Chemistry: from dark clouds to disks

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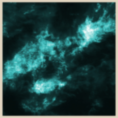
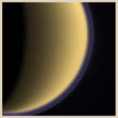
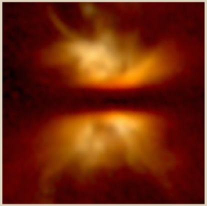
II- From cores to disks

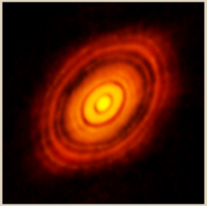
1. The trail of volatile reservoirs from cores to disks
2. Disks irradiation
3. Surface reactions (2)
4. Astrochemical models
5. The interstellar heritage of planetary systems

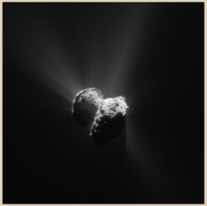
The interstellar heritage of planetary systems







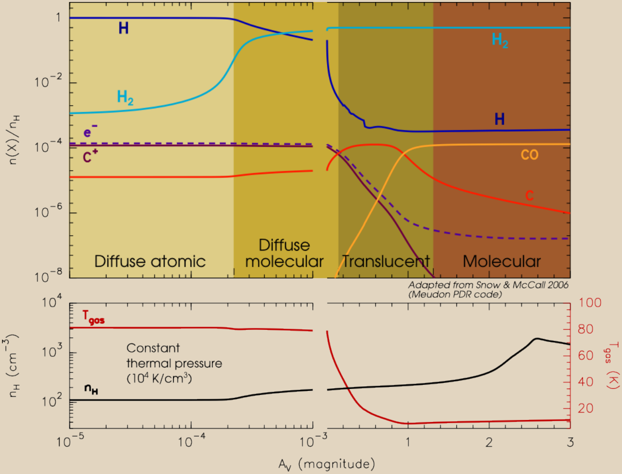




Interstellar phase

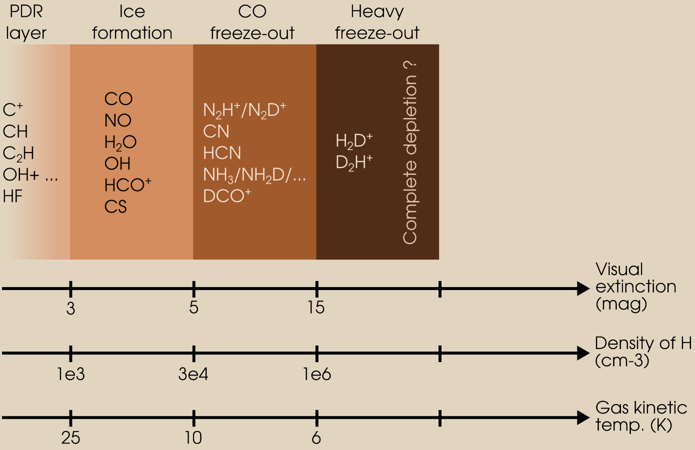
Primitive solar system

Molecular clouds: atomic-to-molecular



Adapted from Snow & McCall 2006 (Meudon PDR code)

Prestellar phase: growing molecular diversity

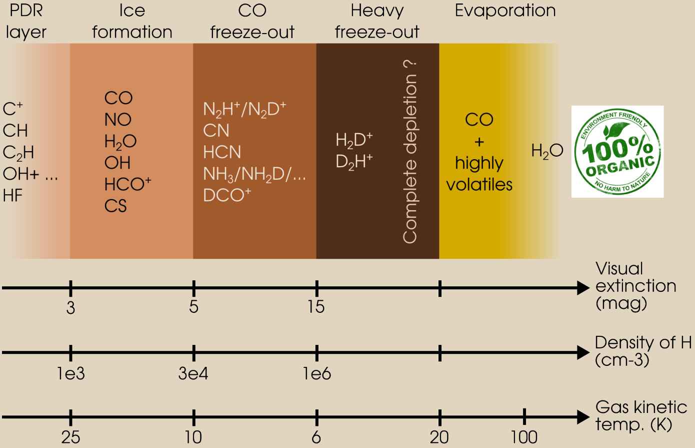


adapted from Bergin & Tafalla 2007

Prestellar phase: growing molecular diversity

- high density: handful of species remain, which are difficult to observe (H_2D^+, D_2H^+, D_3^+) because at high frequency (THz)
- Complete depletion ? Walmsley et al. (2004); Friesen et al. (2014)

Protostellar phase: volatile outburst



PDR layer

C^+
CH
C_2H
OH+ ...
HF

Ice formation

CO
NO
H_2O
OH
HCO^+
CS

CO freeze-out

N_2H^+/N_2D^+
CN
HCN
$NH_3/NH_2D/...$
DCO^+

Heavy freeze-out

H_2D^+
D_2H^+
Complete depletion ?

Evaporation

CO
+
highly volatiles

H_2O

Visual extinction (mag): 3, 5, 15

Density of H (cm-3): 1e3, 3e4, 1e6

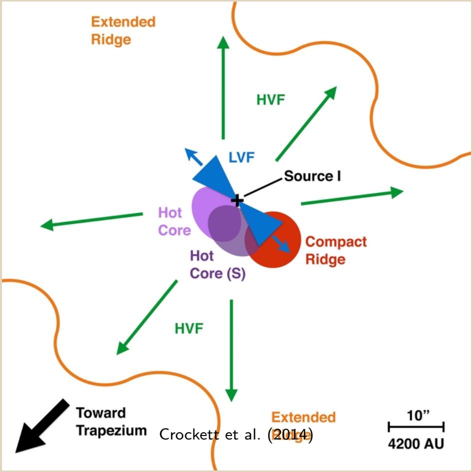
Gas kinetic temp. (K): 25, 10, 6, 20, 100

adapted from Bergin & Tafalla 2007

Organics delivered to early solar system ?

see lecture by D. Bockelée-Morvan

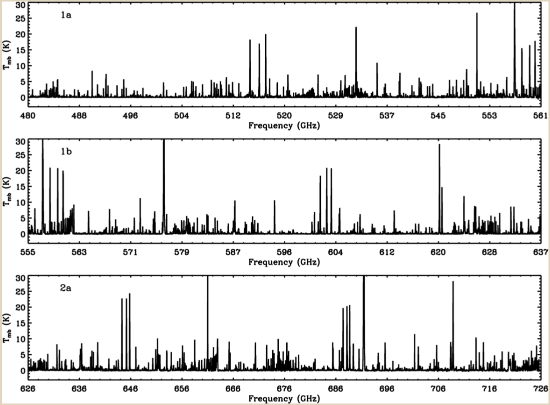
Spectral surveys: Orion KL with Herschel



Crockett et al. (2014)

Orion KL: massive star-forming region

Spectral surveys: Orion KL with Herschel



Crockett et al. (2014)

Spectra dominated by COMs

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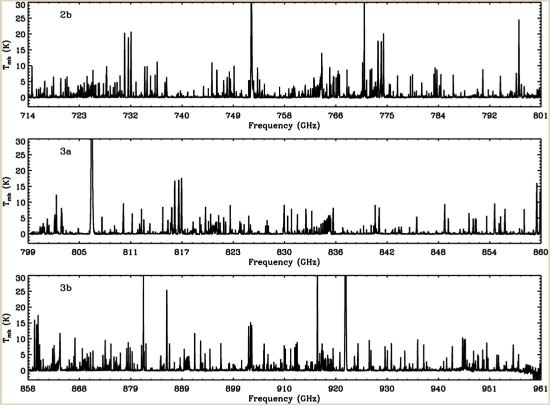

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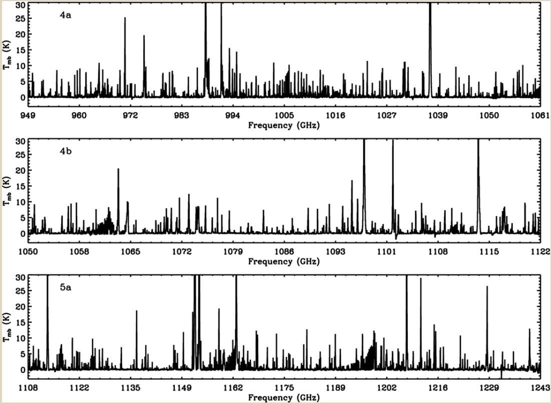

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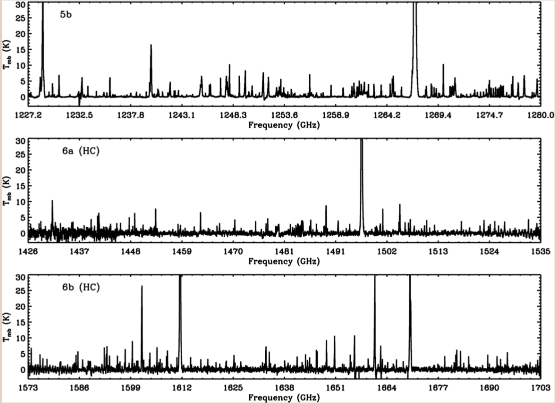

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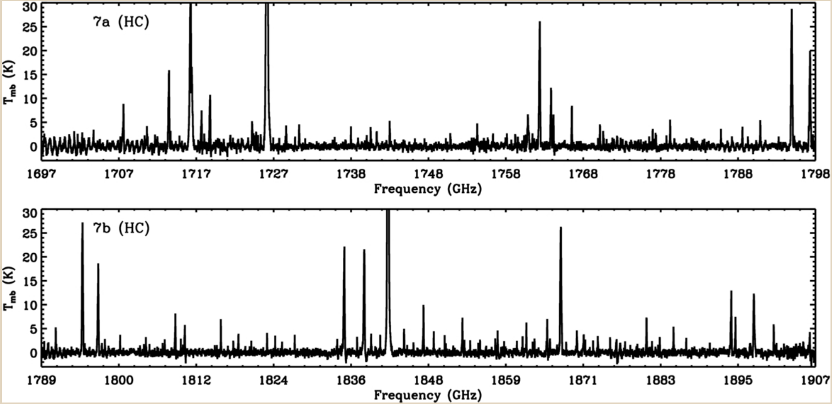
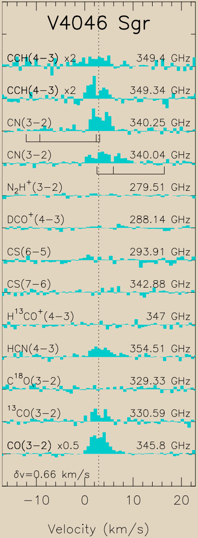


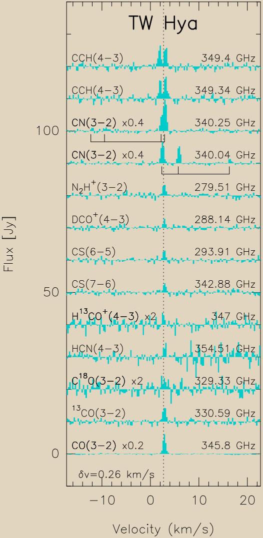
Crockett et al. (2014)

Spectra dominated by COMs

Spectral surveys: TW Hya disk



Kastner et al. (2014)



Punzi et al. (2015)

- Transition disk, ∼ 8 Myr
- Nearest (59.5±0.9 pc, GAIA)
- Essentially: empty
- Wait for A. Dutrey's lecture to see (a little bit) more species and to learn (a lot) more on disks !

The overall picture

- Elemental abundances from stellar nucleosynthesis
- Gas-phase chemistry in molecular clouds ($n_{\mathrm{H}} \approx 1000\,\mathrm{cm}^{-3}$)
- During the next Myr, prestellar phase increases molecular diversity: gas-phase & gas-grain processes
- Depletion of gas-phase species into ices: icy mantles become important reservoirs of heavy elements
- Sublimation in the protostellar phase (hot corinos): T up to ≈ 100 K; part (up to 20%) of the ice mantles returns to the gas-phase;
- photodissociation takes place in the cavity
- Chemistry is – likely only partially – reprocessed during the protostellar phase
- Heavy depletion takes place in the cold/dense regions of protoplanetary disks

Goals and strategy

What are the questions ?

- How can we track the volatile reservoirs if most (if not all) species disappear from the gas phase ?
- Are cometary ices of interstellar origin ?

What are the goals ?

- Know the gas-phase reservoirs on an object-specific basis
- Identify if planetary systems inherited prestellar products

Strategy

- Rely on chemical models to infer the bulk from trace species
- Focus on small species (close to elements) and small networks

Yes we can

- Prestellar phase: see only the tip of the iceberg
- Rely on models to go from the infer the bulk
- Open astrochemical questions:
  - Reservoir of nitrogen: N, N_2, something else ?
  - Reservoir of oxygen: water ice, other ?
  - Reservoir of sulfur: unknown (sum of observable species $\lesssim 1\%$ elemental sulfur
- Known issues in dense clouds
  - nitrogen chemistry is not fully understood (HCN/HNC, isotopic ratios)
  - oxygen is not fully understood (predicted $O_2 \gg$ observed)
  - sulfur: the mystery

But still: we can tell something !

Chemistry: from cores to disks

- All the processes discussed in the context of astrochemistry apply to protoplanetary disks
- The main features are:
  - gas-phase processes
  - surface processes (in water-dominated ices on dust)
  - photo-dissociation regions (PDR) (outskirts of clouds, upper layers of disks)
  - grain size distribution (coagulation in cores, disks)
- Three-body collisions may become efficient in disk midplanes
- To be coupled with dynamical evolution (timescale competition)

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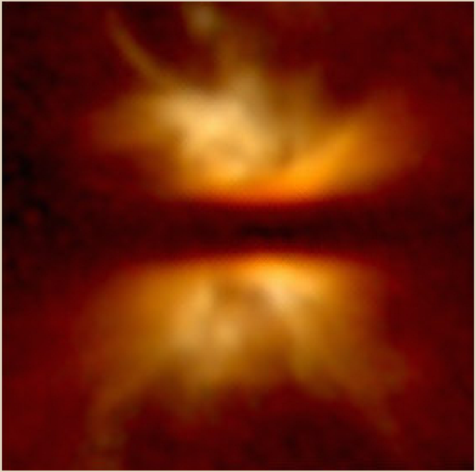
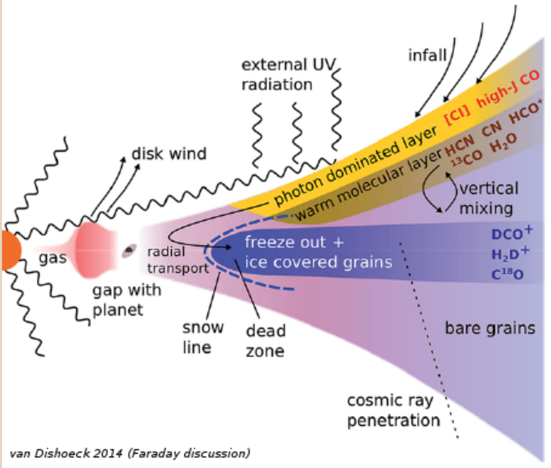
Upper layers of disks



Disks are flared

Upper layers of disks



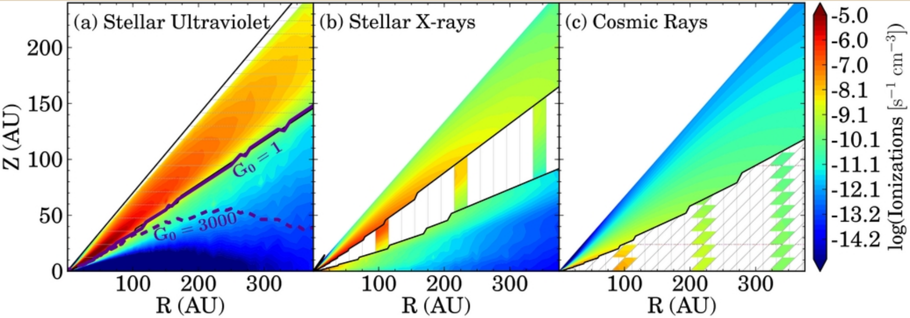
van Dishoeck 2014 (Faraday discussion)

Disks are flared: direct + scattered light

Photodissociation and photoionization

- PDR: photon-dominated region (or photo-dissociation regions)
- Word of caution: for historical reasons, PDRs refer to dense regions ($n_{\mathrm{H}} > 10^4\,\mathrm{cm}^{-3}$); current view is that PDRs are places where UV photons drive the chemistry;
- XDR: X-ray from the central protostar are also important
- UV play a leading role: molecular clouds, upper layer of flared disks
- CN, HCN, HCO^+: probes of the X-ray/UV relative importance (Kastner et al. 2008)
- Important effects in PDR: self-shielding (H_2, CO, N_2), extinction by the dust
- UV field is measured in units of the ISRF (Le Petit et al. 2006)

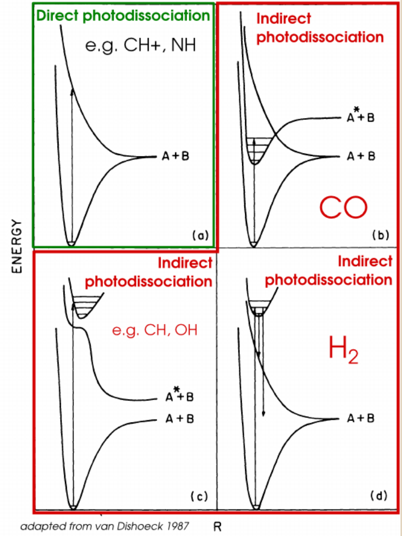
Irradiation of disks



Cleeves et al. (2013)

Cosmic-rays dominate in the midplane regions

UV photodissociation processes



- H_2 and CO photodissociation
- saturation of absorption line
- self-shielding
- mutual shielding (line coincidence)
- UV radiation field evolves when moving inward (PDR models compute this; tables are available)

Selective photodissociation

- Consider two isotopologues, e.g. CO and $C^{18}O$
- Their abundance ratio is the elemental $^{16}O/^{18}O \approx 500$
- Indirect photodissociation favours the more abundant: absorption line of CO is 500 times more opaque than $C^{18}O$
- Photodissociation of CO is 500 times less efficient than $C^{18}O$

$$CO/C^{18}O > 500$$

- also applies to N_2 (Heays et al. 2014):

$$N_2/N^{15}N > (N/^{15}N)_{\rm elemental}$$

(keep this in mind)

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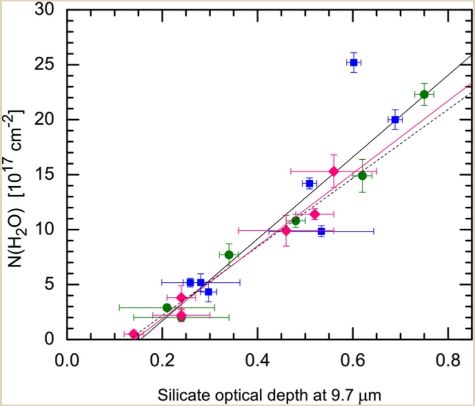
Surface chemistry

- gas-grain processes: accretion, desorption
- chemistry in ices: current view=diffusion limited
- icy grain = third-body in the collision

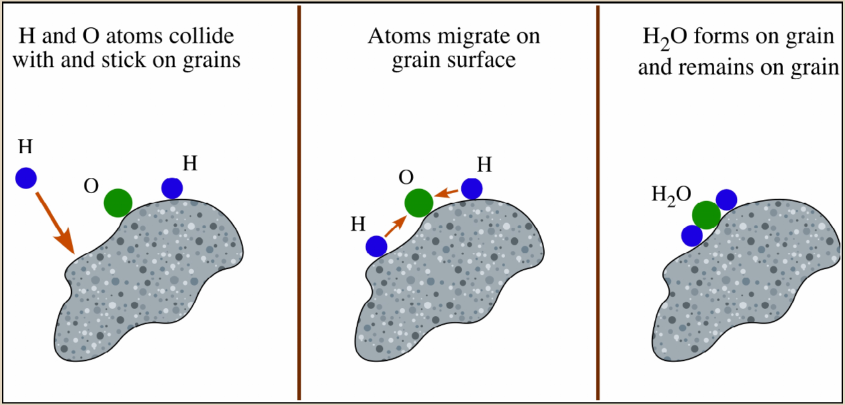
Ice formation



Whittet et al. (2013)

- H_2O ice form at $A_V \approx 3$ mag
- species adsorb into ices
- few 10 of monolayers

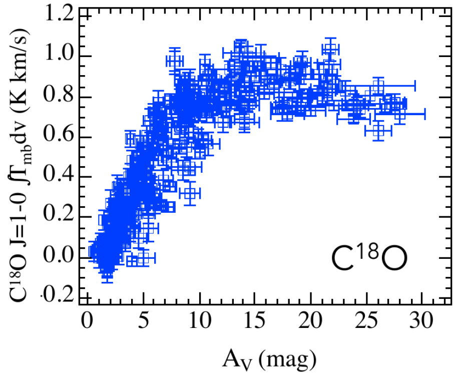
Ice formation



Slide from Bergin

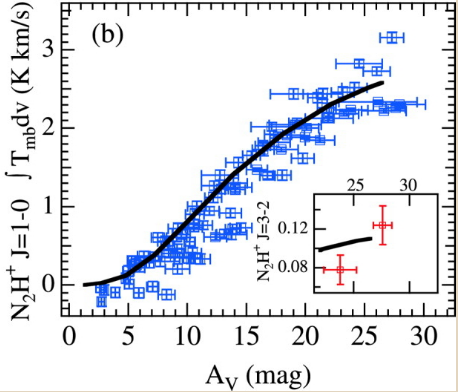
See lecture by E. Dartois (composition, observation, etc)

Molecular freeze-out



- Depletion is systematic (Tafalla et al. 2006)
- C-bearing species disappear from core center
- N-bearing species seem to remain at high densities (Hily-Blant et al. 2008)
- Complete depletion hypothesis: even light species may freeze out (Walmsley et al. 2004; Friesen et al. 2014)

Molecular freeze-out



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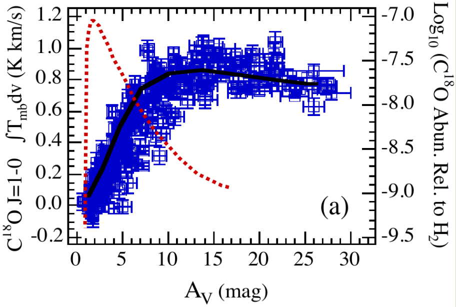

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Chemistry on interstellar grain surface

Usual view: diffusion limited process. Work in progress (you !)

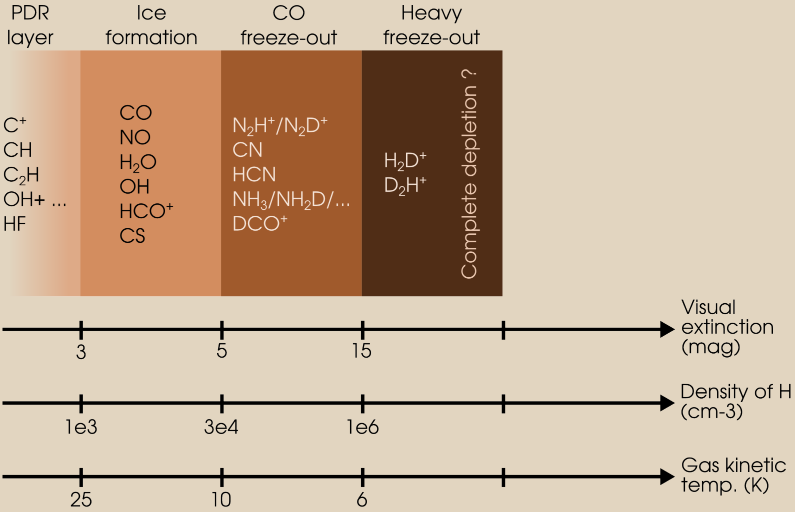
- $k_{\rm hop} = \nu_0 \exp(-\eta E_b/kT_d)$
- ν_0: vibrational freq. of adsorbed species on grain; varies with mass
- $\eta \approx 0.3 - 0.7$
- E_b: binding energy (or energy barrier to overcome for hopping to proceed)
- quantum tunneling: decreases with mass of the particle
- Warning: several caveats
- Surface inhomogeneity (E_b and η both likely to vary spatially)
- Competition between diffusion and reaction unclear

Molecular freeze-out

Depletion is a competition between accretion and evaporation

- Accretion: $k_{\rm acc} = n_d \sigma_d v_{\rm th} S(T, T_d) \approx 10^{-17} (T/10)^{0.5} n_{\rm H}\,{\rm s}^{-1}$
- sticking coefficient $S \approx 1$ (0.8 for H)
- depletion timescale: $\tau_{\rm acc} \approx 10^{10}/n_{\rm H}$ yr
- evaporation timescale (see diffusion): $\tau_{\rm evap} = \nu_0^{-1} \exp(E_b/kT_d)$
- freeze-out = accretion vs evaporation
- freeze-out: controlled by T, $T_{\rm d}$, $n_{\rm H}$
- $T_{\rm grain} > T_{\rm freezeout}$: little freeze-out
- $T_{\rm grain} < T_{\rm freezeout}$: massive freeze-out
- $T_{\rm grain} \sim 10$ K in cores: freeze-out
- Same caveats as before

Depletion in prestellar cores



PDR layer

C^+
CH
C_2H
OH+ ...
HF

Ice formation

CO
NO
H_2O
OH
HCO^+
CS

CO freeze-out

N_2H^+/N_2D^+
CN
HCN
$NH_3/NH_2D/$...
DCO^+

Heavy freeze-out

H_2D^+
D_2H^+

Complete depletion ?

Visual extinction (mag): 3, 5, 15

Density of H (cm-3): 1e3, 3e4, 1e6

Gas kinetic temp. (K): 25, 10, 6

adapted from Bergin & Tafalla 2007

Ice chemistry: a minimalist astrochemical view

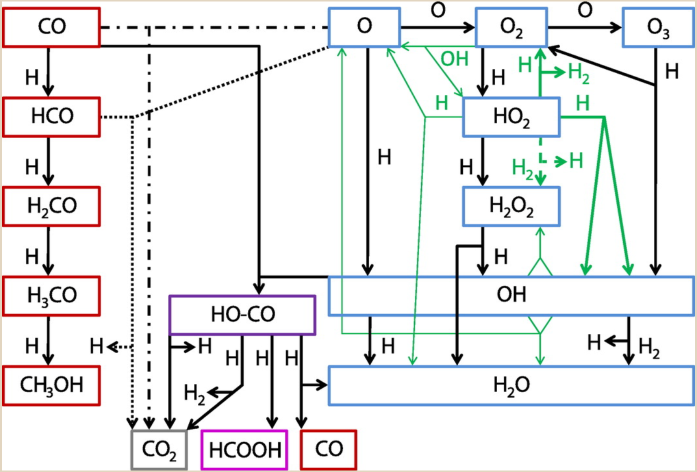
Primary reactions: hydrogenation of ice

- $H + H \longrightarrow H_2$
- O, O_2, O_3 + H → H_2O
- N → NH_3
- CO → CH_3OH (methanol)
- C → CH_4
- and also reactions with other atoms: $CO + O \longrightarrow CO_2$

Other

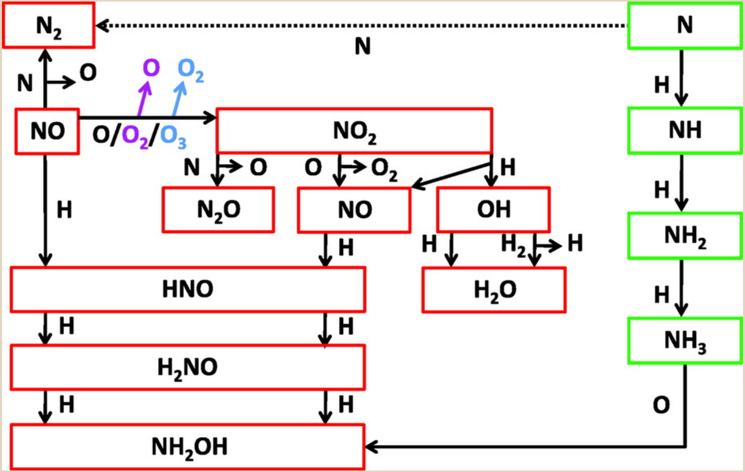
- external source of energy: UV-induced reactions, cosmic rays (see E. Dartois)
- isotopic exchanges

Networks



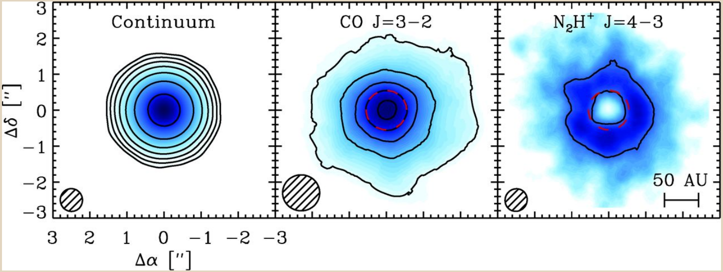
Linnartz et al. (2015)

Networks



Linnartz et al. (2015)

Snow lines



Qi et al. (2013)

- snow line: transition between freeze-out and desorption
- driven by the density and temperature radial and vertical profiles
- radial and vertical snow lines
- species disappear/appear at snow lines
- the CO snow-line: CO is destroyed by $CO + N_2H^+ \longrightarrow N_2 + HCO^+$; spatial anti-correlation between CO and N_2H^+
- Lecture by A. Dutrey

Chemistry in disks

- observations do not sample the disk midplane (yet ?)
- chemistry in disks is very active
- radial/vertical mixing is probably important
- dust settling and growth is essential (dust surface !): time-dependent chemistry and photodissociation
- feedback of chemistry on the turbulence (through ionization)
- chemical timescales can be short: big issue
- A very competitive and very active field of research
- A. Dutrey lecture

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Overview

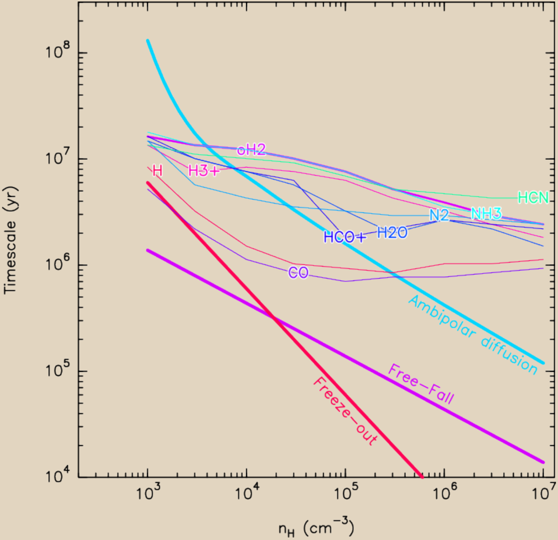
The engine

- The network: typically 100-500 species and tenfold gas-phase reactions
- Philosophy: Small networks vs big networks
- Choice: w/ or w/o ice chemistry
- Important: secondary photons, grain charge

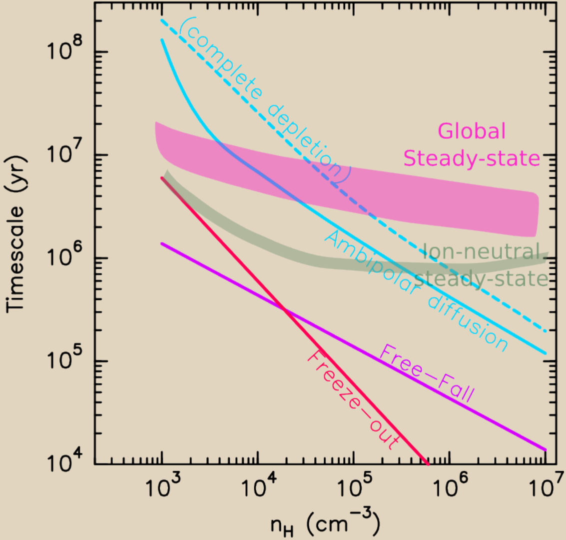
A model

- Boundary conditions (elemental abundances)
- Models: time-dependent (needs initial partitionning) / steady-state
- Physical conditions (0D to 3D); with feedback or not
- Solve a closed system of 1st order ODE (with time or zero-finding)

Timescales


Timescale (yr)
10^8
10^7
10^6
10^5
10^4
10^3
10^4
10^5
10^6
10^7
n_H (cm^{-3})
oH2
H
H3+
HCN
N2
NH3
HCO+
H2O
CO
Ambipolar diffusion
Free–Fall
Freeze–out

Timescales


Timescale (yr)
10^4
10^5
10^6
10^7
10^8
10^3
10^4
10^5
10^6
10^7
n_H (cm^{-3})
(complete depletion)
Global
Steady-state
Ion-neutral
steady-state
Ambipolar diffusion
Free–Fall
Freeze–out

Models vs observations

Models in practice

- Public databases (KIDA, UMIST) and codes (`astrochem`, `nahoon`)
- Boundary conditions

Comparison with observations

- strategy: focus on species or overall agreement (different approach)
- comparison in terms of abundances (abundance ratios more robust)
- or in terms of spectra (line radiative transfer: means problems)
- minimization: figure of merit ? (χ^2 generally not a good one...)
- overall, this is a problem $\rightarrow$ opportunities

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Isotopic ratios

- How can we identify interstellar records in early solar system objects ?
- Are cometary ices (at least partially) of interstellar origin ?
- Strategy: match species at different phases / risky
- Another strategy: isotopic ratios / more robust
- See lecture by C. Burkhardt

The origin of water on Earth and the D/H ratio in water

- Molecular clouds form water
- Water ice during the cold prestellar phase (freeze-out + formation in ices by hydrogenation of O and/or O_2): H_2O/H up to 5×10^{-5}, $\sim$ bulk of volatile oxygen budget
- D/H in the PSN: 2.5×10^{-5}
- D/H in Earth oceans: 1.6×10^{-4}
- One explanation: record of prestellar stage. Why ?

Chemical mass fractionation

- $H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 232\,K$
- Energy difference due to different mass: fundamental energy is $1/2\hbar\omega$, where for a spring, $\omega = \sqrt{k/\mu}$
- Note: exothermicity indeed depends on ortho:para states of all species
- this is a thermoneutral reaction: need to consider the reverse reaction
- at steady-state $k_f/k_r = K(T) = [\mathrm{H_2D^+}][\mathrm{H_2}]/[\mathrm{H_3^+}][\mathrm{HD}] = \exp(-232/T)$
- T decreases → equilibrium shifts to the right, favouring the heaviest species
- fractionation, i.e. deviation from the elemental isotopic ratio:

$$\mathrm{H_2D^+/H_3^+} > (\mathrm{D/H})_{\mathrm{elemental}}$$

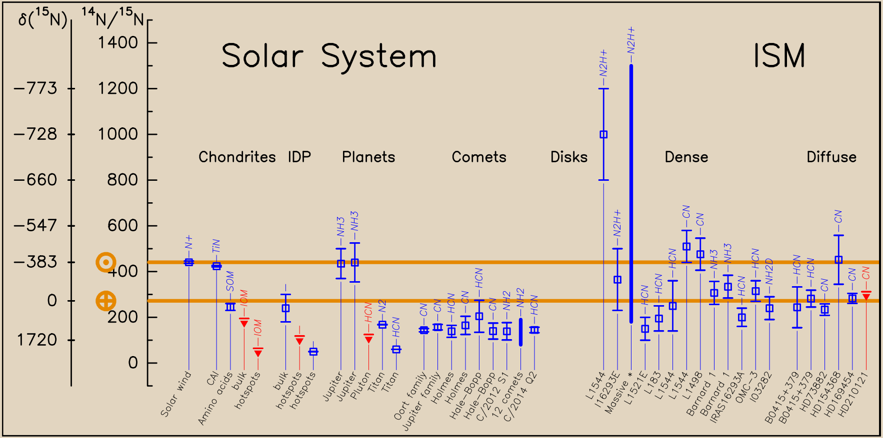
- this fractionation is transfered by chemistry to water (with H_2D+ replacing H_3^+ in the gas-phase)

The origin of water on Earth and the D/H ratio in water

The Cleeves et al. (2014) scenario:

- o:p ratios make $\Delta E \approx 124$ K: fractionation requires $T \leq 50$ K to be efficient: could be midplane, or prestellar phase
- Assume (there are models for this) that cosmic-rays are strongly repealed from disks by the heliosphere: CR flux is reduced by ≈ 100;
- then not enough H_3^+ in the disk (ionization is too low): deuterium fractionation is damped out, hence that of water: never reach the 50-fold enrichment of HDO/H_2O in Earth oceans
- Question: are CR expelled from pp disks ?

The origin of nitrogen in the solar system

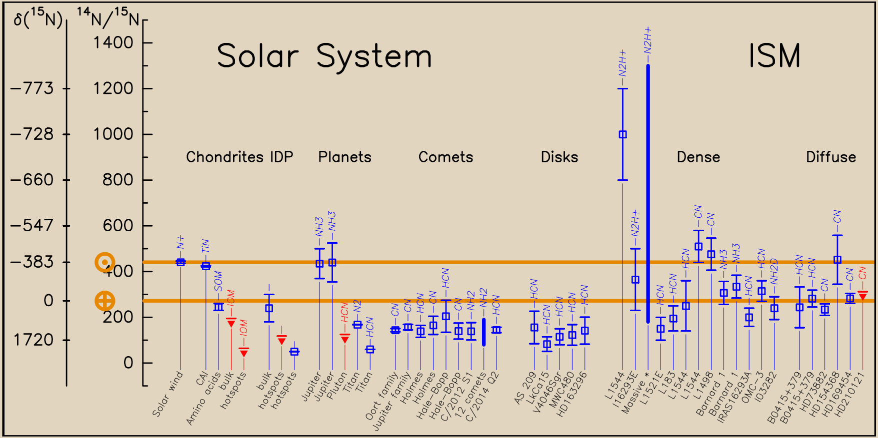


Cometary ratio: 140; elemental (Sun, Jupiter): 441, Earth 272

Origin of the cometary ratio

- comets did not sample the bulk ? spatial inhomogeneity in the PSN ?
- did not trap the bulk ?
- value on Earth ?
- what are the reservoirs of nitrogen in the PSN: N, N_2, other ? what are their isotopic ratios ?
- are the different isotopic ratios due to processes in the PSN ? interstellar (like for water) ?

The origin of nitrogen in the solar system

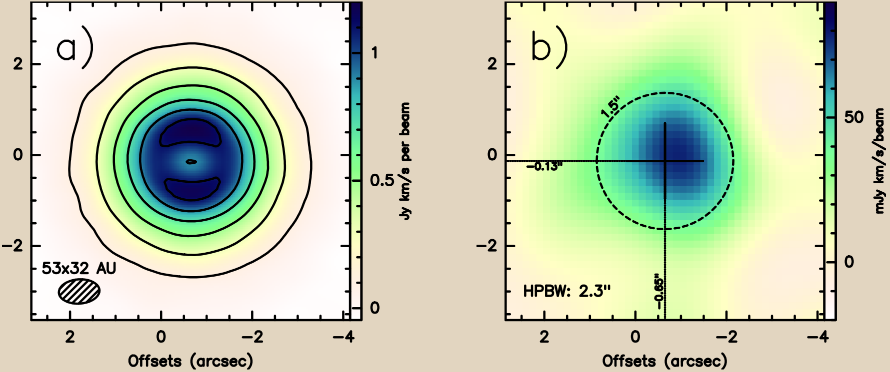


(indirect measurement) HCN in disks ≈ 130; Guzman et al 2017

Origin of the cometary ratio

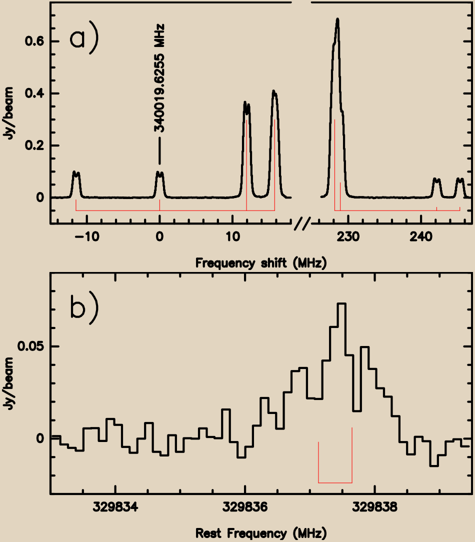
- matching isotopic ratio in disks and comets
- these authors argue towards local processes in the disks: selective photodissociation; no inheritance from prestellar phase
- caveat: indirect measurement (usual method however)
- $H^{13}CN/HC^{15}N$ x $(N/^{15}N) \rightarrow HCN/HC^{15}N$

The CN/C^{15}N ratio in TW Hya

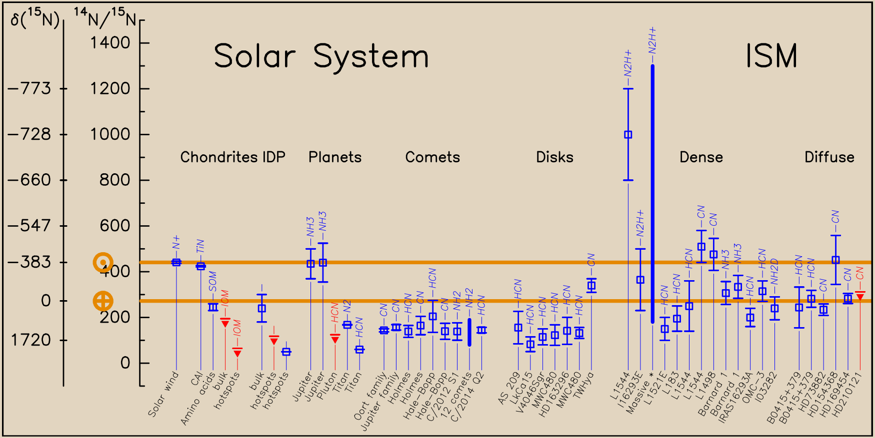


Directly measure CN/C^{15}N isotopic ratio

The CN/C^{15}N ratio in TW Hya



The origin of nitrogen in the solar system



Direct measurement in CN in TW Hya 323 ± 30; Hily-Blant et al 2017

So what ?

The nitrogen isotopic ratio in a galactic context

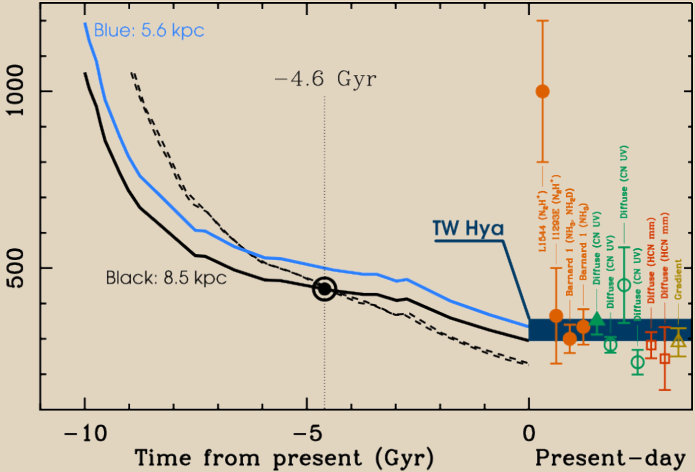
Two reservoirs of nitrogen in disks

- ISM is chemically homogeneous within 1.5 kpc
- $HCN/HC^{15}N=140$ in 5 disks and $CN/C^{15}N=330$ (in one disk)
- Hence, at least one disk carries two isotopic reservoirs

The present-day isotopic ratio in the local ISM

- CN ratio is 330; in very good agreement with direct measurements in local ISM dense cores
- proposal: this is the present-day isotopic ratio in the local ISM
- How to compare present-day isotopic ratios in the local ISM with the 441 ratio in the PSN at -4.6 Gyr at Sun's (unknown) birthplace ?
- answer: ask galactic chemical evolution models

Galactic chemical evolution of nitrogen



Perfect agreement with outward migration scenario (Minchev et al. 2013)

Consequences

- GCE models: today's elemental can not be as low as 140

⇒ HCN traces a fractionated (hence secondary) reservoir

- CN ring emission encompasses Kuiper-belt region: comets did sample the elemental ratio
- evolution of the $N/^{15}N$ ratio in comets over last 4.6 Gyr not needed

New scenario

- new scenario: N_2 is (and was) the main reservoir of nitrogen in disks $\Rightarrow$ must have the elemental isotopic ratio, which was 441 in the PSN
- CN is simply a tracer of this reservoir (consistent with chemical models)
- but N_2 was not trapped into cometary ices (too volatile ???); consistent with Hale-Bopp and ROSETTA results (very low N_2/CO)
- instead, comets trapped a secondary, minor, reservoir (traced by HCN)
- N_2 would have been captured by the Sun and Jupiter (fast ???)
- Earth: mixing of these two volatile nitrogen reservoirs (441 and 140) ?

Nitrogen origin: open questions

- selective photodissociation: radial variation of the isotopic ratio ?
- more CN observations
- origin of the fractionated reservoir: direct measurement of N-isotopic ratio in prestellar cores needed (indeed, done...)
- what could prevent comets from trapping N_2 ?

Summary for lecture 2

- prestellar phase builds molecular diversity and rich ices
- protostellar phase liberates $\approx 20\%$ of the products into the warm cavity: this is still debated
- if not all the ices are processed, interstellar ices may be partially preserved
- Are acometary ices of interstellar origin ? (the O_2 abundance in 67P/G-C: D. Bocklée-Morvan lecture)
- isotopic ratios can be used to establish the link between different evolutionary stages
- this however requires fractionation processes to be known (perhaps not entirely the case for nitrogen)

Concluding remarks

- The interstellar-to-primitive solar system chemical heritage is an extremely active field of research
- Surface chemistry: from laboratory experiments to the astrophysical context
- Comparisons between astrochemical models and observations
- Towards accurate astrochemistry: improved networks (nuclear spin chemistry, isotopic fractionation)
- The initial and boundary conditions: towards astrochemistry clocks
- Overall volatile reservoirs of C, N, O, S, P, from cores to disks: towards the origin of life in planetary systems

Thank you !

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