An infrared spectroscopic approach towards understanding the orientation of dangling OH bonds

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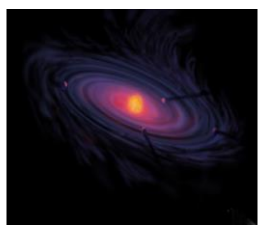
Introduction

Evolution of solar system

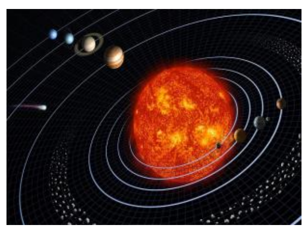
[1]

Eagle Nebula

NASA, ESA, STScI, J. Hester and P. Scowen (Arizona StateUniversity)



Proto-planetary disks



Planetary systems (Solar system)

What is the solar system made of ?

Atoms and Molecules!

[2] Interstellar clouds = the birth place of stars

	Physical properties
Size	3 trillion km 20000 times larger than the Earth–Sun distance (150 million km)
Temp.	10 - 100 K
Density	H_2: 10^3 - 10^5 cm^{-3} (1 atom = 10^{19} cm^{-3})

Extremely low-temperature and low-pressure environments.

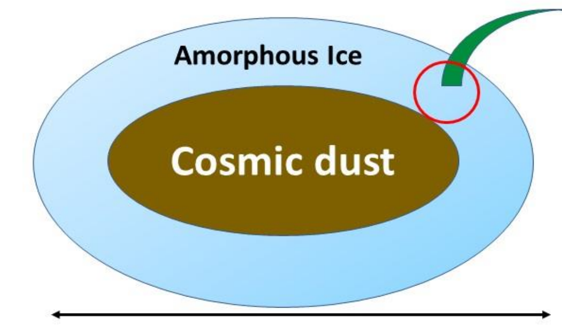
Nevertheless, interstellar clouds are "chemically rich". Around 200 molecules have been discovered.

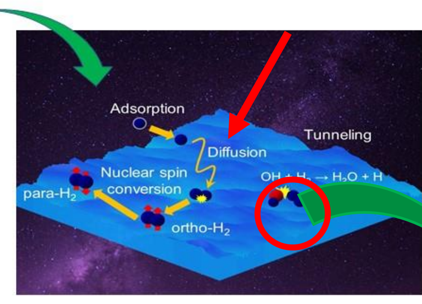
H_2, CO, O_2, H_2O, NH_3, H_2CO, CH_3OH, HCOOH, and fullerene (C_{60}), etc

Interstellar chemistry

How do such molecules evolve in space ?

[3] Gas phase reaction vs Interfacial reaction



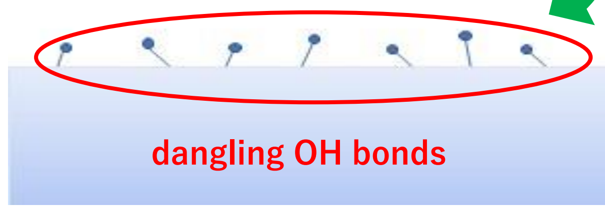


Hama and Watanabe, Chemical Reviews, 113, 8783 (2013).

- cosmic dust: mainly consisted of silicate
- amorphous ice: mainly consisted of H2O

What is the key to understanding the interfacial reaction ?

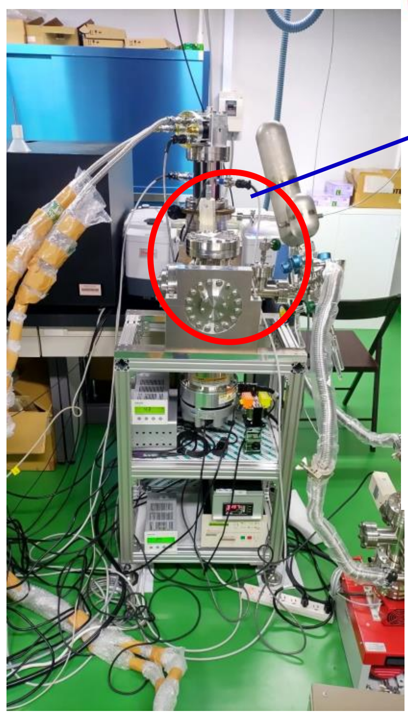
Surface structure !



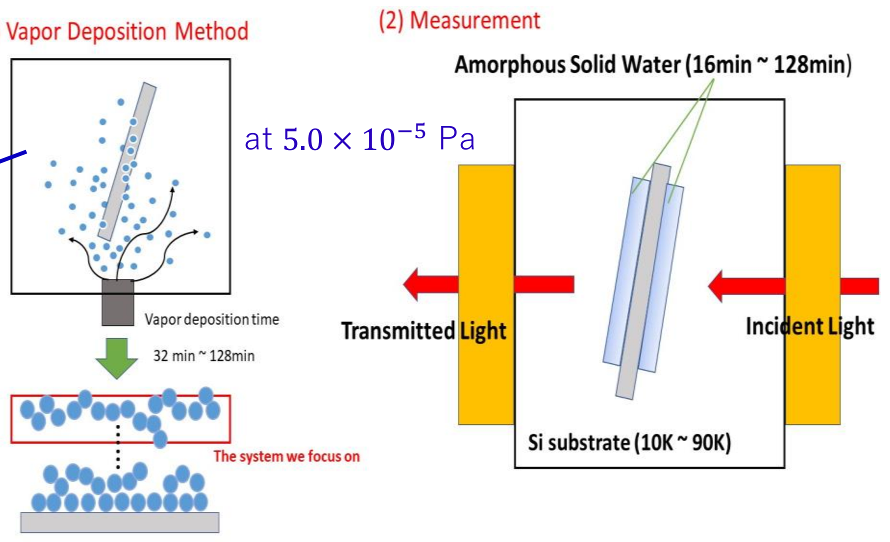
Laboratory study and method of MAIRS

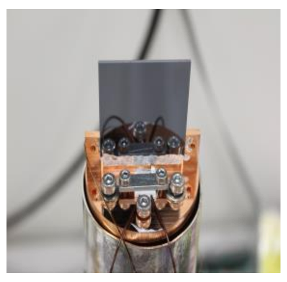
[4]

Experimental procedure



Apparatus in the Utokyo
Ultra-high vacuum chamber, He cryostat (4 K), FT-IR, He-refrigerator etc…

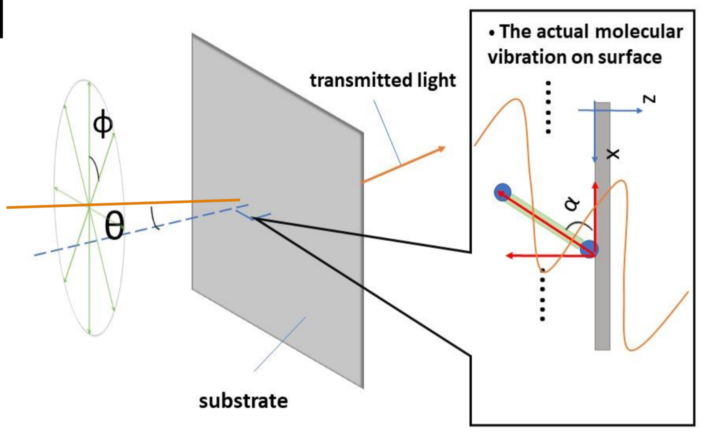




[5] Si-substrate
40 × 40 × 1mm (111)

The principle of Multiple-Angle Incidence Resolution Spectrometry(MAIRS)

[6]



oscillation of electric field

$$S = \begin{pmatrix} S_{obs1} \\ S_{obs2} \\ \vdots \end{pmatrix} = \begin{pmatrix} r_{IP,1} & r_{OP,1} \\ r_{IP,2} & r_{OP,2} \\ \vdots & \vdots \end{pmatrix} \begin{pmatrix} s_{IP} \\ s_{OP} \end{pmatrix} + U \quad -(*)$$

$$= R \begin{pmatrix} s_{IP} \\ s_{OP} \end{pmatrix} + U \quad (U: \text{non-linear term})$$

least squares method

$$\therefore \begin{pmatrix} s_{IP} \\ s_{OP} \end{pmatrix} = (R^T R)^{-1} R^T S \Rightarrow A_{IP} = -\log\left(\frac{s_{IP}^S}{s_{IP}^B}\right) \quad A_{OP} = -\log\left(\frac{s_{OP}^S}{s_{OP}^B}\right)$$

s^S: sample spectrum s^B: background spectrum

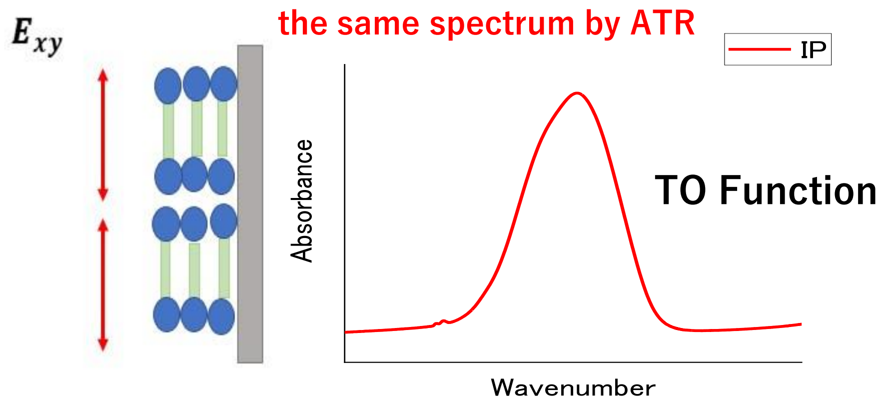
$$R = \begin{pmatrix} \gamma \cos^2\phi_1 + \sin^2\phi\,(\sin^2\theta\tan^2\theta + \cos^2\theta) & \sin^2\phi_1 \tan^2\theta \\ \vdots & \vdots \end{pmatrix}$$

γ: polarization strength ration of **s** polarization and **p** polarization on background

[7]

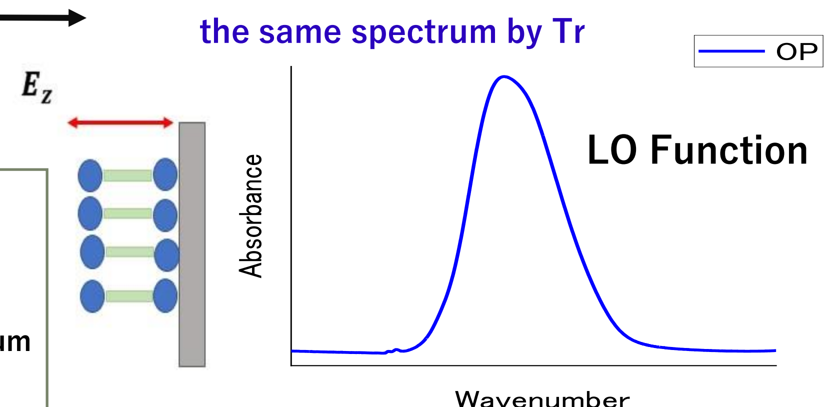
(a) In Plane spectrum

the same spectrum by ATR



(b) Out of Plane spectrum

the same spectrum by Tr

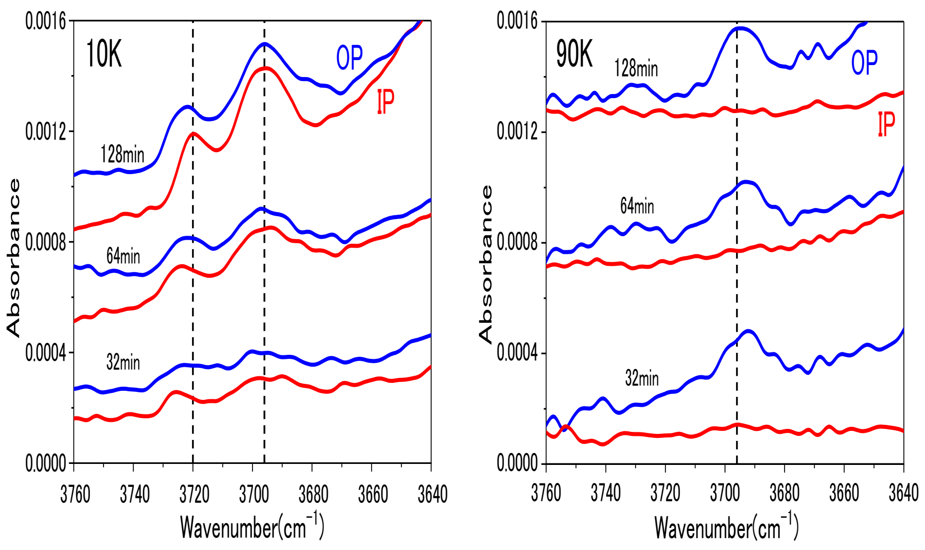


Itoh et al., J. Phys. Chem. A 2009, 113, 7810.
Hasegawa and Shioya, Bull. Chem. Soc. Jpn. 2020, 93, 1127.
Shioya et al, J. Phy. Chem. A 2019, 123, 7177-7183
Hama et al, J. Phy. Chem . Lett. 2020, 11, 7857-7866

Experimental Results

OP/IP spectrum at 10K and 90K (VD time ;128min)

[8]



VD time(min)	32	64	128
Monolayer(ML)	314 MLs	627MLs	1254MLs

1 ML = 0.386 nm

- Both IP and OP spectrum are almost the same at 10K
  → Isotropic property (random)
- Only the OP spectrum at 90K has strong peak at 3698cm^{-1} and the band strength is almost constant
  → Anisotropic property (there is some kind of order)
- The value of A_{OP} at 90K has no dependency on film thickness
  → Dangling OH bonds on outermost surface

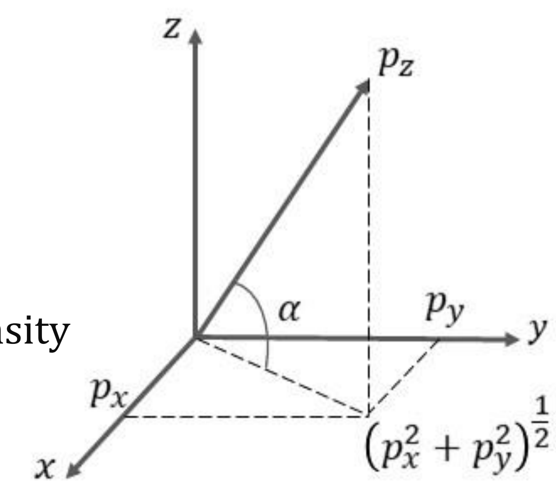
Interesting discovery !

[9] Estimation of the orientation angle

Orientation angle α

$$\alpha = \arctan\sqrt{\frac{2A_{IP}}{A_{OP}}}$$

A: integrated intensity

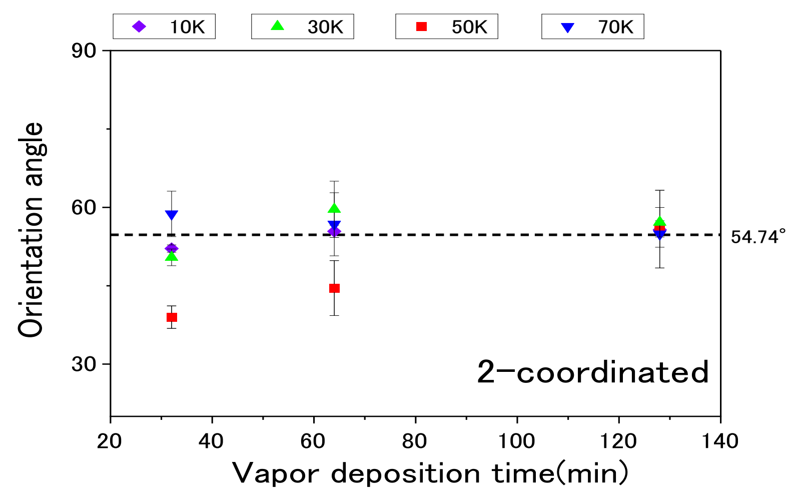


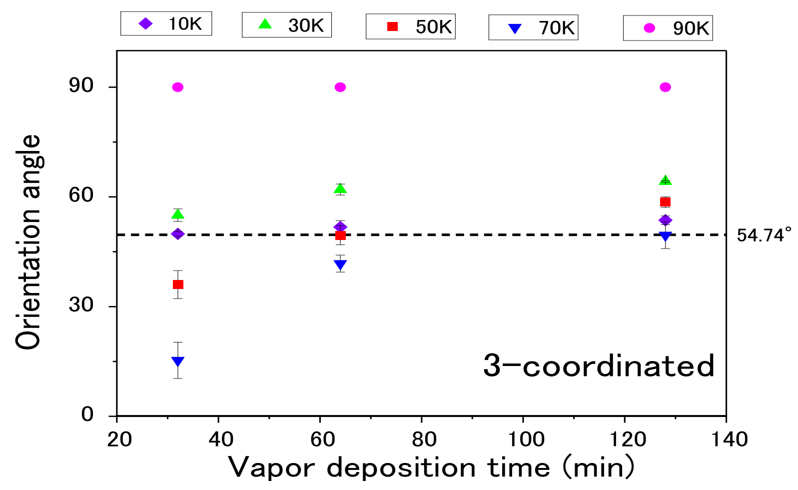
When $A_{IP} = A_{OP}$,

$$\alpha = \arctan\sqrt{2} \approx 54.74°$$

The same to the magic angle

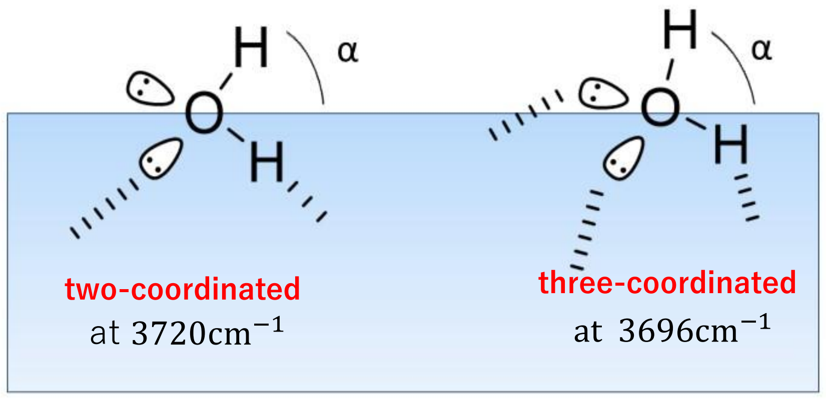
[10] Temperature dependence on orientation angle





Convergence in magic angle!

[11]mage of 2-coordinated and 3-coordinated dangling OH bonds



Buch et al., J. Chem. Phys. 1991, 94, 4091-4092

Conclusion and discussion

- Dangling OH bonds have a local order at a specific temperature(such as 90) !
- Only the 3-coordinated dangling OH bonds exist at 90K
  → This might reflect the surface structure of ASW
- The value of A_{OP} at 90K is almost constant
  → Is the outermost surface of ASW flat and dense?

Why do the 2-coordinated dangling OH bonds disappear at 90K ?

→ Does the structure of 3-dOH under extraordinary circumstances prohibit 2-dOH from developing on the surface ?

One of the example of ASW structure we could deduce