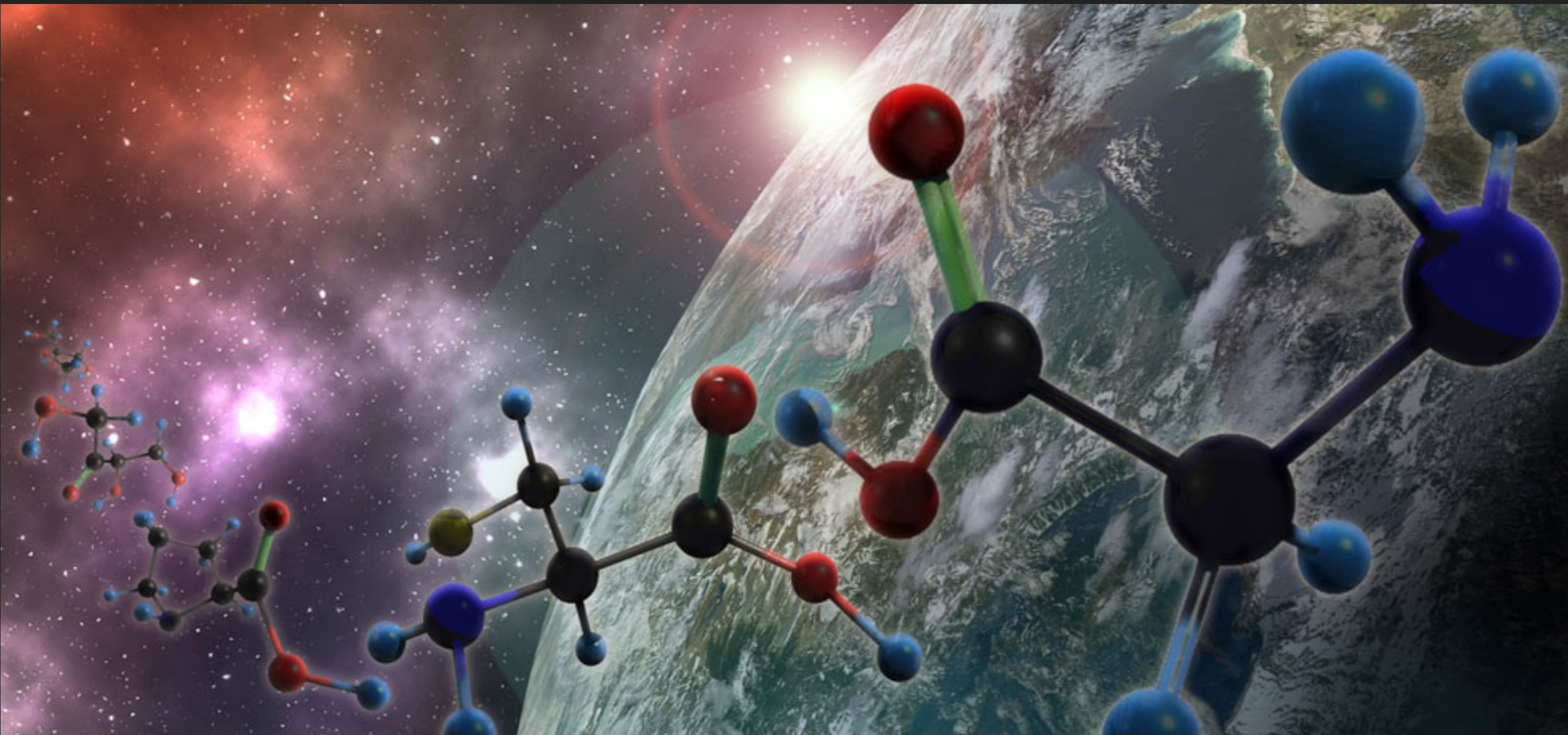


LECTURE 7

STEFANO BOVINO

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Astrochemistry branches



Laboratory Astrochemistry

Quantum Chemistry

Computational Astrochemistry

Observational Astronomy

Spectra, Collisional Coefficients, Atomic/Molecular Data

Chemical Modeling, Simulations, Interpretation of Observations

Astrochemistry branches



Laboratory Astrochemistry

Quantum Chemistry

Computational Astrochemistry

Observational Astronomy

Spectra, Collisional Coefficients, Atomic/Molecular Data

Chemical Modeling, Simulations, Interpretation of Observations

Computational Astrochemistry

Sub-area of Computational Astrophysics

Whatever concerns modeling, chemical kinetics, microphysics

The use of computational tools to understand what we observe

Development of codes for "a priori" studies of astronomical regions

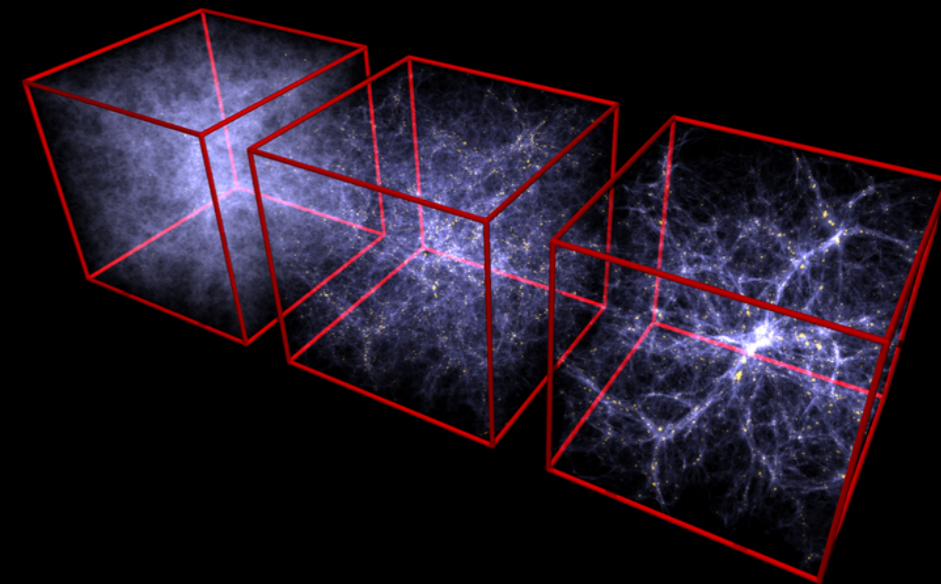
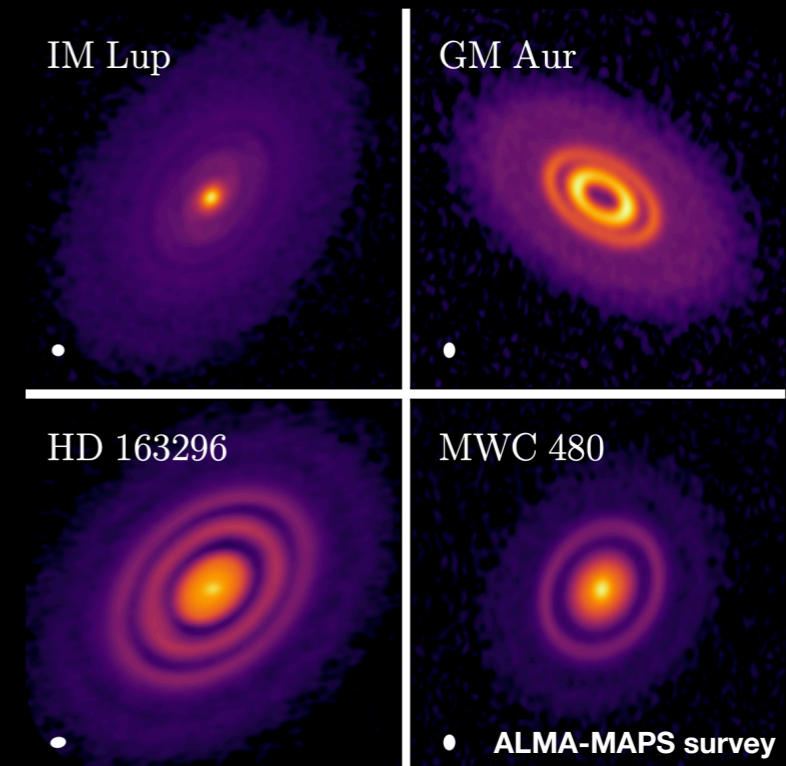
Why do we need models?

- **Observations:**

- Powerful
- Colorful
- Provide a lot of information
- But only provide a single snapshot in time
- Missing three-dimensional information

- **Modeling:**

- Gives us info on the evolution of the object (prior and after the observed stage)



Why chemistry is important (in numerical simulations)

- Needed to compute metal/molecular cooling \rightarrow SF
- Comparison with observations

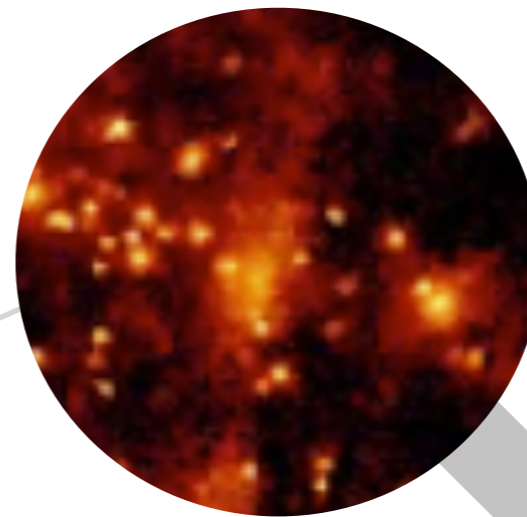
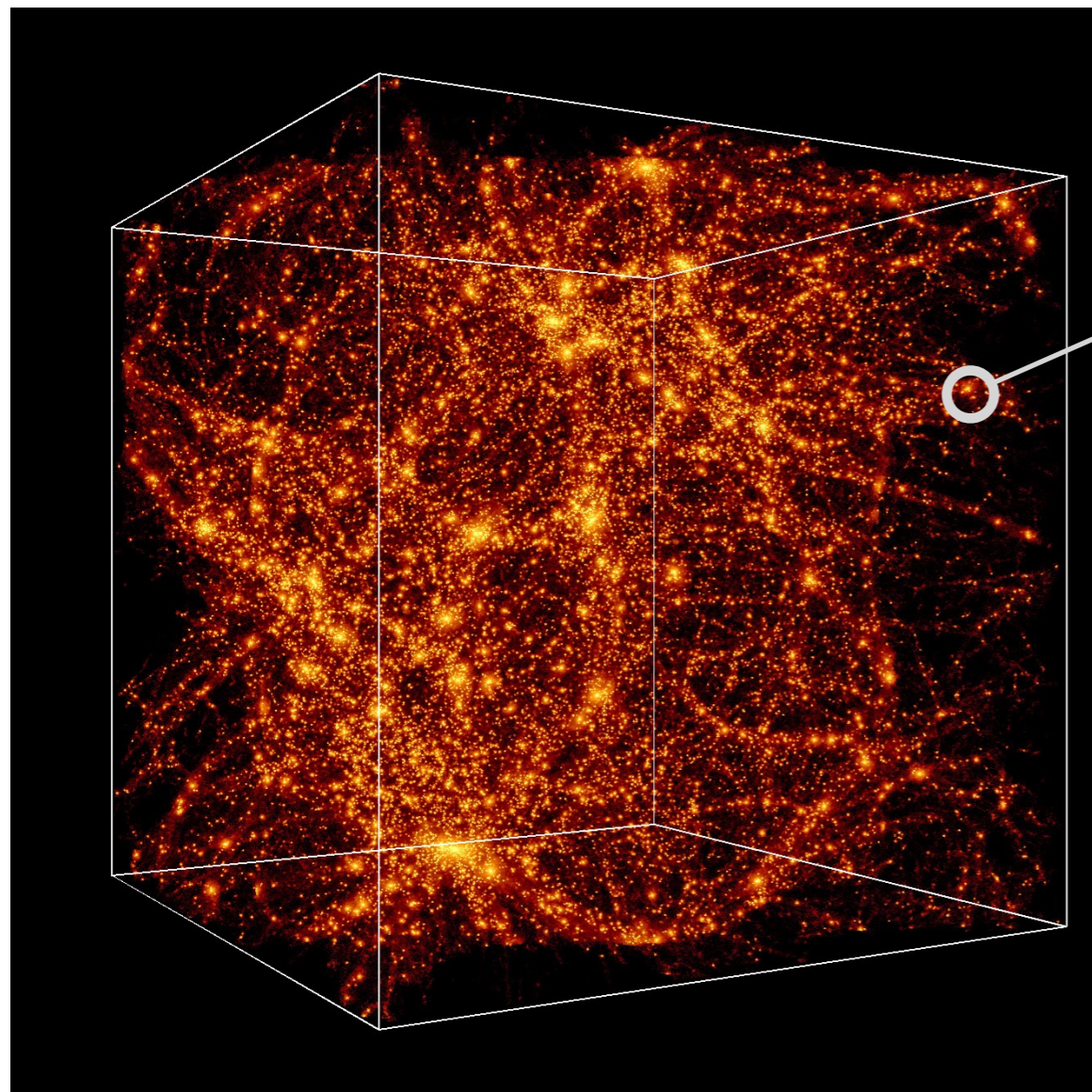
Why chemistry is troublesome (in numerical simulations)

- very CPU demanding
- has a non-linear behaviour
- chemical networks are complex
- connected with many physical processes

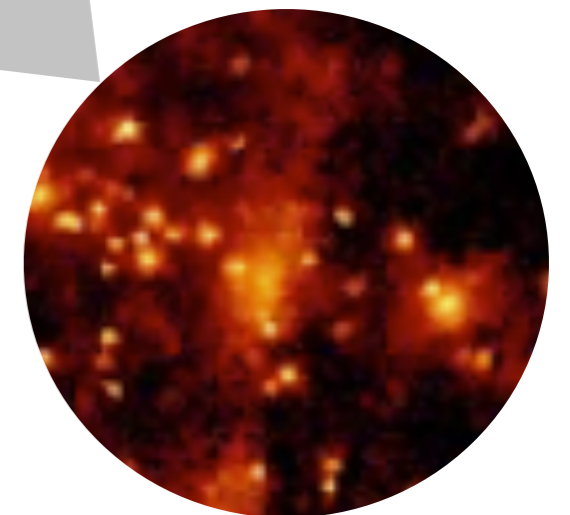
- **Simple (qualitative but very informative):**
 - 0d with fixed physical parameters (often tuned on observations)
 - Time evolution & Sensitivity studies (pseudo time-dependent)
 - Goal: understanding what are the most important processes
 - Interpret observational features (take the comparison with a pinch of salt)

- **Complex (a priori, needed to understand the physics):**
 - Three-dimensional
 - Dynamical information (magnetic fields, turbulence, density fluctuations)
 - Computationally expensive (particularly if chemistry is included)

Hydro-chemistry complexity



ISM particles
Time = t0



ISM particles
Time = t0 + delta t

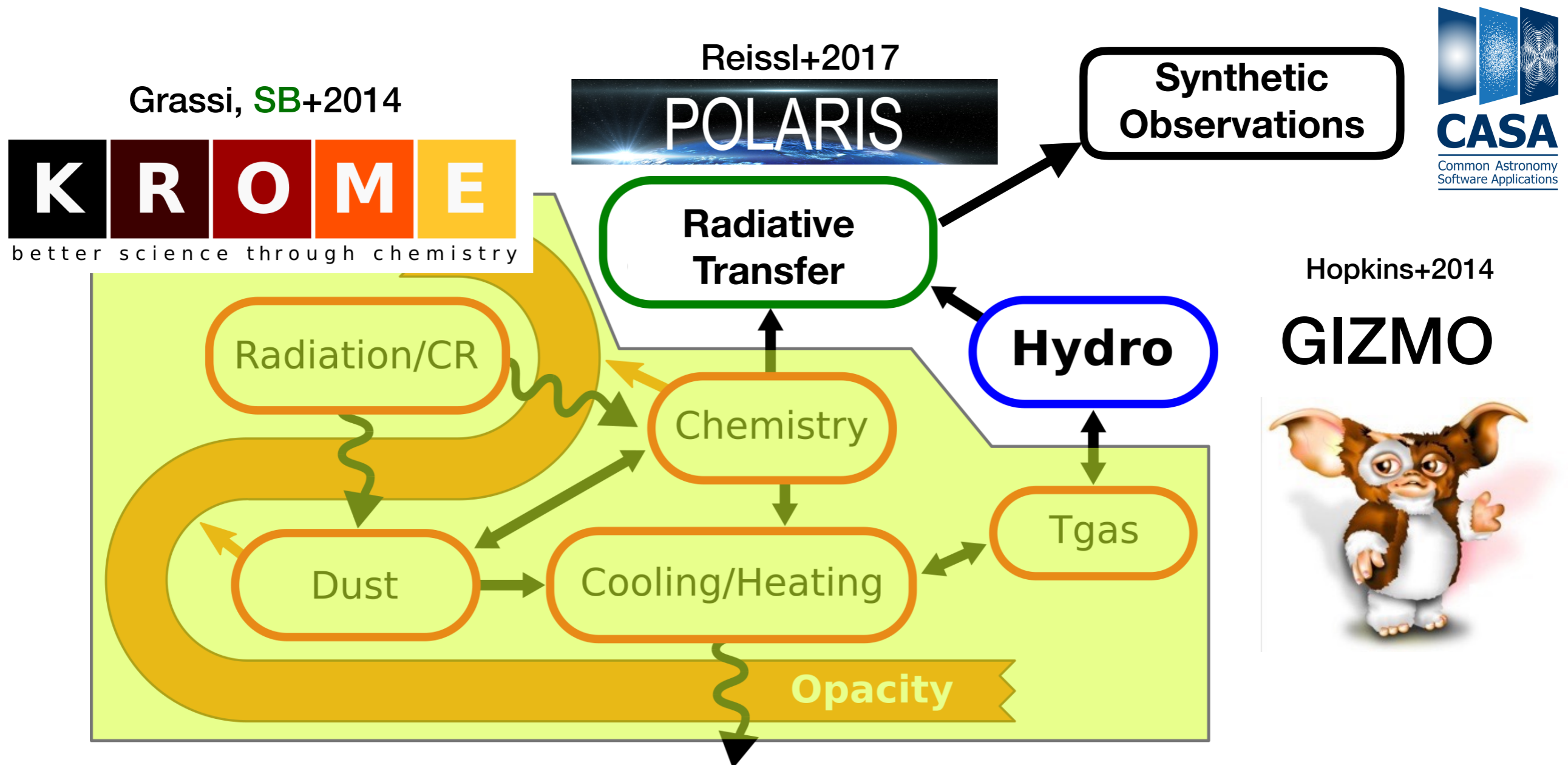
Update a gas volume element every time-step

> 10^6 particles (gas), > 10^4 time-steps

Chemistry is the most intensive part together with the solution of the Poisson equation (gravity solver)

Hydrodynamics + Chemistry

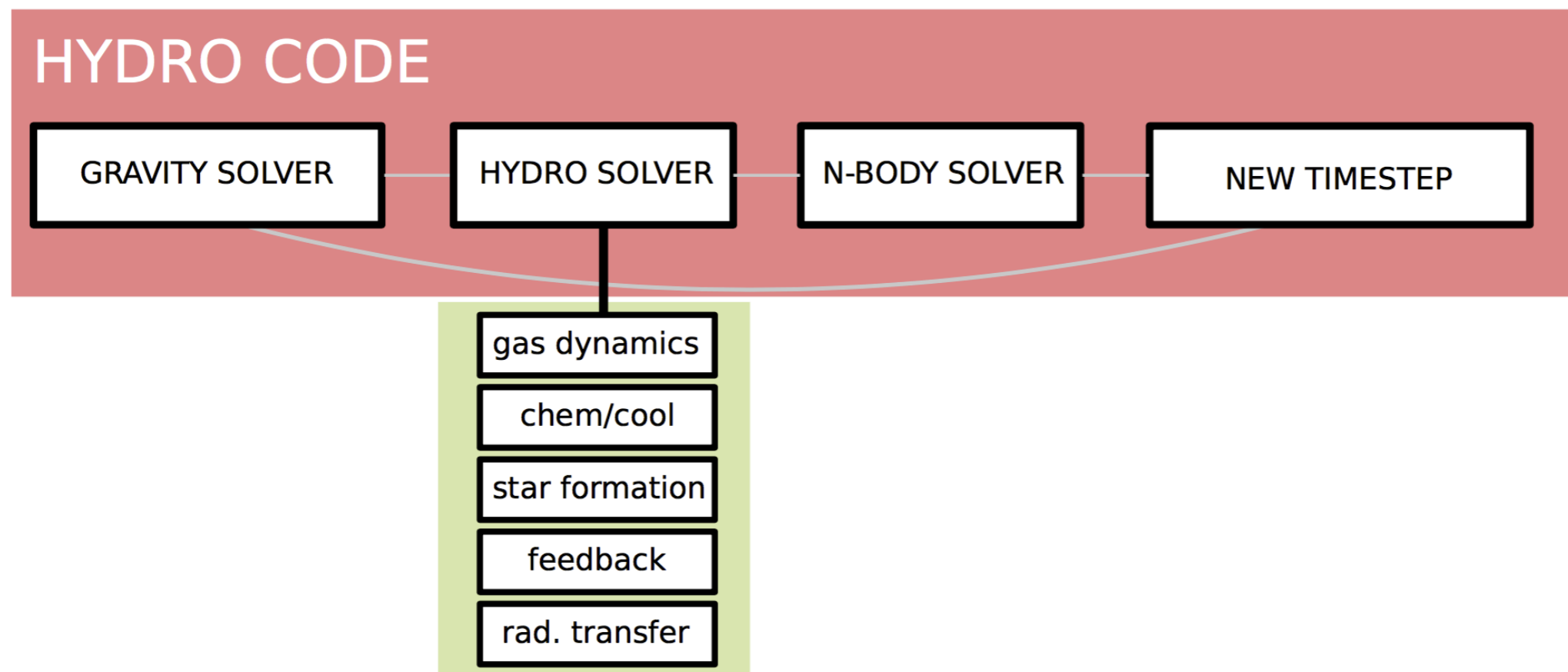
- **GOAL:** compare our simulations with observational data
- **Great advantage:** follow chemistry and microphysics on the fly with hydro



HYDRODYNAMICS - CHEMISTRY COUPLING

Chemistry couples through the energy equation as a source term

$$\frac{\partial(\rho e)}{\partial t} + \nabla[(\rho e + P)v] = S_e \quad (3)$$



ABUNDANCES

- ▶ Absolute quantities (cm^{-3})
- ▶ Relative quantities (abundances or mass fractions)
- ▶ Chemical models compute local densities (n)
- ▶ Observations provide line-of-sights quantities (column densities cm^{-2})

ELEMENTAL ABUNDANCES

- ▶ Total amount of element X is its elemental abundance
- ▶ Abundances are usually measured wrt H nuclei

$$x_X = \frac{n(X)}{n_H}$$

$$n_H = n(\text{H}) + 2n(\text{H}_2) + n(\text{H}^+) + 2n(\text{H}_2^+) + \dots$$

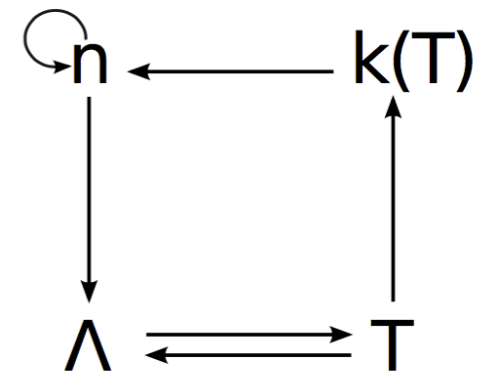
- ▶ In dense clouds sometimes people use :

$$x_X = \frac{n(X)}{n(\text{H}_2)}$$

The problem: mathematically

Stiff: it contains widely varying time scales, i.e., some components of the solution decay much more rapidly than others.

$$\frac{dn_i}{dt} = \overbrace{\sum_{lm} k_{lm}(T) n_l(t) n_m(t)}^{\text{formation}} - \overbrace{\sum_j k_{ij} n_i(t) n_j(t)}^{\text{destruction}}$$
$$\frac{dT}{dt} = \frac{\gamma - 1}{k_B \sum_i n_i} (\Gamma(n, T) - \Lambda(n, T))$$



If in equilibrium

$$\frac{dn_i}{dt} = 0$$

Two types of interstellar regions:

$t_{\text{dyn}} > t_{\text{chem}}$ (steady-state, solved via bisection methods)

$t_{\text{dyn}} < t_{\text{chem}}$ (time-dependent, need a proper solver)

BRIEFLY ON STIFFNESS (CONT'D)

DIFFERENT DEFINITIONS EXIST: a problem is stiff if

- it contains widely varying time scales, i.e., some components of the solution decay much more rapidly than others.
- the stepsize is dictated by stability requirements rather than by accuracy requirements.
- if explicit methods don't work, or work only extremely slowly.
- More generally, a problem is stiff if the eigenvalues of the Jacobian of f differ greatly in magnitude

Explicit vs Implicit methods

- **Explicit:** in order to evaluate y_{n+1} , we use information from time step n
- Forward Euler's method reminder $\rightarrow y_{n+1} = y_n + hf(t_n, y_n)$

it is a single-step method!

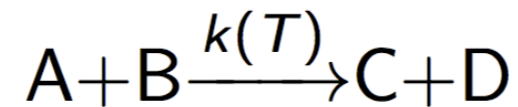


each new time step computation as an initial value problem

Let's introduce the *implicit* methods:

- Backward Euler's method: $y_{n+1} = y_n + hf(t_{n+1}, y_{n+1})$
- it is an algebraic equation to be solved for y_{n+1} Root-finding needed

The core of the problem:



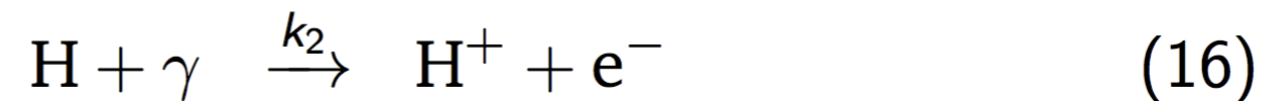
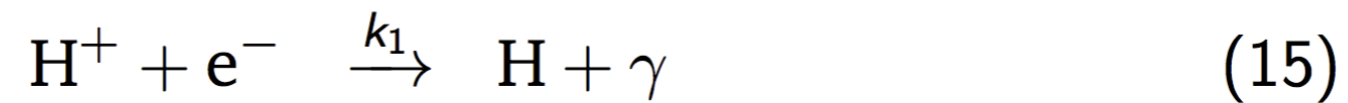
$$k(T) = \left(\frac{8k_b T}{\pi \mu} \right)^{1/2} \frac{1}{(k_B T)^2} \int_0^\infty \sum_{\nu' j'} \sigma_{j' \nu' \leftarrow j=0 \nu=0}(E) e^{-E/k_B T} E dE$$

$$\text{flux} = k(T) n_A(t) n_B(t)$$

↓
ODEs

- ▶ $k(T) \rightarrow$ rate coefficients in $\text{cm}^3 \text{s}^{-1}$ or $\text{cm}^6 \text{s}^{-1}$ or s^{-1}
- ▶ $n(t) \rightarrow$ concentrations in cm^{-3}

A simple chemical network



ODE and Jacobian (an excerpt)

$$\frac{dn_{\text{H}}}{dt} = k_1 n_{\text{H}^+} n_{\text{e}^-} - k_2 n_{\text{H}} \quad (17)$$

$$\frac{\partial^2 n_{\text{H}}}{\partial t \partial n_{\text{H}}} = k_2 \quad \frac{\partial^2 n_{\text{H}}}{\partial t \partial n_{\text{H}^+}} = k_1 n_{\text{e}} \quad (18)$$

RATE COEFFICIENTS ARE KEY PARAMETERS (BUT CAUTION)

How to determine $k(T)$?

- ▶ Experimental (lucky)
- ▶ Langevin (estimate)
 - ▶ valid for ion-molecule reactions
 - ▶ "exothermic", i.e. without barrier
 - ▶ temperature independent
- ▶ Physical considerations (e.g. H=D)
- ▶ *ab initio* calculations (not always available)
 - ▶ solving the Schrödinger equation (2nd order coupled PDEs)

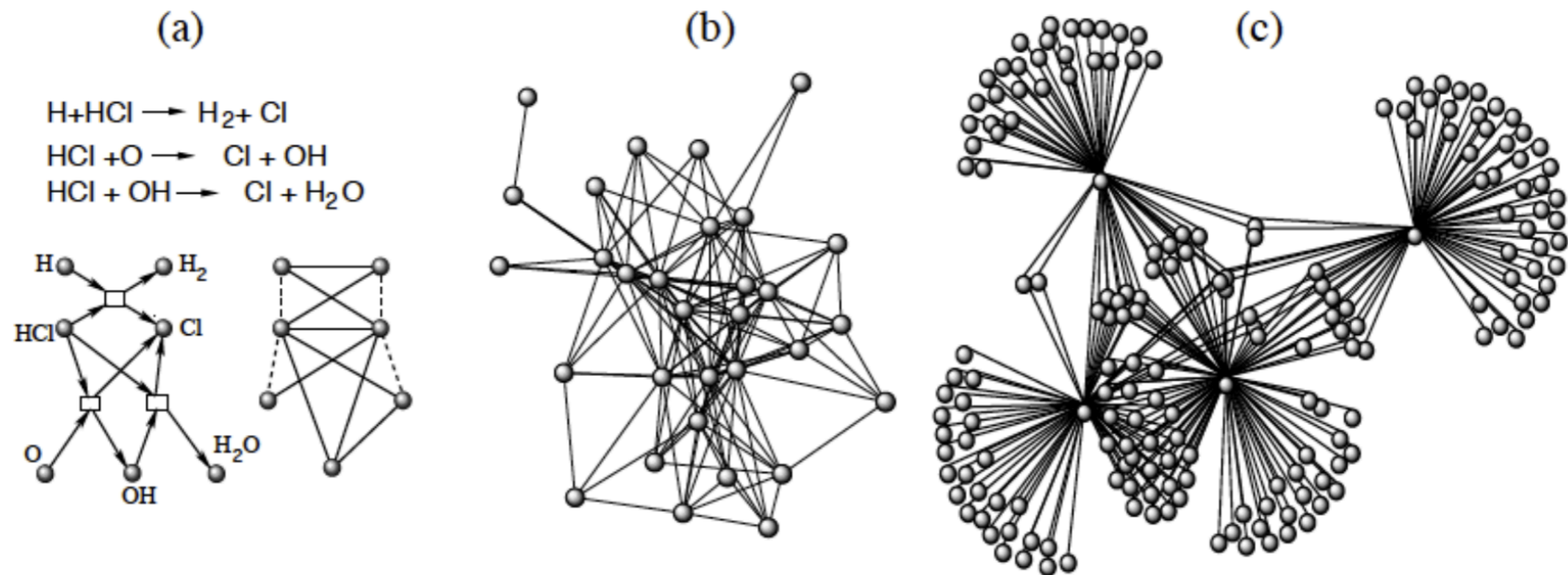
THIS IS A WORK FOR QUANTUM CHEMISTS!

NETWORKS ARE COMPLEX

Astrochemical networks

NODES → chemical species

EDGES → conversion between chemicals



Backward reactions not included, problem with the equilibrium solution

Chemistry is controlled by:

Temperature (kinetic rate coefficient, desorption...)

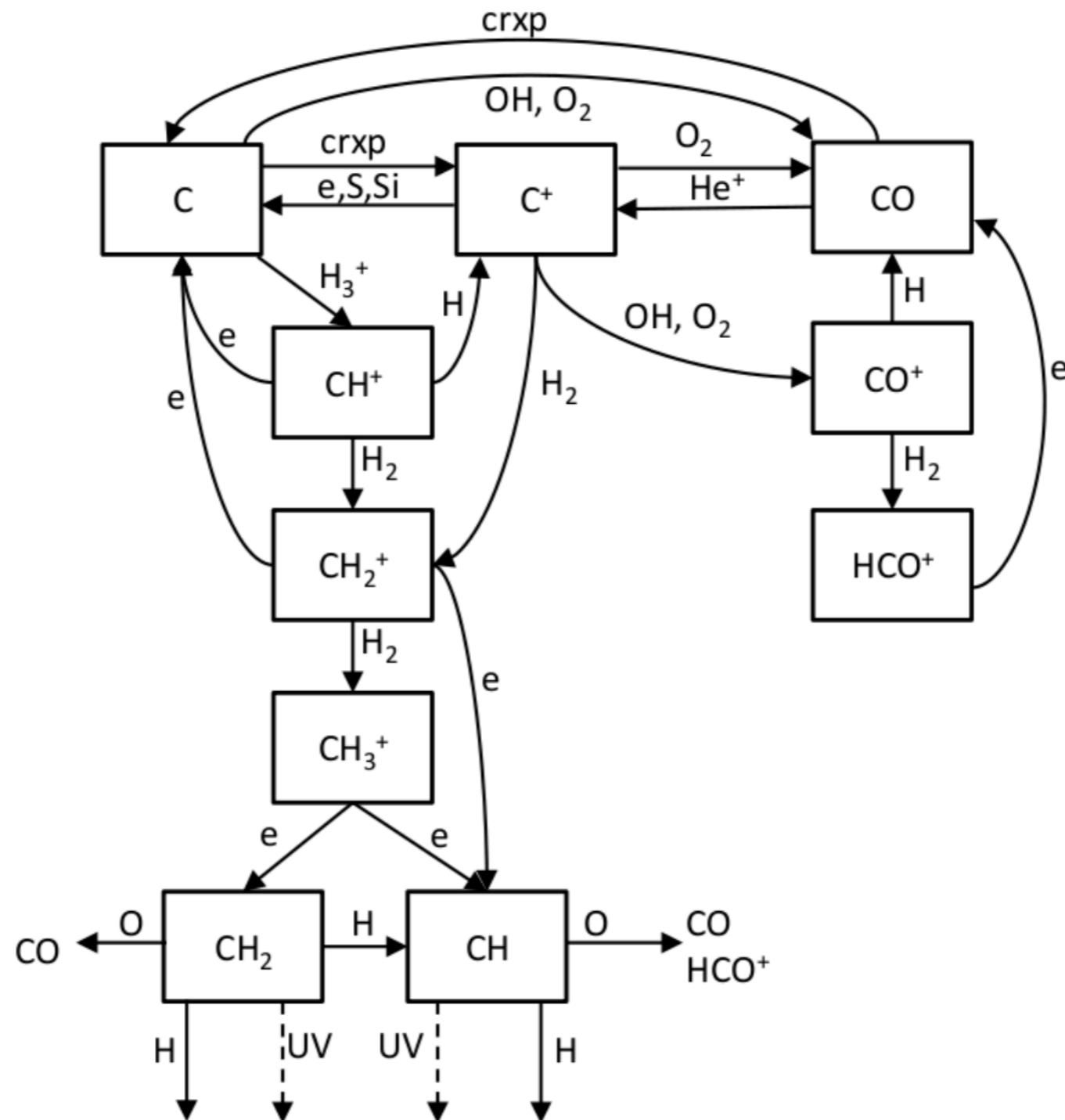
Density (frequency of collisions, ionization, freeze-out)

Ionization: UV, cosmic rays

External UV flux (ISRF)

Cosmic ray ionization rate

CO NETWORK EXAMPLE



- ▶ solve a system of coupled ODEs is computationally expensive (stiff)
- ▶ it requires accurate implicit solvers
- ▶ to build a chemical network is not an easy task
 - ▶ accuracy of rates
 - ▶ availability of rates
 - ▶ how to retrieve the rates
- ▶ reaction rates databases: UMIST, OSU, KIDA (~5000 reactions)
 - ▶ never trust
 - ▶ a lot of uncertainties

EXAMPLE

Problem 1 - nodes (species)

atoms (H, He, C, N, O, Si, Ne, S, P, F, Al, ...)?

species (H, H₂, CO, CH, ...)?

cations and anions (H⁻, H⁺, C³⁺, CH⁻ ...)?

isomers (HOC⁺, HCO⁺, ...)?

isotopes (¹²C¹⁶O, ¹³C¹⁶O, ...)?

fancy stuff (dust, PAH, ...)?

Problem 2 - edges (reactions)

bimolecular (OH⁺ + e⁻ → O + H)?

photochemistry (H⁻ + γ → H + e⁻)

cosmic rays (CO + CR → C + O)

cosmic rays secondary (CO + CRP → C + O)

3-body (H + H + H₂ → H₂ + H₂)

Problem 1 - nodes (species)

atoms (H, He, C, N, O, Si, Ne, S, P, F, Al, ...)?

species (H, H₂, CO, CH, ...)?

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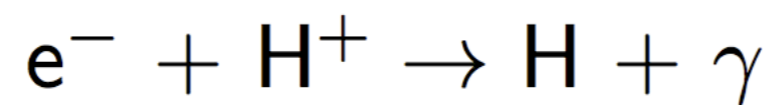
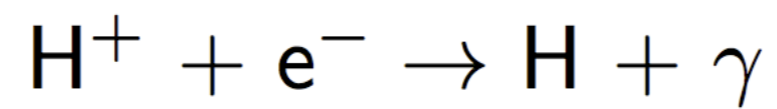
cosmic rays (CO + CR → C + O)

cosmic rays secondary (CO + CRP → C + O)

3-body (H + H + H₂ → H₂ + H₂)

	H	H ⁺	H ⁻	e ⁻	γ	CR
H						
H ⁺	x					
H ⁻	x	x				
e ⁻	x	x	x			
γ	x	x	x	x		
CR	x	x	x	x	x	

chemical reactions “commutes”



	H	H ⁺	H ⁻	e ⁻	γ	CR
H						
H ⁺	x	x			x	x
H ⁻	x	x	x	x		
e ⁻	x	x	x	x	x	x
γ	x	x	x	x	x	x
CR	x	x	x	x	x	x

some pairs are impossible (e.g. H⁻ + H⁻)

	H	H ⁺	H ⁻	e ⁻	γ	CR
H	x	x				
H ⁺	x	x			x	x
H ⁻	x	x	x	x		
e ⁻	x	x	x	x	x	x
γ	x	x	x	x	x	x
CR	x	x	x	x	x	x

some reactions lead to species \notin subset (e.g. $\text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e}^-$)

	H	H ⁺	H ⁻	e ⁻	γ	CR
H	x	x	✓	✓ ✓	✓	✓
H ⁺	x	x	✓	✓	x	x
H ⁻	x	x	x	x	✓	✓
e ⁻	x	x	x	x	x	x
γ	x	x	x	x	x	x
CR	x	x	x	x	x	x

final set of reactions

Final network

$\text{H} + \text{e}^-$	\rightarrow	$\text{H}^+ + 2\text{e}^-$	collisional ionization
$\text{H} + \text{e}^-$	\rightarrow	$\text{H}^- + \gamma$	radiative attachment
$\text{H} + \gamma$	\rightarrow	$\text{H}^+ + \text{e}^-$	photoionization
$\text{H} + \text{CR}$	\rightarrow	$\text{H}^+ + \text{e}^-$	CR ionization
$\text{H}^+ + \text{e}^-$	\rightarrow	$\text{H} + \gamma$	recombination
$\text{H}^+ + \text{H}^-$	\rightarrow	$\text{H} + \text{H}$	mutual recombination
$\text{H}^- + \gamma$	\rightarrow	$\text{H} + \text{e}^-$	electron photodetachment
$\text{H}^- + \text{H}$	\rightarrow	$2\text{H} + \text{e}^-$	collisional detachment
$\text{H}^- + \text{CR}$	\rightarrow	$\text{H} + \text{e}^-$	CR detachment

WHAT WE HAVE TO DO NOW?

- ▶ hunt the rate coefficients you need
- ▶ build the system of rate equations
- ▶ look for an accurate solver to integrate the equations
- ▶ set your initial conditions
- ▶ solve the system and check the results (easiest part, but not always)

DATABASES: KIDA

- ▶ Up-to-date database
- ▶ Involve people with different expertise
- ▶ Include gas-grain reactions
- ▶ Include pre-built networks (for molecular clouds, planetary atmosphere...)
- ▶ Useful as a starting point
- ▶ Suggestion: always re-check in literature if there are new or better rates

<http://kida.obs.u-bordeaux1.fr>

DATABASES: KIDA

WHAT ARE THE TYPES OF REACTIONS?

In KIDA, there are four big families of reactions:

- Unimolecular reactions include dissociations and ionizations by cosmic-ray particles, [secondary UV photons induced by cosmic-ray particles](#) and direct UV photons. ITYPES 1 to 3.
- Bimolecular reactions includes all chemical reactions between two species. ITYPES 4 to 8
- Termolecular reactions are 3-body assisted reactions.
- Surface reactions are reactions occurring at the surface of interstellar grains between adsorbed species.

ITYPE	Description
1	Dissociation or ionization of species due to direct collision with cosmic-ray particles.
2	Dissociation or ionization of species due to UV photons emitted following H ₂ excitation.
3	Dissociation or ionization of neutral species by UV photons with a standard interstellar UV field.
4	Neutral-neutral ($A + B \rightarrow C + D$), ion-neutral ($A^+ + B \rightarrow C^+ + D$, $A^- + B \rightarrow C^- + D$), anion-cation ($A^+ + B^- \rightarrow C + D$) reactions and associative ionization ($A + B \rightarrow AB^+ + e^-$)
5	Exchange reaction $A^+ + B \rightarrow A + B^+$ and $A^+ + B^- \rightarrow A + B$
6	Association reactions between two species (neutral or ionized) stabilized by the emission of a photon ($A + B \rightarrow AB + \text{photon}$ or $A^+ + B \rightarrow AB^+ + \text{photon}$).
7	Association of a neutral species and an anion, resulting in the ejection of the extra electron ($A^- + B \rightarrow AB + e^-$).
8	Recombination of a positive ion with an electron resulting in the dissociation of the molecule ($AB^+ + e^- \rightarrow A + B$) or the emission of a photon ($AB^+ + e^- \rightarrow AB + \text{photon}$) or the attachment of the electron ($A + e^- \rightarrow A^- + \text{photon}$)

DATABASES: KIDA

WHICH FORMULA ARE USED TO COMPUTE THE RATE COEFFICIENTS (FOR GAS-PHASE REACTIONS) FROM THE PARAMETERS STORED IN THE DATABASE?

Five different formula can be used to compute the rate coefficients from the parameters listed in KIDA.

Number (for export)	Name	Formula	Units
1	Cosmic-ray ionization	$k = \alpha\zeta$ (ζ : H_2 cosmic-ray ionization rate)	s^{-1}
2	Photo-dissociation (Draine)	$k = \alpha e^{-\gamma A_v}$ (A_v : visual extinction)	s^{-1}
3	Modified Arrhenius	$k(T) = \alpha(T/300)^\beta e^{-\gamma/T}$	$cm^3 s^{-1}$
4	ionpol1	$k(T) = \alpha\beta (0.62+0.4767\gamma(300/T)^{0.5})$	$cm^3 s^{-1}$
5	ionpol2	$k(T) = \alpha\beta (1+0.0967\gamma(300/T)^{0.5} + \frac{\gamma^2}{10.526} \frac{300}{T})$	$cm^3 s^{-1}$
6	3-body	See here	





For information on the ionpol1 and ionpol2 formula see [here](#).

For information on the visual extinction A_v see [here](#).













SUGGESTION ABOUT QUALITY OF THE RATES

WHAT ARE THE QUALITY INDICATORS OF THE RATE COEFFICIENTS?

Quality indicators are of four types:

-  Not recommended value
-  Not rated value
-  Valid value
-  Recommended value

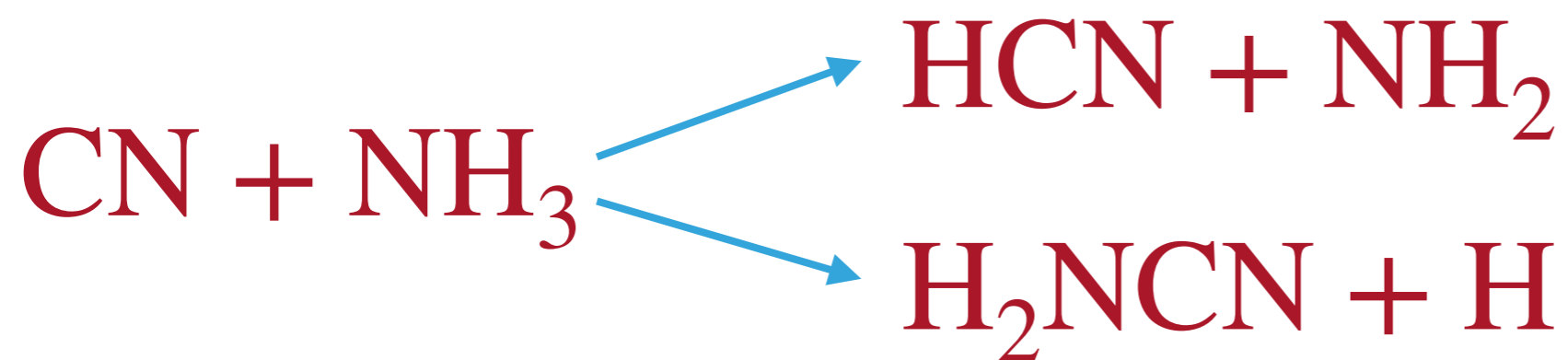
« Not recommended » means that either we have found a mistake in the data or there is a more accurate value to use. We do not erase any value from KIDA, this is why we use this indicator. « Not rated » means that we do not know. « Valid » is used for data with a proper reference (usually papers published by physico-chemists). « Recommended » is used for reactions that have been studied by KIDA experts and a [datasheet](#) explaining the recommendation is also available.




Type	Reaction	α	β	γ	T (K)	Formula 	Evaluation	
Bimo	H + OH	→ O + H ₂	6.86E-14	2.80E+0	1.95E+3	10-280	Modified Arrhenius equation	
		→ O + H ₂	6.99E-14	2.80E+0	1.95E+3	50-200	Modified Arrhenius equation	
Bimo	H ₂ + O	→ H + OH	6.34E-12	0.00E+0	4.00E+3	298-3300	Modified Arrhenius equation	
		→ H + OH	1.46E-12	0.00E+0	9.65E+3	298-3300	Modified Arrhenius equation	
Bimo	H ₃ ⁺ + O ⁻	→ H + O + H ₂	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	C ₂ H ₃ ⁺ + O ⁻	→ O + H ₂ + CCH	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	C ₅ H ₅ ⁺ + O ⁻	→ H + O + H ₂ + C ₅ H ₂	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	C ₇ H ₅ ⁺ + O ⁻	→ H + O + H ₂ + C ₇ H ₂	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	C ₈ H ₄ ⁺ + O ⁻	→ O + H ₂ + C ₈ H ₂	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	C ₉ H ₄ ⁺ + O ⁻	→ O + H ₂ + C ₉ H ₂	7.51E-8	-5.00E-1	0.00E+0	10-280	Modified Arrhenius equation	
Bimo	H ₂ + O(1D)	→ H + OH	1.09E-10	4.94E-2	0.00E+0	50-296	Modified Arrhenius equation	

TYPICAL PROBLEMS

- ▶ Range of temperatures
- ▶ Branching ratios
- ▶ Accuracy
- ▶ Availability
- ▶ Reliability

TYPICAL PROBLEMS



Type	Reaction		α	β	γ	T (K)	Formula 	Evaluation
Bimo	CN + NH₃	→ HCN + NH ₂	2.77E-11	-8.50E-1	0.00E+0	10-298	Modified Arrhenius equation	
		→ H + NH ₂ CN	0.00E+0	0.00E+0	0.00E+0	10-298	Modified Arrhenius equation	

KIDA



What if you have to use this reaction in a high-energy problem

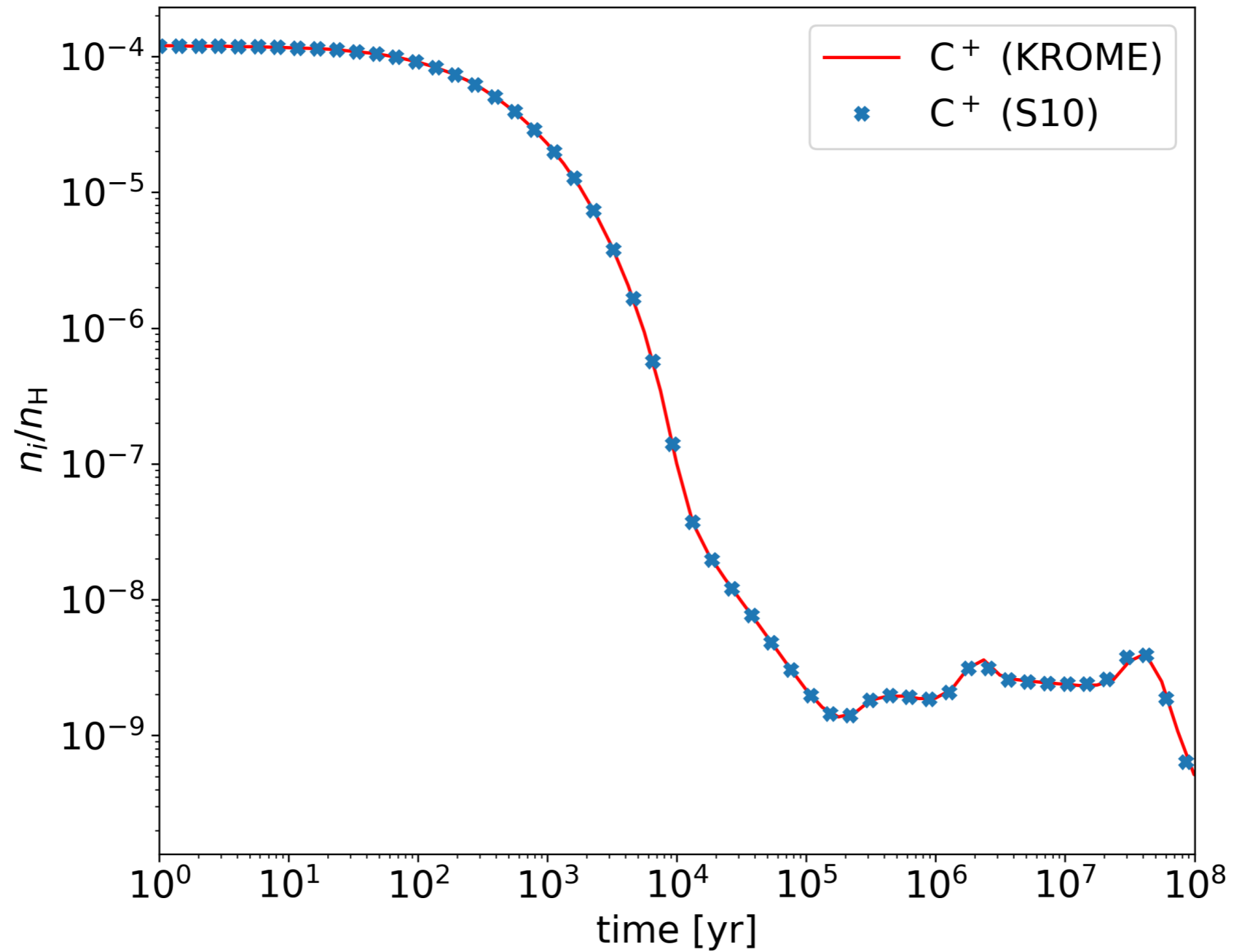
CHARGE CONSERVATION DURING RUNTIME

- ▶ Electrons play a fundamental role in the chemistry
- ▶ Imperative to make sure the electric charge is conserved
- ▶ And check overall charge neutrality

$$n(e^-) = \sum_{\text{cations}} n(i) - \sum_{\text{anions}} n(j) \geq 0$$

- Input parameters: units, proper values
- Initial abundances
- Feasibility of computed chemistry: how to check it?
- Many rates have large uncertainties
- Surface chemistry: stochasticity, desorption/binding energies, porosity, bulk ice vs reactive surface, diffusion between monolayers, etc

BENCHMARKS: THE FUNDAMENTAL STEP



Chemical network:

Set of reactive collisions + ionization + ...

Databases: KIDA, UMIST...

Numerical solver:

Time-dependent: stiff 1st order ODE

Steady-state: zero-finding algorithms (e.g. Newton-Raphson)

Boundary conditions:

Elemental abundances, initial chemical conditions

The engine:

The network: typically 100-500 species and thousands gas-phase reactions

Small vs big networks

With or without ice chemistry

Secondary photons, grain charge

Uncertain processes (chemical desorption...)

A model:

Boundary conditions

Time dependent vs steady-state

Physical framework (0d to 3d)

Solve a system of coupled 1st order ODE

Uncertain processes (chemical desorption...)

Rule of thumb:

Include all the essential chemical processes to simulate accurately the chemistry of the desired molecule(s)

In principle:

More reactions more accurate the solution

In practice:

Risk of increasing the computational costs and introduce uncertainties

Top-down (fast but complex):

Download existing chemical networks and reduce to your needs

Always re-check the network after removal of species/reactions

Bottom-up (slow and risky, but more control):

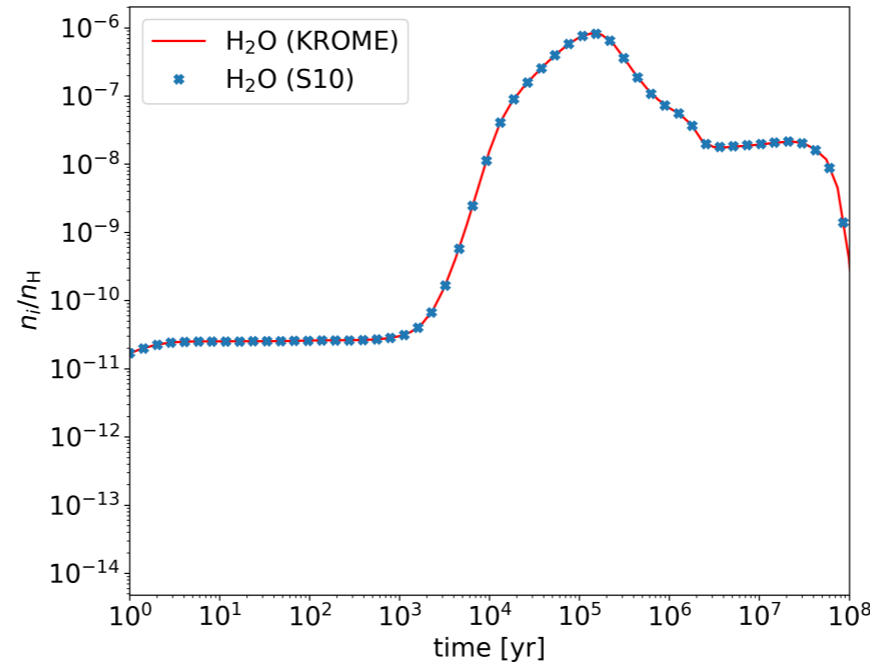
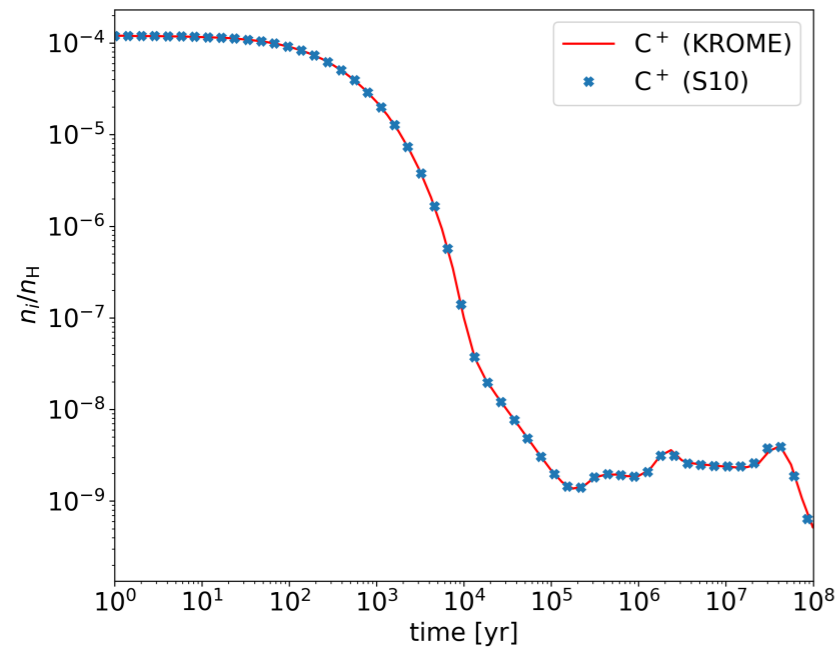
Build a chemical network from scratch starting with the most relevant processes

Things to keep into account:

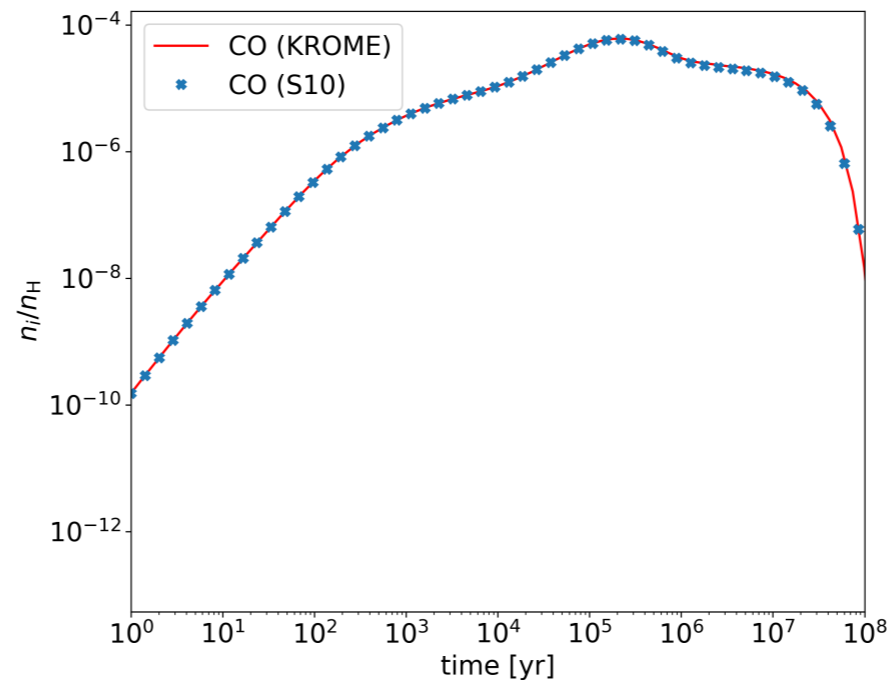
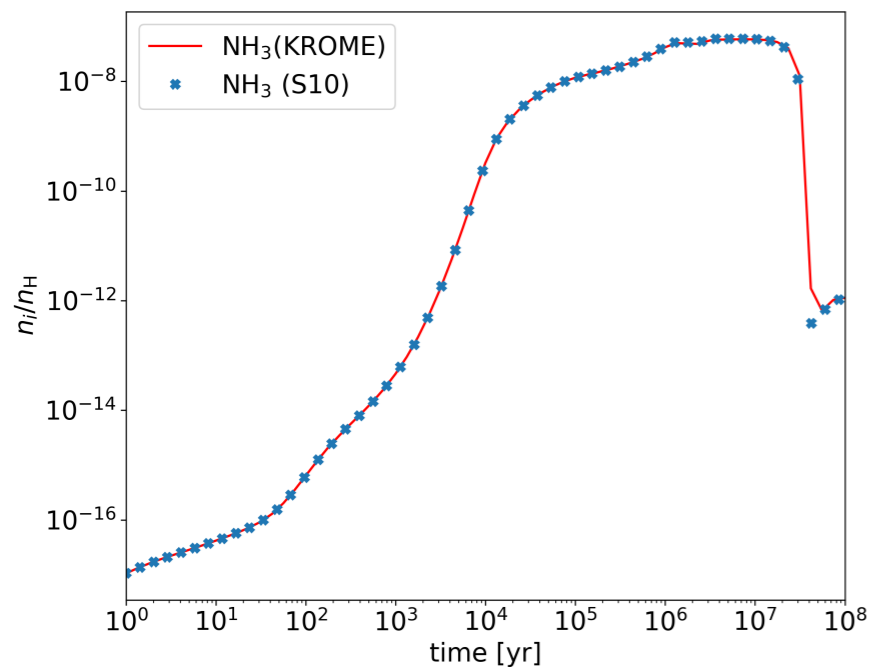
CLOSURE: all species included in the network must have formation/destruction pathways

Sink species might cause problems (but not necessarily)

EXAMPLES: LOW-DIMENSIONALITY MODELS

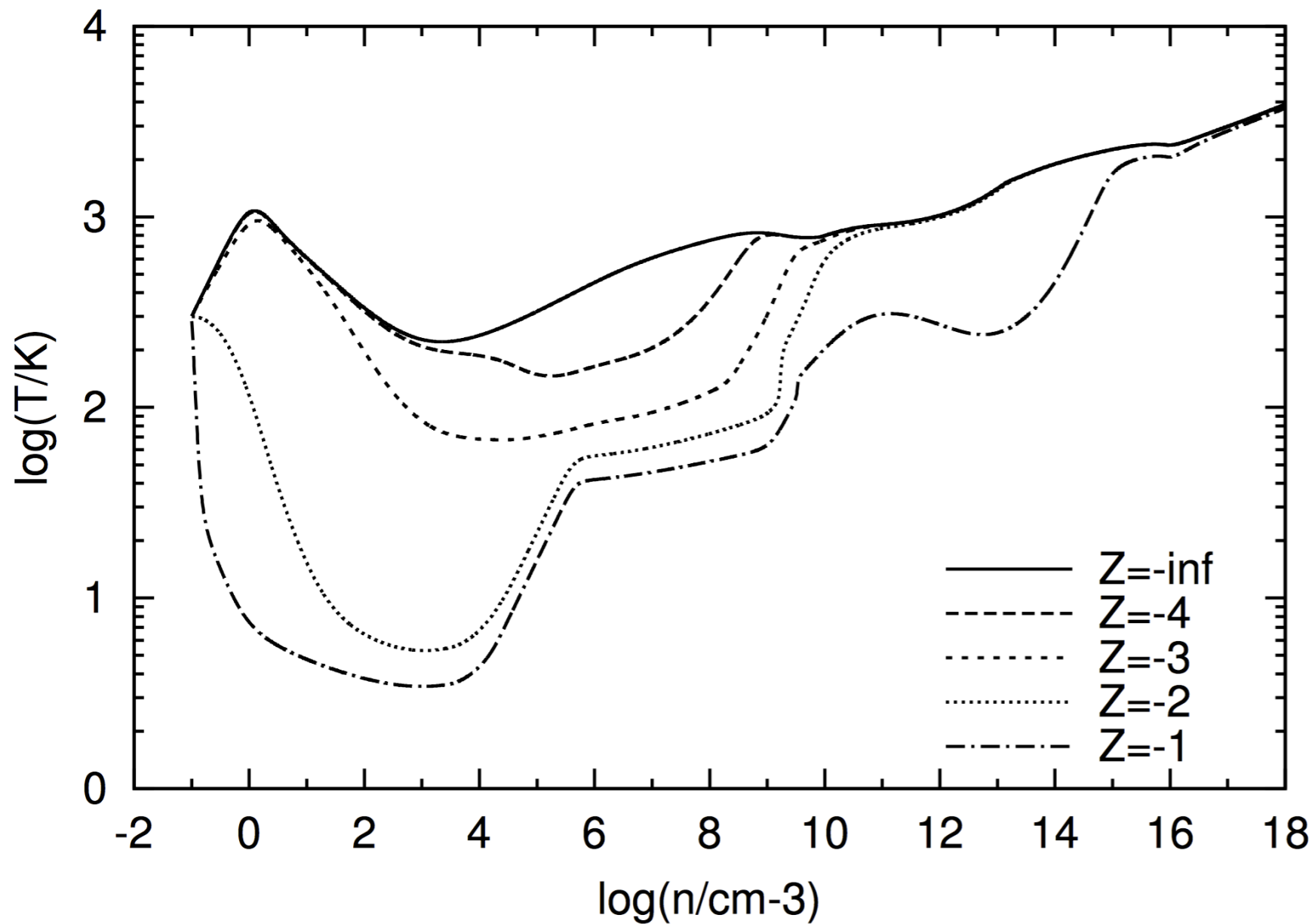


$T = 10 \text{ K}$, $n = 10^4 \text{ cm}^{-3}$
Includes surface chemistry



Recent benchmark
KROME vs Semenov 2010

EXAMPLES: LOW-DIMENSIONALITY MODELS

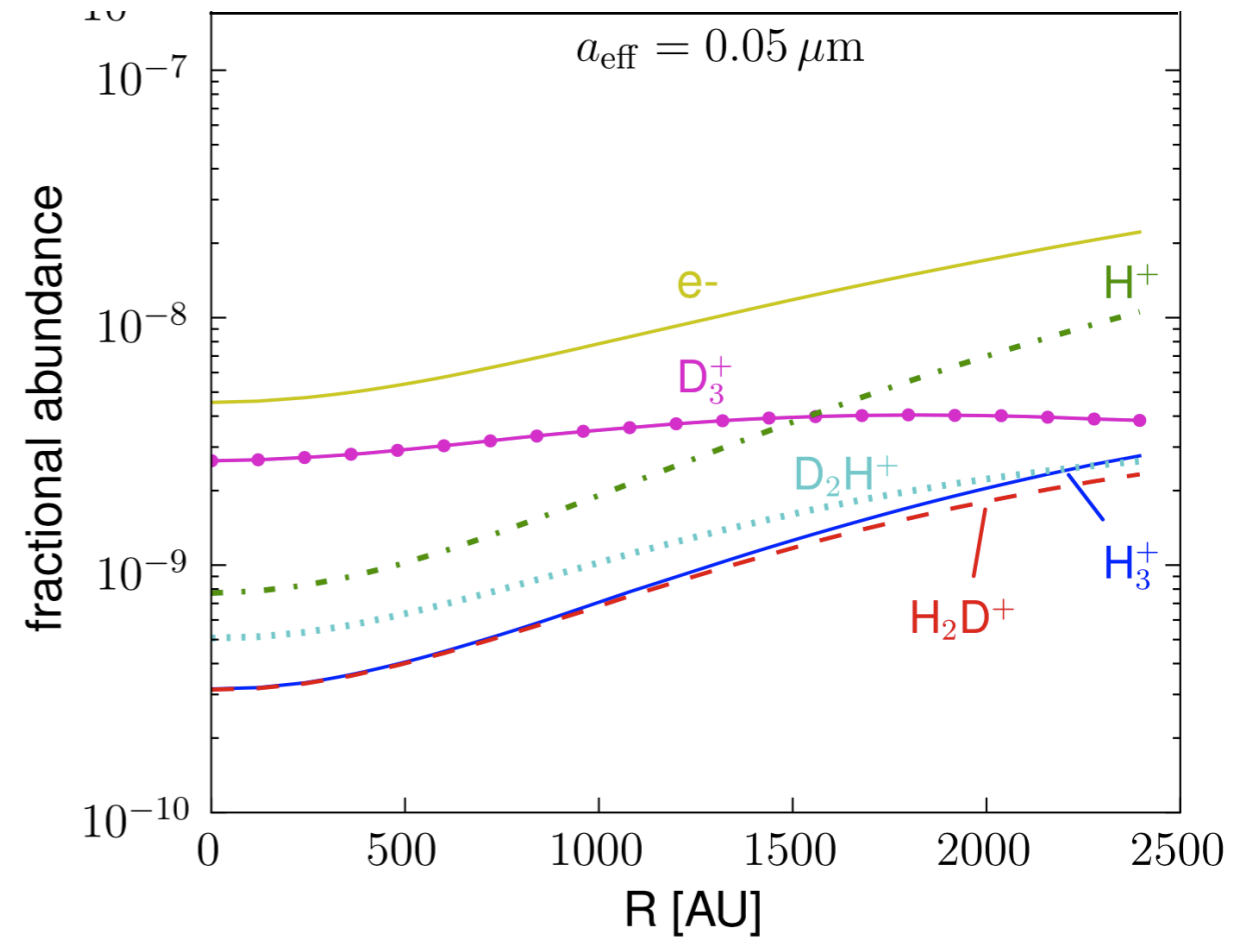
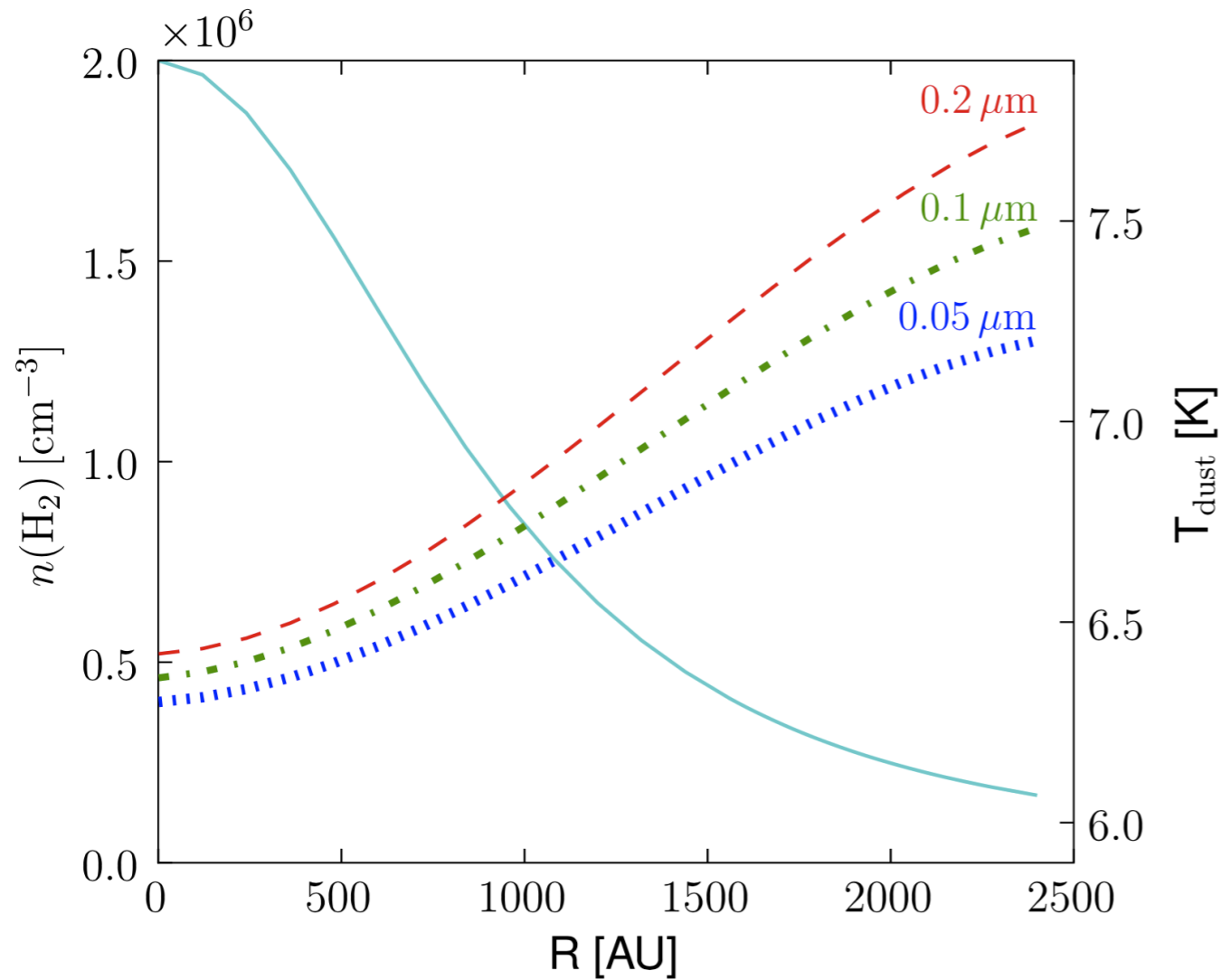


Gravitational collapse
Semi-analytical

$$\frac{d\rho}{dt} = \frac{\rho}{t_{ff}}$$

With cooling/heating

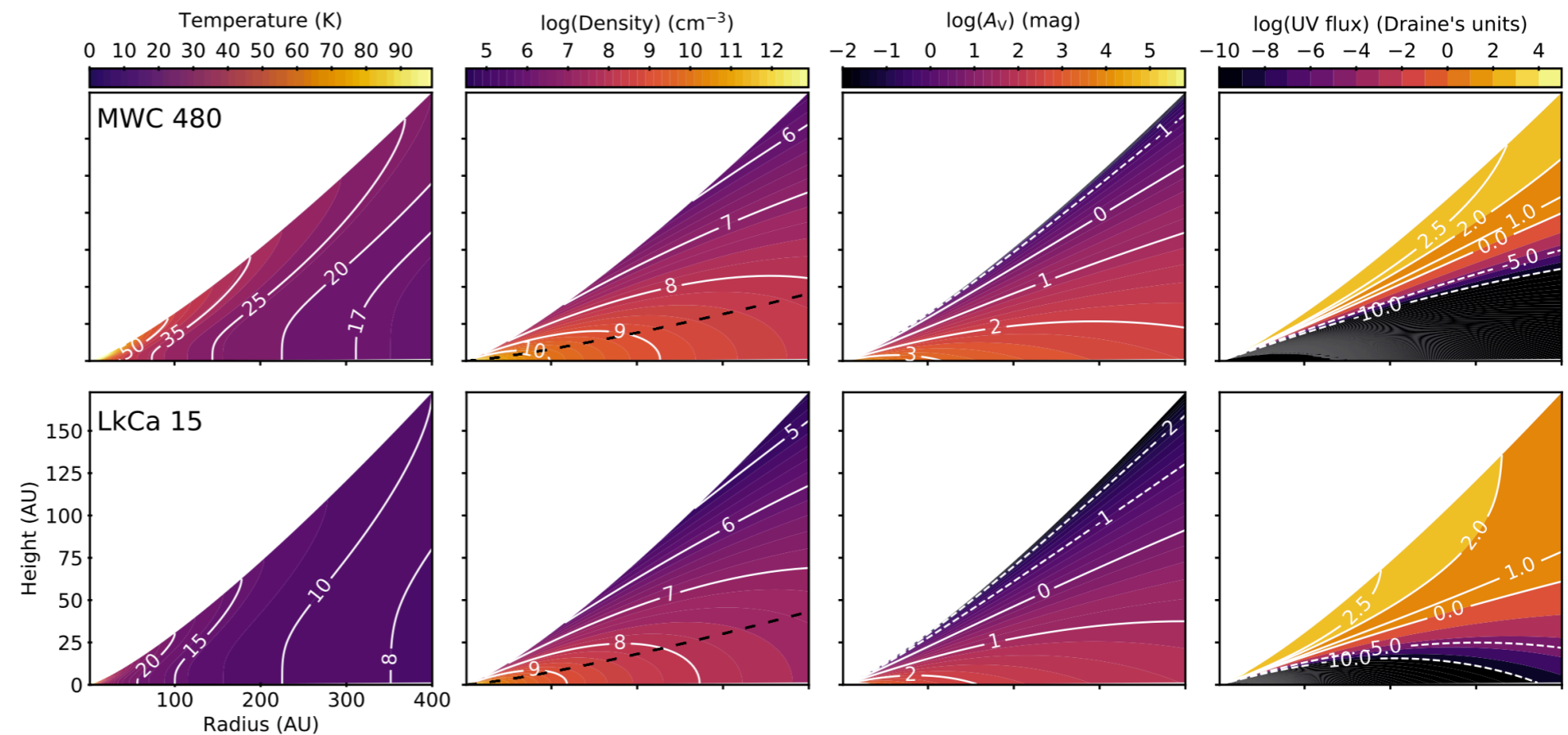
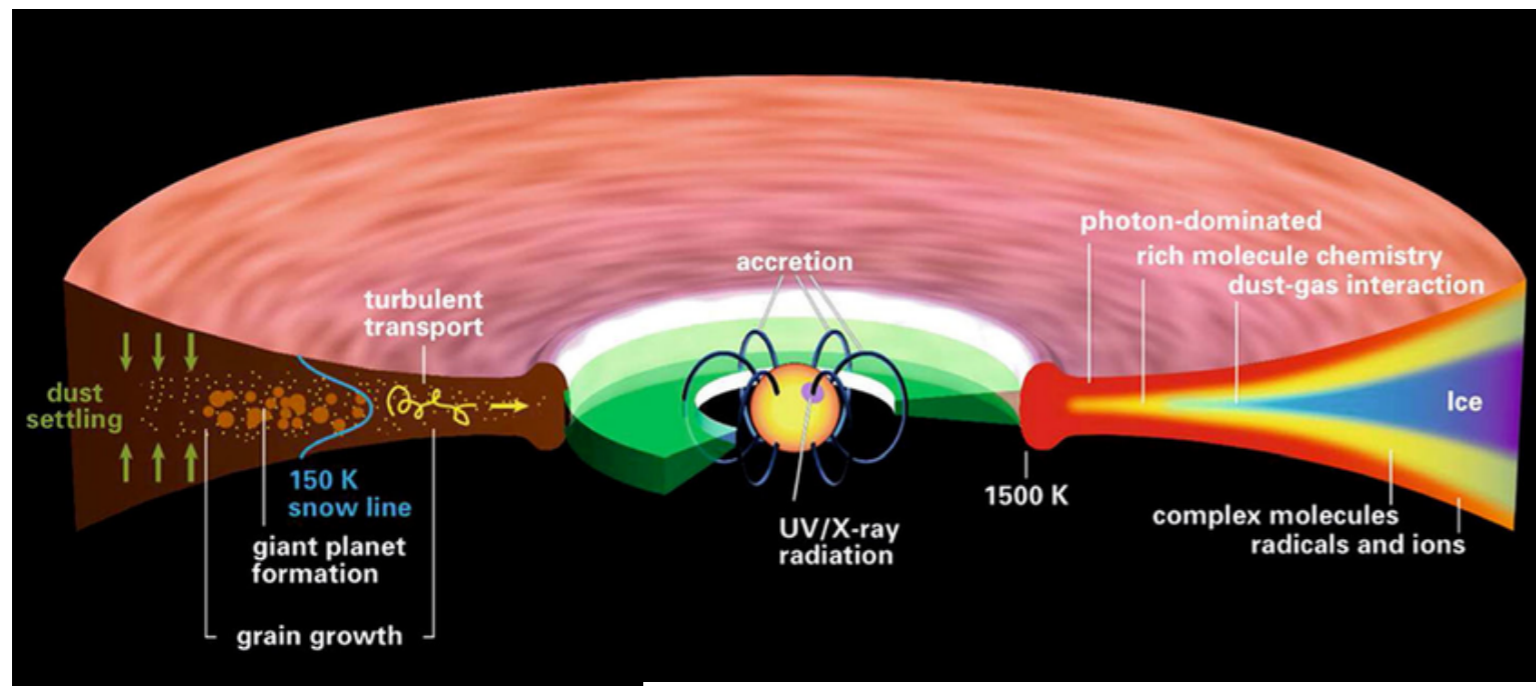
EXAMPLES: LOW-DIMENSIONALITY MODELS



Pseudo 1D

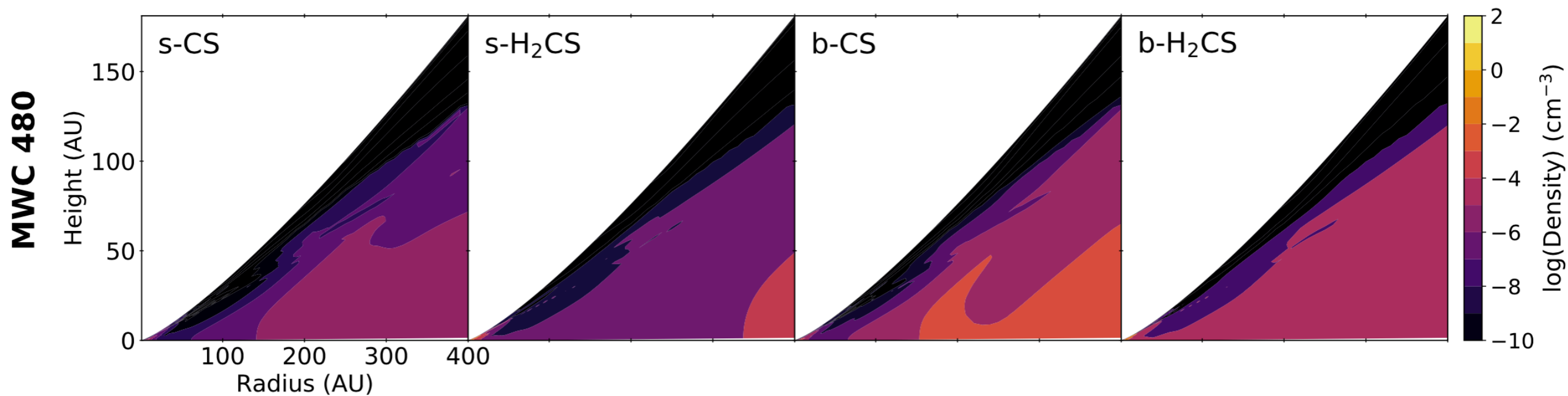
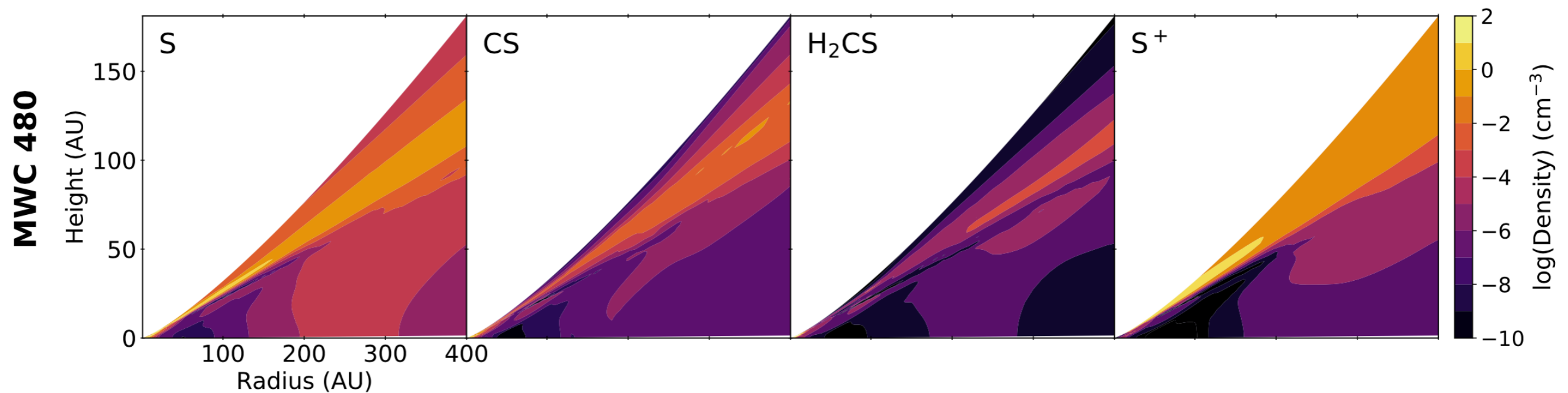
No thermodynamics

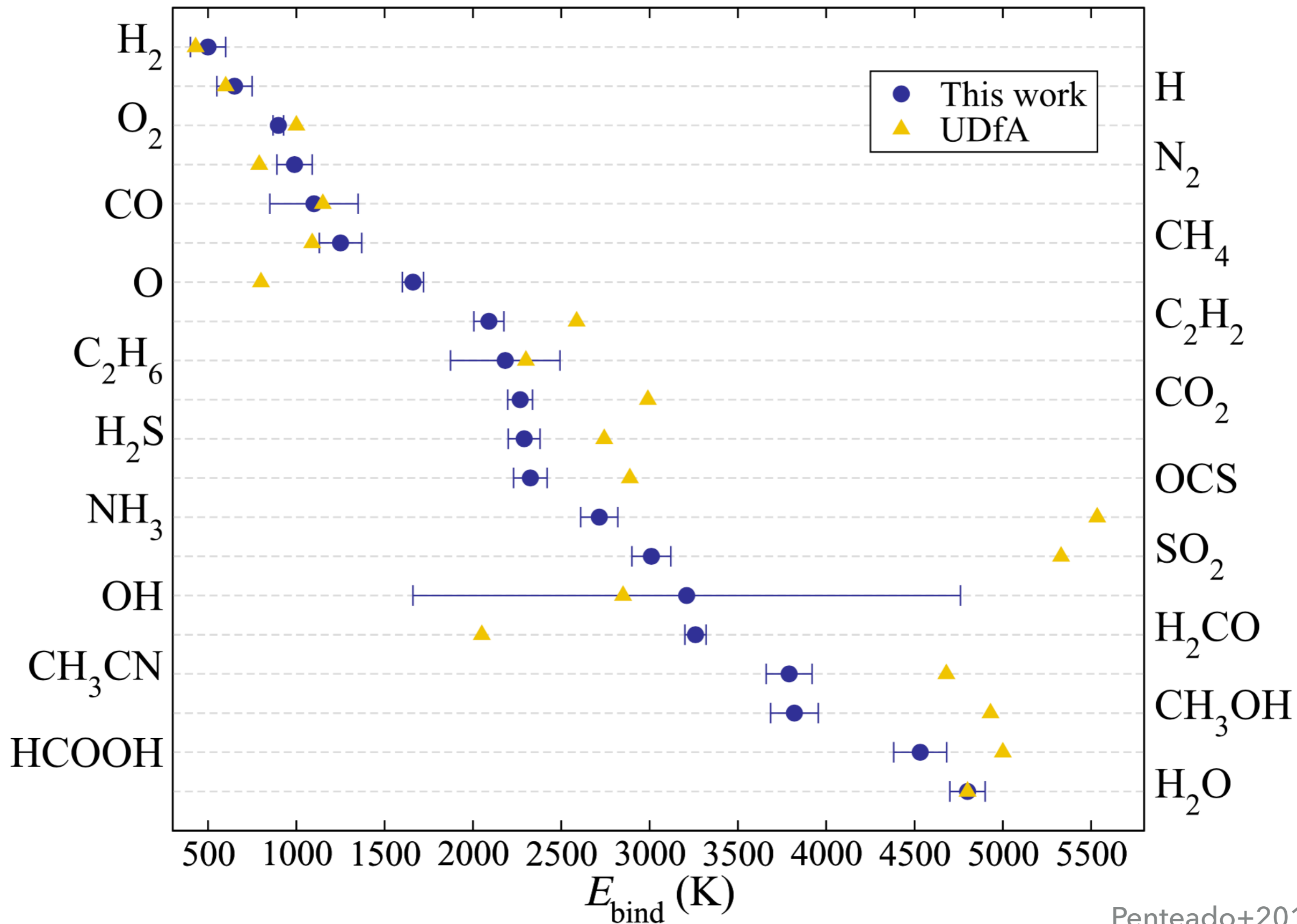
EXAMPLES: LOW-DIMENSIONALITY MODELS

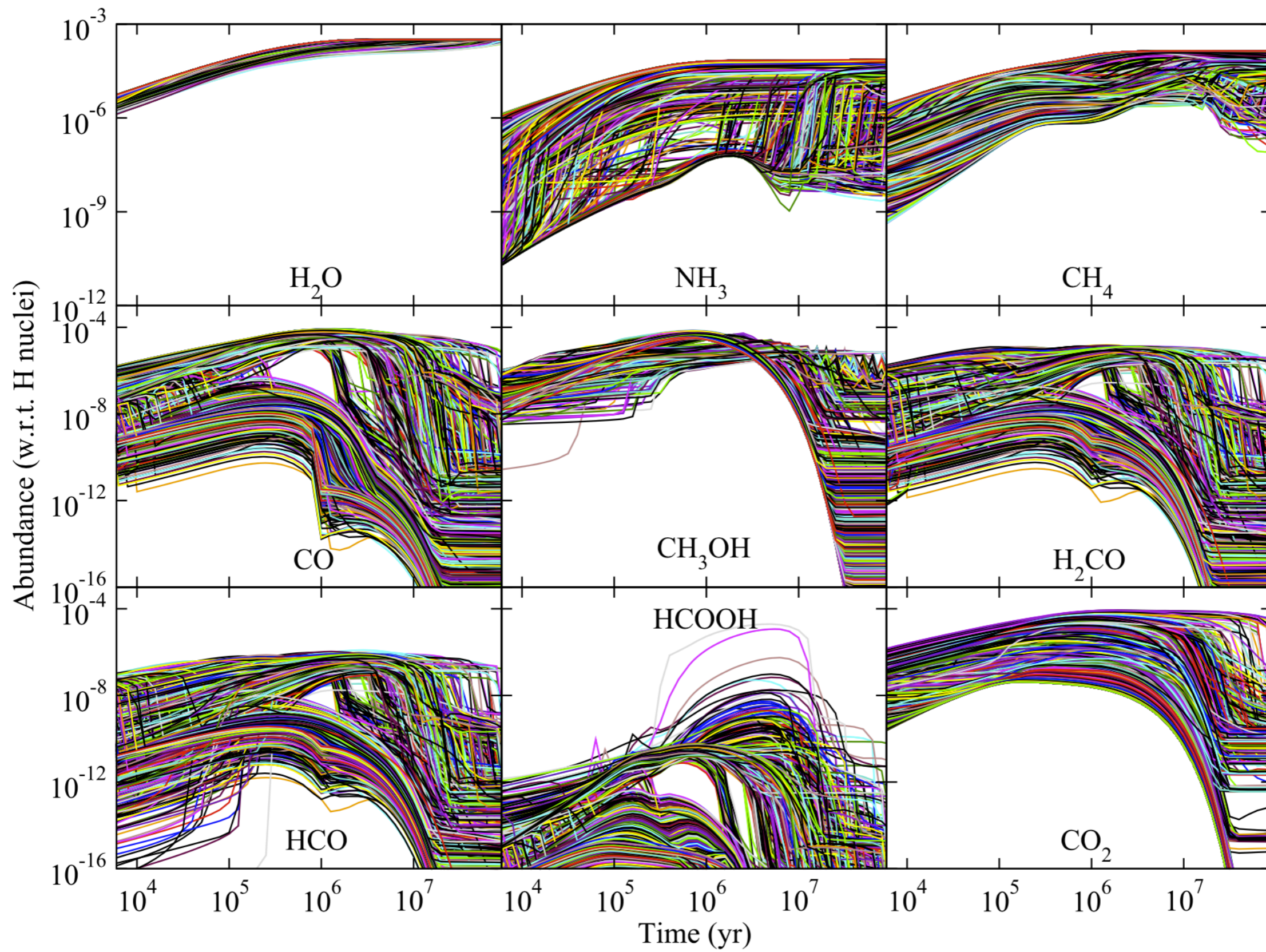


EXAMPLES: LOW-DIMENSIONALITY MODELS

Le Gal+2019







- ▶ A lot of gas-phase reactions rate coefficients are estimates
- ▶ Huge uncertainty on grain-surface chemistry (Binding energy, sticking coefficients, mobility, reactivity, modelling)
- ▶ Uncertainties on key physical parameters (e.g. CRIR)

- ▶ Sensitivity analysis important to identify key uncertainties but not always trivial
- ▶ Problem dependent: ideally one can identify the main reaction fluxes in a specific simulations/model
- ▶ And change the rate regulating those reactions to see how this affects the evolution

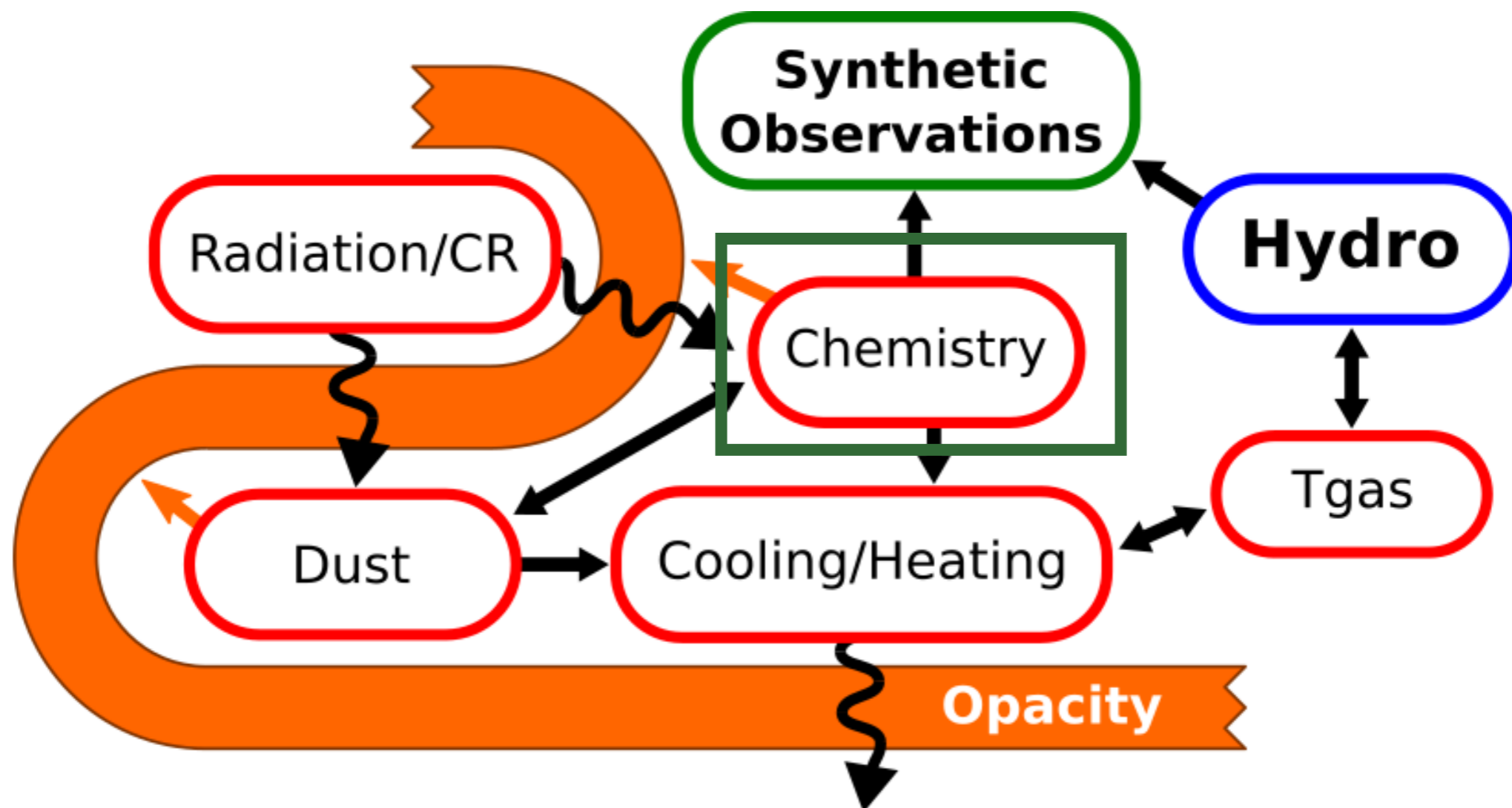
CODES

- **0d codes for gas-grain:**

- **KROME (open source):** www.kromepackage.org
- **ALCHEMIC (MPIA, Heidelberg):** <http://www2.mpia-hd.mpg.de/homes/semenov/>
- **Nahoon (Bordeaux):** <http://kida.astrophy.u-bordeaux.fr/codes.html>
- **ASTROCHEM (Grenoble):** <https://github.com/smaret/astrochem>
- **MAGICKAL (UVa) (private)**
- **CLOUDY (Ferland, no grain, eq.):** <https://www.nublado.org>
- **MEUDON (PDR):** https://ism.obspm.fr/?page_id=33
- **UCLCHEM:** <https://github.com/uclchem/UCLCHEM>
- **THORUS-3DPDR (RT):** http://www.astro.ex.ac.uk/people/th2/torus_html/homepage.html
- **GRAINOBLE (private)**

COMPUTATIONAL ASTROCHEMISTRY IS NOT ONLY NETWORKS

- ▶ Chemical networks are embedded in codes which also solve microphysics



COMPUTATIONAL ASTROCHEMISTRY IS NOT ONLY NETWORKS

convert kinetic energy in something else!

1. radiative loss
2. endothermic reactions
3. gas flows
4. gas-dust interaction

