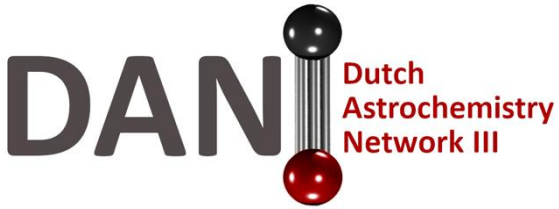
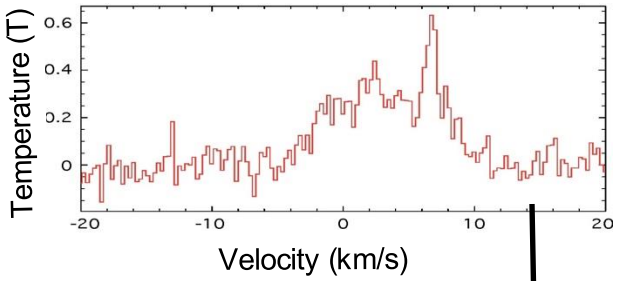
Chemical networks (with modeling)

Valentine Wakelam
Valentine.wakelam@u-bordeaux.fr

Funded by the European Union



Astrochemistry - strategy



Radiative transfert model

Observed abundances

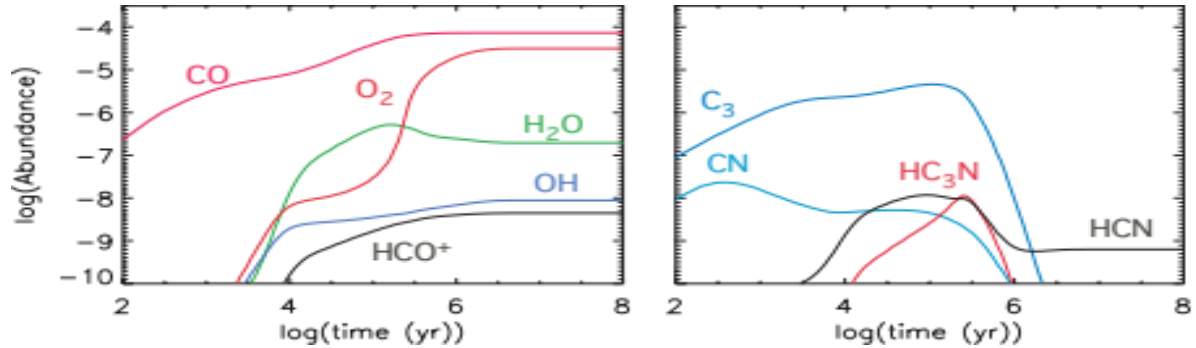
Radiatif-Magneto-Hydrodynamic simulations of star formation

Comparisons

Predictions

Predictions

Chemical model



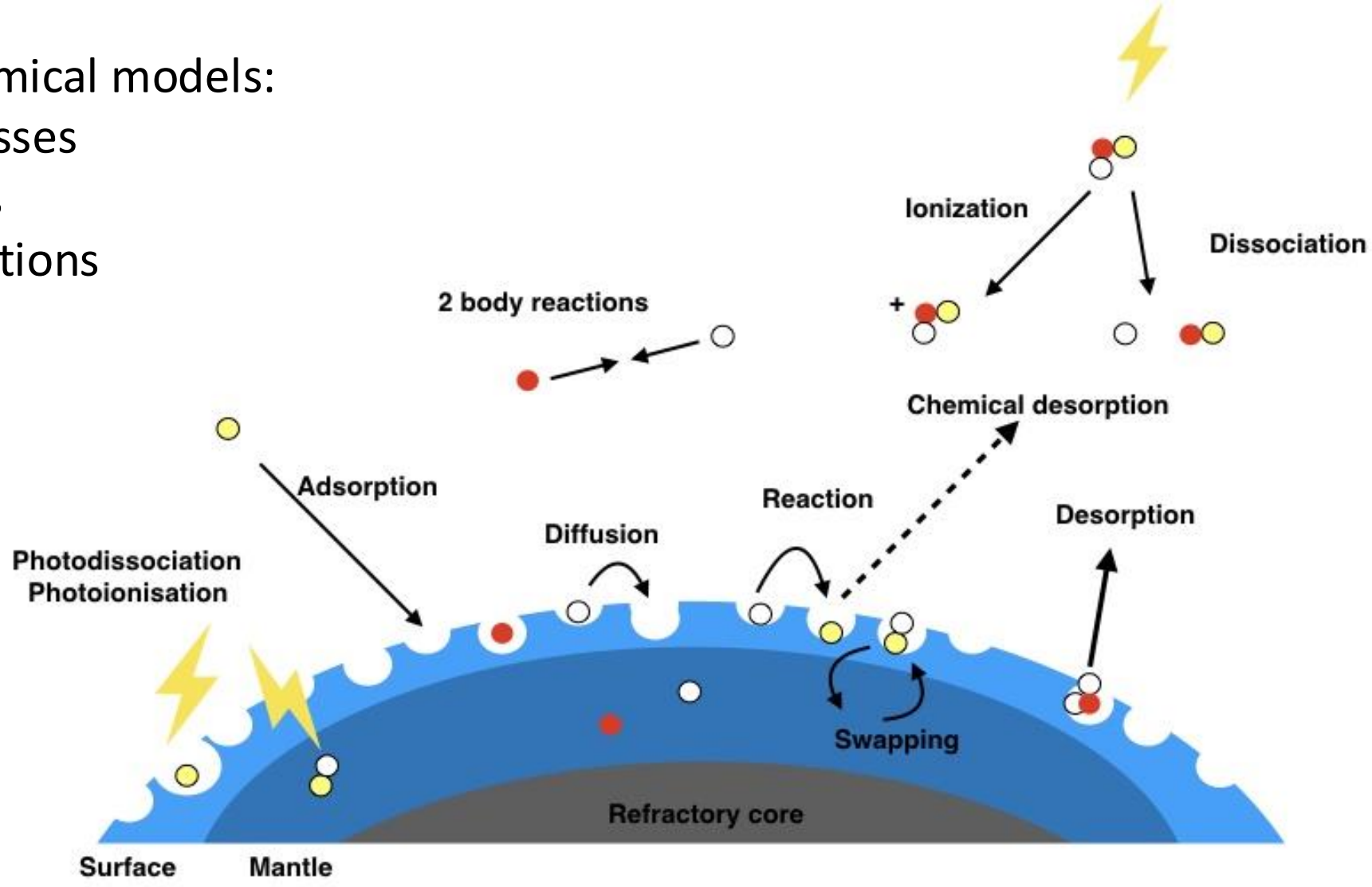
Physical-chemical data

Experimental and theoretical physics and chemistry

Chemical models – gas and grain coupling

Complete astrochemical models:

- Gas-phase processes
- Surface reactions
- Gas-grain interactions

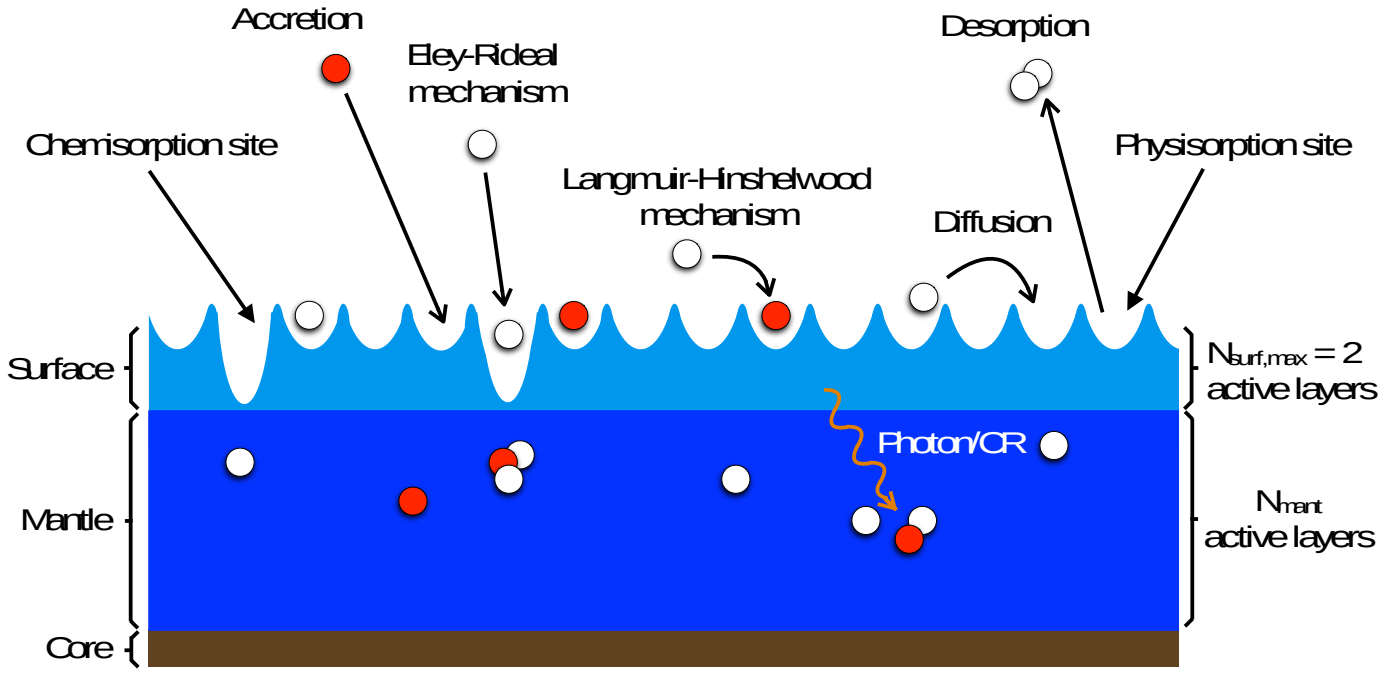


Chemical models – grain surface processes

Surface processes :
- Thermal diffusion
- Tunneling
- Non-diffusion chemistry

Desorption:
- Thermal
- Cosmic-ray heating
- Chemical desorption
- Photpo-desorption
- Cosmic-ray sputtering
- …

Photo-processes



Depending on species binding energies and diffusion energies. In most models diffusion energies are proportional to the binding energies

Chemical models – general considerations

Rate equation approximation (for surface reactions) -> each surface process is represented by a reaction

Solving differential equations for each species at each time step

$$\frac{dn_i(t)}{dt} = \sum_l \sum_j (k_{lj} n_l(t) n_j(t)) - n_i(t) \sum_j (k_{ij} n_j(t)) - k_{\mathrm{ads},i} n_i(t) n_{\mathrm{gr}} + (k_{\mathrm{evap},i} + k_{\mathrm{crd},i})\, n_i^s(t), \quad (2.1)$$

$$\frac{dn_i^s(t)}{dt} = \sum_l \sum_j (k_{lj} n_l^s(t) n_j^s(t)) - n_i^s(t) \sum_j (k_{ij} n_j^s(t)) + k_{\mathrm{ads},i} n_i(t) n_{\mathrm{gr}} - (k_{\mathrm{evap},i} + k_{\mathrm{crd},i})\, n_i^s(t), \quad (2.2)$$

Model parameters:

- Gas and dust temperature
- Irradiation fields (UV, secondary UV, cosmic-rays)
- Density of gas and dust
- Initial conditions (with elemental abundances)
- Geometry of the source
- Chemical network (and many parameters for surface processes)
- ++++

Chemical networks

Chemical networks:
List of chemical reactions (including surface processes and gas-grain interactions.
Each reaction is associated with a number of parameters tabulated to compute the rate coefficients in the conditions of the simulations (can be T dependent, UV or cosmic-ray dependent etc).

As an example, in the chemical networks provided with Nautilus:
584 chemical species
7667 gas-phase chemical reactions
4837 grain-surface reactions and gas-grain interactions (absorption, desortion reactions)

Chemical models – general considerations

Increasing complexity of chemical models

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

Chemical models – general considerations

Increasing complexity of chemical models

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

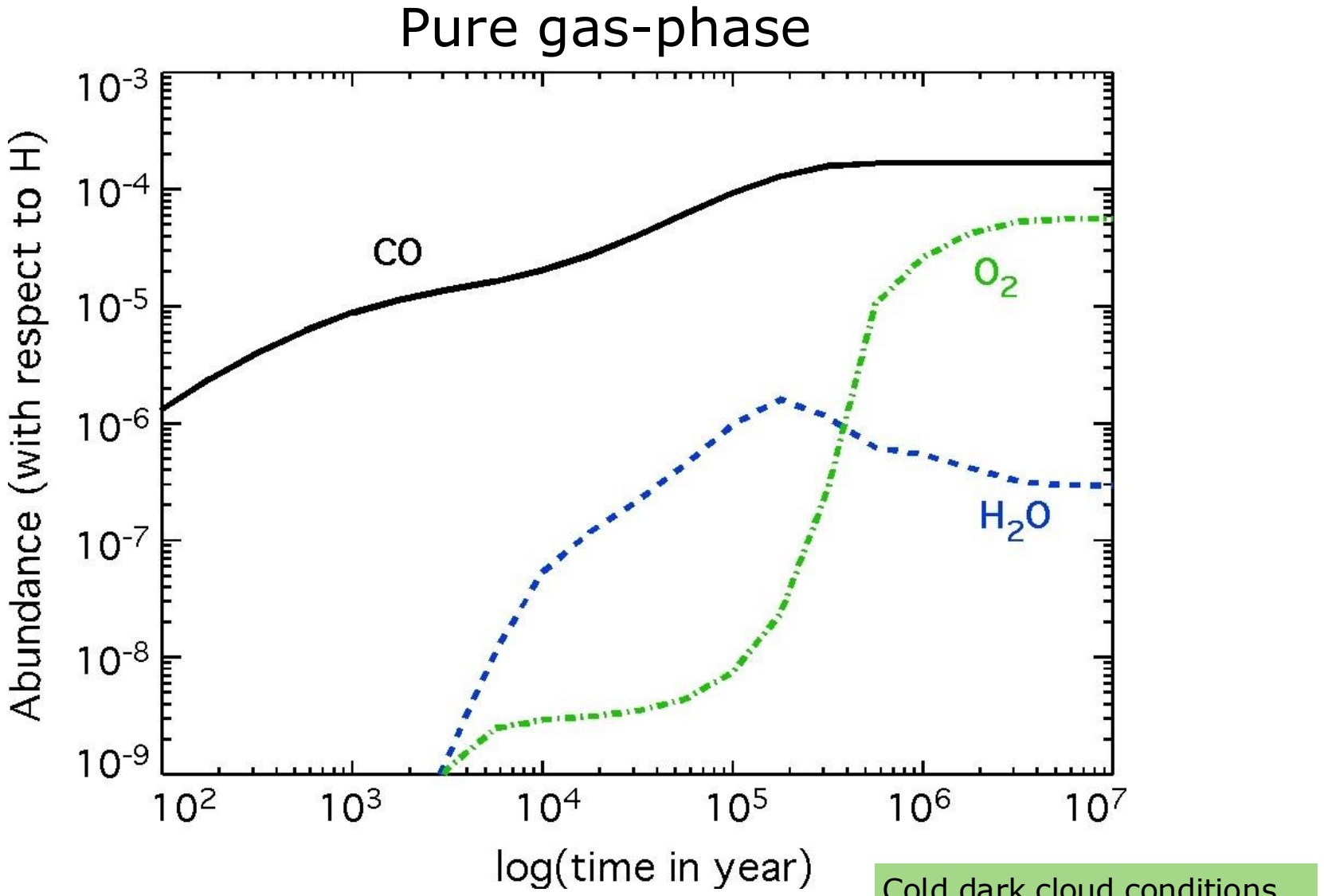
- 0D
- 1D
- 2D

What does this mean?

Dynamic

- Static structrure
- Dynamically active

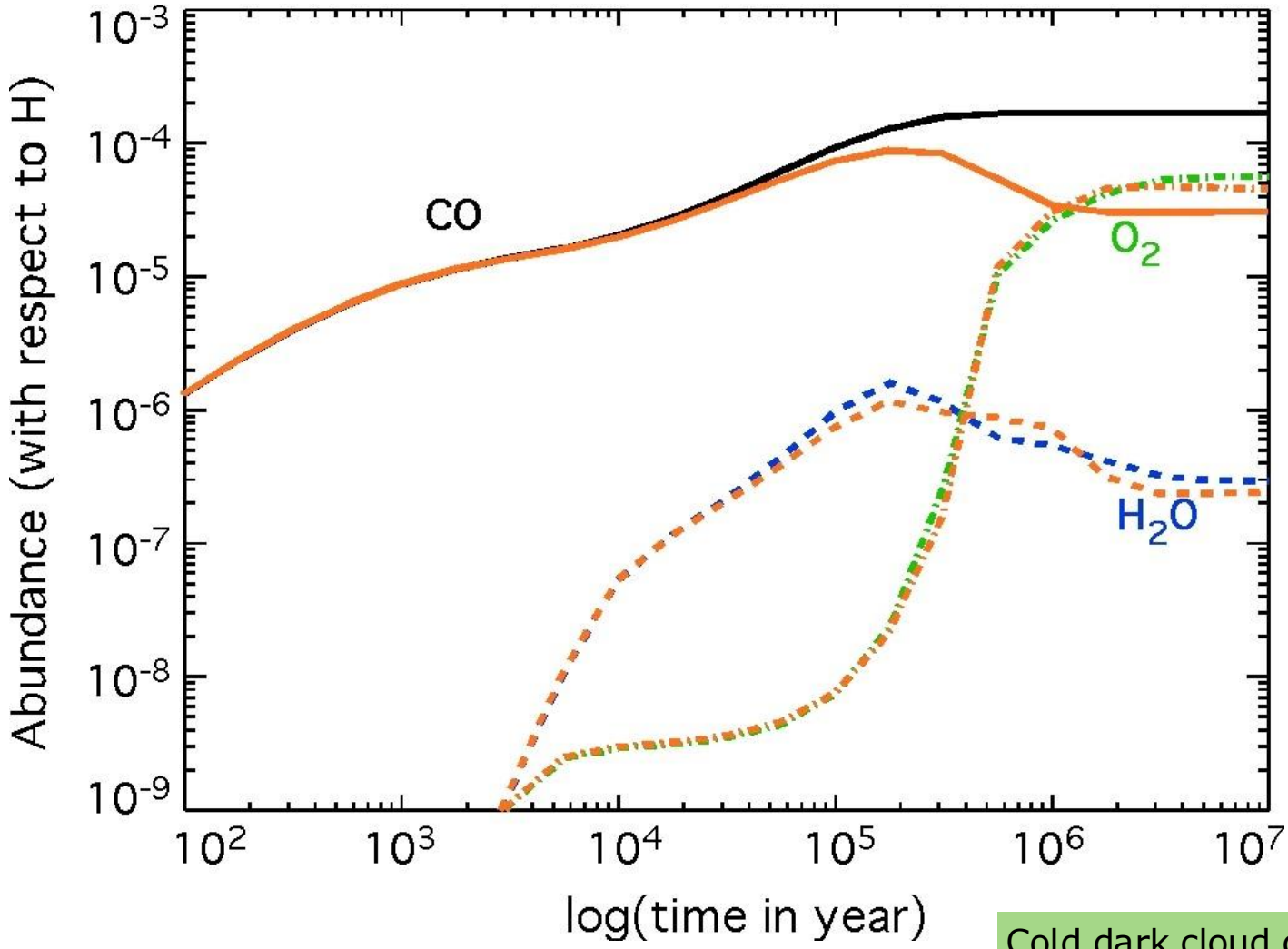
Chemical models – importance of surface processes



Cold dark cloud conditions
(10K, $2 \times 10^4 cm^{-3}$, Av = 30)

Chemical models – importance of surface processes

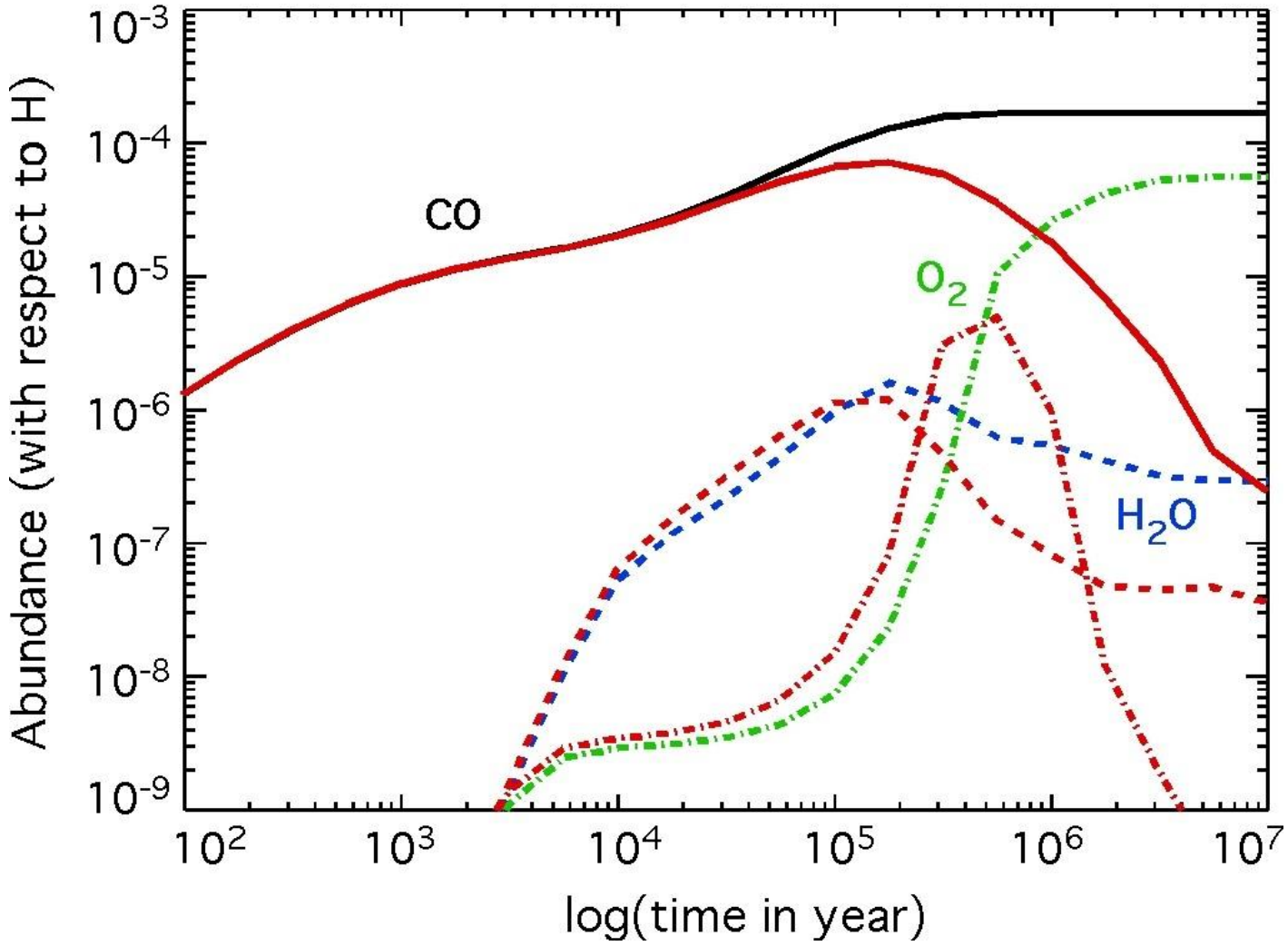
Gas-phase + adsorption/desorption



Cold dark cloud conditions
(10K, $2 \times 10^4 cm^{-3}$, Av = 30)

Chemical models – importance of surface processes

Gas-phase + full surface chemistry

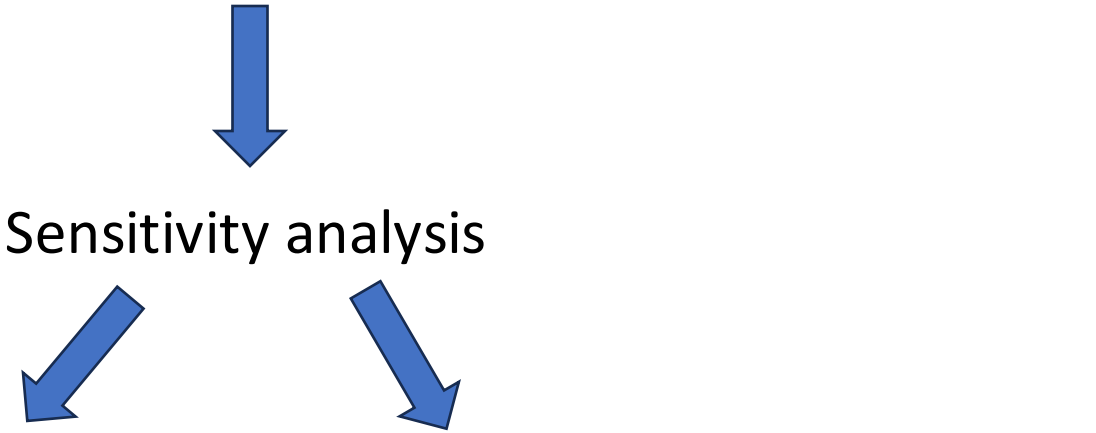


Surface chemistry -> a way to remove species from the gas

Uncertainties

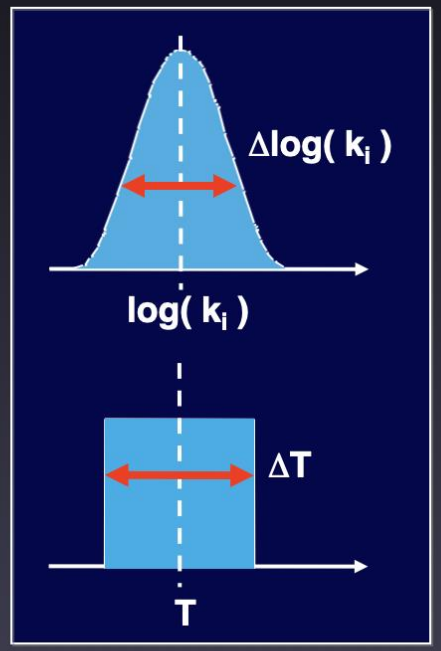
Parameters uncertainties for 0D a gas-phase chemical models:

Gas temperature and density, elemental abundances, initial conditions, cosmic-ray ionization rate, reaction rate coefficients.

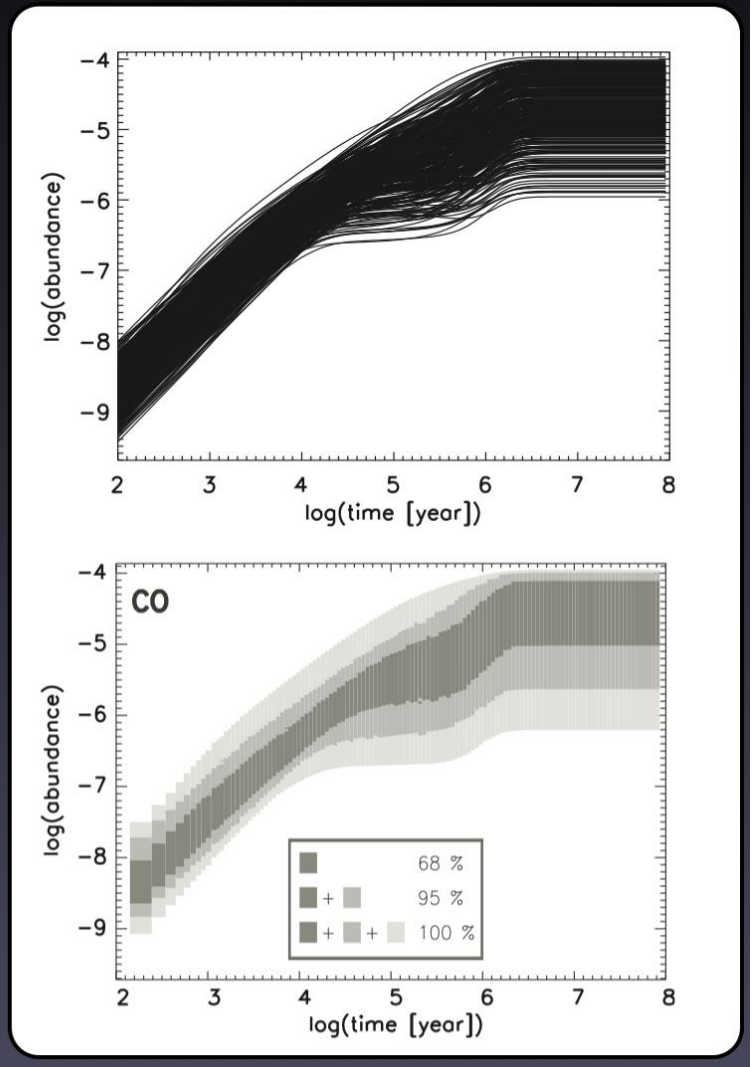


Uncertainties

Parameter uncertainties
(k, T, n etc)



Monte-Carlo
simulations (thousands)



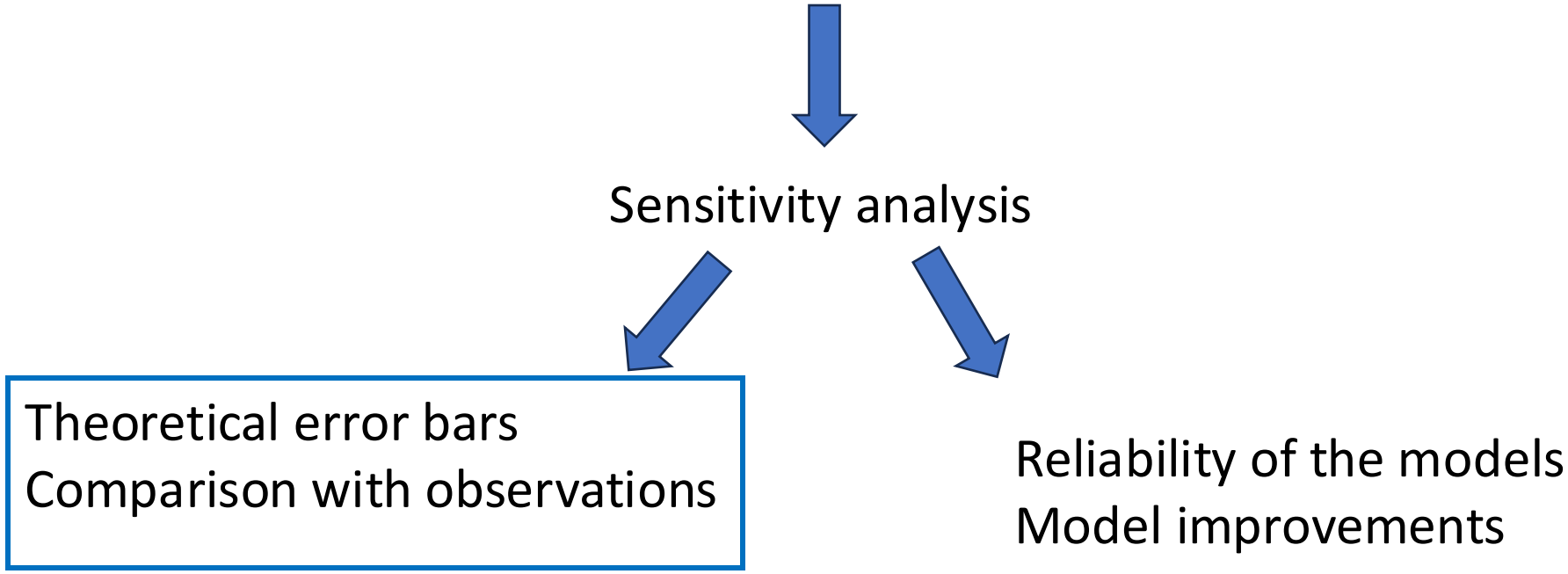
Wakelam, Selsis, Herbst & Caselli (2005)

Wakelam, Herbst & Selsis (2006)

Uncertainties

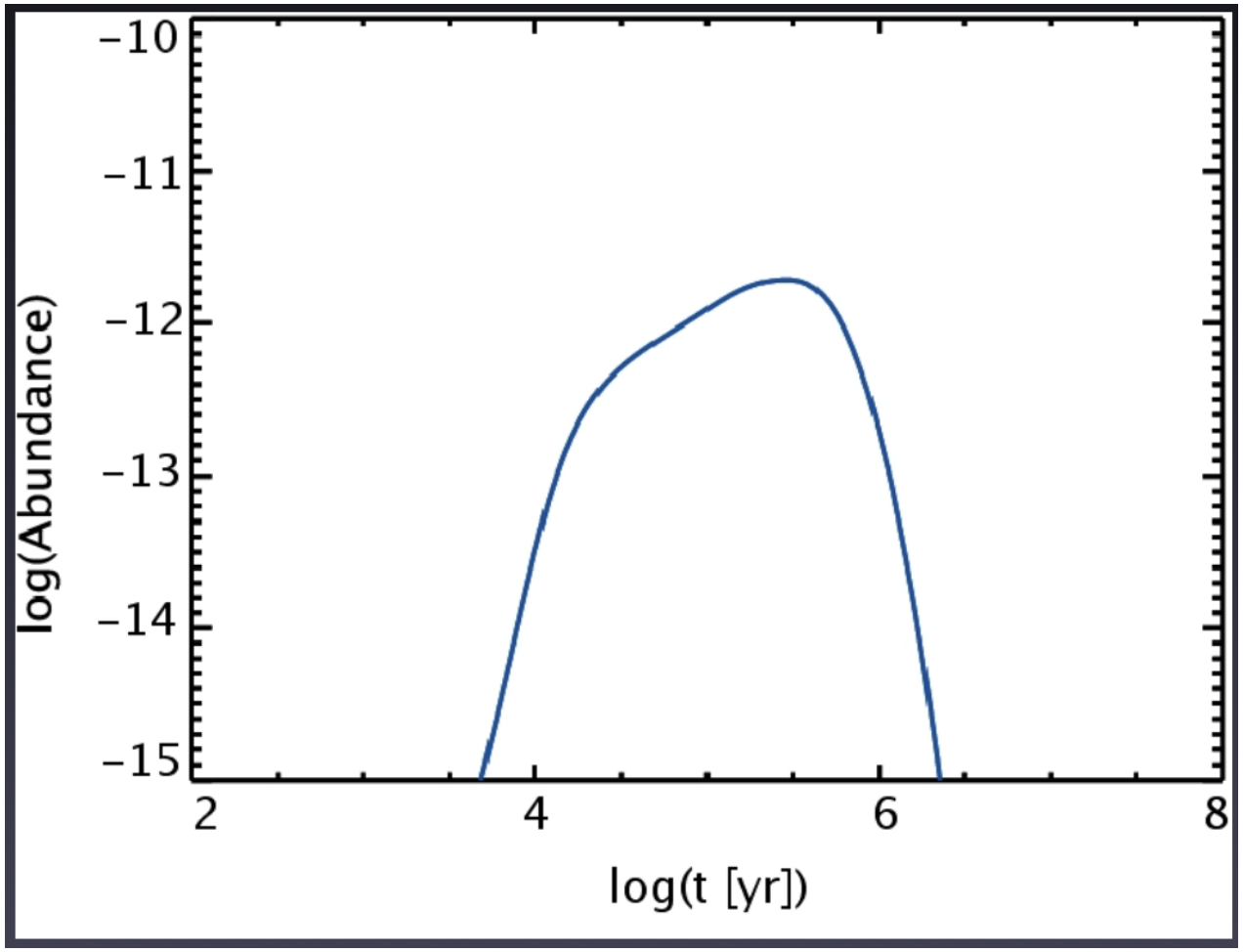
Parameters uncertainties for 0D a gas-phase chemical models:

Gas temperature and density, elemental abundances, initial conditions, cosmic-ray ionization rate, reaction rate coefficients.



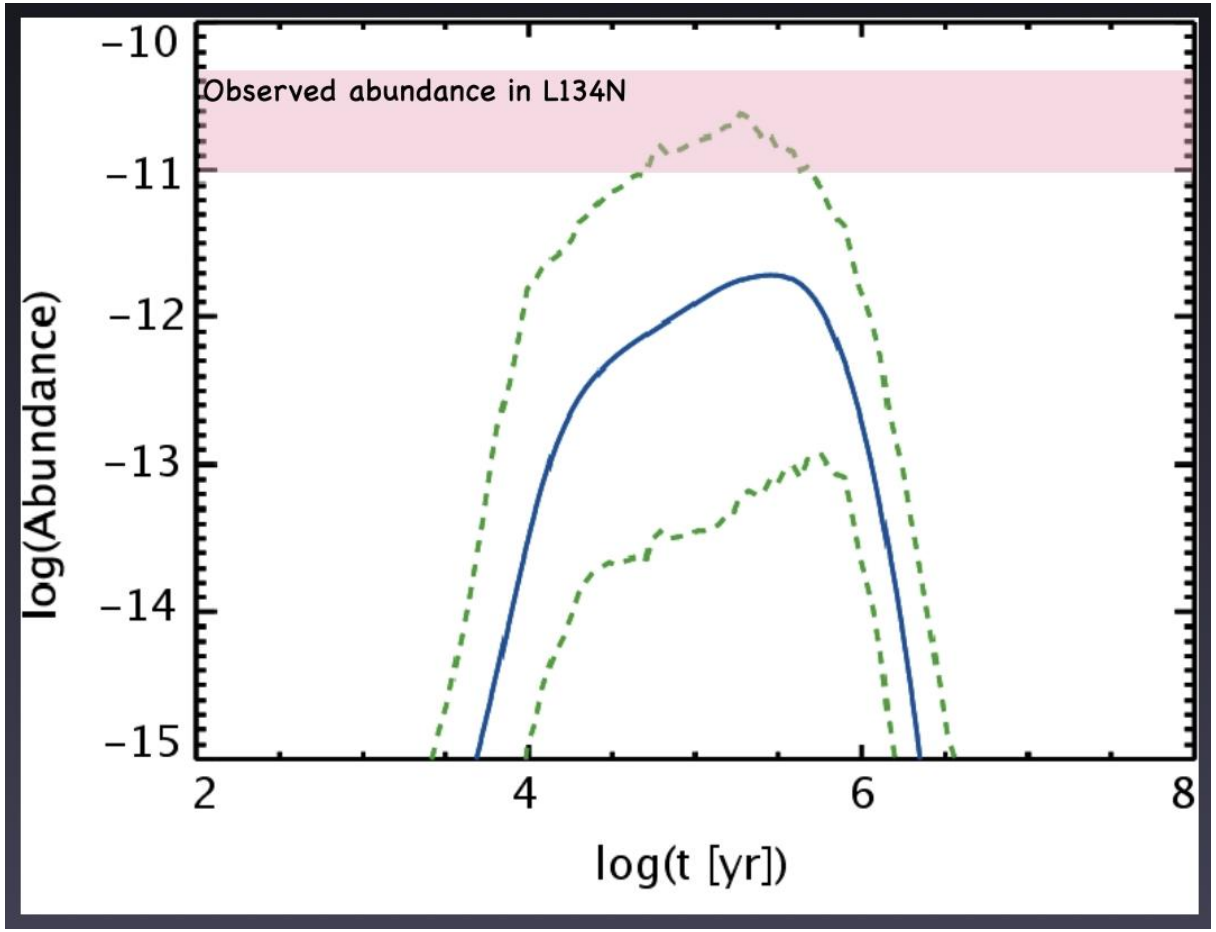
Uncertainties

HC_7N gas-phase abundance in a typical dark cloud



Uncertainties

HC_7N gas-phase abundance in a typical dark cloud –
With error bars due to rate coefficient uncertainties

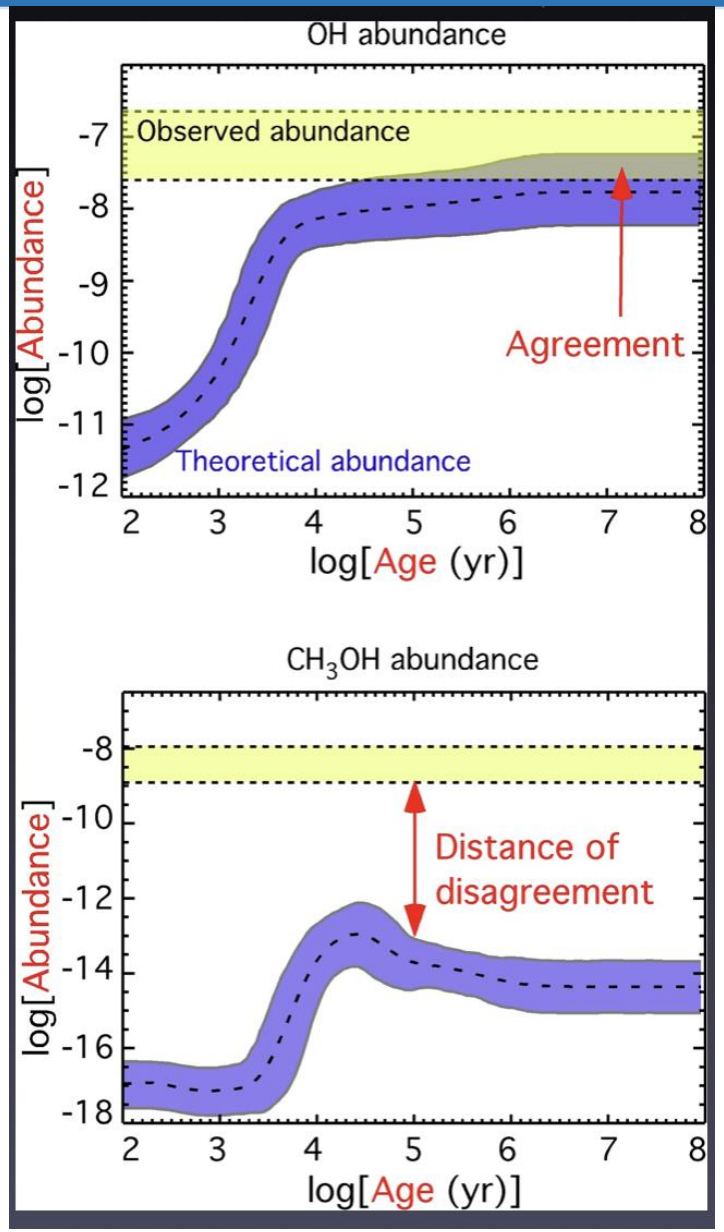


Uncertainties

Comparison with observations:

- Find which molecules are really not reproduced by the model to look for missing processes or wrong chemistry.

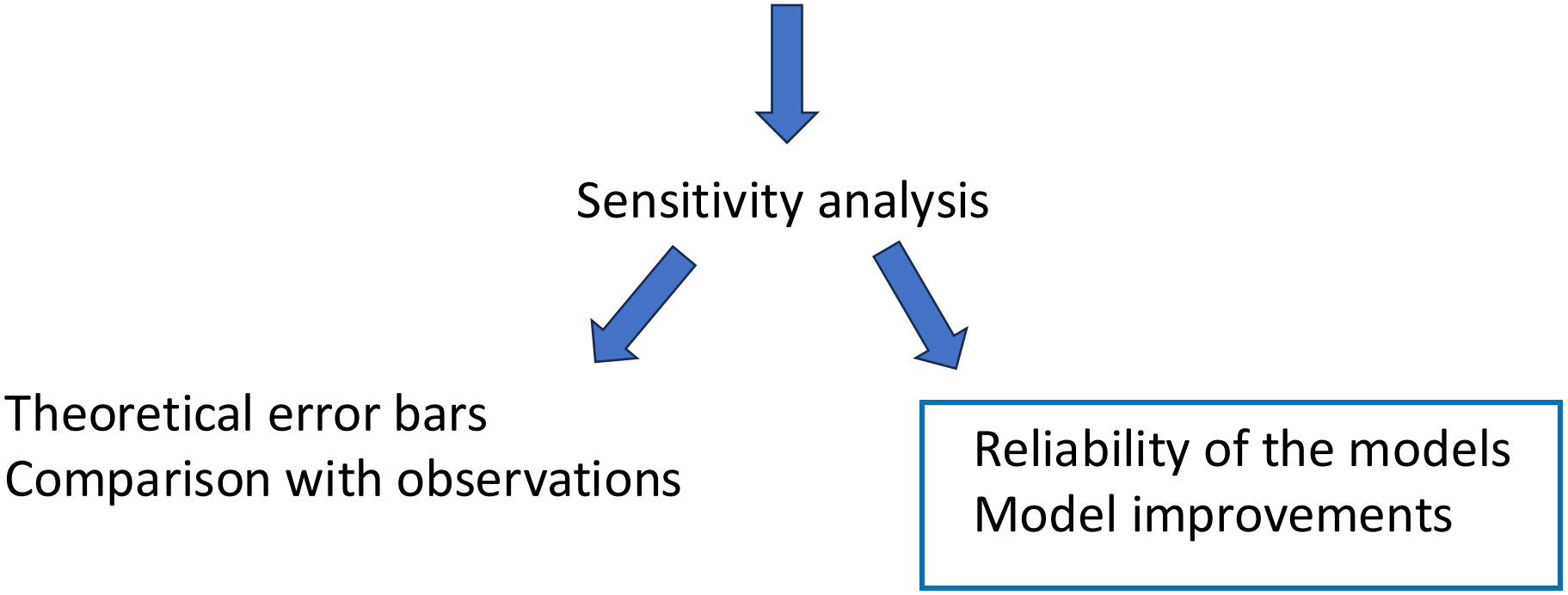
- Constrain “best models” (i.e. sets of parameters)



Uncertainties

Parameters uncertainties for 0D a gas-phase chemical models:

Gas temperature and density, elemental abundances, initial conditions, cosmic-ray ionization rate, reaction rate coefficients.

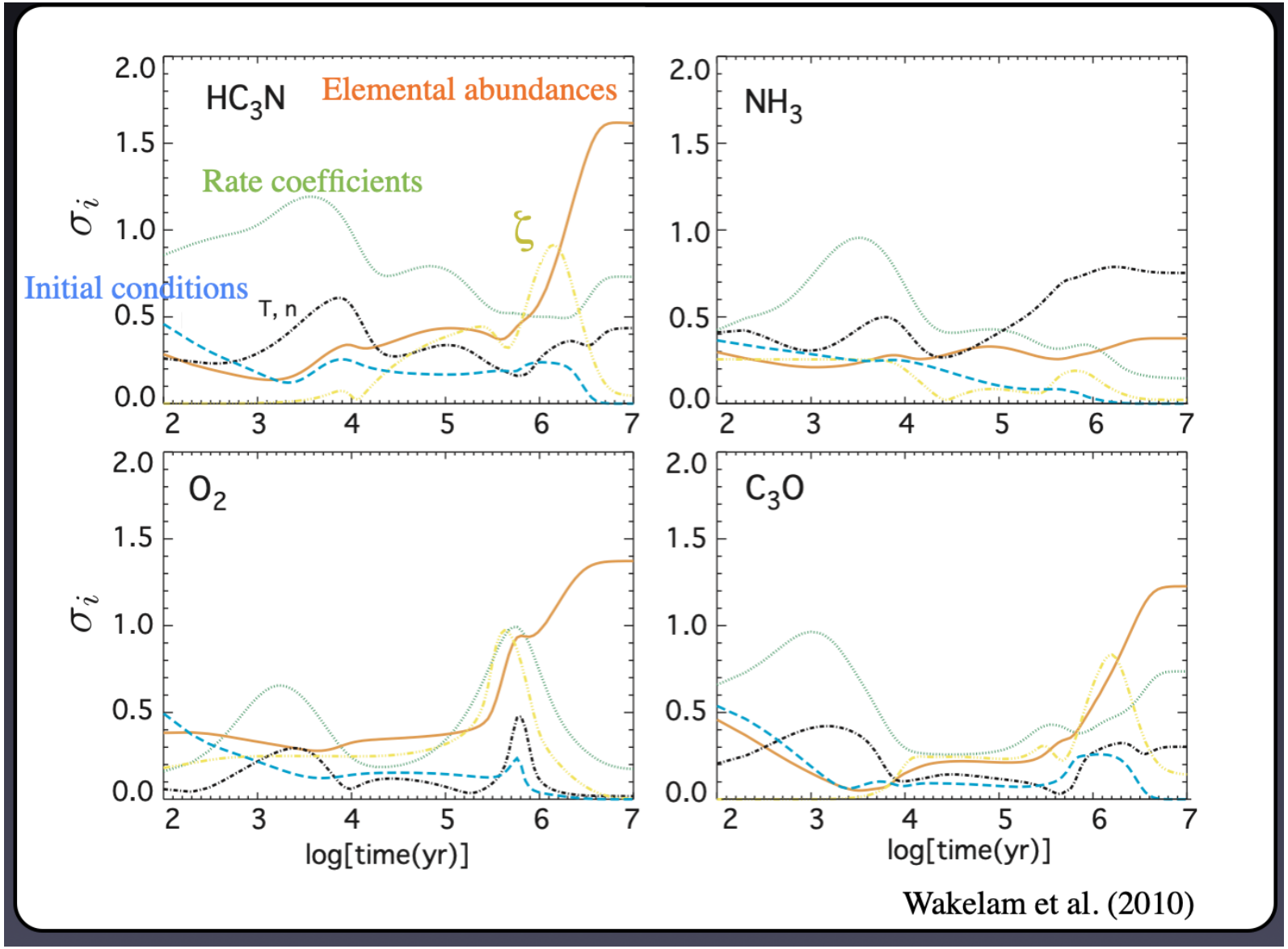


Uncertainties

For example: finding the most crucial parameters

-> Mean standard on the chemical abundances while varying each parameter individually

$$\sigma(t) = \sqrt{\frac{1}{N}\sum_{n=1}^{N}(\log(X_n(t)) - \overline{\log(X(t))})^2}$$

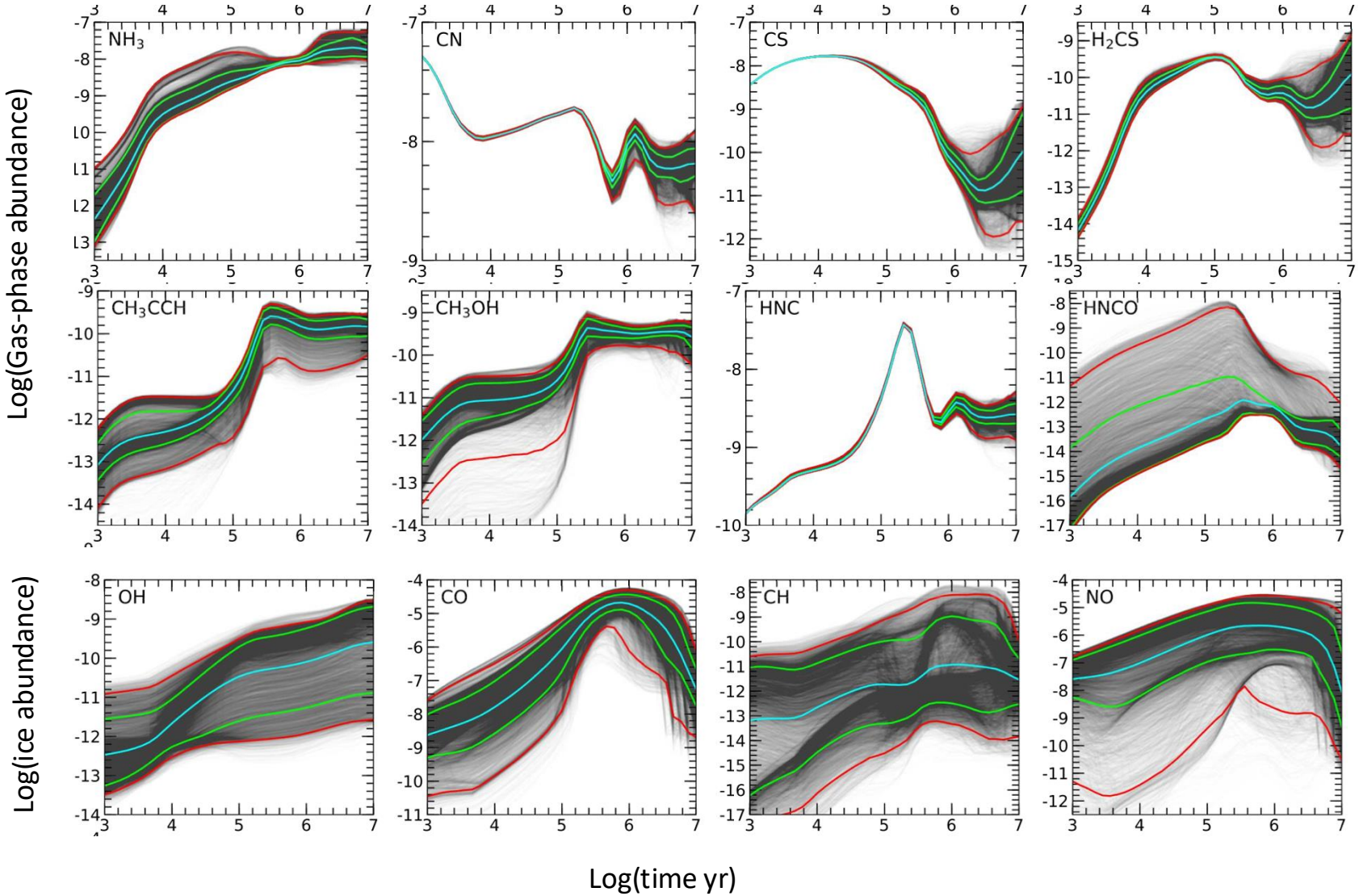


Sensitivity analysis are also for grain processes

Variation of the ratio between binding and diffusion energies between 0.25 and 0.75.

➔ Iqbal et al. (2018)

Other references:
Penteado et al. 2017
++



What is an important reaction?

~8000 gas-phase reactions and ~500 species

Most of them not studied in the lab but they are not all important.

Reaction that produces most or destroys most a species.

Complicated because :

- Depends on the rate coefficient itself but also abundance of the reactants
- Depends on time
- Physical parameters
- Chemical network

$$\frac{dn(i)}{dt} = \sum_{l}\sum_{j} k_{l,j} n(l) n(j) - n(i) \sum_{m} k_{i,m} n(m)$$

Flux producing the molecule

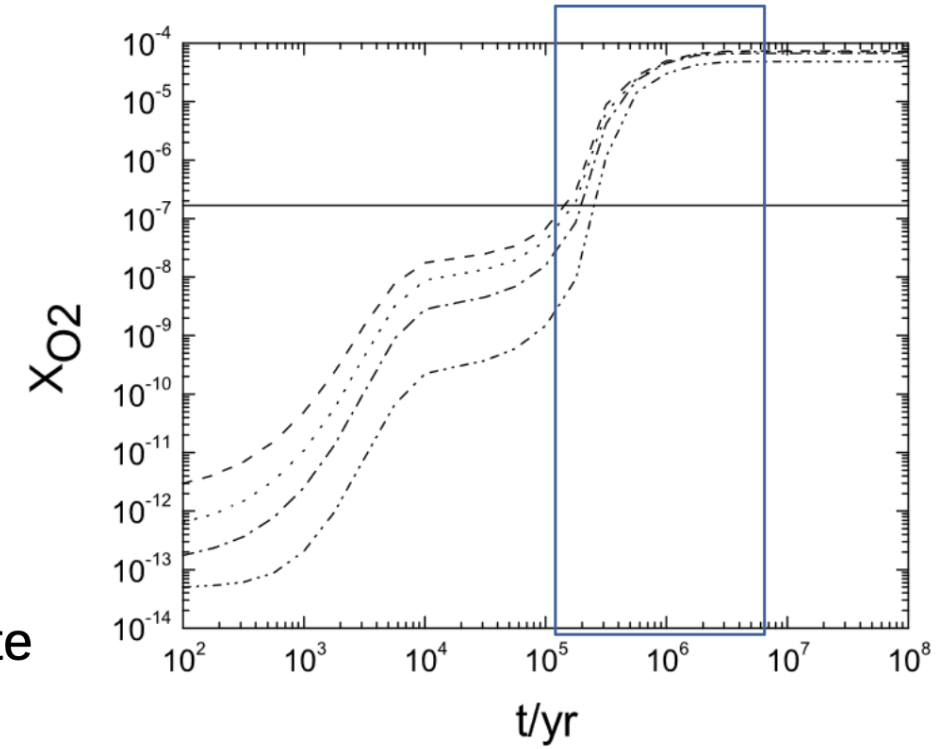
What is an important reaction?

Identification of the most important reaction for O_2 : OH + O → O_2 + H

TABLE 2

VALUES USED FOR RATE COEFFICIENT k_1 AT 10 K

k_1 ($cm^3\ s^{-1}$)	Remarks	Reference
1.76×10^{-10}	osu.1.2007	Smith et al. (2004)
3.5×10^{-11}	Experimental (39–142 K)	Carty et al. (2006)
7.84×10^{-12}	Theoretical without *J*-shifting	This work
5.4×10^{-13}	Theoretical with *J*-shifting	Xu et al. (2007b)



Variation by more of two orders of magnitude on the rate coefficient does not impact much the predicted O2 abundance.

Quan et al. 2010

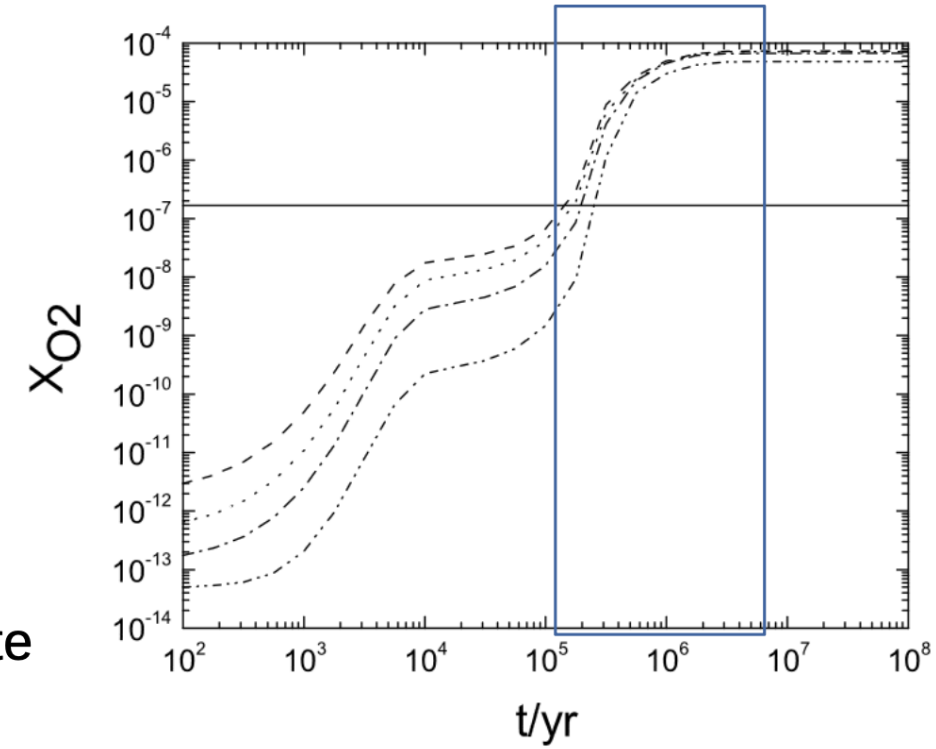
What is an important reaction?

Identification of the most important reaction for O_2 : OH + O → O_2 + H

TABLE 2

VALUES USED FOR RATE COEFFICIENT k_1 AT 10 K

k_1 ($cm^3\ s^{-1}$)	Remarks	Reference
1.76×10^{-10}	osu.1.2007	Smith et al. (2004)
3.5×10^{-11}	Experimental (39–142 K)	Carty et al. (2006)
7.84×10^{-12}	Theoretical without *J*-shifting	This work
5.4×10^{-13}	Theoretical with *J*-shifting	Xu et al. (2007b)



Variation by more of two orders of magnitude on the rate coefficient does not impact much the predicted O2 abundance.

→ main reaction of destruction of OH

Quan et al. 2010

What is an important reaction?

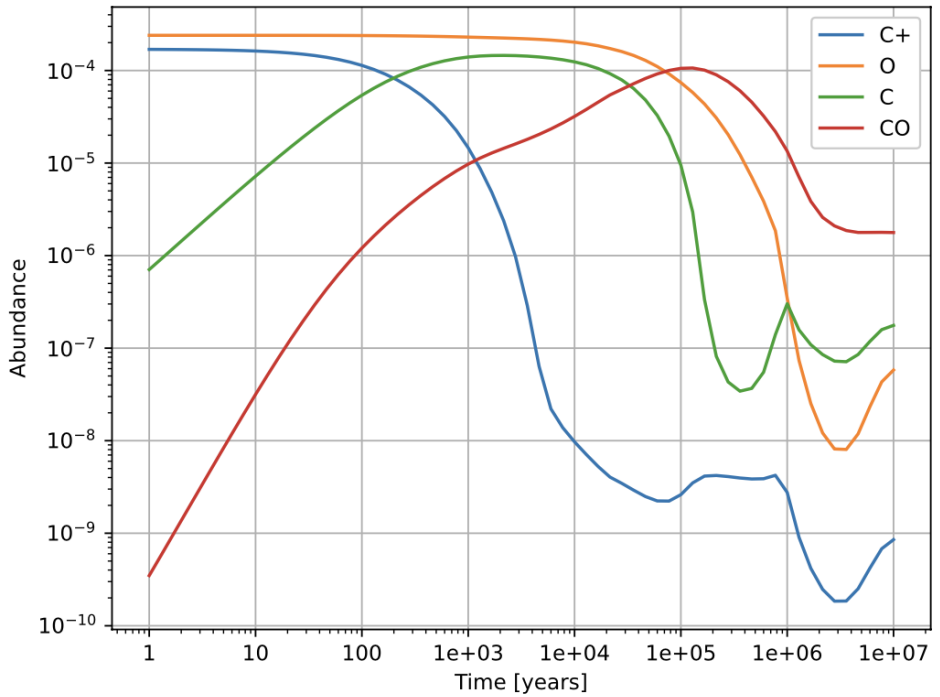
How does CO form ?

$$\frac{dn(i)}{dt} = \sum_l \sum_j k_{l,j} n(l) n(j) - n(i) \sum_m k_{i,m} n(m)$$

Flux producing the molecule

Main reactions for CO at 1e5yr :

	PRODUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	84.6%
4	C + O2 -> O + CO	1.0045830E-14	3.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.2%
4	O2 + C+ -> CO + O+	3.3839354E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	54.6%
99	CO -> JCO	1.4877065E-13	33.3%
4	CO + He+ -> He + O + C+	2.3702264E-14	5.3%
4	CO + H3+ -> H2 + HOC+	1.4322406E-14	3.2%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	1.4%



What is an important reaction?

How does CO form ?

$$\frac{dn(i)}{dt} = \sum_l \sum_j k_{l,j} n(l) n(j) - n(i) \sum_m k_{i,m} n(m)$$

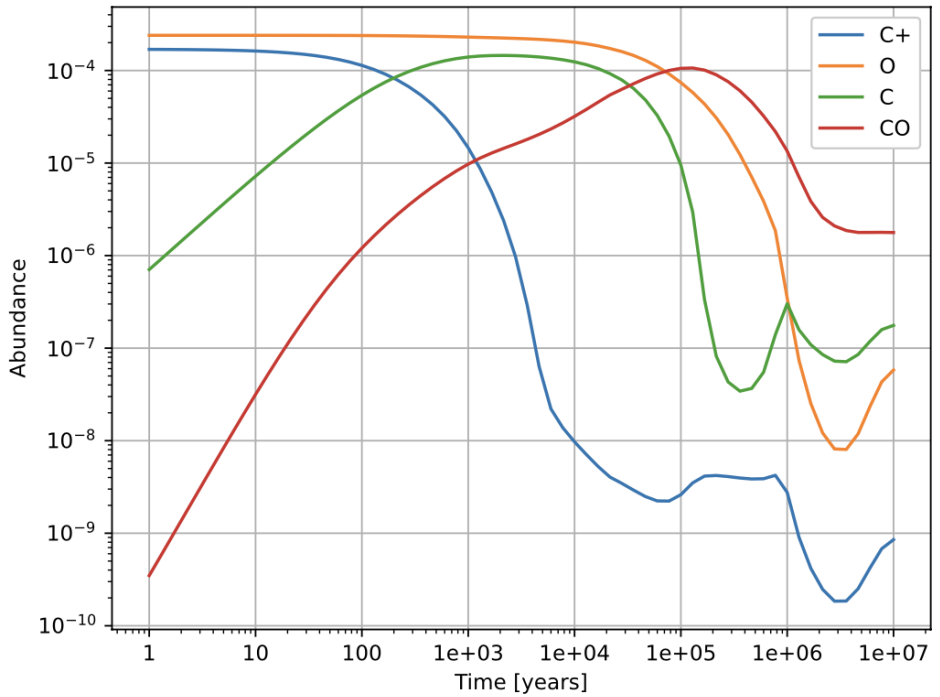
Flux producing the molecule

Main reactions for CO at 1e5yr :

	PRODUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	84.6%
4	C + O2 -> O + CO	1.0045830E-14	3.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.2%
4	O2 + C+ -> CO + O+	3.3839354E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	54.6%
99	CO -> JCO	1.4877065E-13	33.3%
4	CO + He+ -> He + O + C+	2.3702264E-14	5.3%
4	CO + H3+ -> H2 + HOC+	1.4322406E-14	3.2%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	1.4%

Main reactions for HCO+ at 1e5yr :

	PRODUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	86.6%
4	H2 + HOC+ -> H2 + HCO+	1.9626701E-14	7.0%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	2.2%
4	CO + N2H+ -> N2 + HCO+	4.4706682E-15	1.6%
4	H2 + CO+ -> H + HCO+	2.9677614E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	94.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.4%



What is an important reaction?

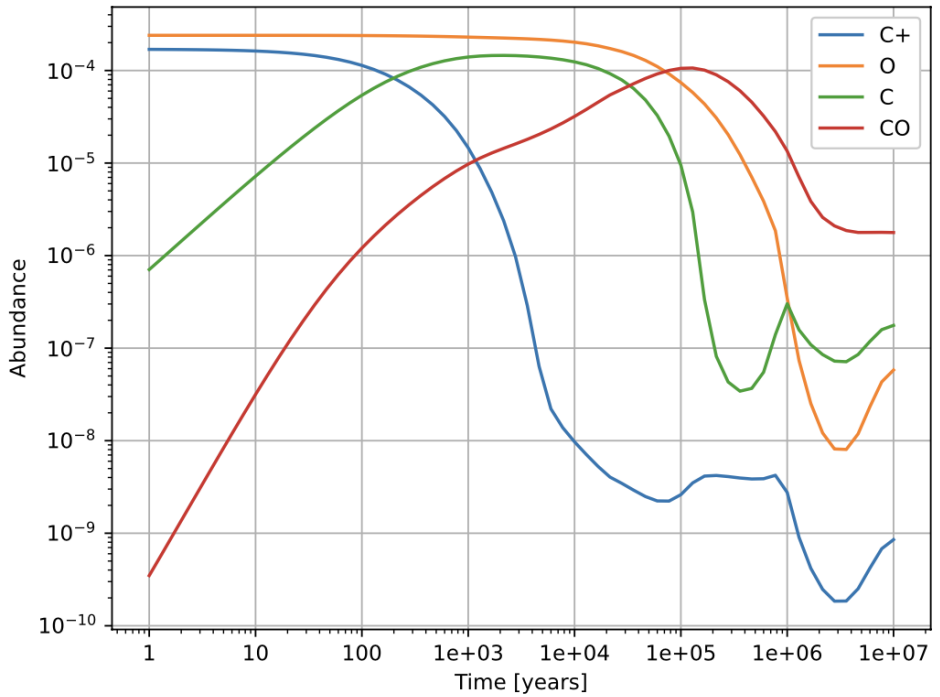
How does CO form ?

$$\frac{dn(i)}{dt} = \sum_l \sum_j k_{l,j} n(l) n(j) - n(i) \sum_m k_{i,m} n(m)$$

Flux producing the molecule

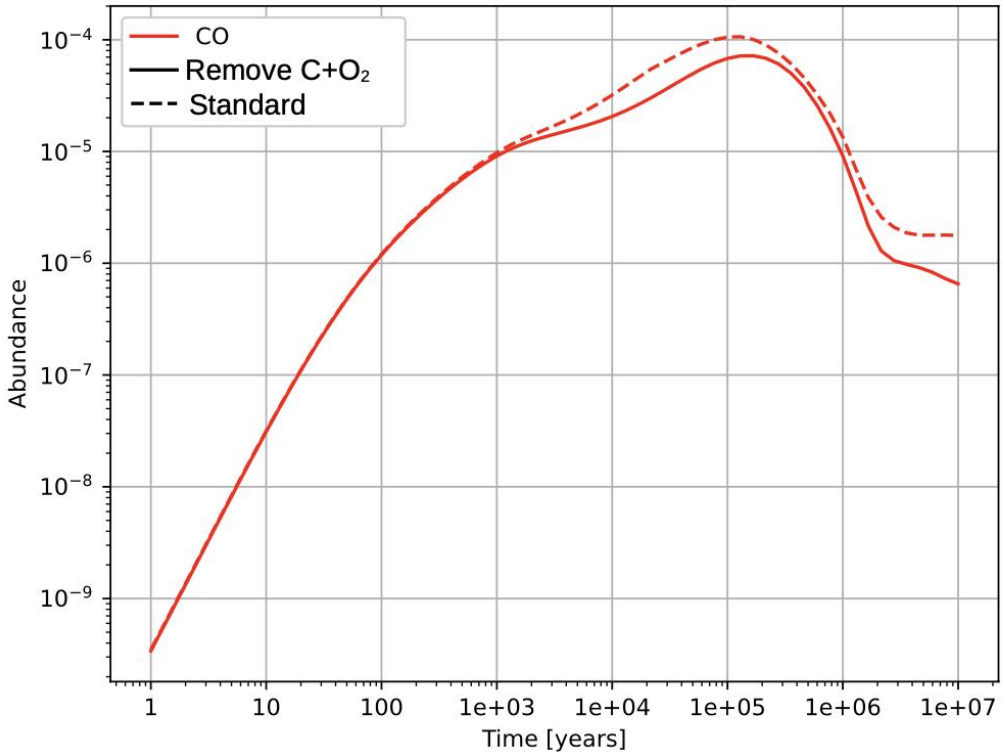
Main reactions for CO at 1e5yr :

	PRODUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	84.6%
4	C + O2 -> O + CO	1.0045830E-14	3.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.2%
4	O2 + C+ -> CO + O+	3.3839354E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	54.6%
99	CO -> JCO	1.4877065E-13	33.3%
4	CO + He+ -> He + O + C+	2.3702264E-14	5.3%
4	CO + H3+ -> H2 + HOC+	1.4322406E-14	3.2%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	1.4%



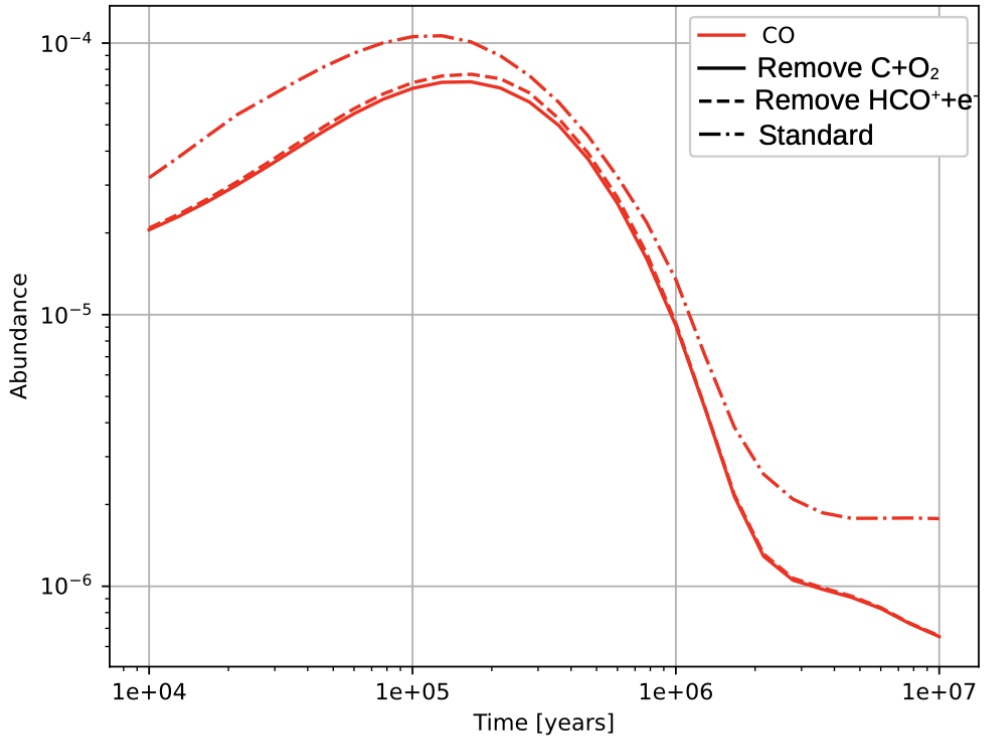
What is an important reaction?

	PRODUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	84.6%
4	C + O2 -> O + CO	1.0045830E-14	3.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.2%
4	O2 + C+ -> CO + O+	3.3839354E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	54.6%
99	CO -> JCO	1.4877065E-13	33.3%
4	CO + He+ -> He + O + C+	2.3702264E-14	5.3%
4	CO + H3+ -> H2 + HOC+	1.4322406E-14	3.2%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	1.4%



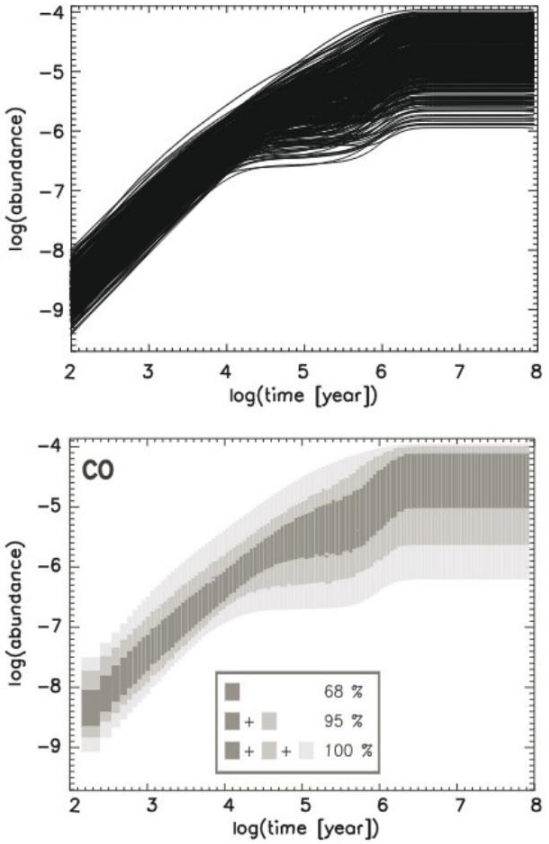
What is an important reaction?

	PRODUCTION (cm-3 s-1)		
8	HCO+ + e- -> H + CO	2.6566927E-13	84.6%
4	C + O2 -> O + CO	1.0045830E-14	3.2%
4	H2O + HCO+ -> CO + H3O+	6.8215483E-15	2.2%
4	O2 + C+ -> CO + O+	3.3839354E-15	1.1%
	DESTRUCTION (cm-3 s-1)		
4	CO + H3+ -> H2 + HCO+	2.4430818E-13	54.6%
99	CO -> JCO	1.4877065E-13	33.3%
4	CO + He+ -> He + O + C+	2.3702264E-14	5.3%
4	CO + H3+ -> H2 + HOC+	1.4322406E-14	3.2%
4	CO + CH5+ -> CH4 + HCO+	6.2696774E-15	1.4%



Many reactions contribute to the formation of CO.

What is an important reaction?



Reaction which variation in rate coefficient impacts the most one species.

- Independent random variation of all rate coefficients (within a factor)
- Compute coefficient correlation

For instance Pearson correlation coefficients:

$$C(X_j, Z) = \frac{\sum_l (X_j^l - \overline{X_j})(Z^l - \overline{Z})}{\sqrt{\sum_l (X_j^l - \overline{X_j})^2 \sum_l (Z^l - \overline{Z})^2}}$$

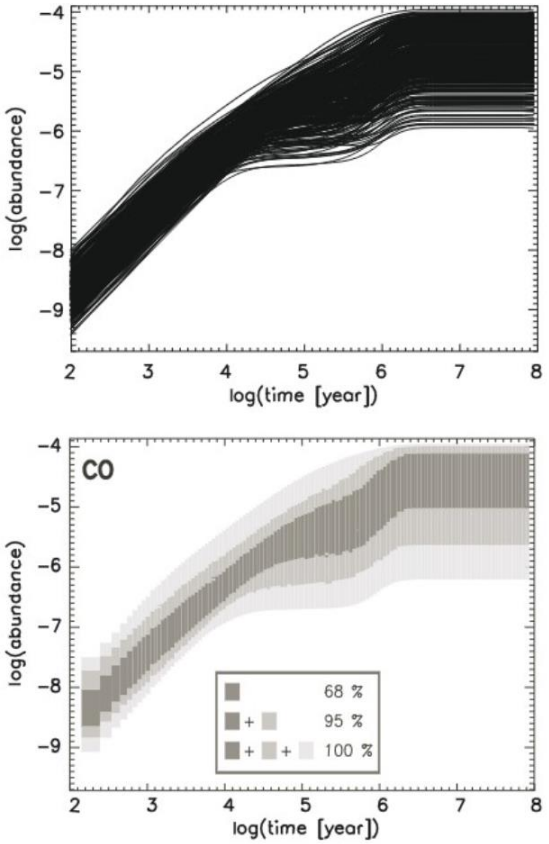
Modified parameter value

Abundance for each set of parameter

Mean abundance

Mean value of the parameter

What is an important reaction?



Reaction which variation in rate coefficient impacts the most one species.

- Independent random variation of all rate coefficients (within a factor)
- Compute coefficient correlation
- Best way to identify indirect impact

Table 3 List of key reactions by number of species influenced.

Reaction	Strongly affected species[1]
$C + H_2 \rightarrow CH_2 + h\nu$	73
$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$	18
$C_2H_2^+ + H_2 \rightarrow C_2H_4^+ + h\nu$	C_2H_2O, C_2H_3, $C_2H_2^+$, C_2HO^+, $C_2H_2N^+$, $C_2H_4^+$
$CH_3^+ + CO \rightarrow C_2H_3O^+ + h\nu$	C_2H_2O, $C_2H_3O^+$
$C_2H_4^+ + e^- \rightarrow C_2H_3 + H$	C_2H_2O, C_2H_3
$HSiO^+ + e^- \rightarrow SiO + H$	Si, SiO
$HSiO^+ + e^- \rightarrow Si + OH$	Si, SiO
$C_3H^+ + H_2 \rightarrow C_3H_3^+ + h\nu$	C_3H_2, H_2C_3, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, $H_3C_3^+$
$C_3H^+ + H_2 \rightarrow H_3C_3^+ + h\nu$	C_3H_2, H_2C_3, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, $H_3C_3^+$
$CH_3^+ + HCN \rightarrow C_2H_4N^+ + h\nu$	C_2H_2N, HC_3N, C_2H_3N, $C_2H_4N^+$
$C_4H_2^+ + H \rightarrow C_4H_3^+ + h\nu$	C_4H_2, C_5H, C_6H_6, $C_4H_3^+$
$CH_3^+ + NH_3 \rightarrow CH_6N^+ + h\nu$	CH_3N, CH_5N
$C_4H_2^+ + O \rightarrow HC_4O^+ + H$	C_3O, HC_4O^+

[1]Right column indicates the number or names of the species influenced strongly by each reaction.

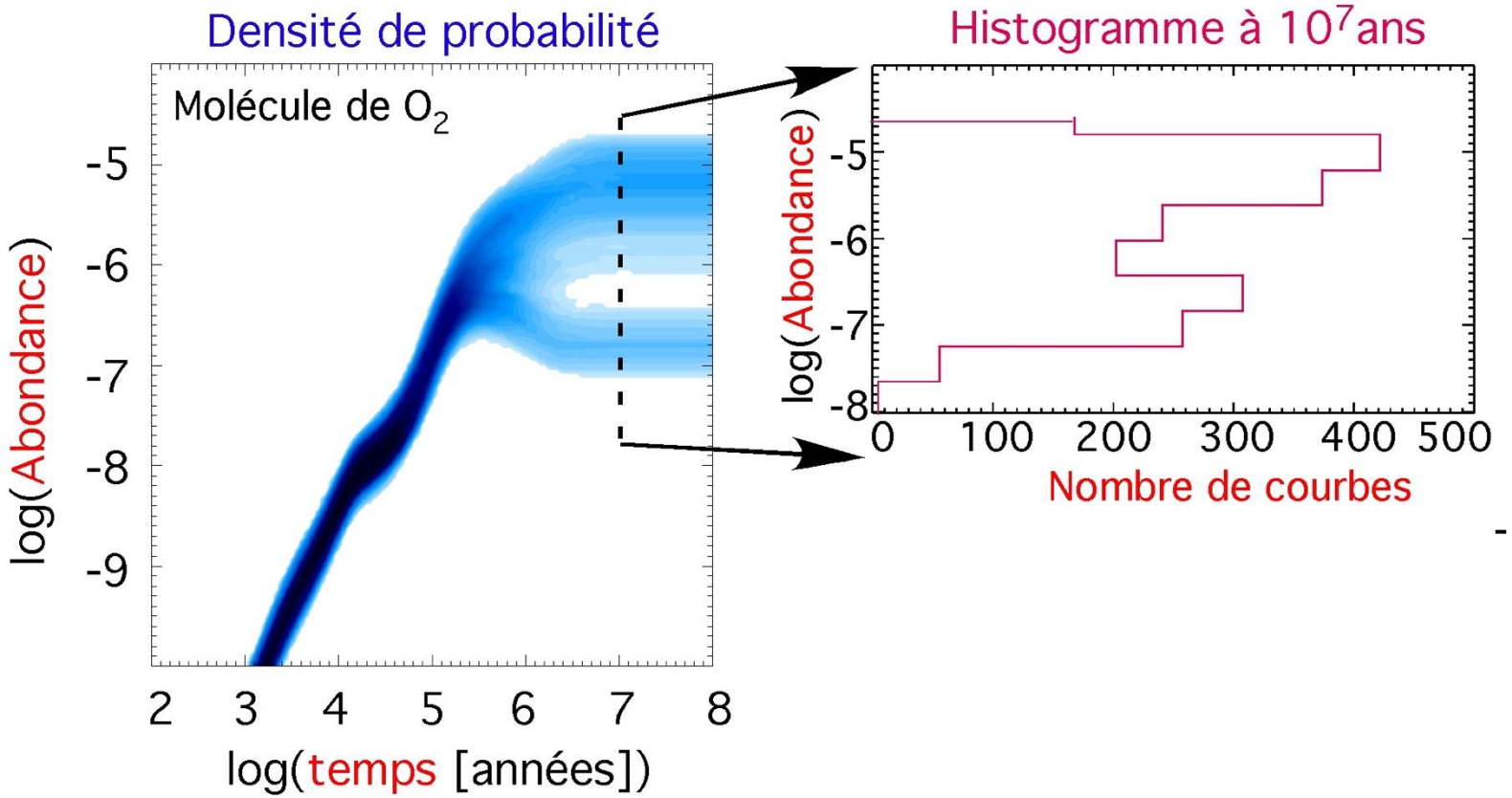
Wakelam et al. (2010)

What is an important reaction?

List of reactions with largest correlation coefficients for species with abundance larger than 1e-12 at 1e5 yr (last kida.uva network).

Reactions	Impacted species
$H_2 + CR \rightarrow H_2^+ + e^-$	187
$He + CR \rightarrow He^+ + e^-$	49
$C_3 + CRP \rightarrow C + C_2$	30
$C + C_3 \rightarrow C_4 + Photon$	CCH, C3, CCO, HCO, OCN, C2H2, c-C3H, C3N, C3O, C3S, l-C3H, c-C3H2, HC3N, HNCCC, l-C3H2, HC3S, HC3O, HC4N, C5O, C3H+, CH3+, c-C3H2+, HC3O+, SiC3H+, HC3NH+, c-C3H3+, H2C3O+, l-C3H3+, H2C3S+, C5H3+
$O + CN \rightarrow N + CO$	N, CN, N2, NC6N, NC8N, N2H+
$H_2 + CH_3^+ \rightarrow CH_5^+ + Photon$	CH4, SiCH3, CH2CCH, C4H3, C2H3+, CH5+
$CO + H_3^+ \rightarrow H_2 + HCO_+$	OH+, H2F+, H2O+, H3+, H3O+
$H_2 + Si^+ \rightarrow SiH_2^+ + Photon$	SiH, SiS, HNSi, SiH2+
$O + H_3^+ \rightarrow H_2 + OH+$	OH+, H2O+, H3O+
$c\text{-}C_3H_2 + Si^+ \rightarrow H + SiC_3H^+$	c-SiC2, l-SiC3, SiC3H+
$C + NH_3 \rightarrow H_2CN + H$	NH3, CH3NH2, CH3NH3+
$H_3O^+ + e^- \rightarrow H + H + OH$	H2O, HCOOH, H3O+
$HF + C^+ \rightarrow H + CF^+$	HF, CF+
$S + CH_3 \rightarrow H + H_2CS$	H2CS, HCCS
$CO + He^+ \rightarrow He + O\ C+$	He+, NH4+
$N + CN \rightarrow C + N_2$	N, N2
$O + CCH \rightarrow CH + CO$	CCH, CCO
$Cl + H_3^+ \rightarrow H_2 + HCl+$	Cl, HCl
$C + C_5O \rightarrow CO + C_5$	C5O, HC5O+
$C + H_2CO \rightarrow CO + CH_2$	HS, H2CO
$Mg + HCO^+ \rightarrow HCO + Mg^+$	Mg, Mg+
$H_2 + C_2H_2^+ \rightarrow C_2H_4^+ + Photon$	C2H2+, C2HO+
$H_2 + C_3H^+ \rightarrow l\text{-}C_3H_3^+ + Photon$	C3H+, l-C3H3+
$H_2 + C_3H^+ \rightarrow c\text{-}C_3H_3^+ + Photon$	C3H+, l-C3H3+
$NH_3 + CH_3^+ \rightarrow CH_3NH_3^+ + Photon$	CH3NH2, CH3NH3+
$C_2H_4^+ + e^- \rightarrow H + C_2H_3$	C2H3, CH3CO
$HC_3NH^+ + e^- \rightarrow H + HNCCC$	HNCCC, C3N-
$CF^+ + e^- \rightarrow C + F$	HF, CF+
$HCS^+ + e^- \rightarrow S + CH$	HCS+, OCS+
$SiNC^+ + e^- \rightarrow Si + CN$	SiN+, SiNC+
$NH_4^+ + e^- \rightarrow H + NH_3$	NH2, NH4+
$C_5H + e^- \rightarrow C_5H^- + Photon$	C5H2, C5H-

Finding weird behaviors with sensitivity analysis



Bistability

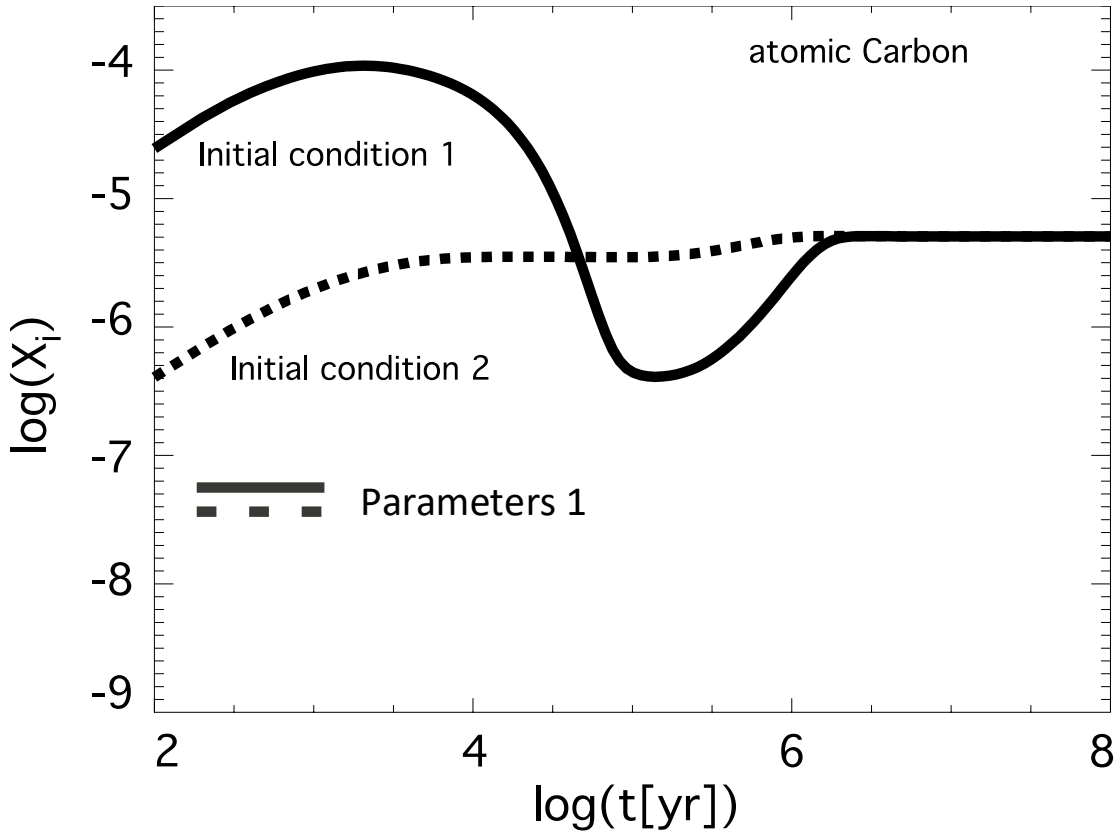
→ Bistability means that the system can exist in two different stable states.

→ In chemistry, it means that a system can evolve in two different states of equilibrium for the same set of physical parameters but depending on the initial conditions.

Bistability

→ Bistability means that the system can exist in two different stable states.

→ In chemistry, it means that a system can evolve in two different states of equilibrium for the same set of physical parameters but depending on the initial conditions.

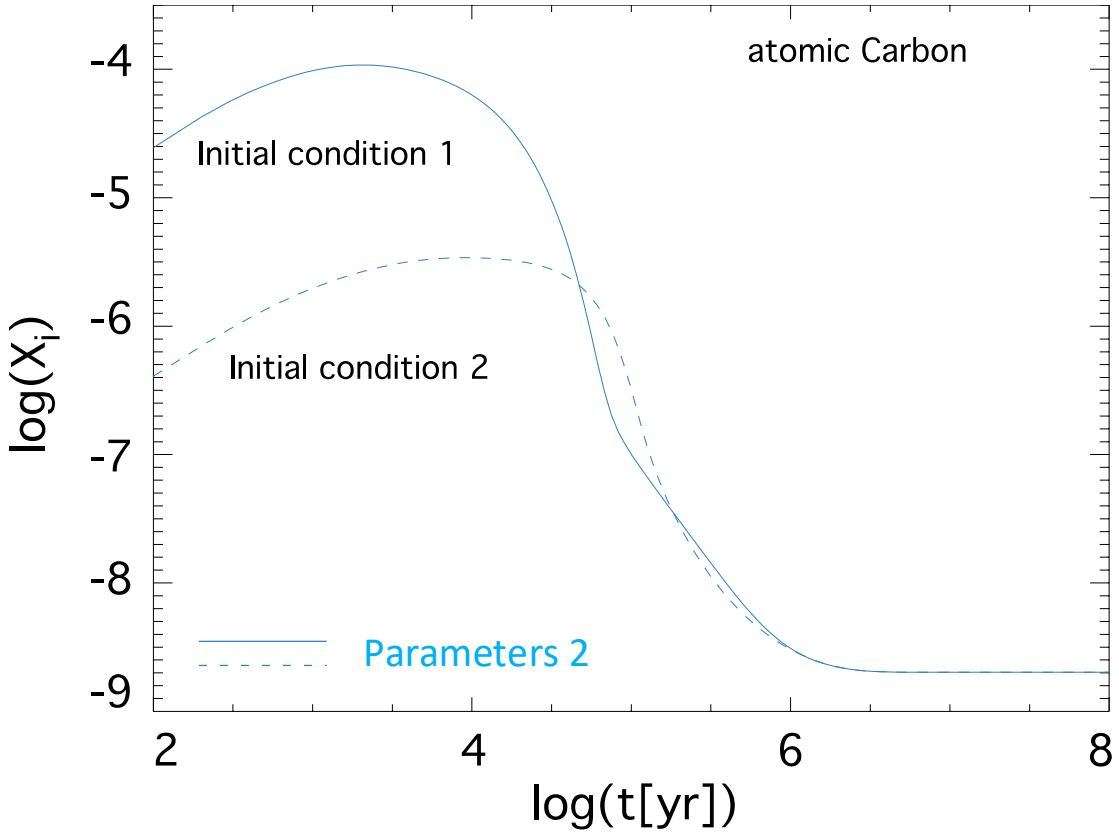


What do I call initial conditions in this case?

Bistability

→ Bistability means that the system can exist in two different stable states.

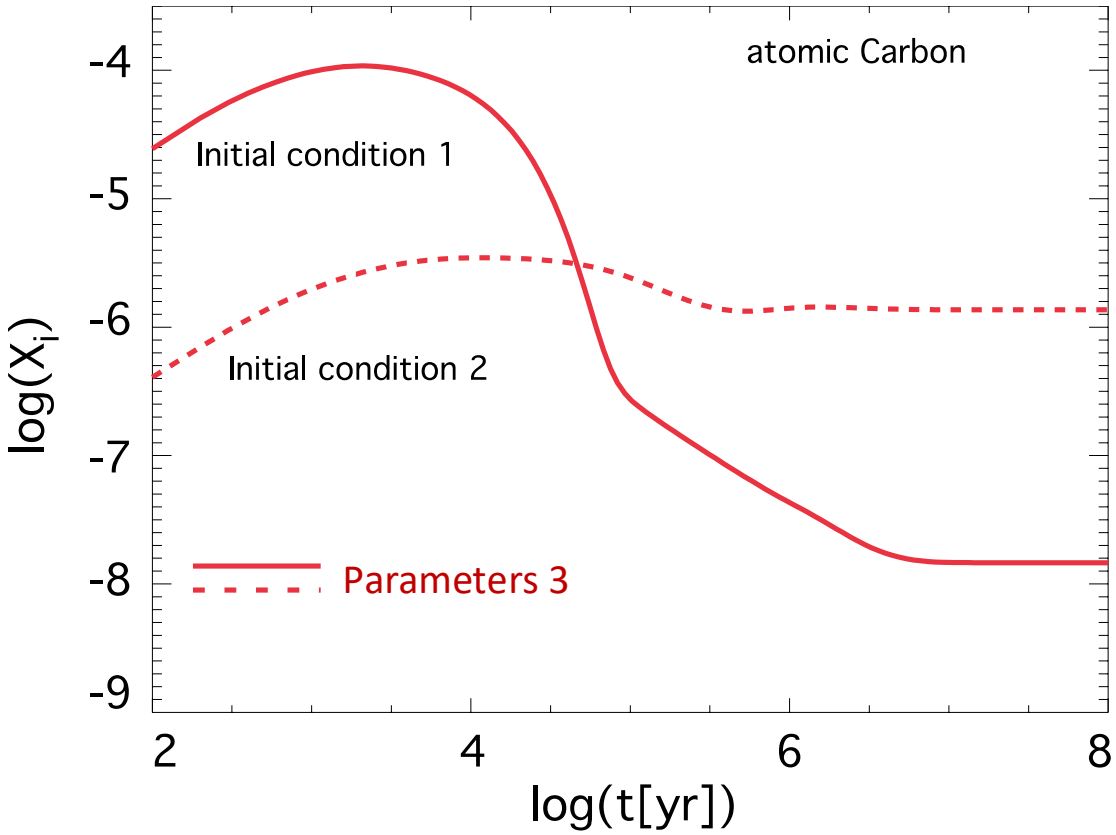
→ In chemistry, it means that a system can evolve in two different states of equilibrium for the same set of physical parameters but depending on the initial conditions.



Bistability

→ Bistability means that the system can exist in two different stable states.

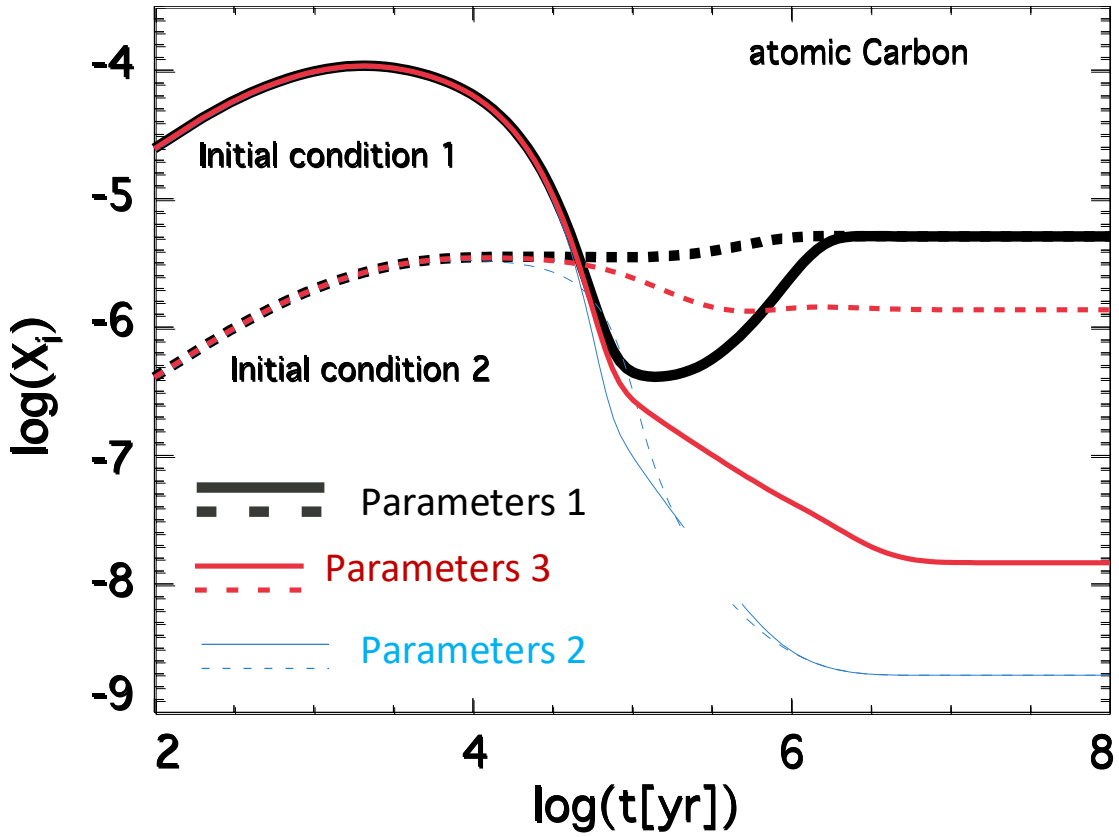
→ In chemistry, it means that a system can evolve in two different states of equilibrium for the same set of physical parameters but depending on the initial conditions.



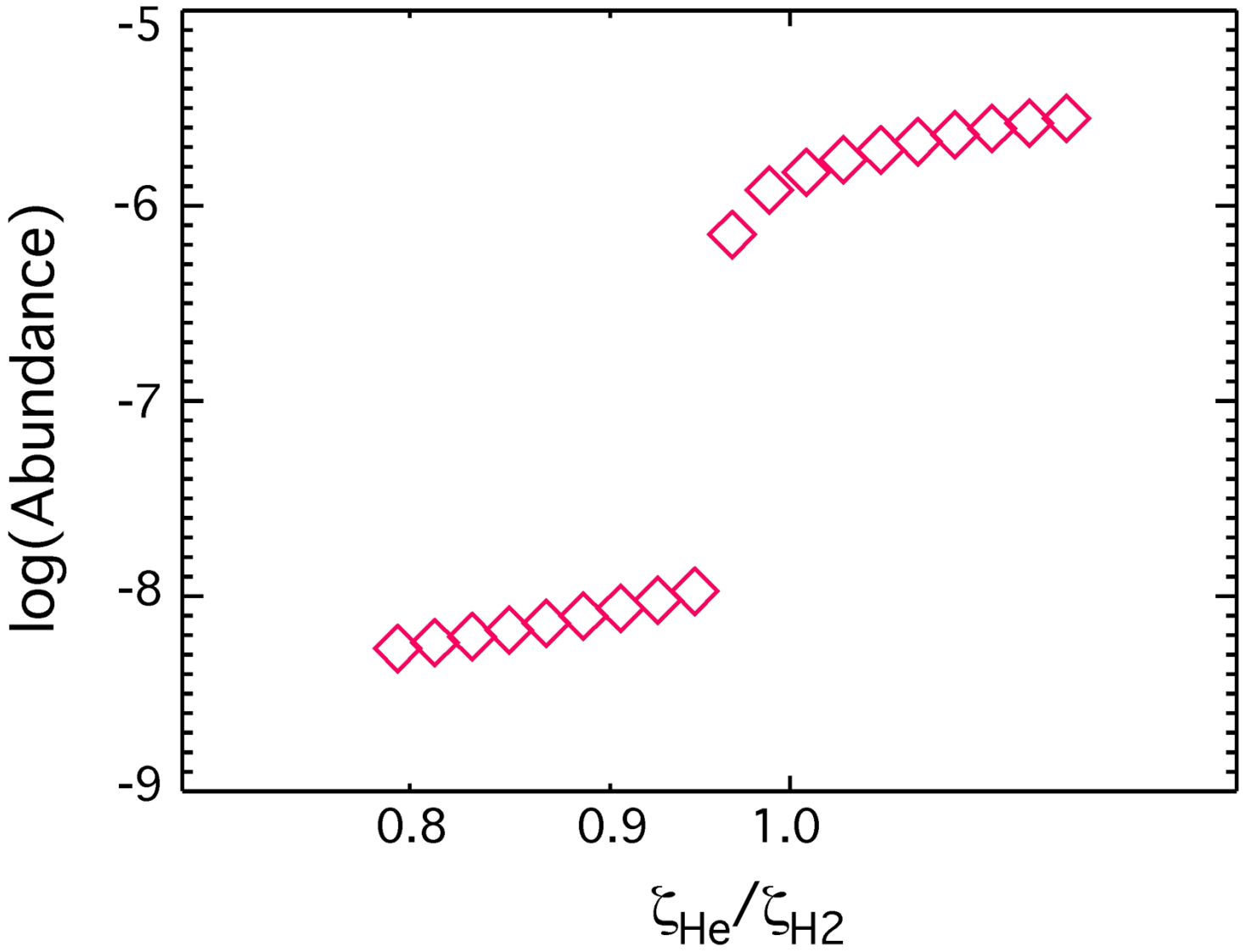
Bistability

→ Bistability means that the system can exist in two different stable states.

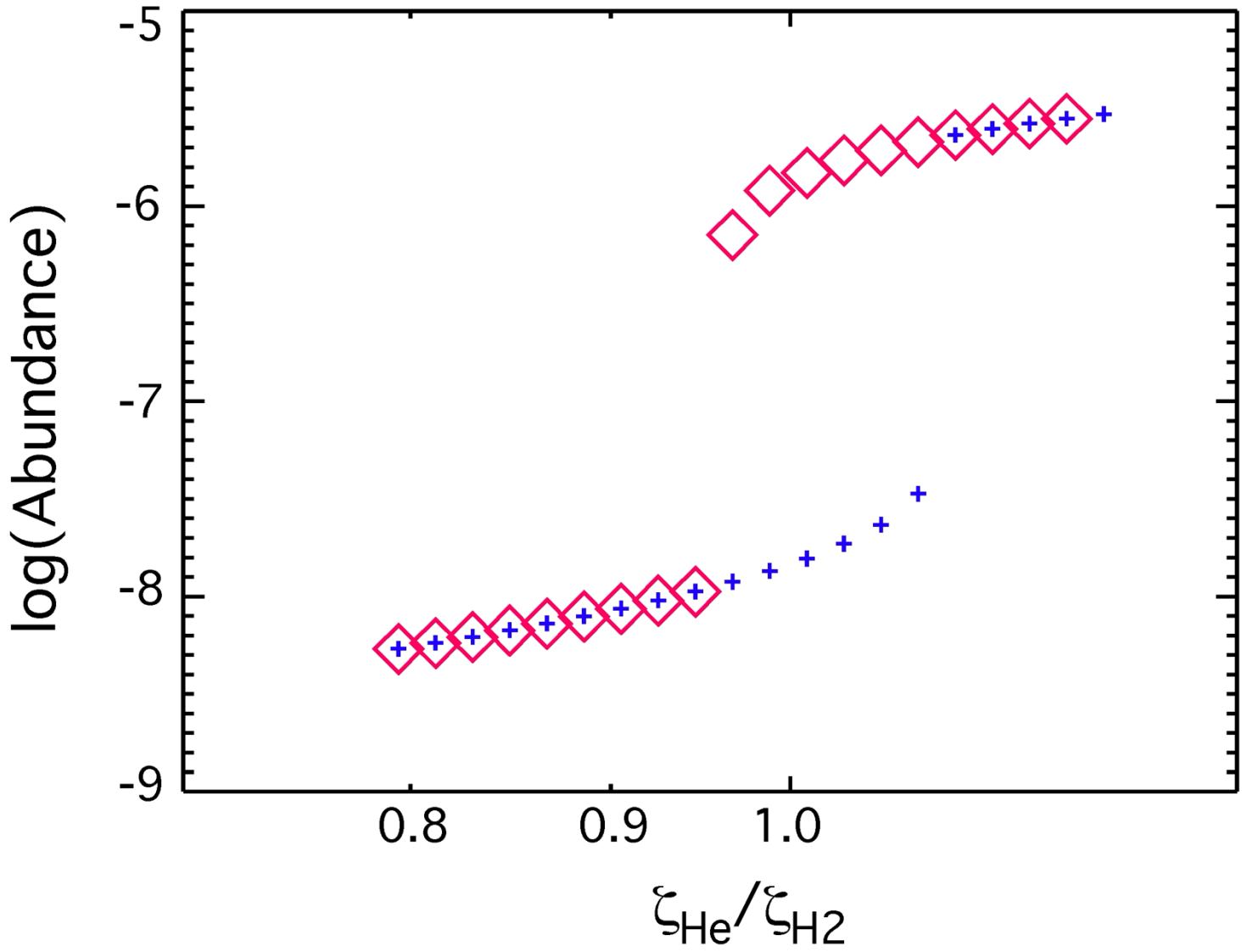
→ In chemistry, it means that a system can evolve in two different states of equilibrium for the same set of physical parameters but depending on the initial conditions.



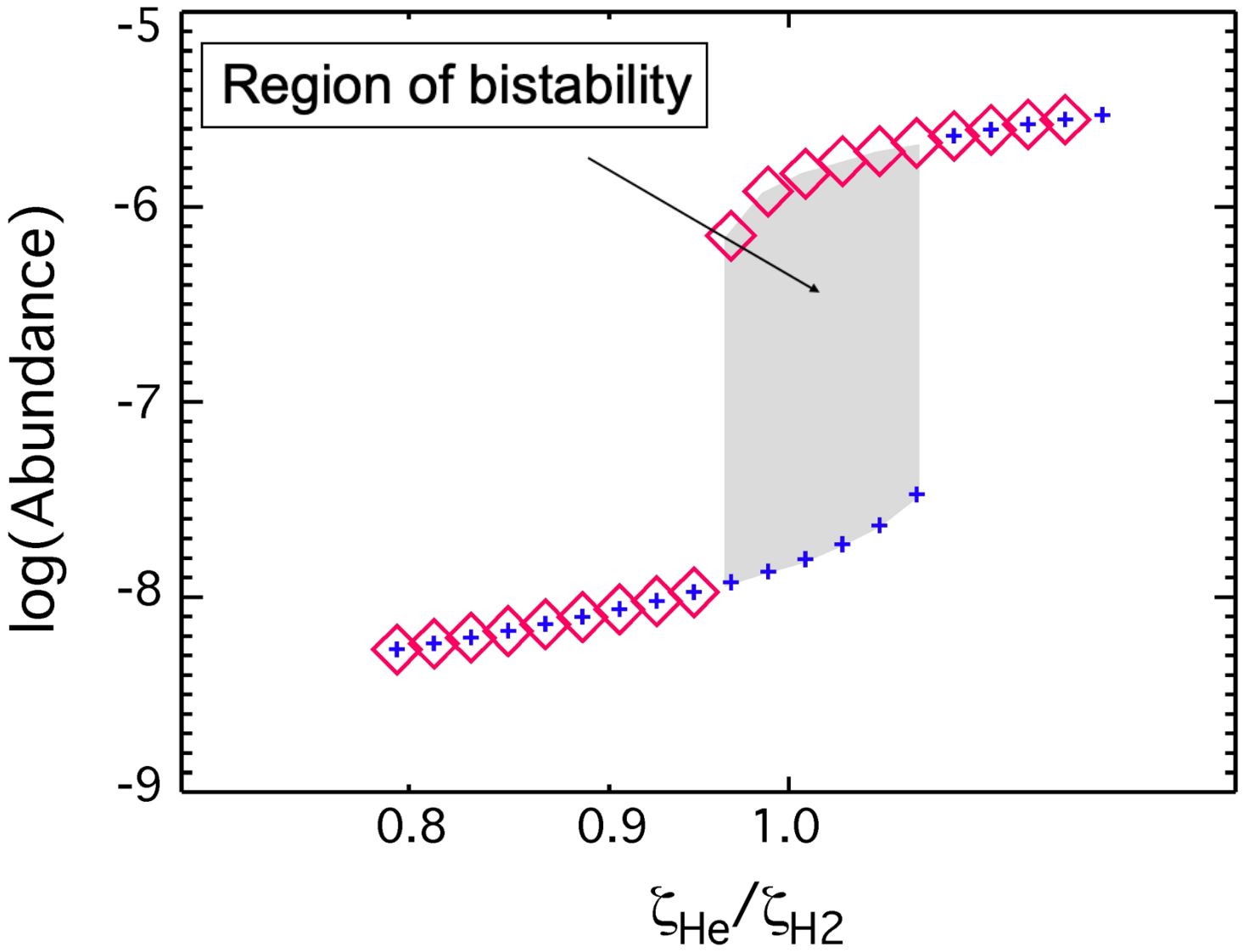
Bistability



Bistability



Bistability



Bistability

References :

- Pineau des Forêts et al. (1992)
- Le Bourlot et al. (1993, 1995a,b)
- Shalabiea & Greenberg (1995)
- Wakelam et al. (2006)
- Dufour (2019, 2021, 2023)
- + many more

Databases of chemical reactions

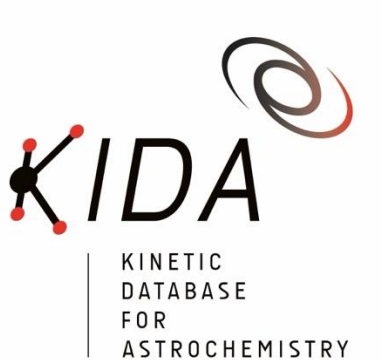
Interstellar medium :
UMIST/UDFA (http://www.udfa.net/), KIDA (https://kida.astrochem-tools.org)
Meudon databases (PdR, Shock ...)

Planetary atmospheres :
NASA-JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies http://jpldataeval.jpl.nasa.gov/
Critical reviews from Journal of Physical and Chemical Reference Data (Atkinson et al., Baulch et al., Herron et al., Tsang et al.,...) http://www.nist.gov/srd/reprints.htm

General databases :
NIST http://kinetics.nist.gov/kinetics/index.jsp, Anicich (ion-neutral) - word or pdf documents

Photo-dissociations :
* Database from LISA http://w3.lisa.univ-paris12.fr/GPCOS/SCOOPweb/SCOOP.html
* Harvard-Smithsonian Center for Astrophysics Molecular Data http://www.cfa.harvard.edu/amp/tools.html
* MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules http://www.atmosphere.mpg.de/enid/2295
* science-softCon UV/Vis+ Spectra Data Base (UV/Vis+Photochemistry Database) http://www.uv-spectra.de/
* SWRI Photo cross sections and rate coefficients http://amop.space.swri.edu/

The KInetic Database for Astrochemistry
http://kida.astrochem-tools.org/



- Database of chemical reactions and associated parameters for the interstellar medium and planetary atmospheres

- Uncritical compilation of data with detailed information (uncertainties, temperature range, bibliographic reference, etc)

- Online consulting interface

- Form to download list of reactions

- You can contribute by submitting data with cvs templates

- Subsets of chemical reactions for specific applications (Titan atmosphere, Hot Jupiters, ISM)

The KInetic Database for Astrochemistry
http://kida.astrochem-tools.org/

For gas-phase reactions:

- Temperature dependent partial reaction rate coefficients for bimolecular reactions
- Photodissociation and ionisation rates (integrated over the ISRF radiation field)
- Photodissociation and ionisation rates due to UV photons induced by cosmic-ray particles (Prasad-Tarafdar mechanism)
- Direct dissociation and ionisations rates by cosmic-ray particles

For surface reactions:

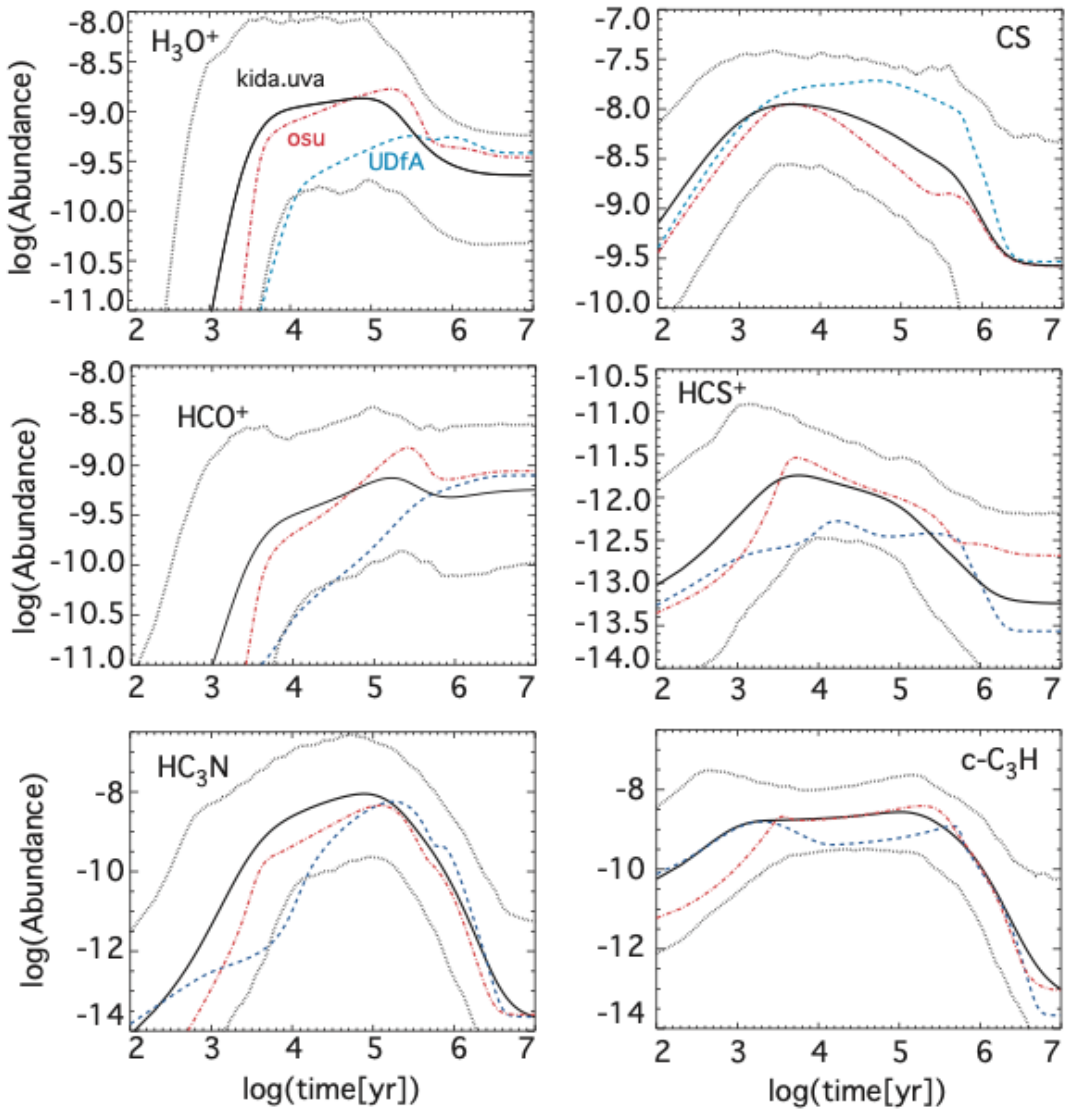
- Possible pathways (with branching ratios)
- Activation energies and barrier width

For species:

- Polarizability, dipole moment and enthalpy of formation
- Diffusion and desorption energies

Comparing gas-phase chemical networks

udf2006 from UMIST
osu-01-2009
kida.uva.2011



From Wakelam et al. (2012)

Reduced networks

Why reducing the networks :

- To have a fast model to couple the chemistry with hydrodynamics
- To run grids of models to compare with observations

Many solutions proposed in the literature:

Estimate the significance of particular species or reactions -> Wiebe et al. (2003)
Flux-reduction scheme -> Grassi et al. (2012)
Iterative sensitive method -> Xu et al. (2009)
Using autoencoders -> Grassi et al. (2022)

+++

However, reduced networks come weaknesses:

- loss of precision (not necessarily a problem)
- valid over a range of conditions.
- valid for a limited number of species.

Emulators of chemical models

- Using grids of gas-grain models to teach neural networks the chemical abundances as a function of time.

- Get a fast emulator of interstellar chemistry over the conditions used for the training.

See for instance Asencio Ramos et al. (2024) and references therein

How to construct a chemical model for a specific application?

- What are the main characteristics of the source?
  - Important chemical processes to include
  - Geometry to consider
- What scenario (time evolution?)?
  - If you do not have the full history : different steps of the modeling to simulate the different steps.
- What are the approximations and are they negligeable?

How to construct a chemical model for a specific application?

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

How to construct a chemical model for a specific application?

Exercise: I want to model the diffuse medium.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

How to construct a chemical model for a specific application?

Exercise: I want to model the diffuse medium.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

How to construct a chemical model for a specific application?

Exercise: I want to model a cold core.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

How to construct a chemical model for a specific application?

Exercise: I want to model a cold core.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- **Gas-phase chemistry + full surface treatment**

Physical parameters

- **Fixed gas temperature, density and visual extinction**
- Evolving gas temperature, density and visual extinction

Geometry

- **0D**
- 1D
- 2D

Dynamic

- **Static structrure**
- Dynamically active

How to construct a chemical model for a specific application?

Exercise:I want to model a proto-stellar envelop.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- Gas-phase chemistry + full surface treatment

Physical parameters

- Fixed gas temperature, density and visual extinction
- Evolving gas temperature, density and visual extinction

Geometry

- 0D
- 1D
- 2D

Dynamic

- Static structrure
- Dynamically active

How to construct a chemical model for a specific application?

Exercise: I want to model a proto-stellar envelop.

Chemistry

- Gas-phase chemistry
- Gas-phase chemistry + adsorption/desorption from the grains
- **Gas-phase chemistry + full surface treatment**

Physical parameters

- Fixed gas temperature, density and visual extinction
- **Evolving gas temperature, density and visual extinction**

Geometry

- **0D**
- **1D**
- 2D

Dynamic

- Static structrure
- **Dynamically active**

How to construct a chemical model for a specific application?

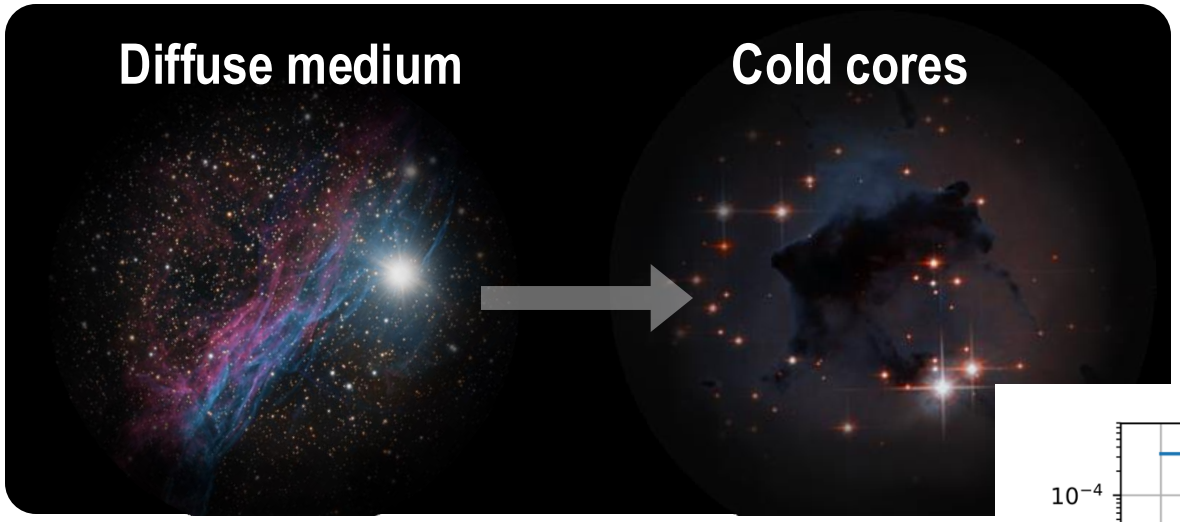
Exercise: I want to model a proto-stellar envelop.

- Need to think about the scenario:
  - Pre-collapse phase (what conditions, how long…)
  - Infall phase (how does the temperature and density increase? For how long?)
  - Deal with the formation of H_2

Example:
- Step 1 of pre-collapse (start from atoms, run the model for cold core conditions for 10^5 or 10^6 yrs)
- Step 2 : isothermal free-fall (increase of the density with a low temperature)
- Step 3: warm-up phase (increase of the temperature with a high density).

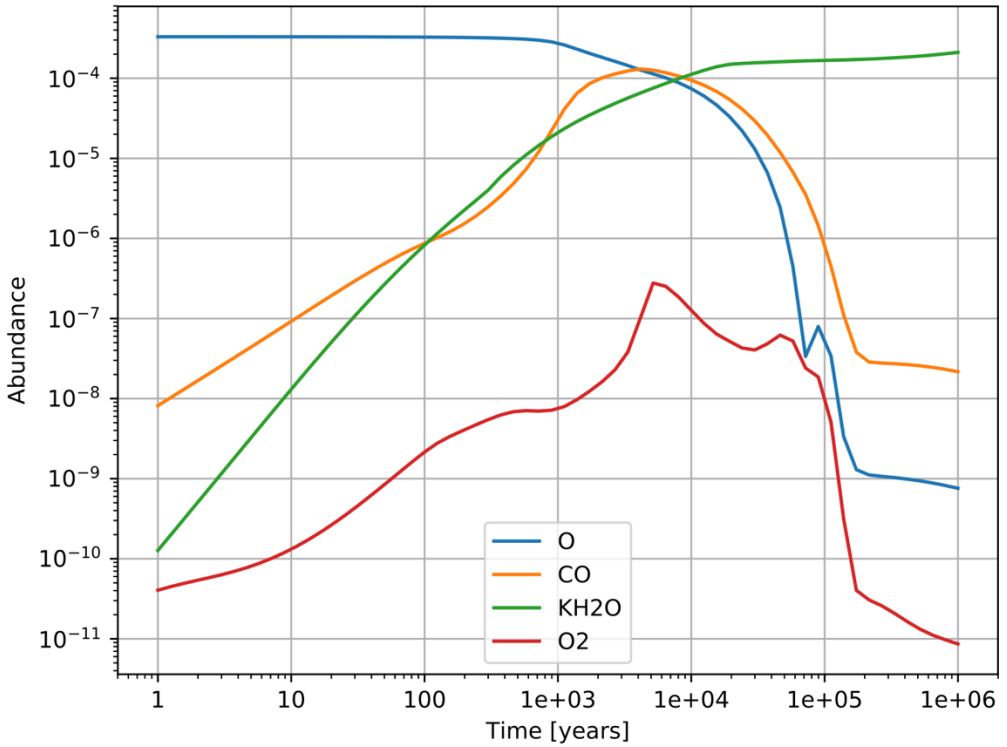
Example : Garrod & Hersbt (2006)

Coupling chemistry with dynamics



Classic approach:

- Hypothesis: physical conditions evolve faster than chemistry.
- Atomic initial conditions (except for H2)
- Keep physical conditions contant (10K, $10^4 cm^{-3}$)
- Compute time dependent chemical abundances

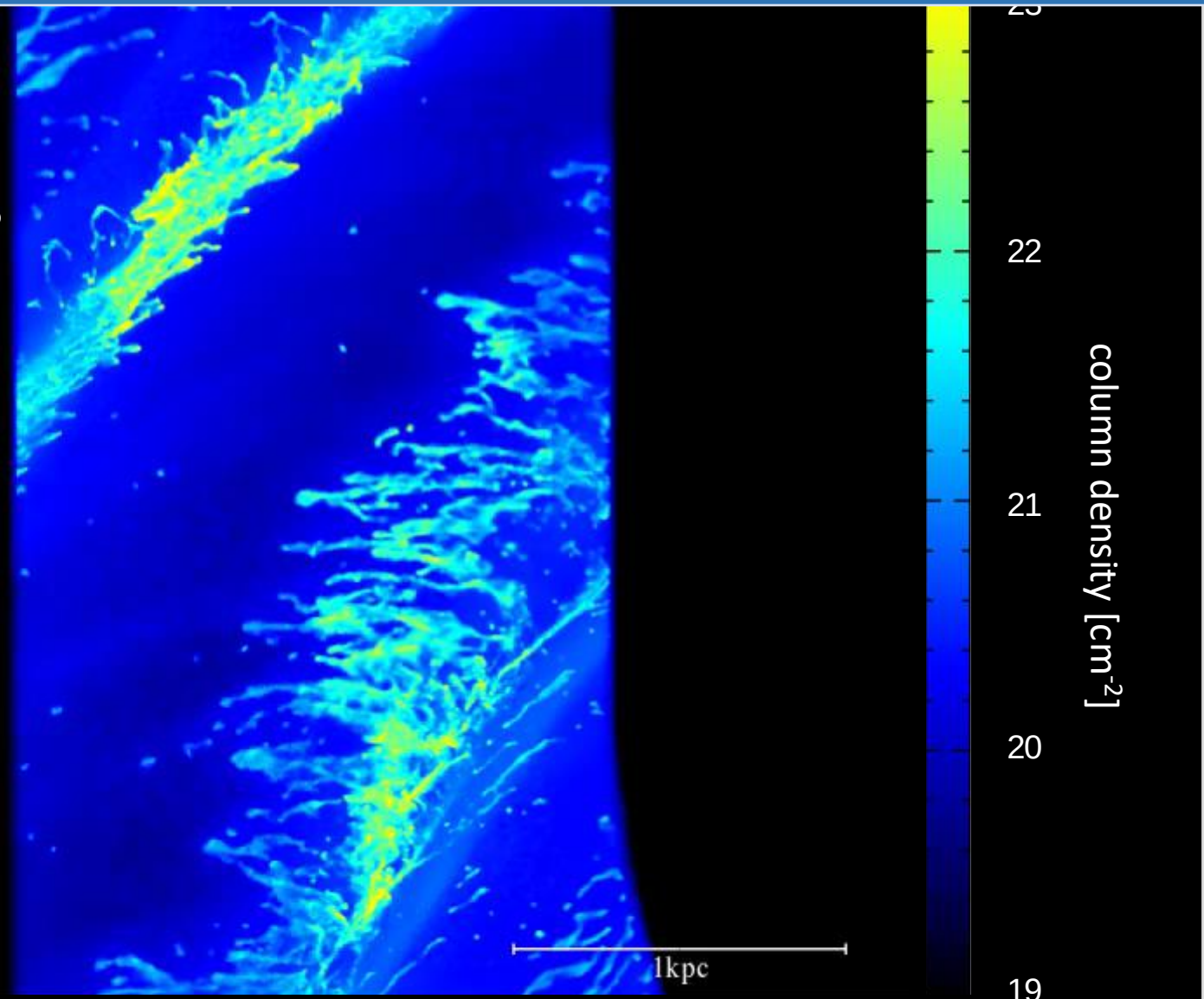


Is this approach valid?

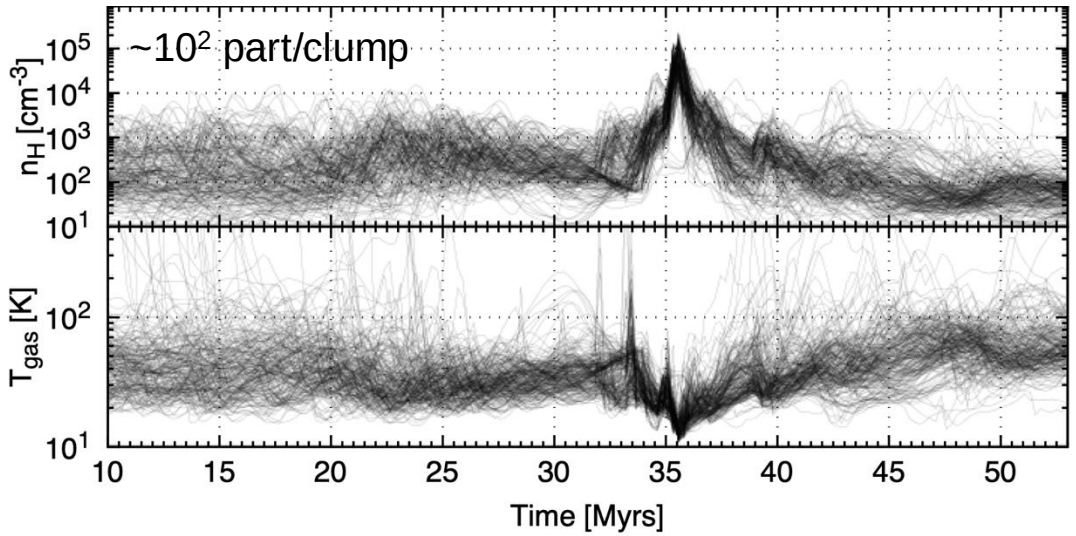
Coupling chemistry with dynamics

- Evolution of a 150x150 pc region:
  - ✓ 10^7 particules of 0.15$M_\odot$ each
  - ✓ over a period of 50 Myr

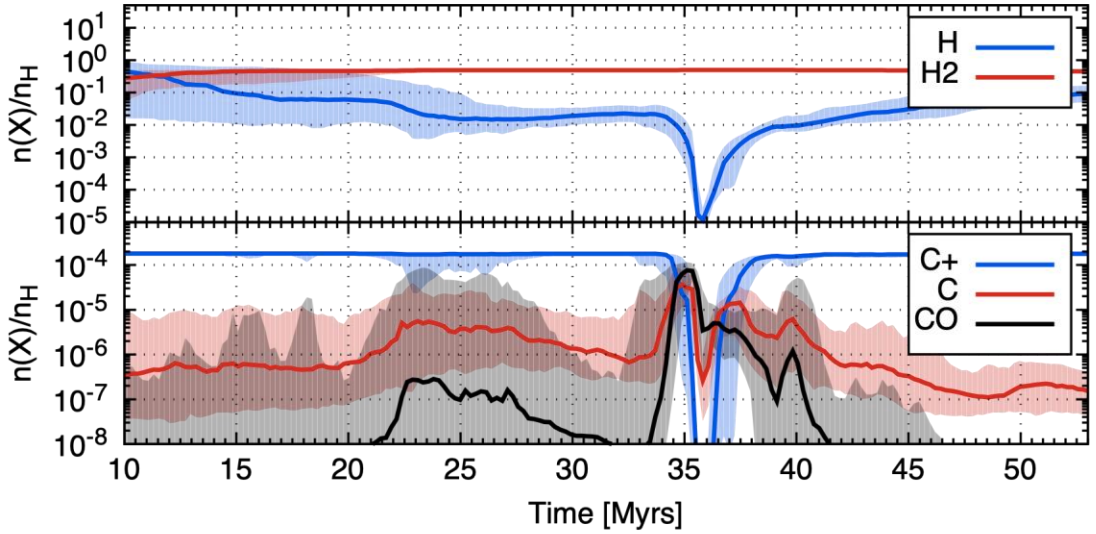
Simulations SPH Bonnel et al. (2013)



Coupling chemistry with dynamics

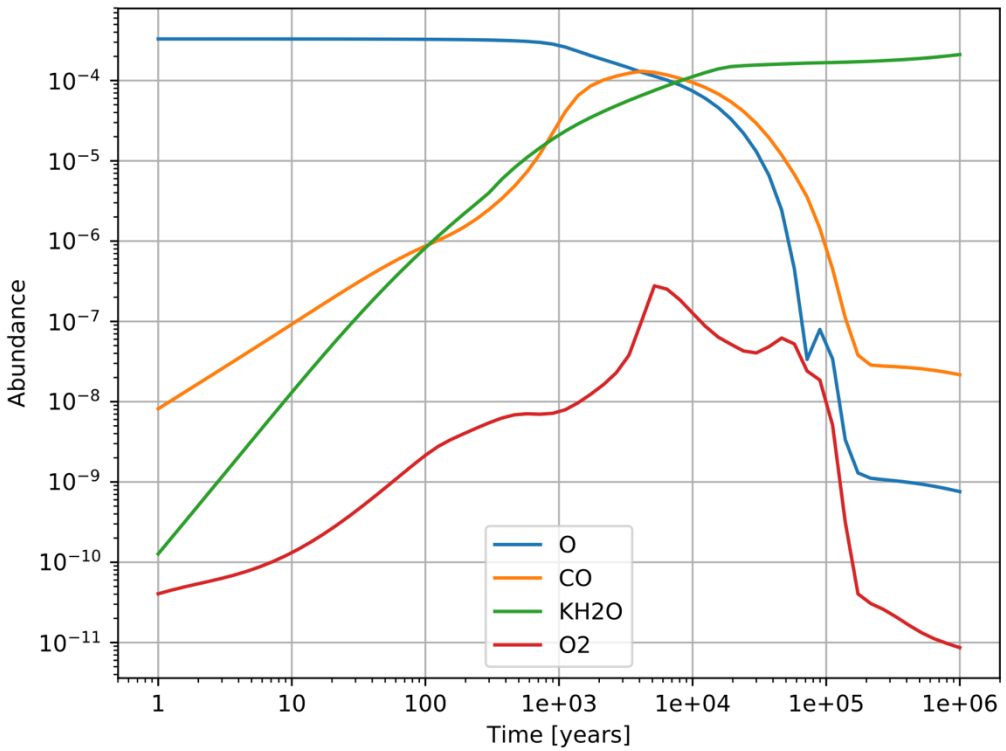


→ Extracting the physical conditions for parcels forming cold cores.

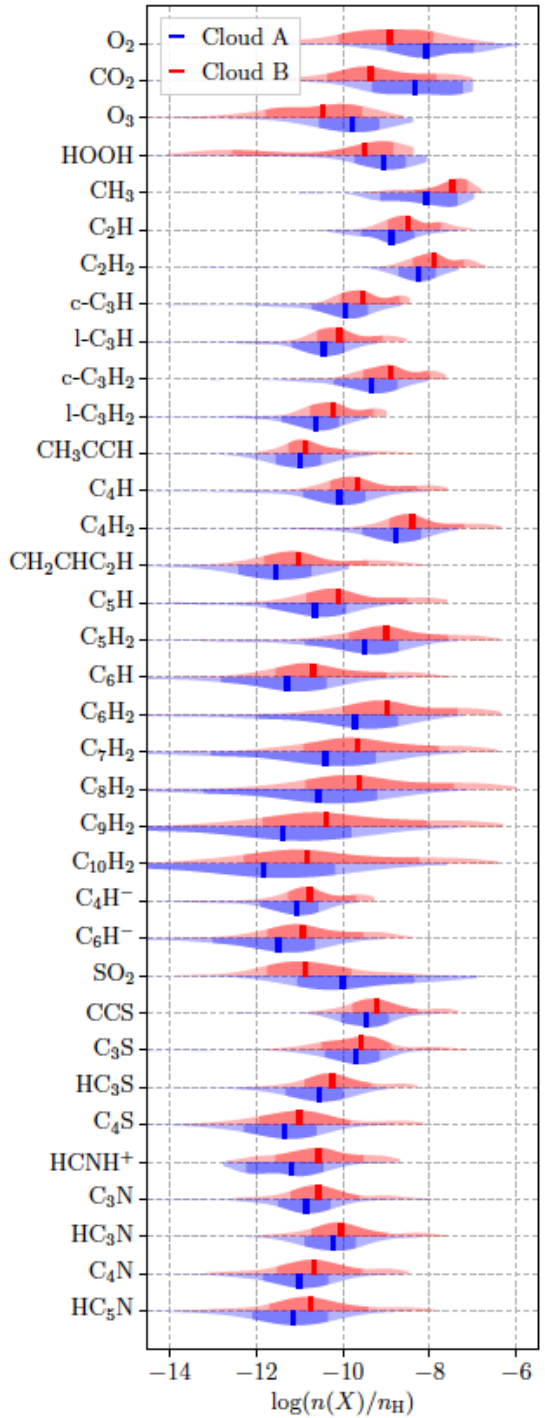


→ Post-process computation of the chemistry for each parcel at each time step.

Classic approach:



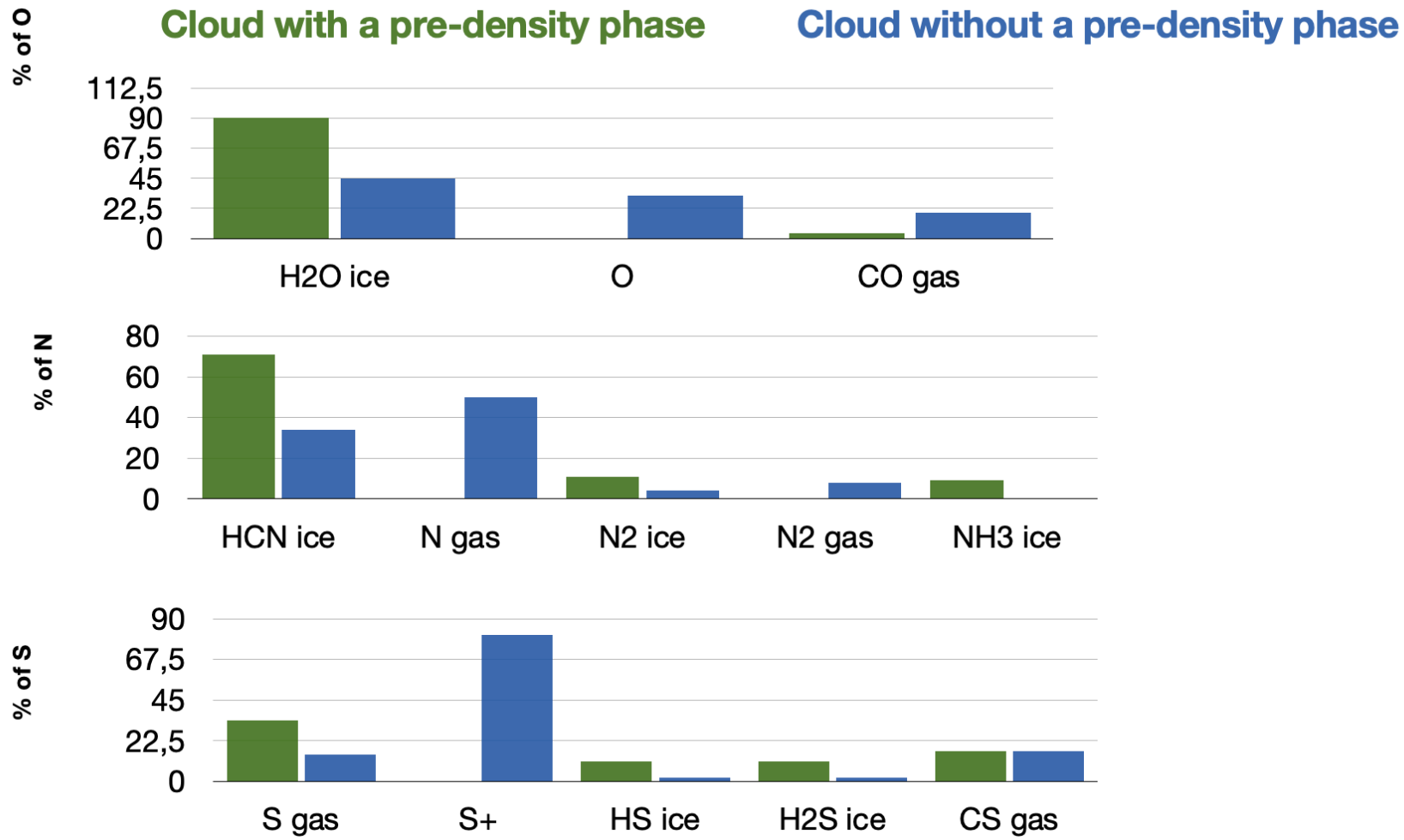
vs



Ruaud et al. 2018

Coupling chemistry with dynamics

Reservoirs of oxygen, nitrogen and sulphur



Take home messages

- In interstellar chemistry, grain-surface reactions need to be considered even though very uncertain.
- Complicated to identify key reactions. So complicated to know in advance if a new rate coefficient estimate will change the model or not.
- The more processes in a network the more stable it will be.
- Different public networks will have different results.
- Your model predictions will depend on the network but also on the physical conditions and their time evolution.