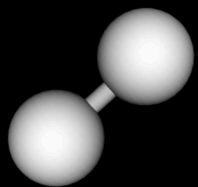
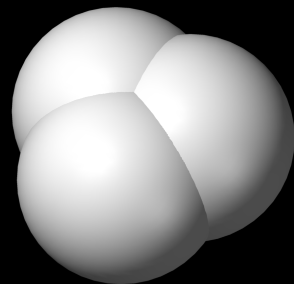
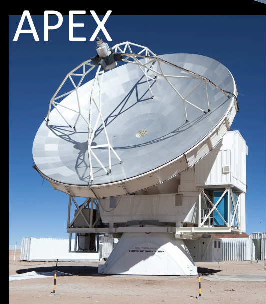
Hydride Isotopologues

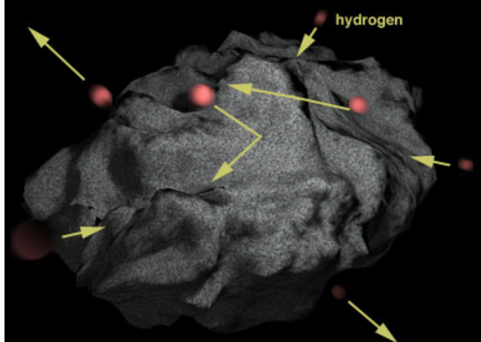
Paola Caselli
Center for Astrochemical Studies
Max-Planck-Institute for Extraterrestrial Physics

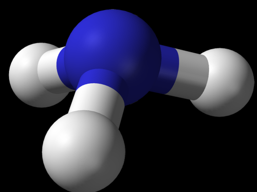


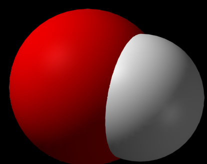


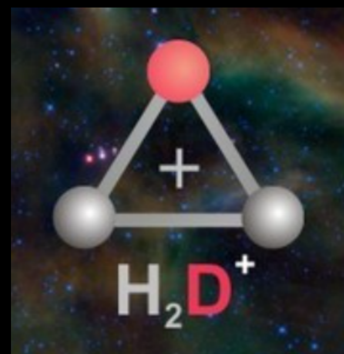
Herschel











Outline

- H_3^+ and its deuterated forms
- Deuterated ammonia
- OD
- Uncertainties and future perspectives

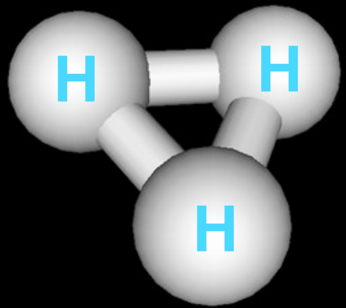
The formation of H_3^+

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

$$H_2 + \text{c.r.} \rightarrow H_2^+ + e^- + \text{c.r.}$$

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

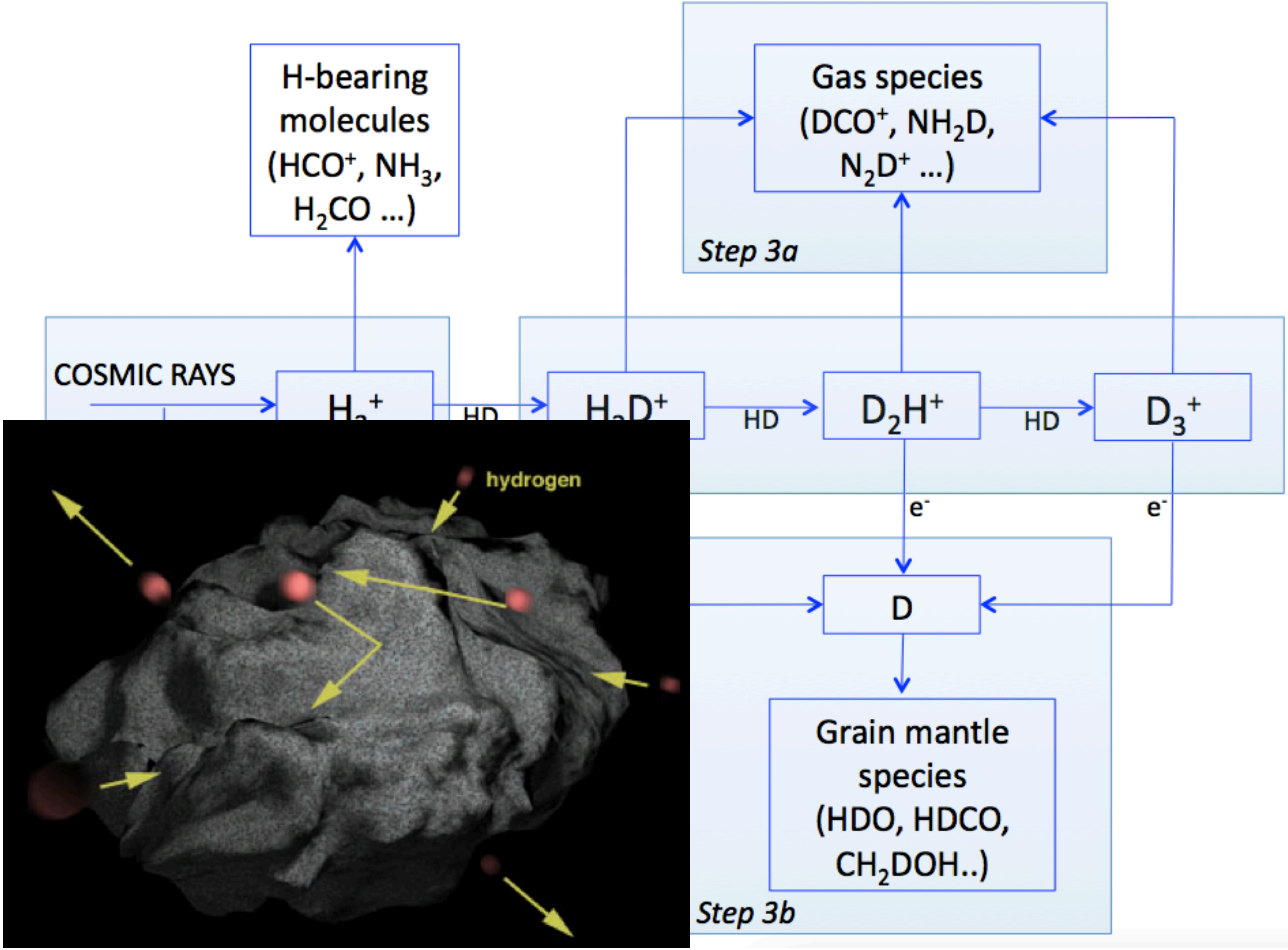
$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 230\ K$ (Watson 1974)

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

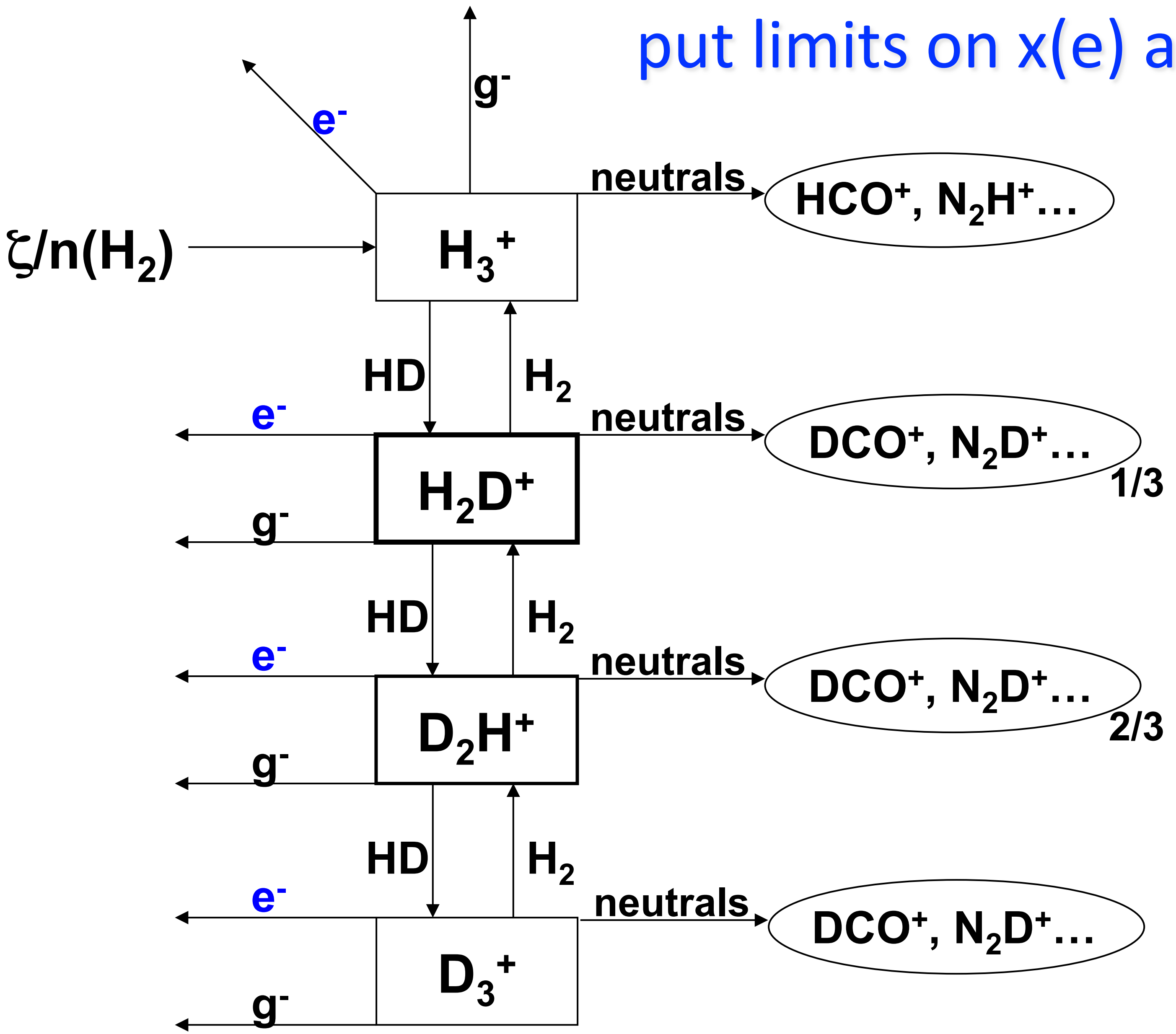
LOWER H_2D^+ and H_3^+ destruction rates	+	HIGHER H_2D^+ formation rate	=	LARGER H_2D^+/H_3^+ abundance ratio and deuterium fractionation

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

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

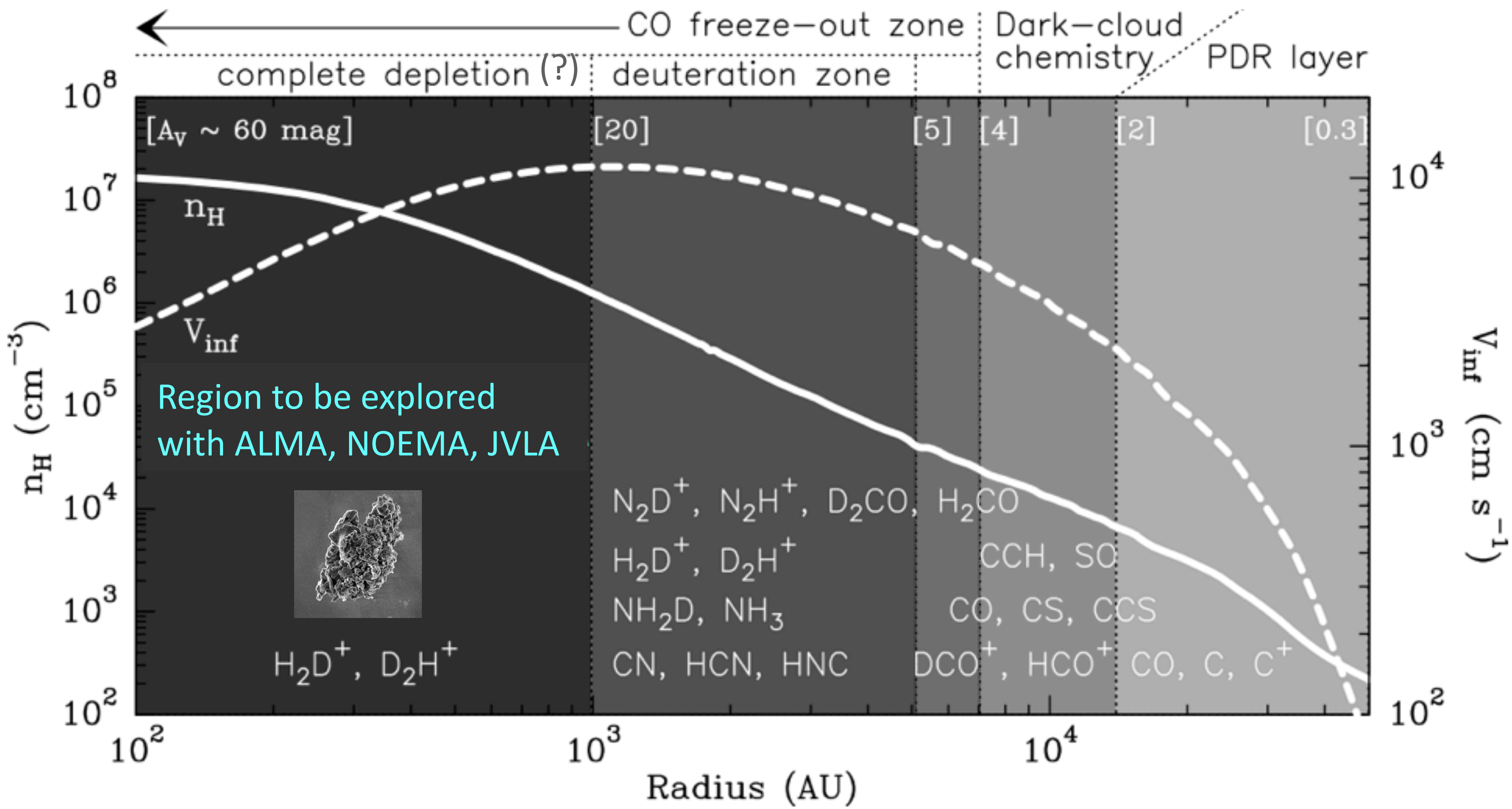

H-bearing molecules (HCO^+, NH_3, H_2CO ...)
Gas species (DCO^+, NH_2D, N_2D^+ ...)
Step 3a
COSMIC RAYS
HD
D_2H^+
HD
D_3^+
e^-
e^-
D
Grain mantle species (HDO, $HDCO$, CH_2DOH..)
Step 3b
hydrogen

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
Caselli 2002
Dalgarno 2006

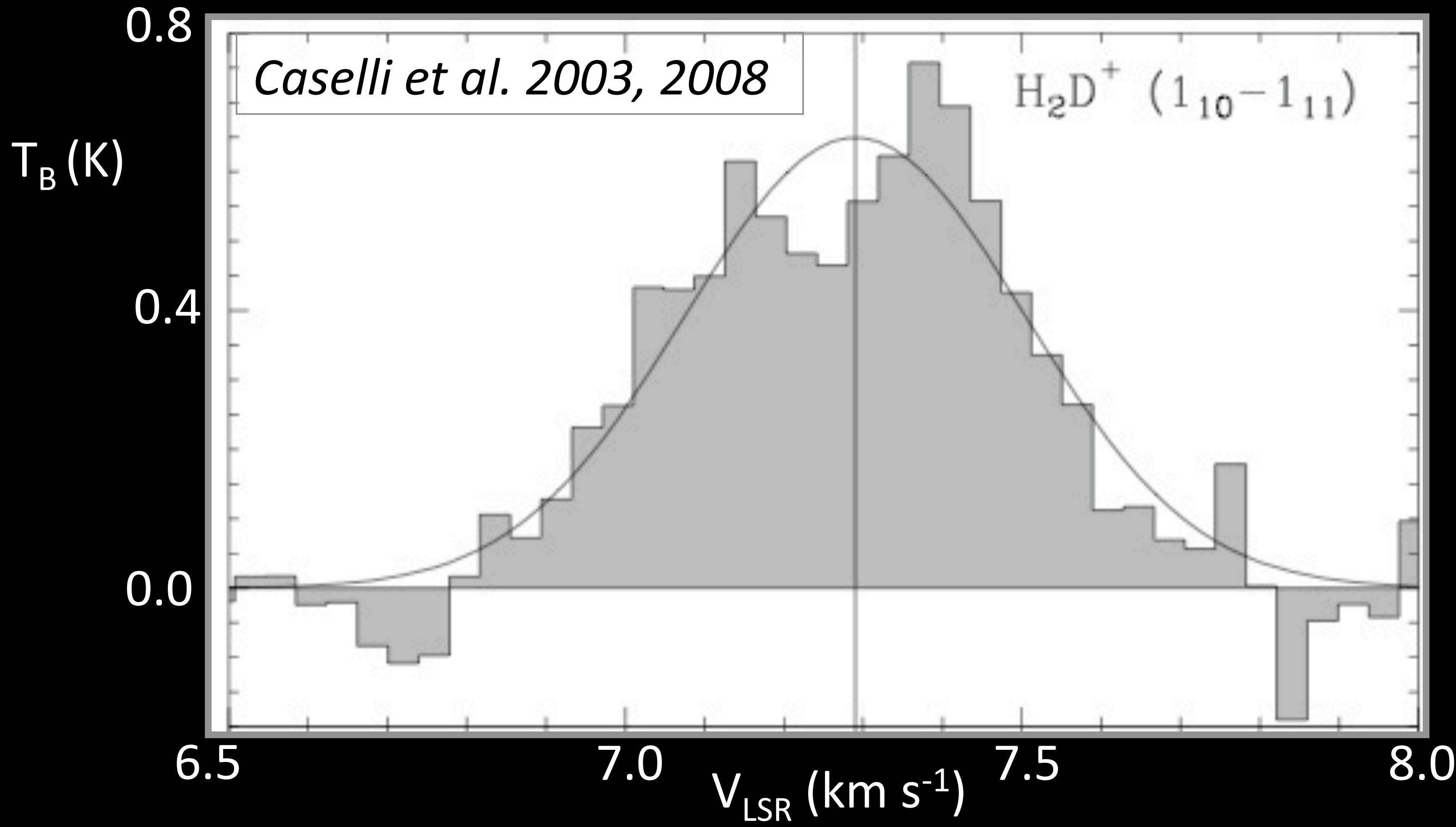
Deuterated molecules are tracers of pre-stellar core centers



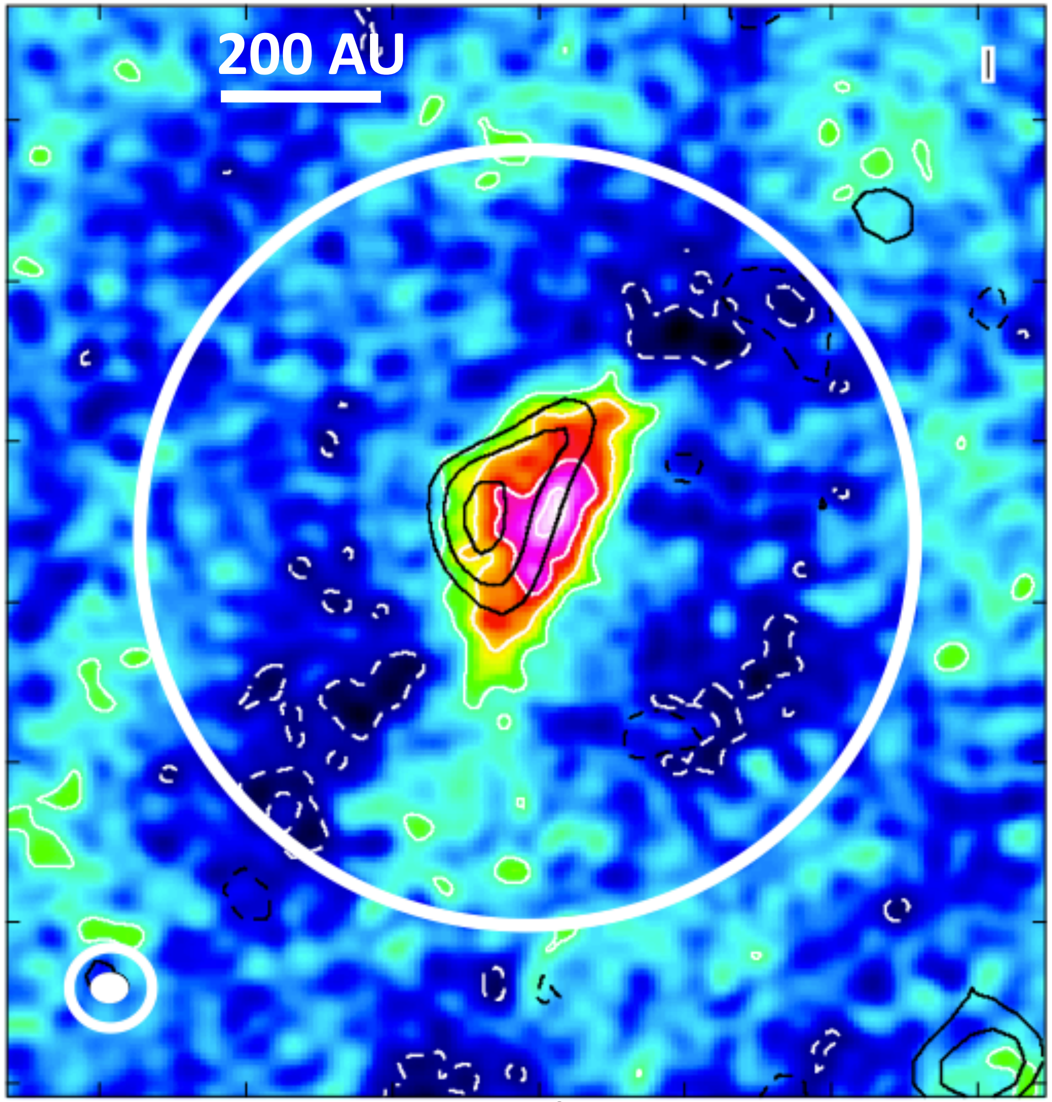
Keto & Caselli 2008, 2010; Caselli 2011, IAU 280; Keto et al. 2015

Surprisingly strong ortho-H_2D^+

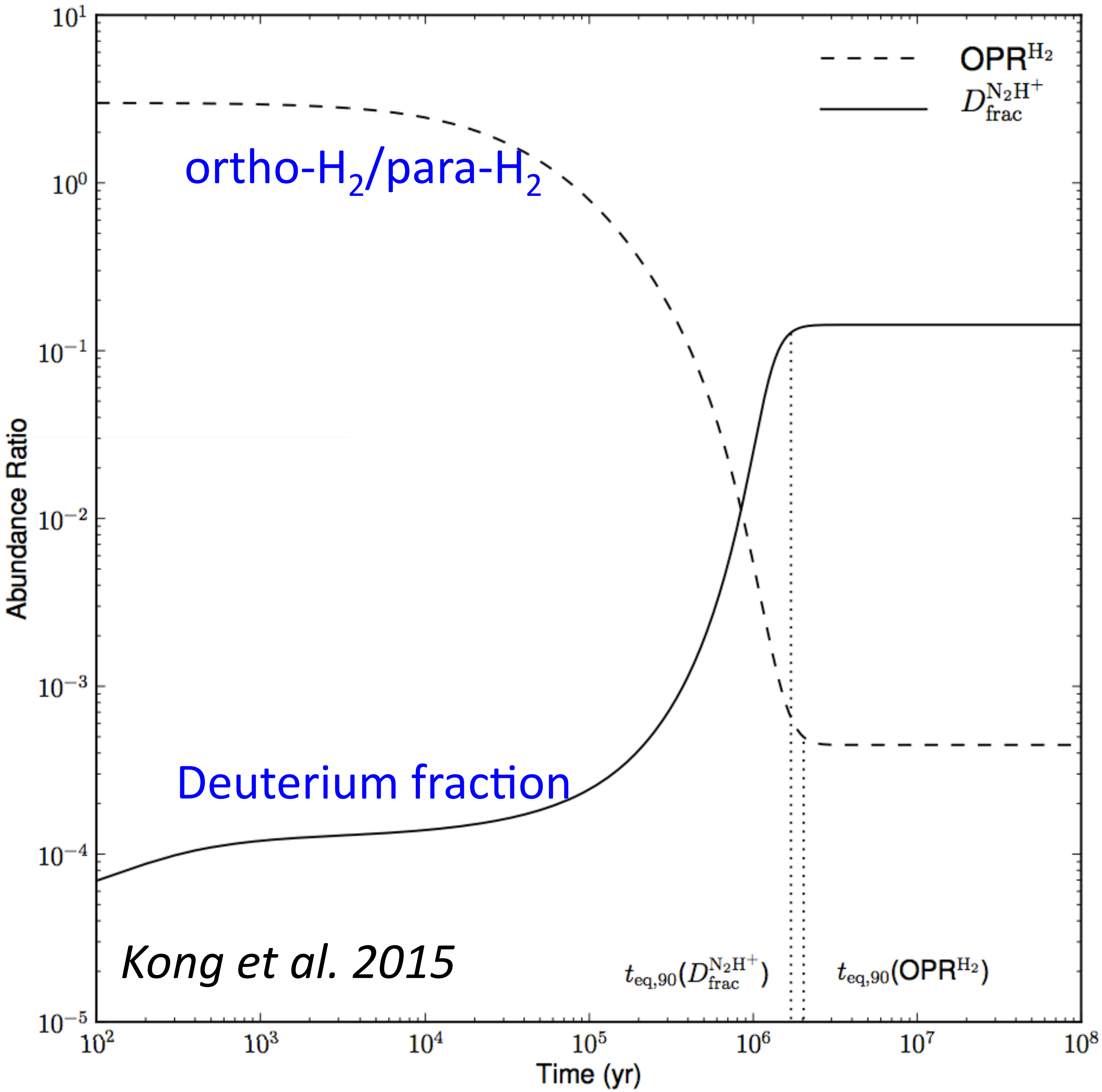
- Led to revision of astrochemical models (*e.g. Roberts et al. 2003*)
- Triggered new laboratory and theory work (*e.g. Hugo et al. 2009*)

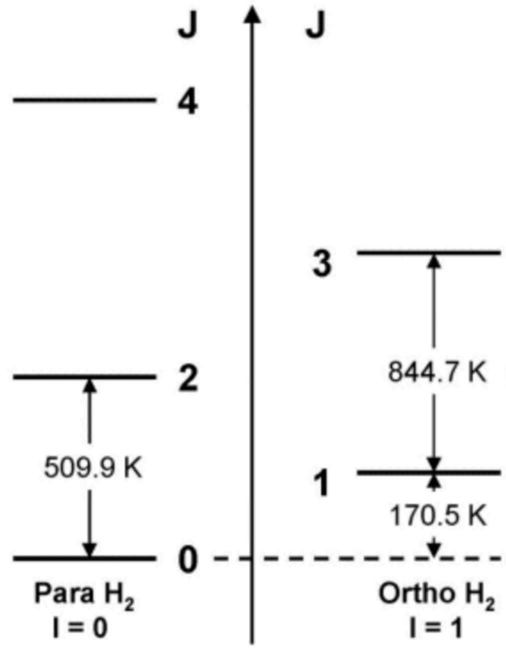


First detection of ortho-H_2D^+ with ALMA



Friesen et al. 2014





$H_3^+ + HD \rightarrow H_2D^+ + p\text{-}H_2$

$H_3^+ + HD \leftarrow H_2D^+ + o\text{-}H_2$

Pagani et al. 1992
Gerlich et al. 2002
Walmsley et al. 2004

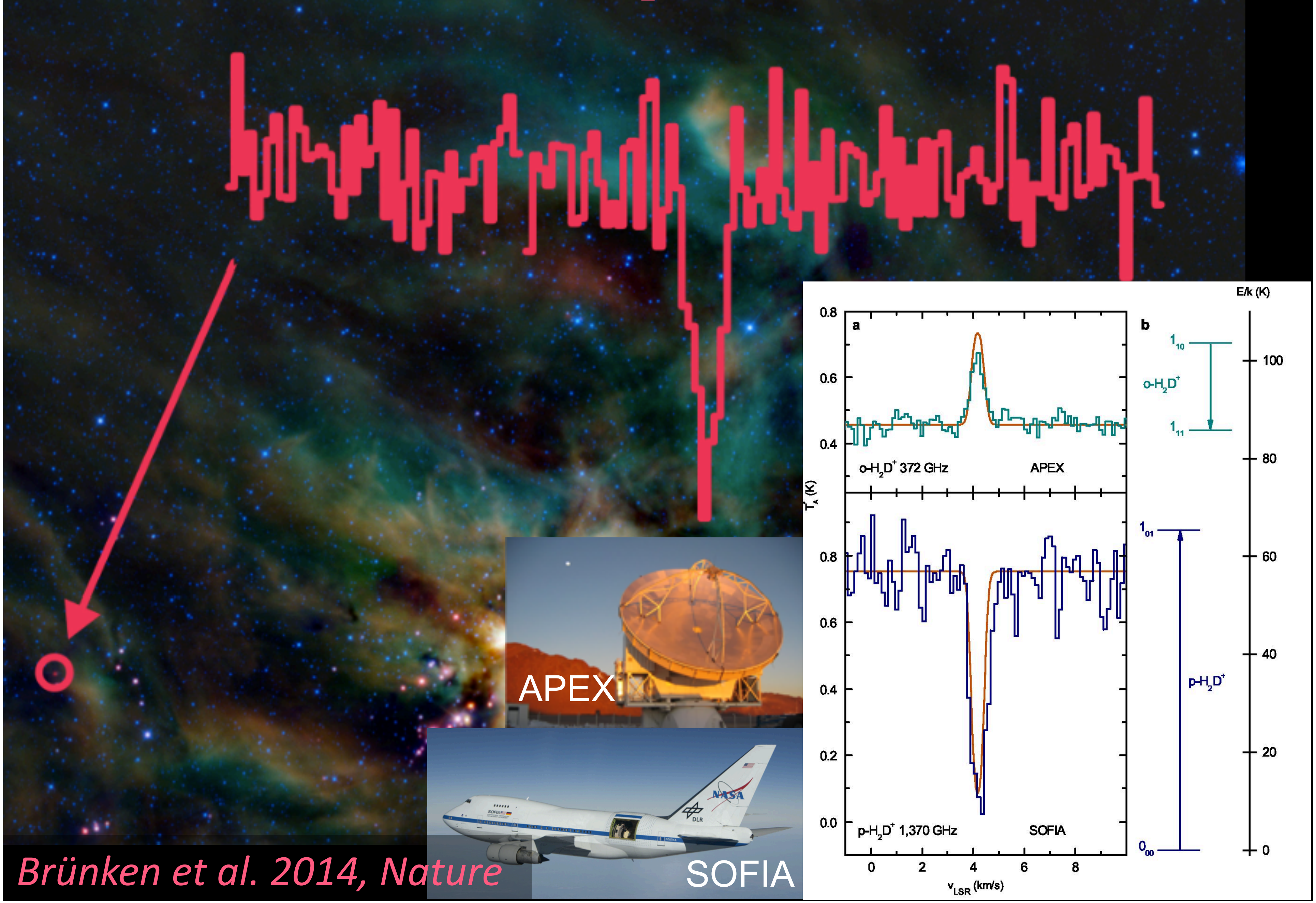
Analytical relation between the H_2 and H_2D^+ ortho-to-para ratios

$$\text{p-H}_2\text{D}^+ + \text{o-H}_2 \overset{k_1}{\Leftrightarrow} \text{o-H}_2\text{D}^+ + \text{p-H}_2$$
$$\text{o-H}_2\text{D}^+ + \text{o-H}_2 \overset{k_2}{\Leftrightarrow} \text{p-H}_2\text{D}^+ + \text{p-H}_2$$
$$\text{o-H}_2\text{D}^+ + \text{o-H}_2 \overset{k_3}{\Leftrightarrow} \text{p-H}_2\text{D}^+ + \text{o-H}_2$$

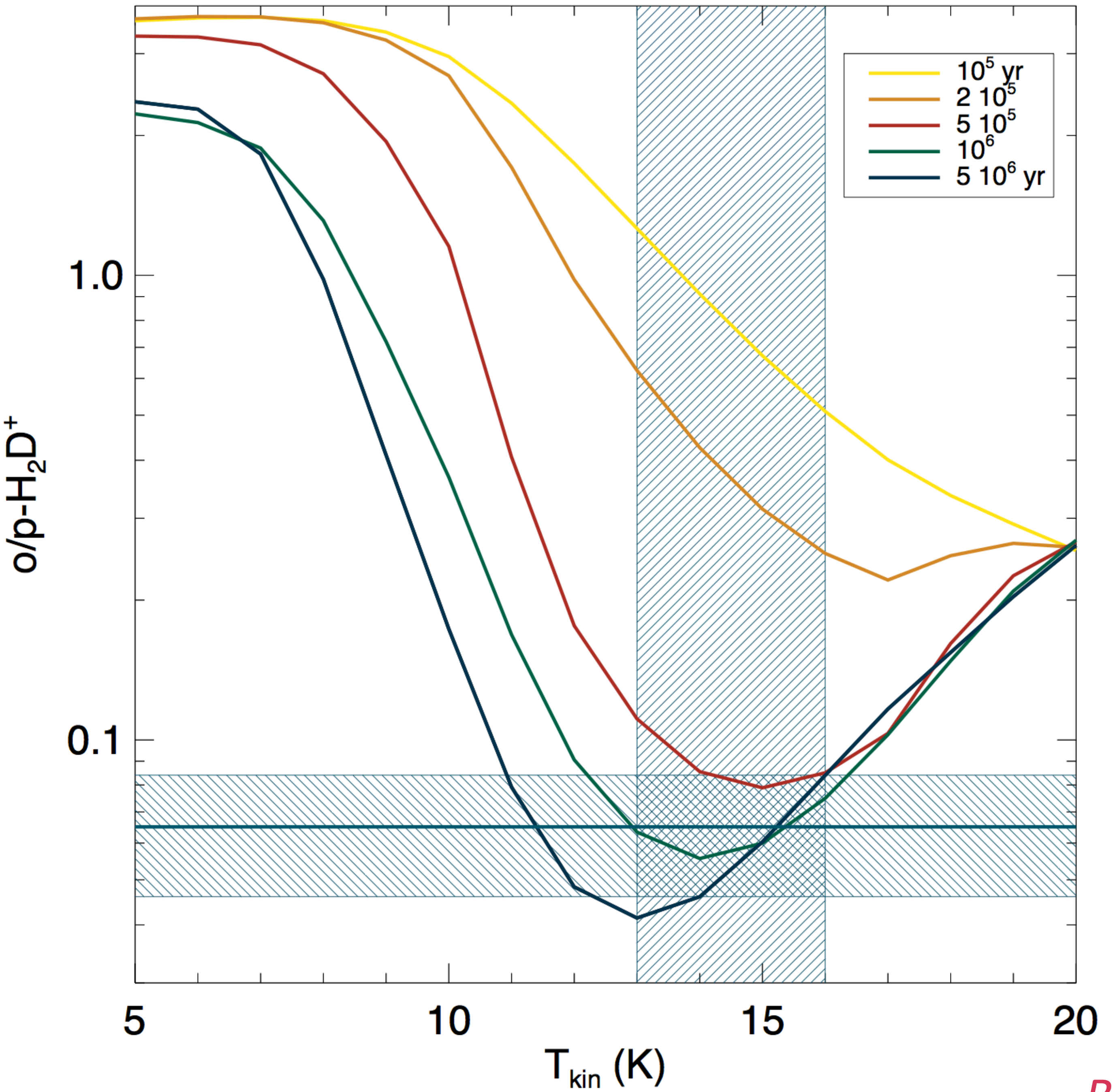
$$\frac{[\text{o-H}_2\text{D}^+]}{[\text{p-H}_2\text{D}^+]} = \frac{(k_1^+ + k_3^-) \times [\text{o-H}_2]/[\text{p-H}_2] + k_2^-}{(k_2^+ + k_3^+) \times [\text{o-H}_2]/[\text{p-H}_2] + k_1^-}$$

Hugo, Asvany & Schlemmer et al. 2009

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

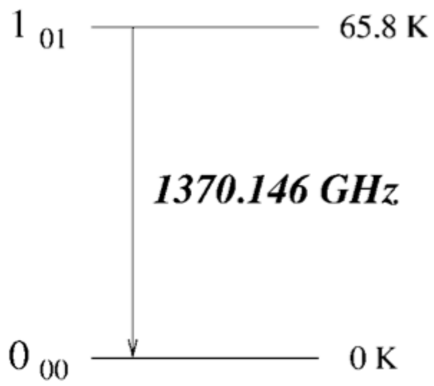


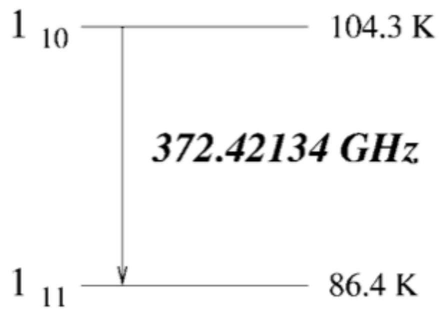
Brünken et al. 2014, Nature

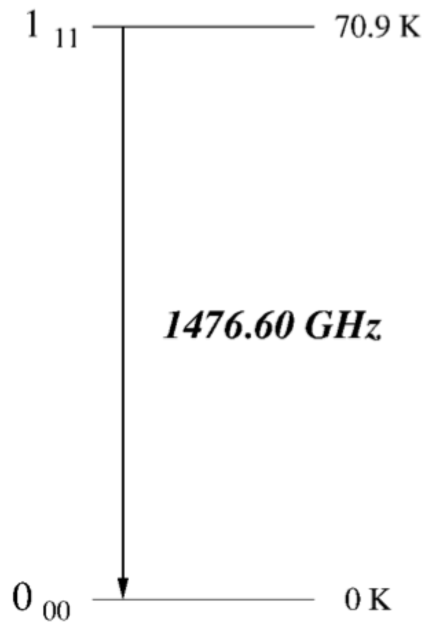


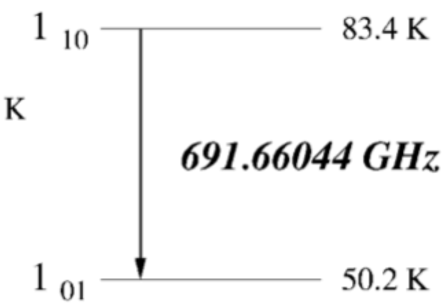
The molecular gas in the cool envelope has been subject to chemical processing for at least one million years (~10 × the free-fall time scale) ➔ ***magnetic support?***

Brünken et al. 2014









PARA H_2D^+

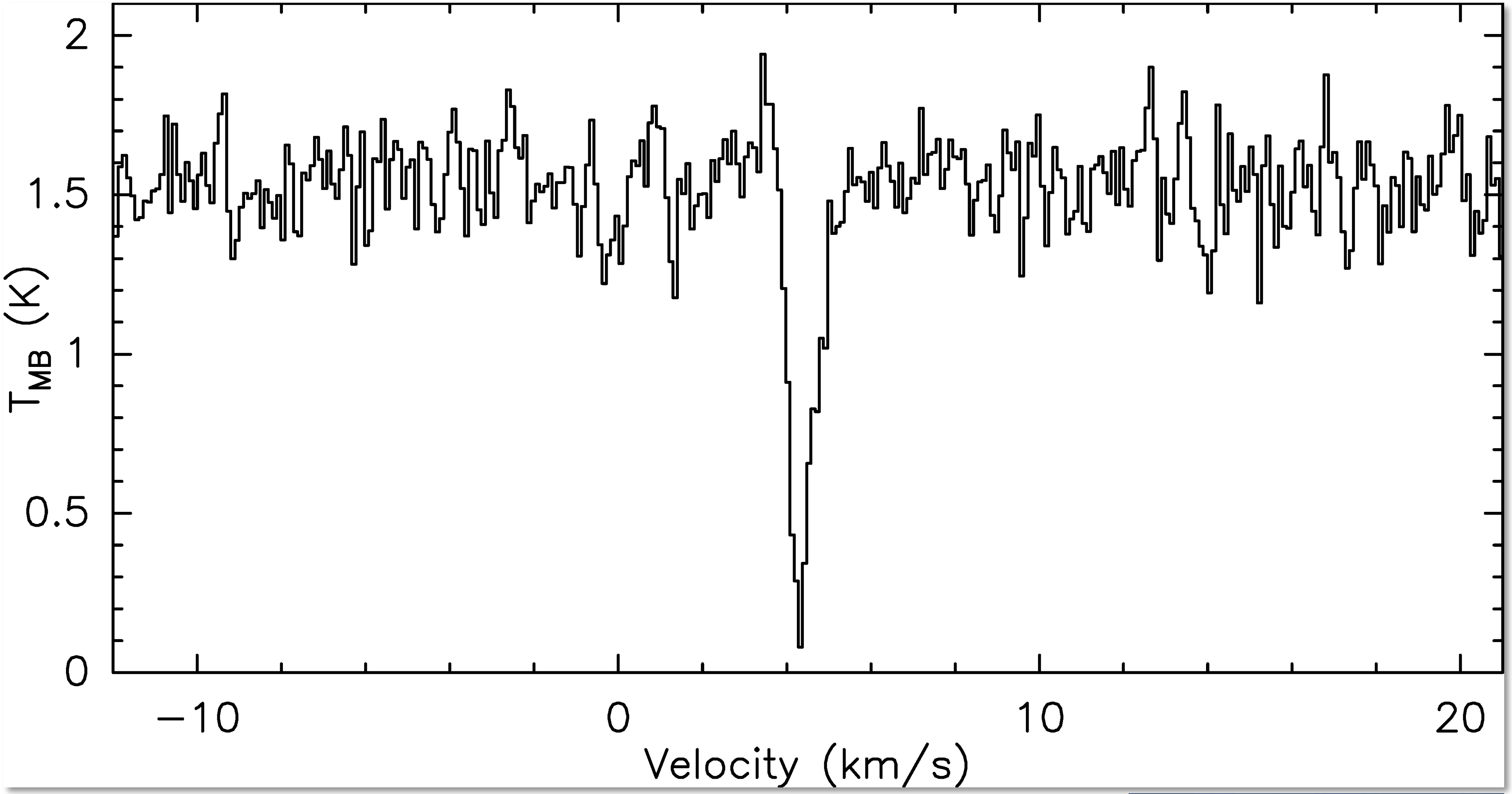
ORTHO H_2D^+

ORTHO D_2H^+

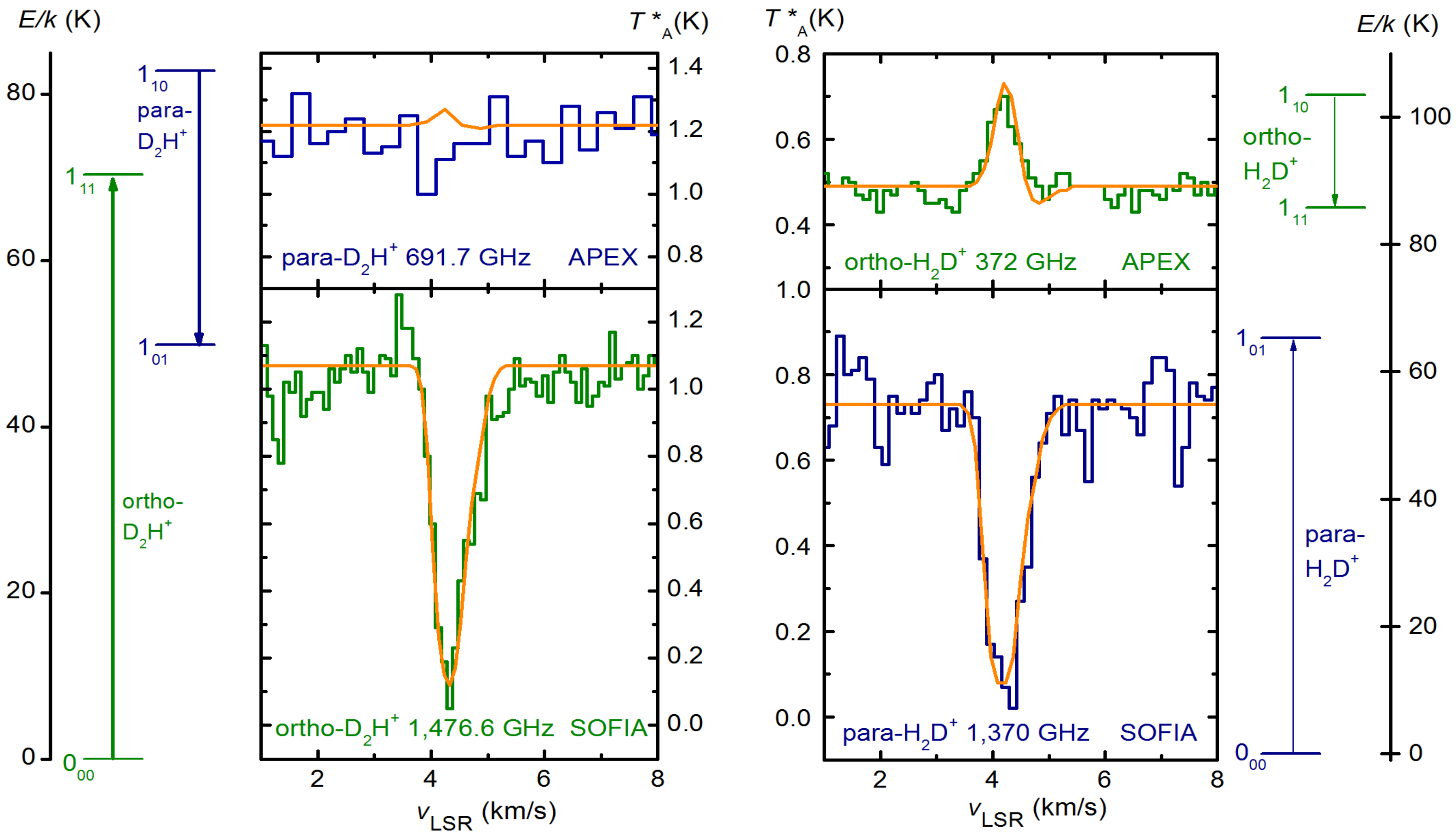
PARA D_2H^+

from Vastel et al. 2004

ortho-D_2H^+ (1_{11}-0_{00}) toward IRAS 16293-2422



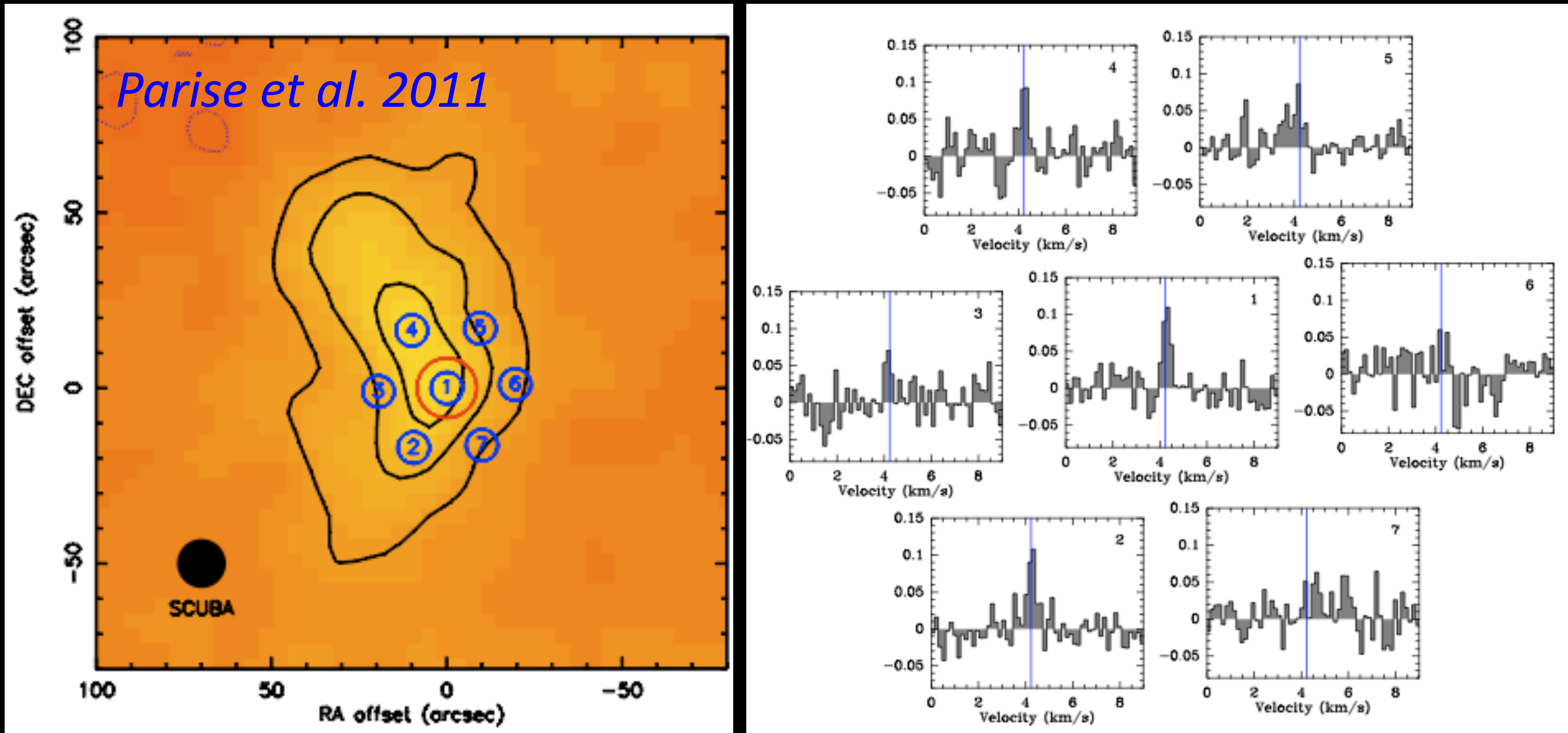
Harju et al., in prep.



Harju et al., in prep.

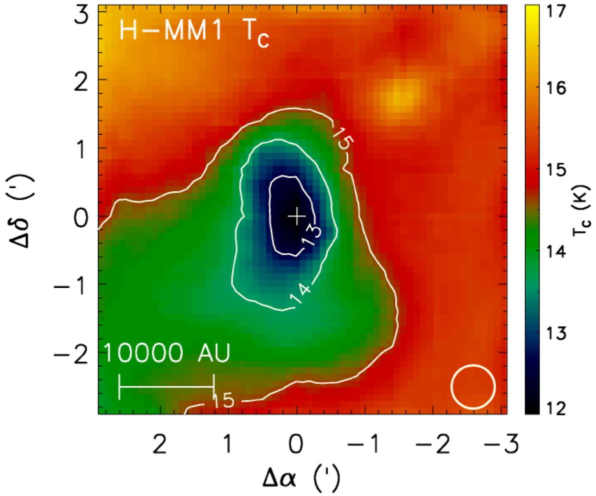
para-D_2H^+

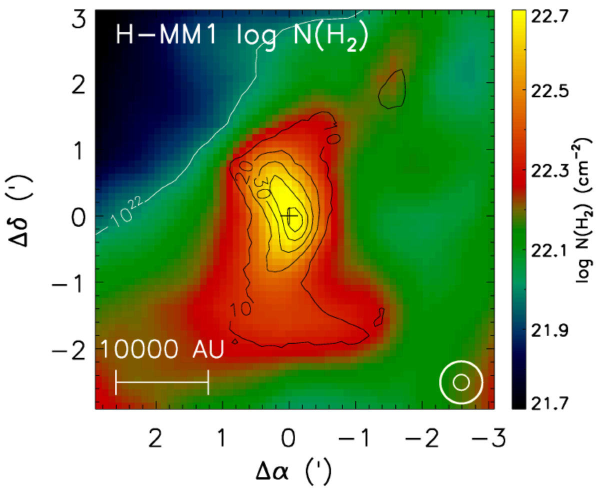
Extended para-D_2H^+ emission (~40'' ~5000 AU) toward L1688/H-MM1 (692 GHz; APEX-CHAMP+)

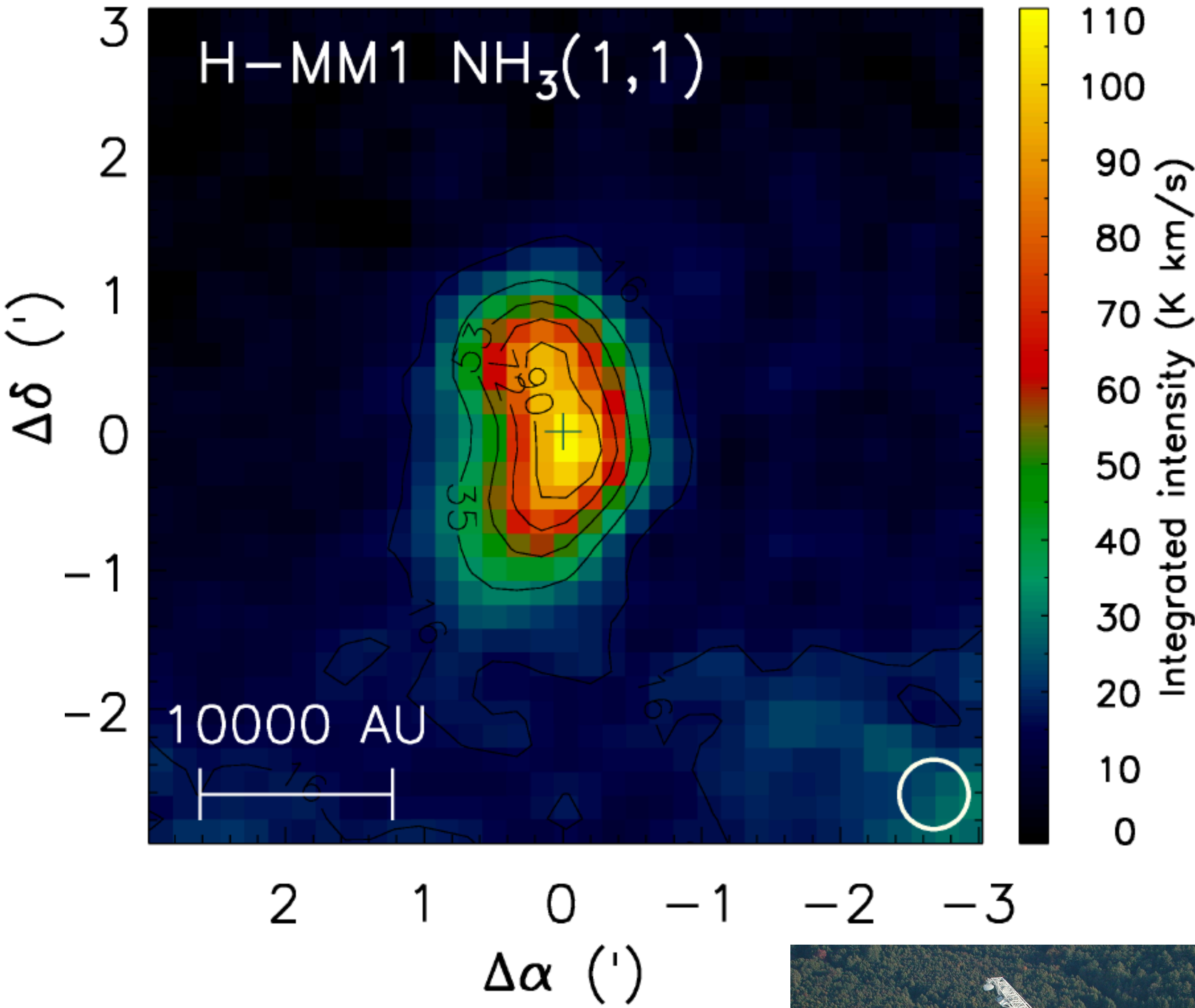


See Vastel et al. (2004) for first detection of para-D_2H^+

Deuteration of ammonia in a starless core

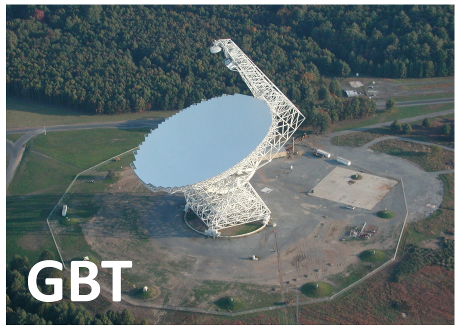




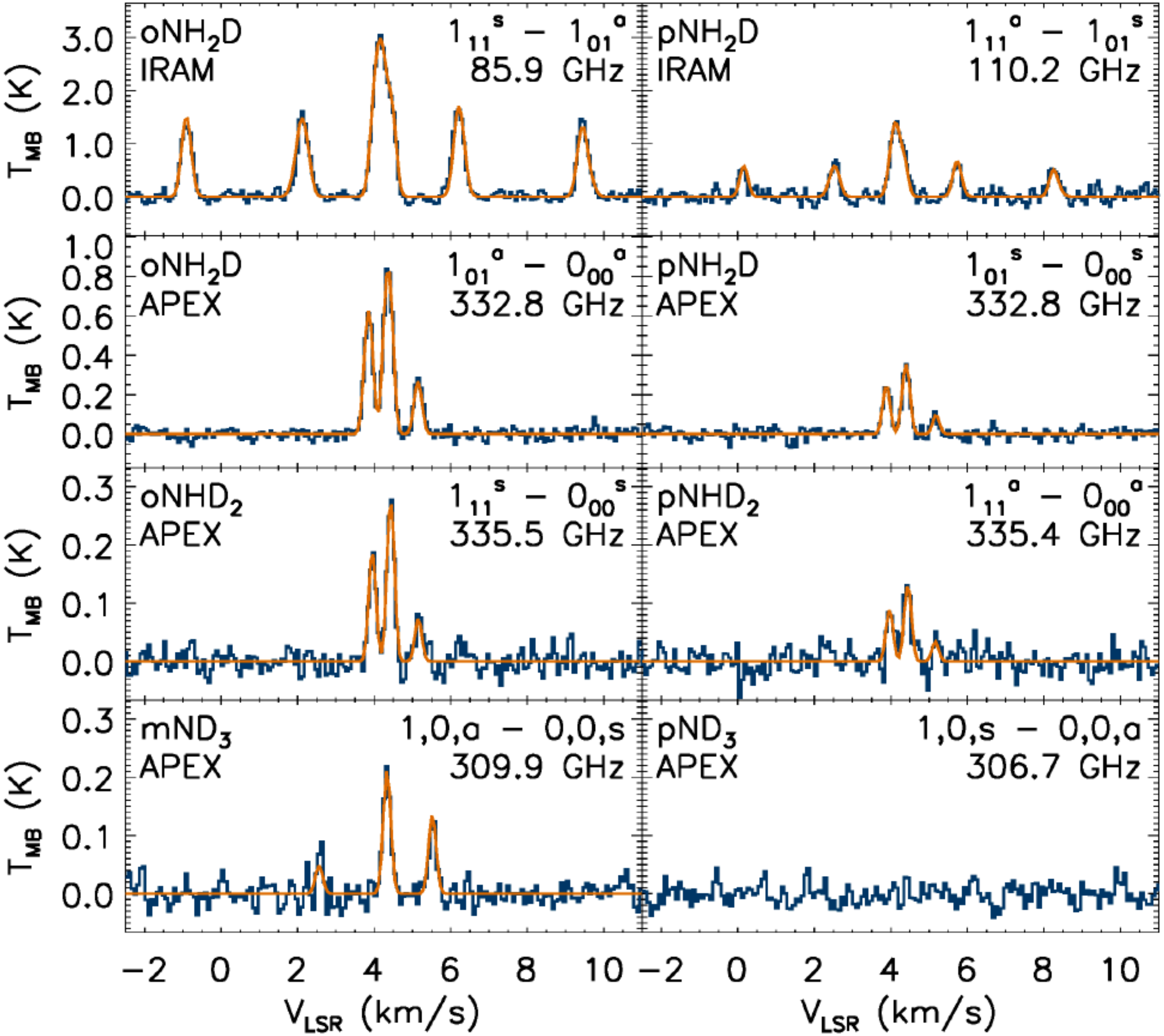


Harju et al. 2017

see also Roueff et al 2005; Lis et al. 2002; Gerin et al. 2006



Gaussian HFS fits

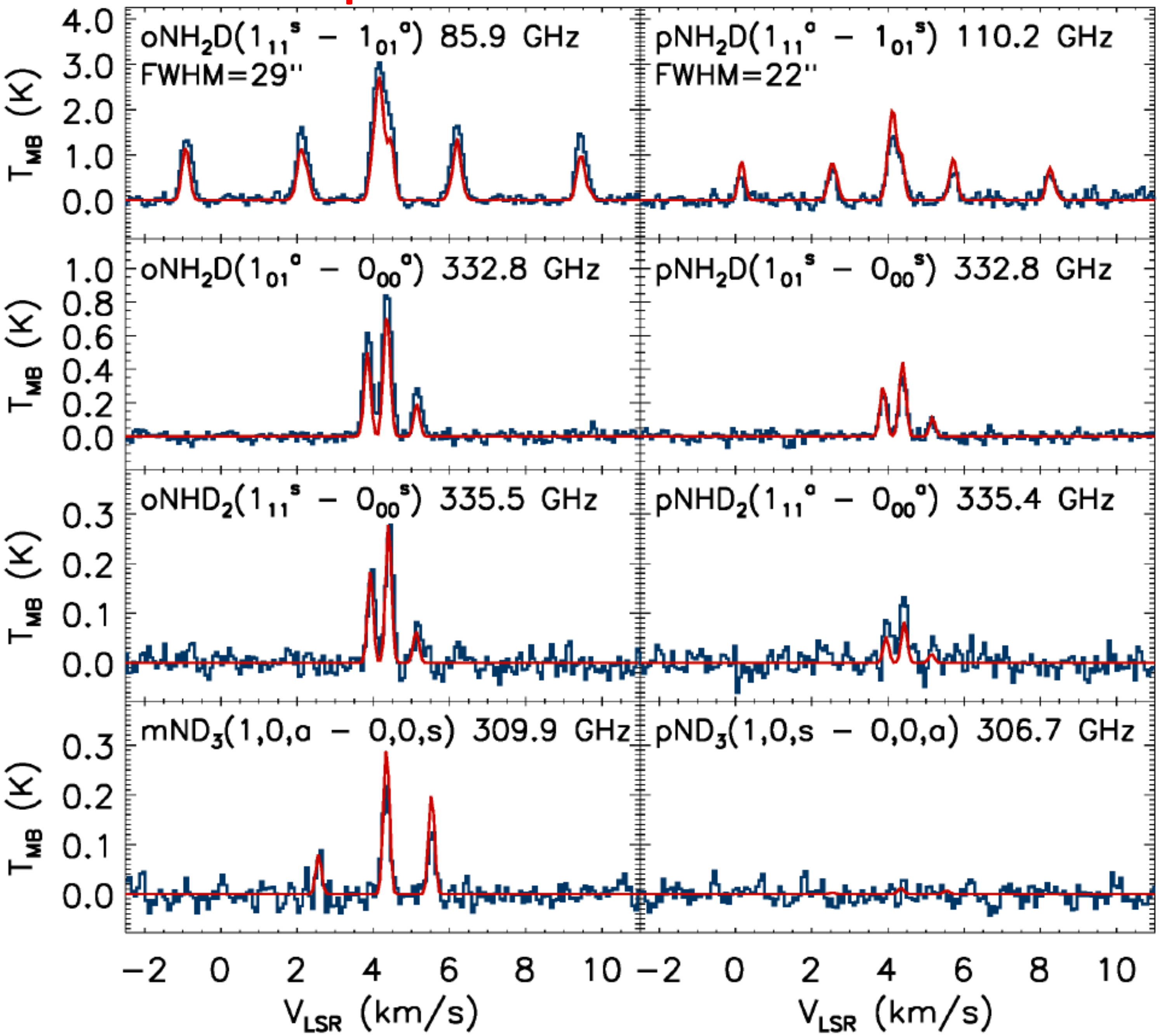


NH_2D/NH_3 ~ 0.6
NHD_2/NH_2D ~ 0.2
ND_3/NHD_2 ~ 0.07
o/p-NH_2D ~ 3
o/p-NHD_2 ~ 2
Consistent with statistical spin ratios

Statistical fractionation and spin ratios fit data better -> full scrambling in reactions forming deuterated ammonia may not be valid (Sipilä et al. 2015).

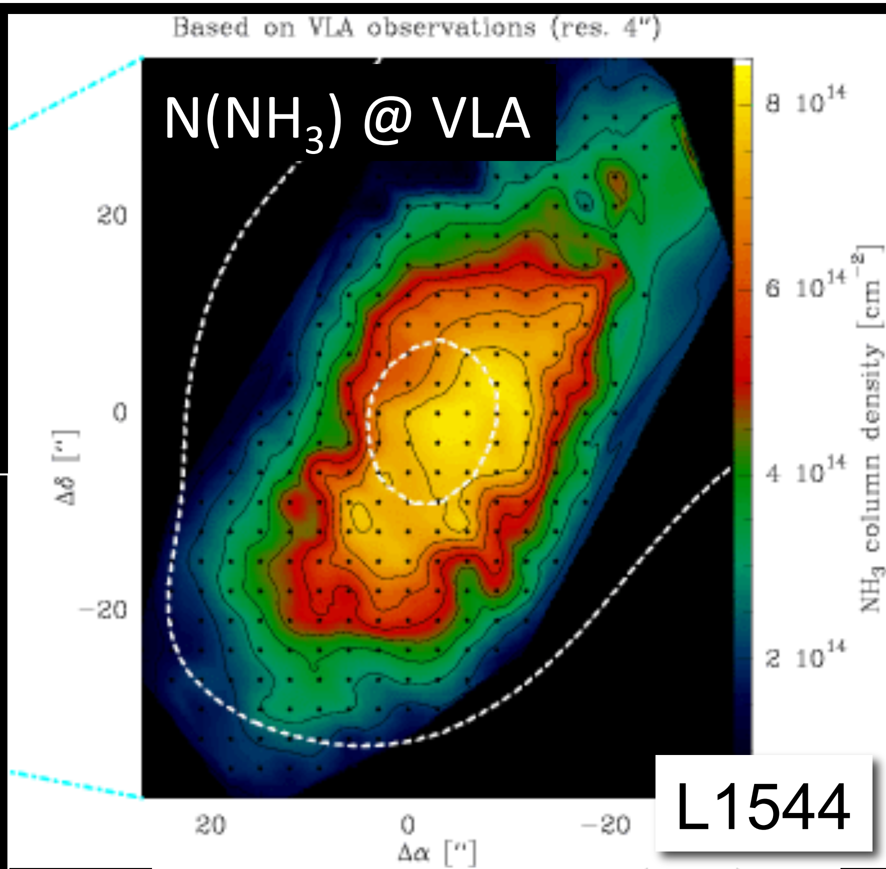
Model results:
o/p-NH_2D ~ 2
o/p-NHD_2 ~ 3
and overproduction of pNH_3 and oH_2D^+

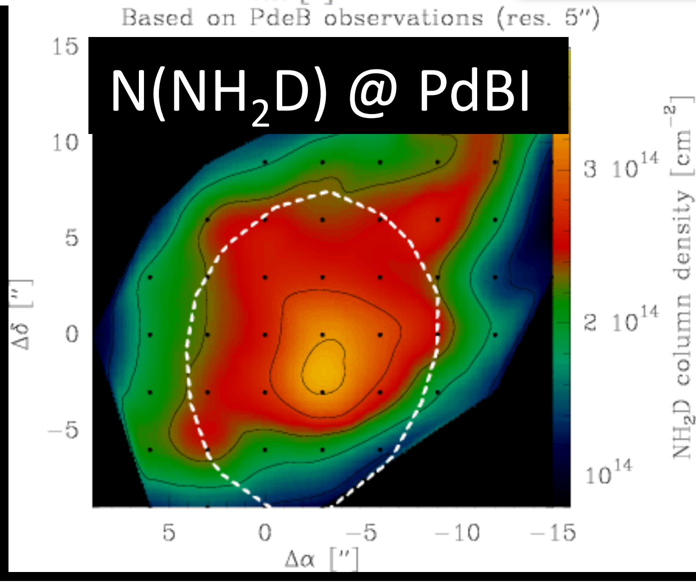
Spectra from dense core model



NH_3 and NH_2D with interferometers in L1544: temperature structure and kinematics.

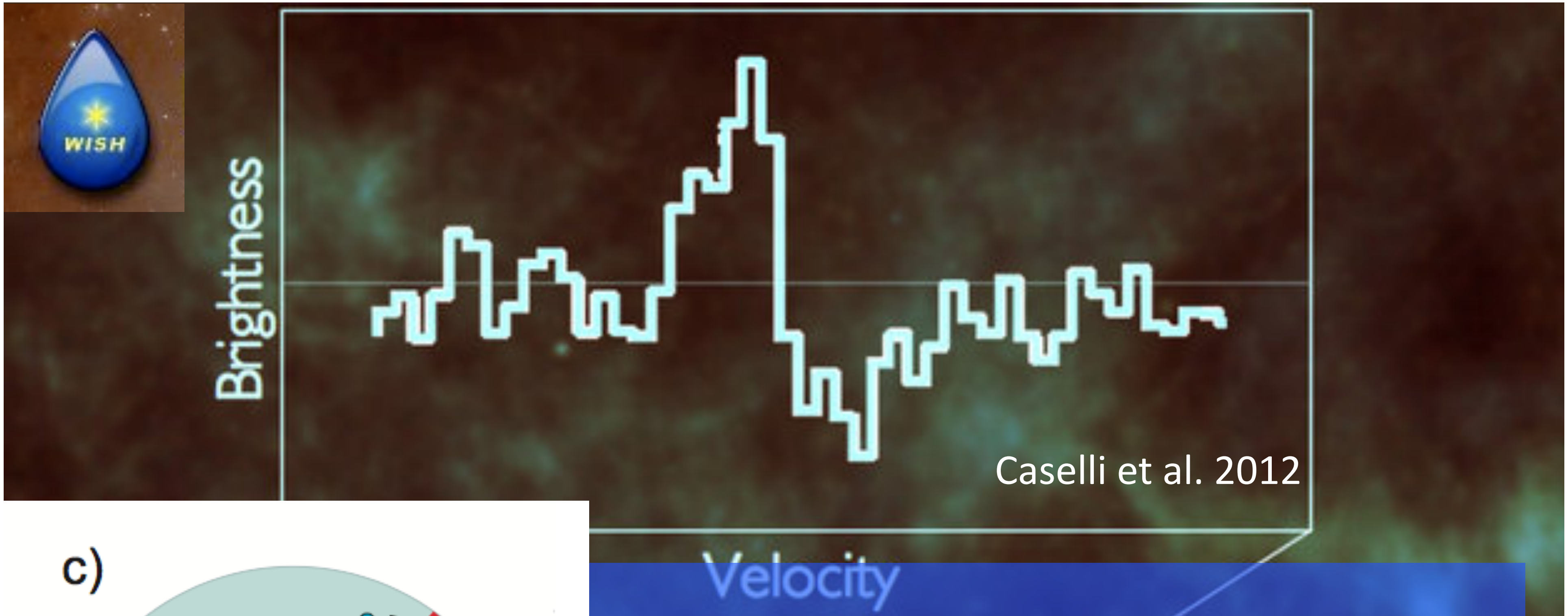
- D-fraction increases to ~0.4 in the central 3000 AU;
- The gas temperature drops to ~6 K in the central 1000 AU;
- Loss of specific angular momentum toward small scales (factor of ~15 from 10000 to 2000 AU).





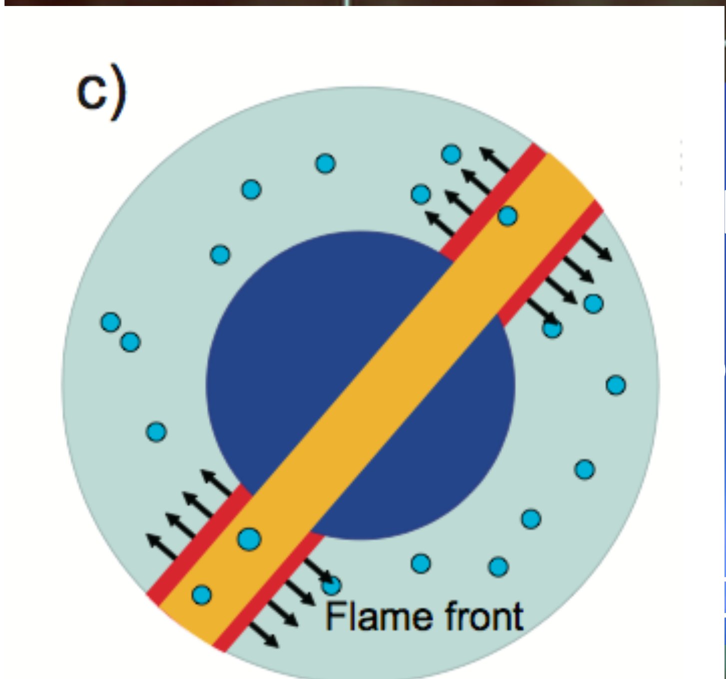
Crapsi, Caselli, Walmsley, Tafalla 2007

First detection of water vapor in a pre-stellar core



l infall within central 1,000 AU;
of water vapor: ~0.5 Earth masses;
f water ice: ~2.6 Jupiter masses;
t for water desorption.

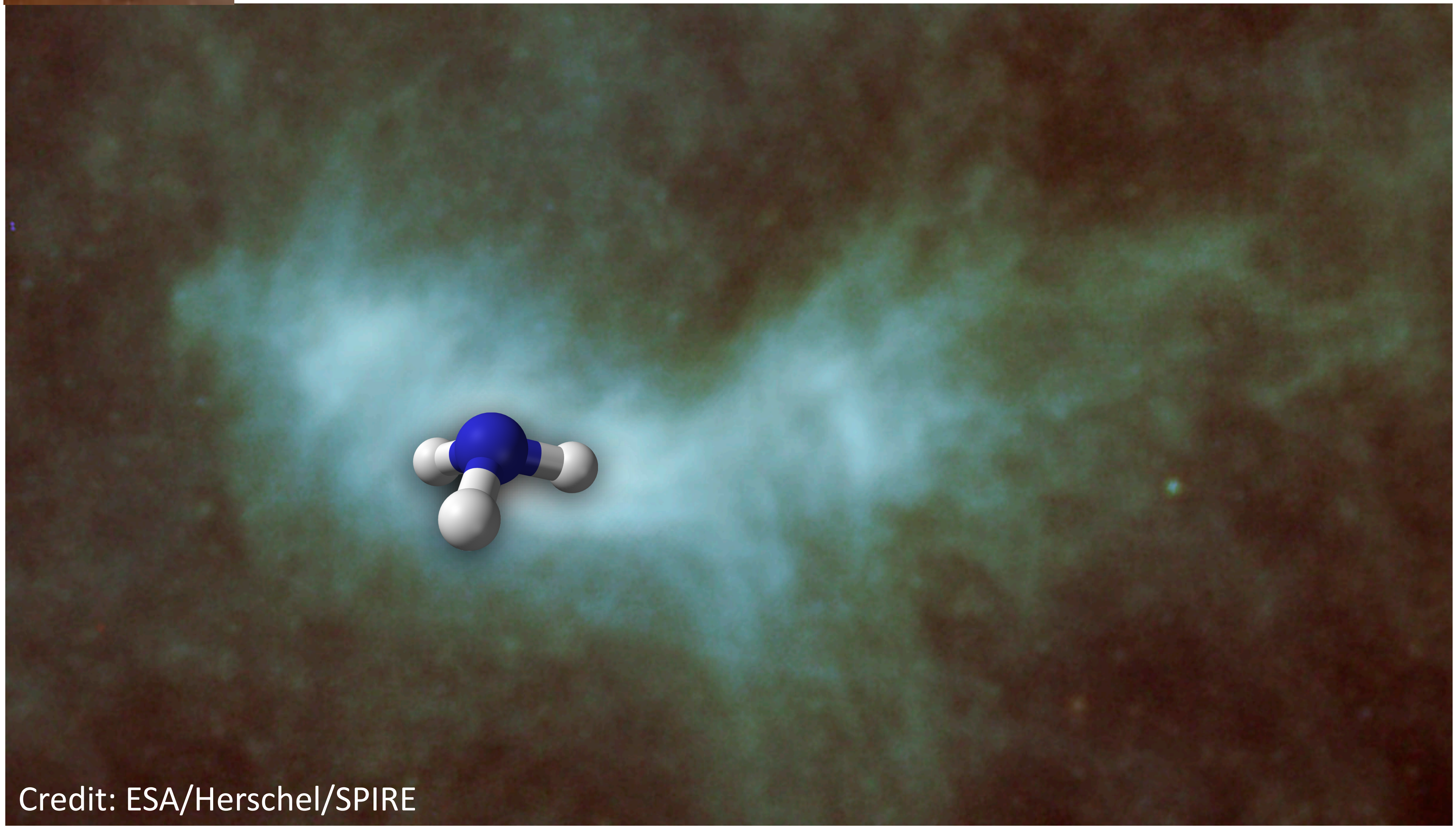
DO upper limits; *Quénard et al. 2015).*

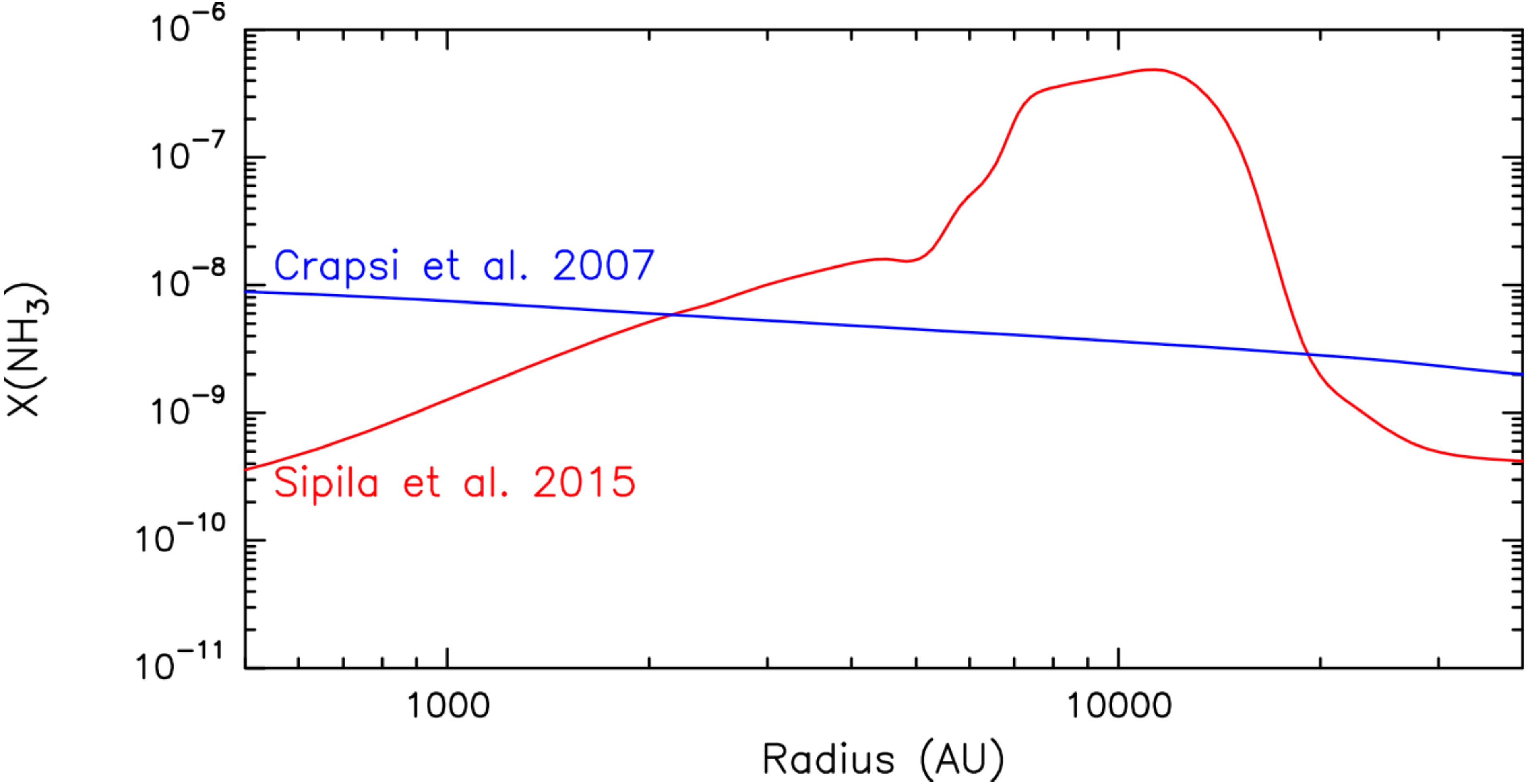


Ivlev et al. 2015

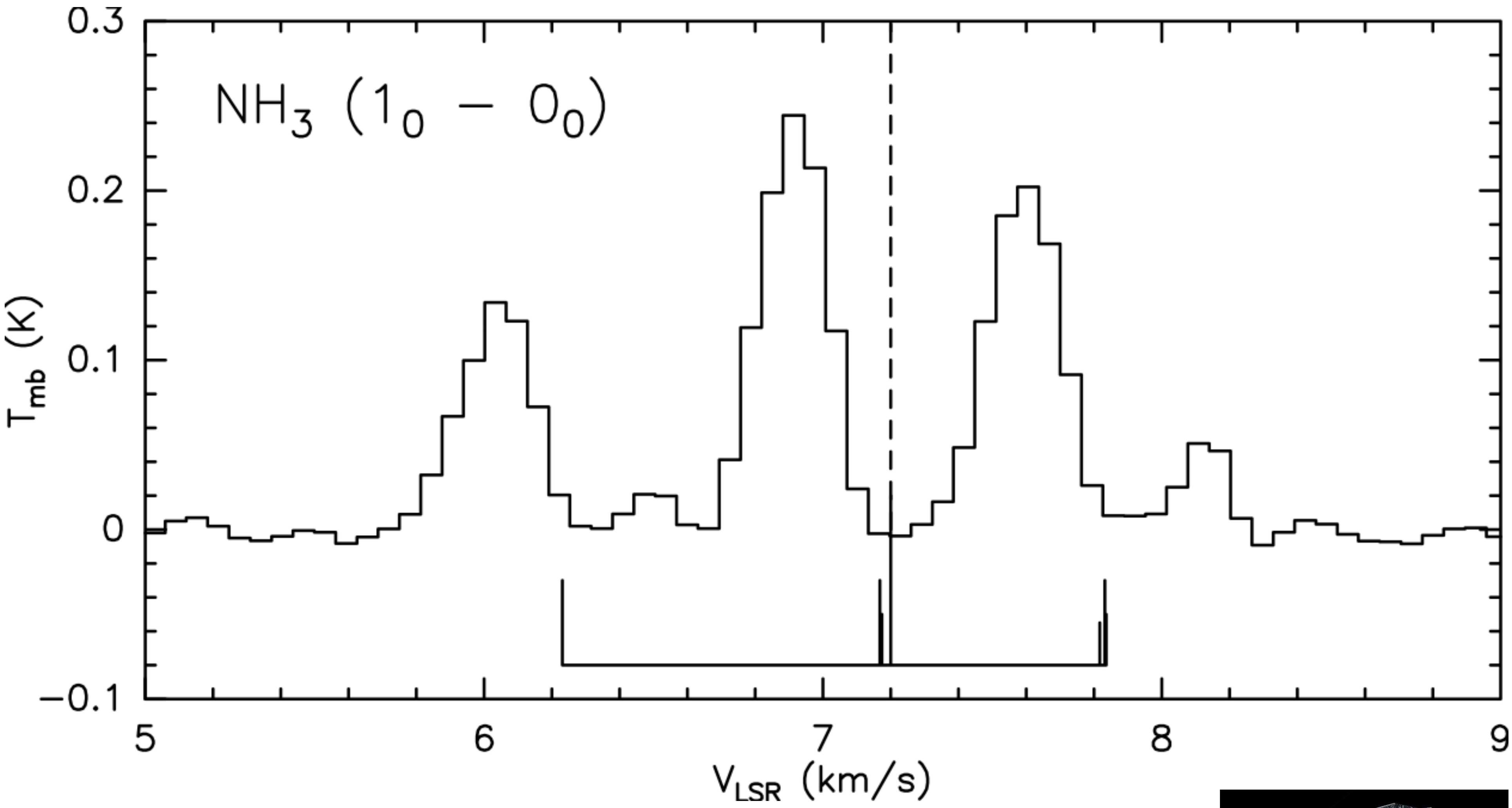
ESA PRESS RELEASE

The ortho-$NH_3(1_0\text{-}0_0)$ spectrum toward L1544 with Herschel

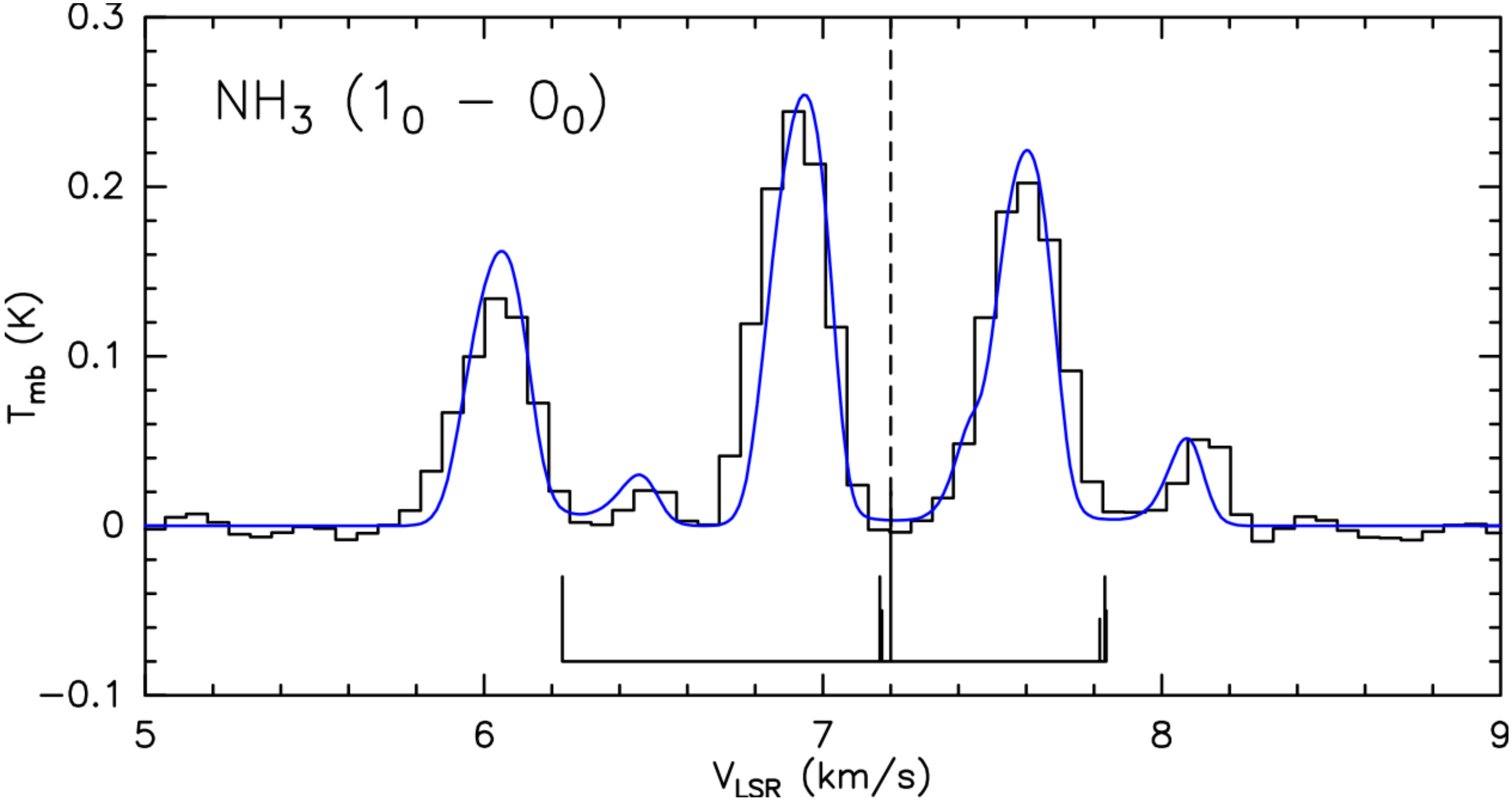




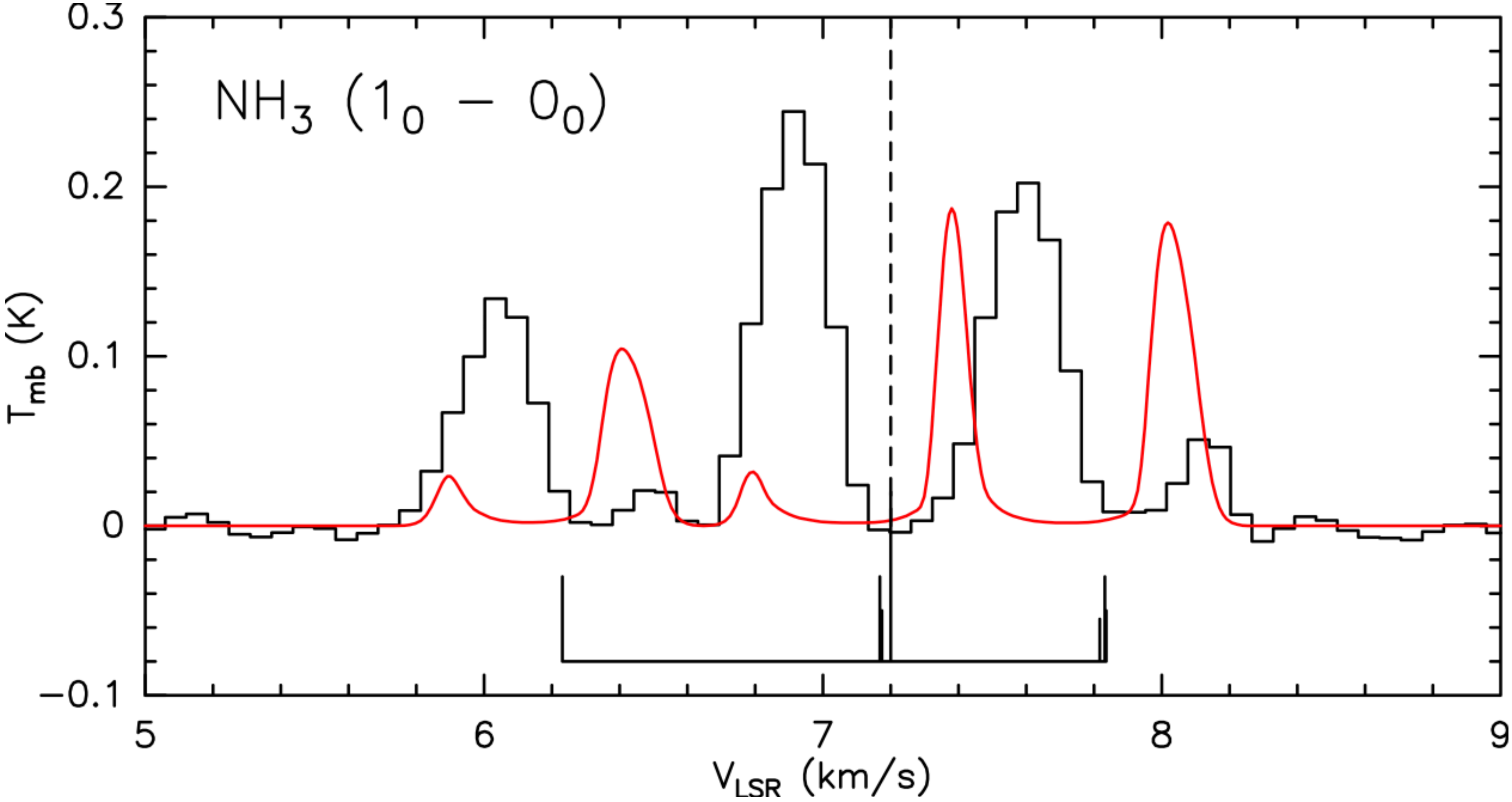
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
$X(NH_3)$
Crapsi et al. 2007
Sipila et al. 2015
1000
10000
Radius (AU)



Caselli, Bizzocchi, Keto et al. , in prep.



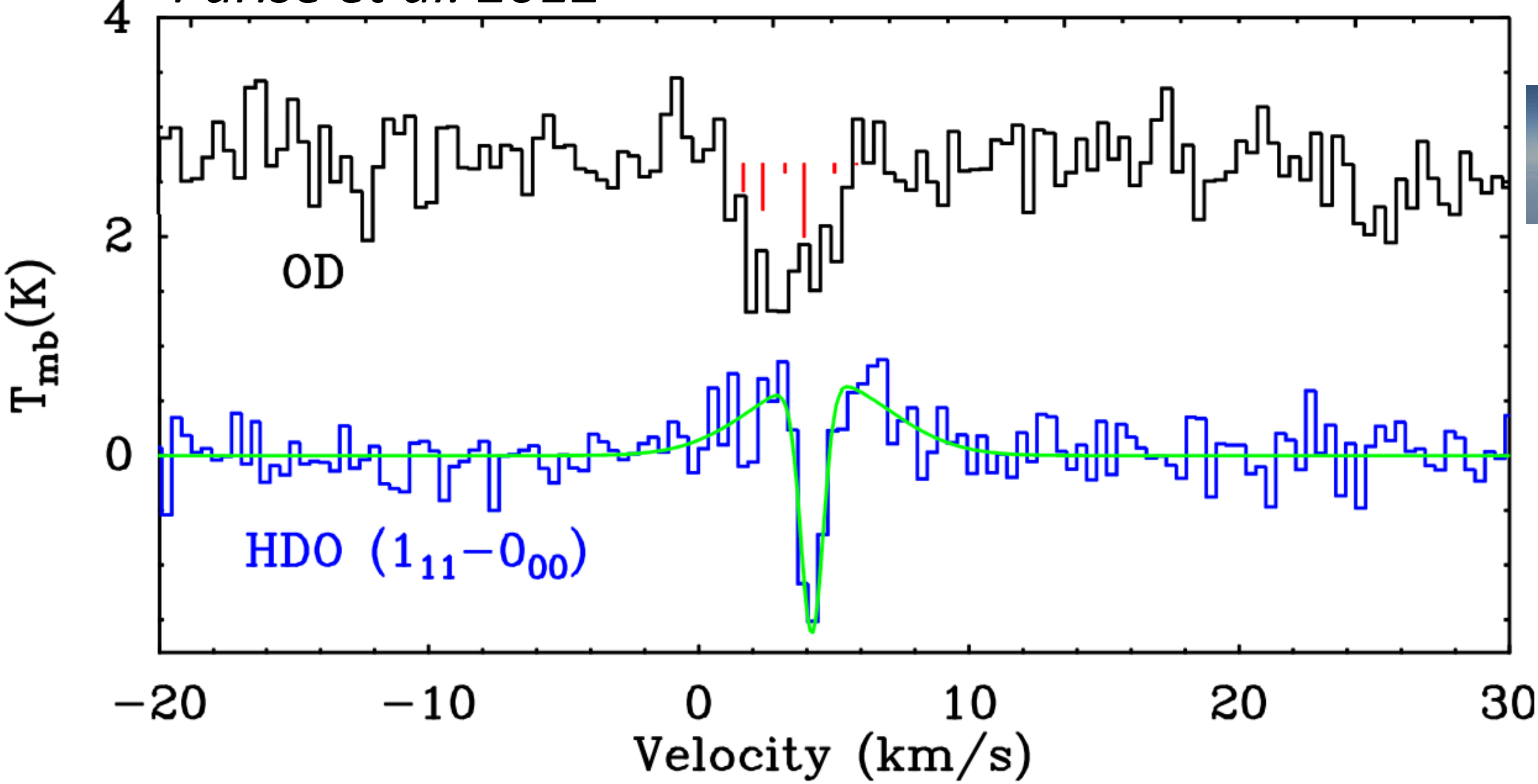
With NH_3 abundance profiled deduced by Crapsi et al. 2007



With NH_3 abundance profiled calculated by Sipilä et al. 2015

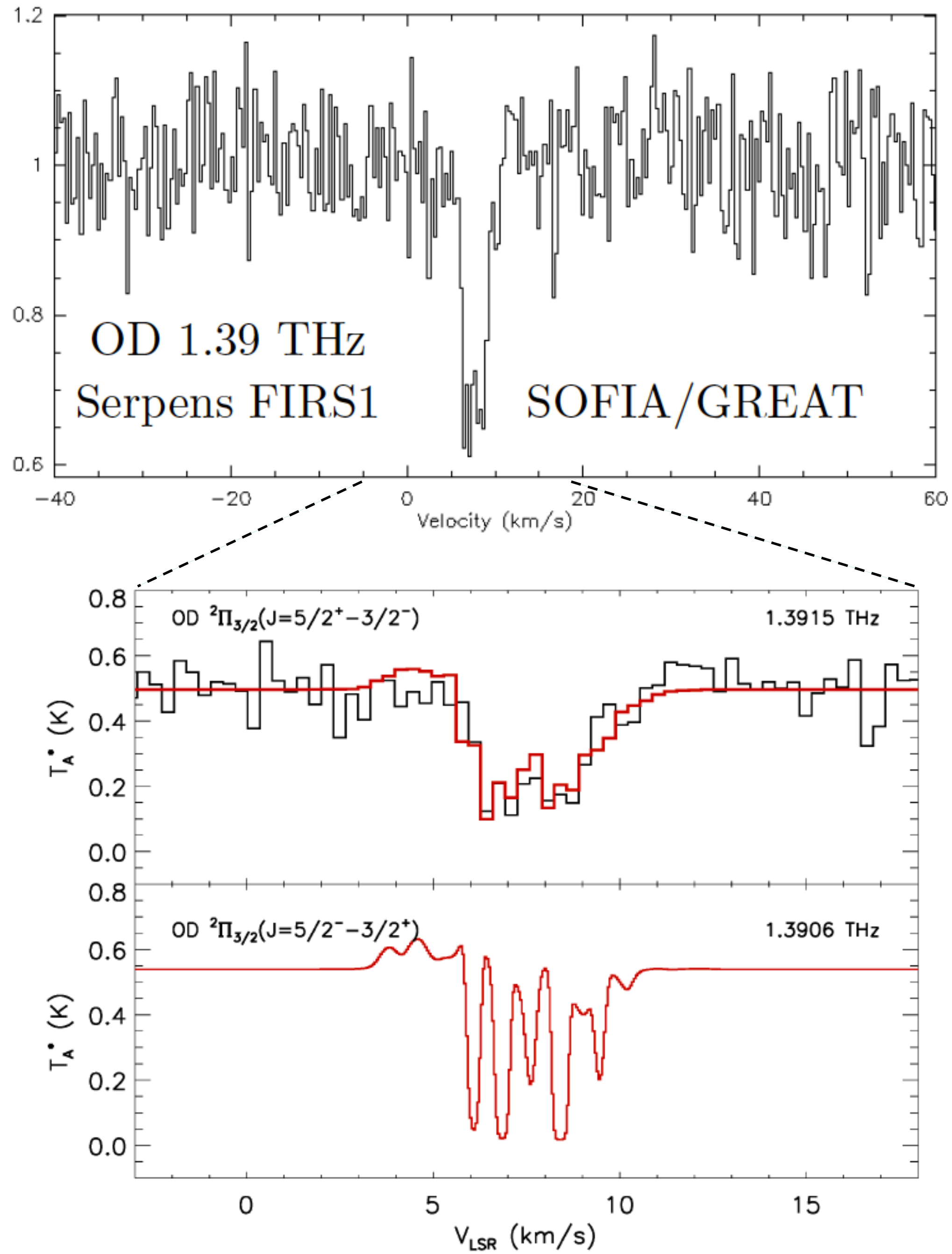
First detection of OD outside the Solar System

Parise et al. 2012



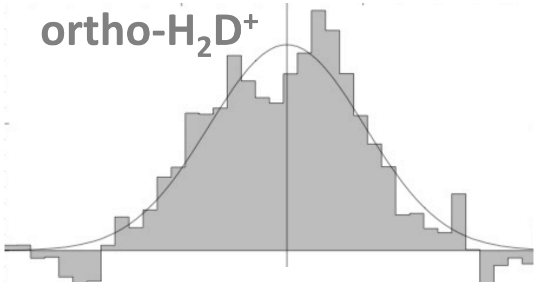
OD/HDO between 17 and 90 (high compared to model predictions ➔ gas phase reprocessing through dissociative recombination of H_2DO^+?)

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

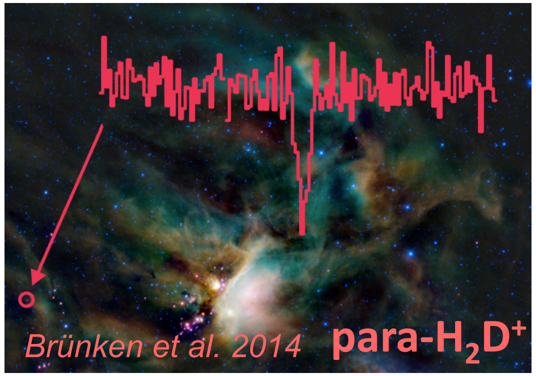


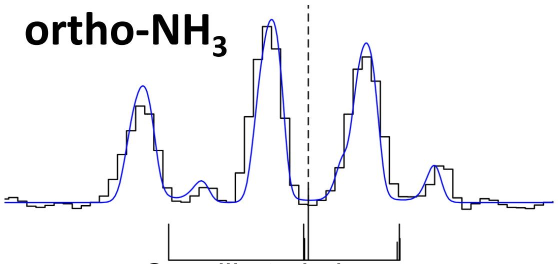
Brünken et al., in prep.

+ new SOFIA OD project accepted

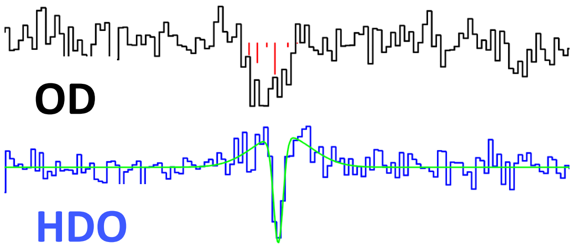


Caselli et al. 2003





Caselli et al., in prep.



Parise et al. 2012

Conclusions and future perspectives

- Observations of deuterated forms of H_3^+ provide constraints on the process of deuterium fractionation in cold environments.

- The ortho-to-para H_2D^+ ratio gives information on the ortho-to-para H_2 ratio, and the chemical age of molecular clouds (if no significant o/p-H_2 conversion on surface).

- Deuterated ammonia is a great tracer of cold gas and has potential to provide detailed information on physical/chemical evolution of dense cores (but more work needed).

- Chemical modeling of static centrally concentrated cores overestimates the central NH_3 freeze-out. Dynamical evolution needs to be taken into account.

- SOFIA observations of OD and OH, together with APEX observations of HDO, can provide more information on Oxygen chemistry (gas-phase vs surface).