Astrochemistry

Astro 736
Nienke van der Marel
Spring 2017

Schedule

- Classes: Thursday 4:00-5:30 PM

- Jan 12th: Introduction to astrochemical processes
- Jan 19th: Clouds and star formation
- Jan 26th: Protoplanetary disks
- Feb 2nd: Ice chemistry
- Feb 9th: NO CLASS
- Feb 16th: Laboratory work (with A. Ding)
- Feb 23rd: Practical session: ALMA, modelling tools and online catalogs
- March 1st: Colloquium Ilse Cleeves
- March 2nd: Student presentations
- March 9th: Reserve class
- April 6th: ALMA preparation workshop (entire IfA)

Exam

- Attendance (don’t miss more than 1 class)
- Student presentation:
  - Present one of the papers from provided list (other papers only after approval)
  - Presentation ~15+5 minutes
  - Ask questions to your fellow students (assigned)
  - Literature background reading
  - How many people want to receive credits? (1 CR)

Introduction to astrochemistry

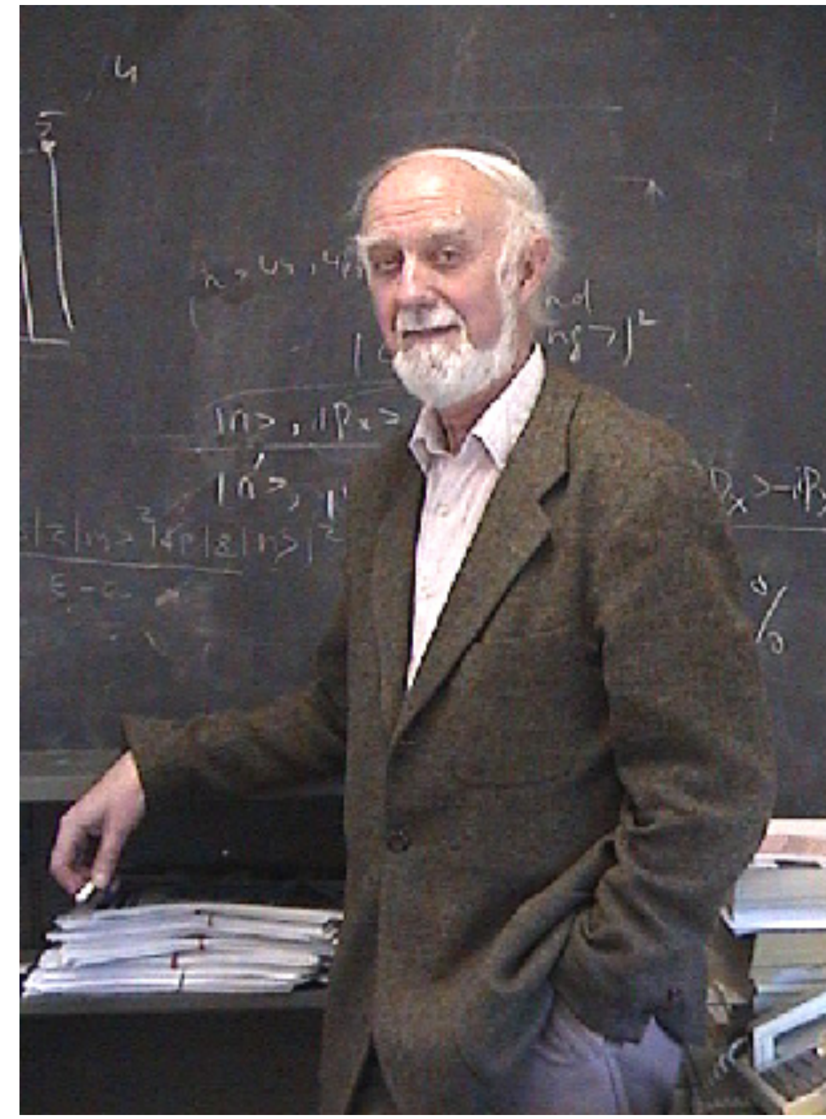
Nienke van der Marel
January 12th 2017

Contents

- Why astrochemistry?
- History
- Spectroscopy
- Formation/destruction processes
- Modeling approaches
- (Some) Observational results

Astrochemistry

- ‘Formation, destruction and excitation of molecules in astronomical environments and their influence on the structure, dynamics and evolution of astronomical objects’
- ‘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’



Alexander Dalgarno
(1928-2015)

Dalgarno 2008

Astrochemistry

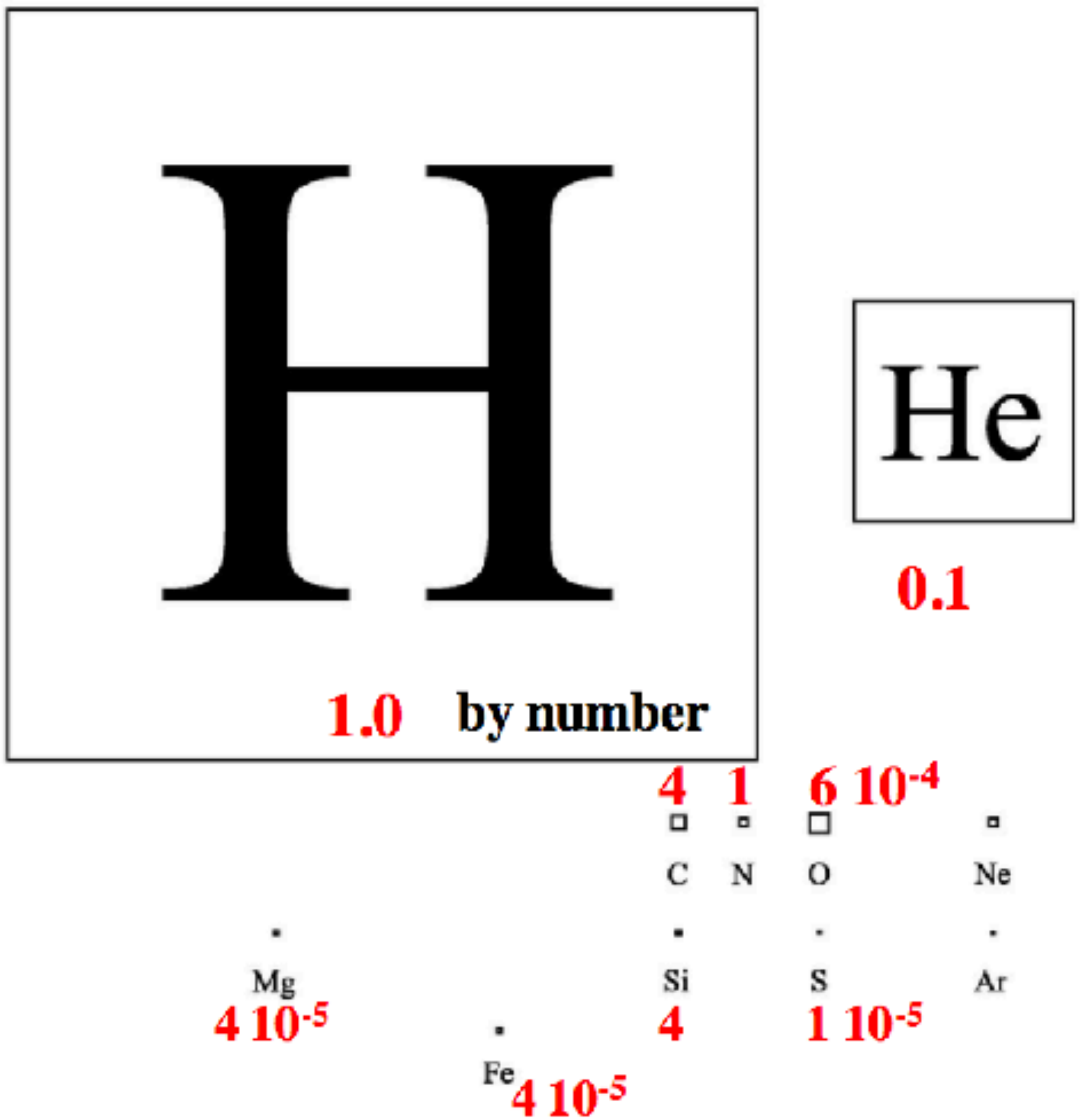
- Molecules are found throughout the universe
  - Molecular clouds, evolved stars, planetary nebulae, protoplanetary disks, stellar and (exo-) planetary atmospheres, solar photosphere, comets, galaxies (nearby to high z), …..
- Understanding their origin gives inside in physical processes and our understanding of the universe

Astrochemistry

- **Conditions very different from those normally encountered in lab on Earth (molecular physics)**
- Typical conditions:
    - Diffuse clouds: T_{kin}~100 K, n~100 cm^{-3}
    - Dense clouds: T_{kin}~10-100 K, n~10^4-10^8 cm^{-3}
    - Hot cores: T_{kin}~100-1000 K, n~10^6-10^8 cm^{-3}
    - Disk mid plane: T_{kin}~10-1000 K, n~10^8-10^{13} cm^{-3}
    - Compare atmosphere at sea level: T_{kin}~300 K, n~3 10^{19} cm^{-3}

Astrochemistry

Astronomical periodical table



McCall 2001

Astrochemistry

Cosmic abundances

Element	Abundance	Element	Abundance
H	1.00	Mg	4.2×10^{-5}
He	0.075	Al	3.1×10^{-6}
C	3.5×10^{-4}	Si	4.3×10^{-5}
N	8.5×10^{-5}	S	1.7×10^{-5}
O	5.5×10^{-4}	Ca	2.2×10^{-6}
Na	2.1×10^{-6}	Fe	4.3×10^{-5}

Astrochemistry

- Enrichment of heavy elements: supernovae, winds, shocks, ….
- Not all elements available for chemistry: lock-up in dust grains (‘depletion’)
- Available forms, depending on conditions:
  - gas molecules
  - ice molecules
  - volatiles (low evaporation temperature)
  - atoms
  - ions
  - radicals (unpaired valence electrons: likely to react)
  - “large molecules”:
    polyaromatic hydrocarbons (PAHs), carbon chains, dust grains, etc.

Astrochemistry

- Dust grains:

  small grains most relevant for chemistry: largest surface

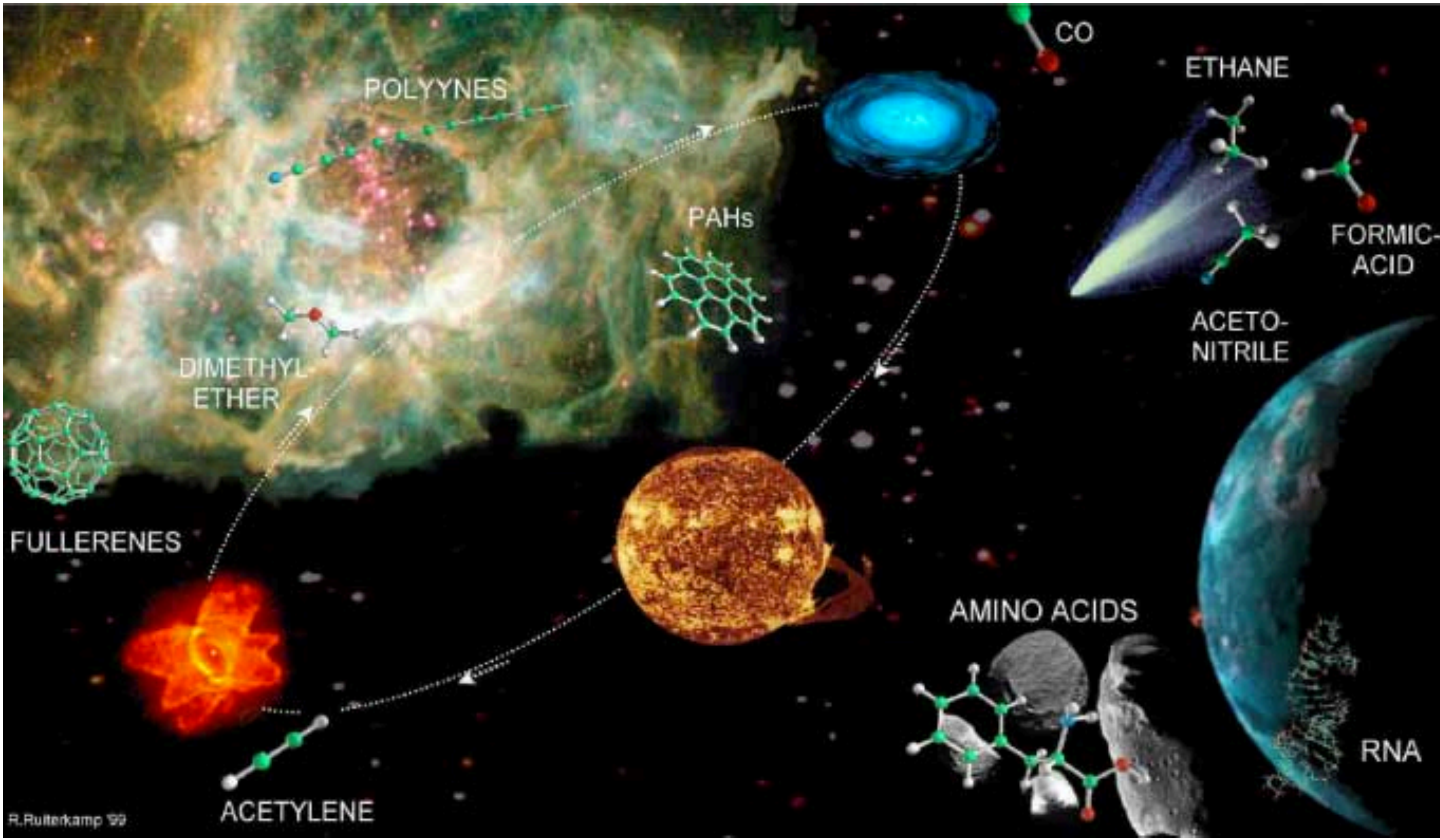
  - Small solid particles ~0.01-0.5 μm in size consisting of silicates and carbonaceous material; ~10^{-12} by number w.r.t. H
  - Most of Si, Mg, Fe incorporated in silicate cores; ~30% of O; ~60% of C in carbonaceous material
  - Cold dense clouds (T_{dust}~10 K): gas-phase species condense on grains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

Astrochemistry

- Time scales:
  - Collision time:~1 month at 10^4 cm^{-3}
  - Chemical time: ~10^5 yr (dark clouds)
  - Star formation: ~10^6 yr
  - Lifetime cloud: ~10^7 yr
- People did not expect to find many molecules since chemical reactions are slow
- Surprise:
  interstellar clouds contain a very rich chemistry!

Astrochemistry

Astrochemistry



Ehrenfreund

Why astrochemistry?

- Molecules as diagnostics of temperature, density, ionisation, velocity, radiation fields, etc.
- Molecules are import coolants of clouds: driving astronomical processes
- Simple molecules form the start of complex organic molecules (COMs) and biomolecules: astrochemical evolution? Origin of life?
- Exotic chemistry: unique chemical laboratory

Why astrochemistry?

- Evolution abundances molecules: *astrochemistry*
- Molecules as physical diagnostics: *astrophysics*
- Progress strongly driven by observations: *technology*
- Explanation observations requires detailed knowledge of molecules: *molecular physics, spectroscopy, quantum chemistry*
  => Very interdisplinary topic!

Astrochemistry

Observations

X-ray, UV, optical, infrared, submm

Clouds, early universe, PDRs, XDRs, shocks, cores, disks, ices, exoplanets, comets

Modeling

Radiative transfer, dynamics, radiation field, chemistry, feedback, chemical evolution

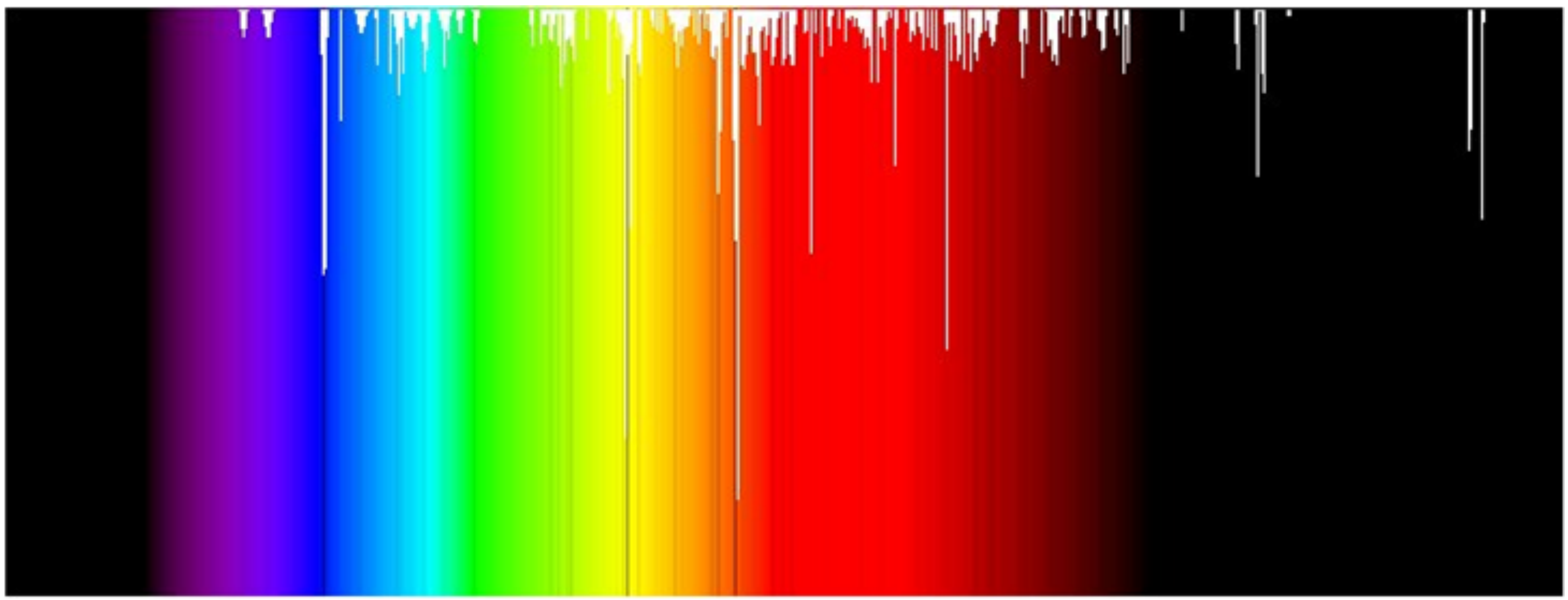
Experimental

Spectroscopy, oscillator strengths, collision rates, reaction rates, grain surface processes, charge exchange, photoprocesses

History

- Diffuse interstellar bands (DIBs):
  narrow absorption features in UV/Opt/IR (~500)

- First discovered in 1922 (Heger)!



- Origin: carbon-bearing molecules, but largely unknown!

History

- DIBs (1920s-1930s)
- Simple gas-phase molecules in optical
  - CH: Swings & Rosenfeld 1937
  - CN: McKellar 1940
  - CH^+: Douglas & Herzberg 1941
- First astrochemical models
  - Kramers & Ter Haar 1946, Bates & Spitzer 1951

History

- 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
- >1970: flood of new molecules

History

- OVRO 230 GHz spectral line survey Orion

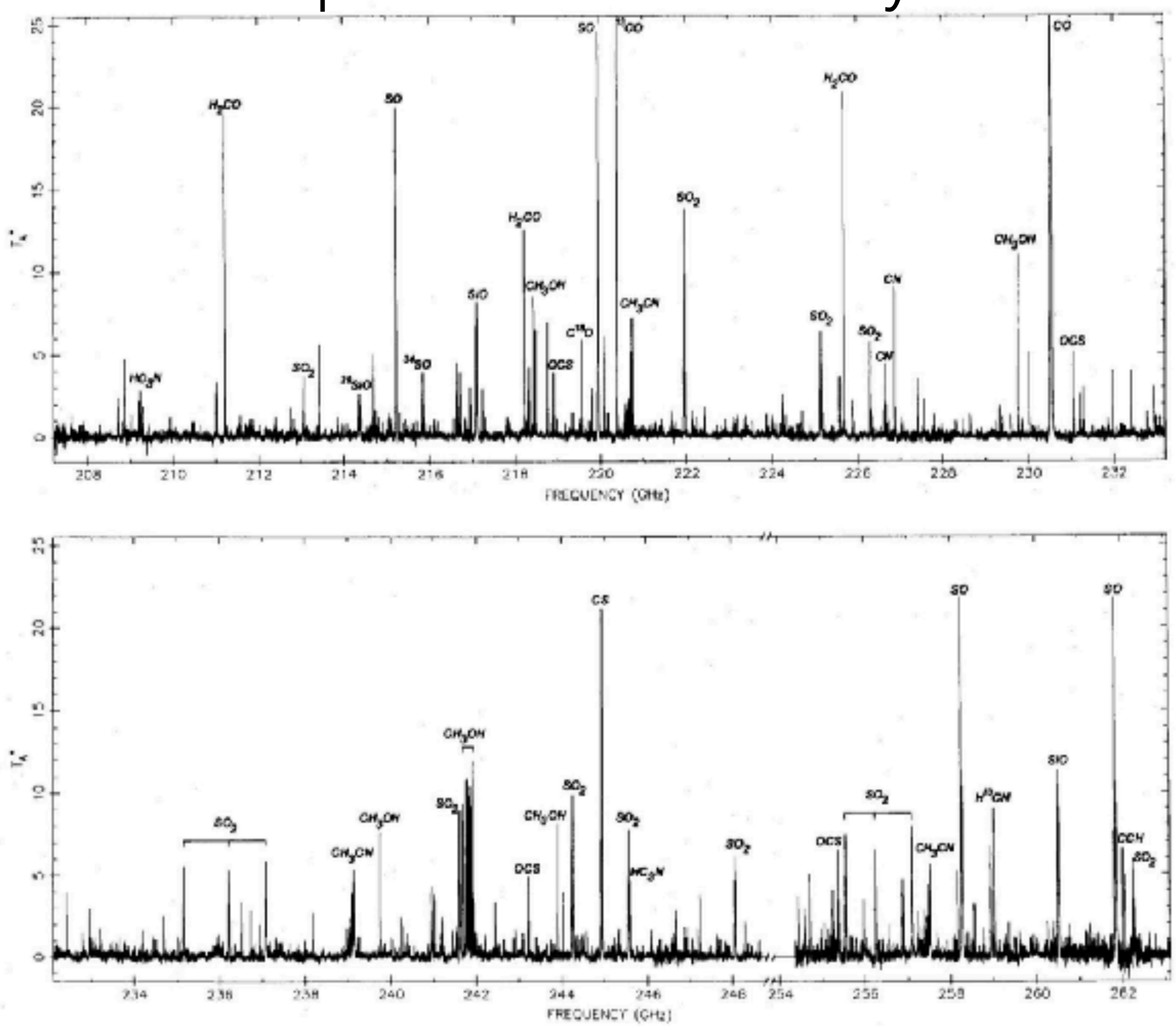


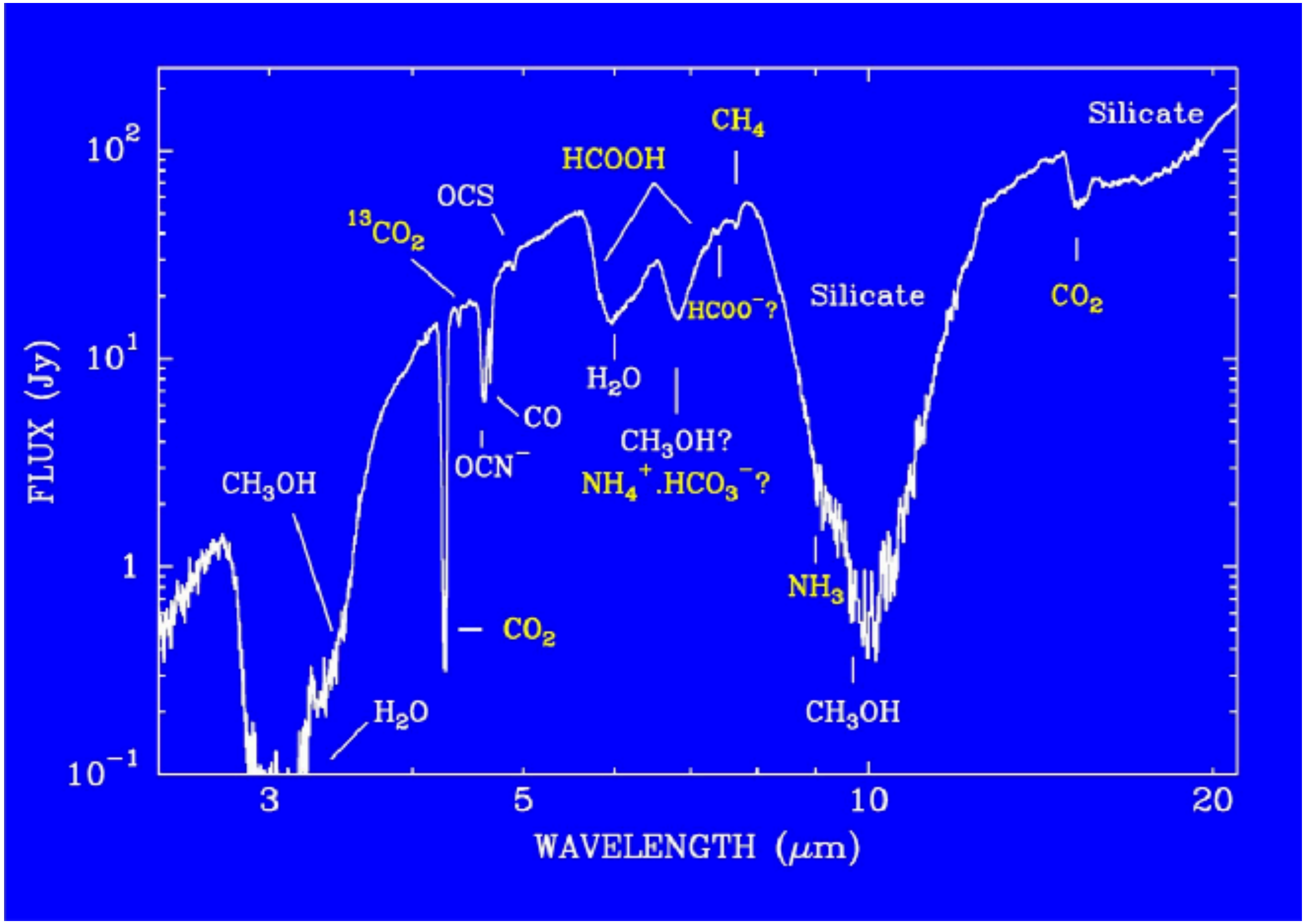
FIG. 1.—Compressed view of the OVRO spectral line survey of OMC-1

Blake+1986, 1987

History

- **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 mm 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 imaging and mapping; limited spectroscopy
  - Ices and silicates toward low mass protostars and disks

History



Infrared spectra:

interstellar ices!

(ISO, YSO W33A)

Later many more with Spitzer

Gibb+2000

History

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H_2	AlCl	CH_2	C_2S	NH_3	CH_4	CH_3OH	CH_3NH_2	$HCOOCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$
CH	PN	H_2S	OCS	H_2CO	SiH_4	CH_3SH	CH_3CCH	CH_3C_2CN	C_2H_5OH	CH_3C_4CN
NH	SiN	NH_2	MgCN	H_2CS	CH_2NH	C_2H_4	CH_3CHO	HC_6H	C_2H_5CN	CH_3CH_2CHO
OH	SiO	H_2O	MgNC	H_2CN	C_5	H_2C_4	c-CH_2OCH_2	C_7H	CH_3C_4H	$(CH_2OH)_2$
O_2(?)	SiS	HNO	NaCN	l-C_3H	l-C_3H_2	CH_3CN	CH_2CHCN	$HOCH_2CHO$	C_8H	
HF	PO	C_2H	SO_2	c-C_3H	c-C_3H_2	CH_3NC	HC_4CN	CH_3COOH	HC_6CN	
C_2	SH	HCN	N_2O	HCCH	H_2CCN	NH_2CHO	C_6H	$H_2CCCHCN$	CH_3CONH_2	N = 11
CN	AlF	HNC	SiCN	HNCO	H_2NCN	H_2CCHO	H_2CCHOH	H_2C_6	CH_2CHCH_3	HC_8CN
CO	FeO	HCO	SiNC	HNCS	CH_2CO	C_5H		CH_2CHCHO		CH_3C_6H
CS	SiC	c-SiC_2		HCCN	HCOOH	C_5N		C_2H_6		
CP		MgCN		C_2CN	C_4H	HC_4N				
NO		MgNC		C_3O	HC_2CN	C_5S(?)				N = 12
NS		AlNC		C_3S	HC_2NC	HC_4H				C_6H_6
SO		HCP	H_3^+	c-SiC_3	C_4Si	CH_2CNH				
HCl	CH^+	C_3	HCO^+	C_3N^-	HNCCC	HC_2CHO				
NaCl	CO^+	C_2O	HOC^+	H_3O^+		c-C_3H_2O				N = 13
KCl	SO^+	CO_2	N_2H^+	$HCNH^+$	H_2COH^+					$HC_{10}CN$
N_2(?)	CF^+		HCS^+	$HOCO^+$	C_4H^-	HC_3NH^+	C_6H^-		C_8H^-	

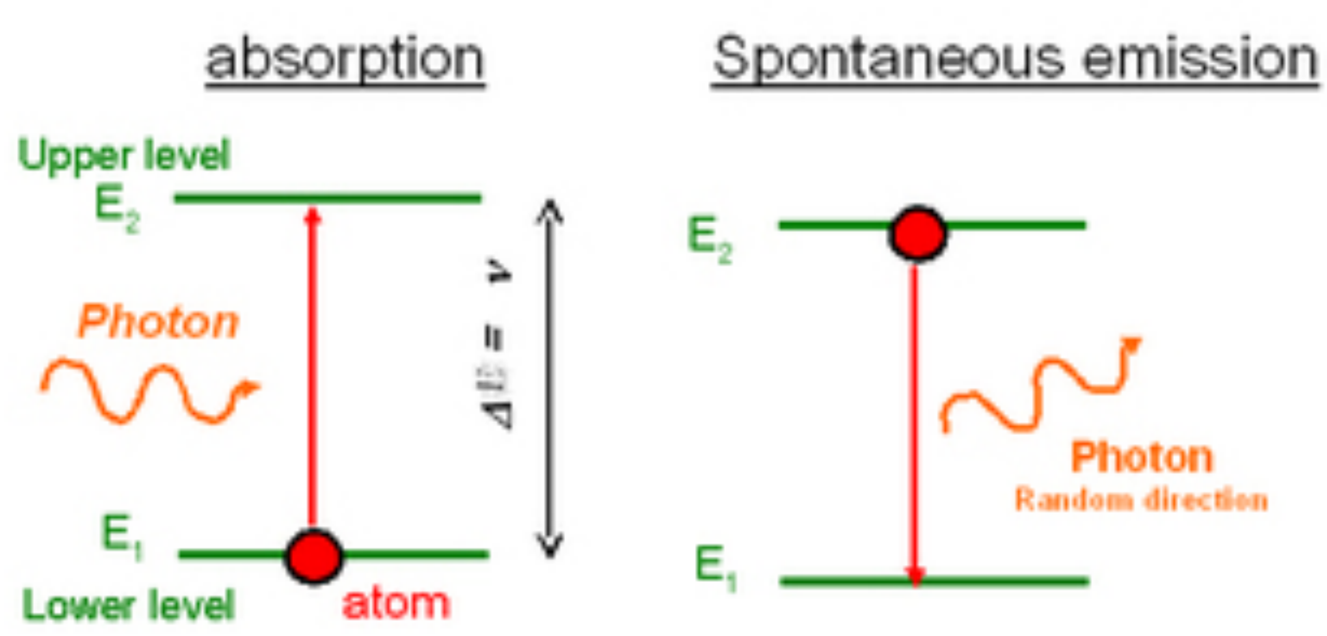
Herbst 2008

History

- Herschel Space Observatory (2009-2013): FIR astronomy
  - H_2O
  - CO transition ladders
  - [OI], [CI], [CII]
  - ArH+ (!!!)
- SOFIA airplane (2010 - now): continuation FIR
- Ground-based NIR telescopes: VLT, Keck, Subaru
- (Sub)millimeter astronomy since 2000s: JCMT, APEX, IRAM, PdBI, SMA, CARMA, ALMA

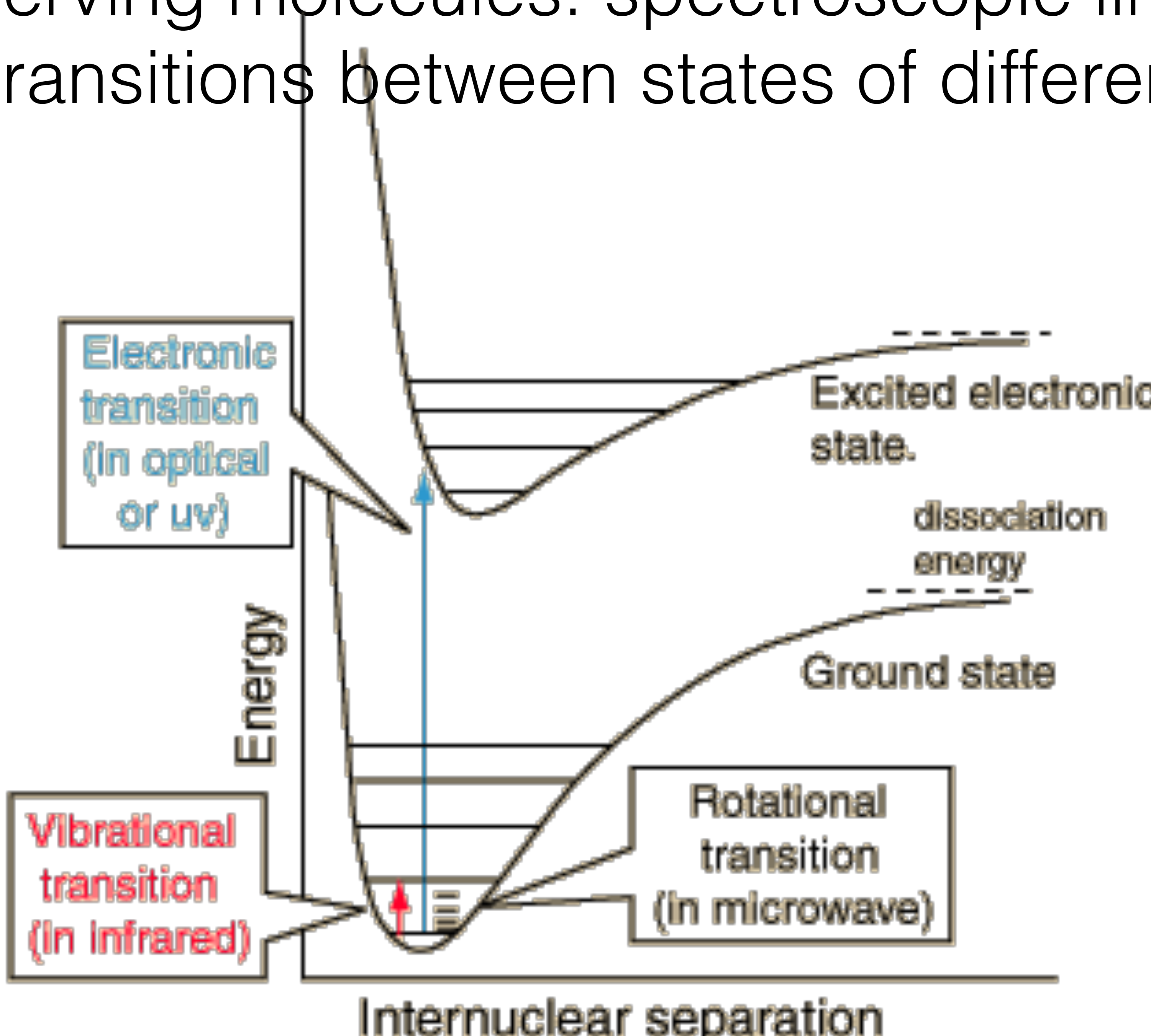
Spectroscopy

- Observing molecular lines
  - absorption: bright background
  - emission: collisional excitation followed by spontaneous emission photon



Spectroscopy

- Observing molecules: spectroscopic lines
  => transitions between states of different energy



Spectroscopy

- Electronic transitions (UV/opt)
  - Atoms:
    - quantum number **n** (1,2,…)
    - orbital angular momentum number **l** (0,1,…,n-1 or *s,p,d,… or S,P,D,…* for heavier atoms: electron interaction)
    - spin angular momentum number **s** (+/- 1/2)
    - total angular momentum **j = l+s**
    - Nomenclature hydrogen series:
      - Transitions to n=1 (Lyman), n=2 (Balmer), n=3 (Paschen), n=4 (Brackett)
      - Successive: α, β, γ, etc… (Ly-α: n=2-1)
      - Balmer series also simply called “hydrogen”: H-α, H-β, etc. (optical: first discovery)
    - Heavier atoms: **J = L+S** *(vector sum: more possibilities)*

Spectroscopy

- Molecules (electronic states):
    - angular momentum orbitals σ, π, δ etc. and total angular momentum Λ = Σ, Π, Δ, etc. (similar as atoms)
    - designation

$$^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)}$$

reflection in the plane through internuclear axis

reflection in center of mass: gerade (even) or ungerade (odd)

spin angular momentum

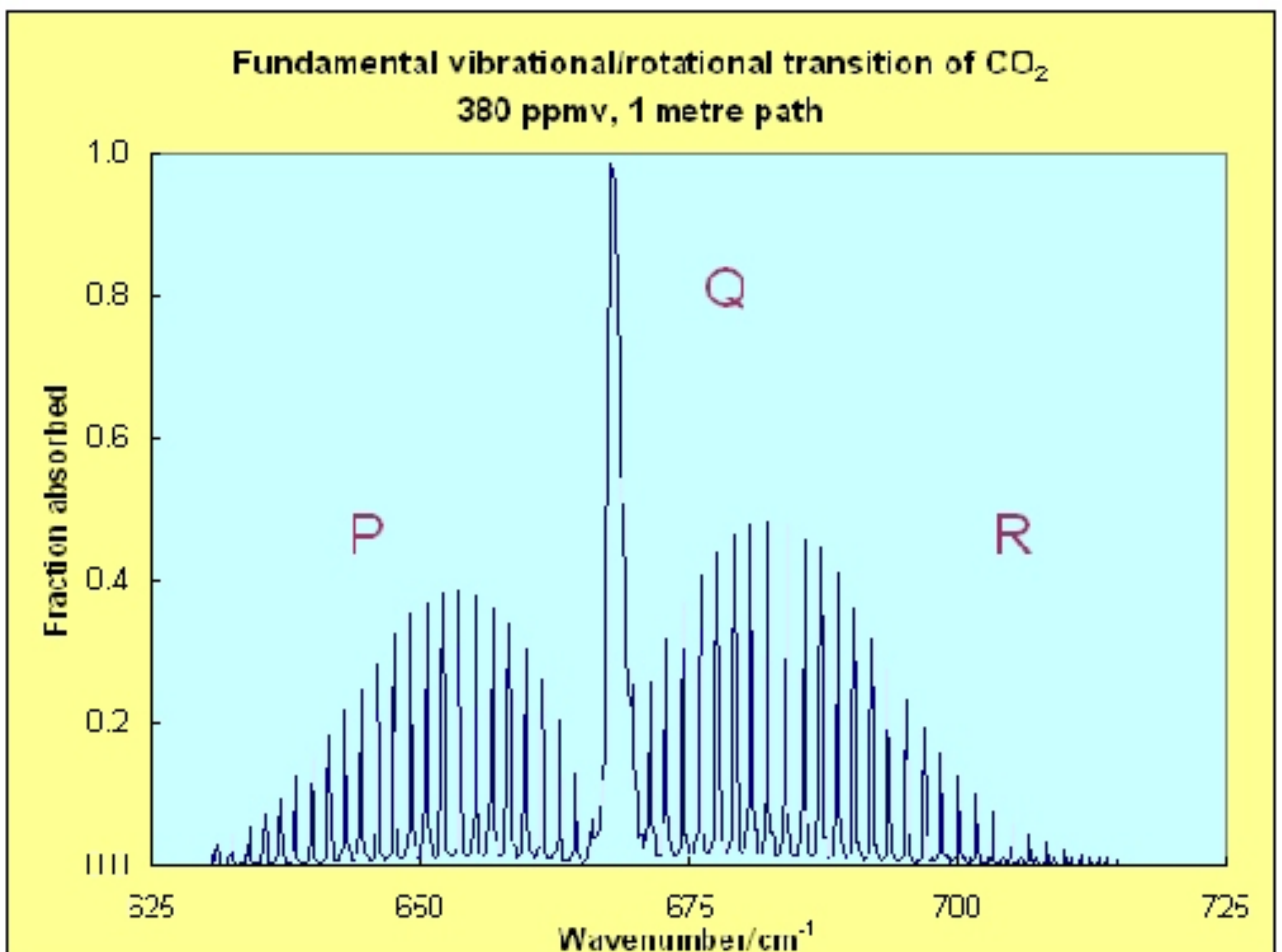
projection angular momentum

Spectroscopy

- Vibrational transitions (infrared): *v=2-1, 1-0, etc.*
  - different vibrational motions: bending or a(symmetric) stretching of molecule groups/bonds (CO, CN, CH, OH, etc.): the heavier, the lower the frequency
  - similarity bond strength ~ binding energies electrons
  - Linear/non-linear molecules (N atoms):
    - linear: 3N-5 modes
    - non-linear: 3N-6 modes
  - Some modes degenerate: same frequency
  - Some modes non-active: no change dipole moment

Spectroscopy

- Usually vibration-rotational transitions (rovibrational)
  - rotational quantum number J:
    $\Delta J=1$ (R branch), $\Delta J=0$ (Q branch), $\Delta J=-1$ (P branch),



Q branch is forbidden in linear molecules, except for perpendicular vibrations.

All non-linear molecules have Q branch as well

wavenumber k (cm^{-1}) = $2\pi/\lambda$ (common unit in IR spectroscopy)

Spectroscopy

- Rotational transitions in (sub)mm: *J=1-0, 2-1, etc.*
- Symmetric molecules have no rotational transition
- Classification according to moments of inertia along 3 axes I_a, I_b, I_c:
    - Spherical top: no dipole moment, so no rotational transition (e.g. CH_4)
    - Linear top (similar to diatomic): $I_a=0$, $I_b=I_c$ (e.g. CO, CO_2)
    - Symmetric top: $I_a < I_b = I_c$ (e.g. NH_3)
      additional quantum number *K:* projection angular momentum on symmetry axis (but *K* cannot change in J transition)
    - Asymmetric top: quantum number $J_{K\text{-}K+}$ (e.g. H_2O, H_2CO, most larger molecules)
- Ortho/para (e.g. H_2O) :
  3 possible ortho (symmetric) spin states, 1 para (asymmetric) spin state

Spectroscopy

- Many selection rules for which transitions between quantum numbers are allowed: complex for larger, asymmetric molecules

- Forbidden lines: transitions that are not allowed according to selection rules, but still happen with much smaller probability (e.g. [OI], [HI]): not happening on Earth!

- Details of molecular spectroscopy beyond the scope of this lecture

- More background: Herzberg 1991, Hollas 1996

Emission

- Most common emission mechanism in space: Collisional excitation + emission photon

- LTE = Local Thermodynamic equilibrium: collisions determine level population when $n>n_{cr}$ (critical density: property of molecule)

- Boltzmann distribution:

$$\frac{n_u}{n_l} = \frac{g_u}{g_l}\exp\left(-h\nu / kT_{ex}\right) = \frac{g_u}{g_l}\exp\left(-(E_u - E_l) / kT_{ex}\right)$$

Emission

- Rate equation

$$\frac{dn_u}{dt} = \underbrace{\left[n_c n_l q_{lu} \right]}_{\substack{\text{coll. exc.} \\ \textbf{Trans. to level u}}} - \underbrace{\left[\underbrace{n_c n_u q_{ul}}_{\text{coll. deexc.}} + \underbrace{n_u A_{ul}}_{\text{spontaneous emission}} \right]}_{\textbf{Trans. out of level u}} = 0$$

$$\Rightarrow \quad \frac{n_u}{n_l} = \frac{n_c q_{lu}}{A_{ul}} \left[\frac{1}{1 + \frac{n_c q_{ul}}{A_{ul}}} \right]$$

- A = Einstein coefficient s^{-1}
- n_c = density of main collision partner (H_2 in molecular clouds)
- q = collisional rate coefficient ($cm^3\ s^{-1}$)
- $q_{lu} = q_{ul}\,(g_u/g_l)\exp(-h\nu/kT)$

Emission

$$\frac{n_u}{n_l} = \frac{n_c q_{lu}}{A_{ul}} \left[\frac{1}{1 + \frac{n_c q_{ul}}{A_{ul}}} \right]$$

- ***Low*** density

$$n_c q_{ul} << A_{ul} \Rightarrow \frac{n_u}{n_l} = \frac{n_c q_{lu}}{A_{ul}}$$

- ***High*** density

$$n_c q_{ul} >> A_{ul} \Rightarrow \frac{n_u}{n_l} = \frac{q_{lu}}{q_{ul}} = \frac{g_u}{g_l} \exp(-\Delta E_{ul} / kT)$$

Thermal distribution

- ***Critical*** density: $n_{\mathrm{crit}} = A_{ul}/q_{ul}$

=> Observe molecules with densities > n_{crit}

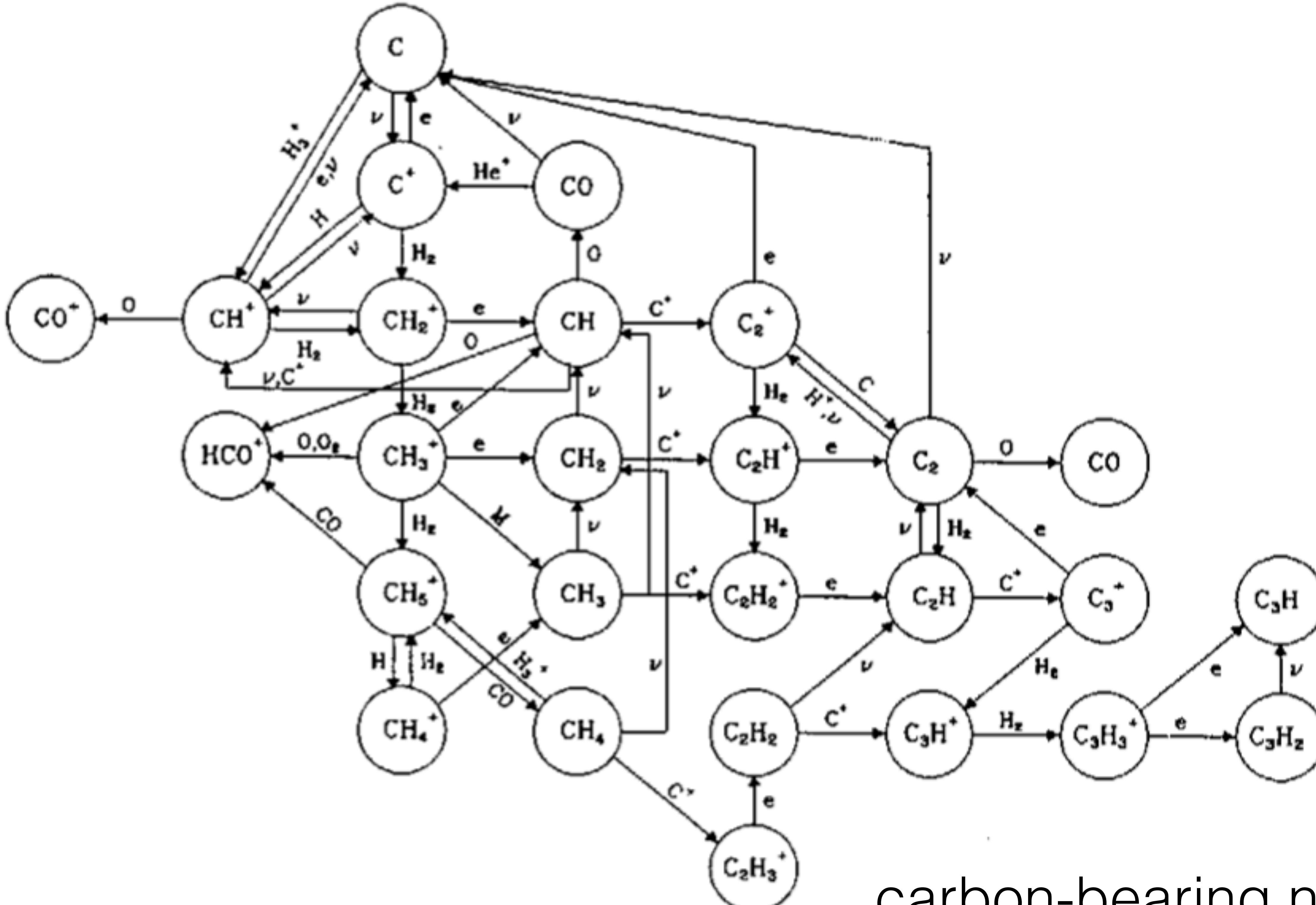
Chemical reactions

- Because of low densities and temperatures, chemistry is controlled by two-body reactions:
  => abundances depend on physical conditions (temperature, density, radiation field, history)

- Three-body reactions not important until $n \sim 10^{12}$ cm^{-3}

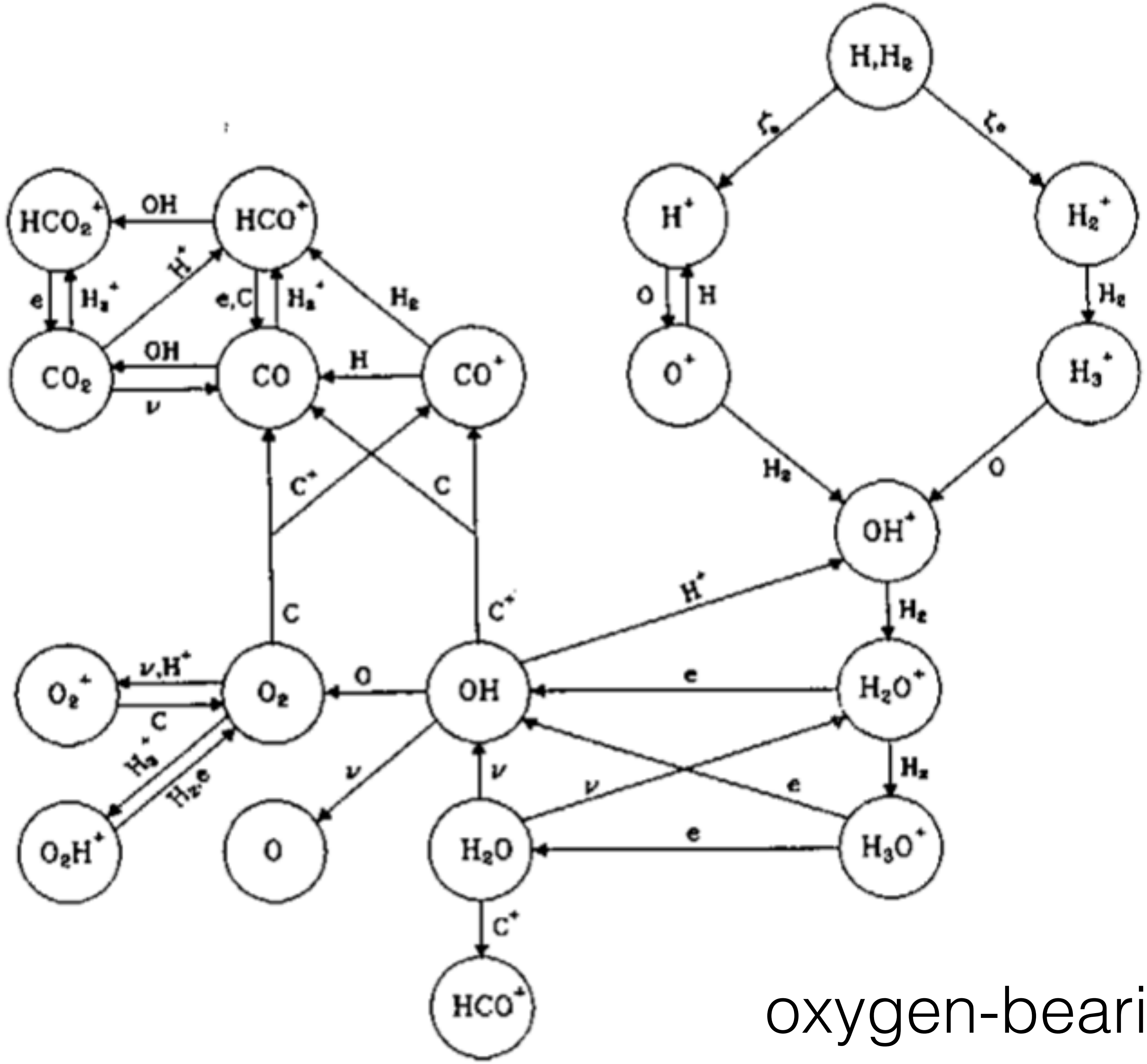
- Reaction rate (often T-dependent):
  $\boldsymbol{k}\, n(x)\, n(y)\ cm^{-3}\ s^{-1}$

Chemical reactions



carbon-bearing network

Chemical reactions



oxygen-bearing network

Types of 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 $X + YZ \Rightarrow XY + Z$

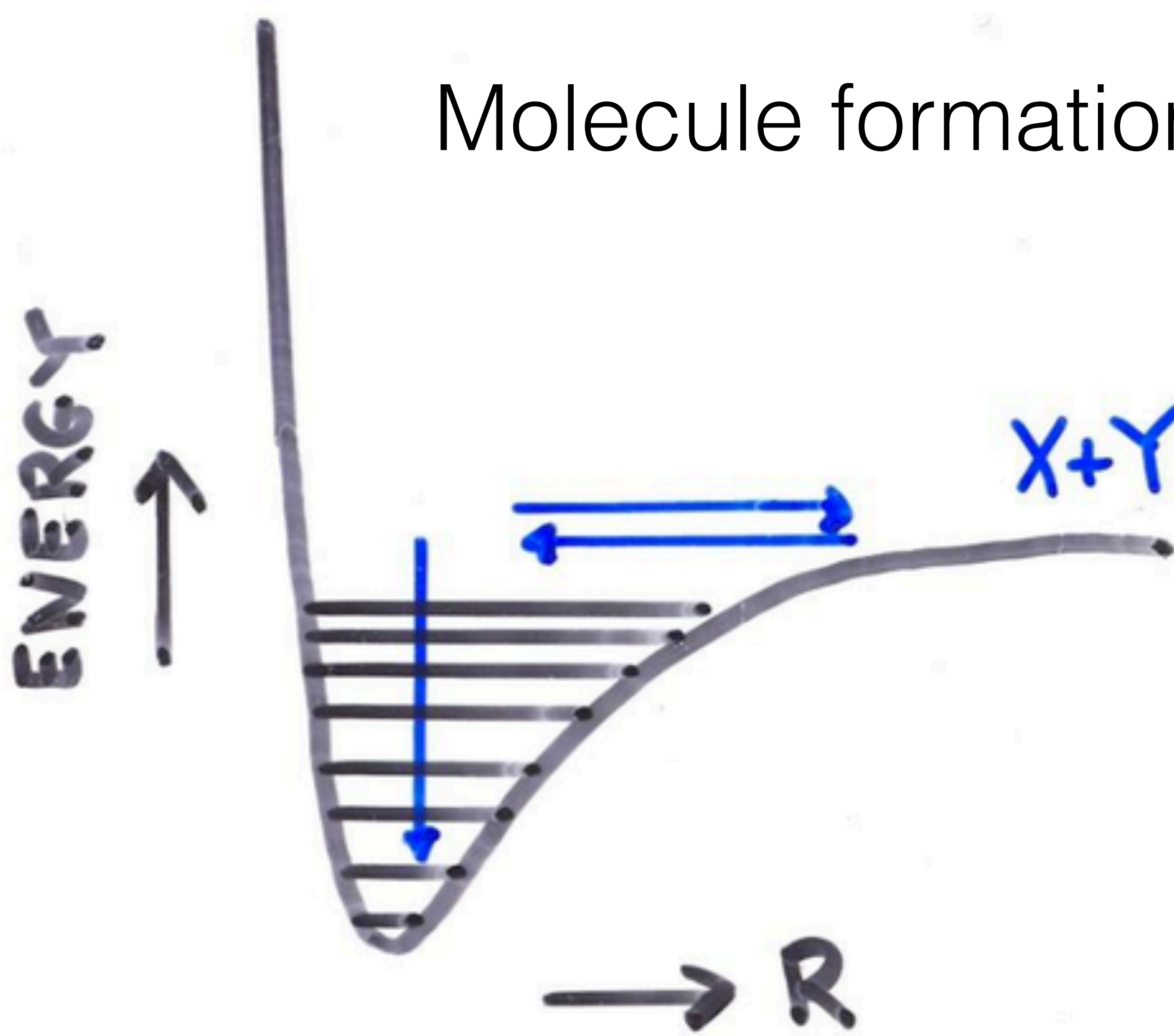
Radiative association

- $X^+ + Y <=> XY^* => XY + h\nu$

collision time
~ 10^{-13} s

transition time
~ 10^{-3} s or 10^{-8} s (vib/elect)

Molecule formation 1:$10^{10 \text{ or } 5}$ collisions: slow

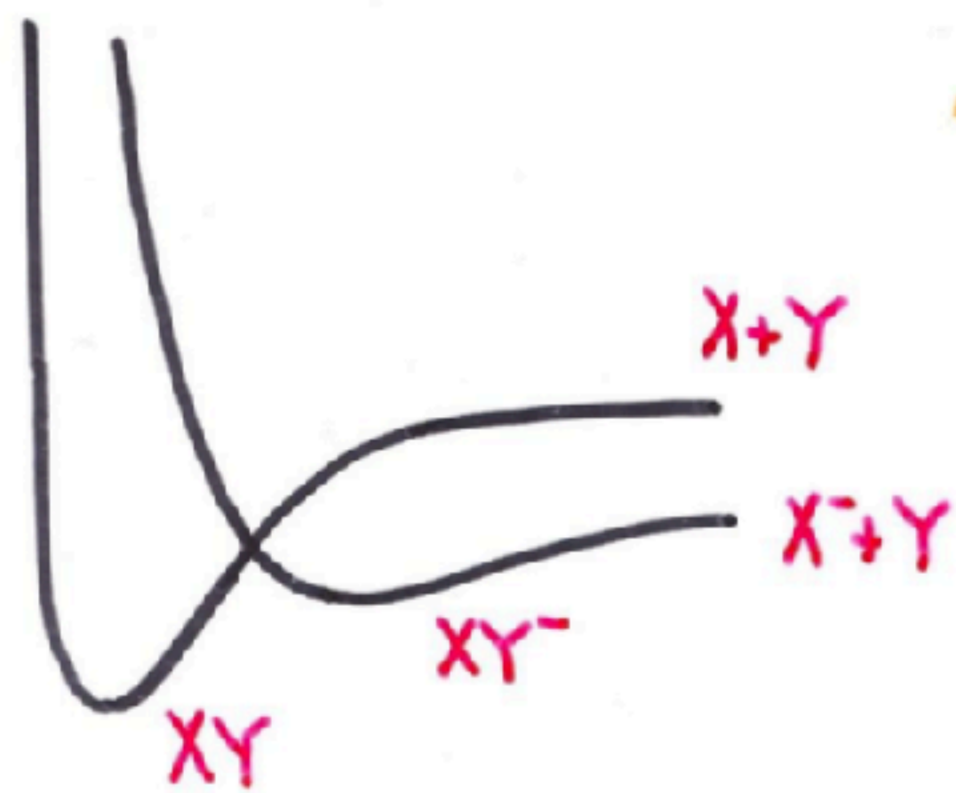


Efficiency larger if destruction time longer:

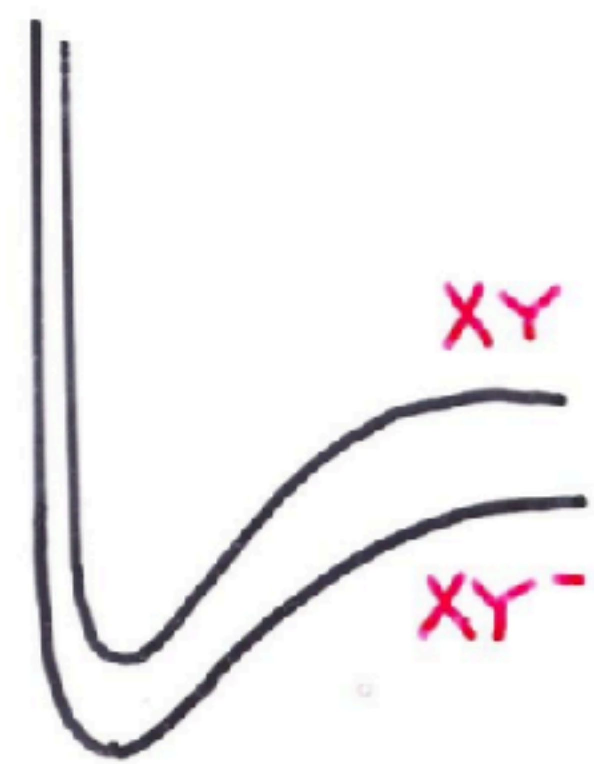
- entrance barrier
- molecule larger

Associative detachment

- $X^- + Y \Rightarrow XY + e$
- First ionization X: $X + e \Rightarrow X^- + h\nu$ (rad. det.: slow)



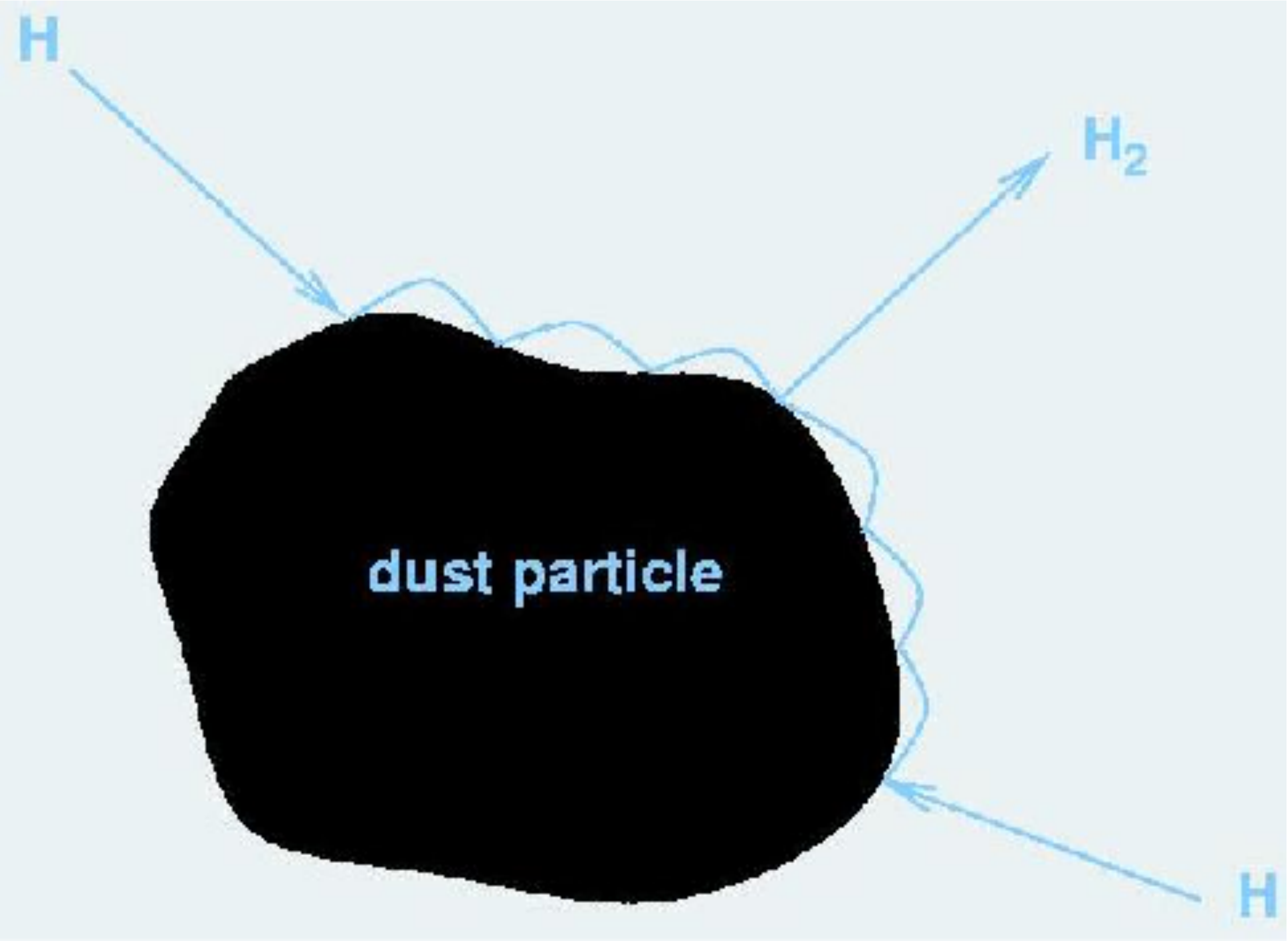
fast



slow

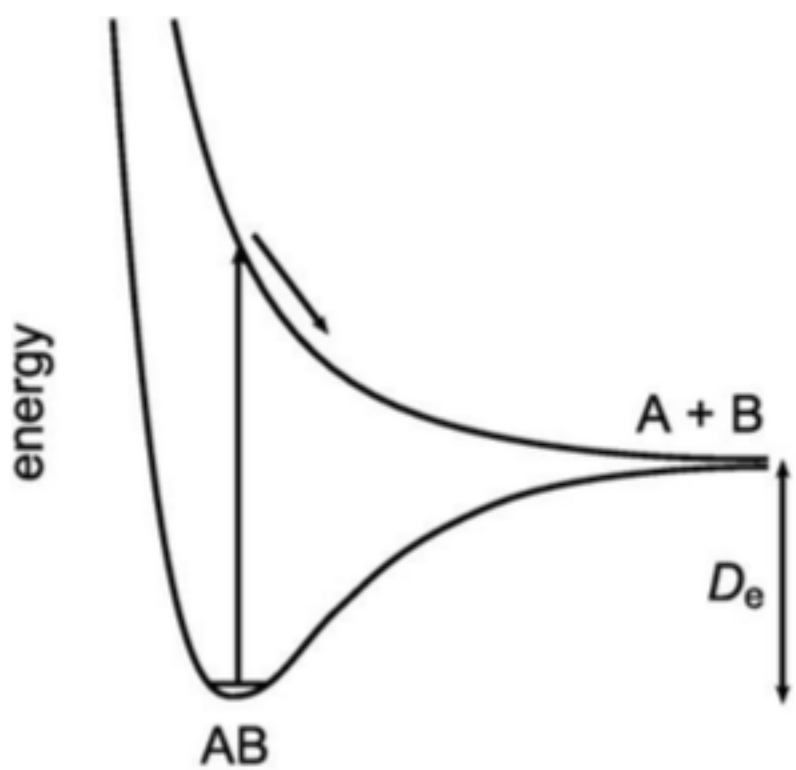
Grain surface

- X+Y:g => XY+g
- Most famous example: molecular hydrogen!

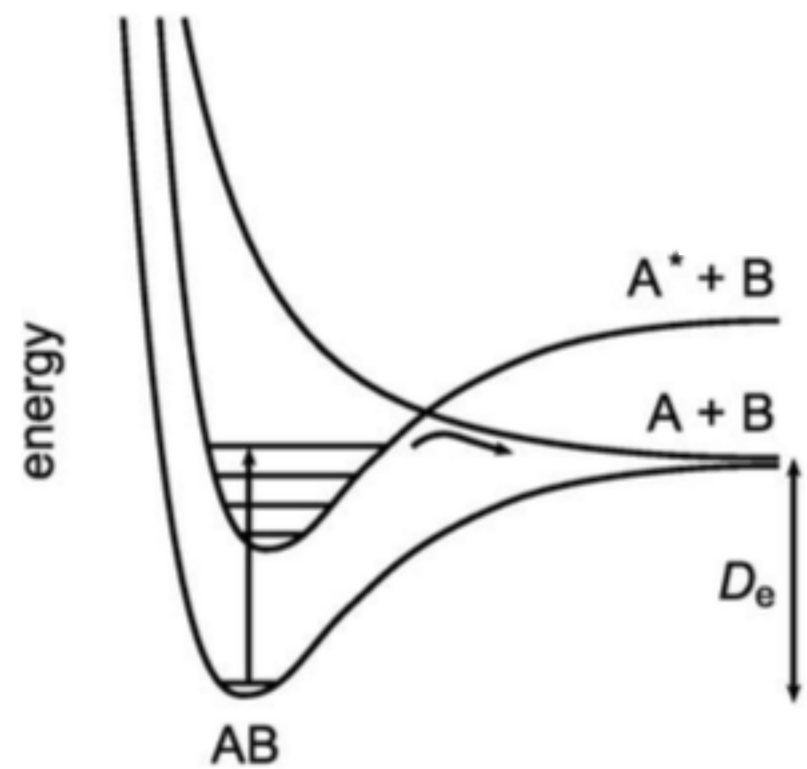


Photodissociation

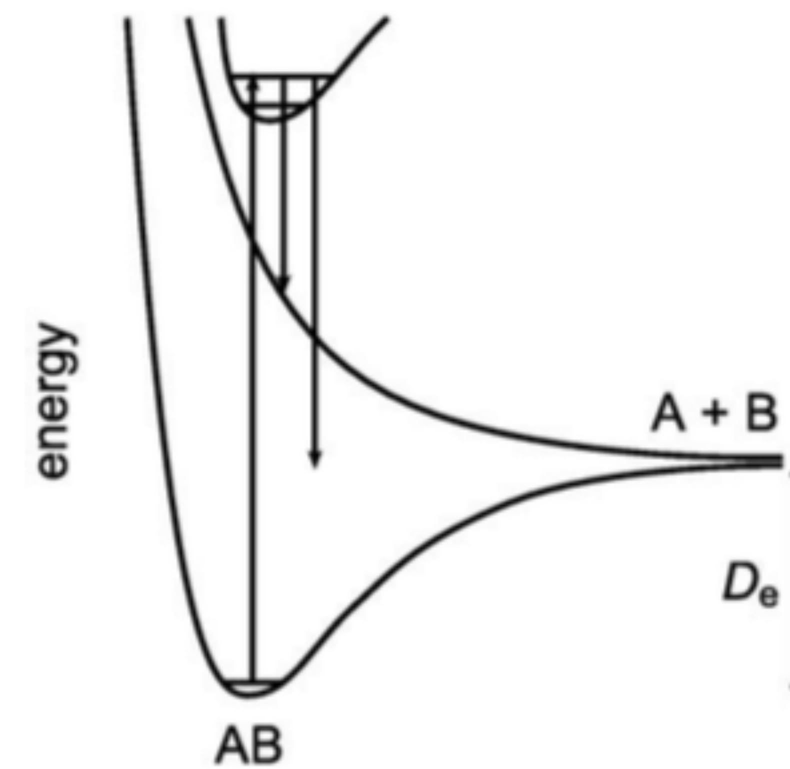
- XY+hv => X+Y



Direct photodissociation



Predissociation (e.g. CO)

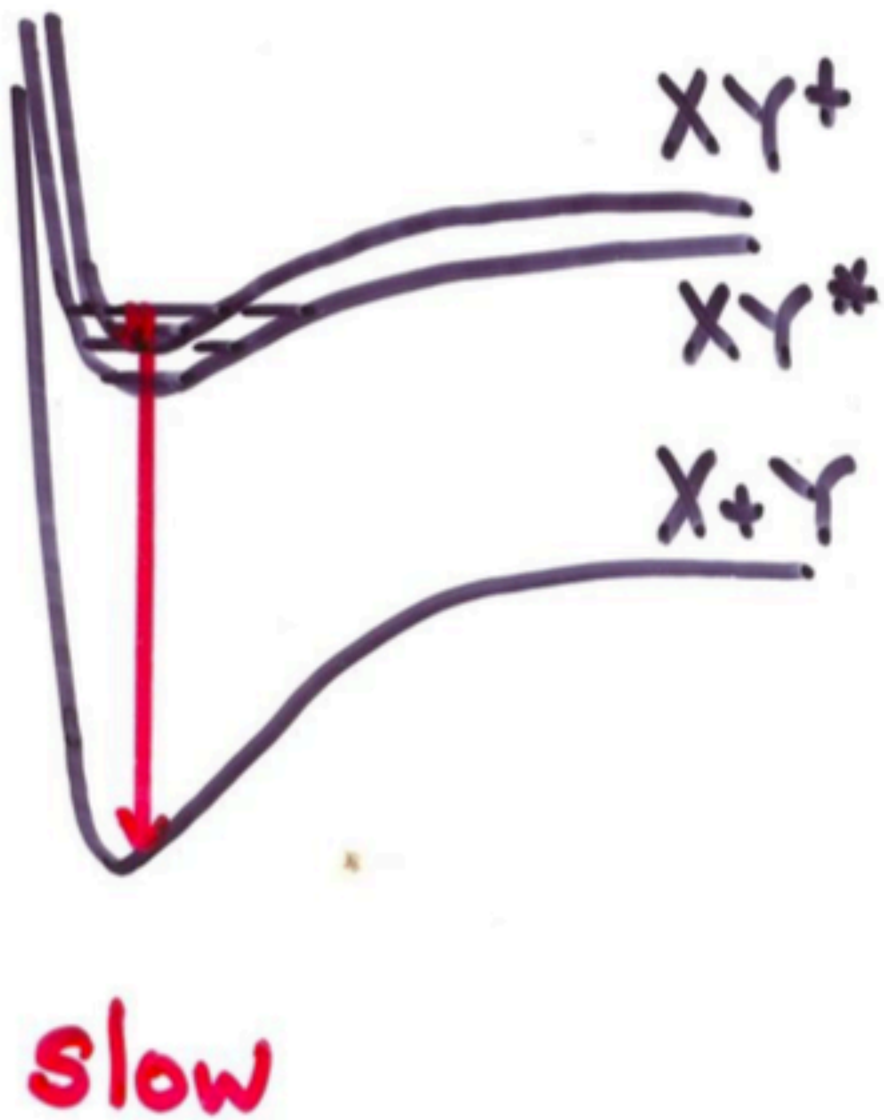


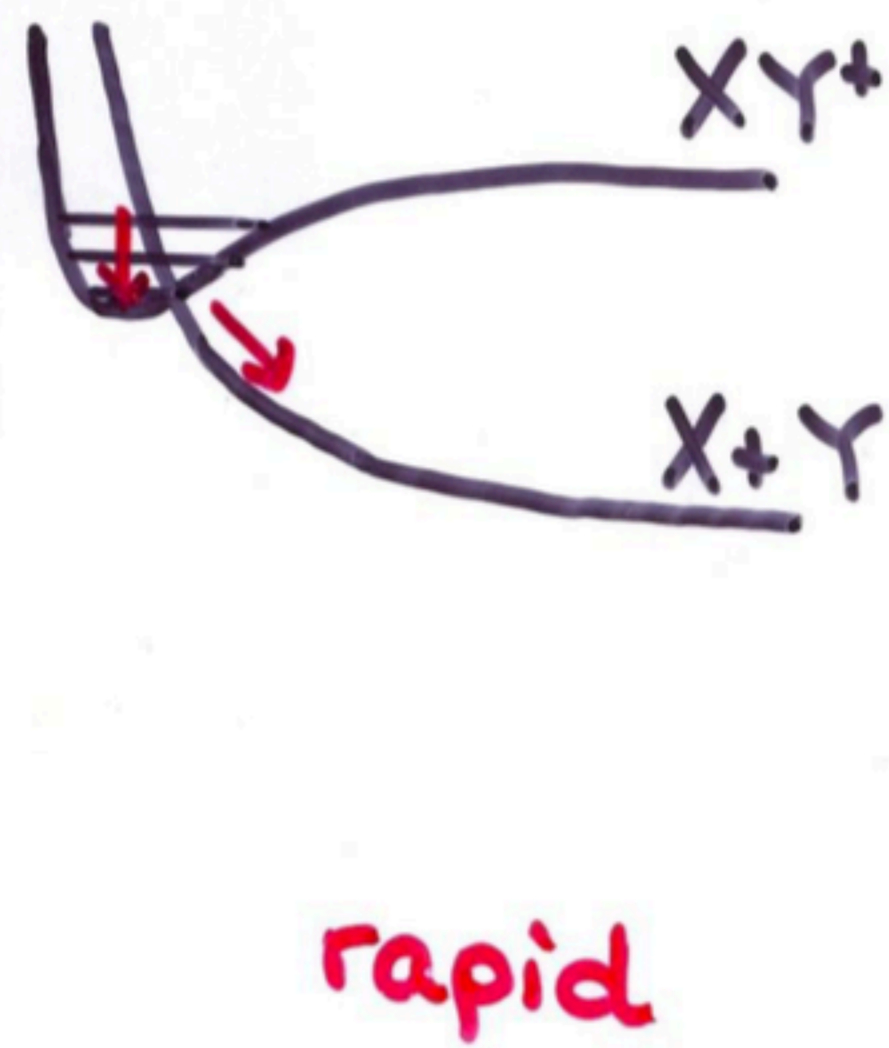
Spontaneous radiative dissociation (e.g. H_2)

Most abundant molecules in clouds:
H_2 and CO => self-shielding

Dissociative recombination

- $XY^+ + e \Rightarrow XY + h\nu \Rightarrow X + Y$





Collisional dissociation

- XY+M => X+Y+M
- Example: destruction H_2 at high temperature (5000 K)
- Note that reverse reaction (association) not possible in universe:
  three-body reaction unlikely!

Ion-molecular reaction

- $X^+ + YZ \Rightarrow XY^+ + Z$
- sometimes charge transfer:
  $X^+ + YZ \Rightarrow X + YZ^+$ (if energy levels available)
- Ion induces dipole moment in molecule when it's approaching => attractive force => capture ion => usually a fast process
- Reaction rate: *Langevin rate* (independent of T)

Neutral-neutral reactions

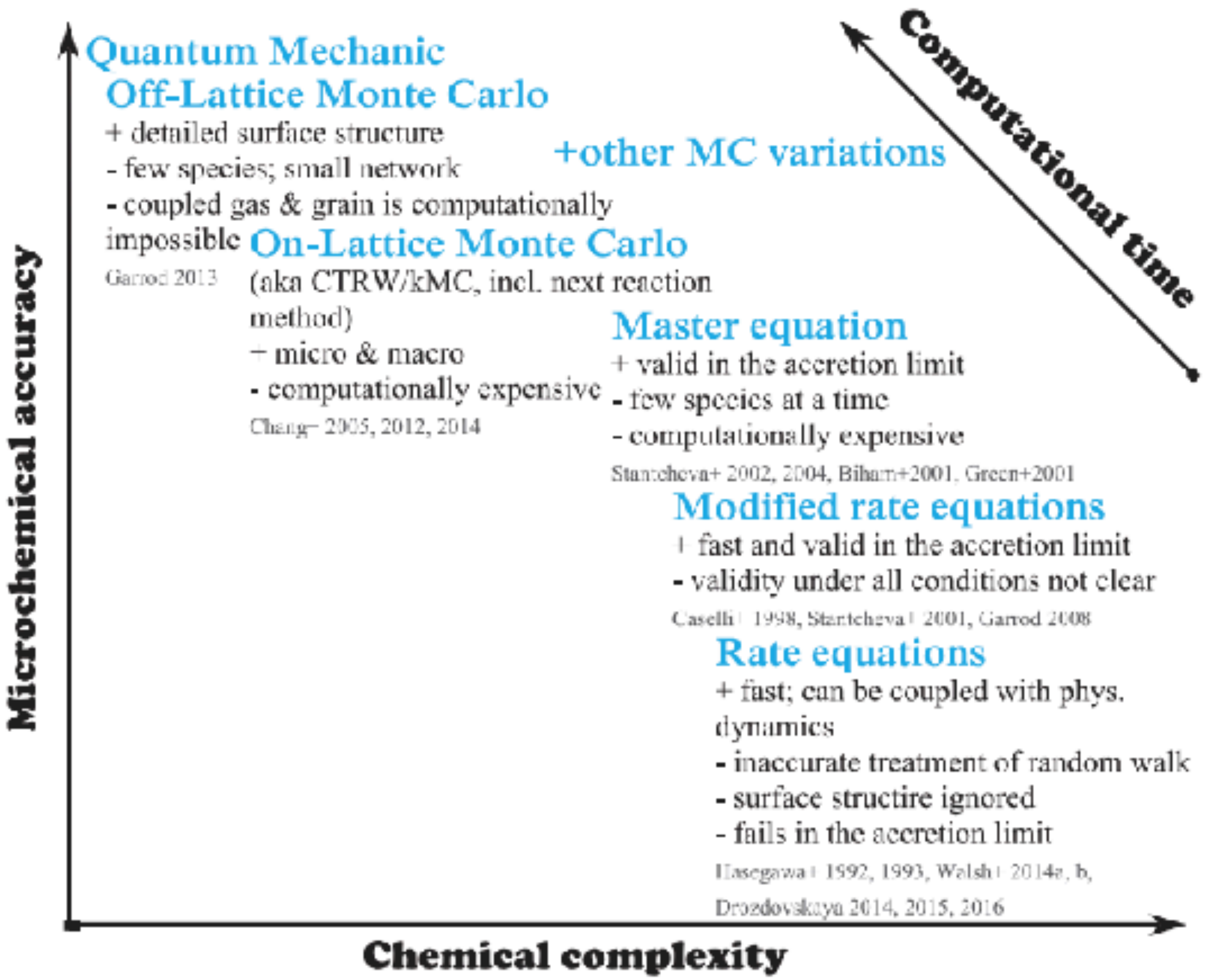
- X+YZ => XYZ => XY +Z
- Long range attraction weak: van der Waals ($1/R^6$)
- Potential energy barriers in both reactions
- Reactions slow at low temperature (although experimental work has shown better results than theory: still on-going work)

Modeling approach

- Many different models: choice depends on the goal
- Distinguish radiative transfer models (RADMC, RATRAN, LIME) from chemical models (chemical networks)
- Generally:
  more complexity ~ more computational time

Modeling approach

- Pure chemistry models

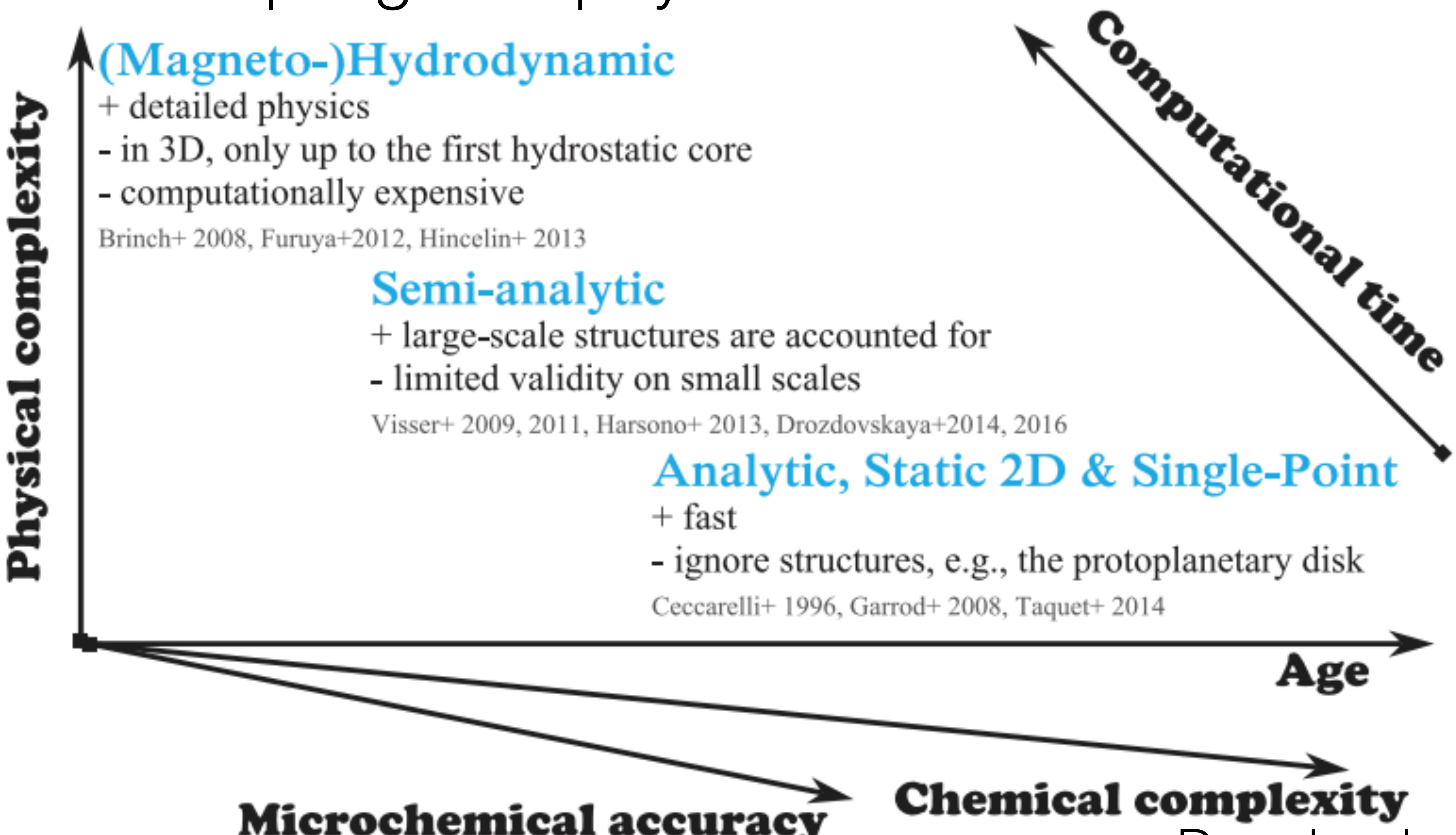


In particular grain chemistry complex: diffusion vs accretion

Drozdovskaya 2016 (thesis)

Modeling approach

- Astrophysical context:
  coupling with physical network



Drozdovskaya 2016 (thesis)

Modeling approach

- Static 2D: no time-dependent physics, only chemistry in certain conditions as function of time (e.g. clouds, disks): can be done as single-point

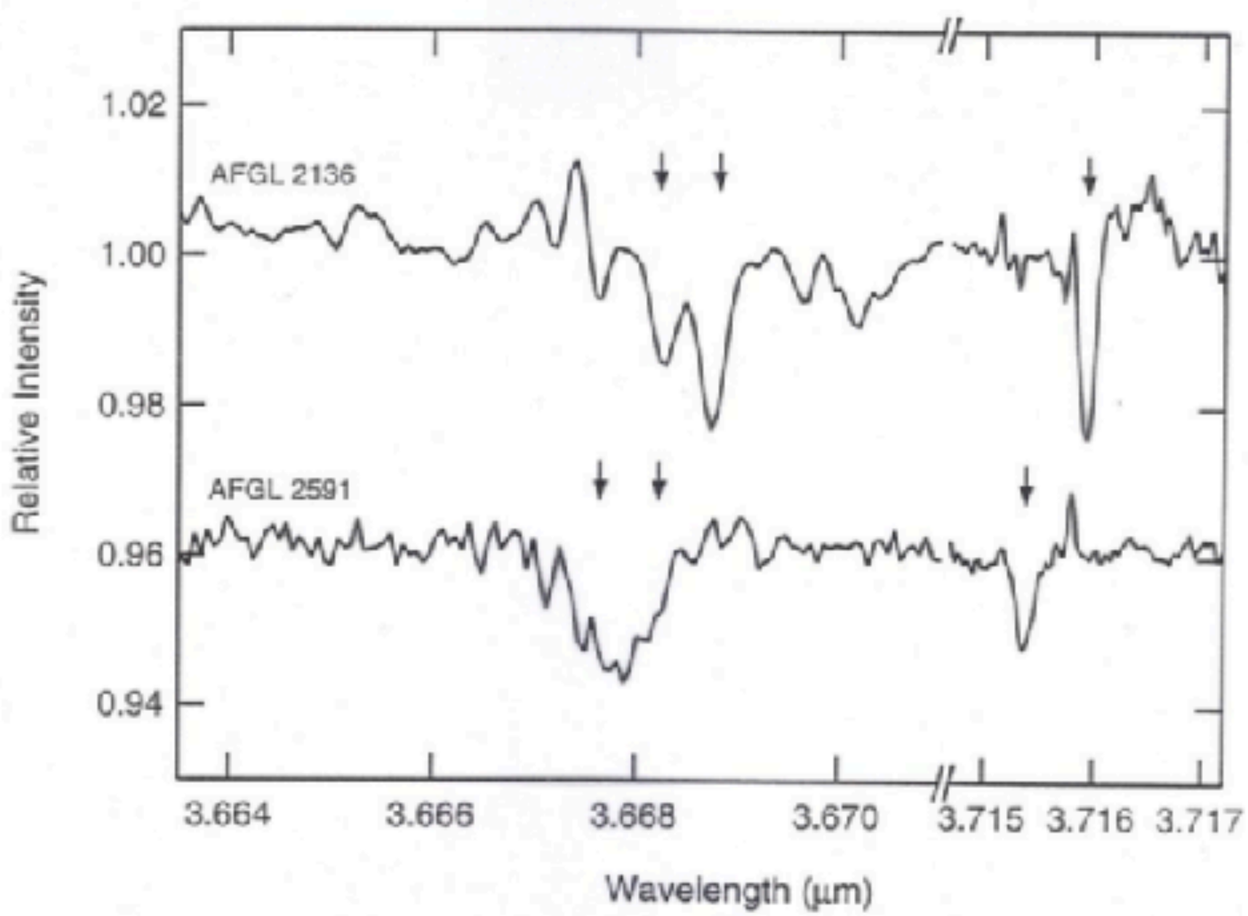
- Semi-analytic: macroscopic physics time-dependence (e.g. Shu collapse of a core)

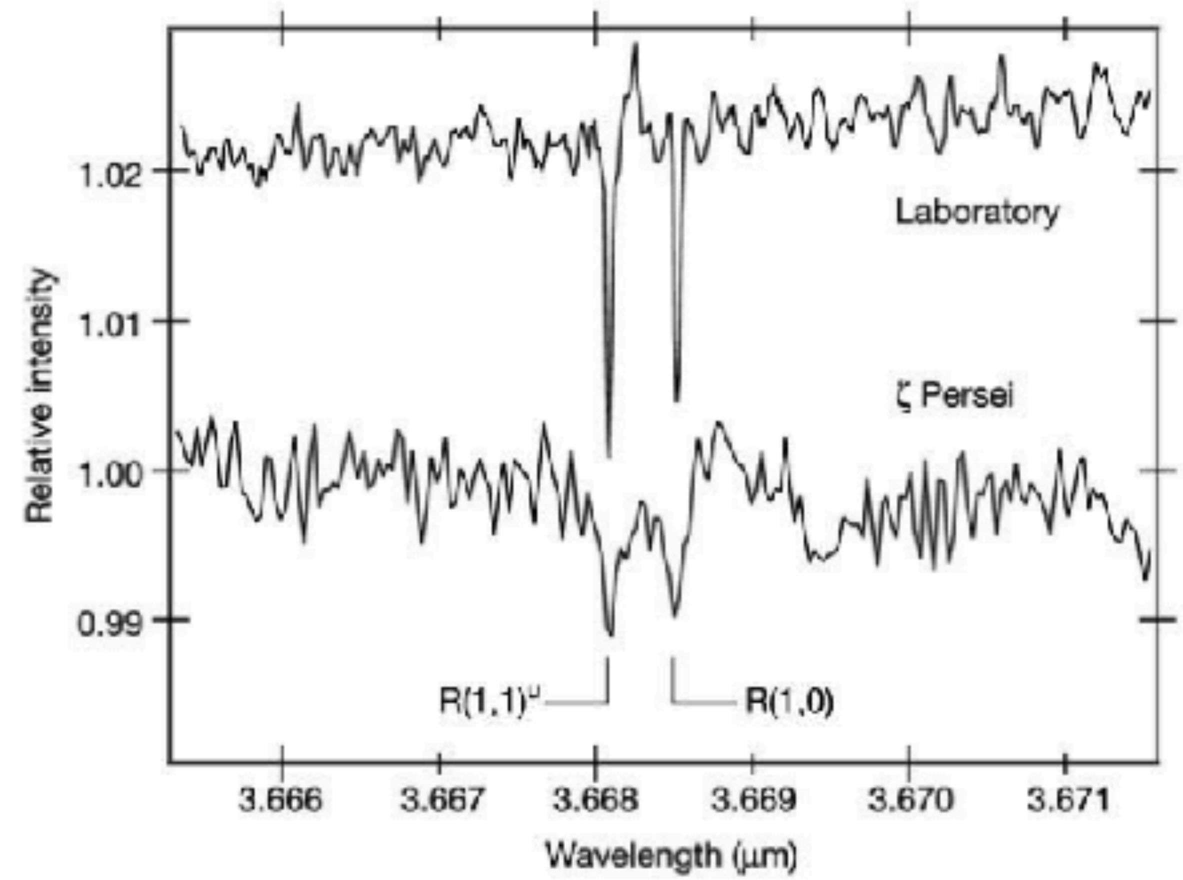
- Hydrodynamic, MHD: detailed physics, very slow (e.g. cloud collapse and star formation)

- Steady state solutions: calculating abundances and temperatures for a given structure/radiation field (e.g. protoplanetary disks: chemical time scales<dynamical, e.g. mixing/turbulence)

Observational highlights

- Interstellar H_3^+: does not exist on Earth!

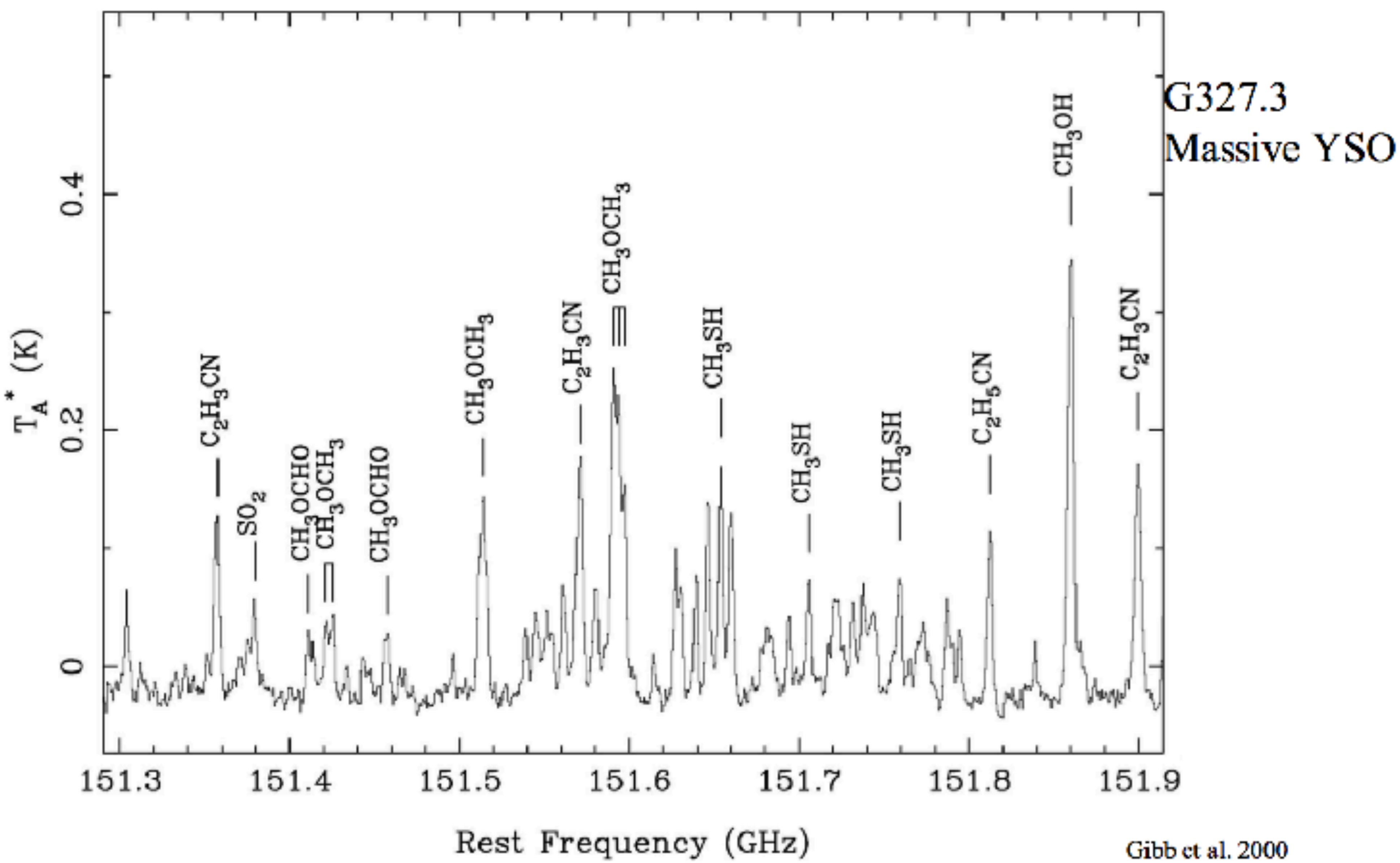




Oka & Geballe 1996
McCall + 1993

Observational highlights

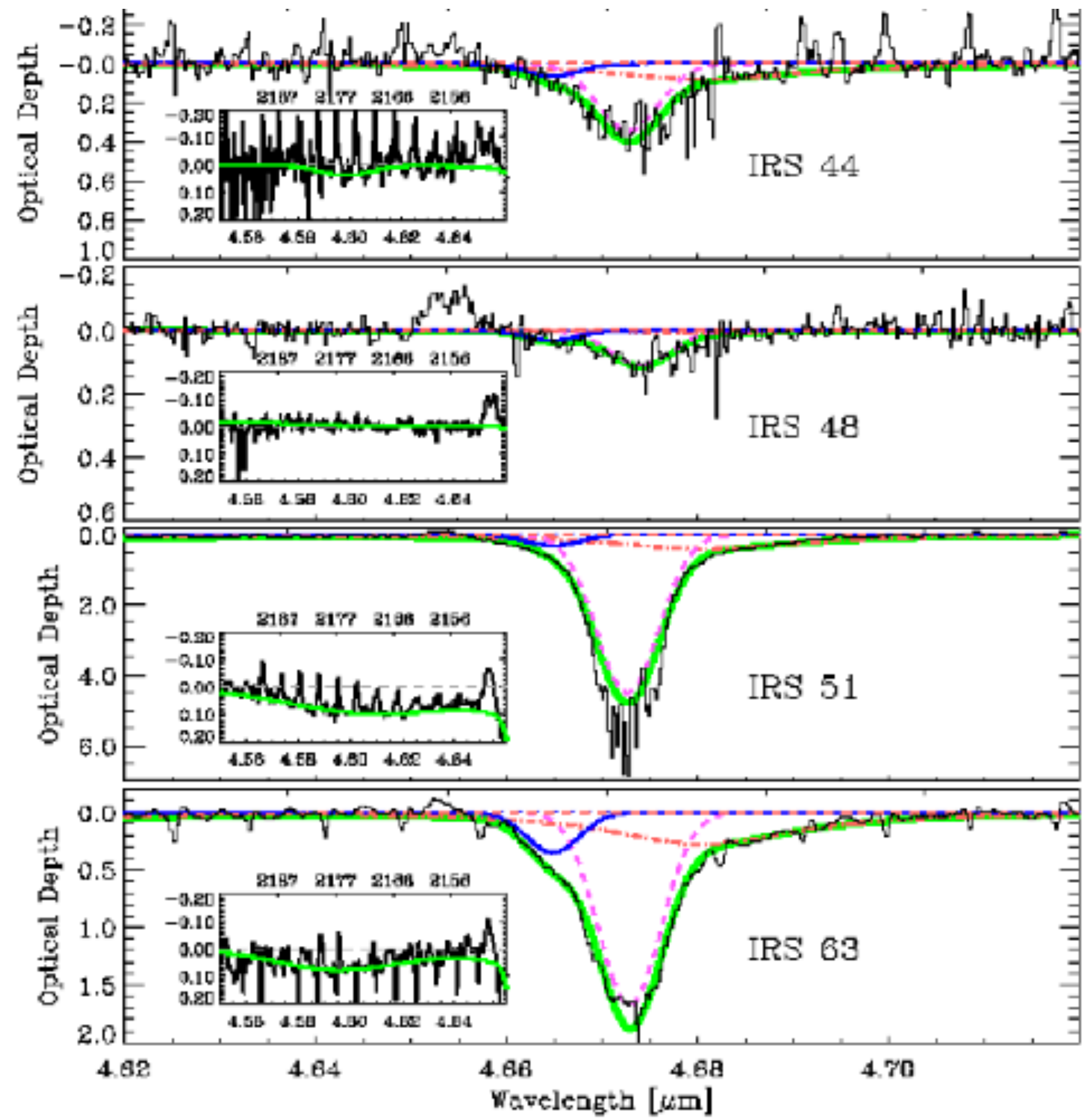
- Massive young core: large amounts of COMs



Gibb+2000

Observational highlights

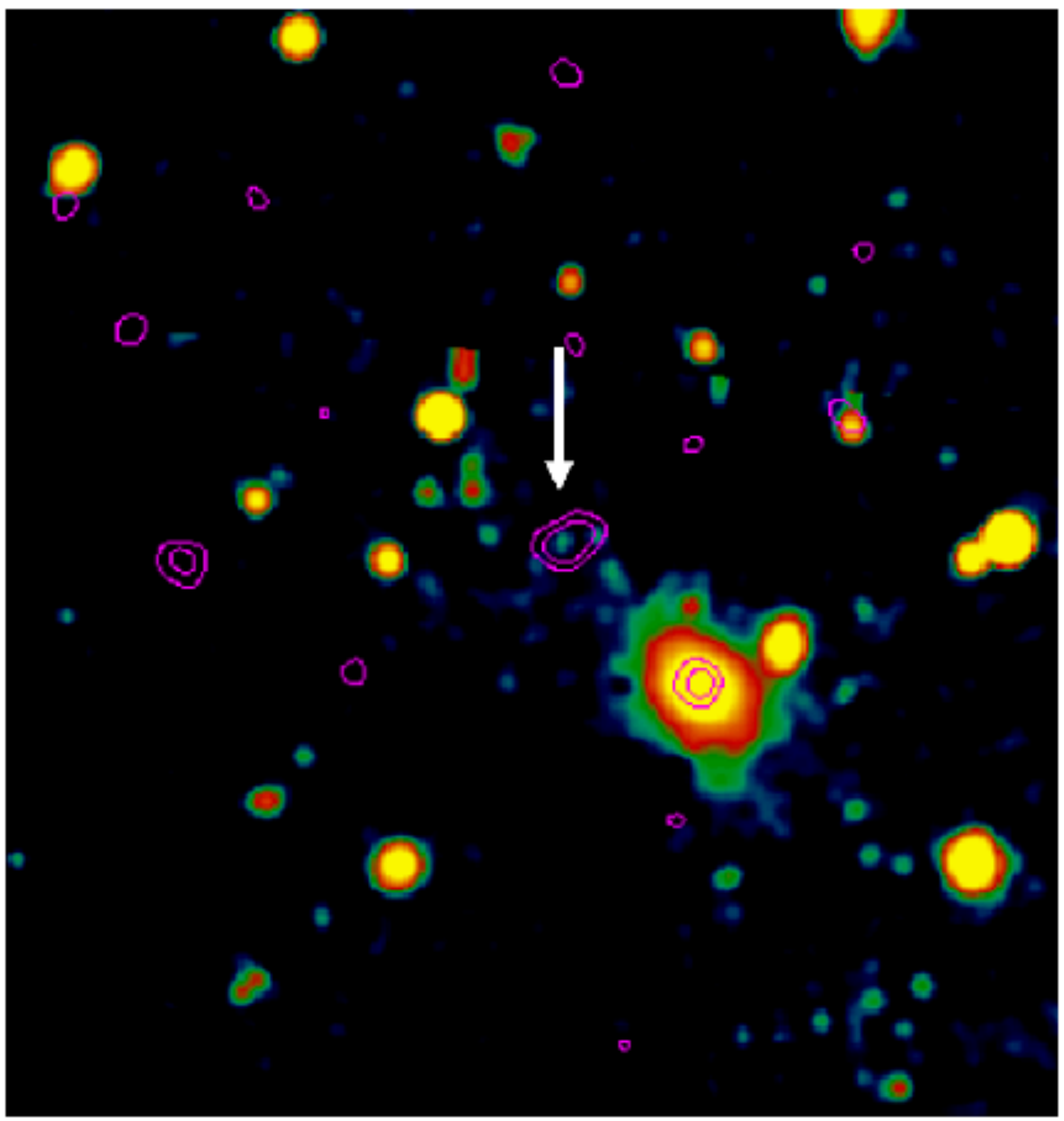
- Ice in protostars (VLT, Spitzer)

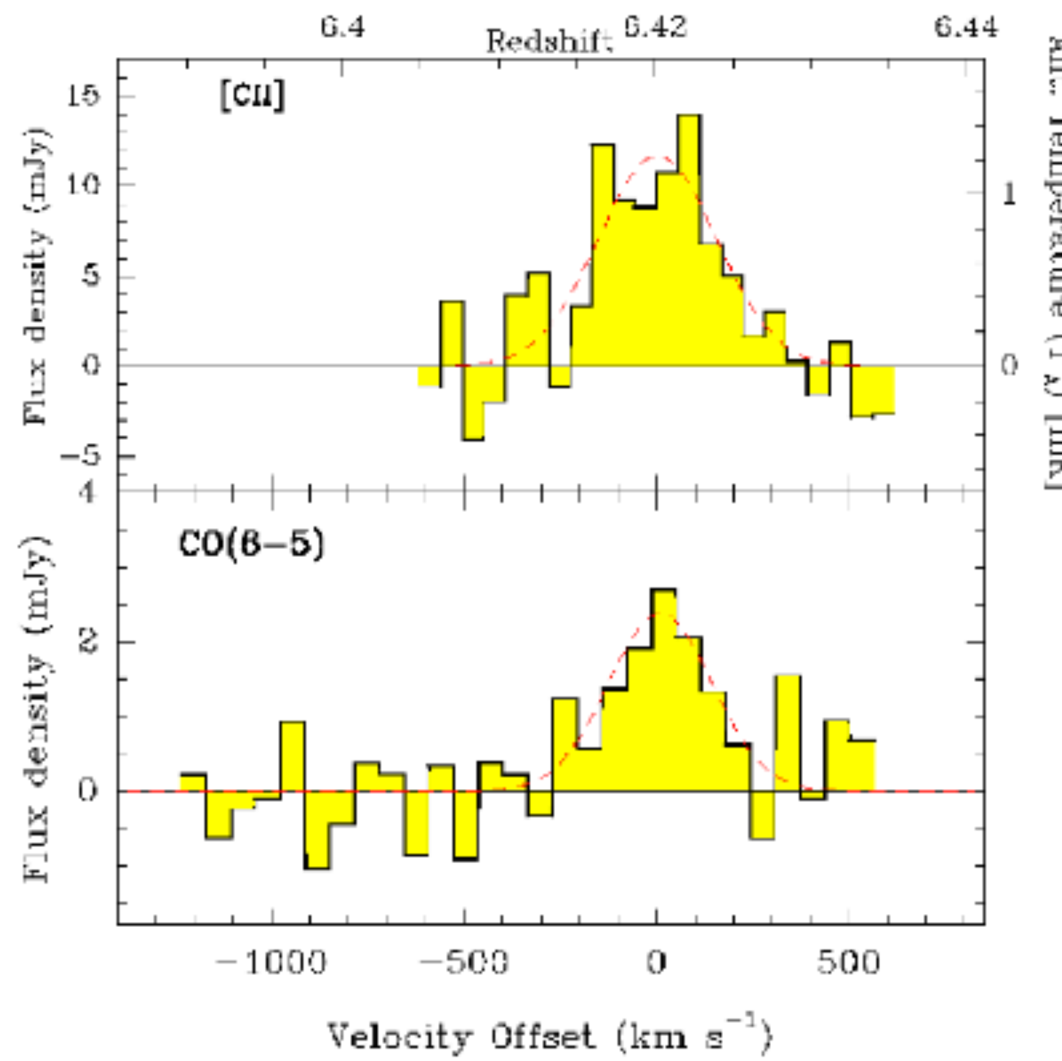


Pontoppidan+2003

Observational highlights

- [CII] and CO 6-5 at z=6.4 quasar:

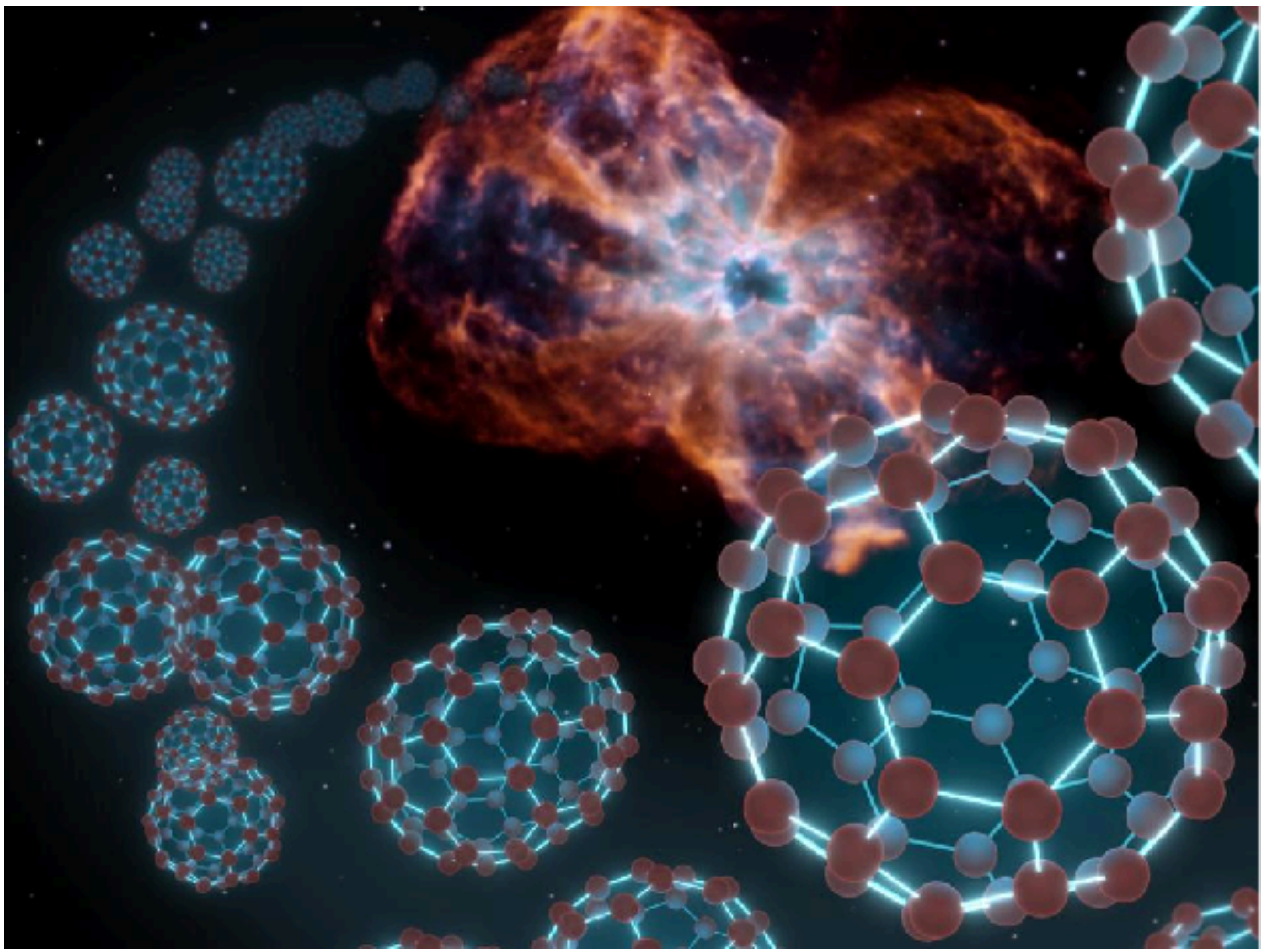




Walter+2003

Observational highlights

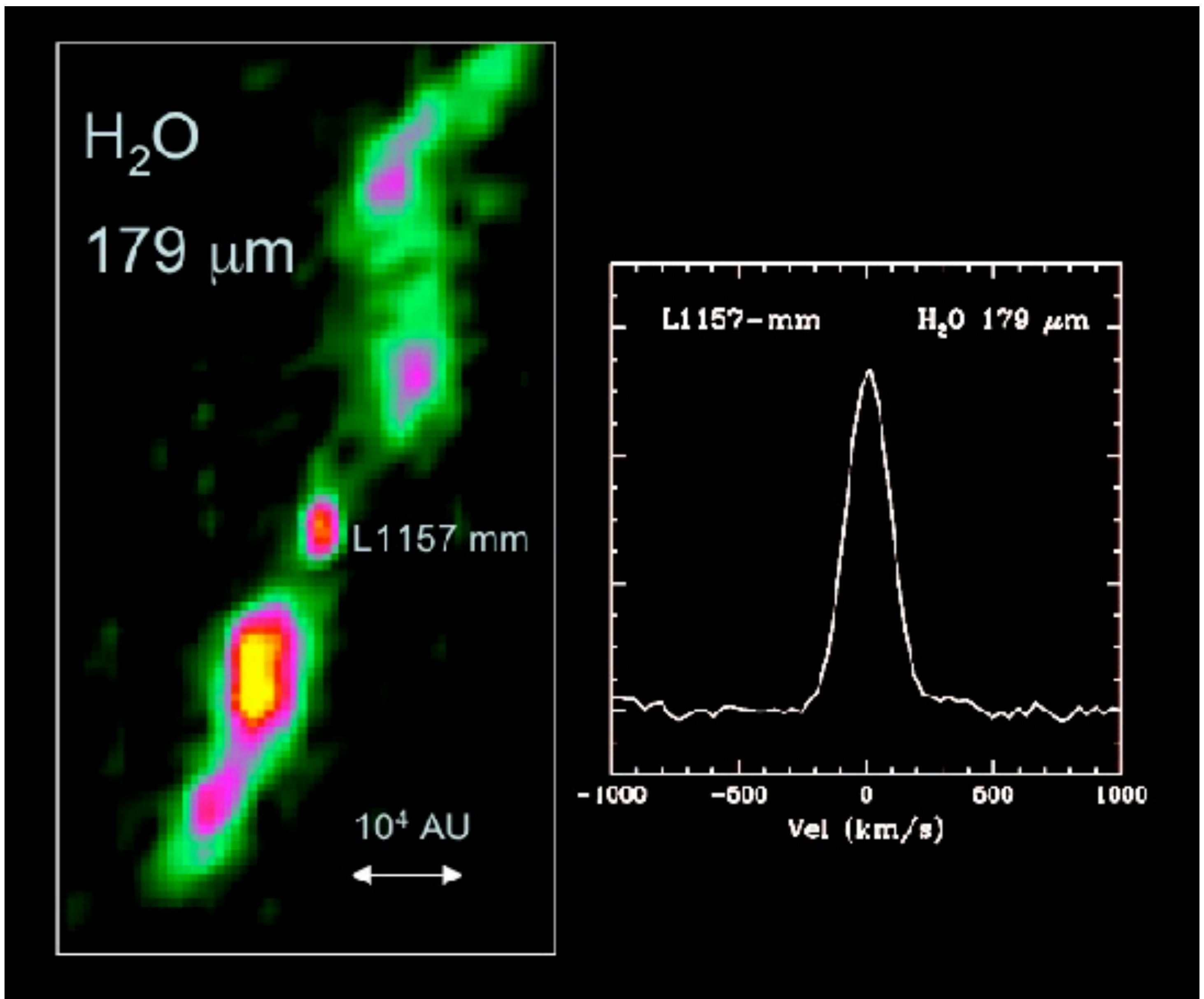
- Buckyballs: C_{60}: large carbon structures (Spitzer)



Cami+2010

Observational highlights

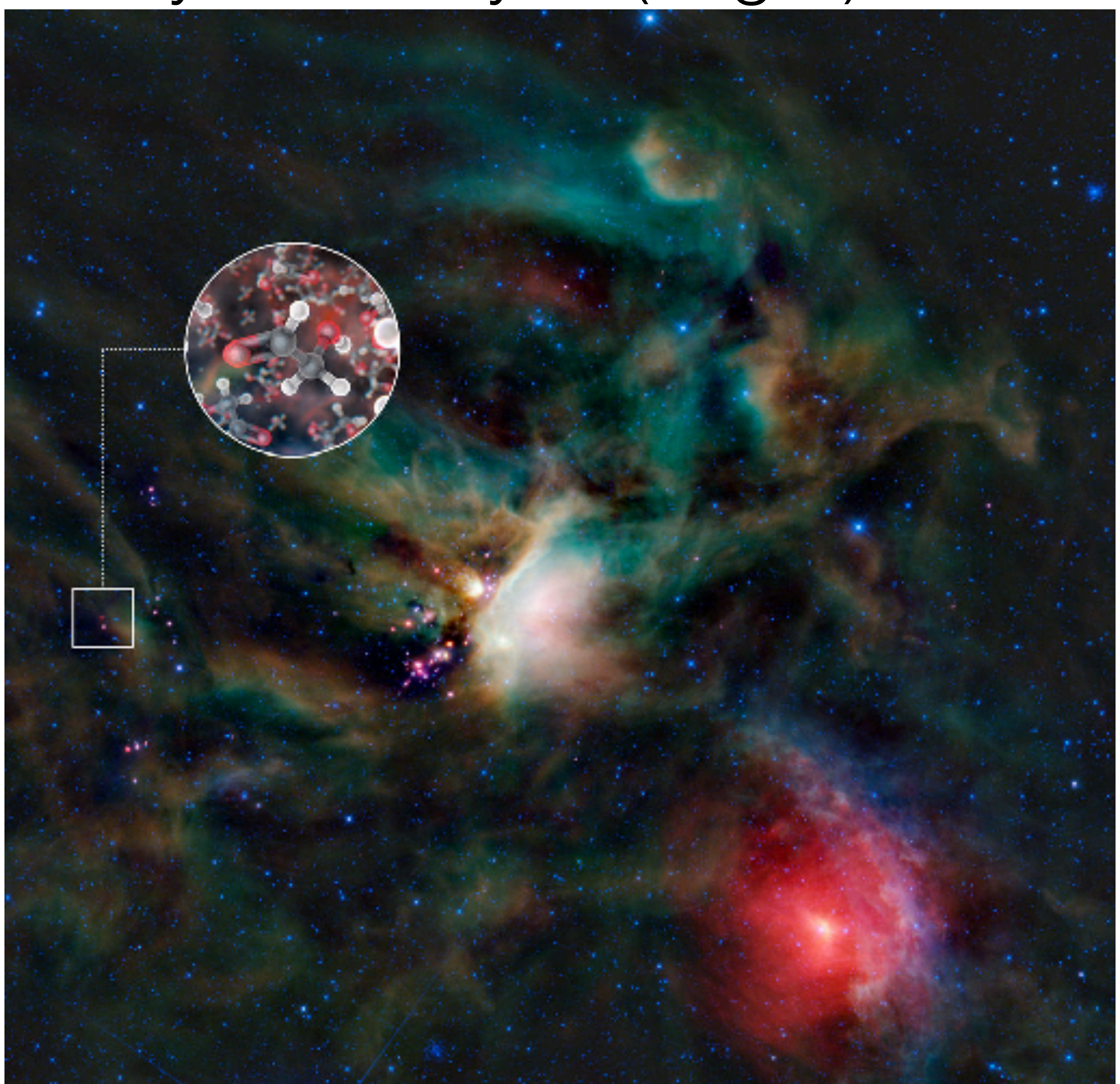
- Water in star forming regions (WISH):
  high-v "bullets" (Herschel PACS) in L1157 outflow

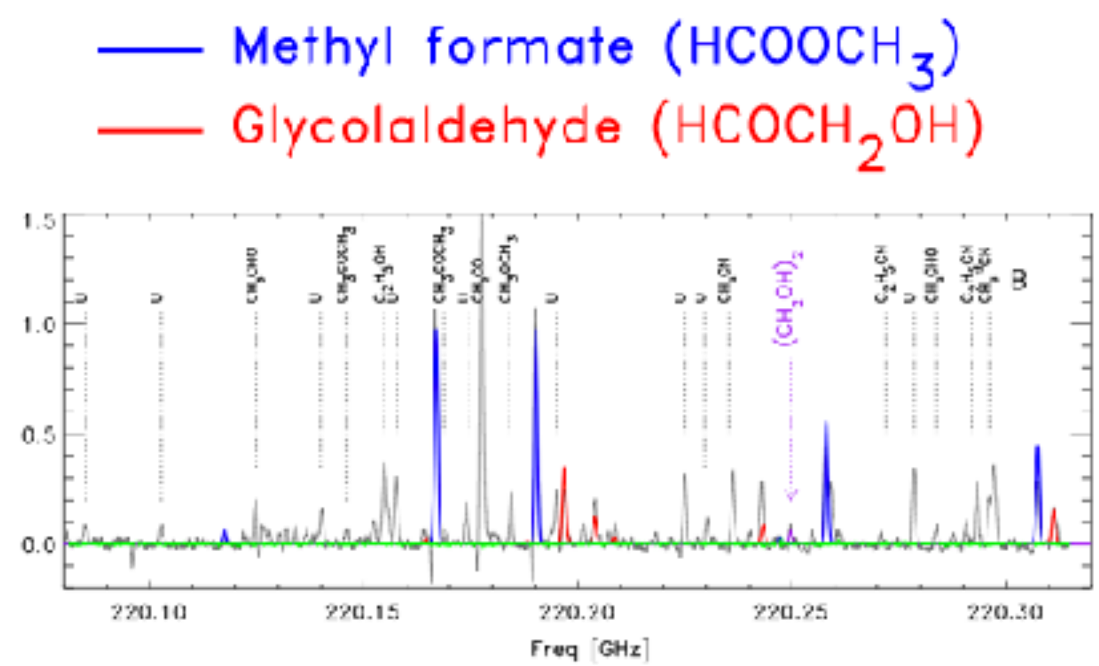


Kristensen+2011,2012

Observational highlights

- Glycolaldehyde (sugar) in IRAS 16293-2422 (ALMA)

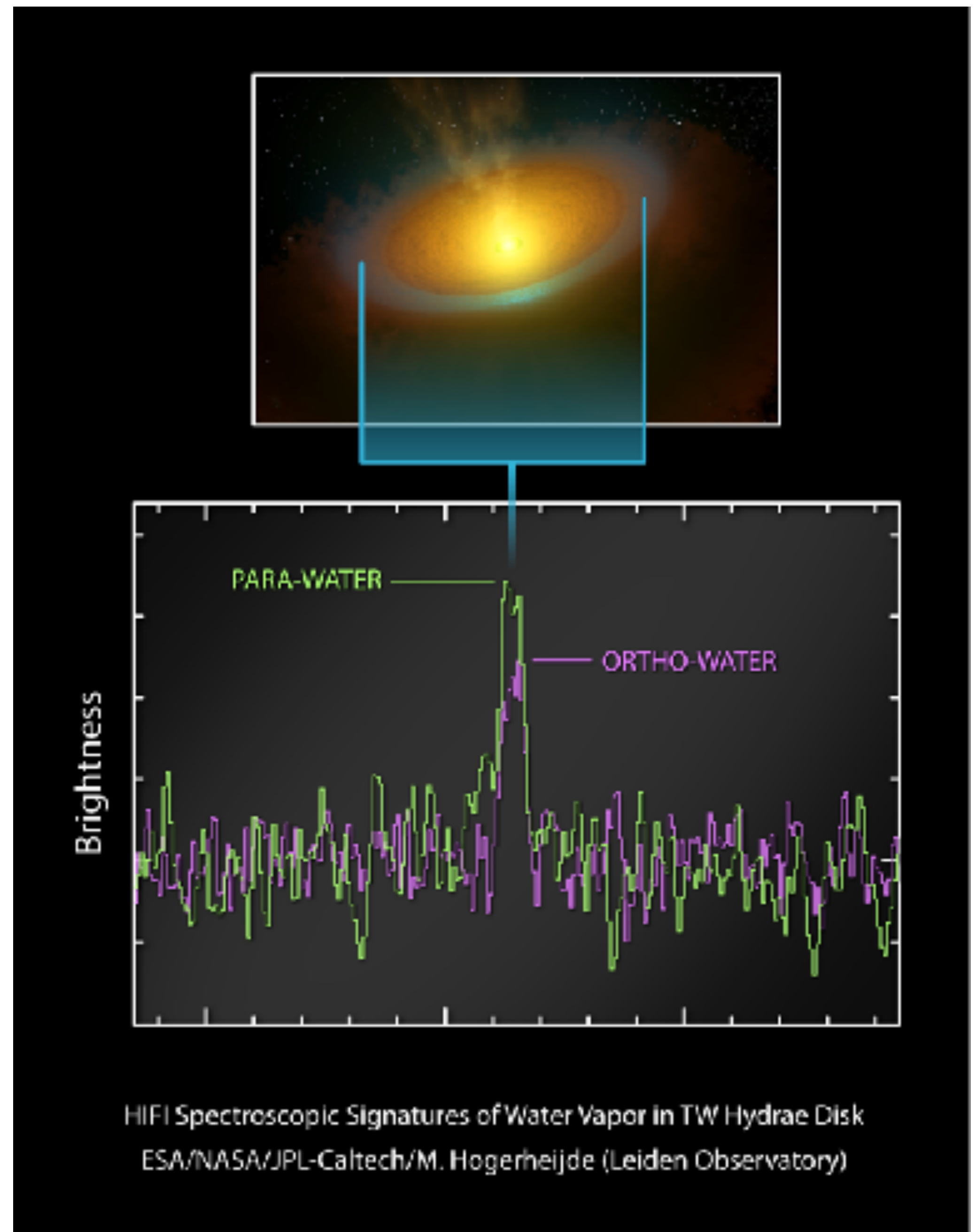




Jorgensen+2012

Observational highlights

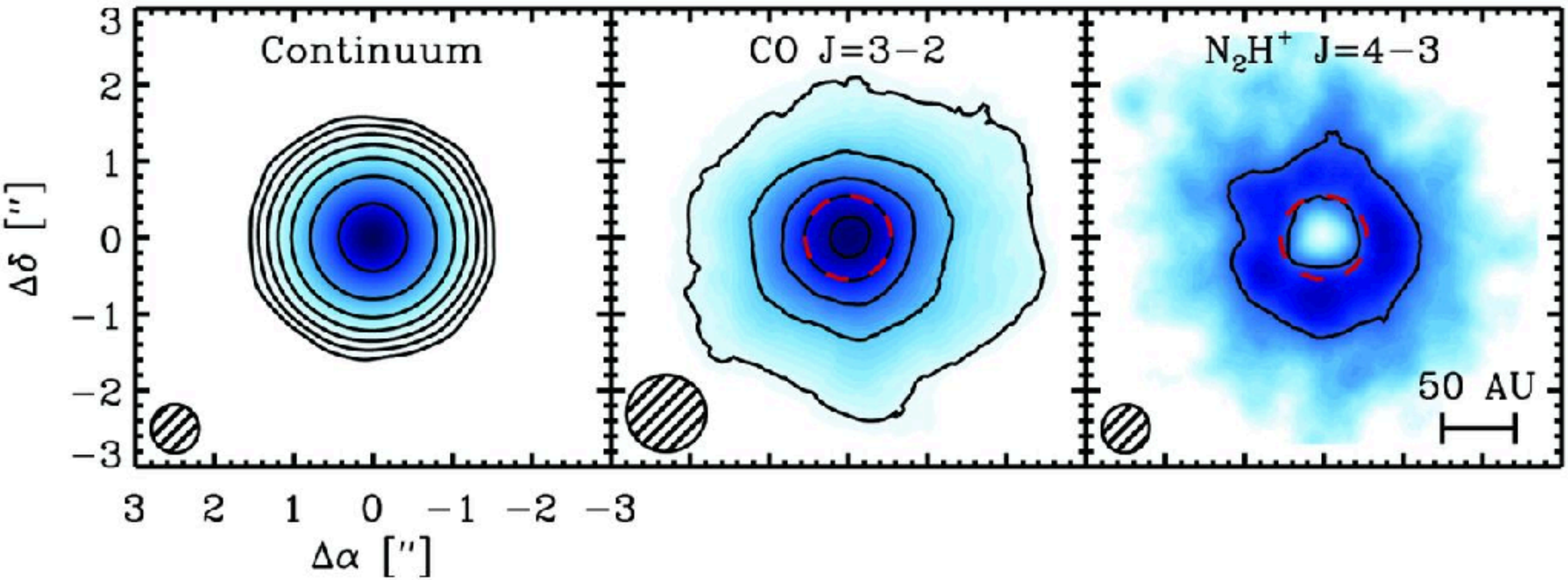
- Water in a protoplanetary disk (TW Hya) with Herschel-HIFI



Hogerheijde+2011

Observational highlights

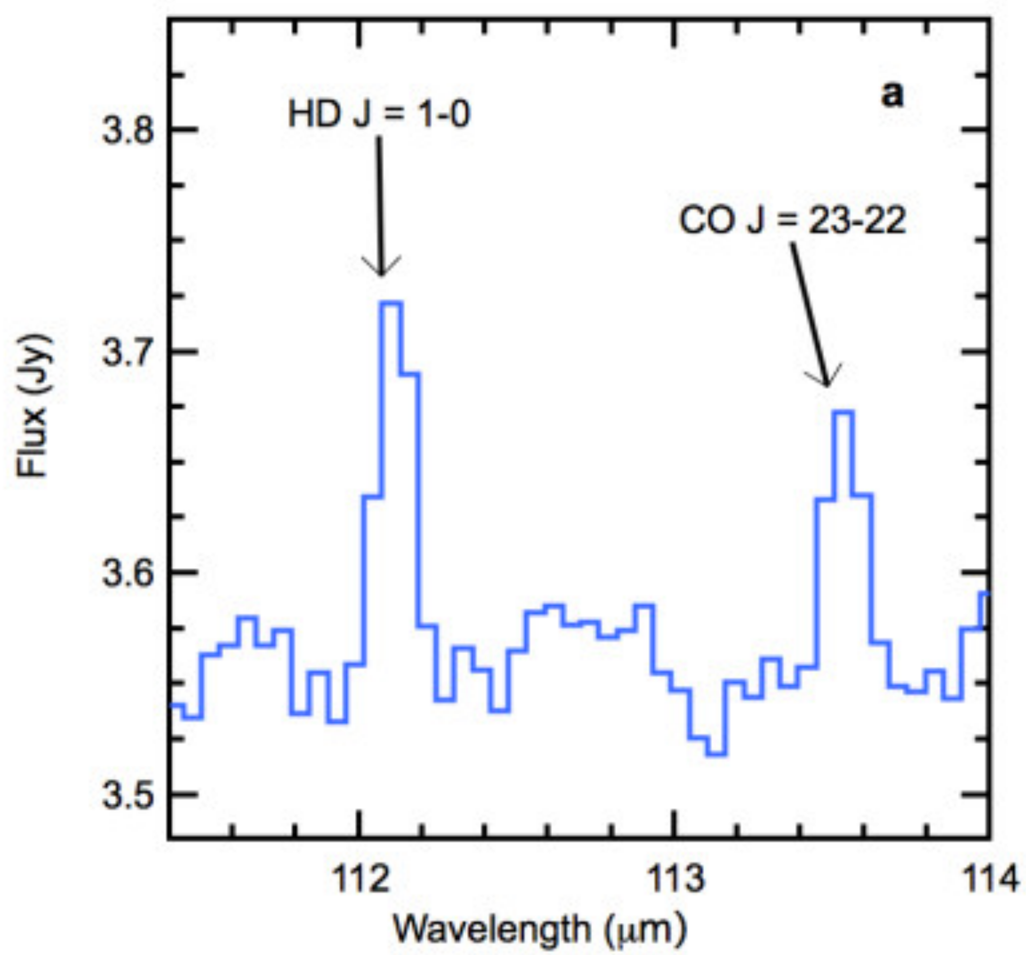
- CO snowline through N_2H^+ (ALMA)



Qi+2013

Observational highlights

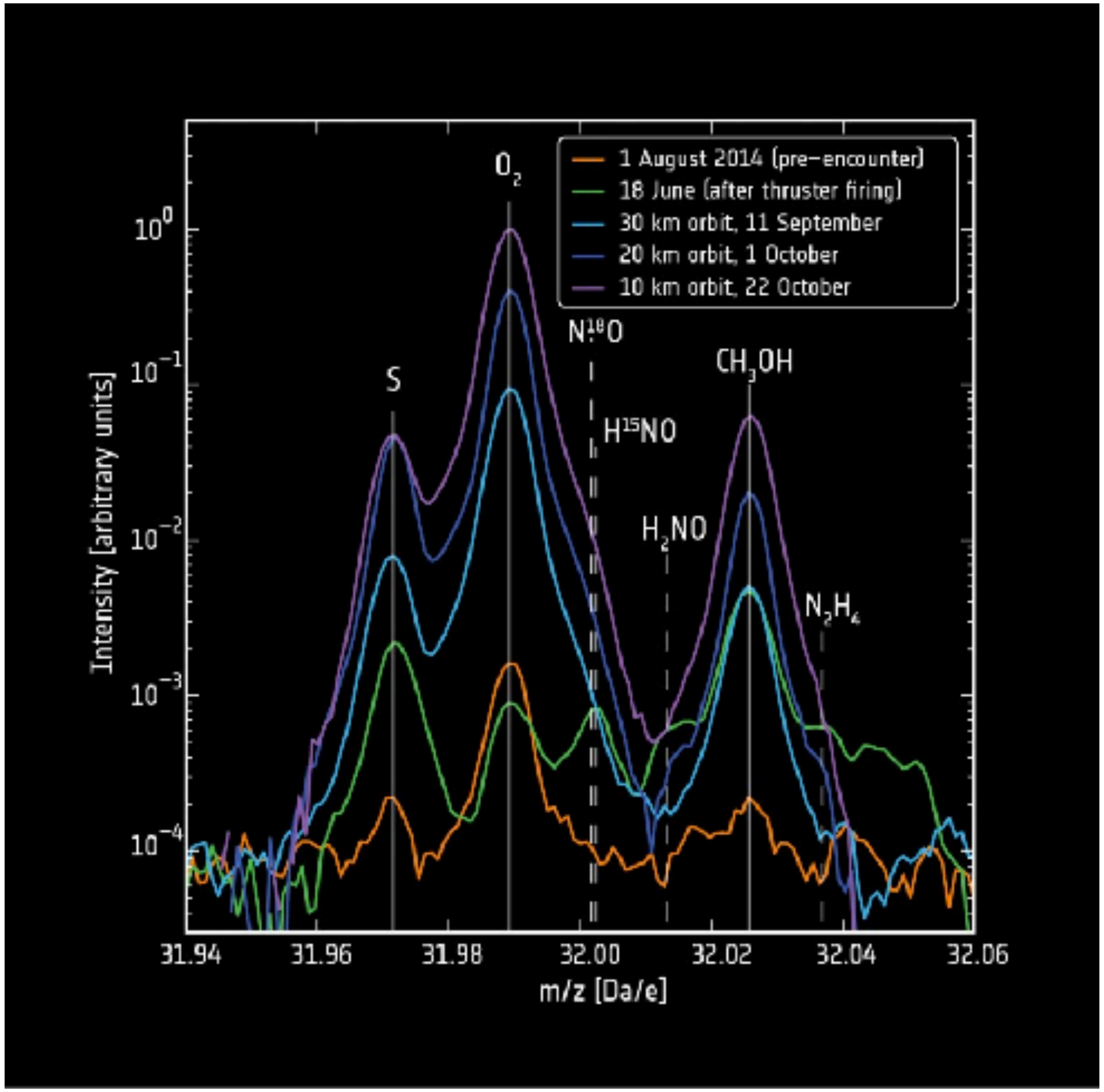
- HD in protoplanetary disk TW Hya (Herschel): direct measurement of disk mass



Bergin+2013

Observational highlights

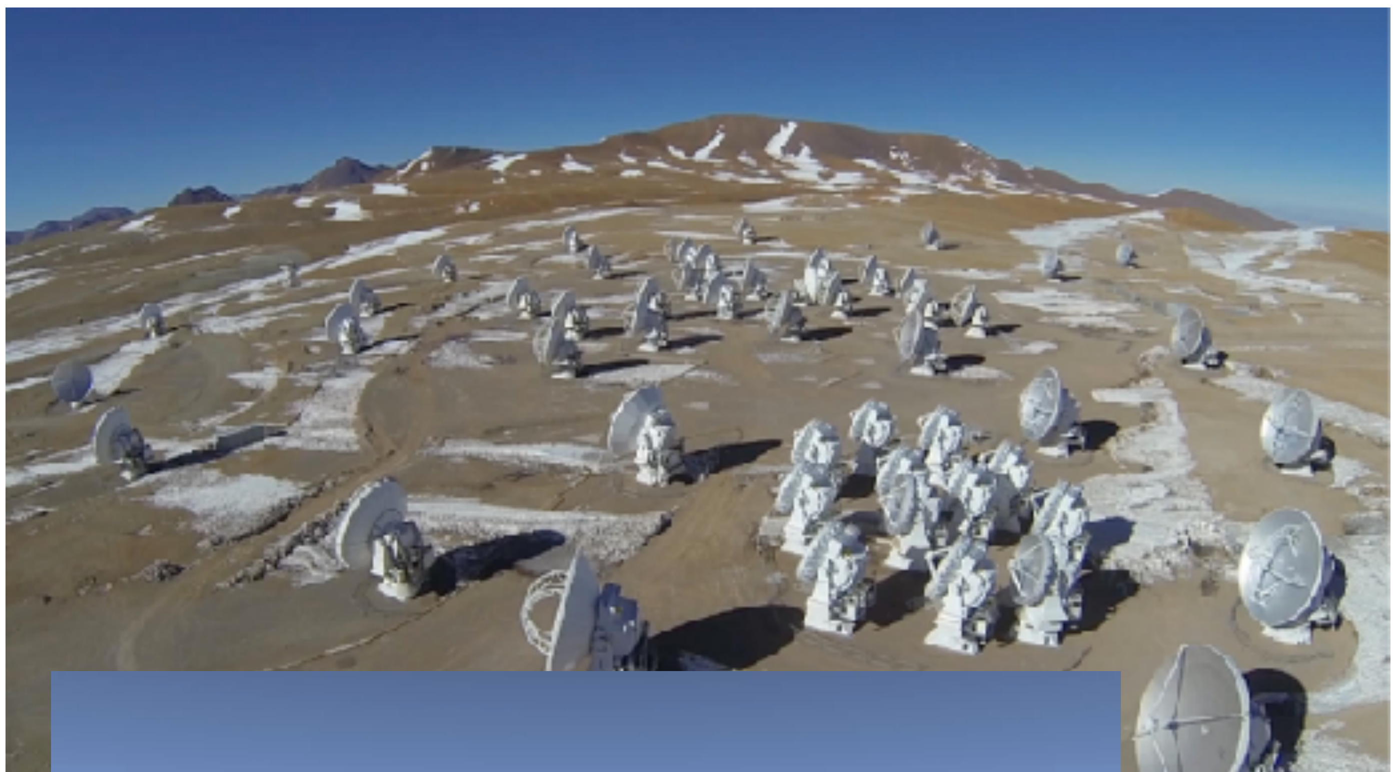
- Molecular oxygen in comet 67P with Rosetta

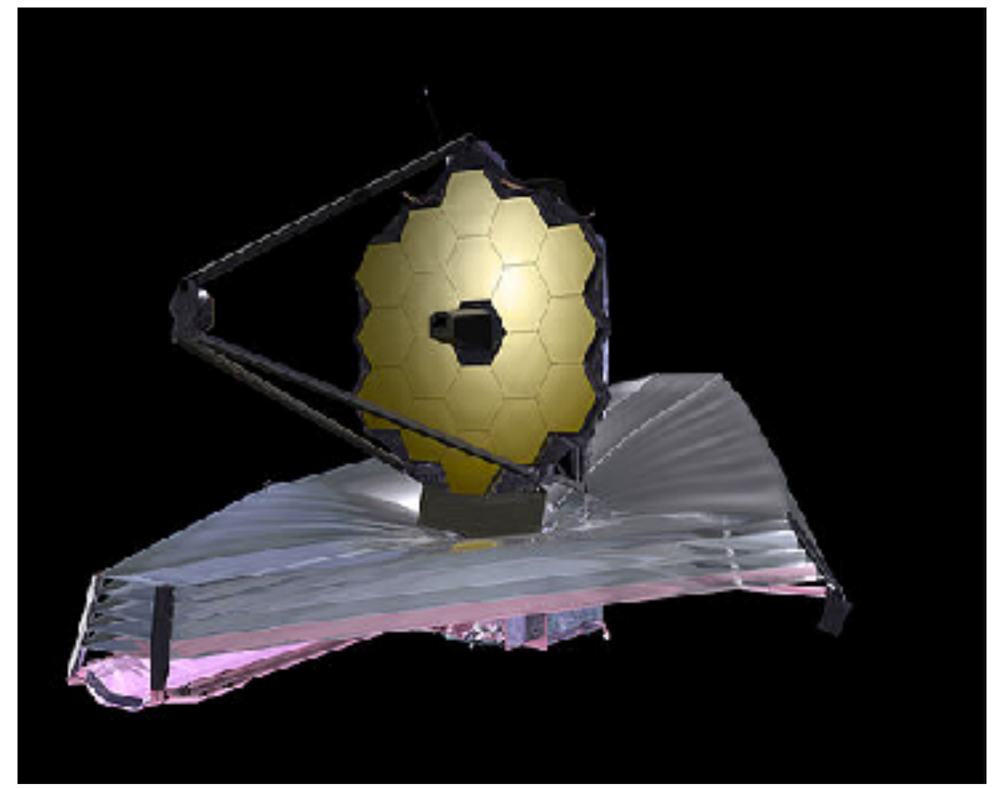


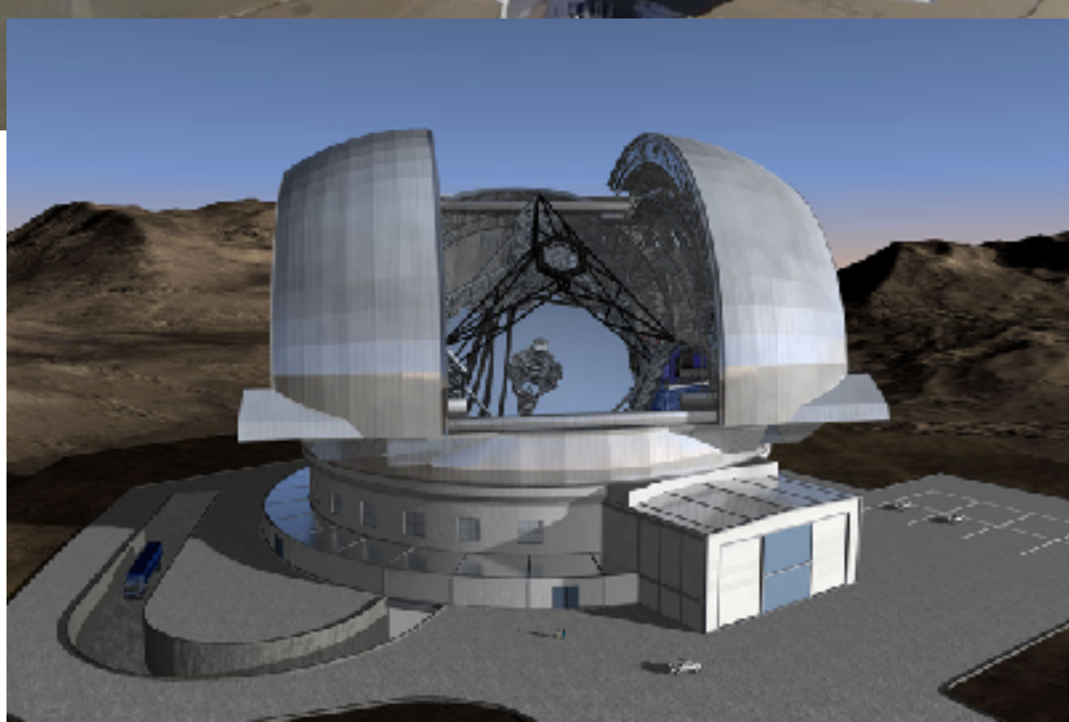
Bieler+2015

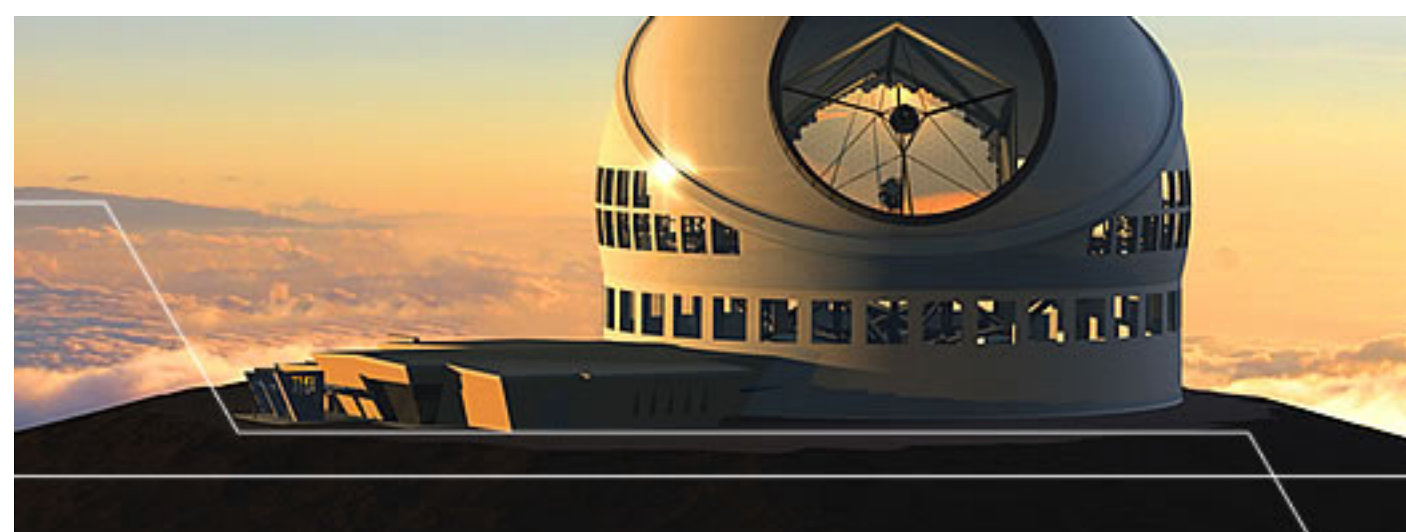
Observational highlights

- Coming up: more ALMA, JWST, E-ELT, TMT









Next week

- Molecular clouds
  - diffuse clouds
  - dark clouds
  - PDRs and XDRs
  - star formation
  - shocks