Deuterated amidogen in the laboratory and in Space

Detection of NHD and ND_2 in space

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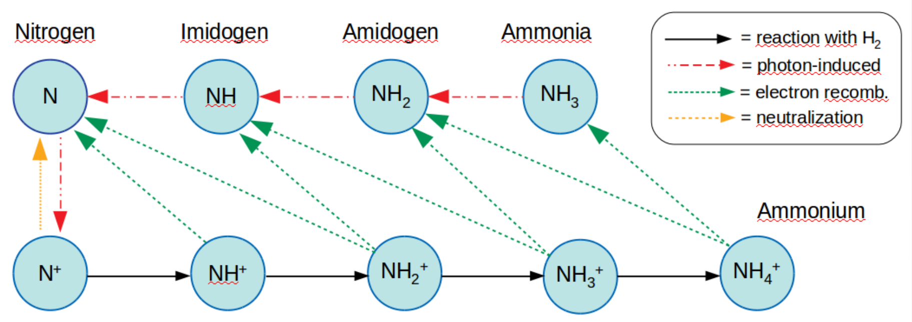
N + H "initial" chemical network



From Gerin, Neufeld and Goicoechea (2016), ARA&A, 54:181.

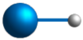
The family of neutral N hydrides

✓ = studied / detected

✗ = not detected

✓ (blue) = studied by CAS/coll

★ = first time by CAS/coll

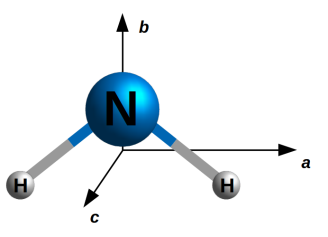


Imidogen	ASTRO	LAB
NH	✓	✓
ND	✓	✓ (blue)
^{15}NH	✗	✓ (blue)
^{15}ND	✗	★

Amidogen	ASTRO	LAB
NH_2	✓	✓
NHD	✗	✓ (blue)
ND_2	✗	✓ (blue)
$^{15}NH_2$	✓	✓
^{15}NHD	✗	★
$^{15}ND_2$	✗	★

Ammonia	ASTRO	LAB
NH_3	✓	✓ (blue)
NH_2D	✓	✓ (blue)
NHD_2	✓	✓
ND_3	✓	✓ (blue)
$^{15}NH_3$	✓	✓
$^{15}NH_2D$	✓	✓
$^{15}NHD_2$	✗	✓
$^{15}ND_3$	✗	✓ (blue)

Molecular and electronic structure of NH_2



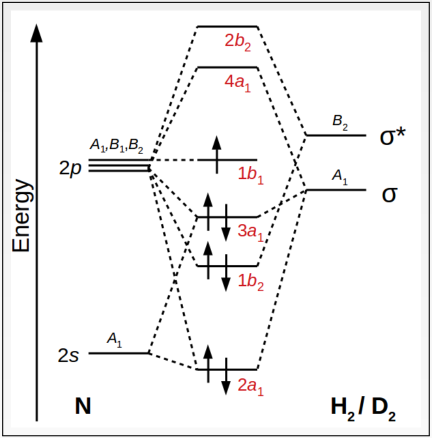
C_{2v} symmetry

$\mu_b = 1.82\,\mathrm{D}$

ortho/*para* statistical weights

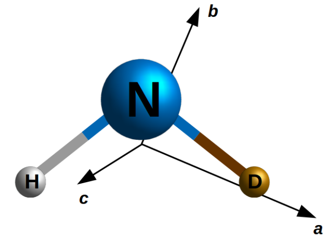
C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	a
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	b
B_2	1	-1	-1	1	c

molecular orbital diagram



$$(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1 \rightarrow \tilde{X}^2B_1$$

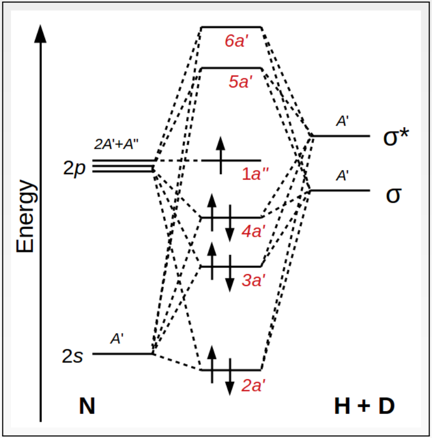
Molecular and electronic structure of NHD



C_s symmetry
$\mu_a = 0.67$ D
$\mu_b = 1.69$ D
~~*ortho*/*para* statistical weights~~

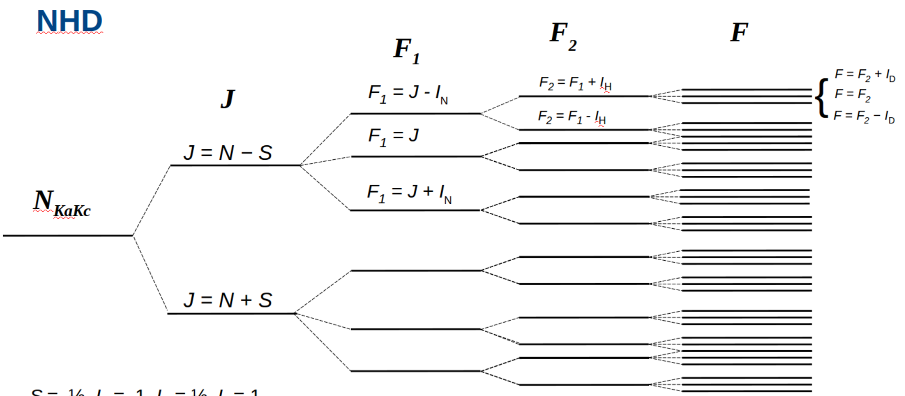
C_s	E	σ_h	
A'	1	1	b, c
A''	1	-1	a

molecular orbital diagram



$$(2a')^2(3a')^2(4a')^2(1a'')^1 \rightarrow \tilde{X}^2A''$$

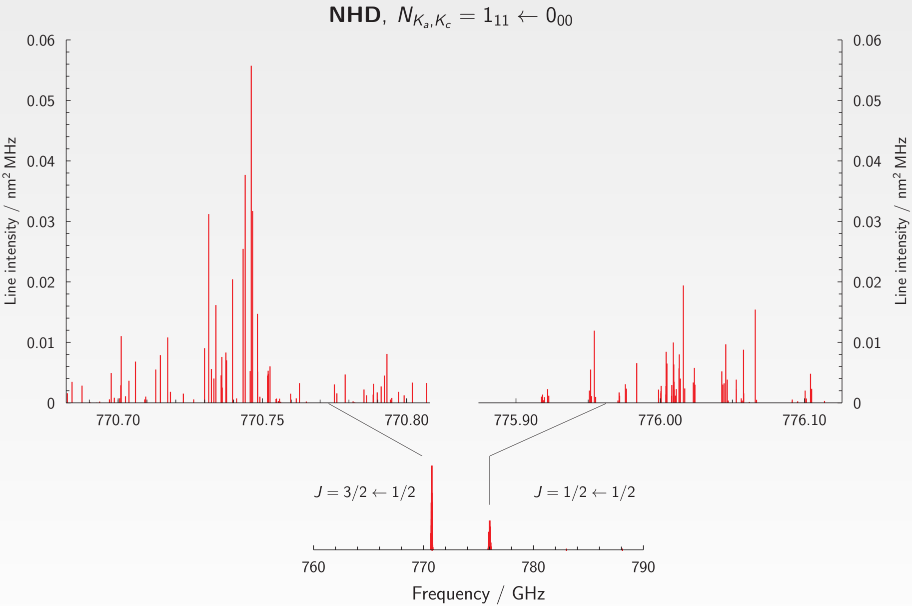
Rotational FS and HFS level scheme



$S = ½, I_N = 1, I_H = ½, I_D = 1$

$\boldsymbol{N + S = J,\ J + I_N = F_1,\ J + I_H = F_2,\ F_2 + I_D = F}$

Fine/Hyperfine spectral patterns



Spectroscopy status of amidogen isotopologues

NH_2

- Submm-wave and FIR spectra well studied:
  (Gendriesch et al. 2001, Martin-Drumel et al. 2014)
- Detected in HMSFCs (Persson et al. 2012)
  and IRAS16293-2422 (Hily-Blant et al. 2010)

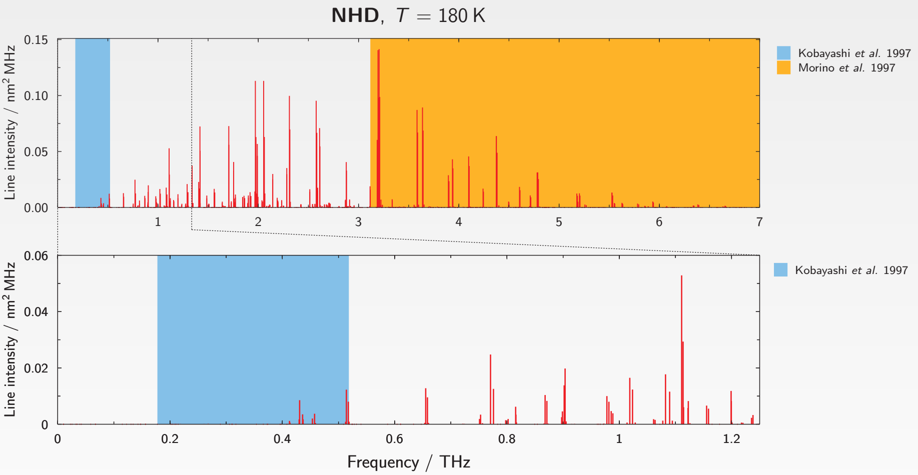
ND_2

- new measurements in the 588–1 131 GHz range done in Bologna
  global analysis with mm, sub-mm, MODR, and FIR data
  (Melosso et al. 2017, *ApJS*)
- Good RFs available, but still not detected/not searched in space

NHD

- Previous measurements provide scarce spectral coverage
  RFs not sufficiently precise for astrophysical purposes (. . . **until recently)**
- new measurements done in Garching (400–1 400 GHz)
  and at AILES@SOLEIL (FIR)
- global analysis TBP (Bizzocchi et al. *submitted to ApJS*)

Spectral coverage plot

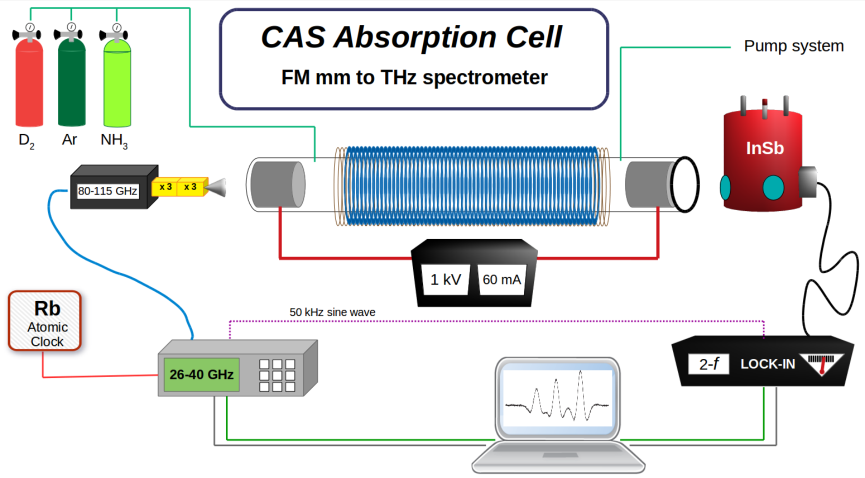


New NHD measurements

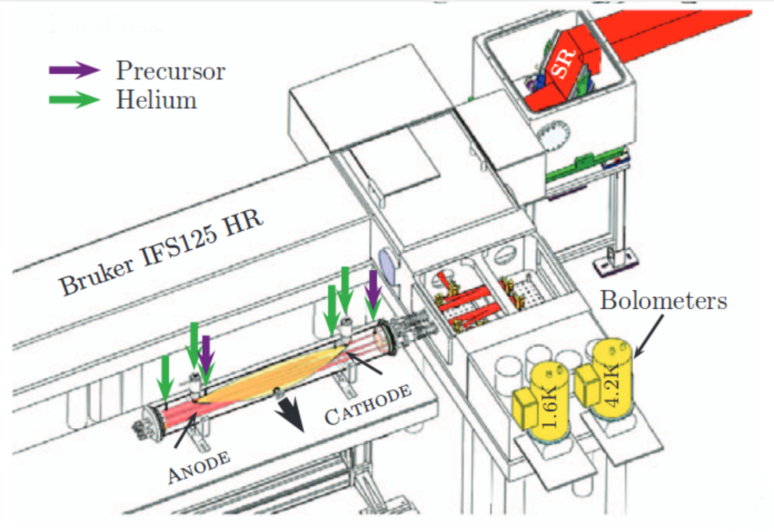
- **sub-mm regime**: 430–1200 GHz at MPE
  (collaboration with Bologna lab: L. Dore, M. Melosso)
  glow discharge of NH_3, D_2, Ar ($P_{tot} = 15 - 25\,\mu$Bar, $T \sim 180$ K)
  positive column: $i = 40 - 70$ mA, $V \approx 2$ kV
  measurement precision 20–50 kHz

- **FIR region**: 60–225 cm^{-1} at AILES beamline (SOLEIL synchrotron)
  (collaboration with O. Pirali and M.A. Martin-Drumel)
  several discharges: typically NH_3, D_2, He ($P_{tot} = 5 - 20$ mBar)
  positive column: $i \approx 100$ mA, $V \approx 4$ kV, room T
  measurement precision ~10 MHz

CASAC spectrometer at MPE

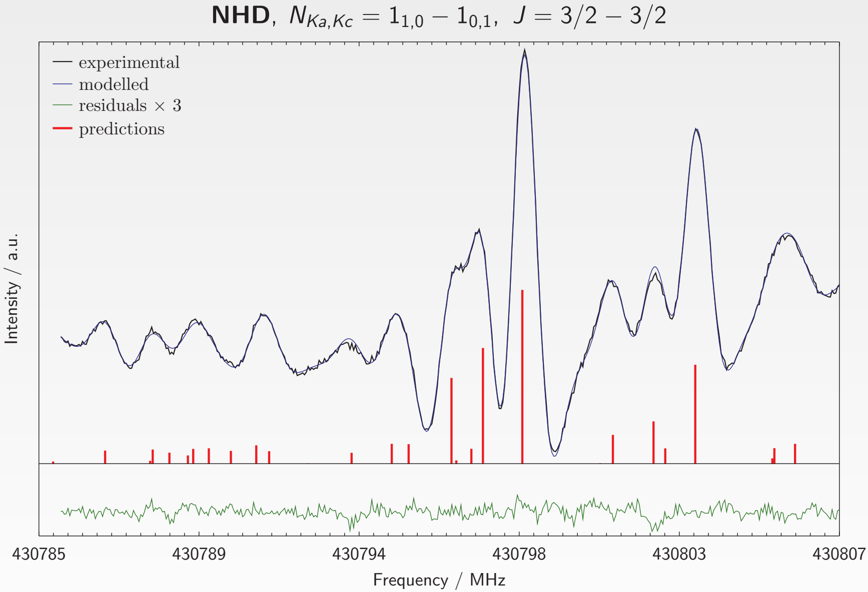


Experimental setup at AILES beamline (SOLEIL)



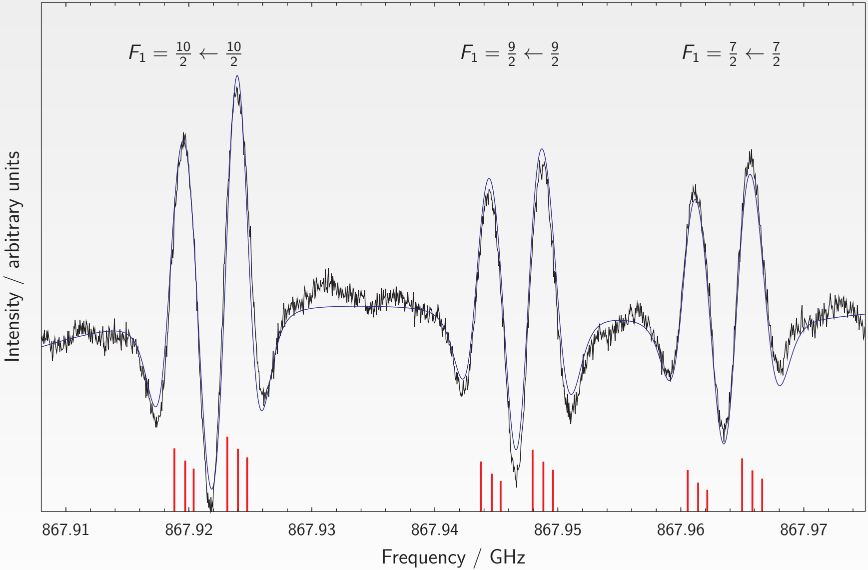
From Martin-Drumel et al. (2011), *Rev. Sci. Instr.*, 82, 113106.

HFS structure in the sub-mm region (1)

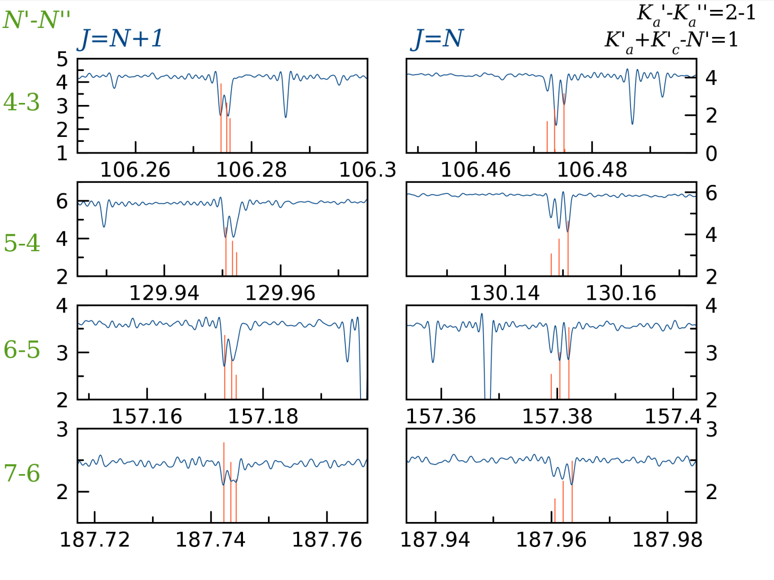


HFS structure in the sub-mm region (2)

$N_{Ka,Kc} = 4_{1,3} \leftarrow 4_{0,4}$, $J = \frac{9}{2} \leftarrow \frac{9}{2}$



HFS structure revealed in the FIR



$^2A''$– rotational–spin effective Hamiltonian

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{fs}} + \hat{H}_{\text{hfs,el–nuc}} + \hat{H}_{\text{hfs,rot–nuc}}$$

$$\hat{H}_{\text{rot}} \subseteq \text{Watson-type} + \text{CDCs}$$

$$\hat{H}_{\text{fs}} \subseteq T^k(\epsilon) \cdot T^k(\mathbf{N}, \mathbf{S}) + \text{Spin–Rot CDCs}$$

$$\hat{H}_{\text{hfs,el–nuc}} \subseteq \sum_i a_F(i)\, T^1(\mathbf{I}_i) \cdot T^1(\mathbf{S}) + \sum_i T^1(\mathbf{I}_i) \cdot T^1(\mathbf{S}, C^2)$$

$$\hat{H}_{\text{hfs,rot–nuc}} \subseteq \sum_i T^2(\mathbf{Q}_i) \cdot T^2(\nabla \mathbf{E}) + T^k(\mathbf{C}) \cdot T^k(\mathbf{N}, \mathbf{I}_i)$$

Hamiltonian parameters

- Rotational and CD constants:
  $A, B, C,\ \Delta_N, \Delta_{NK}, \Delta_K, \delta_N, \delta_K,\ \Phi_N, \Phi_{NNK}, \Phi_{NKK}, \Phi_K, \phi_N, \phi_{NK}, \phi_K,$
  $\ldots$
- Spin–rotation and CD constants:
  $\epsilon_{aa}, \epsilon_{bb}, \epsilon_{cc},\ \Delta^S_J, \Delta^S_{NK} + \Delta^S_{KN}, \Delta^S_K, \delta^S_N, \delta^S_K,$
  $\ldots$
- Electron spin–nuclear spin (i) hyperfine constants:
  $a_F(i),\ T_{aa}(i), T_{bb}(i), T_{cc}(i),$
  $\ldots$
- Rotation–nuclear spin (i) hyperfine constants:
  $\chi_{aa}(i), \chi_{bb}(i), \chi_{cc}(\mathrm{i}),\ C_{aa}(i), C_{bb}(i), C_{cc}(i),$
  $\ldots$

Search for amidogen isotopologues in the ISM

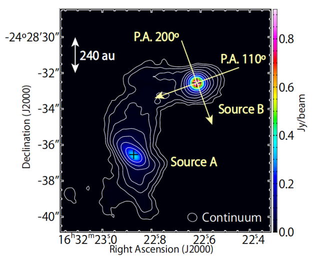
- Observations are difficult from Earth
  rotational lines fall in the sub-mm region
  H_2O *absorption in the atmospher is a major problem*

- These line are best targeted by Space-born facilities like *Herschel*
  Not operative anymore... but
  Herschel legacy data are freely accessible at HSA

- IRAS16293-2422 protostar was a target of the CHESS key project **[Ceccarelli et al. 2010]**
  Full sub-mm to FIR "unbiased" survey was performed
  Source showing extreme deuteration
  (multiply substituted isotopologues found)

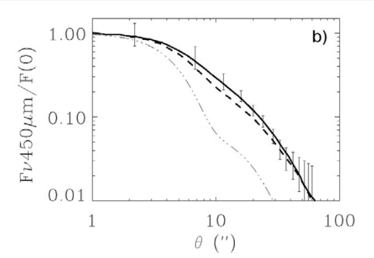
IRAS16293-2422, a prototypical Class 0 protostar

ALMA



Oya et al. (2018)

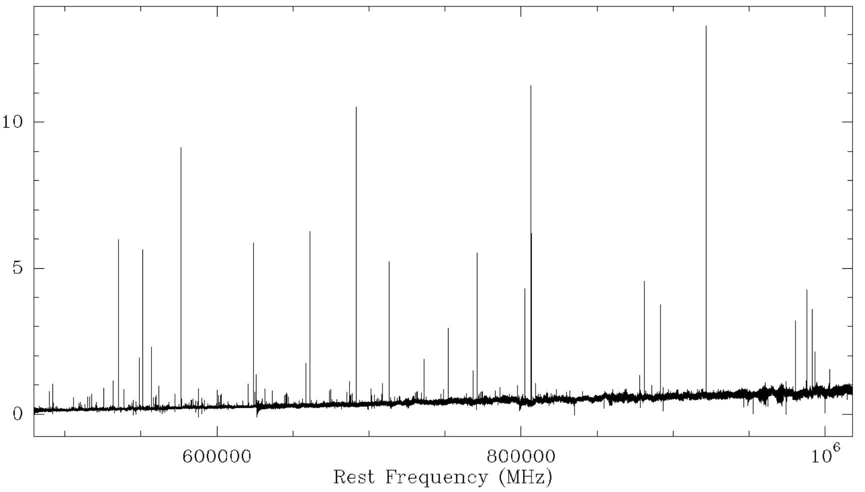
JCMT



Crimier et al. (2010)

Single-dish spectra are dominated by the cold envelope + warm components from inner warm region (dust sublimation)

IRAS16293-2422 survey (CHESS project)



HIFI 1a – 4b bands (from *Herschel* Science Archive)

Nitrogen hydrides in IRAS16293-2422

A&A 521, L42 (2010)
DOI: 10.1051/0004-6361/201015102

Herschel/HIFI: first science highlights

Astronomy & Astrophysics
Special feature

LETTER TO THE EDITOR

First detection of ND in the solar-mass protostar IRAS16293-2422★

A. Bacmann[1,2,30], E. Caux[6,29], P. Hily-Blant[1], B. Parise[10], L. Pagani[8], S. Bottinelli[6,29], S. Maret[1], C. Vastel[6,29], C. Ceccarelli[1,2,30], J. Cernicharo[9], T. Henning[26], A. Castets[1], A. Coutens[6,29], E. A. Bergin[25], G. A. Blake[3], N. Crimier[1,9], K. Demyk[6,29], C. Dominik[12,13], M. Gerin[28], P. Hennebelle[28], C. Kahane[1], A. Klotz[6,29], G. Melnick[18], P. Schilke[10,20], V. Wakelam[2,30], A. Walters[6,29], A. Baudry[2,30], T. Bell[3], M. Benedettini[4], A. Boogert[5], S. Cabrit[8], P. Caselli[7], C. Codella[11], C. Comito[10], P. Encrenaz[8], E. Falgarone[28], A. Fuente[14], P. F. Goldsmith[15], F. Helmich[16], E. Herbst[17], T. Jacq[2,30], M. Kama[12], W. Langer[15], B. Lefloch[1], D. Lis[3], S. Lord[5], A. Lorenzani[11], D. Neufeld[19], B. Nisini[24], S. Pacheco[1], J. Pearson[15], T. Phillips[3], M. Salez[8,28], P. Saraceno[4], K. Schuster[21], X. Tielens[22], F. F. S. van der Tak[16,27], M. H. D. van der Wiel[16,27], S. Viti[23], F. Wyrowski[10], H. Yorke[15], A. Faure[1], A. Benz[31], O. Coeur-Joly[6,29], A. Cros[6,29], R. Güsten[10], and L. Ravera[6,29]

(Affiliations are available on page 5 of the online edition)

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ND, NH

A&A 521, L52 (2010)
DOI: 10.1051/0004-6361/201015253

Astronomy & Astrophysics

LETTER TO THE EDITOR

Nitrogen hydrides in the cold envelope of IRAS 16293-2422★,★★

P. Hily-Blant[1], S. Maret[1], A. Bacmann[1,2], S. Bottinelli[6], B. Parise[10], E. Caux[6], A. Faure[1], E. A. Bergin[25], G. A. Blake[3], A. Castets[1], C. Ceccarelli[1], J. Cernicharo[9], A. Coutens[6], N. Crimier[1,9], K. Demyk[6], C. Dominik[12,13], M. Gerin[28], P. Hennebelle[28], T. Henning[26], C. Kahane[1], A. Klotz[6], G. Melnick[18], L. Pagani[8], P. Schilke[10,20], C. Vastel[6], V. Wakelam[2], A. Walters[6], A. Baudry[2], T. Bell[3], M. Benedettini[4], A. Boogert[5], S. Cabrit[8], P. Caselli[7], C. Codella[11], C. Comito[10], P. Encrenaz[8], E. Falgarone[28], A. Fuente[14], P. F. Goldsmith[15], F. Helmich[16], E. Herbst[17], T. Jacq[2], M. Kama[12], W. Langer[15], B. Lefloch[1], D. Lis[3], S. Lord[5], A. Lorenzani[11], D. Neufeld[19], B. Nisini[24], S. Pacheco[1], T. Phillips[3], M. Salez[8], P. Saraceno[4], K. Schuster[21], X. Tielens[22], F. van der Tak[16,27], M. H. D. van der Wiel[16,27], S. Viti[23], F. Wyrowski[10], and H. Yorke[15]

(Affiliations are available on page 5 of the online edition)

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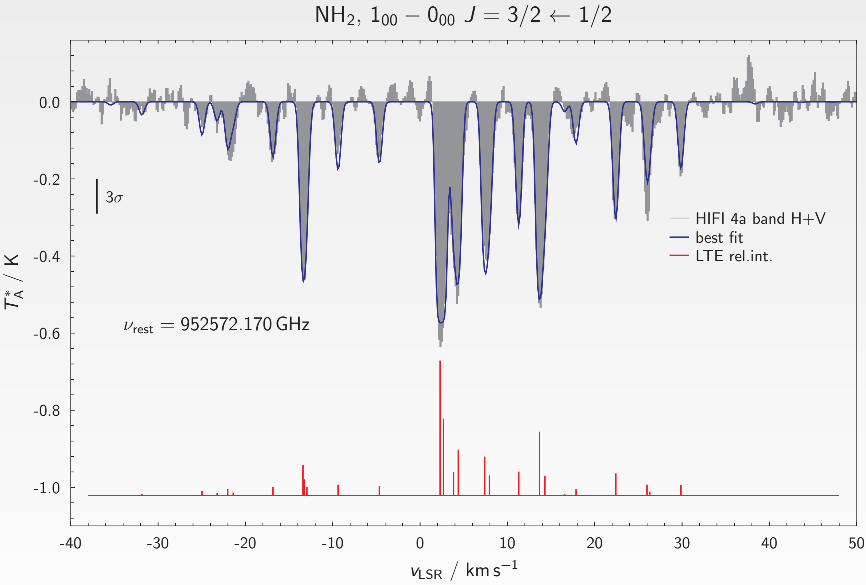
NH_2, o/p-NH_3

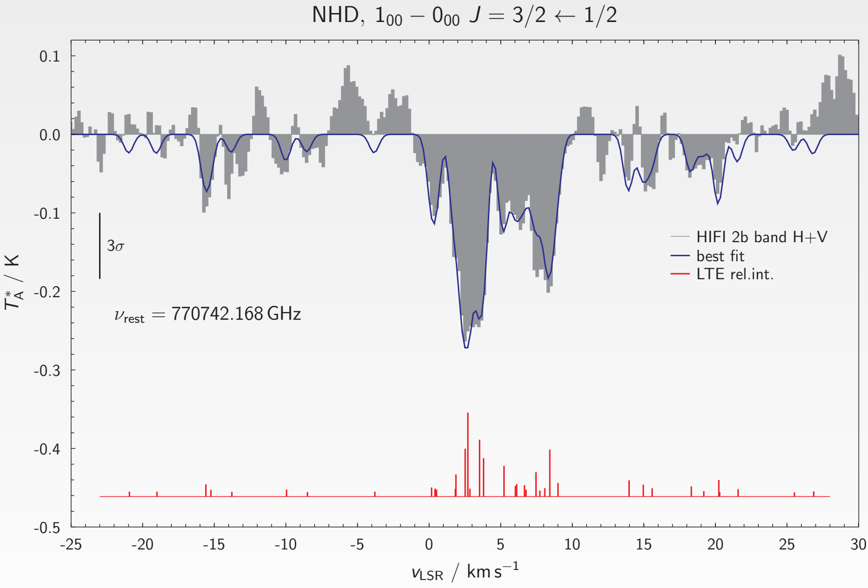
No NH_2 isotopologues searched/detected !

Rest frequencies for NHD and ND_2 were not avaiable until (very) recently

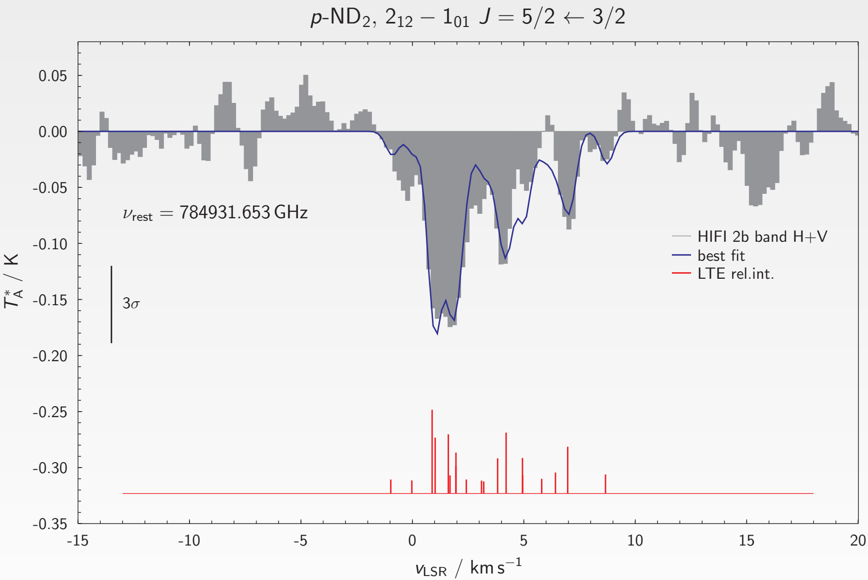
Amidogen: Parent isotopologue



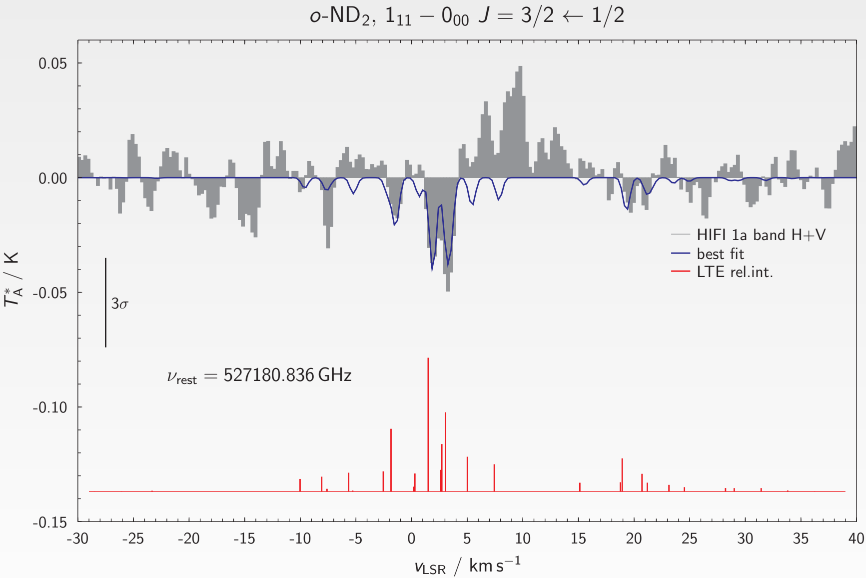
Amidogen: Singly deuterated



Amidogen: Doubly deuterated



Amidogen: Doubly deuterated



IRAS16293-2422: NH_2, NHD, ND_2 results

	N / cm^{-2}	T_{ex} / K	v_{LSR} / $km\,s^{-1}$	Δv / $km\,s^{-1}$
o-$\mathbf{NH_2}$	5.84(24) $\times 10^{13}$	8.6(1)	4.25(1)	0.72(2)
NHD	4.24(63) $\times 10^{13}$	7.3(2)	4.19(3)	0.78(5)
o-$\mathbf{ND_2}$	5.48(77) $\times 10^{12}$	4.5	4.66(6)	0.70
p-$\mathbf{ND_2}$	3.46(10) $\times 10^{11}$	4.5	4.32(2)	0.70

T_{ex} *closer to what found for NH and ND species (Bacmann et a. 2010)*

Amidogen abundace ratios in IRAS16293-2422

- o/p ratio in ND_2:

$$\frac{[o\text{-}ND_2]}{[p\text{-}ND_2]} = 15.8 \rightarrow T_{ex} \approx 4.5\,K$$

- Amidogen deuteration:

$$\frac{[NHD]}{[o\text{-}NH_2]} \sim 0.72 \quad ; \quad \frac{[ND_2]}{[o\text{-}NH_2]} \sim 0.1$$

- **Very high deuteration found!**
  $[ND]/[NH] \sim 30 - 100\%$;
  $[NH_2D]/[NH_3] \sim 10\%$;
  $[D_2CO]/[H_2CO] \sim 5 - 10\%$

Work in progress

- New reduction/deconvolution of HSA data
  improve S/N, better backround subtraction
- Radiative transfer modelling of IRAS16293-2422
  NH_2/H_2 hyperfine collisional rates just published
- Estimate collisional rates for the asymetric NHD species *scaling relations not useful due to different symmetry*

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