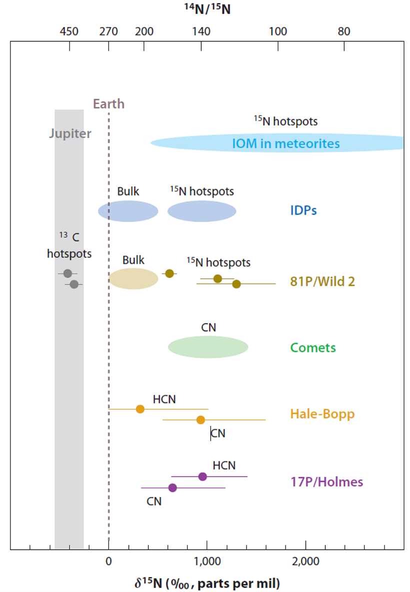
Sub-millimetre spectroscopy of light nitrogen-bearing radicals and ions

Luca Bizzocchi

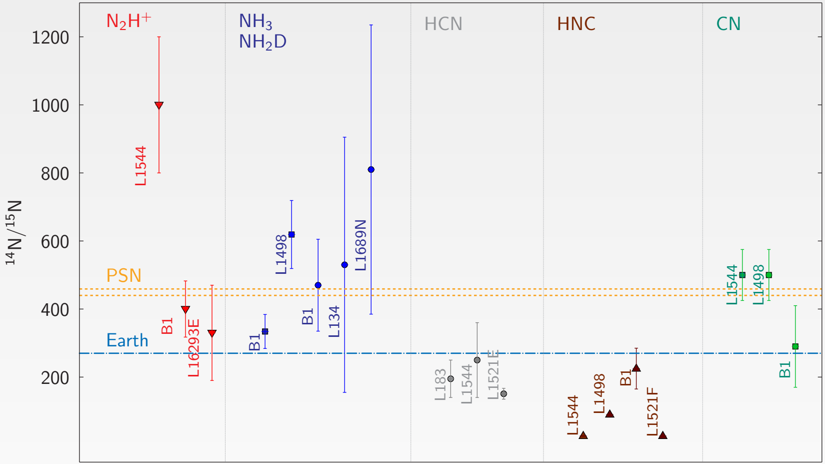
Center for Astrochemical Studies
Max-Planck-Institut für extraterrestrische Physik, Garching, Germany

COST meeting – November 9, 2017– Copenhagen

N isotopic ratio in the Solar System (from Mumma & Charnley 2011)

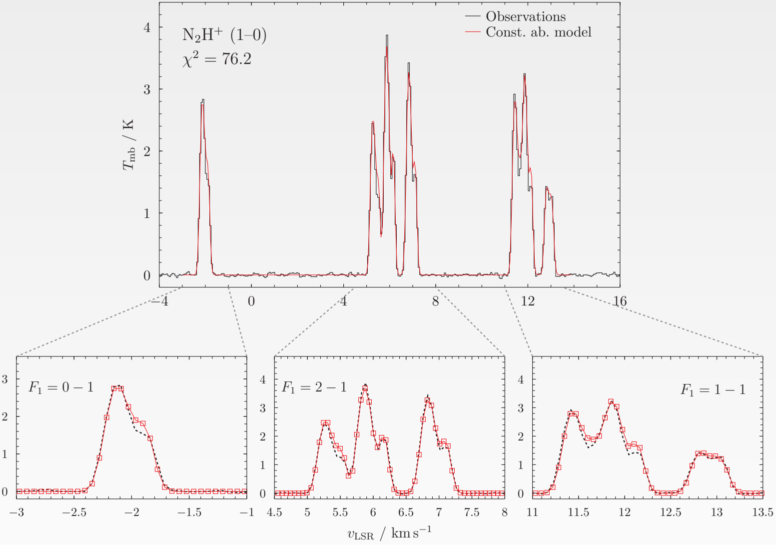


N isotopic ratios in low-mass dense clouds



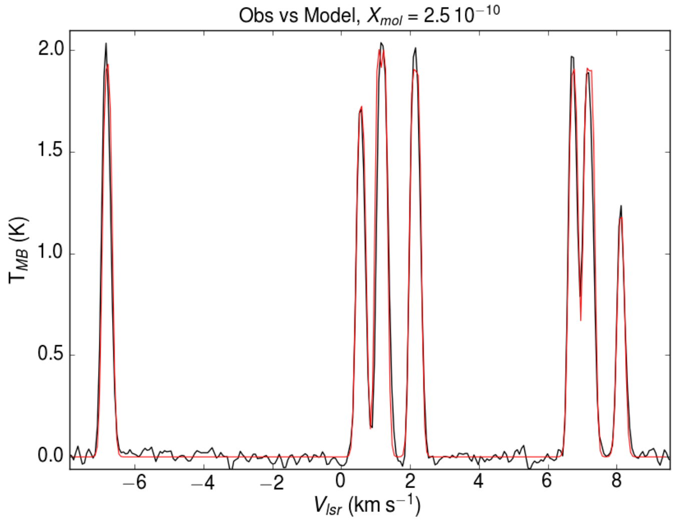
Ikeda+2002, Lis+2010, Gerin+2009, Bizzocchi+2013, Adande+2015, Hily-Blant+2013, Milam & Charnley 2015, Redaelli+ inprep

Interlude: non-LTE modelling of N_2H^+ (1–0) in L1544



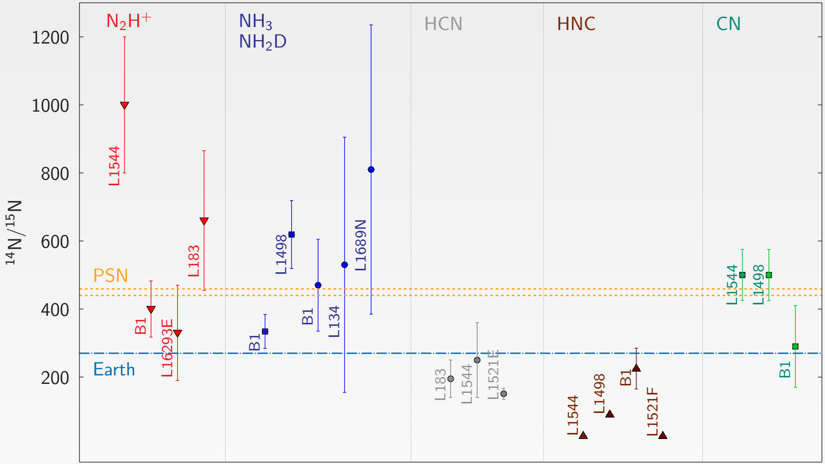
Bizzocchi et al. (2013)

Interlude: non-LTE modelling of N_2H^+ (1–0) in L183



Redaelli at al. *in prep.*

N isotopic ratios in low-mass dense clouds



Ikeda+2002, Lis+2010, Gerin+2009, Bizzocchi+2013, Adande+2015, Hily-Blant+2013, Milam & Charnley 2015, Redaelli+ inprep

N fractionation: summary

- Observational evidences:
  - large $^{14}N/^{15}N$ in cosmomaterials
  - different N reservoirs likely present
  - large variations of $^{14}N/^{15}N$ in ISM too
  - strong dependence on chemical carrier
- Problems:
  - observation data shortage
  - biases
  - N isotopic chemistry not perfectly understood
  - complex relations with D- and ^{13}C-fractionations

What about multiply substituted species?

- very few detected so far
  mainly $^{13}C^{13}C$- or $D^{13}C$-, ($^{15}NH_2D$)
- sensitive probes, provide tight constraint to models
- trace history, different reservoirs
- weak features, line confusion problem
  high-sensitivity / spatial resolution ($\Rightarrow$ ALMA)
  accurate RFs ($\Rightarrow$ improve spectroscopic data base)
- *chemical networks, photo-dissociation rates etc.*

Light nitrogen carriers in the ISM

availability of *highly-precise** rest frequencies

	"main"	^{15}N	^{15}N + D	^{15}N + ^{13}C
NH_3	yes	yes	yes	—
N_2H^+	yes	yes	yes	—
NH_2	yes	yes	?	—
NH	yes	yes	?	—
HCN	yes	yes	yes	yes
HNC	yes	yes	yes	yes
CN	yes	?	—	?

$*$ *directly measured in the lab*

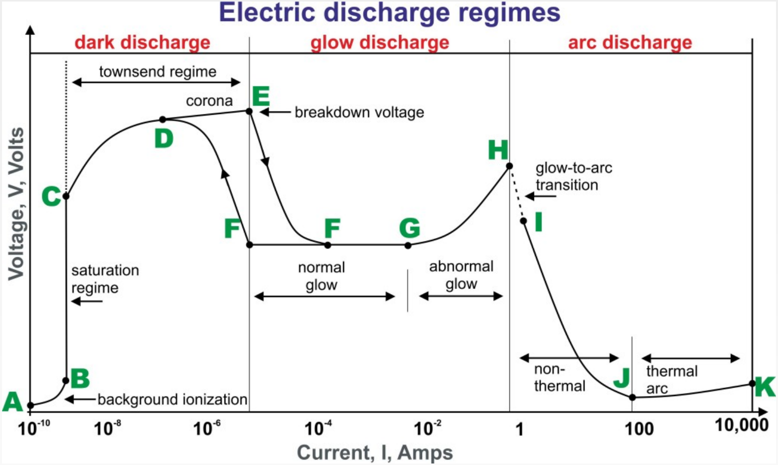
Sources of error for rest frequencies

- incomplete description of rotational the energy manifold
  poor frequency coverage, coarse J, K sampling
- slow convergence of the Hamiltonian expansion
  (critical for light species)
- accidental resonances
  closeby vibrational (Fermi/Coriolis) or electronic (Renner–Teller) states
- Measurements inaccuracies
  congested spectrum, complex HFS patterns, pressure shift

Radical and ions in the laboratory

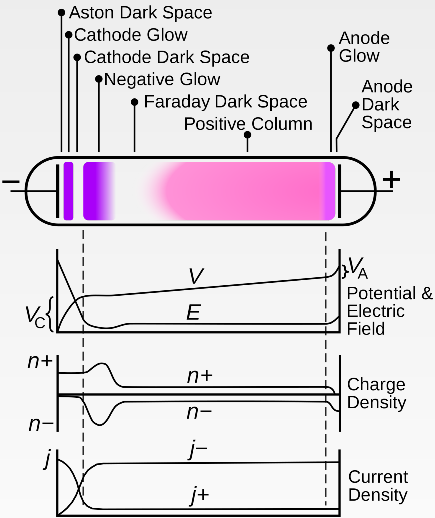
- Unstable in lab conditions ($\tau < 10^{-3}$ s)
  should be generated and studied "on-the-fly"
- Plasma techniques: DC, AC, mw- or rf-discharges
  low samples pressure $\sim$ 1–10 Pa
  low temperature ($\sim$ 77 K practical limit)
- Different plasma regimes:
  "Normal" discharge
  "Anomalous" discharge (magnetically enhanced / *hollow cathode*)

Plasma regimes



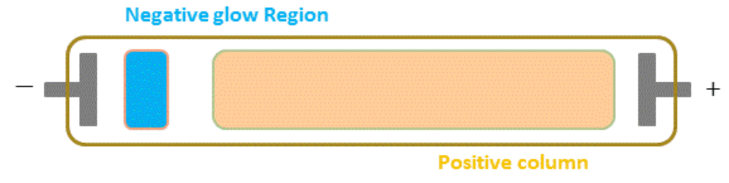
from "Industrial Plasma Engineering: Volume 2"

Glow discharge structure



from "wikipedia common"

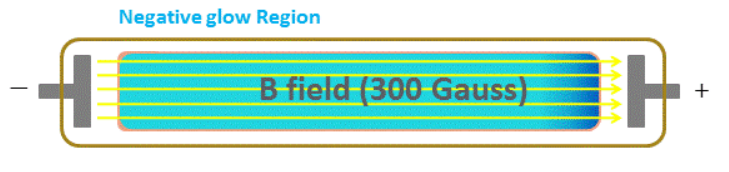
Normal glow discharge



typical conditions: $i \approx 20 - 100\,\mathrm{mA}$, $\Delta V < 1000\,\mathrm{V}$

Magnetically-enhanced "negative" glow discharge

Extended negative glow discharge



typical conditions: $i \approx 2 - 20\,\text{mA}$, $\Delta V \approx 1000 - 5000\,\text{V}$

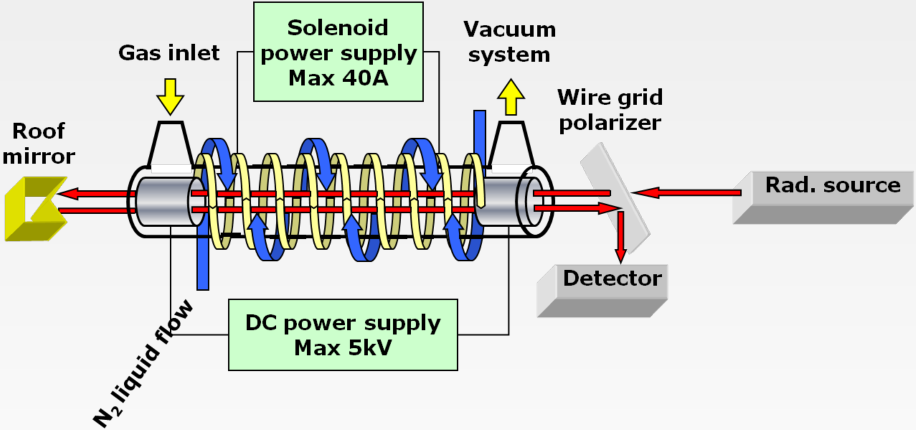
force plasma into the "abnormal" discharge conditions

Magnetically-enhanced “negative” glow discharge

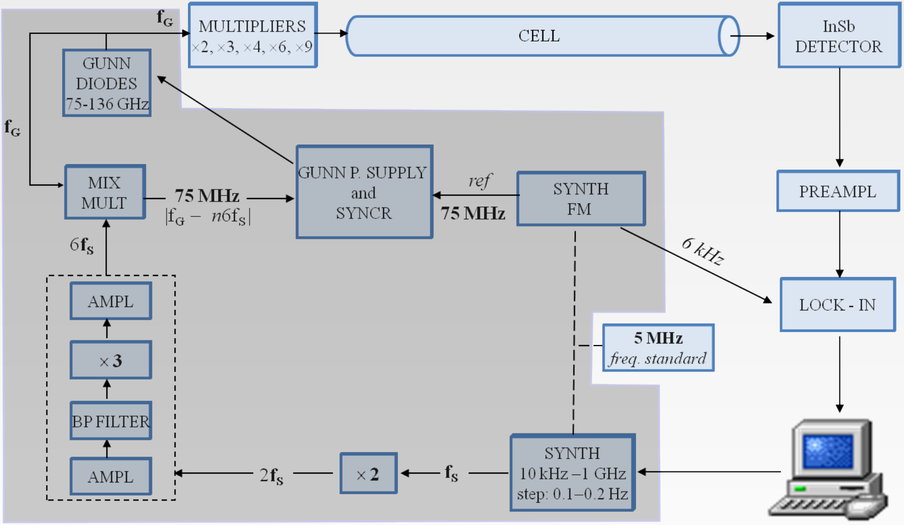
- PROs:
  - extends the plasma region with maximum ion density
  - absence of **E** over long length (no drift)
  - confinement of molecular ions
- CONs:
  - limitation in i/plasma density (“quasi” $i \propto \Delta V$)
  - coaxial **B** present $\Longrightarrow$ Zeeman effect

B-enhanced: optimal for closed-shell molecular ions
normal: used for radical and “high-current” unstable species

The discharge cell



The spectrometer



FM spectroscopy: lineshape analysis

- FM techniques + 2$^{\text{nd}}$ harmonic detection
  The 2$^{\text{nd}}$ derivative of the actual spectral profile is recorded

- Experimental profile modelled as:

$$F_2(\omega) \propto \mathrm{Re} \int_0^\infty J_2(mT)\Phi(T)e^{i\omega T}\mathrm{d}T$$

- Voigt profile function:

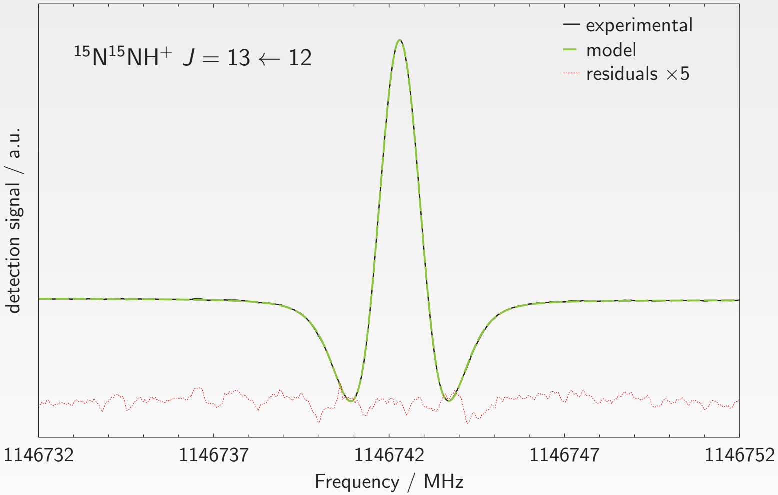
$$\Phi(\Gamma, \alpha_D, T) = \exp\left[-\Gamma T - (\alpha_D T)^2/4\right]$$

- α_D is fixed, the fit yields ω_0, Γ, (+ *empirical parameters*)

$^{15}N^{15}NH^+$ and $^{15}N^{15}ND^+$

- linear closed-shell ions ($^1\Sigma^+$)
- no detectable hyperfine structure
  greater intensity of the $J = 1 \leftarrow 0$ line
- rotational spectrum analysed using simple Hamiltonian
  $H_{\rm rot} = B\hat{J}^2 - D\hat{J}^4 + H\hat{J}^6$
- produced in the "enhhanced" negative glow at 80 K *via*:
  $Ar + {}^{15}N_2 + H_2\ (D_2)$
  $\Delta V = 3.5\,\mathrm{kV}$, $i = 4 - 10\,\mathrm{mA}$

$^{15}N^{15}NH^+$ at 1 THz



Pressure broadening and shift

Pressure broadening (Γ) and pressure shift (s) coefficients are related to the total population transfer rate among rotational states

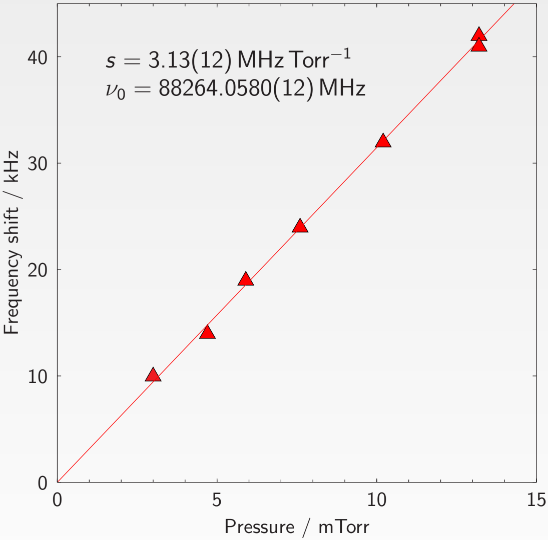
$$\Gamma - \mathrm{i}s = \sigma \langle v \rangle n$$

$$\sigma \leftarrow P(k)$$

$$P(k) = 1 - \sum_{k'} \langle i, k | \mathbf{S} | i, k' \rangle \langle f, k' | \mathbf{S}^* | f, k \rangle$$

Γ and s are experimental determinables

$^{15}N^{15}NH^+$ $J = 1 \leftarrow 0$ pressure shift



$^{15}N^{15}NH^+$ results

$J+1$	J	Observed (MHz)	Obs.-calc. (kHz)	Uncertainty[a] (kHz)	A[b] (s^{-1})
1	0	88 264.0580	−1.1	0.3	3.08(−5)
2	1	176 526.2210[c]		0.6	2.96(−4)
3	2	264 784.5878	−0.8	0.8	1.07(−3)
4	3	353 037.2641	−0.6	0.9	2.63(−3)
5	4	441 282.3524[c]		0.9	5.26(−3)
6	5	529 517.9570	2.2	0.8	9.22(−3)
7	6	617 742.1767	1.3	0.8	1.48(−2)
8	7	705 953.1169	−0.7	0.9	2.23(−2)
9	8	794 148.8830	−2.4	1.1	3.19(−2)
10	9	882 327.5827[c]		1.3	4.40(−2)
11	10	970 487.3141[c]		1.3	5.88(−2)
12	11	1 058 626.1863	2.0	1.1	7.66(−2)
13	12	1 146 742.2976	−1.0	1.5	9.77(−2)
14	13	1 234 833.7625[c]		1.5	1.22(−1)

rms[d] = 1.5 kHz

Constant[e]		Correlation matrix		
B_0 / MHz	44 132.18765(17)	1.000		
D_J / kHz	79.0502(20)	0.934	1.000	
H_J / mHz	50.4(63)	0.871	0.986	1.000

From Dore *et al.* 2017, A&A 604:A26

Is $^{15}N^{15}NH^+$ detectable in ISM?

- $^{14}N^{15}NH^+/^{15}N_2H^+ \approx 20 - 100$ predicted by the chemical model (Dore et al. 2017)
- extreme ^{15}N-enhanced HMSCs are "promising" candidates ($N_2H^+/N^{15}NH^+ \sim 200$, Fontani et al. 2015)
- line peak intensity up to 6 mK can be predicted for the $J = 1 \leftarrow 0$ line
- $\sim$10 hr of telescope time at 0.2 km s^{-1}

Is $^{15}N^{15}NH^+$ detectable in ISM?

- $^{14}N^{15}NH^+/^{15}N_2H^+ \approx 20 - 100$ predicted by the chemical model (Dore et al. 2017)
- extreme ^{15}N-enhanced HMSCs are "promising" candidates ($N_2H^+/N^{15}NH^+ \sim 200$, Fontani et al. 2015)
- line peak intensity up to 6 mK can be predicted for the $J = 1 \leftarrow 0$ line
- $\sim$10 hr of telescope time at 0.2 km s^{-1}
- Recent attempt:
  5 hr of integration on 05358-mm3, σ 2.5 mK,
  $^{14}N^{15}NH^+/^{15}N_2H^+ > 40$

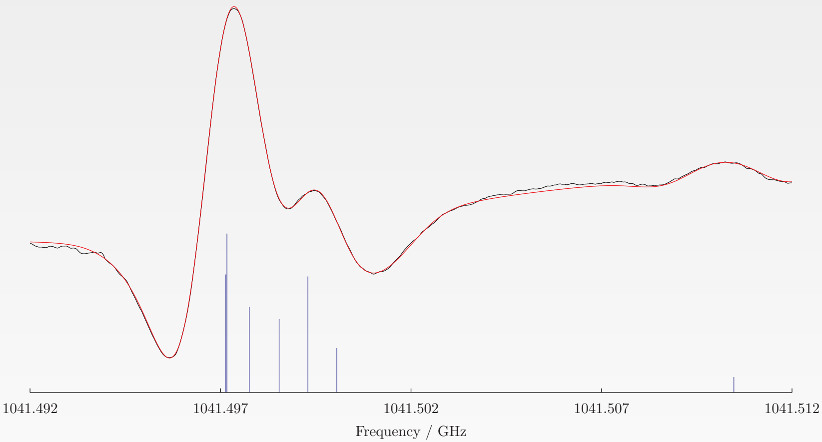
^{15}ND

- diatomic radical with $X^3\Sigma^-$ ground state
- fine + hyperfine structure, Hund's *b*-type coupling scheme

$$\mathbf{N} + \mathbf{S} = \mathbf{J}$$
$$\mathbf{J} + \mathbf{I_N} = \mathbf{F_1}$$
$$\mathbf{F_1} + \mathbf{I_H} = \mathbf{F}$$

- produced in the positive glow at $\sim 85\,\mathrm{K}$ *via*:
  Ar + $^{15}N_2$ + D_2
  $\Delta V = 1\,\mathrm{kV}$, $i = 60\,\mathrm{mA}$

^{15}ND $N = 2 \leftarrow 1$, $J = 2.5 \leftarrow 1.5$



Imidogen Dunham's type analysis

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

- rotation-vibration Dunham's constants:
  Y_{kl} ($\approx \omega_e$, $\omega_e x_e$, B_e, α_e, D_e, ...)
- fine structure constants:
  λ, γ, b, c, *(+ vib-rot dependence terms)*
- hyperfine structure constants:
  eQq, C_I, ... *(+ vib-rot dependence terms)*

mass-scaling relation:

$$X_{kl}^{\alpha} = \left\{ X_{kl}^{0} + \frac{\Delta M_{\mathrm{N}}^{\alpha}}{M_{\mathrm{N}}^{\alpha}} \delta_{kl}^{\mathrm{N}} + \frac{\Delta M_{\mathrm{H}}^{\alpha}}{M_{\mathrm{H}}^{\alpha}} \delta_{kl}^{\mathrm{H}} \right\} \left(\frac{\mu_0}{\mu_\alpha} \right)^{l+k/2+\beta}$$

Imidogen: summary

- new ^{15}ND data recorded in the 487–1043 GHz range
- multi-isotopologue analysis with 1349 data
  4 species, rotational + IR lines, $v_{max} = 6$
- 66 parameters determined: 30(8) *VR*, 13(4) *FS*, 23 *HFS*
- $\sigma_{fit} = 0.873$
- $N, J = 1, 0 \leftarrow 0, 1$ in the ALMA band 8 ($\sigma_{RF} \approx 0.04\,\mathrm{km\,s^{-1}}$)

  (Melosso et al. *in prep*)

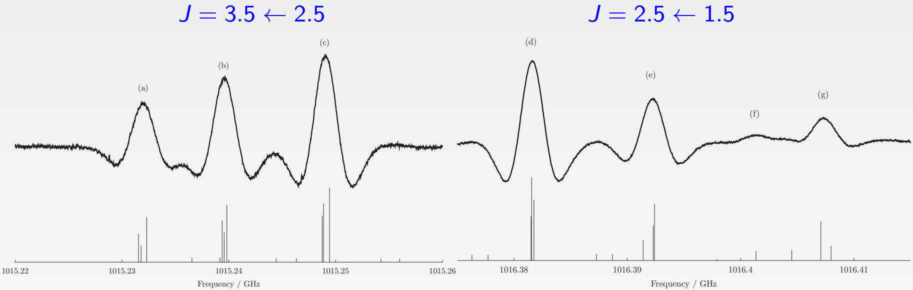
ND_2 and $^{15}ND_2$

- bent triatomic radicals with X^2B_1 ground state
- fine + hyperfine structure
  Hund's *b*-type coupling scheme with two equivalent bosons

$$\mathbf{N} + \mathbf{S} = \mathbf{J}\,, \quad \mathbf{J} + \mathbf{I_N} = \mathbf{F_1}\,, \quad \mathbf{F_1} + \mathbf{I_D} = \mathbf{F}$$
$$(\mathbf{I_D} = \mathbf{I_{D_1}} + \mathbf{I_{D_2}})$$

- spin statistics for $N_{K_a,Kc}$ levels:
  $K_aK_c = ee, oo \rightarrow I_\mathrm{D} = 1$ (3 sublevels)
  $K_aK_c = eo, oe \rightarrow I_\mathrm{D} = 0, 2$ (6 sublevels)

ND_2 $N_{K_a,Kc} = 3_{13} \leftarrow 2_{02}$



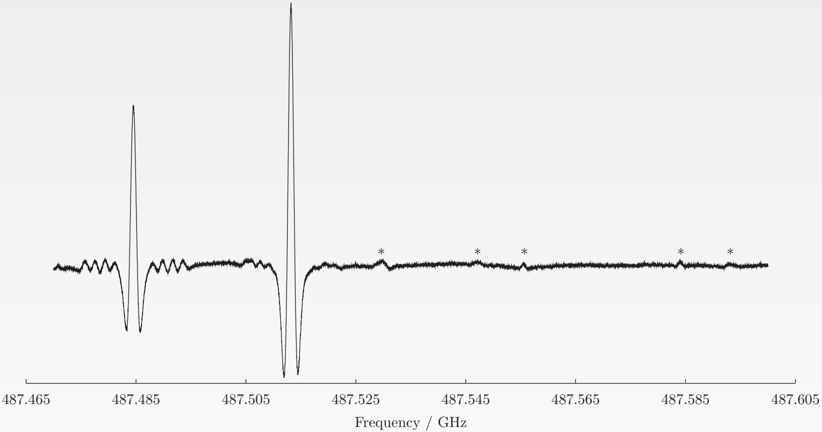
positive glow at $\sim 200\,$K, Ar + $^{15}ND_3$ discharge

$\Delta V = 1\,$kV, $i = 70\,$mA (200 s int. time)

Melosso et al. 2017, ApJS *accepted*

$^{15}ND_2$ and ^{15}ND simultaneous production

$^{15}ND_2$, $N_{KaKc} = 3_{12} \leftarrow 3_{03}$, $J = 3.5 \leftarrow 3.5$ (∗) ^{15}ND, $N, J = 1, 0 \leftarrow 0, 1$

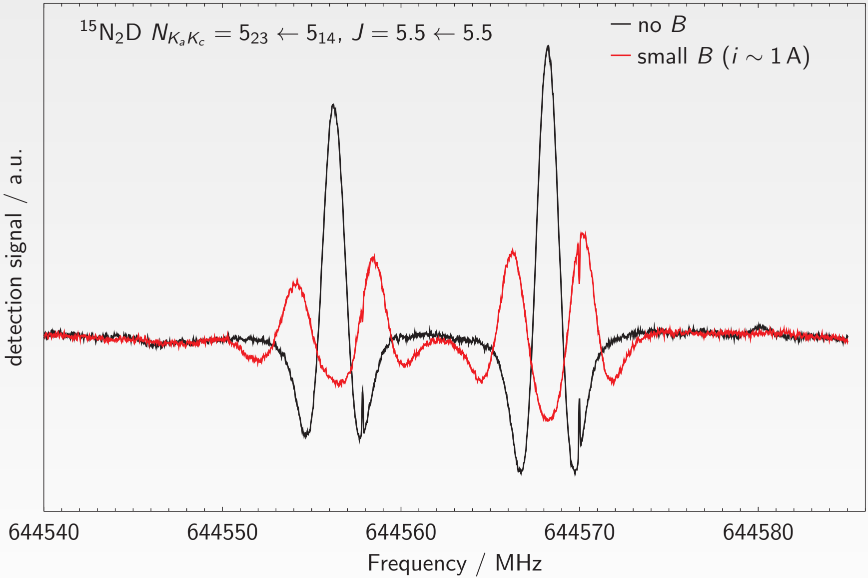


positive glow at $\sim 200\,K$, Ar + $^{15}ND_3$ discharge

$\Delta V = 1\,kV$, $i = 70\,mA$

Melosso et al. *in prep.*

$^{15}ND_2$: effect of applied B



ND_2 and $^{15}ND_2$: results

- ND_2
  - 64 new lines recorded in the 588–1131 GHz range
  - first global fit with all available data (submm + FIR + MODR)
  - 41 parameters determined, $\sigma_{\text{fit}} = 0.87$
  - "good" prediction capability up to 8 THz for ($N \leq 13$, $K_a \leq 17$)
- $^{15}ND_2$
  - 174 new lines recorded in the 264–1051 GHz range
  - 12 rotational transitions with $N \leq 5$ and $Ka \leq 3$
  - 32 parameters determined, $\sigma_{\text{fit}} = 0.84$
  - "good" rest frequency available in the submm and THz regimes

Light nitrogen carriers in the ISM. . . update

availability of *highly-precise** rest frequencies

	"main"	^{15}N	^{15}N + D	^{15}N + ^{13}C
NH_3	yes	yes	yes	—
N_2H^+	yes	yes	yes	—
NH_2	yes	yes	yes	—
NH	yes	yes	yes	—
HCN	yes	yes	yes	yes
HNC	yes	yes	yes	yes
CN	yes	?	—	?

∗ *directly measured in the lab*

What's next on this (sub-)topic?

- ^{15}NHD:
  rotational spectrum unknown
- $C^{15}N$
  only a couple of ISM lines measured, never studied in the lab
- $H^{15}NCO$
  some MW measurements from H. Hocking et al. (1975) mm and submm lines affected by large prediction uncertainties