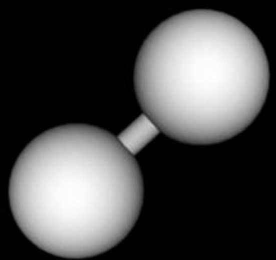
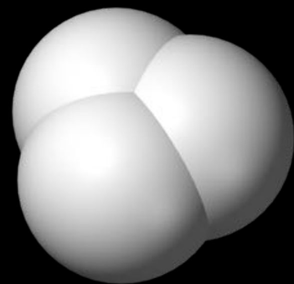
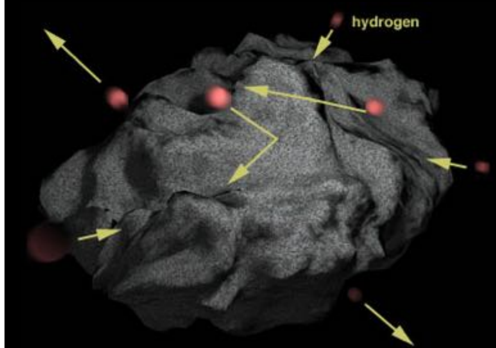
Astrochemistry with SOFIA

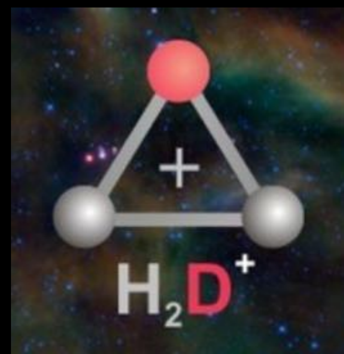
Paola Caselli
Center for Astrochemical Studies
Max-Planck-Institute for Extraterrestrial Physics







FISO Tele-Talk 1 June 2016

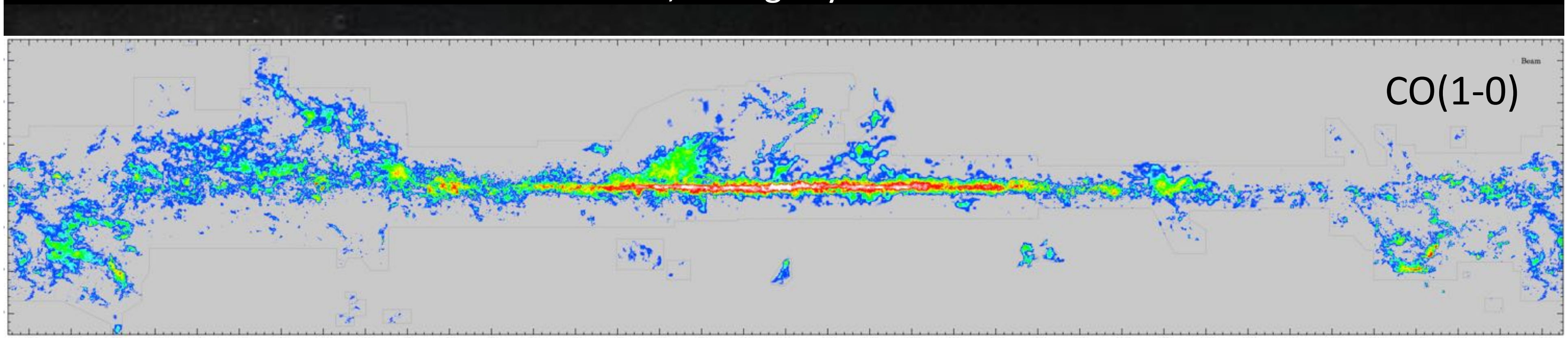


Molecular clouds in the Milky Way

~ 100,000 light years

Molecular clouds in the Milky Way

~ 100,000 light years



Dame, Hartmann & Thaddeus 2001

Interstellar molecules and the seeds of life

Known Interstellar Molecules (Total ~200)

Number of Atoms

2	3	4	5	6	7	8	9
H_2	H_2O	NH_3	SiH_4	CH_3OH	CH_3COH	CH_3CO_2H	CH_3CH_2OH
OH	H_2S	H_3O^+	CH_4	NH_2CHO	CH_3NH_2	HCO_2CH_3	$(CH_3)_2O$
SO	SO_2	H_2CO	CHOOH	CH_3CN	CH_3CCH	CH_3C_2CN	CH_3CH_2CN
SO^+	HN_2^+	H_2CS	HCCCN	CH_3NC	CH_2CHCN	C_7H	$H(CC)_3CN$
SiO	HNO	HNCO	CH_2NH	CH_3SH	HC_4CN	H_2C_6	$H(CC)_2CH_3$
SiS	SiH_2?	HNCS	NH_2CN	C_5H	C_6H	C_8^-?	C_8H
FeO?	H_2D^+	CH_2D^+?	CH_2CN	C_5S?	l-H_2C_2HOH	CH_2OHCHO	C_9^-?
NO	NH_2	CCCN	H_2CCO	HC_2CHO	c-CH_2OCH_2	l-HC_6H	
NS	H_3^+	HCO_2^+	C_4H	CH_2=CH_2	C_7^-		
HCl	NNO	l-CCCH	c-C_3H_2	H_2CCCC			
NaCl	HCO	c-CCCH	l-H_2CCC	HC_3NH^+			
KCl	HCO^+	CCCO	C_5	C_5N			
AlCl	OCS	CCCS	SiC_4	C_6^-?			
AlF	CCH	HCCH	H_3CO^+				
PN	HCS^+	$HCNH^+$	HCCNC				
SiN	c-SiCC	HCCN	HNCCC				
NH	CCO	H_2CN					
SH	CO_2	c-SiC_3					
HD	AlNC						
HF	SiCN						
CH	CCS						
CH^+	C_3						
CN	MgNC						
CO	NaCN						
CS	CH_2						
C_2	MgCN						
SiC	HOC^+						
CP	HCN						
CO^+	HNC						
	KCN?						

10
CH_3COCH_3
$CH_3(CC)_2CN$?
$(CH_2OH)_2$?

11
$H(CC)_4CN$

12
C_6H_6

13
$H(CC)_5CN$

Total: 136

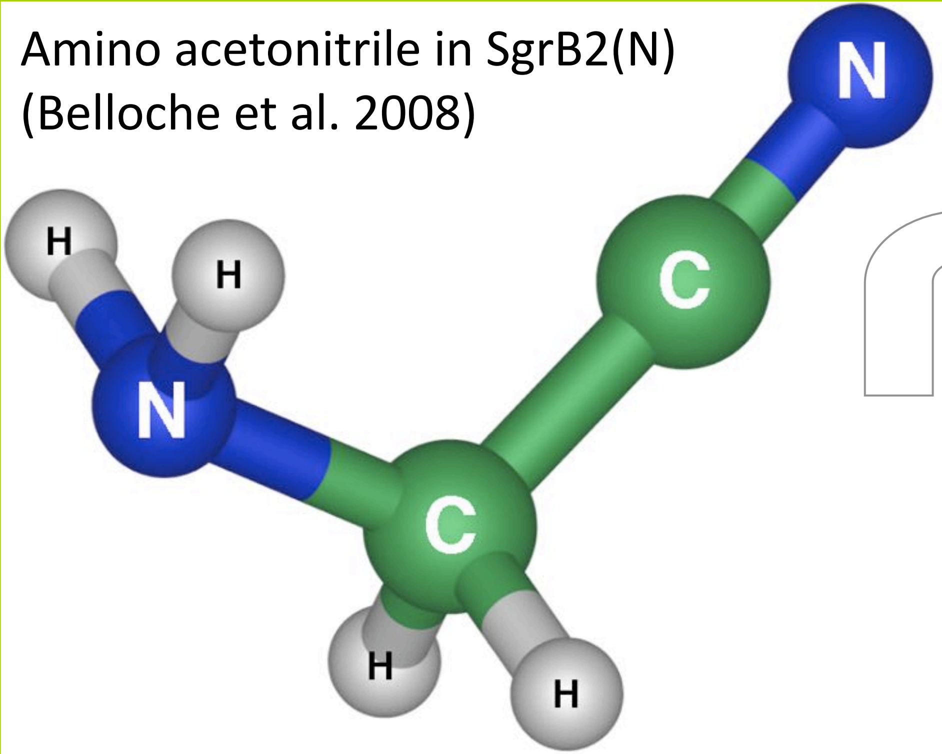
- Organic molecules in green
- Inorganic molecules in pink

http://www.astrochymist.org/astrochymist_ism.html

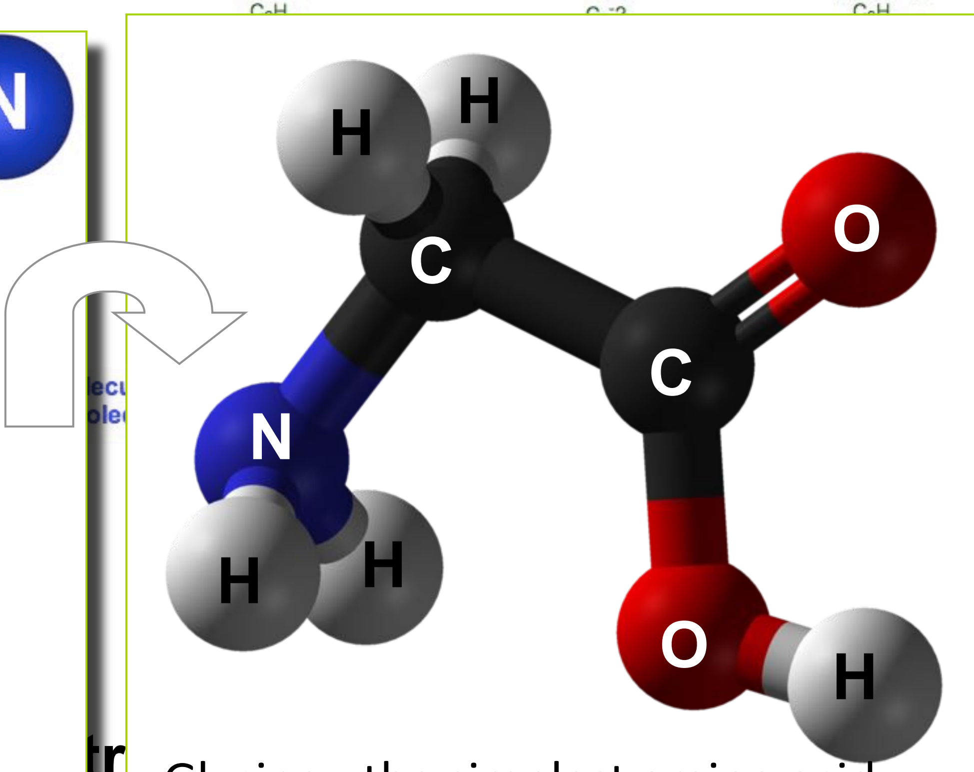
Interstellar molecules and the seeds of life

Known Interstellar Molecules (Total ~200)

Number of Atoms: 2	3	4	5	6	7	8	9
H_2	H_2O	NH_3	SiH_4	CH_3OH	CH_3COH	CH_3CO_2H	CH_3CH_2OH
OH	H_2S	H_3O^+	CH_4	NH_2CHO	CH_3NH_2	HCO_2CH_3	$(CH_3)_2O$
SO	SO_2	H_2CO	CHOOH	CH_3CN	CH_3CCH	CH_3C_2CN	CH_3CH_2CN
SO^+	HN_2^+	H_2CS	HCCCN	CH_3NC	CH_2CHCN	C_7H	$H(CC)_3CN$
SiO	HNO	HNCO	CH_2NH	CH_3SH	HC_4CN	H_2C_6	$H(CC)_2CH_3$
SiS	SiH_2?	HNCS	NH_2CN	C_5H			



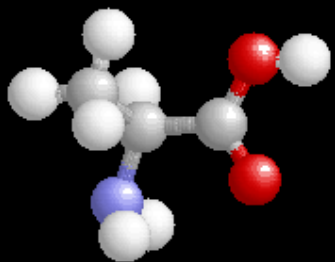
Amino acetonitrile in SgrB2(N) (Belloche et al. 2008)



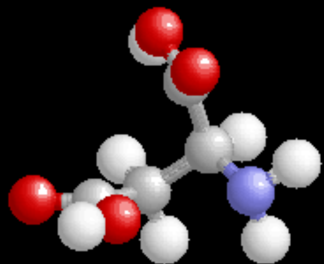
Glycine - the simplest amino acid

Pre-biotic molecules in meteorites

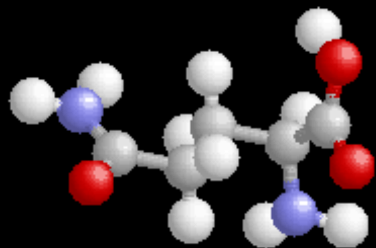
~70 amino acids have been identified in meteorites;
21 of these are used in life.



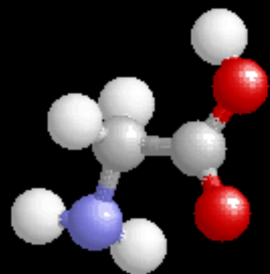
L-Alanine



L-Aspartic Acid

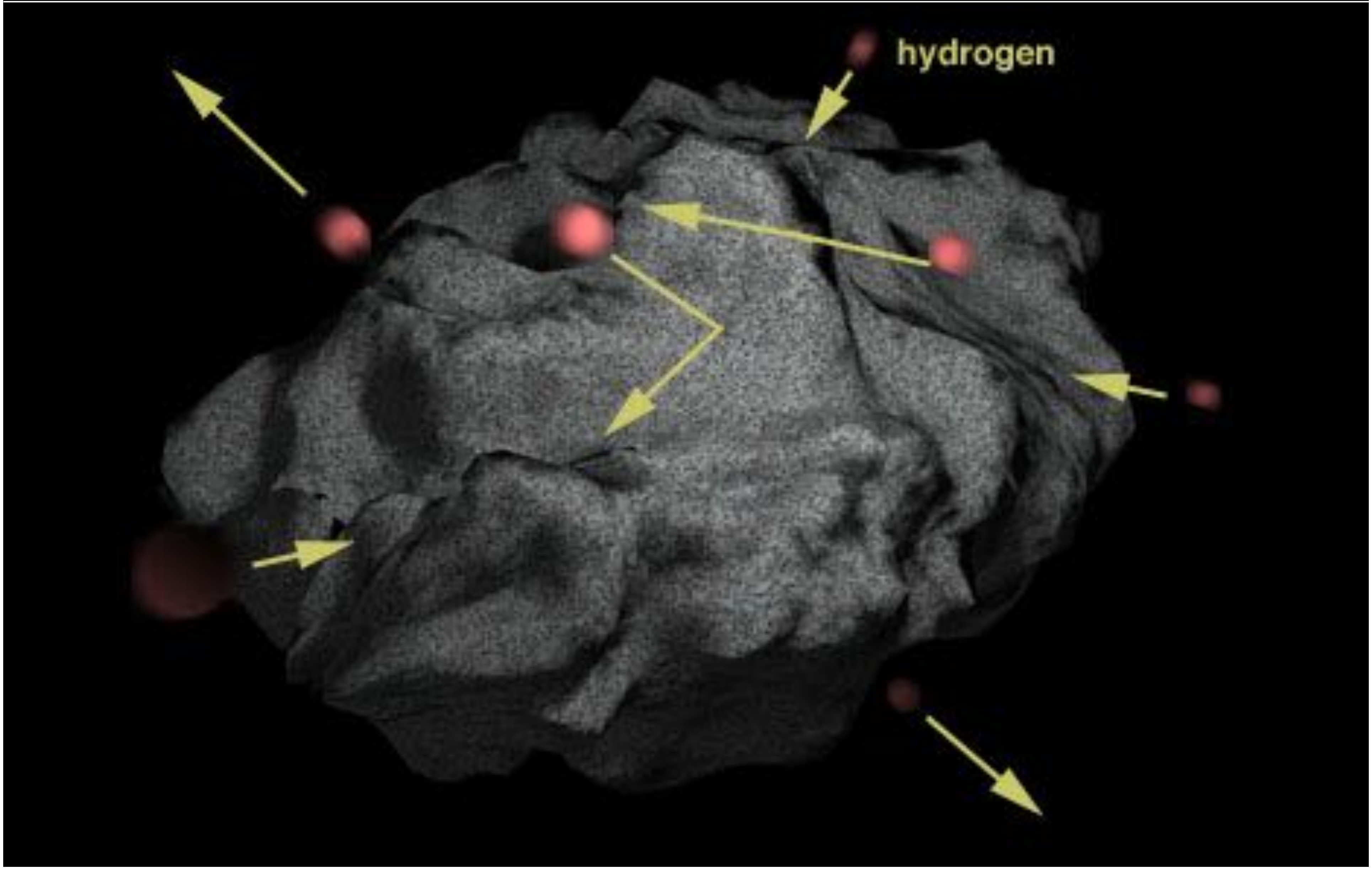


L-Glutamine



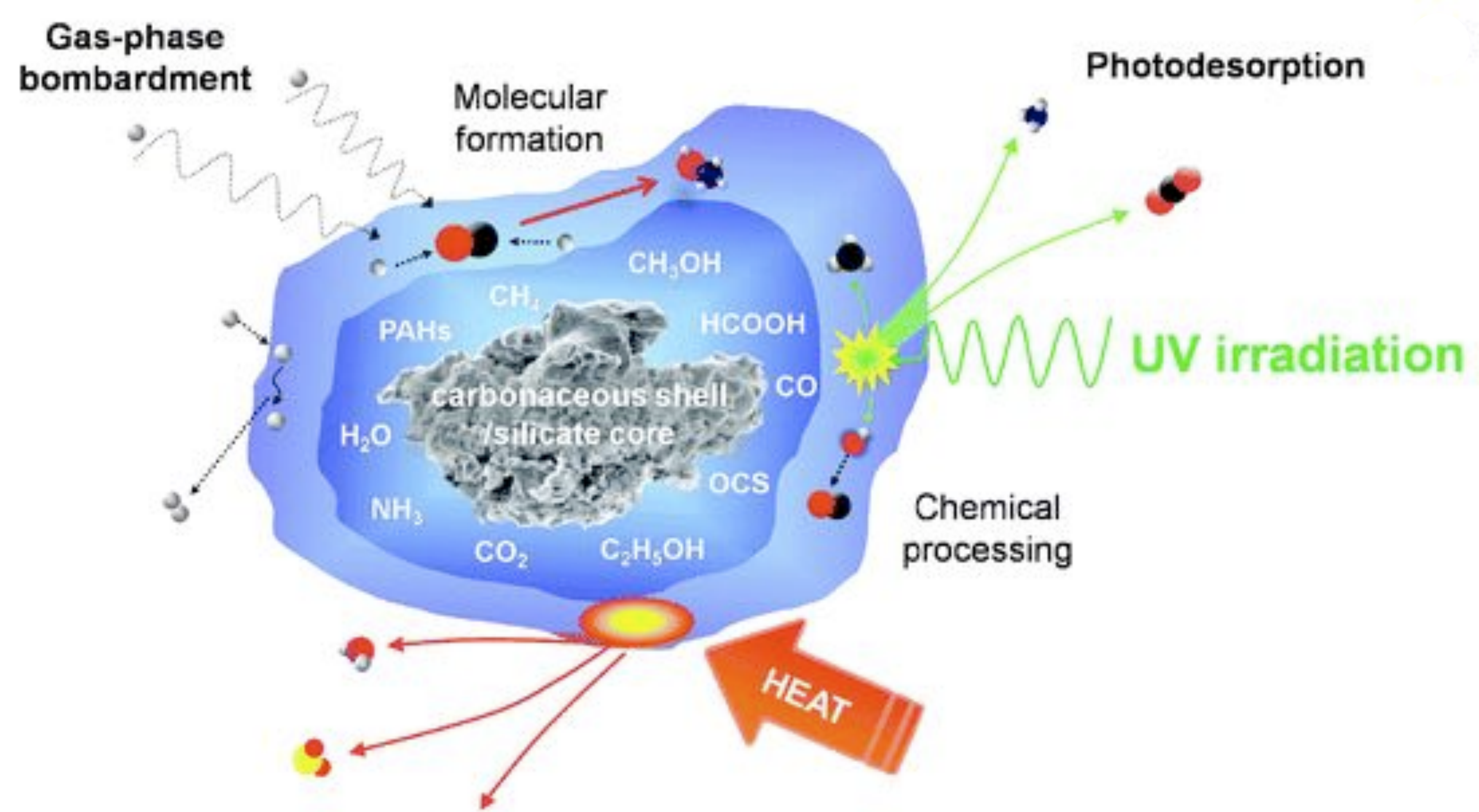
Glycine

Interstellar molecules and the seeds of life



8

Interstellar molecules and the seeds of life



Burke & Brown 2010

Outline

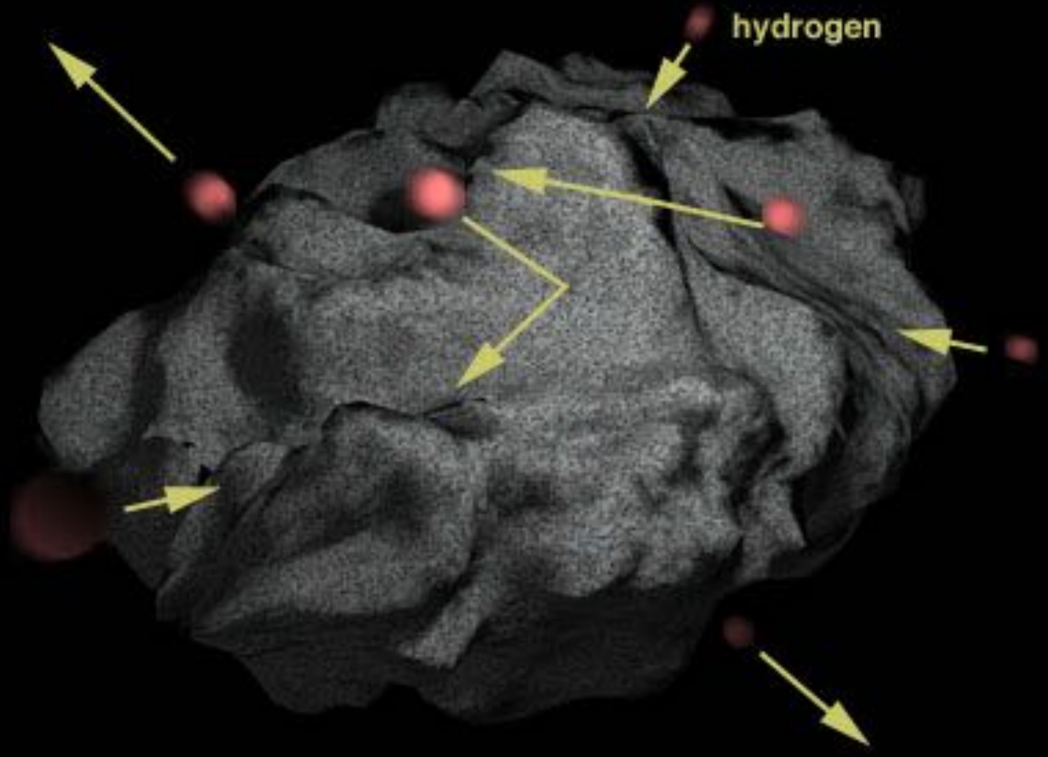
- Formation of H_2
- Formation of H_3^+
- Deuterium fractionation
- The ortho-to-para H_2 ratio
- SOFIA discovery of para-H_2D^+
- SOFIA and oxygen chemistry
- SOFIA and sulfur chemistry

The formation of H_2

The reaction that starts the chemistry in the interstellar medium is the one between two hydrogen atoms to form molecular hydrogen:

$$H + H \rightarrow H_2$$

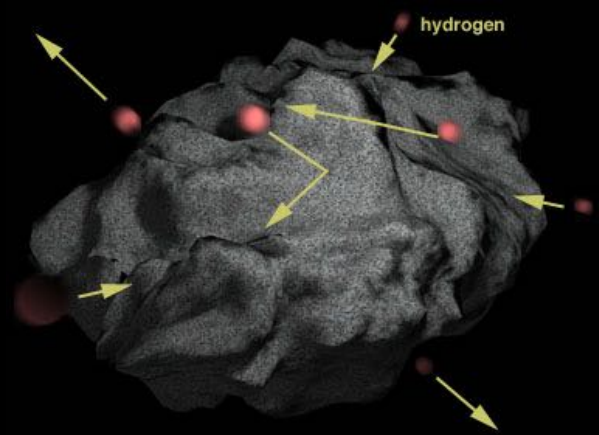
This reaction happens on the surface of dust grains.



11

The H_2 formation rate ($cm^{-3}\ s^{-1}$) is given by (e.g. Gould & Salpeter 1963; Hollenbach & Salpeter 1970; Jura 1974; Pirronello et al. 1999; Cazaux & Tielens 2002; Bergin et al. 2004; Cuppen & Herbst 2005; Cazaux et al. 2008):

$$R_{H_2} = \frac{1}{2} n_H v_H A n_g S_H \gamma$$
$$\cong 10^{-17} - 10^{-16}\ cm^{-3} s^{-1}$$



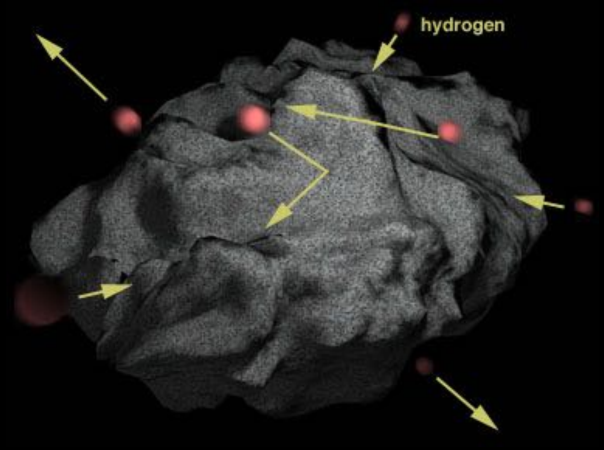
$n_H \equiv$ gas number density
$v_H \equiv$ H atoms speed in gas-phase
$A \equiv$ grain cross sectional area
$n_g \equiv$ dust grain number density
$S_H \equiv$ sticking probability
$\gamma \equiv$ surface reaction probability

12

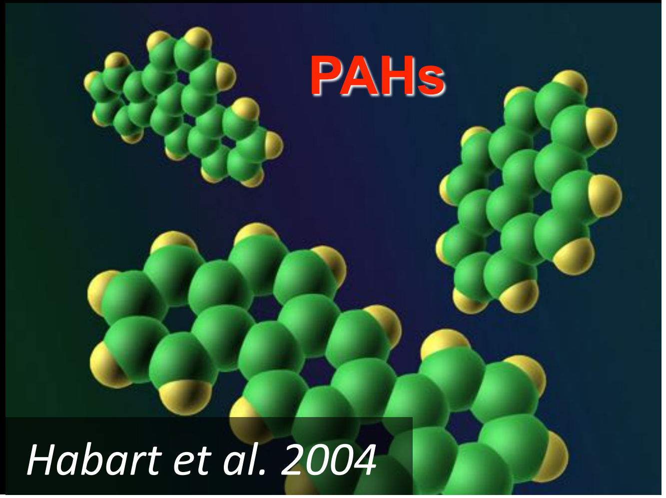
The H_2 formation rate ($cm^{-3}\ s^{-1}$) is given by (e.g. Gould & Salpeter 1963; Hollenbach & Salpeter 1970; Jura 1974; Pirronello et al. 1999; Cazaux & Tielens 2002; Bergin et al. 2004; Cuppen & Herbst 2005; Cazaux et al. 2008):

$$R_{H_2} = \frac{1}{2} n_H v_H A n_g S_H \gamma$$

$$\cong 10^{-17}\ -\ 10^{-16}\ cm^{-3}s^{-1}$$



$n_H \equiv$ gas number density
$v_H \equiv$ H atoms speed in gas-phase
$A \equiv$ grain cross sectional area
$n_g \equiv$ dust grain number density
$S_H \equiv$ sticking probability
$\gamma \equiv$ surface reaction probability



Habart et al. 2004

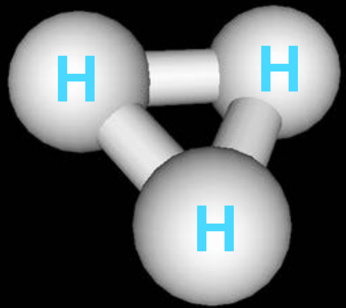
The formation of H_3^+

After the formation of molecular hydrogen, cosmic rays ionize H_2 initiating fast routes towards the formation of complex molecules in dark clouds:

$$H_2 + c.r. \rightarrow H_2^+ + e^- + c.r.$$

Once H_2^+ is formed (in small percentages), it very quickly reacts with the abundant H_2 molecules to form H_3^+, the most important molecular ion in interstellar chemistry:

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



Deuterium Fractionation at T < 20 K

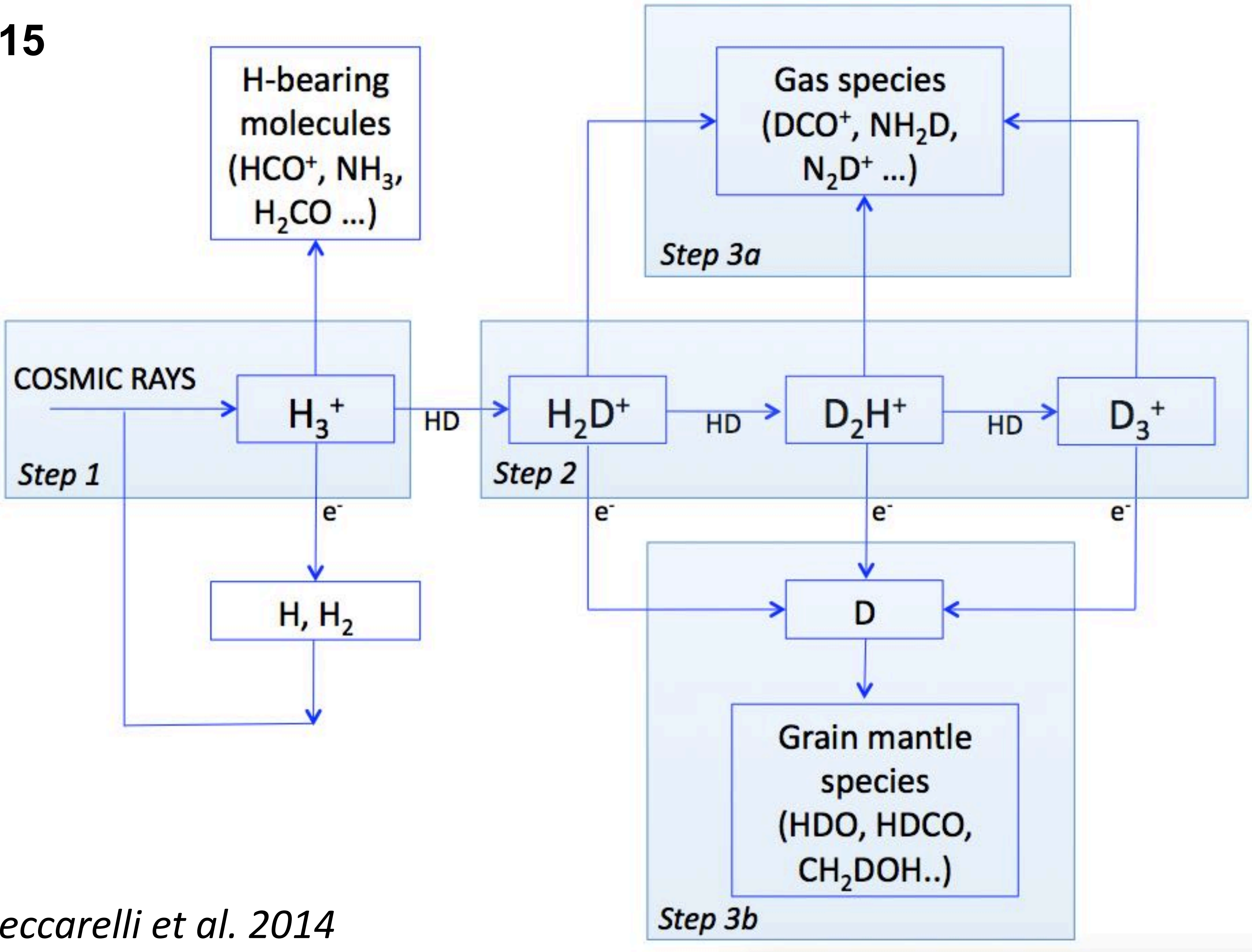
$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 230\ K$ (Watson 1974)

H_2D^+ / H_3^+ increases if the abundance of gas phase neutral species decreases (Dalgarno & Lepp 1984):

LOWER H_2D^+ and H_3^+ destruction rates	+	HIGHER H_2D^+ formation rate	=	LARGER H_2D^+/H_3^+ abundance ratio and deuterium fractionation

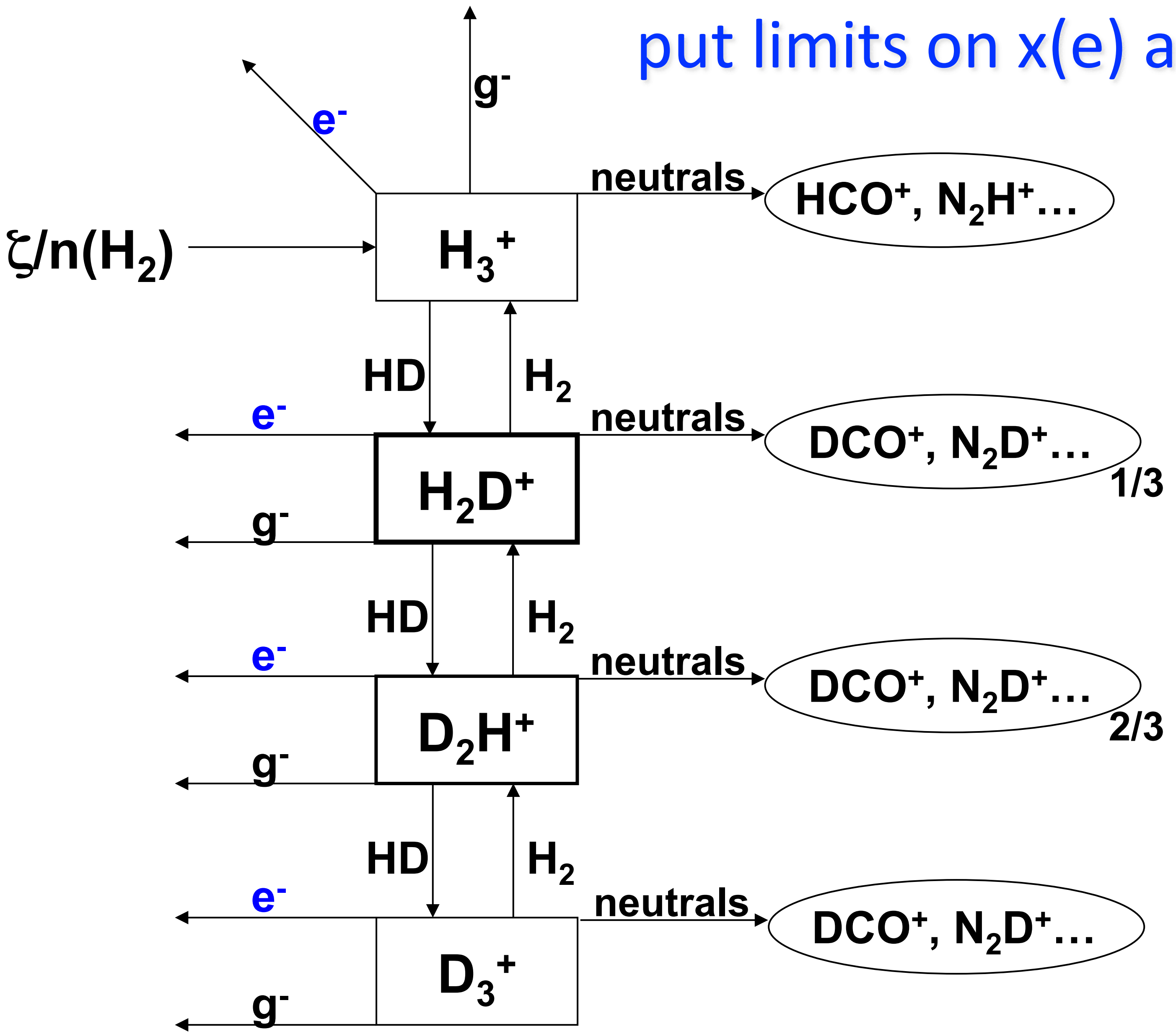
$H_2D^+ + CO \longrightarrow DCO^+ + H_2$

$H_2D^+ + N_2 \longrightarrow N_2D^+ + H_2$



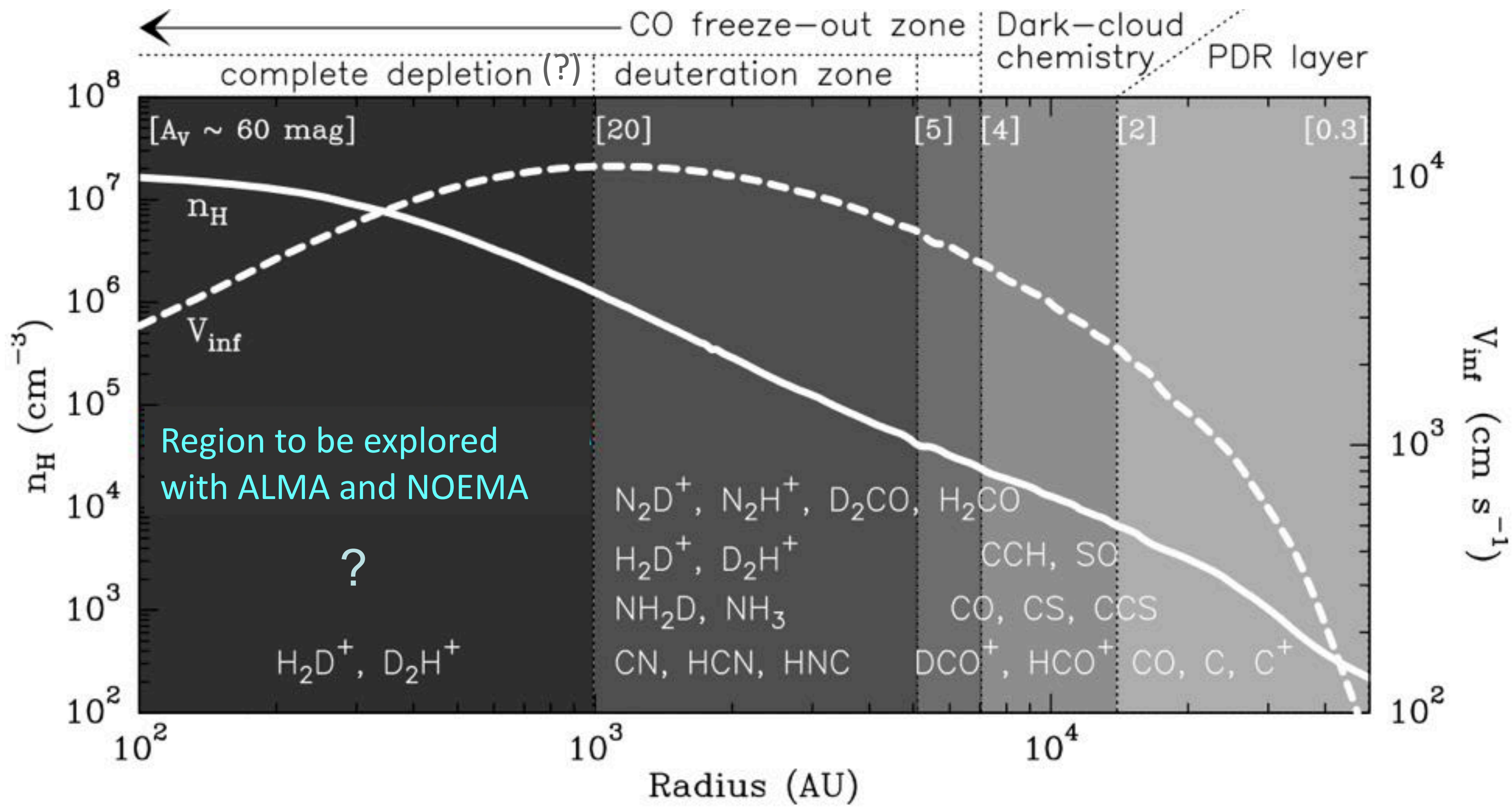
Ceccarelli et al. 2014

Deuterated molecular ions put limits on x(e) and ζ



Guelin et al. 1977
Wootten et al. 1979
Guelin et al. 1982
Bergin et al. 1998
Caselli et al. 1998
Dalgarno 2006

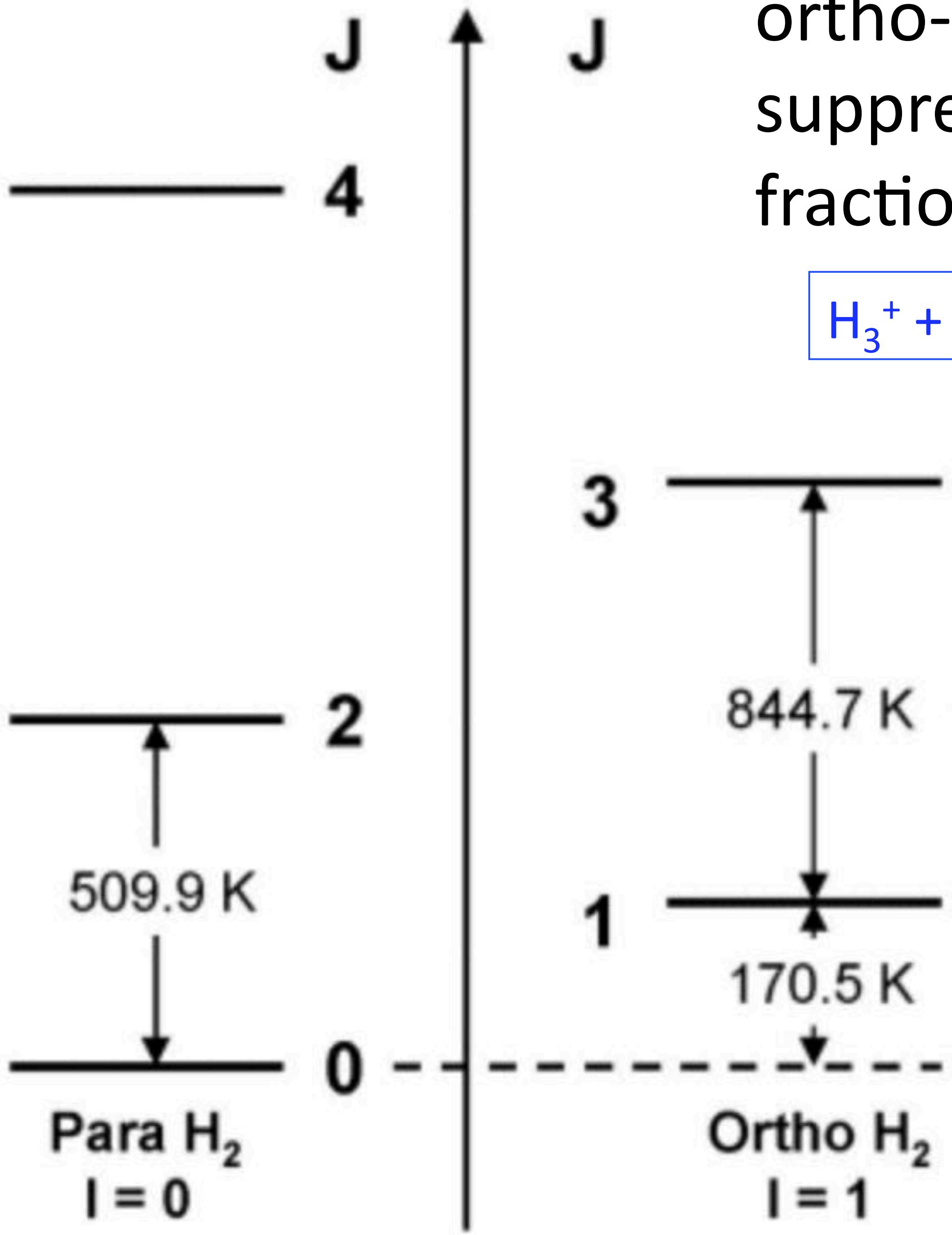
Deuterated molecules are the best tracers of pre-stellar cores



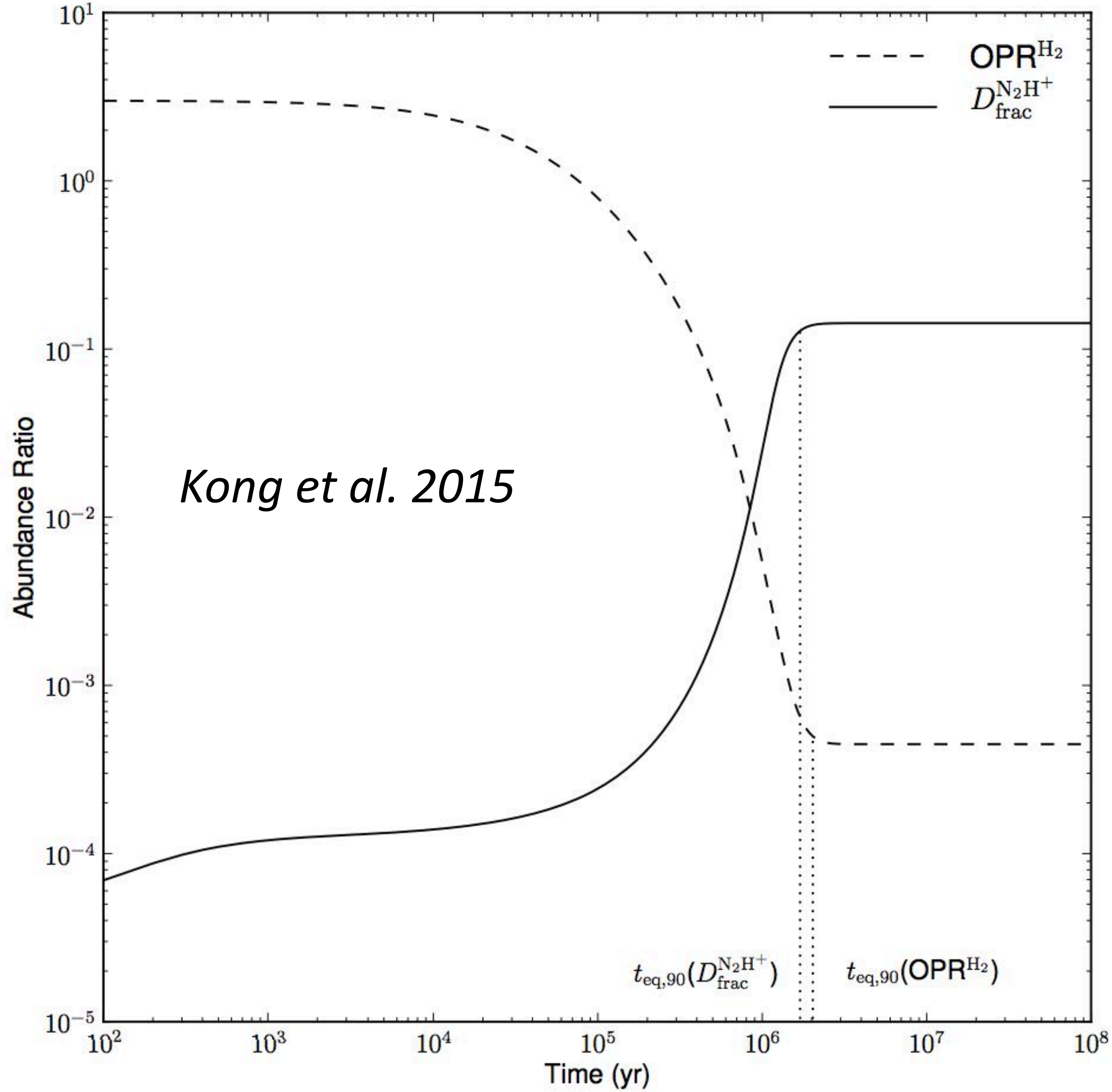
Caselli 2011, IAU 280

ortho-H_2 can slow down / suppress the deuterium fractionation

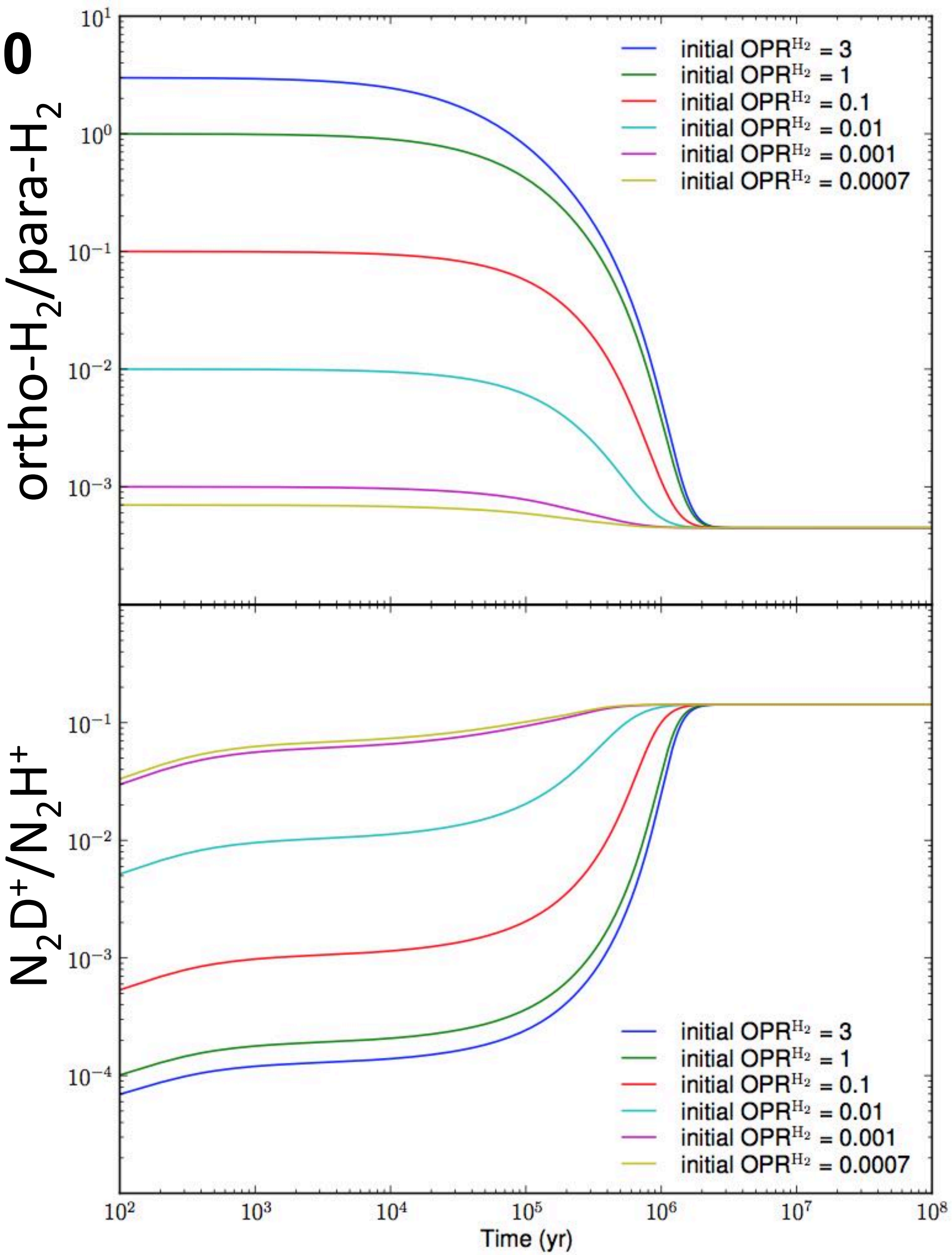
$H_3^+ + HD \longleftrightarrow H_2D^+ + H_2 + 230\ K$



Pagani et al. 1992
Gerlich et al. 2002
Hugo et al. 2009
Kong et al. 2015



OPR^{H_2}
$D_{frac}^{N_2H^+}$
Kong et al. 2015
Abundance Ratio
Time (yr)
$t_{eq,90}(D_{frac}^{N_2H^+})$
$t_{eq,90}(OPR^{H_2})$
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^2
10^3
10^4
10^5
10^6
10^7
10^8



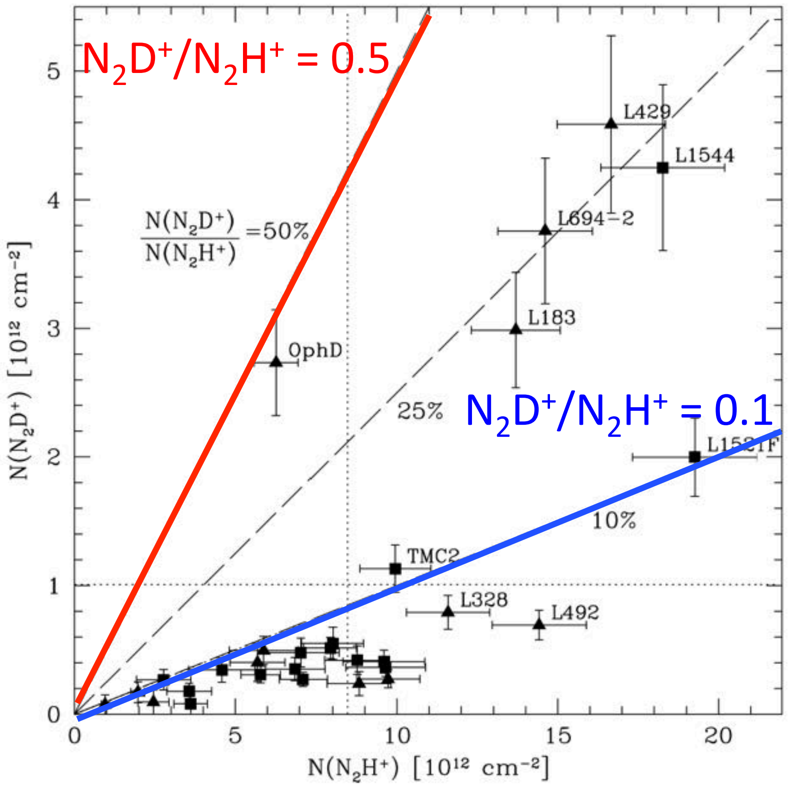
The conversion from ortho to para H_2 is a slow process and it is required to explain the observed large deuterium fractions.

$D_{frac} > 0.1$, requires collapse to be proceeding at rates about 10 times slower than that of free-fall collapse.

Kong et al. 2015

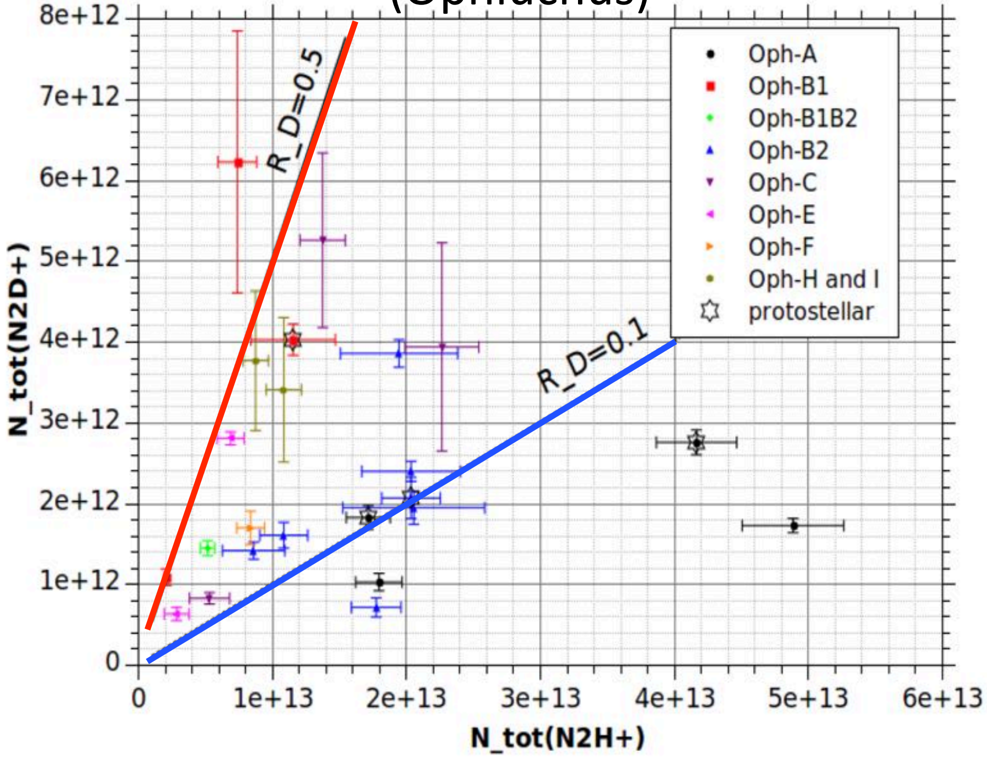
Large (variations of) deuterium fractions

Cores in different molecular clouds



Crapsi et al. 2005

Cores in the same molecular cloud (Ophiuchus)



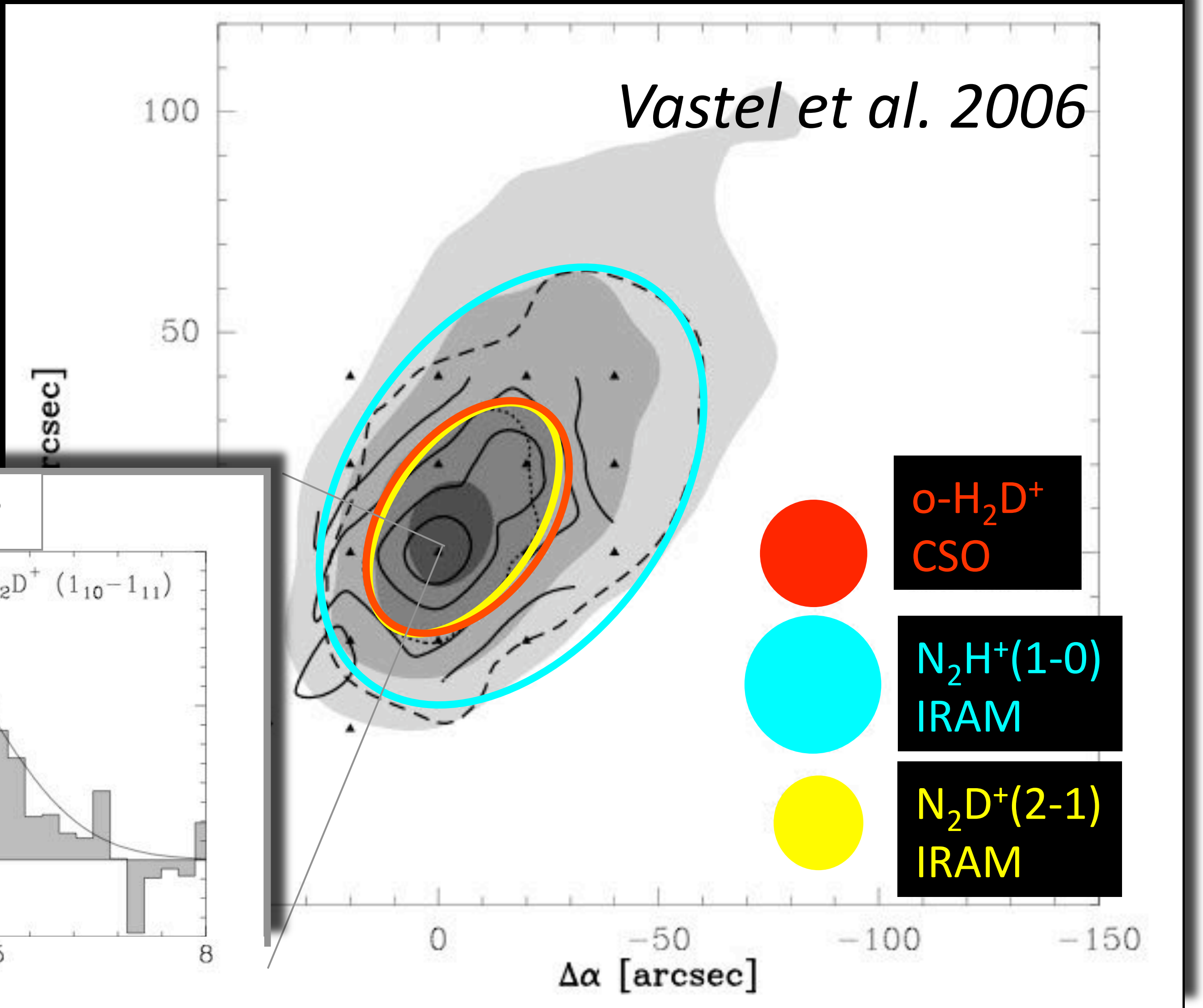
Punanova et al., in prep.

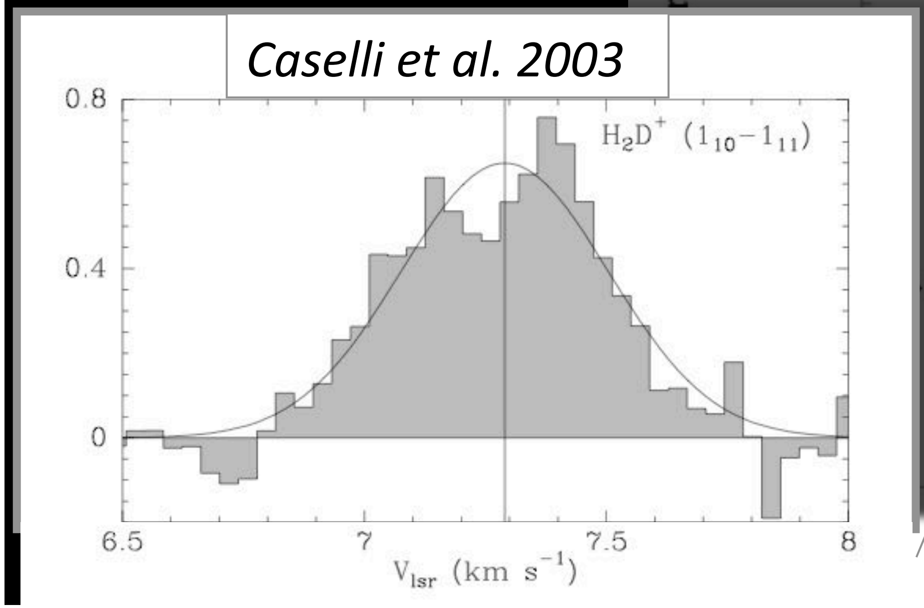
See also Friesen et al. 2010; Friesen, Kirk & Shirley 2013; Schnee et al. 2013

ortho-H_2D^+

The 372 GHz o-H_2D^+ line is strong; its emission is extended ~5000 AU

Only models including all multiply deuterated forms of H_3^+ can reproduce these data (Roberts et al. 2003; Walmsley et al. 2004; Aikawa et al. 2005)



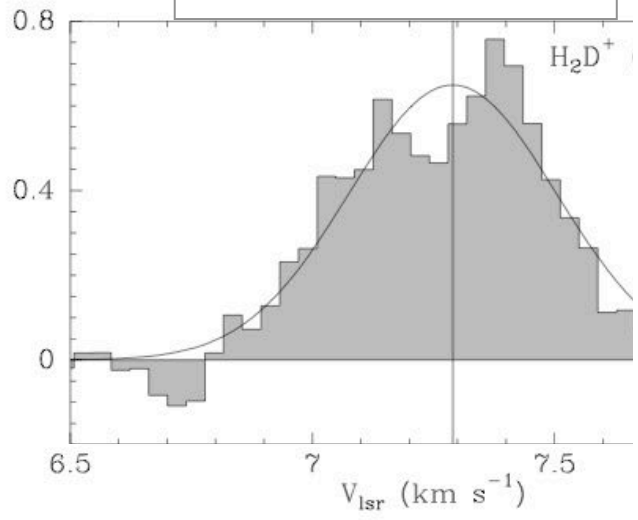


ortho-H_2D^+

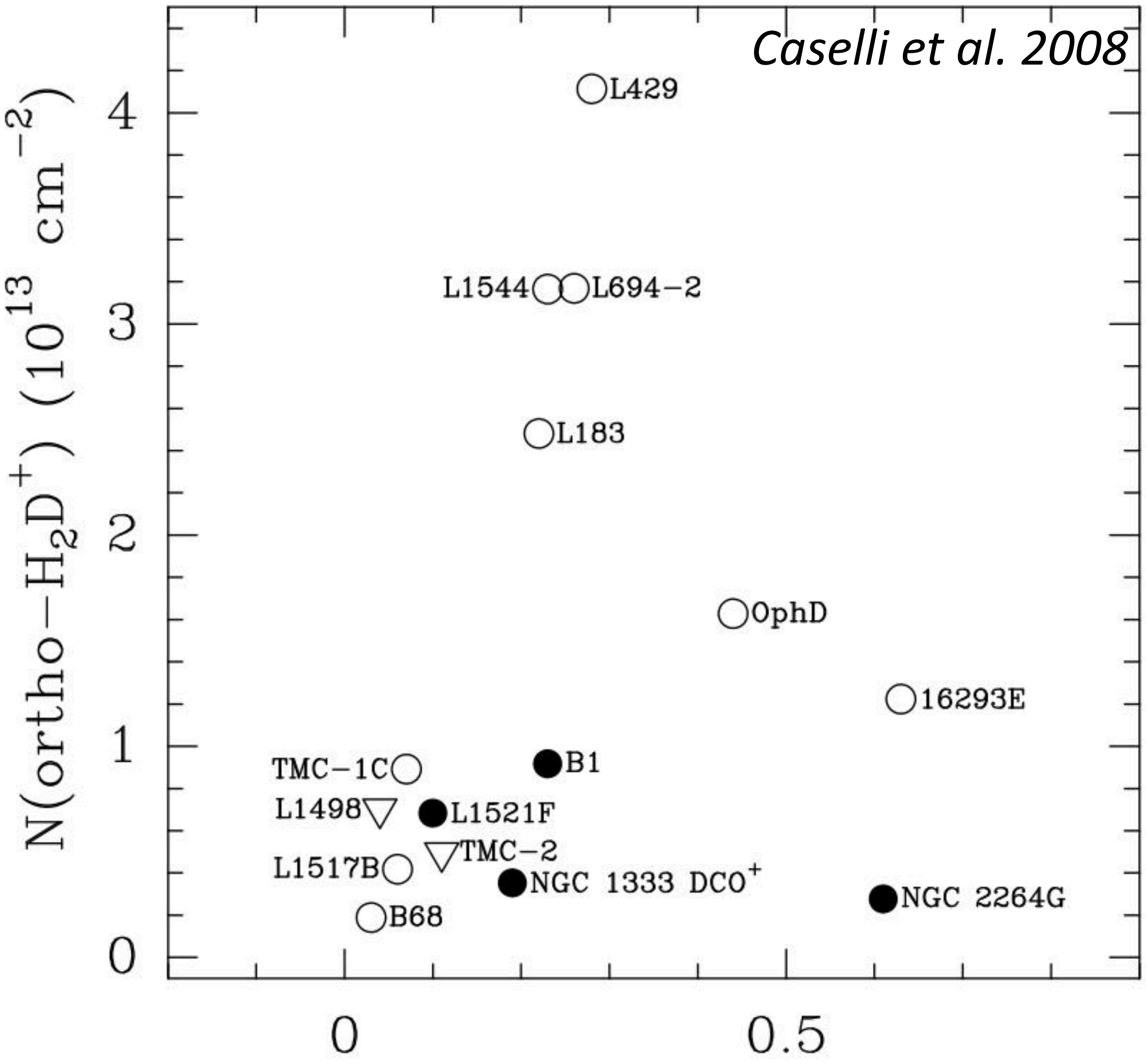
The 372 GHz o-H_2D^+ line

Only models including all multiply deuterated forms of H_3^+ can reproduce these data (Roberts et al. 2003; Walmsley et al. 2004; Aikawa et al. 2005)

Caselli et al. 2003



Caselli et al. 2008

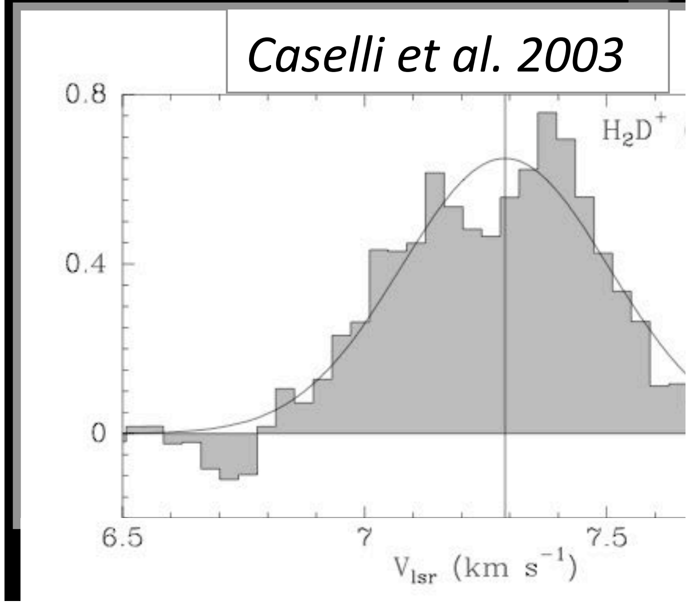


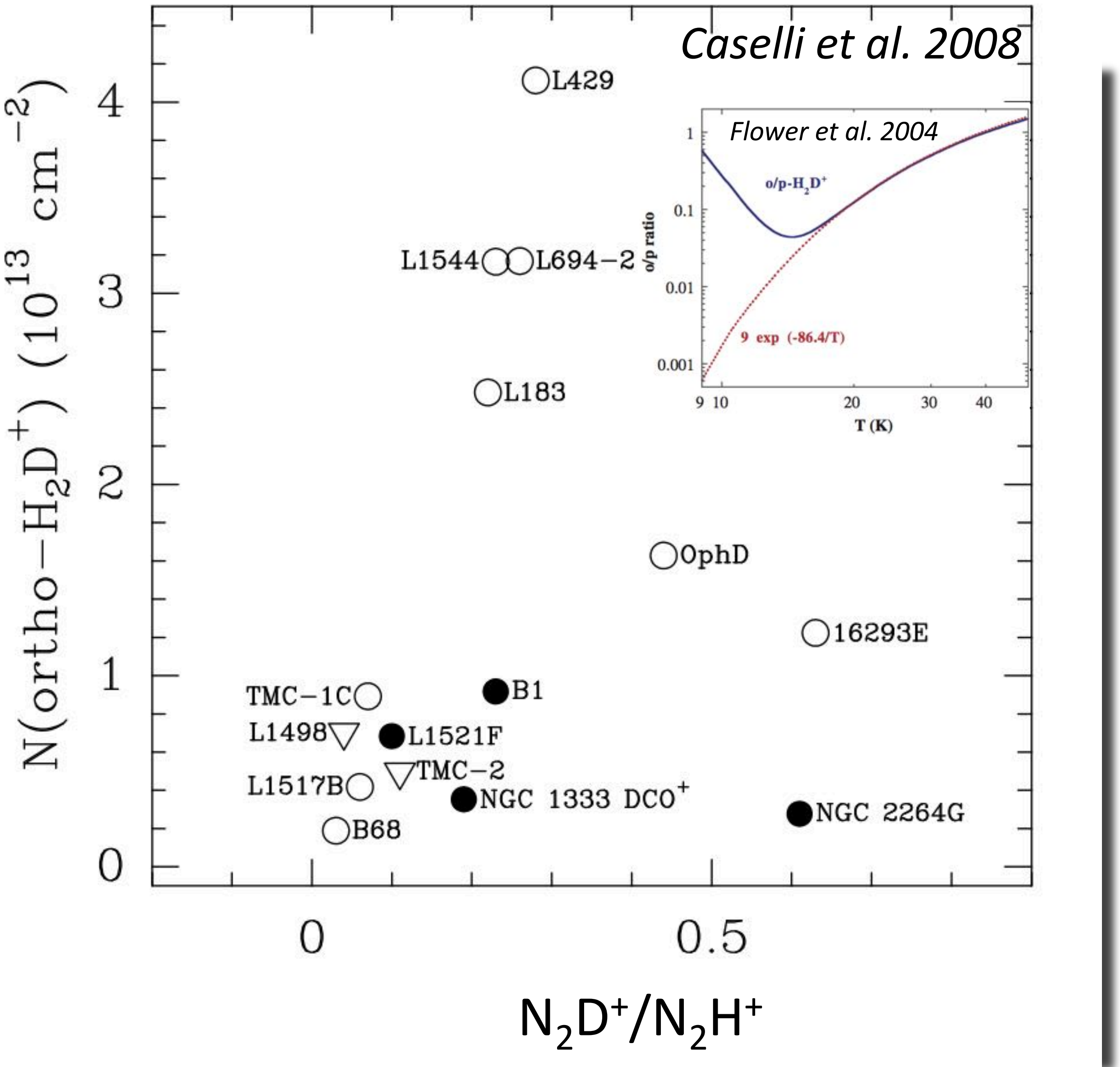
N_2D^+/N_2H^+

ortho-H_2D^+

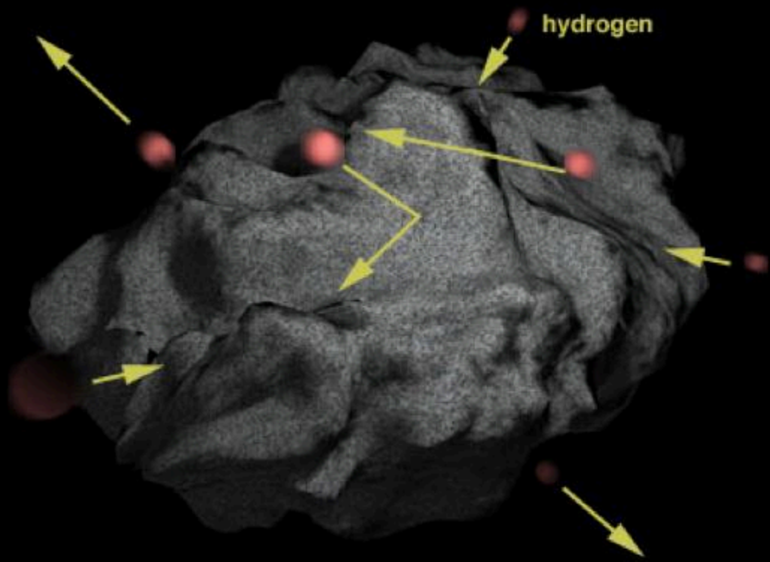
The 372 GHz o-H_2D^+ line

Only models including all multiply deuterated forms of H_3^+ can reproduce these data (Roberts et al. 2003; Walmsley et al. 2004; Aikawa et al. 2005)





How much ortho-H_2 is in molecular clouds?



Upon formation: $oH_2/pH_2 = 3$

In diffuse clouds: $oH_2/pH_2 \sim 0.3\text{-}0.8$ *(Crabtree et al. 2011)*

In the pre-stellar core L183: $oH_2/pH_2 \sim 0.1$ *(Pagani et al. 2009)*

In the starless core B68: $oH_2/pH_2 \sim 0.015$ *(Maret & Bergin 2007)*

In the pre-stellar core L1544: $oH_2/pH_2 \sim 0.003$ *(Kong et al. 2015)*

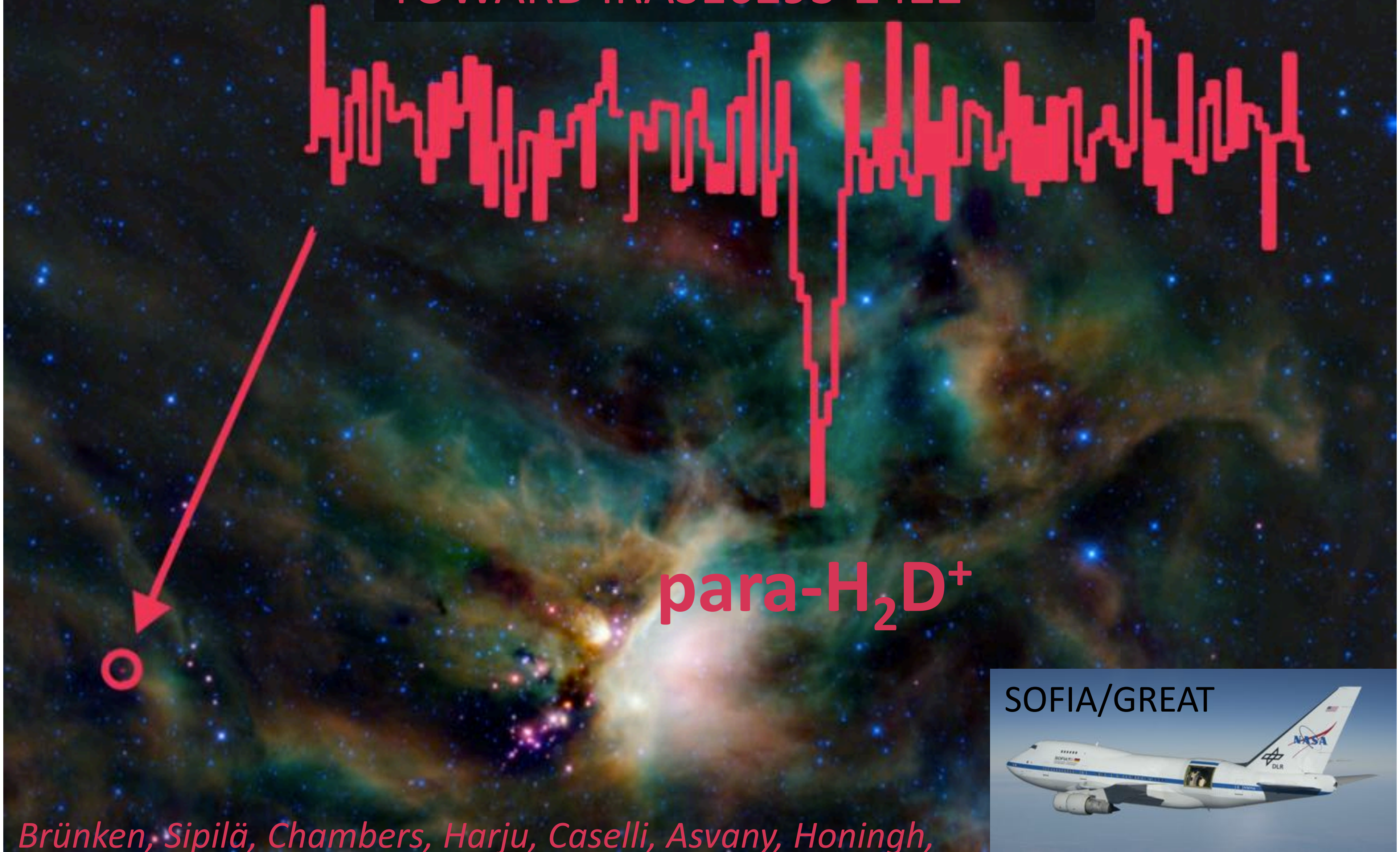
Analytical relation between the H_2 and H_2D^+ ortho-to-para ratios

$$\text{p-}H_2D^+ + \text{o-}H_2 \overset{k_1}{\Leftrightarrow} \text{o-}H_2D^+ + \text{p-}H_2$$
$$\text{o-}H_2D^+ + \text{o-}H_2 \overset{k_2}{\Leftrightarrow} \text{p-}H_2D^+ + \text{p-}H_2$$
$$\text{o-}H_2D^+ + \text{o-}H_2 \overset{k_3}{\Leftrightarrow} \text{p-}H_2D^+ + \text{o-}H_2$$

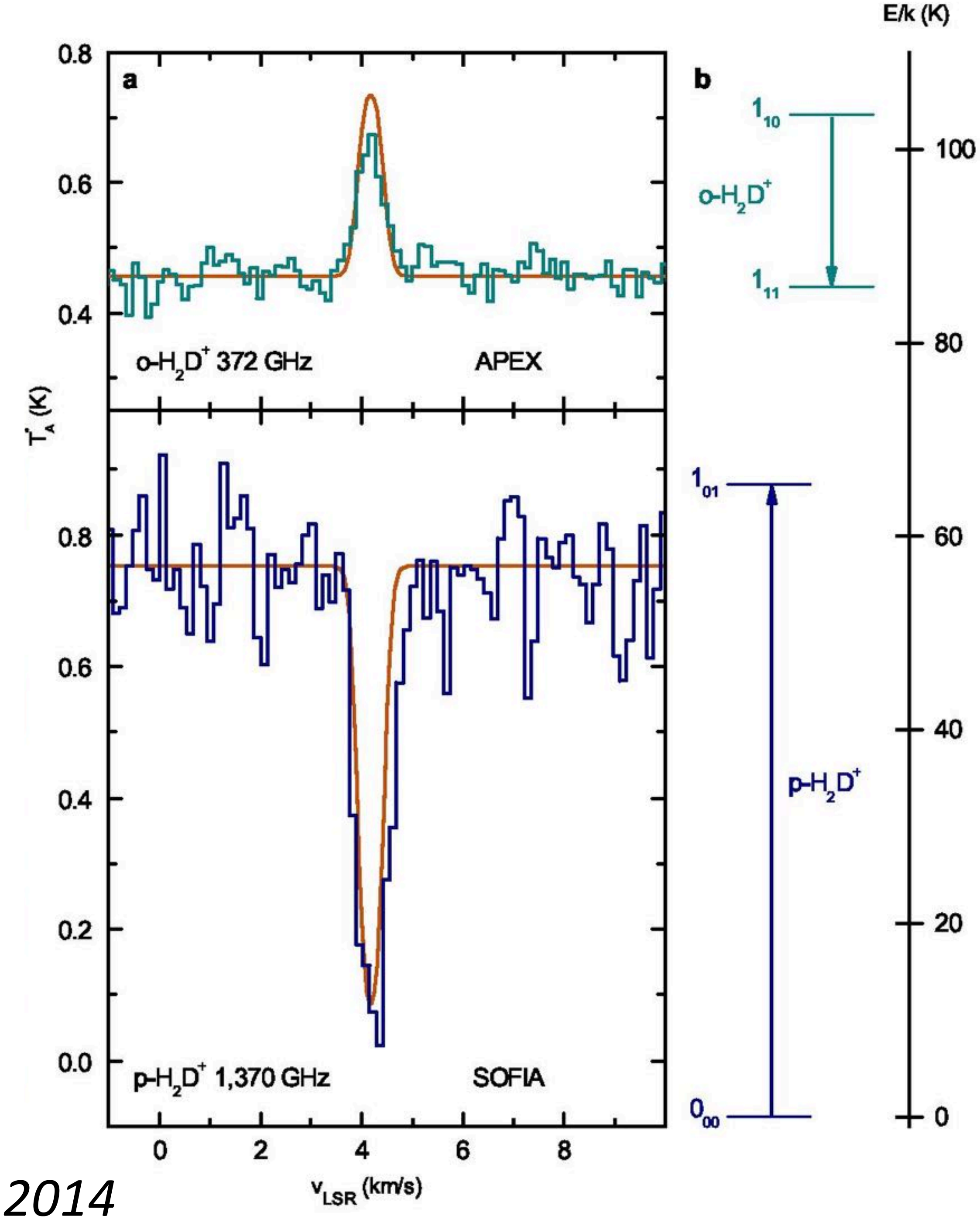
$$\frac{[\text{o-}H_2D^+]}{[\text{p-}H_2D^+]} = \frac{(k_1^+ + k_3^-)\times[\text{o-}H_2]/[\text{p-}H_2] + k_2^-}{(k_2^+ + k_3^+)\times[\text{o-}H_2]/[\text{p-}H_2] + k_1^-}$$

Hugo et al. 2009; Brünken et al. 2014

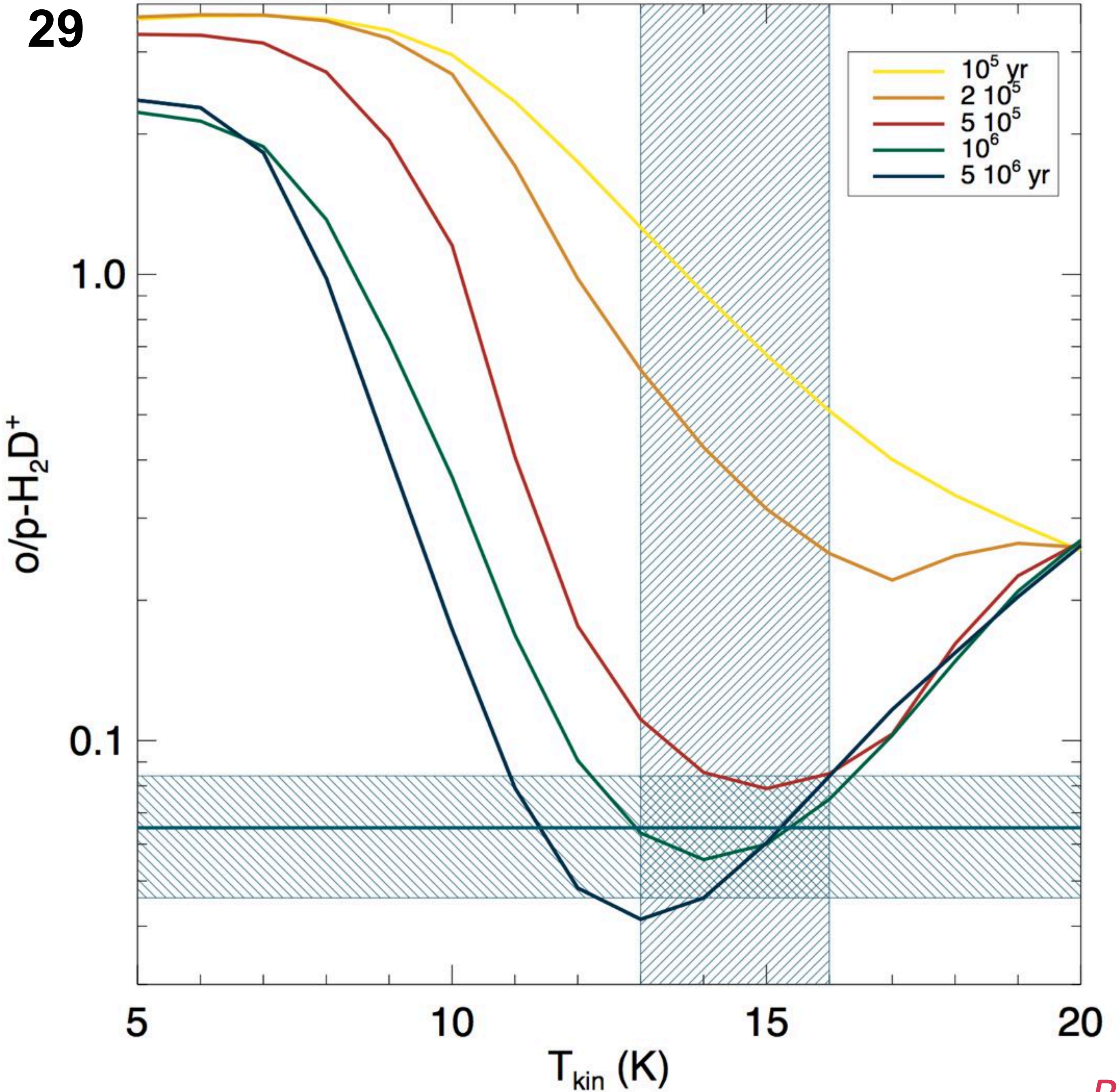
FIRST DETECTION OF para-H_2D^+ TOWARD IRAS16293-2422



Brünken, Sipilä, Chambers, Harju, Caselli, Asvany, Honingh, Kamiński, Menten, Stutzki, Schlemmer 2014, Nature

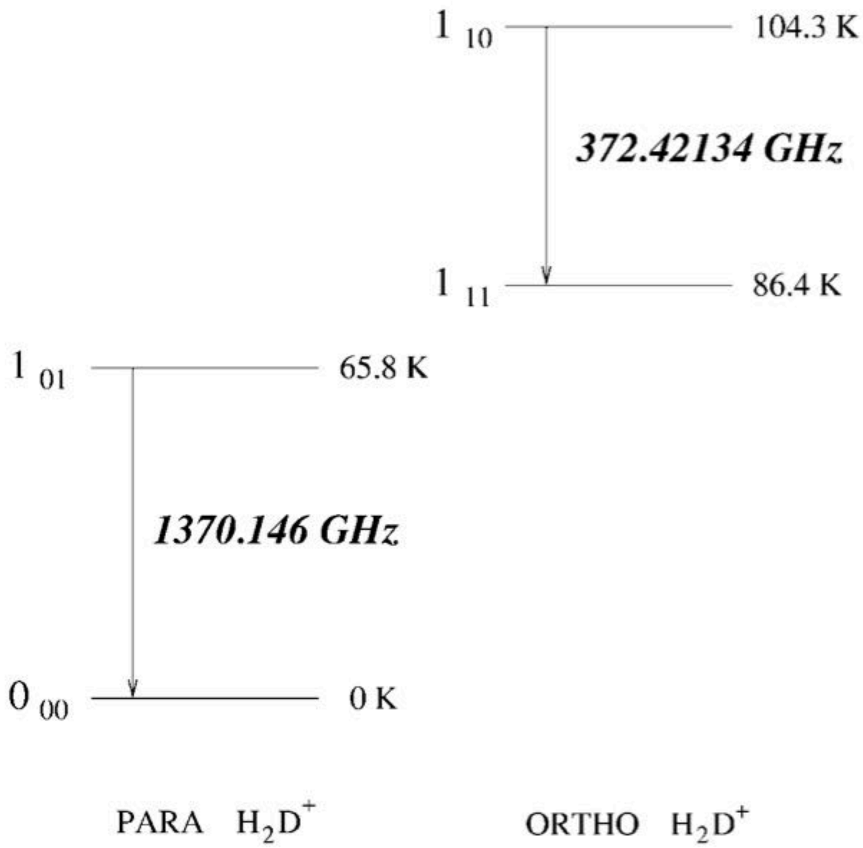


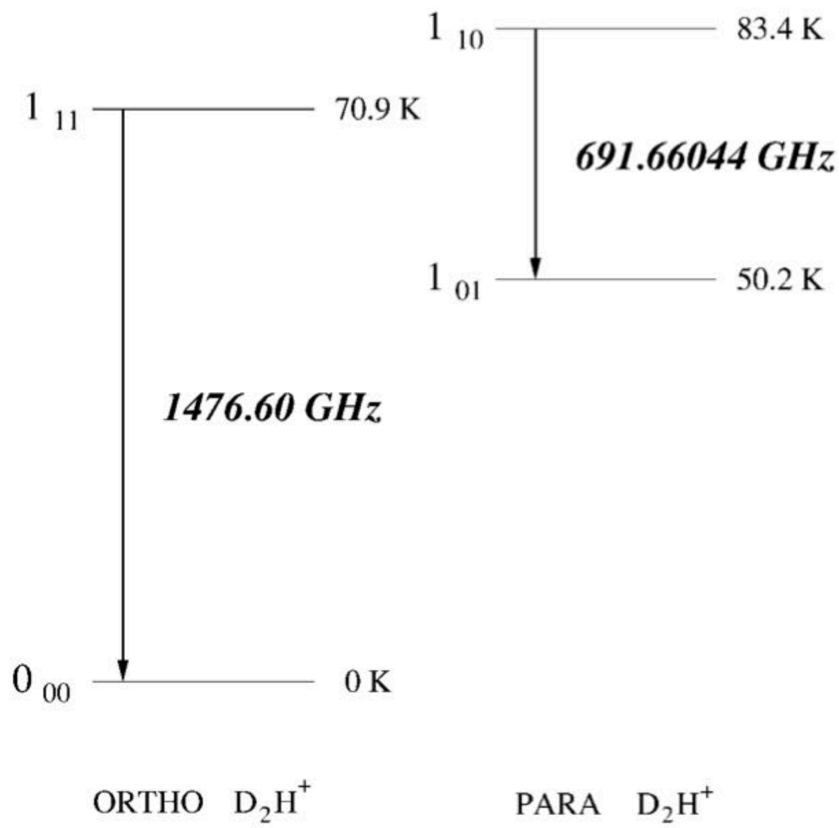
Brünken et al. 2014



The molecular gas in the cool envelope has been subject to chemical processing for at least one million years.

Brünken et al. 2014

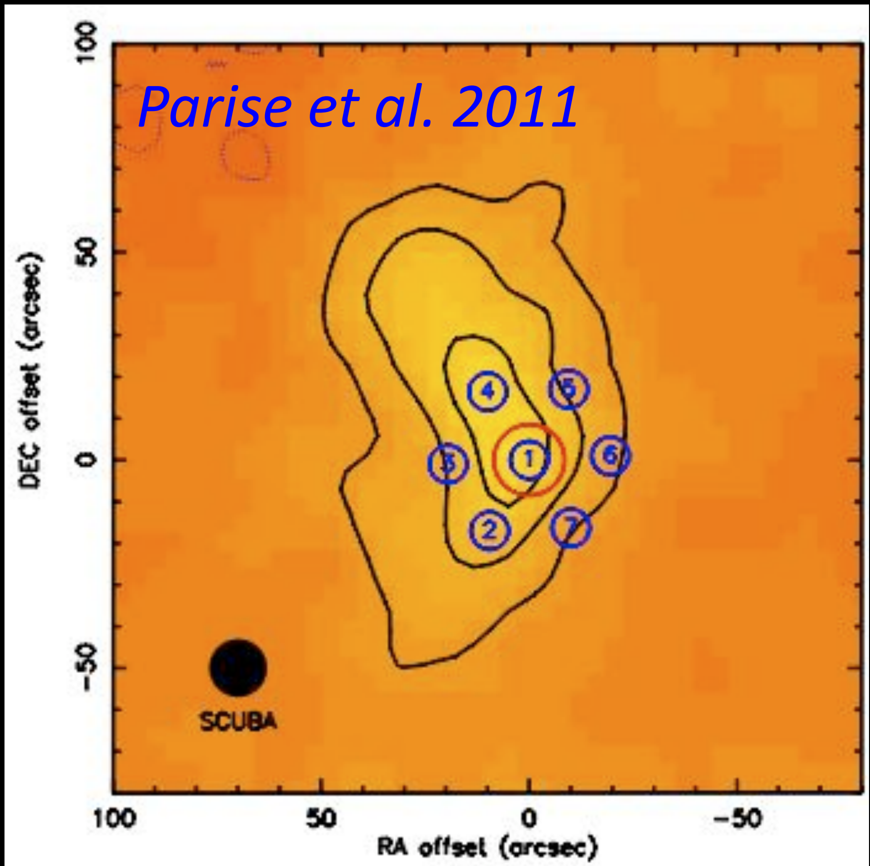


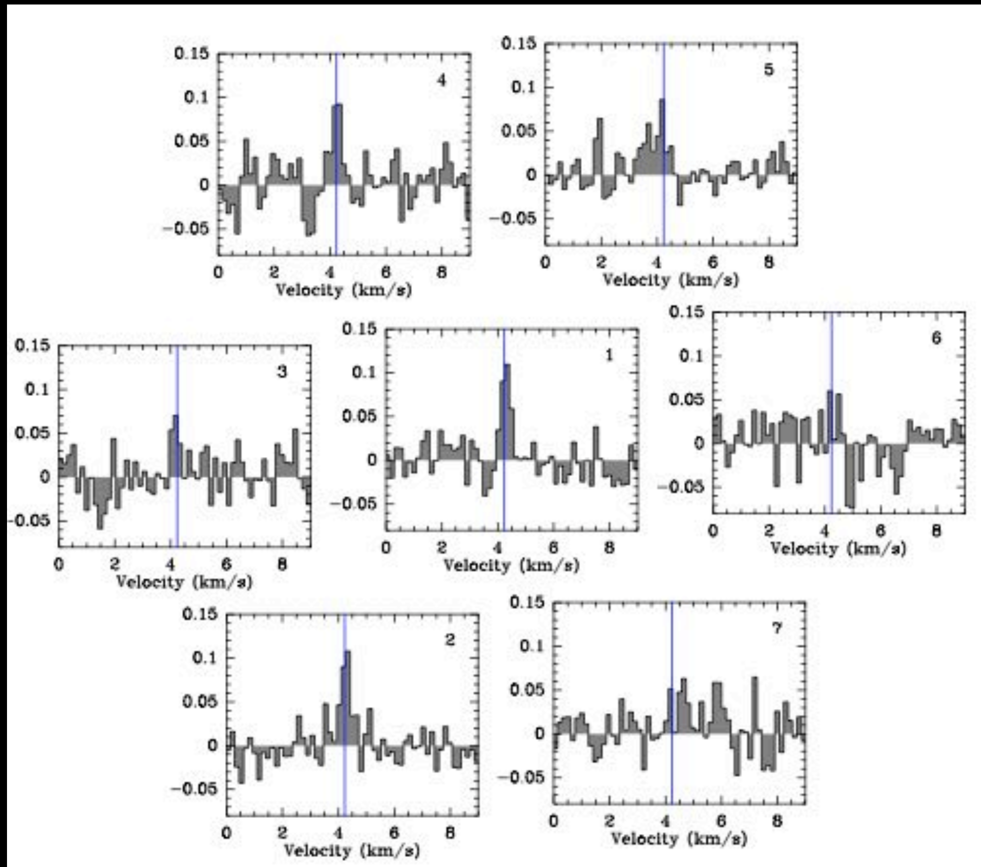


from Vastel et al. 2004

para-D_2H^+

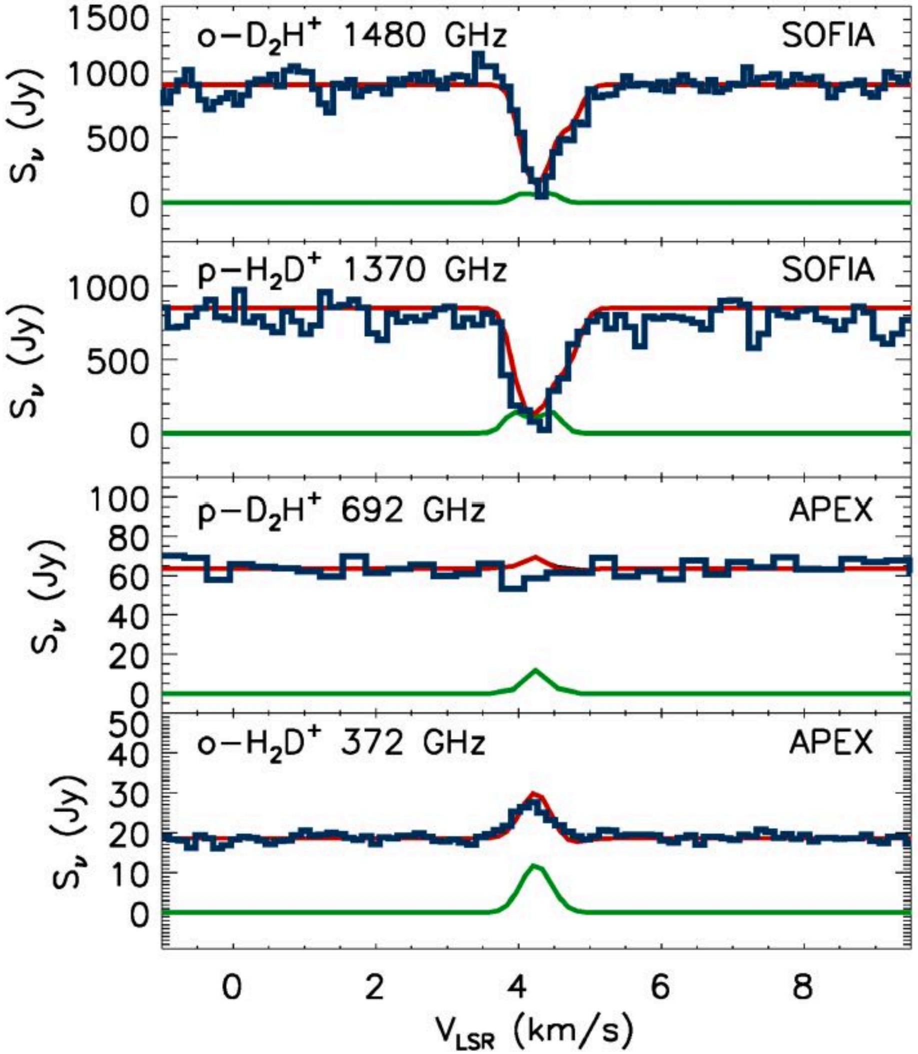
Extended para-D_2H^+ emission (~40'' ~5000 AU) toward L1688/H-MM1 (692 GHz; APEX-CHAMP+)

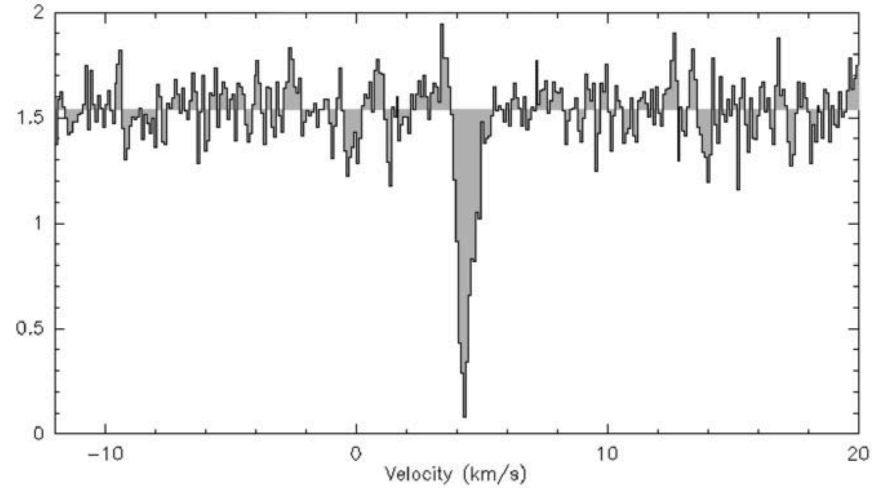


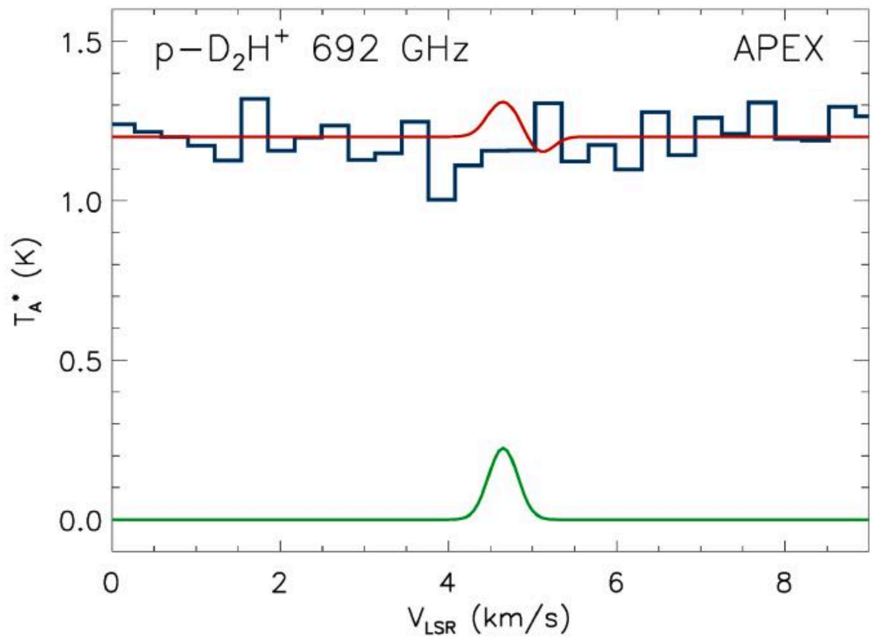


See Vastel et al. (2004) for first detection of para-D_2H^+

ortho-D_2H^+ with SOFIA







Harju, Brünken et al., in prep.

Ro-vibrational lines

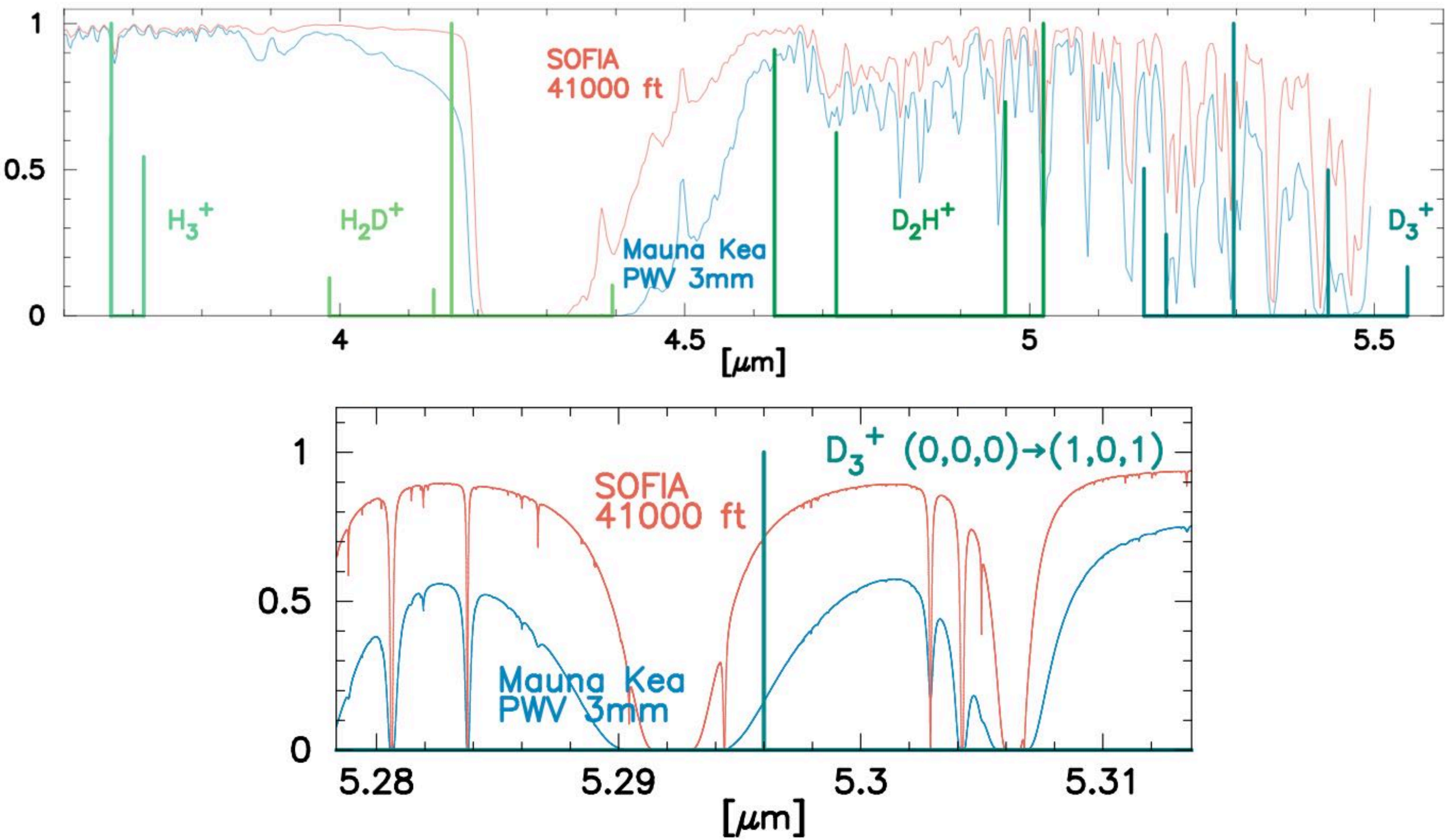
Table 3. Requisite column densities for unit optical depth in the absorption line centre for the deuterated forms of H_3^+. Spectroscopic data from Ramanlal & Tennyson (2004).

Species	Upper level	Lower level	E_l (cm^{-1})	Wavelength (μm)	$N_{\tau=1}$ (cm^{-2})
H_2D^+ (para)	(1, 1, 1)[a]	(0, 0, 0)	0.0	4.162	1.9×10^{14}
H_2D^+ (ortho)	(0, 0, 0)	(1, 1, 1)	60.0	4.395	6.1×10^{14}
H_2D^+ (ortho)	(2, 0, 2)	(1, 1, 1)	60.0	4.136	7.1×10^{14}
H_2D^+ (ortho)	(2, 2, 0)	(1, 1, 1)	60.0	3.985	4.9×10^{14}
D_2H^+ (ortho)	(1, 1, 1)	(0, 0, 0)	0.0	4.965	4.7×10^{14}
D_2H^+ (ortho)	(1, 0, 1)	(0, 0, 0)	0.0	4.72	5.5×10^{14}
D_2H^+ (para)	(1, 1, 0)	(1, 0, 1)	34.9	5.02	6.9×10^{14}
D_2H^+ (para)	(2, 0, 2)	(1, 0, 1)	34.9	4.63	7.6×10^{14}
D_3^+ (ortho)	(0, 1, 1, 0, 1)[b]	(0, 0, 0, 0, 0)	0.0	5.296	2.2×10^{13}
D_3^+ (meta)	(0, 1, 0, 1, 1)	(0, 0, 1, 1, 0)	32.3	5.548	1.6×10^{14}
D_3^+ (meta)	(0, 1, 2, 1, −1)	(0, 0, 1, 1, 0)	32.3	5.198	9.9×10^{13}
D_3^+ (meta)	(0, 1, 2, 1, 1)	(0, 0, 1, 1, 0)	32.3	5.166	9.1×10^{13}
D_3^+ (para)	(0, 1, 1, 0, −1)	(0, 0, 1, 0, 0)	43.6	5.433	4.5×10^{14}

[a] (J, K_a, K_c).
[b] (v_1, v_2, J, G, U).

Flower et al. 2004

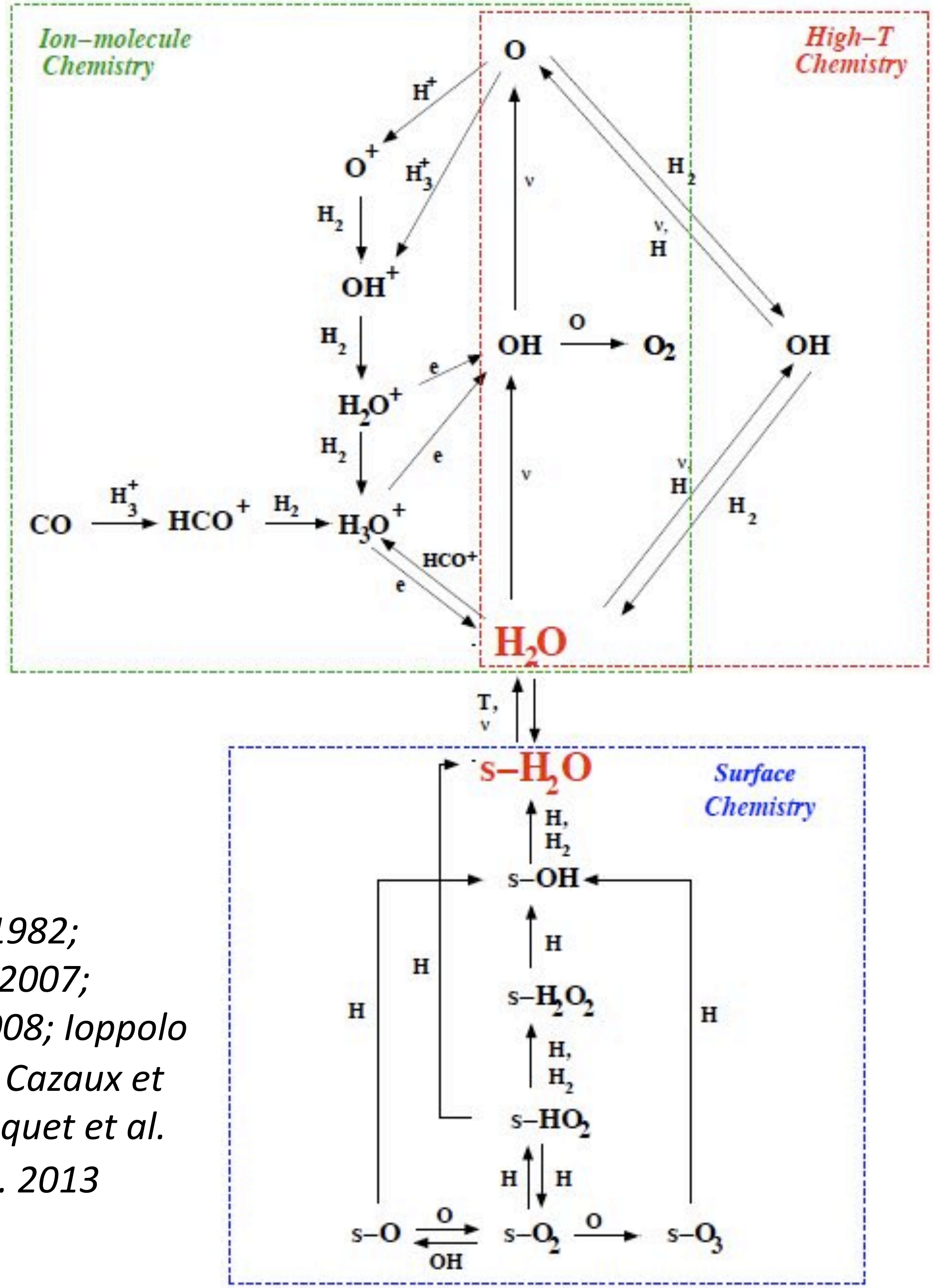
Ro-vibrational lines

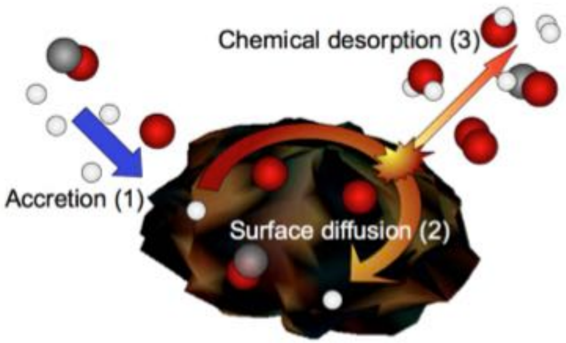


From SOFIA/EXES proposal of Goto et al.

Oxygen Chemistry

van Dishoeck et al. 2011, 2014

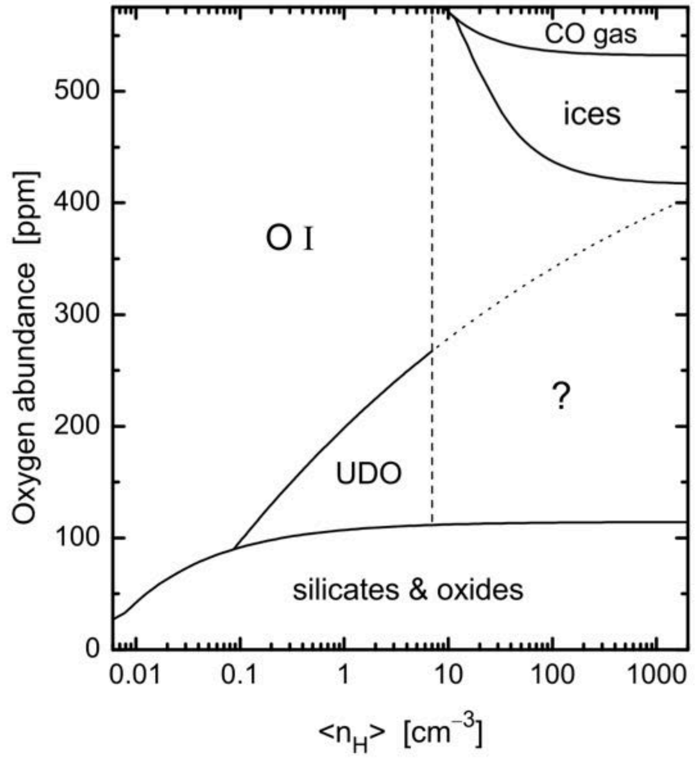


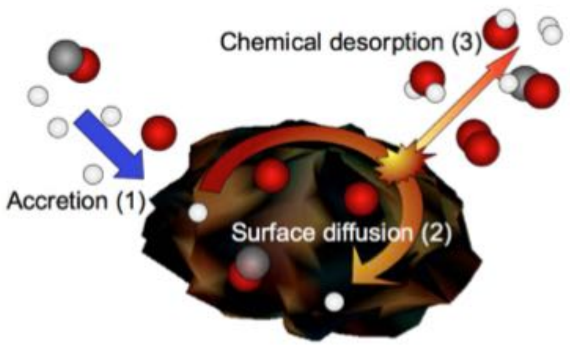


Tielens & Hagen 1982; Cuppen & Herbst 2007; Miyauchi et al. 2008; Ioppolo et al. 2008, 2010; Cazaux et al. 2010, 2011; Taquet et al. 2013; Dulieu et al. 2013

36 Oxygen Chemistry

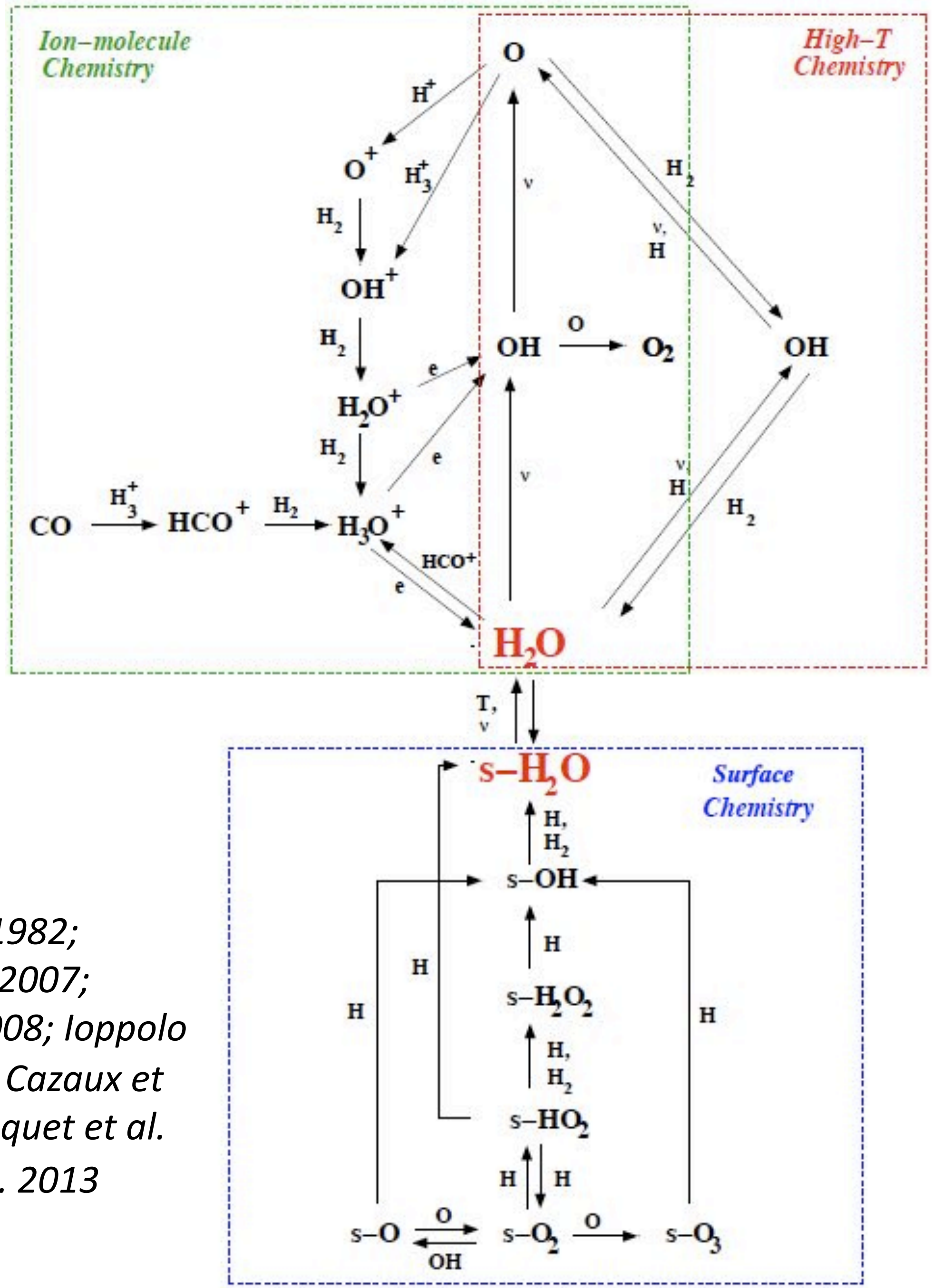
Whittet 2009; Jenkins 2009





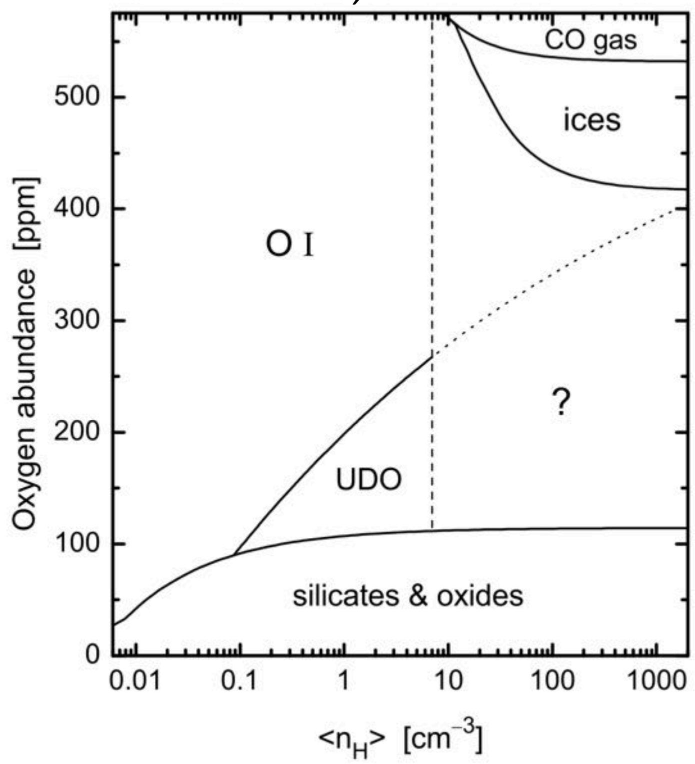
Tielens & Hagen 1982; Cuppen & Herbst 2007; Miyauchi et al. 2008; Ioppolo et al. 2008, 2010; Cazaux et al. 2010, 2011; Taquet et al. 2013; Dulieu et al. 2013

van Dishoeck et al. 2011, 2014

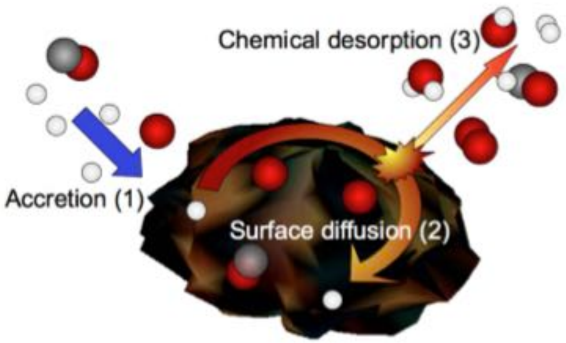


Oxygen Chemistry

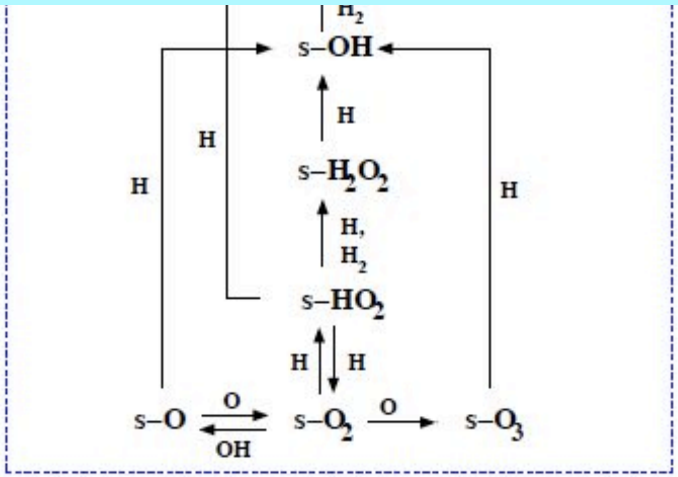
Whittet 2009; Jenkins 2009



It will be important in the future to obtain spectra of the highest quality for stars in lines of sight that sample diffuse-ISM dust over a range of visual extinctions, especially in the waveband containing the 5.85μm carbonyl feature as it should provide the most sensitive quantitative test for oxygenated organics. Both the ***Stratospheric Observatory for Infrared Astronomy*** *and the James Webb Space Telescope will have instruments well matched to this task. –* ***Whittet 2009***

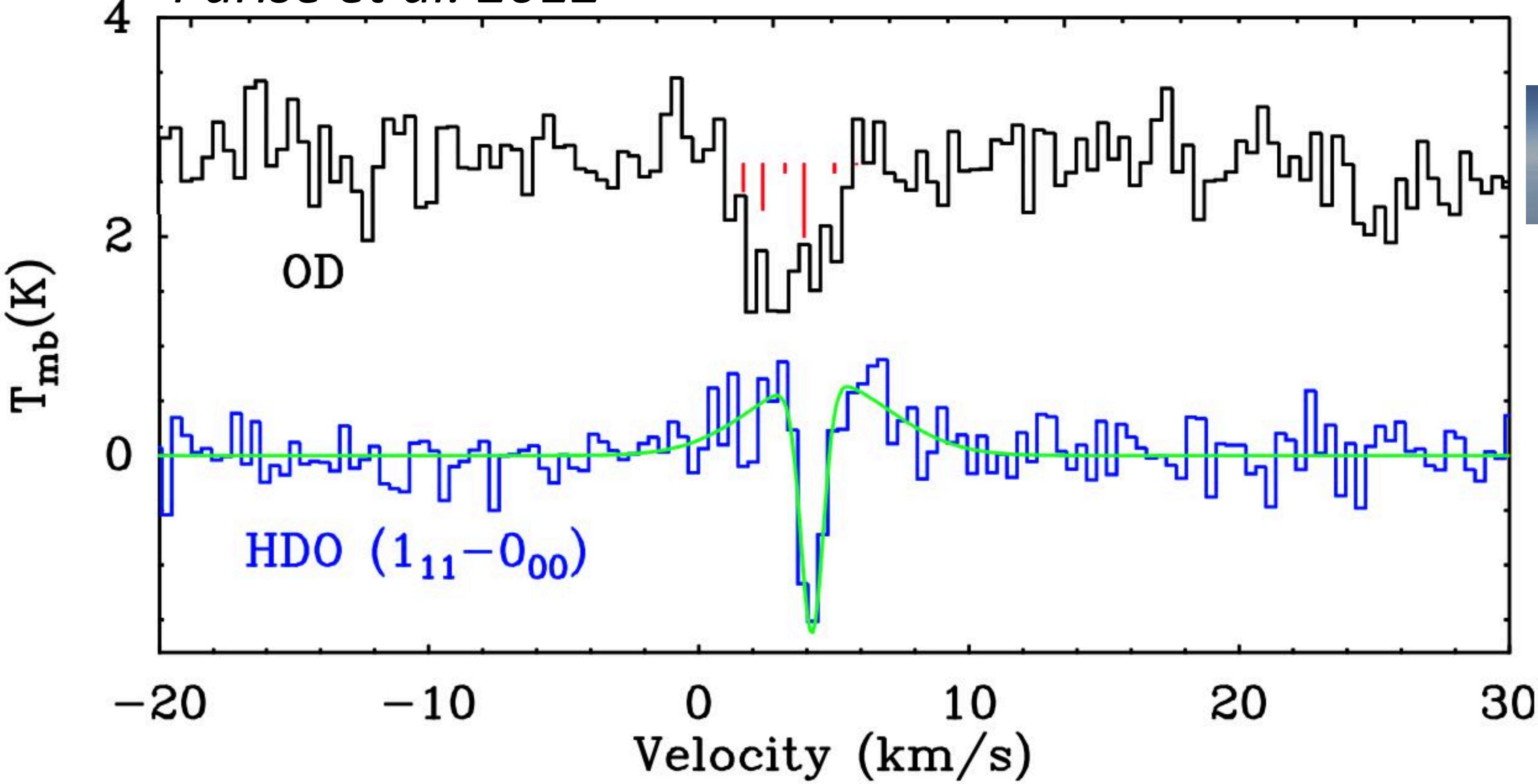


Tielens & Hagen 1982; Cuppen & Herbst 2007; Miyauchi et al. 2008; Ioppolo et al. 2008, 2010; Cazaux et al. 2010, 2011; Taquet et al. 2013; Dulieu et al. 2013



First detection of OD outside the Solar System

Parise et al. 2012



OD/HDO between 17 and 90 (high compared to model predictions ➔ gas phase reprocessing through dissociative recombination of H_2DO^+?)

Parallel observations of OD and OH could provide valuable constraints on the formation and fractionation of water.

The mercapto radical

- Cold SH is unobservable from the ground
- The "ground state" rotational transition

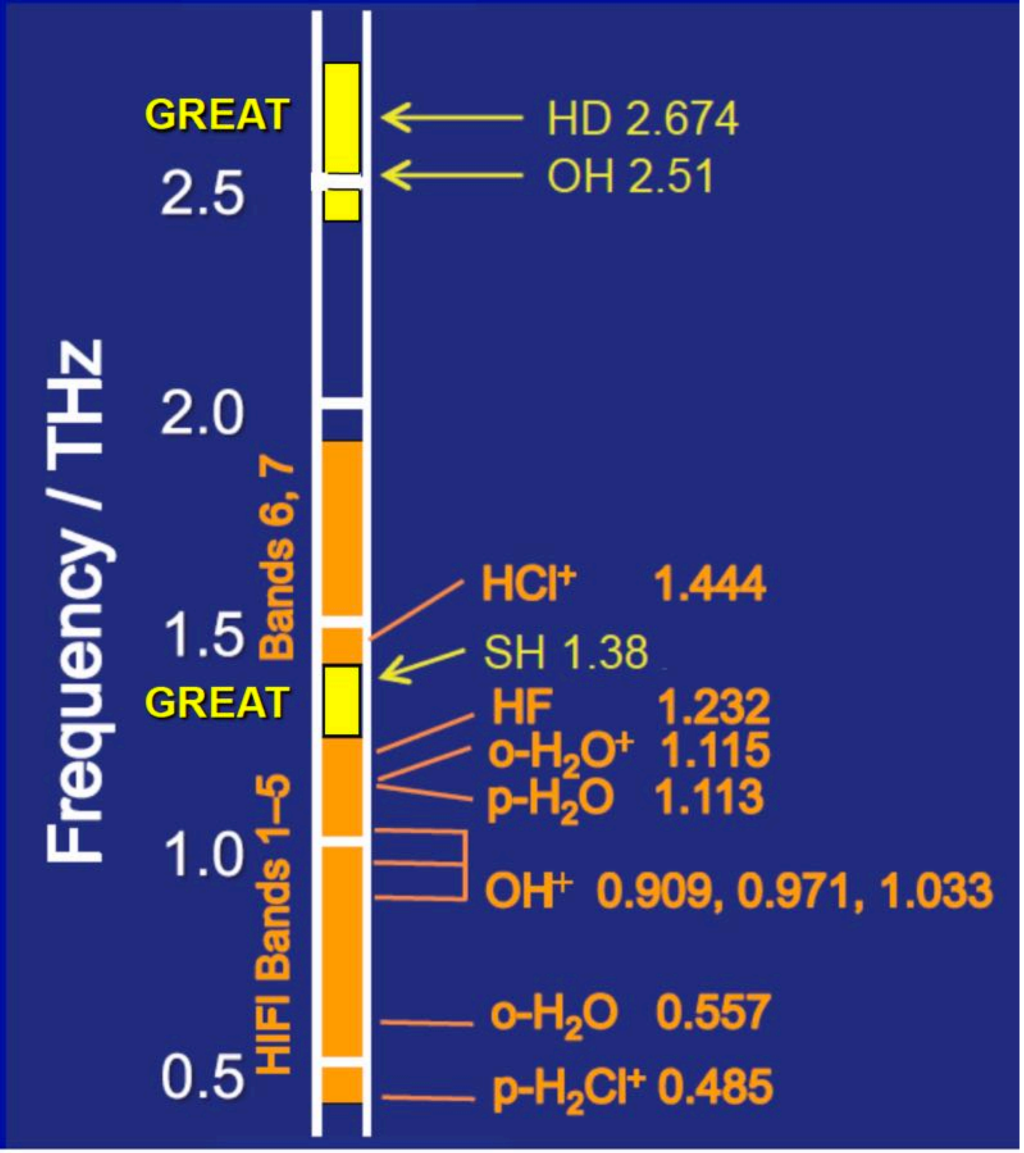
$^2\Pi_{3/2}$ J= 5/2 → 3/2 at 1.383 THz

falls right in the gap between Bands 5 and 6 of *Herschel*'s HIFI spectrometer

Courtesy of David Neufeld

The mercapto radical

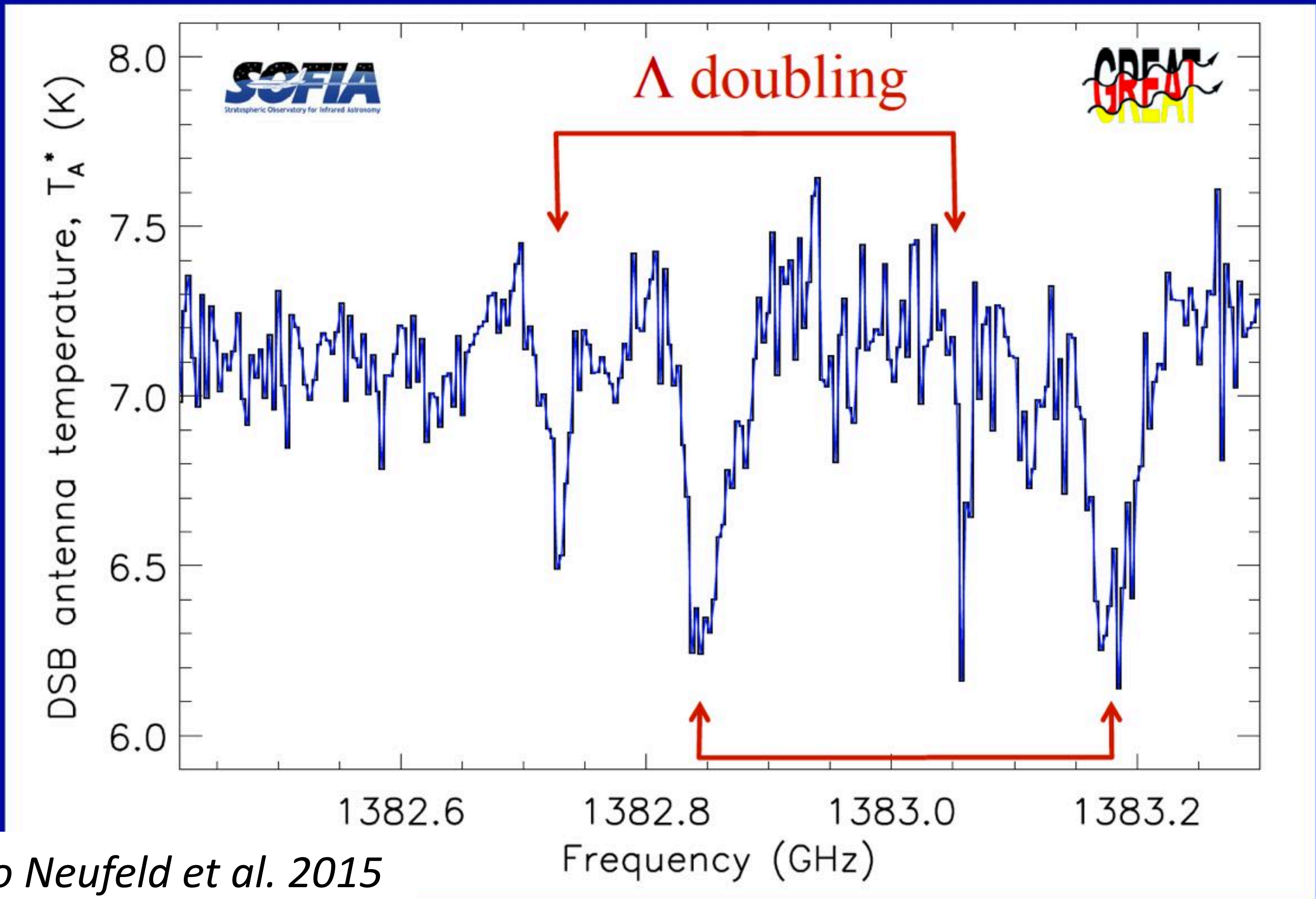
- The GREAT (German REceiver for Astronomy at Terahertz frequencies) spectrometer on SOFIA has a receiver designed to cover this gap in *Herschel*/HIFI coverage (1250 – 1410 GHz)



Courtesy of David Neufeld

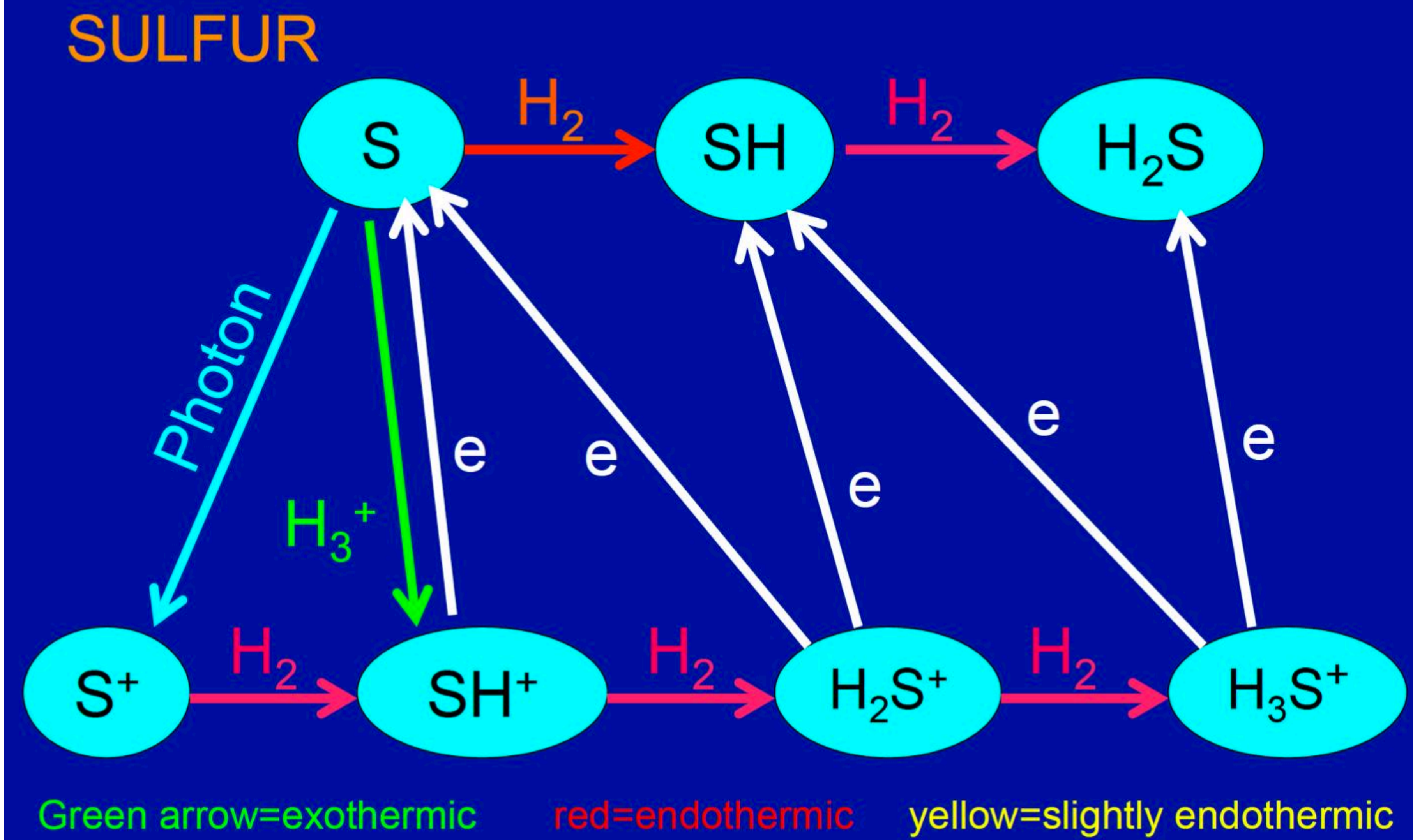
Cycle 0: SH clearly detected in absorption toward W49N

Neufeld et al. 2012, A&A



See also Neufeld et al. 2015

Underlying thermochemistry



Courtesy of David Neufeld

Underlying thermochemistry

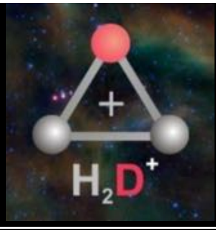
OH and H_2O can be produced via two pathways:

- Low temperature: ion-molecule reactions, then dissociative recombination of H_3O^+
- High temperature: neutral-neutral reactions

SH and H_2S are only produced at elevated temperatures:

- Their presence is evidence for shocks or turbulent dissipation regions

Courtesy of David Neufeld



Summary

With **SOFIA** we can explore the foundations of astrochemistry:

• the deuteration of H_3^+ via HD – the starting point of D fractionation

• the ortho-to-para H_2, via observations of para-H_2D^+ (and ortho-H_2D^+ with APEX) – important for D fractionation and cloud ages

• OH, OD (, carbonyl?) – oxygen chemistry and water fractionation – synergy with Herschel and APEX

• SH unveils the presence of shocks in diffuse clouds