

# Negative and positive ion trapping by isotopic molecules in cryocrystals in case of solid parahydrogen containing electrons and $H_6^+$ radical cations

Yuta Shimizu,<sup>1</sup> Makoto Inagaki,<sup>1</sup> Takayuki Kumada,<sup>2,b)</sup> and Jun Kumagai<sup>1,a)</sup>

<sup>1</sup>Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>2</sup>Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

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We performed electron spin resonance studies of trapped electrons and  $H_6^+$  radical cations produced by radiolysis of solid parahydrogen (p- $H_2$ ), p- $H_2$ –ortho- $D_2$  (o- $D_2$ ), and p- $H_2$ –HD mixtures. Yields of trapped electrons,  $H_6^+$  radical cations, and its isotopic analogs  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) increased with increasing o- $D_2$  and HD concentrations in solid p- $H_2$ . Electrons were found trapped near an o- $D_2$  or an HD in solid p- $H_2$  due to the long-range charge-induced dipole and quadrupole interactions between electrons and isotopic hydrogen molecules.  $H_6^+$  radical cations diffuse in solid p- $H_2$  by repetition of  $H_6^+ + H_2 \rightarrow H_2 + H_6^+$  and are trapped by ortho- $D_2$  or HD to form  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) as isotope condensation reactions. Decay behaviors of these cations by the repetition, isotope condensation, and geminate recombination between electrons and  $H_{6-n}D_n^+$  ( $4 \geq n \geq 0$ ) were reproduced by determining the corresponding reaction rate constants  $k_1$ ,  $k_2$ , and  $k_3$ . Values of 0.045 and 0.0015 L mol<sup>-1</sup> min<sup>-1</sup> were obtained for  $k_1$  ( $H_6^+ + D_2 \rightarrow H_2 + H_4D_2^+$ ) and  $k_2$  ( $H_4D_2^+ + D_2 \rightarrow H_2 + H_2D_4^+$ ), respectively, and the value was quasinull for  $k_3$  ( $H_2D_4^+ + D_2 \rightarrow H_2 + D_6^+$ ). These rate constants suggest that hole mobility drastically decreased in the repetition reaction when  $H_6^+$  radical cations acting as hole carriers formed  $H_4D_2^+$  or  $H_2D_4^+$ . HD and  $D_2$  molecules, therefore, act as electron and hole acceptors in irradiated solid p- $H_2$ –o- $D_2$  and p- $H_2$ –HD mixtures. © 2010 American Institute of Physics. [doi:10.1063/1.3432780]

## I. INTRODUCTION

Electrons trapped in solids at cryogenic temperature have been extensively studied for four decades in the field of radiation chemistry for aqueous matrices,<sup>1</sup> alcohols,<sup>2–6</sup> hydrocarbons,<sup>6,7</sup> and heterocompounds.<sup>4,8</sup> Although most electrons produced by the radiolysis of solid matter recombine with the parent cations, some of them are trapped in local potential minima such as defects, cracks, and distortions to form trapped electrons ( $e_t^-$ ).<sup>9,10</sup> Yields of  $e_t^-$  in solids usually depend on solid crystallinity and polarity. Electrons in glassy solids can be stabilized as  $e_t^-$  by local rearrangement of the surrounding molecules to produce larger free volumes for reducing kinetic energy.<sup>10–12</sup> Polar molecules in solids assist in reducing the potential energy of electron by charge polarization.<sup>3</sup> On the other hand, no electron can be trapped in irradiated molecular crystals, except in irradiated single crystals of  $D_2O$ ,<sup>13</sup> trehalose,<sup>14</sup> and crystals of diols.<sup>2</sup> Large crystallization energy hinders the local rearrangements of molecules in crystals.<sup>9</sup>

Ten years ago, the yields of  $e_t^-$  produced by radiolysis of solid parahydrogen (p- $H_2$ ) were found to significantly increase with increasing  $D_2$  or HD concentrations, whereas no

$e_t^-$  could be detected in their absence by electron spin resonance (ESR) spectroscopy.<sup>15</sup> Recently, we succeeded in detecting  $e_t^-$  in pure p- $H_2$  and found that the isotope effect on  $e_t^-$  yields was 10–24-fold with increasing  $D_2$  and HD concentrations ( $\sim 1$ –8 mol %) in solid p- $H_2$ . This experimental result addresses the following outstanding issues. First, the isotope effect on  $e_t^-$  yields is observed for small concentrations of isotopic hydrogen molecules in irradiated solid p- $H_2$ . Isotope effects on  $e_t^-$  yields in condensed matter have been studied by several researchers.<sup>13,16,17</sup> Wang and Willard<sup>16</sup> reported that  $e_t^-$  yields produced in fully deuterated saturated hydrocarbons such as 3-methylpentane- $d_{14}$ , methylcyclohexane- $d_{14}$ , and 3-methylheptane- $d_{18}$  glasses irradiated using  $\gamma$ -rays at 77 K were around 1.5 times larger than in protiated hydrocarbons. Regarding liquid phases, the survival probability of  $e_t^-$  in liquid  $D_2O$  has been reported to be about 1.1 times higher than in liquid  $H_2O$ .<sup>17,18</sup> Hase and Kawabata<sup>13</sup> detected  $e_t^-$  in irradiated crystalline  $D_2O$  at 4 K using ESR and photoabsorption spectroscopy, in particular, when  $H_2O$  contents in  $D_2O$  were below 3% in volume. Because isotope effects on  $e_t^-$  yields in fully deuterated irradiated solvents were below twofold increases in these reports, except for crystalline  $D_2O$ , 10–24-fold increases obtained by increasing  $D_2$  and HD concentrations ( $\sim 1$ –8 mol %) in solid p- $H_2$  were astonishingly large. In addition, significant amounts of  $e_t^-$  have been yielded in irradiated solid hydrogens that are not in amorphous but crystalline phase. The detection of  $e_t^-$  in solid p- $H_2$  crystals containing small amounts of isotopic

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: kumagai@apchem.nagoya-u.ac.jp.

<sup>b)</sup> Present address: Quantum Beam Science Directorate, Kansai Photon Science Institute, Japan Atomic Energy Agency, 8-1 Umemidai, Kizugawa, Kyoto 619-0215, Japan.

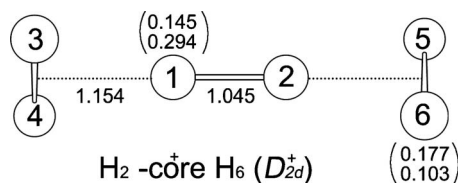


FIG. 1. MP2/cc-pVTZ optimized geometry of  $\text{H}_6^+$  reported by Kurosaki and Takayanagi (Ref. 29). Bond lengths are shown in angstroms. Atomic net charges (upper line) and spin density (lower line) are shown in parentheses. Two side-on  $\text{H}_2$  molecules (3–6) are chemically bound to the  $\text{H}_2^+$ -core (1 and 2).

hydrogen molecules is unusual. Solid hydrogen crystals must be perfect for the following reasons. Hydrogen molecules in solid hydrogen have large zero-point motions, which repair cracks, distortions, and imperfections, maintaining high homogeneity of solid without annealing.<sup>19,20</sup> These occur because molecular hydrogen is light and undergoes small intermolecular interactions. In particular, p- $\text{H}_2$  molecules exclusively have a  $J=0$  rotational quantum state with no electric quadrupole moment. Therefore, solid p- $\text{H}_2$  is free from inhomogeneous electric quadrupole-quadrupole interactions between neighboring p- $\text{H}_2$  molecules. Neither an  $\text{H}_2$  nor a  $\text{D}_2$  has dipole moment and an HD has a negligible dipole moment.<sup>21</sup> The present model of electron trapping cannot account for this isotope effect as the trapping depends on inhomogeneity and polarity in solids.<sup>9–11,21</sup>

$\text{H}_6^+$  radical cations, which are composed of an  $\text{H}_2^+$ -core sandwiched between two side-on  $\text{H}_2$  molecules, have been successfully observed by ESR spectroscopy in solid p- $\text{H}_2$  (Fig. 1).<sup>22</sup> Their isotopic analogs ( $\text{H}_{6-n}\text{D}_n^+$  ( $4 \geq n \geq 1$ )), including  $\text{H}_5\text{D}^+$ ,  $\text{H}_4\text{D}_2^+$ , and  $\text{H}_2\text{D}_4^+$  were also detected.<sup>22</sup> In these analogs, the  $\text{H}_2^+$ -core and side-on  $\text{H}_2$  molecules present in  $\text{H}_6^+$  are replaced by  $\text{D}_2$  or HD molecules. Singly  $\text{D}_2$ -substituted  $\text{H}_4\text{D}_2^+$  is denoted as “ $\text{H}_4\text{D}_2^+$ ” and its doubly HD-substituted counterpart is denoted as “HD-sub.  $\text{H}_4\text{D}_2^+$ .” Note that  $\text{D}_2$ -core  $\text{H}_4\text{D}_2^+$  has not been detected to this date.

Similar to the  $e_t^-$  yields, the total yields of  $\text{H}_6^+$  and  $\text{H}_{6-n}\text{D}_n^+$  ( $4 \geq n \geq 1$ ) increased with increasing ortho- $\text{D}_2$  (o- $\text{D}_2$ ) or HD concentrations. However, these increases have only been investigated by qualitative analysis. In this study, we performed a quantitative decay analysis for the concentrations of  $\text{H}_6^+$  and  $\text{H}_{6-n}\text{D}_n^+$  ( $4 \geq n \geq 1$ ) in irradiated solid p- $\text{H}_2$  at 4.2 K and performed a kinetic analysis for isotope condensation reactions between  $\text{H}_6^+$  and hydrogen isotopic molecules. In other words,  $\text{H}_6^+$  were trapped by o- $\text{D}_2$  and/or HD molecules in solid p- $\text{H}_2$ . Therefore, isotopic hydrogen molecules in solid p- $\text{H}_2$  play an important role in trapping  $\text{H}_6^+$  and electrons. This paper reports isotope effects on the yields and decays of  $e_t^-$  and  $\text{H}_6^+$  in solid p- $\text{H}_2$ , p- $\text{H}_2$ -o- $\text{D}_2$ , and p- $\text{H}_2$ -HD and discusses the trapping mechanisms. We propose new trapping mechanisms of electron and cation by hydrogen isotopic molecules, which have not been accurately considered in the history of radiation chemistry.

## II. EXPERIMENT

p- $\text{H}_2$  molecules were obtained and purified by immersing iron hydroxide  $\text{FeO}(\text{OH})$  into liquid normal  $\text{H}_2$  (>99.999 99%; Taiyo Nippon Sanso Co., Japan) for 10 h at

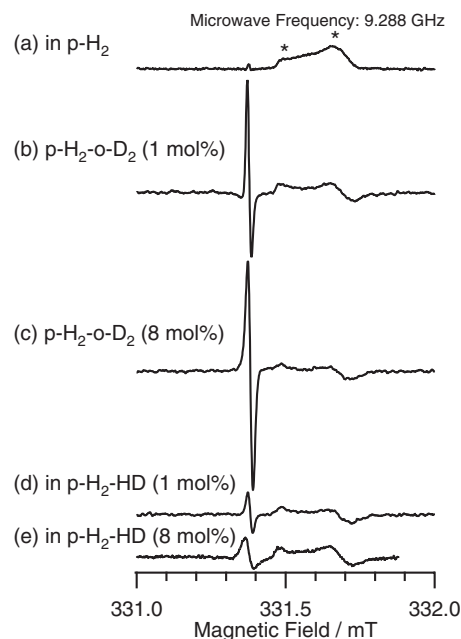


FIG. 2. ESR spectra of  $e_t^-$  produced in  $\gamma$ -ray irradiated solids at 4.2 K. (a) p- $\text{H}_2$ , (b) p- $\text{H}_2$ -o- $\text{D}_2$  (1 mol %), (c) p- $\text{H}_2$ -o- $\text{D}_2$  (8 mol %), (d) p- $\text{H}_2$ -HD (1 mol %), and (e) p- $\text{H}_2$ -HD (8 mol %). Peaks denoted by asterisks were from ESR tubes and Dewar made by radiolysis of quartz. ESR field-modulation frequency, amplitude, and microwave power were 50 kHz, 0.005 mT, and 1 nW, respectively, for p- $\text{H}_2$  and, 50 kHz, 0.01 mT, and 0.1 nW, respectively, for p- $\text{H}_2$ -o- $\text{D}_2$  and p- $\text{H}_2$ -HD mixtures. Peak heights were normalized using field modulation and the square root of microwave power.

14 K in a cryocooler (Daikin UV204SCL). o- $\text{D}_2$  molecules were obtained from normal  $\text{D}_2$  (n- $\text{D}_2$ ) (99.95%; Isotec Inc.) in a similar manner at 18 K. All hydrogen gases, p- $\text{H}_2$ , o- $\text{D}_2$ , and HD (96%; Isotec Inc.) were purified through seven condensation/vaporization cycles at condensation and vaporization temperatures of 10 and 25 K, respectively. The gases were recovered at 25 K. Five p- $\text{H}_2$  samples, namely, p- $\text{H}_2$ , p- $\text{H}_2$ -o- $\text{D}_2$  (1 and 8 mol %), and p- $\text{H}_2$ -HD (1 and 8 mol %) were prepared using different isotopic hydrogen molecule contents. All samples contained 0.1 mol % of He gas (99.9999%; Taiyo Nippon Sanso Co.) for thermal contact. The samples were sealed in quartz cells and immersed in a quartz Dewar filled with liquid He to prepare the solids. Solid samples were irradiated with  $\gamma$ -rays for  $\sim 1$  h to the total dose of 2.88 kGy at the  $^{60}\text{Co}$   $\gamma$ -ray irradiation facility (Nagoya University). The irradiated samples were placed in an X-band ESR spectrometer (JEOL JES-RE1X) to measure the time course of ESR lines at 4.2 K. Microwave frequency and magnetic field of the spectrometer were monitored using a microwave frequency counter (Hewlett-Packard, 53150A, USA) and an NMR field meter (Echo Electronics Co. Ltd., EFM-2000AX, Japan), respectively. Microwave powers of 1.0 and 0.1–1 nW were used to measure the  $\text{H}_6^+$  and  $e_t^-$  lines, respectively.  $\text{H}_6^+$  and  $e_t^-$  yields were determined by double integration of the ESR lines using hexyl radicals in  $\gamma$ -ray irradiated *n*-hexane (>97%; Kanto Chemical Co., Inc., Japan) as a reference. The  $G$ -value, which corresponds to the number of products per 100 eV energy absorbed, has been reported as 4.7, on average, for hexyl radicals under  $\gamma$ - or X-ray irradiation.<sup>9</sup>

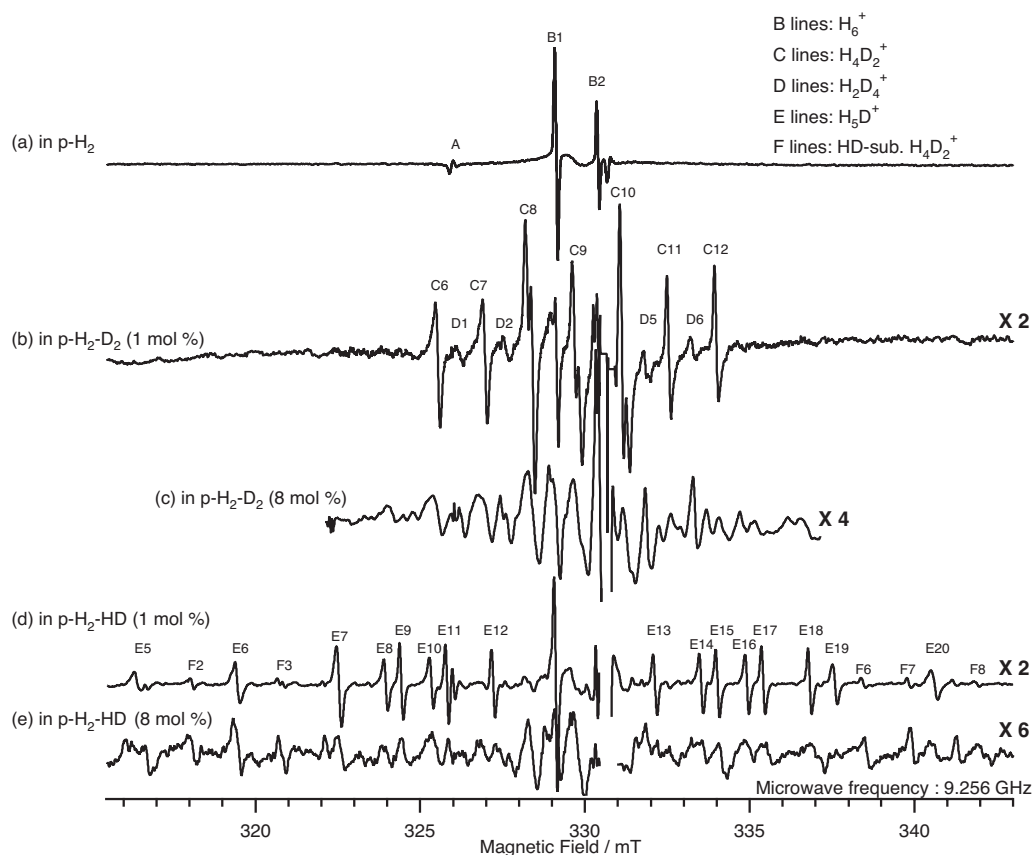


FIG. 3. ESR spectra of  $\gamma$ -ray irradiated solid (a)  $p\text{-H}_2$ , [(b) and (c)]  $p\text{-H}_2\text{-o-D}_2$  mixtures, and [(d) and (e)]  $p\text{-H}_2\text{-HD}$  mixtures measured with a field-modulation frequency of 50 kHz, an amplitude of 0.1 mT, and a microwave power of 1 mW. ESR lines marked as B, C, D, E, and F correspond to  $\text{H}_6^+$ ,  $\text{H}_4\text{D}_2^+$ ,  $\text{H}_2\text{D}_4^+$ ,  $\text{H}_5\text{D}^+$ , and HD-sub.  $\text{H}_4\text{D}_2^+$ , respectively (Ref. 22). The singlet peak marked as A in (a) results from a forbidden transition of H atom radicals.

### III. RESULTS

Figure 2 shows the ESR spectra of  $e_1^-$  produced in solid  $p\text{-H}_2$ ,  $p\text{-H}_2\text{-o-D}_2$ , and  $p\text{-H}_2\text{-HD}$  mixtures. The lines at 331.38 mT ( $g=2.0023$ ) were attributed to  $e_1^-$ . Peak intensity of  $e_1^-$  significantly increased with increasing o- $\text{D}_2$  or HD concentrations in  $p\text{-H}_2$ . The isotope effect on  $e_1^-$  yields was more significant for o- $\text{D}_2$  than for HD. Figure 3 shows the ESR spectra of  $\text{H}_6^+$  [B lines:  $I_{12}$  (nuclear spin quantum number of  $\text{H}_2^+$ -core)=0 and 1;  $I_{34}=I_{56}=0$ ; numbers in subscript corresponds to the atoms in Fig. 1] and  $\text{H}_{6-n}\text{D}_n^+$  ( $4 \geq n \geq 1$ ) produced in  $p\text{-H}_2$ ,  $p\text{-H}_2\text{-o-D}_2$ , and  $p\text{-H}_2\text{-HD}$ . In addition to B lines, ESR lines were observed for  $\text{H}_4\text{D}_2^+$  [C lines:  $I_1=I_2=1/2$ ;  $I_{34}=0$ ;  $I_{56}(\text{o-D}_2)=0$  and 2] and  $\text{H}_2\text{D}_4^+$  [D lines:

$I_{12}=0$  and 1;  $I_{34}(\text{o-D}_2)=I_{56}(\text{o-D}_2)=0$  and 2 for  $\text{H}_2^+$ -core  $\text{H}_2\text{D}_4^+$  and  $I_{12}(\text{o-D}_2)=0$  and 2;  $I_{34}=0$ ;  $I_{56}(\text{o-D}_2)=0$  and 2 for  $\text{D}_2^+$ -core  $\text{H}_2\text{D}_4^+$ ] in irradiated solid  $p\text{-H}_2\text{-o-D}_2$  mixtures. Similarly, ESR lines were also observed for  $\text{H}_5\text{D}^+$  [E lines:  $I_1(\text{H})=1/2$ ;  $I_2(\text{D})=1$ ;  $I_{34}=I_{56}=0$  for HD $^+$ -core  $\text{H}_5\text{D}^+$  and  $I_1=I_2=1/2$ ;  $I_{34}=0$ ;  $I_5(\text{H})=1/2$ ;  $I_6(\text{D})=1$  for  $\text{H}_2^+$ -core  $\text{H}_5\text{D}^+$ ] and HD-sub.  $\text{H}_4\text{D}_2^+$  [F lines:  $I_1=I_2=1/2$ ;  $I_3(\text{H})=I_5(\text{H})=1/2$ ;  $I_4(\text{D})=I_6(\text{D})=1$ ] in irradiated solid  $p\text{-H}_2\text{-HD}$  mixtures. The hyperfine coupling constants (HFCC) for these radical cations is listed in Table I. The precise assignments were discussed in our previous study.<sup>22</sup> Although only 1 mol % of o- $\text{D}_2$  or HD was added to  $p\text{-H}_2$ ,  $\text{H}_4\text{D}_2^+$ , and  $\text{H}_5\text{D}^+$ , ESR intensities were found to be much higher than for

TABLE I. HFCC of  $\text{H}_6^+$  and  $\text{H}_{6-n}\text{D}_n^+$  ( $4 \geq n \geq 1$ ) in mT detected by the analysis of B-F lines.  $A_1$ – $A_6$  indicate the HFCC for the first to sixth atoms in Fig. 1, respectively. Italic values show HFCC for D atoms. Values in parentheses show HFCC values for D atoms multiplied by  $\gamma_p/\gamma_d=6.514$ .

Lines	Species	Core	$g$ value	$A_1$		$A_2$		$A_5$	$A_6$	Remarks
				Iso.	Ani.	Iso.	Ani.			
B	$\text{H}_6^+$	$\text{H}_2^+$	2.00212	20.441	−0.061	20.441	−0.061			
C	$\text{H}_4\text{D}_2^+$	$\text{H}_2^+$	2.0020	21.83	−0.08	19.43	−0.16	<i>1.44</i> (9.38)	<i>1.44</i> (9.38)	
D	$\text{H}_2\text{D}_4^+$	$\text{H}_2^+$	2.0020	21		21		<i>1.44</i> (9.38)	<i>1.44</i> (9.38)	$A_3=A_4=A_5=A_6$
		$\text{D}_2^+$	2.0020	<i>3.35</i> (21.8)		<i>2.98</i> (19.4)		<i>1.44</i> (9.38)	<i>1.44</i> (9.38)	
E	$\text{H}_5\text{D}^+$	$\text{H}_2^+$	2.0020	21.24	−0.10	19.86	−0.10	9.58	<i>1.40</i> (9.12)	
		HD $^+$	2.0020	21.02	−0.12	<i>3.02</i> (19.7)	<i>−0.02</i> (−0.12)			
F	HD-sub. $\text{H}_4\text{D}_2^+$	$\text{H}_2^+$	2.0020	21		21		9.52	<i>1.37</i> (8.92)	$A_3=A_5$ , $A_4=A_6$

TABLE II. Relative yields of  $e_t^-$ ,  $H_6^+$ ,  $H_4D_2^+$ ,  $H_2D_4^+$ ,  $H_5D^+$ , HD-sub.  $H_4D_2^+$ , and H atom radicals produced in p- $H_2$ , p- $H_2$ -o- $D_2$ , and p- $H_2$ -HD mixtures measured 30 min after irradiation.

	Negative $e_t^-$	Positive						Neutral H atom radicals
		$H_6^+$	$H_4D_2^+$	$H_2D_4^+$	$H_5D^+$	HD-sub. $H_4D_2^+$	Total <sup>a</sup>	
p- $H_2$	~7	1	...	...	...	...	1	$6 \pm 1 \times 10^3$
p- $H_2$ - $D_2$ (1 mol %)	70	0.5	1.9	0.4	...	...	2.8	$6 \pm 1 \times 10^3$
p- $H_2$ - $D_2$ (8 mol %)	170	...	$4 \pm 1$	$5 \pm 2$	...	...	$9 \pm 3$	n.d.
p- $H_2$ -HD (1 mol %)	20	0.6	...	...	1.2	0.2	2.0	$5 \pm 1 \times 10^3$
p- $H_2$ -HD (8 mol %)	70	...	...	...	1.7	0.9	2.6	n.d.

<sup>a</sup>The total yield of  $H_6^+$  and  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ).

$H_6^+$  in solid p- $H_2$ -o- $D_2$  [Fig. 2(b)] and p- $H_2$ -HD [Fig. 2(d)], respectively. The B lines were not visible in p- $H_2$ -o- $D_2$  [Fig. 2(c)] and p- $H_2$ -HD [Fig. 2(e)] for o- $D_2$  and HD concentrations of 8 mol %.

Table II shows the relative yields of radical ions detected 30 min after irradiation in p- $H_2$ , p- $H_2$ -o- $D_2$ , and p- $H_2$ -HD mixtures. The yields were obtained by double integration of the corresponding ESR lines. Compared to the  $H_6^+$  yield in p- $H_2$ , the total yields of  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  displayed 2.8- and 9-fold increases upon addition of 1 and 8 mol % o- $D_2$  to p- $H_2$ , respectively. The total yields of  $H_6^+$ ,  $H_5D^+$ , and HD-sub.  $H_4D_2^+$  increased 2- and 2.6-folds upon addition of 1 and 8 mol % HD to p- $H_2$ , respectively. These increases in total yields of  $H_6^+$  and  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) caused by adding HD were less significant than that caused by adding o- $D_2$  at the same concentration. The ratios of the  $H_6^+$ : $H_4D_2^+$ : $H_2D_4^+$  yields would be 97:3:0.03 for p- $H_2$ -o- $D_2$  (1 mol %) and 74:23:1.9 for p- $H_2$ -o- $D_2$  (8 mol %) if  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  were produced statistically with respect to p- $H_2$  and o- $D_2$  concentrations. However, the experimental ratios were 18:68:14 and 0:44:56, respectively. Similarly, the ratios of the  $H_6^+$ : $H_5D^+$ :HD-sub.  $H_4D_2^+$  yields were 30:60:10 for p- $H_2$ -HD (1 mol %) and 0:65:35 for p- $H_2$ -HD (8 mol %). These results clearly show that the  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) species were preferentially produced in solid p- $H_2$ . The yield of H atom radicals was ~6000 times greater than that of  $H_6^+$  and was independent from o- $D_2$  and HD concentrations.

Figure 4 shows the decay behavior of  $e_t^-$ ,  $H_6^+$ ,  $H_4D_2^+$ ,  $H_2D_4^+$ , and H atom radicals produced in p- $H_2$  and p- $H_2$ -o- $D_2$  mixtures. The decay behavior of  $e_t^-$  in p- $H_2$ -o- $D_2$  mixtures was found to be independent of o- $D_2$  concentration and  $\gamma$ -ray dose [Figs. 4(a) and 4(b)].  $H_6^+$  decayed much faster in p- $H_2$ -o- $D_2$  (1 mol %) than that in p- $H_2$ . On the other hand,  $H_4D_2^+$  and  $H_2D_4^+$  decayed in a similar manner in both p- $H_2$ -o- $D_2$  mixtures [Figs. 4(d)-4(f)]. H atom radicals did not decay in p- $H_2$  (Ref. 19) and p- $H_2$ -o- $D_2$  mixtures [Fig. 4(c)]. The absolute yields of  $e_t^-$ ,  $H_5D^+$ , and HD-sub.  $H_4D_2^+$  in p- $H_2$ -HD were lower than those of  $e_t^-$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  in p- $H_2$ -o- $D_2$ , respectively. However, the decay behavior of the corresponding species was almost the same.

Figure 5 shows the decay rates determined using the inverse lifetimes ( $1/\tau_{1/e}$ ) of  $e_t^-$  and  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ).  $H_6^+$  decayed significantly faster than  $H_4D_2^+$ , which decayed a little faster than  $H_2D_4^+$ . The decay rate of  $H_2D_4^+$  was very close to that of  $e_t^-$ .

## IV. DISCUSSION

We would like to describe the radiation chemical reactions of hydrogens before discussing the trapping mechanisms of  $e_t^-$  and  $H_6^+$ . When gaseous  $H_2$  molecules are subjected to ionizing radiation,<sup>9,23</sup> the ionization of  $H_2$  molecules initially produce  $H_2^+$  as



The  $H_2^+$  ions disappear immediately by reacting with neighboring  $H_2$  molecules to form  $H_3^+$  as



The  $H_3^+$  ions recombine with electrons to produce H atom radicals under irradiation:



H atom radicals are also generated by dissociation of  $H_2$  in an excited state:



These ions and H atom radicals are expected to be produced in irradiated solid hydrogen. Although electrons produced in irradiated gaseous  $H_2$  immediately recombine with the cations, very small portions of  $e^-$  can be trapped in the solid phase to form  $e_t^-$  without undergoing recombination. The yield of  $e_t^-$  was about seven times higher than that for  $H_6^+$  in solid p- $H_2$  (cf. Table II). The charge balance suggests a presence of other positive ions beside  $H_6^+$  in irradiated solid p- $H_2$ . Gas phase results indicate that  $H_3^+$  may be the main cationic products in irradiated solid p- $H_2$ . Yields of the other positive ions may be larger when hydrides ( $H^-$ ) are produced in irradiated solid p- $H_2$ .

### A. Trapping mechanism of free electrons by heavier hydrogen isotope molecules

Large increases in  $e_t^-$  yields caused by increases in o- $D_2$  and HD concentrations in irradiated solid p- $H_2$  strongly suggest that isotopic hydrogen molecules play an important role in trapping electrons in p- $H_2$  crystals. We would like to propose the new trapping mechanism of o- $D_2$  and HD-mediated electron. The isotope effect on electron trapping was derived from the difference in rotational constants between these isotopes as follows. Long-range charge-induced dipole and



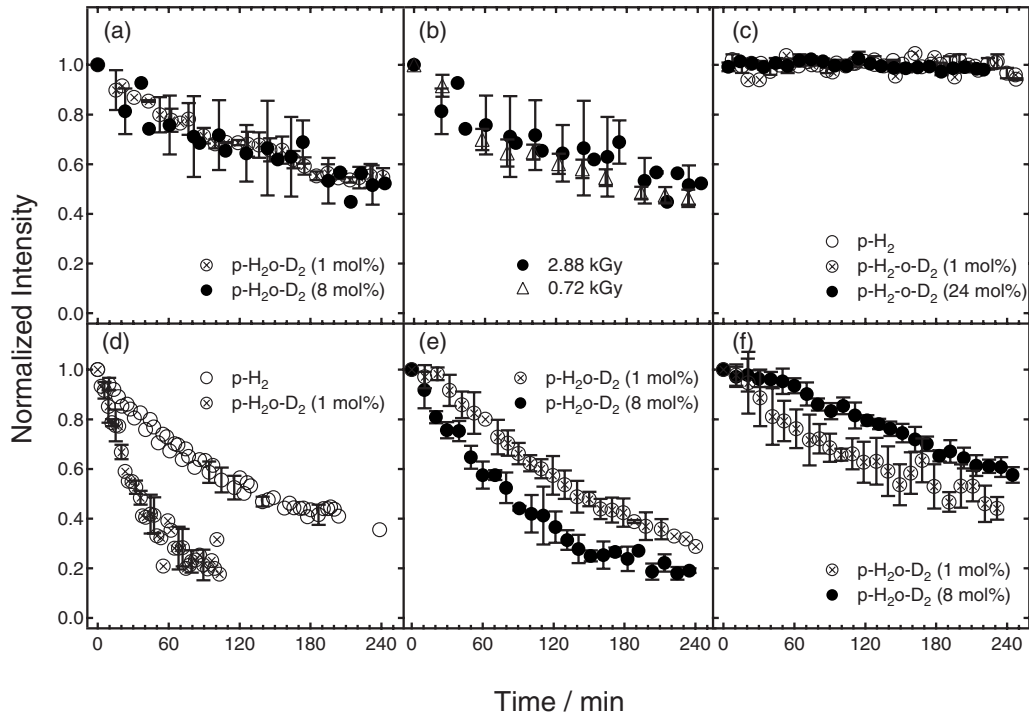


FIG. 4. Decay behaviors of (a)  $e_t^-$ , (b)  $e_t^-$  at different  $\gamma$ -ray irradiation doses, (c) H atom radicals, (d)  $H_6^+$ , (e)  $H_4D_2^+$ , and (f)  $H_2D_4^+$  in p- $H_2$  and p- $H_2$ -o- $D_2$  mixtures. Decay of  $e_t^-$  in (b) were measured in a p- $H_2$ -o- $D_2$  (8 mol %) mixture.

quadrupole interactions between  $e_t^-$  with  $H_2$  or with  $D_2$  were calculated by assuming a point-charge model.<sup>24</sup> Hamiltonian ( $H_s$ ) of the interactions are thus given by

$$H_s = -\alpha e^2/2R^4 + (eQ/R^3 - \gamma e^2/3R^4)P_2(\cos \theta), \quad (5)$$

where  $R$  is the separation between a point charge and  $H_2$  or  $D_2$ .  $\theta$  denotes the orientation of the hydrogen molecule with respect to  $R$  and  $P_2(\cos \theta)$  is the Legendre polynomial.  $\alpha$  and  $\gamma$  are the mean polarizability and its corresponding anisotropy, respectively.  $Q$  is the quadrupole moment of the hydrogen molecule in a molecule-fixed frame. The first and third terms in Eq. (5) describe the charge-induced dipole interaction, while the second term shows the charge-induced quadrupole interactions. Because both p- $H_2$  and o- $D_2$  exclusively have a  $J=0$  rotational state at about 4.2 K, the interaction ( $W_{J=0}$ ) is given by

$$W_{J=0} = \langle \psi_{J=0} | H_s | \psi_{J=0} \rangle + \frac{|\langle \psi_{J=0} | H_s | \psi_{J=2} \rangle|^2}{E_0 - E_2} \\ = -\alpha e^2/2R^4 + \frac{M|eQ/R^3 - \gamma e^2/3R^4|^2}{15\hbar^2}. \quad (6)$$

Here,  $\Psi_J$  and  $E_J$  are the rotational wave function of hydrogen nuclei and the rotational energy for  $J$ , respectively.  $M$  is the moment of inertia of the molecule. Although the first term in Eq. (6) is common to o- $D_2$  and p- $H_2$ , the second term for o- $D_2$  is twice as much as that for p- $H_2$  due to a difference in  $M$ .

Brooks *et al.*<sup>25</sup> calculated that electrons produced in solid hydrogen were stabilized to form trapped electrons called electron bubbles having a radius of 5 Å because of the zero-point energy. At  $R=5$  Å,  $|W_{J=0}|$  was 1.4 meV higher for o- $D_2$  (12.3 meV) than for p- $H_2$  (10.9 meV). Miller *et al.*<sup>26</sup>

also found that  $|W_{J=0}|$  for heteronuclear HD molecules (11.5 meV) was 0.6 meV larger than that for p- $H_2$ . These differences are larger than the thermal energy at 4.2 K as 0.4 meV. Relative  $e_t^-$  yields in irradiated p- $H_2$ , p- $H_2$ -HD(1%), and p- $H_2$ -o- $D_2$ (1%) as 1:3:10, respectively, are in the same order of the  $|W_{J=0}|$  for  $e^-$ -p- $H_2$ ,  $e^-$ -HD, and  $e^-$ -o- $D_2$ , respectively. These results strongly suggest that larger  $|W_{J=0}|$  for o- $D_2$  than that for HD assisted to trapping electrons in the larger yield at 4.2 K.

Assuming a binominal distribution for HD or o- $D_2$  molecules in solid p- $H_2$ , the probability to have one HD or o- $D_2$  molecule in a first layer composed of 12 p- $H_2$  molecules is estimated to be 0.107 and 0.384 for the 1 and 8 mol % samples, respectively. The probability to have two these molecules in a first layer is estimated to be 0.006 and 0.183 for

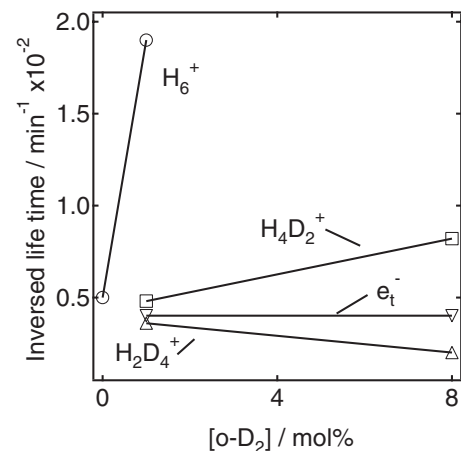


FIG. 5. Decay rates of  $e_t^-$ ,  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  as a function of o- $D_2$  concentration. Decay rates are shown as inverse life times.

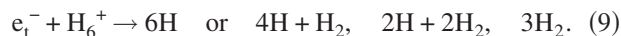
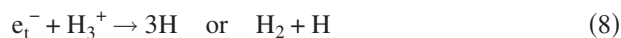
the 1 and 8 mol % samples, respectively. For the 1 mol % samples, it is expected that one  $e_t^-$  mostly interacts with one HD or o- $D_2$  molecule if one  $e_t^-$  occupies a substitutional site of an hcp structure in solid p- $H_2$ . Yields of  $e_t^-$  for the 8 mol % samples including HD or o- $D_2$  molecules increased 3.5 or 2.4 times larger than those of the 1 mol % samples, respectively. The probability to have one HD or o- $D_2$  molecule in a first layer in the 8% samples is estimated 3.8 times larger than those of the 1 mol % samples, which is in agreement with the experimental increases. More than two HD or o- $D_2$  molecules may interact with one  $e_t^-$ , especially in the 8 mol % sample but the probability to have not less than two HD or o- $D_2$  molecules in the first layer is 0.249, which is smaller than that to have one molecule as 0.384. We speculate that the experimental increases in the  $e_t^-$  yields in the 8 mol % samples mainly reflect the pairwise trapping structure. We would like to propose that long-range charge-induced dipole and quadrupole interactions between  $e^-$  and HD or o- $D_2$ , which are larger than  $H_2$ , play an important role in trapping electron in solid p- $H_2$ .

This model, which proposes that isotopic hydrogen molecules trap electrons, may explain the results by Hase and Kawabata,<sup>13</sup> who detected  $e_t^-$  in an irradiated  $D_2O$  single crystal, but not in a  $H_2O$  crystal. Because the strong crystallization energy prevents the local rearrangement of molecules in crystals, no  $e_t^-$  was detected in irradiated  $H_2O$  crystals despite the strong polarizability of  $H_2O$ .<sup>9</sup> Stronger charge-induced dipole and quadrupole interactions with  $e^-$  and D atoms in  $D_2O$  may, therefore, stabilize electrons as  $e_t^-$  in  $D_2O$  single crystals.

Let us estimate the probability to form  $e_t^-$  from  $e^-$  generated by radiolysis. It is reported that five H atom radicals are generated per ionization event through reactions (1)–(4) in the gas phase on average.<sup>23</sup> Assuming that H atom radicals do not undergo recombination during and after irradiation [cf. Fig. 4(c)], the probability was roughly estimated as  $\sim 1/170$ ,  $1/17$ , and  $1/7$  in solid p- $H_2$ , p- $H_2$ -o- $D_2$  (1 mol %), and p- $H_2$ -o- $D_2$  (8 mol %), respectively, using the ratio of the  $e_t^-$  and H atom radical yields.

## B. Decay mechanisms of trapped electrons

Electrons trapped in irradiated solid p- $H_2$  may decay according to the following reactions. One reaction is the attachment of  $e_t^-$  to H atom radicals to produce  $H^-$  [Eq. (7)], and others are recombinations with  $H_3^+$  [Eq. (8)] and  $H_6^+$  [Eq. (9)],



Because the yield of H atom radicals in p- $H_2$  was  $\sim 860$  times larger than for  $e_t^-$  (Table II), the decay rate of  $e_t^-$  should increase with increasing H atom radical concentrations if reaction (7) was the dominant decay process. Note that H atom radicals are homogeneously distributed in solid p- $H_2$  as a result of diffusion, which occurs through repeti-

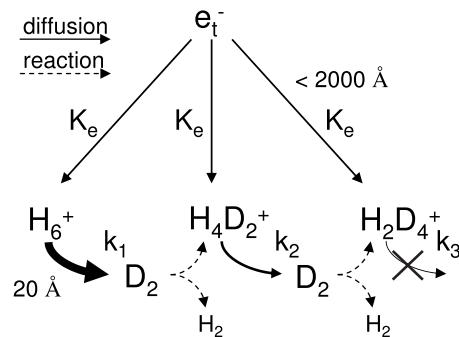


FIG. 6. Schematic representing the reactions of  $e_t^-$ ,  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  in solid p- $H_2$ -o- $D_2$  mixtures. Rate constants  $K_e$ ,  $k_1$ ,  $k_2$ , and  $k_3$  correspond to reactions (9) and (11)–(13), respectively.

tions of the tunneling reaction ( $H+H_2 \rightarrow H_2+H$ ).<sup>19,27</sup> As shown in Fig. 4(b), the decay rates of  $e_t^-$  were dose independent but the yield of H atom radicals produced by radiolysis at a dose of 2.88 kGy was about three to four times higher than at 0.72 kGy.<sup>28</sup> These results indicate that instead of reaction (7), reactions (8) and (9) are the dominant processes for the decay of  $e_t^-$ .

The concentration of  $e_t^-$  ( $[e_t^-]$ ) may depend on the doses. If the decay processes of  $e_t^-$  are dominantly governed by reactions (8) and (9), such as  $H_3^+$  and  $H_6^+$  concentrations, the decay rate should increase with increasing doses. As mentioned above, no difference was observed for the decay rate of  $e_t^-$  at varying doses. We propose that these constant decay rates may be explained by geminate recombination processes with  $H_3^+$  and  $H_6^+$ . Although no experimental evidence for the formation mechanisms of  $H_3^+$  and  $H_6^+$  is available, the formation of  $H_2^+$  by ionization of  $H_2$  molecules is most likely to be the first step in their production.  $H_3^+$  may be produced by reaction (2) immediately after the ionization.<sup>23</sup> Theoretical studies proposed that  $H_6^+$  is produced by rearrangement reaction between H,  $H_3^+$ , and  $H_2$ .<sup>29,30</sup> Therefore, we may assume that reactions between  $e_t^-$  and  $H_3^+$  or  $H_6^+$  as shown in reactions (8) and (9) correspond to the geminate recombination between parent  $H_2^+$  and  $e_t^-$ .

The decay rate constant  $K_e$  was estimated by fitting the exponential decay function,

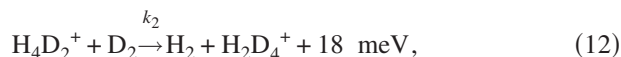
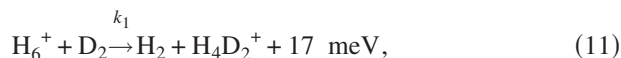
$$-\frac{d[e_t^-]}{dt} = K_e[e_t^-], \quad (10)$$

using experimental results measured for  $0 \text{ min} \leq t \leq 240 \text{ min}$ . The  $K_e$  value was determined to be  $0.004 \pm 0.002 \text{ min}^{-1}$  for p- $H_2$ -o- $D_2$  (1 and 8 mol %). In general,  $[e_t^-]$  follows a nonexponential decay function for geminate recombination in condensed matter due to the inhomogeneous distribution of cations and electrons,<sup>31</sup> but our method almost satisfies the fit.

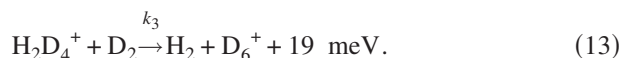
## C. Isotope condensation reactions of $H_6^+$

Figure 6 shows schematic diagrams for reactions involving  $e_t^-$ ,  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  in solid p- $H_2$ -o- $D_2$  mixtures. If  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  only decayed via geminate recombination with  $e_t^-$ , their decay rates would be the same as for  $e_t^-$ . However, while  $H_2D_4^+$  decayed similar to  $e_t^-$ ,

decay rates of  $H_6^+$  and  $H_4D_2^+$  were 6 and 1.5–3 times faster than that for  $e_t^-$  in p- $H_2$ -o- $D_2$  (1 mol %) (Fig. 5). To explain these results, the isotope condensation reactions in solid p- $H_2$ -o- $D_2$  mixtures were assumed to occur as



and



Note that the recombination reactions between  $e_t^-$  and cations are also accompanied by the above reactions. The exothermic energies in reactions (11)–(13) were calculated from differences in zero-point energy between a reactant and a product of  $H_6^+$  and  $H_4D_2^+$ ,  $H_4D_2^+$  and  $H_2D_4^+$ , and  $H_2D_4^+$  and  $D_6^+$ , respectively. These energy differences ranged from 17 to 19 meV and were much higher than the thermal energy at 4.2 K (0.4 meV), suggesting that reverse reactions cannot proceed.

To examine the validity of the proposed condensation reactions, we performed chemical kinetic analysis. The rate equations for  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  can be described as

$$-\frac{d[H_6^+]}{dt} = k_1[D_2][H_6^+] + K_e'[H_6^+], \quad (14)$$

$$-\frac{d[H_4D_2^+]}{dt} = -k_1[D_2][H_6^+] + k_2[D_2][H_4D_2^+] + K_e'[H_4D_2^+], \quad (15)$$

$$-\frac{d[H_2D_4^+]}{dt} = -k_2[D_2][H_4D_2^+] + k_3[D_2][H_2D_4^+] + K_e'[H_2D_4^+], \quad (16)$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are the rate constants for reactions (11)–(13), respectively, and  $K_e'$  is the rate constant for the recombination involving  $e_t^-$ . Figure 7 shows the experimental decay curves of  $H_6^+$  (open circles),  $H_4D_2^+$  (open squares), and  $H_2D_4^+$  (open triangles) in p- $H_2$ -o- $D_2$  mixtures, along with the total decay curve (crosses). The simulated decay curves (broken lines) were found to coincide with experimental curves using  $k_1$  of  $0.045 \text{ L mol}^{-1} \text{ min}^{-1}$ ,  $k_2$  of  $0.0015 \text{ L mol}^{-1} \text{ min}^{-1}$ , and  $k_3$  of  $0 \text{ L mol}^{-1} \text{ min}^{-1}$  for both p- $H_2$ -o- $D_2$  samples (1 and 8 mol %).  $K_e'$  was determined to be  $0.0058 \text{ min}^{-1}$  for p- $H_2$ -o- $D_2$  (1 mol %) and  $0.0039 \text{ min}^{-1}$  for p- $H_2$ -o- $D_2$  (8 mol %) from the total decay curves, in close agreement with the  $K_e$  value obtained in the previous section ( $0.004 \pm 0.002 \text{ min}^{-1}$ ).

The rate-determining steps for reactions (11)–(13) may be the diffusion of  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  in solid p- $H_2$ . Noticeable differences between  $k_1$ ,  $k_2$ , and  $k_3$  thus reflect differences in mobility between  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$ .  $H_6^+$ ,  $H_4D_2^+$ , and  $H_2D_4^+$  may diffuse via repeated hole hopping reactions as

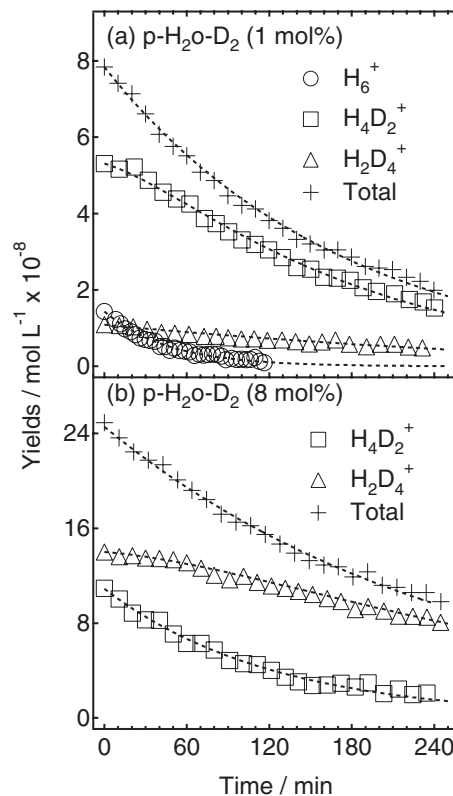
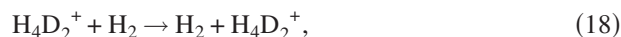
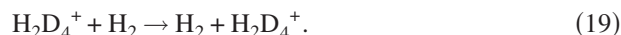


FIG. 7. Time course of the yields of  $H_6^+$  (open circles),  $H_4D_2^+$  (open squares), and  $H_2D_4^+$  (open triangles) and the total yield (crosses) in p- $H_2$ -o- $D_2$ : (a) 1 mol % and (b) 8 mol %. Broken lines are simulated decays obtained using  $K_e'$ ,  $k_1$ ,  $k_2$ , and  $k_3$  in Eqs. (14)–(16).



and



The mobility of  $H_6^+$  may drastically decrease with increasing number of deuterium atoms in  $H_6^+$ . Our hole hopping diffusion model described by the isotope condensation of  $H_6^+$  is also sufficient to explain results observed for  $H_5D^+$  and HD-sub.  $H_4D_2^+$  was produced preferentially and decayed slower than  $H_6^+$  in p- $H_2$ -HD mixtures.<sup>22</sup>

## V. SUMMARY

We found that the yields of  $e_t^-$  and  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) increased significantly with increasing o- $D_2$  or HD concentrations in irradiated solid p- $H_2$ , suggesting that both  $e_t^-$  and  $H_6^+$  are trapped by isotopic hydrogen molecules. Previous general methods, used to trap ionic species in local potential energy minima produced by cracks, distortions, and imperfections in the solids, could not be applied to electron and ion trapping in solid p- $H_2$  because of its self-annealing property. Isotope effects on induced dipole and quadrupole moments are proposed to generate local minima, allowing ionic species to be trapped in solid p- $H_2$ . Electrons produced in solid p- $H_2$  were stabilized by neighboring o- $D_2$  and HD because the interaction energy between electrons and o- $D_2$  or HD was greater than with p- $H_2$ . Previous reports<sup>13,16–18</sup> on

the enhancement of yields or electron lifetimes in several irradiated deuterated molecular crystals may be partly explained by our proposed mechanisms.

The chemical dynamics was elucidated quantitatively for the isotope condensation of  $H_6^+$  to form  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ).  $H_6^+$  diffused via repeated hole hopping in solid p- $H_2$  and reacted with o- $D_2$  or HD to produce  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ). The diffusion rates of  $H_{6-n}D_n^+$  ( $4 \geq n \geq 1$ ) by hole hopping were extremely slower than for  $H_6^+$ .

## ACKNOWLEDGMENTS

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