NanoSpace

DAN Dutch Astrochemistry Network III

Laboratory Spectroscopy

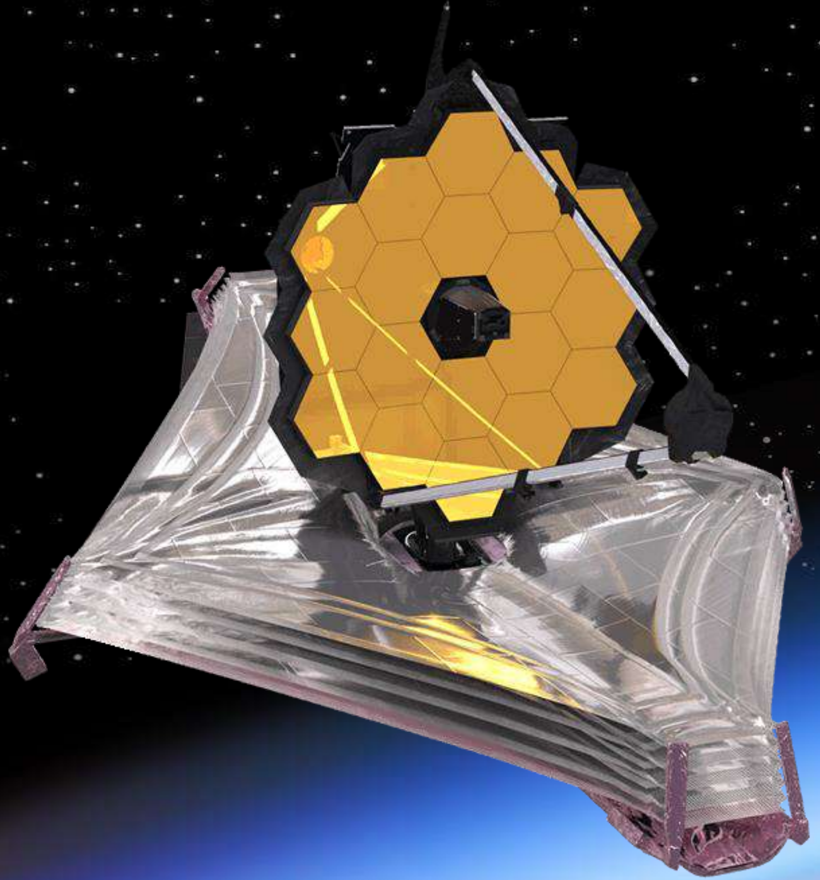
Sergio Ioppolo

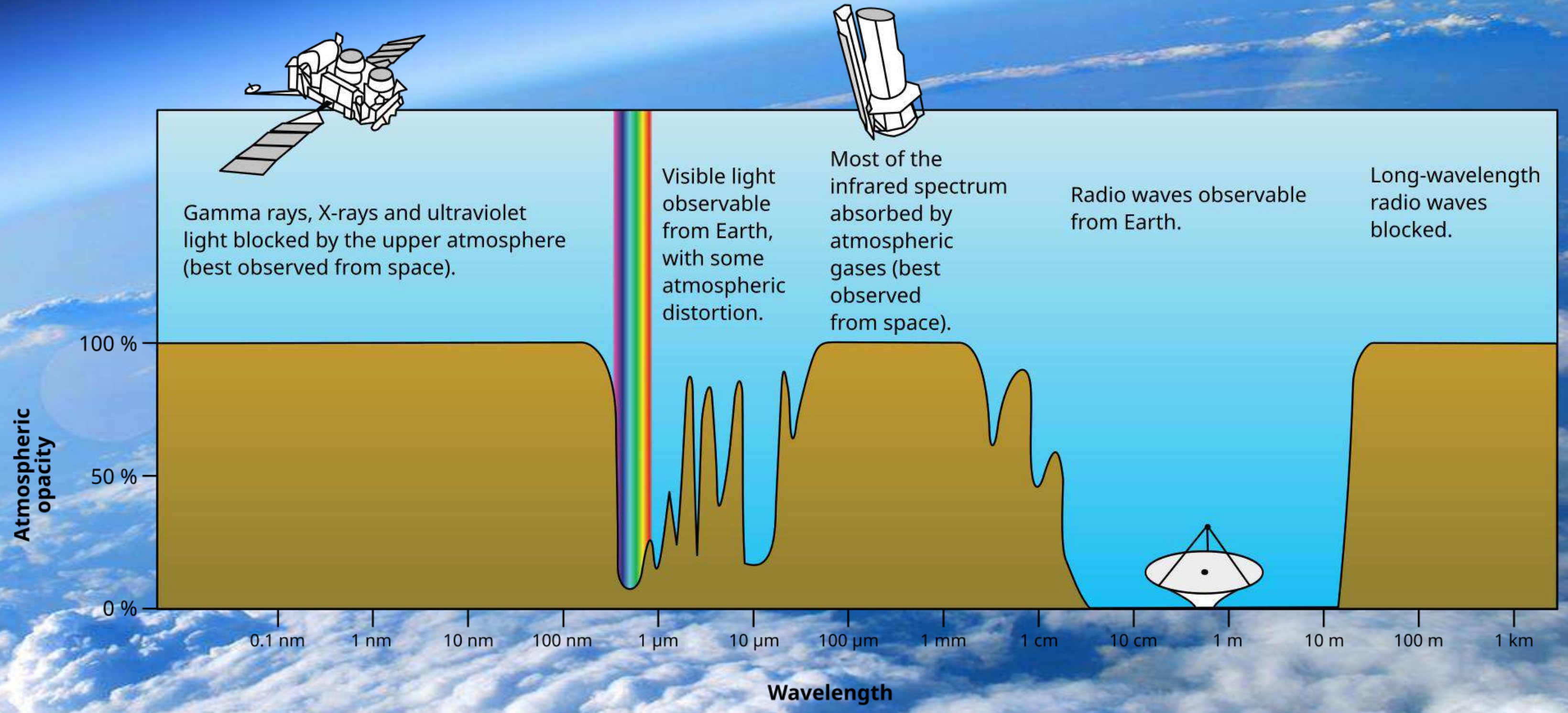
InterCat, Department of Physics and Astronomy, Aarhus University

AARHUS UNIVERSITY

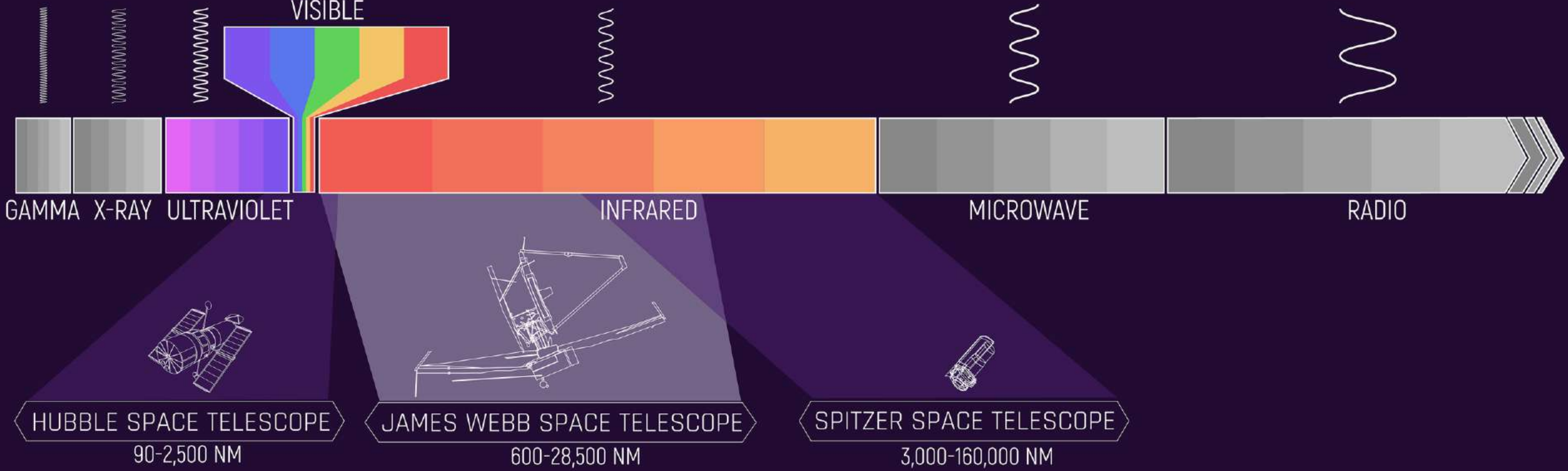
cost
EUROPEAN COOPERATION
IN SCIENCE & TECHNOLOGY

Funded by
the European Union

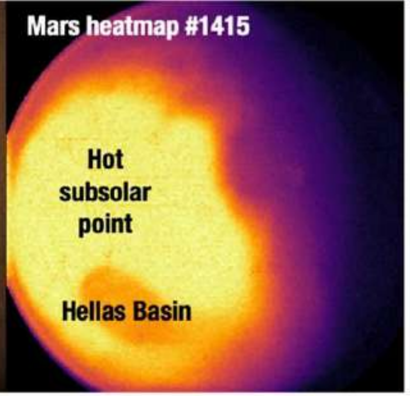



Gamma rays, X-rays and ultraviolet light blocked by the upper atmosphere (best observed from space).
Visible light observable from Earth, with some atmospheric distortion.
Most of the infrared spectrum absorbed by atmospheric gases (best observed from space).
Radio waves observable from Earth.
Long-wavelength radio waves blocked.
100 %
50 %
0 %
Atmospheric opacity
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
10 cm
1 m
10 m
100 m
1 km
Wavelength

ELECTROMAGNETIC SPECTRUM

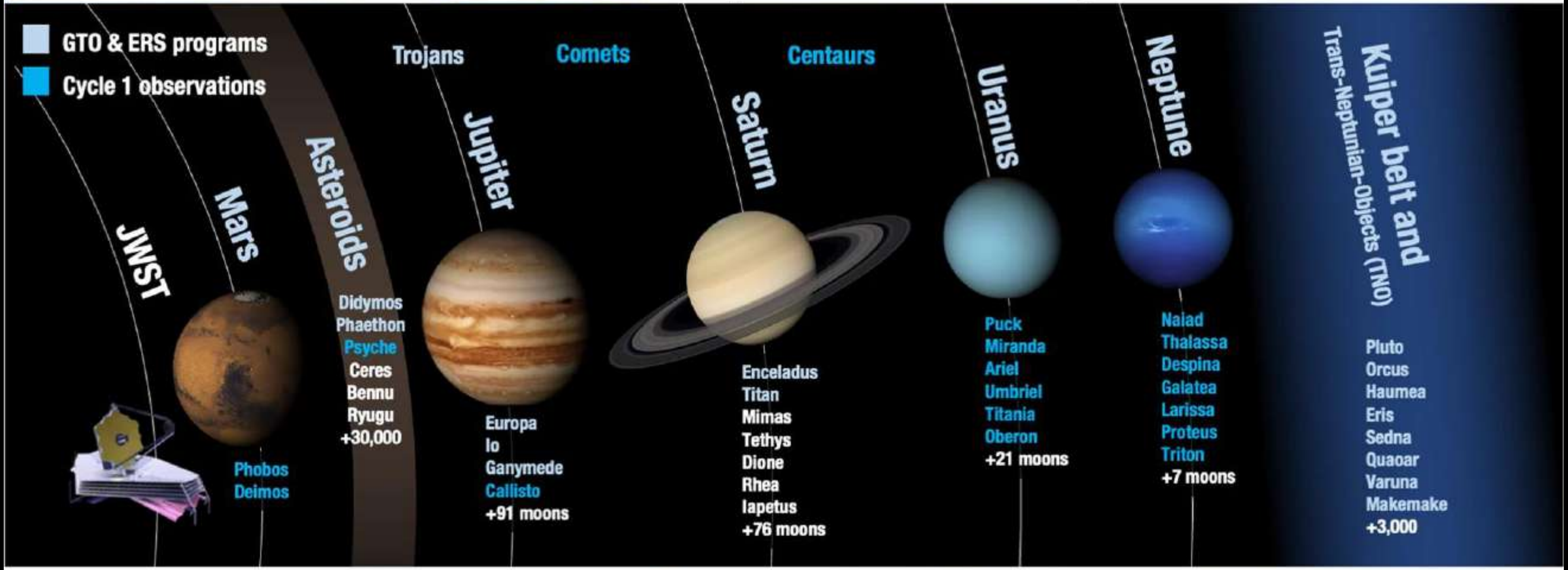


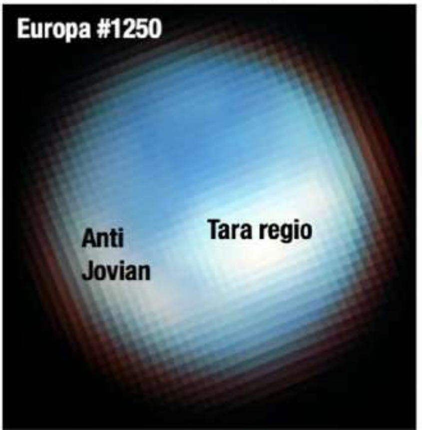

Mars surface #1415

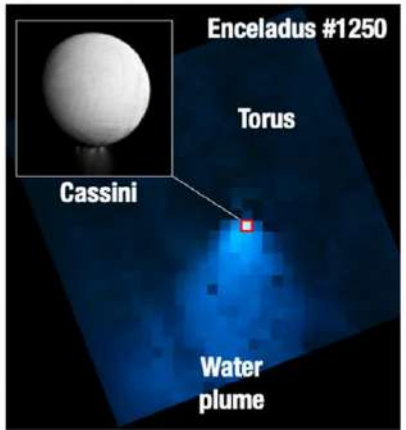

Mars heatmap #1415


Main belt comet #1252


Saturn #1247

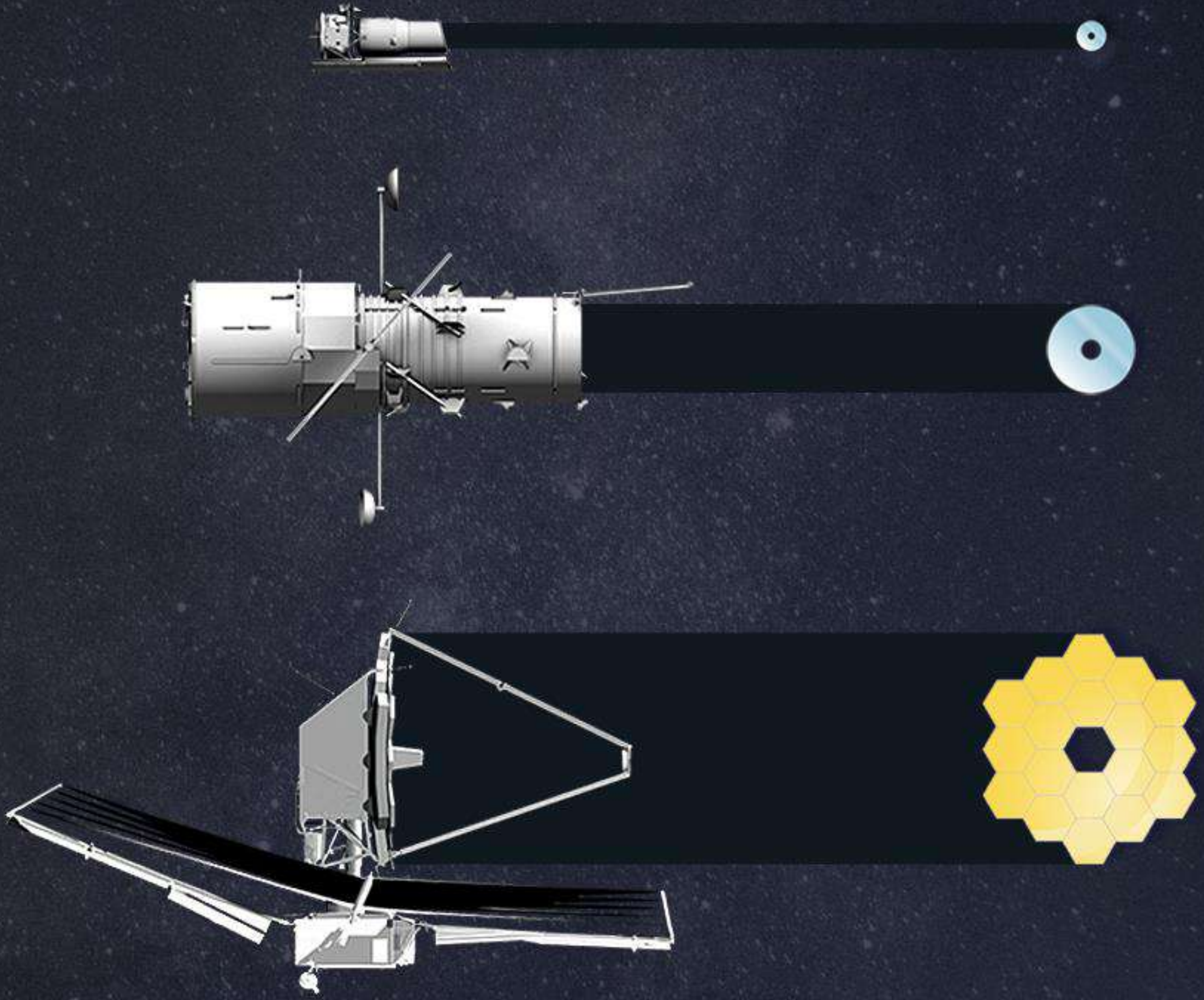



Europa #1250


Enceladus #1250


Uranus #2739


Neptune #2739

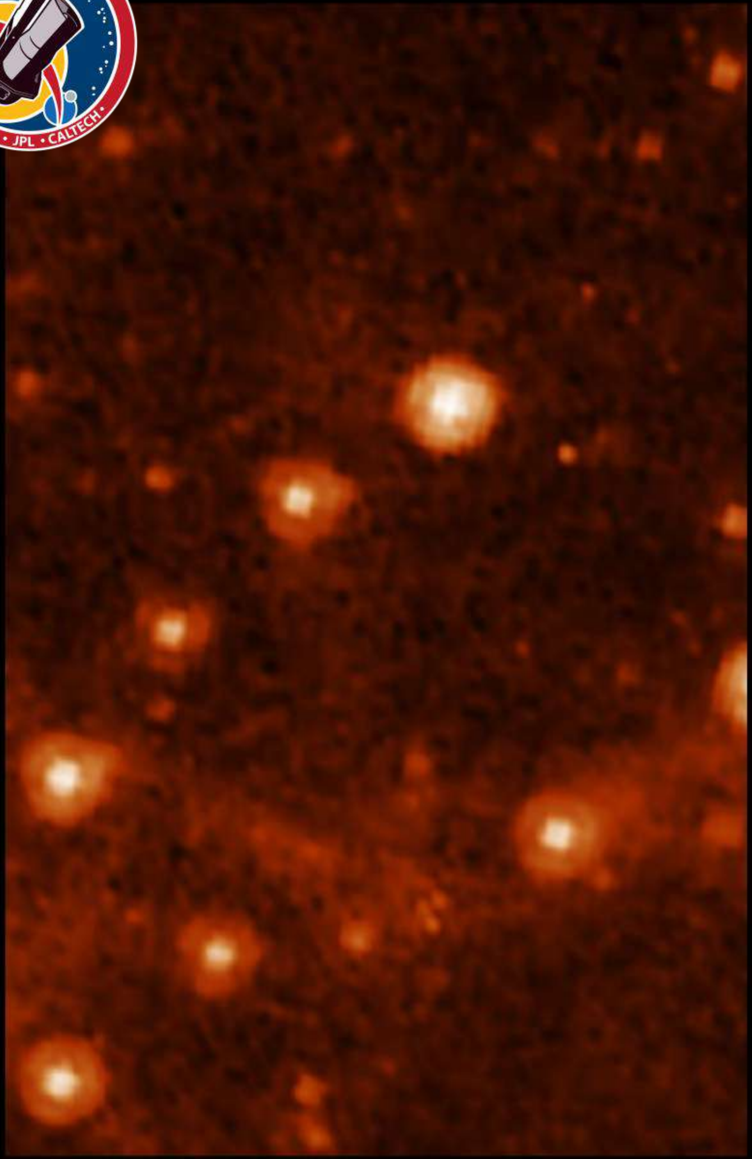


Spitzer
0.85 meters

Hubble
2.4 meters

Webb
6.6 meters

SPITZER SPACE TELESCOPE
NASA • JPL • CALTECH

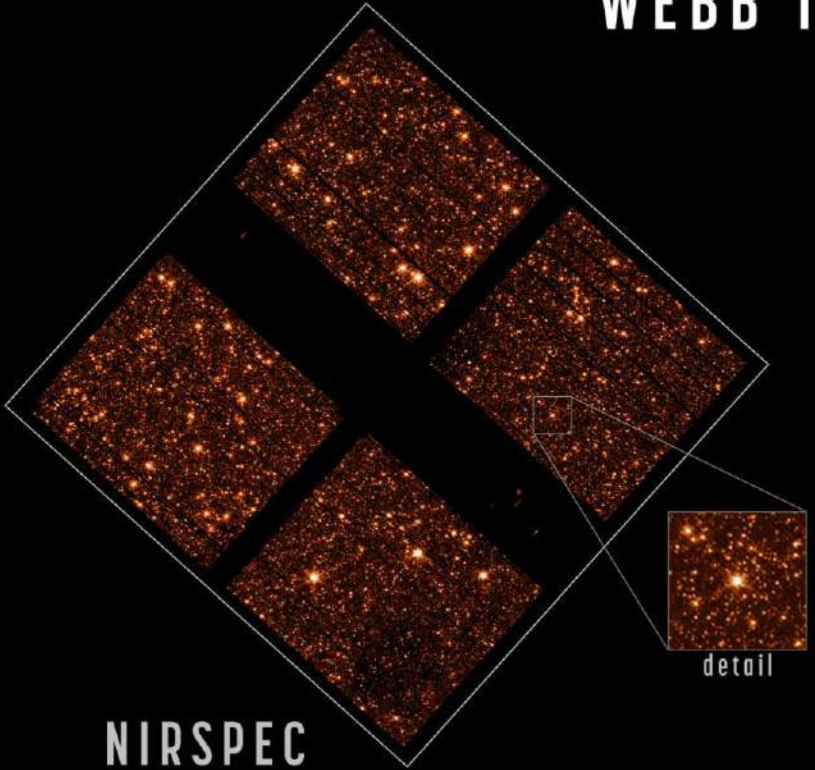


SPITZER IRAC 8.0μ

NASA | ESA | CSA
jwst

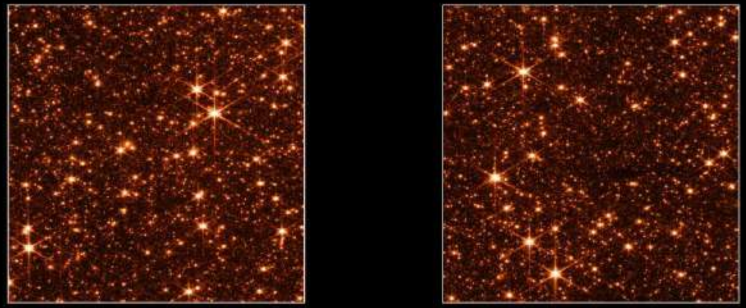
WEBB MIRI 7.7μ

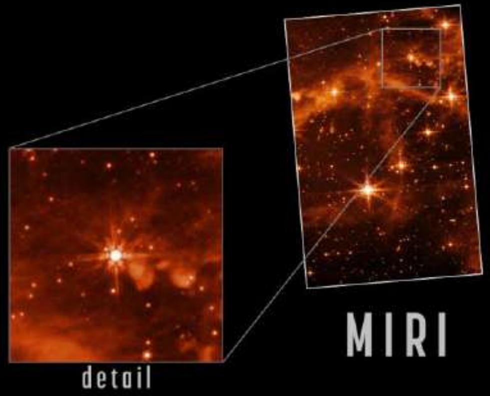
WEBB TELESCOPE IMAGE SHARPNESS CHECK



NIRSPEC

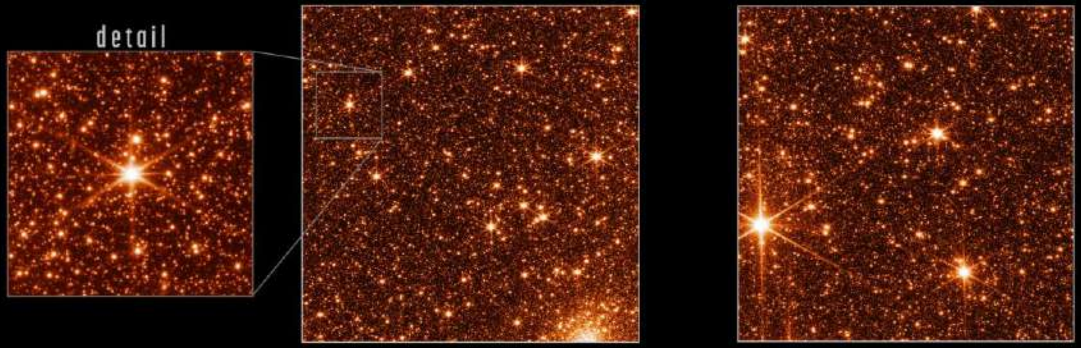
NIRCAM



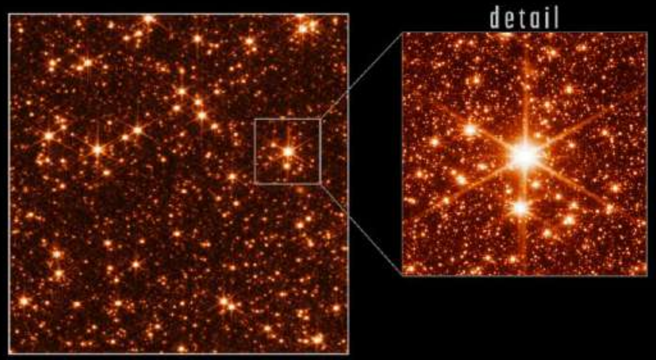


MIRI

FINE GUIDANCE SENSOR



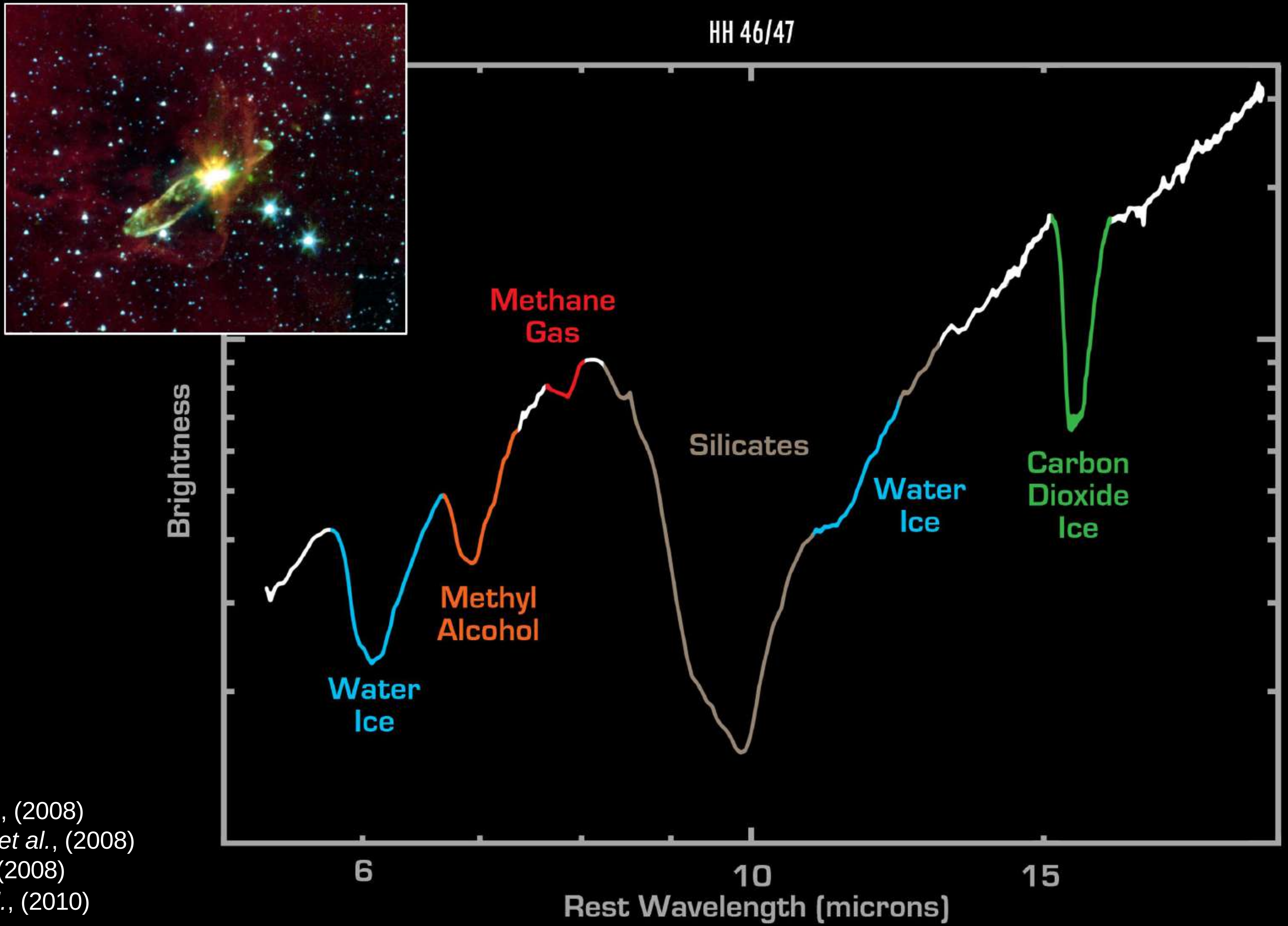
NIRISS



JAMES WEBB SPACE TELESCOPE

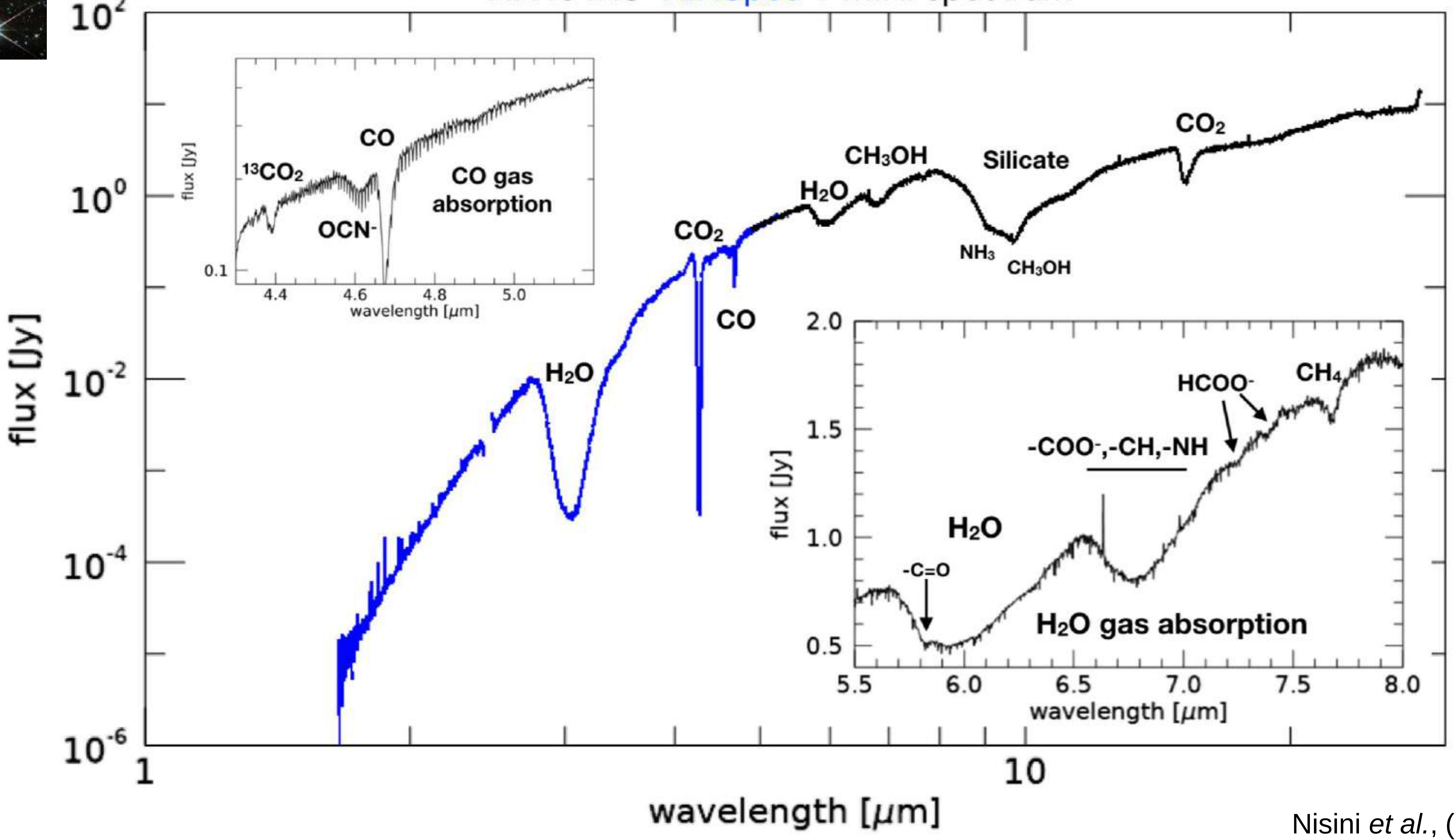
HH 46/47

NIRCam Filters | F115W F187N F200W F335M F444W F470N



Boogert *et al.*, (2008)
Pontoppidan *et al.*, (2008)
Öberg *et al.*, (2008)
Bottinelli *et al.*, (2010)

HH46 IRS NIRSpec + MIRI spectrum



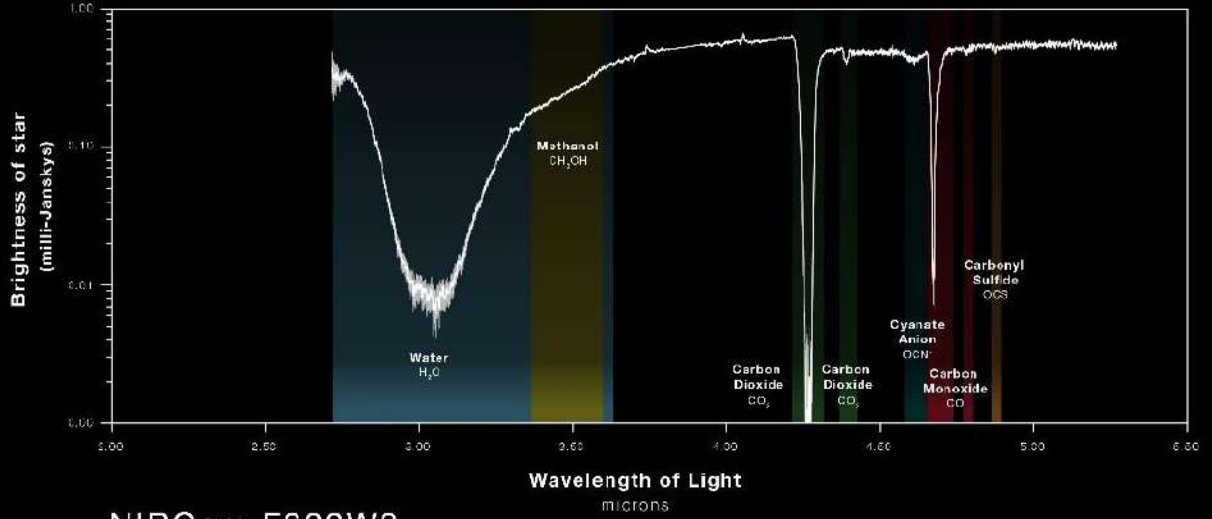
Nisini *et al.*, (2024)

WEBB
SPACE TELESCOPE

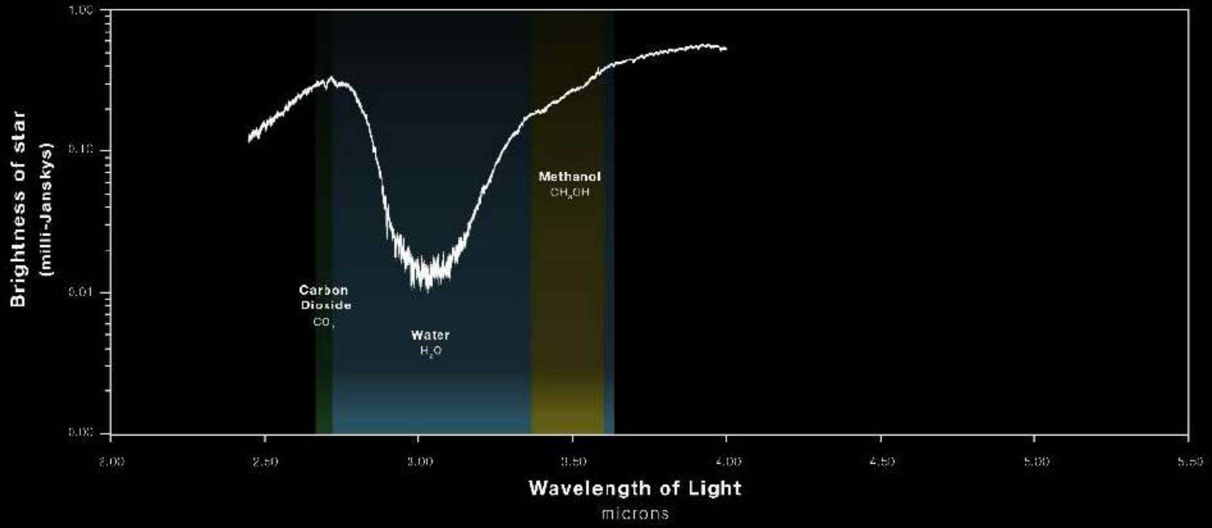
CHAMAELEON | DARK CLOUD BACKGROUND STAR NIR38

ICE CHEMICAL COMPOSITION

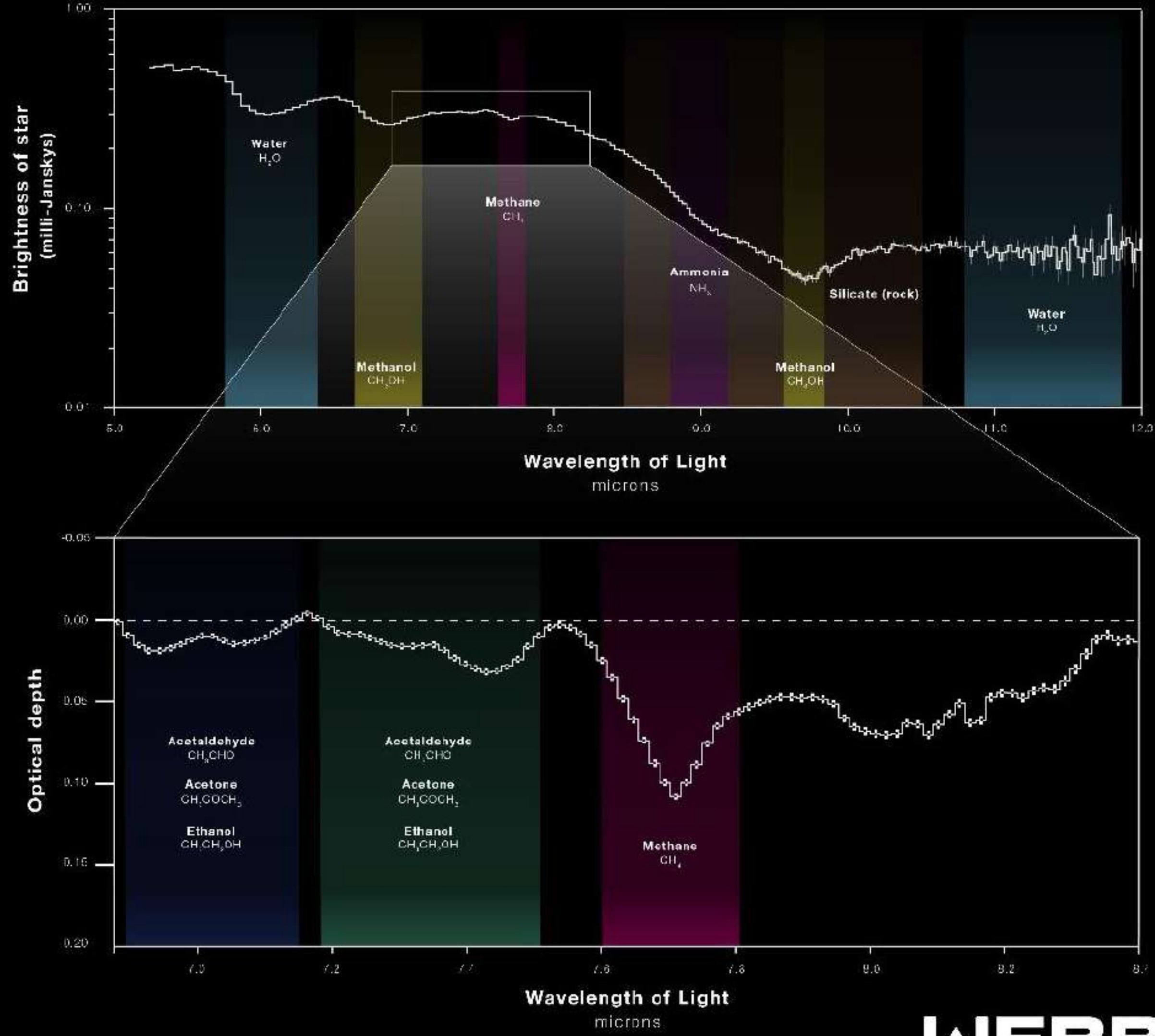
NIRSpec G395H



NIRCam F322W2



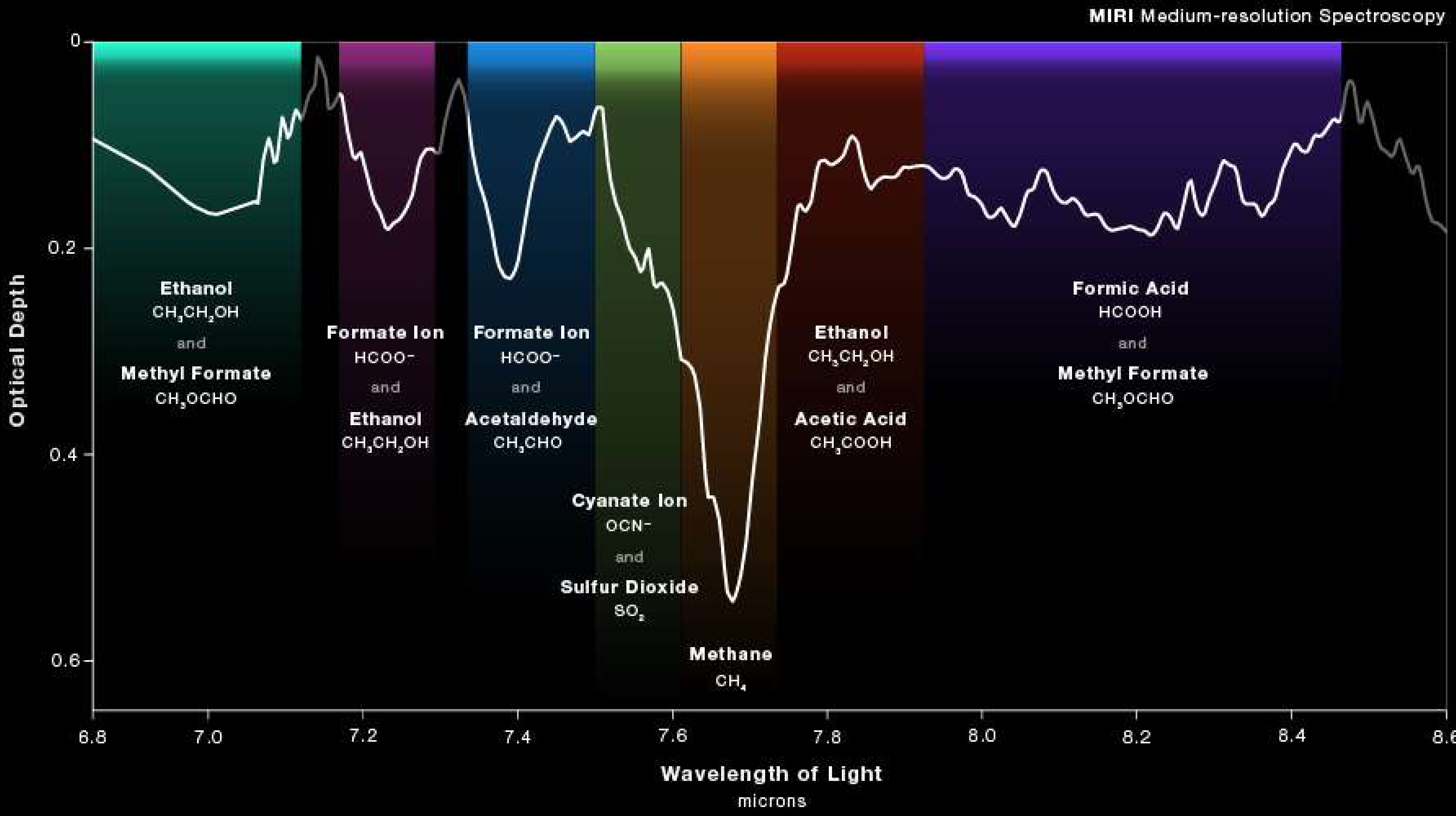
MIRI LRS P750L



WEBB
SPACE TELESCOPE

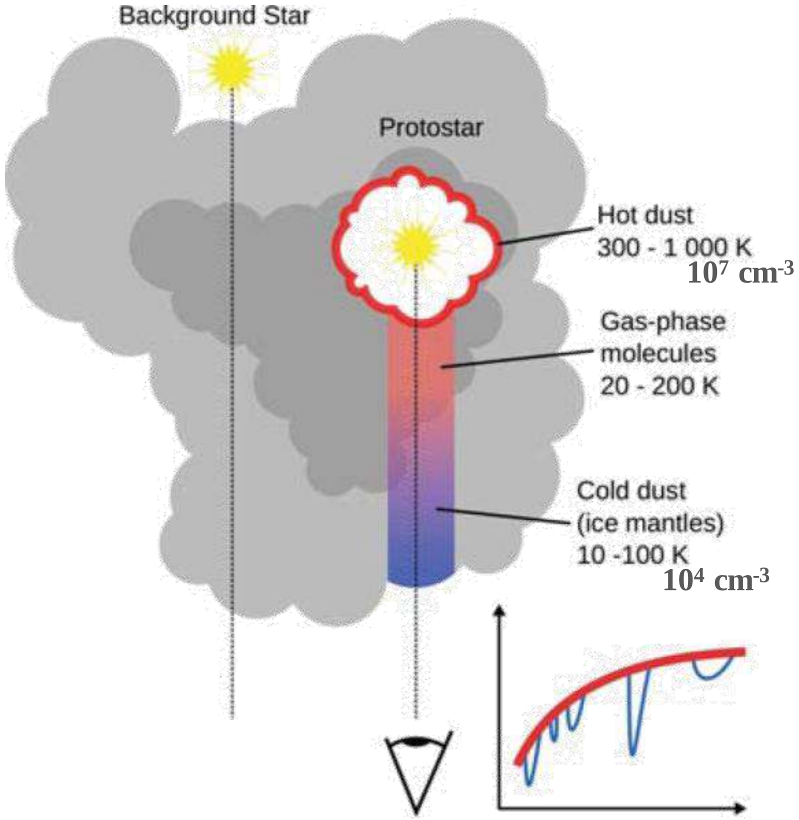
NGC 1333 IRAS 2A PROTOSTAR

COMPLEX ORGANIC MOLECULES

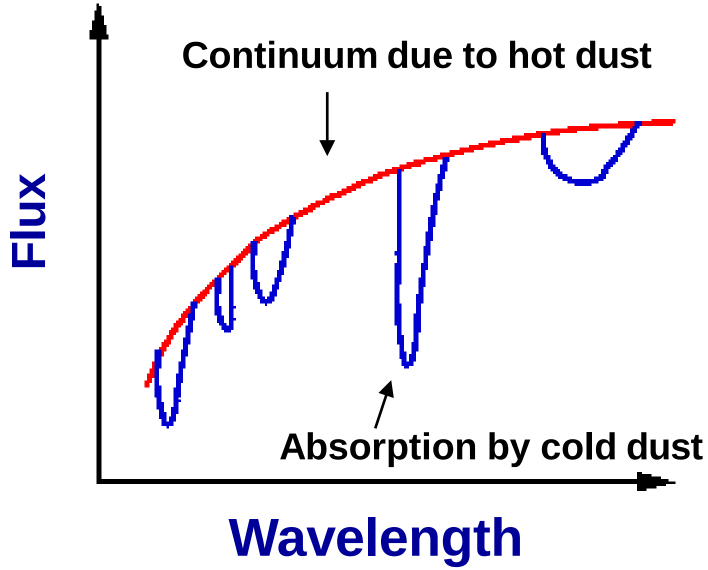


WEBB
SPACE TELESCOPE

Infrared: absorption gas and solids

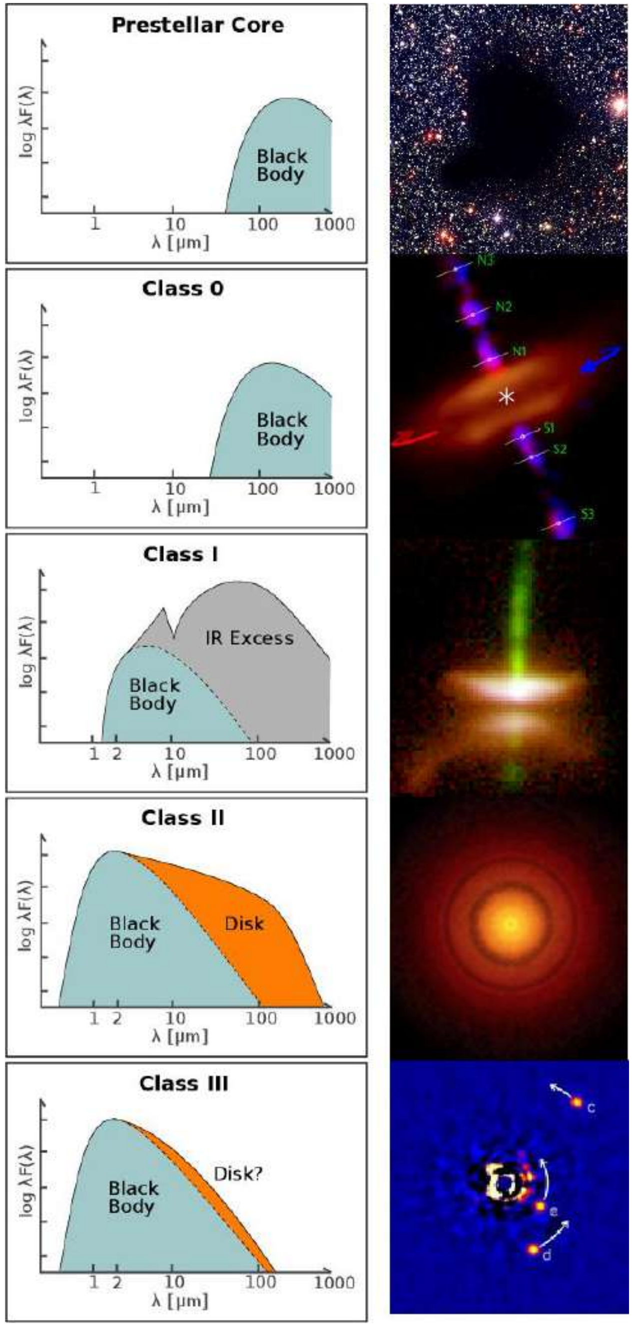


Spectral energy distributions (SED)



Vibrational transitions of gases *and* solids

Spectral energy distributions (SEDs)



The prestellar core is the dark cloud B68 as observed by VLT/FORS1.

The Class 0 object is the HH212 protostar in Orion as observed by ALMA16.

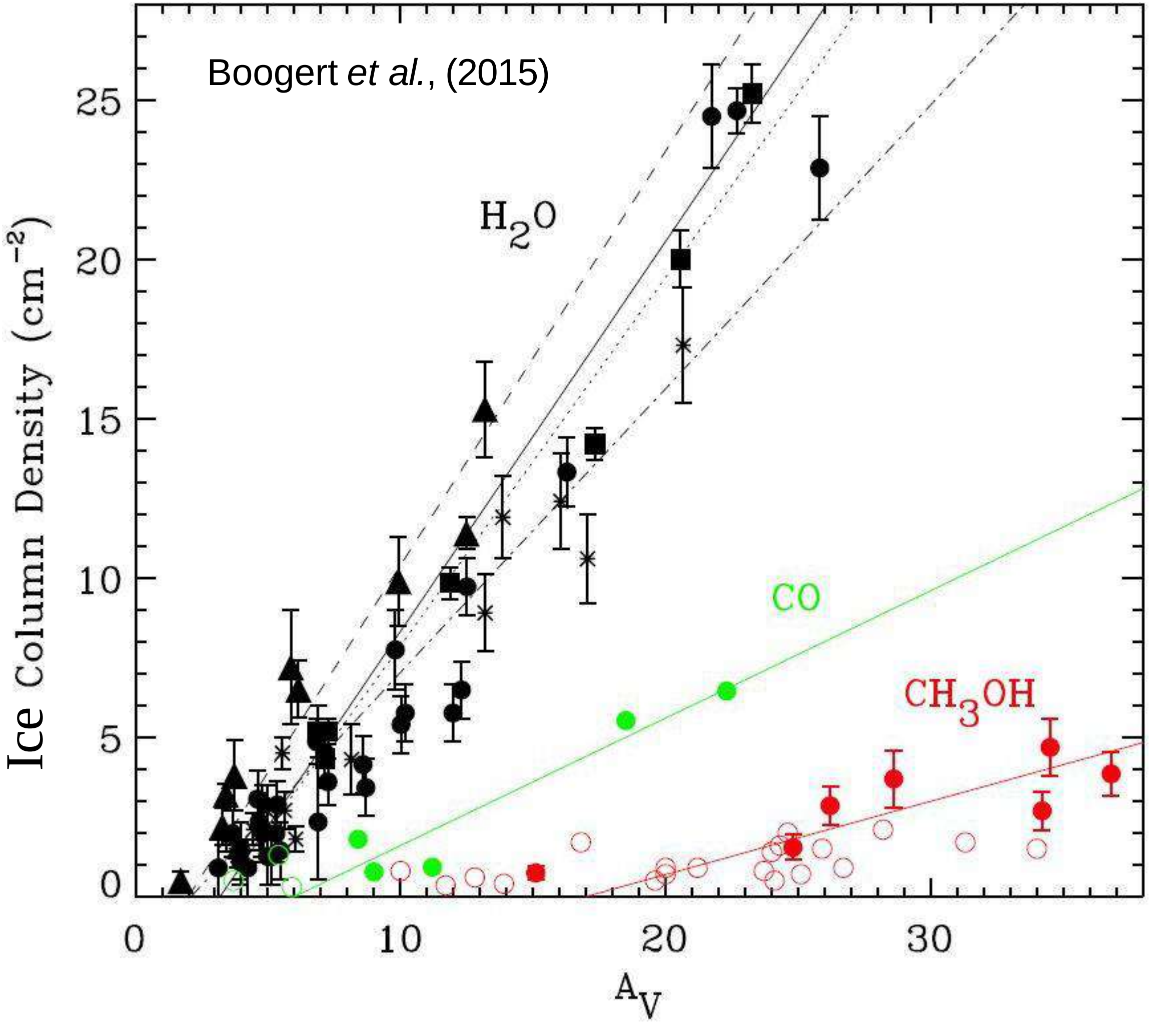
The Class I object is HH30 as observed by the Hubble Space Telescope.

The Class II object is an ALMA view of the proto-planetary disk surrounding the young star TW Hydrae.

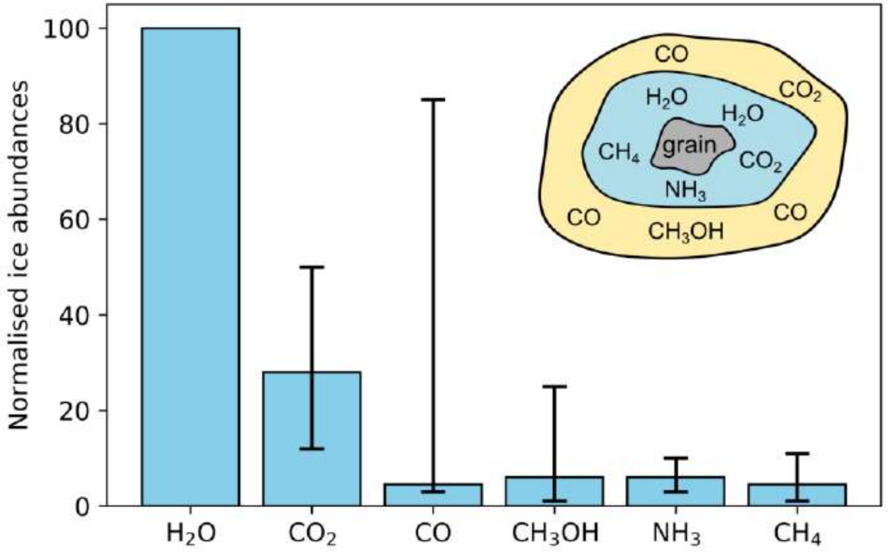
The Class III object is the image of the system HR 8799 with three orbiting planets. The image has been acquired at the Keck II telescope.

Bianchi *et al.*, (2019)

Ice formation threshold

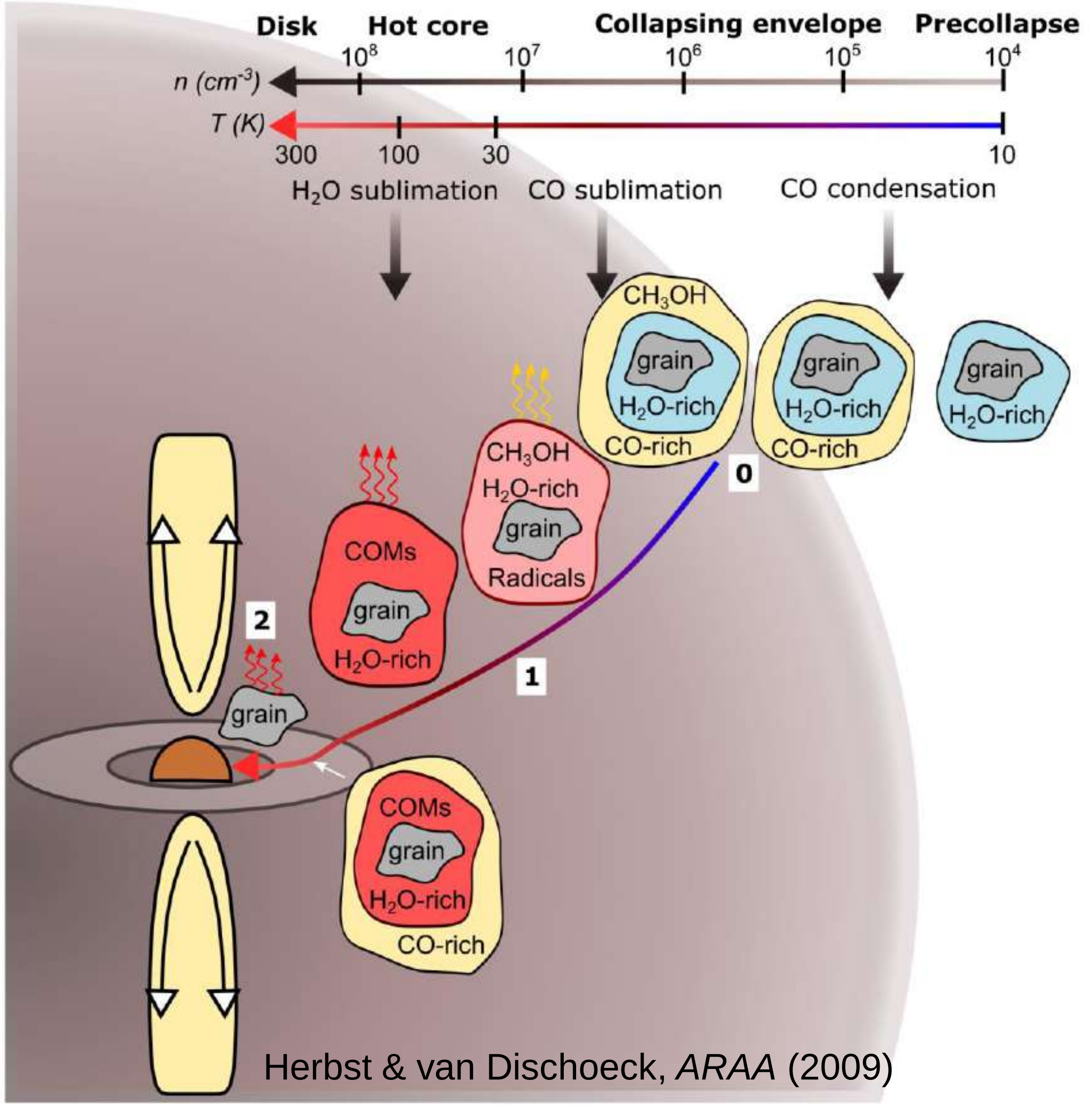

Boogert *et al.*, (2015)

Öberg, *Chem. Rev.* (2016)

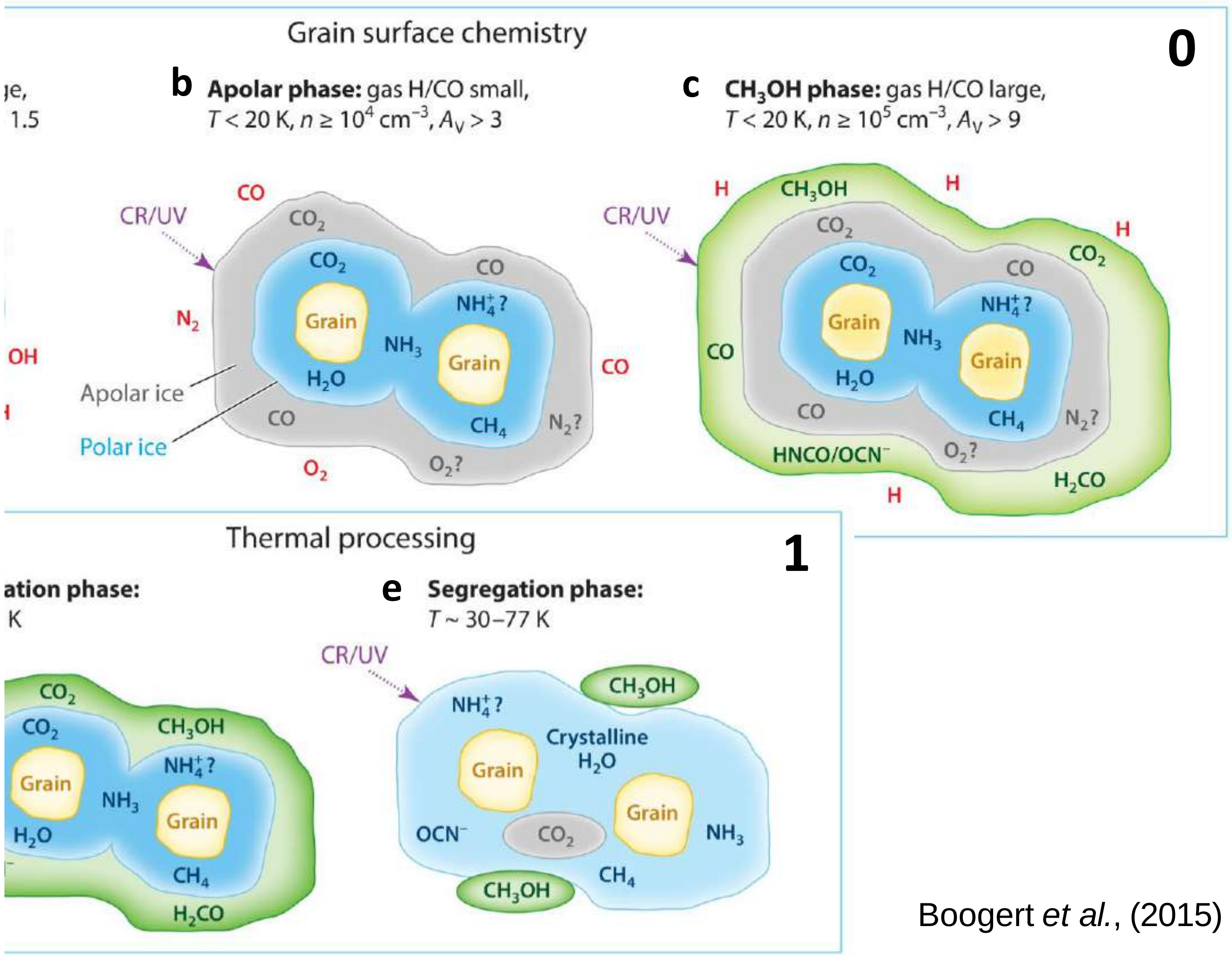


H_2O ice formation starts at $A_V < 3$ mag; CO and CH_3OH ice deeper into cloud

Ice different phases

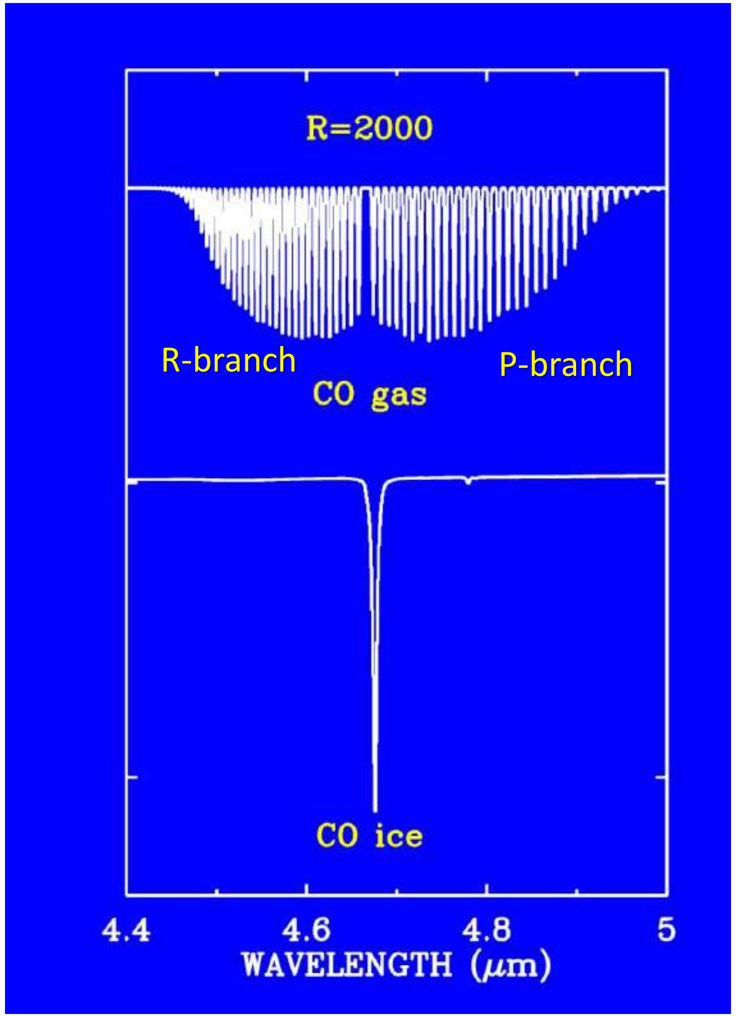


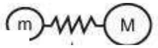
Herbst & van Dischoeck, *ARAA* (2009)



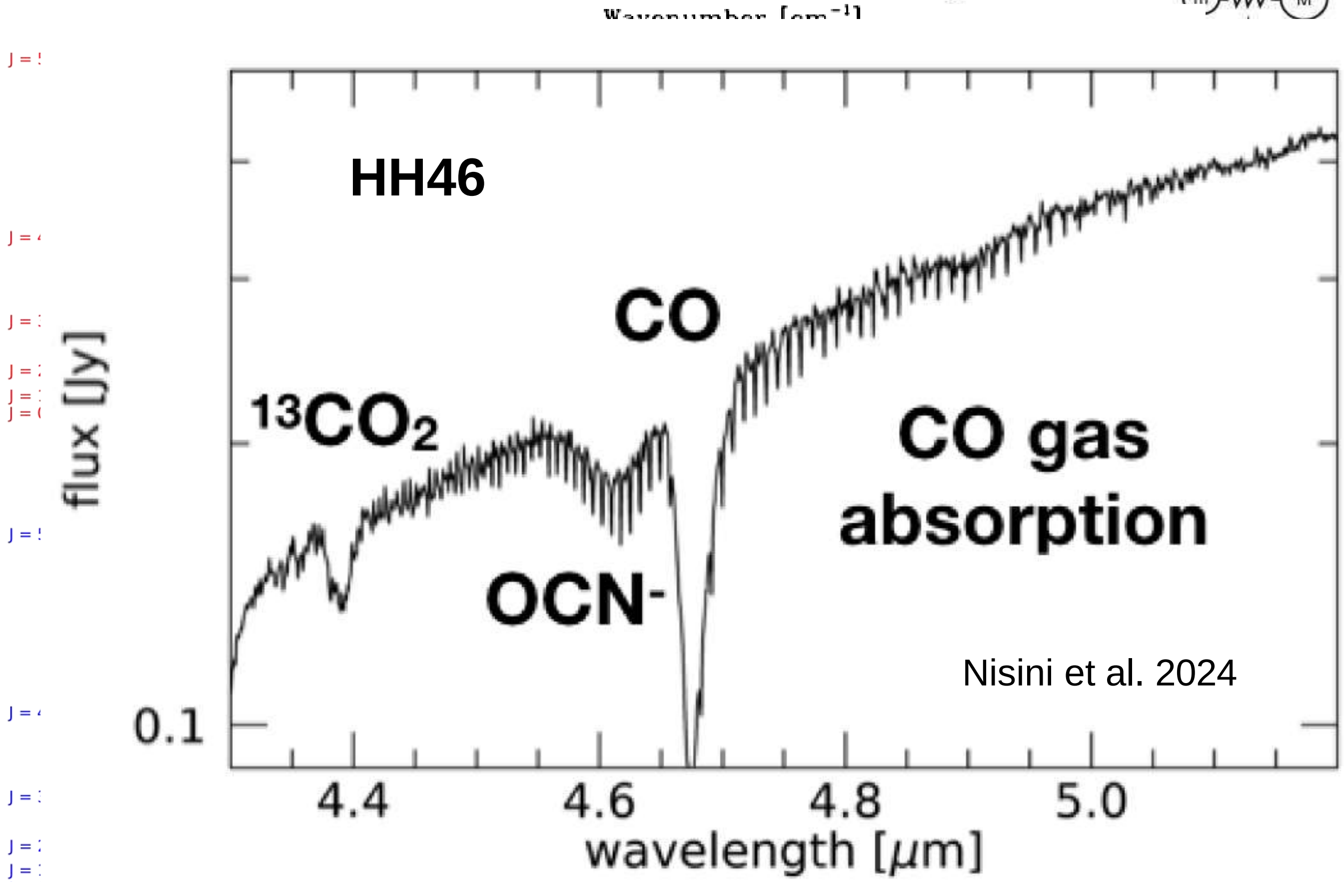
Boogert *et al.*, (2015)

Gas versus Ice: IR





k = Force constant



Nisini et al. 2024

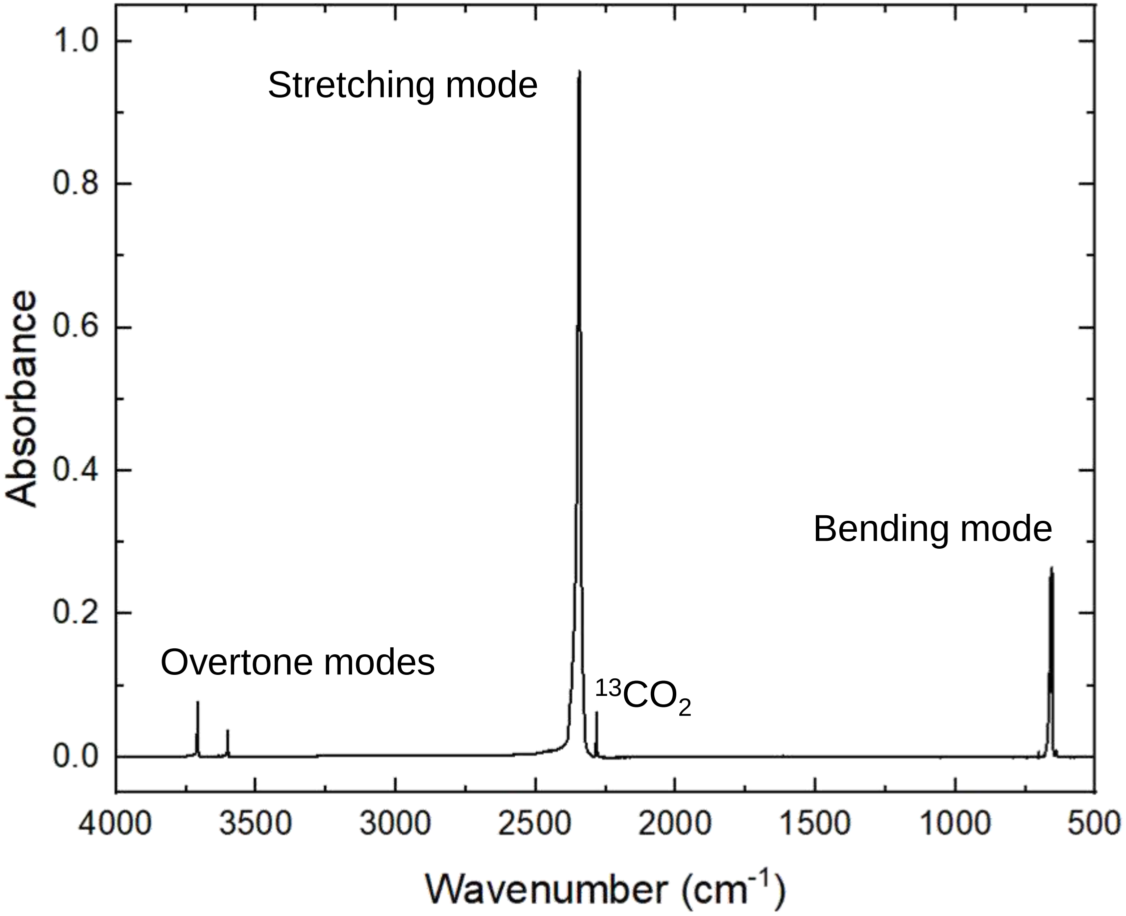
T

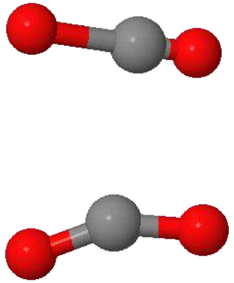
3-0	5	6350.4404	6350.4420	6350.436
4-0	1	8414.4702	8414.4686	8414.458

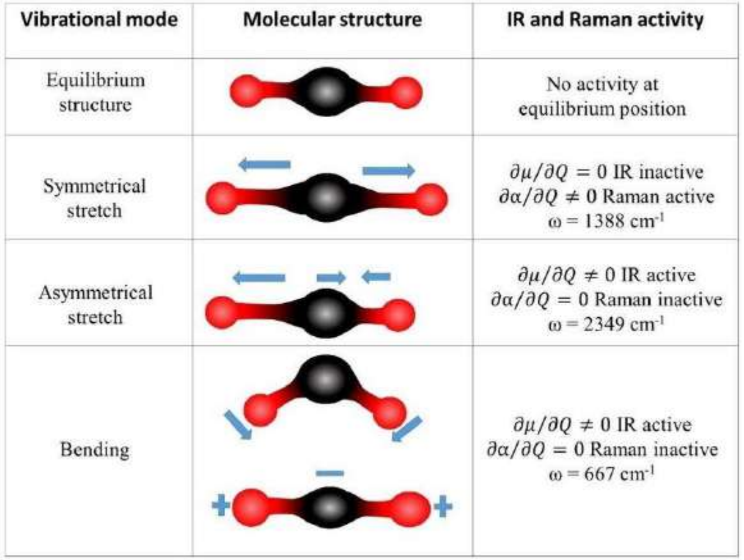
Pontoppidan *et al.* (2003)

Rank *et al.*, (1965)

Vibrational motions CO_2



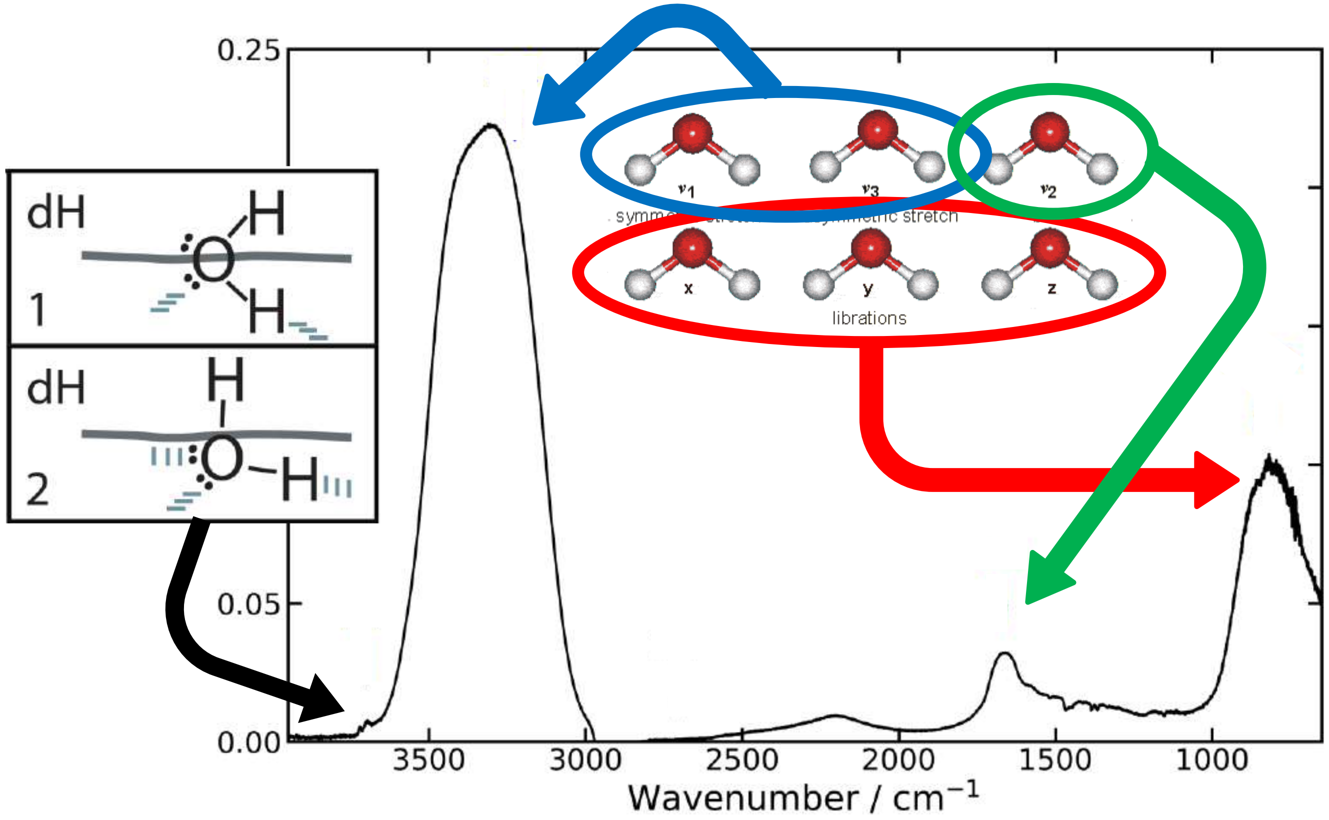




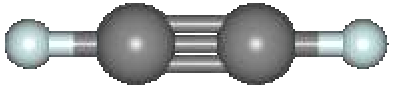
Vibrational mode	Molecular structure	IR and Raman activity
Equilibrium structure		No activity at equilibrium position
Symmetrical stretch		$\partial\mu/\partial Q = 0$ IR inactive $\partial\alpha/\partial Q \neq 0$ Raman active $\omega = 1388\ cm^{-1}$
Asymmetrical stretch		$\partial\mu/\partial Q \neq 0$ IR active $\partial\alpha/\partial Q = 0$ Raman inactive $\omega = 2349\ cm^{-1}$
Bending		$\partial\mu/\partial Q \neq 0$ IR active $\partial\alpha/\partial Q = 0$ Raman inactive $\omega = 667\ cm^{-1}$

Ehrenfreund *et al.*, (1997)

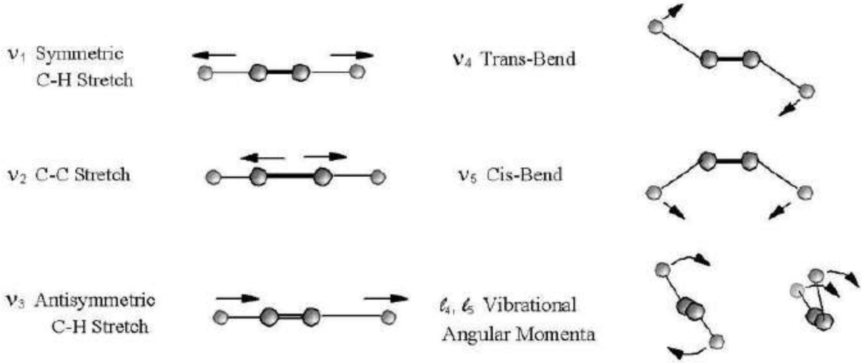
Vibrational motions H_2O

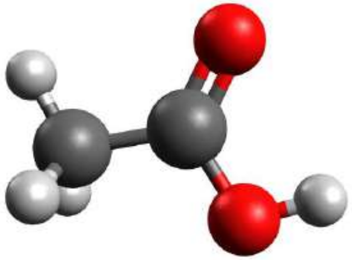


More complex modes

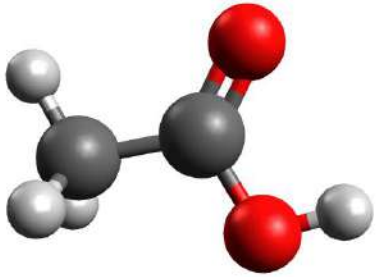


C_2H_2

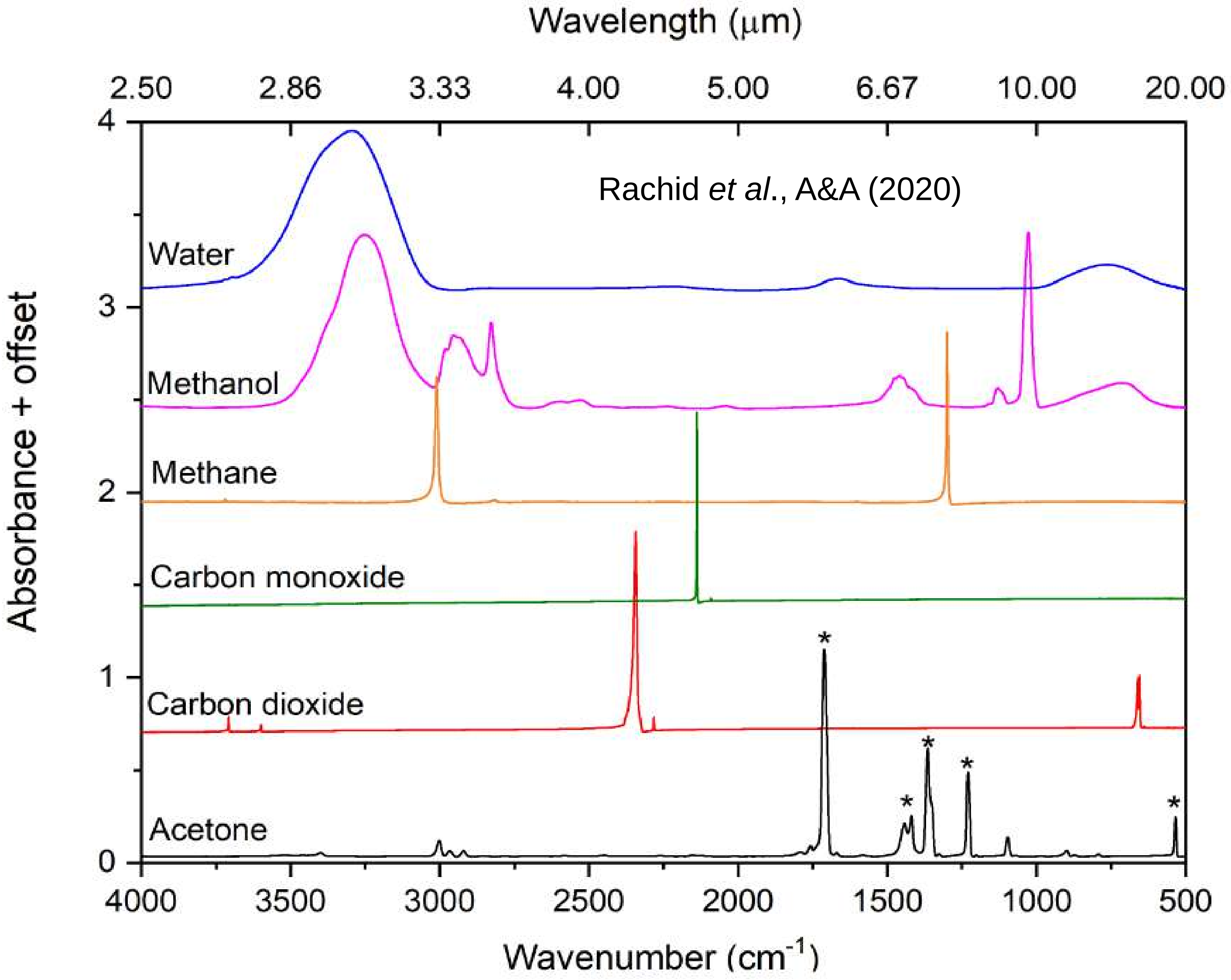




Acetic acid



Leiden Ice Database for Astrochemistry


Rachid *et al*., A&A (2020)

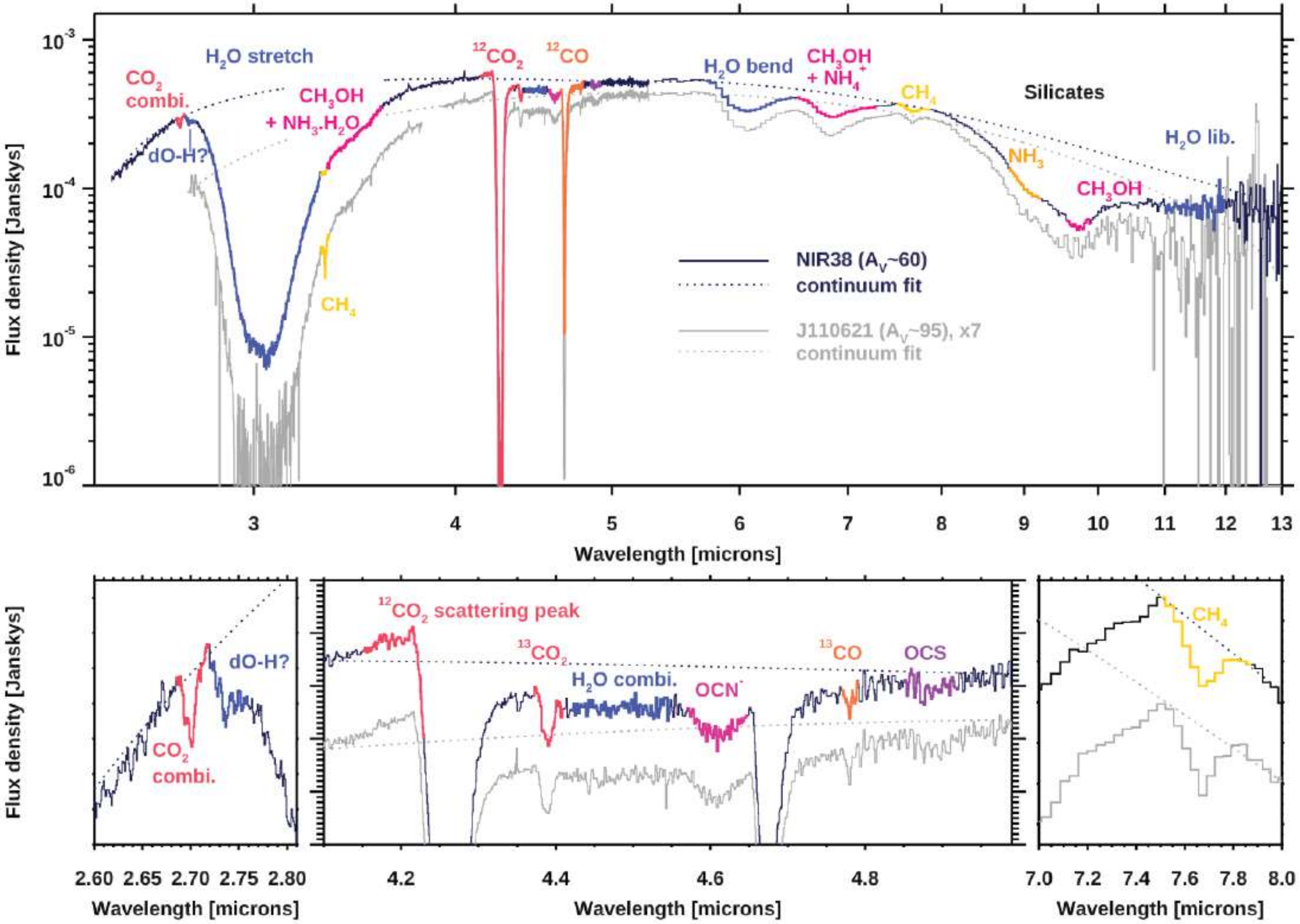
Ice at high Av (Ice Age program)

ERS: PI McClure, co-PI Boogert, co-PI Linnartz,
co-I Ioppolo + 46 co-Is

Cycle 1: **PI McClure, co-**I Ioppolo + 25 co-Is

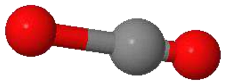
400 hours of observational time in first year to study cosmic ices

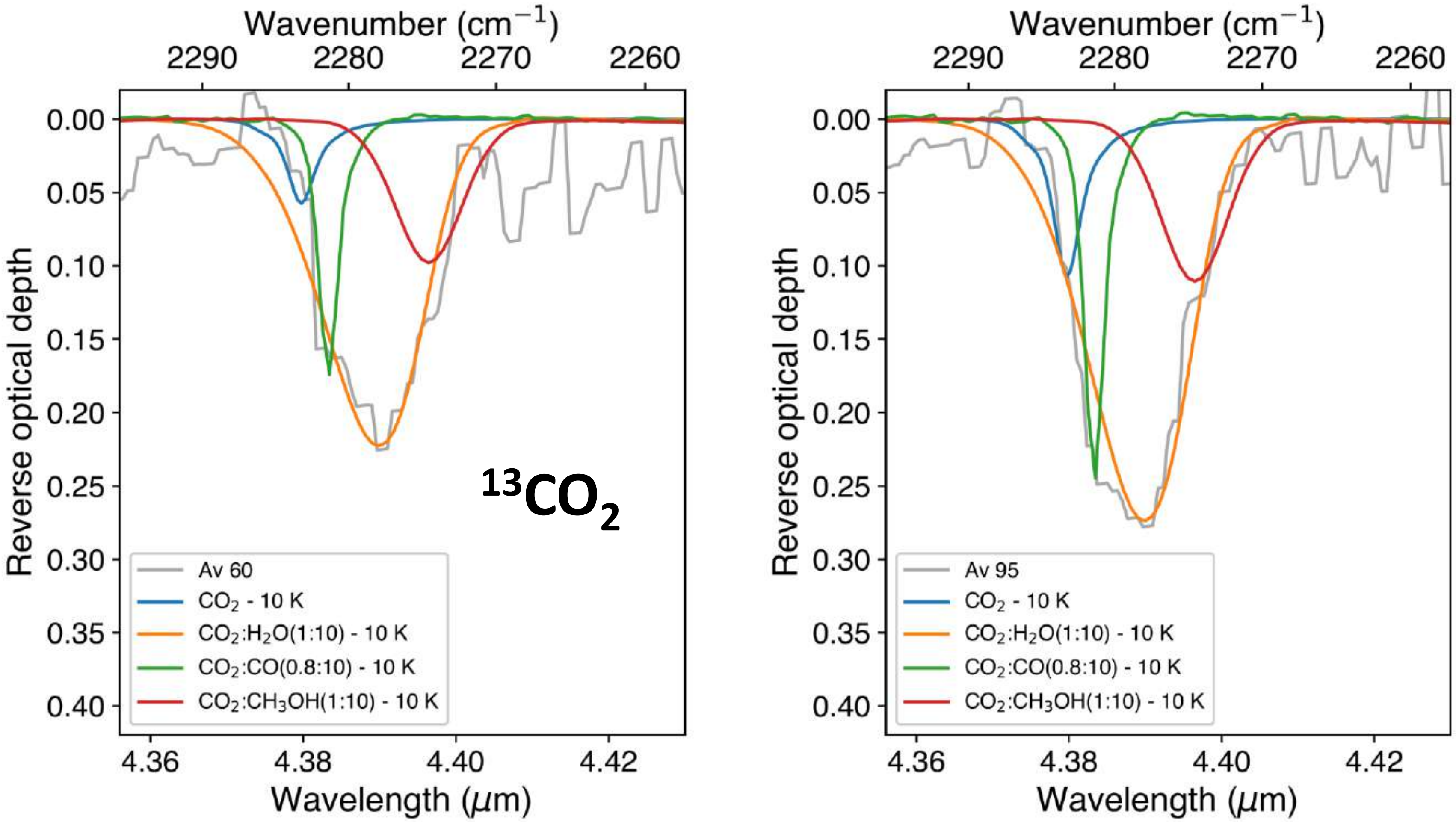
Exercise will use LIDA



McClure *et al.*, Nat. Astron. (2023)

$^{13}CO_2$ ice at high Av (Ice Age program)



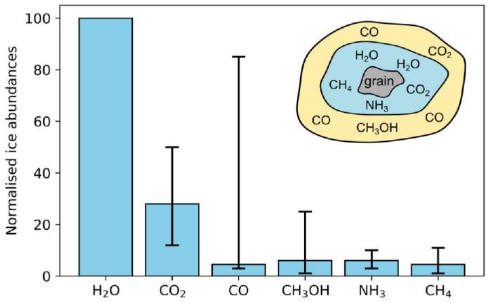


Cold CO_2 in dense cores

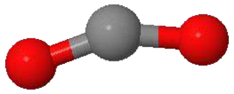
McClure *et al.*, Nat. Astron. (2023)

CO_2 ice toward different objects

Solid CO_2 is a good indicator of the temperature history in the envelopes of young stars



Pontoppidan *et al.*, ApJ (2008)



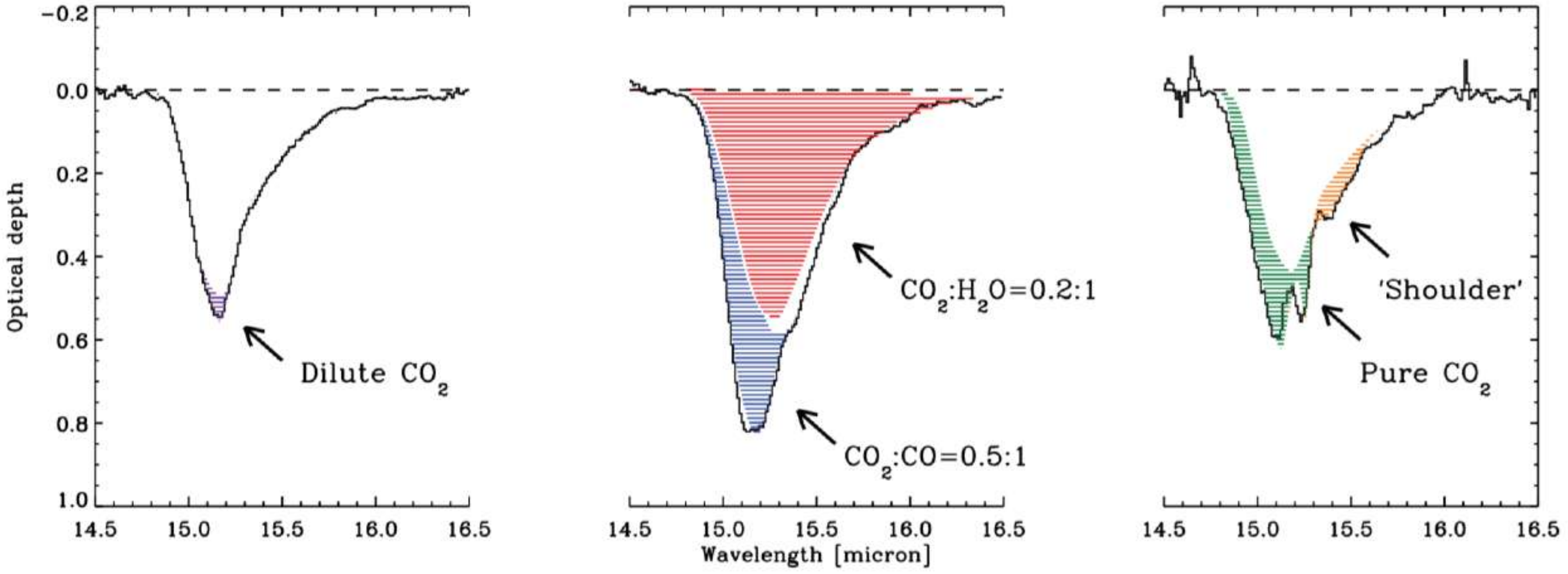
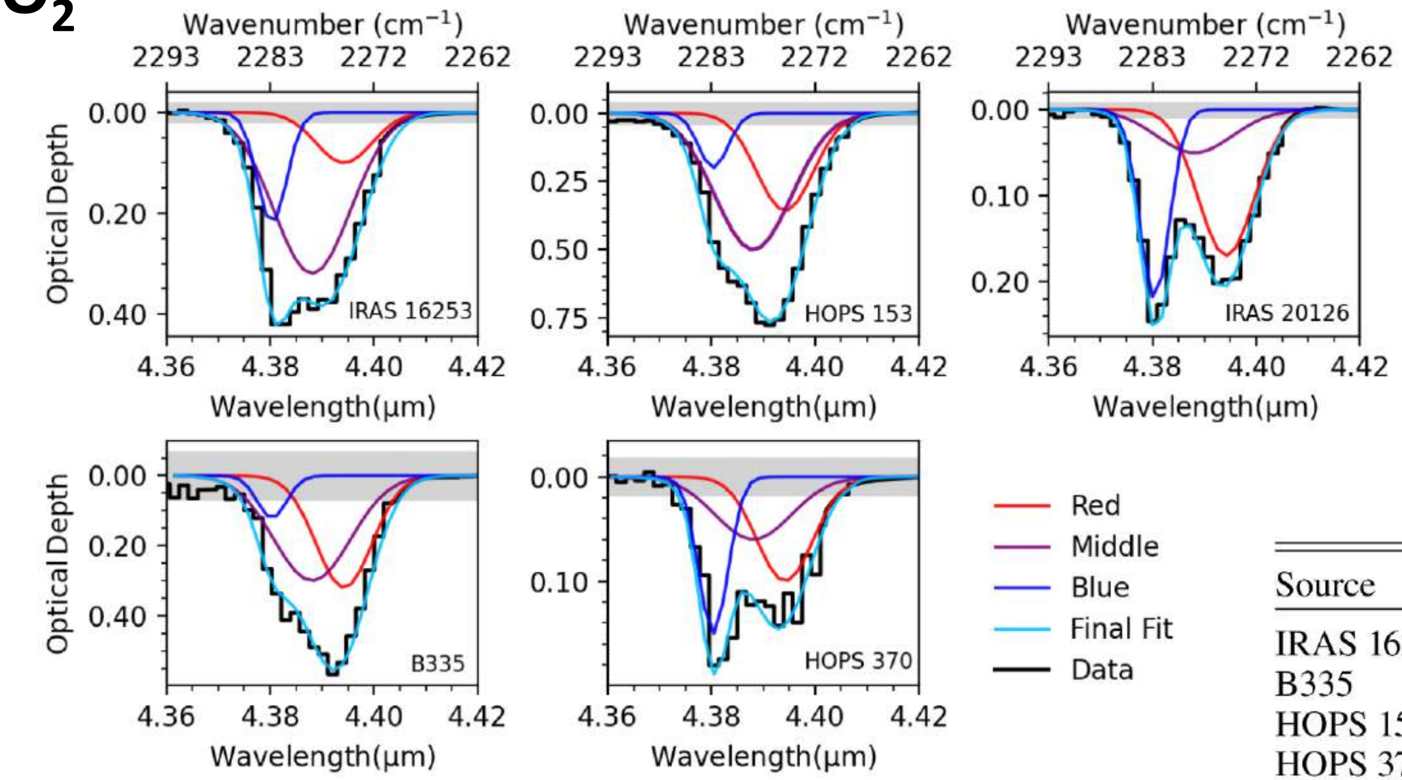
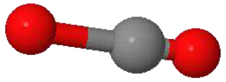


FIG. 3.—Sketch of the five different components used to fit the CO_2 band. The spectra used to illustrate the components are (*left to right*) IRS 51, SVS 4-5, and RNO 91.

Investigating Protostellar Accretion Across the Mass Spectrum (IPA program)

$^{13}CO_2$



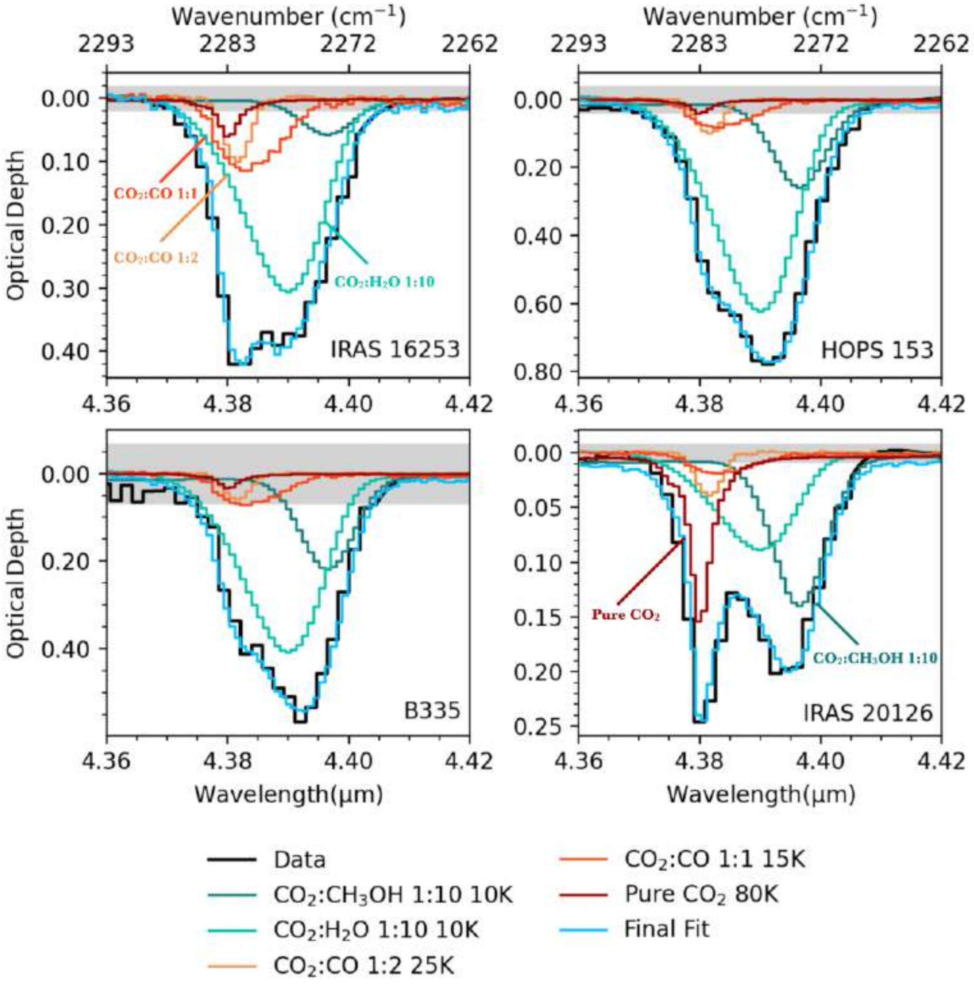


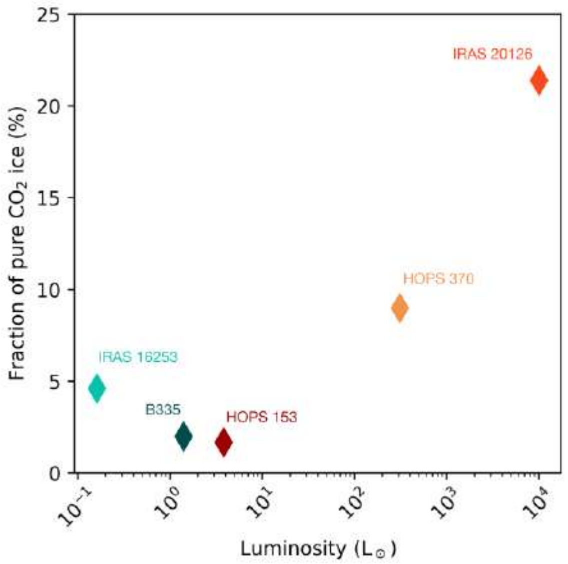
Source	Distance (pc)	Luminosity ($L_\odot$)	Stellar mass ($M_\odot$)
IRAS 16253	140	0.16	0.12–0.17
B335	165	1.4	0.25
HOPS 153	390	3.8	0.6
HOPS 370	390	310	2.5
IRAS 20126	1550	10^4	12

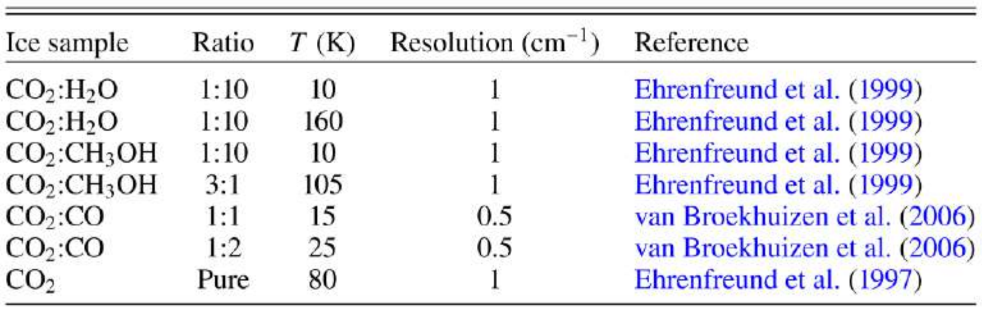
Brunken *et al.*, A&A (2024)

Investigating Protostellar Accretion Across the Mass Spectrum (IPA program)

$^{13}CO_2$





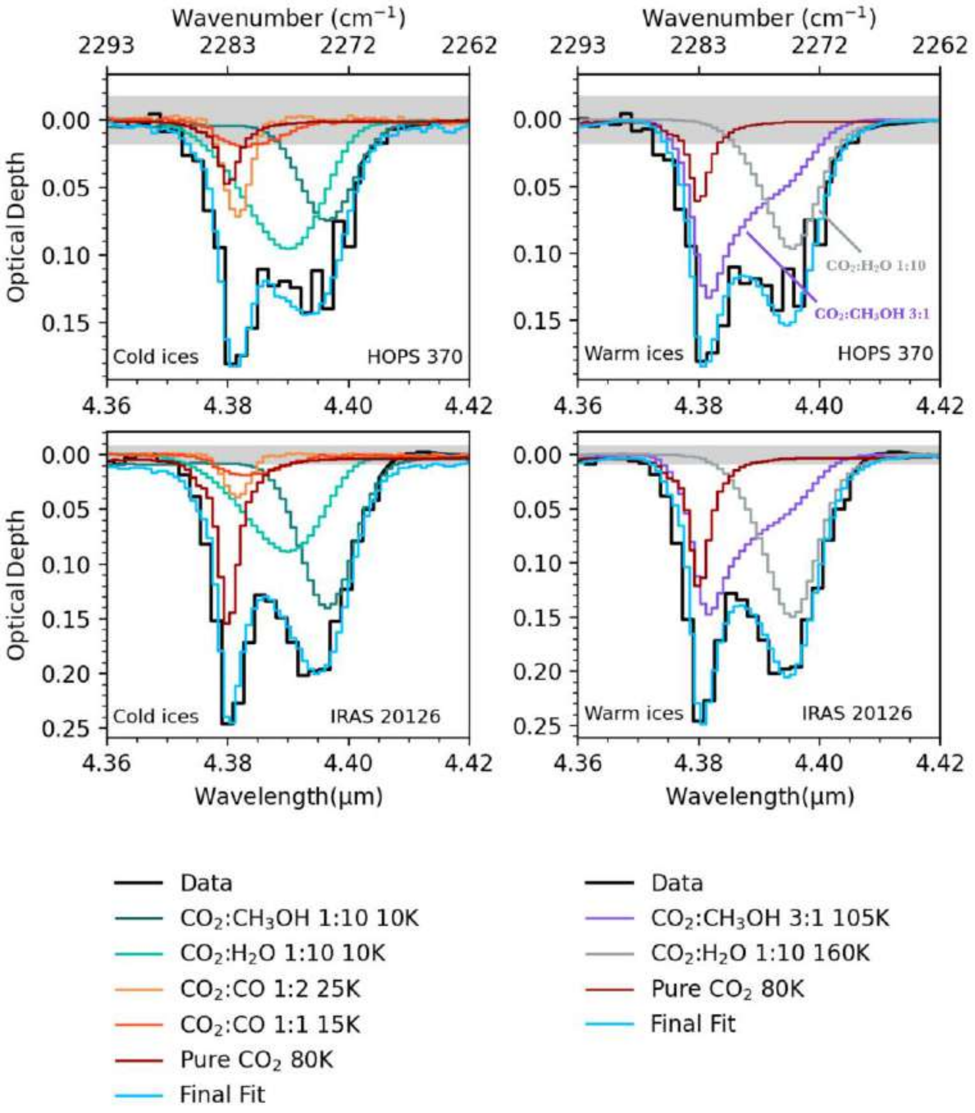


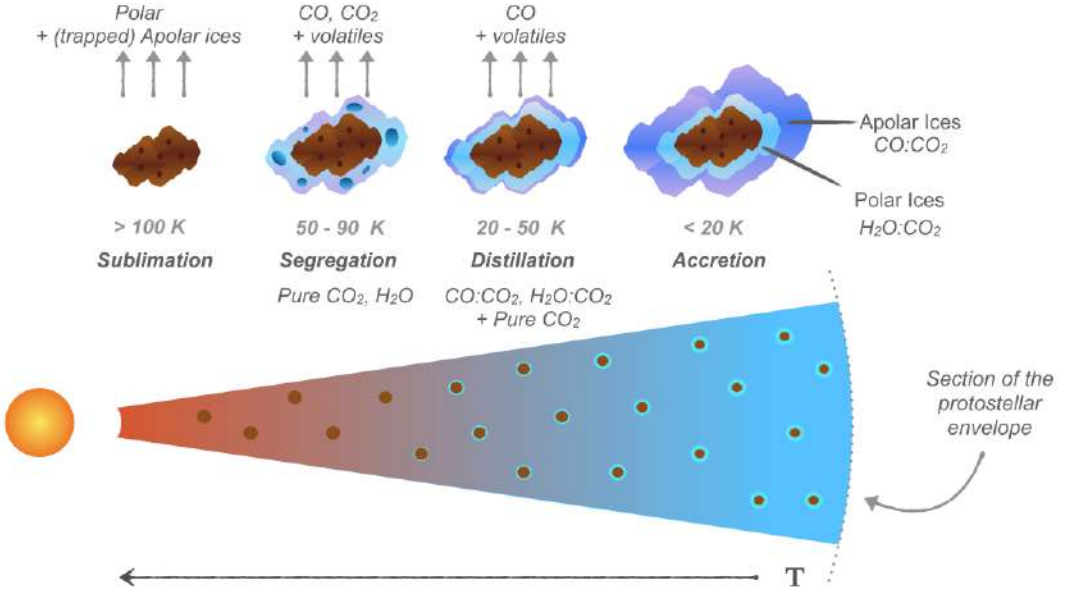
Ice sample	Ratio	T (K)	Resolution (cm^{-1})	Reference
CO_2:H_2O	1:10	10	1	Ehrenfreund et al. (1999)
CO_2:H_2O	1:10	160	1	Ehrenfreund et al. (1999)
CO_2:CH_3OH	1:10	10	1	Ehrenfreund et al. (1999)
CO_2:CH_3OH	3:1	105	1	Ehrenfreund et al. (1999)
CO_2:CO	1:1	15	0.5	van Broekhuizen et al. (2006)
CO_2:CO	1:2	25	0.5	van Broekhuizen et al. (2006)
CO_2	Pure	80	1	Ehrenfreund et al. (1997)

Brunken *et al.*, A&A (2024)

Investigating Protostellar Accretion Across the Mass Spectrum (IPA program)

$^{13}CO_2$





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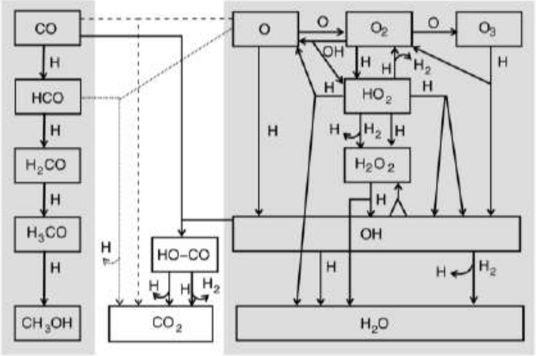
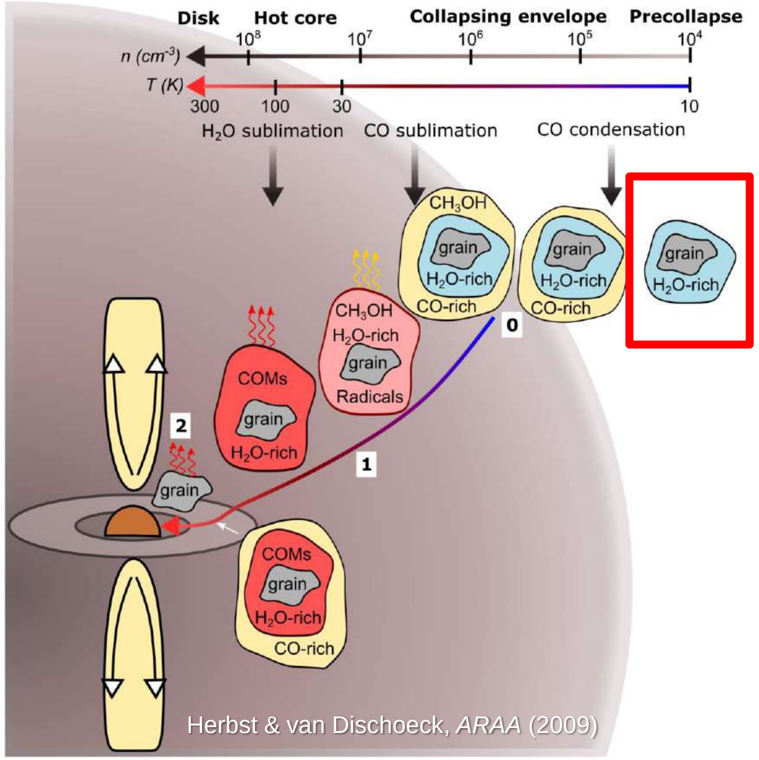
$CO_2:CO$	1:1	15	0.5	van Broekhuizen et al. (2006)
$CO_2:CO$	1:2	25	0.5	van Broekhuizen et al. (2006)
CO_2	Pure	80	1	Ehrenfreund et al. (1997)

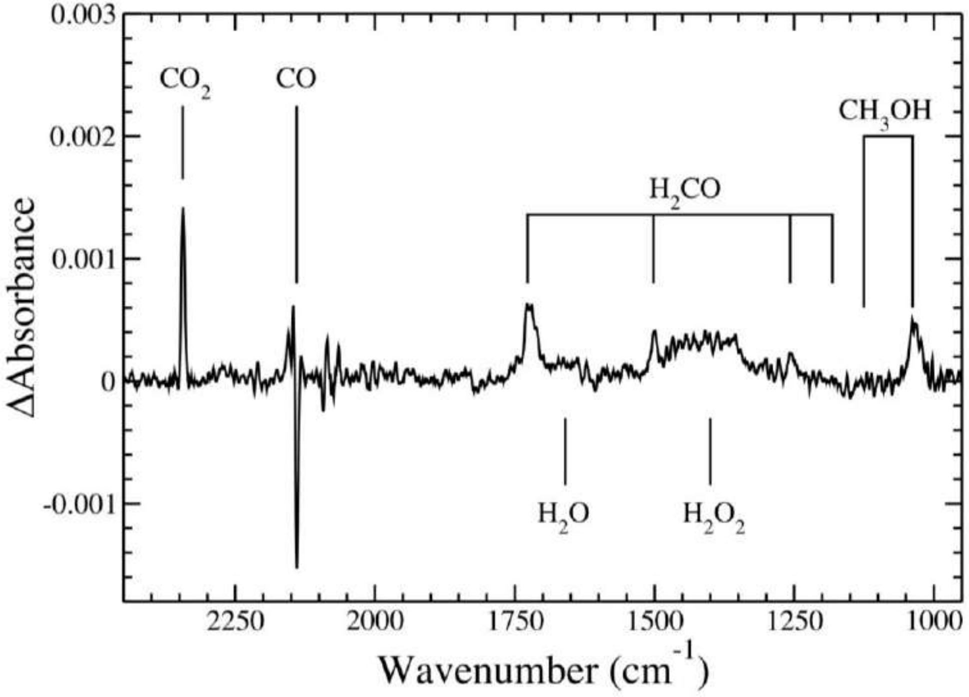
Brunken *et al.*, A&A (2024)

Surface Formation of CO_2 in Space



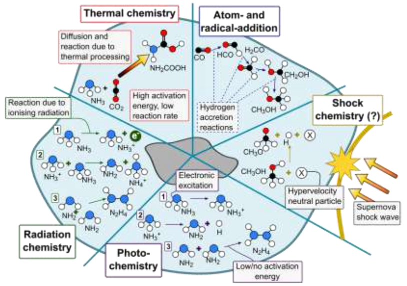


Herbst & van Dischoeck, *ARAA* (2009)

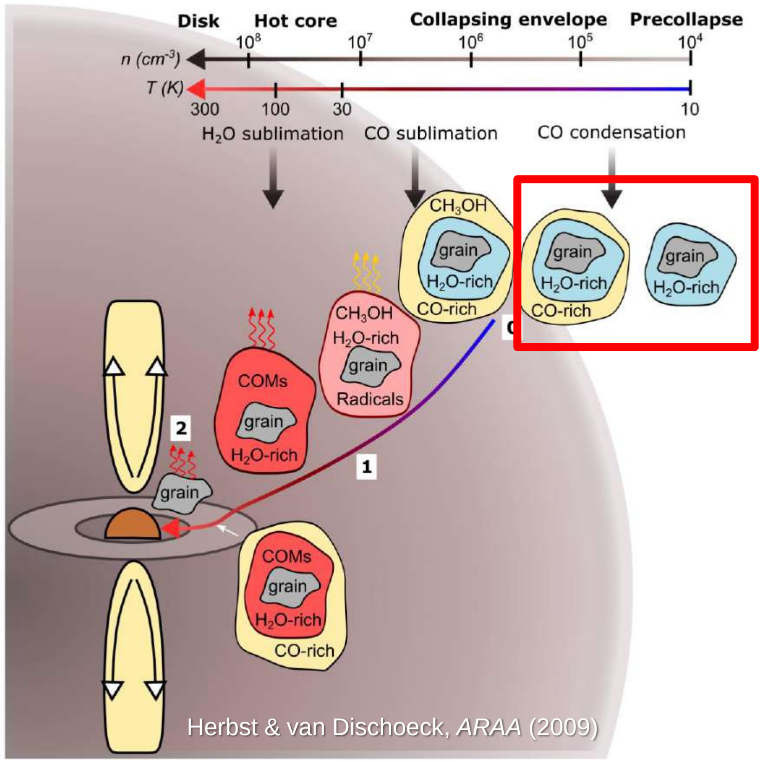


Oba *et al.*, ApJL (2010)
Ioppolo *et al.*, MNRAS (2011)
Noble *et al.*, ApJ (2011)

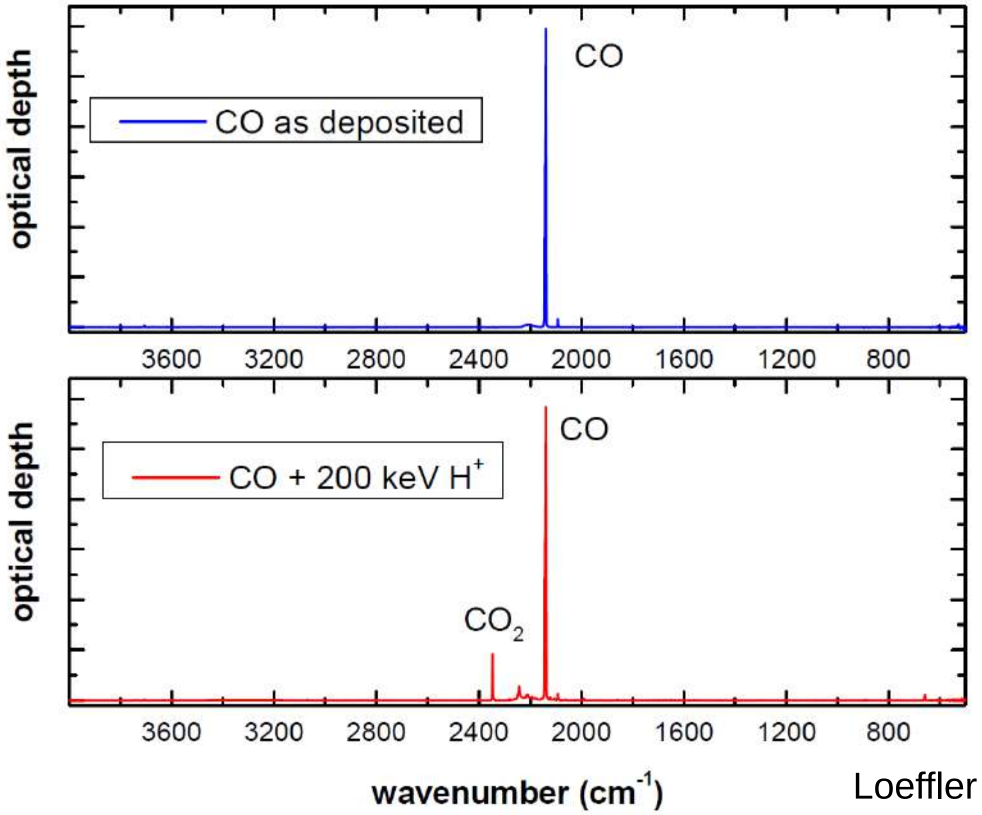
Surface Formation of CO_2 in Space



Arumainayagam *et al.*, CSR (2019)



Herbst & van Dischoeck, *ARAA* (2009)



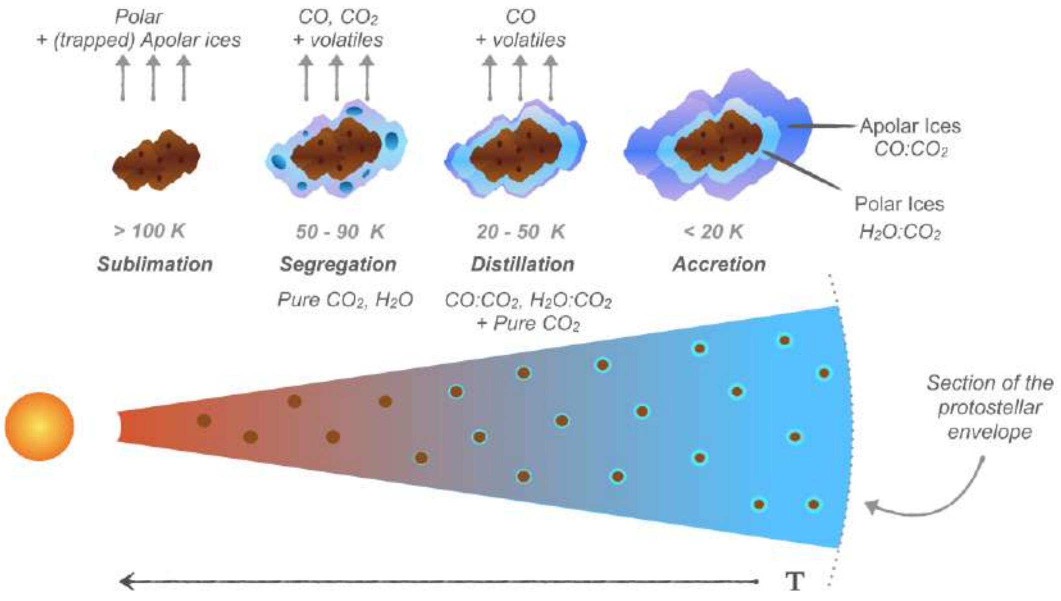
Loeffler *et al.*, A&A (2005)

Open question on structure of CO_2 in ices

- Is CO_2 mixed up with other frozen components, or is it segregated in multilayer structures?

- Has it attained a crystalline arrangement, or does it have an amorphous structure?

- Can we reproduce all the above conditions in the lab?



Infrared profile of CO_2 ice bands

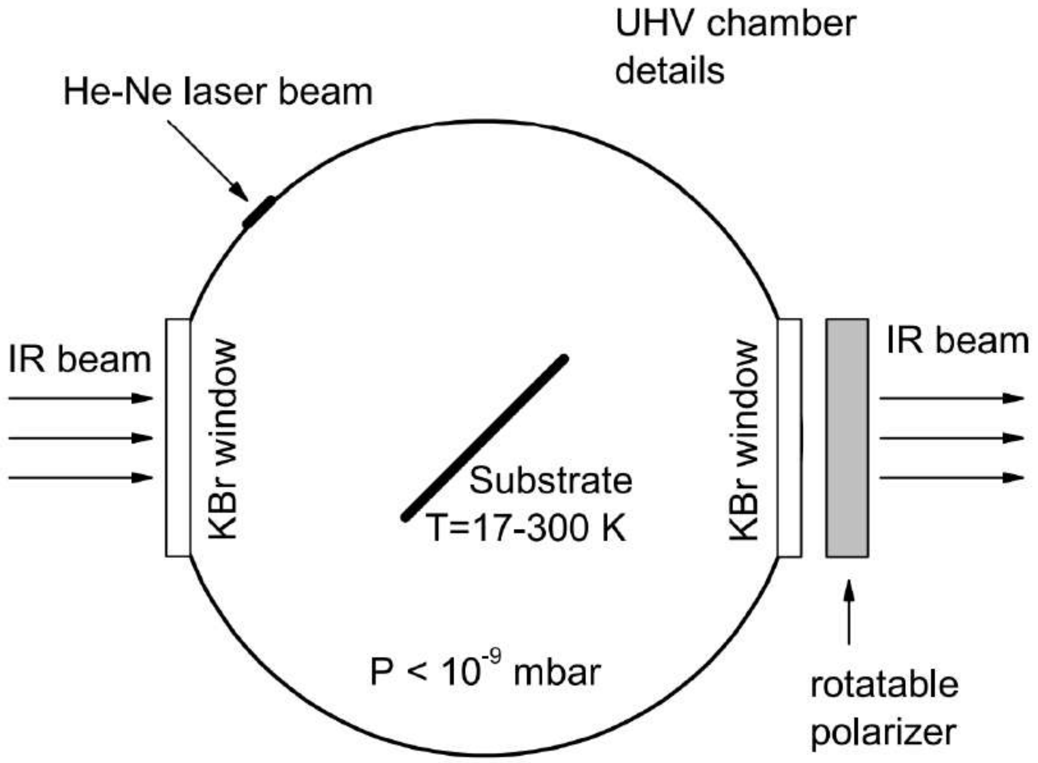


Fig. 1. Schematic depiction of the ultra high vacuum chamber.

Baratta and Palumbo, A&A (2017)

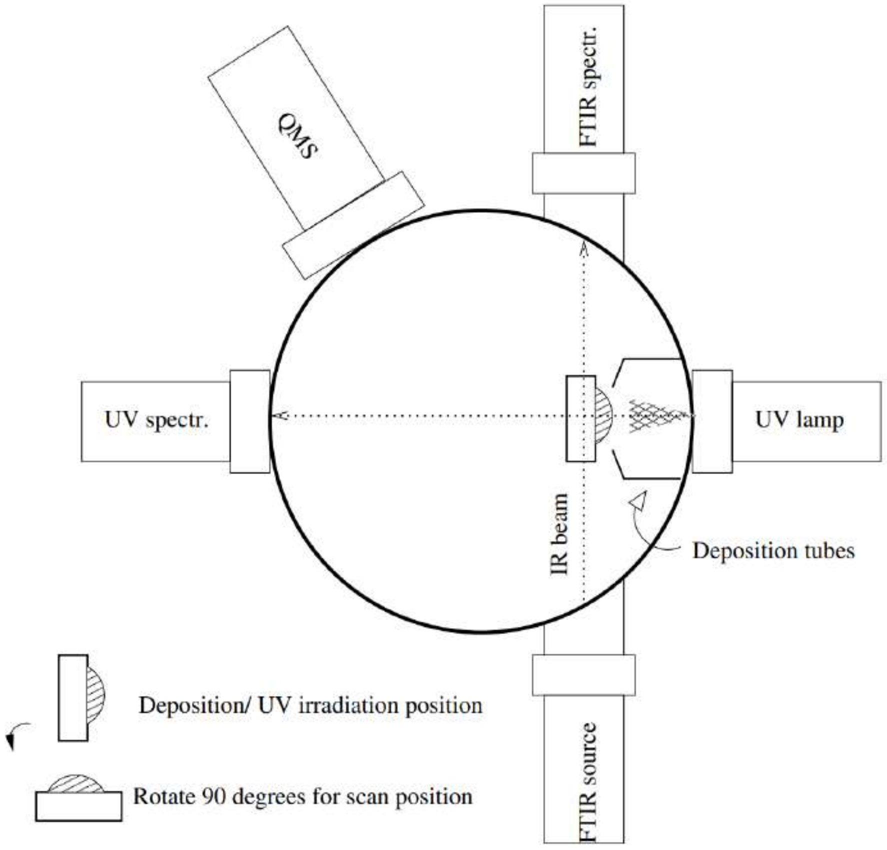
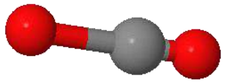
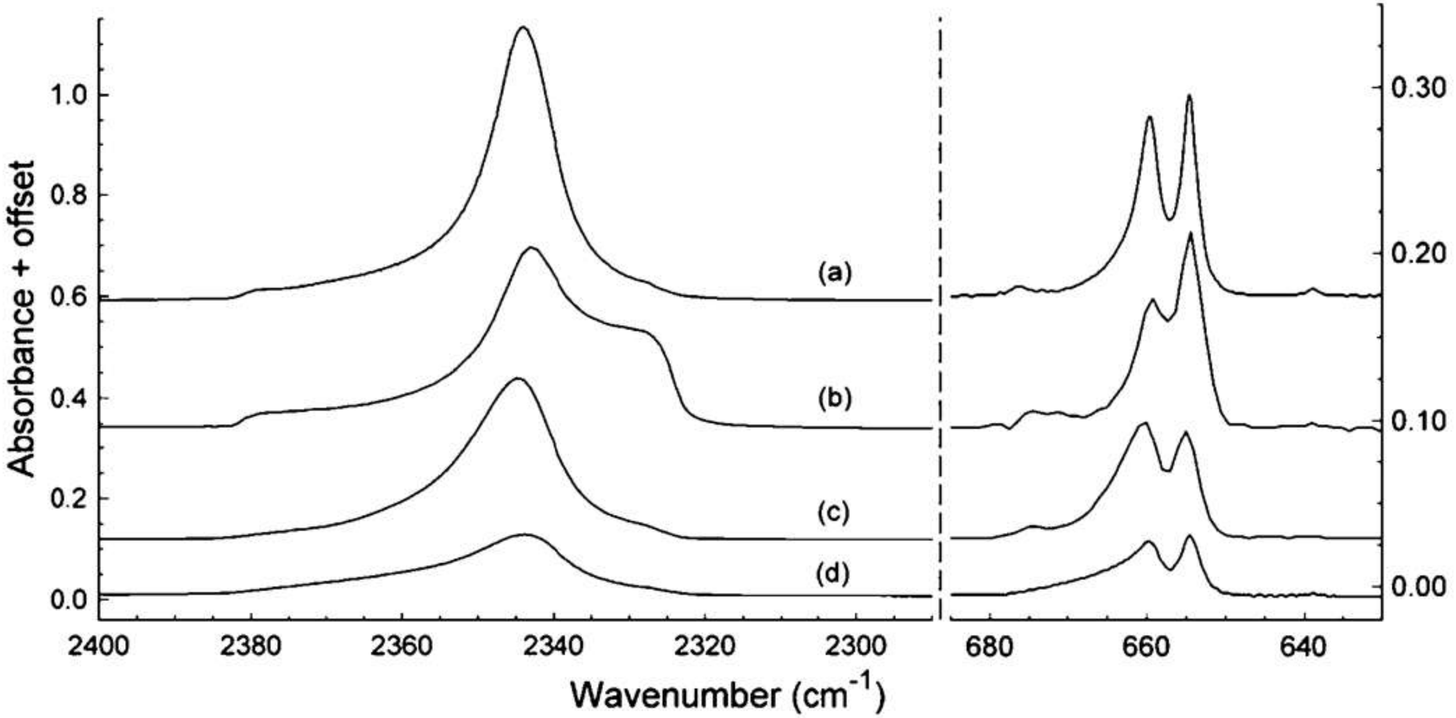


Fig. 2. Schematic representation of the upper level of the main chamber of the ISAC experimental set-up, where gas deposition onto the cold substrate forms an ice layer that is UV irradiated. FTIR and QMS techniques allow in situ monitoring of the solid and gas phases.

Escribano *et al.*, PNAS (2013)

Infrared profile of CO_2 ice bands





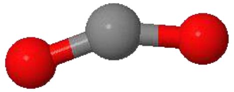
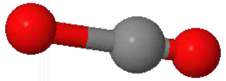


Figure 1. Infrared spectra of the ν_3 (left) and ν_2 (right) bands of CO_2 ices made near 10 K. The ice thickness was 0.10 μm in each case and the substrate chosen was KBr. Spectra were calculated (Swanepoel 1983) using the optical constants of (a) Ehrenfreund et al. (1997), (b) Hudgins et al. (1993), (c) Baratta & Palumbo (1998), and (d) Rocha & Pilling (2014). Spectra are offset for clarity.

Gerakines and Hudson, ApJL (2015)

Infrared profile of CO_2 ice bands



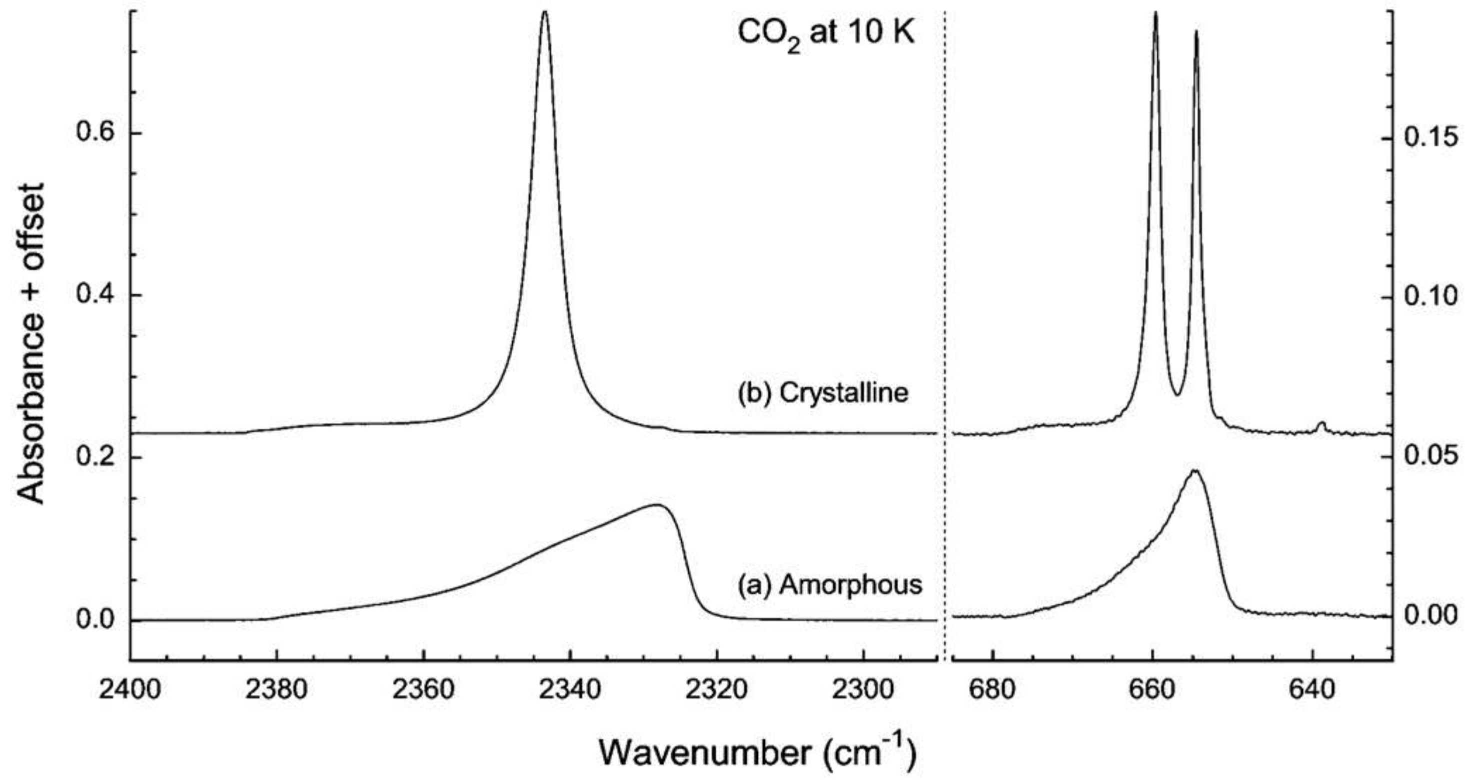
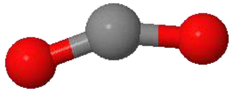
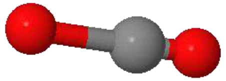


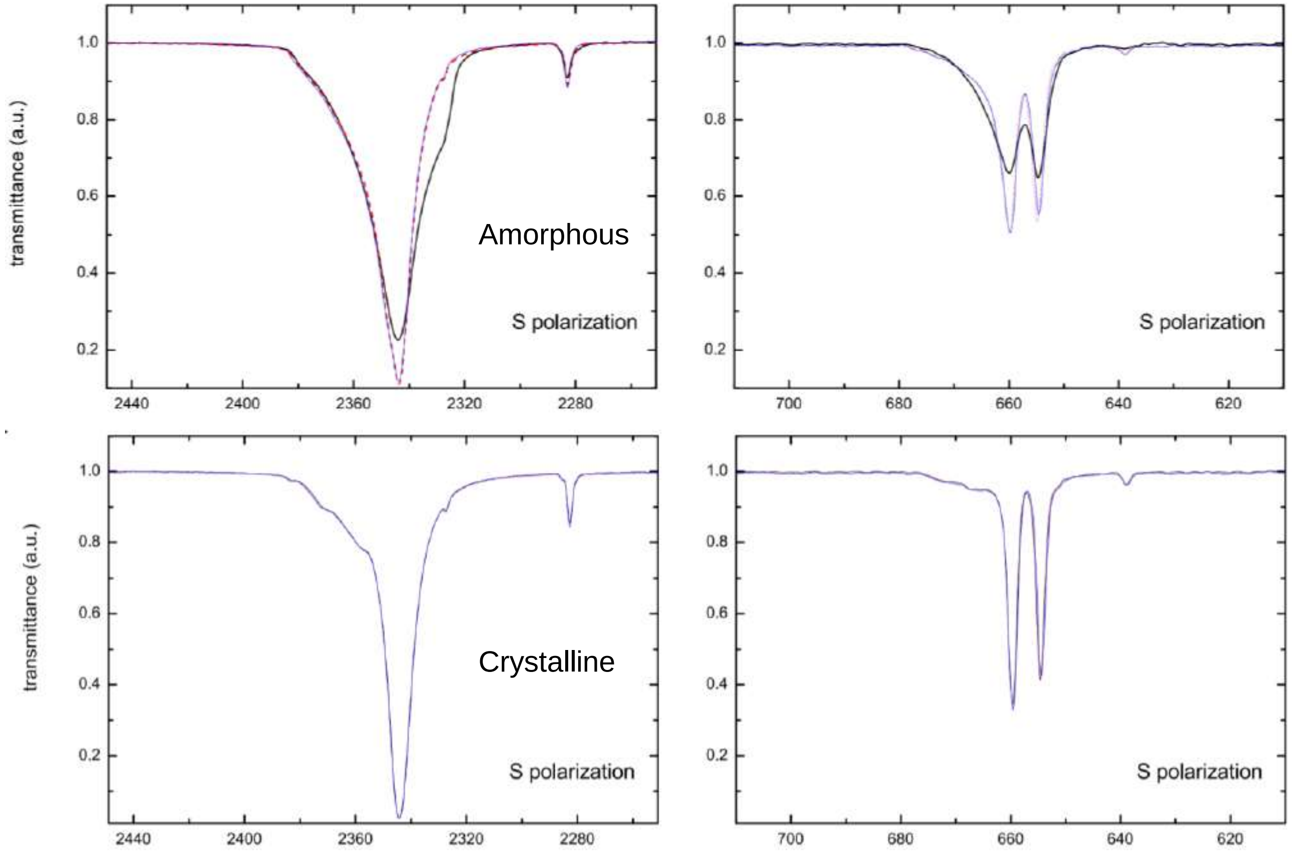
Figure 2. Infrared spectra of the ν_3 (left) and ν_2 (right) bands of solid CO_2. The CO_2 ice sample was grown at 10 K to give (a) an amorphous solid that (b) crystallized on warming to 70 K and then was recooled to 10 K to give the spectrum shown. The thickness of the initial sample was about 0.03 μm. Spectra are offset for clarity.

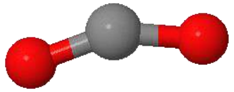


Gerakines and Hudson, ApJL (2015)

Infrared profile of CO_2 ice bands



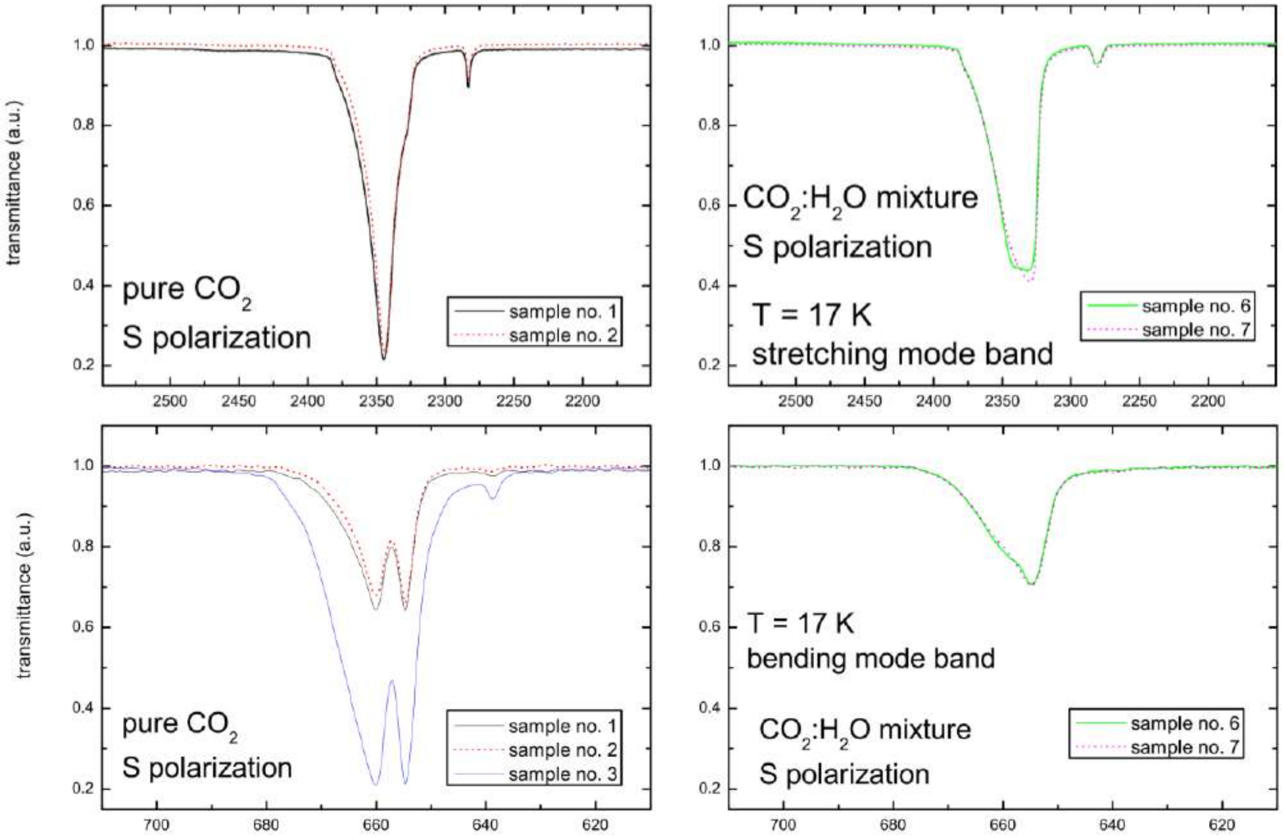




Figures 9 and 10. Infrared spectra of solid CO_2. (Top panels) Spectra are acquired after sample deposition at 17 K, after thermal annealing to 77 K and after cooling down to 17 K. (Bottom panels) Spectra are acquired after sample deposition at 70 K, after thermal annealing to 77 K and after cooling down to 17 K.

Baratta and Palumbo, A&A (2017)

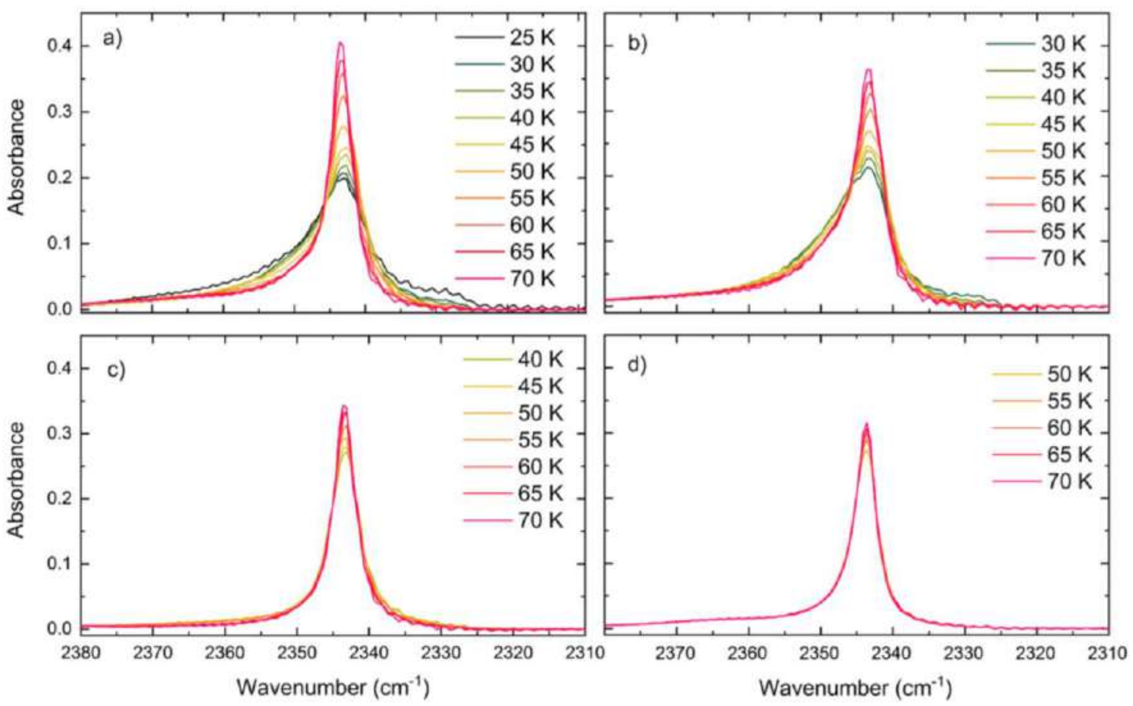
Infrared profile of CO_2 ice bands

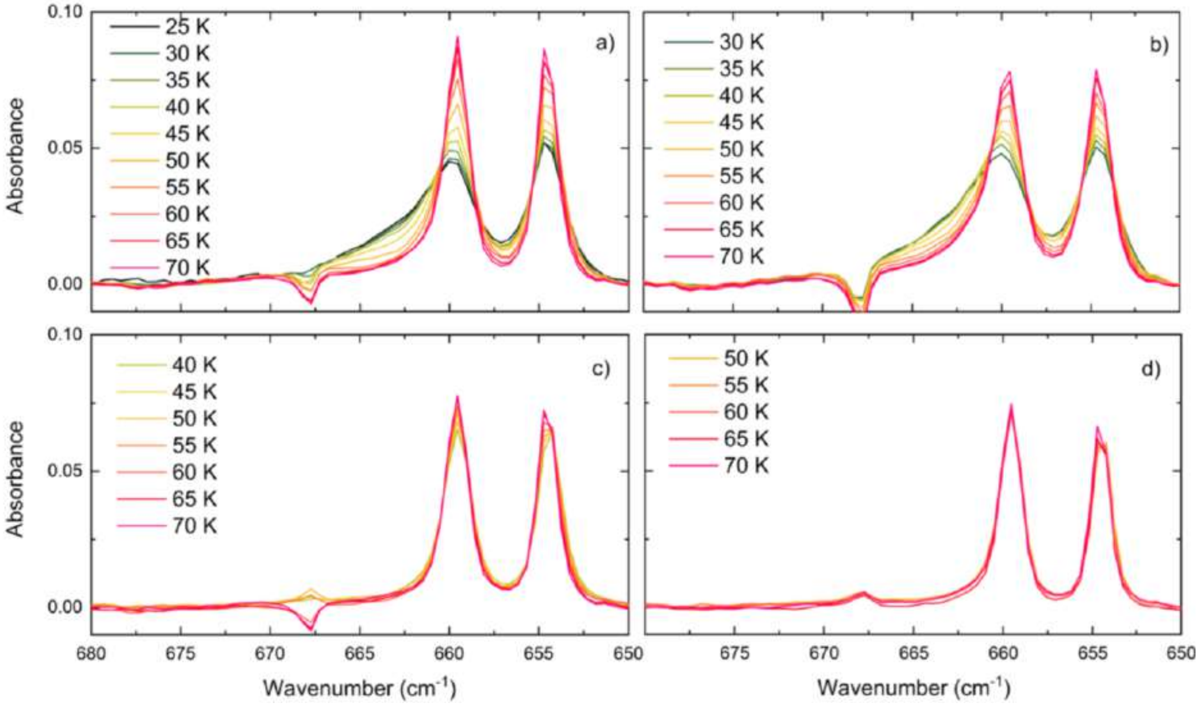


Figures 3 and 4. Infrared spectra of pure solid CO_2 deposited at 17 K (left panels) compared to infrared spectra of CO_2:H_2O mixtures deposited under analog conditions (right panels).

Baratta and Palumbo, A&A (2017)

Infrared profile of CO_2 ice bands





Mifsud *et al.*, JMS (2022)

Crystallization of CO_2 ice

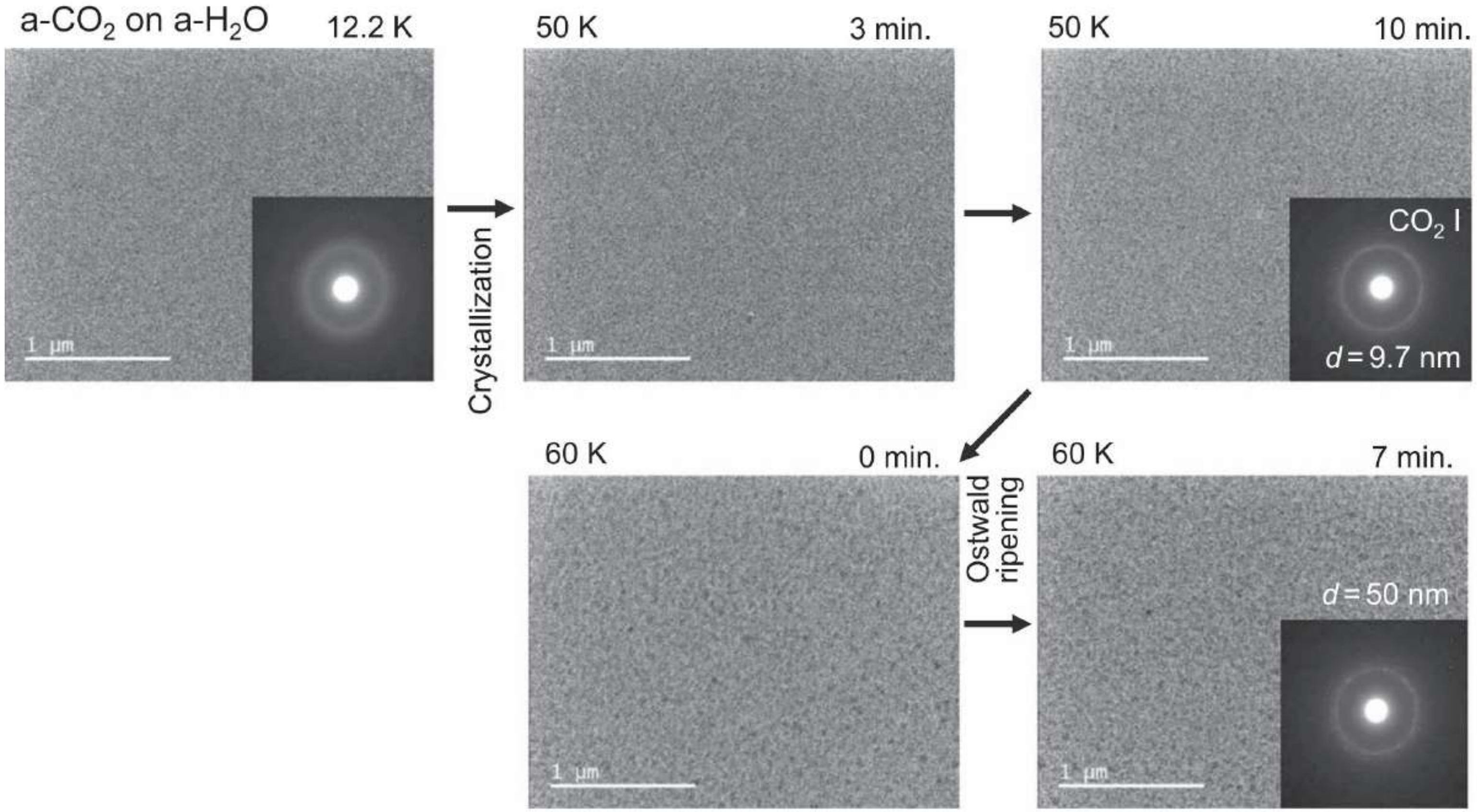
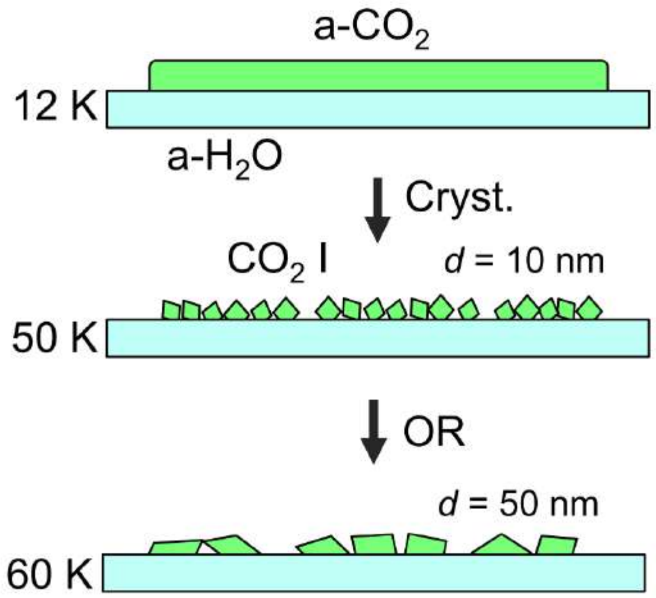
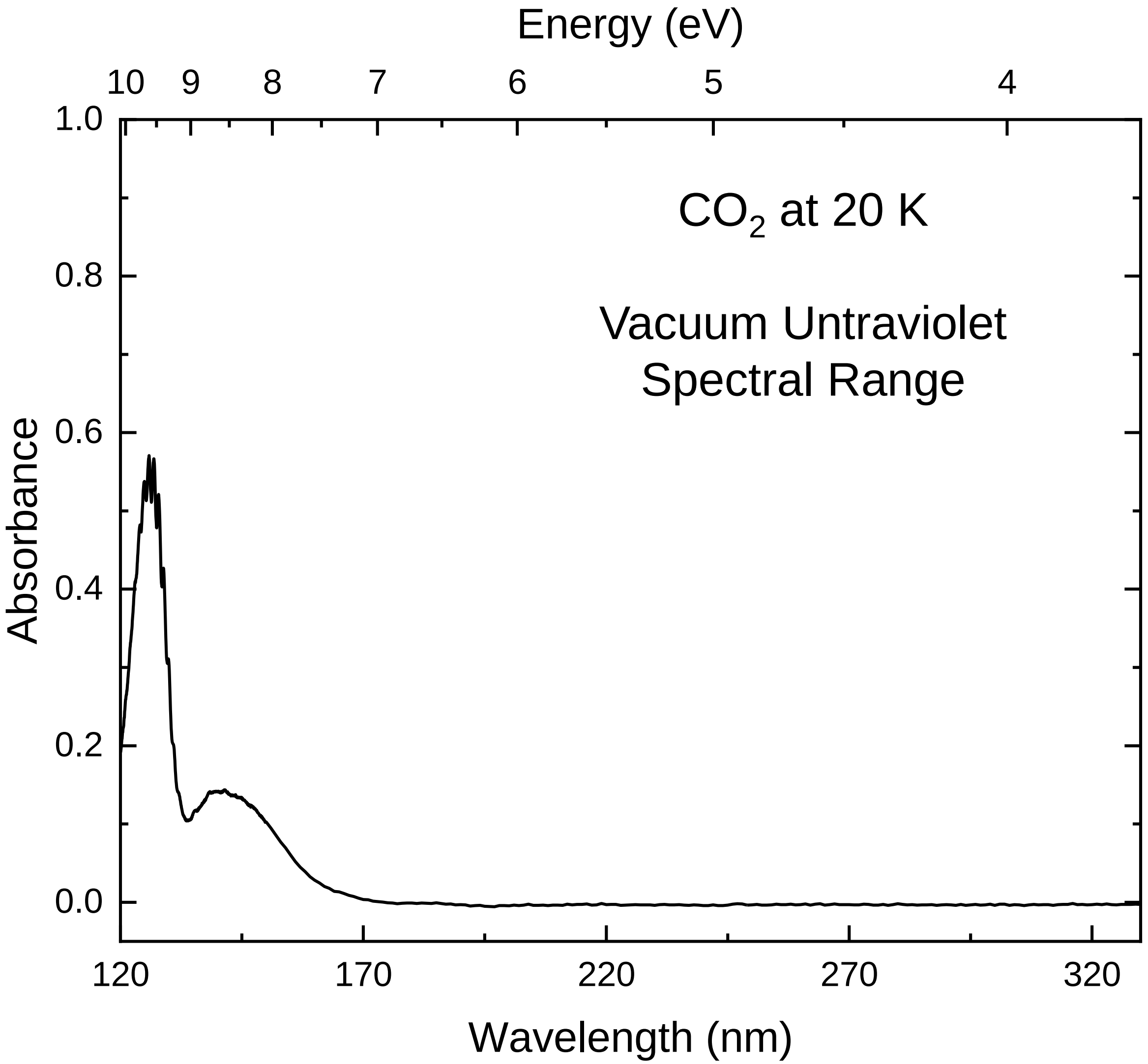


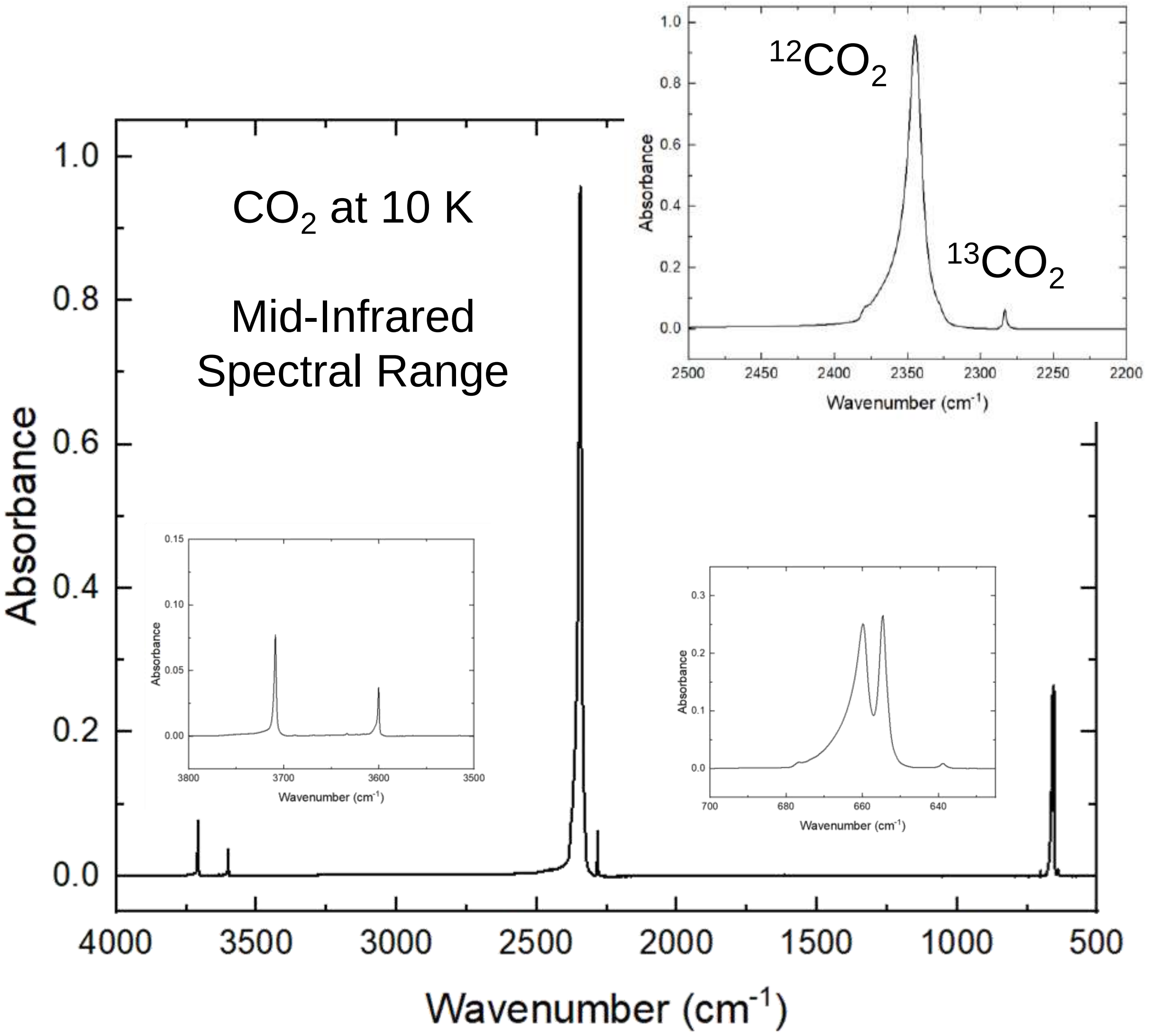
Figure 5. TEM observation of the crystallization of a-CO_2 on a-H_2O substrate at 50 and 60 K.



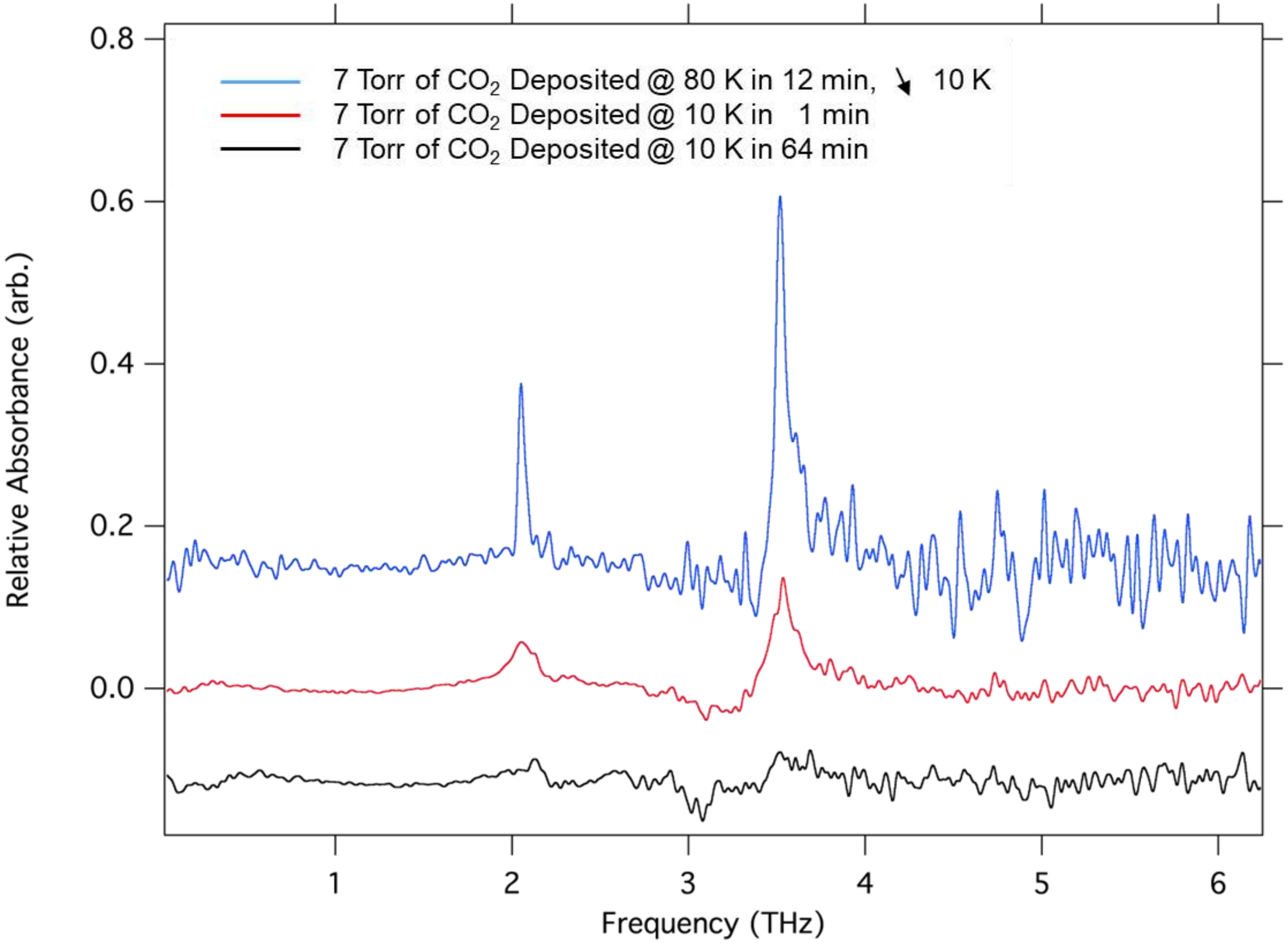
Kouchi *et al.*, ApJ (2021)

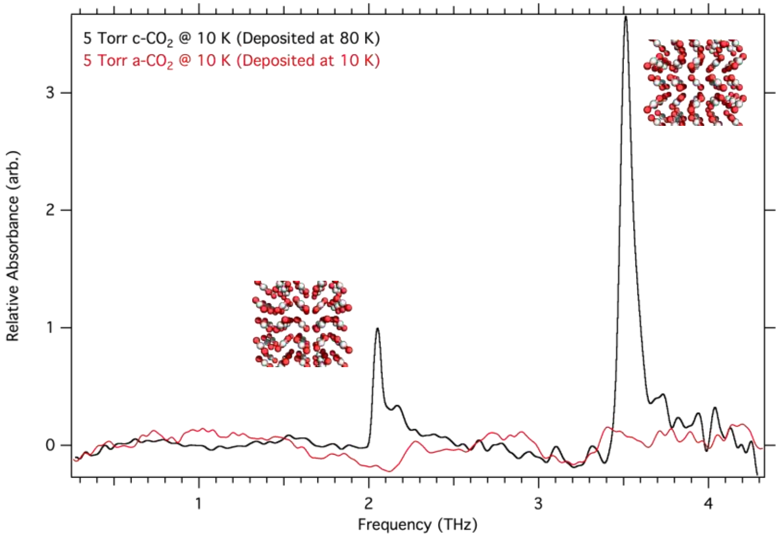
CO_2 - From VUV to Far-IR

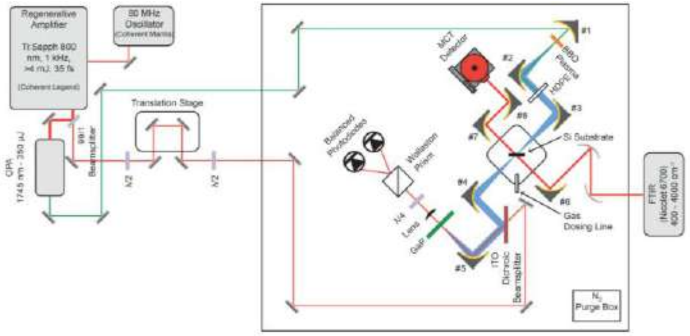




CO_2 – in the Far-IR (THz)







McGuire *et al.*, PCCP (2016)

RAIR Spectra of CO_2 ice

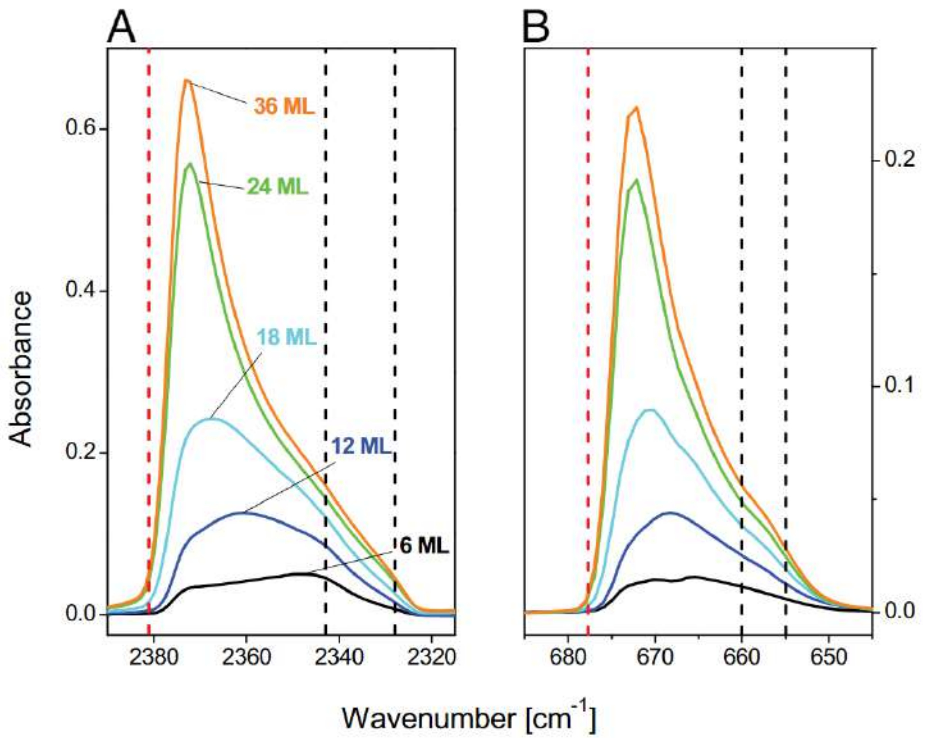
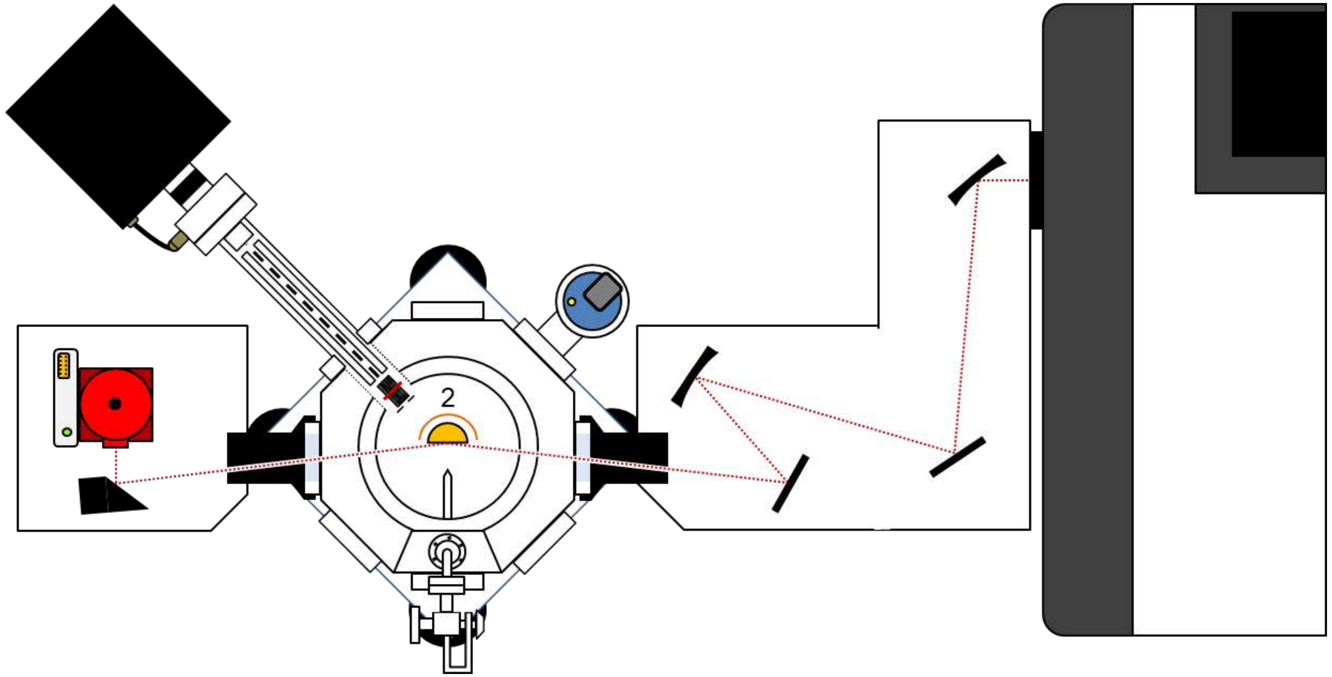


Fig. 3. RAIR spectra of CO_2 samples deposited at 14 K with a growing thickness between 6 and 36 ML. Black dashed lines mark the wavenumber position, in decreasing frequency, of the ν_3 and X modes (*A*) and of the ν_{2b} and ν_{2a} components (*B*). Red dashed lines indicate the observed wavenumber for the LO modes in transmission spectra of pure crystals at a 30° incidence (19).

Escribano *et al.*, PNAS (2013)



Surface selection rule

RAIR active

RAIR inactive

Ioppolo *et al.*, RSI (2013)

HFML - FELIX Laboratory

HFML
Science in High Magnetic Fields

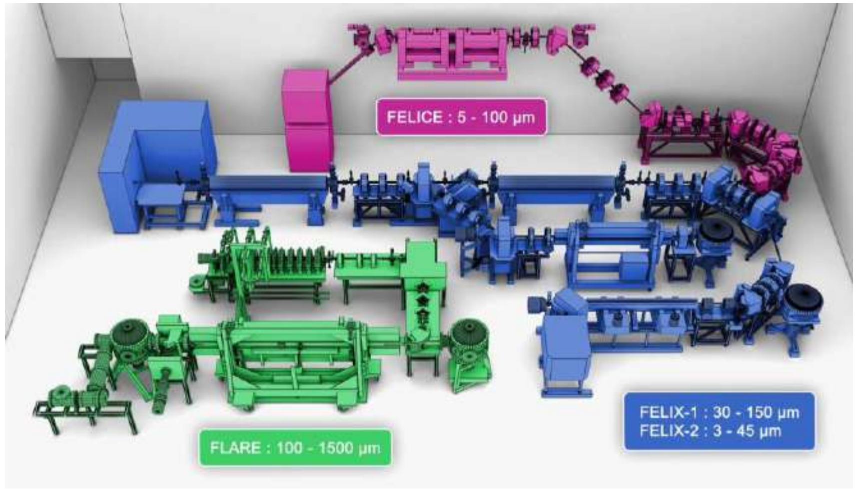
FELIX
Free Electron Lasers for Infrared eXperiments

Wide tunability

High intensity

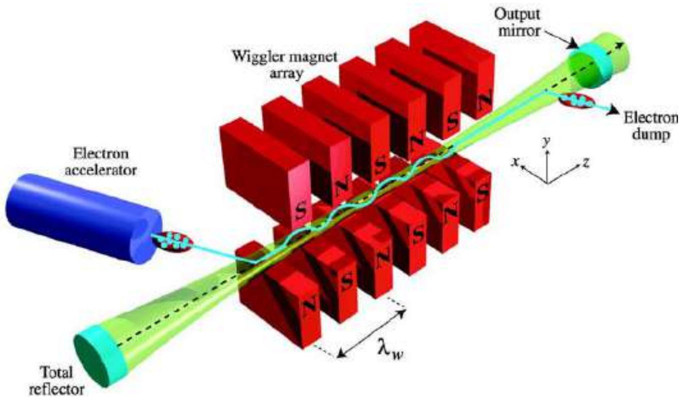
Ultrashort pulses

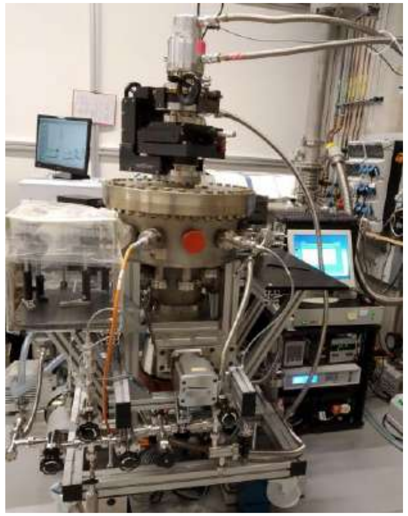
Radboud University
Nijmegen, The Netherlands

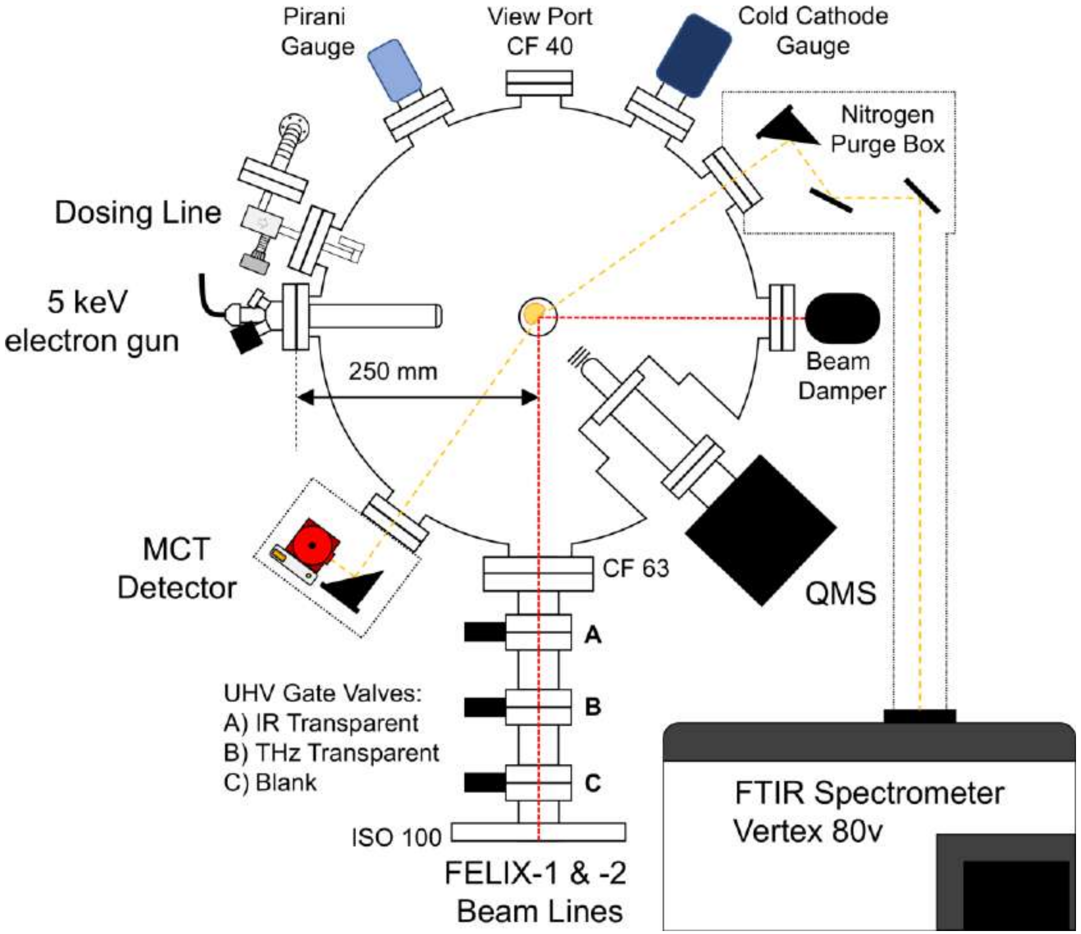


Lab Ice Surface Astrophysics (LISA)

- **FEL-1 & FEL-2 End Station:**
- **UHV Chamber (P = 1x10^{-10} mbar)**
- **Analytical Tools (FTIR & QMS)**
- **Sample Manipulation (Rotation + XYZ)**
- **Source (5 keV electron gun)**

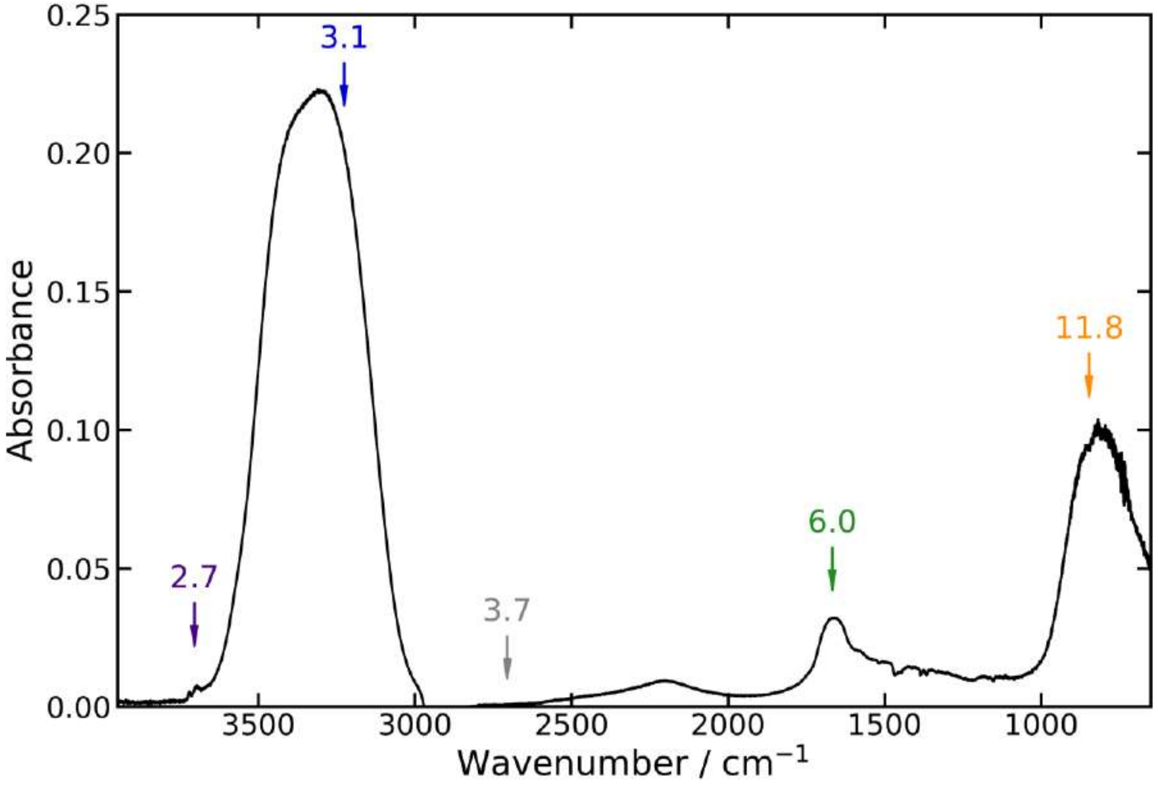




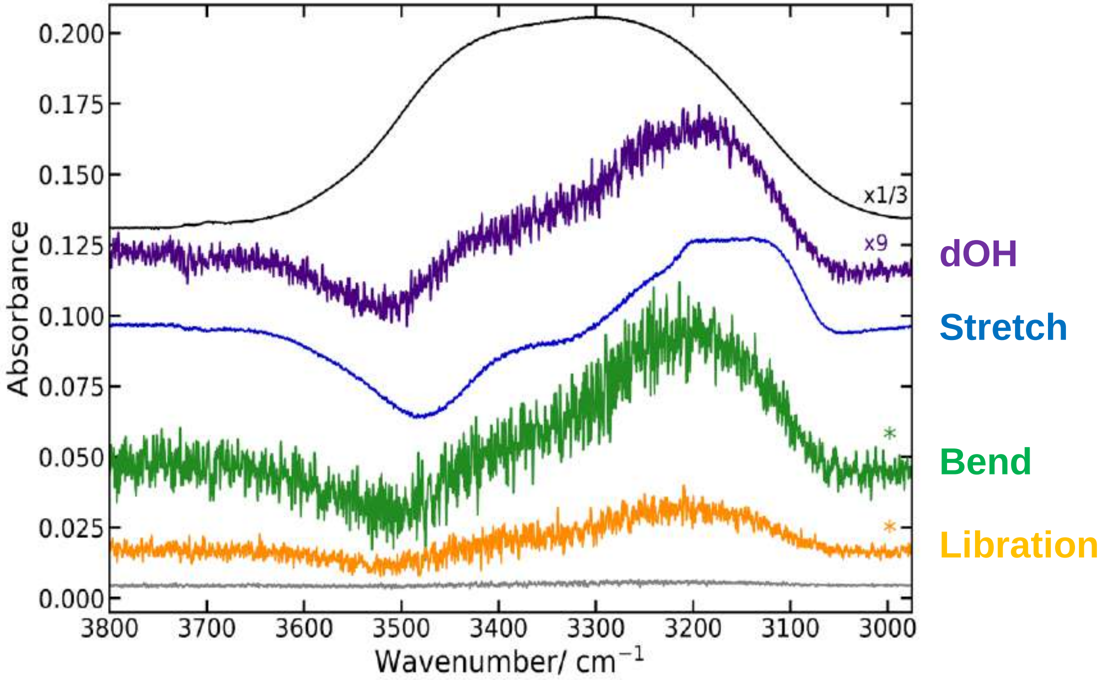


Selective IR-induced Spectral Changes

Amorphous Solid Water (ASW):



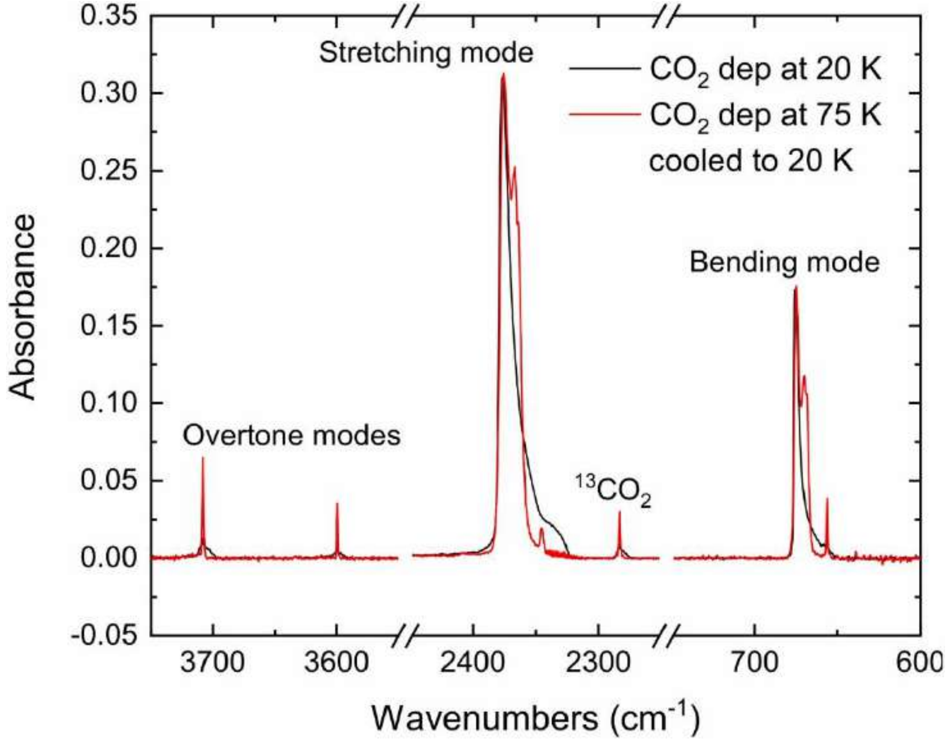
Vibrational excitation heats ice locally causing crystallization-like effects (increased number of H-bonds)

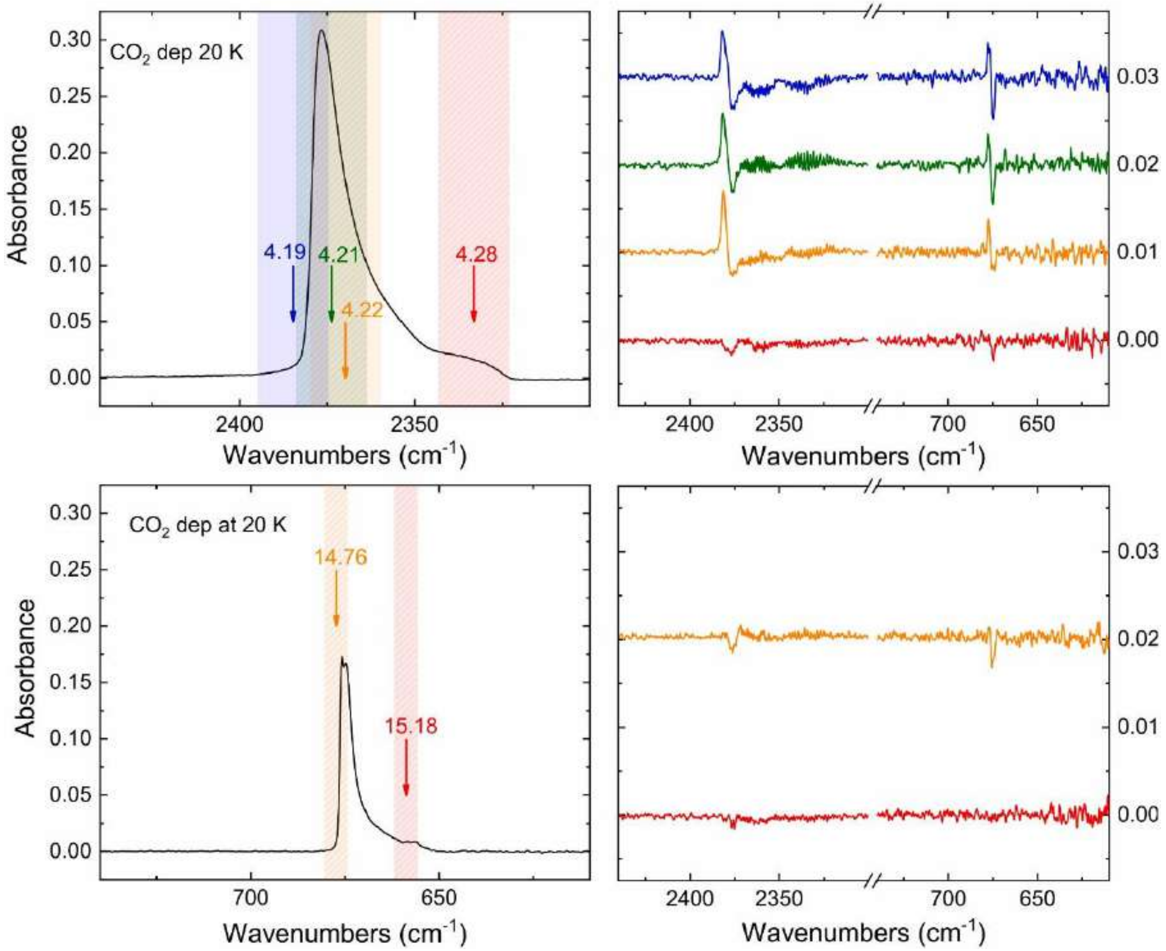


Noble *et al.*, JPCC (2020), Cuppen *et al.*, JPCA (2022)

Selective IR-induced Spectral Changes

Pure CO_2 ices

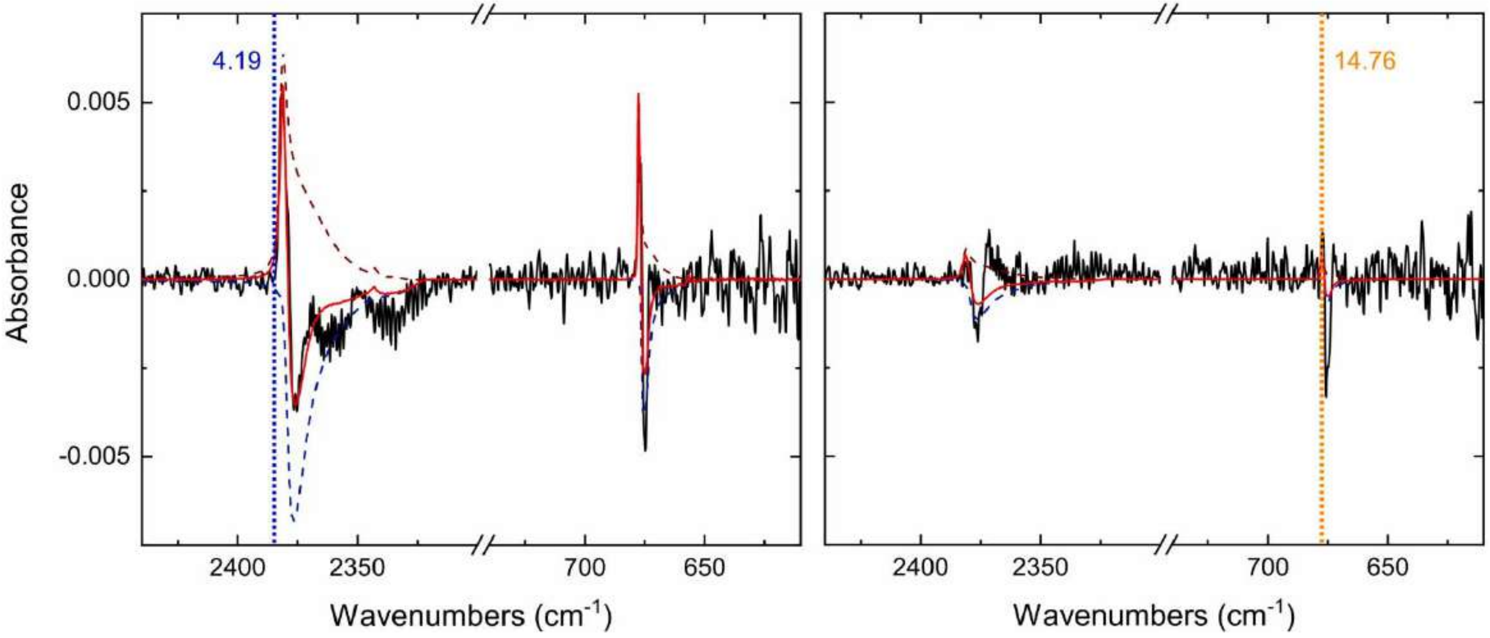


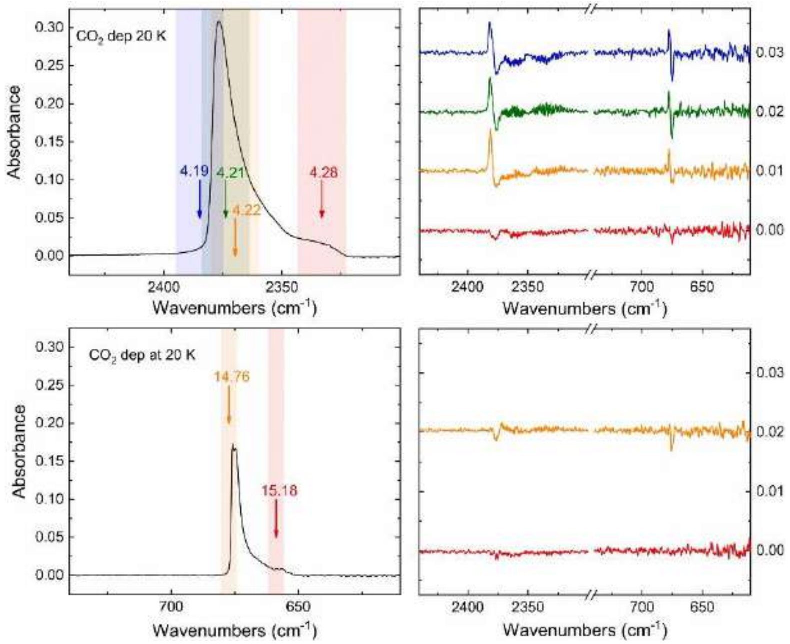


Ioppolo *et al.*, JMS (2022)

Selective IR-induced Spectral Changes

Pure CO_2 ices

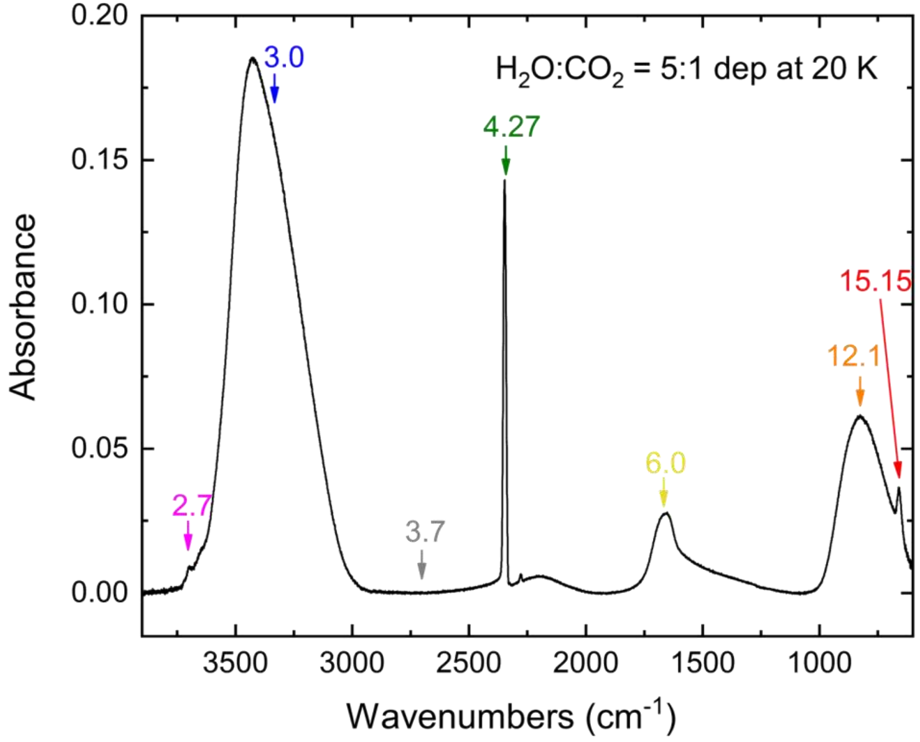


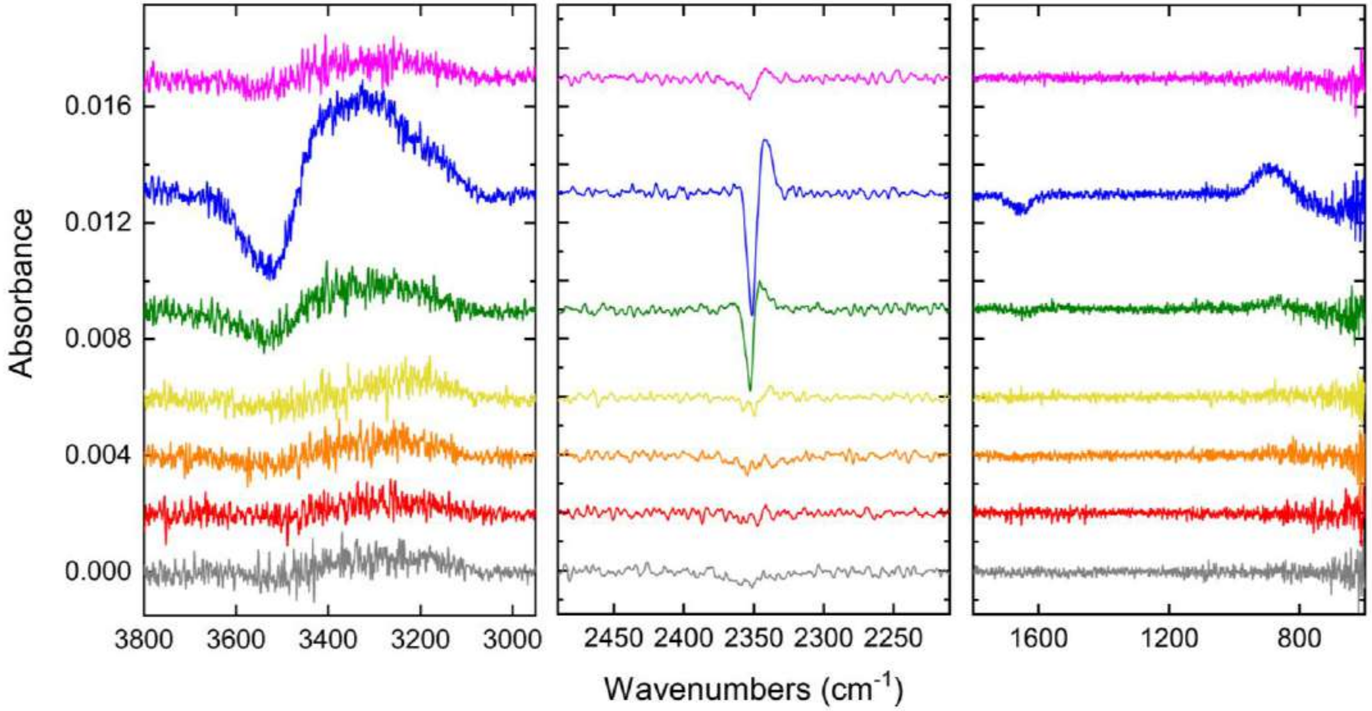


Ioppolo *et al.*, JMS (2022)

Selective IR-induced Spectral Changes

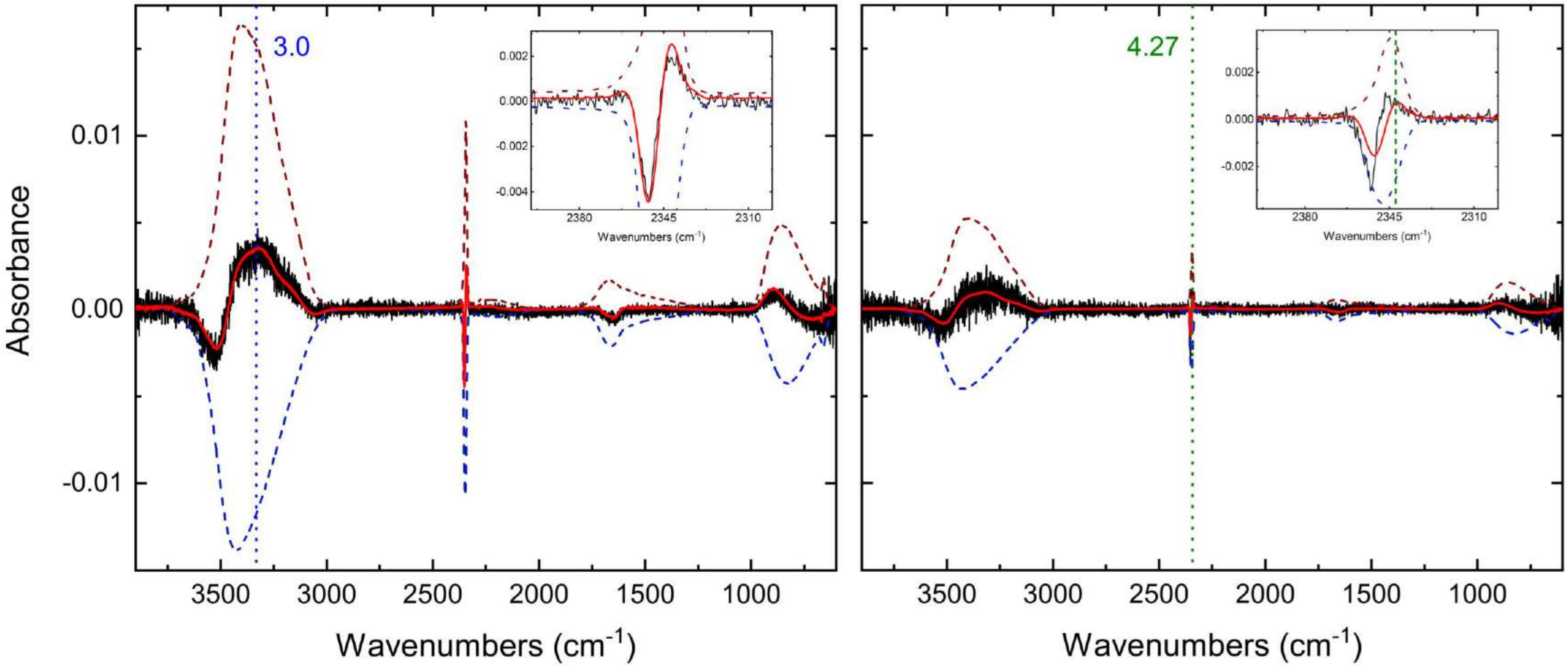
$H_2O:CO_2$ mixed ices





Schrauwen *et al.*, in press

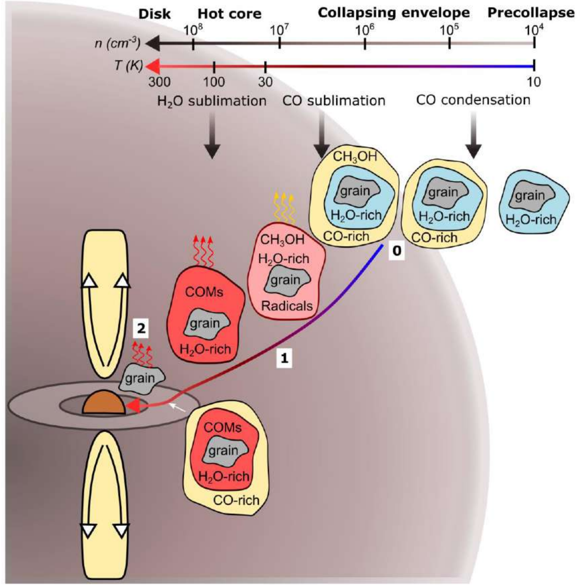
Selective IR-induced Spectral Changes



Schrauwen *et al.*, in press

Key Points

- Solid H_2O, CO, CO_2 are some of the most abundant species detected in ice grain mantles in the ISM
- Debate on the structure (amorphous vs crystalline) of CO_2 samples obtained in laboratory by thin-film techniques is still open – but converging
- IRFEL irradiation of CO_2-rich ices suggests that the ice behaves as an amorphous material when deposited at low temperatures
- Complementary spectroscopic VUV/IR/THz techniques can help understanding the physicochemical evolution of interstellar ices



QUESTIONS