Interstellar cold dust surface chemistry: a key to understanding molecular evolution in space

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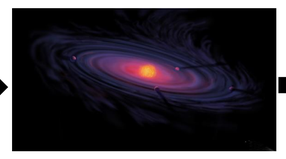
Introduction

Interstellar chemistry

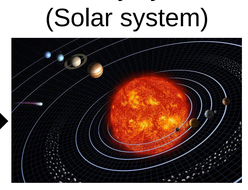
The formation of planetary systems (Solar system)
How do interstellar atoms evolve into molecules and solids?

Interstellar clouds (10–100 K)

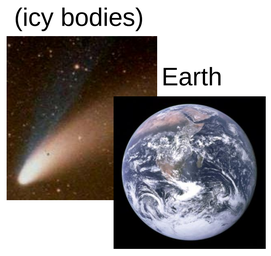
Proto-planetary disks



Planetary systems (Solar system)

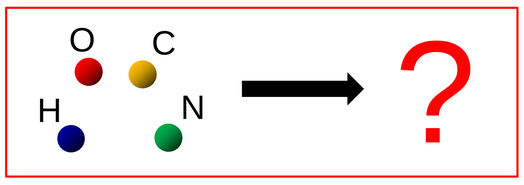


Comets (icy bodies)

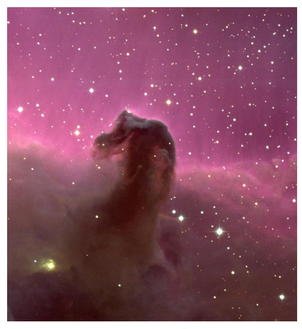


Earth

Molecular evolution



Interstellar clouds: the birth places of stars



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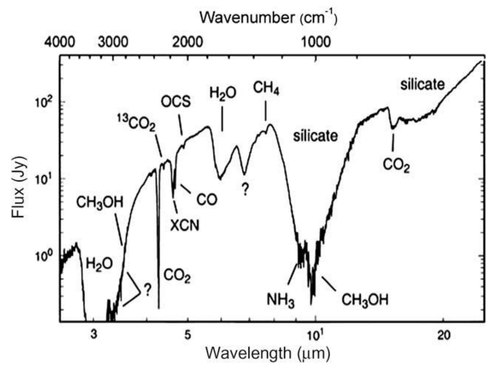
Physical properties	
Size	3 trillion km 20000 times larger than the Earth–Sun distance (150 million km)
Temp.	10 - 100 K
Density	H_2: 10^3 - 10^5 cm^{-3} (1 atom = 10^{19} cm^{-3})

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…

How are molecules formed in interstellar clouds?

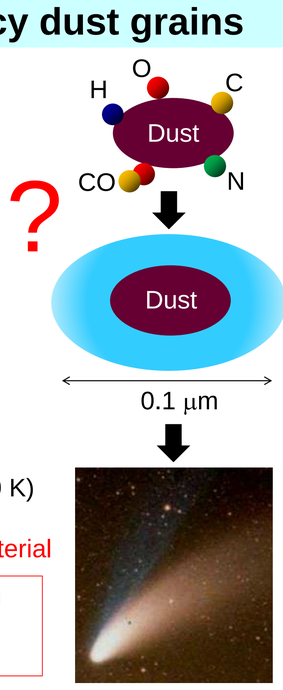
Infrared observation: icy dust grains



Gibb et al. Astrophys. J. (2000).

Silicate dust covered with H_2O ice (T_{cry}=140 K)
Similar chemical constituents to comets
Icy grains are the precursors of planetary material

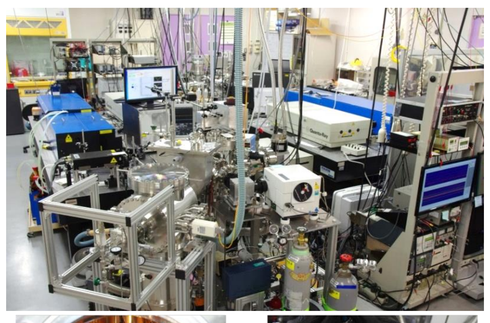
Gas-phase chemistry cannot explain the observational results
Dust surface chemistry is key



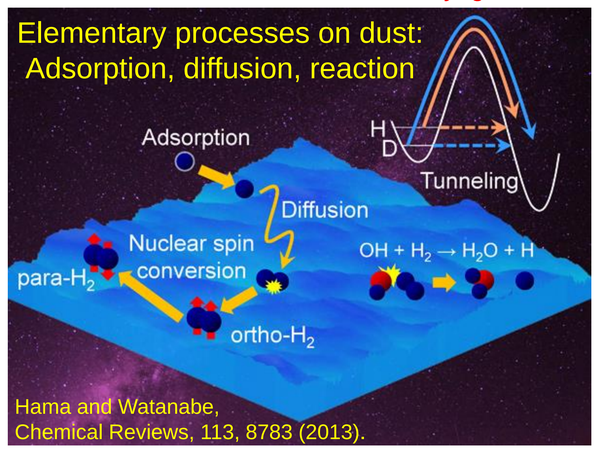
Laboratory study for interstellar dust surface chemistry

Experimental setup: an interdisciplinary science

Machines in Hokkaido Univ.
Ultra-high vacuum chamber, He cryostat (4 K), lasers, FT-IR, H-atom source etc…



Interstellar chemistry covers quantum chemistry, spectroscopy, and surface physics, as well as vacuum science and cryogenics



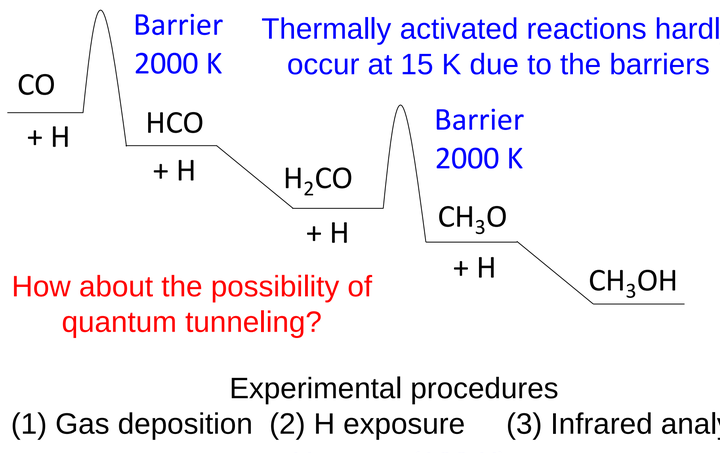
(1) Surface diffusion of H atom on water ice: thermal hopping vs quantum tunneling
Hama et al., Astrophys. J. (2012). Kuwahata and Hama et al., Phys. Rev. Lett. (2015).

(2) Surface chemical reactions driven by quantum tunneling
Hama and Watanabe, Chem. Rev. (2013)., Hama et al., PNAS (2015).

(3) Nuclear-spin isomers of H_2O desorbed from ice and the origin of water in space
Hama et al., Science (2016). Hama et al., Astrophys. J. Lett. (2018).

H_2CO and CH_3OH formation at 15 K by tunneling

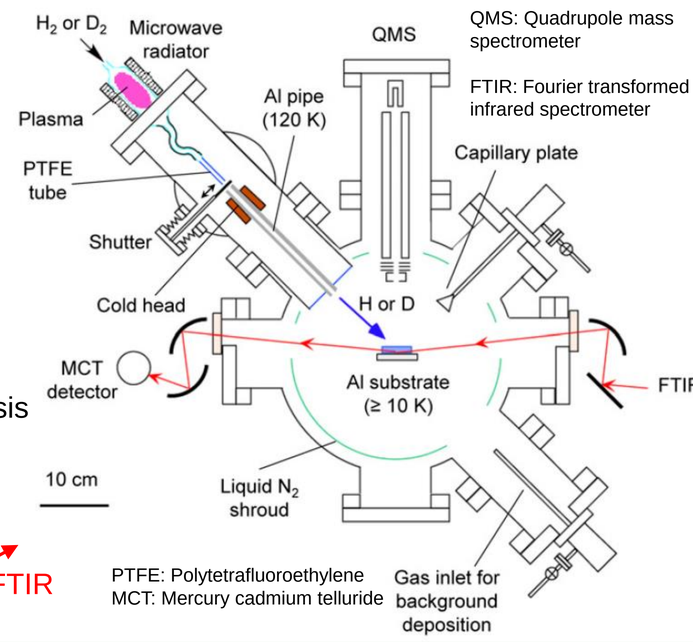
H atom addition reactions to CO:
$CO + H \rightarrow HCO$ $HCO + H \rightarrow H_2CO$
$H_2CO + H \rightarrow CH_3CO$ $CH_3CO + H \rightarrow CH_3OH$



Thermally activated reactions hardly occur at 15 K due to the barriers

How about the possibility of quantum tunneling?

H atom source: Microwave-induced plasma.
Cooled to 120 K with a cold Al pipe.
Flux: 4-5 × 10^{14} atoms cm^{-2} s^{-1}
(2 s = 1 monolayer (ML) = 10^{15} cm^{-2} s^{-1})

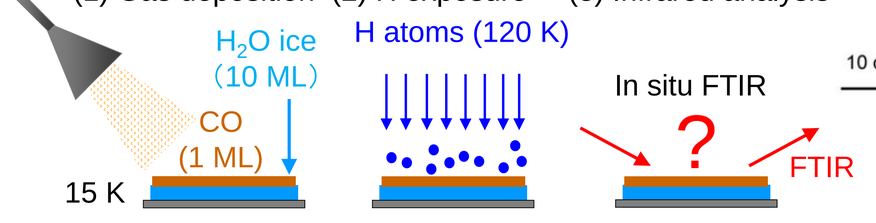


QMS: Quadrupole mass spectrometer

FTIR: Fourier transformed infrared spectrometer

PTFE: Polytetrafluoroethylene
MCT: Mercury cadmium telluride

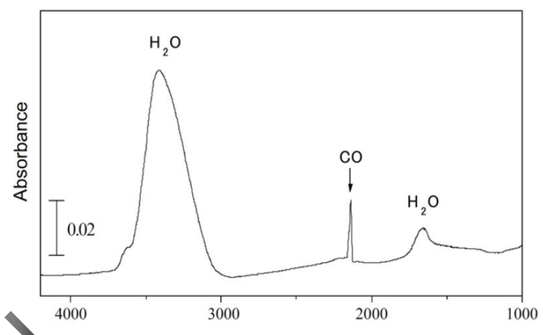
Experimental procedures
(1) Gas deposition (2) H exposure (3) Infrared analysis



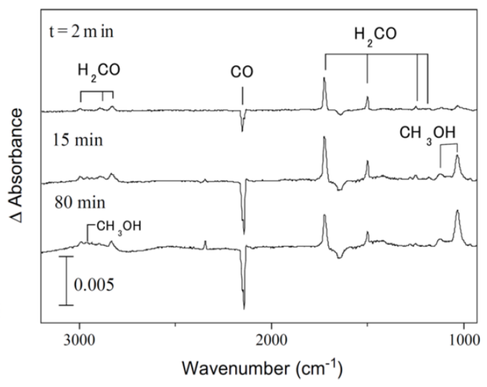
Experimental Results

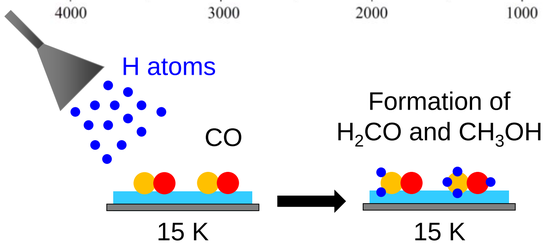
Cold H atom addition reactions to CO at 15 K

CO on H_2O ice at 15 K



Differential spectra during H exposure



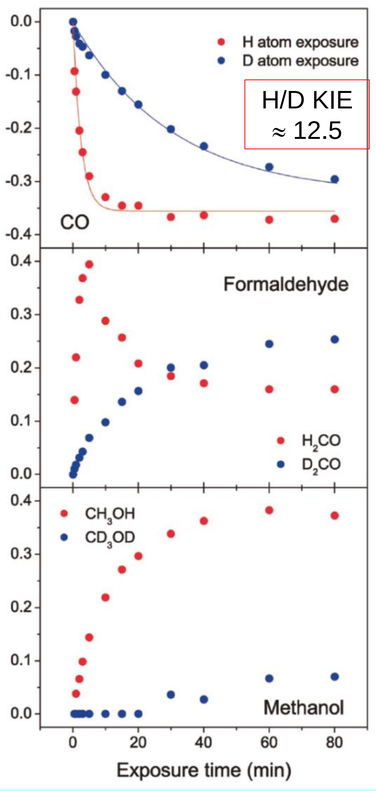


Chemical compositions of ice grains (%)

H_2O	100	CO	5-8
CO_2	20-13	CH_4	<2
NH_3	7-15	HCCOH	< 0.09
H_2CO	2-3	CH_3OH	4-17

2 hrs exposure = Lifetime of interstellar clouds (~10^7 years)
H_2CO and CH_3OH can be formed from CO in interstellar clouds !!

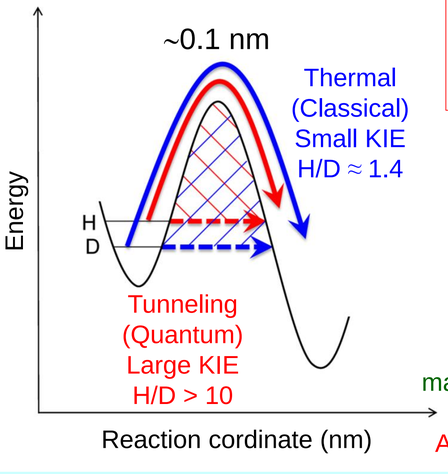
Large H/D kinetic isotope effect → Quantum tunneling!



De Broglie wavelength (nm) for particles with kinetic energy E_k

$$\lambda = h/mv = h/(2mE_k)^{1/2}$$

E_k (kJ mol^{-1})	H (1)	D (2)	C (12)
0.08 (10 K)	0.98 nm	0.69 nm	0.28 nm
2.5 (300 K)	0.18 nm	0.13 nm	0.05 nm



λ is larger than the typical barrier width (~0.1 nm) of chemical reaction, especially at low temp.

Tunneling rate k_q (s^{-1}) for reaction having a rectangular potential

$$k_q \approx \nu G \approx \nu \exp\left\{\frac{-2a[2\mu E_{ac}]^{1/2}}{\hbar}\right\}$$

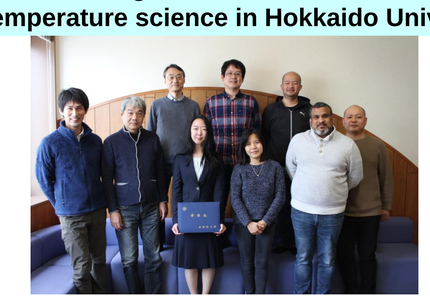
G = Tunneling probability: Barrier width (a) and mass (μ) are important, as well as barrier height (E_{ac})
ν = frequency factor (10^{13} s^{-1}):
Adsorption time of H atoms is also important for k_q

Conclusions: Molecular evolution by quantum tunneling

Tunneling reactions are efficient at low temp.
(1) λ is larger than the typical barrier width (~0.1 nm) of reaction.
(2) Long-time interaction of reactants on dust ↔ Single collision in gas phase

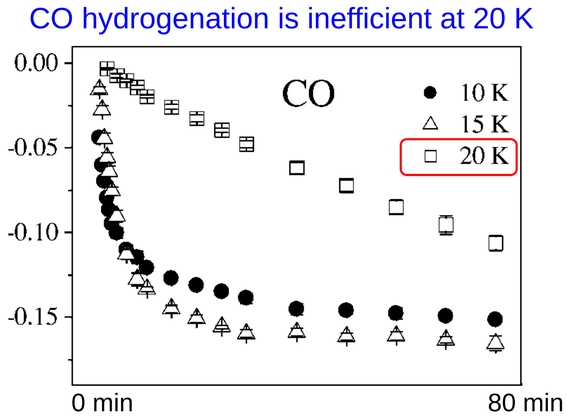
Many reactions driven by quantum tunneling
H-addition
Monoxide→ Aldehyde, Alcohol, and Amine
$CO + H \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3OH$
$NO + H \rightarrow\rightarrow\rightarrow NH_2OH$
Oxygen → Hydrogen-peroxide, and Water
$O_2 + H \rightarrow\rightarrow H_2O_2$ $H_2O_2 + H \rightarrow H_2O + OH$ (tunneling)
Aromatic → Aliphatic
$C_6H_6 + H \rightarrow C_6H_{12}$
(Benzene → Cyclohexane)
H-transfer
Water-formation
$OH + H_2$: $H_2O + H$

Acknowledgements: Institute of low temperature science in Hokkaido Univ.



Why is tunneling effective at low temperature? Long-time adsorption of H atoms is critical for tunneling

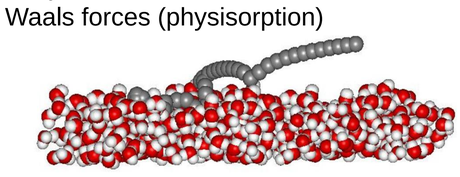
CO hydrogenation is inefficient at 20 K



H atoms can barrierlessly adsorb on the dust surface through van der Waals forces (physisorption)

H atom on amorphous ice:
E = 300-650 K (1 kcal/mol)

$$t = \nu^{-1} \exp(E/k_B T)$$



Adsorption time (t) on ice (E = 450 K, ν = 10^{13} s^{-1})

Temp. (K)	Time (s)
10	10^6 (1 month)
20	10^{-3} (1 ms)
30	10^{-7} (100 ns)