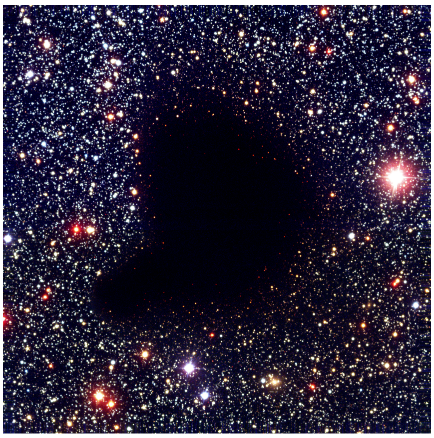
Chemistry: from dark clouds to disks

P. Hily-Blant

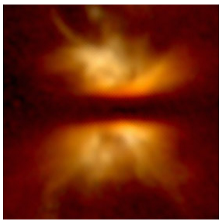
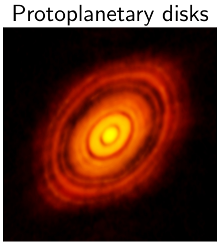
I- The building blocks

From clouds to stars to planets



The interstellar heritage of planetary systems

These lectures

Prestellar cores	Protostars	Protoplanetary disks
		
0.1 pc (2e4 AU, 3e12 km)	5000 AU	100 AU

Why chemistry ?

To know the chemical content of the gas

- What is the Universe made of ?
- Formation/destruction of the species
- Galactic chemical evolution
- Interstellar heritage of planetary systems

To probe the physical conditions

- Kinetic temperature, density, ionization fraction, non-thermal motions
- Trace kinematics through line profiles
- Equation of state: cooling, heating
- To compute physical processes: magnetic fields, multi-fluid

Astrochemistry

Quoting Dalgarno (2008)

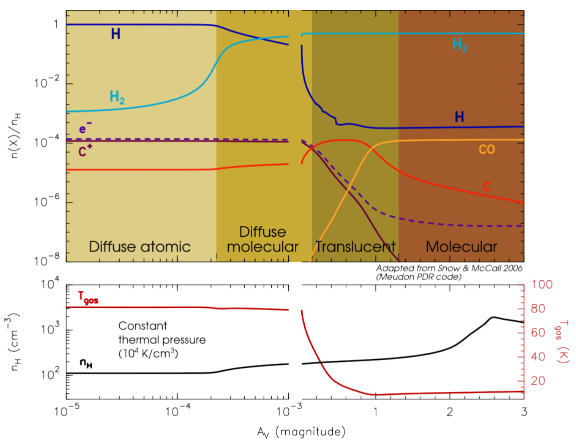
> *"The essential subject matter of astrochemistry is the formation, destruction, and excitation of molecules in astronomical environnements and their influence on the structure, dynamics, and evolution of astronomical objects. The molecules provide powerful diagnostics probes of the ambient physical conditions in which they are found. Progress in astrochemistry rests upon a diversity of observational, experimental, and theoretical skills and a broad knowledge of chemistry and astronomy."*

History of deuterium

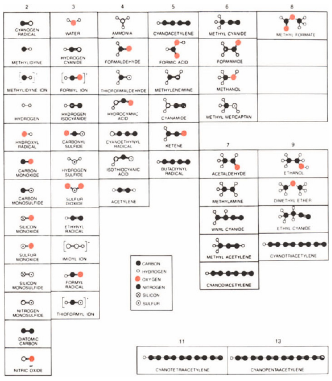
- H, D, He, Li, Be (B, and isotopologues)
- History of deuterium: a clue of the history since the Big Bang
- Initial D/H=2.7 $\times 10^{-5}$
- Today, local ISM: 2.3 $\times 10^{-5}$
- D/H where/when the PSN formed (-4.6 Gyr, $z = 1.4$): 2.5 $\times 10^{-5}$
- But Earth oceans: 1.6 $\times 10^{-4}$
- See C. Burkhardt lecture

Is D/H telling us something about solar system formation ?

Molecular clouds: the atomic-to-molecular transition



Interstellar species



Prasad et al. (1987)

List of interstellar species in 1987

Interstellar species: a broad choice

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	C_{70} *
C_2**	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	C_{60}^+ *
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O 2016			
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	CH_3NCO 2015	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^+ (?)								

~200 species

SiO	CO_2 *	HSCN	$NCCNH^+$ 2015
SiS	NH_2	H_2O_2	
CS	H_3^+ (*)	C_3H^+	
HF	SiCN	HMgNC	
HD	AlNC	HCCO 2015	
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
TiO	Si_2C 2015
ArH^+	
N_2	
NO^+ ?	

CDMS list of ISM species; see also `www.astrochymist.org`

This lecture

Today

- General characteristics of interstellar chemistry
- The elemental abundances (unusual aspects of)
- Overview of gas-phase processes and orders of magnitudes
- The interplay between theory, models, and observations

Tomorrow

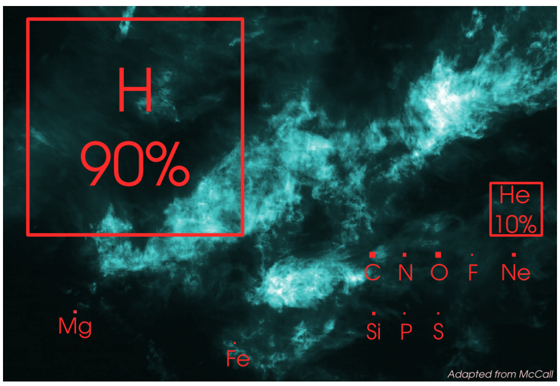
- Chemistry from cores to disks: similarities and differences
- Time-dependent vs steady-state: influence of the initial conditions
- Isotopic ratios as tracers of the history

I- The building blocks

Abundances

- Absolute quantities (cm^{-3})
- Relative quantities (abundances, or concentrations)
- Chemical models compute local densities
- Observations provide line-of-sight quantities (column densities)
- Column density ratios: more robust

The astrochemist table of elements



Interstellar chemistry is dominated by hydrogen

Elemental abundances

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

$$\boxed{[\mathrm{X}] = n(\mathrm{X})/n_\mathrm{H}}$$

- $n_\mathrm{H} = n(\mathrm{H}) + 2n(\mathrm{H_2}) + n(\mathrm{H^+}) + 2n(\mathrm{H_2^+}) + \dots$
- Warning: in dense, fully molecular gas, some authors use abundances wrt $\mathrm{H_2}$ molecules

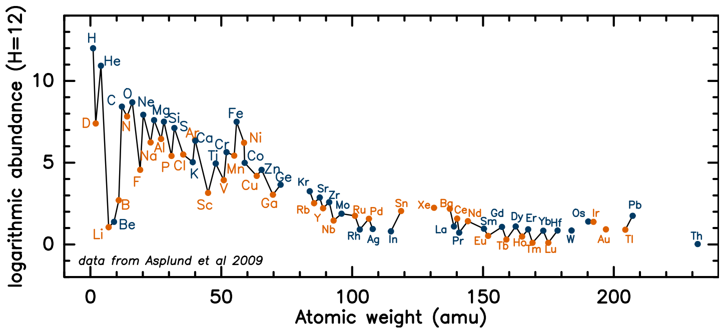
$$n(\mathrm{X})/n(\mathrm{H_2}) = 2n(\mathrm{X})/n_\mathrm{H}$$

- Advice: always use wrt H nuclei; in any case, make it explicit (and say it in your captions)
- In this lecture: wrt n_H

Cosmic abundances

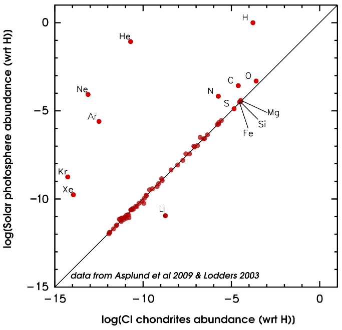
- Elemental abundances are functions of space and time: galactic chemical evolution (GCE) models (Matteucci 2012)
- So-called *cosmic abundances* or *cosmic abundance standard*
- Derived from observations of stellar atmospheres
- Quite model-dependent: although precise, not necessarily accurate !
- General reference: Asplund et al. (2009)
- Related lectures: M. Gounelle, H. Leroux, C. Engrand, L. Nittler

Solar abundances (1): photosphere



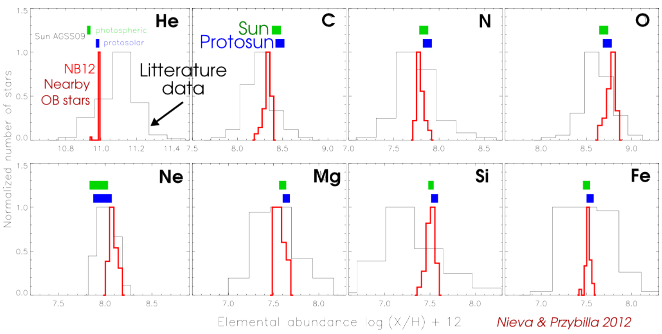
- Sun photosphere + (1D–3D) radiative transfer modeling
- Representative of the abundances -4.6 Gyr at the Sun's birthplace

Solar abundances (2): CI chondrites



- Mass spectroscopy of primitive meteorites; more direct
- Most primitive are CI chondrites
- Do not trace highly volatiles (H, C, N, O, noble gases); often normalized to Si (non volatile)
- General reference: Lodders (2003, 2010)
- Lectures from M. Gounelle, L. Nittler, F. Ciesla, C. Engrand

Cosmic Abundance Standard (CAS)



- local ISM abundances from B-type stars (Nieva & Przybilla 2012)
- radiative transfer modeling

Is the Sun representative of the present-day local ISM ?

Cosmic Abundance Standard (CAS)

	Cosmic Standard		Orion nebula		Young	ISM		Sun[k]		
Elem.	B stars – this work[a]		Gas	Dust[d]	F&G stars[e]	Gas	Dust[j]	GS98	AGSS09	CLSFB10
He	10.99 ± 0.01	…	10.988 ± 0.003^b	…	…	…	…		10.93 ± 0.01	
C	8.33 ± 0.04	214 ± 20	8.37 ± 0.03^c	~0	8.55 ± 0.10	7.96 ± 0.03^f	123 ± 23	8.52 ± 0.06	8.43 ± 0.05	8.50 ± 0.06
N	7.79 ± 0.04	62 ± 6	7.73 ± 0.09^b	…	…	7.79 ± 0.03^g	0 ± 7	7.92 ± 0.06	7.83 ± 0.05	7.86 ± 0.12
O	8.76 ± 0.05	575 ± 66	8.65 ± 0.03^c	128 ± 73	8.65 ± 0.15	8.59 ± 0.01^h	186 ± 67	8.83 ± 0.06	8.69 ± 0.05	8.76 ± 0.07
Ne	8.09 ± 0.05	123 ± 14	8.05 ± 0.03^c	…	…	…	…	8.08 ± 0.06	7.93 ± 0.10	…
Mg	7.56 ± 0.05	36.3 ± 4.2	$6.50{:}^c$	33.1 ± 4.2:	7.63 ± 0.17	6.17 ± 0.02^i	34.8 ± 4.2	7.58 ± 0.05	7.60 ± 0.04	…
Si	7.50 ± 0.05	31.6 ± 3.6	6.50 ± 0.25^c	28.4 ± 4.3	7.60 ± 0.14	6.35 ± 0.05^i	29.4 ± 3.6	7.55 ± 0.05	7.51 ± 0.03	…
Fe	7.52 ± 0.03	33.1 ± 2.3	6.0 ± 0.3^c	32.1 ± 2.5	7.45 ± 0.12	5.41 ± 0.04^i	32.9 ± 2.3	7.50 ± 0.05	7.50 ± 0.04	7.52 ± 0.06

Notes. [a] Including nine stars from Orion (NS11), in units of log(El/H) + 12 / atoms per 10^6 H nuclei – computed from average star abundances (mean values over all individual lines *per element*, equal weight per line), the uncertainty is the standard deviation; [b] Esteban et al. (2004); [c] Simón-Díaz & Stasińska (2011); [d] difference between the cosmic standard and Orion nebula gas-phase abundances, in units of atoms per 10^6 H nuclei; [e] Sofia & Meyer (2001); [f] value determined from strong-line transitions (Sofia et al. 2011), which is compatible with data from the analysis of the [C II] 158 μm emission (Dwek et al. 1997). Weak-line studies of C II] λ2325 Å indicate a higher gas-phase abundance $\varepsilon(C) = 8.11 \pm 0.07$ (Sofia 2004), which corresponds to 84 ± 28 ppm of carbon locked up in dust; [g] Meyer et al. (1997), corrected accordingly to Jensen et al. (2007); [h] Cartledge et al. (2004); [i] Cartledge et al. (2006). The uncertainty in the ISM gas-phase abundances is the standard error of the mean; [j] difference between the cosmic standard and ISM gas-phase abundances, in units of atoms per 10^6 H nuclei; [k] photospheric values of Grevesse & Sauval (1998, GS98), Asplund et al. (2009, AGSS09) and Caffau et al. (2010, CLSFG10).

Metallicity of the Sun unexpectedly high

Present-day local ISM abundances

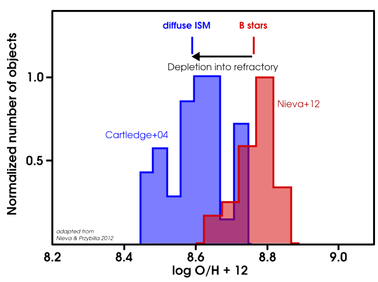
Element	Protosun		Protosun, GCE corrected[a]		CAS	$d\varepsilon(\mathrm{El.})/dR_g$	CAS+$d\varepsilon(\mathrm{El.})/dR_g$	
	AGSS09	CLSFB10	AGSS09	CLSFB10		dex kpc^{-1}	$R_g = 6$ kpc	$R_g = 5$ kpc
C	8.47 ± 0.05	8.54 ± 0.06	8.53 ± 0.05	8.60 ± 0.06	8.33 ± 0.04	-0.103 ± 0.018[b]	8.54 ± 0.05	8.64 ± 0.05
N	7.87 ± 0.05	7.90 ± 0.12	7.95 ± 0.05	8.01 ± 0.12	7.79 ± 0.04	-0.085 ± 0.020[c]	7.96 ± 0.05	8.05 ± 0.05
O	8.73 ± 0.05	8.80 ± 0.07	8.77 ± 0.05	8.84 ± 0.07	8.76 ± 0.05	-0.035[d,e]	8.83 ± 0.05	8.87 ± 0.05
Mg	7.64 ± 0.04	...	7.68 ± 0.04	...	7.56 ± 0.05	-0.039[d]	7.64 ± 0.05	7.68 ± 0.05
Si	7.55 ± 0.04	...	7.63 ± 0.04	...	7.50 ± 0.05	-0.045[d]	7.59 ± 0.05	7.64 ± 0.05
Fe	7.54 ± 0.04	7.56 ± 0.06	7.68 ± 0.04	7.70 ± 0.06	7.52 ± 0.03	-0.052[d]	7.62 ± 0.03	7.68 ± 0.03

- Solar photosphere not necessarily representative of the local ISM
- Birthplace of the Sun is unknown
- Outward migration more likely (Nieva & Przybilla 2012; Minchev et al. 2013; Hily-Blant et al. 2017) but see Martínez-Barbosa et al. (2015)

Chemical homogeneity

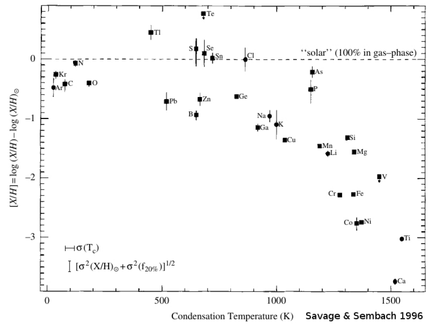
- Local ISM (within 1.5 kpc) is chemically homogeneous at a 10% level
- Allows meaningful comparisons between star and planet forming regions in the local ISM
- Choice of a set of elemental abundances: sun, B-stars
- Recommended litterature: Sofia & Meyer (2001); Asplund et al. (2009); Nieva & Przybilla (2012)

Refractories and volatiles



- In astrochemistry: refractory ≡ dust (condensation temp.)
- Depletion of elements into refractory in the diffuse ISM
- Dust abundances: indirect estimates (extinction models)

Depletion of elements



Refractories and volatiles

Elem. X	Adopted $(X/\mathrm{H})_{\mathrm{ref}}$	A_X	B_X	z_X
C	8.46 ± 0.04	-0.101 ± 0.229	-0.193 ± 0.060	0.803
N	7.90 ± 0.11	-0.000 ± 0.079	-0.109 ± 0.111	0.550
O	8.76 ± 0.05	-0.225 ± 0.053	-0.145 ± 0.051	0.598
Mg	7.62 ± 0.02	-0.997 ± 0.039	-0.800 ± 0.022	0.531
Si	7.61 ± 0.02	-1.136 ± 0.062	-0.570 ± 0.029	0.305
P	5.54 ± 0.04	-0.945 ± 0.051	-0.166 ± 0.042	0.488
Cl	5.33 ± 0.06	-1.242 ± 0.129	-0.314 ± 0.065	0.609
Ti	5.00 ± 0.03	-2.048 ± 0.062	-1.957 ± 0.033	0.430
Cr	5.72 ± 0.05	-1.447 ± 0.064	-1.508 ± 0.055	0.470
Mn	5.58 ± 0.03	-0.857 ± 0.041	-1.354 ± 0.032	0.520
Fe	7.54 ± 0.03	-1.285 ± 0.044	-1.513 ± 0.033	0.437
Ni	6.29 ± 0.03	-1.490 ± 0.062	-1.829 ± 0.035	0.599
Cu	4.34 ± 0.06	-0.710 ± 0.088	-1.102 ± 0.063	0.711
Zn	4.70 ± 0.04	-0.610 ± 0.066	-0.279 ± 0.045	0.555
Ge	3.70 ± 0.05	-0.615 ± 0.083	-0.725 ± 0.054	0.690
Kr	3.36 ± 0.08	-0.166 ± 0.103	-0.332 ± 0.083	0.684

- Jenkins (2009, 2014): $A_X \sim$ consumption rate, $B_X \sim$ propensity towards depletion ($z_X \sim$ scaling factor)
- Not all elements have the same propensity towards depletion

ISM: Volatiles = cosmic - refractory = gas + ice

Initial conditions

- Elements are partitioned among species by chemical processes
- Sum of all abundances of that element is its elemental abundance
- The different species may be called *reservoirs*
- For some species, one reservoir dominates
- E.g. in moderately dense clouds ($n_{\mathrm{H}} \approx 10^3\,\mathrm{cm}^{-3}$), the main reservoir of the carbon element is CO, and $n(\mathrm{CO}) \lesssim n_{\mathrm{tot}}(\mathrm{C})$

Initial conditions = elemental abundances + initial partitioning

Recommended values

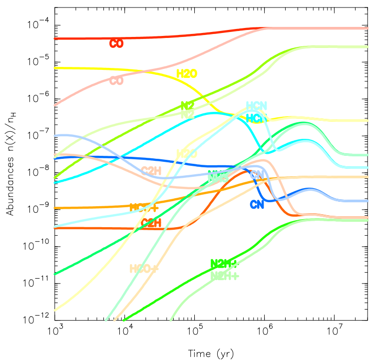
Table 1. Fractional elemental abundances, n_X/n_H, and their adopted distribution across the phases of the medium; this compilation is based upon the studies of Anders & Grevesse (1989), Savage & Sembach (1996), Gibb et al. (2000) and Sofia & Meyer (2001). The fractional abundance of the PAH is $n_{PAH}/n_H = 1.0 \times 10^{-6}$. Numbers in parentheses are powers of 10.

Element	Fractional abundance	Gas phase	PAH	Grain mantles	Grain cores
H	1.00	1.00			
He	1.00 (−1)	1.00 (−1)			
C	3.55 (−4)	8.27 (−5)	5.40 (−5)	5.53 (−5)	1.63 (−4)
N	7.94 (−5)	6.39 (−5)		1.55 (−5)	
O	4.42 (−4)	1.24 (−4)		1.78 (−4)	1.40 (−4)
Mg	3.70 (−5)				3.70 (−5)
Si	3.37 (−5)				3.37 (−5)
S	1.86 (−5)	1.47 (−5)		3.93 (−6)	
Fe	3.23 (−5)	1.50 (−8)			3.23 (−5)

Flower & Pineau des Forêts (2003)

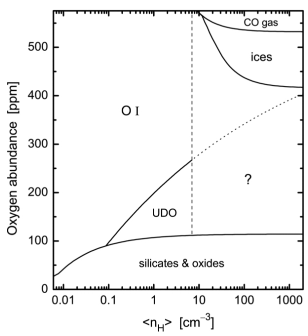
- Not a unique choice
- consider varying the C/O, N/N_2 etc (Le Gal et al. 2014)
- Advice: always quote the adopted values in the article

Influence of the initial partitioning: example



- One set of elemental abundances
- Two sets of initial partitioning (e.g. corresponding to slightly different A_V)
- *molecular* case:
  - H_2=1
  - C^+=1
  - O=1
- *mixed* case:
  - H_2=67%
  - C/C^+=1
  - O/H_2O=1
- Note: identical steady-state

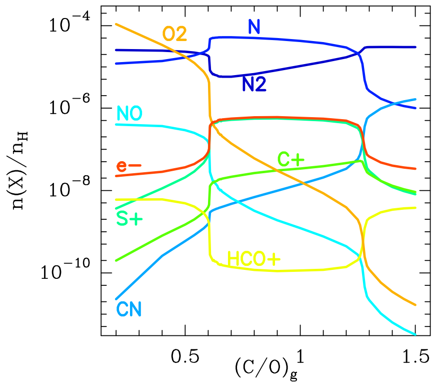
Missing reservoirs



Whittet (2010)

- Oxygen: on third can not be accounted for by known reservoirs
- Carbon: dust (200–300 ppm) + volatile (100–200 ppm), total (200–300 ppm)

Influence of the elemental abundances: the C/O ratio



Variation of the gas-phase elemental abundance of C and O

I- The building blocks

Interstellar chemistry is ruled by kinetics

- Takes place in the CNM: from diffuse ($n_\mathrm{H} \sim 100\,\mathrm{cm}^{-3}$) to dense ($n_\mathrm{H} > 10^4\,\mathrm{cm}^{-3}$) clouds
- Low density: no time to reach equilibrium
- IS chemistry is driven by kinetics

Kinetics vs equilibrium

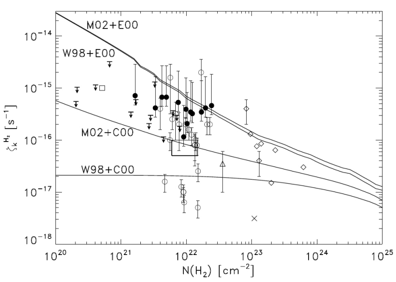
$$\mathrm{AB} + \mathrm{C} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A} + \mathrm{BC}$$

- Thermodynamics:
$$K(T) = \frac{[A]\cdot[BC]}{[AB]\cdot[C]}$$
- Kinetics:
$$\frac{dn(\mathrm{A})}{dt} = -\frac{dn(\mathrm{AB})}{dt} = k(T)n(\mathrm{AB})n(\mathrm{C})$$
- Detailed balance ($t \to \infty$):
$$K = \frac{k_f}{k_r} \propto \exp(-\Delta G/kT)$$

Consequences

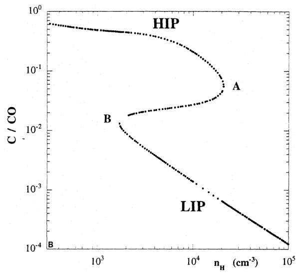
- Low temperature: exothermic reactions dominate (ion-neutral)
- Backward reactions not included: $t \to \infty$ does not converge towards equilibrium (molecular clouds lifetime is limited)
- steady-state $\neq$ equilibrium
- Example: HCN/HNC ≈ 1 in cold clouds; HCN is 65.5 kJ/mol below HNC, equilibrated abundance ratio would be HCN/HNC$= 10^{170}$
- Example: carbon is mostly in CO; but $[\mathrm{CH_4}][\mathrm{H_2O}]/[\mathrm{CO}][\mathrm{H_2}]^3 > 10^{500}$ at equilibrium through $\mathrm{CO} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{CH_4} + \mathrm{H_2O}$;
- time-dependent/steady-state, various timescales (from yr to few Myr)
- $\tau \sim 1/(k(T)n_\mathrm{H}[\mathrm{X}]) \sim [10^{-11}\,10^4\,10^{-5}]^{-1} \sim 0.1$ Myr

Ionization



- Driven by cosmic ray ionization $\zeta \approx 10^{-17} - 10^{-16}\,\mathrm{s}^{-1}$
$$x_e = n_e/n_\mathrm{H} \propto (\zeta/n_\mathrm{H})^{0.5}$$
- in the deep interior: secondary photons (fluorescence of collisionally excited $\mathrm{H_2}$)

Steady-state: complications



Le Bourlot et al. (1995)

- In most cases, steady-state does not depend on history
- In some instances, steady-state does depend on history: bistable character

Gas and dust

- Two components: volatiles (gas+ice) and refractory (dust)
- Dust (1% in mass) but pivotal role: thermal balance, chemistry, dynamics
- Charge state (or ionization fraction): controls dissipative effects (Ohm, Hall, etc), coupling with magnetic fields
- Charge: both gas and dust
- Ionization: cosmic rays + secondary photons, direct UV

Control parameters

- Temperature (kinetic rate coefficients, evaporation)
- Density (frequency of collisions, ionization, freeze-out)
- Elemental abundances (C/O ratio, sulfur, etc)
- Ionization: UV, cosmic-rays
- External UV flux (ISRF) (diffuse ISM, upper layers in disks)
- Cosmic-ray ionization rate ζ (essentially through $\zeta/n_{\rm H}$)

Chemistry in dilute interstellar gas

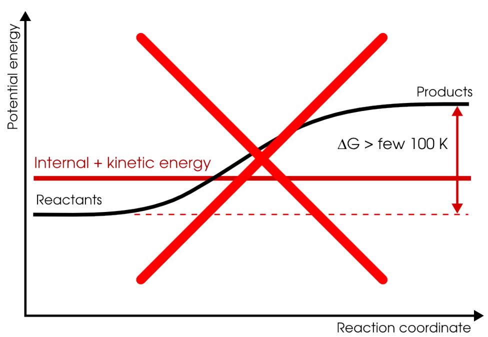
- Dominated by bi-molecular collisions and uni-molecular
- No three-body collisions
- During the collision, formation of an activated complex
  $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB}^*$, lifetime $\sim 10^{-12}$ s
- Stabilize complex: remove energy; otherwise $\mathrm{AB}^* \longrightarrow \mathrm{A} + \mathrm{B}$ will occur
- Third-body collision most unlikely
- Only reactions involving molecules: $\mathrm{AB} + \mathrm{C} \longrightarrow \mathrm{A} + \mathrm{BC}$
- Emission of a photon: $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB} + h\nu$

Bi-molecular collisions

$$\mathrm{AB} + \mathrm{C} \xrightarrow{k} \mathrm{A} + \mathrm{BC}, \quad k(T)\ \mathrm{cm^3\,s^{-1}}$$

- low density: only bi-molecular collisions
- reaction involves inelastic collisions with destruction/creation of bonds
- the overall energy balance involves primarily the formation enthalpy:
  $\Delta G = \Delta H - T\Delta S \approx \Delta H$ at low T
- exoergic reaction: ΔG larger than a few 100 K
- endoergic reaction: ΔG smaller than a few -100 K
- thermoneutral reaction: $|\Delta G|$ within a few 100 K
- kinetic rate are measured and/or computed theoretically

Exoergic reactions only



- Endoergic reactions
- ΔG too large: are not considered

Energetic properties of principal species

species	PA[b] (eV)	IE[c]	DE[d]	k_L
He	1.84	24.581		x1e-9 cm3 s-1
H	2.65	13.595		
N	3.39	14.545		
O_2	4.38	12.071	5.116	
H_2	4.39	15.426	4.478	
O	5.04	13.615		0.80 ± 0.40
N_2	5.13	15.581	9.759	1.90 ± 0.40
NO	5.51	9.264	6.497	1.25 ± 0.40
CO_2	5.68	13.769	5.453	2.00 ± 0.60
CH_4	5.72	12.99	4.406	2.40 ± 0.30
CO	6.15	14.014	11.09	2.00 ± 0.20
OH	6.2	12.90	4.392	
C	6.42	11.265		
HCCH	6.65	11.41	4.9	3.40 ± 0.80
S	6.86	10.357		
C_2	6.9	12.15	6.21	
H_2O	7.22	12.62	5.114	5.40 ± 0.60
HCN	7.43	13.91	5.65	7.80 ± 0.80
CH	7.7	10.64	3.465	
NH_3	8.85	10.15	4.38	4.50 ± 0.50

[a]The last column gives experimental rate constants k_L for the Langevin reaction $H_3^+ + X \rightarrow H_2 + HX^+$. Values of k_L are approximate averages

Oka (2013)

- PA: proton affinity
- IE: ionization energy
- DE=dissociation energy
- $X + H_3^+ \longrightarrow XH^+ + H_2 + \Delta E$, ΔE = PA(X)-PA(H_2)
- H_3^+ is a proton donnor

General references

- Not possible to acknowledge the wide field of astrochemistry
- Partial choice of most valuable readings:
  - Very general: Watson (1976), Klemperer (2006), Bergin (2009), Oka (2013)
  - Cold cloud chemistry foundation: Herbst & Klemperer (1973), Prasad et al. (1987)
  - Complex organic molecules: Herbst & van Dishoeck (2009)
  - A. Dalgarno†, J. Black, E. van Dishoeck

I- The building blocks

Overview of astrochemical modelling

Chemical network

- set of reactive collisions + ionization, etc
- historical databases: Herbst& Klemperer 1977, Prasad & Huntress 1980, Millar et al 1991
- derived general databases: KIDA (inherited from OSU), UMIST

Numerical solver

- time-dependent: stiff 1st order ODE (`DVODE`)
- steady-state: zero-finding algorithms (e.g. Newton-Raphson)

Boundary conditions

- Elemental abundances and initial partitioning

Types of reactions and orders of magnitude

Type	Example	$k(T)$
CR ionization	$He + CRP \longrightarrow He^+ + e^-$	10^{-16}–$10^{-17}\,s^{-1}$
ion-neutral	$CO + H_3^+ \longrightarrow HCO^+ + H_2$	$10^{-9}\,cm^3\,s^{-1}$
neutral-neutral	$N + CH \longrightarrow CN + H$	$10^{-11}\,cm^3\,s^{-1}$
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Photodissociation	$H_2O + h\nu \longrightarrow OH + H$	$10^{-9}\exp(-\gamma A_V)\,cm^3\,s^{-1}$

Langevin rates

- proton-hop reaction: $H_2 + H_2^+ \longrightarrow H_3^+ + H + 1.74eV$
- ion-dipole: key factor = polarizability α (cm^3)
- approaching H_2^+ polarizes H_2 inducing a dipole moment
- charge-induced dipole potential, or Langevin potential: $V_L = -\alpha e^2/2r^4$
- cross-section: $\sigma_L = \pi r_L^2 = 2\pi\frac{e}{v}(\alpha/\mu)^{1/2}$, μ: reduced mass
- impact parameter $b < r_L$ leads to reaction
- Langevin rate (cgs units): $k_L = \int v\sigma_L(v)f(v)dv$:

$$k_L = 2\pi e(\alpha/\mu)^{1/2}, \qquad \alpha \approx 1\text{Å}^3$$

- $k_L \approx 10^{-9}\ cm^3\,s^{-1}$, for all systems
- k_L: ind. of T, hence dominate at low-T

Langevin rates

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Oka (2013)

Langevin rates and H_3^+ drive interstellar chemistry

Langevin rates

Table 3 The number of reactions of different types that are included in the OSU kinetic database (version osu-09–2008) for astrochemistry (Wakelam et al. 2010)

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Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
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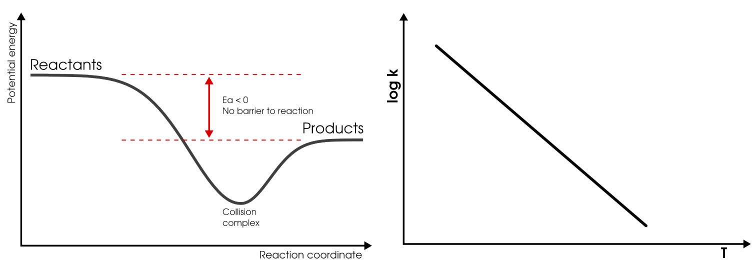
Internal photo-processes[a]	$CO + h\nu \rightarrow C + O$	192

[a] External photo-processes are those induced by the interstellar radiation field; internal photo-processes are induced by radiation generated in dark clouds by the interaction of molecules, especially H_2, with cosmic rays. Further details and examples are given in Section 4.5.

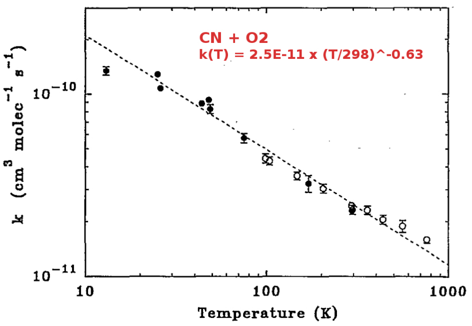
Smith (2011)

Barrierless reactions



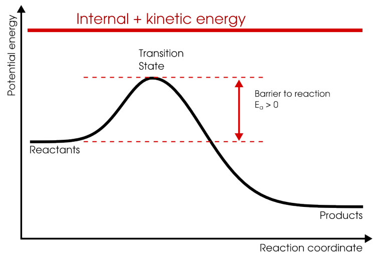
- radical-radical reaction (e.g. $CN + O_2$)
- $k(T) = \alpha(T/300)^\beta$, $\approx 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ at 10 K

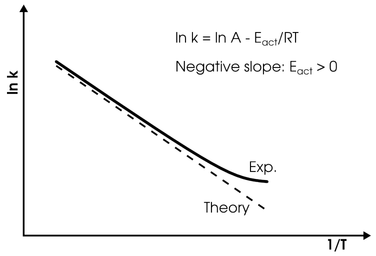
Example: CN + O_2



Sims I. R. et al, J Chem Phys 1994

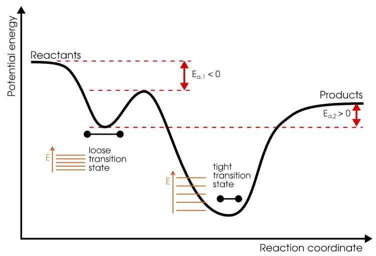
Arrhenius-type reactions

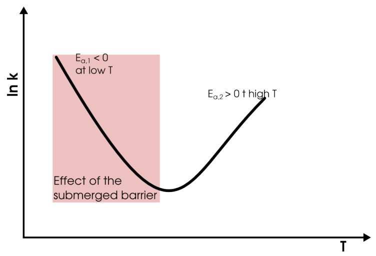




- neutral-neutral reaction
- $k(T) = A\exp(-E_a/T)$, $\approx 10^{-11}\ \mathrm{cm^3\,s^{-1}}$ at 10 K
- A $(\mathrm{cm^3\,s^{-1}})$: pre-exponential factor; rate of collisions
- E_a (K): activation energy
- $\exp(-E_a/T)$: fraction of colliders with kinetic energy larger than E_a (M-B distrib.)

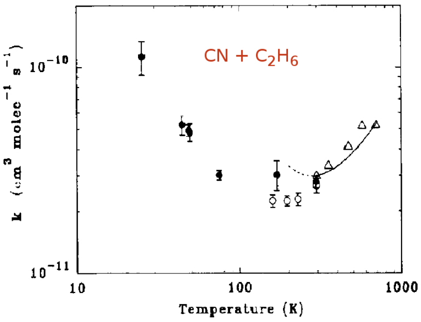
Special case: submerged barrier





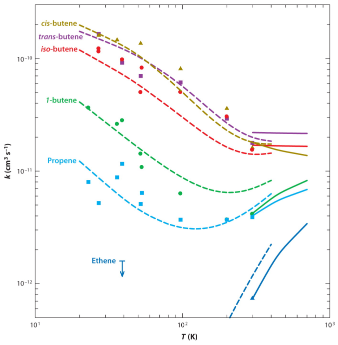
- rate increases at low-T up to $10^{-10}\,\mathrm{cm^3\,s^{-1}}$
- observed in many neutral-neutral reactions involving radicals and unsaturated species
- must be fast at 300 K
- was evidenced using CRESU method (France/Rennes)

Example: CN + C_2H_6



Sims I. R. et al, Chem Phys Let 1993

Fast n-n at low-T



Smith (2011)

Reactions with atomic oxygen

Types of reactions and orders of magnitude

Type	Example	$k(T)$
CR ionization	$He + CRP \longrightarrow He^+ + e^-$	10^{-16}–$10^{-17}\,s^{-1}$
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Photodissociation	$H_2O + h\nu \longrightarrow OH + H$	$10^{-9}\exp(-\gamma A_V)\,cm^3\,s^{-1}$

- Kinetic rate coefficients are usually written as:

$$k(T) = \alpha\,(T/300)^\beta\,\exp(-\gamma/T)\;cm^3\,s^{-1}$$

- Modified Arrhenius form
- $\gamma \sim \Delta G$, or $\gamma \sim E_a$

Gas-phase chemistry: typical sequence

1. Chemistry starts with ions
   - $H_2 + CRP \longrightarrow H_2^+ + e^-$ (85% of the time)
   - $He + CRP \longrightarrow He^+ + e^-$
   - He^+ will ionize/dissociate almost anything
2. Ions then collide primarily with H and H_2
   - $H_2 + H_2^+ \longrightarrow H_3^+$: small proton affinity, universal proton donnor
   - $X + H_3^+ \longrightarrow XH^+ + H_2$
3. *Hydrogen abstractions*: $XH^+ + H_2 \longrightarrow XH_2^+ + H$, etc
   - until saturation: NH_4^+, CH_5^+, H_3O^+
4. *Dissociative recombinations*: $XH_n^+ + e^- \longrightarrow XH_{n-1} + H$
   - Example: H_2O, NH_3, HCO^+, CHn
   - Difficulty: branching ratios of output channels

Kinetic rate coefficients

$$k(T)\ ?$$

Theoretical calculations of kinetic coefficients

Non-reactive collisions

- Born-Oppenheimer approximation
- Potential energy surface (PES) down to $\sim$10 K precision
- PES-fitting
- Dynamics on the PES
- Averaging over Maxwell-Boltzmann velocity distribution

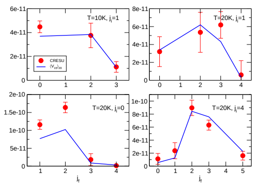
Reactive collisions

- B-O approximation
- Compute energetics for different approaching 3D geometry
- Search for extrema (minimum, saddle points)
- Compute dynamics along this path

Measurements of kinetic coefficients

- Laboratory experiments: down to 50 K (e.g. Bordeaux) + numerical extrapolations downwards; 5 K (Rennes)
- Different techniques: usually, measure the disappearance of reactants (w/o disentangling among products)
- General reference: Smith (2011)

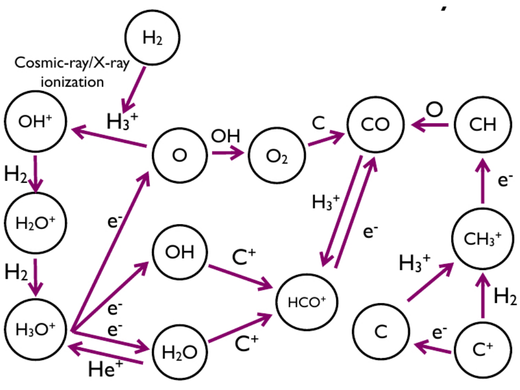
Experiments vs theory: non-reactive systems



- Absolute agreement between theory and experiments; Sims, Faure et al (Rennes/Grenoble collab.)
- Quantum resonances in CO-H_2 inelastic collisions; Costes & Naulin 2016

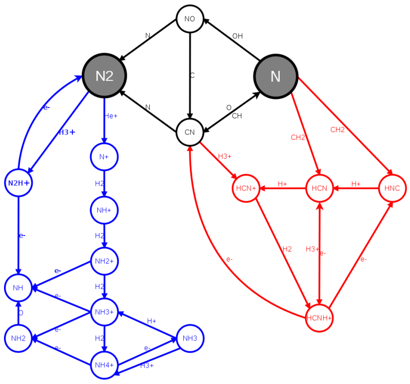
- Validation of theory and experiments is obtained jointly
- Non-reactive systems first
- reactive systems so far limited to 3 atoms (e.g. F + H_2 $\longrightarrow$ HF + H)

Gas-phase chemical networks



From E. Bergin

Gas-phase chemical networks



Hily-Blant et al. (2013); Le Gal et al. (2014)

Networks

Table 3 The number of reactions of different types that are included in the OSU kinetic database (version osu-09–2008) for astrochemistry (Wakelam et al. 2010)

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Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46	
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1	
Neutral-neutral reactions	$C + C_2H_2 \rightarrow C_3\,H + H$	382	$\sim 10^{-11}$ up to 10^{-10}
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + h\nu$	16	
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539	$\sim 10^{-7}\,T^{\alpha}$, α=0.5-1
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + h\nu$	16	
Anion-cation recombination	$HCO^+ + H^- \rightarrow H_2 + CO$	36	
Electron attachment	$C_6H + e \rightarrow C_6H^- + h\nu$	4	
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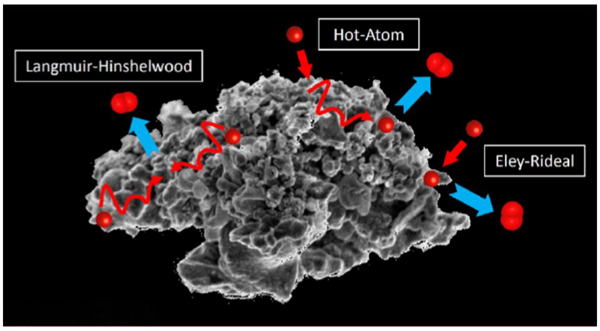
[a] External photo-processes are those induced by the interstellar radiation field; internal photo-processes are induced by radiation generated in dark clouds by the interaction of molecules, especially H_2, with cosmic rays. Further details and examples are given in Section 4.5.

I- The building blocks

The limits of gas-phase processes

- Formation of $\mathrm{H_2}$ in the present-day universe: too slow (2-body radiative association, three-body)
- formation of water in prestellar cores and protostars (van Dishoeck 2014)
- methanol
- aceto-nitrile NH_2CH_2CN (Belloche et al. 2008), precursor of glycine amino-acid ?

Surface chemistry: the formation of $\mathrm{H_2}$



Linnartz et al. (2015)

Usual description: H atoms adsorb on the surface, migrate (tunnelling, thermal hopping), encounter and form a $\mathrm{H_2}$ molecule, liberating 4.5 eV, evenly distributed among phonon, kinetic, and internal energy.

Surface chemistry: the formation of $\mathrm{H_2}$

- Formation of $\mathrm{H_2}$ on grains: pseudo one-order kinetics

$$\frac{dn(\mathrm{H_2})}{dt} = Rn(\mathrm{H})n_\mathrm{H}$$

- In the above: $n_\mathrm{H} \propto n_g$; $R \approx 2-3\times10^{-17}\,\mathrm{cm^3\,s^{-1}}$ (Jura 1975)
- Fully molecular gas requires $\mathrm{H_2}$ self-shielding
- S: sticking probability; ϵ: probability of reaction upon encounter; a: average dust size;
- $R = 1/2\epsilon S\Sigma_g v_\mathrm{th} n(\mathrm{H})$

Surface of dust

- First parameter from astrochemical point of view: total grain surface per unit volume
- formation of H_2, chemistry, UV extinction, thermal balance
- For MRN-like size distribution ($n(a) \propto a^{-3.5}$), surface in small grains (mass in large grains): coagulation decreases surface available for chemistry (and extinction, and photoelectric effect with secondary photons, hence charge, etc !)
- Grain growth in disks (see Dartois and Dutrey lectures)

Interrupted here: continuation in Lecture 2

I- The building blocks

Summary for today

- Chemistry is not an option
- Chemistry is a serious field of research in astrophysics
- Time-dependent calculations depend on the initial conditions
- Set of elemental abundances is a fundamental problem
- Understand gas-phase processes in the pre-stellar phase to determine the initial conditions of protoplanetary disks
- My opinion: grain-surface chemistry is an experimentally- and observationally-driven field

End of Part 1

Tomorrow: 8:30 am

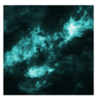
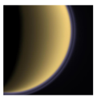
To which extent is the product of the pre-stellar chemistry preserved in primitive planetary systems ?

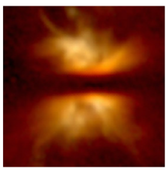
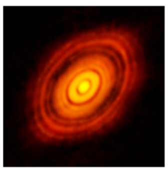
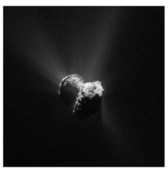
Chemistry: from dark clouds to disks

P. Hily-Blant

II- From cores to disks

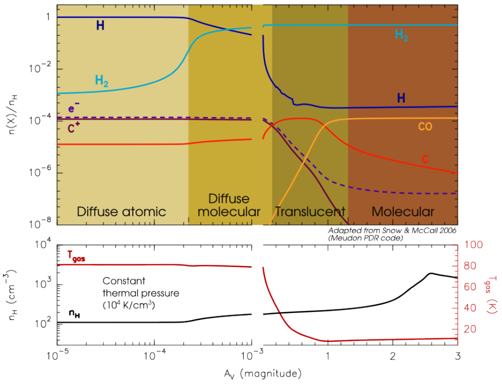
The interstellar heritage of planetary systems

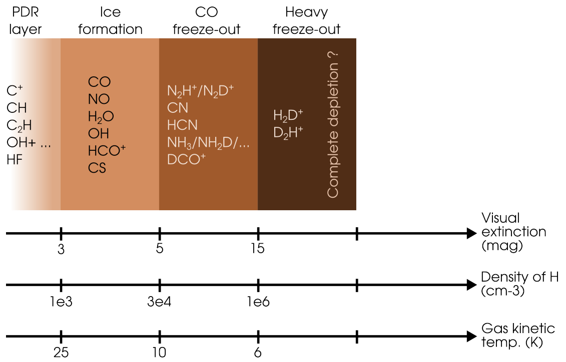




Interstellar phase   Primitive solar system

Molecular clouds: atomic-to-molecular



Prestellar phase: growing molecular diversity

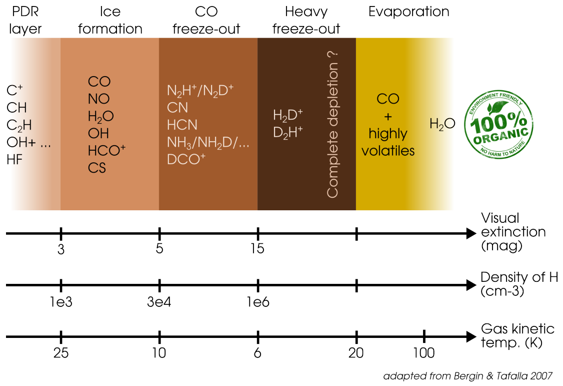


adapted from Bergin & Tafalla 2007

Prestellar phase: growing molecular diversity

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

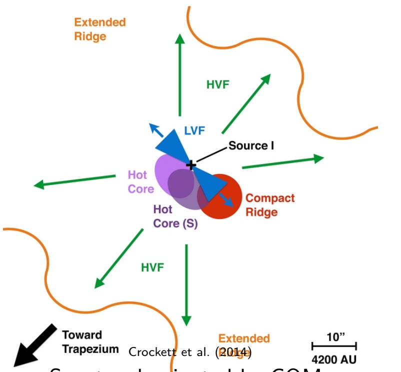
Protostellar phase: volatile outburst



Organics delivered to early solar system ?

see lecture by D. Bockelée-Morvan

Spectral surveys: Orion KL with Herschel

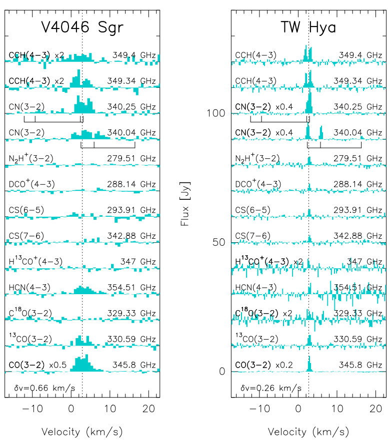


Crockett et al. (2014)

Spectra dominated by COMs

Orion KL: massive star-forming region

Spectral surveys: TW Hya disk



Kastner et al. (2014) Punzi et al. (2015)

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

The overall picture

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

Goals and strategy

What are the questions ?

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

What are the goals ?

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

Strategy

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

Yes we can

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

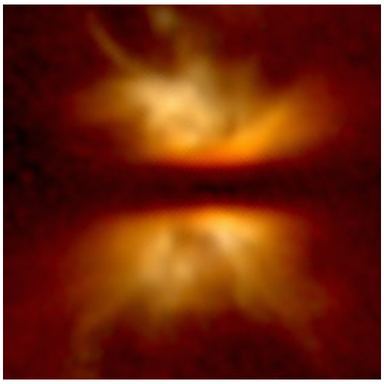
But still: we can tell something !

Chemistry: from cores to disks

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

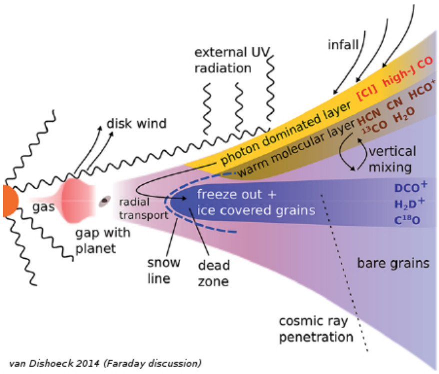
II- From cores to disks

Upper layers of disks



Disks are flared

Upper layers of disks

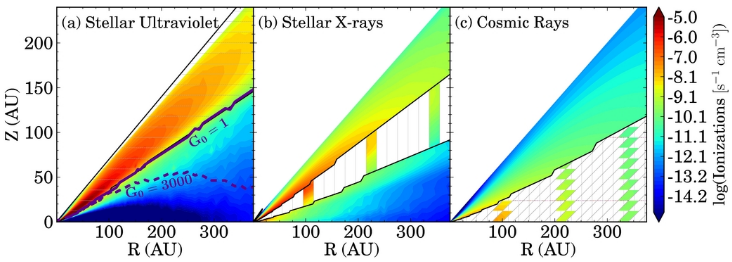


Disks are flared: direct + scattered light

Photodissociation and photoionization

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

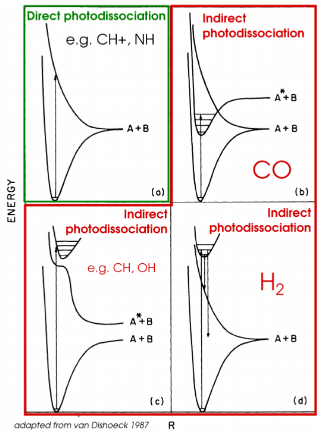
Irradiation of disks



Cleeves et al. (2013)

Cosmic-rays dominate in the midplane regions

UV photodissociation processes



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

Selective photodissociation

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

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

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

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

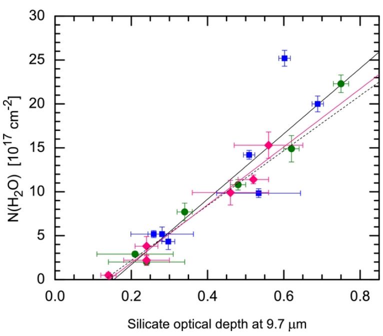
(keep this in mind)

II- From cores to disks

Surface chemistry

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

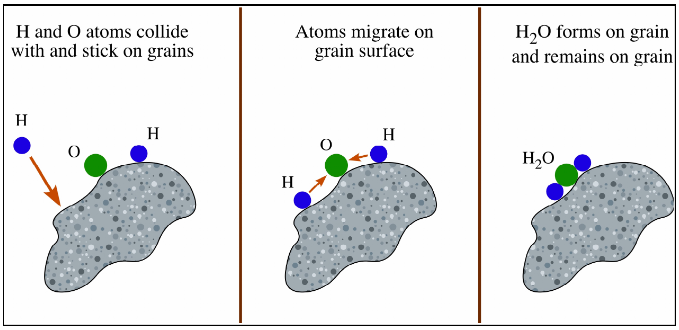
Ice formation



Whittet et al. (2013)

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

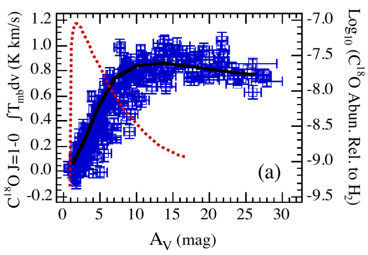
Ice formation



Slide from Bergin

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

Molecular freeze-out



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

Chemistry on interstellar grain surface

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

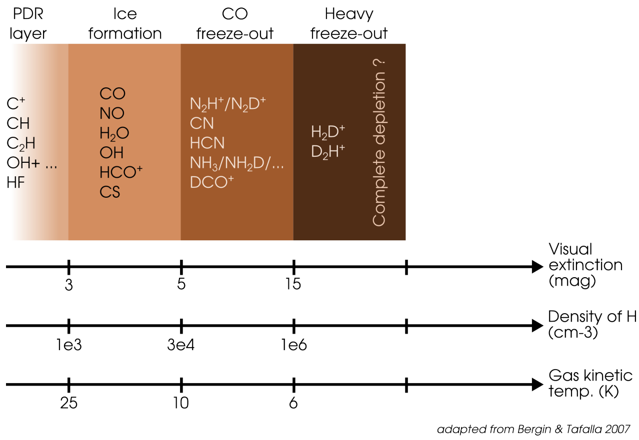
- $k_{\rm hop} = \nu_0 \exp(-\eta E_b / kT_d)$
- ν_0: vibrational freq. of adsorbed species on grain; varies with mass
- $\eta \approx 0.3 - 0.7$
- E_b: binding energy (or energy barrier to overcome for hopping to proceed)
- quantum tunneling: decreases with mass of the particle
- Warning: several caveats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

Molecular freeze-out

Depletion is a competition between accretion and evaporation

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

Depletion in prestellar cores



Ice chemistry: a minimalist astrochemical view

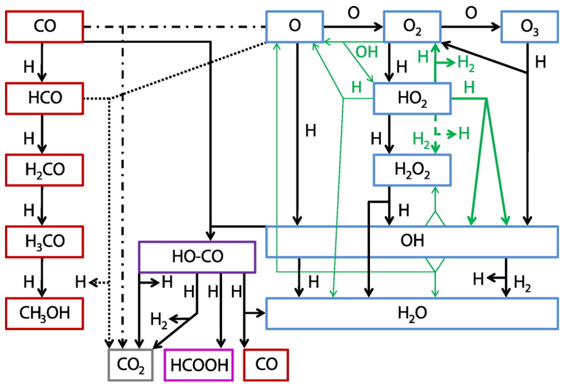
Primary reactions: hydrogenation of ice

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

Other

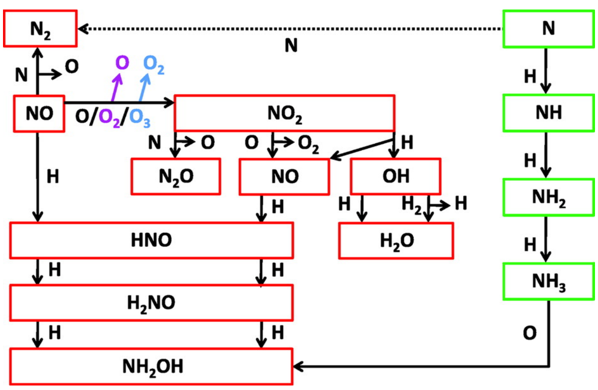
- external source of energy: UV-induced reactions, cosmic rays (see E. Dartois)
- isotopic exchanges

Networks



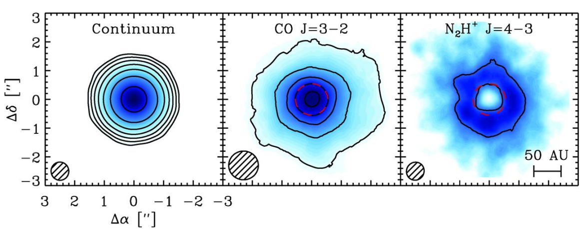
Linnartz et al. (2015)

Networks



Linnartz et al. (2015)

Snow lines



Qi et al. (2013)

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

Chemistry in disks

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

II- From cores to disks

Overview

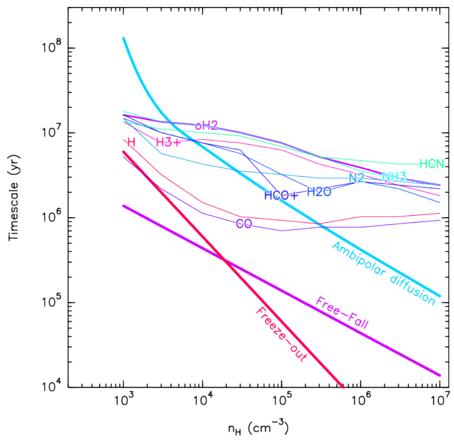
The engine

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

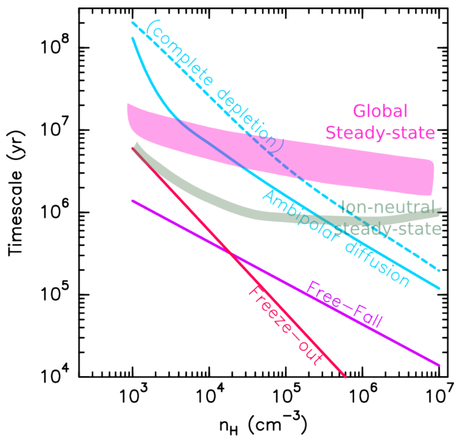
A model

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

Timescales



Timescales



Models vs observations

Models in practice

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

Comparison with observations

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

II- From cores to disks

Isotopic ratios

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

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

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

Chemical mass fractionation

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

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

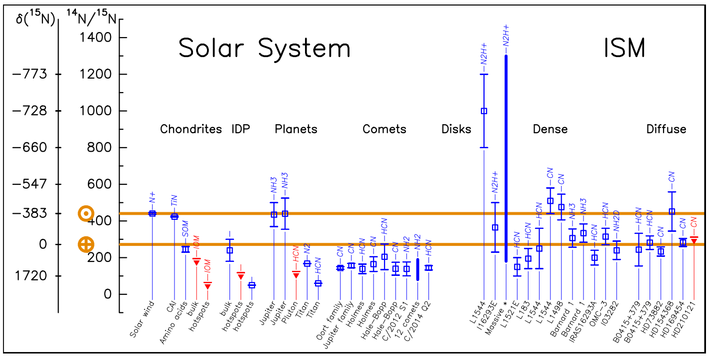
- this fractionation is transfered by chemistry to water (with H_2D+ replacing H_3^+ in the gas-phase)

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

The Cleeves et al. (2014) scenario:

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

The origin of nitrogen in the solar system

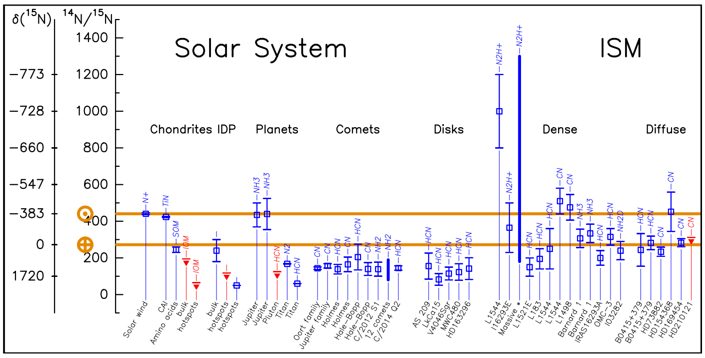


Cometary ratio: 140; elemental (Sun, Jupiter): 441, Earth 272

Origin of the cometary ratio

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

The origin of nitrogen in the solar system

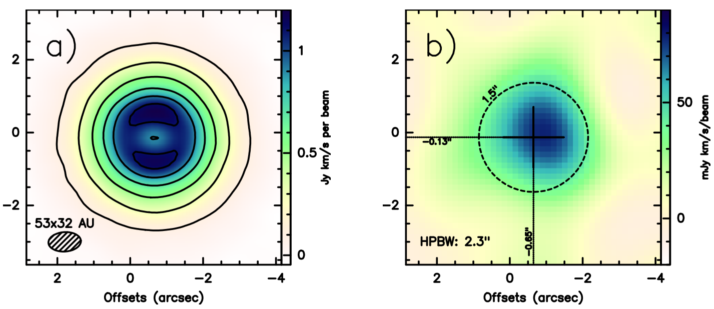


(indirect measurement) HCN in disks ≈ 130; Guzman et al 2017

Origin of the cometary ratio

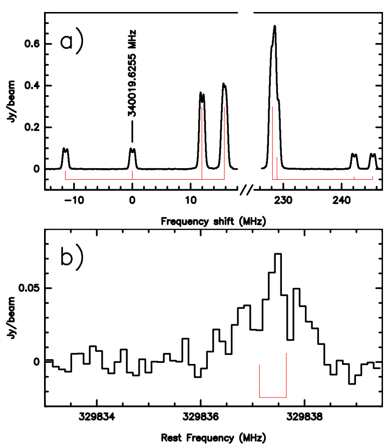
- matching isotopic ratio in disks and comets
- these authors argue towards local processes in the disks: selective photodissociation; no inheritance from prestellar phase
- caveat: indirect measurement (usual method however)
- $H^{13}CN/HC^{15}N$ x $(N/^{15}N) \rightarrow HCN/HC^{15}N$

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

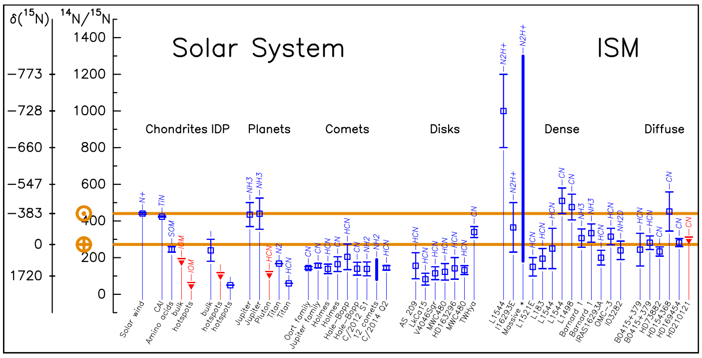


Directly measure $CN/C^{15}N$ isotopic ratio

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



The origin of nitrogen in the solar system



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

So what ?

The nitrogen isotopic ratio in a galactic context

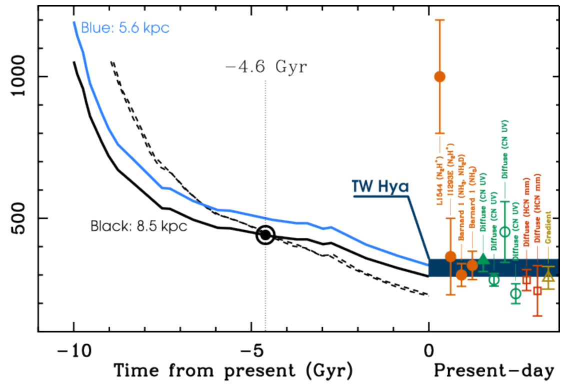
Two reservoirs of nitrogen in disks

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

The present-day isotopic ratio in the local ISM

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

Galactic chemical evolution of nitrogen



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

Consequences

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

$\Rightarrow$ HCN traces a fractionated (hence secondary) reservoir

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

New scenario

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

Nitrogen origin: open questions

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

Summary for lecture 2

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

Concluding remarks

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

Thank you !

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