

# Decay Behaviors of $\text{H}_2^-$ Anions in Solid Parahydrogen: Effect of Nuclear Spins on Chemical Reactions

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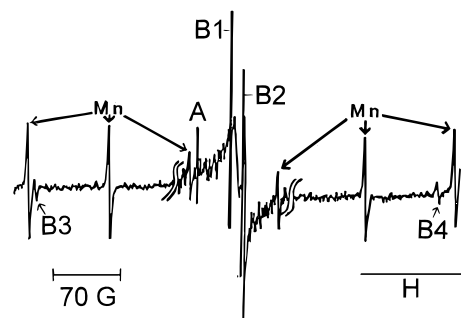
Decay processes of  $\text{H}_2^-$  anions in  $\gamma$ -ray-irradiated solid parahydrogen were studied by using an ESR spectrometer. The following interesting results were obtained. First, the initial yields of ortho- $\text{H}_2^-$  anions in the  $\gamma$ -irradiated solid parahydrogen were 3 times as large as those of para- $\text{H}_2^-$  anions. Second, the yields of para- $\text{H}_2^-$  anions decrease faster than those of ortho- $\text{H}_2^-$  anions upon storage of the irradiated samples at 4.2 K. Third, the decay rate of  $\text{H}_2^-$  anions is accelerated by the addition of HD and  $\text{D}_2$  molecules. Fourth,  $\text{H}_2^-$  anions at 2.2 K decay faster than at 4.2 K. According to the parity conservation rule in a homonuclear diatomic molecule, the energy of ortho- $\text{H}_2^-$  anions at the ground state is lower than that of para- $\text{H}_2^-$  anions, whereas that of ortho- $\text{H}_2$  molecules is higher than that of para- $\text{H}_2$  molecules at low temperatures. The first and second results are ascribed to para  $\rightarrow$  ortho conversion of  $\text{H}_2^-$  anions. The third result indicates that nearby HD and  $\text{D}_2$  accelerate the decay of  $\text{H}_2^-$  anion or broaden the spectra by superhyperfine interactions. The fourth result suggests a coherent tunneling mechanism of decay of  $\text{H}_2^-$  anions in the solid parahydrogen.

## Introduction

The solid hydrogen is a matrix of great interest that shows remarkable quantum phenomena.<sup>1,2</sup> Recently, Miyazaki has proposed that the solid parahydrogen (p- $\text{H}_2$ ), which has no nuclear spin moment, is a very useful matrix for a high-resolution ESR spectroscopy at ultralow temperatures, at which unstable species are trapped. Because of the absence of their superhyperfine interactions, the spectra narrow drastically.<sup>3</sup> In the  $\gamma$ -ray-irradiated solid p- $\text{H}_2$ , we have found the new stable species of  $\text{H}_2^-$  anions for the first time, which are unstable in the gas phase.<sup>4</sup> In addition, the new observation gives additional interesting results. para- $\text{H}_2^-$  (p- $\text{H}_2^-$ ) and ortho- $\text{H}_2^-$  (o- $\text{H}_2^-$ ) are formed in the ratio of 1:3,<sup>4</sup> though the purity of p- $\text{H}_2$  molecules in the solid is higher than 95%. It suggests that para  $\rightarrow$  ortho conversion has occurred during the irradiation, while in the case of the  $\text{H}_2$  molecule, ortho  $\rightarrow$  para conversion generally occurs at low temperatures. If the para  $\rightarrow$  ortho conversion of  $\text{H}_2^-$  anions still occurs after the irradiation, it should be detectable. In this study, we have examined the time evolution of the storage of para- and ortho- $\text{H}_2^-$  anions in the  $\gamma$ -irradiated solid p- $\text{H}_2$  at 2.2 and 4.2 K. Effects of HD and  $\text{D}_2$  on the decay processes of  $\text{H}_2^-$  anions were also studied.

## Experimental Section

p- $\text{H}_2$  samples were synthesized by normal hydrogen liquid passing through a column of iron(III) hydroxide ( $\text{FeO}(\text{OH})$ ) at 14 K. The purity of p- $\text{H}_2$  was more than 95 mol %. The solidified samples were irradiated at 4.2 K with  $\gamma$ -rays from a Co-60 source to a total dose of 0.3 kGy. In order to reduce the amounts of color centers in  $\gamma$ -irradiated quartz, we have used a new cryostat for  $\gamma$ -irradiation. In some cases, the samples were irradiated with X-rays (60 kV, 45 mA) at 4.5 K. The radical



**Figure 1.** ESR spectra of  $\text{H}_2^-$  anions in  $\gamma$ -ray-irradiated solid parahydrogen at 4.2 K measured in a wide range of magnetic field. The peaks, indicated by B1, B2, B3, and B4, are attributed to  $|I=1, I_z=0\rangle$ ,  $|0,0\rangle$ ,  $|1,1\rangle$ , and  $|1,-1\rangle$  states of  $\text{H}_2^-$  anions, respectively.

species produced were measured by ESR spectroscopy at 4.2 and 2.2 K. The 2.2 K was produced by evacuating the liquid helium by a rotary pump. The relative yields of  $\text{H}_2^-$  anions were obtained by measuring the peak heights of the ESR spectra. It was verified that the influence of the color centers on the peak height is almost negligible, because the signals originating from color centers did not decay at all during the measurements. The details of the experimental procedure were described in the previous paper.<sup>5</sup>

## Results

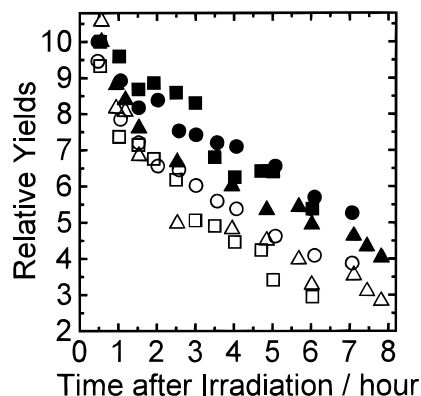
Figure 1 shows the ESR spectrum of the solid parahydrogen  $\gamma$ -ray-irradiated at 4.2 K. The peaks, indicated by B1, B2, B3, and B4, are of  $\text{H}_2^-$  anions, while the peak indicated by A is due to other species that has not been identified yet. B1, B2, B3, and B4 peaks are attributed to the states  $|I=1, I_z=0\rangle$ ,  $|0,0\rangle$ ,  $|1,1\rangle$ , and  $|1,-1\rangle$  of  $\text{H}_2^-$ , where  $I$  and  $I_z$  indicate the spin quantum number and the spin magnetic quantum number, respectively.<sup>4</sup> Thus, the B2 peak is of p- $\text{H}_2^-$  and the others, B1, B3, and B4, are of o- $\text{H}_2^-$ . As discussed above, it is interesting that the yields of o- $\text{H}_2^-$  are by 3 times larger than

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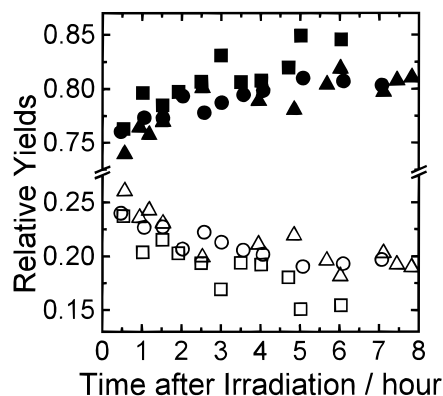
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**Figure 2.** Yields of H<sub>2</sub><sup>-</sup> anions in  $\gamma$ -irradiated solid p-H<sub>2</sub> as a function of storage time at 4.2 K. (●, ■, ▲) B1 (o-H<sub>2</sub><sup>-</sup>) peak in Figure 1; (○, □, △) B2 (p-H<sub>2</sub><sup>-</sup>) peak in Figure 1. Circles, squares, and triangles are the results in three different samples.



**Figure 3.** Ratios of the yields of o-H<sub>2</sub><sup>-</sup> (●, ■, ▲) and p-H<sub>2</sub><sup>-</sup> (○, □, △) to the total yields of H<sub>2</sub><sup>-</sup> anions against storage time at 4.2 K (see text).

those of p-H<sub>2</sub><sup>-</sup>, while the concentration of p-H<sub>2</sub> in the solid is greater than 95%. Though ortho-H<sub>2</sub> molecules (o-H<sub>2</sub>) at 6 mol % were added to the solid p-H<sub>2</sub>, the ratio of the yields of o-H<sub>2</sub><sup>-</sup> to those of p-H<sub>2</sub><sup>-</sup> was not changed.

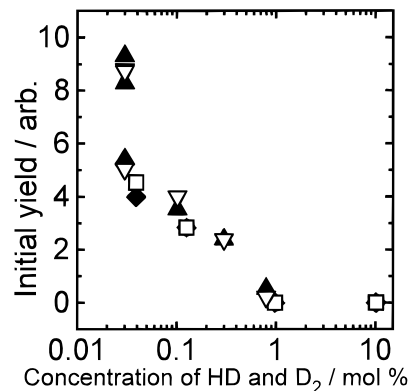
Figure 2 shows time course of the yields of H<sub>2</sub><sup>-</sup> anions upon storage of  $\gamma$ -irradiated solid p-H<sub>2</sub> at 4.2 K. The yields of B1 (*I*<sub>B1</sub>) and B2 (*I*<sub>B2</sub>) peaks in Figure 1, corresponding to o-H<sub>2</sub><sup>-</sup> and p-H<sub>2</sub><sup>-</sup>, are shown. The experiments have been done for three different samples, depicted by circles, squares, and triangles, respectively. As shown in the figure, the reproducibility of these data is good. The yields of B3 peak (*I*<sub>B3</sub>) and B4 peak (*I*<sub>B4</sub>) could not be measured because of their poor S/N ratio. But they are expected to be the same as those of B1, since they are attributed to ortho-H<sub>2</sub> and just separated by their spin magnetic quantum number (*I*<sub>z</sub>), which are not degenerated.<sup>4</sup>

Figure 3 shows the ratios of the yields of p-H<sub>2</sub><sup>-</sup> and o-H<sub>2</sub><sup>-</sup> to the total yields of H<sub>2</sub><sup>-</sup> anions that are obtained from Figure 2 as *I*<sub>B2</sub>/(3*I*<sub>B1</sub> + *I*<sub>B2</sub>) and 3*I*<sub>B1</sub>/(3*I*<sub>B1</sub> + *I*<sub>B2</sub>), respectively. Note that their denominators indicate the total yields of H<sub>2</sub><sup>-</sup> anions (*I*<sub>H2-</sub>) calculated as

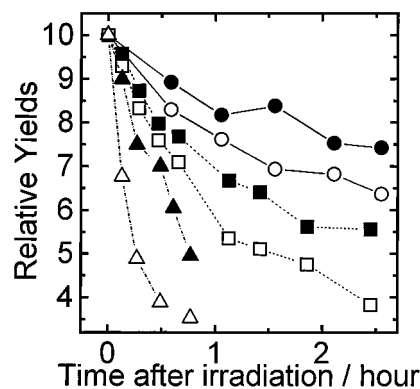
$$I_{H_2^-} = I_{o-H_2^-} + I_{p-H_2^-} = I_{B1} + I_{B2} + I_{B3} + I_{B4} = 3I_{B1} + I_{B2} \quad (1)$$

The ratio of o-H<sub>2</sub><sup>-</sup> increases upon the storage, while that of p-H<sub>2</sub><sup>-</sup> decreases.

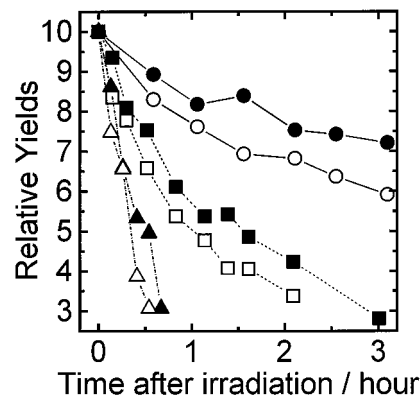
Figure 4 shows the initial yields of B1 and B2 peaks in Figure 1, corresponding to o-H<sub>2</sub><sup>-</sup> and p-H<sub>2</sub><sup>-</sup>, respectively, in  $\gamma$ -irradiated p-H<sub>2</sub>-HD-D<sub>2</sub> mixtures as a function of concentrations of HD and D<sub>2</sub> molecules at 4.2 K. The initial yields of H<sub>2</sub><sup>-</sup> anions decrease as the concentration of HD and D<sub>2</sub> in the solid increases.



**Figure 4.** Initial yields of H<sub>2</sub><sup>-</sup> anions in  $\gamma$ -irradiated solid p-H<sub>2</sub> at 4.2 K as a function of concentrations of HD (▲, ▼) or D<sub>2</sub> (◆, □) molecules. Data depicted by ◆ and □ contain 0.03 mol % HD. (▲, ◆) B1 (o-H<sub>2</sub><sup>-</sup>) peak in Figure 1; (▼, □) B2 (p-H<sub>2</sub><sup>-</sup>) peak in Figure 1.

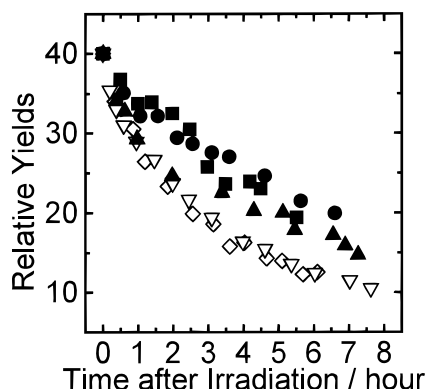


**Figure 5.** Relative yields of H<sub>2</sub><sup>-</sup> anions in  $\gamma$ -irradiated p-H<sub>2</sub>-HD mixtures against storage time at 4.2 K. (●, ■, ▲) o-H<sub>2</sub><sup>-</sup> and (○, □, △) p-H<sub>2</sub><sup>-</sup>, obtained from B1 and B2 peaks in Figure 1. Circles, squares, and triangles correspond to the HD concentrations at 0.03, 0.01, and 0.30 mol %, respectively. All the yields at *t* = 0 are normalized to 10.



**Figure 6.** Relative yields of H<sub>2</sub><sup>-</sup> anions in  $\gamma$ -irradiated p-H<sub>2</sub>-D<sub>2</sub> mixtures against storage time at 4.2 K. (●, ■, ▲) o-H<sub>2</sub><sup>-</sup> and (○, □, △) p-H<sub>2</sub><sup>-</sup>, obtained from B1 and B2 peaks in Figure 1. Circles, squares, and triangles correspond to the D<sub>2</sub> concentrations at 0, 0.01, and 0.10 mol %, respectively. All the samples contain 0.03 mol % HD. And all the yields at *t* = 0 are normalized to 10.

Figures 5 and 6 show the time course of relative yields of o-H<sub>2</sub><sup>-</sup> and p-H<sub>2</sub><sup>-</sup> in  $\gamma$ -irradiated p-H<sub>2</sub>-HD and p-H<sub>2</sub>-D<sub>2</sub> mixtures upon the storage of the sample at 4.2 K, respectively, where all the yields at *t* = 0 are normalized to 10. The yields of the anions in the solids containing 0.03, 0.10, and 0.30 mol % HD are shown in Figure 5, and those in the solids containing 0, 0.01, and 0.1 mol % D<sub>2</sub> are shown in Figure 6. It is pointed out that, in Figures 4 and 5, the results in the sample containing 0.03 mol % HD are obtained from pure solid parahydrogen,



**Figure 7.** Time course of the total yields of  $\text{H}_2^-$  anions in  $\gamma$ -irradiated solid  $\text{p-H}_2$  at 4.2 K ( $\bullet$ ,  $\blacksquare$ ,  $\blacktriangle$ ) and 2.2 K ( $\diamond$ ,  $\nabla$ ). The experiments were done for three samples at 4.2 K and for two samples at 2.2 K.

**TABLE 1: Parities of Wave Functions on Exchanging Each Proton in a  $\text{H}_2$  Molecule or a  $\text{H}_2^-$  Anion<sup>a</sup>**

	vibration	rotation	electron	nuclear spin	total
para- $\text{H}_2$	sym	sym	sym	anti	anti
ortho- $\text{H}_2$	sym	anti	sym	sym	anti
para- $\text{H}_2^-$	sym	anti	anti	anti	anti
ortho- $\text{H}_2^-$	sym	sym	anti	sym	anti

<sup>a</sup> The abbreviations sym and anti represent symmetric and antisymmetric of wave functions, respectively.

which contains 0.015% D atoms estimated from the natural abundance of D and H. Similarly, all the samples shown in Figure 6 inevitably contain 0.03 mol % HD. Both  $\text{o-H}_2^-$  and  $\text{p-H}_2^-$  anions decay faster proportional to the concentration of HD or  $\text{D}_2$ .

Figure 7 shows the time course of the total yields of  $\text{H}_2^-$  anions ( $I_{\text{n-H}_2^-}$ ) at 4.2 and 2.2 K. The experiments were done for three samples at 4.2 K and for two at 2.2 K. It is interesting that  $\text{H}_2^-$  anions at 2.2 K apparently decay faster than at 4.2 K.

## Discussion

**Conversion of  $\text{p-H}_2^-$  Anions to  $\text{o-H}_2^-$  Anions.** We now consider the problems why  $\text{p-H}_2^-$  anions decay faster than  $\text{o-H}_2^-$  and why the initial yields of  $\text{o-H}_2^-$  anions are higher than those of  $\text{p-H}_2^-$  anions. In a homonuclear diatomic molecule, its quantum state is restricted by its parity on exchanging each proton in a molecule. Since a proton is a fermion, the total parity of the wave function of the molecule ( $\Psi_{\text{molecule}}$ ) should be antisymmetric. Besides, it is represented as a product of that of each quantum state ( $\varphi$ ), which is written as  $\Psi_{\text{molecule}} = \varphi_{\text{vibration}} \times \varphi_{\text{rotation}} \times \varphi_{\text{electron}} \times \varphi_{\text{nuclear spin}}$ .<sup>6</sup> Parities of wave functions on exchanging each proton in a  $\text{H}_2$  molecule and a  $\text{H}_2^-$  anion are summarized in Table 1. Since a rotational wave function of a  $\text{p-H}_2$  molecule is symmetric and that of an  $\text{o-H}_2$  molecule is antisymmetric,  $\text{p-H}_2$  and  $\text{o-H}_2$  are in  $J = 0$  and  $J = 1$  rotational states at low temperatures, respectively. So the energy level of  $\text{o-H}_2$  molecule at the ground state is 170.5 K higher than that of  $\text{p-H}_2$ . Accordingly,  $\text{o-H}_2$  molecules convert into  $\text{p-H}_2$  molecules by themselves, when magnetic perturbations exist around them. On the contrary, the electronic state of electrons in a  $\text{H}_2^-$  anion is  $^2\Sigma_u^+$ , which means antisymmetric on the exchanging, while that in  $\text{H}_2$  molecule is  $^1\Sigma_g^+$ , which means symmetric.<sup>7,8</sup> Then,  $\text{p-H}_2^-$  and  $\text{o-H}_2^-$  anions at ground states are in  $J = 1$  and  $J = 0$  rotational states, respectively. Therefore, the energy of  $\text{o-H}_2^-$  anion becomes lower than that of  $\text{p-H}_2^-$  at 4 K. Accordingly, the result in Figure 3 is explained

**TABLE 2: Decay Rate of  $\text{H}_2^-$  Anions and Yields of  $\text{H}_2^-$  Anions and H Atoms in X-ray-Irradiated  $\text{p-H}_2$  at 4.5 K**

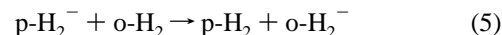
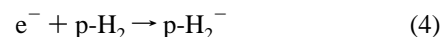
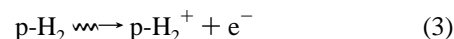
	irradiation time (min)	
	17	150
decay rate <sup>a</sup> (arb unit)	0.087	0.056
yields of $\text{H}_2^-$ (arb unit)	0.43	3.5
yields of H (arb unit)	$2.5 \times 10^3$	$2.3 \times 10^4$

<sup>a</sup> Obtained by the kinetic plot of pseudo-first-order reaction for the data.

as para  $\rightarrow$  ortho conversion of  $\text{H}_2^-$  anion under the magnetic perturbation caused by an unpaired electron in it.



When  $\text{o-H}_2$  at 6 mol % was added to  $\text{p-H}_2$ , the ratio of the initial yields of  $\text{o-H}_2^-$  to those of  $\text{p-H}_2^-$  in the irradiated solid is the same as that in the irradiated pure  $\text{p-H}_2$ . Thus, the higher yields of  $\text{o-H}_2^-$  anions compared to those of  $\text{p-H}_2^-$  cannot be ascribed to the electron transfer from  $\text{p-H}_2^-$  anion to  $\text{o-H}_2$  molecule (reaction 5).

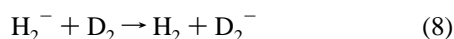
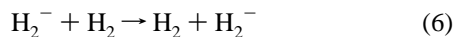


The high initial yields of  $\text{o-H}_2^-$  are probably due to the para  $\rightarrow$  ortho conversion of  $\text{p-H}_2^-$  during  $\gamma$ -irradiation (reaction 2). In contrast with the case of  $\text{H}_2$  molecules,  $\text{p-H}_2^-$  anions convert into  $\text{o-H}_2^-$ .

**Decay Mechanism of  $\text{H}_2^-$  Anions.**  $\text{H}_2^-$  anions would migrate in the solid and finally meet to react with other species in the solid. Now, we will discuss the mechanism of the decay of  $\text{H}_2^-$  anions. Table 2 shows decay rates of  $\text{H}_2^-$  anions and initial yields of H atoms and  $\text{H}_2^-$  anions at 4.5 K in the solid parahydrogen irradiated by X-rays at 17 and 150 min. In spite of the large difference in their irradiation times, both decay rates are the same within their experimental errors, while the yields of  $\text{H}_2^-$  anions and H atoms increase linearly with an increase of the irradiation time. As accompanied by the yields of  $\text{H}_2^-$  anions, those of cations are also expected to increase with an increase of the irradiation time for conservation of their charge in the solid. If  $\text{H}_2^-$  anions react with H atoms by the electron transfer reaction,  $\text{H}_2^- + \text{H} \rightarrow \text{H}_2 + \text{H}^-$ , or neutralize with cations, the decay rate of  $\text{H}_2^-$  anions must be proportional to the yields of H atoms or cations, respectively. However, as discussed above, it does not depend upon the yields of H atoms or cations, suggesting that the disappearance process of  $\text{H}_2^-$  anions is due to neither the reaction with H atoms nor that with cations.

Now, the effect of the addition of HD and  $\text{D}_2$  on the decay of  $\text{H}_2^-$  anions will be discussed. Figure 4 shows that the initial yields of B1 ( $\text{o-H}_2^-$ ) and B2 ( $\text{p-H}_2^-$ ) peaks in Figure 1 decrease as the concentration of HD and  $\text{D}_2$  in the solid increases. Moreover, Figures 5 and 6 show that the decay rates of both  $\text{o-H}_2^-$  and  $\text{p-H}_2^-$  anions are accelerated by addition of HD and  $\text{D}_2$  molecules, indicating that  $\text{H}_2^-$  anions interact with HD and  $\text{D}_2$  molecules. When  $\text{H}_2^-$  anions (probably electrons in  $\text{H}_2^-$ ), HD, and  $\text{D}_2$  migrate in the solid (reaction 6) and meet, they disappear by some reaction with HD or  $\text{D}_2$  molecules.<sup>9,10</sup> Note that  $\text{HD}^-$  or  $\text{D}_2^-$  anions are never created, because reactions 7

and 8 are endothermic processes, which are derived from ground state vibrational energies of H<sub>2</sub>, HD, and D<sub>2</sub> molecules.



In these experiments, the ESR spectrum of HD<sup>-</sup> and D<sub>2</sub><sup>-</sup> anions could not be detected.

So, it is probable that nearby HD and D<sub>2</sub> accelerate the decay of H<sub>2</sub><sup>-</sup> anion or broaden the spectra by superhyperfine interactions. To clarify the problem, we are now planning additional experiments.

**Temperature Dependence of the Decay of H<sub>2</sub><sup>-</sup> Anions.** Figure 7 shows that the H<sub>2</sub><sup>-</sup> anions at 2.2 K decay faster than those at 4.2 K. Though the decay rate should decrease with decreasing temperature in the classical theory, it increases at lower temperature in this work. The decay rate is probably controlled by the rate for the diffusion of electron in H<sub>2</sub><sup>-</sup> anions (reaction 6). Therefore, the data suggest that the electron in H<sub>2</sub><sup>-</sup> anions migrate faster at the lower temperatures. It is probable that the reaction occurs via tunneling because of the light mass of an electron. Moreover, its inverse temperature dependence of the diffusion rate is probably caused by repetition of coherent tunneling: particle transfer without phonon absorption or emission.<sup>11</sup> For example, Kiefl et al. previously reported that muon, whose mass is about 1/9 of a proton, migrates in ionic solids by coherent tunneling processes at ultralow temperatures.<sup>12,13</sup> The rate for the diffusion increases clearly with

decreasing temperature. By the same behavior as this, the temperature dependence on the decay of H<sub>2</sub><sup>-</sup> anions shown in Figure 7 suggests that H<sub>2</sub><sup>-</sup> anions diffuse in the solid parahydrogen by coherent tunneling.

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