Astrochemistry

the summary

Astro 736

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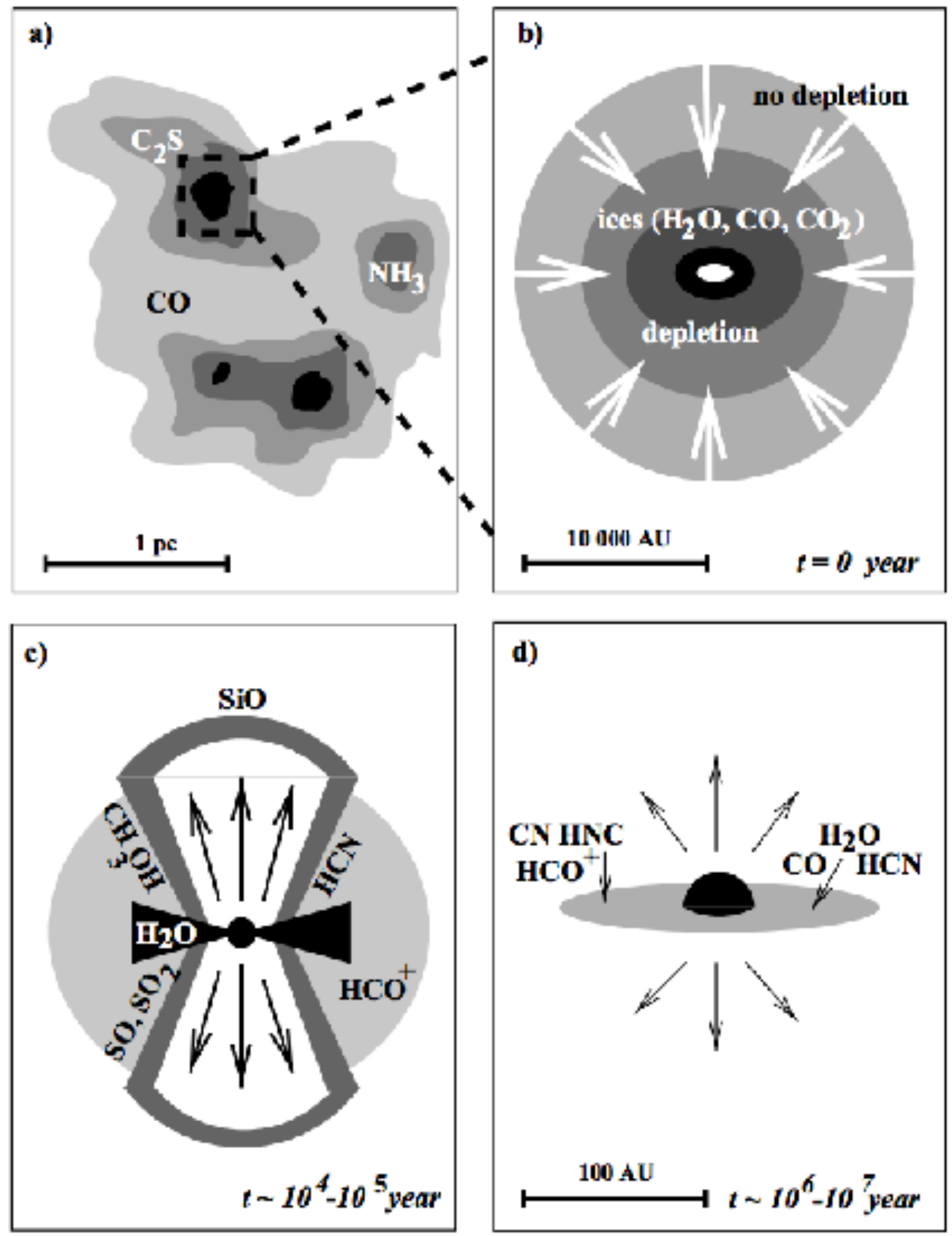
Astrochemistry

- **When the first interstellar molecules were discovered, chemists were very surprised. Why?**
  - Conditions in space are very unsuitable for chemistry: time scales long!
  - 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}

Star and planet formation



Range of environments for different chemistry!

Astrochemistry

- **Why is study of astrochemistry important? What do we learn from it?**

    - Diagnostics of physical conditions: density, temperature, ionization, velocity, radiation fields, etc.

    - Coolants of clouds: drivers of processes

    - Start of COMs and biomolecules: origin of life?

    - Exotic laboratory for fundamental chemistry

Astrochemistry

Observations

X-ray, UV, optical, infrared, submm

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

Modeling

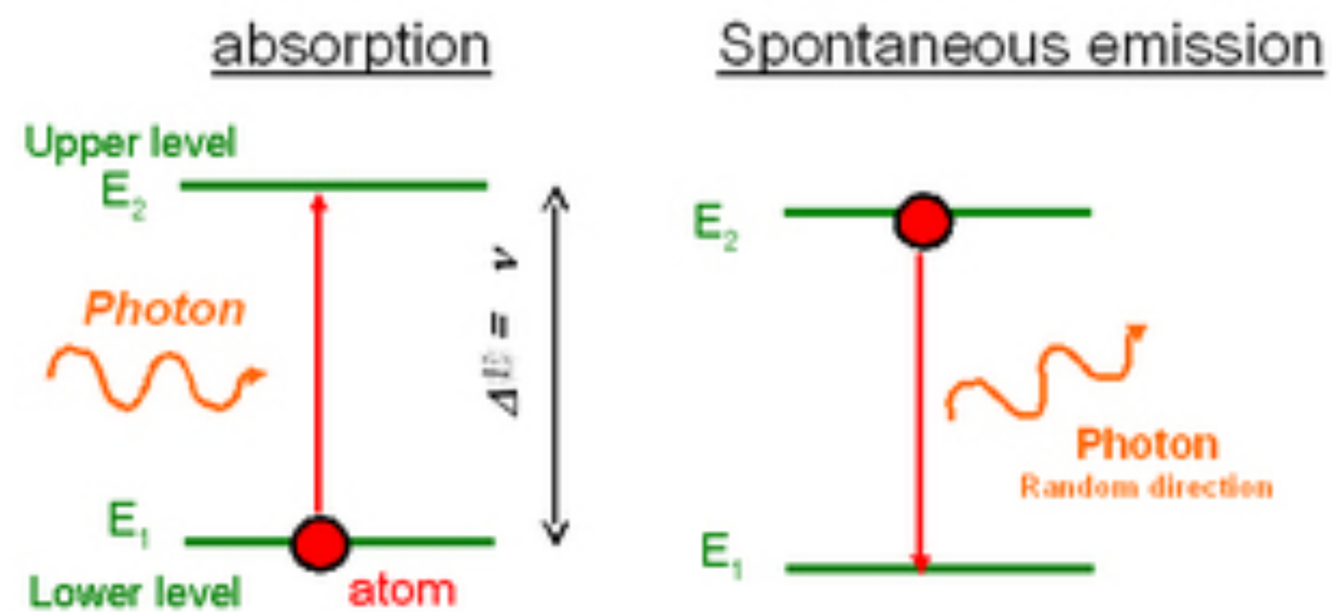
Radiative transfer, dynamics, radiation field, chemistry, feedback, chemical evolution

Experimental

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

Spectroscopy

- **How do we observe molecules?**
  - Emission/absorption lines from energy transitions
    - Electronic (optical)
    - Vibrational (IR)
    - Rotational (submm)

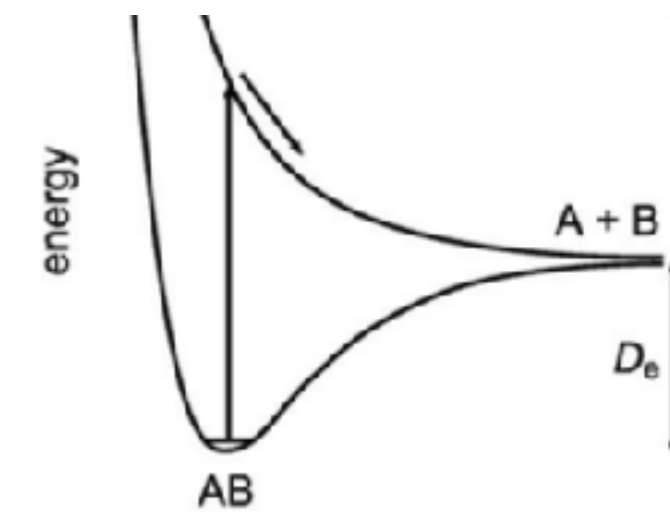


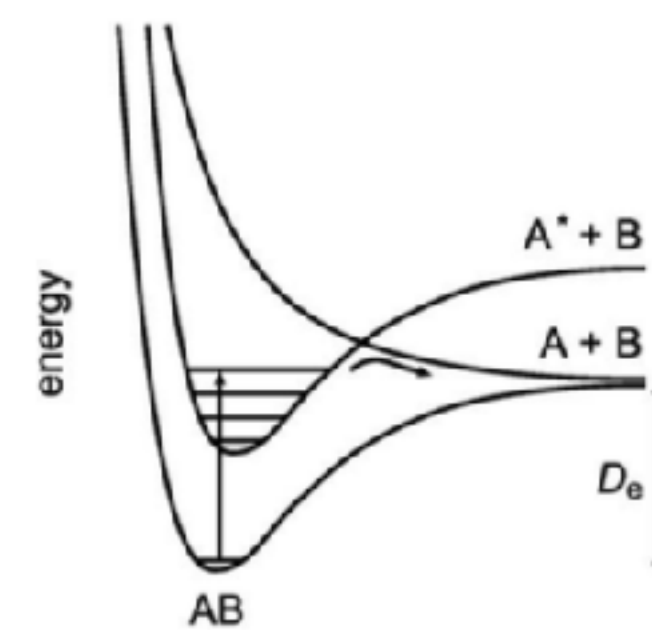
Chemical reactions

- **What types of chemical reactions exist and why do molecules not randomly react with each other?**

  - Formation (association) and destruction (dissociation), often with the release or capture of a photon or electron

  - Energy barriers (and potential crossings) determine reaction rate





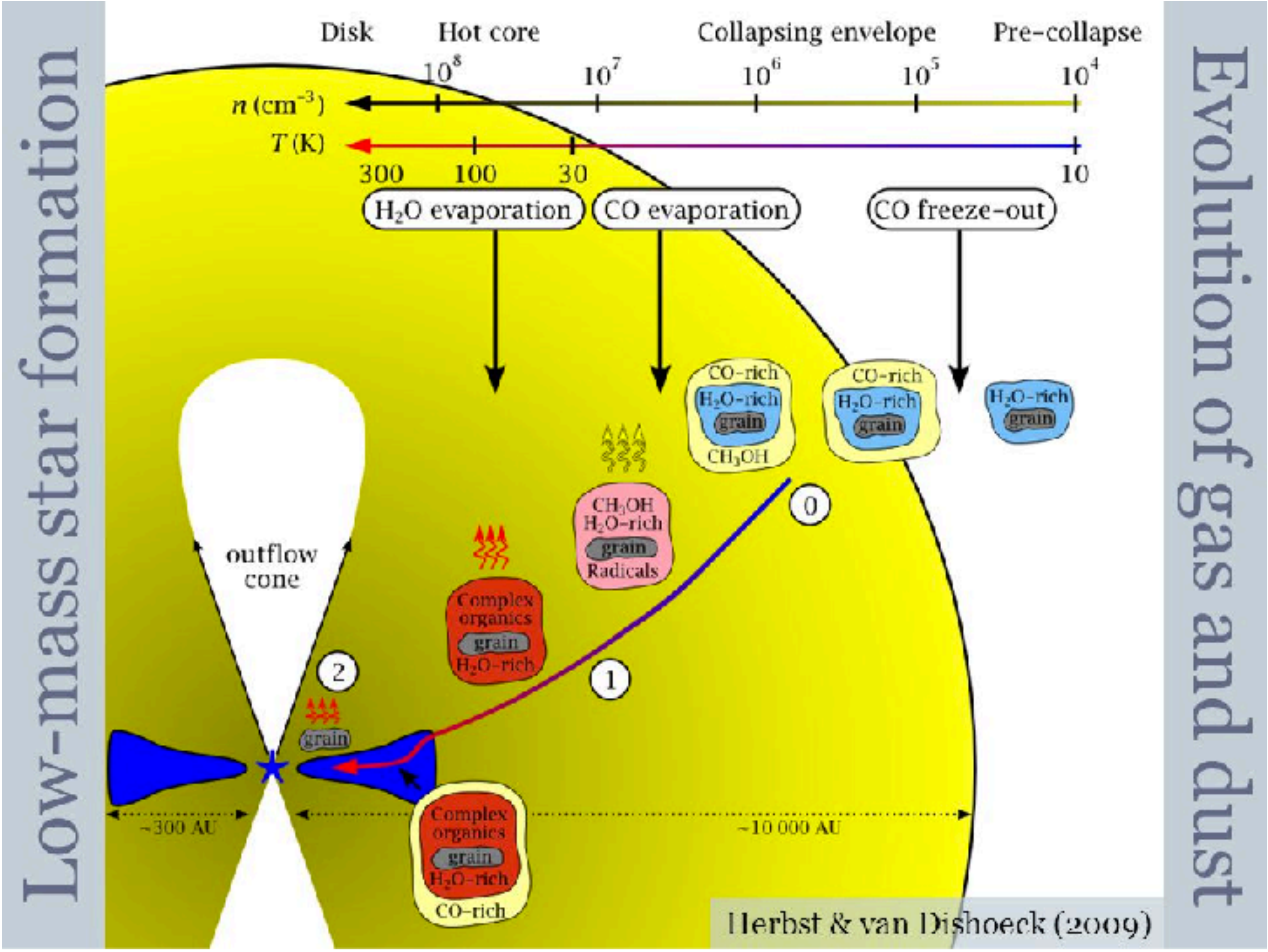
Chemical reactions

- **Why are ion reactions more efficient than neutral reactions?**
  - Ion induces dipole moment in molecule when it's approaching => attractive force => capture ion => usually a fast process
  - Neutral reactions: long-range interaction weak (van der Waals, $1/R^6$)
  - Reaction rate: *Langevin rate* (independent of T)
  - $X^+ + YZ \Rightarrow XY^+ + Z$

Ice

- **Why is ice (solid state) chemistry so important for astrochemistry and how do we study it?**
  - Ice chemistry is required to efficiently form complex organic molecules: observed abundances cannot be explained by gas-phase chemistry
  - An ice matrix allows radicals to diffuse through the matrix before formation
  - Link with comets/origin of life
  - Study:
    - Laboratory work (incl. theoretical calculations)
    - Gas observations
    - Ice spectroscopy

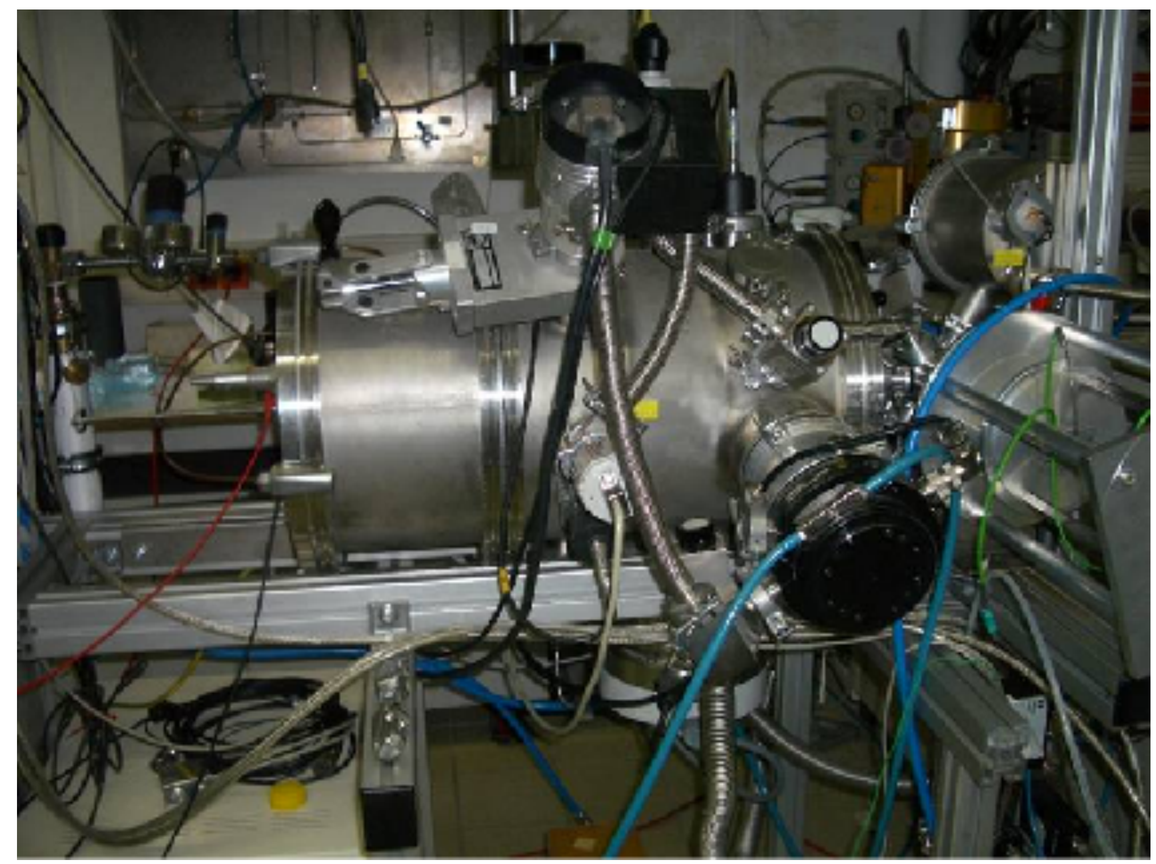
Ice



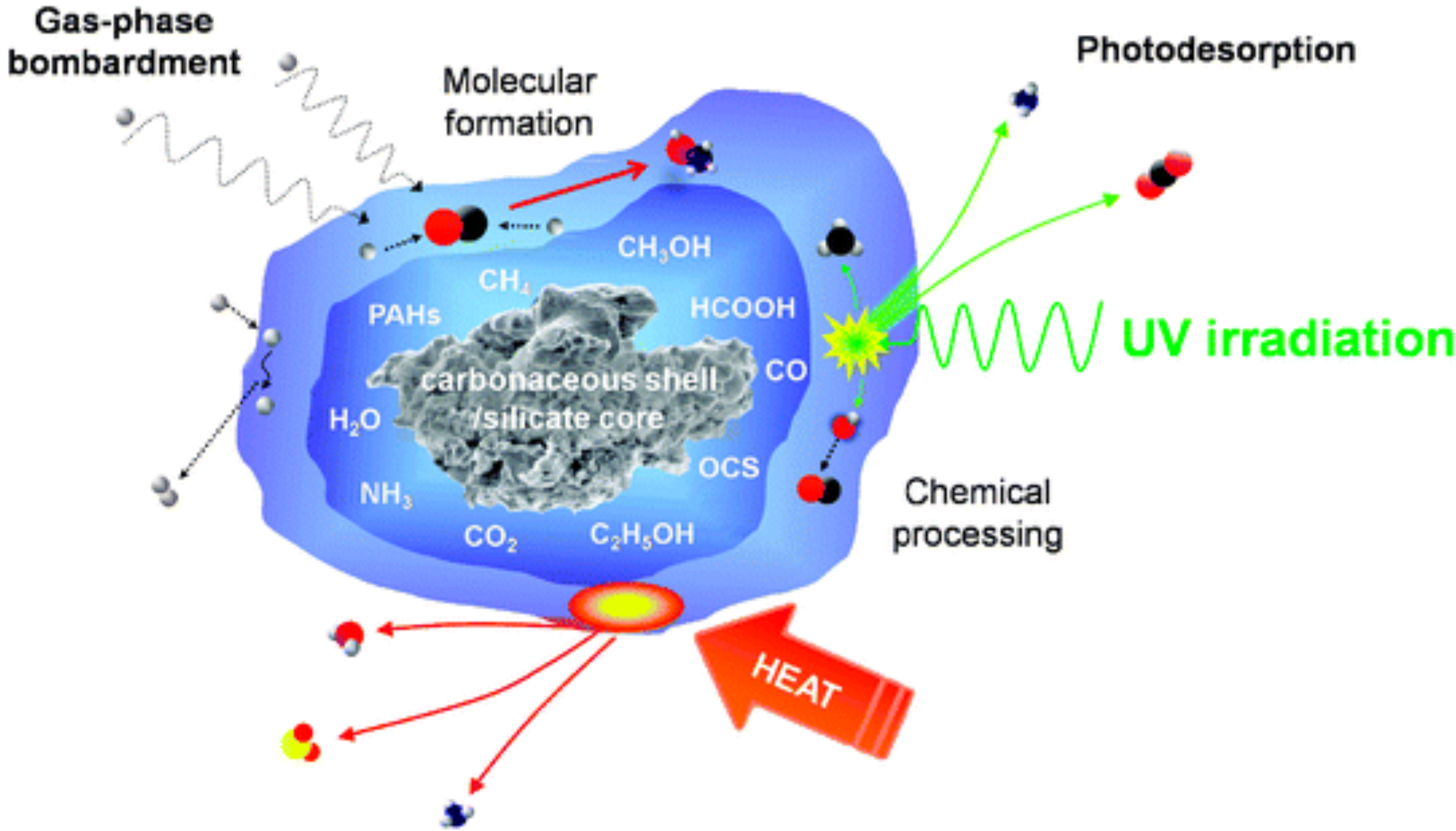
Low-mass star formation
Evolution of gas and dust
Disk
Hot core
Collapsing envelope
Pre-collapse
10^8
10^7
10^6
10^5
10^4
n (cm^{-3})
T (K)
300
100
30
10
H_2O evaporation
CO evaporation
CO freeze-out
CO-rich
H_2O-rich
grain
CH_3OH
CO-rich
H_2O-rich
grain
H_2O-rich
grain
0
CH_3OH
H_2O-rich
grain
Radicals
outflow cone
Complex organics
grain
H_2O-rich
1
2
grain
Complex organics
grain
H_2O-rich
CO-rich
~300 AU
~10 000 AU
Herbst & van Dishoeck (2009)

Ice

- **Why do we need to perform laboratory work to explain ice spectra?**
  - Ice chemistry cannot be computed directly due to the quantum mechanical complexity of a matrix of molecules
    - shape of vibrational features (environment and history)
    - chemical formation/destruction
  - Reaction rates (also under radiation fields) often unknown
  - But difficult to perform: ultra-high vacuum and low T required!



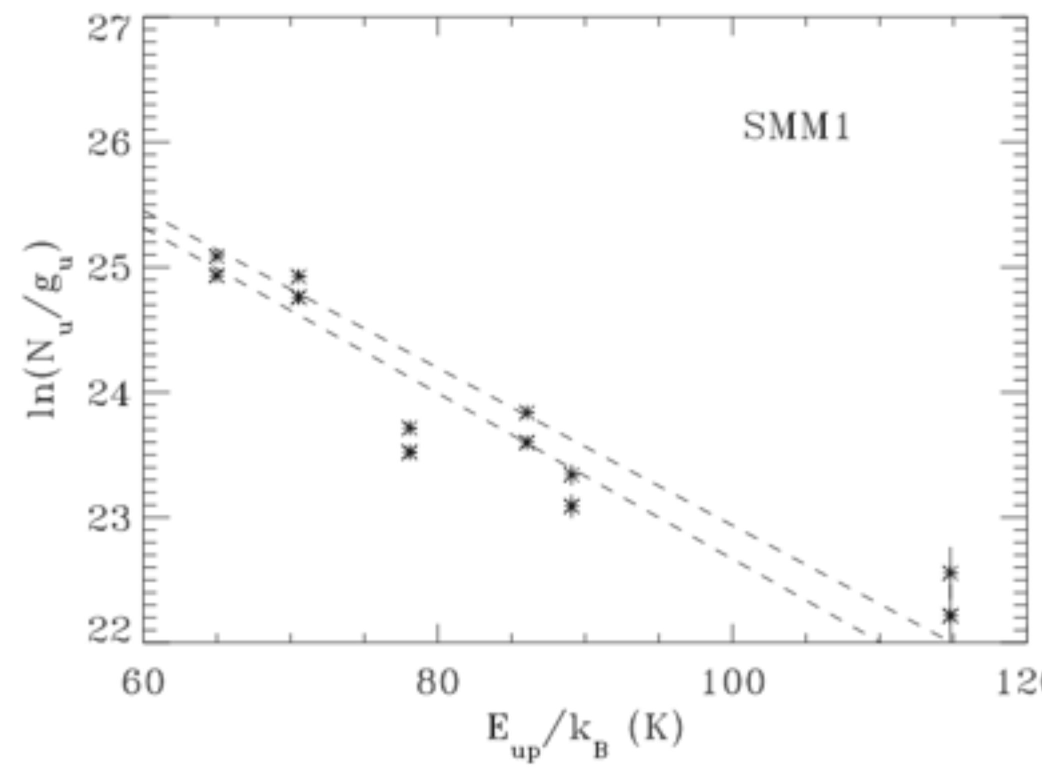
Ice



Gas-phase bombardment
Molecular formation
Photodesorption
UV irradiation
Chemical processing
HEAT
carbonaceous shell /silicate core
CH_3OH
CH_4
PAHs
HCOOH
CO
H_2O
OCS
NH_3
CO_2
C_2H_5OH

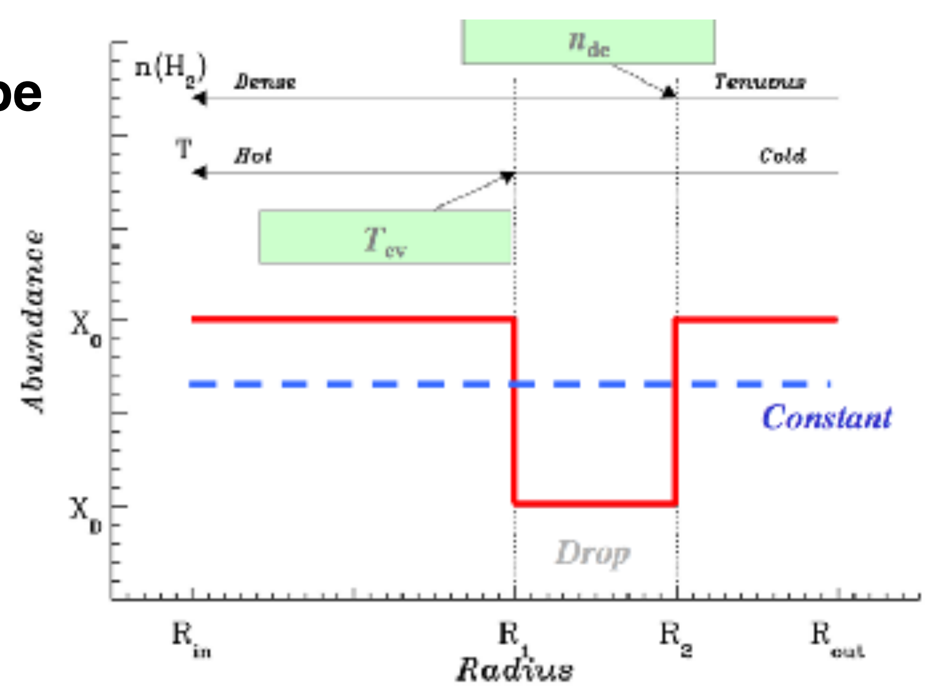
Ice

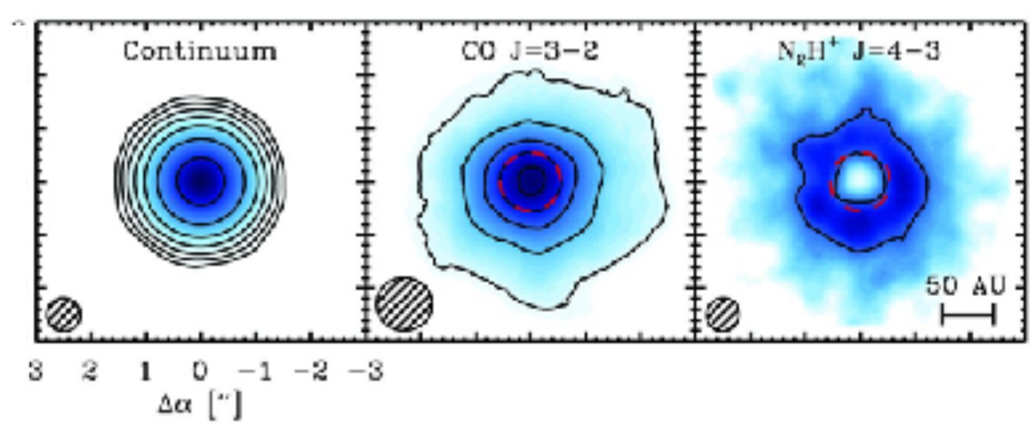
- **How can we learn more about ice from gas observations?**
  - Rotational diagrams: N_{mol} & T
  - Abundances and ratios
  - Snowlines: e.g. N_2H^+ only where CO is frozen out



steep slope/low T (~15 K) indicates photodesorption

Envelope model



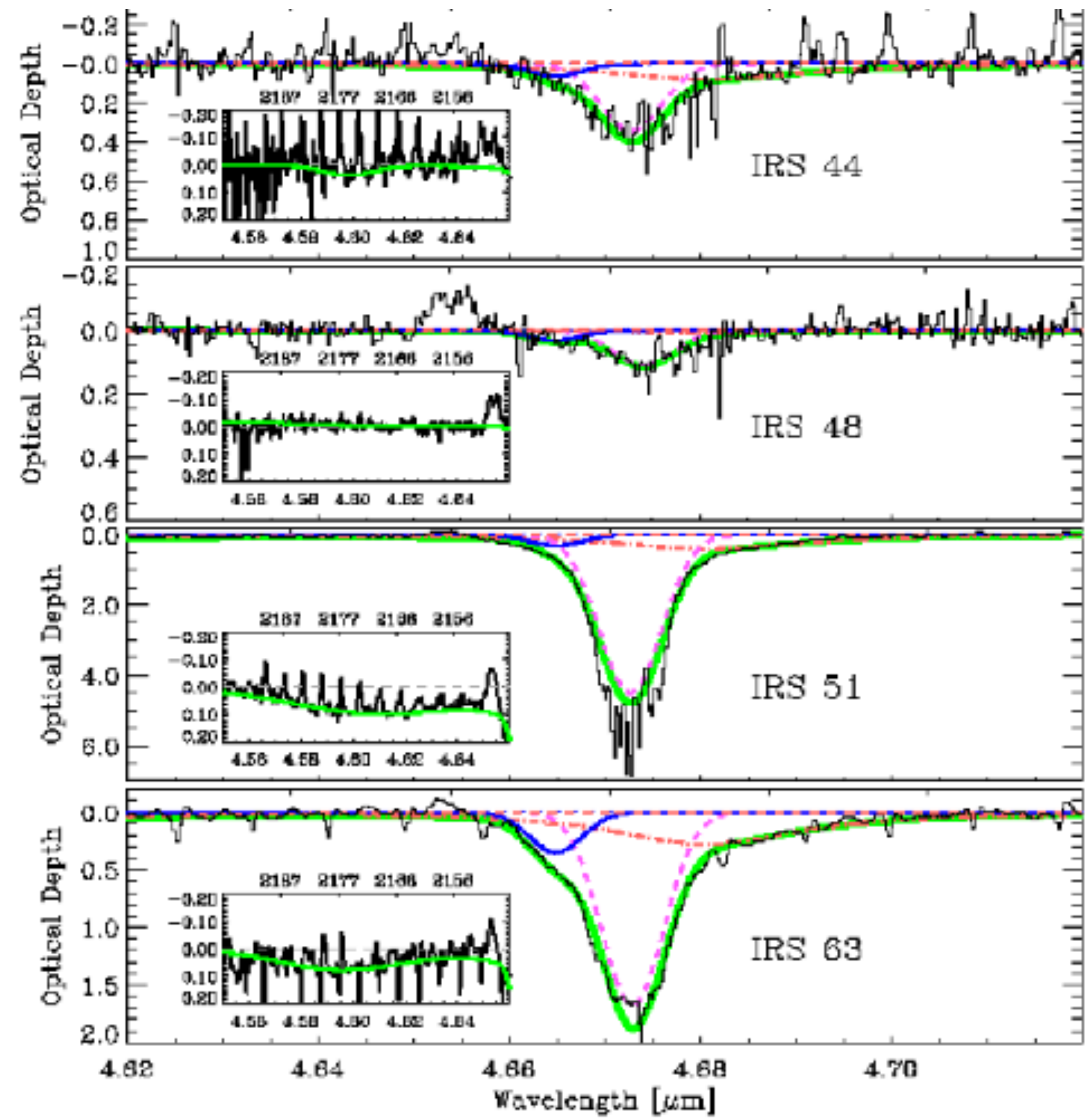


Disk N_2H^+ ring

Oberg et al. 2011
Jorgensen et al. 2004
Qi et al. 2013

Ice

- **What are the features in an interstellar ice spectrum?**
- Absorption
  (need background source)
- Infrared wavelengths
- Broad vibrational feature due to dispersion bond strengths
- Narrow rovibrational features from gas lines

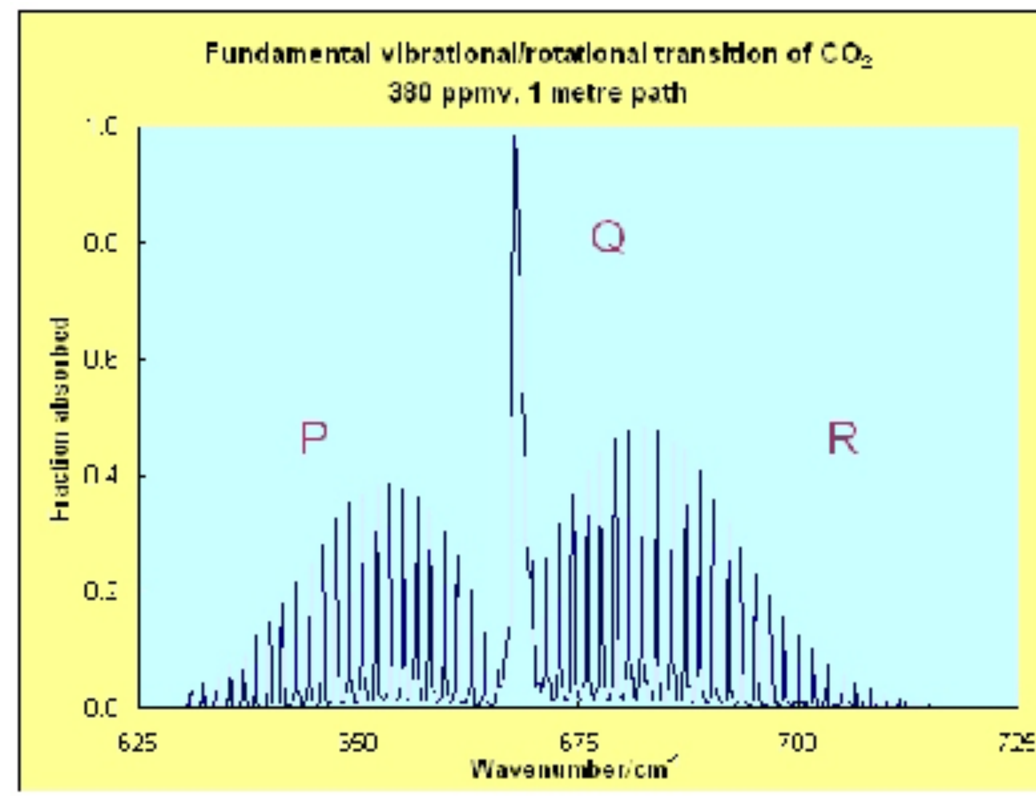


Spectroscopy

- **What is a rovibrational spectrum? Why does it look like this?**

- A rovibrational transition is a vibration in combination with a rotation
  (R: $\Delta J=+1$, Q: $\Delta J=0$, P: $\Delta J=-1$)

- Q only allowed for non-linear molecules



Spectroscopy

- **What is the critical density and LTE?**
  - Molecular density needs to be > n_{crit} in order to be in LTE (Local Thermodynamic equilibrium: collisions determine level population)
    => critical density: property of molecule
  - Most common emission mechanism in space: Collisional excitation + emission photon (two-body reactions only due to low densities)
  - Boltzmann distribution:

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

(ground for rotational diagrams)

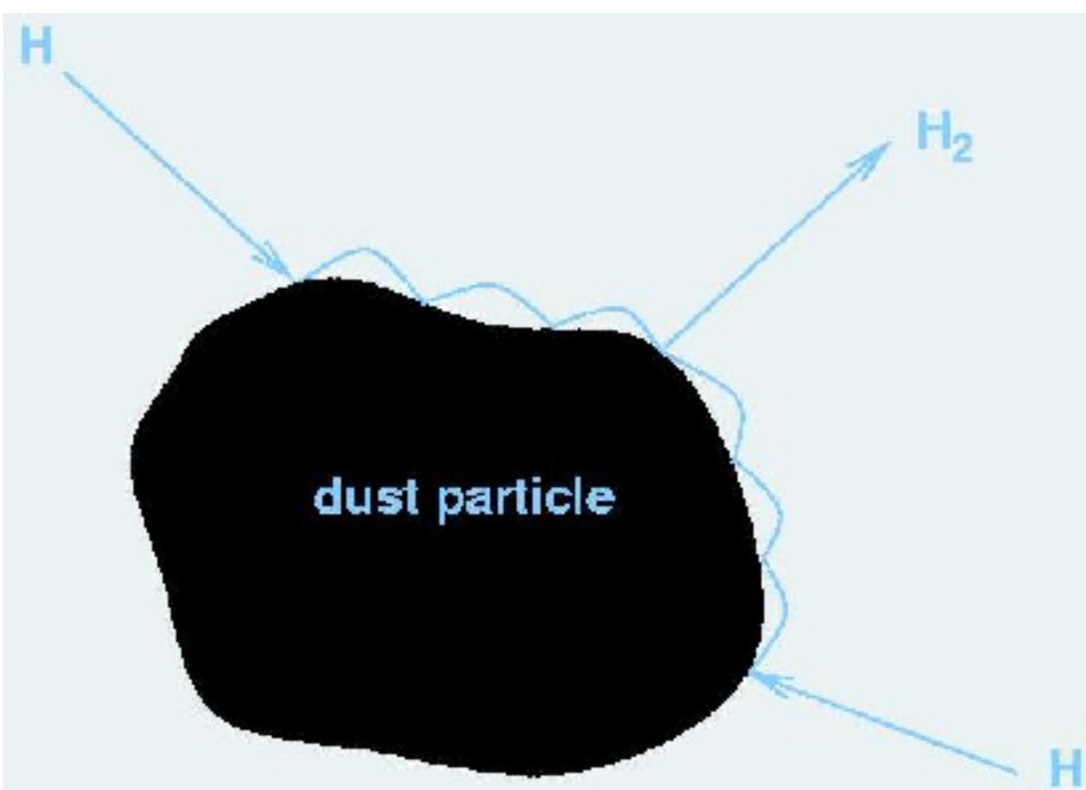
Spectroscopy

- **What is a forbidden transition?**
  - This is a transition that is not allowed according to QM selection rules. In reality, they can happen but with much lower probability. The low densities in space make them more probable to occur as collisions are more rare than on Earth.
  - Notation: [OI], [HI], [CI], etc.

Hydrogen

- **H_2 is the most abundant molecule in space, how is it formed?**

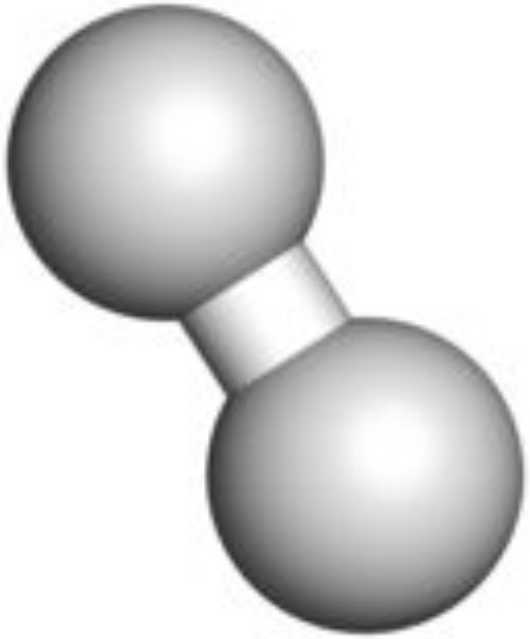
  - Gas-phase reaction inefficient: formation on dust grains, where grains acts as catalyser



Langmuir-Hinshelwood
or
Eley-Rideal (high T: short adsorption time)

Hydrogen

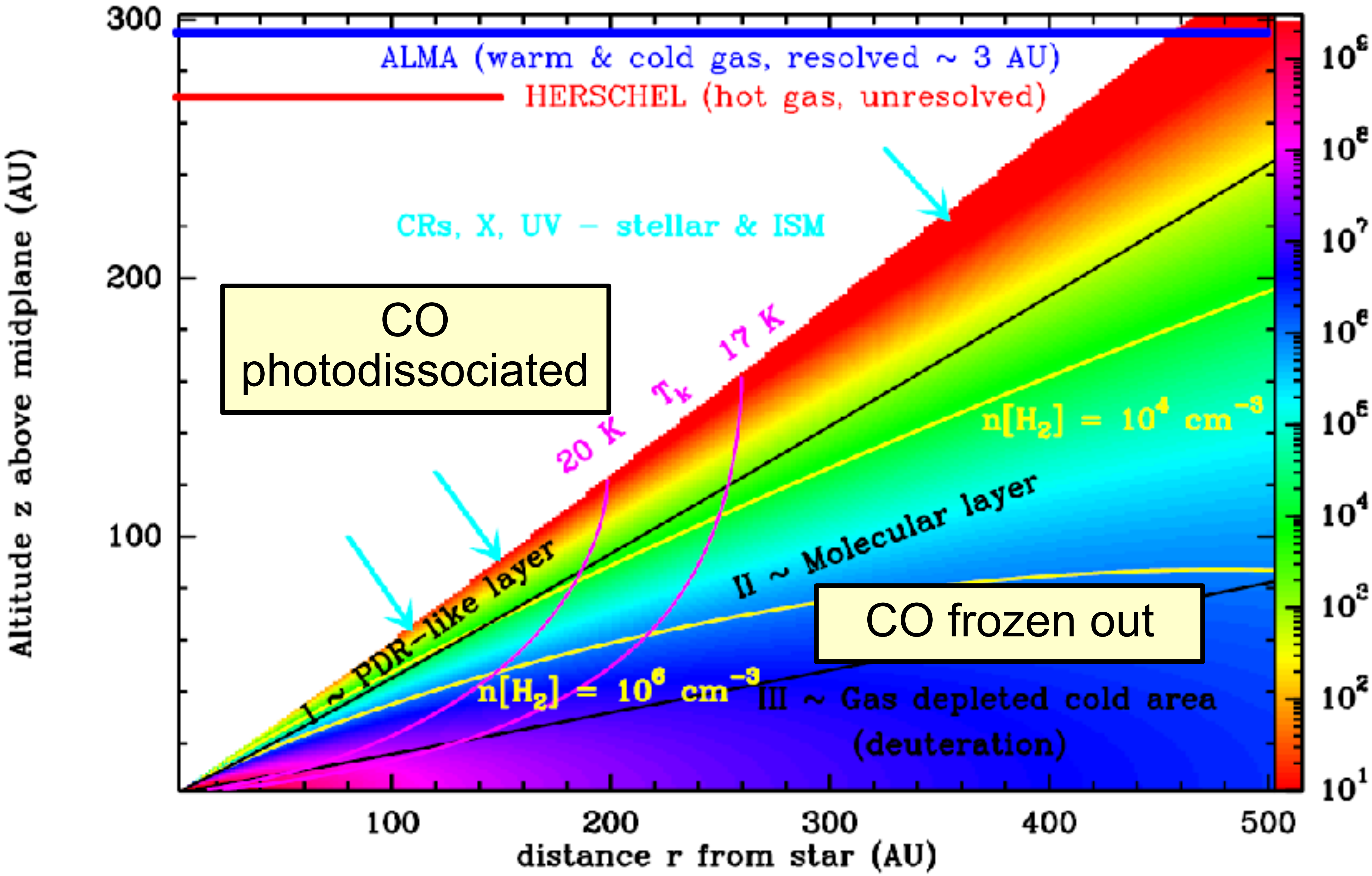
- **H_2 is the most abundant molecule in space, why don't we observe it regularly?**
    - It is a symmetric molecule and has no permanent dipole moment, thus no regular rotational transitions: quadrupole rovibrational transitions are allowed, but more rare and in the infrared, thus harder to observe



CO

- **What is our next most-abundant molecule and what are the issues with converting its abundance to density?**
  - CO, which is >10 000x less abundant than H_2
  - CO/H_2 is not constant: CO is frozen out at <20 K and photo dissociated in presence of a stellar radiation field, although it can self-shield as well at sufficient densities (H_2 as well!)
  - CO quickly becomes optically thick and is thus not tracing the full density: rarer CO isotopologues are often required

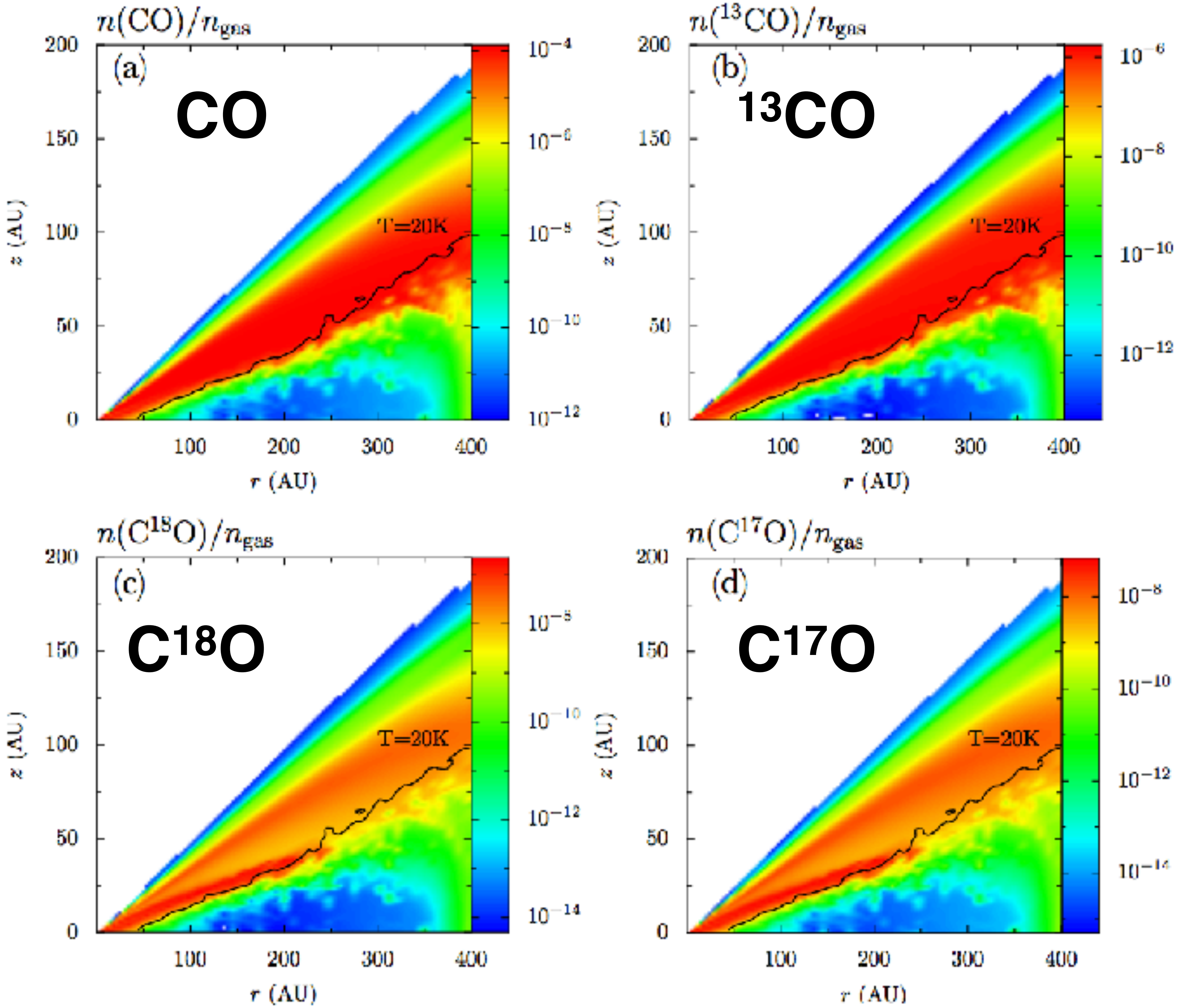
CO



ALMA (warm & cold gas, resolved ~ 3 AU)
HERSCHEL (hot gas, unresolved)
CRs, X, UV – stellar & ISM
CO photodissociated
20 K
T_k
17 K
$n[H_2] = 10^4$ cm^{-3}
I ~ PDR-like layer
II ~ Molecular layer
CO frozen out
$n[H_2] = 10^6$ cm^{-3}
III ~ Gas depleted cold area (deuteration)
Altitude z above midplane (AU)
distance r from star (AU)
300
200
100
100
200
300
400
500
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^8

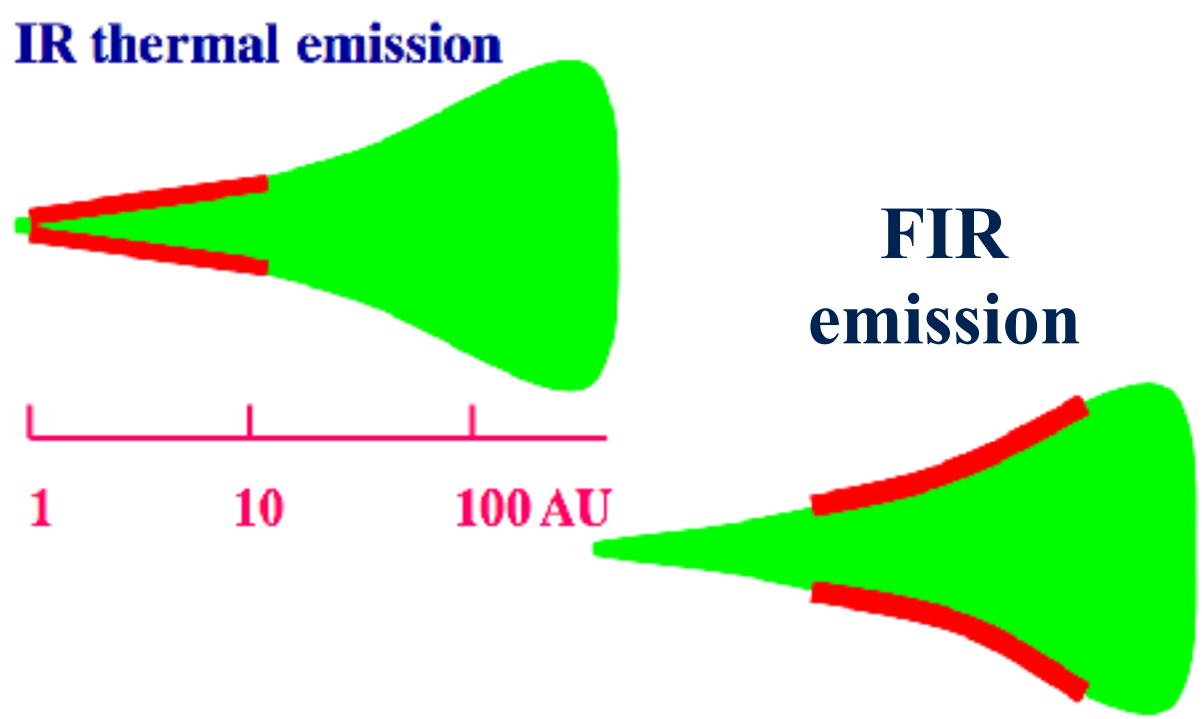
CO

CO isotopologues: Optical depth

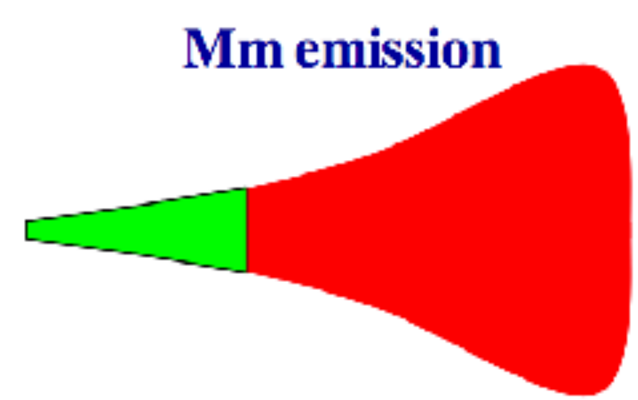


Disks

- **Why do we need different telescopes (wavelength ranges) to study the full structure of protoplanetary disks?**



Large range of temperatures and densities: modelling usually required to interpret emission



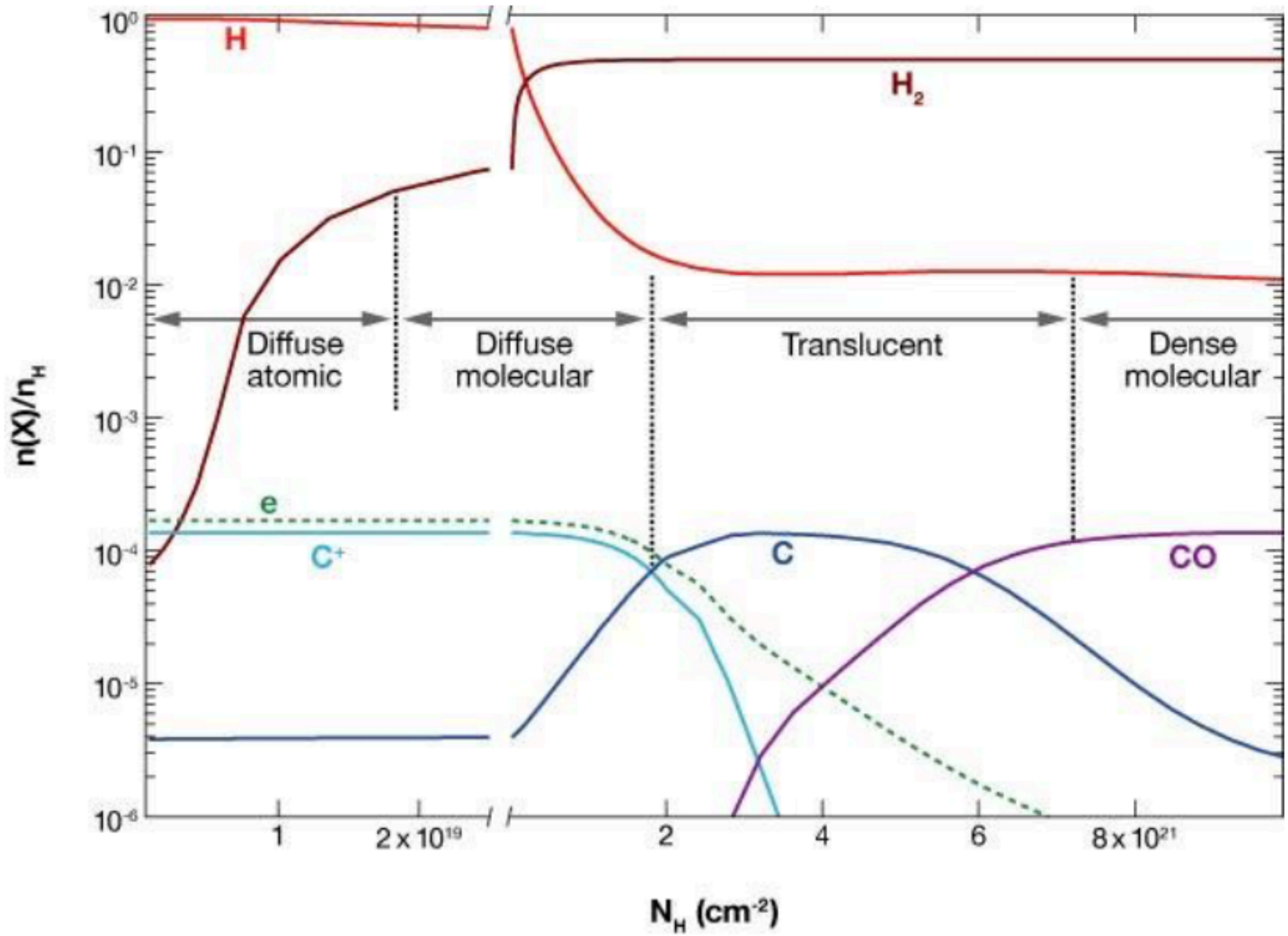
Clouds

- **What are PDRs and what is their role in clouds?**
  - Photon-dominated regions are regions with low density: UV-photons control the physical/chemical state cloud T~25-100 K (edge-center), n~100-500 $cm^{-3,}$ A_V ~ 1 mag
  - Typical: diffuse/translucent clouds, inner part of prestellar clouds (also upper layers disks)
  - mostly simple diatomic molecules (e.g. H_2, HD, CH, CH^+): gas-grain chemistry not important and quick photodissociation by ISRF
  - Dark clouds and protostellar cores:

    $T \approx 10$ K, $n_H \approx 10^4$-10^5 $cm^{-3,}$ A_V>5 mag

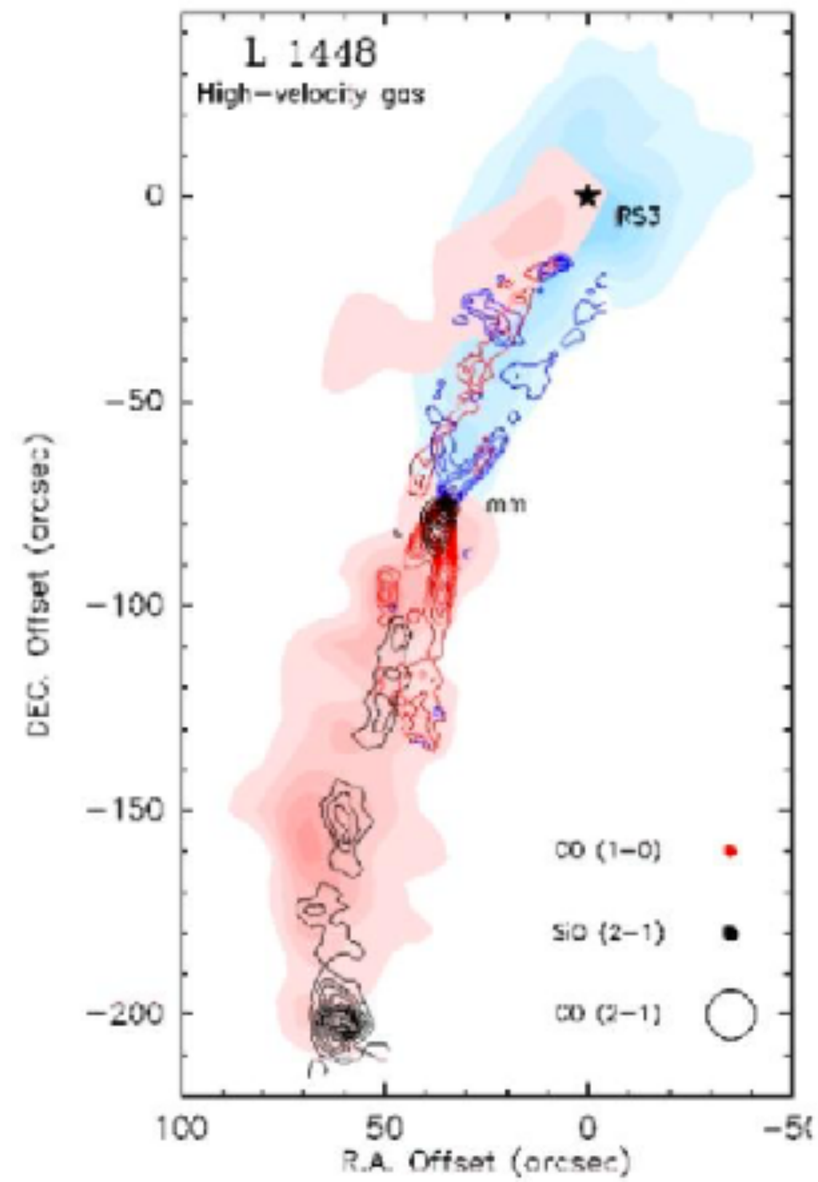
    - Ice and gas-grain chemistry significant!
    - strongest lines at mm wavelengths (low-J)

Clouds


H
H2
Diffuse atomic
Diffuse molecular
Translucent
Dense molecular
e
C+
C
CO
n(X)/nH
NH (cm-2)
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
1
2 x 10^19
2
4
6
8 x 10^21

Shocks

- **Where can we find shocks and how does the chemistry change in shocks?**
  - Shocks are found along e.g. molecular outflow walls in star-forming clouds: it is a disturbance with $v > c_s$: material cannot respond dynamically thus it compresses, heats and accelerates: irreversible change
  - Molecules are (photo)dissociated, ice mantles are sputtered, molecular reactions with energy barrier are enhanced, grains are destroyed (Si, Fe)



Astrochemistry

- **Why is this the right time to study astrochemistry?**
- ALMA, JWST, E-ELT, TMT, SPICA….