Since 1959

# Surface Science of Water Ice


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Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
EyeNetAqua Solutions Pvt. Ltd.
DeepSpectrum Innovations Pvt. Ltd.

Associate Editor

Professor-in-charge

International Centre for Clean Water

# Ice – why should we care?

**Ice is big in scale - 10 percent of the land area on Earth is covered with glacial ice. Glacierized areas cover over 15 million square kilometers.**

**Ice is there everywhere, including in space - naturally**

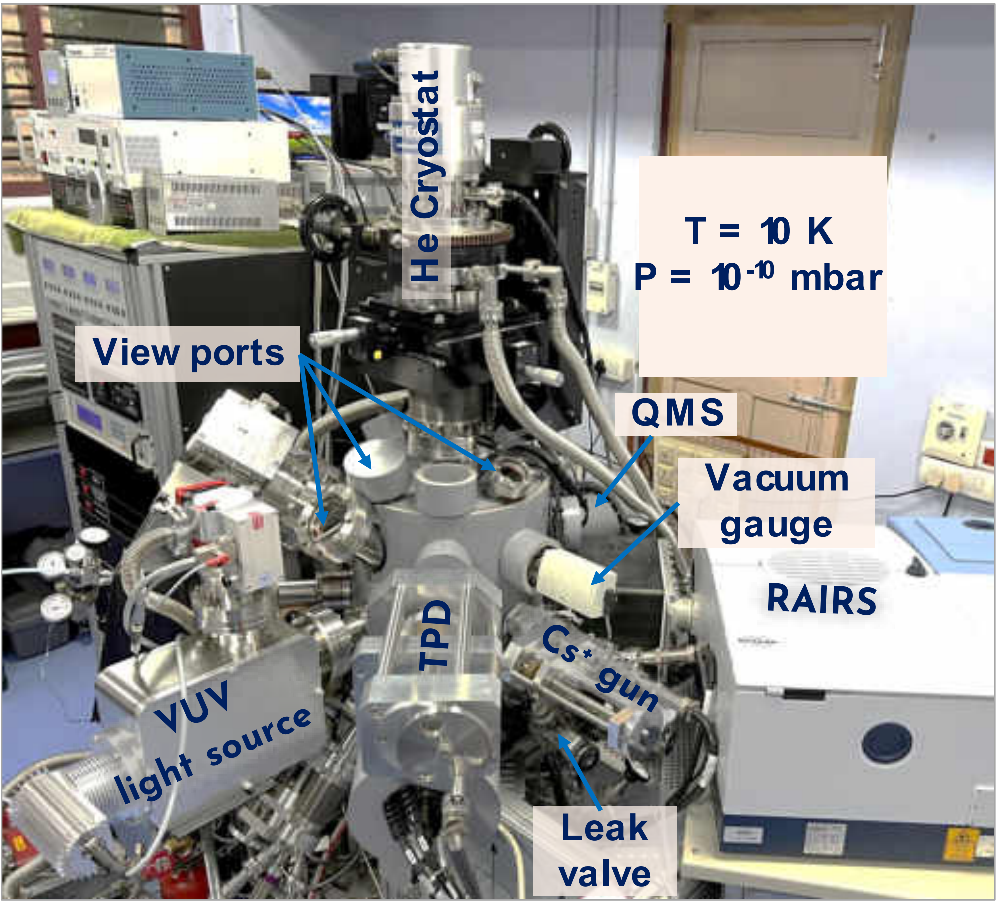
**Ice could be a vehicle for life on Earth - astrobiology**

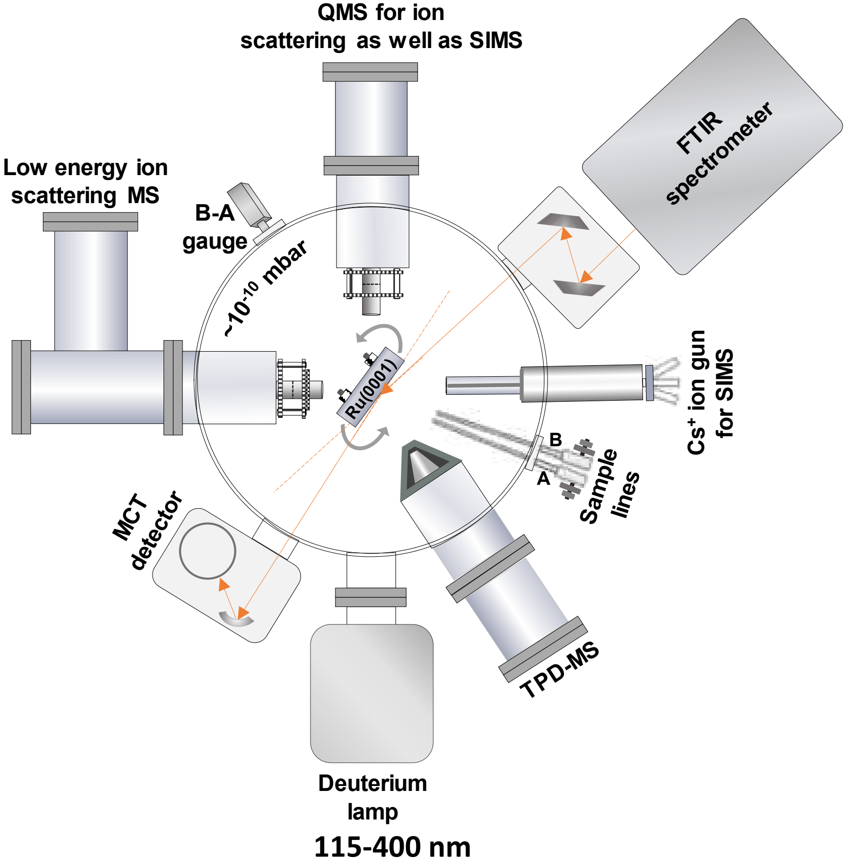
**Ice can make clathrates**

**Water is not understood – especially in its condensed form**

**Condensed molecular solids are all ices**

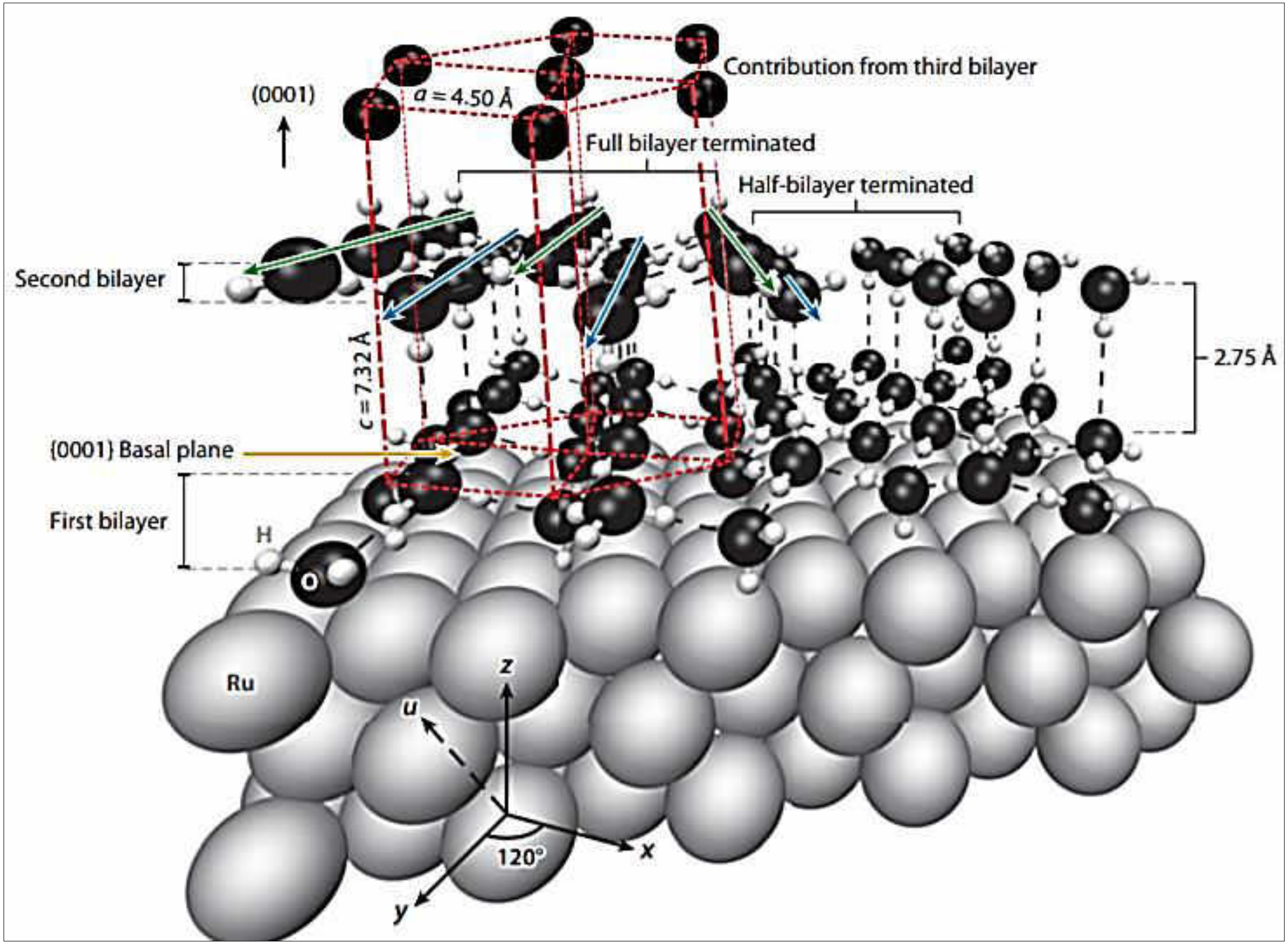
# Instrumentation




Bag, S. *et al.*, *Rev. Sci. Instrum.* **2014**, *85*, 014103/1-014103/7

Viswakarma, *G. et al., J. Phys. Chem. Lett.*, **2023**, *14*, 2823–2829




Bag, S. *et al.*, *Annu. Rev. Anal. Chem.* **2013**, *6*, 97–118

# Instrumentation

$$H^+ + H_2O \text{ (liquid)} \rightarrow H_3O^+$$

$$H^+ + H_2O \text{ (solid)} \rightarrow ?$$

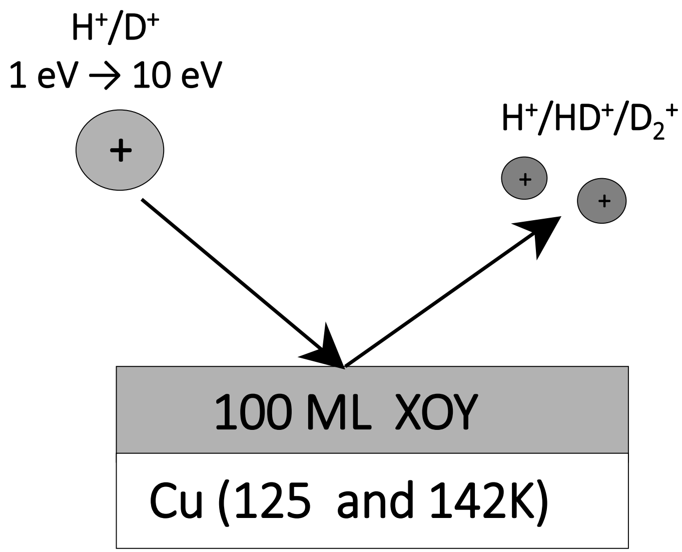
**(at ultralow energy)**

$$\uparrow$$

$$\tfrac{1}{2} H_2$$

Soumabha Bag, Martin R. S. McCoustra and T. Pradeep, J. Phys. Chem. C, 115 (2011) 13813-13819.

# <u>Chemical exchange (or mixing)</u>



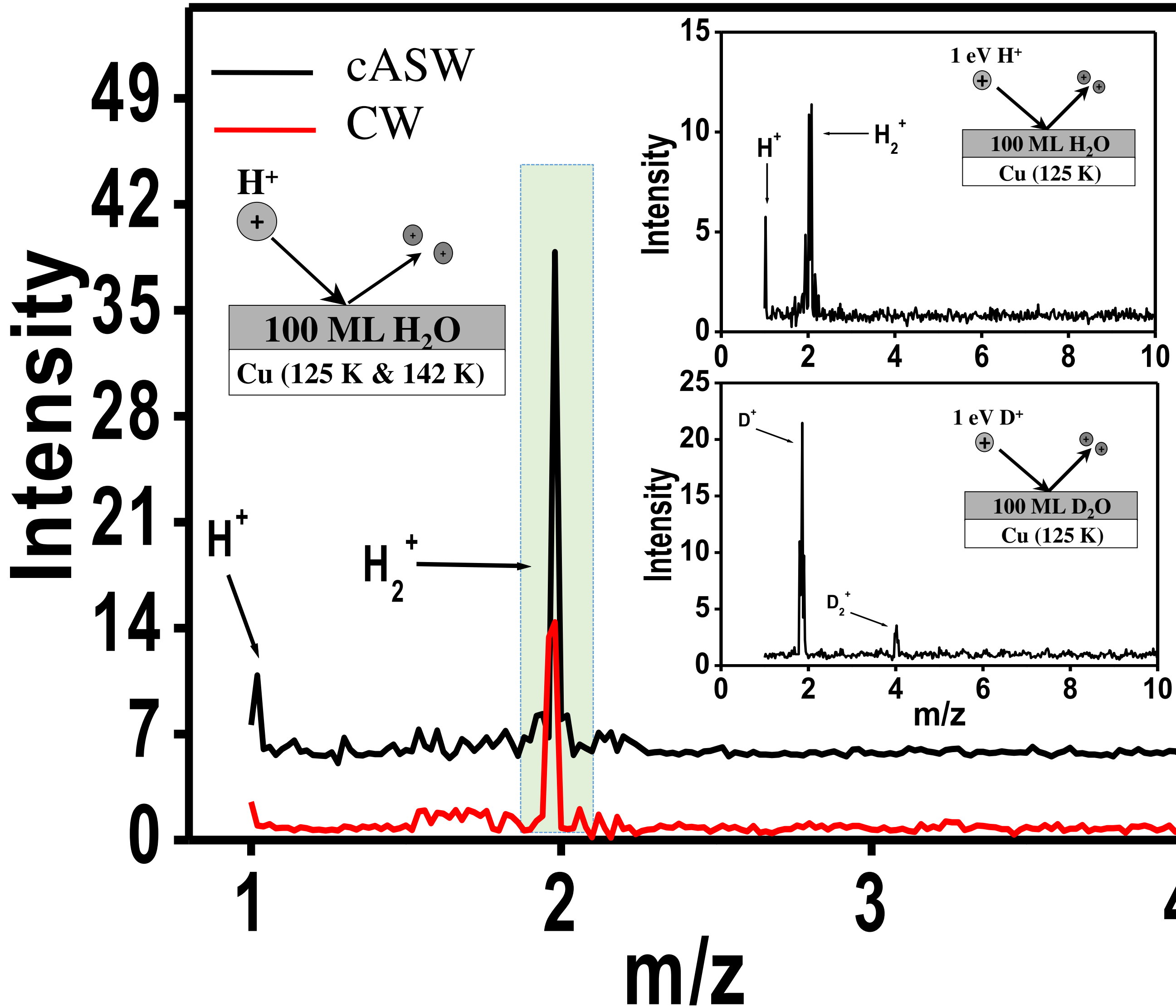

[X= H, D, Me, Et, Pr, But, Pen]
[Y= H, D]

Ultra-low energy (1-10 eV) $H^+/D^+$ ions were subjected to collide on various molecular solids

ML = Monolayer
1 ML ≈ $1.1 \times 10^{15}$ molecules/cm$^2$*



*Moon, E.-S.; Kang, H.; Oba, Y.; Watanabe, N.; Kouchi, A. Astrophys. J. **2010**, 713, 906



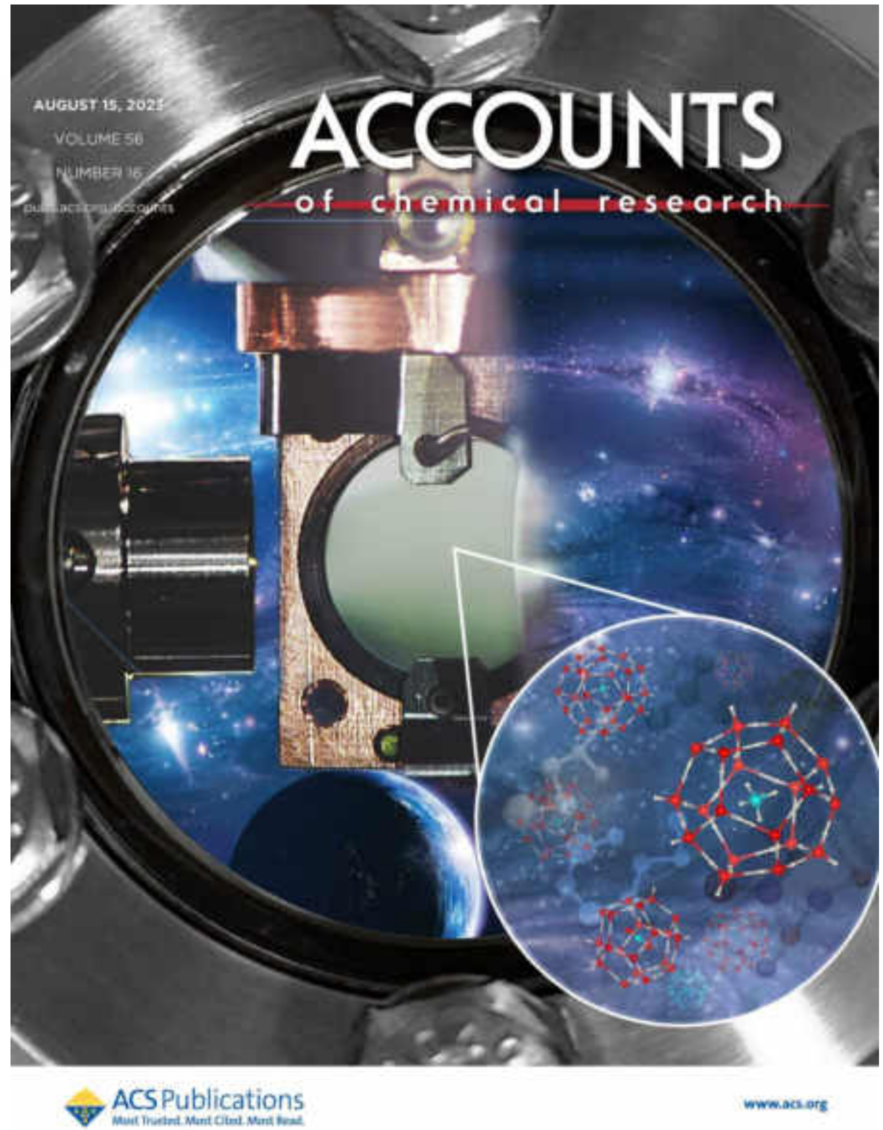

**Mass spectrum upon the bombardment of 1 and 2 eV $H^+$ on amorphous ice (cASW) & crystalline ice (CW)**

ACCOUNTS
of chemical research
pubs.acs.org/accounts Article

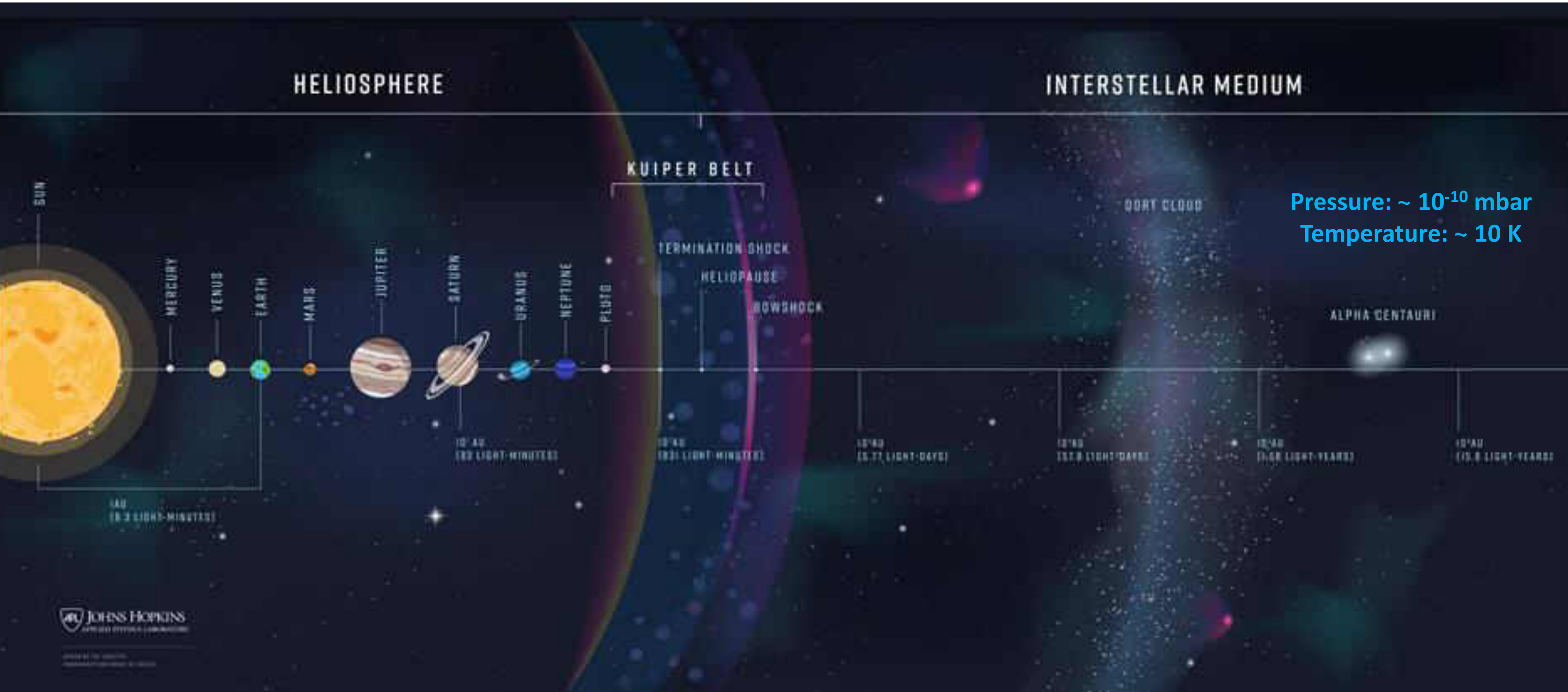
# Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,* and Thalappil Pradeep*

Cite This: https://doi.org/10.1021/acs.accounts.3c00317 Read Online



# Interstellar medium



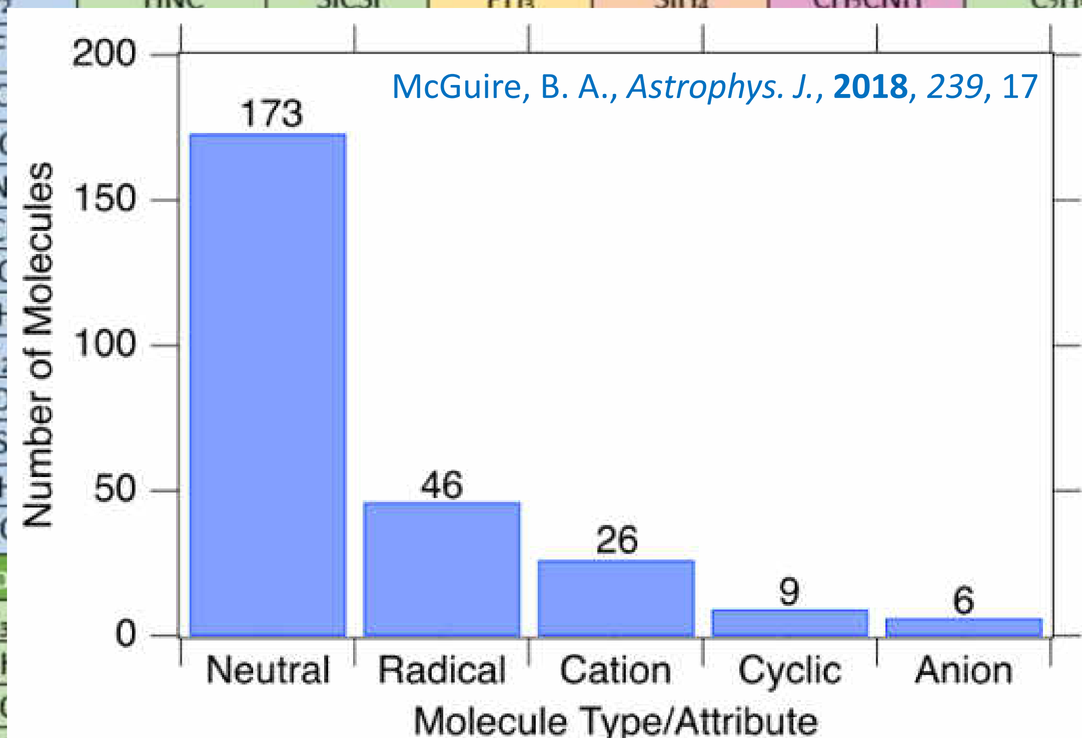

Diffuse clouds: T ~ 100 K, n ~ 100 molecules per $cm^3$
Dense clouds: T ~ 10-100 K, n ~ $10^4$-$10^8$ molecules per $cm^3$
On Earth sea level: T ~ 300 K, n ~ $3\times10^{19}$ molecules per $cm^3$

https://spaceref.com/science

# Interstellar molecules

260

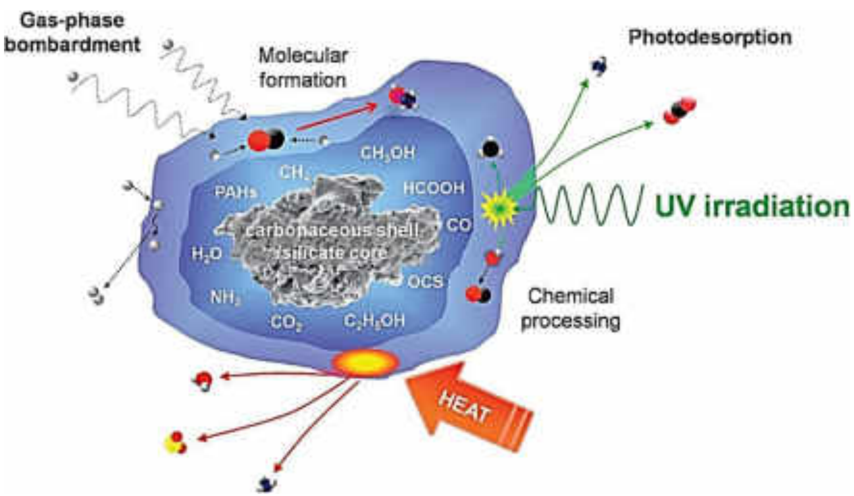
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2 atoms | CS | $HCO^+$ | KCN | $H_3O^+$ | HCOOH | *l*-$HC_4N$ | $CH_2CHCHO$ | $CH_3OCH_2OH$ |
| $H_2$ | HF | $HCS^+$ | FeCN | $NH_3$ | $H_2CNH$ | *c*-$H_2C_3O$ | $CH_2CCHCN$ | 11 atoms |
| AlF | SH | $HOC^+$ | $HO_2$ | c-$SiC_3$ | $H_2C_2O$ | $C_5N^-$ | $H_2NCH_2CN$ | $HC_9N$ |
| AlCl | $SH^+$ | $H_2O$ | $TiO_2$ | $CH_3$ | $H_2NCN$ | E-HNCHCN | $CH_3CHNH$ | $CH_3C_6H$ |
| $C_2$ | FeO | $H_2S$ | $C_2N$ | $C_3N^-$ | $HNC_3$ | $SiH_3CN$ | $CH_3SiH_3$ | $C_2H_5OCHO$ |
| CH | $O_2$ | HNC | SiCSi | $PH_3$ | $SiH_4$ | $CH_3CNH$ | $C_2H_5N$ | $CH_3OC(O)CH_3$ |
| $CH^+$ | CF | | | | | | CO | 12 atoms |
| CN | PC | | | | | | ms | *c*-$C_6H_6$ |
| CO | AlC | | | | | | H | $C_3H_7CN$ |
| $CO^+$ | CN | | | | | | CN | *t*-$C_2H_5OCH_3$ |
| CP | HC | | | | | | O | >12 atoms |
| CSi | TiC | | | | | | OH | $C_{60}$ |
| HCl | ArH | | | | | | N | $C_{60}^+$ |
| KCl | $N_2$ | | | | | | | $C_{70}$ |
| NH | NC | | | | | | $NH_2$ | c-$C_6H_5CN$ |
| NO | NS | | | | | | | $CO(CH_2OH)_2$? |
| NS | LiH | | | | | | 5 | $C_{14}H_{10}$? |
| NaCl | CrO | | | | | | SH | $C_{14}H_{10}^+$ |
| OH | 3 ato | | | | | | CHO | $C_6H_5OH$ |
| $OH^+$ | $C_3$ | | | | | | O | |
| PN | $C_2H$ | | | | | | ms | |
| SO | $C_2O$ | | | | | | N | |
| $SO^+$ | $C_2S$ | CCP | HOCO | $CH_2CN$ | $HC_3NH^+$ | $C_7H$ | $(CH_3)_2CO$ | |
| SiN | $CH_2$ | AlOH | $H_2CO$ | $CH_4$ | $HC_2CHO$ | $H_2C_6$ | $(CH_2OH)_2$ | |
| SiO | HCN | $H_2O^+$ | $H_2CN$ | $HC_3N$ | $NH_2CHO$ | $CH_2OHCHO$ | $CH_3CH_2CHO$ | |
| SiS | HCO | $H_2Cl^+$ | $H_2CS$ | $HC_2NC$ | $C_5N$ | *l*-$C_6H_2$ | $CH_3CHCH_2O$ | |

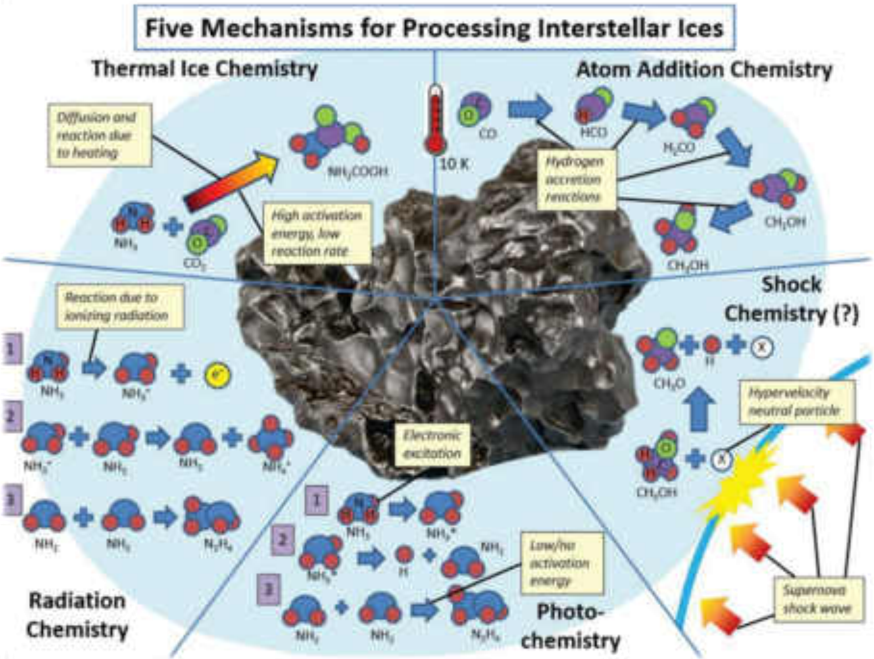





Arumainayagam, C. R. *et al., Chem. Soc. Rev.*, **2019**, *48*, 2293–2314

# Interstellar ices




**Silicates and carbonaceous material – 0.01-0.5 µm**

Arumainayagam, C. R. *et al., Chem. Soc. Rev.,* **2019**, *48*, 2293–2314

# Applications of clathrate hydrates

**"Ice on fire" burning of methane hydrate**

**Applications:**

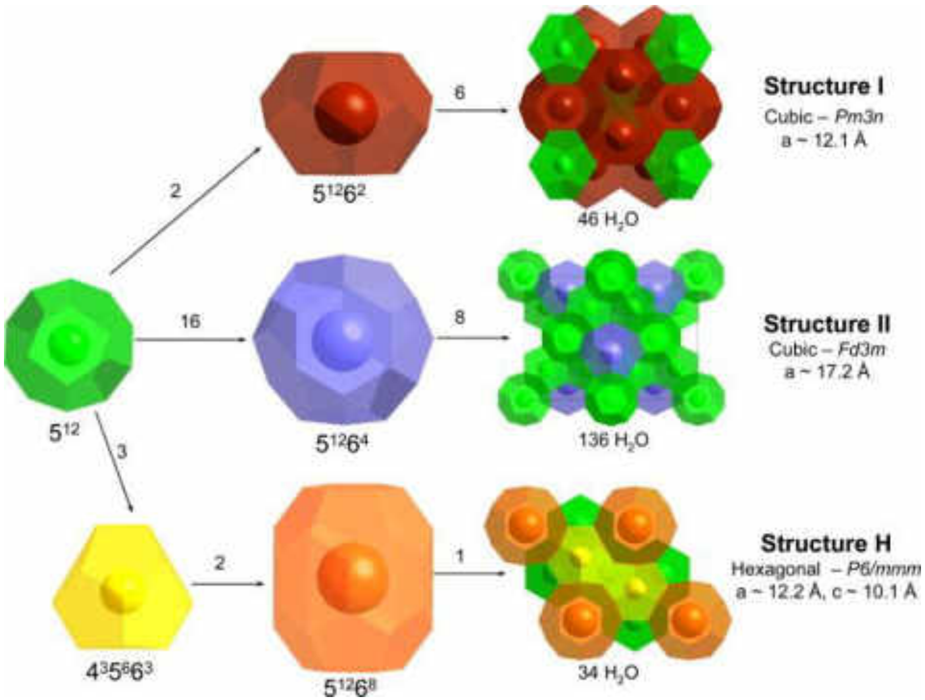
- Renewable energy source.
- Storage of natural gases and hydrogen ($H_2$).
- Separation of flue gases and desalination of seawater.
- Flow assurance in gas pipelines.

**Gas hydrate plug recovered from a subsea pipeline**



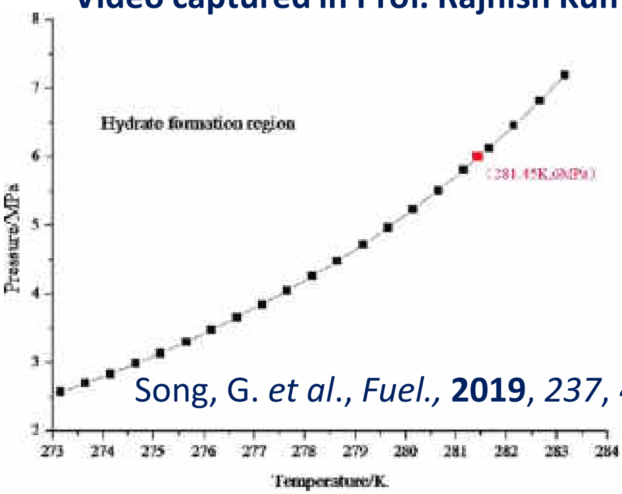
Koh, A.C. *et al., Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 237-257

# Clathrate hydrates



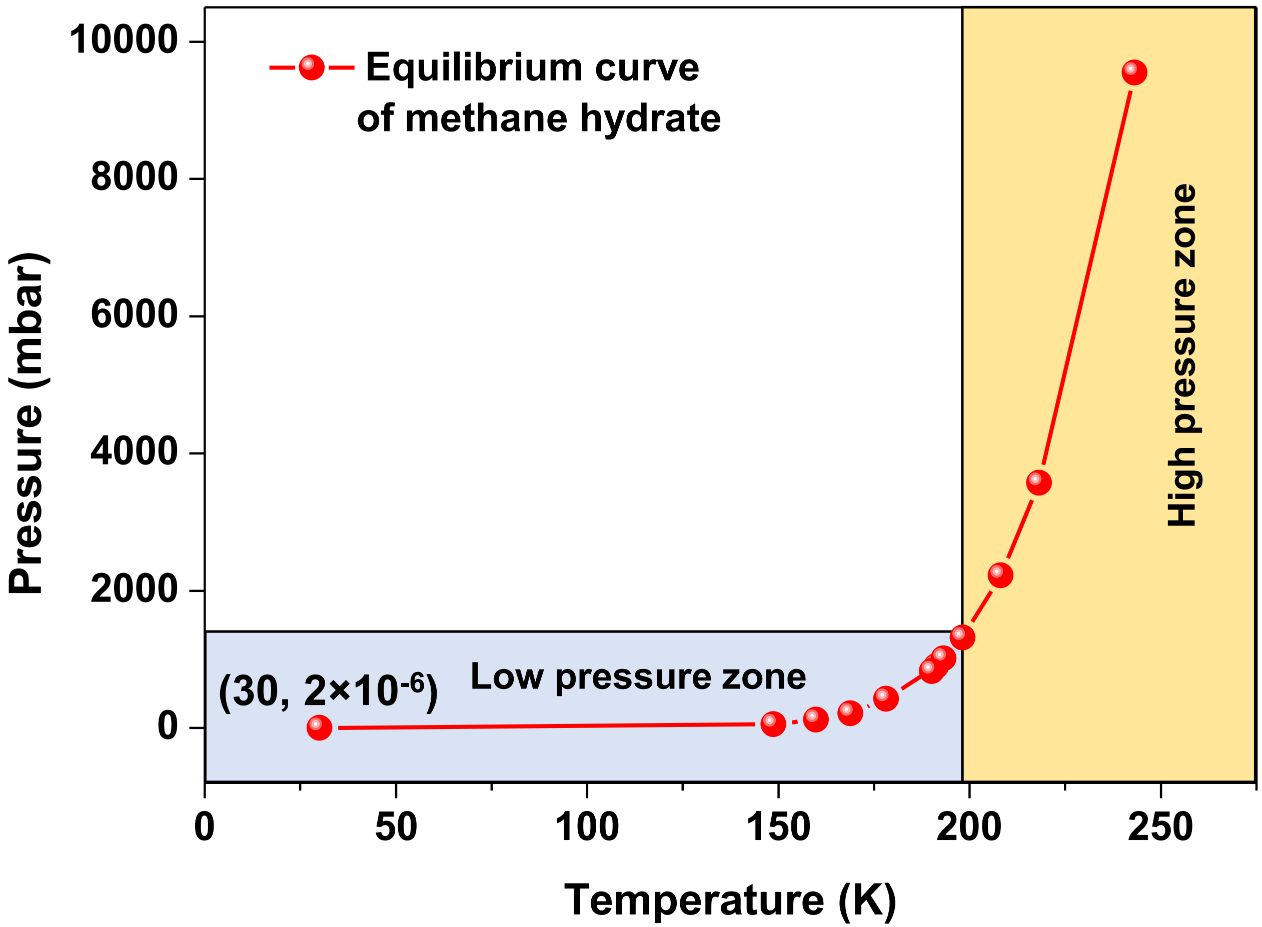

Strobel, T. A. *et al.*, *Chem. Phys. Lett.*, **2009**, *478*, 97–109

**Video captured in Prof. Rajnish Kumar's lab**




Song, G. *et al.*, *Fuel.*, **2019**, *237*, 475-485

# Clathrate hydrates at extreme low pressure

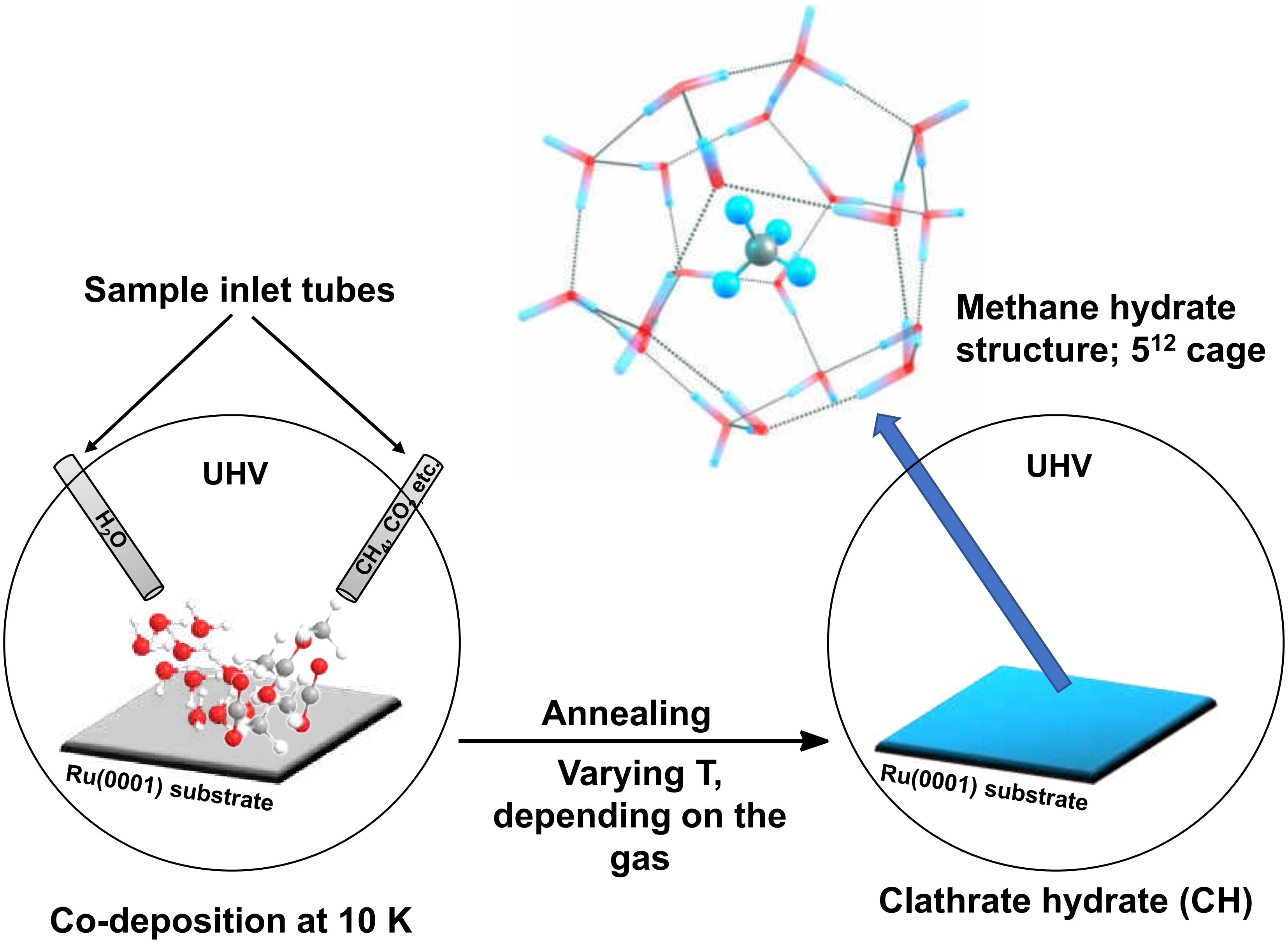



Sloan, E.D.; Koh, C. A., *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008

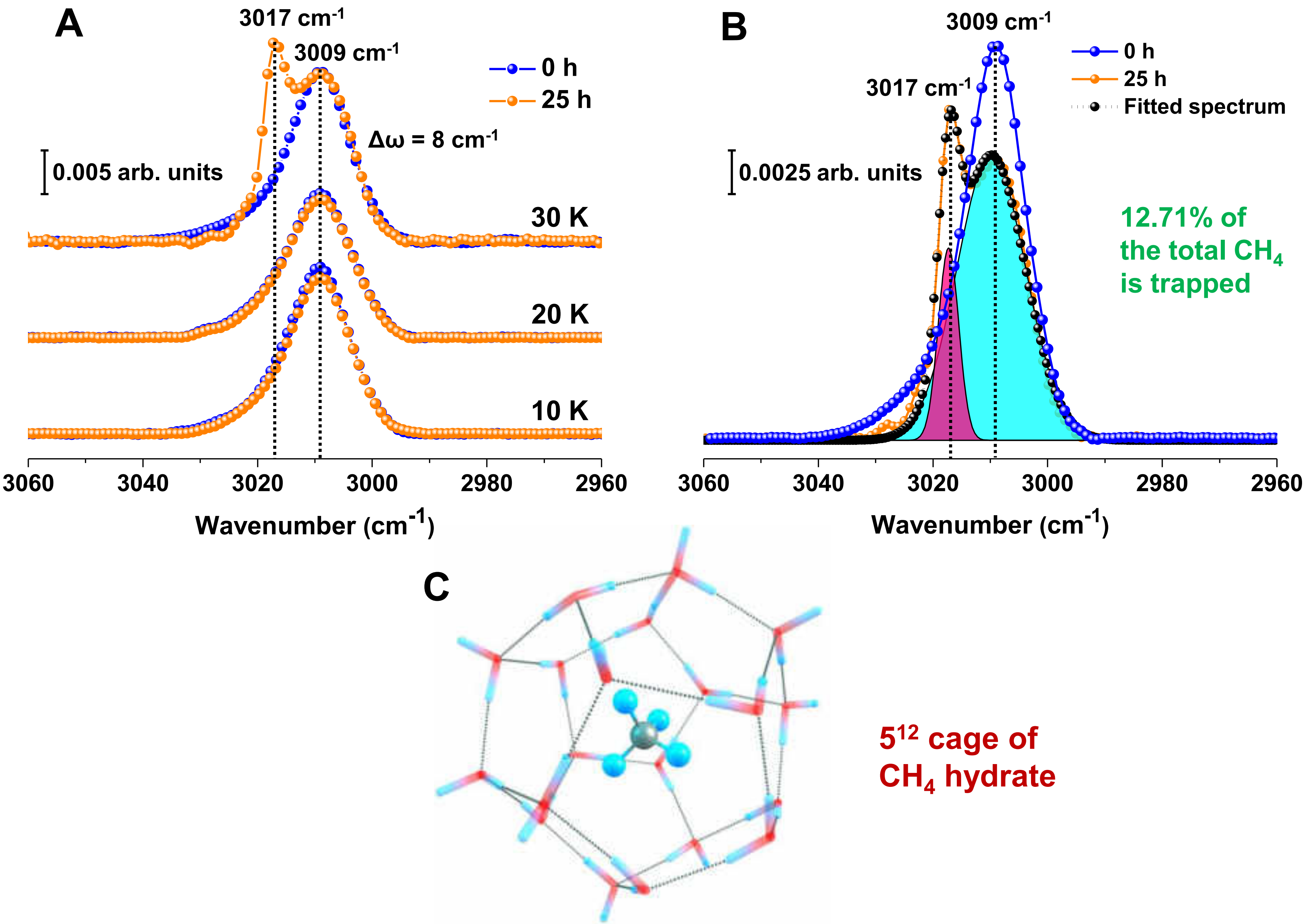
# ***Clathrate hydrates in interstellar environment***

Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.*, **2019**, *116*, 1526-1531

# Experimental method

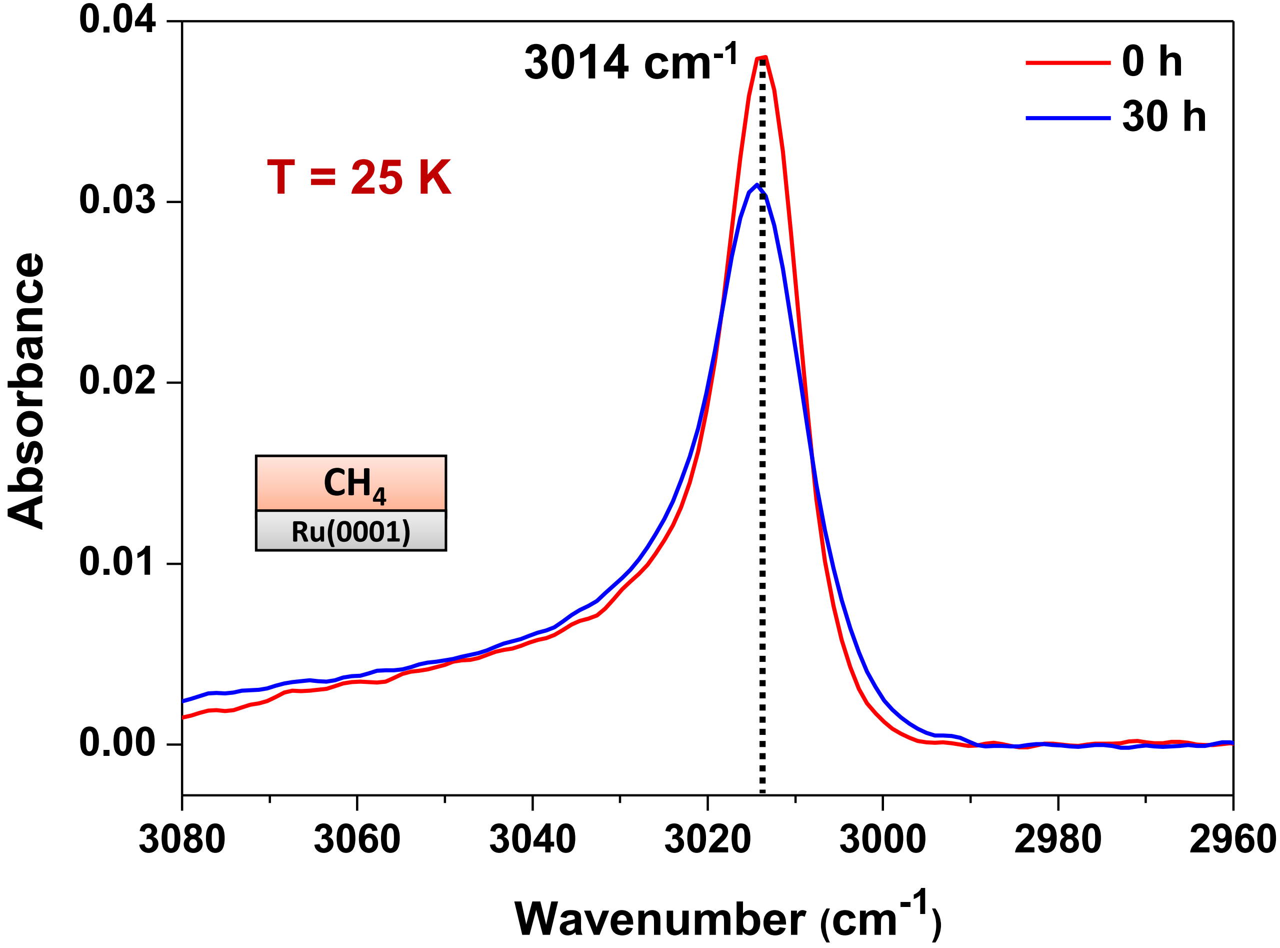


# Clathrate hydrates in interstellar environment




Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

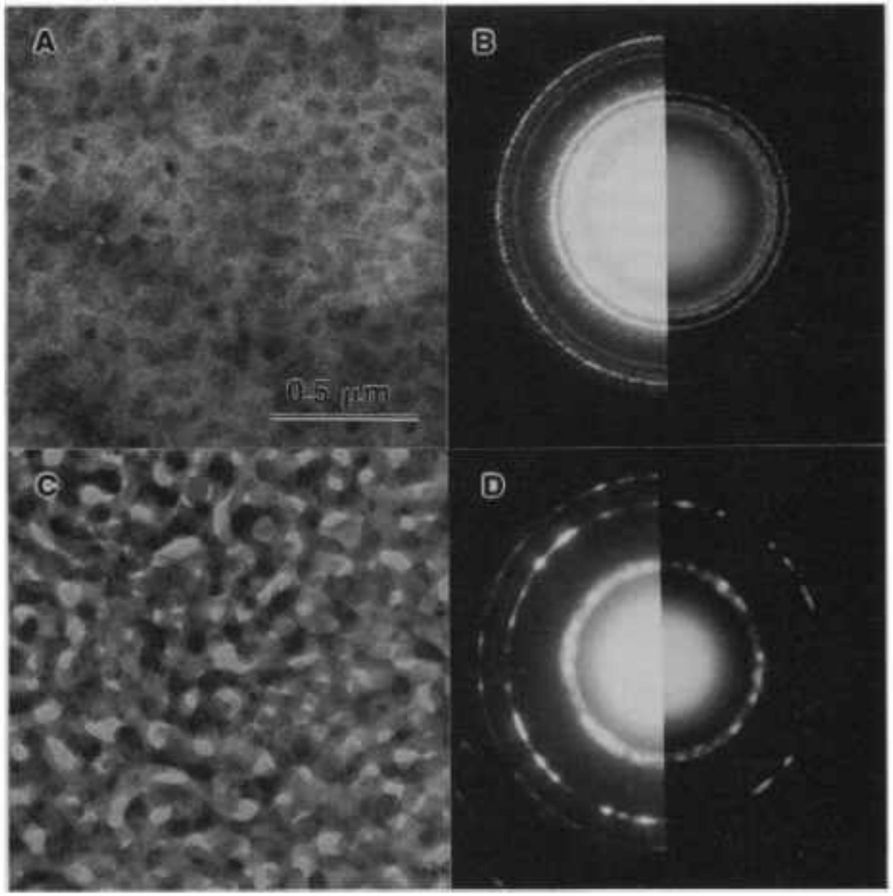
# Clathrate hydrates in interstellar environment

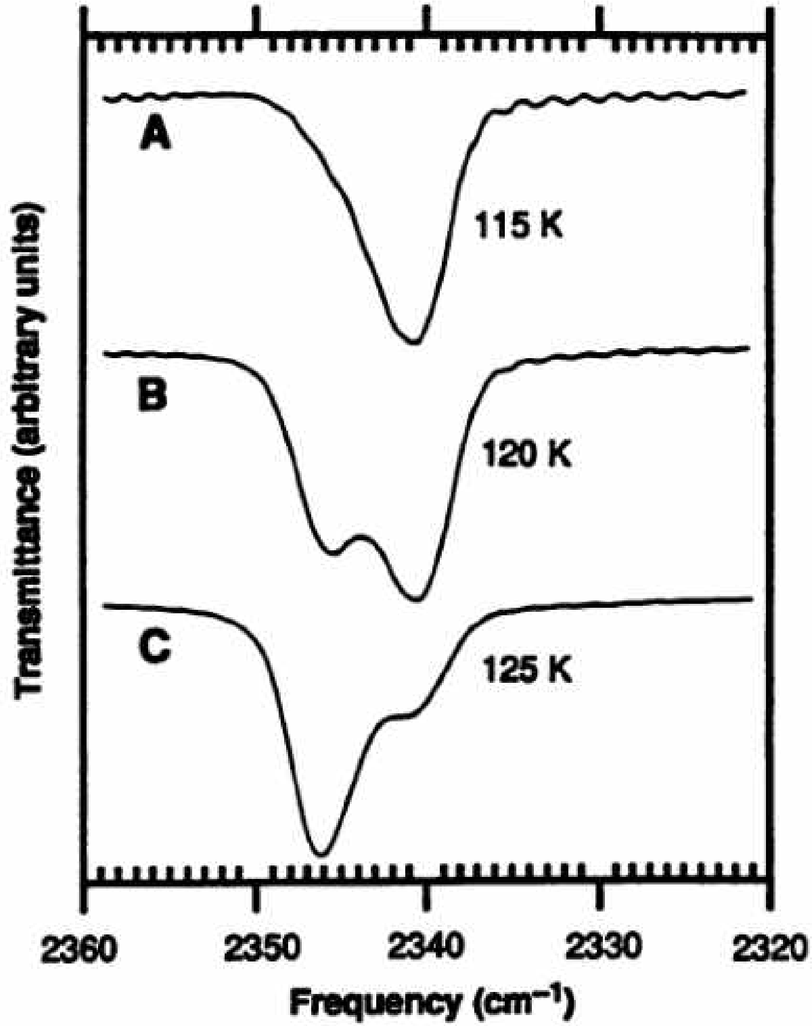



Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

# Clathrate hydrate at low pressure

P = $10^{-6}$ Torr



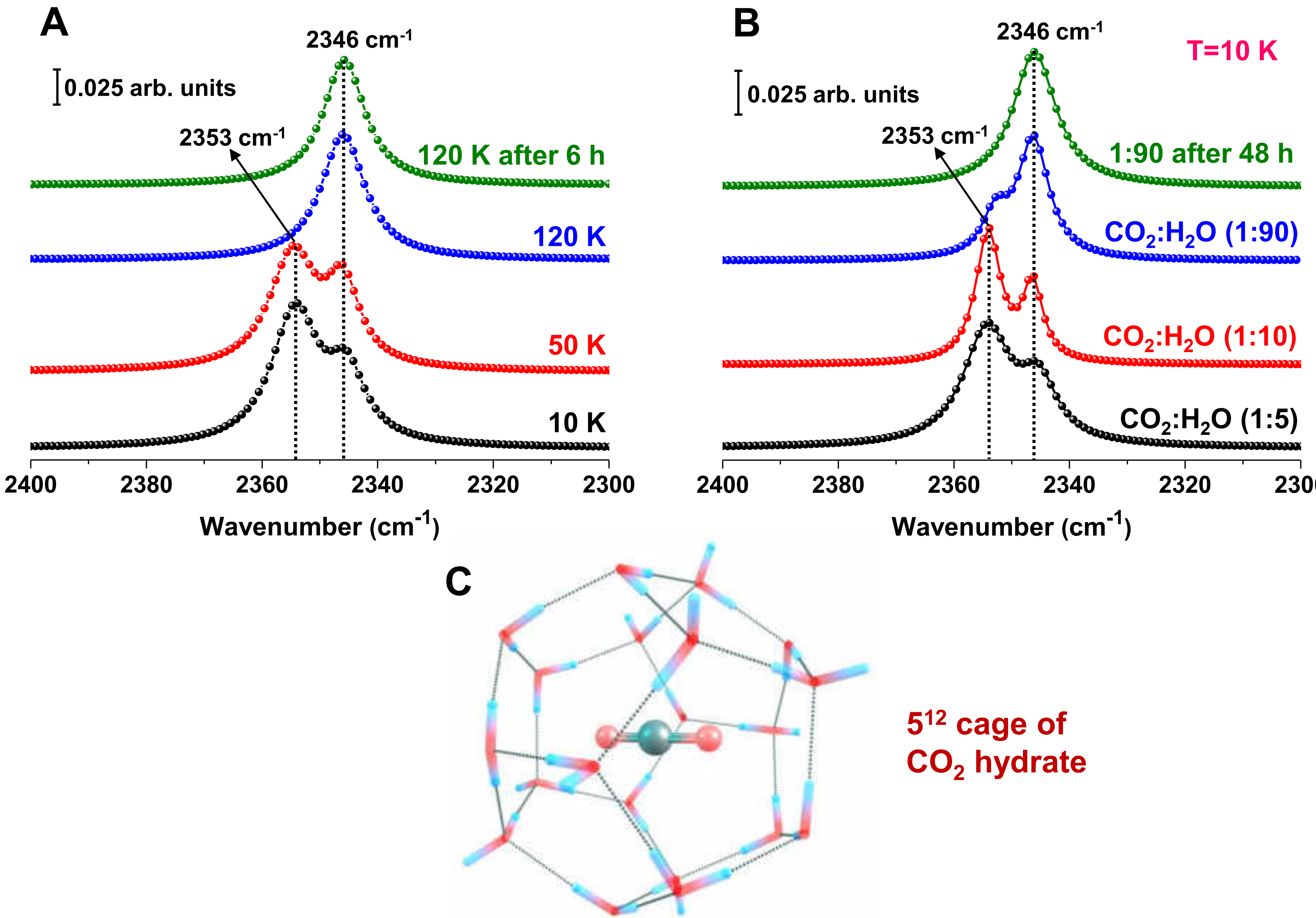

**Here, $CO_2$ hydrate was used as a local sensitive probe towards the formation of methanol hydrate**

**$H_2O$:$CH_3OH$:$CO_2$ = 100:50:1**



Blake, D. *et al., Science* **1991**, *254*, 5031, 548-551

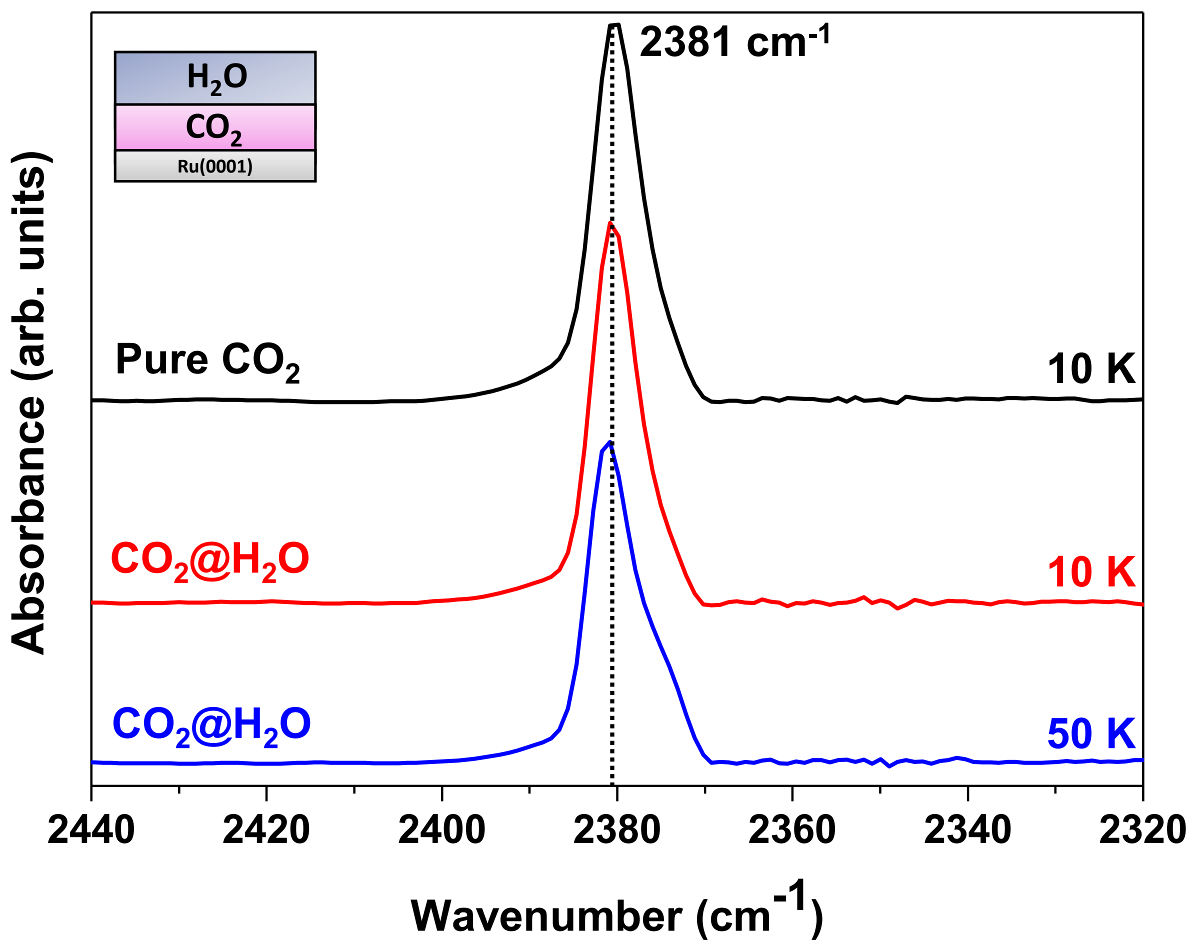
# Clathrate hydrates in interstellar environment




$5^{12}$ cage of $CO_2$ hydrate

Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

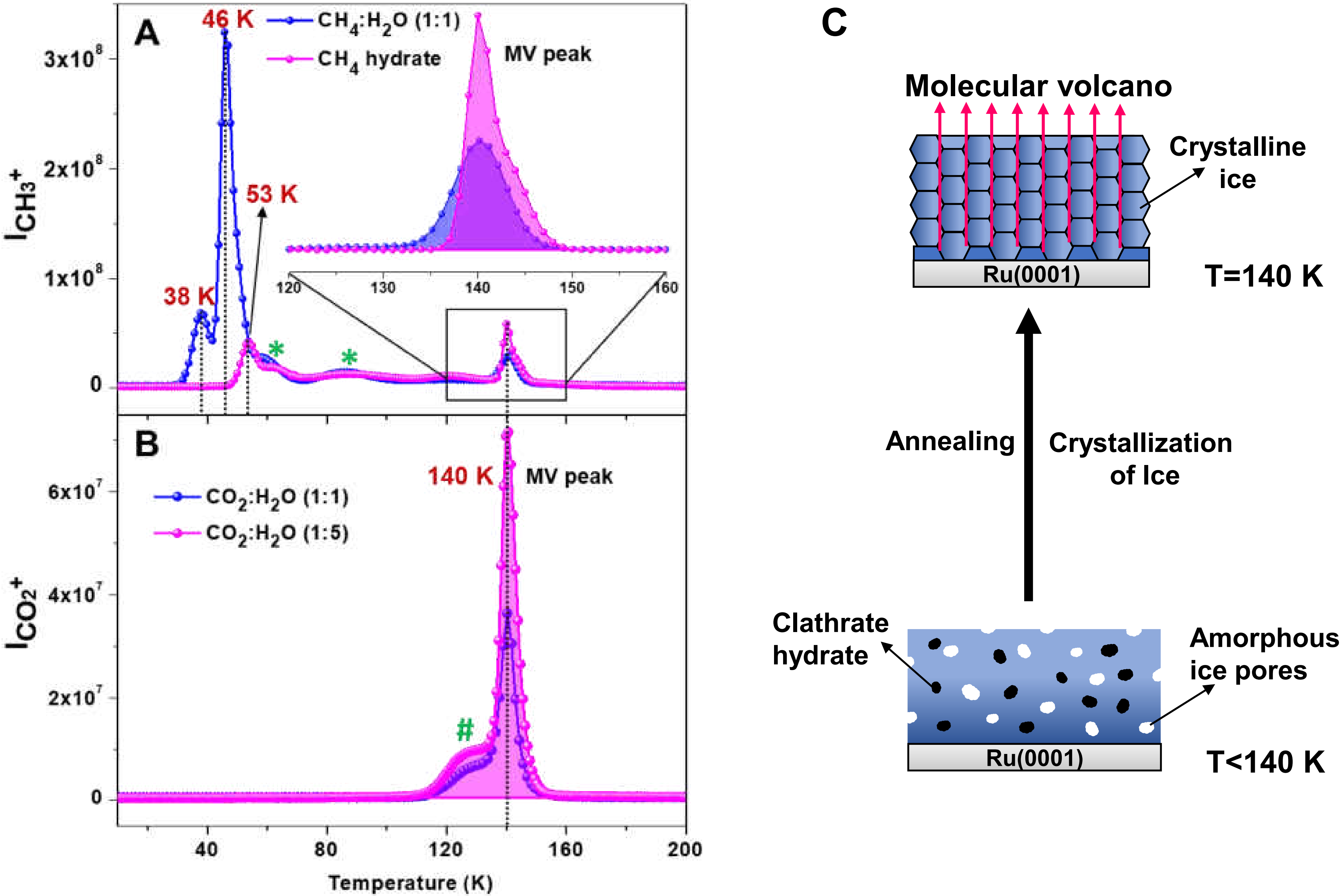
# Clathrate hydrates in interstellar environment






Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

# Clathrate hydrates in interstellar environment



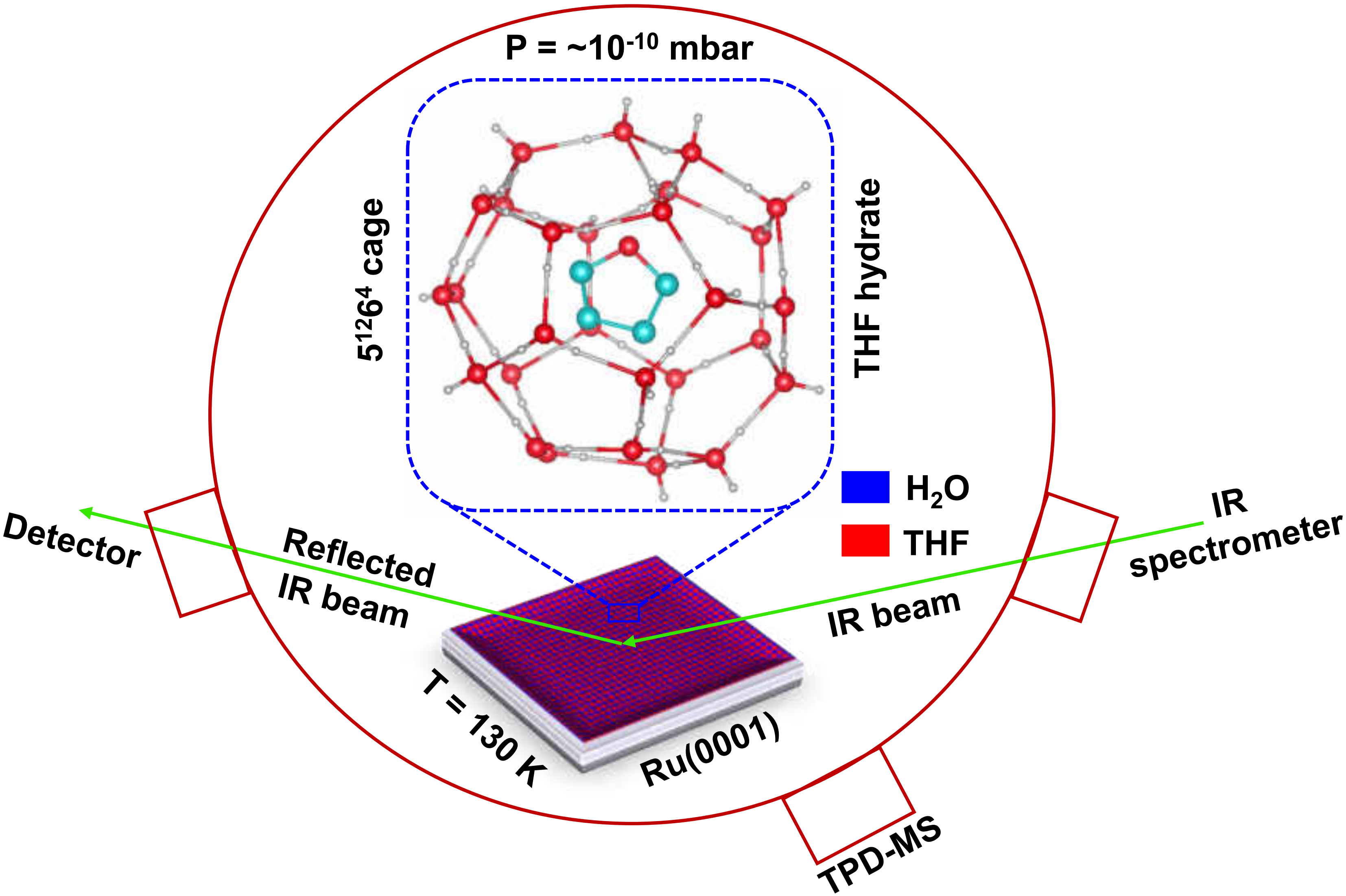



Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

## ***Spontaneous formation of tetrahydrofuran hydrate in ultrahigh vacuum***

Ghosh, J. *et al.*, *J. Phys. Chem. C* **2019**, *123*, 16300-16307

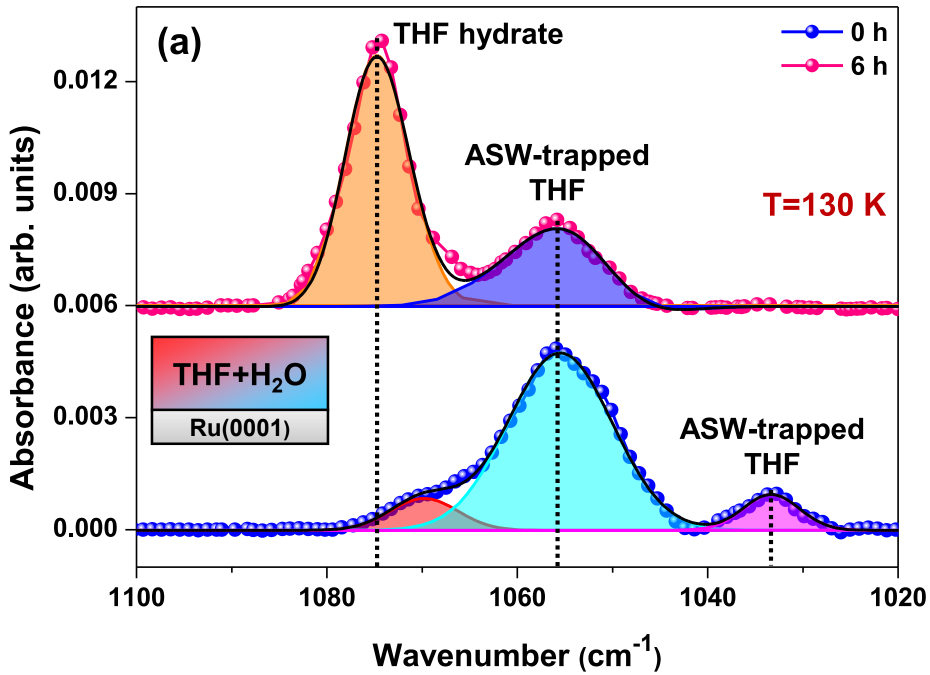
# Formation of THF hydrate in UHV

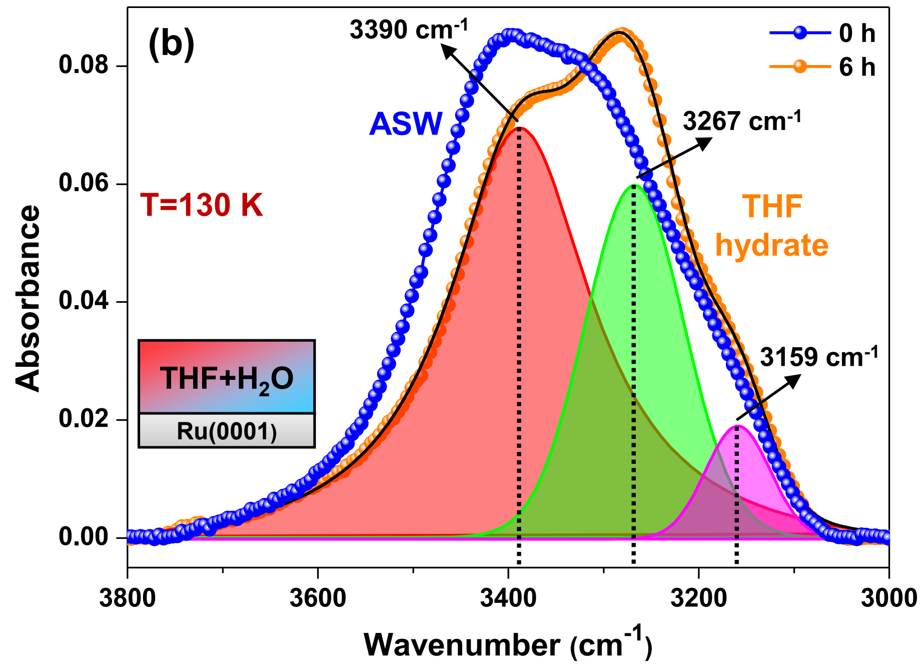





Ghosh, J. *et al., J. Phys. Chem. C* **2019**, *123*, 16300-16307

# Formation of THF hydrate in UHV






Ghosh, J. *et al., J. Phys. Chem. C* **2019**, *123*, 16300-16307

Many hydrates

# ***Formation of cubic ice via clathrate hydrate, prepared in ultrahigh vacuum at cryogenic conditions***

Ghosh, J. *et al., J. Phys. Chem. Lett.* **2020**, *11*, 26-32

# Cubic ice via clathrate hydrate

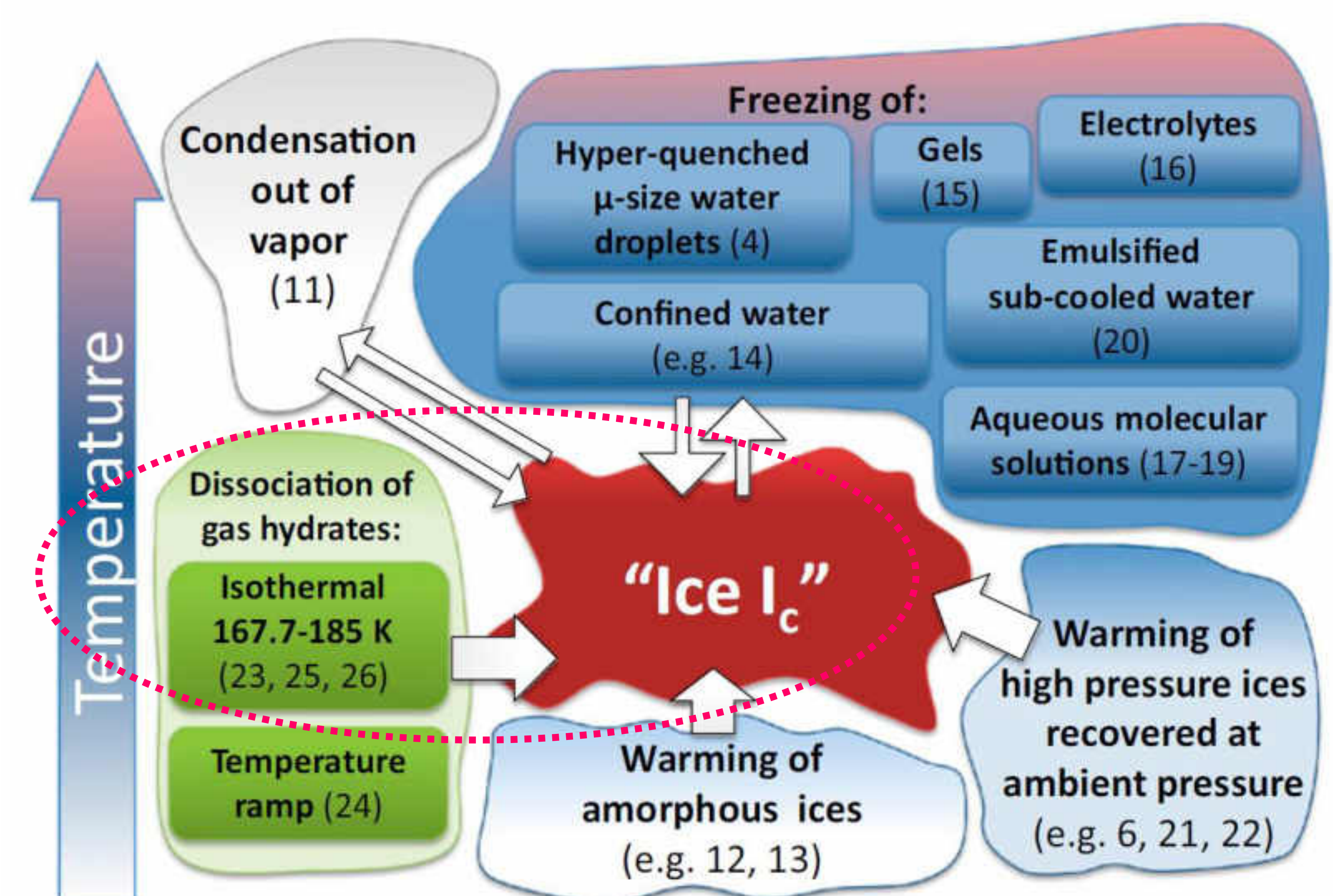
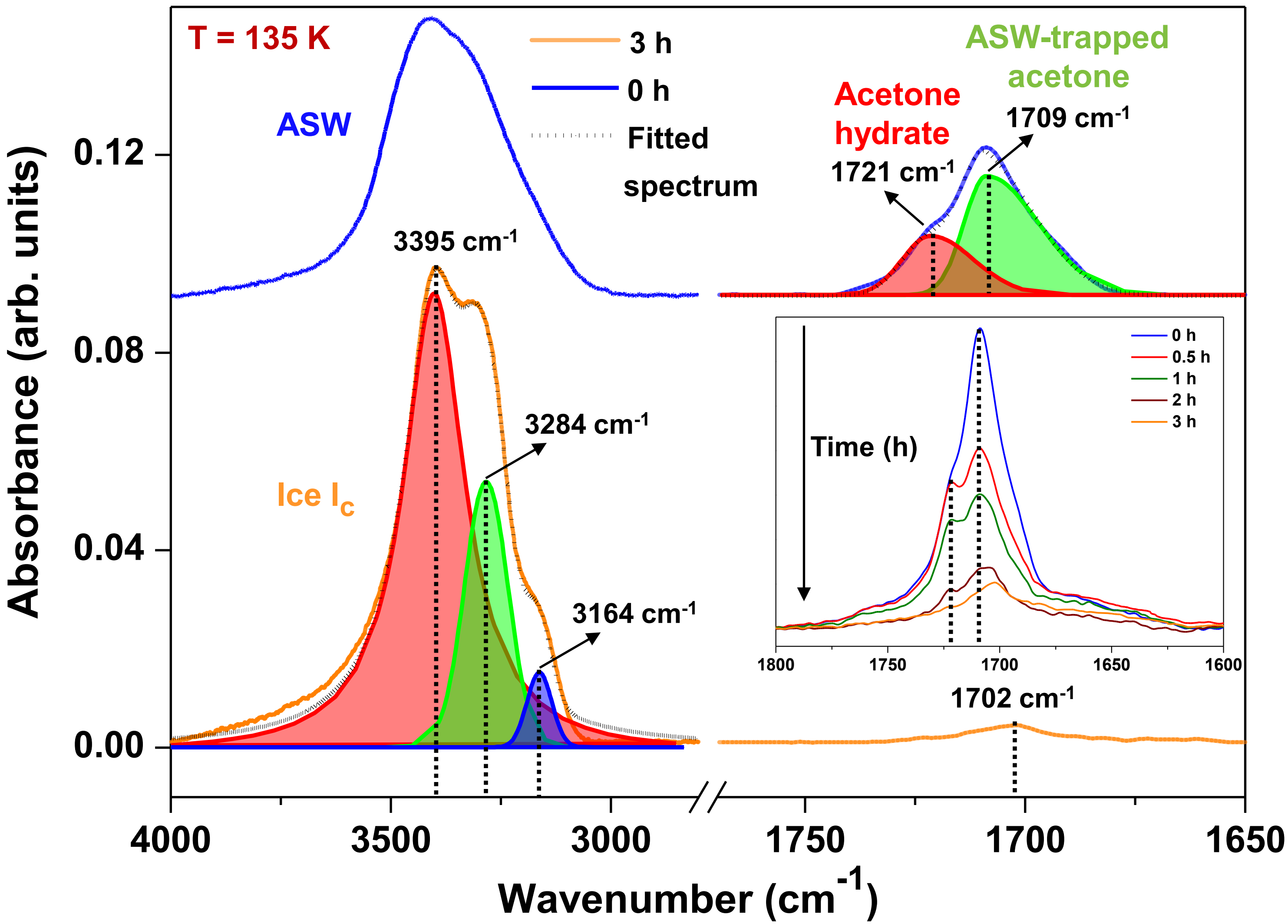



**Fig. 2.** Main established routes of forming "ice I$_c$".

Kuhs, W. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2012,** *109*, 21259-21264

# Cubic ice via clathrate hydrate




Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26-32

# Diffraction pattern of cubic ice

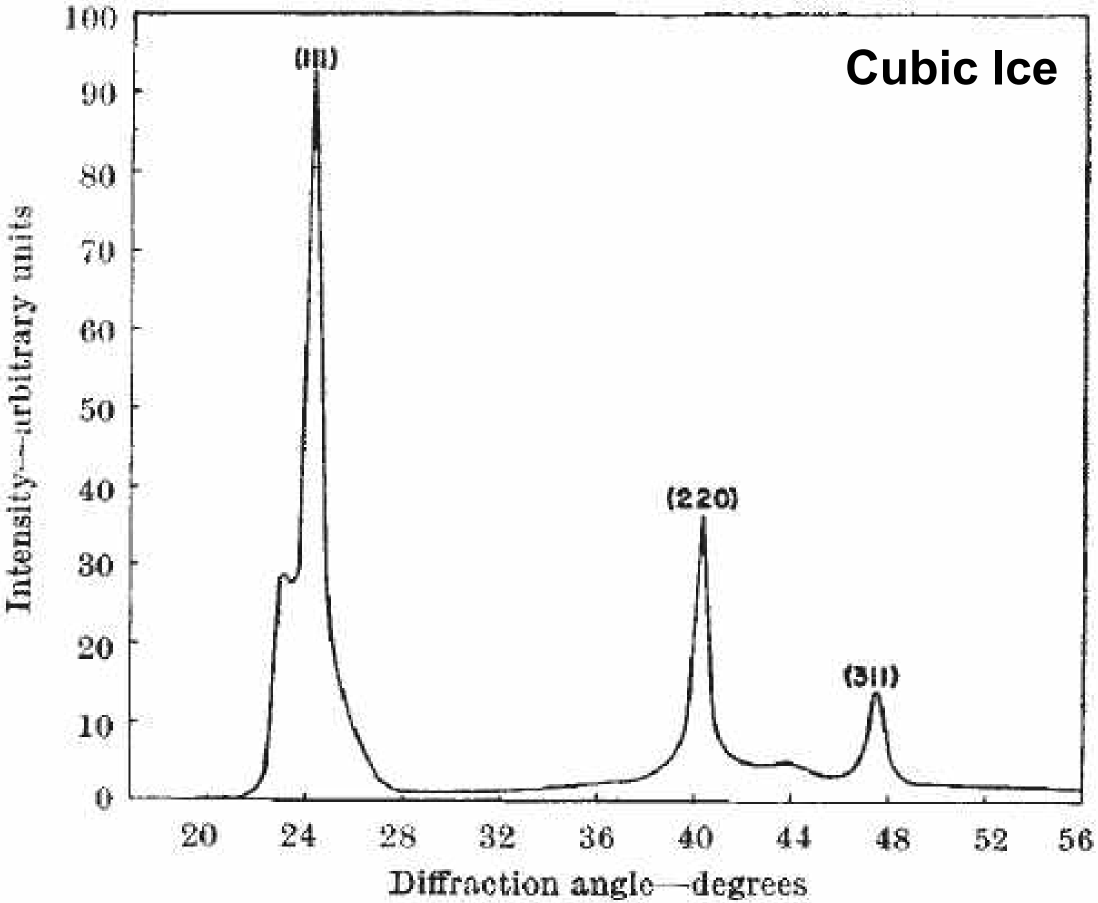
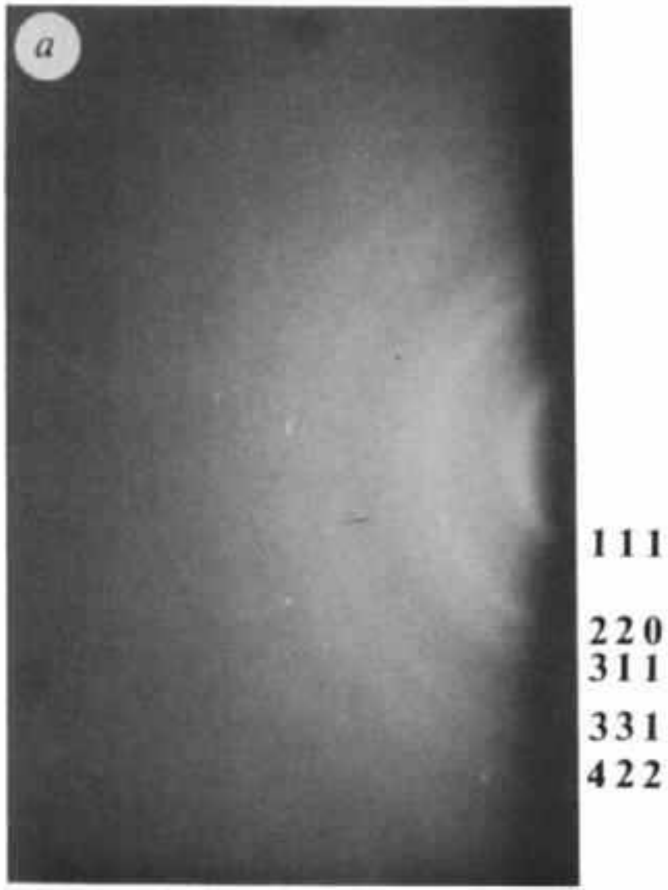


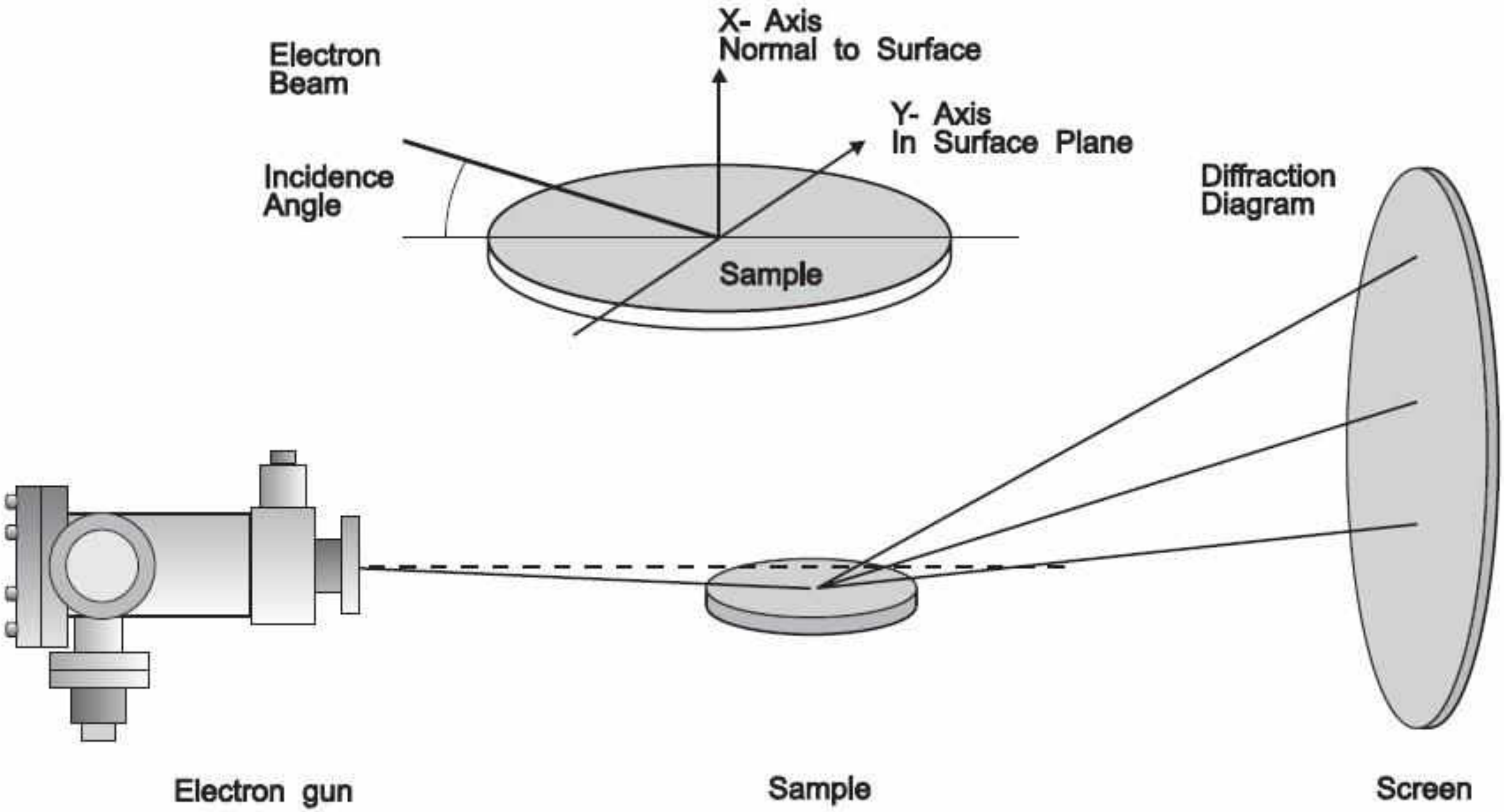

Fig. 3. X-ray diffraction pattern of diamond-cubic ice in the presence of vitreous ice




Dowell, L. G. *et al.*, *Nature* **1960**, *168,* 1144-1148

Kouchi, A. *et al.*, *Nature* **1990**, *344,* 134-135

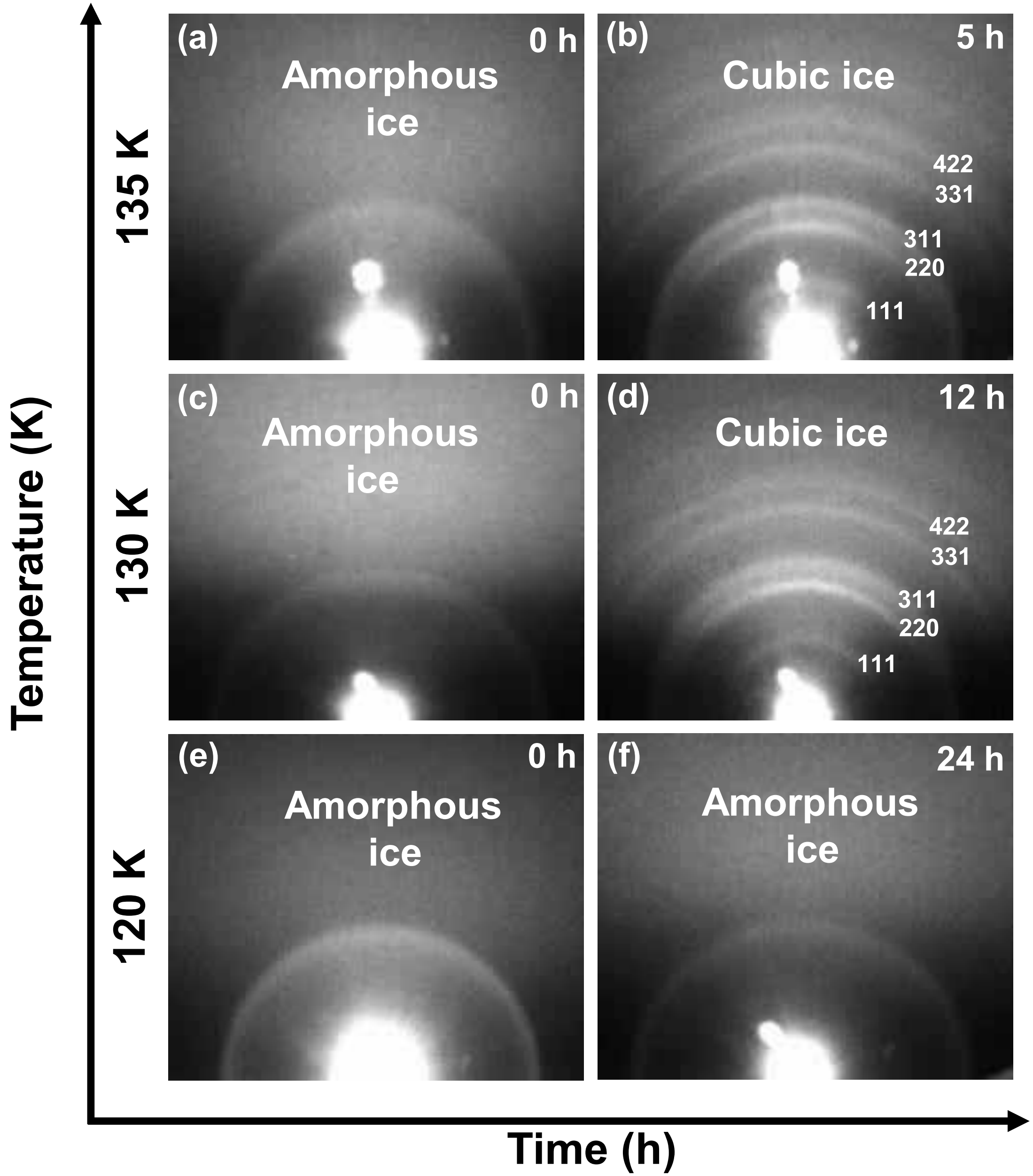
# RHEED set-up






https://www.staibinstruments.com/products/rheed/

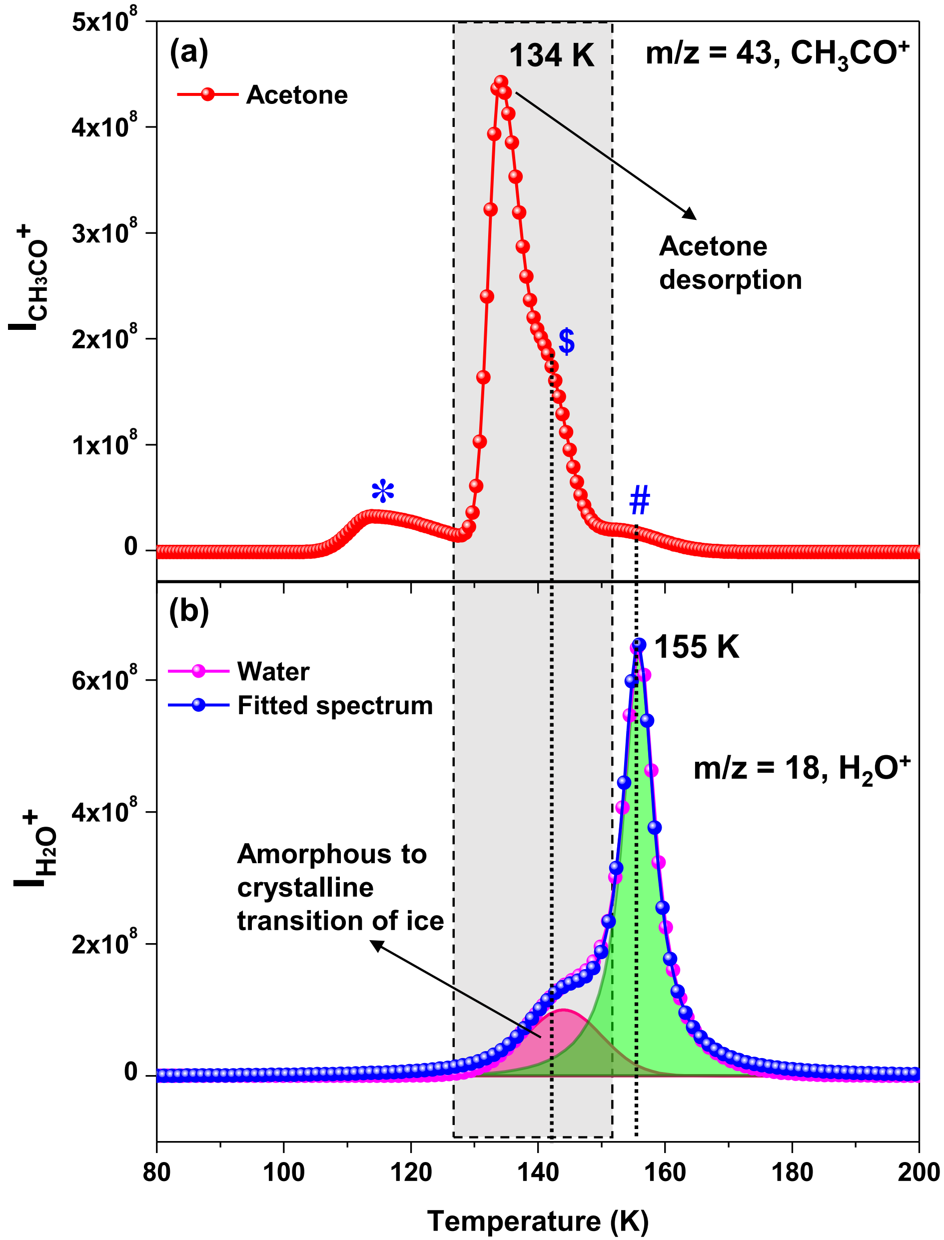
# Cubic ice via clathrate hydrate




Dr. Ryutaro Souda, NIMS, Tsukuba, Japan

Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26-32

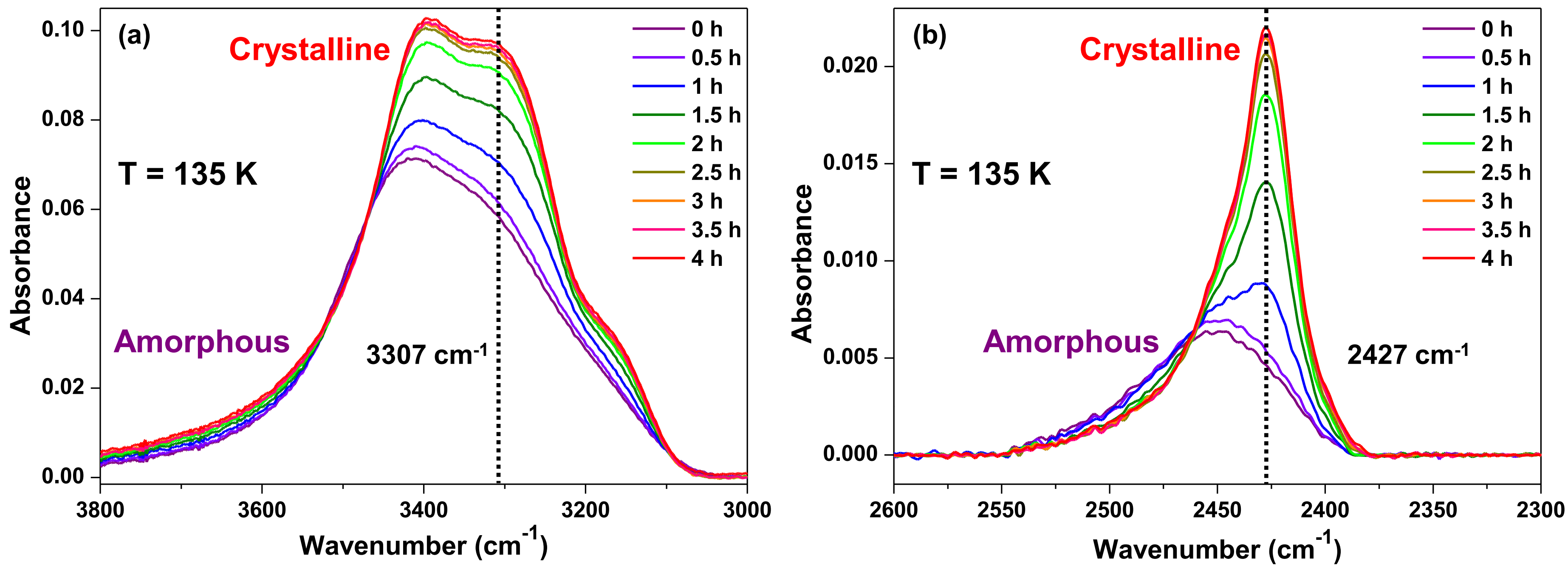
# Cubic ice via clathrate hydrate




Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26-32

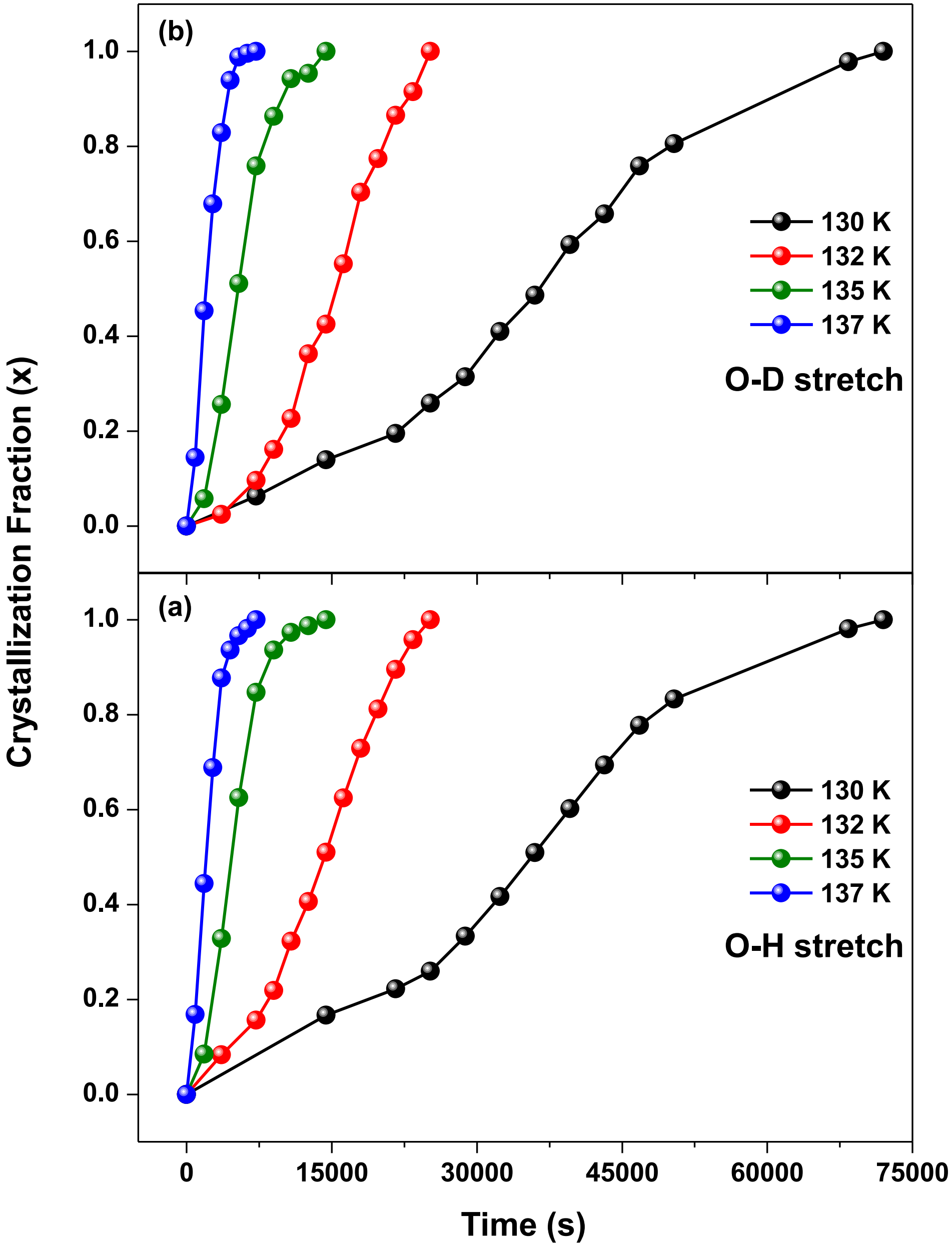
# Cubic ice via clathrate hydrate

acetone:HDO (5% $D_2O$ in $H_2O$ solution)




Ghosh, J. *et al., J. Phys. Chem. Lett.* **2020**, *11*, 26-32

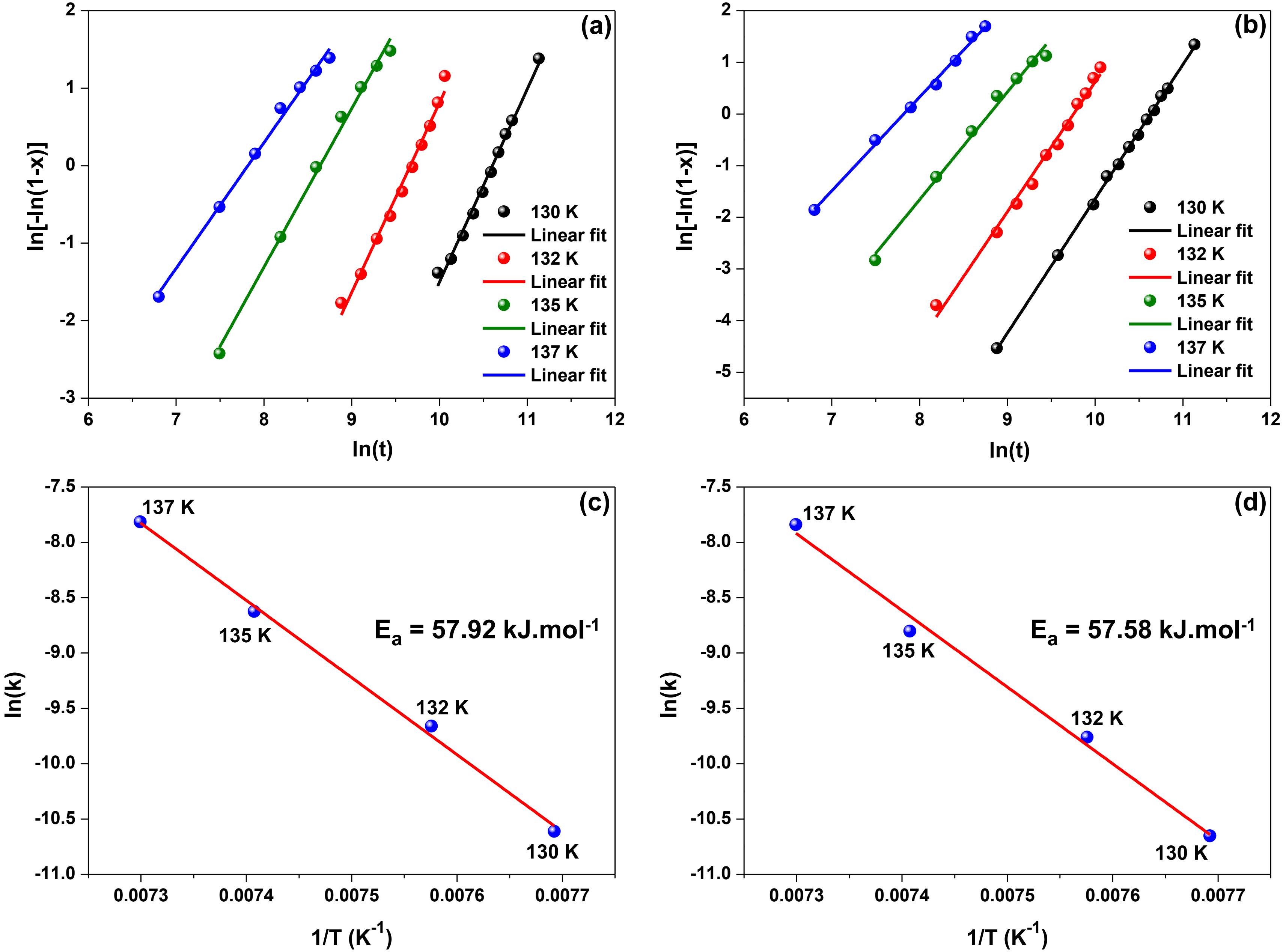
# Cubic ice via clathrate hydrate






Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26-32

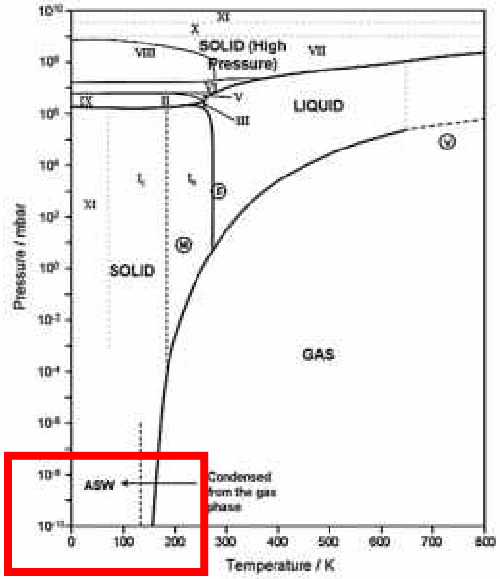
# Cubic ice via clathrate hydrate



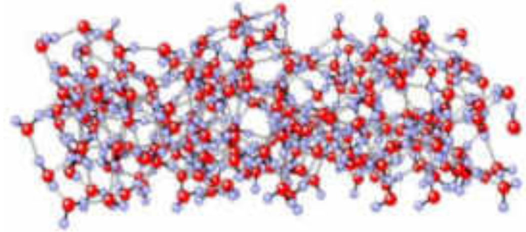



Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26-32

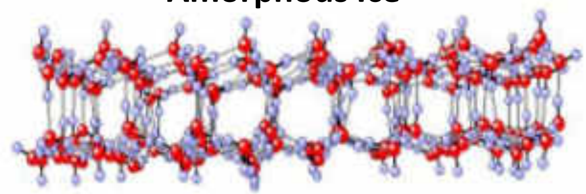
# Water ice




Mason, N. J. *et al.*, *Faraday Discussions.*, **2006**, *133*, 311–329



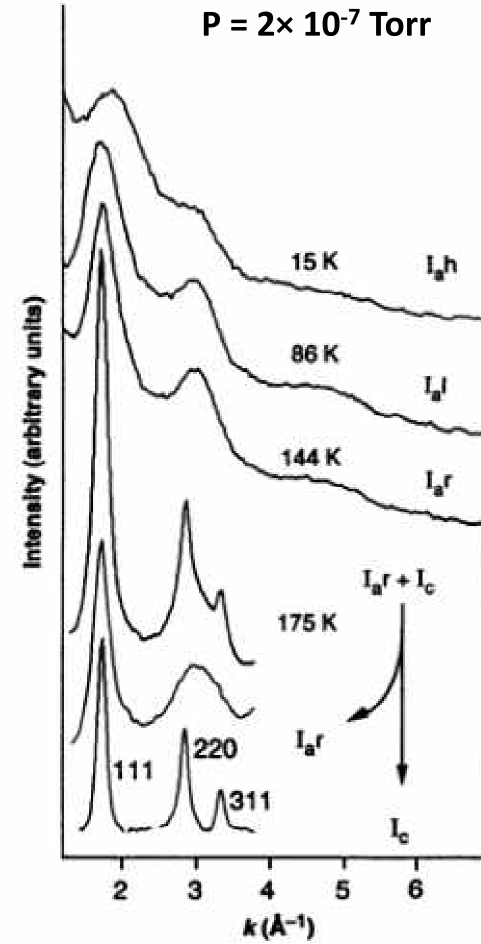
Amorphous Ice

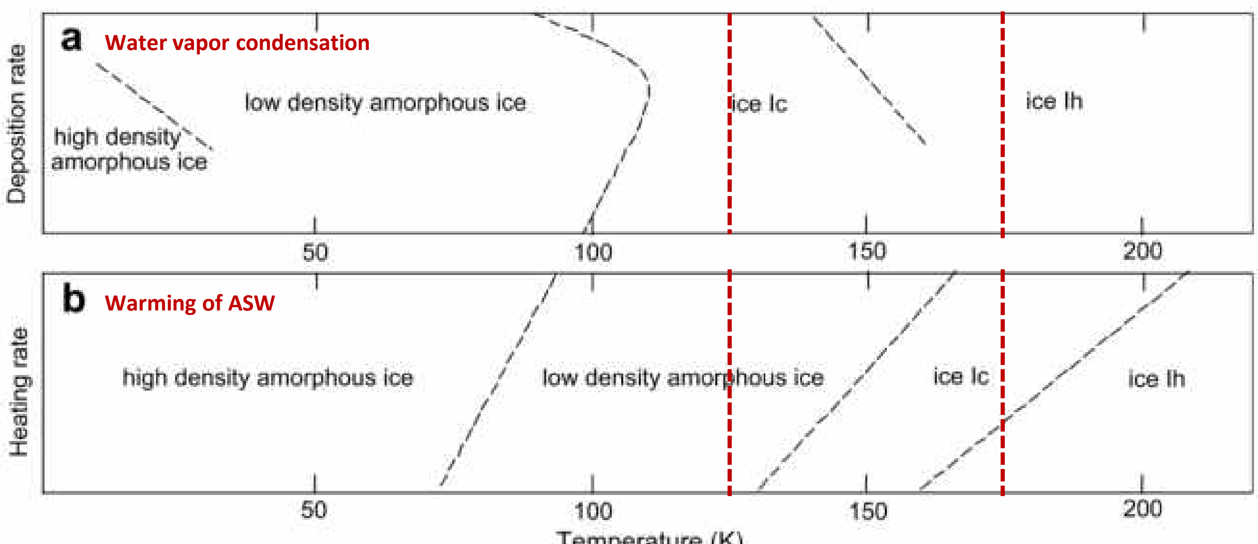


Crystalline Ice, T >135 K

Suter, M. T. *et al.*, *Chem., Phys.* **2006**, *326,* 281–288

Selected area electron diffraction



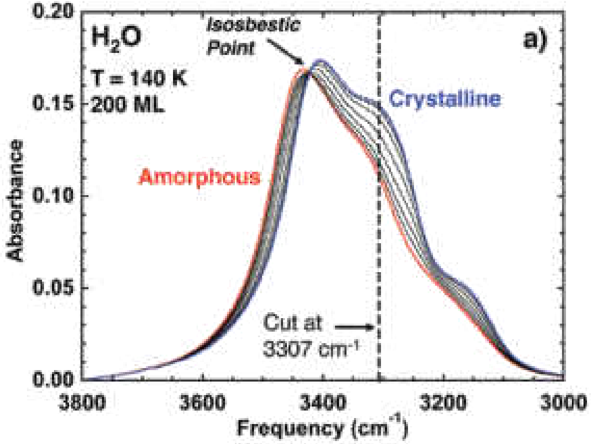

Jenniskens, P. & Blake, *Science.* **1994**, *265*, 753–756

Watanabe, N & Kouchi, A., *Prog. Surf. Sci.*, **2008**, *83*, 439–489

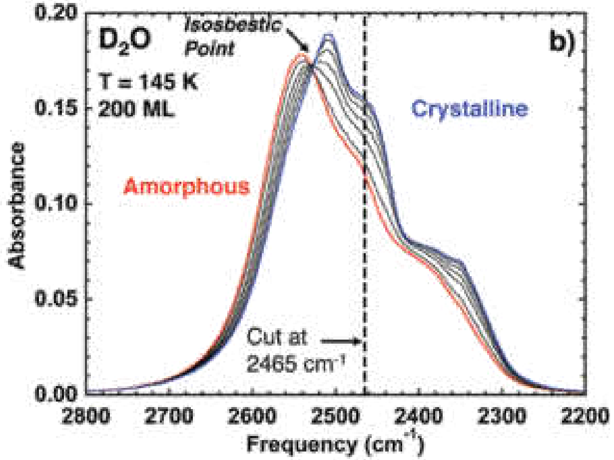
Phenomena

# Crystallisation

O-H stretch

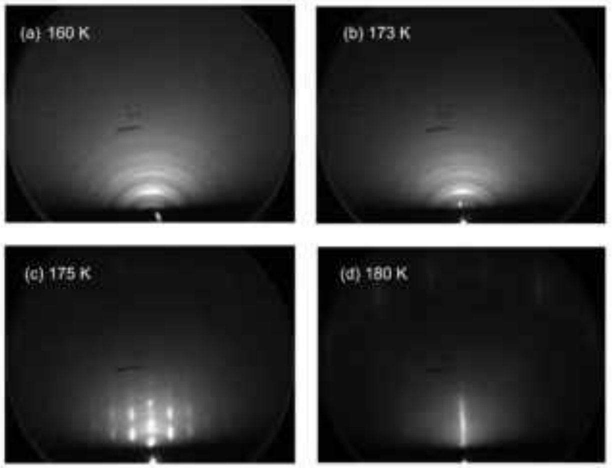



O-D stretch

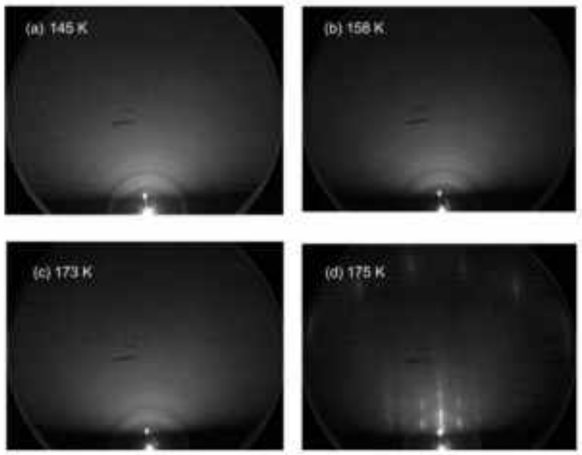



Smith, R. S. *et al., J. Phys. Chem. A.*, **2011**, *115*, 5908–5917

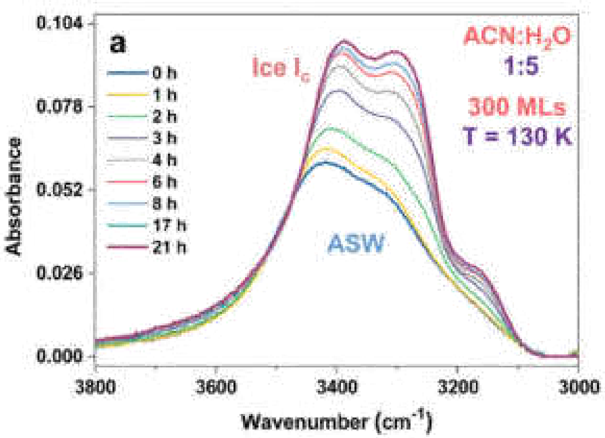
RHEED pattern

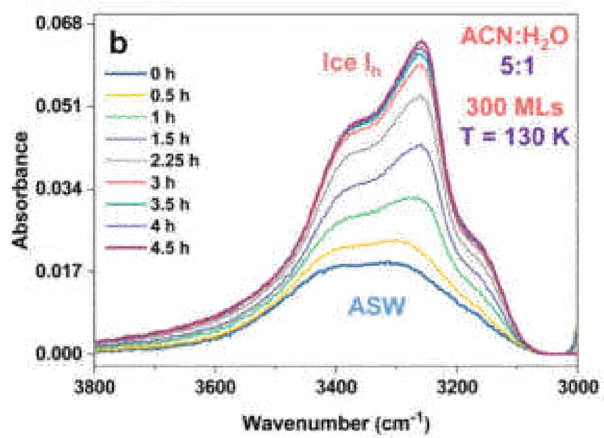



(1-propanol (2 L)/$H_2O$ (50 L)/Pt(111))




(Methanol (2 L)/$H_2O$ (50 L)/Pt(111))

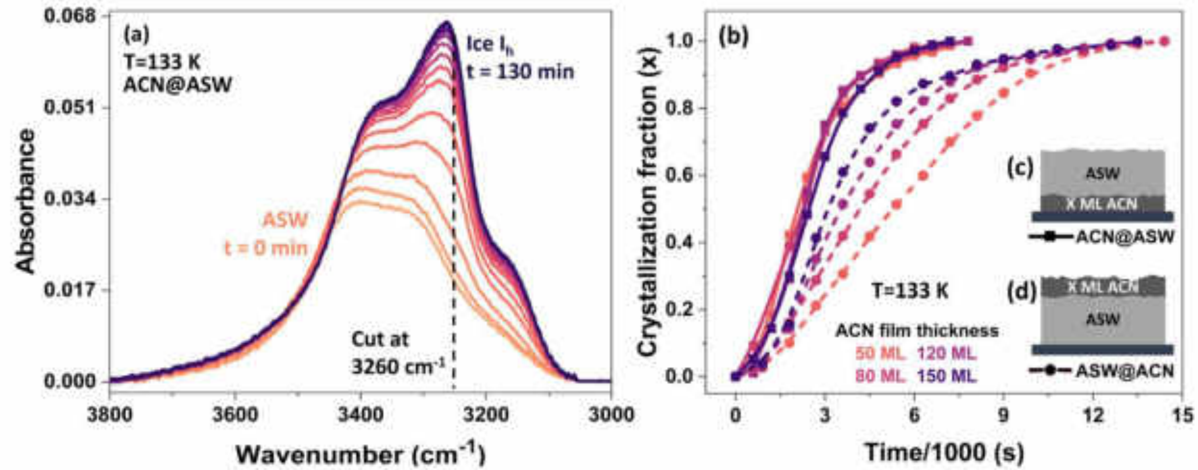


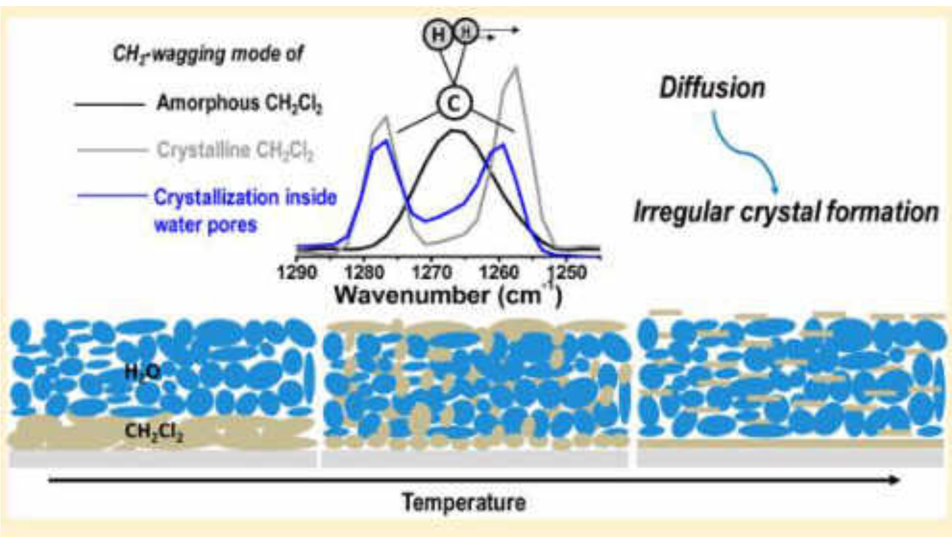

Viswakarma, *G. et al., Phys. Chem. Chem. Phys.*, **2021**, *23*, 24052–24060

Souda, R. *et al., Langmuir.*, **2022**, *38*, 14422–14429

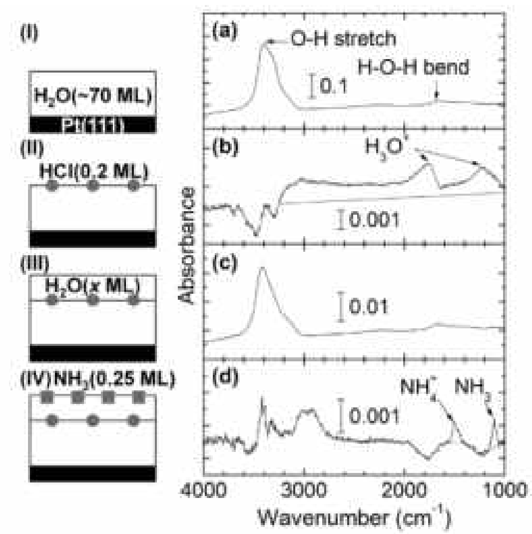
# Diffusion




Viswakarma, *G. et al., Phys. Chem. Chem. Phys.*, **2022**, *24,* 26200–26210

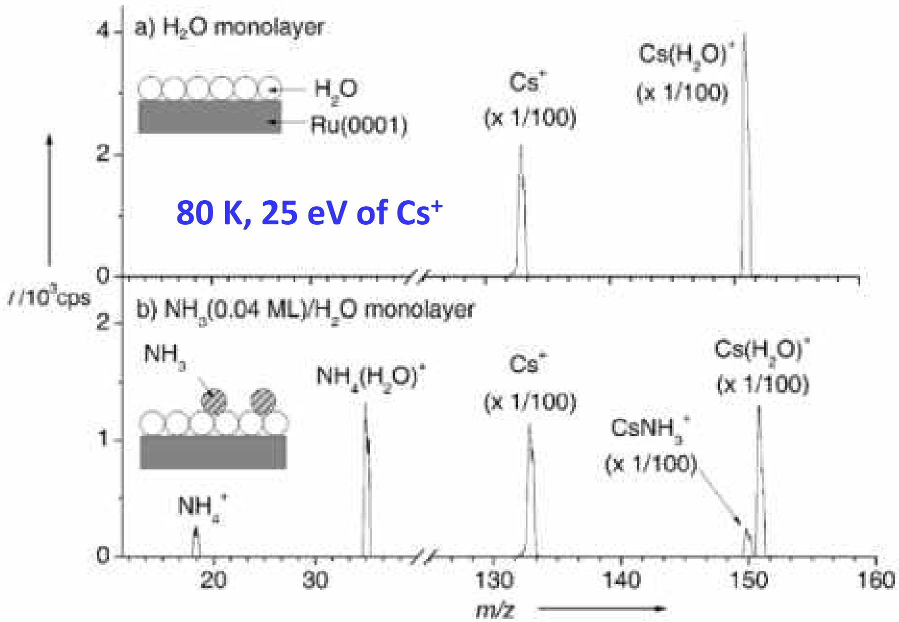


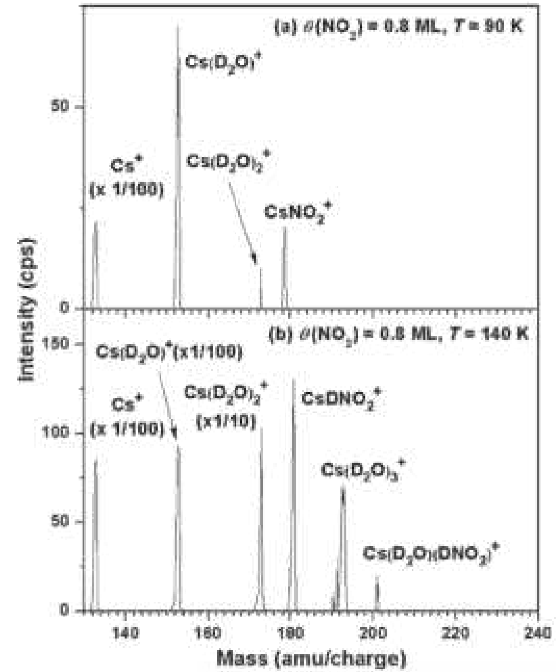

Bhuin, R.G. *et al., J. Phys. Chem. C.,* **2016**, *120*, 13474−13484



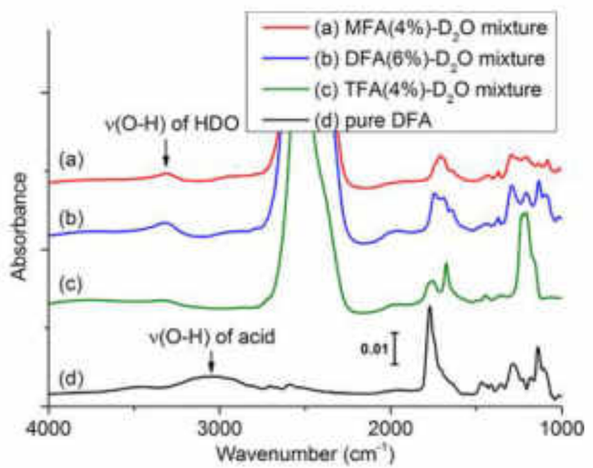

Lee, D. H., *et al., J. Phys. Chem. C.*, **2019**, *123*, 3657–3663

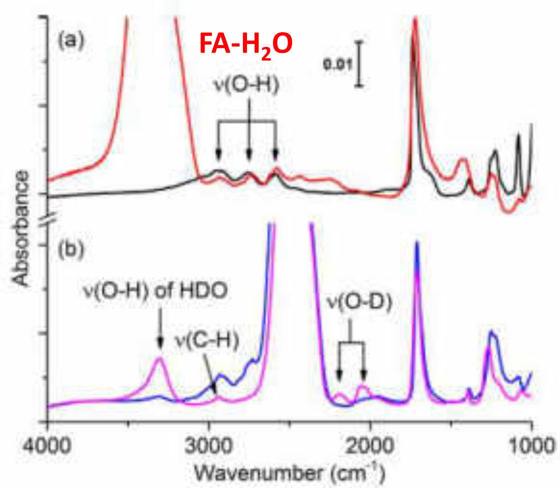
# Chemical reaction

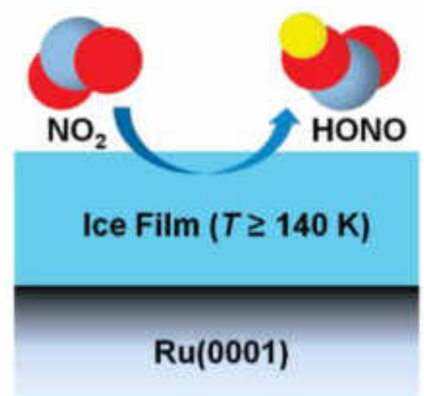



Kang, H., *Angew. Chem. Int. Ed.*, **2012**, *51*, 1-5



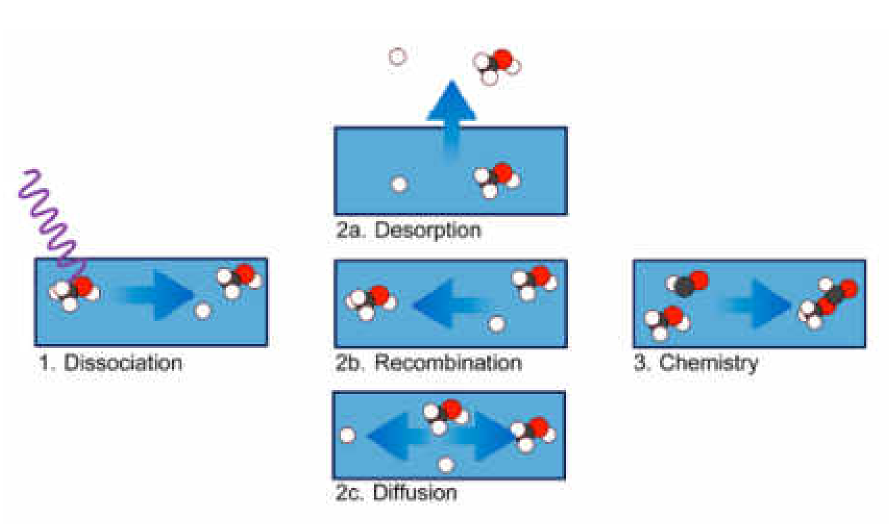



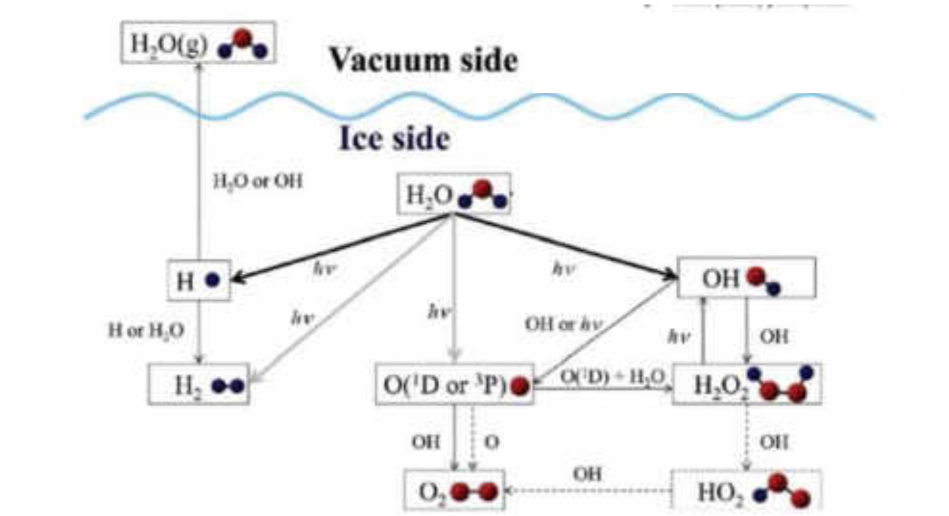

Park, Y. *et al., J. Phys. Chem. Lett.*, **2018**, *9*, 4282−4286

Kim, S. *et al., J. Phys. Chem. Lett.*, **2010**, *1*, 3085−3089

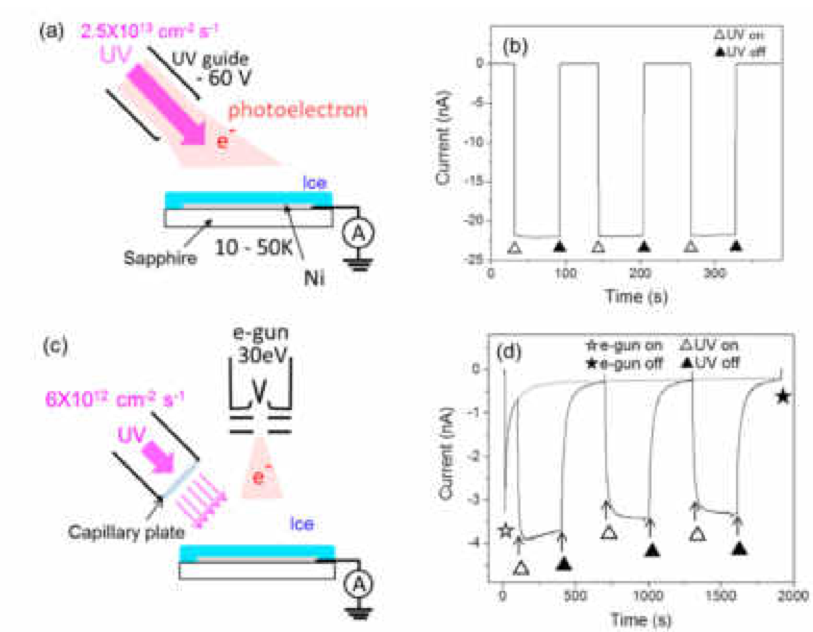
# Photochemistry of molecular solids

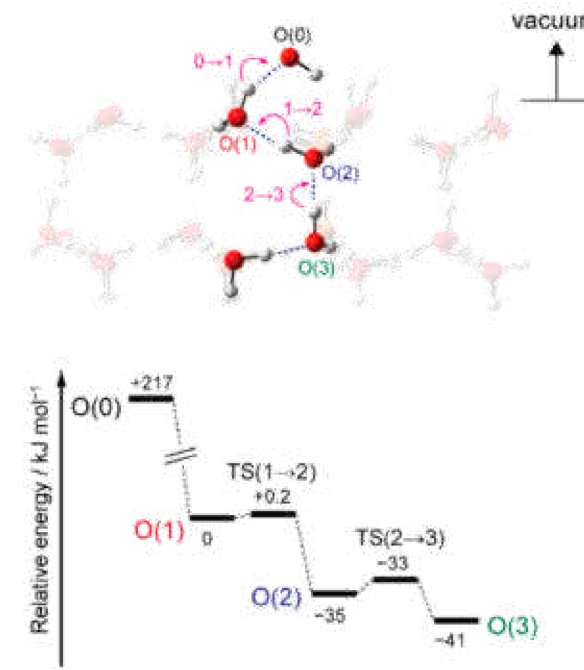



Öberg. K. *Chem. Rev.,* **2016,** *116*, 9631–9663




Arumainayagam, C. R. *et al. Chem. Soc. Rev.,* **2019**, *48*, 2293–2314

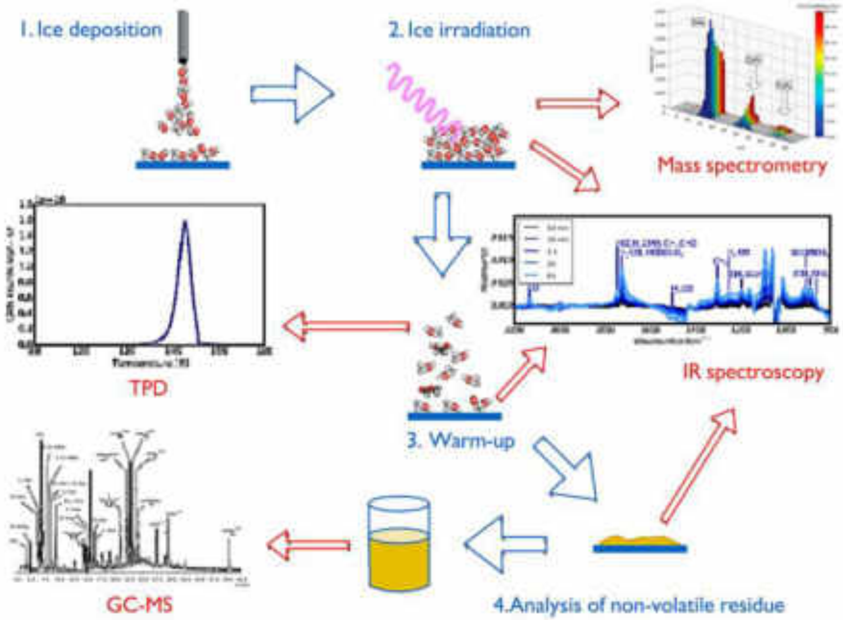


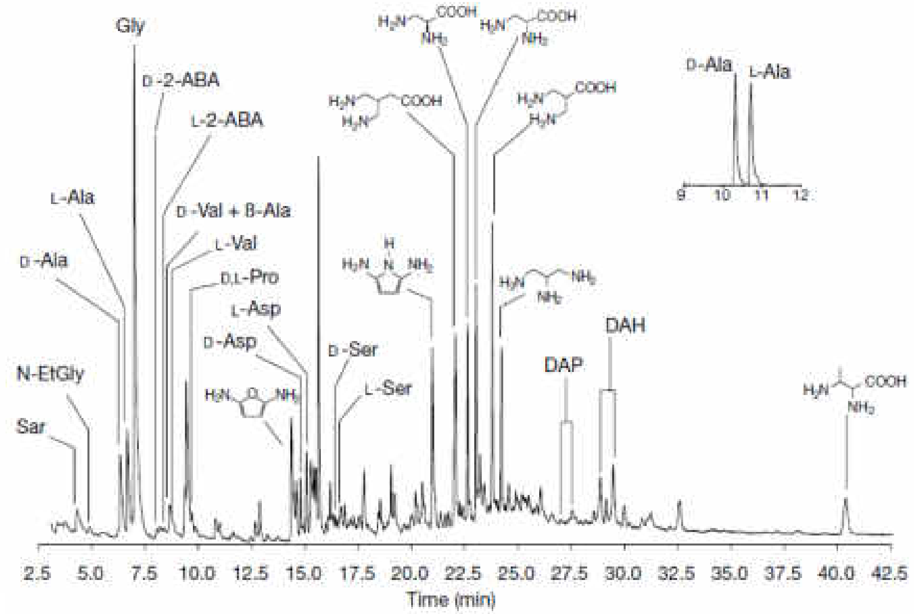






Tsuge, M. & Watanabe, N., *Acc. Chem. Res.*, **2021**, *54*, 471–480

# Origin of life




| |
|---|
| Al substrate: 12 K temperature |
| $H_2O:CH_3OH:NH_3:CO:CO_2 = 2:1:1:1:1$ |
| **UV flux = $1.5\times10^{15}$ photons.$s^{-1}$ for 24 hours** |
| 6 M HCl at 110 °C for 24 h under argon atmosphere |
| Caro G.M.M. *et al., Nature,* **2002**, *416*, 403–406 |

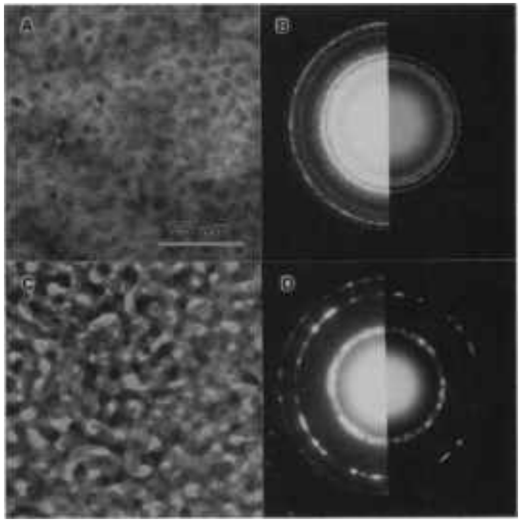
Öberg, K., *Chem. Rev.,* **2016,** *116*, 9631−9663

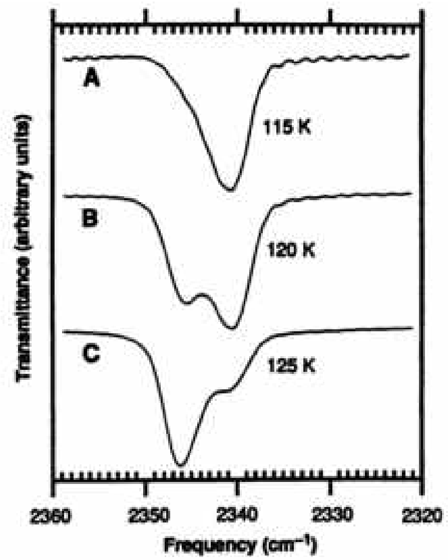
Caro, G.M.M. *et al., Nature.*, **2002**, *416*, 403–406

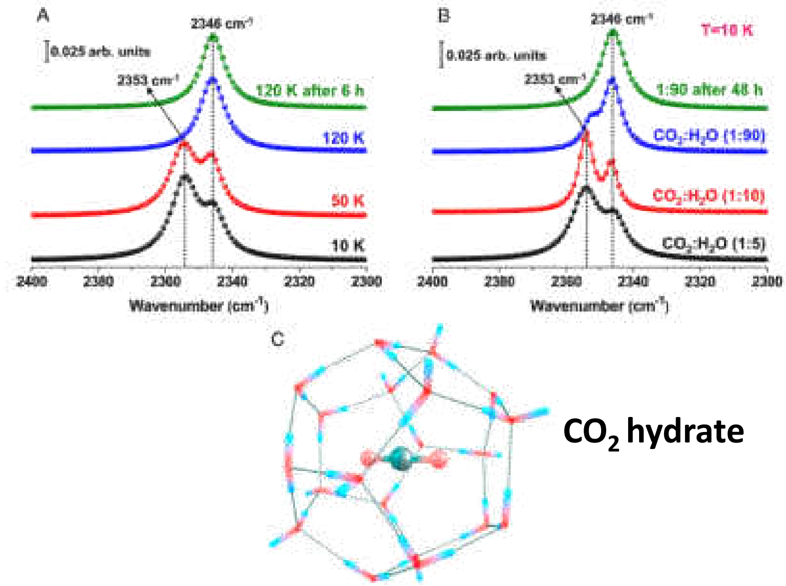
# Clathrate hydrate formation in vacuum

P = $10^{-6}$ Torr

$H_2O:CH_3OH:CO_2 = 100:50:1$

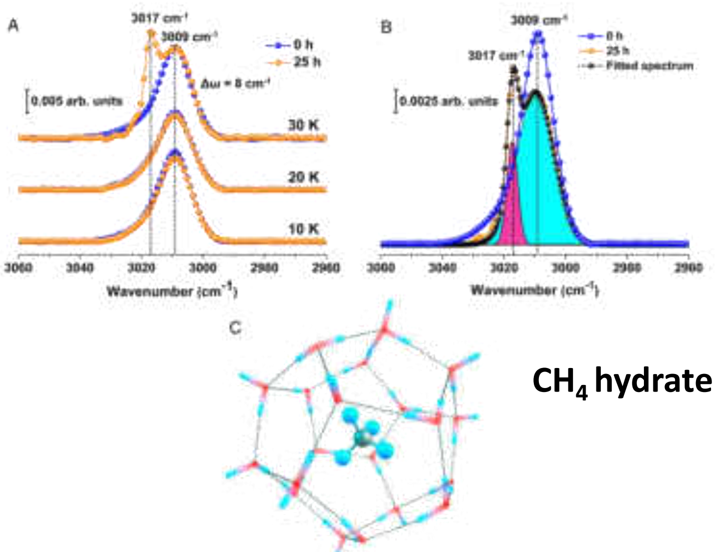


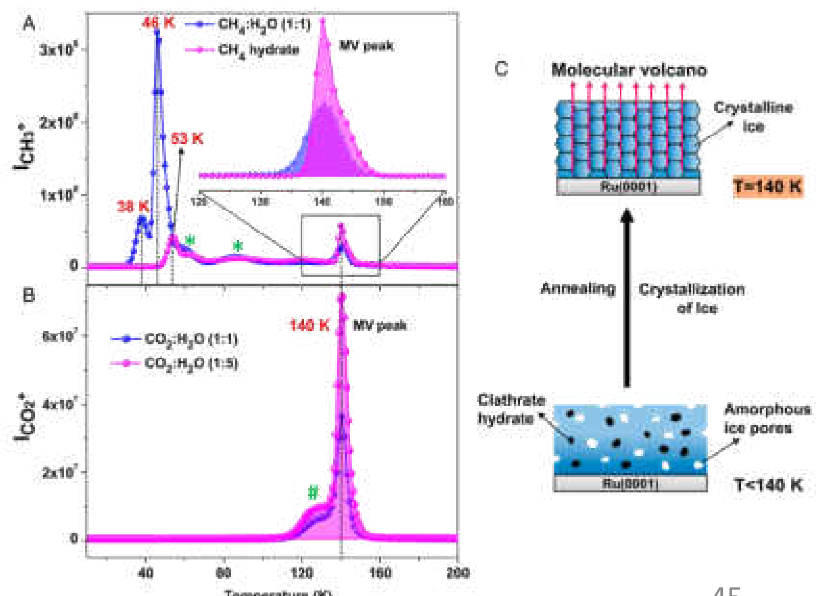




$CO_2$ hydrate

Blake, D. *et* al., Science., **1991**, *254*, 548–551



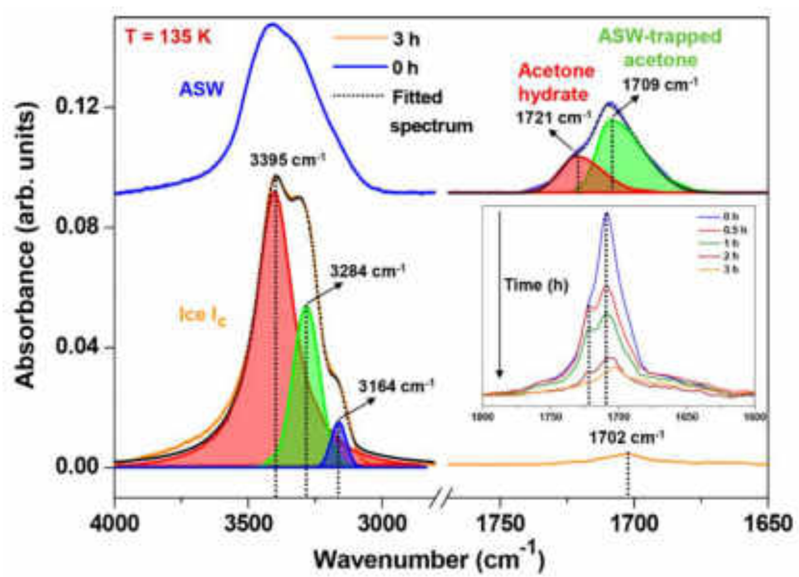

$CH_4$ hydrate

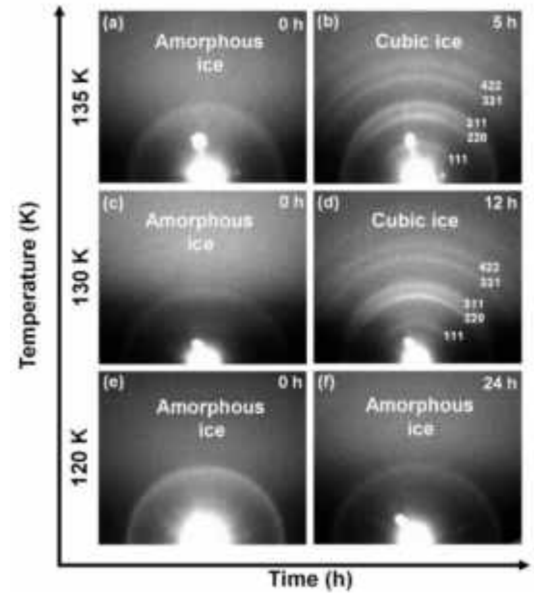




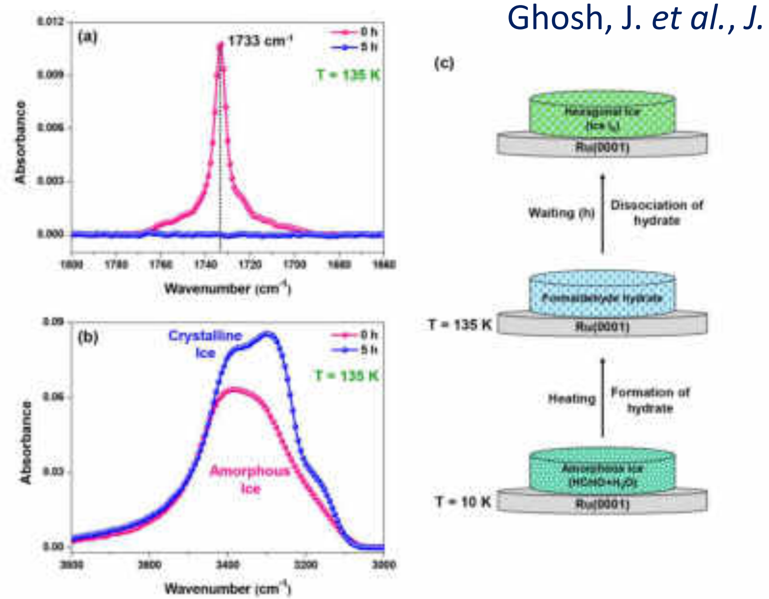

Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **2018,** *116*, 1526-1531

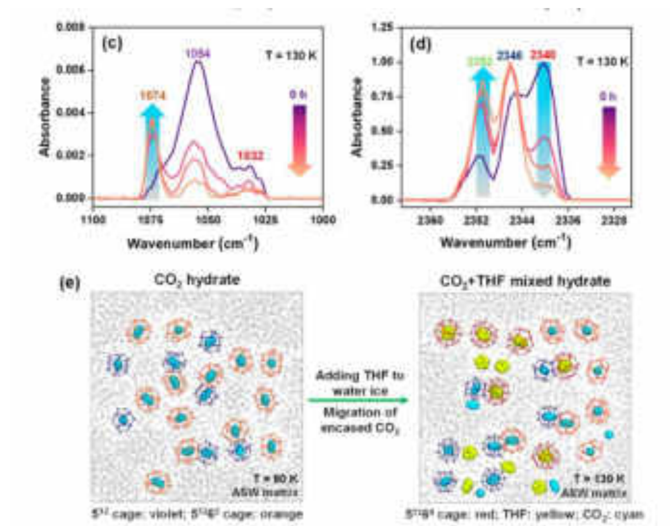
# Transformation of clathrate hydrate under UHV




Ghosh, J. *et al.*, *J. Phys. Chem. Lett.*, **2020**, *11*, 26–32



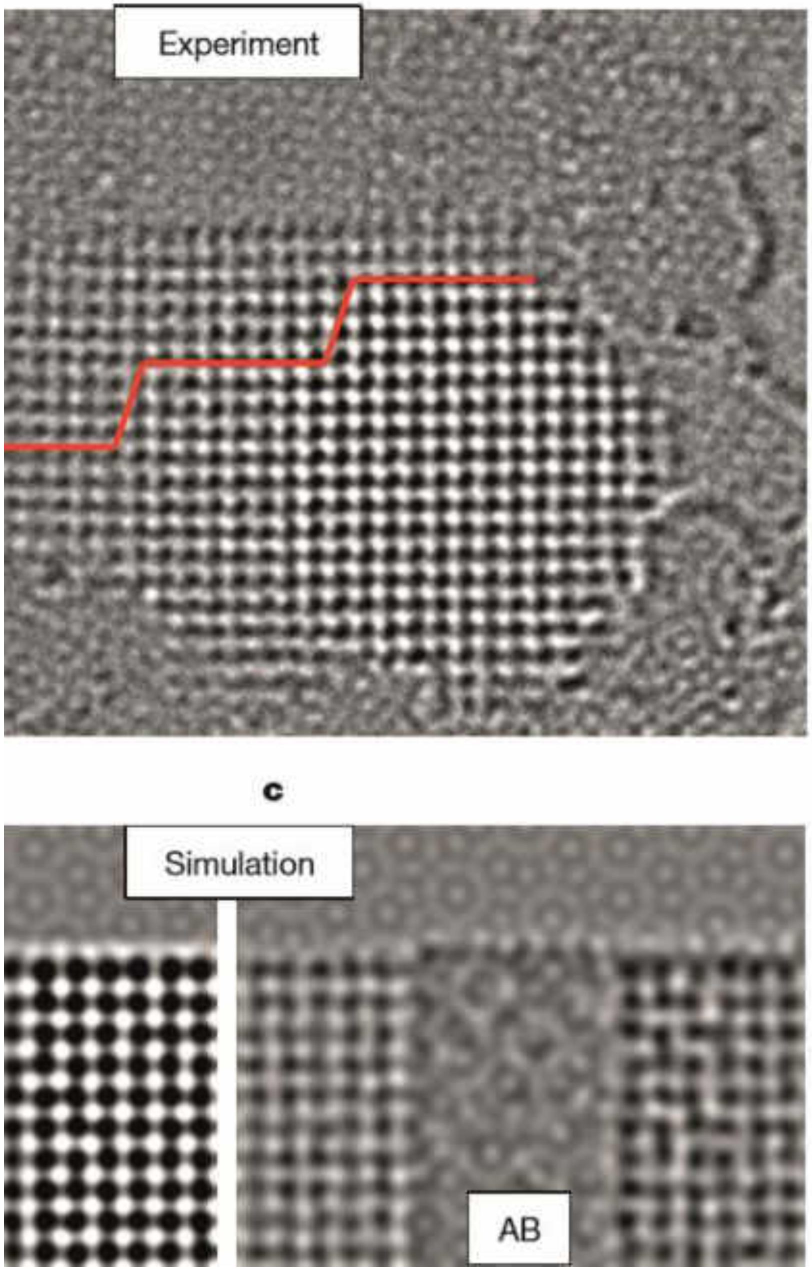



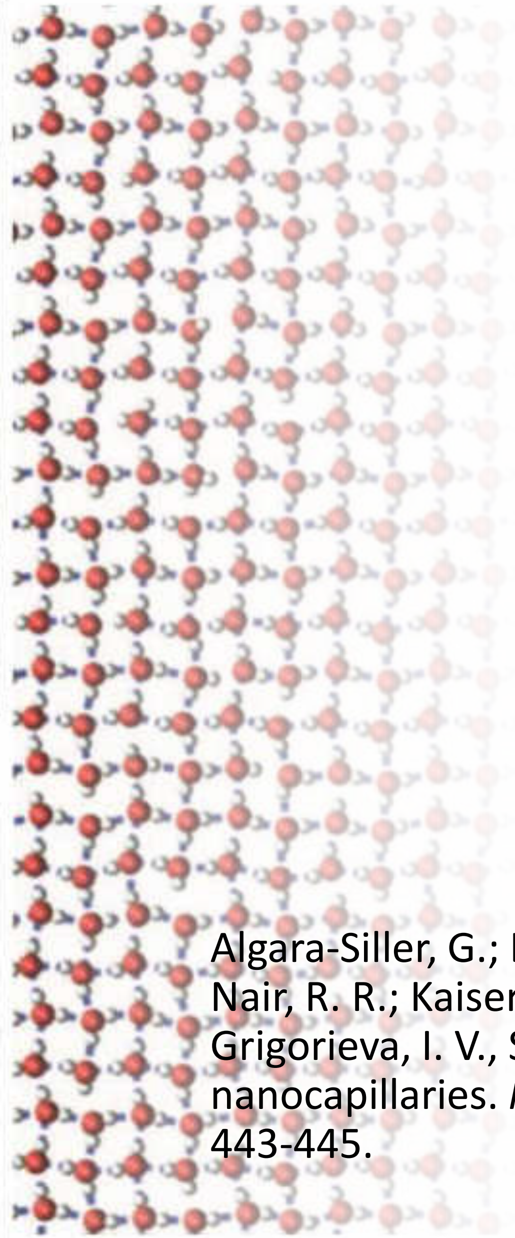

Viswakarma, *G. et al.*, *J. Phys. Chem. Lett.*, **2023**, *14*, 2823–2829

Ghosh, J. *et al.*, *J. Phys. Chem. C.*, **2021**, *125*, 4532–4539

CryoEM

# Observing clathrate hydrates?



Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015,** *519* (7544), 443-445.

## *Existence of acetaldehyde clathrate hydrate and its dissociation leading to cubic ice under ultrahigh vacuum and cryogenic conditions*

Vishwakarma G. *et al*., ***J. Phys. Chem. Lett*.** 2023, *14*, 5328−5334

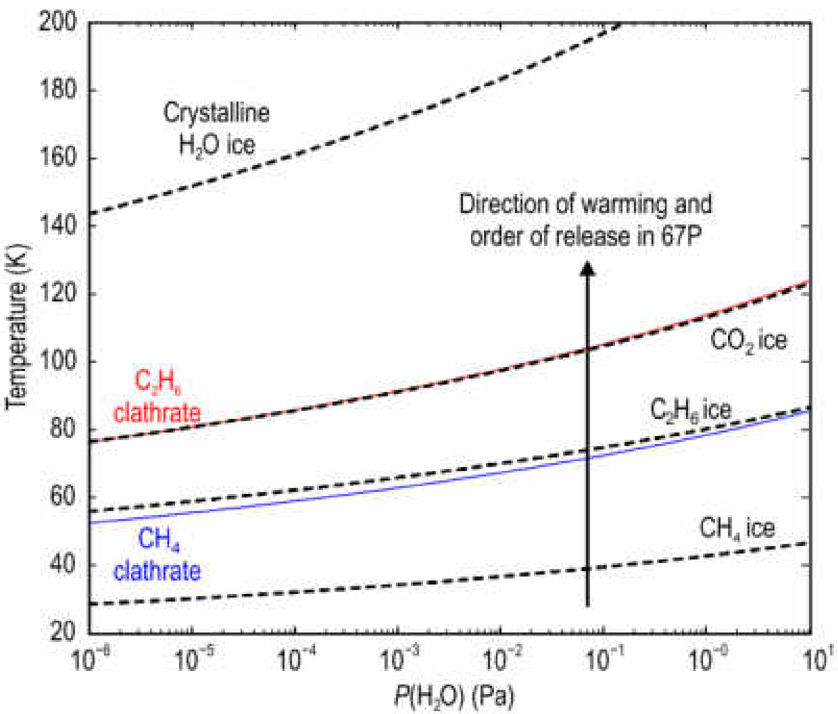
# Motivation

SPACE SCIENCES

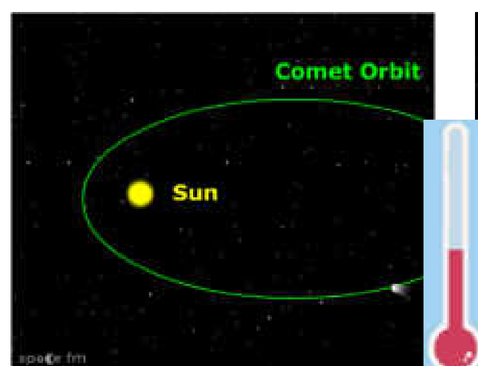
## The presence of clathrates in comet 67P/Churyumov-Gerasimenko

Adrienn Luspay-Kuti,[1]* Olivier Mousis,[2] Myrtha Hässig,[1,3] Stephen A. Fuselier,[1,4] Jonathan ... [5] Be...ard Marty,[6] Kathleen E. Mandt,[1,4] Peter Wurz,[3,7] Martin Rubin[3]

...0.1126/sciadv.1501781




Equilibrium curves of clathrates and pure condensates in the cometary environment.

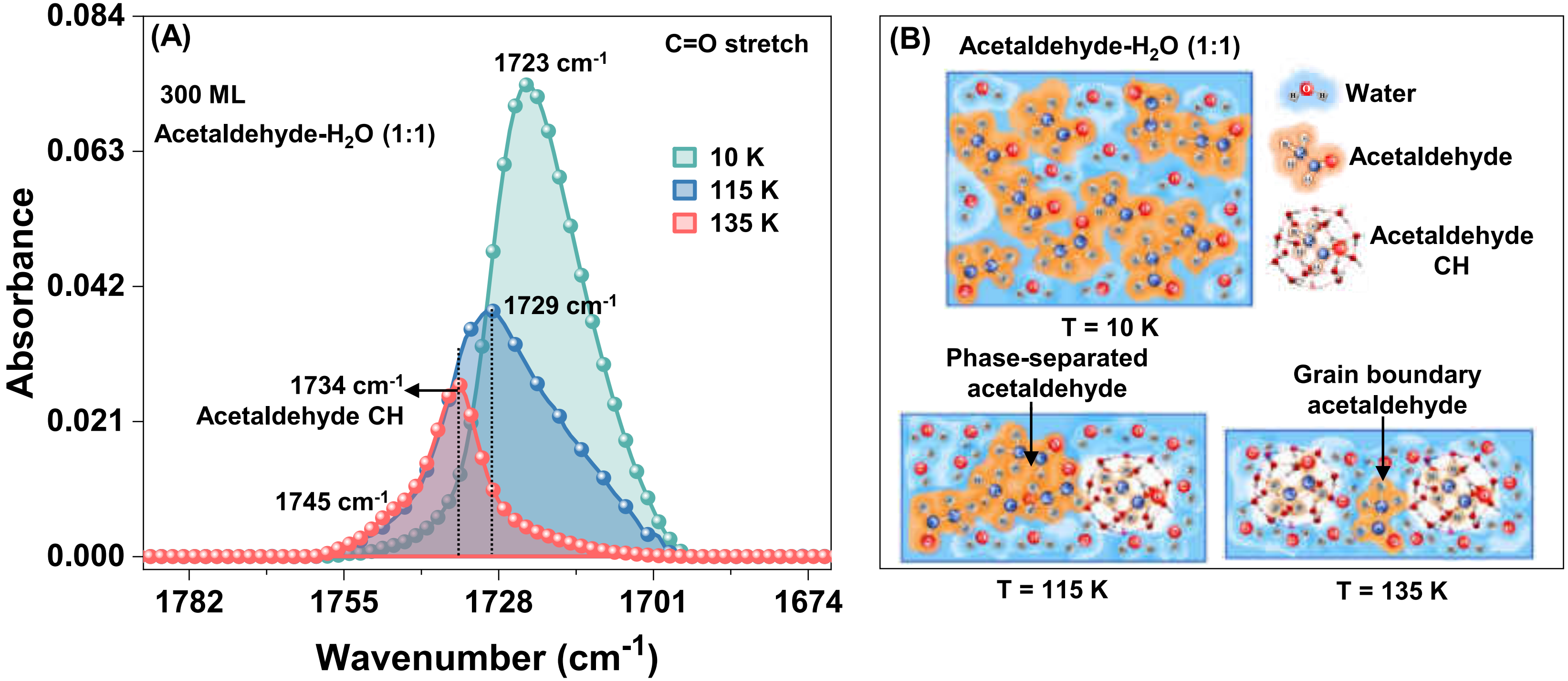

https://www.space.fm/astronomy/planetary systems/comets.html

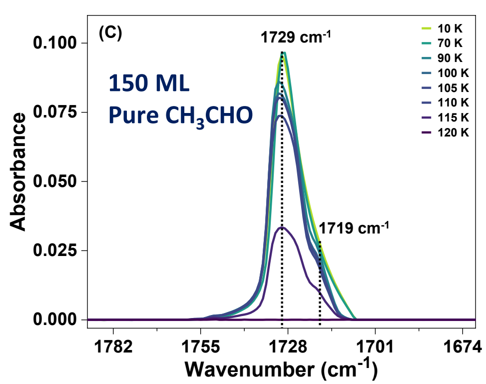
https://photojournal.jpl.nasa.gov/catalog/PIA21749

Luspay-Kuti, A. *et al.*, *Sci. Adv.* **2016**, *2*, e1501781

# Formation of acetaldehyde clathrate hydrate

## 300 ML $CH_3CHO+H_2O$ (1:1)




| Gaseous phase | Clathrate hydrate | Condensed phase |
|---|---|---|
| 1746 $cm^{-1}$ | 1734 $cm^{-1}$ | 1729 $cm^{-1}$ |

# Formation of acetaldehyde clathrate hydrate

**Dielectric and nuclear magnetic resonance characterization of unstable clathrate hydrates of acetaldehyde and propionaldehyde**[1]

D. W. DAVIDSON, S. R. GOUGH, AND J. A. RIPMEESTER
*Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9*

Received May 10, 1976

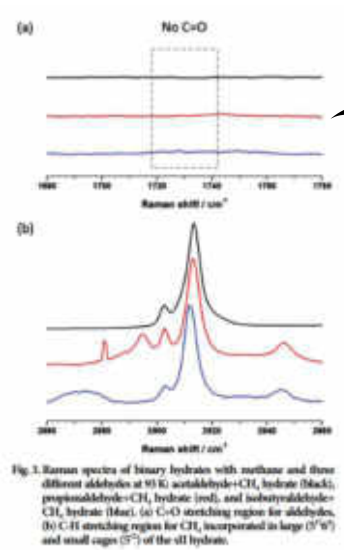
Davison, D. W. *et al.*, *Can. J. Chem.* **1976**, *54*, 3085-3088

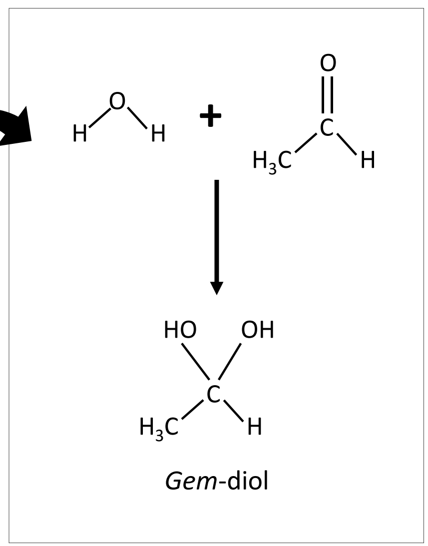
**Thermodynamic and spectroscopic identification of aldehyde hydrates**

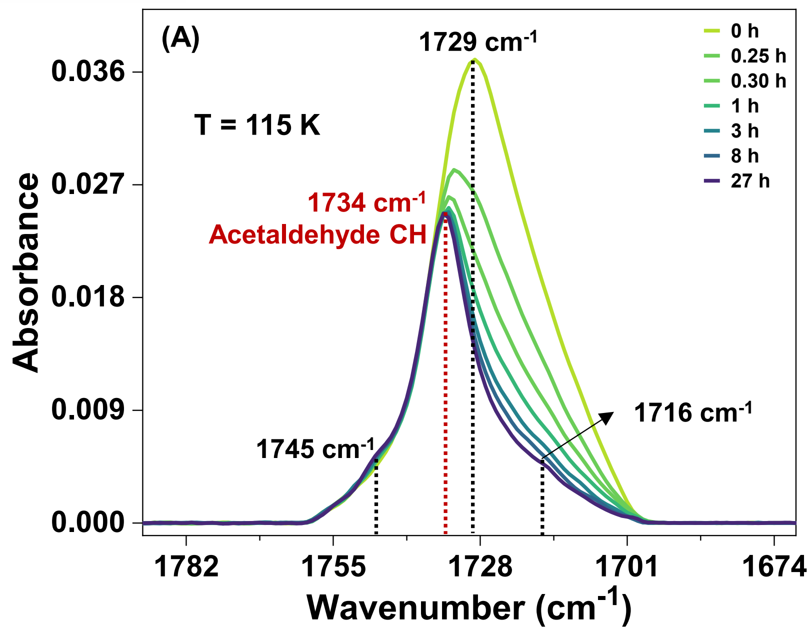
**Hyery Kang, Yun-Ho Ahn, Dong-Yeun Koh, and Huen Lee**[†]

Department of Chemical and Biomolecular Engineering (BK21+ Program), KAIST,
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea

(*Received 3 November 2015 • accepted 25 January 2016*)



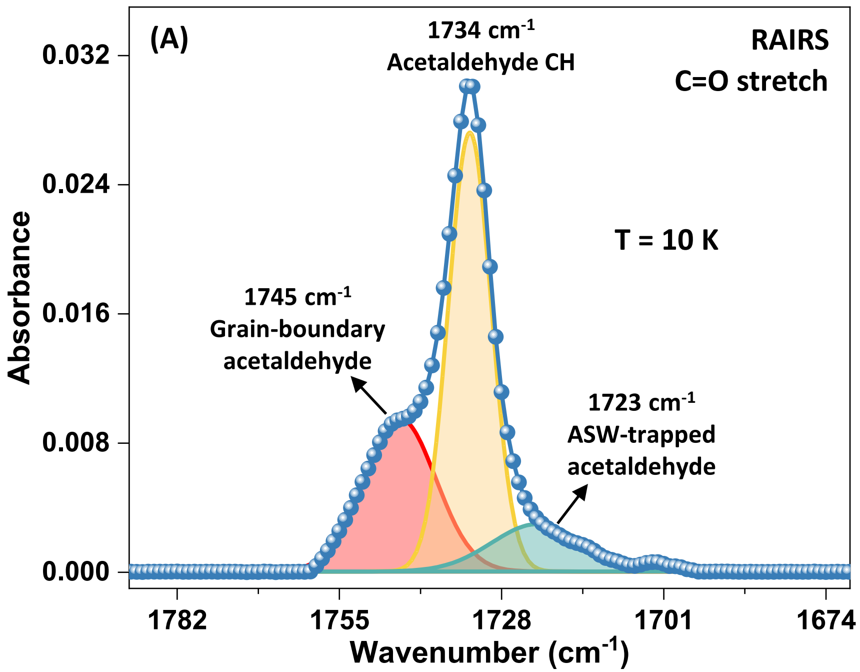




Kang, H. *et al.*, *Korean J. Chem. Eng.* **2016**, *33*, 1897-1902

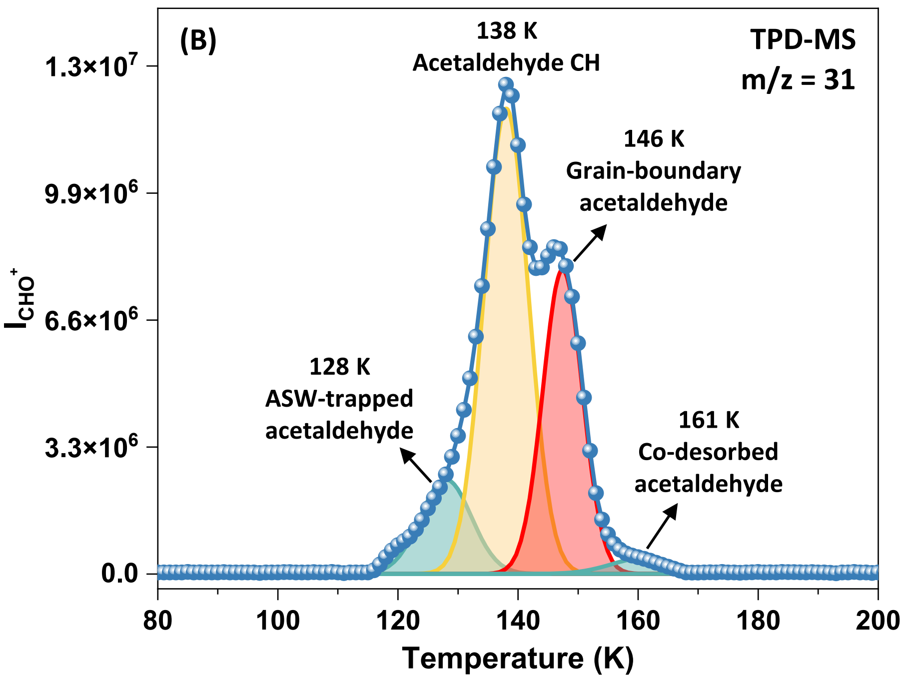
# Formation of acetaldehyde clathrate hydrate

## RAIRS at 10 K



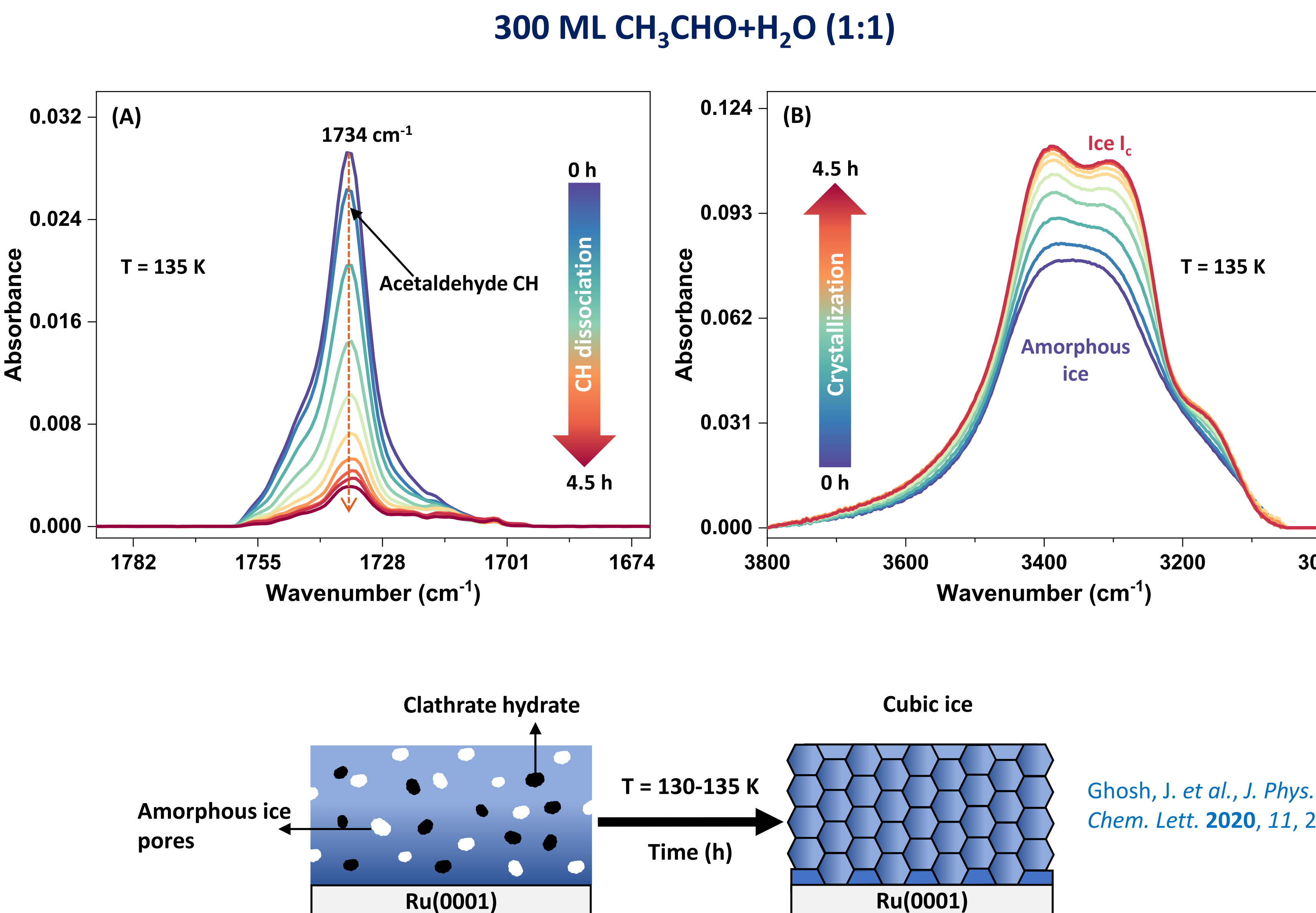

| Peak position ($cm^{-1}$) | 1745 | 1734 | 1723 |
|---|---|---|---|
| Amount of $CH_3CHO$ (%) | 32 | 55 | 13 |

## TPD-MS



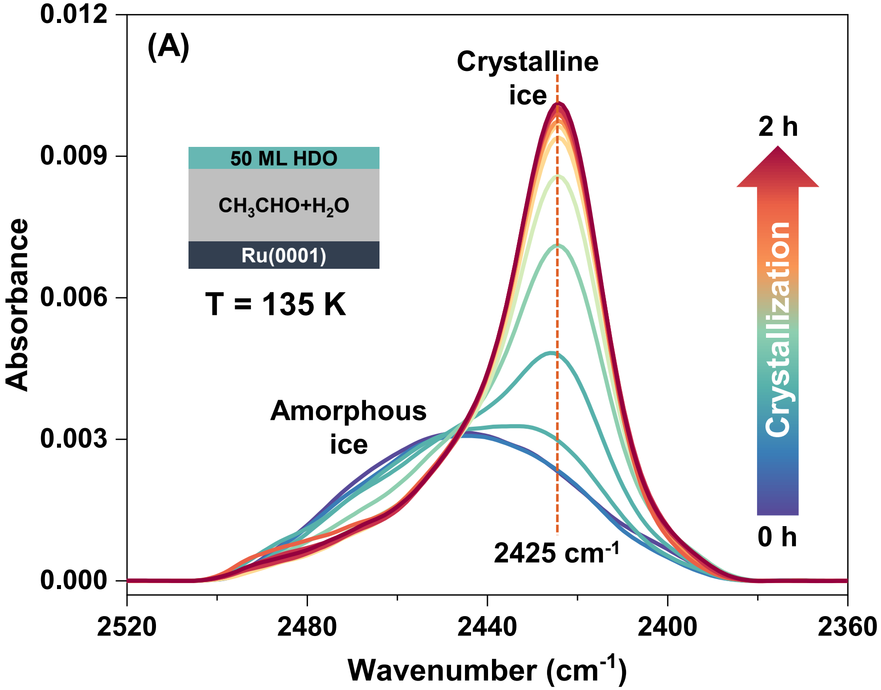

| Peak position (K) | 128 | 138 | 146 | 161 |
|---|---|---|---|---|
| Amount of $CH_3CHO$ (%) | 12 | 54 | 31 | 3 |

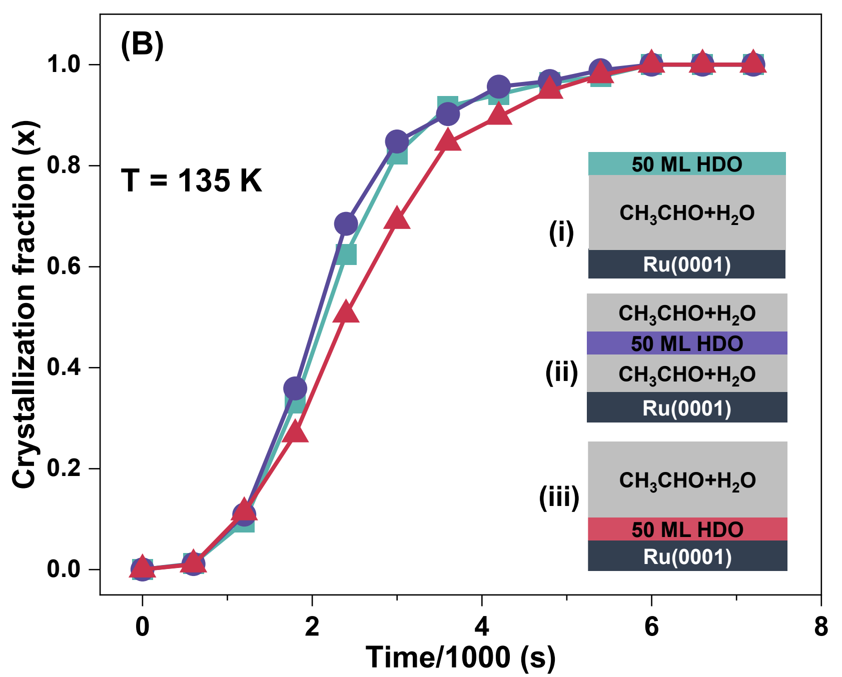
# Formation of cubic ice via dissociation of clathrate hydrate

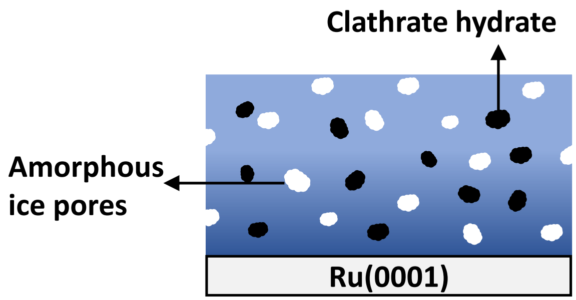


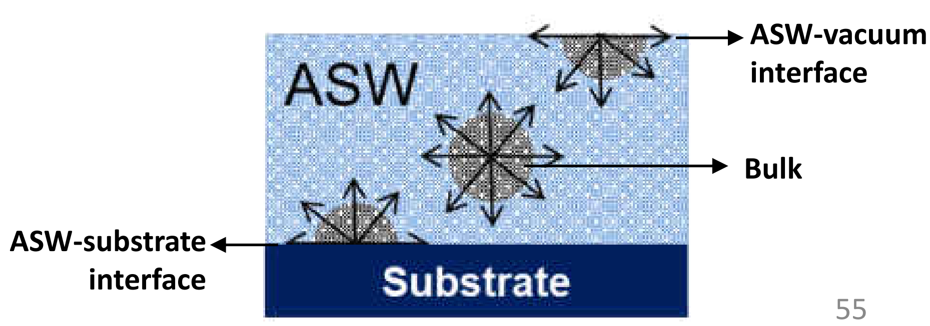

Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26–32

# Crystallization mechanism

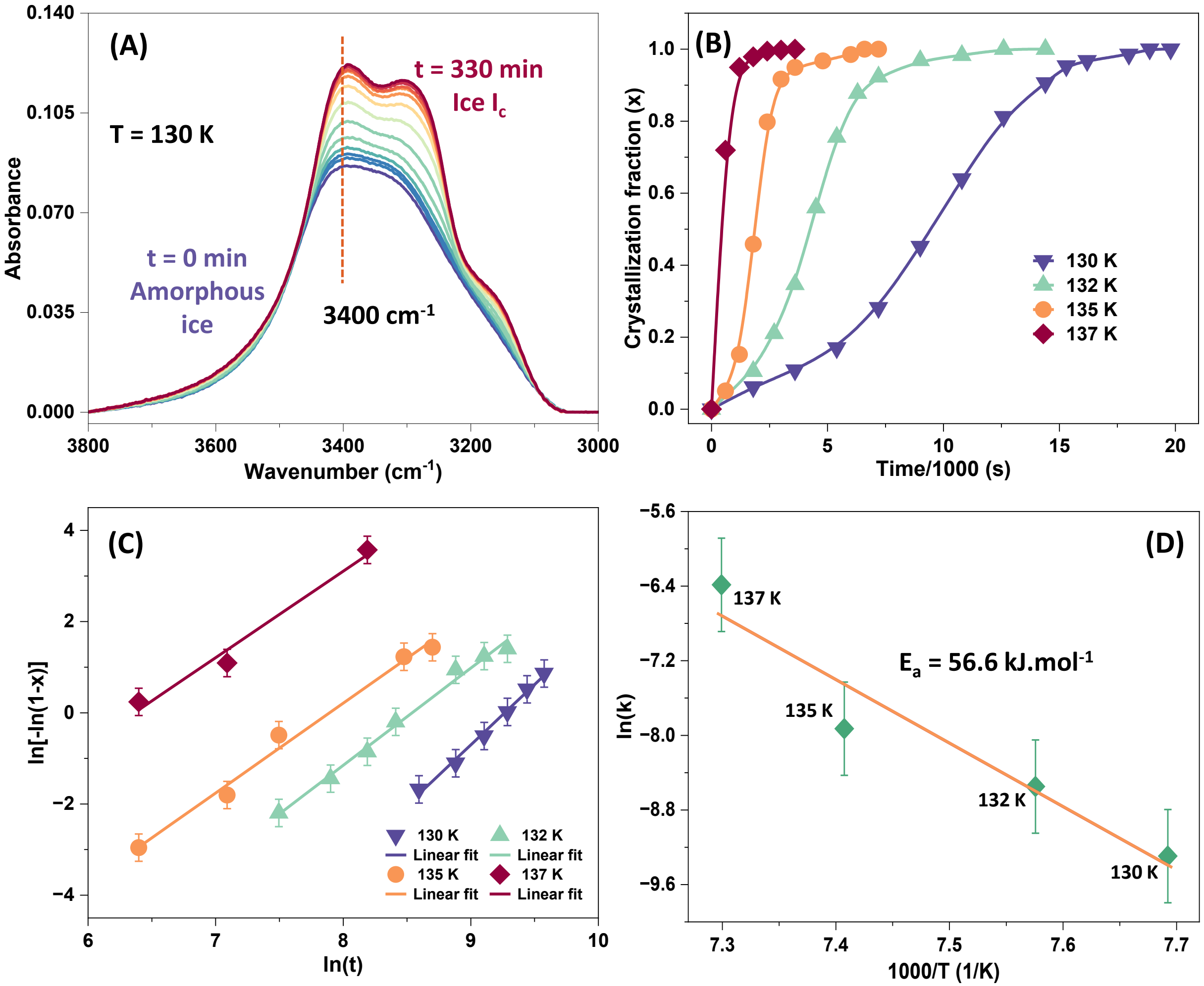


# Crystallization Kinetics



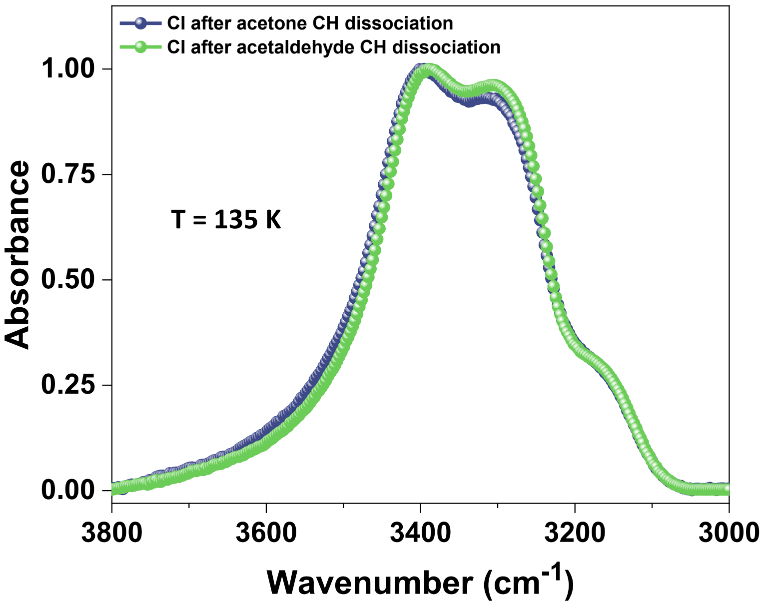

Avrami equation

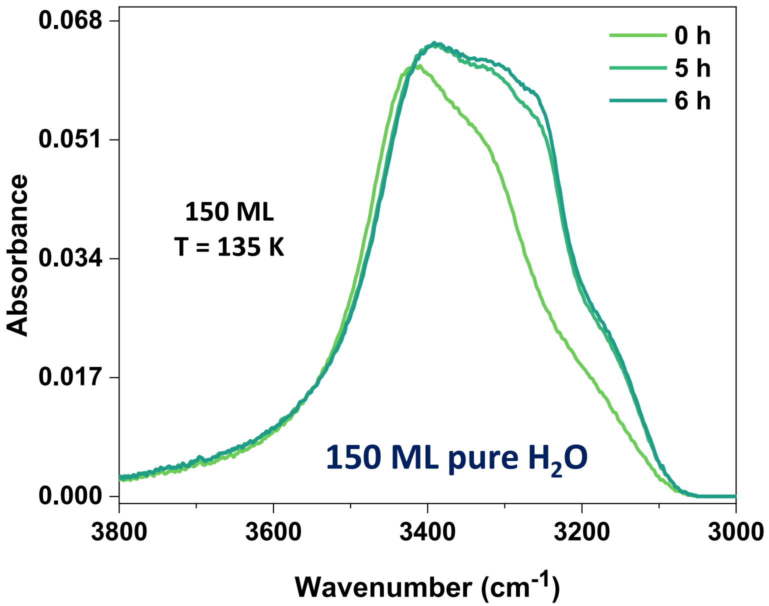
$$x(t) = 1 - \exp(-k \cdot t)^n$$

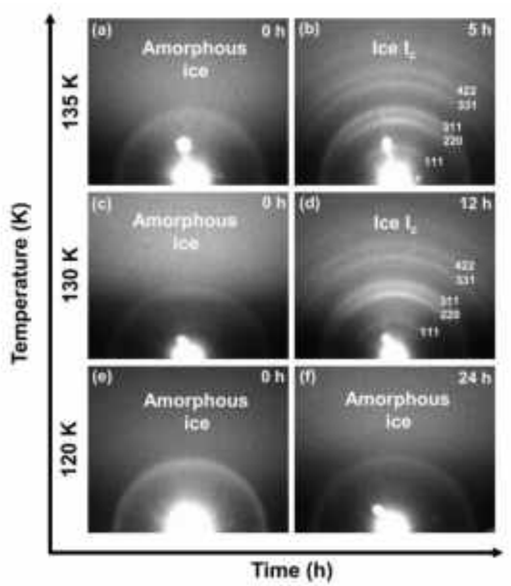
$$\ln(-\ln[1 - x(t)]) = n \ln(t) + n \ln k$$

Activation energy ($E_a$) for crystallization of pure ASW film = 60–77 kJ·mol$^{-1}$

# Control experiments




Time-dependent RHEED images of 300 MLs of acetone:$H_2O$ (1:1) at 120, 130, and 135 K.

Ghosh, J. *et al.*, *J. Phys. Chem. Lett.* **2020**, *11*, 26–32

**Few additional experiments**

(1) $CH_3CHO$+$D_2O$ (1:1)

(2) $CH_3CHO$@$H_2O$ (150 @150 ML)

(3) $CH_3CHO$+$H_2O$ (1:10, 1:20)

# *Facile crystallization of ice $I_h$ via formaldehyde hydrate in ultrahigh vacuum under cryogenic conditions*

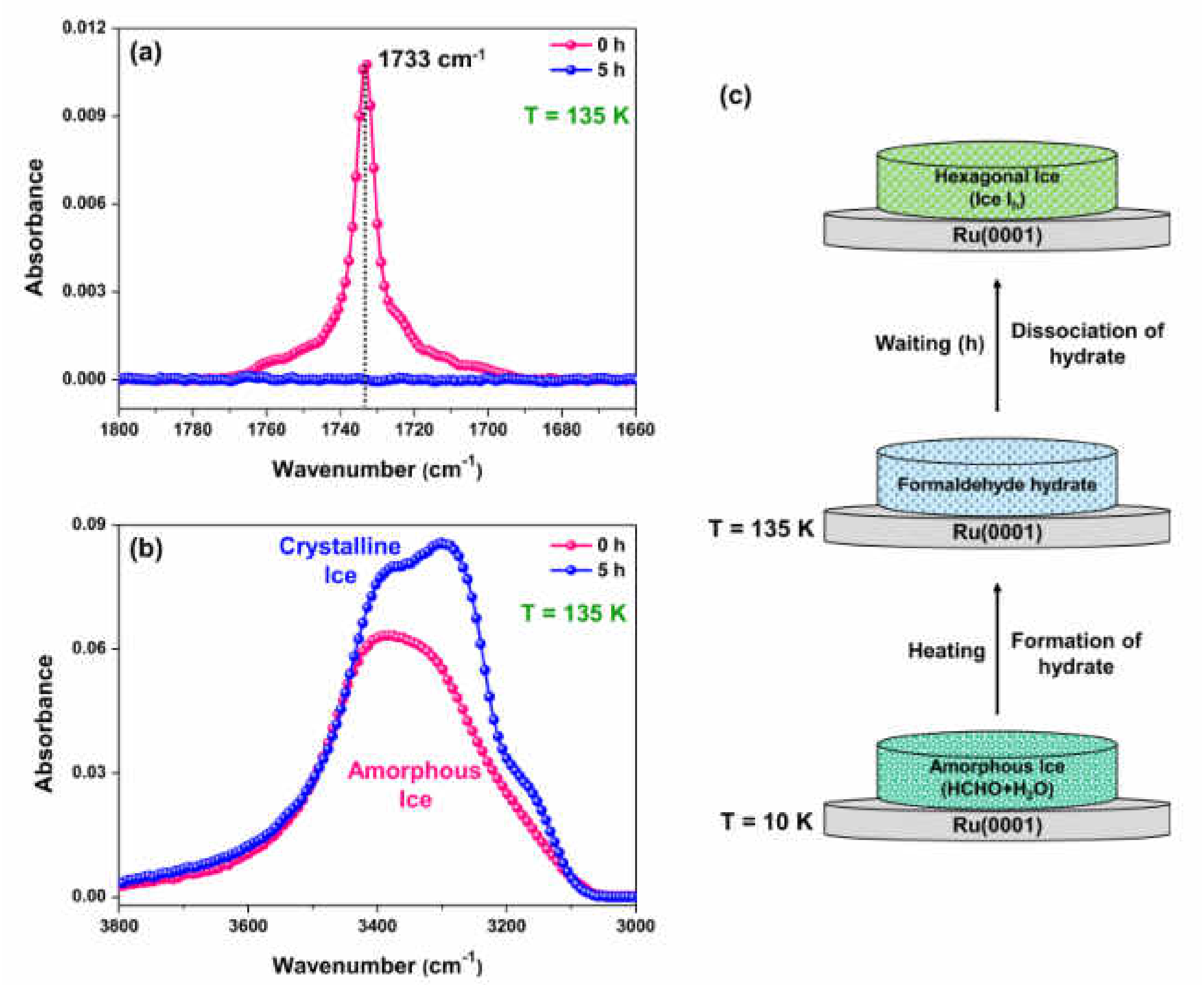
Jyotirmoy Ghosh,‡ **Gaurav Vishwakarma**,‡ Subhadip Das, and Thalappil Pradeep

Ghosh J. *et al.*, ***J. Phys. Chem. C*** 2021, *125*, 4532–4539

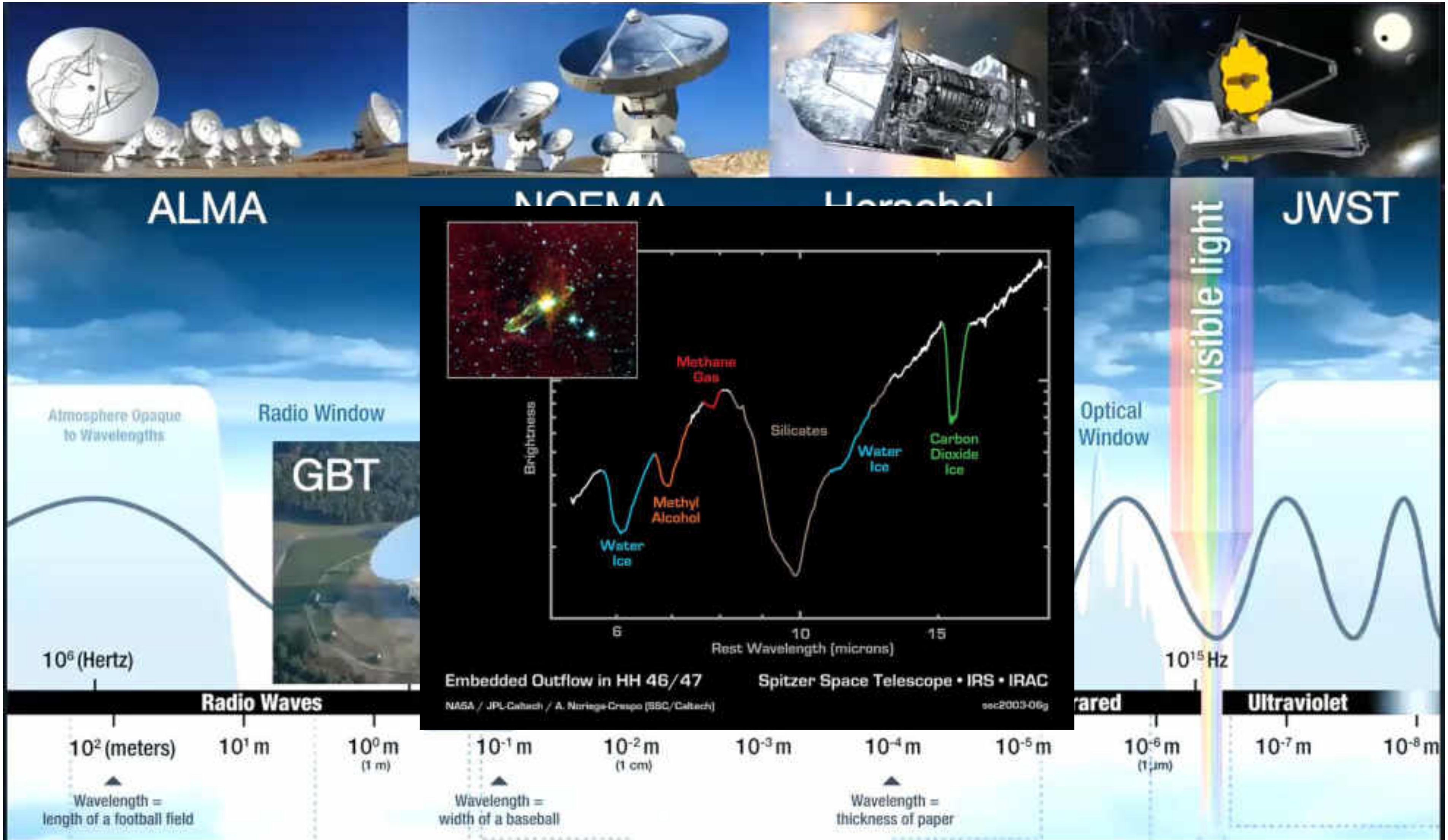
‡ Contributed equally

# Formation of hexagonal ice via clathrate hydrate

**300 ML HCHO+$H_2O$ (1:1)**

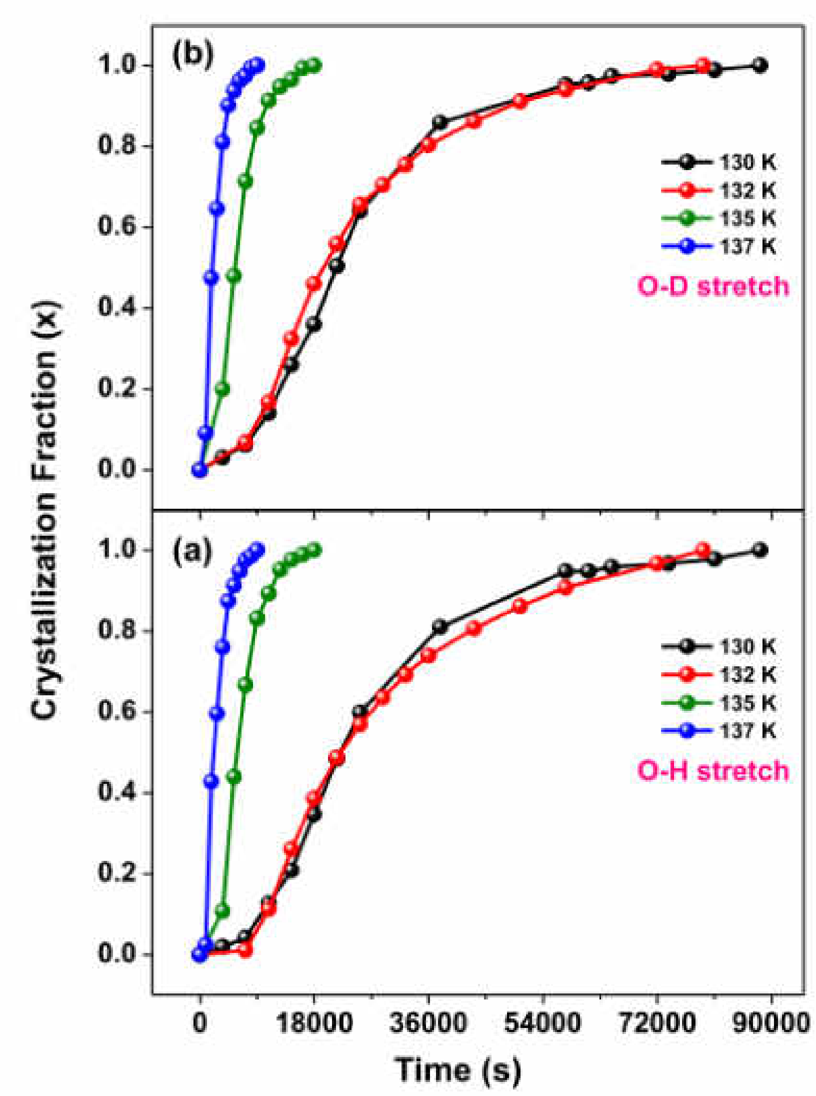


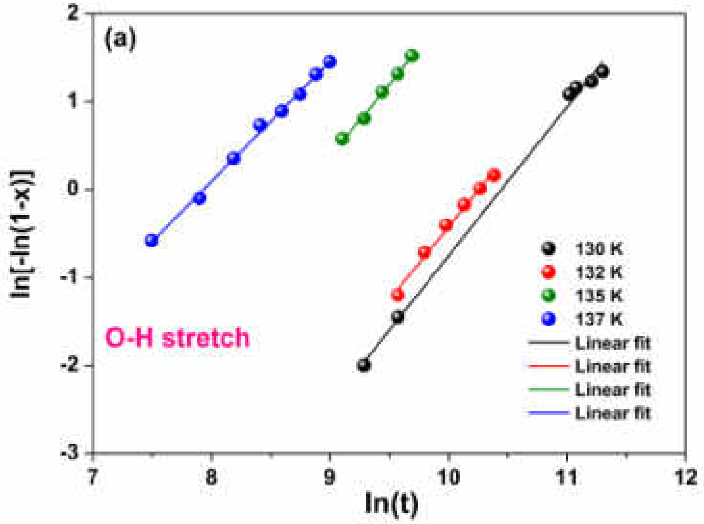
# Astronomical spectroscopy

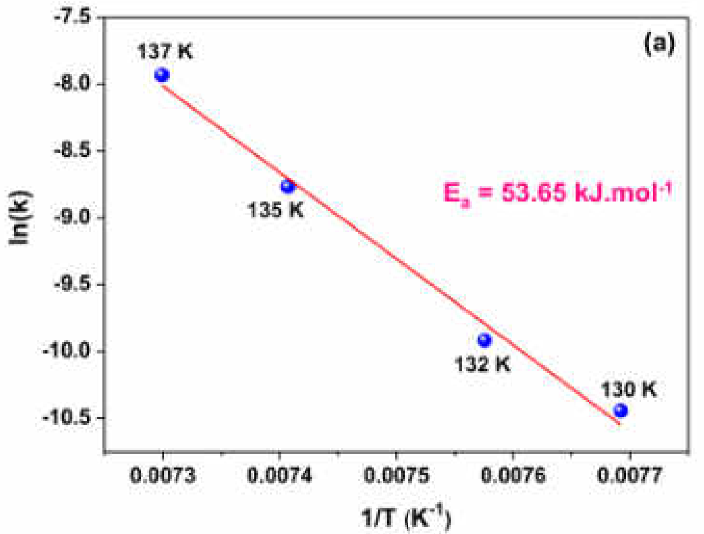



Science Mission Directorate. "Introduction to the Electromagnetic Spectrum" NASA Science. 2010. National Aeronautics and Space Administration.

# Crystallization Kinetics



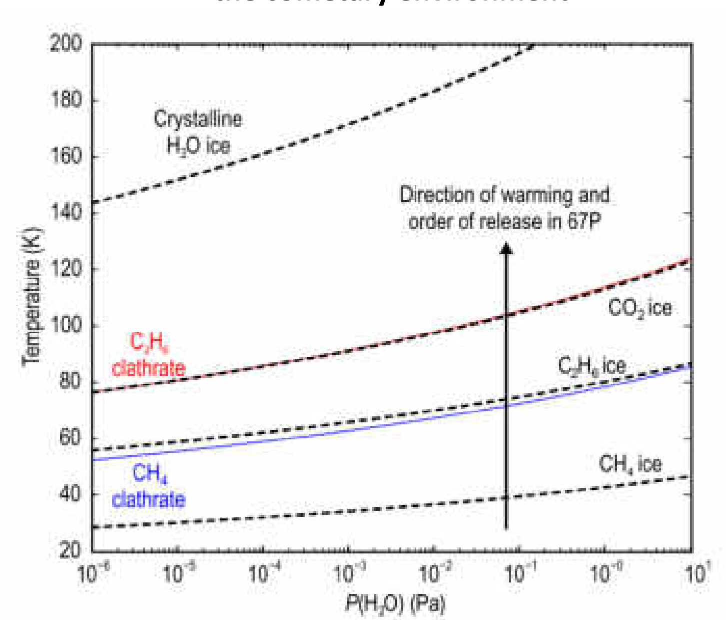



# Conclusions

- We have shown that the dissociation of formaldehyde CH makes hexagonal ice in UHV at 130-135 K, much below the usual crystallization temperature, 155 K.

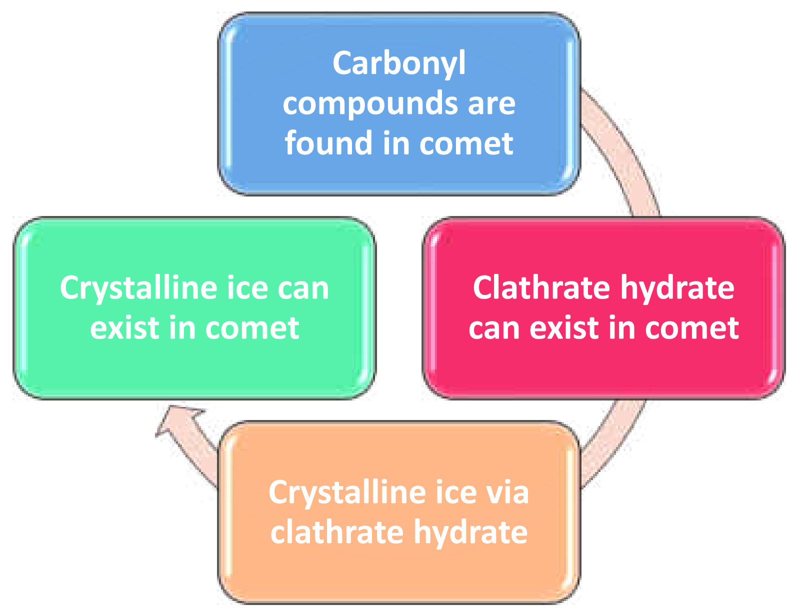
- Associated crystallization-kinetics and activation energy ($E_a$) for the process were also evaluated.

**Equilibrium curves of clathrates and pure condensates in the cometary environment**




Luspay-Kuti, A. *et al.*, *Sci. Adv.* **2016**, *2*, e1501781

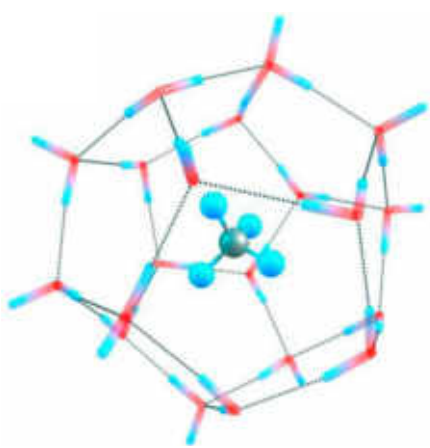
**Missing puzzle**



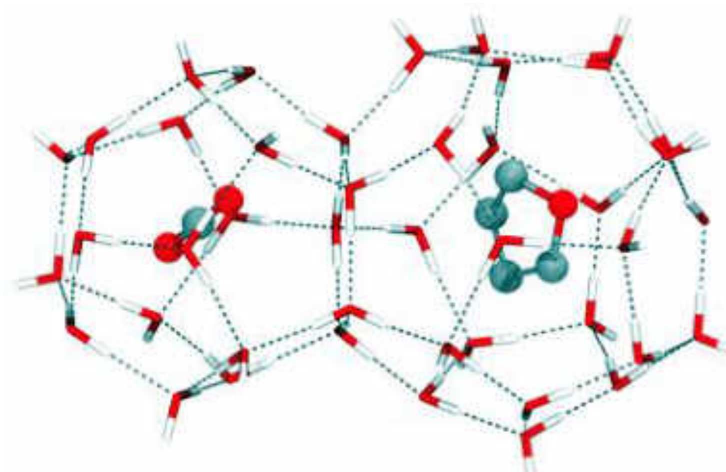

**Acetone, acetaldehyde, and formaldehyde**

# *Induced migration of $CO_2$ from hydrate cages to amorphous solid water under ultrahigh vacuum and cryogenic conditions*

Vishwakarma G. *et al.*, ***J. Phys. Chem. Lett.*** 2023, *14*, 2823-2829

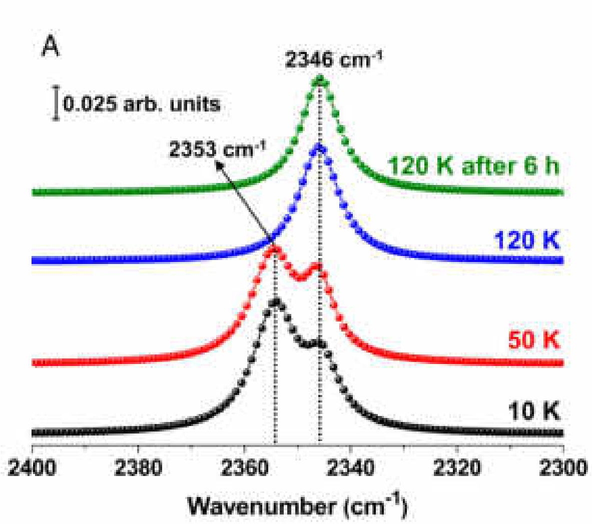


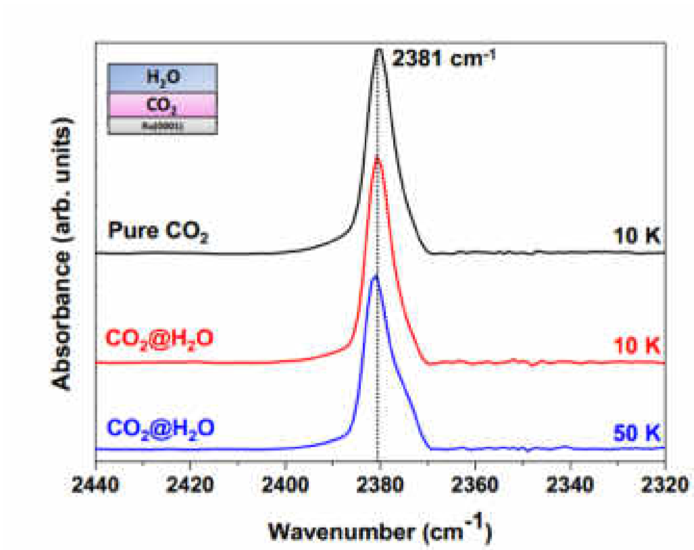
**$CH_4$@$5^{12}$**

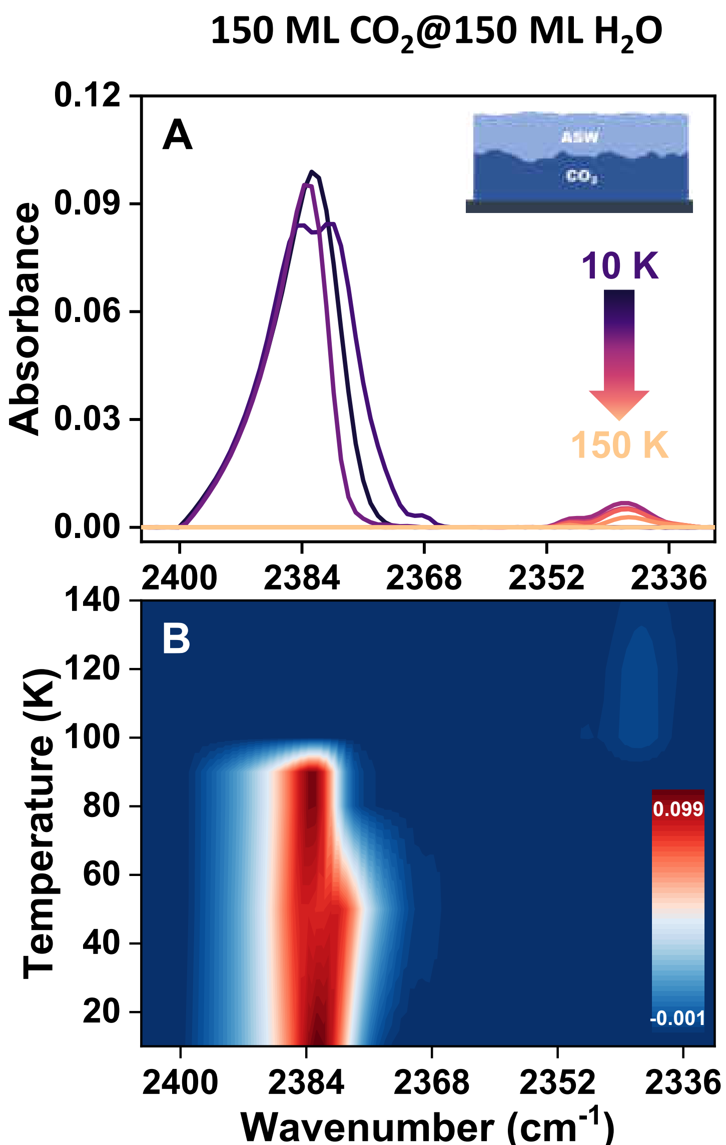


**$CO_2$@$5^{12}$ and THF@$5^{12}6^4$ cage**

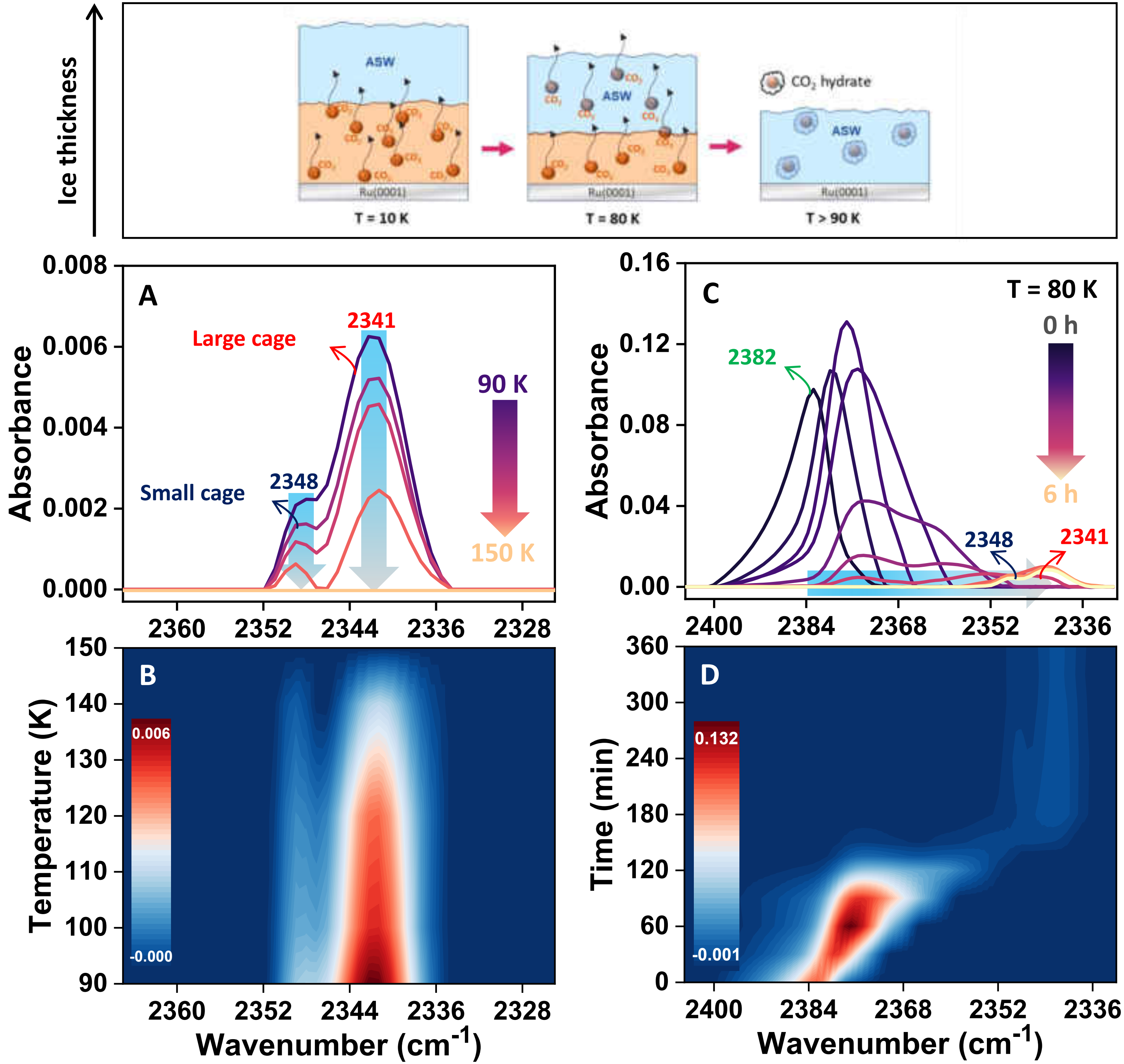
# Clathrate hydrates in interstellar environment



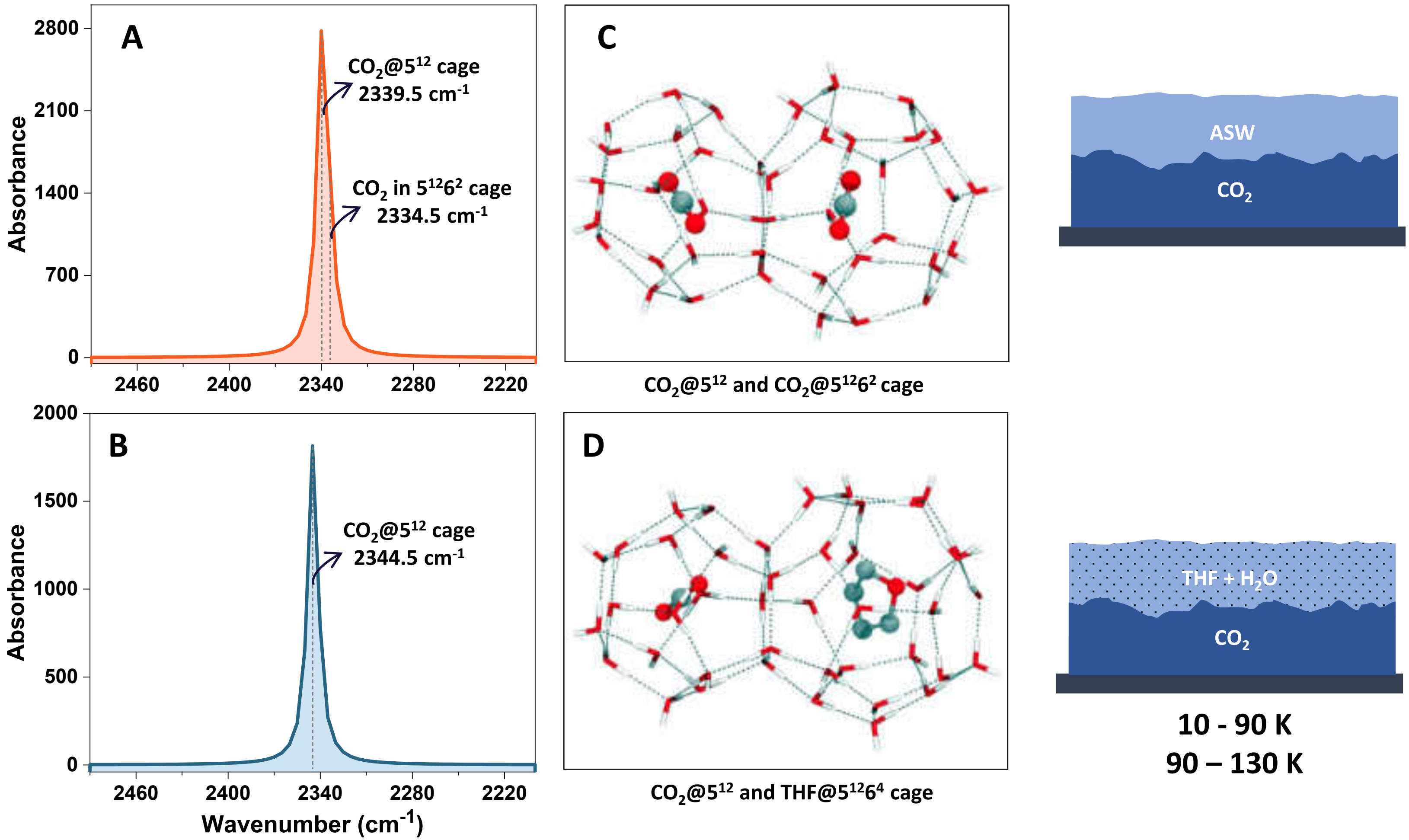



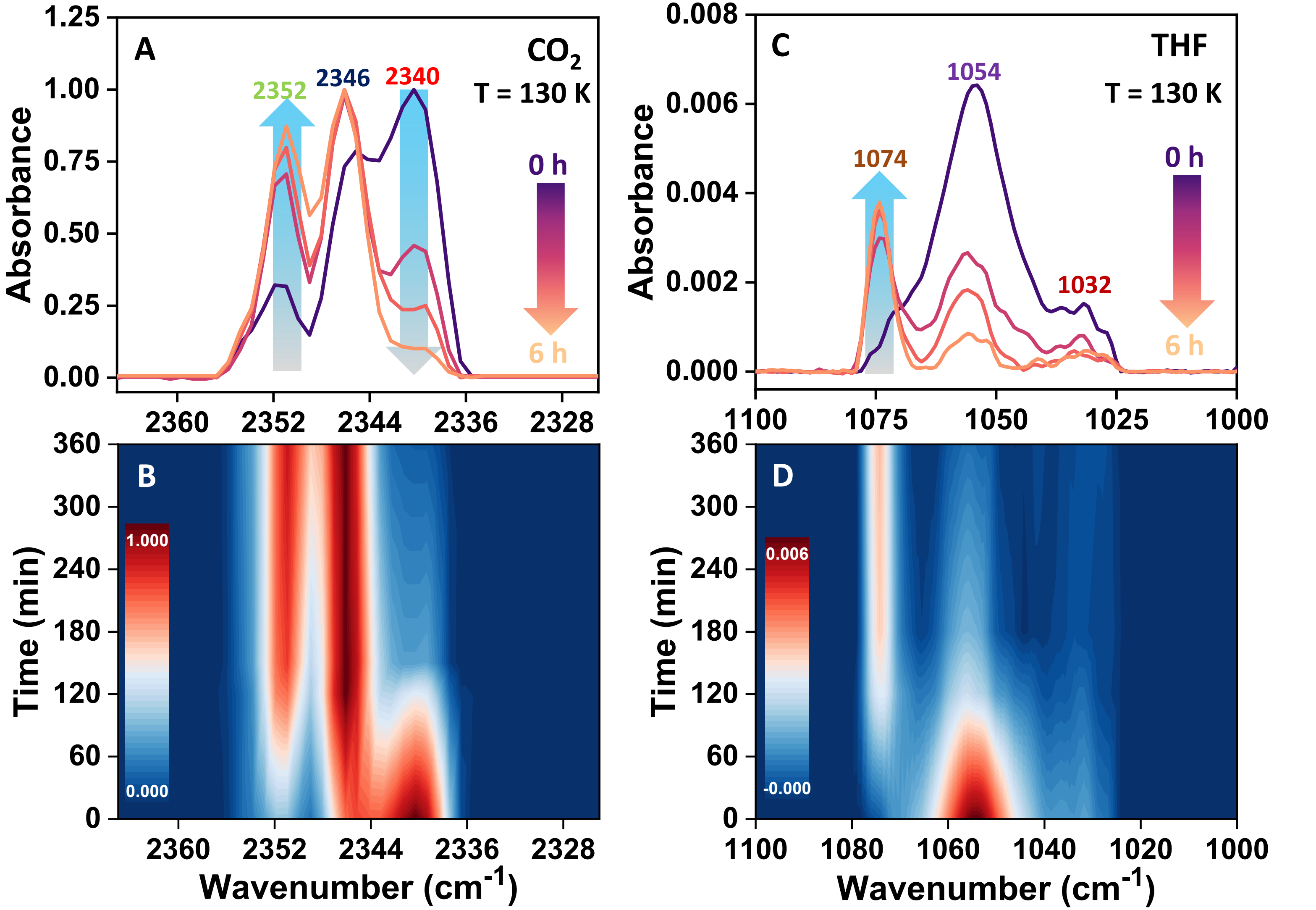

Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531



Ice thickness
ASW
Ru(0001)
T = 10 K
T = 80 K
$CO_2$ hydrate
T > 90 K
A
Absorbance
Large cage
2341
Small cage
2348
90 K
150 K
C
T = 80 K
2382
0 h
6 h
2348
2341
B
Temperature (K)
0.006
-0.000
Wavenumber ($cm^{-1}$)
D
Time (min)
0.132
-0.001
Wavenumber ($cm^{-1}$)


A
Absorbance
2800
2100
1400
700
0
2460
2400
2340
2280
2220
$CO_2$@$5^{12}$ cage
2339.5 $cm^{-1}$
$CO_2$ in $5^{12}6^2$ cage
2334.5 $cm^{-1}$
B
Absorbance
2000
1500
1000
500
0
$CO_2$@$5^{12}$ cage
2344.5 $cm^{-1}$
Wavenumber ($cm^{-1}$)
C
$CO_2$@$5^{12}$ and $CO_2$@$5^{12}6^2$ cage
D
$CO_2$@$5^{12}$ and THF@$5^{12}6^4$ cage
ASW
$CO_2$
THF + $H_2O$
$CO_2$
10 - 90 K
90 – 130 K

# Mixed clathrate hydrate of $CO_2$-THF

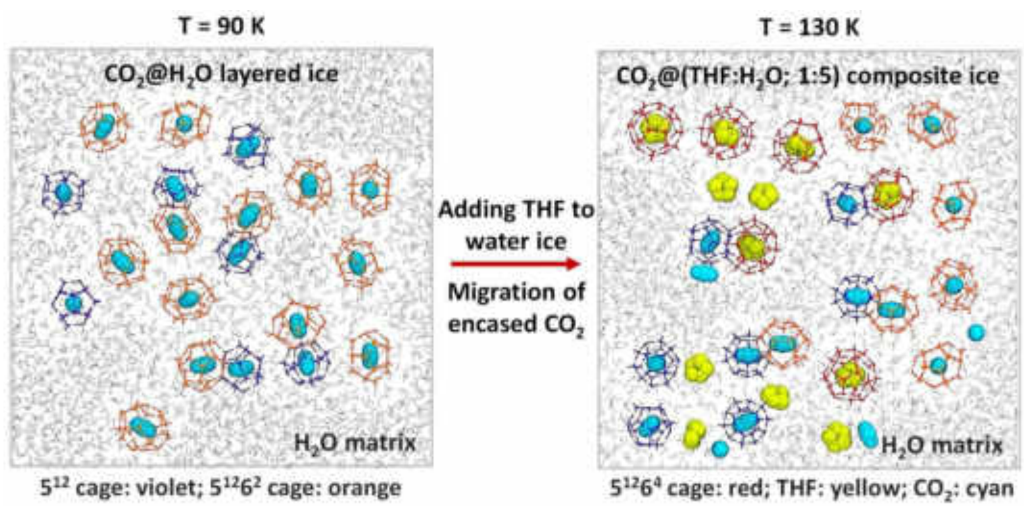


# Conclusions

- We have studied the migration of $CO_2$ from the CH cages to the matrix of ASW in presence of THF under UHV and cryogenic conditions.

- We demonstrated the partitioning of $CO_2$ in $CO_2@5^{12}$ and $CO_2@5^{12}6^2$ cages of sI at 90 K without the 'help guest'.

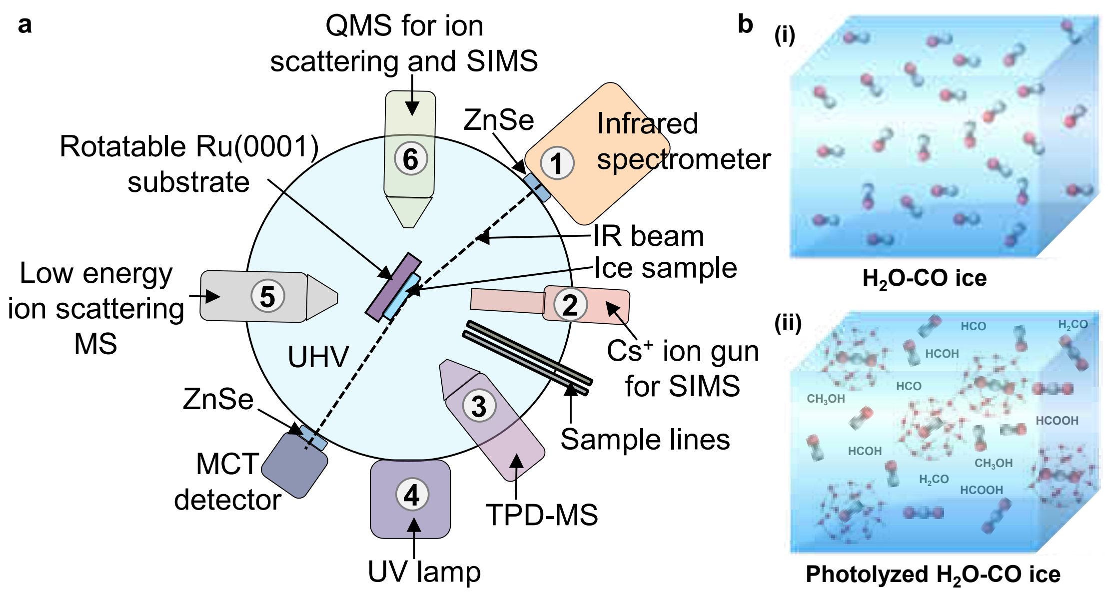
- We have prepared mixed CH of $CO_2$ with THF.

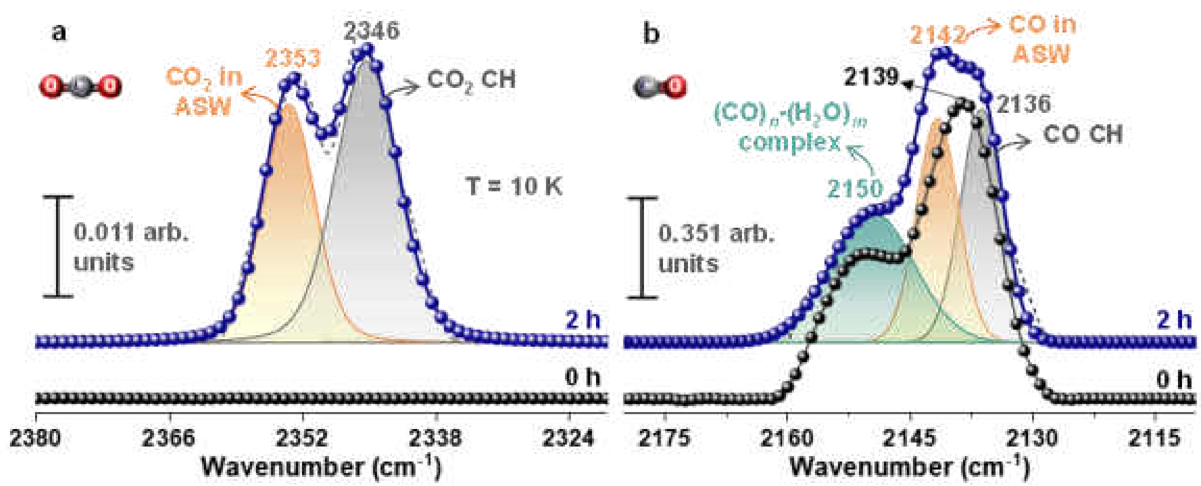


# ***Partitioning photochemically formed $CO_2$ into clathrate hydrate in interstellar conditions***

Vishwakarma, G. *et al*., **2023** (Under consideration)

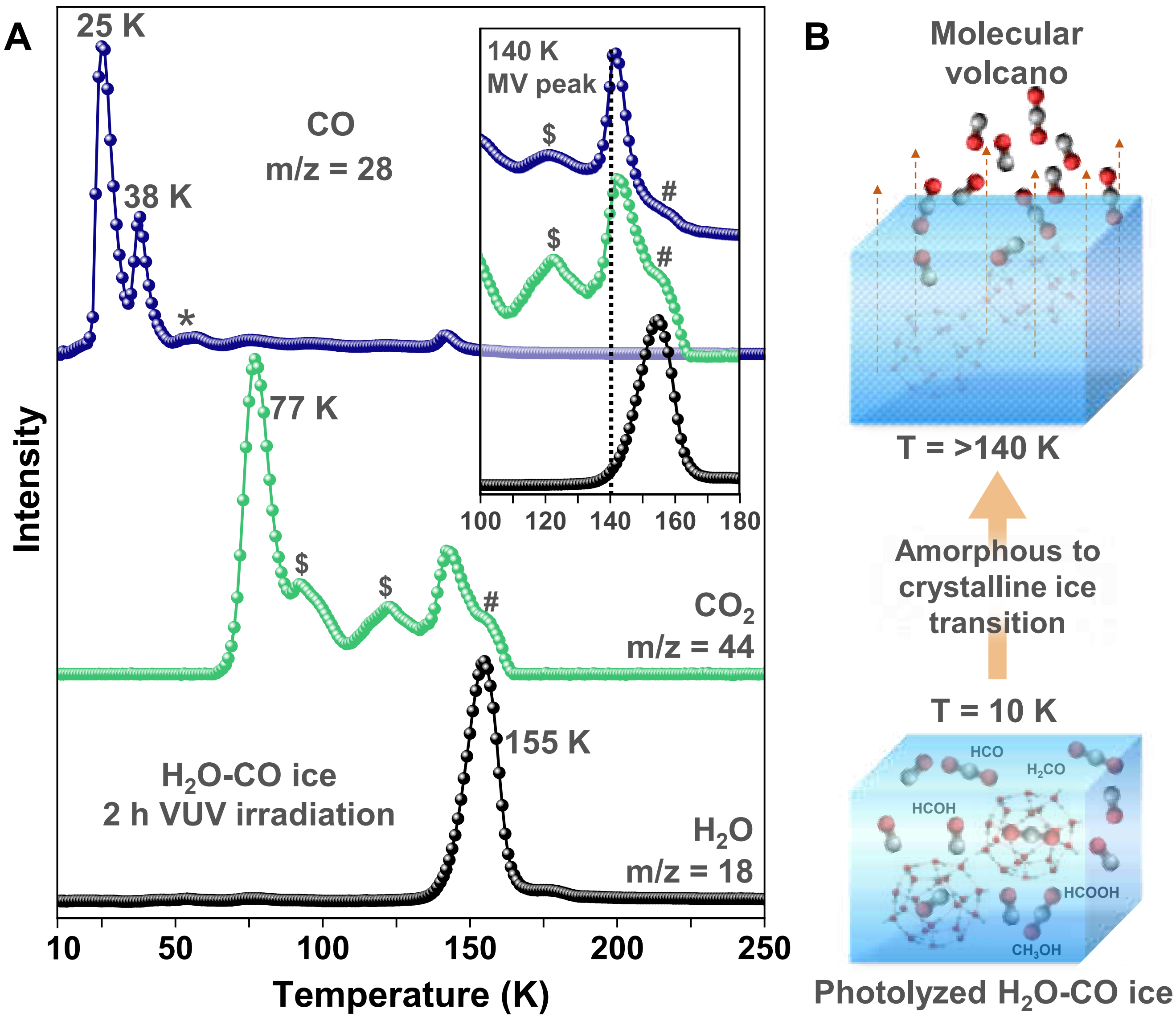
# Partitioning photochemically formed $CO_2$



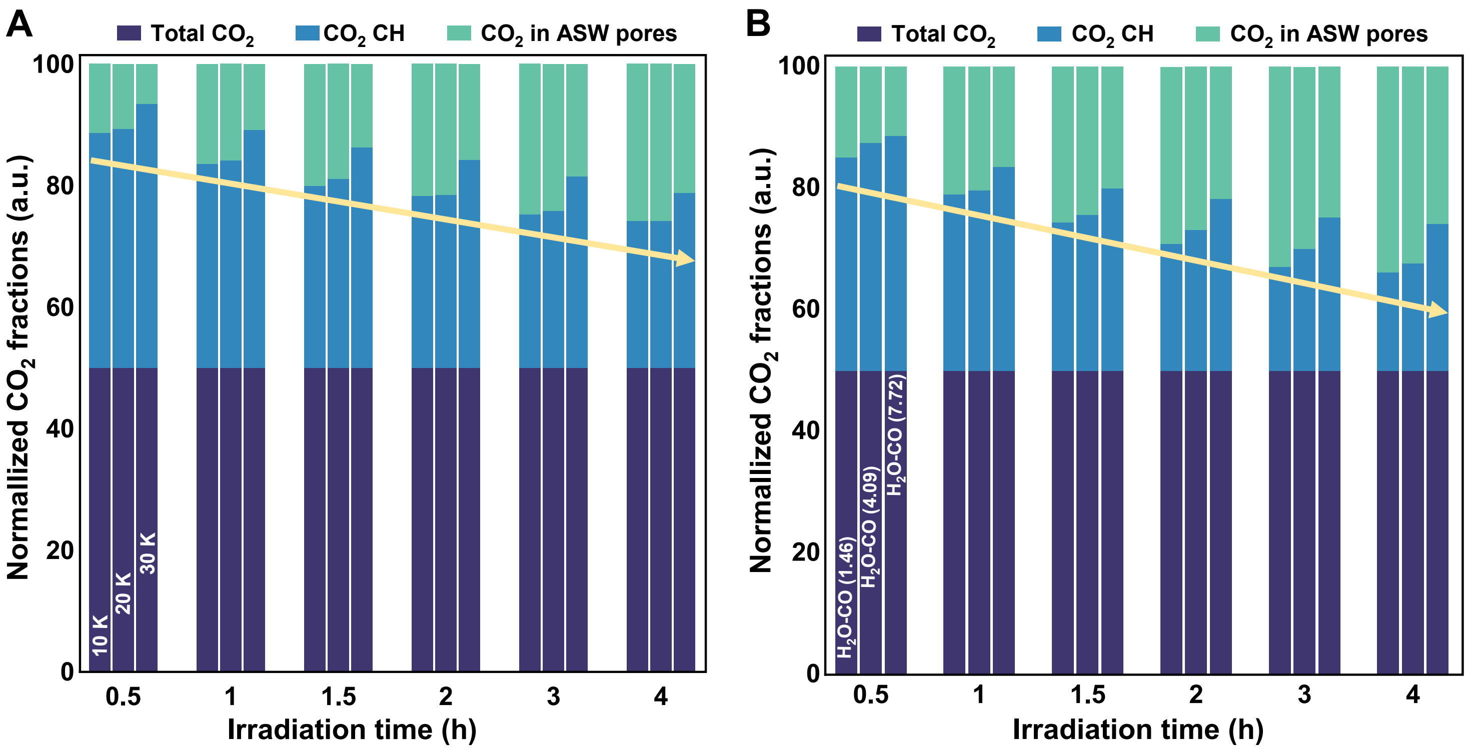
# Partitioning photochemically formed $CO_2$

## TPD mass spectrometric analysis of photolyzed $H_2O$-CO mixture



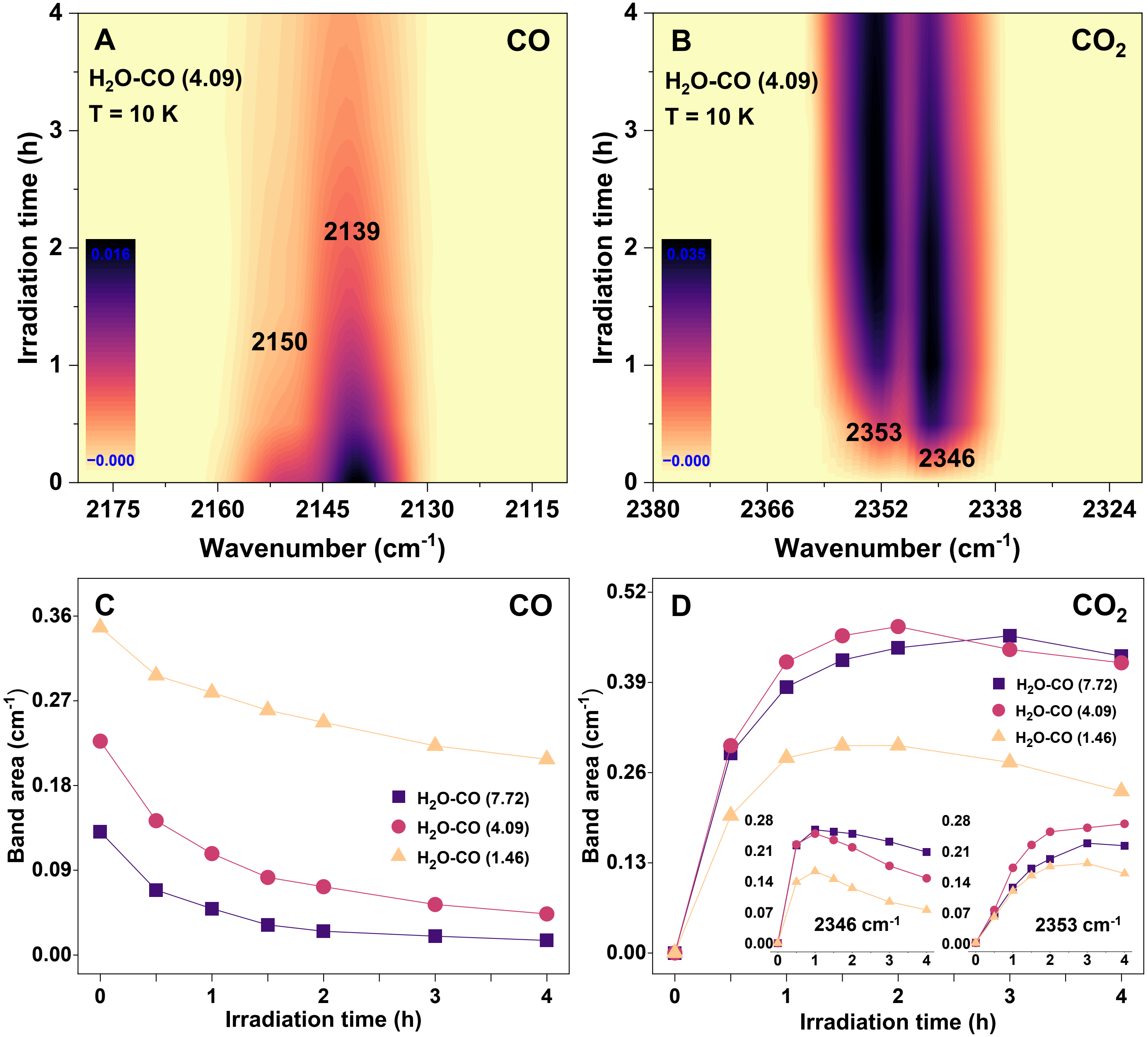
# Partitioning photochemically formed $CO_2$

## Trends of photochemically produced $CO_2$ partitioning at different temperatures and $H_2O$-CO compositions



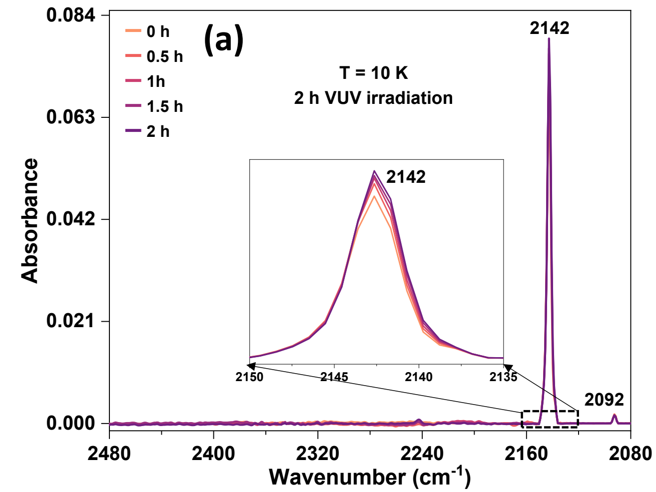
# Partitioning photochemically formed $CO_2$

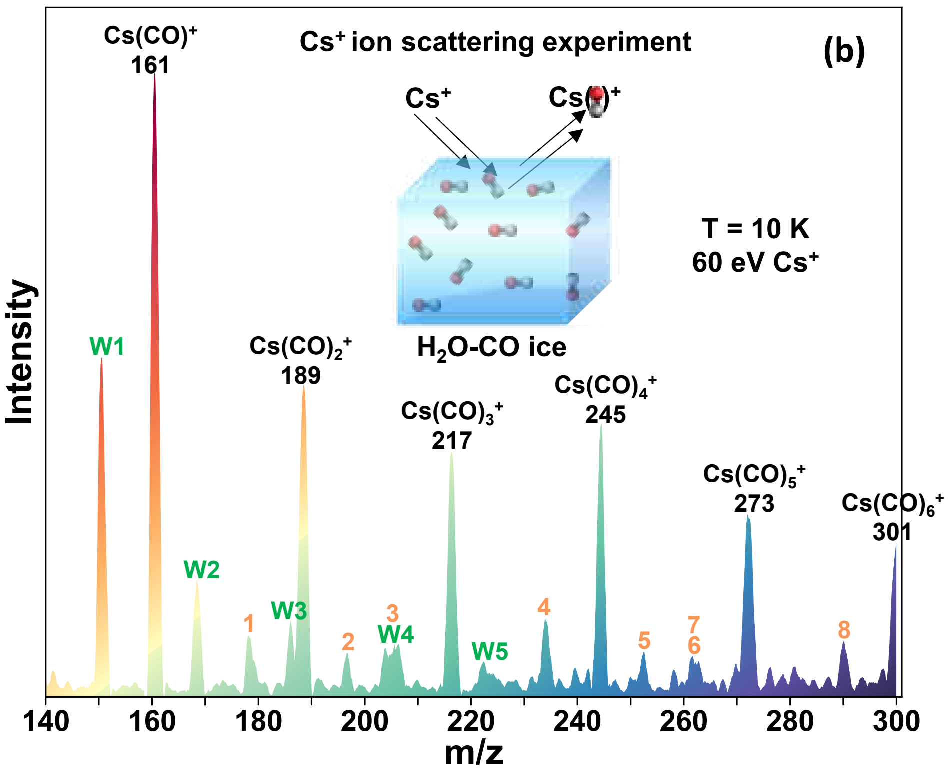
## Composition-dependent experiments



# Surface structure of $H_2O$-CO ice

## $Cs^+$ ion scattering analysis of the surface of (a) unirradiated, (b) irradiated $H_2O$-CO mixture




Complex = m/z

(1) $CO(H_2O)$ = 179

(2) $CO(H_2O)_2$ = 197

(3) $H_2O(CO)_2$ = 207

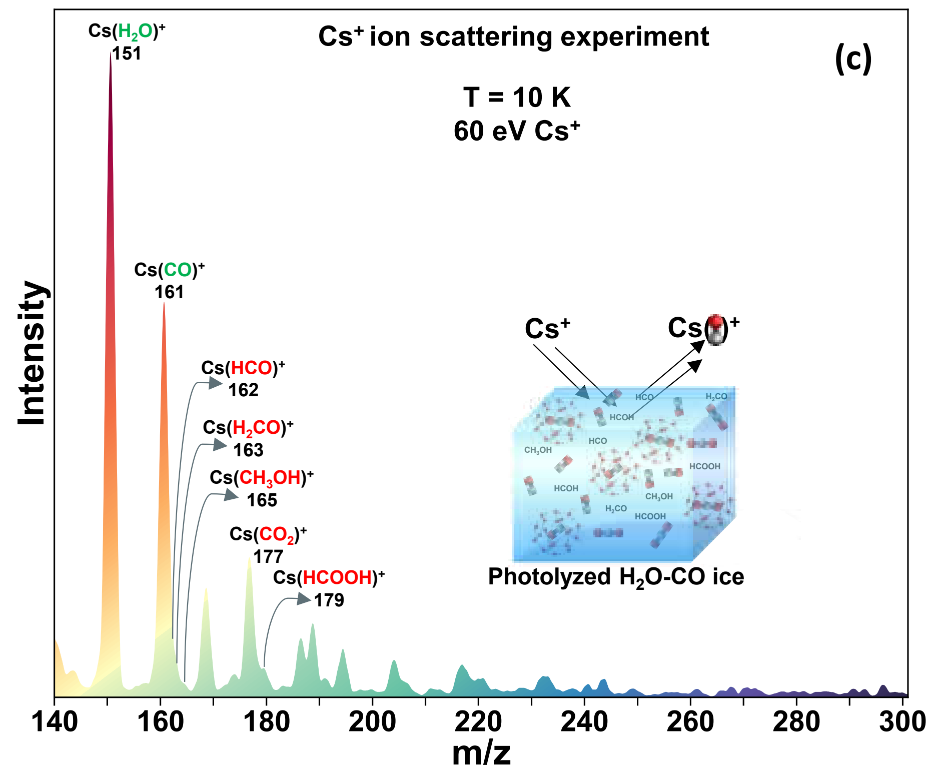
(4) $H_2O(CO)_3$ = 235

(5) $(H_2O)_2(CO)_3$ = 253

(6) $(CO)_2(H_2O)_4$ = 261

(7) $H_2O(CO)_4$ = 263

(8) $H_2O(CO)_5$ = 291



# Existence of clathrate hydrates under UHV

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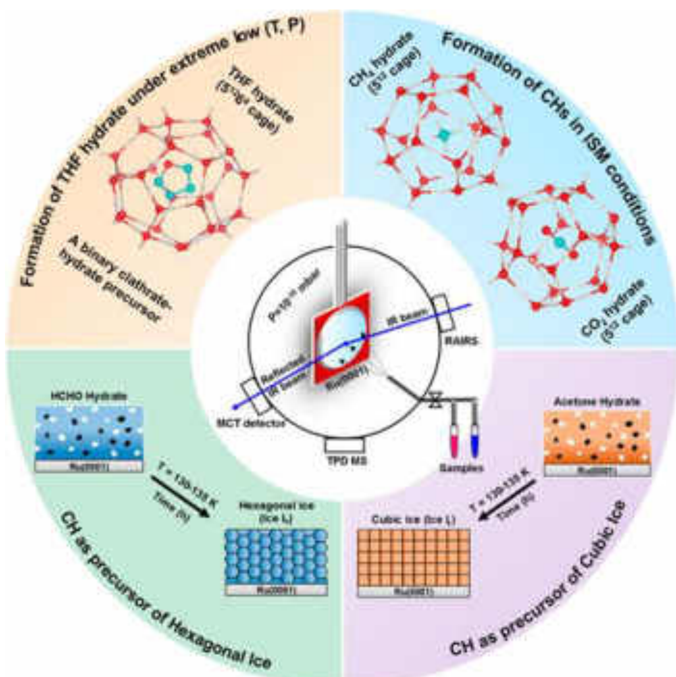
Article

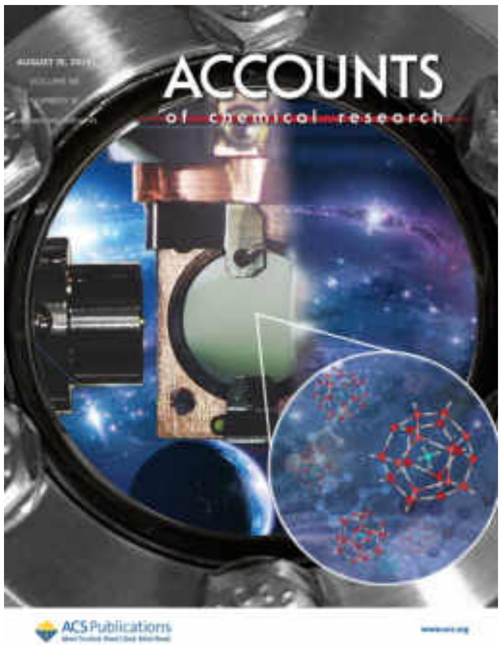
## Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,* and Thalappil Pradeep*

Cite This: https://doi.org/10.1021/acs.accounts.3c00317

Read Online

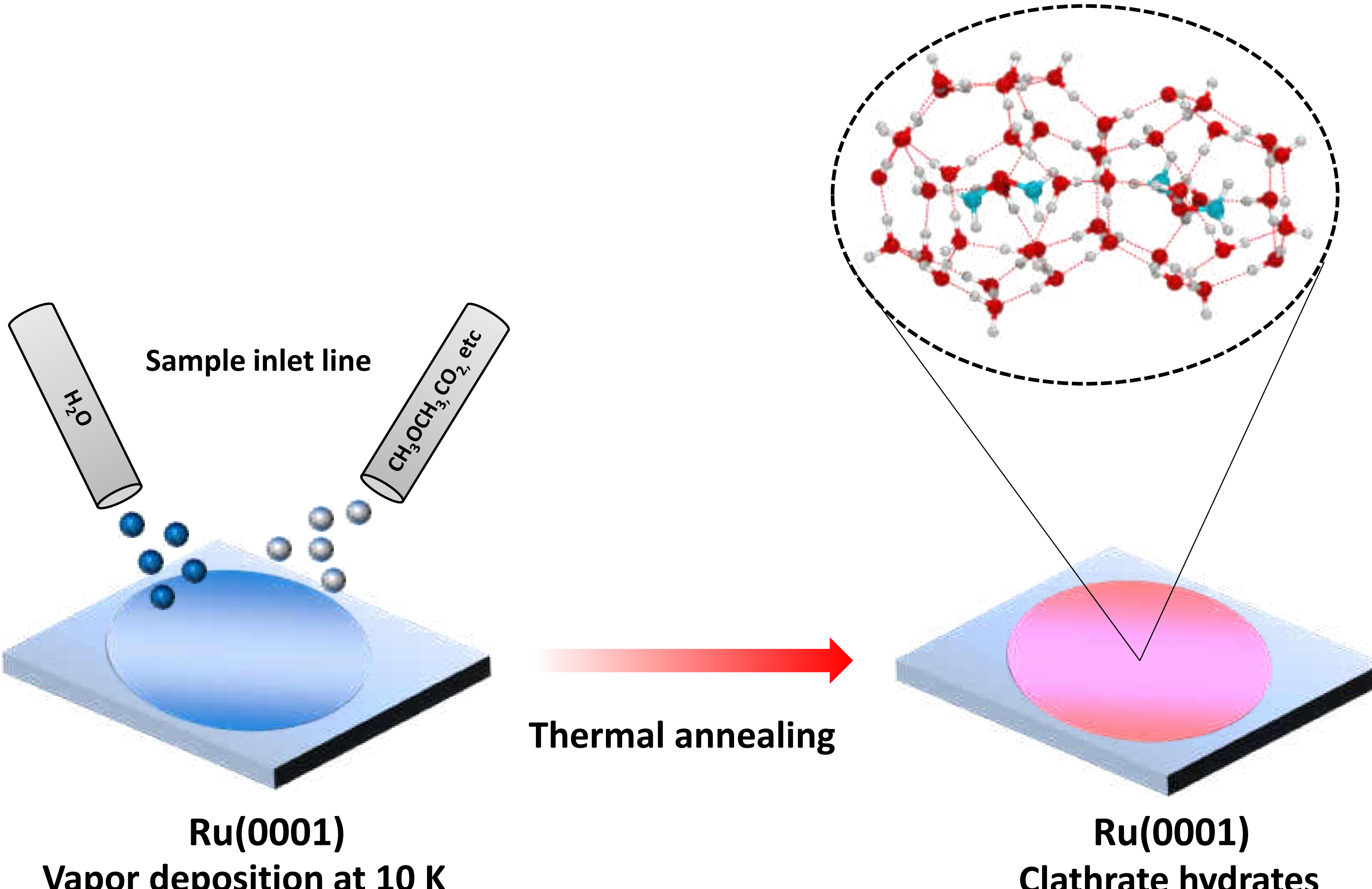


Thank you

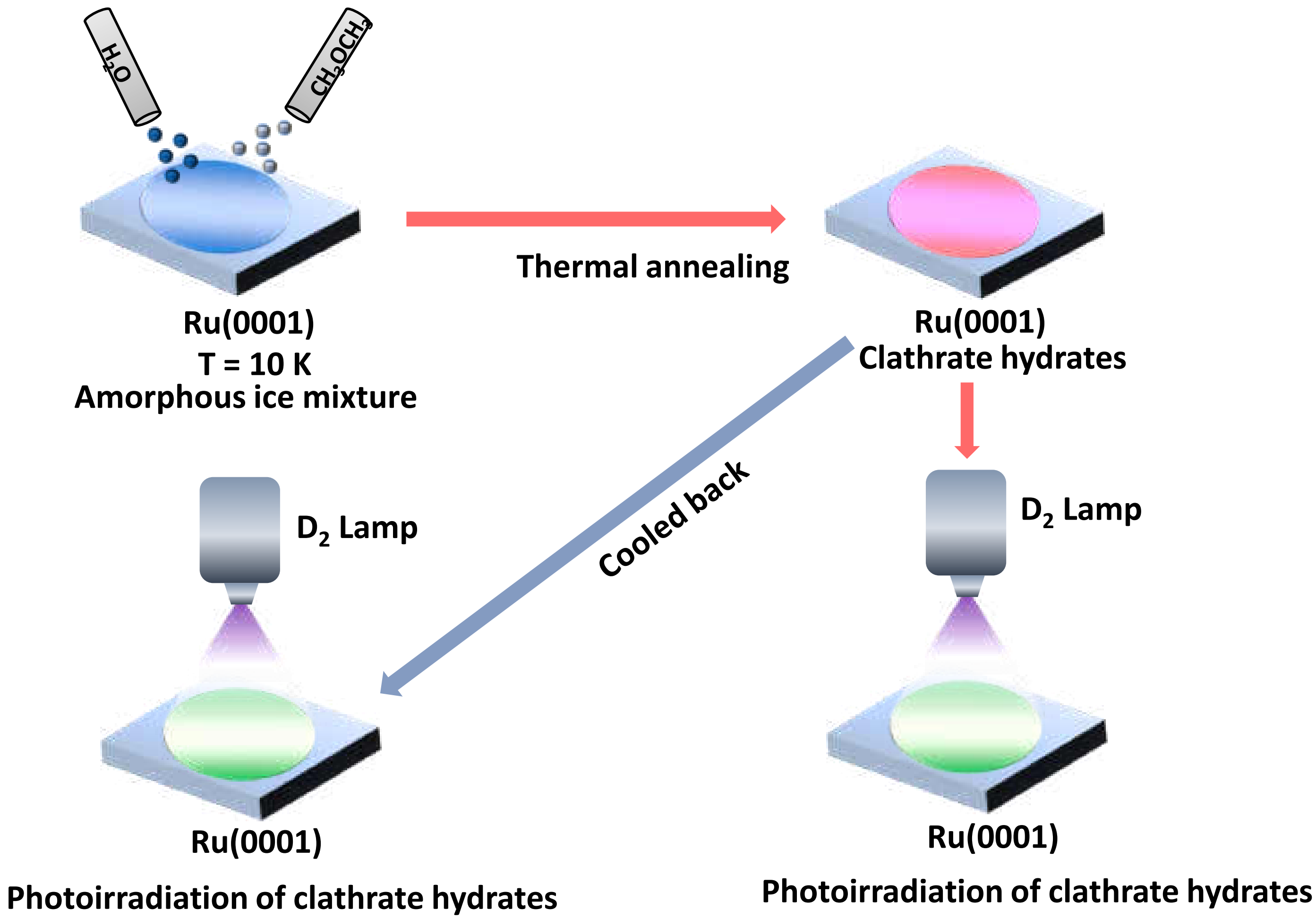
# Research proposal - 1

**Examine the formation of mixed clathrate hydrates and the interplay between different guest molecules within the structure.**



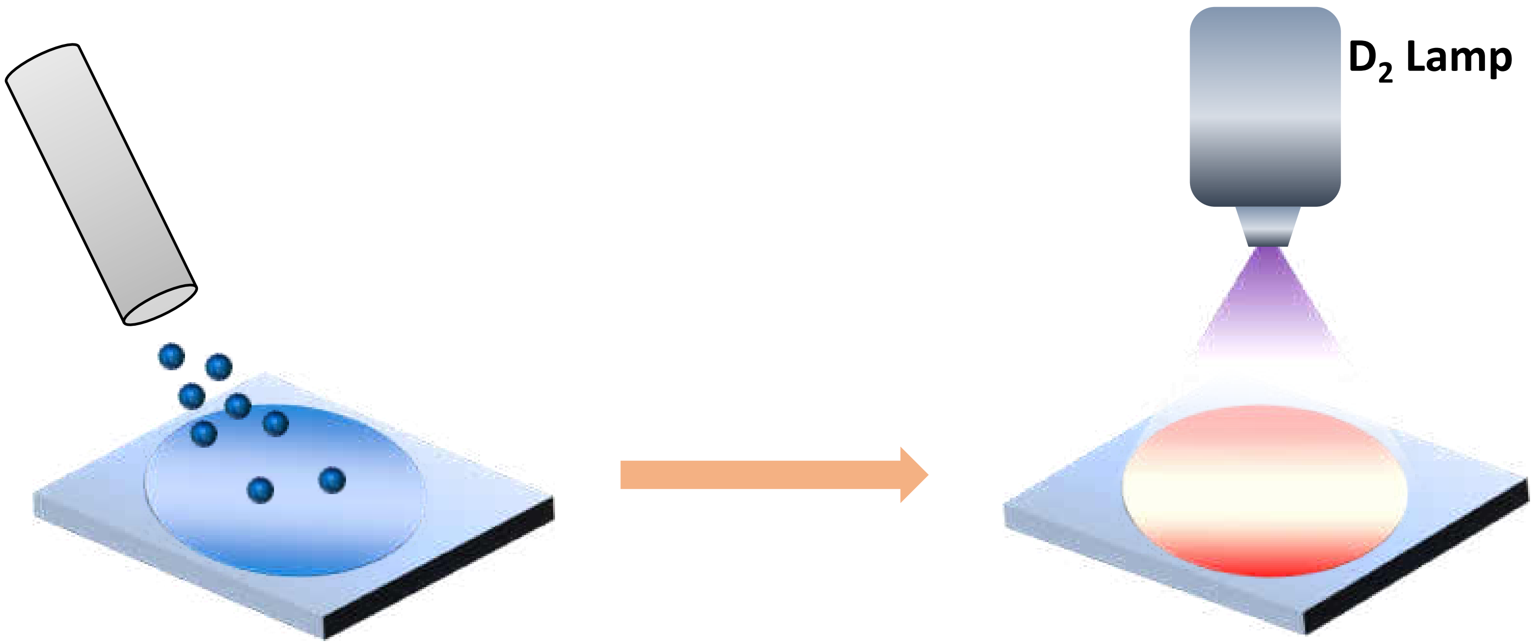
# Research proposal - 2

**Fate of clathrate hydrates under vacuum ultraviolet (VUV) radiation.**



# Research proposal - 3

**Explore the chemistry behind the formation of complex molecules under vacuum ultraviolet radiation.**




**Ru (0001)**

**T = 10 K**

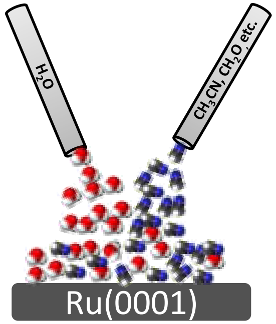
**Small molecules**

**Ru (0001)**

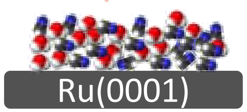
**T = 10 K**

**Big complex molecules**

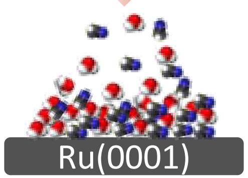
# Experimental procedure




Ice deposition

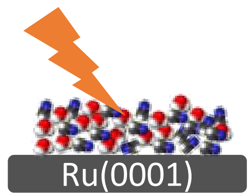



Deposited ice

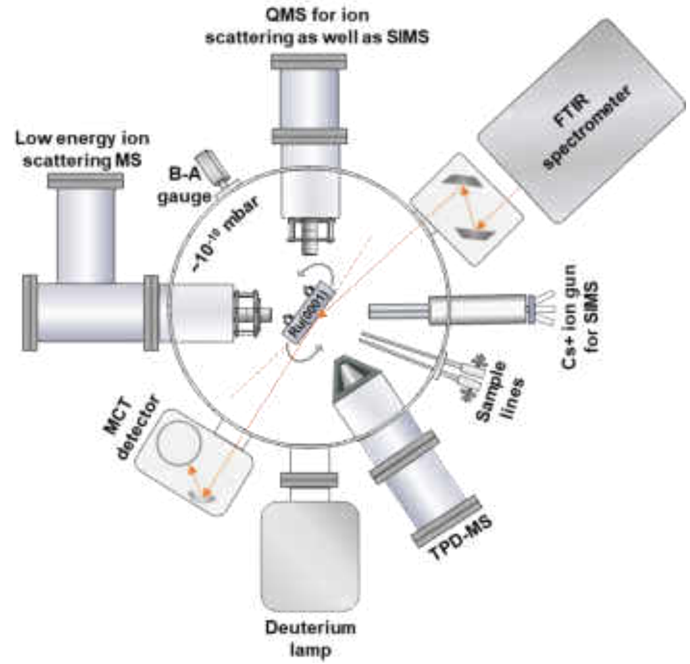



Thermal processing of ices

- Low energy ion scattering (LEIS)
- TPD-MS
- RAIRS
- Low energy $Cs^+$ ion gun
- Vacuum UV lamp

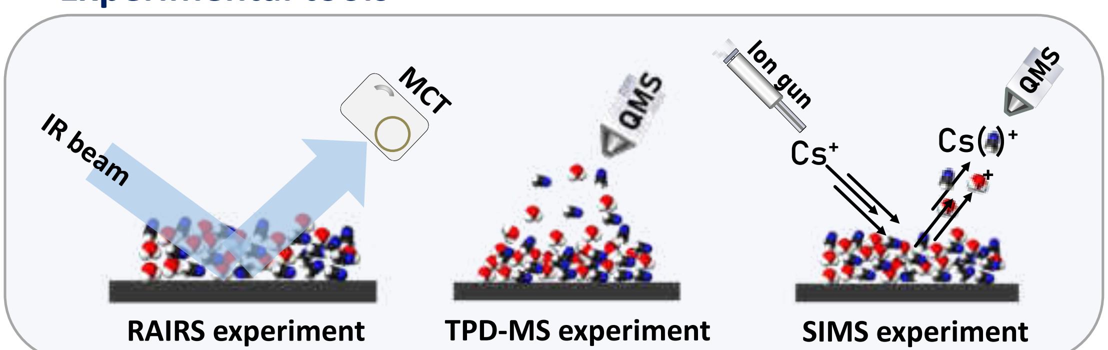



Photochemical processing of ices




Schematic diagram of the experimental setup

## Experimental tools



# Molecules detected in interstellar medium

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2 atoms | CS | $HCO^+$ | KCN | $H_3O^+$ | HCOOH | *l*-$HC_4N$ | $CH_2CHCHO$ | $CH_3OCH_2OH$ |
| $H_2$ | HF | $HCS^+$ | FeCN | $NH_3$ | $H_2CNH$ | *c*-$H_2C_3O$ | $CH_2CCHCN$ | 11 atoms |
| AlF | SH | $HOC^+$ | $HO_2$ | c-$SiC_3$ | $H_2C_2O$ | $C_5N^-$ | $H_2NCH_2CN$ | $HC_9N$ |
| AlCl | $SH^+$ | $H_2O$ | $TiO_2$ | $CH_3$ | $H_2NCN$ | E-HNCHCN | $CH_3CHNH$ | $CH_3C_6H$ |
| $C_2$ | FeO | $H_2S$ | $C_2N$ | $C_3N^-$ | $HNC_3$ | $SiH_3CN$ | $CH_3SiH_3$ | $C_2H_5OCHO$ |
| CH | $O_2$ | HNC | SiCSi | $PH_3$ | $SiH_4$ | $CH_2CNH$ | $C_2H_5N$ | $CH_3OC(O)CH_3$ |
| $CH^+$ | $CF^+$ | HNO | $S_2H$ | HCNO | $H_2COH^+$ | $C_5S$ | $(NH_2)_2CO$ | 12 atoms |
| CN | PO | MgCN | HCS | HOCN | $C_4H^-$ | 7 atoms | 9 atoms | *c*-$C_6H_6$ |
| CO | AlO | MgNC | HSC | HSCN | HC(O)CN | $C_6H$ | $CH_3C_4H$ | $C_3H_7CN$ |
| $CO^+$ | $CN^-$ | $N_2H^+$ | NCO | $H_2O_2$ | HNCNH | $CH_2CHCN$ | $CH_3CH_2CN$ | *t*-$C_2H_5OCH_3$ |
| CP | $HCl^+$ | $N_2O$ | $OCN^-$ | l-$C_3H^+$ | $CH_3O$ | $HC_5N$ | $(CH_3)_2O$ | >12 atoms |
| CSi | TiO | NaCN | 4 atoms | HMgNC | $H_2NCO^+$ | $CH_3CHO$ | $CH_3CH_2OH$ | $C_{60}$ |
| HCl | $ArH^+$ | OCS | $C_3H^*$ | HCCO | $NCCNH^+$ | $NH_2CH_3$ | $HC_7N$ | $C_{60}^+$ |
| KCl | $N_2$ | $SO_2$ | *l*-$C_3H^+$ | $CH_3Cl$ | $NH_3D^+$ | *c*-$C_2H_4O$ | $C_8H$ | $C_{70}$ |
| NH | $NO^+$ | *c*-$SiC_2$ | $C_3N$ | CNCN | 6 atoms | $H_2CCHOH$ | $CH_3C(O)NH_2$ | c-$C_6H_5CN$ |
| NO | $NS^+$ | $CO_2$ | $C_3O$ | MgCCH | $C_5H$ | $C_6H^-$ | $C_8H^-$ | $CO(CH_2OH)_2$? |
| NS | LiH | $NH_2$ | $C_3S$ | NCCP | *l*-$C_4H_2$ | $CH_3NCO$ | $C_3H_6$ | $C_{14}H_{10}$? |
| NaCl | CrO | $H_3^+$ | $C_2H_2$ | 5 atoms | $C_2H_4$ | $HC_5O$ | $CH_3CH_2SH$ | $C_{14}H_{10}^+$ |
| OH | 3 atoms | SiCN | $HC_2N$ | $C_5$ | $CH_3CN$ | 8 atoms | $CH_3NHCHO$ | $C_6H_5OH$ |
| $OH^+$ | $C_3$ | AlNC | $HCNH^+$ | $C_4H$ | $CH_3NC$ | $CH_3C_3N$ | $HC_7O$ | |
| PN | $C_2H$ | SiNC | HNCO | $C_4Si$ | $CH_3OH$ | $HC(O)OCH_3$ | 10 atoms | |
| SO | $C_2O$ | HCP | HNCS | *c*-$C_3H_2$ | $CH_3SH$ | $CH_3COOH$ | $CH_3C_5N$ | |
| $SO^+$ | $C_2S$ | CCP | $HOCO^+$ | $CH_2CN$ | $HC_3NH^+$ | $C_7H$ | $(CH_3)_2CO$ | |
| SiN | $CH_2$ | AlOH | $H_2CO$ | $CH_4$ | $HC_2CHO$ | $H_2C_6$ | $(CH_2OH)_2$ | |
| SiO | HCN | $H_2O^+$ | $H_2CN$ | $HC_3N$ | $NH_2CHO$ | $CH_2OHCHO$ | $CH_3CH_2CHO$ | |
| SiS | HCO | $H_2Cl^+$ | $H_2CS$ | $HC_2NC$ | $C_5N$ | *l*-$C_6H_2$ | $CH_3CHCH_2O$ | |

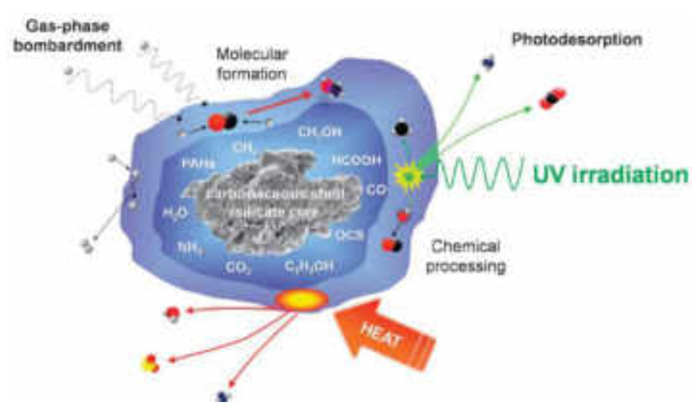
Arumainayagam, C. R. *et al., Chem. Soc. Rev.* **2019**, *48*, 2293–2314

**Table 9.** Total number of detections for each facility listed in §4.

| Facility | # | Facility | # |
|---|---|---|---|
| IRAM 30-m | 64 | SMA | 2 |
| NRAO 36-ft | 33 | SEST | 2 |
| GBT 100-m | 28 | SOFIA | 2 |
| NRAO/ARO 12-m | 27 | Hat Creek 20-ft | 2 |
| Yebes 40-m | 19 | IRTF | 2 |
| Nobeyama 45-m | 15 | PdBI | 2 |
| NRAO 140-ft | 13 | OVRO | 2 |
| Bell 7-m | 8 | MWO 4.9-m | 2 |
| ALMA | 8 | Hubble | 1 |
| SMT | 7 | IRAS | 1 |
| Herschel | 7 | BIMA | 1 |
| Parkes | 5 | NRL 85-ft | 1 |
| FCRAO 14-m | 5 | ATCA | 1 |
| ISO | 5 | Mitaka 6-m | 1 |
| APEX | 4 | McMath Solar Telescope | 1 |
| Onsala 20-m | 4 | UKIRT | 1 |
| KPNO 4-m | 4 | Odin | 1 |
| Effelsberg 100-m | 4 | FUSE | 1 |
| Algonquin 46-m | 3 | KAO | 1 |
| Mt. Wilson | 3 | Mt. Hopkins 60-in | 1 |
| Spitzer | 3 | Aerobee-150 Rocket | 1 |
| Haystack | 3 | Millstone Hill 84-ft | 1 |
| CSO | 2 | Goldstone | 1 |

JWST

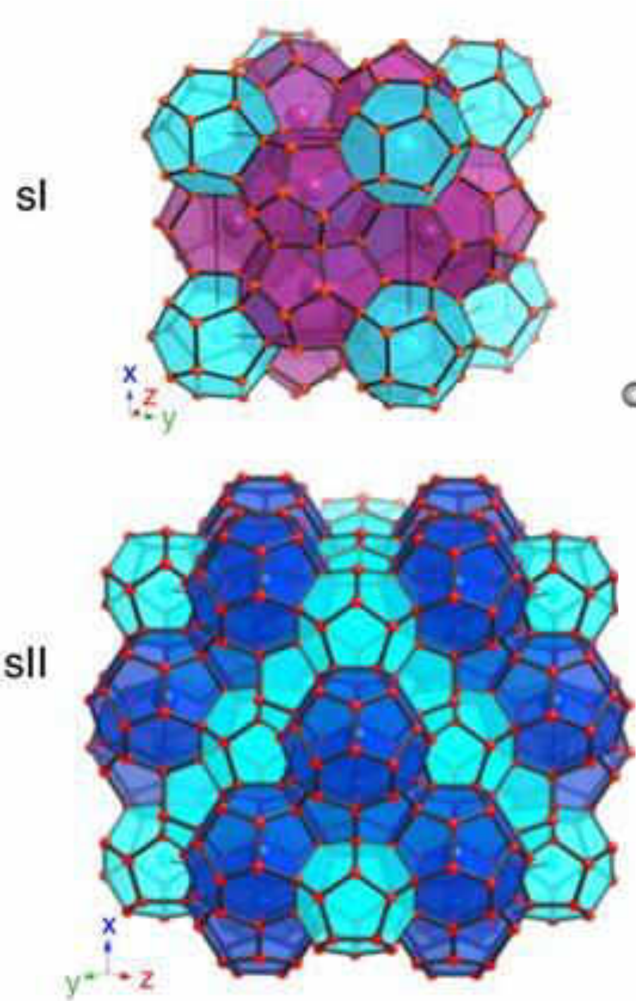
arXiv:2109.13848 [astro-ph.GA]



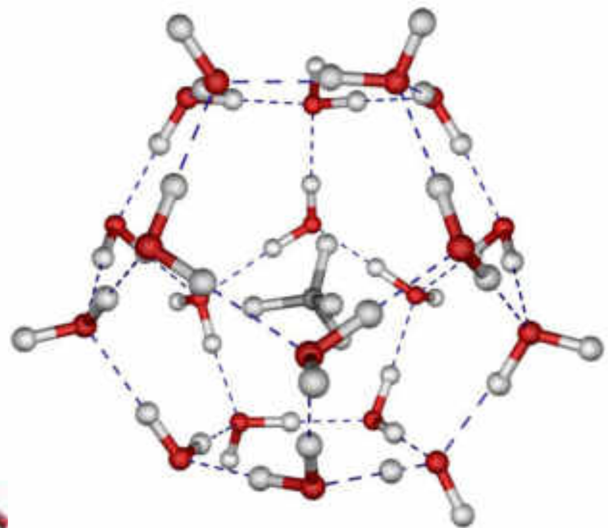

## Materials

| | | |
|---|---|---|
| $H_2O$, $CO_2$, CO, | $CH_3CHO$, | $CH_3CN$, |
| $CH_4$, HCHO, | $CH_3COCH_3$, | $(CH_2)_4O$ |

# What is clathrate hydrate?




**Unit cells**



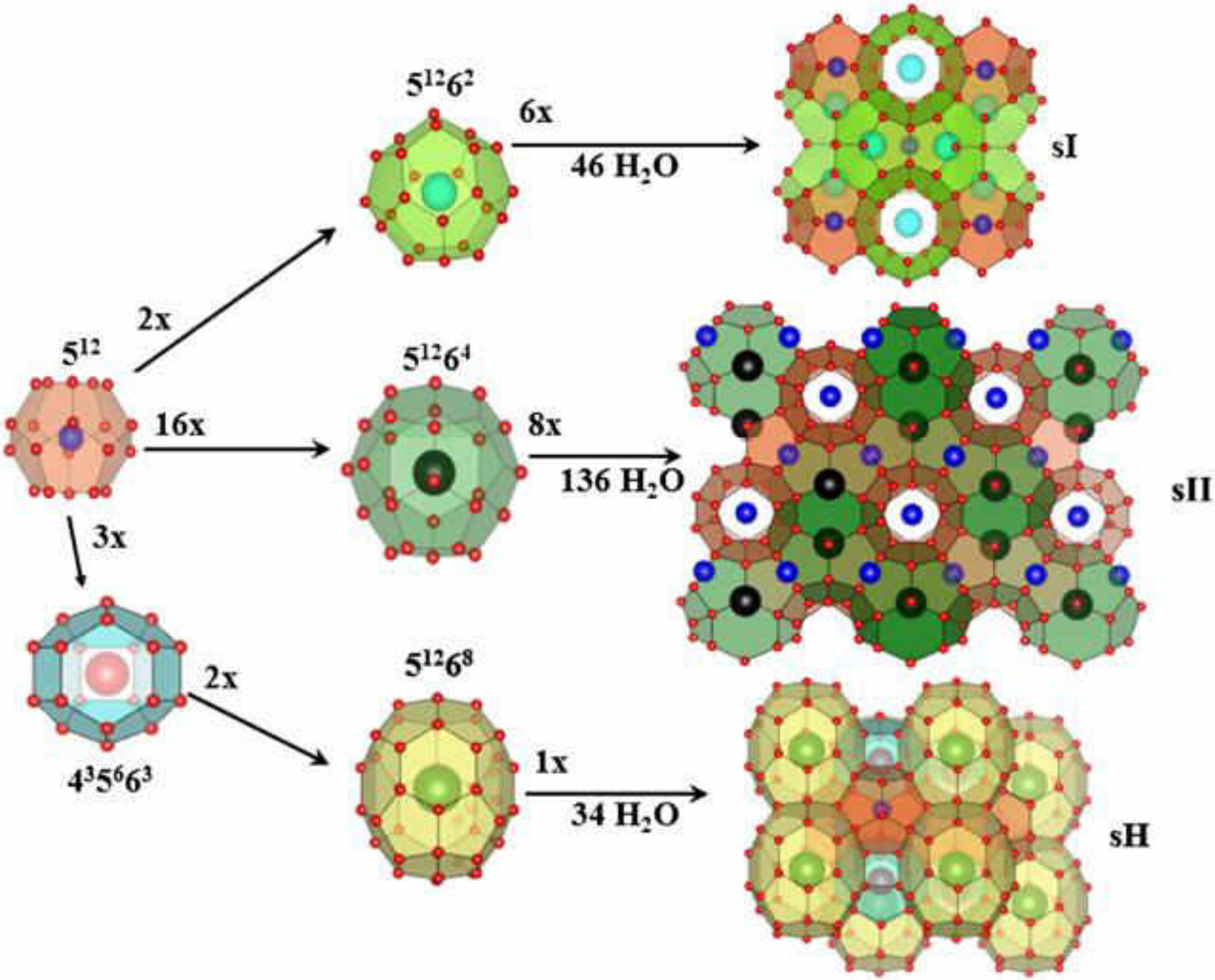
**Methane trapped inside $5^{12}$ cage of hydrate**

**Occurrence:**
**Deep ocean layers, permafrost region, marine sediments at high P and moderate T**

- **1810** — Chlorine hydrate discovered by Sir Humphrey Davy
- **1934** — Hammerschmidt discovered hydrates as pipeline plugs; provides Hammerschmidt equation
- **1965** — Makogon first discovered the natural source of methane hydrate
- **1987** — Ripmeester and coworkers discovered a new hydrate structure, termed as sH hydrate

Ranieri, U. *et al.*, *Nat. Commun.* **2017**, *8*, 1076

# Classification of clathrate hydrates




Methane, ethane, carbon dioxide, etc...

Propane, iso-butane, natural gases, etc…

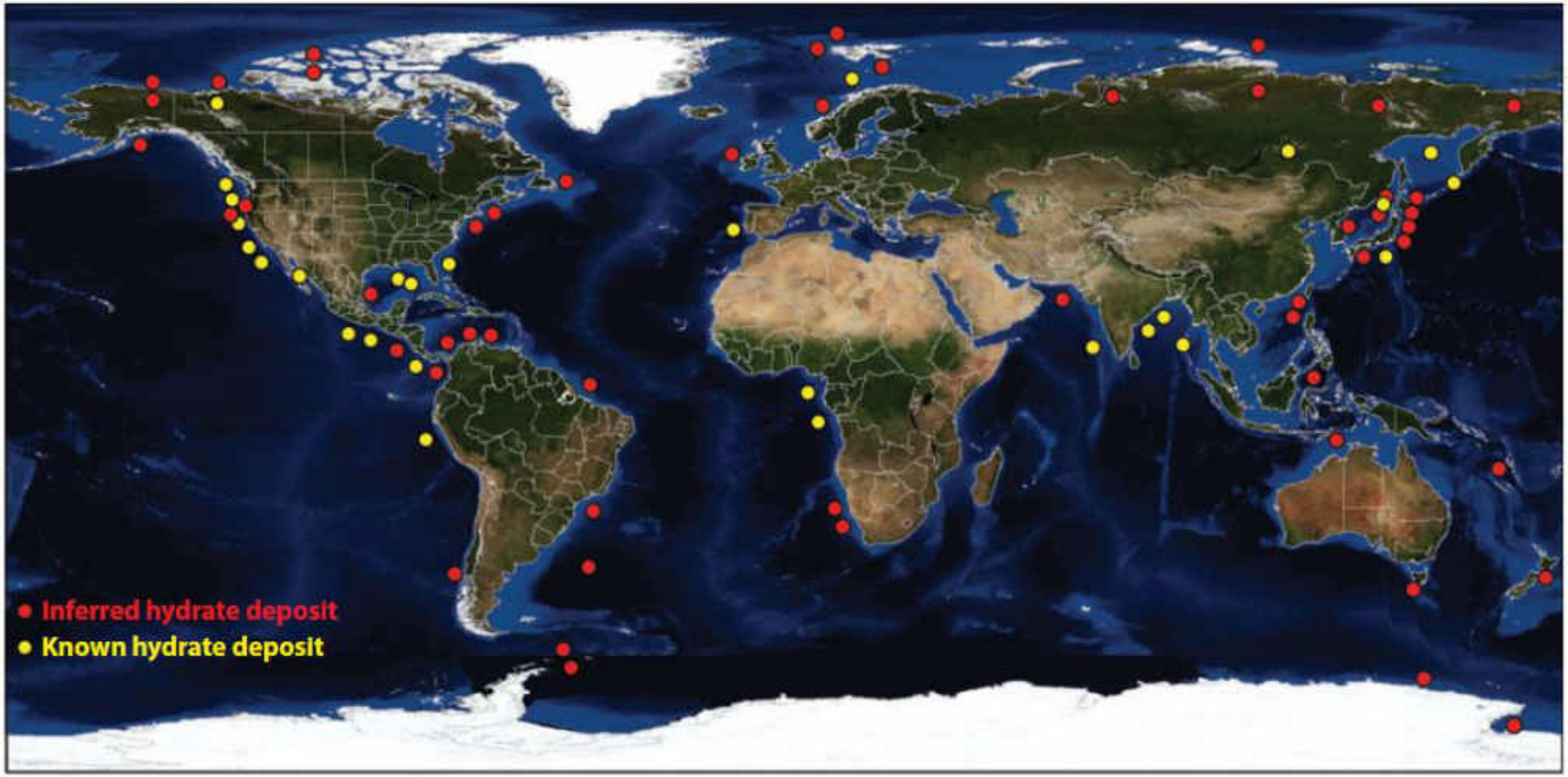
Methane+neo hexane, methane+cycl oheptane, etc…

**Examples**



Warrier, P. *et al.*, *J. Chem. Phys.* **2016**, *145*, 21705

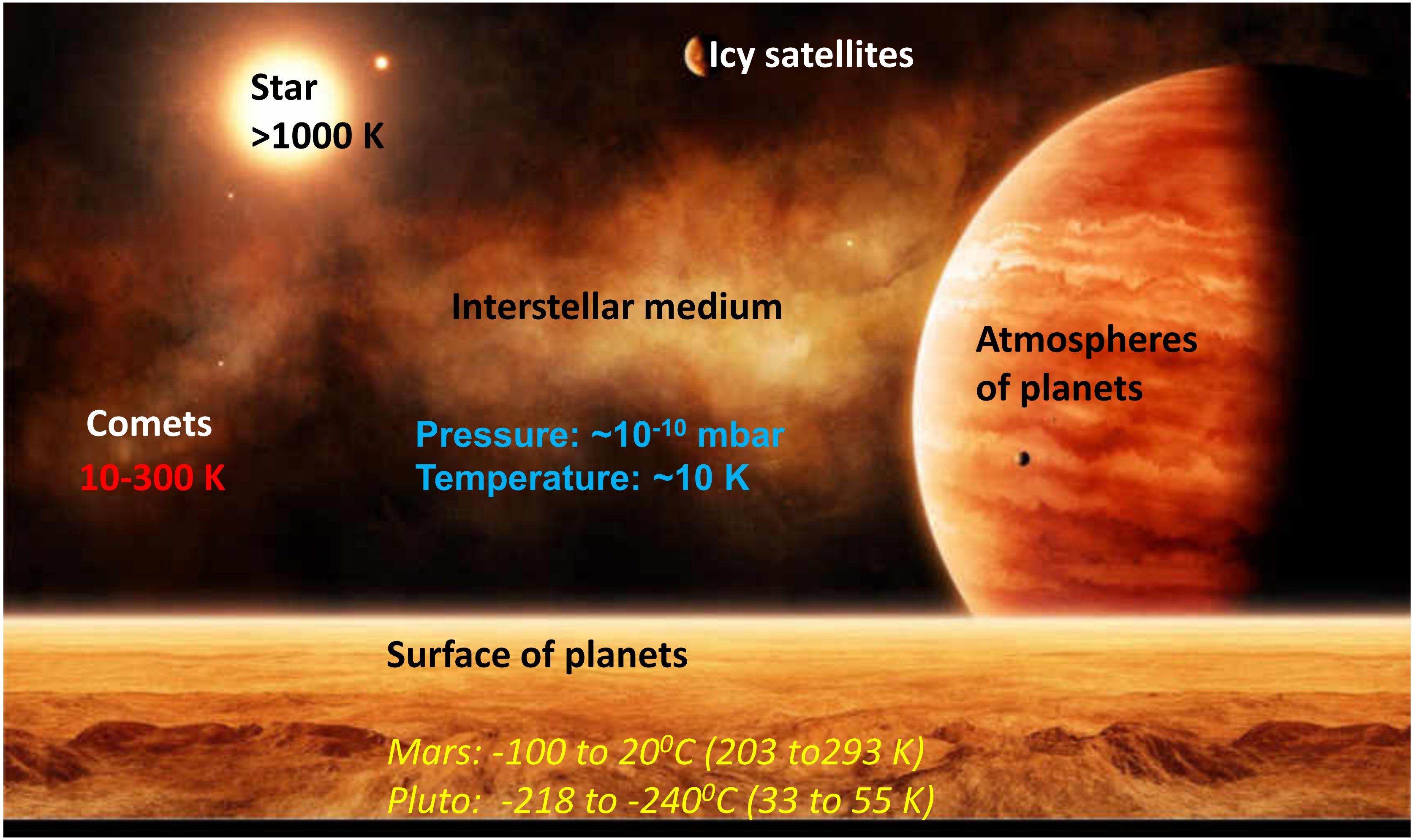
# Occurrence of clathrate hydrates






Hester, K. C. *et al., Annu. Rev. Mar. Sci.* **2009**, *1*, 303-327

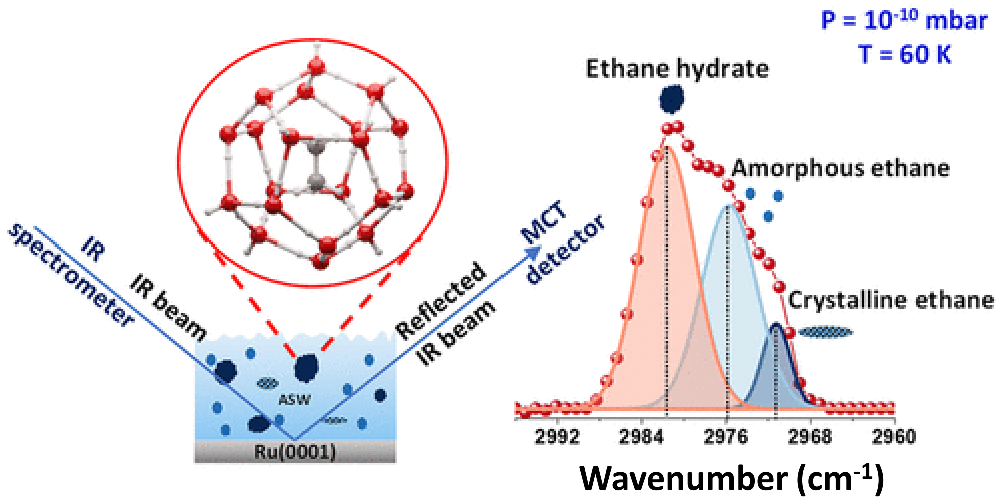
# Interstellar medium (ISM)



# Work done

## Formation of ethane clathrate hydrate in ultrahigh vacuum by thermal annealing

Malla, B. K. *et al., J. Phys. Chem. C.,* **2022**, *42*, 17983–17989



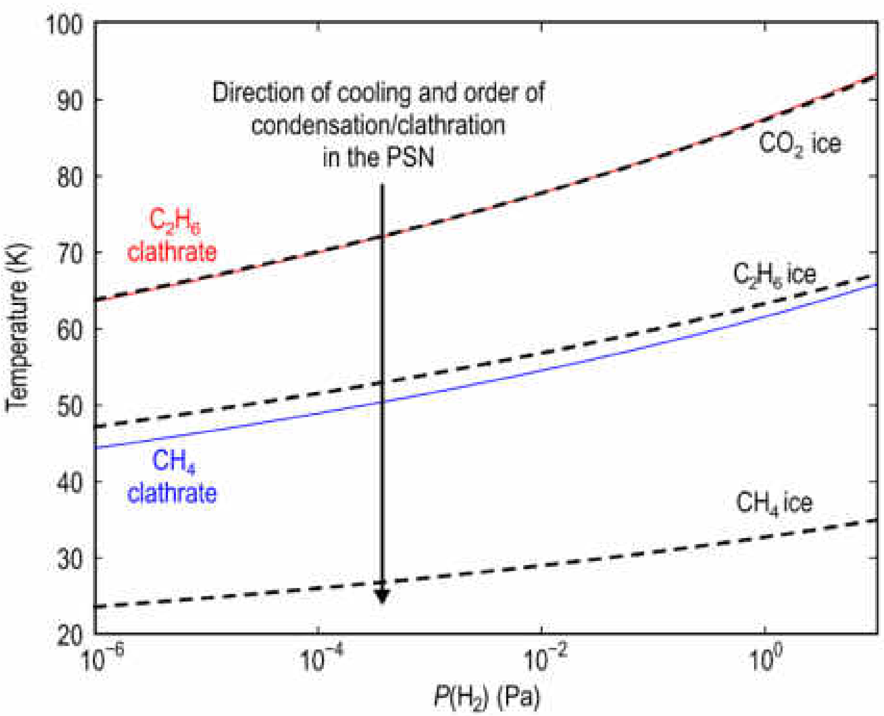
# Background

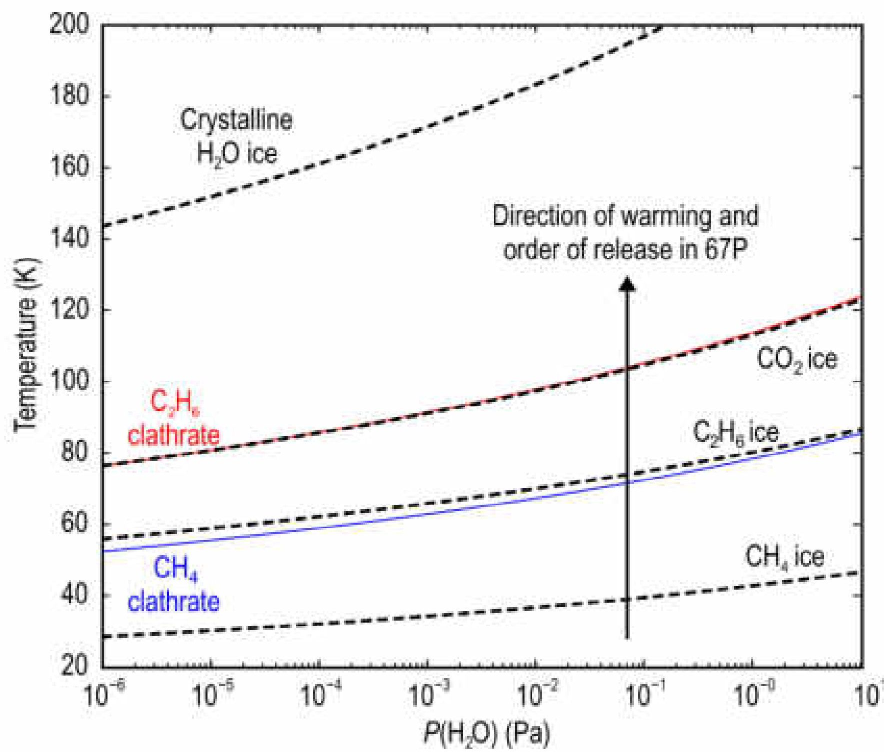
RESEARCH ARTICLE | SPACE SCIENCES

## The presence of clathrates in comet 67P/Churyumov-Gerasimenko

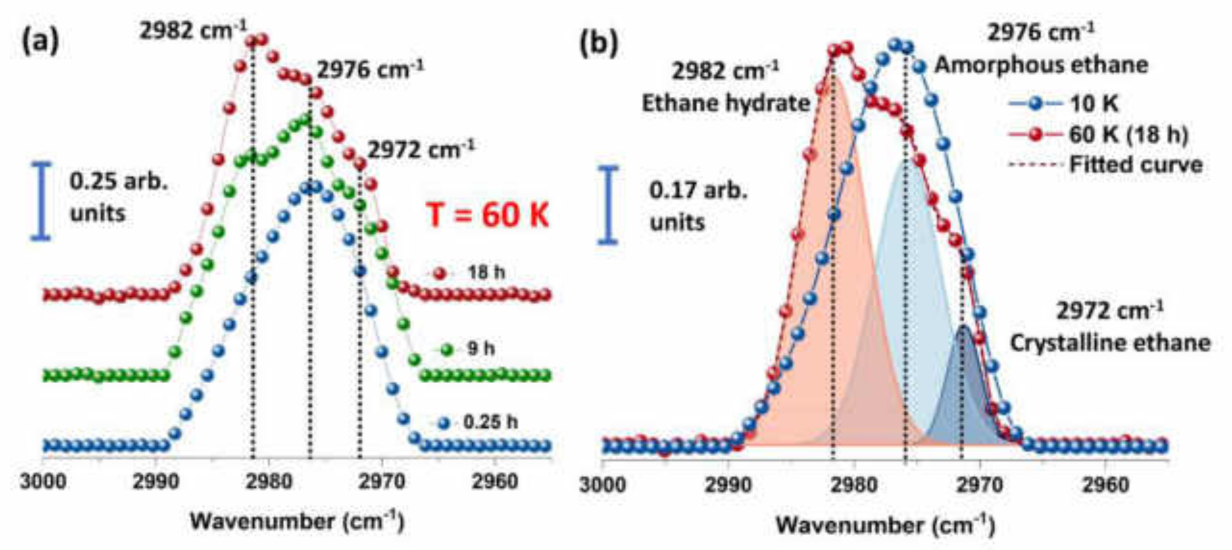
ADRIENN LUSPAY-KUTI, OLIVIER MOUSIS, MYRTHA HÄSSIG, STEPHEN A. FUSELIER, JONATHAN I. LUNINE, BERNARD MARTY, KATHLEEN E. MANDT, PETER WURZ, AND MARTIN RUBIN Authors Info & Affiliations

SCIENCE ADVANCES • 8 Apr 2016 • Vol 2, Issue 4 • DOI: 10.1126/sciadv.1501781

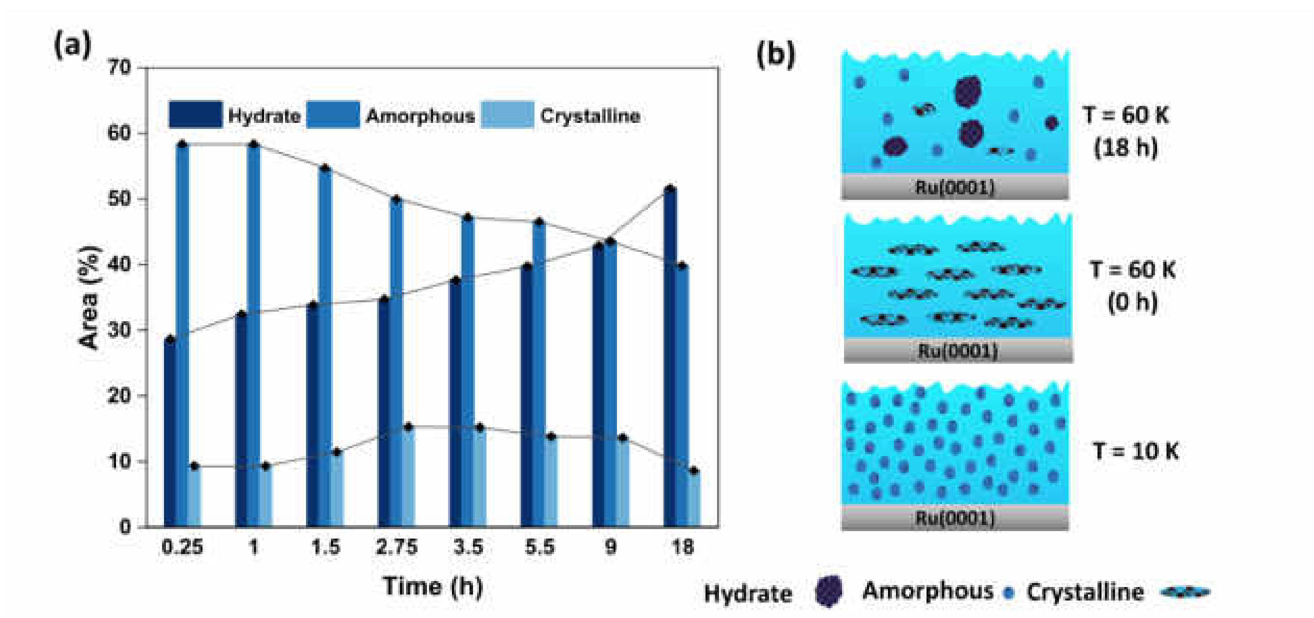


# Results and discussion

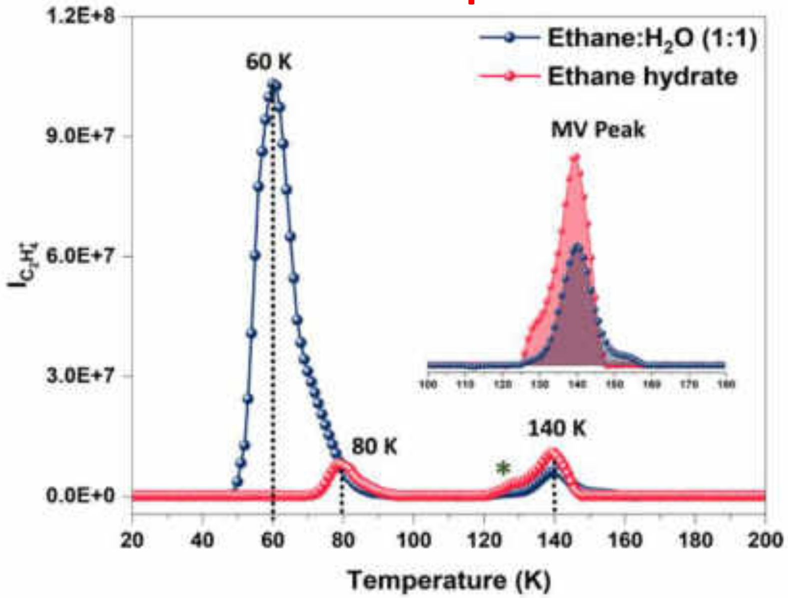


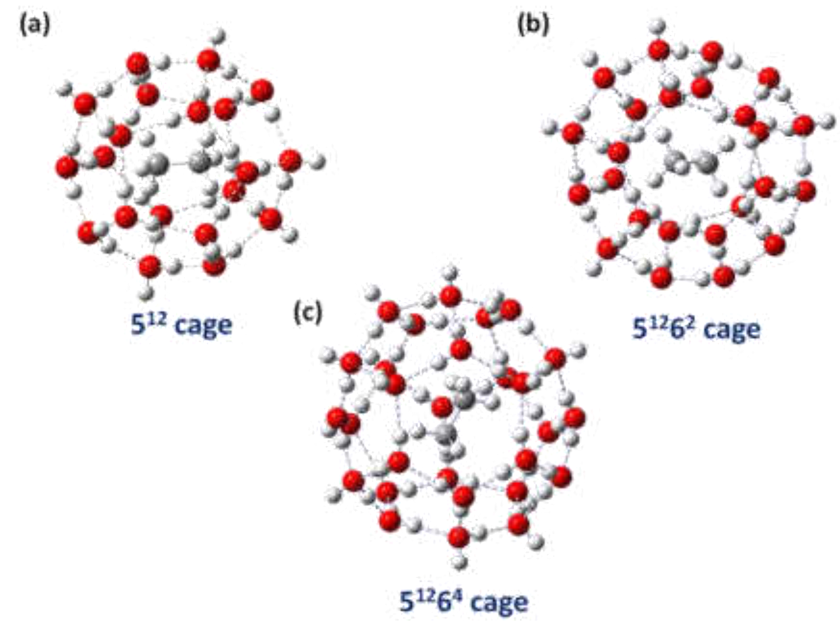

C-H antisymmetric stretching region

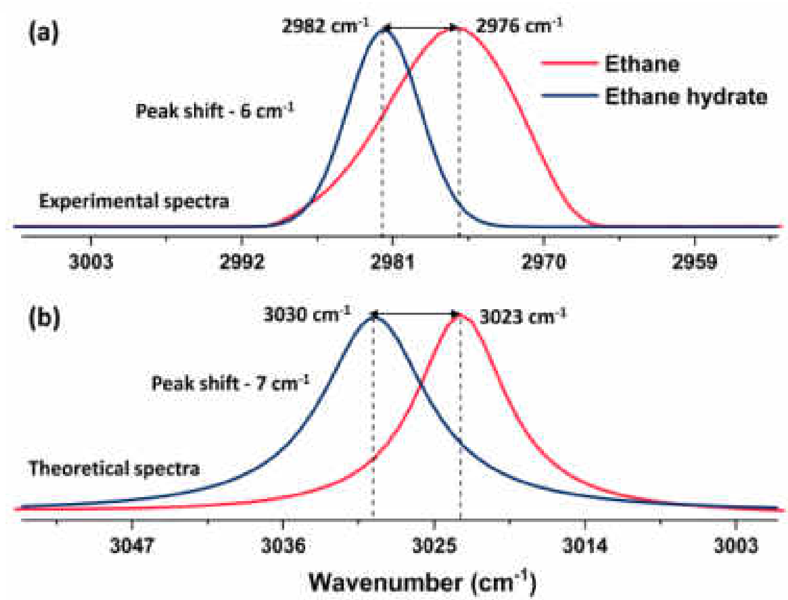


# Results and discussion

TPD-MS plot



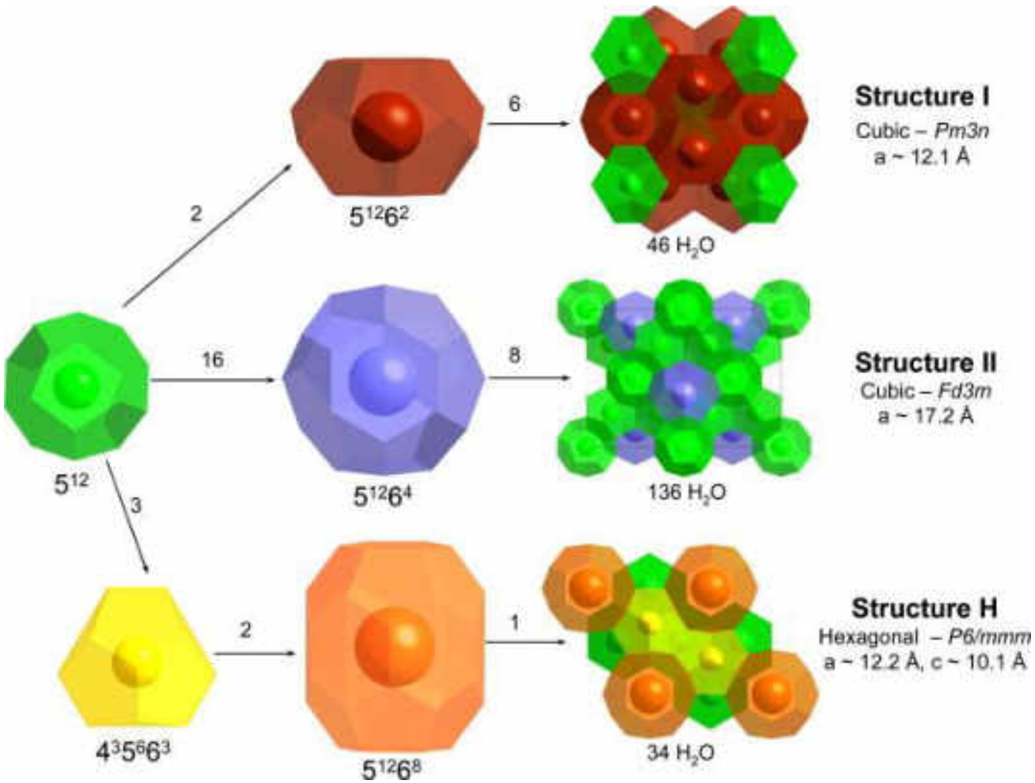



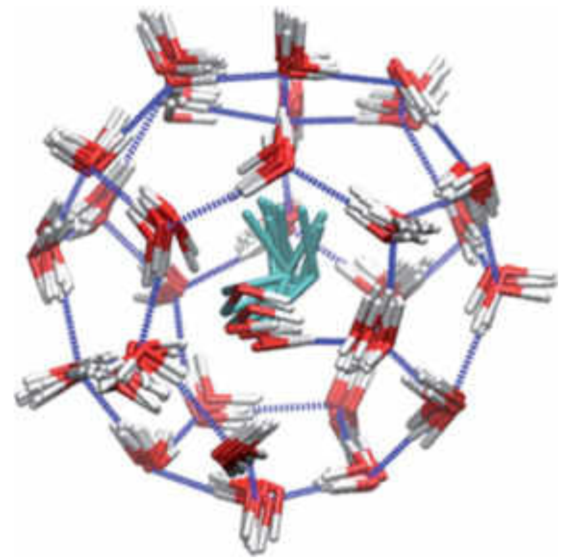
**From Dr. Jyotirmoy**

**From Gaurav**

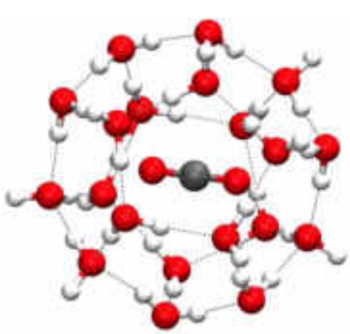
# Clathrate hydrates



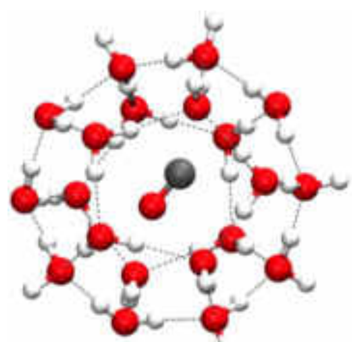

Strobel, T. A. *et al.*, *Chem. Phys. Lett.* **2009**, *478*, 97–109



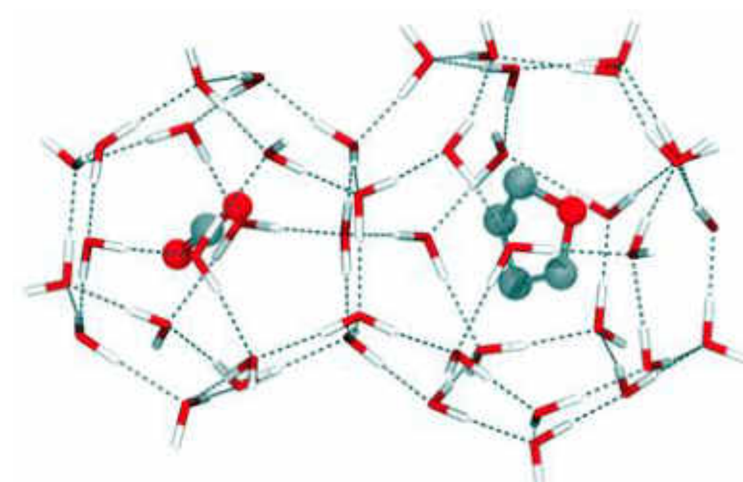
Udachin, K. *et al.*, *J. Chem. Phys.* **2011**, *134*, 121104



**$CO_2$@$5^{12}$**



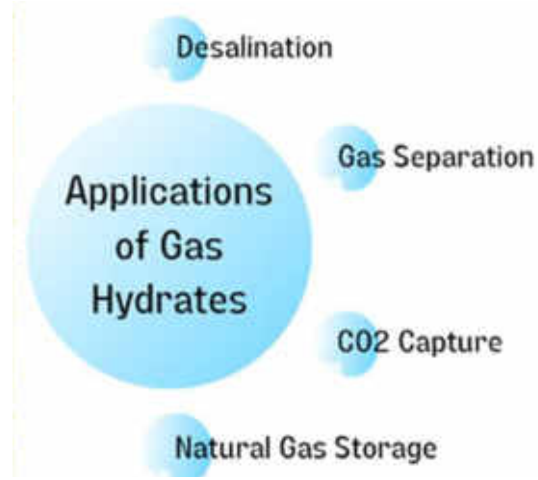
**CO@$5^{12}$**



**$CO_2$@$5^{12}$ and THF@$5^{12}6^4$ cage**

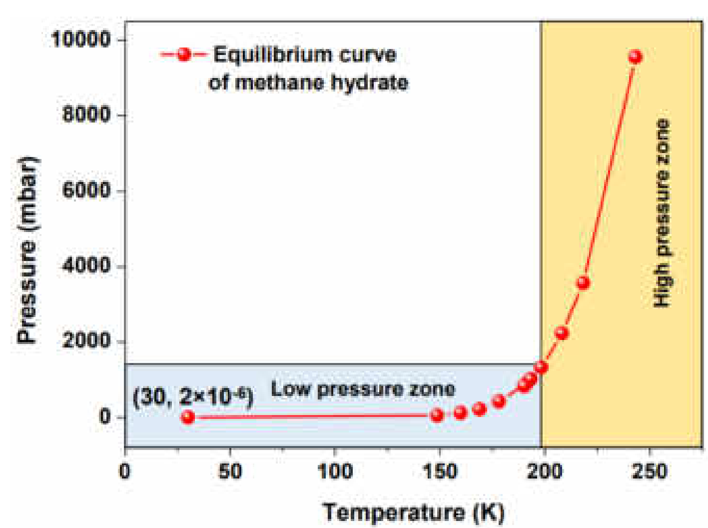
# Properties and applications of clathrate hydrates

“Ice on fire” burning of methane hydrate




Veluswamy, H. P. and Upadhye, N., *Energy Fuels* **2022**, *36*, 2323-2350

Methane clathrate block embedded in the sediment of hydrate ridge

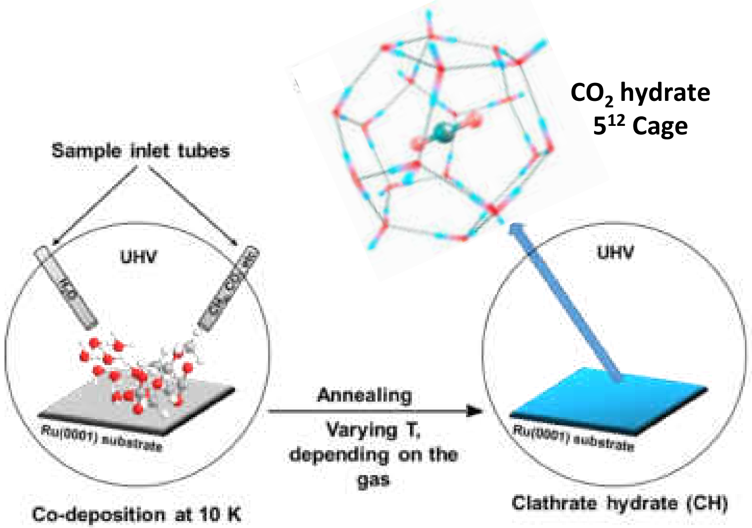


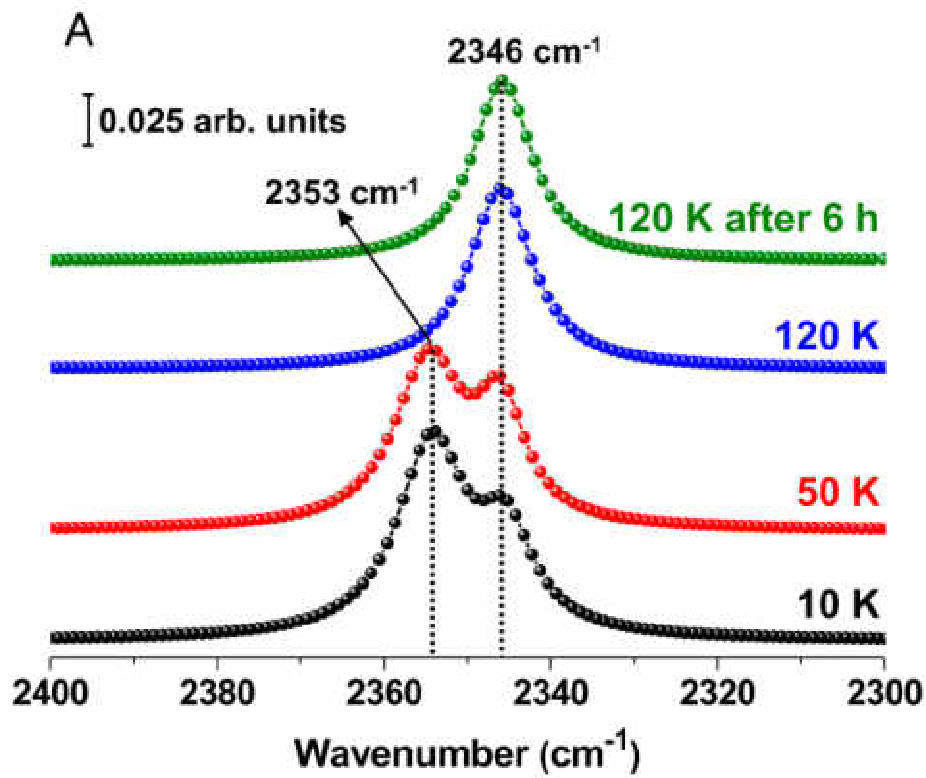

https://en.wikipedia.org/wiki/Clathrate_hydrate

Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

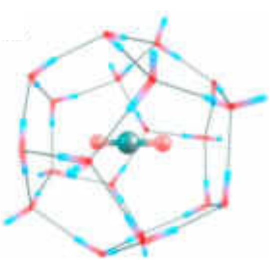
# Clathrate hydrates in interstellar environment

## Experimental method

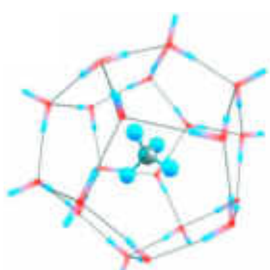



Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531



$CO_2@5^{12}$



$CH_4@5^{12}$

**T = 10-30 K**

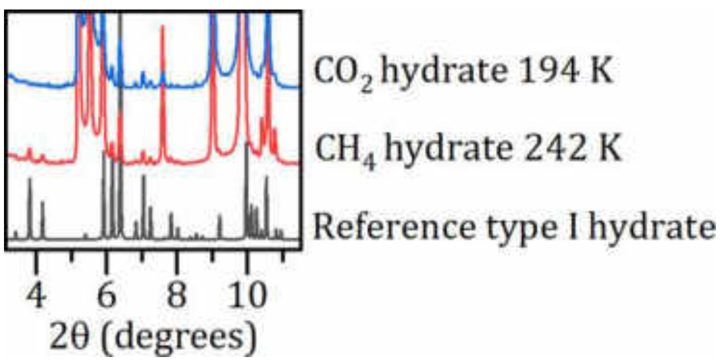
**P = $10^{-10}$ mbar**

# In situ synchrotron X-ray diffraction experiments

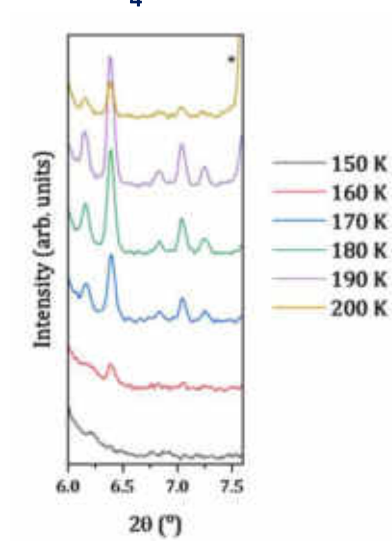
## In Situ X-Ray Diffraction Study on Hydrate Formation at Low Temperature in a High Vacuum

Robert P.C. Bauer, Aravind Ravichandran, John S. Tse,* Narayan Appathurai, Graham King, Beatriz Moreno, Serge Desgreniers, and Ramaswami Sammynaiken

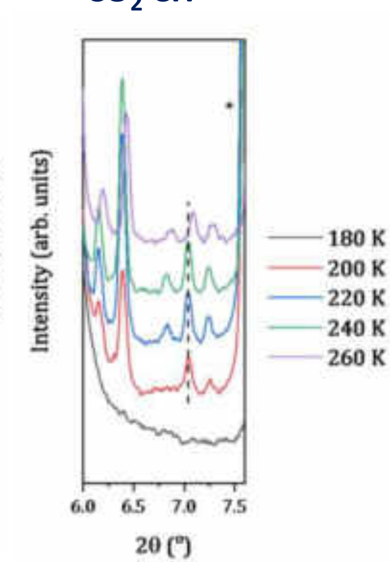
Cite This: *J. Phys. Chem. C* 2021, 125, 26892−26900 Read Online




**$CH_4$ CH**

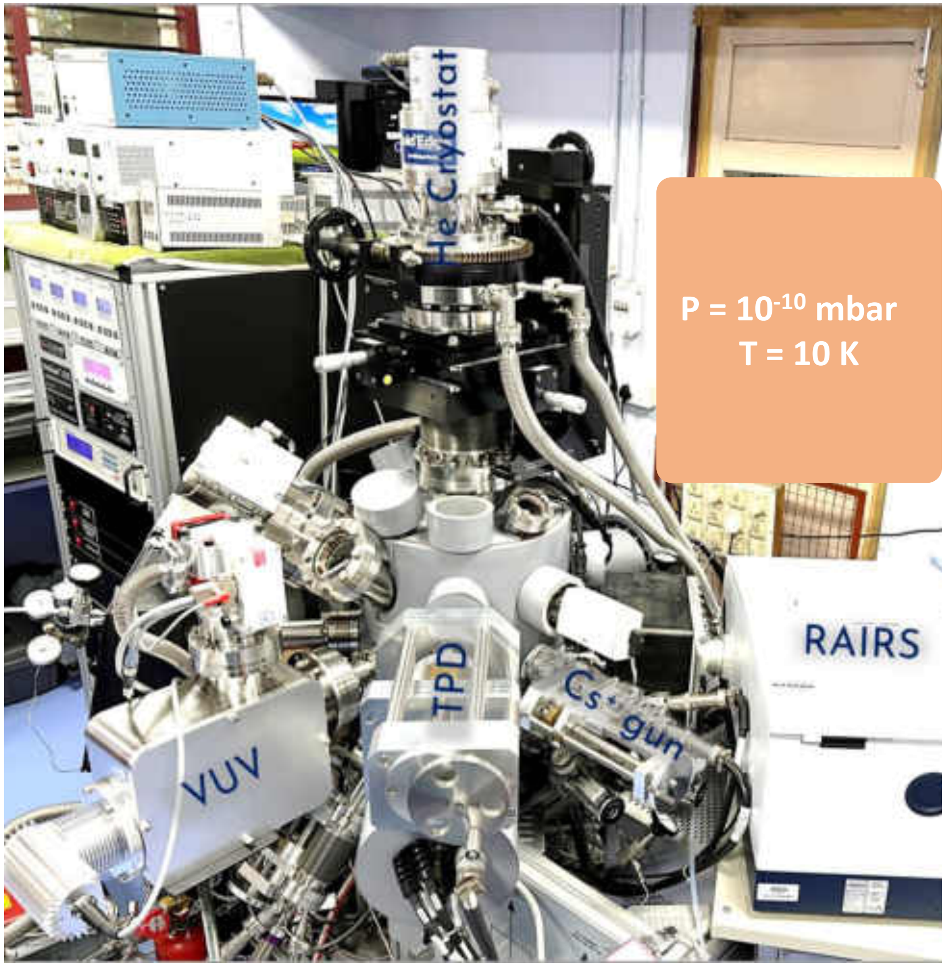



**$CO_2$ CH**



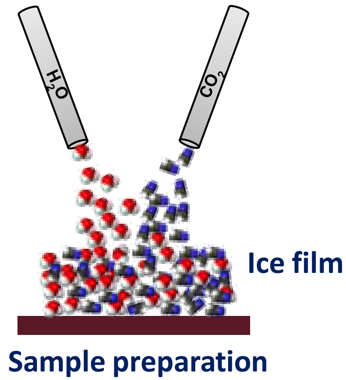

Bauer, R. P. C. *et al.*, *J. Phys. Chem. C* **2021**, *125*, 26892−26900

# Instrumentation

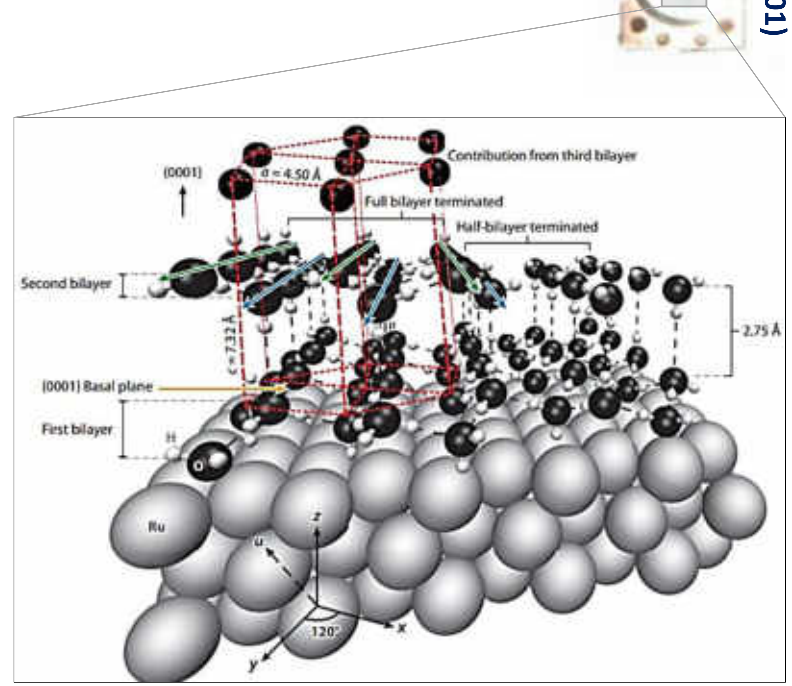



P = $10^{-10}$ mbar
T = 10 K

Bag, S. *et al.*, *Rev. Sci. Instrum*. **2014**, *85*, 014103



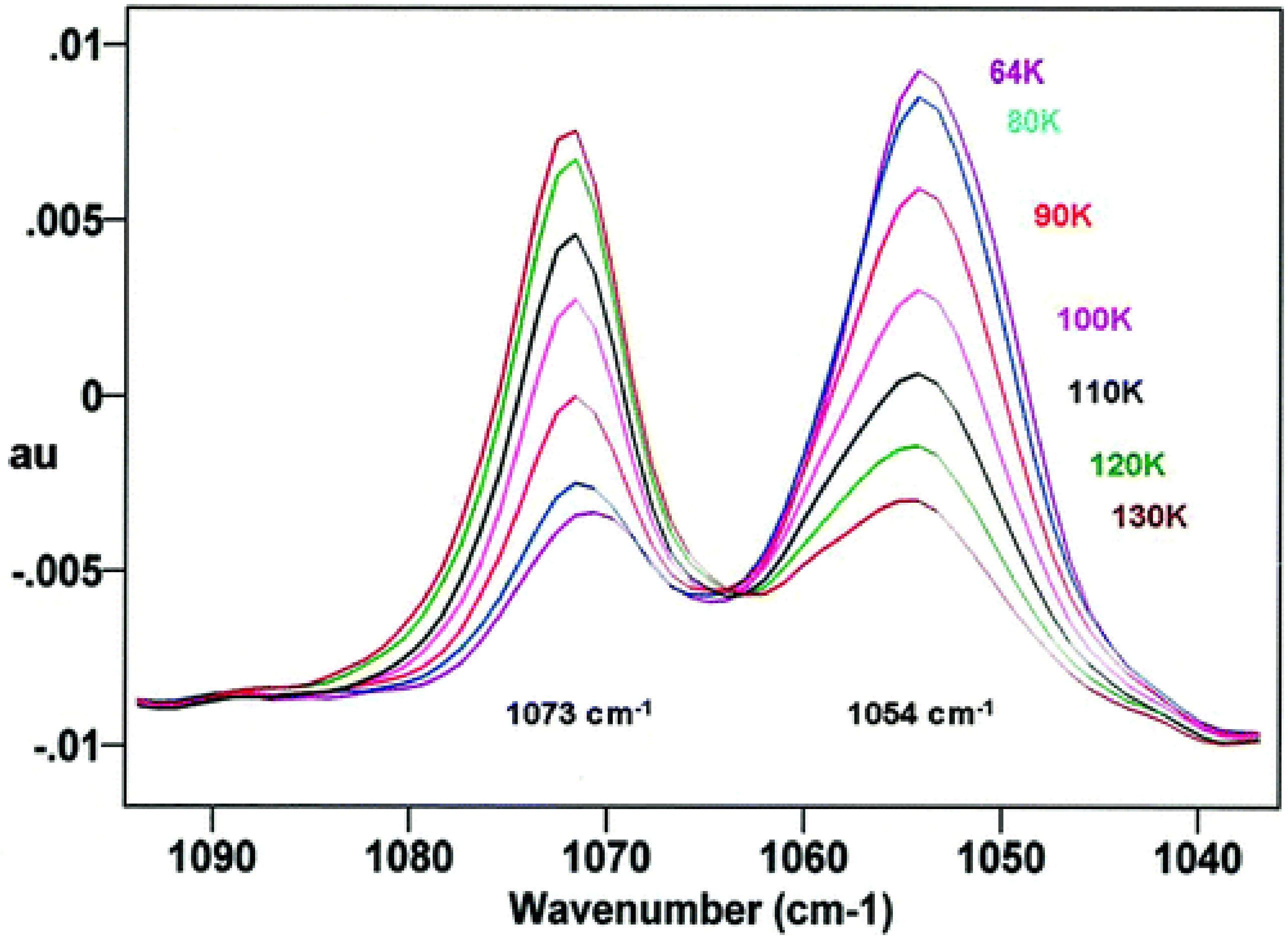





Bag, S. *et al.*, *Annu. Rev. Anal. Chem.* **2013**, *6*, 97–118

THF hydrate slides below

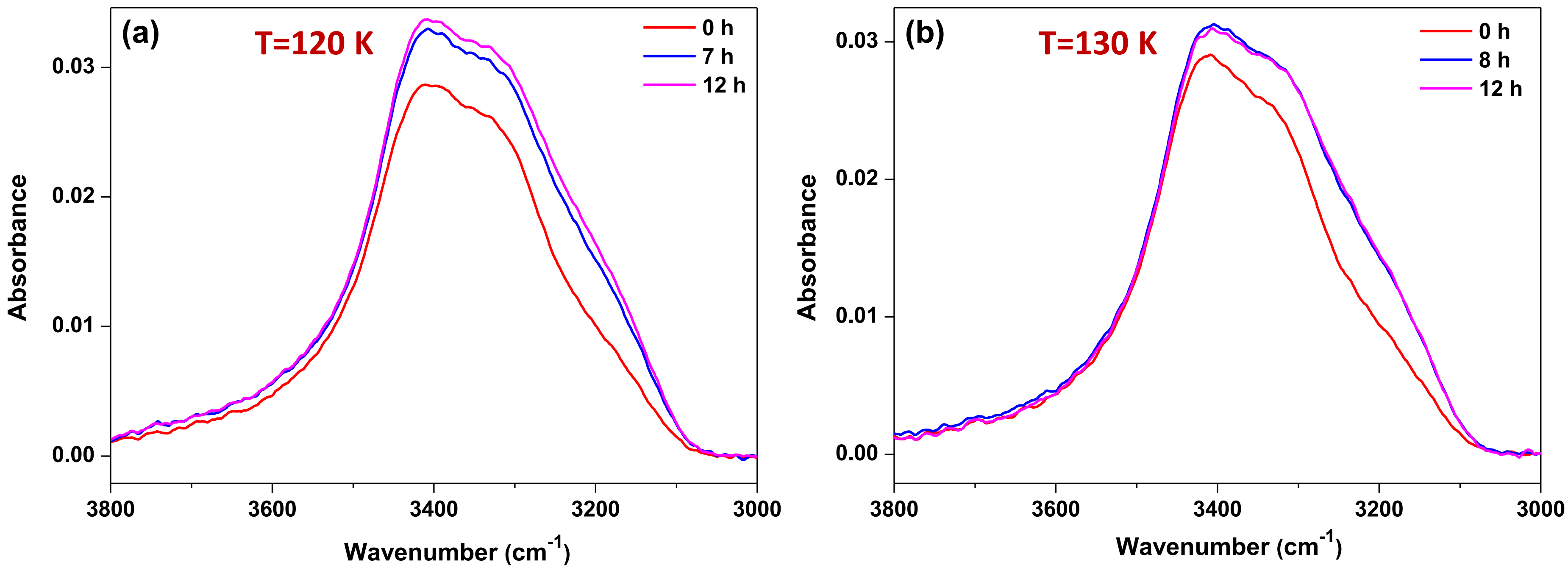
# Formation of THF hydrate






Monreal, I. A. *et al., J. Phys. Chem. A* **2011**, *115*, 5822-5832

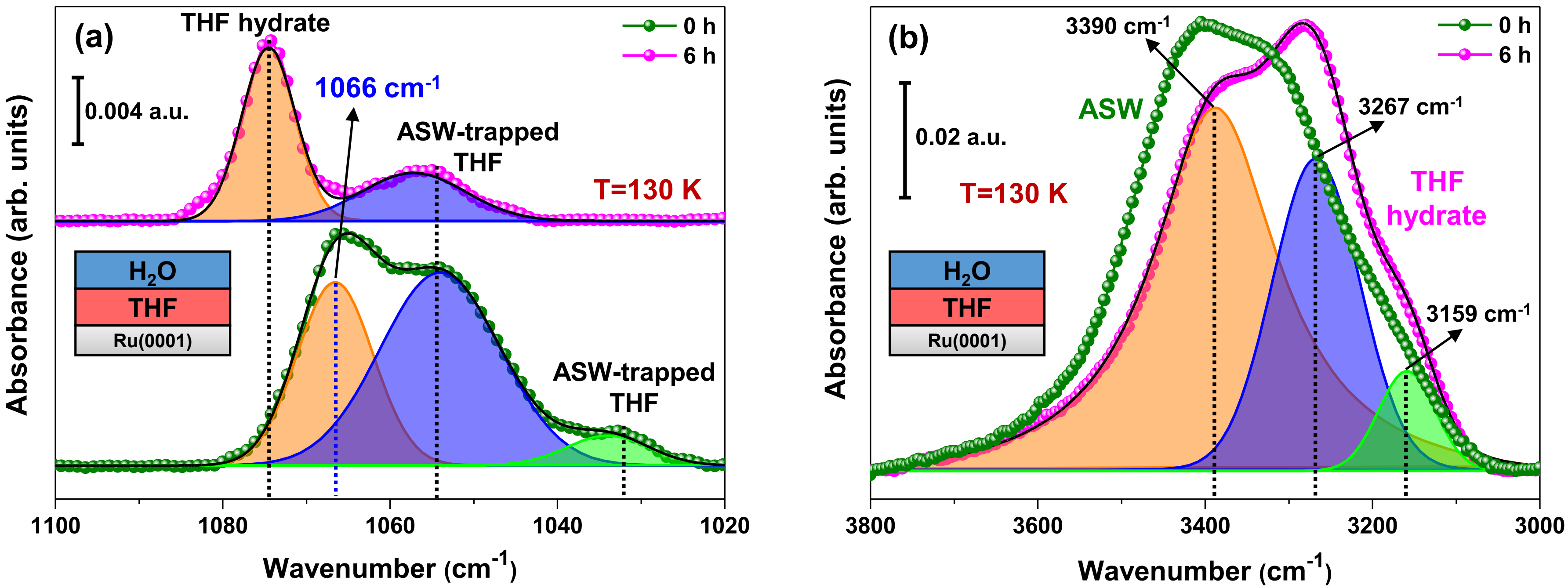
# Formation of THF hydrate in UHV






Ghosh, J. *et al., J. Phys. Chem. C* **2019**, *123*, 16300-16307

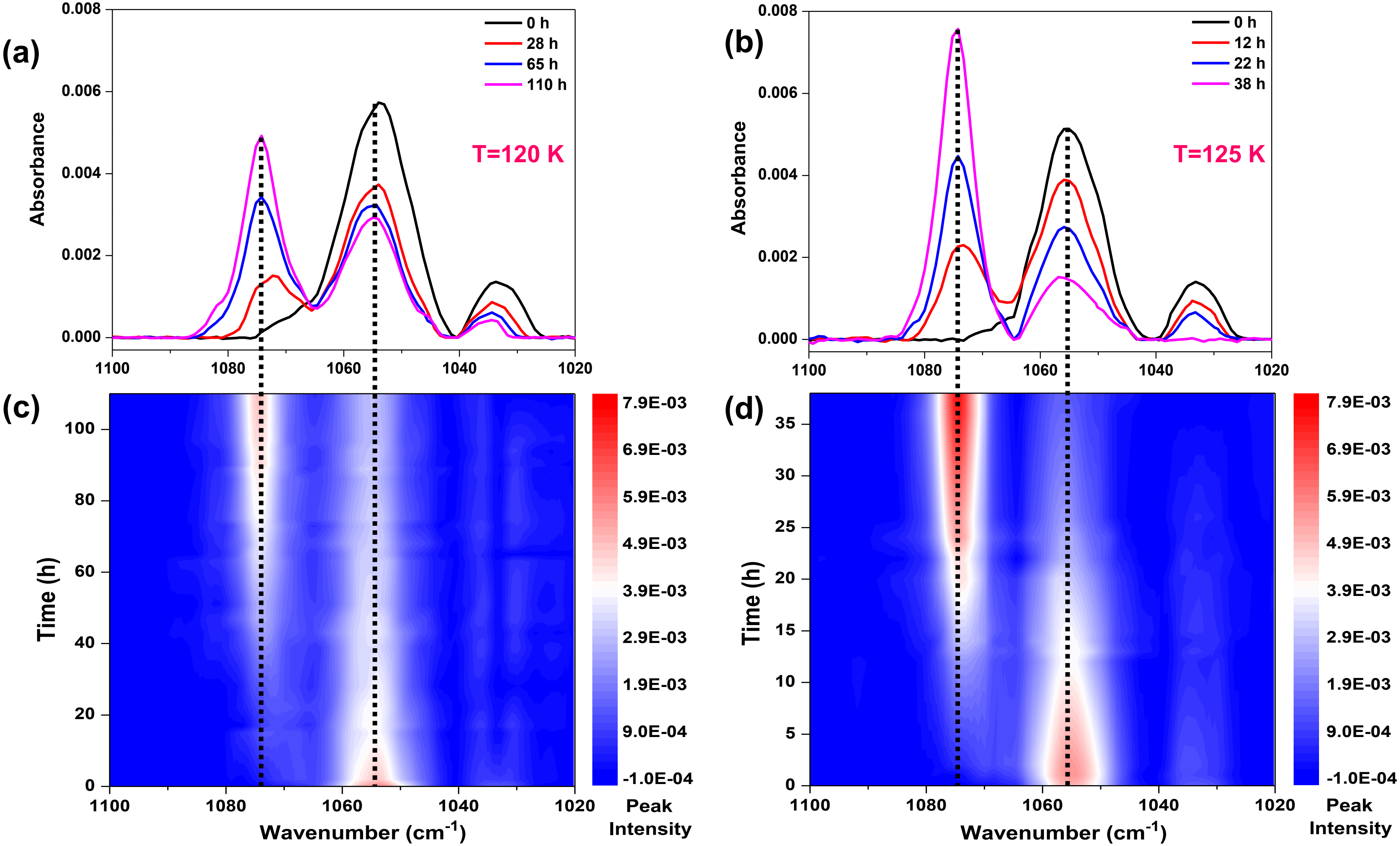
# Formation of THF hydrate in UHV






Ghosh, J. *et al., J. Phys. Chem. C* **2019**, *123*, 16300-16307

# Formation of THF hydrate in UHV






Ghosh, J. *et al.*, *J. Phys. Chem. C* **2019**, *123*, 16300-16307

# Formation of THF hydrate in UHV

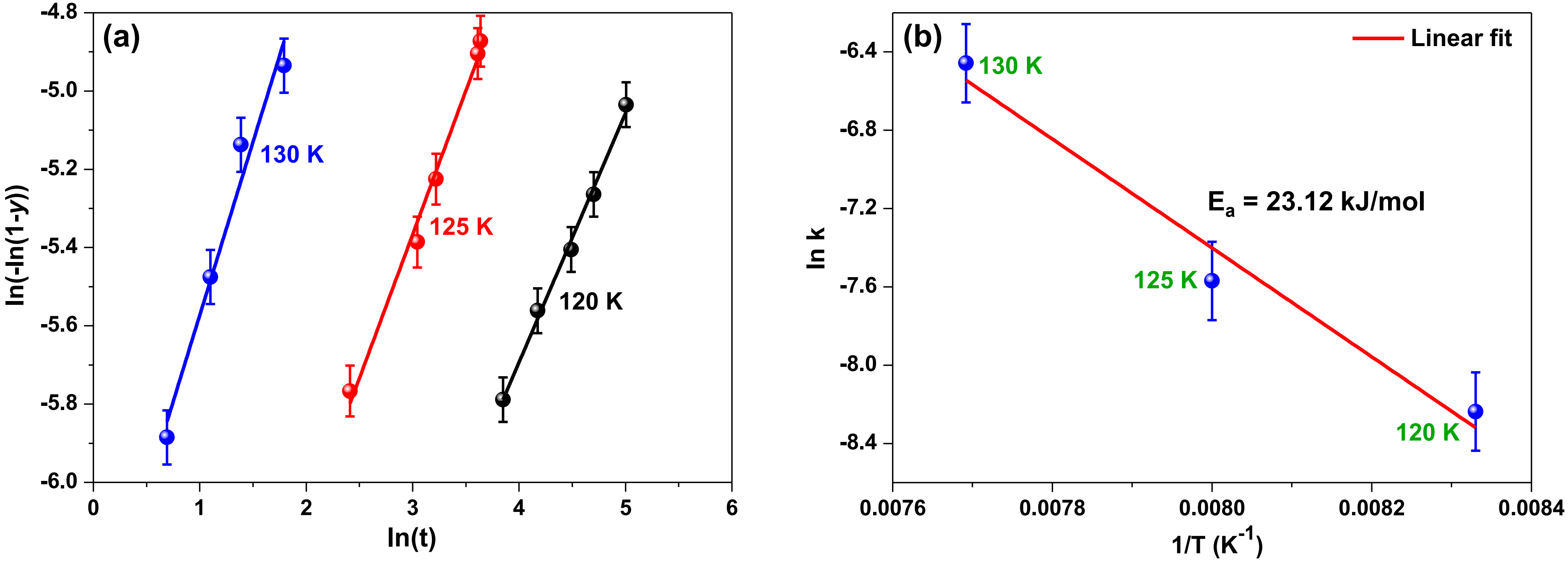
Avrami equation,

$y(t) = 1 - \exp[-k(T).t]^n$

$\ln(-\ln[1 - y(T)]) = n \ln(t) + n \ln k(T)$

Arrhenius equation,

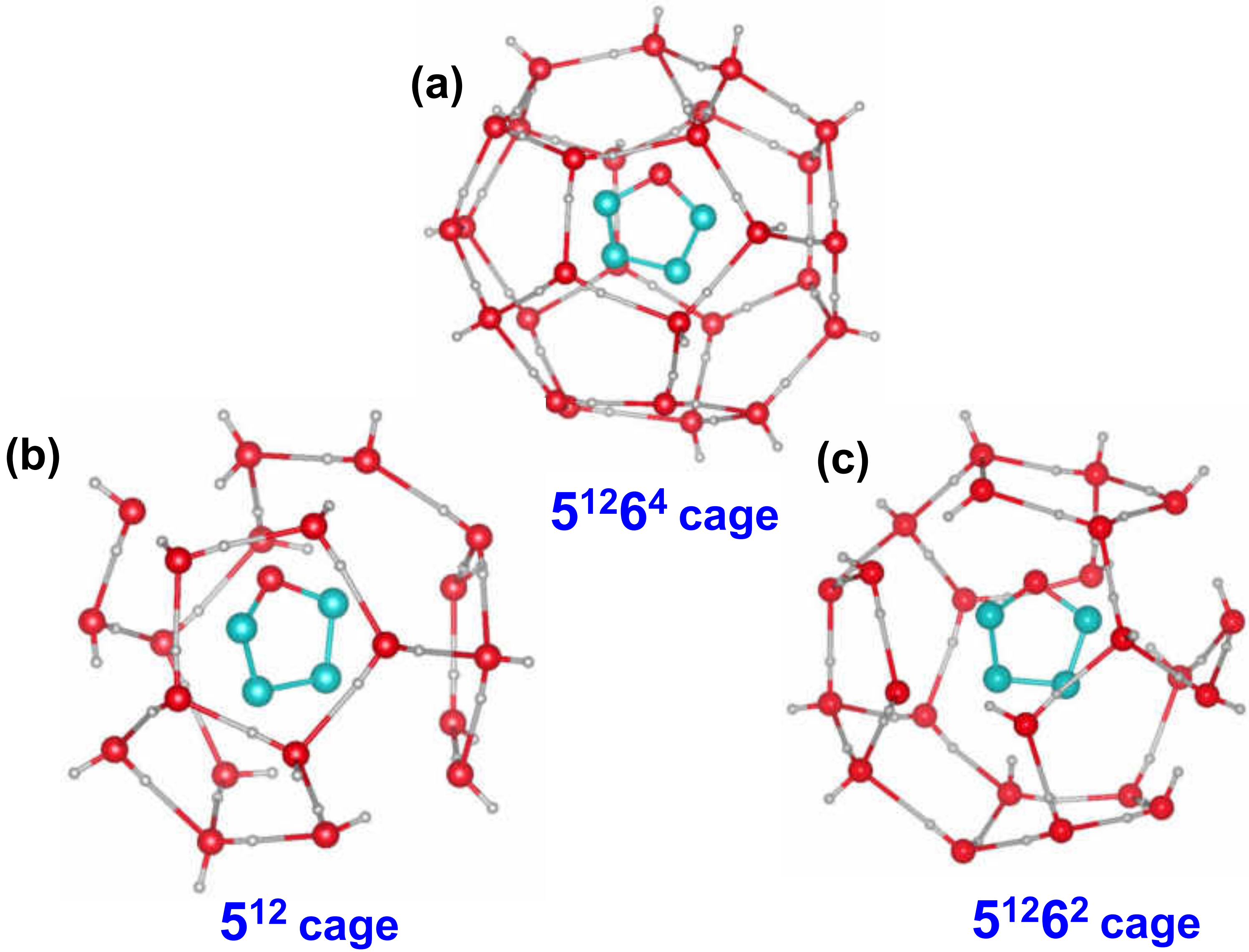
$k = A.\exp[-E_a/RT]$






Ghosh, J. *et al.*, *J. Phys. Chem. C* **2019**, *123*, 16300-16307

# Formation of THF hydrate in UHV



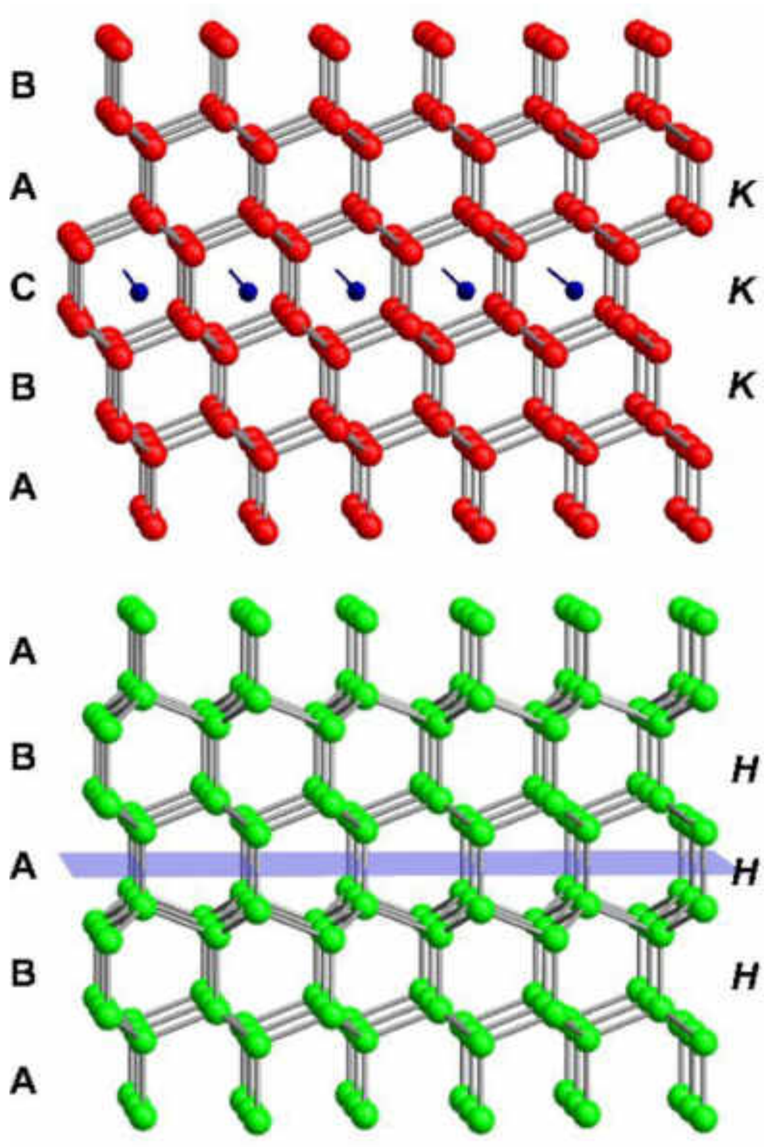

Ghosh, J. *et al., J. Phys. Chem. C* **2019**, *123*, 16300-16307

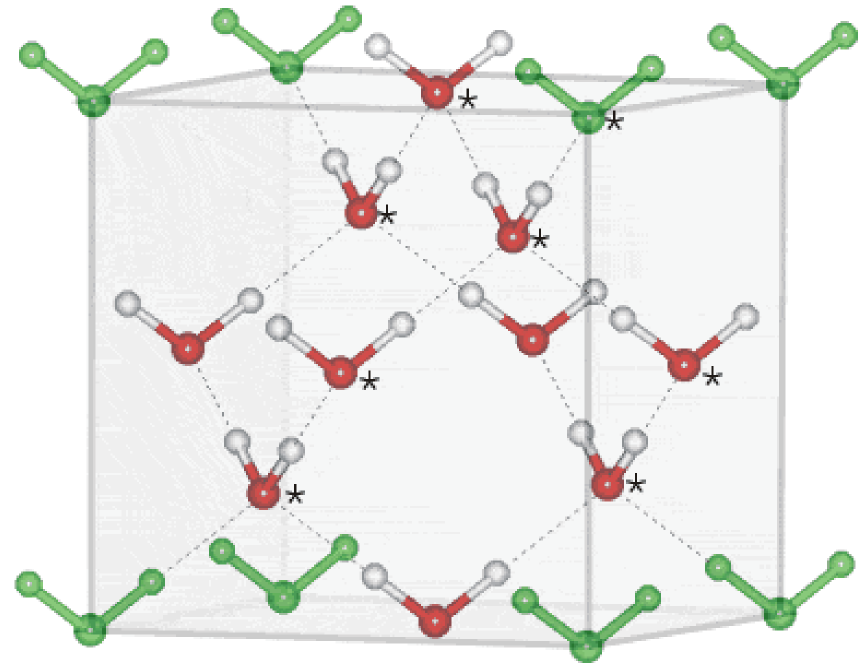
Cubic ice slide (one slide) below

# Structure of cubic ice

Ice $I_c$

Ice $I_h$



**Unit cell of cubic ice**

http://www1.lsbu.ac.uk/water/cubic_ice.html



Kuhs, W. F. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2012,** *109*, 21259-21264