Irradiated Ammonia for Polarized Solid Targets

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Jefferson Lab

Outline

Irradiated ammonia: a brief history
Behavior of irradiated ammonia
Radicals in ammonia
Summary, conjectures, and questions

Chronology of irradiated ammonia

1979: Niinikoski and Rieubland [CERN] irradiate NH_3 with a low dose of protons at 77 K. Reaches 90+% at 2.5 T and 0.3 K.

Tapio Niiniikoski

1980: Seely et al. [SLAC] irradiate NH_3 and ND_3 with a low dose of 20 GeV electrons at 1 K.
Reaches 75% (NH_3) and 25% (ND_3) at 5 T and 1 K.

Mike Seely

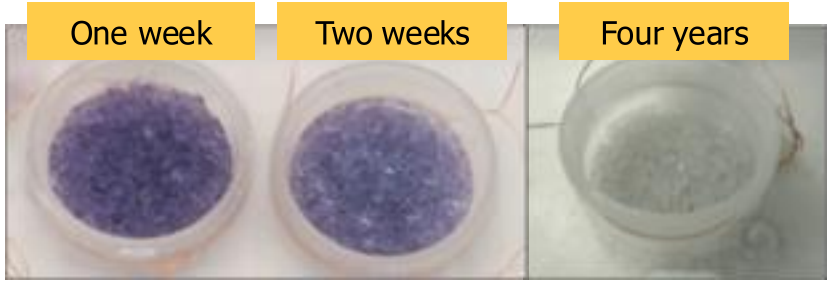
1980: Meyer et al. [Bonn] irradiate NH_3 and ND_3 with high dose of electrons at 87 K. Reaches 60% (NH_3) and 16% (ND_3) and 2.5 T and 0.5 K.

Werner Meyer

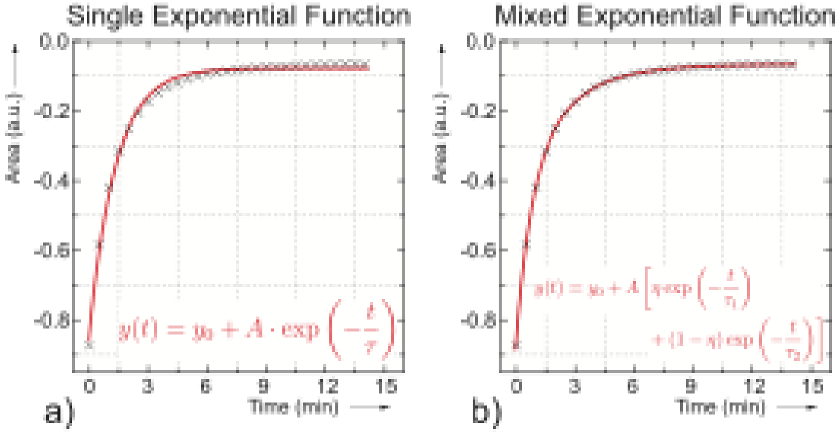
1990: Crabb et al. [Michigan] irradiate NH_3 with 10 GeV electrons at 87 K. Reaches 95% at 5 T and 1 K.

Don Crabb

Behavior of irradiated ammonia



Alexander Berlin, PhD thesis, Bochum University (2015)



Alexander Berlin, PhD thesis, Bochum University (2015)

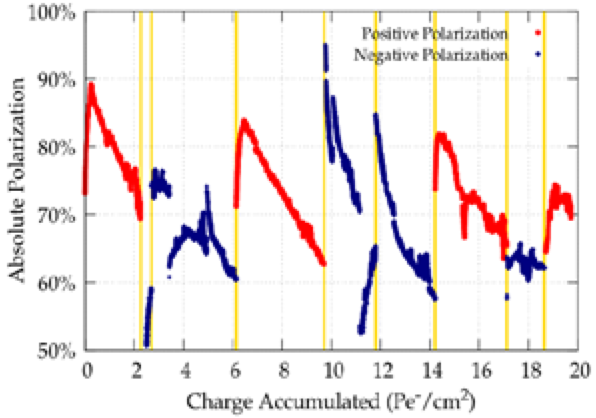
It turns purple

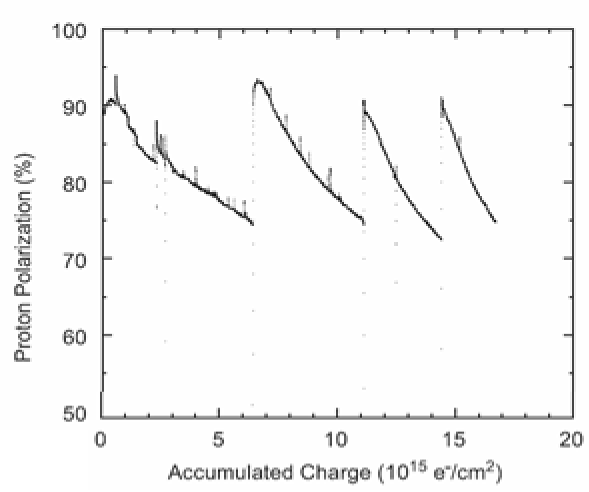
At 77 K the color slowly fades over time (not so for ND_3).
The polarizability remains (albeit slower).
Spin relaxation also slows.
→ Color centers are not *essential* for dynamic polarization.

NH_3

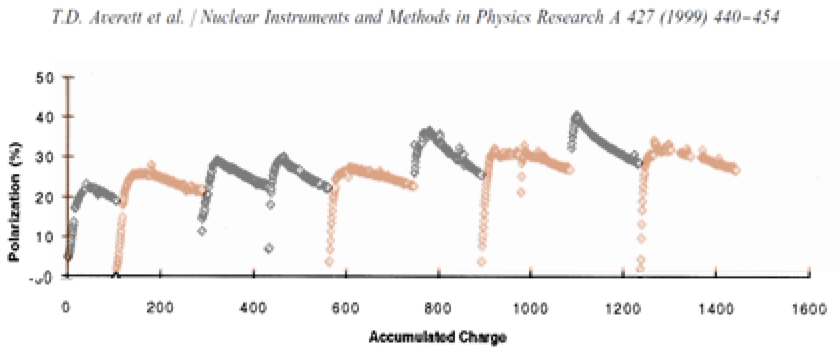
A single exponential can describe the **spin-up curve**.
Two spin-lattice times are required for the **relaxation curve.**
This is especially true for freshly-irradiated materials.

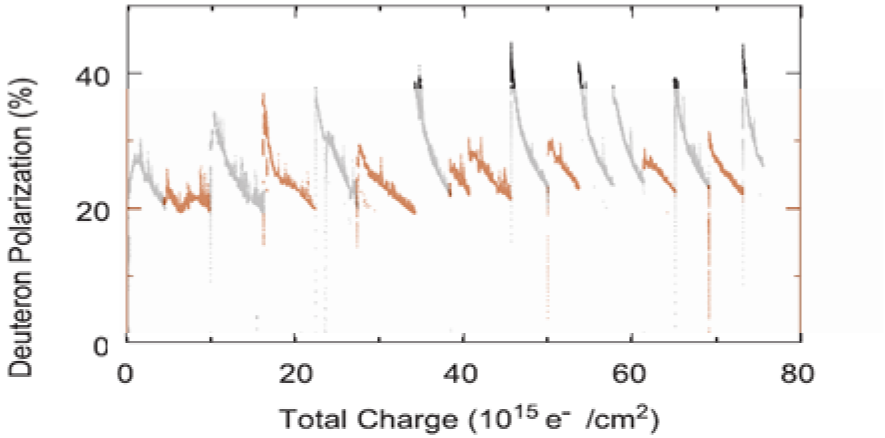
Behavior of irradiated ammonia





Radiation damage to NH_3 can be repaired multiple times by annealing the sample, up to a practical end of life of about 20 Pe$^-$ cm^{-2}



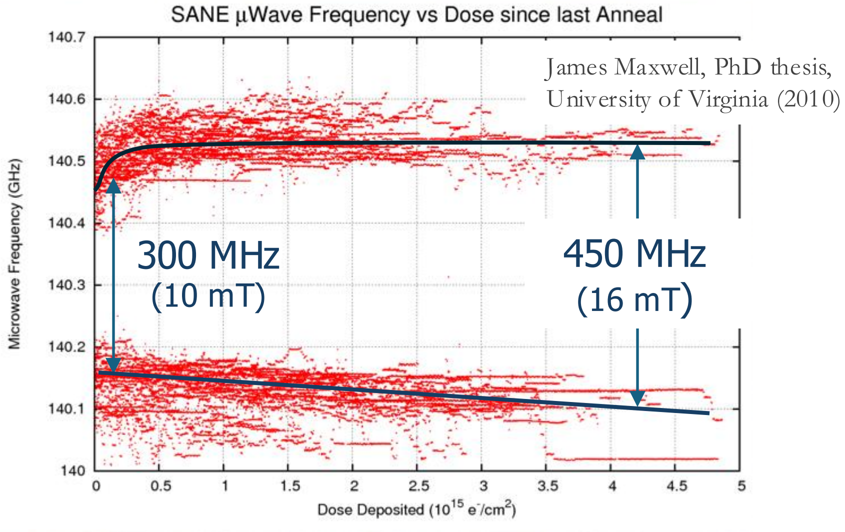


The polarization of ND_3 benefits significantly from a "cold dose" at 1 K.

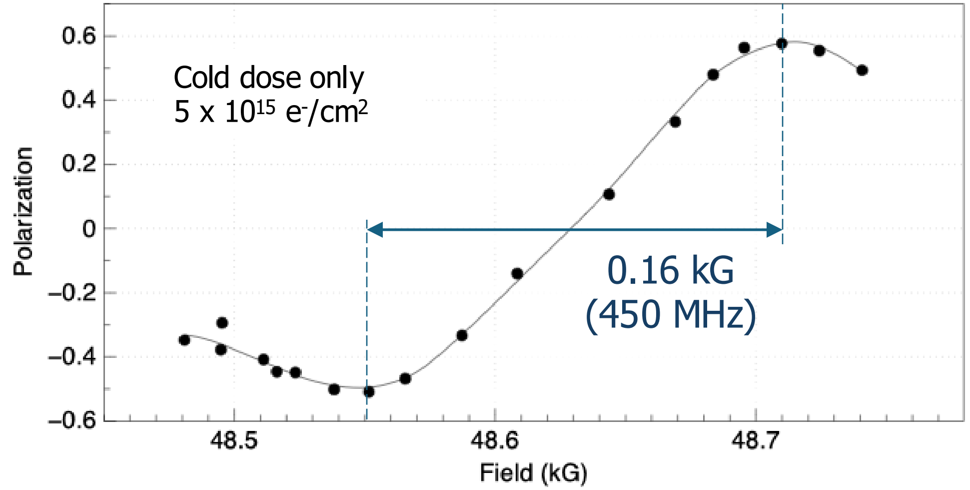
It is up to 4x more radiation resistant than NH_3.

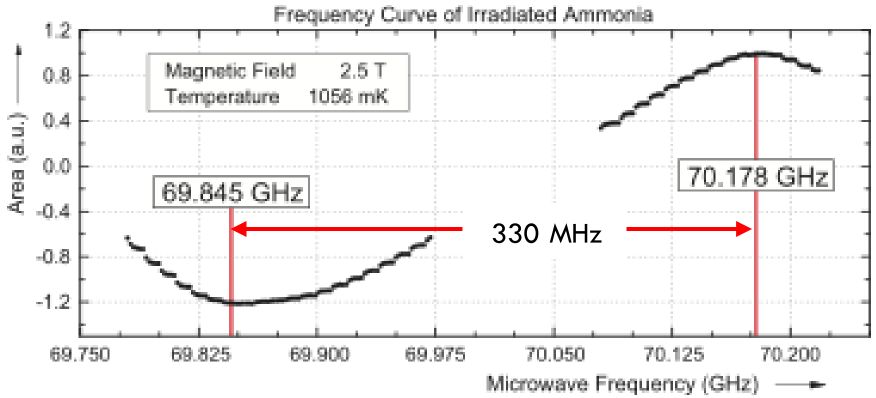
Behavior of irradiated ammonia

In NH_3 at 1K/5T the optimum frequencies are initially about 300 MHz apart and separate to 450 MHz with cold dose



Mike Seely, PhD thesis, Yale University (1992)



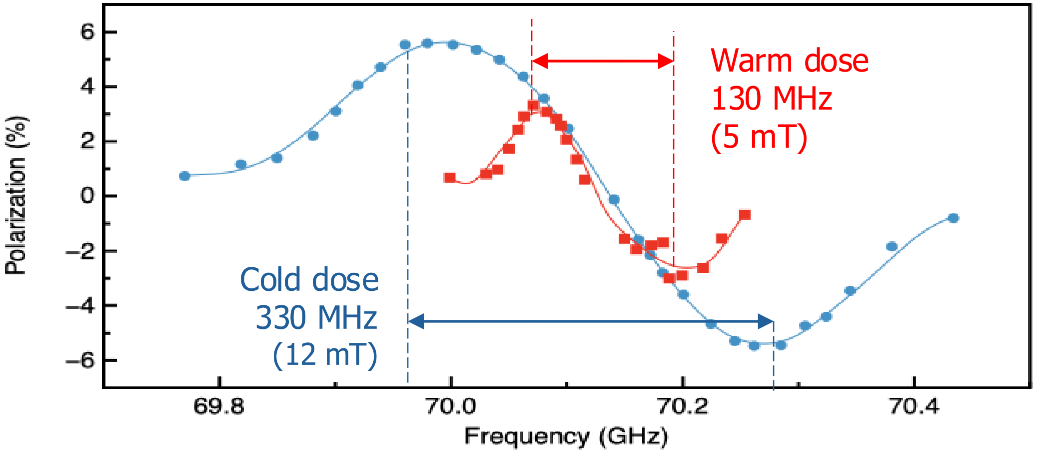


Alexander Berlin, PhD thesis, Bochum University (2015)

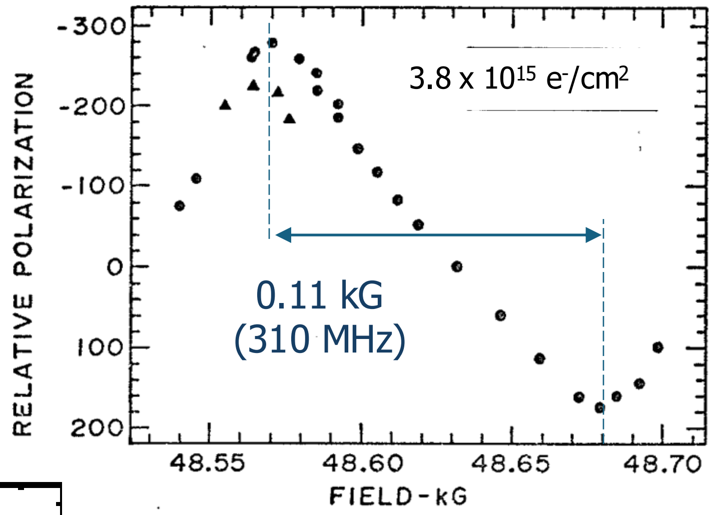
The frequency separation (warm dose only) is about the same at 2.5 T

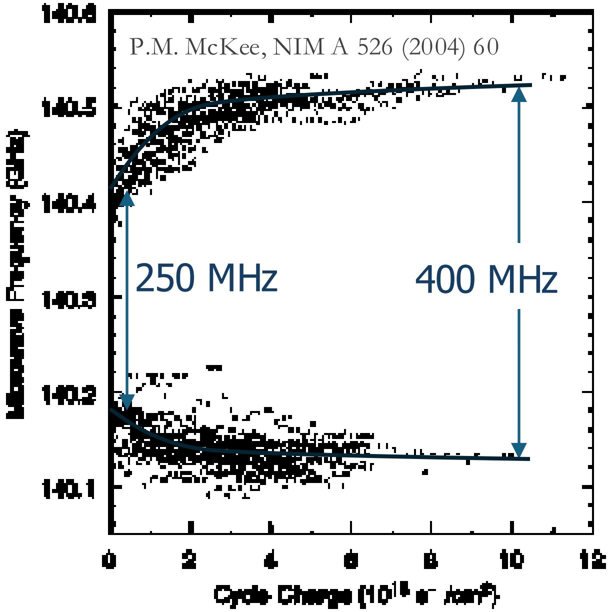
Behavior of *deuterated* ammonia

W. Meyer, NIM A 526 (2004) 12

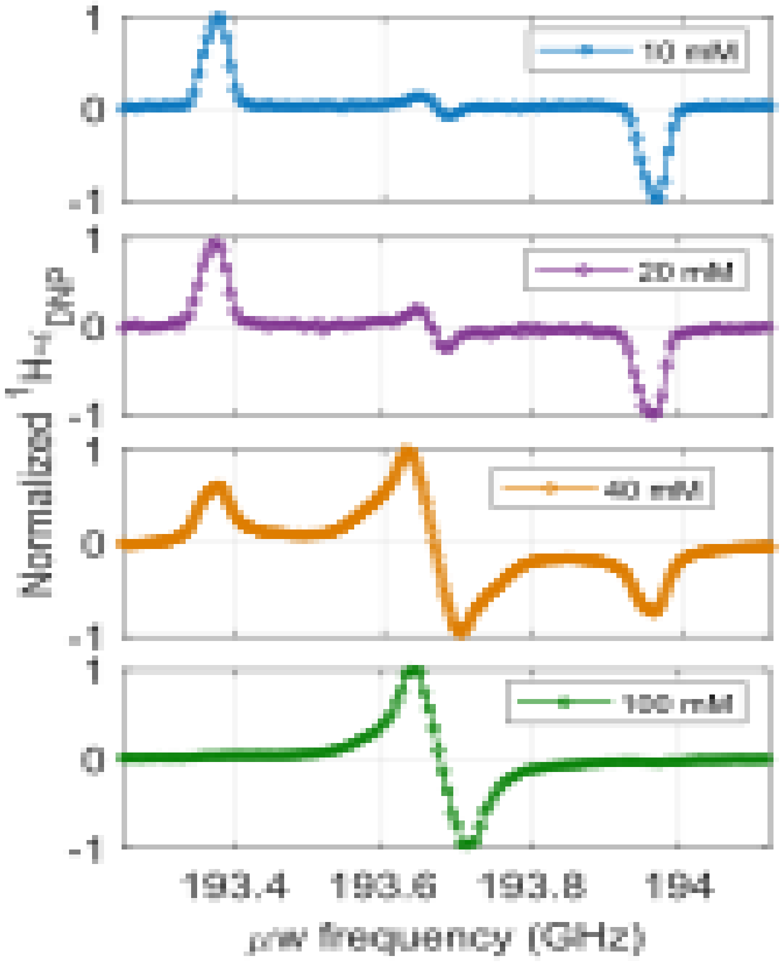


Mike Seely, PhD thesis, Yale University (1992)





A transition from the SE to TM with increasing concentration of trityl OX063

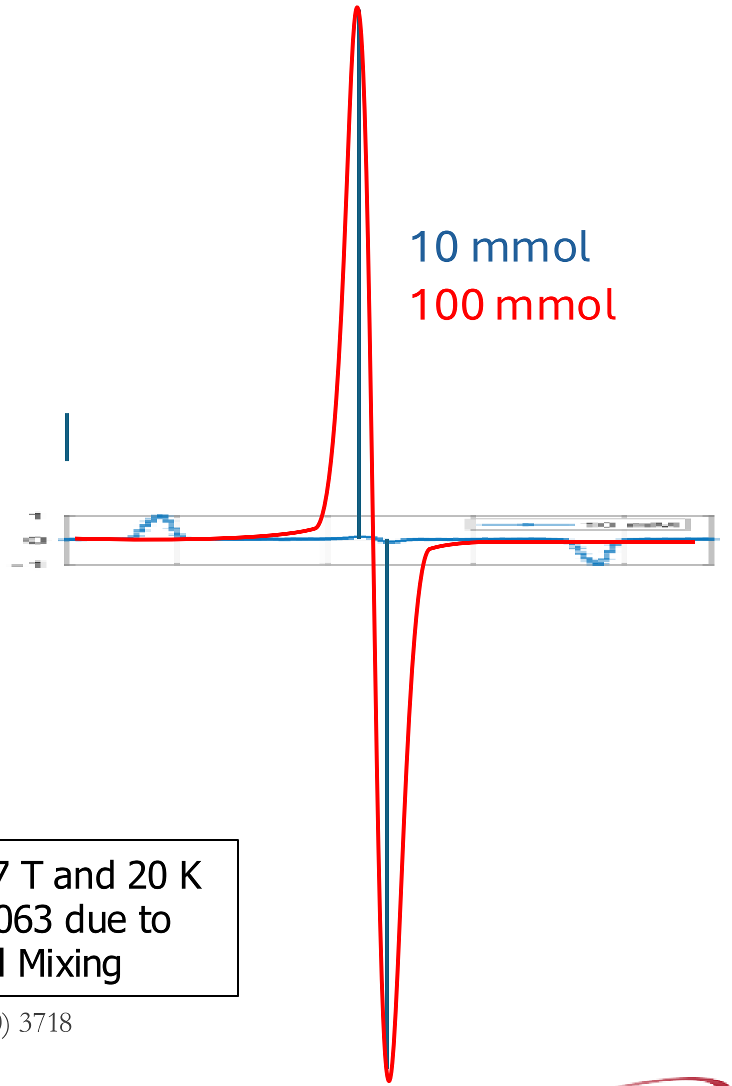


SE: 10 TM: 1.6

SE: 19 TM: 5

SE: 14 TM: 30

SE: 2 TM: 110

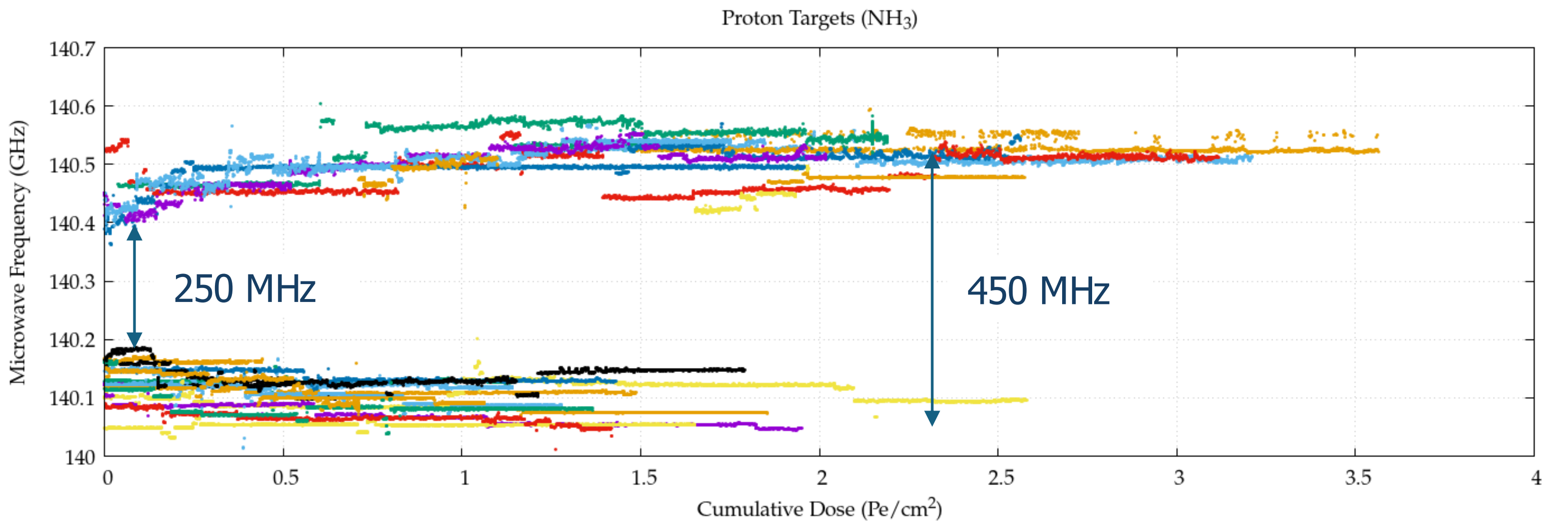


^{1}H enhancement factors at 7 T and 20 K in DMSO*/water + trityl-OX063 due to the Solid Effect and Thermal Mixing

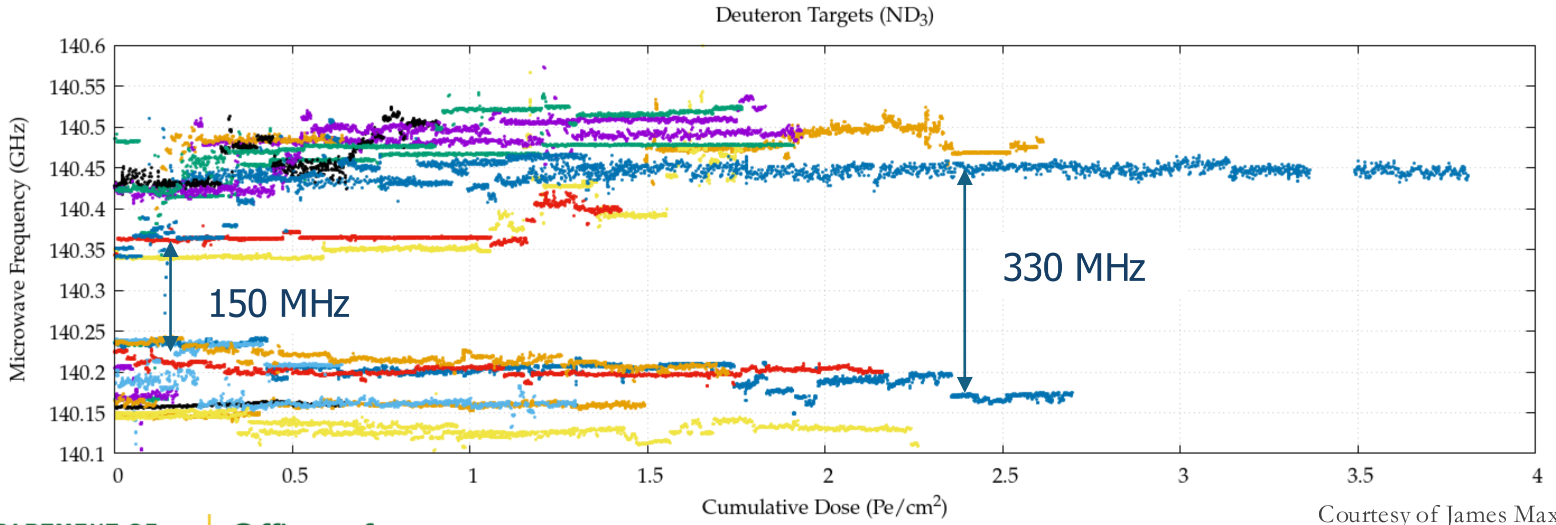
A. Equbal et al, J. Phys. Chem. Lett (2020) 3718

*dimethyl sulfoxide

Behavior of *deuterated* ammonia



Run Group C
Protons follow the usual script



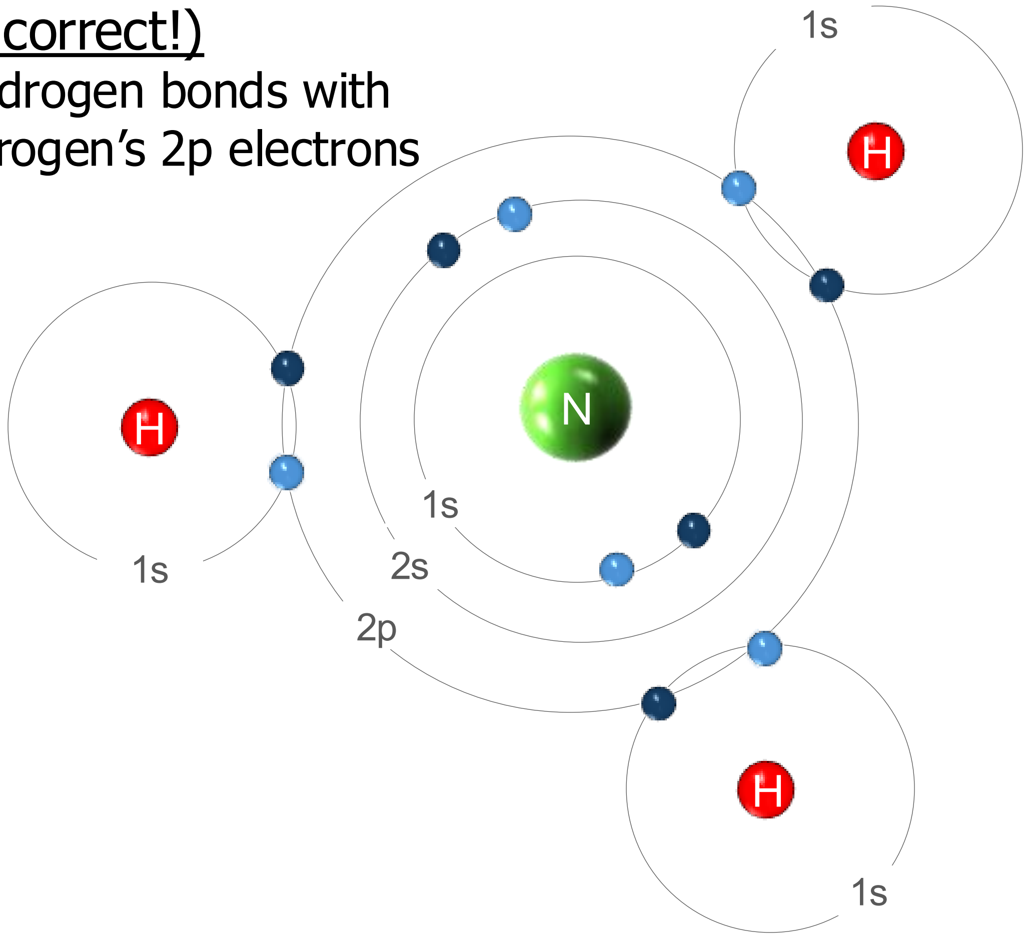
Run Group C
Deuteron data is inconclusive

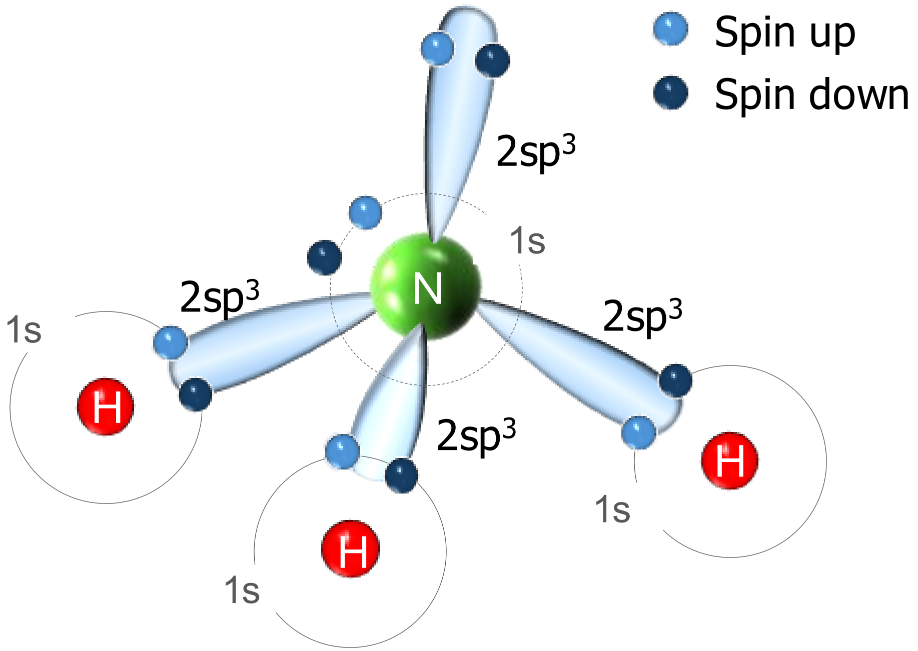
Courtesy of James Maxwell

The ammonia molecule

<u>Physicist's model (incorrect!)</u>

Hydrogen bonds with nitrogen's 2p electrons





<u>Chemist's model</u>

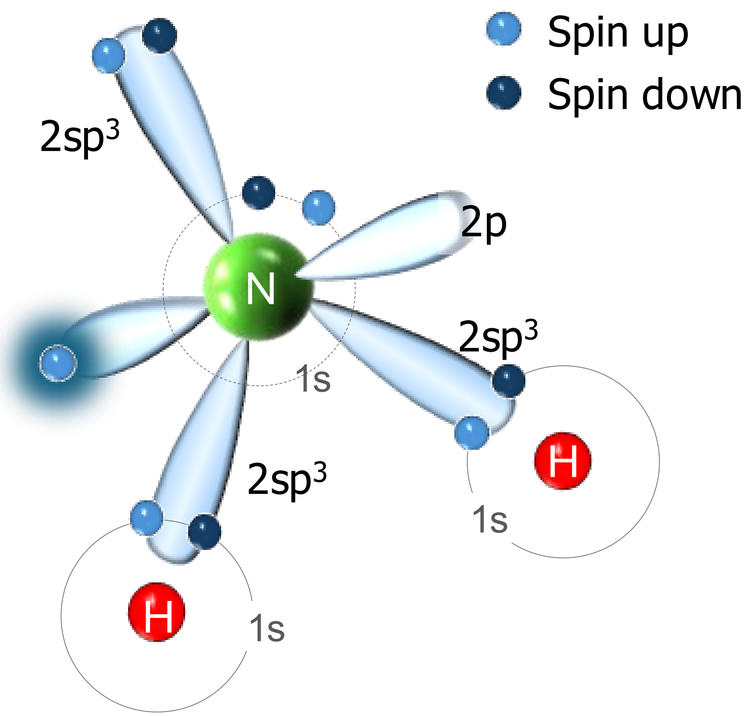
Hydrogen & Nitrogen bond via four 2sp^3 hybrid orbitals

Radicals in irradiated ammonia

EPR studies at 0.33 T (X-band) and 2.5 T (V-band) have found that the dominate species produced by radiation at 87 K is the amine radical $\bullet NH_2$ (or $\bullet ND_2$)

M. Symons, 2nd Pol. Target Materials Workshop (1979)
"At 77 K only $\bullet NH_2$ radicals are obtained."

$$NH_3 \rightarrow \bullet NH_3^+ + e^-$$
$$\bullet NH_3^+ + NH_3 \rightarrow \bullet NH_2 + NH_4^+$$
$$NH_4^+ + e^- \rightarrow NH_3 + \bullet H$$
$$NH_3 + \bullet H \rightarrow \bullet NH_2 + H_2$$



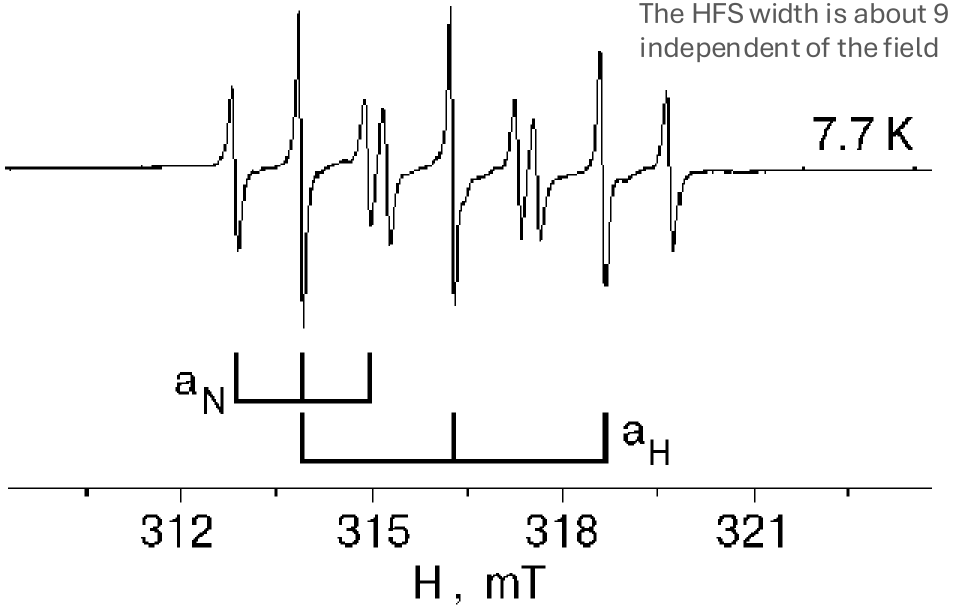
Amine radical $\bullet NH_2$ $^2B_1$ configuration

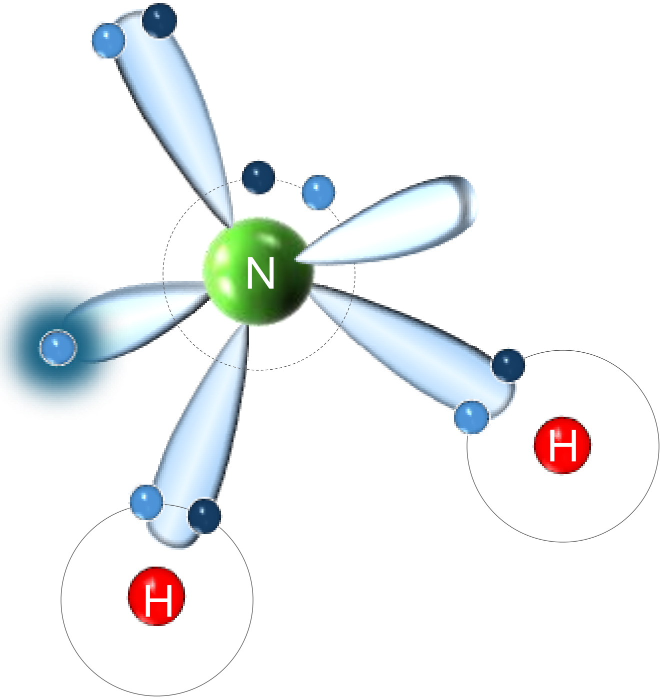
Radicals in irradiated ammonia

Hyperfine splitting: $\mathcal{H}_{HF} = \boldsymbol{s} \cdot \boldsymbol{a} \cdot \boldsymbol{I}$

The hyperfine interaction with the Nitrogen and Hydrogen nuclei produces $(2n_N I_N+1)\,(2n_H I_H+1) = 3 \times 3 = 9$ lines

The HFS width is about 9 mT (250 MHz), independent of the field



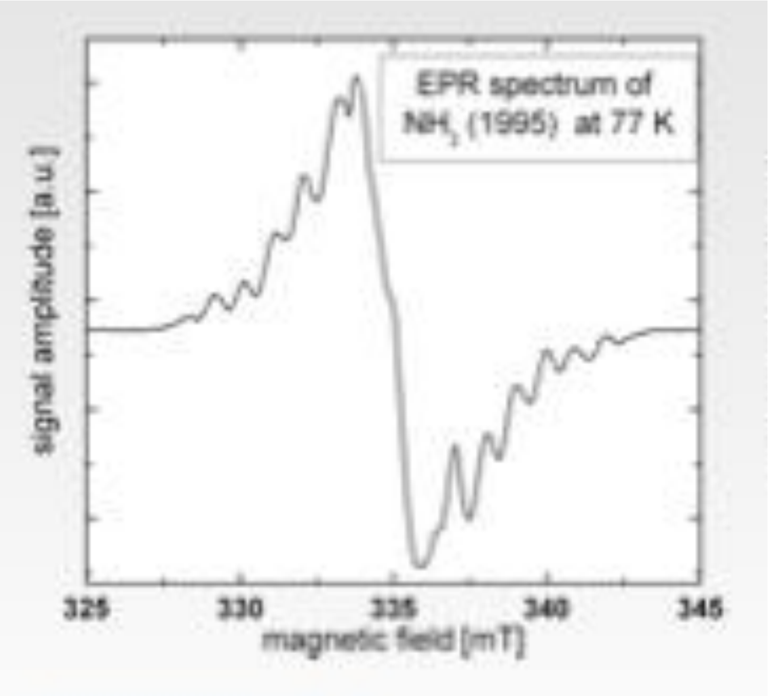


•NH_2 radical trapped in solid Argon matrix at 7.7 K

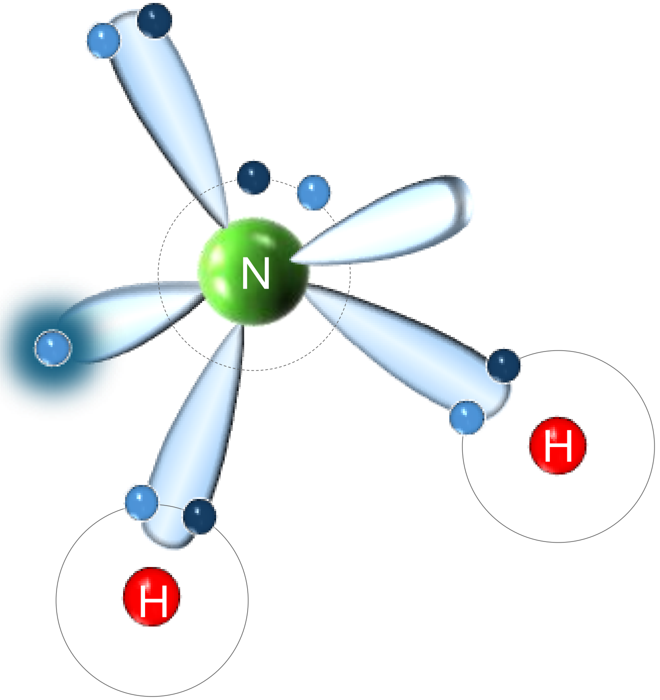
E.Y. Misochko et al, *Low Temp. Phys.* 26, 727–735 (2000)

Radicals in irradiated ammonia

Dipolar Broadening: $\mathcal{H}_{sI} = \hbar^2 \left(\frac{\mu_0}{4\pi}\right) \gamma_s \gamma_I \left[\frac{\vec{s}\cdot\vec{I}}{r^3} - \frac{3(\vec{s}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5}\right]$



Dipolar broadening increases the width by about 50%, independent of field.

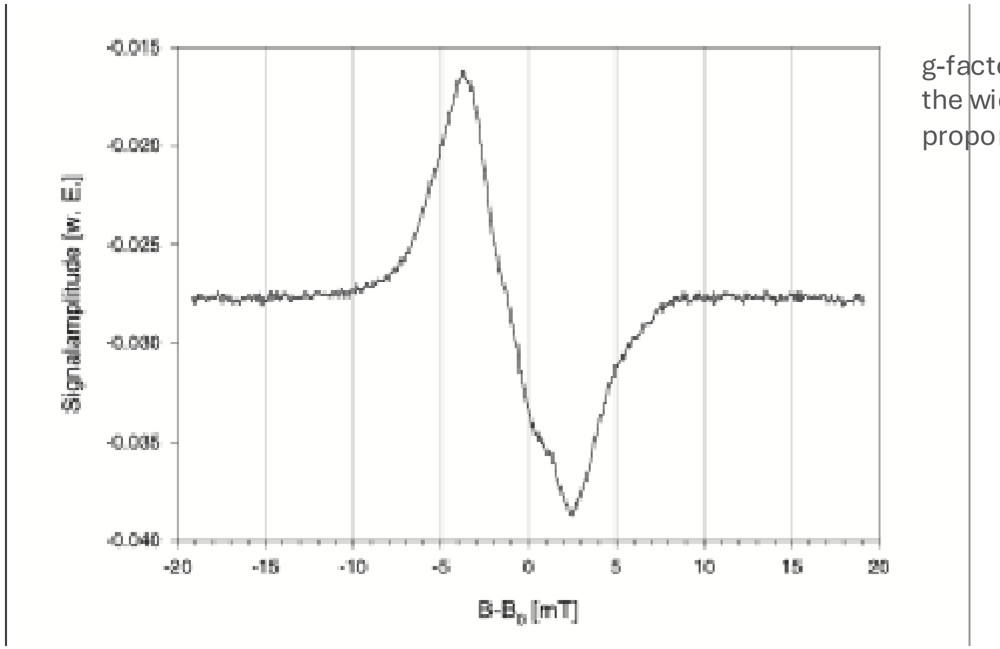


$\bullet NH_2$ radical in warm-irradiated NH_3

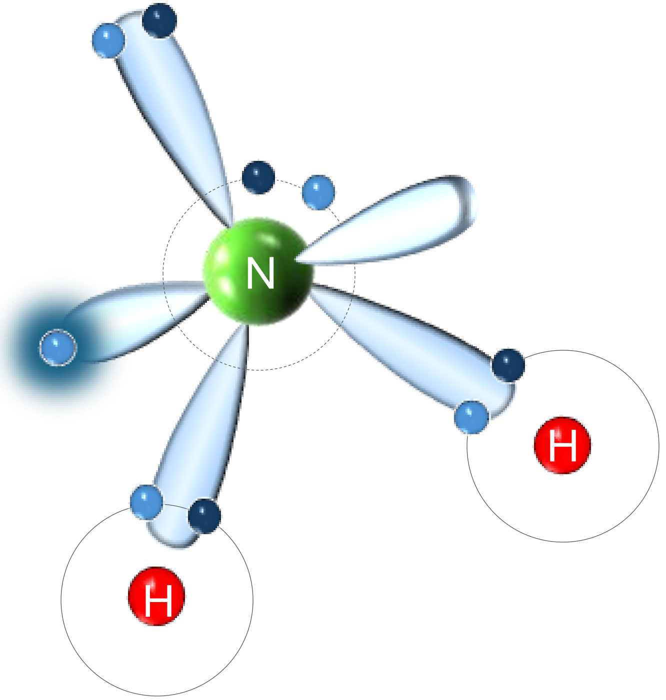
Alexander Berlin, PSTP2011, St. Petersburg

Radicals in irradiated ammonia

g-factor anisotropy $\mathcal{H}_{SO} = \boldsymbol{s} \cdot \boldsymbol{g} \cdot \boldsymbol{B}$



g-factor anisotropy increases the width by about 20%, proportional to the field.



•NH_2 radical at 2.5 T

Jorg Heckmann PhD Thesis, Bochum (2004)

Radicals in irradiated ammonia

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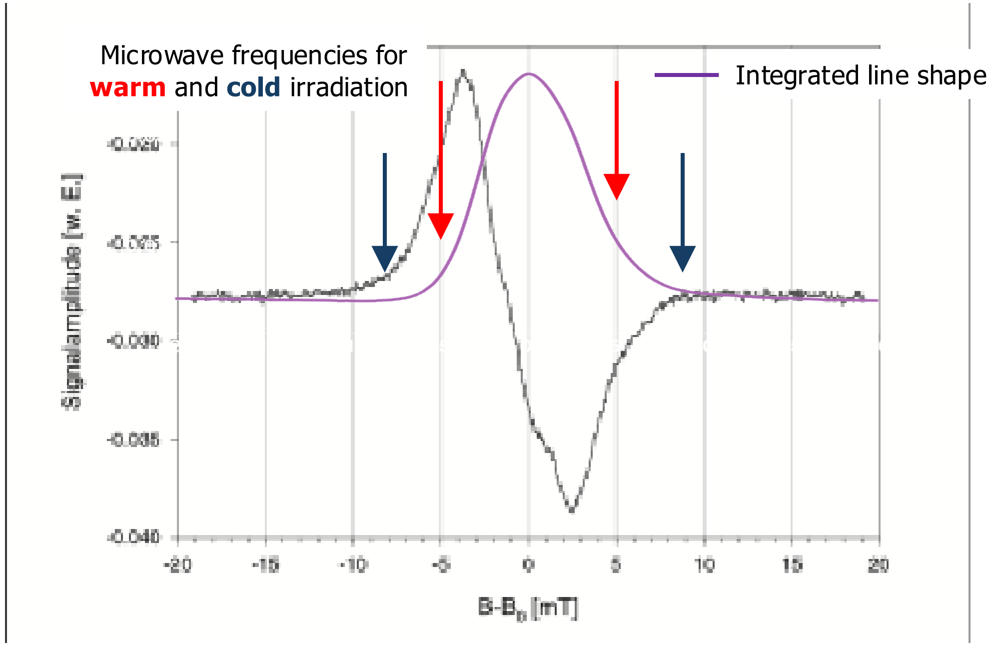

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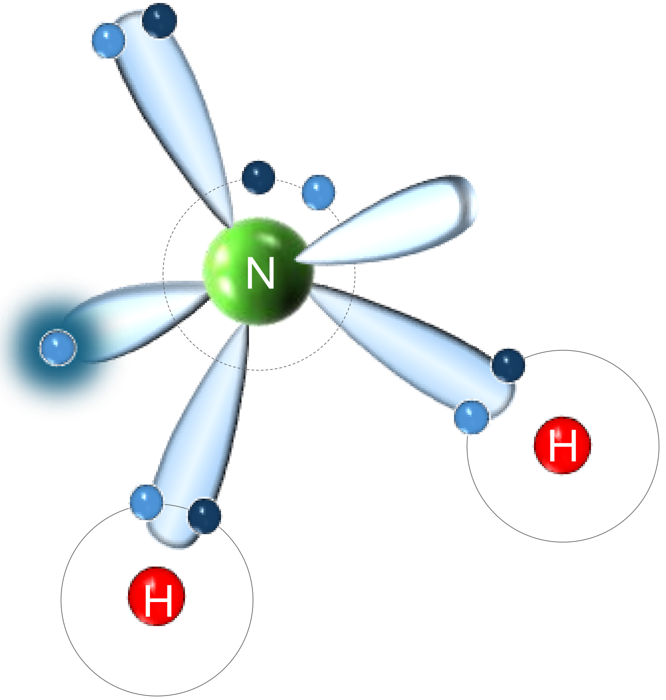
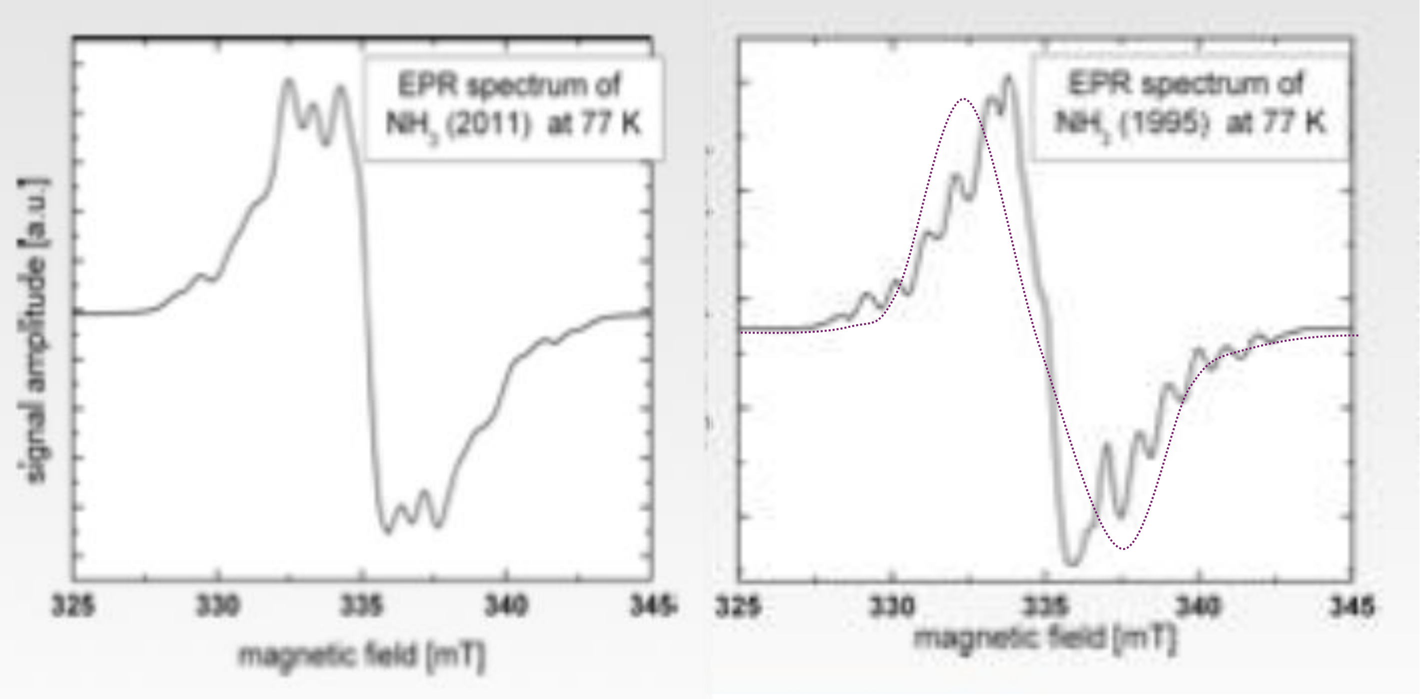
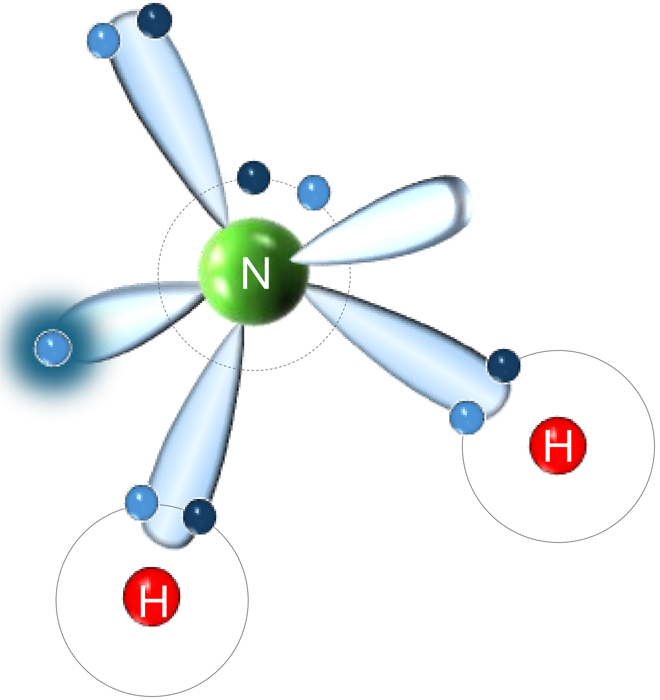


Radicals in irradiated ammonia

Alexander Berlin, PSTP2011, St. Petersburg





•**NH_2** radical in fresh, warm-irradiated NH_3

Alexander Berlin, PSTP2011, St. Petersburg

•**NH_2** radical 16-year-old warm-irradiated NH_3

Is the color center missing?

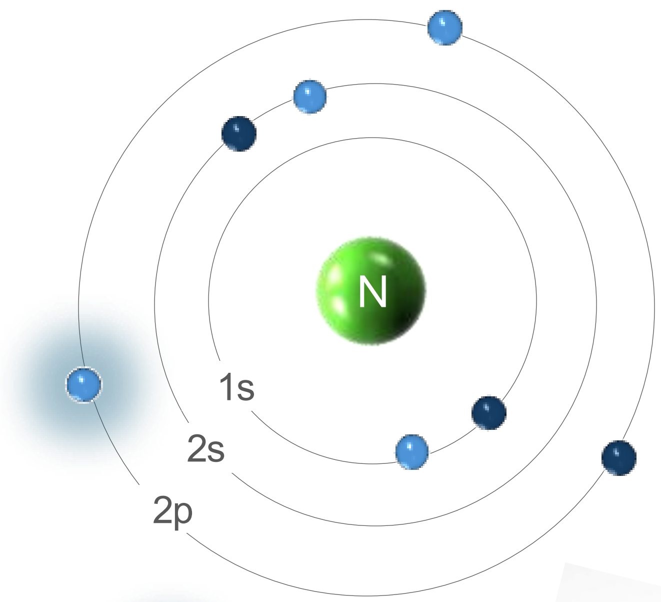
Radicals in irradiated ammonia

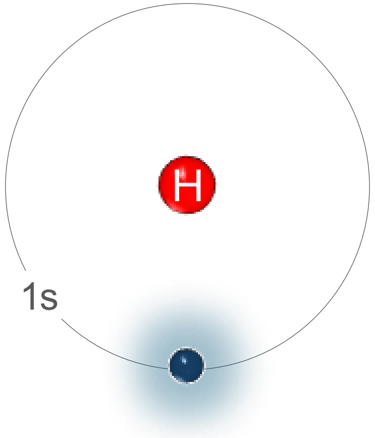
Other radicals have been observed at 77 K, such as

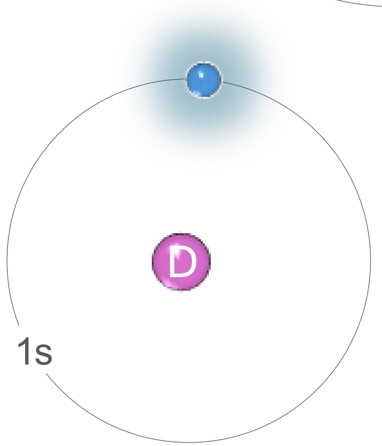
- atomic hydrogen
- atomic deuterium
- atomic nitrogen-14
- atomic nitrogen-15
- "hydrazine radical?"

L.G. DeMarco, A.S. Brill, and D.G. Crabb
J. Chem. Phys 108 (1998) 1423

Also J. Heckmann & A. Berlin (Bochum)







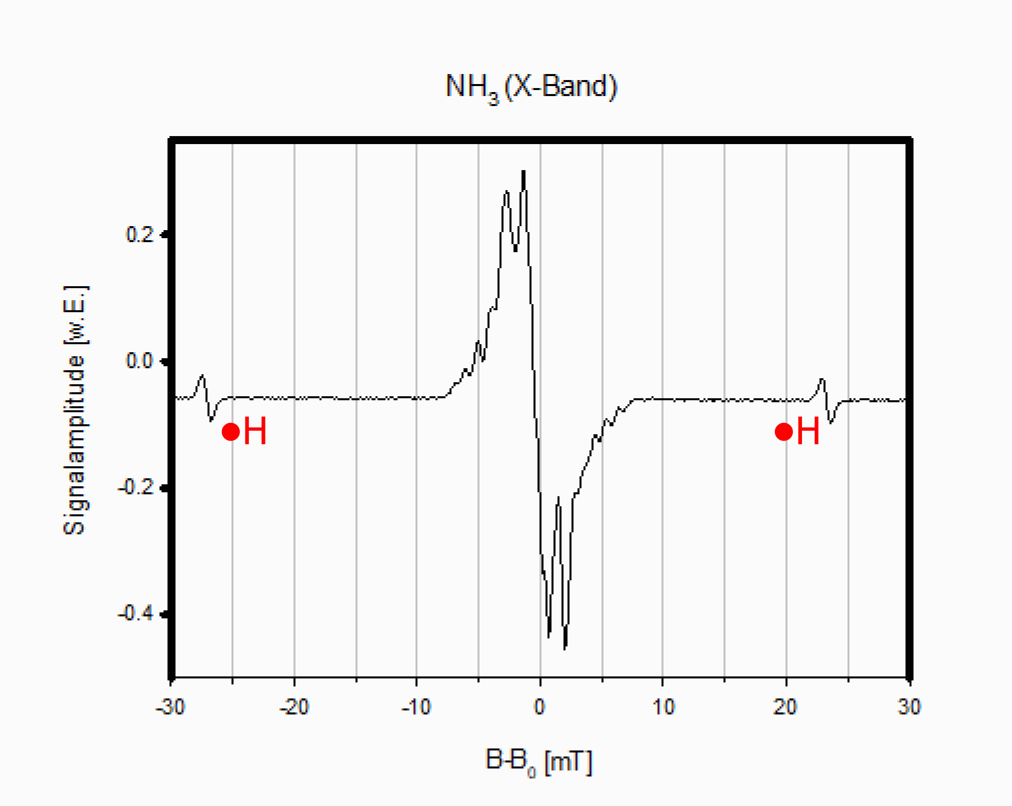
Radicals in irradiated ammonia

Atomic hydrogen

The HFS of hydrogen is about 50 mT (1.4 GHz), far outside our microwave scan

- ✗ DNP
- ✓ Spin-relaxation

It decays about 30 K warmer than •NH_2
Symons: NH_3 + •H → •NH_2 + H_2 ??

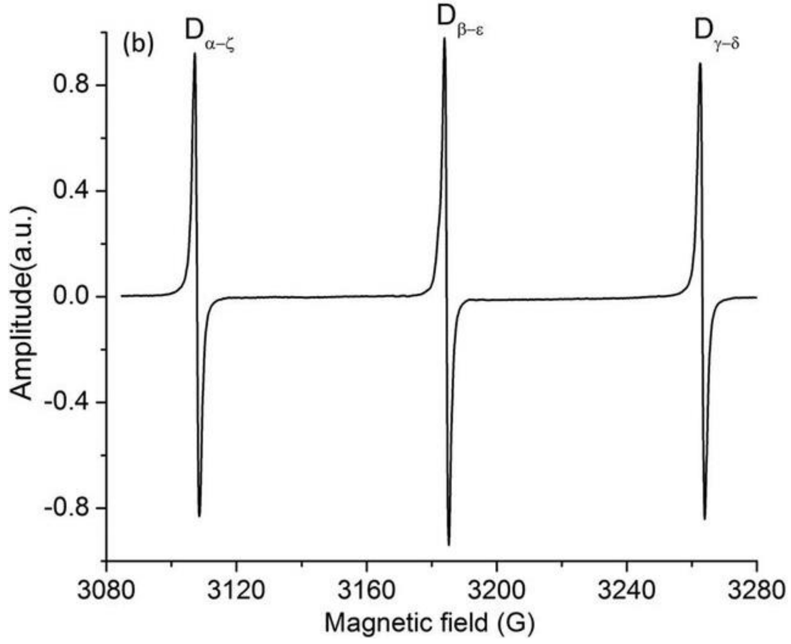


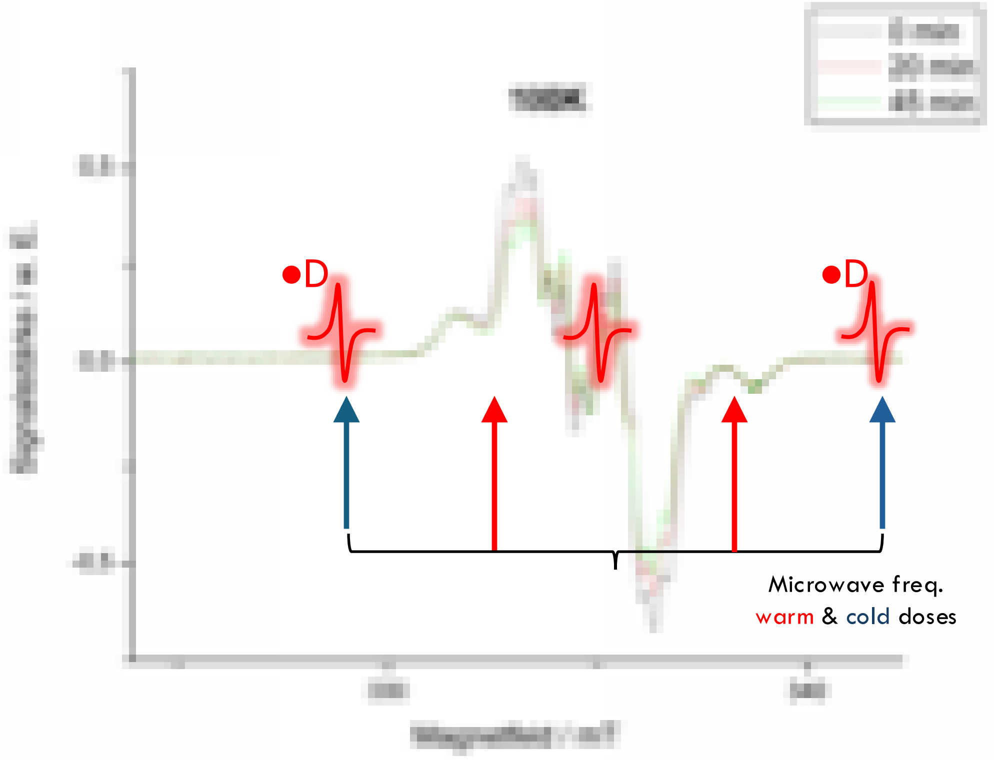
•NH_2 and •H radicals in warm irradiated NH_3
Jorg Heckmann, PhD thesis, Bochum (2004)

Radicals in irradiated ammonia

Atomic deuterium

HFS is much smaller than ^1H, about 15 mT, low-to-high





x-band spectra of irradiated **ND_3** at 100 K

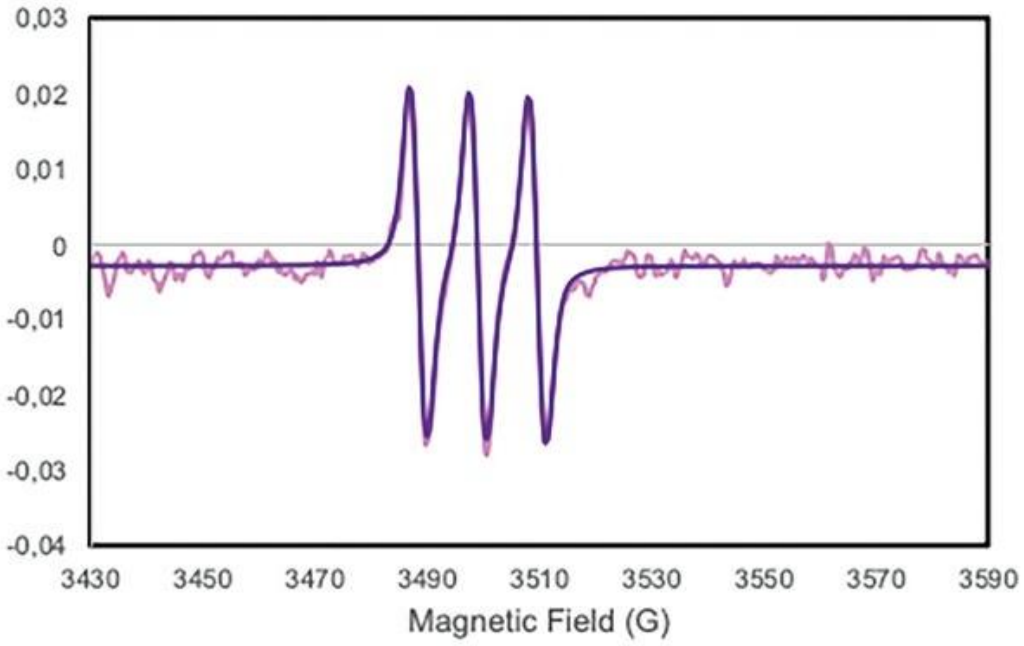
Alexander Berlin, PhD thesis, Bochum (2015)

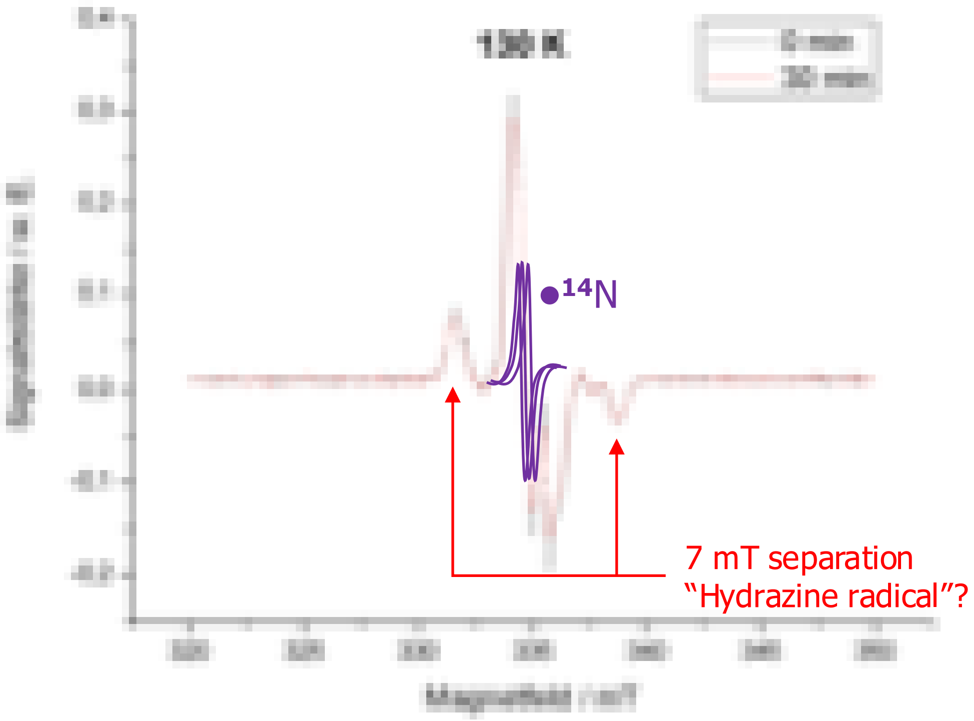
Demarco: "… the free radicals (●ND_2) decay at a higher temperature than do the D atoms."

Radicals in irradiated ammonia

By 130 K, the $\bullet ND_2$ radicals have completely disappeared, leaving resonance lines from one or more unidentified species.

HFS in ^{14}N is narrower still, 1 mT





x-band spectra of irradiated **ND_3** at 130 K

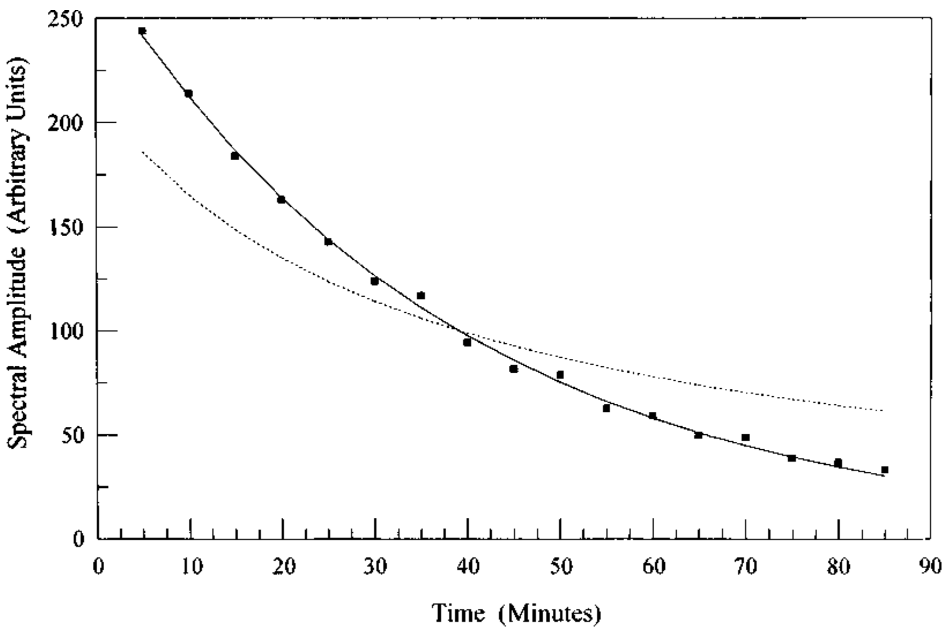
Alexander Berlin, PhD thesis, Bochum (2015)

Summary, Conjectures, Questions

- When ammonia is irradiated at 87 K, the *dominant* species are $\bullet NH_2$ and $\bullet ND_2$
- The principle broadening mechanisms are the hyperfine and dipolar interactions
- Other radicals are produced, each with a different activation temperature

- Atomic hydrogen $\bullet H$ is probably the main source of radiation damage in NH_3
- Atomic deuterium $\bullet D$ is not as damaging and may *improve* the polarization of ND_3

- What ***is*** the "cold dose"?
- Does it have to be cold?
- How cold?
- How long does it last at 77 K?
- Can we perform *in situ* monitoring at 1 K?



Decay of H-atom resonance at 102 K.
Solid line: First-order fit
Dotted line: Second-order fit

L. DeMarco et al, J. Chem. Phys., Vol. 108, No. 4, 22 January 1998