Experimental determination of the mechanism of the tunneling diffusion of H atoms in solid hydrogen: Physical exchange versus chemical reaction

Takayuki Kumada

Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
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The pressure effect on the recombination rate constant of H atoms in solid H_2 has been studied by electron spin resonance spectroscopy. It has been found that the rate constant was independent of pressure up to 13 MPa in the temperature range below 4 K, while it significantly decreases with an increase in pressure in the range above 5 K. The low temperature behavior observed indicates that H atoms diffuse in solid H_2 "chemically" through the $H + H_2 \rightarrow H_2 + H$ reaction not by the physical exchange mechanism.

I. INTRODUCTION

It is well known that H atoms diffuse in solid H_2 via quantum mechanical tunneling in the temperature range below 4 K (Refs. [1]–[6]); however, fundamental mechanism of this has not yet been understood. In particular, it is quite difficult to distinguish whether the H atoms migrate through "chemical diffusion" or "physical diffusion." Here, chemical diffusion means that the H atom moves from the previous trapping site to the next trapping site by the $H + H_2 \rightarrow H_2 + H$ chemical reaction between H and one of its surrounding H_2 molecules, while physical diffusion corresponds to the normal diffusion of H atom by exchanging its position with neighboring H_2 molecules in solid H_2. In 1980s, both Nagoya's group[1,7] and Moscow's group[5] experimentally showed that the $D + DH \rightarrow D_2 + H$ and $D + H_2 \rightarrow DH + H$ chemical reactions occur by quantum tunneling in low-temperature solid HD and D_2 containing H_2, independently; however, these two groups derived totally different conclusions for the tunneling diffusion of H atoms in solid H_2. Nagoya's group stated that the $H + H_2 \rightarrow H_2 + H$ reaction should be the dominant mechanism for the H atom diffusion in solid H_2. On the other hand, Moscow's group concluded that the H atom diffusion is completely due to physical diffusion. The purpose of the present study is to put a period to this controversial subject.

As the simplest and typical physical diffusion, the tunneling diffusion of ^{3}He atoms in solid ^{3}He has been extensively studied in the past.[8,9] Using various experimental techniques,[10–13] it has been well established that ^{3}He atoms diffuse through three- and four-atom cyclic exchange mechanisms in ^{3}He solid. Notice that the three- or four-atom exchanges require the least disturbance for the surrounding atoms. One of the most important experimental findings in the solid ^{3}He system is that the tunneling exchange rate is strongly dependent on the pressure. In fact, it is well known that the tunneling exchange rate significantly decreases with an increase in pressure. This finding simply implies that the effect of pressure on the H atom diffusion coefficient in solid H_2 should give a definitive evidence in determining whether H atoms diffuse via chemical diffusion or physical diffusion.

Recently, we have developed a high-pressure handling system designed for electron spin resonance (ESR) measurement. We have succeeded in pressuring solid H_2 up to 22 MPa, and applied this technique to the study of the thermally activated diffusion of H atom above 5.5 K; however, we could not extend the measurement in the range below 4 K, because the concentration of H atoms produced by our x-ray irradiation system was too low to measure the tunneling diffusion coefficient of H atoms in solid H_2 by quantum tunneling. Very recently, we have found that the yield of H atoms produced by the ultraviolet photolysis of O_2-doped solid H_2 is much larger than that by x-ray irradiation of solid H_2 we have used so far. Using this technique, we studied the effect of pressure on the tunneling diffusion of H atoms in solid H_2.

II. EXPERIMENT

The experimental procedure is similar to that used in our previous ESR study of O_2-doped solid D_2 and HD.[14] Normal-H_2 (n-H_2) gas containing O_2 (500–1500 ppm) was slowly (10–100 sccm) introduced into the quartz sample cell whose bottom tip was cooled down to 4.5 K using the He-flow cryostat (Scientific Inc. Model 9650). The gas was condensed to be an O_2-doped H_2 solid at the bottom tip. Because of a large difference in both boiling and melting temperatures between H_2 and O_2, a lot of O_2 clusters are probably formed in the solid. Then, the solid was pushed down to the cavity center of the X-band ESR spectrometer (JEOL JES TE-200), and irradiated with a low-pressure mercury lamp for 3–7 h through the cavity window. The time evolution of the H atom concentration in the UV-irradiated solid H_2 sample was measured using the ESR spectrometer in the temperature range between 3.4 and 6.5 K. In a high-pressure measurement, extra H_2 gas was added to fill up the bottom tip of the cell before irradiation, and pressurized with He gas.

III. RESULT AND DISCUSSION

After the UV photolysis of the O_2-doped solid H_2 sample, ESR signals of H, HO_2, and unassigned small signals at $g \approx 2$ were observed. Since both the ESR linewidth and power saturation behavior of the H signal were very similar to those measured in γ- and x-ray irradiated pure n-H_2 solid,[2,3] H atoms produced in this O_2-doped H_2 solid are well separated from other paramagnetic species such as O_2 and trapped in substitutional sites of solid H_2 fully surrounded by H_2 molecules.[15] The H atoms are produced by the following scheme:[16–18]
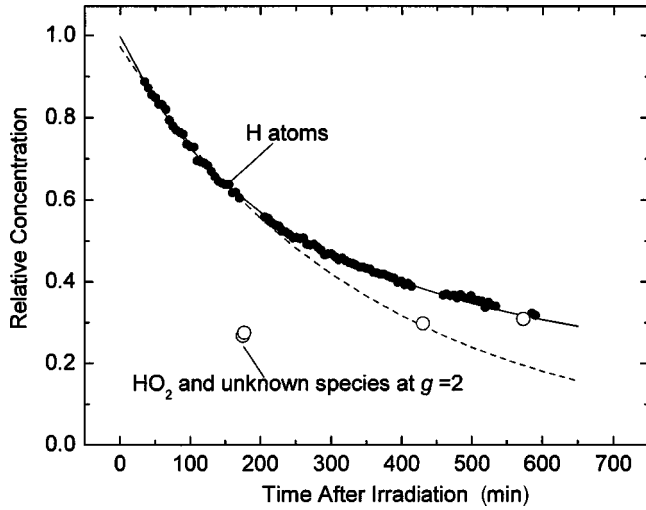
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FIG. 1. Relative concentration of H atoms $[H(t)]$, HO_2 and unknown species observed around $g \approx 2$ produced by the UV photolysis of O_2-doped solid n-H_2 measured at 3.4 K and 0 MPa. The solid line represents the fit of $[H(t)]$ to Eq. (1). The dashed line shows the fit of $[H(t)]$ at $t < 200$ min to the exponential decay function.
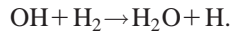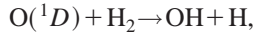
$$O_2 + h\nu(\lambda = 184.9 \text{ nm}) \rightarrow O(^3P) + O(^3P),$$

$$O(^3P) + O_2 \rightarrow O_3,$$

$$O_3 + h\nu(\lambda \leq 310 \text{ nm}) \rightarrow O(^1D) + O_2,$$

$$O(^1D) + H_2 \rightarrow OH + H,$$
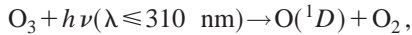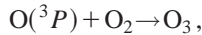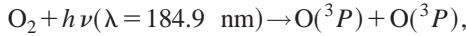
$$OH + H_2 \rightarrow H_2O + H.$$

Figure 1 compares the concentrations of H atoms $[H(t)]$, HO_2, and unknown species observed at $g \approx 2$ as a function of the time t after UV irradiation at 3.4 K. $[H(t)]$ does not decrease logarithmically but can be well reproduced by the second-order decay kinetics as

$$[H(t)] = \frac{1}{\frac{1}{[H(0)]} - k_{rec}t}, \quad (1)$$

where k_{rec} is the second-order recombination rate constant. On the other hand, the concentrations of HO_2 and unknown species were found to only slightly increase. This result indicates that the main channel of the H-atom decay is not due to $H + O_2 \rightarrow HO_2$ but to the recombination $H + H \rightarrow H_2$.

Figure 2 shows the time evolution of the H atom concentration measured in a pressurized solid at 3.4 K. No pressure effect was observed up to 13 MPa. Figure 3 plots $k_{rec}(P,T)/k_{rec}(0 \text{ MPa}, 3.4 \text{ K})$ at the pressure $P = 0$ MPa and 13 MPa determined by fitting $[H(t)]$ to Eq. (1) as a function of temperature T. As reported in Ref. 4, k_{rec} at 0 MPa was found to be proportional to T in the range between $1.3 \leq T \leq 4.2$ K, and to exponentially increase with an increase in T in the range above 5 K. k_{rec} is independent of pressure up to 13 MPa below 4.2 K, whereas it remarkably decreases with an increase in pressure for $T \geq 5$ K.
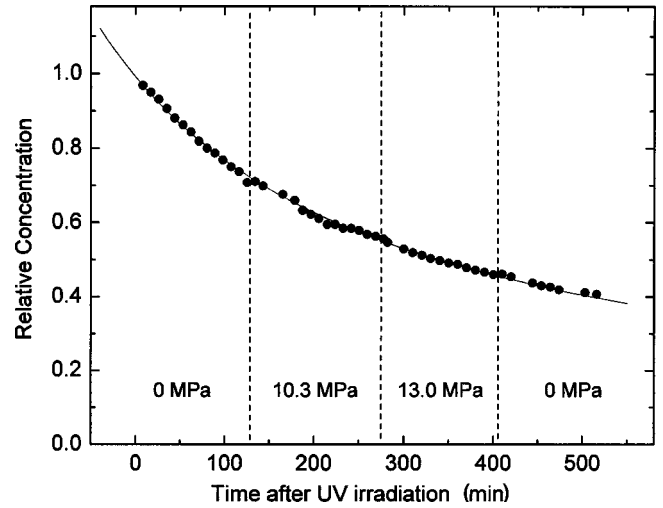

FIG. 2. Relative concentration of H atoms produced by the UV photolysis of O_2-doped solid n-H_2 measured at 3.4 K and 0–13 MPa. The solid line represents the fit of $[H(t)]$ to Eq. (1).

It is known that the rate-determining step of the H atom decay is the diffusion of H atoms in solid n-H_2.[3] Then, the sharp increase in k_{rec} with T above 5 K is indicative of the H atom diffusion by thermally activated processes. The decrease in k_{rec} with the increase in P was found to be due to the decrease in the number of thermally produced vacancies which assist the H atom diffusion in solid H_2.[19] On the other hand, the small temperature dependence of k_{rec} for $T \leq 4.2$ K shows that the H atoms diffuse in solid H_2 by quantum tunneling.[4,6] In particular, it is theoretically explained that the $k_{rec} \propto T$ relation is due to the one-phonon quantum tunneling mechanism.[6] Therefore, the absence of the pressure effect on k_{rec} below 4.2 K shows that the tunneling probability of H atoms in solid H_2 does not depend on P. What does the result imply about the tunneling diffusion mechanism of H atoms in solid H_2?

Now, let us discuss the above-mentioned experimental findings by assuming that the tunneling diffusion is com-
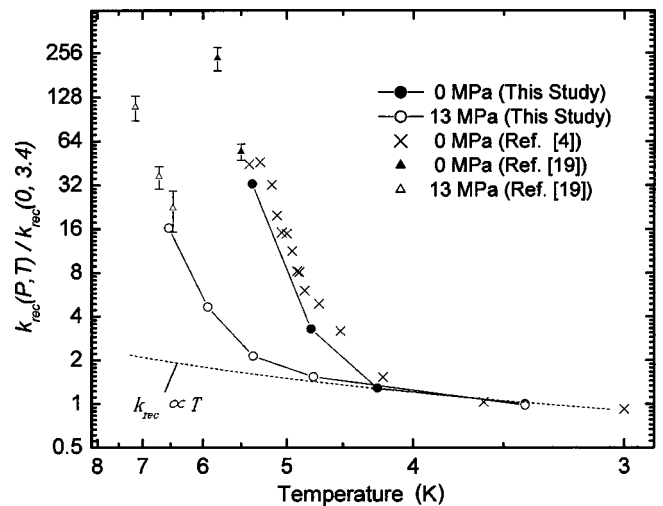

FIG. 3. Arrhenius plot of k_{rec} at 0 and 13 MPa normalized to that at 0 MPa and 3.4 K.
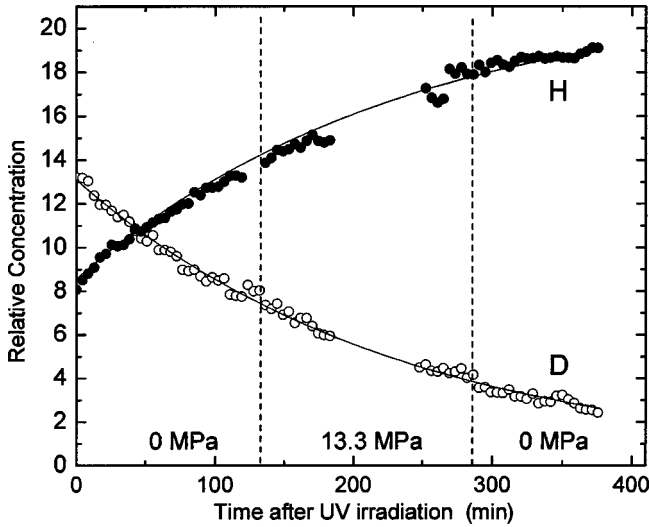
FIG. 4. Time evolution of the concentrations of H and D atoms produced by the UV photolysis of O_2-doped solid HD measured at 3.4 K and 0 and 13 MPa. The solid lines show the fit of the H and D concentrations to the exponential decay and association functions, respectively.

pletely due to physical diffusion. Here, we apply the model of the physical diffusion, which is well established in the solid ^{3}He system, to the tunneling diffusion of H atoms in solid H_2. It is known that the rate-determining step of the physical diffusion is the free volume formation required for exchanging particles in solids by compressing their surroundings.[8,9] The free energy δE to produce the free volume ΔV can be written as

$$\delta E = P\Delta V + \frac{1}{2\beta}\frac{(\Delta V)^2}{V_0}, \qquad (2)$$

where β is the compressibility of the solid and V_0 is the equilibrium volume of exchanging particles. When the pressure of hcp solid ^{3}He increases from 11.8 to 18.8 MPa, δE increases by 23 K (49% of δE at 0 MPa) and the diffusion coefficient of the ^{3}He atoms is reduced to $\sim 1/20$. Delriieu and Sullivan[9] established in the solid ^{3}He system, that when solid H_2 is pressurized from 0 to 11 MPa, δE increases by 73 K (51%), and the diffusion coefficient of H_2 molecules is reduced to be 1/80. If we apply the same model to the H atom diffusion in solid H_2, the physical diffusion coefficient of H atoms in solid H_2 is also expected to decrease drastically with the increase in pressure. Our experimental data, however, do not show any pressure effect on k_{rec} at $T \leq 4$ K, strongly indicating that the tunneling diffusion of the H atoms in solid H_2 is not due to the physical exchange.

If H atoms diffuse by chemical diffusion in solid H_2, how does the diffusion coefficient depend on pressure? In order to understand the pressure effect on the tunneling reaction, H $+H_2 \rightarrow H_2 + H$, in solid H_2, we measured the rate constant for the $D + DH \rightarrow D_2 + H$ reaction in solid HD at 0 MPa and 13 MPa. Figure 4 shows the time evolution of the concentration of D and H atoms produced by the UV photolysis of

O_2-doped solid HD. Both of the decrease in D and increase in H concentrations are due to the tunneling reaction of the D atom with one of the neighboring HD molecules, $D + DH \rightarrow D_2 + H$. The reaction rate constant obtained here (2.53×10^{-27} cm^3 molecule^{-1} s^{-1}) is consistent with that reported in x- and γ-irradiated solid HD.[1,7,20] We have found that the reaction rate constant is independent of pressure up to 13 MPa. This result strongly suggests that the pressure effect on the $H + H_2 \rightarrow H_2 + H$ reaction in solid H_2 is not expected either. Thus, the absence of pressure effect on k_{rec} in solid H_2 observed in the low-temperature region indicates that the tunneling diffusion of H atoms in solid H_2 proceeds by chemical diffusion.

The barrier height for the $H + H_2 \rightarrow H_2 + H$ reaction is known to be 4600 K,[21] which is significantly larger than that for the physical diffusion of H atoms in solid H_2 (~ 100 K).[22] Why does the tunneling diffusion of H atoms in solid H_2 proceed by chemical diffusion instead of physical diffusion? This is simply because both reduced mass m and barrier width L for the $H + H_2$ reaction are remarkably smaller than those for the physical exchange. The tunneling probability P_{tunnel} with kinetic energy E depends on m and L as $P_{tunnel} \propto \exp(-\int \sqrt{2m(U-E)}dL/\hbar)$ within the WKB approximation,[23] where U is the barrier height and $\hbar$ is Plank's constant. The $H + H_2$ reaction system has an $m = 2/3$ atomic mass unit (amu) and $L = 1.14$ Å.[21] On the other hand, as ^{3}He atoms in hcp ^{3}He solid diffuse by the cyclic exchange of three neighboring ^{3}He atoms, one H atom and its neighboring two H_2 molecules in solid H_2 should cyclically exchange their positions together with the displacement of at least three surrounding H_2 molecules to produce a free volume for the physical exchange. For example, the value of $m^{1/2}L$ for the H_2-H_2-H_2 exchange is calculated to be 6.4 in units of amu$^{1/2}$Å.[9] Since total mass of exchanging particles for the H-H_2-H_2 exchange is 5, the value of $m^{1/2}L$ is estimated to be 5.9. Consequently, although the barrier height for the $H + H_2$ reaction is much larger than that of physical exchange, the value of $(mU)^{1/2}L$ for the $H + H_2$ reaction can be even smaller. Of course, this estimation may be too crude to determine the diffusion mechanism of H atoms in solid H_2; however, we can point out the possibility that chemical diffusion could be the dominant process for the tunneling diffusion of H atoms in solid H_2, even though the barrier height for chemical diffusion is much higher than that for physical diffusion.

IV. CONCLUSION

We have studied the effect of pressure on the recombination of H atoms produced by the UV photolysis of O_2-doped solid H_2 in order to determine whether H atoms in solid H_2 diffuse by the physical exchange of positions with neighboring H_2 molecules, or by the $H + H_2 \rightarrow H_2 + H$ tunneling chemical reaction. The rate constant for the H atom recombination in solid H_2 was found to be independent of pressure up to 13 MPa, especially in the low-temperature region below 4 K. This result indicates that the H atoms diffuse through the repetition of $H + H_2 \rightarrow H_2 + H$ tunneling reaction in solid H_2 in the temperature range at $T \leq 4$ K.

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