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Clathrate Hydrates in Interstellar Environment

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ACS
Sustainable
Chemistry & Engineering

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Dr. Ashutosh Singh



Materials, Methods and Devices for Futuristic Technologies (MDFT-2023)



2007 12 12

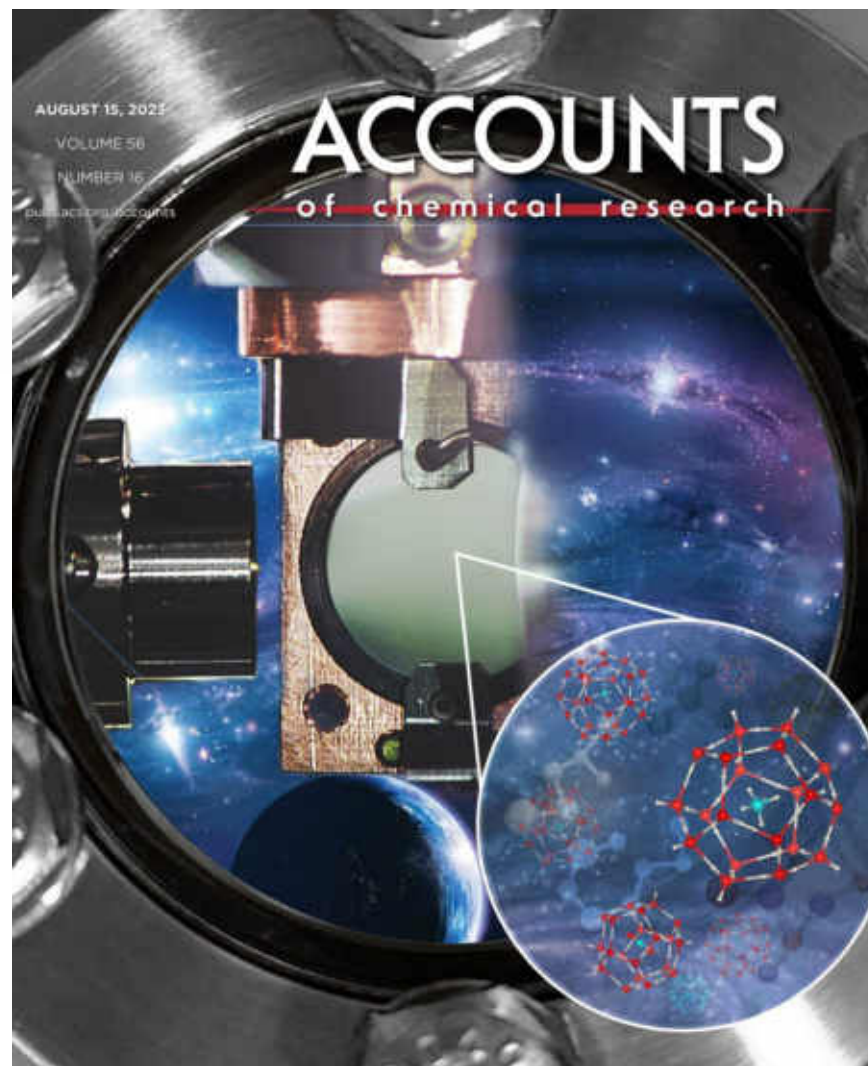


Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

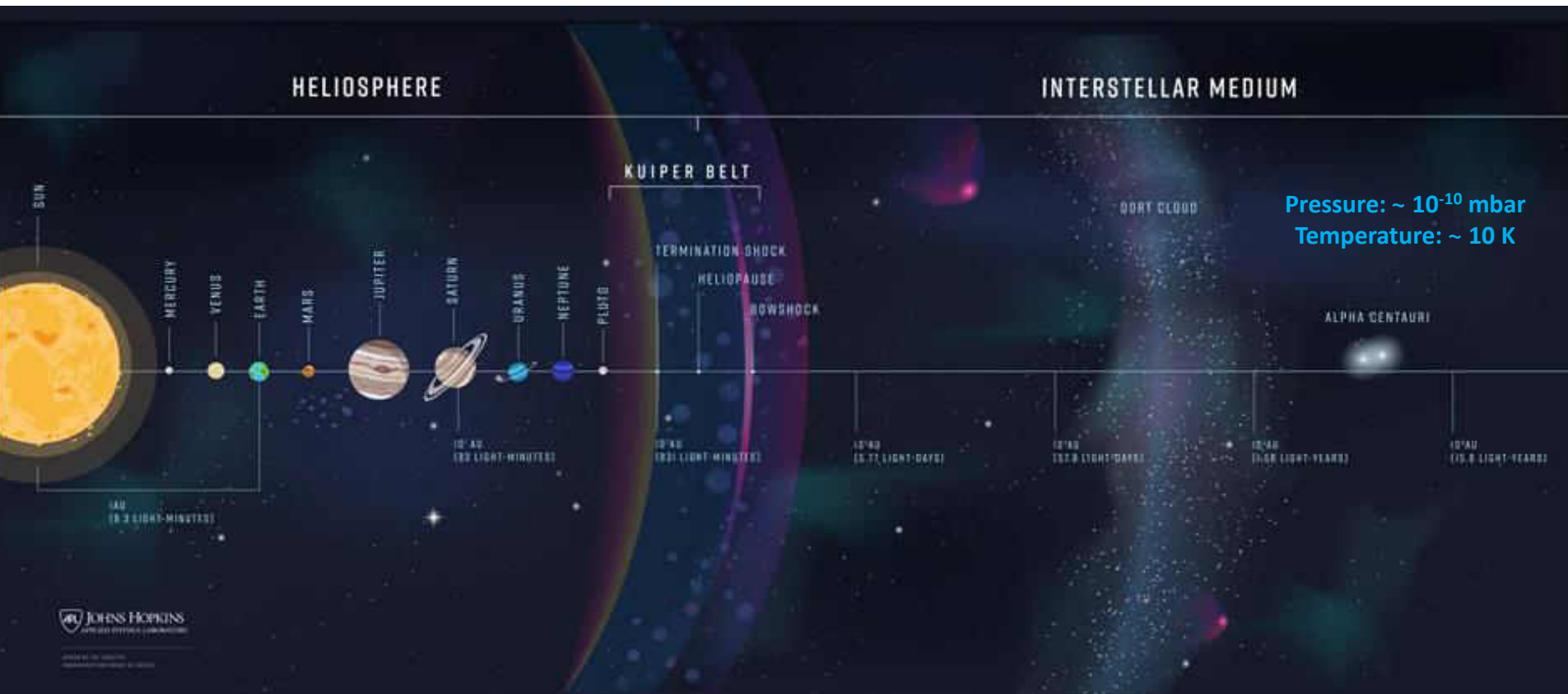
Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,* and Thalappil Pradeep*

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

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Interstellar medium



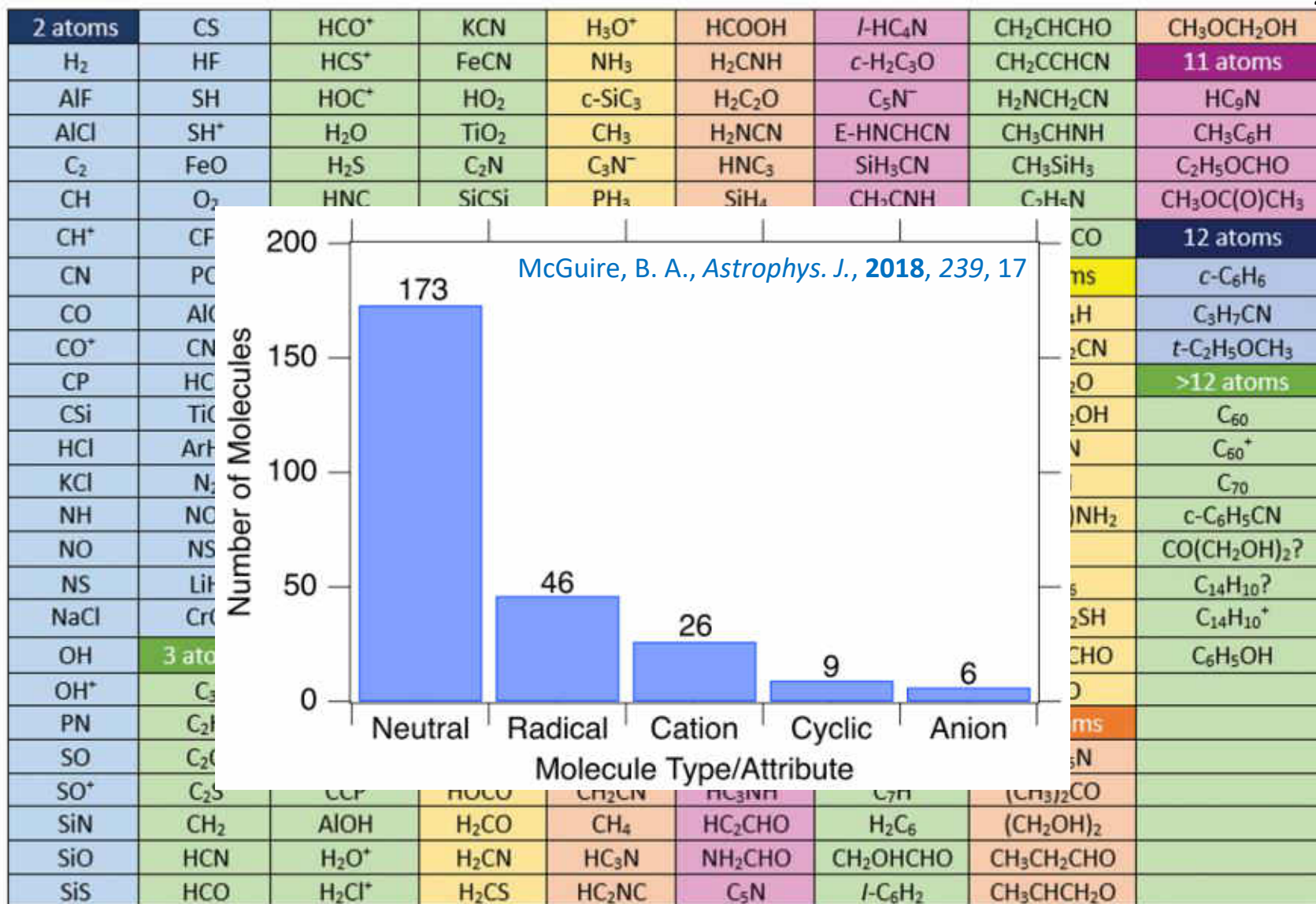
Diffuse clouds: $T \sim 100$ K, $n \sim 100$ molecules per cm^3

Dense clouds: $T \sim 10$ - 100 K, $n \sim 10^4$ - 10^8 molecules per cm^3

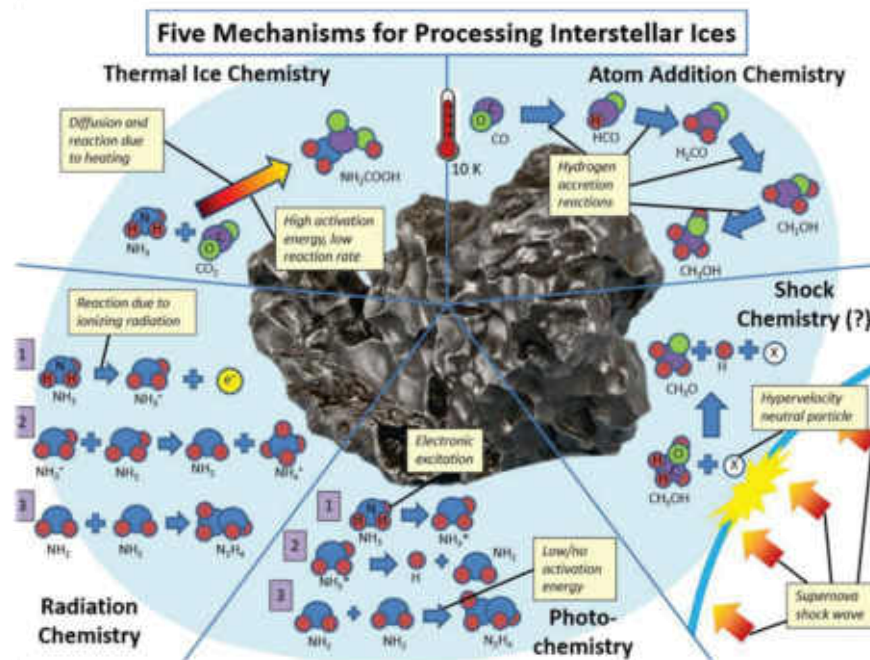
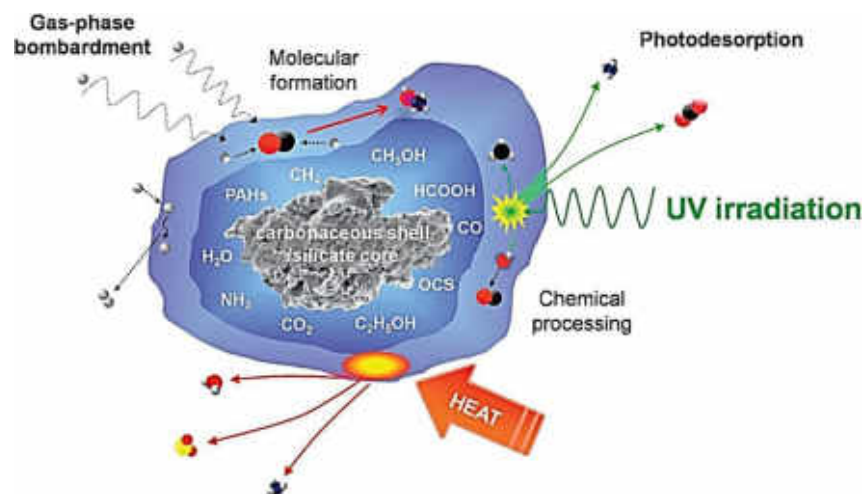
On Earth sea level: $T \sim 300$ K, $n \sim 3 \times 10^{19}$ molecules per cm^3

Interstellar molecules

260



Interstellar ices



Silicates and carbonaceous material – 0.01-0.5 μm

Applications of clathrate hydrates



“Ice on fire” burning of methane hydrate

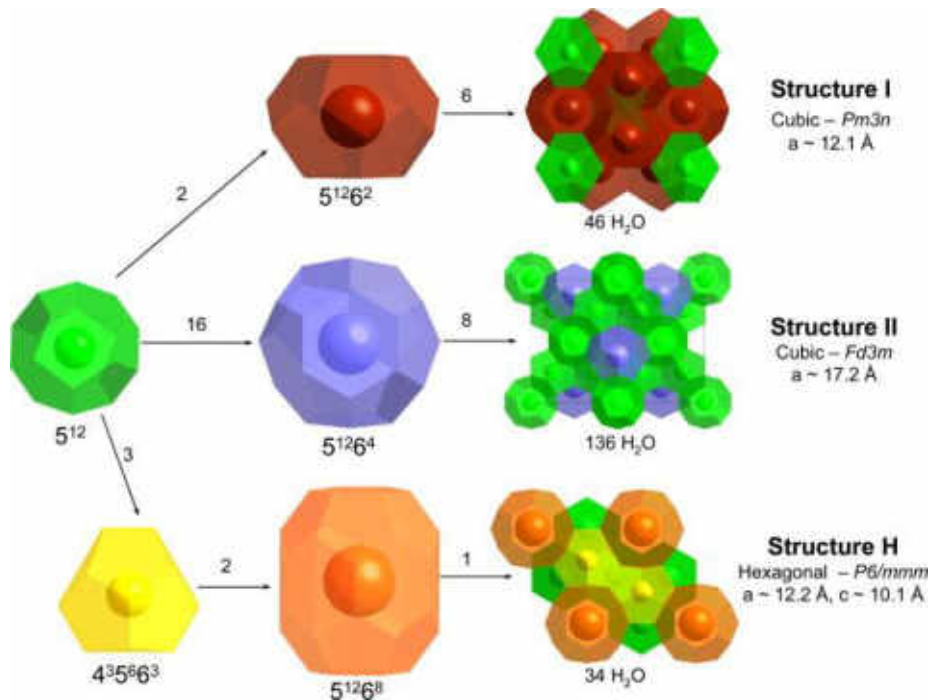


Gas hydrate plug recovered from a subsea pipeline

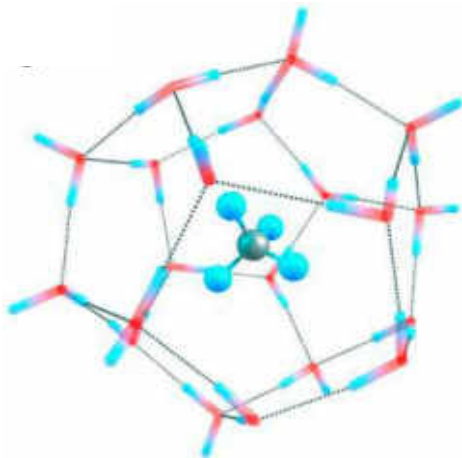
Applications:

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

Clathrate hydrates



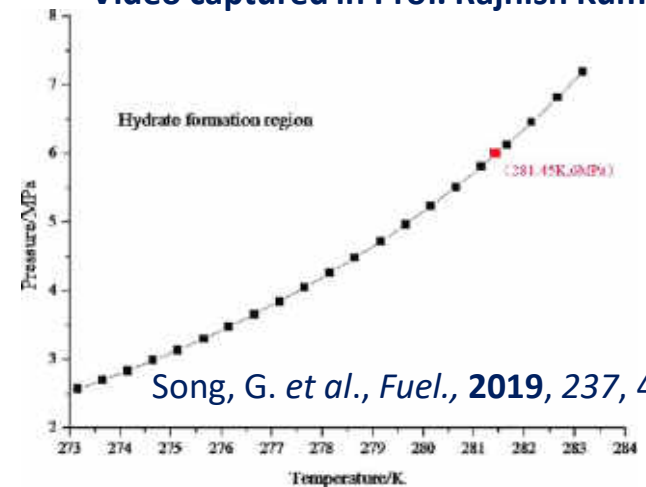
Strobel, T. A. *et al.*, *Chem. Phys. Lett.*, **2009**, 478, 97–109



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

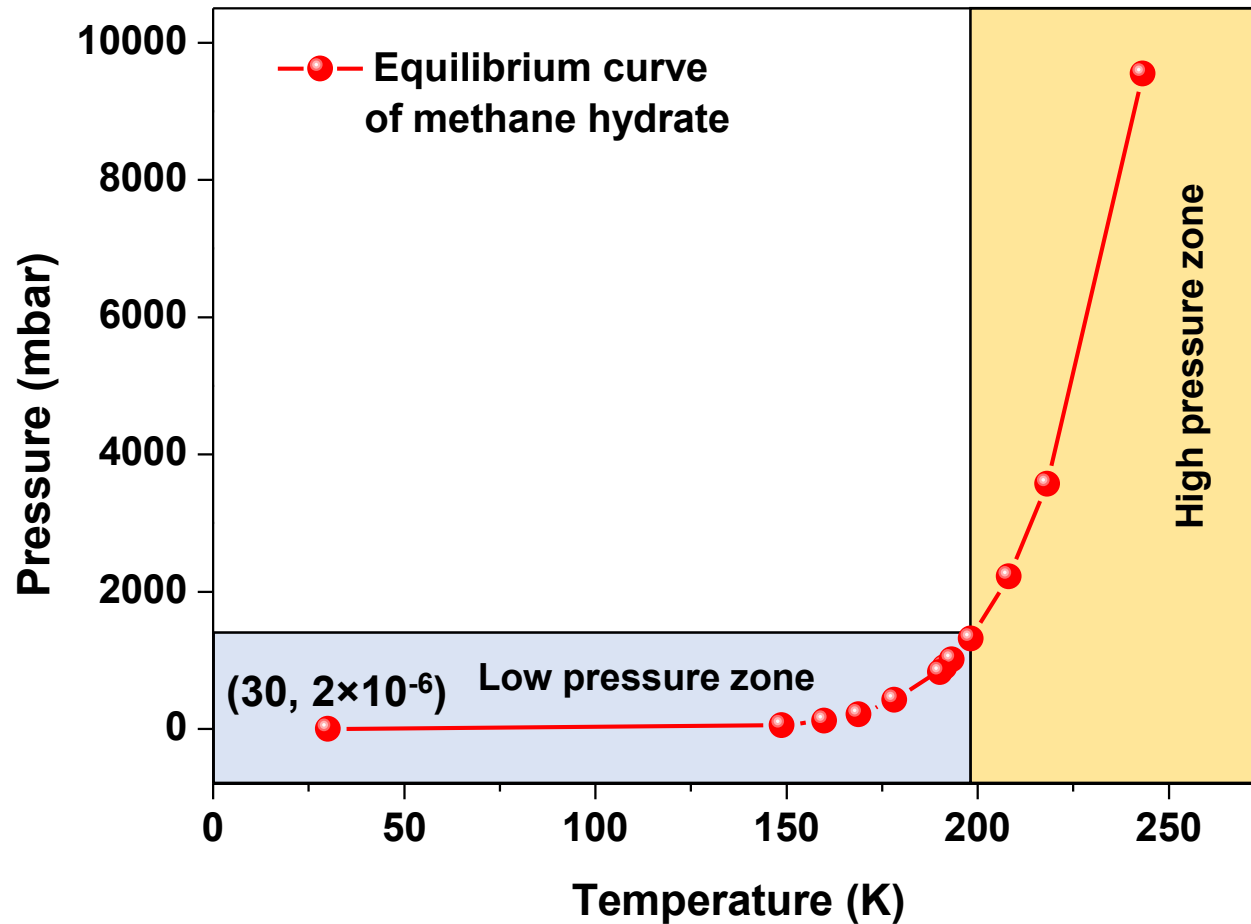


Video captured in Prof. Rajnish Kumar's lab



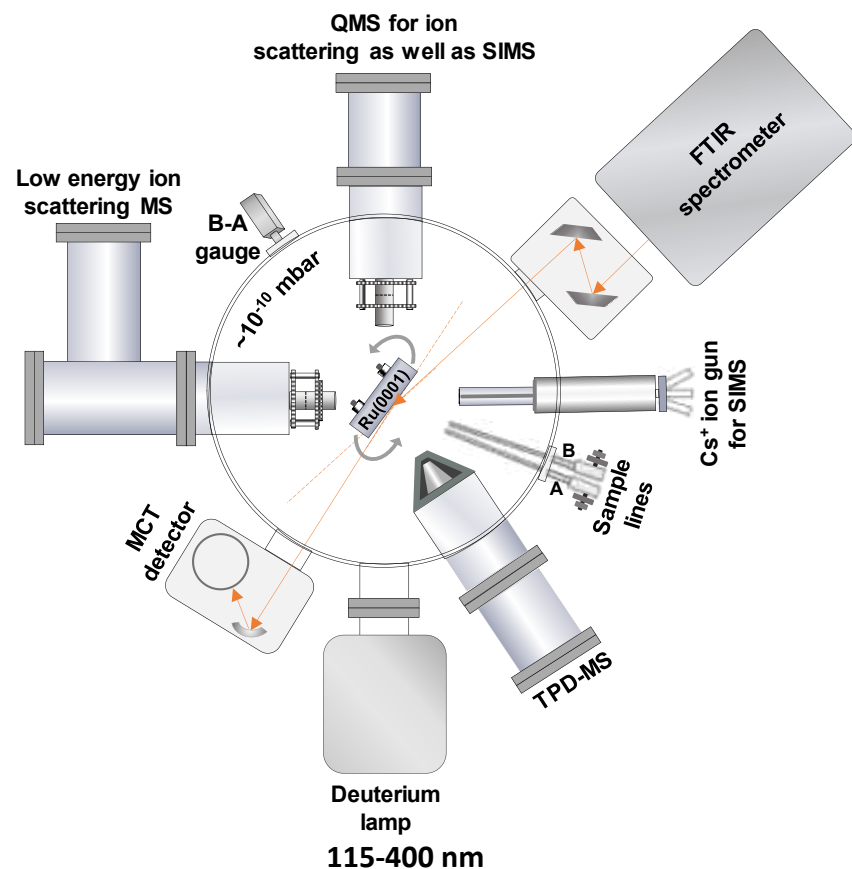
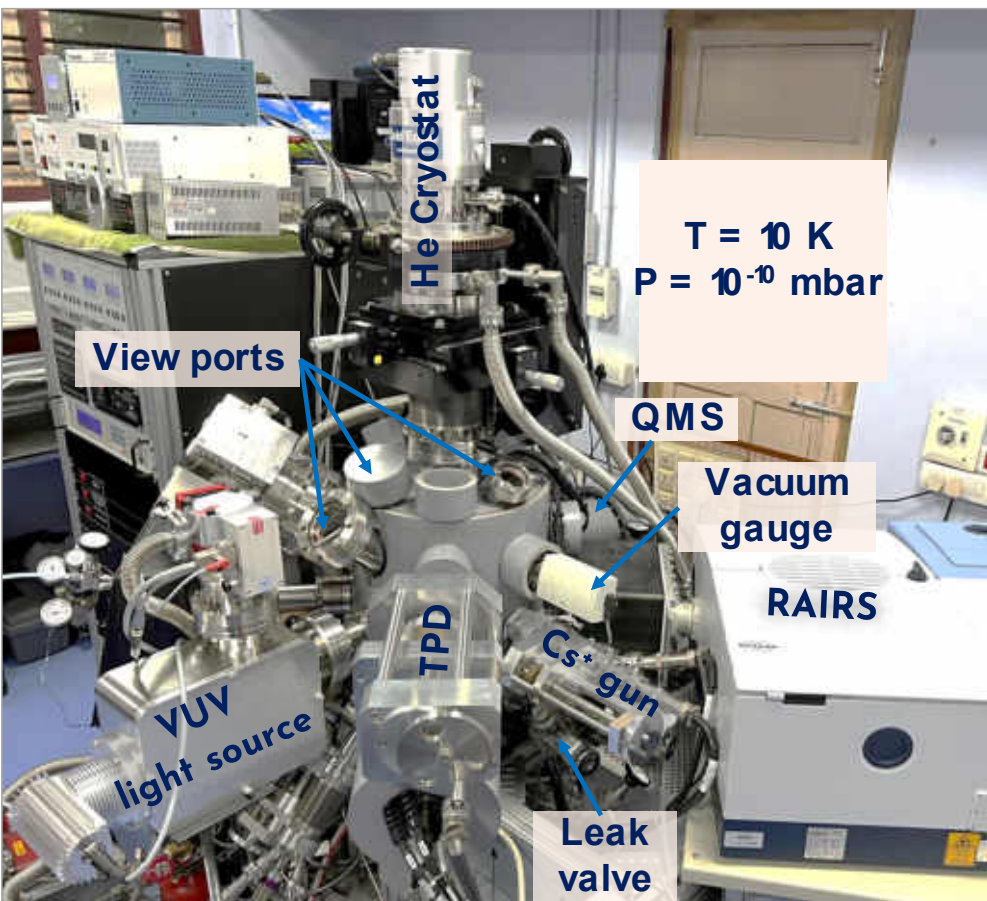
Song, G. *et al.*, *Fuel.*, **2019**, 237, 475-485

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

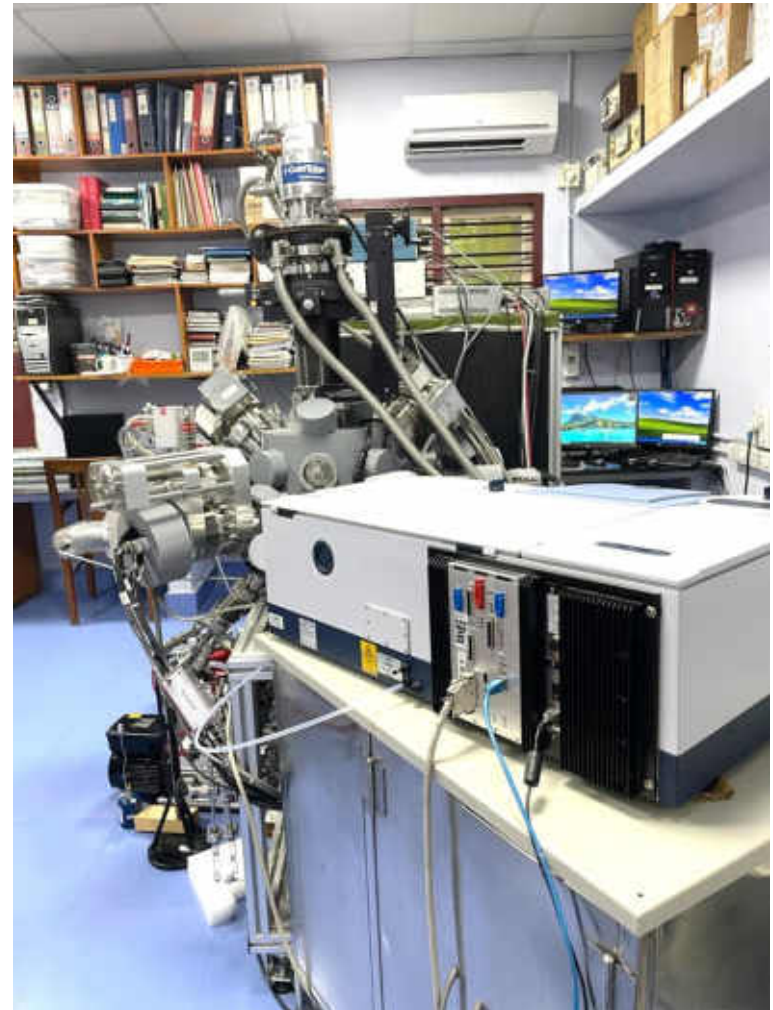
Instrumentation



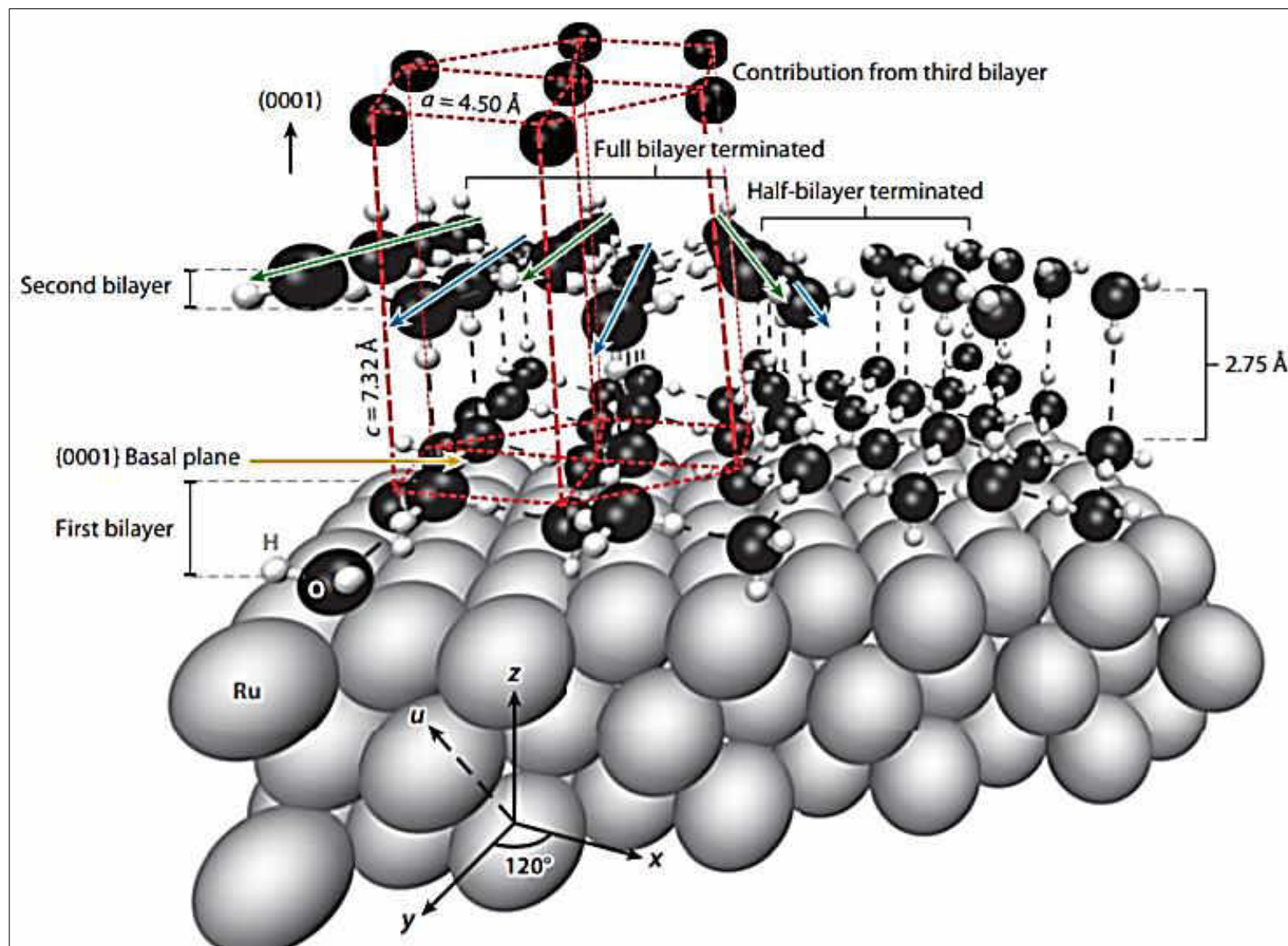
Bag, S. et al., *Rev. Sci. Instrum.* **2014**, 85, 014103/1-014103/7

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

Instrumentation



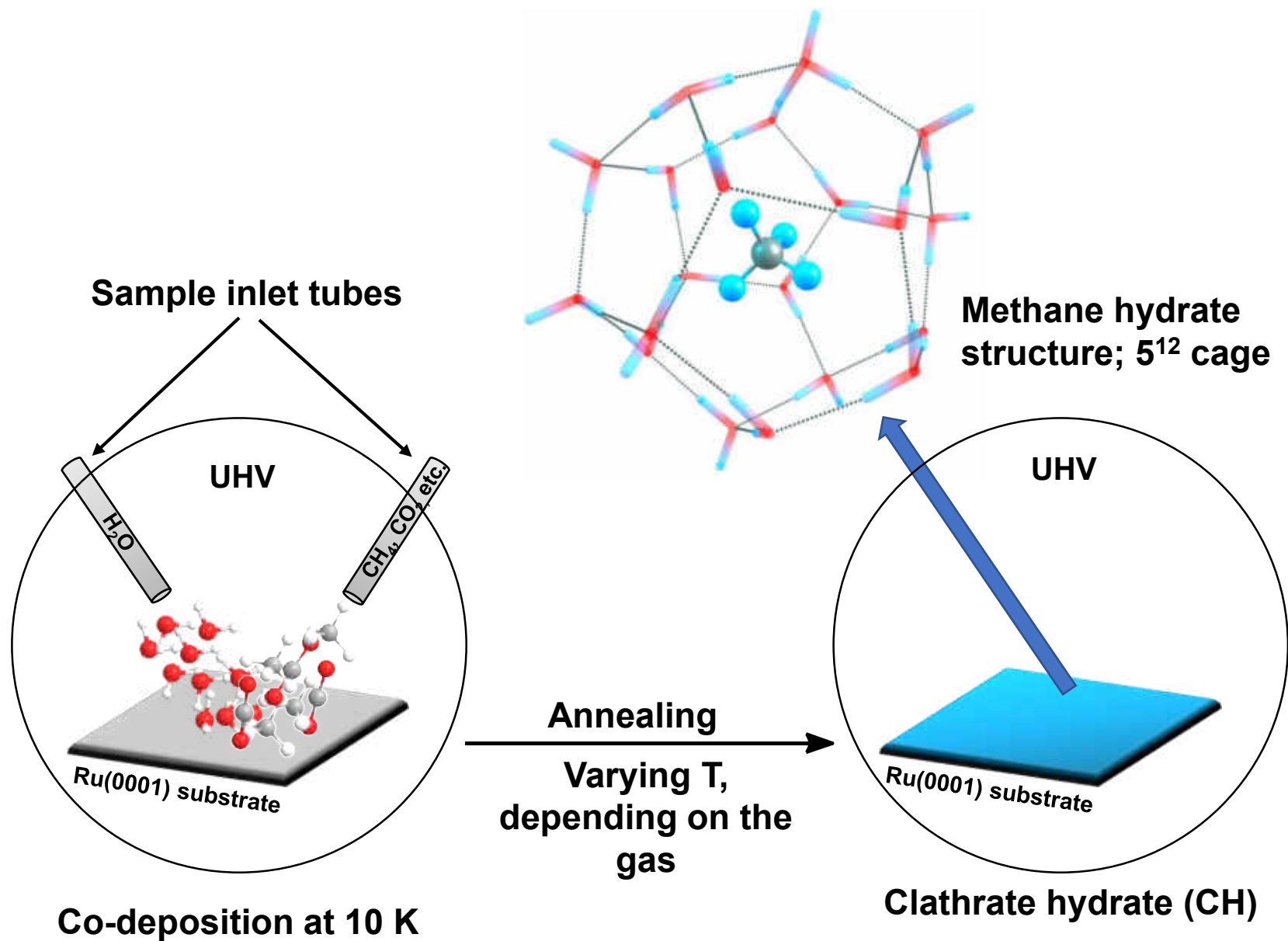
Ice instrument located in HSB-148, IIT Madras



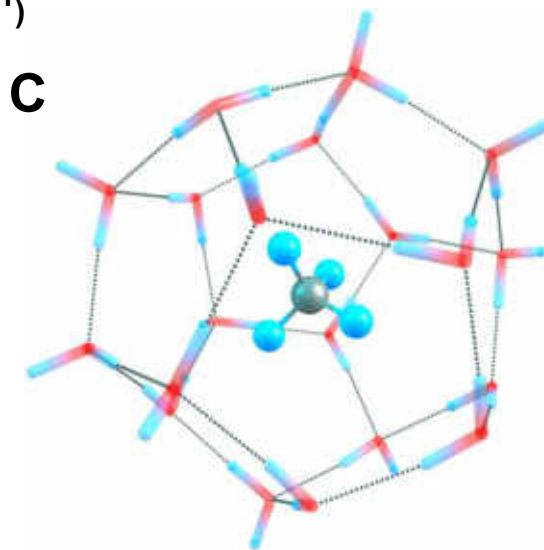
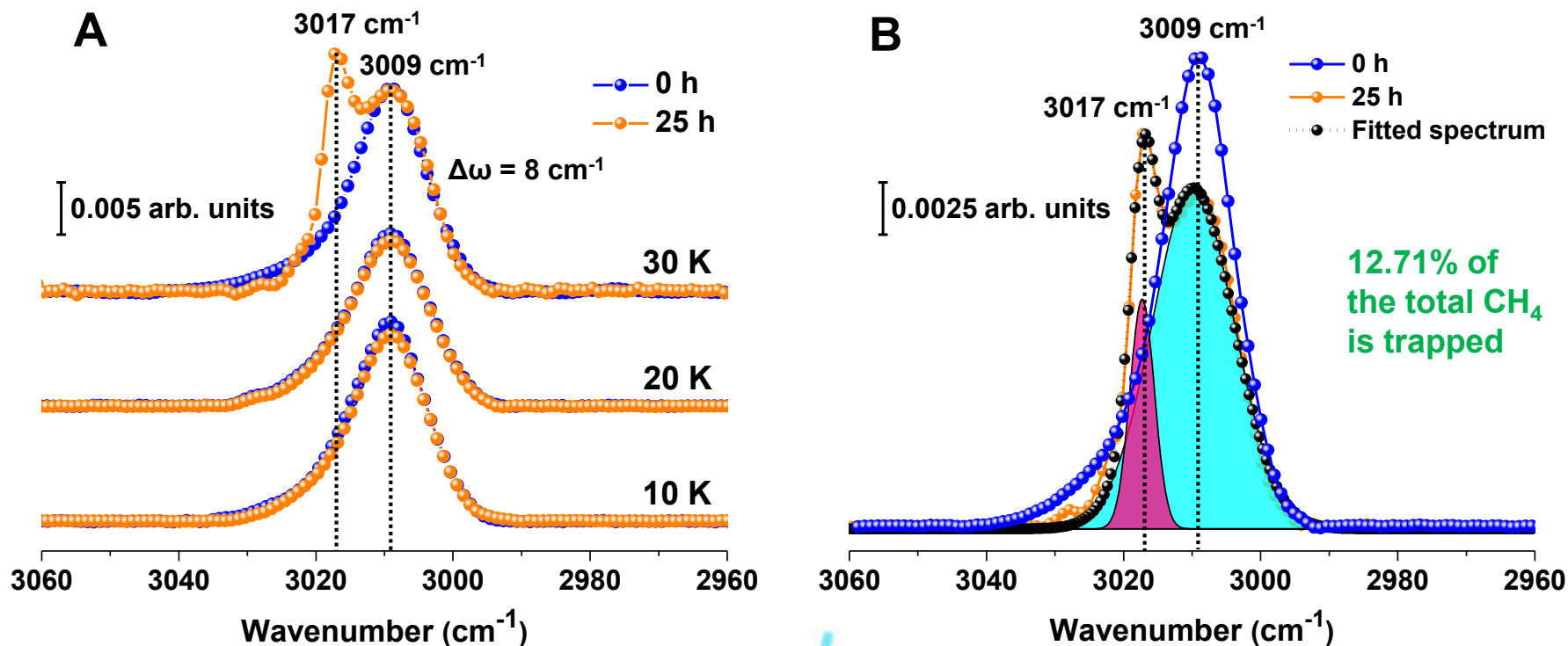
Clathrate hydrates in interstellar environment

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

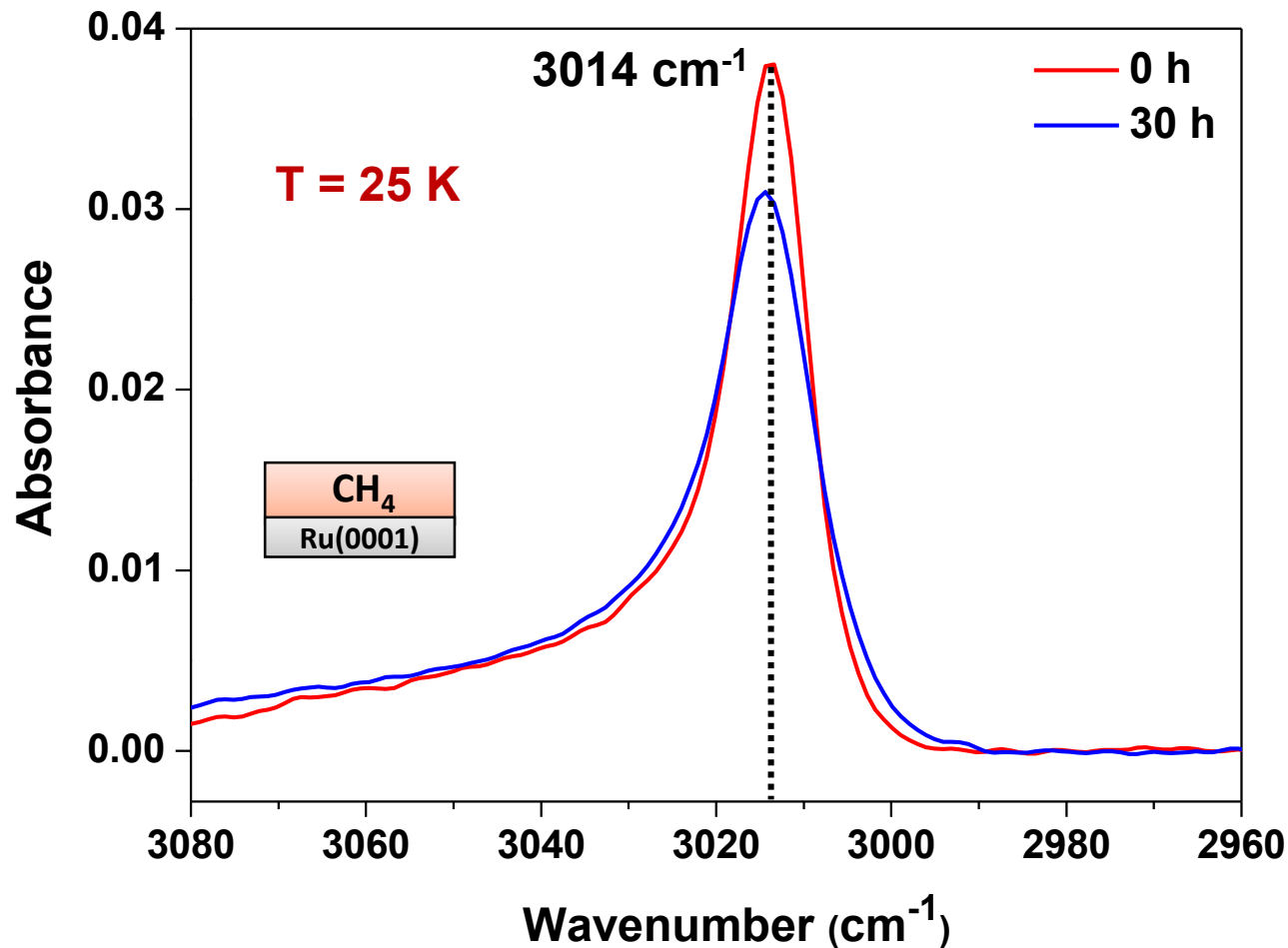
Experimental method



Clathrate hydrates in interstellar environment

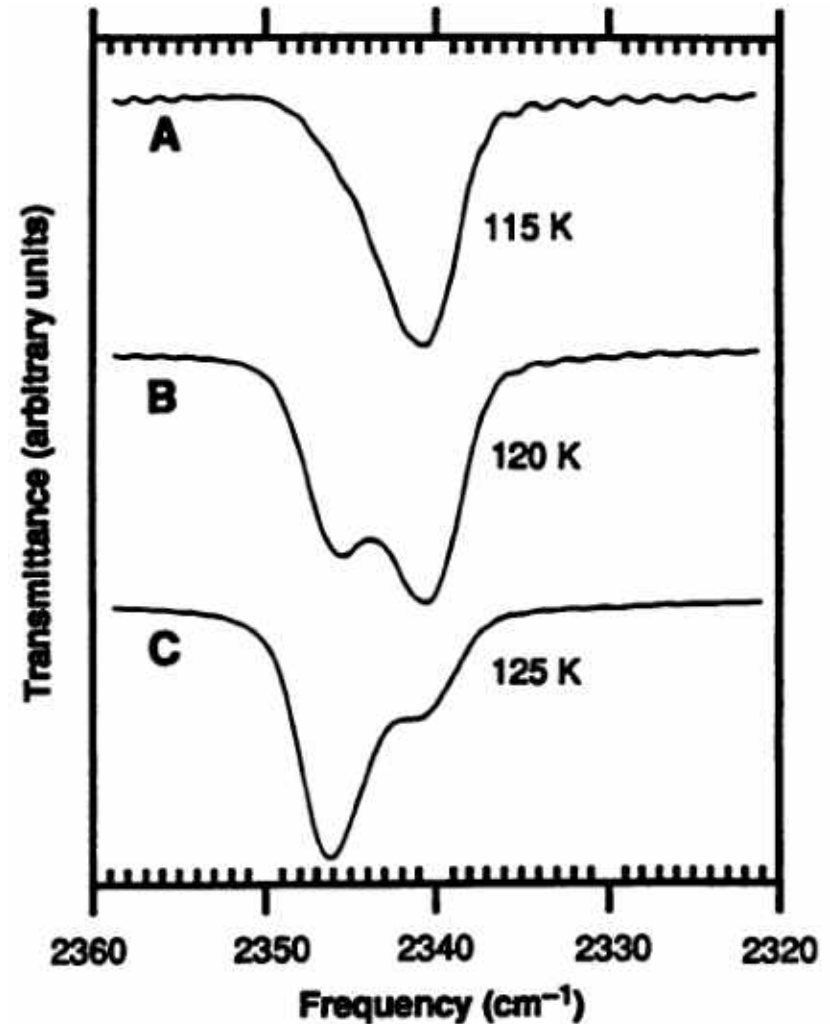
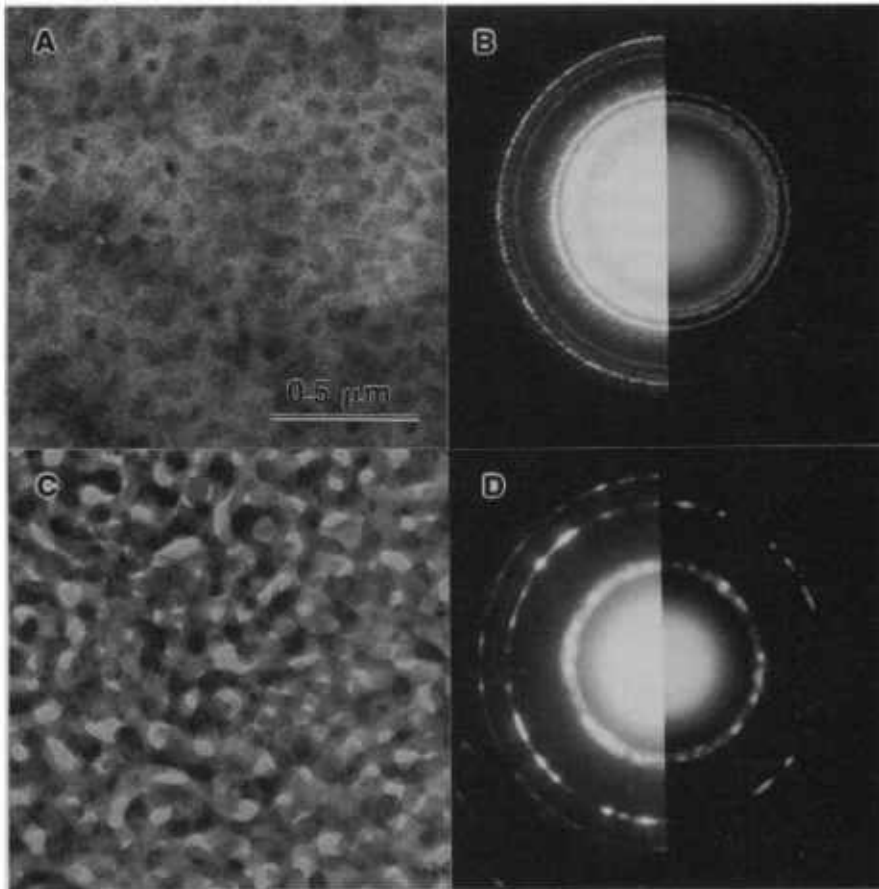


Clathrate hydrates in interstellar environment



Clathrate hydrate at low pressure

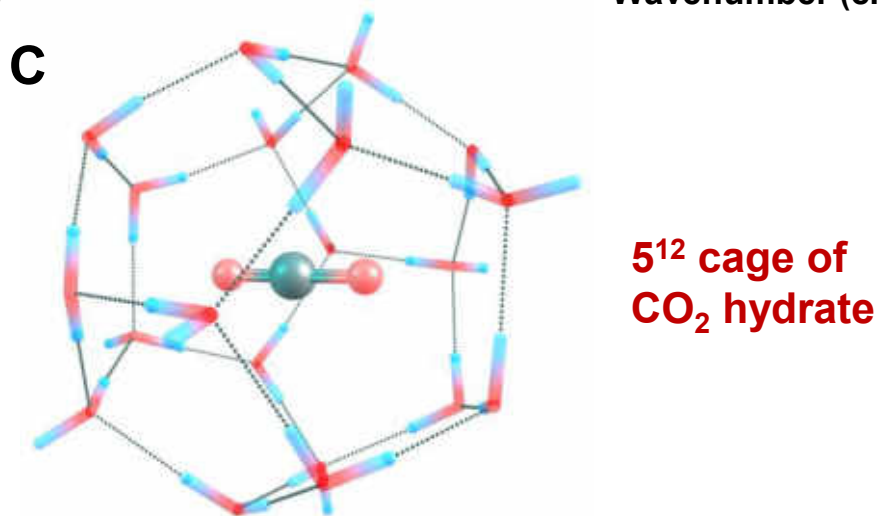
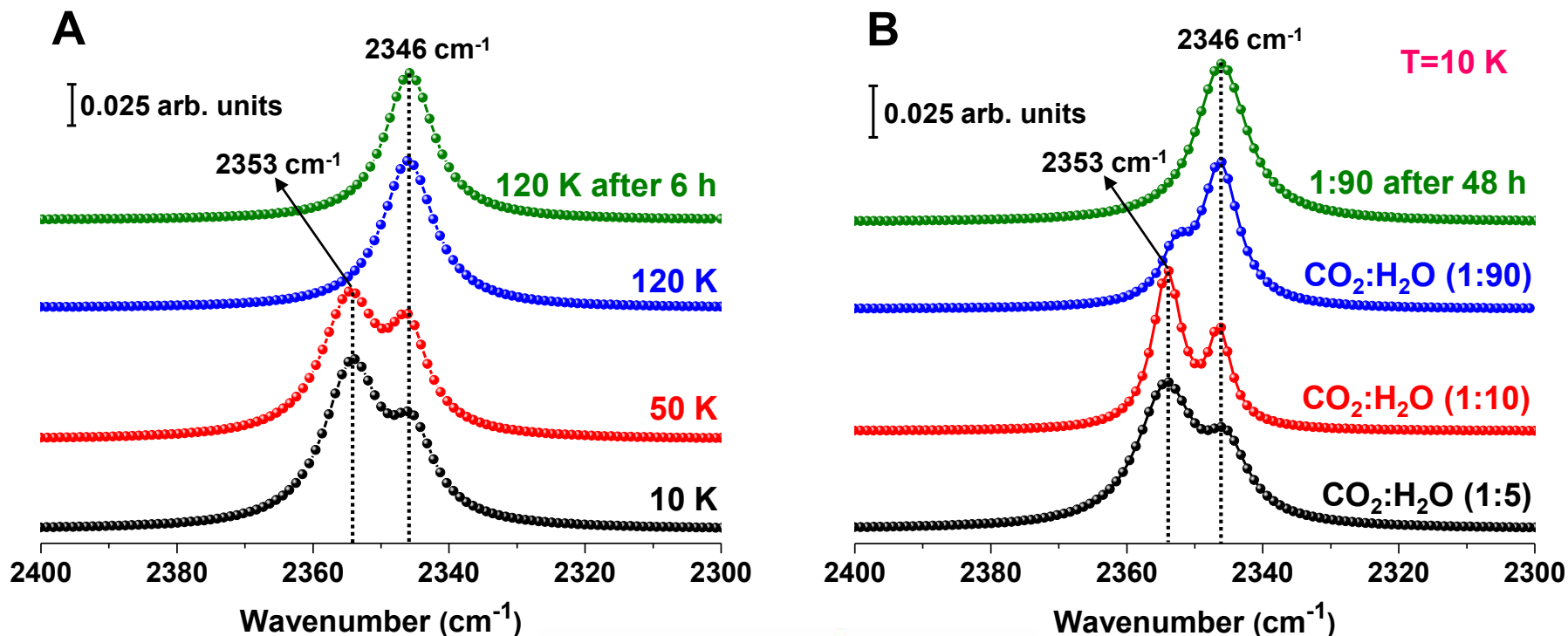
$P = 10^{-6}$ Torr



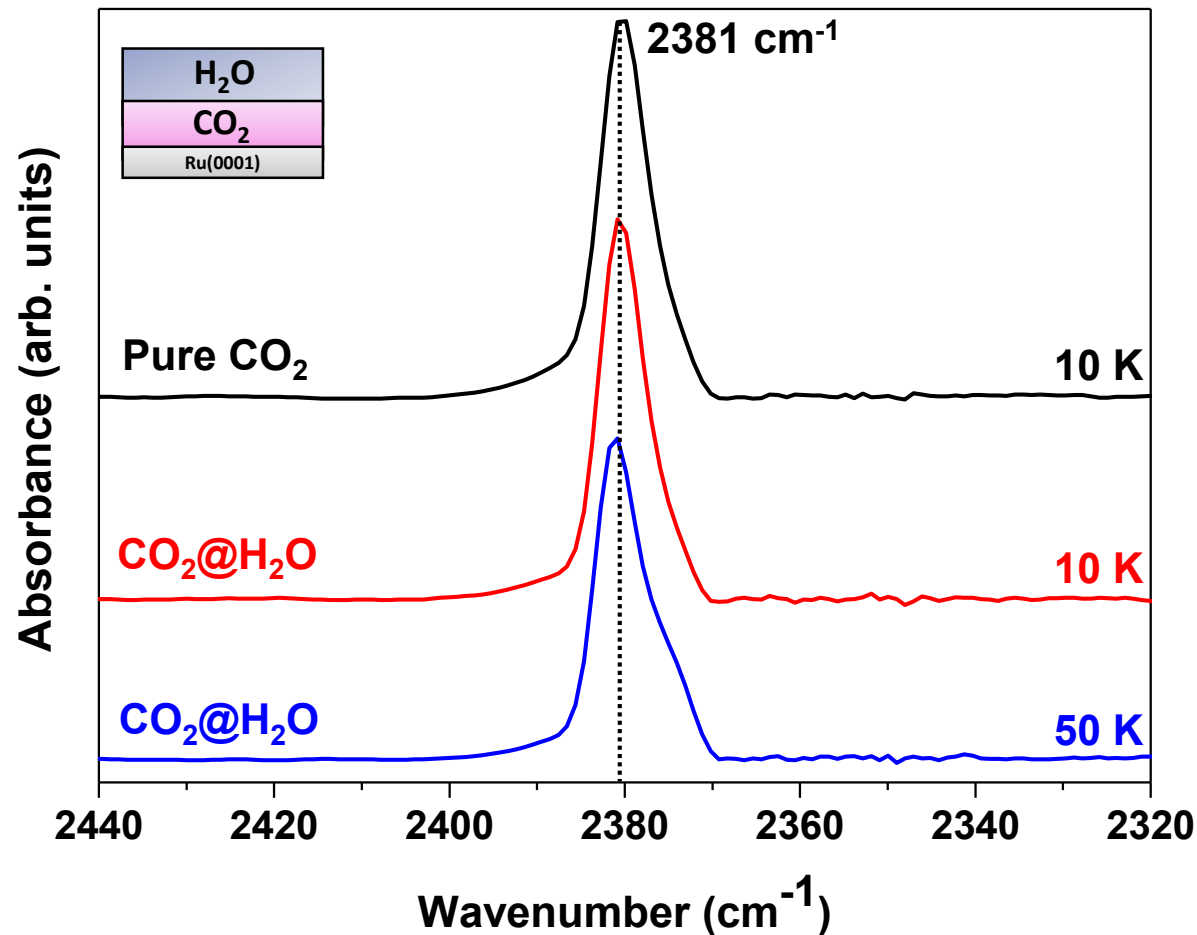
Here, CO_2 hydrate was used as a local sensitive probe towards the formation of methanol hydrate

$\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}_2 = 100:50:1$

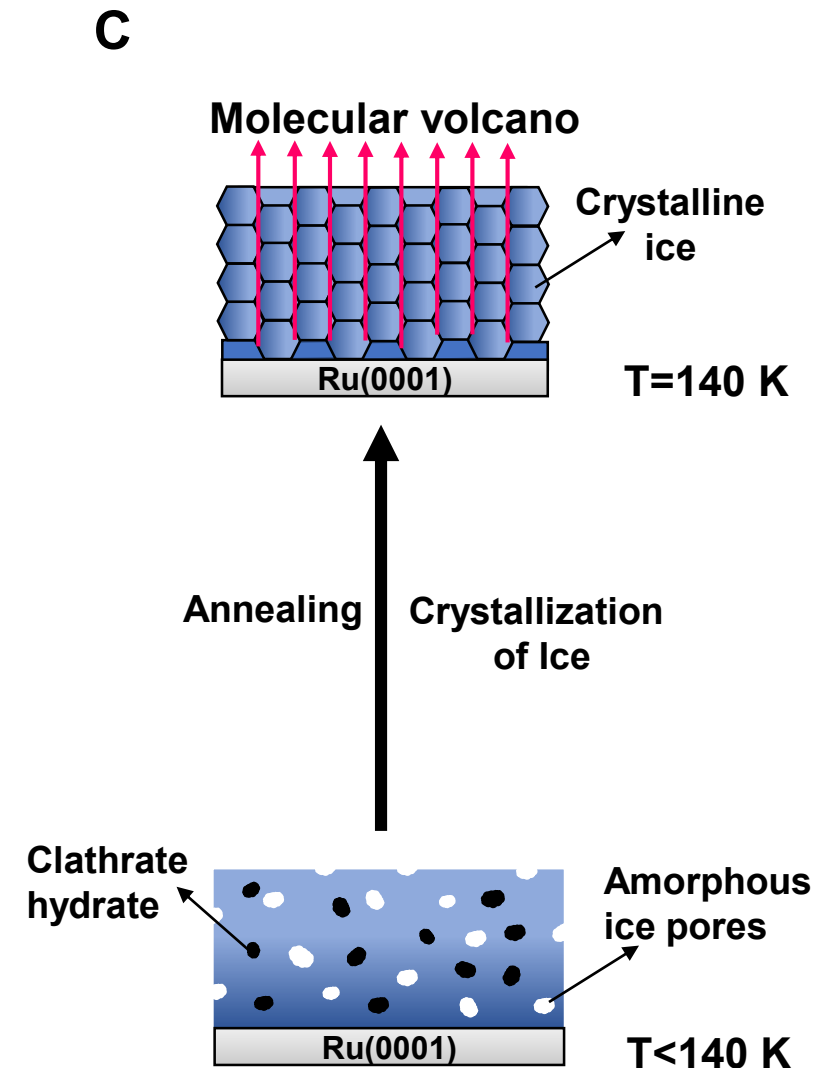
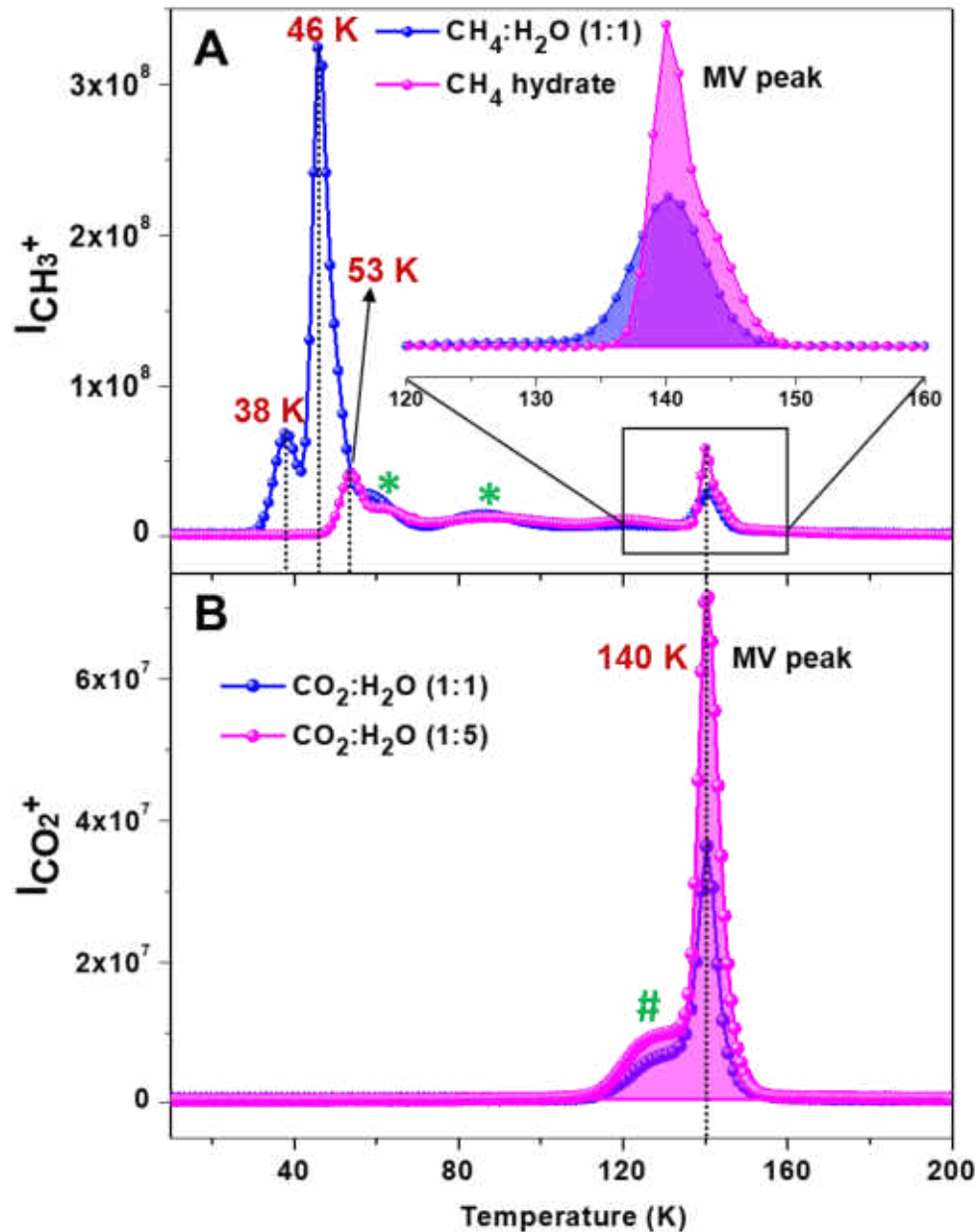
Clathrate hydrates in interstellar environment



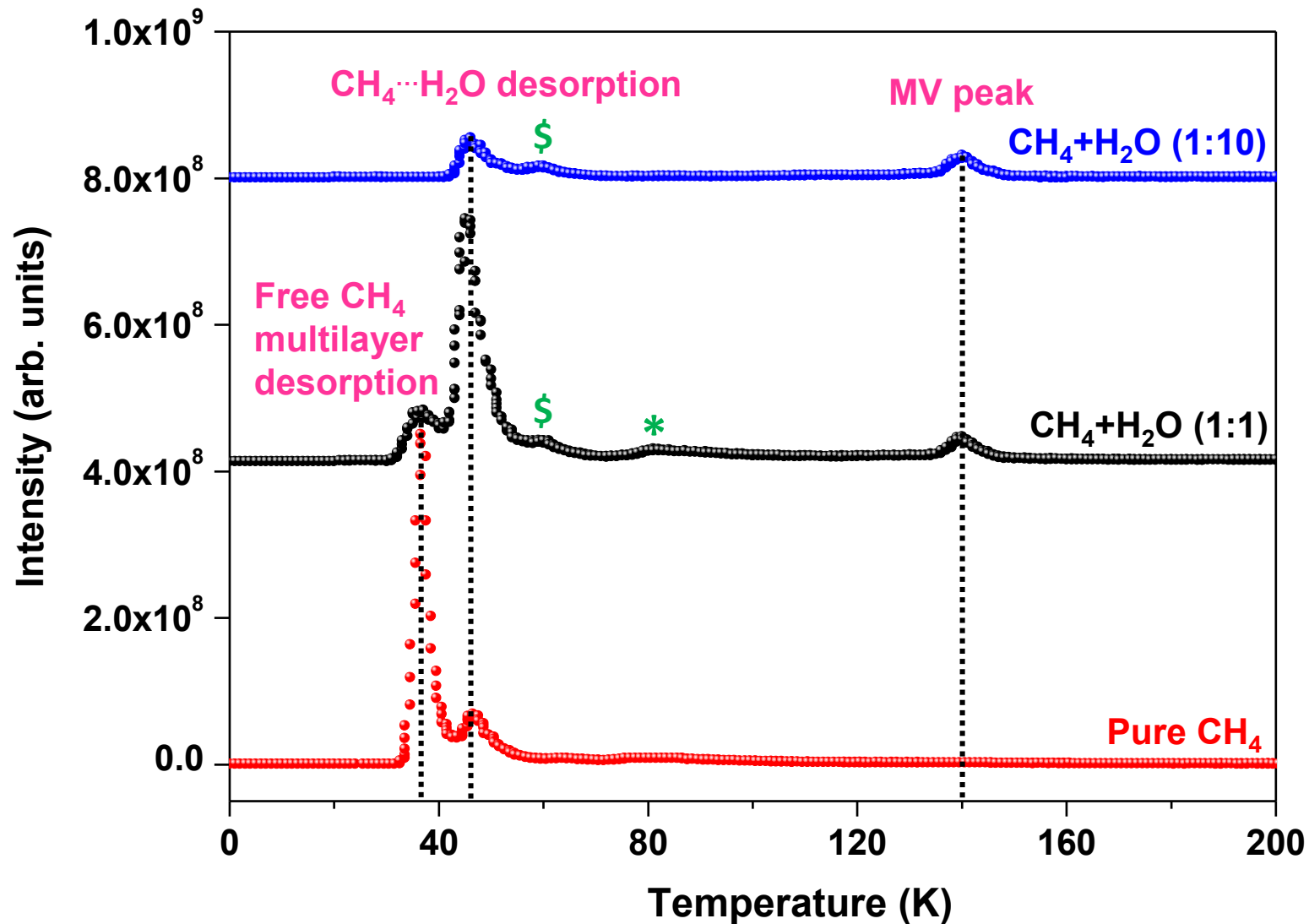
Clathrate hydrates in interstellar environment



Clathrate hydrates in interstellar environment



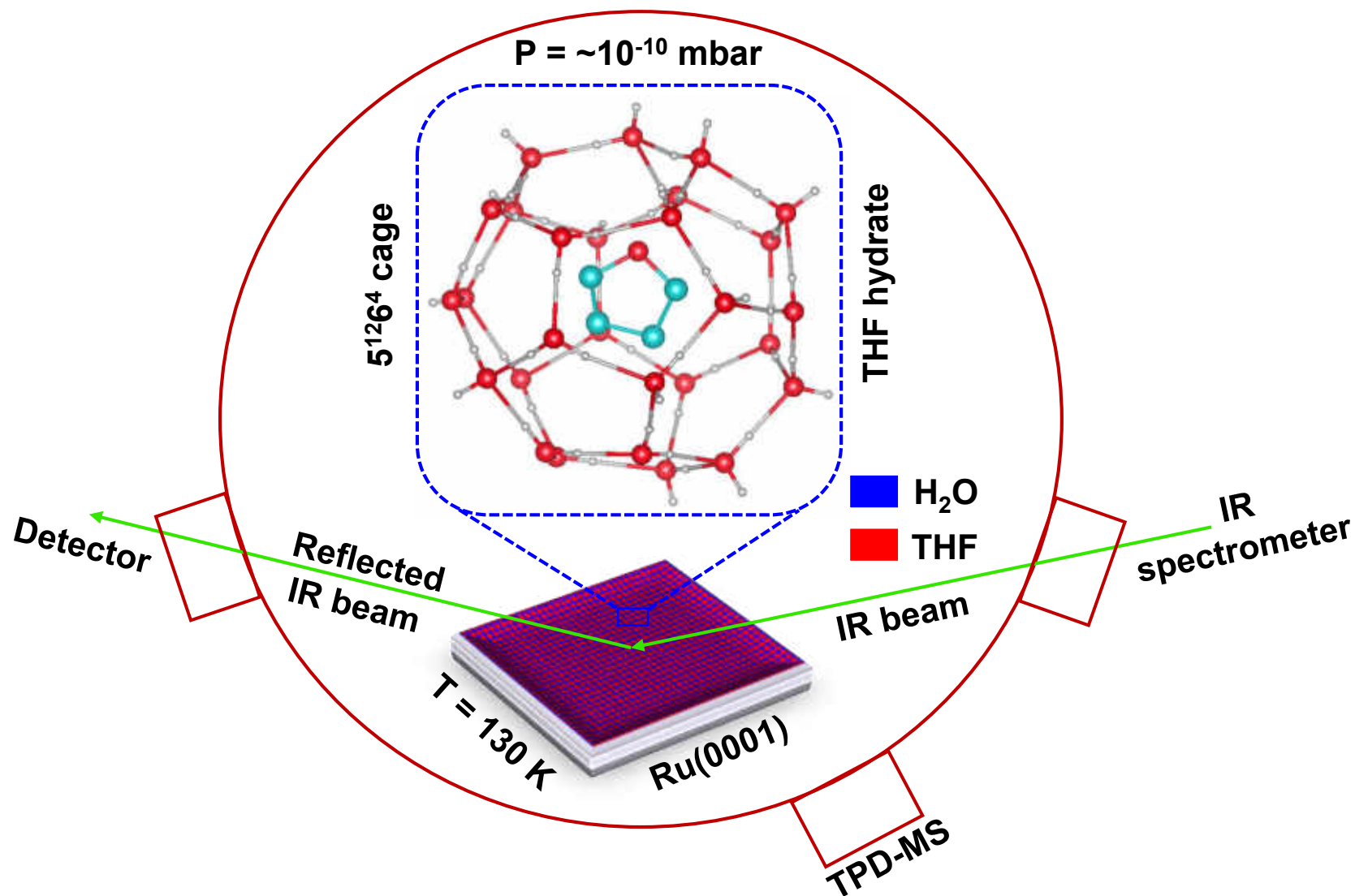
Clathrate hydrates in interstellar environment



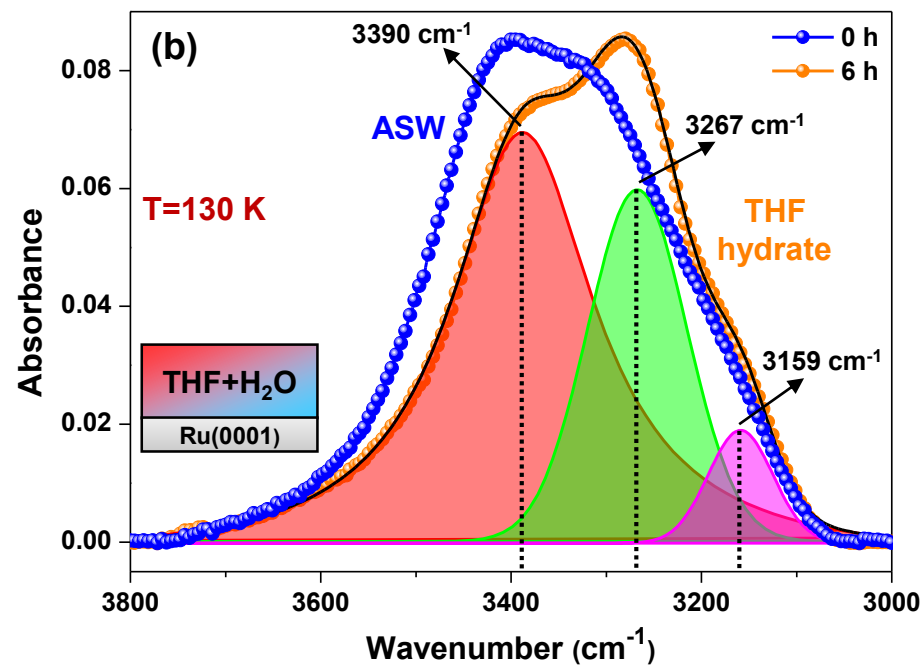
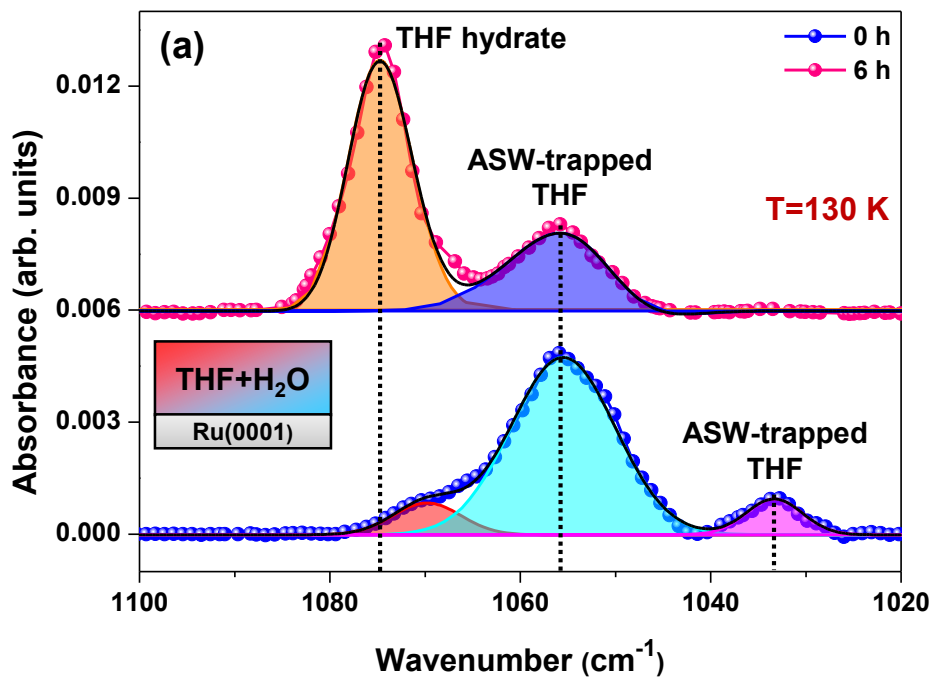
Spontaneous formation of tetrahydrofuran hydrate in ultrahigh vacuum

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

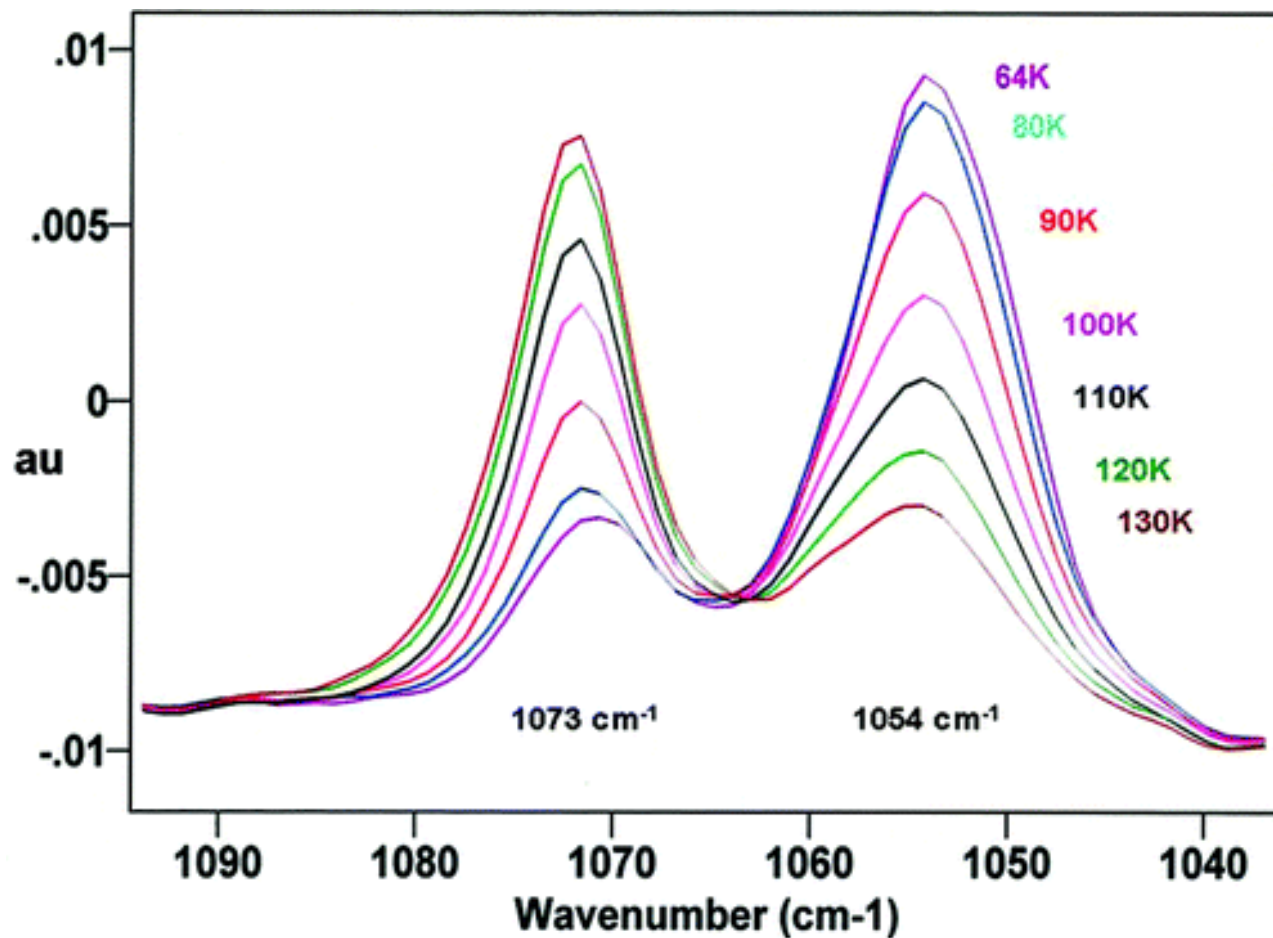
Formation of THF hydrate in UHV



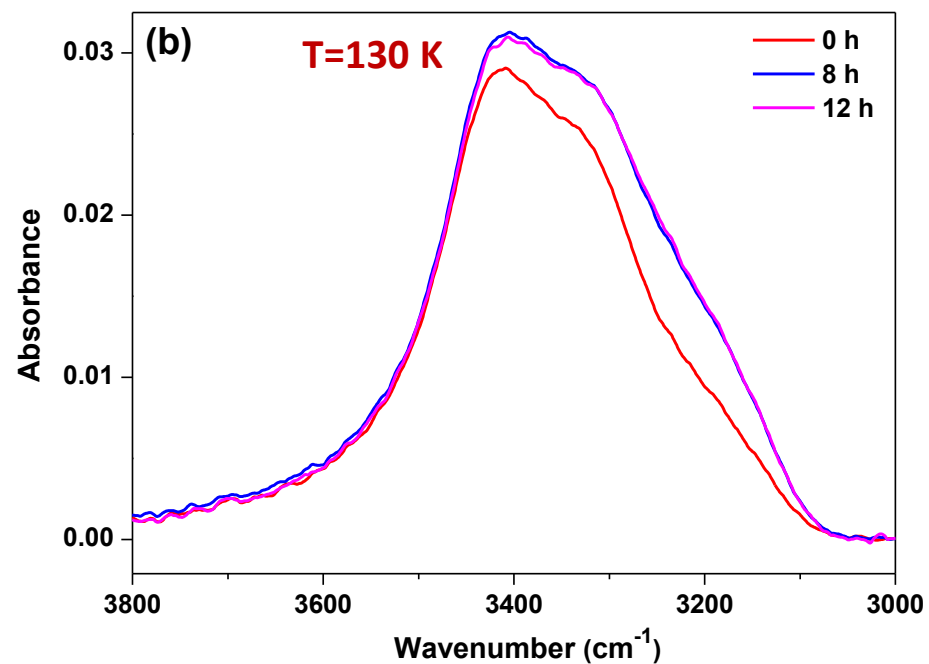
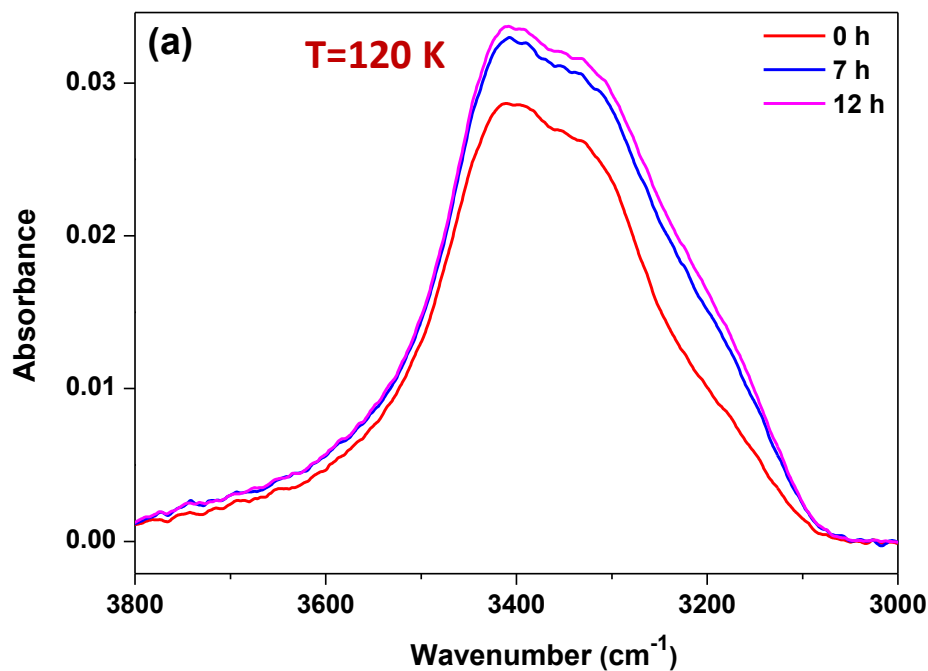
Formation of THF hydrate in UHV



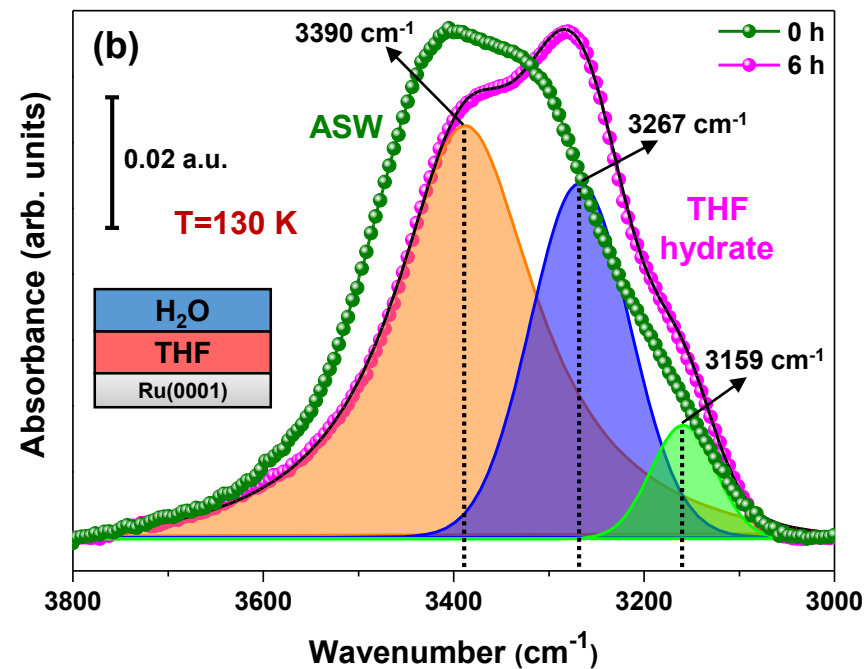
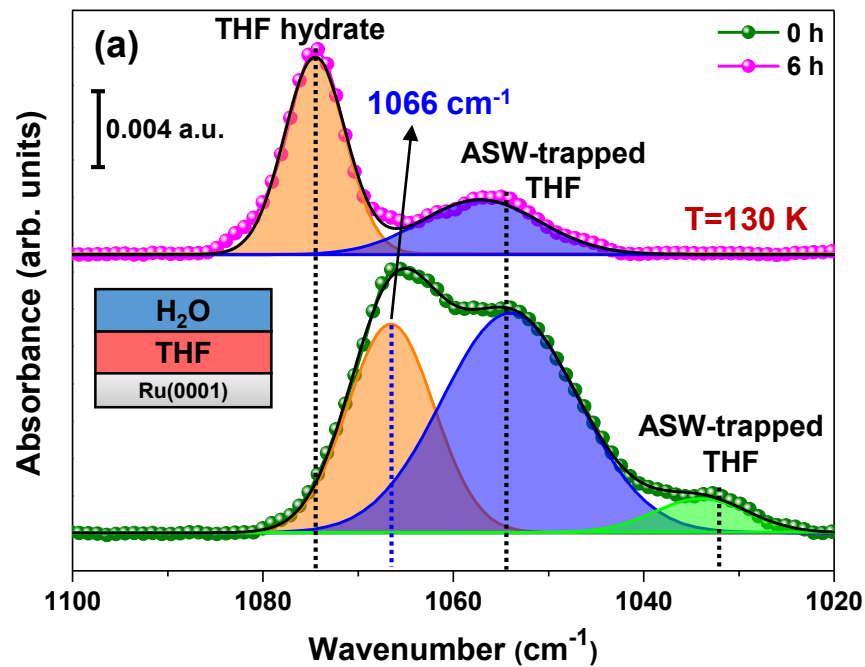
Formation of THF hydrate



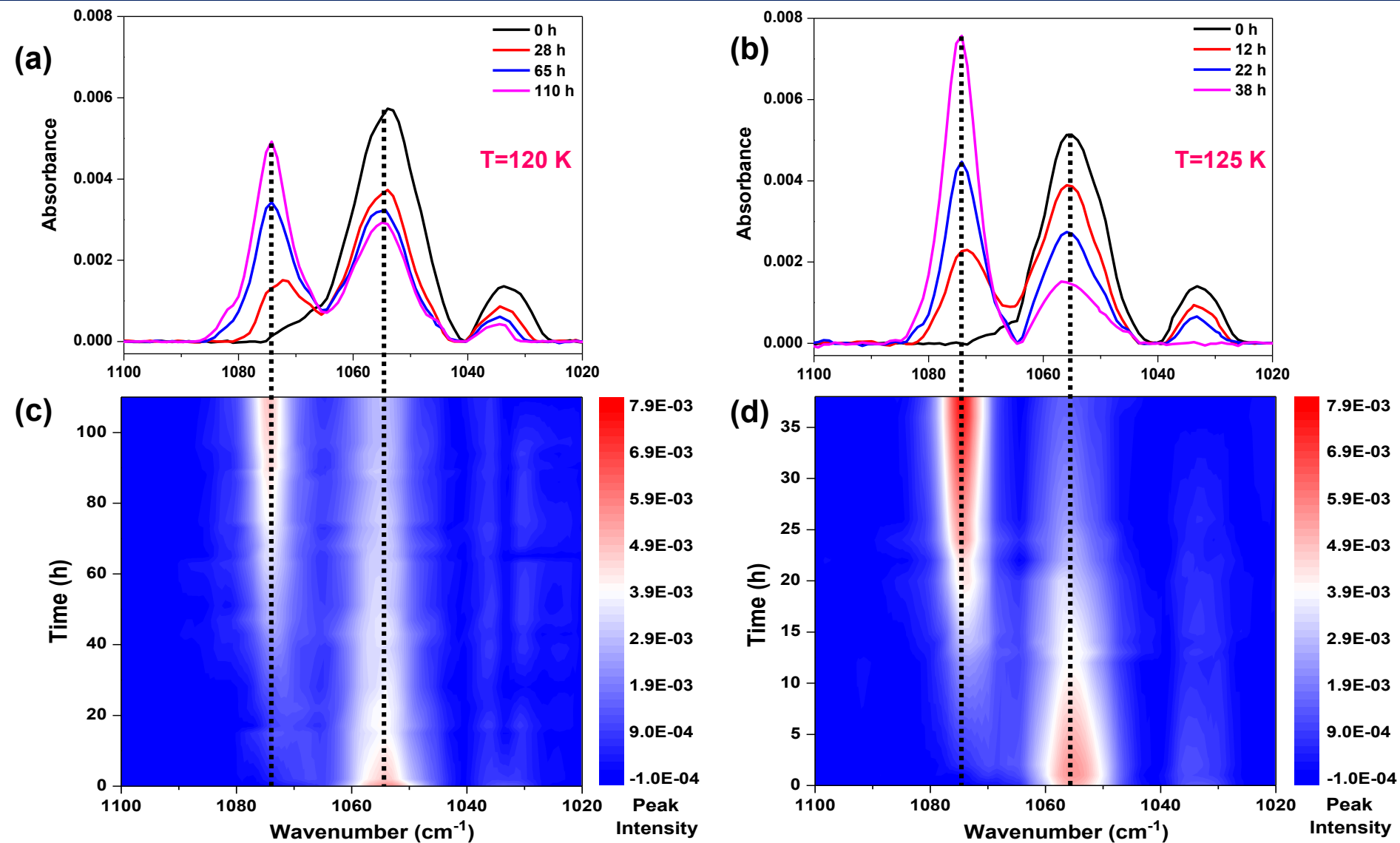
Formation of THF hydrate in UHV



Formation of THF hydrate in UHV



Formation of THF hydrate in UHV



Formation of THF hydrate in UHV

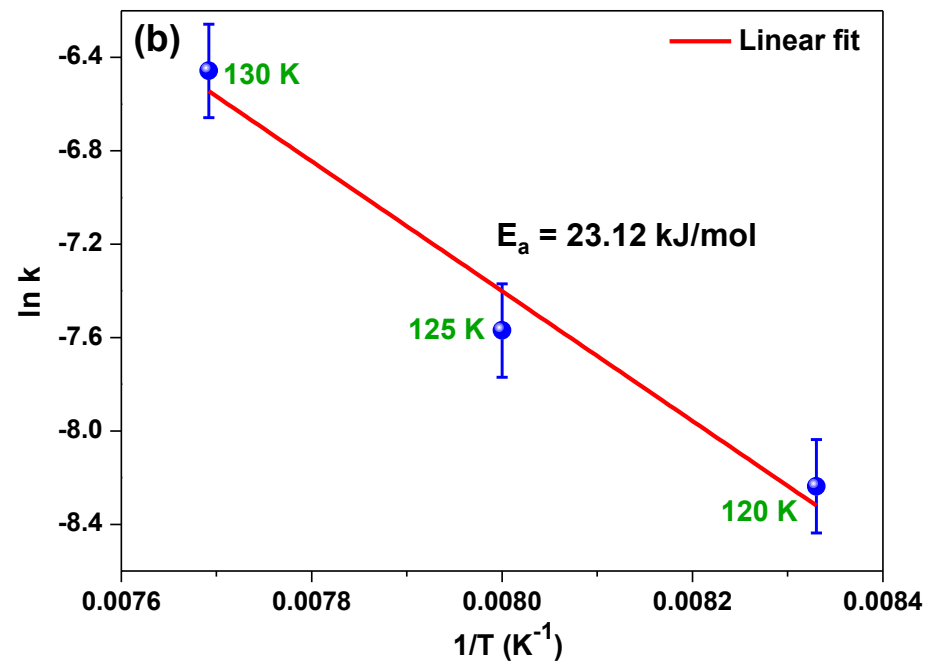
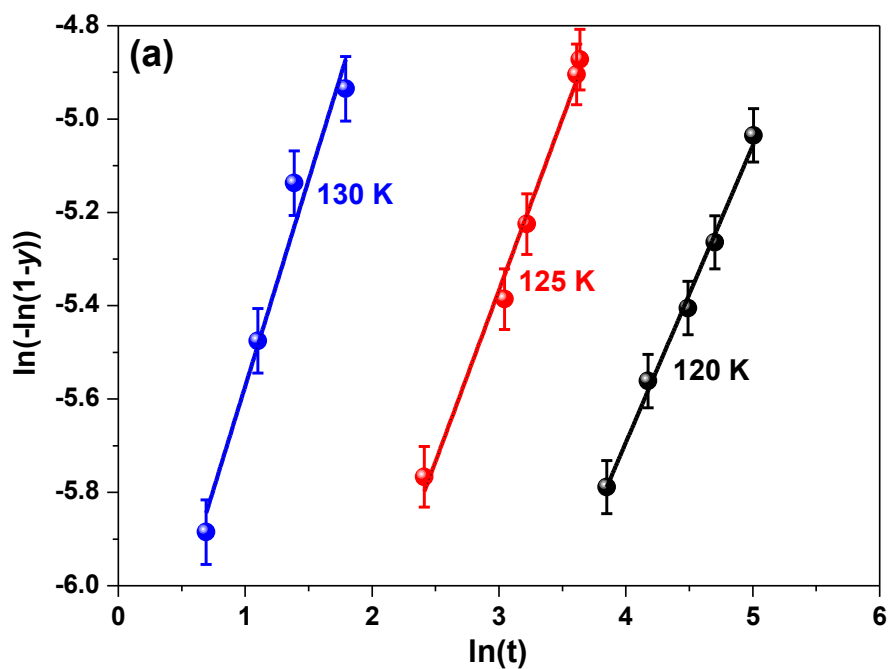
Avrami equation,

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

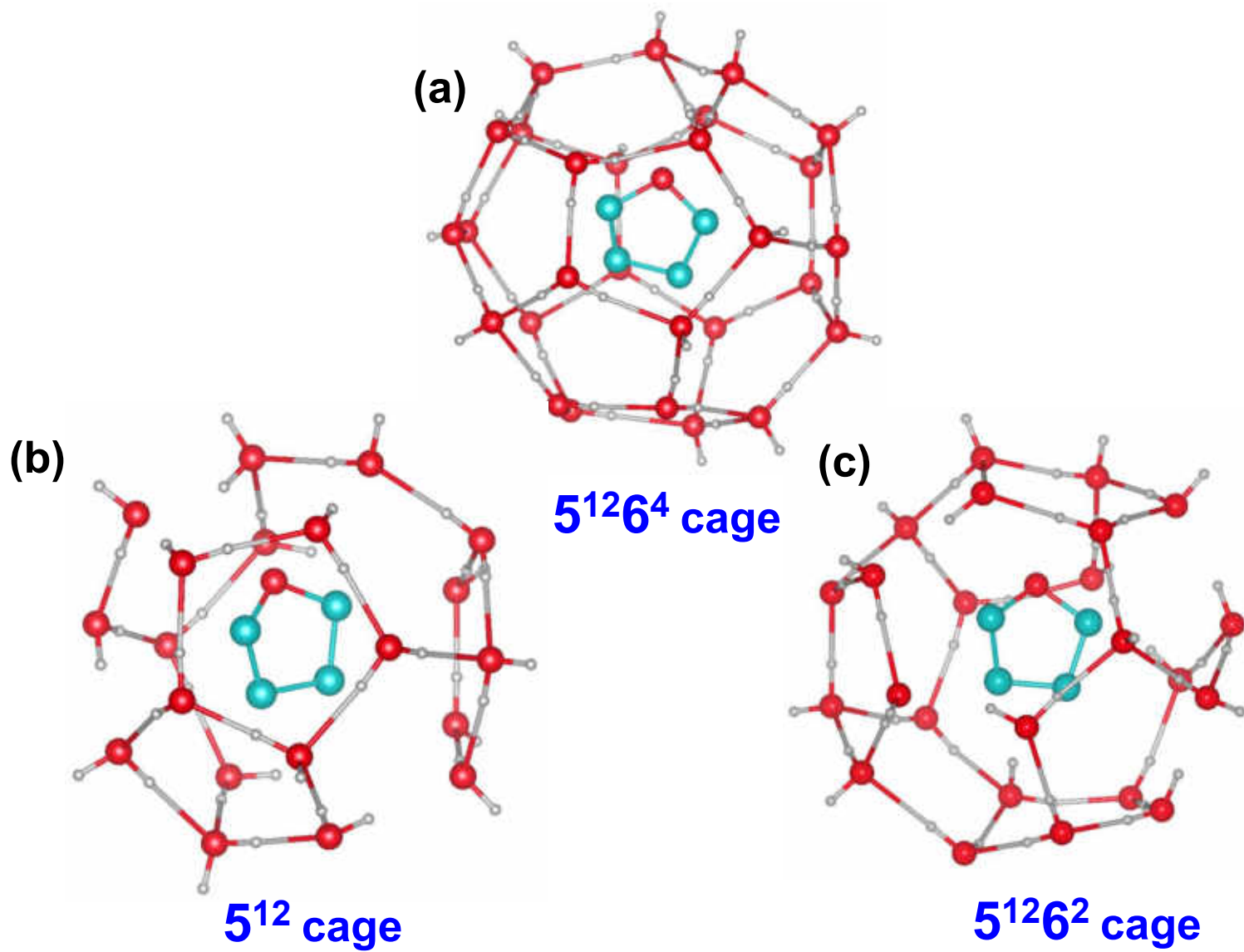
$$\ln (-\ln [1 - y(T)]) = n \ln (t) + n \ln k(T)$$

Arrhenius equation,

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



Formation of THF hydrate in UHV



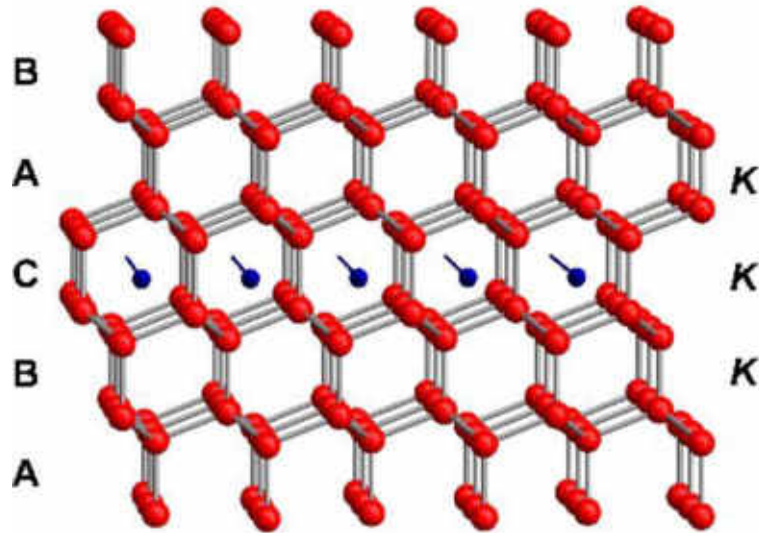
Many hydrates

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

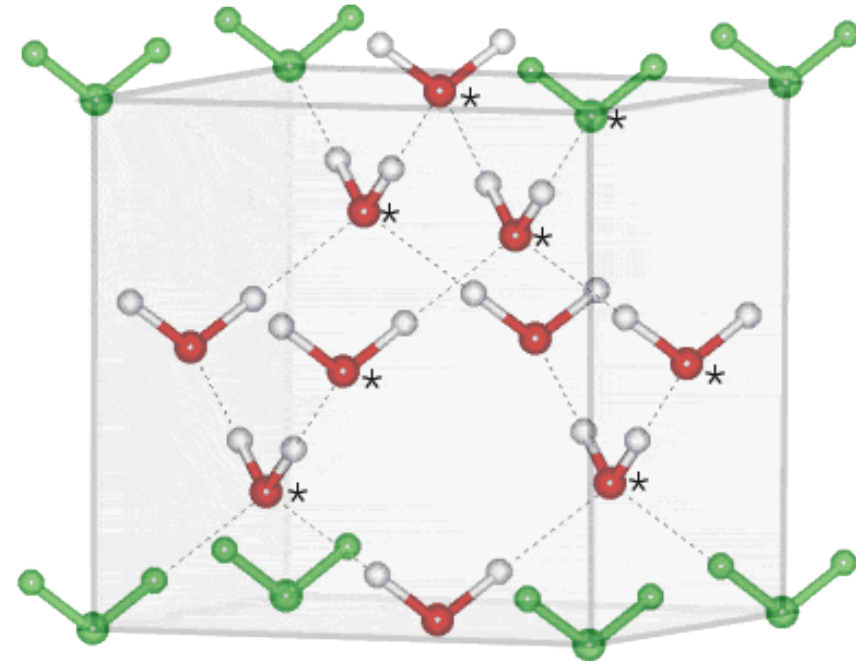
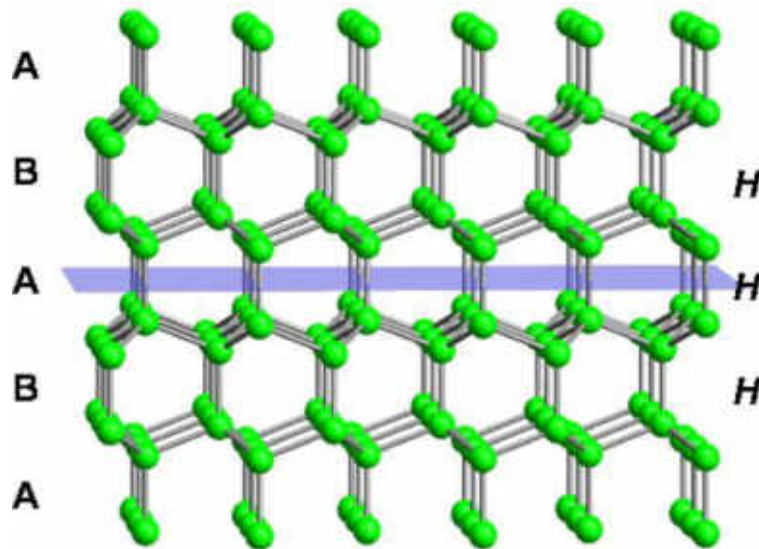
Ghosh, J. et al., *J. Phys. Chem. Lett.* **2020**, 11, 26-32

Structure of cubic ice

Ice I_c



Ice I_h



Unit cell of cubic ice

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

Cubic ice via clathrate hydrate

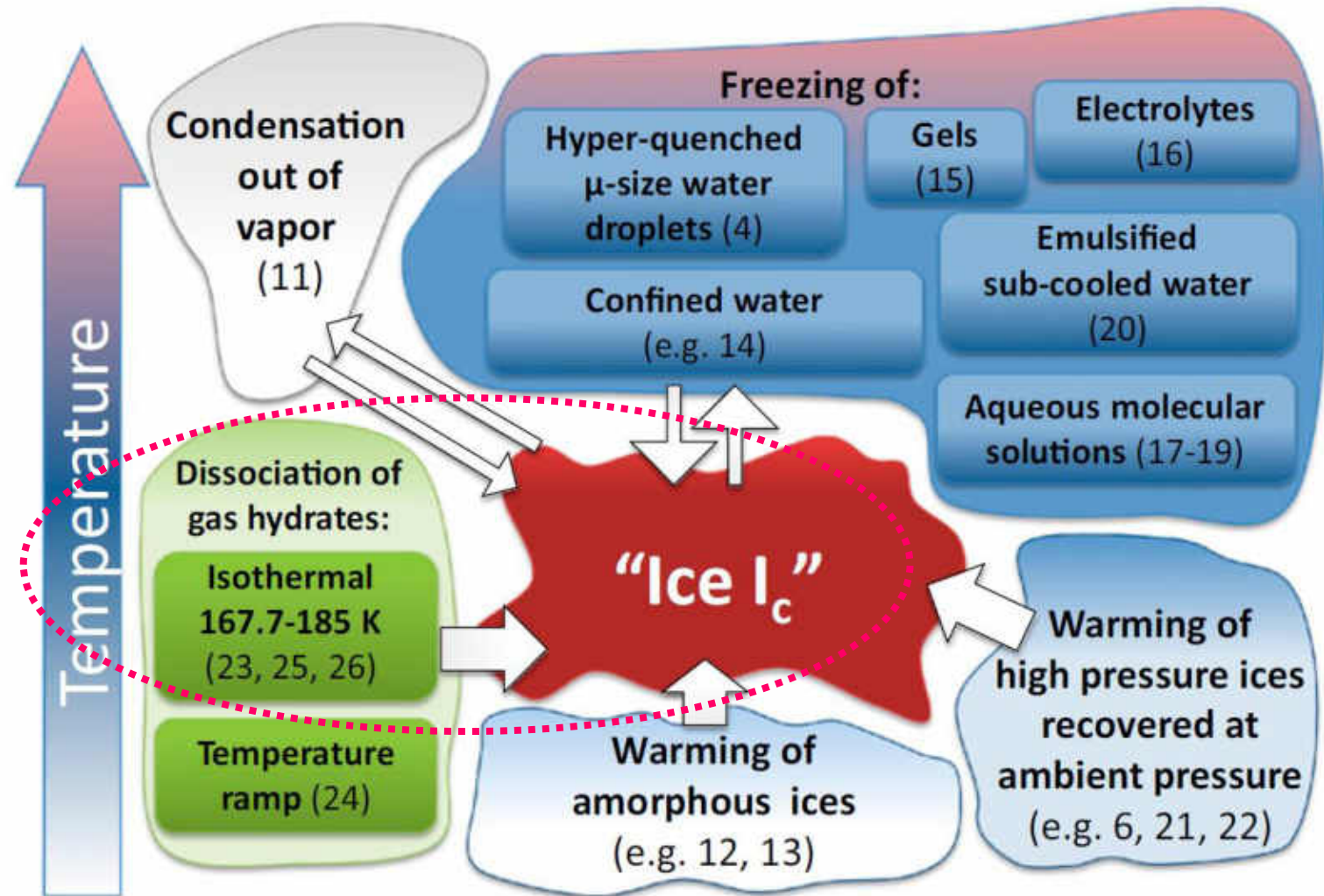
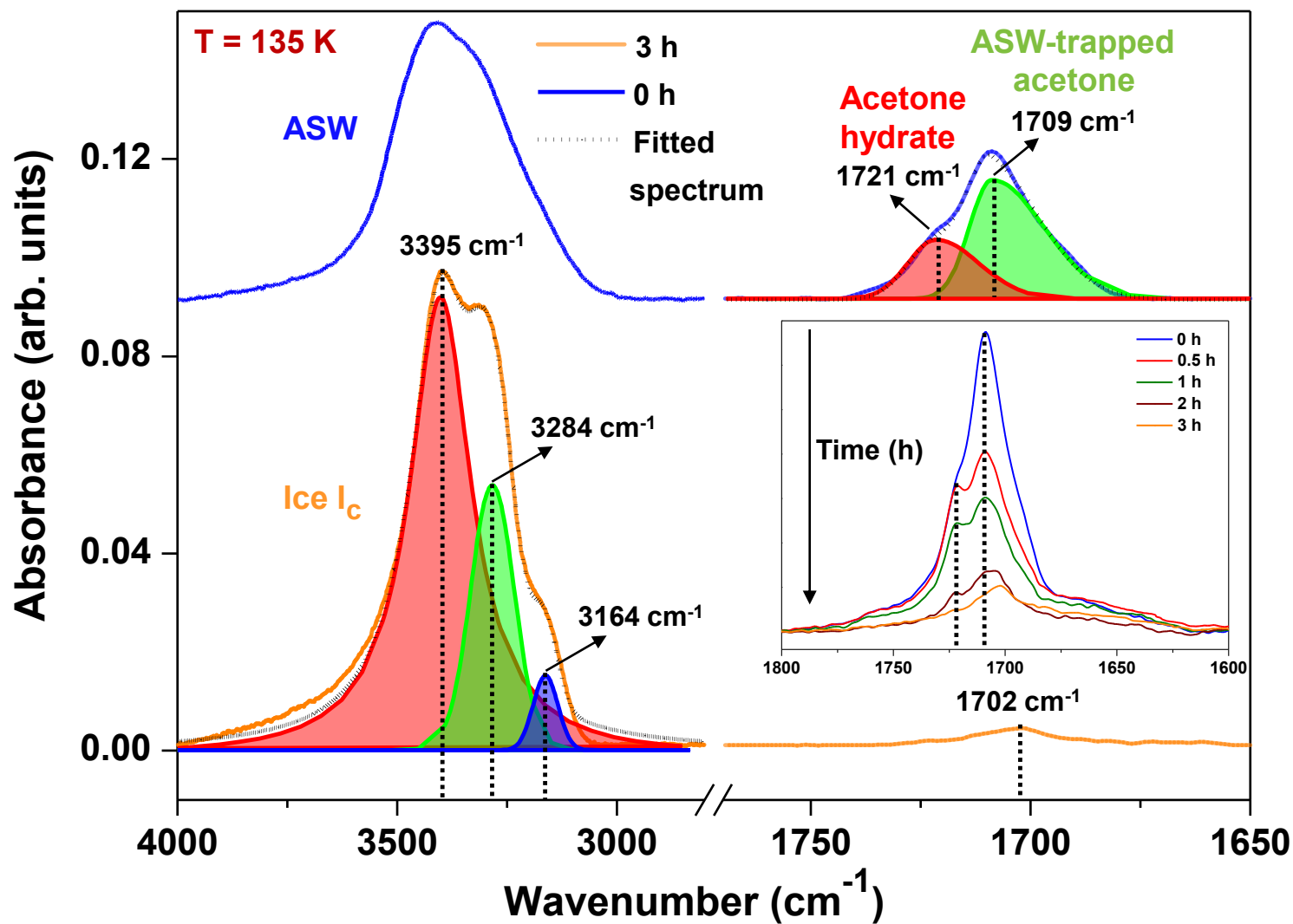


Fig. 2. Main established routes of forming "ice I_c".

Cubic ice via clathrate hydrate



Diffraction pattern of cubic ice

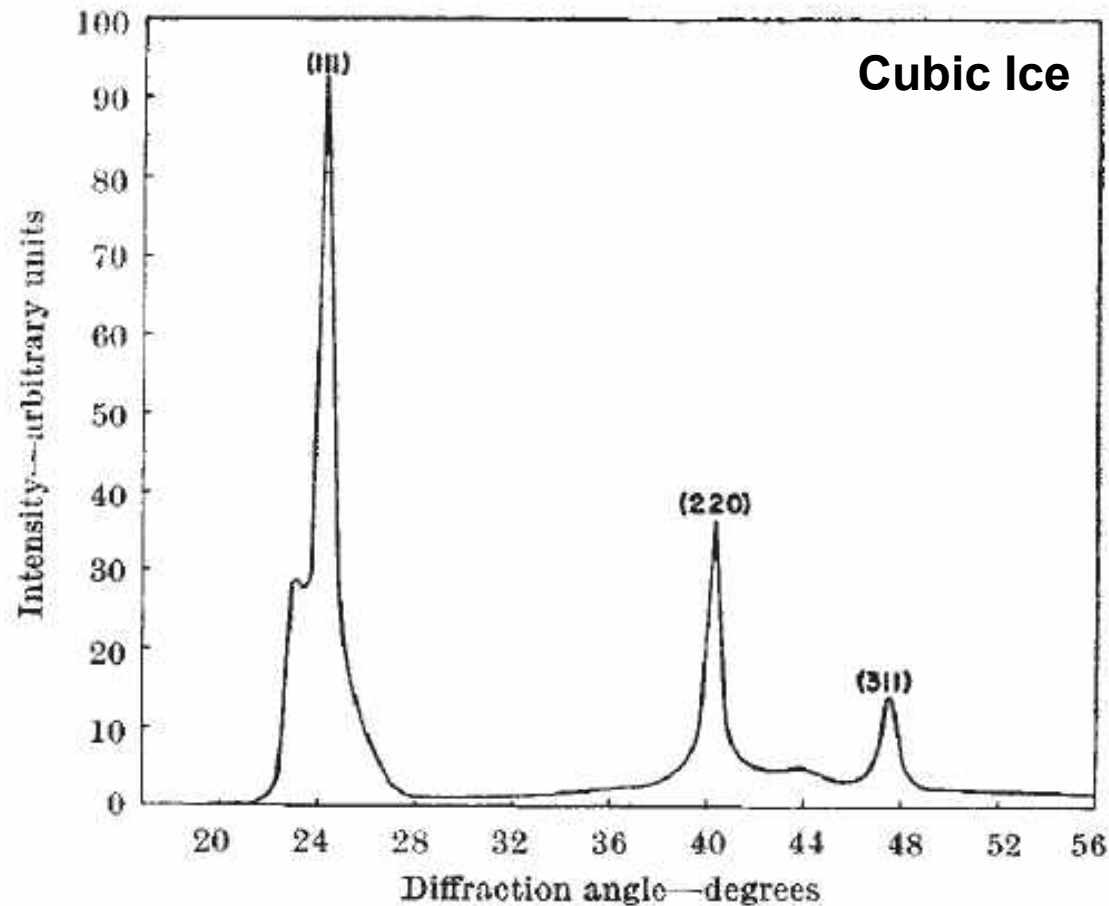
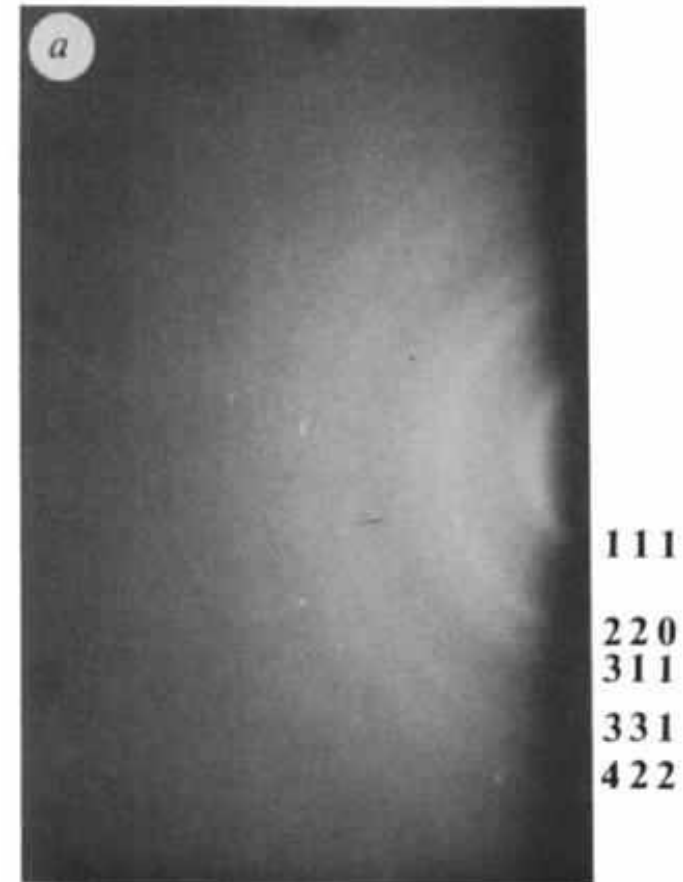


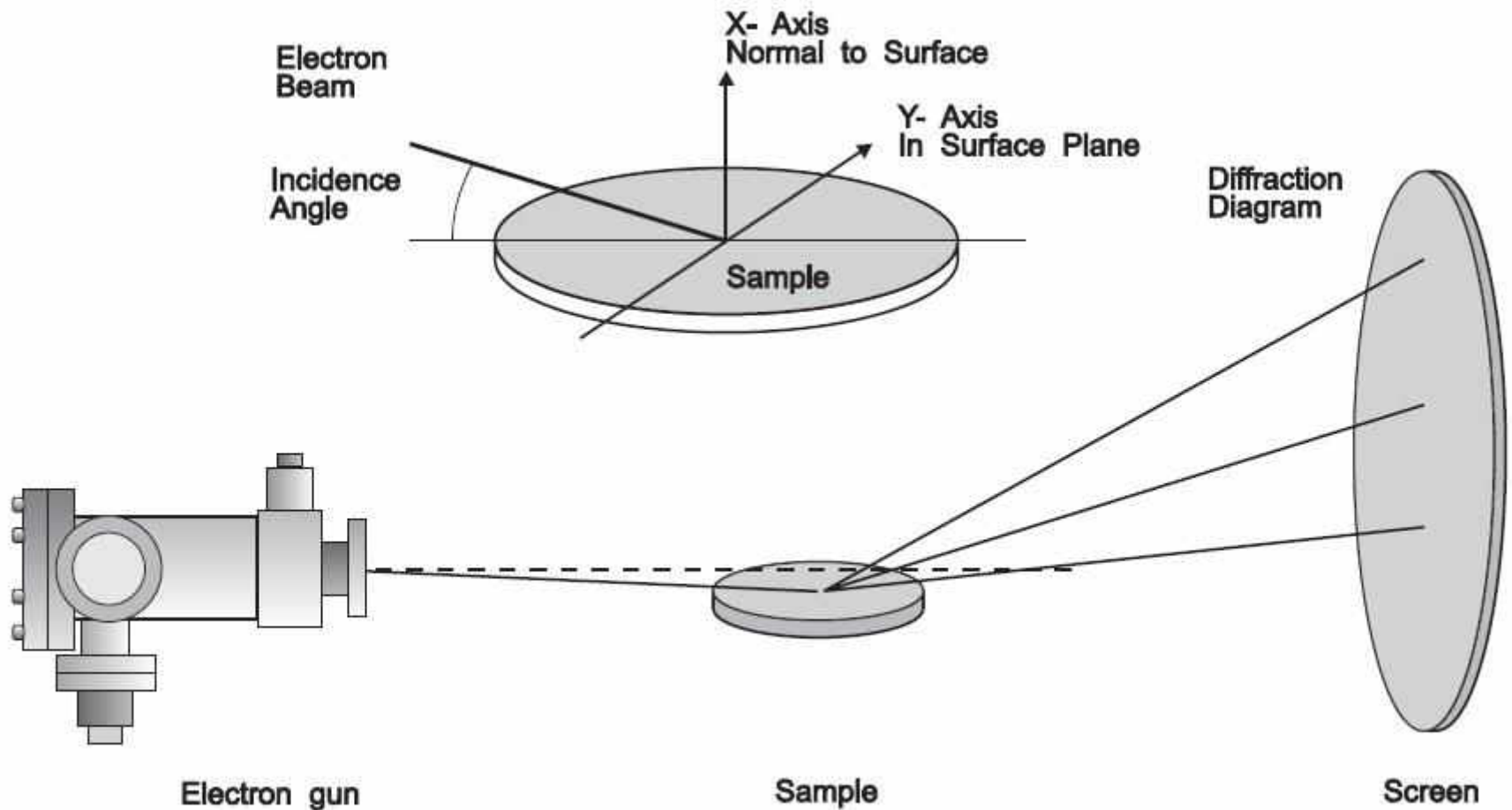
Fig. 3. X-ray diffraction pattern of diamond-cubic ice in the presence of vitreous ice



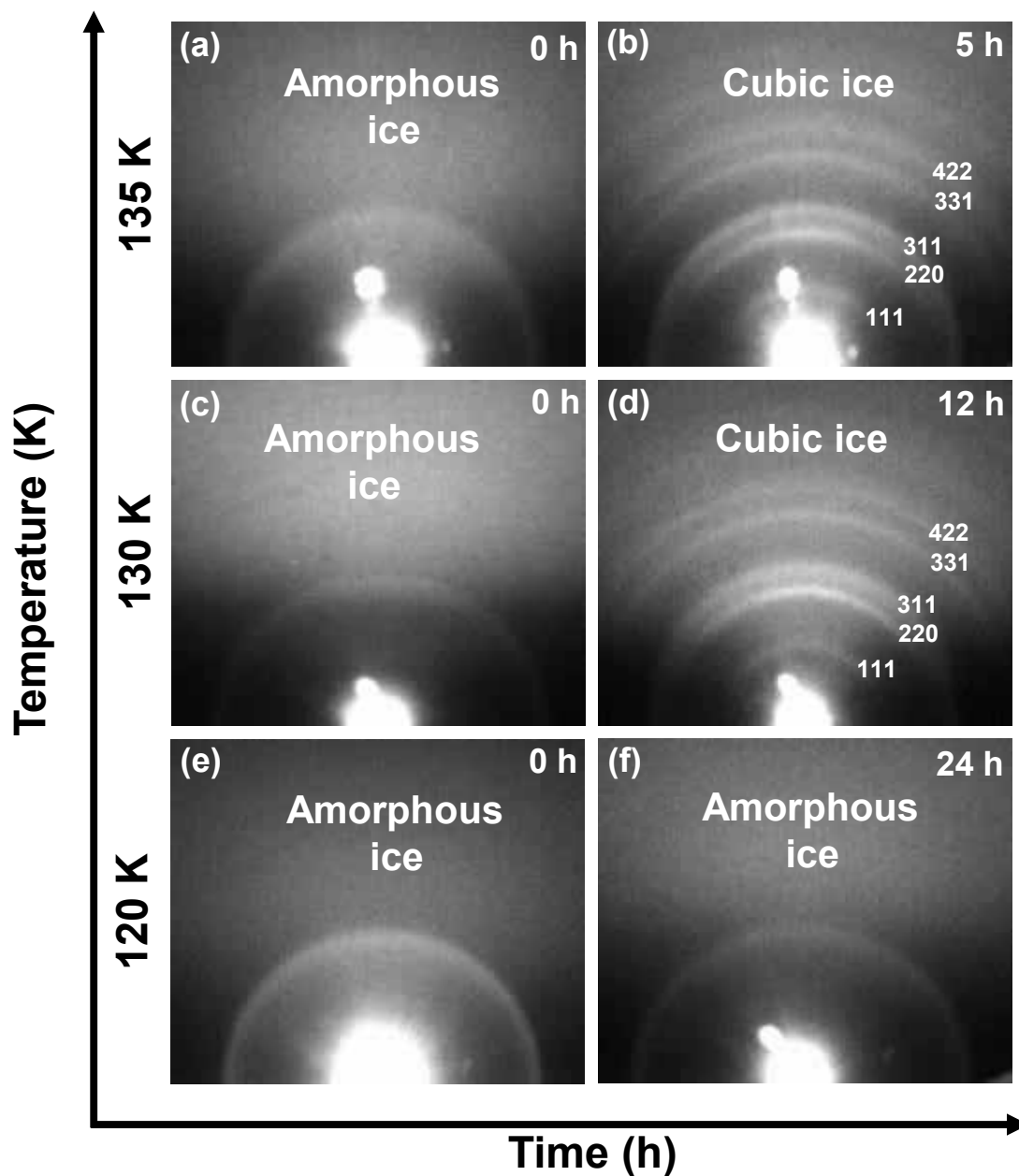
Dowell, L. G. *et al.*, *Nature* **1960**, 168, 1144-1148

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

RHEED set-up

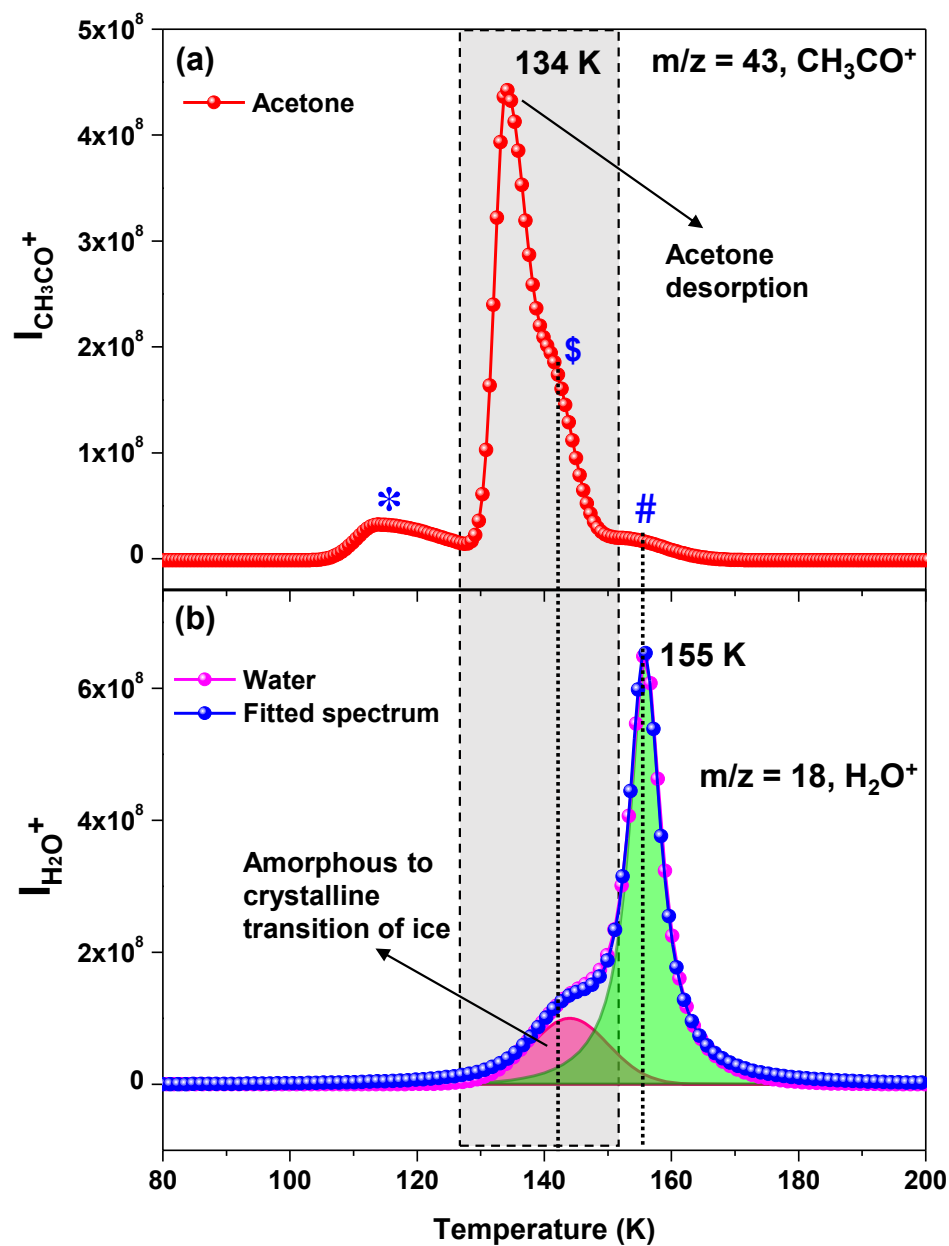


Cubic ice via clathrate hydrate

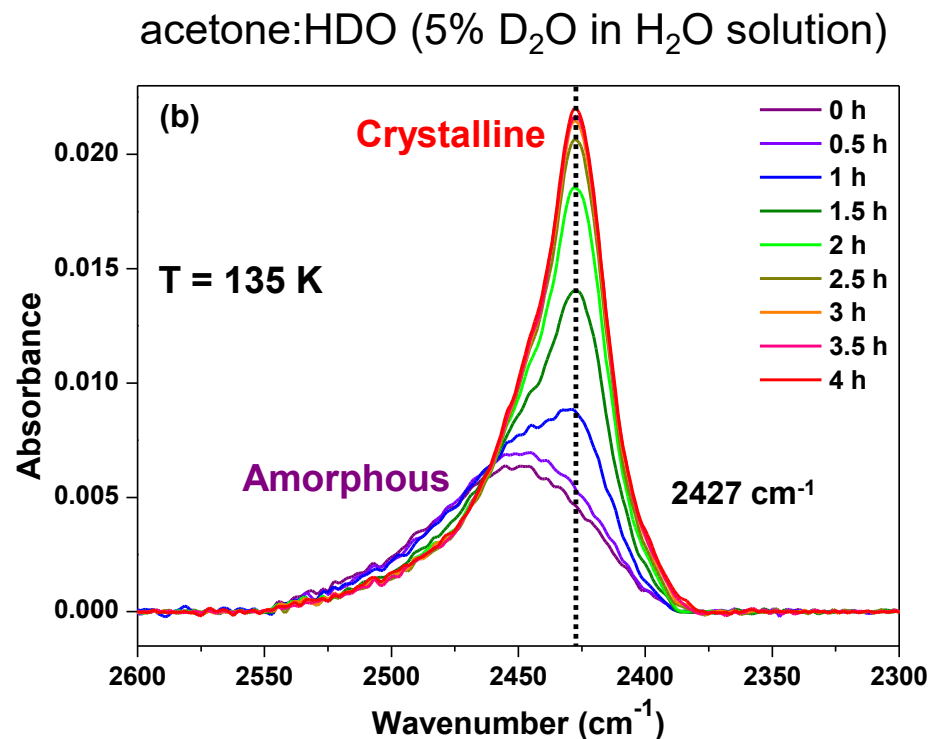
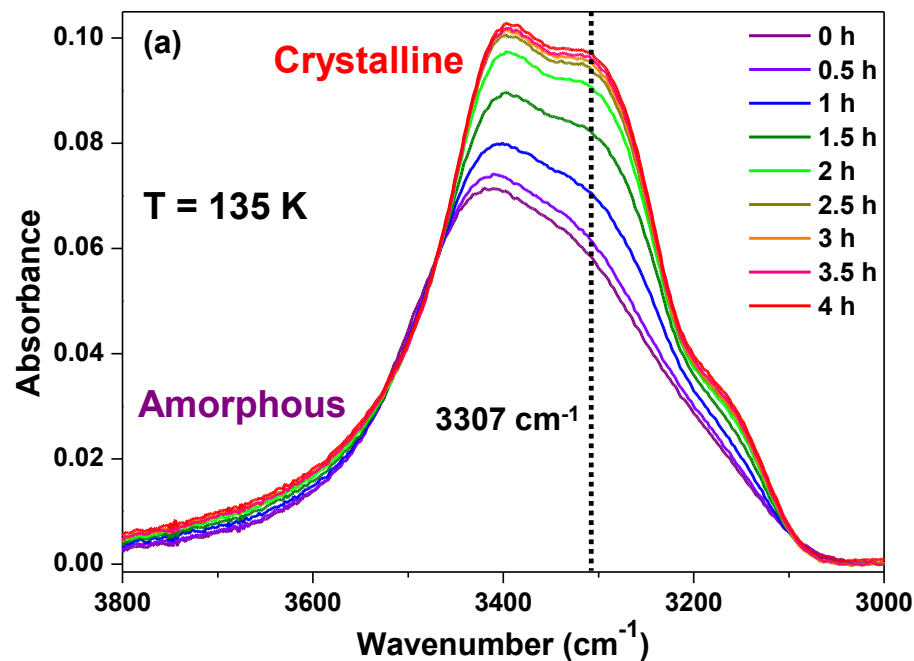


Dr. Ryutaro Souda,
NIMS, Tsukuba,
Japan

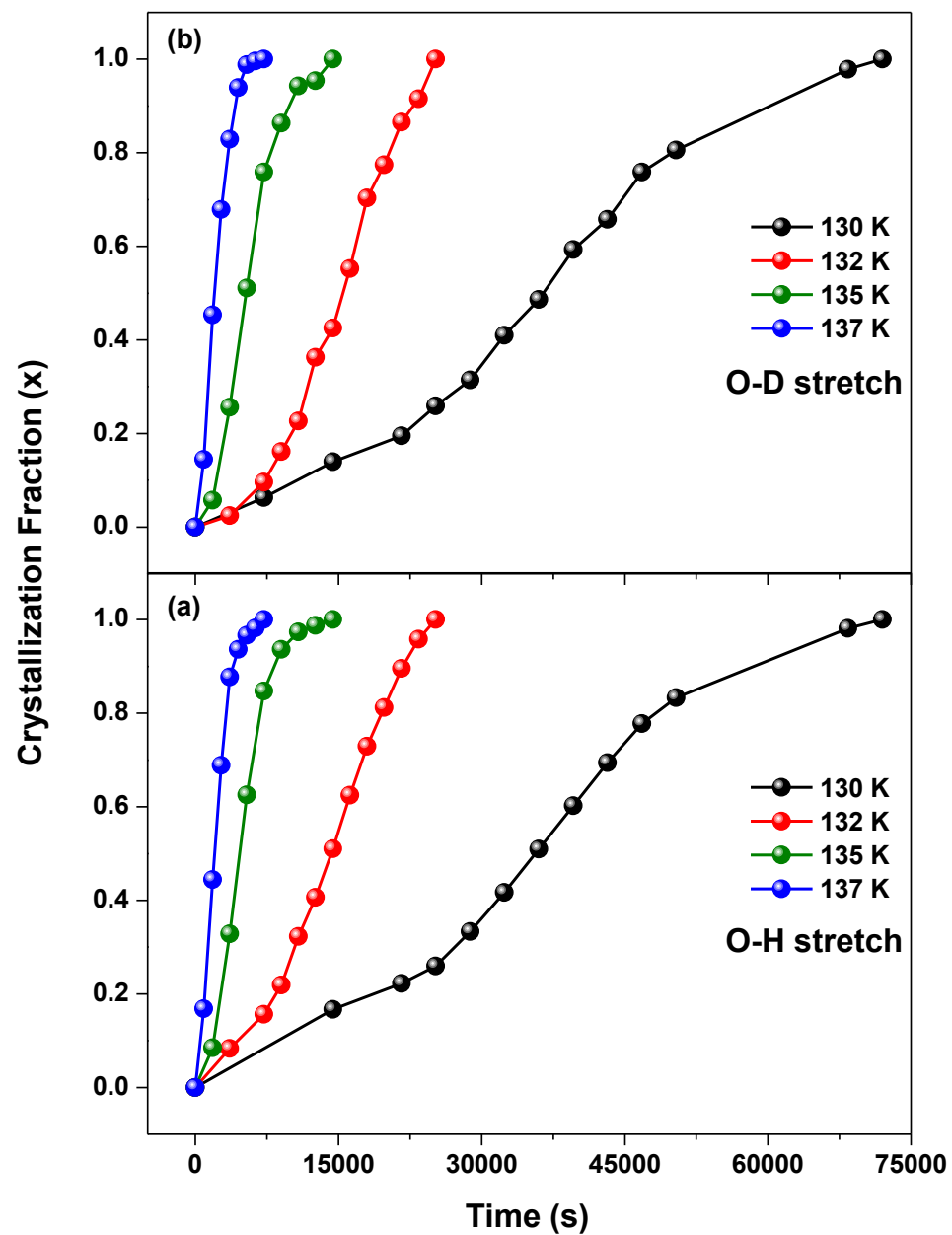
Cubic ice via clathrate hydrate



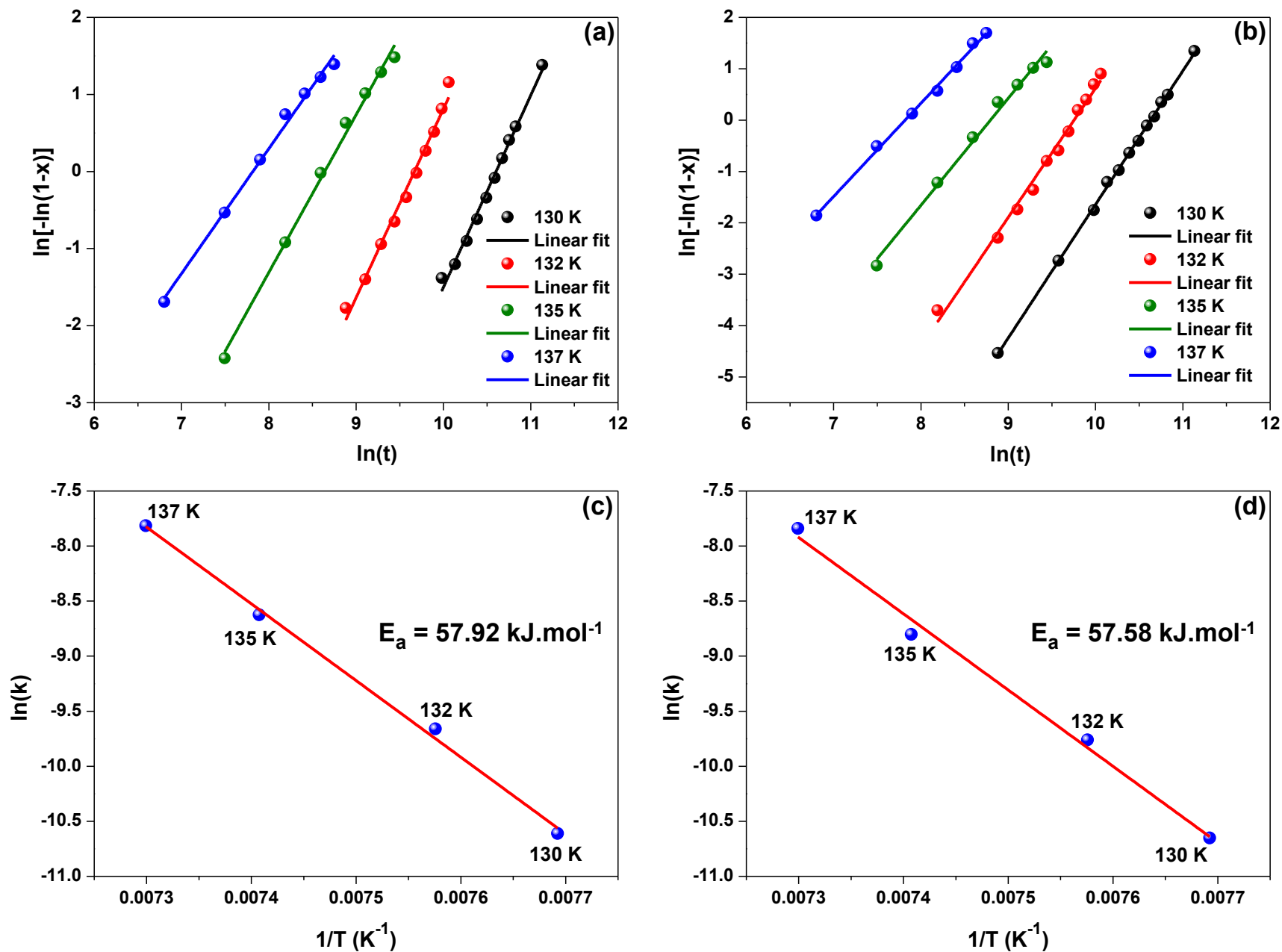
Cubic ice via clathrate hydrate



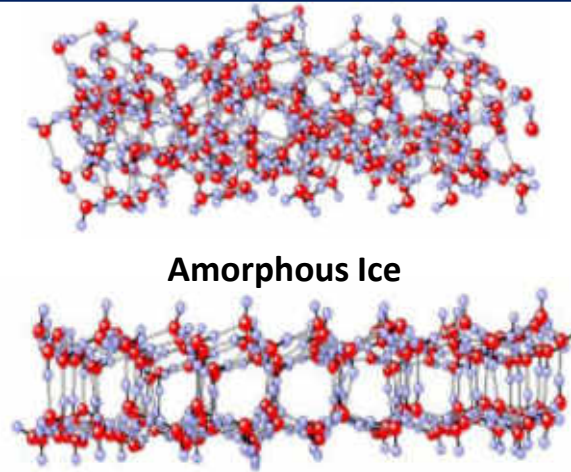
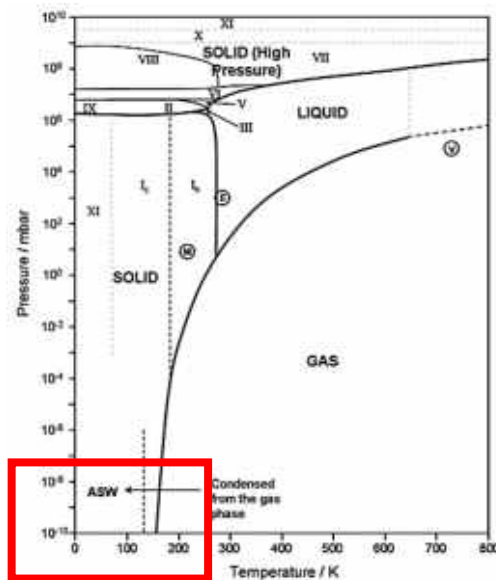
Cubic ice via clathrate hydrate



Cubic ice via clathrate hydrate

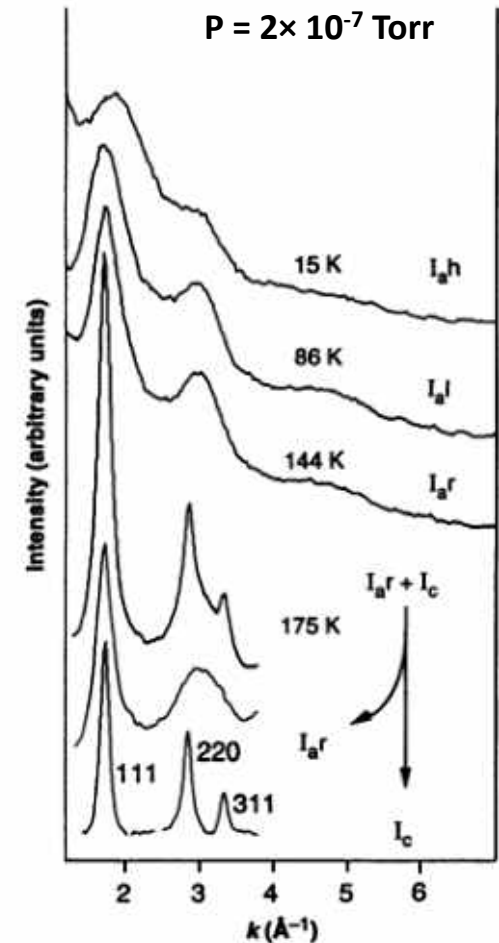


Water ice



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

Selected area electron diffraction

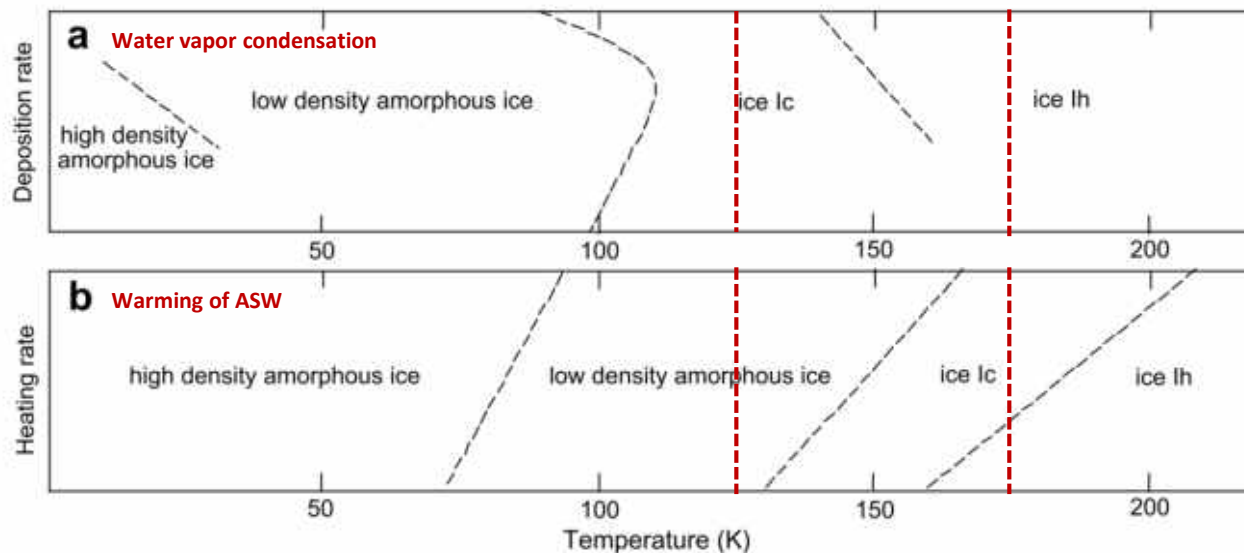


Jenniskens, P. & Blake, *Science*. **1994**, 265, 753–756

44

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

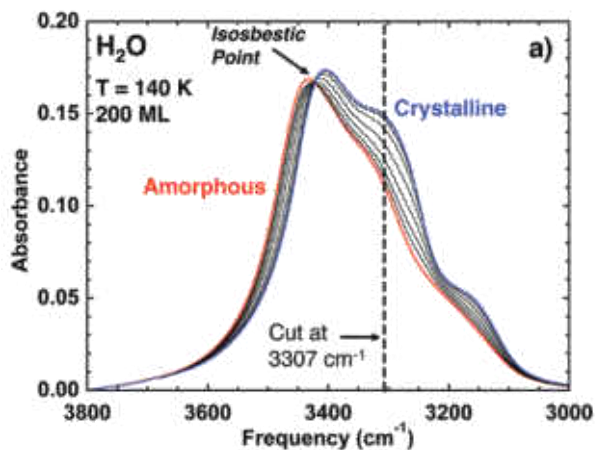
Mason, N. J. et al., *Faraday Discussions.*, **2006**, 133, 311–329



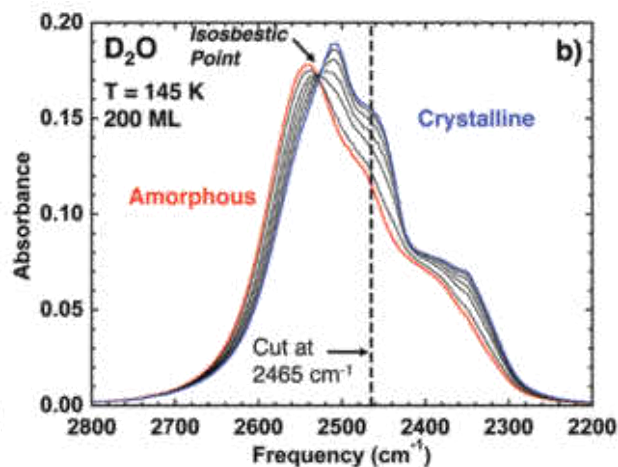
Photochemistry

Crystallisation

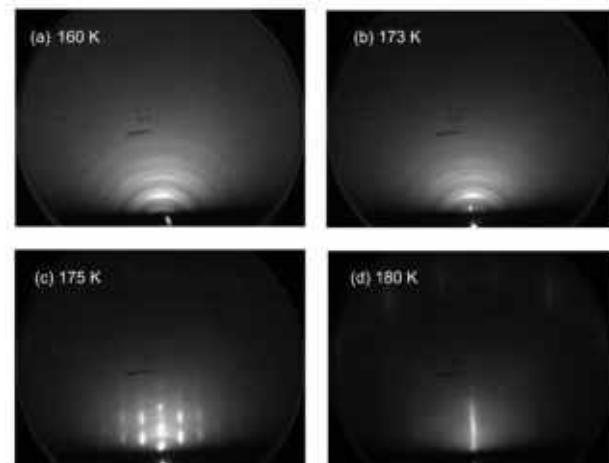
O-H stretch



O-D stretch

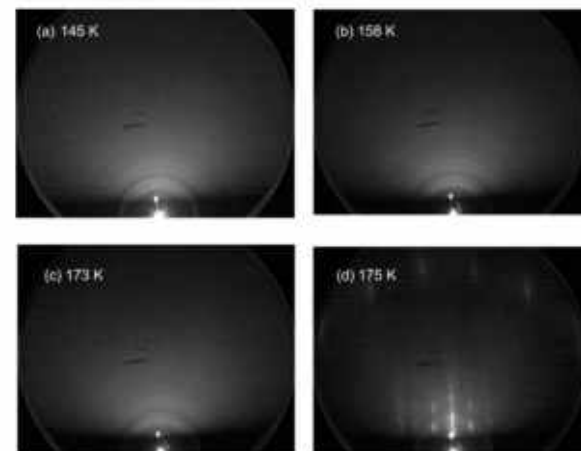
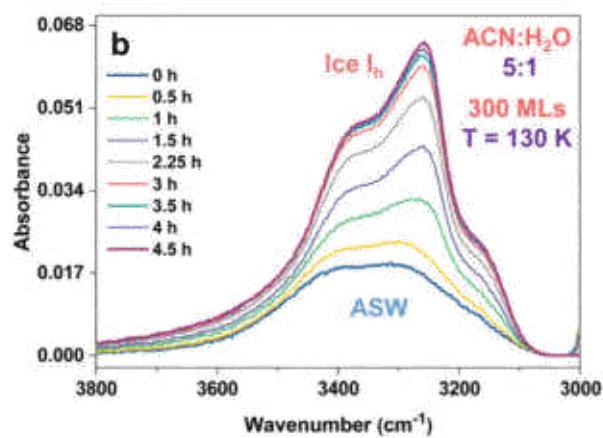
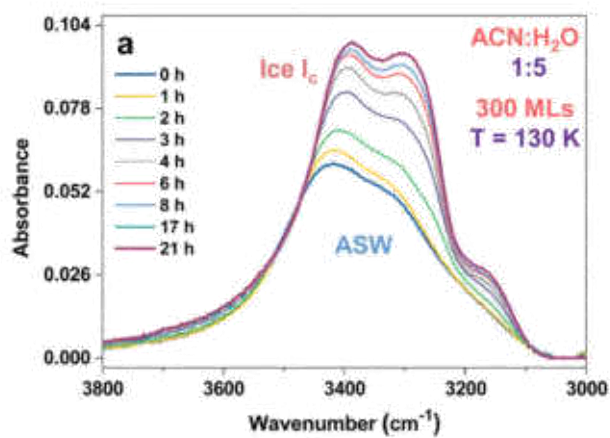


RHEED pattern



(1-propanol (2 L)/H₂O (50 L)/Pt(111))

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

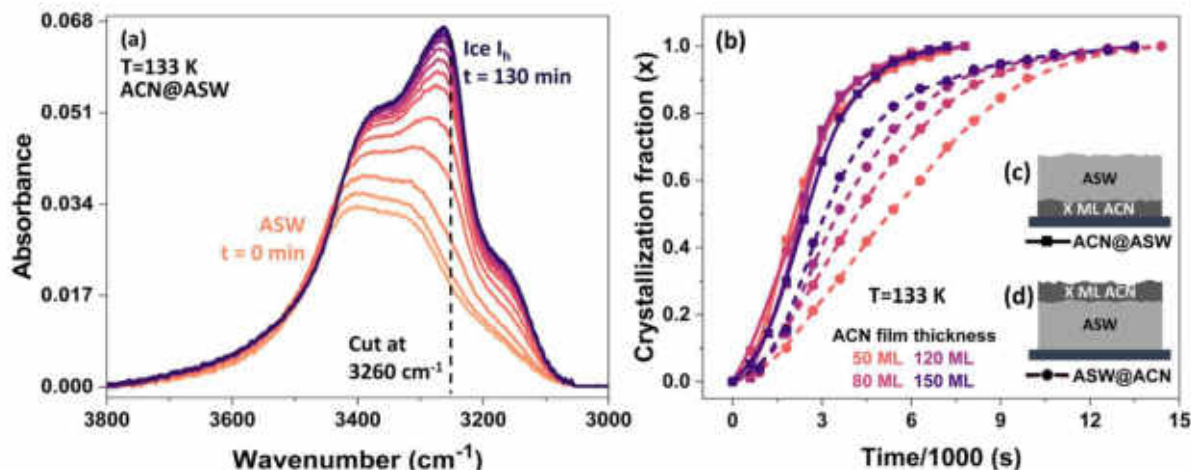


(Methanol (2 L)/H₂O (50 L)/Pt(111))

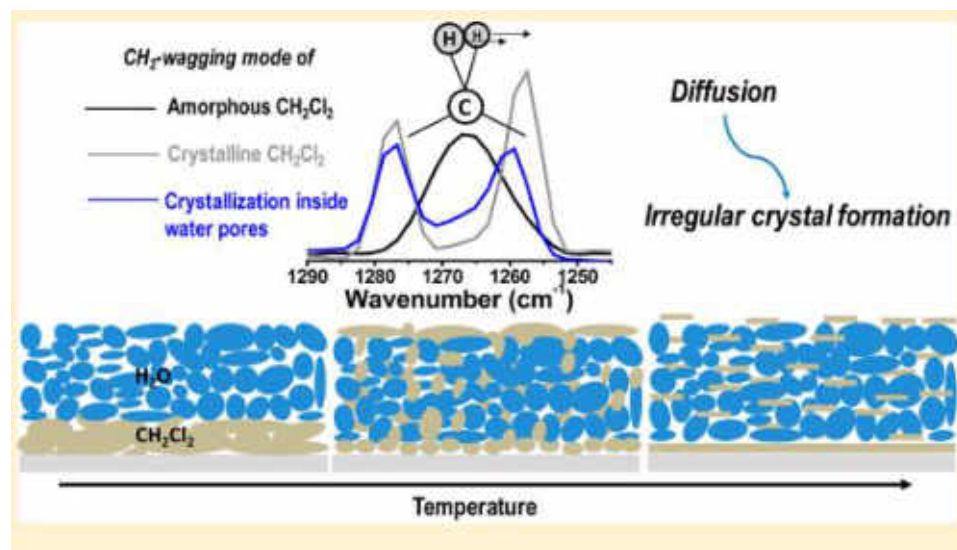
Viswakarma, G. *et al.*, *Phys. Chem. Chem. Phys.*, **2021**, 23, 24052–24060

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

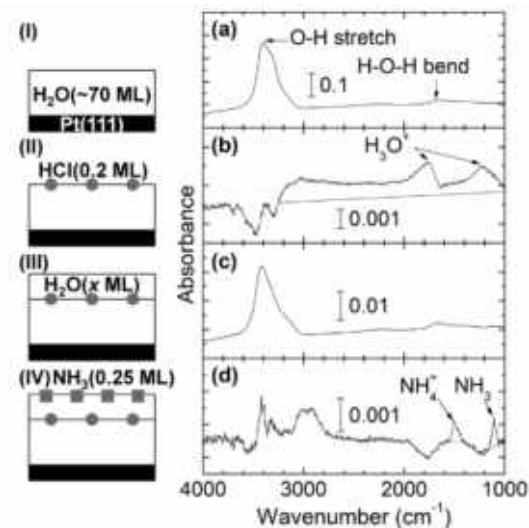
Diffusion



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

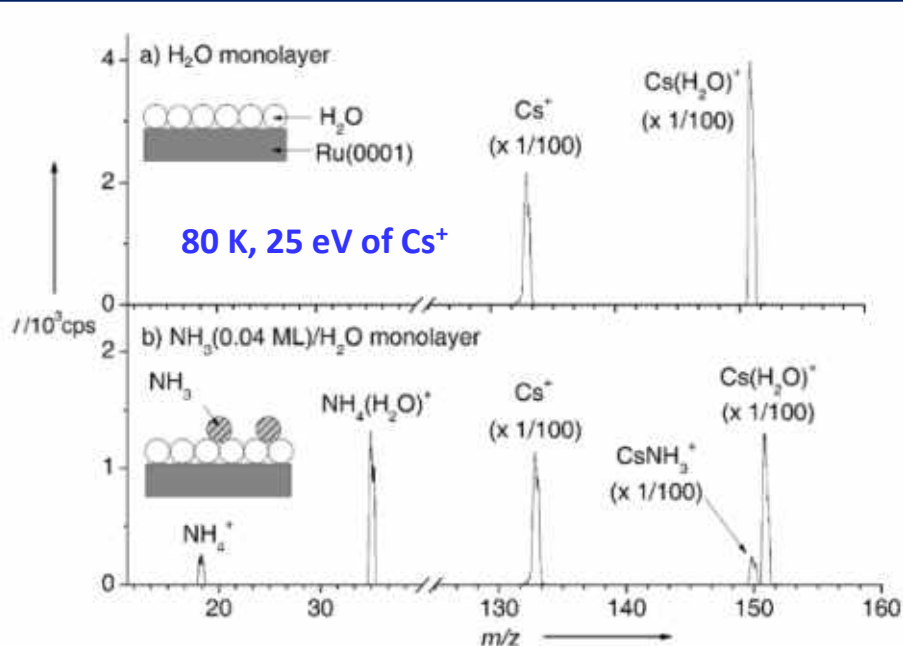


Bhuin, R.G. et al., *J. Phys. Chem. C.*, **2016**, 120, 13474–13484

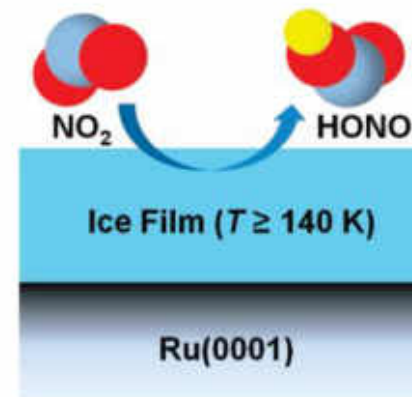
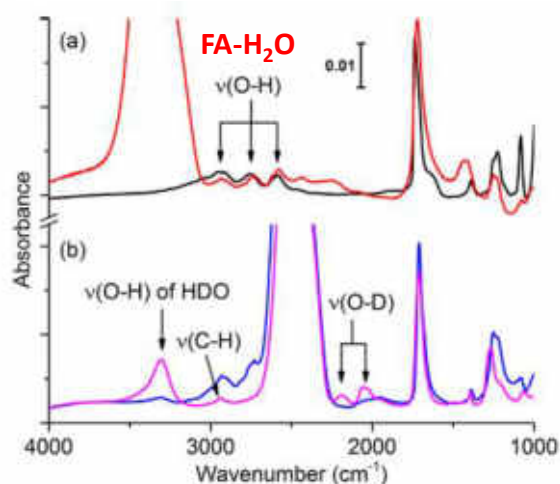
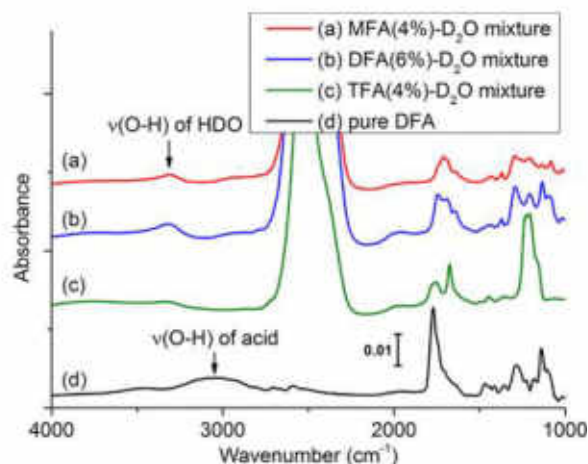
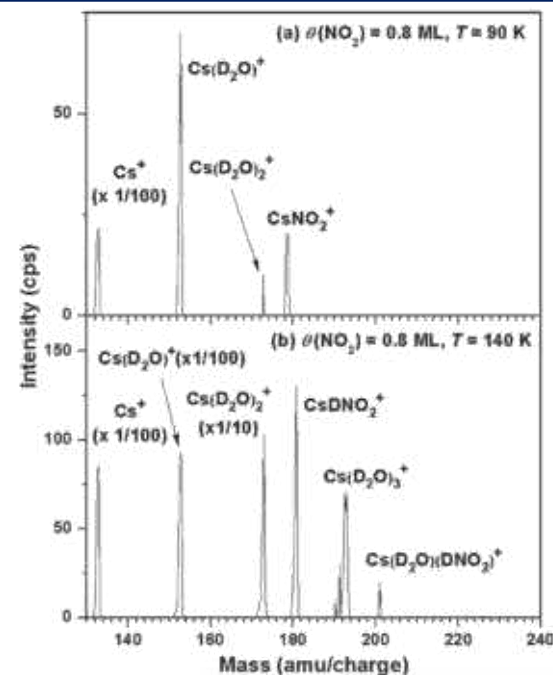


Lee, D. H., et al., *J. Phys. Chem. C.*, **2019**, 123, 3657–3663

Chemical reaction



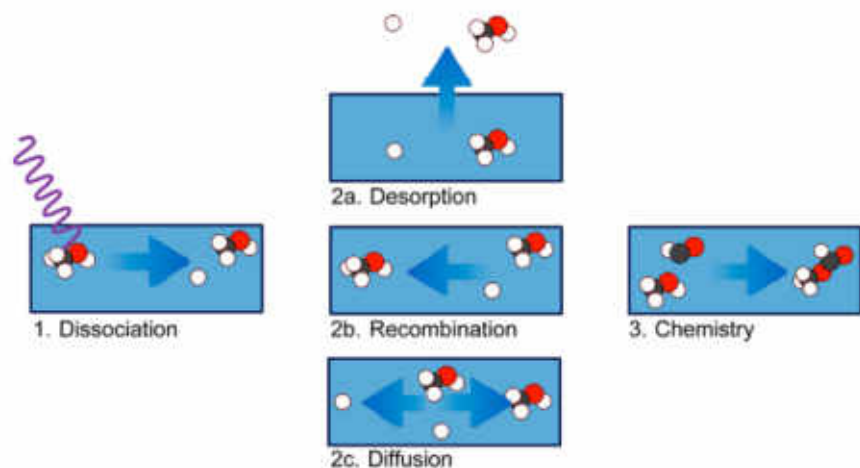
Kang, H., *Angew. Chem. Int. Ed.*, **2012**, 51, 1-5



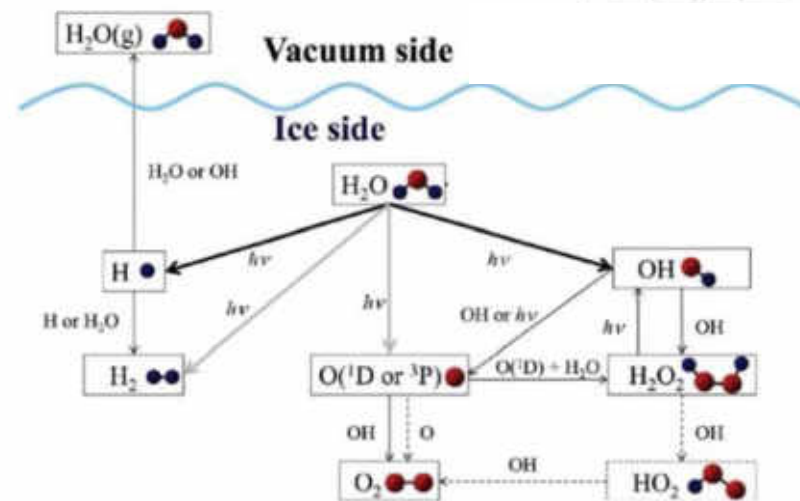
Park, Y. et al., *J. Phys. Chem. Lett.*, **2018**, 9, 4282–4286

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

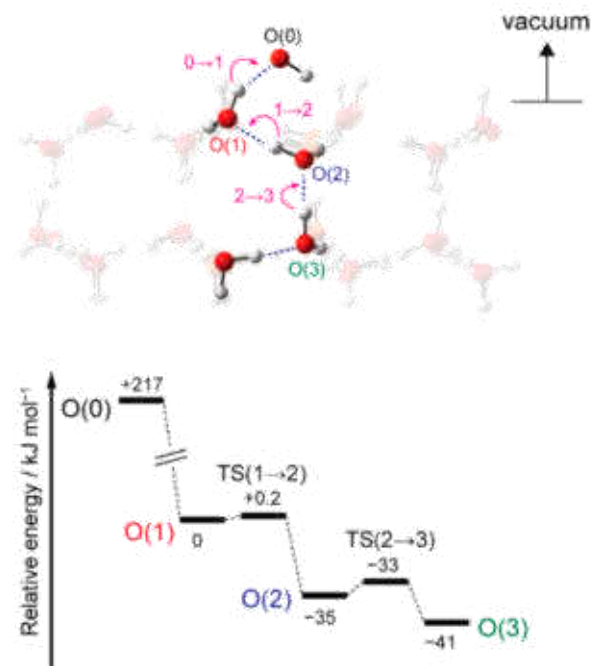
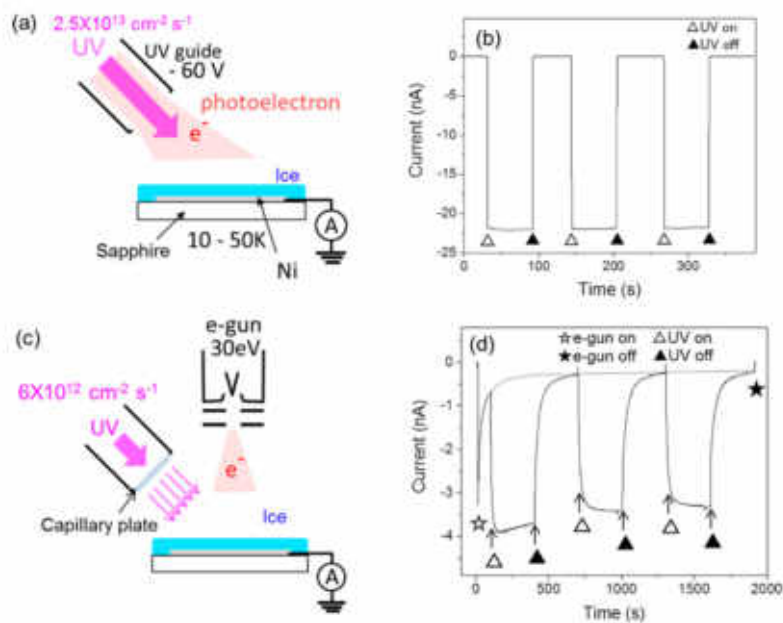
Photochemistry of molecular solids



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

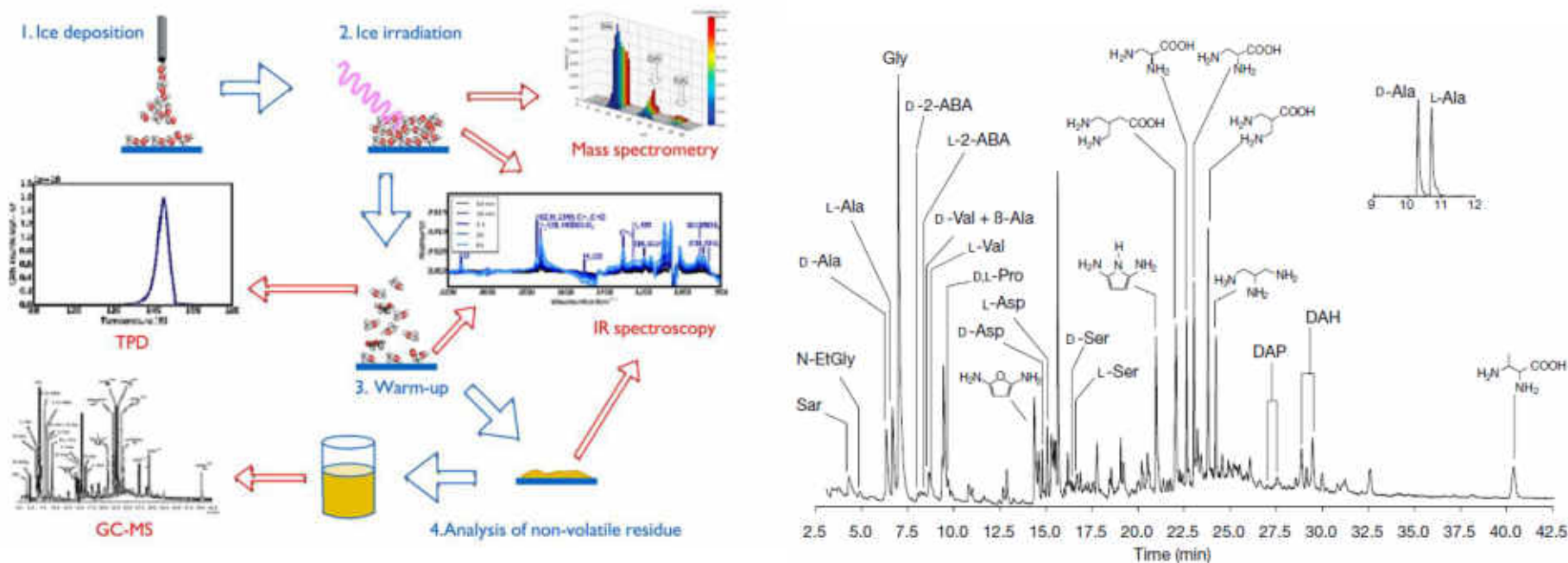


Arumainayagam, C. R. *et al. Chem. Soc. Rev.*, **2019**, *48*, 2293–2314



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

Origin of life



Al substrate: 12 K temperature

$\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO}:\text{CO}_2 = 2:1:1:1:1$

UV flux = 1.5×10^{15} photons.s⁻¹ for 24 hours

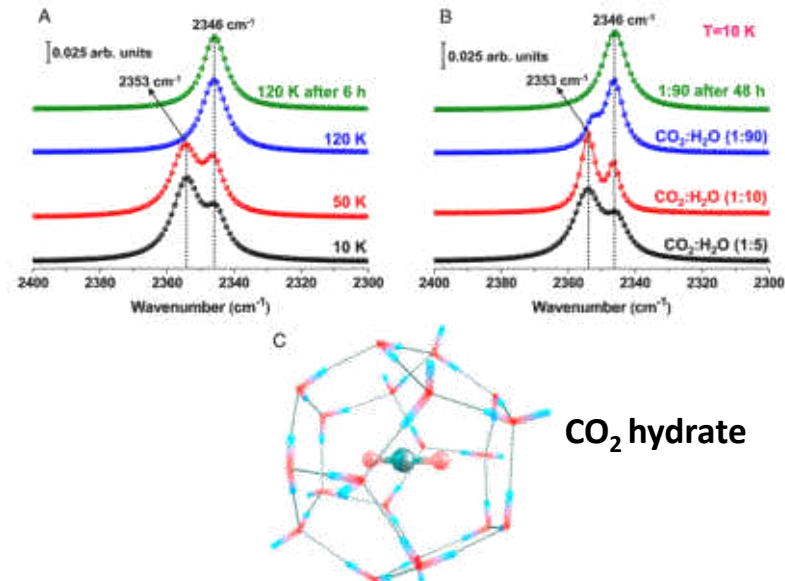
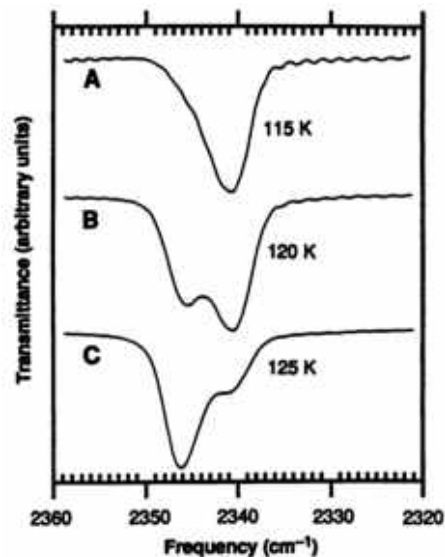
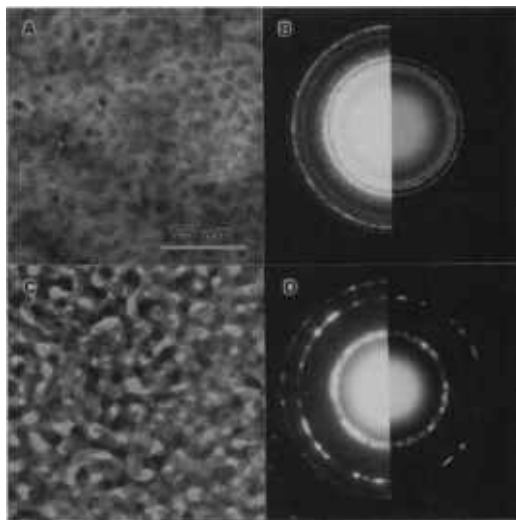
6 M HCl at 110 °C for 24 h under argon atmosphere

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

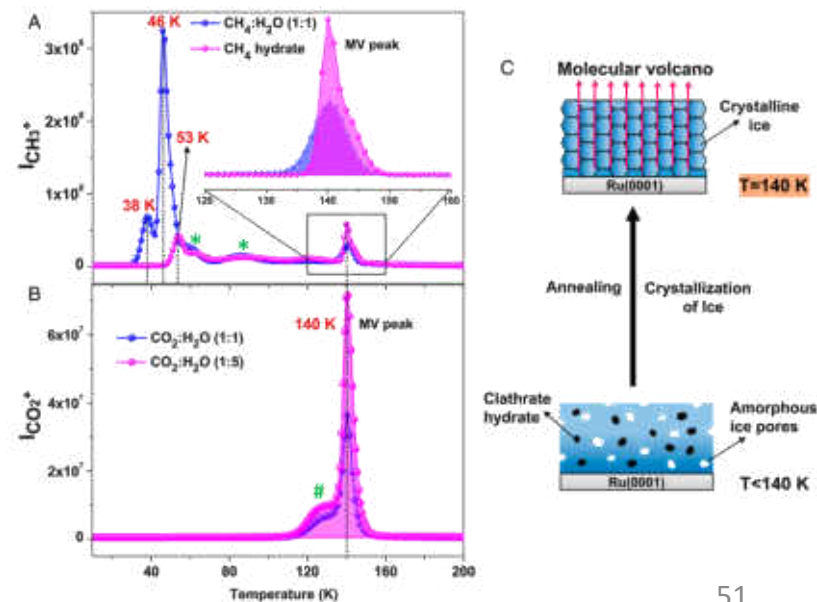
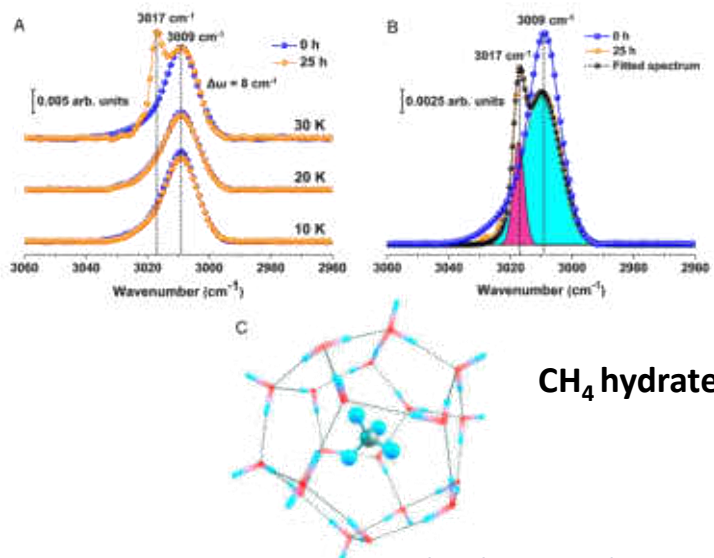
Clathrate hydrate formation in vacuum

$P = 10^{-6}$ Torr

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

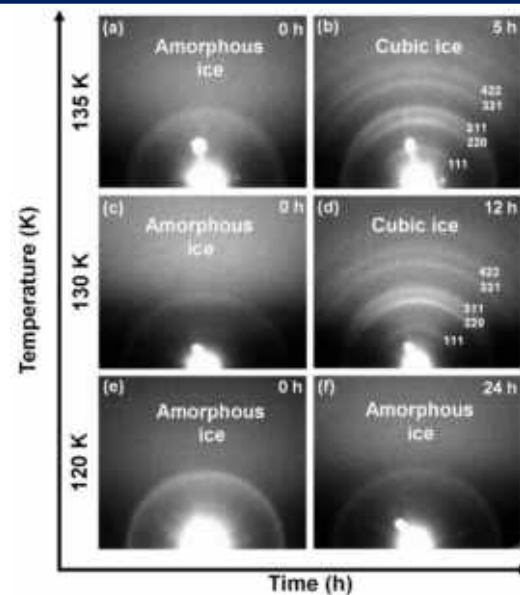
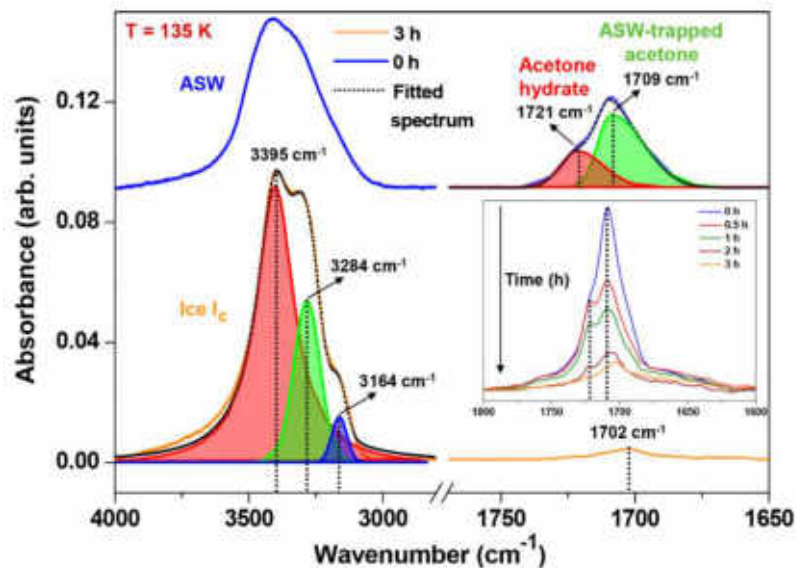


Blake, D. et al., Science., 1991, 254, 548–551

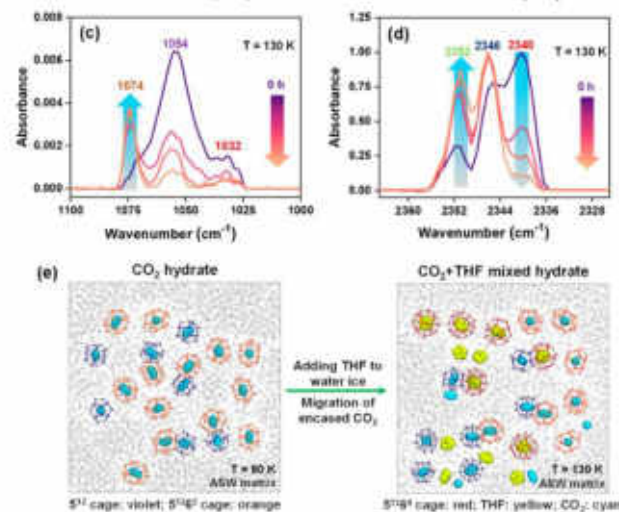
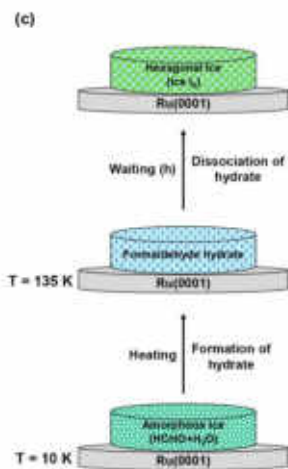
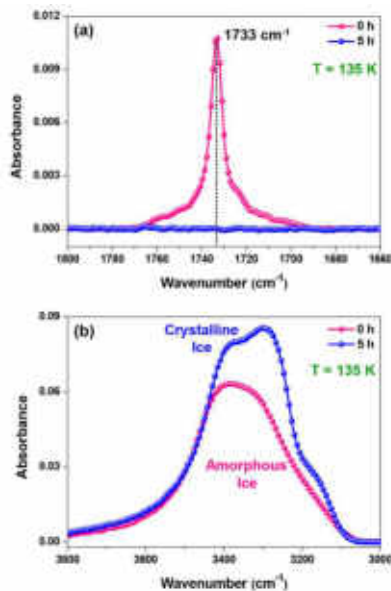


Ghosh, J. et al., Proc. Natl. Acad. Sci. U.S.A., 2018, 116, 1526-1531

Transformation of clathrate hydrate under UHV



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



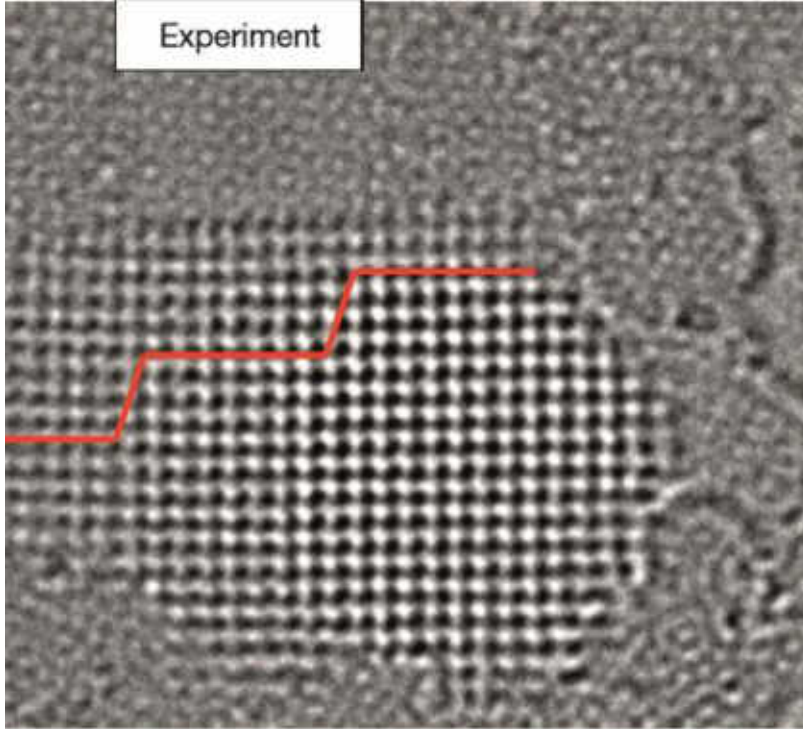
Viswakarma, G. et al., *J. Phys. Chem. Lett.*, **2023**, 14, 2823–2829

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

CryoEM

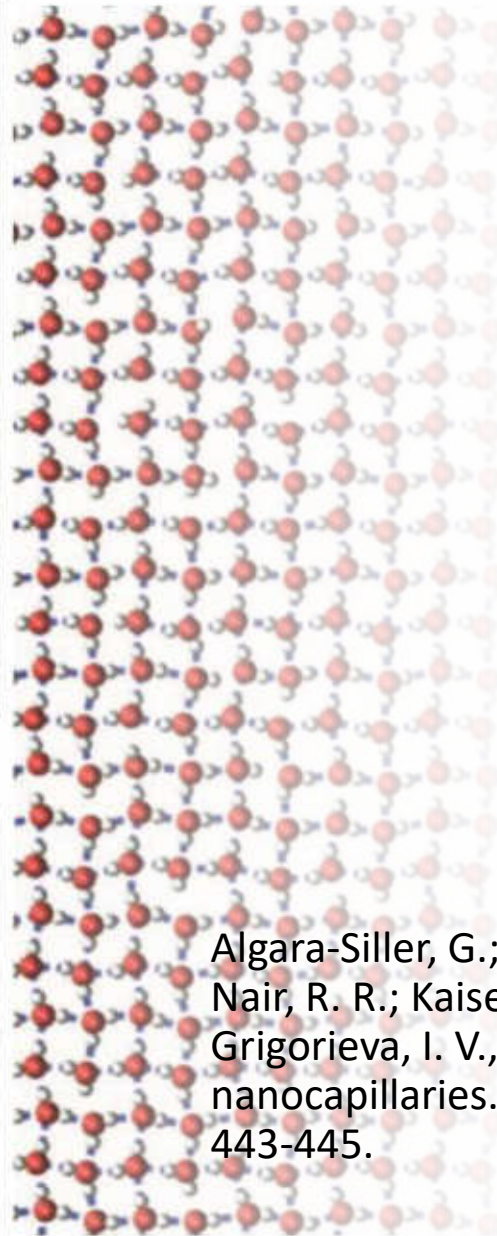
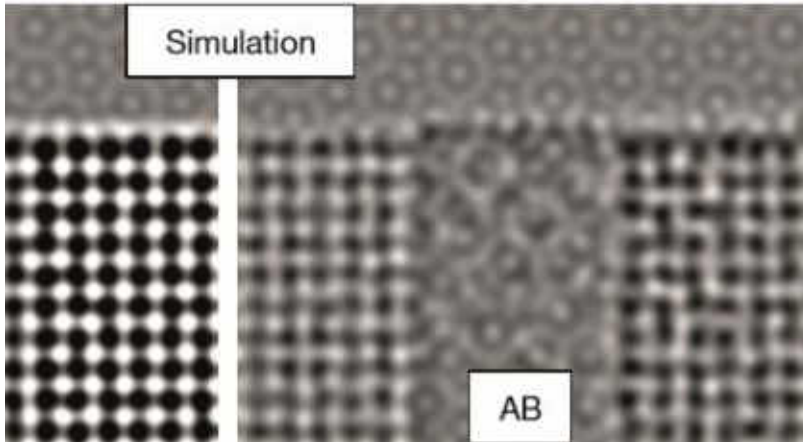
Observing clathrate hydrates?

Experiment



c

Simulation



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.

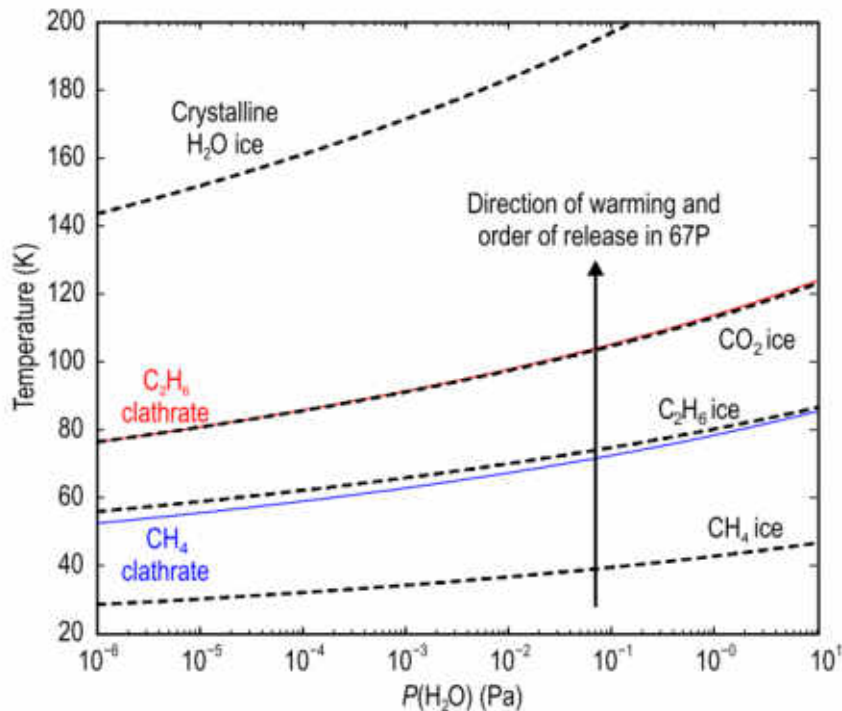
Existence of acetaldehyde clathrate hydrate and its dissociation leading to cubic ice under ultrahigh vacuum and cryogenic conditions

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

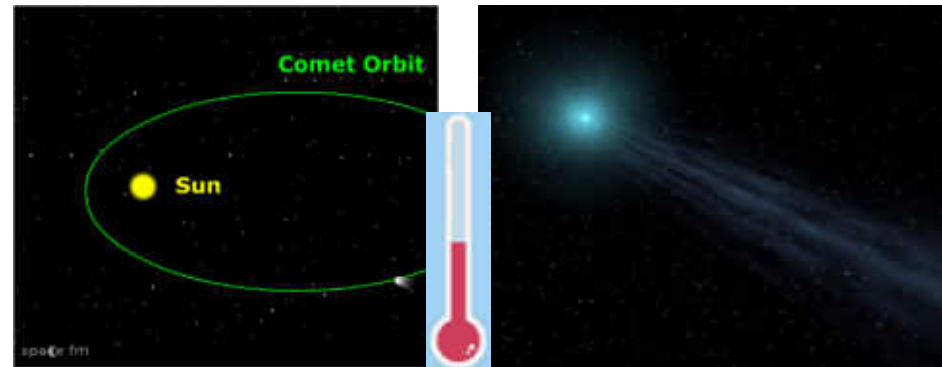
SPACE SCIENCES

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 I. ⁵ Bernard Marty,⁶ Kathleen E. Mandt,^{1,4} Peter Wurz,^{3,7} Martin Rubin³

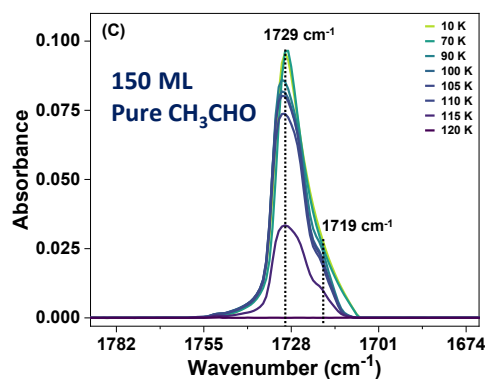
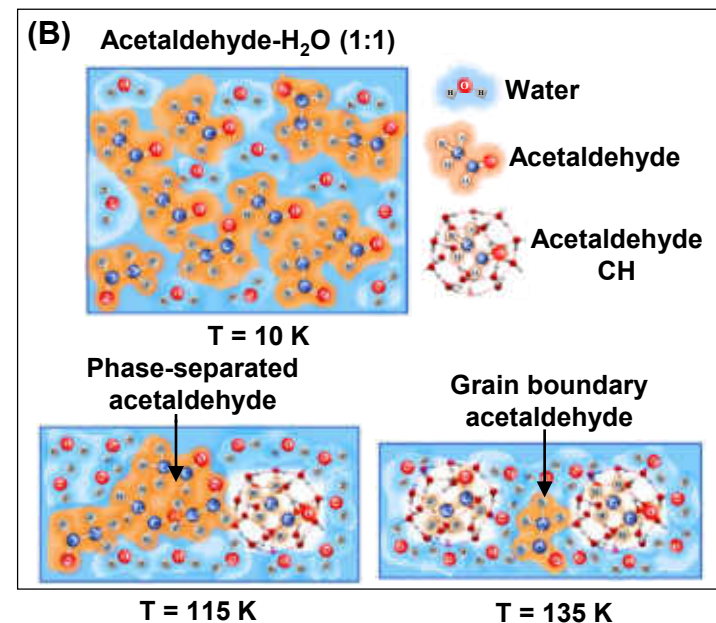
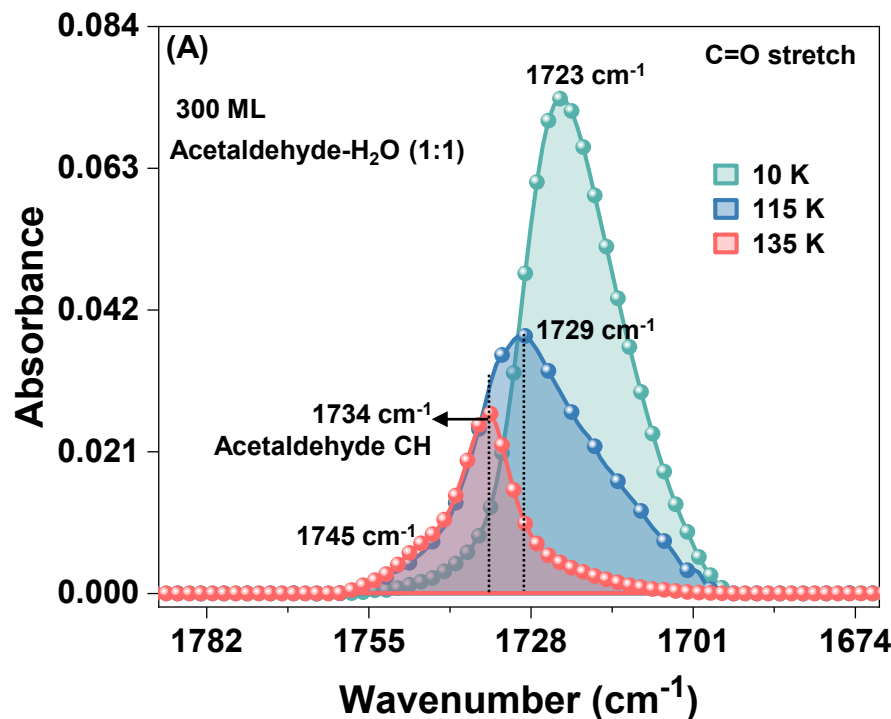


Equilibrium curves of clathrates and pure condensates in the cometary environment.



Formation of acetaldehyde clathrate hydrate

300 ML $\text{CH}_3\text{CHO}+\text{H}_2\text{O}$ (1:1)



Gaseous phase
1746 cm^{-1}

Clathrate hydrate
1734 cm^{-1}

Condensed phase
1729 cm^{-1}

Formation of acetaldehyde clathrate hydrate

Dielectric and nuclear magnetic resonance characterization of unstable clathrate hydrates of acetaldehyde and propionaldehyde¹

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

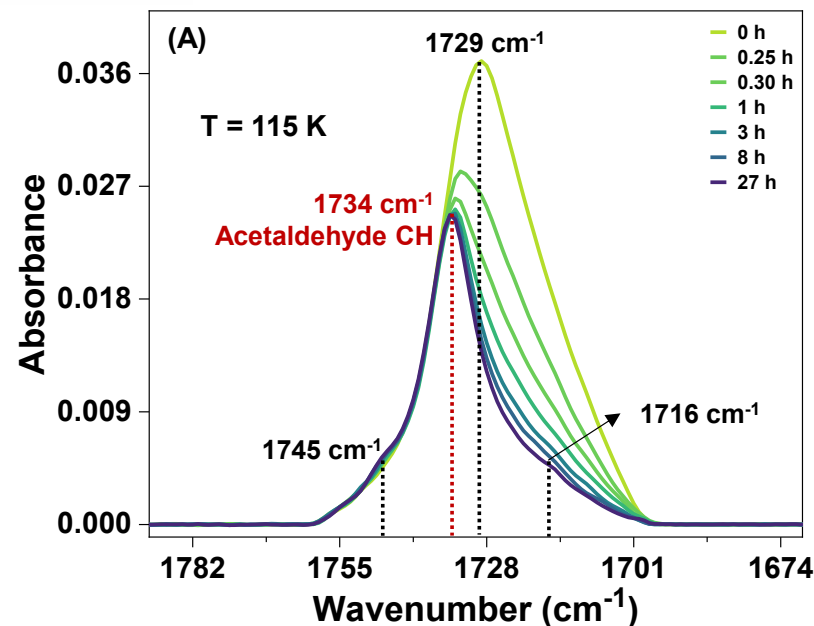
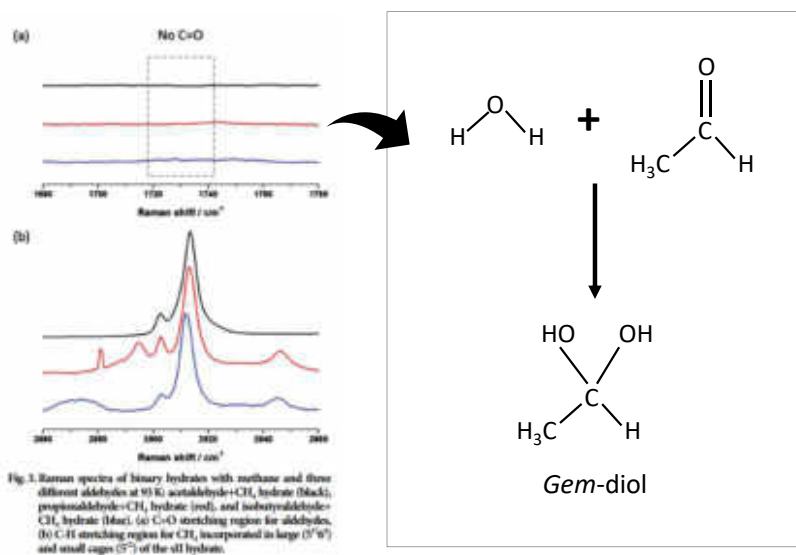
Thermodynamic and spectroscopic identification of aldehyde hydrates

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

Department of Chemical and Biomolecular Engineering (BK21+ Program), KAIST,

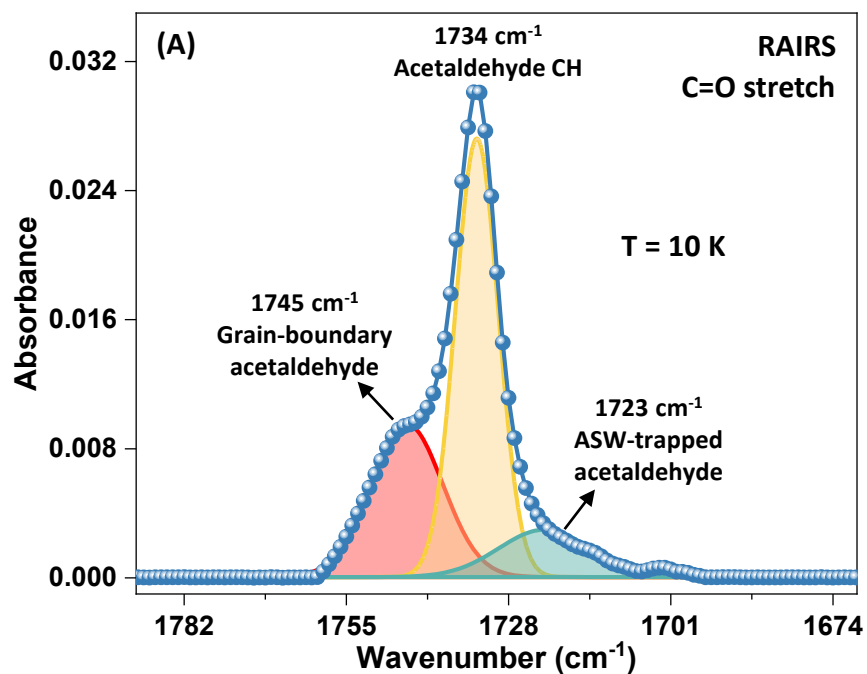
291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea

(Received 3 November 2015 • accepted 25 January 2016)



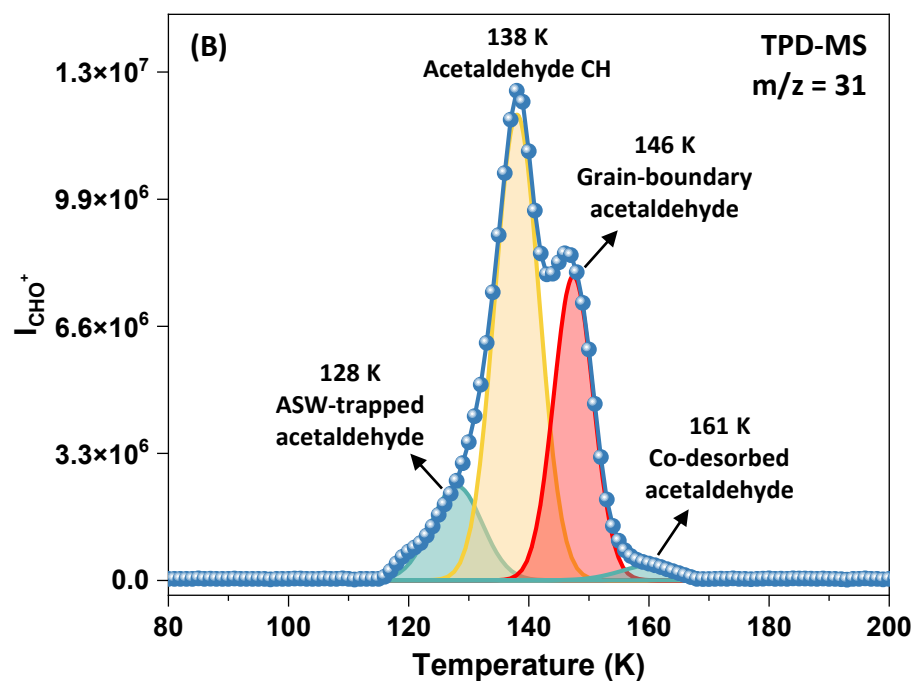
Formation of acetaldehyde clathrate hydrate

RAIRS at 10 K



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

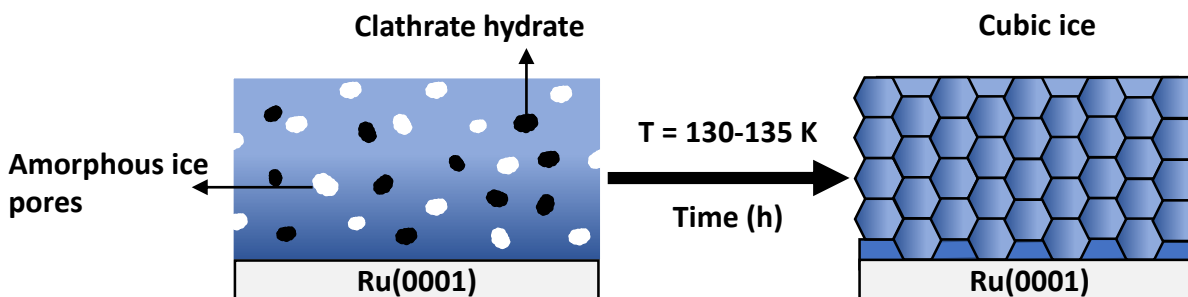
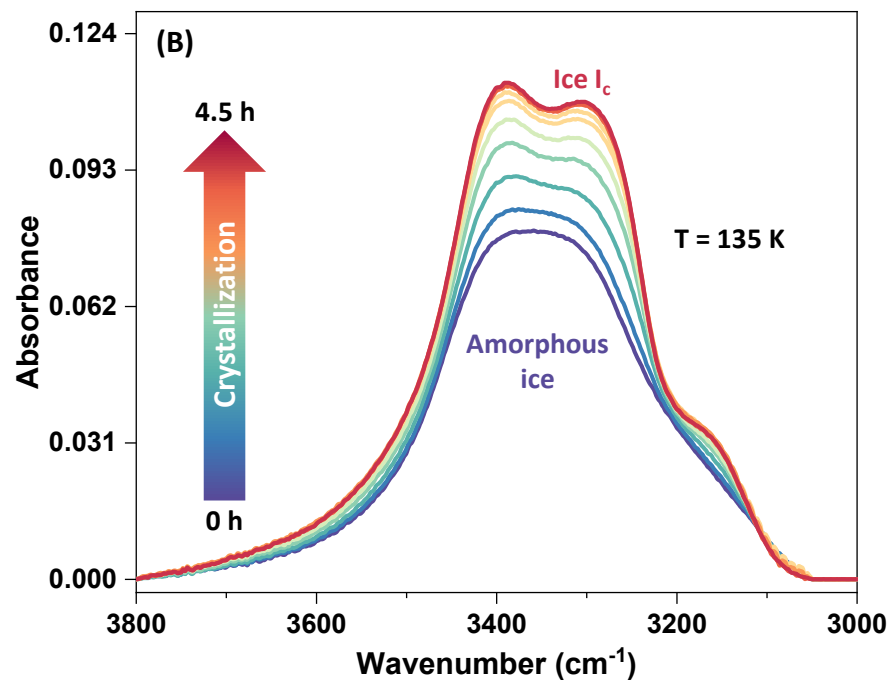
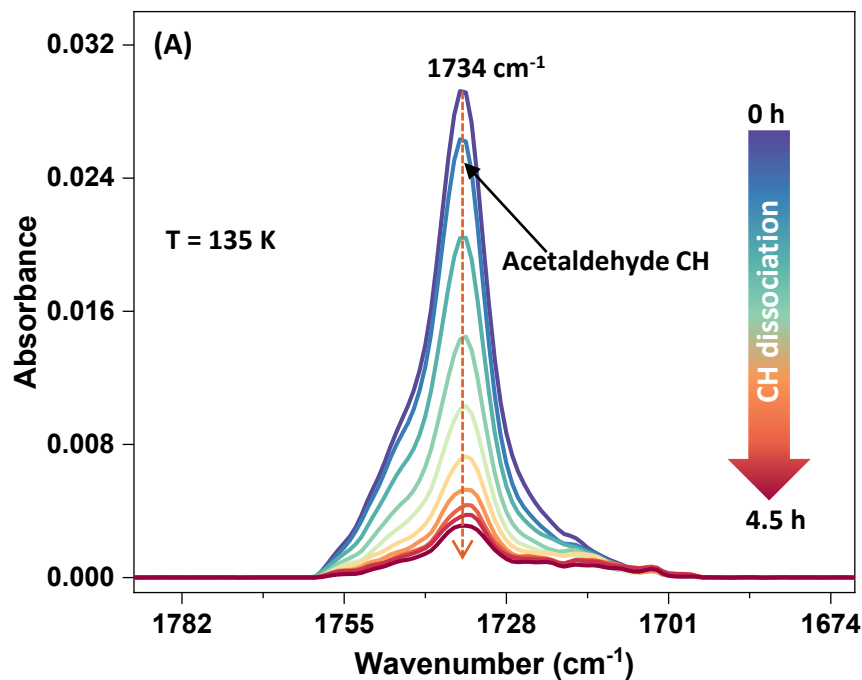
TPD-MS



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

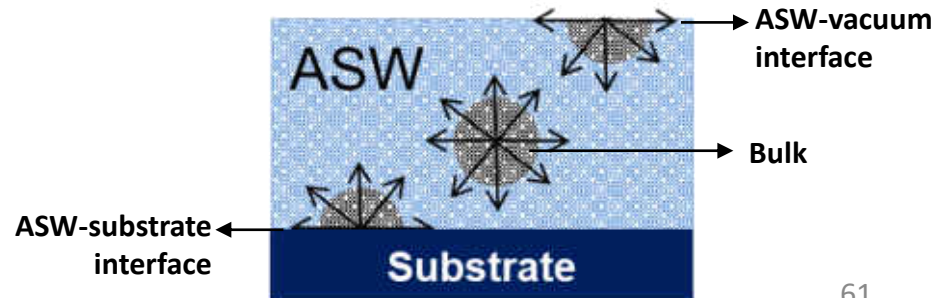
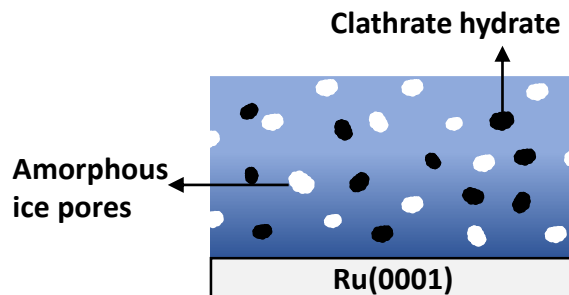
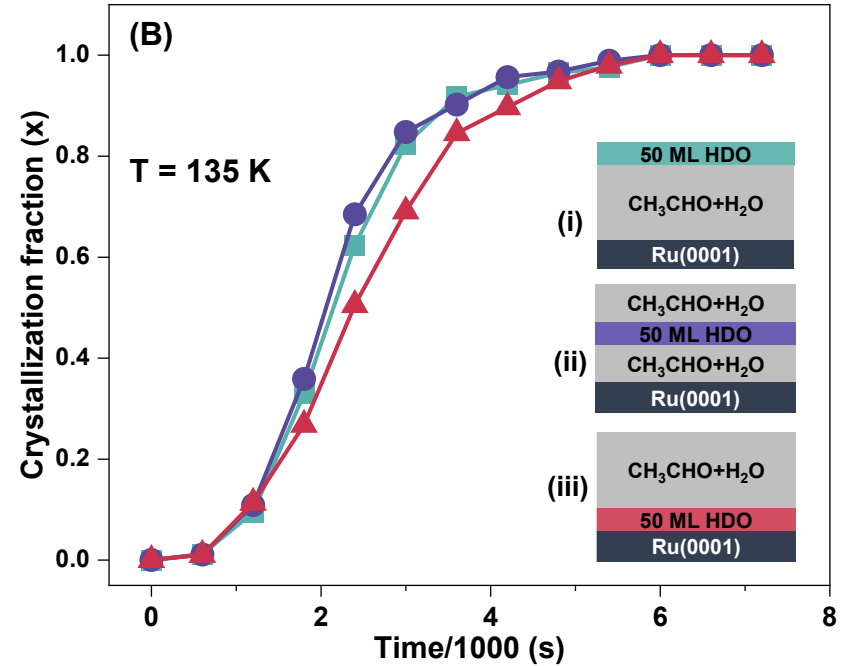
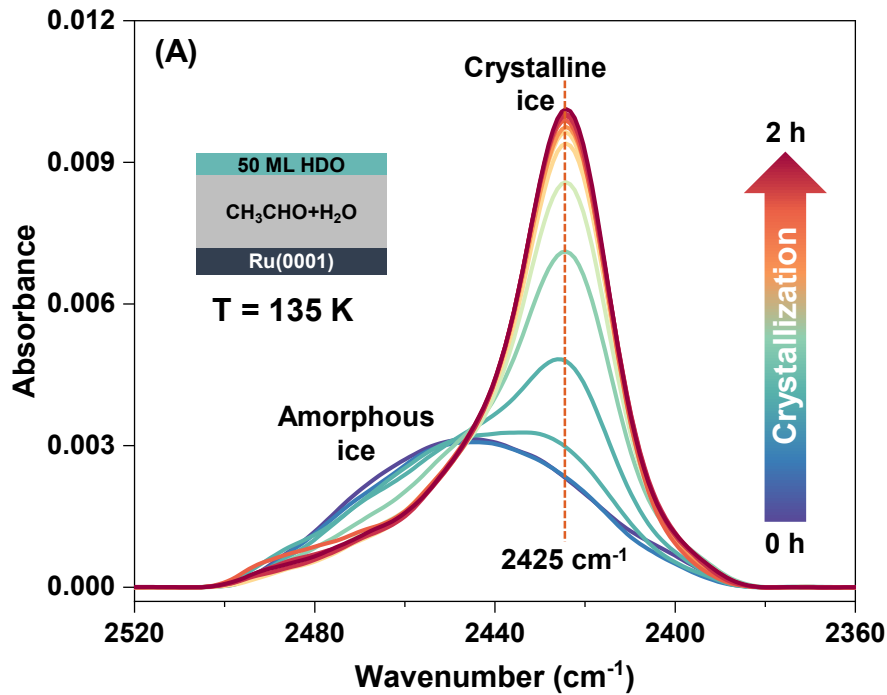
Formation of cubic ice via dissociation of clathrate hydrate

300 ML $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$ (1:1)

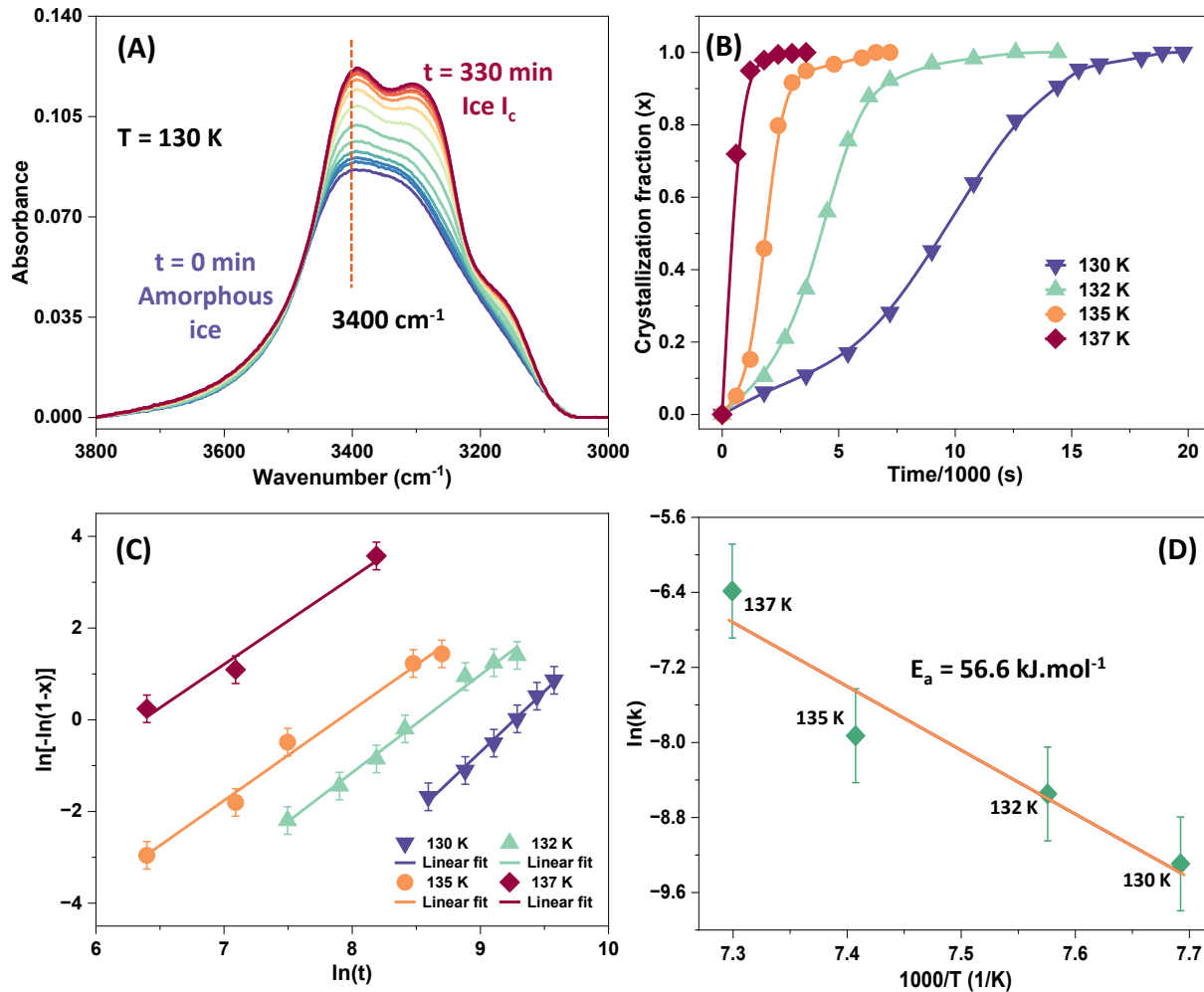


Ghosh, J. et al., *J. Phys. Chem. Lett.* **2020**, *11*, 26–32

Crystallization mechanism



Crystallization Kinetics



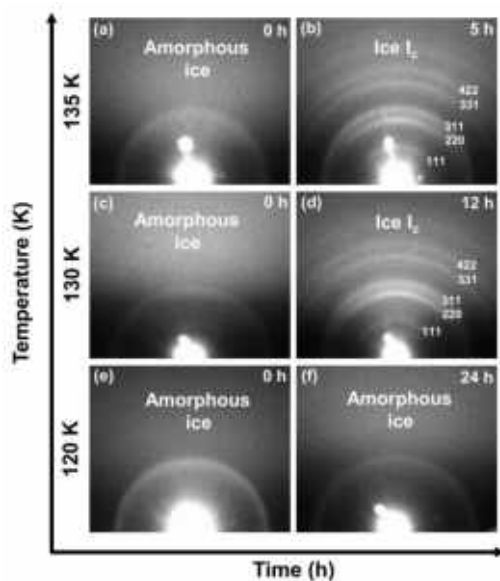
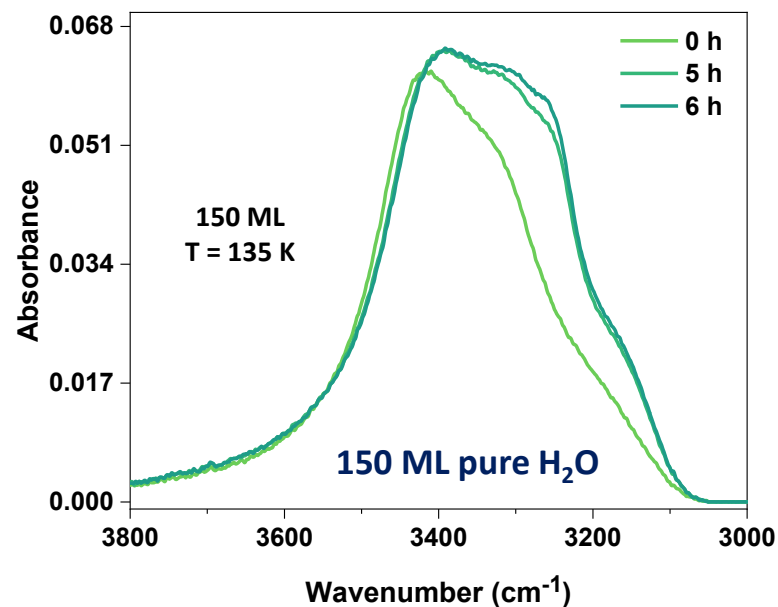
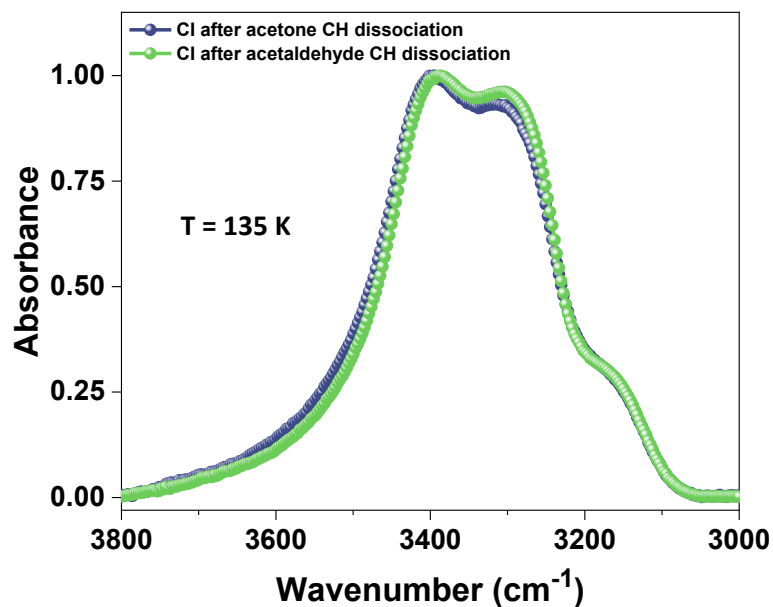
Avrami equation

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

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

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

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) $\text{CH}_3\text{CHO} + \text{D}_2\text{O}$ (1:1)
- (2) $\text{CH}_3\text{CHO} @ \text{H}_2\text{O}$ (150 @ 150 ML)
- (3) $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$ (1:10, 1:20)

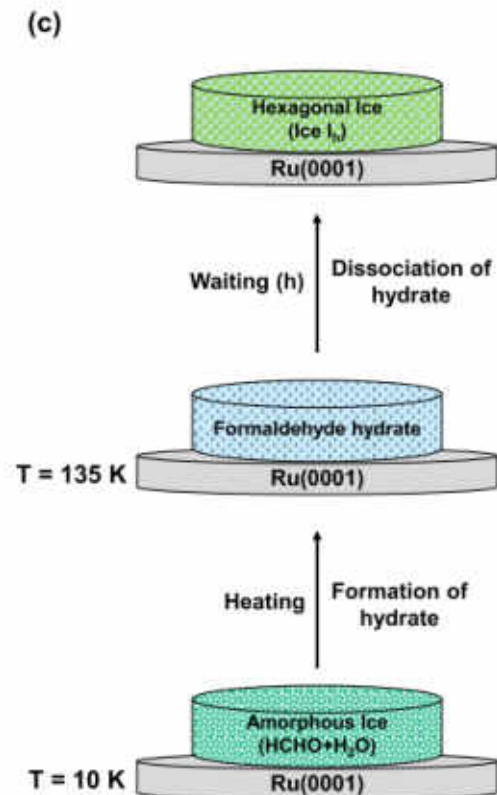
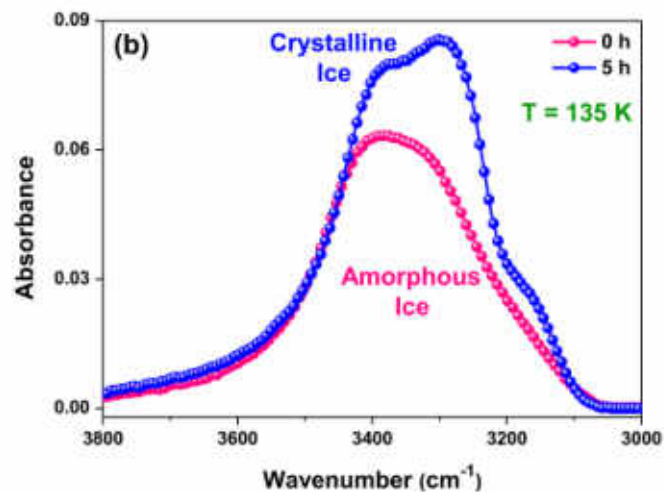
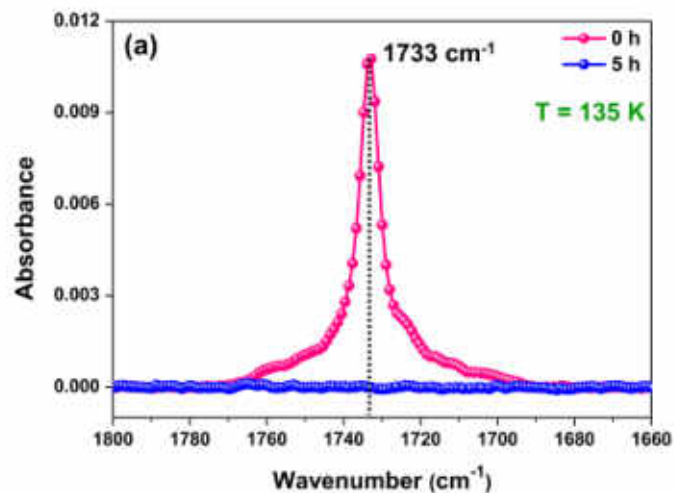
Facile crystallization of ice I_h via formaldehyde hydrate in ultrahigh vacuum under cryogenic conditions

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

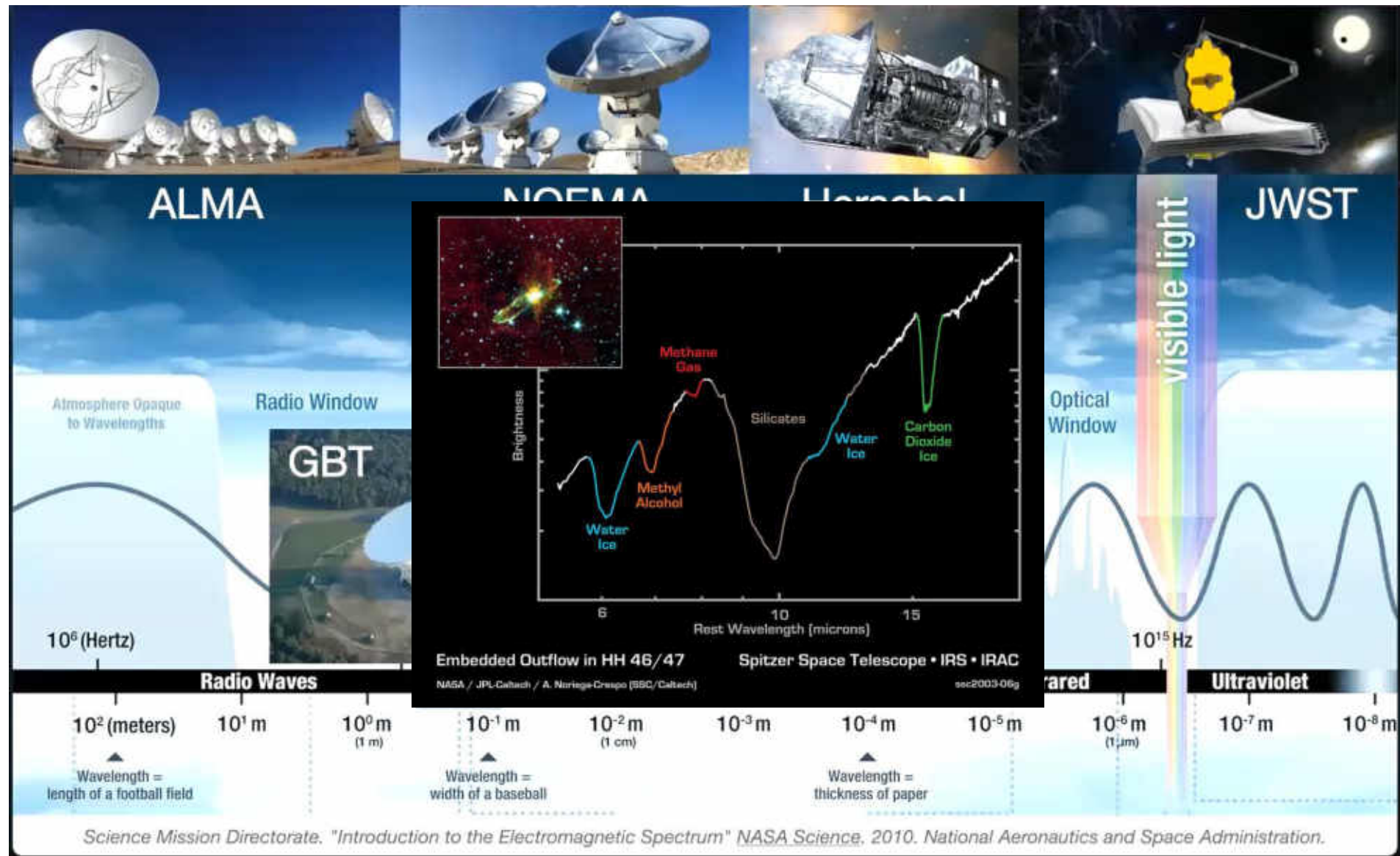
Ghosh J. *et al.*, *J. Phys. Chem. C* 2021, 125, 4532–4539

Formation of hexagonal ice via clathrate hydrate

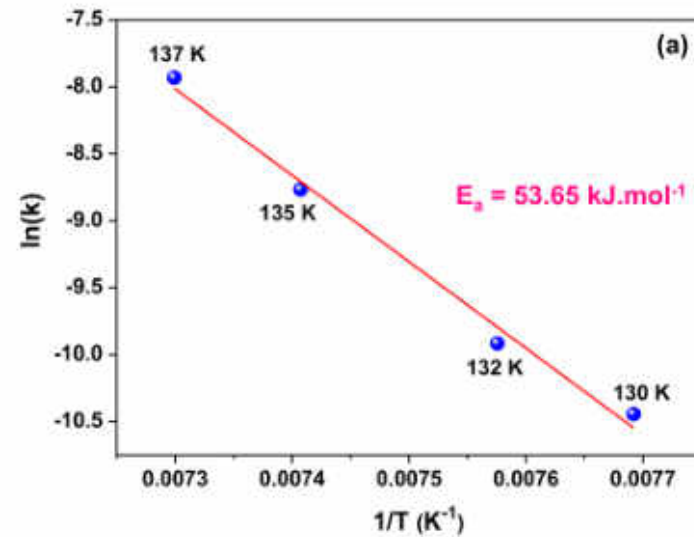
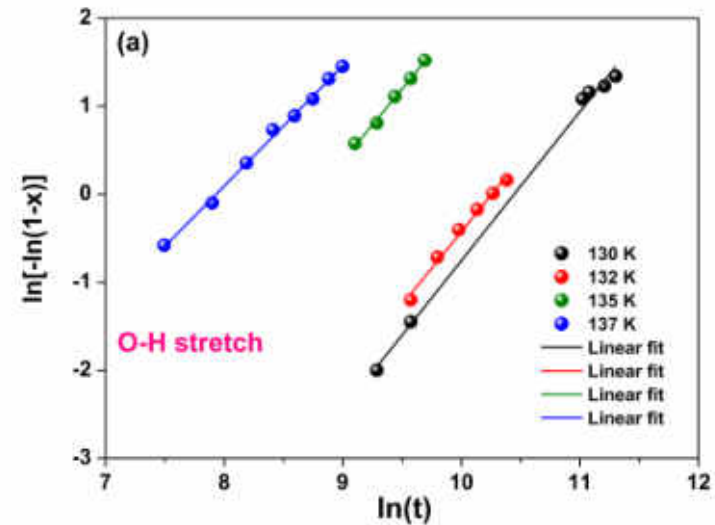
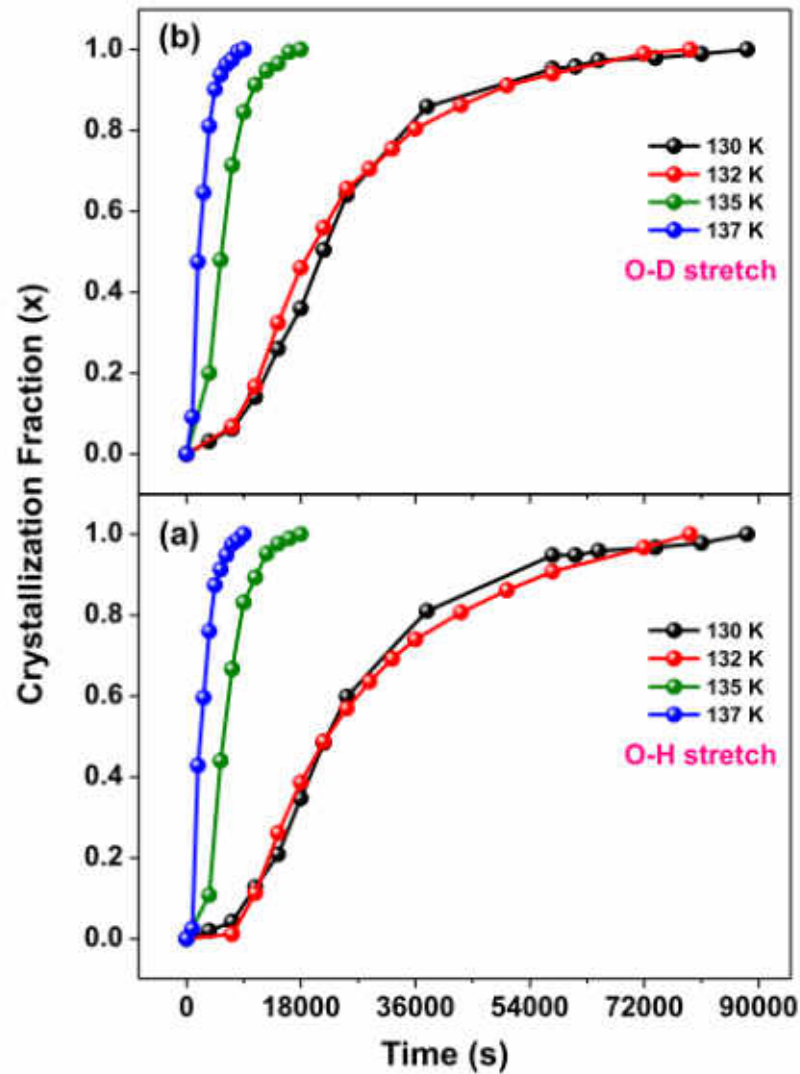
300 ML HCHO+H₂O (1:1)



Astronomical spectroscopy



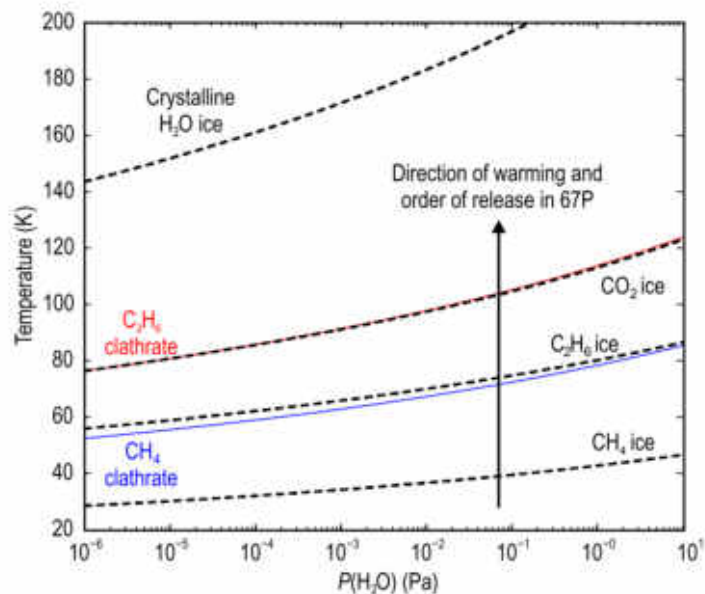
Crystallization Kinetics



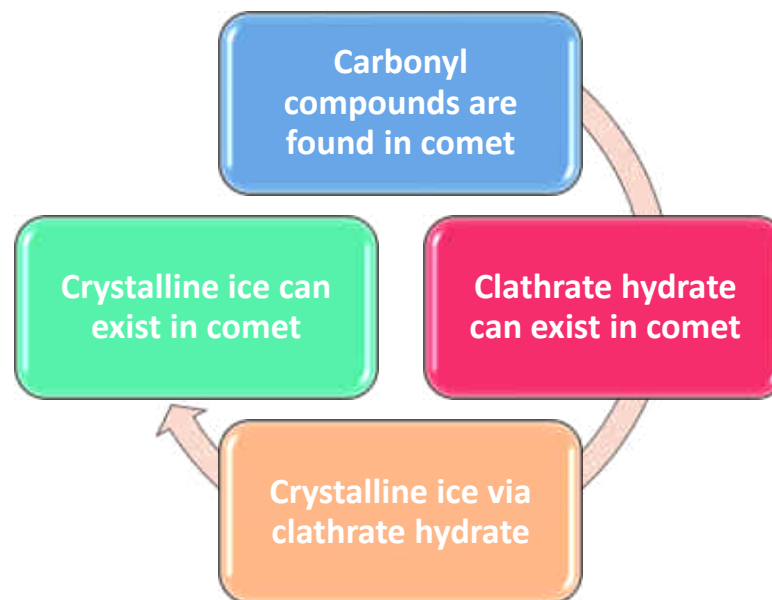
Conclusions

- ▲ 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

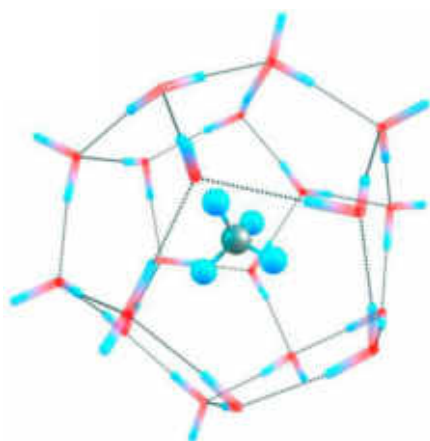


Missing puzzle

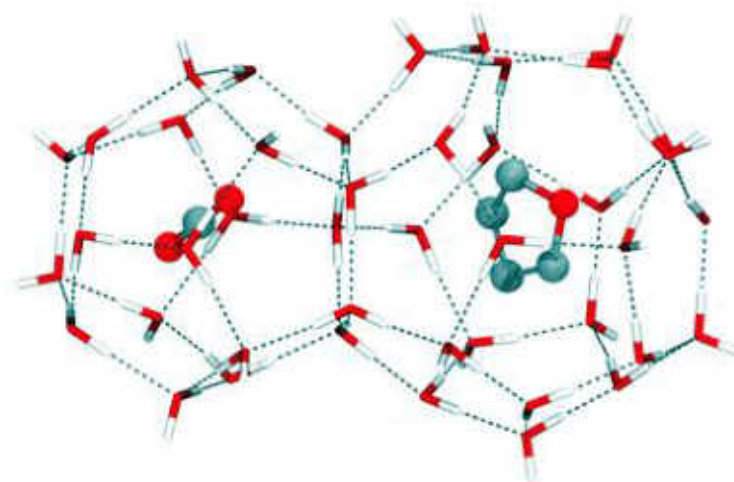


Induced migration of CO₂ from hydrate cages to amorphous solid water under ultrahigh vacuum and cryogenic conditions

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

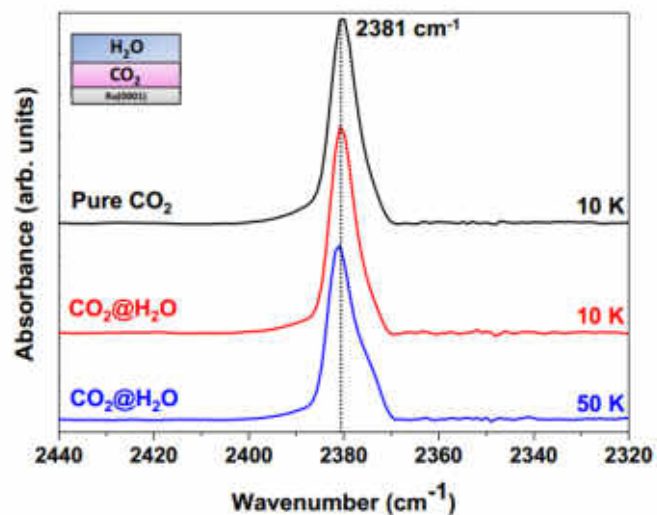
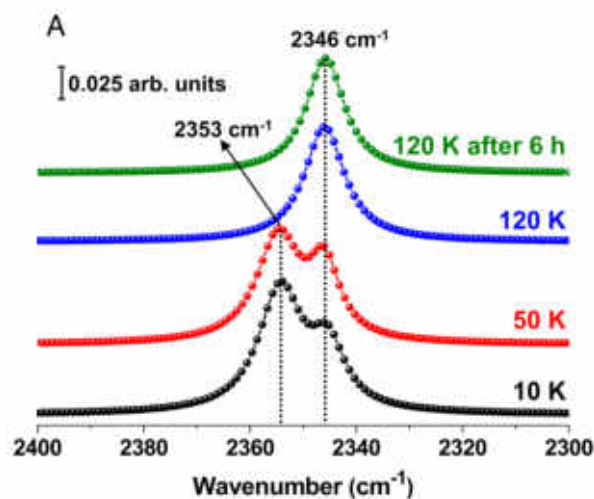


CH₄@5¹²

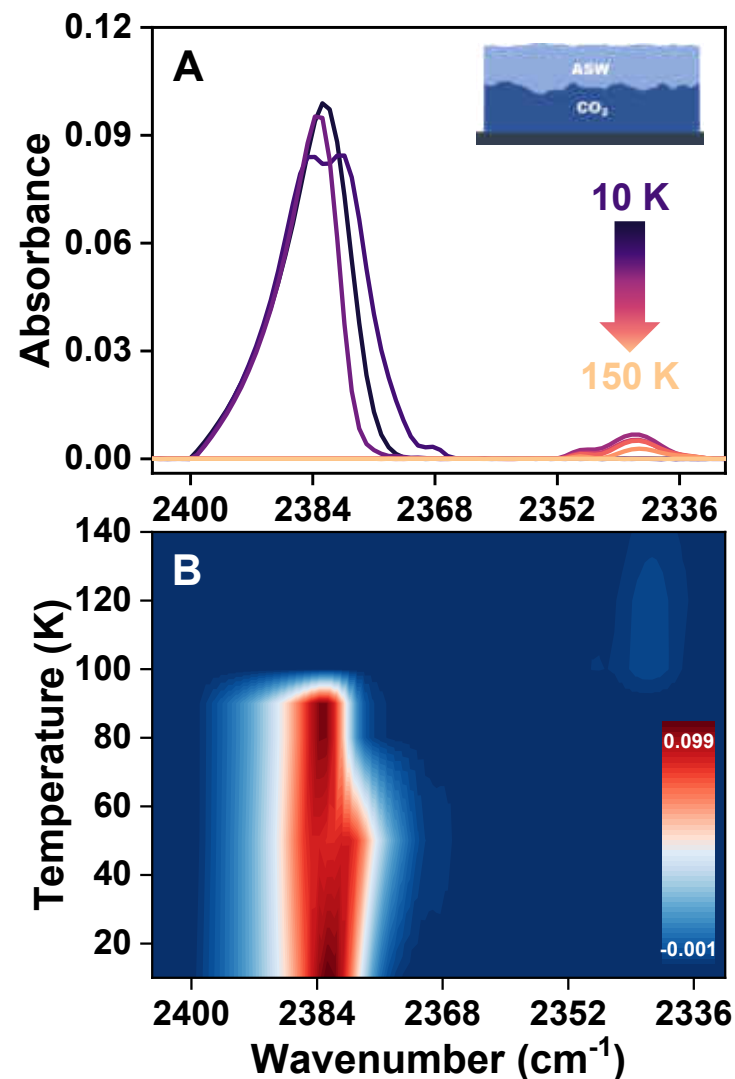


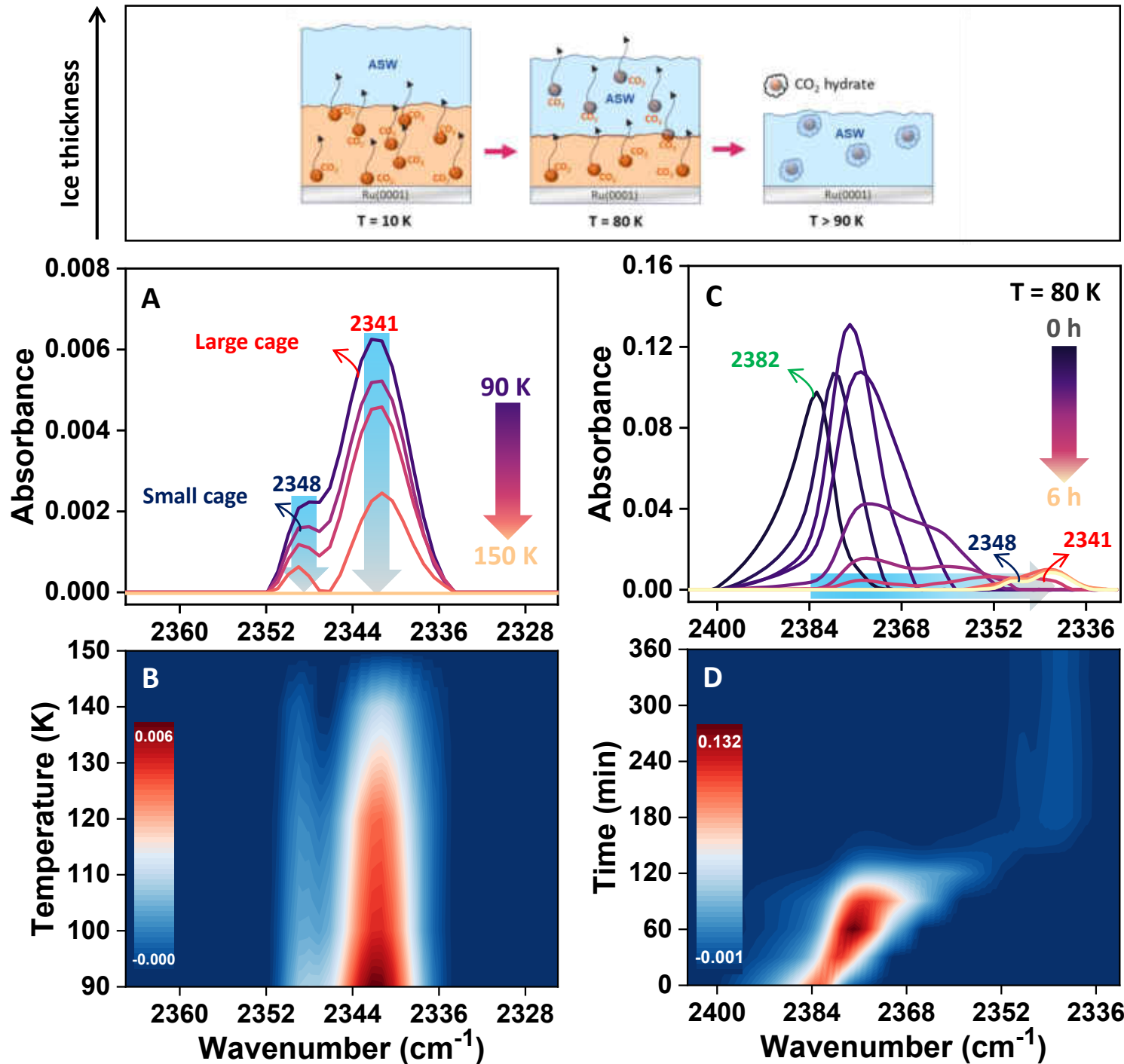
CO₂@5¹² and THF@5¹² 6⁴ cage

Clathrate hydrates in interstellar environment

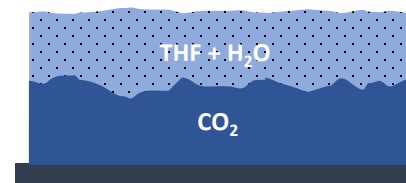
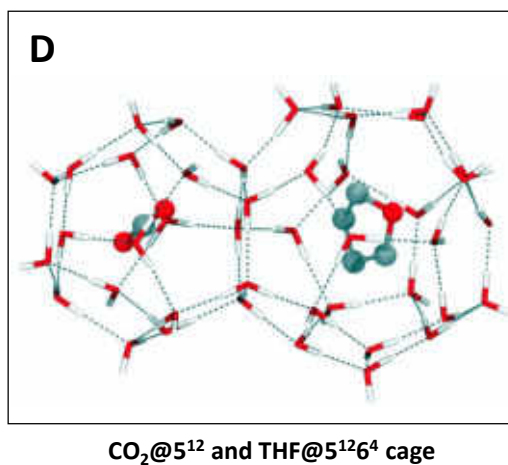
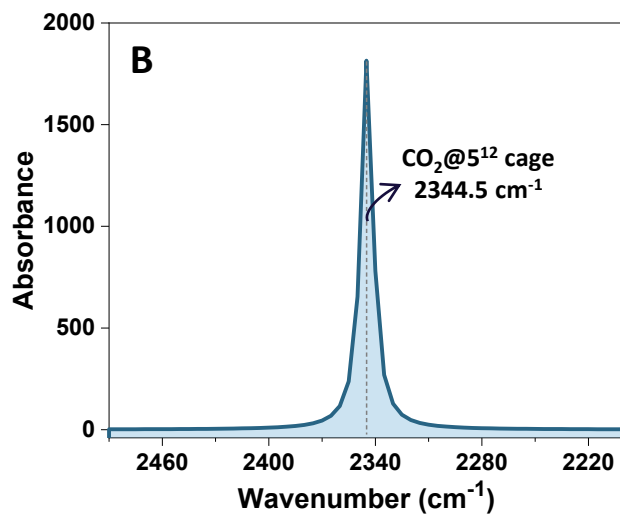
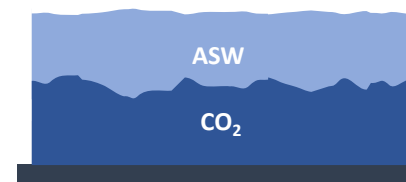
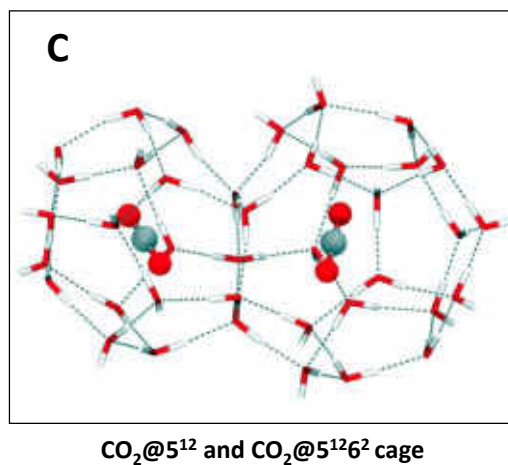
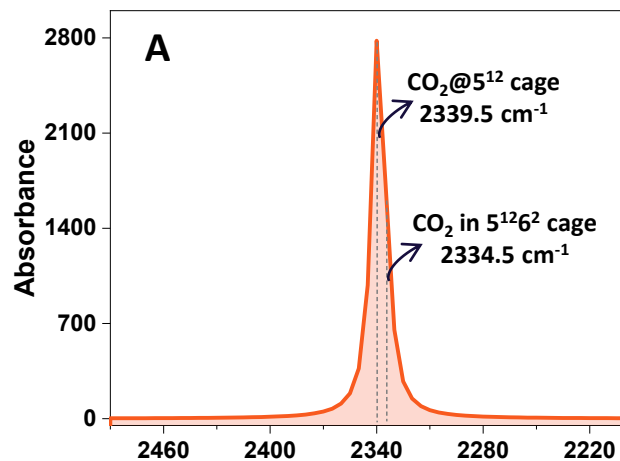


150 ML CO₂@150 ML H₂O



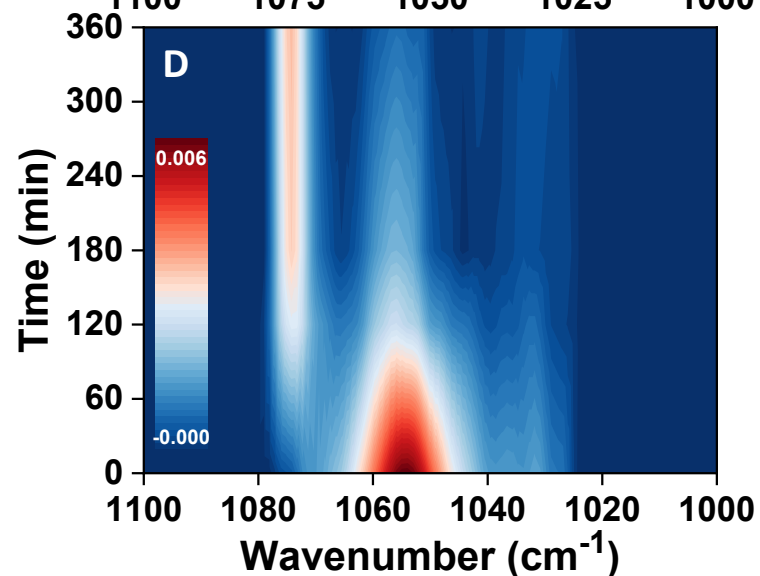
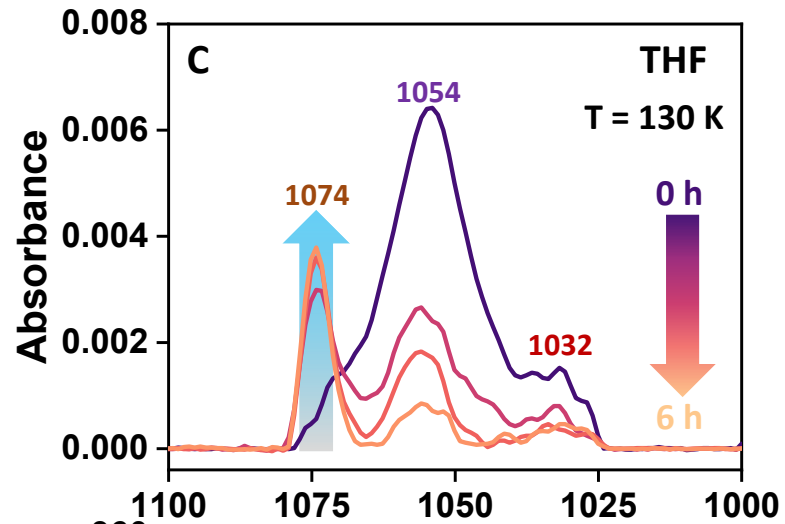
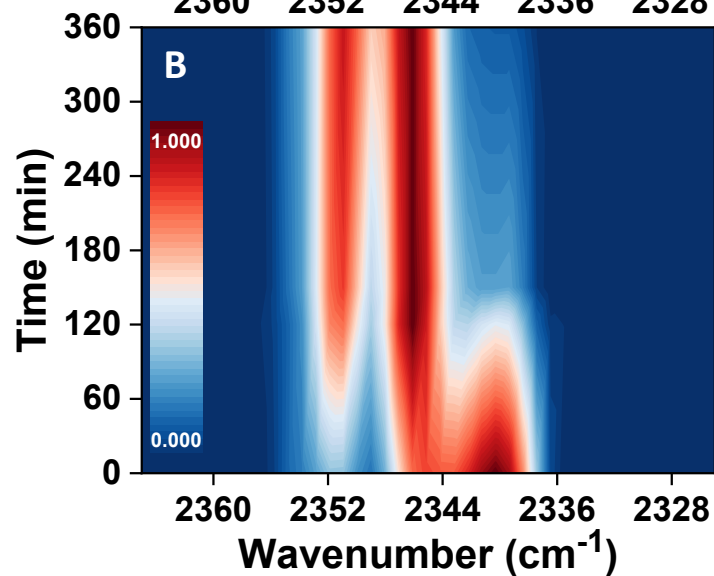
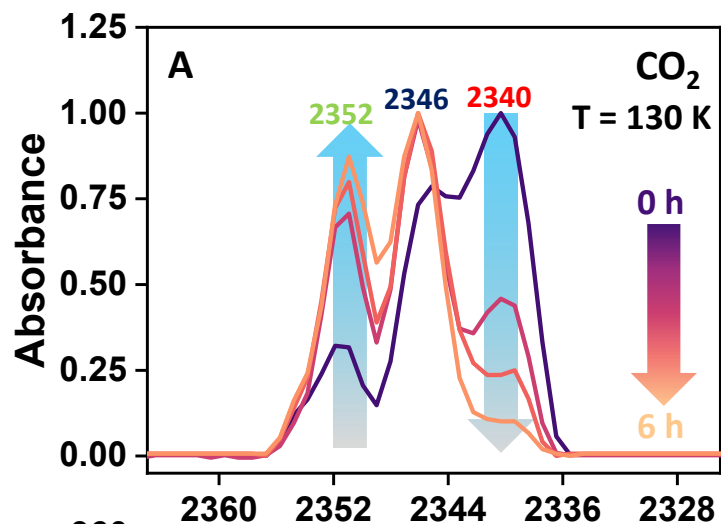


Quantum chemical calculation



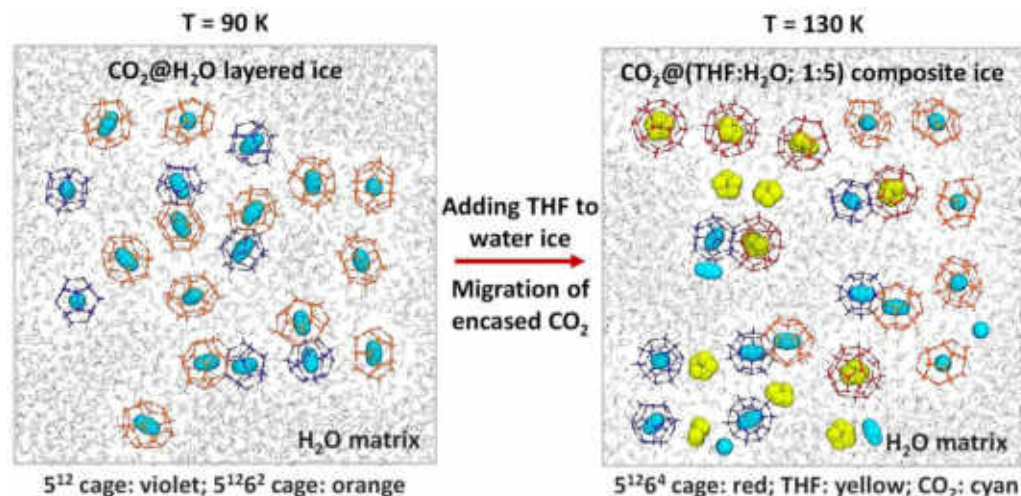
10 - 90 K
90 - 130 K

Mixed clathrate hydrate of CO₂-THF



Conclusions

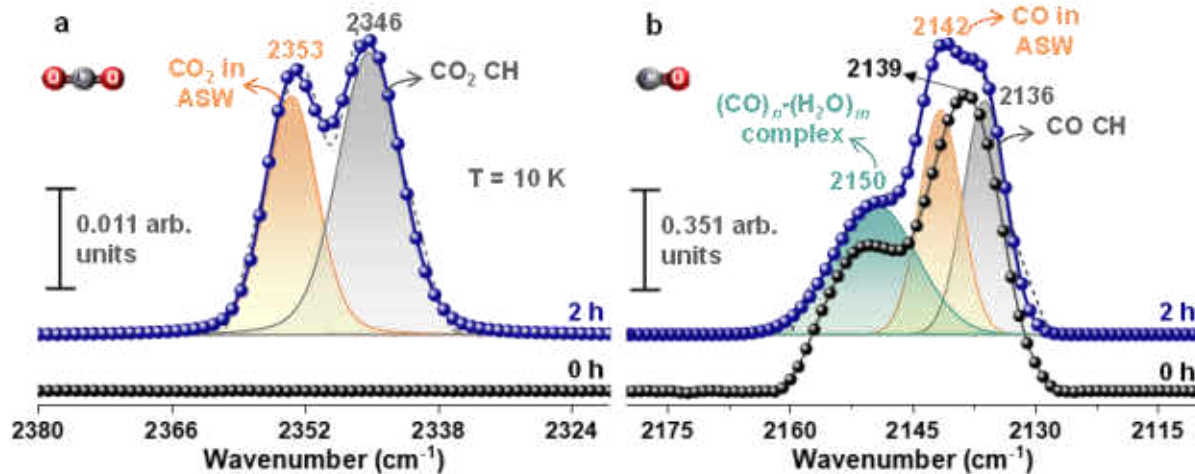
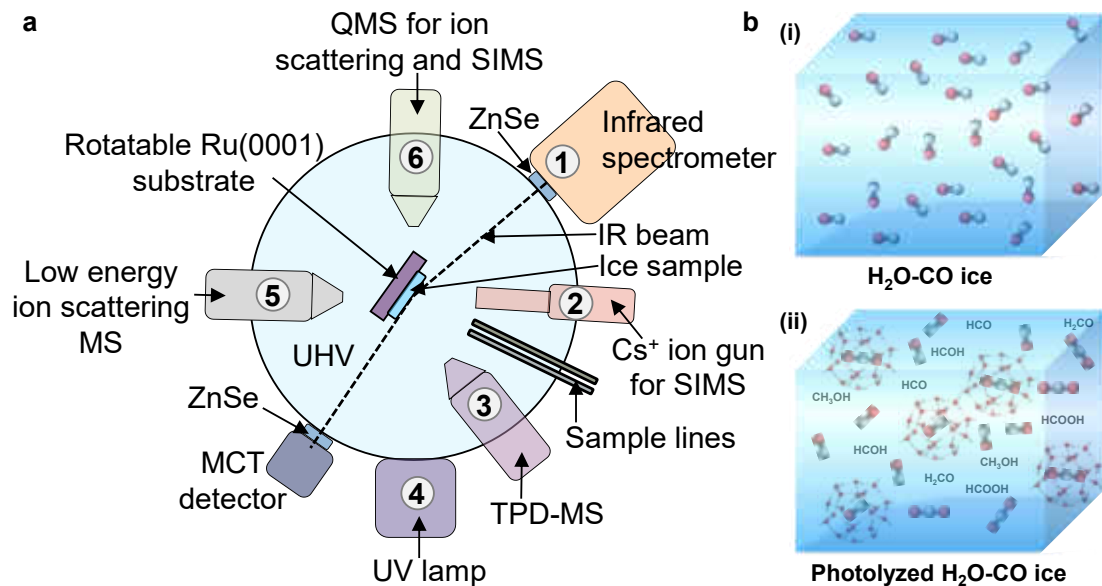
- ▲ We have studied the migration of CO_2 from the CH cages to the matrix of ASW in presence of THF under UHV and cryogenic conditions.
- ▲ We demonstrated the partitioning of CO_2 in $\text{CO}_2@5^{12}$ and $\text{CO}_2@5^{12}6^2$ cages of sl at 90 K without the 'help guest'.
- ▲ We have prepared mixed CH of CO_2 with THF.



Partitioning photochemically formed CO₂ into clathrate hydrate in interstellar conditions

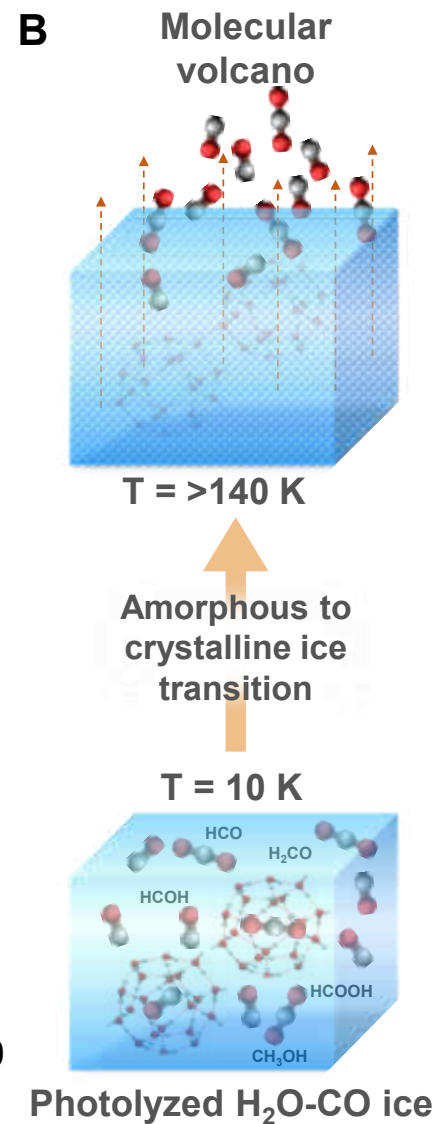
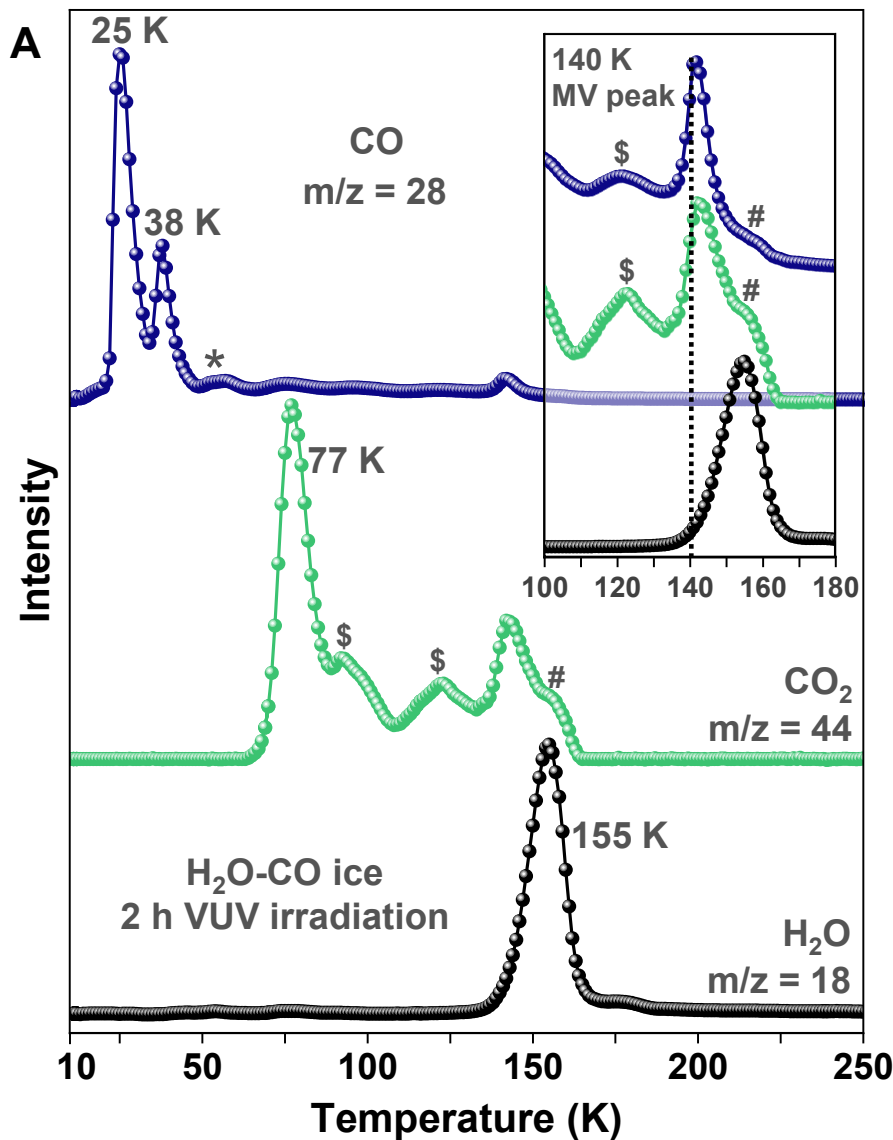
Vishwakarma, G. *et al.*, **2023** (Under consideration)

Partitioning photochemically formed CO_2



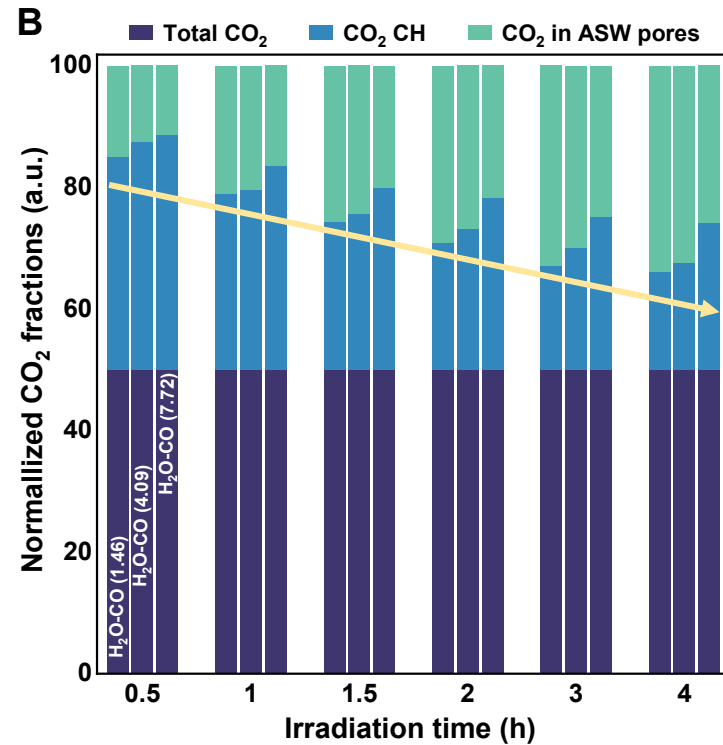
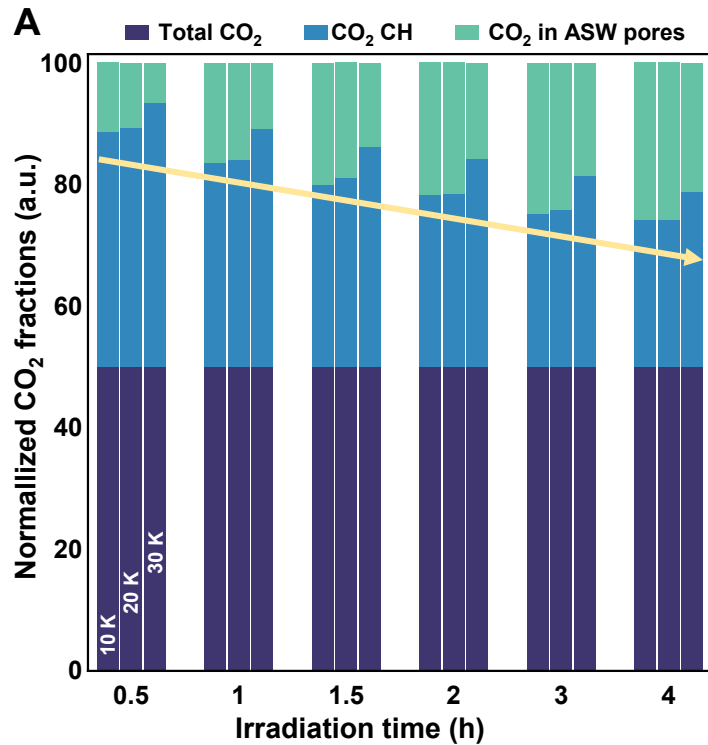
Partitioning photochemically formed CO_2

TPD mass spectrometric analysis of photolyzed H_2O - CO mixture



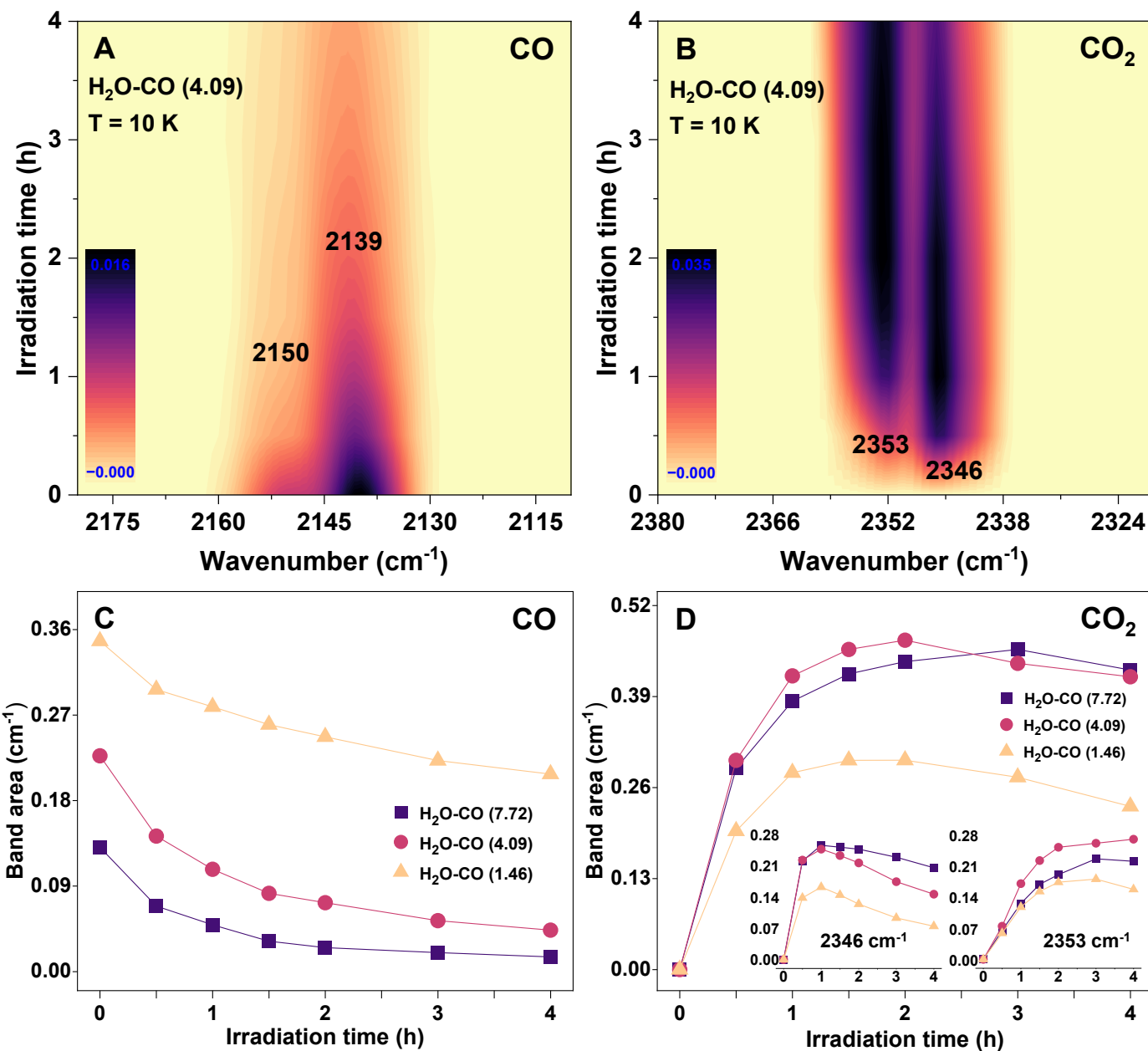
Partitioning photochemically formed CO₂

Trends of photochemically produced CO₂ partitioning at different temperatures and H₂O-CO compositions



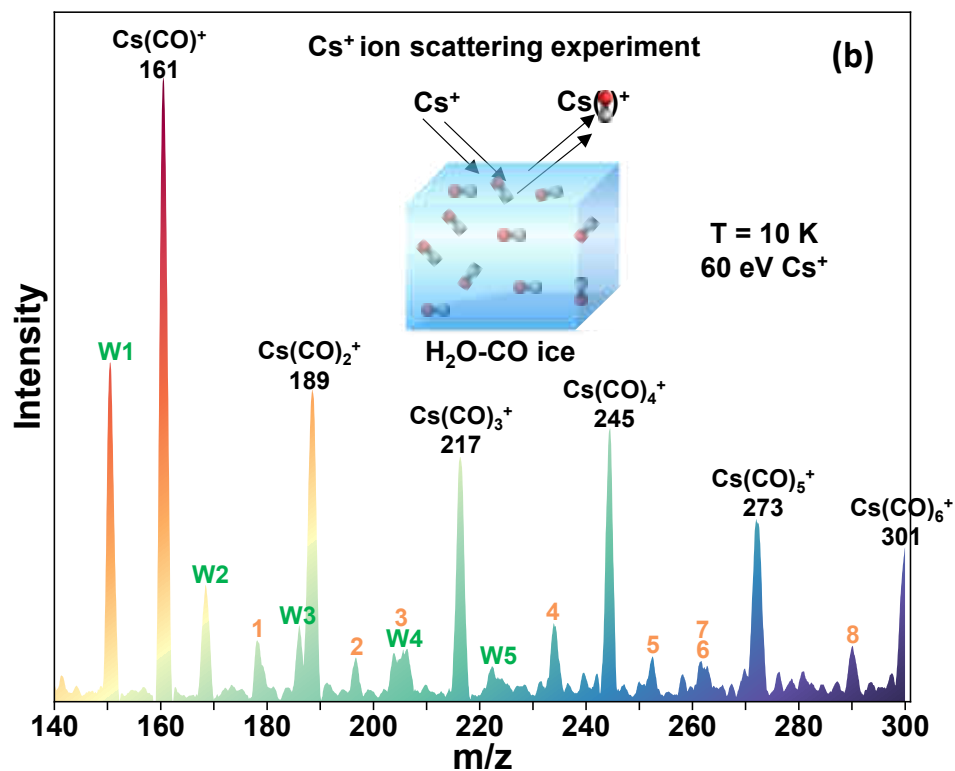
Partitioning photochemically formed CO₂

Composition-dependent experiments

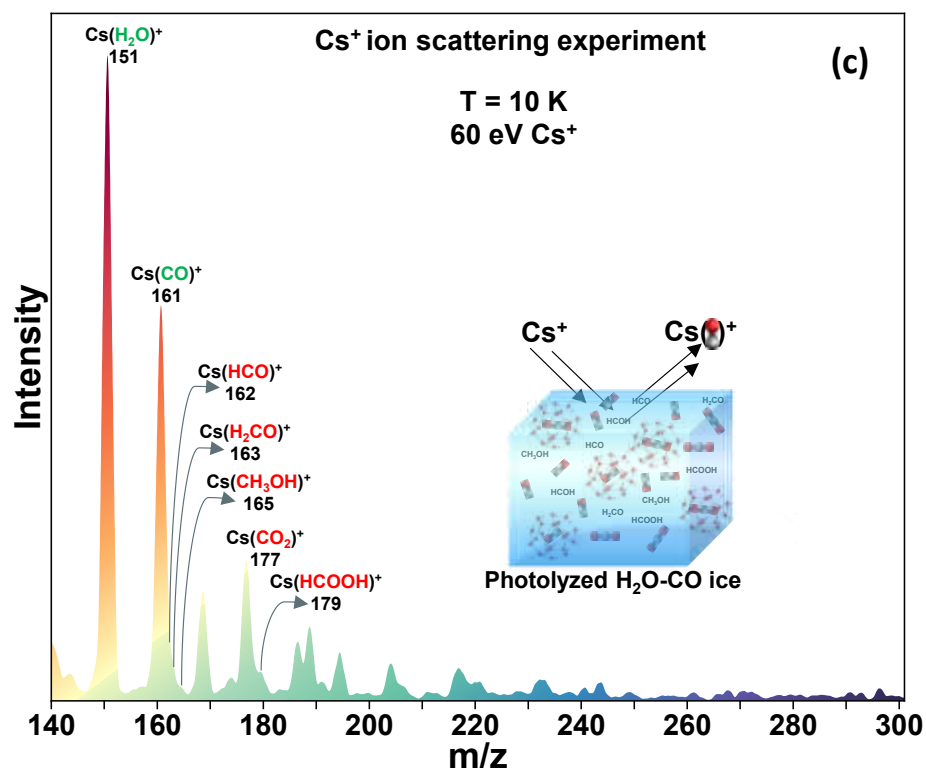
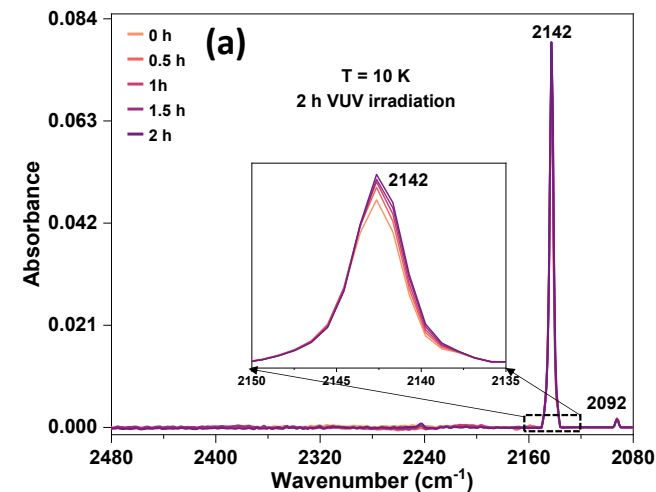


Surface structure of H₂O-CO ice

Cs⁺ ion scattering analysis of the surface of (a) unirradiated, (b) irradiated H₂O-CO mixture



(1) CO(H ₂ O) = 179	(3) H ₂ O(CO) ₂ = 207	(6) (CO) ₂ (H ₂ O) ₄ = 261
(2) CO(H ₂ O) ₂ = 197	(4) H ₂ O(CO) ₃ = 235	(7) H ₂ O(CO) ₄ = 263
	(5) (H ₂ O) ₂ (CO) ₃ = 253	(8) H ₂ O(CO) ₅ = 291



Existence of clathrate hydrates under UHV

ACCOUNTS

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Article

Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

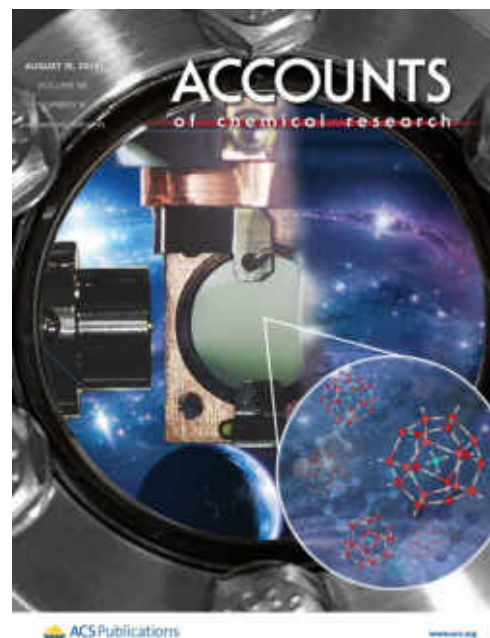
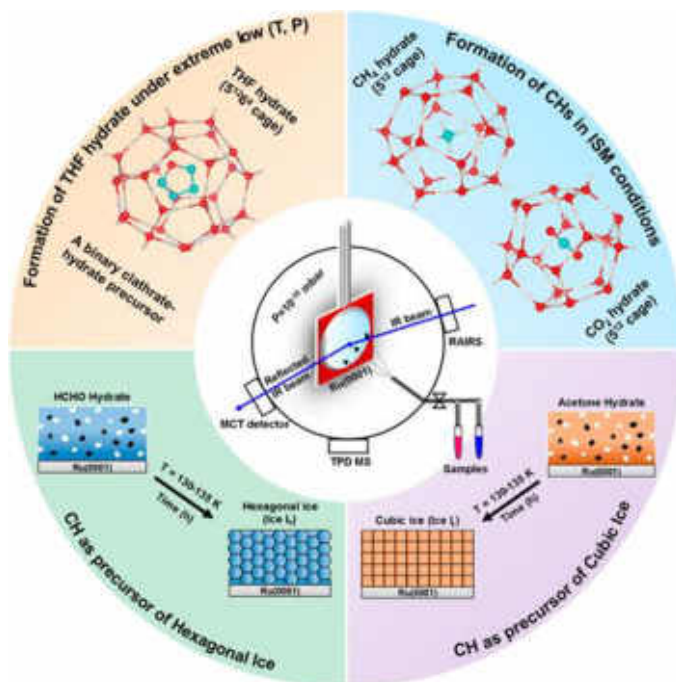
Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,^{*} and Thalappil Pradeep^{*}



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



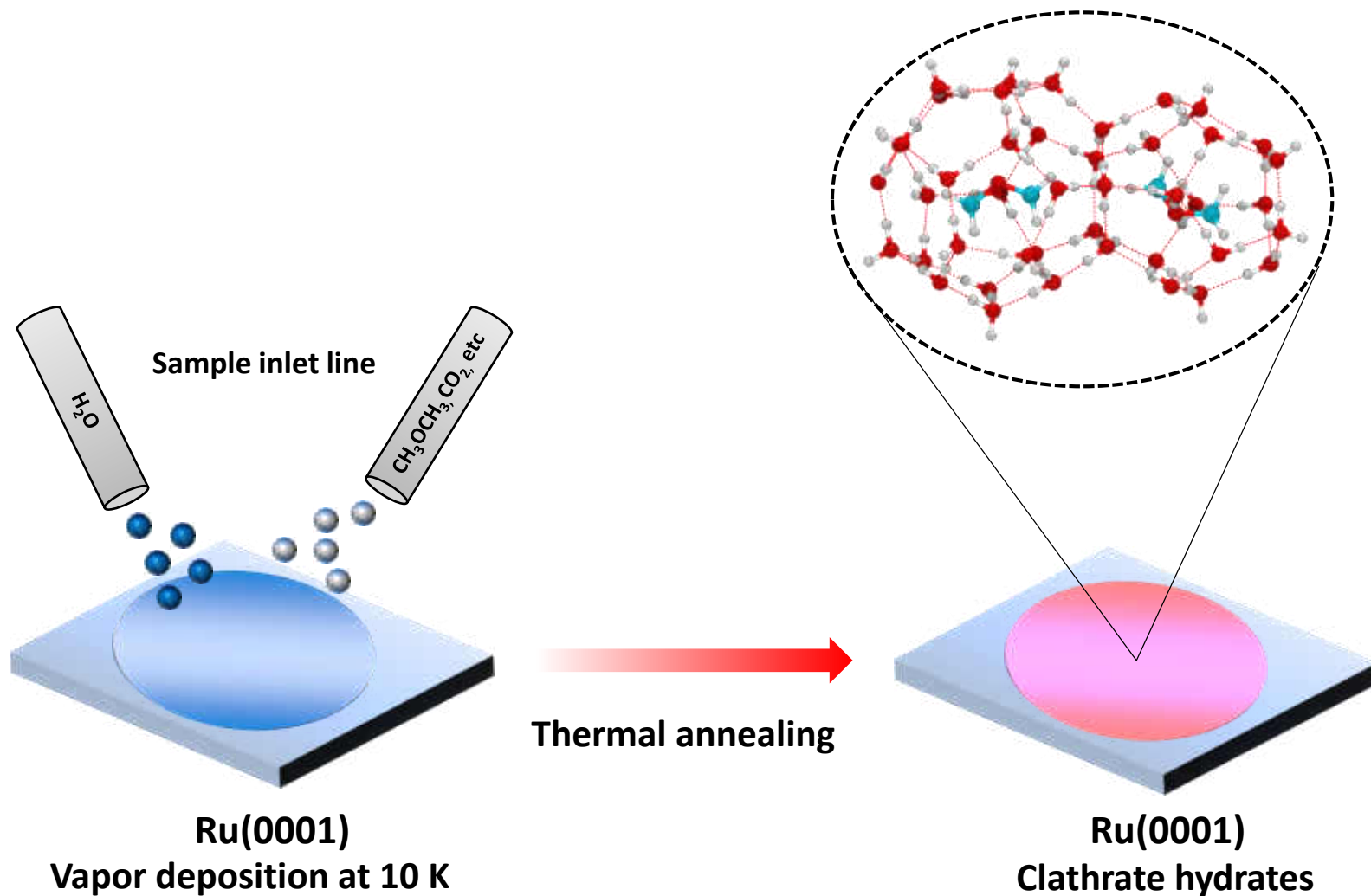
Read Online



Thank you

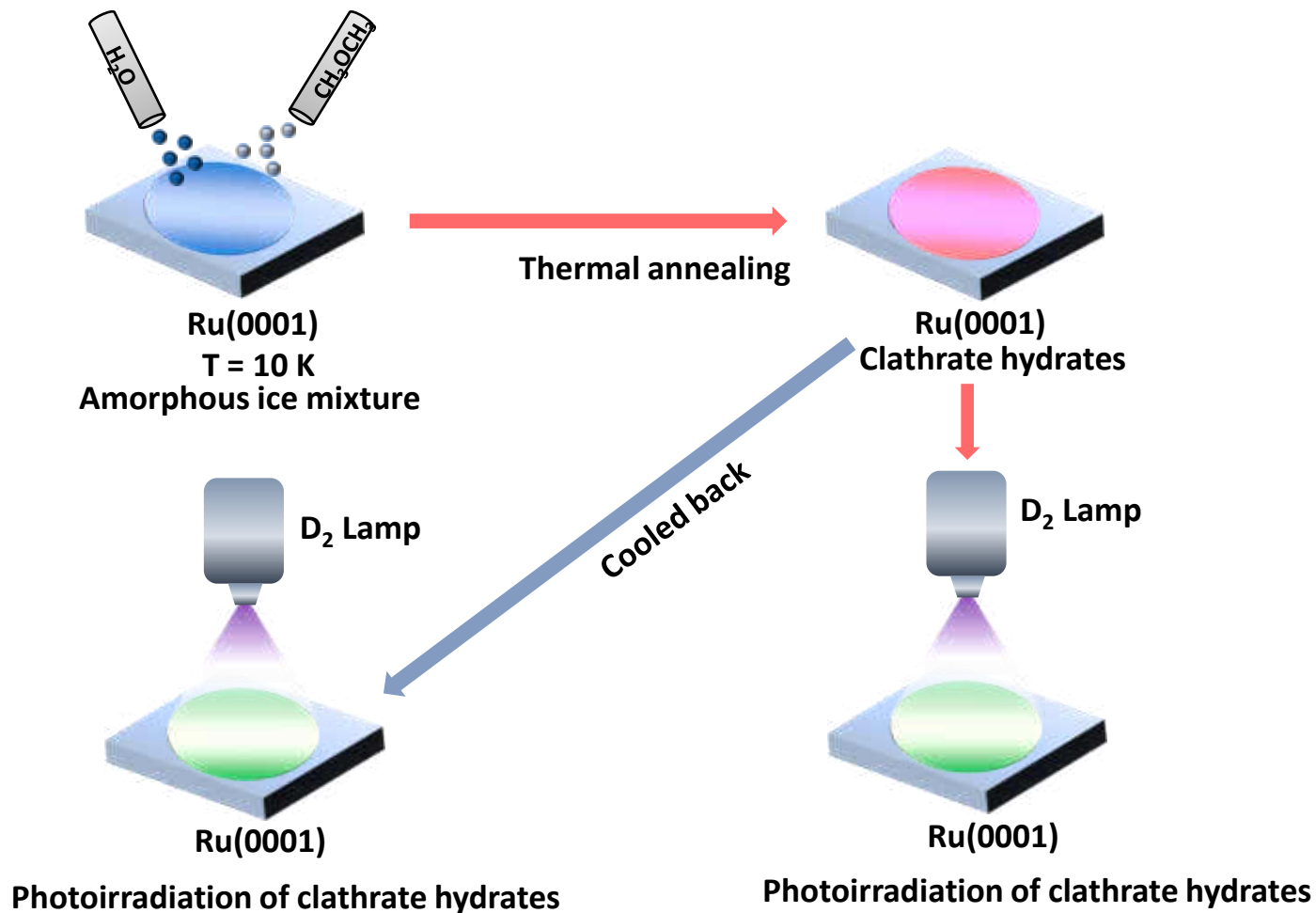
Research proposal - 1

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



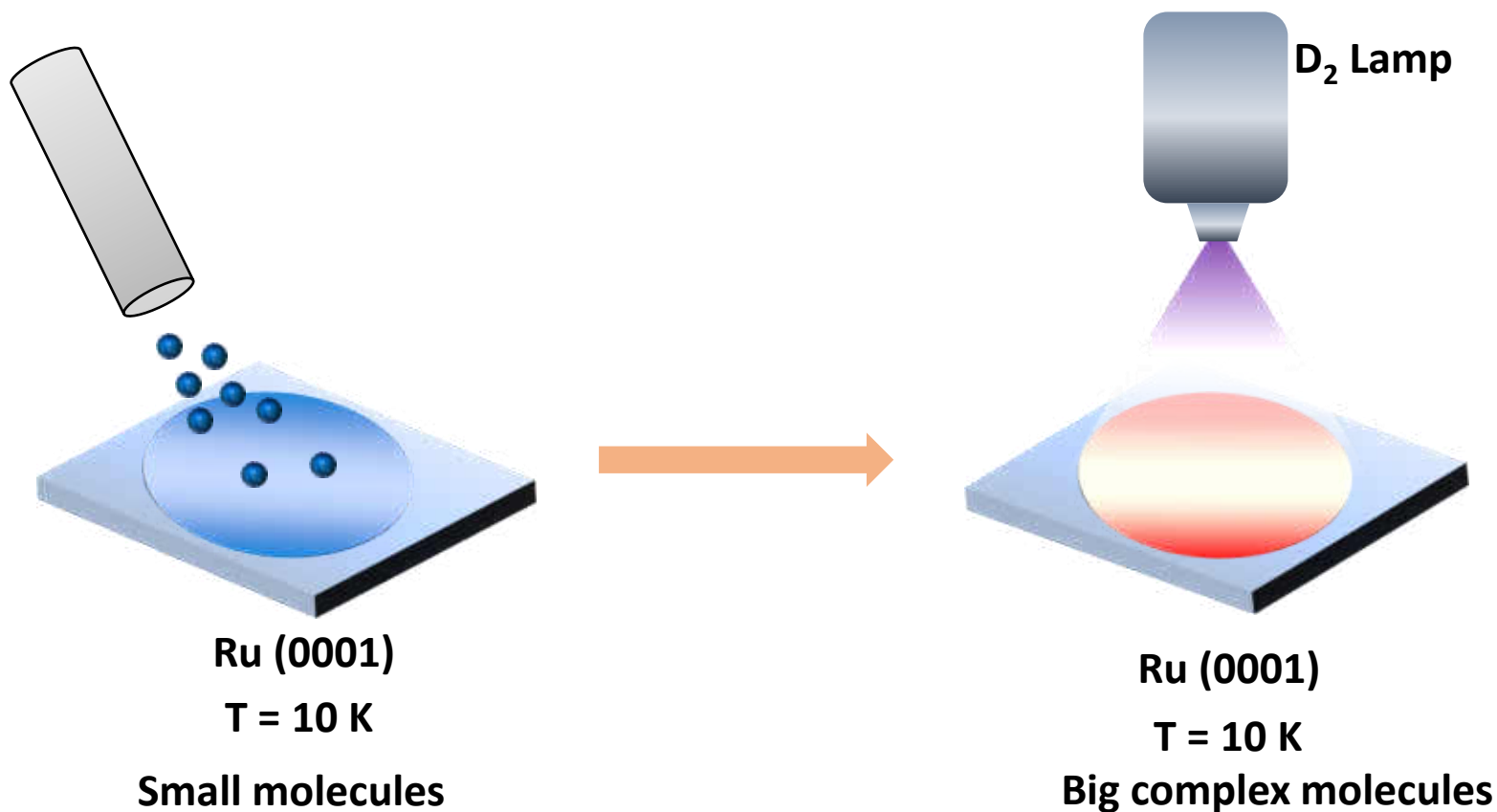
Research proposal - 2

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

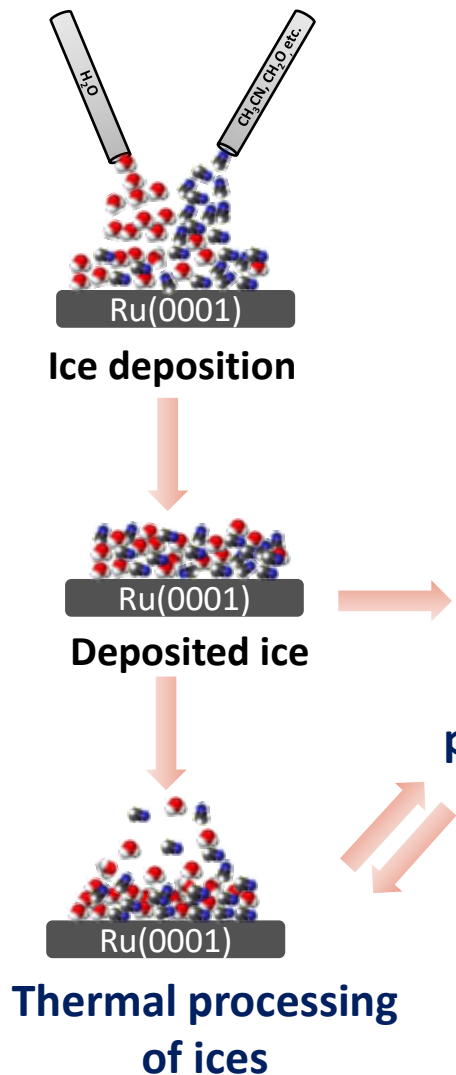


Research proposal - 3

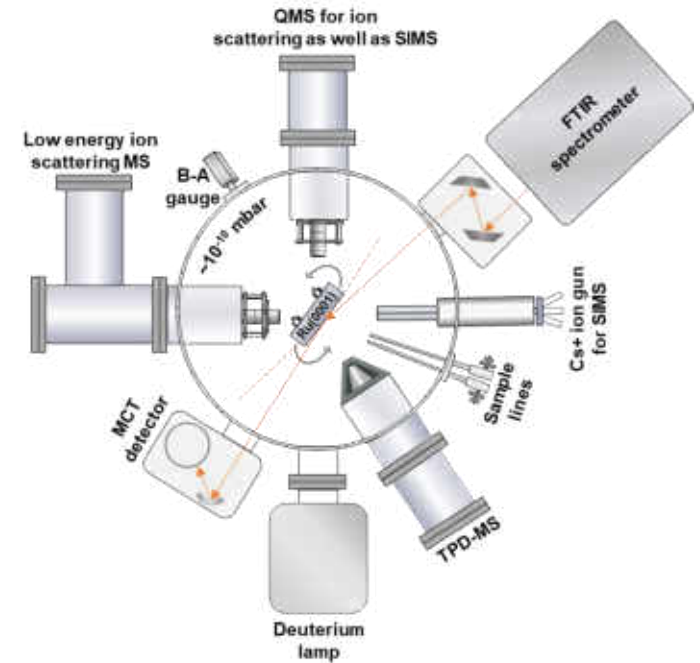
Explore the chemistry behind the formation of complex molecules under vacuum ultraviolet radiation.



Experimental procedure

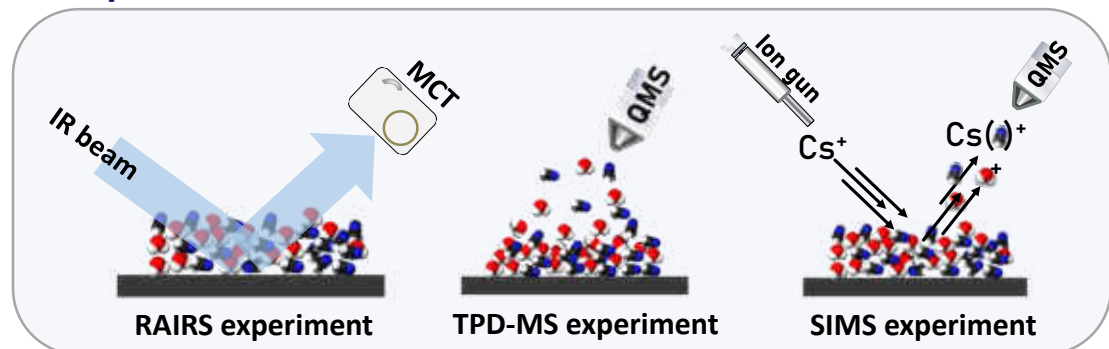


- ▲ Low energy ion scattering (LEIS)
- ▲ TPD-MS
- ▲ RAIRS
- ▲ Low energy Cs⁺ ion gun
- ▲ Vacuum UV lamp



Schematic diagram of the experimental setup

Experimental tools



Molecules detected in interstellar medium

2 atoms	CS	HCO ⁺	KCN	H ₃ O ⁺	HCOOH	<i>l</i> -HC ₄ N	CH ₂ CHCHO	CH ₃ OCH ₂ OH
H ₂	HF	HCS ⁺	FeCN	NH ₃	H ₂ CNH	<i>c</i> -H ₂ C ₃ O	CH ₂ CCHCN	11 atoms
AlF	SH	HOC ⁺	HO ₂	<i>c</i> -SiC ₃	H ₂ C ₃ O	C ₅ N ⁺	H ₂ NCH ₂ CN	HC ₄ N
AlCl	SH ⁺	H ₂ O	TiO ₂	CH ₃	H ₂ NCN	E-HNCHCN	CH ₃ CHNH	CH ₃ C ₆ H
C ₂	FeO	H ₂ S	C ₂ N	C ₃ N ⁺	HNC ₃	SiH ₃ CN	CH ₃ SiH ₃	C ₂ H ₅ OCHO
CH	O ₂	HNC	SiCSi	PH ₃	SiH ₄	CH ₂ CNH	C ₂ H ₅ N	CH ₃ OC(O)CH ₃
CH ⁺	CF ⁺	HNO	S ₂ H	HCNO	H ₂ COH ⁺	C ₅ S	(NH ₂) ₂ CO	12 atoms
CN	PO	MgCN	HCS	HOCN	C ₄ H ⁺	7 atoms	9 atoms	<i>c</i> -C ₅ H ₆
CO	AlO	MgNC	HSC	HSCN	HC(O)CN	C ₅ H	CH ₃ C ₄ H	C ₅ H ₇ CN
CO ⁺	CN ⁺	N ₂ H ⁺	NCO	H ₂ O ₂	HNCNH	CH ₂ CHCN	CH ₃ CH ₂ CN	<i>t</i> -C ₂ H ₅ OCH ₃
CP	HCl ⁺	N ₂ O	OCN ⁺	<i>l</i> -C ₃ H ⁺	CH ₃ O	HC ₃ N	(CH ₃) ₂ O	>12 atoms
CSi	TiO	NaCN	4 atoms	HMgNC	H ₂ NCO ⁺	CH ₃ CHO	CH ₃ CH ₂ OH	C ₆₀
HCl	ArH ⁺	OCS	C ₃ H ⁺	HCCO	NCCNH ⁺	NH ₂ CH ₃	HC ₇ N	C ₆₀ ⁺
KCl	N ₂	SO ₂	<i>l</i> -C ₃ H ⁺	CH ₃ Cl	NH ₃ D ⁺	<i>c</i> -C ₂ H ₄ O	C ₈ H	C ₇₀
NH	NO ⁺	<i>c</i> -SiC ₂	C ₃ N	CNCN	6 atoms	H ₂ CCHOH	CH ₃ C(O)NH ₂	<i>c</i> -C ₆ H ₅ CN
NO	NS ⁺	CO ₂	C ₃ O	MgCCH	C ₅ H	C ₆ H ⁺	C ₈ H ⁺	CO(CH ₂ OH) ₂ ?
NS	LiH	NH ₂	C ₃ S	NCCP	<i>l</i> -C ₄ H ₂	CH ₃ NCO	C ₃ H ₆	C ₁₄ H ₁₀ ?
NaCl	CrO	H ₃ ⁺	C ₂ H ₂	5 atoms	C ₃ H ₄	HC ₅ O	CH ₃ CH ₂ SH	C ₁₄ H ₁₀ ⁺
OH	3 atoms	SiCN	HC ₃ N	C ₅	CH ₃ CN	8 atoms	CH ₃ NHCHO	C ₆ H ₅ OH
OH ⁺	C ₃	AlNC	HCNH ⁺	C ₄ H	CH ₃ NC	CH ₃ C ₃ N	HC ₇ O	
PN	C ₂ H	SiNC	HNCO	C ₄ Si	CH ₃ OH	HC(O)OCH ₃	10 atoms	
SO	C ₂ O	HCP	HNCS	<i>c</i> -C ₃ H ₂	CH ₃ SH	CH ₃ COOH	CH ₃ C ₅ N	
SO ⁺	C ₂ S	CCP	HOCO ⁺	CH ₂ CN	HC ₃ NH ⁺	C ₇ H	(CH ₃) ₂ CO	
SiN	CH ₂	AlOH	H ₂ CO	CH ₄	HC ₂ CHO	H ₂ C ₆	(CH ₂ OH) ₂	
SiO	HCN	H ₂ O ⁺	H ₂ CN	HC ₃ N	NH ₂ CHO	CH ₂ OHCHO	CH ₃ CH ₂ CHO	
SiS	HCO	H ₂ Cl ⁺	H ₂ CS	HC ₂ NC	C ₅ N	<i>l</i> -C ₆ H ₂	CH ₃ CHCH ₂ O	

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

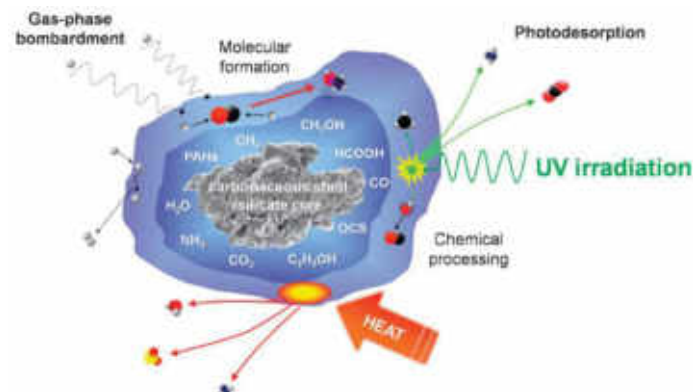
JWST

arXiv:2109.13848 [astro-ph.GA]

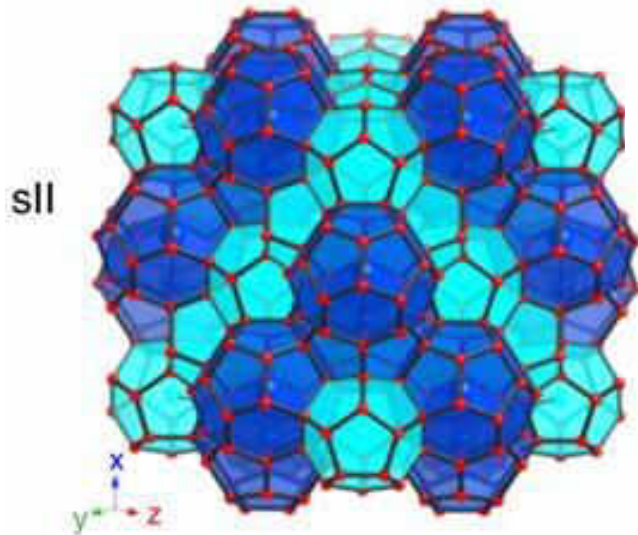
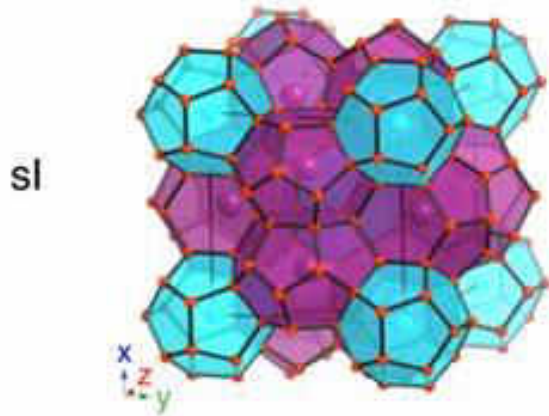
Arumainayagam, C. R. *et al.*, *Chem. Soc. Rev.* **2019**, 48, 2293–2314

Materials

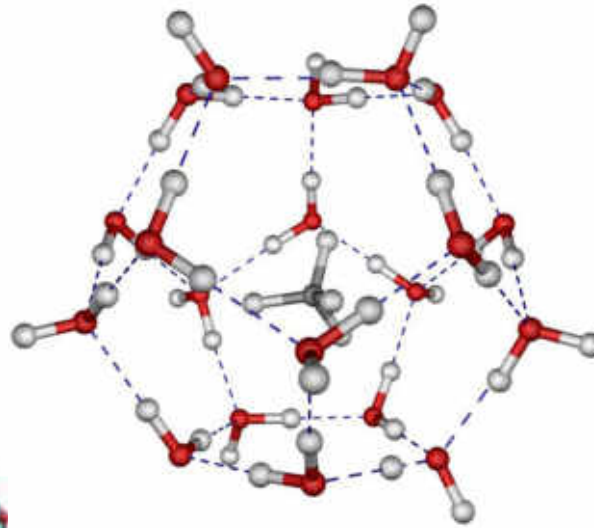
H₂O, CO₂, CO, CH₃CHO, CH₃CN, CH₄, HCHO, CH₃COCH₃, (CH₂)₄O



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

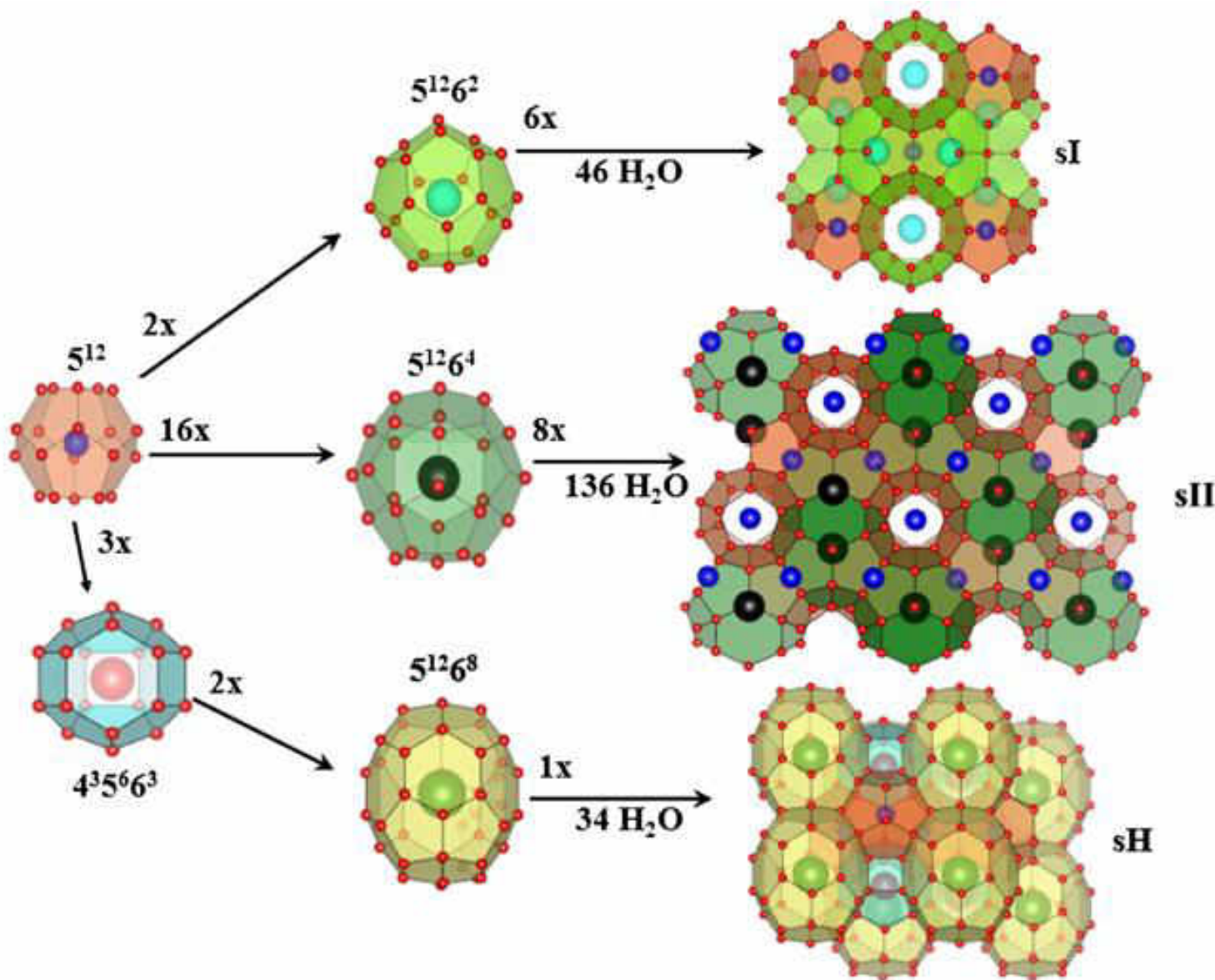
1965

Makogon first discovered the
natural source of methane
hydrate

1987

Ripmeester and coworkers
discovered a new hydrate
structure, termed as sH hydrate

Classification of clathrate hydrates



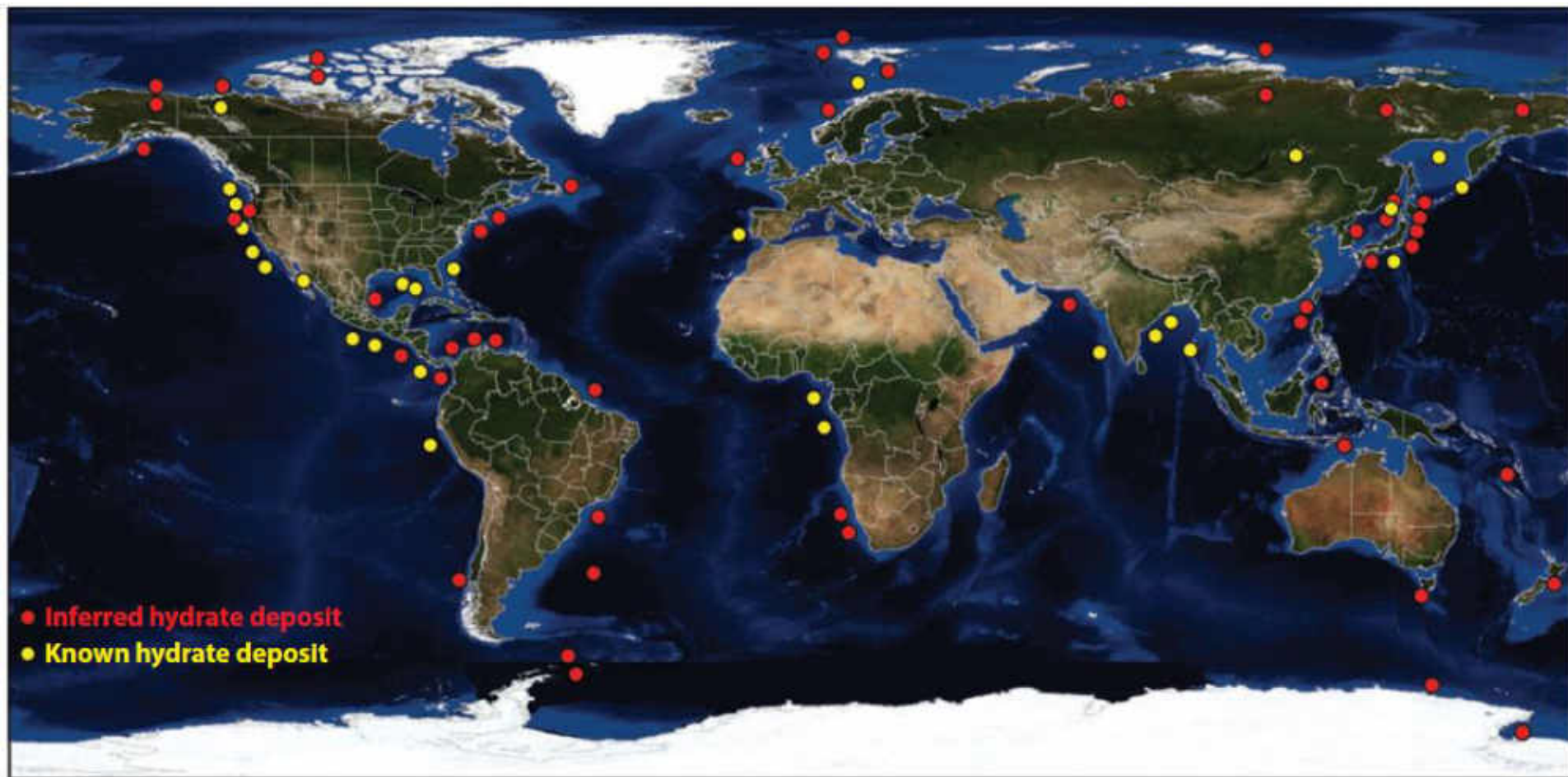
Methane,
ethane, carbon
dioxide, etc...

Propane, iso-
butane,
natural gases,
etc...

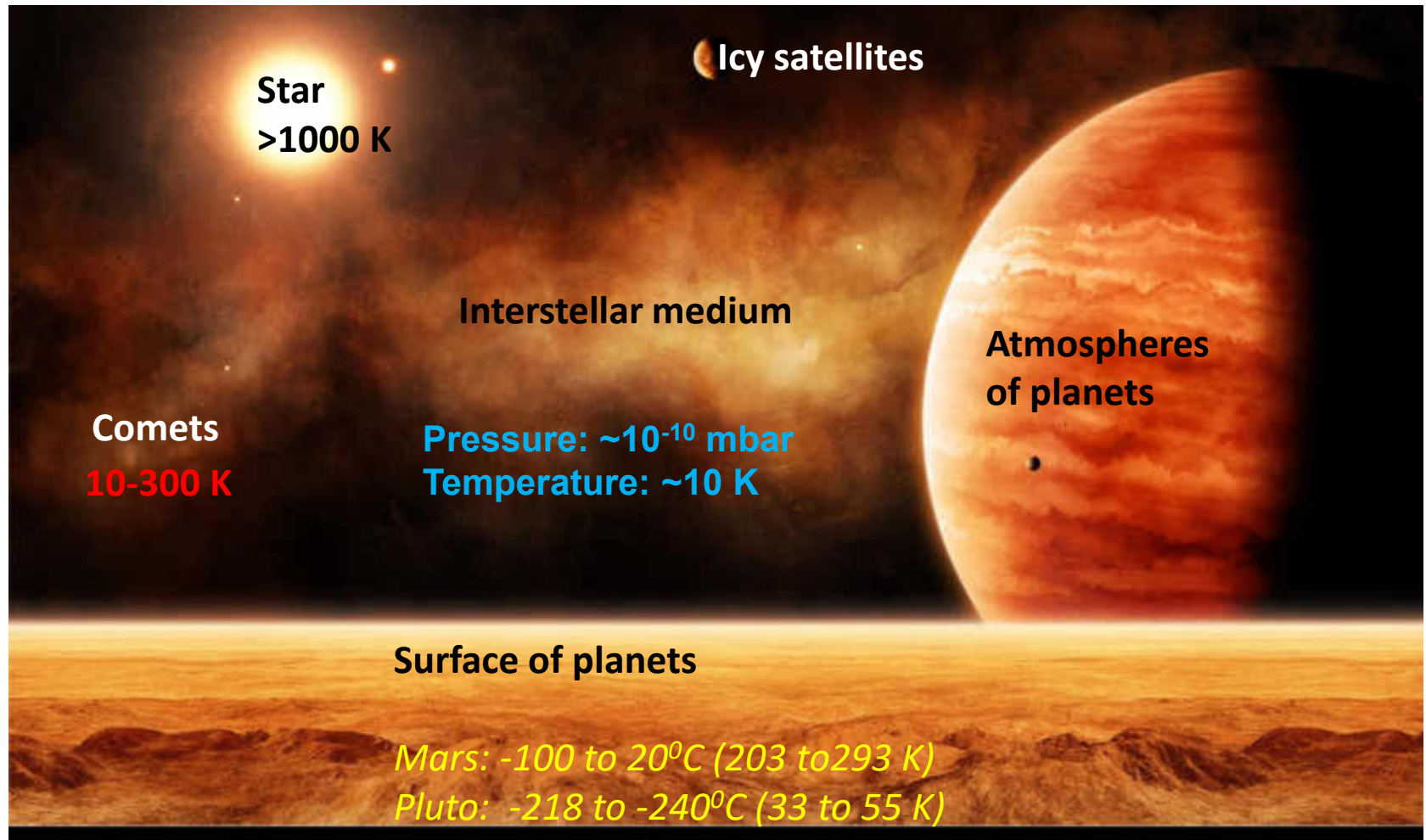
Methane+neo
hexane,
methane+cycl
oheptane,
etc...

Examples

Occurrence of clathrate hydrates

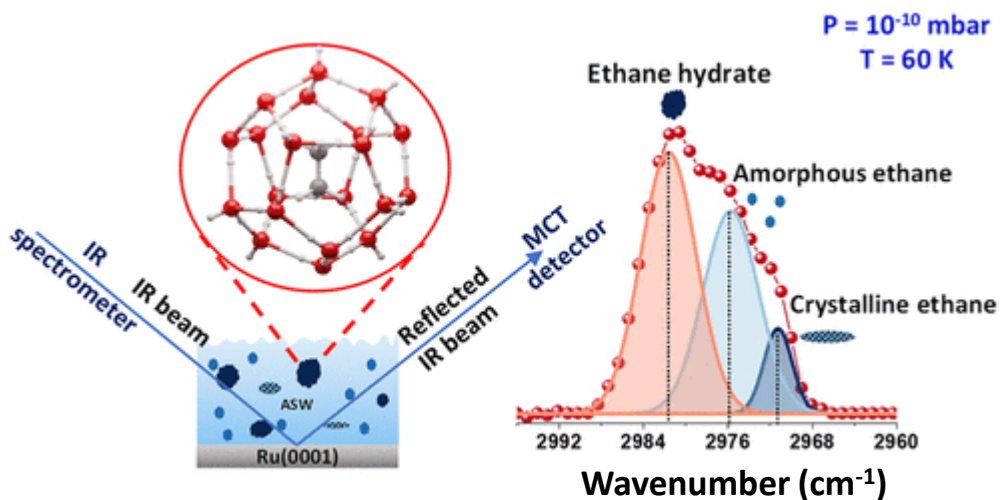


Interstellar medium (ISM)



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

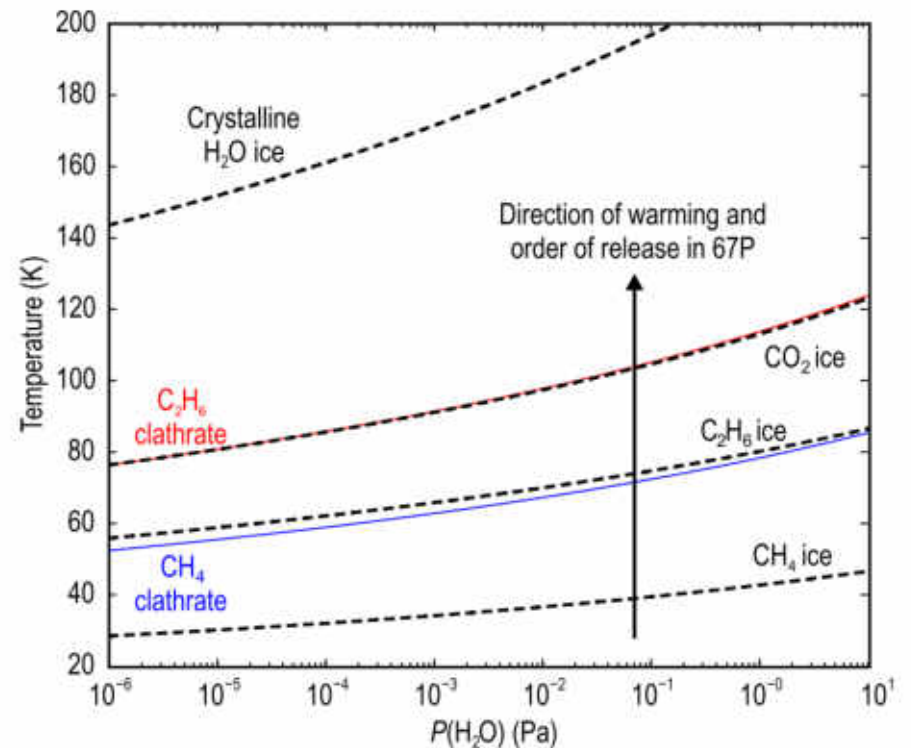
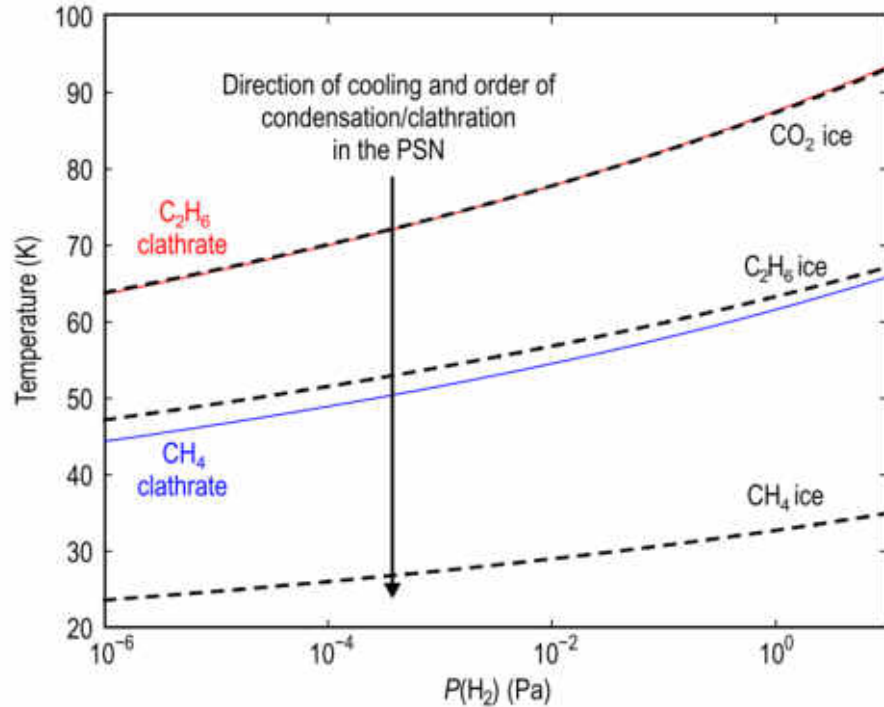


The presence of clathrates in comet 67P/Churyumov-Gerasimenko

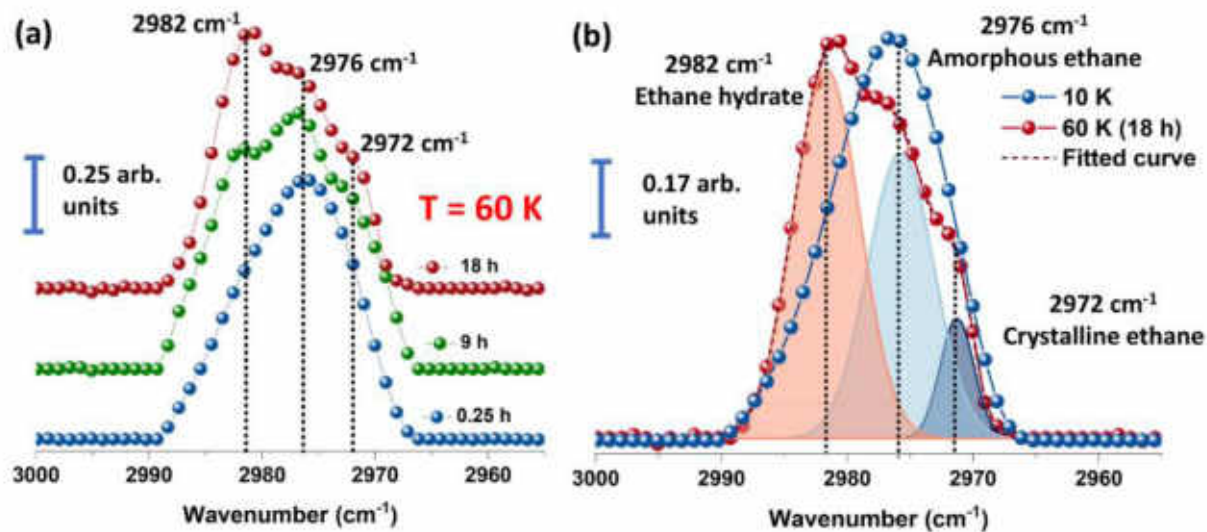
ADRIEN LUSPAY-KUTI, OLIVIER MOUSIS, MYRTHA HÄSSIG, STEPHEN A. FUSELIER, JONATHAN I. LUNINE, BERNARD MARTY, KATHLEEN E. MANDT, PETER WURZ

AND MARTIN RUBIN [Authors Info & Affiliations](#)

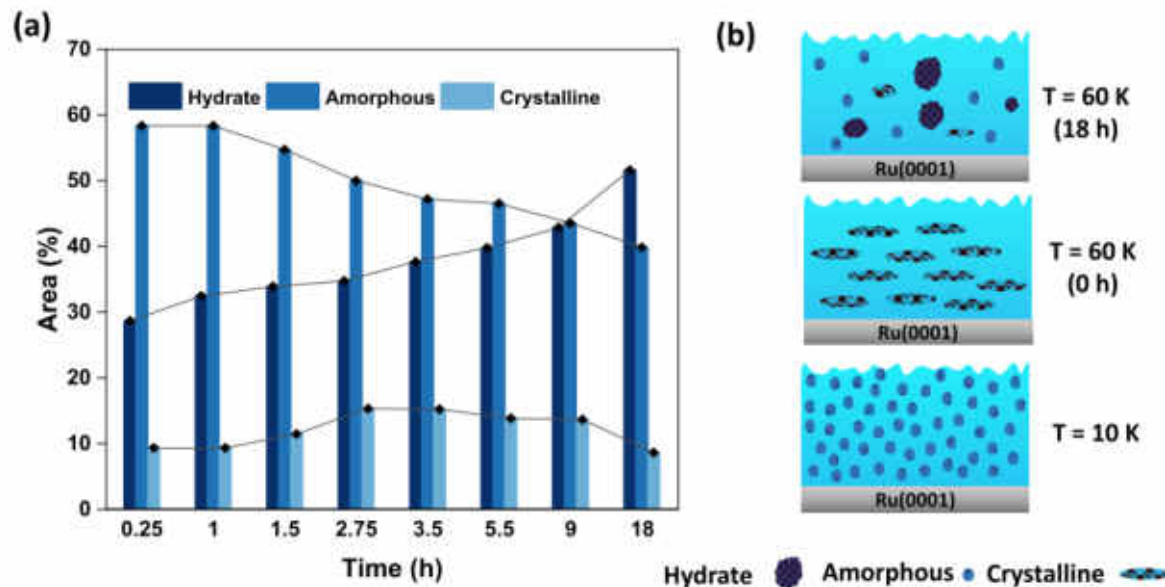
SCIENCE ADVANCES • 6 Apr 2016 • Vol 2, Issue 4 • DOI:10.1126/sciadv.1501781



Results and discussion

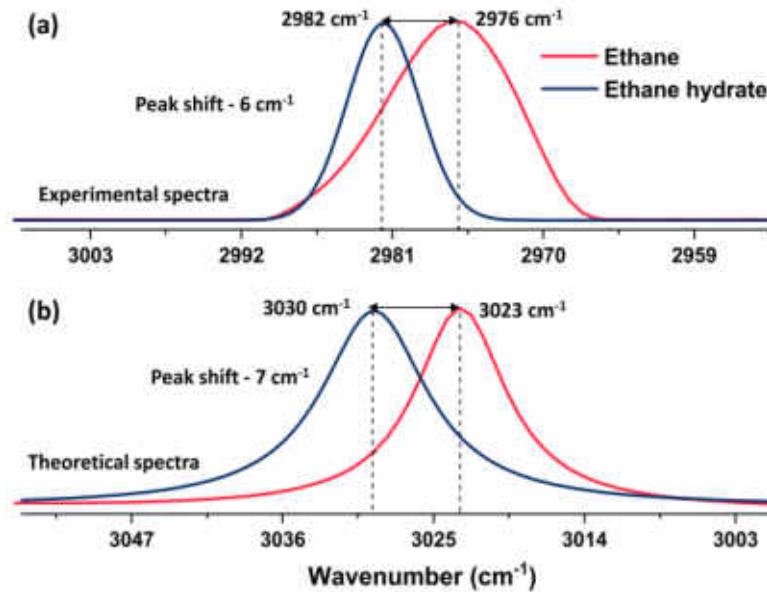
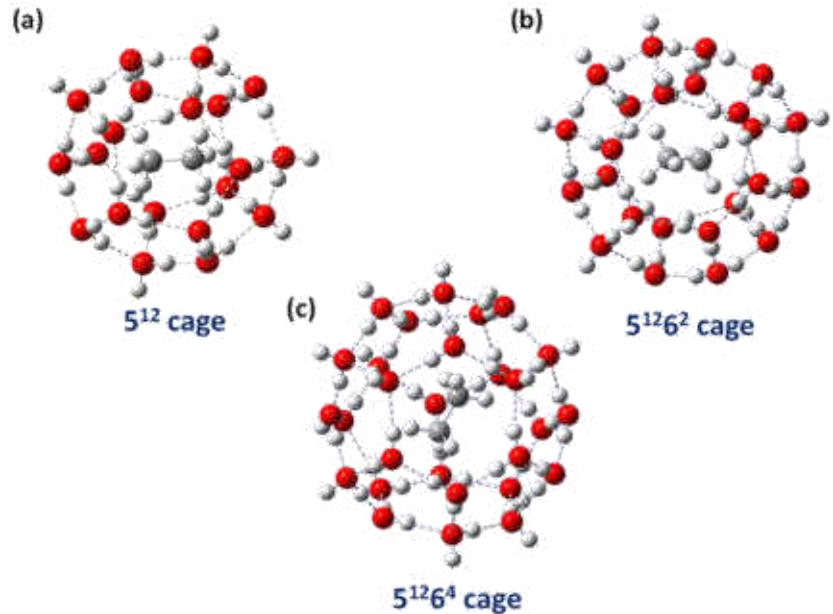
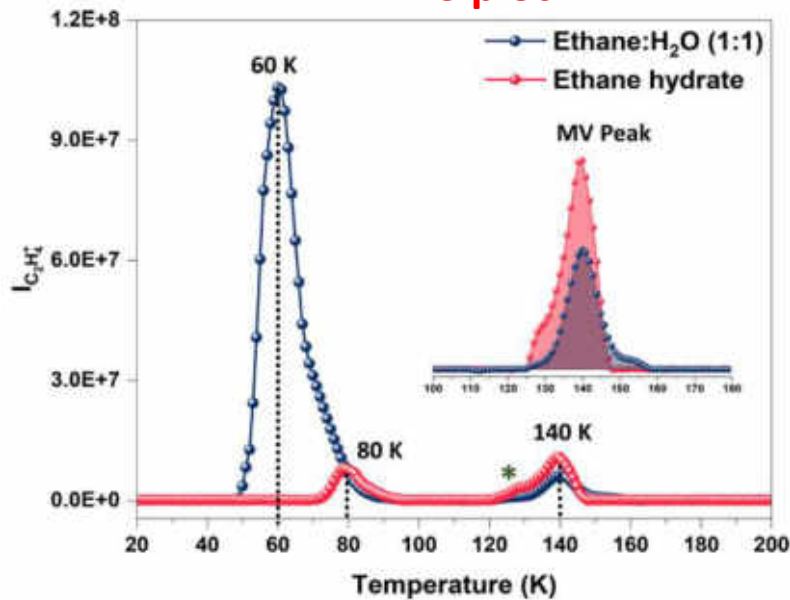


C-H antisymmetric stretching region



Results and discussion

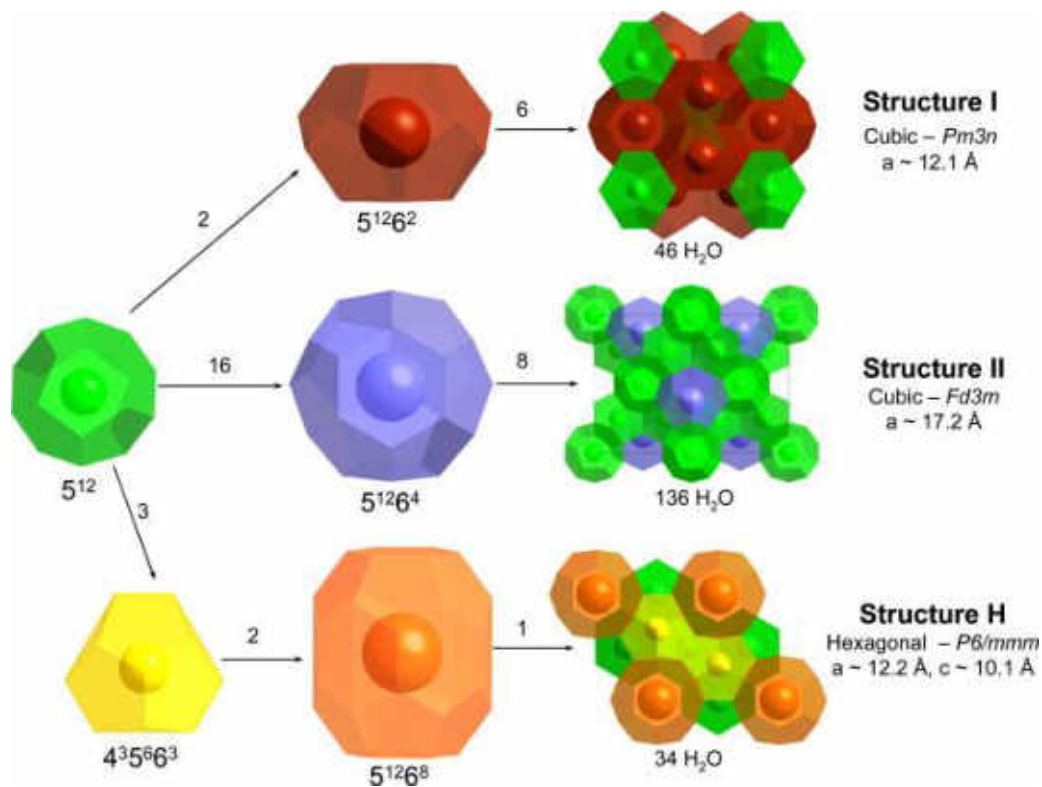
TPD-MS plot



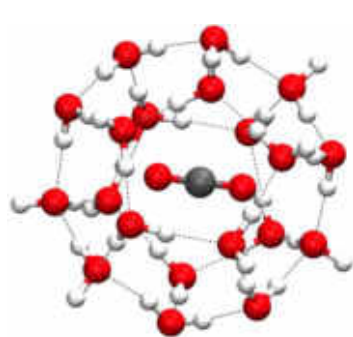
From Dr. Jyotirmoy

From Gaurav

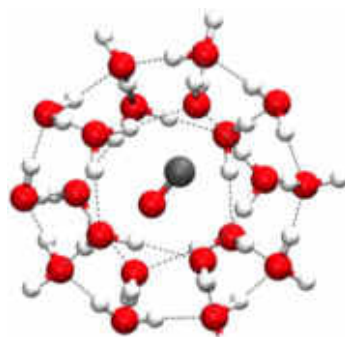
Clathrate hydrates



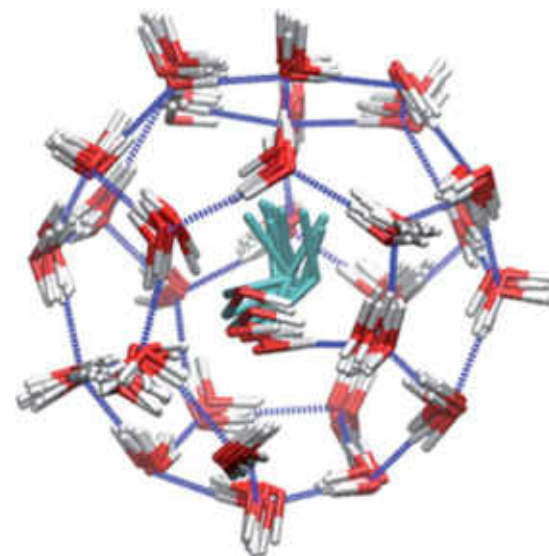
Strobel, T. A. *et al.*, *Chem. Phys. Lett.* **2009**, 478, 97–109



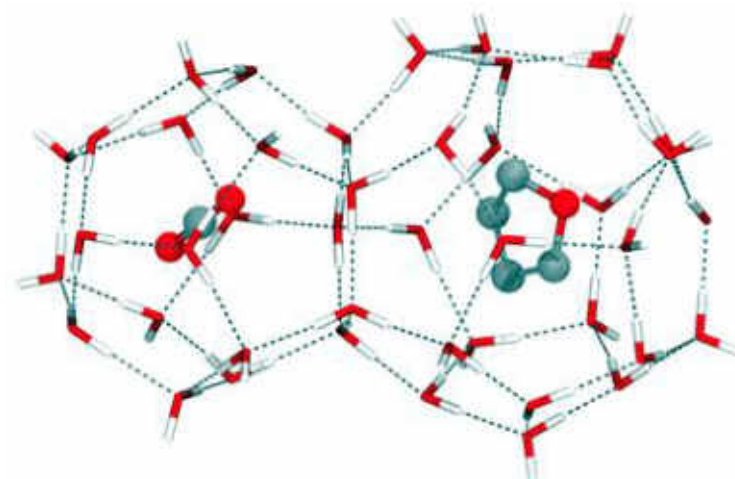
$\text{CO}_2@5^{12}$



$\text{CO}@5^{12}$



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



$\text{CO}_2@5^{12}$ and $\text{THF}@5^{12}6^4$ cage

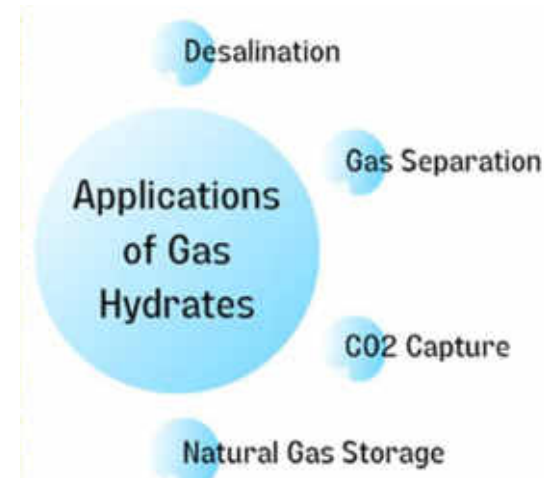
Properties and applications of clathrate hydrates



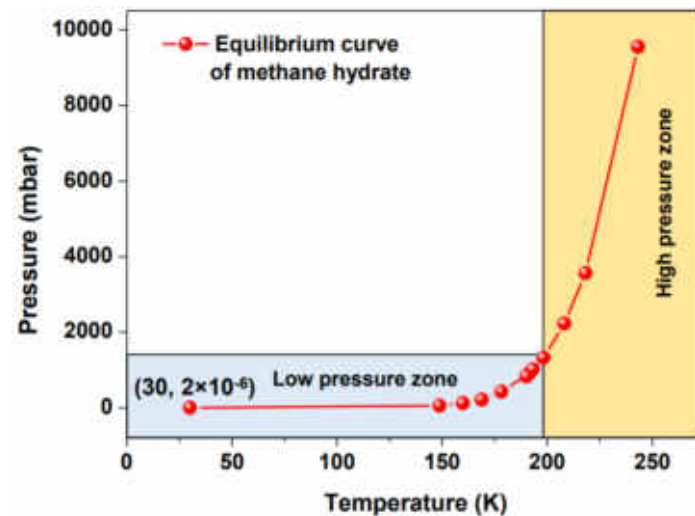
“Ice on fire” burning of methane hydrate



Methane clathrate block embedded in the sediment of hydrate ridge

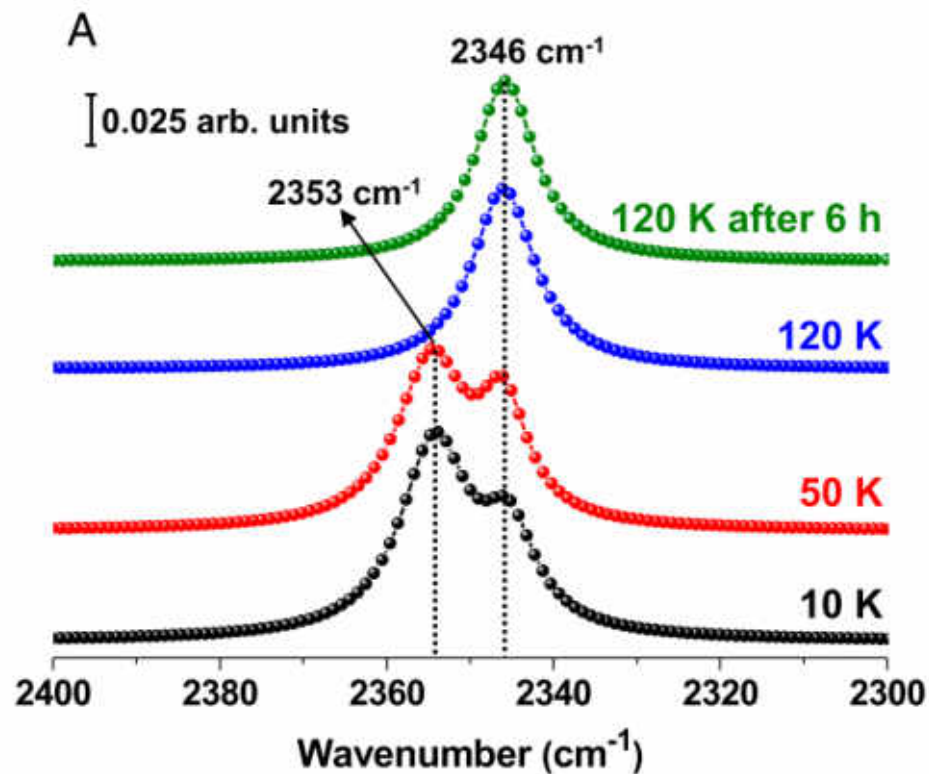
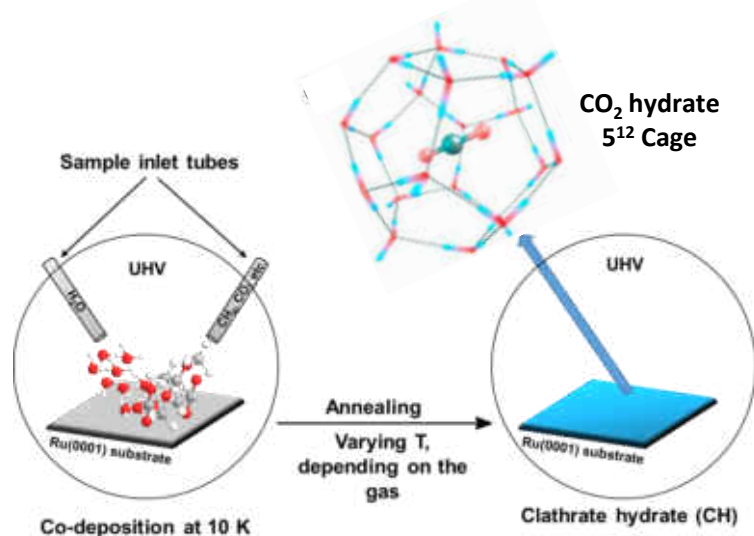


Veluswamy, H. P. and Upadhye, N., *Energy Fuels* **2022**, 36, 2323-2350

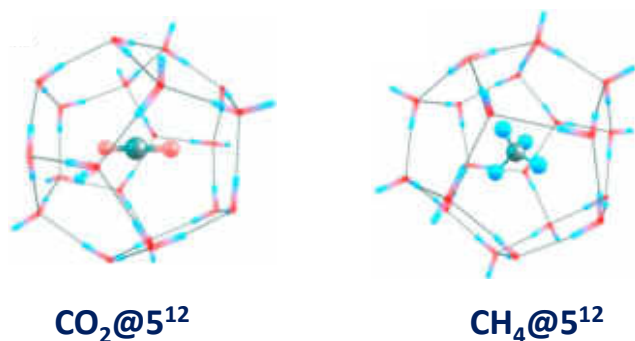


Clathrate hydrates in interstellar environment

Experimental method



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



T = 10-30 K
P = 10⁻¹⁰ mbar

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

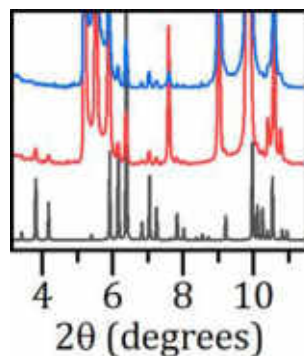
Robert P.C. Bauer, Aravind Ravichandran, John S. Tse,* Narayan Appathurai, Graham King, Beatriz Moreno, Serge Desgreniers, and Ramaswami Sammynaiken



Cite This: *J. Phys. Chem. C* 2021, 125, 26892–26900

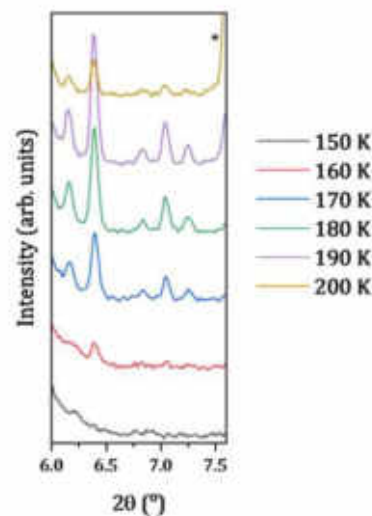


Read Online

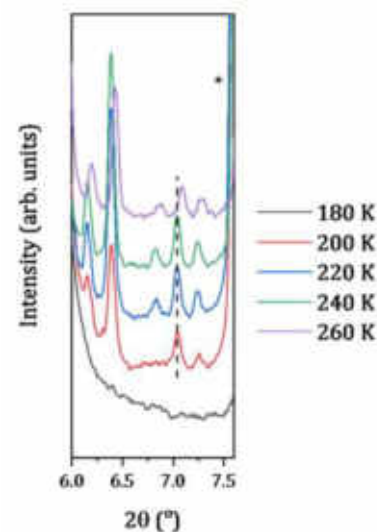


CO₂ hydrate 194 K
CH₄ hydrate 242 K
Reference type I hydrate

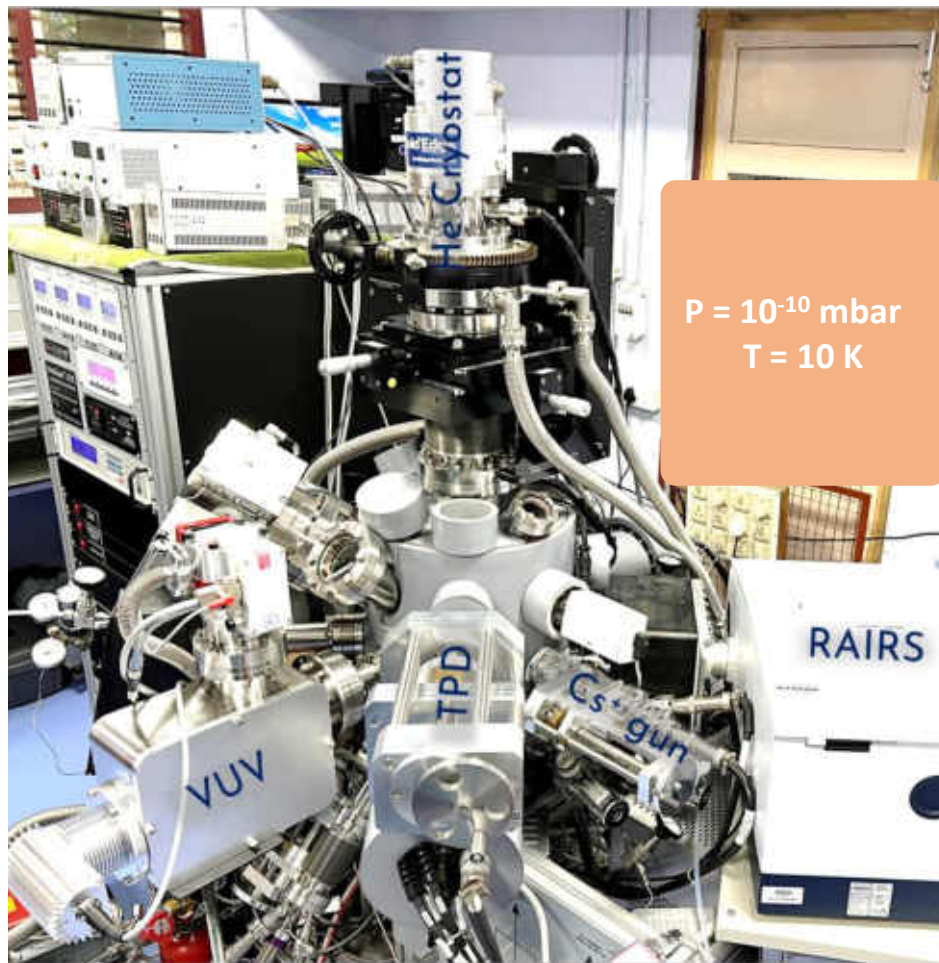
CH₄ CH



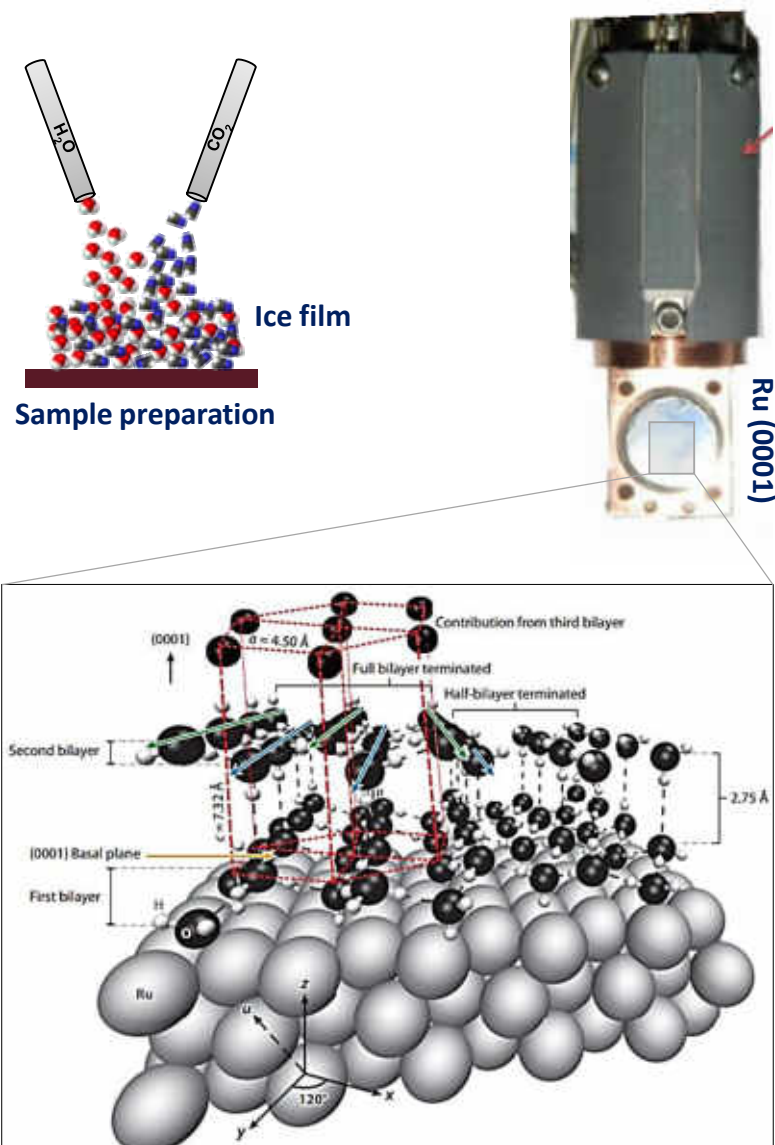
CO₂ CH



Instrumentation



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



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