ASTROCHEMISTRY : FROM STARS TO PLANETS

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Table

Table

1. **Why molecules?**
   - **It all begins with nuclei**
   - **Relevance**
2. Where molecules?
   - Hot to cold
   - Dense to thin
   - Ionized, Plasmas, PDRs
3. When molecules?
   - Early universe
   - Disks
   - Planets
4. How to detect?
   - Rotation
   - IR and other
5. How to model?
   - Qualitative/Quantitative
   - Ab initio
6. Conclusion

Chemistry = molecules

ISM

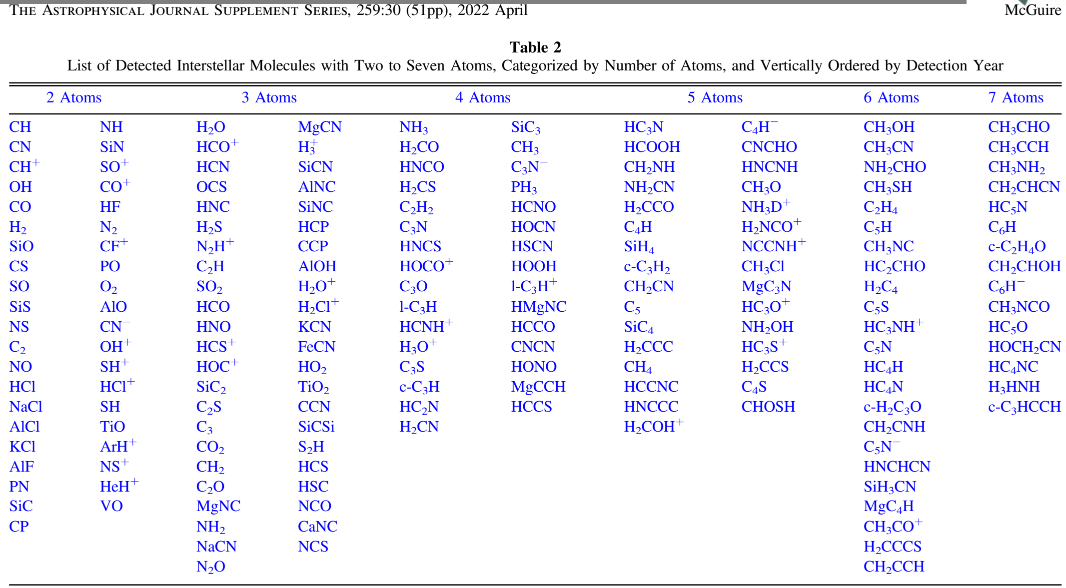

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Table 2

List of Detected Interstellar Molecules with Two to Seven Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

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	H_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	

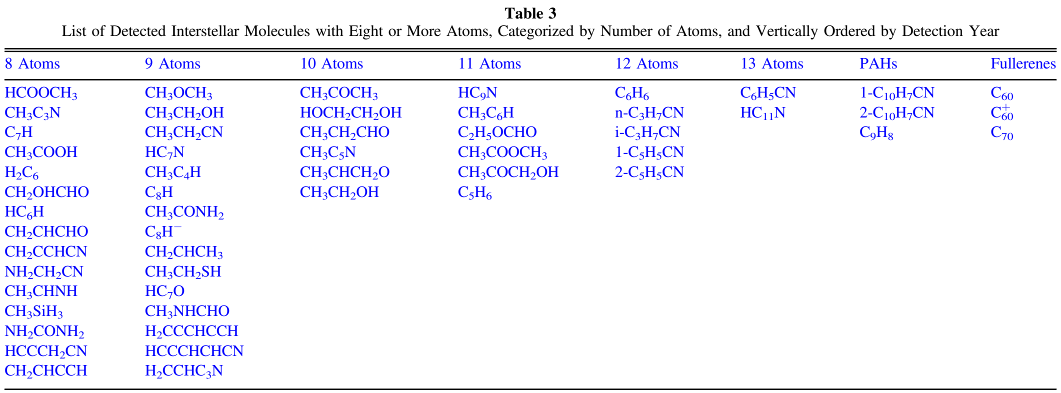
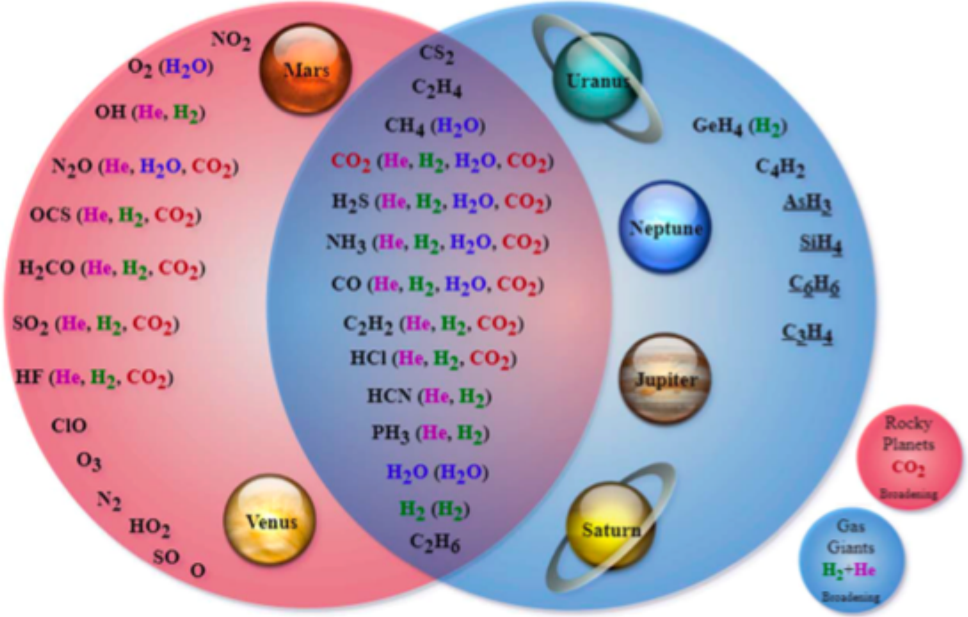


Table 3

List of Detected Interstellar Molecules with Eight or More Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

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_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						

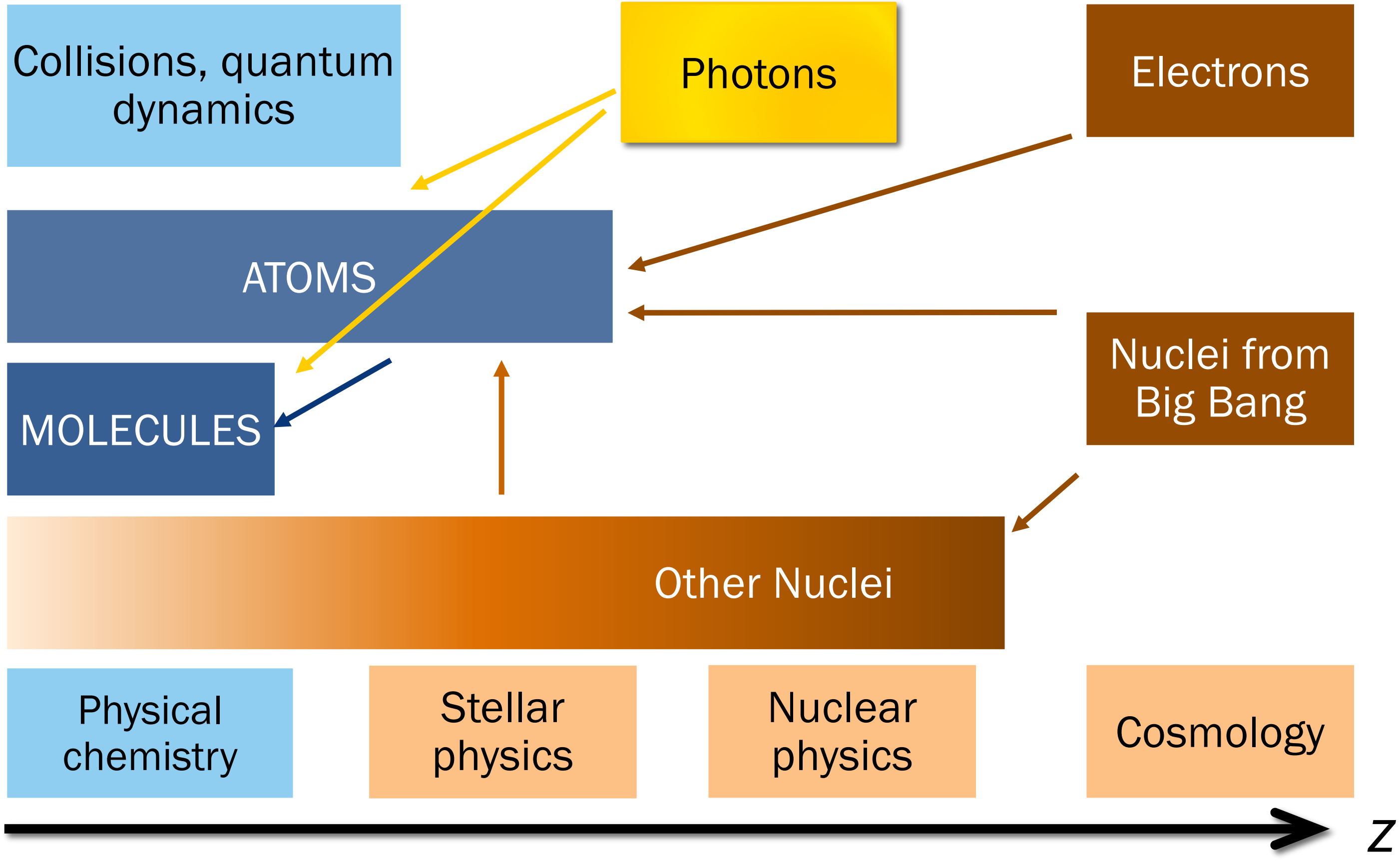
Chemistry = molecules



Planetary atmospheres main gases and prominent molecules

I. Gordon et al.

A Hierarchy of Ingredients



Collisions, quantum dynamics

Photons

Electrons

ATOMS

MOLECULES

Nuclei from Big Bang

Other Nuclei

Physical chemistry

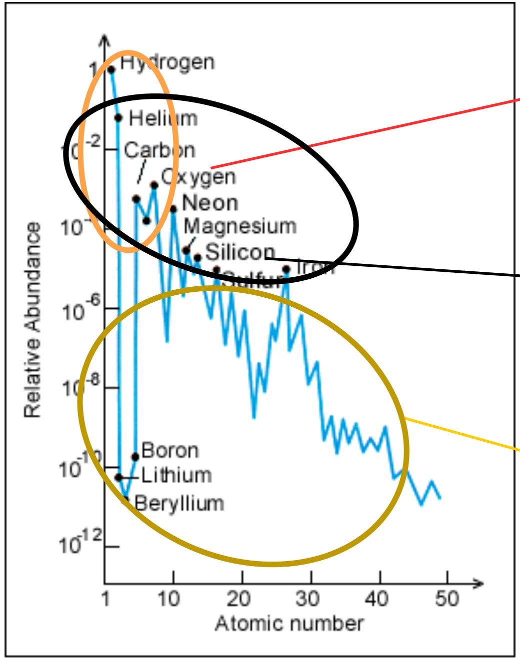
Stellar physics

Nuclear physics

Cosmology

NUCLEAR PHYSICS

Elemental abundances in the Milky Way



Organic chemistry main elements:
H >> O ~ C > N

He + Some heavier elements

Little P, Alkalines, Halogens
VERY little Li, Be, B

FIGURE 3.46 — A summary of the cosmic abundances of the elements and their isotopes.

MOLECULAR PHYSICS

Why looking for molecules ?

- Molecules display a nearly infinite of variety:
  - from the simplemost, H_2, the transition-elements containing molecules to the molecules of life, and the polymers, the PAH's .
  - All categories have been observed in extraterrestrial environments, from meteorites to the edge of the Universe.
- Molecules (and in particular isotopologues) are a beacon for history

- Molecules

are seen in nearly any environment: binding energies from to a few eV → to a few Kelvin

- In Astrophysics,

  The abundance of nuclei is determinental for the abundances of the various molecules: interplay of GeV/MeV to eV/μeV physics (15 orders of magnitude), interplay of high and low energy astrophyics, including super novae
- Measures of fundamental constants history

Tool	Some results
Thermodynamics and kinetics	Out of equilibrium situations, timescales
Spectroscopy	Fundamental constants, identification, abundances
Spectral lineshapes	Opacities, atmospheres (planets and cool stars)
Isotopic compositions	Detailed history, past nuclear physics
Molecular presence and abundances	Physical and chemical characterization, atmospheric composition
Mass spectrometry (probes)	Up to large molecules, polymers

Why is Astrochemistry both an ancient and a modern problem?

Is it good old spectroscopy again, in a new guise? Yes, and difficult.

- Think of the hyperfine structure of ND_2H, the rotational-torsional spectroscopy of CH_3-O-CH_3, to the ro-vibrational spectroscopy of exotic ions (H_3CH_2CN)+ or radicals (CHNH). All these species are known, and some have been discovered by astrophysical spectroscopy.
- **Spectroscopy** ranges from GHz to THz and beyond (cm -> sub-mm, FIR, IR). We have all the instruments, and everything in the spectral line is significant. ‘’Every photon counts’’
- **Spectral line shapes are not in equilibrium**, they are broadened by the Doppler effect and by collisions, they are heterogeneous and optically thick.
- **Spectra of highly excited atoms** is very difficult to model

Why is Astrochemistry both an ancient and a modern problem?

- ***It's also about***: finding a flower in a meadow of weeds. Weeds are common and hardy. Flowers are rare, their signals weak, but what an achievement to find **urea $O{=}C(NH_2)_2$** - the first biomolecule synthesized in the 19th century, which proved that chemistry was universal- sugars and amino acids (these, in meteorites, and perhaps in cometsj).

- ***It's also about***: characterizing the atmospheres of other stars and their planets similar to Neptune, or superbly strange like the Trappist system: 5 planets - IR star. Study meteorology there and one day find bio-signed molecules.

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   - It all begins with nuclei
   - Relevance

2. **Where molecules?**
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   - **Dense to thin**
   - **Ionized, Plasmas, PDRs**

3. When molecules?
   - Early universe
   - Disks
   - Planets

4. How to detect?
   - Rotation
   - IR and other

5. How to model?
   - Qualitative/Quantitative
   - Ab initio

6. Conclusion

A list (not exhaustive…)

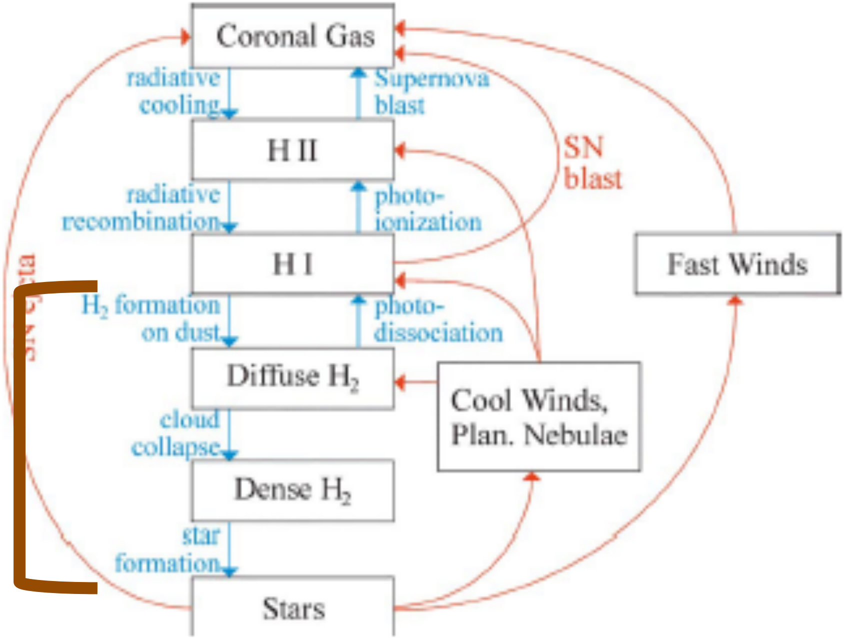
Not mentioned:
PAH 's;
Intergalactic

Object	Conditions
PDR	gradients in ionization temperature. Photophysics dominat.
HI regions	Very low density, equilibrium very slow to reach
Molecular ISM + grains	Cold, some molecules freeze out (deplete) on grain surfaces. Gas and surface chemistru
YSO	Factories of COM's
Dying stars	Factories of COM's
Disks	Tracers of future history. Gradients in space, turbulence, Keplerian motion
Stellar atmospheres	From cool to hot molecules or atomic plasmas. Specific tracers
Planetary atmospheres	From diffuse to dense, vast ranges
Extragalactic	Metallicities, star formation rates
Early universe	Only H, He e-; traces of D, Li

James Graham's Conception of The ISM as a Complex System

The Interstellar Medium
Astronomy 216
Spring 2008

Al Glassgold
University of California, Berkeley



T and radiation compatible with chemistry

Conditions of interstellar gases

- Large range in temperature & density
  $T \approx 10 - 10^6$ K $n \approx 10^{-3} - 10^6$ cm^{-3}
- Even dense regions are “ultra-high vacuum”
  lab UHV: 10^{-10} Torr ($n \approx 4 \times 10^6$ cm^{-3})
  (STP conditions: $n = 3 \times 10^{19}$ cm^{-3})

Ionized gases

H II regions - bright nebulae associated with regions of star formation & molecular clouds; ionized by stellar UV photons from early-type (OB) stars

$T \approx 10^4$ K & $n_e \approx 0.1 - 10^4$ cm^{-3}

Warm Ionized Medium (WIM)

$T \approx 8000$ K & $n_e \approx 0.025$ cm^{-3}

Hot Ionized Medium (HIM) - tenuous gas pervading the ISM, ionized by electron impact

$T \approx 4.5 \times 10^5$K & $n_e \approx 0.035$ cm^{-3}

Neutral gases

Cool clouds (CNM)

$T \approx 100$ K & $n \approx 40$ cm^{-3}

Warm neutral gas (WNM)

$T \approx 7500$ K & $n \approx 0.5$ cm^{-3}

Cold dark clouds ($M \approx 10 - 1000\ M_\odot$)

$T \geq 10$ K & $n \approx 10^2 - 10^4$ cm^{-3}

Giant molecular clouds ($M \approx 10^3 - 10^5\ M_\odot$)

$T \geq 20$ K & $n \approx 10^2 - 10^4$ cm^{-3}

with high density cores & clumps that form stars.

Where are molecules? (simplified)

Main gas depend on object scrutinized

- ISM, YSO, Stars :
  H, H_2, (He), oy cold plasma e^-
- Comets : H_2O
- Atmospheres: H_2, CH_4, NH_3, N_2, SO_2, O_2 (Earth), mixtures

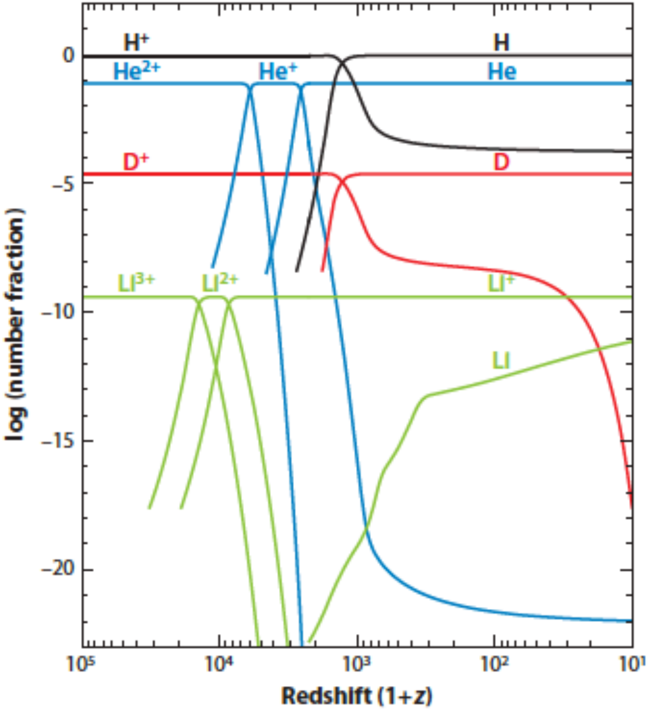
The main gas is very often optically inactive in microwave, not necessarily in IR
Active molecule as traces.

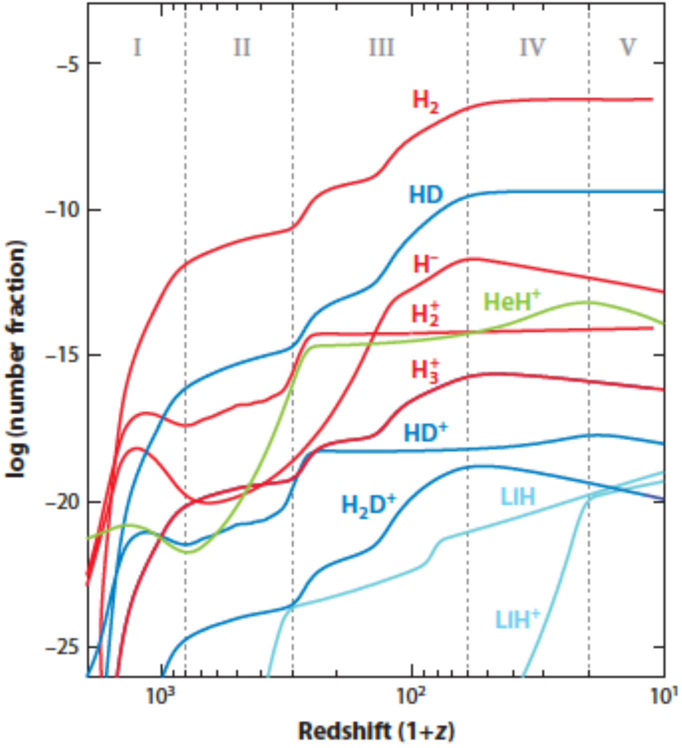
Special mention: early universe: Chemistry before stars

The Dawn of Chemistry

Daniele Galli and Francesco Palla

INAF-Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, 50125 Firenze, Italy; email: galli@arcetri.astro.it, palla@arcetri.astro.it





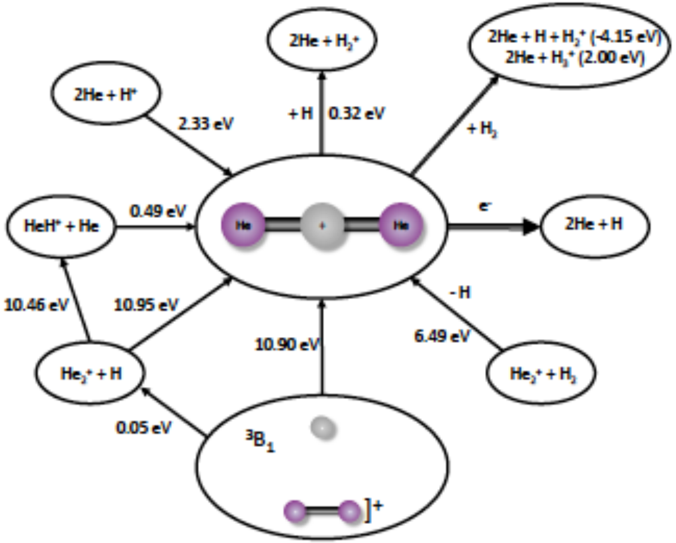
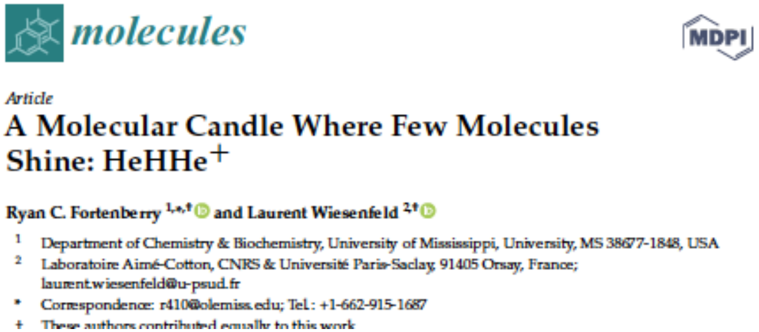


Figure 2. The pathways and ZPVE-corrected energetics for the creation and destruction of $^{1}\Sigma_{g}^{+}$ HeHHe^{+}. Positive energies favor the products based on the direction of the arrow. Negative energies favor the reactants.



molecules

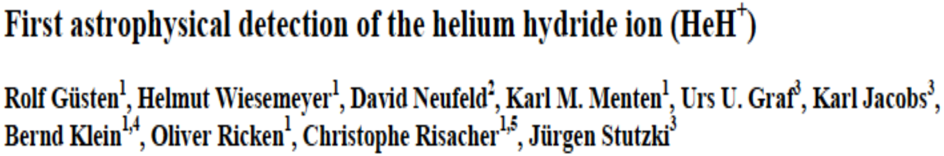
MDPI

Article

A Molecular Candle Where Few Molecules Shine: HeHHe^{+}

Ryan C. Fortenberry [1,*,†] and **Laurent Wiesenfeld** [2,†]

[1] Department of Chemistry & Biochemistry, University of Mississippi, University, MS 38677-1848, USA
[2] Laboratoire Aimé-Cotton, CNRS & Université Paris-Saclay, 91405 Orsay, France; laurent.wiesenfeld@u-psud.fr
[*] Correspondence: r410@olemiss.edu; Tel.: +1-662-915-1687
[†] These authors contributed equally to this work



First astrophysical detection of the helium hydride ion (HeH^{+})

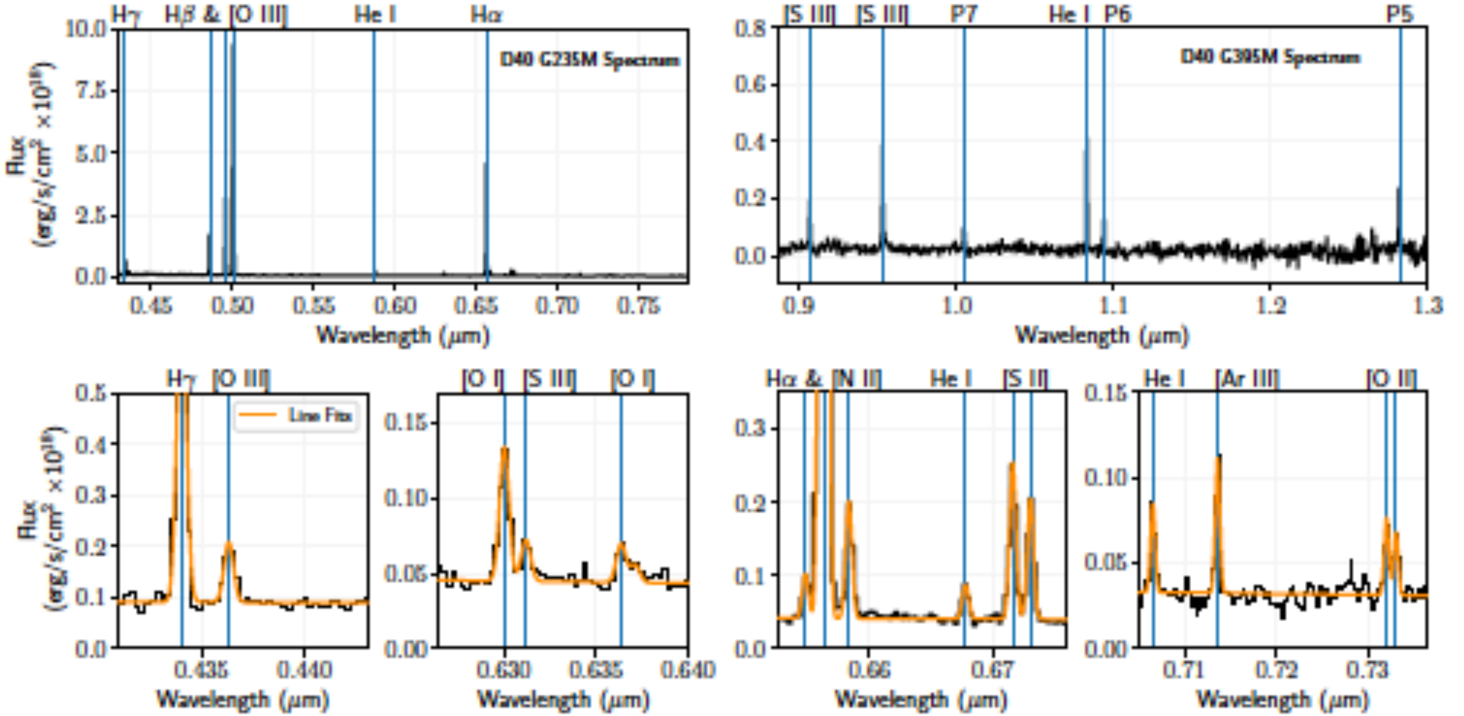
Rolf Güsten[1], Helmut Wiesemeyer[1], David Neufeld[2], Karl M. Menten[1], Urs U. Graf[3], Karl Jacobs[3], Bernd Klein[1,4], Oliver Ricken[1], Christophe Risacher[1,5], Jürgen Stutzki[3]

Extra galactic

CECILIA: Direct O, N, S, and Ar Abundances in Q2343-D40, a Galaxy at $z \sim 3$

Noah S. J. Rogers,[1] Allison L. Strom,[1,2] Gwen C. Rudie,[3] Ryan F. Trainor,[4] Menelaos Raptis,[4] and Caroline von Raesfeld[1,2]

Direct Gas-Phase Abundances at $z \sim 3$ 3



IMAGES, SPECIFIC CASES

* **Dense clouds**

T ~ 5- 10 K, n ~ 10^5 cm^{-3}

x_e ~ 10^{-8}

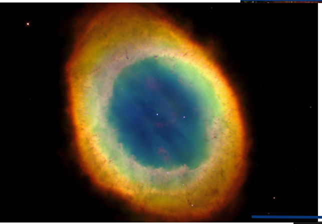
Tracers : CO, HCO+, N2H+,H2D+

* **Diffuse clouds**

T ~ 100 K, n ~ 10^2 cm^{-3}

x_e ~ 10^{-4}

Tracers : OH, CH^+, HC

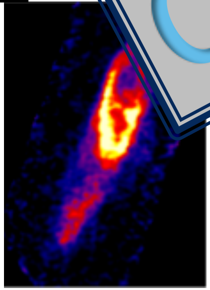


* **Photo**

T

C+

Oldies but Goodies



* **Jets**

T ~ 10-1000 K, n ~ 10^{4-7} cm^{-3}

Tracers : CO, HCO+, SiO

Star forming regions/ YSO environments

T ~ 5- 300 K, n ~ 10^{4-7} cm^{-3}

x_e ~ $10^{-9-1\text{à}}$

Tracers : CO, HCO+,H2O

H2CO,CH3OH,

N,S containing molecules

* **Dense clouds**
$T \sim 5\text{-} 10$ K, $n \sim 10^5$ cm^{-3}
$x_e \sim 10^{-8}$
Tracers : CO, HCO+, N2H+,H2D+

* **Diffuse clouds**
$T \sim 100$ K, $n \sim 10^2$ cm^{-3}
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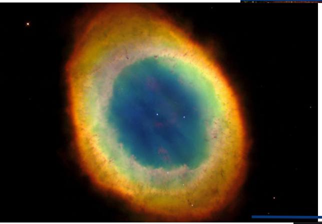
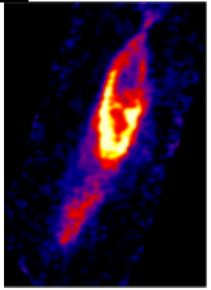
Tracers : OH, CH^+, HCO^+



* **Photon-Dominated Regions**
$T \sim 1000$ K, $n \sim 10^4$ cm^{-3}
$x_e \sim 10^{-4}$
Tracers : CN, CH, $CH^{+,}$ C+



* Jets

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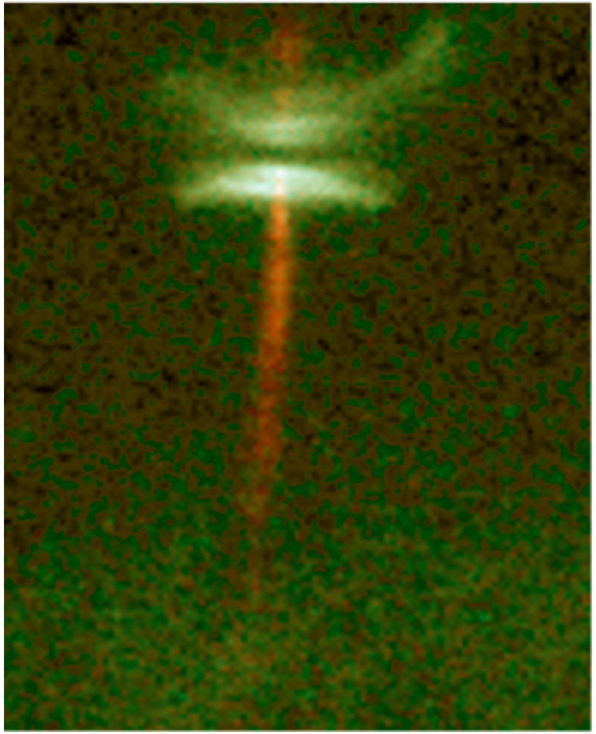
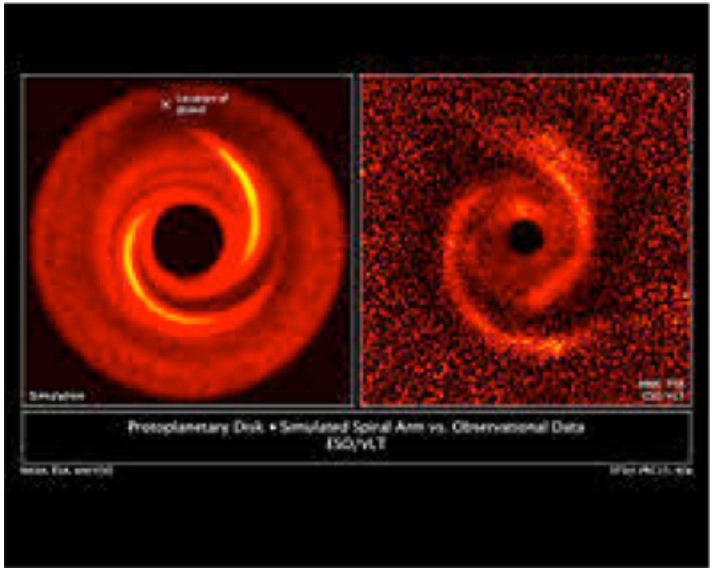
Star forming regions/ YSO environments

$T \sim 5\text{-} 300$ K, $n \sim 10^{4\text{-}7}$ cm^{-3}
$x_e \sim 10^{-9-\text{1à}}$
Tracers : CO, HCO+,H2O
H2CO,CH3OH,
N,S containing molecules

Protoplanetary disks





Protoplanetary Disk • Simulated Spiral Arm vs. Observational Data
ESO/VLT

Protoplanetary Disks

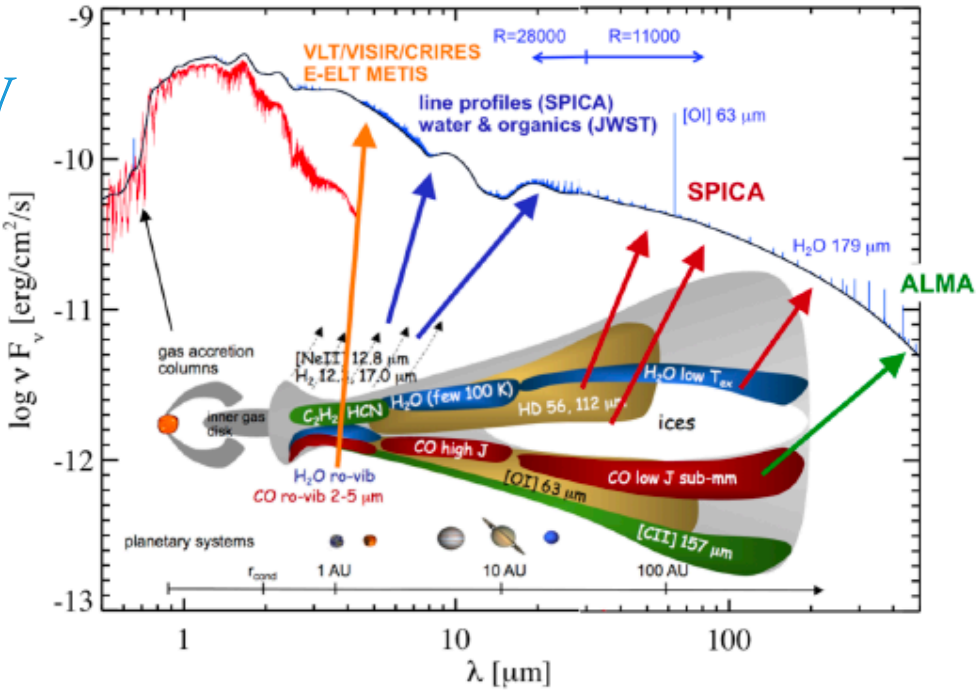


Figure 2. An overview of line emission from near-IR to submm wavelengths from planet forming disks and existing and upcoming instrumentation to detect it. The model SED is that of a typical T Tauri disk using two different spectral resolutions ($R = 28\,000$ and $R = 11\,000$ relevant for the planned SMI and SAFARI instruments onboard the proposed SPICA mission).

I Kamp, WF Thi et al.

Postpone the atmospheres…

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3. Conclusion

How to detect?
A note on units

1 kcal/mole ≈ 43 meV ≈ 503 K ≈ 350 cm-1 ≈ 10 THz

Chemistry

Thermodynamics

Spectroscopy

Electron, atomic, nuclear physics

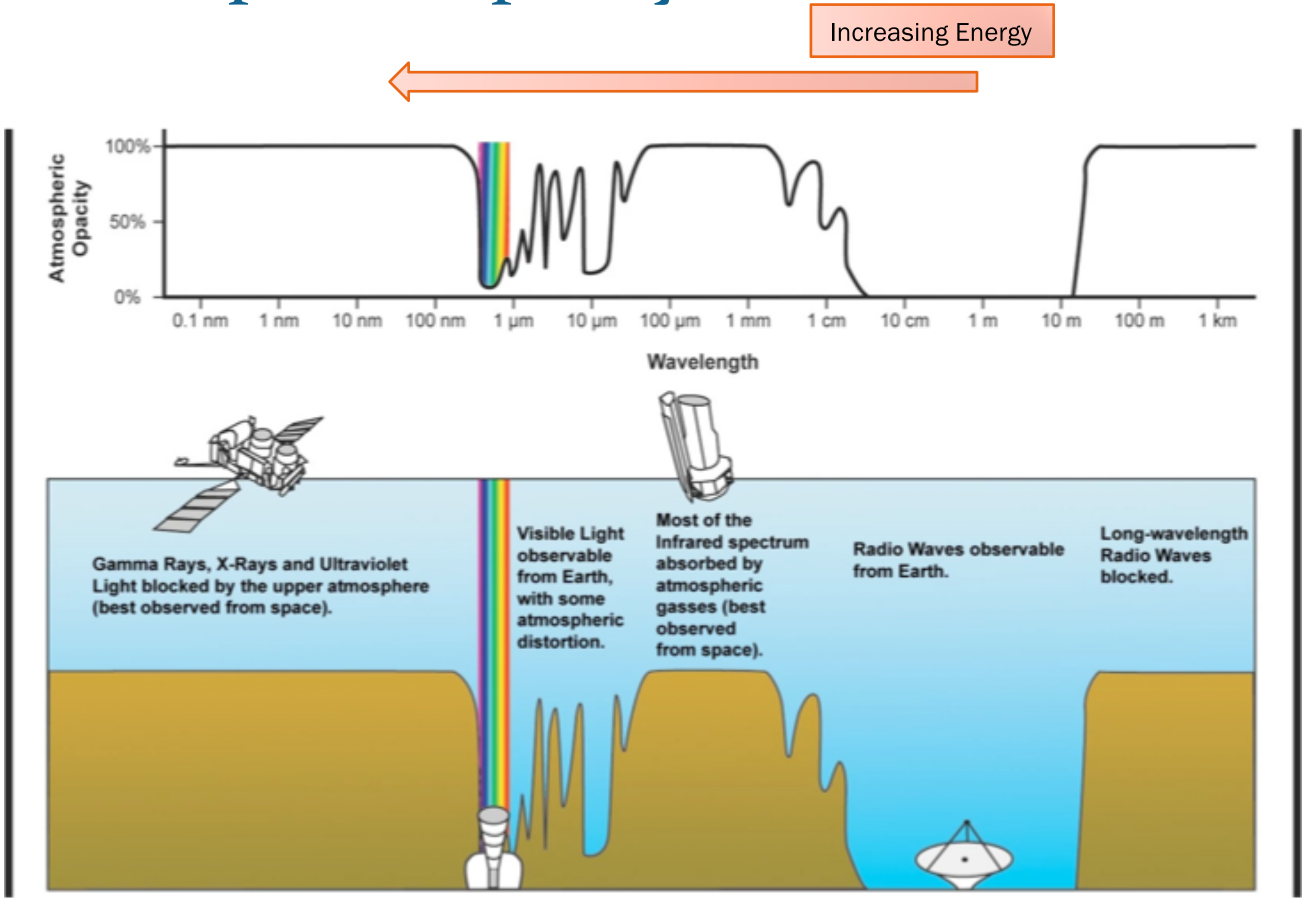
- **Probes:** many ways to deal with molecules, from chromatography to mass spectrometry. Valid for example in our atmosphere, for planetary probes (Cassini, Rosetta,…)

- **Telescopes:** wavelengths from cm to sub-Å, from radio waves to gamma-rays, from µeV to GeV (cosmic rays). Single optics (dish or mirror) or interferometry (ALMA,Plateau de Bures, VLA, VLTI, Gemini)

Quantum states		Energies	Type of radiation	How to detect
Hyperfine structure		kHz → MHz	Longwave to radio	**Usually indirectly detected**
Fine structure (mostly atoms		100GHz → a few THz	microwave to FIR	**ground & space** **Favorable for high-z atomic gasses**
Rotation		0.5 → 60 cm-1	millimiter to sub-mm	**ground (mostly) and space / plane/balloons**
Vibration		100 → A few 1000 cm-1	FIR to IR	**Space and balloons** **Favorable for high-z molecular gasses**
Electronic transitions	Molecules	up to a few eV	visible, UV	**ground and space**
	Atoms	up to a few keV	Visible → X-rays	**ground and space**

1 kcal/mole ≈ 43 meV ≈ 503 K ≈ 350 cm-1 ≈ 10 THz

Atmospheric opacity



Atmospheric opacity

Gamma rays, nuclear physics

Violent events, supernovae

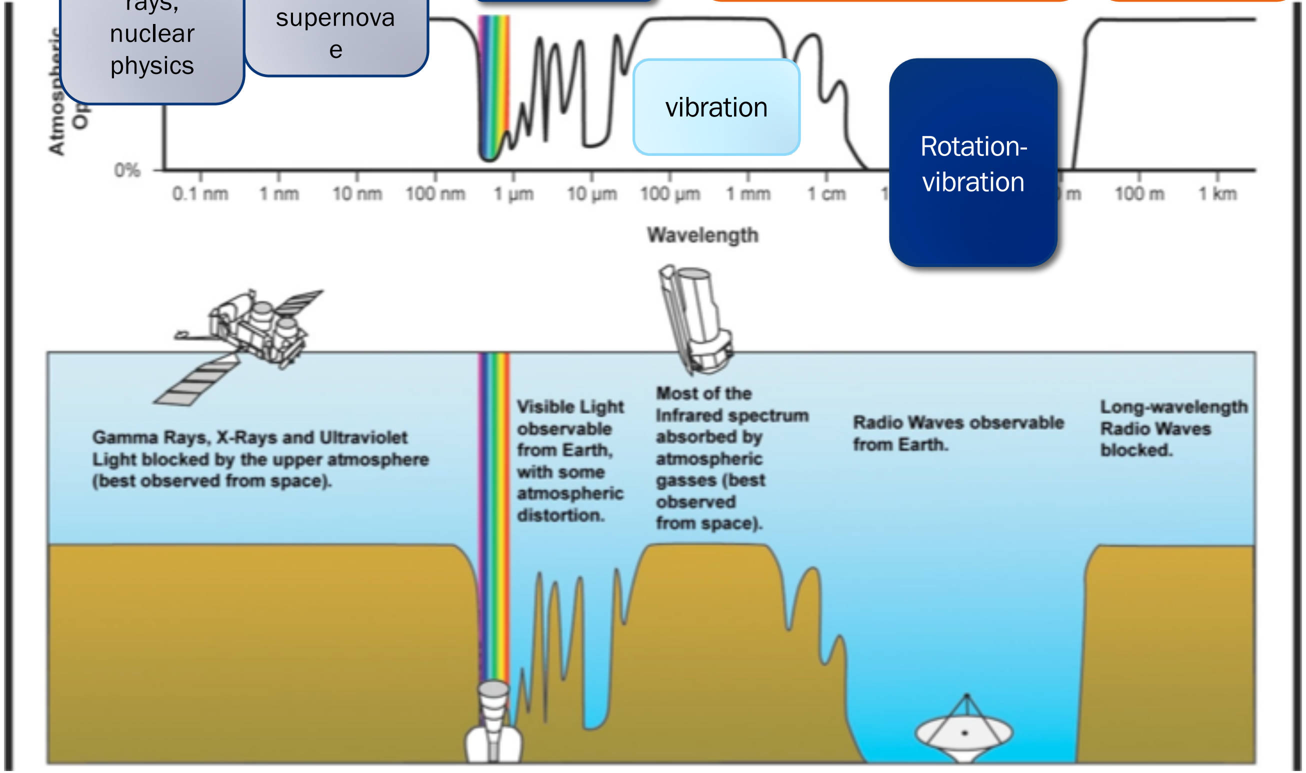
Hot gas

high-z atoms cosmological background

high-z molecules

vibration

Rotation-vibration



Gamma Rays, X-Rays and Ultraviolet Light blocked by the upper atmosphere (best observed from space).

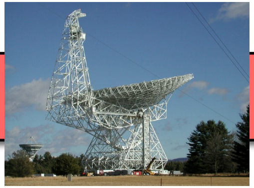
Visible Light observable from Earth, with some atmospheric distortion.

Most of the Infrared spectrum absorbed by atmospheric gasses (best observed from space).

Radio Waves observable from Earth.

Long-wavelength Radio Waves blocked.

GBT, VLA < 50 GHz



IRAM 80… 270 GHz

ALMA 80… 950 GHz

Herschel 480 … 1910 GHz (HIFI)

esa

HERSCHEL

Space Observatory

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	Atoms	up to a few keV	Visible → X-rays	**ground and space**

1 kcal/mole ≈ 43 meV ≈ 503 K ≈ 350 cm-1 ≈ 10 THz

Young stellar object: solar mass binary

The ALMA-PILS survey: inventory of complex organic molecules towards IRAS 16293-2422 A

J. Jørgensen et al., Niels Bohr Inst. et al.

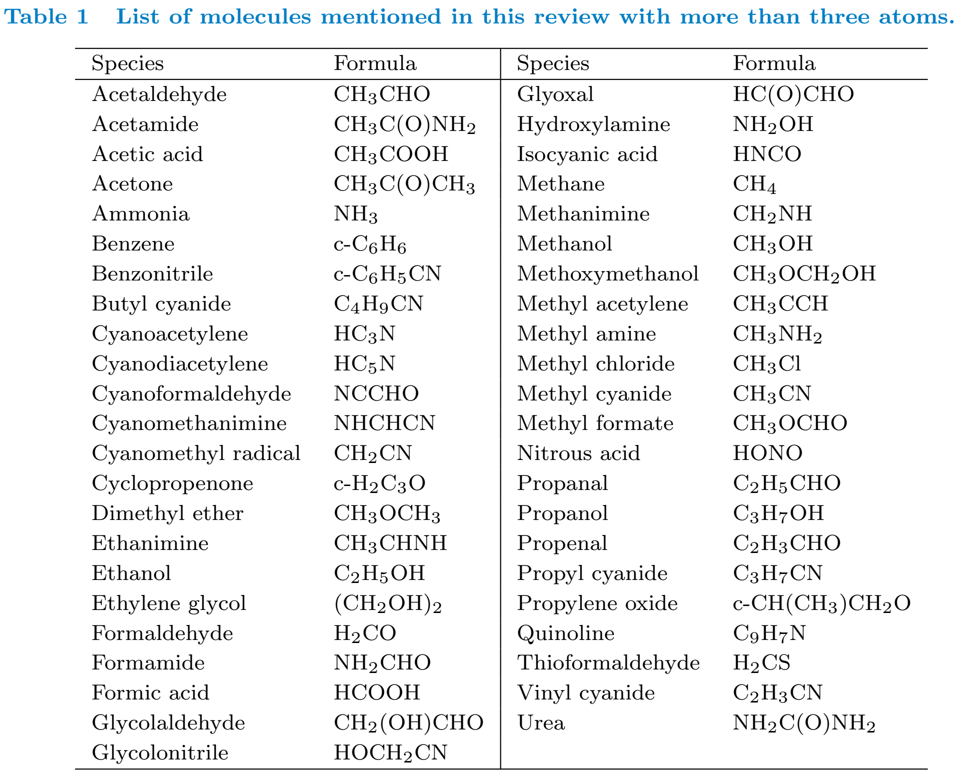
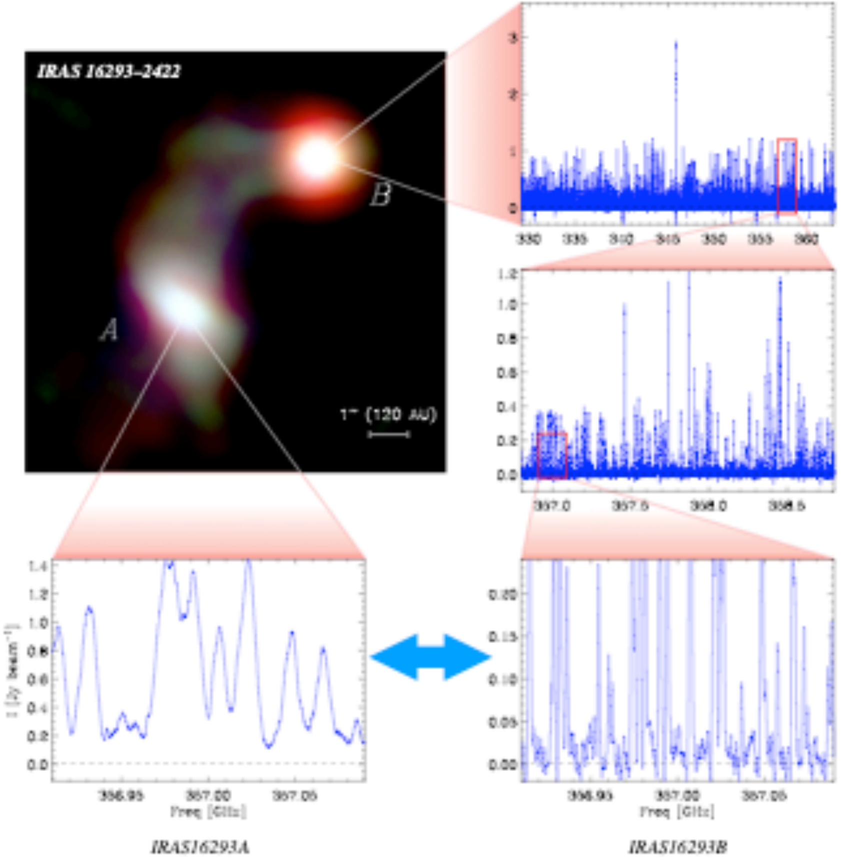


Table 1 List of molecules mentioned in this review with more than three atoms.

Species	Formula	Species	Formula
Acetaldehyde	CH_3CHO	Glyoxal	$HC(O)CHO$
Acetamide	$CH_3C(O)NH_2$	Hydroxylamine	NH_2OH
Acetic acid	CH_3COOH	Isocyanic acid	$HNCO$
Acetone	$CH_3C(O)CH_3$	Methane	CH_4
Ammonia	NH_3	Methanimine	CH_2NH
Benzene	c-C_6H_6	Methanol	CH_3OH
Benzonitrile	c-C_6H_5CN	Methoxymethanol	CH_3OCH_2OH
Butyl cyanide	C_4H_9CN	Methyl acetylene	CH_3CCH
Cyanoacetylene	HC_3N	Methyl amine	CH_3NH_2
Cyanodiacetylene	HC_5N	Methyl chloride	CH_3Cl
Cyanoformaldehyde	$NCCHO$	Methyl cyanide	CH_3CN
Cyanomethanimine	$NHCHCN$	Methyl formate	CH_3OCHO
Cyanomethyl radical	CH_2CN	Nitrous acid	$HONO$
Cyclopropenone	c-H_2C_3O	Propanal	C_2H_5CHO
Dimethyl ether	CH_3OCH_3	Propanol	C_3H_7OH
Ethanimine	CH_3CHNH	Propenal	C_2H_3CHO
Ethanol	C_2H_5OH	Propyl cyanide	C_3H_7CN
Ethylene glycol	$(CH_2OH)_2$	Propylene oxide	c-$CH(CH_3)CH_2O$
Formaldehyde	H_2CO	Quinoline	C_9H_7N
Formamide	NH_2CHO	Thioformaldehyde	H_2CS
Formic acid	$HCOOH$	Vinyl cyanide	C_2H_3CN
Glycolaldehyde	$CH_2(OH)CHO$	Urea	$NH_2C(O)NH_2$
Glycolonitrile	$HOCH_2CN$		

The ALMA-PILS survey: inventory of complex organic molecules towards IRAS 16293-2422 A



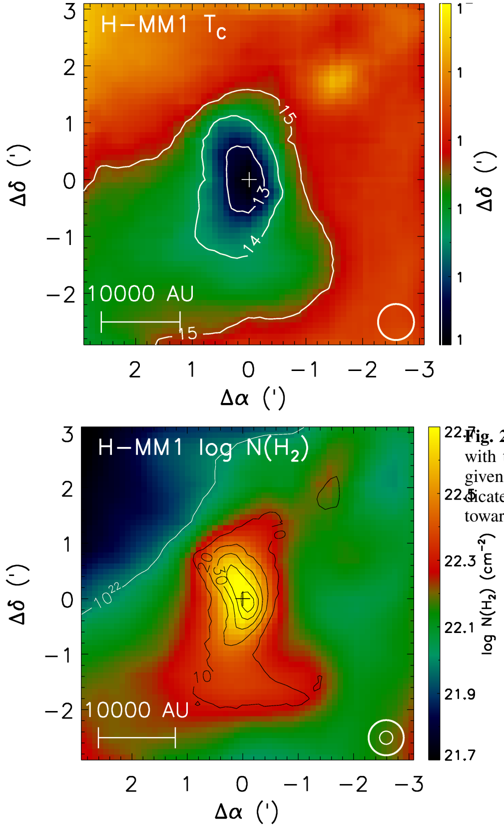


Fig. 1. Dust colour temperature (T_C, top) and the H_2 column density ($N(H_2)$, bottom) maps of H-MM1 as derived from Herschel/SPIRE maps at 250, 350, and 500 μm. The distribution of the 850 μm emission observed with SCUBA-2 is indicated with black contours on the $N(H_2)$ map. The contour levels are 10 to 50 by 10 MJy sr^{-1}. The column

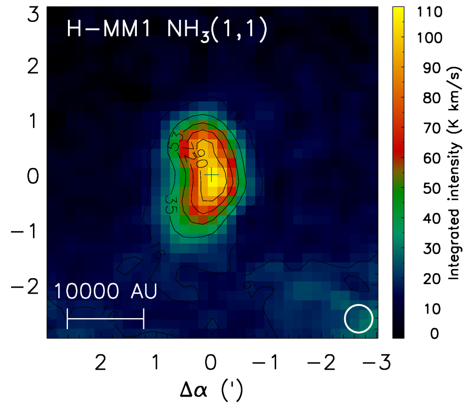


Fig. 2. Integrated $NH_3(1,1)$ intensity (T_{MB}) map of H-MM1 observed with the GBT. The intensity unit is K km s^{-1}, and the colour scale is given on the right. The 32″ beam size of the GBT at 23.7 GHz is indicated in the bottom right. The APEX and IRAM spectra were taken towards the position indicated with a plus sign.

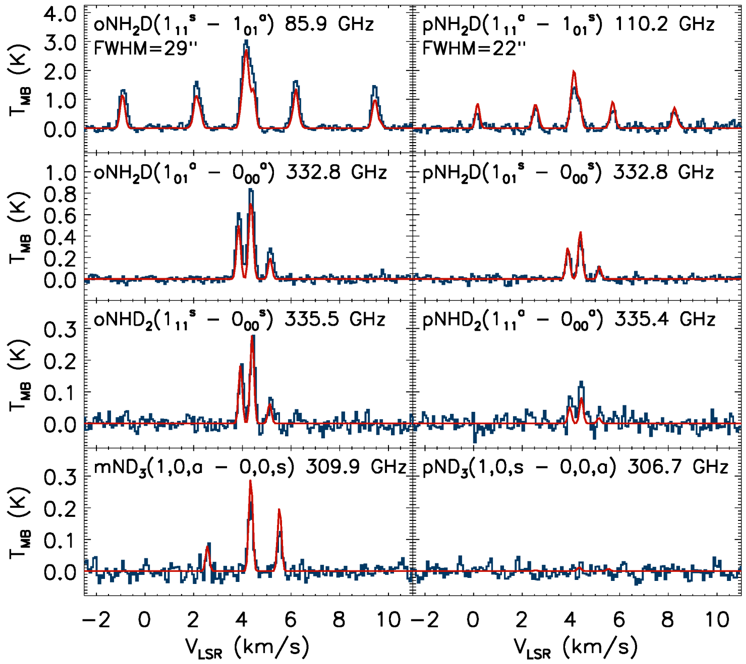


Fig. 16. Deuterated ammonia spectra produced by the core model at the time 3 10^5 yr (red curves) together with the observed spectra (histograms).

Starless core Ophiuchus/H-MM1

Harju at al. 2016

Stellar atmosphere : case of brown dwarf

Tannock at al., MNRAS, 2022

A 1.46–2.48 μm spectroscopic atlas of a T6 dwarf (1060 K) atmosphere with IGRINS: first detections of H_2S and H_2, and verification of H_2O, CH_4, and NH_3 line lists

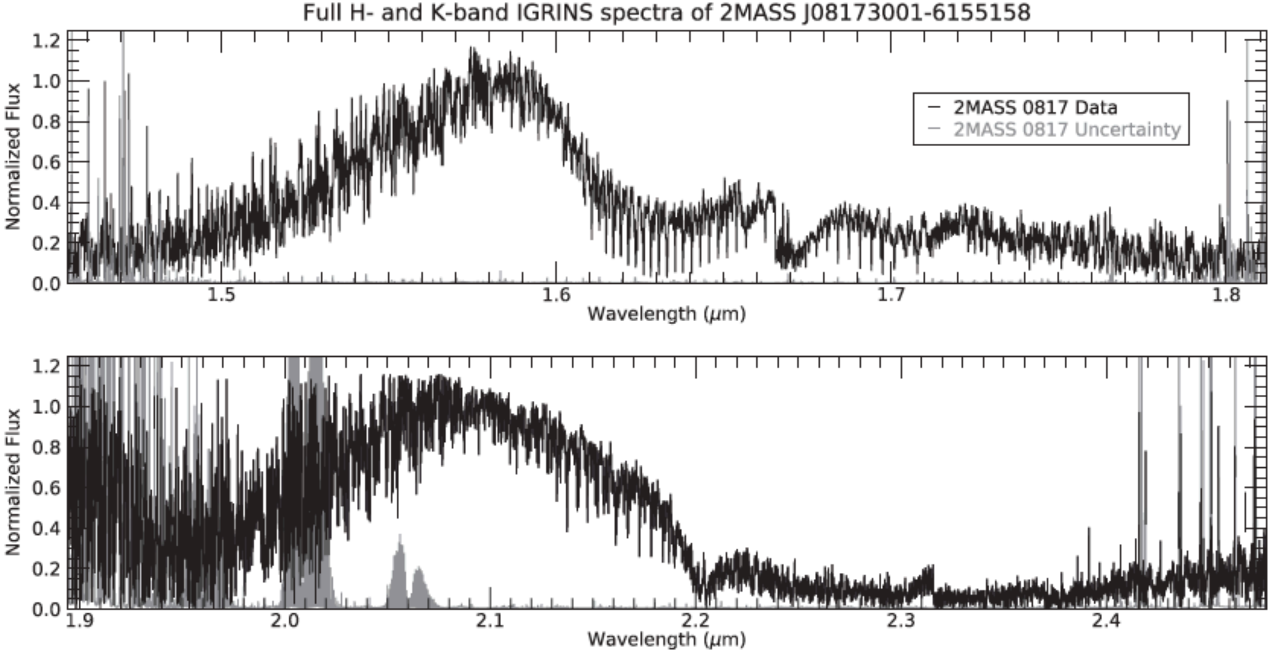
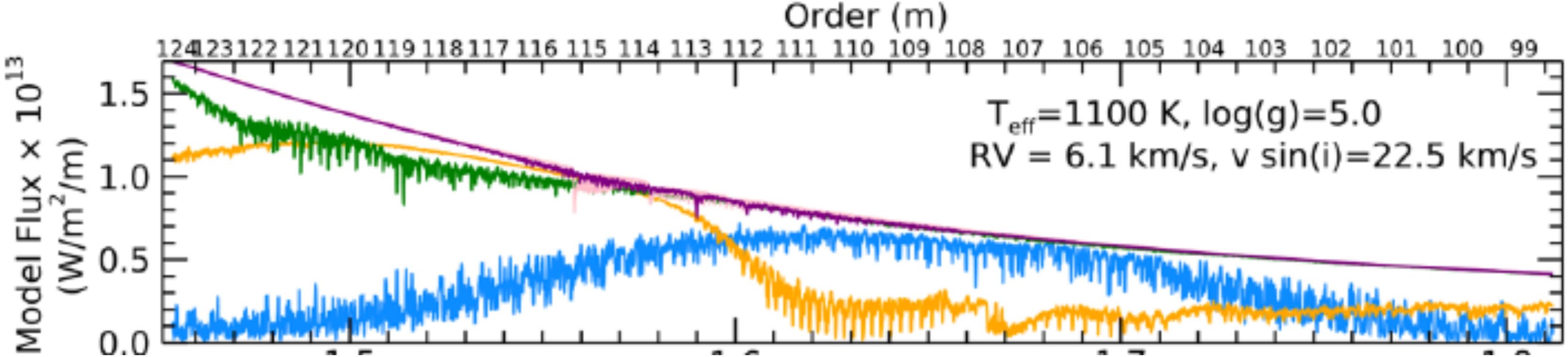
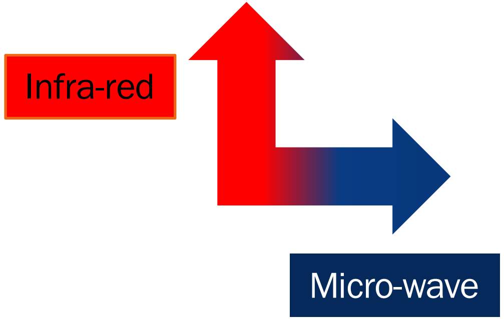


Figure 2. The full *H*- and *K*-band IGRINS spectra of 2MASS J08173001−6155158 with epochs combined and the orders stitched together. This figure does not include the quadratic correction described in Section 3.1. These data appear noisy, but in fact have S/N ≃ 300 at the peak of the *H*-band spectrum and S/N ≃ 200 at the *K*-band peak. The apparent noise spikes are all absorption features, and can be seen in detail in the full set of figures in the Appendix, available in the Online Supplementary Material.





Infra-red

Micro-wave

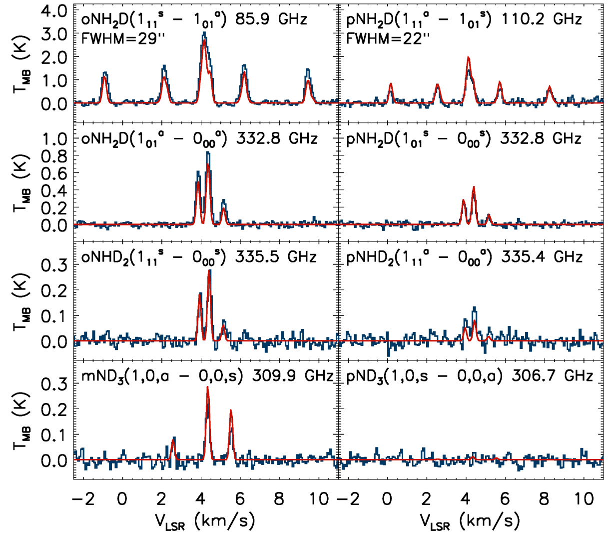
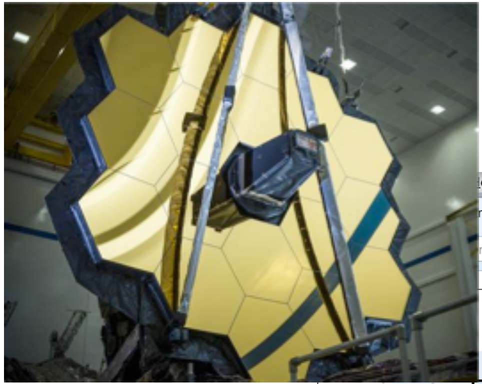
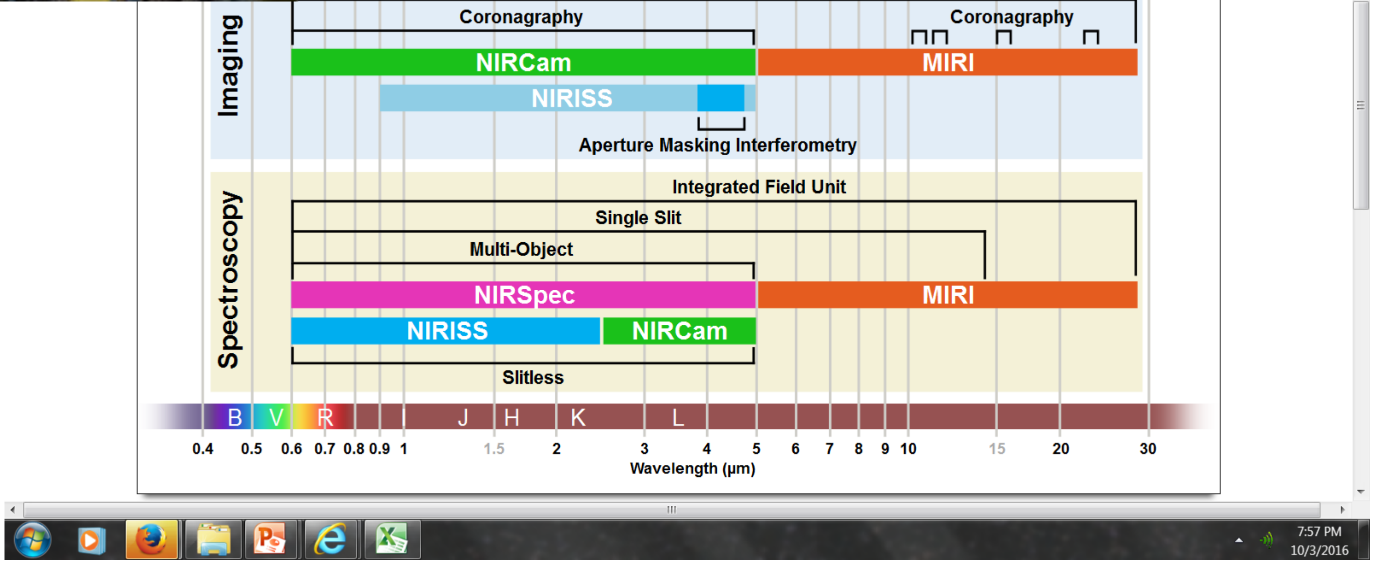


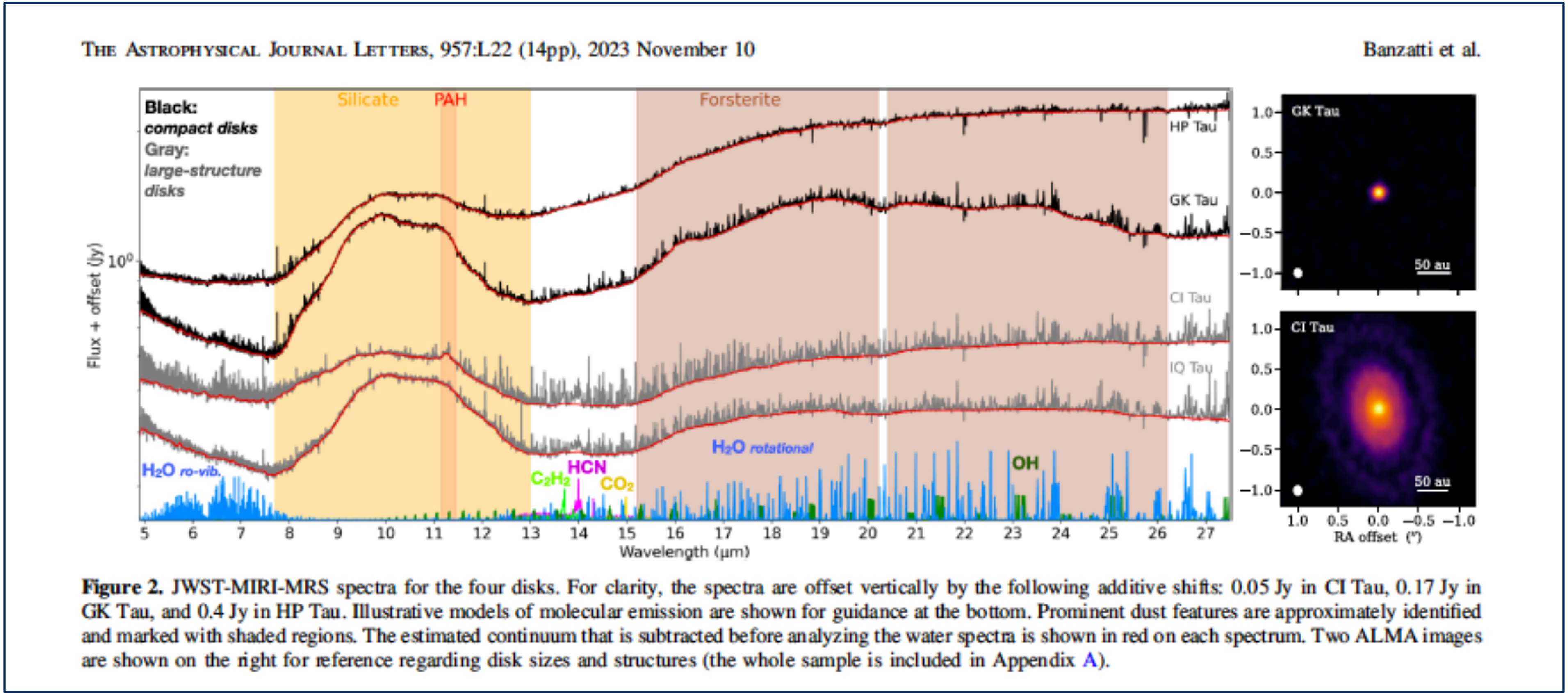
Fig. 16. Deuterated ammonia spectra produced by the core model at

Special topic : JWST





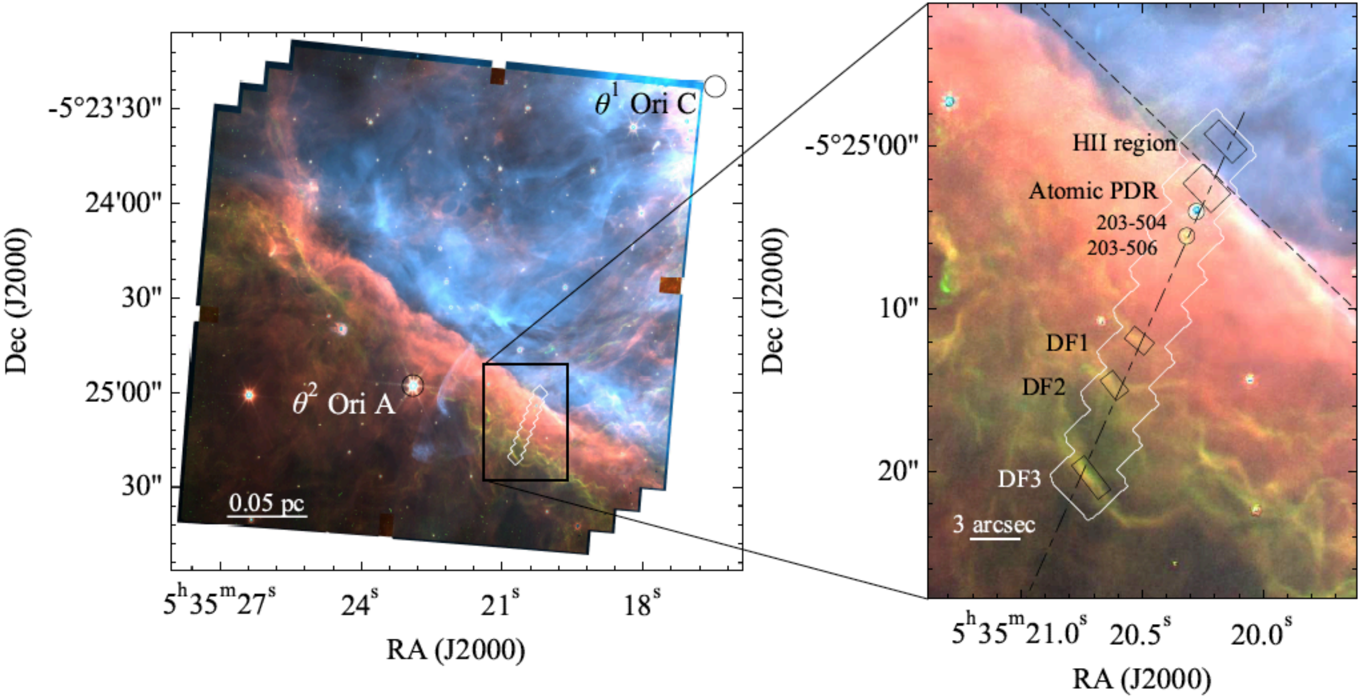
Protoplanetary Disks



The Astrophysical Journal Letters, 957:L22 (14pp), 2023 November 10 Banzatti et al.

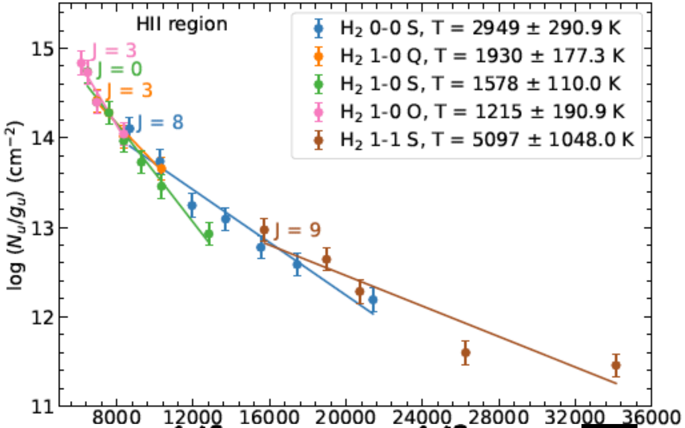
Figure 2. JWST-MIRI-MRS spectra for the four disks. For clarity, the spectra are offset vertically by the following additive shifts: 0.05 Jy in CI Tau, 0.17 Jy in GK Tau, and 0.4 Jy in HP Tau. Illustrative models of molecular emission are shown for guidance at the bottom. Prominent dust features are approximately identified and marked with shaded regions. The estimated continuum that is subtracted before analyzing the water spectra is shown in red on each spectrum. Two ALMA images are shown on the right for reference regarding disk sizes and structures (the whole sample is included in Appendix A).

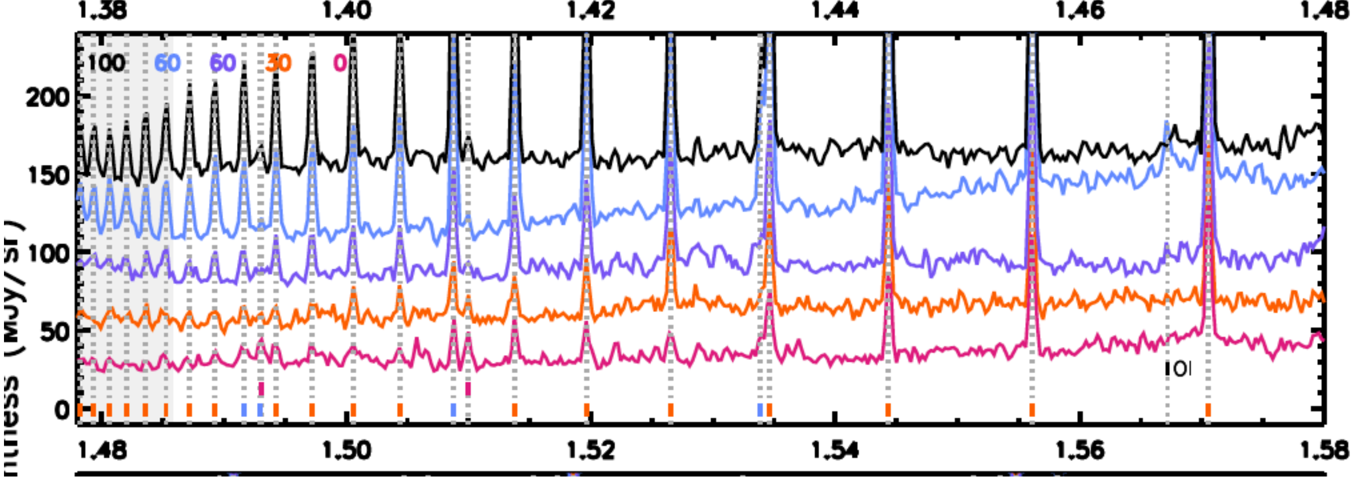
PDR (photon dominated region): here the Orion Bar



PDRs4ALL coll., JWST Early Science Release 2023-202x

H_2 Δj=0,±2 detection
Quadrupolar (E2) transitions

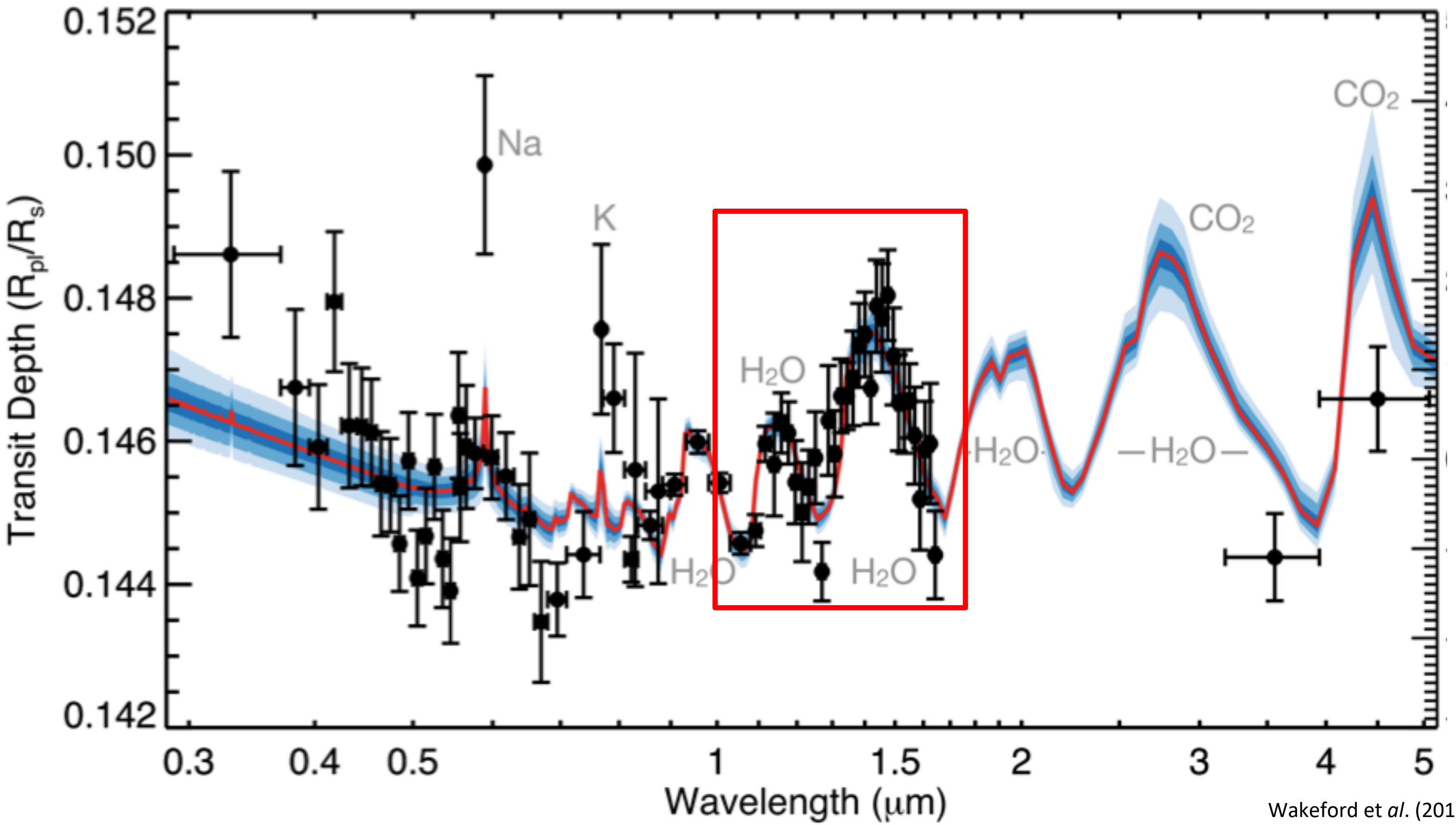




[redacted]

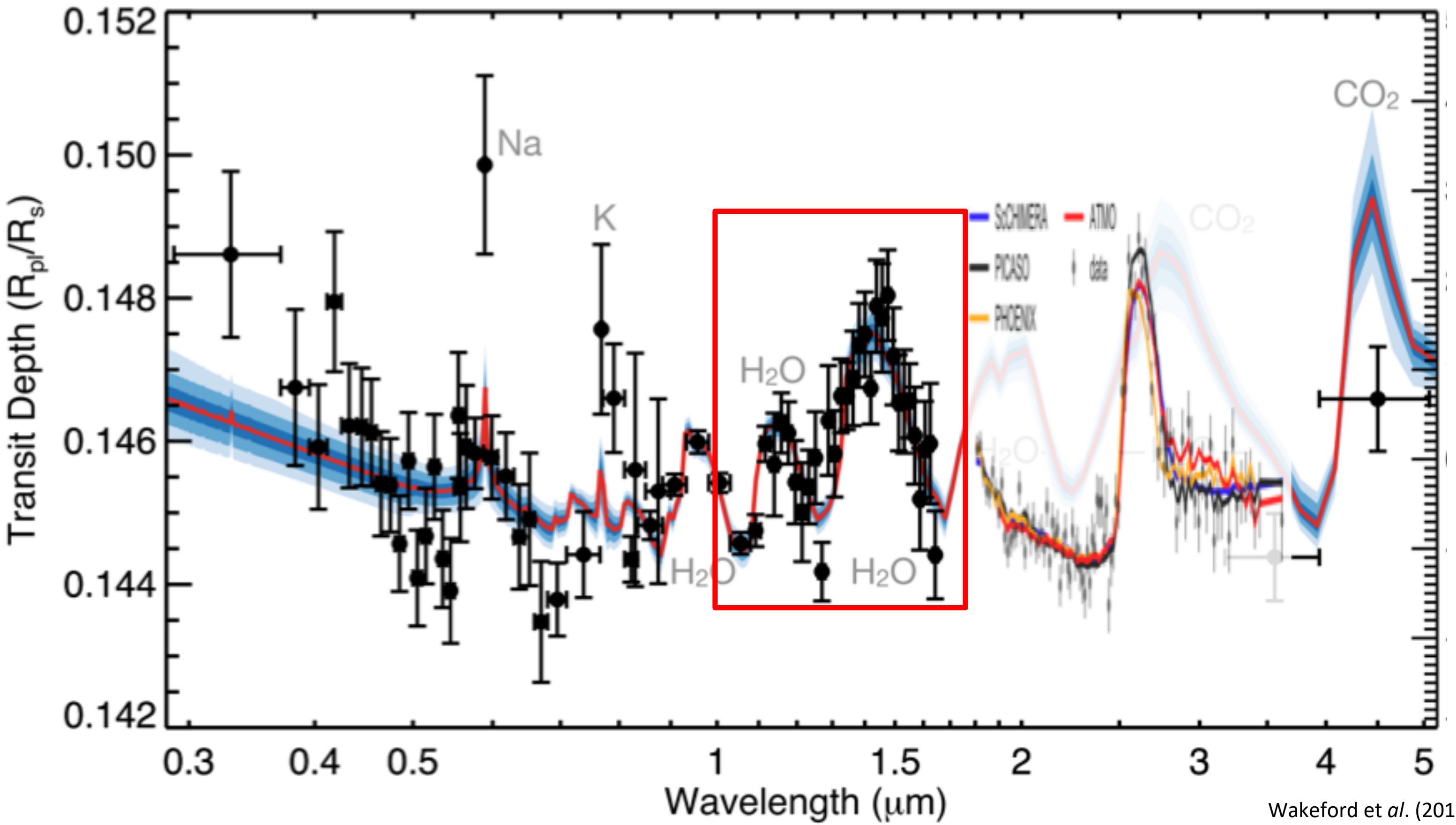
PDRs4ALL coll., JWST Early Science Release 2023-202x

Before and after JWST



Wakeford et *al*. (2018) TJTEC Early (2022)

Before and after JWST

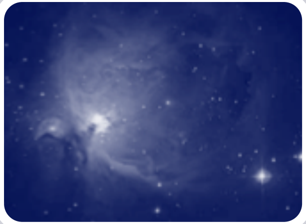


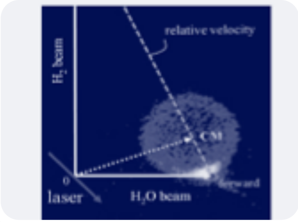
Wakeford et *al*. (2018) TJTEC Early (2022)

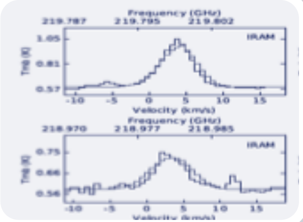
Table

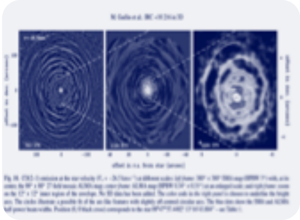
1. Why molecules?
   - It all begins with nuclei
   - Relevance
2. Where molecules?
   - Hot to cold
   - Dense to thin
   - Ionized, Plasmas, PDRs
3. When molecules?
   - Early universe
   - Disks
   - Planets
4. How to detect?
   - Rotation
   - IR and other
5. **How to model?**
   - **Qualitative/Quantitative**
   - **Ab initio**
6. Conclusion

The tripod









Observations

Laboratory

- Experiments
- Theory

Models

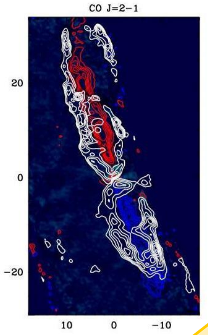
Object

From observation to modelling

On the sky

Line catalogs

Spectrum:
Line positions
and shapes



Excitation model

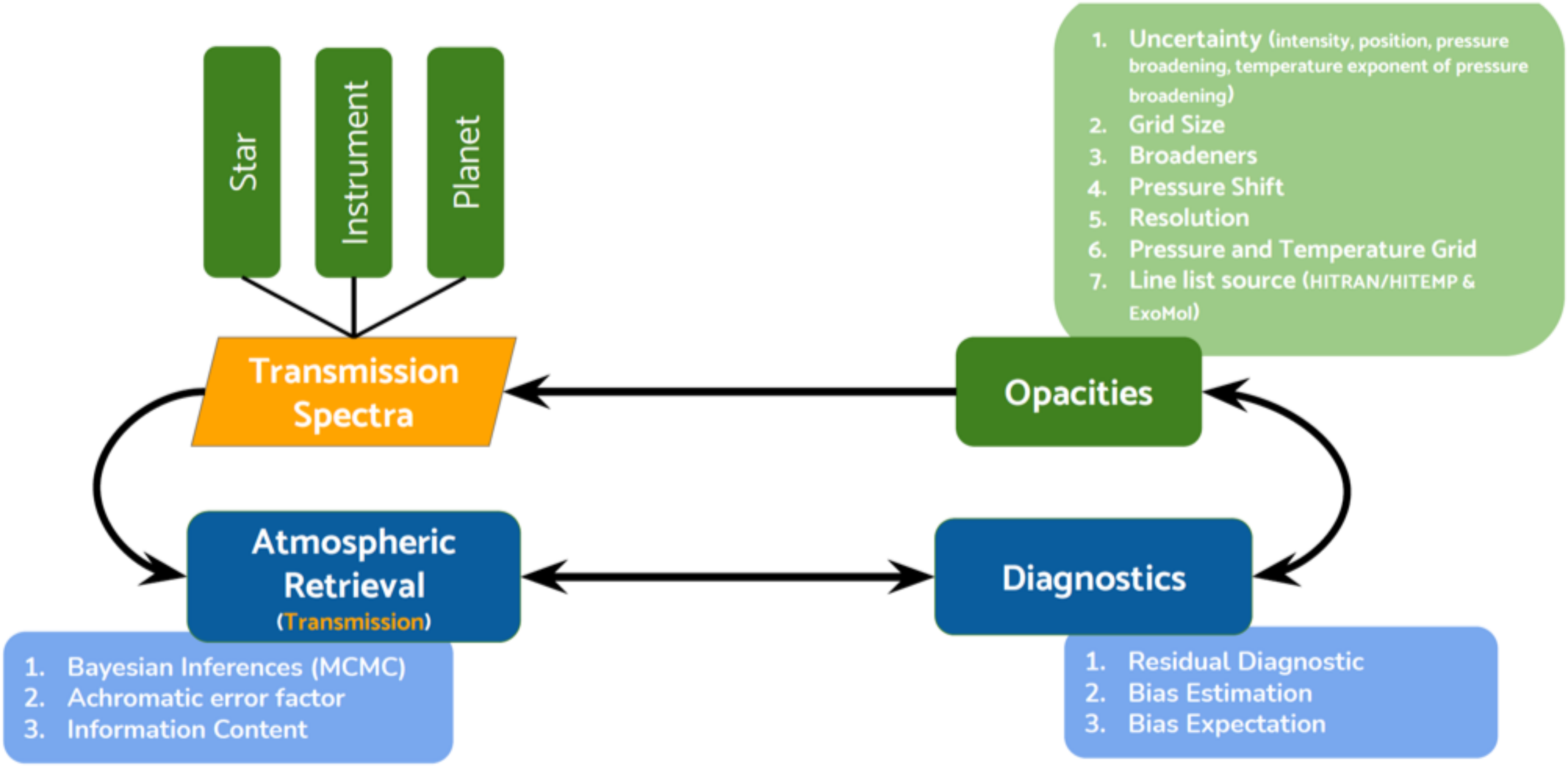
Abundances, speeds,
Cartography

Model:
chemistry, history

Chemistry:
reactions kinetics

Compatibility,
Further studies

Assessing the extent of the opacity challenge for exoplanetary sciences



1. Uncertainty (intensity, position, pressure broadening, temperature exponent of pressure broadening)
2. Grid Size
3. Broadeners
4. Pressure Shift
5. Resolution
6. Pressure and Temperature Grid
7. Line list source (HITRAN/HITEMP & ExoMol)

1. Bayesian Inferences (MCMC)
2. Achromatic error factor
3. Information Content

1. Residual Diagnostic
2. Bias Estimation
3. Bias Expectation

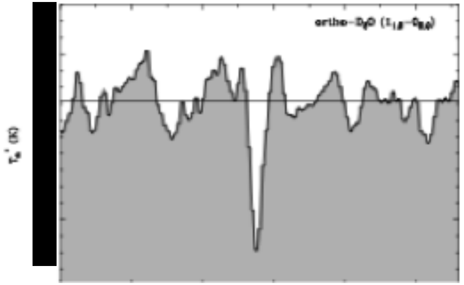
(Niraula et al., 2022)

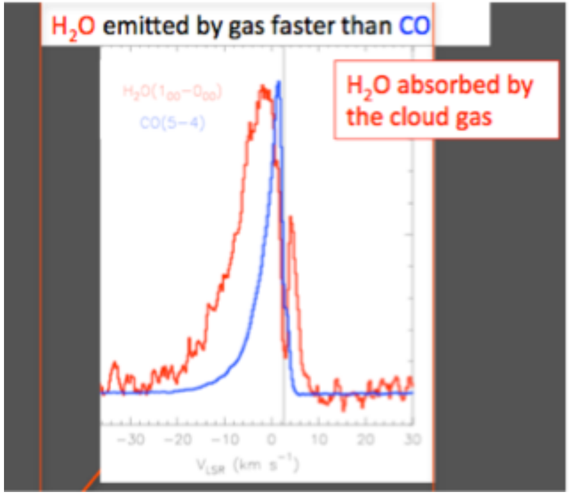
MICROSCOPIC DATA, COLLISIONS

Our work in Grenoble, than Paris

Rotational spectrum detected by HIFI /Herschel

D_2O



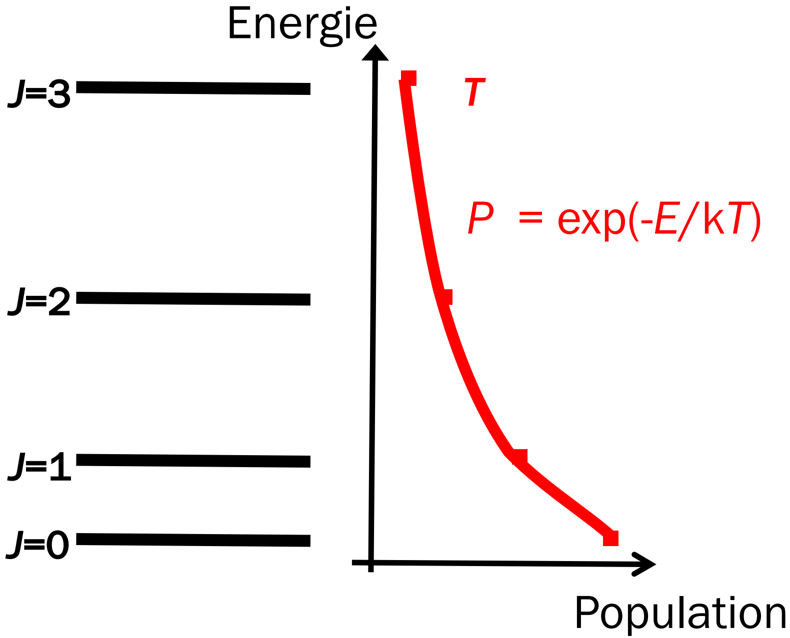

H_2O emitted by gas faster than CO

H_2O absorbed by the cloud gas

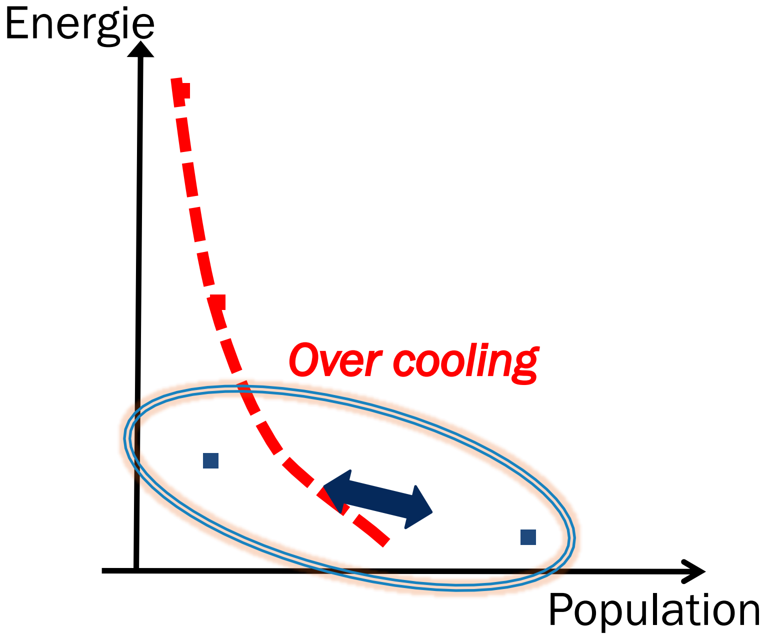
(the CHESS collaboration, Ceccarelli et al., star forming regions and shocks)

Level population

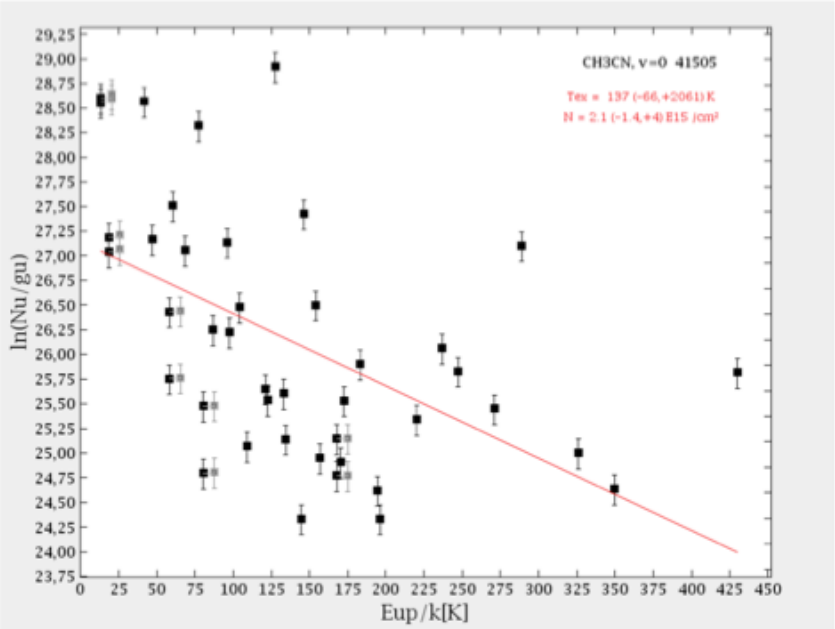
LTE



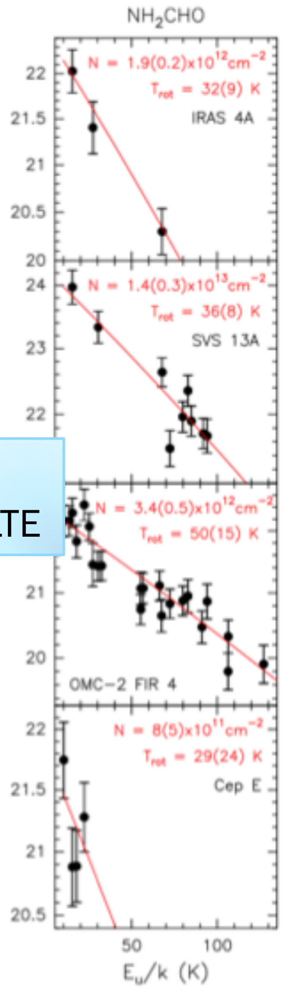
No temperature at all



Example



No LTE



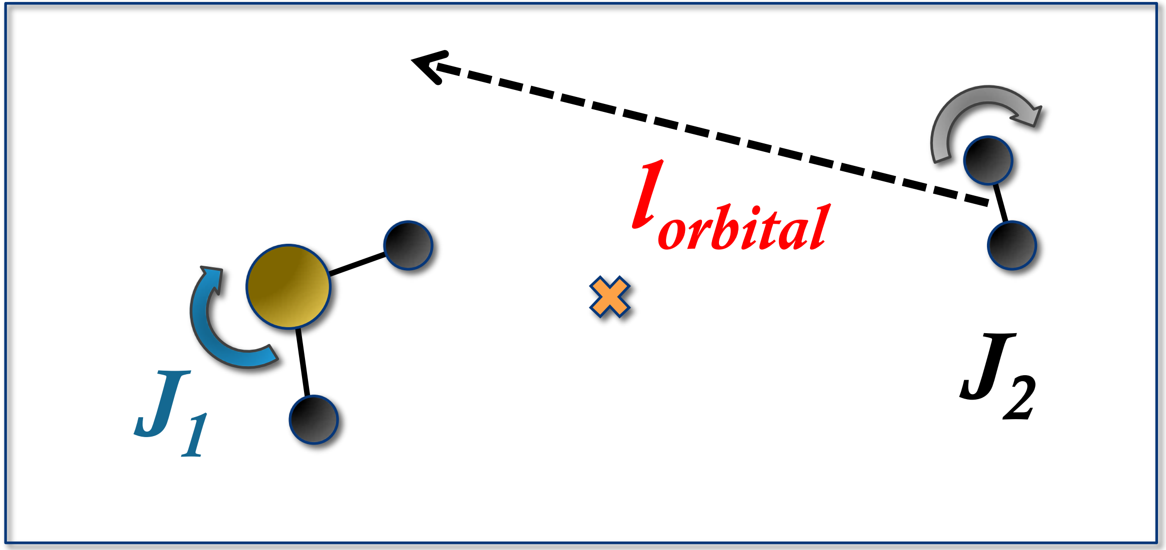
LTE

Courtesy of C. Ceccarelli, C. Kahane
Al-Edhari

Classical view for reaching LTE

- $l_{\text{orbital}} = p\,b = m\,v\,b$

  (m reduced mass; b impact parameter; v relative velocity) . **Exchange l <-> J** makes LTE



** : isotopologs also computed*

H_2O *	• Full D potential (9D) with H_2, rigid potential with He • Full rotational analysis, Class./Quantum • Partial vibrational analysis, Class./Quantum dynamics • Isotopologues, HDO,D_2O,$H_2{}^{18}O$	MANY COLLABORATIONS
CO *	• Potential with CO and H2 vibration • High precision rotational analysis	M. Wernli PhD
HC_3N	• Rigid rotor potential with H2 (4D) • Full rotational analysis, Quantum dynamics	M. Wernli PhD
NH_3 *	• 5D potential with H2 & inversion • All isotopologues NDH2, NHD2, ND3	Several Post-Docs
H_2CO	• Rigid rotor, full potential with H2 • Overcooled, absorbs the CMB	N. Troscompt PhD
$HCOOCH_3$	• Full potentiel with He • Overcooling	Coll. K. Szalewicz
HNCO	• Full potentiel with He, H2	E. Sahnoun PhD
c-C_3H_2*	• Full potentiel with He, H2 • Unstable molecule	M. Ben Khalifa PhD
CH_3CN	• Full potentiel with He, H2 • C_{3v} symmetry -> peculiar spectroscopy	M. Ben Khalifa PhD/post doc
C^+	• Interaction with H2 • Fine structure transition	Coll NASA-JPL

$HCO^+ – H_2$

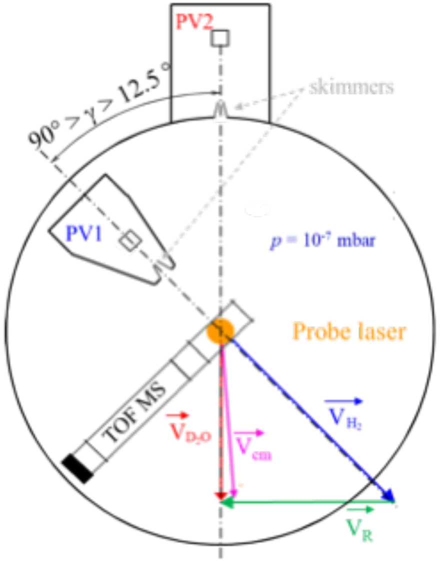
$SiO – H_2$

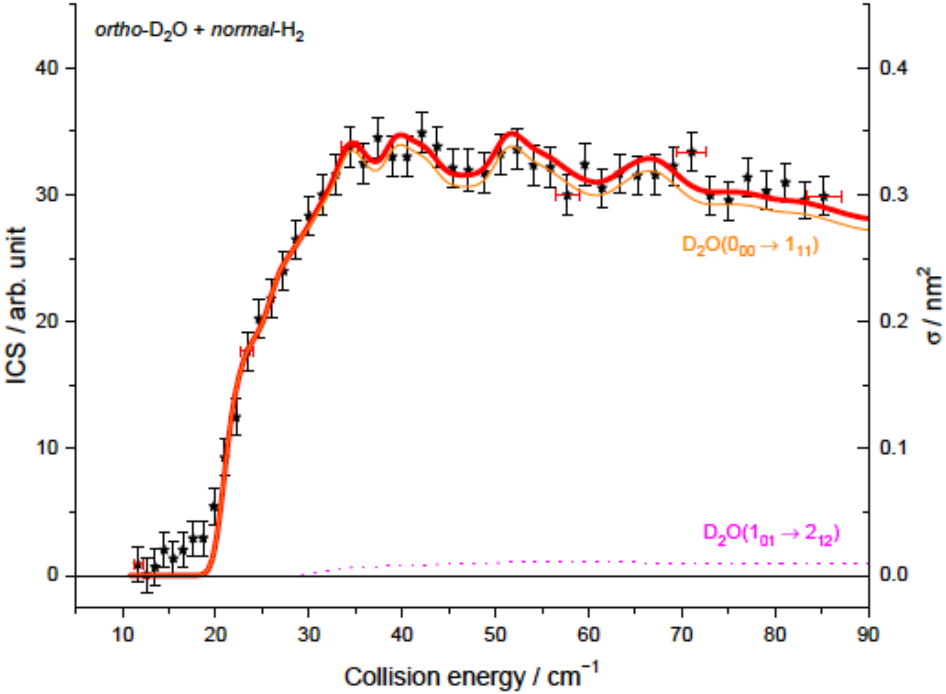
$SO_2 – H_2$

$HCl – He,H_2$

HMgNC – He

Bergeat, LW, Faure, 2020-2022

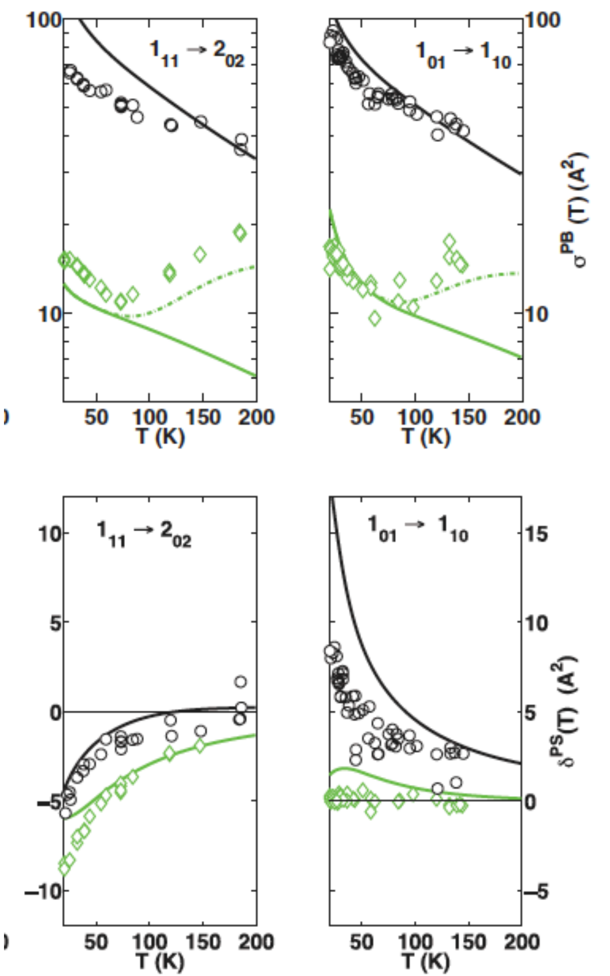




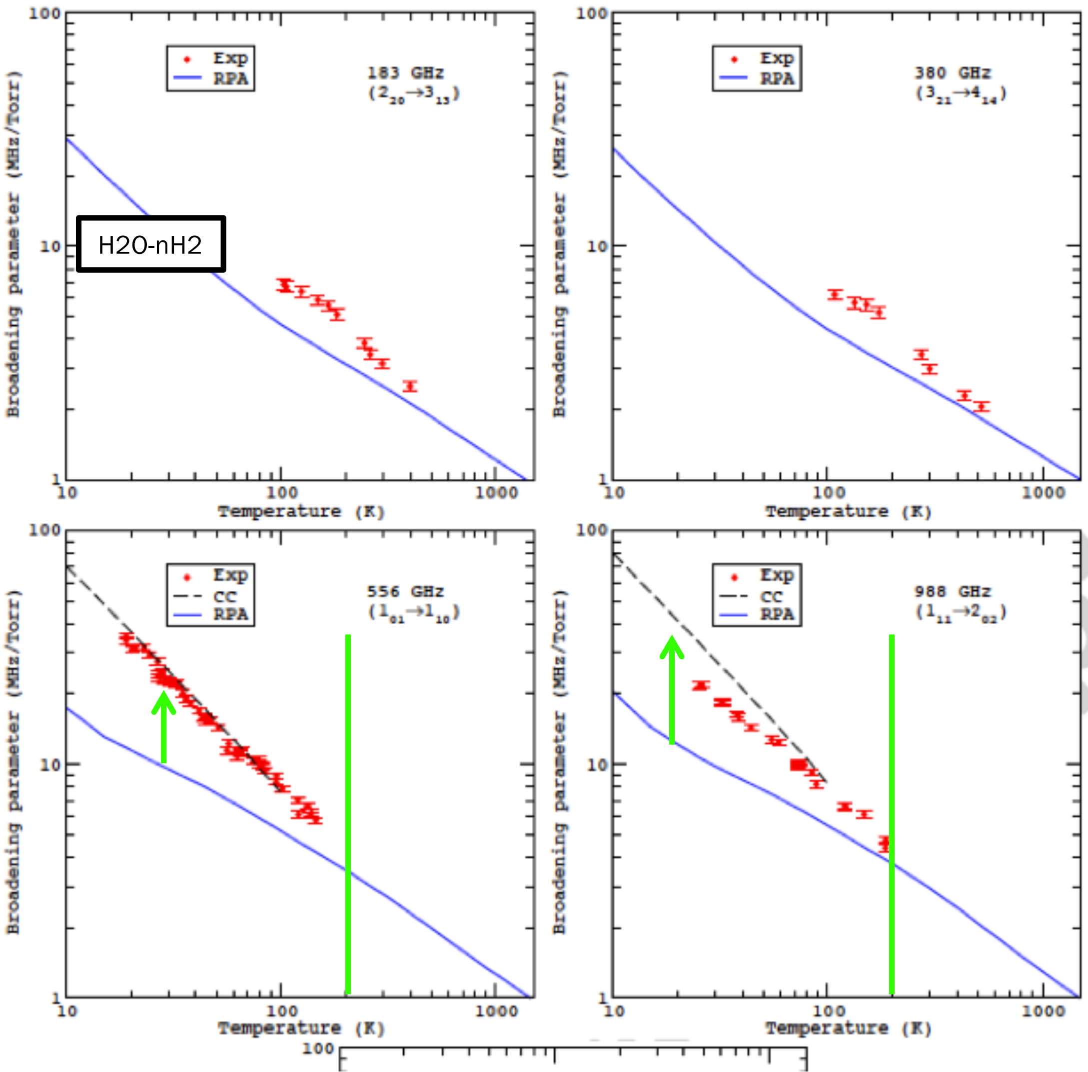
Bergeat et al, PRL 2020/Molecules 2022

Pressure broadening and shift H2O –H2

Drouin, LW, 2012



A. Faure, LW, B Drouin, J Tennyson, JQSRT, 2012.



H2O-nH2

Moving to atmospheres

CO_2

- PES CO2 –He CO2 –H2
- Dynamics of collision
- Ro-vib in progress
- Pressure Broadening, Opacities

MIT – Harvard – U. Paris collaboration

CH_4

- PES CH4 –H2

Grenoble Tunis
(E. Sahnoun)

Computation on national supercomputers

- Relevant computations:

  opacity is the MAIN BOTTLENECK for atmpospheres.

- Quantum mechanical dynamics: matrix algebra

- Heavy on computation, massively parallel setups.

- Main project is HPC
- 10^6 scalar CPU hours is ordinary for a project)
- For atmospheres (higher T), 10^7 hours projected : large project for present day computing power.
- MIT-U. Saclay-CNRS joint endeavour being set up

Work in team

- **Lab. Aimé Cotton, Paris-Saclay**

Olivier Dulieu, Alex Voute

- **Grenoble**

Alexandre Faure

- **Tunis**

Nejmeddine Jaïdane

Emna Sahnoun

Malek Ben Khalifa (now, Leuven, BE)

- **MIT / Harvard**

Julie de Wit

Prajwal Niraula

Iouli Gordon

- Many collaborations through **the COST action** « Our astrochemical History »

Extreme case: ultra-small, ultra precise spectroscopic telescope

SPECULOOS (Chili- U Liège)

1m telescopes in La Silla and Tenerife

HARPS on the 3.6 m telescope LaSilla

RS=120,000 (measured)

The other extreme: VLT/ESO (Chili)