X-band ESR study of radicals and their spin relaxation in solid hydrogens

Japan Atomic Energy Agency (JAEA)
(old name: Japan Atomic Energy Research Institute(JAERI))
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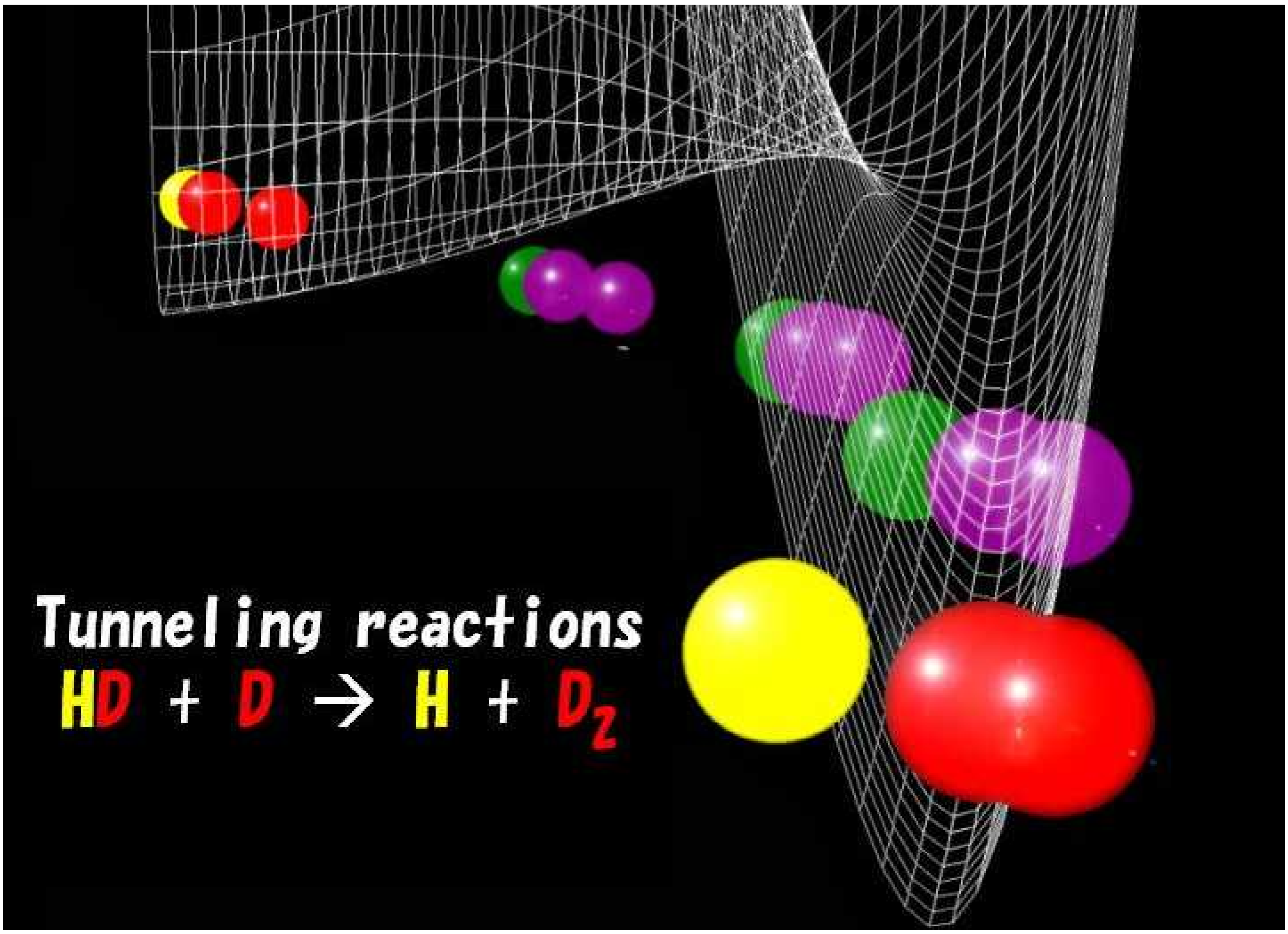
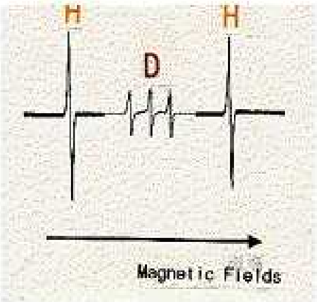
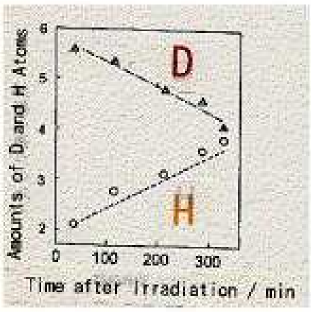
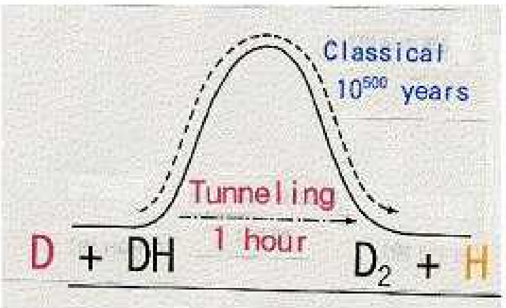


ESR study in γ-ray irradiated solid HD







Tunneling reactions
in solid hydrogen

↓

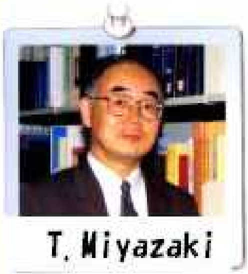
Local environment
Energy dissipation

↓

ESR spectroscopy
Spin-relaxation

Nagoya and JAEA (JAERI) — Russian group

1980's



T. Miyazaki

Japan-Soviet joint seminars

I. I. Lukashevich
V. Shevtsov
E. B. Gordon
Y. Kagan et. al.

1995

T. Kumada (Me)

1999 V. Shevtsov

2002 E. B. Gordon

Closed on 1990's

2003

2005

Now, I'm the best person who covers these studies!

NUCLEAR INSTRUMENTS AND METHODS 11[illegible] (1974) 477-485; © NORTH-HOLLAND PUBLISHING CO.

DNP aided by H

$P_H = 3\ \%$

DYNAMIC POLARIZATION OF PROTONS AND DEUTERONS IN SOLID DEUTERIUM HYDRIDE*

JOHNDALE C. SOLEM

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

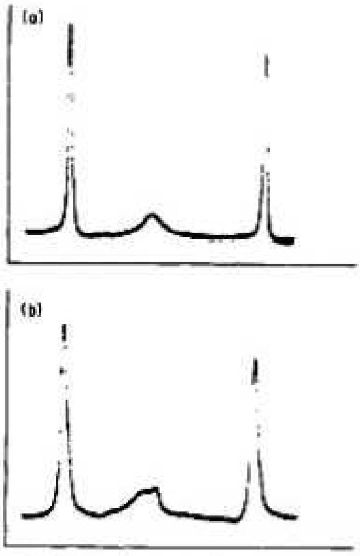


Fig. 3. EPR spectrum of an irradiated solid HD sample prepared from gas containing 3×10^{-4} O_2 impurity. (a) 4.2 K, (b) 1.2 K. The two narrow resonances are ascribed to H-atoms trapped in the HD lattice and the broad central resonance is ascribed to the radical O_2D. The centers of the H-atom resonances are separated by 504 G.

Relaxation times for two samples

Material	T_1 at 4.2 K		T_1 at 1.2 K	
	Low field resonance	High field resonance	Low field resonance	High field resonance
Purified HD	95 ms	95 ms	–	–
Purified HD and 3×10^{-3} O_2	0.14 ms	0.14 ms	0.25 ms	0.29 ms

Optimize parameters!
- H-atom concentration
- Add O_2 for relaxation

Index

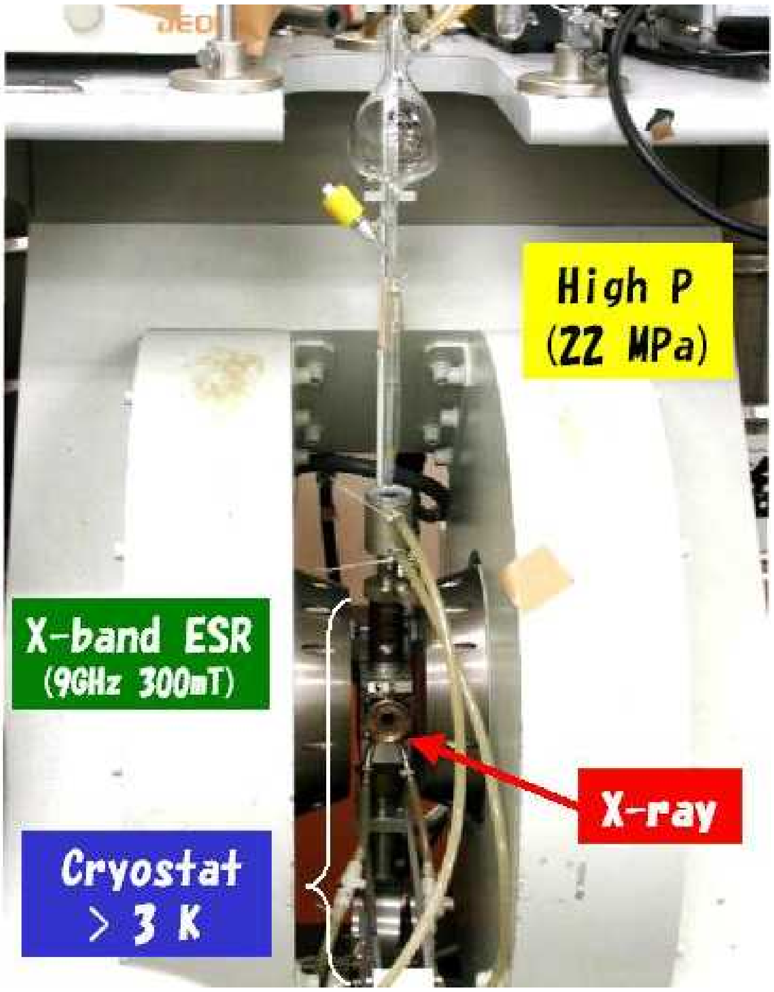
1. Experimental Setup
2. Trapping sites
3. Linewidth
4. Radiolysis
5. Spin relaxation

Experiments at JAEA (JAERI)

mainly by Me

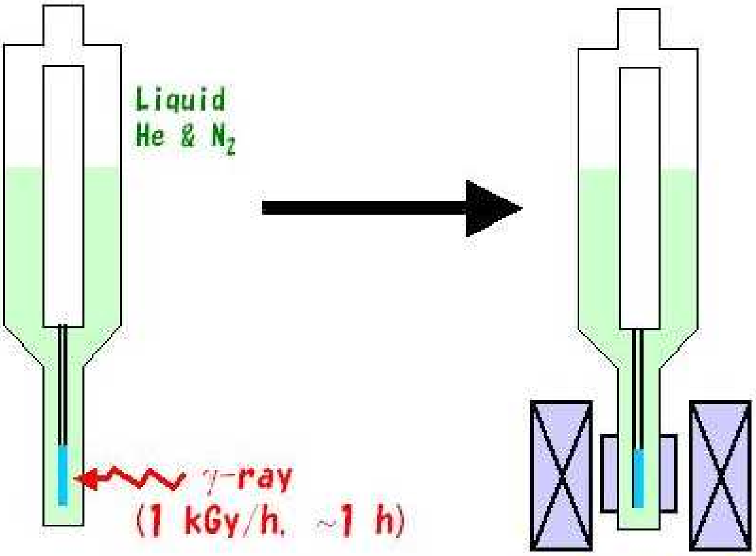
- $n\text{-}H_2$
- HD ($n\text{-}H_2$: 3%, $n\text{-}D_2$: 2%)
- $n\text{-}D_2$
- $p\text{-}H_2$ ($o\text{-}H_2$: 0.2%)

$H_2 \xrightarrow{\text{x-ray}} H + H$ (0.1 ppm)



Experiments at Nagoya

(Miyazaki's lab.)



$H_2 \rightsquigarrow H + H$ (3ppm)

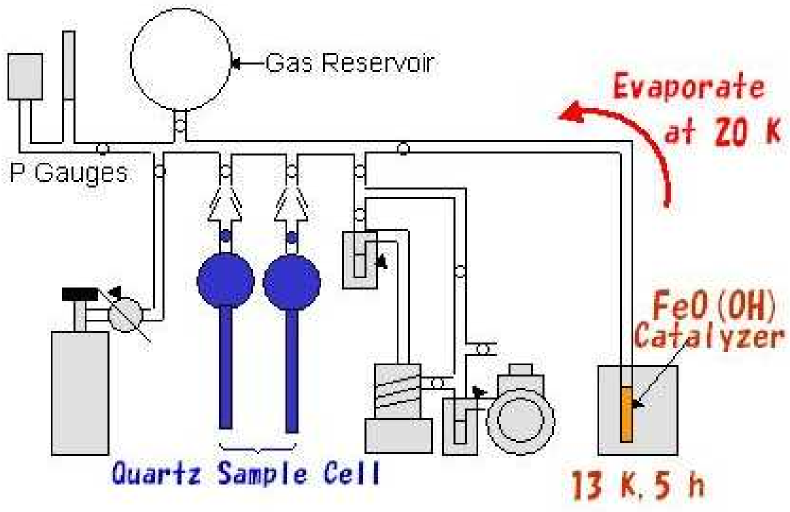
X-band ESR

1.9 - 4.2 K

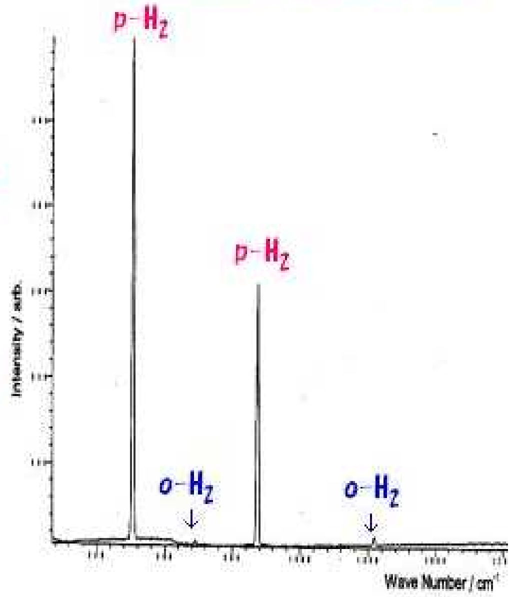
Quadruple-walled
Quartz Dewer
(5000 Euro)

Preparation of para-H_2

- Glass vacuum line



- Raman Spectrum



p-H_2 gas (99.8 %) is produced

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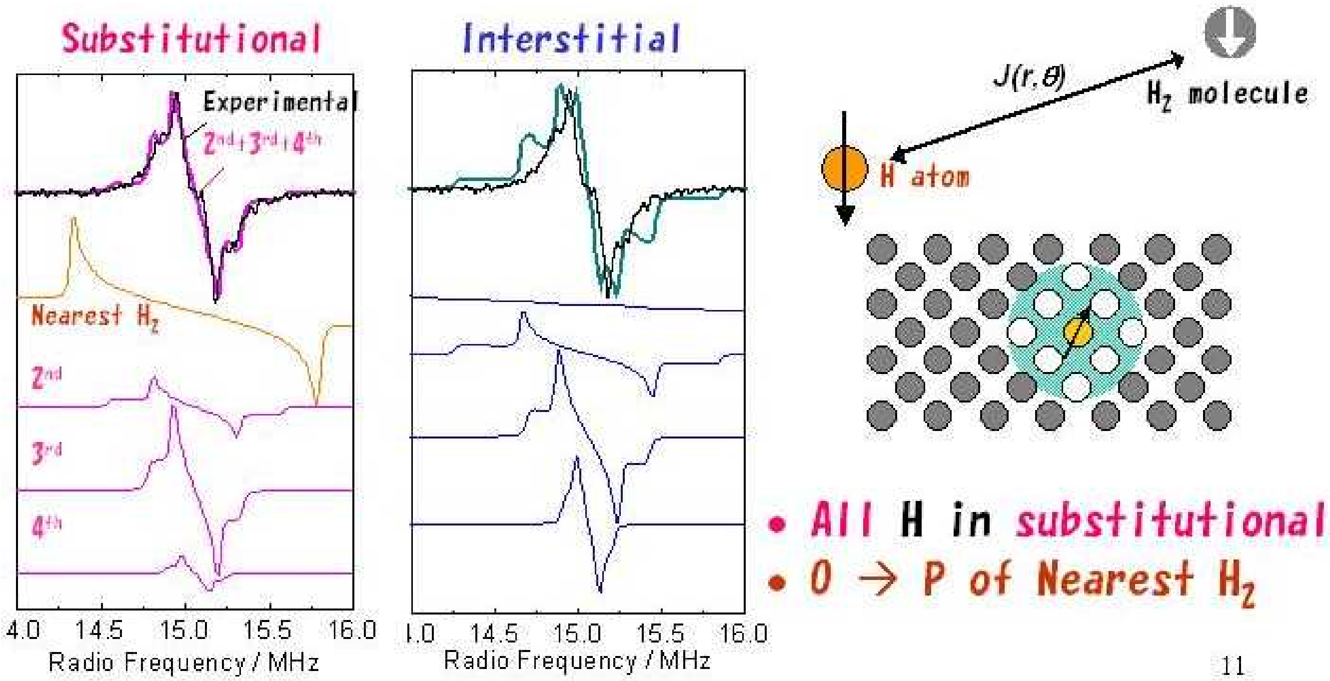
1. Experimental Setup (p-H_2, n-H_2, HD, D_2)
2. Trapping sites
3. Linewidth
4. Radiolysis
5. Spin relaxation

ENDOR study of H atoms in solid H_2

(Electron-Nuclear spin DOuble Resonance)

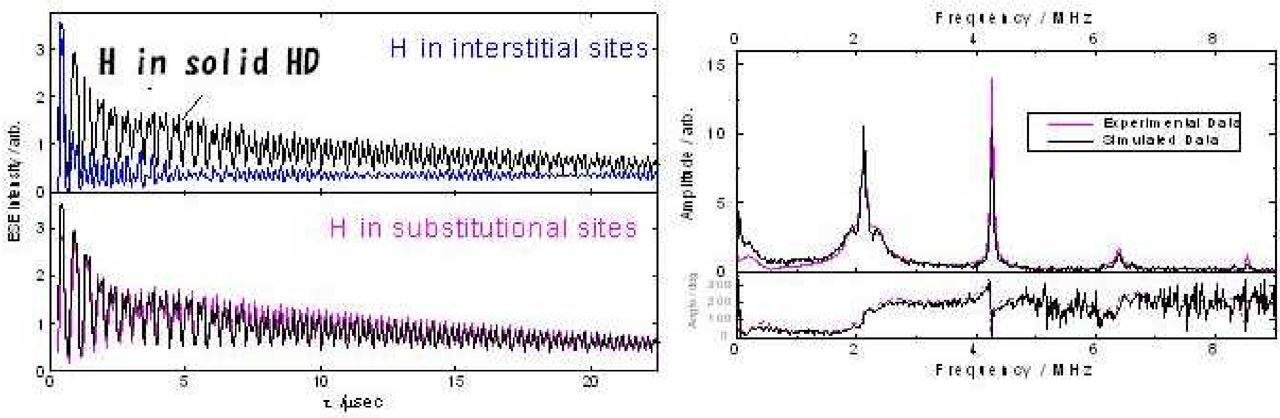
T. Kumada, et al., Chem. Phys. Lett. **288**, 755-759 (1998)



- All H in substitutional
- O → P of Nearest H_2

Electron Spin Echo of H in HD and D_2

T. Kumada, et al., J. Chem. Phys. 111, 10974-10978 (1999).

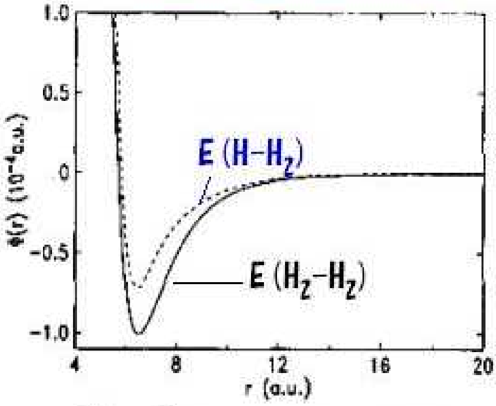


All H and D atoms are also in substitutional sites of solid HD and D_2

Monte-Carlo study of H atoms in solid H_2

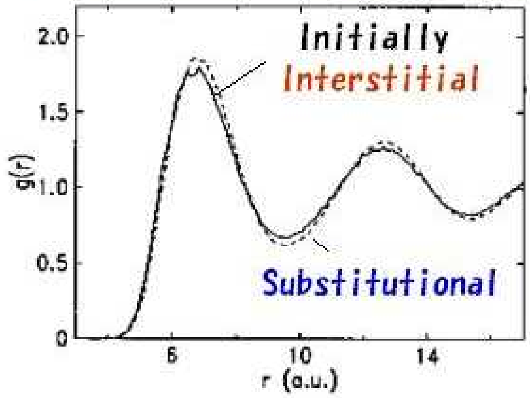
D. Li and V. Voth, JCP **100**, 1785 (1994)

•Pair potential



H atoms are more stable in substitutional sites

•Distribution H_2 around H



Interstitial→Substitutional

(Self-annealing effect)

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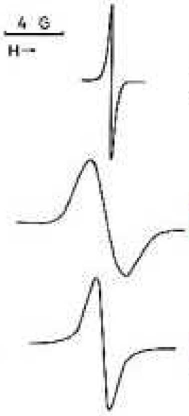
1. Experimental Setup (p-H_2, n-H_2, HD, D_2)
2. Trapping sites — All in substitutional
3. Linewidth
4. Radiolysis
5. Spin relaxation

- **ESR linewidth**
  - Trapping sites are homogeneous
  - No anisotropy in H atom
  - Very slow spin-lattice relaxation
  - Superhyperfine interaction → Yes!



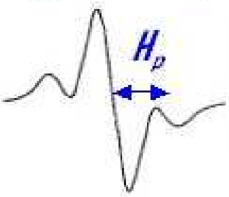
H in p-H_2 < 0.006 mT

H and D in HD 0.27 mT ⇒ Should be ~0.27 mT at 2.5 T

H and D in D_2 0.12 mT

∧∧

- **ESR spin flip-flop satellite line**



H_p=0.5 mT, H_d=0.08 mT at X-band ⇒ H_p=4.1 mT, H_d=0.7 mT at 2.5 T

Narrow enough for Solid Effect

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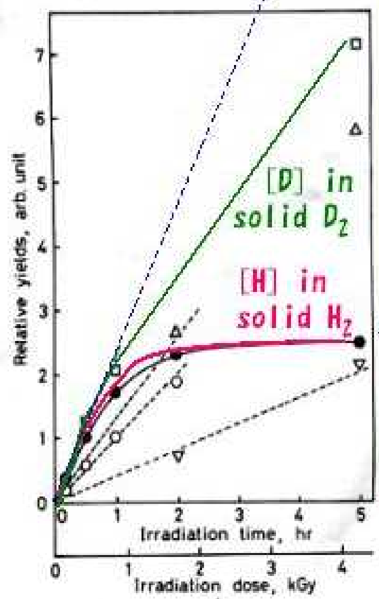
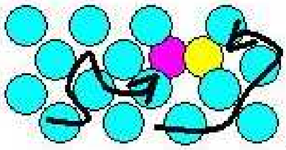
1. Experimental Setup (p-H_2, n-H_2, HD, D_2)
2. Trapping sites — All in substitutional
3. Linewidth — Narrow enough for Solid Effect
4. Radiolysis
5. Spin relaxation

Radiolysis of solid hydrogens

T. Miyazaki et al., Radiat. Phys. Chem. **36**, 501 (1990)



← 3 ppm



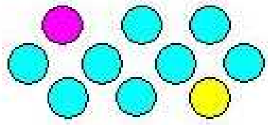
Bulk recombination

$HD : p\text{-}H_2 : o\text{-}H_2 : o\text{-}D_2 : p\text{-}D_2$

= 100 : 12 : 38 : 33 : 17

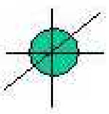
Enhance T_{1n}^{-1}

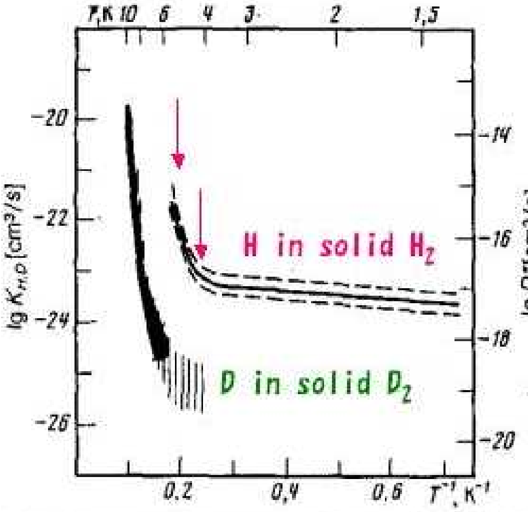
Spoil DNP



H(D) atoms remained

High yields of H ⟷ Less bulk recombination

J=1  Enhance T_1^{-1}	Ortho-H_2 $I = 1$ (75 %)		Para-D_2 $I = 1$ (33 %)
J=0 	Para-H_2 $I = 0$ (25 %)	HD $I_H = ½$, $I_D = 1$ (100 %)	Ortho-D_2 $I = 0, 2$ (66 %)



A. S. Iskovskikh et al., JETP **64**, 1085 (1986)

How about higher dose rate?

↓

Heating by γ-rays

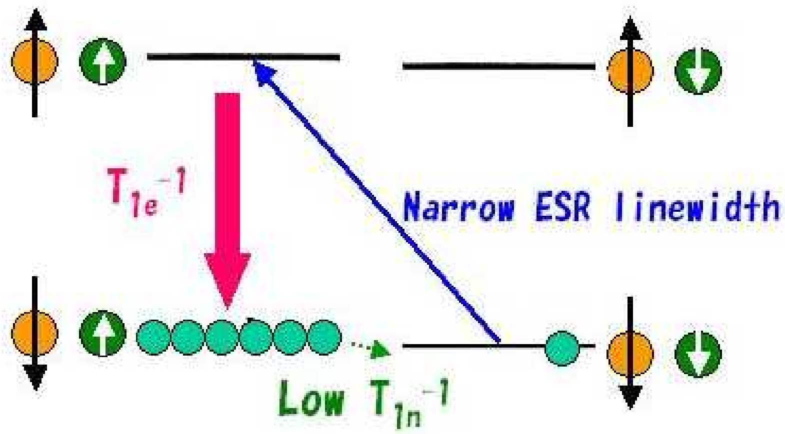
↓

Enhance Bulk recombination

- Nagoya: H in HD : 5 ppm
- Solem : H in HD : 100 ppm
- Collins: H in HD: 300 ppm with o-H_2 and p-D_2 at ~3 %

Index

1. Experimental Setup (p-H_2, n-H_2, HD, D_2)
2. Trapping sites — All in substitutional
3. Linewidth — Narrow enough for Solid Effect
4. Radiolysis — By-products o-H_2, p-D_2
5. Spin relaxation



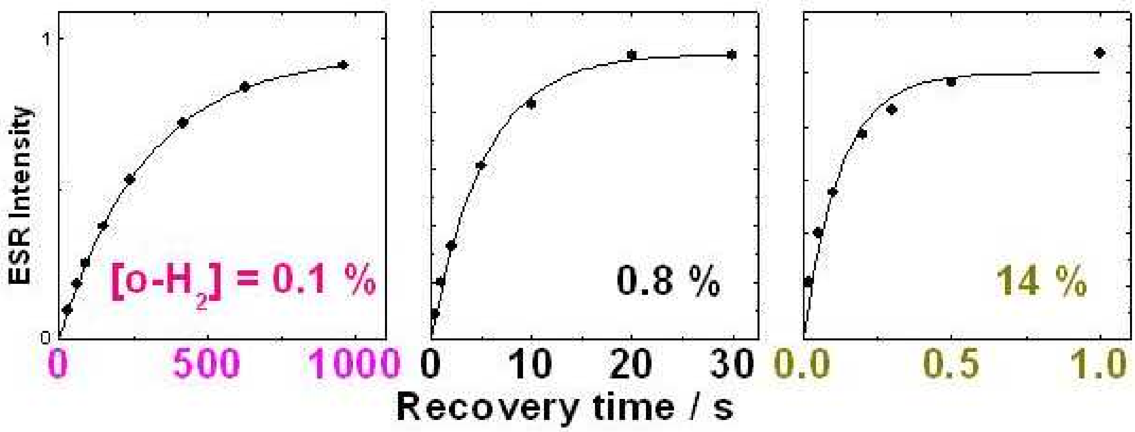
We need high T_{1e}^{-1} and low T_{1n}^{-1}

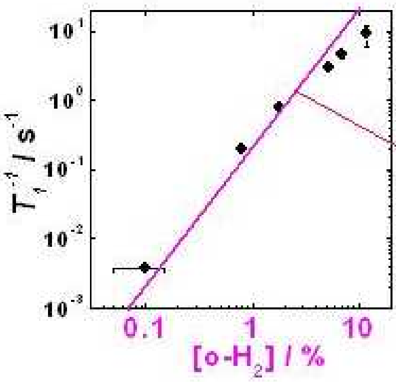
Lower T_{1n}^{-1} in highly purified HD

How about T_{1e}^{-1} in this case?

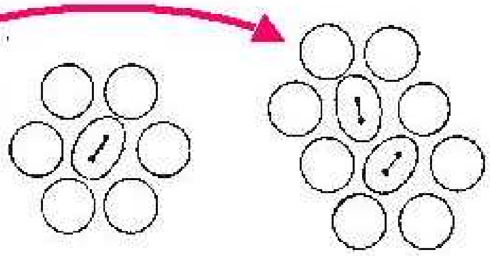
T_{1e} in solid p-H_2

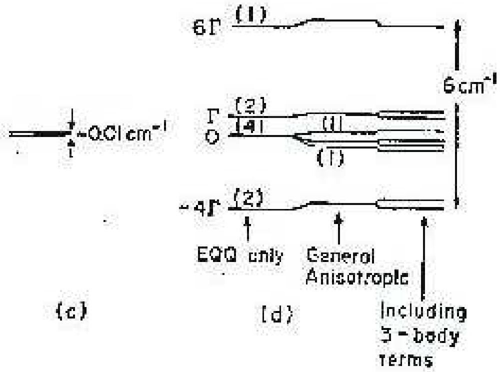
T. Kumada et al., JCP 116, 1109 (2002)

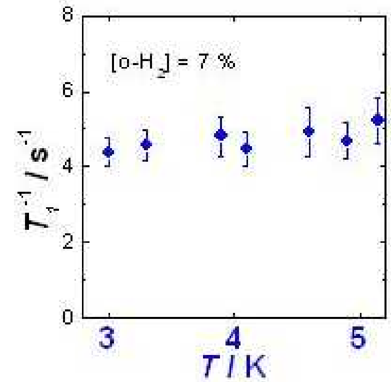




$T_{1e}^{-1} \propto [o\text{-}H_2]^2$



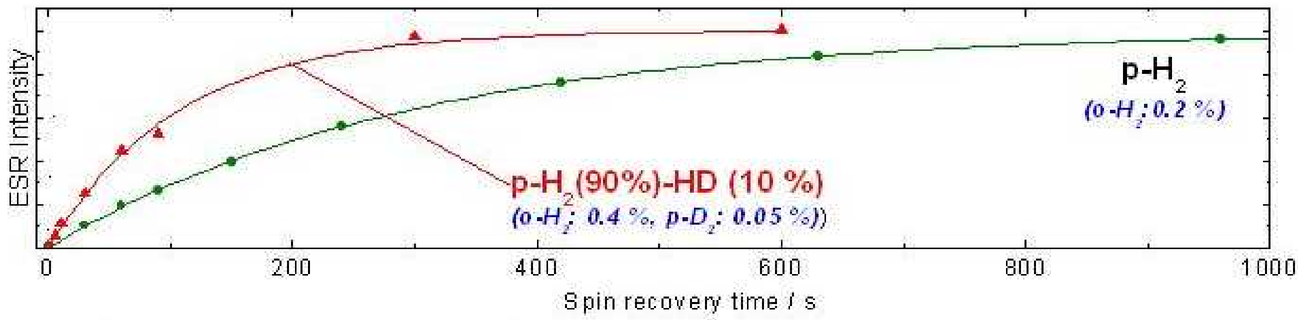


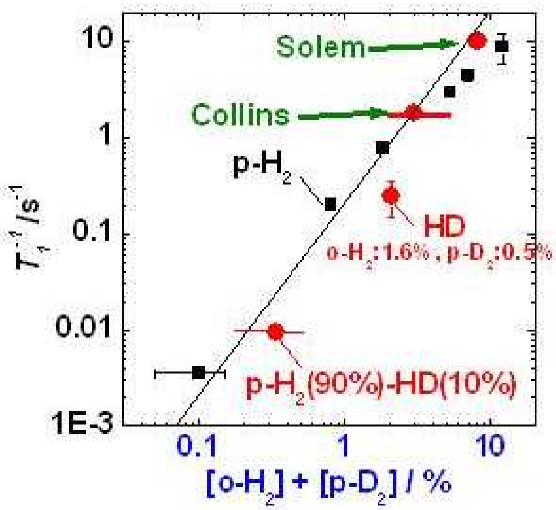


Independent of T

Zeeman energy (0.3 cm^{-1}) → q-q int. of o-H$_2$ pair (<6 cm^{-1})

T_{1e} in solid HD





T_{1e} depends only on [o-H$_2$]+[p-D$_2$]

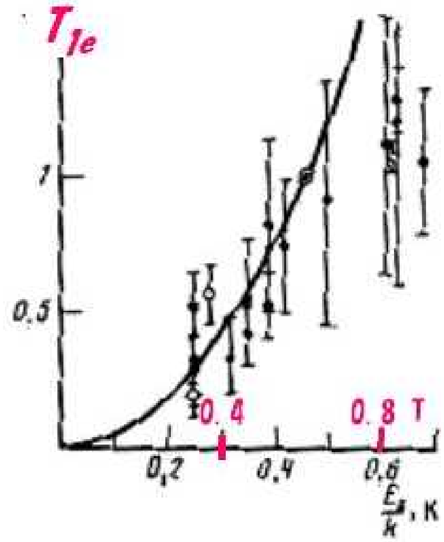
Whether p-H$_2$ or HD does not matter!

↓

T_{1e} → 10^3 s in highly purified HD

T_{1e} (H) at DNP condition

A. S. Iskovskikh et al., JETP **64**, 1085 (1986)

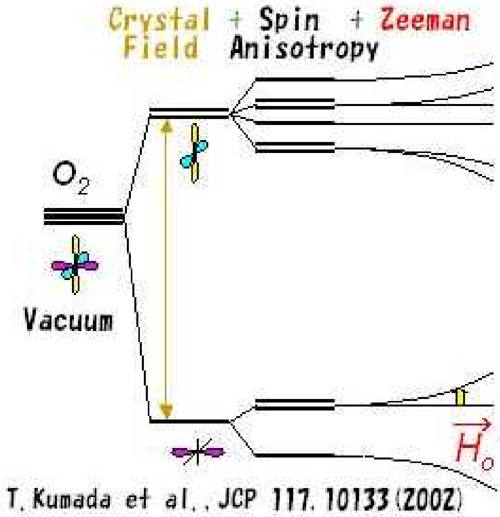


T_{1e} increases with H_0

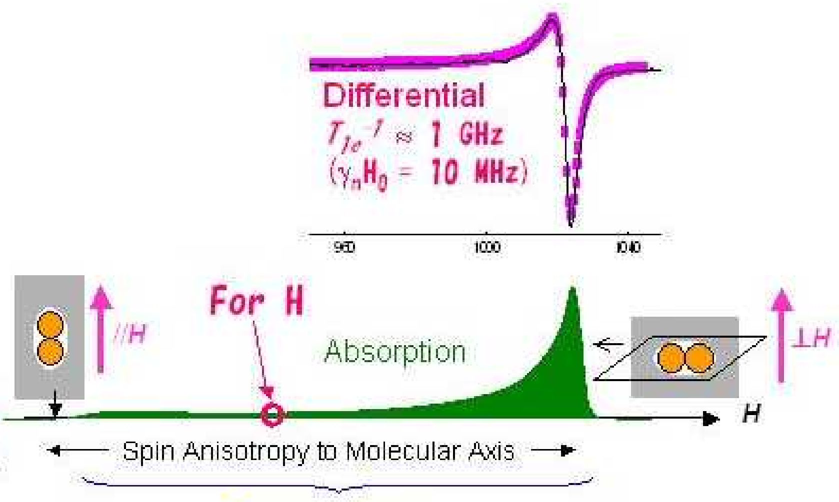
T_{1e} is independent of [H] (Not shown)

$T_{1e} \gg 10^3$ s at DNP condition

Solem added O_2, T_{1e}(H) = 100 ms → 0.1 ms



T. Kumada et al., JCP 117, 10133 (2002)



O_2 enhance both T_{1e}^{-1}(H) and T_{1n}^{-1} → Spoil DNP

Summary on DNP with H atom

1. Trapping sites — Excellent
2. Linewidth — Excellent
3. Radiolysis — By-product o-H_2 and p-D_2
4. Spin relaxation — $T_{1e} \gg 1000$ s in purified HD

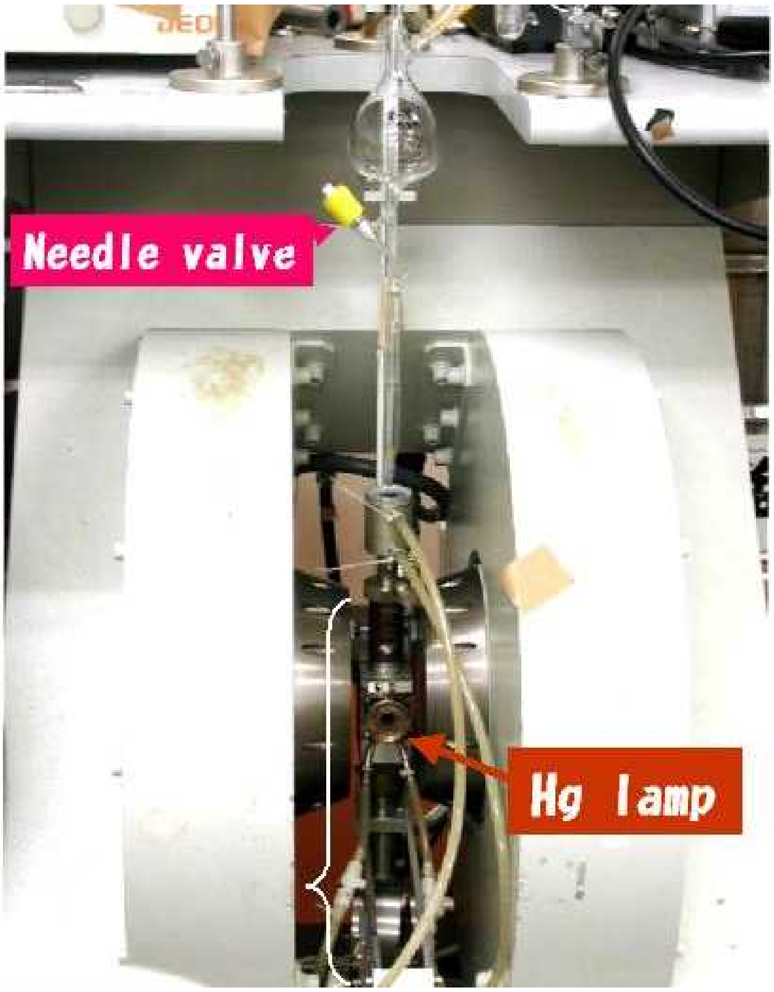
DNP in highly purified HD is impossible!

Only "poor" polarization with "poor" purity

How about CH_3 ?

Experiment

- **Sample**
  pH_2-CH_3I (0.06%)
- **Deposition rate**
  4 mmol / 1 h
- **UV illumination**
  Mercury lamp 10 min
  $CH_3I \rightarrow CH_3 + I$
- **CH_3 produced in p-H_2**
  ≈ 10 ppm (0.001 %)



1000 ppm isolated in solid p-H_2

M. E. Fajardo and S. Tam, JCP108, 4237 (1998)

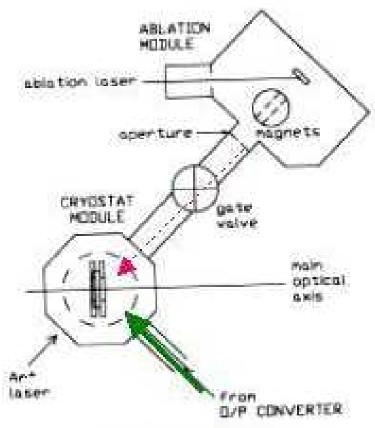
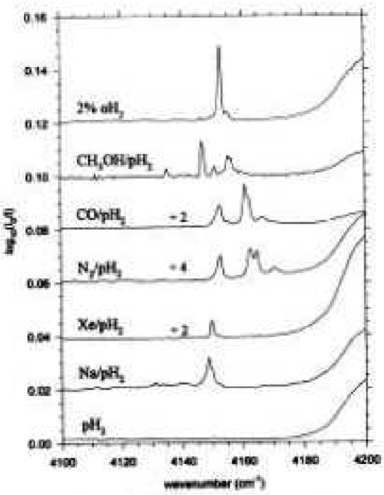


FIG. 1. Experimental diagram.

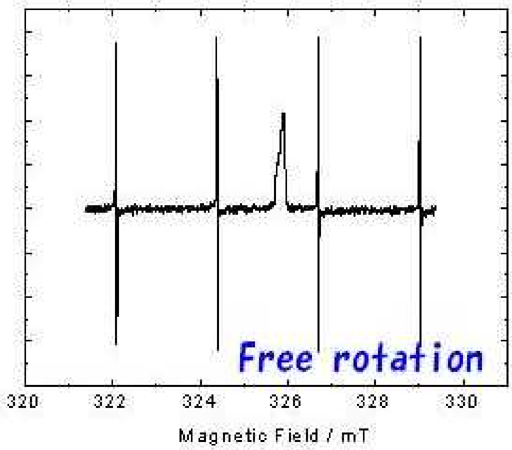


Deposition on cold substrate at 2 K for IR study

1. [guest] = 1000 ppm.
2. Millimeter thick.
3. Optically transparent.

Linewidth of CH_3 in solid HD

CH_3 in p-H_2 (ΔH = 0.02 mT)



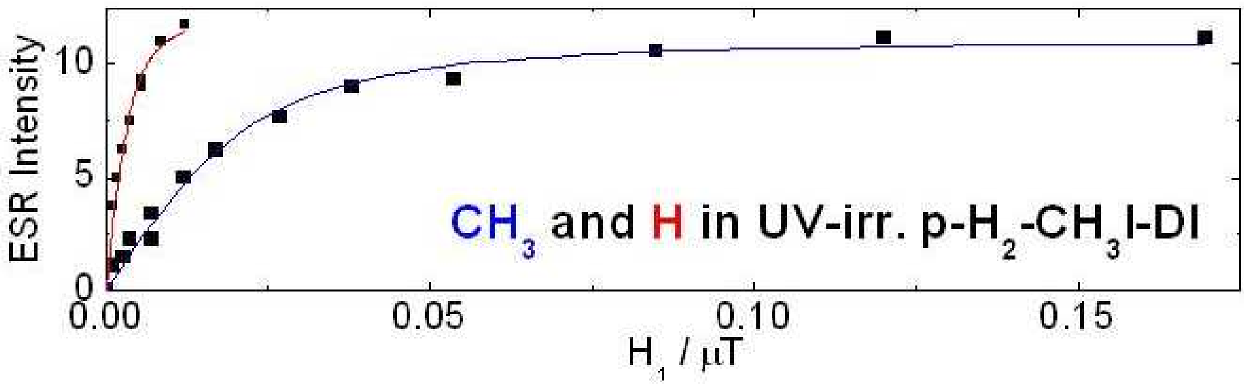
Linewidth (mT)

	H	CH_3 (CD_3)	
p-H_2	<0.006	0.02	
D_2	0.12	0.12	Superhyperfine
HD	0.27		Superhyperfine

Should be 0.27 mT in HD at 2.5 T

Narrow enough for solid effect !

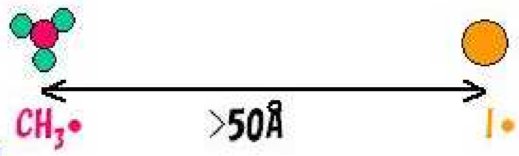
Microwave power saturation of CH_3 in solid p-H_2



0.2 ms < $T_{1e}(CH_3)$ < 10 ms, $T_{1e}(H) \approx 5$ s

- **Promising**
  - High yields with mercury lamp
  - No o-H_2, p-D_2

- **Check points**

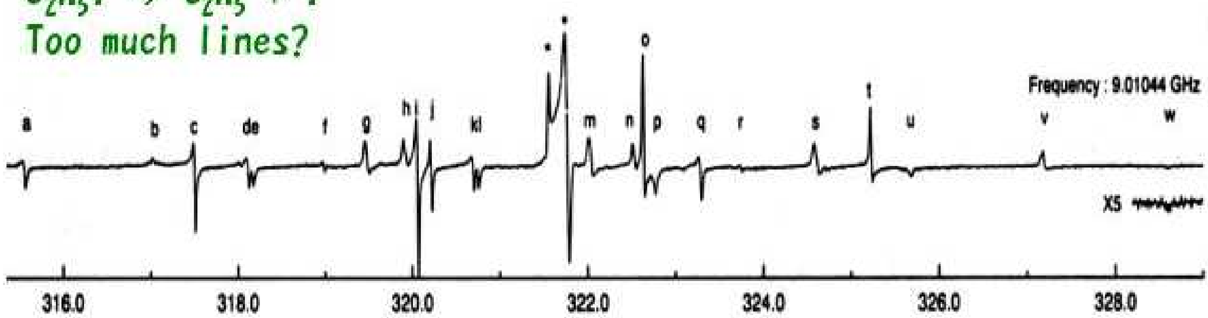


  - I atoms → enhance T_{1n}^{-1}

May be $(CH_3I)_2 \xrightarrow{h\nu} 2CH_3 + I_2$
If not, use $CH_3N_2CH_3 \xrightarrow{h\nu} 2CH_3 + N_2$.

•C_2H_5

$C_2H_5I \rightarrow C_2H_5 + I$
Too much lines?



•N (^4S)

NO → N + O but small cross section
By-product: O atom and N(±3/2) ↔ N(±1/2)

•NH_2

Not observed in UV-illuminated NH_3 in solid H_2 → Why?

See "Photochemistry of small molecules" H. Okabe, Wiley 1978

Conclusion for DNP of solid HD

- Use CH_3 instead of H atom
- Arrange set up for isolation of CH_3I
- Use $CH_3N_2CH_3$ and so on, if I atoms spoil DNP
- Use other photoproducts, if $T_{1e}(CH_3)$ is still long

Goal of our study

Determination of mesoscale structure
Of polymers using DNP and SANS

2006	2007	2008	2009

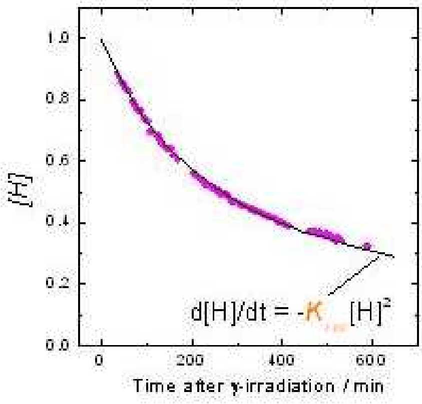
Build up DNP system for laboratory →

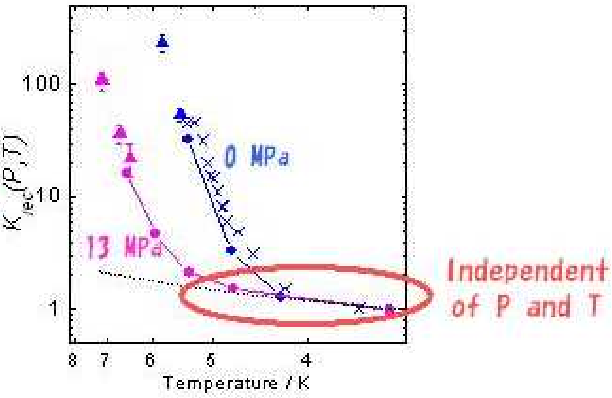
Synthesize polymers designed for DNP →

Build up DNP system for SANS →

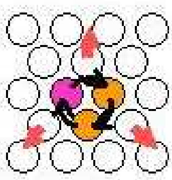
Contact me if you are interested in our project!

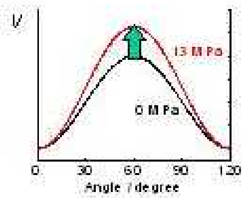
Tunneling diffusion by $H + H_2 \rightarrow H_2 + H$





★ physical exchange model
$D(13\ MPa) \ll D(0\ MPa)$ → No





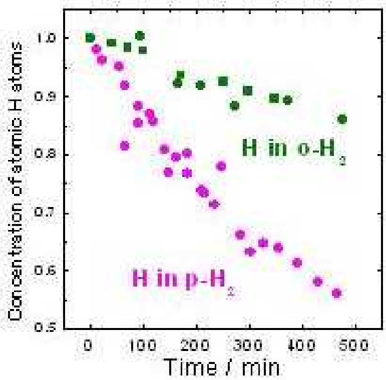
★ $H + H_2 \rightarrow H_2 + H$,
$k(13\ MPa) = k(0\ MPa)$ → Yes (eg. No P effect on $D + DH \rightarrow D_2 + H$)

H atoms in solid H_2 diffuse by the $H + H_2$ tunneling reaction below 4 K

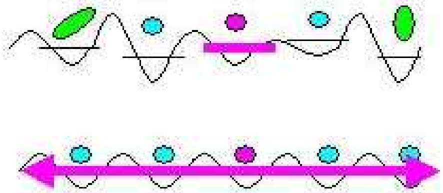
T. Kumada, Phys. Rev. B 68, 052301-1-4 (2003).

Effect of surrounding environment on $H + H_2 \rightarrow H_2 + H$

- Decay of H atoms in solid H_2



- Tunneling reaction
  - in solid n-H_2
  - in solid p-H_2



We should know the local environment around reactants.

T. Kumada et al., J. Low Temp. Phys. 122, 265-278 (2001)
T. Kumada et al., J. Chem. Phys. 116, 1109-1119 (2002).

Radiolysis of gaseous H_2

P. C. Souers, Hydrogen properties for fusion energy, Univ. California (1986)

CALCULATED RADIATION DAMAGE EVENTS IN H_2 GAS BOMBARDED WITH ONE 16 fJ (100 keV) ELECTRON THAT LOSES ALL ITS ENERGY

Processes	Products	Number of events	Ion pairs
Ionization	$H_2^+ + e^-$	2 377	0.87
	$H^+ + e^- + H$	341	0.12
	$2(H^+ + e^-)$	14	0.01
		2 732	1.00
Excitation	$H_2^* \rightarrow H_2 + h\nu$	1788	1.16
	$H_2^* \rightarrow 2H$	740	
	$H_2^* \rightarrow H^* + H$	614	
	$H_2^* \rightarrow 2H^*$	28	
Atom production (sum from above)		3 105	1.14

NOTE: There is no further reaction or recombination of the radiation damage products.

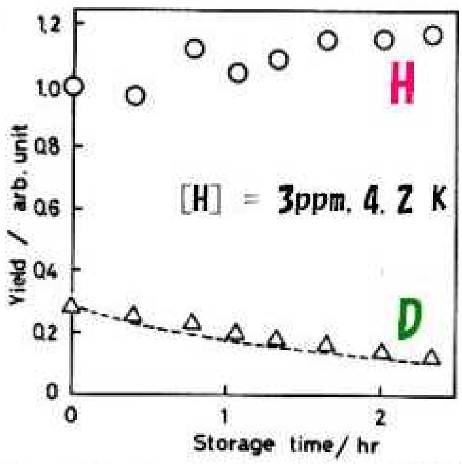
$H_2^+ + H_2 \rightarrow H_3^+ + H$

$H_3^+ + e^- \rightarrow$ { 3H ; $H_2 + H$ }

14000 H atoms

Radiation energy 100 keV →
- 60 keV: H-H dissociation
- 40 keV: The others

$\tau_{1/2(H)}$: Lifetime of H in solid HD



T. Miyazaki et al., JCP 93, 3352 (1989)

No decrease in [D] + [H]

↓

No recombination within 2 h

↓

$\tau_{1/2(H)} > 10^5$ s for [H]=3ppm

↓

$\tau_{1/2(H)} \geq 1$ h for [H]=100 ppm

Radiolysis of H_2

P. C. Souers, Hydrogen properties for fusion energy, Univ. California (1986)

CALCULATED RADIATION DAMAGE EVENTS IN H_2 GAS BOMBARDED WITH ONE 16 fJ (100 keV) ELECTRON THAT LOSES ALL ITS ENERGY

Processes	Products	Number of events	Ion pairs
Ionization	$H_2^+ + e^-$	2377	0.87
	$H^+ + e^- + H$	341	0.12
	$2(H^+ + e^-)$	14	0.01
		2732	1.00
Excitation	$H_2^* \rightarrow H_2 + h\nu$	1788	1.16
	$H_2^* \rightarrow 2H$	740	
	$H_2^* \rightarrow H^* + H$	614	
	$H_2^* \rightarrow 2H^*$	28	
Atom production (sum from above)		3105	1.14

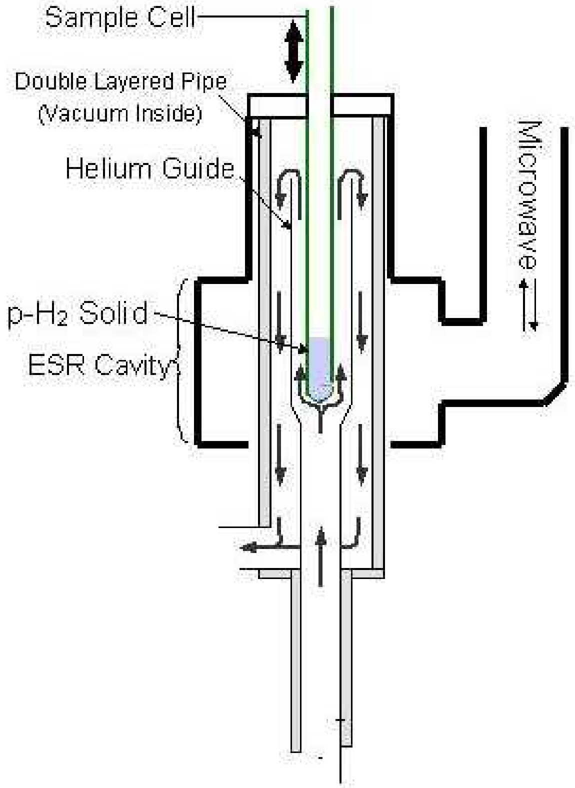
NOTE: There is no further reaction or recombination of the radiation damage products.

$H_2^+ + H_2 \rightarrow H_3^+ + H$

$H_3^+ + e^- \rightarrow \{ 3H,\ H_2 + H$

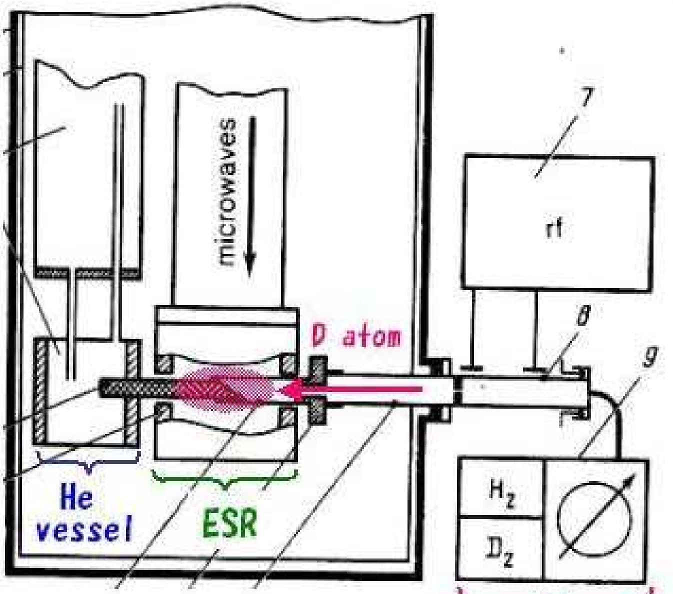
14000 H atoms

Radiation energy 100 keV → { 60 keV: H-H dissociation; 40 keV: The others



D atoms in solid D_2 produced by discharge

I. S. Iskovskikh et al., JETP **64**, 1085 (1986)



Advantage

$[D] = 3000$ ppm in solid D_2

Disadvantage

$HD \rightarrow H_2, D_2, HD$ (1:1:2)

ESR Linewidth

Solid	Place	Produced by	ΔH(4 K)	ΔH(1 K)
HD	Miyazaki	γ-ray	0.27	0.27
	Kumada	X-ray	0.27	0.27
		UV	0.28	
	Collins	Tritium	0.3	0.3
	Solem	X-ray	1.1	2.0
D_2	Miyazaki	γ-ray	0.12	0.12
	Kumada	X-ray	0.12	0.27
		UV	0.13	
	Shevtsov	Discharge	0.12	0.12

Solem probably overestimated the width.

Sweep rate: 6 mT/s →

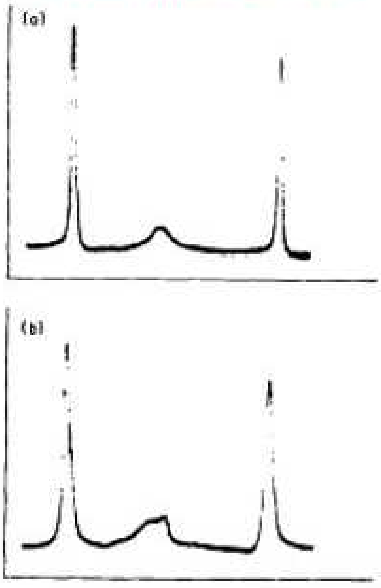


Fig. 3. EPR spectrum of an irradiated solid HD sample prepared from gas containing 3 × 10 [illegible] O_2 impurity. (a) 4.2 K, (b) 1.2 K. The two narrow resonances are ascribed to H-atoms trapped in the HD lattice and the broad central resonance is ascribed to the radical O_2D. The centers of the H-atom resonances are [illegible] separated by 504 G