# WG4: Isotopic Chemistry

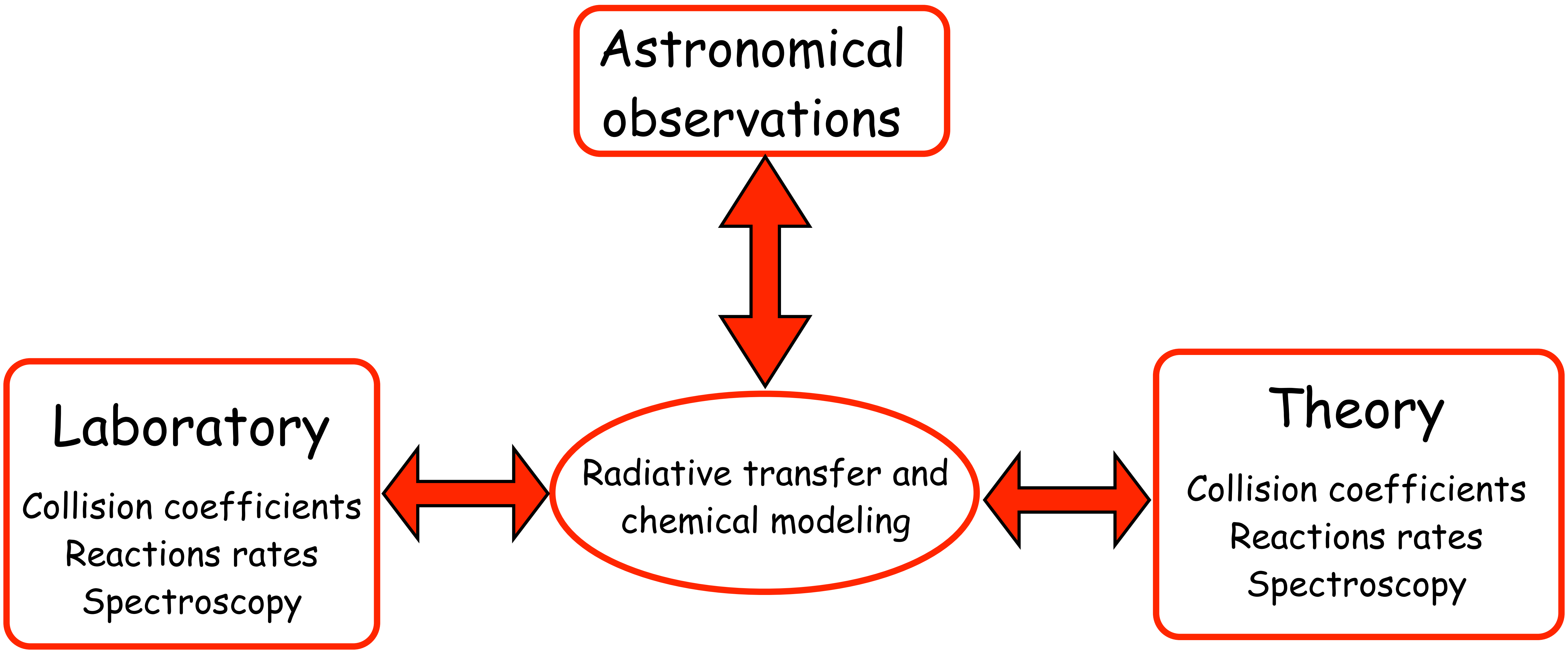
## A view from the astronomer

Charlotte Vastel

May 28th, 2015

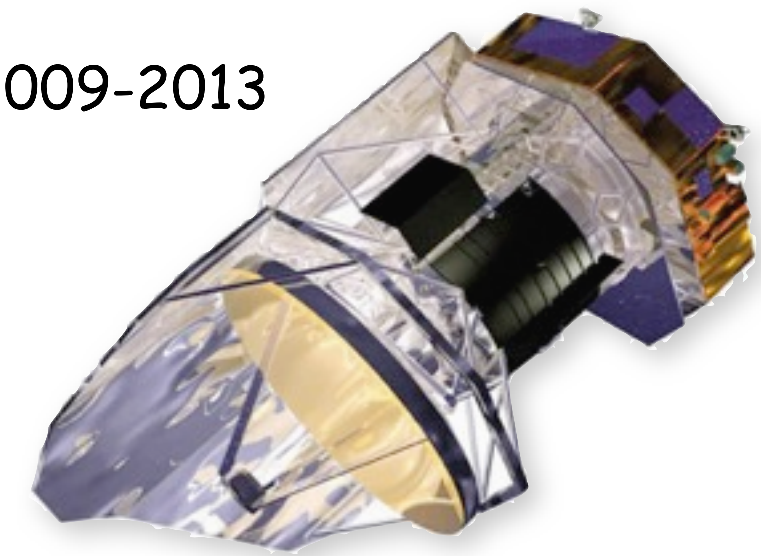
# Our Astro-Chemical History

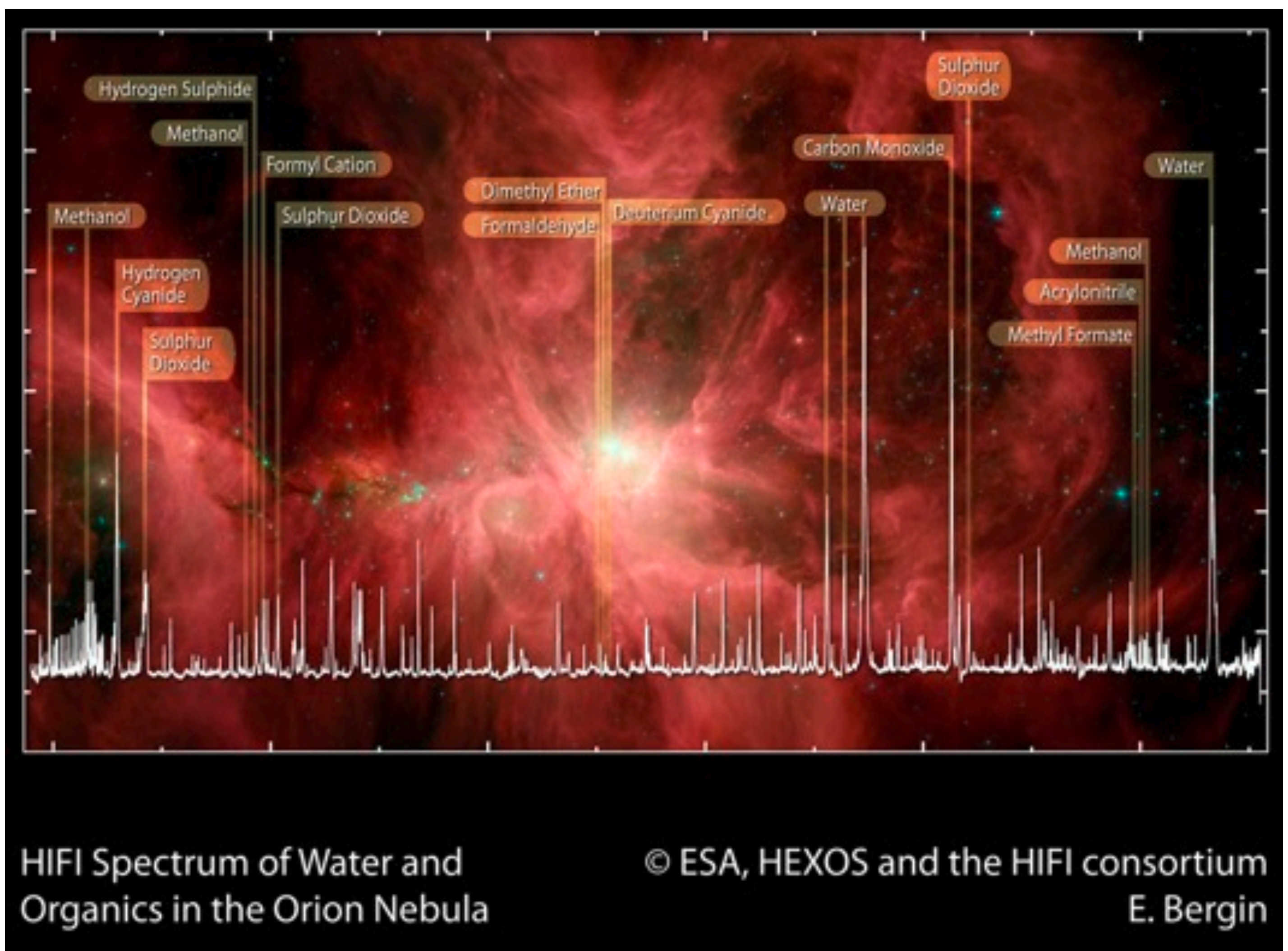
The main objective of the Action is to bring together astrophysical and chemical laboratories to focus on the molecular evolution towards complexity, from star formation to the present day Solar System, and to provide innovative experimental and theoretical chemical schemes.

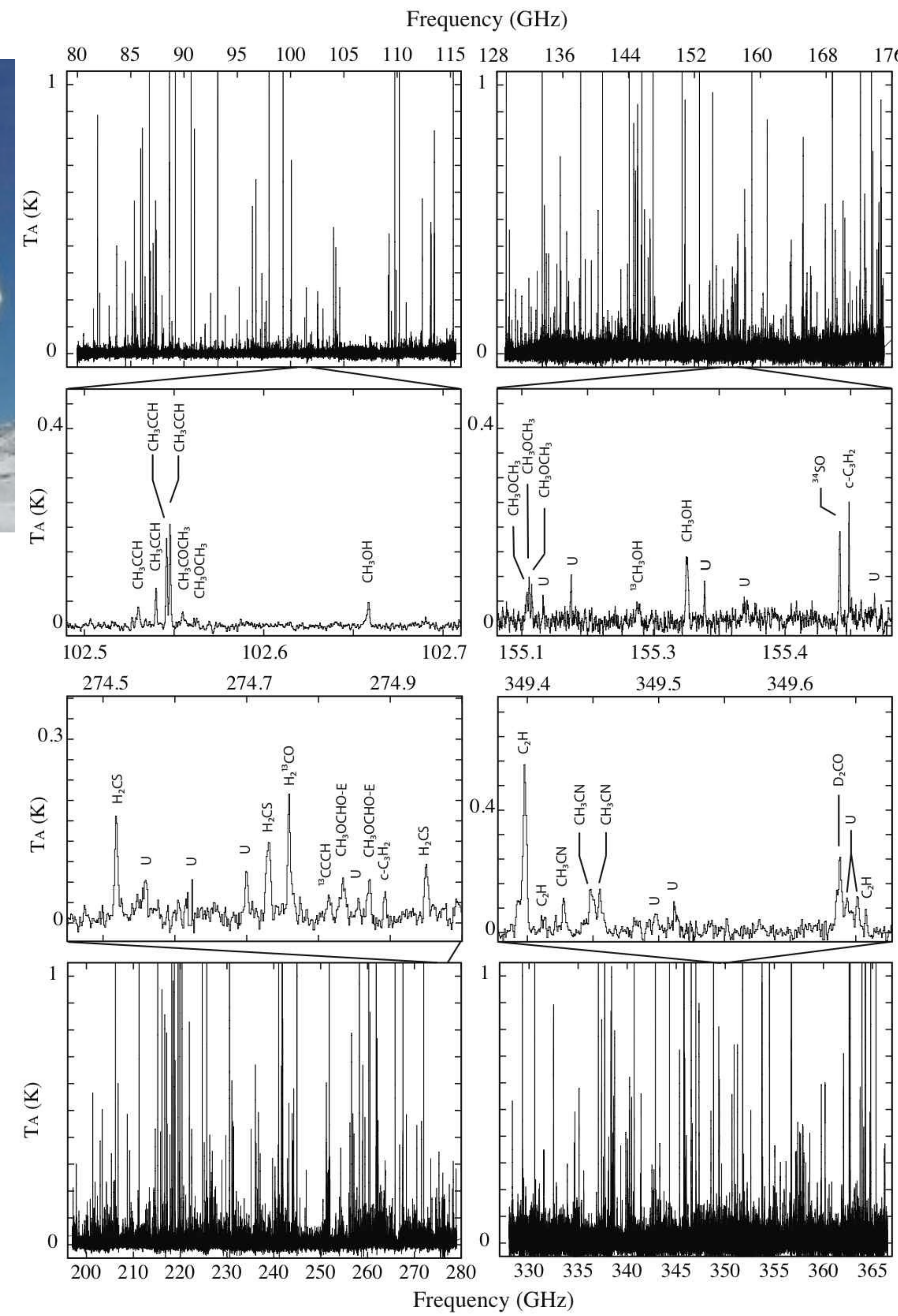


# Golden age for astrochemistry

2009-2013

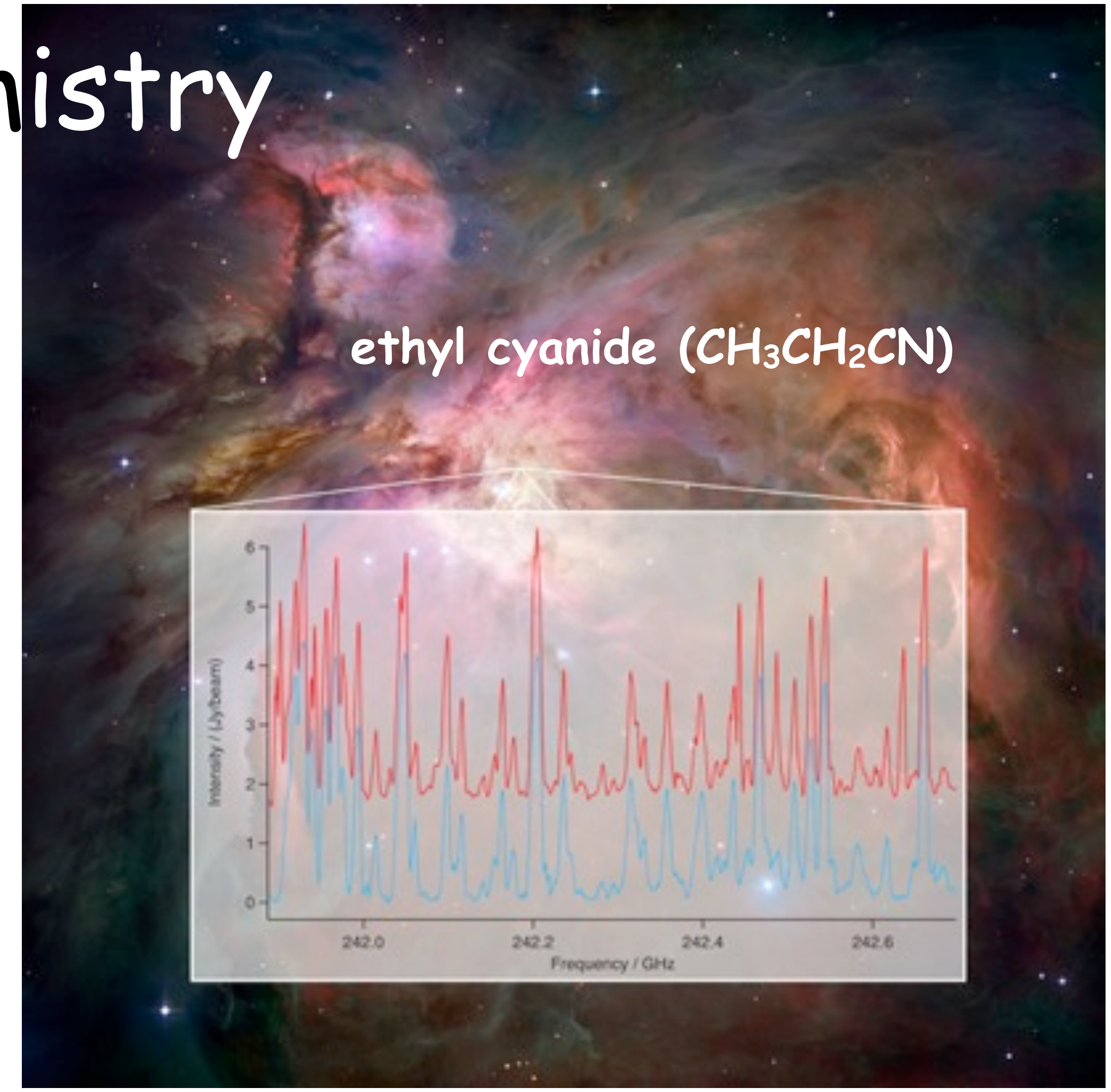



IRAS16293: Caux et al. 2012

# Golden age for astrochemistry





## SOLIS: 1st Large Program with NOEMA

**(1) Understand organic chemistry in space**

**(2) Determine how it evolves during the process of formation of Solar-type systems**

(see B. Lefloch's presentation)

# The astronomers periodic table

How abundant is one element presented by the size of its white square.

| 2 atoms | 3 atoms | 4 atoms | 5 atoms | 6 atoms | 7 atoms | 8 atoms | 9 atoms | 10 atoms | 11 atoms | 12 atoms | >12 atoms |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | $C_3$ * | c-$C_3H$ | $C_5$ * | $C_5H$ | $C_6H$ | $CH_3C_3N$ | $CH_3C_4H$ | $CH_3C_5N$ | $HC_9N$ | c-$C_6H_6$ * | $HC_{11}N$ |
| AlF | $C_2H$ | l-$C_3H$ | $C_4H$ | l-$H_2C_4$ | $CH_2CHCN$ | $HC(O)OCH_3$ | $CH_3CH_2CN$ | $(CH_3)_2CO$ | $CH_3C_6H$ | n-$C_3H_7CN$ | $C_{60}$ * |
| AlCl | $C_2O$ | $C_3N$ | $C_4Si$ | $C_2H_4$* | $CH_3C_2H$ | $CH_3COOH$ | $(CH_3)_2O$ | $(CH_2OH)_2$ | $C_2H_5OCHO$ | i-$C_3H_7CN$<br>2014 | $C_{70}$ * |
| $C_2$** | $C_2S$ | $C_3O$ | l-$C_3H_2$ | $CH_3CN$ | $HC_5N$ | $C_7H$ | $CH_3CH_2OH$ | $CH_3CH_2CHO$ | $CH_3OC(O)CH_3$ | | |
| CH | $CH_2$ | $C_3S$ | c-$C_3H_2$ | $CH_3NC$ | $CH_3CHO$ | $C_6H_2$ | $HC_7N$ | | | | |
| $CH^+$ | HCN | $C_2H_2$* | $H_2CCN$ | $CH_3OH$ | $CH_3NH_2$ | $CH_2OHCHO$ | $C_8H$ | | | | |
| CN | HCO | $NH_3$ | $CH_4$ * | $CH_3SH$ | c-$C_2H_4O$ | l-$HC_6H$ * | $CH_3C(O)NH_2$ | | | | |
| CO | $HCO^+$ | HCCN | $HC_3N$ | $HC_3NH^+$ | $H_2CCHOH$ | $CH_2CHCHO$ (?) | $C_8H^-$ | | | | |
| $CO^+$ | $HCS^+$ | $HCNH^+$ | $HC_2NC$ | $HC_2CHO$ | $C_6H^-$ | $CH_2CCHCN$ | $C_3H_6$ | | | | |
| CP | $HOC^+$ | HNCO | HCOOH | $NH_2CHO$ | | $H_2NCH_2CN$ | $CH_3CH_2SH$ (?) | | | | |
| SiC | $H_2O$ | HNCS | $H_2CNH$ | $C_5N$ | | $CH_3CHNH$ | | | | | |
| HCl | $H_2S$ | $HOCO^+$ | $H_2C_2O$ | l-$HC_4H$ * | | | | | | | |
| KCl | HNC | $H_2CO$ | $H_2NCN$ | l-$HC_4N$ | | | | | | | |
| NH | HNO | $H_2CN$ | $HNC_3$ | c-$H_2C_3O$ | | | | | | | |
| NO | MgCN | $H_2CS$ | $SiH_4$ * | $H_2CCNH$ (?) | | | | | | | |
| NS | MgNC | $H_3O^+$ | $H_2COH^+$ | $C_5N^-$ | | | | | | | |
| NaCl | $N_2H^+$ | c-$SiC_3$ | $C_4H^-$ | HNCHCN | | | | | | | |
| OH | $N_2O$ | $CH_3$ * | $HC(O)CN$ | | | | | | | | |
| PN | NaCN | $C_3N^-$ | HNCNH | | | | | | | | |
| SO | OCS | $PH_3$ | $CH_3O$ | | | | | | | | |
| $SO^+$ | $SO_2$ | HCNO | $NH_4^+$ | | | | | | | | |
| SiN | c-$SiC_2$ | HOCN | $H_2NCO^+$ (?) | | | | | | | | |
| SiO | $CO_2$ * | HSCN | | | | | | | | | |
| SiS | $NH_2$ | $H_2O_2$ | | | | | | | | | |
| CS | $H_3^+$ (*) | $C_3H^+$ | | | | | | | | | |
| HF | SiCN | HMgNC | | | | | | | | | |
| HD | AlNC | | | | | | | | | | |
| FeO ? | SiNC | | | | | | | | | | |
| $O_2$ | HCP | | | | | | | | | | |
| $CF^+$ | CCP | | | | | | | | | | |
| SiH ? | AlOH | | | | | | | | | | |
| PO | $H_2O^+$ | | | | | | | | | | |
| AlO | $H_2Cl^+$ | | | | | | | | | | |
| $OH^+$ | KCN | | | | | | | | | | |
| $CN^-$ | FeCN | | | | | | | | | | |
| $SH^+$ | $HO_2$ | | | | | | | | | | |
| SH | $TiO_2$ | | | | | | | | | | |
| $HCl^+$ | $C_2N$<br>2014 | | | | | | | | | | |
| TiO | | | | | | | | | | | |
| $ArH^+$ | | | | | | | | | | | |
| $NO^+$ ?<br>2014 | | | | | | | | | | | |

# Molecules in the Interstellar Medium or Circumstellar Shells (as of 10/2014: CDMS catalog)

More than 180 molecules unambiguously detected

Isotopologues (H, C, N, O, S) are not listed

# Our working group

WG1: Chemistry in cold diluted gas
WG2 icy grain surface chemistry
WG3 UV and X-ray photochemistry
**WG4: Isotopic Chemistry (Octavio Roncero and myself as coordinators)**

- **The core of this Action relies on data coming from ground and space telescopes**. For most large observational programs, the data are private to the consortium for a limited amount of time, less than two years usually. Having an established network of laboratories capable of using the data and exploiting it fully keeps the scientific content within the European laboratories.

- The next generation of instruments and experiments are the IR James Webb Space Telescope, the ALMA and NOEMA interferometer. In order to fully understand their flow of data and making effective consortia that affirm strongly the European presence, a fully established network of laboratory is a necessity.

# Our working group

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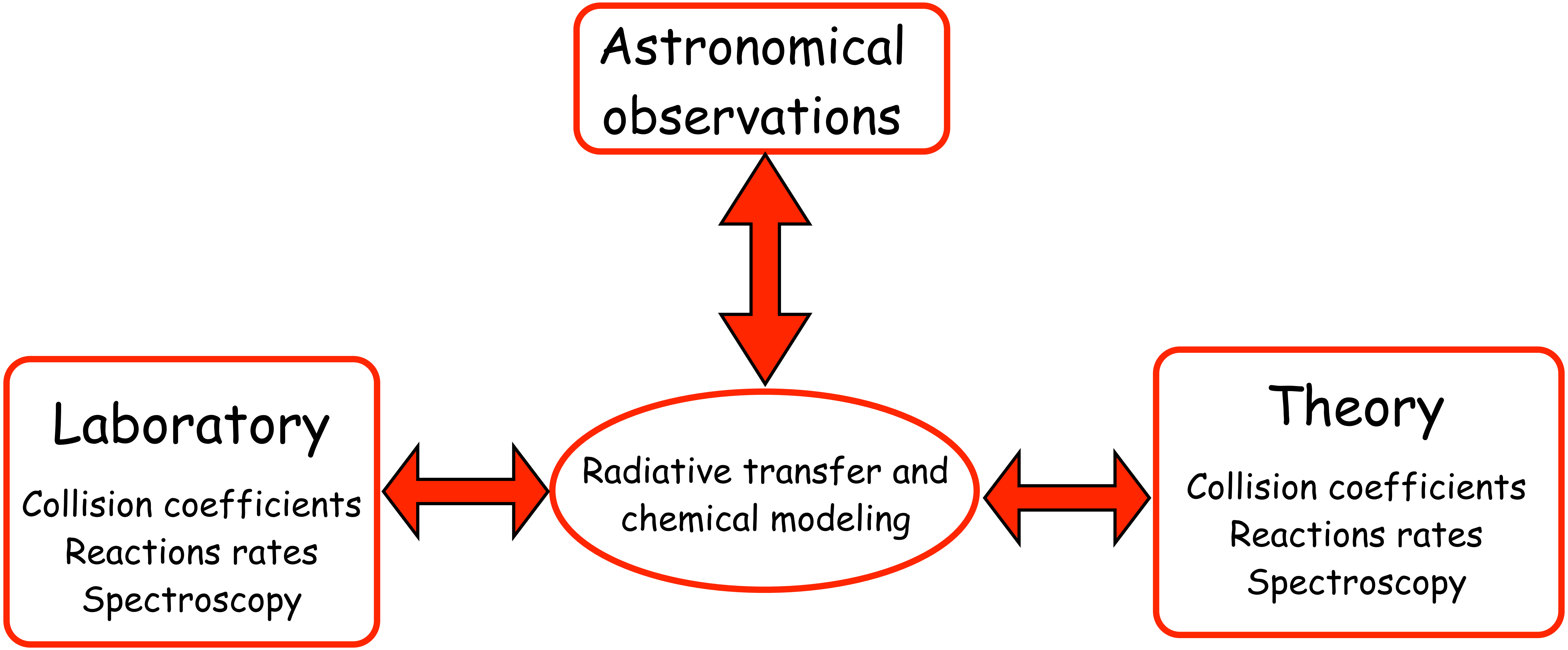


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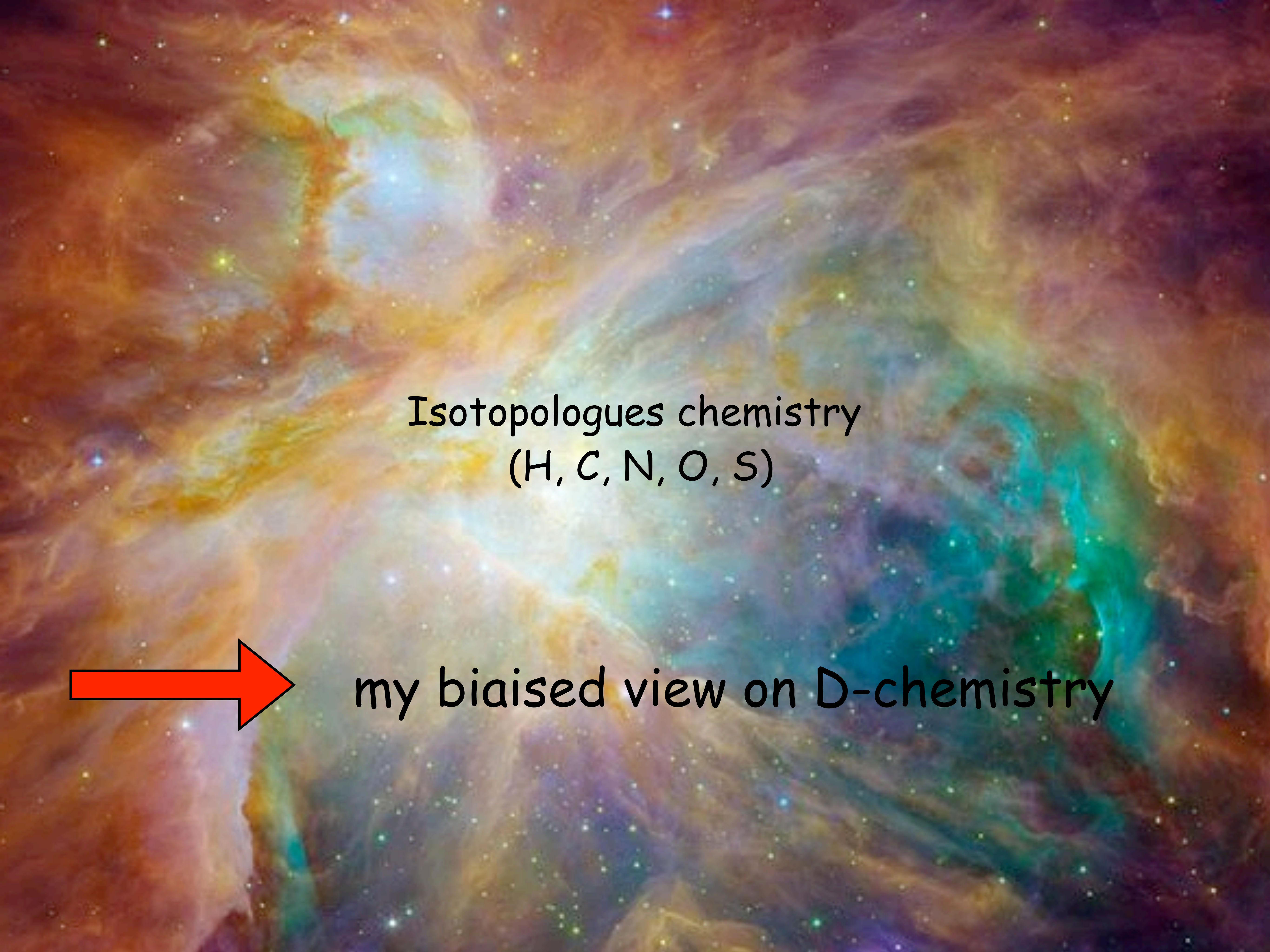
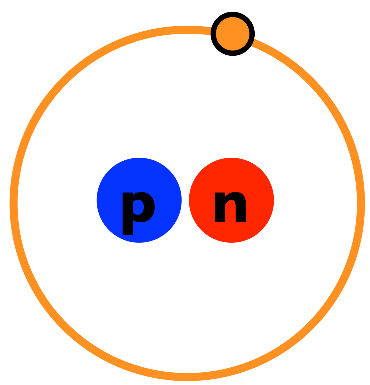
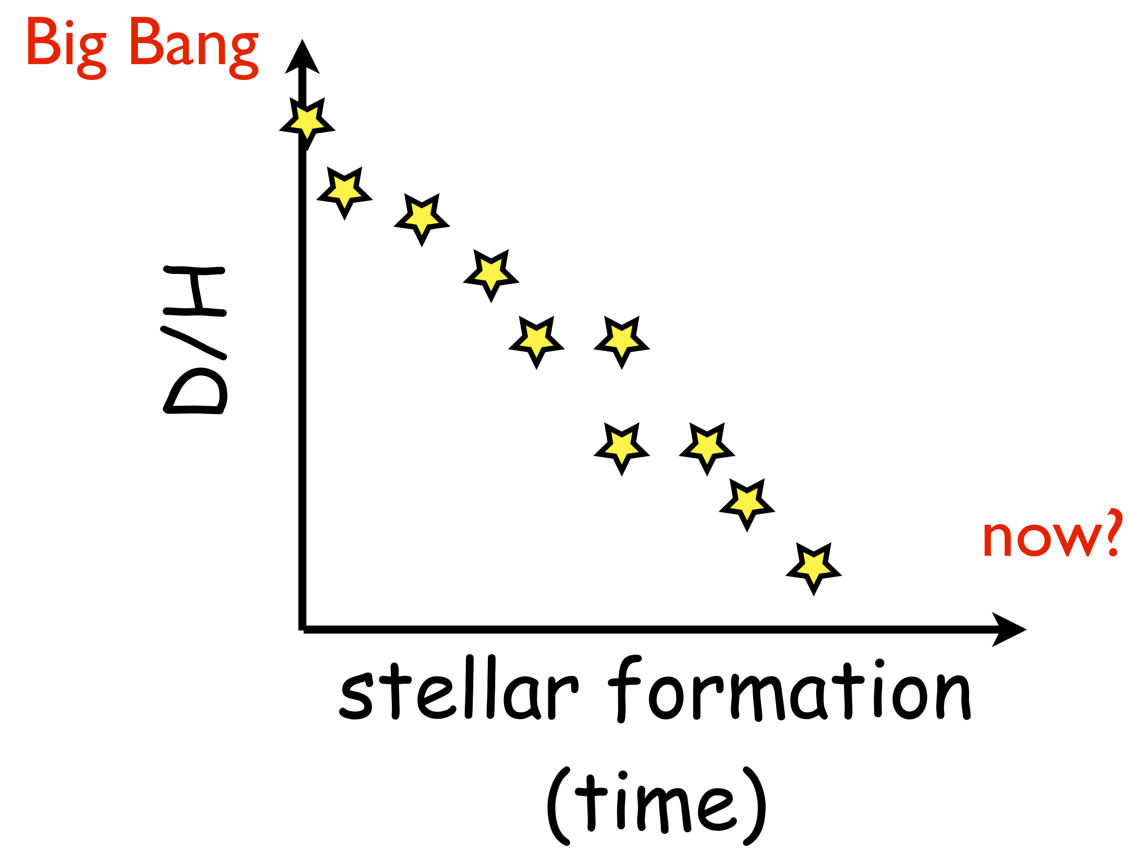

Isotopologues chemistry
(H, C, N, O, S)
my biaised view on D-chemistry

# *D: the fossil atom*

Deuterium was formed during the Big Bang nucleosynthesis (along with H, He, Li and Be).

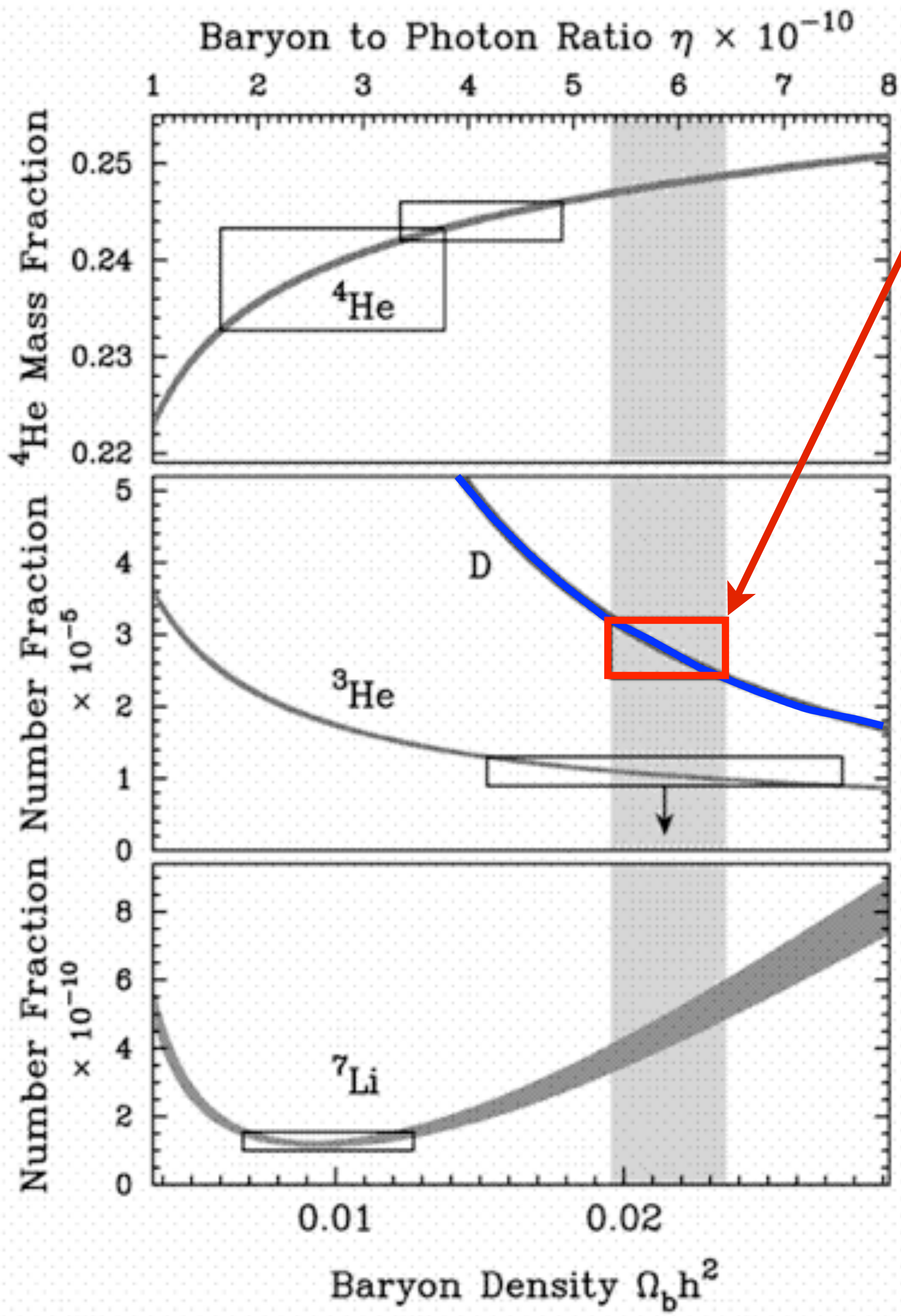



Formed during BBN, D is a fragile isotope, easily destroyed at high temperatures. The expansion of the universe cooled the universe and cut this conversion (-->$^{4}$He) short before it could be completed.
High temperatures inside stars lead to a constant destruction of D, transformed in heavier elements. This decreasing abundance in time is called **astration**.
The remaining D is therefore representative of the Universe rate of expansion and its density.

# *The fossil atom*

Deuterium was formed during the primeval Big Bang nucleosynthesis with D/H proportional to baryon density.




QSOs: D/H close to the primeval value

VLT: D/H=2.82 $10^{-5}$ @z=2.6

WMAP (2009): D/H = 2.7 $10^{-5}$

A precise estimate of the baryon density removes a degree of liberty to the cosmological models.

Kirkman et al. 2003/ Burles et al. 2001

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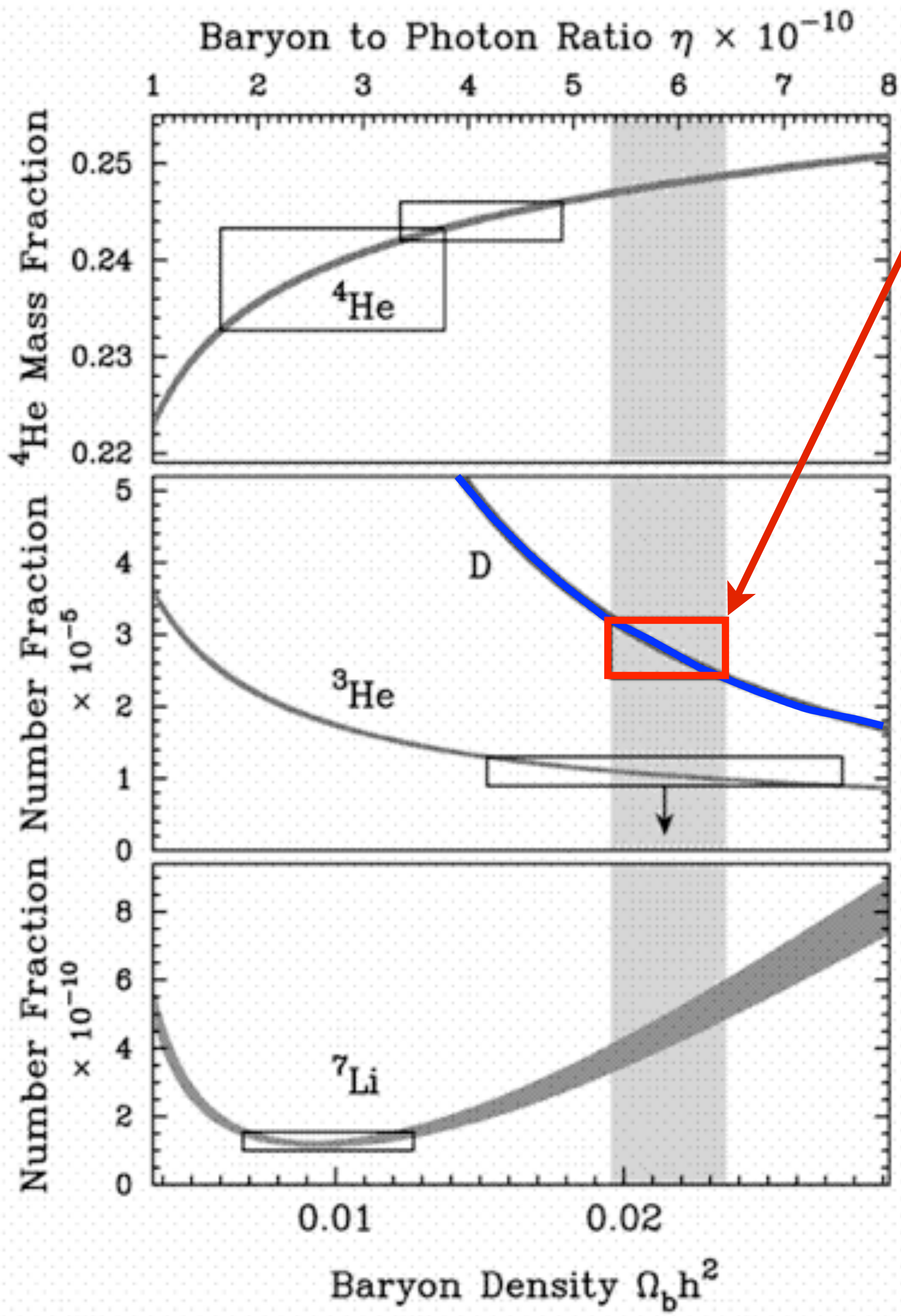



QSOs: D/H close to the primeval value

VLT: D/H=2.82 $10^{-5}$ @z=2.6

WMA

A p

rem

cos

Kirkma

Quasars: very energetic and distant active galactic nucleus

# *Deuterated molecules in the interstellar medium*

| D | | | D2 | | D3 |
|---|---|---|---|---|---|
| $HD$ | $C_2D$ | $CH_3CCD$ | $CHD_2OH$ | $D_2CO$ | $ND_3$ |
| $HDO$ | $DCO^+$ | $HDCS$ | $CHD_2CCH$ | $CH_2DCCD$ | $CD_3OH$ |
| $HDS$ | $N_2D^+$ | $CH_3OD$ | $D_2CS$ | $D_2O$ | |
| $H_2D^+$ | $NH_2D$ | $C_4D$ | $NHD_2$ | $D_2H^+$ | |
| $DCN$ | $HDCS$ | $CH_2DOH$ | $CHD_2OH$ | $D_2S$ | |
| $DNC$ | $DC_5N$ | $CH_2DCN$ | | $c\text{-}C_3D_2$ | |
| $CH_2DCCH$ | $C_2D$ | $DC_3N$ | | | |
| | c-C3HD | $ND$ | | | |

Abundances much larger (several orders of magnitudes) wrt the cosmic D/H abundance ($1.5\ 10^{-5}$ ; Linsky et al. 2007).

Main chemical reactions extracting D from HD (main D reservoir in dense regions):

$$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + \Delta E_1,$$

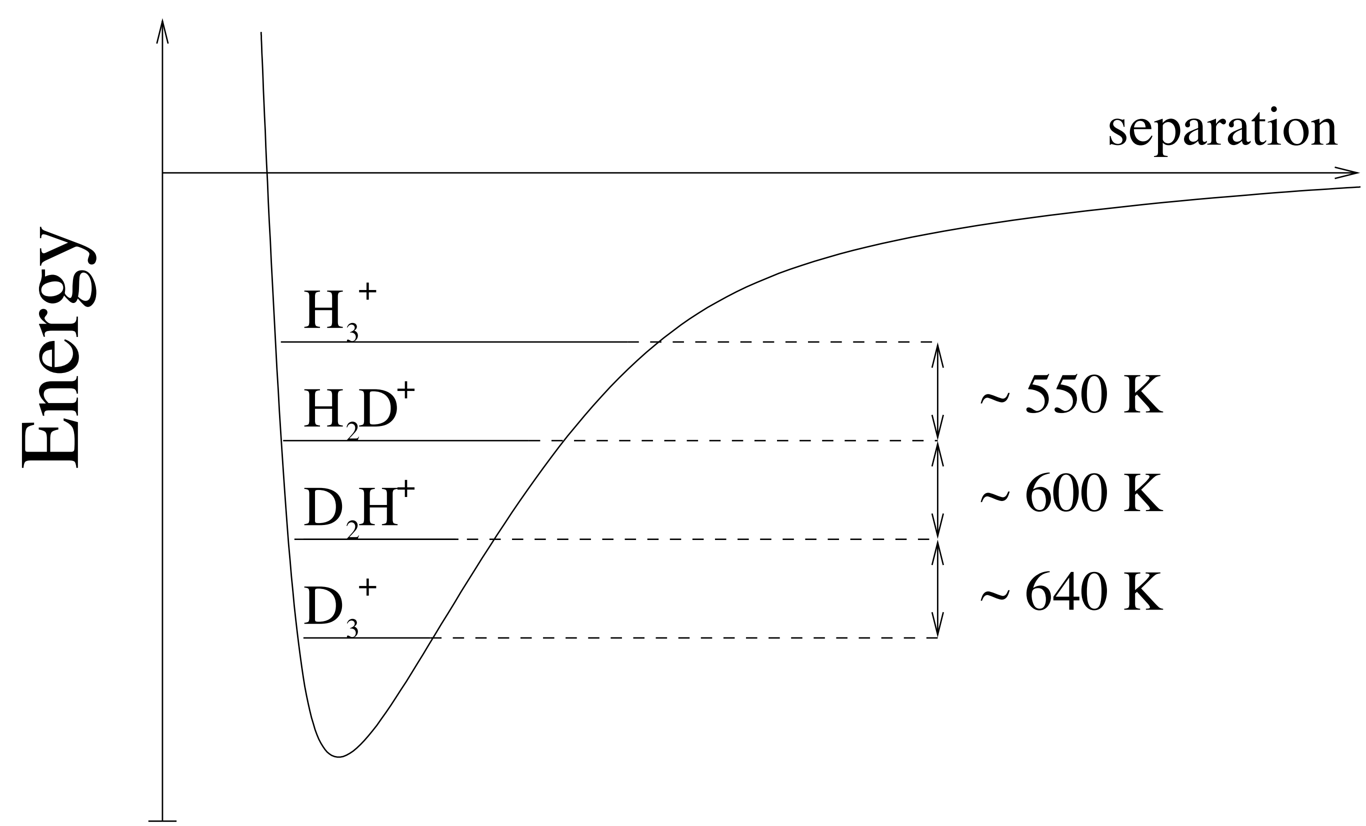
T ≤ 20 K

$$CH_3^+ + HD \longrightarrow CH_2D^+ + H_2 + \Delta E_2,$$
$$C_2H_2^+ + HD \longrightarrow C_2HD^+ + H_2 + \Delta E_3,$$

T ≤ 70 K

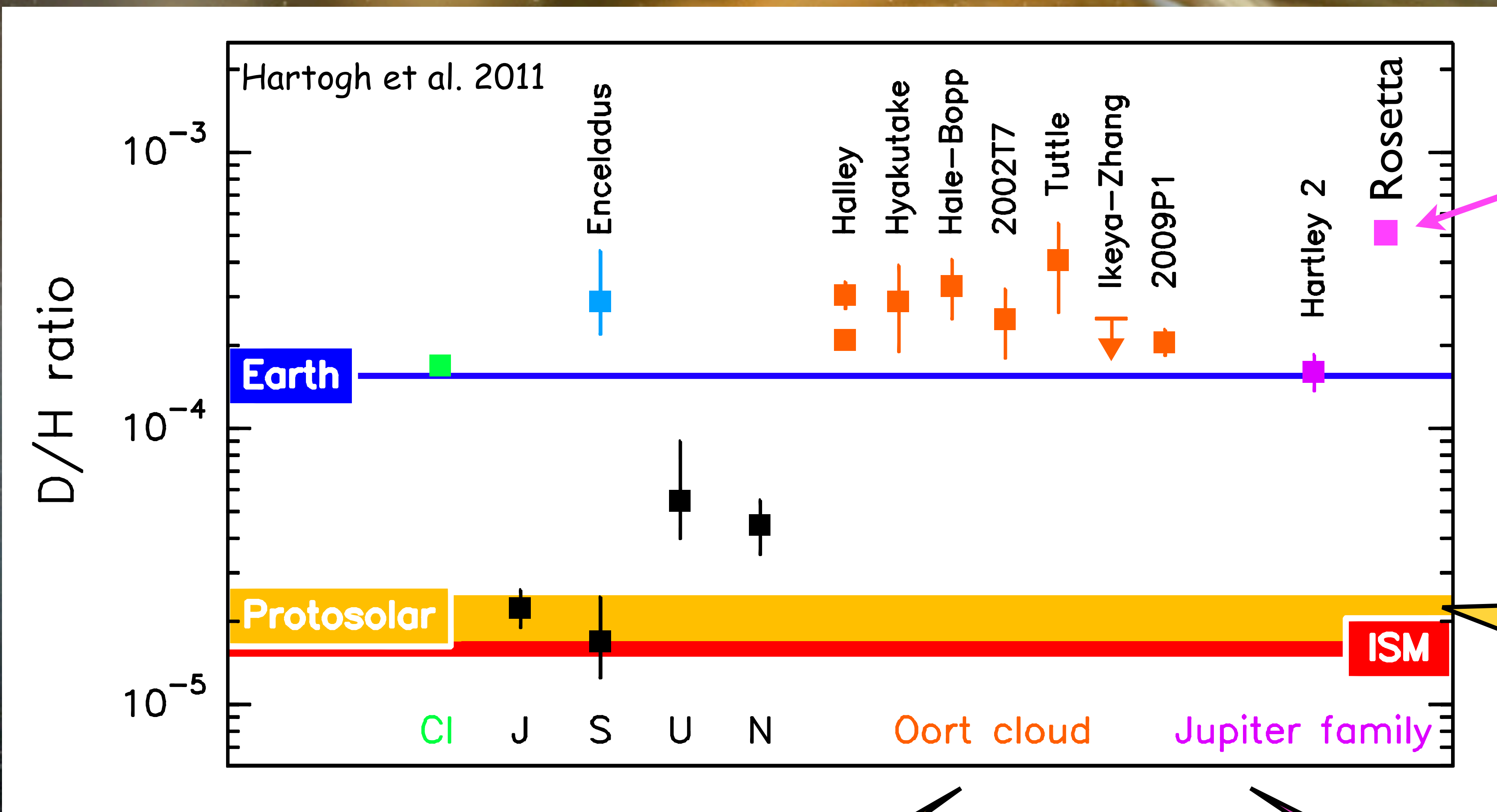
Exothermic reactions, $\Delta E_1/k$~230 K, $\Delta E_2/k$~375 K, $\Delta E_3/k$~550 K. In the cold regions (10-20K), backwards reactions are not efficient despite the $H_2$ high abundance.

D species abundances are very different from one source to another.
Why??
Chemical fractionation that forces D to stabilize in heavier molecules, in cold dense regions.



# Isotopic fractionation: water

Comets are among the most primitive bodies left from the planetesimal building stage of the Solar Nebula




Altwegg et al. 2015

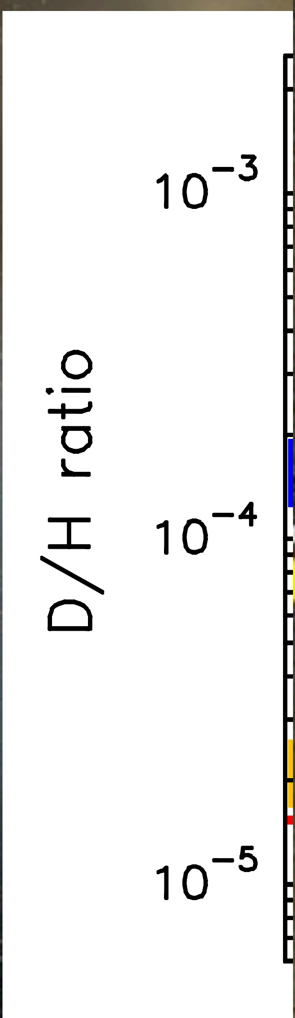
$^{3}He/^{4}He$ measurements in the solar wind combined with solar models.

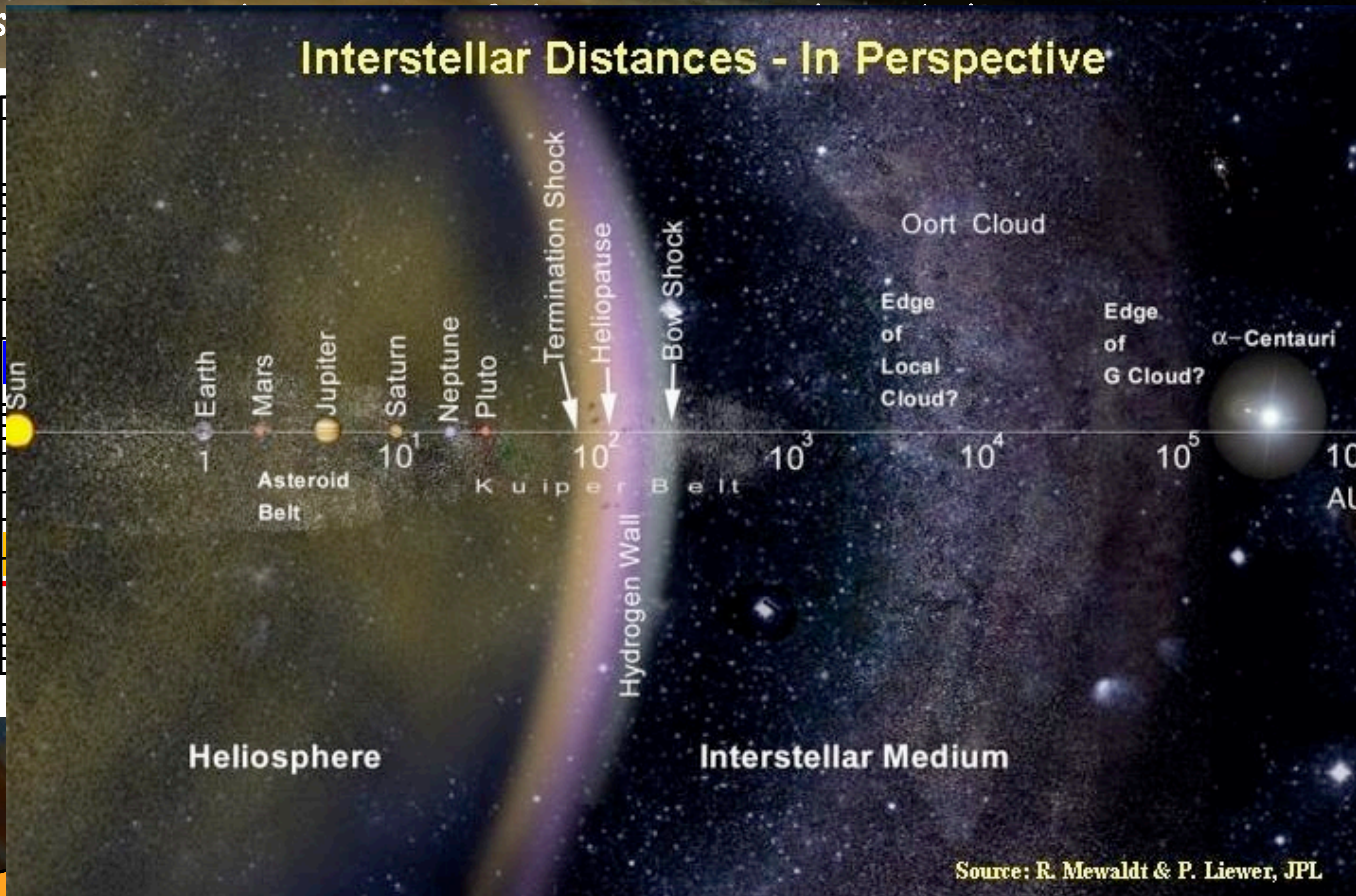
These comets may have originated from radii near the gas giants and subsequently ejected to the Oort cloud (>5,000 au).

These comets are believed to originate from the Kuiper belt, which exists beyond the orbits of the giant planets at radii between 30 and 50 AU
potential source of water on the Earth!
Hartogh et al. 2011, Nature

# Isotopic fractionation: water

Comets

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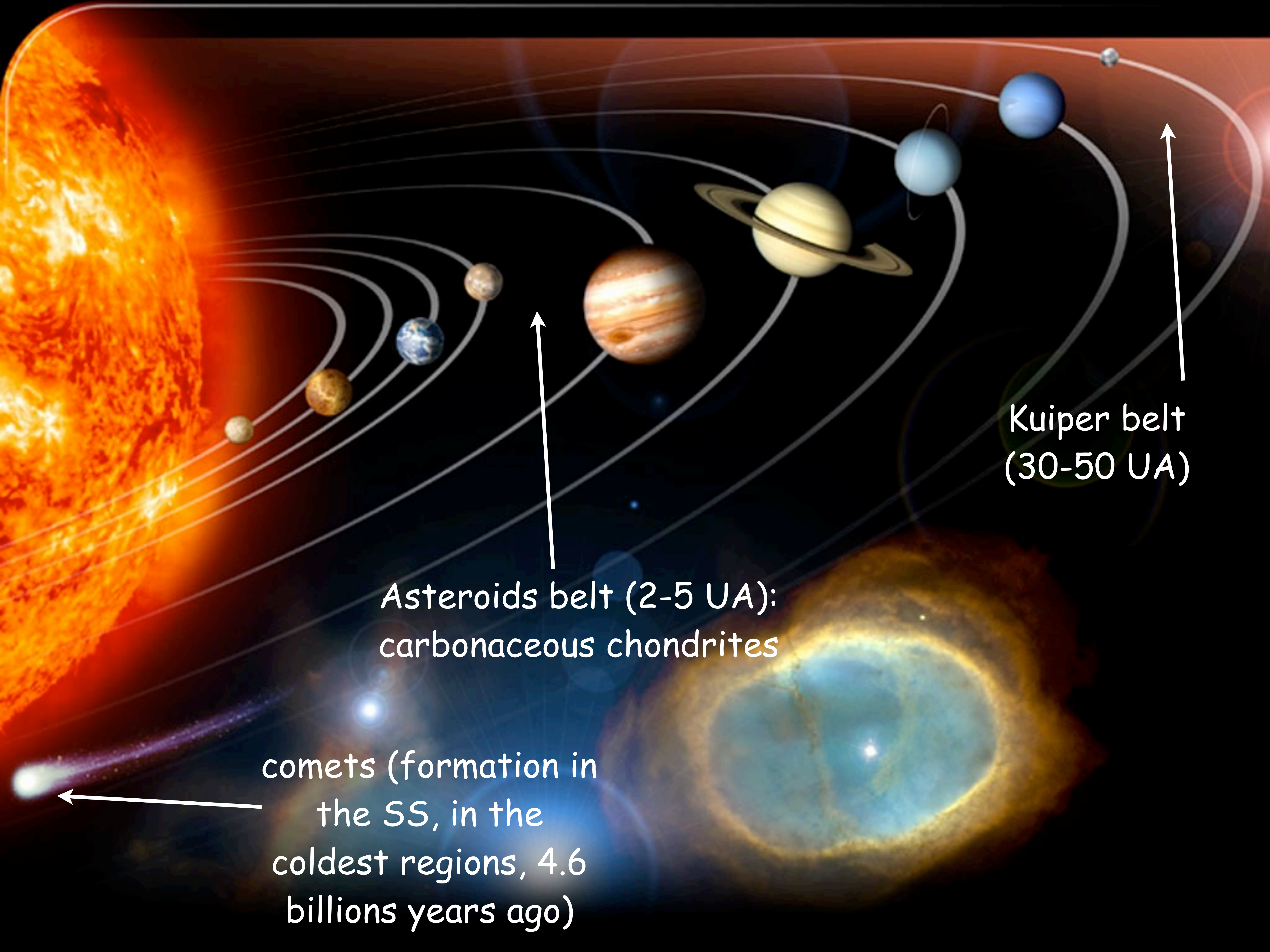
ok


Kuiper belt
(30-50 UA)
Asteroids belt (2-5 UA):
carbonaceous chondrites
comets (formation in
the SS, in the
coldest regions, 4.6
billions years ago)

# WG4: Isotopic Chemistry

## A view from the theoretician

Octavio Roncero

May 28th, 2015