Isotopic fractionation of deuterium, carbon and nitrogen

Jean Christophe Loison, Bordeaux
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Evelyne Roueff, Observatoire de Paris

Introduction
principles of gas phase fractionation reactions
Deuterium fractionation in warm conditions
new analysis of D, ^{13}C and ^{15}N chemistries
Comparison between models and observations
Conclusions

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MSME Laboratoire Modélisation et Simulation Multi Echelle
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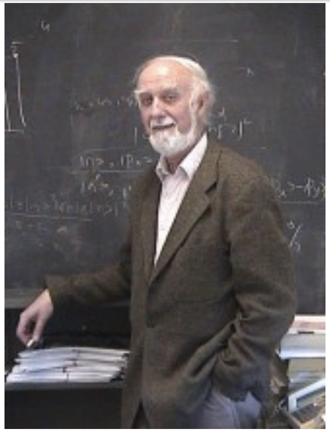

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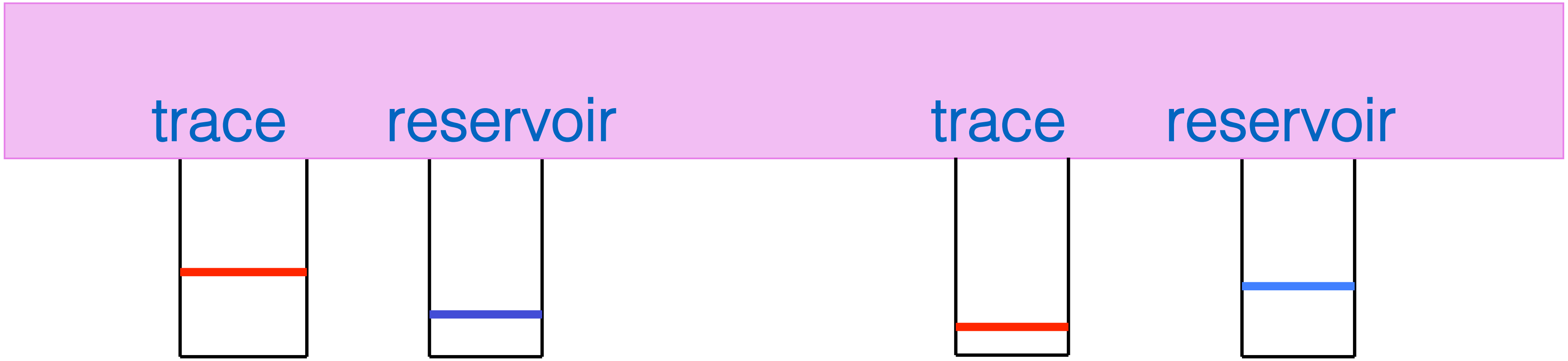
Low temperature thermodynamics

Basic mechanism : H_{eavy} / L_{ight} exchange reactions in the gas phase

$$\text{A-L}_{ight}^{(+)} + \text{B-H}_{eavy} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \text{A-H}_{eavy}^{(+)} + \text{B-L}_{ight} + \Delta E_0$$



trace reservoir trace reservoir

HD, D
^{13}CO, $^{13}C^+$
^{15}N, ^{15}NN

H_2, H
^{12}CO, $^{12}C^+$
^{14}N, N_2

Equilibrium constant: $K(T) = k_f / k_r >> 1$ if $kT << \Delta E_0$

$k_f = k_L$; $k_r << k_f$

adapted from E. Herbst

Reaction equilibrium constant

$$\text{A-H}^+ + \text{B-D} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{A-D}^+ + \text{B-H} + \Delta E_0$$

$$K(T) = exp(-\Delta G/kT) = exp(\Delta S/k)exp(\Delta H/T)$$

more precisely

$$K(T) = \frac{k_f}{k_r} = (\frac{m_{AD^+} \cdot m_{BH}}{m_{AH^+} \cdot m_{BD}})^{3/2} \times \frac{q(AD^+) \cdot q(BH)}{q(AH^+) \cdot q(BD)} \times exp(\Delta E_0/kT)$$

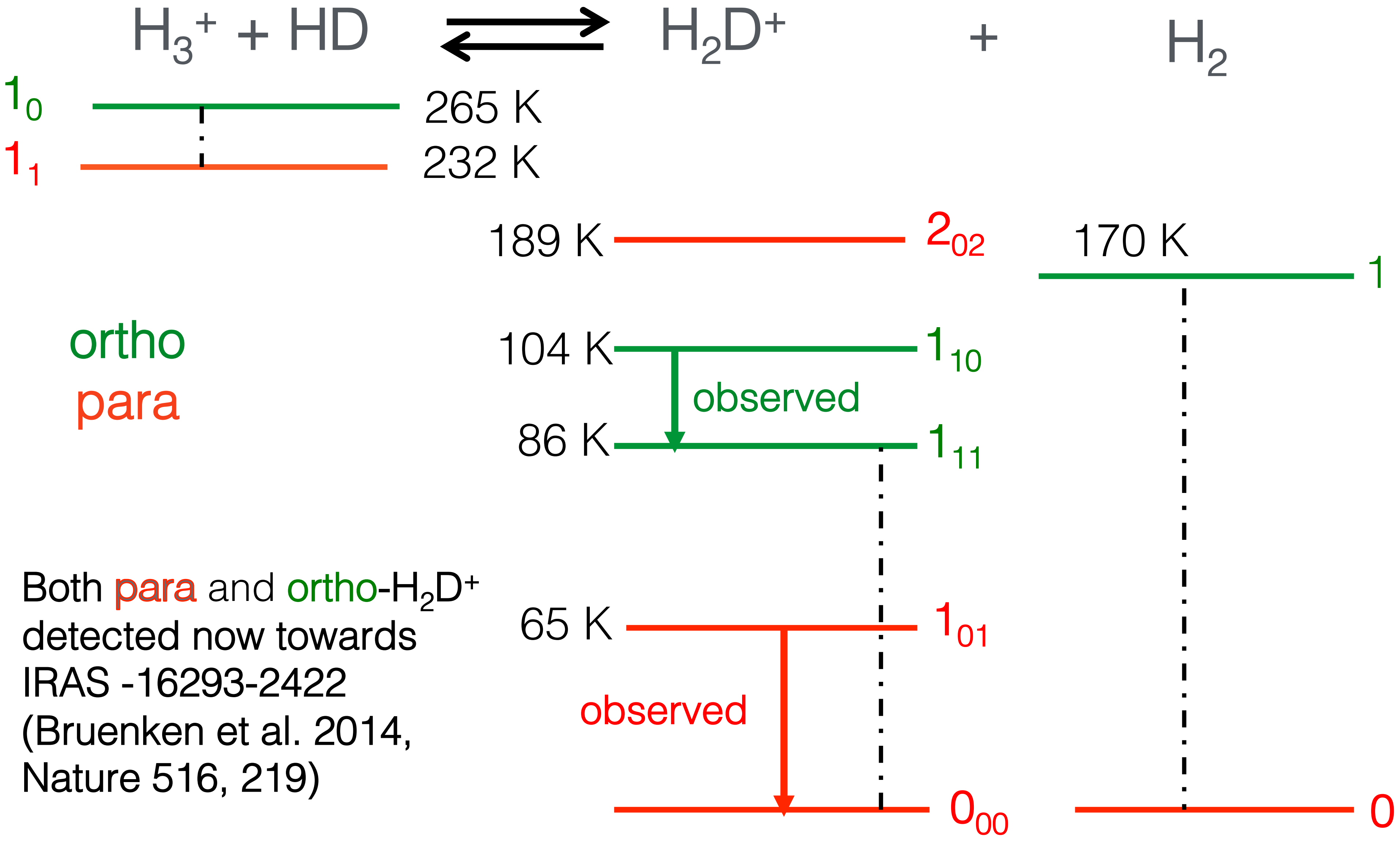
Internal partition functions : include rotation, nuclear spin, symmetry number

$$q(T) = \sum_i g_i \times exp(-E_i/kT)$$

Expression used in astrophysical studies (Terzieva + Herbst, MNRAS 317, 563)

$$K(T) = f(B, M) \times exp(\Delta E_0/kT)$$

State to state chemistry : example of H_3^+ + HD exchange



Both para and ortho-H_2D^+ detected now towards IRAS -16293-2422 (Bruenken et al. 2014, Nature 516, 219)

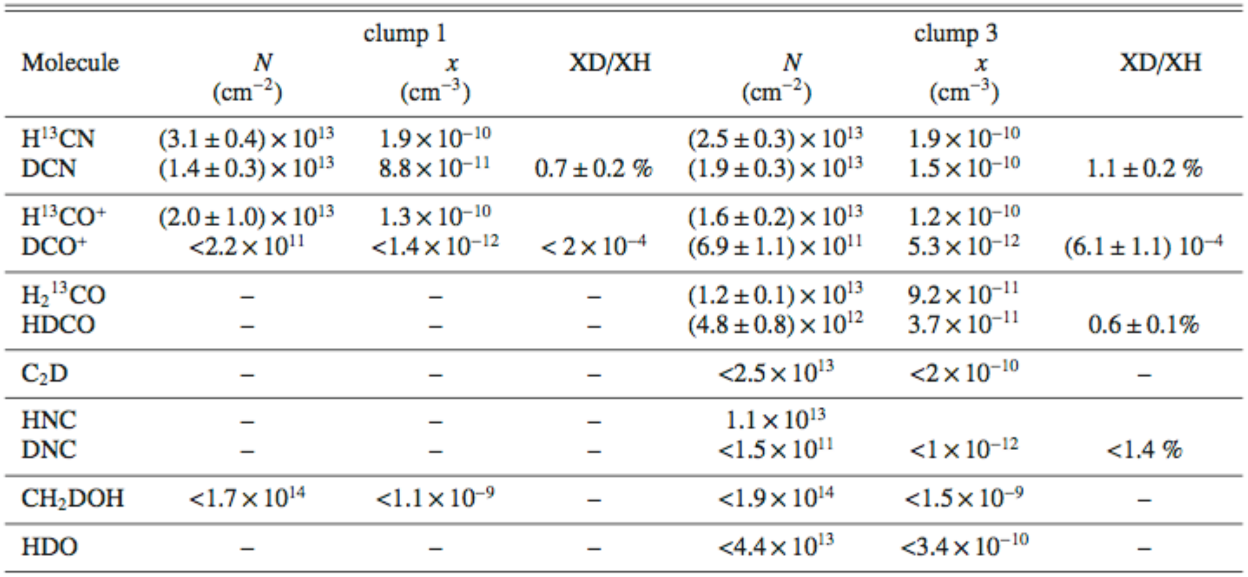
Gas phase deuteration fractionation at moderate temperatures

$CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2$ $\Delta E \approx 650K$ *Roueff et al. 2013, JPCA117, 9959*

$$CH_2D^+ + O \longrightarrow DCO^+ + H_2$$
$$CH_2D^+ + N \longrightarrow DNC^+ + H_2$$
$$CH_2D^+ + H_2 \longrightarrow CH_4D^+ + H_2$$
$$CH_4D^+ + e \longrightarrow CH_2D + H_2$$
$$CH_2D + O \longrightarrow HDCO + H$$

"Warm" chemistry starring CH_2D^+ in the Orion Bar (Parise et al. 2009, AA508, 737)

Table 7. Summary of column densities, abundances, and D/H ratios in the observed molecules.



Molecule	clump 1 N (cm^{-2})	 x (cm^{-3})	 XD/XH	clump 3 N (cm^{-2})	 x (cm^{-3})	 XD/XH
$H^{13}CN$	$(3.1 \pm 0.4) \times 10^{13}$	1.9×10^{-10}		$(2.5 \pm 0.3) \times 10^{13}$	1.9×10^{-10}	
DCN	$(1.4 \pm 0.3) \times 10^{13}$	8.8×10^{-11}	0.7 ± 0.2 %	$(1.9 \pm 0.3) \times 10^{13}$	1.5×10^{-10}	1.1 ± 0.2 %
$H^{13}CO^+$	$(2.0 \pm 1.0) \times 10^{13}$	1.3×10^{-10}		$(1.6 \pm 0.2) \times 10^{13}$	1.2×10^{-10}	
DCO^+	$<2.2 \times 10^{11}$	$<1.4 \times 10^{-12}$	$< 2 \times 10^{-4}$	$(6.9 \pm 1.1) \times 10^{11}$	5.3×10^{-12}	$(6.1 \pm 1.1)\ 10^{-4}$
$H_2{}^{13}CO$	–	–	–	$(1.2 \pm 0.1) \times 10^{13}$	9.2×10^{-11}	
HDCO	–	–	–	$(4.8 \pm 0.8) \times 10^{12}$	3.7×10^{-11}	0.6 ± 0.1%
C_2D	–	–	–	$<2.5 \times 10^{13}$	$<2 \times 10^{-10}$	–
HNC	–	–	–	1.1×10^{13}		
DNC	–	–	–	$<1.5 \times 10^{11}$	$<1 \times 10^{-12}$	<1.4 %
CH_2DOH	$<1.7 \times 10^{14}$	$<1.1 \times 10^{-9}$	–	$<1.9 \times 10^{14}$	$<1.5 \times 10^{-9}$	–
HDO	–	–	–	$<4.4 \times 10^{13}$	$<3.4 \times 10^{-10}$	–

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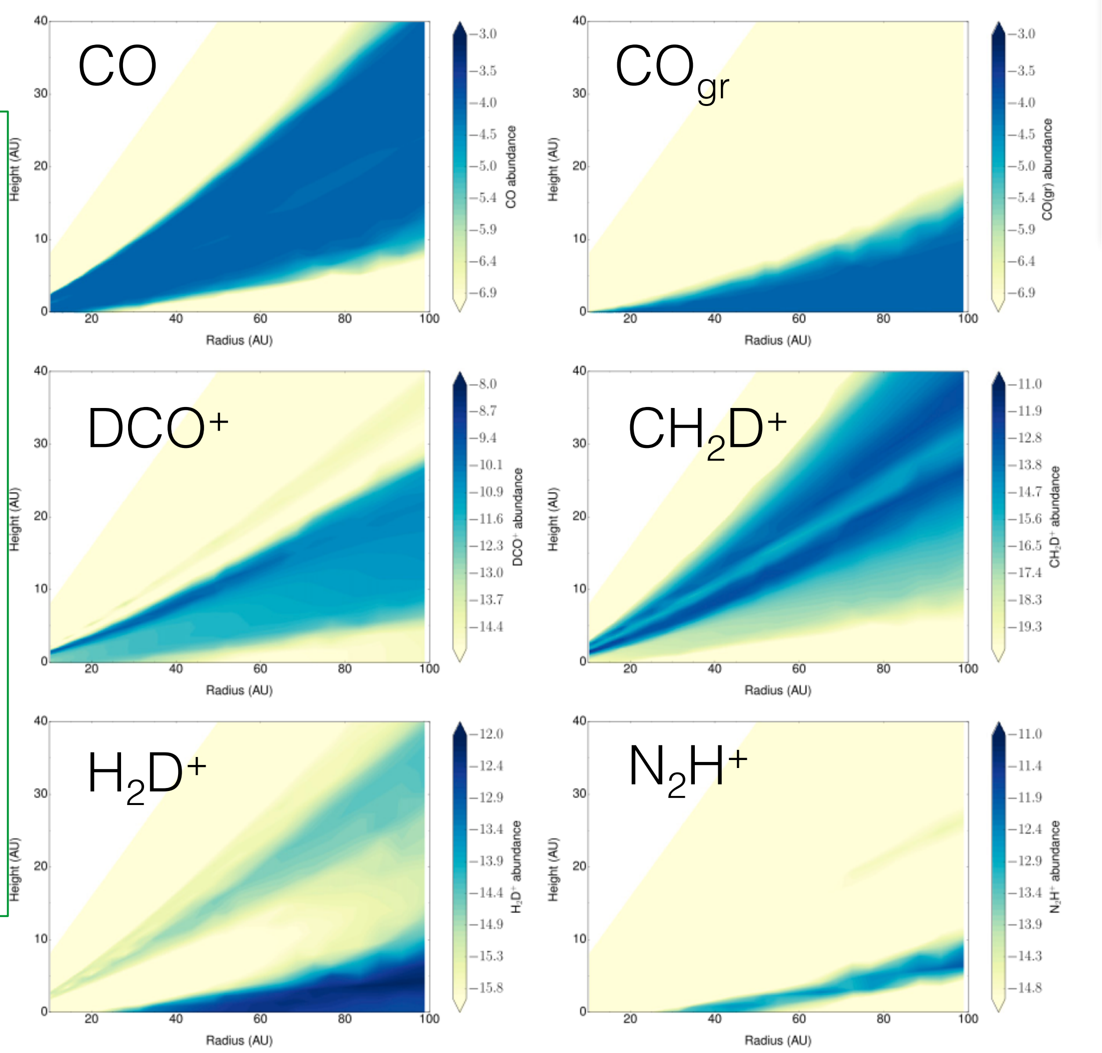
$CH_2D^+ + O \longrightarrow DCO^+ + H_2$

DCO⁺ detected in various disks (DM Tau Guilloteau 2006, TWHya Oberg et al. 2012, HD163296 Matthews et al 2013, LkCa15, IMLup, ….SMA DISC project)

DCO⁺ as a probe of ionization in the warm disk surface
Favre et al. 2015, ApJL 802, L23

DCO⁺ observed in the inner layers of the disk may rather trace ionization than the CO snow line as previously suggested by Matthews et al. 2013, AA557, A132



Search for isotopic exchange reactions

Type A : direct exchange

$$K_{eq} = \frac{k_{\rightarrow}}{k_{\leftarrow}} = f_{B,M} \times exp(-\Delta E/kT)$$

$$^{15}NN + N_2H^+ \rightleftharpoons {}^{15}NNH^+ + N_2$$

$f(B,M)$ depends on rotational constants and symmetry
(Terzieva+Herbst MNRAS317, 563, 2000)

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Type B : reactions involving adduct formation and leading to direct products without isomerization

$^{15}N^+ + N_2 \rightleftharpoons {}^{15}NN + N^+$

$$k_{\rightarrow} + k_{\leftarrow} = k_{capture}$$

$$k_{\rightarrow} = k_{capture} \times \frac{f(B,M)}{[f(B,M) + exp(-\Delta E/kT)]}$$

$$k_{\leftarrow} = k_{capture} \times \frac{exp(-\Delta E/kT)}{[f(B,M) + exp(-\Delta E/kT)]}$$

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Type C : reactions involving adduct formation with isomeric pathways

$^{13}C + HCN \rightleftharpoons H^{13}CN + C$

The isotopic isomerization reaction competes with the dissociation of the adduct. The rate constant depends on the location of the transition state, and statistical calculations are generally required to estimate the isomerization reaction rate constant

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Type D : other exothermic channels

→ Isotopic exchange does not proceed

$\cancel{^{15}N + NO \rightleftharpoons {}^{15}NO + N}$

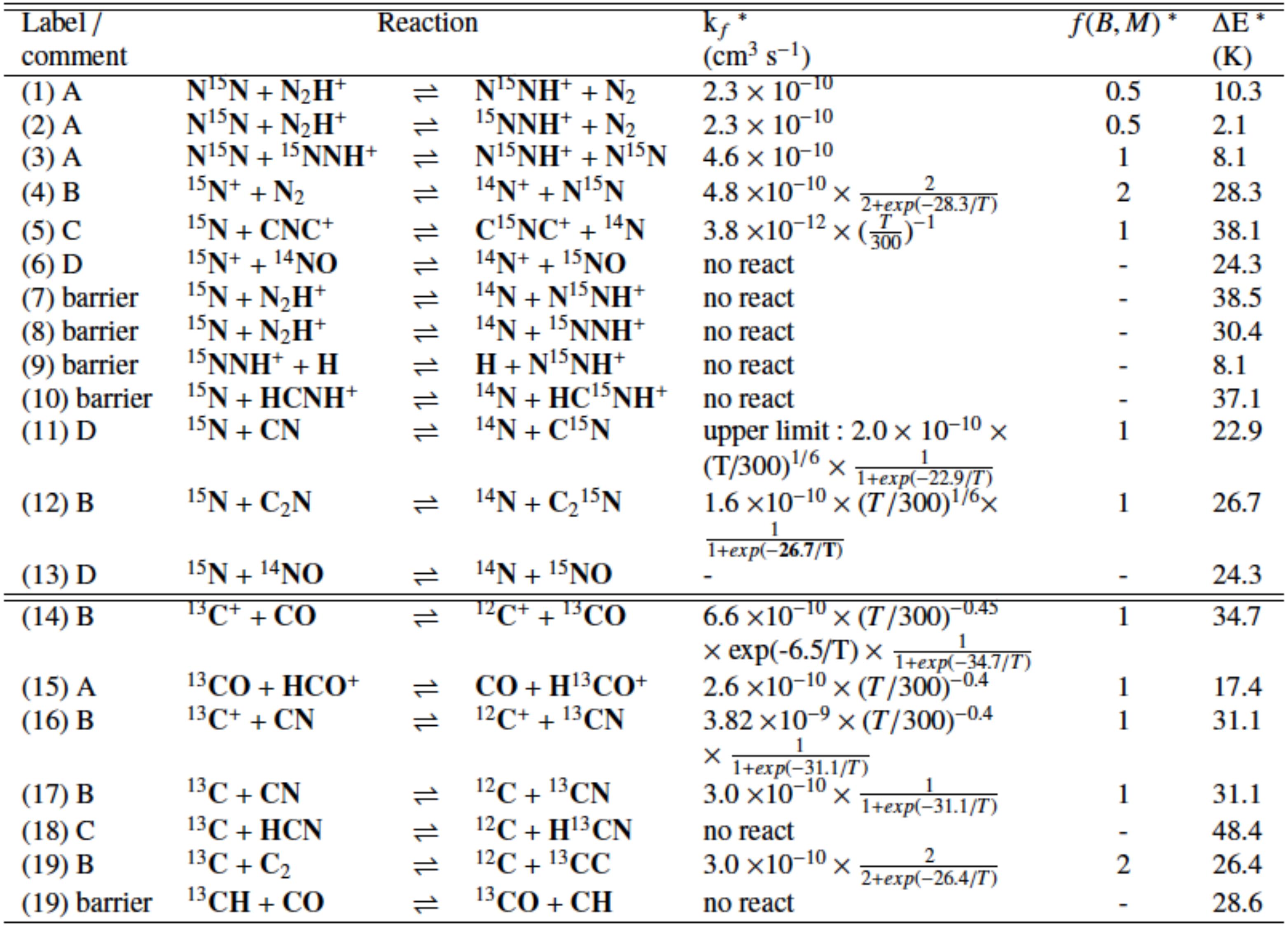
Carbon + oxygen fractionation reactions in CO and HCO^+

Evaluation of ΔE (K) from ZPEs

	Theory				Exp
	MR 2014	**LGFA 84**	**L98**	**HKD77**	**SA80**
$^{13}C^+ + CO \rightleftarrows {}^{13}CO + C^+$	34.5	35	36.0		40±6
$^{13}C^+ + C^{18}O \rightleftarrows {}^{13}C^{18}O + C^+$	35.4	36	37.5		
$HCO^+ + {}^{13}CO \rightleftarrows H^{13}CO^+ + CO$	17.8	9	20	16.5	12±5
$HCO^+ + C^{18}O \rightleftarrows HC^{18}O^+ + CO$	6.4	14	7.5	6.2	15±5
$HCO^+ + {}^{13}C^{18}O \rightleftarrows H^{13}C^{18}O^+ + CO$	24.2	22	27	22.6	
$H^{13}CO^+ + {}^{13}C^{18}O \rightleftarrows H^{13}C^{18}O^+ + {}^{13}CO$	6.4	13	7.0	6.1	
$HC^{18}O^+ + {}^{13}CO \rightleftarrows H^{13}CO^+ + C^{18}O$	11.4	-5	12.5	10.3	<5
$HC^{18}O^+ + {}^{13}C^{18}O \rightleftarrows H^{13}C^{18}O^+ + C^{18}O$	17.8	8	19.5	16.4	

MR2014: Mladenovic+ Roueff, AA566, A144, 2014 ; results with D reported as well and HOC^+ isotopologues
LGFA84: Langer et al. ApJ277, 581, 1984; *reporting HKD77*
L98: Lohr, JCP108, 8012, 1998
HKD77: Henning et al. internal report MPI/PAE Astro 135, 1977
SA80: Smith+Adams, ApJ 242, 424, 1980

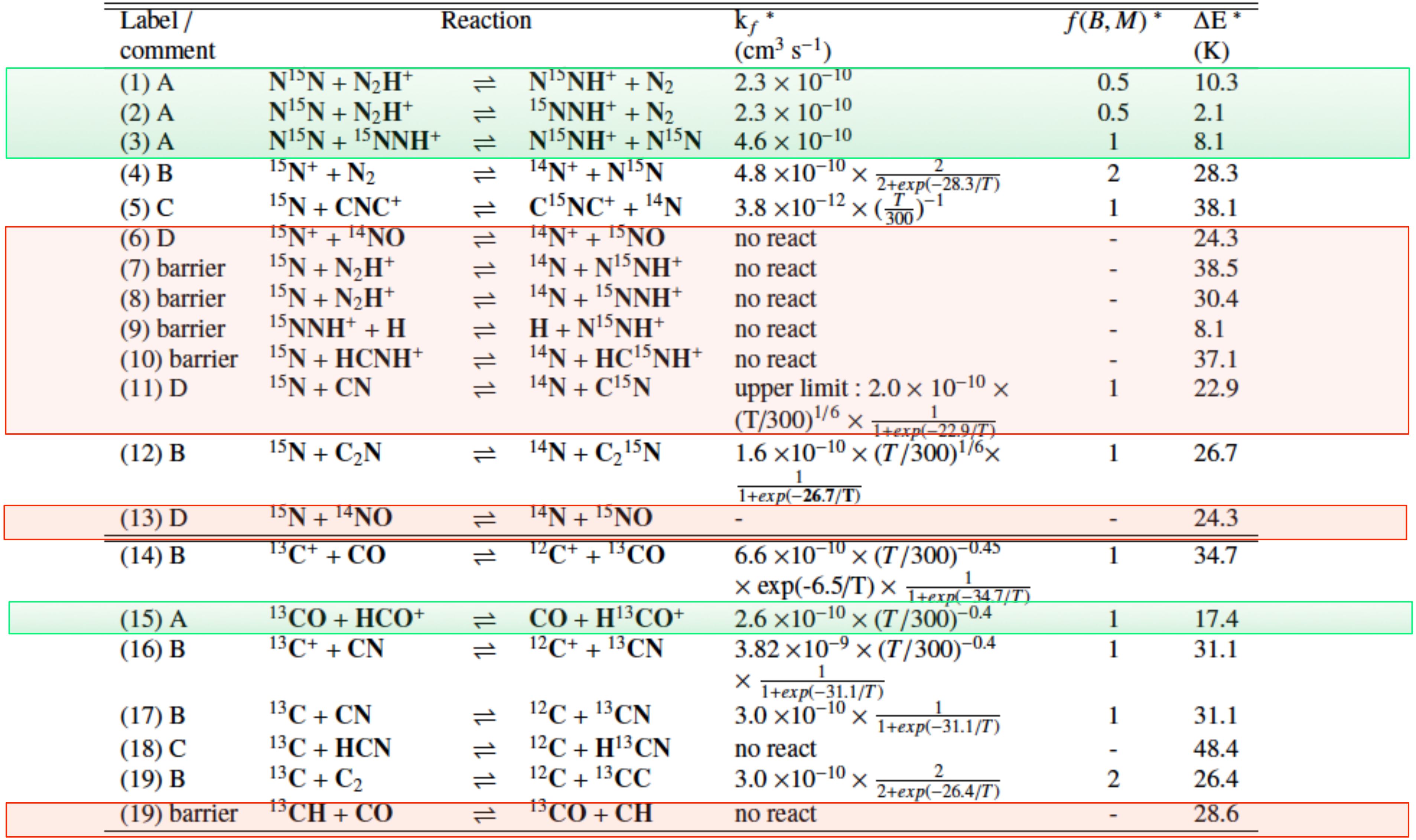
Revisiting fractionation reaction



Label / comment	Reaction			k_f * ($\mathrm{cm^3\ s^{-1}}$)	$f(B,M)$ *	ΔE * (K)
(1) A	$\mathrm{N^{15}N + N_2H^+}$	$\rightleftharpoons$	$\mathrm{N^{15}NH^+ + N_2}$	2.3×10^{-10}	0.5	10.3
(2) A	$\mathrm{N^{15}N + N_2H^+}$	$\rightleftharpoons$	$\mathrm{^{15}NNH^+ + N_2}$	2.3×10^{-10}	0.5	2.1
(3) A	$\mathrm{N^{15}N + {}^{15}NNH^+}$	$\rightleftharpoons$	$\mathrm{N^{15}NH^+ + N^{15}N}$	4.6×10^{-10}	1	8.1
(4) B	$\mathrm{^{15}N^+ + N_2}$	$\rightleftharpoons$	$\mathrm{^{14}N^+ + N^{15}N}$	$4.8 \times 10^{-10} \times \frac{2}{2+exp(-28.3/T)}$	2	28.3
(5) C	$\mathrm{^{15}N + CNC^+}$	$\rightleftharpoons$	$\mathrm{C^{15}NC^+ + {}^{14}N}$	$3.8 \times 10^{-12} \times (\frac{T}{300})^{-1}$	1	38.1
(6) D	$\mathrm{^{15}N^+ + {}^{14}NO}$	$\rightleftharpoons$	$\mathrm{^{14}N^+ + {}^{15}NO}$	no react	-	24.3
(7) barrier	$\mathrm{^{15}N + N_2H^+}$	$\rightleftharpoons$	$\mathrm{^{14}N + N^{15}NH^+}$	no react	-	38.5
(8) barrier	$\mathrm{^{15}N + N_2H^+}$	$\rightleftharpoons$	$\mathrm{^{14}N + {}^{15}NNH^+}$	no react	-	30.4
(9) barrier	$\mathrm{^{15}NNH^+ + H}$	$\rightleftharpoons$	$\mathrm{H + N^{15}NH^+}$	no react	-	8.1
(10) barrier	$\mathrm{^{15}N + HCNH^+}$	$\rightleftharpoons$	$\mathrm{^{14}N + HC^{15}NH^+}$	no react	-	37.1
(11) D	$\mathrm{^{15}N + CN}$	$\rightleftharpoons$	$\mathrm{^{14}N + C^{15}N}$	upper limit : $2.0 \times 10^{-10} \times (T/300)^{1/6} \times \frac{1}{1+exp(-22.9/T)}$	1	22.9
(12) B	$\mathrm{^{15}N + C_2N}$	$\rightleftharpoons$	$\mathrm{^{14}N + C_2{}^{15}N}$	$1.6 \times 10^{-10} \times (T/300)^{1/6} \times \frac{1}{1+exp(-\mathbf{26.7/T})}$	1	26.7
(13) D	$\mathrm{^{15}N + {}^{14}NO}$	$\rightleftharpoons$	$\mathrm{^{14}N + {}^{15}NO}$	-	-	24.3
(14) B	$\mathrm{^{13}C^+ + CO}$	$\rightleftharpoons$	$\mathrm{^{12}C^+ + {}^{13}CO}$	$6.6 \times 10^{-10} \times (T/300)^{-0.45} \times \exp(-6.5/T) \times \frac{1}{1+exp(-34.7/T)}$	1	34.7
(15) A	$\mathrm{^{13}CO + HCO^+}$	$\rightleftharpoons$	$\mathrm{CO + H^{13}CO^+}$	$2.6 \times 10^{-10} \times (T/300)^{-0.4}$	1	17.4
(16) B	$\mathrm{^{13}C^+ + CN}$	$\rightleftharpoons$	$\mathrm{^{12}C^+ + {}^{13}CN}$	$3.82 \times 10^{-9} \times (T/300)^{-0.4} \times \frac{1}{1+exp(-31.1/T)}$	1	31.1
(17) B	$\mathrm{^{13}C + CN}$	$\rightleftharpoons$	$\mathrm{^{12}C + {}^{13}CN}$	$3.0 \times 10^{-10} \times \frac{1}{1+exp(-31.1/T)}$	1	31.1
(18) C	$\mathrm{^{13}C + HCN}$	$\rightleftharpoons$	$\mathrm{^{12}C + H^{13}CN}$	no react	-	48.4
(19) B	$\mathrm{^{13}C + C_2}$	$\rightleftharpoons$	$\mathrm{^{12}C + {}^{13}CC}$	$3.0 \times 10^{-10} \times \frac{2}{2+exp(-26.4/T)}$	2	26.4
(19) barrier	$\mathrm{^{13}CH + CO}$	$\rightleftharpoons$	$\mathrm{^{13}CO + CH}$	no react	-	28.6

Roueff, Loison, Hickson, 2015, A&A 576, A99

Revisiting fractionation reaction



Label / comment	Reaction			k_f * ($cm^3 s^{-1}$)	$f(B, M)$ *	ΔE * (K)
(1) A	$N^{15}N + N_2H^+$	$\rightleftharpoons$	$N^{15}NH^+ + N_2$	2.3×10^{-10}	0.5	10.3
(2) A	$N^{15}N + N_2H^+$	$\rightleftharpoons$	$^{15}NNH^+ + N_2$	2.3×10^{-10}	0.5	2.1
(3) A	$N^{15}N + {}^{15}NNH^+$	$\rightleftharpoons$	$N^{15}NH^+ + N^{15}N$	4.6×10^{-10}	1	8.1
(4) B	$^{15}N^+ + N_2$	$\rightleftharpoons$	$^{14}N^+ + N^{15}N$	$4.8 \times 10^{-10} \times \frac{2}{2+exp(-28.3/T)}$	2	28.3
(5) C	$^{15}N + CNC^+$	$\rightleftharpoons$	$C^{15}NC^+ + {}^{14}N$	$3.8 \times 10^{-12} \times (\frac{T}{300})^{-1}$	1	38.1
(6) D	$^{15}N^+ + {}^{14}NO$	$\rightleftharpoons$	$^{14}N^+ + {}^{15}NO$	no react	-	24.3
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(8) barrier	$^{15}N + N_2H^+$	$\rightleftharpoons$	$^{14}N + {}^{15}NNH^+$	no react	-	30.4
(9) barrier	$^{15}NNH^+ + H$	$\rightleftharpoons$	$H + N^{15}NH^+$	no react	-	8.1
(10) barrier	$^{15}N + HCNH^+$	$\rightleftharpoons$	$^{14}N + HC^{15}NH^+$	no react	-	37.1
(11) D	$^{15}N + CN$	$\rightleftharpoons$	$^{14}N + C^{15}N$	upper limit : $2.0 \times 10^{-10} \times (T/300)^{1/6} \times \frac{1}{1+exp(-22.9/T)}$	1	22.9
(12) B	$^{15}N + C_2N$	$\rightleftharpoons$	$^{14}N + C_2{}^{15}N$	$1.6 \times 10^{-10} \times (T/300)^{1/6} \times \frac{1}{1+exp(-\mathbf{26.7/T})}$	1	26.7
(13) D	$^{15}N + {}^{14}NO$	$\rightleftharpoons$	$^{14}N + {}^{15}NO$	-	-	24.3
(14) B	$^{13}C^+ + CO$	$\rightleftharpoons$	$^{12}C^+ + {}^{13}CO$	$6.6 \times 10^{-10} \times (T/300)^{-0.45} \times exp(-6.5/T) \times \frac{1}{1+exp(-34.7/T)}$	1	34.7
(15) A	$^{13}CO + HCO^+$	$\rightleftharpoons$	$CO + H^{13}CO^+$	$2.6 \times 10^{-10} \times (T/300)^{-0.4}$	1	17.4
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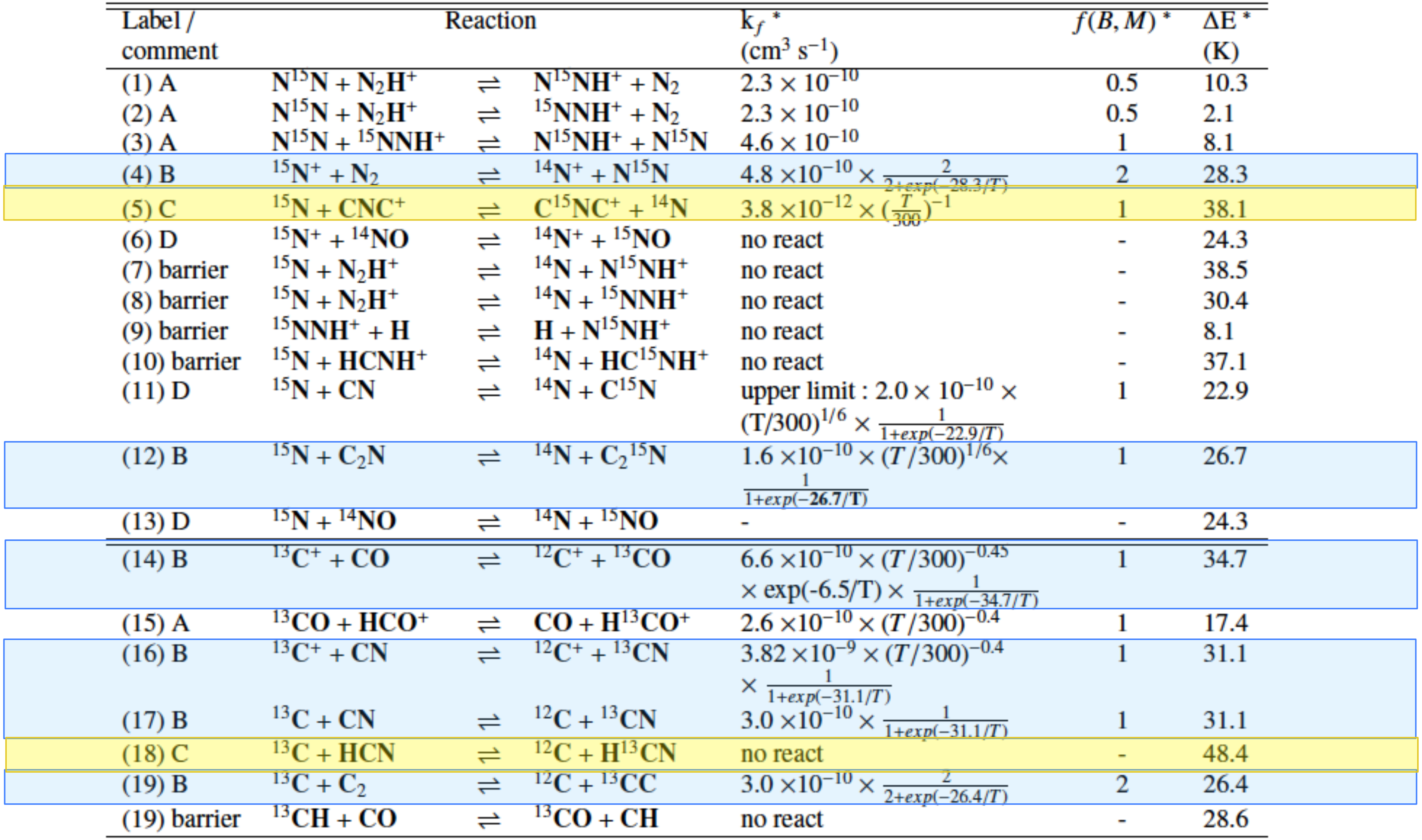
(19) B	$^{13}C + C_2$	$\rightleftharpoons$	$^{12}C + {}^{13}CC$	$3.0 \times 10^{-10} \times \frac{2}{2+exp(-26.4/T)}$	2	26.4
(19) barrier	$^{13}CH + CO$	$\rightleftharpoons$	$^{13}CO + CH$	no react	-	28.6

Type A : direct exchange

Type D : other reactive channels available

Revisiting fractionation reaction



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(14) B	$^{13}C^+ + CO$	$\rightleftharpoons$	$^{12}C^+ + {}^{13}CO$	$6.6 \times 10^{-10} \times (T/300)^{-0.45} \times exp(-6.5/T) \times \frac{1}{1+exp(-34.7/T)}$	1	34.7
(15) A	$^{13}CO + HCO^+$	$\rightleftharpoons$	$CO + H^{13}CO^+$	$2.6 \times 10^{-10} \times (T/300)^{-0.4}$	1	17.4
(16) B	$^{13}C^+ + CN$	$\rightleftharpoons$	$^{12}C^+ + {}^{13}CN$	$3.82 \times 10^{-9} \times (T/300)^{-0.4} \times \frac{1}{1+exp(-31.1/T)}$	1	31.1
(17) B	$^{13}C + CN$	$\rightleftharpoons$	$^{12}C + {}^{13}CN$	$3.0 \times 10^{-10} \times \frac{1}{1+exp(-31.1/T)}$	1	31.1
(18) C	$^{13}C + HCN$	$\rightleftharpoons$	$^{12}C + H^{13}CN$	no react	-	48.4
(19) B	$^{13}C + C_2$	$\rightleftharpoons$	$^{12}C + {}^{13}CC$	$3.0 \times 10^{-10} \times \frac{2}{2+exp(-26.4/T)}$	2	26.4
(19) barrier	$^{13}CH + CO$	$\rightleftharpoons$	$^{13}CO + CH$	no react	-	28.6

Type B reactions : reactions involving adduct formation and leading to direct products without isomerization

Type C reactions : reactions involving adduct formation with isomerization pathways. More work to be done

Time dependent chemical models

D, ^{13}C + ^{15}N containing molecules

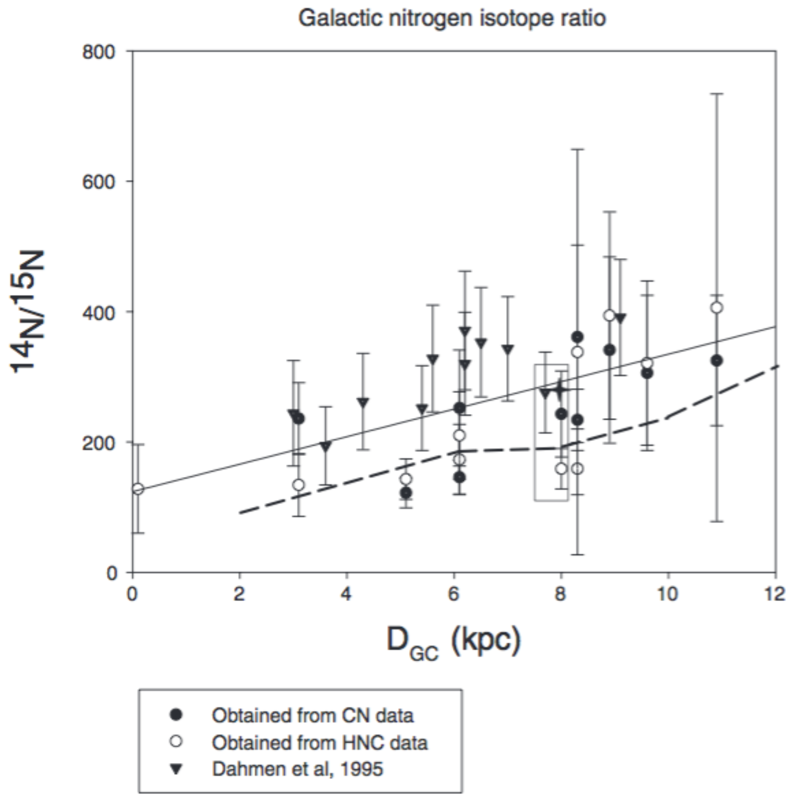
307 atomic + molecular species
5440 chemical gas phase reactions
o/p ratio of H_2 fixed
involved in $H_2D^+ + (o/p)\text{-}H_2 \longrightarrow H_3^+ + H$
and $N^+ + (o/p)\text{-}H_2 \longrightarrow NH^+ + H$

✏ Comparison with available observations
✏ Test the hypothesis that ^{13}C containig molecules are in elemental isotopic ratios
✏ discuss the influence of the elemental ^{14}N / ^{15}N ratio

Elemental abundances	TMC1 like	Prestellar core
C / H	4.15 10^{-5}	1.4 10^{-5}
O / H	6.0 10^{-5}	2.0 10^{-5}
N / H	6.4 10^{-5}	2.1 10^{-5}
S / H	8.0 10^{-8}	8.0 10^{-8}
D / H	1.5 10^{-5}	1.5 10^{-5}
^{12}C / ^{13}C	68	68
^{14}N/^{15}N	440 274	440 274
Physical conditions		
n_H (cm^{-3})	2 10^4	2 10^5
T (K)	10	10
ζ (s^{-1}) per H_2	1.3 10^{-17}	1.3 10^{-17}
o/p ratio of H_2	10^{-3}	10^{-3}
Radiation field	NO	NO

the elemental ^{14}N / ^{15}N ratio

From Adande & Ziurys, 2012, ApJ 744, 194



protosolar nebula: ^{14}N / ^{15}N = 440±6 (Marty et al. 2011, Sci 332 1533, from Genesis mission)

Galactic value?

^{14}N / ^{15}N = 237 ± 25 (from absorbed HCN towards B0415 + 379) (Lucas & Liszt 1998, AA 337, 246

^{14}N / ^{15}N = 123.8(5.2) + 21.1(37.1) D_{GC}(kpc)

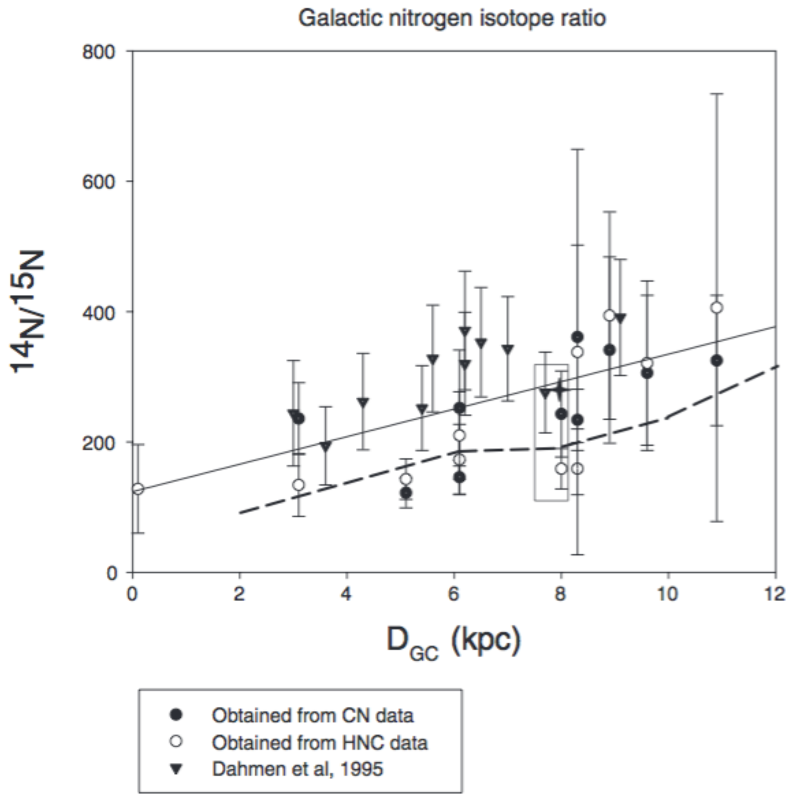
⇨ 290±40 at D≈7.9 kpc (Adande & Ziurys 2012)

^{14}N / ^{15}N = 274 ±18 (Ritchey et al 2015, ApJ 804, L3, from ISM CN)

60% increase of ^{15}N in the last 4.6 Gyrs
Hot CNO cycle; secondary production of ^{15}N from novae outbursts ?

the elemental ^{14}N / ^{15}N ratio

From Adande & Ziurys, 2012, ApJ 744, 194



proto**solar nebula**: ^{14}N / ^{15}N = 440±6 (Marty et al. 2011, Sci 332 1533, from Genesis mission)

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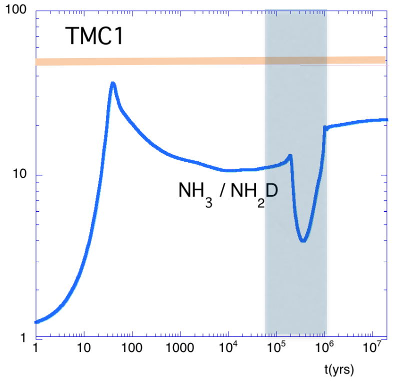
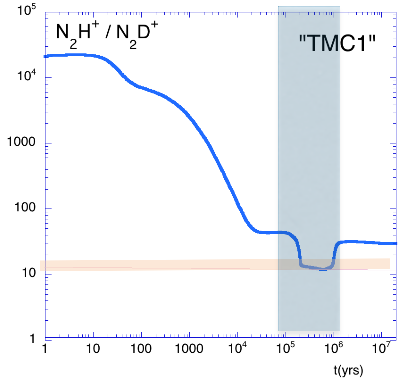
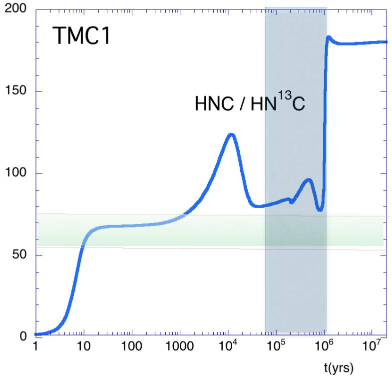
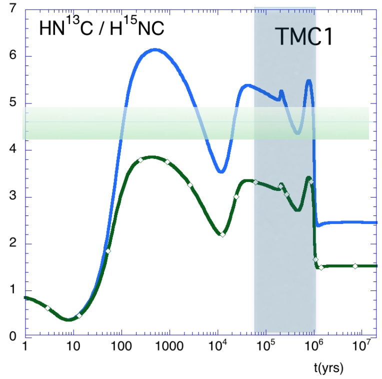
60% increase of ^{15}N in the last 4.6 Gyrs
Hot CNO cycle; secondary production of ^{15}N from novae outbursts ?

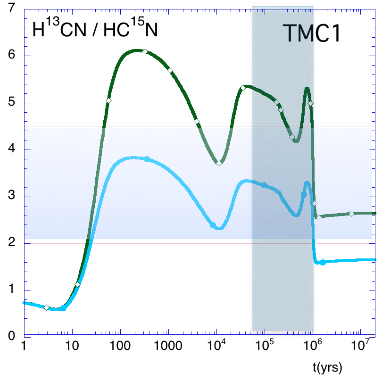
^{12}C/^{13}C = 91.4±1.3 from solar photosphere (Ayres et al. 2013, ApJ 765, 46); Genesis data to come?
^{12}C/^{13}C = 68 in the local ISM
30% increase of ^{13}C since formation of the sun

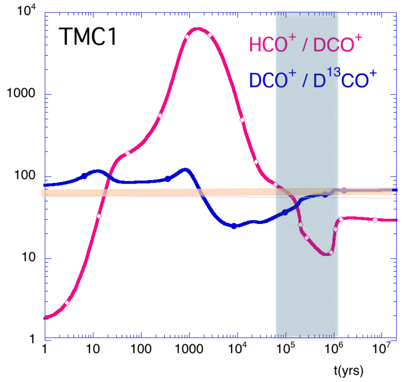












Model results TMC1 conditions

Time window ≈ 10^5 – 10^6 yrs

Observations

Tiné et al. 2000, AA356, 1039

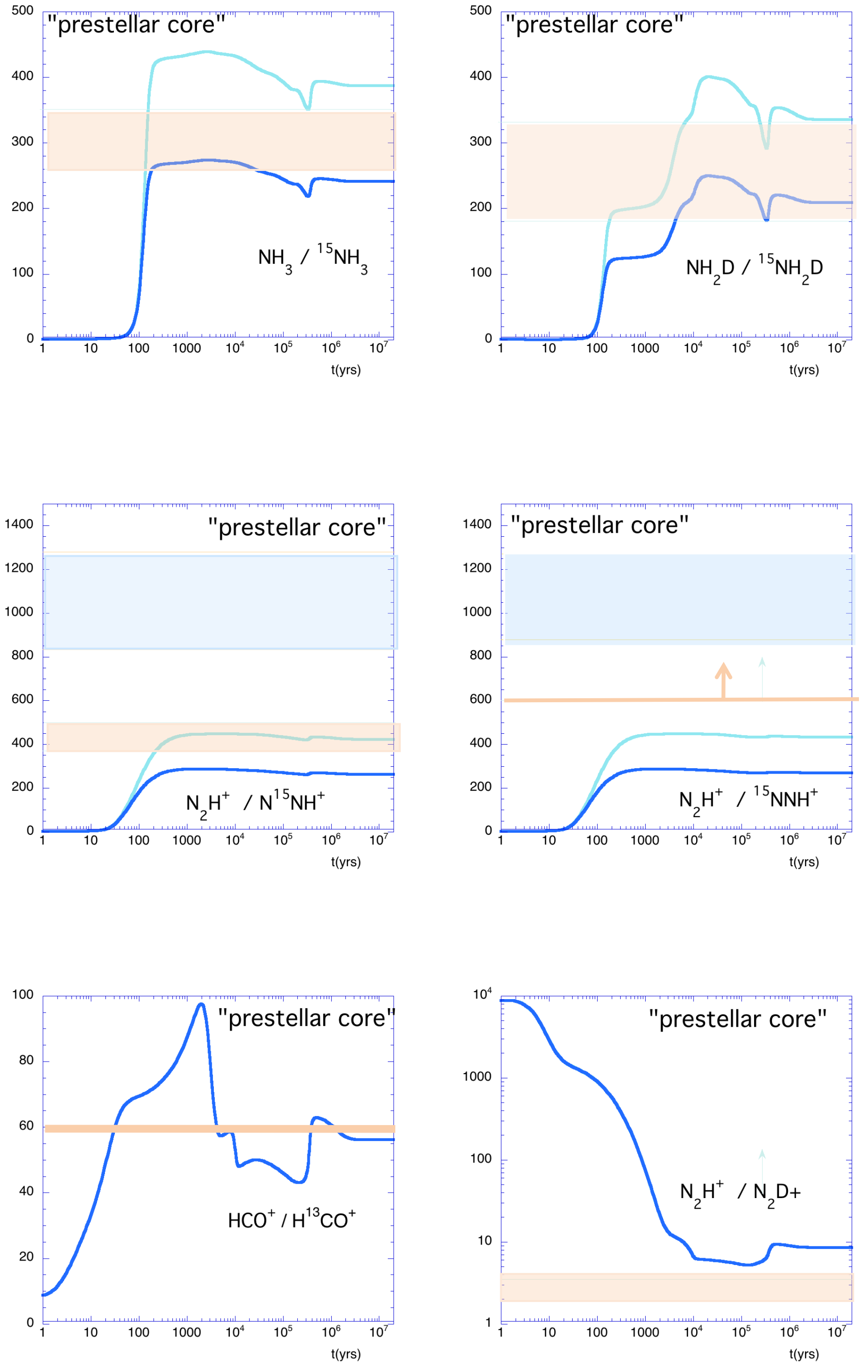
Hily-Blant et al 2013, AA557, A65

Liszt & Ziurys 2012, ApJ 747, 55

Test of the $^{14}N/^{15}N$ ratio :
No clear conclusion

HNC / $HN^{13}C$ not in the isotopic ratio

Similar conclusion for HCN / $H^{13}CN$



prestellar core conditions

Observations

B1: Daniel et al. 2013, A&A560, A3

L1544: Bizzocchi 2013, A&A555, A109

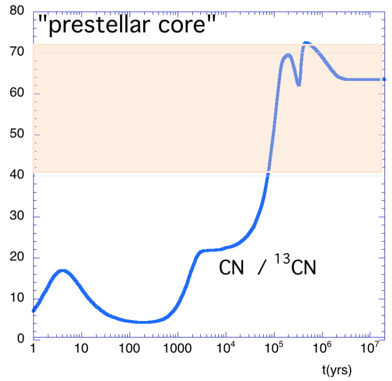
Steady state conditions reached at ≈ 1Myr

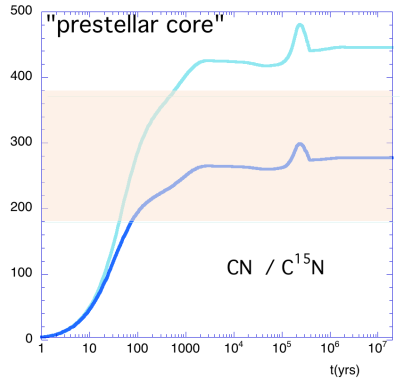
Deuterium fractionation ≈ OK

$^{14}N/^{15}N$ ratio in NH_3 and NH_2D
NH_2D more enriched in ^{15}N than NH_3 (slightly enhanced ZPEs from NH^+ -$^{15}NH^{+\,[4.8K]}$, ND^+ - $^{15}ND^{+\,[7K]}$)

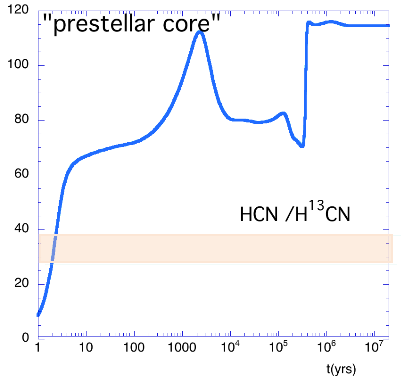
No agreement for N_2H^+
Role of collisional excitation?

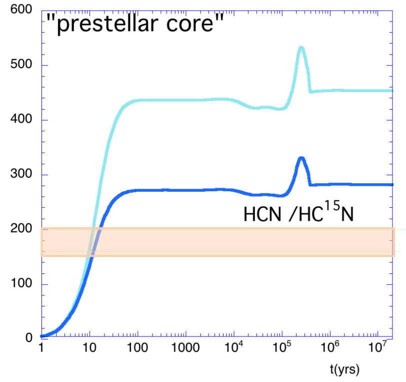
B1

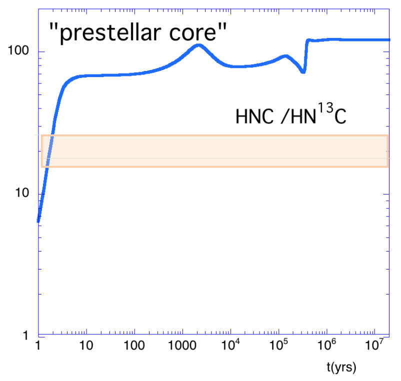


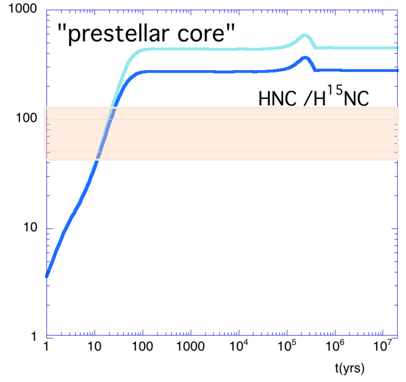


prestellar core conditions









Models with ^{14}N/ ^{15}N=274 in better agreement with observations

However, observations modeled with density + temperature profile

Possibility of reanalysis of the observations by introducing collisional excitation rates with H_2 (cf talk by F. Lique)

Carbon chains: another challenge for isotopic studies

Different ^{13}C positions in C_2H

TMC1: $C^{13}CH$ / ^{13}CCH = 1.6 (Sakai et al. 2011, A&A 512, A31)
Orion Bar PDR: $C^{13}CH$ / ^{13}CCH = 1.4 (Cuadrado et al. 2015, AA575, A82)

$H + {}^{13}CCH \Rightarrow C^{13}CH + H$ $\Delta E \approx 8.1K$ (Tarroni, private communication 2010)
$\Delta E = 7.5K$ (Morgan+Fortenberry 2015, submitted to JPCA)

Only at work for low T conditions

suggestion by Cuadrado et al:

$^{13}C^+ + C_2H \rightleftarrows C^+ + {}^{13}CCH$ $\Delta E \approx 55K$ (28.2K from Morgan+ Fortenberry 2015)

$^{13}C^+ + C_2H \rightleftarrows C^+ + C^{13}CH$ $\Delta E \approx 63K$ (35.7K from Morgan+ Fortenberry 2015)

However $C^+ + C_2H \rightarrow C_3^+ + H$. Then, according to our rule, the reaction should not take place.

Other possibilities?
Under warm conditions
$C_2 + H_2 \rightarrow C_2H + H$ exothermic reaction with a barrier of ≈ 1420K
$^{13}CC + H_2 \rightarrow {}^{13}CCH + H$ different barriers? (suggestion of JC Loison)
$\rightarrow C^{13}CH + H$ $[\Delta^{ZPE} (C_2 - {}^{13}CC) = 26.4K]$

Summary and conclusions

✏ Careful analysis of spectroscopic properties and intermolecular potential surfaces critical to understand isotopic exchange

✏ $^{15}N + N_2H^+$ exchange found unlikely (as well as $^{15}N + HCNH^+$ and $^{15}N^+ + NO$)

✏ very large observed $N_2H^+/^{15}NNH^+$ and $N_2H^+/N^{15}NH^+$ not reproduced by our models

✏ NH_3 / $^{15}NH_3$ > NH_2D / $^{15}NH_2D$ may be explained by the different ZPEs involved in $N^+ + H_2$ isotopic variants IF $N^+ + p\text{-}H_2$ is a real endothermicity.

✏ Interdependence of C and N chemistries.

✏ an even slight enrichment of CO reservoir leads to a significant depletion in minor species

✏ elemental abundance of interstellar ^{15}N? Suggestion of a $^{14}N/^{15}N$ ratio of 274 ±18 may help in the interpretation of observations.

✏ dependence of the model results on elemental abundances, and in particular to the C/O ratio