50 Years of Matrix Isolation of Atomic Free Radicals

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Impurity-Helium Solids

-Very large concentrations of free radicals can be stabilized. Eg. $2 \cdot 10^{19}$ cm^{-3} D in D_2 (~0.1%), more for N in N_2. Studies of rates of tunneling chemical reactions, studies of atomic diffusion in disordered media.

- Structural and magnetic properties of nanoparticles.

-Novel porous medium. Studies of He in disordered medium.

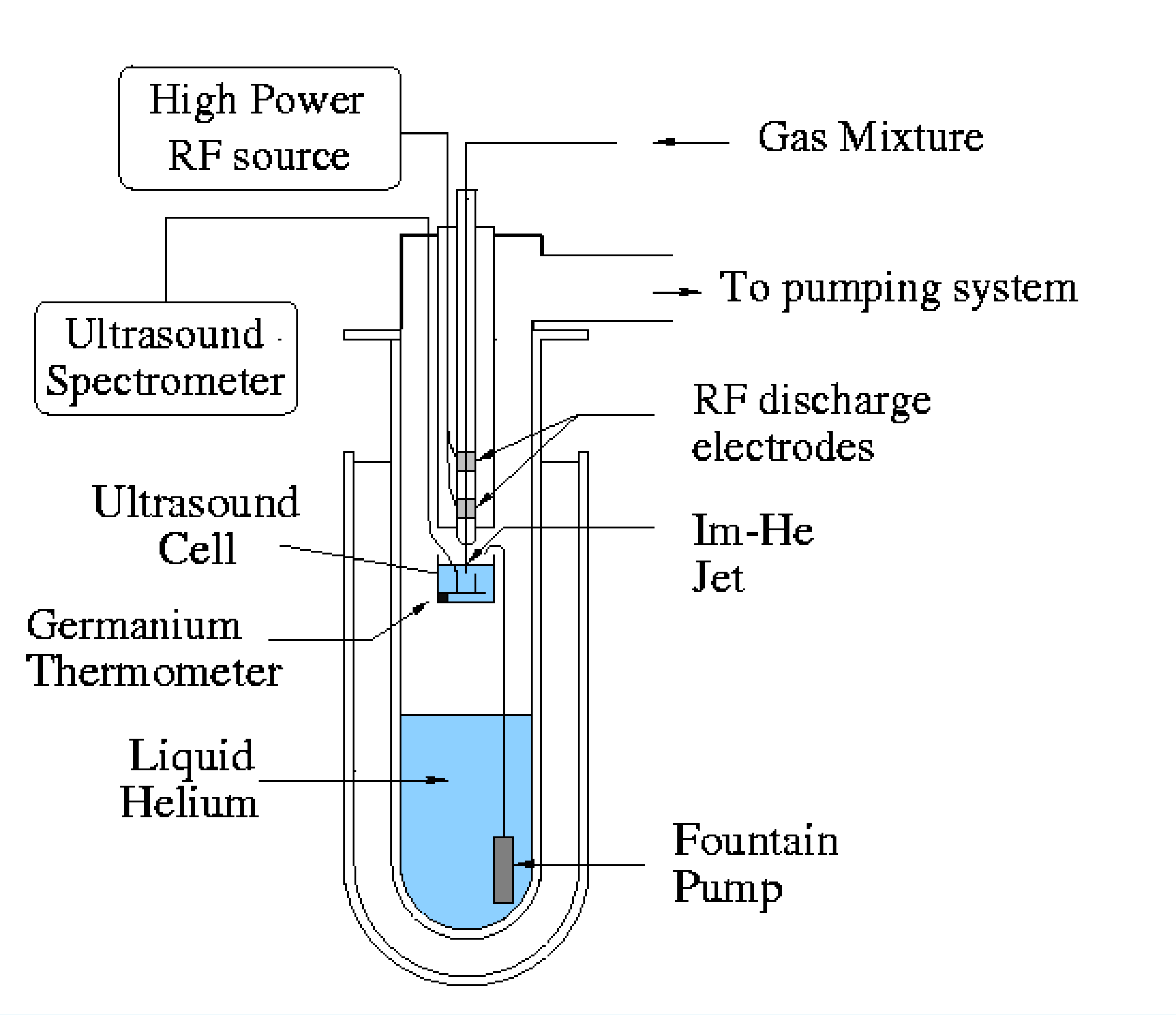
- Quantum effects in H-containing solids.

- High energy densities are obtainable.

- Suggested as moderators for ultracold neutrons (D_2).

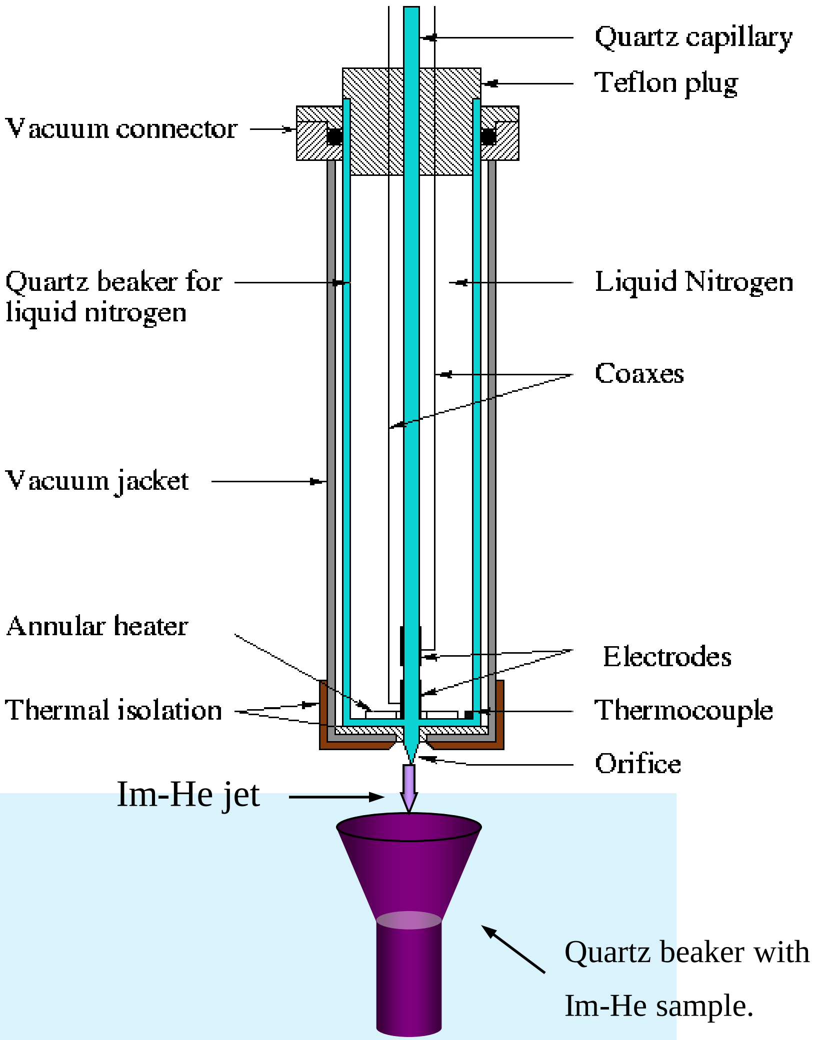
- Materials with large internal surfaces. Catalysis.

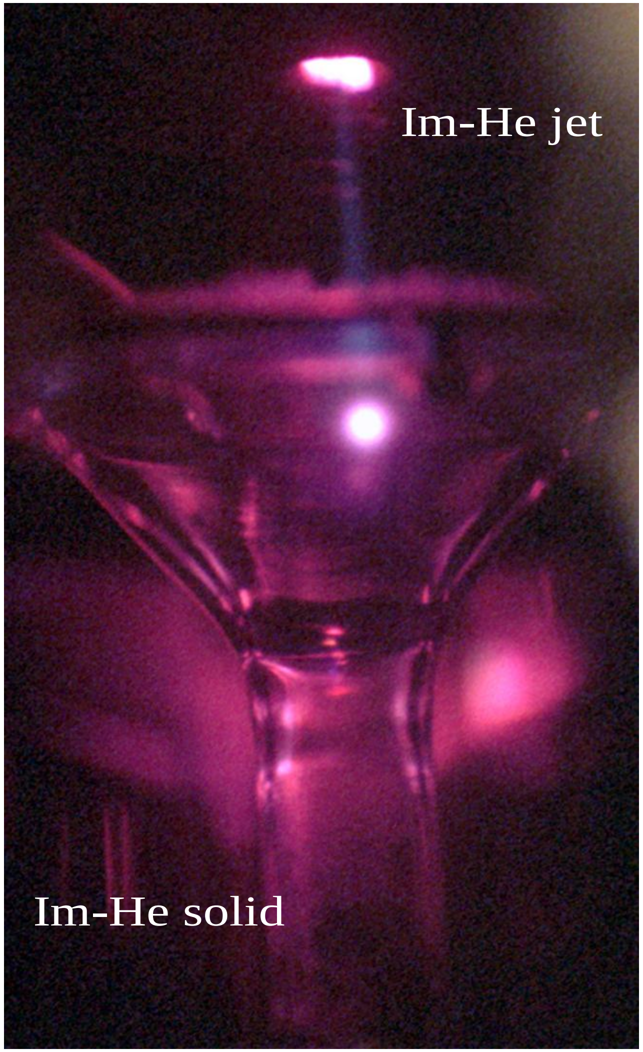
Sample preparation:



E.B.Gordon, L.P. Mezhov-Deglin and O.F. Pugachev, JETF Lett, 19, 63 (1974)

Sample preparation .





Conditions during sample preparation:
Pressure ~5 Torr (Temperature ~1.5 K)
Gas mixture composition - [Im]/[He]=1-5 %)
Gas flux ~5*10^{19} atom and molecules per sec
Distance between source orifice and liquid helium surface in beaker ~2 cm

E.B.Gordon, L.P. Mezhov-Deglin and O.F. Pugachev, JETF Lett, 19, 63 (1974)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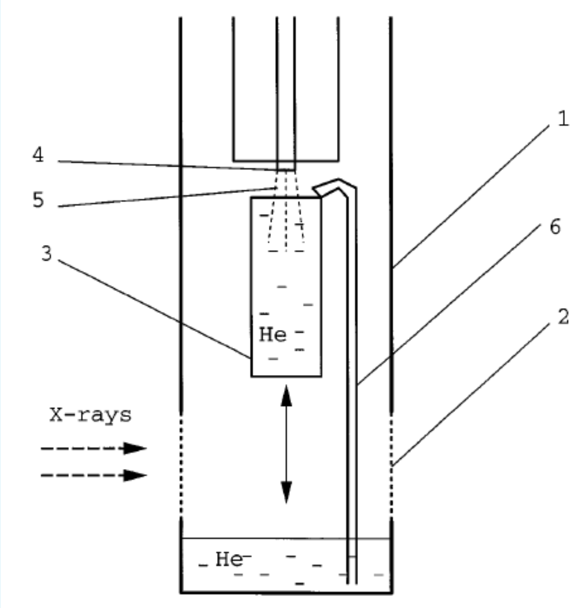
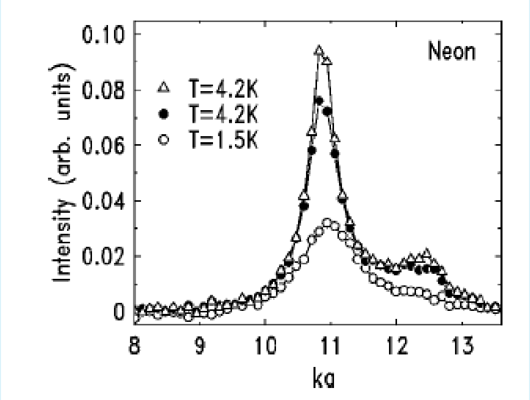
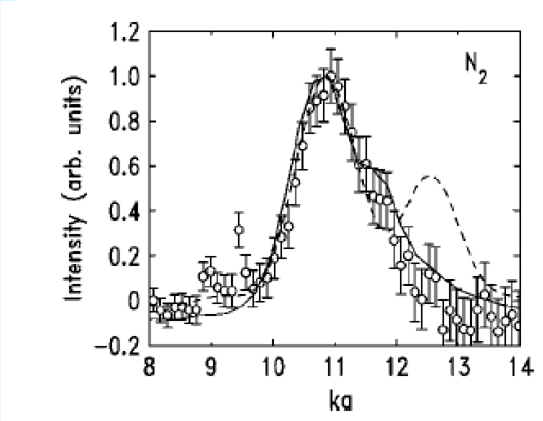
X-ray Diffraction Studies of the Im-He Condensates

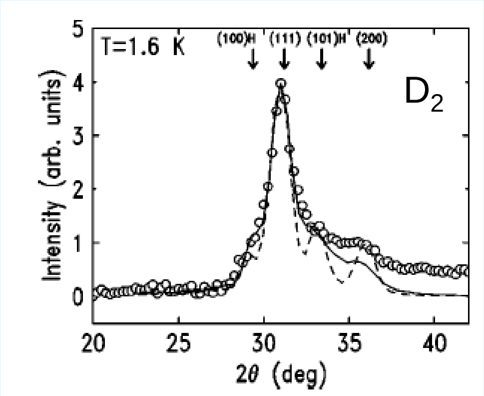


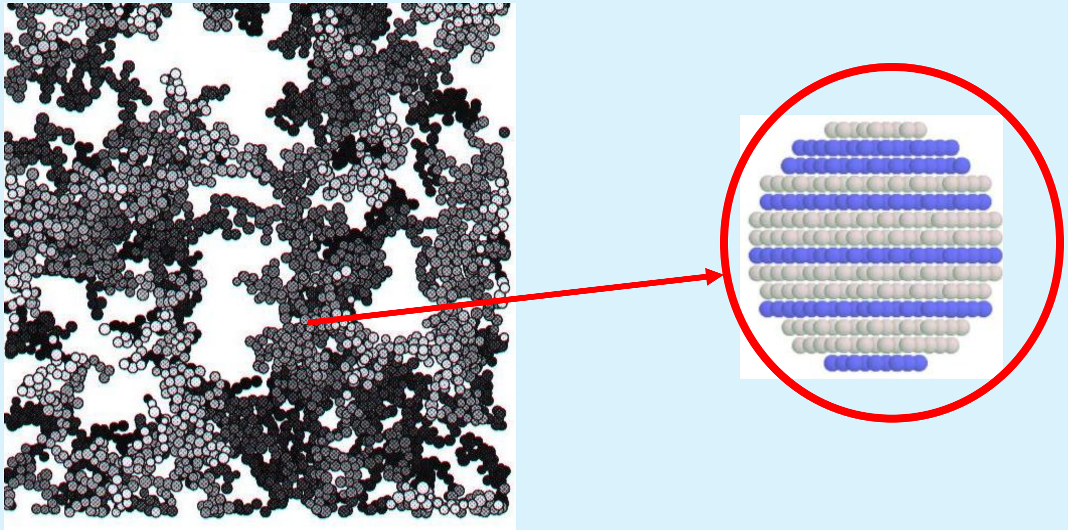
X-ray studies were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory.

X-ray Diffraction Studies of the Im-He Solids









Connected, aerogel-like structures consisting of closed-packed building blocks with defects.

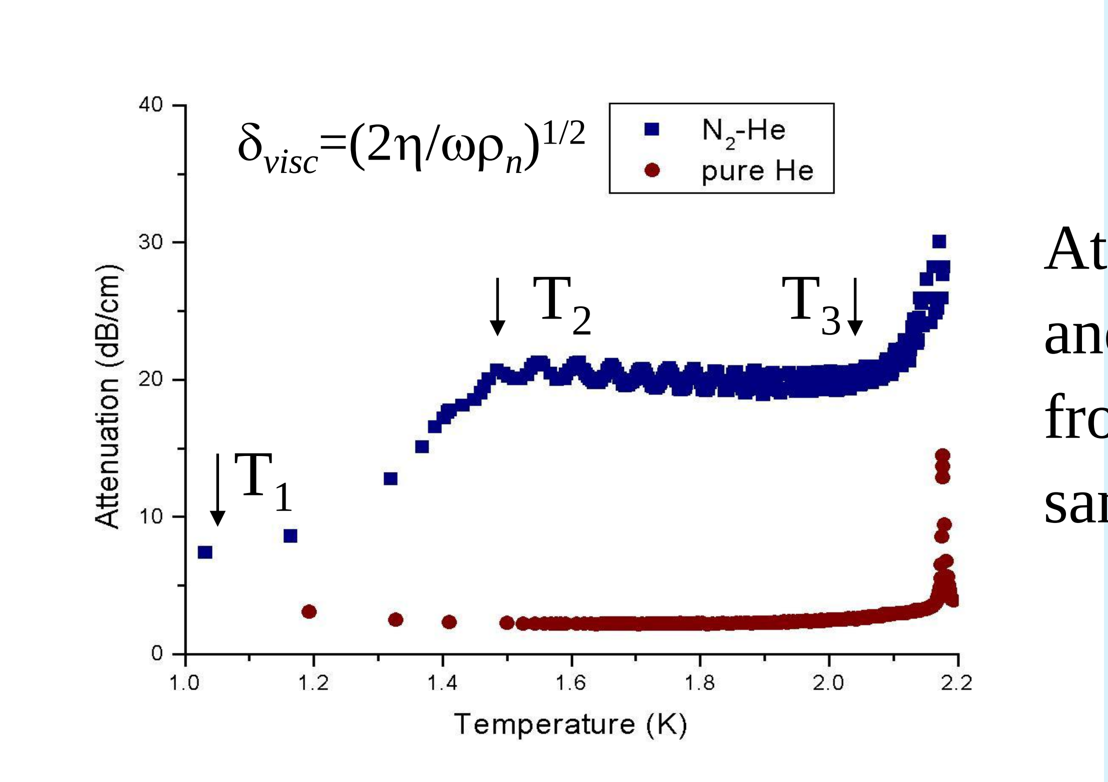
Typical block size 5-9 nm, quite narrow size distribution (~1 nm). Atomic densities ~10^{19}-10^{21} cm^{-3}.

Wide distribution of pore sizes (8-860 nm) detected by ultrasound measurements.

S.I. Kiselev, et al., *PRB* **65**, 024517 (2001); E.P. Bernard, et al., *PRB* **69**, 104201 (2004)

Previous work done at Cornell:

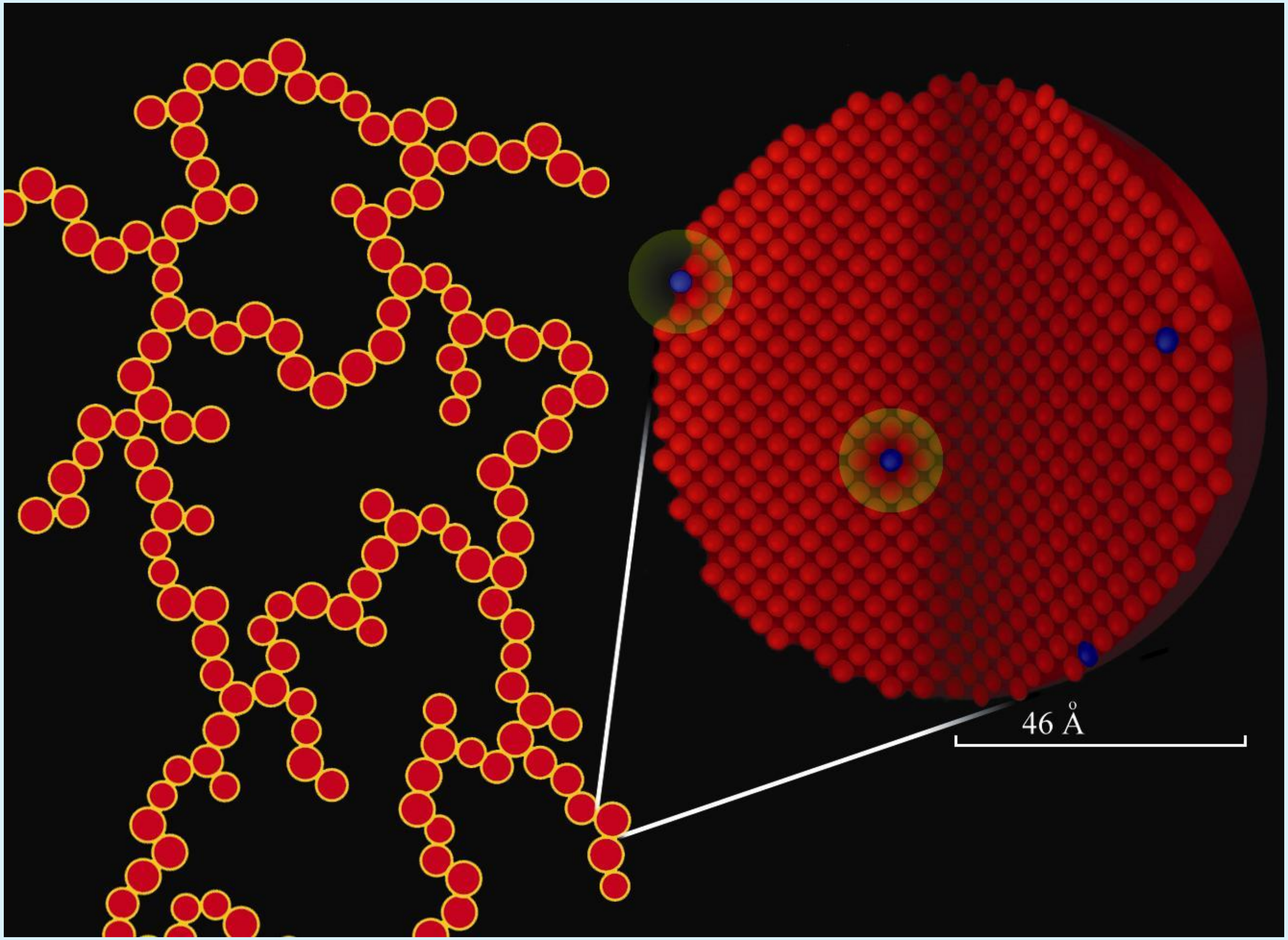
Ultrasound to explore the Structure of Im-He solids



Attenuation grows as more and more helium decouples from the pores of N_2-He sample.

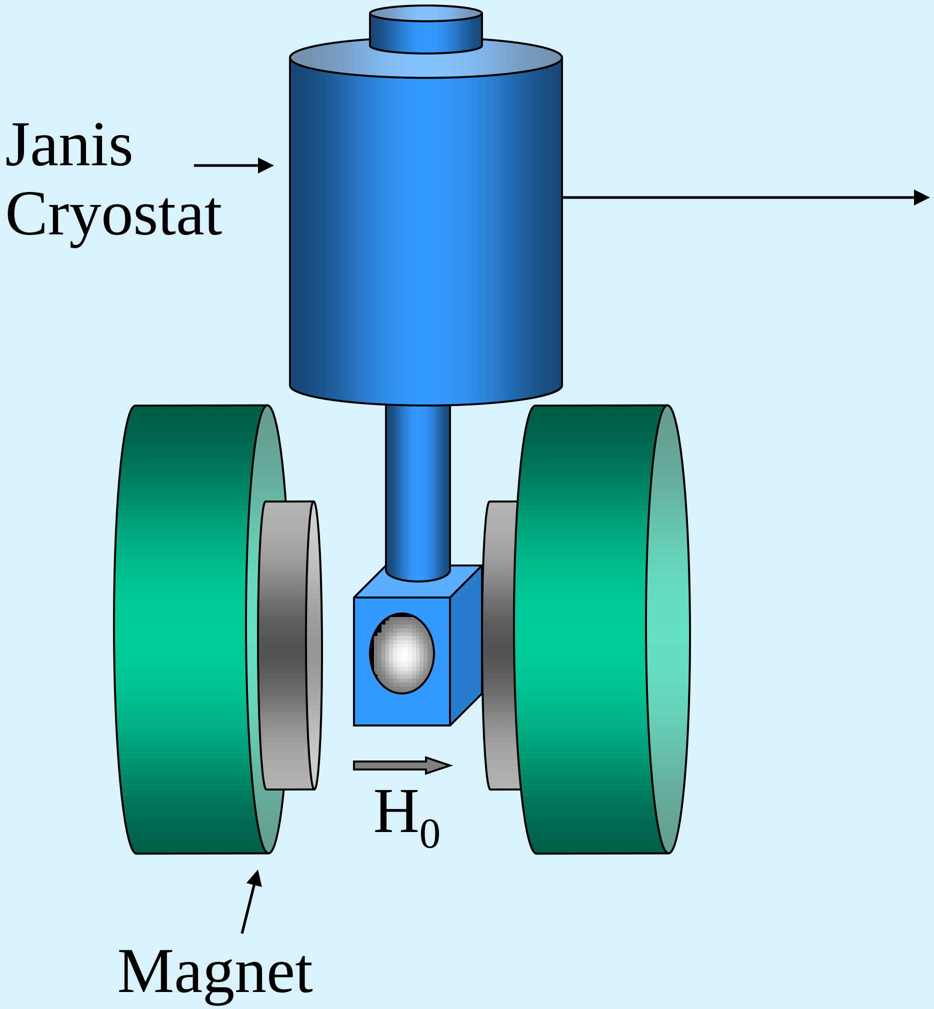
Attenuation of 5 MHz ultrasound in helium in N_2-He solid.

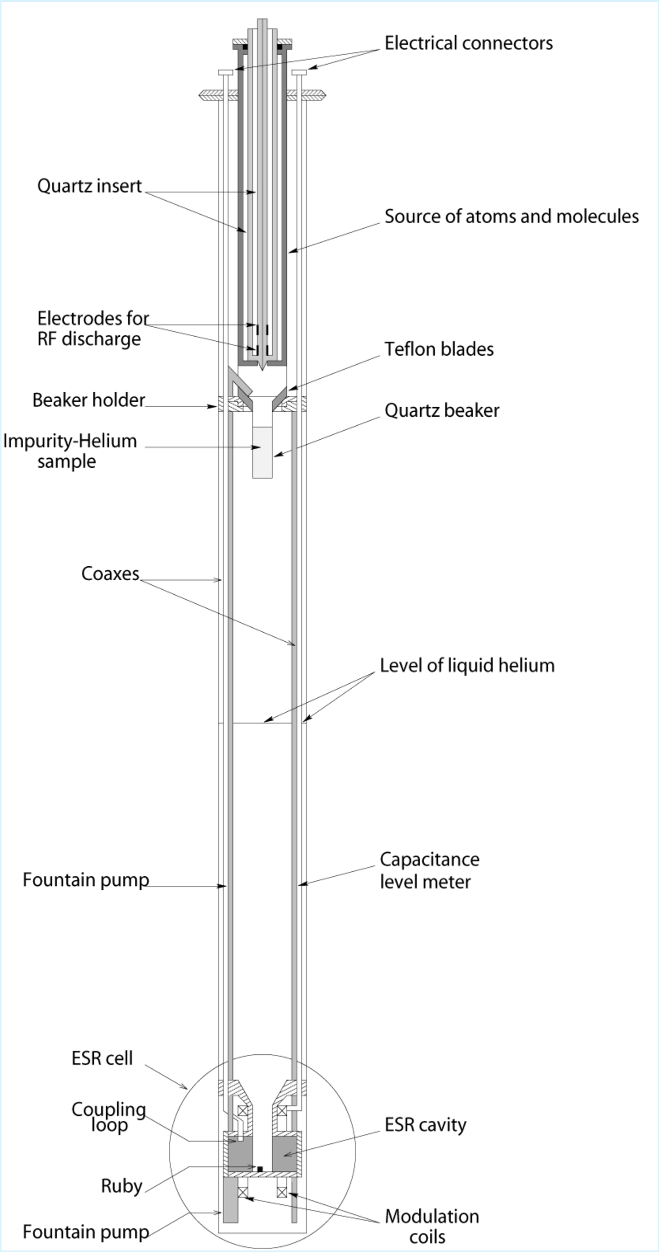
An idealized view of a deuterium-helium solid



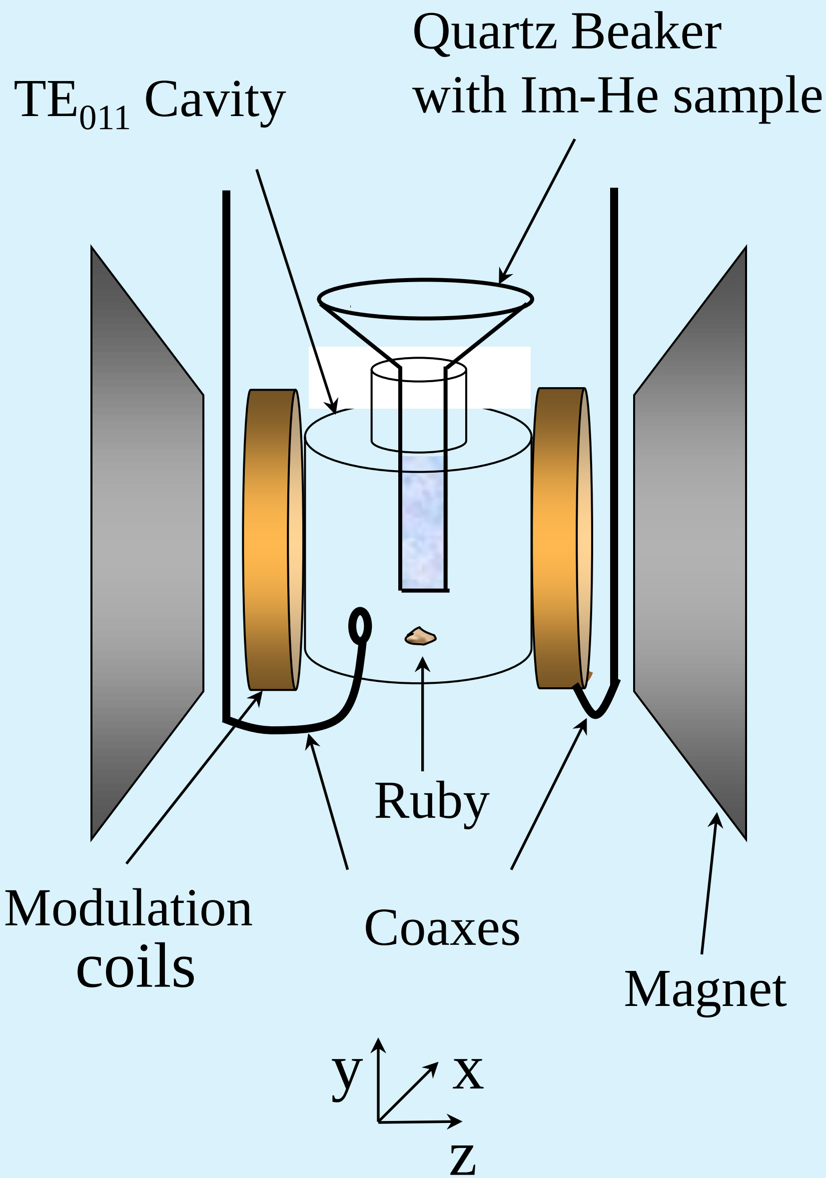
Red shows deuterium molecules arranged in an FCC lattice. The molecules are in spherical J = 0 rotational states. Yellow shows a monolayer of ^{4}He solidified on the helium surface. The surrounding superfluid ^{4}He is not shown. Blue shows deuterium atoms substituted within the molecular lattice. The green spheres show the first five coordination shells around each atom, where the ESEEM signal is explicitly simulated.

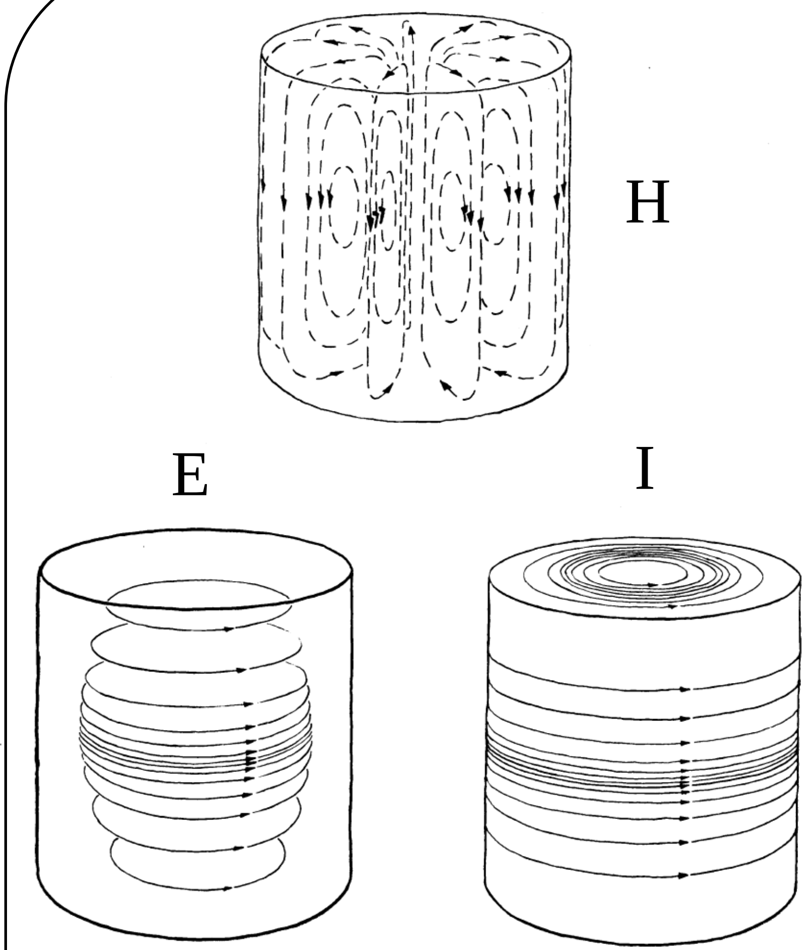
CW ESR Experiment





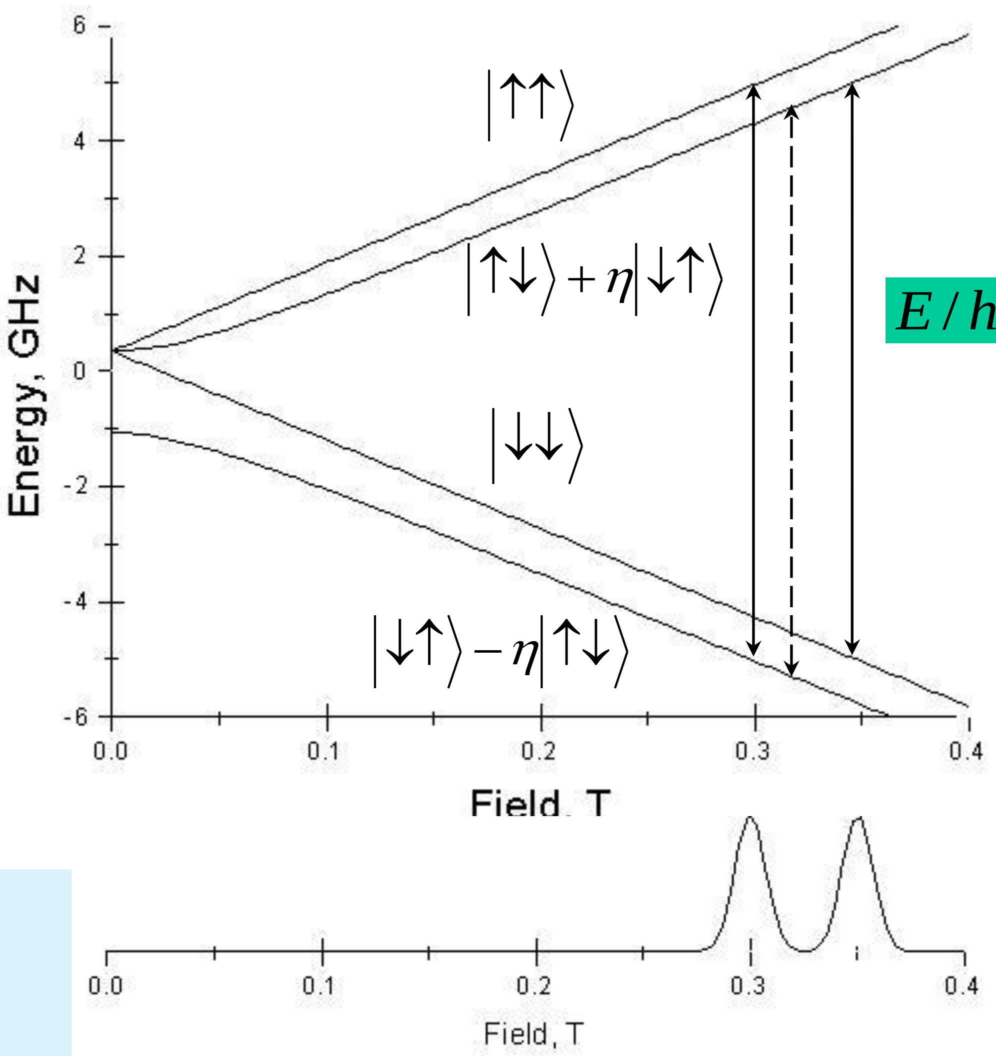
ESR cell.





Schematic field distributions in cylindrical TE$_{011}$ cavity.

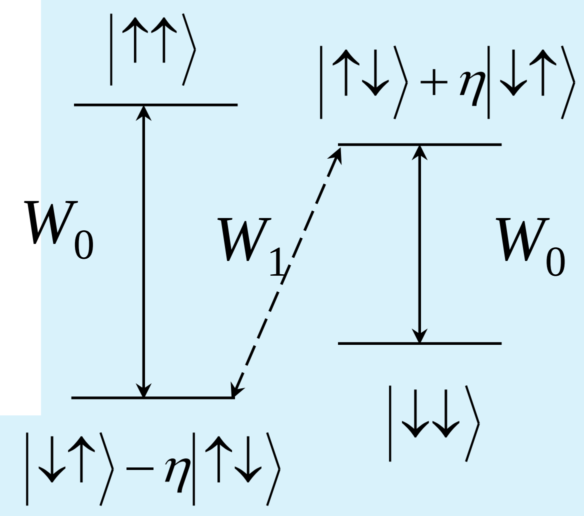
Hydrogen atom in magnetic field.



$\Delta M_S = \pm 1$, and $\Delta M_I = 0$ or

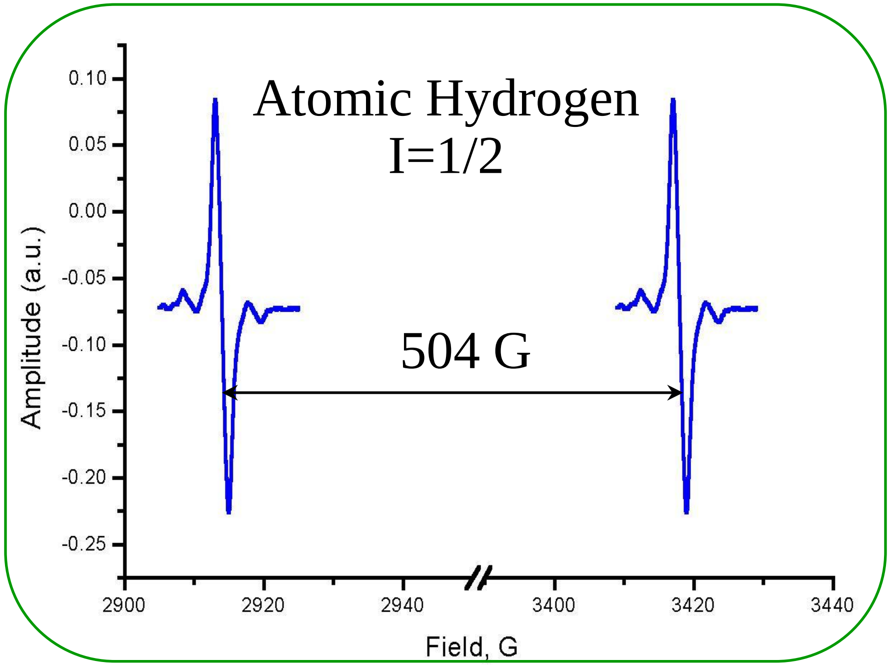
$\Delta M_S = \pm 1$, and $\Delta M_I = \mp 1$

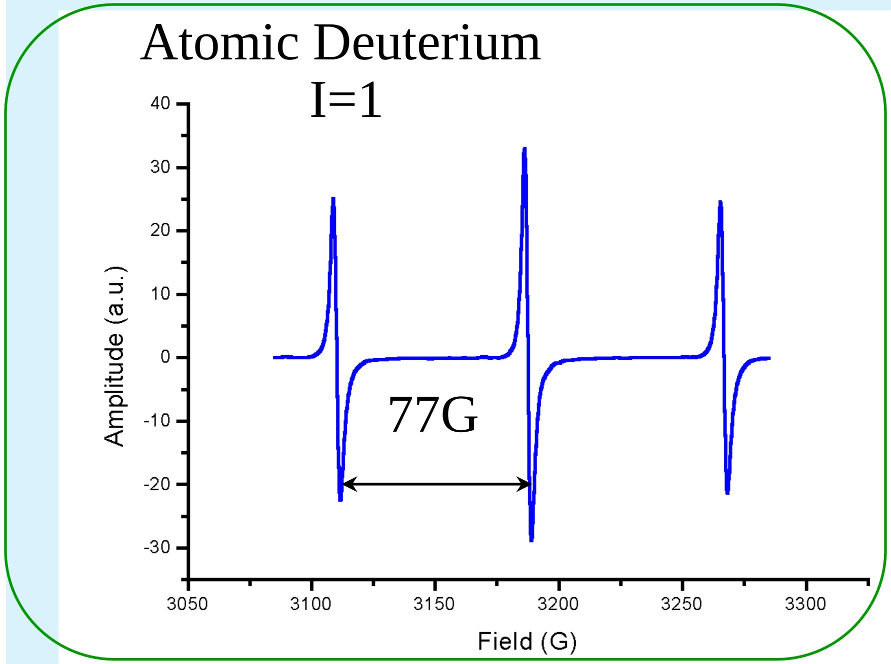
$E/h = 9.07\,\text{GHz}$



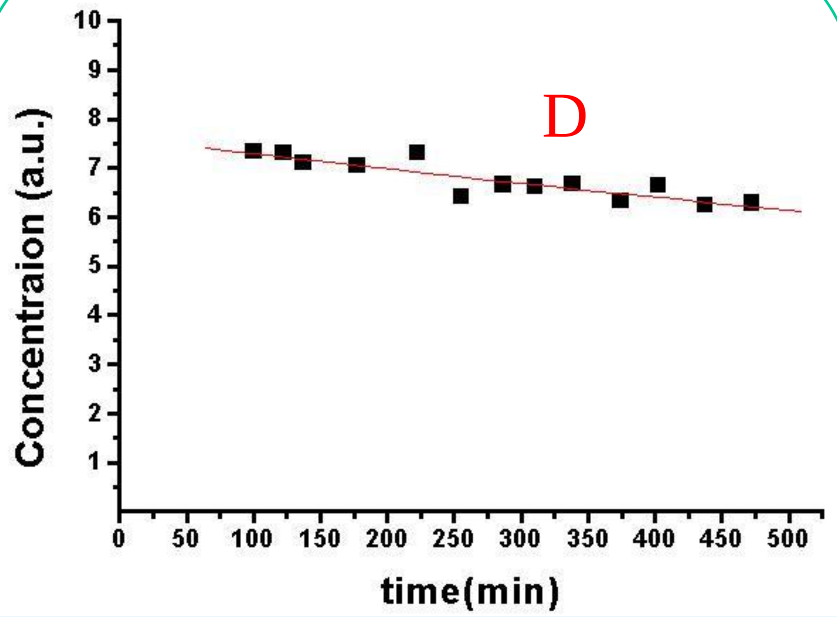
$$W_1 \sim \eta^2 W_0 \sim \frac{1}{170}$$

ESR hyperfine structure for interactions with nuclei of different magnetic moments.



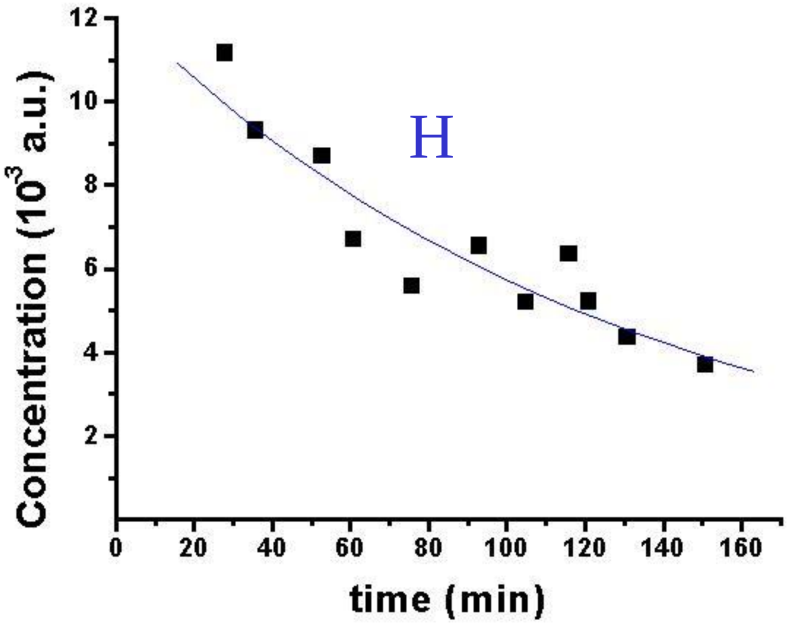


Effect of storage of H and D in Im-He solid at T=1.4 K.



Mixture used D_2:He=1:20

$\tau = 2500 \pm 500$ min

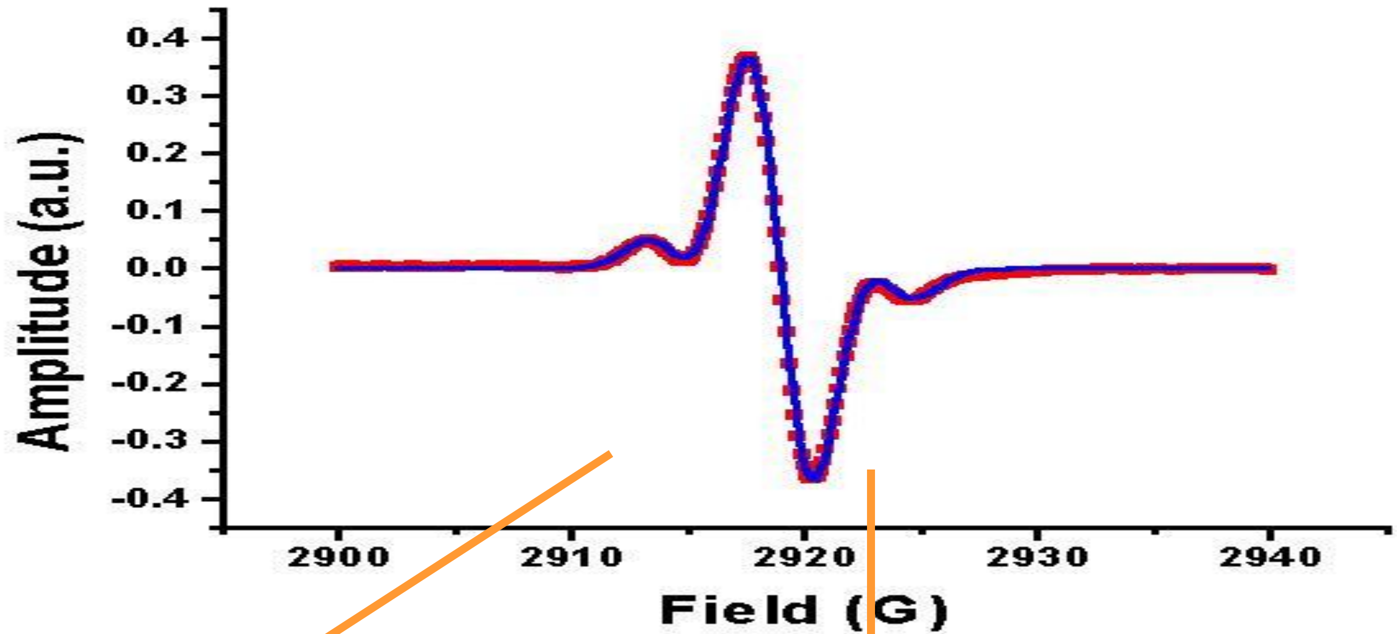


Mixture used H_2:Ne:He=1:4:100

$\tau = 130 \pm 20$ min

Low field ESR lines of H atoms

Sample formed by gas mixture
H_2:D_2:He = 1:4:1000



$$\Delta H_{\text{fitted}} = 4.3 \pm 0.1\,\text{G}$$

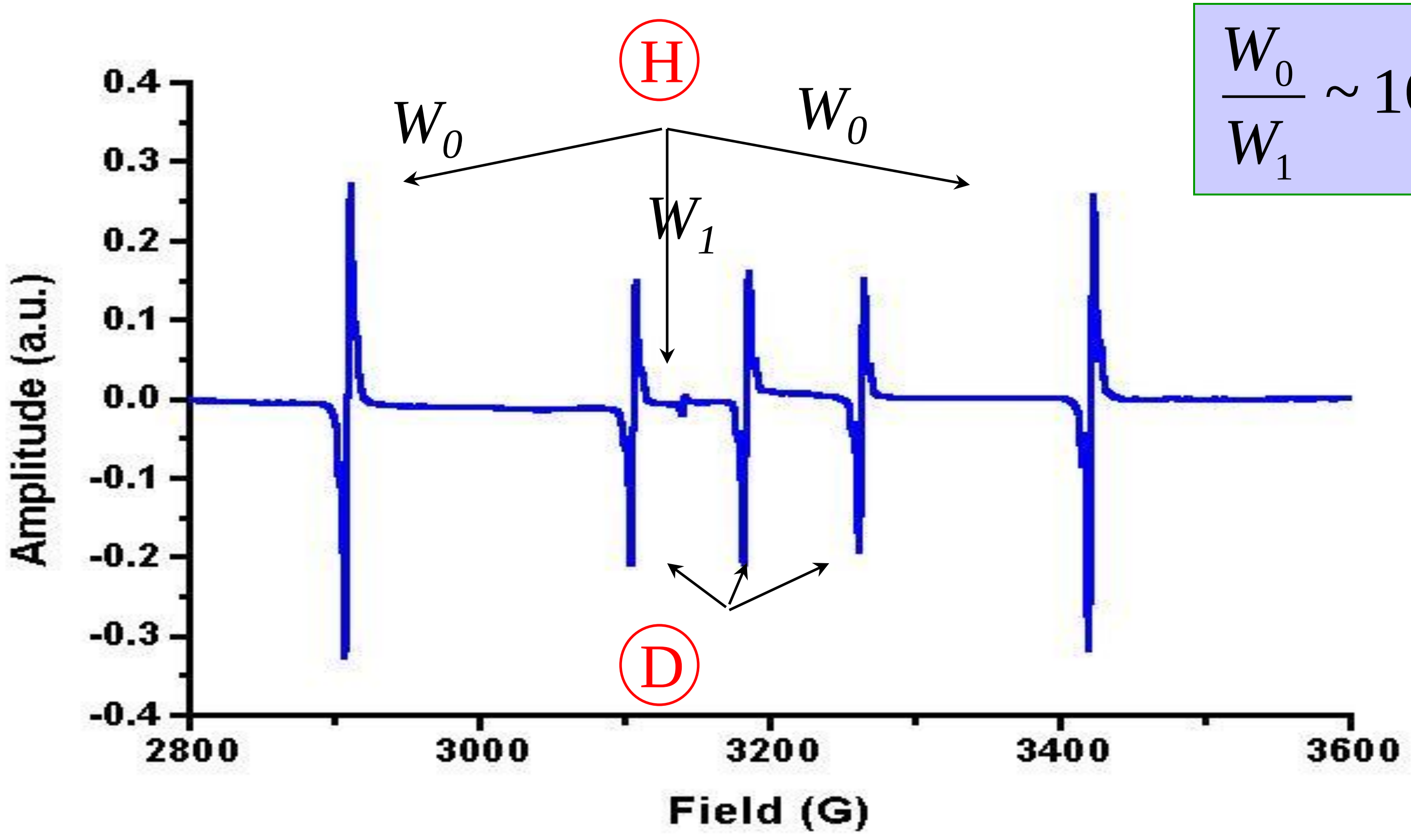
$$\Delta H_{\text{theory}} = H_0 \frac{g_N \beta_N}{g_e \beta_e} = 4.3\,\text{G}$$

$$\langle r \rangle_n = 0.73 (g_e \beta_e / H)^{1/3} n^{1/6} (I_{\text{sat}} / I_{\text{main}})^{-1/6}$$

$$\frac{I_{\text{sat}}}{I_{\text{main}}} \approx .11 \Rightarrow \langle r \rangle_n = 2.2\,\text{Å}$$

for two protons near H atom

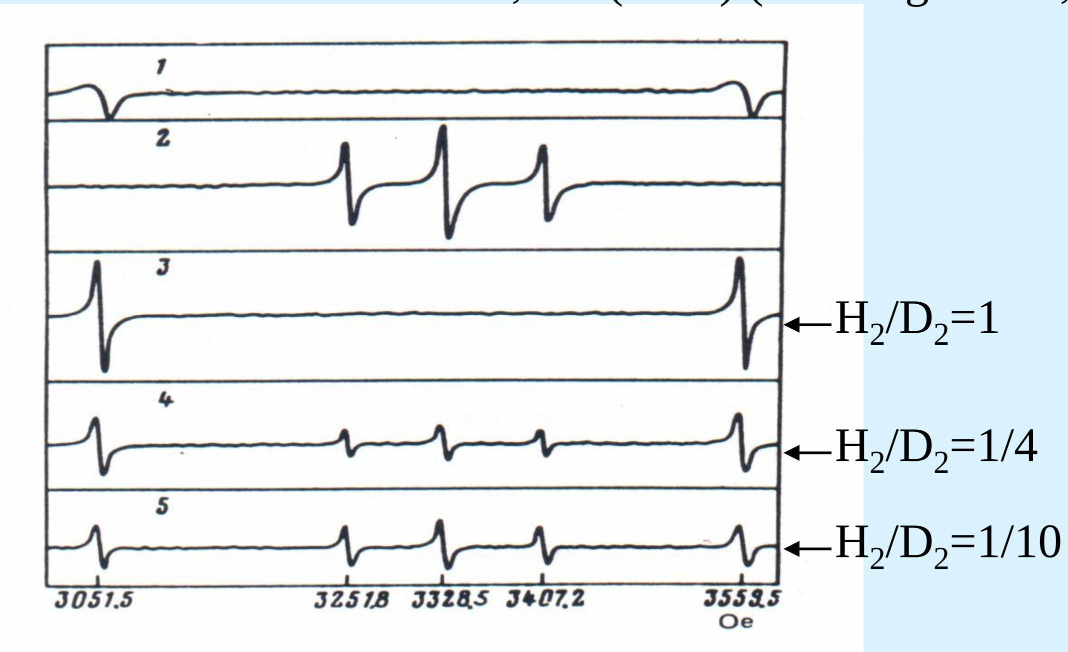
ESR spectra of hyperfine structures H and D atoms in HD-D_2-He solid (mixture used - H_2:D_2:He=1:4:100)



$$\frac{W_0}{W_1} \sim 160$$

Exchange tunneling reactions

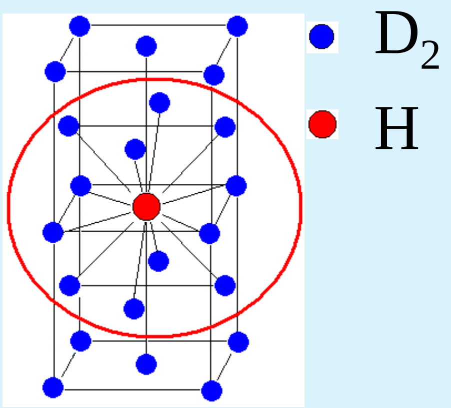
Gordon et all JETP Letters 37,282 (1983) (Chernogolovka, Russia)

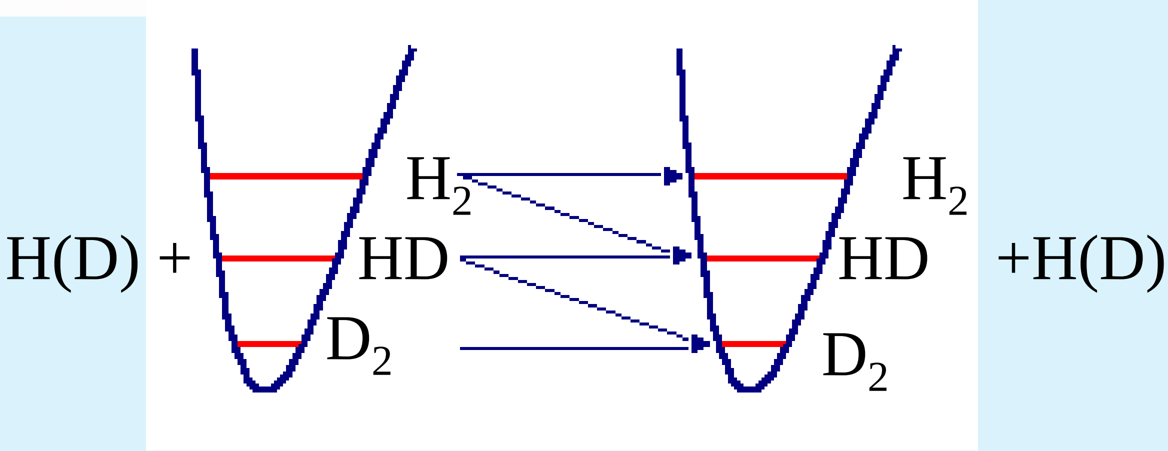


T<1.8K

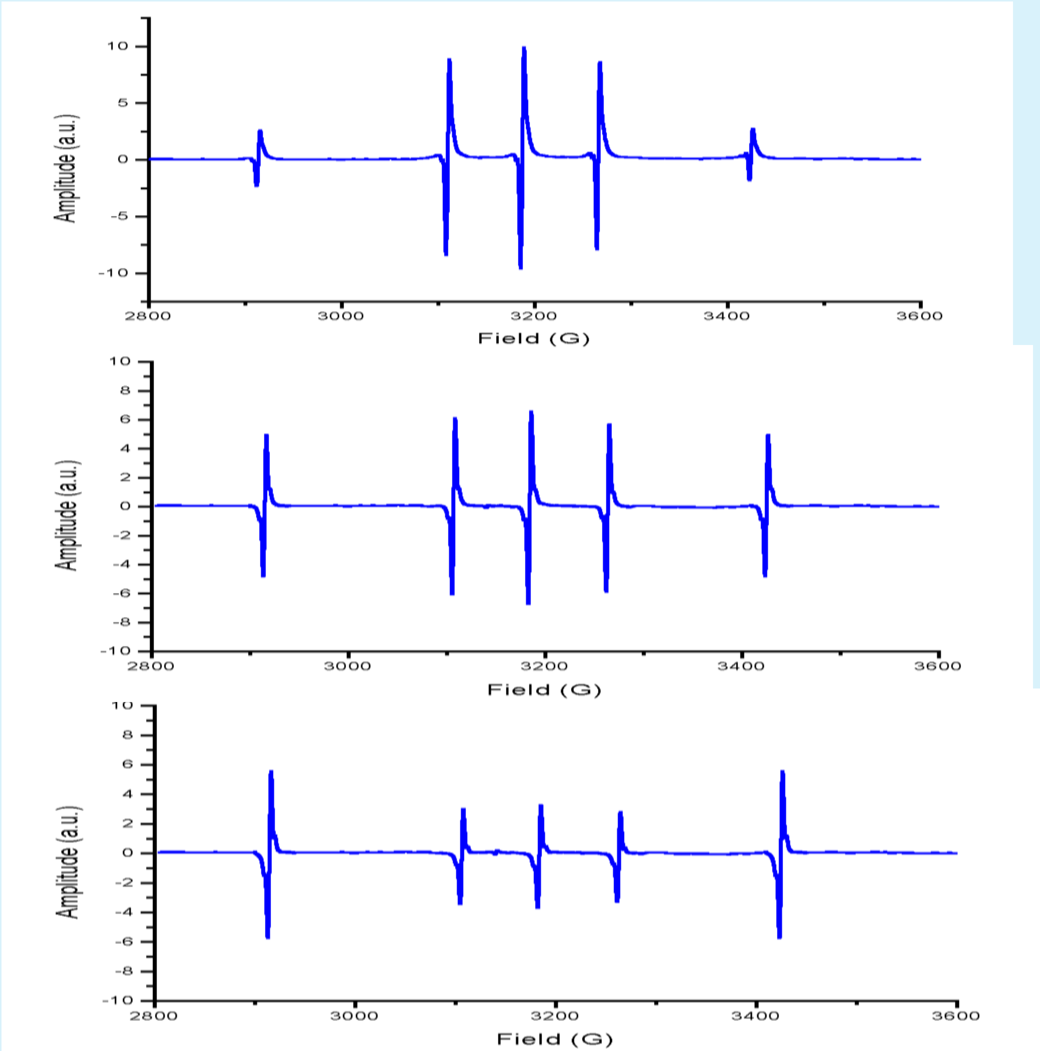
FIG. 1. EPR spectra of H and D atoms for different mixtures: 1—H_2:Ne: He = 1:1:40; 2—D_2: He = 1:20; 3—H_2:D_2:Ne: He = 1:1:1:60; 4—H_2:D_2: He = 1:4:100; 5—H_2:D_2: He = 1:10:220.

1) $D+H_2 \rightarrow HD+H$
2) $D+HD \rightarrow D_2+H$
3) $H+H_2 \rightarrow H_2+H$
4) $H+D_2 \rightarrow HD+D$
5) $H+HD \rightarrow HD+H$
6) $H+HD \rightarrow H_2+D$
7) $D+D_2 \rightarrow D_2+D$
8) $D+HD \rightarrow HD+D$





Time evolution of the ESR spectra of the H and D atoms in HD-D_2-He solid (mixture used - H_2:D_2:He=1:8:180)



t=23 min

t=205 min

t=479 min

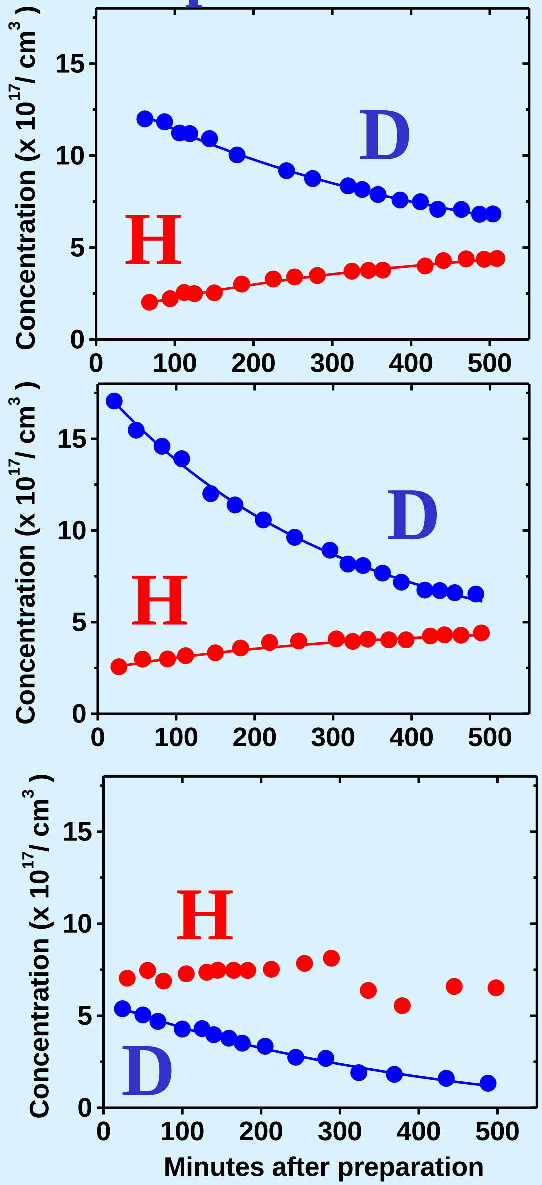
$\color{blue}{D}$+H_2 → HD+$\color{red}{H}$,

$\color{blue}{D}$+HD → D_2+$\color{red}{H}$

ESR spectra from H atoms (doublet) and D atoms (triplet) in H_2-D_2-He solid at T=1.37 K taken at different times after sample preparation. (H_2:D_2:He=1:8:180)

V.V. Khmelenko et al., Physica Scripta, T102, 118 (2002)

Time evolution of average concentrations of H and D atoms for different make up mixtures.

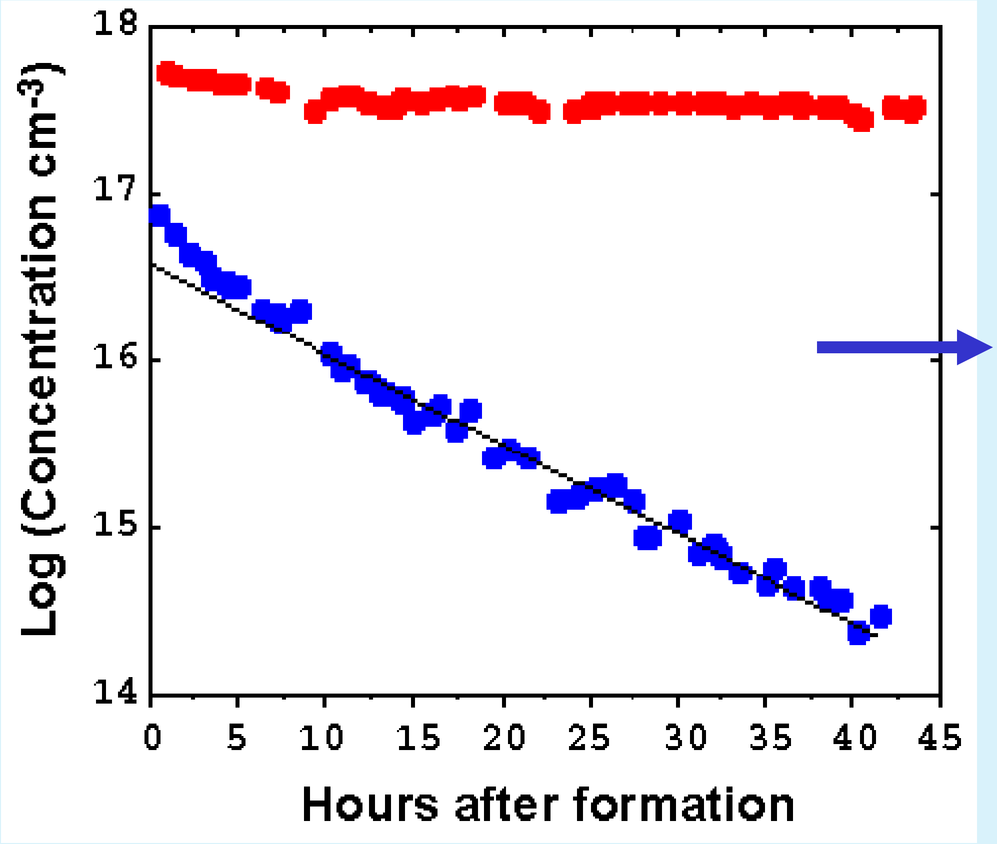


H_2:D_2:He=1:20:420

H_2:D_2:He=1:8:180

H_2:D_2:He=1:4:100

H and D atoms in HD-D_2-helium solids



D+H_2=HD+H, k =5.4x10^{-2} cm^{3}mol^{-1}s^{-1}

D+HD=D_2+H, k'=1.9x10^{-3} cm^{3}mol^{-1}s^{-1}

$$-\frac{d[\mathbf{D}]}{dt} = k[\mathbf{HD}]\cdot[\mathbf{D}] = k'[\mathbf{D}]$$

$[H]_{max}$ ~10^{18} cm^{-3}

E.P. Bernard et al., J. Low Temp. Phys. 138, 839 (2005)

Low Temperature Tunneling Reactions.

Calculated rate constant for the first order kinetics, k'.

(1)	$H_2 + D \rightarrow H + HD$	$5.4 \cdot 10^{-2}$
(2)	$HD + D \rightarrow H + D_2$	$1.3 \cdot 10^{-4}$
(3)	$DH + D \rightarrow D + HD$	$2.2 \cdot 10^{-5}$
(4)	$D_2 + D \rightarrow D + D_2$	$3.7 \cdot 10^{-8}$
(5)	$H_2 + H \rightarrow H + H_2$	$2.0 \cdot 10^{-2}$
(6)	$HD + H \rightarrow H + DH$	$1.0 \cdot 10^{-4}$
(7)	$DH + H \rightarrow D + H_2$	$< 10^{-51}$
(8)	$D_2 + H \rightarrow D + DH$	$< 10^{-51}$

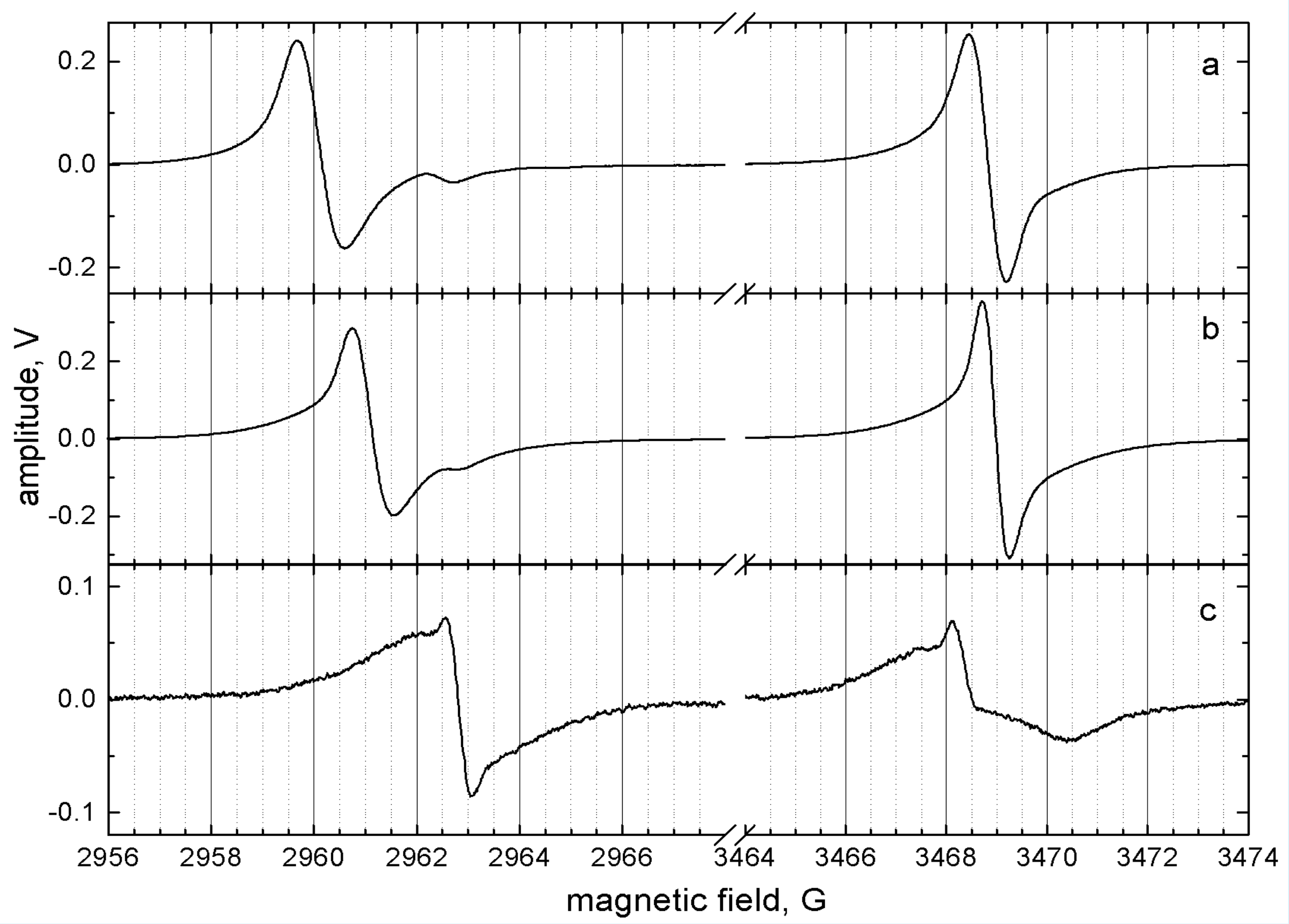
$$-\frac{d[\mathbf{D}]}{dt} = k[\mathbf{H_2}] \cdot [\mathbf{D}] = k'[\mathbf{D}]$$

rate for $D + HD \rightarrow D_2 + H$

(1.9×10^{-3} $cm^3 mol^{-1} s^{-1}$)

Takayanagi and Sato, J. Chem. Phys. **92**, 2862 (1990)

ESR Spectra of H atoms in H-Kr Samples

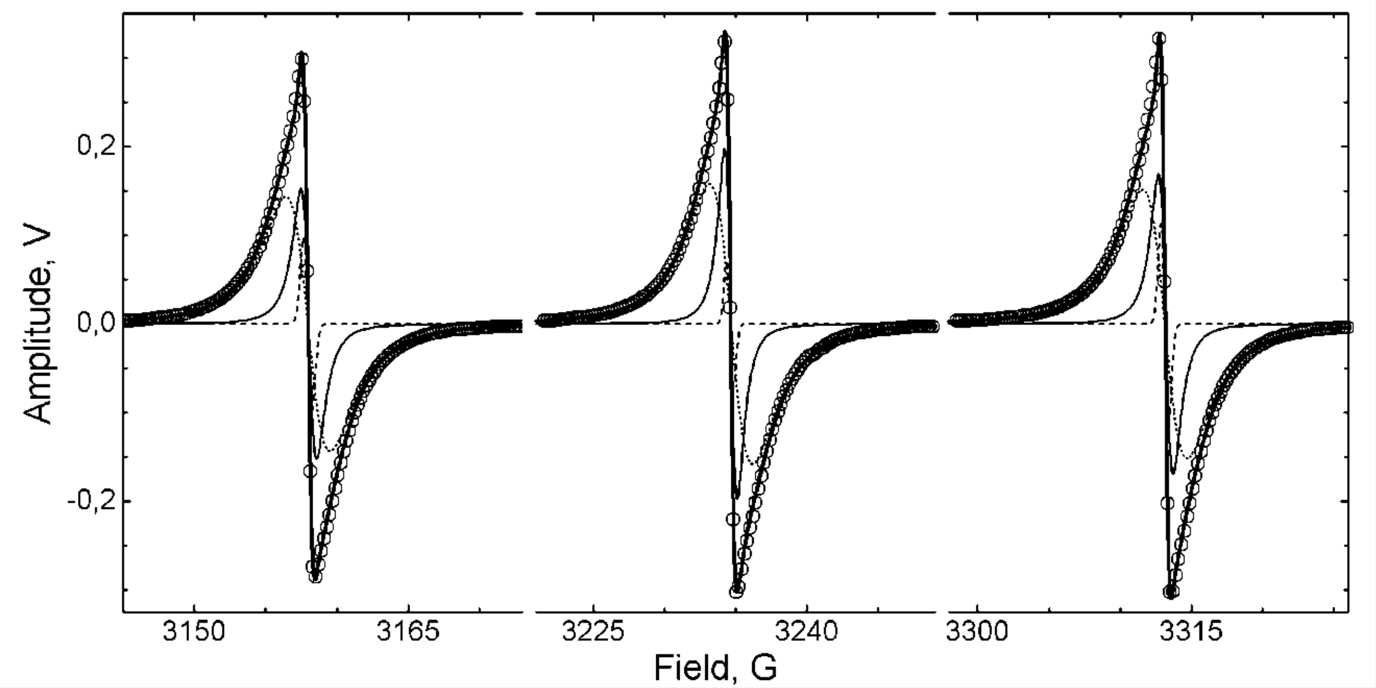


(a) As-prepared sample from gas mixture H_2:Kr:He= 1:1:200.

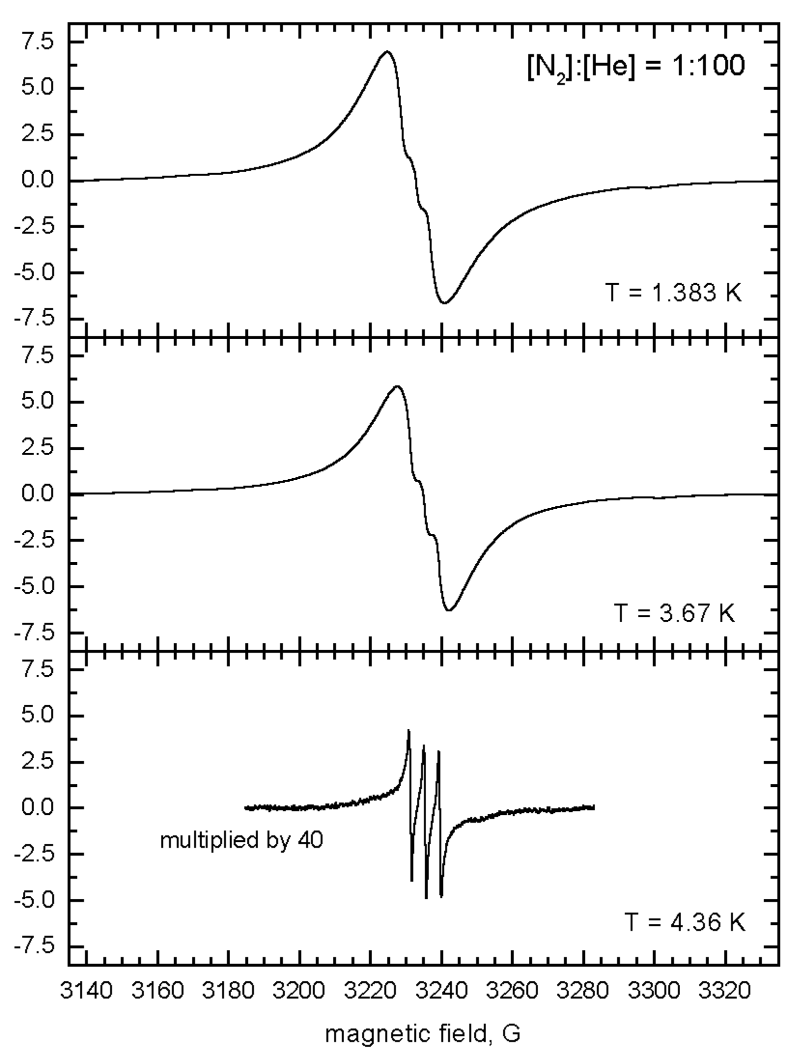
(b) As-prepared sample from gas mixture H_2:Kr:He= 1:50:10,000.

(c) Sample (a) after annealing to 14.5 K and cooling to 1.35K. Amplification increased by a factor 15.

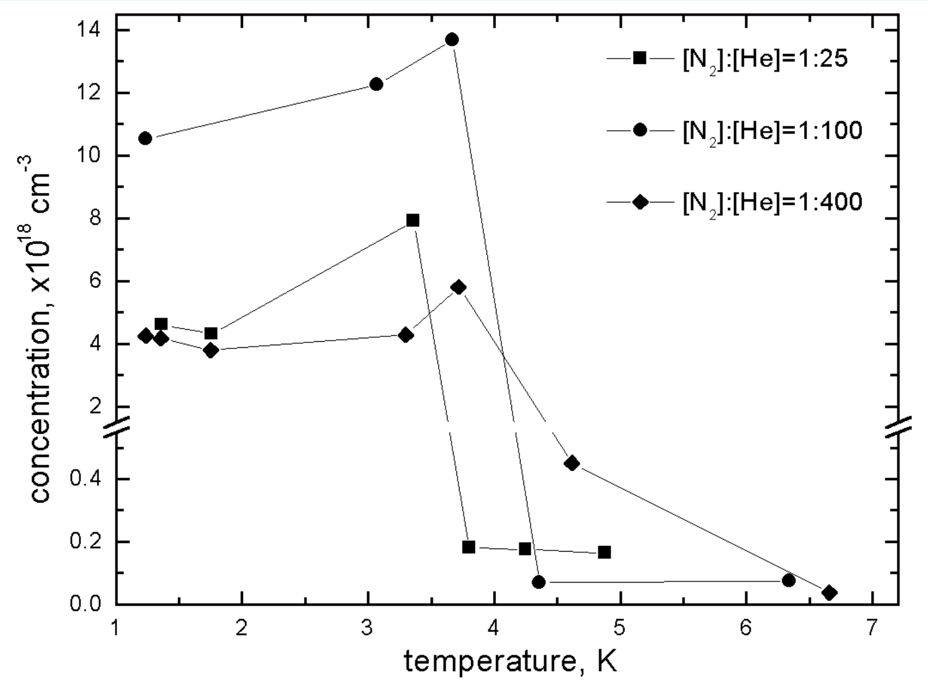
Exchange narrowing of ESR spectra of D atoms in D-Kr-He solids



ESR investigations of N atoms in N_2-He solids



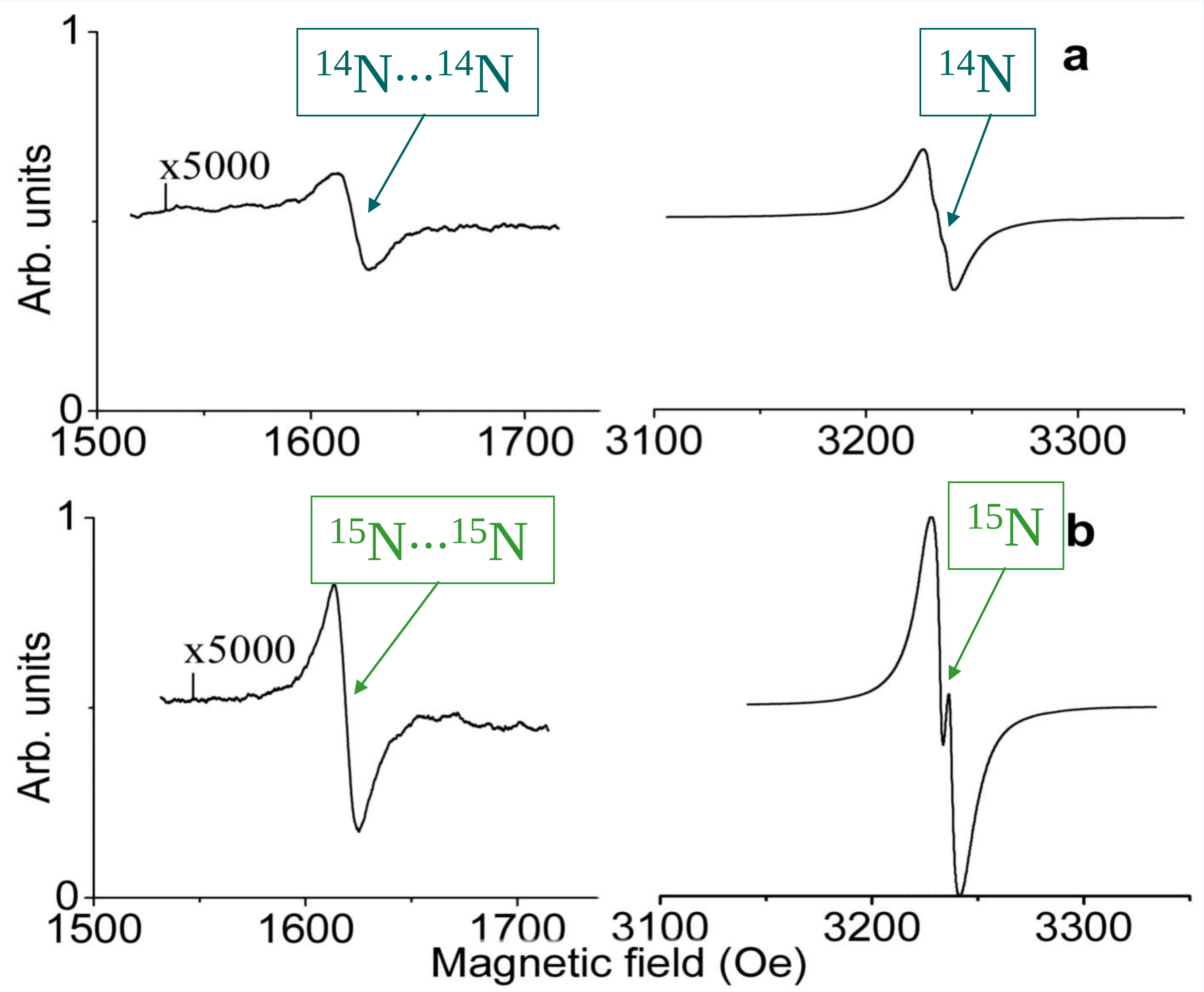
Changes of ESR spectra of nitrogen atoms trapped in sample condensed from gaseous mixture $[N_2]$:[He]=1:100



The temperature dependence of the average concentration of N atoms in N_2-He solids created by different nitrogen-helium gas mixtures

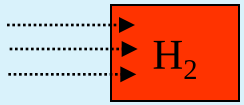
$$[N]_{max\ av} = 1.0*10^{19}\ cm^{-3}$$

ESR spectra of nitrogen atoms and spin-pair radicals in nitrogen –helium solids at T=1.35K



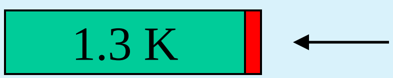
Experiments with H in H_2

Irradiation of H_2 by β, γ, x –rays:



- Jen, *Maryland* , (1957-1960) — T>4.2 K
- Webeler, *NASA*, *Cleveland* (1975) — T=0.3-1.0 K
- Souers, *Livermore* (1980-) — T>4.2 K
- Miyazaki, *Nagoya*, (1980-) — T>1.8 K

Flash condensing on a cold surface:



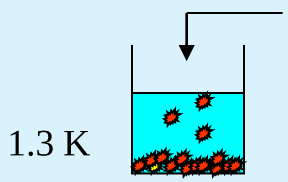
H + H_2

- Lukashevich, *KIAE*, *Moscow* (1978)
- Shevtsov, *Turku*, *Finland* (1992-1998)

T>1.3 K

or into superfluid ^{4}He:

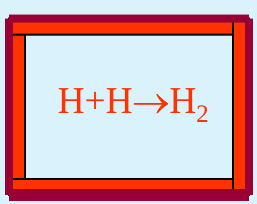
H + H_2



- Gordon *et al.* *Chernogolovka*, *Russia* (1974-)
- Lee, Khmelenko *Cornell* (1998-)

T>1.3 K

Growing from recombination of H↓:



- Vasiliev *et al.* *Turku*, *Finland* (2004-) — T=0.05-1.0 K

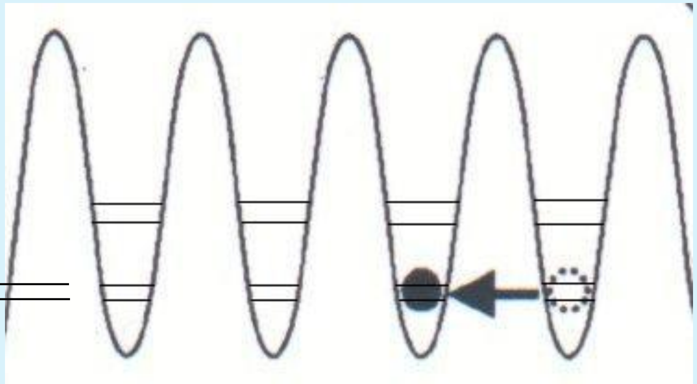
10^5-10^6 smaller deposition rate

Recombination of H atoms in solid H_2

Quantum diffusion:

$$\Delta \cdot \tau_{hop} \approx \hbar$$

$$D_{sp} \approx \frac{a^2}{\tau_{hop}} \approx \frac{a^2 \Delta}{\hbar} \qquad \Delta = 10^{-3} - 10^{-1}\,\mathrm{K}$$



105 K

$$D_{sp} \approx 10^{-7}\,\mathrm{cm}^2/s \quad \text{at} \quad \Delta = 10^{-2}\,\mathrm{K}$$

Yu. Kagan *et al.* JETP Lett. 36,253-256(1982) (Moscow, Russia)

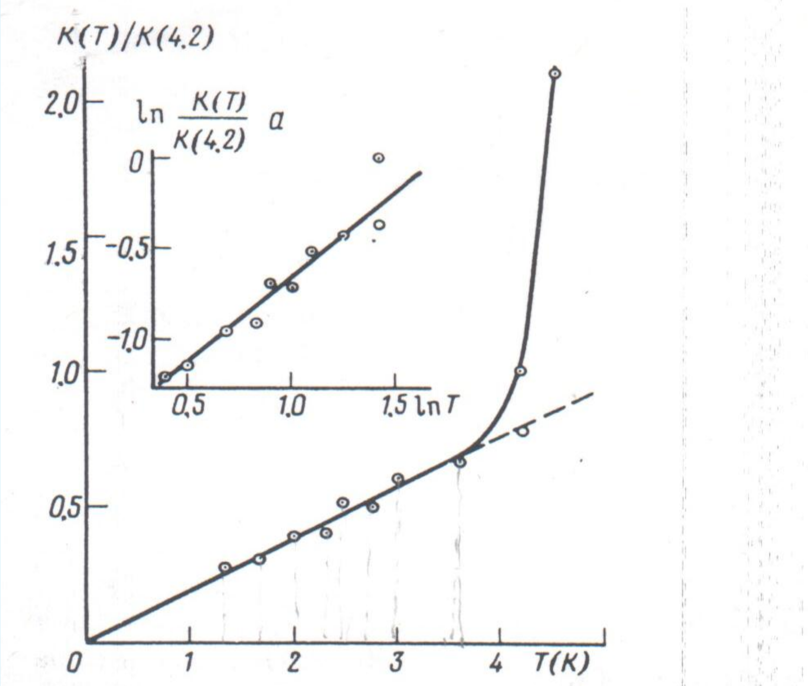


FIG. 2. $K(T)$ for H atoms in solid H_2 for 1.35 K < T < 4.2 K.

For 1.3<T<4.2 K

K_H = AT, A = (2±1) 10^{-24} $cm^3 s^{-1} K^{-1}$

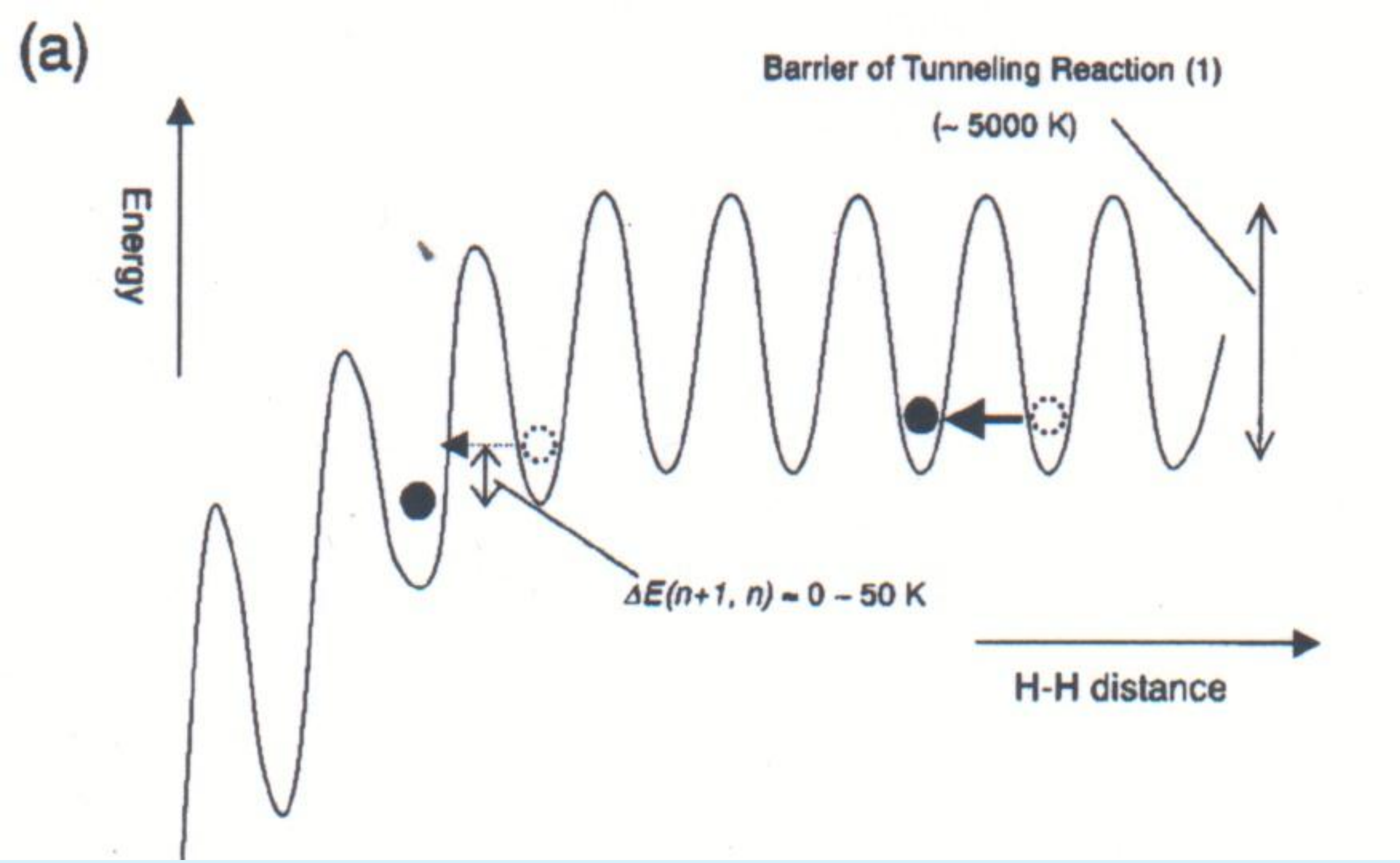
$$D_{rec} \approx 10^{-17}\,\mathrm{cm}^2/s$$

A.V Ivliev *et al.* JETP Lett. 36, 472-475 (1982) (Moscow, Russia)

Recombination of H atoms in solid H_2

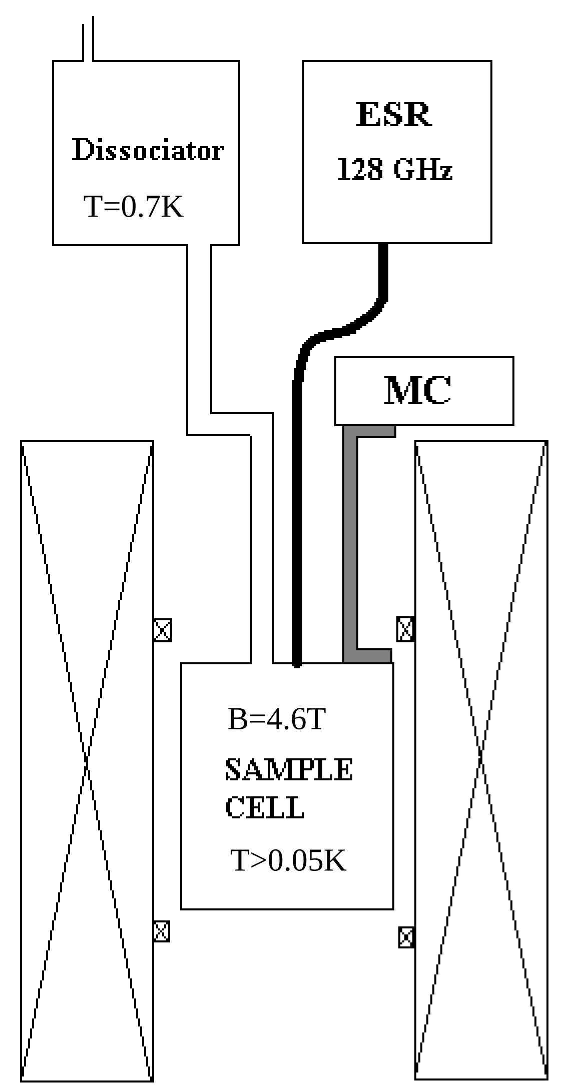
$H+H2 \rightarrow H_2+H$, $H+H \rightarrow H_2$

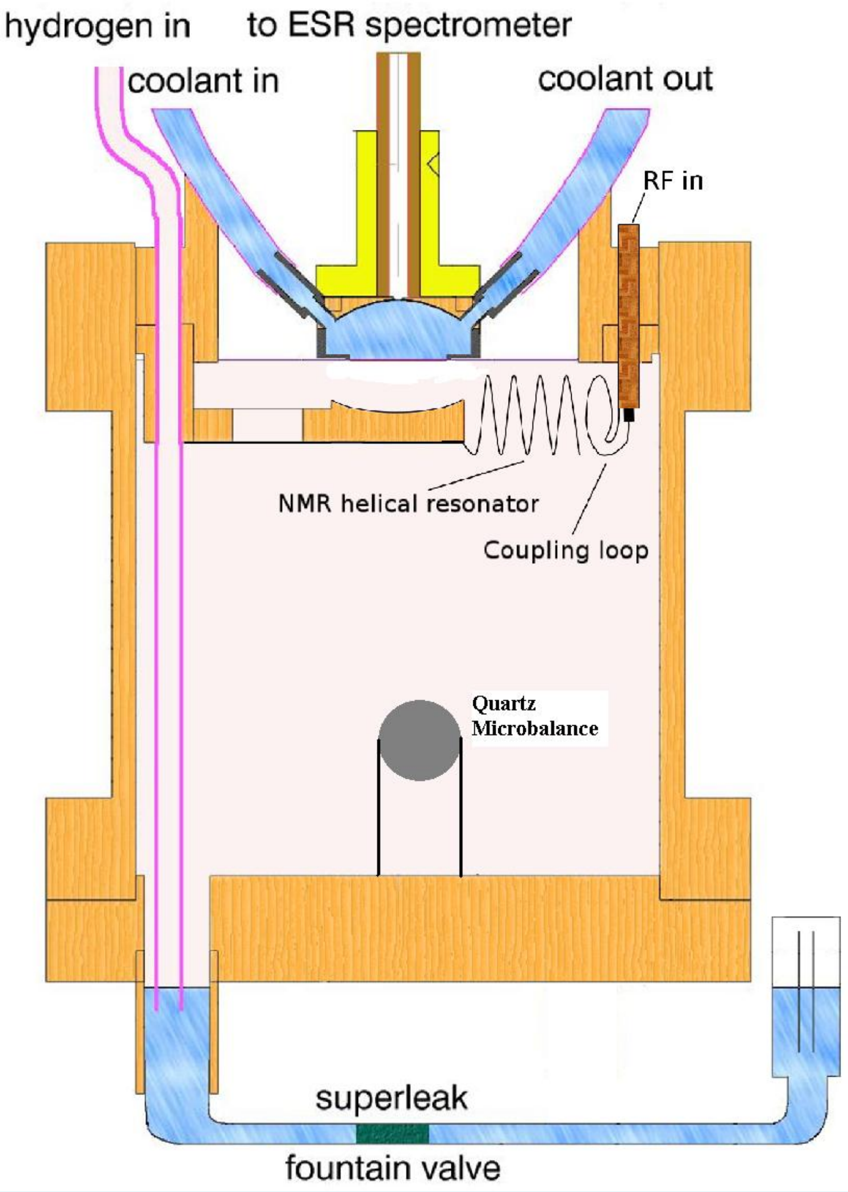
Kumada and Miyazaki
Journal of Chem. Phys.,116, 1109 (2002)



Schematic mechanism for the recombination of H atoms in solid H_2. Potential energy against H-H distance

Experimental setup

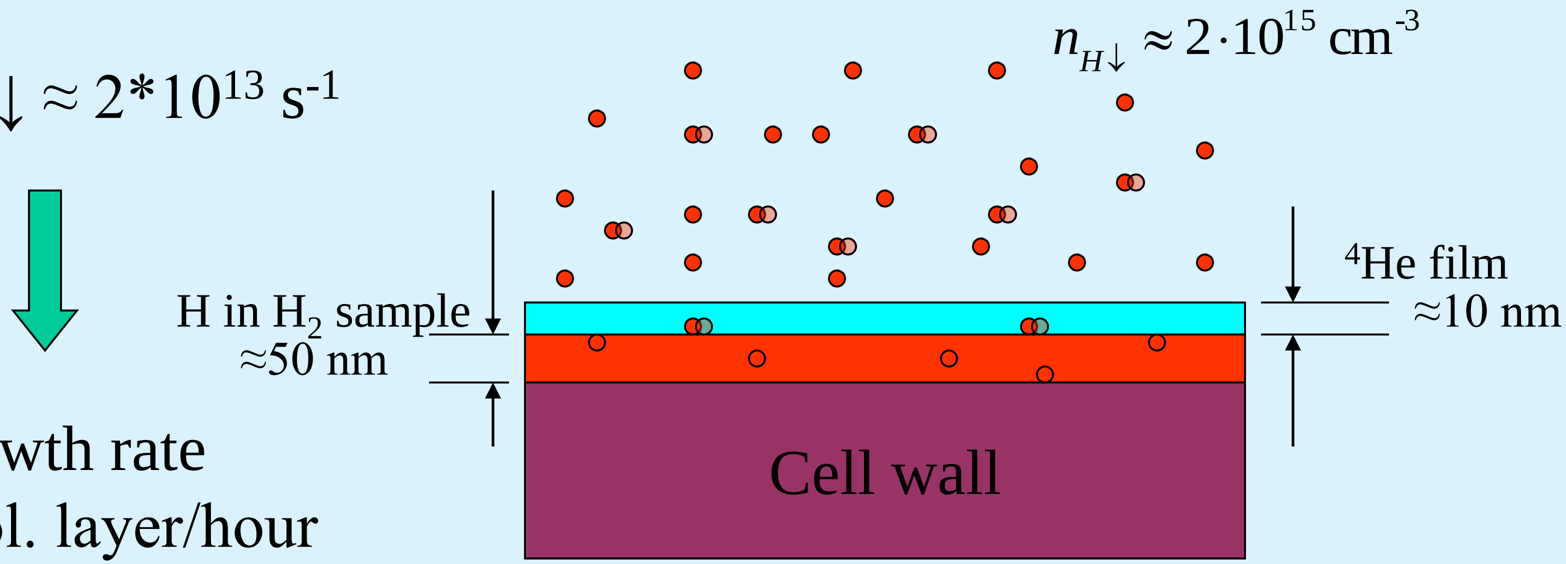




Preparation of H in H_2 sample

flux of H↓ ≈ $2*10^{13}$ s^{-1}

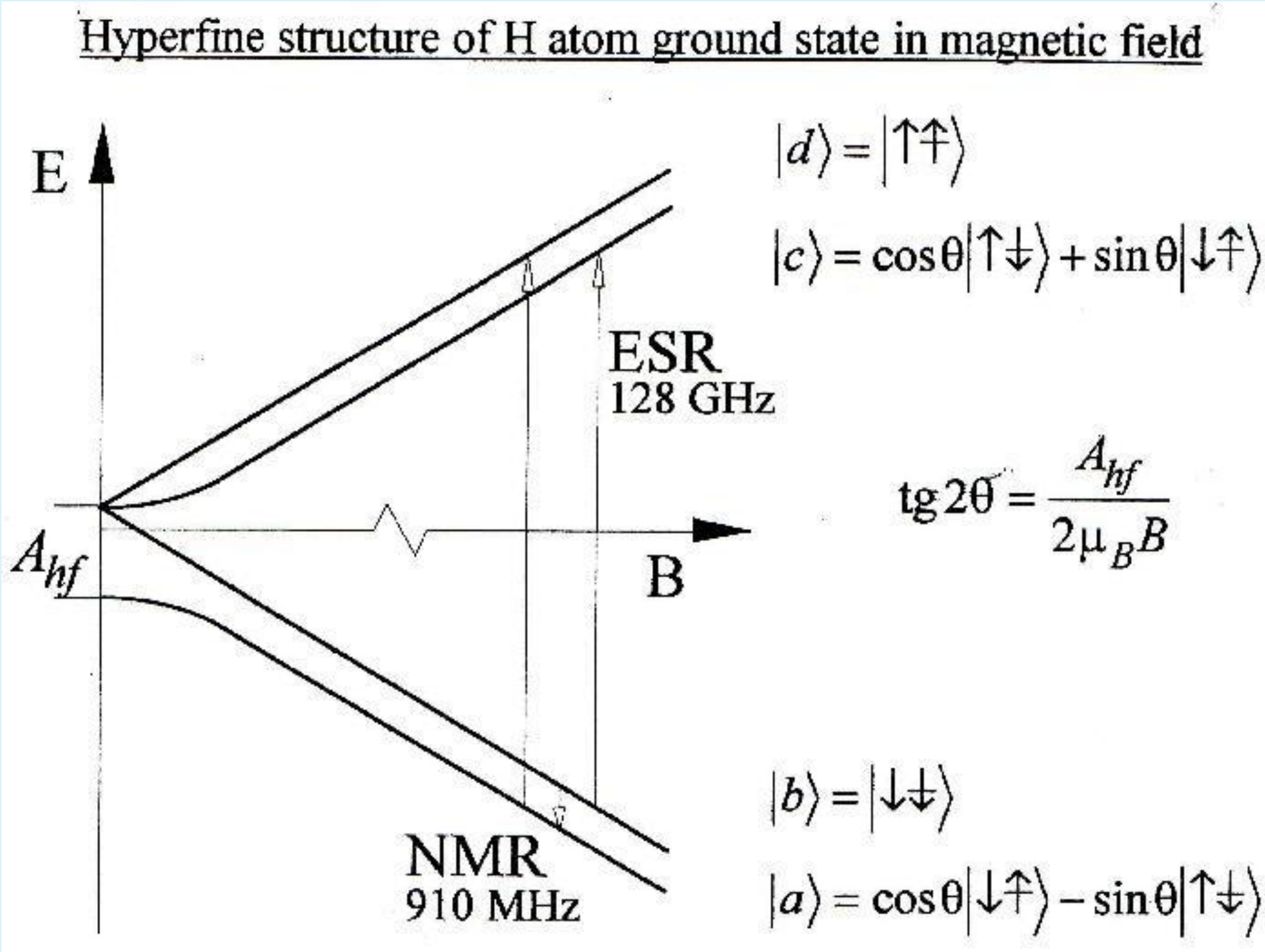
Film growth rate
≈ 0.5 mol. layer/hour



After one week of coating we get
50 nm thick H_2 film
with 50 ppm of H, or $n_H \approx 10^{18}$ cm^{-3}

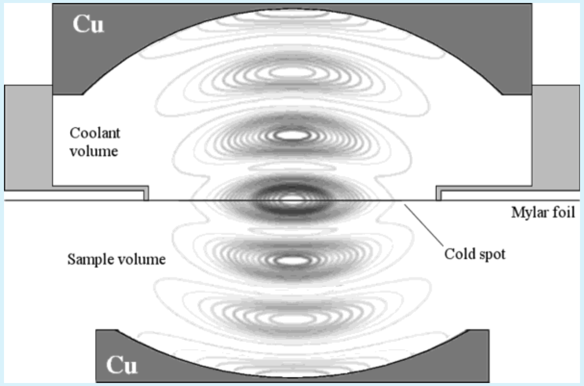
Optimal coating temperature ≈ 300 mK

Sample is stable for weeks of observation

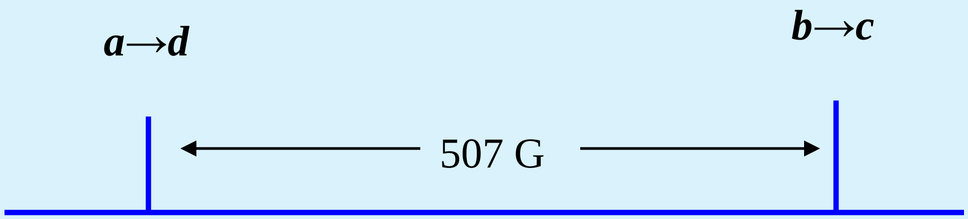


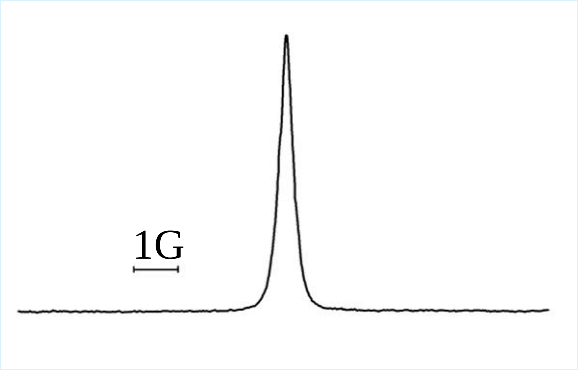
$\boldsymbol{a} + \boldsymbol{b} \rightarrow$ orho-H_2, I=1 $\boldsymbol{a} + \boldsymbol{a} \rightarrow$ para-H_2, I=0

H↓ ESR spectra

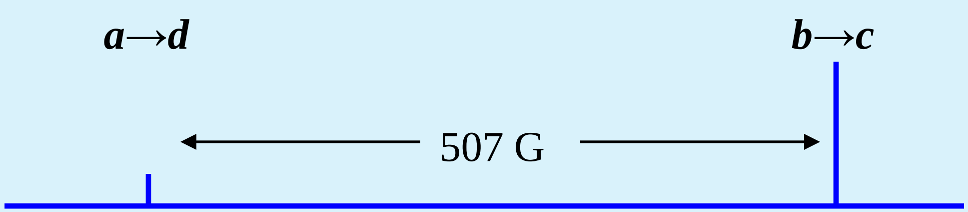


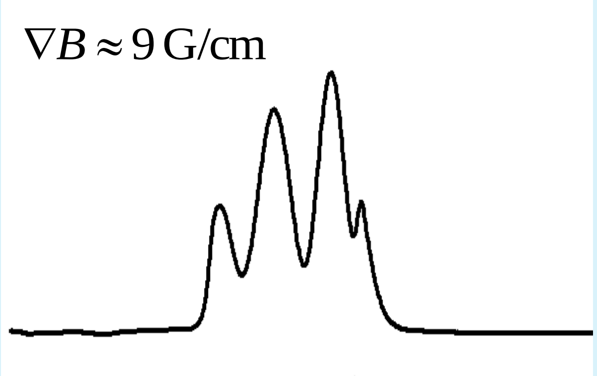
during coating:





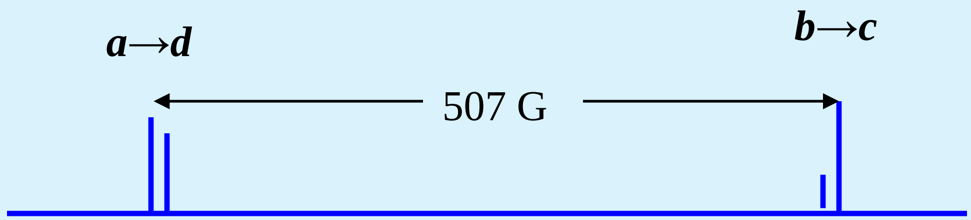
Switching off the dissociator,
getting doubly polarized sample:

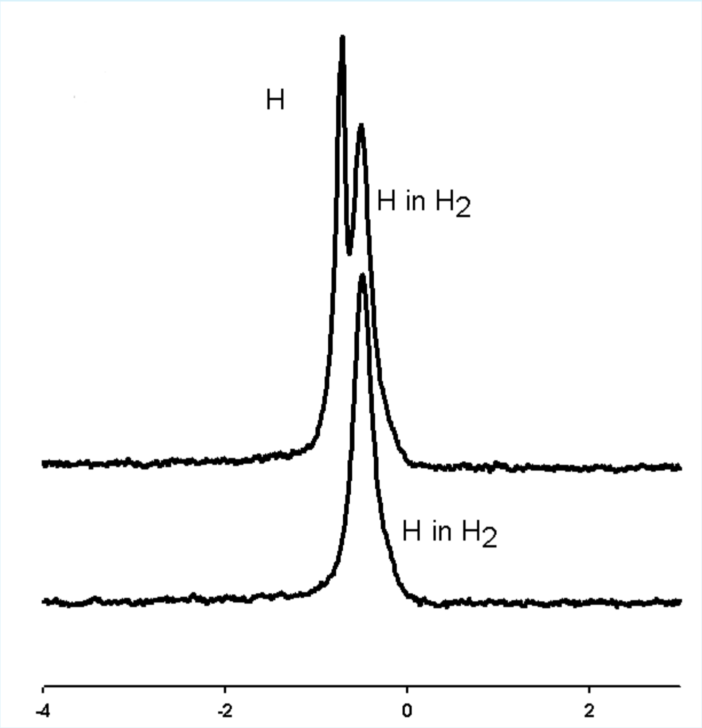




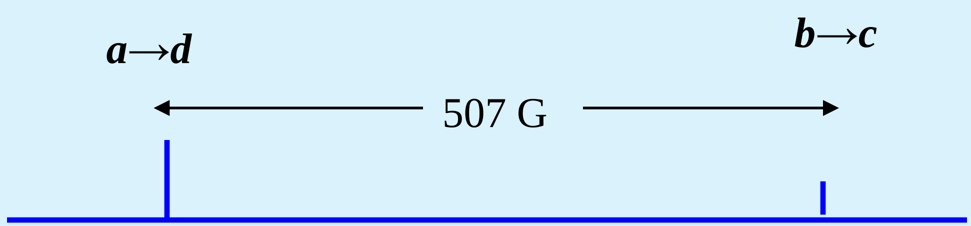
ESR spectra with H in H_2

H gas and H in H_2

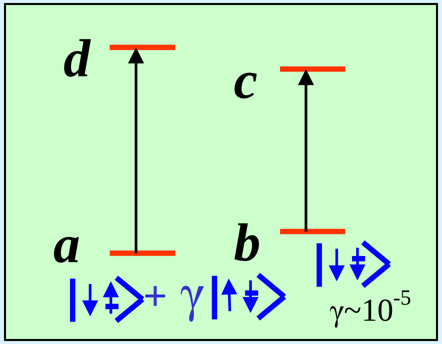


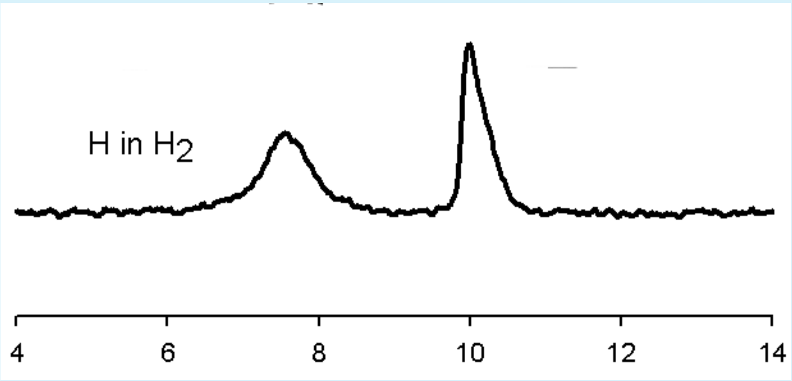


H in H_2 only

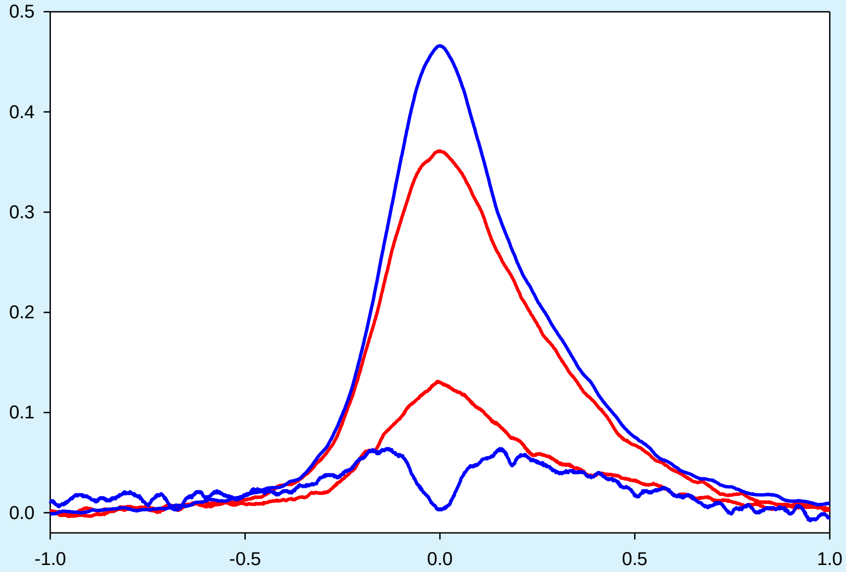


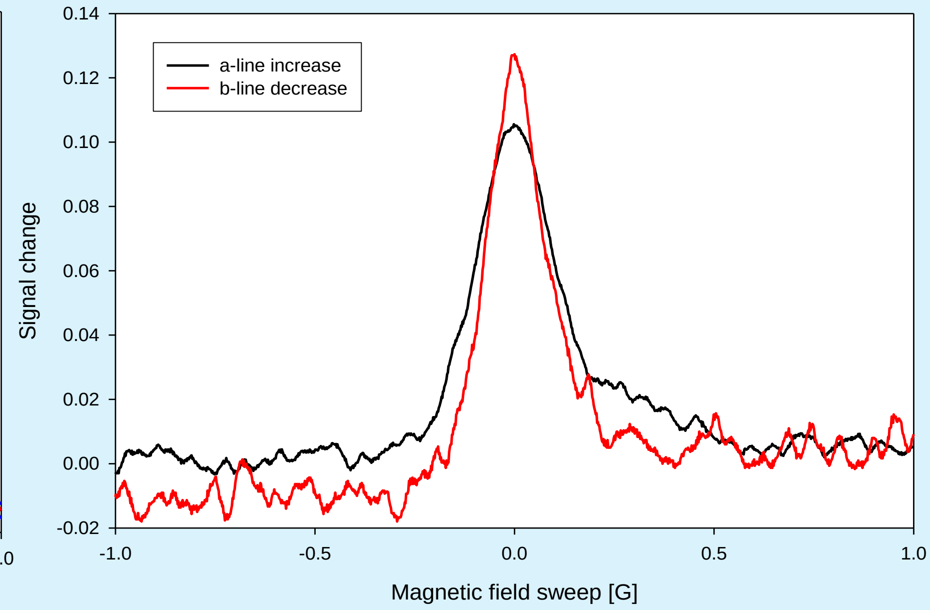
in a magnetic field gradient:





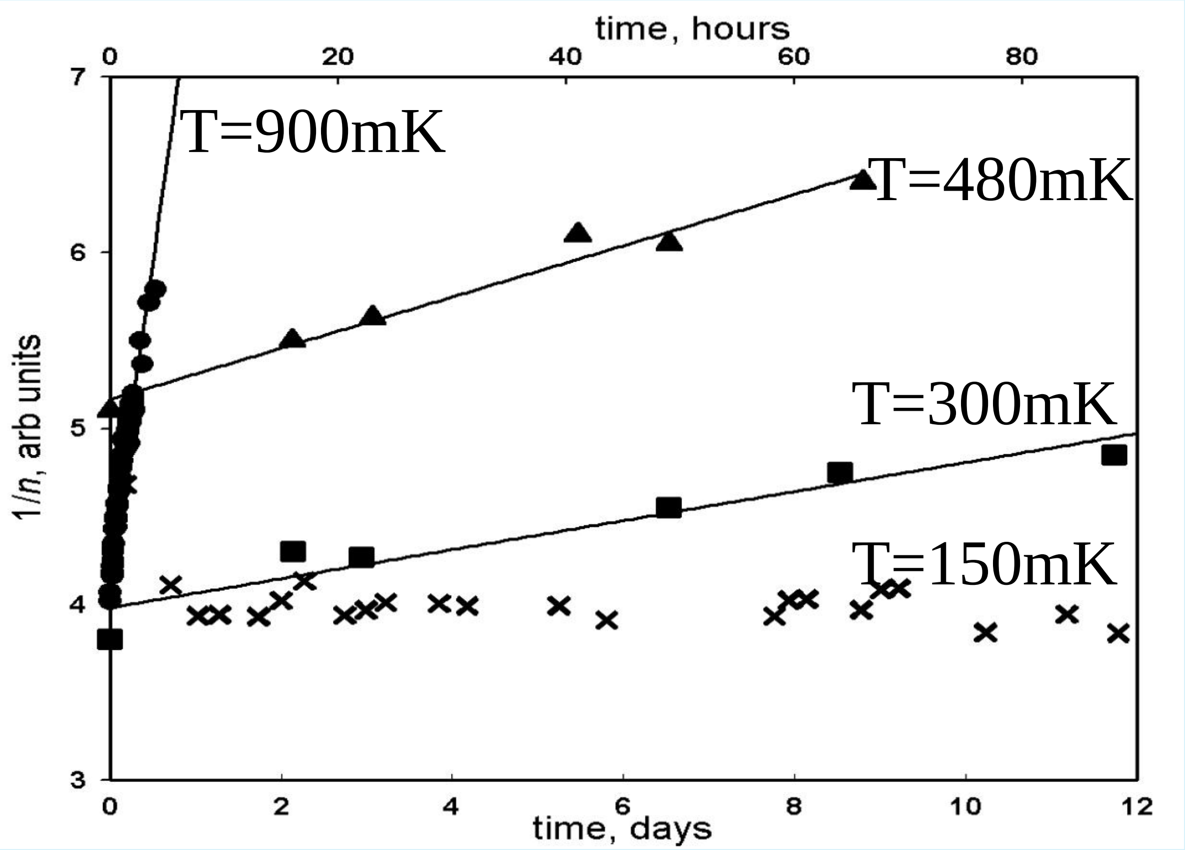
Burning the hole in ESR lines





$$D_{sp} \approx \frac{l^2}{t} \leq 10^{-8} \frac{\text{cm}^2}{s}$$

H atoms recombination at T< 1 K



$$[H] = 10^{18}\ cm^{-3}$$

$$\frac{dn}{dt} = -K_{rec}n^2$$

$$\frac{K_{rec}(850)}{K_{rec}(480)} \approx 20$$

Relaxation of NMR transition

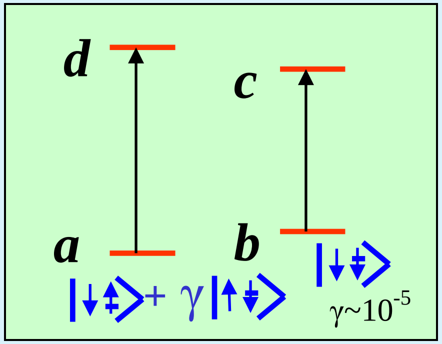
T=150mK

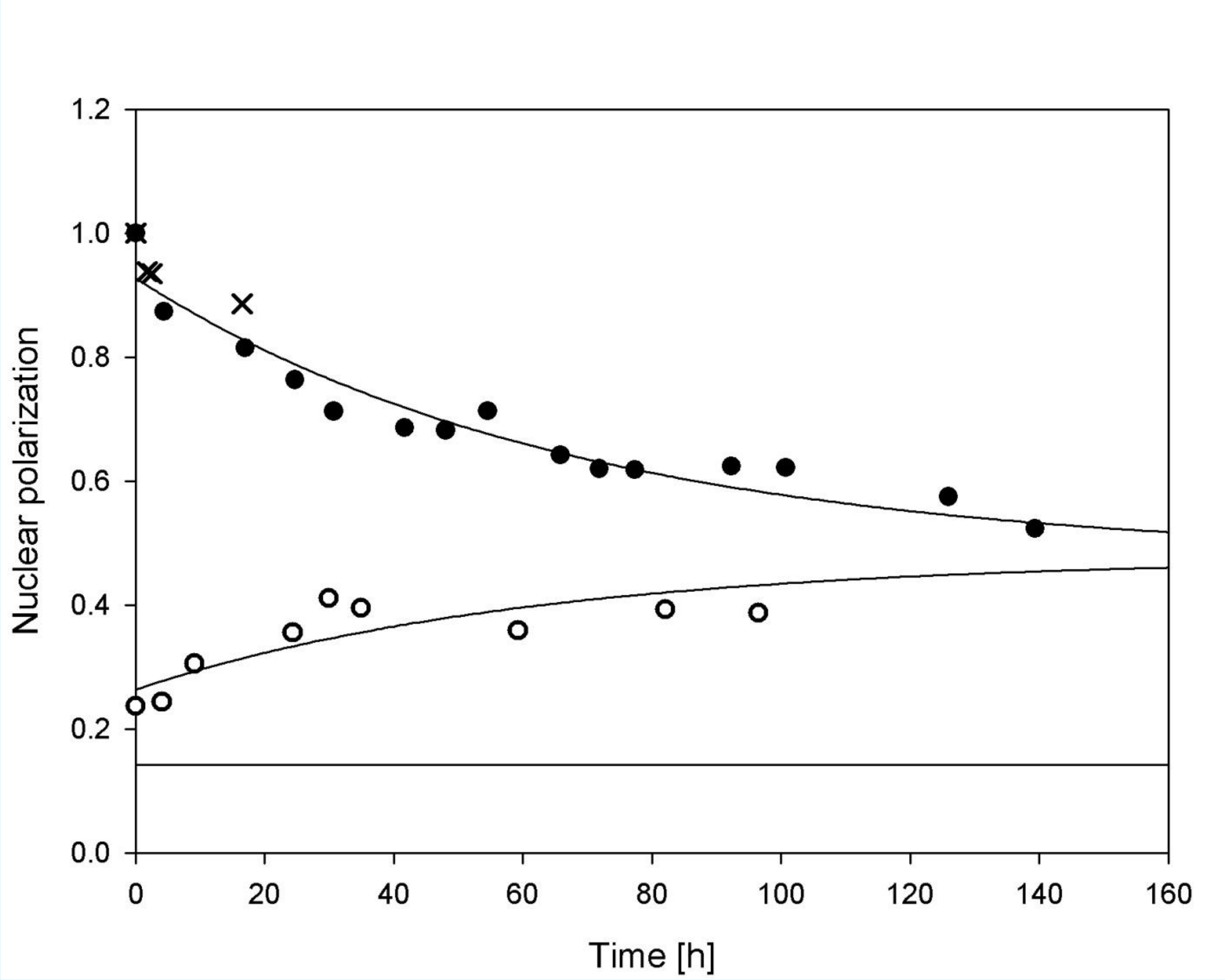
T_{ba}~ 60 h

$$\Delta E_{ab} \approx 43\,\text{mK}$$

$$\frac{n_a}{n_b} = e^{\frac{43}{150}} \approx 1.33$$

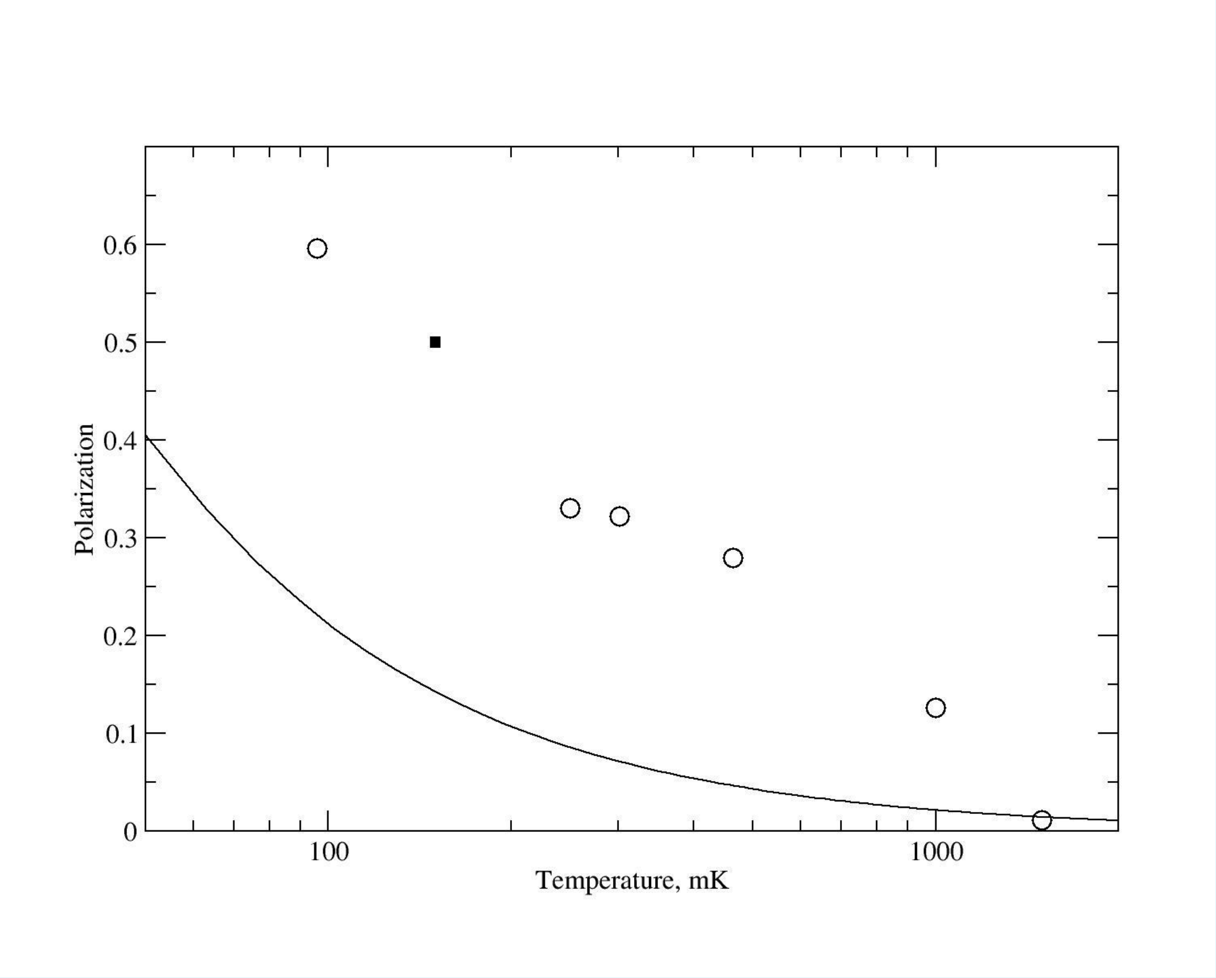
$$\left(\frac{n_a}{n_b}\right)_\infty = 3$$





Non- Boltzmann populations ratio at steady state

Steady state polarization of H atoms in molecular hydrogen films



○–recent Cornell data, ■–data point from Ahokas *et al.* PRL **97** 095301 (2006), Boltzmann distribution - solid curve.

Conclusions

- **I. Im-He Condensates – Observed:**
- **A. Very high Concentrations of Atomic Radicals**
- **B. Tunneling Exchange Reactions studied for H isotopes including influence of substrates**
- **C. Spin pair radicals in N-N_2 samples.**

- **II. H in H_2 films observed:**
- **A. Large departure of Populations of two lowest hf states from Boltzmann Distribution**
- **(substrate dependence)**
- **B. Overhauser Effect with rapid relaxation through forbidden Transition**
- **C. Very Long a-b relaxation time <u>but</u> impossible to fully saturate.**

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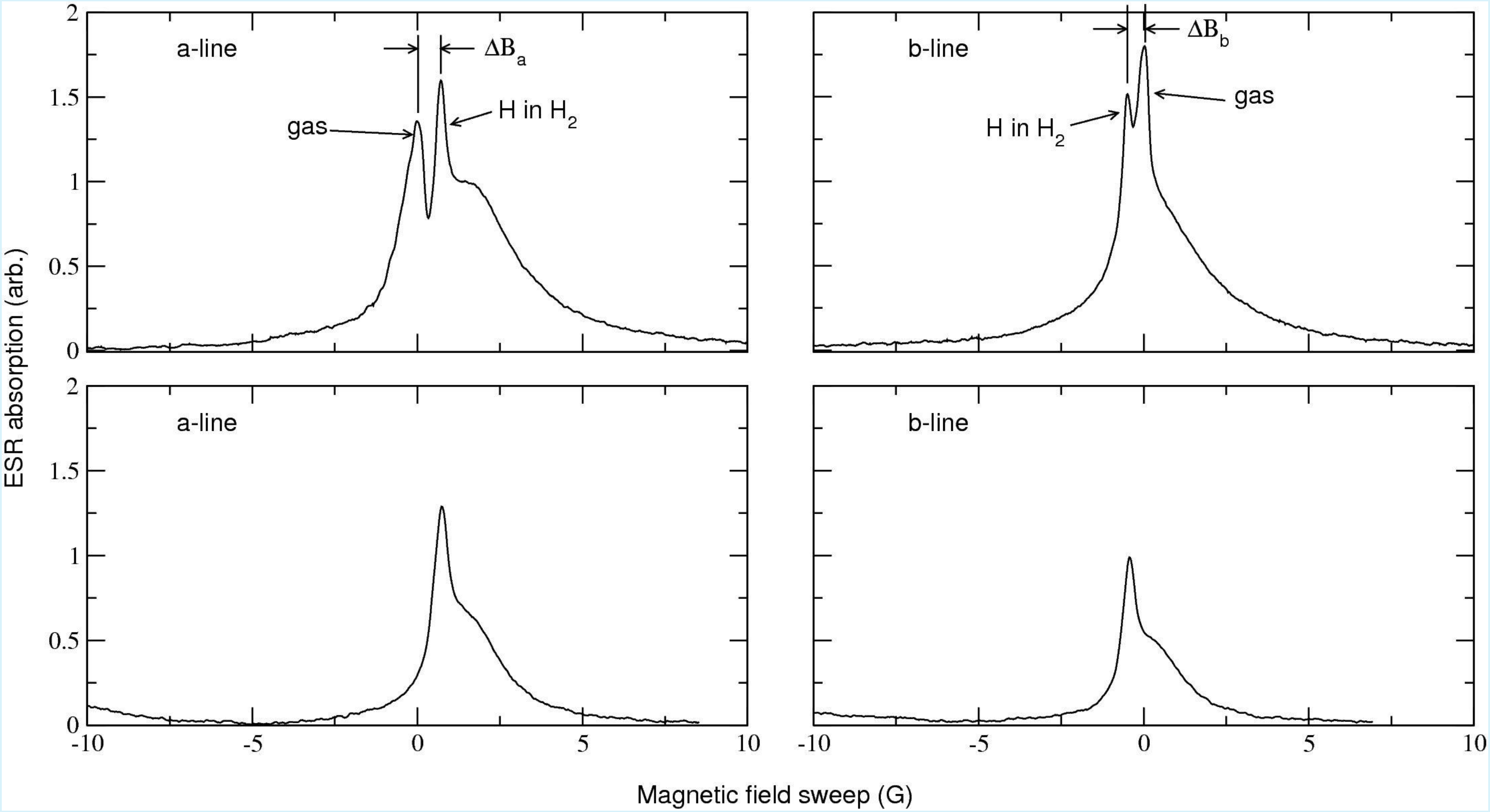
ESR spectra of H atoms in solid H_2 and gas phase



Steady state polarization of H atoms in molecular hydrogen films