Ice chemistry

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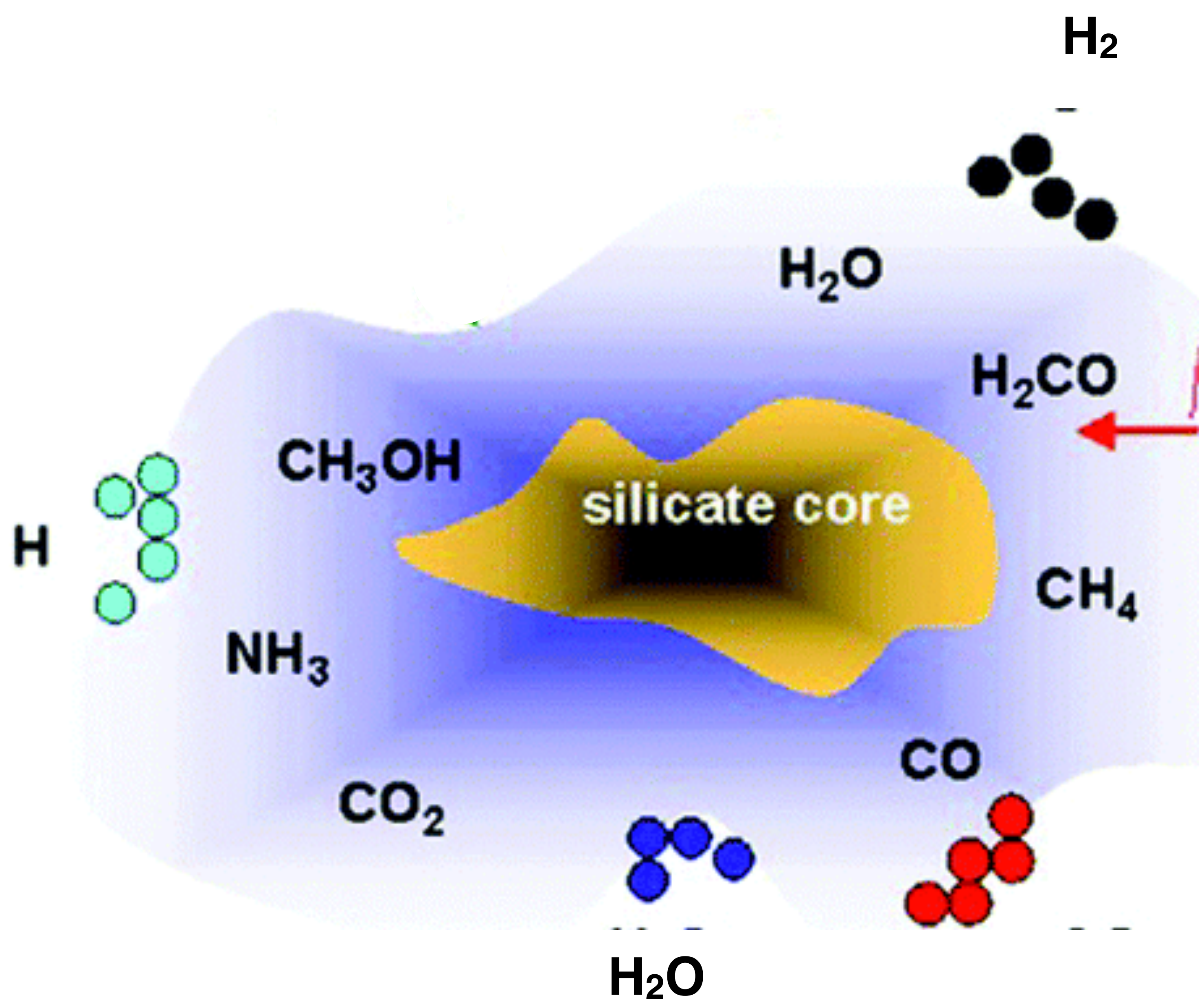
- Spectral features
- Observations
- Ice processing
- Ice history
- Comets

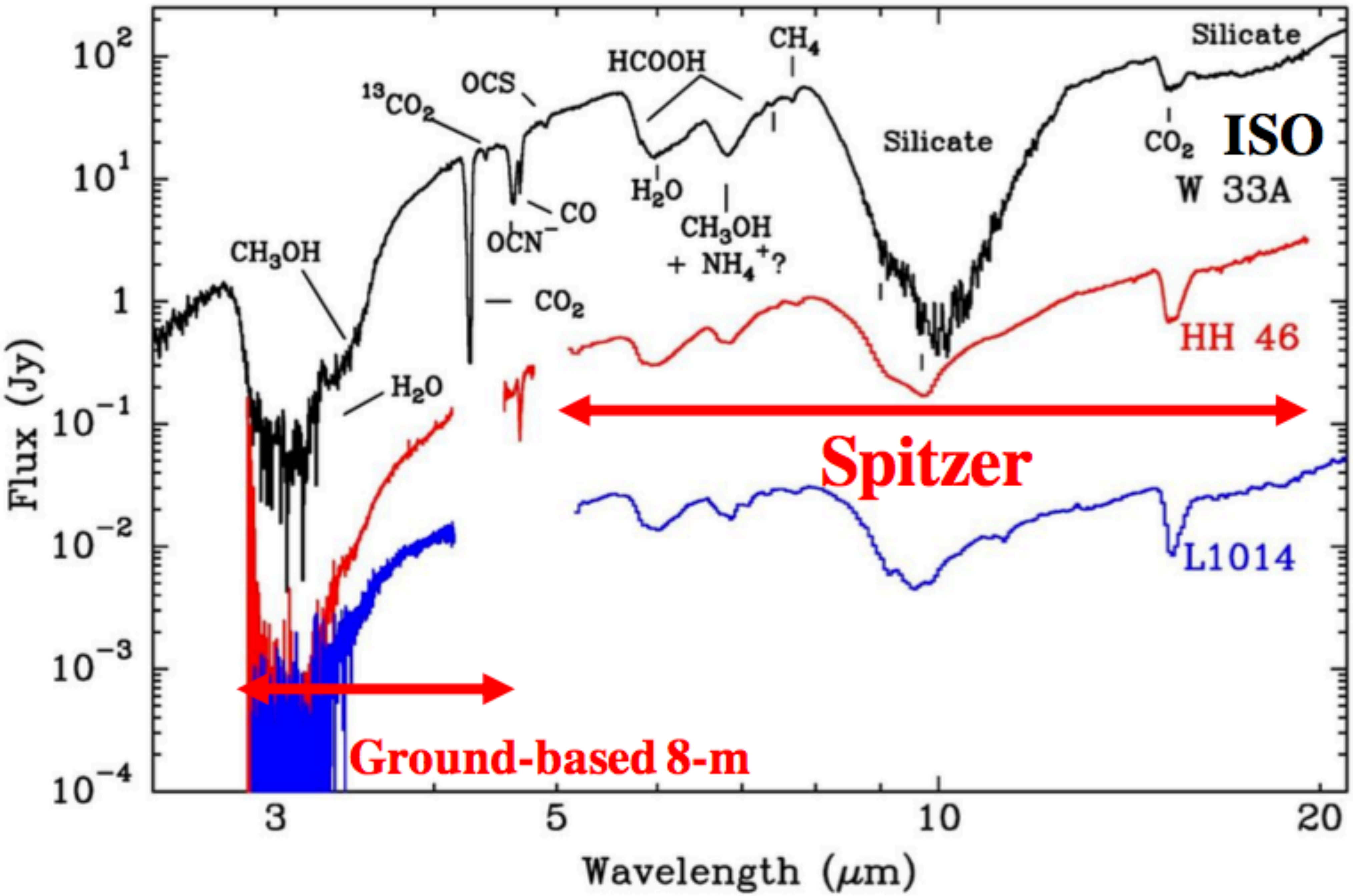
Interstellar ice

- Ice forms on dust grains



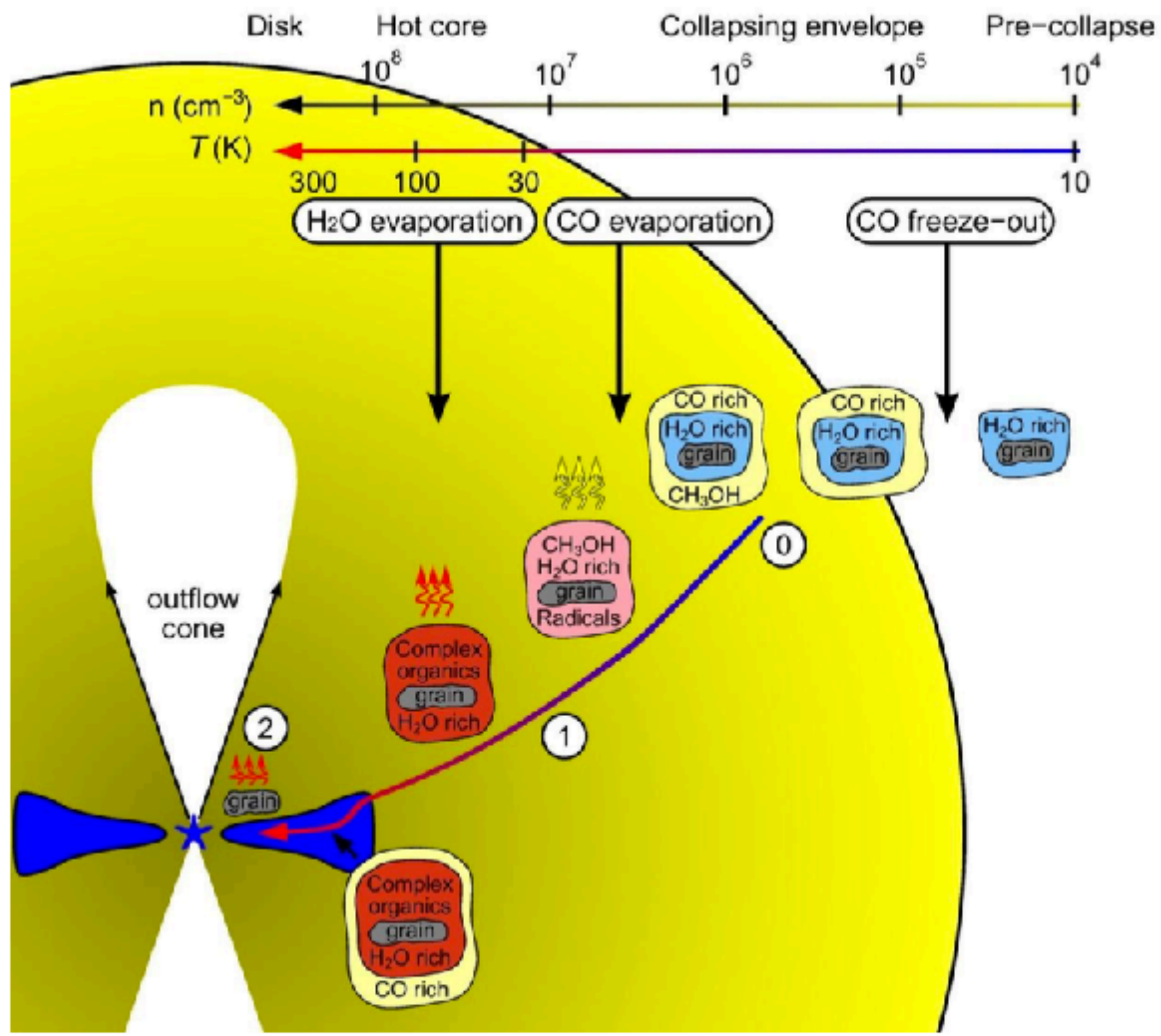
Interstellar ice

- Absorption spectra: need for background source



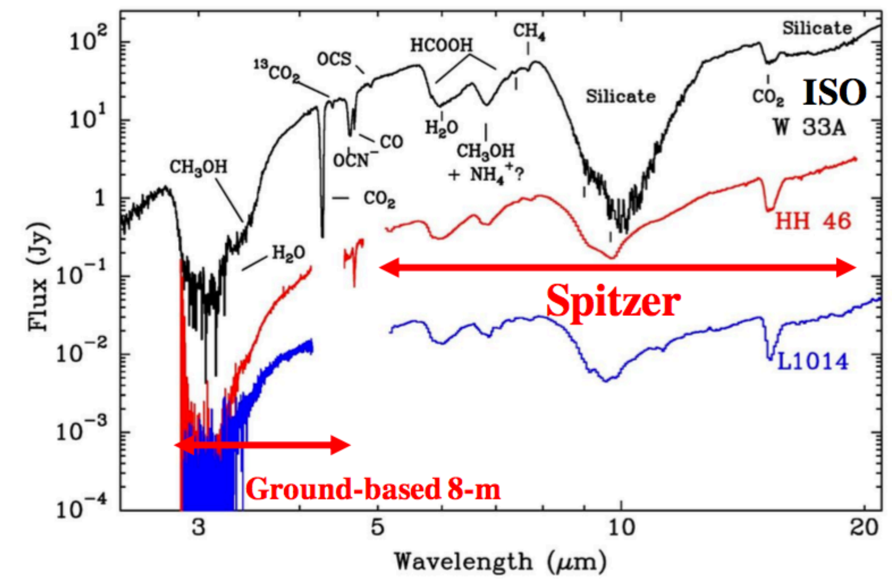
Interstellar ice

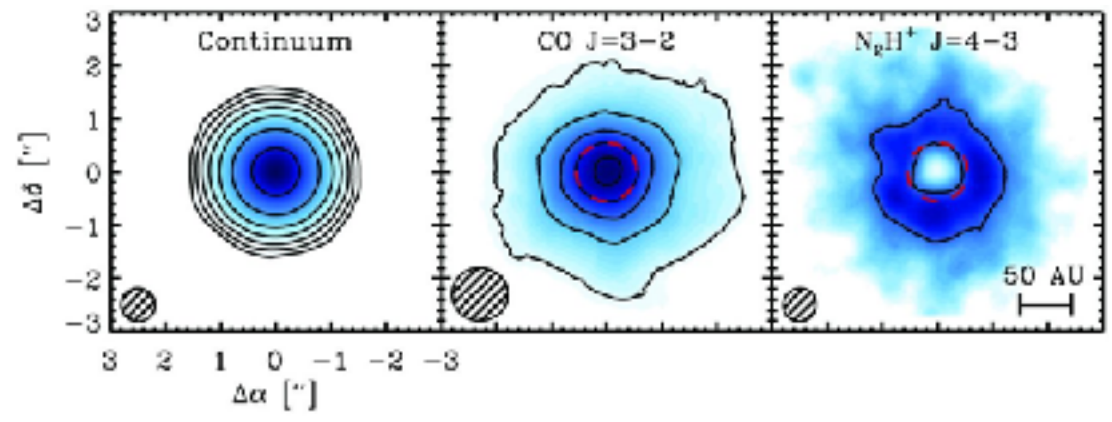
- Low temperature and high density (collisions): =>Relevant in all stages of star and planet formation



Interstellar ice

- How do we know that it exists?
  - Absorption spectra in mid infrared
  - Abundances of molecules (e.g. H_2O, CO_2, CH_3OH, complex organic molecules) too high to be explained by gas-phase chemistry alone
  - Presence of molecules (e.g. N_2H^+) that can only form when another molecule (CO) is frozen out





Interstellar ice

Sublimation temperatures for pure ices as measured in lab; values in space are lower because of longer timescales

Species	T_{evap} (lab) (K)
H_2O	150
CH_3OH	99
HCN	95
SO_2	83
NH_3	78
CO_2	72
H_2CO	64
H_2S	57
CH_4	31
CO	25
N_2	22

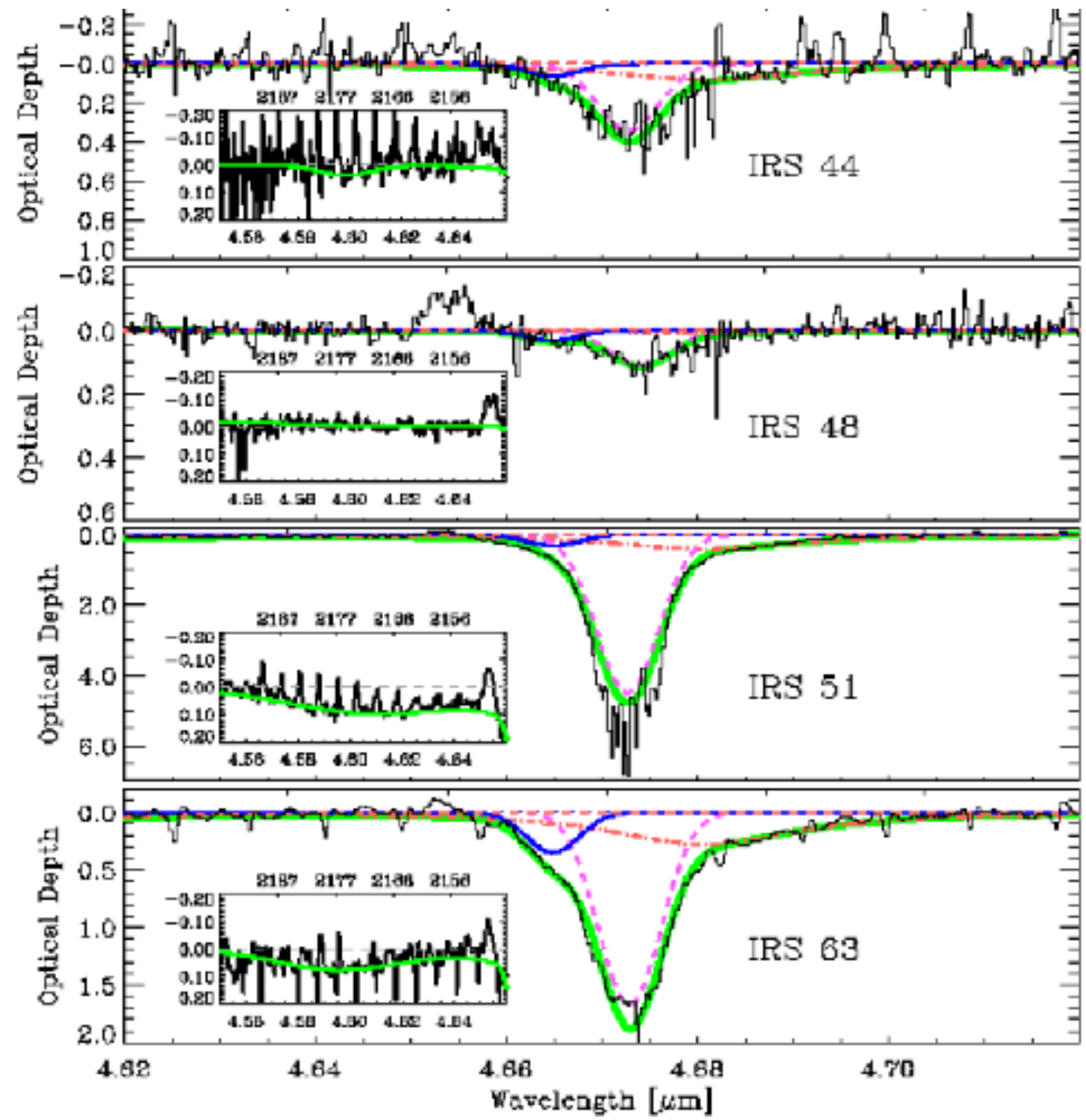
Collings et al. 2004

Spectra

- Type of transition: vibrational absorption => vibration of intermolecular bond

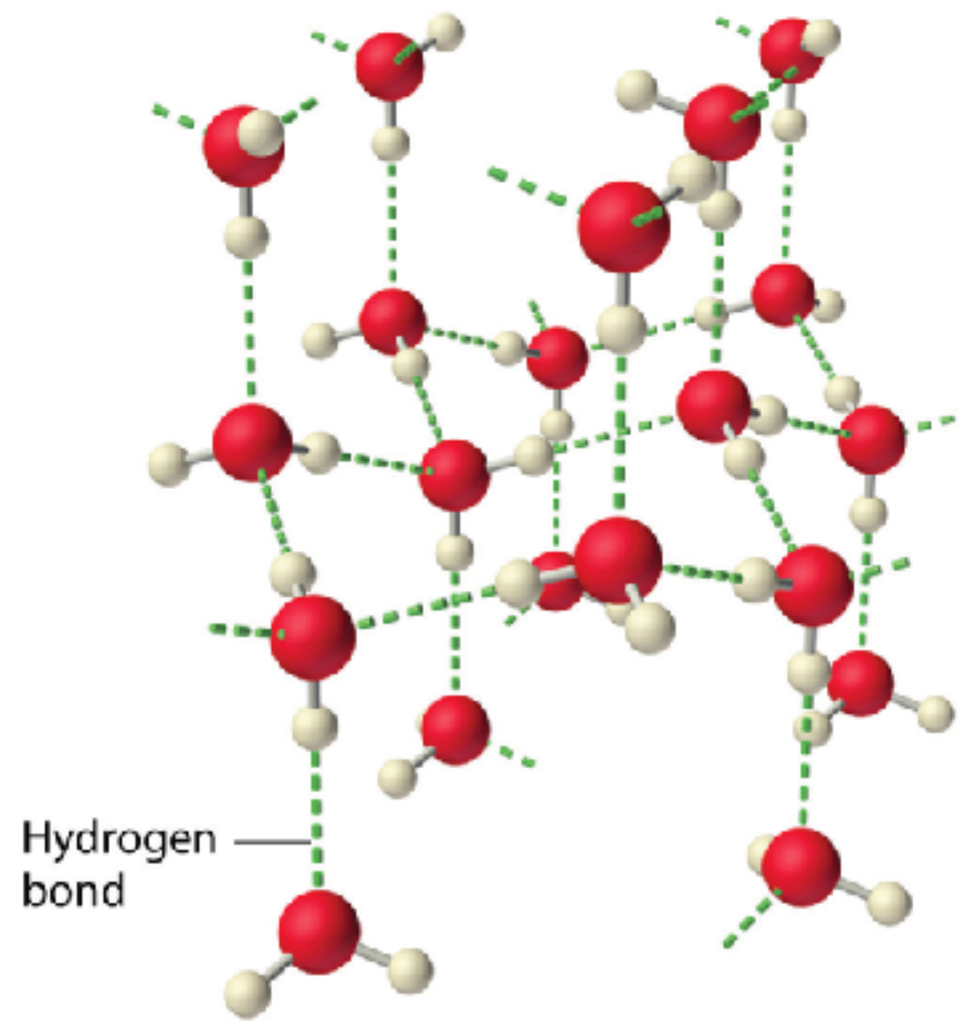
- Why not emission?

- Gas vs solid state: why do the spectral features look different?



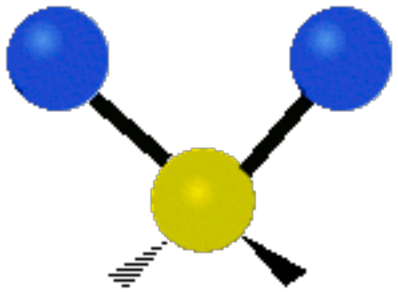
Spectra

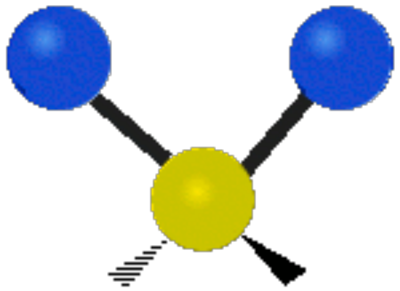
- Type of transition: vibrational
- Why not emission?
  => Vibrational energies >>100 K:
  ices are evaporated long before excitation
- Gas vs solid state: why do the spectral features look different?
  - **Gas**: ***lines***
    => rovibrational transitions ($\Delta J=0,\pm1$)
  - **Solid state**: ***broad absorption band***
    => width determined by dispersion of bond strengths
    => peak is blue-shifted: larger energy required to vibrate intermolecular bonds



Spectra

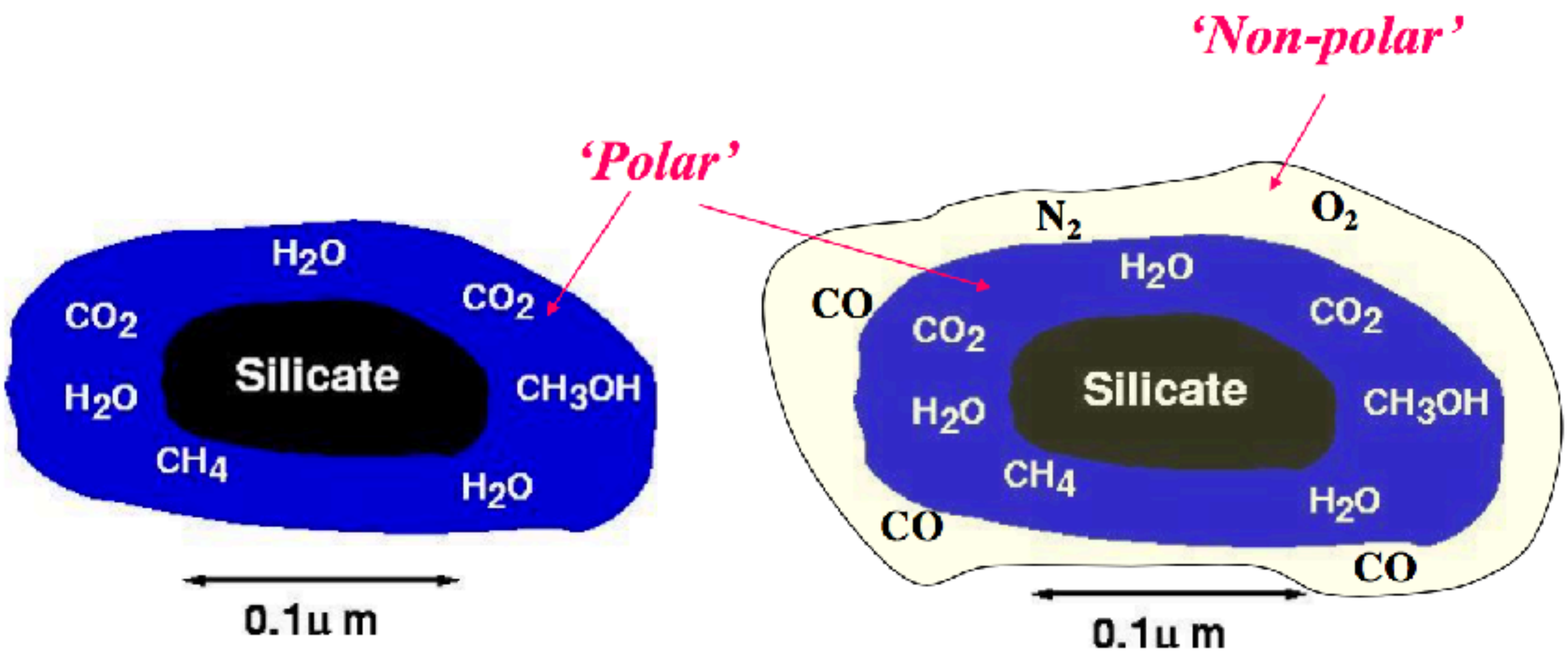
- Vibrations:
  - stretching
  - bending
  - libration (slight rotation)
- Now imagine these inside an ice matrix!





Spectra

- Due to origin of the features, the shape of the spectral features depends strongly on the environment (bonds)!
- Particular difference:
  polar (H_2O-rich) vs **non-polar** (H_2O-poor) ice: why?

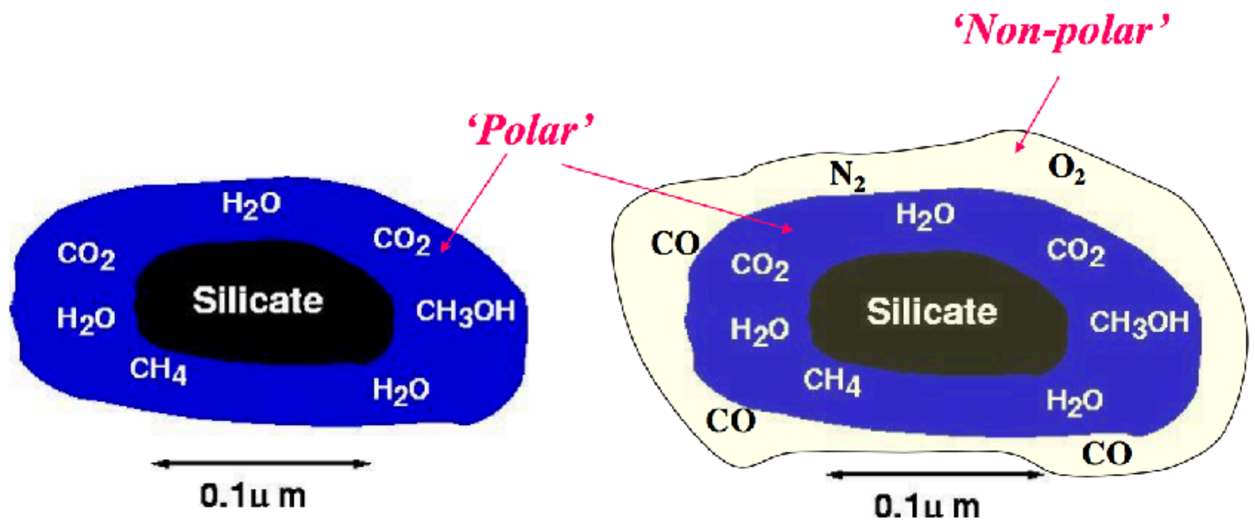


Spectra

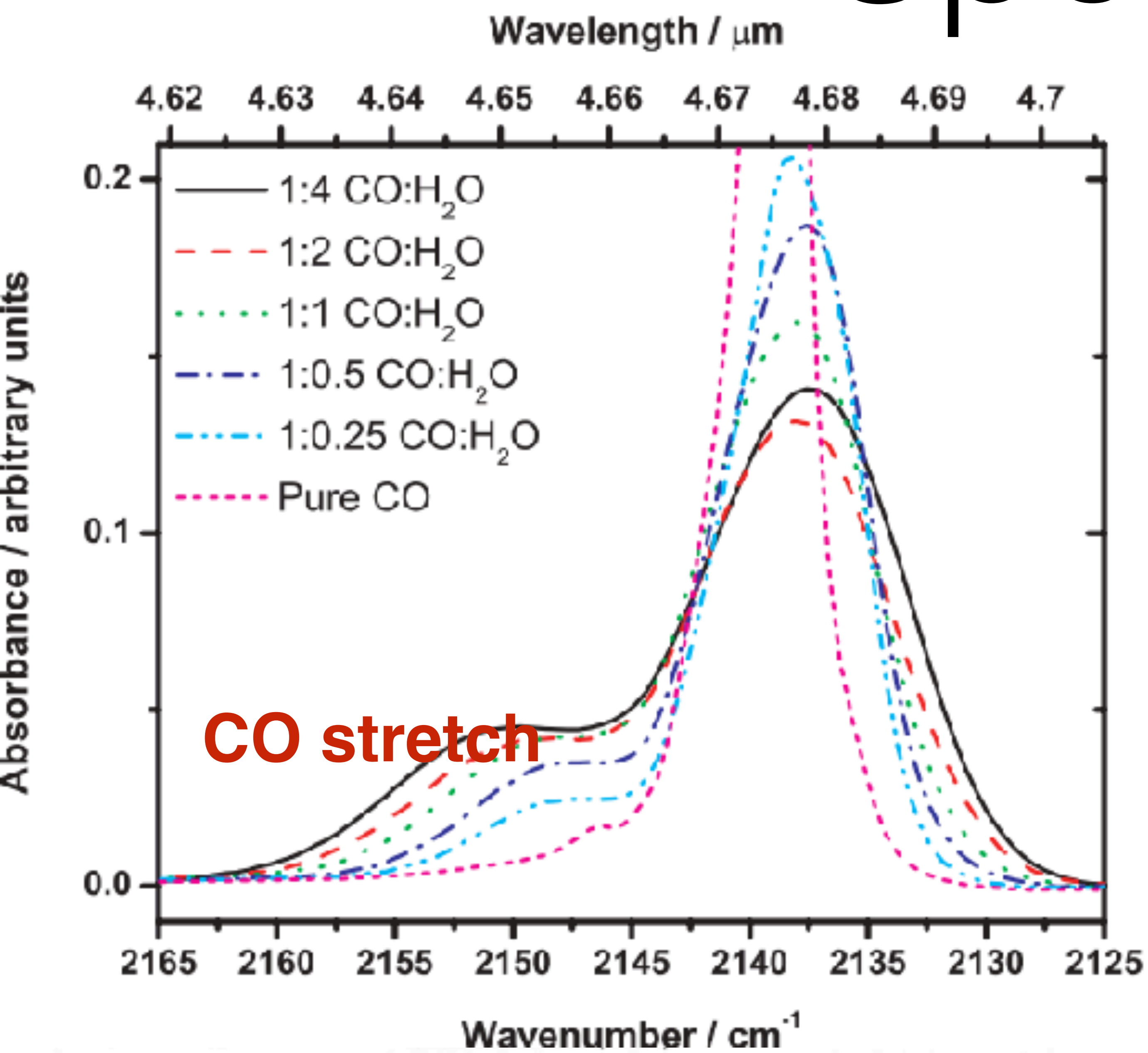
- Due to origin of the features, the shape of the spectral features depends strongly on the environment (bonds)!

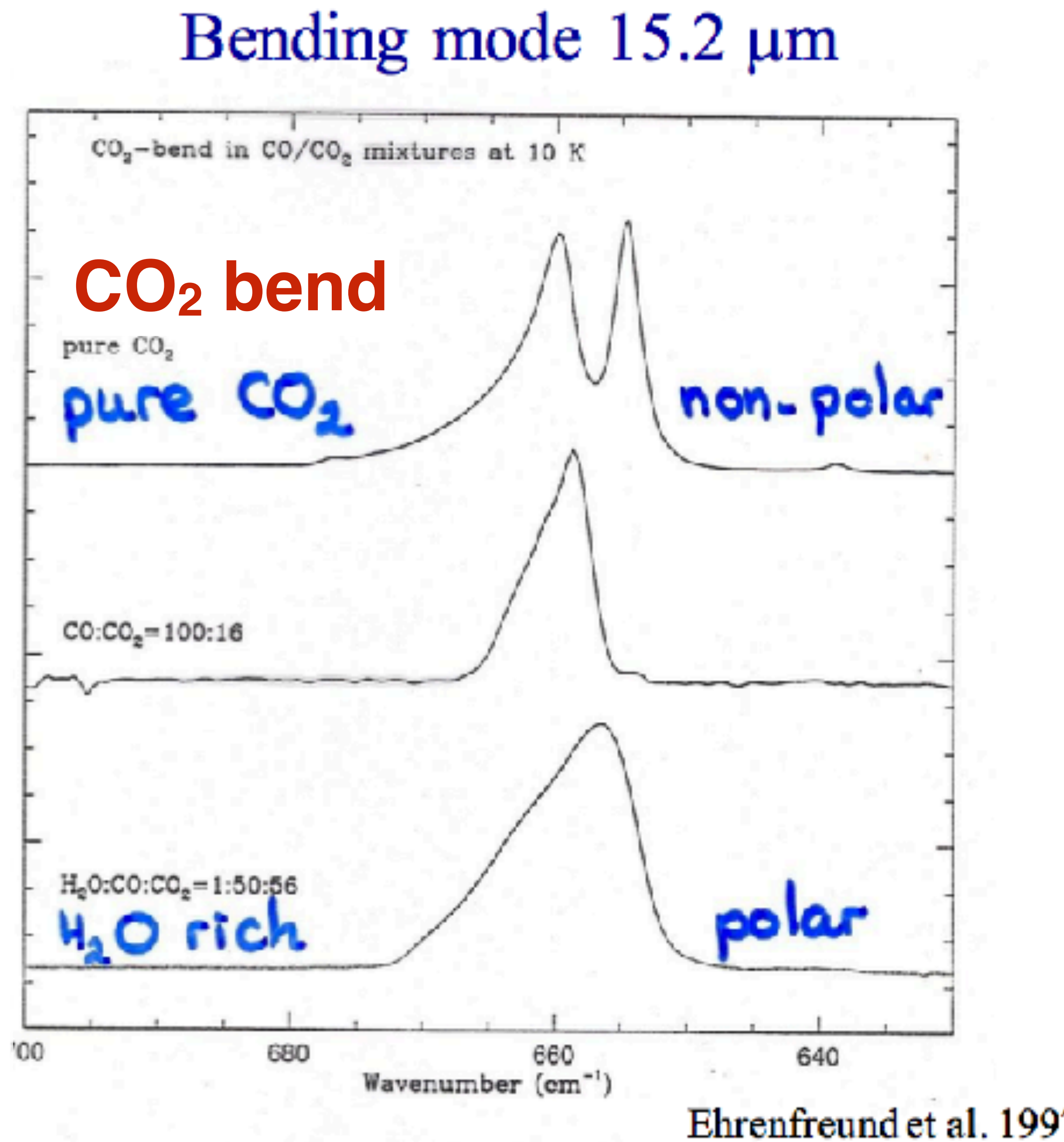
- Particular difference:
  polar (H_2O-rich) vs **non-polar** (H_2O-poor) ice: why?
  => hydrogen bonds vs van der Waals bonds

- Also notice: layered structure of polar and non-polar ices => relevant in interstellar environments!



Spectra

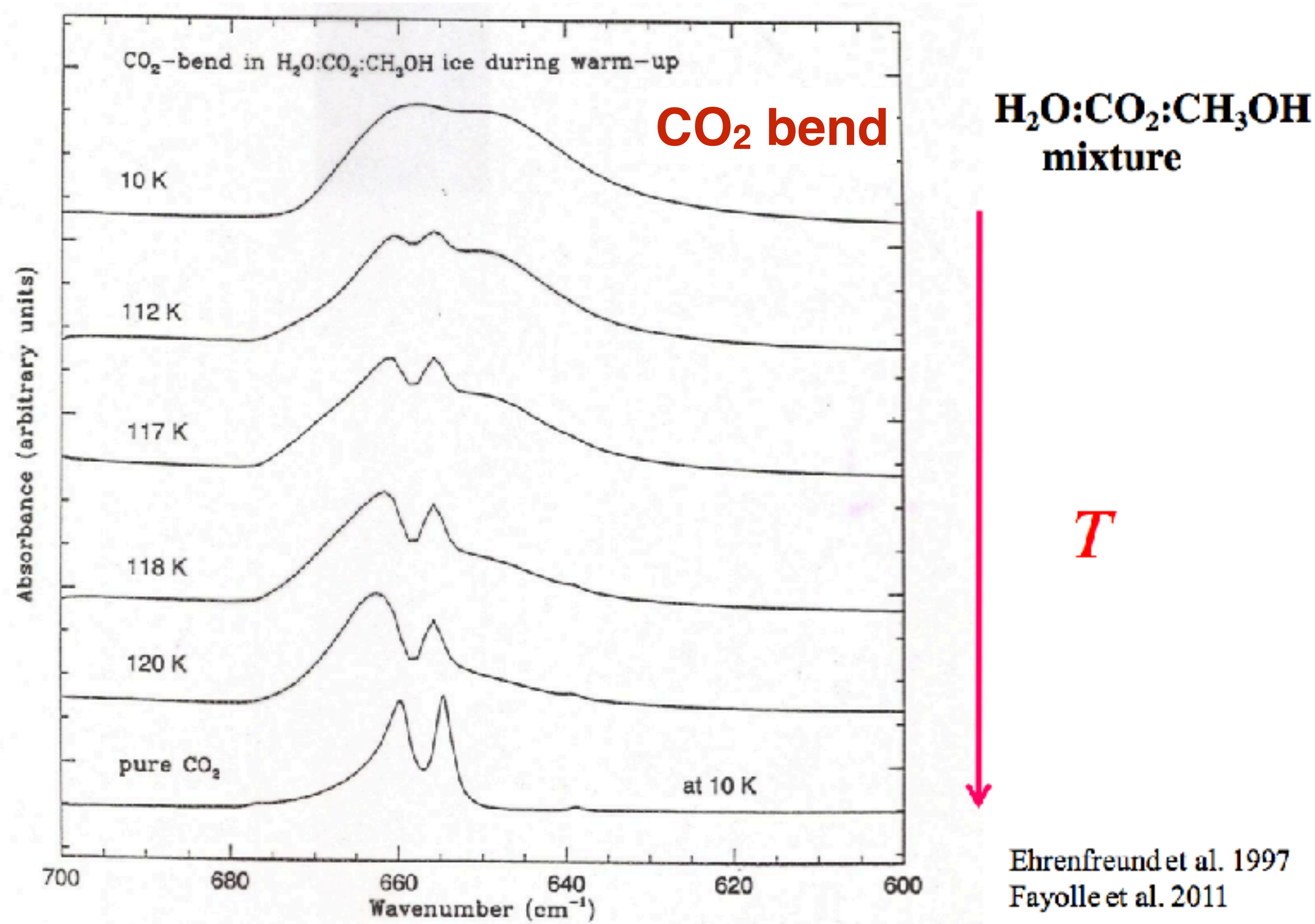




=> dependence on environment…

Ehrenfreund et al. 1997
Bouwman et al. 2007
talk Maissa!

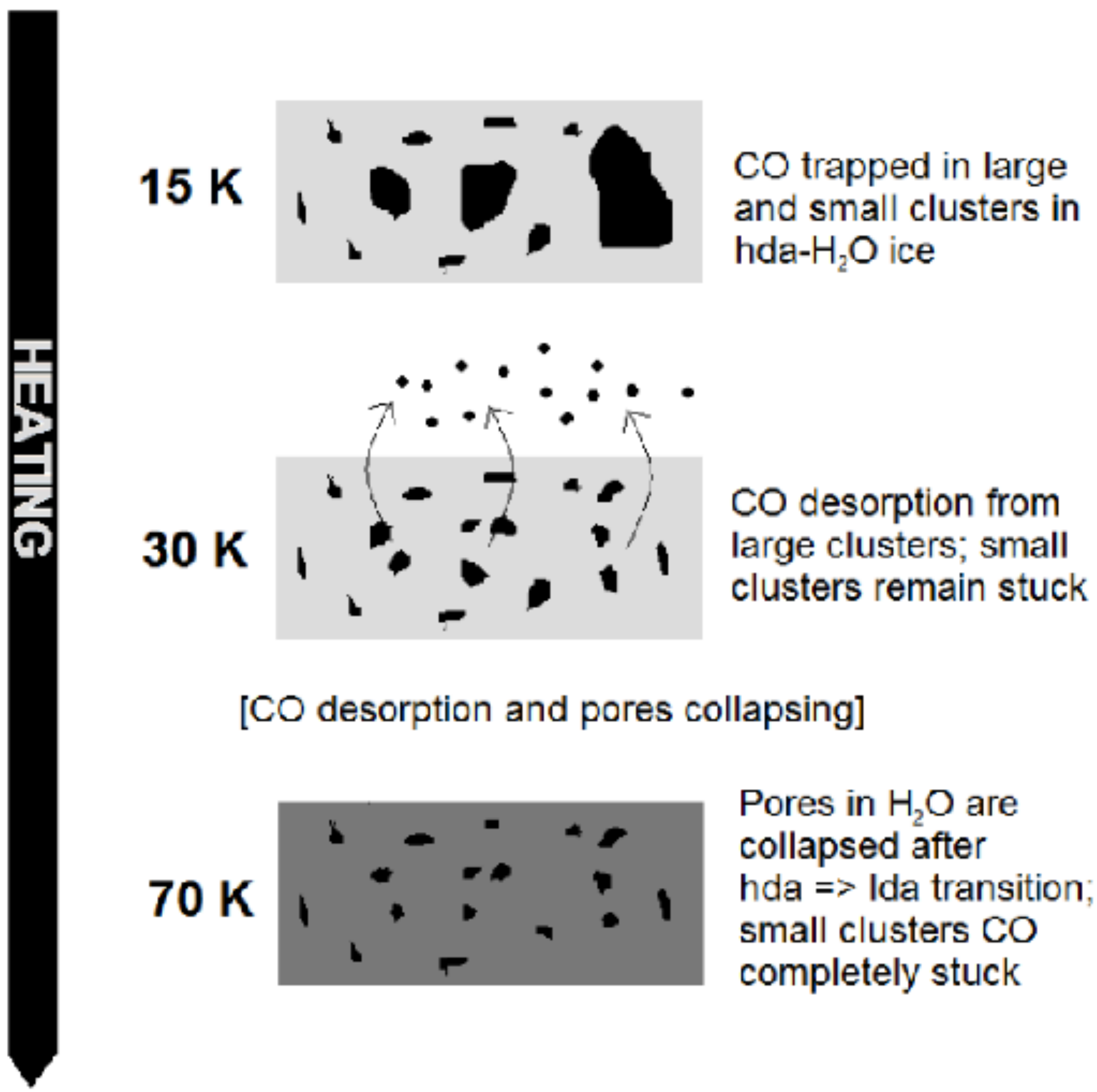
Spectra



Ehrenfreund et al. 1997
Fayolle et al. 2011

=> dependence on temperature…

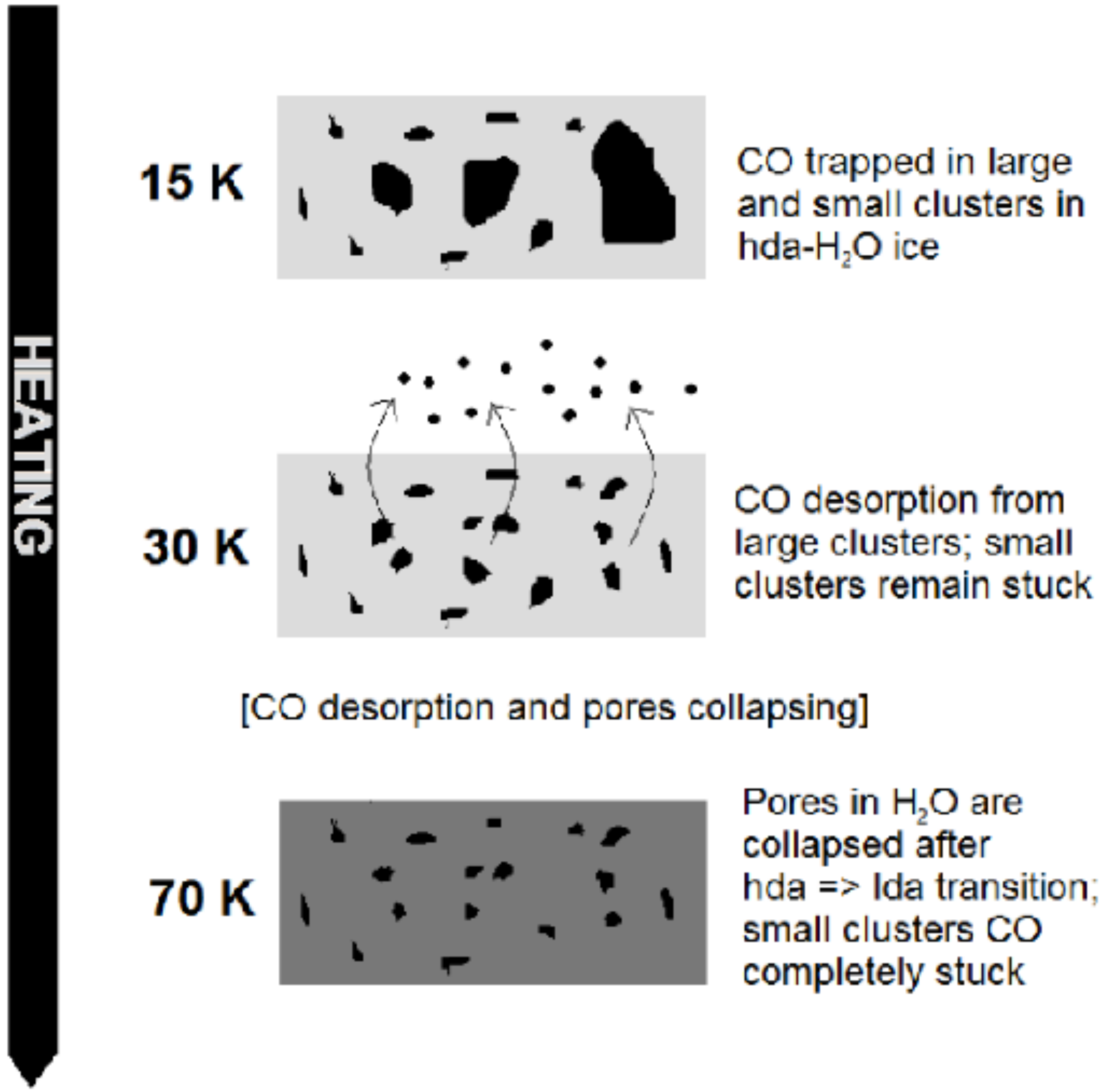
Spectra



=> dependence on history…

Collings et al. 2004

Spectra



Summary: very difficult to match observations with lab spectra!

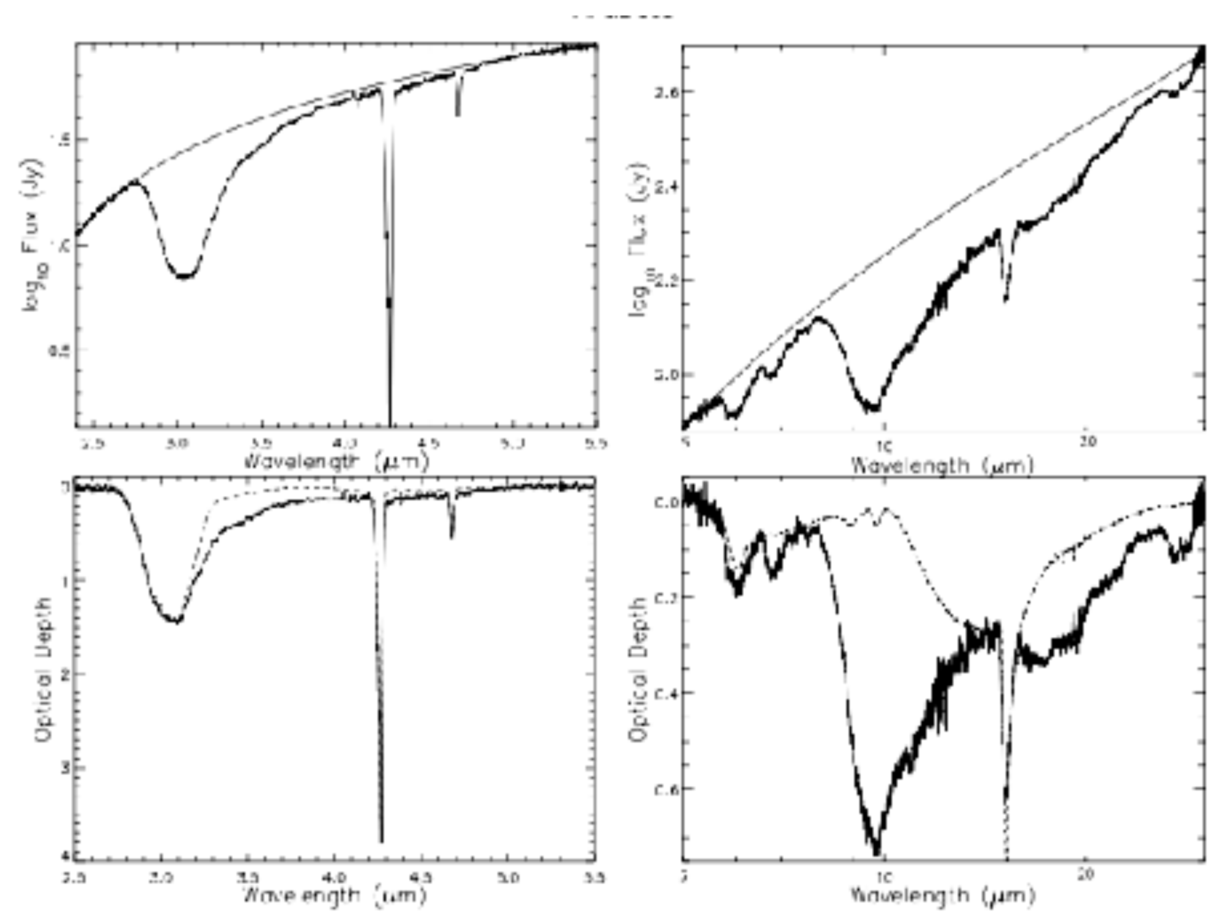
=> dependence on history…

Collings et al. 2004

Observations

- First ice observations with *ISO* (2.5-30 μm) on 15 high-mass YSOs in 1990s

- Larger samples of dozens of low-mass YSOs with e.g. Spitzer (5-20 μm) and VLT-ISAAC (3-5 μm, L/M) in 2000s



e.g. Gibb et al. 2004
Boogert et al. 2008
Pontoppidan et al. 2003

Observations

- Detections of e.g. H_2O, CO, CO_2, CH_3OH, H_2CO, CH_4, HCOOH, NH_3, OCN^-, etc.
- Large variety in features, abundances and properties across the sample

e.g. Gibb et al. 2004
Boogert et al. 2008
Pontoppidan et al. 2003

Observations

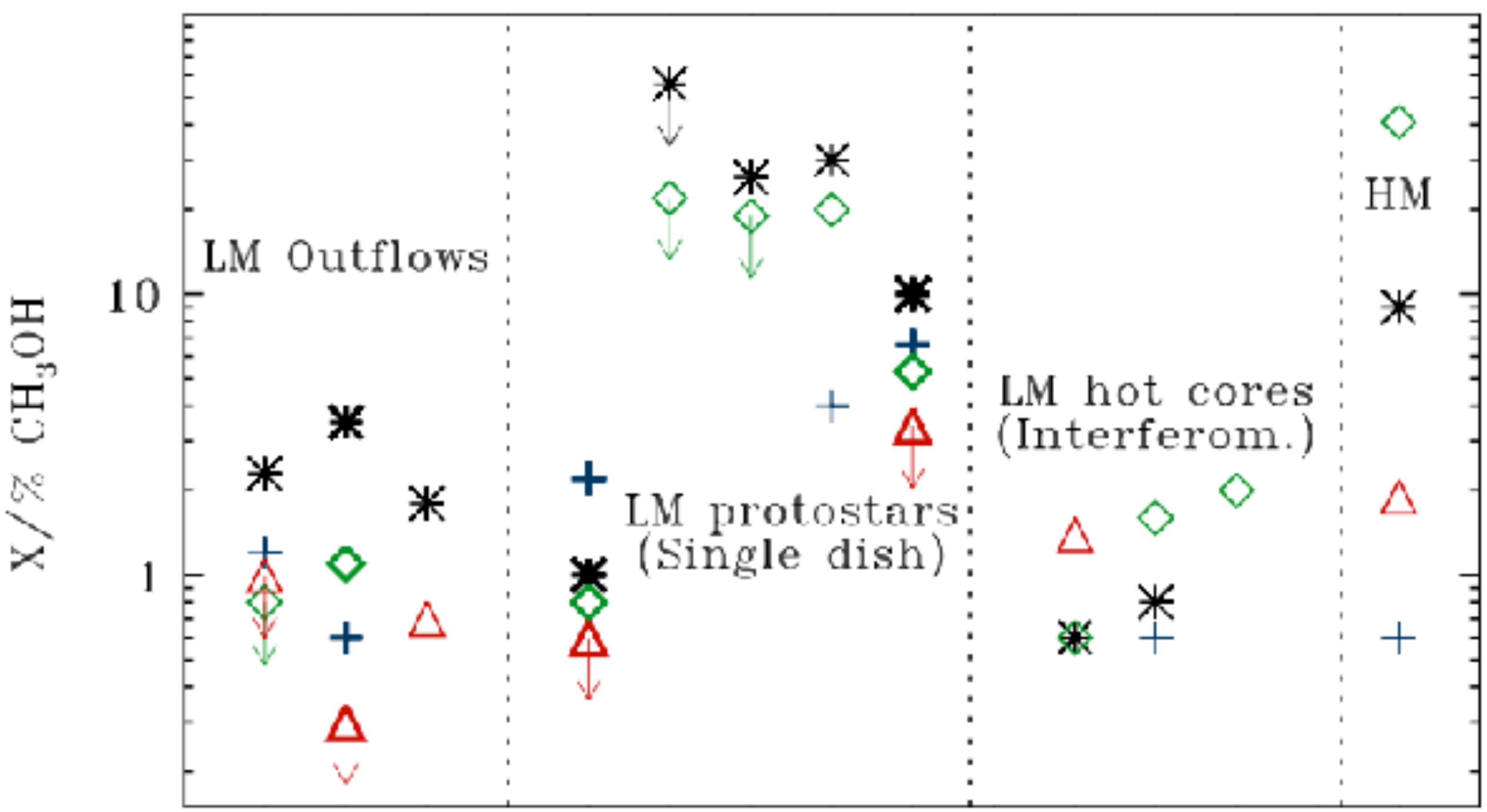
Species	High-mass YSO NGC 7538 IRS9	Low-mass YSO HH46
H_2O	100	100
CO	10	20
CO_2	16	32
CH_3OH	9	6
H_2CO	<3	
HCOOH	2	3
CH_4	1	5
NH_3	10	
OCN^-	0.8	0.6

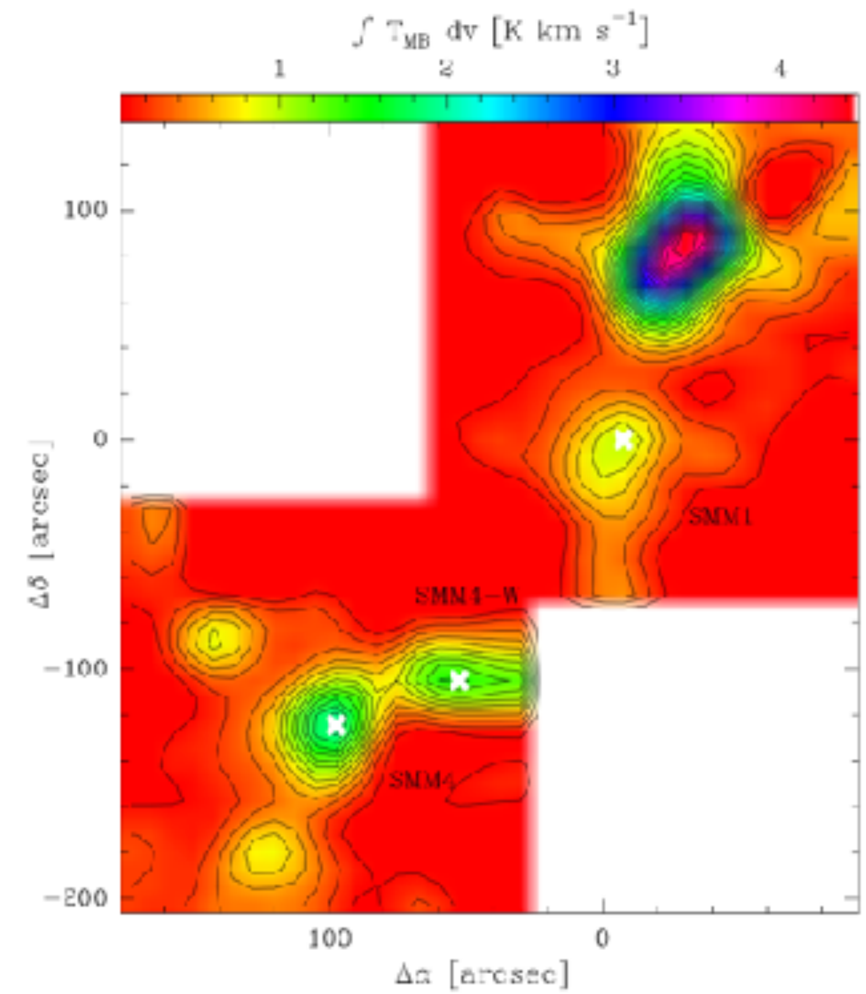
~10^{-4} w.r.t. H_2

Highly variable source by source due to low T_{evap}

Observations

- Gas-phase molecules can be indicators of ice as well => origin is ice chemistry
- Example:
  Serpens cores: $HCOOCH_3$, CH_3CHO and C_2H_5OH: products of CH_3OH





Oberg et al. 2011
Talk Christian!

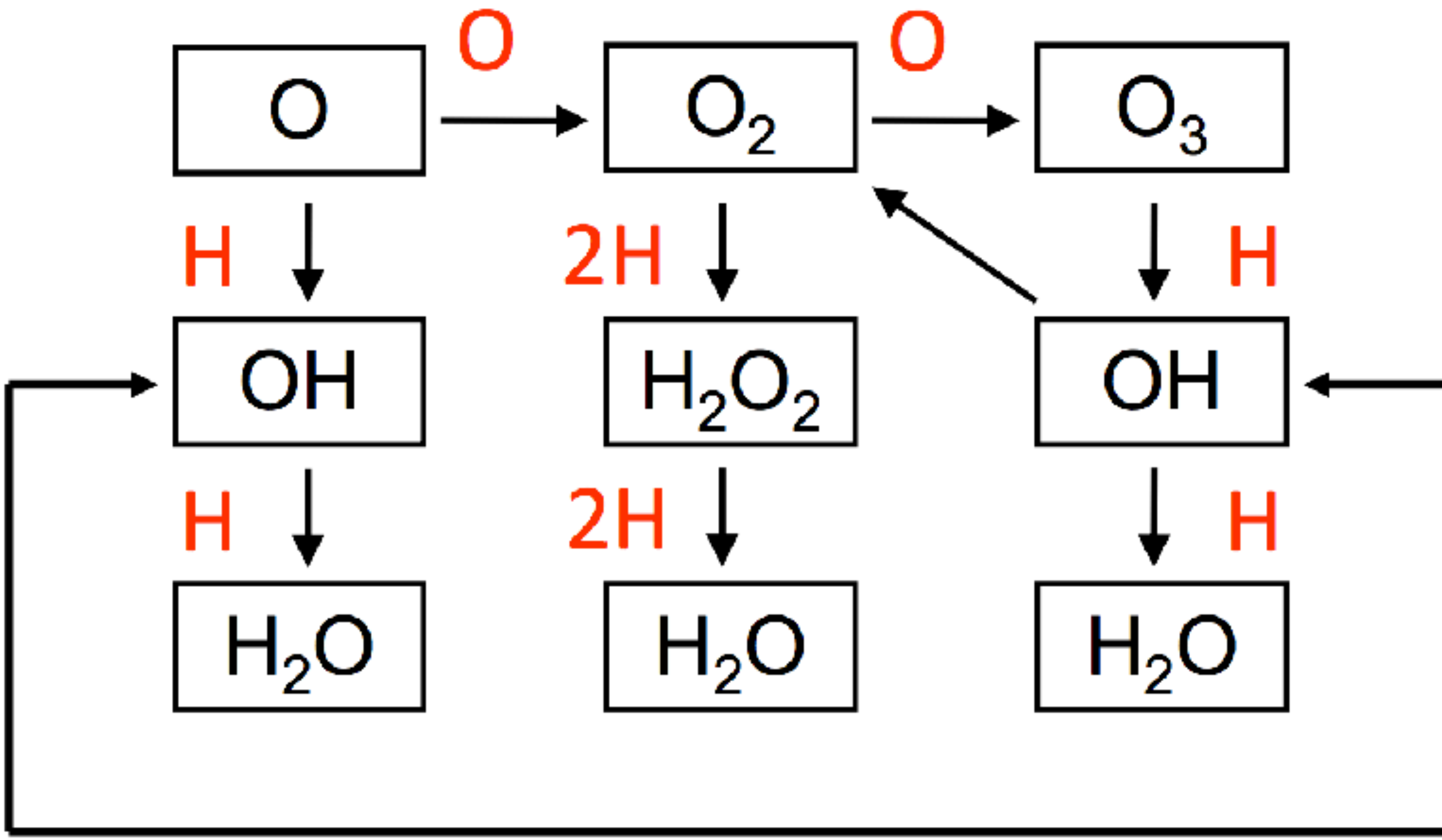
Ice processing

- Gas-grain chemistry: relevant for $n_H > 10^4$ cm^{-3} (collisions sufficiently rapid)

- Atoms and molecules arrive on grain, diffuse around, potentially react (if reaction barrier low) and potentially return to the gas phase

- Typical:
  - low density environment => large abundance H
  => hydrogenation ices (H_2O, CH_4, NH_3)
  - high density environment => large abundance O
  => oxidation O_2, CO, CO_2

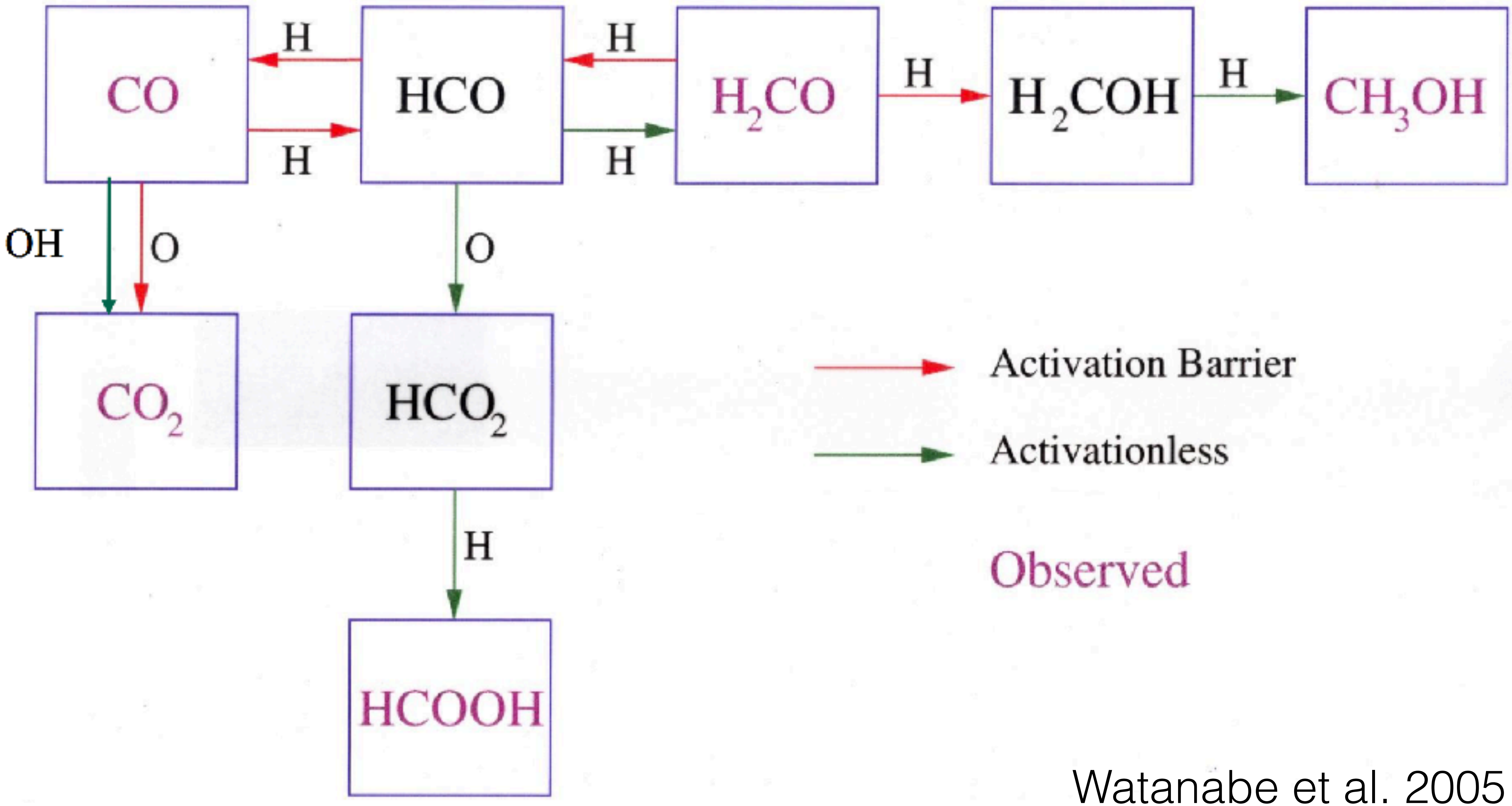
Ice processing



Tielens & Hagen 1982

Postulated in 1982, since 2000s testable in laboratory!

Ice processing



Watanabe et al. 2005
Ioppolo et al. 2011

Ice processing

- Desorption mechanisms:
  - Thermal evaporation
    - see T_{evap} table => large range, but also environment dependence
    - Non-polar species (CO, O_2, …) desorb at lower T than polar species (H_2O, CH_3OH, …)
  - Cosmic-ray spot heating
  - UV heating (can also trigger/induce ice reactions!)
  - Exothermic chemical reactions
  - Grain-grain collisions, shocks (sputtering)

Interstellar ice

Species	T_{evap} (lab) (K)
H_2O	150
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Collings et al. 2004

Ice processing

- Desorption mechanisms:
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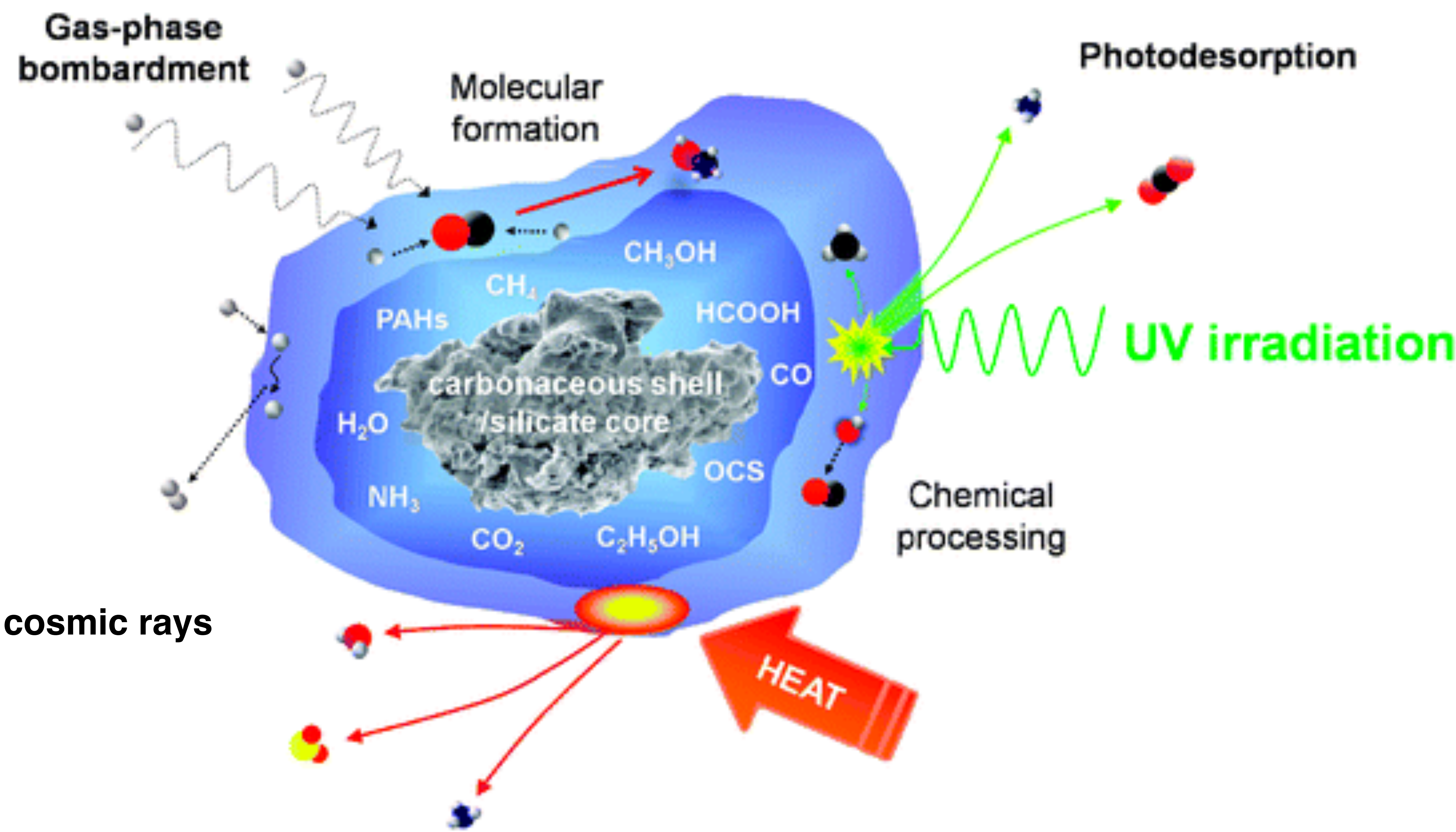
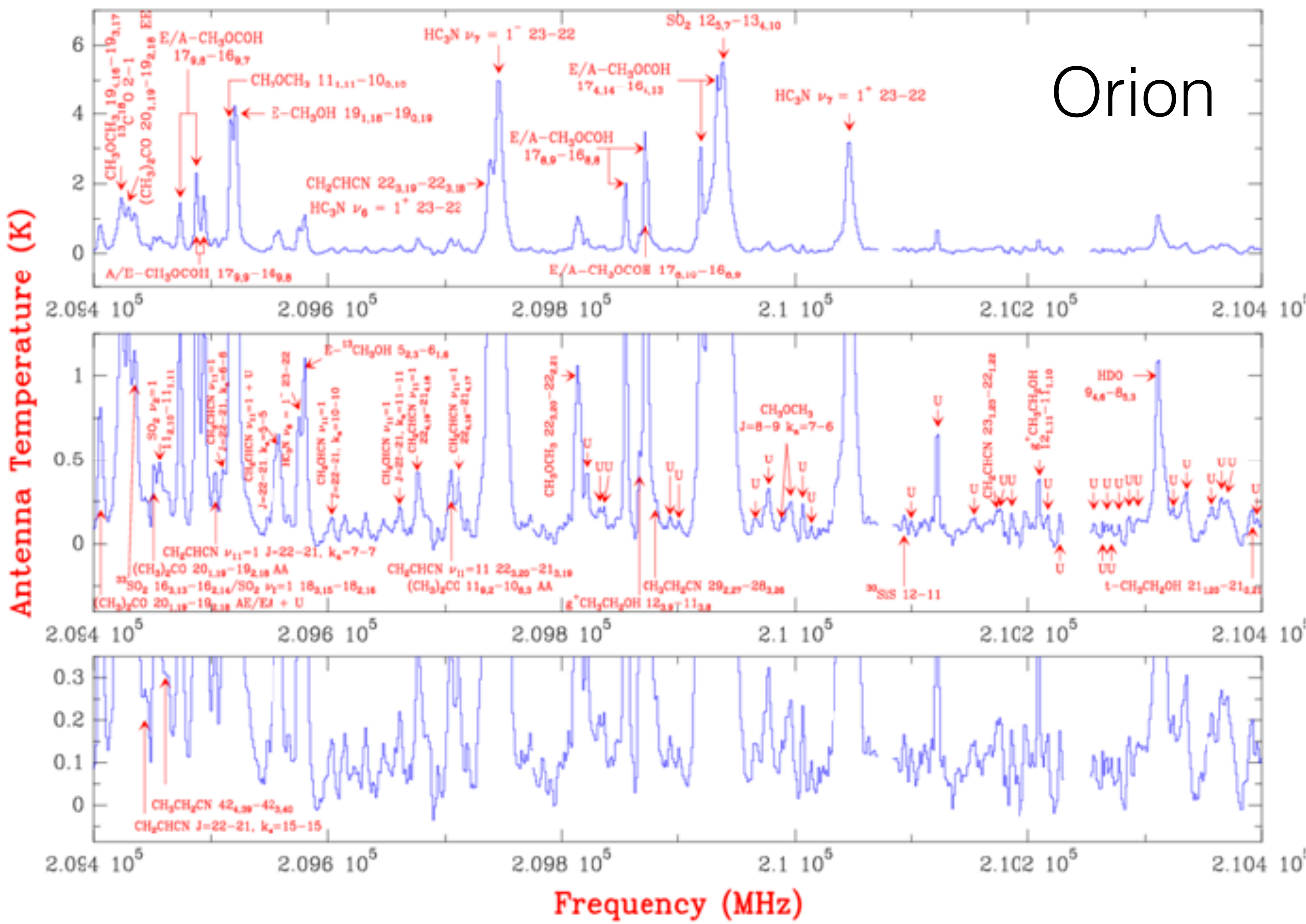
    - Non-polar species (CO, O_2, …) desorb at lower T than polar species (H_2O, CH_3OH, …)
  - Cosmic-ray spot heating
  - UV heating (can also trigger/induce ice reactions by production radicals!)
  - Exothermic chemical reactions
  - Grain-grain collisions, shocks (sputtering)

Ice processing

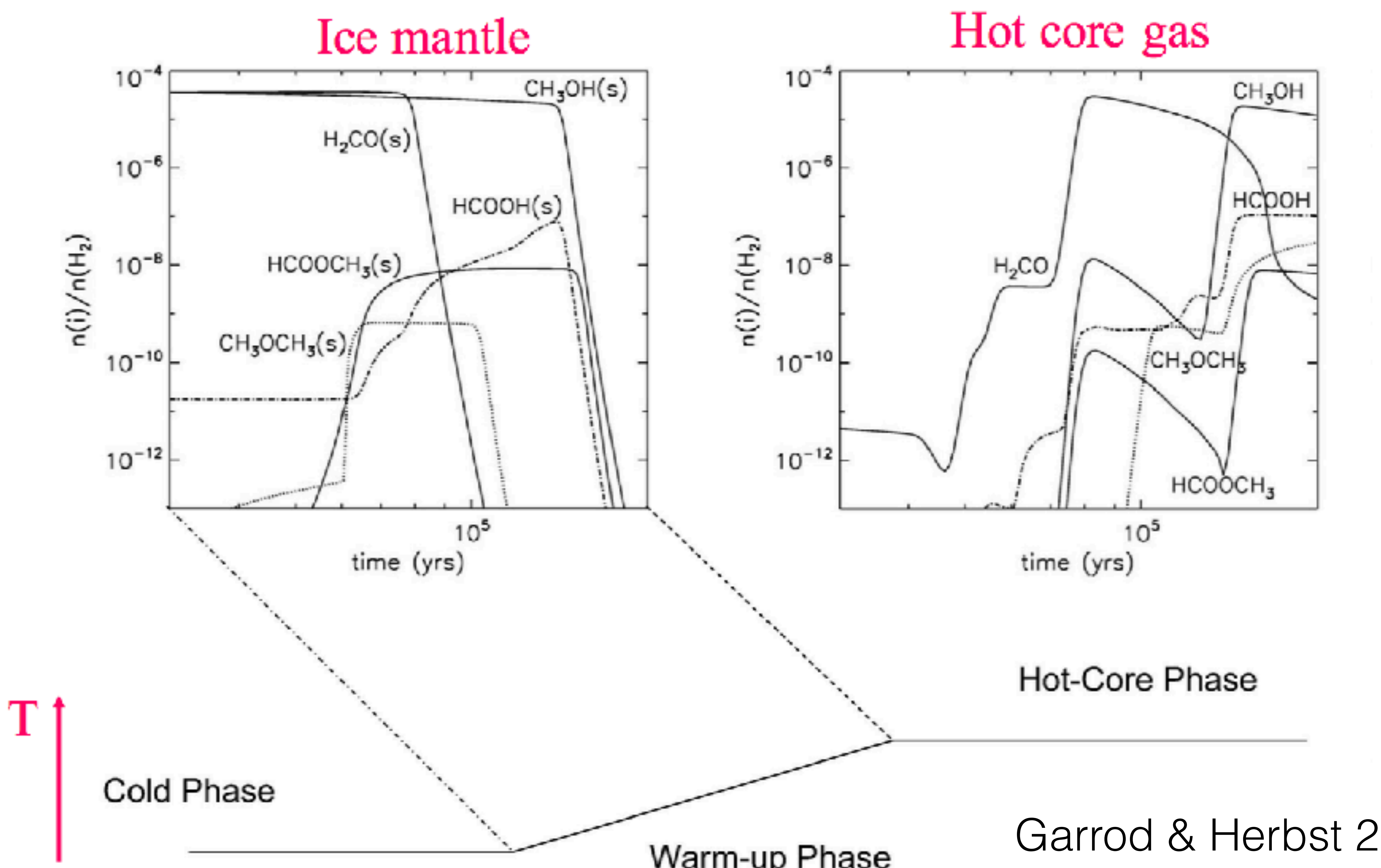


Ice history

- Particularly interesting: hot cores => COMs!



Ice history



Garrod & Herbst 2006
Garrod et al. 2008

Ice history

- So what is the origin of COMs? Three generations:

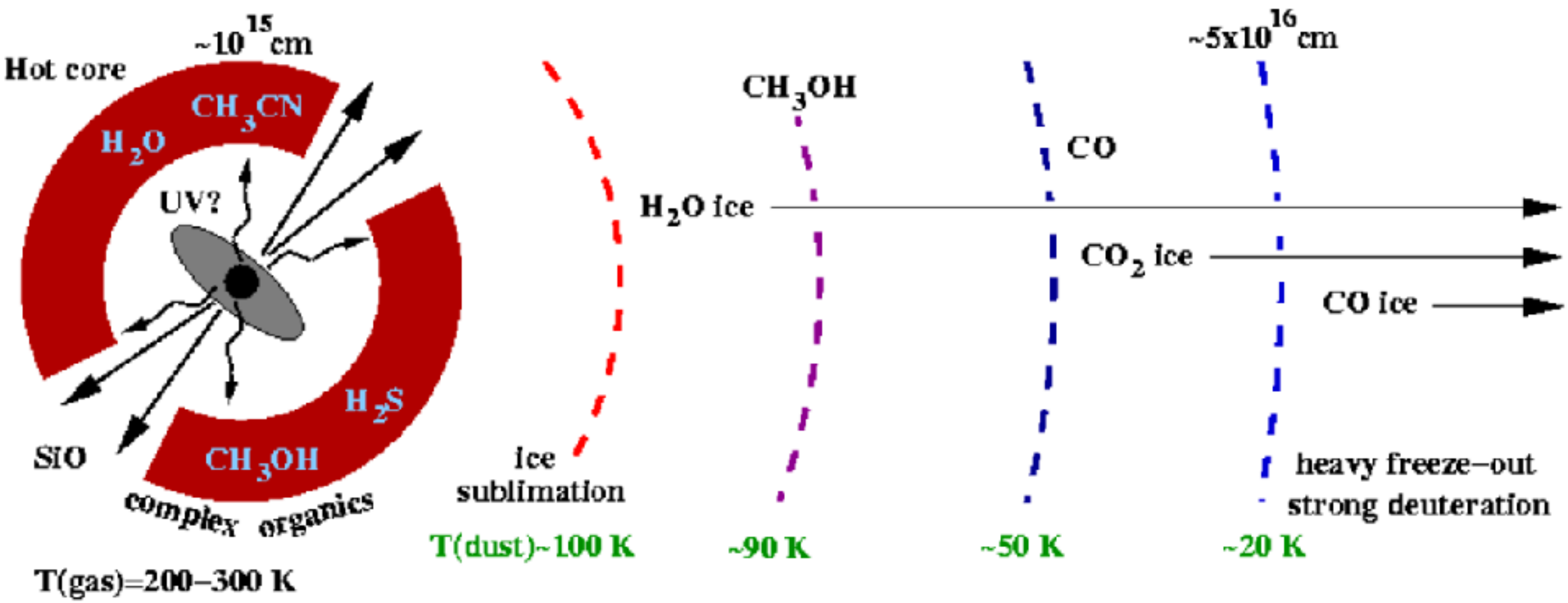
- **Zeroth generation**:
  formed on ices in cold (~10 K) dark clouds: CH_3OH

- **First generation**:
  formed in ices by reactions with radicals at slightly elevated temperatures (20-40 K)
  => Needs a little UV to produce radicals, e.g. by cosmic- ray induced photons

- **Second generation**:
  formed in hot (>100 K) gas from reactions with evaporated species

Herbst & van Dishoeck 2009

Ice history



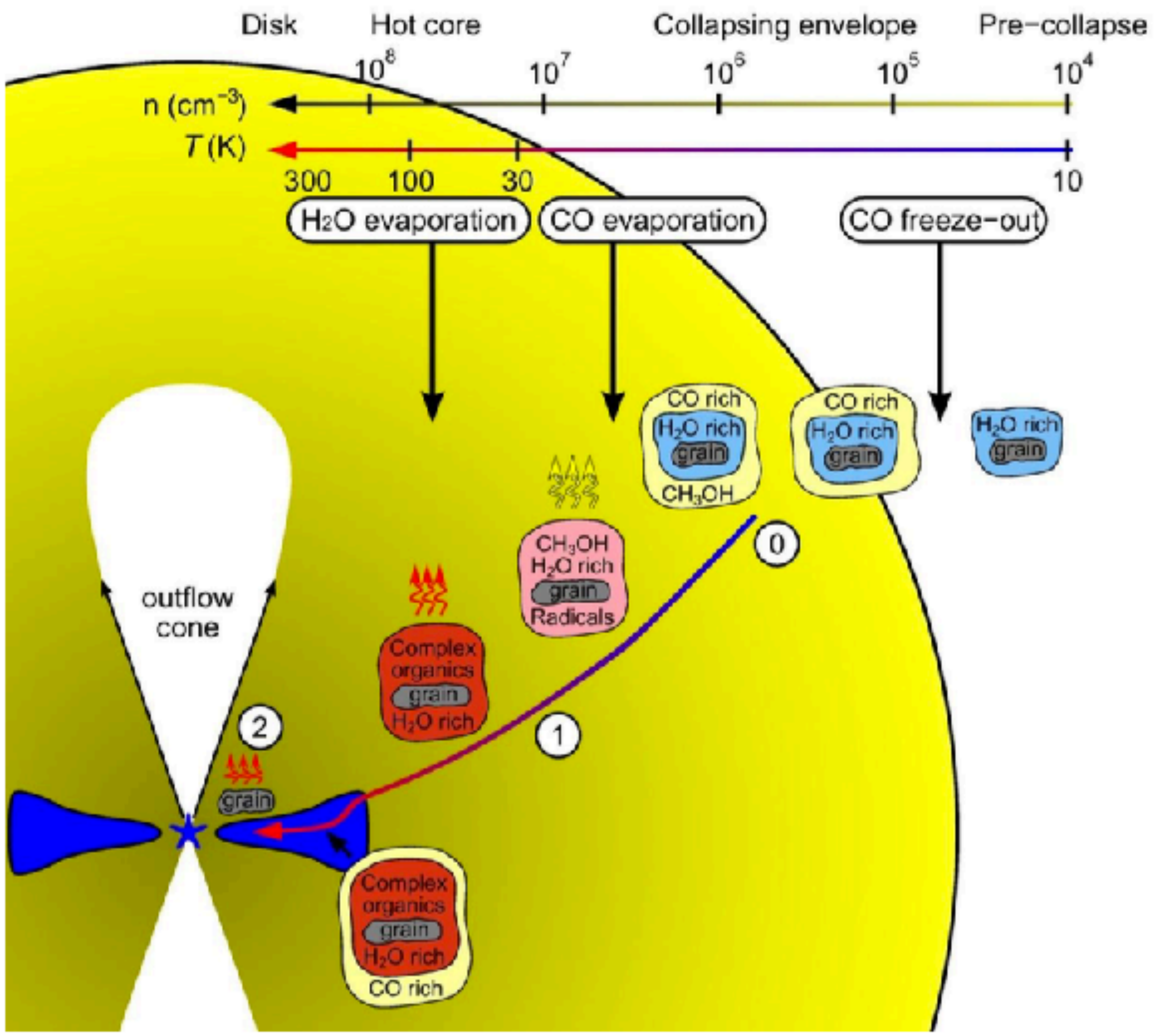
2nd generation

1st generation

0th generation

Ice history

- Heavy freeze-out of molecules onto grains in cold pre-stellar phase
- Grain surface reactions produce new species
- Protostar heats surroundings
    - Ice evaporation
    - Hot core chemistry
- Fraction of ices and gas ends up in disks; remainder is dispersed



Visser et al. 2009

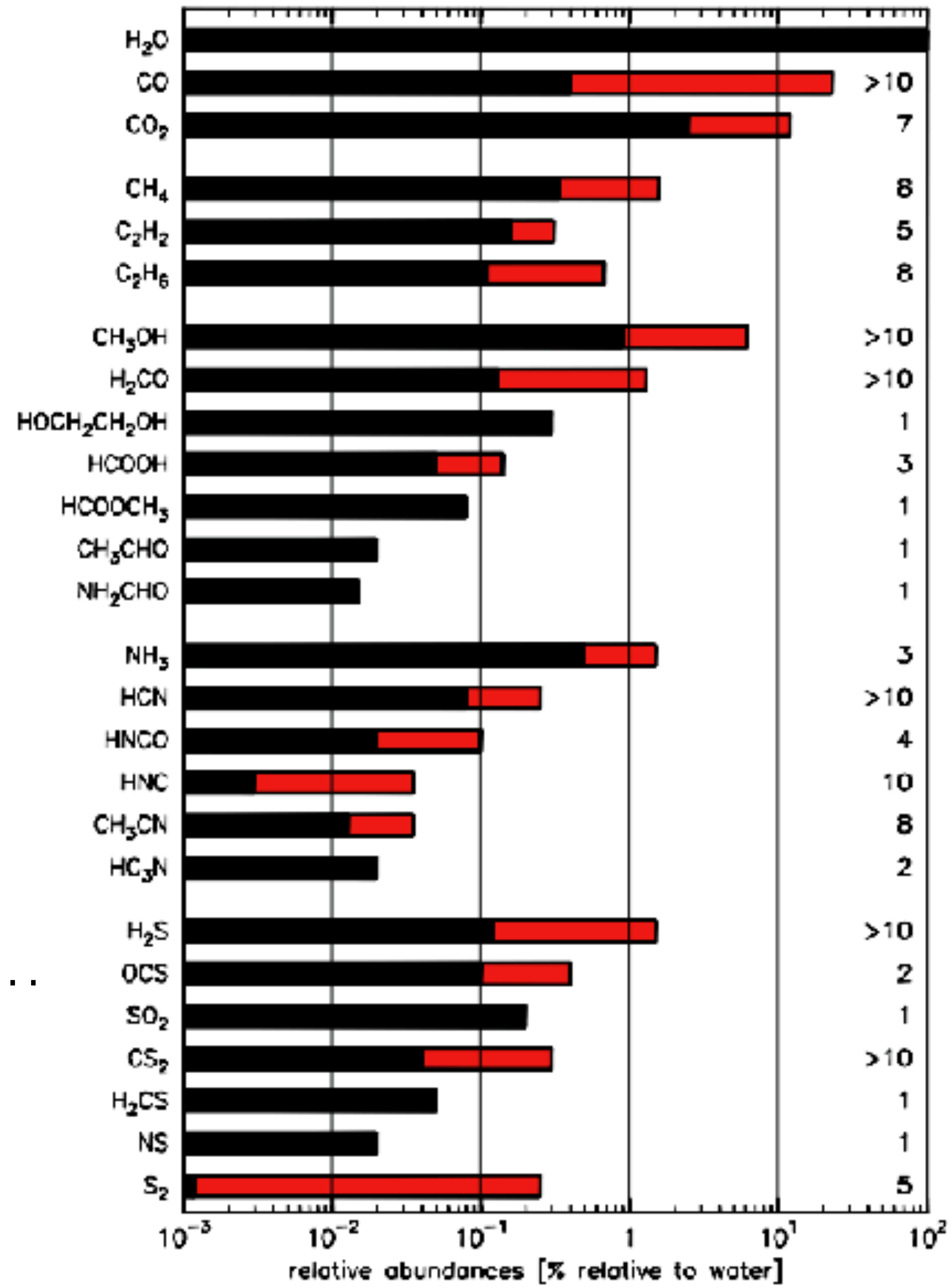
Comets

- Comets: remnants of planetesimals that formed the outer planets

- Most of their life: Kuiper belt or Oort cloud
=> bulk composition is pristine: window on disk chemistry at time of planet formation

Comets

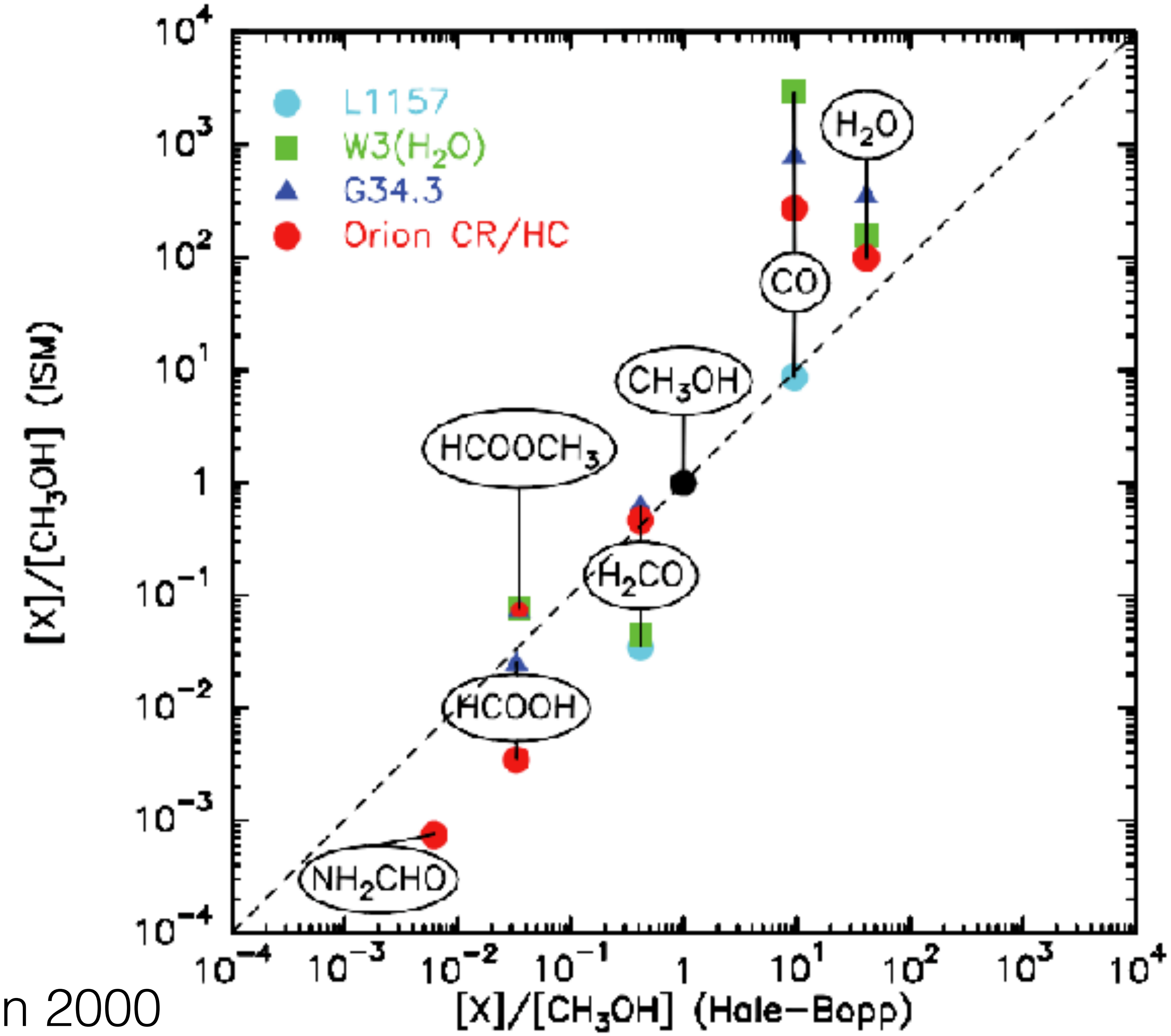
- In situ studies:
  - Deep Impact (9P/Tempel1)
  - EPOXI (103P/Hartley2)
  - STARDUST (81P/Wild2)
  - ROSETTA (67P/Churyumov–Gerasimenko)
- Majority studies: gas phase spectroscopy in the coma (IR/submm)
- Bulk composition is H_2O, CO, CO_2,…
- Processing upon approaching Sun: evaporation and photodissociation



Bockelee-Morvan 2011

Comets

- Somewhat similar ice abundances protostars and comets



Bockelee-Morvan 2000

Comets

- Similar ice abundances protostars and comets and large chemical diversity between comets:
  => mix of original cold core and high T materials

- Long period and short period comets have similar diversity:
  => argument for pristine chemical diversity

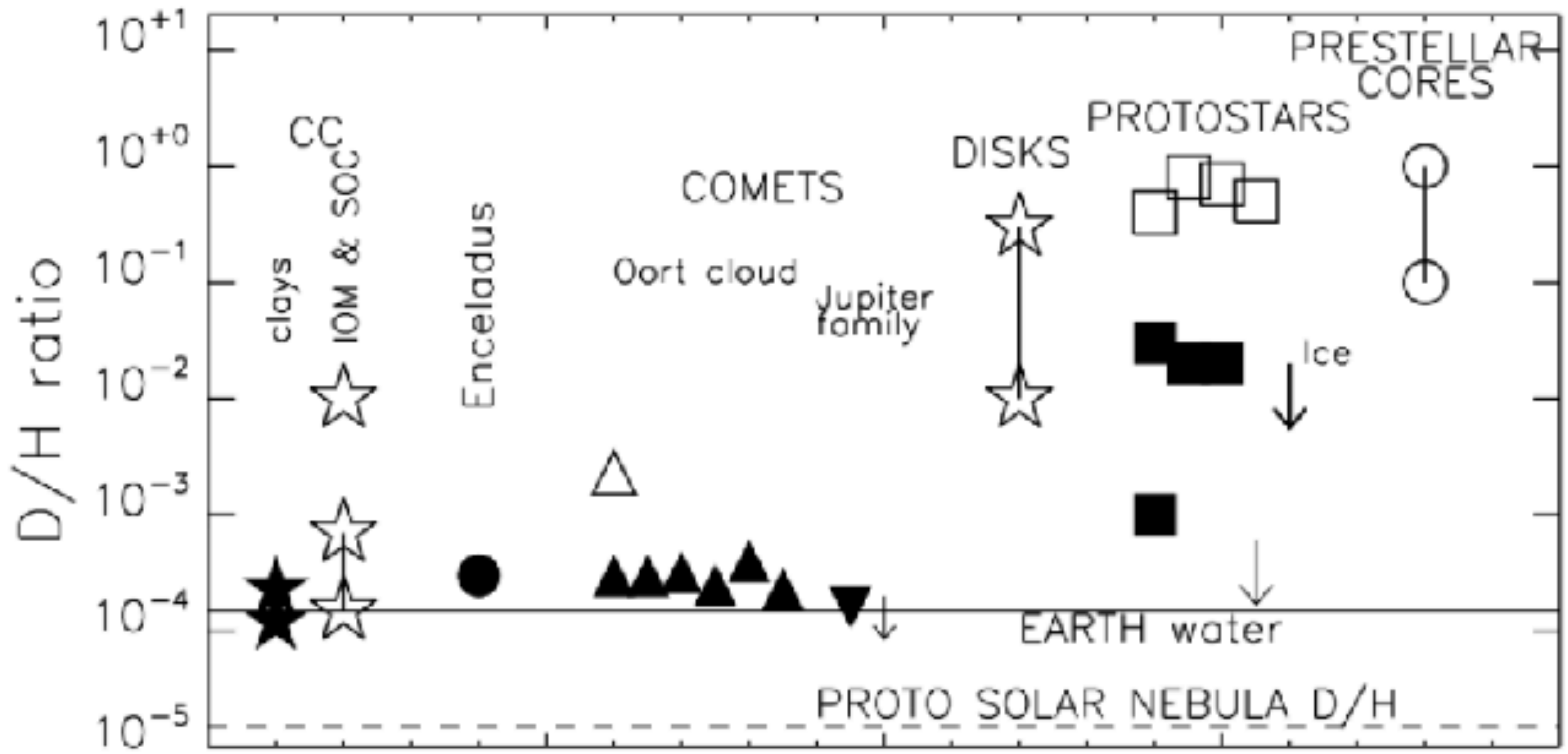
- Major question: is the coma representative for the nucleus composition?

Species	Protostar ices	Comets
H_2O	100	100
CO	3-10	6-30
CO_2	10-35	2-20
CH_3OH	1-25	2
H_2CO	1-7	0.2-1
HCOOH	0.4-2	0.1
NH_3	1-10	0.5-2
CH_4	0.5-2	1

Bockelee-Morvan 2011

Comets

- Isotopic ratios (e.g. D/H, $^{14}N/^{15}N$) important diagnostic for physical/chemical conditions



D/H in Solar System >> protostellar objects:
most measurements of SS objects are from within 20 AU
=> deuteration higher at larger radii/lower temperatures (H_3^+, H_2D^+ formation)

Ceccarelli et al. 2014 (PPVI)

In two weeks

- Laboratory work
  - Experimental setups
  - Type of studies
  - Comparison with astronomical results