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Decay Dynamics of H Atoms in Solid Hydrogen at 4.2 K. Controlling Factor of Tunneling Reaction $H + para\text{-}H_2 \rightarrow para\text{-}H_2 + H$

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H atoms produced by the γ-ray irradiation of solid *para*-H_2 (p-H_2) and solid *normal*-H_2 (n-H_2) decay gradually when the irradiated sample is stored at 4.2 K. *ortho*-H_2 (o-H_2) molecules at the sites nearest an H atom in solid n-H_2 convert to p-H_2 molecules by interacting with the H atom. H atoms in solid H_2 decay by the process of tunneling diffusion $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ and finally recombine with other H atoms. The rate constants for the tunneling reaction were obtained from the decay rates of H atoms in solid H_2 at various concentrations of o-H_2. When solid n-H_2 is stored for 10 h at 4.2 K after γ-ray irradiation, a number of o-H_2 molecules change into p-H_2 molecules by a catalytic chain reaction induced by mobile H atoms. The G value of the o-H_2 yields from H atoms amounts to $1{-}2.6 \times 10^4$. The rate constant for the tunneling reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ decreases drastically with increasing numbers of o-H_2 molecules, which exist as orientational defects in solid p-H_2. It was concluded that a very small amount of energy (ca. 2 cal mol^{-1}) affects the tunneling reaction at very low temperatures.

Introduction

Generally, a chemical reaction takes place if the reactants pass over the potential energy barrier for the reaction, the barrier height of which is greater than about 10 kcal mol^{-1} (≑5000 K). Thus, strong interaction with reactants is necessary for controlling the reaction. A tunneling reaction that takes place by passing through the potential energy barrier via quantum mechanical tunneling, however, occurs at a low temperature, such as 4 K. It is expected that a small interaction energy would affect the tunneling reaction significantly at cryogenic temperatures. Most of the previous studies on tunneling reactions have been limited to tunneling reactions at low temperature. The controlling factors of tunneling reaction have seldom been studied except for tunneling reactions in solid hydrogen.

Since the reaction of a hydrogen−hydrogen molecule can be considered as a prototypical bimolecular reaction, the study of the tunneling of this reaction is very important to the theory of chemical kinetics. Solid hydrogen is a matrix of great interest that shows remarkable quantum phenomena.[1,2] Since the reaction of the hydrogen−hydrogen molecule in solid hydrogen is a simple system, the controlling factors of the tunneling reaction can be elucidated in this system. New studies on the temperature effects on tunneling reactions suggest that the vacancy formation and the local motion of reactants play important roles in tunneling reactions.[3] The inverse temperature dependence of the rate constant for the tunneling reaction $H_2^- + H_2 \rightarrow H_2 + H_2^-$ in solid parahydrogen indicates that phonon scattering affects the tunneling reaction.[4]

When n-H_2 (*normal*-hydrogen) or p-H_2 (*para*-hydrogen) is irradiated in the solid phase with γ-rays at 4.2 K, the H atoms decay gradually after the irradiated sample is stored at 4.2 K. The H atoms in solid p-H_2 decay faster than those in solid n-H_2, which consists of 75% o-H_2 (*ortho*-hydrogen) and 25% p-H_2.[5] As discussed in detail previously,[5] H atoms do not migrate by trap-to-trap tunneling of H atoms but by repetition of the tunneling reaction $H + H_2 \rightarrow H_2 + H$. This mechanism was determined from the facts that H atoms are trapped in the substitutional sites of hydrogen crystals and that the rate constant for the tunneling reaction $H + H_2$ obtained from the decay rate of H atoms in solid H_2 is similar to that calculated theoretically from the reliable potential energy surface for the reaction. In the previous paper,[5] the difference in the decay rates of H atoms between p-H_2 and n-H_2 was interpreted in terms of the difference in the rate constants between $H + p\text{-}H_2$ (rotational quantum number $J = 0$) and $H + o\text{-}H_2$ ($J = 1$). Recently, the ENDOR spectra of H atoms in n-H_2 indicate that almost all o-H_2 molecules at the sites nearest an H atom convert to p-H_2 molecules.[6] This result indicates that almost all of the H atoms in solid n-H_2 diffuse by the same reaction, $H + p\text{-}H_2$, as that for H atoms in solid p-H_2. Therefore, we cannot ascribe the difference in the decay rate of H atoms between solid p-H_2 and solid n-H_2 to the difference in the rotational quantum states of H_2. The amount of H atoms produced by γ-ray irradiation of solid p-H_2 decreases to roughly half the initial yields at 10 h after the irradiation, but available data on the impact of storage times less than 10 h were very lacking in the previous study.[5] In this study, we have re-examined the decay of H atoms in p-H_2 and n-H_2 in more detail after the irradiated samples are stored for 10 h. It will be concluded here that o-H_2 molecules at the second and third nearest sites around an H atom affect the tunneling reaction $H + p\text{-}H_2$.

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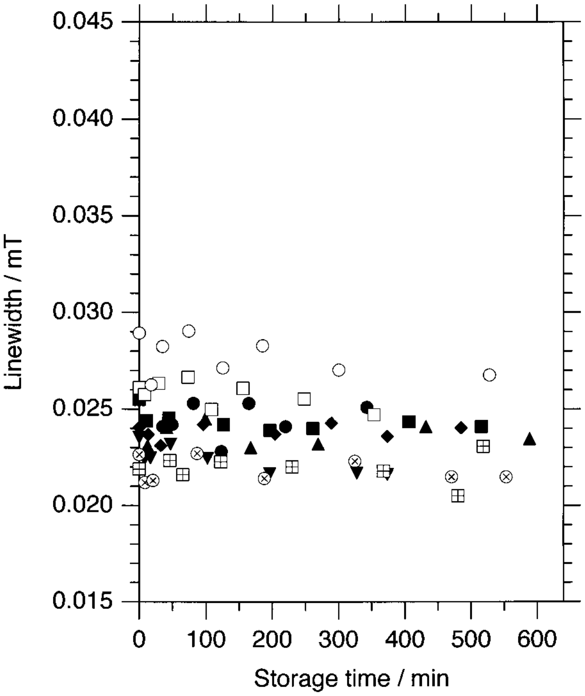

Figure 1. ESR line widths of H atoms at 4.2 K against storage time after γ-ray irradiation of solid p-H_2 at 4.2 K. (■, ●, ▲, ▼, ◆, ⊞, ⊗) p-H_2, (□) p-H_2−o-H_2 (6.3%) mixture, (○) p-H_2−o-H_2 (12.2%)mixture.

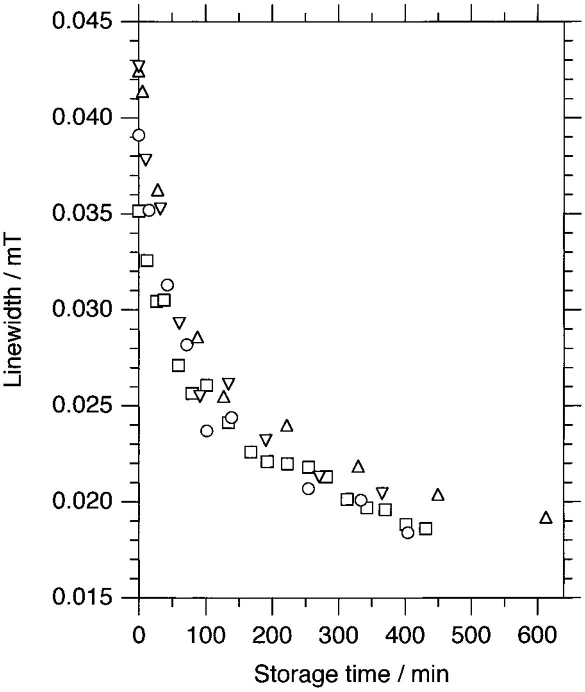

Figure 2. ESR line widths of H atoms at 4.2 K against storage time after γ-ray irradiation of four samples (□, ○, △, ▽) of solid n-H_2 at 4.2 K..

Experimental Section

Normal hydrogen (n-H_2) was more than 99.999 mol % pure. n-H_2 consists of 75% o-H_2 and 25% p-H_2. p-H_2 was synthesized by passing n-H_2 liquid through a column of iron(III) hydroxide (FeO(OH)) at 14 K. p-H_2 contains about 3% o-H_2 just after synthesis; this was measured by Raman spectroscopy. When p-H_2 gas is sealed in an ESR tube and stored at room temperature, the concentration of the o-H_2 impurity increases gradually by $p\text{-}H_2 \rightarrow o\text{-}H_2$ conversion. The real concentration of o-H_2 during the ESR measurement of the sample p-H_2 is roughly 8%.

Hydrogen, sealed in a fused quartz sample tube, was solidified by rapidly cooling the sample tube from room temperature to 4.2 K. The sample was irradiated at 4.2 K with γ-rays from a ^{60}Co source to a total dose of 0.18−2.8 kGy, which was measured by the Fricke dosimetry. The H atoms, produced by radiolysis, were measured at 4.2 K by the JEOL JES-RE1X ESR spectrometer at a low microwave power level that does not result in saturation of the signals of the hydrogen atoms. The amounts of the hydrogen atoms were obtained by double integration of signals using the ES-PRIT425 computer system (JEOL). The amount of p-H_2 was measured by a gas chromatograph, which consisted of a thermal conductivity detector and a column (14 cm long) of 0.5 nm molecular sieves at 77 K. An example of a gas chromatogram was shown in the previous paper.[5]

Results

Figure 1 shows the effect of storage time on the ESR line widths at the maximum slope of the H atom signals in solid p-H_2 at 4.2 K after γ-ray irradiation. The line widths are constant during the storage of the irradiated sample. The average line width after 400 min is 0.023 ± 0.0015 mT. The ESR line widths of H atoms in p-H_2 containing 6.3% and 12.2% o-H_2 are also shown here.

TABLE 1: ESR Line Widths at Maximum Slope of H Atoms after 400 min of Storage of γ-Ray-Irradiated Solid H_2 at 4.2 K

sample	line widths, mT
p-H_2[a]	0.023 ± 0.0015
p-H_2[a]−o-H_2 (6.3%)[b]	0.025
p-H_2[a]−o-H_2 (12.2%)[b]	0.027
n-H_2[c]	0.019 ± 0.0008

[a] p-H_2 contains ~8% o-H_2. [b] 6.3% or 12.2% p-H_2 was added to p-H_2. [c] n-H_2 contains 75% o-H_2.

Figure 2 shows the effect of storage time on the ESR line widths of H atoms in γ-ray-irradiated n-H_2 at 4.2 K. The line widths are narrowed significantly after 200 min and then decrease gradually. The final line widths after 400 min in the n-H_2 containing 75% o-H_2 are 0.019 ± 0.0008 mT at 4.2 K, which is slightly narrower than those in the p-H_2 containing o-H_2 at about 8% as an impurity. The ESR line widths after 400 min of storage of the irradiated sample are summarized in Table 1.

Figure 3 shows the effect of o-H_2 on the decay of H atoms in solid H_2 at 4.2 K. The H atoms decay quite slowly in solid n-H_2, which contains 75% o-H_2, denoted by the closed symbols (■, ●, ▲). When 12.2% o-H_2, denoted by the symbol (▼), and 6.3% o-H_2, denoted by the symbol (◆), are added, the H atoms clearly decay. H atoms in solid p-H_2, denoted by the open symbols (□, ○), decay quickly.

Table 2 shows the amount of p-H_2 in γ-ray-irradiated solid n-H_2 at 4.2 K after a dose of 2.8 kGy. Since n-H_2 originally contains 25% p-H_2, the difference of the measured value from 25% corresponds to the yields of p-H_2. In sample A, solid n-H_2 was stored for 0.6 h at 4.2 K before γ-ray irradiation and was then irradiated at 4.2 K for 1.4 h. Since the concentration of p-H_2 is 26.7%, the yields of p-H_2 produced by this treatment are 1.7% (26.7−25). This p-H_2 was formed by the conversion from o-H_2. The amount (26.6%) of p-H_2 in sample B, which was stored at 4.2 K for 2.0 h without γ-ray irradiation, is approximately the same as that (26.7%) in the γ-ray-irradiated

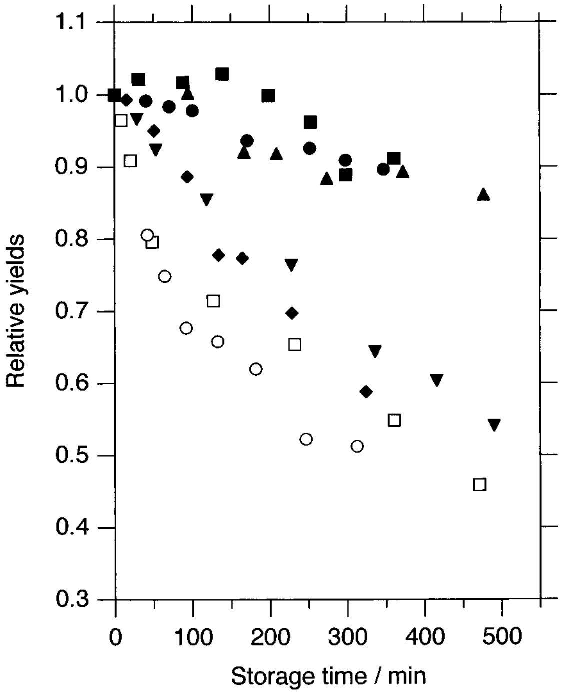

Figure 3. Effect of o-H_2 on the decay of H atoms in solid H_2 at 4.2 K after γ-ray irradiation at 4.2 K. The initial concentration of H atoms in all samples are around 1×10^{-7} mol cm^{-3}. (■, ●, ▲) n-H_2 containing 75% o-H_2, (▼) p-H_2−o-H_2 (12.2%) mixture, (◆) p-H_2−o-H_2 (6.3%) mixture, (□, ○) p-H_2.

TABLE 2: Amounts of p-H_2 from γ-Ray Irradiation of Solid n-H_2 at 4.2 K to a Dose of 2.8 kGy[a]

sample, experimental condition	p-H_2, %
A, stored for 0.6 h at 4.2 K and then γ-irradiated for 1.4 h	26.7 ± 0.4[b]
B, stored for 2.0 h at 4.2 K without γ-irradiation	26.6 ± 0.5[b]
C, stored for 0.6 h at 4.2 K before irradiation, γ-irradiated for 1.4 h, and then stored for 10 h at 4.2 K	36.2 ± 0.4[c]
D, stored for 12 h at 4.2 K without γ-irradiation	34.3 ± 0.4[d]

[a] n-H_2 contains initially 25% p-H_2. [b] Standard deviation obtained from 4 runs. [c] Standard deviation obtained from 6 runs. [d] Standard deviation obtained from 10 runs.

sample A. o-H_2 in the sample without irradiation converts to p-H_2 interacting with other o-H_2 molecules which have nuclear magnetic moments.[1] The amount (36.2%) in sample C, which was stored at 4.2 K for 10 h after γ-ray irradiation, is higher than those (34.3%) in sample D, which was stored at 4.2 K for 12 h without γ-ray irradiation. The difference in the amounts of sample C and sample D is due to the conversion of o-H_2 by the interaction of mobile H atoms during storage for 10 h (cf. Discussion).

Discussion

Local Environment around H Atoms. The previous studies concluded that H atoms are trapped in substitutional sites of the H_2 crystal.[6,7] The ENDOR spectrum of H atoms in γ-ray-irradiated n-H_2 indicates that o-H_2 molecules at the sites nearest to the H atom convert to p-H_2 molecules, while o-H_2 molecules exist at the second and third nearest sites.[6] The analysis of ESR spin−flip lines of H atoms in solid n-H_2 shows that most of the o-H_2 molecules at the nearest sites convert to p-H_2 molecules.[7]

The ESR line width of H atoms is determined by the superhyperfine interaction with the nuclear magnetic moment of o-H_2 molecules around the H atoms. Since the nuclear magnetic moment of p-H_2 is zero, p-H_2 molecules do not contribute to the ESR line width. The initial ESR line width of H atoms just after γ-ray irradiation of n-H_2 at 4.2 K is 0.043 mT, but it decreases to 0.019 mT after 400 min (cf. Figure 2, and Table 1). The results indicate that the local concentration of o-H_2 molecules near H atoms in solid n-H_2 decreases during the storage at 4.2 K. Table 1 shows that the ESR line (0.019 mT) of the H atoms in solid n-H_2 consisting of 75% o-H_2 is slightly narrower than that (0.023 mT) in solid p-H_2, which includes about 8% o-H_2 as an impurity. The narrower line in solid n-H_2 indicates that the local concentration of o-H_2 molecules near the H atoms in solid n-H_2 is slightly lower than that in solid p-H_2, though the total concentration of o-H_2 molecules in n-H_2 is of course much higher than that in p-H_2. The ortho−para conversion of H_2 molecules is induced by the interaction of electron spins of H atoms. As will be discussed, the H atoms in solid n-H_2 decay more slowly than those in solid p-H_2. H atoms in solid n-H_2 stay at the same site for longer times than do H atoms in solid p-H_2. Thus, the ortho−para conversion of o-H_2 molecules near an H atom in solid n-H_2 takes place efficiently.

Catalytic Chain Reaction of o-H_2−p-H_2 Conversion by H Atoms. o-H_2 molecules in solid n-H_2 convert to p-H_2 molecules by two processes: interacting with other o-H_2 molecules and interacting with the H atoms produced by γ-ray irradiation. When solid n-H_2 consisting of 25% p-H_2 and 75% o-H_2 is stored for 12 h at 4.2 K without γ-ray irradiation, the amount of p-H_2 in sample D of Table 2 increases to 34.3%. The ortho−para conversion in this case is caused by the nuclear magnetic moment of other o-H_2 molecules. The rate constant for the conversion was estimated at 4.36×10^{-6} (mol fraction)$^{-1}$ s^{-1}, which coincides with the reported value (4.72×10^{-6} (mol fraction)$^{-1}$ s^{-1}).[1]

When solid n-H_2 is irradiated with γ-rays and stored for 10 h at 4.2 K, the amount of p-H_2 in γ-ray-irradiated sample C becomes 36.2 ± 0.4%, which is ~1.1−2.7% larger than those (34.3 ± 0.4%) in sample D without γ-ray irradiation. When the irradiated sample is warmed to room temperature just after γ-ray irradiation, the amount of p-H_2 in γ-ray-irradiated sample A is the same as that in sample B without γ-ray irradiation. Therefore, the ortho−para conversion does not take place during γ-ray irradiation, but by the storage of the sample after the irradiation.

The ENDOR and ESR spin−flip lines of H atoms in solid n-H_2 show that almost all o-H_2 molecules at the sites nearest an H atom convert to p-H_2 molecules, while o-H_2 molecules at the second, third, and fourth sites do not change.[6,7] So it is expected that H atoms will convert a number of o-H_2 molecules to p-H_2 molecules during their migration when the sample is stored after irradiation.

The G value (which is defined by the number of molecules formed from the absorption of 100 eV of radiation energy) of p-H_2 molecules in γ-ray-irradiated solid n-H_2 was estimated by the following procedure. When solid n-H_2 is irradiated by γ-rays to a dose of 2.8 kGy measured by the Fricke dosimetry, n-H_2 absorbs the radiation energy of 3.14×10^{19} eV g^{-1}. Since the yields (~1.1−2.7%) of p-H_2 molecules correspond to ~$3.3-8.1 \times 10^{21}$ molecules g^{-1}, G values for the production of p-H_2 were estimated as $1.1-2.6 \times 10^4$ [$3.3-8.1 \times 10^{21} \times 100/(3.14 \times 10^{19})$]. Since an H atom is trapped in a substitutional site and surrounded with 12 H_2 molecules, the number of initial o-H_2 molecules surrounding the H atom is 9 (12×0.75) in solid n-H_2, which consists of 75% o-H_2. If H atoms do not migrate at all and convert the o-H_2 molecules in the nearest neighbors to p-H_2, the G value for the production of p-H_2 is expected to be only 21.6 (2.4×9). Here, the G value of H atoms produced by the γ-ray irradiation of solid n-H_2 dosed with 2.8 kGy is 2.4.[8] The very large G values ($1.1-2.6 \times 10^4$) obtained experimentally indicate that the ortho−para conversion is a chain reaction caused by the migration of H atoms.

When an H atom hops to the next site, it encounters seven new H_2 molecules. Thus, the H atom meets 5.25 (7×0.75) o-H_2 molecules in one jump and converts them to p-H_2. The jump frequency of H atoms in solid n-H_2 is 1.0 s^{-1},[5] and thus, H atoms jump 3.6×10^4 times ($1 \times 10 \times 60 \times 60$) during the storage of irradiated solid n-H_2 for 10 h. If all H atoms effectively convert o-H_2 molecules in the nearest neighbors during their migration, the G value for the production of p-H_2 is expected to be 4.5×10^5 ($2.4 \times 5.25 \times 3.6 \times 10^4$), which is much larger than the experimental G values ($1.1-2.6 \times 10^4$). The difference between the experimental G values and the expected ones is probably due to the migration region of H atoms. A portion of H atoms diffuse through the region rich in o-H_2 and convert o-H_2 efficiently to p-H_2. The rest of them diffuse through the region rich in p-H_2 without converting o-H_2. Thus, the experimental G values are smaller than the value estimated by the model anticipating all H atoms to convert o-H_2 to p-H_2 during their migration.

Effect of o-H_2 Impurity on the Tunneling Reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$. Though H atoms decay fast in solid H_2 at temperatures above 4.2 K by a thermally activated process, they decay slowly by a tunneling process below this temperature. As discussed in the Introduction and the previous paper,[5] H atoms migrate in solid H_2 by the repetition of the tunneling reaction $H + H_2 \rightarrow H_2 + H$ below 4.2 K. Since the neighbors nearest an H atom are p-H_2 molecules in both solid n-H_2 and solid p-H_2, the H atom reacts with the p-H_2 molecule. The rate constant for the tunneling reaction can be obtained by the following process, the details of which were discussed in the previous paper.[5] The H atoms diffuse through the solid H_2 and recombine with other H atoms through second-order kinetics when the matrix can effectively remove the recombination energy. The rate constant (k_H) for the decay of H atoms is expressed as

$$k_H = 4\pi r(D_H + D_H) \tag{1}$$

where D_H and r are the diffusion coefficient of H atoms and the contact distance between two H atoms in a recombination reaction, respectively. Then the rate constant ($k(H + p\text{-}H_2)$) for the reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ is related to the jump frequency (ν) and concentration of p-H_2 (C_{H_2})

$$k(H + p\text{-}H_2) = \nu / C_{H_2} \tag{2}$$

$$\nu = 6D_H/l^2 \tag{3}$$

l is the trap-to-trap distance for H atoms in a substitutional site. The rate constants for the tunneling reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ are summarized in Table 3. The rate constant of n-H_2, in which the concentration of o-H_2 is 75%, is also shown, taken from ref 5. The value of $k(H + p\text{-}H_2)$ obtained in solid p-H_2 is 110 $cm^3\ mol^{-1}\ s^{-1}$, which is larger than the value (43 $cm^3\ mol^{-1}\ s^{-1}$) reported previously.[5] Though the amount of H atoms in solid p-H_2 decreases drastically during storage for 10 h to half the initial yield, only two data were previously obtained during storage times less than 10 h. Since many data were obtained 10 h after γ irradiation, the rate constant in this study is more reliable than the value in the previous paper.[5]

TABLE 3: Rate Constants for Tunneling Reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ in Solid Hydrogen at 4.2 K[a]

sample	rate constant, $cm^3\ mol^{-1}\ s^{-1}$
p-H_2[b]	110 ± 20[c]
p-H_2[b]−o-H_2 (6.3%)	84
p-H_2[b]−o-H_2 (12.2%)	68
p-H_2−o-H_2 (75%)[d]	24[e]

[a] The errors of the values are about 20%. [b] p-H_2 itself contains about 8% o-H_2. [c] Mean value of 7 runs. [d] The sample is n-H_2. [e] Mean value of the previous results (ref 5). The previous paper assumed that the rate constant obtained in solid n-H_2 consists of $k(H + o\text{-}H_2)$ and $k(H + p\text{-}H_2)$. Since the nearest neighbors around an H atom in solid n-H_2 are p-H_2 molecules, the rate constant in solid n-H_2 represents $k(H + p\text{-}H_2)$ (see text). Thus, the $k(H + o\text{-}H_2)$ in ref 5 was incorrect.

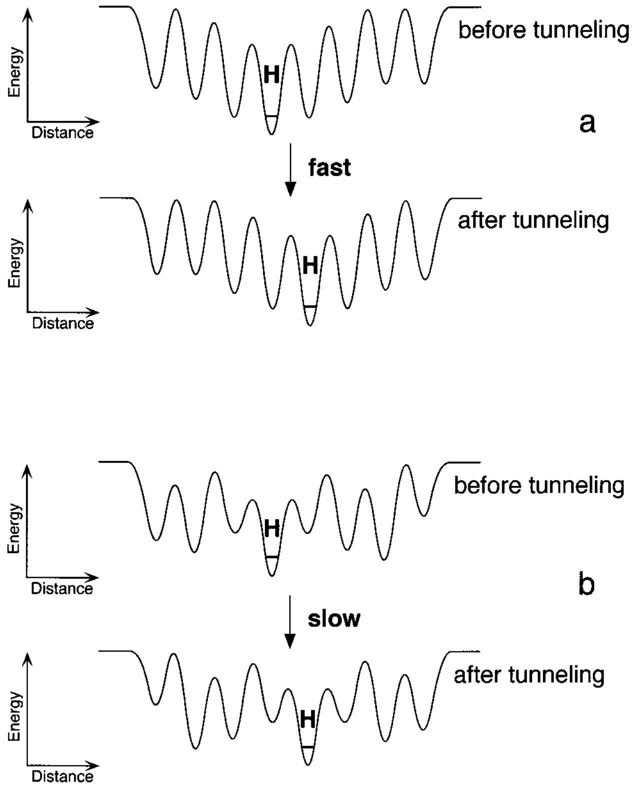

Figure 4. Schematic diagram of the potential energy around an H atom and a visual model of the multidimensional tunneling reaction in (a) solid p-H_2 and (b) solid n-H_2.

Table 3 shows that the rate constants for the tunneling reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$ at 4.2 K decrease with the increasing concentration of o-H_2 though o-H_2 molecules do not interact directly with H atoms. p-H_2 molecules are in the rotational quantum state of $J = 0$ that has spherical symmetry. o-H_2 molecules, however, are in the state of $J = 1$ and rotate in some direction. Thus, when o-H_2 molecules exist in pure crystal p-H_2, they disturb the periodicity of the crystal as the orientational defects. The tunneling reaction in the solid phase should be considered as a multidimensional tunneling process, accompanied by the local rearrangement of the surrounding molecules.

Figure 4 shows a schematic picture of the multidimensional tunneling reaction of an H atom in solid hydrogen. Figure 4a shows tunneling in pure crystal p-H_2. An H atom trapped in the hydrogen crystal causes some distortion in the lattice, which was pointed out by ENDOR spectroscopy[6] and theoretical calculation.[10] The potential energy around the H atom in pure crystal p-H_2 is periodic and symmetrical, bearing some distortion near the trapping site (cf. Figure 4a). When an H atom jumps to the next site by tunneling reaction, the distribution of the potential energy shifts to the next site. Since the shape of the potential energy in the pure p-H_2 crystal before tunneling is the same as that at the next site after the tunneling, the tunneling takes place fast, as shown in Figure 4a. Figure 4b shows tunneling in crystal n-H_2, which contains 75% o-H_2. o-H_2 molecules disturb the periodic distribution of the potential energy near an H atom. The tunneling reaction in the presence of o-H_2 molecules is accompanied by the shift of the asymmetrical distribution of the potential energy, resulting in the retardation of the tunneling reaction (cf. Figure 4b).

The quantum tunneling diffusion of muonium in solid is also a multidimensional tunneling phenomenon and is affected significantly by the presence of impurities. The hopping rate of muonium in KCl crystal is suppressed by the addition of Na as an impurity.[11] The orientational defects in solid N_2 retard the muonium hopping rate.[12] The muonium hopping rate in solid N_2 is also suppressed by the presence of H_2 impurities.[12] Theoretical studies of the impurity effect on the tunneling diffusion were conducted by Kagan et al.[11,13] The hopping rate (ν) by tunneling is given as

$$\nu \doteqdot 2\lambda J^2\Omega(T)/[\xi^2 + \Omega(T)^2] \qquad (4)$$

where λ is a factor determined by the crystal structure, J is the tunneling matrix element, and ξ is the energy shift between the initial and final states due to the disorder caused by impurities. $\Omega(T)$ is the damping factor corresponding to the final state level broadening caused by the phonon scattering, and it is proportional to temperature by T^{α}, where $\alpha = \sim 3-9$. When the energy shift by impurities is large and $|\xi| \gg \Omega(T)$, eq 4 is written as

$$\nu \doteqdot 2\lambda J^2\Omega(T)/\xi^2 \qquad (5)$$

The tunneling reaction in solid hydrogen can be discussed qualitatively by this model. The rate constant for the tunneling reaction H + p-H_2 in solid p-H_2 is 110 $cm^3\ mol^{-1}\ s^{-1}$ at 4.2 K, whereas that in solid n-H_2 is 24 $cm^3\ mol^{-1}\ s^{-1}$. Though the nearest neighbors of an H atom in solid n-H_2 are p-H_2 molecules, the energy shift (ξ) in solid n-H_2 from the o-H_2 impurities in the second and third layers around the H atom is larger than that in solid p-H_2 because of the large amount of o-H_2 in solid n-H_2. Thus, eq 5 indicates that the jump frequency, which corresponds to the rate constant of the H atom, in solid n-H_2 is lower than that in solid p-H_2.

It is very interesting that the presence of o-H_2 affects the rate of the tunneling reaction $H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$. The energy shift ($\xi$) caused by the orientational defects in solid N_2 is estimated to be about 1 K (2 cal mol^{-1}); it affects drastically the rate of quantum diffusion of muonium below 20 K.[12] Though little information on the energy shift due to the orientational defects of o-H_2 in solid p-H_2 is available, it may be estimated at about 1 K (2 cal mol^{-1}), since the orientational energy of o-H_2 molecules from the electric quadrupole−quadrupole interaction in solid p-H_2 is 0.8 K.[2] It is a new and surprising example of a chemical reaction wherein an amount of energy as small as 2 cal mol^{-1} can affect a rate of reaction whose barrier height amounts to 10 kcal mol^{-1}.[14] When a reaction occurs at room temperature by the reactants passing over the potential energy barrier, an interaction energy of above ca. 1 kcal mol^{-1} is necessary for controlling the reaction. Since a tunneling reaction takes place at ultralow temperature, the extremely small energy affects the rate of the chemical reaction.

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References and Notes

(1) Souers, P. C. *Hydrogen Properties for Fusion Energy*; University of California Press: Berkeley, CA, 1986.

(2) Meyer, H. *Low Temp. Phys.* **1998**, *24*, 381.

(3) Miyazaki, T.; Kumada, T.; Komaguchi, K.; Aratono, Y. *Radiat. Phys. Chem.* **1997**, *50*, 523.

(4) Kumada, T.; Kitagawa, N.; Mori, S.; Kumagai, J.; Aratono, Y.; Miyazaki, T. *J. Low Temp. Phys.* **1999**, *114*, 413.

(5) Miyazaki, T.; Hiraku, T.; Fueki, K.; Tsuchihashi, Y. *J. Phys. Chem.* **1991**, *95*, 26.

(6) Kumada, T.; Kitagawa, N.; Noda, T.; Kumagai, J.; Aratono, Y.; Miyazaki, T. *Chem. Phys. Lett.* **1998**, *288*, 755.

(7) Miyazaki, T.; Iwata, N.; Fueki, K.; Hase, H. *J. Phys. Chem.* **1990**, *94*, 1702.

(8) Miyazaki, T.; Kato, M.; Fueki, K. *Radiat. Phys. Chem.* **1990**, *36*, 501.

(9) Silvera, I. F. *Rev. Mod. Phys.* **1980**, *52*, 393.

(10) Li, D.; Voth, G. A. *J. Chem. Phys.* **1994**, *100*, 1785.

(11) Kadono, R. *Appl. Magn. Reson.* **1997**, *13*, 37.

(12) Storchak, V. G.; Brewer, J. H.; Morris, G. D. *Hyperfine Interact.* **1994**, *85*, 31.

(13) Kagan, Yu.; Prokofev, N. V. Zh. *Eksp. Teor. Fiz.* **1986**, *90*, 2176.

(14) Tunneling reaction is affected by the misalignment of energy levels between the initial and final states, which may be caused by temperature (T) in addition to impurities. The amount (Ω) of the misalignment at T (K) is roughly estimated by the following equation (cf. Kagan, Yu.; Maksimov, L. A.; Prokofev, N. V. *JETP Lett.* **1982**, *36*, 253): $\Omega \doteqdot 10^6\omega_D(T/\omega_D)^9$, where ω_D is Debye temperature. Ω in solid hydrogen at 4 K is about 2.6×10^{-5} K ($10^6 \times 100(4/100)^9$), which is much smaller than the energy shift (about 1 K) due to orientational defects of o-H_2 in solid parahydrogen. Thus, the temperature at 4 K does not affect tunneling reaction.