Gas-phase processes

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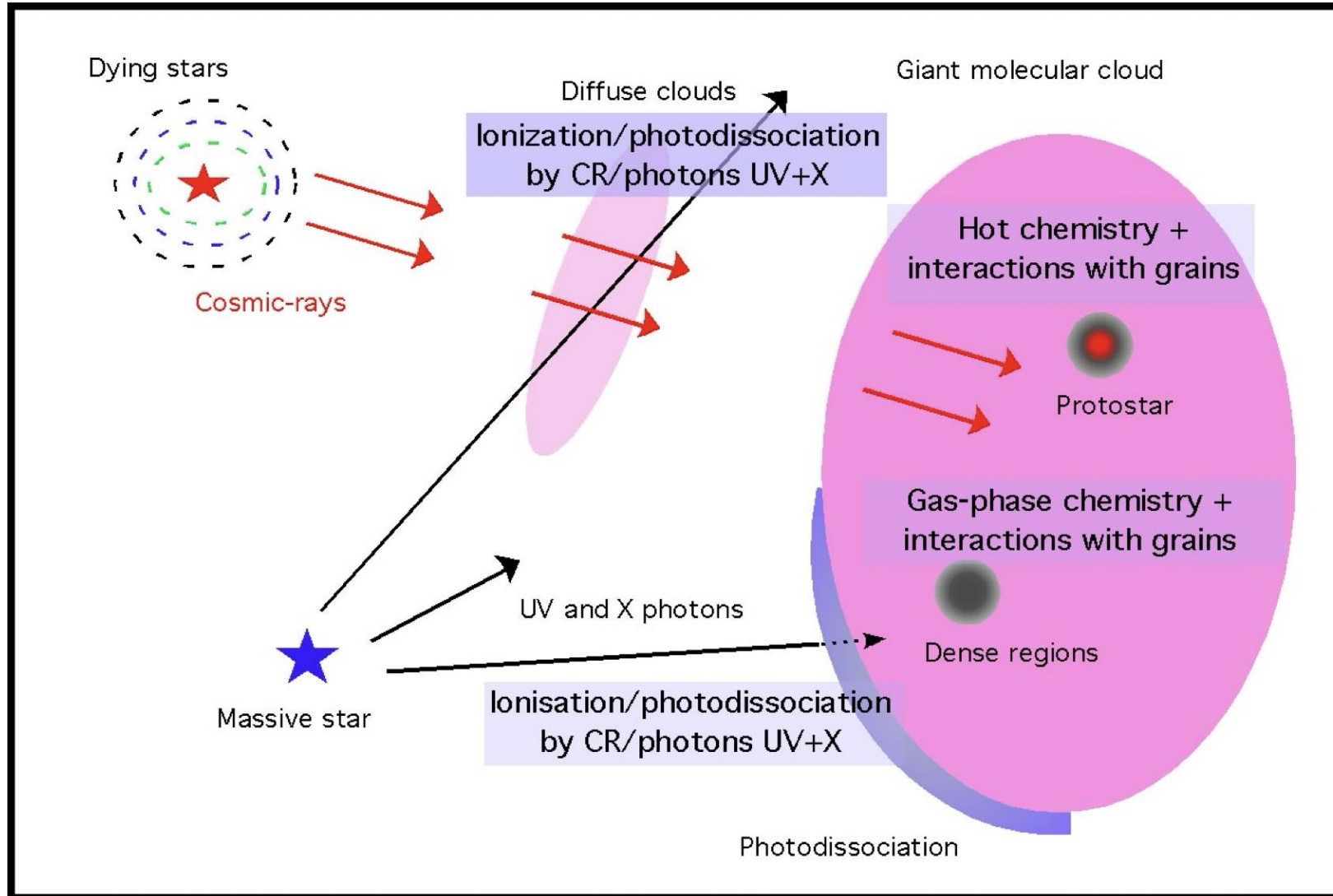
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Main processes depending on the interstellar region

Dying stars

Cosmic-rays

Diffuse clouds

Giant molecular cloud

Ionization/photodissociation by CR/photons UV+X

Hot chemistry + interactions with grains

Protostar

Gas-phase chemistry + interactions with grains

UV and X photons

Massive star

Ionisation/photodissociation by CR/photons UV+X

Dense regions

Photodissociation

Interstellar medium

Large variety of objects (diffuse medium, cold cores, protostellar-envelops).
Large variety of physical conditions (densities between 1 particule/cm^3 and 10^{14} particules/cm^3, temperatures between 5 and 1000K).

For comparison on Earth:

Densities ~$10^{21}cm^{-3}$
Temperatures ~300K

Notion of density : nbr of particules per cm^3 (usually proton H)
$n_H = n(H) + 2n(H_2)$

# Gas-phase processes

1st order reactions :
- Ionization and dissociation by UV photons
- Ionization and dissociation by cosmic-rays
- Ionization and dissociation by cosmic-ray induced photons

2sd order reactions :
- Ion-molecule reactions ($A^+ + B \rightarrow C^+ + D$)
- Exchange reactions ($A^+ + B \rightarrow A + B^+$ or $A+ + B- \rightarrow A + B$)
- Electronic recombinations ($AB^+ + e^- \rightarrow A + B$, $AB^+ + e^- \rightarrow AB + h\nu$, $A + e^- \rightarrow A^- + h\nu$)
- Neutral-neutral reactions ($A + B \rightarrow C + D$)
- Radiative associations ($A + B \rightarrow AB + h\nu$ or $A^+ + B \rightarrow AB^+ + h\nu$)
- Electron attachment ($C + e^- \rightarrow C^-$)

General statements on chemical kinetics

$$ABC + h\nu \xrightarrow{k1} AB + C$$

$$ABC + h\nu \xrightarrow{k2} A + BC$$

First order reaction (The rates of the reactions depend on the concentration of only one reactant.)
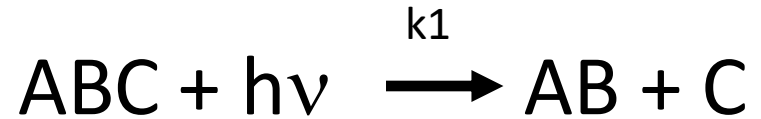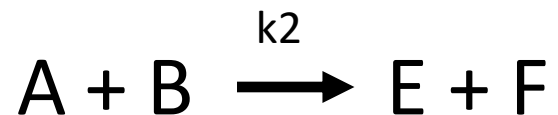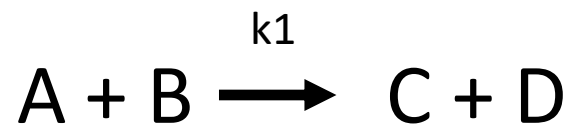
Rate of reaction : $k\, n_{ABC}$

k_1 and k_2 : rate coefficients.
$K_{tot} = k_1 + k_2$ is the total rate coefficient – rate ($cm^{-3}\, s^{-1}$) at which ABC disappears.
$BR_1 = k_1 / k_{tot}$ and $BR_2 = k_2/k_{tot}$ are the branching ratios of channel 1 and 2
$BR_1 + BR_2 = 1$

General statements on chemical kinetics

$$A + B \xrightarrow{k1} C + D$$

$$A + B \xrightarrow{k2} E + F$$

Second order reaction

Rate of reaction : $k\ n_A\ n_B$

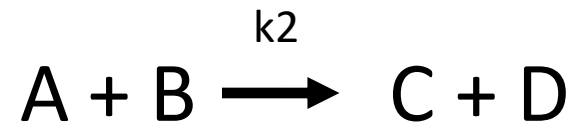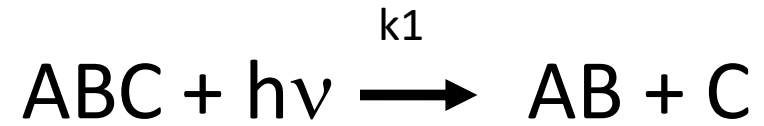k_1 and k_2 : partial rate coefficients.
$K_{tot} = k_1 + k_2$ is the total rate coefficient – rate ($cm^{-3}\ s^{-1}$) at which A and B disappear.
$BR_1 = k_1 / k_{tot}$ and $BR_2 = k_2/k_{tot}$ are the branching ratios of channel 1 and 2
$BR_1 + BR_2 = 1$

General statements on chemical kinetics

$$ABC + h\nu \xrightarrow{k1} AB + C$$

$$A + B \xrightarrow{k2} C + D$$

$$C + E \xrightarrow{k3} CE + h\nu$$
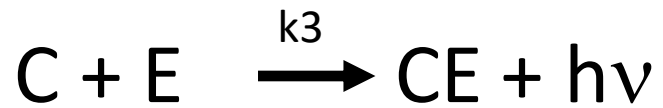
$$\frac{dn_C}{dt} = k_1 n_{ABC} + k_2 n_A n_B - k_3 n_C n_E$$

Gas-phase chemical models = solving the kinetic equation as a function of time for all species

$$\frac{dn_i}{dt} = \sum_{l,j} k_{lj} \, n_l n_j - ni \sum_m k_{im} n_m$$

Define fractional abundance for every species i:
X(i) = n(i) / n_H

n_H = n(H) + 2 n(H_2) (i.e. all hydrogen, in mostly-neutral regions)

Equilibrium chemistry:
Minimizing the free energy of a system. All chemical processes are balanced. Closed system.
reactants $\rightleftharpoons$ products

Steady-state:
Chemical abundances do not evolve but the system is not balanced. The system is not closed.
dn_i/dt = 0

Non equilibrium chemistry and not steady-state in many cases

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Gas-phase photo-processes
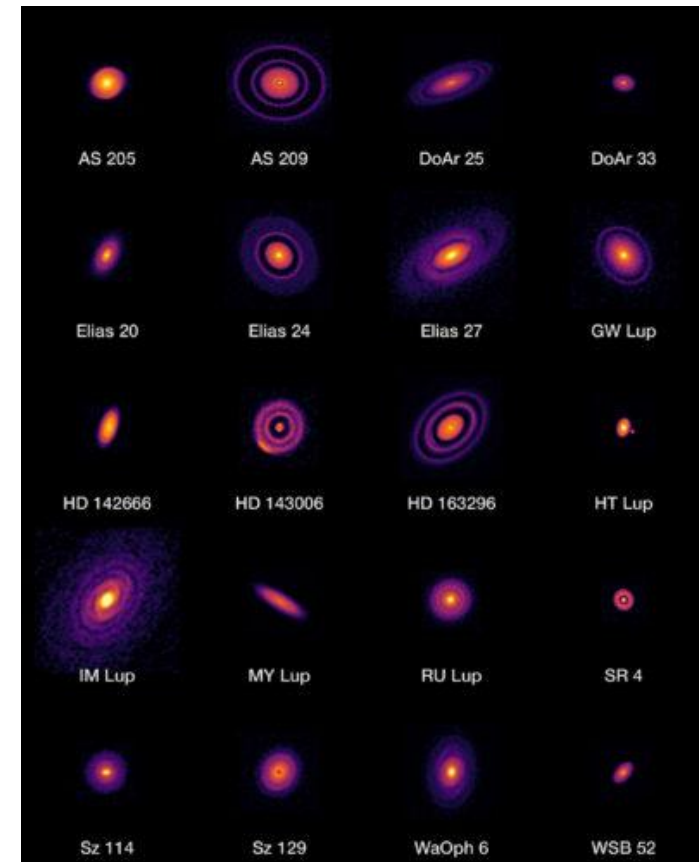
Diffuse medium

The Horsehead Nebula
(VLT KUEYEN + FORS 2)

ESO PR Photo 02a/02 (25 January 2002)   © European Southern Observatory

Photo-dominated regions

Atmospheres of protoplanetary disks

AS 205   AS 209   DoAr 25   DoAr 33
Elias 20   Elias 24   Elias 27   GW Lup
HD 142666   HD 143006   HD 163296   HT Lup
IM Lup   MY Lup   RU Lup   SR 4
Sz 114   Sz 129   WaOph 6   WSB 52

Gas-phase photo-processes

Sources of irradiation for the diffuse medium and PdRs :

UV interstellar radiation coming from the massive stars of the Galaxy (< 13.6 eV / 912 Å) (ex: Draine 1978)

All photons with E> 912 Å /13.6 eV are rapidly absorbed by the atoms of hydrogen around the stars.

Star-Birth Clouds · M16 HST · WFPC2
PRC95-44b · ST ScI OPO · November 2, 1995
J. Hester and P. Scowen (AZ State Univ.), NASA

Color image constructed from three separate images taken in the light of emission from different types of atoms. Red : S+, Green : Hydrogen, Blue : O++.

Gas-phase photo-processes

Sources of irradiation for protoplanetary disks
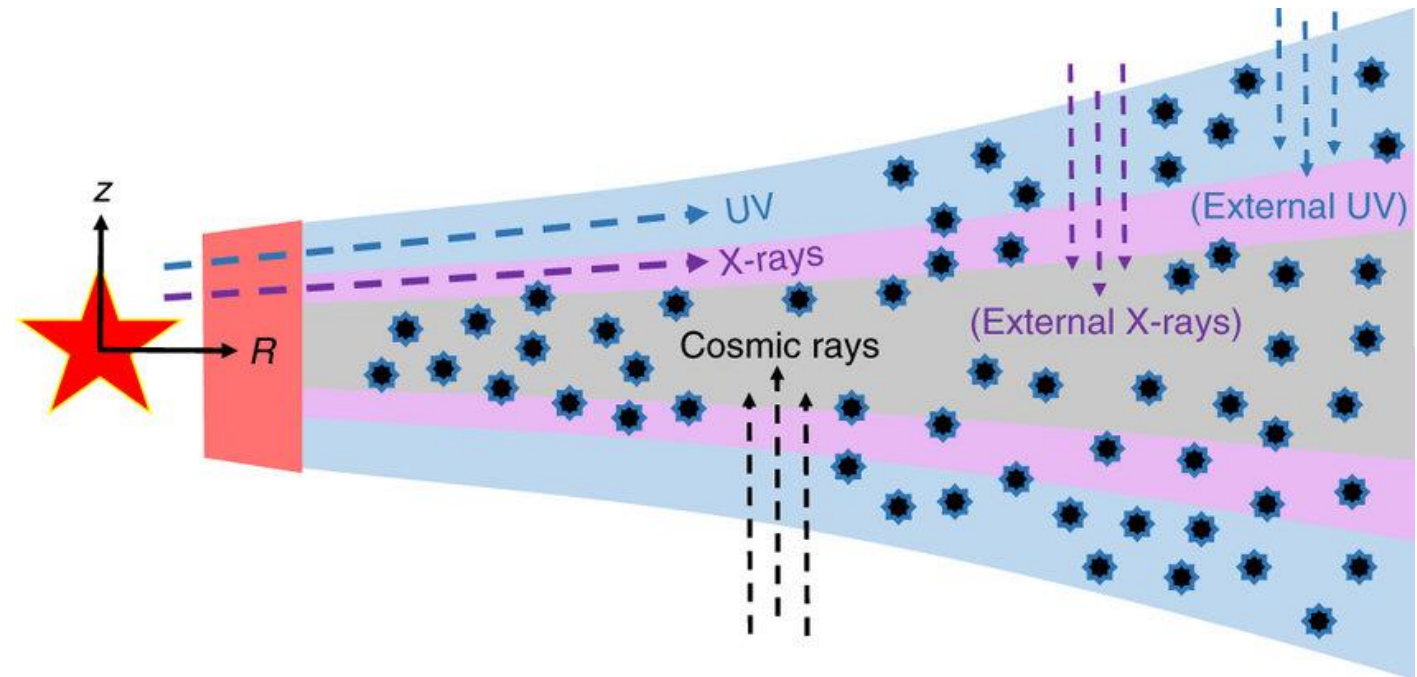
Gas-phase photo-processes

Photo-dissociation

$$AB + h\nu \longrightarrow A + B$$

Photo-ionization

$$AB + h\nu \longrightarrow AB^+ + e^-$$

1st order reaction with respect to A and B (or AB^+)

Photodissociation rate (in s^{-1}) of a molecule going from the lower energy level l to the upper level u by absorption:

$$k_{phot} = \int \sigma_{u,l}(\lambda) x_l I(\lambda) d\lambda$$

Cross section of photodissociation (cm^{-2})

Mean intensity of radiation ($cm^{-2}s^{-1}Å^{-1}$)

fraction of population in level l

In astrochemical models and databases (for the mean intensity of radiation of the interstellar medium:

$$k_{Phot} = \alpha \times e^{-\gamma Av} \ (s^{-1})$$

α and γ are specific to the species while Av is the visual extinction.

Gas-phase photo-processes

To learn more about the photo-processes in the gas-phase:

https://home.strw.leidenuniv.nl/~ewine/photo/

Overview Papers

- Heays, Bosman, van Dishoeck 2017, Astron. Astrophys. arXiv
- van Hemert & van Dishoeck 2008, Chemical Physics 343, 292
- van Dishoeck et al. 2006, Faraday Discussions 133, 855
- van Dishoeck 1988, in "Rate Coefficients in Astrochemistry"
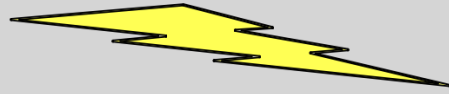
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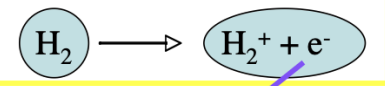
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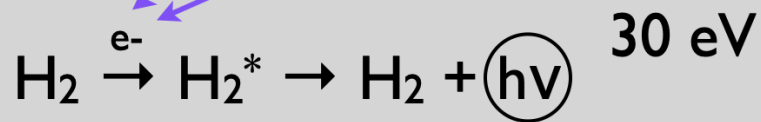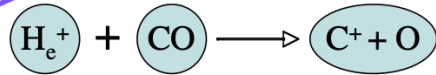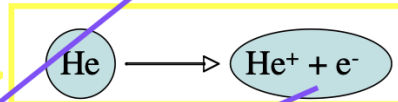
Impact of cosmic-rays

Cosmic-Ray Particles
(protons, electrons, Fe...)

10 - 100 MeV ζ_{H2}

$H_2 \longrightarrow H_2^+ + e^-$

$H_2^+ + H_2 \longrightarrow H_3^+ + H$

ζ_{He}

$He \longrightarrow He^+ + e^-$

$He^+ + CO \longrightarrow C^+ + O$

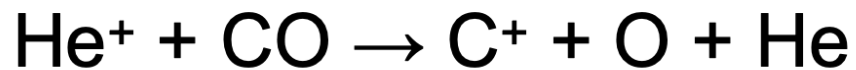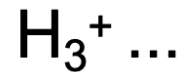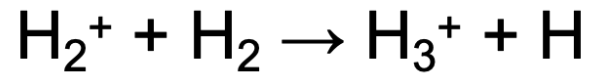$H_2 \overset{e^-}{\rightarrow} H_2^* \rightarrow H_2 + h\nu$ 30 eV

Indirect UV photons produced inside cold cores (Prasad & Tarafdar 1980 mechanism)

Impact of cosmic-rays

Starting points of molecular formation and destruction

$H_2 + \gamma \rightarrow H_2^+ + e^-$ Starting point of formation
$H_2^+ + H_2 \rightarrow H_3^+ + H$
$H_3^+ \ldots$

Starting point of destruction

$He + \gamma \rightarrow He^+ + e^-$
$He^+ + CO \rightarrow C^+ + O + He$
$\ldots$

Impact of cosmic-rays

In astrochemical models: 2 types of reactions

- Direct ionization by cosmic-rays – mostly for atoms, strongly dominated by ionization of H_2 and He

- Ionization and dissociation by the UV photons produced by cosmic-rays

$$k_{CR} \text{ and } k_{CRP} = \alpha \times \zeta \ (s^{-1})$$

H_2 cosmic-ray ionization rate (in s^{-1})

References : Prasad & Huntress 1980, Gredel et al. (1989)

Impact of cosmic-rays

N2	CR	N	N		5.000e+00
H	CR	H+	e-		4.600e-01
He	CR	He+	e-		5.000e-01
N	CR	N+	e-		2.100e+00
O	CR	O+	e-		2.800e+00
CO	CR	C	O		5.000e+00
CO	CR	CO+	e-		3.000e+00
H2	CR	H	H		1.000e-01
H2	CR	H	H+	e-	2.200e-02
H2	CR	H+	H-		3.000e-04
H2	CR	H2+	e-		9.300e-01

Direct process: rate of the order of a few 10^{-17} s^{-1} (for $\zeta = 10^{-17}$ s^{-1})

NH	CRP	H	N	3.690e+02
NH	CRP	NH+	e-	7.100e+00
NO	CRP	N	O	2.990e+02
NO	CRP	NO+	e-	2.370e+02
NS	CRP	N	S	5.000e+02
O2	CRP	O	O	7.810e+02

Direct process: rate of the order of a few 10^{-15} s^{-1} (for $\zeta = 10^{-17}$ s^{-1})

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Bimolecular reactions: Temperature dependent rate coefficients

$$A + B \longrightarrow C + D$$

$$\Delta_r H_{(T,p)} = (\Delta_f H_C + \Delta_f H_D) - (\Delta_f H_A + \Delta_f H_B)$$
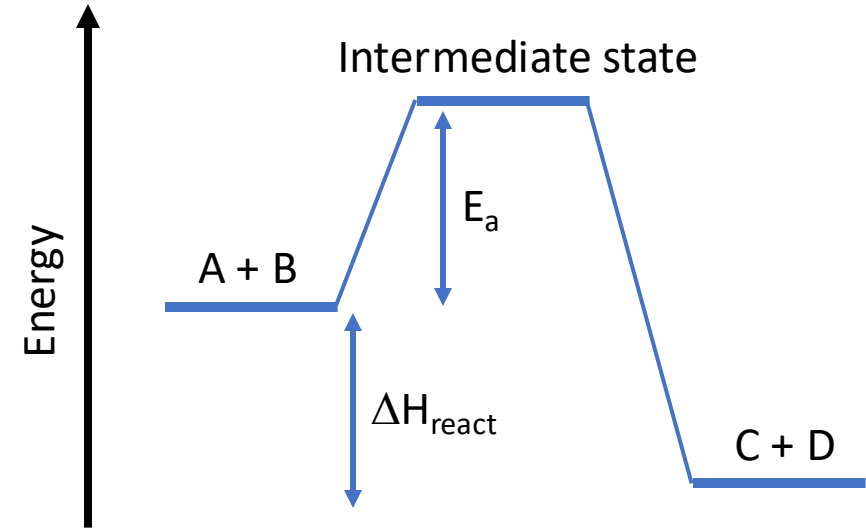
Enthalpy of reaction (J mol^{-1})

Enthalpy of formation of each species

Enthalpy of formation for atoms = 0

Negative enthalpy = exothermic reaction

Positibe enthalpy = endothermic reaction

Bimolecular reactions: Temperature dependent rate coefficients

Modified Arrhenius law : empirical law that fits the data

$$k = \alpha \, (T/300)^{\beta} \exp(-\gamma/T)$$

Unit : $cm^3 s^{-1}$

Experiments at different temperatures then fitting the temperature dependence to get the parameters.
α, β and γ are tabulated in databases.

To be important at low temperature, γ has to be null and the reaction has to be exothermic.

Bimolecular gas-phase reactions

Example of various estimates from experiments and theoretical calculations for reaction N + NO -> O + N$_2$

Very difficult to get temperatures at low temperature.
Be careful with extrapolations at low temperature.
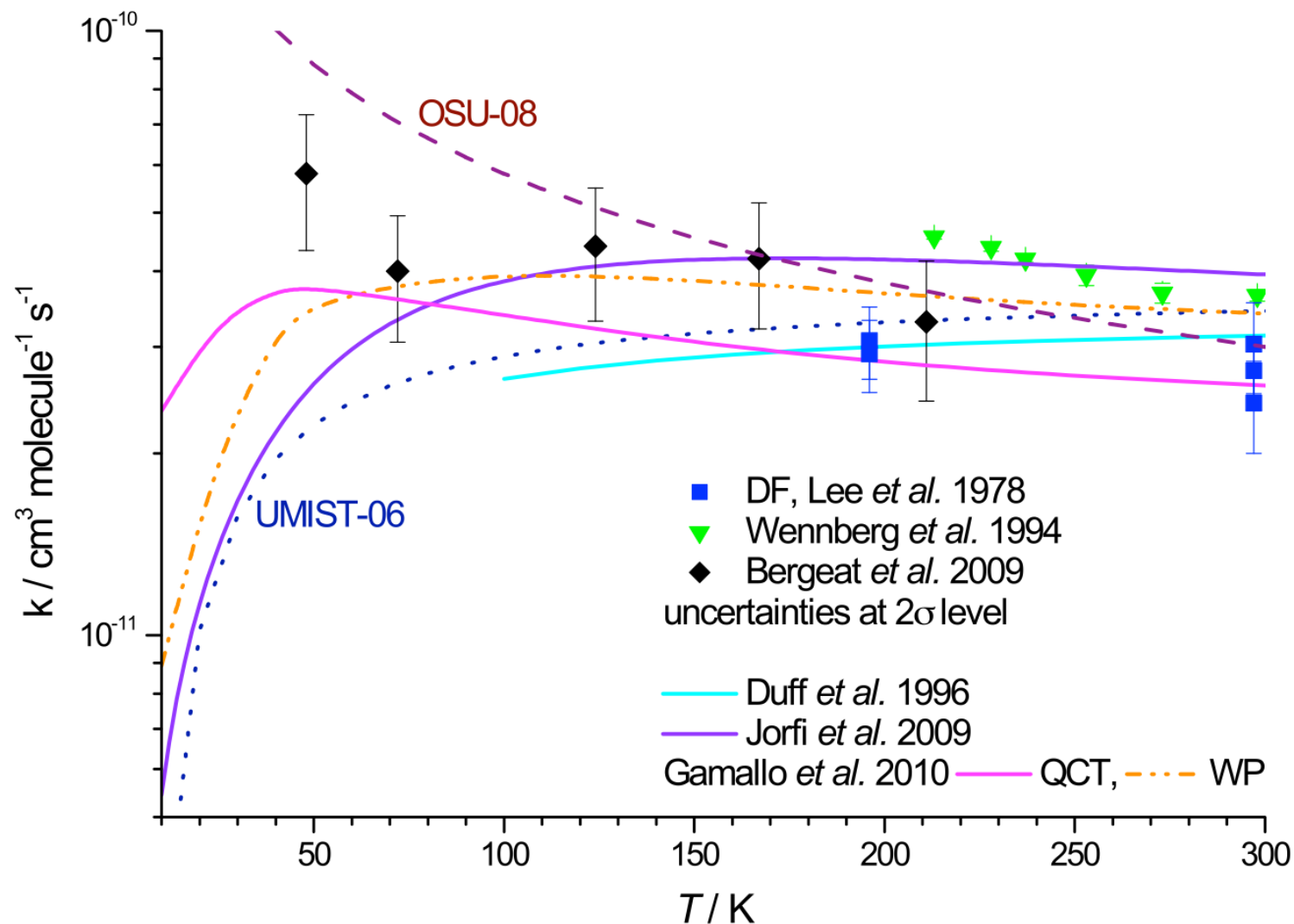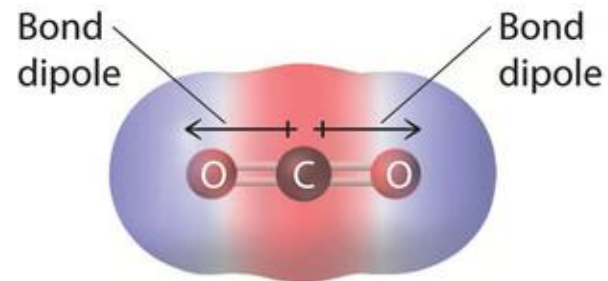
Bimolecular gas-phase reactions : ion-neutral reactions

Many ion-neutral reactions are barrier less and exothermic: very important for ISM chemistry.
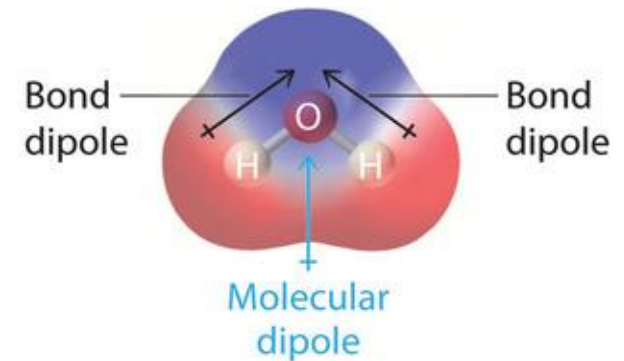
Two types of ion-neutral reactions:
- ions + non-polar neutrals
- ions + polar neutrals

Symetric linear species do not have a dipole moment.

Molecules with dipole moment: non-uniform distributions of positive and negative charges on the various atoms.

(a) No net dipole moment

(b) Net dipole moment

Bimolecular gas-phase reactions : ion-neutral reactions

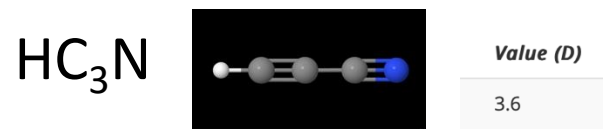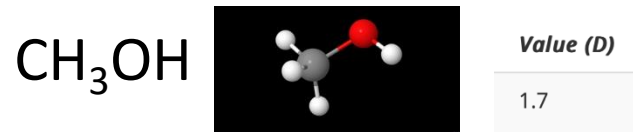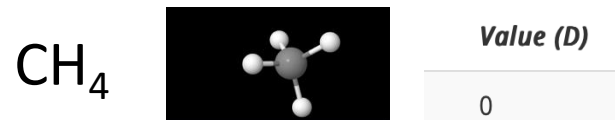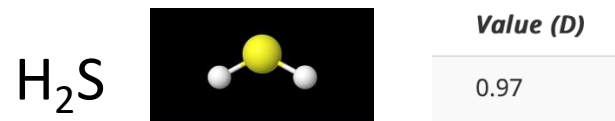Which species have dipole moments?

O H_2S

N_2 CH_4

CO CH_3OH

H_2O HC_3N

CO_2

Which species have dipole moments?

O

Value (D)

0

N$_2$

Value (D)

0

CO

Value (D)

0.112

H$_2$O

Value (D)

1.8546 ±0.004

CO$_2$

Value (D)

0

H$_2$S

Value (D)

0.97

CH$_4$

Value (D)

0

CH$_3$OH

Value (D)

1.7

HC$_3$N

Value (D)

3.6

Bimolecular gas-phase reactions : ion-neutral reactions

ions + polar neutrals

For non-measured reactions, modification of the classical approach:

First determine the temperature T for wich the x parameter = 2 :

$$x = \frac{\mu_D}{(2\alpha_{\text{pola}}k_B T)^{1/2}},$$

→ dipole moment of the neutral reactant

Then two expressions depending on the temperature:

Between 10K and T: $k(T) = \alpha\beta(0.62 + 0.4767\gamma(300/T)^{0.5})$

Between T and 100K: $k(T) = \alpha\beta(1 + 0.0967\gamma(300/T)^{0.5} + (\gamma^2/10.526) \times (300/T)).$

α = branching ratio
β = Langevin rate
γ = x at 300K

More explanations in Woons & Herbst (2009) and Wakelam et al. (2010)

Bimolecular gas-phase reactions : ion-neutral reactions

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α = branching ratio
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γ = x at 300K

Given in databases with the correct T range which depends on the reaction.

l. (2010)

Bimolecular gas-phase reactions : neutral-neutral reactions

- Great majority of ISM molecules are neutral, unsaturated (hydrogen-poor) molecules or free radicals.

- For a long time considered to be inefficient at low temperature (many of them have high activation barriers).

- Since the early 2000, the CRESU apparatus started to measure reactions at low temperature.

Bimolecular gas-phase reactions : neutral-neutral reactions

Formamide NH_2CHO (observed in massive star forming regions, low mass protostellar envelops and shock regions).

Controversy around the reaction $NH_2 + H_2CO \rightarrow NH_2CHO + H$ that was proposed as an efficient gas-phase pathway to form formamide.

Baronne et al. (2015)

T(K)	k(10) cm^3s^{-1}	α	β	γ
10-300	2.23e-10	2.60E-12	-2.10E+0	2.69E+1

Method: Calculations

Skouteris et al. (2017)

T(K)	k(10) cm^3s^{-1}	α	β	γ
10-300	2.89e-11	7.79E-15	-2.56E+0	4.88E+0

Method: Calculations

Bimolecular gas-phase reactions : neutral-neutral reactions

Formamide NH_2CHO (observed in massive star forming regions, low mass protostellar envelops and shock regions).

Controversy around the reaction $NH_2 + H_2CO \rightarrow NH_2CHO + H$ that was proposed as an efficient gas-phase pathway to form formamide.

Douglas et al. (2022)
Calculations + measurements

Channel			T(K)	k(10) cm^3s^{-1}	α	β	γ	F_0	g	Type uncert
$H_2CO + NH_2$	$\rightarrow$	$HCO + NH_3$	10-140	5.59e-12	9.67E-17	-2.88E+0	-1.17E+1	1.2	0	logn

Channel			T(K)	k(200) cm^3s^{-1}	α	β	γ
$H_2CO + NH_2$	$\rightarrow$	$HCO + NH_3$	140-350	7.80e-16	4.21E-18	9.80E+0	-1.84E+3

Channel			T(K)	k(200) cm^3s^{-1}	α	β	γ
$H_2CO + NH_2$	$\rightarrow$	$H + NH_2CHO$	110-350	5.43e-18	8.35E-14	0.00E+0	1.93E+3

Bimolecular gas-phase reactions : radiative associations

Two species colliding to form a short-lived intermediate that can stabilize by the emission of a photon.

$$A + B \longrightarrow AB^* \longrightarrow AB + h\nu$$

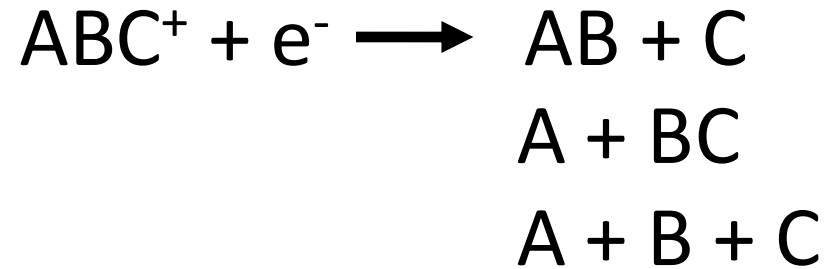Can only occur at low density.

Very little experiments done.

Thoery is complicated.

Rate coefficients are low.

COMs formation using such processes should be taken with care.

Type of reaction that would definitly to be studied in the lab !!!

References : Herbst et al. 1982, 2021

Bimolecular gas-phase reactions : electronique recombination

$$ABC^+ + e^- \longrightarrow AB + C$$
$$A + BC$$
$$A + B + C$$

- Release a lot of energy.
- High rate coefficients (of the order $10^{-7} - 10^{-6}$ $cm^3 s^{-1}$ at 10K).
- Very often the end of formation of neutrals.
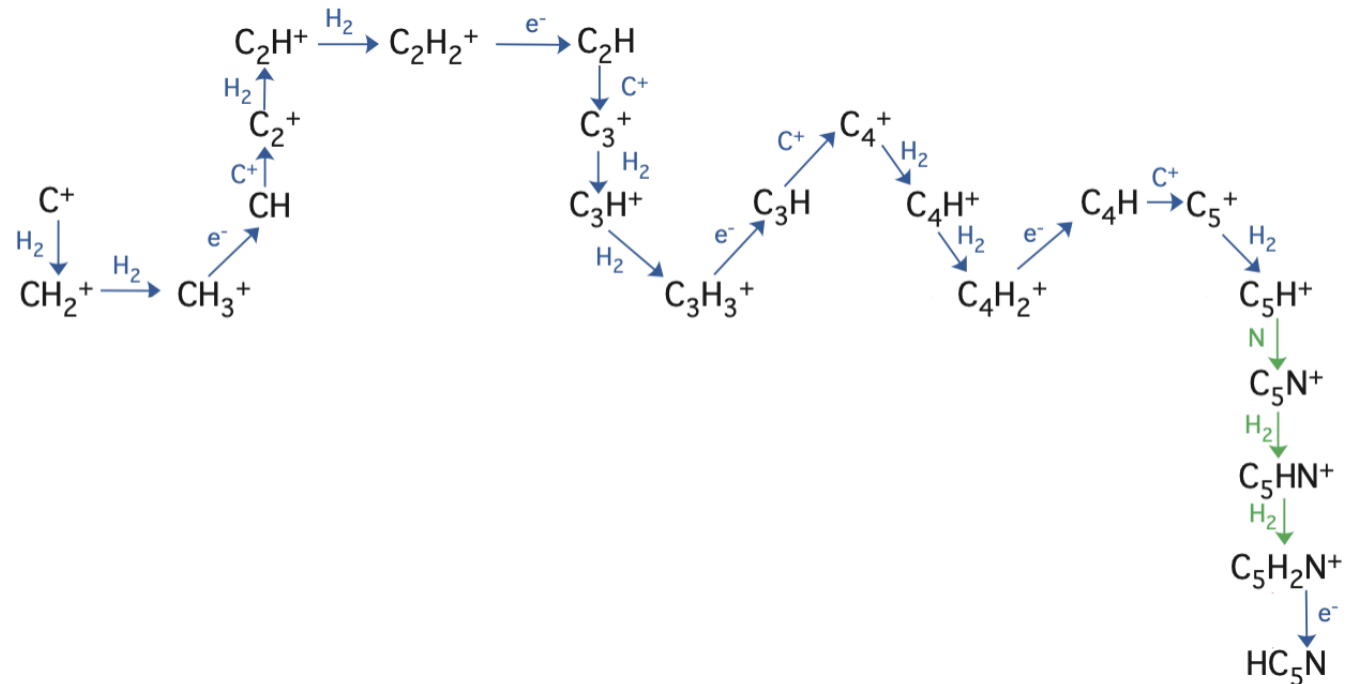
Formation of anions

- A new chemical area of interstellar molecules opened in 2006 with the discovery of C_6H^- in space by McCarthy et al.
- Followed by C_4H^- (Cernicharo et al. 2007), C_8H^- (Brünken et al. 2007), C_3N^- (Thaddeus et al. 2008), C_5N^- (Cernicharo et al. 2008), CN^- (Agúndez et al. 2010), $C_{10}H^-$ (Remijan et al. 2023), C_7N^- (Cernicharo et al. 2023)

Main chemical pathways

Electronique attachment: $C_4H + e^- \rightarrow C_4H^- + h\nu$

Associative detachment: $C_4^- + H \rightarrow C_4H + e^-$

Charge exchange: $C_4^+ + H^- \rightarrow C_4 + H$

Anion-cation reactions: $C_4^+ + CN^- \rightarrow C_3 + C_2N$

The example of H_2 formation

Association radiative : $H(1s) + H(1s) \rightarrow HH^* \rightarrow H_2 + h\nu$

HH* would need the emission of a 4.5 eV to stabilize, which is forbidden.

Other possible reactions:

$H^- + H \rightarrow H_2 + e^-$ or $H + H_2^+ \rightarrow H_2 + H^+$

Ionisation in the ISM not enough

The example of H_2 formation

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Other possible reactions:

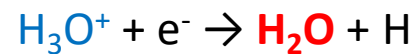$$H^- + H \rightarrow H_2 + e^- \qquad \text{or} \qquad H + H_2^+ \rightarrow H_2 + H^+$$
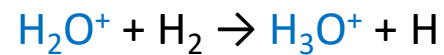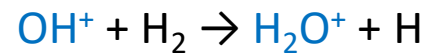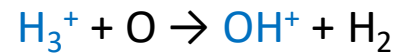
> Ionisation in the ISM not enough

The only efficient way: formation on the grains

$$H + H + \text{grain} \rightarrow H_2 + \text{grain}$$

Consortium paper on H_2 formation : Wakelam et al. (2017)
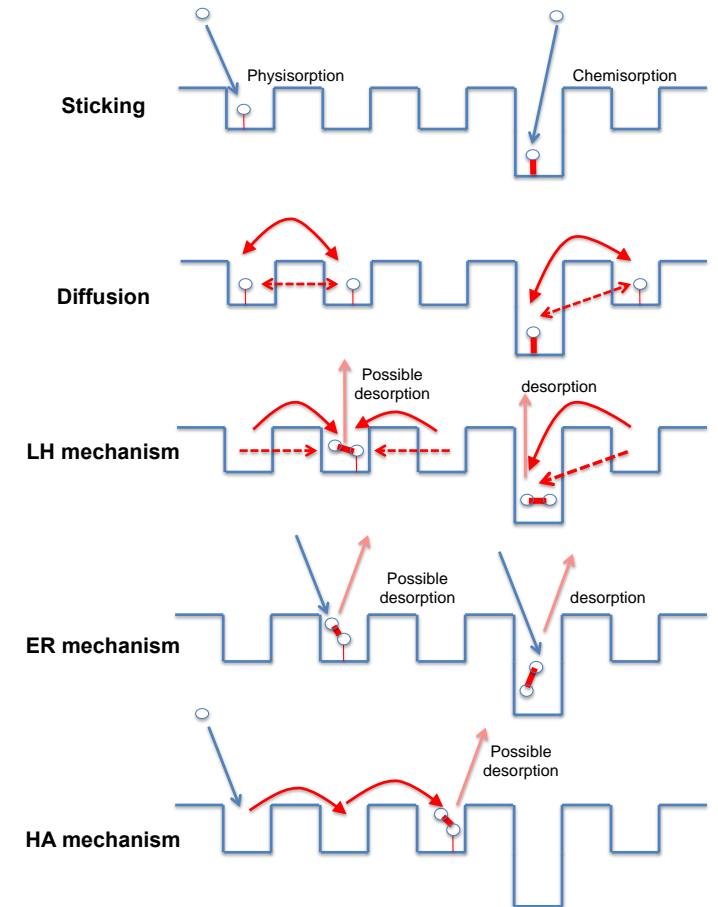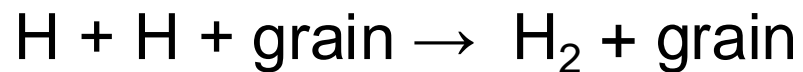
Main chemical pathways to the formation of O_2 and H_2O in the gas-phase

$H_2 + \gamma \rightarrow H_2^+ + e^-$

$H_2^+ + H_2 \rightarrow H_3^+ + H$

$H_3^+ + O \rightarrow OH^+ + H_2$

$OH^+ + H_2 \rightarrow H_2O^+ + H$

$H_2O^+ + H_2 \rightarrow H_3O^+ + H$

$H_3O^+ + e^- \rightarrow OH + H_2$ $\qquad$ $O + OH \rightarrow O_2 + H$

$H_3O^+ + e^- \rightarrow H_2O + H$
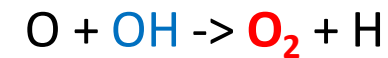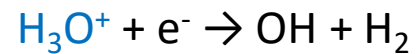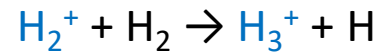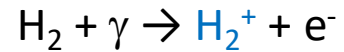
The example of O_2 formation

Gas-phase chemical models predict that:

- half of the oxygen in the form of O_2

- the other half in CO

- So that O_2/CO ~ 0.5
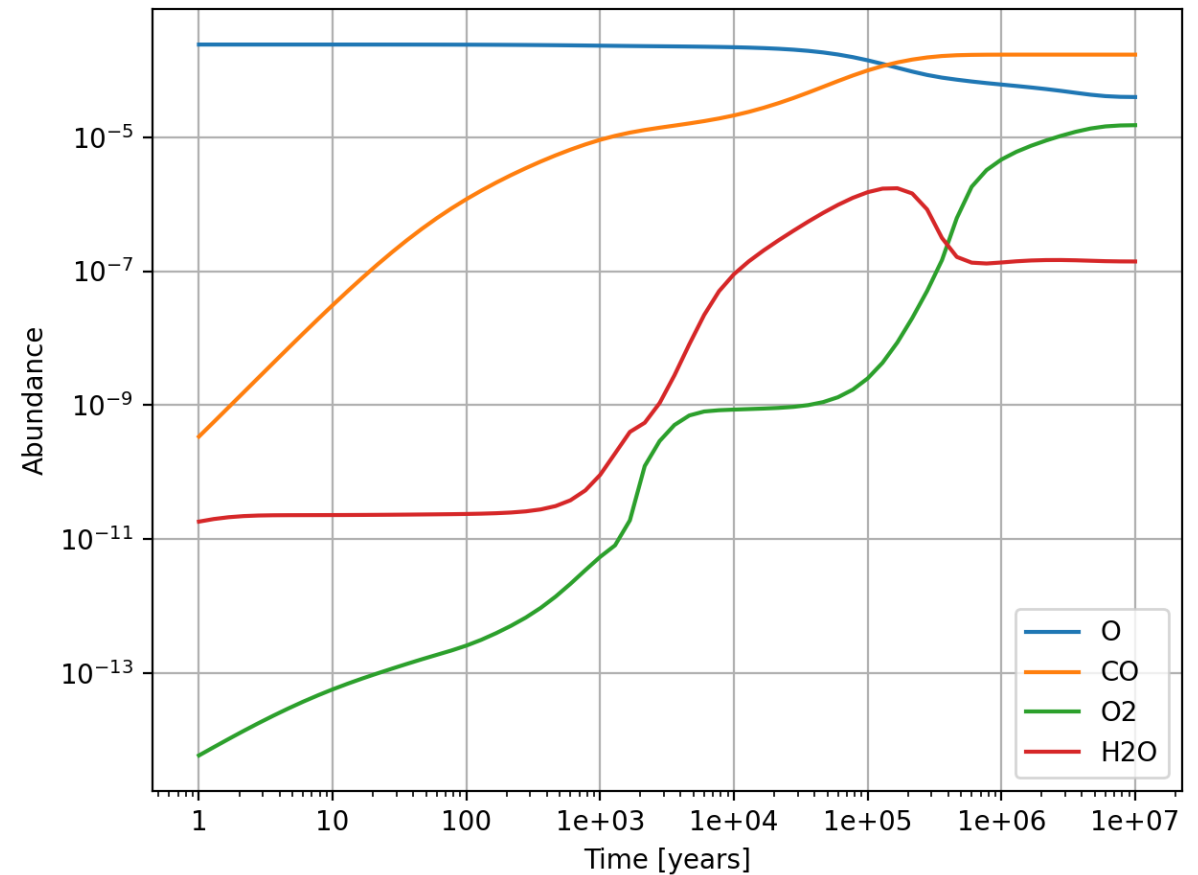
The example of O_2 formation

Ground based telescopes from 1985 to 1997:

Galactic sources: $O^{18}O$ (234 GHz, $N_J: 2_1 \rightarrow 0_1$)

- Goldsmith et al,. 1985, ApJ 289, 613
- Liszt & van den Bout, 1985, ApJ 291, 178
- Pagani et al., 1993, A&A 274, L13
- Fuente et al., 1993, A&A 275, 558
- Maréchal et al., 1997, A&A 318, 252 ⇒ $O_2/CO < 0.1$ (3 σ)
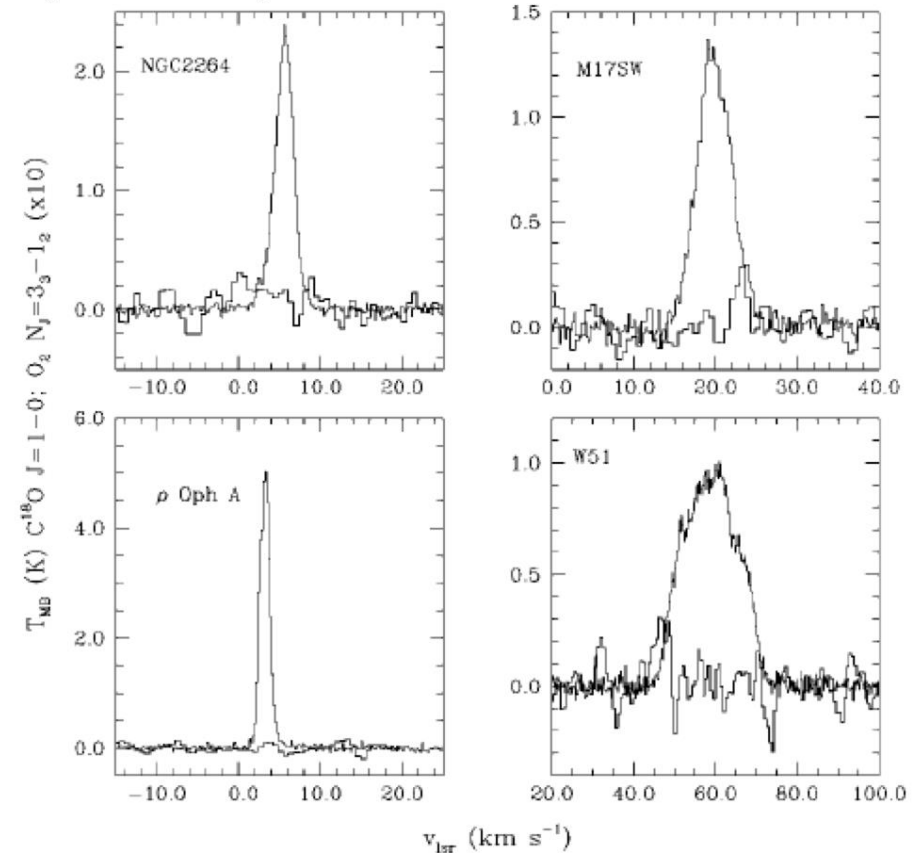
Extra galactic sources: $O^{16}O$ (119 GHz, $N_J: 1_1 \rightarrow 1_0$)

- Liszt, 1985, ApJ 298, 281L
- Combes et al., 1991, A&A 248, 607
- Liszt, 1992, ApJ 386, 139
- Combes et al., 1997, A&A 327, L17 ⇒ $O_2/CO < 0.006$ (3 σ)

The example of O_2 formation

Quest for the interstellar O_2

First space telescope: Submillimeter Wave Astronomy Satellite
O_2 at 487 GHz ($N_J = 3_3 - 1_2$)

SWAS : 1998-2005

No detection : O_2 abundance $< 3 \times 10^{-7}$ **Goldsmith et al. (2000)**

The example of O_2 formation

Quest for the interstellar O_2

Second space telescope: Odin
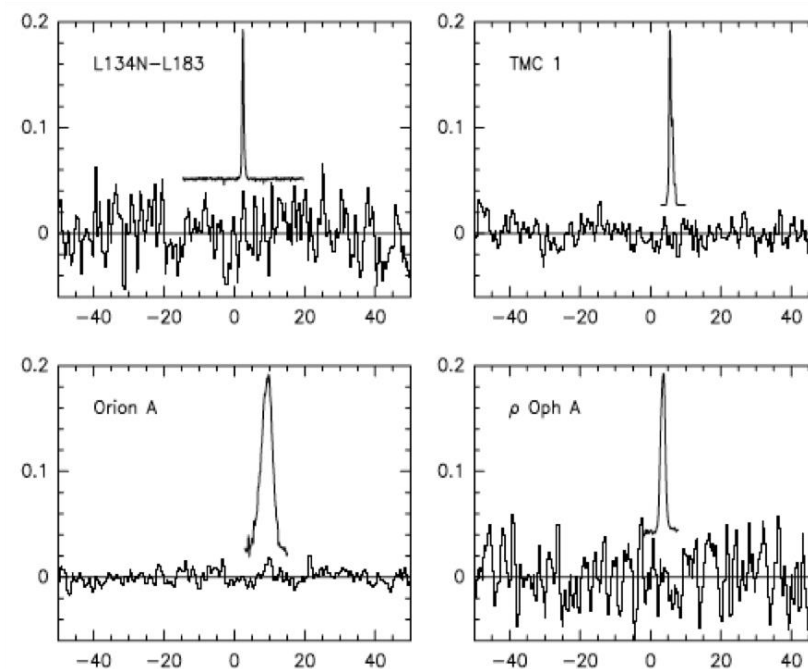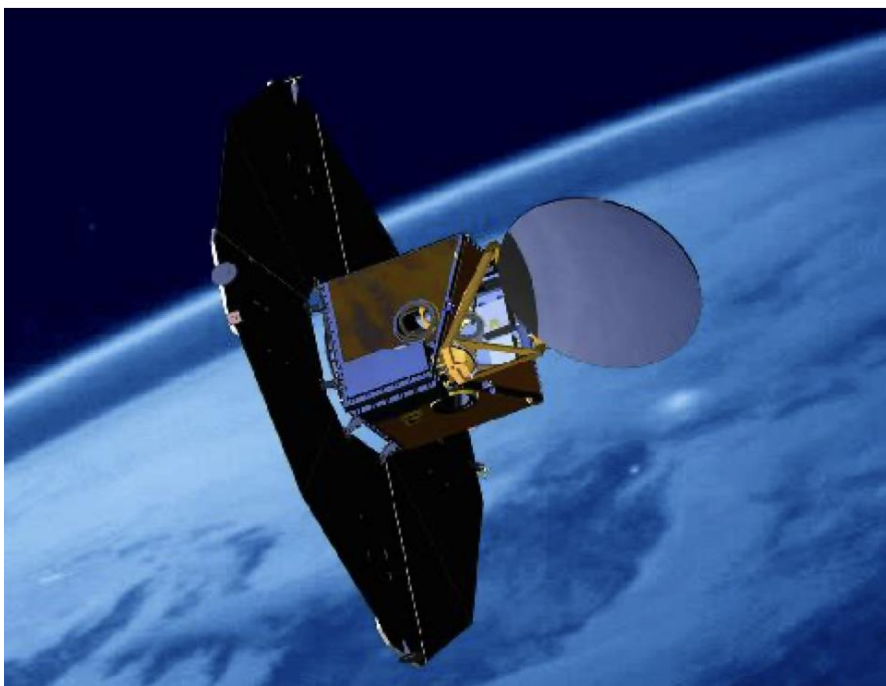
No detection : < 5-10x10^{-8}   **Pagani et al. (2003)**

The example of O_2 formation

Quest for the interstellar O_2

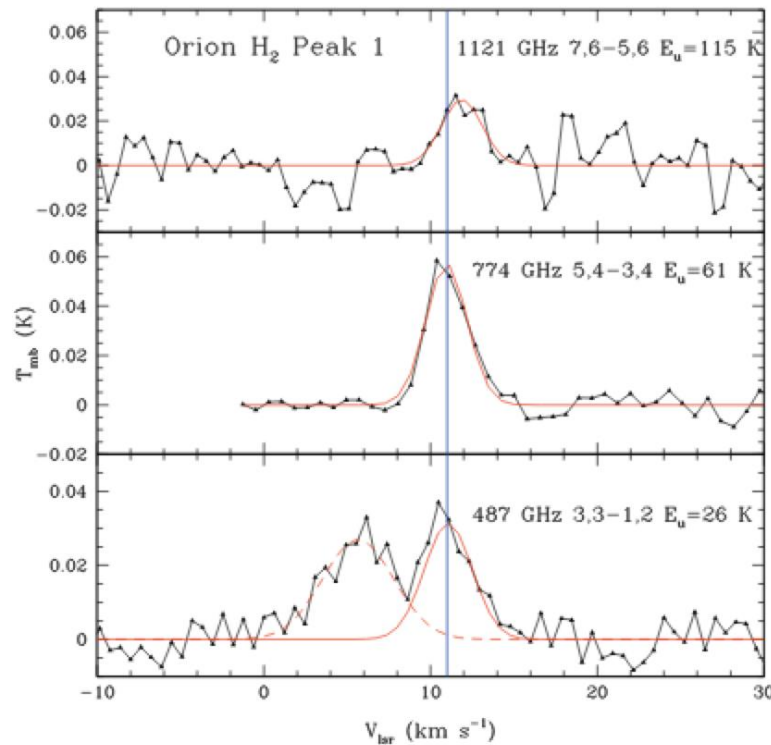**With a reanalysis of Odin's data, first detection in 2006.**
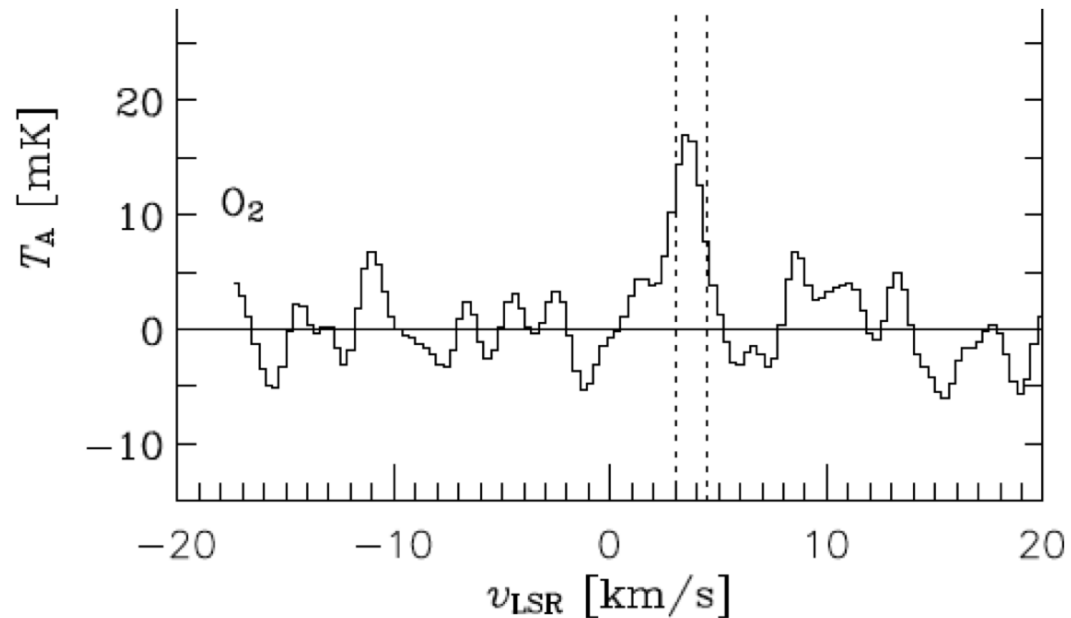
~(3-5)x10^{-8} Larsson et al. (2007)
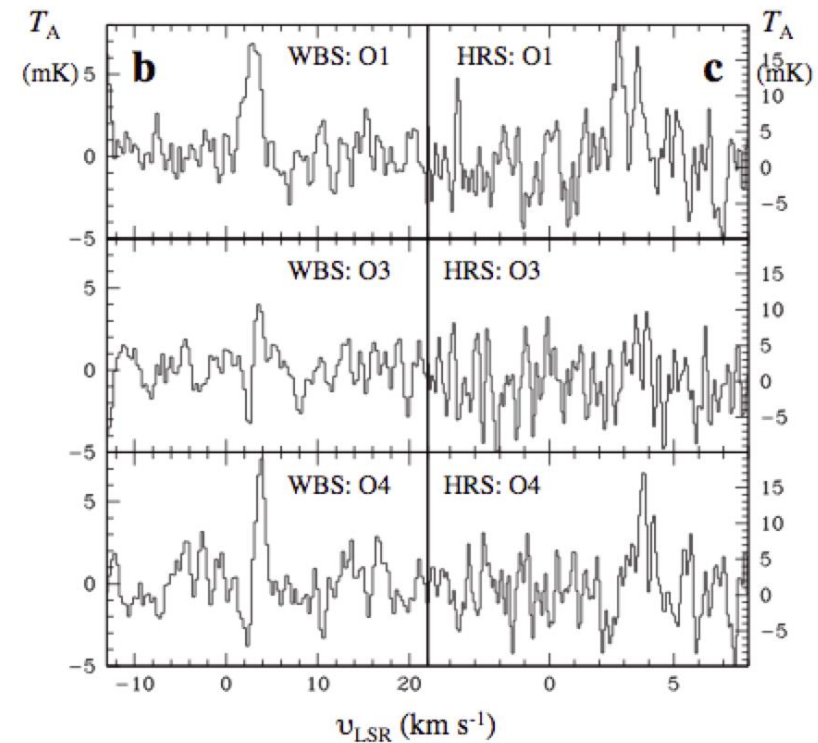
The example of O$_2$ formation

Quest for the interstellar O₂

Confirmation with Herschel but many non-detection

Liseau et al. (2012)

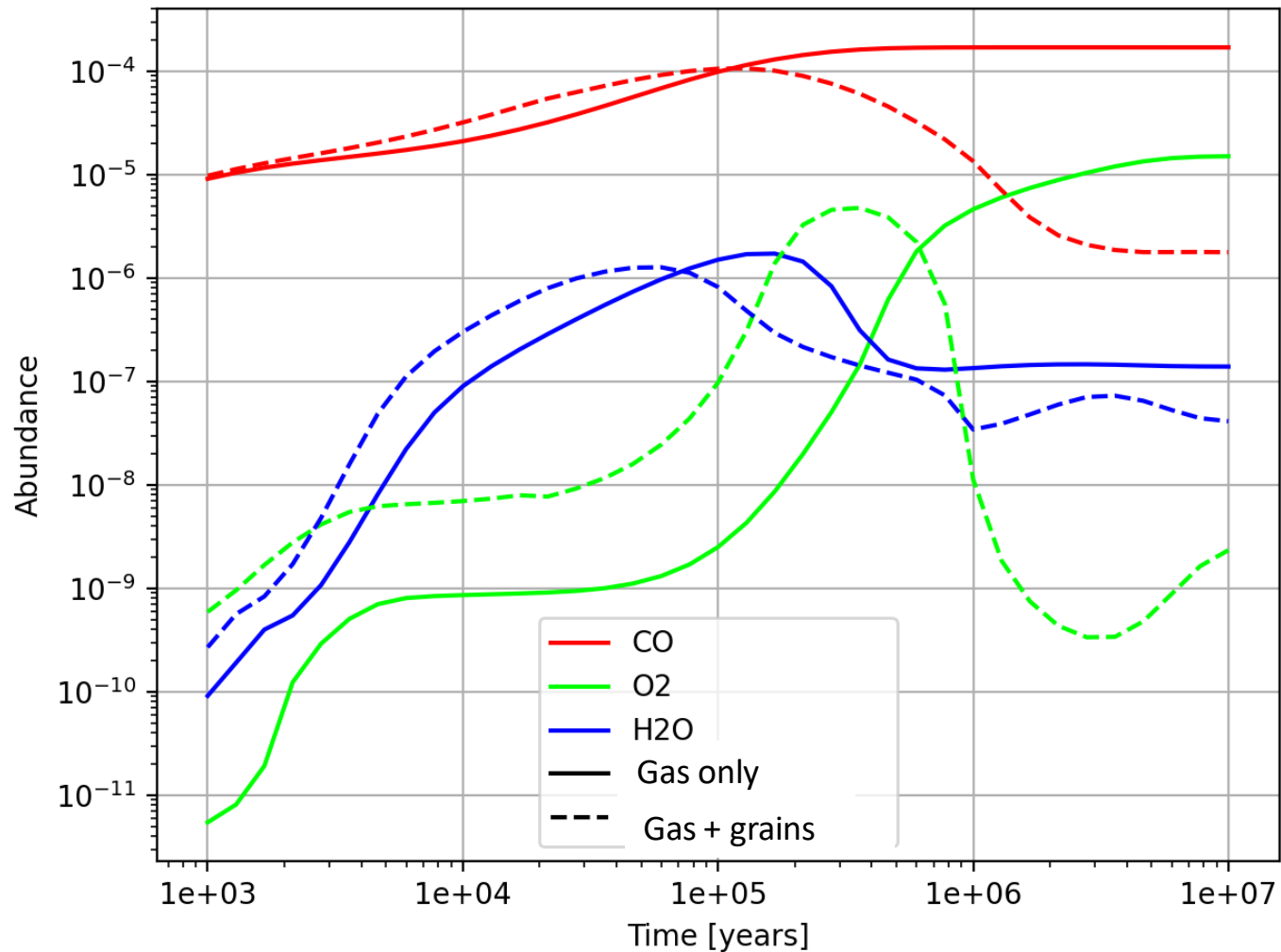**Goldsmith et al. (2011)**

Same abundances as previously determined.

The example of O_2 formation

Source	Column density (cm^{-3})	Abundance (with respect to H_2)	Reference
TMC1 - NH_3	$< 6.8 \times 10^{14}$	$< 7.7 \times 10^{-8}$	Pagani et al. (2003)
L134N - NH_3	$< 1.1 \times 10^{15}$	$< 1.7 \times 10^{-7}$	Pagani et al. (2003)
L429	$< 1.1 \times 10^{16}$	$< 9.2 \times 10^{-8}$	Wirström et al. (2016)
Oph D	$< 1.2 \times 10^{16}$	$< 1.1 \times 10^{-7}$	Wirström et al. (2016)
L1544	$< 8.2 \times 10^{15}$	$< 6.3 \times 10^{-8}$	Wirström et al. (2016)
L694-2	$< 1.6 \times 10^{16}$	$< 1.6 \times 10^{-7}$	Wirström et al. (2016)
Sgr A	$< 1.4 \times 10^{16}$	$< 5 \times 10^{-8}$	Sandqvist et al. (2015)
IRAS4 (protostar)	$< 1.2 \times 10^{15}$	$< 5.7 \times 10^{-9}$	Yıldız et al. (2013)
IRAS4 (cloud)	$(2.8 - 4.3) \times 10^{15}*$	$(4.3 - 2.2) \times 10^{-7}*$	Yıldız et al. (2013)
Orion bar	$< 1 \times 10^{16}$	-	Melnick et al. (2012)
IRAS16293-2422	$< 1.7 \times 10^{15}$	$< 1.2 \times 10^{-7}$	Pagani et al. (2003)
IRAS16293-2422	$< 9 \times 10^{19}$	-	Taquet et al. (2018)
ρ Oph A	$< 3.4 \times 10^{15}$	$< 9.3 \times 10^{-8}$	Pagani et al. (2003)
ρ Oph A	10^{15}	5×10^{-8}	Larsson et al. (2007)
ρ Oph A	$(3 - 6) \times 10^{15}$	$\sim 5 \times 10^{-8}$	Liseau et al. (2012)
Orion	6.5×10^{15}	$(0.3 - 7.3) \times 10^{-6}$	Goldsmith et al. (2011)
Orion A	$< 1.9 \times 10^{15}$	$< 8.9 \times 10^{-8}$	Pagani et al. (2003)
NGC2071	$< 2.6 \times 10^{15}$	$< 1.5 \times 10^{-7}$	Pagani et al. (2003)
NGC6334I	$< 5.0 \times 10^{15}$	$< 7.1 \times 10^{-8}$	Pagani et al. (2003)
(G0.26 - 0.01)	$< 5.6 \times 10^{16}$	$< 7.6 \times 10^{-7}$	Pagani et al. (2003)
M17SW	$< 7.3 \times 10^{15}$	$< 5.7 \times 10^{-7}$	Pagani et al. (2003)
S68FIRS1	$< 1.6 \times 10^{15}$	$< 9.7 \times 10^{-8}$	Pagani et al. (2003)
G34.3 + 0.2	$< 5.2 \times 10^{15}$	$< 5.2 \times 10^{-8}$	Pagani et al. (2003)

Listed in Wakelam et al. (2019)

The example of O_2 formation

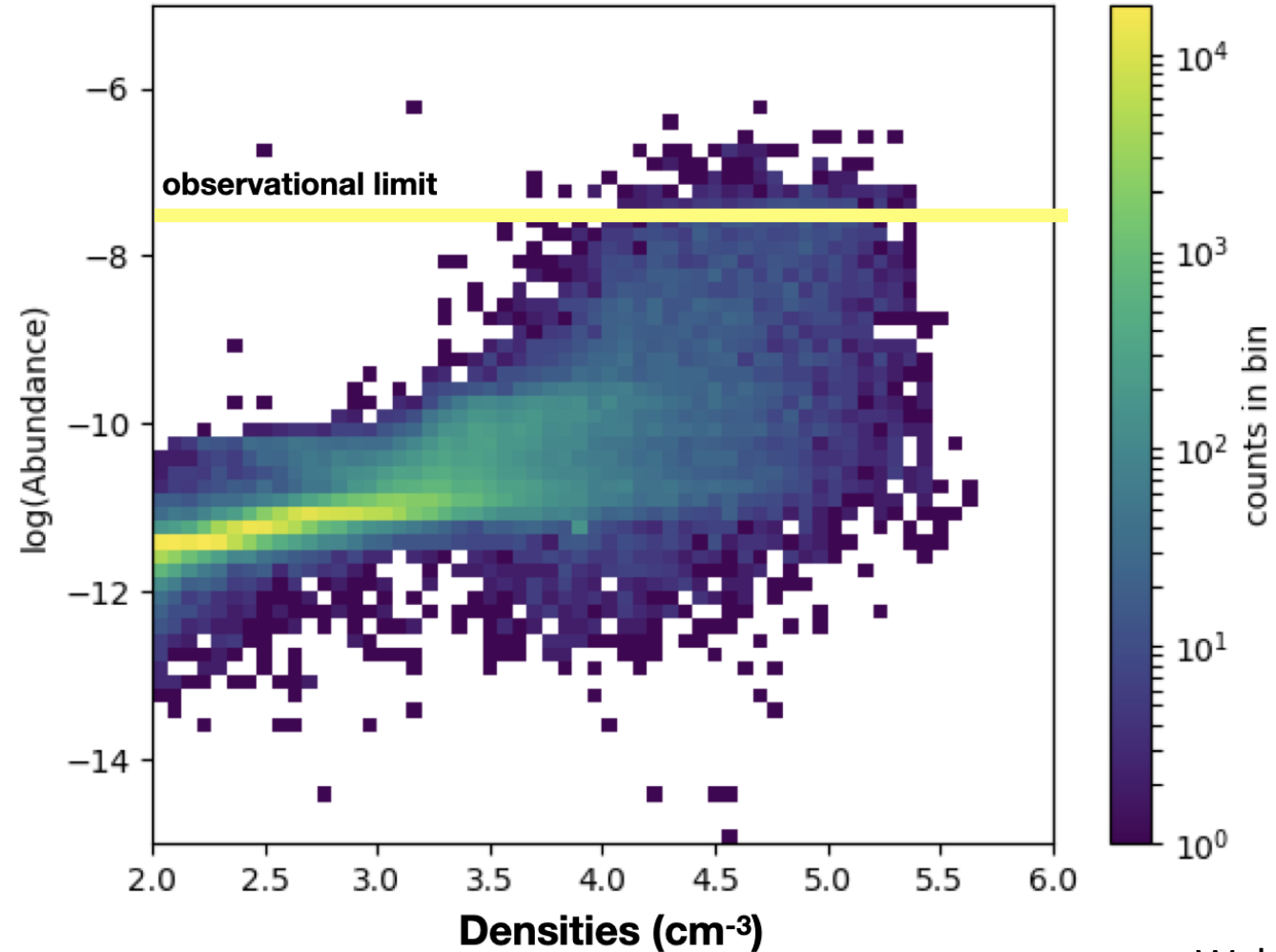## Why isn't there any O_2 in the gas?

The example of O$_2$ formation

Why isn't there any O$_2$ in the gas?

Proposed scenario:

Using hydrodynamical simulations to follow the evolution of the ISM in a galactic arm.

-> The diversity of the history of the physical conditions leads to a very low abundance of O$_2$ in the gas.

Wakelam et al. (2019)

Messages to take home

There are many processes involved in the gas-phase chemistry.

Determination of rate coefficients:
- For some processes, there can be estimate of the rate coefficients (example capture rate for ion-neutral reactions).
- Experiments or quantum calculations (there can be polemics)
- Most of them in databases are guessed or estimated based on chemical similarities

Better have uncertain rate coefficients than a smaller network. The more the reactions, the less the chemical abundances are sensitive to the exact rate coefficients.

-> Where efforts need to be done: radiative associations

Exercises:

What's the effet of density?

What's the effect of cosmic-ray ionization rate?

What's the effect of temperature?

If we have time:
- Tests with and without grain surface chemistry
- Test different densities (compare the effect if grains surfaces are considered)
- Change the ionization of H2
- Change the AV and/or the UV field (show that it reaches steady state at low Av)