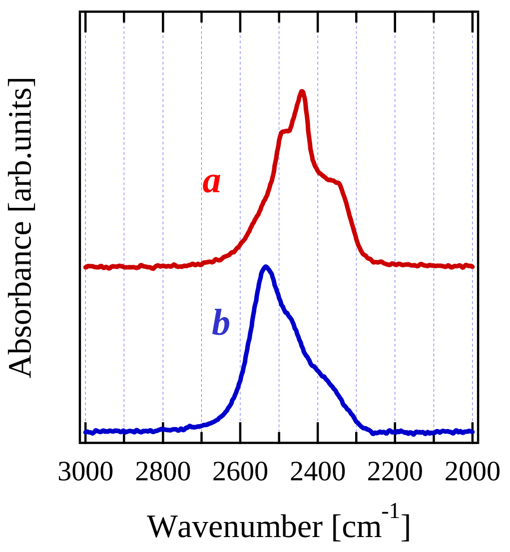
T. Kondo, et al., J. Chem. Phys. 126 (2007) 181103, 1-5.

Analysis of IRAS spectra

Experimental result



OD stretch mode



a : Crystalline ice

b : Amorphous solid water

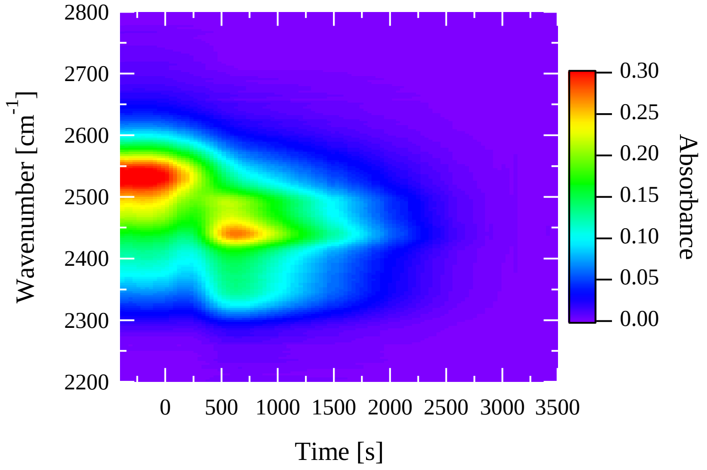
Absorption intensity

$$I(\upsilon) = a\sigma_{Cryst} I_{Cryst}(\upsilon) + b\sigma_{ASW} I_{ASW}(\upsilon)$$

$$\sigma_{ASW} = 0.67\sigma_{Cryst}$$

c.f. E. Backus, *et al*., Phys. Rev. Lett. **92** (2004) 236101.

Fitting result

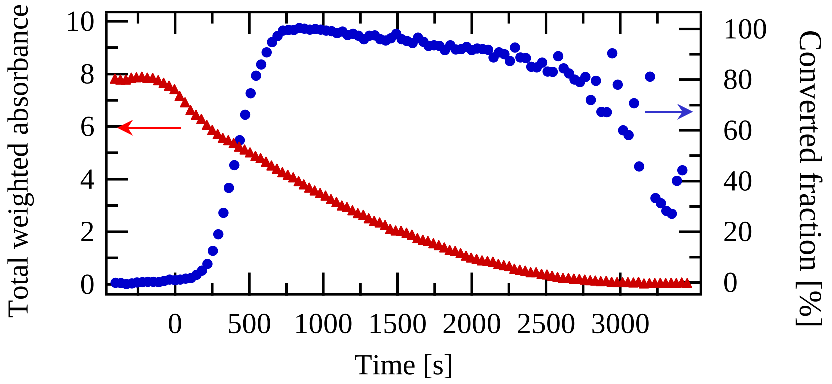


Converted fraction

$$Fraction = \frac{0.67a}{0.67a + b}$$

Total weighted absorbance

$$\frac{0.67a + b}{(0.67a + b)_{initial}}$$

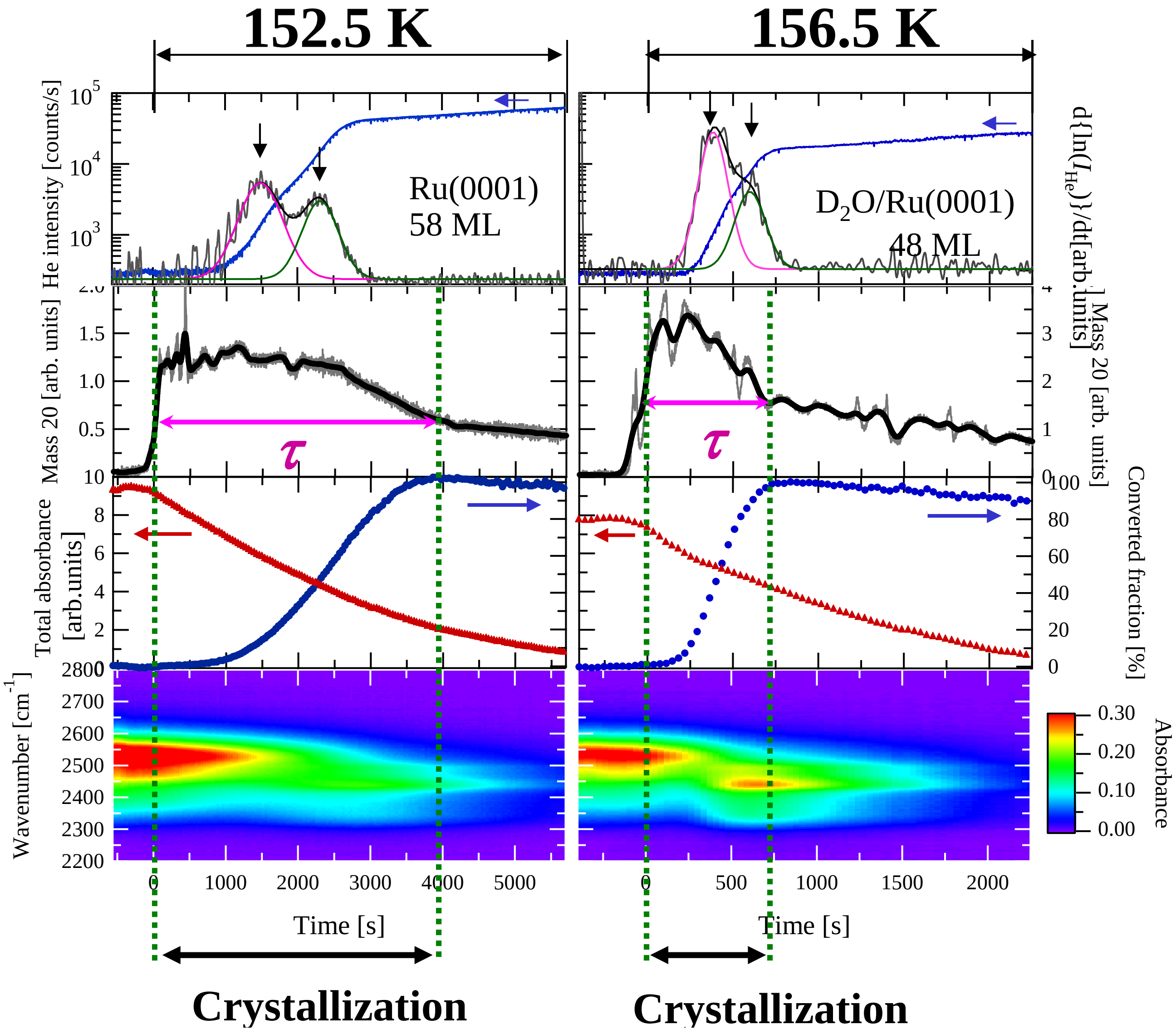


Crystallization of ASW on Ru(0001)

ヘリウム原子線散乱
HAS
（表面の状態）

等温脱離種計測
ITPD
（脱離水分子の数）

反射赤外吸収分光
IRAS
（ν_{OD}:バルクの状態）



結晶化中における下地露出を伴うモフォロジー変化を示唆！

検証：理論モデルを用いた結晶化メカニズムの解析

Classical nucleation and growth model of isothermal solid-state phase transformation kinetics

$$\chi(t) = 100\left\{1 - \exp\left(-(kt)^n\right)\right\}[\%]$$

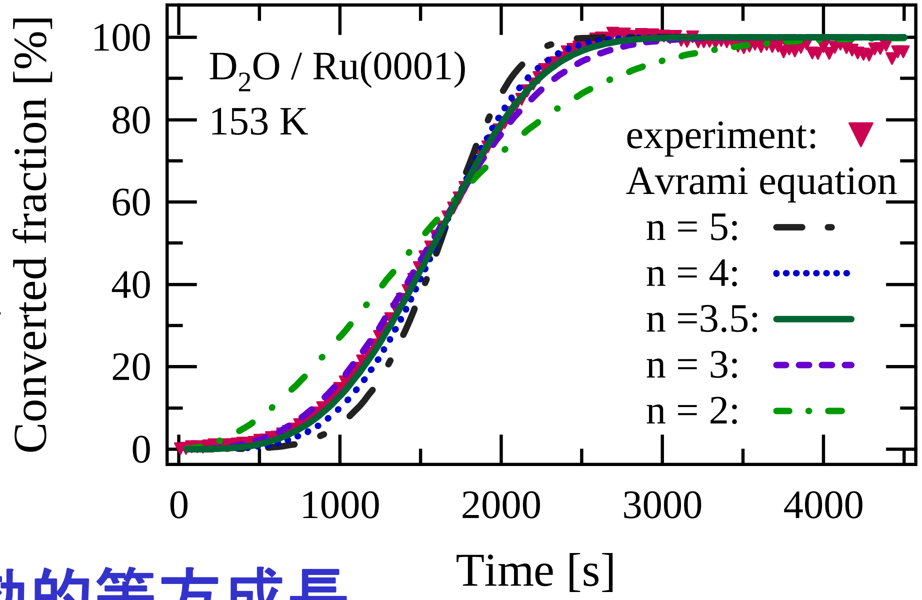
χ: converted fraction [%]
t: time [s]
k: crystallization rate constant
n : parameter (mechanism of the crystallization)

M. J. Avrami, J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).

n **= 1.4 :Heterogeneous growth**

n **= ~4.0 :Random nucleation and homogeneous growth**

Water in Confining Geometries, edited by V. Buch and J. P. Devlin (Springer-Verlag, Berlin, 2003)



Our result is well fitted by
n **= ~3.5 :ランダム核形成、実効的等方成長**

検証：理論モデルを用いた結晶化メカニズムの解析

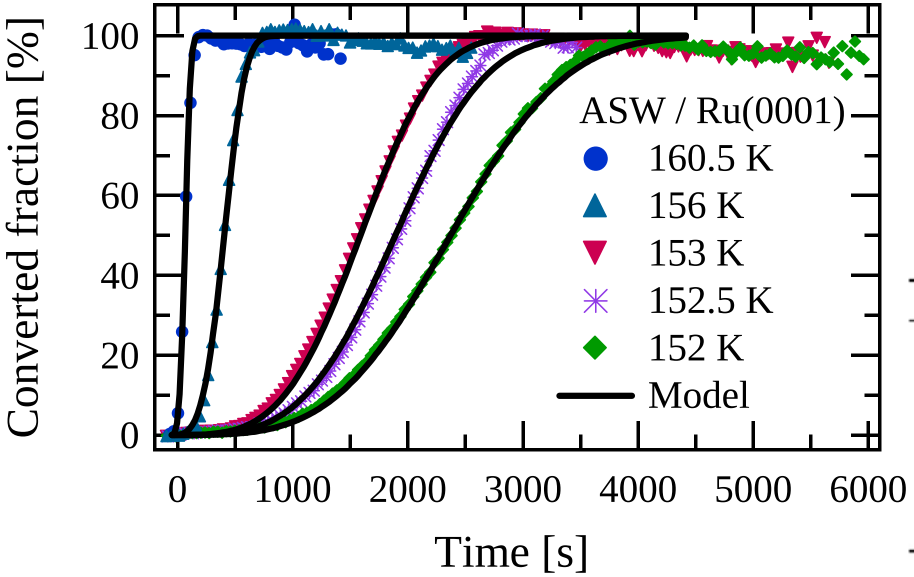
バルク内でのランダム核形成、実効的等方成長である

↓

更に進んだ理論モデルを用いることが可能になる

考慮する**3**要素
- ***(1)*** *結晶化時の脱離*
- ***(2)*** *形成核の有限サイズ*
- ***(3)*** *表面、界面、バルクそれぞれからの成長*

E. H. G. Backus *et al.*, J. Chem. Phys. **121**, 1038 (2004).

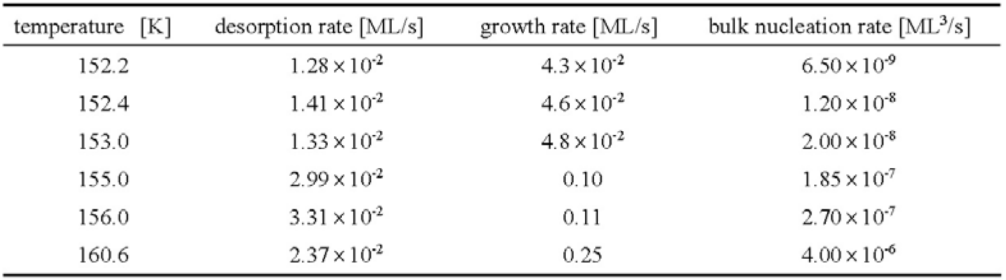


For the model, “bulk nucleation” is applied

Nucleation grain diameter is selected as 3 ML

P. Ahlström, *et al.*, Phys. Chem. Chem. Phys. **6**, 1890 (2004).

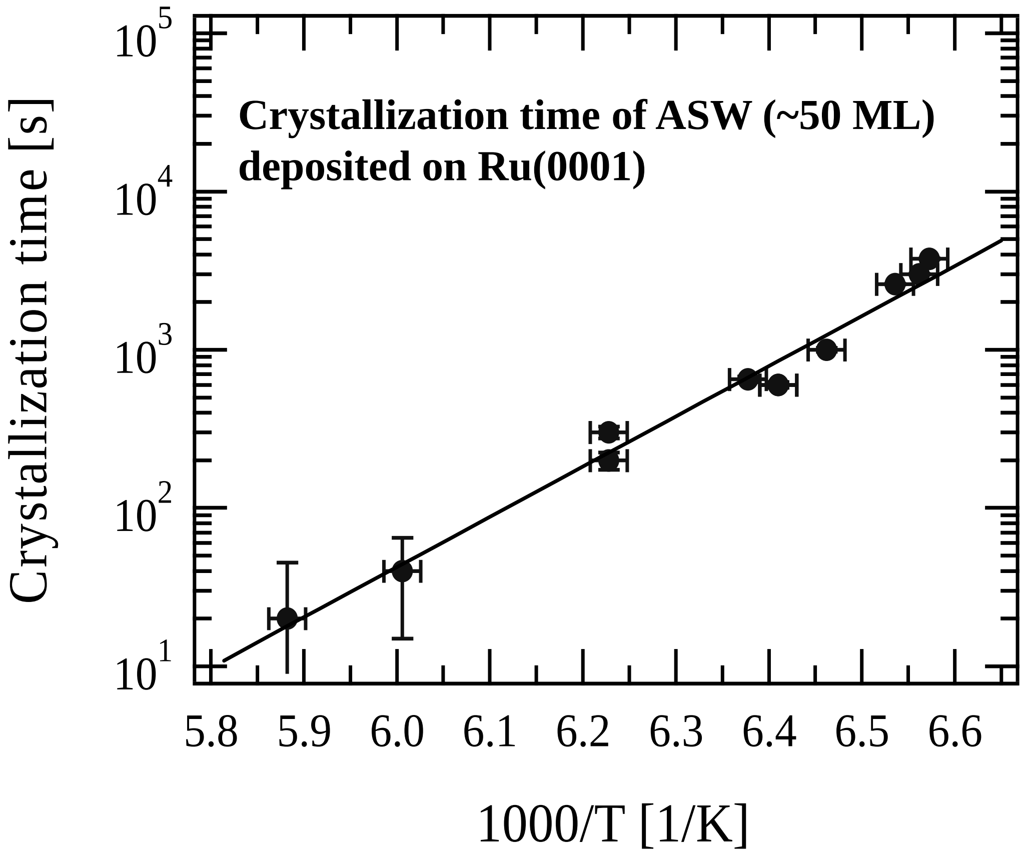
導出した**Growth-rate**と**nucleation-rate**



temperature [K]	desorption rate [ML/s]	growth rate [ML/s]	bulk nucleation rate [ML^3/s]
152.2	1.28×10^{-2}	4.3×10^{-2}	6.50×10^{-9}
152.4	1.41×10^{-2}	4.6×10^{-2}	1.20×10^{-8}
153.0	1.33×10^{-2}	4.8×10^{-2}	2.00×10^{-8}
155.0	2.99×10^{-2}	0.10	1.85×10^{-7}
156.0	3.31×10^{-2}	0.11	2.70×10^{-7}
160.6	2.37×10^{-2}	0.25	4.00×10^{-6}

ランダム核形成、等方成長メカニズムであることが確認された

Activation energy of the ASW (~50 ML) crystallization on Ru(0001)



Arrhenius equation

$$k = A\exp\left(\frac{-E}{RT}\right)$$

$$\ln(k) = -\frac{E}{R}\frac{1}{T} + \ln(A)$$

k : rate coefficient of the reaction

T : temperature

A : pre-exponential factor (frequency factor)

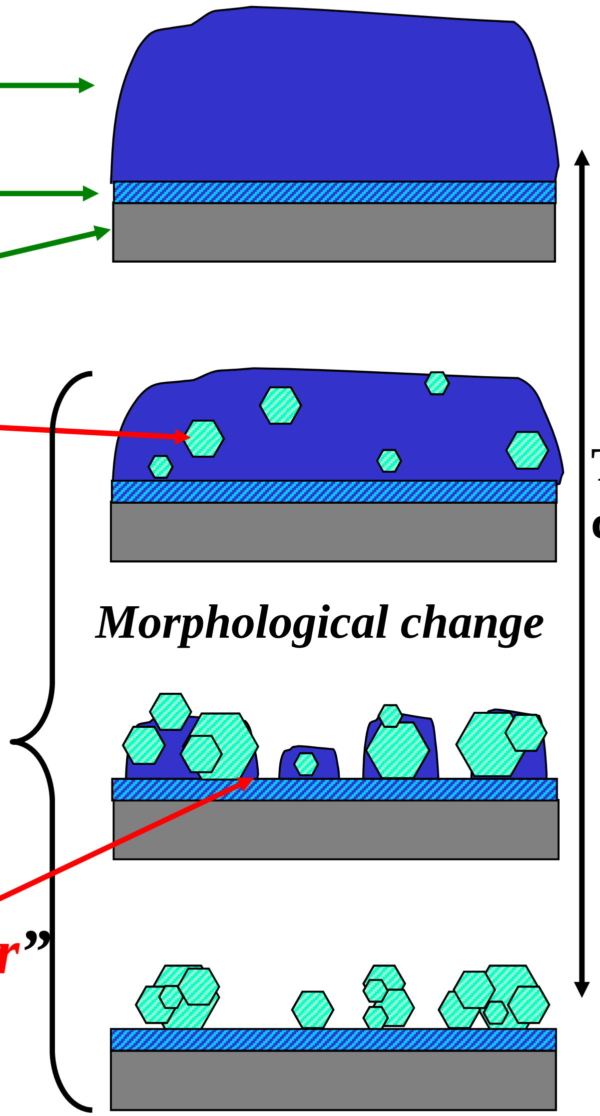
E : activation energy of the reaction

R : gas constant (or Boltzmann constant)

$E_{crystallize}$=650 ± 25 meV

T. Kondo, et al., J. Chem. Phys. 126 (2007) 181103, 1-5.

まとめ：Ru(0001)表面におけるアモルファス氷の結晶化



Amorphous solid water

first-water-layer

Ru(0001)

Crystalline ice grain

Morphological change

Time for the ASW crystallization:

“τ” in ITPD

“Random nucleation”

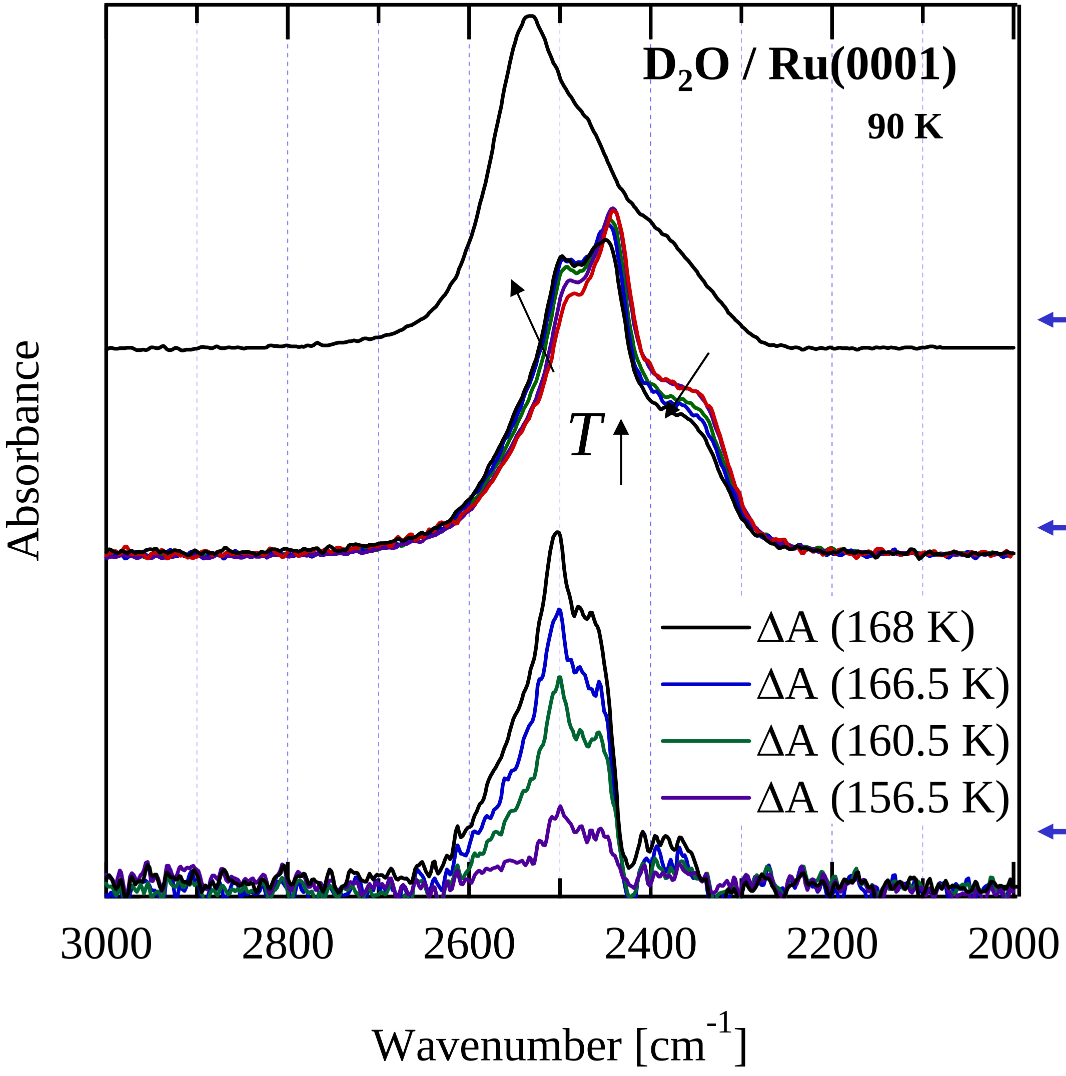
“effectively homogeneous growth”

“appearance of the first-water-layer”

$E_{crystallize}$=650 ± 25 meV

T. Kondo, et al., J. Chem. Phys. 126 (2007) 181103, 1-5.

形成される結晶氷のIRASスペクトルにおける違い



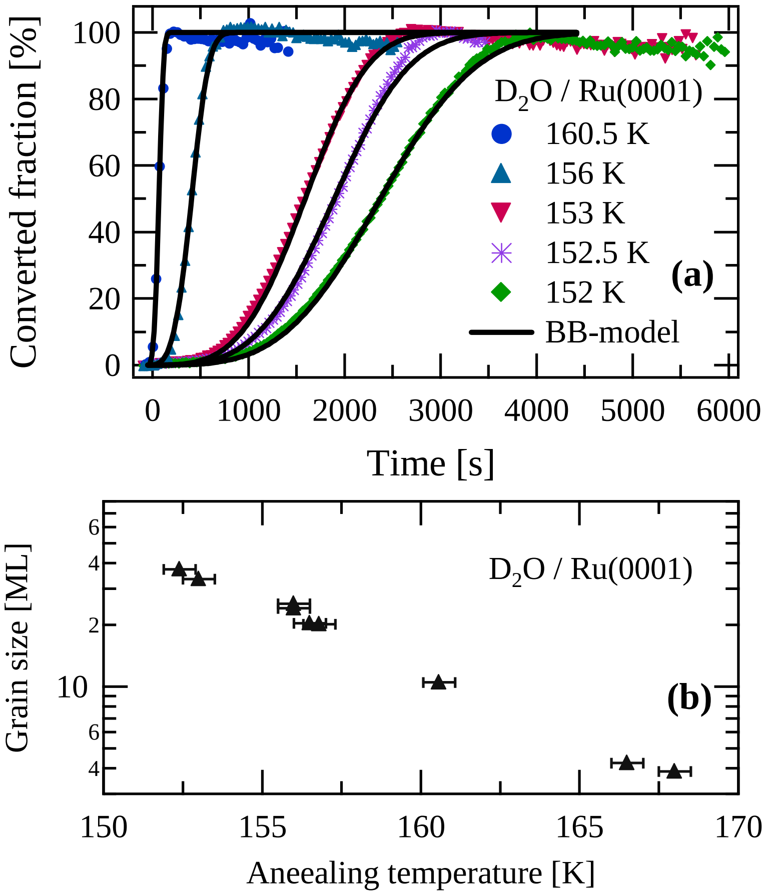
アモルファス氷

結晶氷

結晶氷間の差スペクトル

T. Kondo, et al., Chem. Phys. Lett. 448 (2007) 121-126.

平均的氷結晶グレインサイズの見積もり



$$R_{CI} \approx 0.5\left[J_N(T)\int_0^{\infty}(1-\chi(t))dt \right]^{-1/3}$$

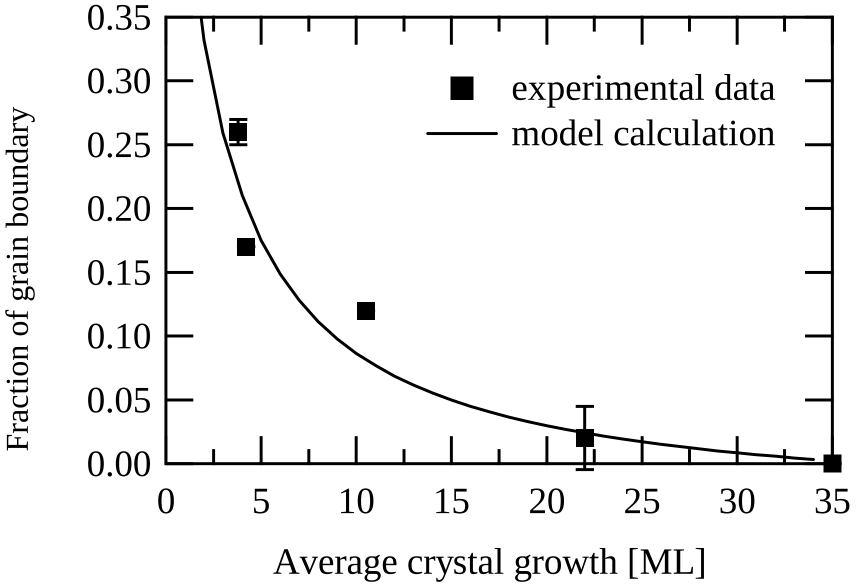
$\chi(t)$: the fraction of the conversion from ASW to CI at the time t

$J_N(T)$: the crystalline nucleation rate derived from model analysis

T : the isothermal annealing temperature

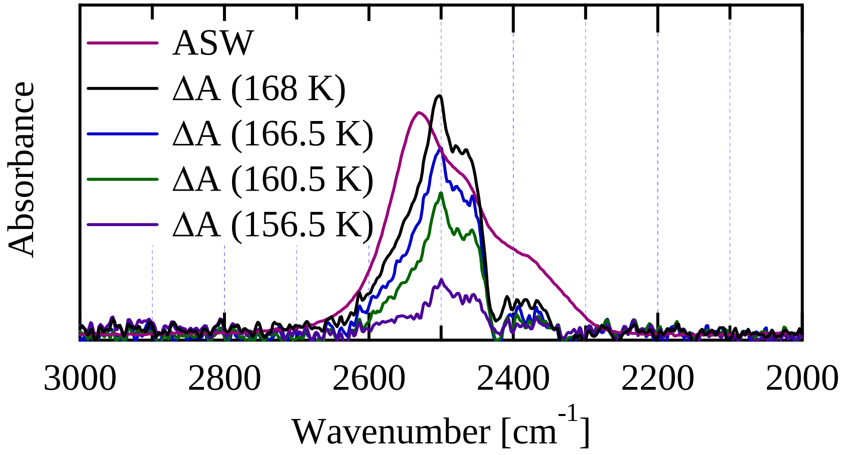
T. Kondo, et al., Chem. Phys. Lett. 448 (2007) 121-126.

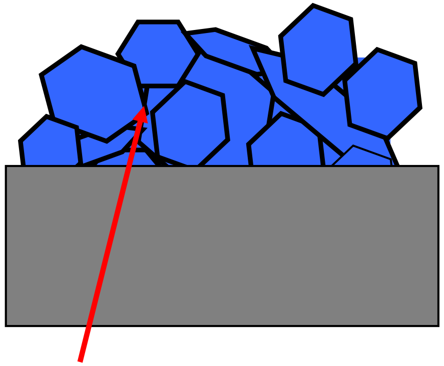
スペクトル成分量がグレインサイズの面積に対応している



$$S=\frac{(4/3)\pi(r^*+R_{CI})^3-(4/3)\pi\{(r^*+R_{CI})-0.5\}^3}{(4/3)\pi(r^*+R_{CI})^3}$$

r^* : critical nuclei size





氷グレイン一氷グレイン界面
の水分子振動に対応

赤外分光による初の観測

T. Kondo, et al., Chem. Phys. Lett. 448 (2007) 121-126.

Crystallization of ASW(D_2O) on CO/Ru(0001)

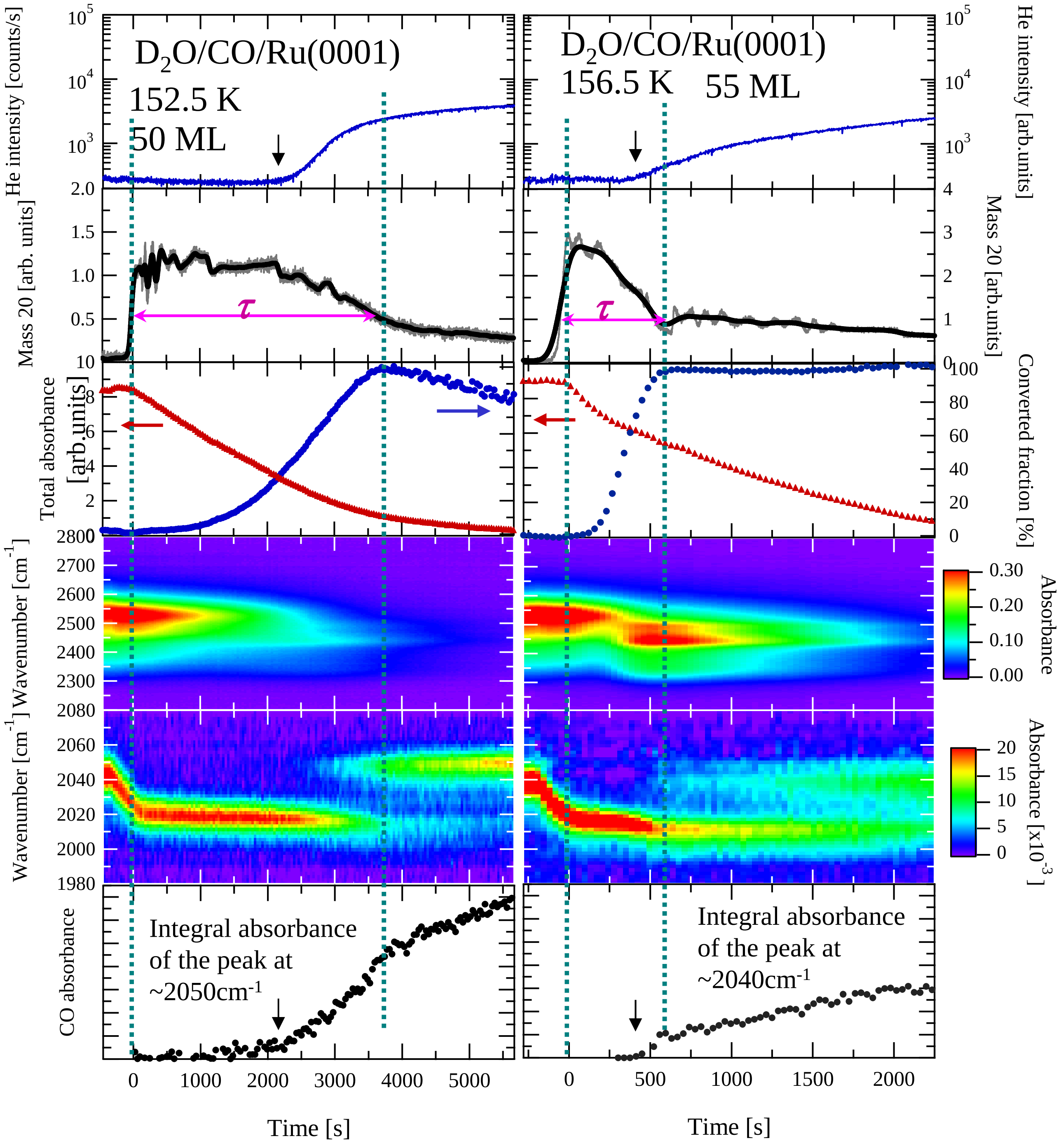
T. Kondo, et al., J. Chem. Phys. 127 (2007) 094703, 1-14.

ヘリウム原子線散乱
HAS
（表面の状態）

ITPD
（脱離水分子の数）

反射赤外吸収分光
IRAS
（ ν_{OD}:バルクの状態）

反射赤外吸収分光
IRAS
（ν_{CO}:界面の状態）



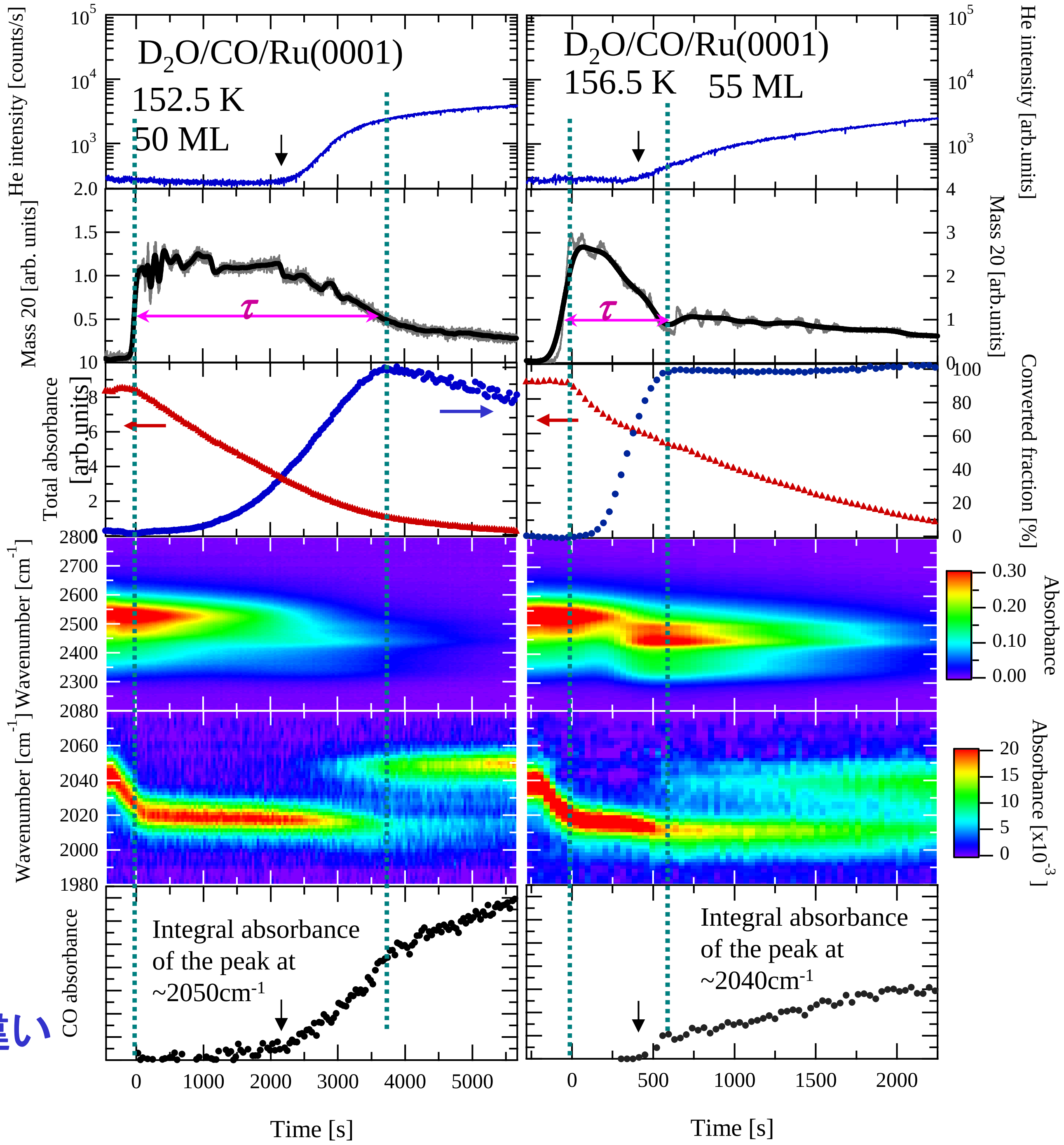
新たに分かる主な事柄:

(1) Ru(0001)の場合と
同じ結晶化メカニズム
及びキネティックス

(2) 極初期に界面が変化

(3) 結晶化中における
下地表面の曝露を
伴うモフォロジー変化

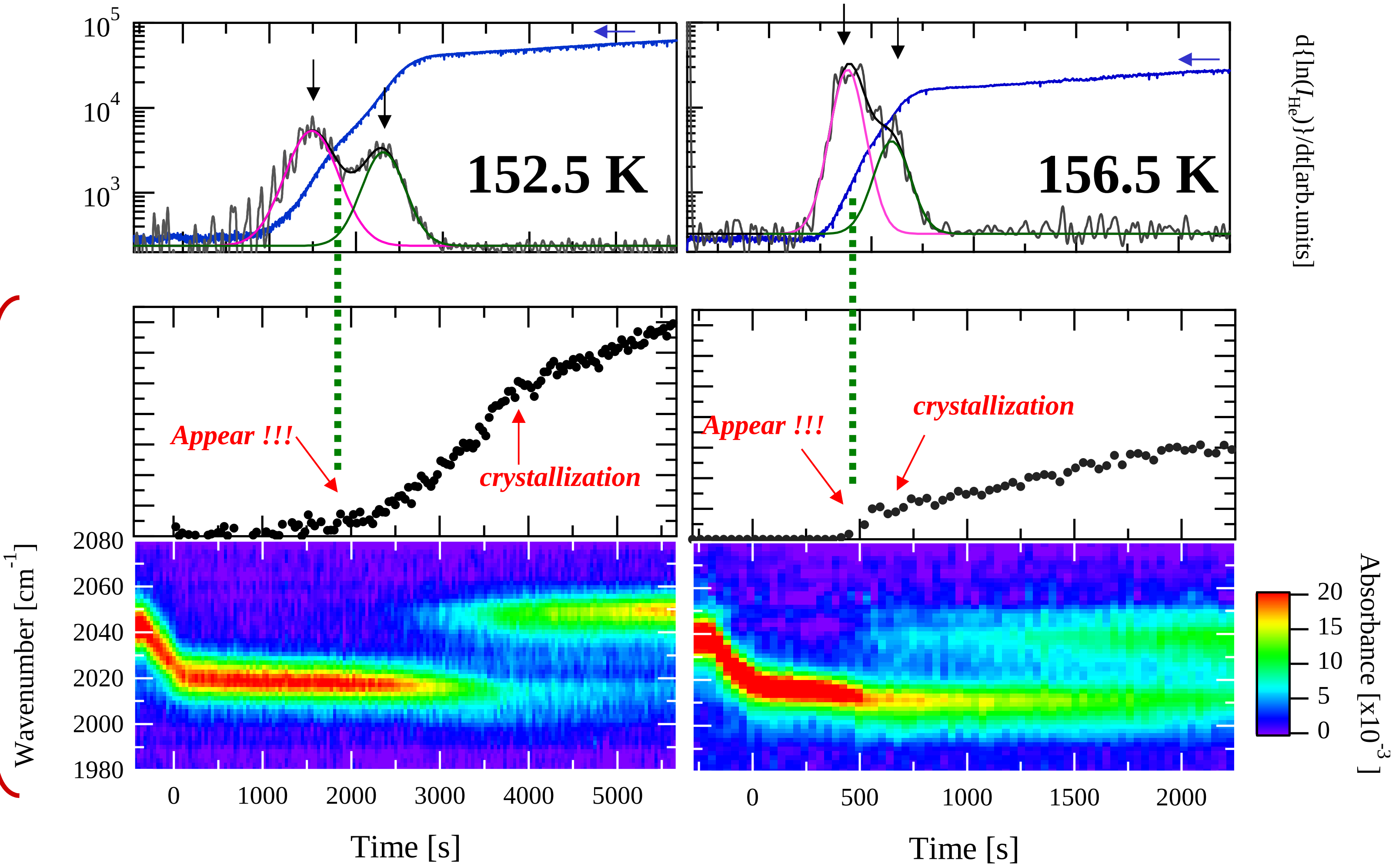
(4) HASのみが捉えた
ポテンシャル凹凸の違い



検証：下地表面が露出するタイミングの比較

Ru(0001)でのHAS

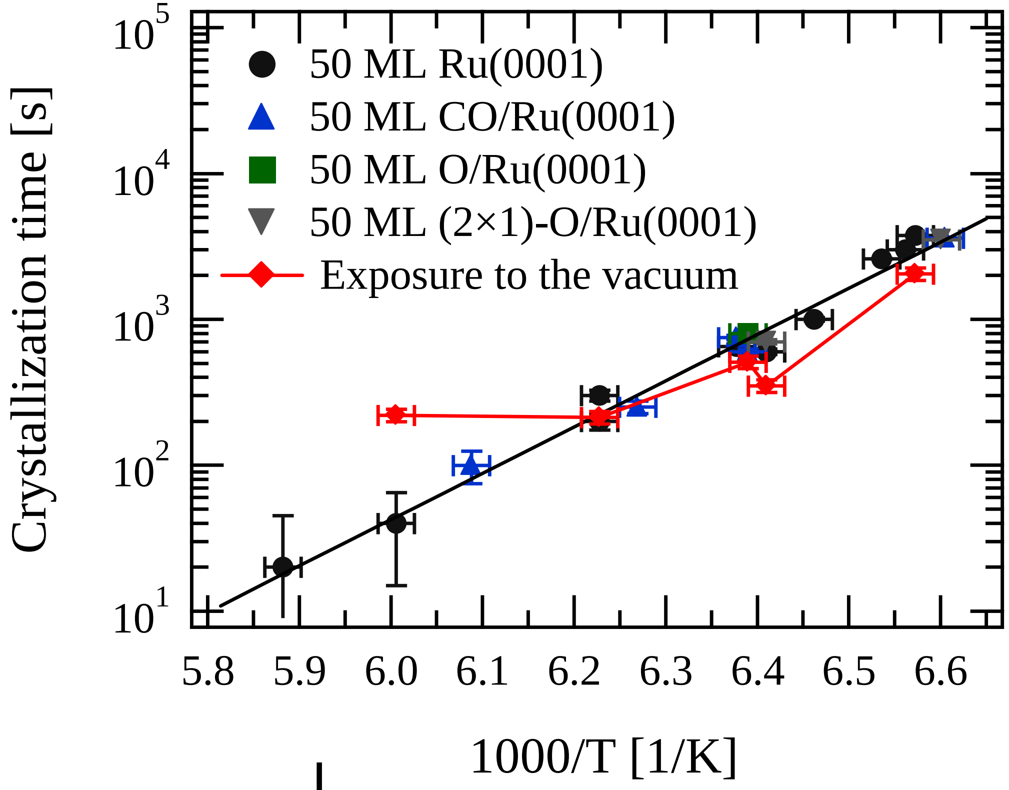
CO/Ru(0001)でのIRAS



非常に似たタイミングで下地が析出している

結晶グレインのサイズや分布が似ていることを示唆している

Activation energy of the ASW (~50 ML) crystallization on Ru(0001)



Arrhenius equation

$$k = A\exp\left(\frac{-E}{RT}\right)$$

$$\ln(k) = -\frac{E}{R}\frac{1}{T} + \ln(A)$$

k : rate coefficient of the reaction

T : temperature

A : pre-exponential factor (frequency factor)

E : activation energy of the reaction

R : gas constant (or Boltzmann constant)

$$E_{crystallize} = 650 \pm 25 \text{ meV}$$

↓

(1) 活性化エネルギーが下地に依らない

(2) 結晶化中の下地露出と結晶化の競争が起きている

結論

非破壊同時計測によりRu(0001)でのアモルファス氷(ASW)結晶化を調べた結果、以下のことが分かった：

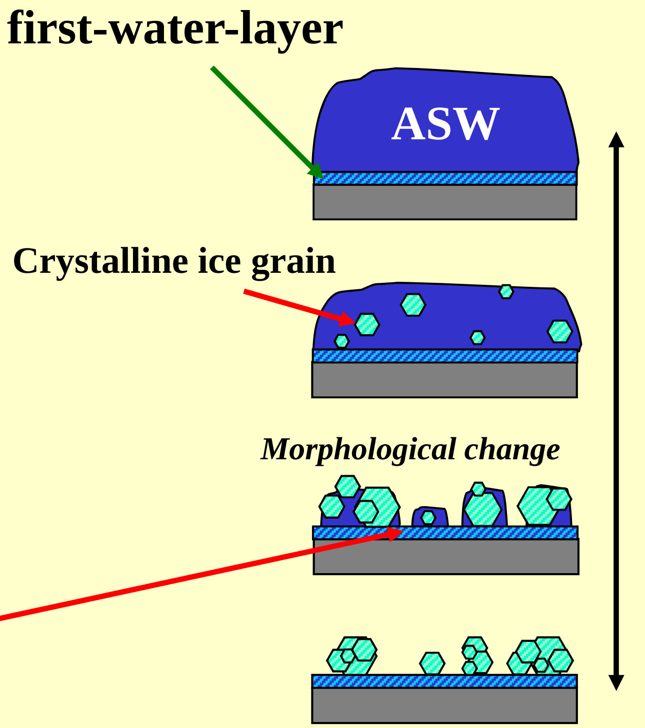
(1) **オリジナルのITPD解釈が正しい**
（脱離率の変化が結晶化の変化と対応）

(2) アモルファス氷の結晶化は下地によらず**バルク内からのランダム核形成**および**実効的等方成長**である
（Ru(0001)からのtemplate effectはおきない）

(3) 結晶化の最中に**下地の露出を伴うモフォロジーの変化**が起きている

(4) ポテンシャル凹凸は下地によって異なる
（よく定義された氷表面作成に際して極めて重要ーHASのみが捉えた！！）

T. Kondo, et al., Surf. Sci. 600 (2006) 3570-3574.
T. Kondo, et al., Chem. Phys. Lett. 448 (2007) 121-126.
T. Kondo, et al., J. Chem. Phys. 126 (2007) 181103, 1-5.
T. Kondo, et al., J. Chem. Phys. 127 (2007) 094703, 1-14.



Time for the ASW crystallization:
“τ” in ITPD

$$E_{crystallize} = 650 \pm 25\ \mathrm{meV}$$