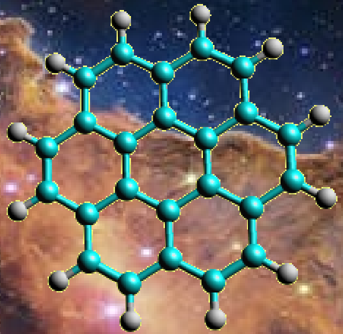
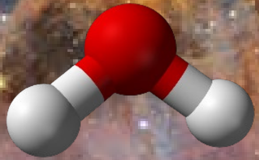
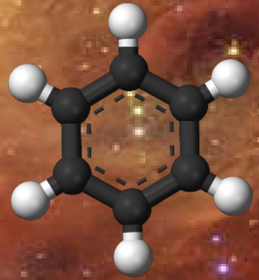
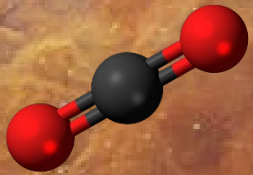
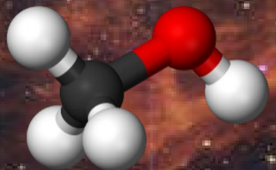
Astrochemistry: from the past to the future











Ewine F. van Dishoeck

Leiden Observatory/MPE

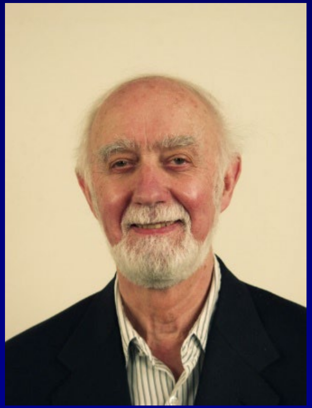
FIR-submm symposium in honor of Thijs de Graauw, Leiden, April 3 2025

European Research Council

INTERCAT Center for Interstellar Catalysis

We owe much to our (grand)fathers of astrochemistry

Townes



Dalgarno

Trained in atomic, molecular, chemical physics

Kaifu

Winnewisser

Thaddeus

Walmsley

Herbst

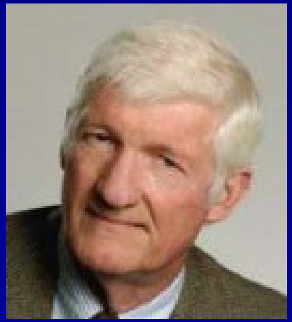
Tielens

We owe just as much to the instrument builders!

Thijs!!

Tom Phillips

Richard Hills



Jack Welch

Where it all started….

Keukenhof, May 1982

Thanks to all for shaping the field of astrochemistry!

What is astrochemistry?
(a.k.a molecular astrophysics)

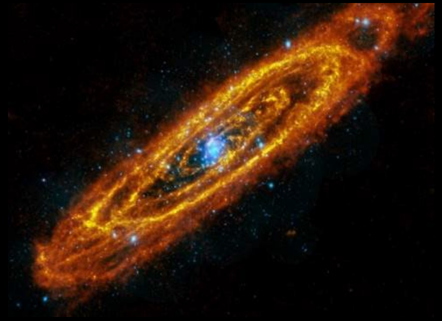
- **Formation, destruction and excitation of molecules in astronomical environments**

- **Molecules as probes of physical structure ISM**

- **Trail of molecules from clouds to planets: *origins***

Molecules found throughout the Universe
Focus here on solar neighborhood

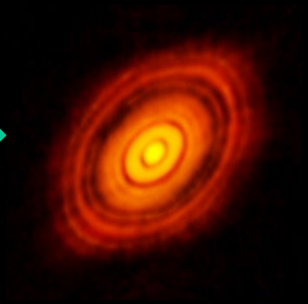
From the biggest to the smallest scales with the same molecules!



High z

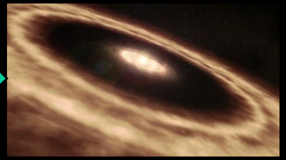
Cloud

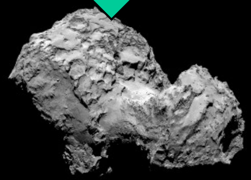
PDRs,
Protostars



Disk

Inner disk



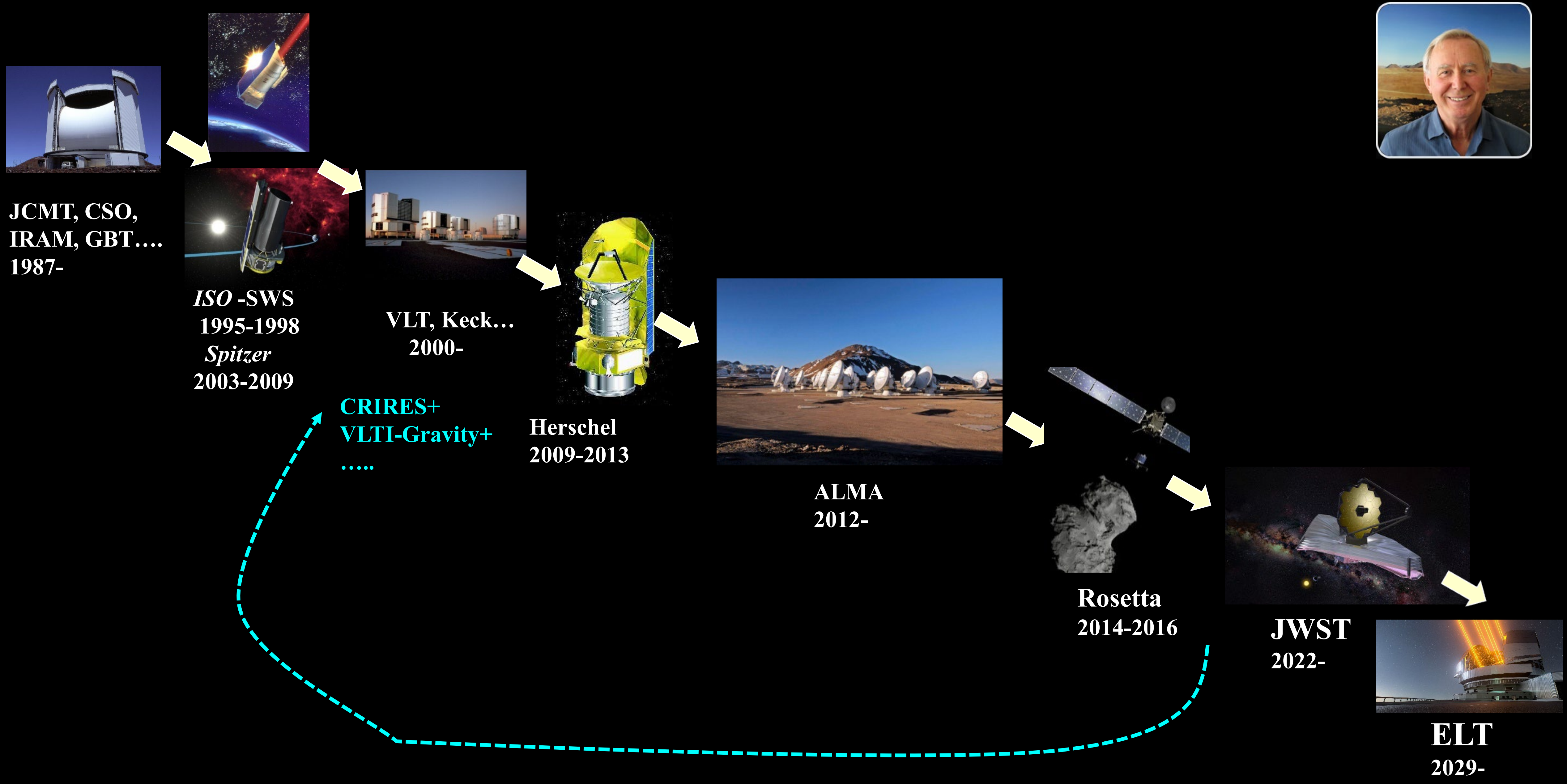


Planet

Comet

Following the trail of molecules from clouds to disks and planets

Astrochemistry driven by new facilities at IR and mm



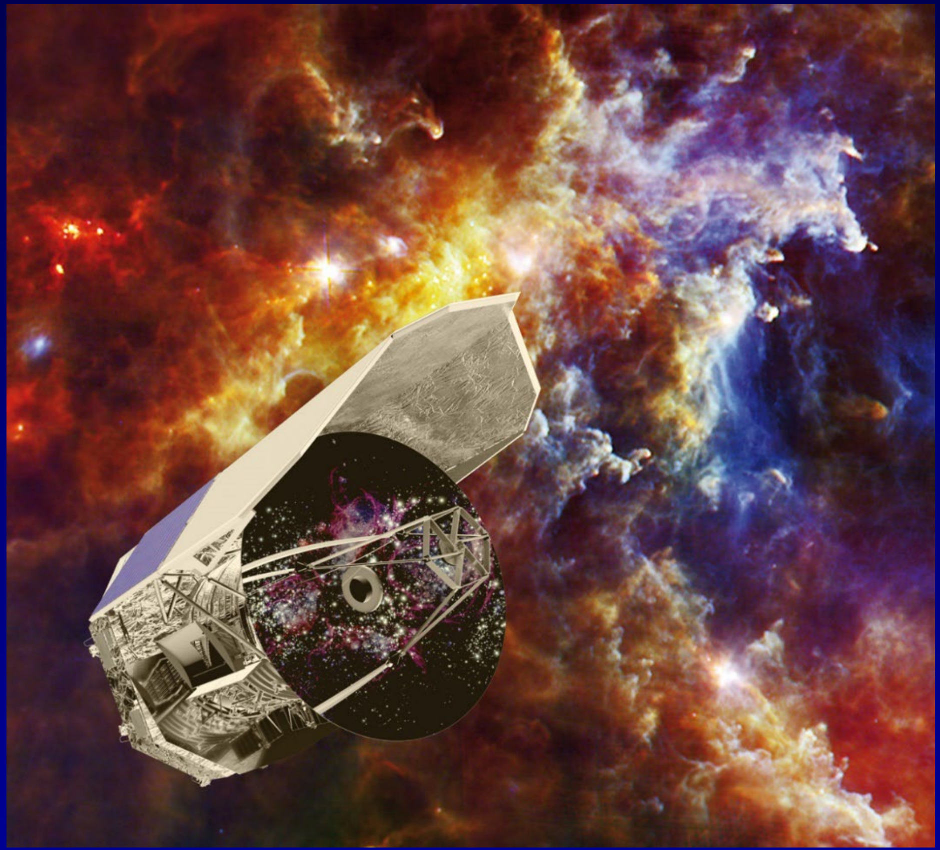
This talk: a few astrochemistry themes

- Hydrides
- Ices
- Water
- Complex organic molecules

- Future directions

I. Diffuse clouds: Hydrides

a *Herschel-HIFI* legacy



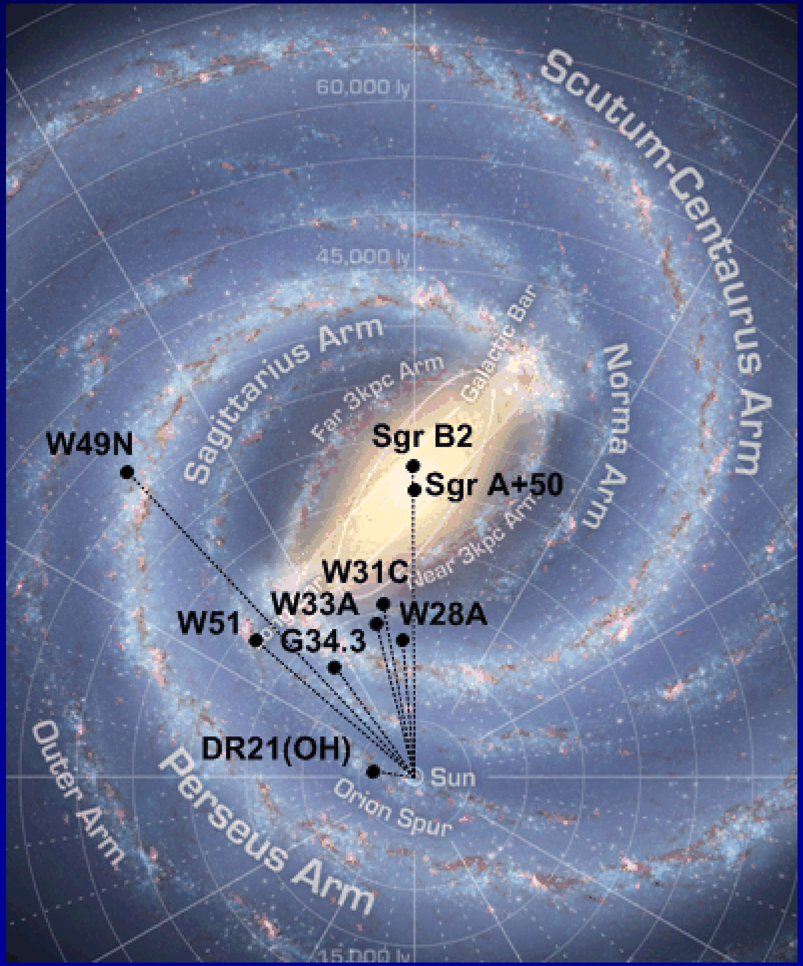
3.5m telescope

Beam 20-47”
scale of clouds

Hydrides have their primary rotational transitions in far-infrared
Building blocks of astrochemical gas-phase networks

Diffuse and translucent clouds

Testing ion-molecule chemistry

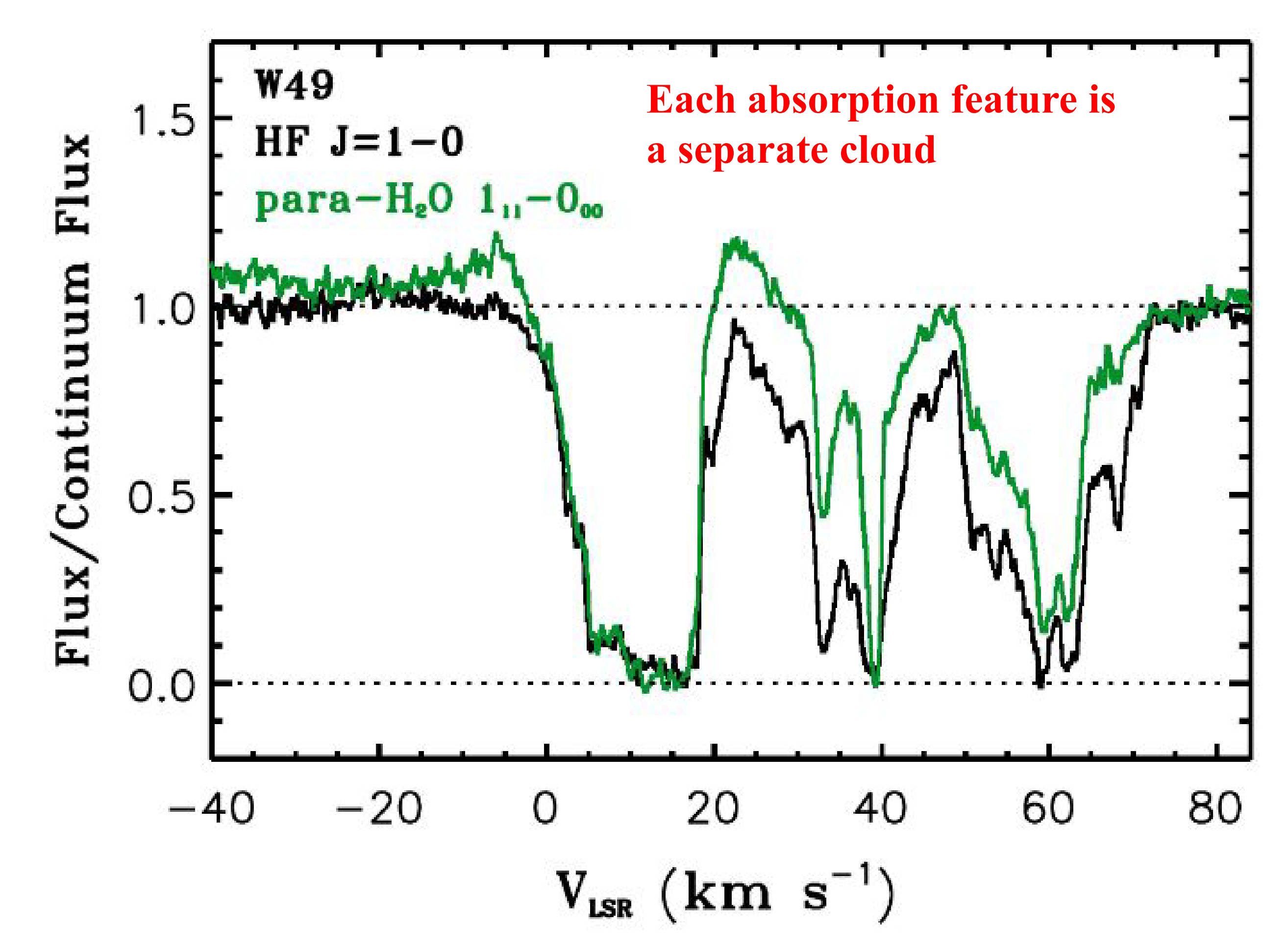


Gerin et al. 2016, ARA&A

- Absorption against bright far-IR continuum
- Clouds n~10^2 cm^{-3}, A_V ~few mag
- All molecules in ground level→simple analysis
- *Precision astrochemistry* (factor of ~2)

Gerin et al. 2010

Absorption lines

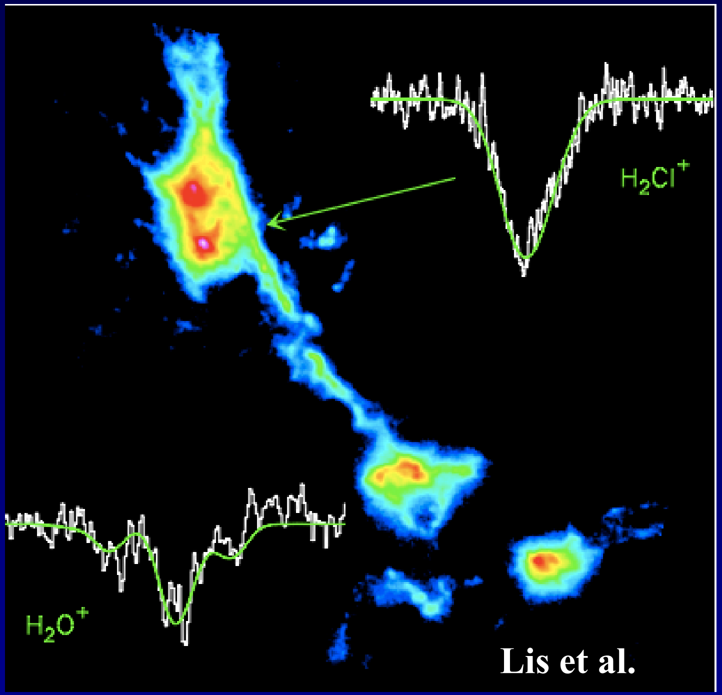


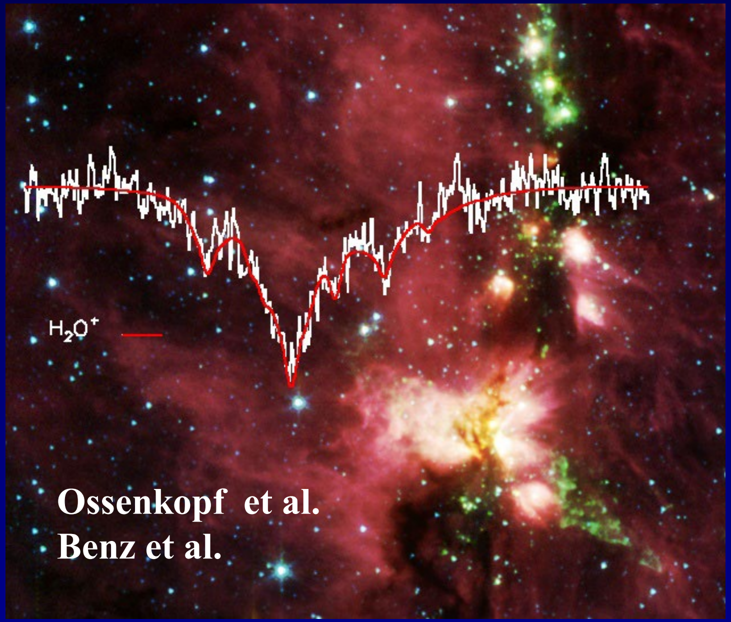
Water
o/p=3

Neufeld et al. 2010,
Sonnetrucker et al. 2010
Godard et al. 2012
Emprechtinger et al. 2012
Flagey et al. 2013

- **HF as tracer of H_2 column density because of simple chemistry F + $H_2 \rightarrow$ HF**
- **Constant H_2O/H_2 abundance of $5x10^{-8}$, consistent with ion-molecule chemistry**

Surprise: strong OH^+, H_2O^+



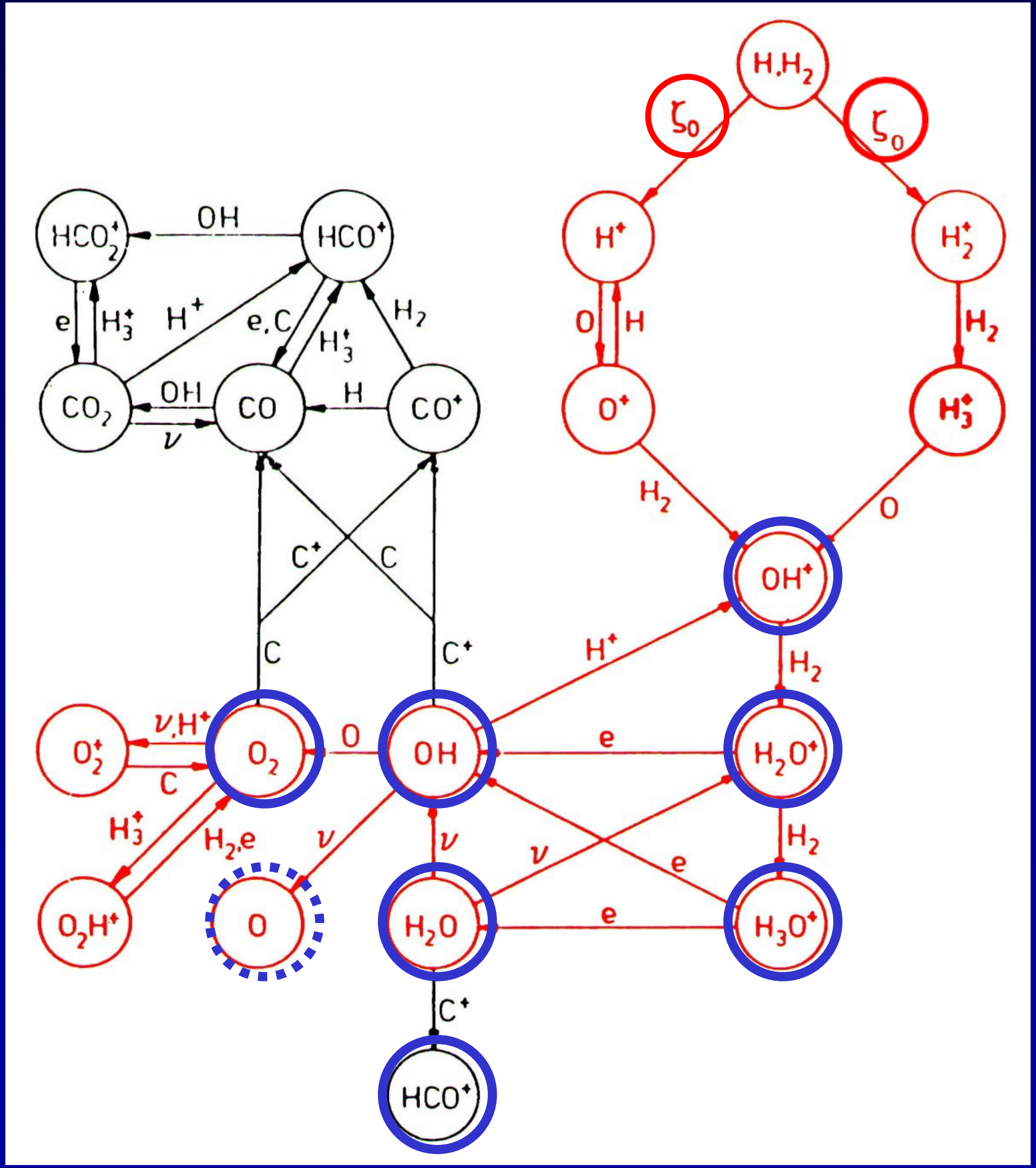


Seen along all lines of sight, from diffuse to dense clouds, And even in high redshift galaxies!

Points to a ISM phase with H/H_2~10

Ossenkopf et al., Benz et al., Bruderer et al., Gerin et al., Wyrowski et al., Gupta et al., Schilke et al., Lis et al. 2010; Neufeld et al. 2012, de Luca et al. 2012, Indriolo et al. 2013, Monje et al. 2013....
OH^+ detection with APEX Wyrowski et al. 2010

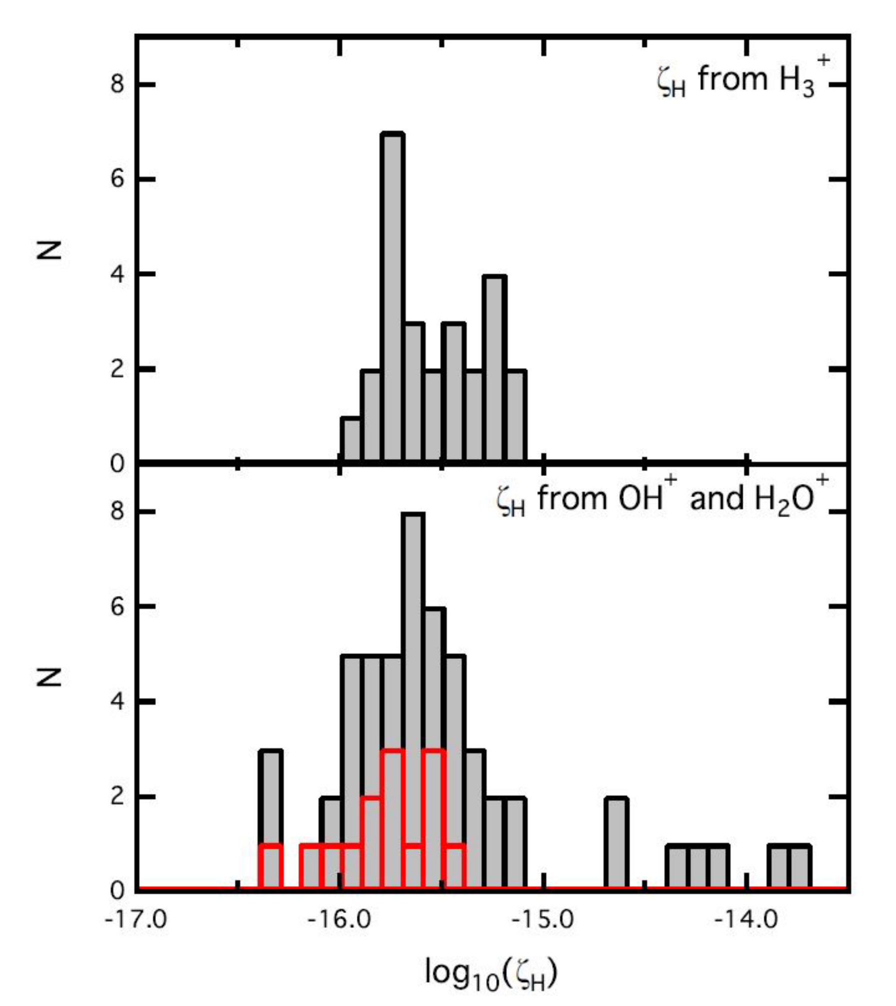
All key species in oxygen chemistry detected!



Initiated by cosmic ray ionization

Network from Black & Dalgarno 1977

Cosmic ray ionization rates



Red: denser material associated with continuum source

H_3^+ as probe

Geballe & Oka 1996
Van der Tak & vD 2000
McCall et al. 2003
Indriolo & McCall 2012

OH^+ and H_2O^+

Indriolo et al. 2015

ArH^+

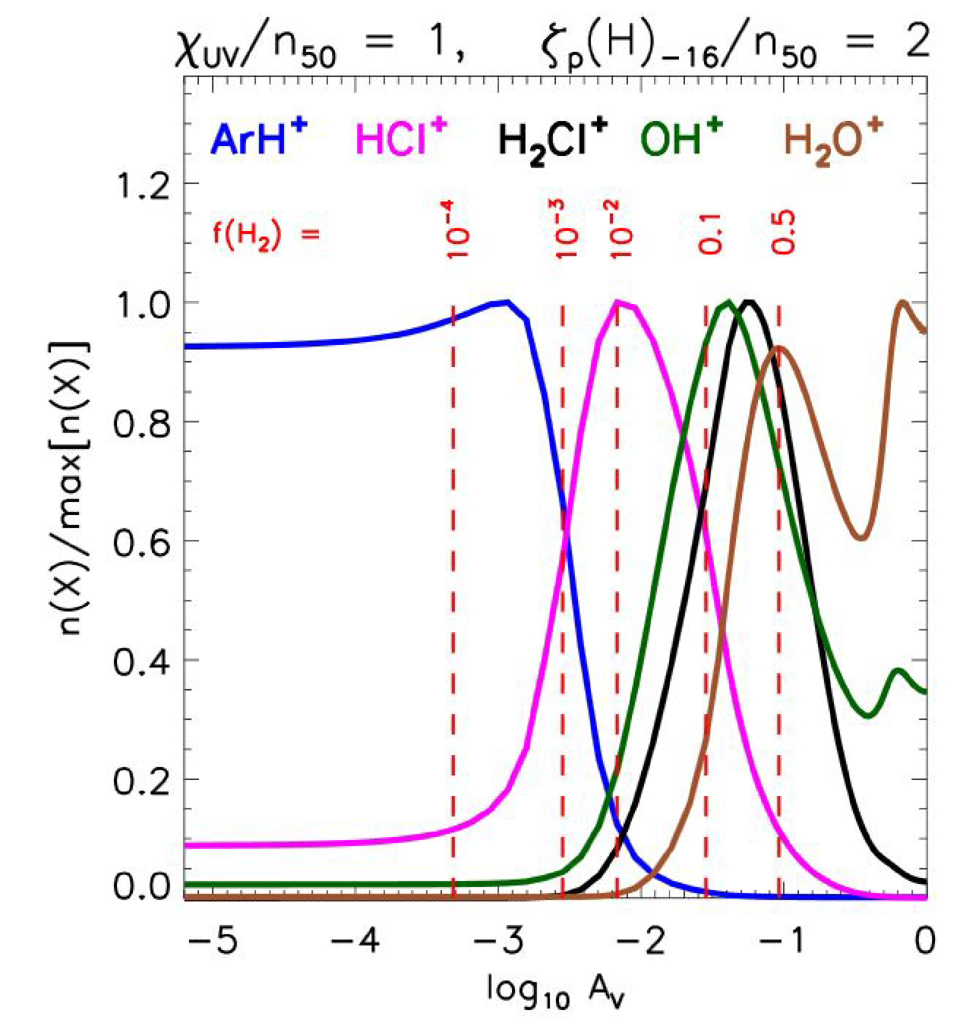
Neufeld & Wolfire 2017

Obolentseva et al. 2024 suggest lower mean values ~6×10^{-17} s^{-1}

See also van Dishoeck & Black 1986

Ions probing ISM structure

HeH$^+$
SOFIA
Güsten et al. 2019



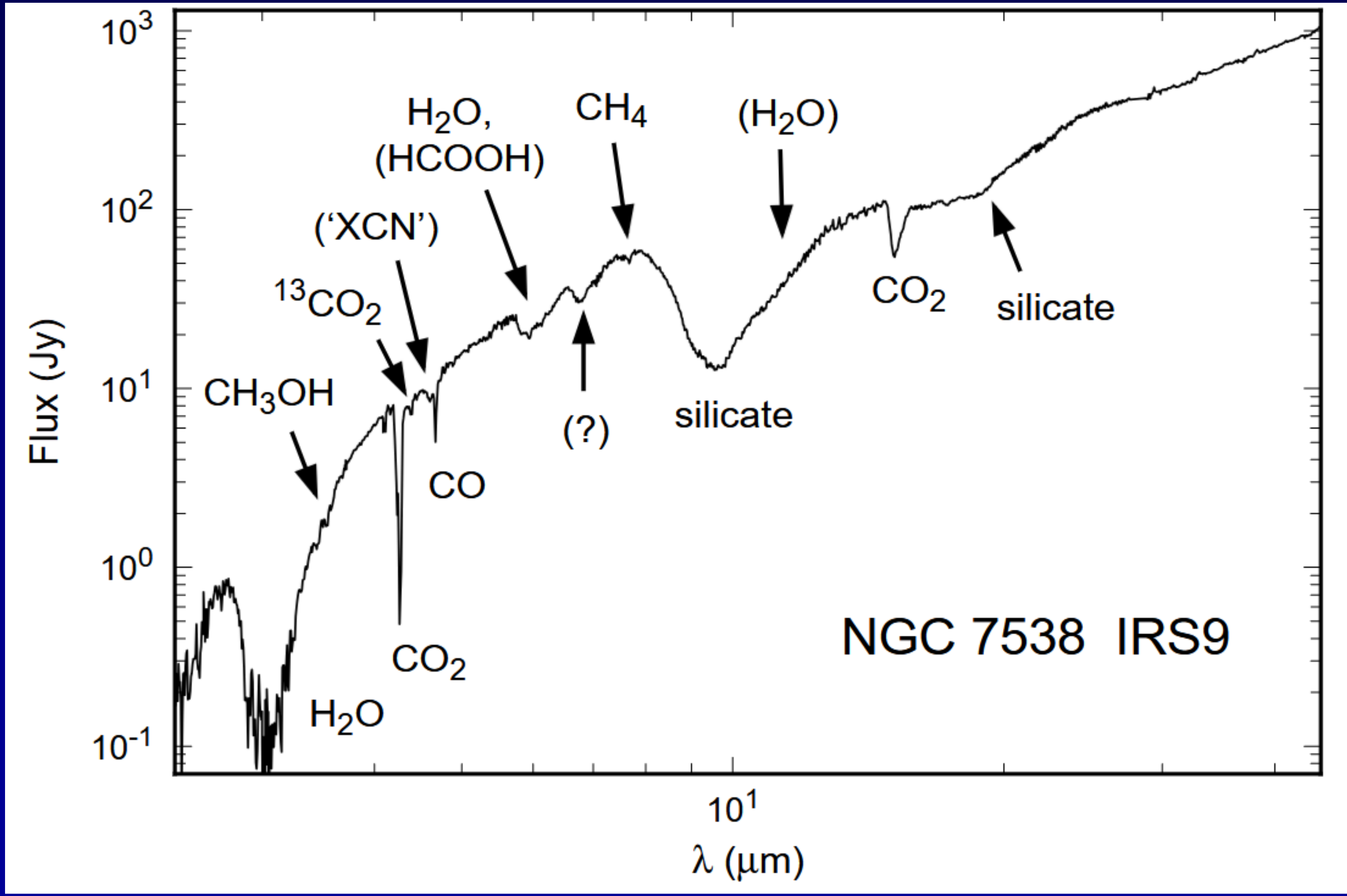
Neufeld & Wolfire 2016

Hydrodynamical simulations of GMCs and galaxies have to be consistent with these data, as well as C+ → C → CO transition

Future prospects for hydrides

- ISM in (distant) galaxies
  - Red-shifted lines with ALMA WSU (high frequency) bands
- Galactic ISM
  - Many more lines of sight (maps) with heterodyne instrument
  - Herschel-HIFI did well! APEX continuing, new space
    - Is there a killer science case?

II. Icy universe opened up by ISO-SWS



Ices contain a major fraction of the elemental budgets!

Whittet et al. 1996

Detection of solid CO_2

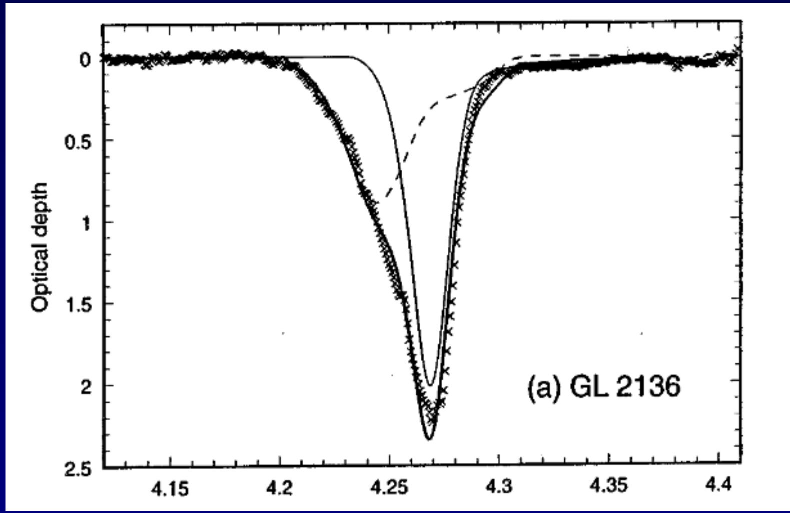
Detection of CO_2 ice in dense clouds at ~15% w.r.t. H_2O

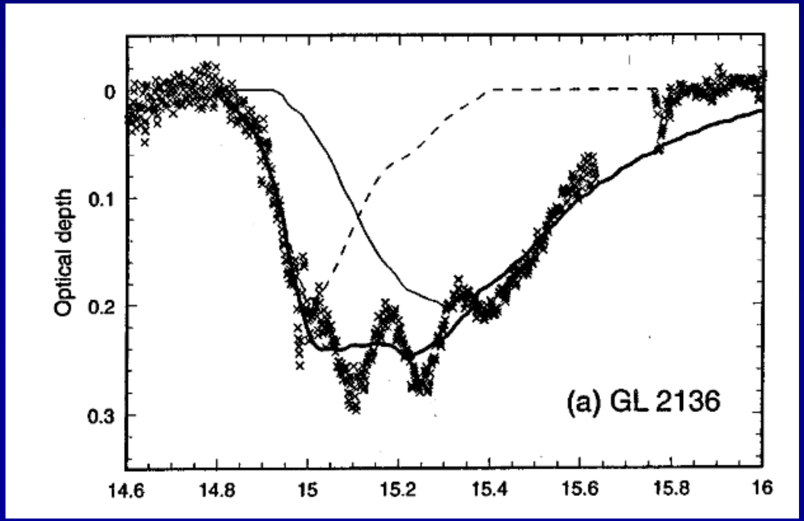
Astron. Astrophys. 315, L345–L348 (1996)

ASTRONOMY AND ASTROPHYSICS

SWS observations of solid CO_2 in molecular clouds*

Th. de Graauw[1,2], D.C.B. Whittet[3], P.A. Gerakines[3], O.H. Bauer[4], D.A. Beintema[1,5], A.C.A. Boogert[2], D.R. Boxhoorn[1], J.E. Chiar[3], P. Ehrenfreund[6], H. Feuchtgruber[4,5], F.P. Helmich[6], A.M. Heras[5], R. Huygen[7], D.J.M. Kester[1], D. Kunze[4], F. Lahuis[5], K.J. Leech[5], D. Lutz[4], P.W. Morris[5,8], T. Prusti[5], P.R. Roelfsema[1,5], A. Salama[5], S.G. Schaeidt[4,5], W.A. Schutte[6], H.W.W. Spoon[8], A.G.G.M. Tielens[9], E.A. Valentijn[1], B. Vandenbussche[5,7], E.F. van Dishoeck[6], P.R. Wesselius[1], E. Wieprecht[4,5], and C.M. Wright[4]





These ISO-SWS data on high-mass protostars remain unique since too bright for JWST!

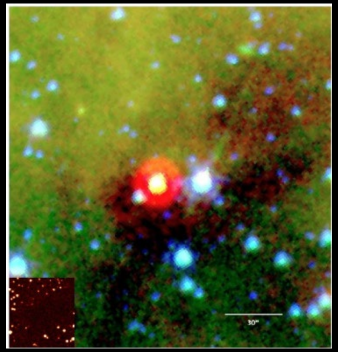
Using band profiles as diagnostics of environment and heating (lab data!)

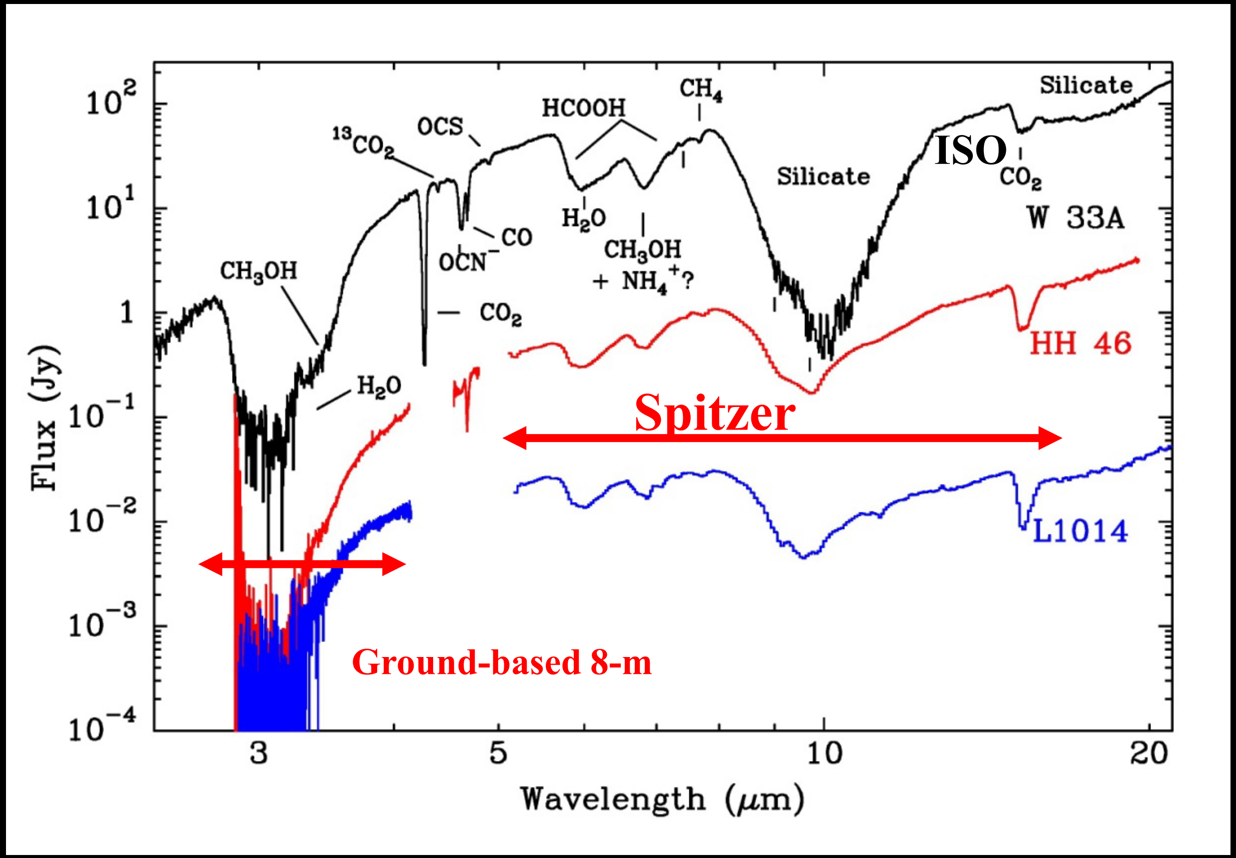
From ISO to *Spitzer*: raw sensitivity

From 10^5 to <0.1 L_{sun} objects!

HH 46: solar-mass YSO

L1014: substellar YSO



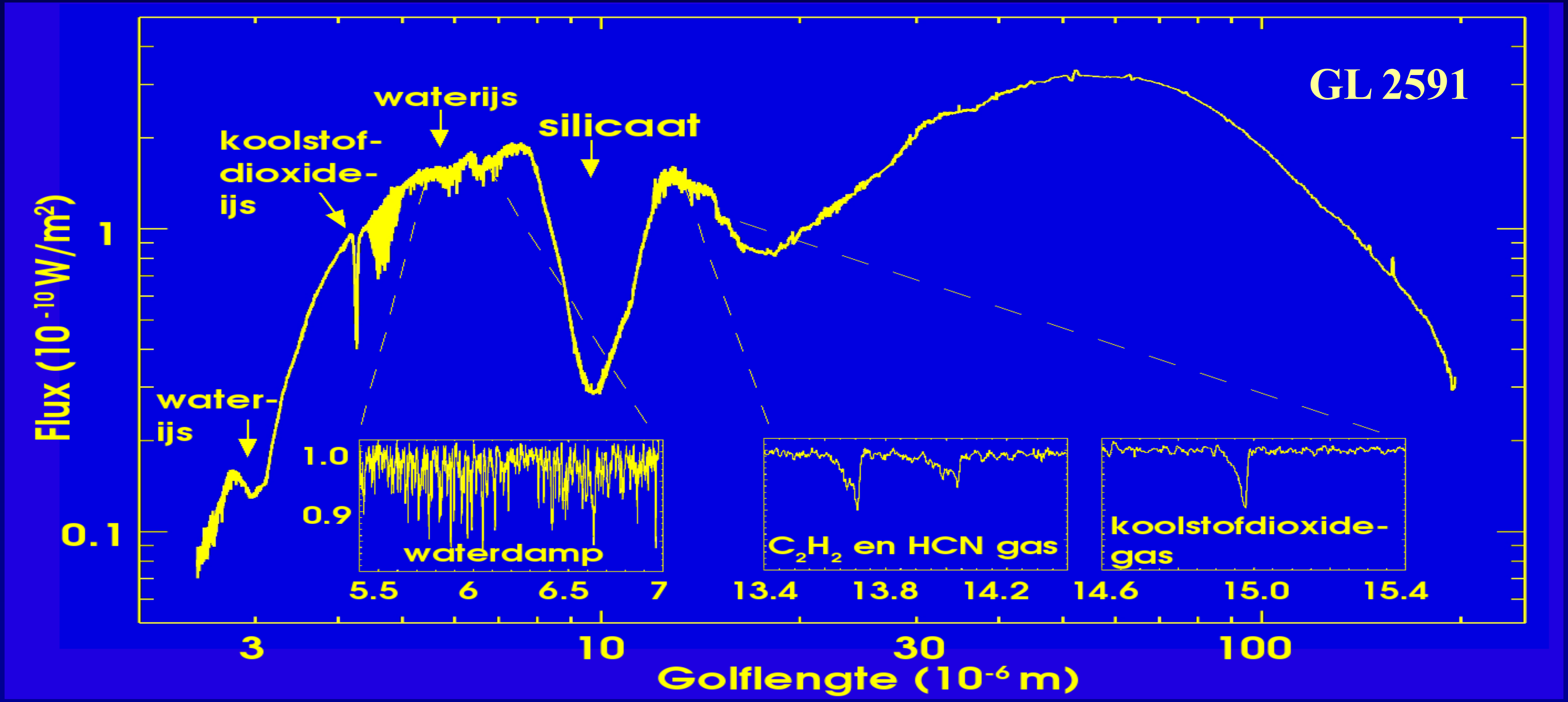


Note similarity ices over large range of luminosities 0.1-10^5 L_{Sun}

And now with JWST: see talk Melissa McClure

Boogert et al. 2004, 2008, 2015
Pontoppidan et al. 2008
Öberg, et al. 2008, 2011
Bottinelli et al. 2010, 2015

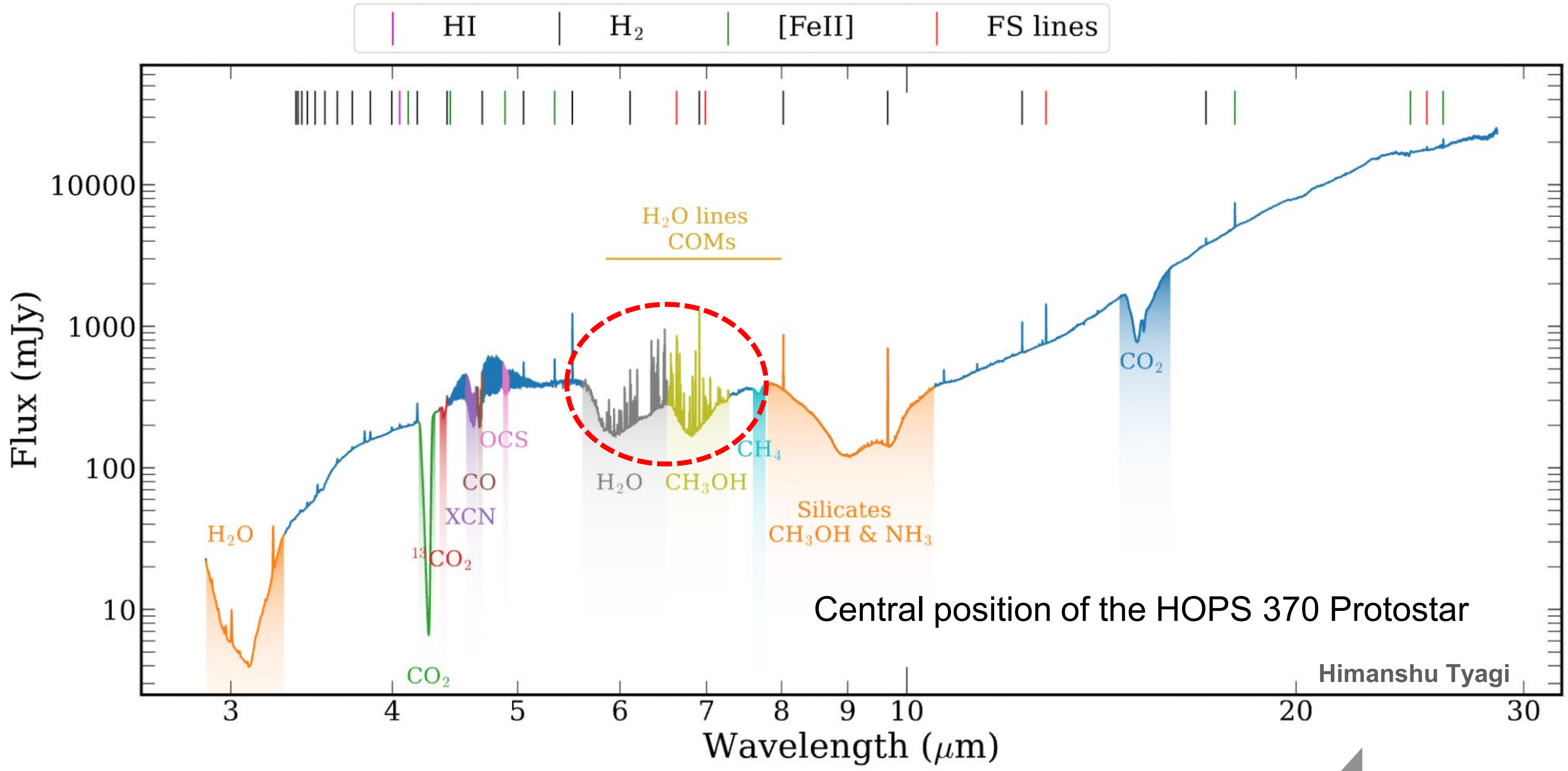
ISO-SWS: Ice *and* gas



vD & Helmich 1996
Boonman, Lahuis et al. 2003
van Dishoeck et al. 1996

- So far only for high-mass protostars, *now also solar-mass protostars with JWST*

Full 3-27 μm JWST spectra are rich in gas and ice features



Detection of HDO ice
Slavicinska+2024

Thermal processing of ices from 4 micron $^{13}CO2$ ice feature
Brunken+2024

12C/13C in ices
Brunken et al. 2024b, JOYS+

Spatial variations in $^{13}CO2$ feature

Tyagi+2025.

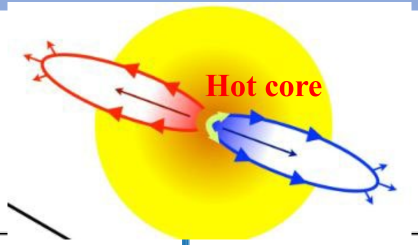
Tentative detection of CH_3CN ice

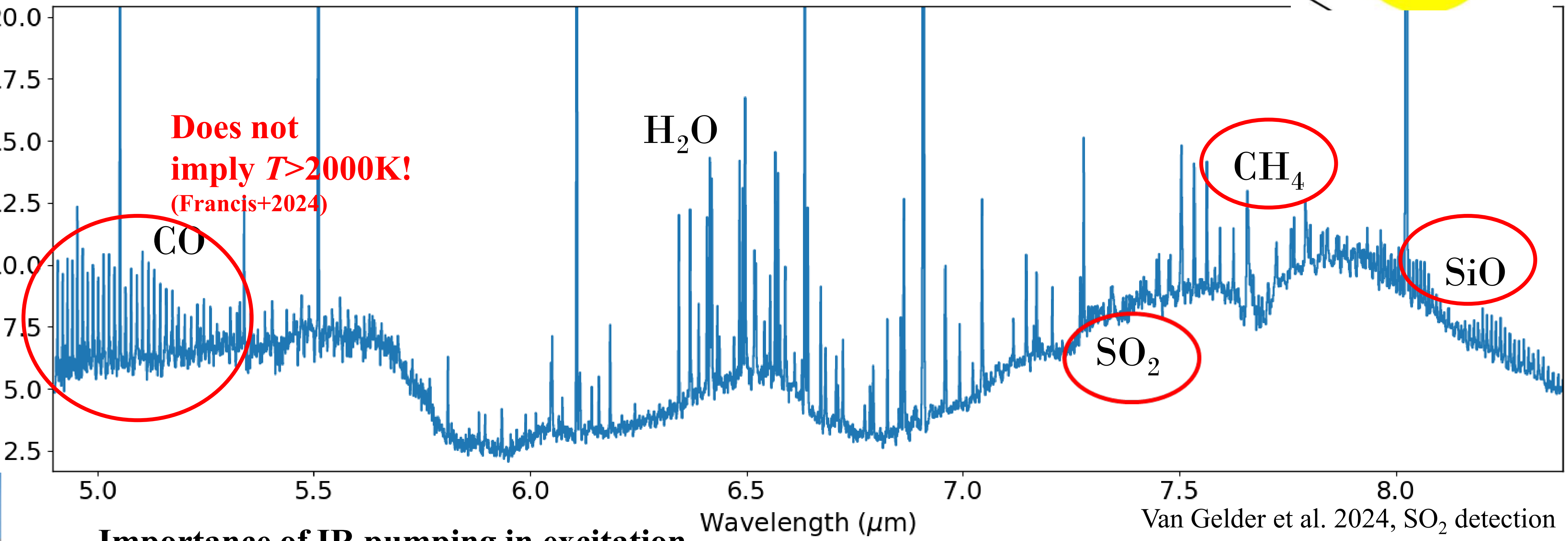
Nazari+2024

Recent ice studies with IPA

Low mass: very rich molecular spectra

L1448-mm: Class 0 low-mass YSO: **hot core vs dense shocks**

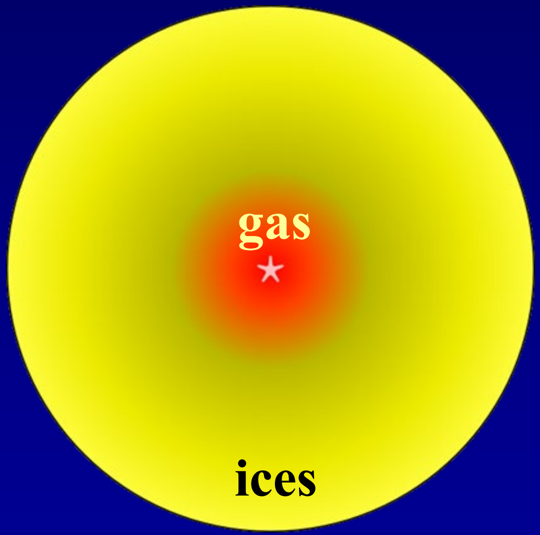




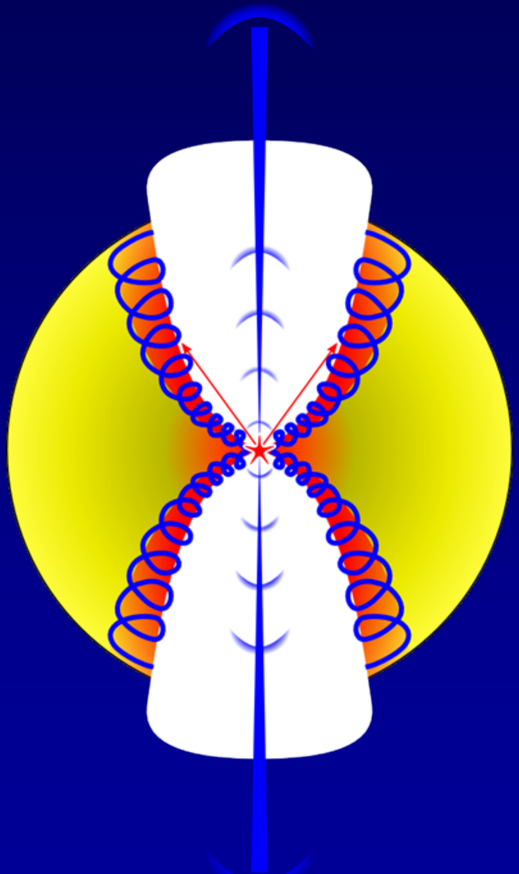
Importance of IR pumping in excitation

Van Gelder et al. 2024, SO_2 detection
Van Gelder, Francis et al. 2024b

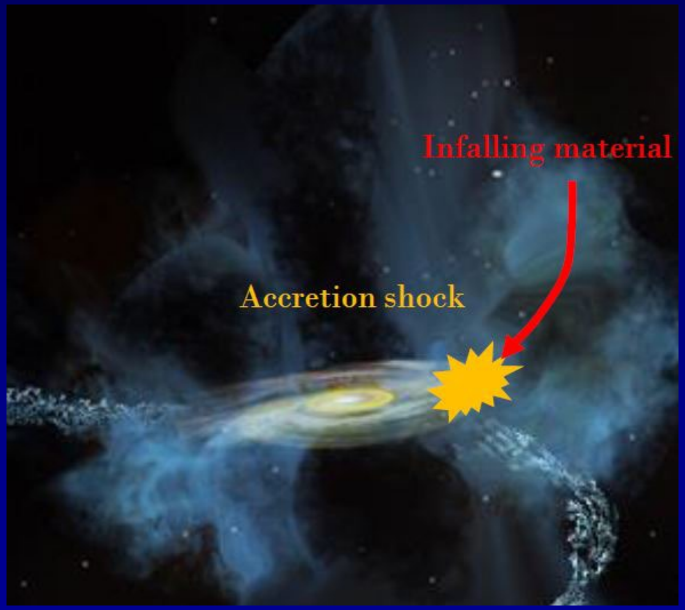
Warm gas: origin molecules on 100 au scale?



Hot core:
Sublimation of ices

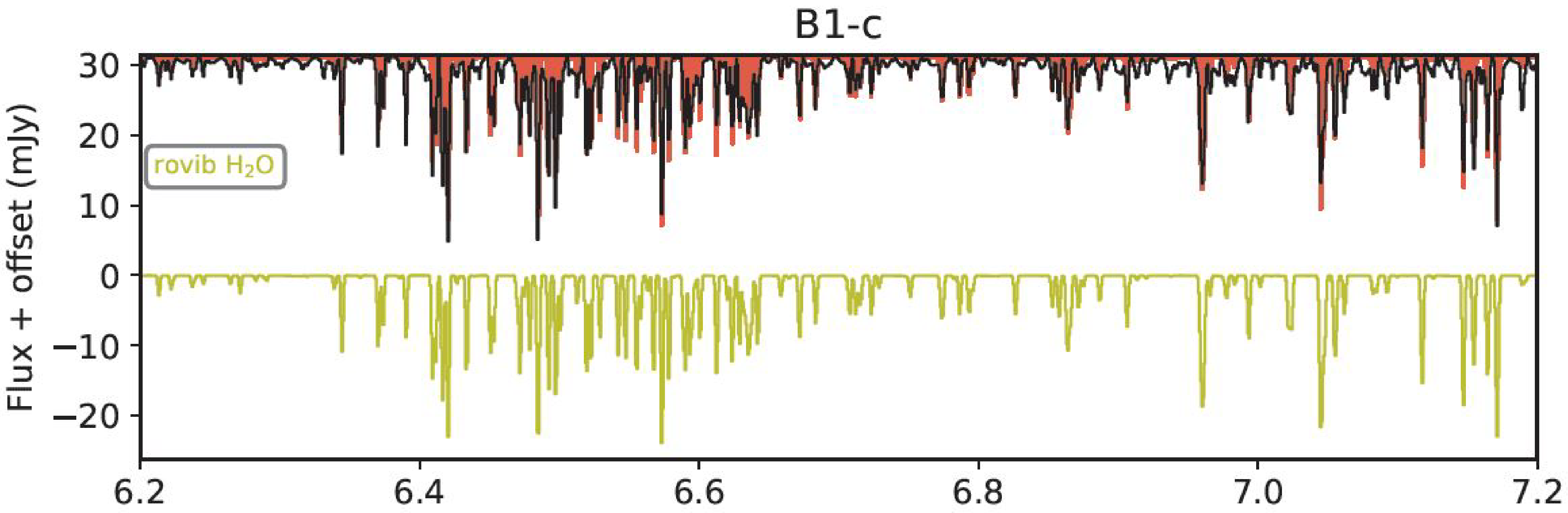


Dense outflow shocks



Accretion shock onto disk

Class 0 protostar: hot core absorption



Data + model

Model

Low-mass protostar with hot core seen in complex molecules with ALMA

Van Gelder et al. 2024b

Future directions and prospects

- *Imaging* hot core chemistry
  - Thermal sublimation?
  - Dense outflow shocks?
  - Accretion shocks onto disk?

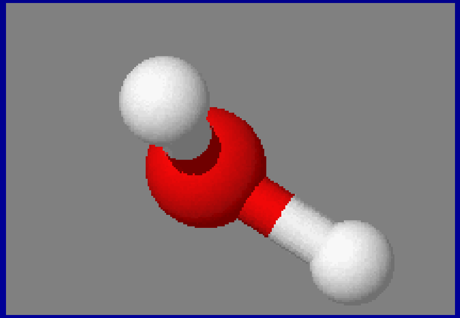
- Need high spectral and spatial resolution data
  - ELT-METIS
  - R~10^5 mid-IR spectrometer in space
  - ALMA WSU and 2040+ (see also water and COMs)

III. Water

90 papers

- Where and how is water formed in space?
- Which physical components does water trace?
- What is the water ‘trail’ from clouds to disks to planets?

Wikipedia-Mitchidr

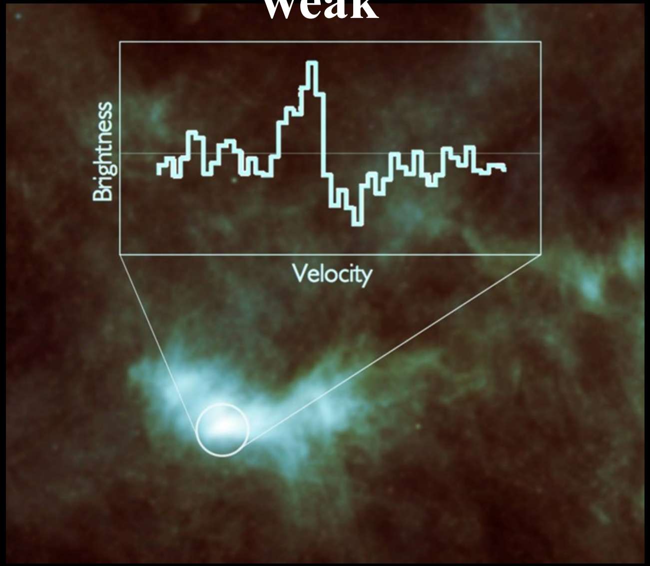


vD, Bergin, Lis & Lunine 2014, PPVI
vD, Kristensen et al. 2021

Water from clouds to disks

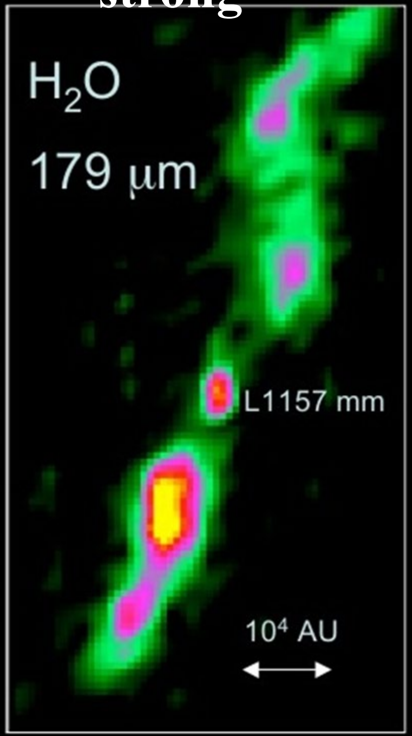
vD et al. 2014, 2021

Dense cloud
weak



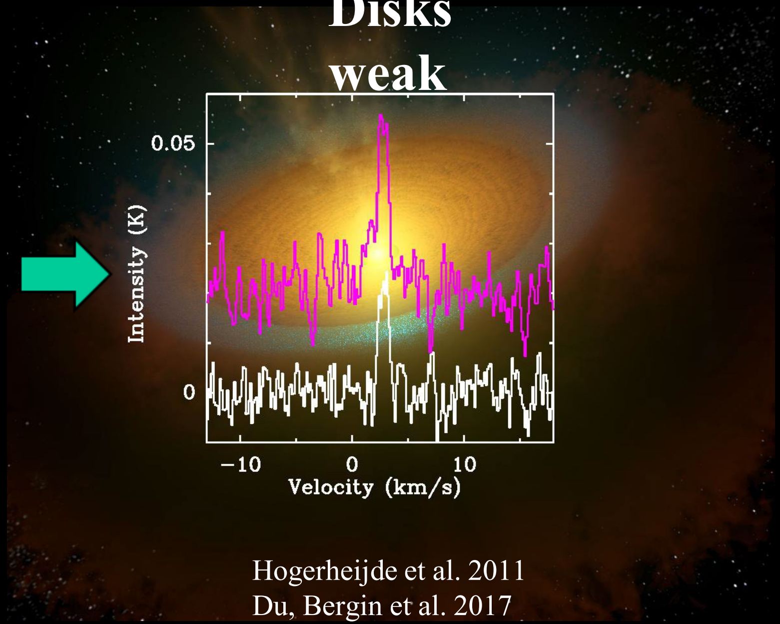
Caselli et al. 2012

Protostar + outflow
strong



Nisini et al. 2010

Disks
weak



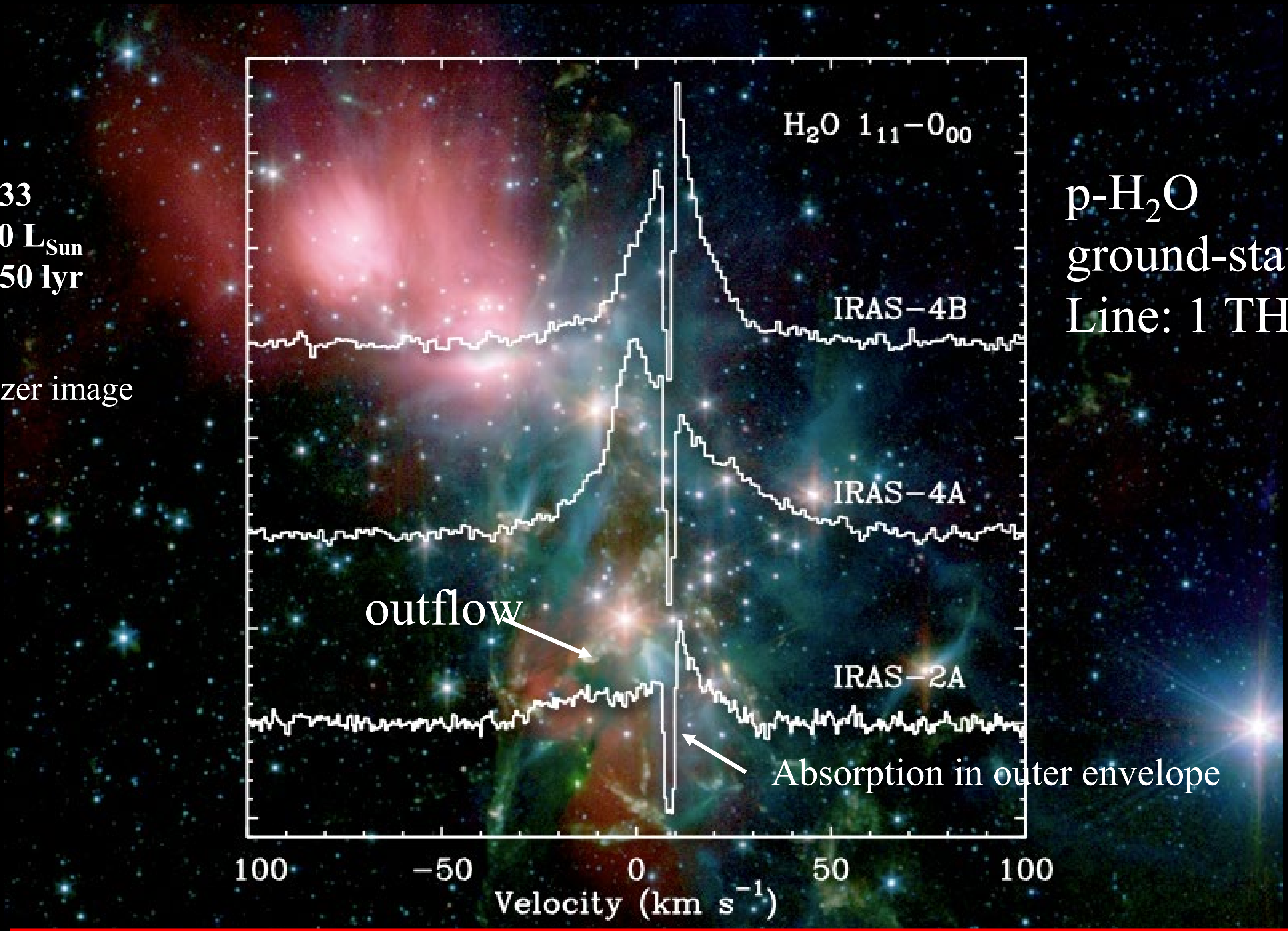
Hogerheijde et al. 2011
Du, Bergin et al. 2017

- Water is mostly ice in cold clouds
- Water formed abundantly in shocks (but lower abundance than expected due to UV)
- Water is locked up quickly in large bodies in disks

Protostars: beautiful line profiles, multiple components

N1333
L~20 L_{Sun}
D~750 lyr

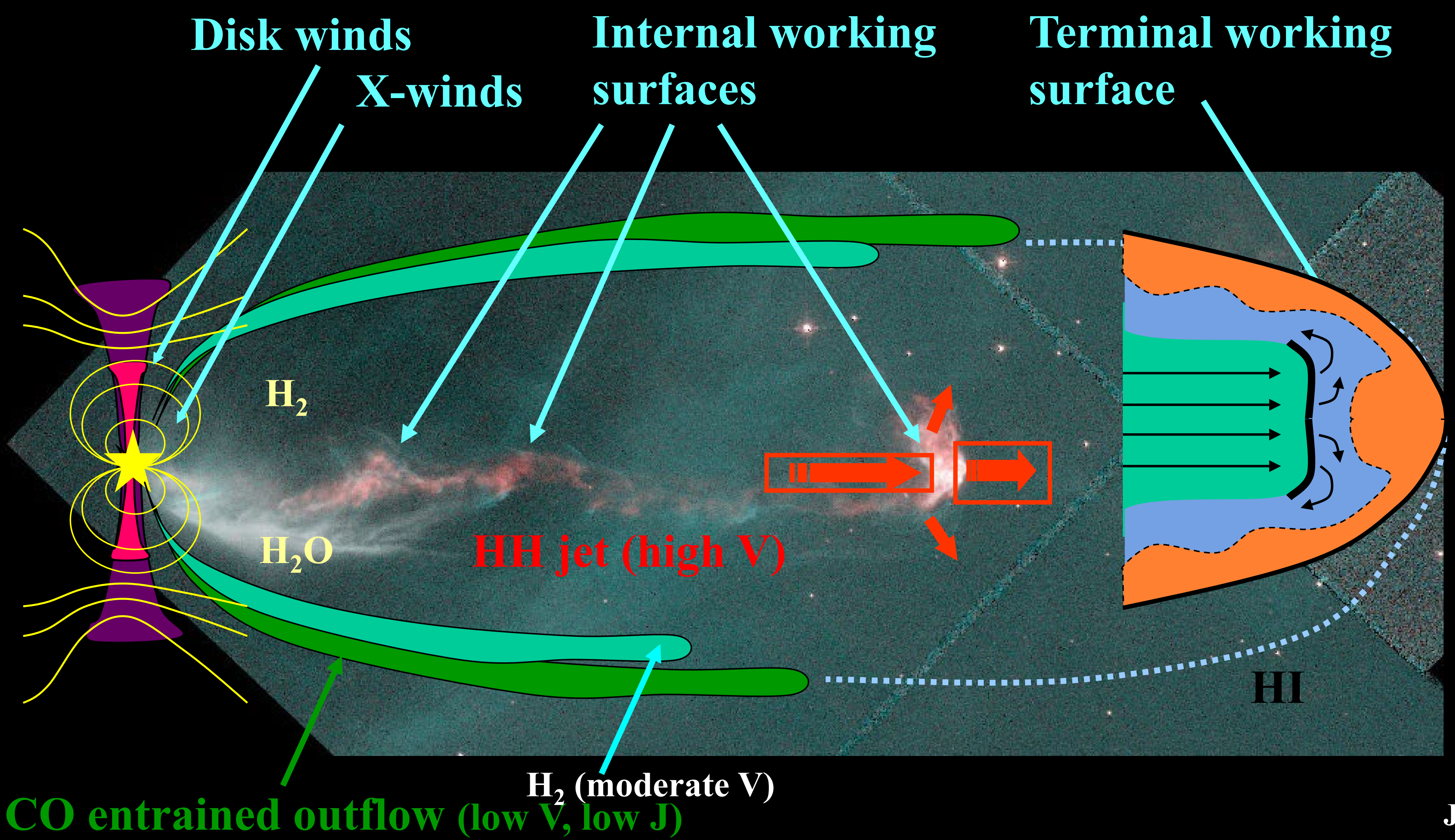
Spitzer image



Kristensen et al. 2010, 2012

Future: images of H_2O components on subarcsec scale, link with JWST!

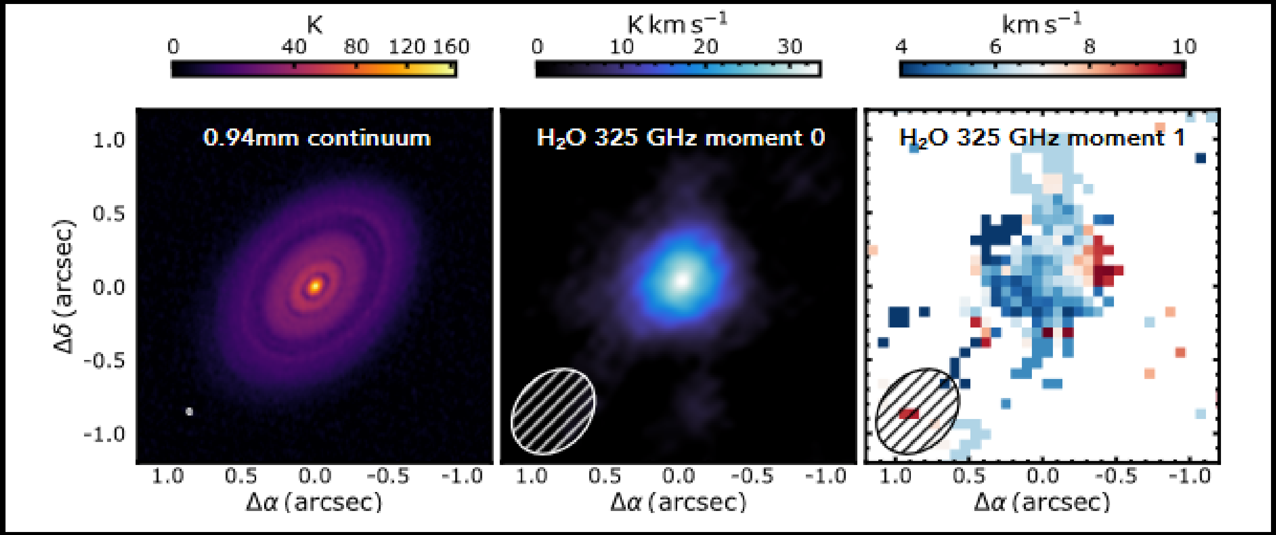
Interlinked physics and chemistry of outflows:
Jets, winds ⇒ wide-angle cavities



J. Bally 2016

Imaging warm water with ALMA

Blue=water
Red=dust cont



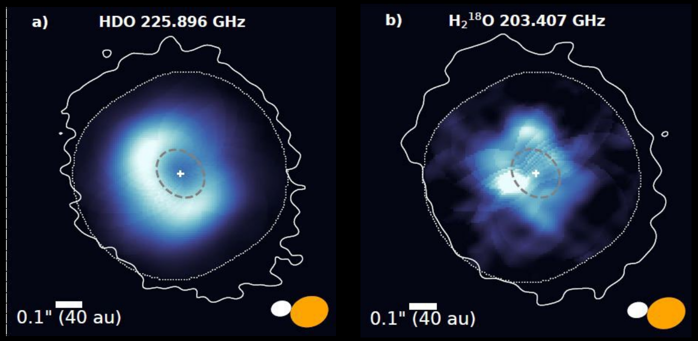
Facchini et al. 2024

≥4 Earth oceans of water vapor within 17 au radius

Why is not much more water observations + imaging done with ALMA?

HDO/H_2O and D_2O/H_2O from cloud to disk and comets: inheritance water in disk

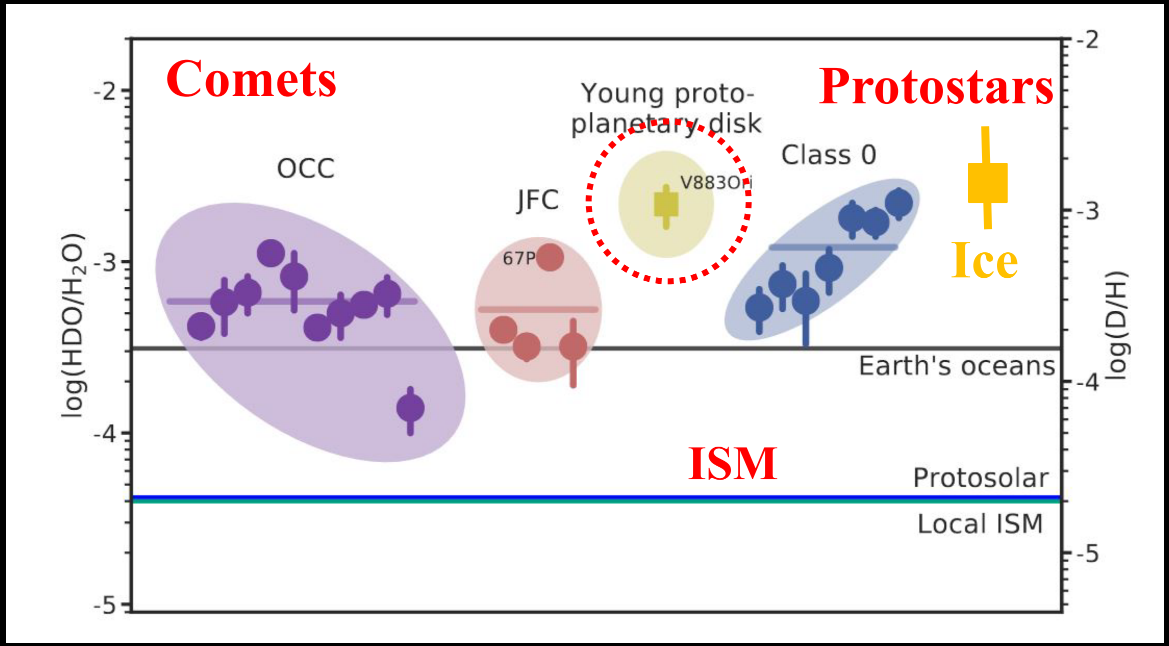
HDO **$H_2{}^{18}O$**



ALMA images V883 Ori disk

Tobin, van 't Hoff, et al. 2023, Nature

Press release March 8 2023

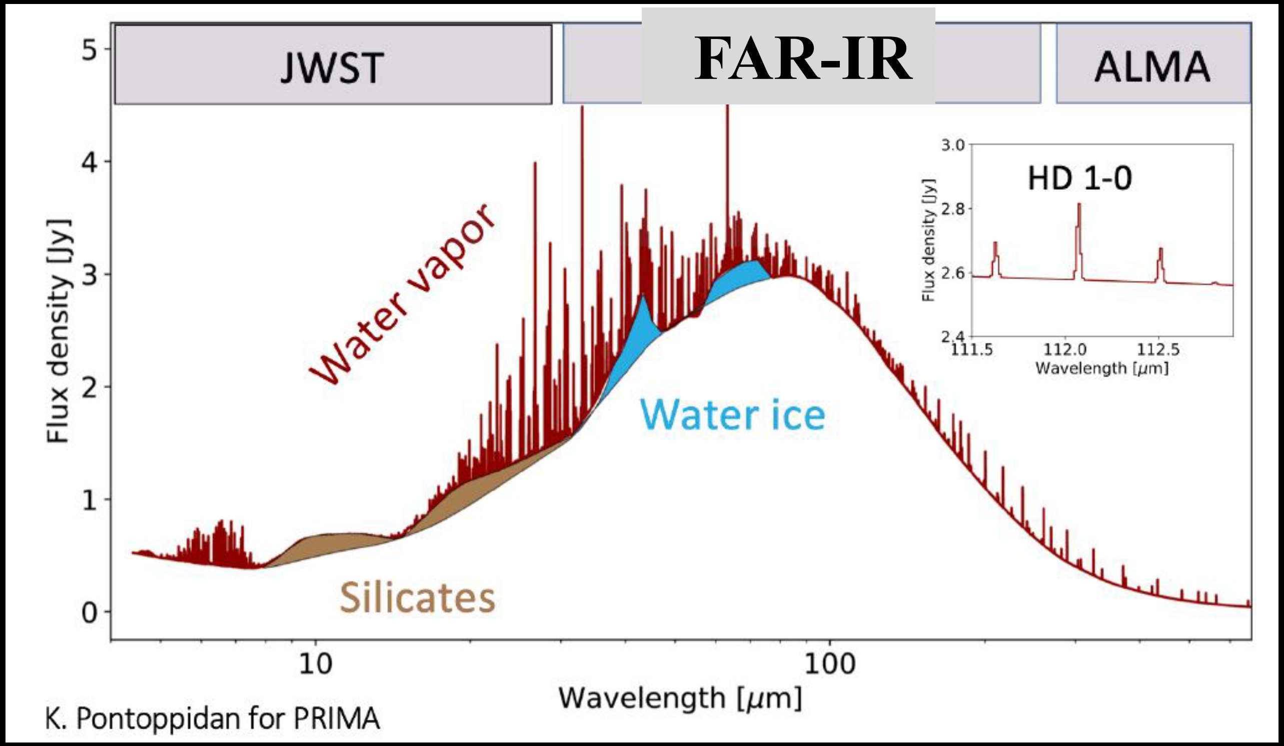


Also $D_2O/HDO >> HDO/H_2O$

See also:
Jensen et al. 2021, vD et al. 2021
Coutens et al. 2012, 2014
Persson et al. 2014, Furuya et al. 2016

JWST
Slavicinska+2024, 2025

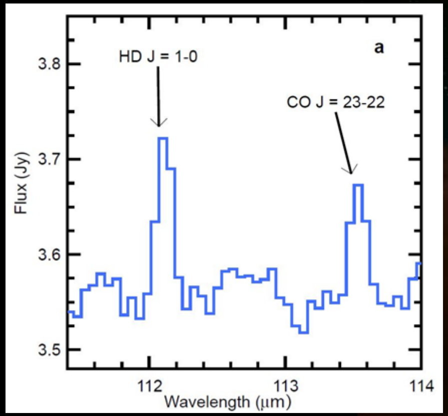
Importance of far-infrared for planet-forming disks



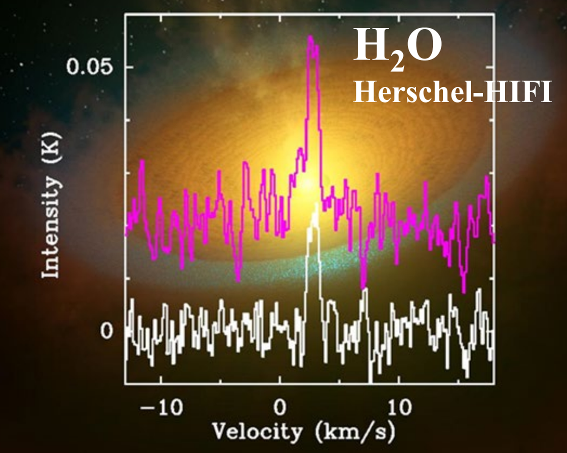
J. Glenn slides
Poster AAS 2023

- **Water vapor**
- **Water ice**
- **HD: disk mass**
- **Crystalline silicates**
- **….**

Major FIR driver: see talks Bergin, Notsu, McClure

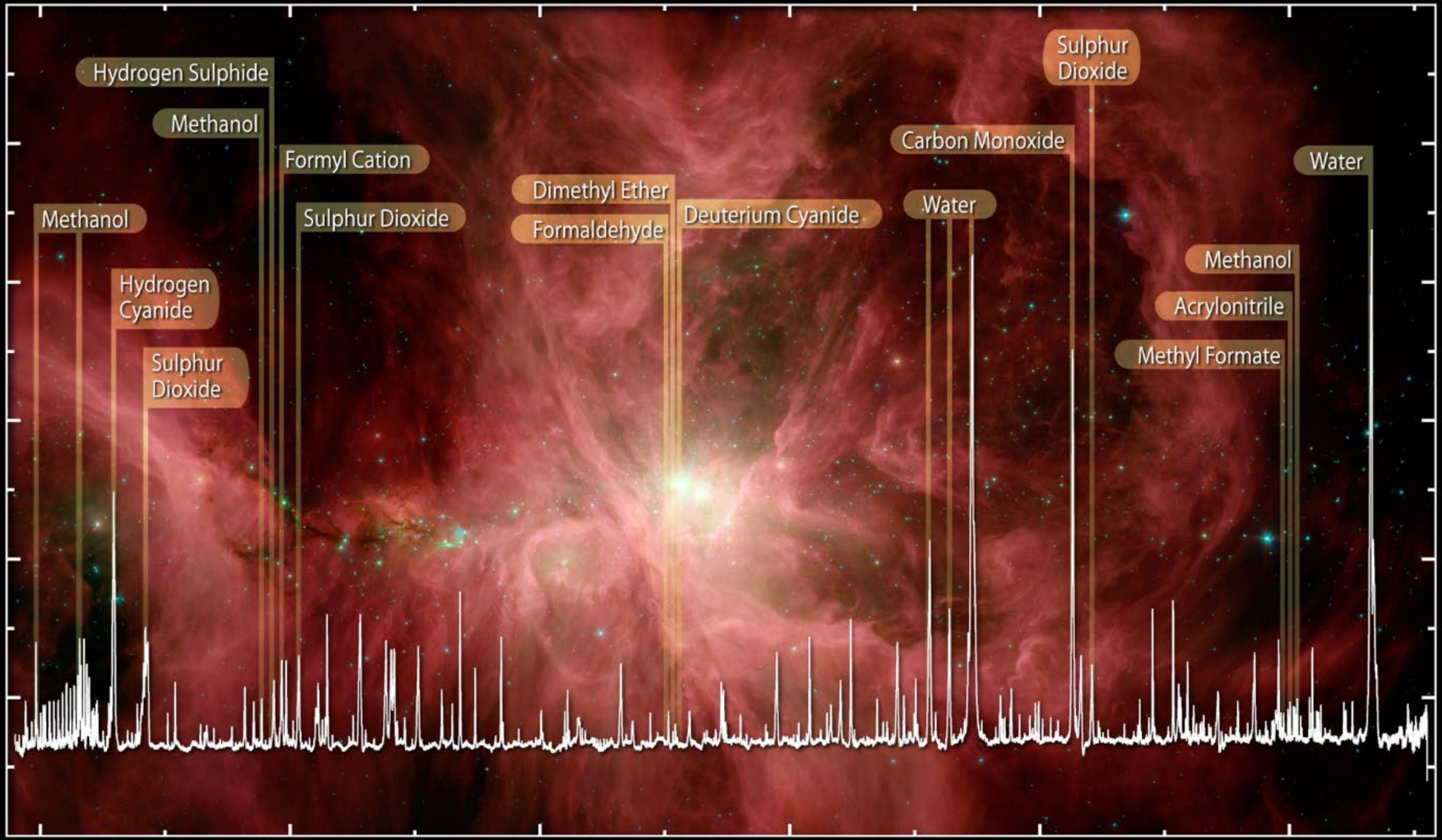


Bergin et al. 2013



(No?) Need for heterodyne resolution?

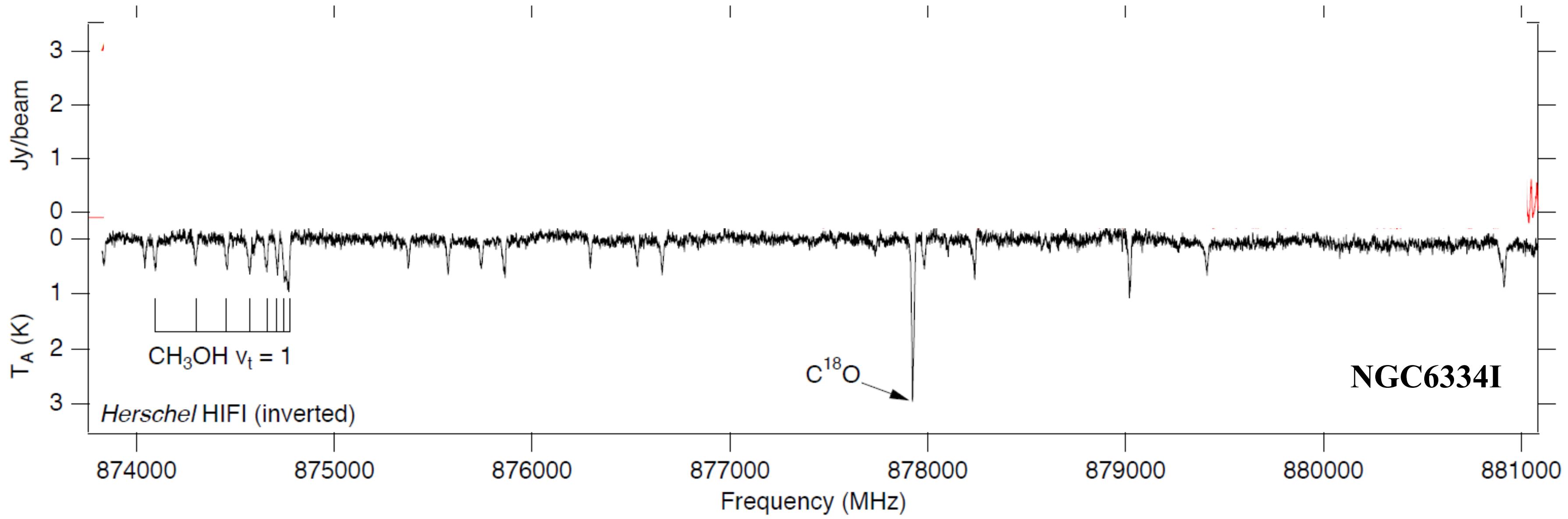
IV. Complex molecules



HIFI Orion spectrum

Bergin et al. 2010
Crockett et al. 215

ALMA vs Herschel
sensitivity to small scale emission

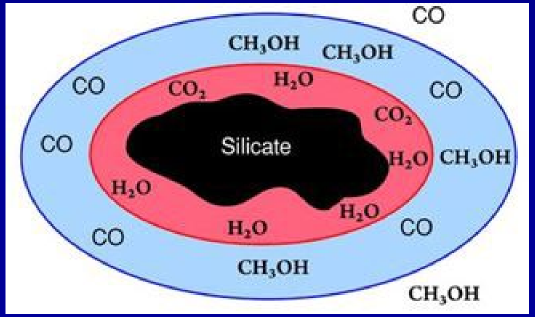


McGuire et al. 2019

High frequency windows still largely unexplored after >10 year ALMA!!

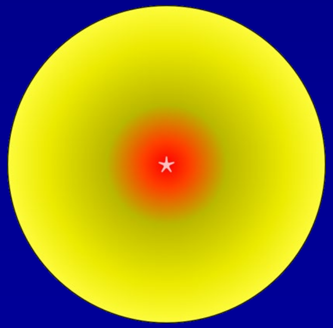
COM science questions

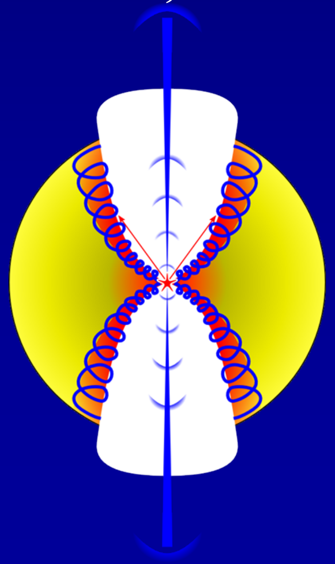
- How far does complexity go?
- Grain surface vs gas-phase formation?
- Similarities vs differences sources?
  - COMs as physical diagnostics
- COMs from clouds to disks



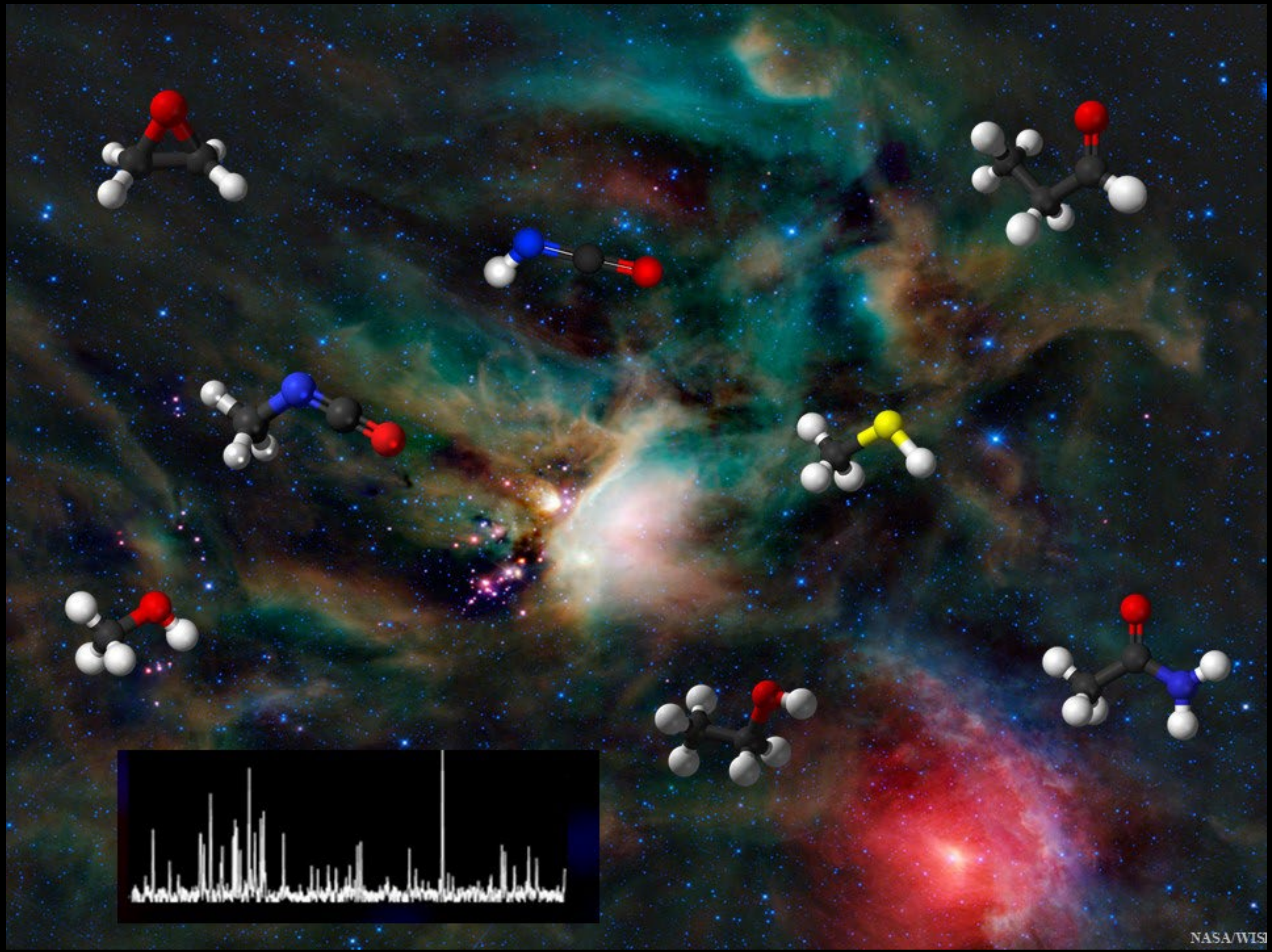
COM study approaches

- Complete COM inventory in a single source (“Fab 4”)
- Selected COMs in many sources
- “Big game hunting”
- New frequency ranges, e.g. cm, submm
- High angular resolution
  - hot core, outflow/disk wind, accretion shock



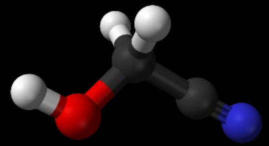


Warm star-forming regions reveal rich chemistry on solar system scales

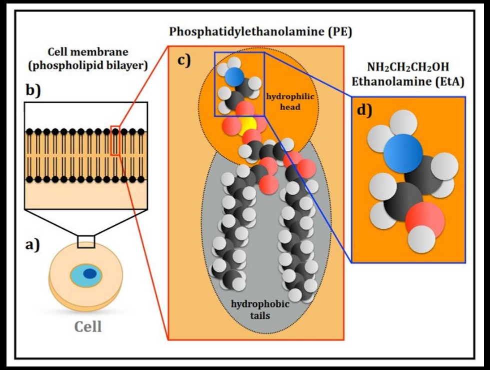


ALMA: precision astrochemistry (abundance ratios to 20%)
minor species down to 10^{-12} w.r.t. H_2

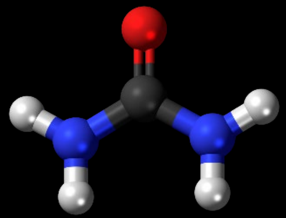
Toward biological molecules



Glycolonitrile

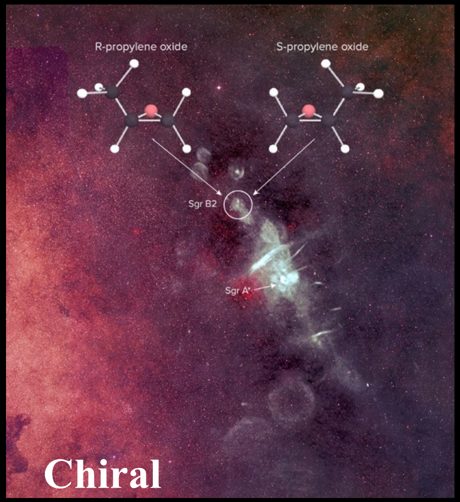


Rivilla+



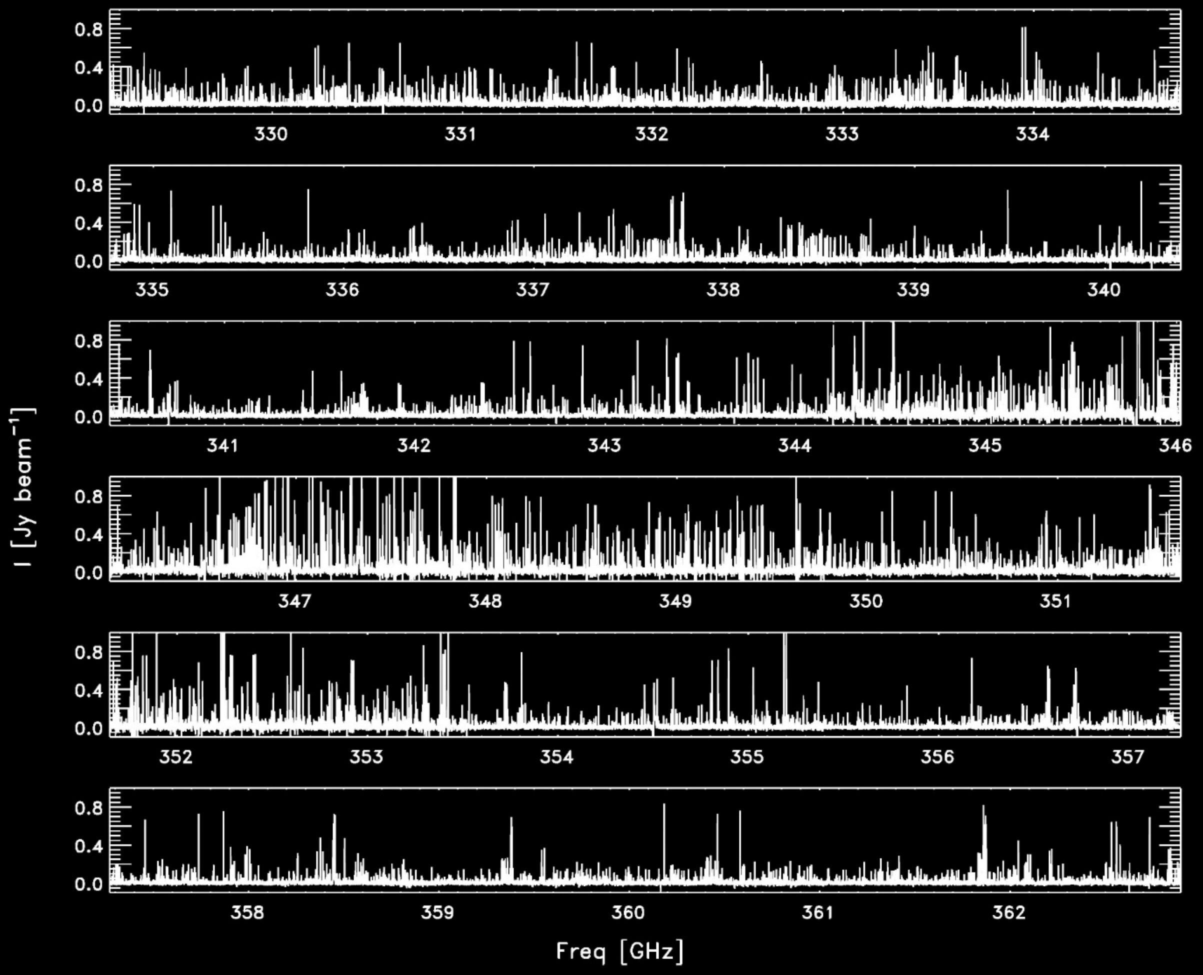
Urea

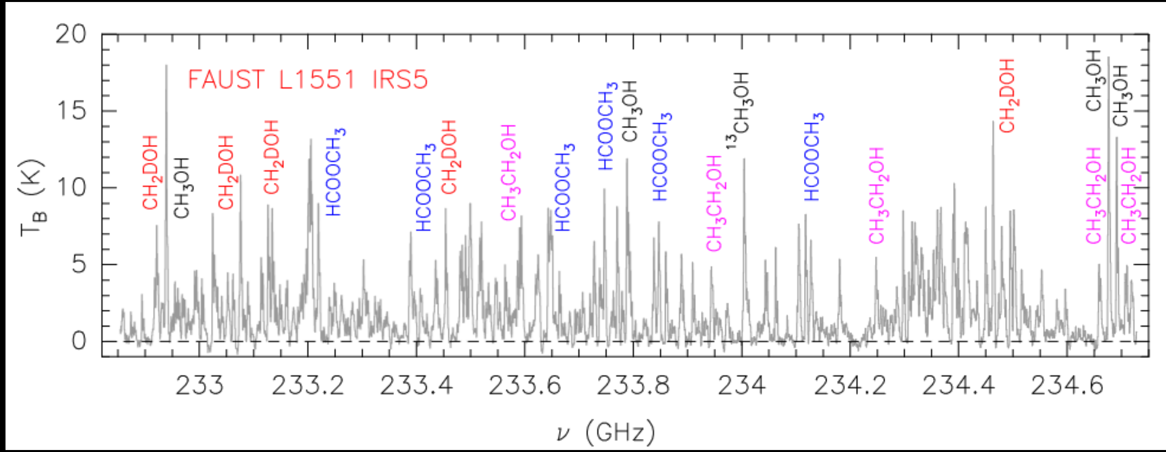
Belloche+



McGuire+

Many thousands of lines



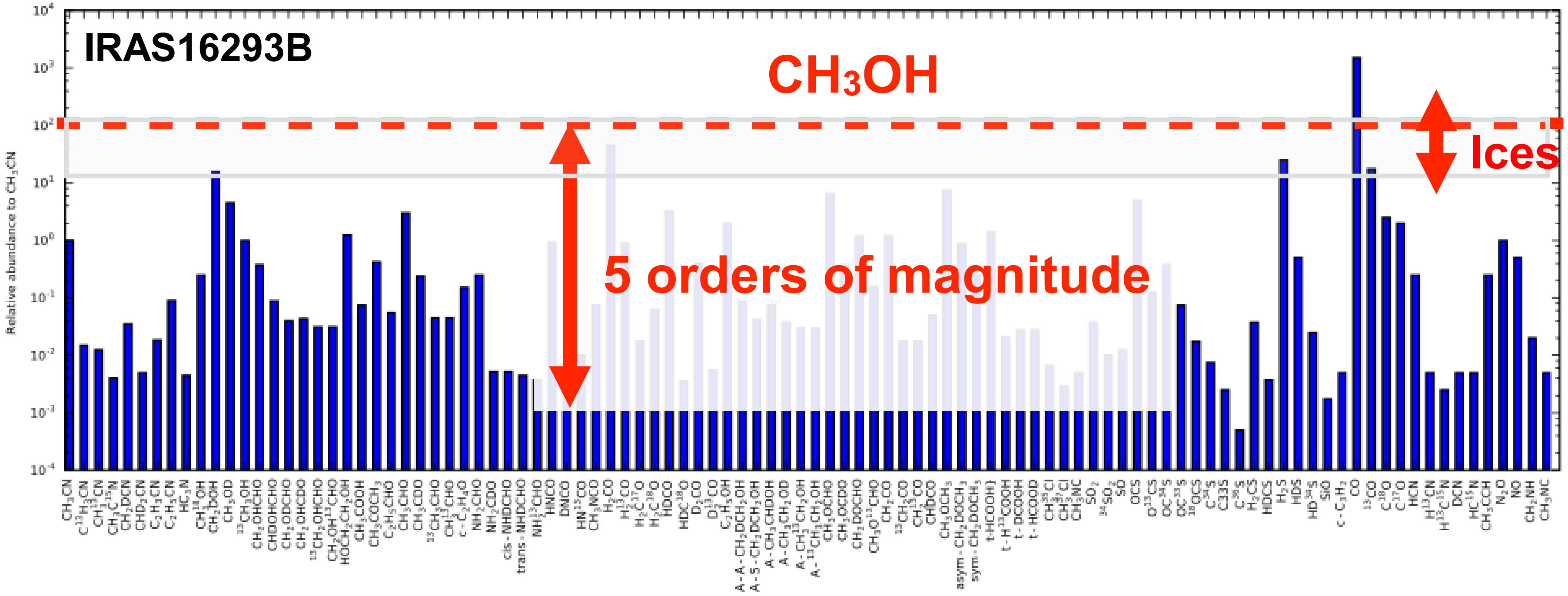


FAUST survey Bianchi et al. 2021 ++
PEACHES survey Yang et al.
REMOCA, CALYPSO surveys Belloche et al.
……..

PILS, COMPASS surveys: Jørgensen+ 2016, 2018

More systematic broadband surveys of large samples with ALMA WSU, need faster analysis tools!

Protostellar chemical fingerprint: gas vs ice

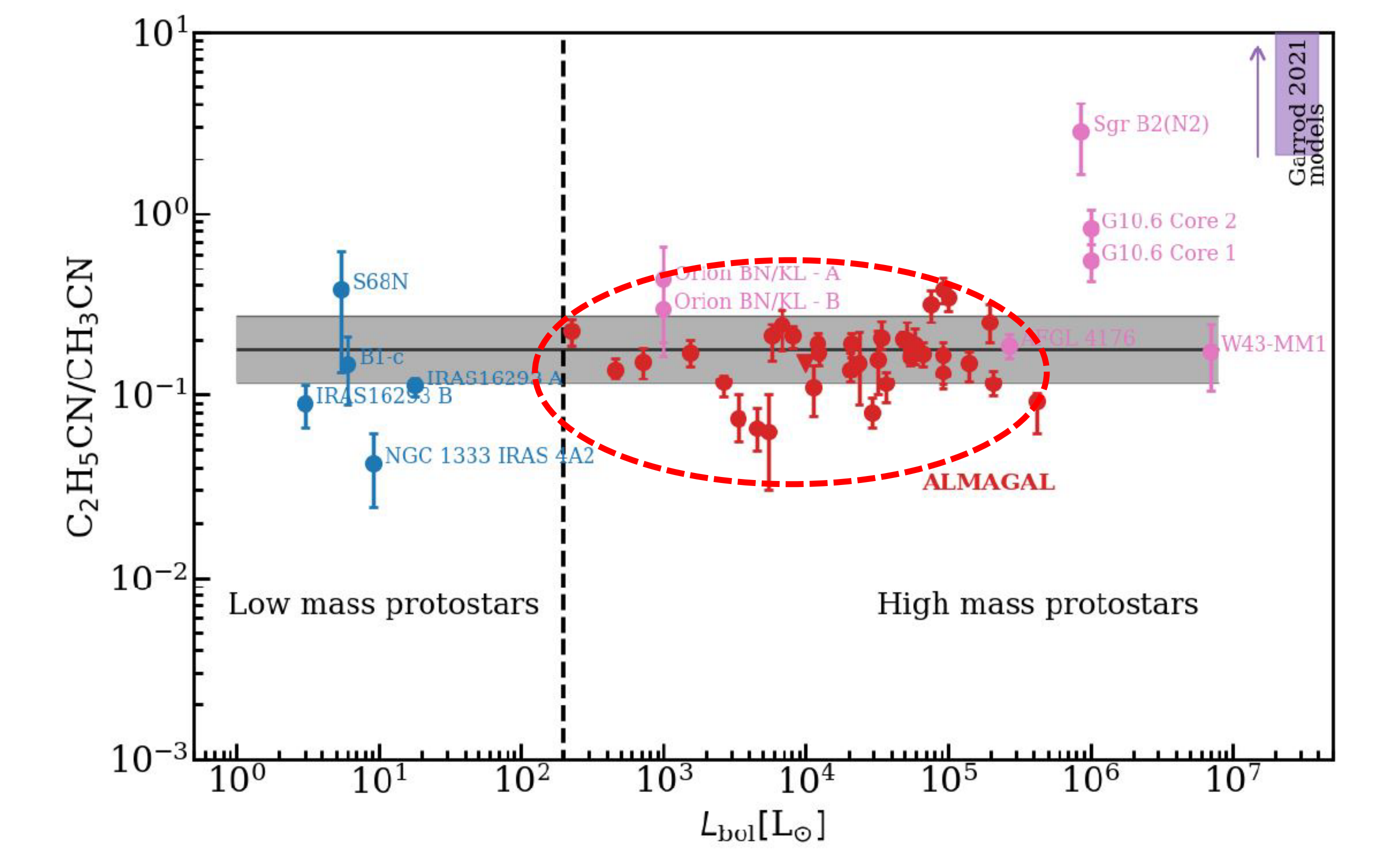


- More than 100 molecular species (including isotopologues)
- High deuteration fraction

ALMA: Much lower abundances and higher dynamic range than we can ever see in ices

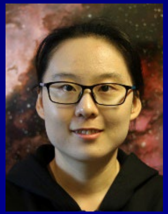
Figure credit: Hannah Calcutt & Marit Fiechter

From individual sources to large samples: constant abundance ratios



Nazari et al. 2021, 2022
Van Gelder et al. 2020, 2021

Coletta et al. 2020, …



Chen et al. 2023

Small spread over many orders of luminosity, for many abundance ratios

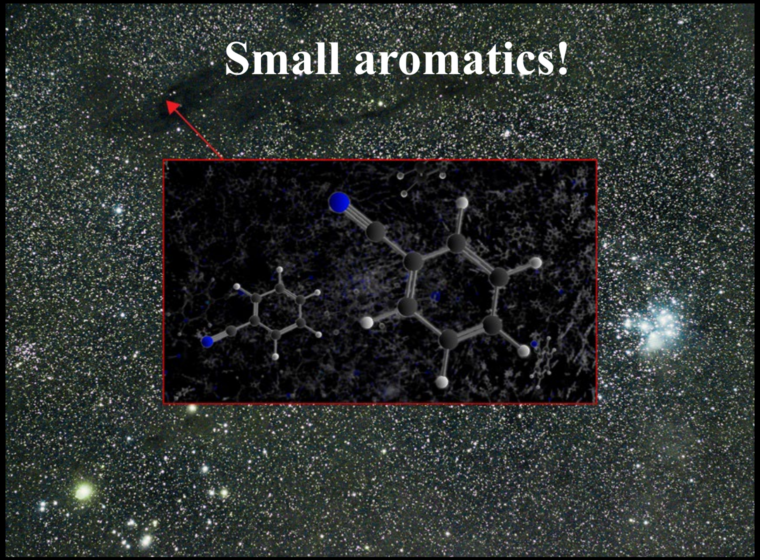
Points to formation in ices in pre-stellar phase under similar conditions

Several COMs now seen in ices with JWST (Rocha et al. 2024, Chen et al. 2025)

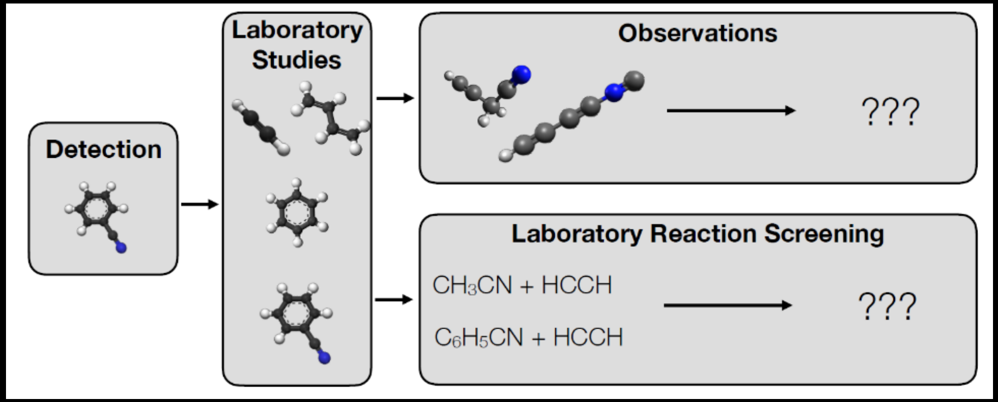
Renewed focus on cold clouds

heavy molecules

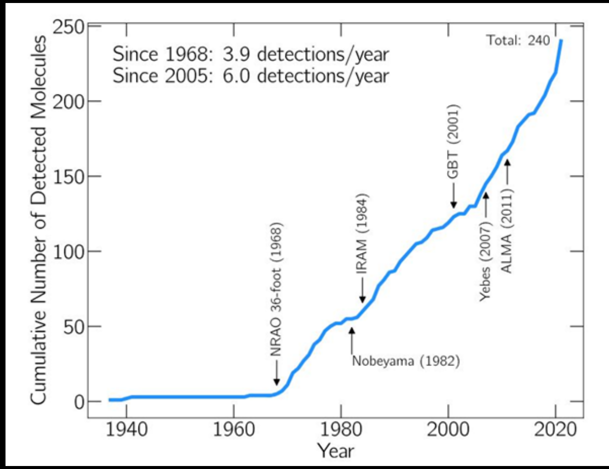
TMC-1

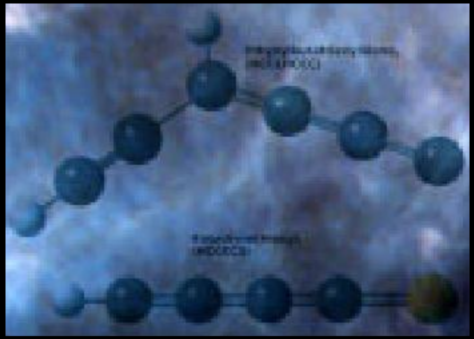


McGuire et al. 2018, 2021 **GBT**



Rate of detections





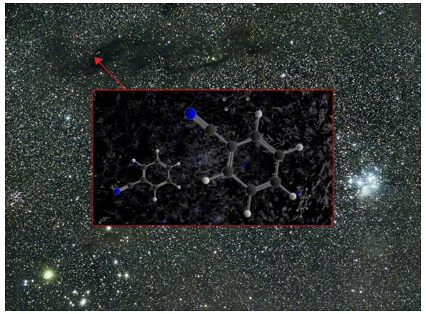
Quijote **Yebes survey at ~20-40 GHz**
Many aliphatic molecules
Cernicharo et al. 2021-2024

Science case for ngVLA

More than 300 different molecules detected

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-C_2H_4O
CS	PO	C_2H	AlOH	$HOCO^+$	HOOH	c-C_3H_2	CH_3Cl	HC_2CHO	CH_2CHOH
SO	O_2	SO_2	H_2O^+	C_3O	l-C_3H^+	CH_2CN	MgC_3N	H_2C_4	C_6H^-
SiS	AlO	HCO	H_2Cl^+	l-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-C_3H	MgCCH	HCCNC	C_4S	HC_4N	H_3HNH
NaCl	SH	C_2S	CCN	HC_2N	HCCS	HNCCC	CHOSH	c-H_2C_3O	c-C_3HCCH
AlCl	TiO	C_3	SiCSi	H_2CN		H_2COH^+		CH_2CNH	

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-$C_{10}H_7CN$	C_{60}
CH_3C_3N	CH_3CH_2OH	$HOCH_2CH_2OH$	CH_3C_6H	n-C_3H_7CN	$HC_{11}N$	2-$C_{10}H_7CN$	C_{60}^+
C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	i-C_3H_7CN		C_9H_8	C_{70}
CH_3COOH	HC_7N	CH_3C_5N	CH_3COOCH_3	1-C_5H_5CN			
H_2C_6	CH_3C_4H	CH_3CHCH_2O	CH_3COCH_2OH	2-C_5H_5CN			
CH_2OHCHO	C_8H	CH_3CH_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						



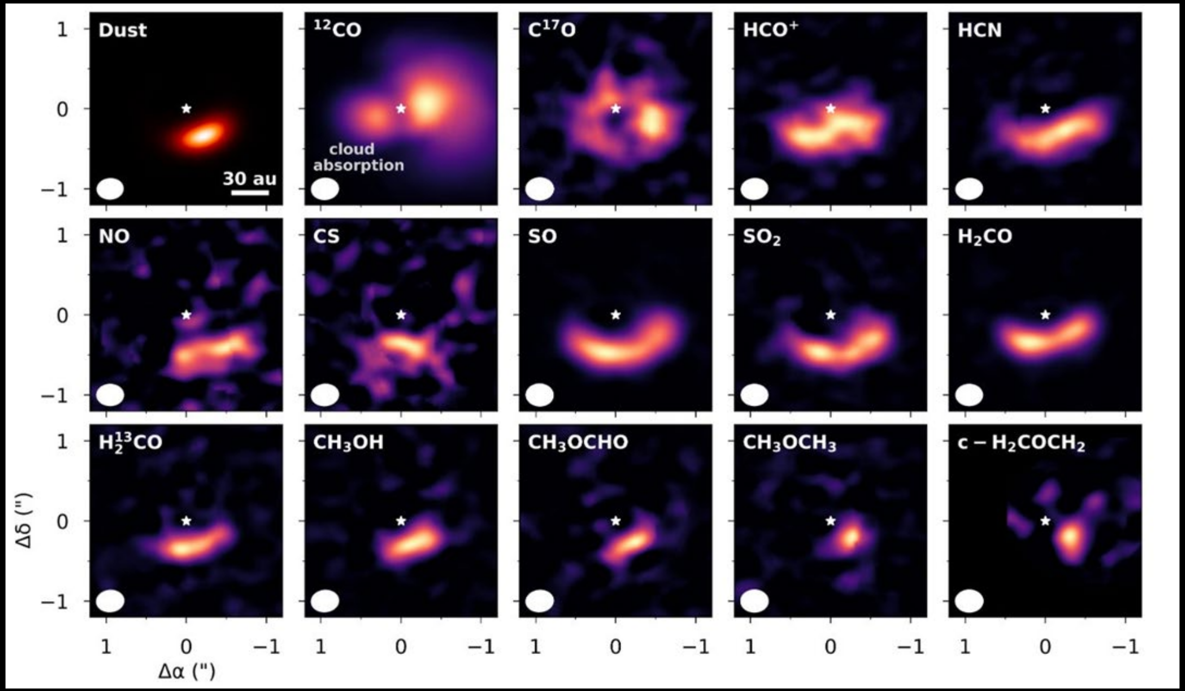
cyanopyrene

Abundances down to 10^{-12} w.r.t. H_2

McGuire 2022, 2024

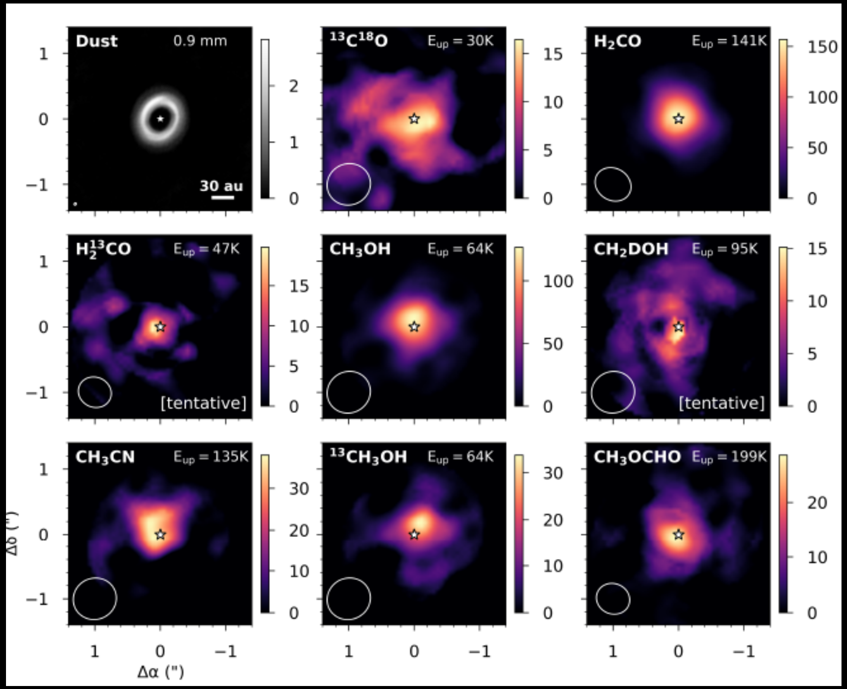
Simple and complex molecules in disks

IRS48 dust trap = ice trap!

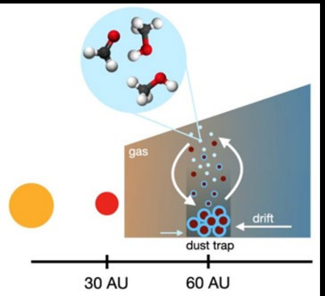


van der Marel et al. 2021, Booth et al. 2021, 2022, 2024

HD 100453



Booth et al., subm.

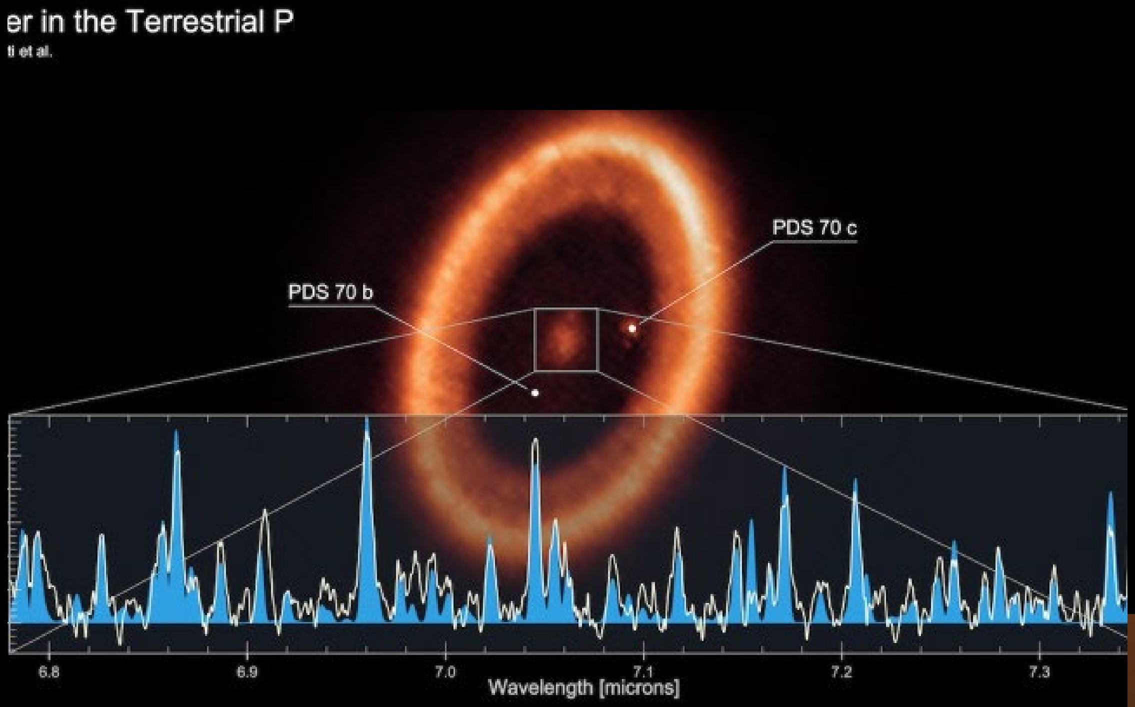


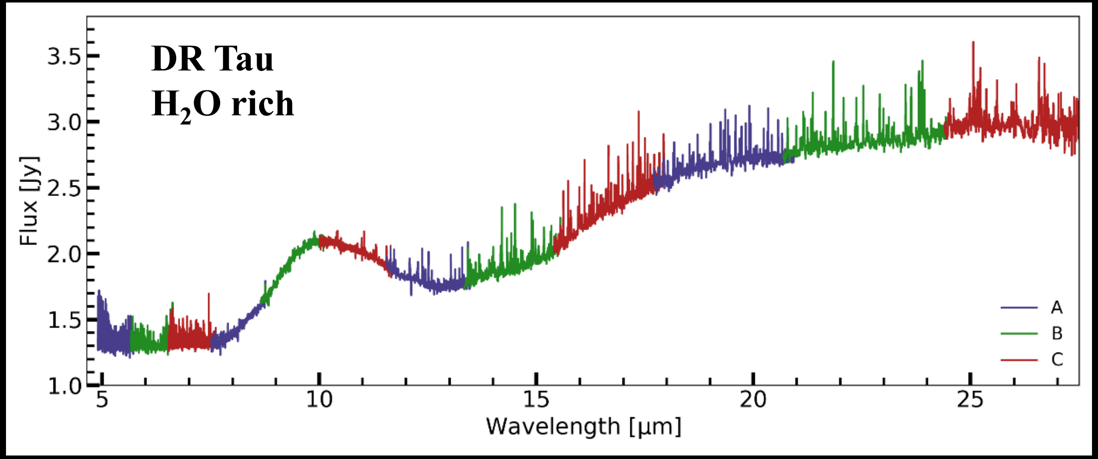
COMs in warm disks are inherited from previous cold phase

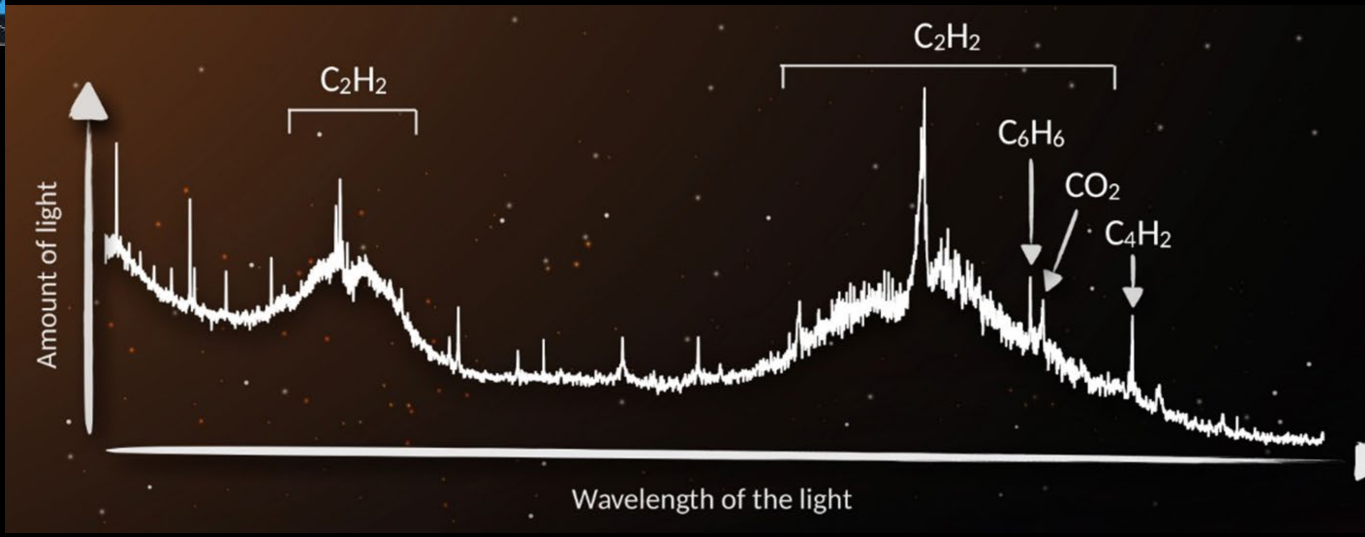
(Note: these data required long integrations at modest resolution (~30 au) with ALMA)

Chemistry in disks needs WSU and ALMA2040+

Inner ~1 au of protoplanetary disks: large diversity in JWST spectra





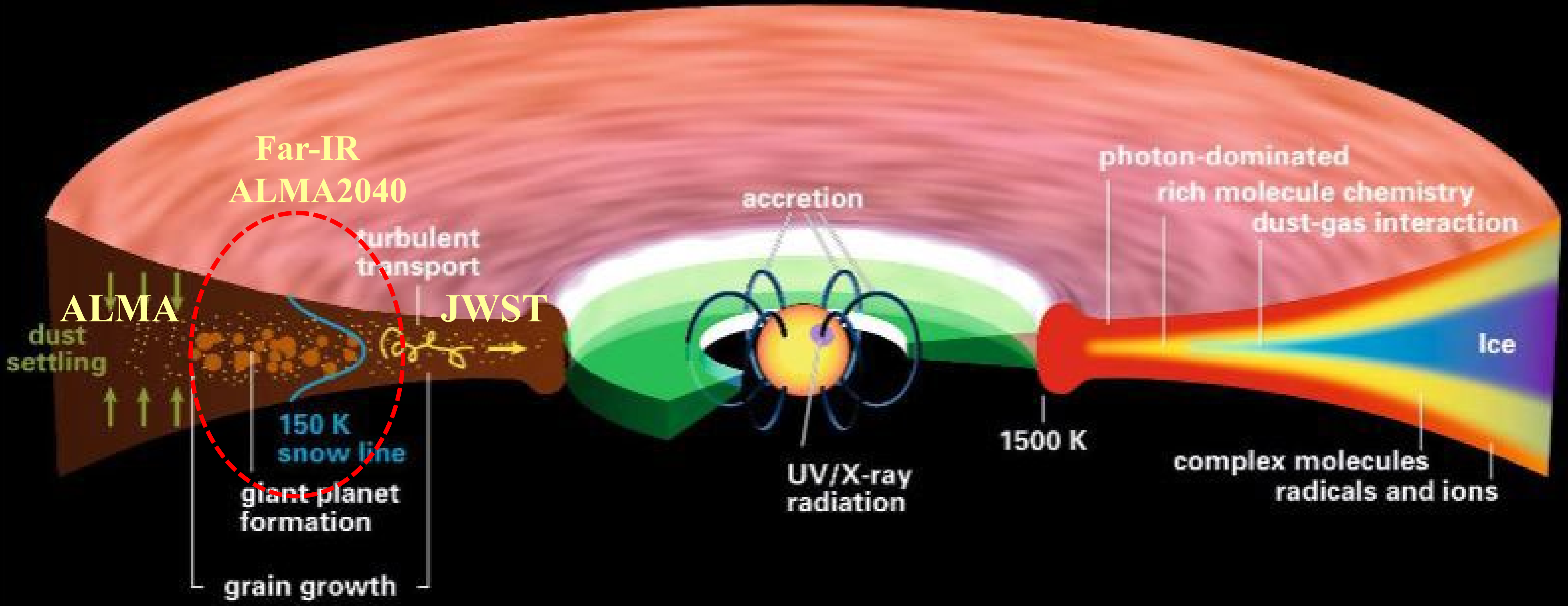


Water-rich vs hydrocarbon rich

MINDS: Perotti et al. 2023, Temmink et al. 2024, Tabone et al. 2023, Gasman et al. 2023…
JDISCS: Banzatti et al. 2023, 205, Pontoppidan et al. 2024, Colmenares et al. 2024, …

Future: probing and imaging the critical 1-10 au planet-forming zones

Current facilities are "blind" for this region



Elucidating the critical role of snowlines and dust traps in setting planetary composition for large disk samples

Requires Far-IR and ALMA2040 sensitivity

Henning & Semenov 2013

Future needs

- ALMA WSU
- ALMA 2040+: factor 3-10 enhanced sensitivity

- Far-IR PRIMA
- Mid-Far-IR: high spectral resolution (balloons, e.g. POEMM; Grex-plus; space)
- Far-IR interferometer? need killer science case

Thanks to Thijs in shaping the field across the world

….and for enabling so much good science and always being "ahead of the curve"