The Prebiotic Potential and Molecular Diversity of Space Environments

Past Projects and Future Possibilities with SOFIA

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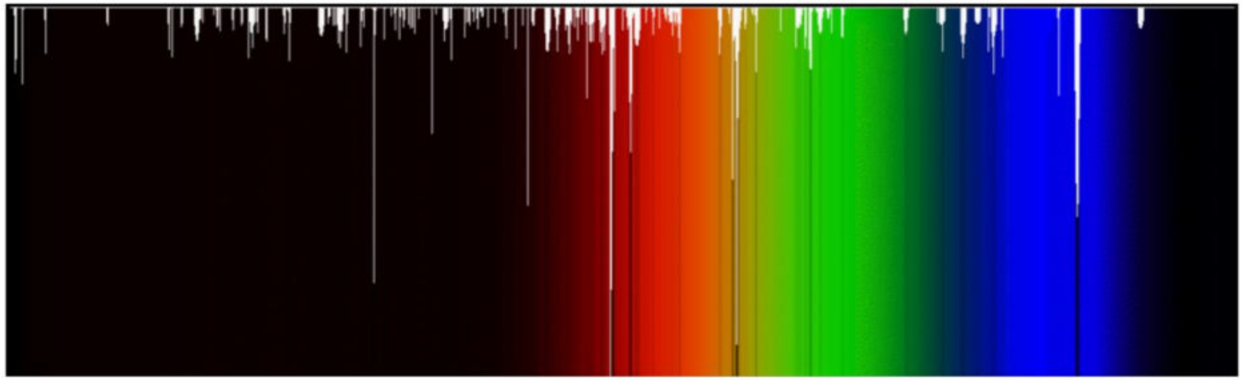
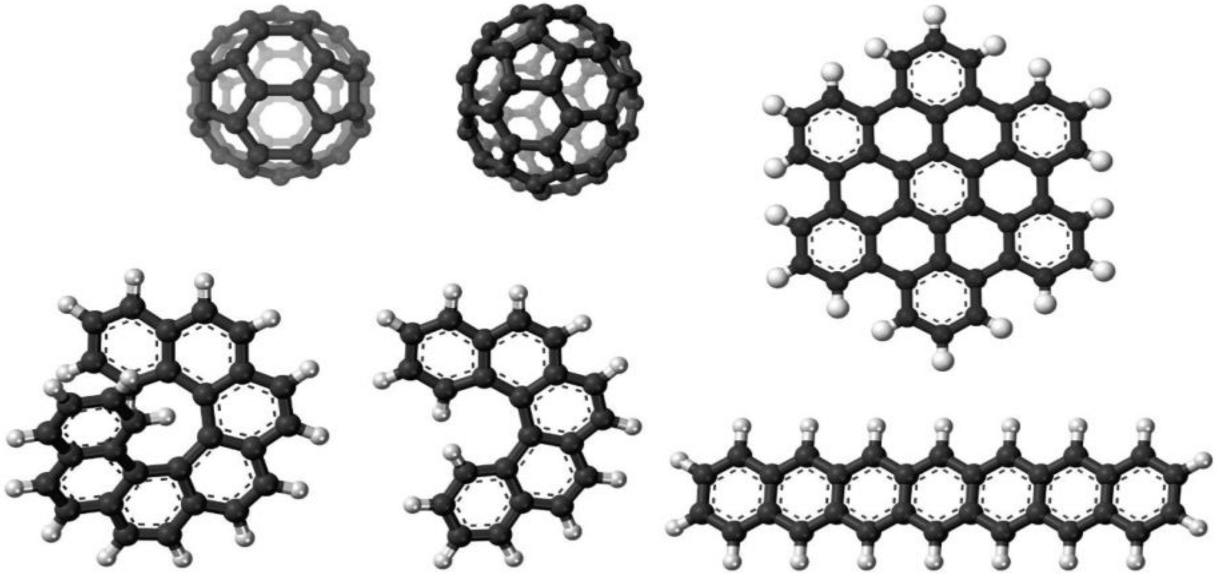
The Early Years of Astrochemistry (1922-1942)

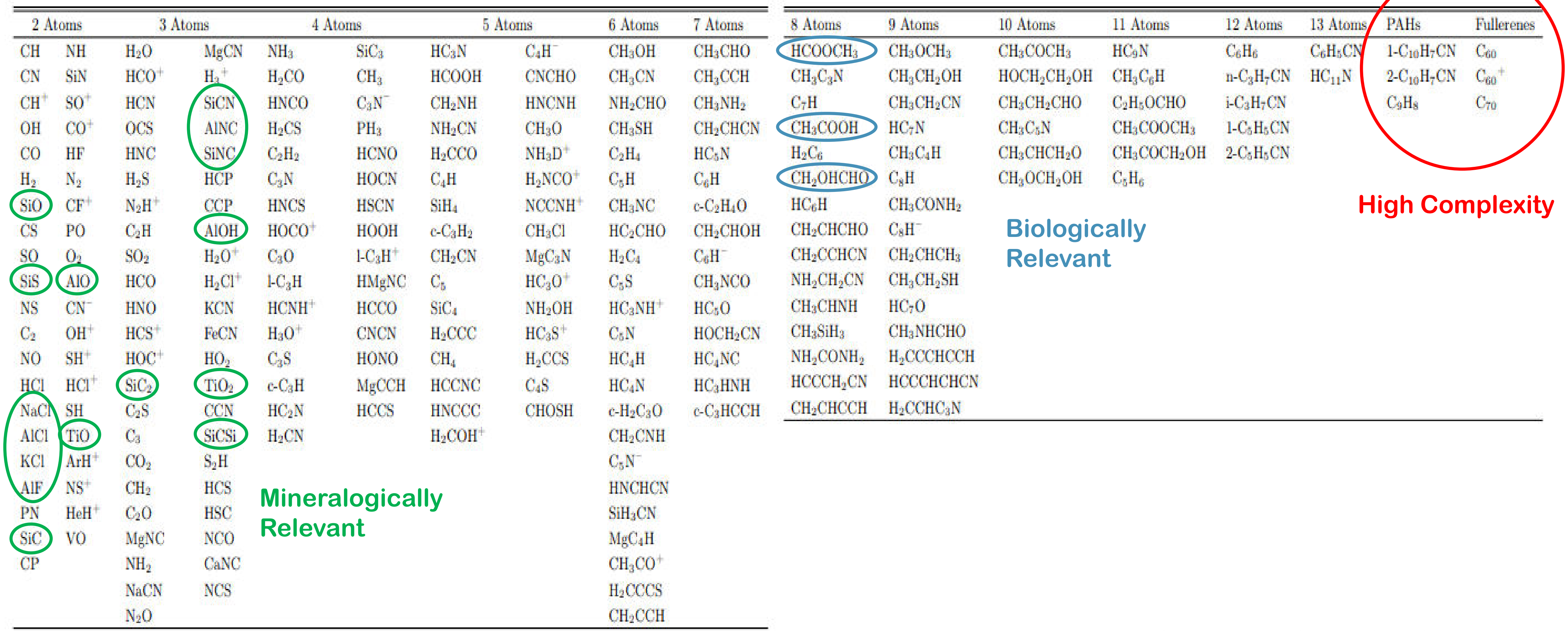




Feldman, *Can. J. Phys.* **79**, 89.

Modern Astrochemistry (1963 – Present)

Molecules are Everywhere!



2 Atoms		3 Atoms		4 Atoms		5 Atoms		6 Atoms	7 Atoms
CH	NH	H_2O	MgCN	NH_3	SiC_3	HC_3N	C_4H^-	CH_3OH	CH_3CHO
CN	SiN	HCO^+	H_3^+	H_2CO	CH_3	HCOOH	CNCHO	CH_3CN	CH_3CCH
CH^+	SO^+	HCN	SiCN	HNCO	C_3N^-	CH_2NH	HNCNH	NH_2CHO	CH_3NH_2
OH	CO^+	OCS	AlNC	H_2CS	PH_3	NH_2CN	CH_3O	CH_3SH	CH_2CHCN
CO	HF	HNC	SiNC	C_2H_2	HCNO	H_2CCO	NH_3D^+	C_2H_4	HC_5N
H_2	N_2	H_2S	HCP	C_3N	HOCN	C_4H	H_2NCO^+	C_5H	C_6H
SiO	CF^+	N_2H^+	CCP	HNCS	HSCN	SiH_4	$NCCNH^+$	CH_3NC	$c\text{-}C_2H_4O$
CS	PO	C_2H	AlOH	$HOCO^+$	HOOH	$c\text{-}C_3H_2$	CH_3Cl	HC_2CHO	CH_2CHOH
SO	O_2	SO_2	H_2O^+	C_3O	$l\text{-}C_3H^+$	CH_2CN	MgC_3N	H_2C_4	C_6H^-
SiS	AlO	HCO	H_2Cl^+	$l\text{-}C_3H$	HMgNC	C_5	HC_3O^+	C_5S	CH_3NCO
NS	CN^-	HNO	KCN	$HCNH^+$	HCCO	SiC_4	NH_2OH	HC_3NH^+	HC_5O
C_2	OH^+	HCS^+	FeCN	H_3O^+	CNCN	H_2CCC	HC_3S^+	C_5N	$HOCH_2CN$
NO	SH^+	HOC^+	HO_2	C_3S	HONO	CH_4	H_2CCS	HC_4H	HC_4NC
HCl	HCl^+	SiC_2	TiO_2	$c\text{-}C_3H$	MgCCH	HCCNC	C_4S	HC_4N	HC_3HNH
NaCl	SH	C_2S	CCN	HC_2N	HCCS	HNCCC	CHOSH	$c\text{-}H_2C_3O$	$c\text{-}C_3HCCH$
AlCl	TiO	C_3	SiCSi	H_2CN		H_2COH^+		CH_2CNH	
KCl	ArH^+	CO_2	S_2H					C_5N^-	
AlF	NS^+	CH_2	HCS					HNCHCN	
PN	HeH^+	C_2O	HSC					SiH_3CN	
SiC	VO	MgNC	NCO					MgC_4H	
CP		NH_2	CaNC					CH_3CO^+	
		NaCN	NCS					H_2CCCS	
		N_2O						CH_2CCH	

8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13 Atoms	PAHs	Fullerenes
$HCOOCH_3$	CH_3OCH_3	CH_3COCH_3	HC_9N	C_6H_6	C_6H_5CN	$1\text{-}C_{10}H_7CN$	C_{60}
CH_3C_3N	CH_3CH_2OH	$HOCH_2CH_2OH$	CH_3C_6H	$n\text{-}C_3H_7CN$	$HC_{11}N$	$2\text{-}C_{10}H_7CN$	C_{60}^+
C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	$i\text{-}C_3H_7CN$		C_9H_8	C_{70}
CH_3COOH	HC_7N	CH_3C_5N	CH_3COOCH_3	$1\text{-}C_5H_5CN$			
H_2C_6	CH_3C_4H	CH_3CHCH_2O	CH_3COCH_2OH	$2\text{-}C_5H_5CN$			
CH_2OHCHO	C_8H	CH_3OCH_2OH	C_5H_6				
HC_6H	CH_3CONH_2						
CH_2CHCHO	C_8H^-						
CH_2CCHCN	CH_2CHCH_3						
NH_2CH_2CN	CH_3CH_2SH						
CH_3CHNH	HC_7O						
CH_3SiH_3	CH_3NHCHO						
NH_2CONH_2	$H_2CCCHCCH$						
$HCCCH_2CN$	HCCCHCHCN						
CH_2CHCCH	H_2CCHC_3N						

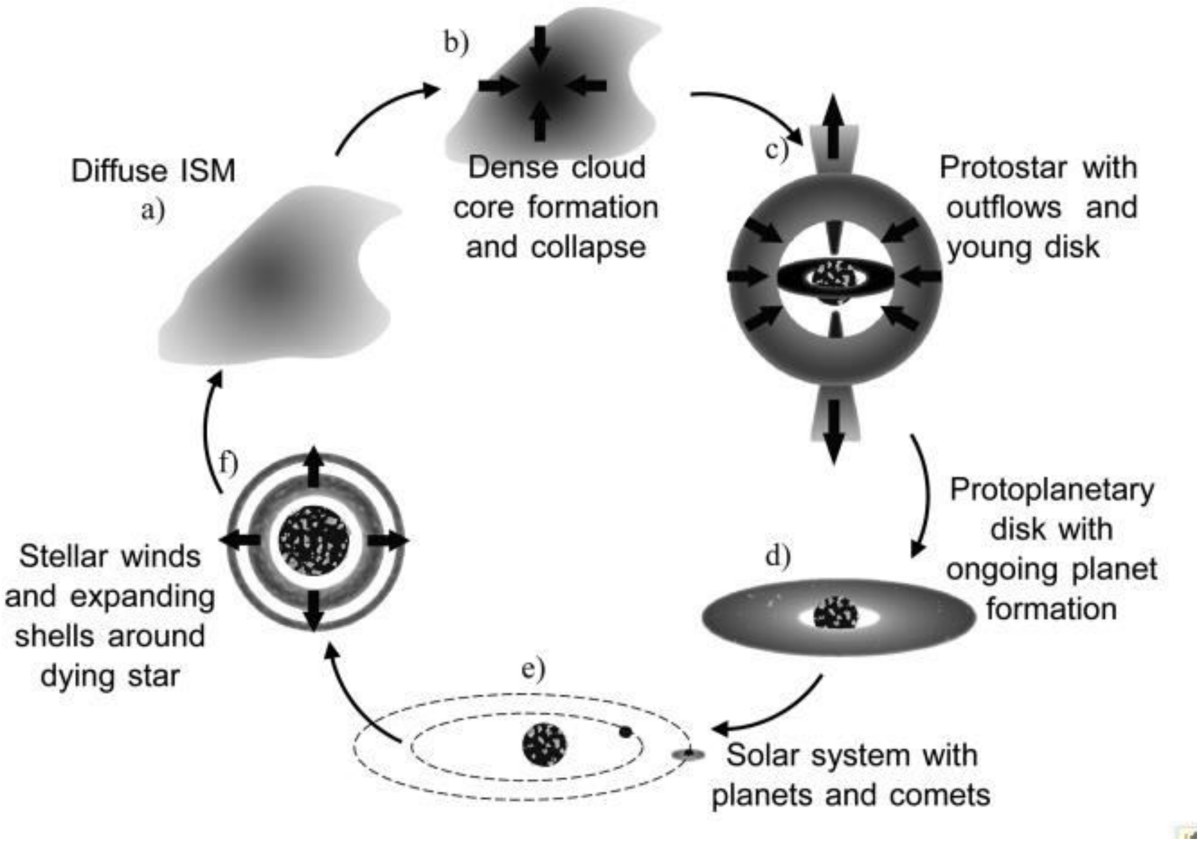
Mineralogically Relevant

Biologically Relevant

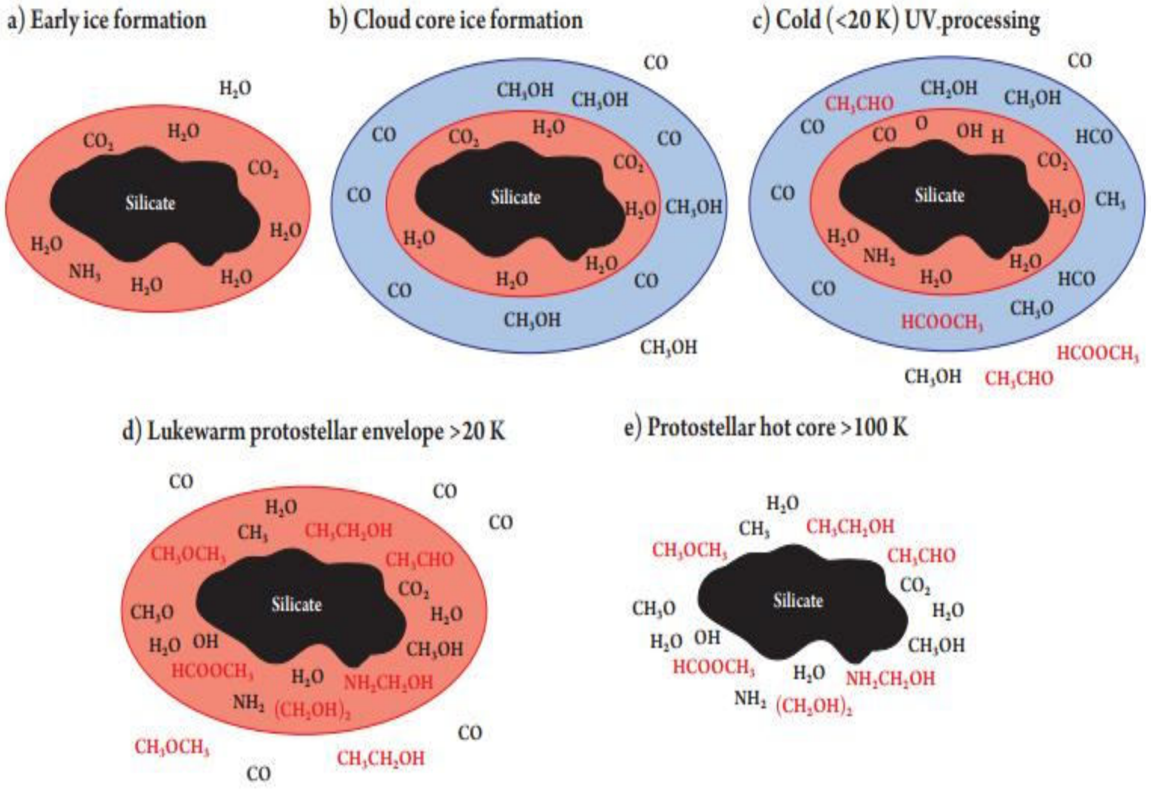
High Complexity

McGuire, *Astrophys. J. Suppl.* accepted.

Cosmic Chemistry Cycle

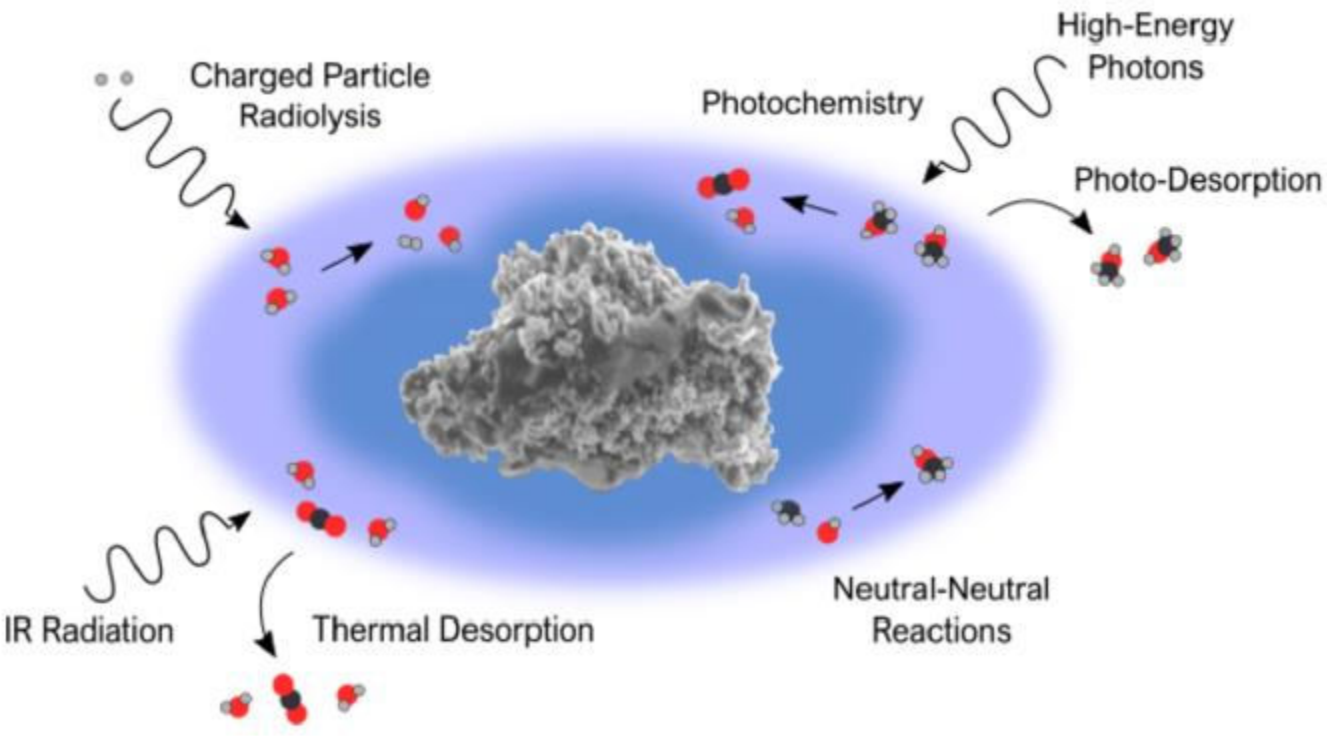


Öberg, *Chem. Rev.* **116**, 9631.

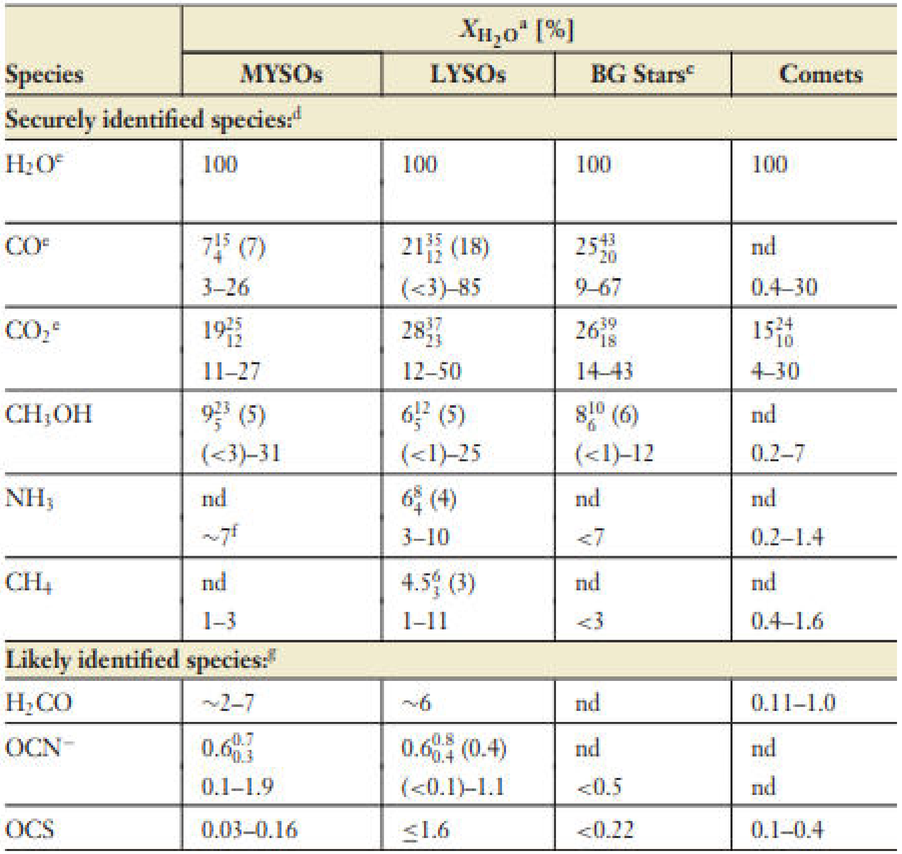


Öberg et al., *Astrophys. J.* **716**, 825.

Ices – the Factories of Interstellar Molecular Complexity!



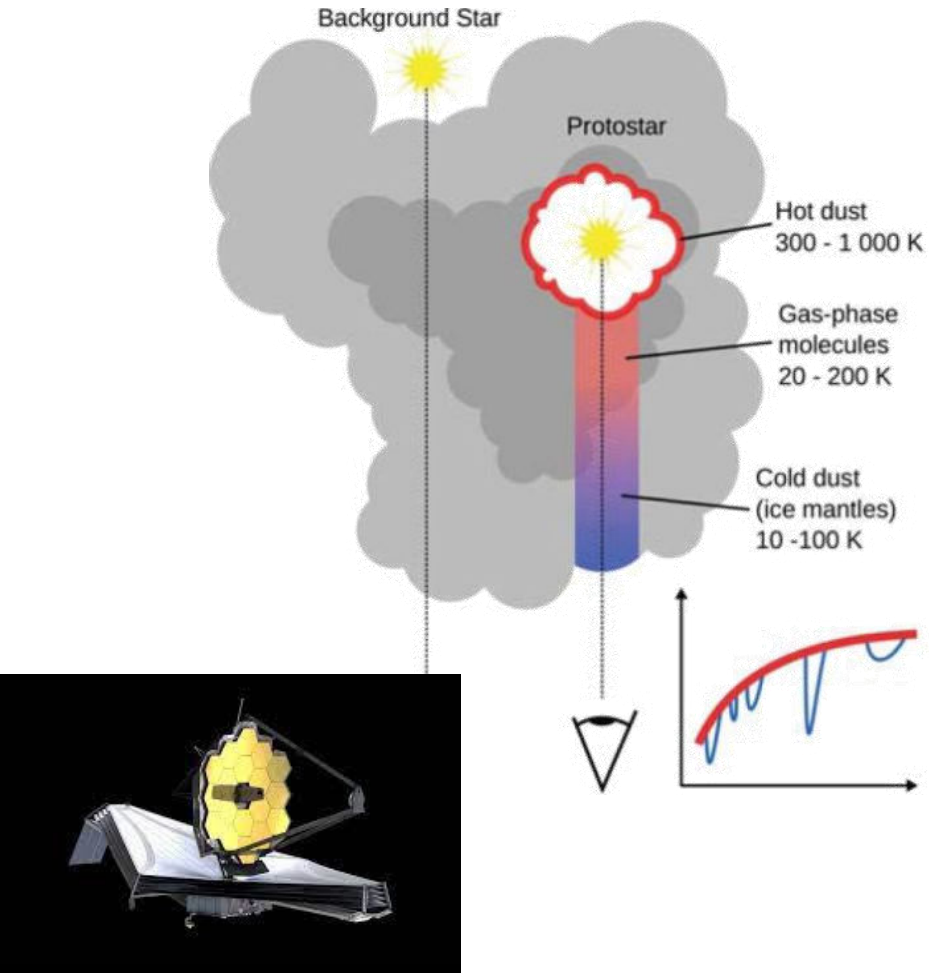
Herczku et al., *Rev. Sci. Instrum.* **92**, 084501.

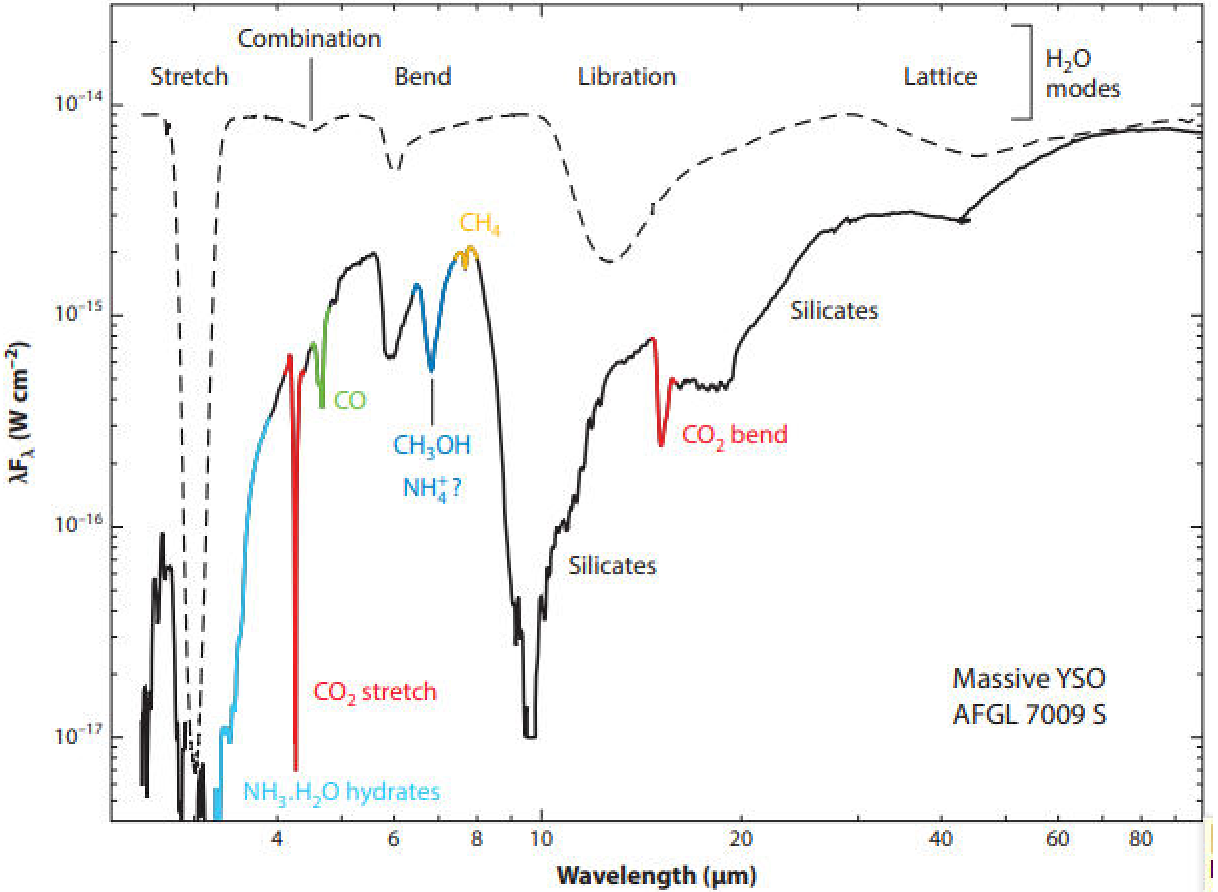


Species	X_{H_2O}[a] [%]			
	MYSOs	LYSOs	BG Stars[c]	Comets
Securely identified species:[d]				
H_2O[e]	100	100	100	100
CO[e]	7_4^{15} (7) 3–26	21_{12}^{35} (18) (<3)–85	25_{20}^{43} 9–67	nd 0.4–30
CO_2[e]	19_{12}^{25} 11–27	28_{23}^{37} 12–50	26_{18}^{39} 14–43	15_{10}^{24} 4–30
CH_3OH	9_5^{23} (5) (<3)–31	6_5^{12} (5) (<1)–25	8_6^{10} (6) (<1)–12	nd 0.2–7
NH_3	nd ~7[f]	6_4^{8} (4) 3–10	nd <7	nd 0.2–1.4
CH_4	nd 1–3	4.5_3^{6} (3) 1–11	nd <3	nd 0.4–1.6
Likely identified species:[g]				
H_2CO	~2–7	~6	nd	0.11–1.0
OCN^-	$0.6_{0.3}^{0.7}$ 0.1–1.9	$0.6_{0.4}^{0.8}$ (0.4) (<0.1)–1.1	nd <0.5	nd nd
OCS	0.03–0.16	≤1.6	<0.22	0.1–0.4

Boogert et al., *Annu. Rev. Astron. Astrophys.* **53**, 541.

Constraining the Chemical Compositions of Icy Mantles





Boogert et al., *Annu. Rev. Astron. Astrophys.* **53**, 541.

Constraining the Chemical Compositions of Icy Mantles

- Several telescopes available to collect mid-IR and THz spectra
- Laboratory spectral data needed to interpret observations

Image credits: NASA, USRA (Universities Space Research Association), and L-3 Communications Integrated Systems

Advantages of THz Spectroscopy Compared to Mid-IR

- Mid-IR
  - Only intra-molecular vibrational modes can be observed
  - Different molecules sharing functional moieties may be hard to identify

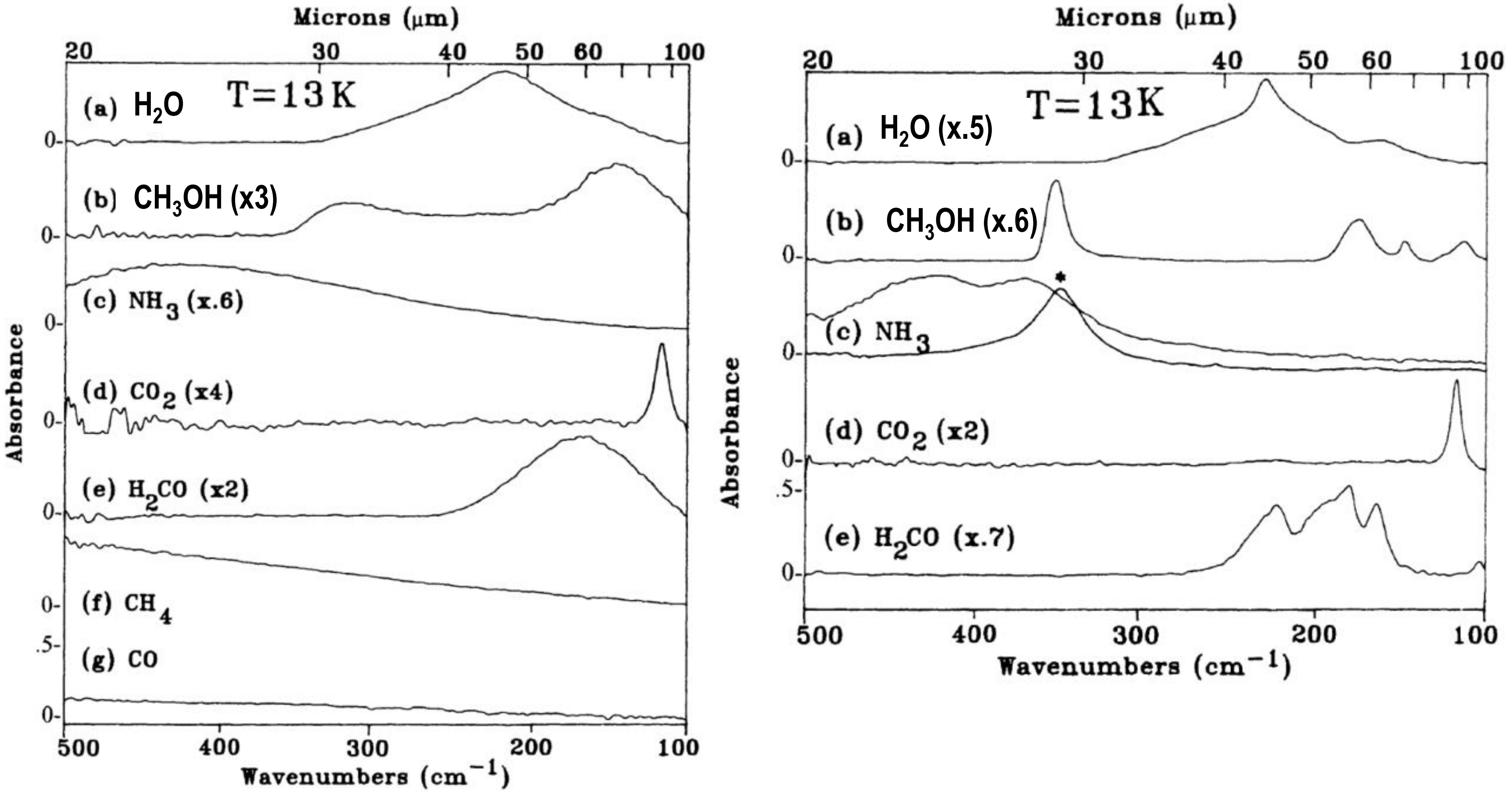
- THz
  - Lower energy vibrations are probed, including inter-molecular ones
  - Technique is sensitive to long-range interactions between molecules and ice structure

Advantages of THz Spectroscopy Compared to Mid-IR

- **Mid-IR**
  - **Transitions can only be observed in absorption**
  - **A mid-IR source (e.g., a YSO) behind the line of sight is needed, greatly reducing the number of astronomical settings that may be studied**

- **THz**
  - **Low energetic transitions mean that at <150 K absorption can occur against the background continuum**
  - **Molecules may therefore be studied via their emission signals**

Early Forays into Laboratory Far-IR Spectroscopy

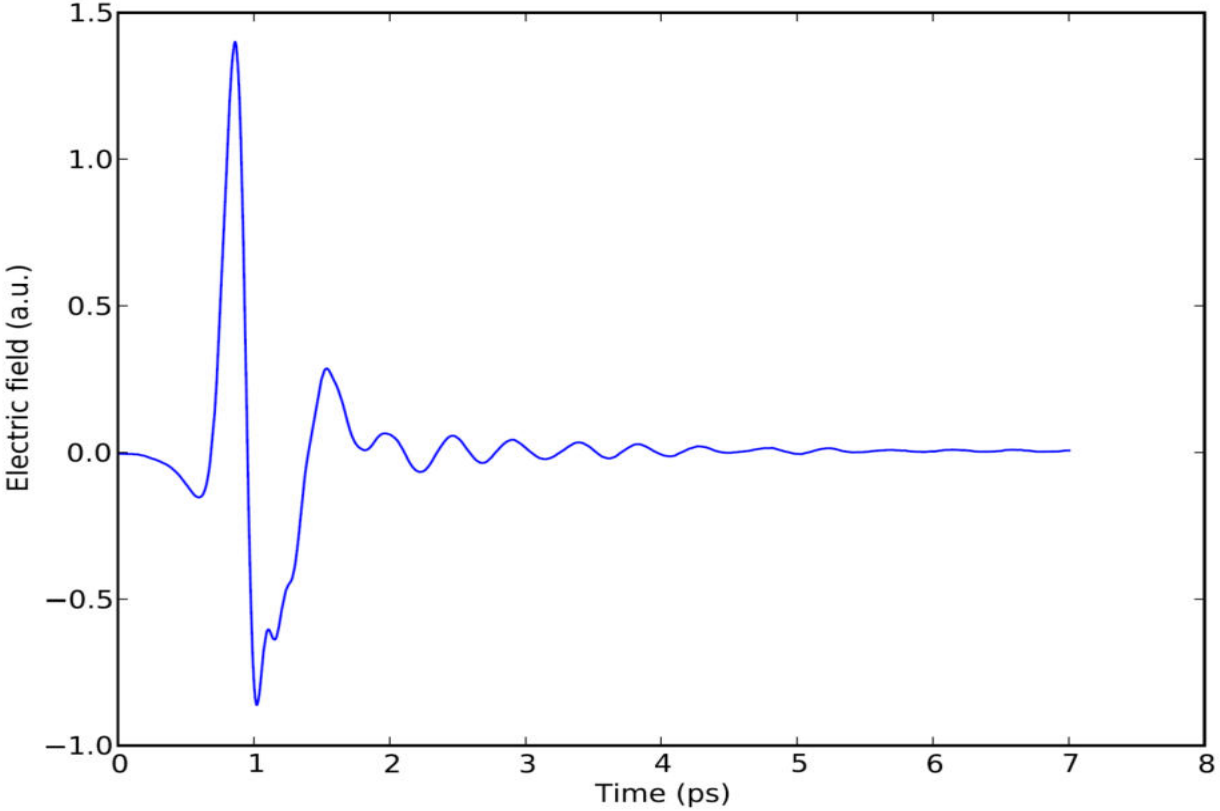


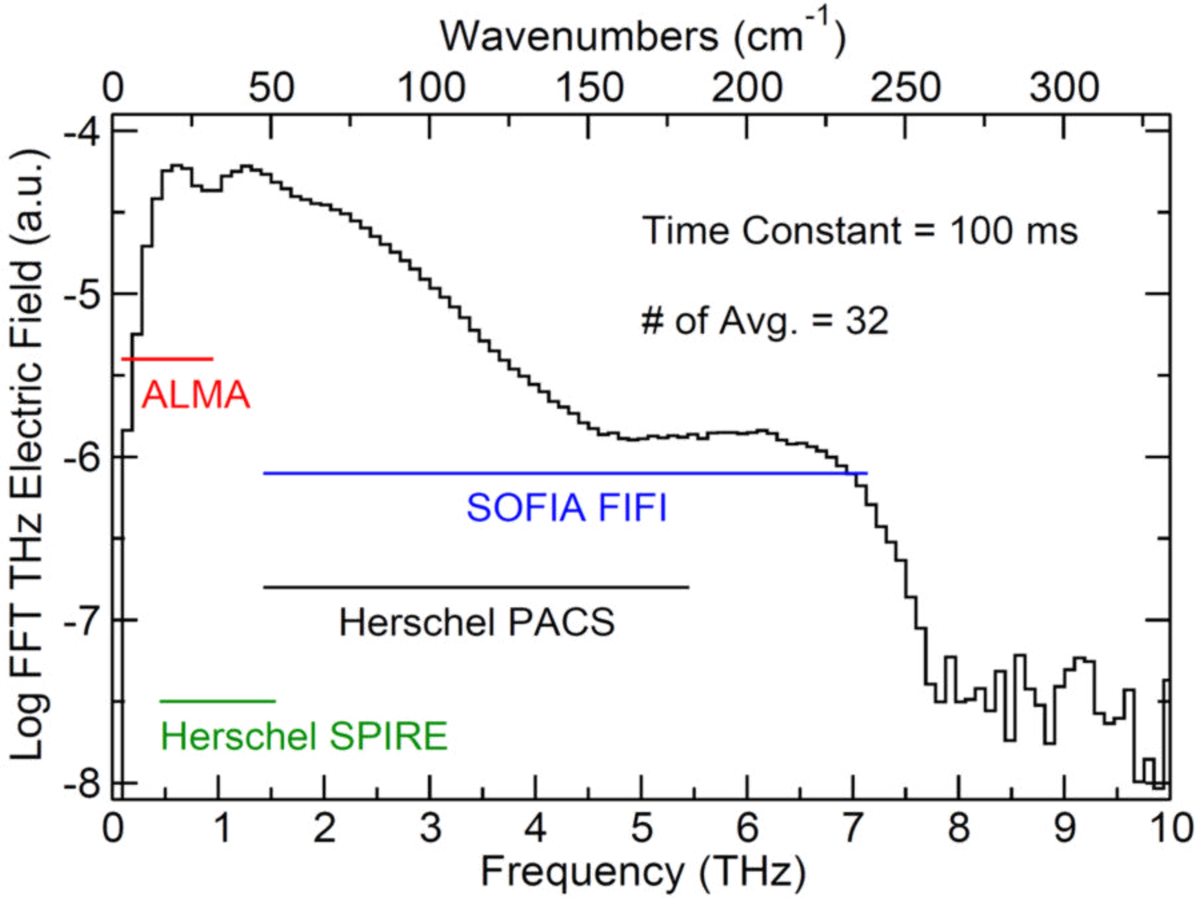
Moore and Hudson, *Radiat. Phys. Chem.* **45**, 779.

- **Noticeable differences in the spectra of amorphous (left) and crystalline (right) ices.**
- **Indication of the usefulness of THz spectroscopy.**

Time-Domain (TD) THz Spectroscopy in the Laboratory
An Example from Caltech

Collect a signal in the time domain……and Fourier transform numerically



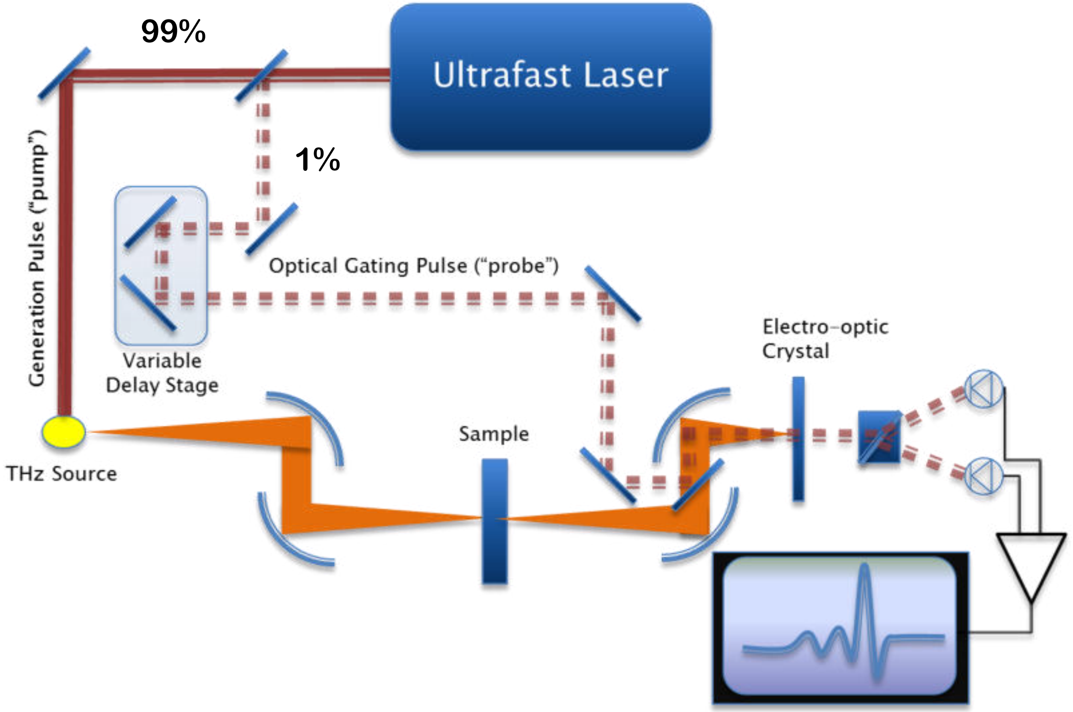


Allodi et al., *Phys. Chem. Chem. Phys.* **16**, 3442.

Time-Domain (TD) THz Spectroscopy in the Laboratory
An Example from Caltech

Laboratory TD-THz spectroscopy can be broken down into two very basic concepts:

- **THz Pulse Generation**
  - ***via two-colour plasma***
- **THz Detection**
  - ***via electro-optical sampling***



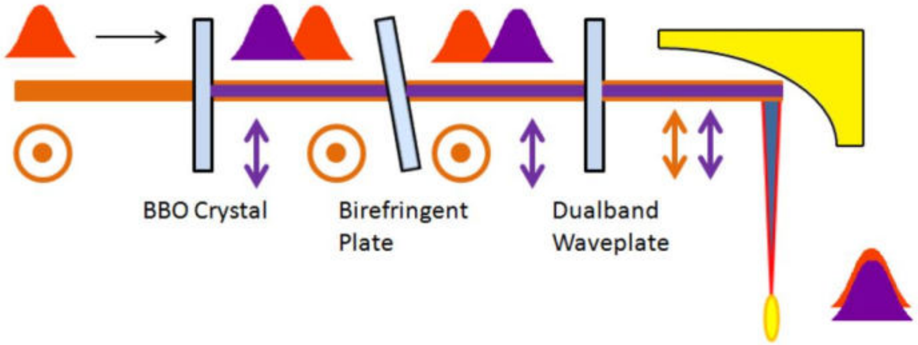
Time-Domain (TD) THz Spectroscopy in the Laboratory
An Example from Caltech

THz Pulse Generation

- BBO – frequency double amplified 800 nm output to 400 nm
- Calcite – compensate for phase delay between 400 and 800 nm pulses
- Dual-Band Wave-Plate – align polarisations
- Focus 400 and residual 800 nm light to form plasma in air

Mechanism:

- 800 nm light generates plasma
- 400 nm light accelerates electrons in plasma
- Accelerated electrons emit THz pulses

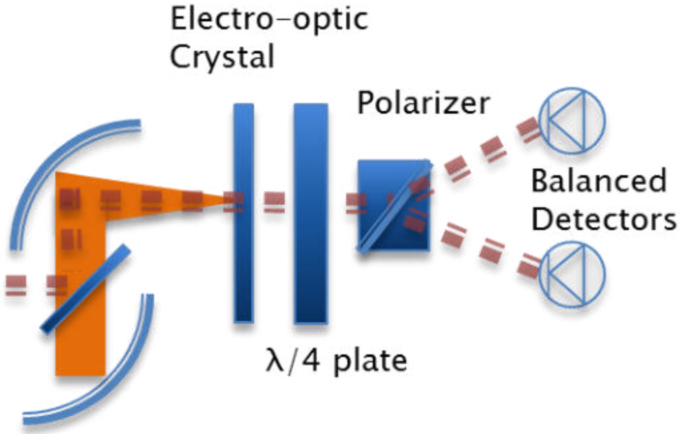


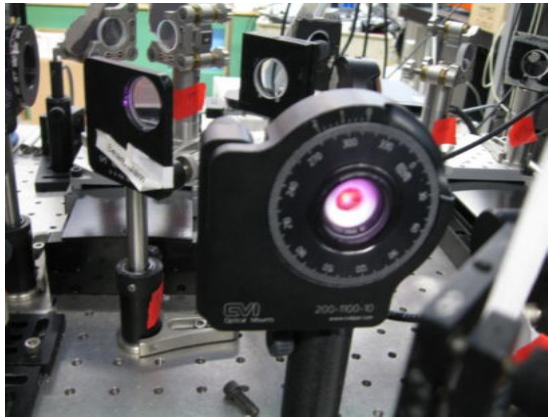
Time-Domain (TD) THz Spectroscopy in the Laboratory

An Example from Caltech

THz Detection

- THz beams are focused down onto a crystal (ZnTe or GaP)
- THz pulse causes a rotation in the polarisation of the probe beam in the crystal (Pockels Effect)
- Magnitude of polarisation change is linear to applied THz electric field (so measure THz electric field not intensity)
- A pair of balanced detectors sees a difference in signal



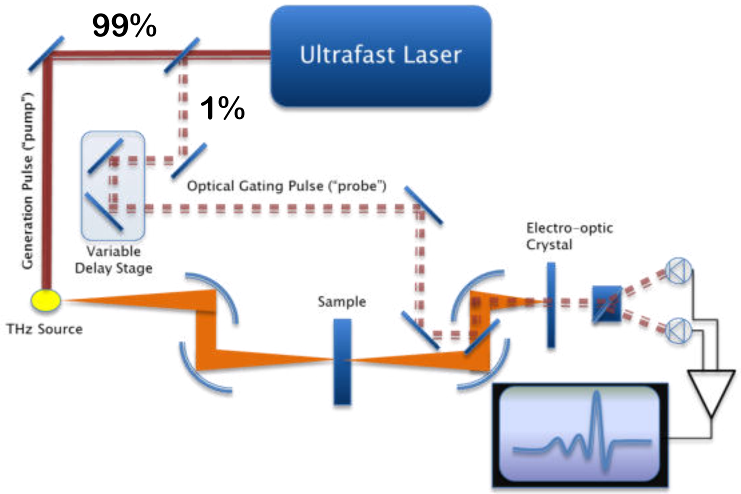


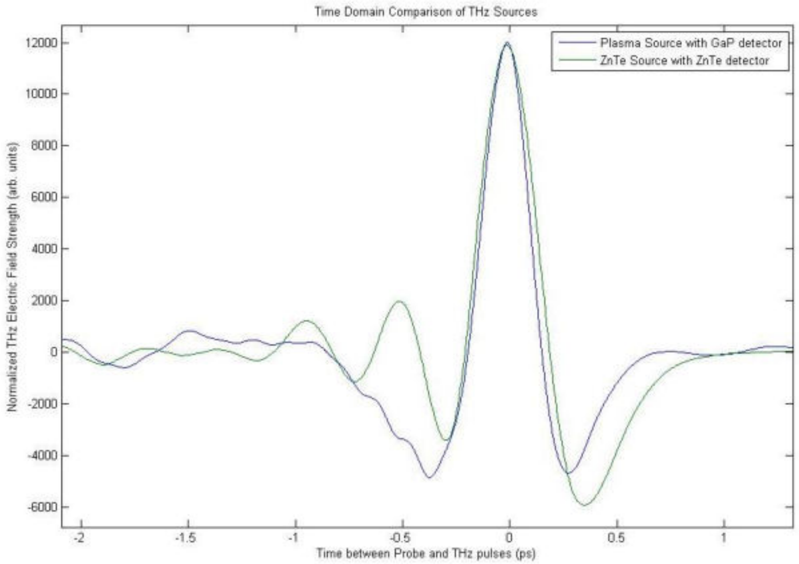
Time-Domain (TD) THz Spectroscopy in the Laboratory

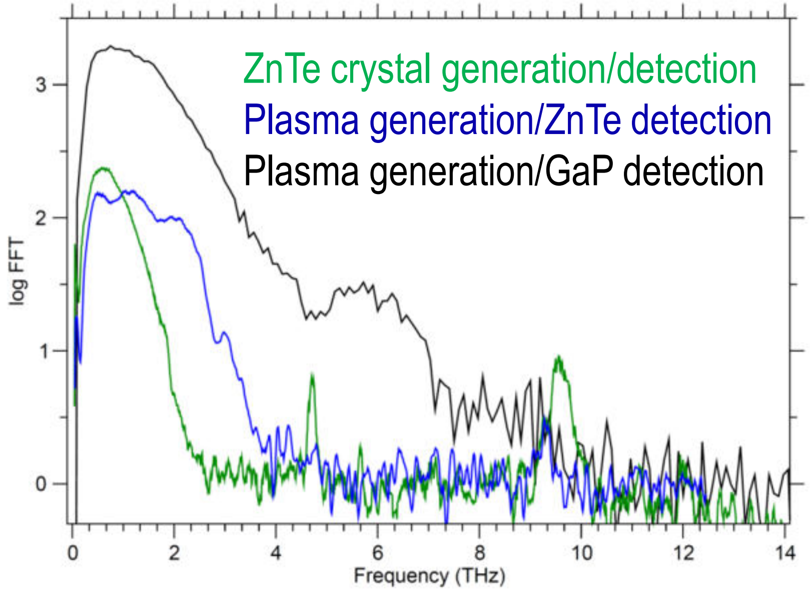
An Example from Caltech

Opto-Mechanical Delay

- Allows the entire THz waveform to be stepped through
- The electric field is measured as a function of delay time
- FFT of the temporal waves gives spectral distribution in the frequency domain.

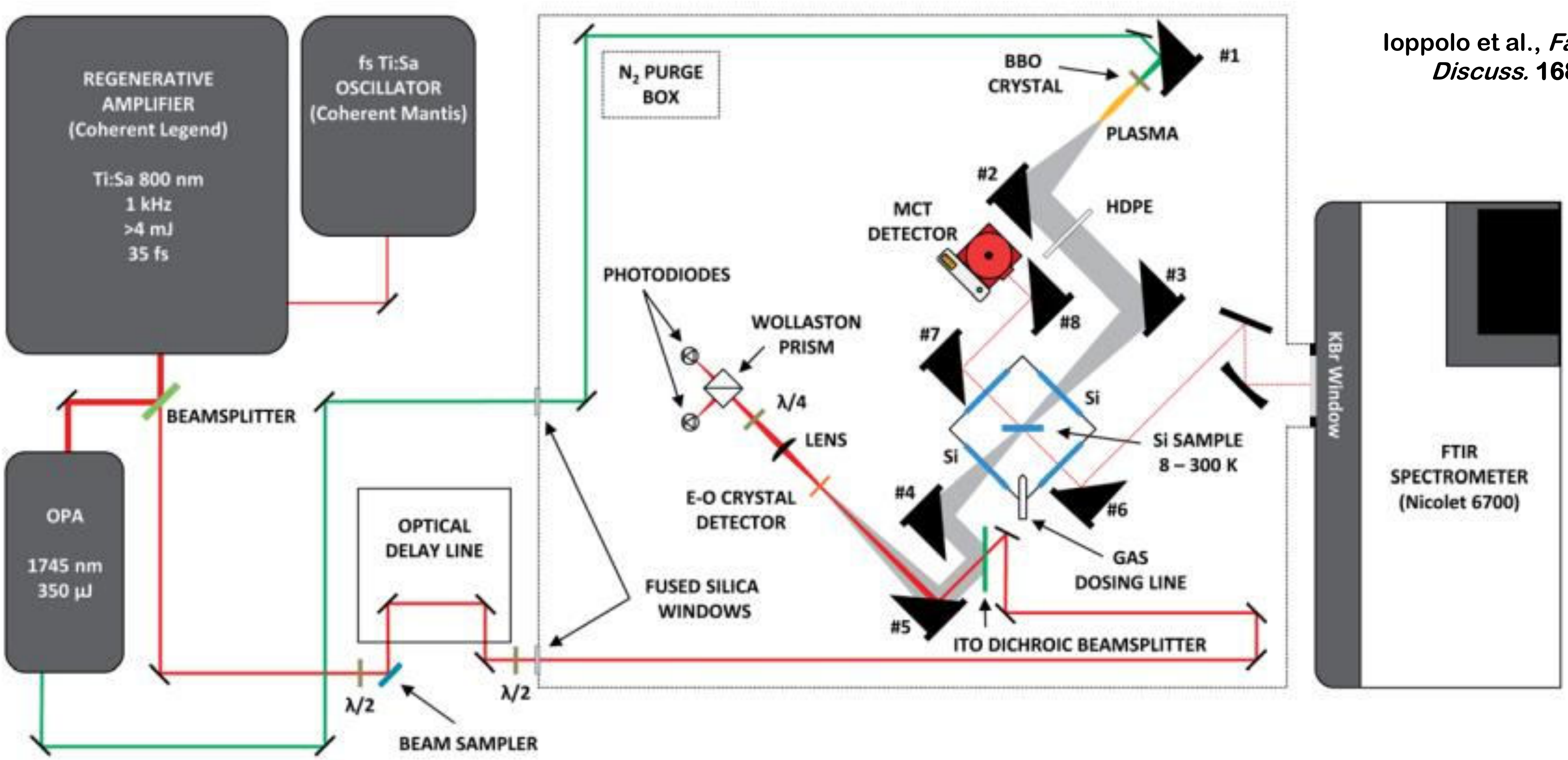






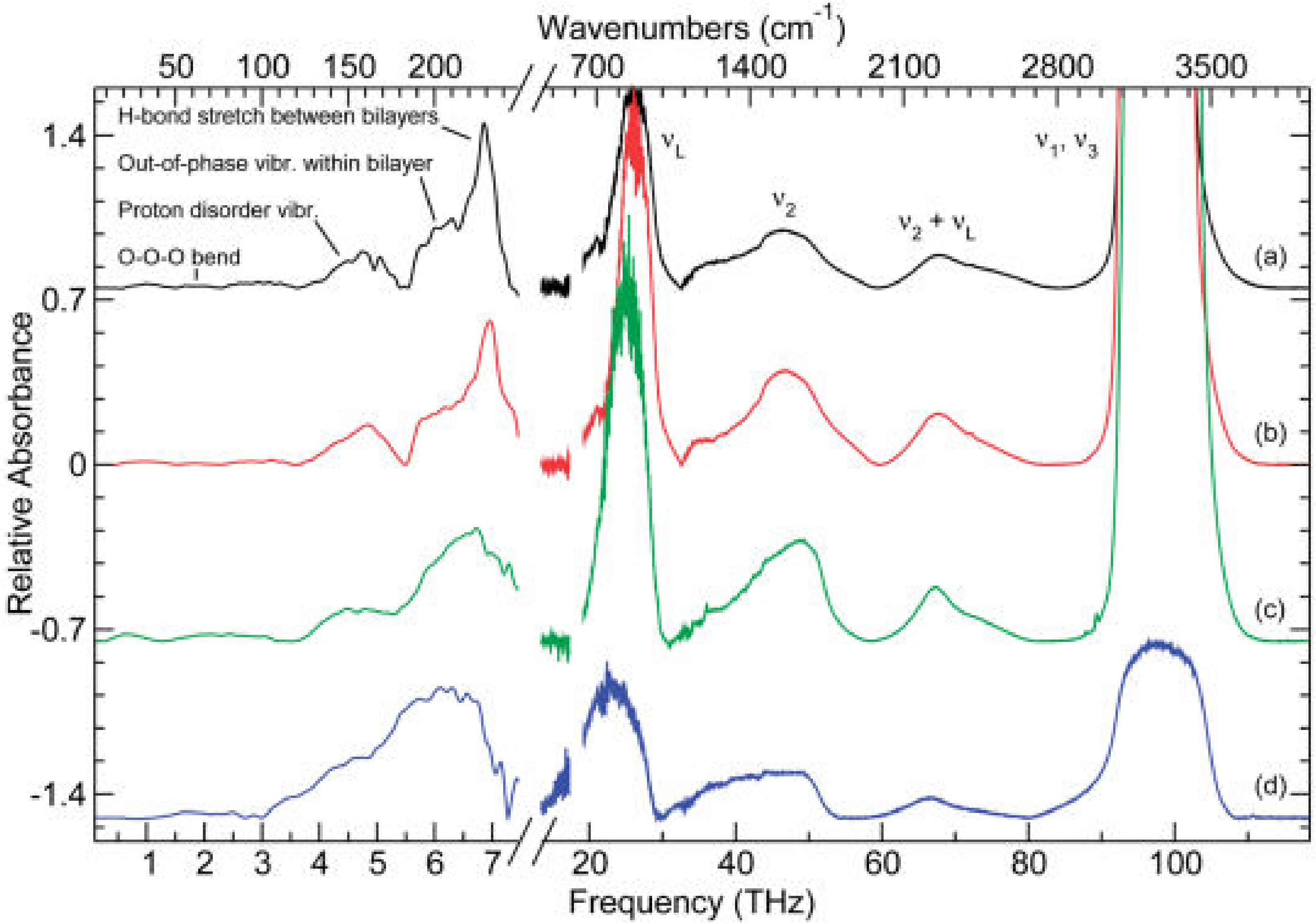
Time-Domain (TD) THz Spectroscopy in the Laboratory
An Example from Caltech

Ioppolo et al., *Faraday Discuss.* **168**, 461.



THz Spectra of Astrophysical Ice Analogues

Comparisons with Mid-IR Spectra for H_2O



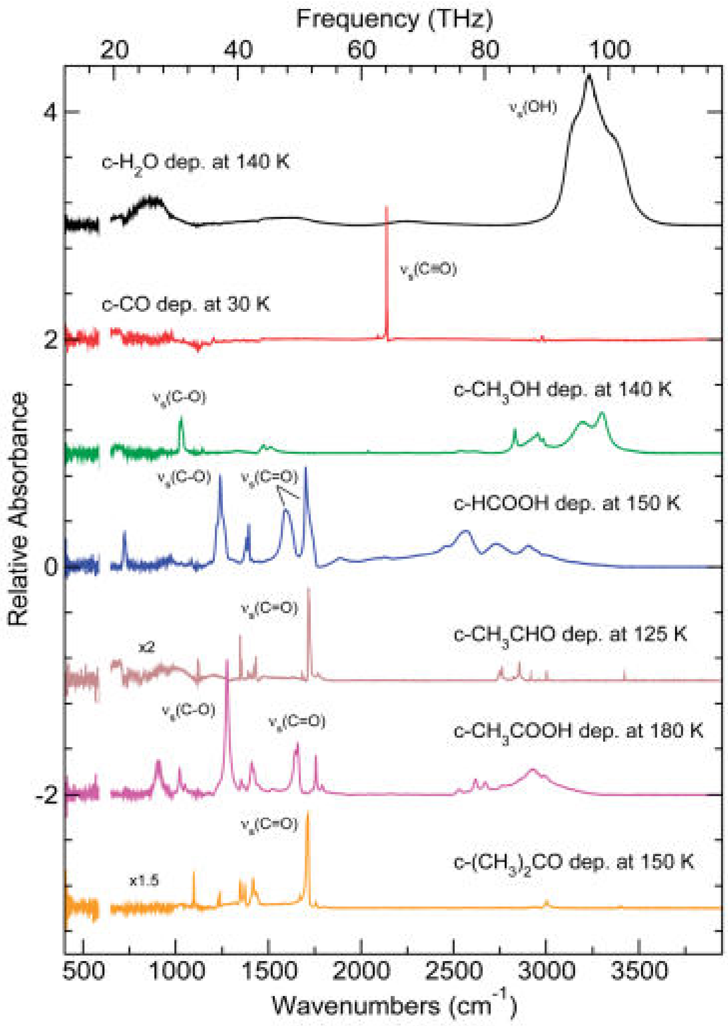
- Four absorptions in the H_2O mid-IR spectrum
- Peak appearances vary due to temperature and phase.

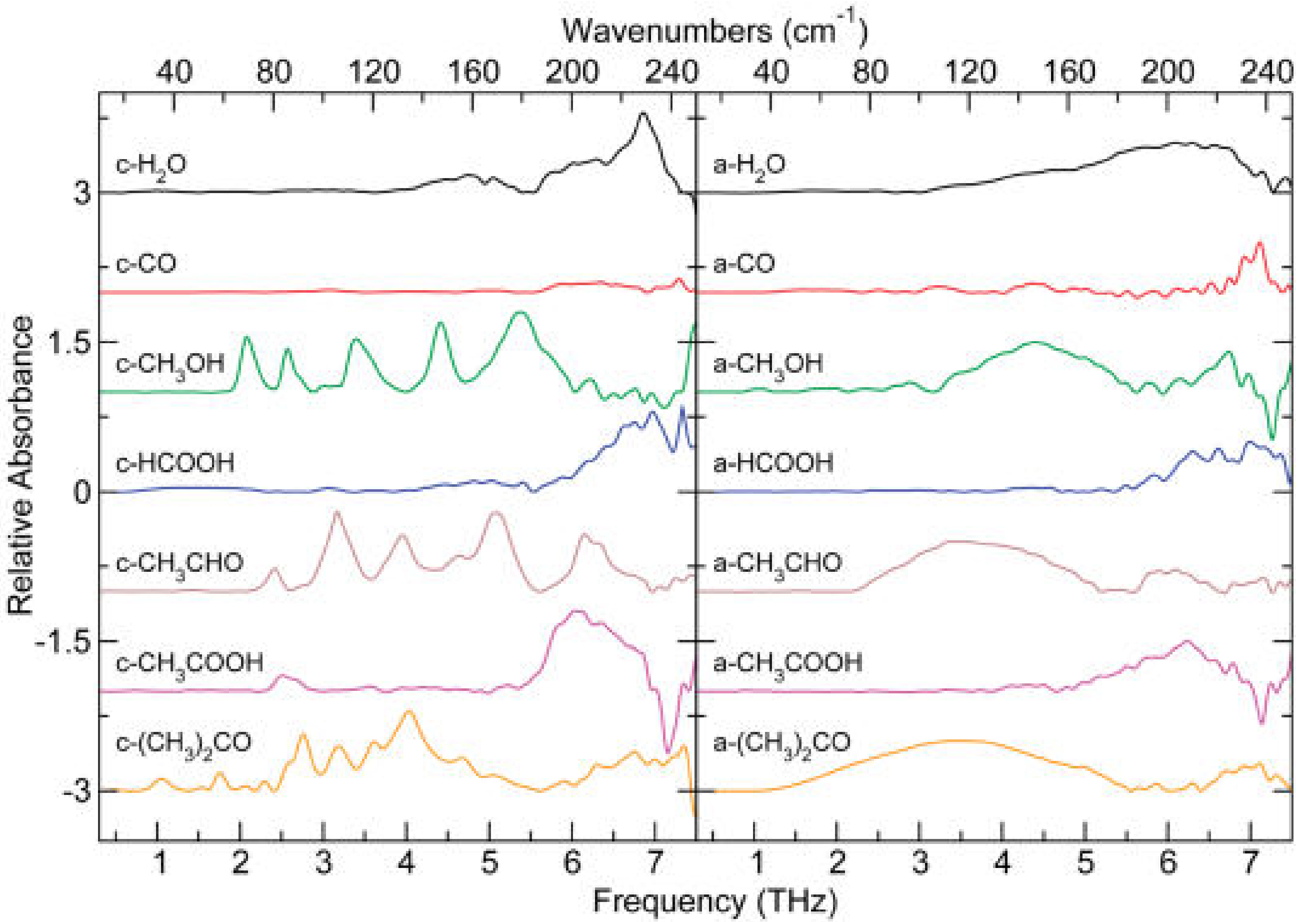
- THz spectra contains many weak features.
- Four strong absorptions in crystalline H_2O.

Ioppolo et al., *Faraday Discuss.* **168**, 461.

THz Spectra of Astrophysical Ice Analogues

Comparisons with Mid-IR Spectra for Other Molecules

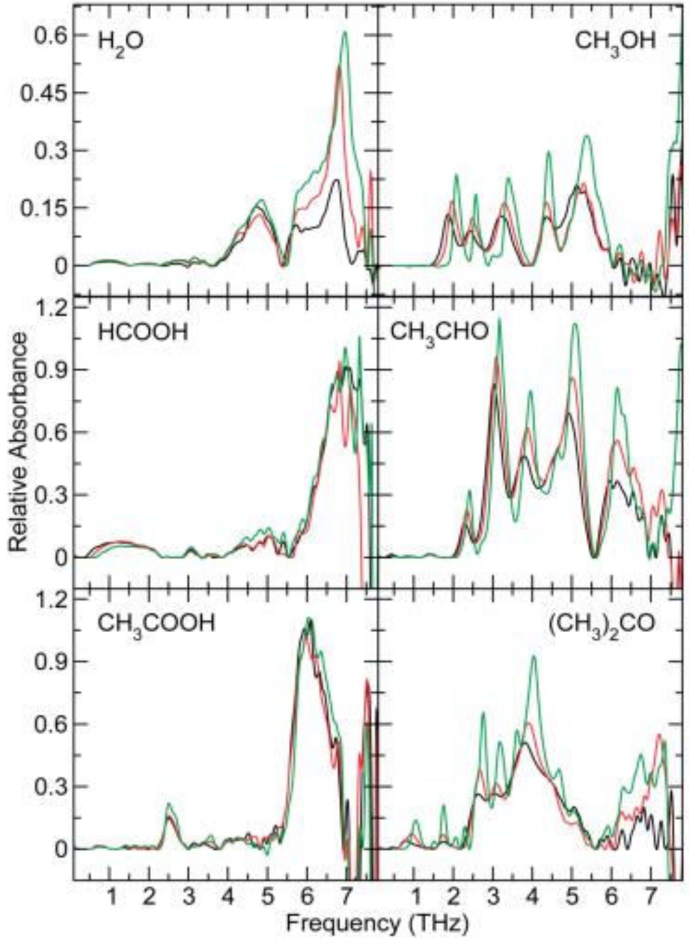




Ioppolo et al., *Faraday Discuss.* 168, 461.

THz Spectra of Astrophysical Ice Analogues

The Temperature Effect



Ioppolo et al., *Faraday Discuss.* **168**, 461.

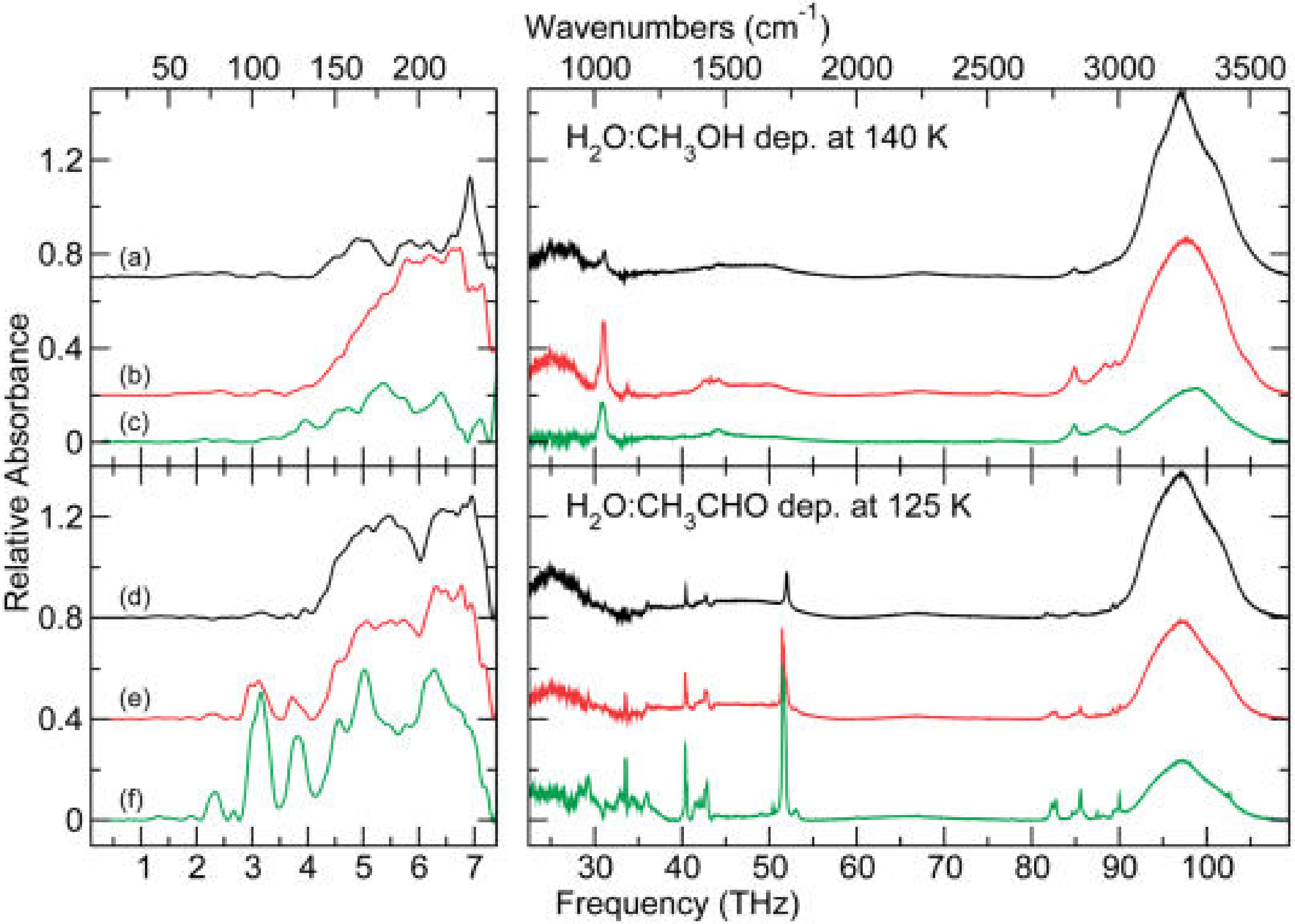
- THz peaks in crystalline ices are stronger, sharper, and blue-shifted at lower temperatures.
- Peak shifting and broadening results from the anharmonicity of vibrational potential.
- Hot bands are red-shifted due to decrease in the spacing between vibrational levels.
- At low temperature, only lower vibrational states are populated and so bands are blue-shifted and sharper.
- Different vibrational minima corresponding to different crystal structures will exhibit different bands.
- Intramolecular torsional modes may be apparent.

THz Spectra of Astrophysical Ice Analogues

The Composition Effect

- **Contaminant species may alter the intermolecular H-bonding networks in ices.**

- **If the peaks of a contaminant affect those of the bulk ice independent of contaminant concentration, and these peaks also grow proportionally to their concentration, then segregation may have occurred (e.g., CO_2, CH_3CHO).**



Allodi et al., *Phys. Chem. Chem. Phys.* **16**, 3442.

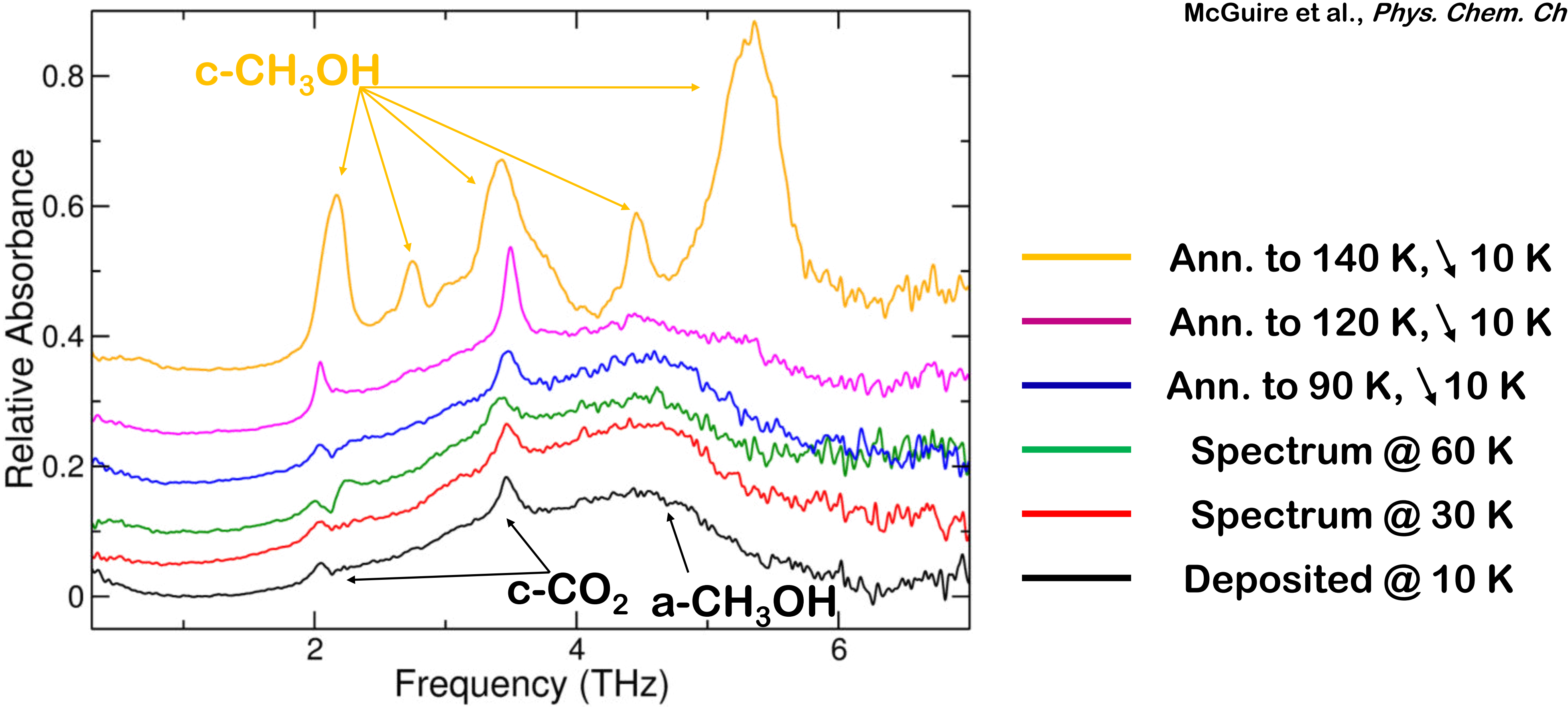
Ioppolo et al., *Faraday Discuss.* **168**, 461.

THz Spectra of Astrophysical Ice Analogues

The Composition Effect

Thermal processing of mixed $CH_3OH:CO_2$ 1:1 ice

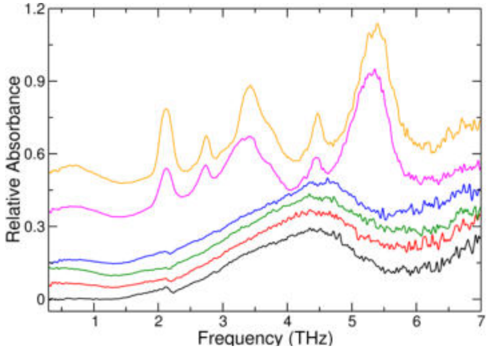
McGuire et al., *Phys. Chem. Chem. Phys.* **18**, 20199.



THz Spectra of Astrophysical Ice Analogues

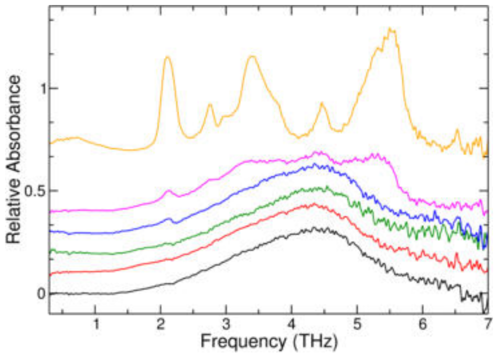
The Composition Effect

10:1



CH_3OH >>

3:1



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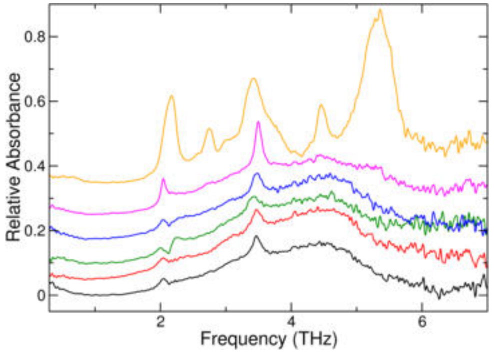

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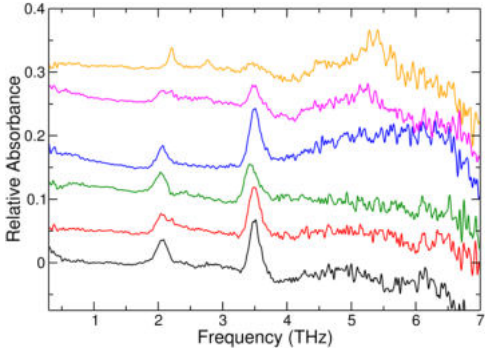
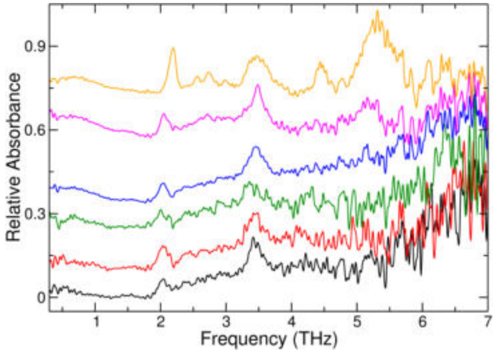


<<CO_2

1:3



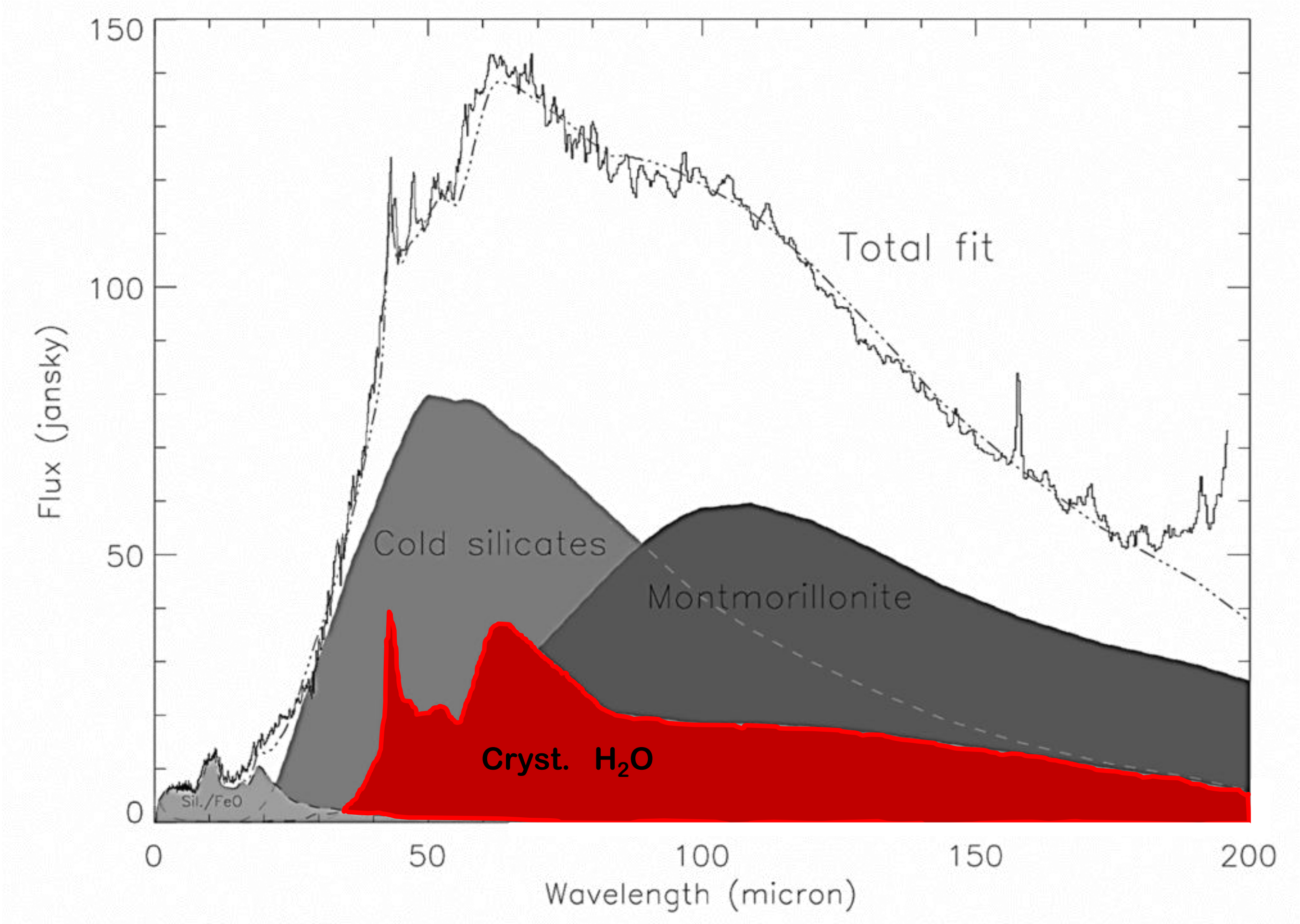
McGuire et al., *Phys. Chem. Chem. Phys.* **18**, 20199.

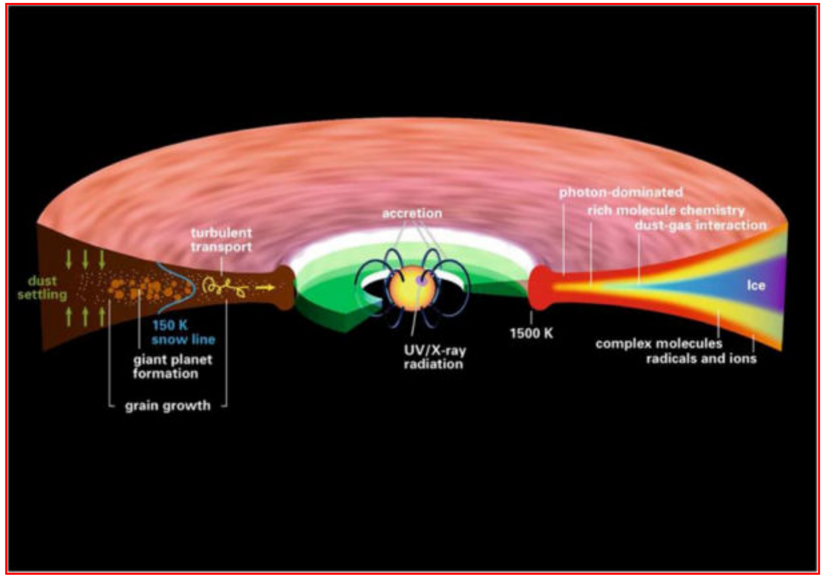
Key Points of THz Laboratory Astrochemistry

- THz spectroscopy offers an additional and complementary analytical tool to mid-IR spectroscopy.
- THz spectroscopy is not limited to a particular line of sight, offering a wider choice of observable targets.
- THz spectroscopy is sensitive to the temperature, structure, and chemical composition of an astrophysical ice.
- Further laboratory spectra must be acquired to aid in deciphering astrophysical observations.

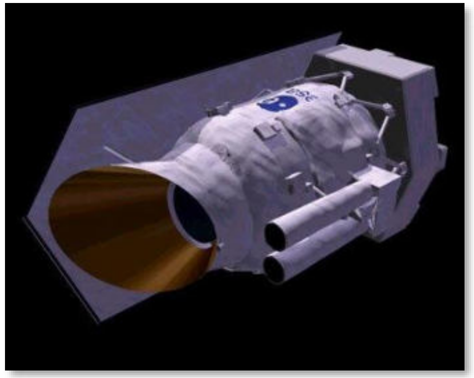
Detection of Ices in Protoplanetary Disks

ISO Data - Herbig Ae Stars HD142527

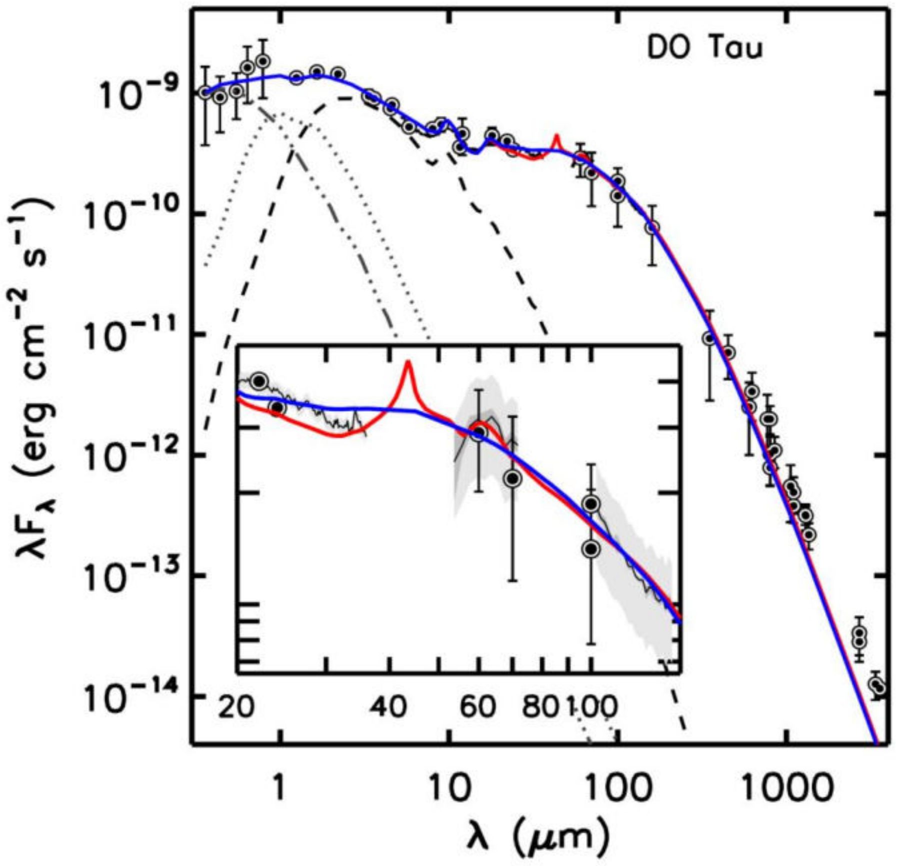




Malfait et al. (1999)



Detection of Trans-Neptunian Ices
PACS Data - T Tauri Stars



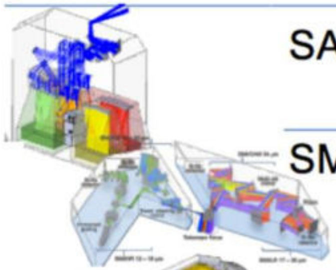
with water ice

with silicates and graphite

McClure, PhD Thesis (2014)

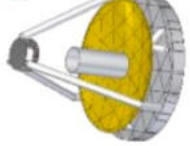
A Missed Opportunity
SPace Infrared telescope for Cosmology and Astrophysics

Launch: JAXA's H3 launch vehicle
Orbit: L2
Nominal mission lifetime: 3 years
Goal: 5 years

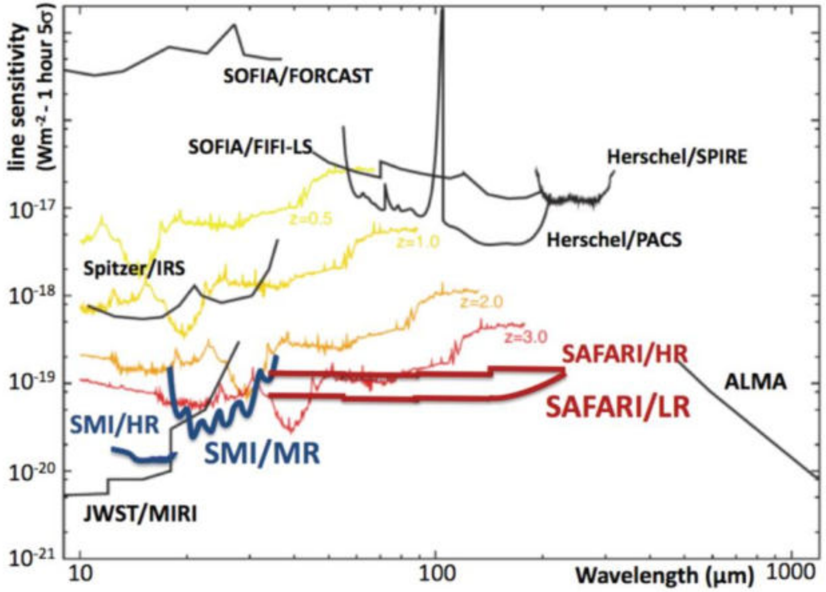


SAFARI: 34-230 μm background limited spectroscopy, *R*~300-11000
100, 200, 350 μm imaging polarimeter

SMI: 17-36 μm background limited spectroscopy, *R*~100-2000
12-18 μm spectroscopy at *R*~28000
10'x12' survey camera and *R*~100 spectrometer

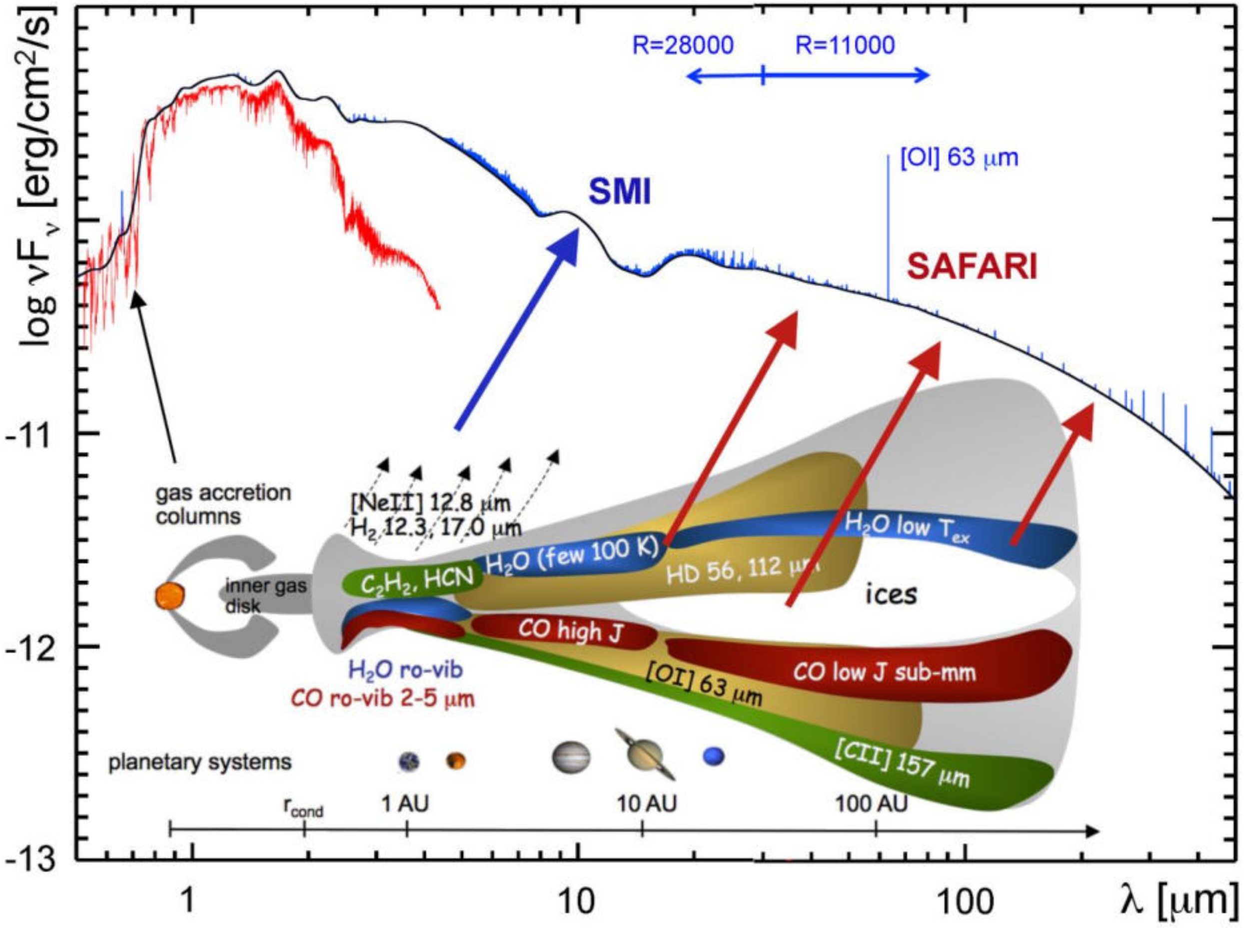


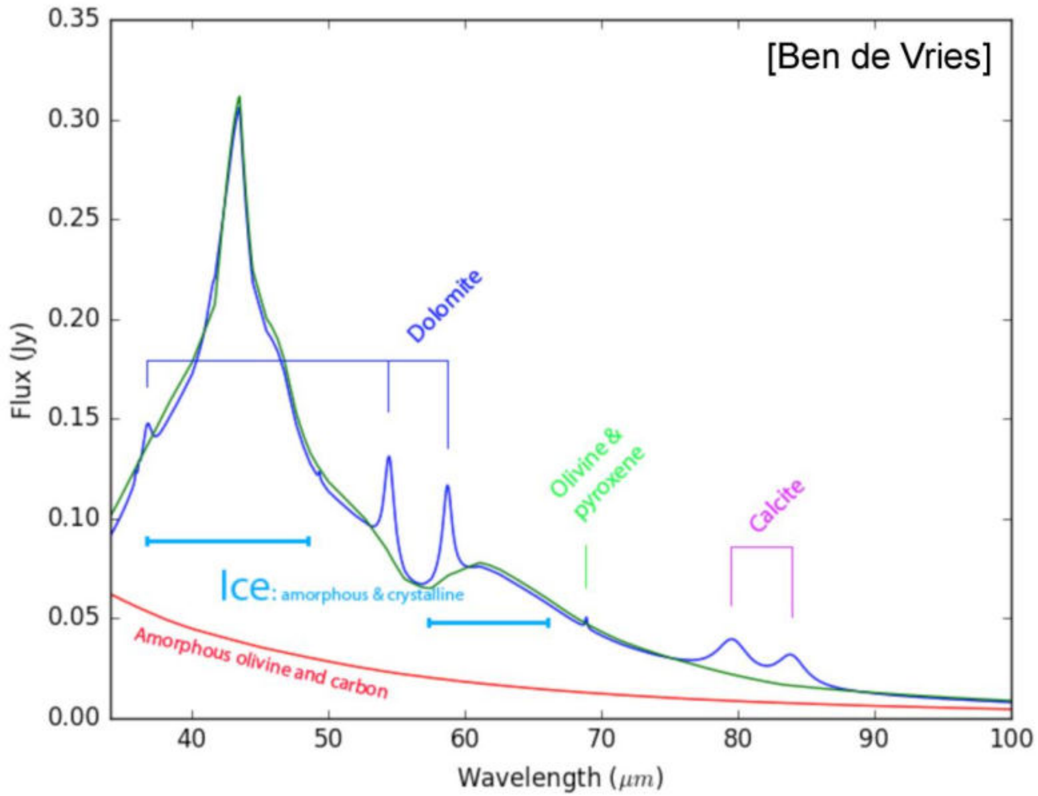
2.5 meter <8K Ritchey-Chrétien telescope assembly
Mechanical coolers combined with passive V-groove cooling
JAXA H3 launcher



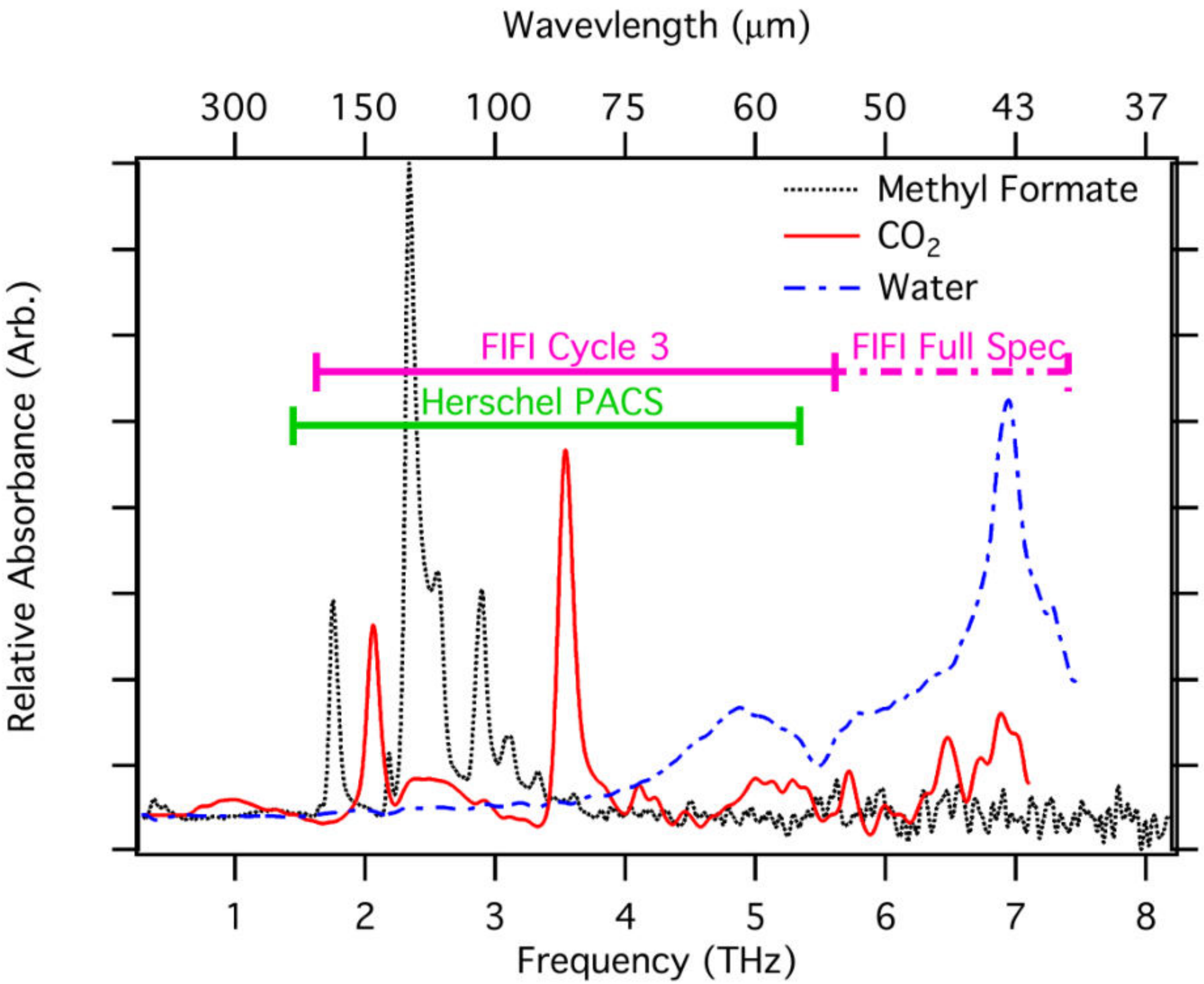
A Missed Opportunity

SPace Infrared telescope for Cosmology and Astrophysics

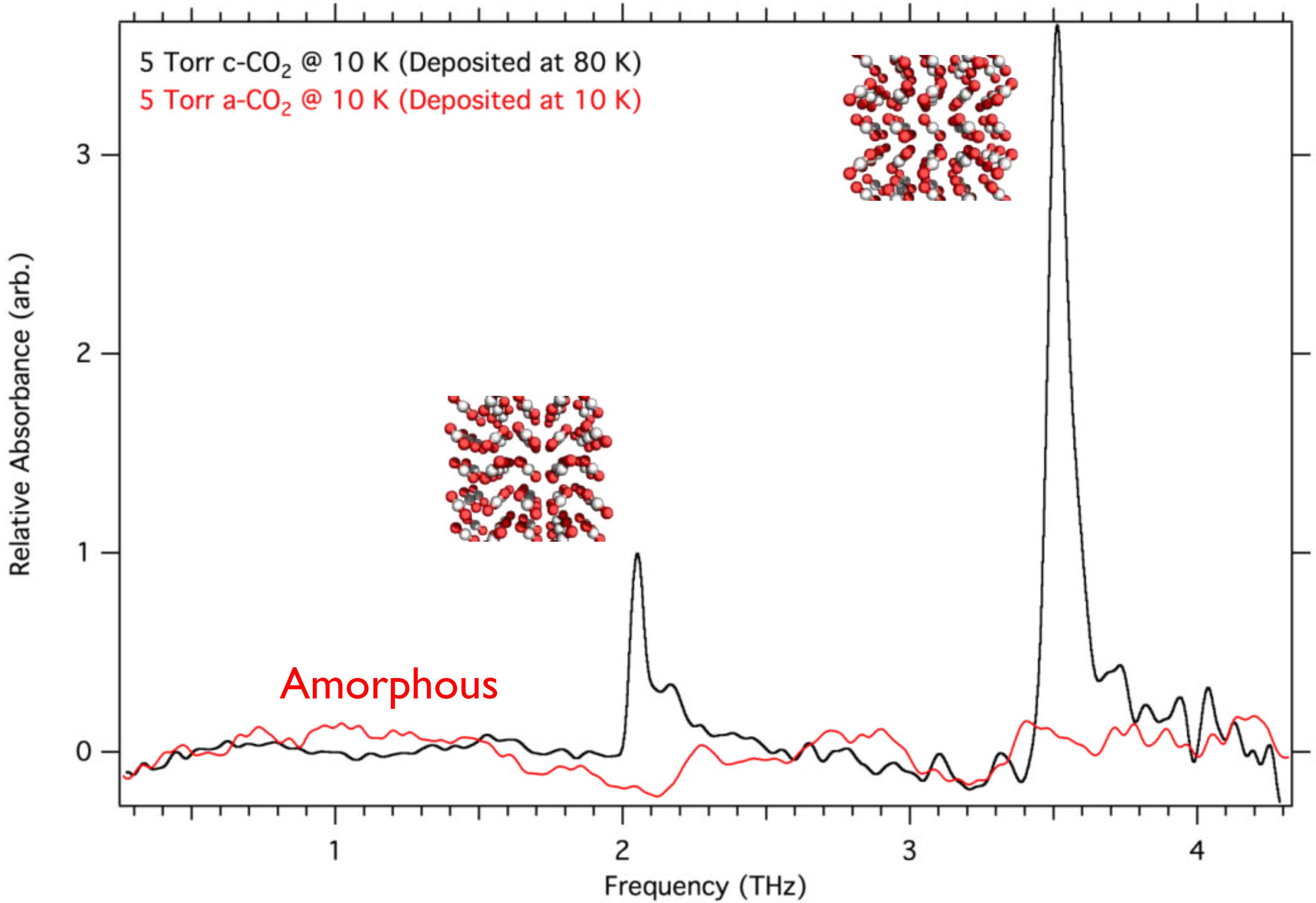




Potential Detection of COMs in the THz

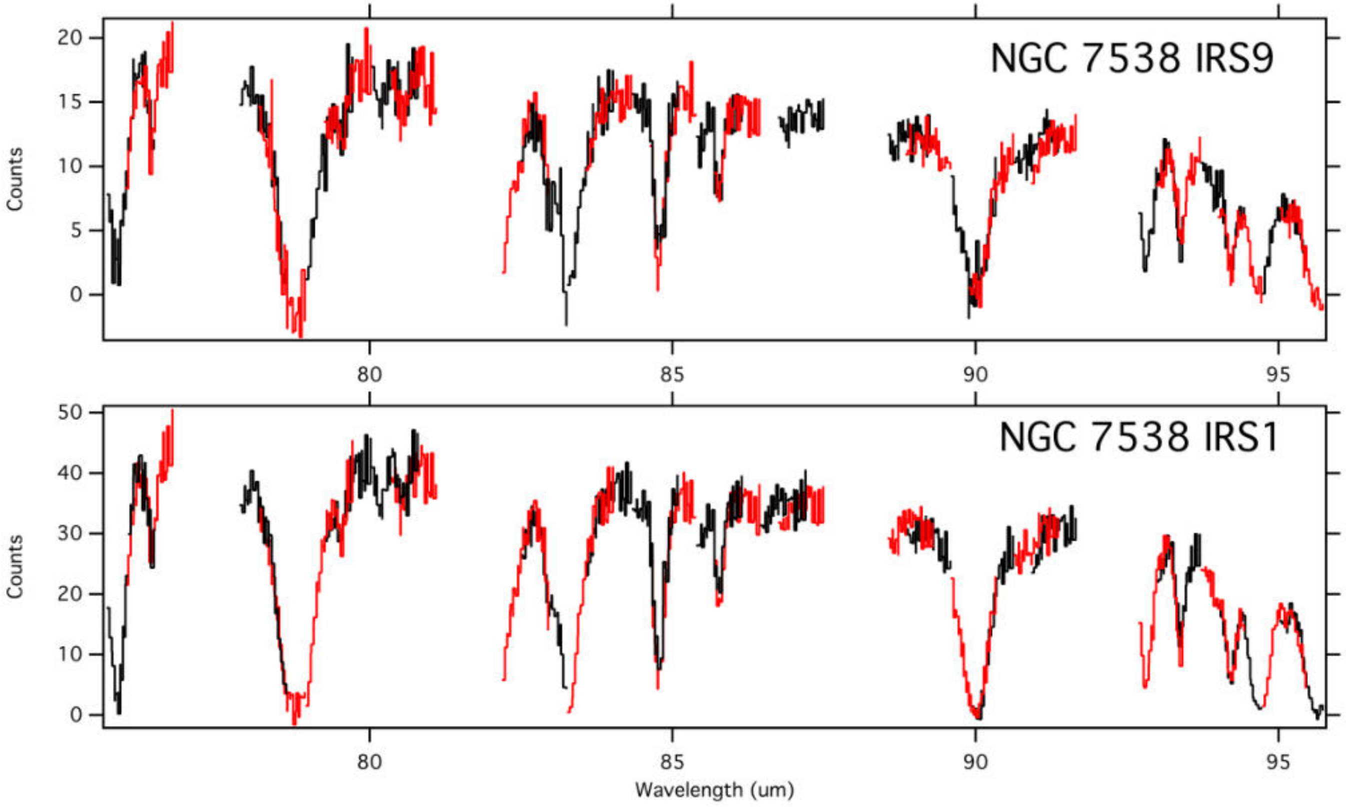


CO_2 - Amorphous vs crystalline Ice

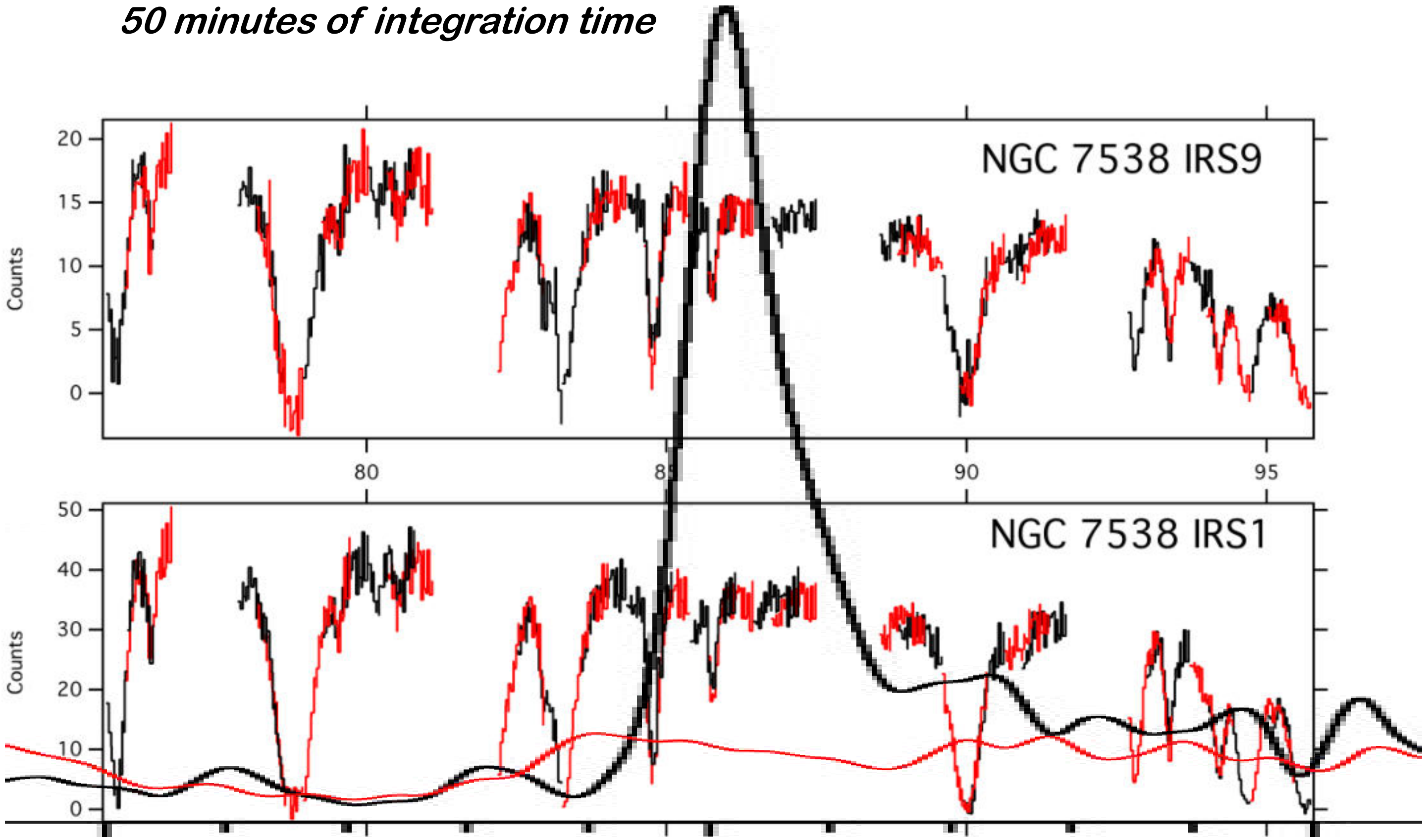


SOFIA Observations Cycle 3

50 minutes of integration time

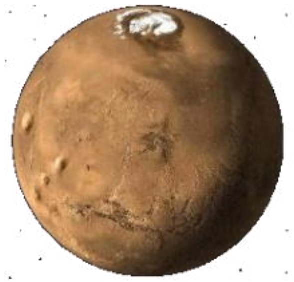


SOFIA Observations Cycle 3

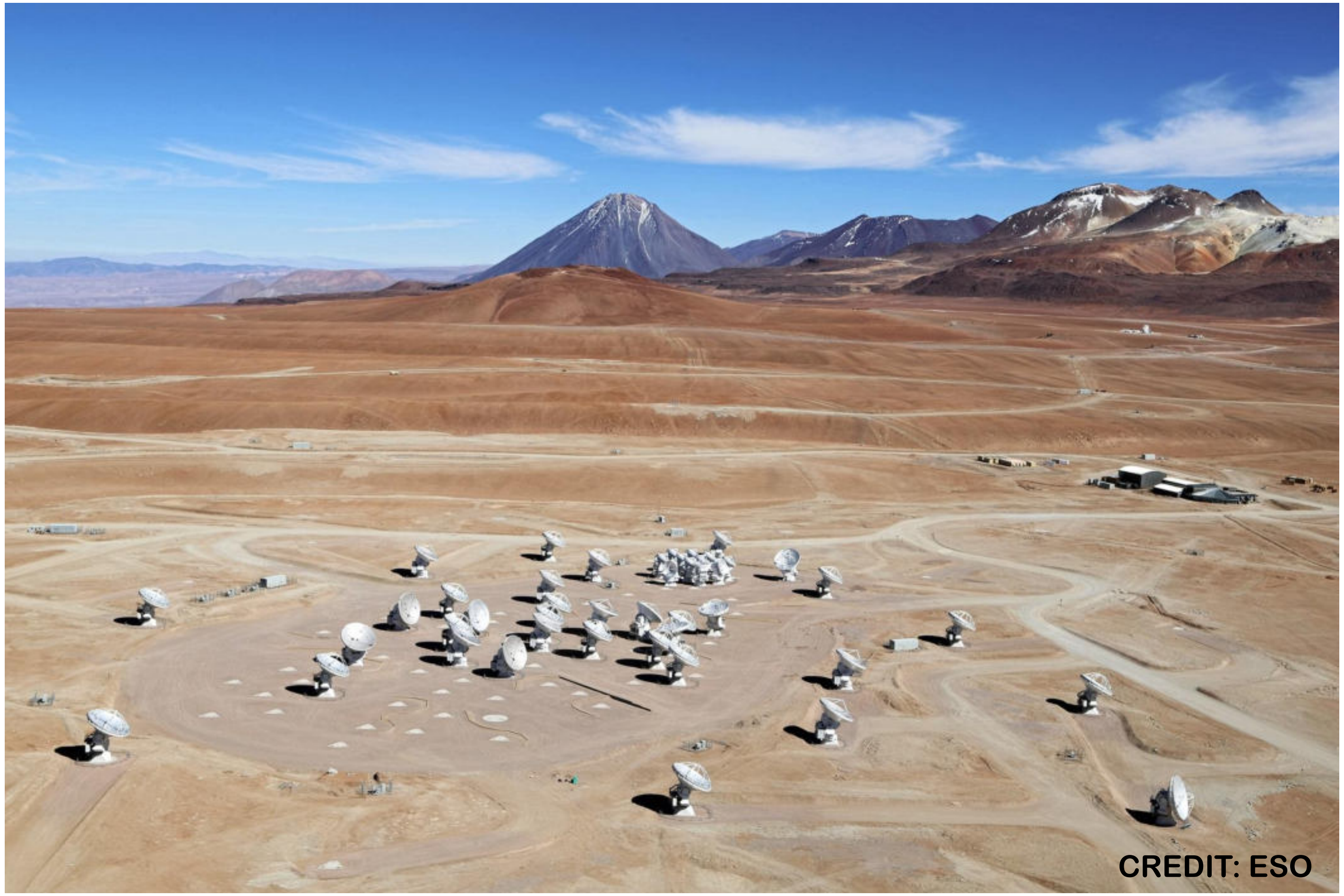


50 minutes of integration time

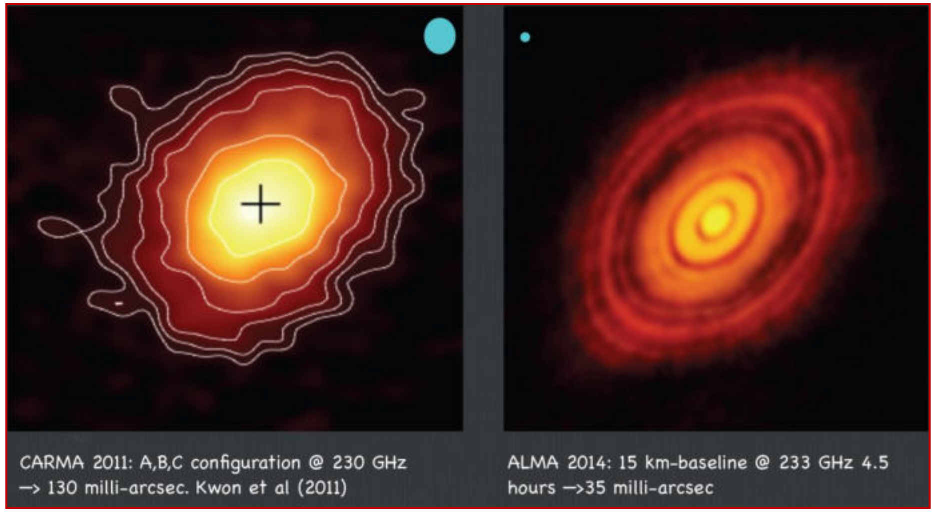
4 THz **3 THz**



ALMA - Atacama Large Millimeter/submillimeter Array



CREDIT: ESO

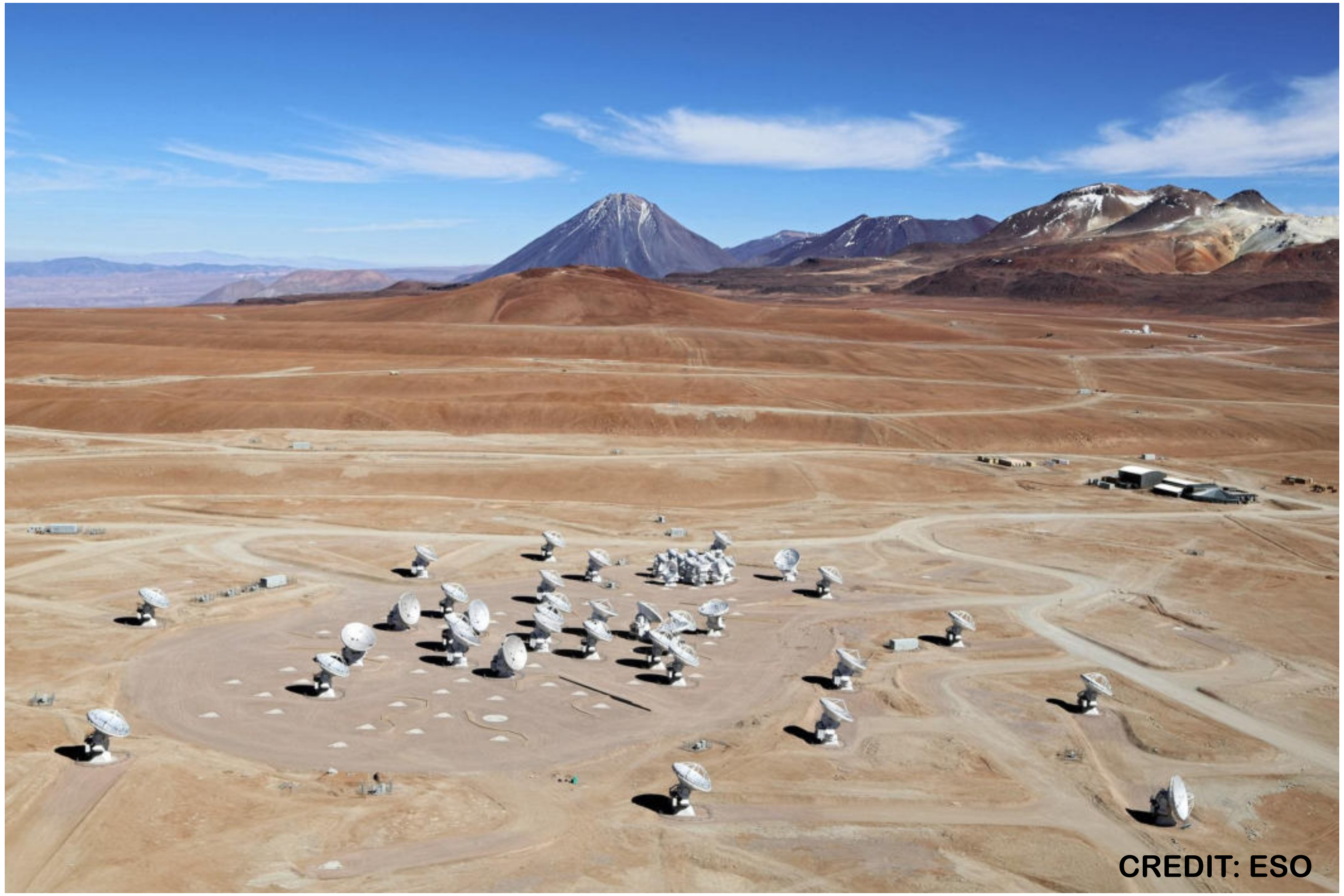


CARMA 2011: A,B,C configuration @ 230 GHz —> 130 milli-arcsec. Kwon et al (2011)

ALMA 2014: 15 km-baseline @ 233 GHz 4.5 hours —>35 milli-arcsec

CREDIT: B. Saxton, NRAO/NSF

ALMA - Atacama Large Millimeter/submillimeter Array



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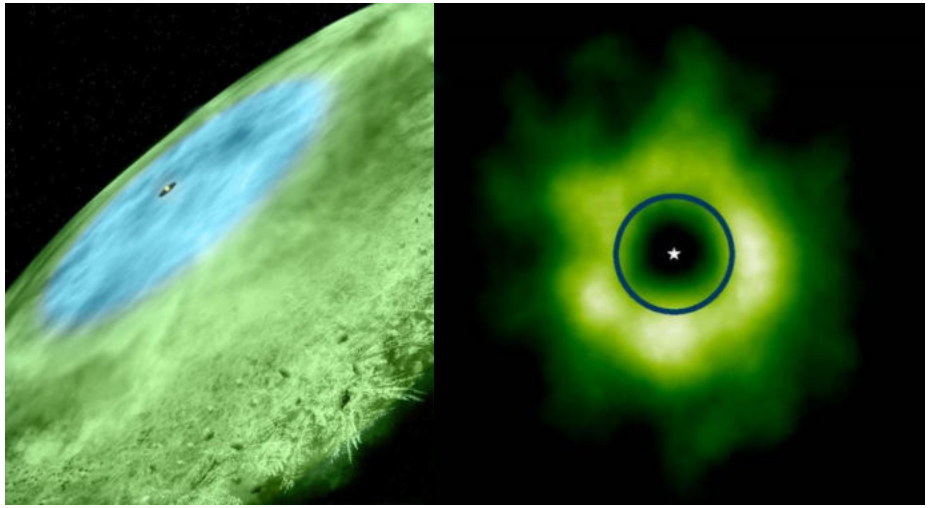
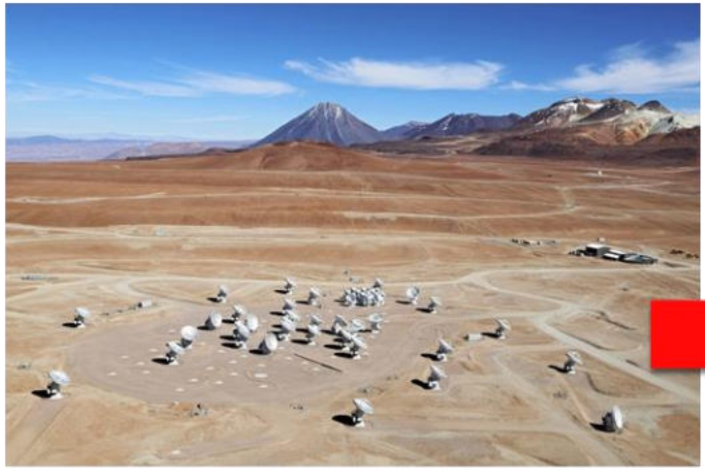


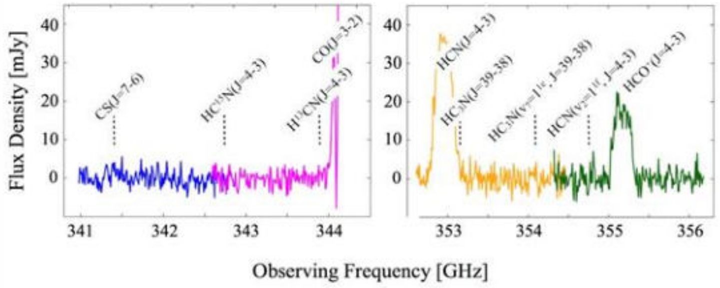
CREDIT: P. Salomé, Paris Obs.
K. Öberg, Harvard

ALMA - Atacama Large Millimeter/submillimeter Array
Emission Spectroscopy

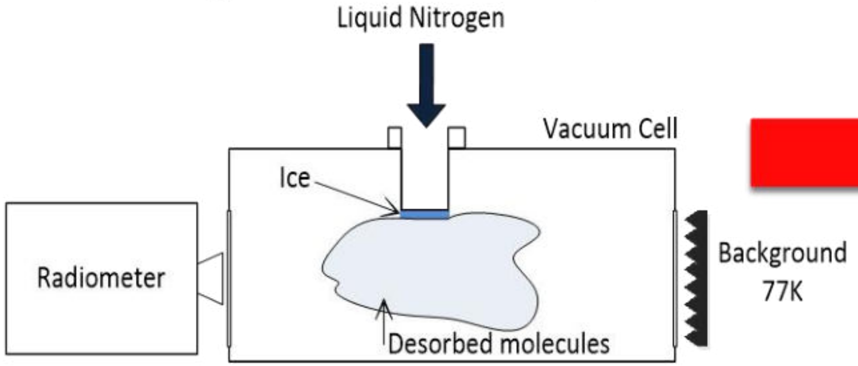
(sub)mm Observations

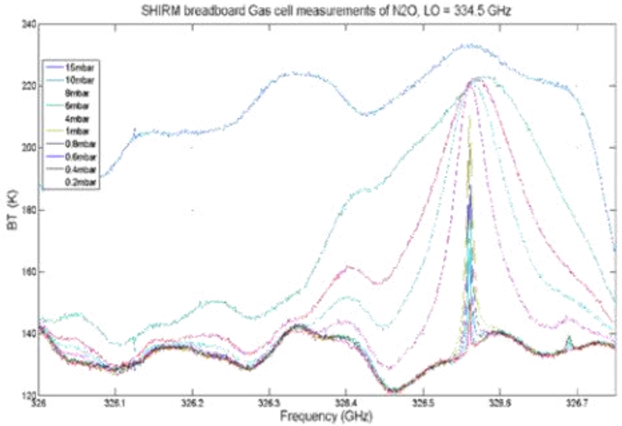


ALMA

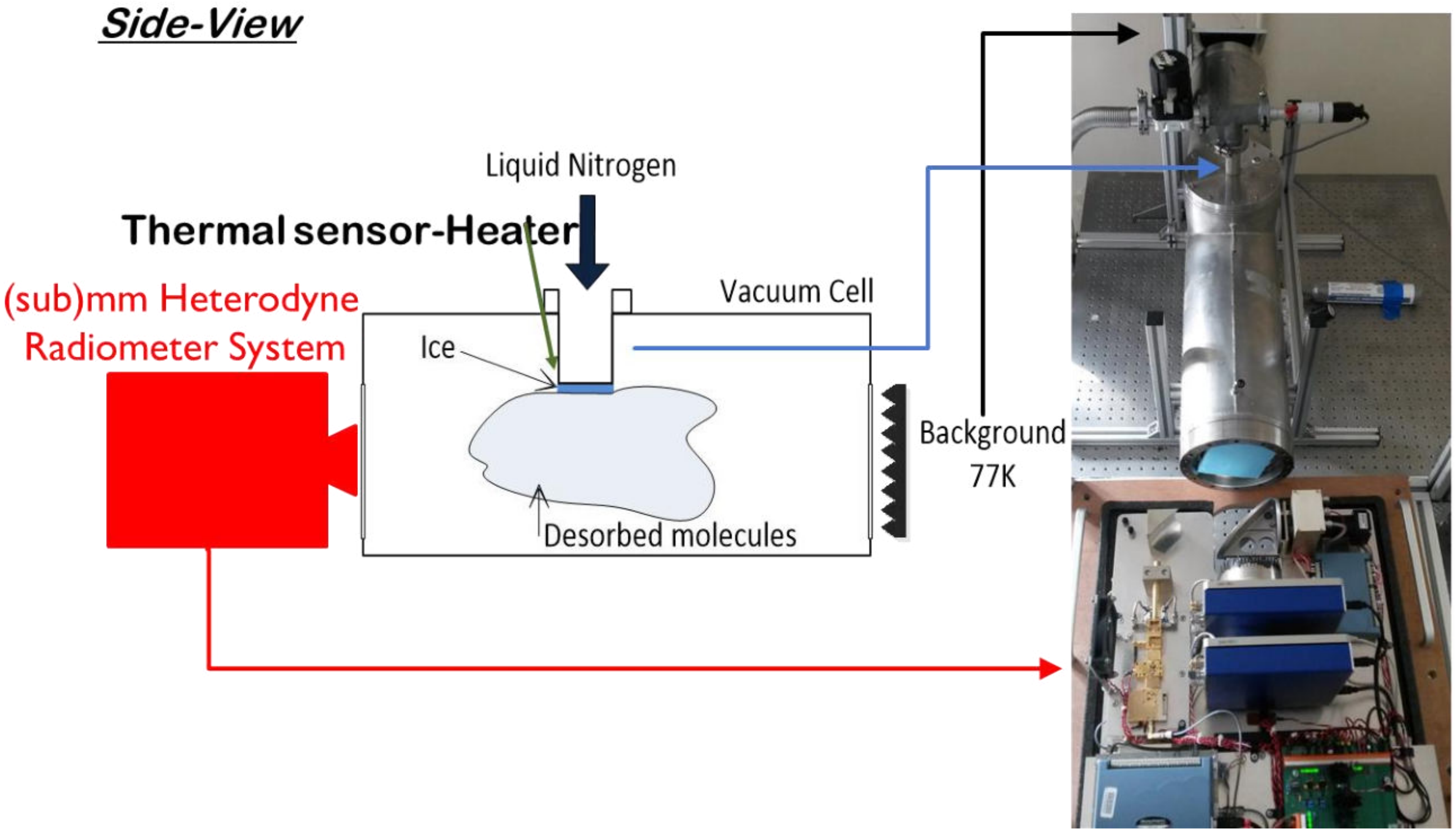


Laboratory Measurements





THz Desorption Emission Spectroscopy



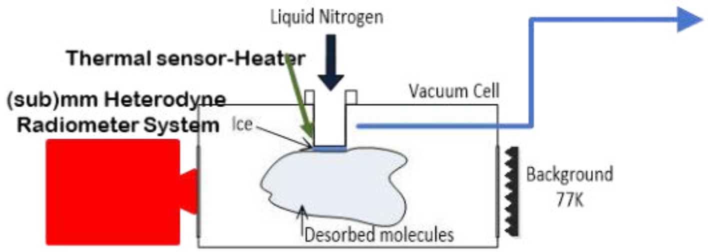
Top-View

RAL Space
SCIENCE DRIVEN, TECHNOLOGY ENABLED

Auriacombe et al., MNRAS in prep.

THz Desorption Emission Spectroscopy

Side-View



RAL Space
SCIENCE DRIVEN, TECHNOLOGY ENABLED

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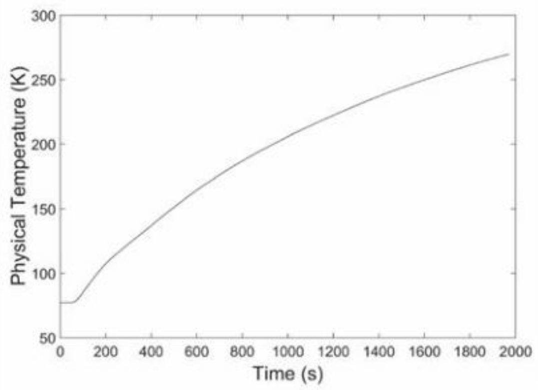
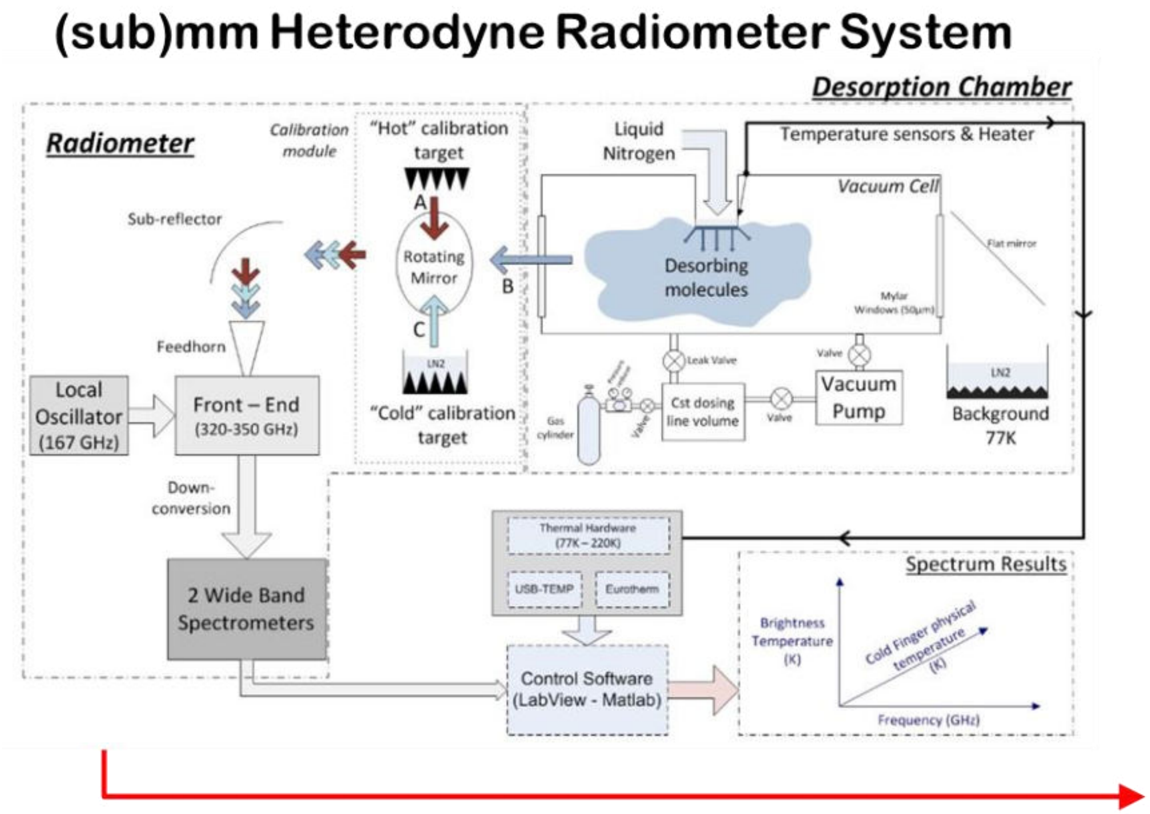
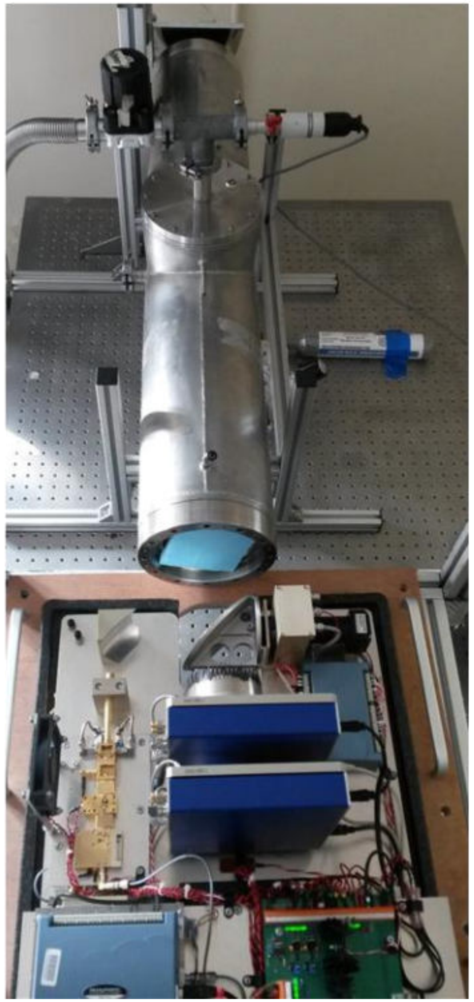


THz Desorption Emission Spectroscopy





Top-View

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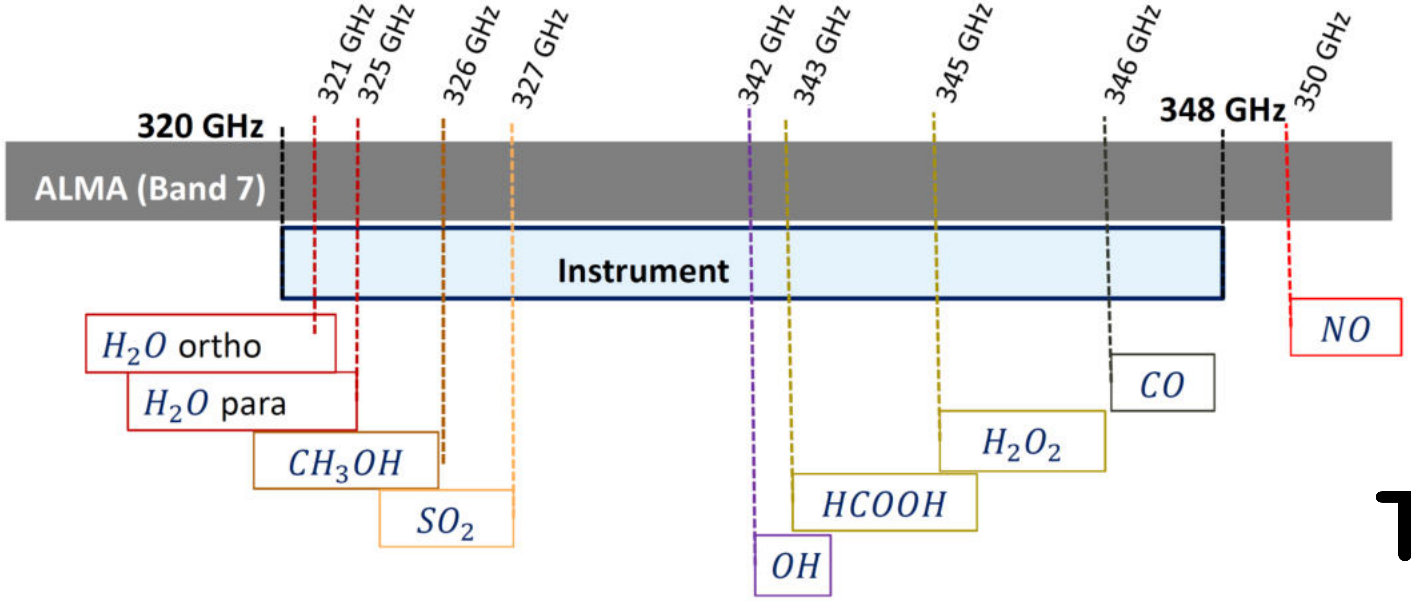
THz Desorption Emission Spectroscopy

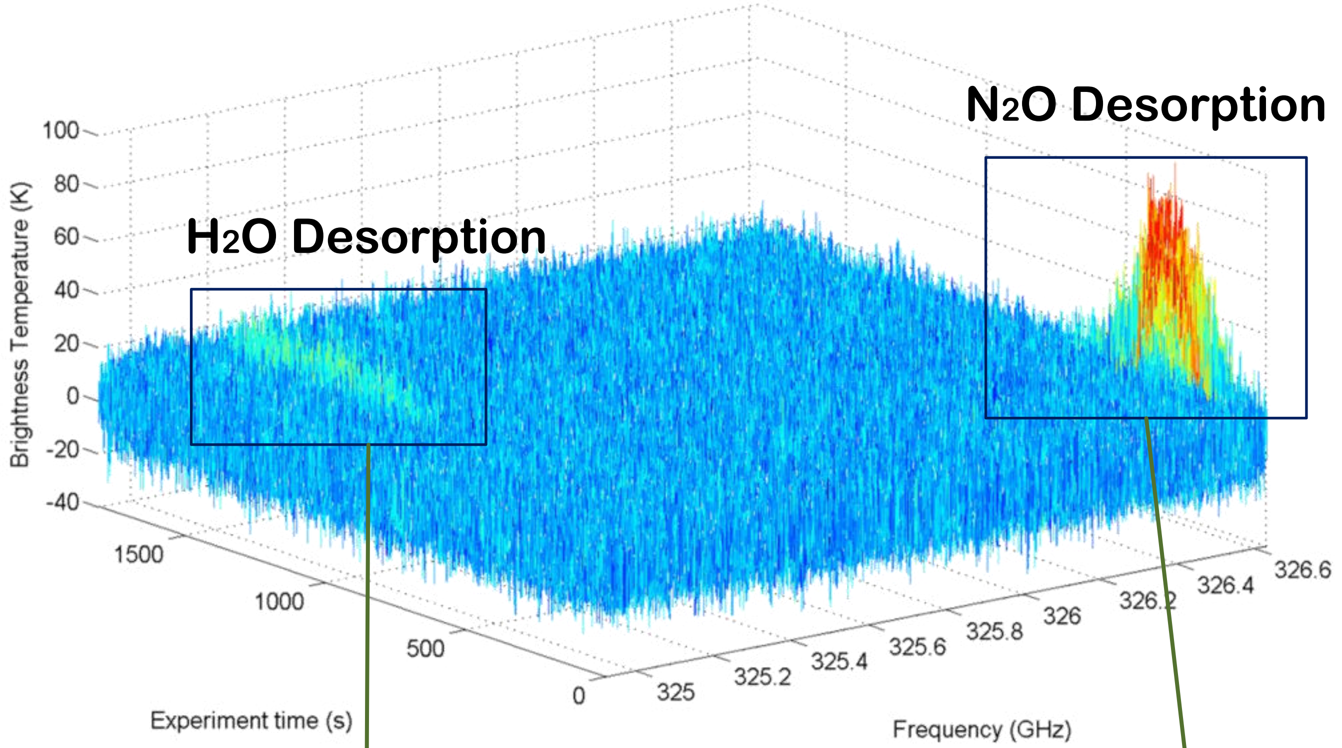


Target Molecules

Experiment:

Molecules	Frequency Line
Water	325,15 GHz
Methanol	326 GHz,…
Nitrous Oxide (N_2O)	326,55 GHz

THz Desorption Emission Spectroscopy



H_2O Desorption

- Start:~ 230 K
- Peak: ~ 250 K

N_2O Desorption

- Start: ~ 90 K
- Peak: ~ 130 K

Final Remarks

- Need for airborne or spaceborne observatory instruments with appropriate bandwidth, resolution, and sensitivity.

- THz ice spectroscopy has the potential to identify the presence and temperature of COMs in interstellar ices and to characterize physics and chemistry of the ISM.

- THz Desorption Emission Spectroscopy can be used to study thermal desorption of COMs. More technology development needed to study non-thermal processes.

Thanks for your attention!
Any questions?

Key Papers:

- Allodi et al. (2014), *Phys. Chem. Chem. Phys.* **16**, 3442
- Ioppolo et al. (2016), *Faraday Discuss.* **168**, 461
- McGuire et al. (2016), *Phys. Chem. Chem. Phys.* **18**, 20199
- Mifsud et al. (2021), *Front. Astron. Space Sci.* **8**, 757619

Thanks to Collaborators at:

University of Kent

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