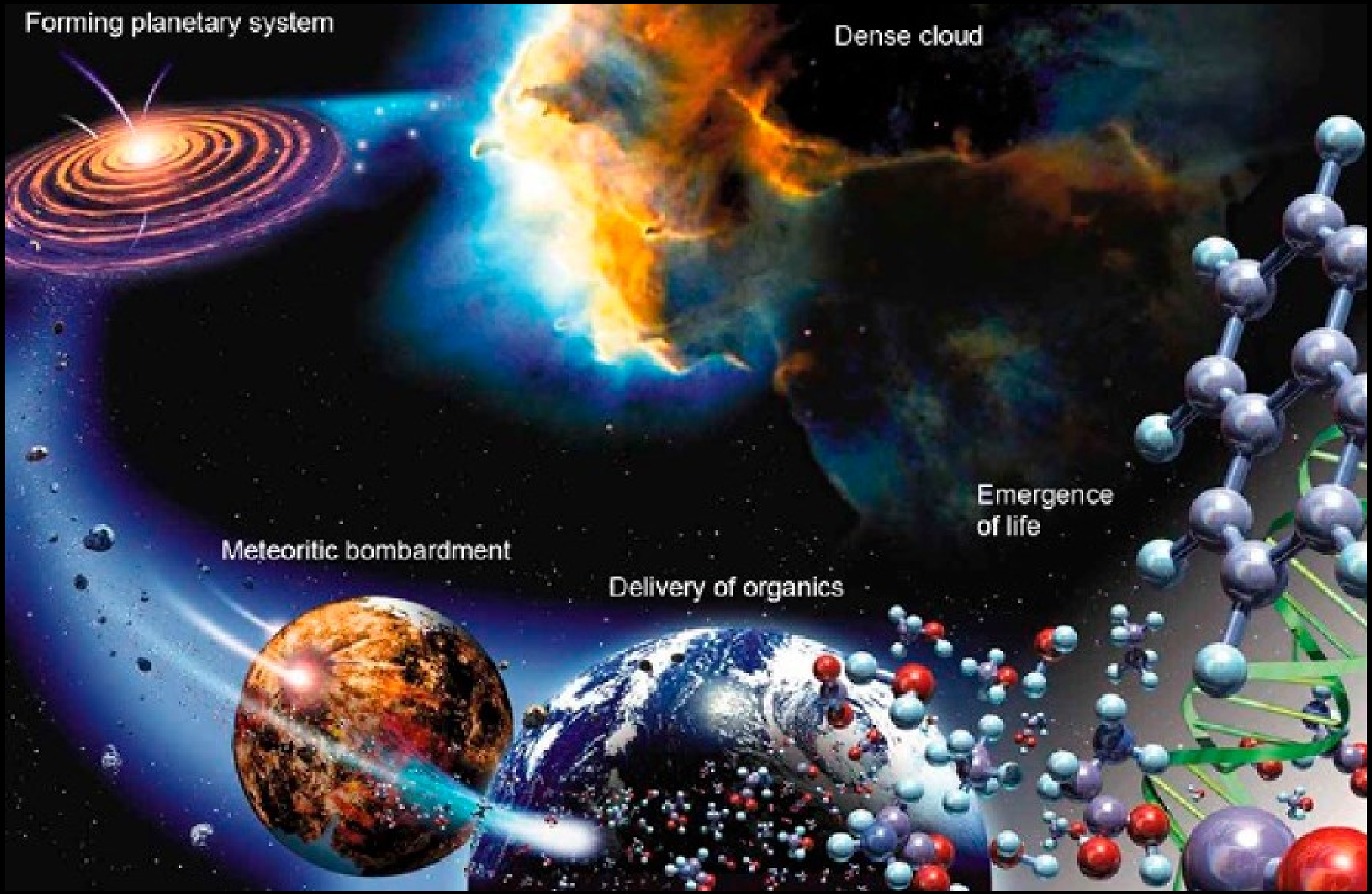
Master course: Astrochemistry I:

Basic principles and recent results



Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

Master course: Astrochemistry I:

Basic principles and recent results

Welcome!
Master students (M1 & M2) + Everyone interested

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The Molecular Universe

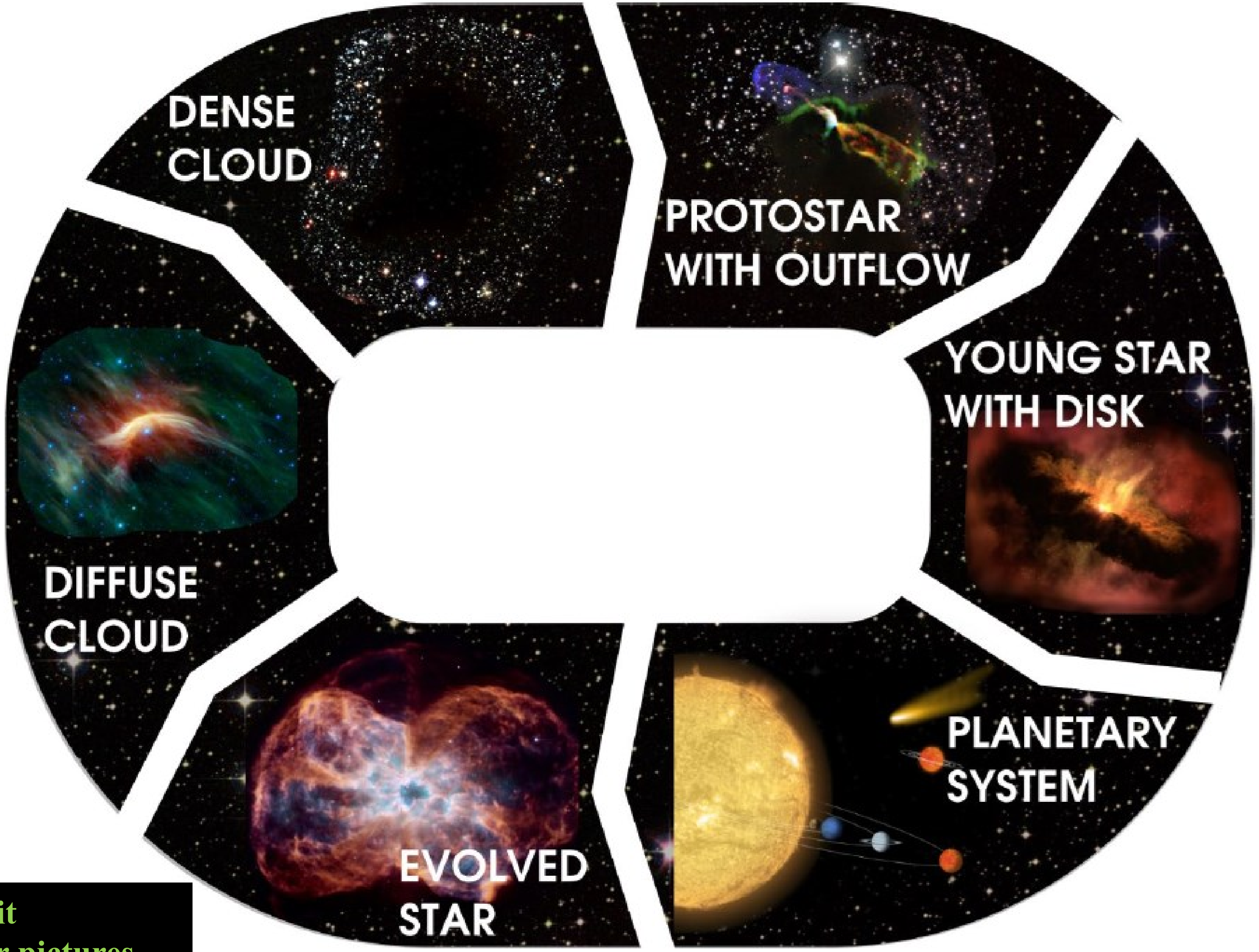


Figure by M. Persson; credit NASA/ESA/ESO/ALMA for pictures.

Outline of course

- Introduction; Basic molecular processes I
- Basic molecular processes II
- Chemistry in the Early Universe
- Chemistry in diffuse clouds; PDRs, XDRs
- Chemistry in shocks
- Chemistry in dark clouds & pre-stellar cores
- Chemistry in star-forming regions; disks; relation to Solar System; comets

Background reading

- See literature list:
  - Tielens (2013) – Molecular Universe
  - van Dishoeck et al. (2013) – H_2O; (2014) Faraday discussions
- Books on subject: Tennyson, Tielens, Draine, etc.
- Relevant reviews summarized for each lecture
- Some homework and self-study required to get most out of the class
- Course website: https://hrodmarsson-group.space/teaching/

Organization

- Lectures & problem sessions: 8 x 3hrs (06/10/26-20/01/27)
  - Homework problems
  - Look at problems before sessions
- 3 ECTS units – Oral exam on appointment
- Required background
  - Radiation processes (Planck function, Einstein coefficients)
  - Statistical physics (Maxwell, Boltzmann distributions)
  - Quantum physics (H atom, molecular spectroscopy)
  - Molecular spectroscopy
-

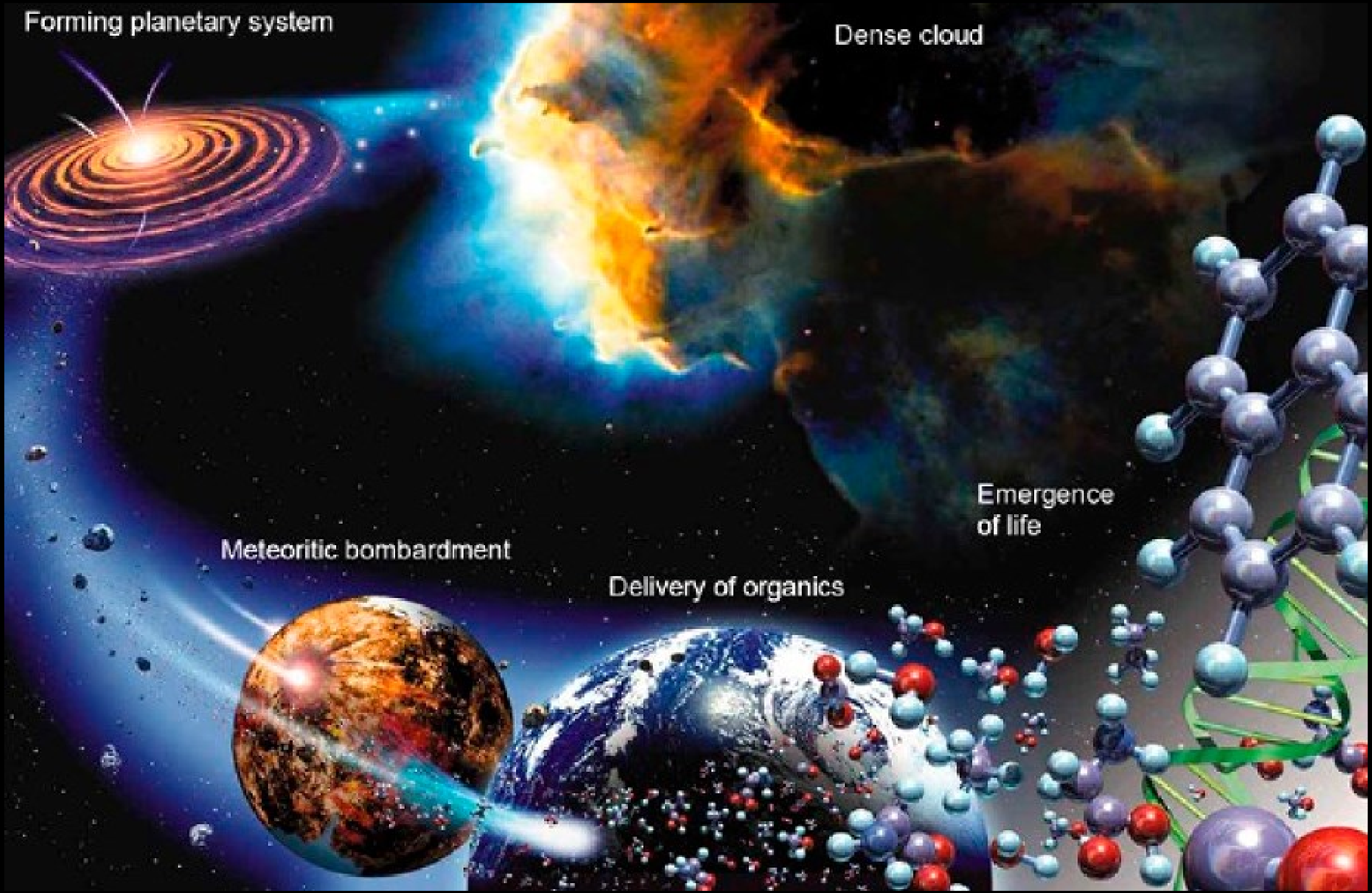
Master course: Astrochemistry I:

Lecture 1: Introduction; basic processes

Reading list:

Water review:
van Dishoeck *et al.* (2013) Chemical Reviews
Sections 1&2

van Dishoeck (2014) Faraday discussions



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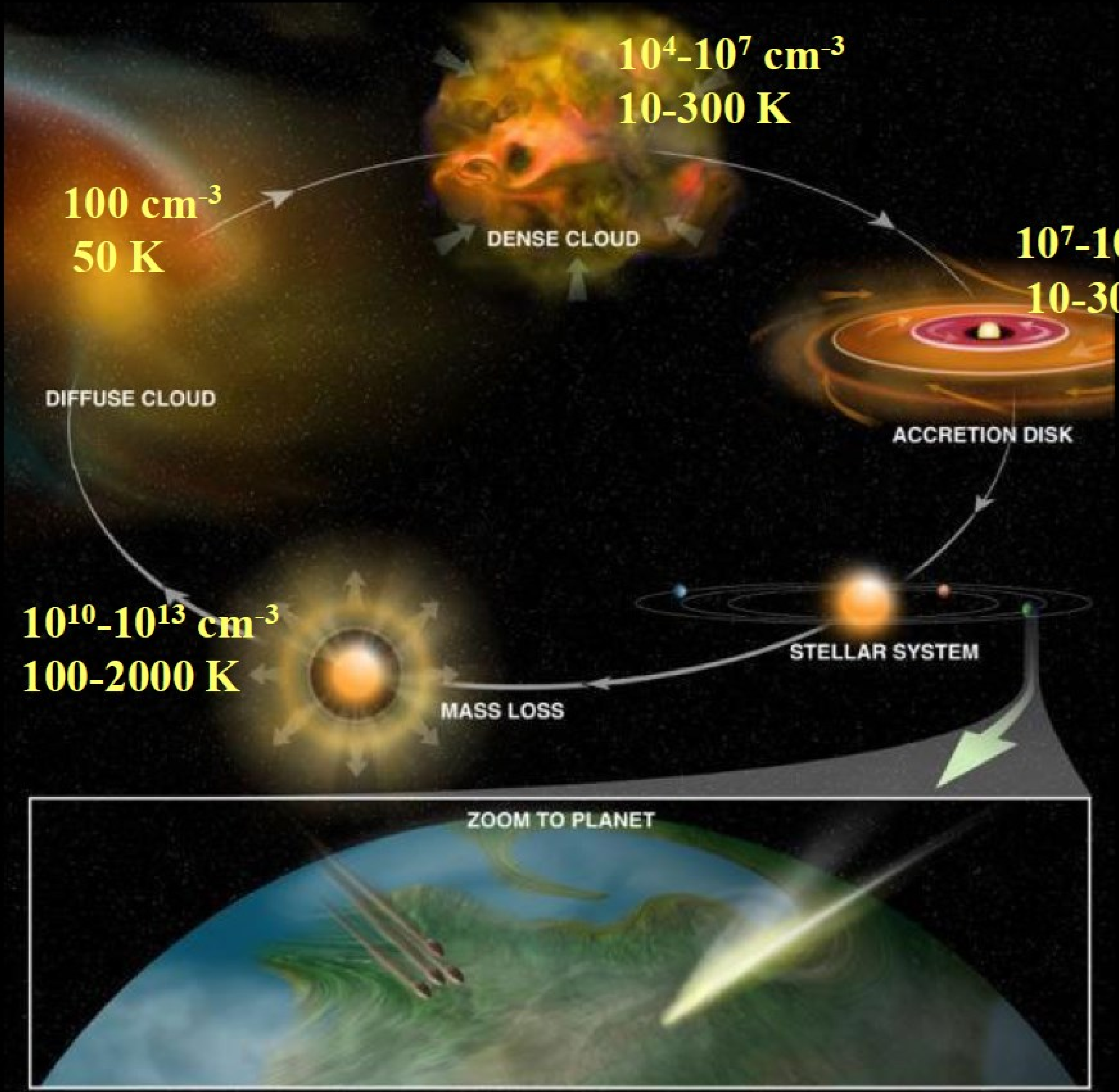
What is astrochemistry?
(or molecular astrophysics)

- ‘Formation, destruction and excitation of molecules in astronomical environments and their influence on the structure, dynamics and evolution of astronomical object.’
- ‘Blending of astronomy and chemistry in which each area enriches the other in a *mutually stimulating* interaction’
- ‘Astrophysics is almost entirely applied atomic, molecular and optical physics’
- **Dalgarno, ARA&A, 2008**

1.1 Introduction

- Molecules are found throughout the universe
  - Molecular clouds, evolved stars, planetary nebulae, protoplanetary disks, stellar and (exo)planetary atmospheres, solar photosphere, comets, galaxies (nearby to high z),…
- Some typical conditions
  - Diffuse clouds: $T_{\mathrm{kin}} \sim 100$ K, $n \sim 100$ cm^{-3}
  - Dense clouds: $T_{\mathrm{kin}} \sim 10\text{-}100$ K, $n \sim 10^4\text{-}10^7$ cm^{-3}
  - Shocks: $T_{\mathrm{kin}} \sim 200\text{-}2000$ K, $n \sim 10^4\text{-}10^5$ cm^{-3}
  - Hot cores: $T_{\mathrm{kin}} \sim 100\text{-}1000$ K, $n \sim 10^6\text{-}10^8$ cm^{-3}
  - Disk midplane: $T_{\mathrm{kin}} \sim 10\text{-}1000$ K, $n \sim 10^8\text{-}10^{13}$ cm^{-3}
  - Compare atmosphere at sea level: $T_{\mathrm{kin}} \sim 300$ K, $n \sim 3\text{x}10^{19}$ cm^{-3}
- → Conditions very different from those normally encountered in lab on Earth: ***molecular physics***

From clouds to stars and planets



10^4-10^7 cm^{-3}
10-300 K

100 cm^{-3}
50 K

10^7-10^{13} cm^{-3}
10-3000 K

10^{10}-10^{13} cm^{-3}
100-2000 K

B. Saxton
NRAO

Time scales

- Collision time: ~1 month at 10^4 cm^{-3}
- Chemical time: ~10^5 y (dark clouds)
- Star formation: ~10^6 yr
- Lifetime cloud: ~10^7 yr

- → Do not expect to find many molecules since chemical reactions are slow
- *Surprise: interstellar clouds contain very rich chemistry!*

Where are molecules found?

Horsehead nebula

Dark pre-stellar core B68

ESO-VLT
Alves *et al*. 2001

Star-forming clouds

HST Carina nebula

Typical sizes: up to a few light years (10^{18} cm ~ 100000x distance from Earth to Sun)
Typical masses: up to 10^5 M_{Sun}

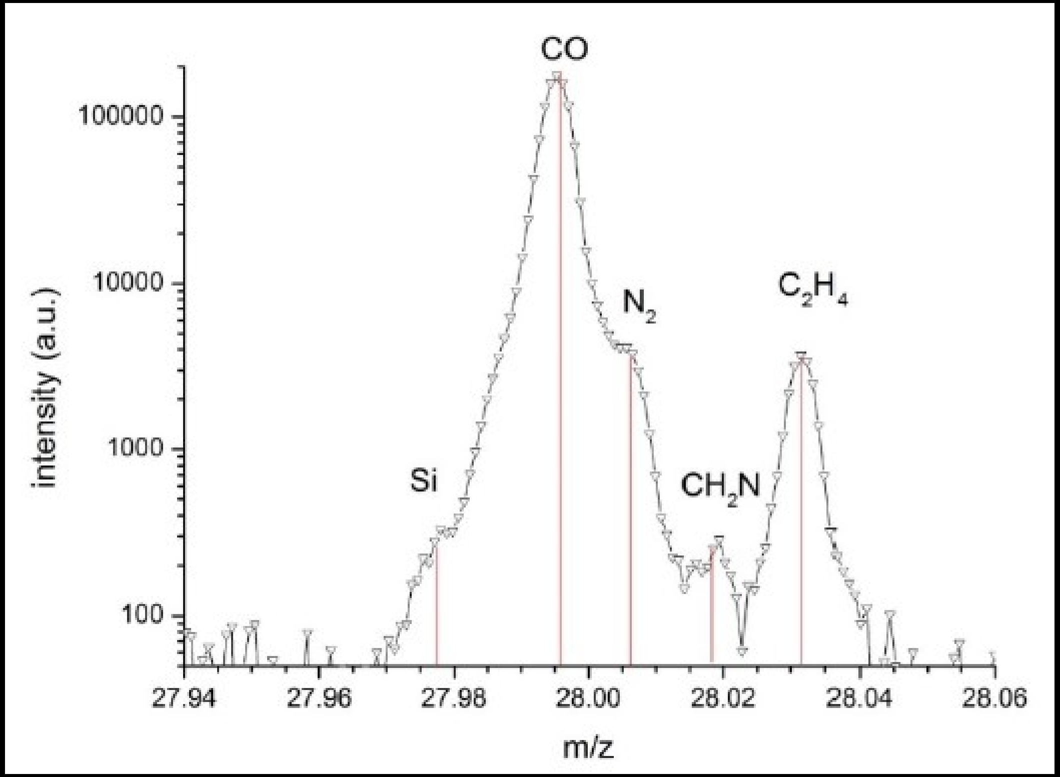
Introduction - continued

- Interstellar clouds are birthplaces of new stars and planets
  - Evolution of molecule abundances: ***astrochemistry***
  - Molecules as physical diagnostics: ***astrophysics***
  - Incorporation into exoplanetary atmospheres: ***astrobiology***
- Progress strongly driven by observations: ***technology***

- →***Very interdisciplinary topic!***

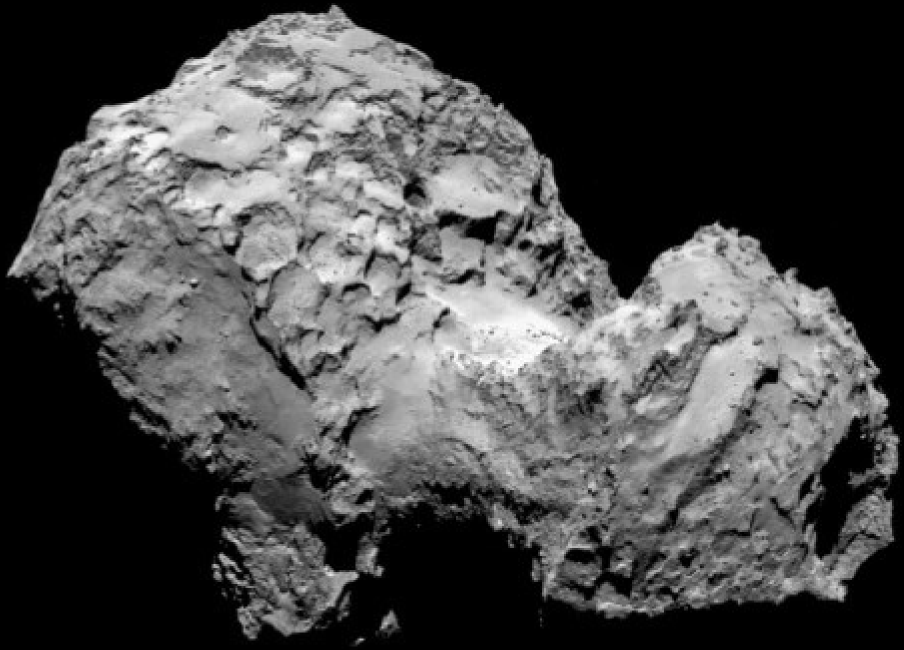
Link with comets – Rosetta

Mass spectrometry gases



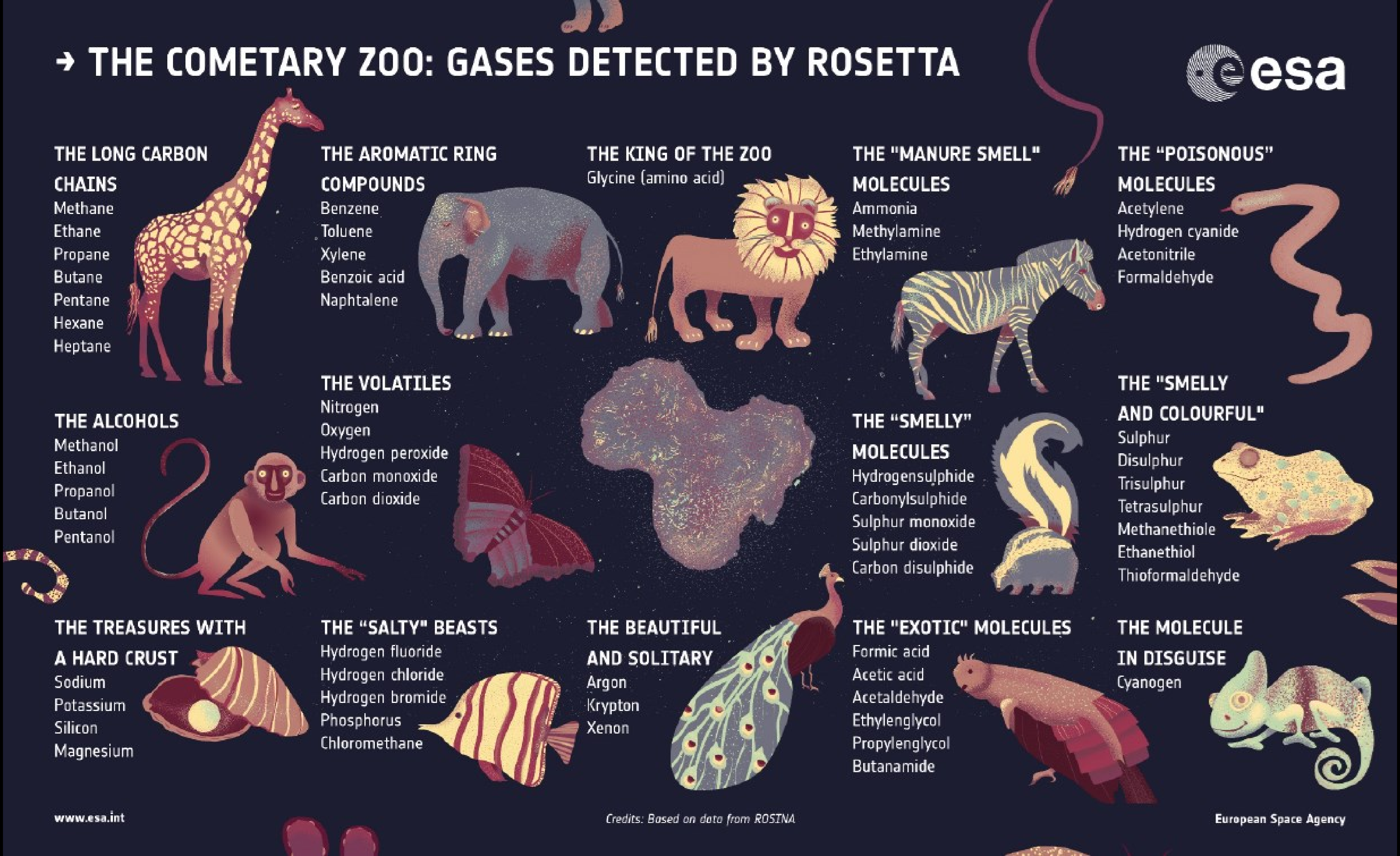
ROSINA: Altwegg, Rubin et al. (2016)
Glycine detected!

Comet 67P / G-C



ESA-OSIRIS team

→ THE COMETARY ZOO: GASES DETECTED BY ROSETTA



THE LONG CARBON CHAINS

Methane
Ethane
Propane
Butane
Pentane
Hexane
Heptane

THE AROMATIC RING COMPOUNDS

Benzene
Toluene
Xylene
Benzoic acid
Naphtalene

THE KING OF THE ZOO

Glycine (amino acid)

THE "MANURE SMELL" MOLECULES

Ammonia
Methylamine
Ethylamine

THE "POISONOUS" MOLECULES

Acetylene
Hydrogen cyanide
Acetonitrile
Formaldehyde

THE ALCOHOLS

Methanol
Ethanol
Propanol
Butanol
Pentanol

THE VOLATILES

Nitrogen
Oxygen
Hydrogen peroxide
Carbon monoxide
Carbon dioxide

THE "SMELLY" MOLECULES

Hydrogensulphide
Carbonylsulphide
Sulphur monoxide
Sulphur dioxide
Carbon disulphide

THE "SMELLY AND COLOURFUL"

Sulphur
Disulphur
Trisulphur
Tetrasulphur
Methanethiole
Ethanethiol
Thioformaldehyde

THE TREASURES WITH A HARD CRUST

Sodium
Potassium
Silicon
Magnesium

THE "SALTY" BEASTS

Hydrogen fluoride
Hydrogen chloride
Hydrogen bromide
Phosphorus
Chloromethane

THE BEAUTIFUL AND SOLITARY

Argon
Krypton
Xenon

THE "EXOTIC" MOLECULES

Formic acid
Acetic acid
Acetaldehyde
Ethylenglycol
Propylenglycol
Butanamide

THE MOLECULE IN DISGUISE

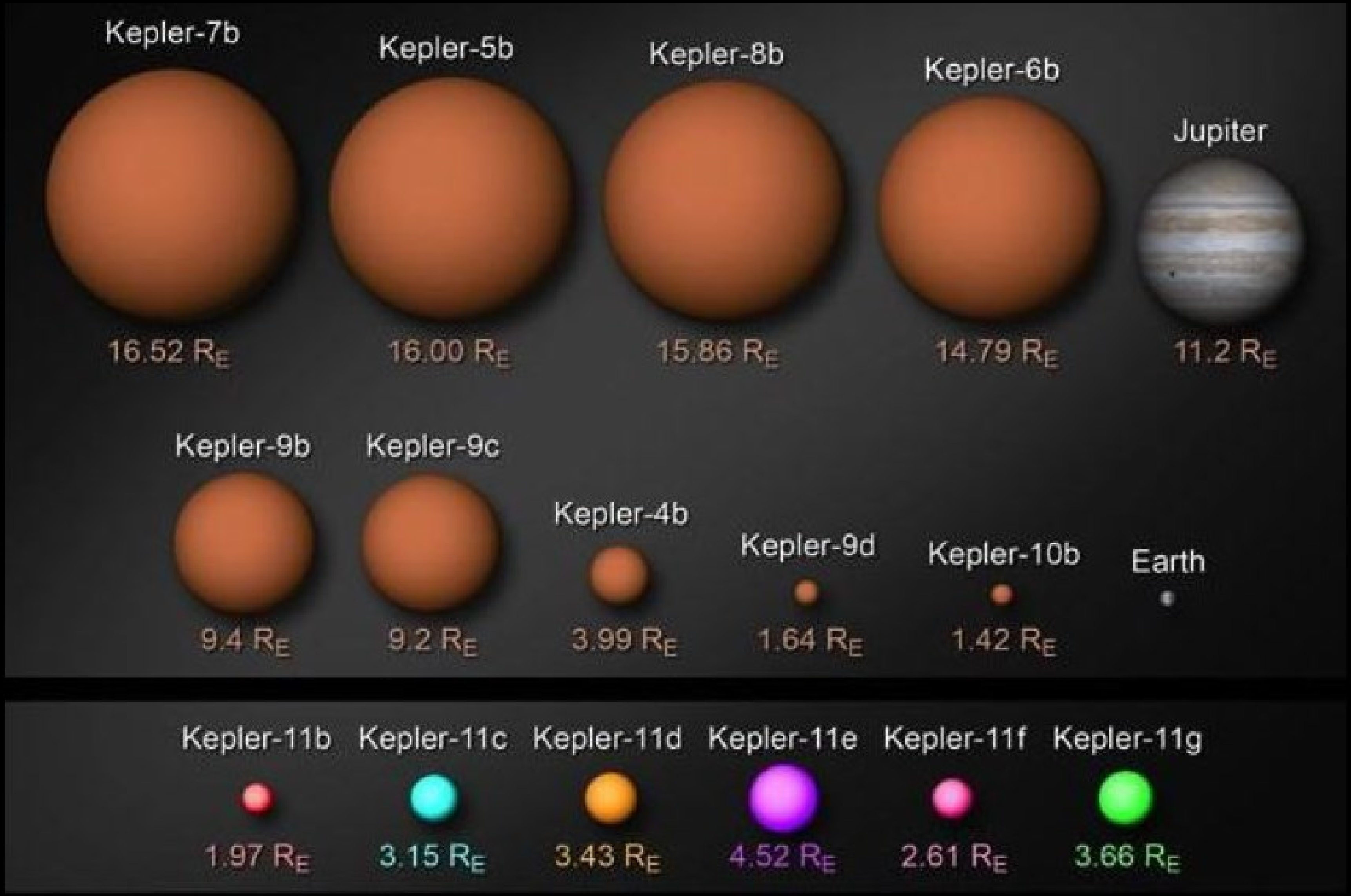
Cyanogen

www.esa.int

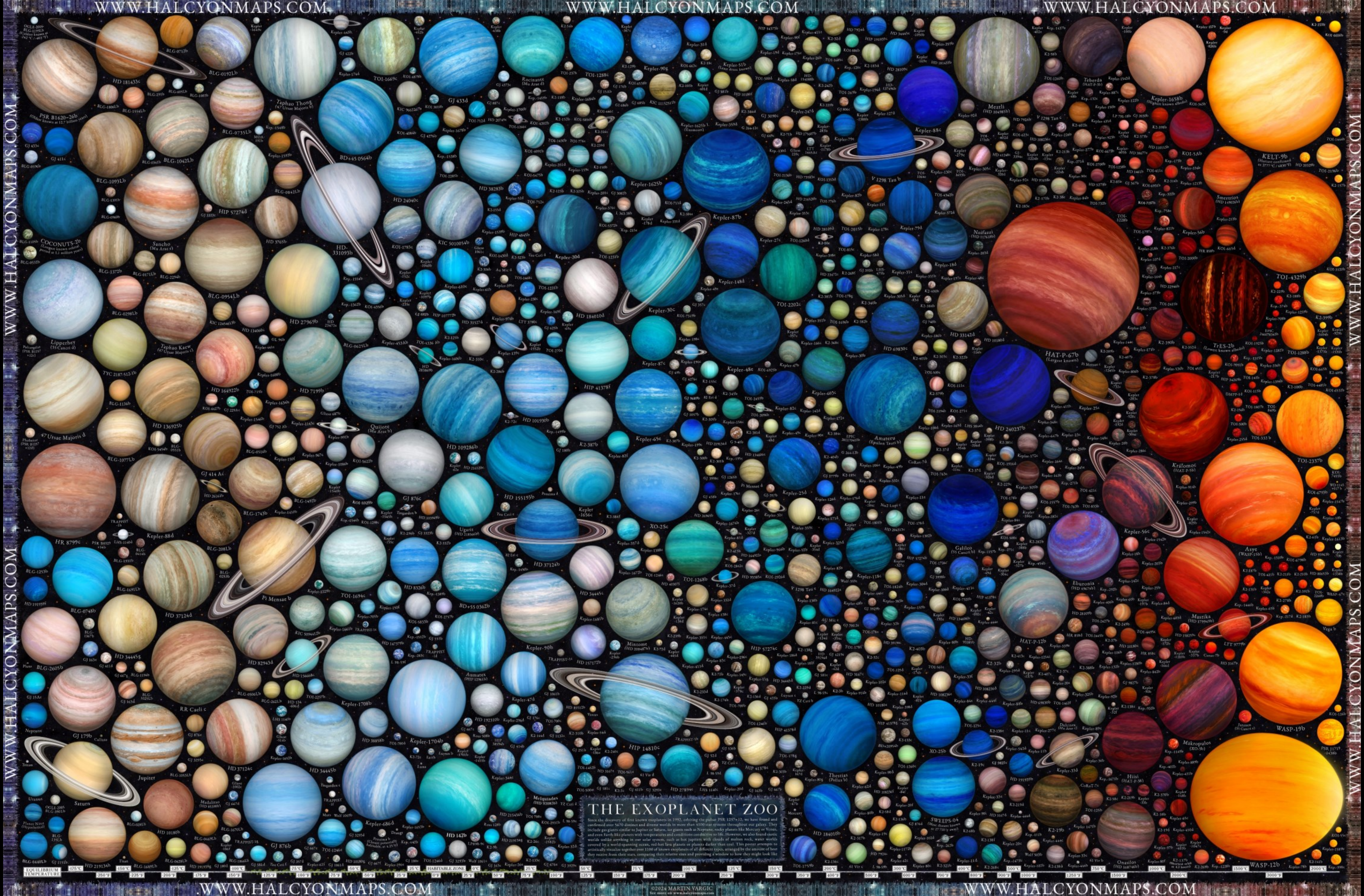
Credits: Based on data from ROSINA

European Space Agency

Exoplanets – what are their building blocks?



Kepler: Borucki et al. 2011, Batalha et al. 2013
Today: >6200 exoplanets - https://exoplanetarchive.ipac.caltech.edu/docs/counts_detail.html

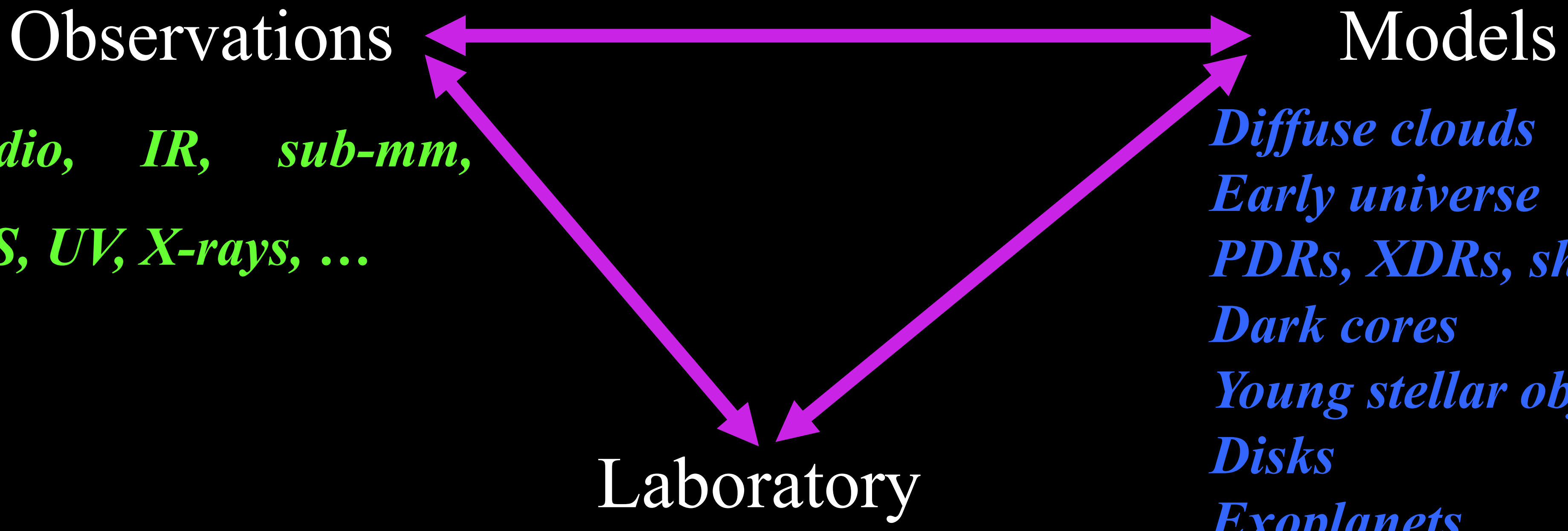


THE EXOPLANET ZOO

Since the discovery of first known exoplanets in 1992, orbiting the pulsar PSR 1257+12, we have found and confirmed over 5670 distinct and diverse worlds in more than 4100 star systems throughout our galaxy. They include gas giants similar to Jupiter or Saturn, ice giants such as Neptune, rocky planets like Mercury or Venus, and even Earth-like planets with temperatures and conditions conductive to life. However, we also found exotic worlds unlike anything in our solar system, such as hot jupiters with clouds of molten rock, water worlds covered by a world-spanning ocean, red-hot lava planets or planets darker than coal. This poster attempts to artistically visualize together over 1100 of known exoplanets of all different types, arranged by the amount of heat they receive from their stars, comparing their relative sizes and providing a window to how they might look like

See more on www.halcyonmaps.com

Approach



Observations

Radio, IR, sub-mm,

VIS, UV, X-rays, …

Models

Diffuse clouds
Early universe
PDRs, XDRs, shocks
Dark cores
Young stellar objects
Disks
Exoplanets

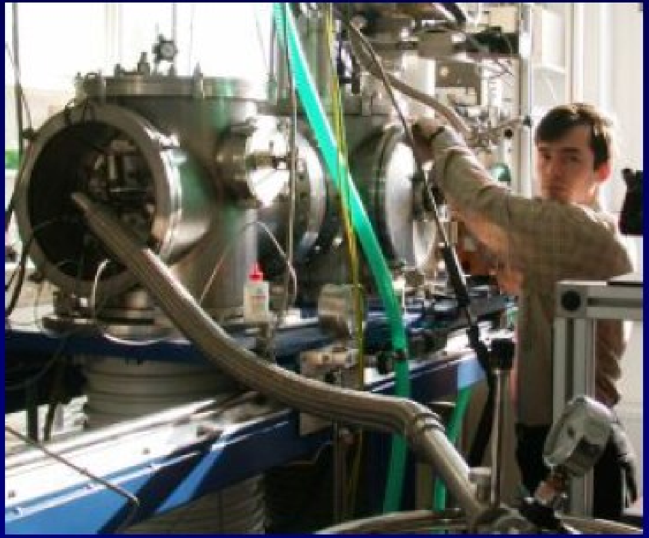
Laboratory

Spectroscopy, oscillator strengths, …
Collision rates, photo-rates, radiative association,
Charge exchange, chemical reactions,
Grain surface processes….

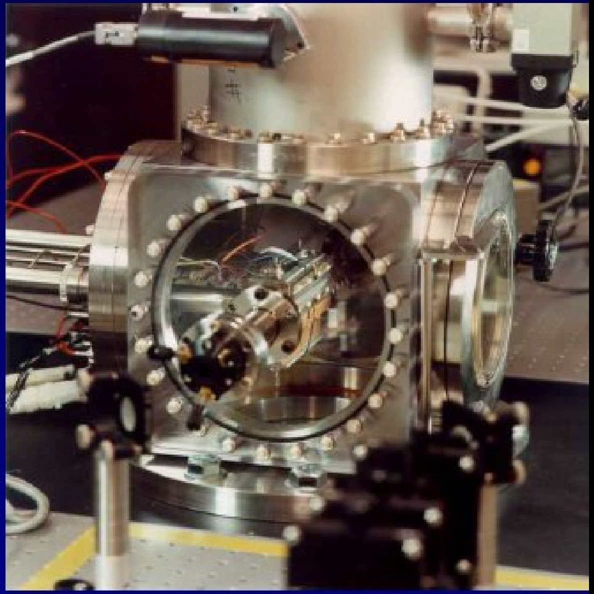
Fantastic experiments

Spectroscopy

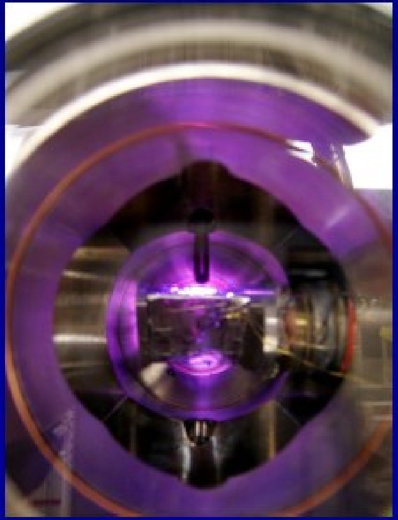
He droplets



Cavity Ringdown Spectroscopy



UV plasma

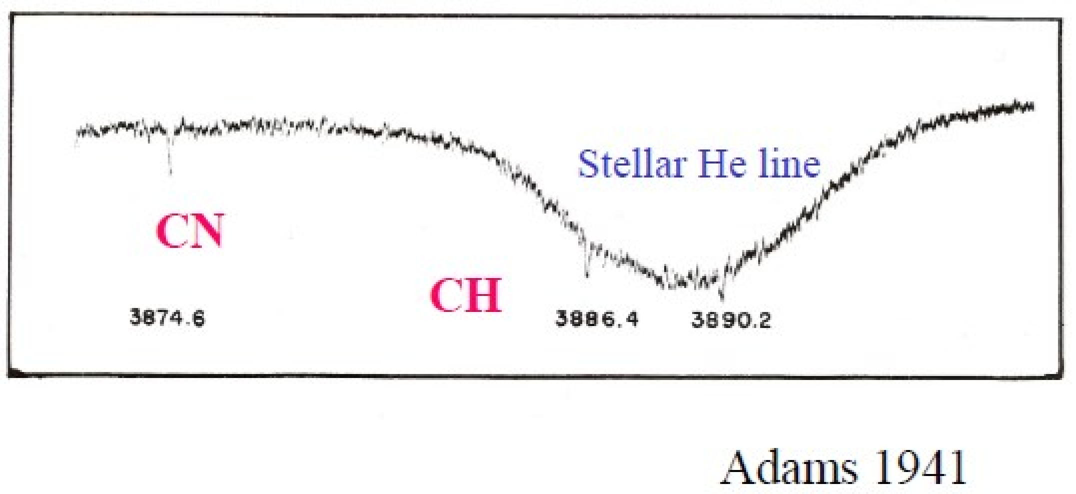


UHV surface science

Crossed beam experiments

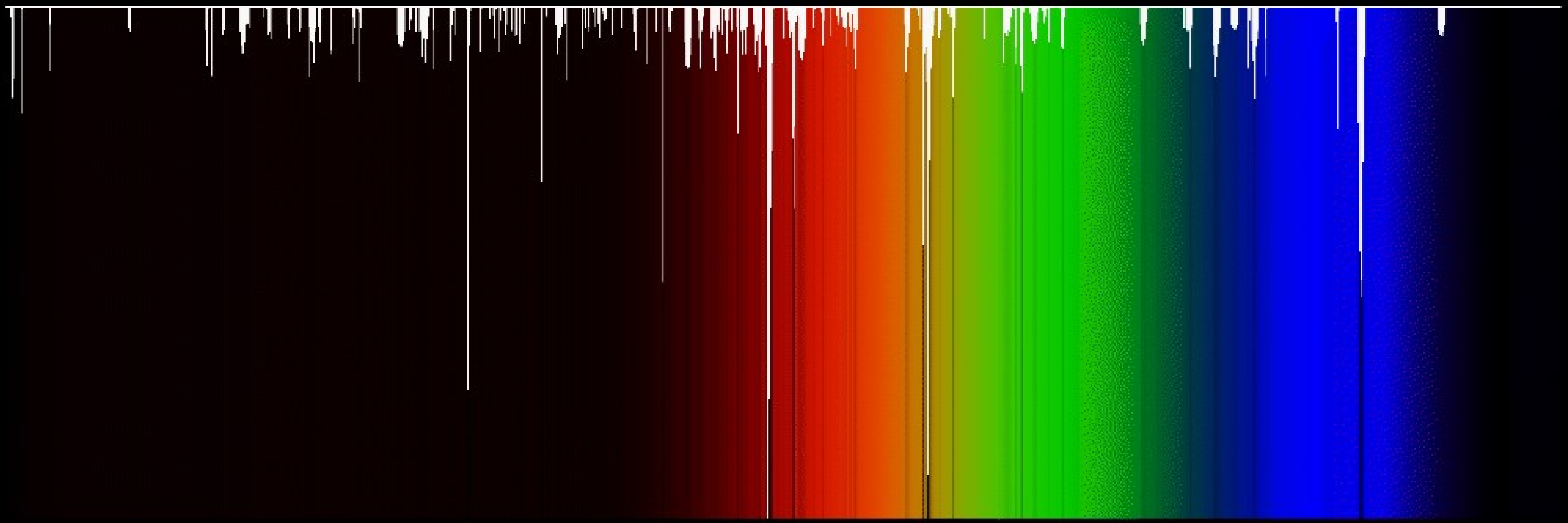
1.2 Some history

- Diffuse interstellar bands discovered in 1922 by Mary Lea Heger, 1934 by Merrill
  - Still not identified in 2014! Since 2015: C_{60}^+ carrier of 4-5 DIBs.
- Sharp bands due to small gas phase molecules identified in 1937-1940
  - CH: Swings & Rosenfeld 1937
  - CN: McKellar 1940
  - CH^+: Douglas & Herzberg 1941
- First astrochemical models
  - Kramers & ter Haar 1946
  - Bates & Spitzer 1951



Adams 1941

Diffuse interstellar bands (DIBs)



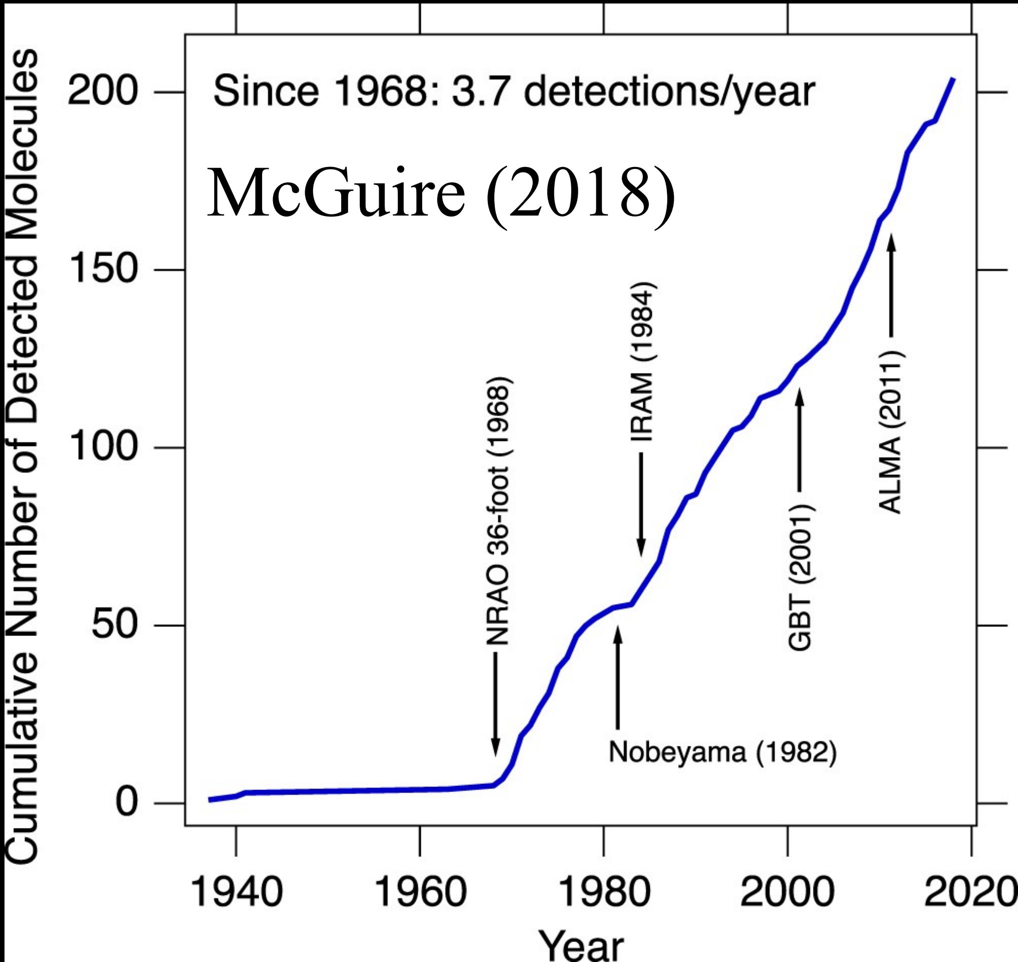
IAU symposium 297
Cami & Cox 2013, ed.

Courtesy: P. Jenniskens, F.-X. Desert

- Over 600 DIBs are known
- The carriers of the DIBs are unidentified
- DIBs are likely due to large carbon-bearing molecules
- C_{60}^+ is one of the candidates for 4-5 DIBs (now confirmed, but took 20 years)

History continued

- Development of radio astronomy
  - H I 21 cm: Ewen & Purcell 1951; Oort & Muller 1951
  - OH 18 cm: Weinreb et al. 1963
  - NH_3 1 cm: Cheung, Townes et al. 1968
    - First polyatomic molecule!
  - H_2O 1 cm (22 GHz): Cheung et al. 1969
- Development of UV astronomy
  - 1970: H_2
- Development of millimeter astronomy
  - 1970: CO
  - After 1970: flood of new molecules
  - After 2019: An avalanche! 150 new species!



McGuire (2018)

Orion molecular cloud

D=400 pc

HST image

Nearby high-mass star-forming cloud with strongest lines

Orion 230 GHz survey OVRO

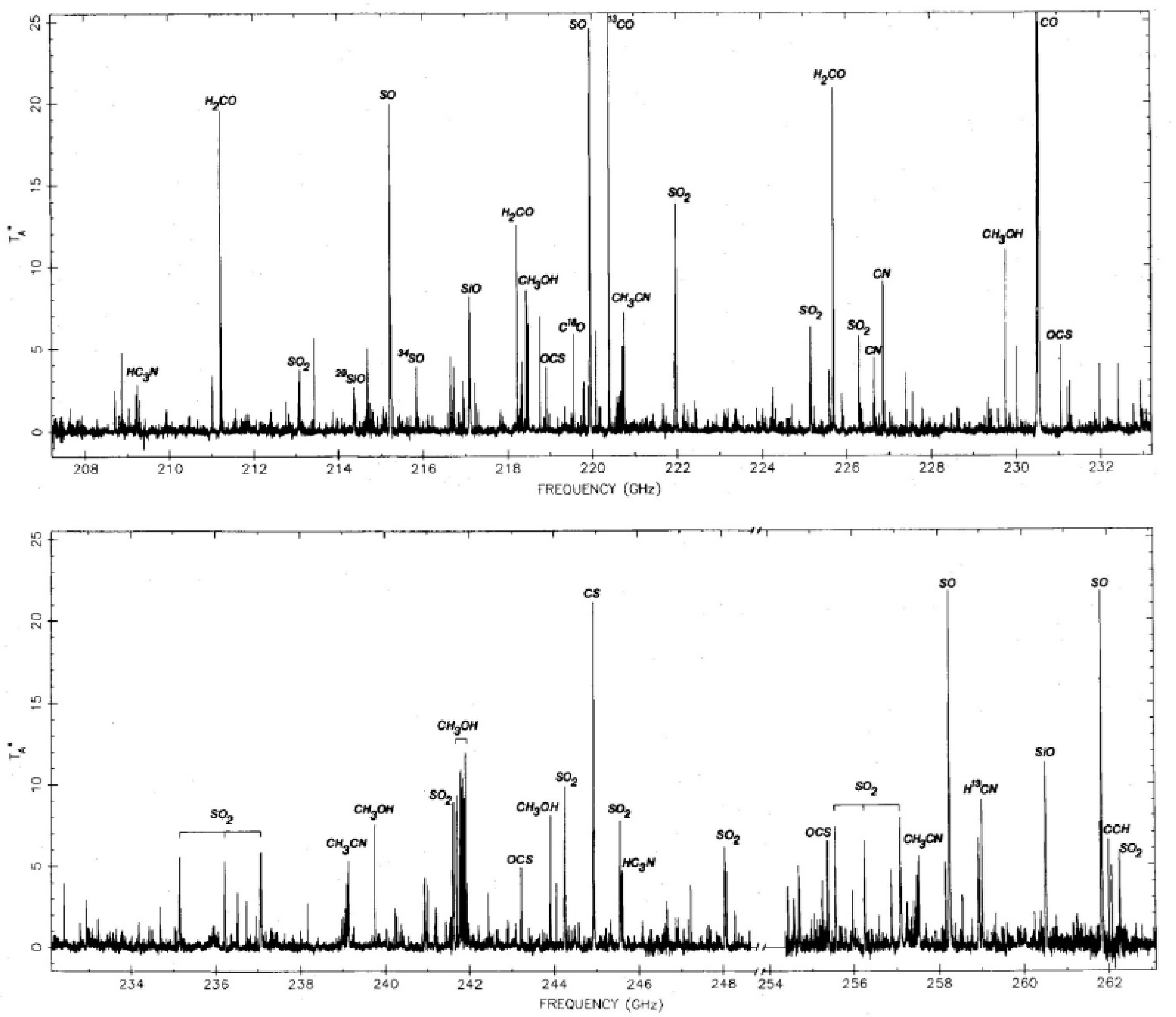


FIG. 1.—Compressed view of the OVRO spectral line survey of OMC-1

Sutton et al. (1985)
Blake et al. (1986)
Blake et al. (1987)

History continued

- Development of IR astronomy
  - 1983: ***IRAS***
    - First full-sky survey at 12, 25, 60 and 100 μm
    - Cirrus clouds and dust properties
    - Presence of very small dust particles (10-100 Å), large molecules (PAHs)
  - 1995-98: ***Infrared Space Observatory (ISO)***
    - First complete 2-200 μm spectra
    - Nature and composition of grains (silicates, ices) and PAHs
    - H_2O, OH, [O I] far-IR lines
    - Symmetric molecules: C_6H_6, CH_3, C_2H_4, CO_2, ….
    - H_2 lines as probe of shocks and PDRs
  - 2003-2009: ***Spitzer Space Telescope***
    - High sensitivity imgin and mapping; low-resolution spectroscopy
    - Ices, silicates, PAHs toward low mass protostars and disks
    - Detection of C_{60}!
  - 1980's – now: ***Ground*** and ***airborne*** IR instruments
- *Home exercise: check websites of various telescopes*

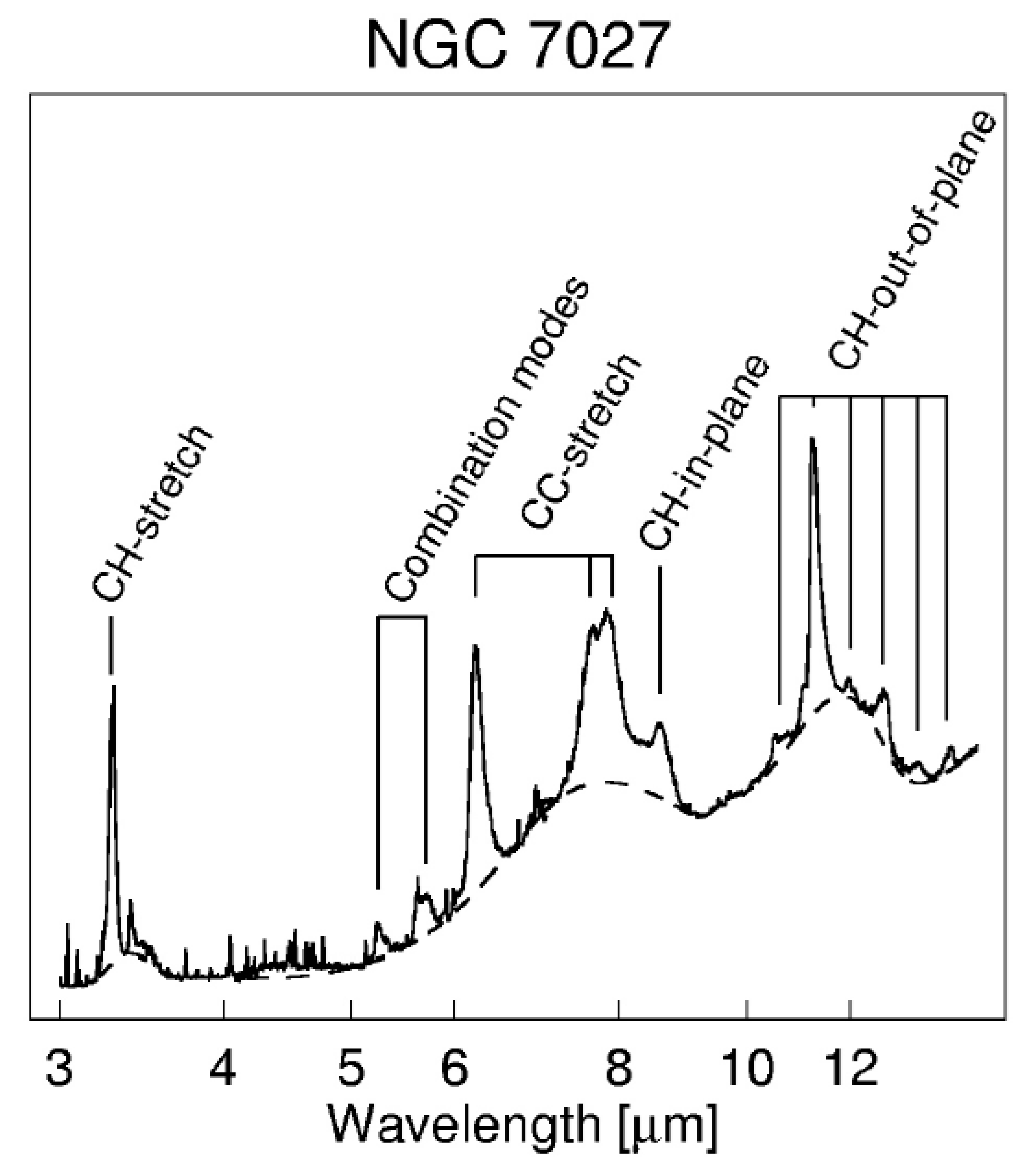
Unidentified Infrared Bands due to PAHs?

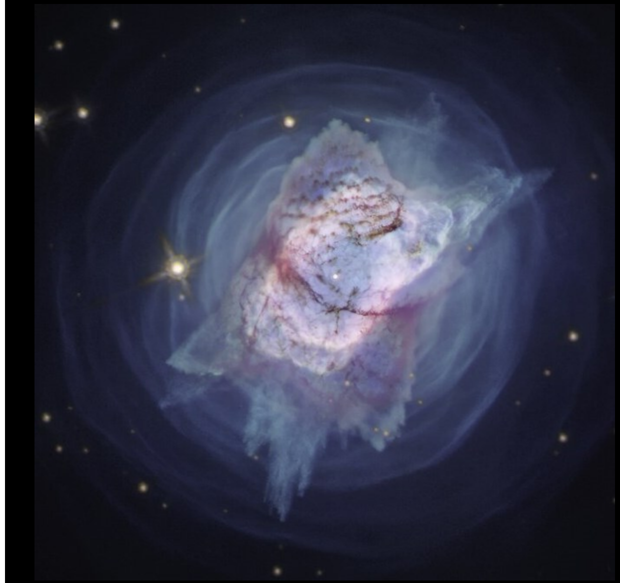
Seen through Universe
Tracers of UV
→Star formation!

US/NL:
Tielens, Allamandola, et al.

France:
Puget, Léger, Omont

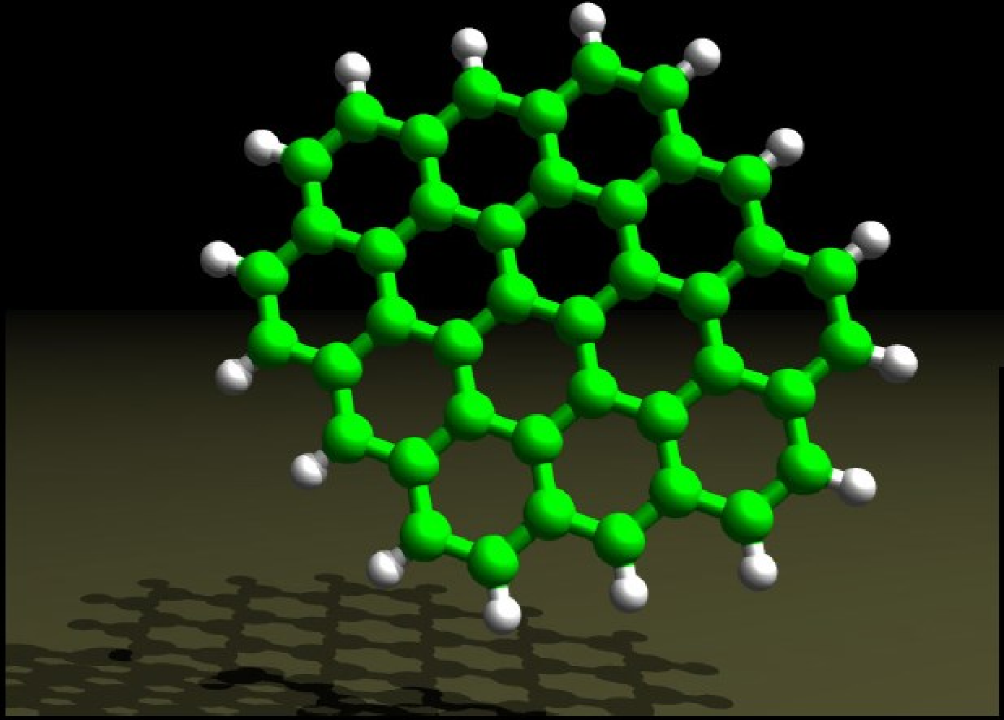
Credit: NASA, ESA, and J. Kastner (RIT)



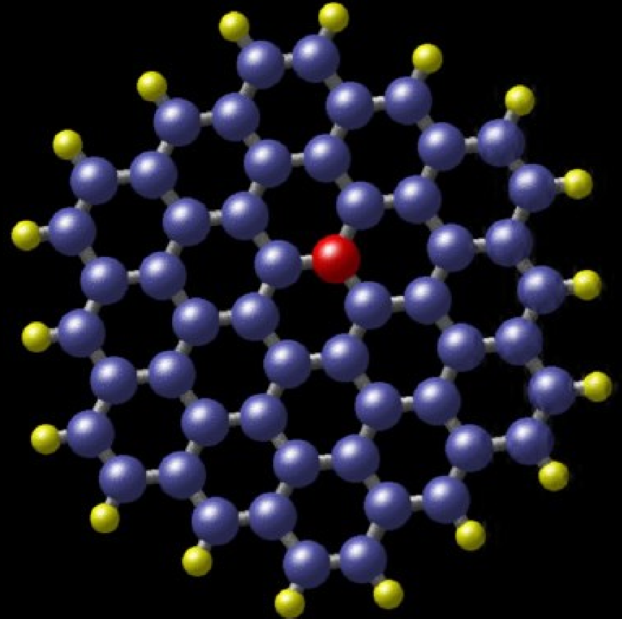


Credit: NASA, ESA, and J. Kastner (RIT)

Polycyclic Aromatic Hydrocarbons (PAHs)

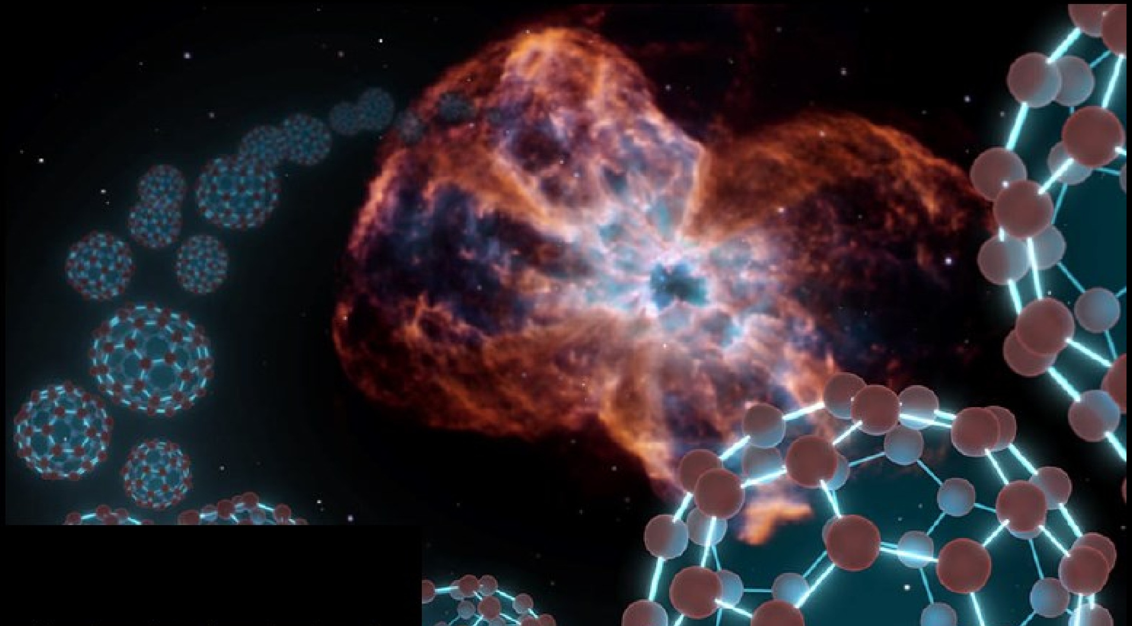


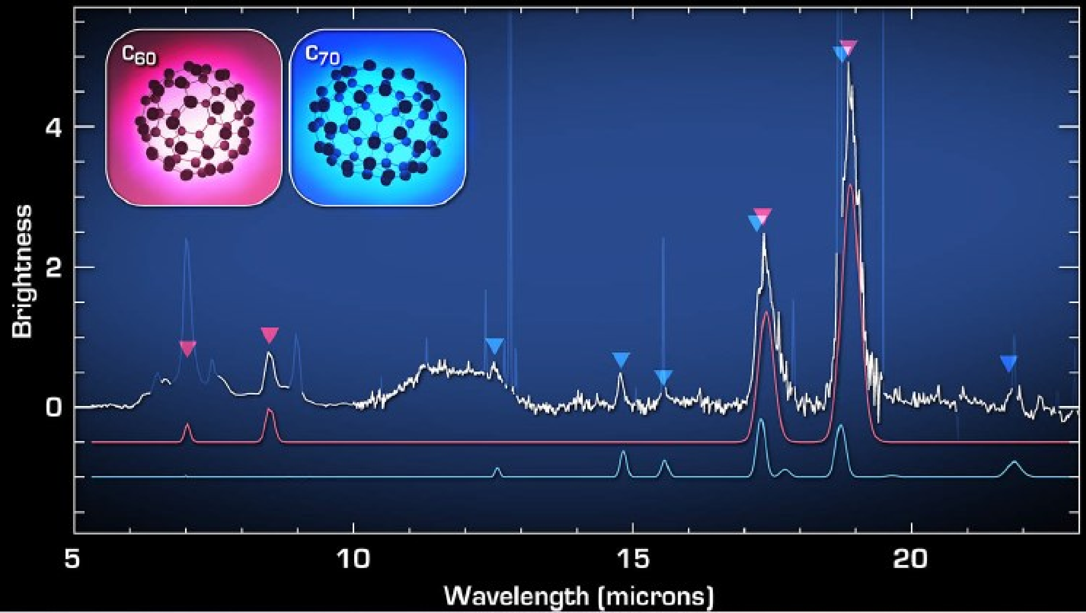
Only detected as a *class* of molecules



PAHN: N-containing PAHs

Detection of interstellar buckminsterfullerenes

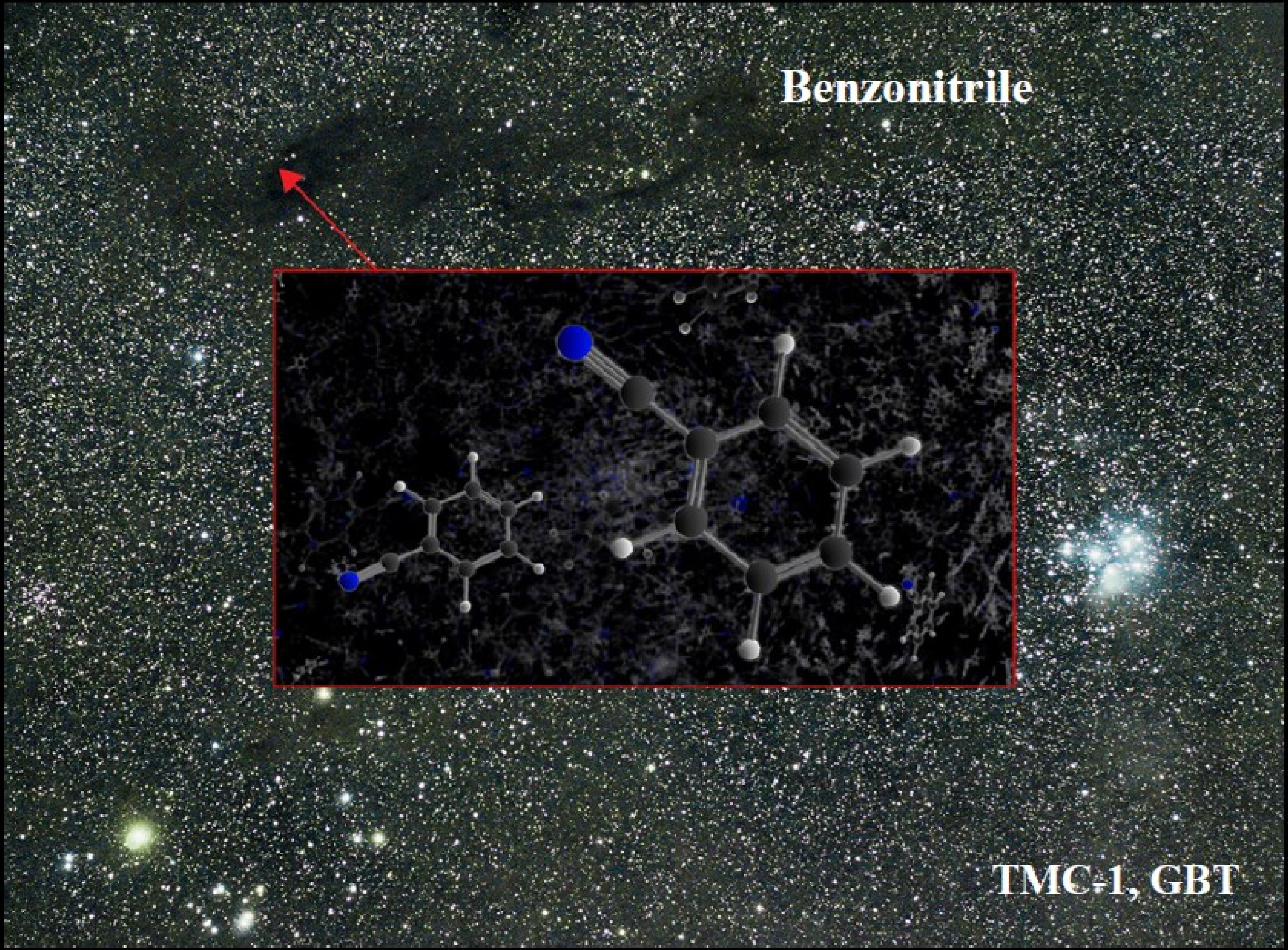




Predicted by Harry Kroto
when he was working on
long carbon chains in space in late
1980’s

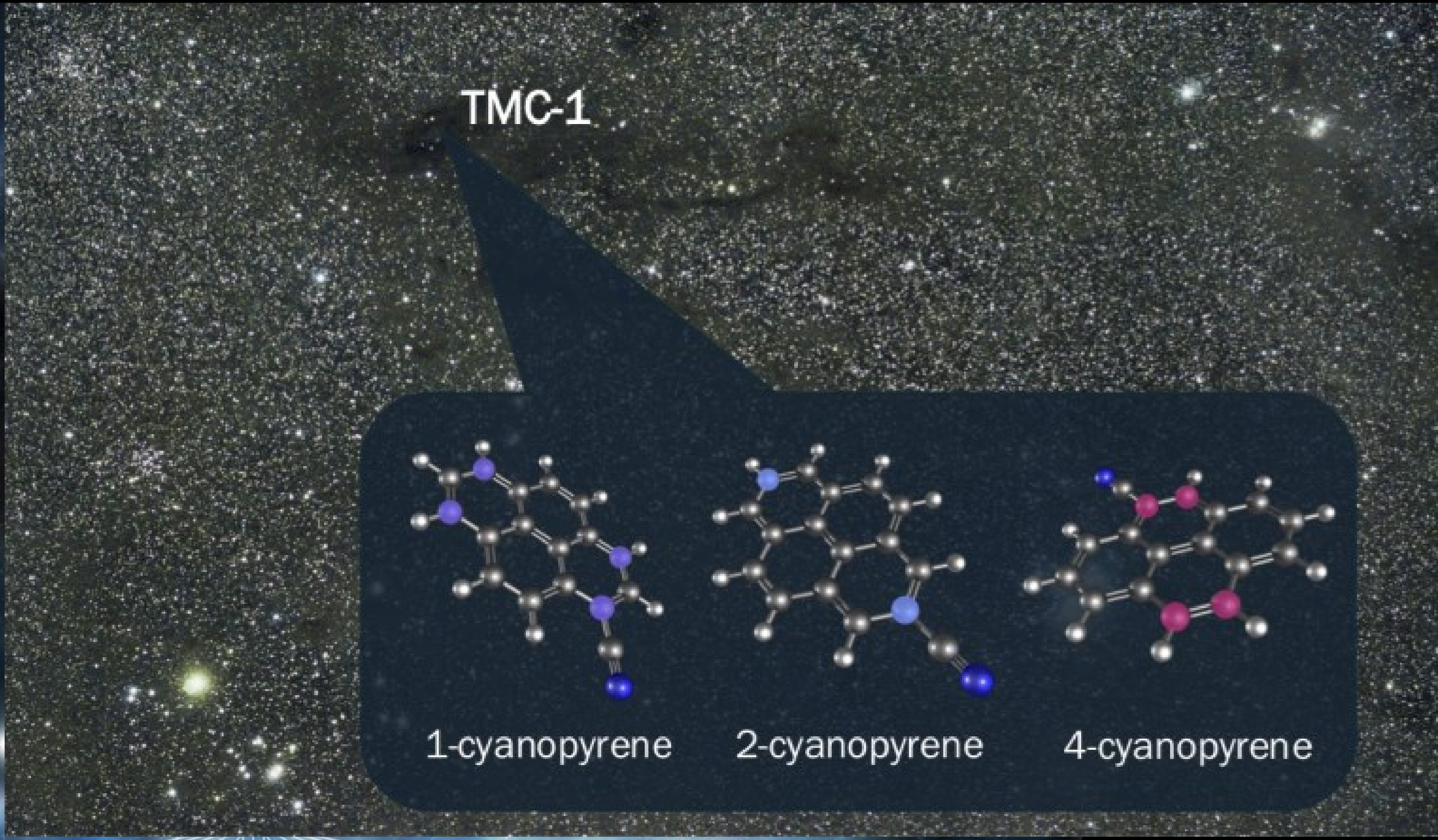
Cami et al. 2010

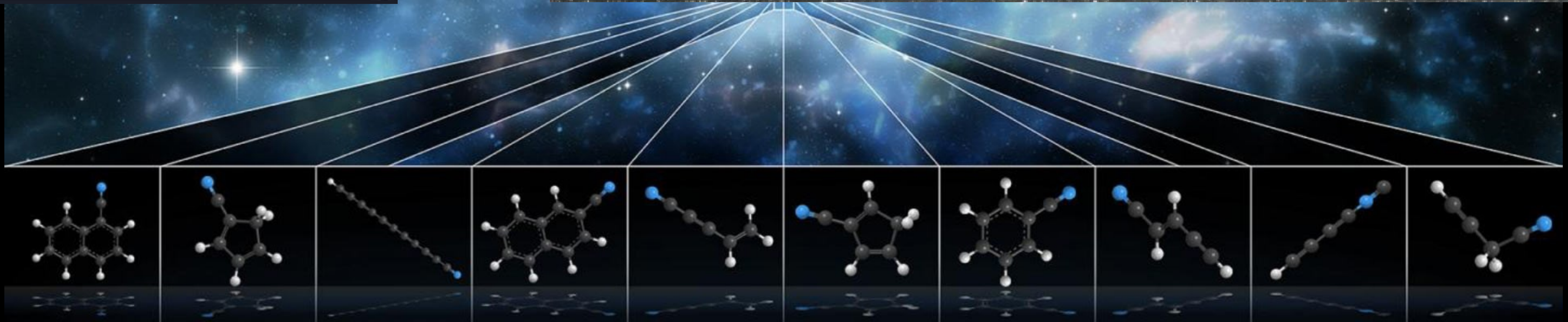
Radio detection of benzonitrile



McGuire et al. 2018, Science

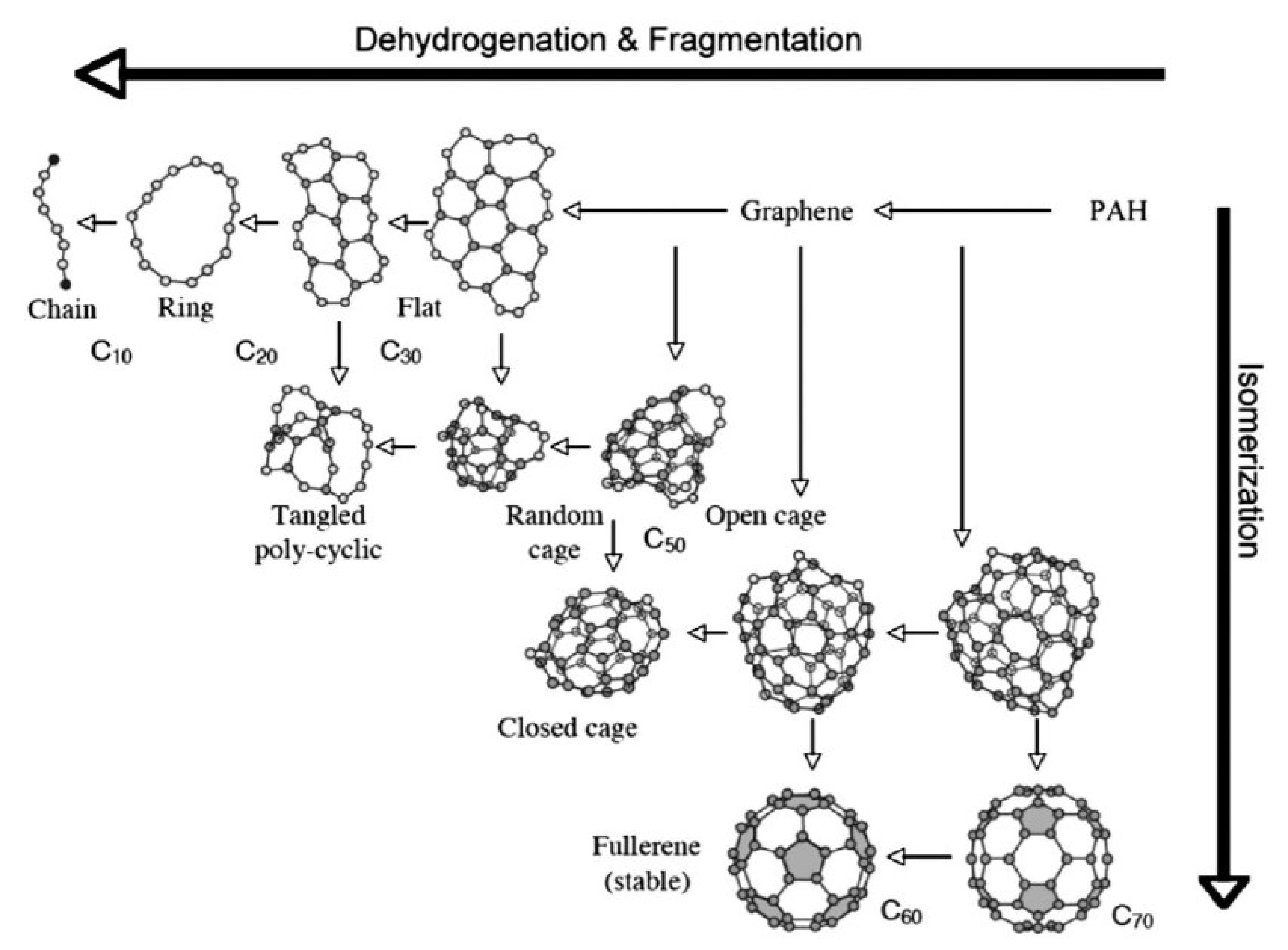
Cyano-naphthalene, cyano-coronene and more





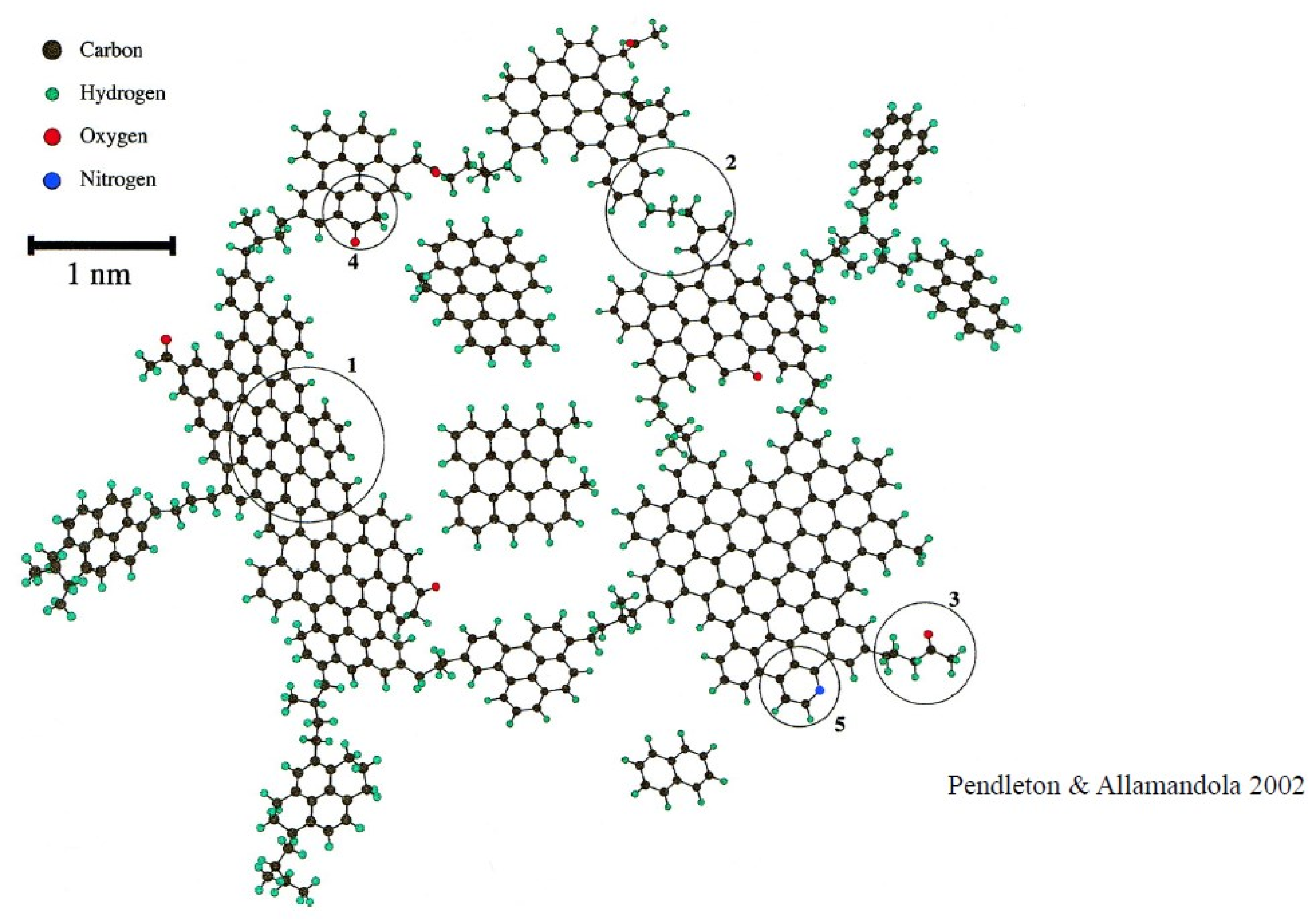
McGuire
Wenzel et al
2024-2025

Top-down chemistry from PAHs to fullerenes



Tielens 2013

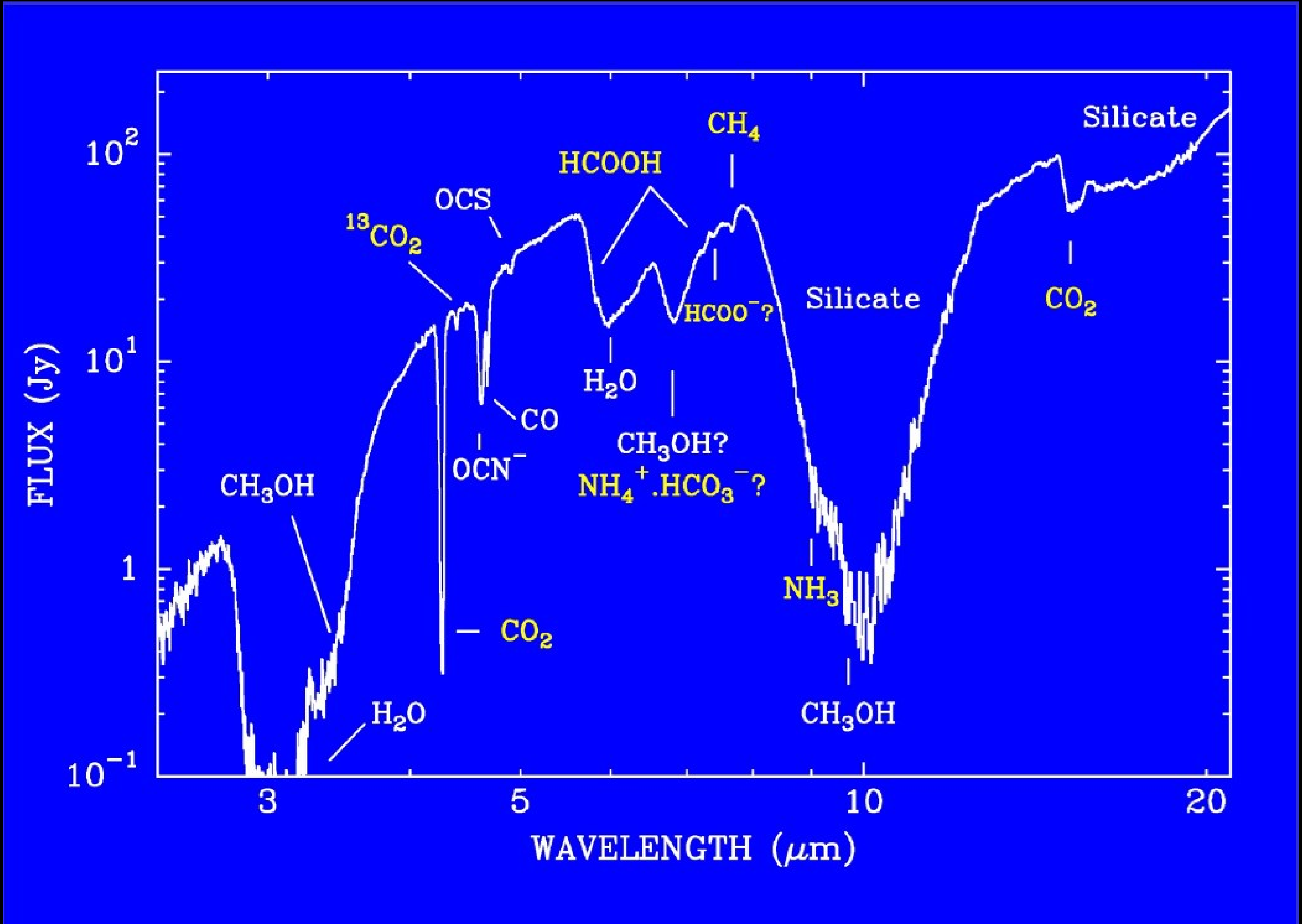
Carbonaceous material



Pendleton & Allamandola 2002

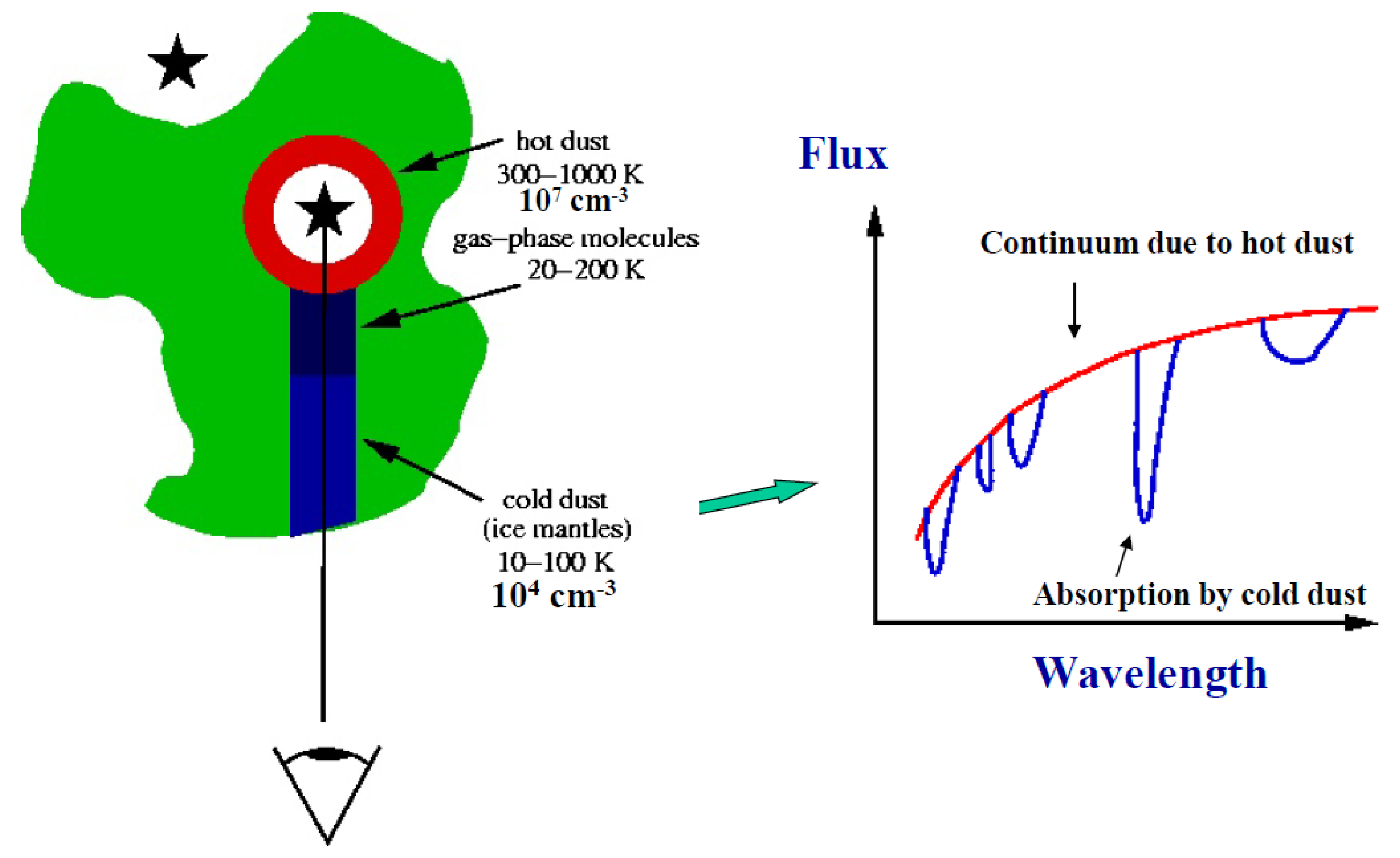
PAHs and compositions of grains discussed in Astrochem II

Inventory of ices



Gibb et al. (2004)

Infrared: absorption of gas and solids



Vibrational transitions of gases *and* solids

1.3 Composition of clouds

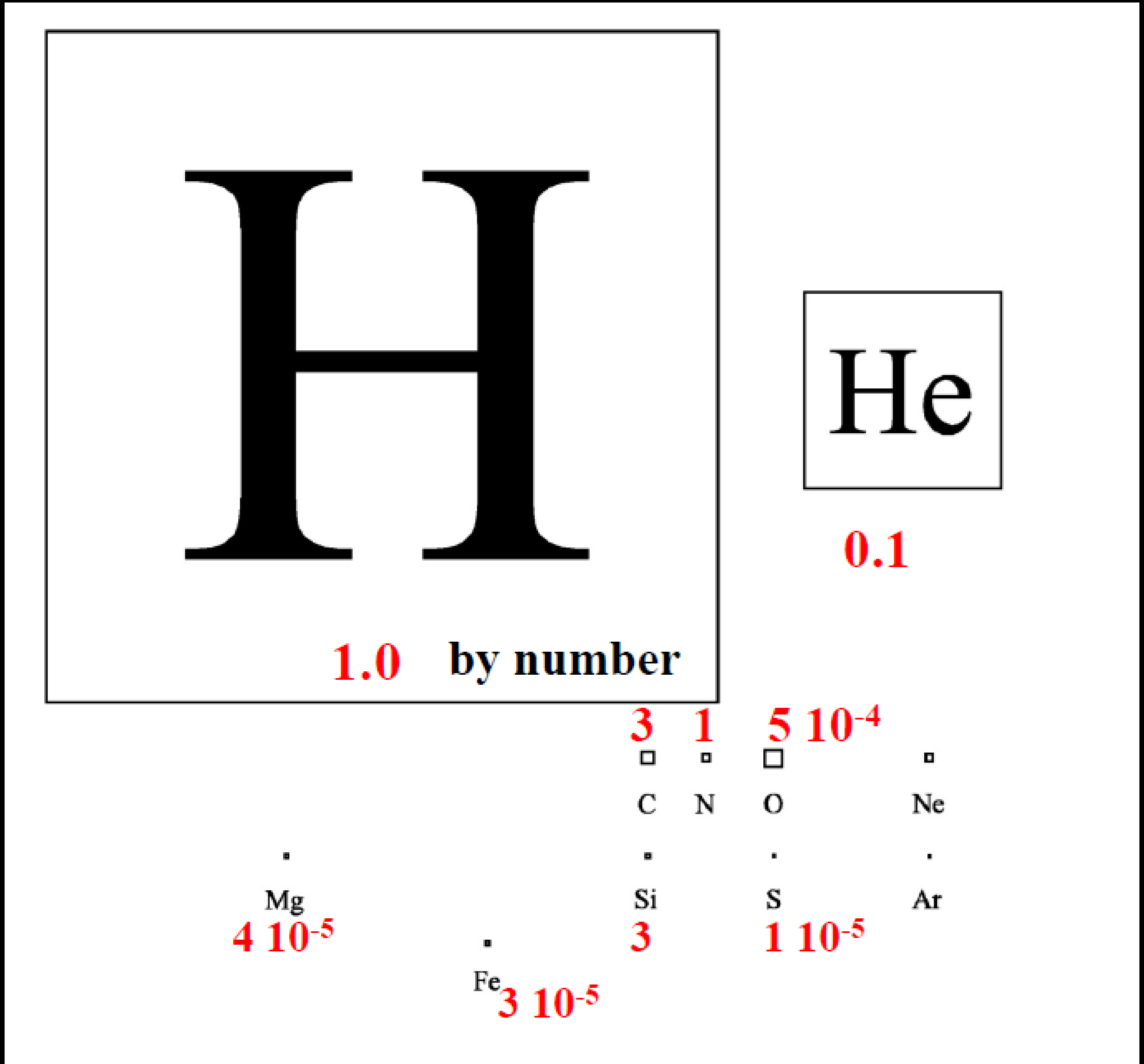
- Cosmic (solar) composition of elements

Asplund et al. (2009) ARA&A

Element	**Abundance**	**Element**	**Abundance**
H	1.00	Mg	4.0×10^{-5}
He	0.085	Al	2.8×10^{-6}
C	2.7×10^{-4}	Si	3.2×10^{-5}
N	6.8×10^{-5}	S	1.3×10^{-5}
O	4.9×10^{-4}	P	2.6×10^{-7}
Na	1.7×10^{-6}	Fe	3.2×10^{-5}

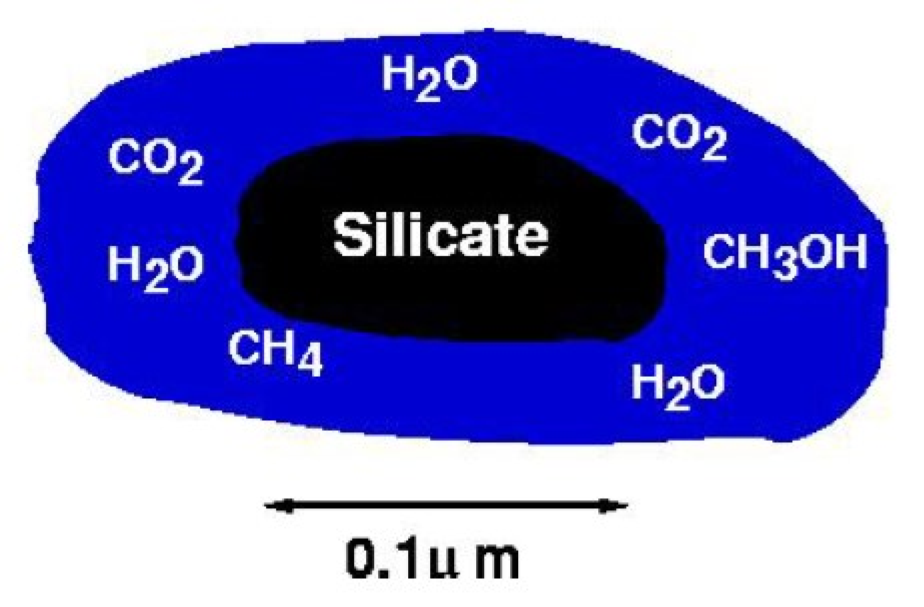
- Interstellar space is continuously enriched with heavy elements from dying stars through red-giant winds, novae, supernovae
- Interstellar abundances may differ slightly from solar abundances but homogeneous throughout ISM
- Not all these atoms available for gas phase chemistry, some locked up in grains (‘depletion’)

The astronomer‘s periodic table



McCall 2001

Interstellar grains



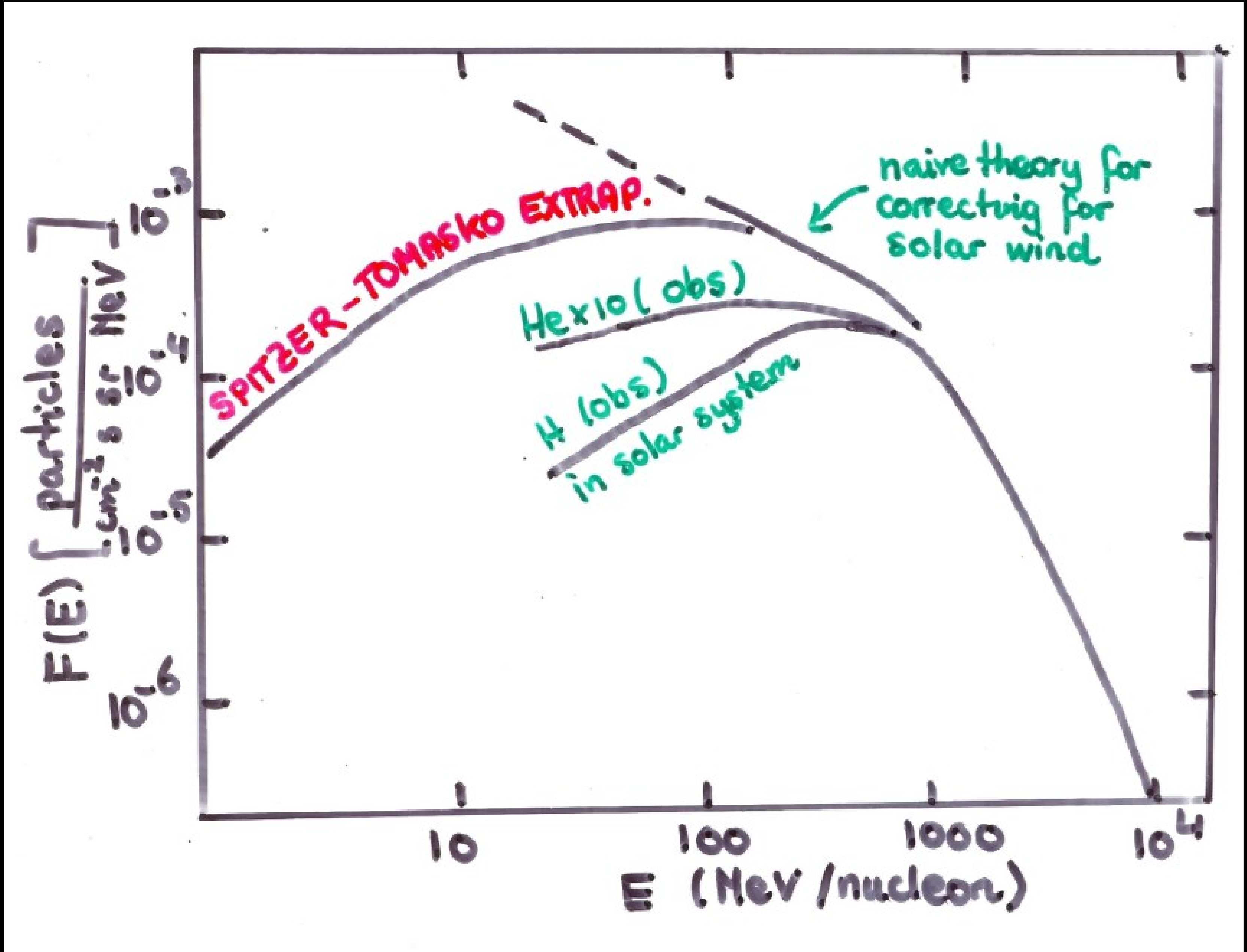
- Small solid particles ~0.01-0.5 μm in size consisting of silicates and carbonaceous material;
  - $\sim 10^{-12}$ by number wrt H
- Most of Si, Mg, Fe incorporated in silicate cores;
  - ~30% of O; ~60% of C in carbonaceous material
- Cold dense clouds ($T_{\mathrm{dust}} \sim 10$ K): gas-phase species condense on grains forming an icy mantle

Cosmic rays

- In regions in which UV photons cannot penetrate, ionization is provided by ***cosmic rays***
- Cosmic rays were discovered in 1912 through balloon experiments. They consist of high energy nuclei with GeV energies (protons, electrons, He, Fe nuclei, …)
- Ionization is mostly due to cosmic rays with E = 5-500 MeV, which cannot be observed directly due to solar wind

  → extrapolation required
- Conservative estimate (Spitzer & Tomasko): $\xi_{CR} = 4\text{x}10^{-18}\ \text{s}^{-1}$
- Curent best estimate: $\xi_H \sim 2\text{x}10^{-16}\ \text{s}^{-1}$ in diffuse clouds, decreasing to ~few x $10^{-17}\ \text{s}^{-1}$ in dense clouds

Observed cosmic rays



1.4 Observational techniques diffuse clouds

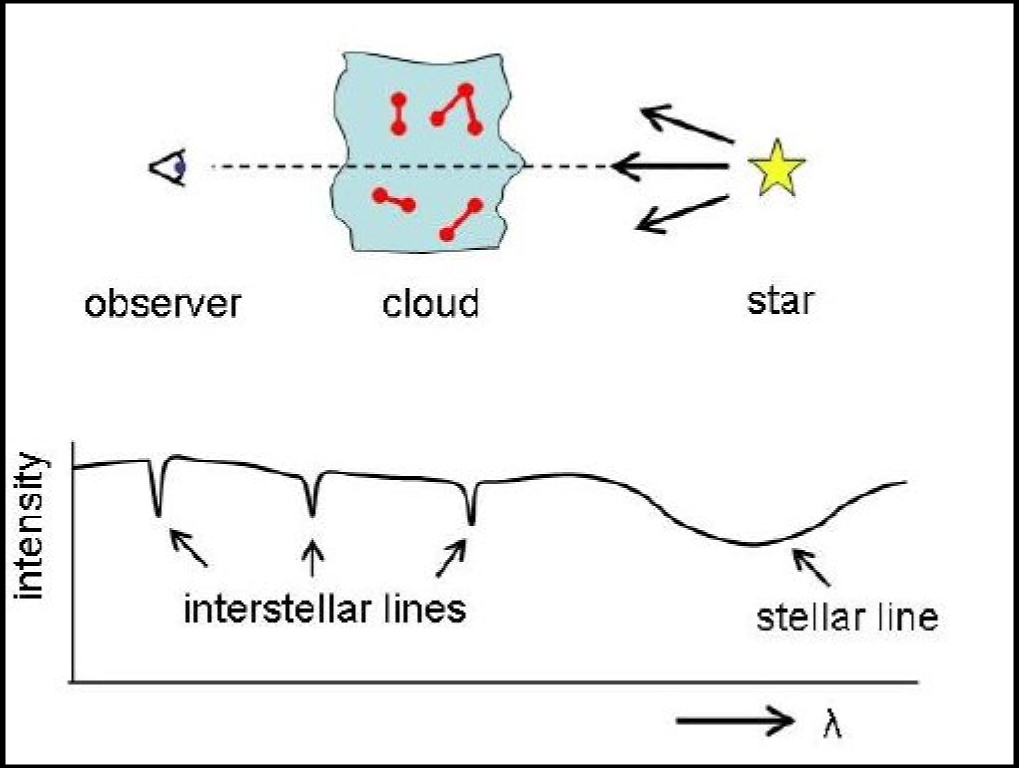
- Diffuse clouds ≡ clouds with total visual extinction $A_V \leq 1$ mag
- Visible + UV light from background stars not completely obscured
- If $A_V \leq 0.3$ mag → virtually all hydrogen in atomic form → diffuse atomic clouds
- If 0.3 mag $\leq A_V \leq$ 1 mag → significant fraction of hydrogen is molecular
- Note:

$$A_V = \frac{N_H}{1.8\ x\ 10^{21} cm^2}$$

With $N_{\mathrm{H}} = N(\mathrm{H}) + 2N(\mathrm{H}_2)$

Observations of diffuse clouds

- Observed primarily by absorption lines at visible (since 1900‘s) and UV wavelengths (since 1970‘s)
- Classical example: line-of-sight toward ζ Oph
- Spectra show sharp interstellar lines super-imposed on broad stellar lines

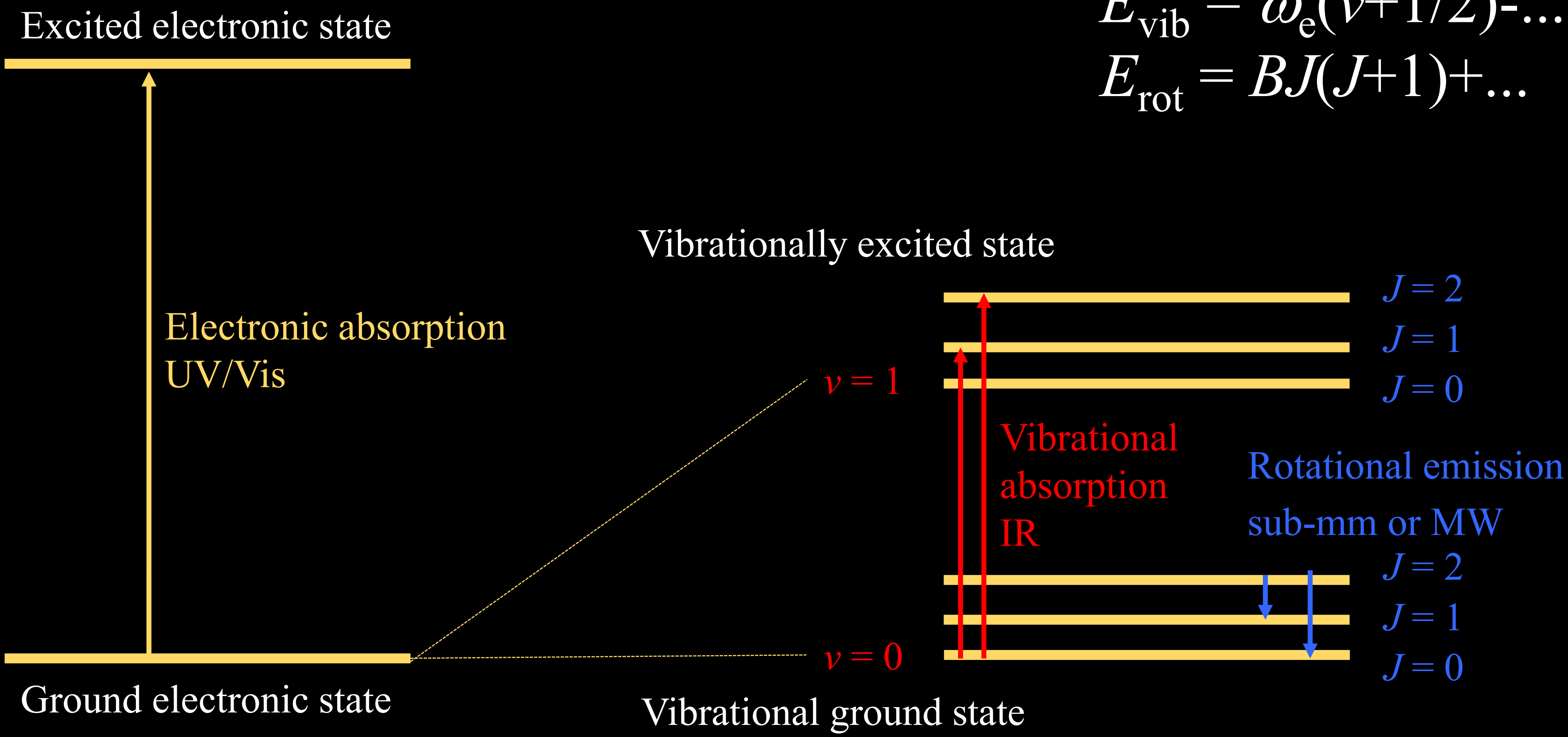


Molecular spectroscopy

$$E = E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}}$$

$$E_{\mathrm{vib}} = \omega_e(v+1/2)-\ldots$$

$$E_{\mathrm{rot}} = BJ(J+1)+\ldots$$



Excited electronic state

Electronic absorption
UV/Vis

Ground electronic state

Vibrationally excited state

$v = 1$

$J = 2$

$J = 1$

$J = 0$

Vibrational
absorption
IR

Rotational emission
sub-mm or MW

$v = 0$

$J = 2$

$J = 1$

$J = 0$

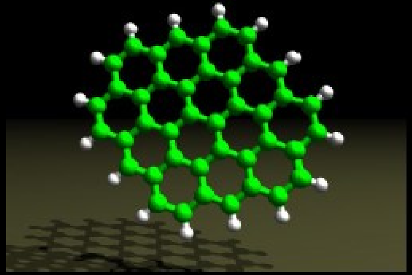
Vibrational ground state

Dense clouds

- Opaque at visible and UV wavelengths → molecules shielded from dissociating UV radiation
- Millimeter emission: ***rotational*** transitions
  - *Limitation:* molecule must have permanent dipole moment → cannot observe H_2, C_2, N_2, CH_4, C_2H_2, ...
  - *Advantage:* many molecules down to low abundances; lines in emission → map
- Infrared absorption: ***vibrational*** transitions
  - *Limitation:* need background IR source → only info along line of sight
  - *Advantage:* symmetric molecules + solid state
- Earth‘s atmosphere prevents observations of key molecules: H_2O, O_2, CO_2

From visible to infrared light

HH 46 star-forming region

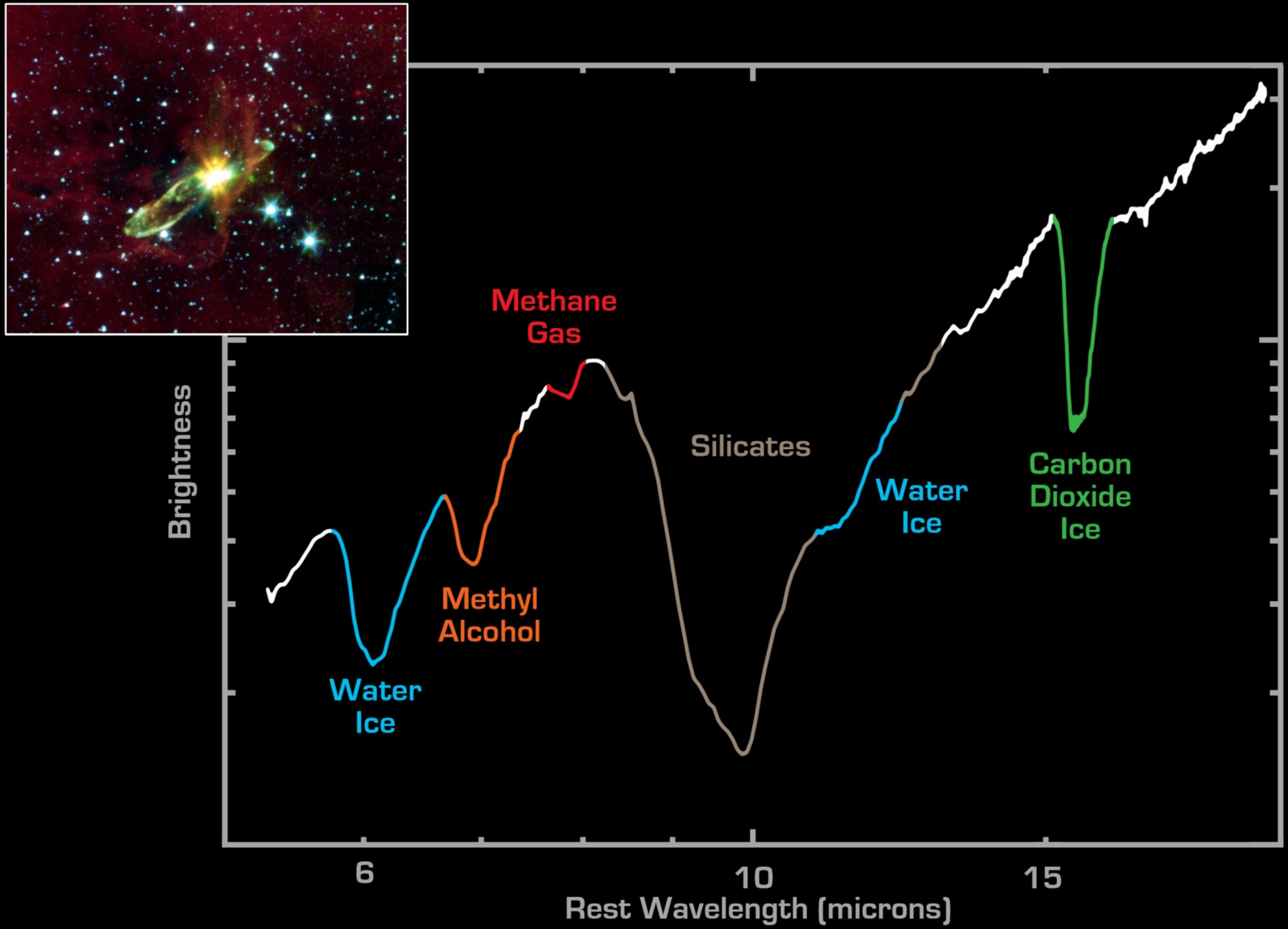


Spitzer image:

Red= 8 μm: PAH
Green= 4.5 μm: H_2
Blue= 3 μm: stars

Noriega-Crespo et al. 2004
Spitzer animation

Need long wavelengths to penetrate dusty regions



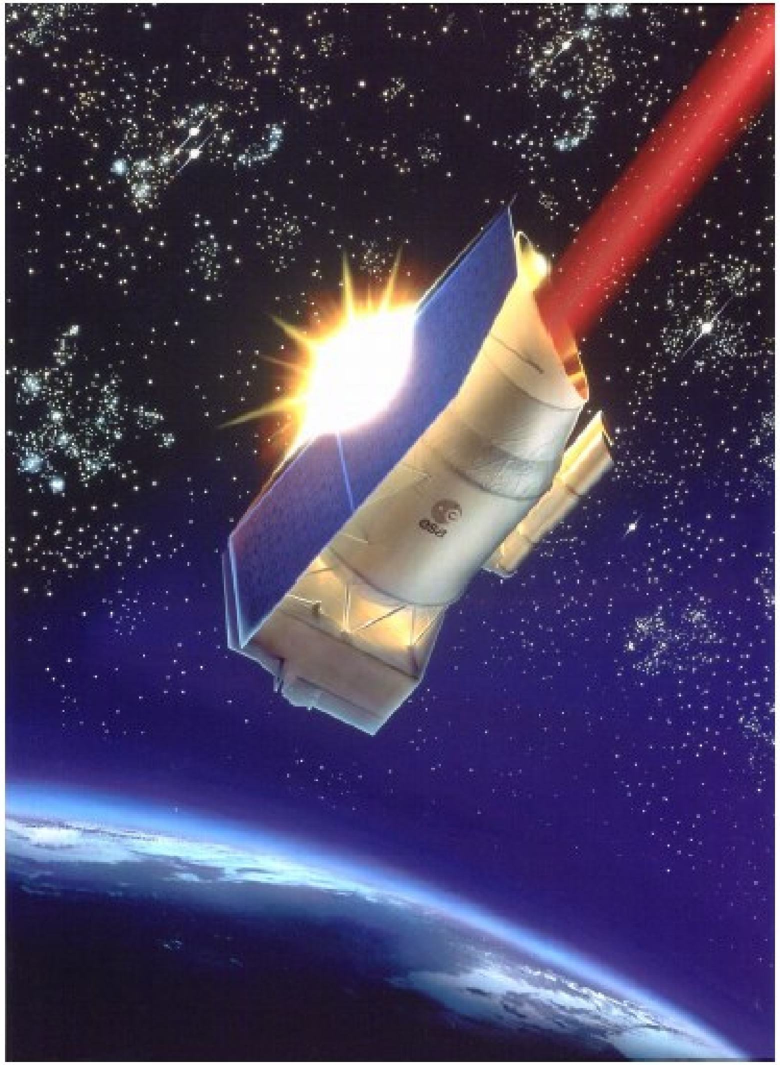
Embedded Outflow in HH 46/47

Spitzer Space Telescope • IRS • IRAC

NASA / JPL-Caltech / A. Noriega-Crespo (SSC/Caltech)

ssc2003-06g

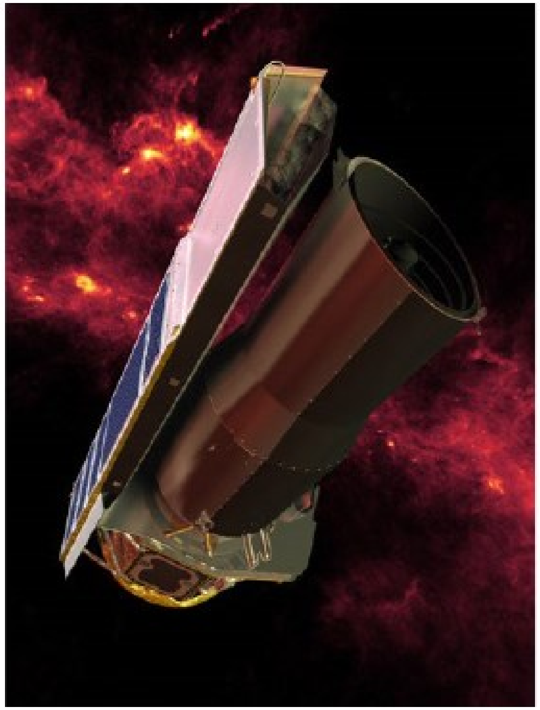
Infrared observatories



ISO 1995-1998

VLT

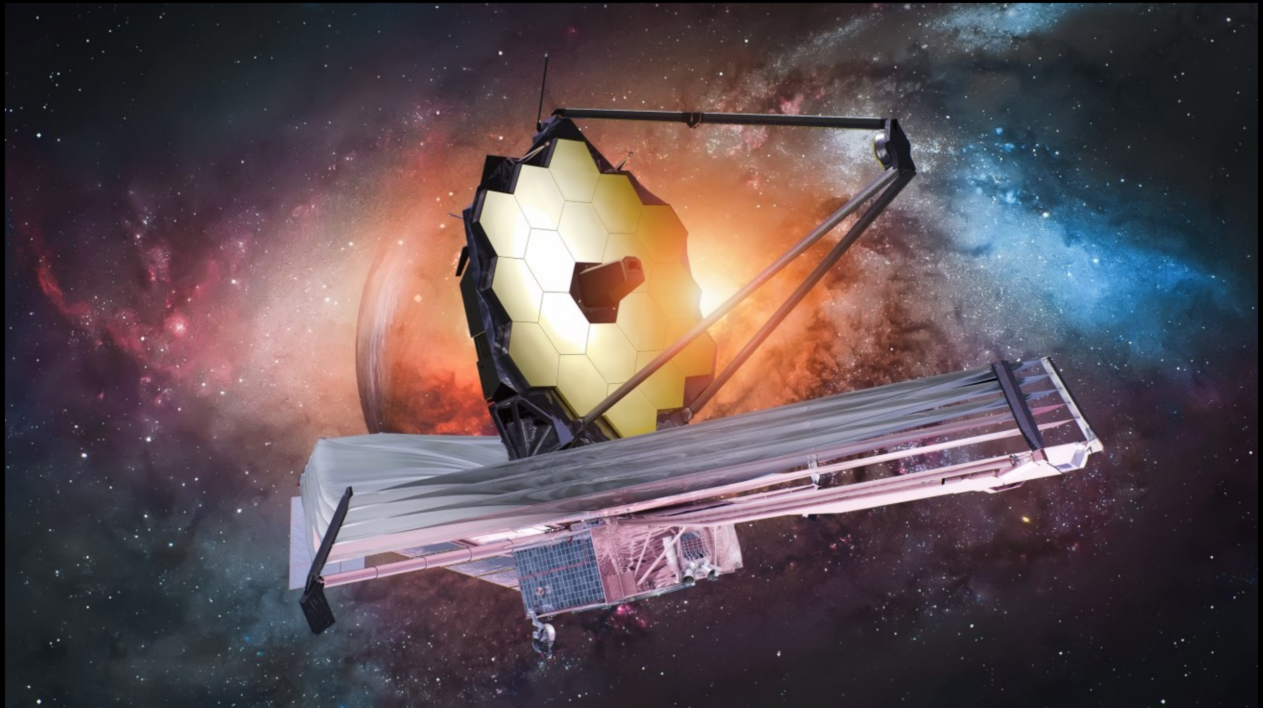
Keck



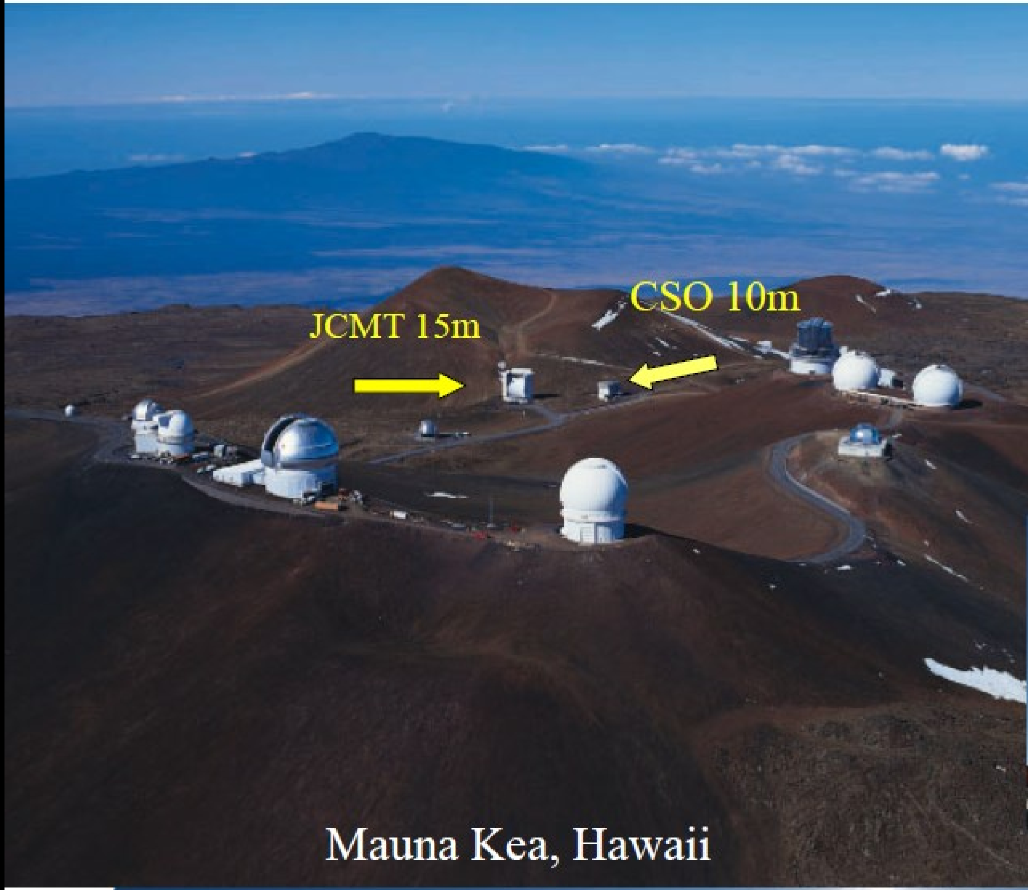
Spitzer 2003-2009

James Webb Space Telescope (JWST)

- Launched in December 2021
- Could be operational for 20+ yrs
- Four instruments:
    - Mid Infrared Instrument (MIRI) (5 – 28 μm)
    - Near Infrared Camera (NIRCam) (0.6 – 5.0 μm)
    - Near Infrared Imager and Slitless Spectrograph (NIRISS) (0.6 – 5.0 μm)
    - Near Infrared Spectrograph (NIRSpec) (0.6 – 5.3 μm)



Sub-mm/Far-IR observatories



APEX

Herschel 2009-2013

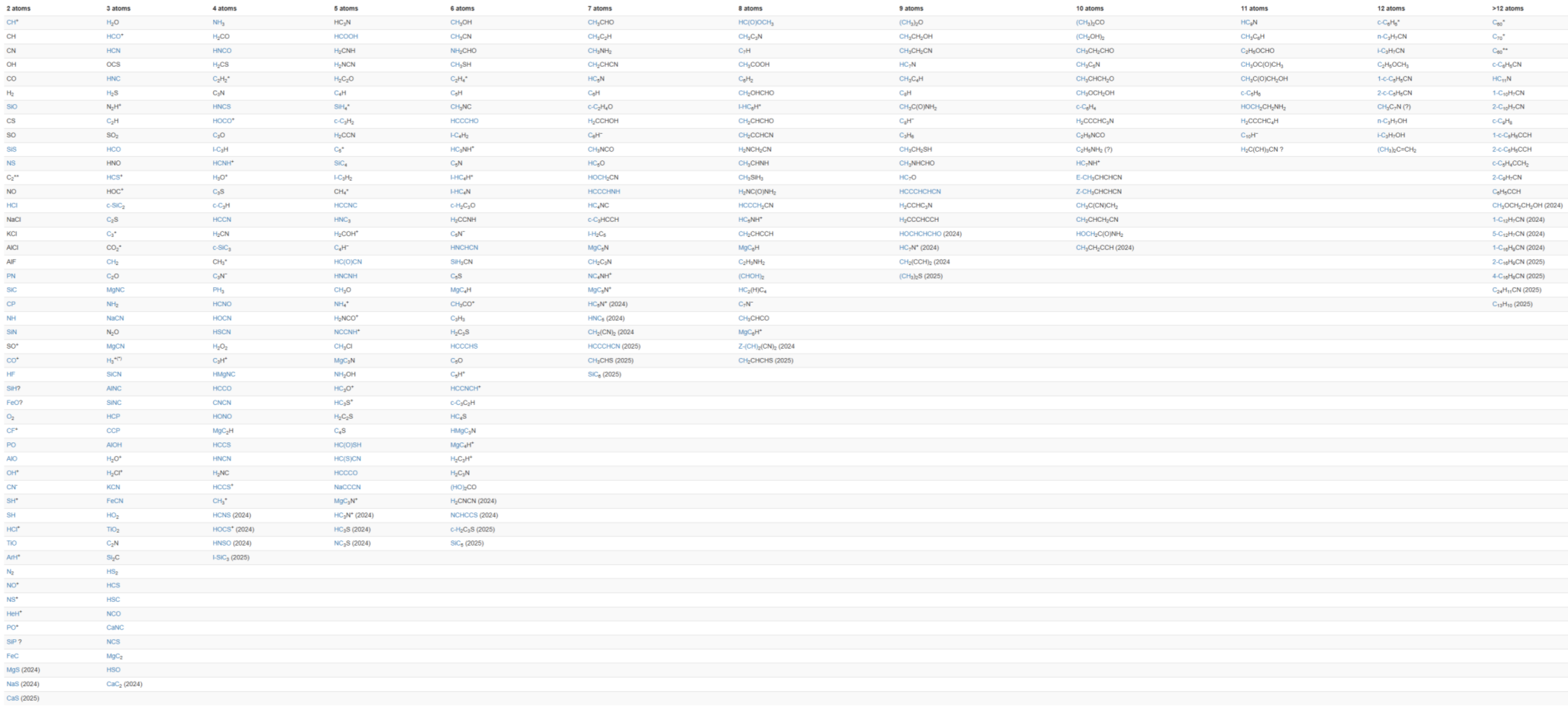
Bulk of gas-phase molecules, no solids

Atacama Large millimeter array (ALMA)

- 54 x 12m + 12 x 7m antennae
  - Up to 10000 times faster than existing arrays
- Millimeter/submillimeter wavelengths
  - 7 – 0.35 mm (30-900 GHz)

Inauguration March 13, 2013

1.5 Identified interstellar molecules



2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
CH^+	H_2O	NH_3	HC_3N	CH_3OH	CH_3CHO	$HC(O)OCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$	HC_9N	c-C_6H_6*	C_{60}*
CH	HCO^+	H_2CO	HCOOH	CH_3CN	CH_3C_2H	CH_3C_3N	CH_3CH_2OH	$(CH_2OH)_2$	CH_3C_6H	n-C_3H_7CN	C_{70}*
CN	HCN	HNCO	H_2CNH	NH_2CHO	CH_3NH_2	C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	i-C_3H_7CN	C_{60}^+*
OH	OCS	H_2CS	H_2NCN	CH_3SH	CH_2CHCN	CH_3COOH	HC_7N	CH_3C_5N	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$	c-C_6H_5CN
CO	HNC	C_2H_2*	H_2C_2O	C_2H_4*	HC_5N	C_6H_2	CH_3C_4H	CH_3CHCH_2O	$CH_3C(O)CH_2OH$	1-c-C_5H_5CN	$HC_{11}N$
H_2	H_2S	C_3N	C_4H	C_5H	C_6H	CH_2OHCHO	C_8H	CH_3OCH_2OH	c-C_5H_6	2-c-C_5H_5CN	1-$C_{10}H_7CN$
SiO	N_2H^+	HNCS	SiH_4*	CH_3NC	c-C_2H_4O	l-HC_6H*	$CH_3C(O)NH_2$	c-C_6H_4	$HOCH_2CH_2NH_2$	CH_3C_7N (?)	2-$C_{10}H_7CN$
CS	C_2H	$HOCO^+$	c-C_3H_2	HCCCHO	H_2CCHOH	CH_2CHCHO	C_8H^-	H_2CCCHC_3N	H_2CCCHC_4H	n-C_3H_7OH	c-C_9H_8
SO	SO_2	C_3O	H_2CCN	l-C_4H_2	C_6H^-	CH_2CCHCN	C_3H_6	C_2H_5NCO	$C_{10}H^-$	i-C_3H_7OH	1-c-C_5H_5CCH
SiS	HCO	l-C_3H	C_5*	HC_3NH^+	CH_3NCO	H_2NCH_2CN	CH_3CH_2SH	$C_2H_5NH_2$ (?)	$H_2C(CH)_3CN$?	$(CH_3)_2C{=}CH_2$	2-c-C_5H_5CCH
NS	HNO	$HCNH^+$	SiC_4	C_5N	HC_5O	CH_3CHNH	CH_3NHCHO	HC_7NH^+			c-$C_5H_4CCH_2$
C_2**	HCS^+	H_3O^+	l-C_3H_2	l-HC_4H*	$HOCH_2CN$	CH_3SiH_3	HC_7O	E-$CH_3CHCHCN$			2-C_9H_7CN
NO	HOC^+	C_3S	CH_4*	l-HC_4N	HCCCHNH	$H_2NC(O)NH_2$	HCCCHCHCN	Z-$CH_3CHCHCN$			C_6H_5CCH
HCl	c-SiC_2	c-C_3H	HCCNC	c-H_2C_3O	HC_4NC	$HCCCH_2CN$	H_2CCHC_3N	$CH_3C(CN)CH_2$			$CH_3OCH_2CH_2OH$ (2024)
NaCl	C_2S	HCCN	HNC_3	H_2CCNH	c-C_3HCCH	HC_5NH^+	$H_2CCCHCCH$	CH_2CHCH_2CN			1-$C_{12}H_7CN$ (2024)
KCl	C_3*	H_2CN	H_2COH^+	C_5N^-	l-H_2C_5	CH_2CHCCH	HOCHCHCHO (2024)	$HOCH_2C(O)NH_2$			5-$C_{12}H_7CN$ (2024)
AlCl	CO_2*	c-SiC_3	C_4H^-	HNCHCN	MgC_5N	MgC_6H	HC_7N^+ (2024)	CH_3CH_2CCH (2024)			1-$C_{16}H_9CN$ (2024)
AlF	CH_2	CH_3*	HC(O)CN	SiH_3CN	CH_2C_3N	$C_2H_3NH_2$	$CH_2(CCH)_2$ (2024				2-$C_{16}H_9CN$ (2025)
PN	C_2O	C_3N^-	HNCNH	C_5S	NC_4NH^+	$(CHOH)_2$	$(CH_3)_2S$ (2025)				4-$C_{16}H_9CN$ (2025)
SiC	MgNC	PH_3	CH_3O	MgC_4H	MgC_5N^+	$HC_2(H)C_4$					$C_{24}H_{11}CN$ (2025)
CP	NH_2	HCNO	NH_4^+	CH_3CO^+	HC_5N^+ (2024)	C_7N^-					$C_{13}H_{10}$ (2025)
NH	NaCN	HOCN	H_2NCO^+	C_3H_3	HNC_5 (2024)	CH_3CHCO					
SiN	N_2O	HSCN	$NCCNH^+$	H_2C_3S	$CH_2(CN)_2$ (2024	MgC_6H^+					
SO^+	MgCN	H_2O_2	CH_3Cl	HCCCHS	HCCCHCN (2025)	Z-$(CH)_2(CN)_2$ (2024					
CO^+	$H_3^{+(*)}$	C_3H^+	MgC_3N	C_5O	CH_3CHS (2025)	CH_2CHCHS (2025)					
HF	SiCN	HMgNC	NH_2OH	C_5H^+	SiC_6 (2025)						
SiH?	AlNC	HCCO	HC_3O^+	$HCCNCH^+$							
FeO?	SiNC	CNCN	HC_3S^+	c-C_3C_2H							
O_2	HCP	HONO	H_2C_2S	HC_4S							
CF^+	CCP	MgC_2H	C_4S	$HMgC_3N$							
PO	AlOH	HCCS	HC(O)SH	MgC_4H^+							
AlO	H_2O^+	HNCN	HC(S)CN	$H_2C_3H^+$							
OH^+	H_2Cl^+	H_2NC	HCCCO	H_2C_3N							
CN^-	KCN	$HCCS^+$	NaCCCN	$(HO)_2CO$							
SH^+	FeCN	CH_3^+	MgC_3N^+	H_2CNCN (2024)							
SH	HO_2	HCNS (2024)	HC_3N^+ (2024)	NCHCCS (2024)							
HCl^+	TiO_2	$HOCS^+$ (2024)	HC_3S (2024)	c-H_2C_3S (2025)							
TiO	C_2N	HNSO (2024)	NC_3S (2024)	SiC_5 (2025)							
ArH^+	Si_2C	l-SiC_3 (2025)									
N_2	HS_2										
NO^+	HCS										
NS^+	HSC										
HeH^+	NCO										
PO^+	CaNC										
SiP ?	NCS										
FeC	MgC_2										
MgS (2024)	HSO										
NaS (2024)	CaC_2 (2024)										
CaS (2025)											

- For updates, see:
- https://cdms.astro.uni-koeln.de/classic/molecules
- https://www.astrochymist.org/
- Some identifications challenged

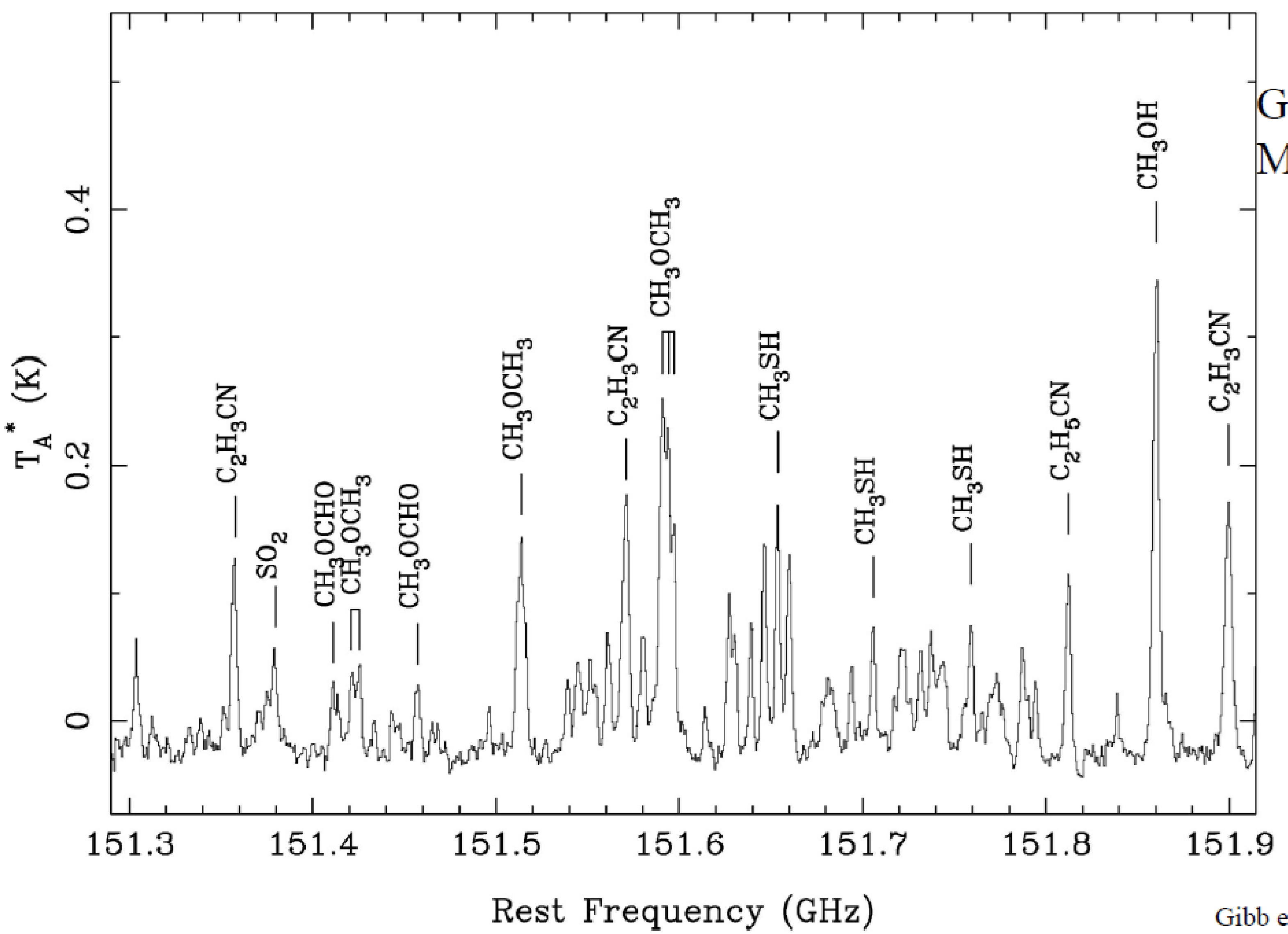
Diversity of molecules

- Over 360 different molecules found
- ‘Ordinary’ molecules
  - NH_3, H_2O, H_2CO, CH_3CH_2OH, ...
- ‘Exotic‘ molecules
  - HCO^+, N_2H^+, HCCCCCCCN, ...

→Unusual molecules

(rare on Earth but not in space)

Millimeter spectra: myriads of lines!

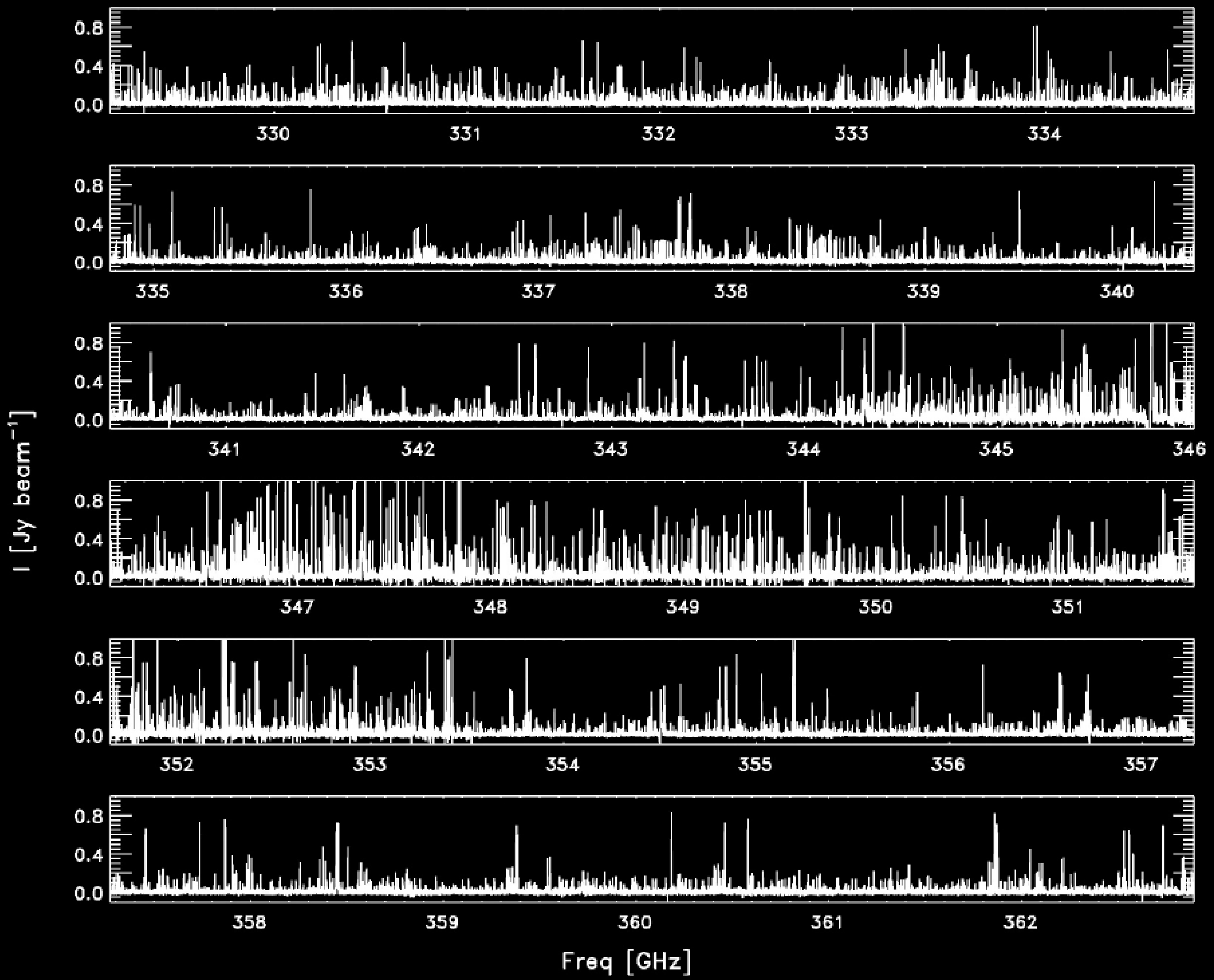


G327.3
Massive YSO

Gibb et al. 2000

- **Not all lines identified**

Molecular inventories of protostars
ALMA full spectral survey of IRAS 16293–2422



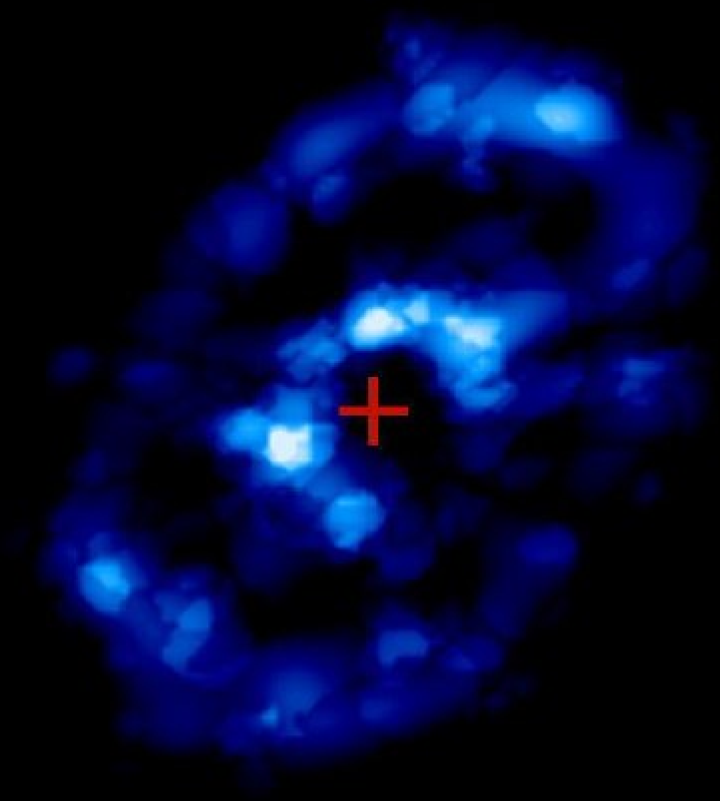
PILS

Jørgensen, vD
+ 2016

- **ALMA also produces an image of each line!**

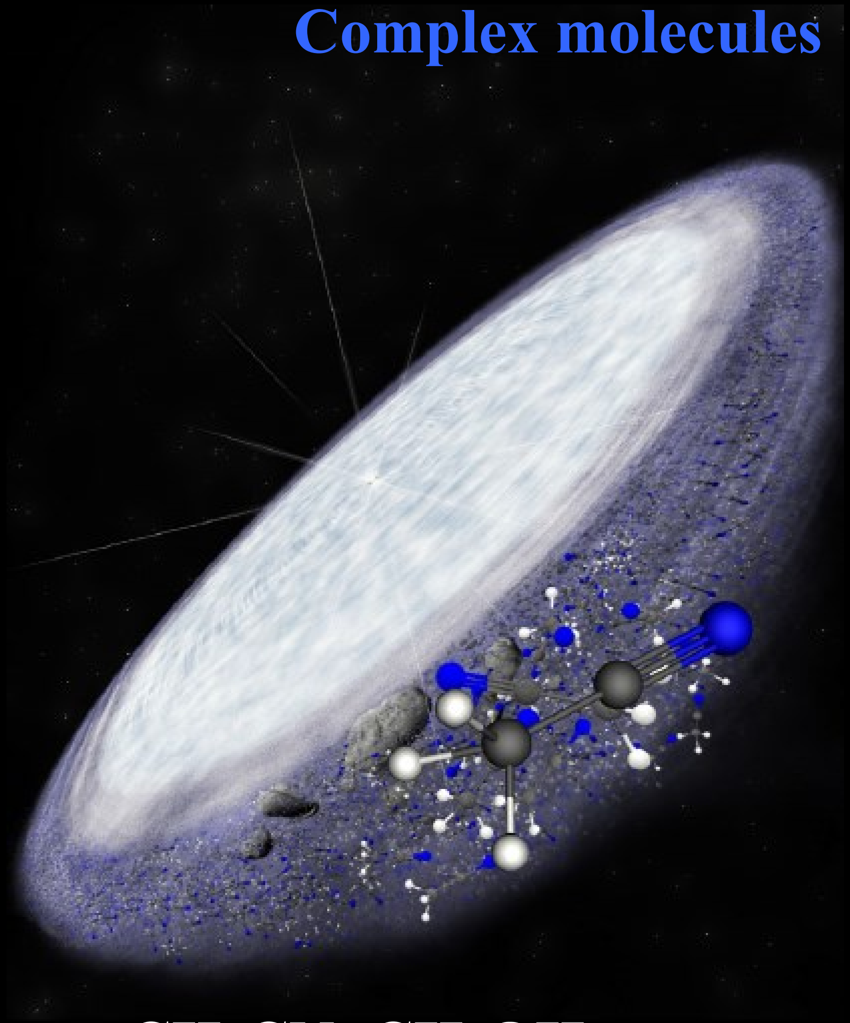
Molecules in protoplanetary disks

Snowlines



DCO^+ in IM Lup

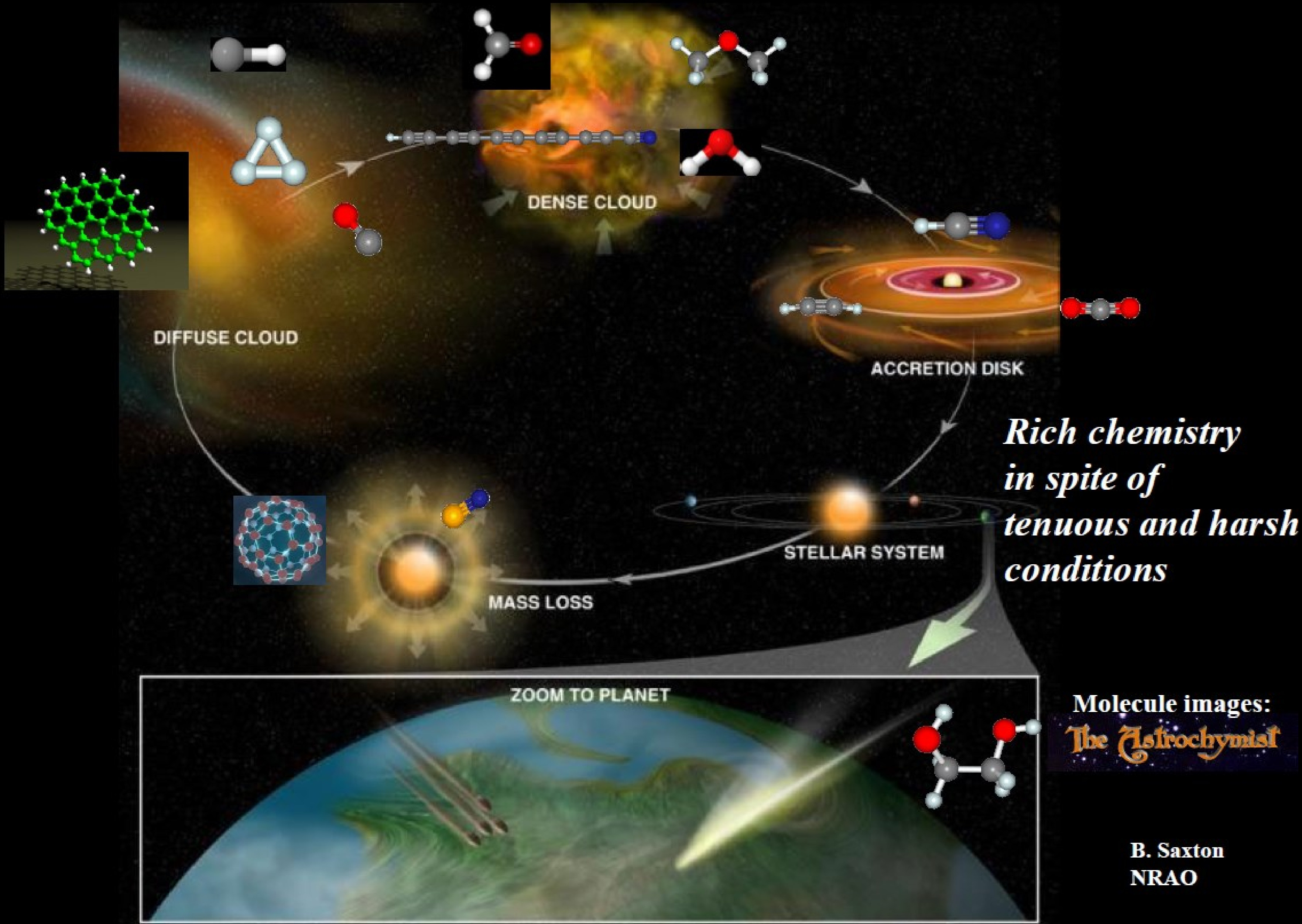
Complex molecules



CH_3CN, CH_3OH

K. I. Öberg et al. (2015a, b)

From clouds to stars and planets



Rich chemistry in spite of tenuous and harsh conditions

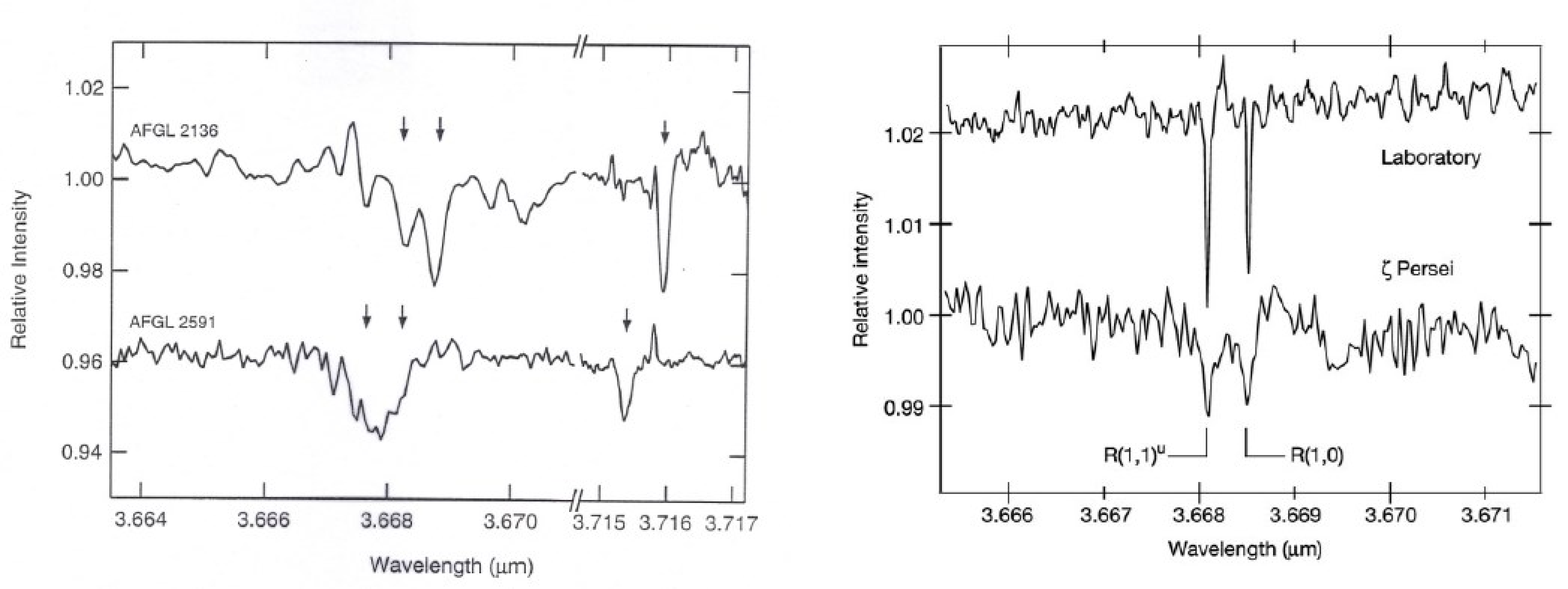
Molecule images:

B. Saxton
NRAO

Some detections

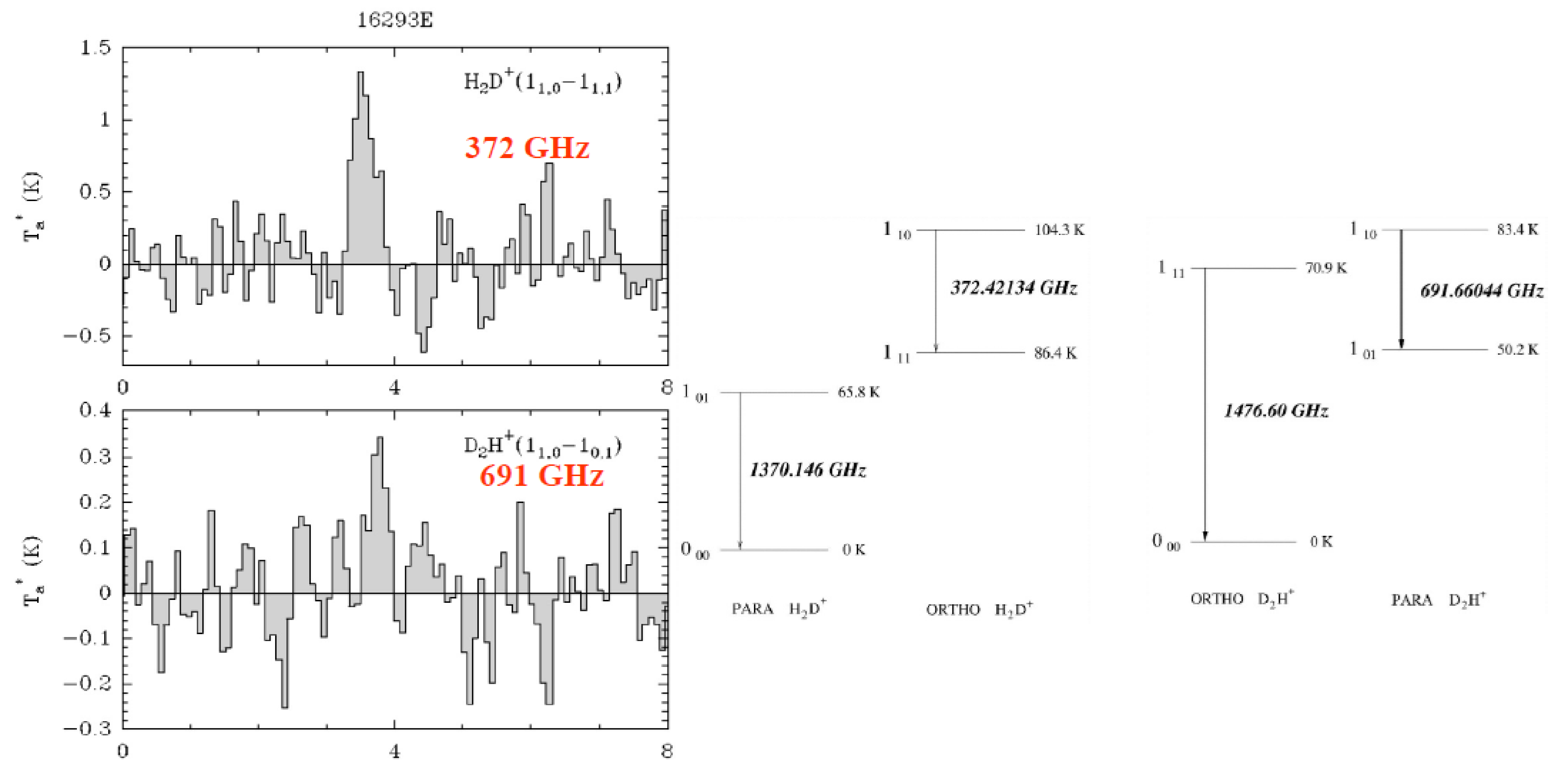
- H_3^+, H_2D^+, D_2H^+: cornerstones ion-molecule chemistry
- OH^+, H_2O^+, H_2Cl^+: small hydrides
- ArH^+, HeH^+: The first noble gas molecules
- C_3, C_4, C_6H_2, CH_3CHCH_2: carbon chains
- Cyclic C_2H_4O, C_2H_4S, C_3H_2, others
- C_6H_6, C_6H_5-CN, PAH-CN: (Cyano-)benzene, (cyano-)PAHs
- C_4H^-, C_6H^-, C_8H^-, $C_{10}H^-$: first negative ions
- D_2CO, ND_3, CD_3OH: doubly+triply deuterated
- NaCN, AlCN, SiN, SiCSi, MgCN, metal-containing species
- O_2 confirmed in a few places
- Unconvincing & controversial: glycine, tryptophan...

Interstellar H_3^+



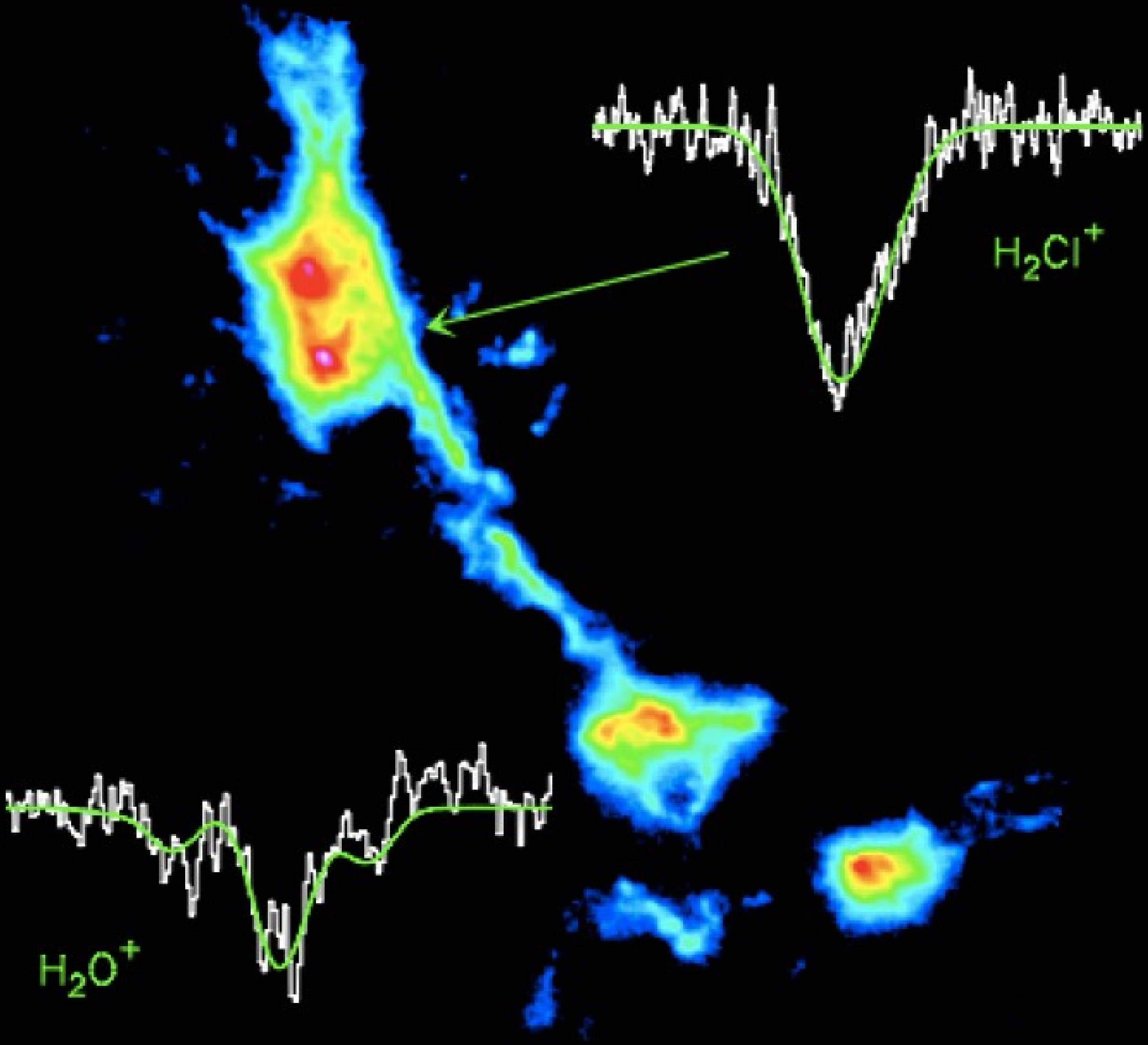
Oka & Geballe (1996)
McCall et al. (1999, 2003)

H_2D^+ & D_2H^+



Stark et al. (1999)
Caselli et al. (2003)
Vastel et al. (2006)

Detection of H_2O^+ & H_2Cl^+



- H_2O^+ widespread throughout our own and other galaxies
- H_2Cl^+ confirms simple Cl chemistry

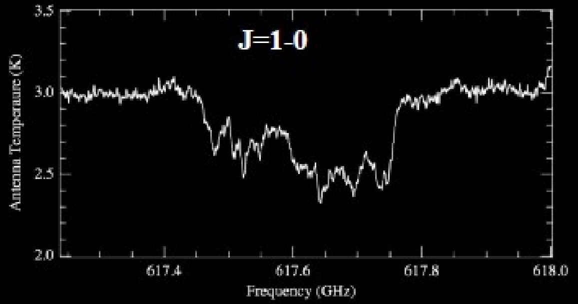
Gerin et al., Ossenkopf et al, Benz et al., Bruderer et al., Wyrowski et al., Gupta et al., Schilke et al., Lis et al., Herschel/HIFI special issue 2010

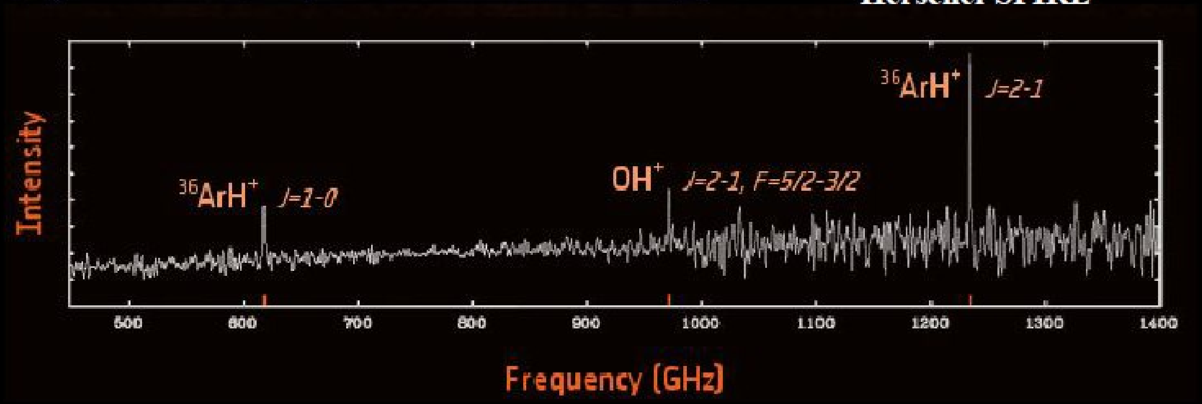
First interstellar noble gas molecule found

$^{36}ArH^+$

Crab nebula
Hubble+ Herschel

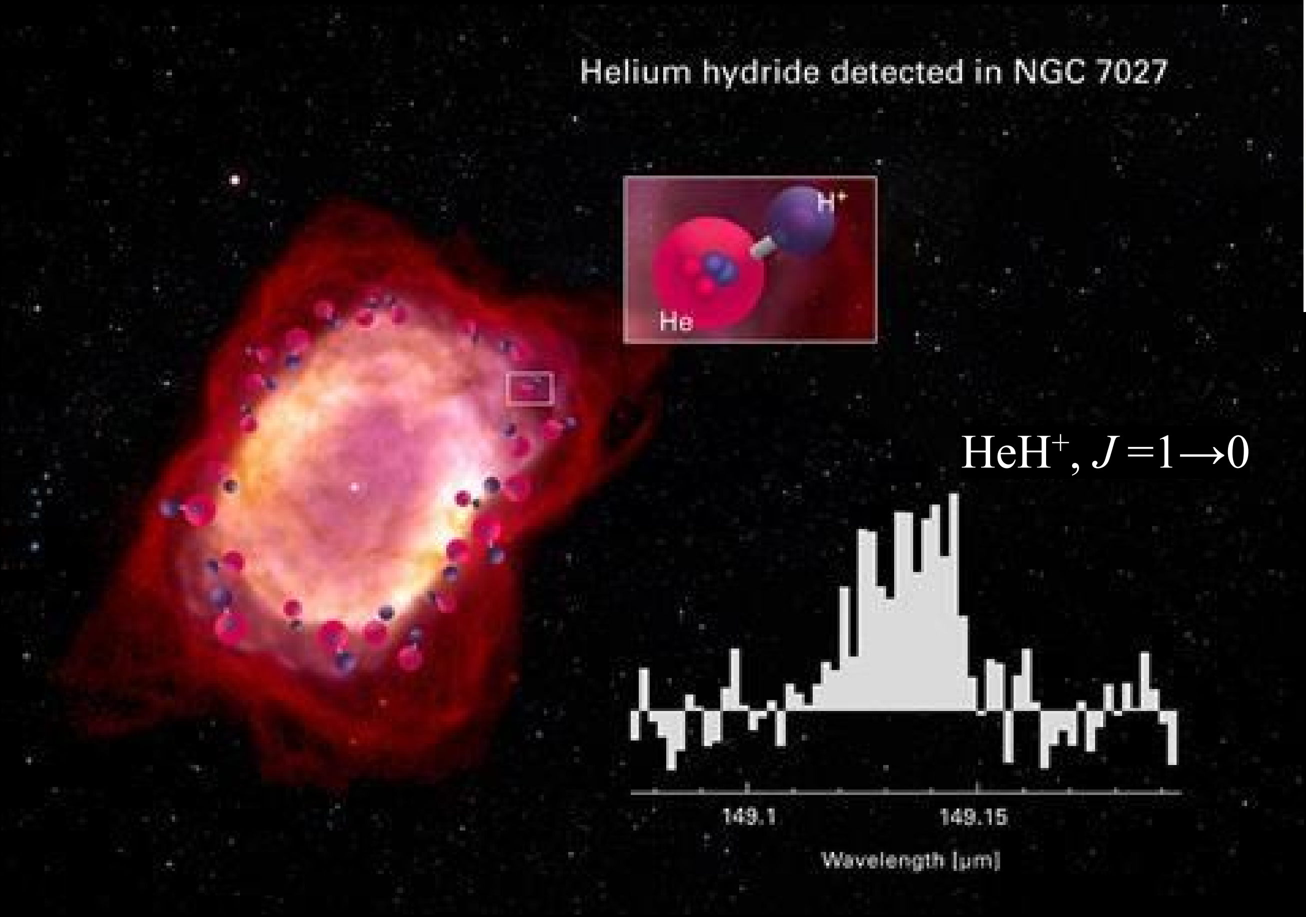
Barlow et al. 2013
Herschel-SPIRE





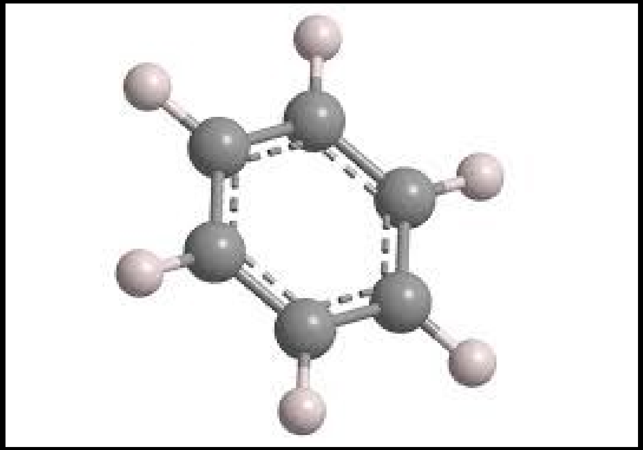
Schilke et al. 2014
Herschel-HIFI Sgr B2

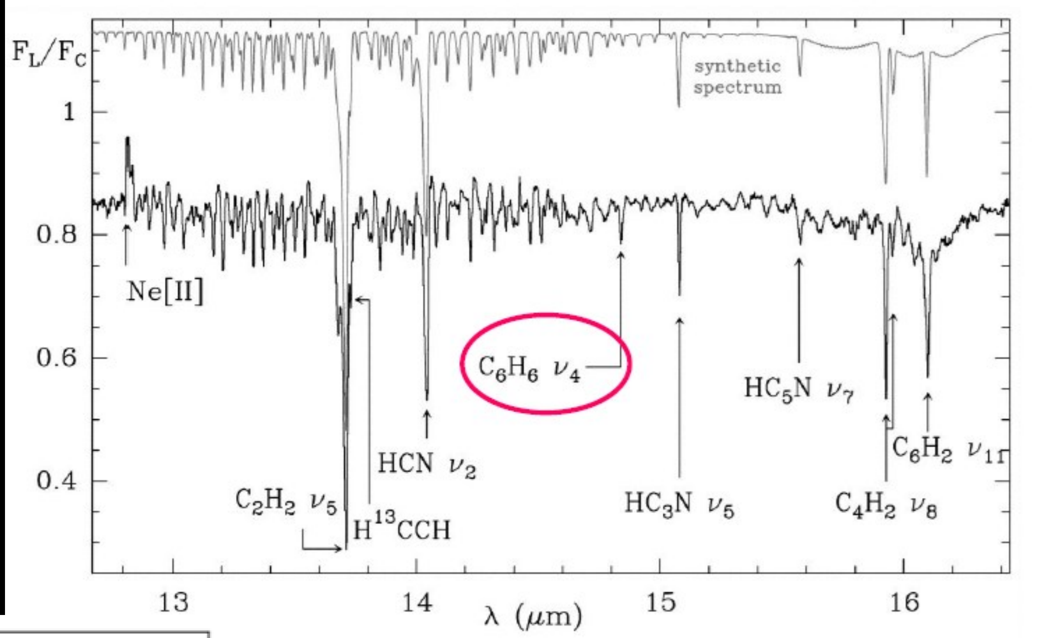
First noble gas made by Universe

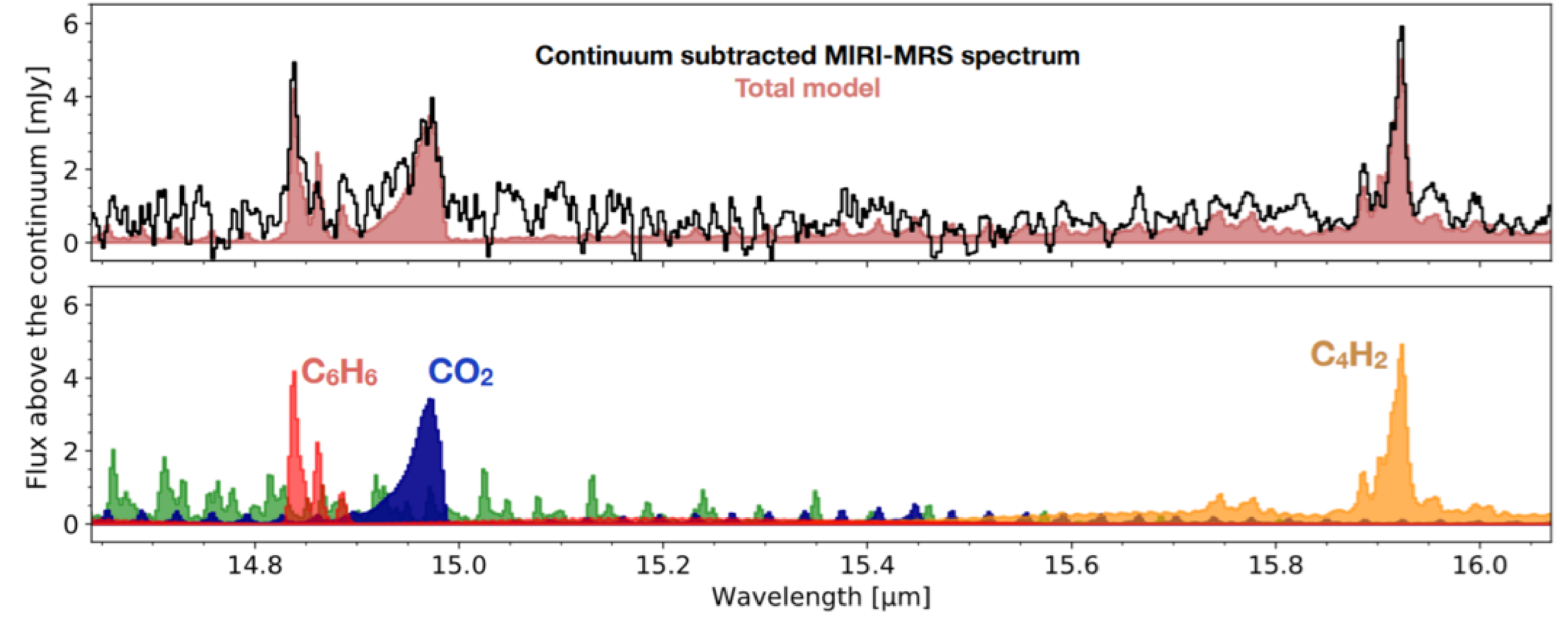


- First molecule in the Universe
- Important for cooling
- Detected with SOFIA

Detection of benzene



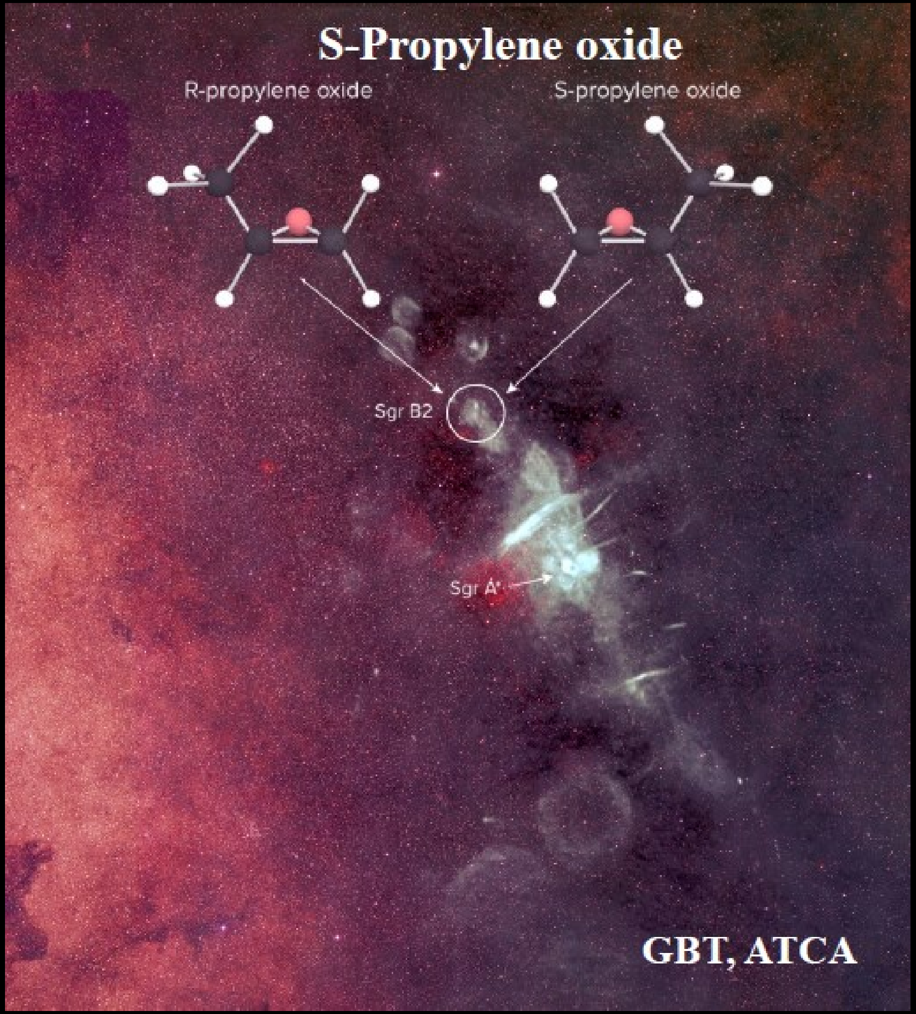




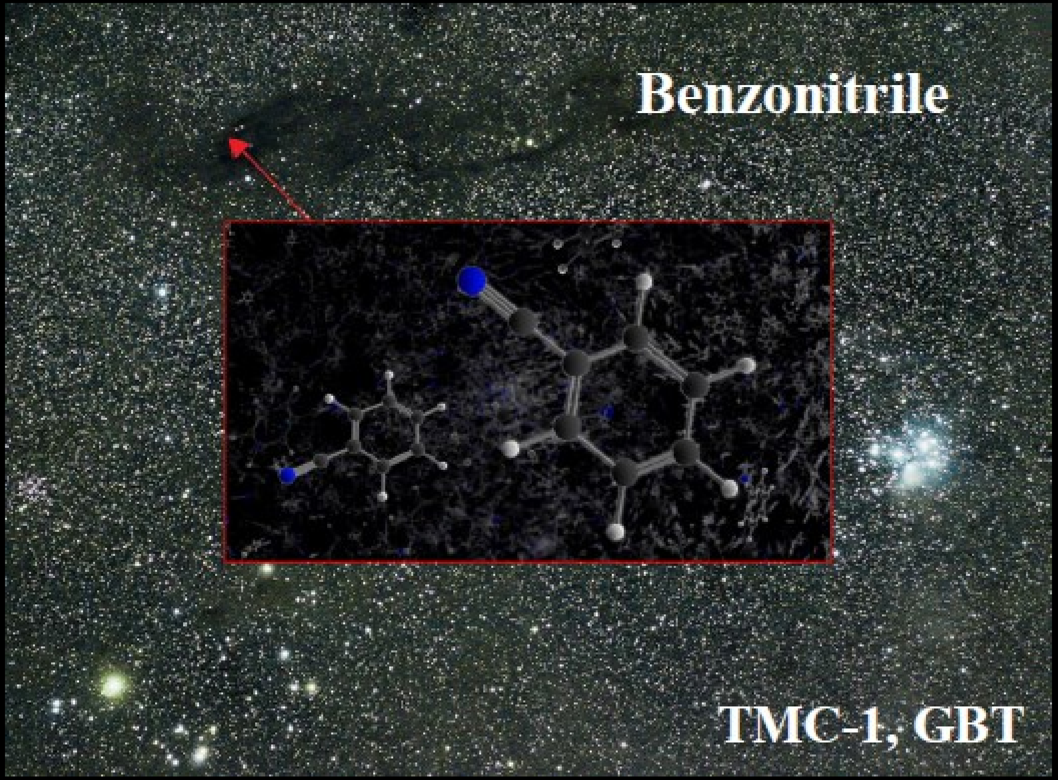
Circumstellar:
Cernicharo et al. (2001)

Protoplanetary disk:
Tabone et al. (2023)

First chiral and aromatic molecules in radio



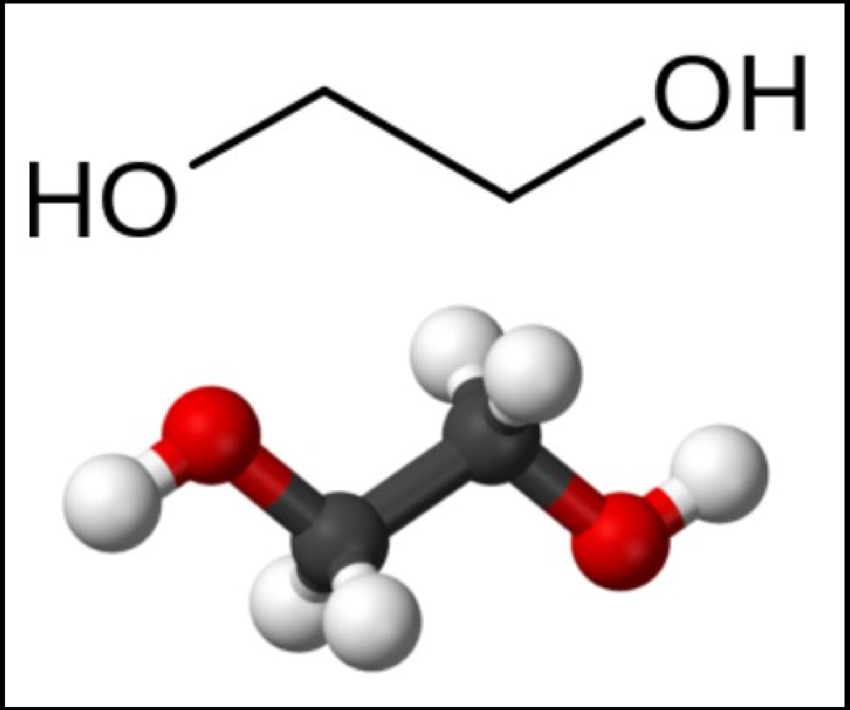
McGuire, Carrol, Blake et al. (2016) Science

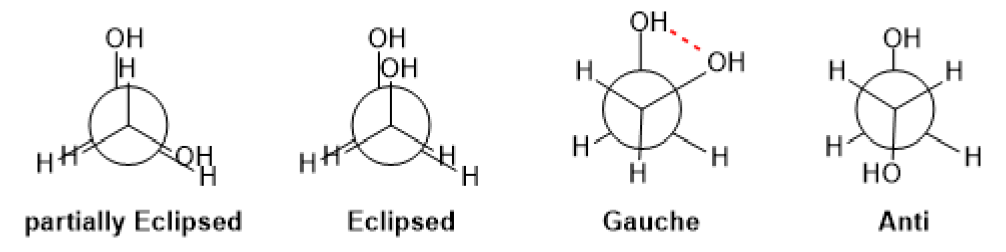


McGuire et al. (2018) Science

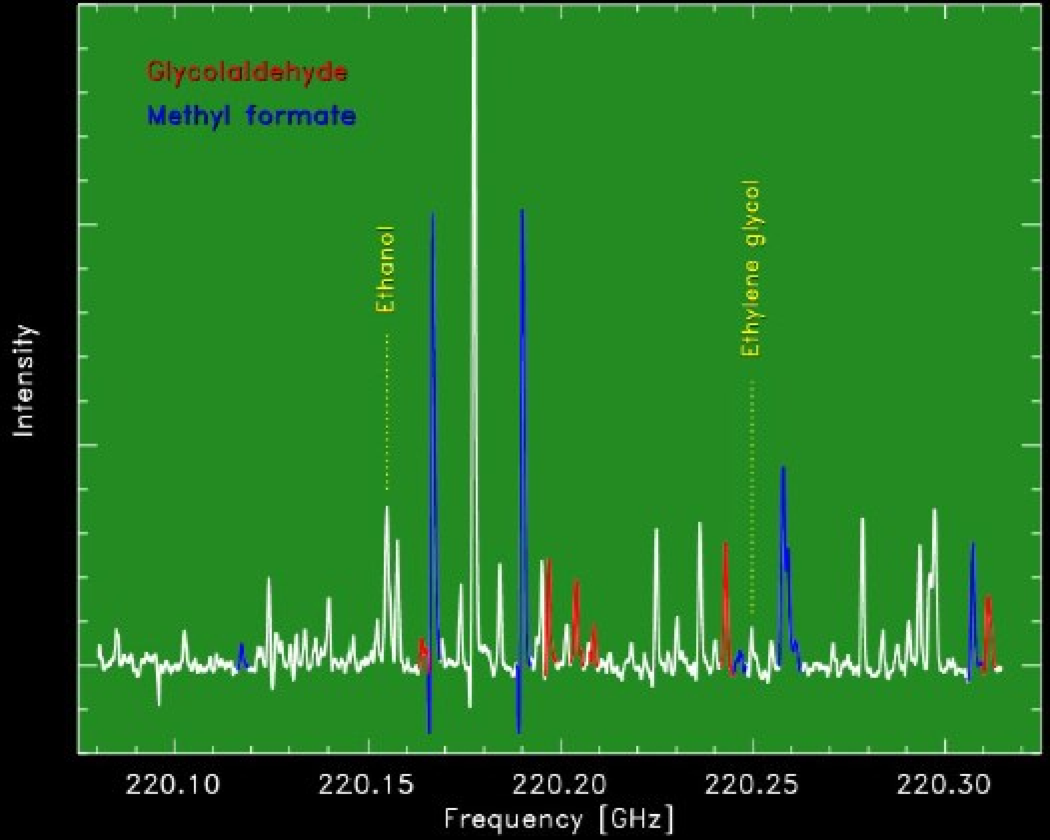
Note: not yet possible to measure left/right ratio, need polarized light

Interstellar antifreeze





Identifying weak lines in a forest
Need at least three lines that match exactly
No anti-coincidences



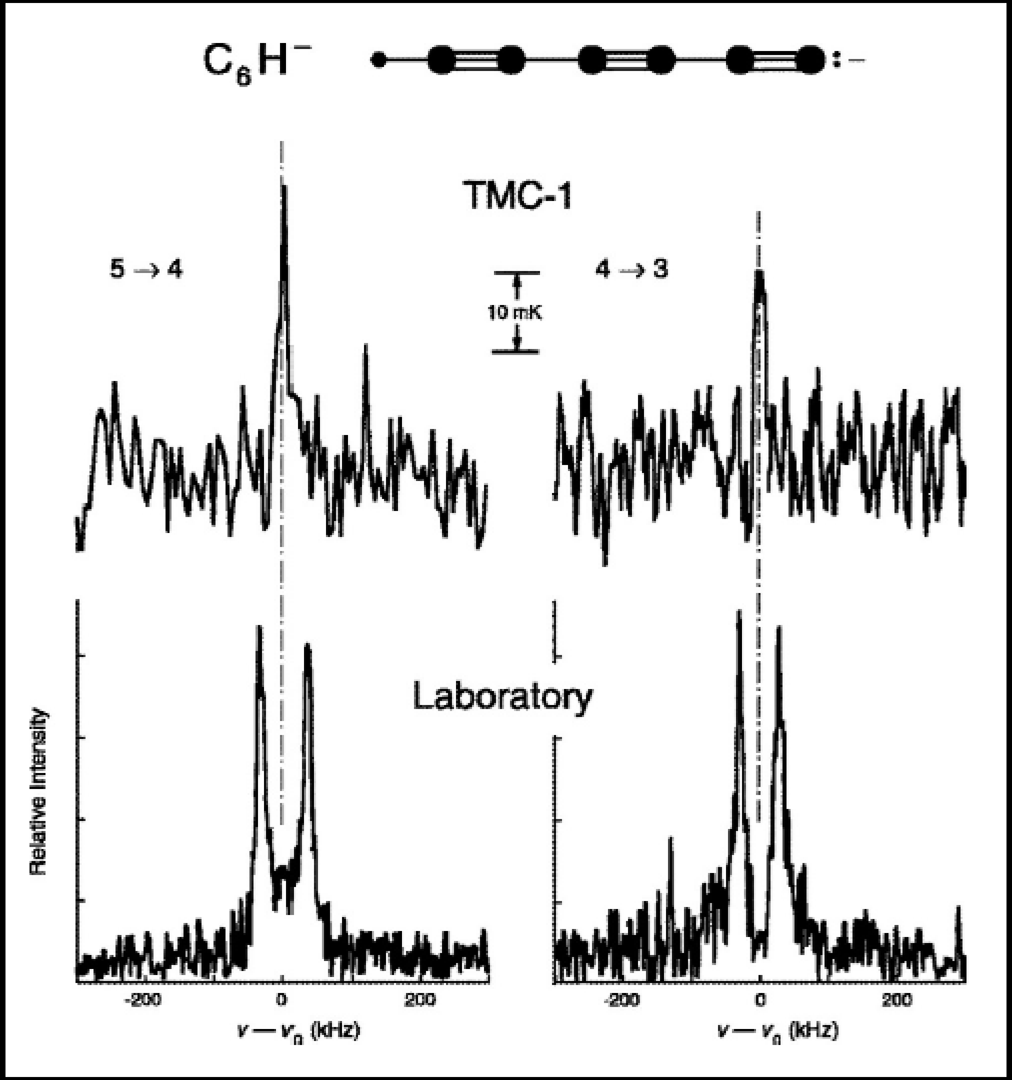
Jörgensen et al. (2012, 2016)

Negative ions

Predicted in the 1970s

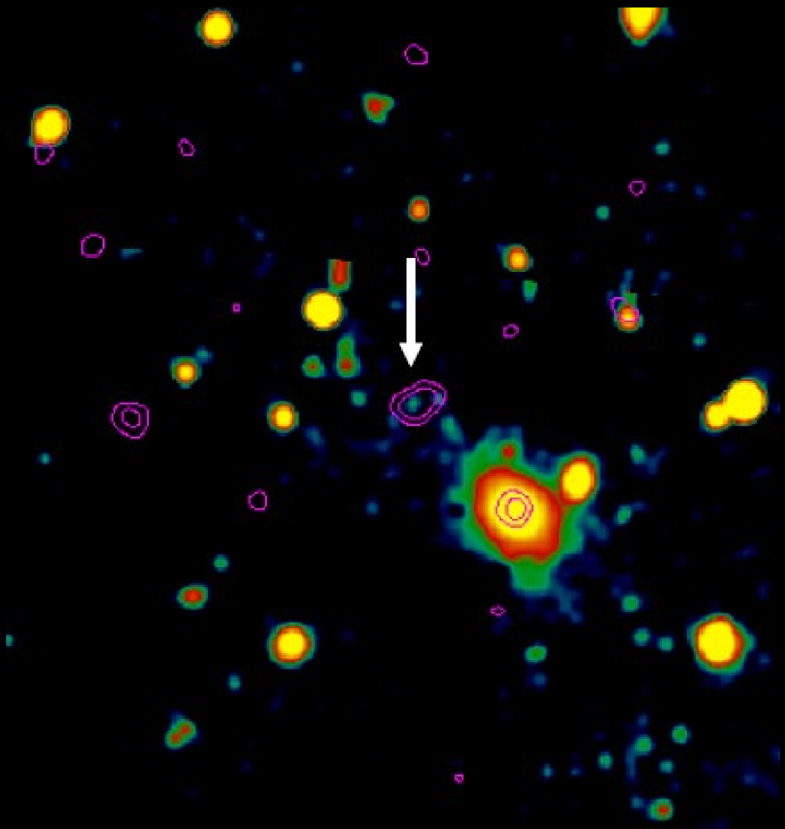
Not detected until late 2000s

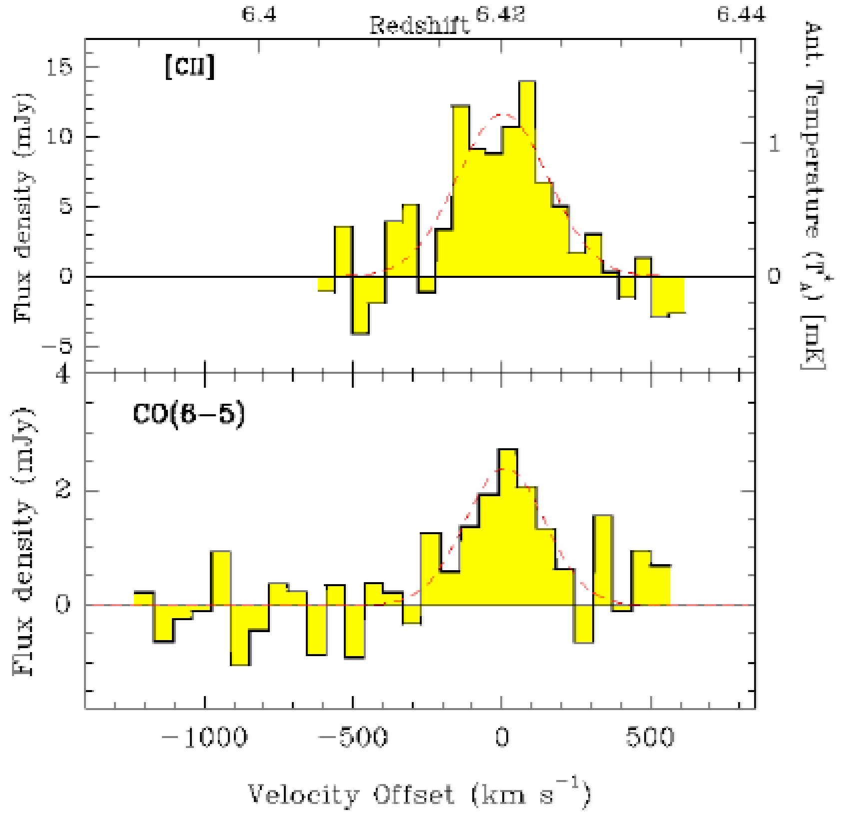
Larger ions more easily formed than smaller ions



McCarthy et al. (2007)

Molecules at high redshift z=6-7



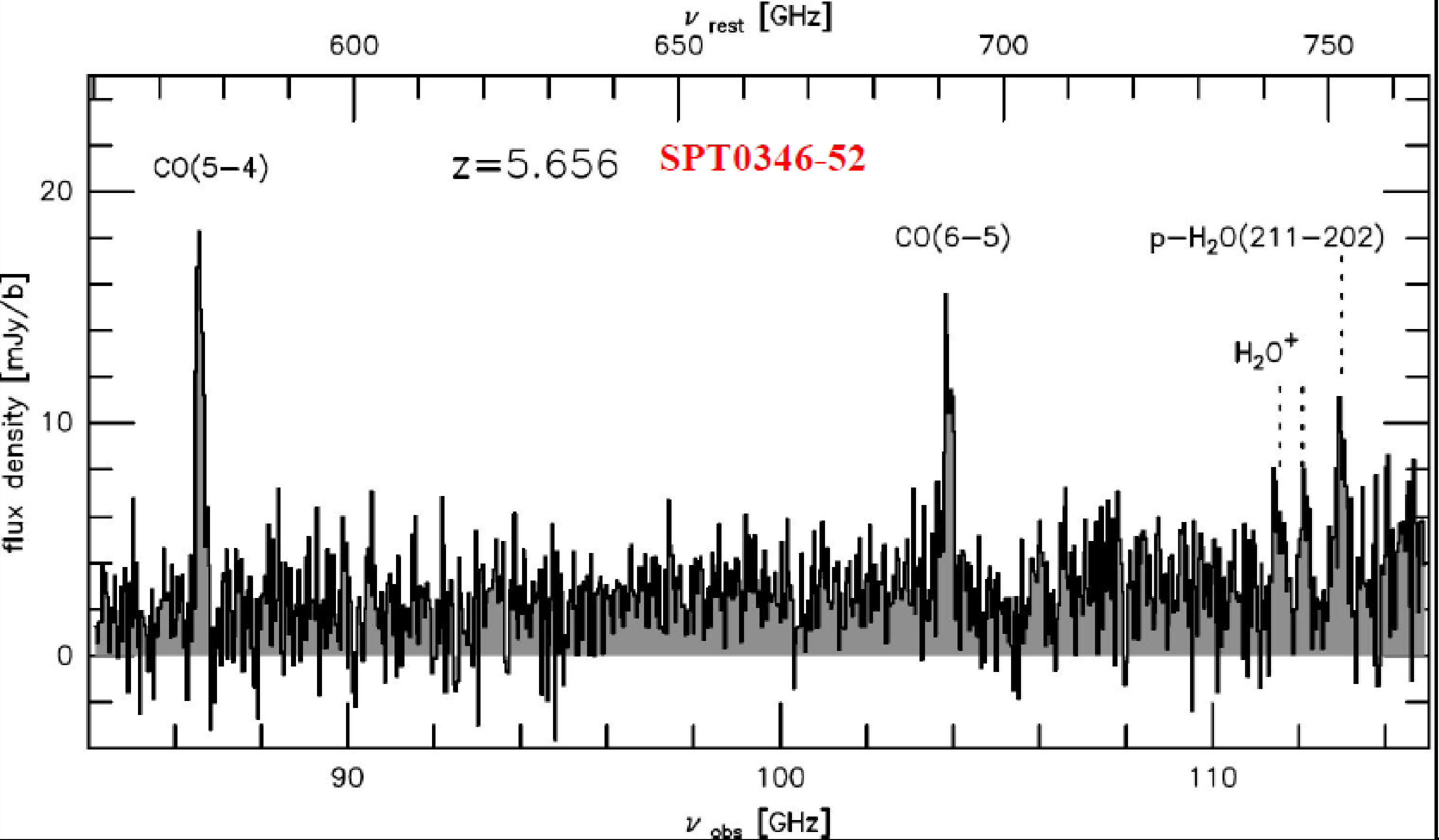


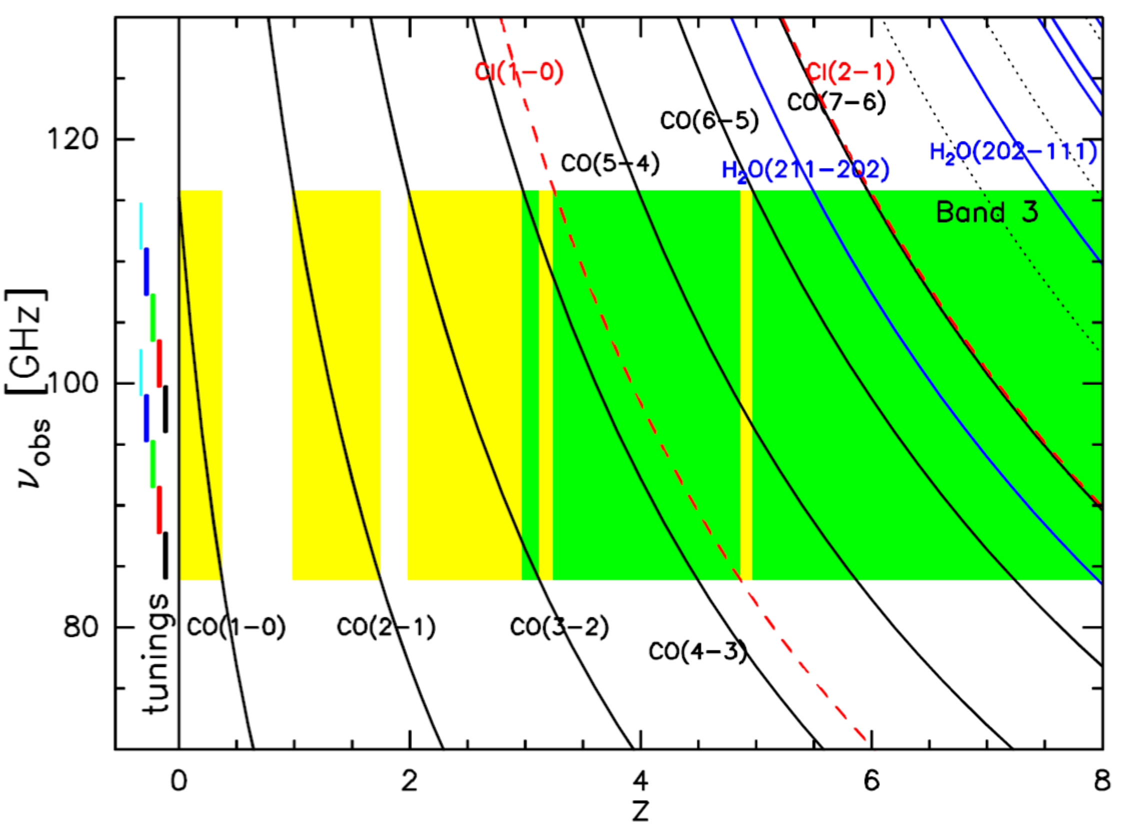
Walter et al. 2003, Maiolino et al. 2005
Venemans et al. 2017

CO and C^+ ([C II]) in quasars SDSS J1148+5251 at z=6.4
Lines shifted by factor 1+z
Current record: [C II] at z=7.54

$$1 + z = \frac{1}{\sqrt{1 - v^2/c^2}}$$

High-z spectroscopy sub-mm galaxies





CO, H_2O and even H_2O^+ at z=5.66!
Also detected: HCO^+, HCN, CN at high z

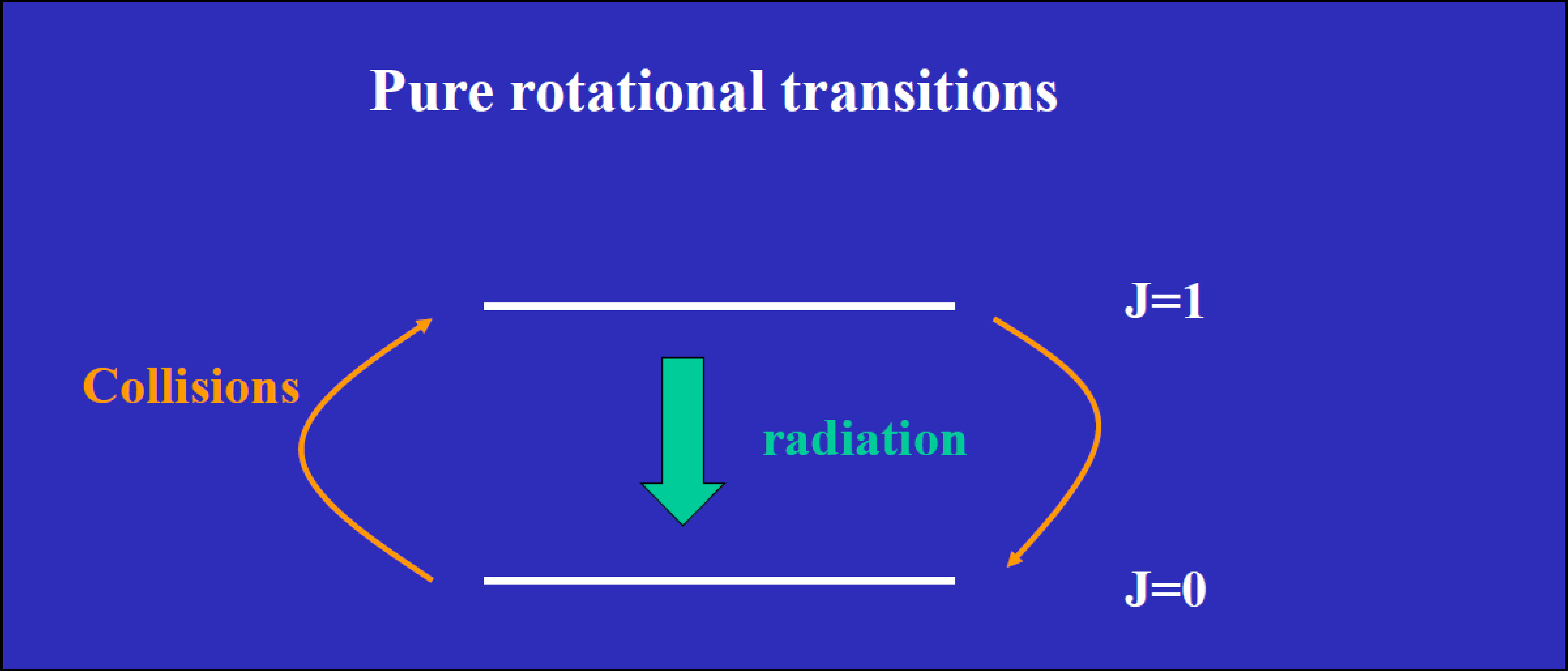
Weiss et al. 2013, ALMA 3 mm survey

1.6 Importance of molecules

- Exotic chemistry: unique laboratory
- Astrochemical evolution
- Molecules as diagnostics of temperature T_{kin}, density n_{H}, velocity, …
- Molecules as coolants
- Radiation escapes from cloud → net kinetic energy lost → cloud cools down

$$\mathbf{CO}(J\!=\!\mathbf{0}) \xrightarrow{\text{Collisions}} \mathbf{CO}(J\!=\!\mathbf{1}) \xrightarrow{\text{Radiation}} \mathbf{CO}(J\!=\!\mathbf{0})$$

Molecular excitation



- Population distribution not in thermodynamic equilibrium but determined by competition between radiative and collision processes
- Critical density ∝ $\mu^2\upsilon^3$ → higher frequencies probe higher densities and temperatures

1.7 Questions addressed

- What are the chemical processes leading to formation and destruction of molecules? What causes chemical diversity?
- How well are basic molecular processes known from experiments or theory?
- What is the evolution of molecules in the universe, from their creation at high redshifts to interstellar clouds to incorporation in new solar systems?
- How can molecules be used as physical and chemical diagnostics of physical structure, evolution, cosmic-ray ionization, primordial D, ...

1.8 Basic molecular processes: gas phase

- Because of low temperatures and densities in clouds, chemistry is not in thermodynamic equilibrium but controlled by two body reactions → abundances depend on physical conditions (T, n, radiation field), history, ...
- Three body reactions do not become important until $n > 10^{12}$ cm^{-3}
- Although models contain thousands of reactions, only few different types of processes
- Rate of reaction: $\underbrace{k}_{\text{rate coefficient in cm}^3\text{ s}^{-1}}\, n(\mathrm{X})n(\mathrm{Y})$ cm^{-3} s^{-1}

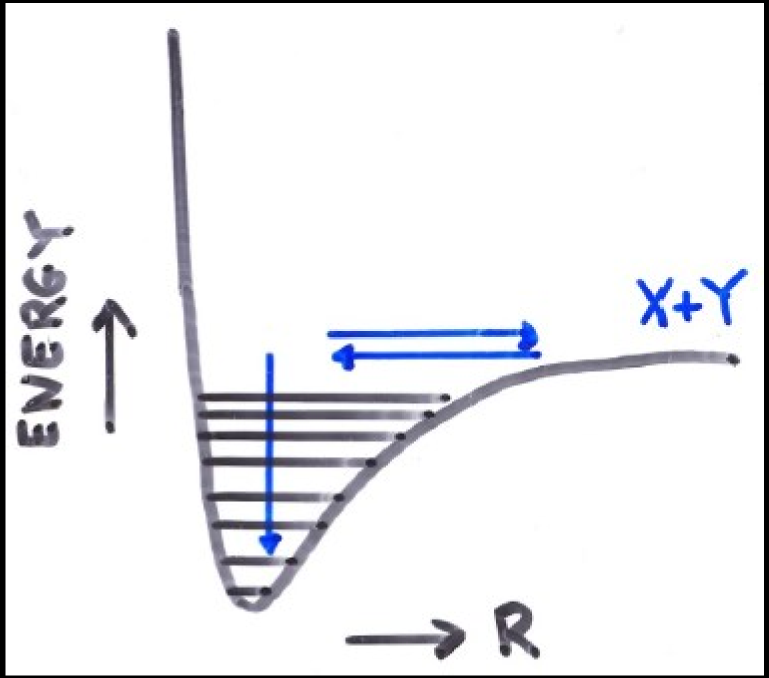
Van Dishoeck 1988
Tielens Ch. 4

Types of chemical reactions

- Formation of bonds
  - Radiative association: $X^+ + Y \rightarrow XY^+ + h\nu$
  - Associative detachment: $X^- + Y \rightarrow XY + e^-$
  - Grain surface: $X + Y{:}g \rightarrow XY + g$
- Destruction of bonds
  - Photodissociation: $XY + h\nu \rightarrow X + Y$
  - Dissociative recombination: $XY^+ + e^- \rightarrow X + Y$
  - Collisional dissociation: $XY + M \rightarrow X + Y + M$
- Rearrangement of bonds
  - Ion-molecule reactions: $X^+ + YZ \rightarrow XY^+ + Z$
  - Charge-transfer reactions: $X^+ + YZ \rightarrow X + YZ^+$
  - Neutral-neutral reactions: $X + YZ \rightarrow XY + Z$

1.9 Radiative association

- $X + Y \underset{\tau_D}{\overset{\tau_C}{<=>}} XY^* \xrightarrow{\tau_R} XY + h\nu$
- Energy conservation → a photon must be emitted, which is a very slow process



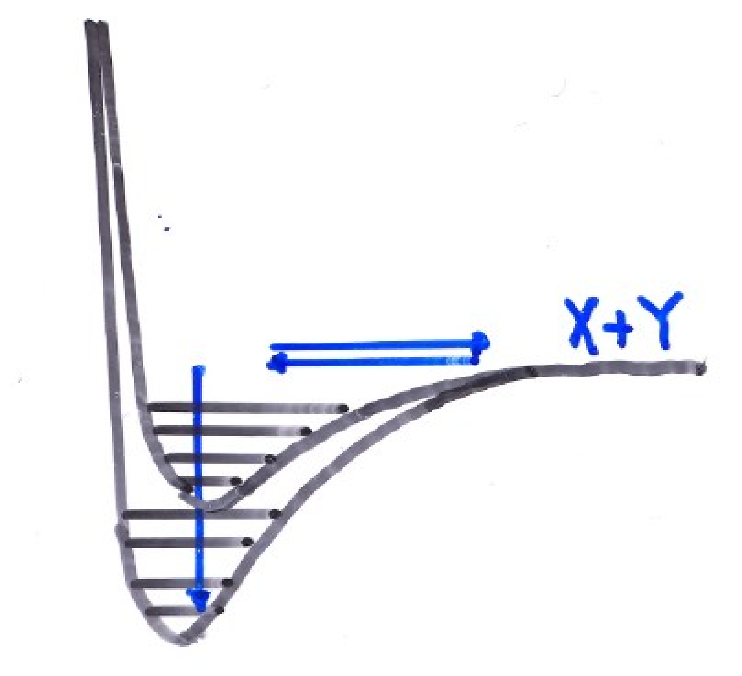
$\tau_R = 10^{-2}\text{-}10^{-3}$ s vibrational transition

$\tau_{Rc,d} = 10^{-13}$ s collision time

→Molecule formation occurs only in 1:10^{10} collisions

Radiative association continued

- Process becomes more efficient if more electronic states are available



$\tau_r = 10^{-8}$ s electronic transition

$\tau_{c,d} = 10^{-13}$ s collision time

→Efficiency increased to 1:10^5 collisions

Radiative association continued

- Efficiency can be enhanced if:
  - Electronic states are available: τ_r shorter
  - Entrance channel has a barrier: τ_d longer
  - Molecule larger: τ_d longer
- Radiative association is extremely difficult to measure in laboratory because 3-body processes dominate under most lab conditions.
- Many rate coefficients are based on theory; overall uncertainties 1-2 orders of magnitude
- Exception: $\mathbf{C^+ + H_2 \rightarrow CH_2^+ + \boldsymbol{h\nu}}$
  - $k \sim 10^{-15}$ cm^3 s^{-1} within factor of 2-3
  - Initiates carbon chemistry

Experiment vs theory

- $\mathrm{X} + \mathrm{Y} \underset{k_D}{\overset{k_C}{<=>}} \mathrm{XY}^*$
- $\mathrm{XY}^* \xrightarrow{k_R} \mathrm{XY} + h\nu$
- $\mathrm{XY}^* + \mathrm{M} \xrightarrow{k_M} \mathrm{XY} + \mathrm{M}$

Measured in experiments

$$k_{eff} = k_c \frac{k_r + k_m[M]}{k_d + k_r + k_m[M]} \longrightarrow k_{eff} = k_{ra} + k_{3b}[M]$$

$$k_{ra} = \left(\frac{k_c}{k_d}\right) k_r$$

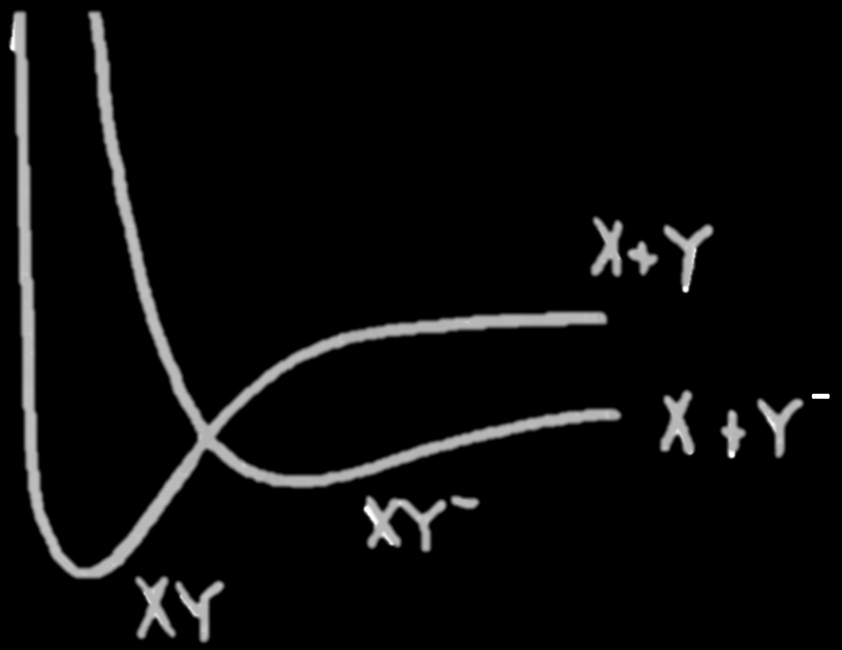
Theory + required by astrochemists

1.10 Associative detachment

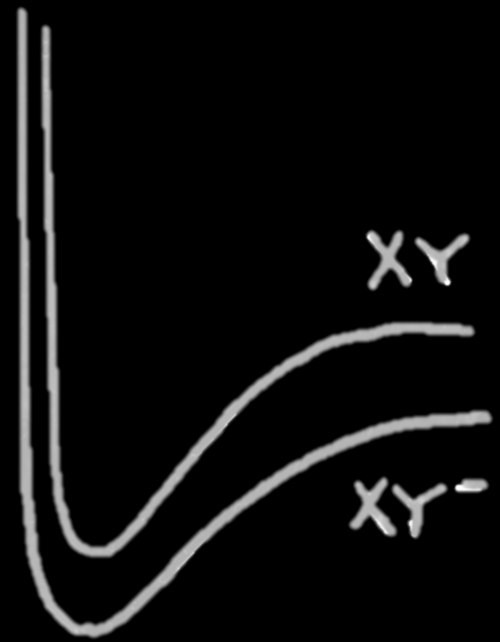
- Usually not important in cold clouds, but can play a role in partly ionized regions and early universe
- Form negative ions by radiative attachment*
  - $X + e^- \rightarrow X^- + h\nu$ slow process
- Form molecule by associative detachment
  - $X^- + Y \rightarrow XY + e^-$

*Note: rate for electron attachment is faster for larger molecules

Associative detachment continued



fast

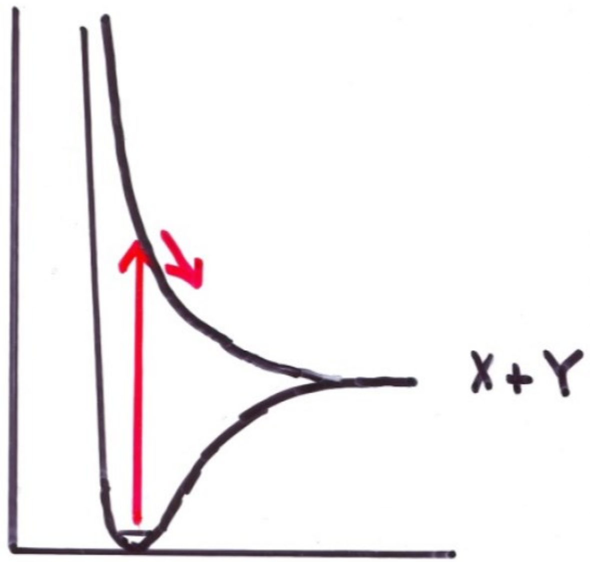


slow

- Examples: $H + e^- \rightarrow H^- + h\nu$
  $H^- + H \rightarrow H_2 + e^-$ fast
  $S + e^- \rightarrow S^- + h\nu$
  $S^- + CO \rightarrow OCS + e^-$ fast

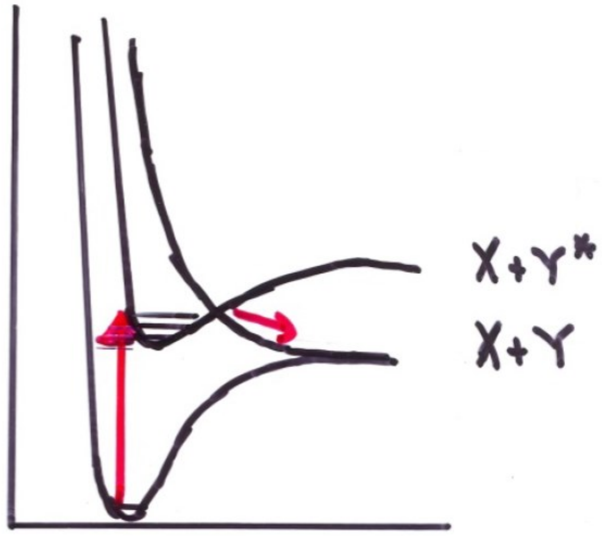
1.11 Photodissociation

- $XY + h\nu \rightarrow X + Y$



Direct photodissociaton

$OH, H_2O, CH, CH_2,...$



Predissociaton

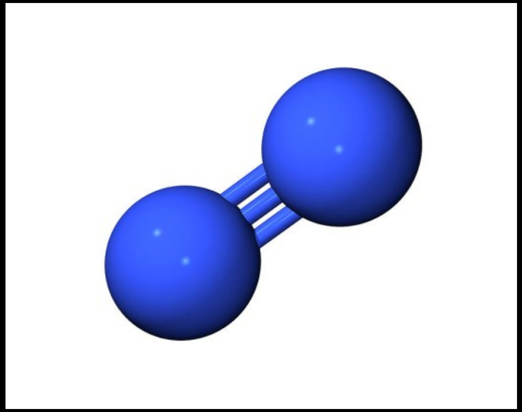
$CO, N_2,...$

- Experiment available for stable molecules, but not for radicals or ions
- Small molecules: quantum chemical calculations of potential surfaces of excited states + transition dipole moments, followed by nuclear dynamics to obtain cross sections

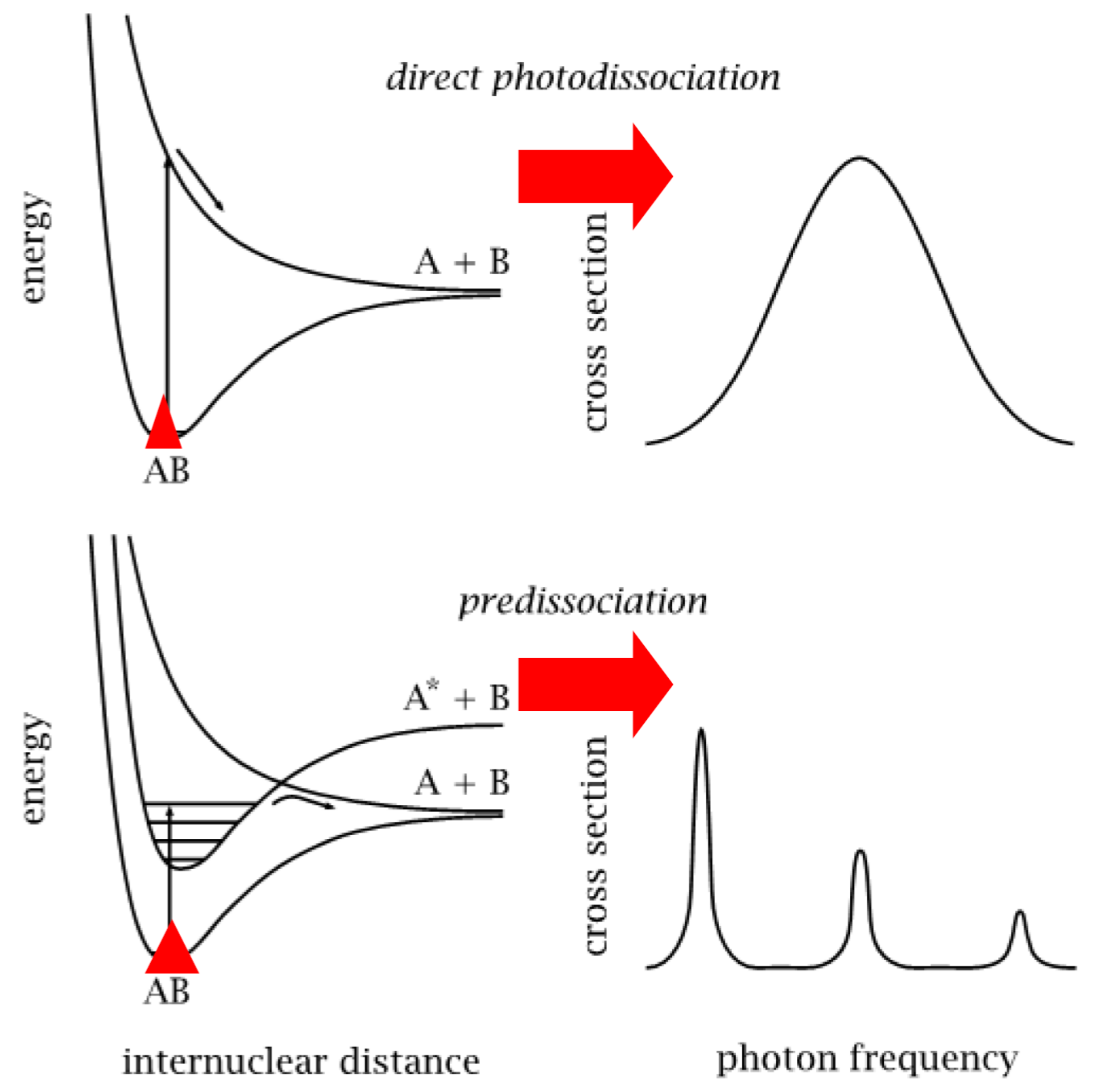
Photodissociation and predissociation

Indirect photodissociation

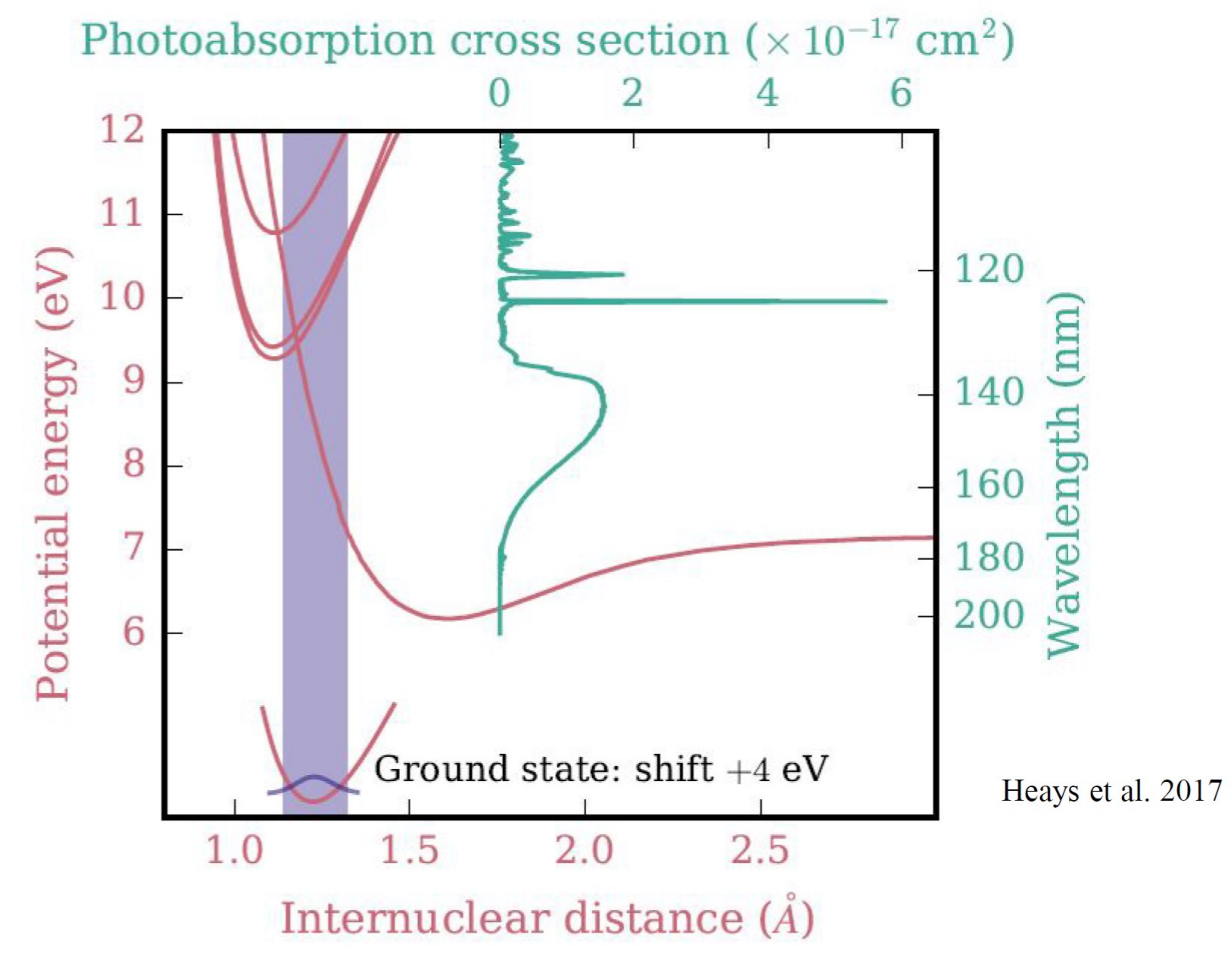
Predissociation



Li et al. 2013



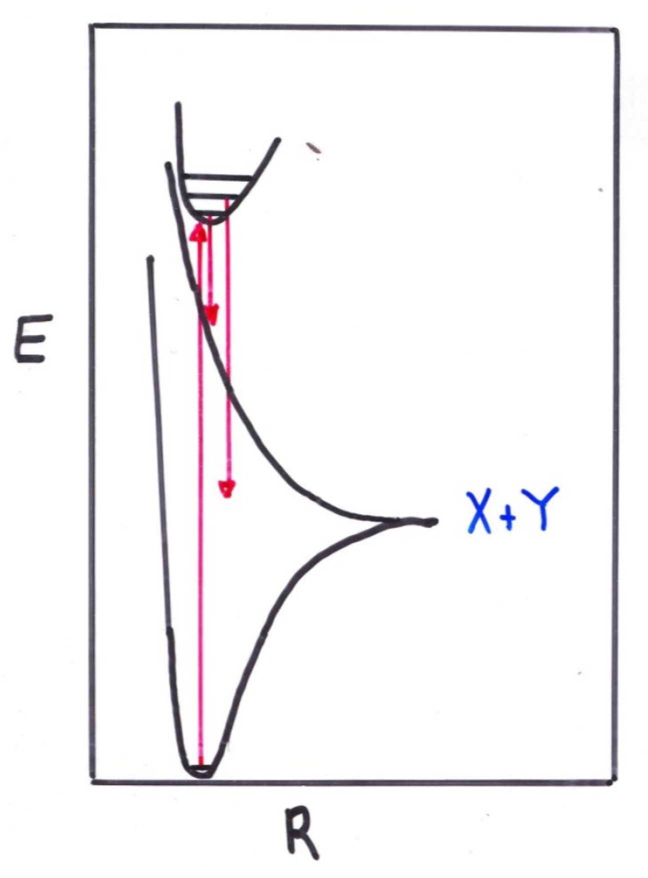
Cross section shape



Heays et al. 2017

Franck Condon principle: reflects vibrational wavefunction ground state

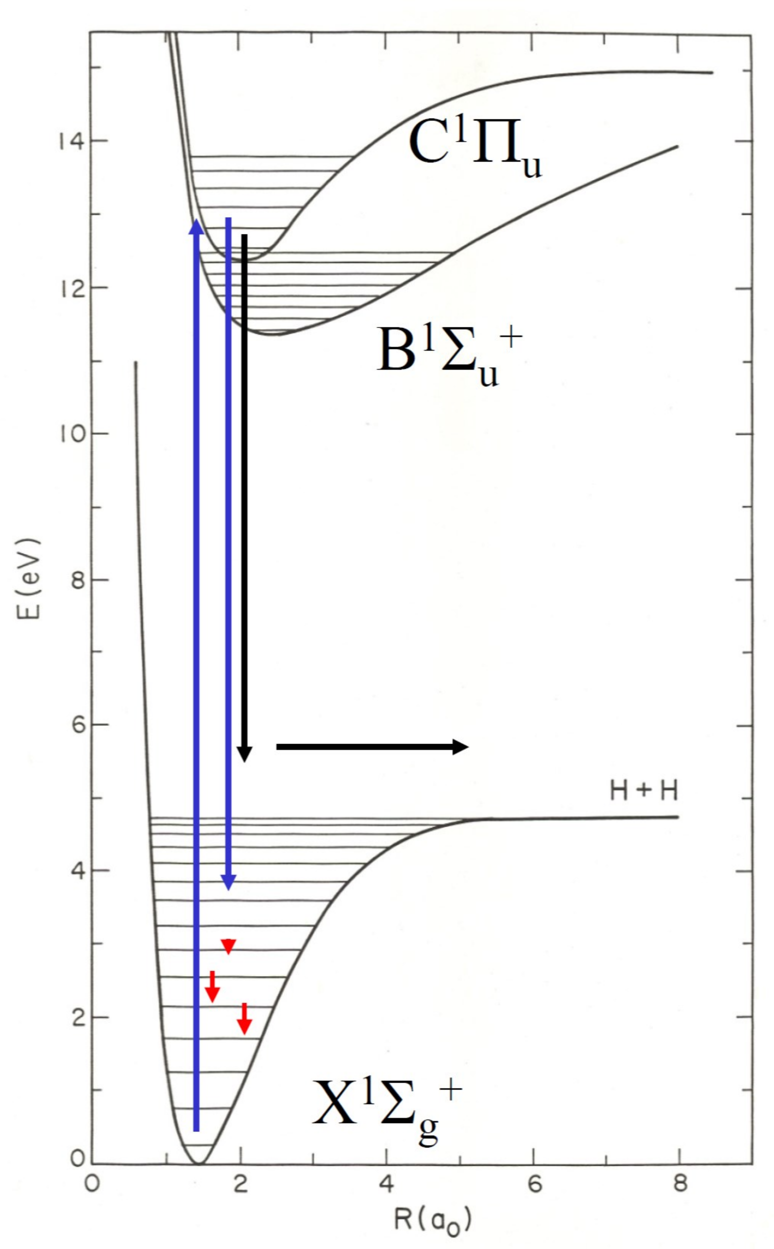
Photodissociation continued



Spontaneous radiation dissociation
Example: H_2

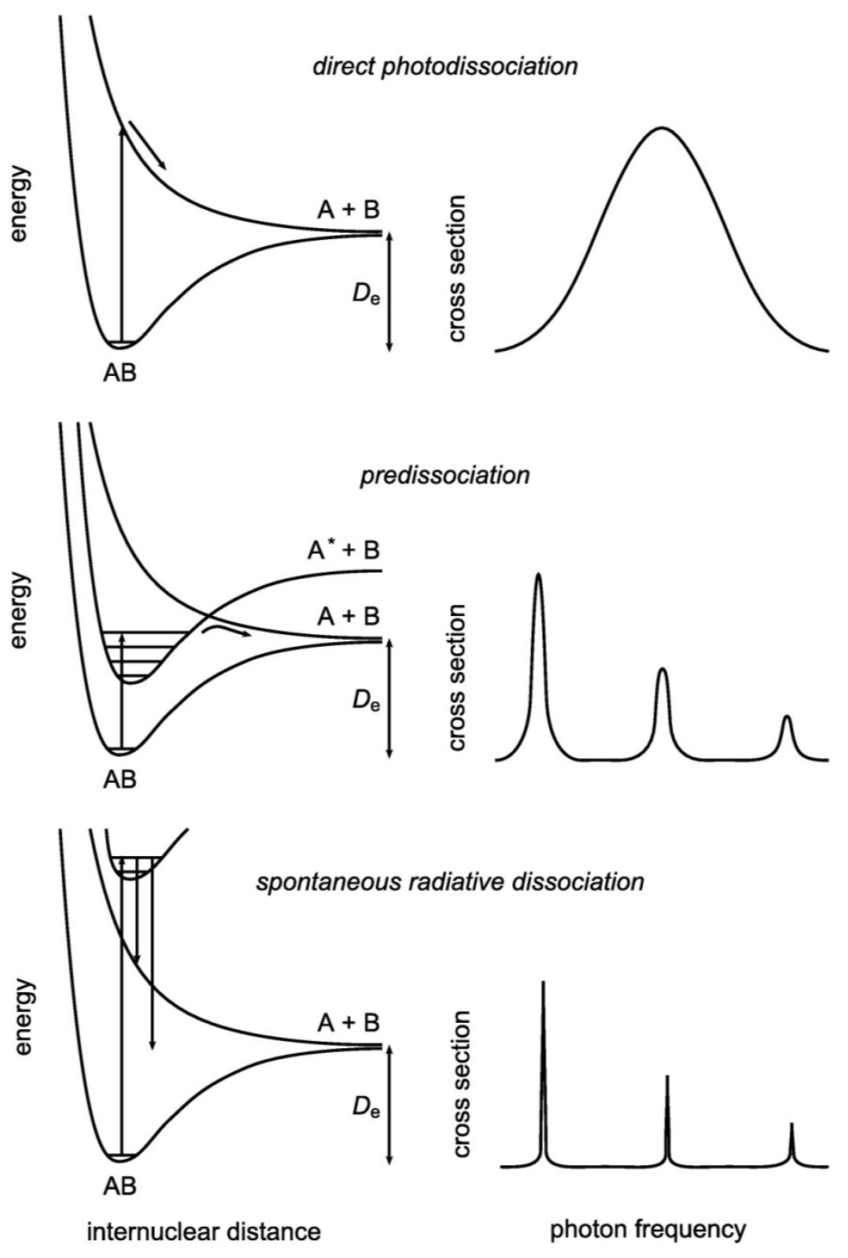
- Photodissociation of both H_2 and CO occurs by line absorption → self-shielding important inside clouds
- Photoionization: $XY + h\nu \rightarrow XY^+$
  $\rightarrow X^+ + Y$

H_2 spontaneous radiative dissociation



- 90% of absorptions into B and C states are followed by emission back into bound vibrational levels of the X state
- 10% of the absorptions are followed by emission into the unbound vibrational continuum, leading to dissociation

Summary processes – small molecules



Direct p.d.

Ex: H_2^+, OH, H_2O

Predissociation

Ex: CO

Spontaneous radiative dissociation

Ex: H_2

Photodissociation rate

- Continuum photodissociation

$$k_{pd} = \int \sigma(\lambda) I(\lambda) d\lambda$$

where σ_{pd} is the cross section in cm^2, I=radiation field

- Discrete photodissociation

$$k_{pd} = \sum \frac{\pi e^2}{m_e c^2} \lambda_{line}^2 f_{line} \eta_{line} I(\lambda_{line})$$

where f is oscillator strength and η is the dissociation probability.

Interstellar radiation field

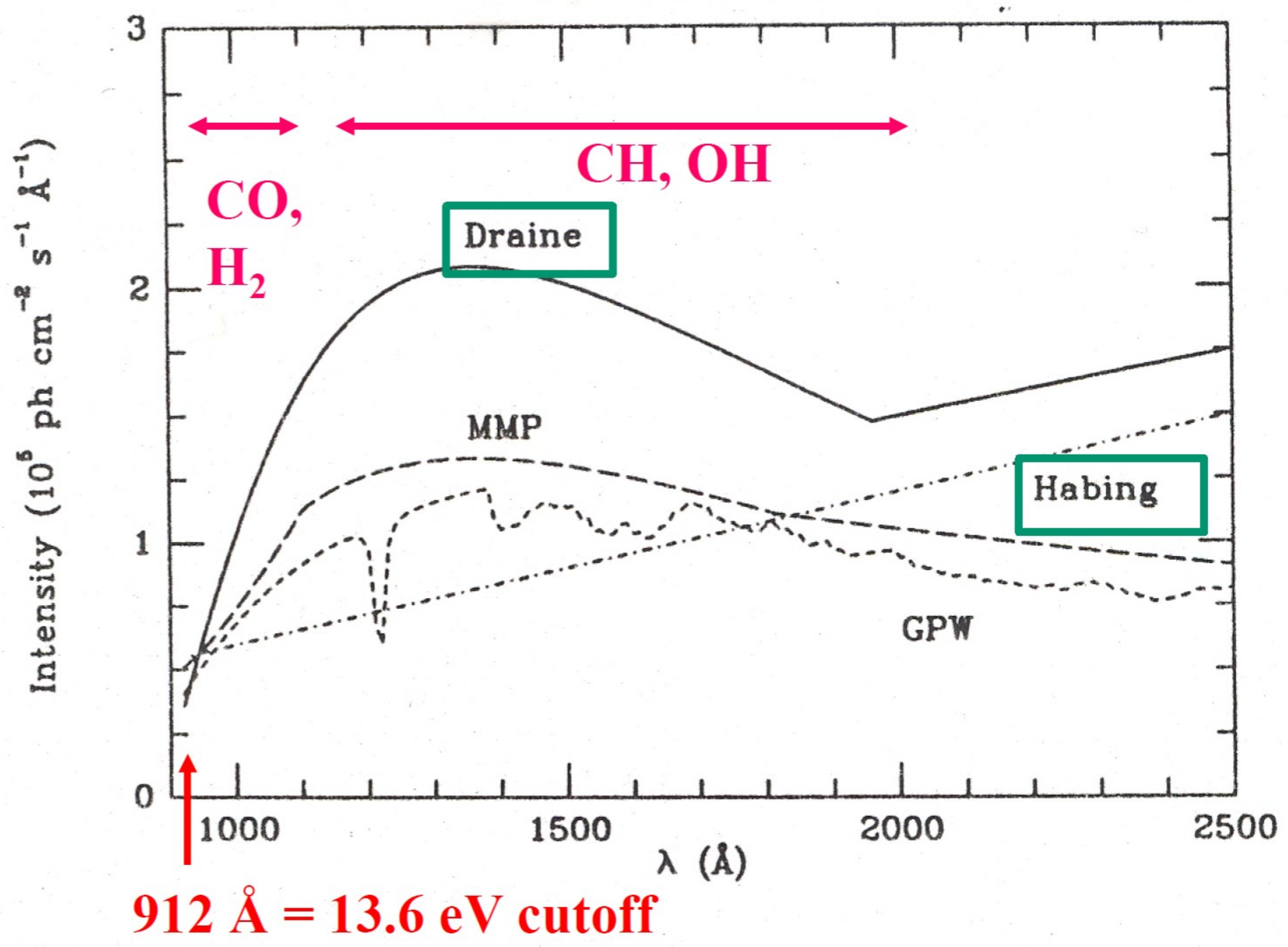
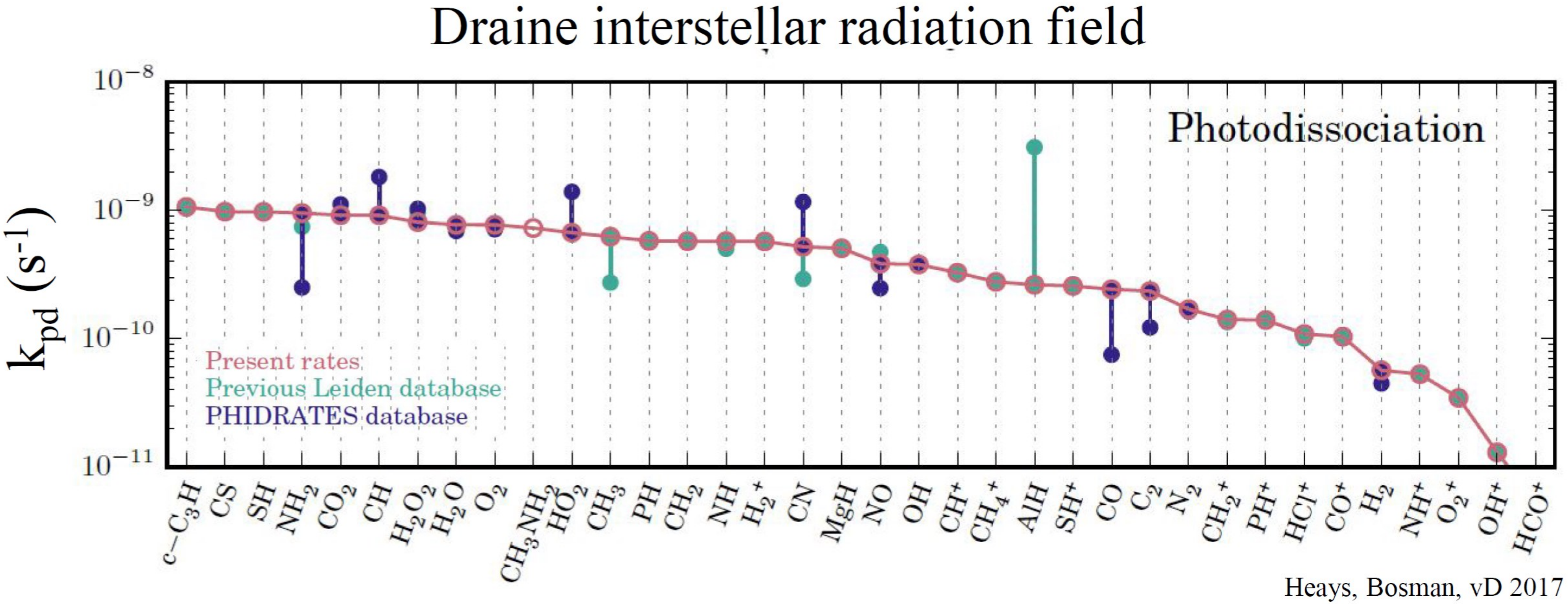


Figure 5. *The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).*

Average radiation provided by young O + B stars in solar neighborhood

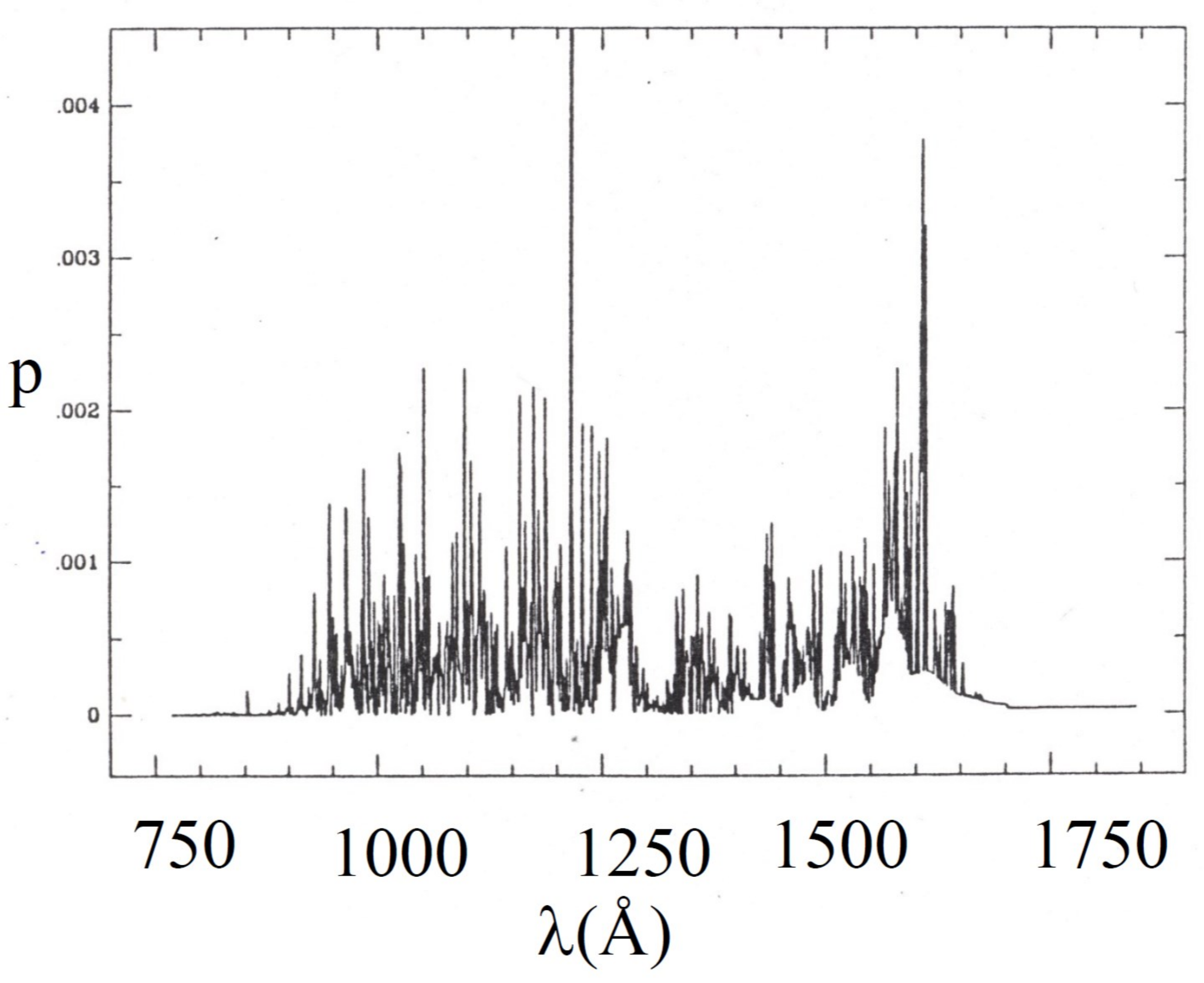
Photodissociation rates



Heays, Bosman, vD 2017

Question: what is the typical lifetime of an interstellar molecule in a diffuse cloud?

Cosmic-ray induced radiation



$$H_2 + CR \rightarrow H_2^+ + e^*$$
$$H_2 + e^* \rightarrow H_2^* + e$$
$$H_2^* \rightarrow H_2 + h\nu$$

Prasad & Tarafdar 1983
Gredel et al. 1987

Detailed line + continuum spectrum peaking around 1600 Å and continuing below 912 Å

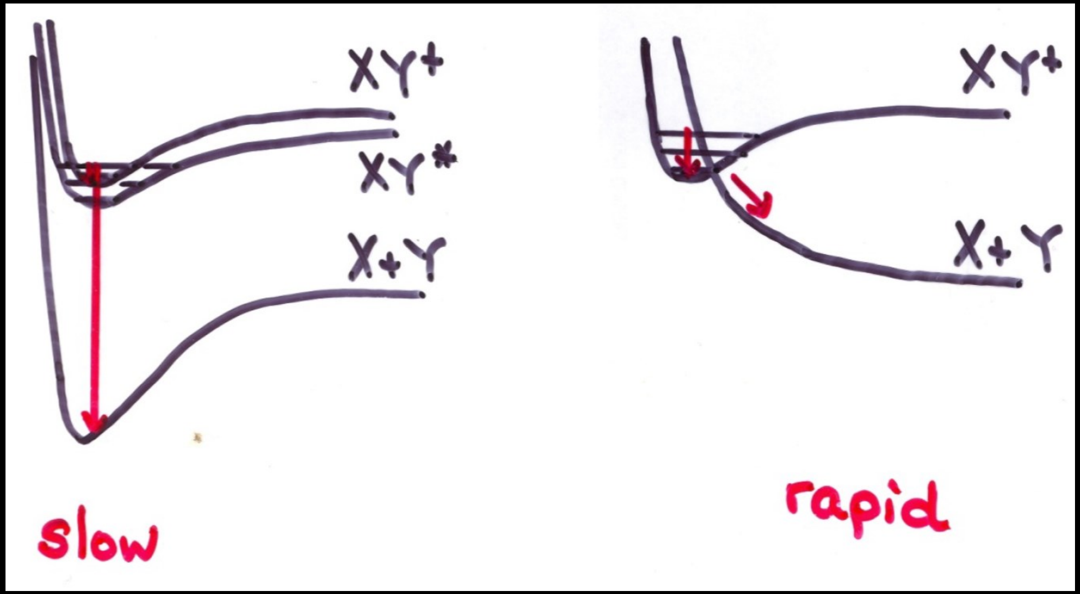
Other radiation fields

- Ly-α dominated
  - Shocks, ...
- Stellar blackbodies $T_{\mathrm{eff}} = 4000\text{-}10000$ K
  - Disks, cool PDRs, ...
- Solar radiation $T_{\mathrm{eff}} = 5000$ K + Ly-α
  - Comets

1.12 Dissociative recombination

- Atomic ions: $X^+ + e^- \rightarrow X + h\nu$ ***Radiative: slow***
- Molecular ions: $XY^+ + e^- \rightarrow XY + h\nu$ ***Radiative: slow***

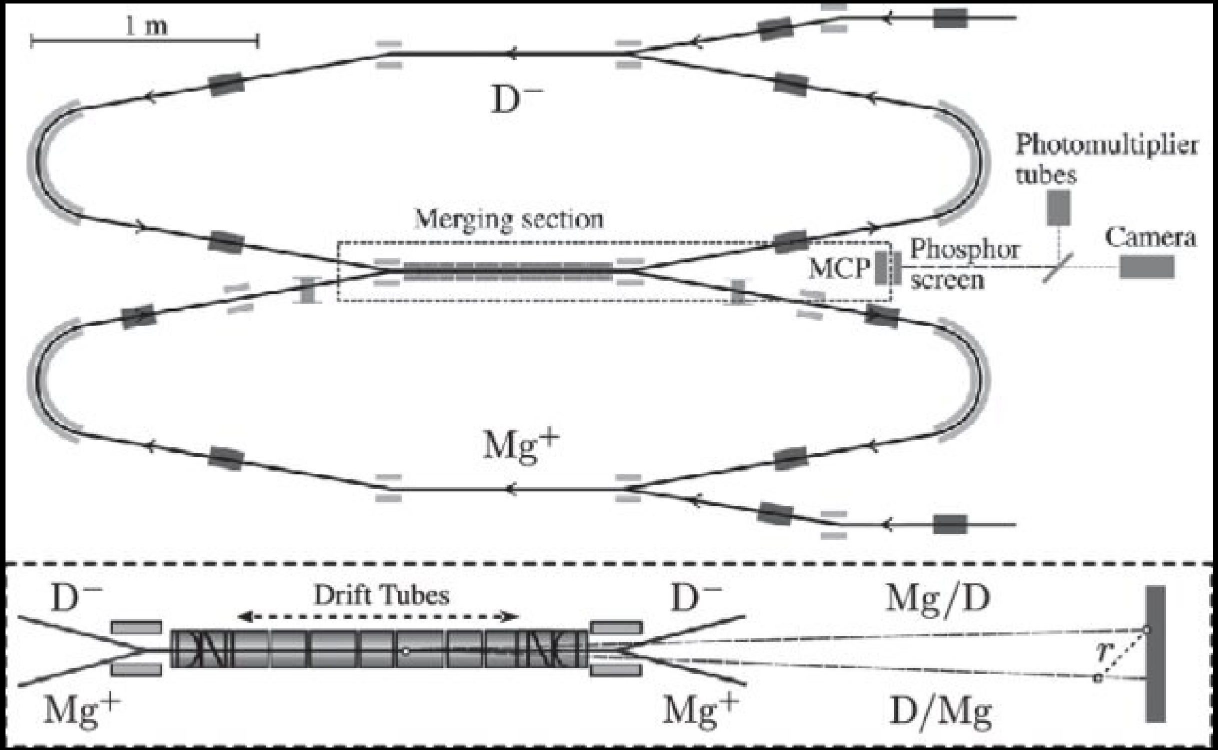
$\rightarrow X + Y$ ***Dissociative: rapid at low T***



- Need curve crossing between XY^+ and repulsive XY potential for reaction to proceed fast.

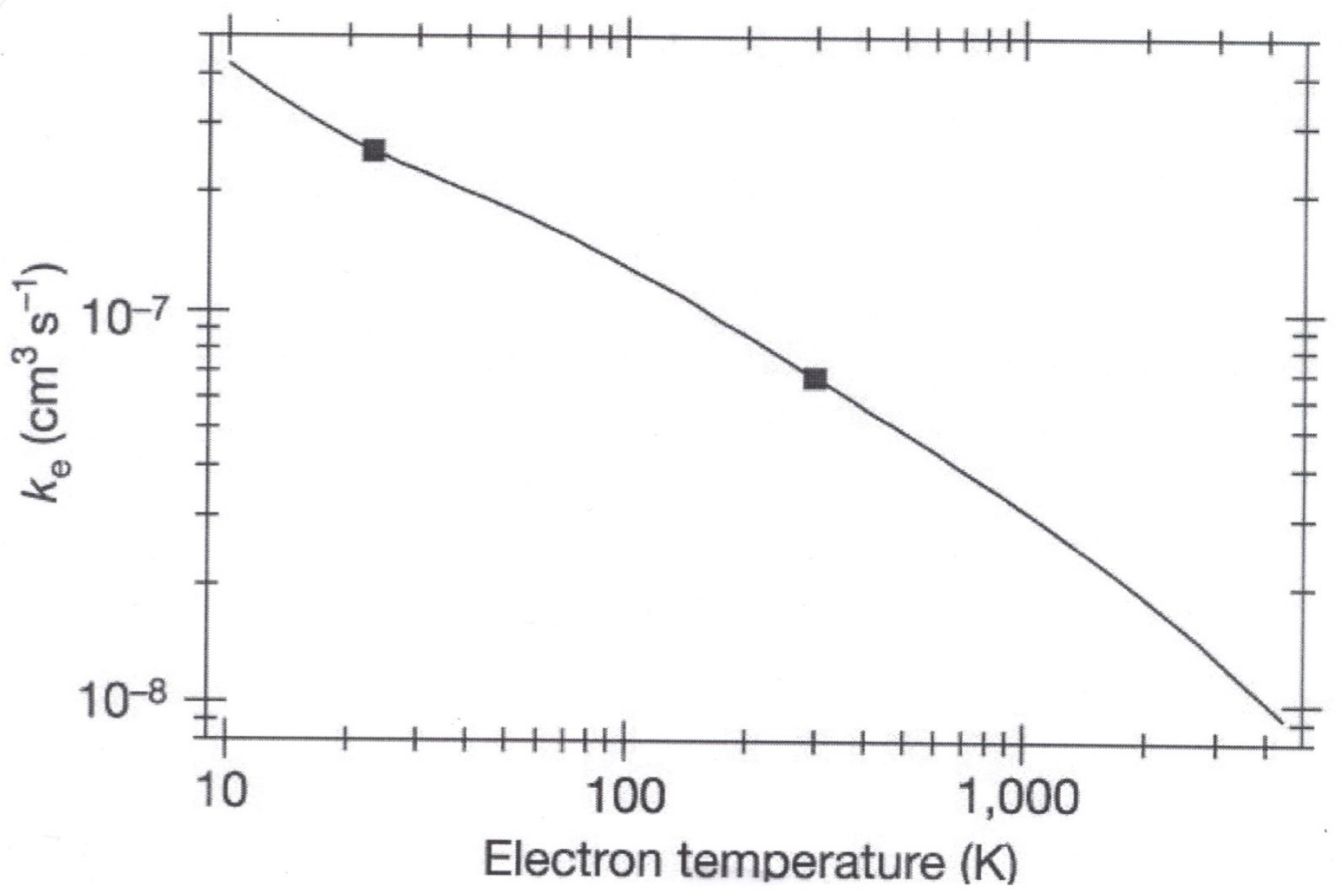
Storage ring experiments

- DESIREE in Stockholm (formely CRYRING)
- Also Aarhus, Heidelberg



Grumer et al. (2022)

$H_3^+ + e^-$ DR rate



McCall et al. (2003)

- Literature values range from < 10^{-12} to 10^{-7} cm^3 s^{-1} at 300 K over last 25 years.
- High rate coefficients now also reproduced by theory, even without curve crossing.
- Rates for other molecules known accurately.

DR products

- $$\left.\begin{aligned} XH_n^{+} + e^{-} &\longrightarrow XH_{n-1} + H \\ &\longrightarrow XH_{n-2} + H_2 \\ &\longrightarrow \ldots\ldots \end{aligned}\right\}$$

  Branching ratios:

  Major uncertainty!

- Example: $$\begin{aligned} H_3O^{+} &\longrightarrow H_2O + H \\ &\longrightarrow OH + H_2 \\ &\longrightarrow OH + H + H \\ &\longrightarrow O + H_2 + H \end{aligned}$$

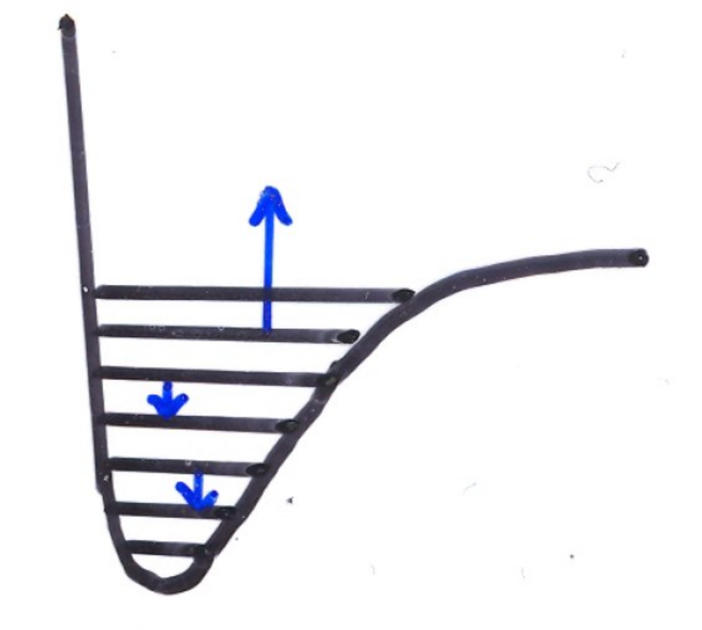
H_3O^+ DR products

Product	**Vejby-C. et al. 97**	**Buhr et al. 10**
$H_2O + H$	**33%**	**17%**
$OH + H_2$	18%	12%
$OH + H + H$	48%	71%
$O + H_2 + H$	1%	0%

- Major surprise experiments: 3-body products (e.g. OH + H + H) abundant!
- See also Jensen et al. (2000), Neau et al. (2000)

1.13 Collisional dissociation

- If *T* high (~5000 K), H_2 destroyed by collisions



- $H + H_2 \rightarrow H + H + H$
- $He + H_2 \rightarrow He + H + H$
- $H_2 + H_2 \rightarrow H_2 + H + H$

H_2 no dipole moment → significant population in high v at high T → large dissociation rate

CO small dipole moment → radiative stabilization rapid → not much population in high v → small dissociation rate

1.14 Collisional rate coefficients

- Calculation of molecular excitations requires availability of rate coefficients with H_2 (o,p), H, He, and e (see exercises)
- State-to-state rate coefficients from theory
  - Ab initio calculation of potential surface(s)
  - Molecular dynamics on surfaces
- Major effort by various quantum chemical groups
- Limited tests against experiments
  - Accuracy varies from ~20% to order of magnitude

See RADEX exercise, van der Tak et al. (2020)

Astronomical Units

- pc = parsec = 206,265 AU = 3.086×10^{18} cm
- $M_\odot$= solar mass = 1.99×10^{33} g
- $L_\odot$= solar luminosity = 3.90×10^{33} erg s^{-1}
- eV = 1.602×10^{-12} erg
- Å = 10^{-8} cm
- Jansky = 10^{-23} erg s^{-1} cm^{-2} Hz^{-1}
- Rayleigh = 10^6 photons s^{-1} cm^{-2} $(4\pi \text{ sr})^{-1}$
- Debye = 10^{-18} esu cm
- Kcal/mol = 6.947×10^{-14} erg $atom^{-1}$