Since 1959

Surface Science of Clathrate Hydrates

Thalappil Pradeep

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https Professor-in-charge org

International Centre for Clean Water

Co-founder

InnoNano Research Pvt. Ltd.

InnoDI Water Technologies Pvt. Ltd.

VayuJAL Technologies Pvt. Ltd.

Aqueasy Innovations Pvt. Ltd.

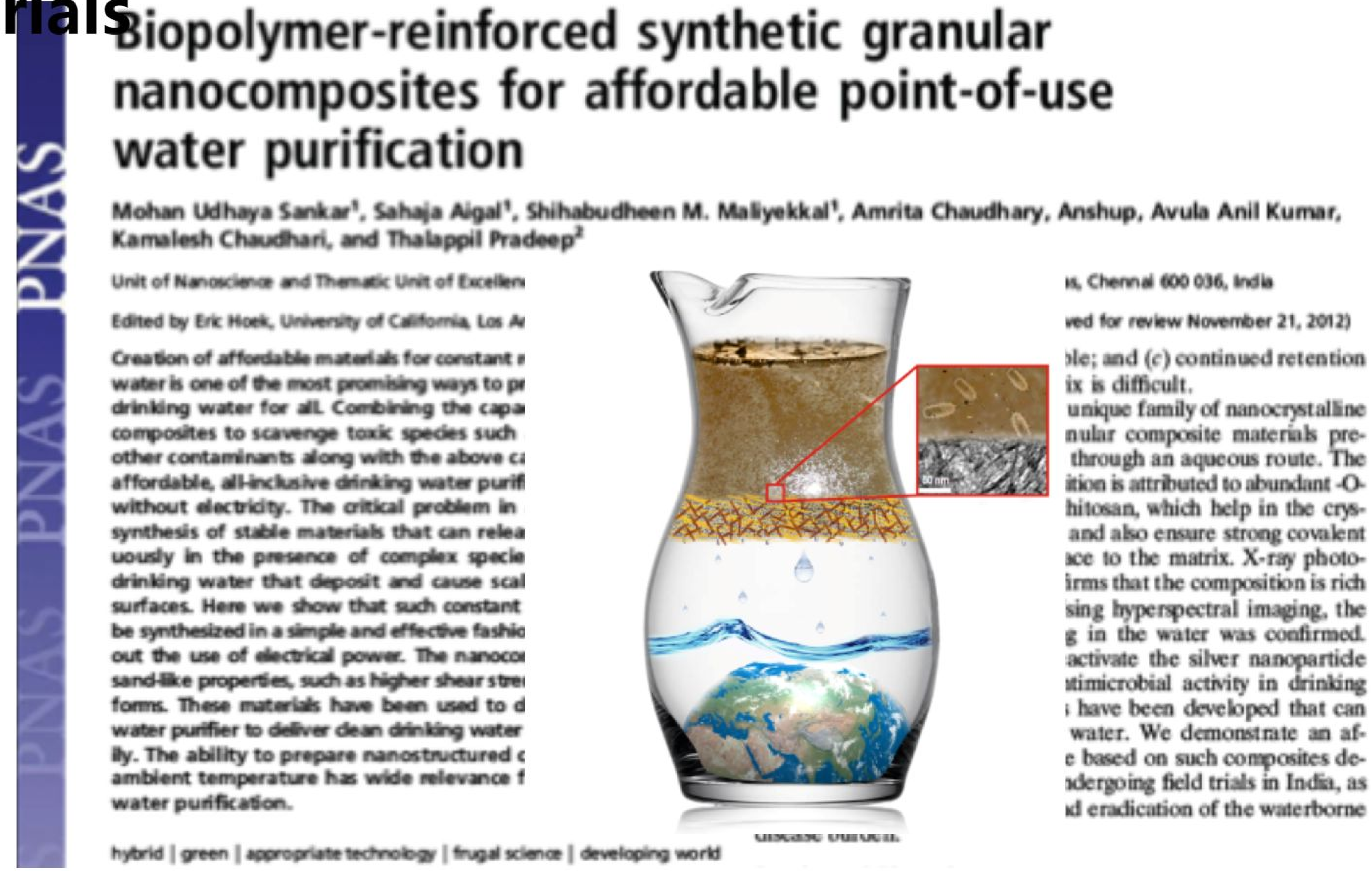
Hydromaterials Pvt. Ltd.

EyeNetAqua Solutions Pvt. Ltd.

An ocean of opportunities

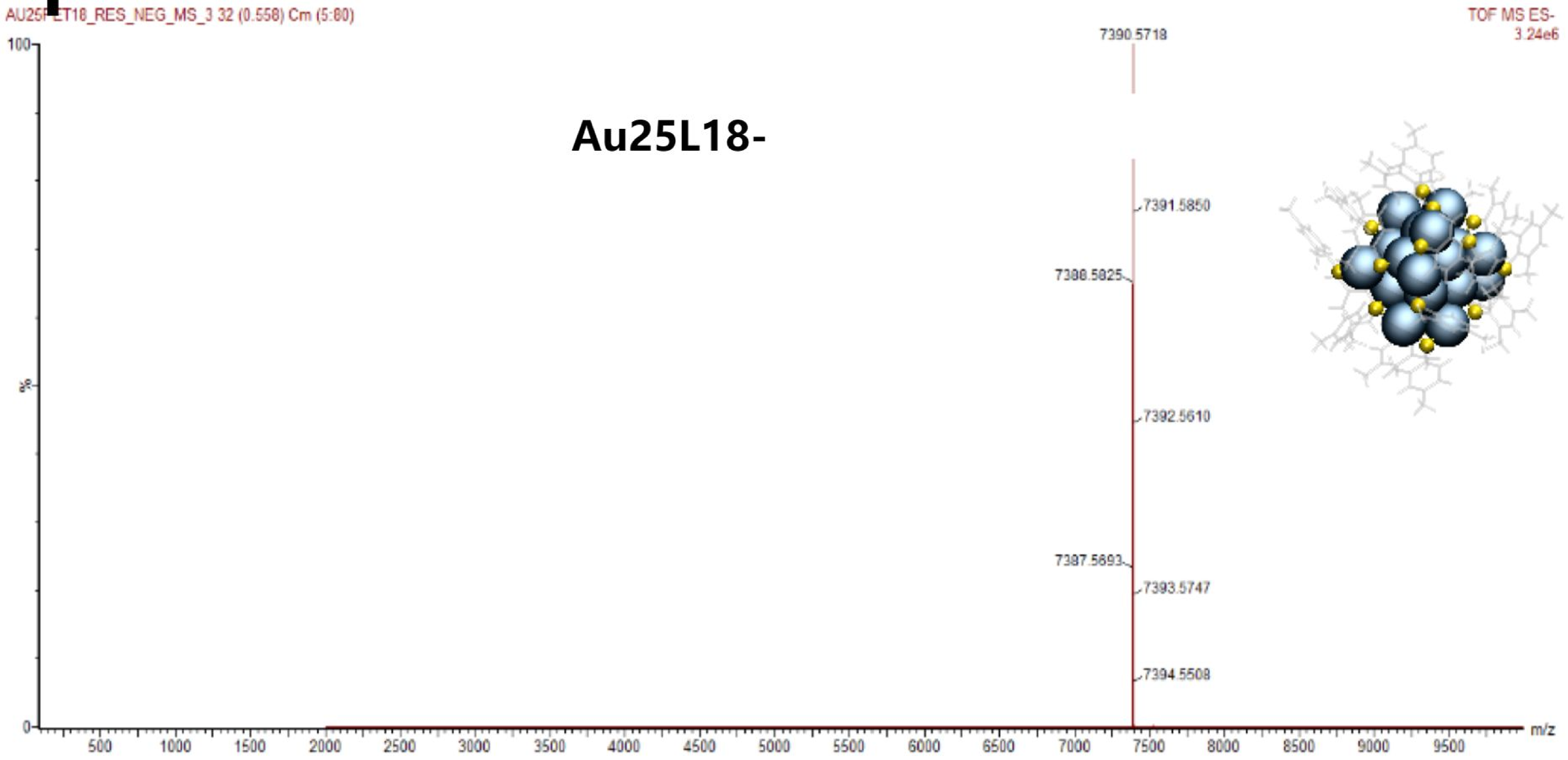
Water presents a unique opportunity to find a purpose in life.

Water positive mate rials



M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.,* 110 (2013) 8459-8464.

Nanomaterials are now atomically precise



T. Pradeep et. al. *Acc. Chem. Res.* 2018 ; 2019.

Clean water for everyone

ACS Sustainable Chemistry & Engineering Editori
al, December 2016

Across the countr y

International Centre for Clean Water

IIT Madras Research Park

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

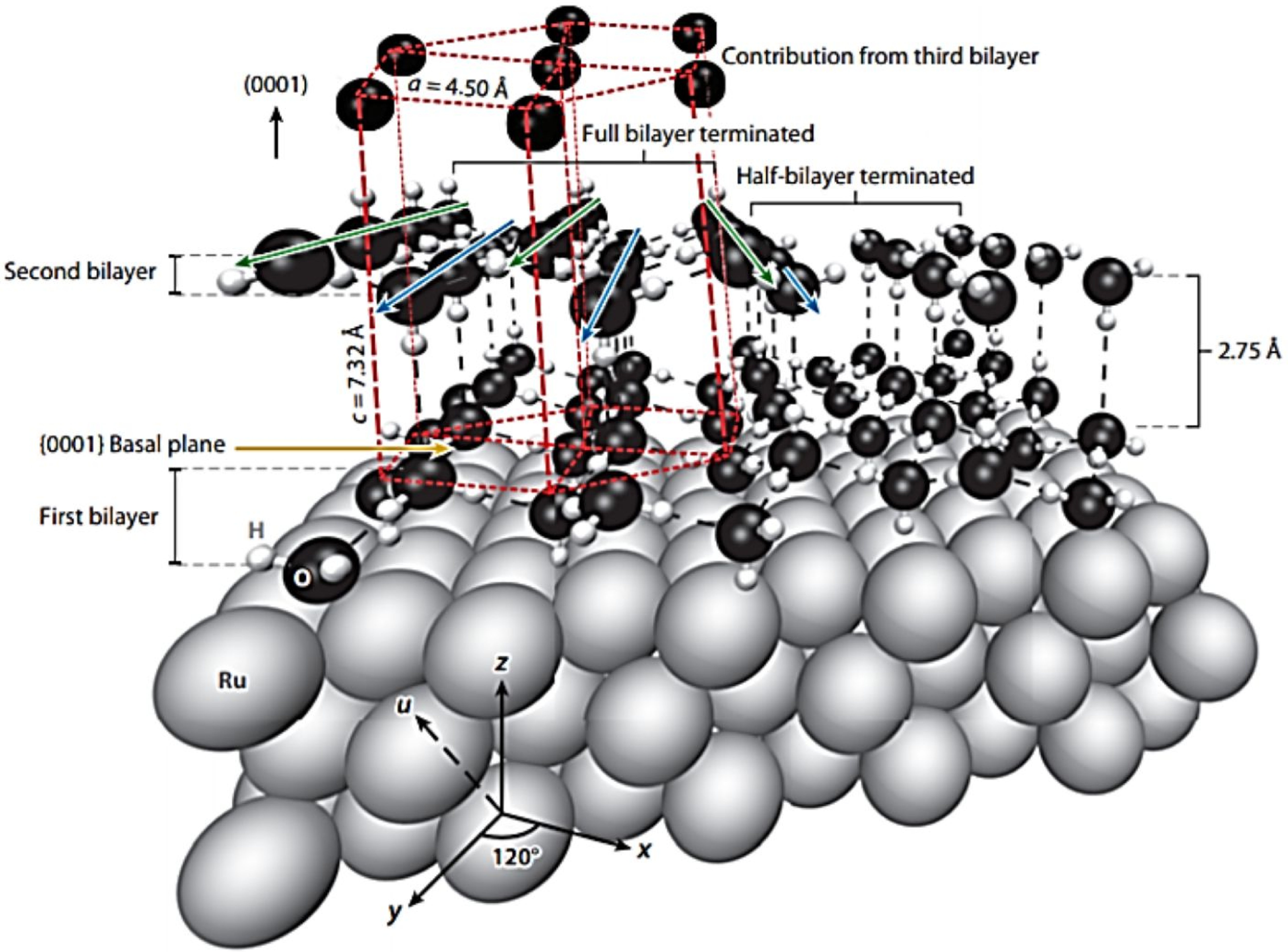
Condensed molecular solids are all ices

Instrumentation

115-400 nm

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

Viswakarma, *G. et al., J. Phys. Chem. Lett.,* **2023**, *14*, 2823–28
29



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

Instrumentation

$H^+ + H_2O$ (liquid) $\rightarrow H_3O^+$

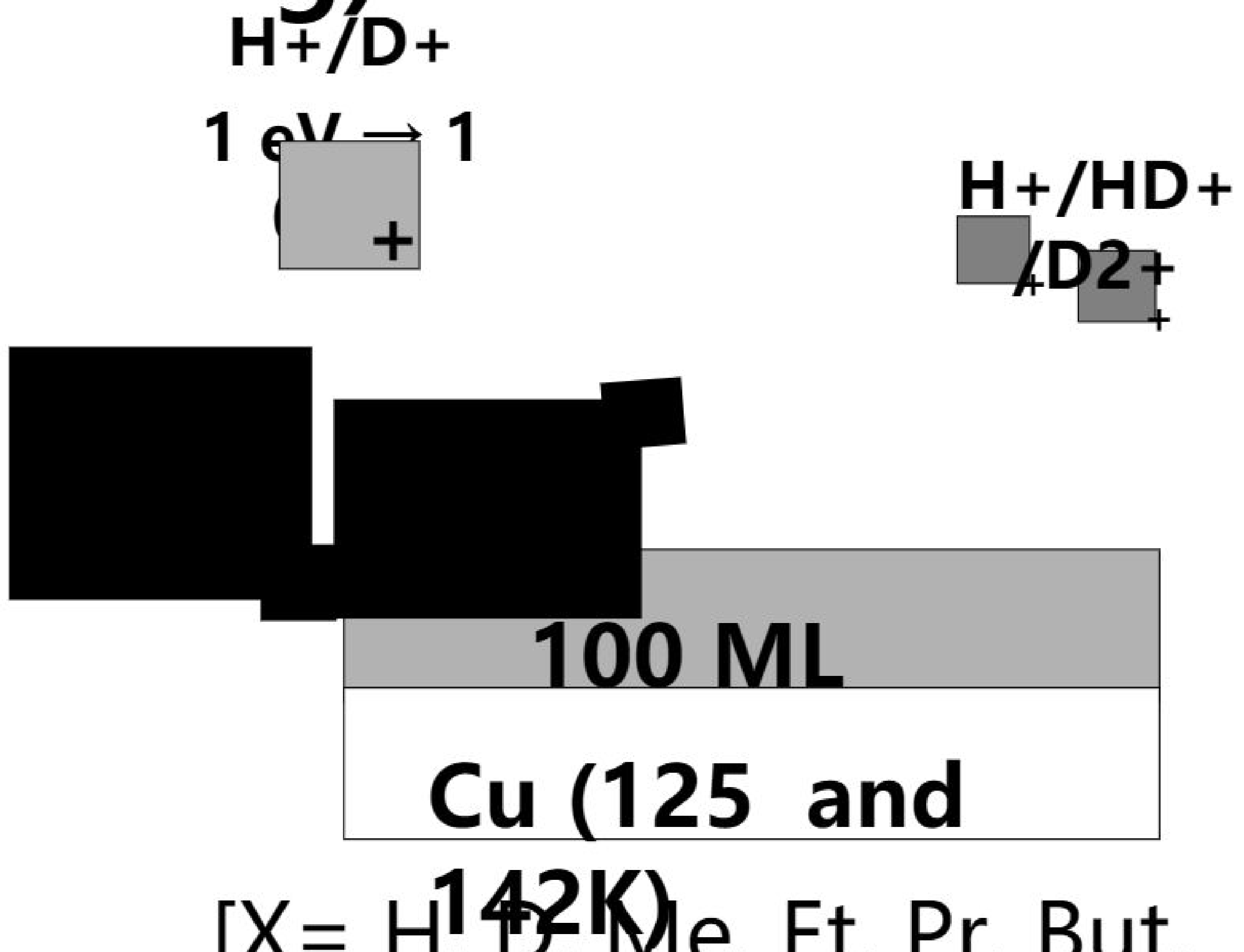
$H^+ + H_2O$ (solid) $\uparrow\rightarrow$?

$\frac{1}{2}$(at ultralow energy)

H_2

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

Chemical exchange (or mi xing)



[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 × 1015 molecules /cm2*

*Moon, E.-S.; Kang, H.; Oba, Y.; Watanabe, N.; Kouchi, A. Astrophys. J. **2** cASW

CW

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

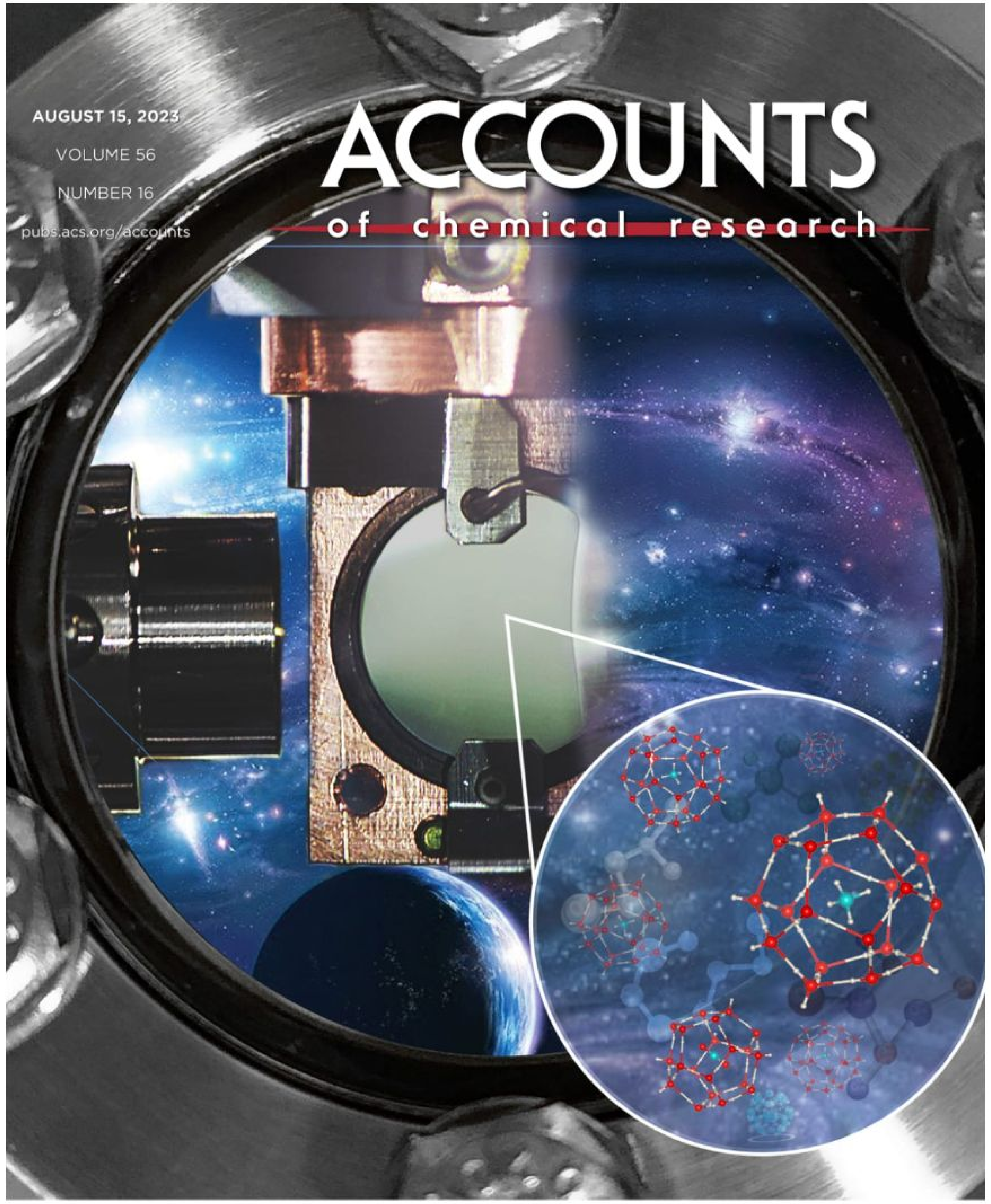
ACCOUNTS of chemical research

pubs.acs.org/accounts Article

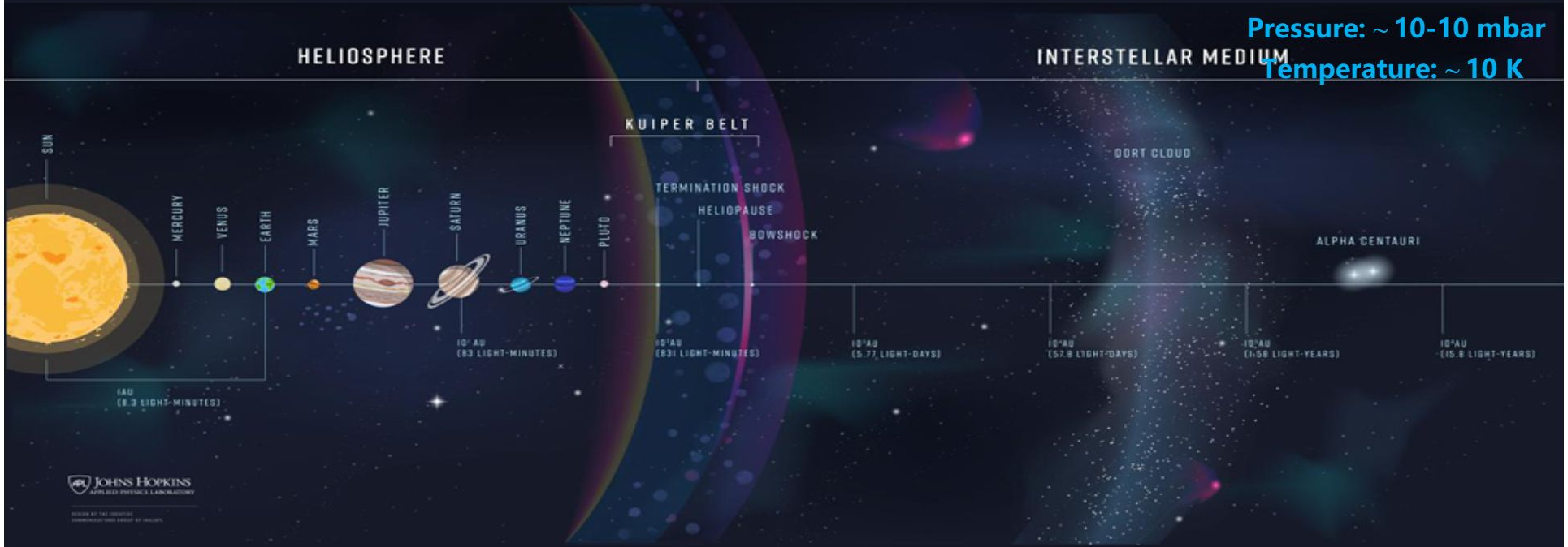
Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

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

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



Interstellar medium



Pressure: ~ 10-10 mbar
Temperature: ~ 10 K

Diffuse clouds: T ~ 100 K, n ~ 100 molecules per cm 3

Dense clouds: T ~ 10-100 K, n ~ 104-108 molecules per cm3

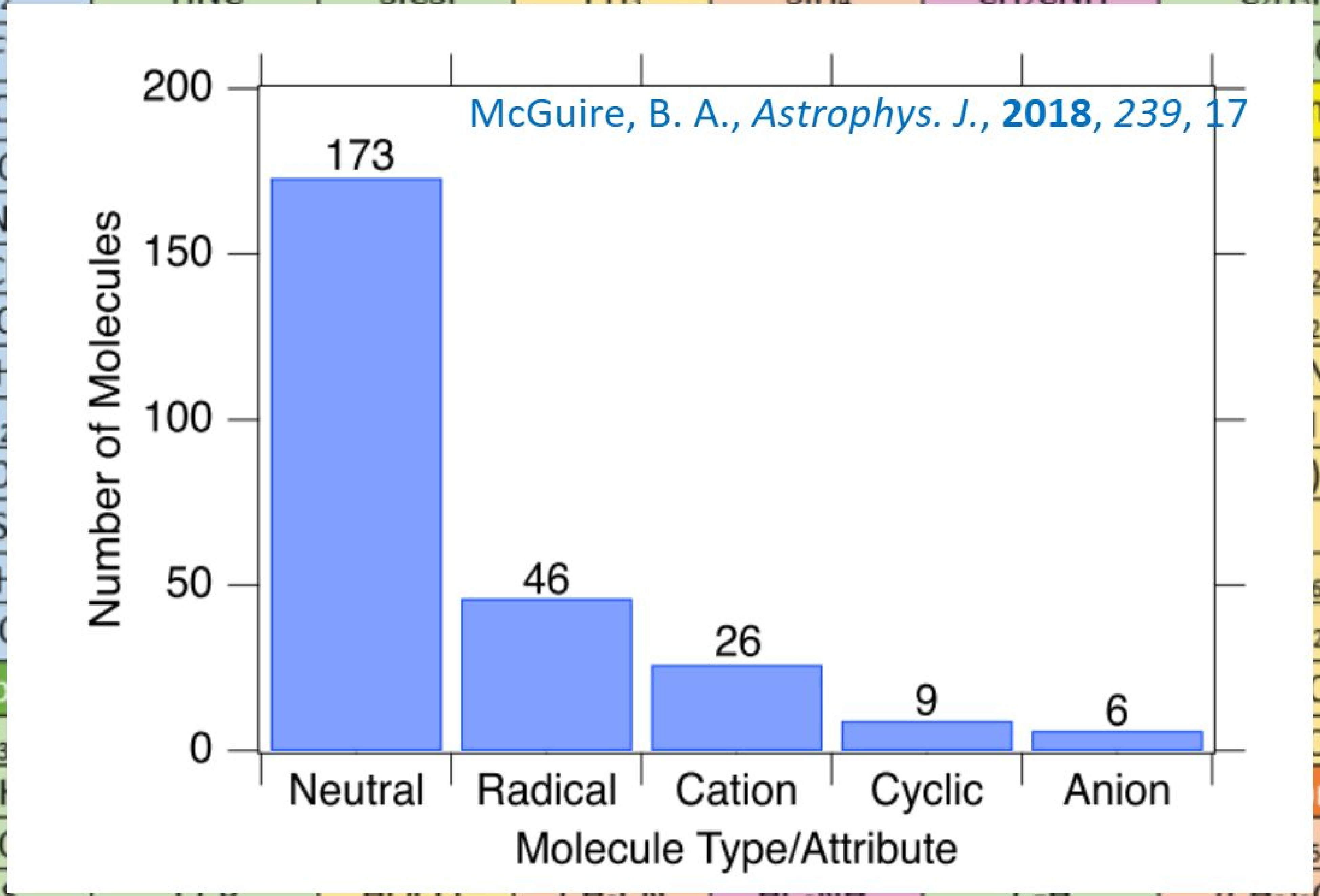
On Earth sea level: T ~ 300 K, n ~ 3×1019 molecules per cm3

https://spaceref.com/science

Interstellar molecules

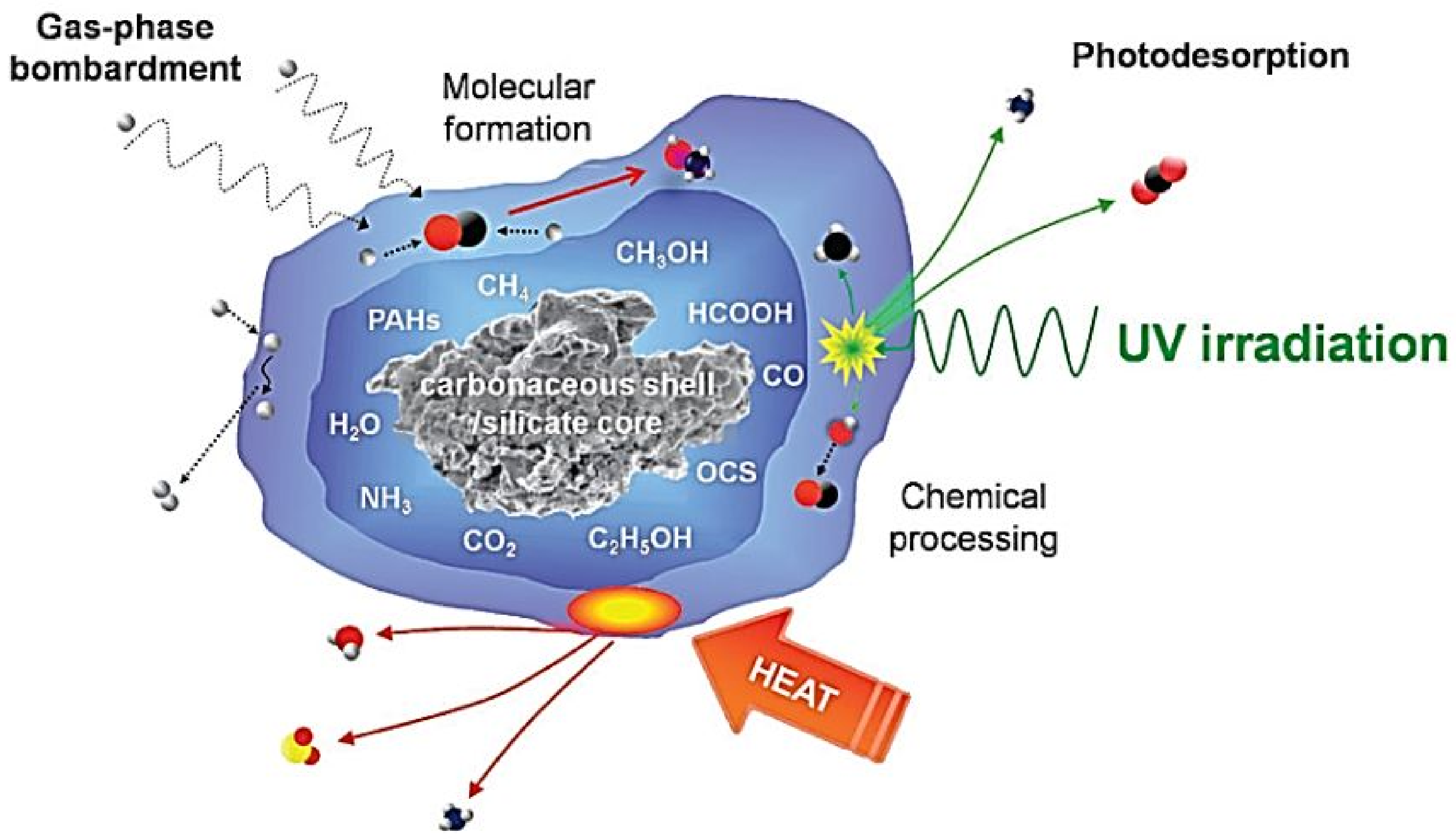
260

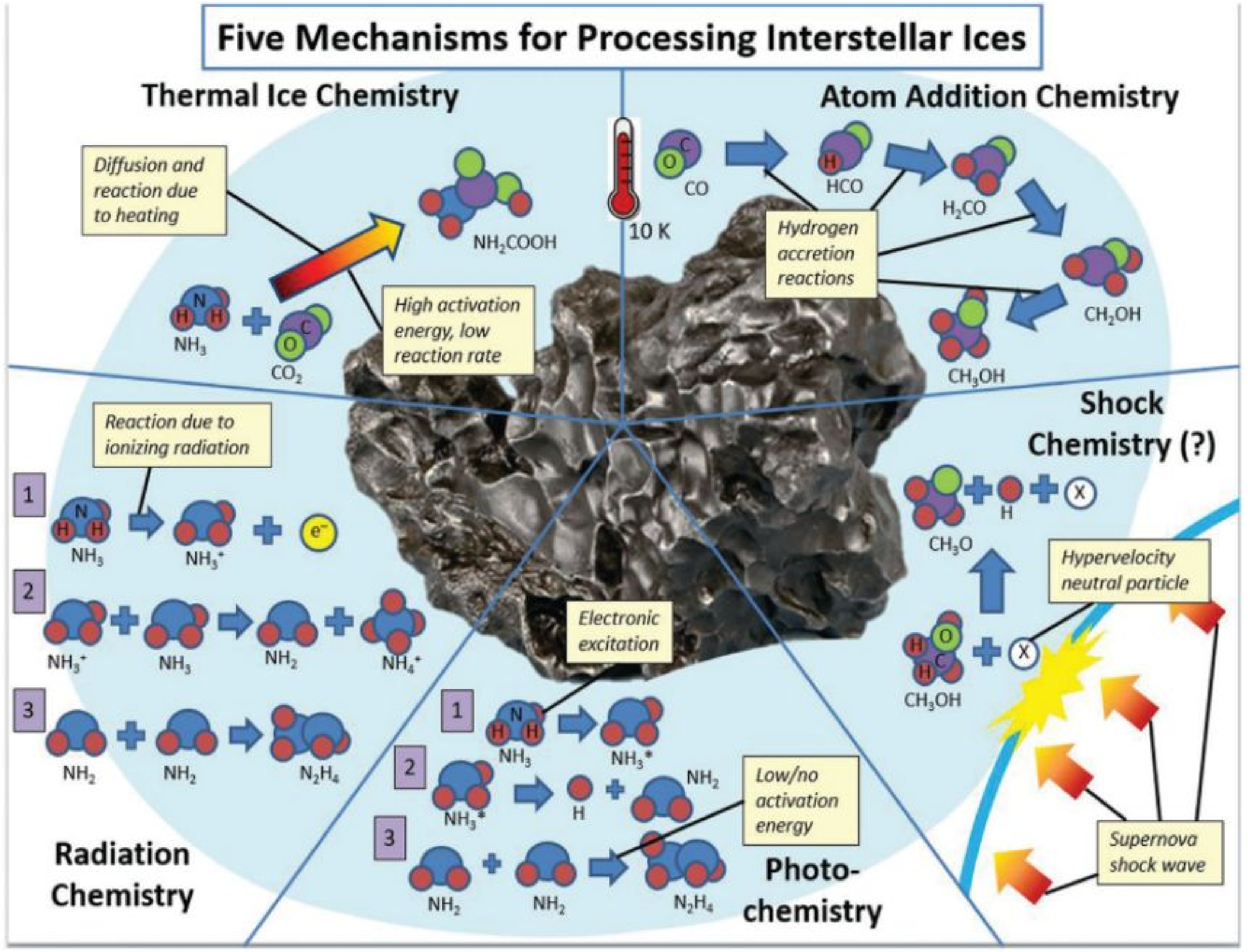
2 atoms	CS	HCO^+	KCN	H_3O^+	HCOOH	*l*-HC_4N	CH_2CHCHO	CH_3OCH_2OH
H_2	HF	HCS^+	FeCN	NH_3	H_2CNH	*c*-H_2C_3O	CH_2CCHCN	11 atoms
AlF	SH	HOC^+	HO_2	c-SiC_3	H_2C_2O	C_5N^-	H_2NCH_2CN	HC_9N
AlCl	SH^+	H_2O	TiO_2	CH_3	H_2NCN	E-HNCHCN	CH_3CHNH	CH_3C_6H
C_2	FeO	H_2S	C_2N	C_3N^-	HNC_3	SiH_3CN	CH_3SiH_3	C_2H_5OCHO
CH	O_2	HNC	SiCSi	PH_3	SiH_4	CH_2CNH	C_2H_5N	$CH_3OC(O)CH_3$
CH^+	CF						CO	12 atoms
CN	PC						ms	*c*-C_6H_6
CO	Al						H	C_3H_7CN
CO^+	CN						CN	*t*-$C_2H_5OCH_3$
CP	HC						O	>12 atoms
CSi	Ti						OH	C_{60}
HCl	ArH						N	C_{60}^+
KCl	N_2							C_{70}
NH	NO						)NH_2	c-C_6H_5CN
NO	NS							$CO(CH_2OH)_2$?
NS	LiH						6	$C_{14}H_{10}$?
NaCl	CrO						SH	$C_{14}H_{10}^+$
OH	3 ato						CHO	C_6H_5OH
OH^+	C_3						O	
PN	C_2H						ms	
SO	C_2						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 μ m

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

Applications of clathrate hydrates

"Ice on fire" burning of methane hydrate

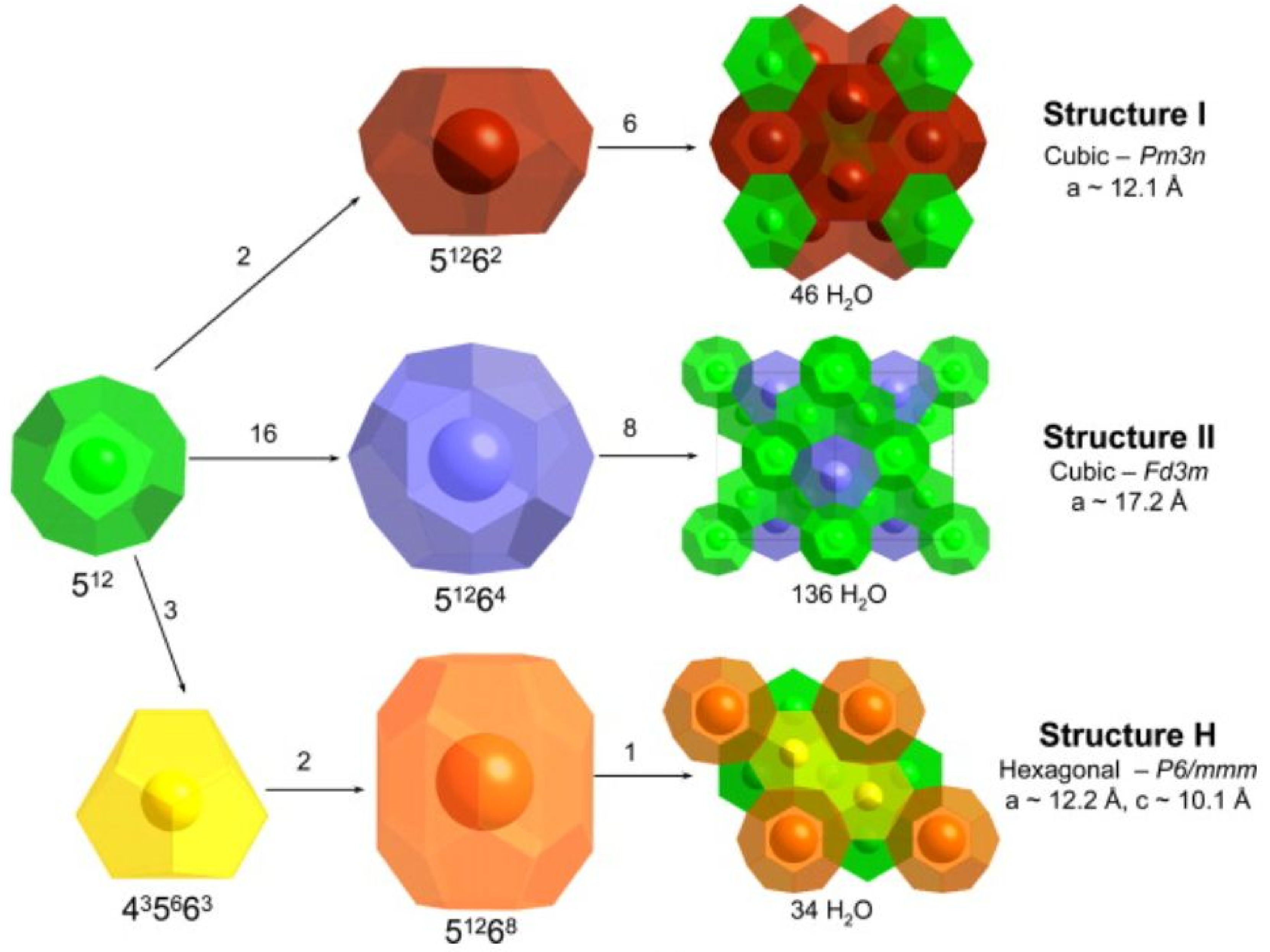
Applications:

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

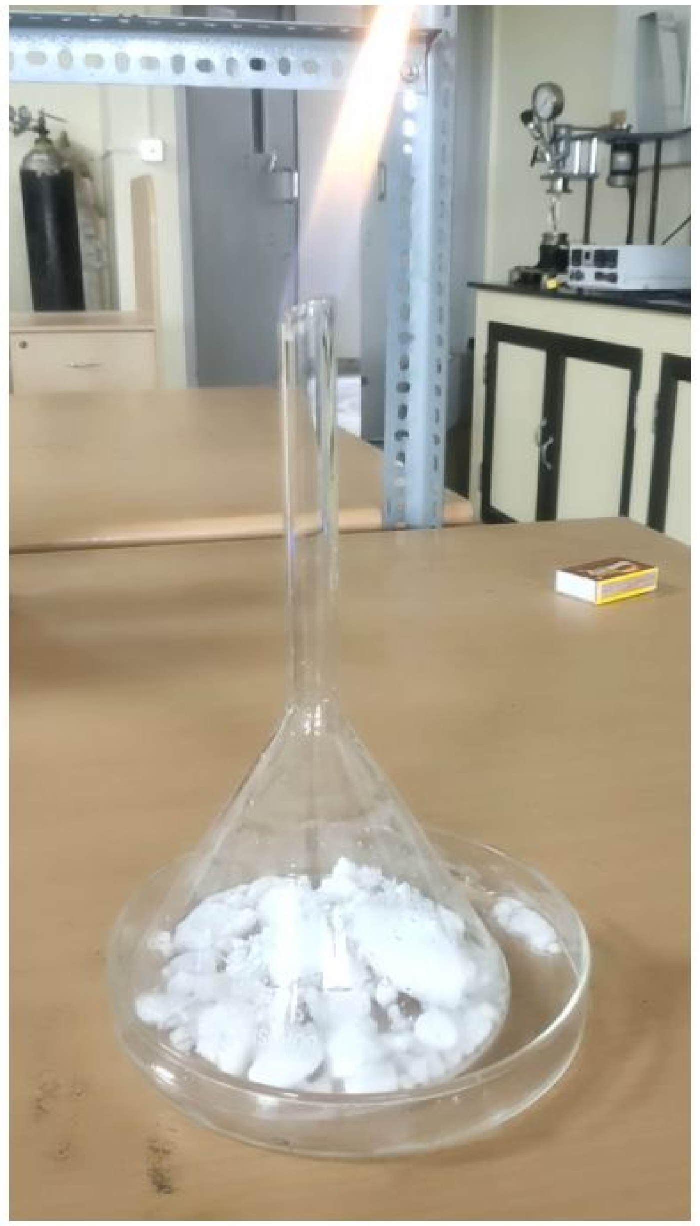
Gas hydrate plug recovered from a subsea pipeline

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

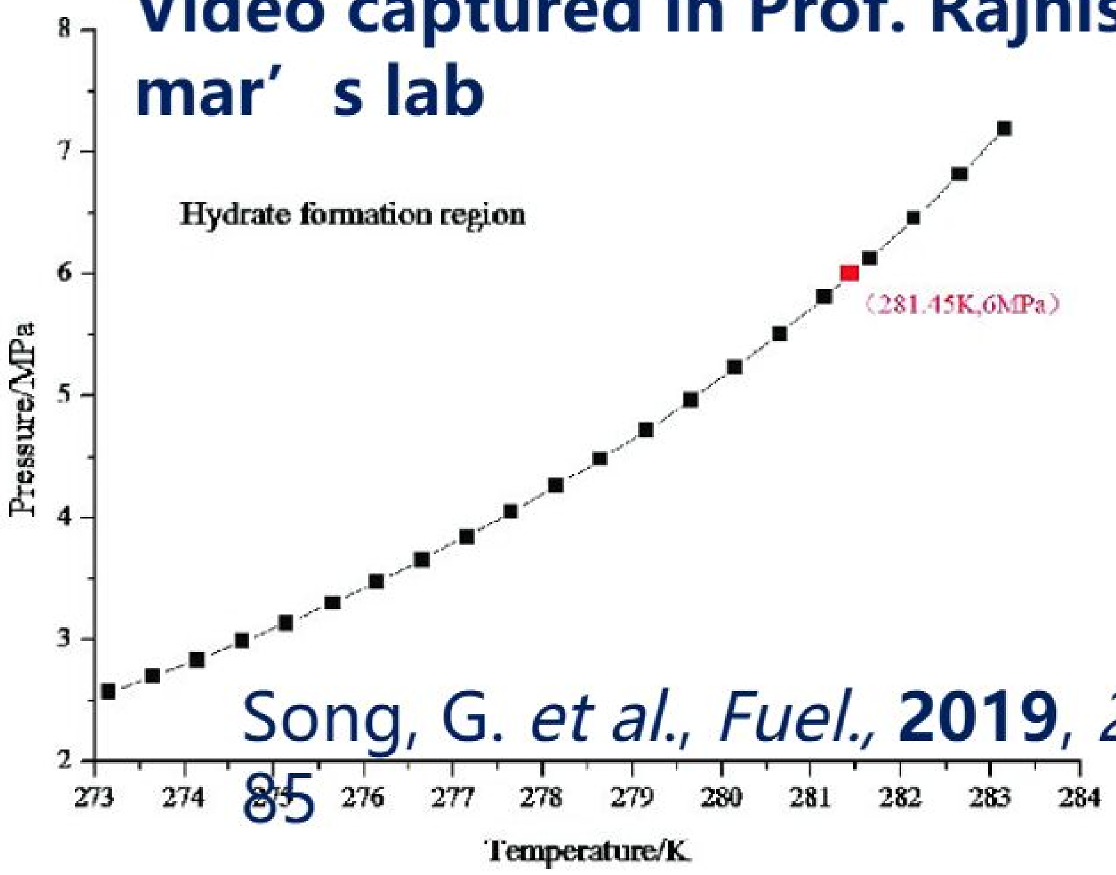
Clathrate hydrates



Strobel, T. A. *et al.*, *Chem. Phys. Lett.*, **2009**, *478*, 97–106

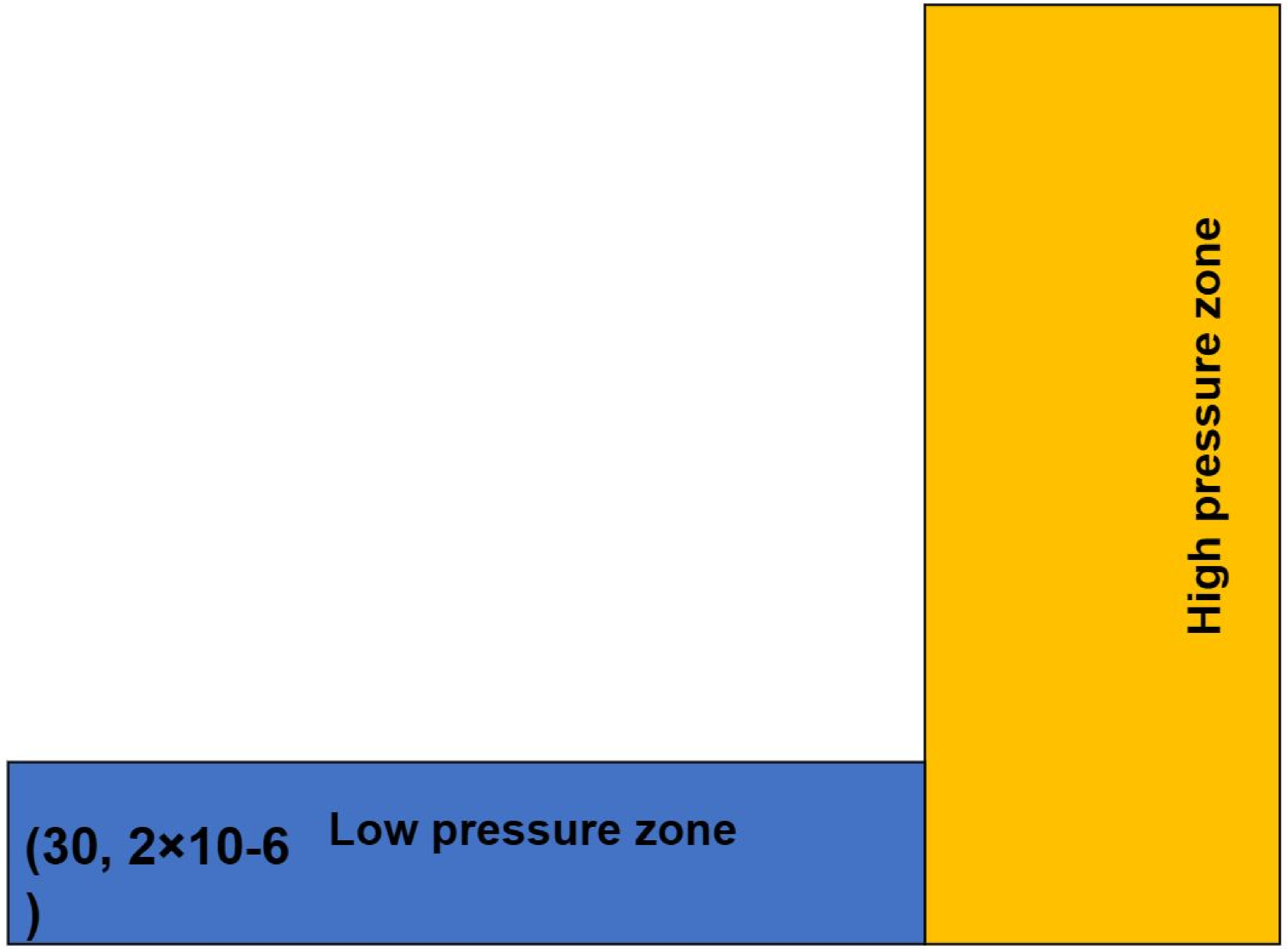


Video captured in Prof. Rajnish Kumar's lab



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

Clathrate hydrates at extreme low pressure

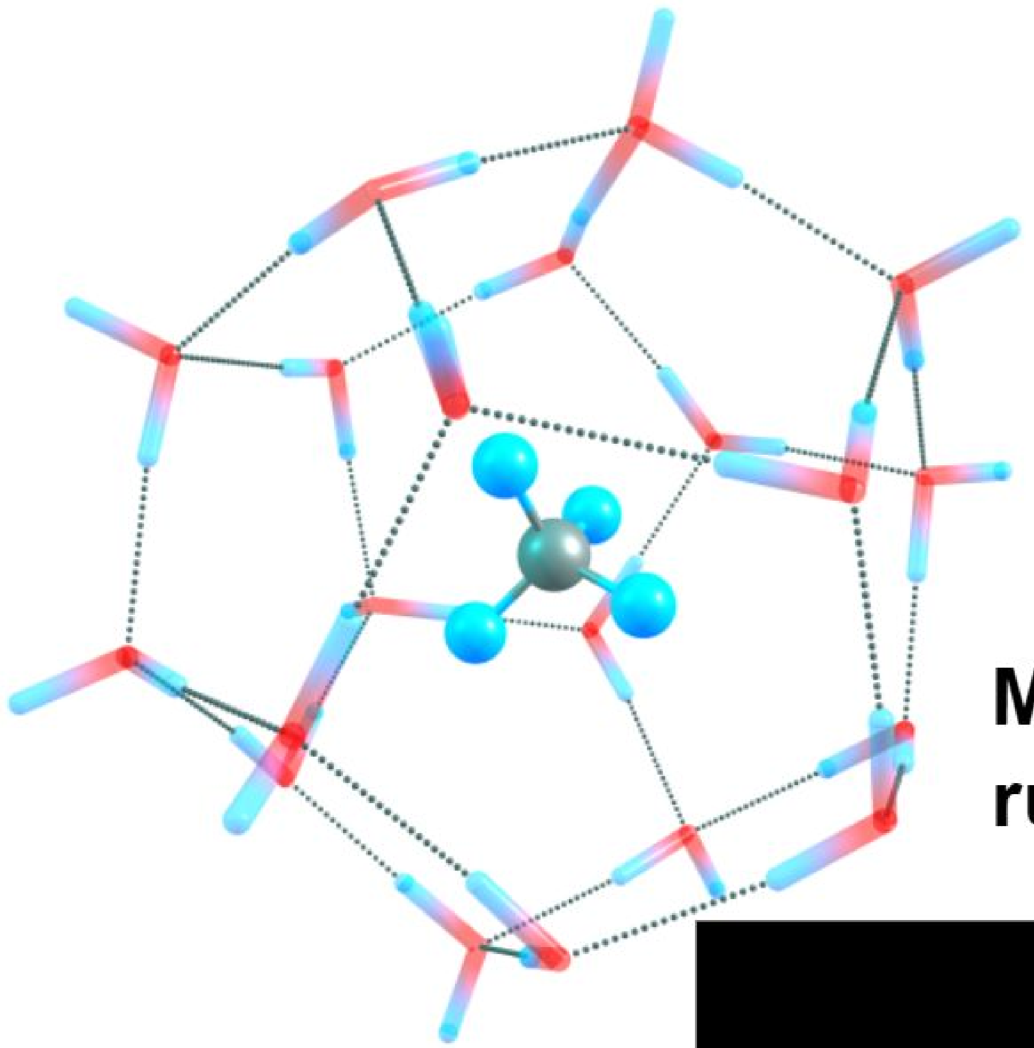


Sloan, E.D.; Koh, C. A., *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008

Clathrate hydrates in interstellar environment

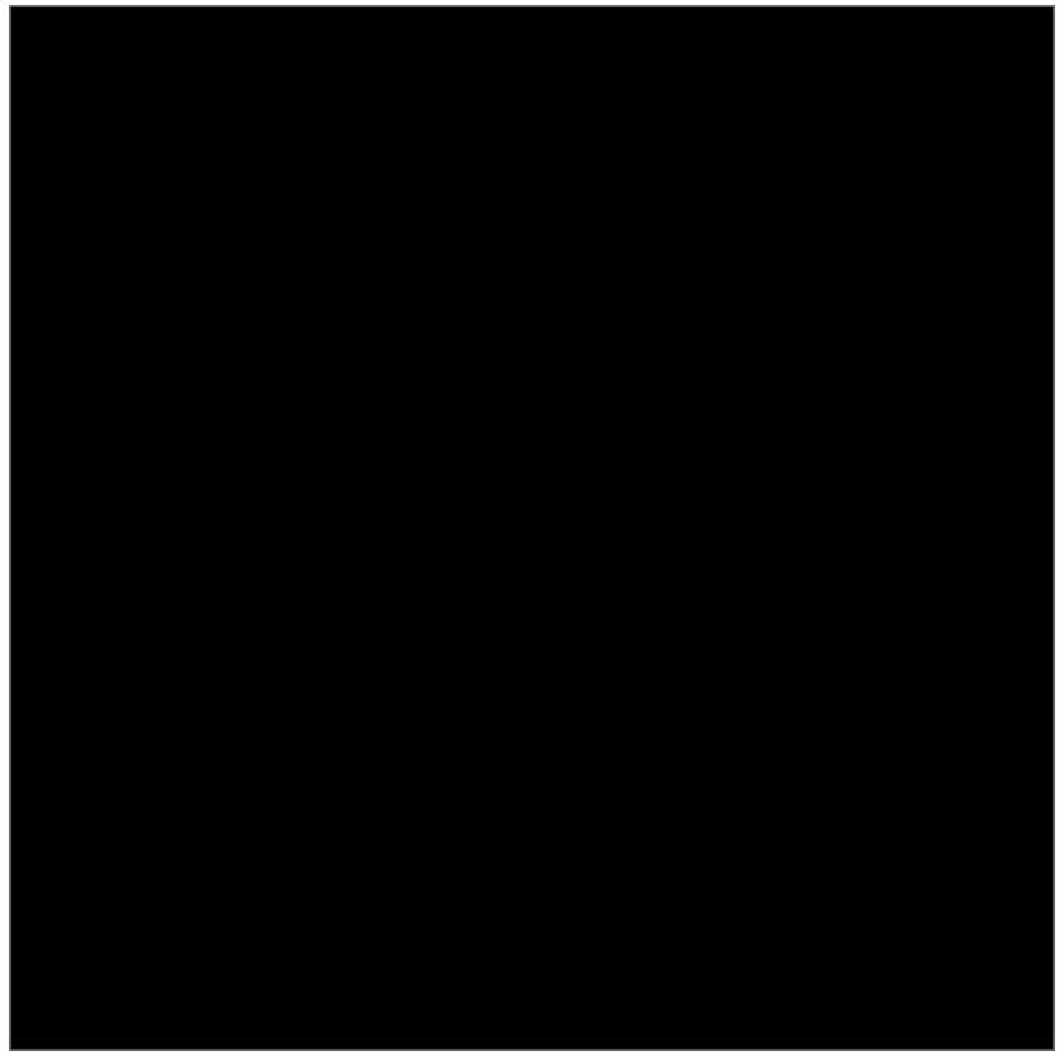
Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.*, **2019**, *116*, 1526-1531

Experimental method



Methane hydrate st
ructure; 512 cage

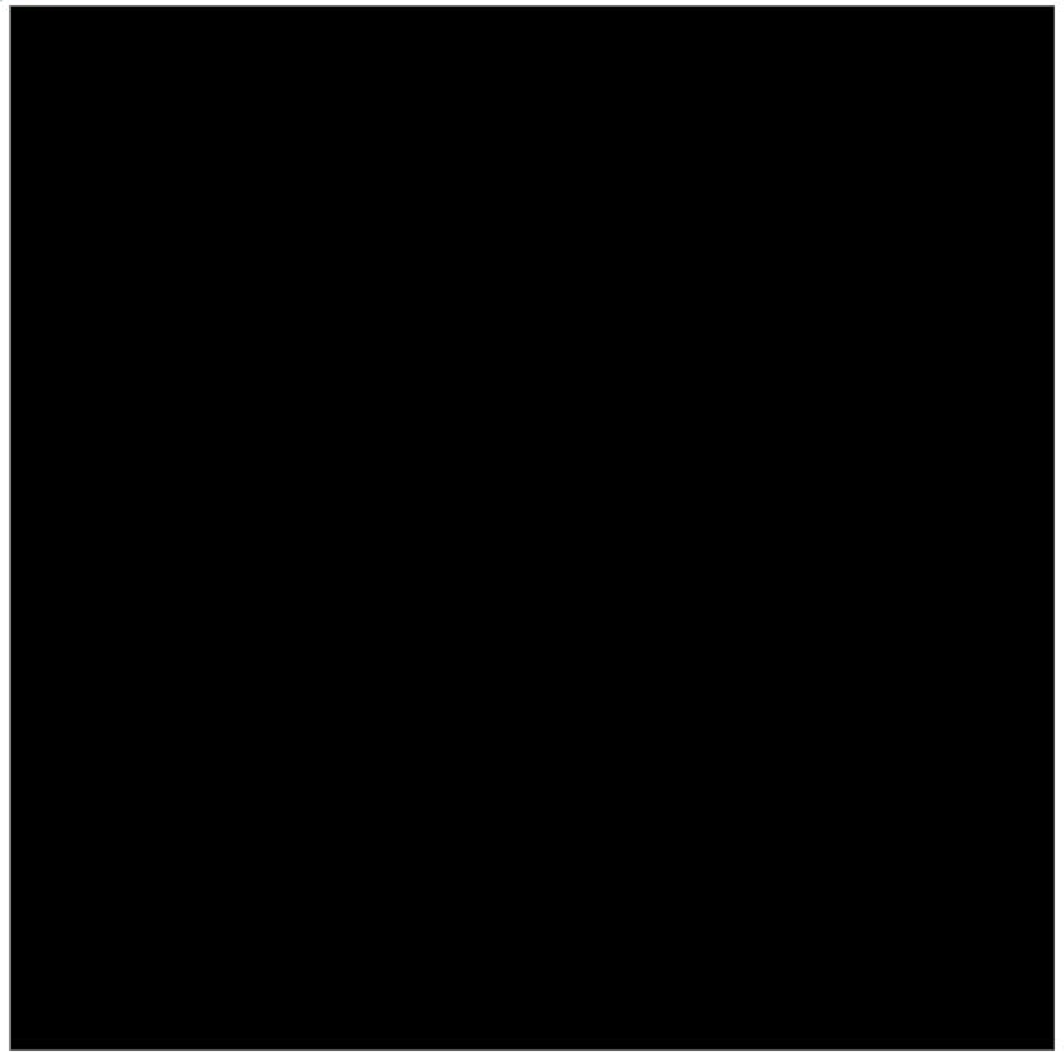
Sample inlet tubes



Co-deposition at 10 K

Annealing

Varying T, dependin
g on the gas



Clathrate hydrate (CH)

Clathrate hydrates in interstellar environment

A

3017 cm-1

3009 cm-1

Δω = 8 cm-1

0.005 arb. units

30 K

20 K

10 K

B

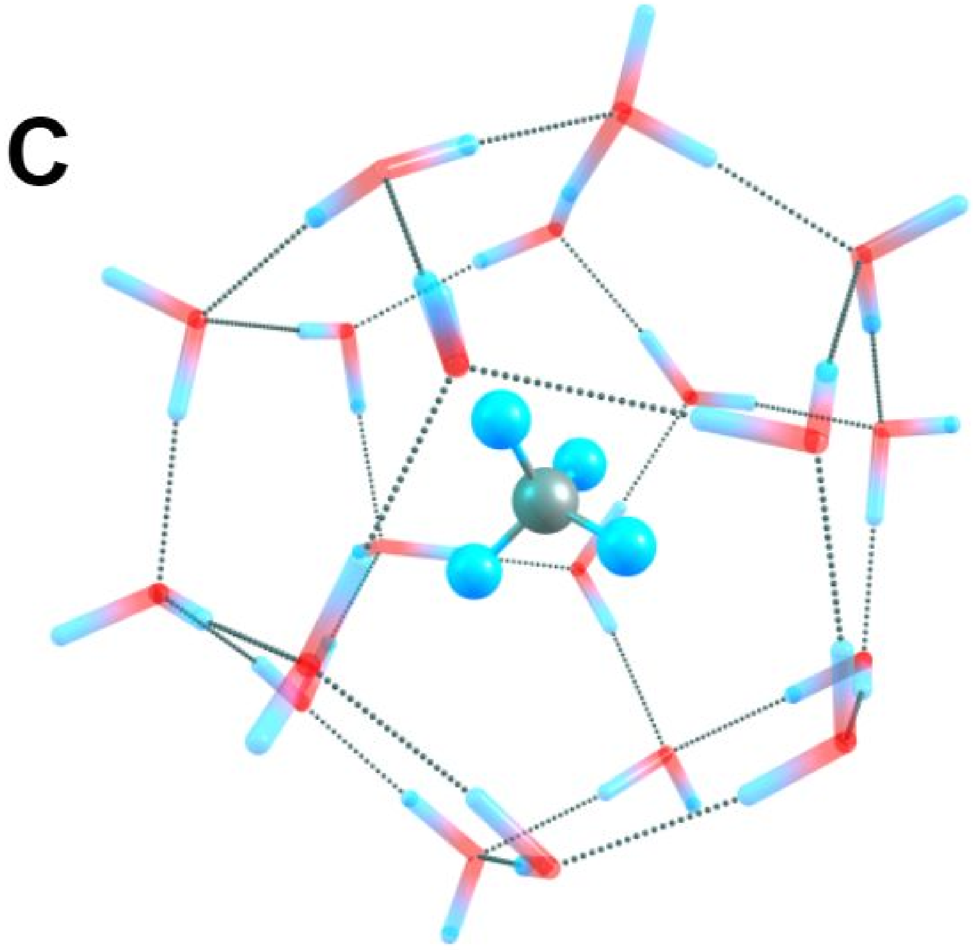
3009 cm-1

3017 cm-1

0.0025 arb. units

12.71% of the total CH4 is trapped

C



512 cage of CH4 hydrate

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

Clathrate hydrates in interstellar environment

3014 cm-
1

T = 25 K

[redacted]

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

Clathrate hydrates in interstellar environment

A

2346 cm-1

0.025 arb. units

2353 cm-1

120 K after 6 h

120 K

50 K

10 K

B

2346 cm-1

T=10 K

0.025 arb. units

2353 cm-1

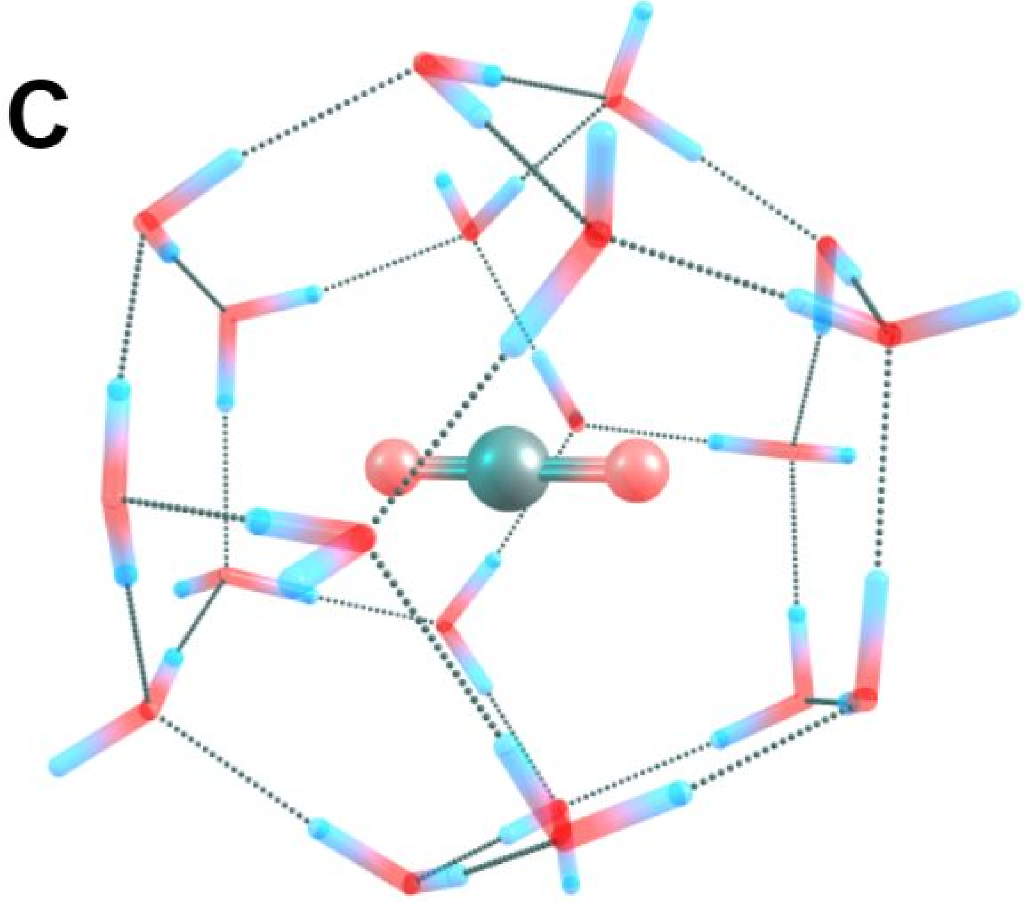
1:90 after 48 h

CO2:H2O (1:90)

CO2:H2O (1:10)

CO2:H2O (1:5)

C



512 cage of CO2 hydrate

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

Clathrate hydrates in interstellar environment

[redacted]

2381 cm-
1

Pure CO
2

10
K

CO2@H2
O

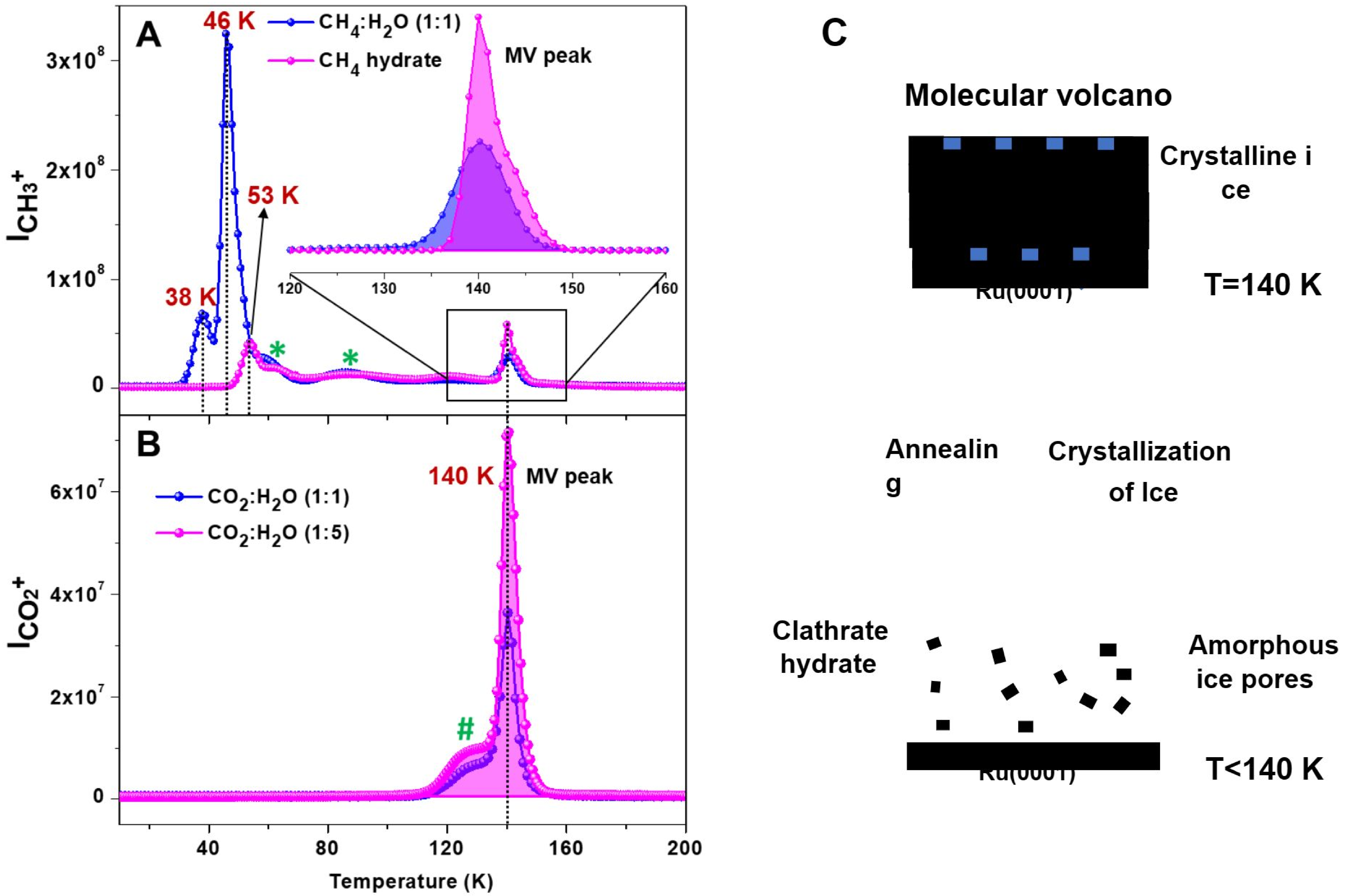
10
K

CO2@H2
O

50
K

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

Clathrate hydrates in interstellar environment

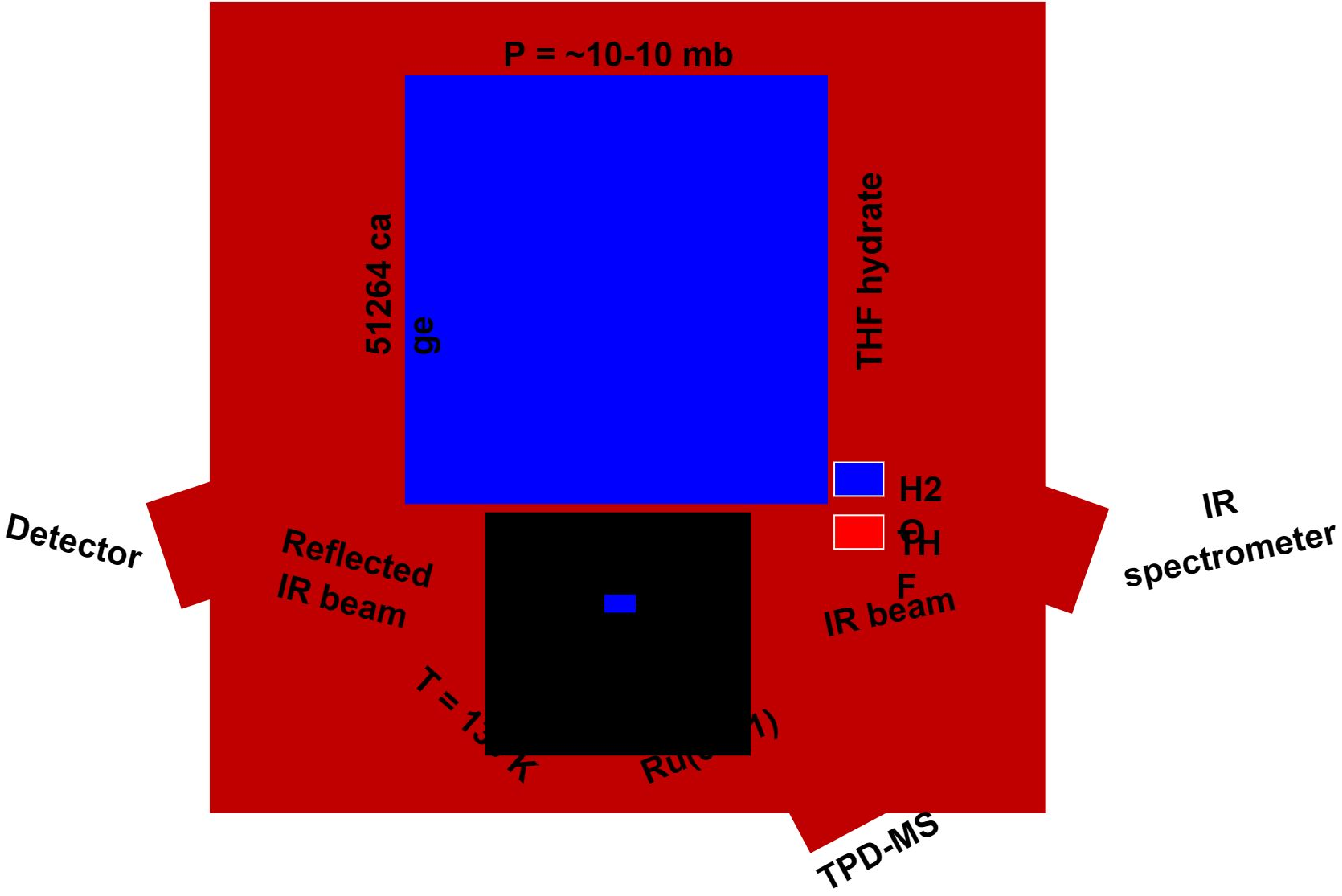


Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

Spontaneous formation of tetrahydrofuran hydrate i n 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

(a)

THF hydrate

ASW-trapped THF

T=130 K

[redacted]

ASW-trapped THF

(b)

3390 cm-1

ASW

3267 cm-1

T=130 K

THF hydrate

3159 cm-1

[redacted]

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

Many hydra
tes

Formation of cubic ice via clathrate hydrate, prepare d in ultrahigh vacuum at cryogenic conditions

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

Cubic ice via clathrate hydrate

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

Cubic ice via clathrate hydrate

T = 135 K

ASW-trapped acetone

Acetone hydrate

1709 cm-1

ASW

1721 cm-1

3395 cm-1

3284 cm-1

Time (h)

Ice Ic

3164 cm-1

1702 cm-1

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

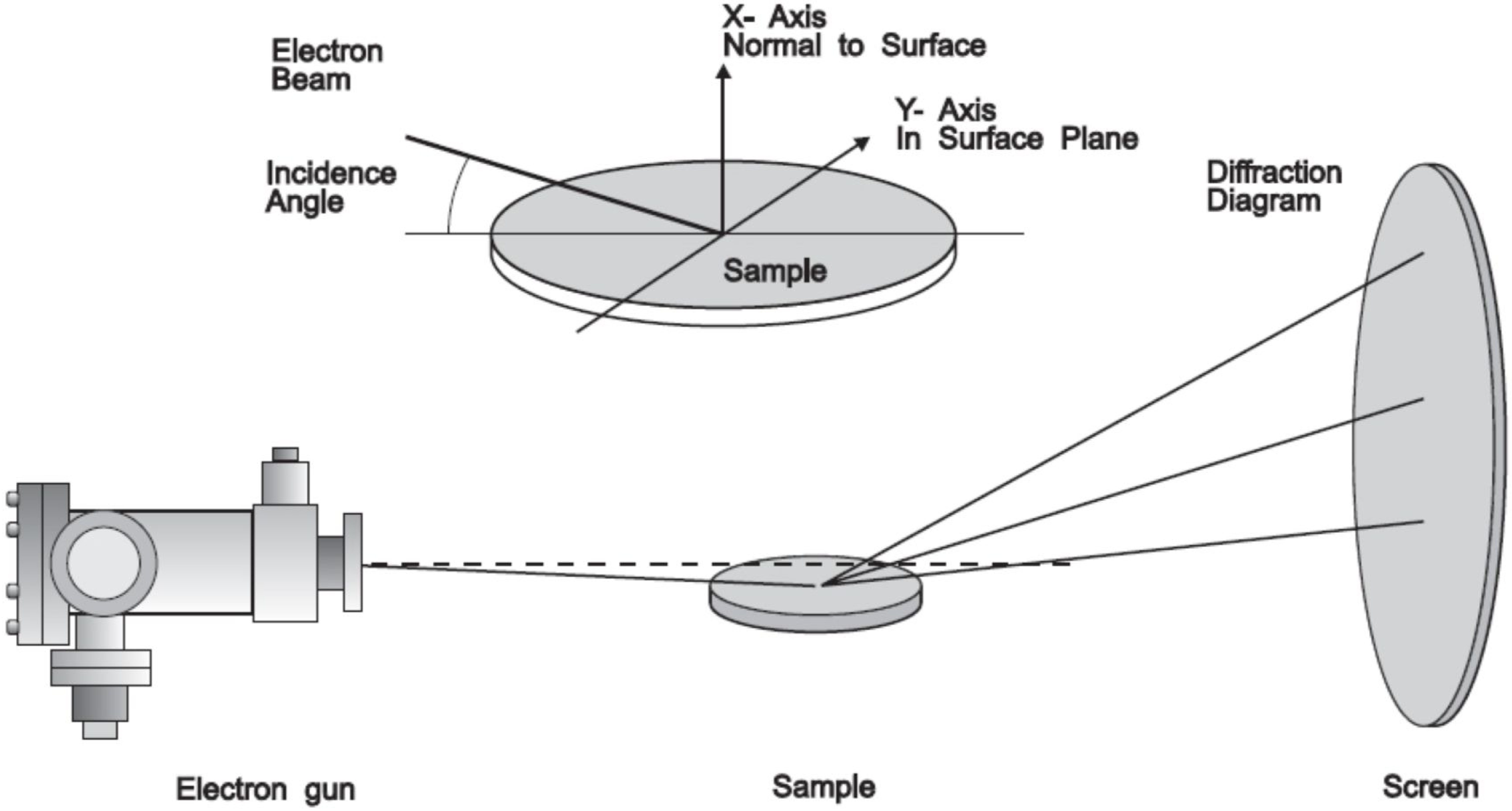
Diffraction pattern of cubic ice

Cubic Ice

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

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

RHEED set-up



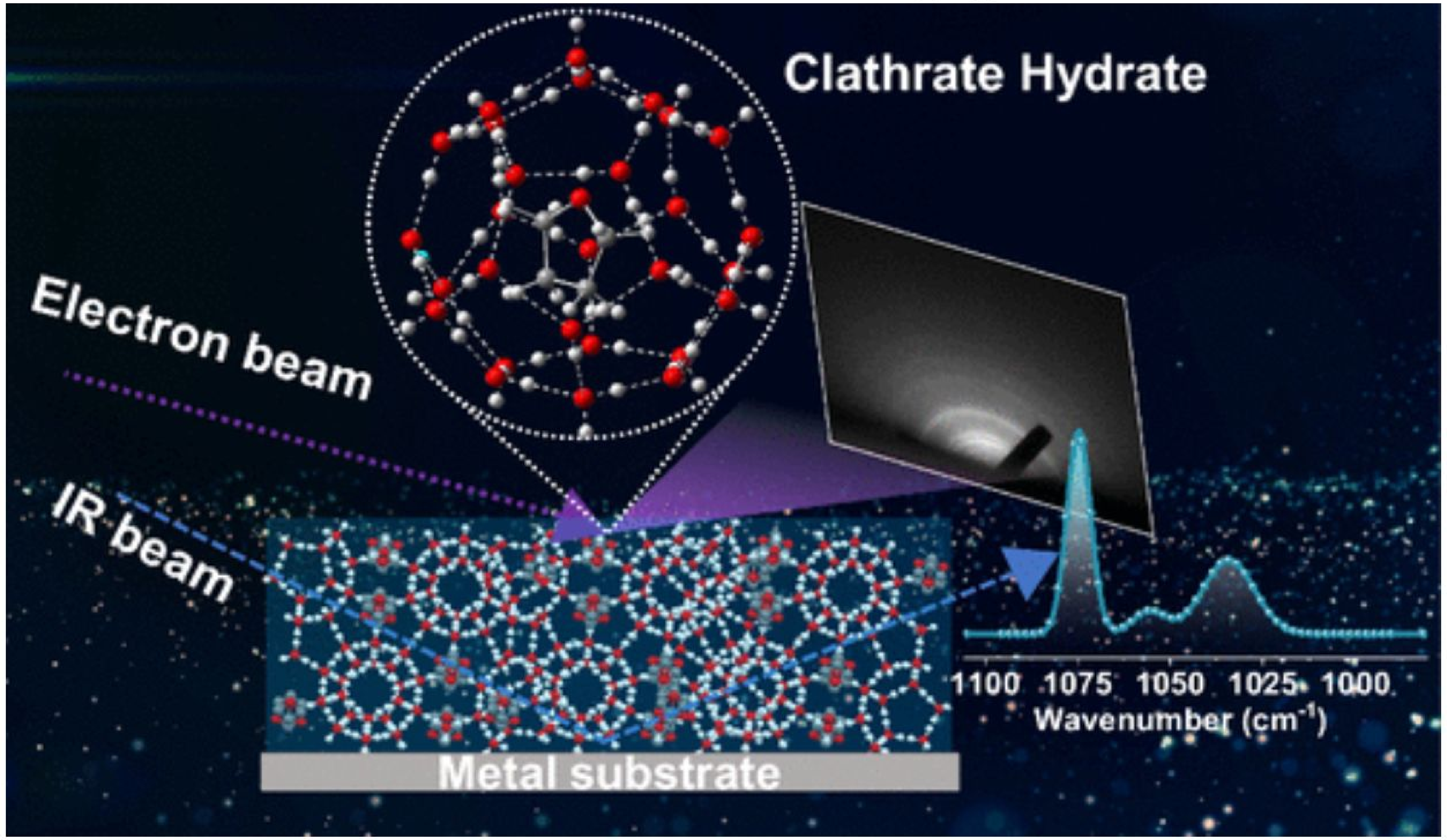
https://www.staibinstruments.com/products/rheed/

Cubic ice via clathrate hydrate

Dr. Ryutaro Souda, NIMS, Tsukuba, Japan

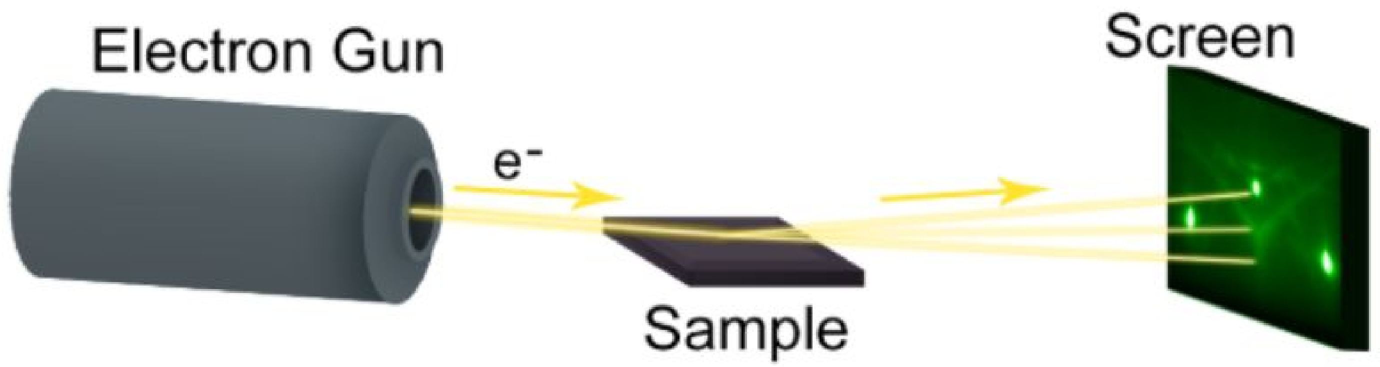
Ghosh, J. *et al., J. Phys. Chem. Lett.* **2020**, *11*, 26-32

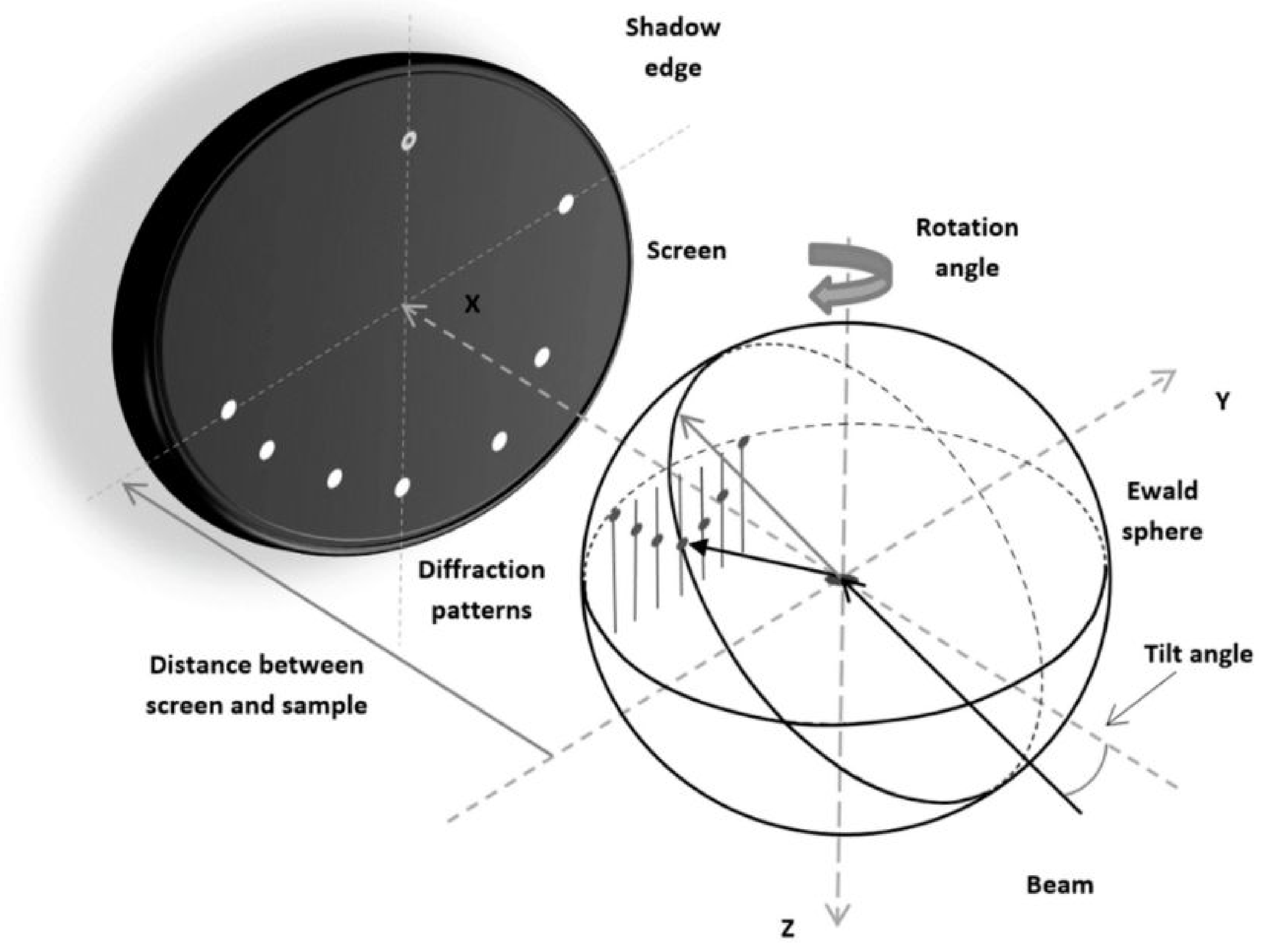
Growth of Clathrate Hydrates in Nanoscale Ice Films Observed Using Electron Diffraction and Infrared Spectroscopy

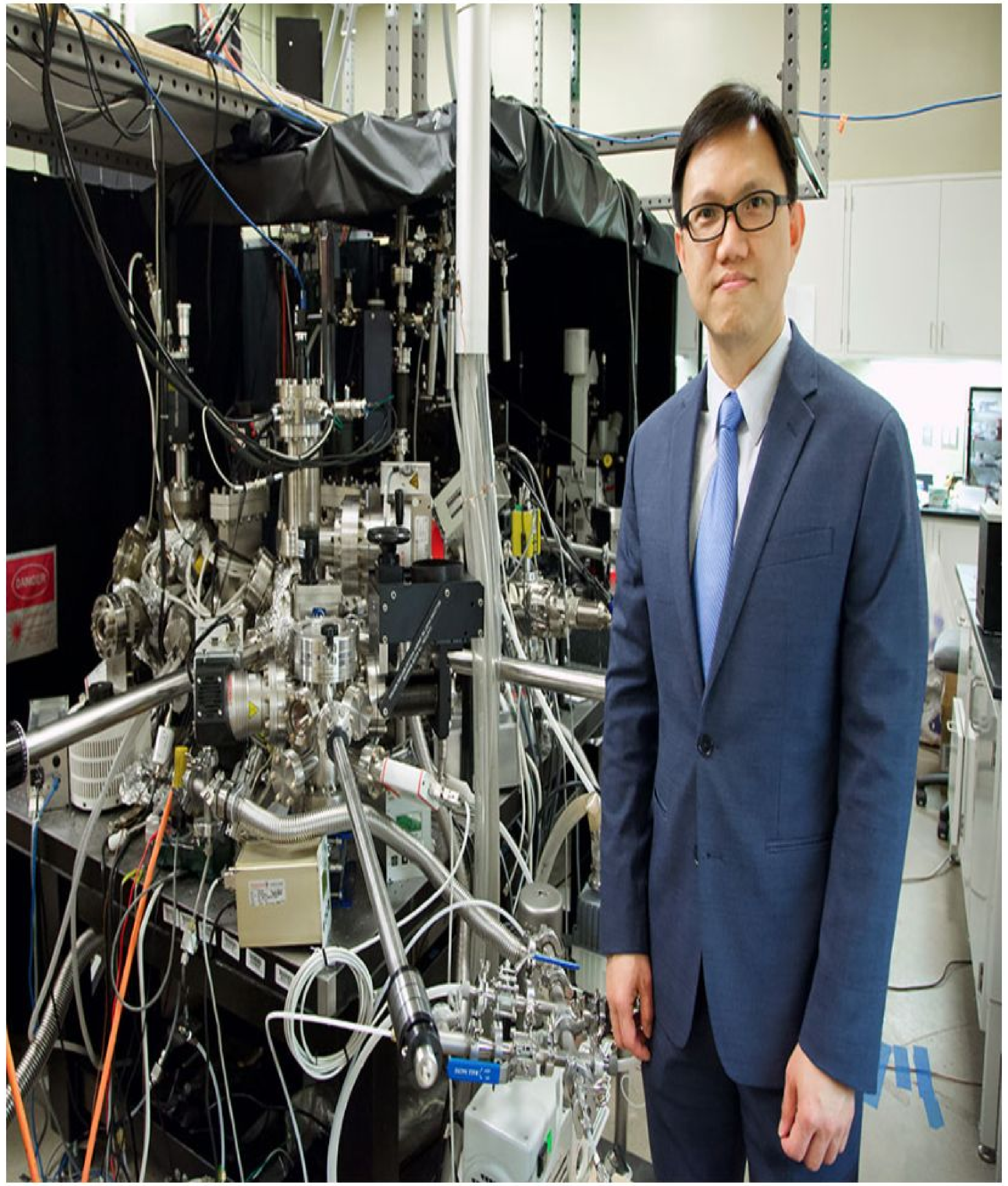


Malla, B. K. *et al., J. Phys. Chem. Lett.* ***2025****, 16, 1, 365–371*

Reflection high energy electron dif fraction



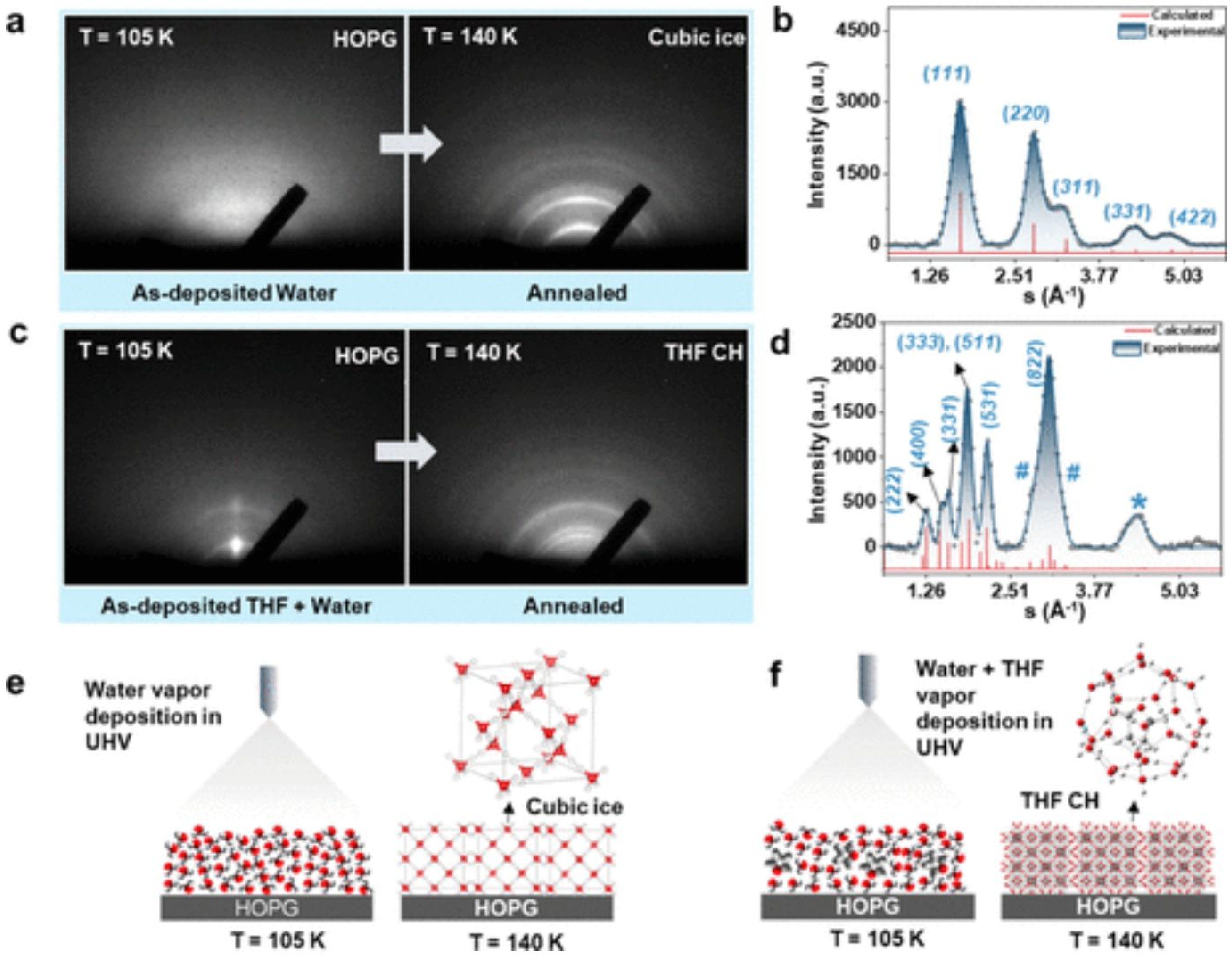




Instrument at UoH

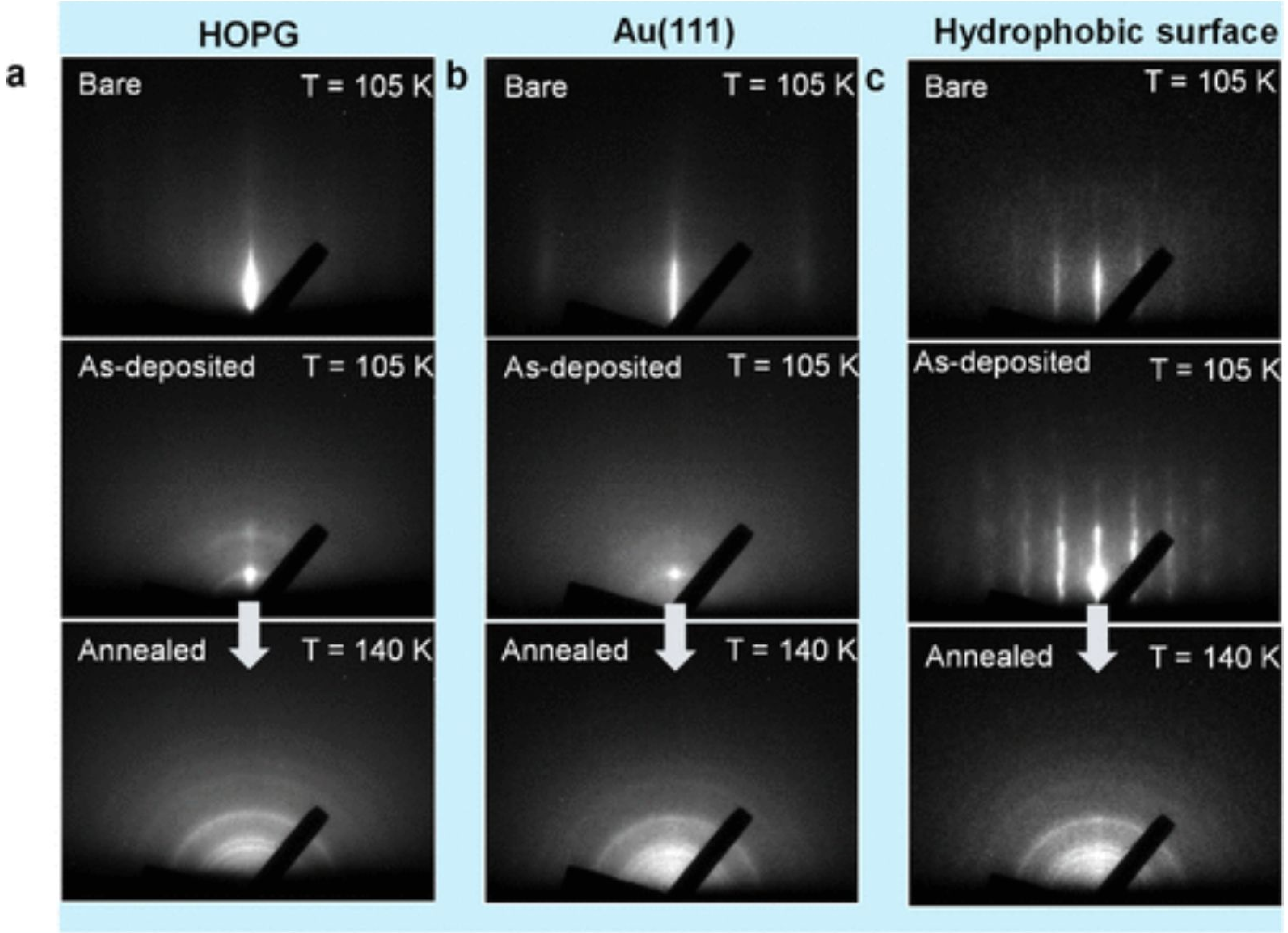
S. Hasegawa., in Characterization of Material, Wiley, **2012**, 1

RHEED study



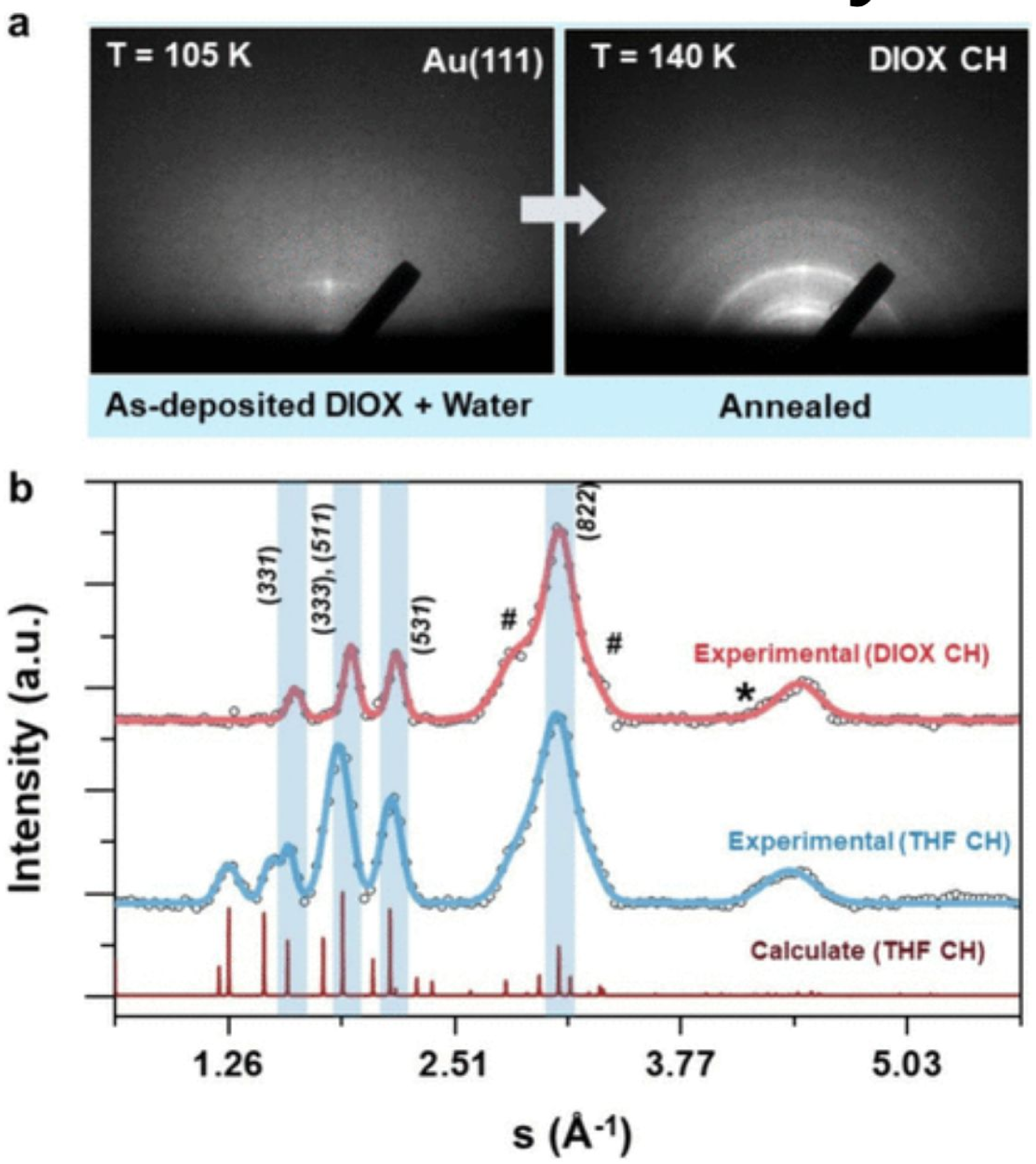
Malla, B. K. *et al., J. Phys. Chem. Lett.* ***2025****, 16, 1, 365–371*

RHEED study



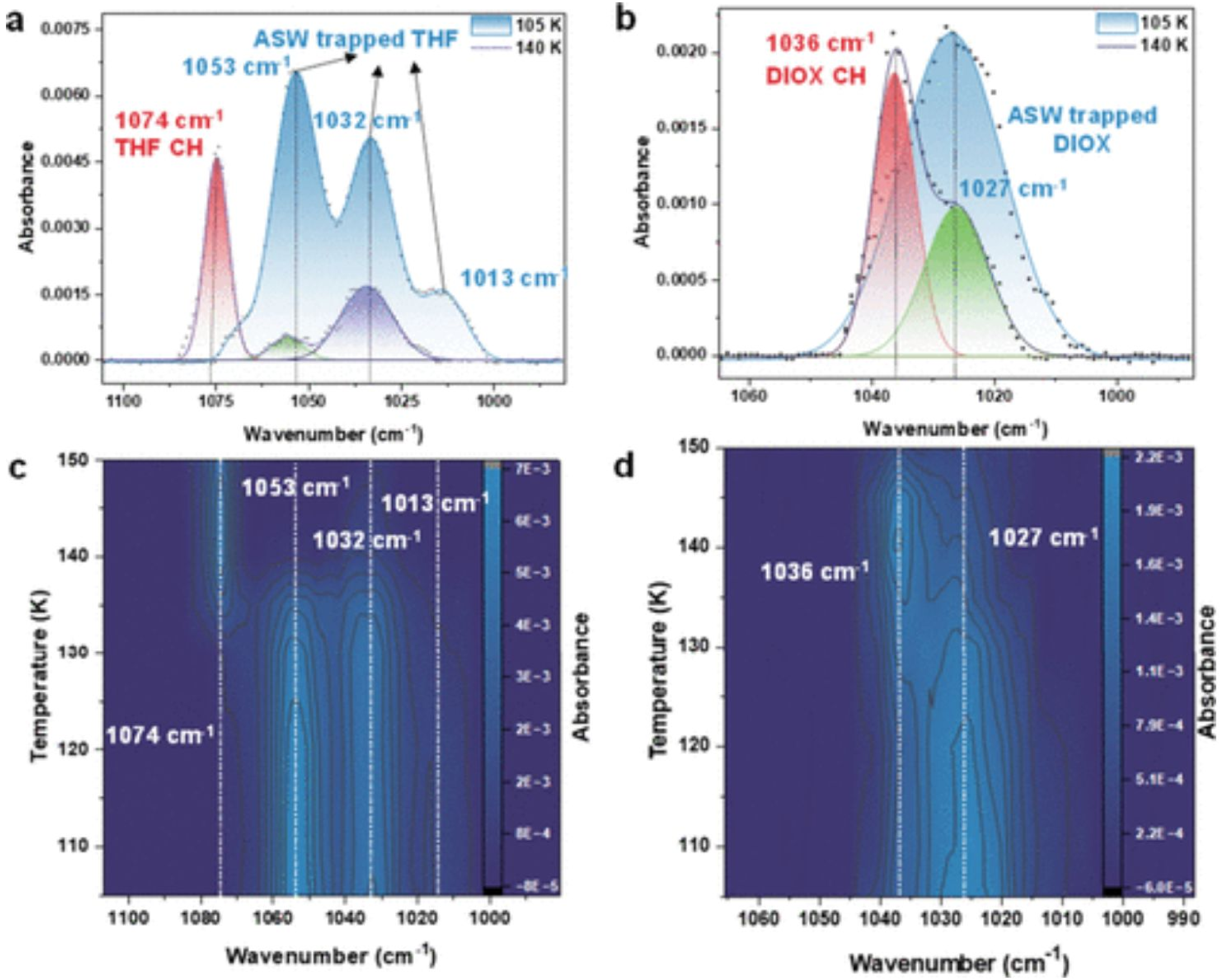
Malla, B. K. *et al., J. Phys. Chem. Lett.* ***2025****, 16, 1, 365–371*

RHEED study



Malla, B. K. *et al., J. Phys. Chem. Lett.* ***2025****, 16, 1, 365–371*

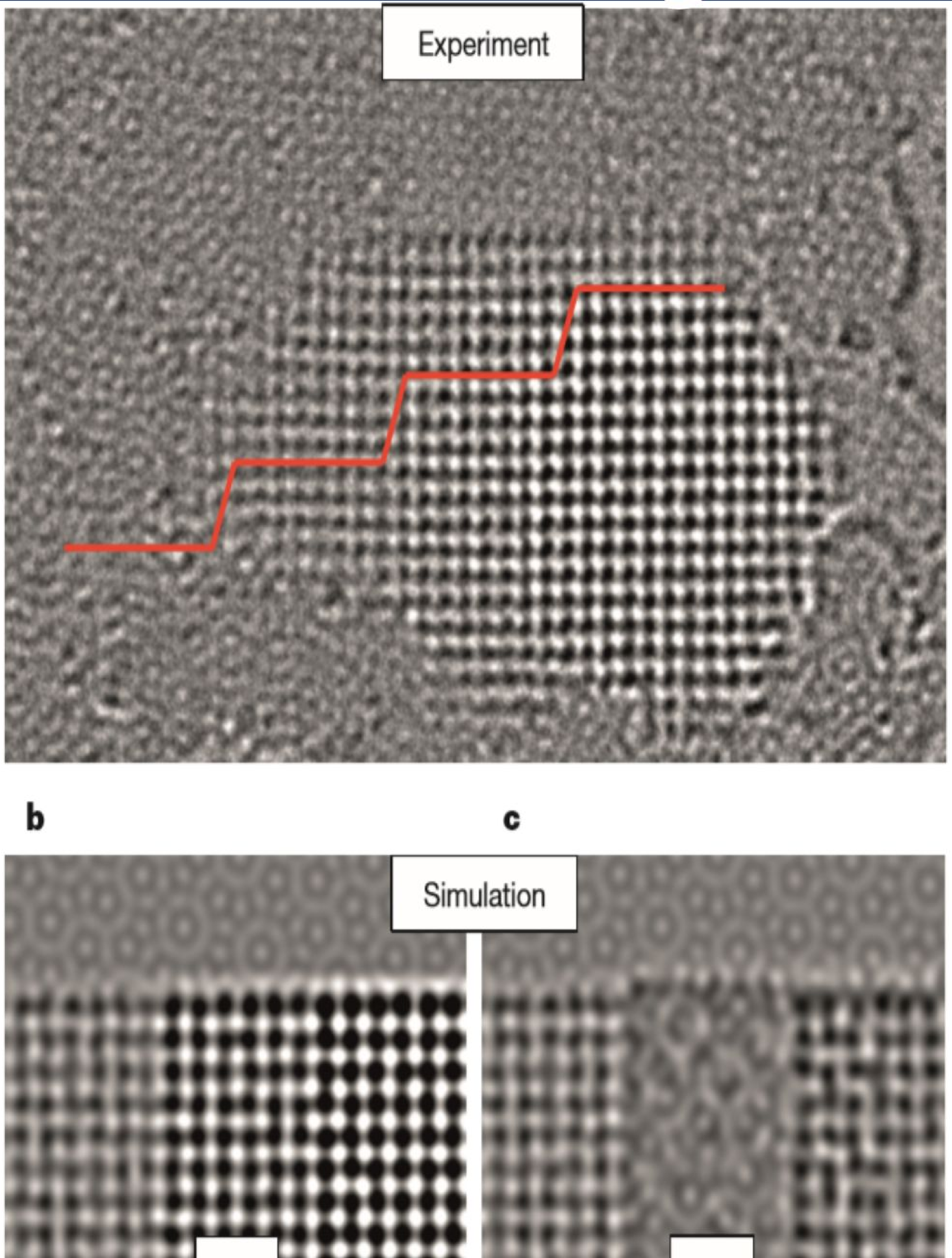
RAIRS study

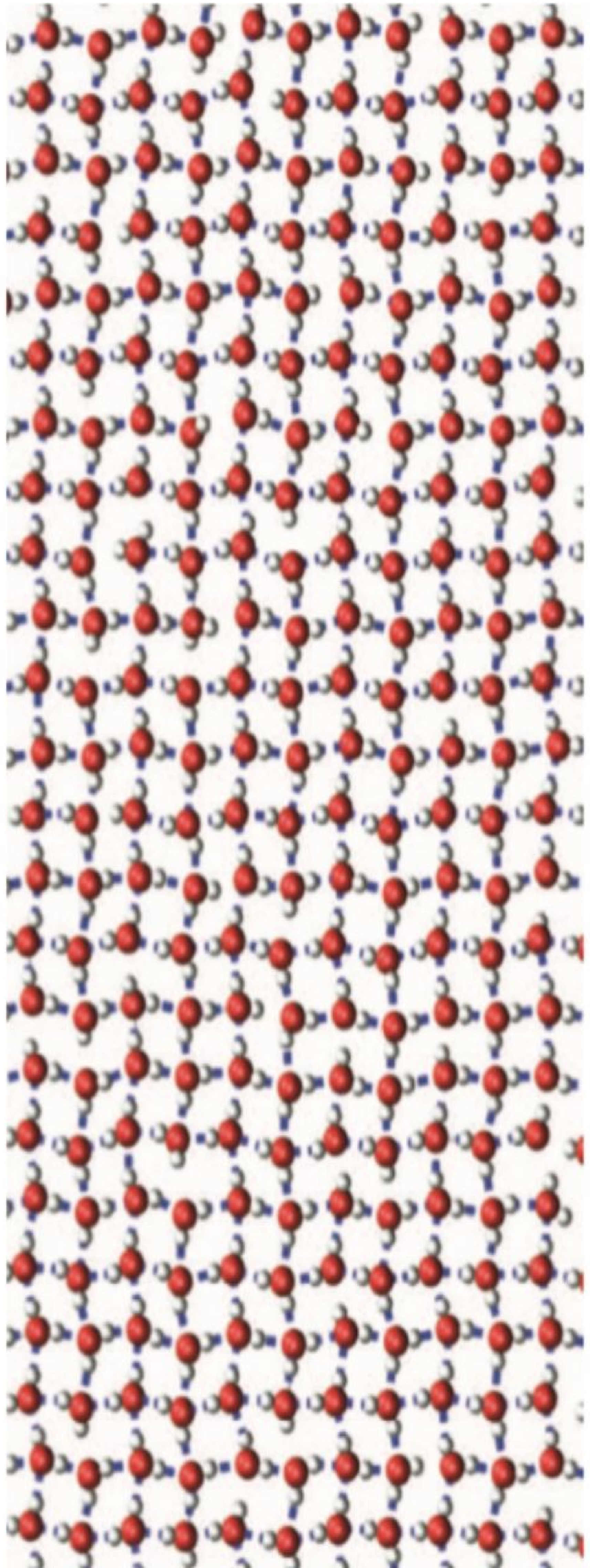


Malla, B. K. *et al., J. Phys. Chem. Lett.* ***2025****, 16, 1, 365–371*

Phenomena

Observing clathrate hydrates?



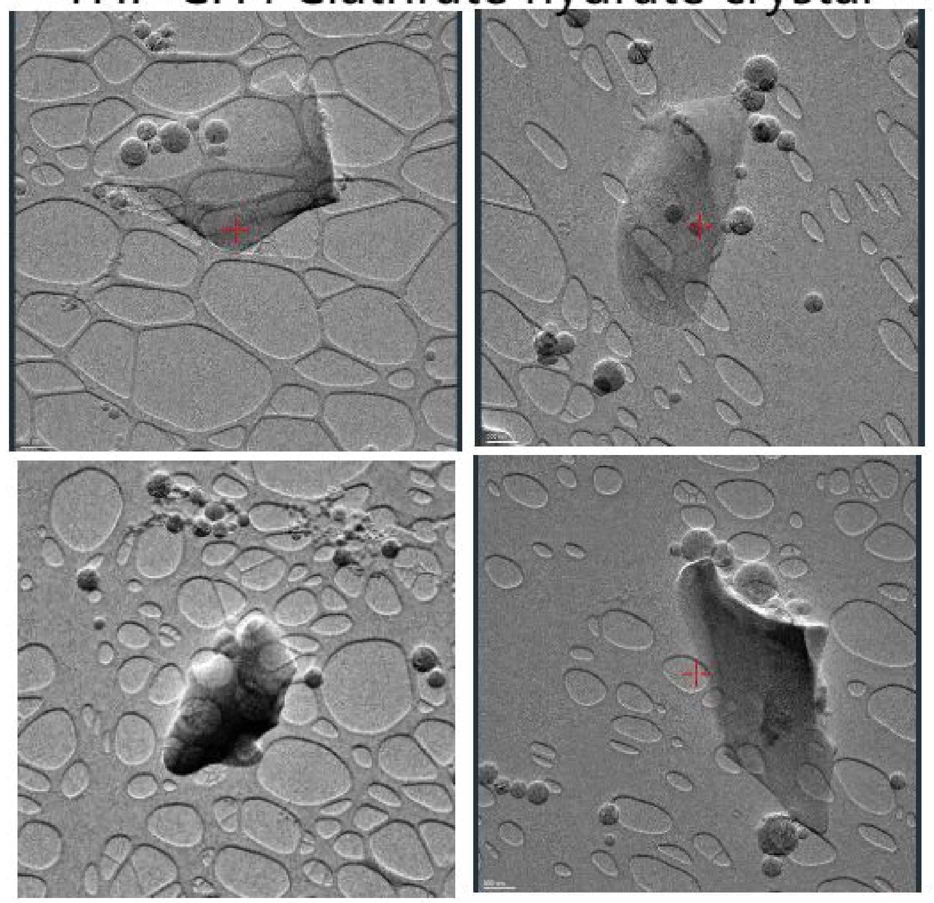


Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015,** *519* (7544), 443-445.

Electron diffraction of nanometer-scale crystals of clathrate hydrate

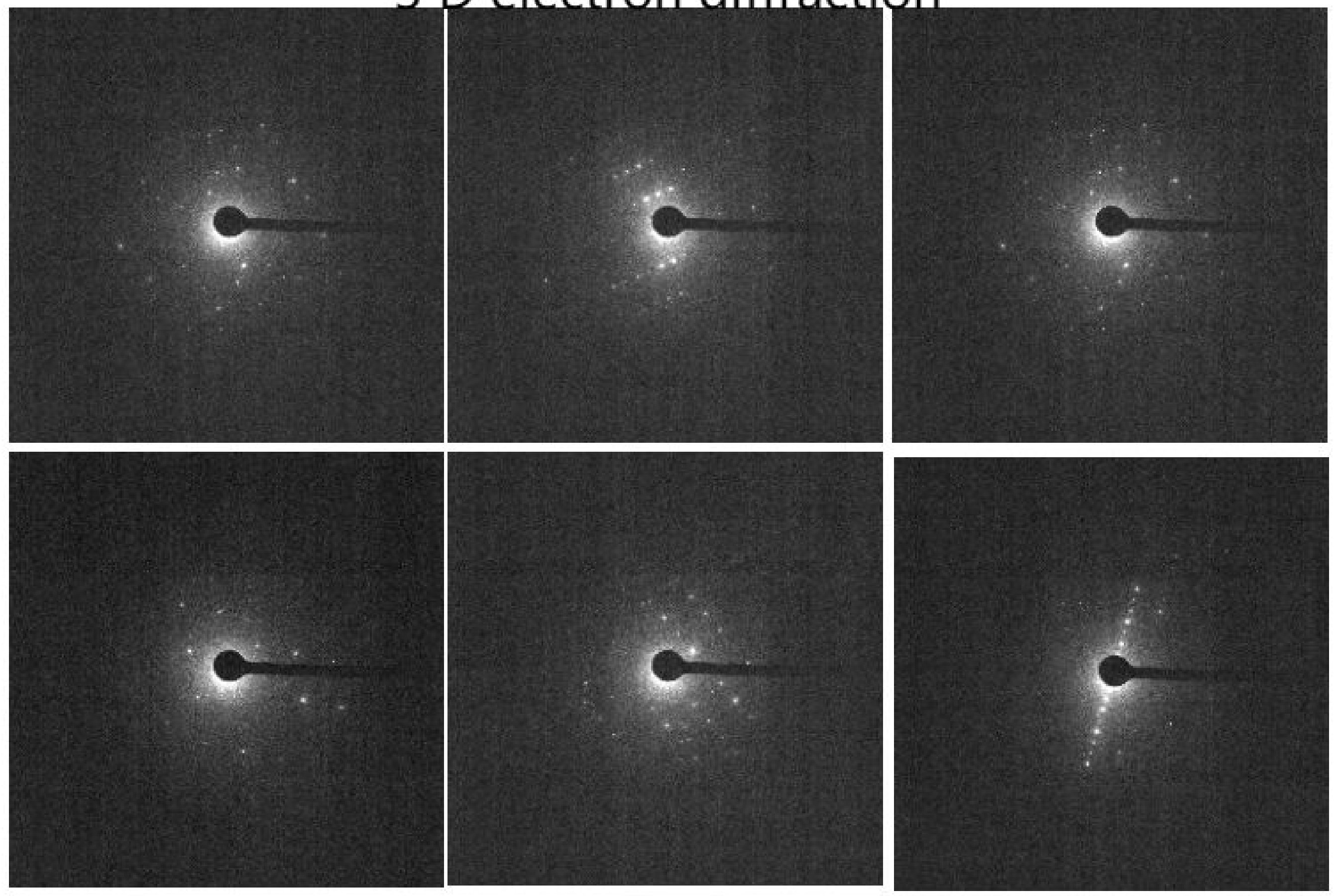
(a)

THF-CH4 Clathrate hydrate crystal

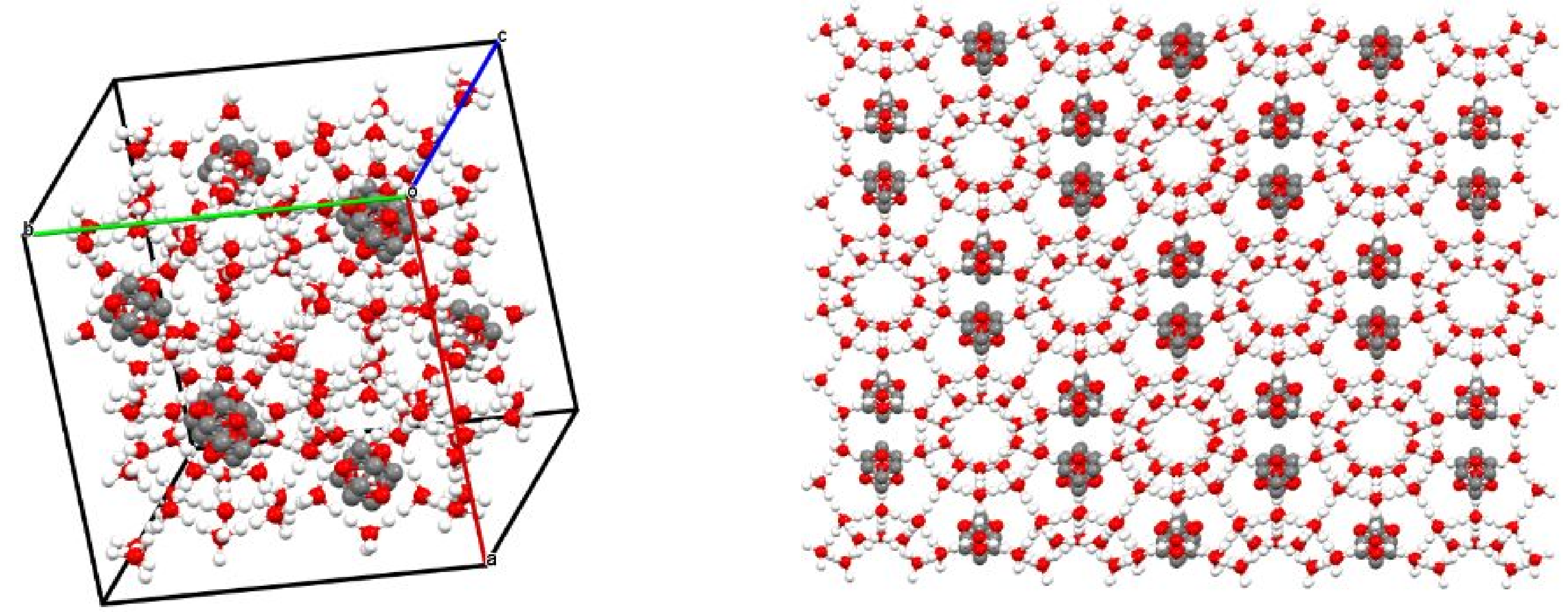


(b)

3 D electron diffraction



(c)

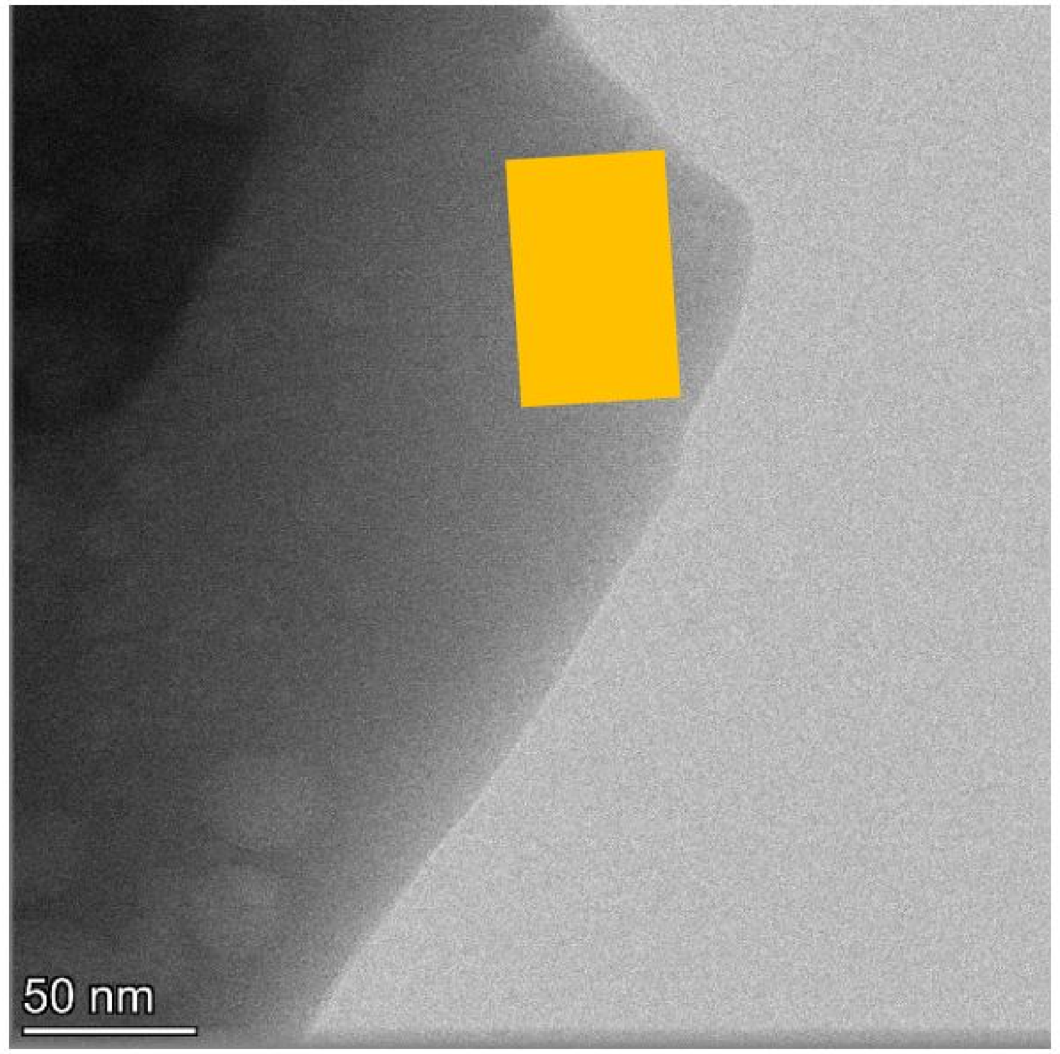


Crystal structure

Unpublished

Imaging of CH planes under Cryo-EM

(a)



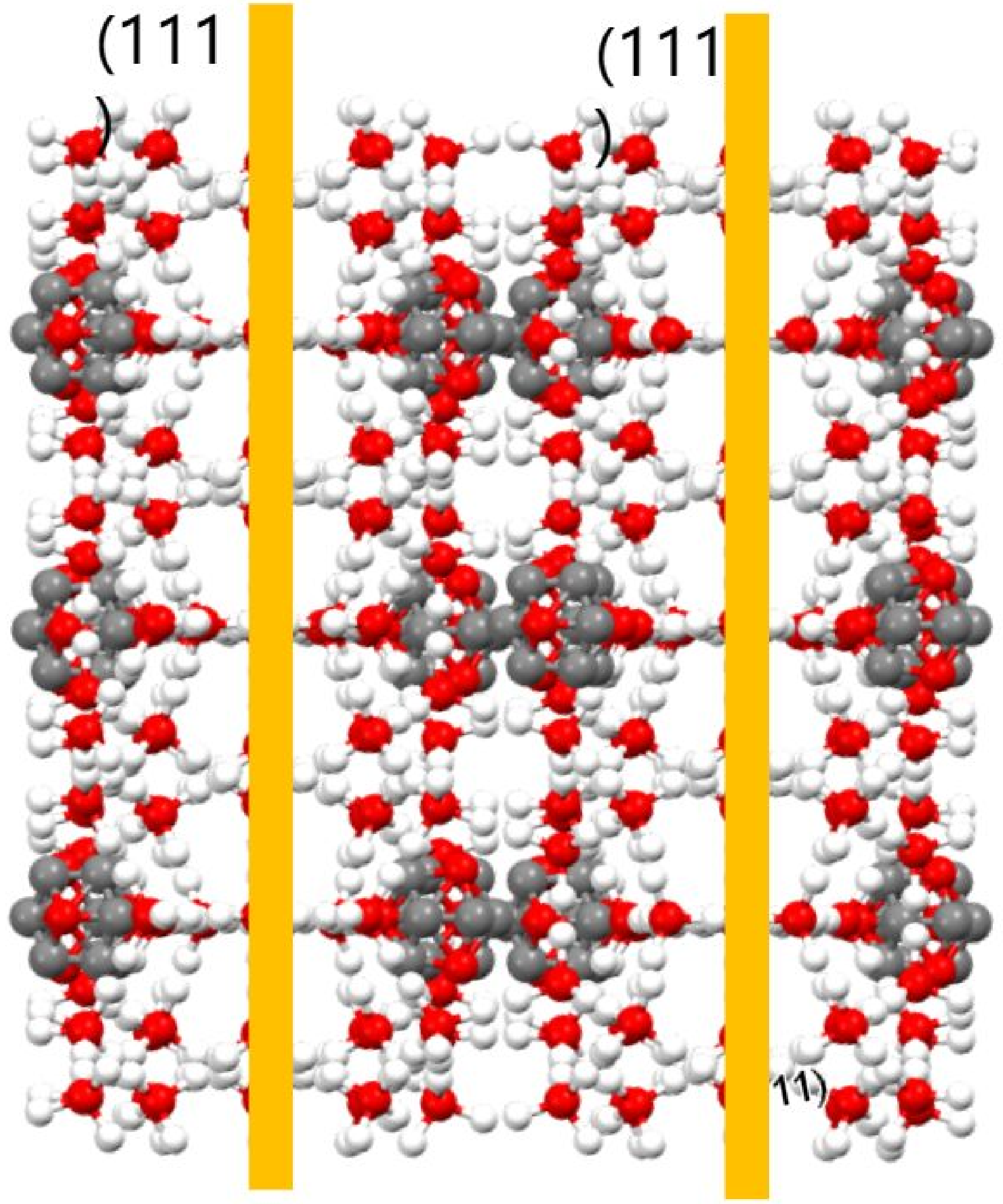
(b)

(1)

(3)

9.36 Å

(c)



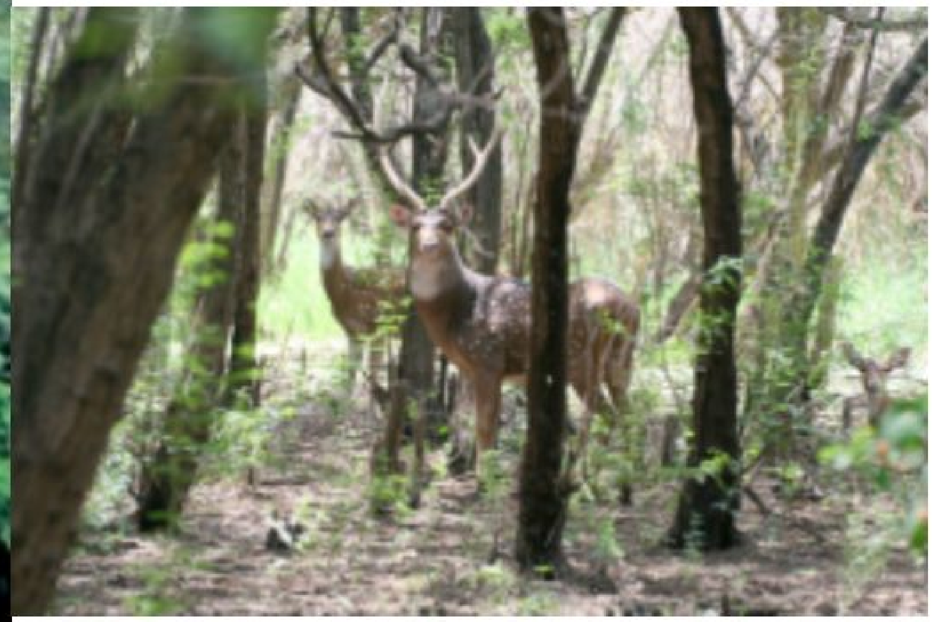
Unpublished


thermo scientific

International Centre for Clean Water

https://iccw.world

Indian Institute of Technology Madras



murthi/V. Kamakoti

Associate Editor

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pradeep RESEARCH GROUP

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Thank you all