

Surface Chemistry of the ISM

— Experimental approach to grain surface processes —

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Institute of Low Temperature Science, Hokkaido University, Japan

1. Introduction

2. H₂ formation on ice

Surface diffusion, Ortho-to-para ratios

3. Formation of H₂O, H₂CO, CH₃OH, etc.

4. Prospects

Molecular cloud



- Birthplace of stars and planets
- $10\text{ K} < T$
- $n_{\text{gas}} \sim 10^{4-6}\text{ cm}^{-3}$
- Many species > 140
- Ice dust : $\sim 10^{-8}\text{ cm}^{-3}$

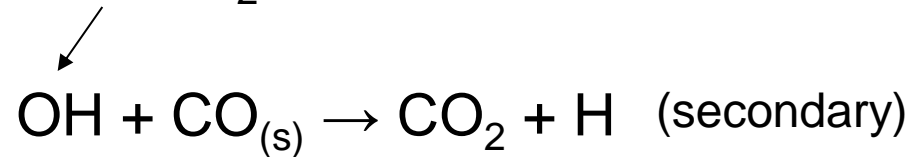
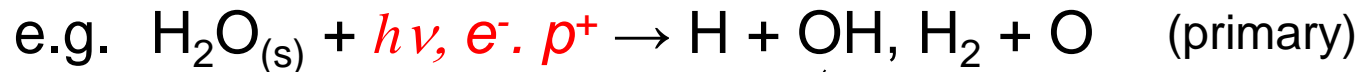
Gas phase reactions

- mainly,
ion-molecule reactions
- reaction network models

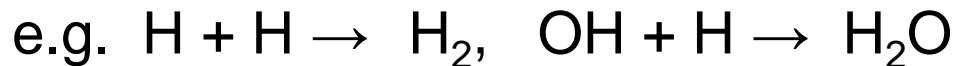
Solid phase reactions on/in ice dust

necessary for
 H_2 , H_2O , organic molecules

Energetic process (irradiation of ice mantle)



Nonenergetic surface reaction on ice



What's the advantage of surface reaction
compared to gas phase reaction?

In the core of dense clouds,

H atom flux > UV, e⁻, p⁺ fluxes



Important !

Nonenergetic surface reaction on ice

$A + BC \rightarrow ABC$ without external energy input like UV and cosmic ray

e.g. $H + H \rightarrow H_2$, $OH + H \rightarrow H_2O$

What's the advantage of surface reaction
compared to gas phase reaction?

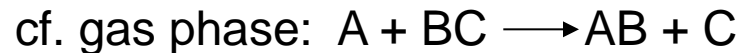
Advantages of grain surface processes

☆ Low temperature surfaces accumulate reactants

- Long interaction (residence) time enables reactions having small cross sections to proceed. → e.g. tunneling reactions

☆ The surface can act as a third body for reactions (excess energy absorber).

- Simple addition reactions can proceed without dissociation.



☆ Catalytic effect

- Reactions, Ortho-to-para (nuclear spin) conversion, etc.

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H₂ formation on ice dust



- To maintain the number density of H₂ in MC, the formation rate needs to balance with destruction rate by cosmic ray.



~ 1 molecule / day / dust assuming $n_d \sim 10^{-12} n_H$

- Accretion rate of H atom on dust ~ 1 /day in MC
- Sticking coefficient of H atom ~1 @ 10 K (MD calc. & experiment)

If H atom migrates on the dust surface significantly at 10 K,
the formation rate can reach at ~1 molecule /day.

Need to know the **surface diffusion of H atom** on ice grain at 10 K!

Theoretical approach to H₂ formation on ice

- ☆ Gould & Salpeter 1963; Hollenbach & Salpeter 1970, 1971

First estimation of H₂ formation rate on dust by semi-classical model

$$R_G = \frac{1}{2} \gamma \bar{v}_H n_g n_H \bar{\sigma}_g$$

→ The **Key factor** depending on **diffusion rate**.

Assuming **tunneling diffusion on periodic potential**,

Observation can be reproduced at the dust temp of 5~20K.

- ☆ Smoluchowski 1979

Taking tunneling diffusion on **nonperiodic** potential of ice,

diffusion rate: 3 orders smaller than previous reports.

 H₂ formation at 10K

Hard to predict diffusion theoretically.

Experimental approach is desirable.

Activation energy for the diffusion of H atom on ice

☆ First set of experiments where H₂ detected after H deposition

Perets et al. (2005)

40meV

×

Matar et al. (2008)

22meV

○

} H₂ formation at 10 K

Assuming thermal hopping

☆ More recent experiments (direct H atom detection on ice)

Watanabe et al. (2010)

~ 22meV

>30meV

Dominant !

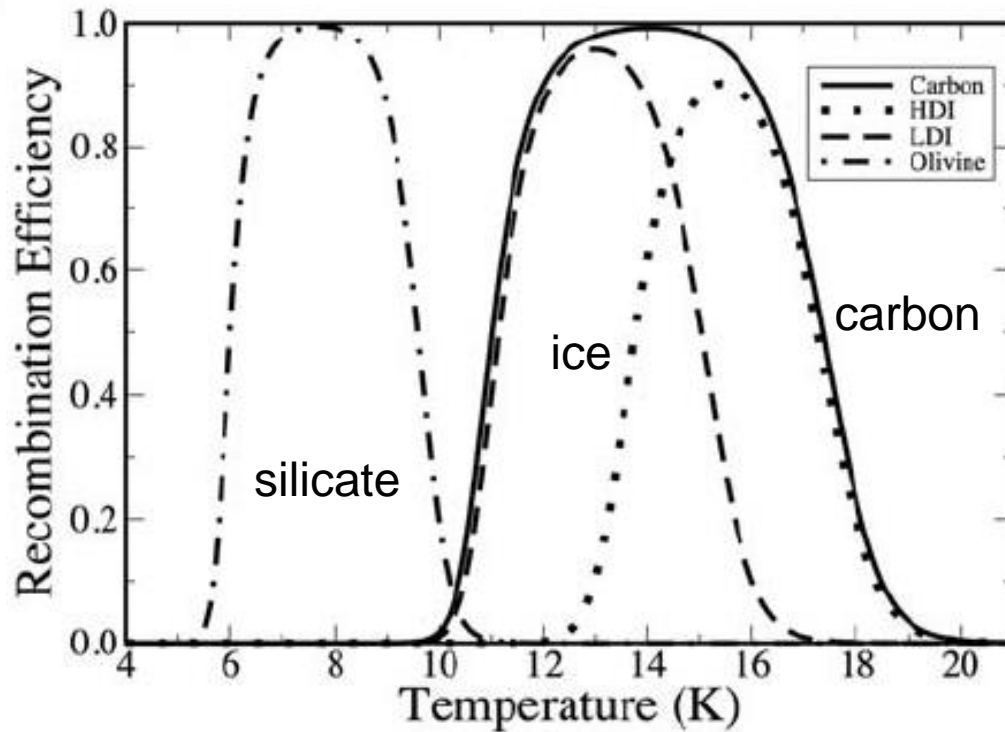
Kuwahata et al. (2015) diffusion on ice: thermal hopping + tunneling

Experiments can reproduce the H₂ abundance well.

Further information about H₂ formation,

see Wakelam et al. *Molecular Astrophys.* 9, 1 (2017)

H₂ formation on dust strongly depends on temperatures



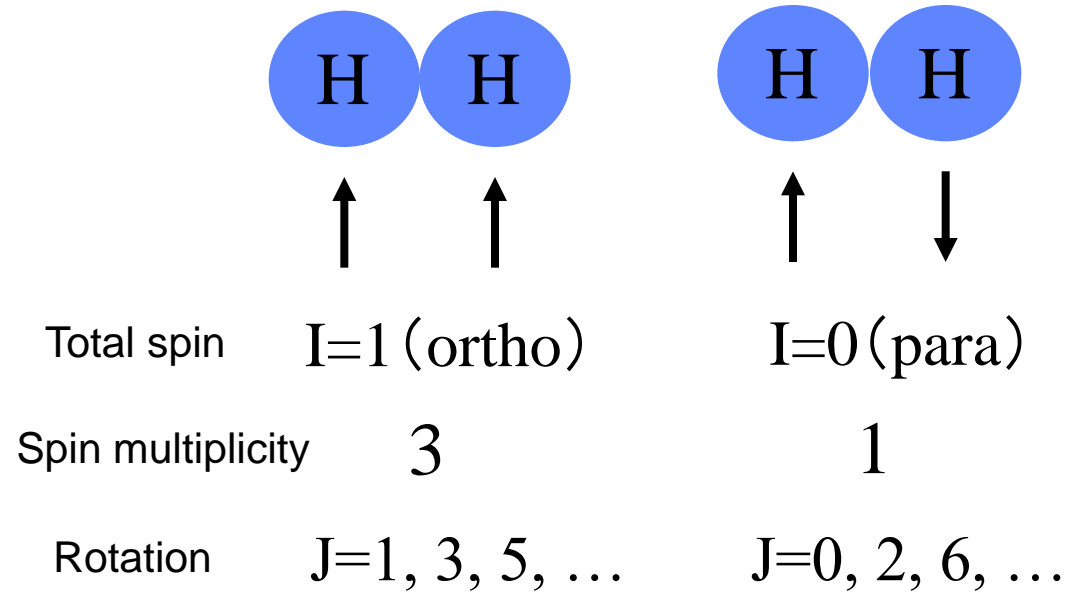
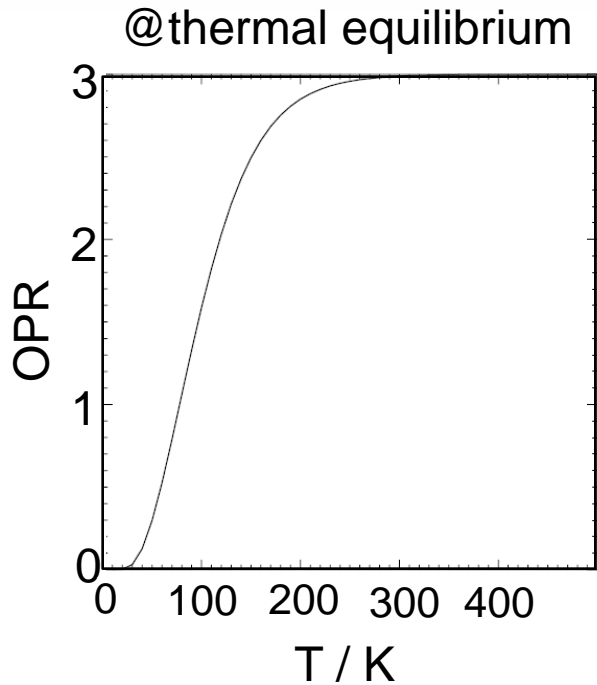
Temperature window available for H₂ formation on dust (Vidali+ 2006)

Sticking coefficient of H atom drops significantly at around 20 K

Formation process at higher temp.

- H abstraction reaction from hydrogenated surface ($\text{HX} + \text{H} \rightarrow \text{H}_2 + \text{X}$)
- Photolysis of hydrogenated solid such as H₂O and PAH

Ortho-to-para ratio (OPR) of H₂

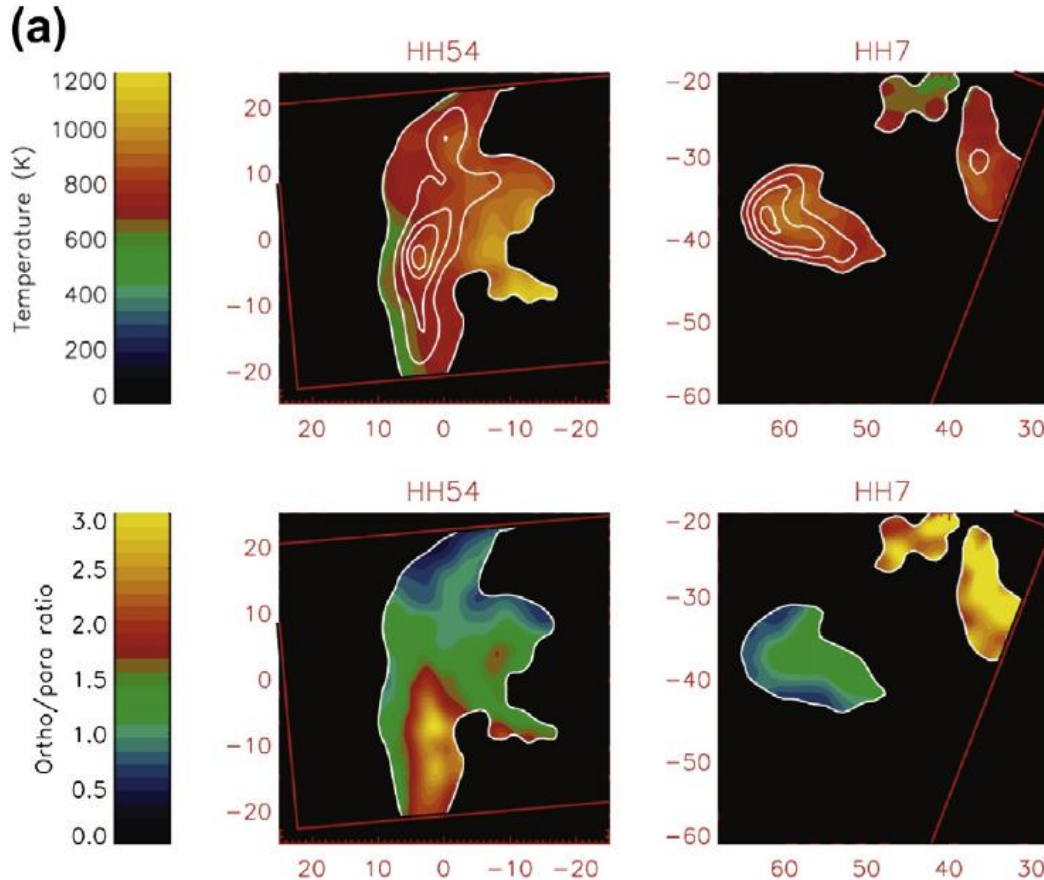


Radiative transformation (O ↔ P) is forbidden

$$\text{OPR} = N_{\text{ortho}} / N_{\text{para}} = \frac{\sum_{v, J=\text{odd}} g_I (2J+1) \exp(-E_{v,J} / kT)}{\sum_{v, J=\text{even}} g_I (2J+1) \exp(-E_{v,J} / kT)}$$

OPR at high temperature limit = **3** (e.g. 0.01 @30K)

Observations of OPRs for H₂



@ PDRs

OPRs ~ 1

lower than 3 expected from rotational temps.

e.g. Harbart *et al.* 2003, 2011
Fleming *et al.* 2010

@ Shock regions

Upper : rotational 600-1000 K

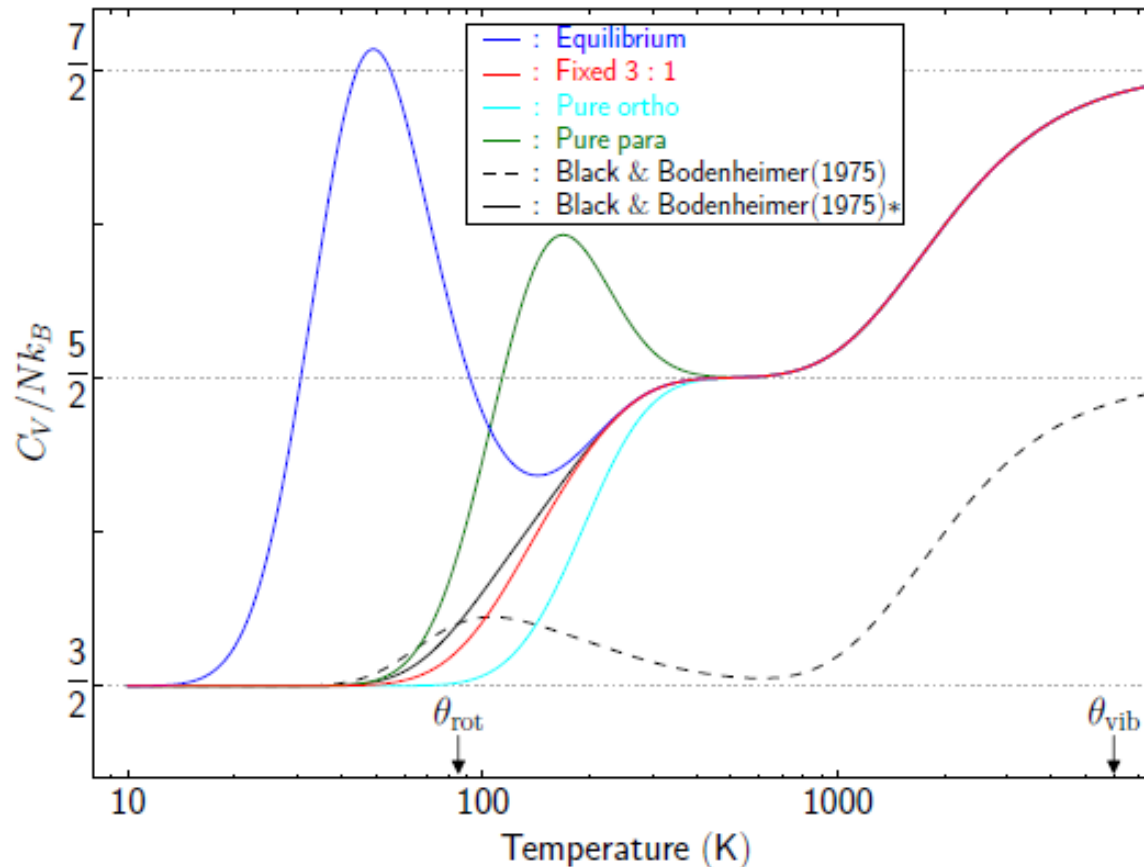
Lower : OPR 0.5-3

Neufeld *et al.* *ApJ* 649, 816 (2006)

The OPRs are out-of-equilibrium !

Importance of OPR for H₂

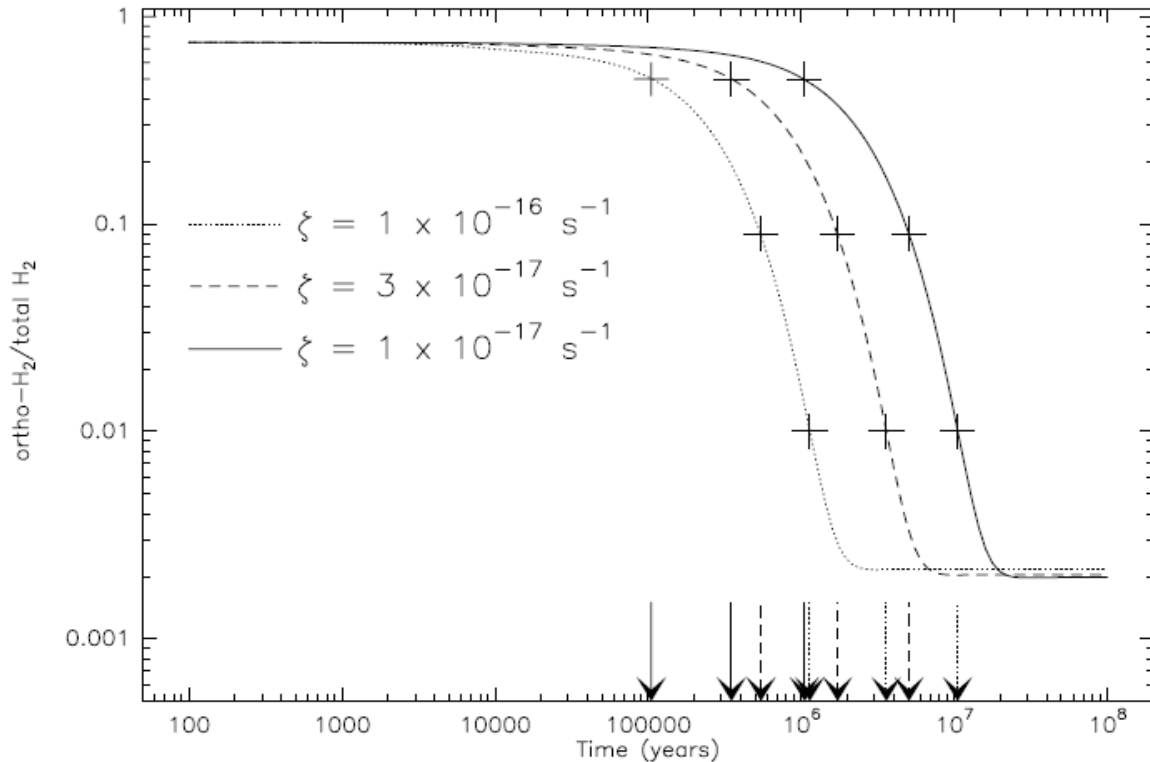
- ☆ The OPR affects dynamics of core formation in star-forming region.



Heat capacity of H₂ gas with different OPRs
(Vaytet *et al.* A&A 563, A85 (2014))

Importance of OPR for H₂

- ★ Slow conversion process between two spin isomers has been used as a tracer of the age of clouds.



Variation of ortho-abundance at different cosmic-ray fields by spin-exchange reactions in gas phase. The OPR starts from 3 in this model (Pagani *et al.* A&A 551, A38 (2013))

Importance of OPR for H₂

☆ The OPR can control chemical evolution in molecular clouds.

The lowest $\Delta E_{o-p} \sim 170 \text{ K} \longrightarrow$ The OPR of H₂ significantly affects chemistry in molecular clouds

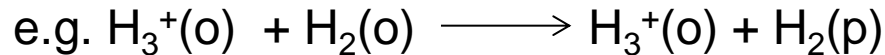


Important species for deuterium enrichment in molecules

What **is the meaning of** the observed OPR (spin temperature) ?
controls

⊘ radiative process \longrightarrow *spin temp can be a tracer of physicochemical history of molecules...*

☆ OPR can change in **gas phase** by spin exchange reaction, but slow.

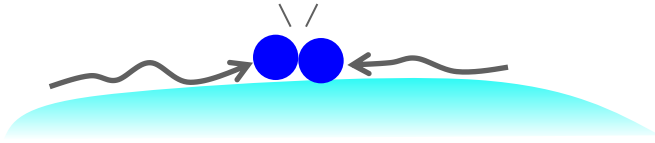


☆ **Little is known** about how the OPR behaves on **grains** (temp., structure, composition, etc).

Look at how the OPRs of H_2 behave on ice dust at ~ 10 K !

Experimental findings in OPR of H₂ on ice at ~10 K

OPR of nascent H₂ on ice



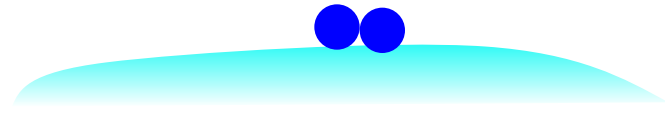
Theory : ~3 without exp. evidence

OPR of nascent H₂ formed by recombination is ~3

Watanabe *et al.* 2010

Gavilan *et al.* 2012

OP conversion on ice with time
No theoretical prediction



First observed by IR

Buch & Devlin 1993

OPR of H₂ decreases significantly for several minutes

Watanabe *et al.* 2010

Large isotope effect on conversion rate

H₂ (~370s) >> D₂

Sugimoto & Fukutani 2011

Hama *et al.* 2012

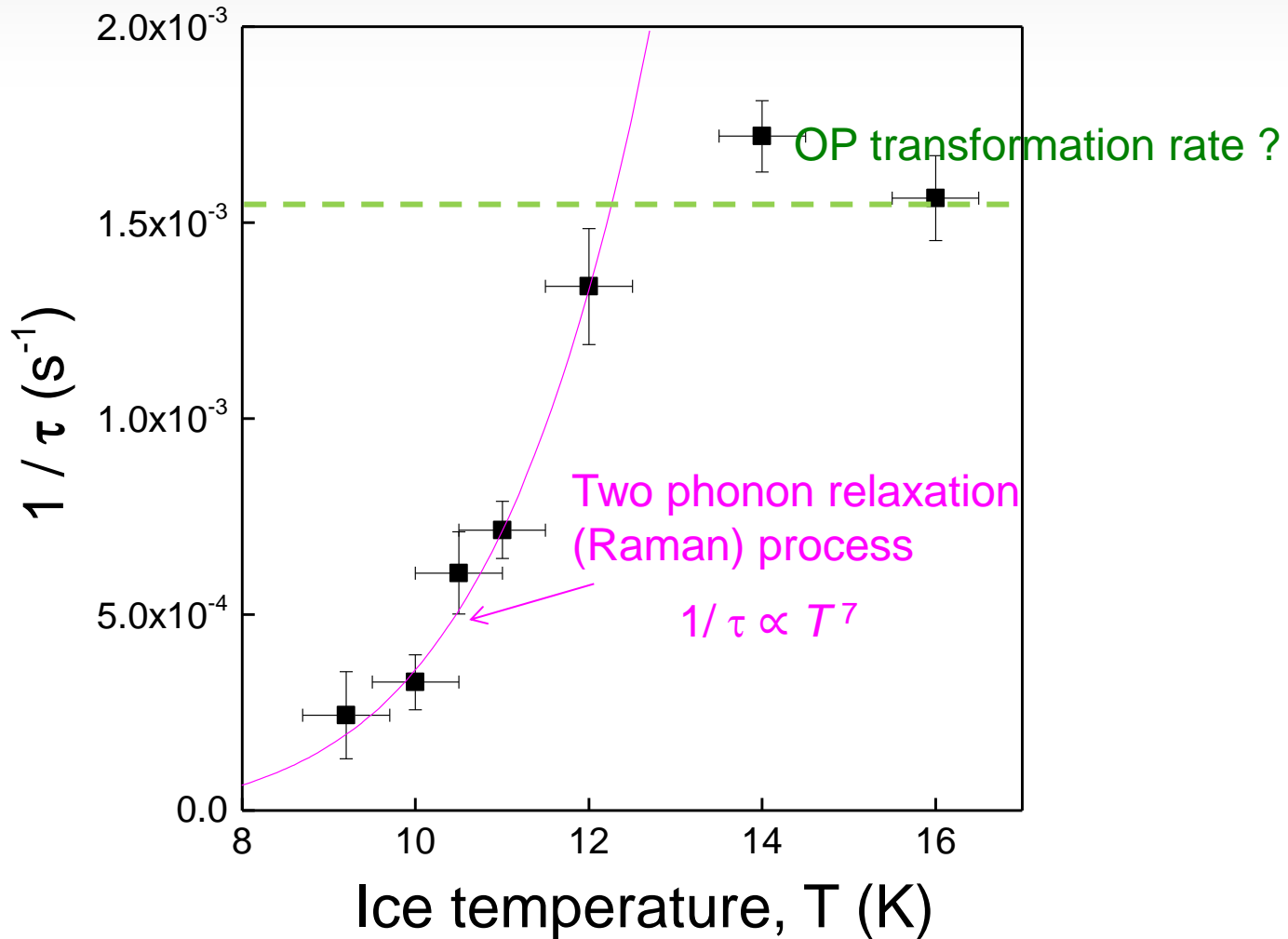
Trace O₂ molecules accelerate the OP conversion for D₂

Chehrouri *et al.* 2011

Temperature dependence of OP conversion

Ueta *et al.*, 2016

OP conversion rate vs surface temperature

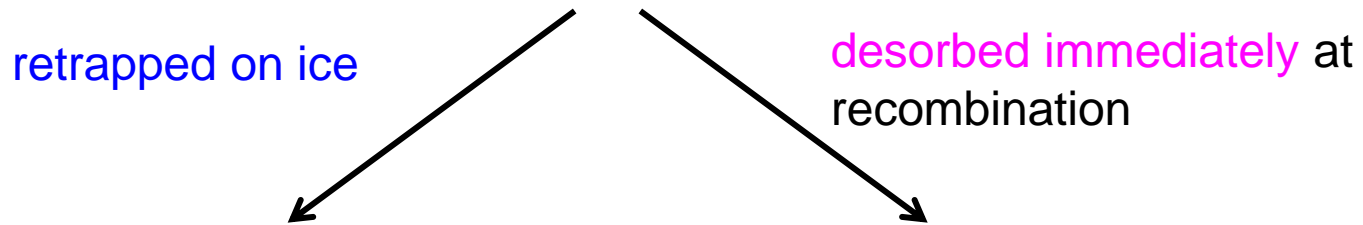


Steep increase of conversion rate cannot be explained by state-mixing alone.

Energy dissipation process should be considered.

Astrochemical story for OPR of H₂ molecule starting from the ice grain

The OPR of nascent H₂ ~ 3 on ice (ASW)



OPR decreases rapidly on ASW.
OPR depends on the dust temp and when
H₂ is released in gas phase

OPR ~ 3

OP conversion in gas phase

e.g. for the gas phase reactions, see

D. Gerlich *et al.*, *Philos. Trans. A. Math. Phys. Eng. Sci.* **364**, 3007 (2006).

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Main components in an ice dust mantle

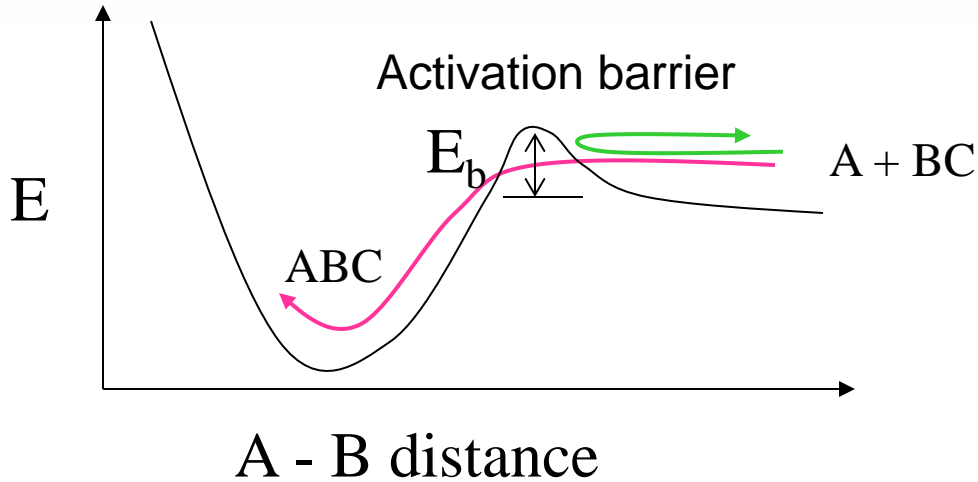
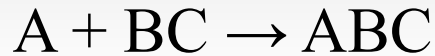
(from Gibb *et al.* 2004)

Molecules	W33A high	NGC7538 IRS9/high	Elias29 low	Elias16 field
H ₂ O	100	100	100	100
CO	8.1	17	5.0	25
CO ₂	13.2	23	19.7	24
H ₂ CO	3.1	2.2	—	—
CH ₃ OH	17	4.3	<15.6	<2.9
CH ₄	1.5	1.5	<1.6	—
NH ₃	15	15	<7.3	<10

Gas phase
synthesis

How these primordial molecules are produced on ice dust?

Tunneling reaction: key process for molecular formation



Q1: Why does it occur?

Ans1: because of the wave nature of atoms

$$\lambda = \frac{h}{\sqrt{2mkT}}$$

(free particle case)

Q2: Probability of the tunneling reaction

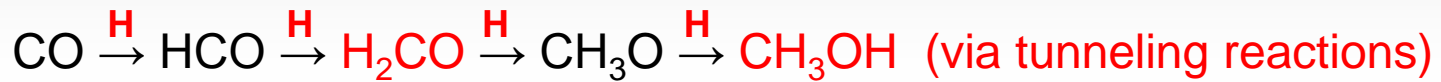
Ans2:

$$P = \exp\left[-2a\sqrt{\frac{2m(E_b - E_0)}{\hbar^2}}\right] \quad (\text{in the case of rectangular barrier})$$

Tunneling reaction becomes prominent

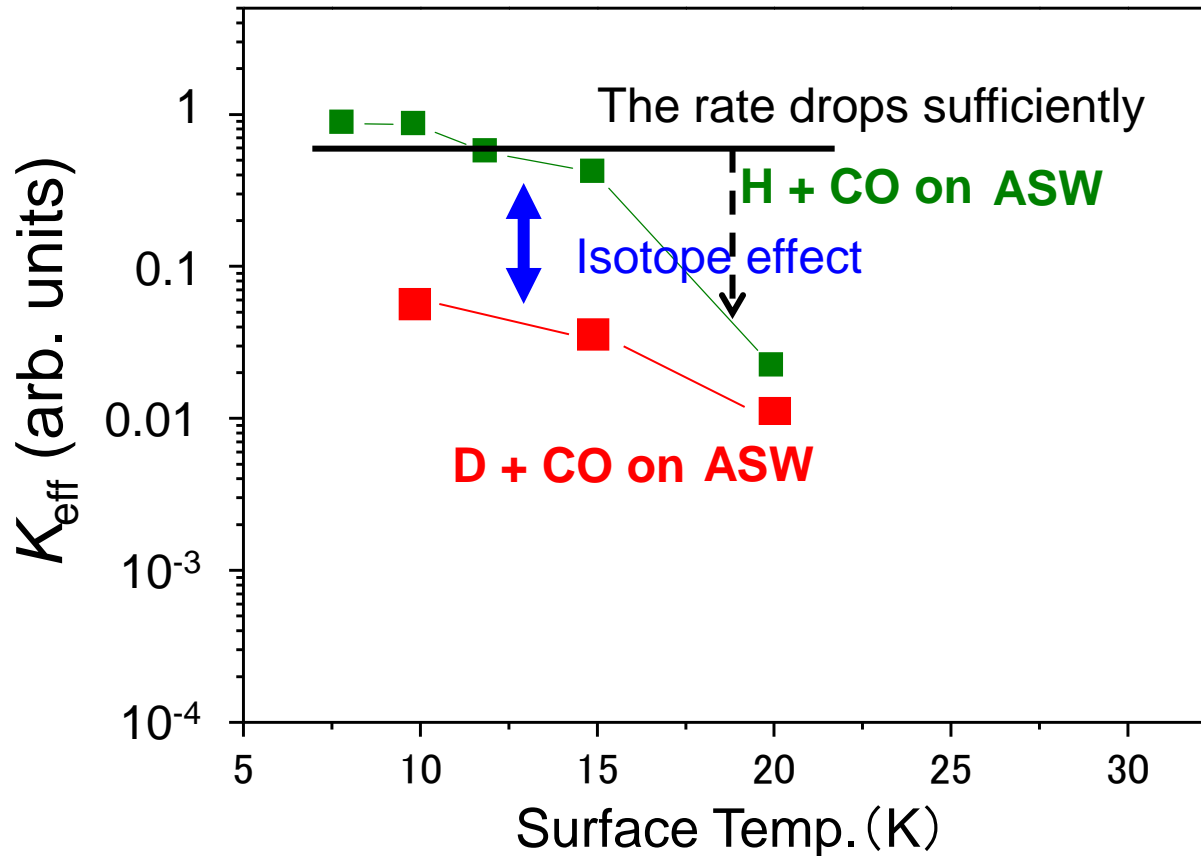
with **low mass particle at low temperatures !**

Formaldehyde & methanol formation on dust grains



e.g. Watanabe & Kouchi *ApJ* 571, L173 (2002)+, .

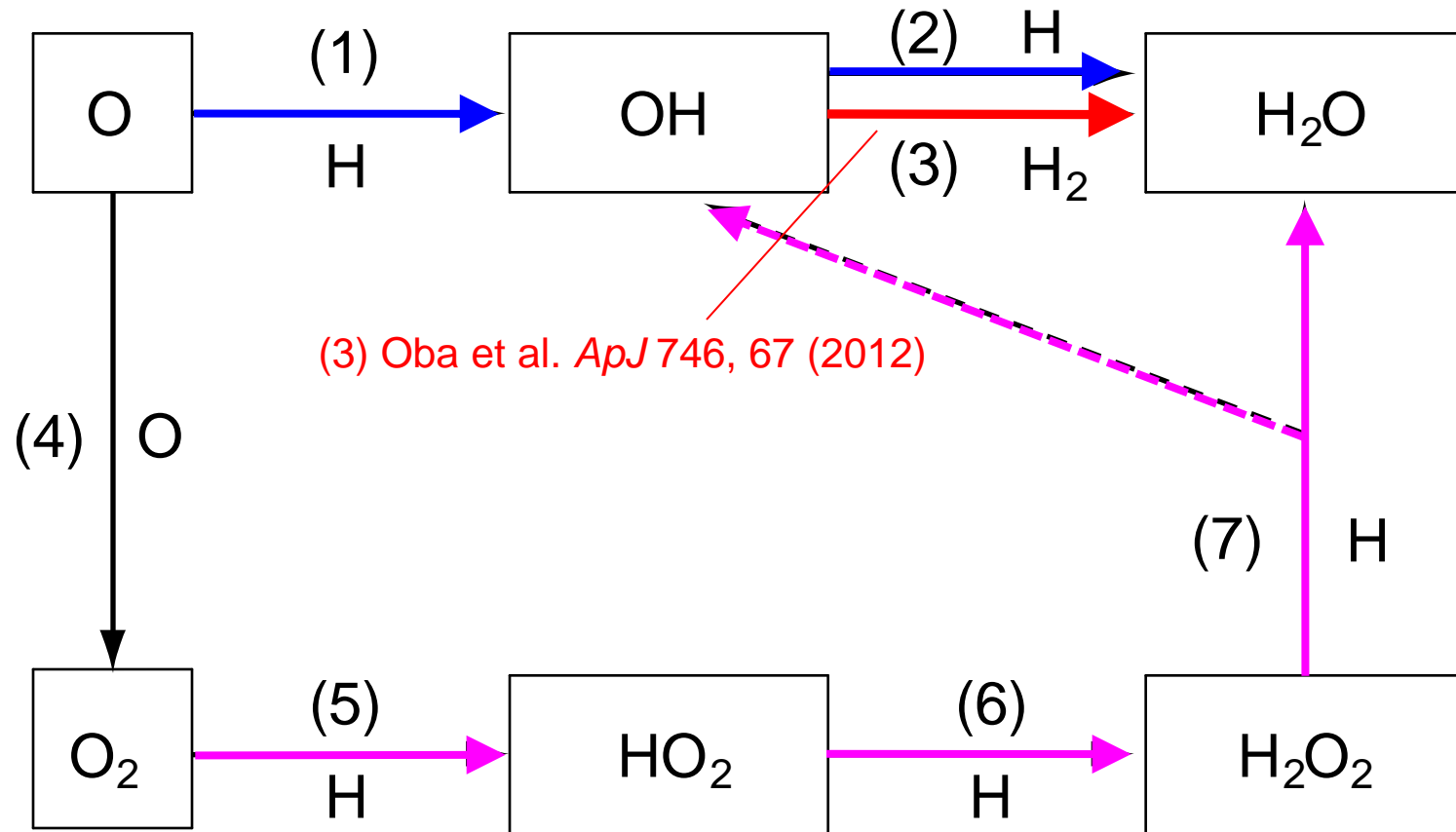
Fuchs et al. *AA* 505, 629 (2009)+, Pirim et al. *JPCA* 114, 3320 (2010)



Hidaka et al. *JCP* 126, 204707 (2007)

Water ice formation on dust grains

(1)+(2): Dulieu et al. *AA* 512 A30 (2010); Jing et al. *ApJ* 741 L9 (2011)

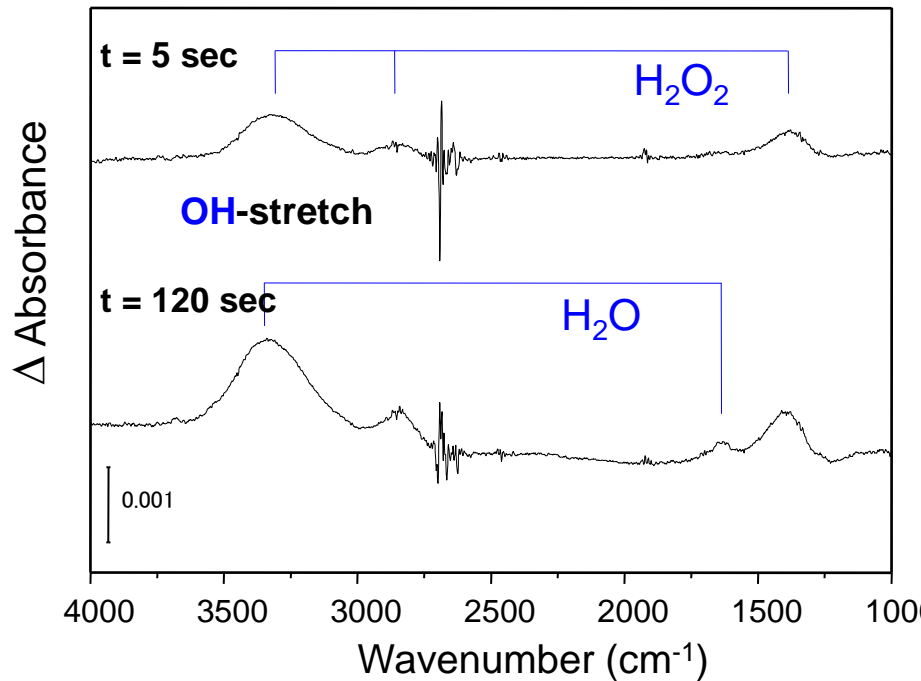


(5)+(6)+(7): e.g. Miyauchi *CPL* 456, 27 (2008)+; Ioppolo et al. *ApJ* 686, 1474 (2008)+.
can be a dominant route in MC (Cuppen & Herbst 2007)

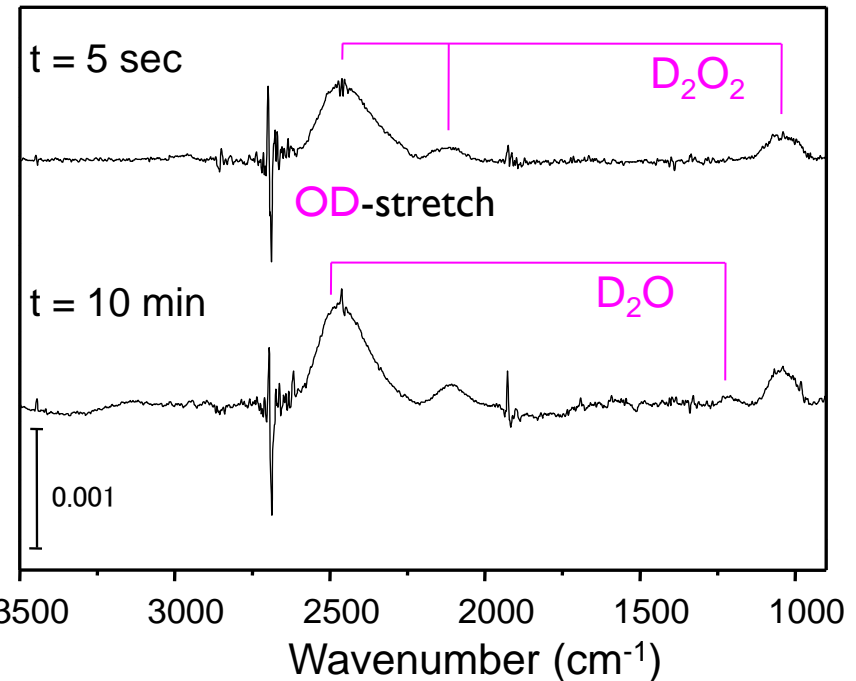
Variation of IR absorption spectra



Solid $O_2(10K) + H$



Solid $O_2(10K) + D$



This process works in MC (10min in exp. $\rightarrow 10^5$ yr in MC)

The produced solid is amorphous phase, not crystalline !

Other molecular formation on the surfaces

- $\text{CO} + \text{O} \rightarrow \text{CO}_2$ Roser et al. *ApJ* 555, L61 (2001), Raut & Baragiola *ApJ* 737, L14 (2011)
- $\text{CO} + \text{thermal OH} \rightarrow \text{CO}_2 + \text{H}$ Oba et al. *ApJ* 712, L74 (2010)
- $\text{N} \xrightarrow{\text{H}} \text{NH} \xrightarrow{\text{H}} \text{NH}_2 \xrightarrow{\text{H}} \text{NH}_3$ e.g. Hidaka et al. *PCCP* 13, 15798 (2011),
Fedoseev et al. *MNRAS* 446, 449 (2015)
- $\text{NO} \xrightarrow{3\text{H}} \text{NH}_2\text{OH}$ Congiu et al. *ApJ* 750, L12 (2012)
- $\text{HCN} \xrightarrow{2\text{H}} \text{CH}_2\text{NH} \xrightarrow{2\text{H}} \text{CH}_3\text{NH}_2$ Theule et al. *AA* 534, A64 (2011)
- C_6H_6 (benzene) $\xrightarrow{6\text{H}}$ C_6H_{12} (cyclohexane) Hama et al. *JPCLet* 5, 3843 (2014)

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- COM, PAH formation by energetic process
Starting from simple ices
- Surface diffusion of heavy species (O atom, radicals...)
- What is the reaction-rate limited process?
e.g. “Diffusion rate vs Tunneling rate” in tunneling reactions
- The mechanism of nuclear spin conversion on the surface
- More quantitative data (surface number density, rate constant, etc)

For more info about dust surface chemistry,

see [Watanabe & Kouchi, Prog. Surf. Sci. 83, 439 \(2008\)](#)

[Hama & Watanabe, Chem. Rev. 113, 8783 \(2013\)](#)