MASTER

**EVIDENCE FOR THE FORMATION AND MOTION OF
MOLECULAR HYDROGEN IN IRRADIATED LITHIUM HYDRIDE**

Herman R. Leider

July 2, 1969

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Lawrence Radiation Laboratory
UNIVERSITY OF CALIFORNIA
LIVERMORE

UCRL-50698

**EVIDENCE FOR THE FORMATION AND MOTION OF
MOLECULAR HYDROGEN IN IRRADIATED LITHIUM HYDRIDE**

Herman R. Leider

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

EVIDENCE FOR THE FORMATION AND MOTION OF MOLECULAR HYDROGEN IN IRRADIATED LITHIUM HYDRIDE

Abstract

It has been reported in a previous study that the motionally narrowed hydrogen seen with pulsed nuclear magnetic resonance in irradiated $\text{Li}({}^1\text{H}, {}^3\text{H})$ does not have the same isotopic composition as the original lithium hydride. This experiment has been repeated with a different isotopic composition to extend the range of the data. The hydrogen that

gives rise to the motionally narrowed NMR signal has been shown to be in high density gas bubbles that must form by diffusion processes. We propose that the difference in isotopic composition is due to the mass dependence in the diffusion coefficient, and arguments are given to support the idea that the diffusing species is molecular hydrogen.

Discussion

It is well established that irradiation of lithium hydride results in considerable decomposition of this material into lithium metal and hydrogen gas that remain trapped in the lattice. This is true whether the source of the radiation is external, such as γ -irradiation of LiH ,¹⁻⁴ or internal, such as in lithium hydride containing ${}^3\text{H}$.^{1,2}

The hydrogen that is produced has properties expected of the gaseous molecular form^{2,3}; in particular, an ortho-para transition has been observed³ that is a positive indication of diatomic hydrogen. Furthermore, no paramagnetism has been detected in irradiated LiH by electron spin resonance that is not associated with either colloidal lithium metal or F-centers, even when irradiated at liquid nitrogen temperature.¹ If irradiation were to produce atomic hydrogen,

trapped somehow in the lattice, paramagnetism due to these atoms would be detectable. This, too, is evidence that the "free" hydrogen present is diatomic in nature. The V-center absorption spectrum in irradiated LiH has also been attributed to molecular H_2 .⁵ More direct evidence that hydrogen is present in gaseous form is the recent observation of cubic voids in irradiated LiH by electron microscope techniques.⁶ These voids are predominantly oriented with their walls parallel to the $[100]$ crystallographic directions. Upon observation of these voids, a nuclear magnetic resonance experiment (NMR) was performed on an irradiated single crystal to observe the angular variation of the spin-echo T_2 -relaxation time of the gaseous hydrogen as a function of crystal orientation relative to the applied magnetic field.⁷ The results are entirely

consistent with the picture of hydrogen gas trapped in a cubic bubble. The variation of the NMR relaxation time with crystal orientation is as would be predicted from a model where loss of phase coherence of the H_2 magnetic moments is due to interactions with the bubble walls.

Having firmly established that irradiation of lithium hydride produces diatomic hydrogen that is ultimately trapped in voids as a dense gas, it remains to be explained how microscopic pockets of gas actually form. A particularly important clue is found in the observation that for $Li(^1H, ^3H)$ the ratio of "free" tritium to hydrogen found by NMR is significantly different from the isotopic ratio of the material.²

Consider the following model. We assume that in $Li(^1H, ^3H)$ the steady-state concentration of gaseous species containing 1H and/or 3H is determined by the efficiency of the radiation process in ionizing the $^1H^-$ and $^3H^-$ ions and by the rate at which the species formed recombine with lithium. The gas that collects in bubbles is assumed to sample the steady-state distribution of molecules or atoms produced in the system by radiation. We assume that the efficiency of ionization for $^1H^-$ and $^3H^-$ is the same and, therefore, that the relative concentration of 1H - and 3H -containing species as formed is statistically determined. Diatomic molecules exist in the gas bubbles, and we know that NMR sees only three-fourths of 1H_2 and 3H_2 because of the ortho-para equilibrium, but that all $^1H^3H$ is seen. However, the weight given to the signal from $^1H^3H$ is one-half that from 1H_2 or 3H_2 as its contribution to the spin count,

since each molecule of $^1H^3H$ has only one atom of each kind rather than two.

On the basis of the foregoing, three cases are easily visualized:

Case A: Radiation produces a monatomic specie (1H or 3H) that diffuses as a monatomic specie.

Production by radiation, $H_{(c)}^- \rightarrow H_{(c)} + e$,

$$\frac{d[{}^1H]}{dt} = k[{}^1H^-] \quad (1a)$$

$$\frac{d[{}^3H]}{dt} = k[{}^3H^-] \quad (1b)$$

Recombination, $H_{(c)} + Li_{(c)} \rightarrow LiH_{(c)}$,

$$- \frac{d[{}^1H]}{dt} = KD_{1H} [{}^1H] \quad (2a)$$

$$- \frac{d[{}^3H]}{dt} = KD_{3H} [{}^3H] = K \frac{\sqrt{3}}{3} D_{1H} [{}^3H] \quad (2b)$$

The terms in square brackets, $[]$, always represent concentrations or fractional concentrations. D_i is the appropriate diffusion coefficient of the i th specie. We assume that diffusion coefficients of similar 1H and 3H species differ only by a mass term.

At steady state:

$$k[{}^1H] = KD_{1H} [{}^1H] \quad (3a)$$

$$k[{}^3H] = K \frac{\sqrt{3}}{3} D_{1H} [{}^3H] \quad (3b)$$

so that

$$\frac{[{}^3H]}{[{}^1H]} = \sqrt{3} \frac{[{}^3H^-]}{[{}^1H^-]} = \sqrt{3} R_I \quad (4)$$

Here we assume that, since the gas appears as diatomic molecules, the formation of molecules occurs after the atoms

reach the bubbles. Since the number of $^1\text{H}_2$, $^3\text{H}_2$ and $^1\text{H}^3\text{H}$ molecules depends on the quantity of each type of atom,

$$\left[^1\text{H}_2 \right] \propto \left[^1\text{H} \right]^2 \quad (5a)$$

$$\left[^3\text{H}_2 \right] \propto \left[^3\text{H} \right]^2 \quad (5b)$$

and

$$\left[^1\text{H}^3\text{H} \right] \propto 2 \left[^1\text{H} \right] \left[^3\text{H} \right] \quad (5c)$$

since $2\text{H} \rightleftharpoons \text{H}_2$. Now the ratio of ^3H atoms to ^1H atoms is

$$R' = \frac{\left[^3\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]}{\left[^1\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]} \quad (6a)$$

and the observed spin ratio is

$$R = \frac{\frac{3}{4} \left[^3\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]}{\frac{3}{4} \left[^1\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]} \quad (6b)$$

Using relations (4) and (5)

$$R_A = R_I \left(\frac{\frac{9}{4} R_I + \sqrt{3}}{\sqrt{3} R_I + \frac{3}{4}} \right) \quad (7)$$

R_A is plotted as a function of composition in Fig. 1 as curve A.

Case B: Radiation produces a diatomic specie ($^1\text{H}_2$, $^1\text{H}^3\text{H}$, or $^3\text{H}_2$), which then diffuses as a diatomic specie.

Production by radiation, $2\text{H}_{(c)}^- \rightarrow \text{H}_{2(c)} + 2e$,

$$\frac{d \left[^1\text{H}_2 \right]}{dt} = k \left[^1\text{H}^- \right]^2 \quad (8a)$$

$$\frac{d \left[^3\text{H}_2 \right]}{dt} = k \left[^3\text{H}^- \right]^2 \quad (8b)$$

$$\frac{d \left[^1\text{H}^3\text{H} \right]}{dt} = 2k \left[^1\text{H}^- \right] \left[^3\text{H}^- \right] \quad (8c)$$

Recombination, $\frac{1}{2} \text{H}_{2(c)} + \text{Li}_{(c)} \rightarrow \text{LiH}_{(c)}$,

$$- \frac{d \left[^1\text{H}_2 \right]}{dt} = K D_{^1\text{H}_2} \left[^1\text{H}_2 \right] \quad (9a)$$

$$- \frac{d \left[^3\text{H}_2 \right]}{dt} = K \frac{\sqrt{3}}{3} D_{^1\text{H}_2} \left[^3\text{H}_2 \right] \quad (9b)$$

$$- \frac{d \left[^1\text{H}^3\text{H} \right]}{dt} = K \frac{\sqrt{2}}{2} D_{^1\text{H}_2} \left[^1\text{H}^3\text{H} \right] \quad (9c)$$

At steady state:

$$k \left[^1\text{H}^- \right]^2 = K D_{^1\text{H}_2} \left[^1\text{H}_2 \right] \quad (10a)$$

$$k \left[^3\text{H}^- \right]^2 = K \frac{\sqrt{3}}{3} D_{^1\text{H}_2} \left[^3\text{H}_2 \right] \quad (10b)$$

$$2k \left[^1\text{H}^- \right] \left[^3\text{H}^- \right] = K \frac{\sqrt{2}}{2} D_{^1\text{H}_2} \left[^1\text{H}^3\text{H} \right] \quad (10c)$$

As in case A, the observed ratio,

$$R = \frac{\frac{3}{4} \left[^3\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]}{\frac{3}{4} \left[^1\text{H}_2 \right] + \frac{1}{2} \left[^1\text{H}^3\text{H} \right]} \quad (11)$$

Using 9 (a,b and c),

$$R_B = R_I \left(\frac{\frac{3}{4} \sqrt{3} R_I + \sqrt{2}}{\sqrt{2} R_I + \frac{3}{4}} \right) \quad (12)$$

This is plotted as curve B in Fig. 1.

Case C: Radiation produces a diatomic species ($^1\text{H}_2$, $^3\text{H}_2$, and $^1\text{H}^3\text{H}$) that must dissociate into atoms in order to diffuse (^1H and ^3H).

Production by radiation, $2\text{H}_{(c)}^- \rightarrow \text{H}_{2(c)} + 2e$,

$$\frac{d \left[^1\text{H}_2 \right]}{dt} = k \left[^1\text{H}^- \right]^2 \quad (13a)$$

$$\frac{d[{}^3\text{H}_2]}{dt} = k[{}^3\text{H}^-]^2 \quad (13b)$$

$$-\frac{d[{}^3\text{H}_2]}{dt} = K D_{3\text{H}} [{}^3\text{H}] = 2K \frac{\sqrt{3}}{3} D_{1\text{H}} [{}^3\text{H}_2] \quad (14b)$$

$$\frac{d[{}^1\text{H}{}^3\text{H}]}{dt} = 2k[{}^1\text{H}^-][{}^3\text{H}^-] \quad (13c)$$

Recombination, $\text{H}_{2(c)} \rightleftharpoons 2\text{H}_{(c)}$; $\text{H}_{(c)} + \text{Li}_{(c)} \rightarrow \text{LiH}_{(c)}$,

$$-\frac{d[{}^1\text{H}_2]}{dt} = K D_{1\text{H}} [{}^1\text{H}] = 2K D_{1\text{H}} [{}^1\text{H}_2] \quad (14a)$$

$$\begin{aligned} -\frac{d[{}^1\text{H}{}^3\text{H}]}{dt} &= K D_{1\text{H}} [{}^1\text{H}] + K D_{3\text{H}} [{}^3\text{H}] \\ &= K D_{1\text{H}} [{}^1\text{H}{}^3\text{H}] + K \frac{\sqrt{3}}{3} D_{1\text{H}} [{}^1\text{H}{}^3\text{H}] \end{aligned} \quad (14c)$$

Fig. 1. The ratio of ${}^3\text{H}$ spins to proton spins plotted as a function of composition for three cases.

Proceeding as before, we get

$$R_C = R_I \left(\frac{\frac{3\sqrt{3} + 3}{8} R_I + 1}{R_I + \frac{3\sqrt{3}}{8}} \right), \quad (15)$$

which is plotted as curve C. On examination of Table I and Fig. 1, it is evident that cases B and C are not distinguished by the experimental results, and thus, either case may be valid. However, there are several plausibility arguments against case C. The energy of dissociation of hydrogen molecules is so large that it would seem unlikely that dissociation would be a common event. Moreover, if such a dissociation did occur appreciably, one would expect to have seen some evidence for the presence of atomic hydrogen by such a sensitive probe as electron spin resonance, even if its average existence were short-lived.

Table I shows the results of NMR determination of the $^3\text{H}/^1\text{H}$ ratio² for two compositions of $\text{Li}(^1\text{H}, ^3\text{H})$ along with the calculated values of this ratio for cases A, B, and C; the values of the isotopic ratios

for these two compositions are also shown. Figure 1 contains the plots for the two points representing the two compositions, the curve for the isotopic ratio, and the values calculated for the three cases discussed above. For the composition at 0.475 atom fraction of $^3\text{H}^-$, the point represents measurements on several samples stored at temperatures of from $\sim 25^\circ\text{C}$ to $\sim 250^\circ\text{C}$. The point at 0.61 atom fraction of $^3\text{H}^-$ is from a single sample that was stored at 75°C . The width in composition for each point represents the range of composition the sample has seen due to the radioactive decay of ^3H . Although the experimental uncertainty in these measurements is quite large, it seems that case A is not a good description of results. Consequently, we may say that in the radiation decomposition of lithium hydride, the formation of bubbles of hydrogen gas proceeds by the production of hydrogen molecules and their subsequent aggregation into bubbles, probably by diffusion of molecules through the lattice to nucleation sites.

Table I. Isotopic ratios and observed and calculated $^3\text{H}/^1\text{H}$ ratios for two compositions of $\text{Li}(^1\text{H}, ^3\text{H})$.

$[^3\text{H}^-]$	Isotopic ratio, R_I	R_A	R_B	R_C	$R_{(\text{obs.})}$
0.475	0.905-0.83	1.47	1.16	1.12	1.2 ± 0.2
0.610	1.564-1.38	2.38	1.82	1.84	1.6 ± 0.3

References

1. F. E. Pretzel et al., "Properties of Lithium Hydride: V. Vacancy Formation, Cavitation and Lithium Precipitation in Irradiated Lithium Hydride," J. Appl Phys. **33** (Suppl.), 510 (1962); the unabridged version is Radiation Effects on Lithium Hydride, Los Alamos Scientific Laboratory, N. M., Rept. LA-2463 (1961).
2. P. C. Souers, T. A. Jolly, and C. F. Cline, "Pulsed Nuclear Magnetic Resonance Study of Irradiated Lithium Hydride," J. Phys. Chem. Solids **28**, 1717 (1967).
3. P. C. Souers et al., Pulsed Nuclear Magnetic Resonance of Gamma-Irradiated Lithium Hydride, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71517 (1969); P. C. Souers et al., NMR and Electron Microscopy Studies on Irradiated Lithium Hydride, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71835 (1969).
4. H. W. Newkirk and H. R. Leider, Thermal Annealing of Irradiated Lithium Hydride: I. Measurement of Stored Energy, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71850 (1969); H. R. Leider, Thermal Annealing of Irradiated Lithium Hydride: II. A Proposed Mechanism, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71851 (1969).
5. F. E. Pretzel and C. C. Rushing, "Properties of Lithium Hydride: II. Optical Absorption by Color Centers," J. Phys. Chem. Solids **17**, 232 (1961).
6. T. Imai, Observation of Bubbles in Gamma-Irradiated Lithium Hydride, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71730 (1969); and Phil. Mag. (to be published).
7. P. C. Souers, T. S. Blake, and R. M. Penpraze, NMR Anisotropy in Irradiated Lithium Hydride, Lawrence Radiation Laboratory, Livermore, Rept. UCRL-71698 (1969); and Phil. Mag. (to be published).

Distribution

LRL Internal Distribution

Michael M. May	
G. Dorough	
H. Weed	
A. Karo	
B. Rubin	
G. D. Snider	
H. Otsuki	
J. S. Kane	
A. J. Rothman	
D. Coronado	3
C. Cline	
H. Leider	20
T. Imai	
P. C. Souers	
T. Blake	
H. Newkirk	
J. Mitchell	
R. Penpraze	
G. Smith	
C. Griffith	
J. B. Holt	
R. H. Conit	
TID Berkeley	
TID File	30

External Distribution

C. H. Ice	3
J. H. Owen	
Savannah River Laboratory	
Aiken, South Carolina	
D. T. Vier	
J. Anderson	
Los Alamos Scientific Laboratory	
Los Alamos, New Mexico	
F. Fushimi	3
Mound Laboratory	
Miamisburg, Ohio	

External Distribution (Continued)

W. Wilson
Sandia Laboratories
Livermore, California

P. W. Levy
Brookhaven National Laboratory
Upton, New York

TID-4500 Distribution, UC-4, Chemistry

207

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65.

GL/dh