Spin-state chemistry of deuterated ammonia

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Outline

- Formation of NH_2D, NHD_2, and ND_3
- Expected nuclear spin ratios
- Models and observations

Deuteration of ammonia I

- NH_2D, NHD_2, and ND_3 are most efficently formed in reactions between NH_3 and deuterated ions, followed by dissociative recombination (Rodgers & Charnley 2001 ApJ 553, 613)
- Deuteration along the primary production chain $NH^+ \overset{H_2}{\rightarrow} NH_2^+ \overset{H_2}{\rightarrow} NH_3^+ \overset{H_2}{\rightarrow} NH_4^+$ is probably less important
- In prestellar cores the most likely agents are H_2D^+, D_2H^+, and D_3^+, e.g., $NH_3 \overset{H_2D^+}{\rightarrow} NH_3D^+ \overset{e^-}{\rightarrow} NH_2D$

Deuteration of ammonia II

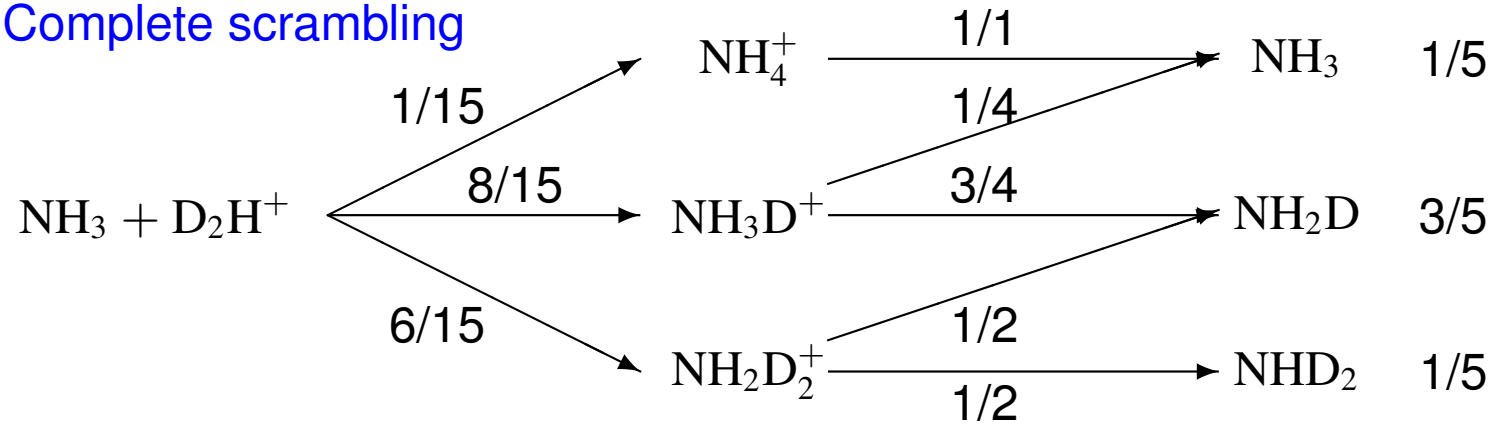
- Chemistry models usually assume that ion-molecule reactions occur through intermediate reaction complexes where nuclei are completely mixed, e.g.,

$$\mathrm{NH_3}+\mathrm{D_2H^+} \rightarrow (\mathrm{NH_4D_2^+})^{\ddagger} \rightarrow \begin{cases} \mathrm{NH_4^+} & + & \mathrm{D_2} & (1/15) \\ \mathrm{NH_3D^+} & + & \mathrm{HD} & (8/15) \\ \mathrm{NH_2D_2^+} & + & \mathrm{H_2} & (6/15) \end{cases}$$

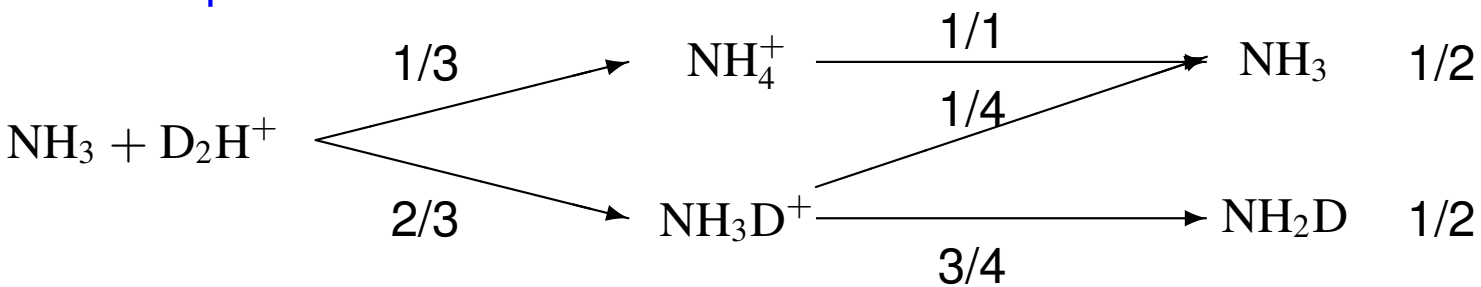
- In this scenario $\mathrm{NHD_2}$ and $\mathrm{ND_3}$ can be formed directly from $\mathrm{NH_3} + \mathrm{D_2H^+}$ and $\mathrm{NH_3} + \mathrm{D_3^+}$
- Spin selection rules in reactive collisions are needed for estimating the abundances of different spin species

Reaction $NH_3 + D_2H^+$

Complete scrambling



Proton hop



In both schemes, o/pNH_3 is $\sim$ conserved and o/p-$NH_2D = 2\,\mathrm{o/p}NH_3 + 1$. In the upper scheme, o/p$NHD_2 = \mathrm{o/p}D_2H^+$.

Formation on grains

- Molecules are formed through H (or D) atom additions, e.g., $\mathrm{N}^* \xrightarrow{\mathrm{H}^*} \mathrm{NH}^* \xrightarrow{\mathrm{H}^*} \mathrm{NH}_2^* \xrightarrow{\mathrm{H}^*} \mathrm{NH}_3^*$
  (grain surface species indicated with *)
- The degree of deuterium fractionation depends on the atomic $\mathrm{D}^*/\mathrm{H}^*$ ratio
- Fractionation ratios are supposed to be statistical (Brown & Millar 1989, MNRAS 240, 25P):

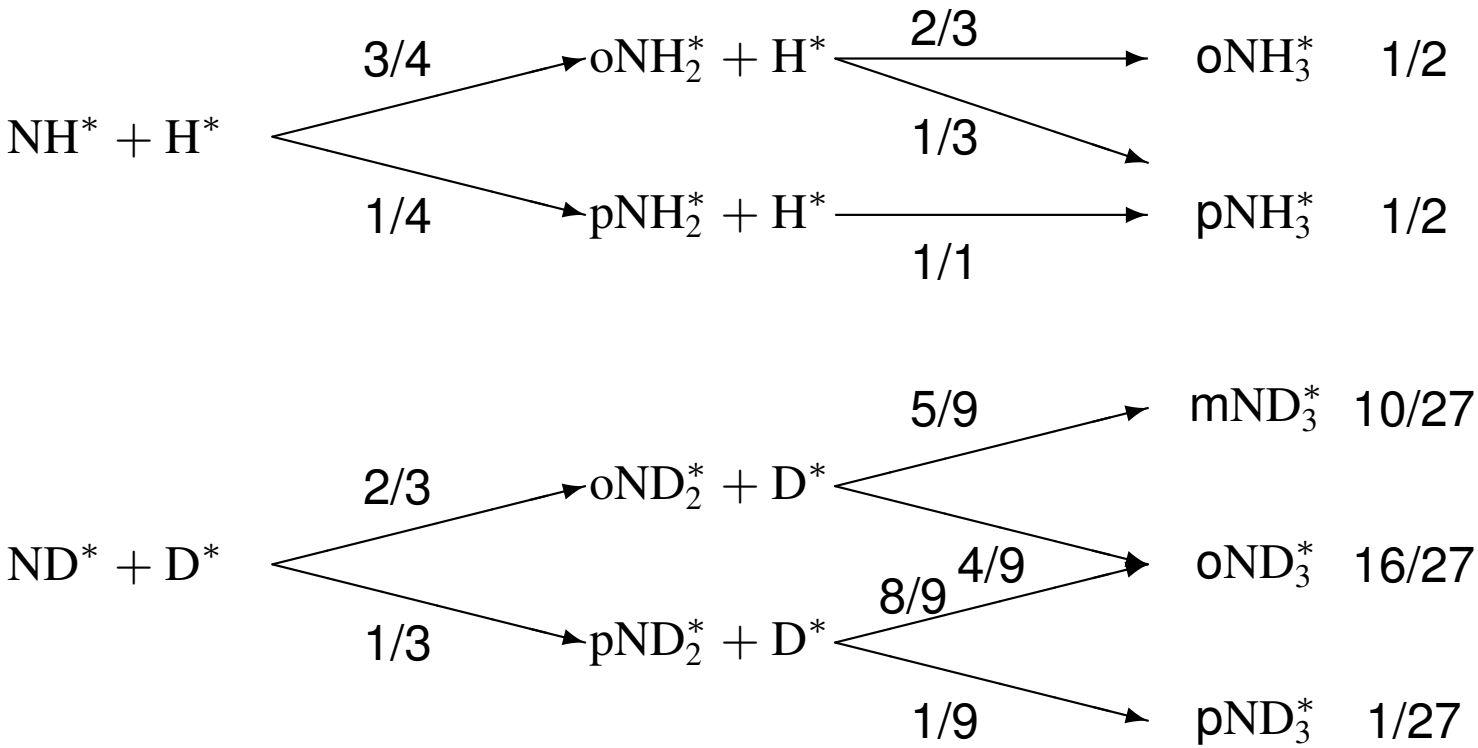
$$\begin{aligned} \mathrm{NH_2D^*}/\mathrm{NH_3^*} &\approx 3\,\mathrm{D}^*/\mathrm{H}^* \\ \mathrm{NHD_2^*}/\mathrm{NH_2D^*} &\approx \mathrm{D}^*/\mathrm{H}^* \\ \mathrm{ND_3^*}/\mathrm{NHD_2^*} &\approx \tfrac{1}{3}\,\mathrm{D}^*/\mathrm{H}^* \end{aligned}$$

- Spin ratios should correspond to the statistical weights:

o:p-$\mathrm{NH_3^*}$	=	1:1	o:p-$\mathrm{NH_2D^*}$	=	3:1
o:p-$\mathrm{NHD_2^*}$	=	2:1	o:m:p-$\mathrm{ND_3^*}$	=	16:10:1

Statistical ratios

- Reactions where one H or D nucleus is added to a complex (like on grain surfaces) result in statistical spin ratios



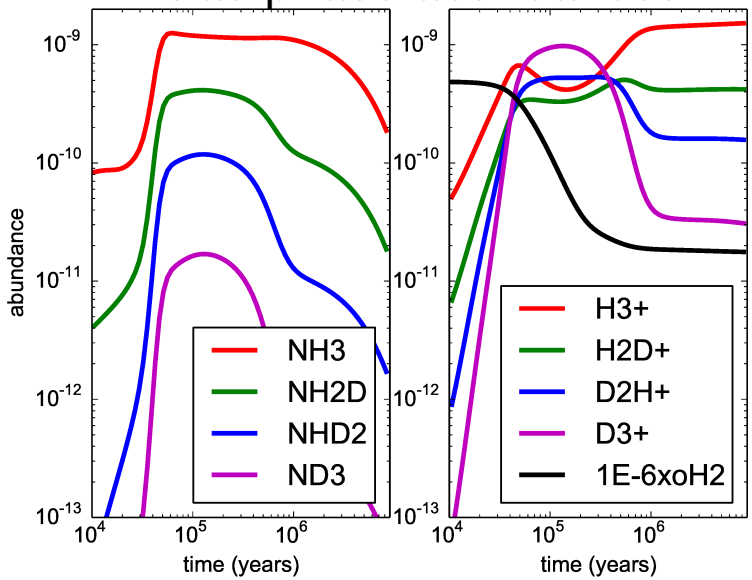
- Proton/deuteron hop or abstraction reactions in the gas-phase should follow the same spin selection rules

Chemistry model

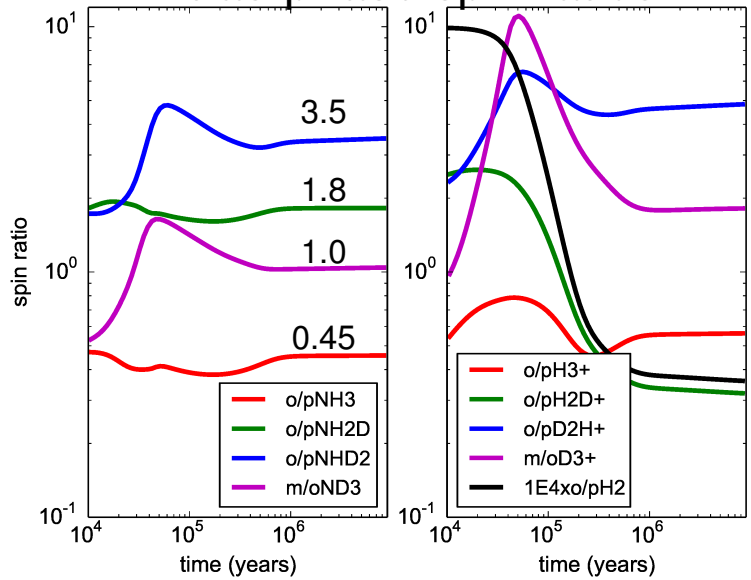
- Gas-grain chemistry code *pyRate* developed by Olli Sipilä
- The reaction set distinguishes the different nuclear spin states of light hydrogen molecules, nitrogen hydrides, water, and their deuterated forms
- Branching ratios calculated using symmetry rules
  (Sipilä, Harju, Caselli & Schlemmer 2015, A&A 581, A122)
- Predicts time variations and deviations from statistical spin ratios in the gas (*and also on grains except at very late stages*)

Dense dark cloud model, $n(\mathrm{H_2}) = 5 \times 10^5$ cm^{-3}, $T = 10$ K

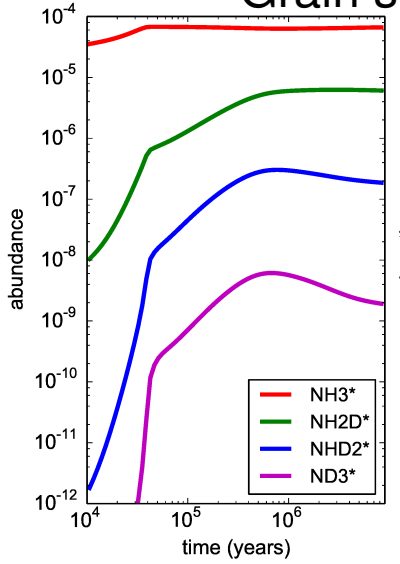
Gas-phase abundances

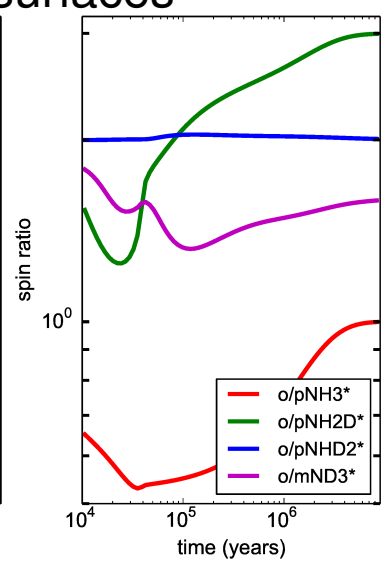


Gas-phase spin ratios



Grain surfaces





$\mathrm{o/pNH_2D*} = 3$

$\mathrm{o/pNHD_2*} = 2$

$\mathrm{o/mND_3*} = 1.6$

$\mathrm{o/pNH_3*} = 1$

Observations of deuterated ammonia

- NH_3, NH_2D, NHD_2, and ND_3 have been observed previously towards Barnard 1 (Perseus) and L1689 N (Ophiuchus)
  Lis et al. 2002, ApJ 571, L55
  Roueff et al. 2005, A&A 438, 585
  Gerin et al. 2006, A&A 454, L63
  Lis et al. 2006, ApJ 636, 916
  Roueff et al. 2015, A&A 576, A99
  Daniel et al. 2016, MNRAS 457, 1535
  Lis et al. 2016, ApJ 827, 133
  Results:
  -$[NH_2D]/[NH_3] \geq [NHD_2]/[NH_2D] \approx 0.2$,
  -$[ND_3]/[NHD_2] = 0.05 - 0.10$,
  -o/p$NH_2D \sim 3$, o/p$NHD_2 \sim 2$.
- Recently also towards the starless core Oph/H-MM1
  Harju, Daniel, Sipilä, Caselli et al. 2017, A&A 600, A61

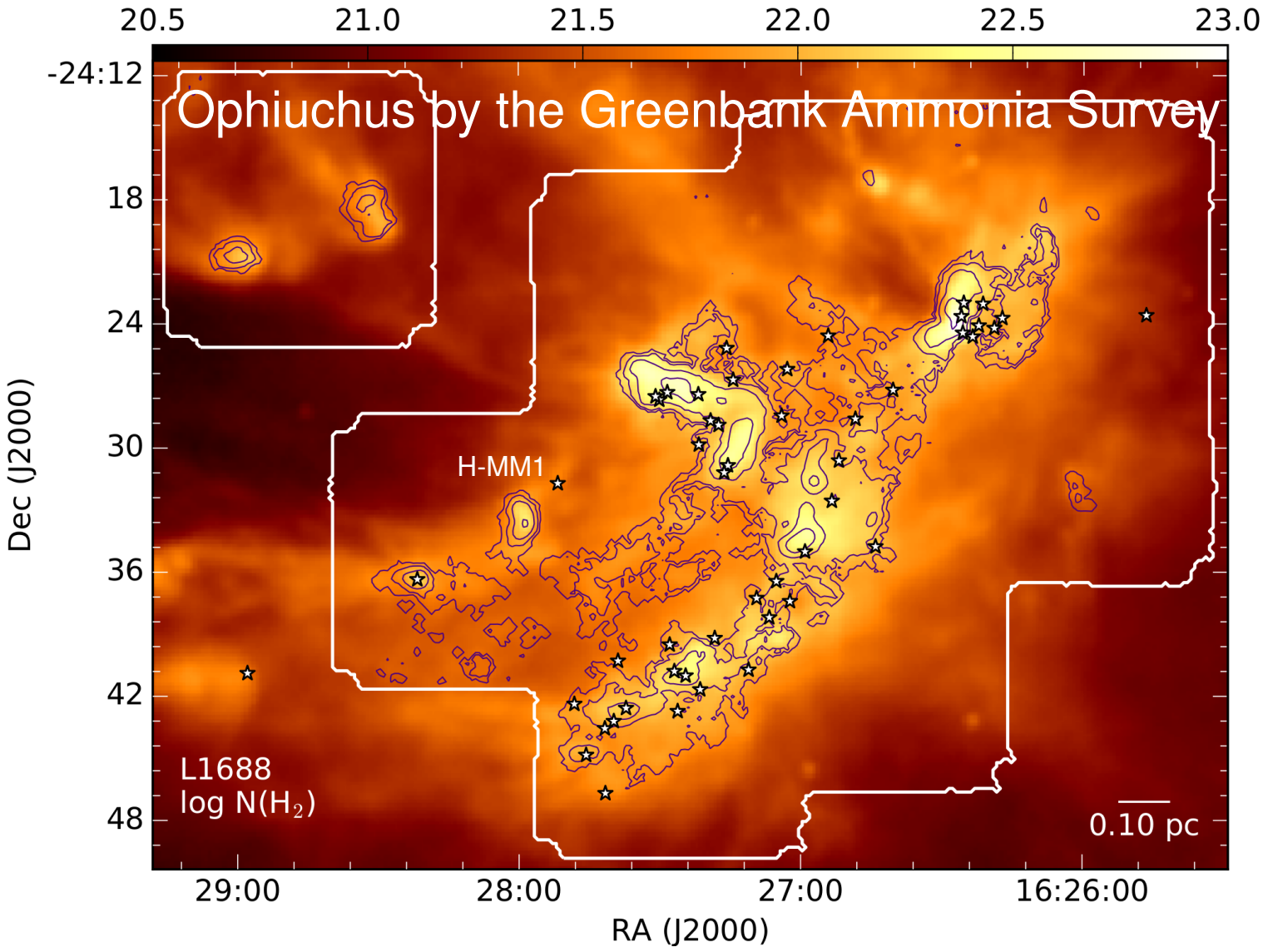
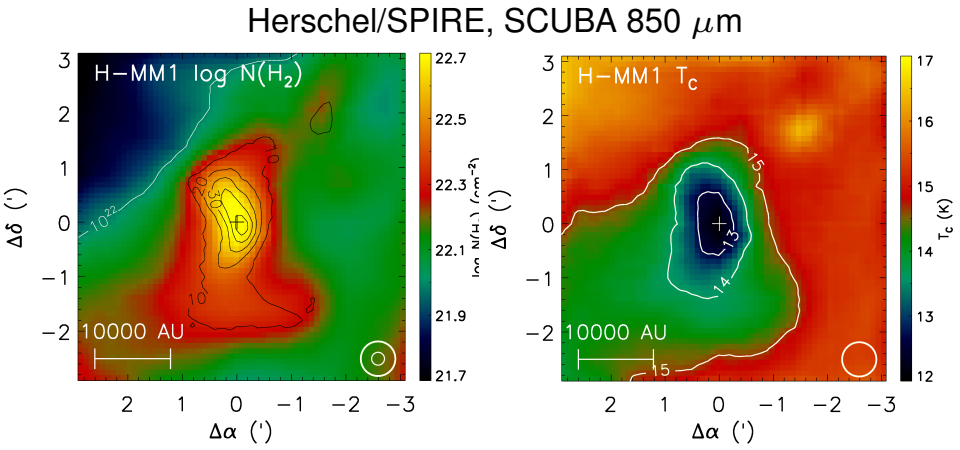
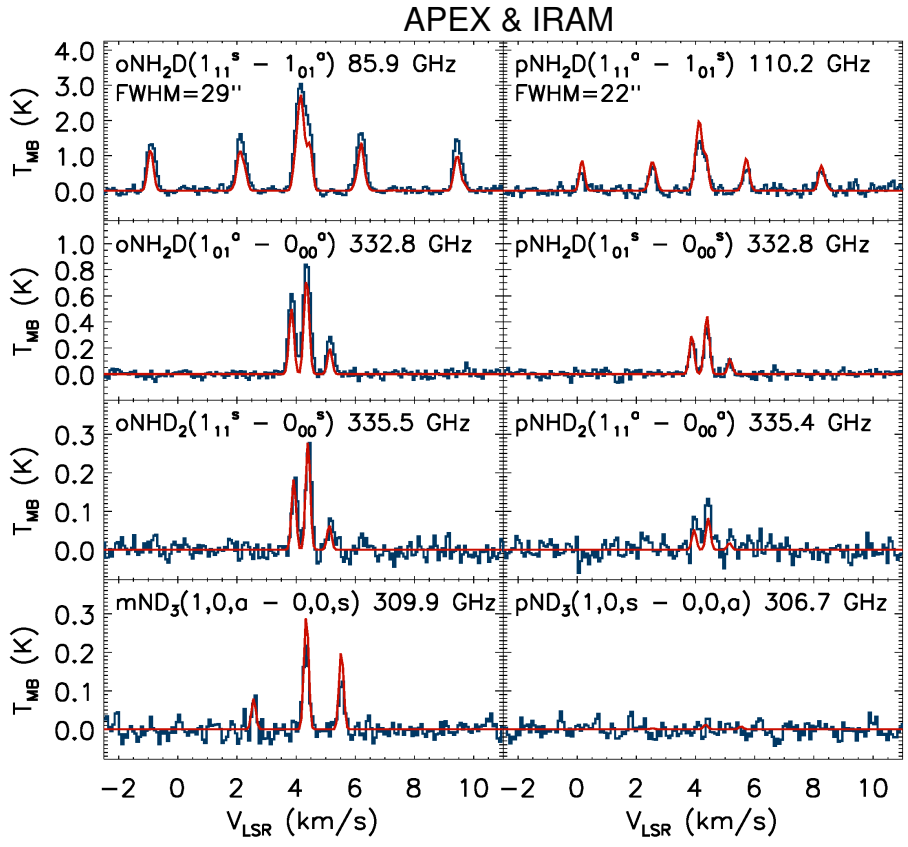


Image: $N(\mathrm{H_2})$ from Herschel, contours: integrated $\mathrm{NH_3}(1,1)$ intensity, Friesen & Pineda et al. 2017, arXiv 1704.06318

Oph/H-MM1





-Rotational lines of o+p-NH_2D, o+p-NHD_2, and m+p-ND_3, and inversion lines of p-NH_3 towards the centre of the core were observed with APEX 12m, IRAM 30m, and GBT 100m

-A hydrostatic model (MBES) constructed based on the dust continuum and NH_3 observations.

-Chemical abundances (as functions of radius and time) were calculated using *pyRate*

-Spectral lines simulated using Mika Juvela's programs

Observed and modelled spin ratios

- Abundance ratios derived from the observed spectra:

NH_2D/NH_3	0.39 ± 0.02 (o:p-NH_3 = 1:1)
NHD_2/NH_2D	0.22 ± 0.02
ND_3/NHD_2	0.06 ± 0.01 (o:m:p-ND_3 = 18:10:1)
o/p-NH_2D	3.0 ± 0.2
o/p-NHD_2	2.4 ± 0.4

  Consistent with statistical spin ratios

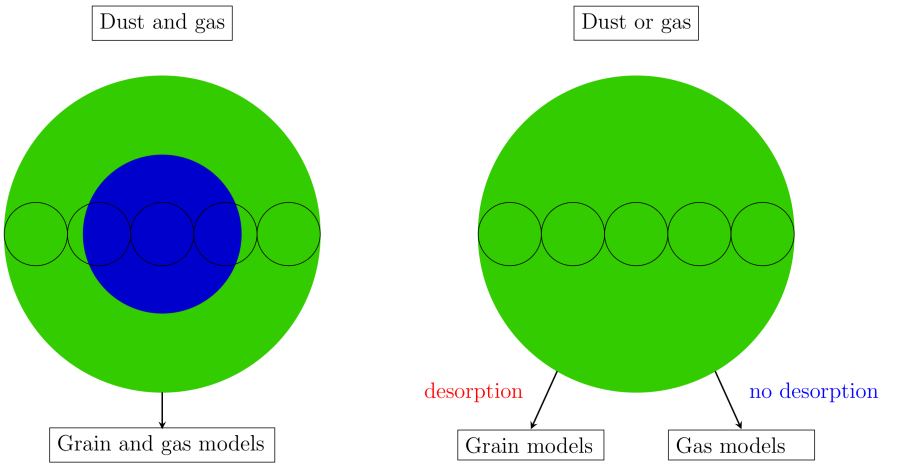
- Agree with previous observations towards two cores (Roueff et al. 2005 A&A 438, 585; Daniel et al. 2016 MNRAS 457, 1535)
- The best-fit chemistry model predicts, however, o/p-$NH_2D \sim 2$, o/p-$NHD_2 \sim 4$

Possible explanations for the discrepancy

- Contribution from grain surface chemistry?
  In the A&A paper this was considered unlikely because
  -the core is cold and probably well shielded
  -the observations pertain gas-phase molecules
  -evaporated molecules are rapidly reprocessed by ion-molecule reactions
- The complete scrambling hypothesis is not valid?
  -interchanges of nuclei in the reaction complex may be hindered by potential barriers
  -nuclei do not have equivalent positions
  -few experimental or theoretical studies of relevant reactions

ALMA Cycle 4

ALMA time granted for mapping H-MM1 in o+p-NH_2D, o+p-NHD_2, and CH_3OH at $\lambda = 3\,\mathrm{mm}$ (Band 3) and 1 mm (Band 7)
-Band 3: ACA+12m
-Band 7: ACA+TP
-angular resolution $3 - 4''$

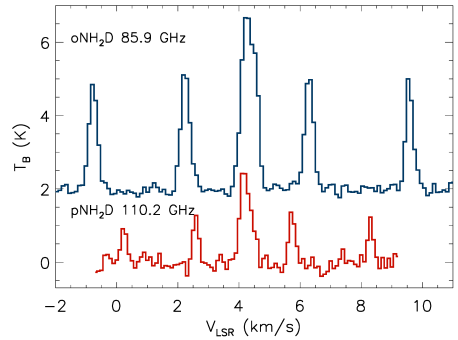


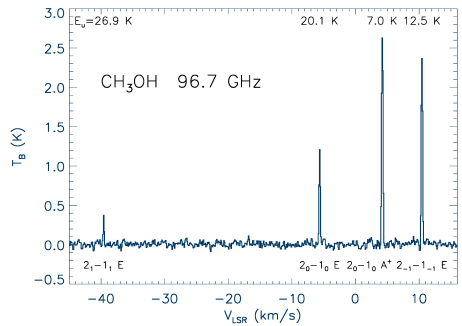
Do we see different spin ratios in the core nucleus where desorption from grains is very unlikely?

Project completed in April, Band 3 data received
Thanks for Jaime Pineda for quick data reduction.

ALMA results

-o+pNH_2D integrated intensity maps are similar to the SCUBA 450μm and 850μm dust continuum maps.
-CH_3OH concentrates strongly on the core's eastern edge, which is more shielded from the interstellar radiation field.
-CH_3OH lines are only slightly broader than the NH_2D lines.
-Rotational temperatures derived from three $E - CH_3OH$ lines are $\sim 10K$.
-Peak fractional abundances:
$X(E - CH_3OH) \leq 3.5 \times 10^{-9}$ in the desorption layer $(A/E \sim 1.5)$
$X(o{-}NH_2D) \leq 7 \times 10^{-9}$ in the core.





Preliminary conlusions from ALMA data

- NH_2D is confined to the dense core and shows a flat column density distribution, that is, it is depleted in the centre.
- The analysis of o/p-NH_2D is still under way.
- CH_3OH indicates enhanced desorption on the eastern side of the core. Not correlated with NH_2D.
- No evidence for high temperatures or large velocity dispersion in the gas traced by CH_3OH
- Possible explanations:
  -Reactive desorption plus asymmetric illumination (Vasyunin & Herbst 2013)
  -CH_3OH traces a past shock related to an external event or the core formation (cf. Lis et al. 2016, ApJ 827, 133)