

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

Yuta Shimizu,¹ Makoto Inagaki,¹ Takayuki Kumada,^{2,b)} and Jun Kumagai^{1,a)}

¹Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

²Advanced 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⁻¹ min⁻¹ 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,¹ alcohols,²⁻⁶ hydrocarbons,^{6,7} and heterocompounds.^{4,8} 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^-).^{9,10} 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.¹⁰⁻¹² Polar molecules in solids assist in reducing the potential energy of electron by charge polarization.³ On the other hand, no electron can be trapped in irradiated molecular crystals, except in irradiated single crystals of D_2O ,¹³ trehalose,¹⁴ and crystals of diols.² Large crystallization energy hinders the local rearrangements of molecules in crystals.⁹

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.¹⁵ 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 (~ 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.^{13,16,17} Wang and Willard¹⁶ 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 γ -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 .^{17,18} Hase and Kawabata¹³ 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 (~ 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

^{a)} Author to whom correspondence should be addressed. Electronic mail: kumagai@apchem.nagoya-u.ac.jp.

^{b)} Present address: Quantum Beam Science Directorate, Kansai Photon Science Institute, Japan Atomic Energy Agency, 8-1 Umemidai, Kizugawa, Kyoto 619-0215, Japan.

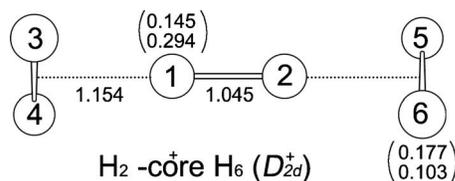


FIG. 1. MP2/cc-pVTZ optimized geometry of H_6^+ reported by Kurosaki and Takayanagi (Ref. 29). Bond lengths are shown in angstroms. Atomic net charges (upper line) and spin density (lower line) are shown in parentheses. Two side-on H_2 molecules (3–6) are chemically bound to the H_2^+ -core (1 and 2).

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.^{19,20} These occur because molecular hydrogen is light and undergoes small intermolecular interactions. In particular, p- H_2 molecules exclusively have a $J=0$ rotational quantum state with no electric quadrupole moment. Therefore, solid p- H_2 is free from inhomogeneous electric quadrupole-quadrupole interactions between neighboring p- H_2 molecules. Neither an H_2 nor a D_2 has dipole moment and an HD has a negligible dipole moment.²¹ The present model of electron trapping cannot account for this isotope effect as the trapping depends on inhomogeneity and polarity in solids.^{9–11,21}

H_6^+ radical cations, which are composed of an H_2^+ -core sandwiched between two side-on H_2 molecules, have been successfully observed by ESR spectroscopy in solid p- H_2 (Fig. 1).²² Their isotopic analogs ($H_{6-n}D_n^+$ ($4 \geq n \geq 1$)), including H_5D^+ , $H_4D_2^+$, and $H_2D_4^+$ were also detected.²² In these analogs, the H_2^+ -core and side-on H_2 molecules present in H_6^+ are replaced by D_2 or HD molecules. Singly D_2 -substituted $H_4D_2^+$ is denoted as “ $H_4D_2^+$ ” and its doubly HD-substituted counterpart is denoted as “HD-sub. $H_4D_2^+$.” Note that D_2 -core $H_4D_2^+$ has not been detected to this date.

Similar to the e_t^- yields, the total yields of H_6^+ and $H_{6-n}D_n^+$ ($4 \geq n \geq 1$) increased with increasing ortho- D_2 (o- 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 H_6^+ and $H_{6-n}D_n^+$ ($4 \geq n \geq 1$) in irradiated solid p- H_2 at 4.2 K and performed a kinetic analysis for isotope condensation reactions between H_6^+ and hydrogen isotopic molecules. In other words, H_6^+ were trapped by o- D_2 and/or HD molecules in solid p- H_2 . Therefore, isotopic hydrogen molecules in solid p- H_2 play an important role in trapping H_6^+ and electrons. This paper reports isotope effects on the yields and decays of e_t^- and H_6^+ in solid p- H_2 , p- H_2 -o- D_2 , and p- 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- H_2 molecules were obtained and purified by immersing iron hydroxide $FeO(OH)$ into liquid normal H_2 (>99.999 99%; Taiyo Nippon Sanso Co., Japan) for 10 h at

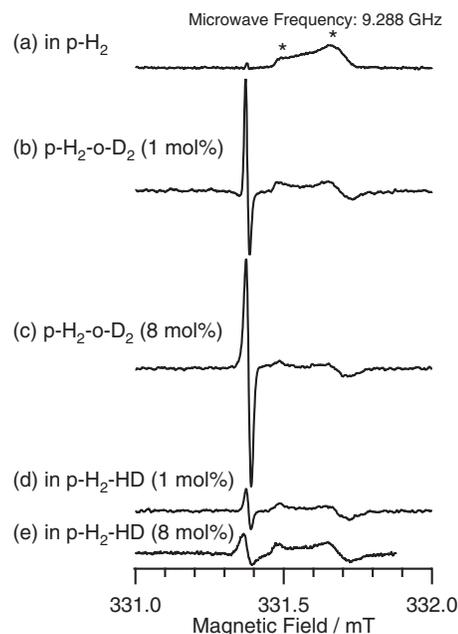


FIG. 2. ESR spectra of e_t^- produced in γ -ray irradiated solids at 4.2 K. (a) p- H_2 , (b) p- H_2 -o- D_2 (1 mol %), (c) p- H_2 -o- D_2 (8 mol %), (d) p- H_2 -HD (1 mol %), and (e) p- H_2 -HD (8 mol %). Peaks denoted by asterisks were from ESR tubes and Dewar made by radiolysis of quartz. ESR field-modulation frequency, amplitude, and microwave power were 50 kHz, 0.005 mT, and 1 nW, respectively, for p- H_2 and, 50 kHz, 0.01 mT, and 0.1 nW, respectively, for p- H_2 -o- D_2 and p- 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- D_2 molecules were obtained from normal D_2 (n- D_2) (99.95%; Isotec Inc.) in a similar manner at 18 K. All hydrogen gases, p- H_2 , o- 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- H_2 samples, namely, p- H_2 , p- H_2 -o- D_2 (1 and 8 mol %), and p- 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 γ -rays for ~ 1 h to the total dose of 2.88 kGy at the ^{60}Co γ -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 H_6^+ and e_t^- lines, respectively. H_6^+ and e_t^- yields were determined by double integration of the ESR lines using hexyl radicals in γ -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 γ - or X-ray irradiation.⁹

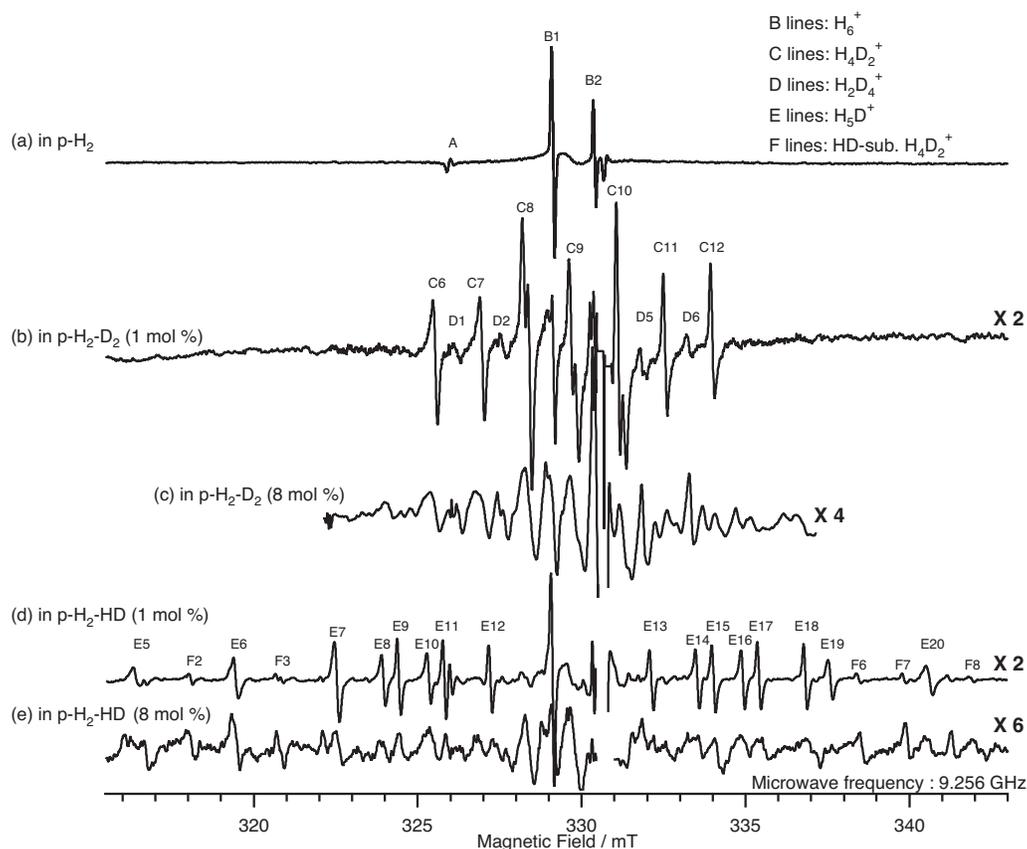


FIG. 3. ESR spectra of γ -ray irradiated solid (a) $p\text{-H}_2$, [(b) and (c)] $p\text{-H}_2\text{-o-D}_2$ mixtures, and [(d) and (e)] $p\text{-H}_2\text{-HD}$ mixtures measured with a field-modulation frequency of 50 kHz, an amplitude of 0.1 mT, and a microwave power of 1 mW. ESR lines marked as B, C, D, E, and F correspond to H_6^+ , H_4D_2^+ , H_2D_4^+ , H_5D^+ , and HD-sub. H_4D_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- D_2 or HD concentrations in $p\text{-H}_2$. The isotope effect on e_1^- yields was more significant for o- D_2 than for HD. Figure 3 shows the ESR spectra of H_6^+ [B lines: I_{12} (nuclear spin quantum number of 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 H_4D_2^+ [C lines: $I_1=I_2=1/2$; $I_{34}=0$; $I_{56}(\text{o-D}_2)=0$ and 2] and H_2D_4^+ [D lines:

$I_{12}=0$ and 1; $I_{34}(\text{o-D}_2)=I_{56}(\text{o-D}_2)=0$ and 2 for H_2^+ -core H_2D_4^+ and $I_{12}(\text{o-D}_2)=0$ and 2; $I_{34}=0$; $I_{56}(\text{o-D}_2)=0$ and 2 for D_2^+ -core H_2D_4^+] in irradiated solid $p\text{-H}_2\text{-o-D}_2$ mixtures. Similarly, ESR lines were also observed for H_5D^+ [E lines: $I_1(\text{H})=1/2$; $I_2(\text{D})=1$; $I_{34}=I_{56}=0$ for HD $^+$ -core H_5D^+ and $I_1=I_2=1/2$; $I_{34}=0$; $I_5(\text{H})=1/2$; $I_6(\text{D})=1$ for H_2^+ -core H_5D^+] and HD-sub. H_4D_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.²² Although only 1 mol % of o- D_2 or HD was added to $p\text{-H}_2$, H_4D_2^+ , and H_5D^+ , ESR intensities were found to be much higher than for

TABLE I. HFCC of 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	H_6^+	H_2^+	2.00212	20.441	−0.061	20.441	−0.061			
C	H_4D_2^+	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	H_2D_4^+	H_2^+	2.0020	21		21		<i>1.44</i> (9.38)	<i>1.44</i> (9.38)	$A_3=A_4=A_5=A_6$
		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	H_5D^+	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. H_4D_2^+	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-H₂, p-H₂-o-D₂, and p-H₂-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 ^a	
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 ± 1	5 ± 2	9 ± 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.

^aThe total yield of H_6^+ and $H_{6-n}D_n^+$ ($4 \geq n \geq 1$).

H_6^+ in solid p-H₂-o-D₂ [Fig. 2(b)] and p-H₂-HD [Fig. 2(d)], respectively. The B lines were not visible in p-H₂-o-D₂ [Fig. 2(c)] and p-H₂-HD [Fig. 2(e)] for o-D₂ and HD concentrations of 8 mol %.

Table II shows the relative yields of radical ions detected 30 min after irradiation in p-H₂, p-H₂-o-D₂, and p-H₂-HD mixtures. The yields were obtained by double integration of the corresponding ESR lines. Compared to the H_6^+ yield in p-H₂, 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-D₂ to p-H₂, 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-H₂, 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-D₂ 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-H₂-o-D₂ (1 mol %) and 74:23:1.9 for p-H₂-o-D₂ (8 mol %) if H_6^+ , $H_4D_2^+$, and $H_2D_4^+$ were produced statistically with respect to p-H₂ and o-D₂ 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-H₂-HD (1 mol %) and 0:65:35 for p-H₂-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-H₂. The yield of H atom radicals was ~6000 times greater than that of H_6^+ and was independent from o-D₂ 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-H₂ and p-H₂-o-D₂ mixtures. The decay behavior of e_t^- in p-H₂-o-D₂ mixtures was found to be independent of o-D₂ concentration and γ -ray dose [Figs. 4(a) and 4(b)]. H_6^+ decayed much faster in p-H₂-o-D₂ (1 mol %) than that in p-H₂. On the other hand, $H_4D_2^+$ and $H_2D_4^+$ decayed in a similar manner in both p-H₂-o-D₂ mixtures [Figs. 4(d)–4(f)]. H atom radicals did not decay in p-H₂ (Ref. 19) and p-H₂-o-D₂ mixtures [Fig. 4(c)]. The absolute yields of e_t^- , H_5D^+ , and HD-sub. $H_4D_2^+$ in p-H₂-HD were lower than those of e_t^- , $H_4D_2^+$, and $H_2D_4^+$ in p-H₂-o-D₂, 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 H₂ molecules are subjected to ionizing radiation,^{9,23} the ionization of H₂ molecules initially produce H_2^+ as



The H_2^+ ions disappear immediately by reacting with neighboring H₂ 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 H₂ 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 H₂ 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-H₂ (cf. Table II). The charge balance suggests a presence of other positive ions beside H_6^+ in irradiated solid p-H₂. Gas phase results indicate that H_3^+ may be the main cationic products in irradiated solid p-H₂. Yields of the other positive ions may be larger when hydrides (H⁻) are produced in irradiated solid p-H₂.

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

Large increases in e_t^- yields caused by increases in o-D₂ and HD concentrations in irradiated solid p-H₂ strongly suggest that isotopic hydrogen molecules play an important role in trapping electrons in p-H₂ crystals. We would like to propose the new trapping mechanism of o-D₂ 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

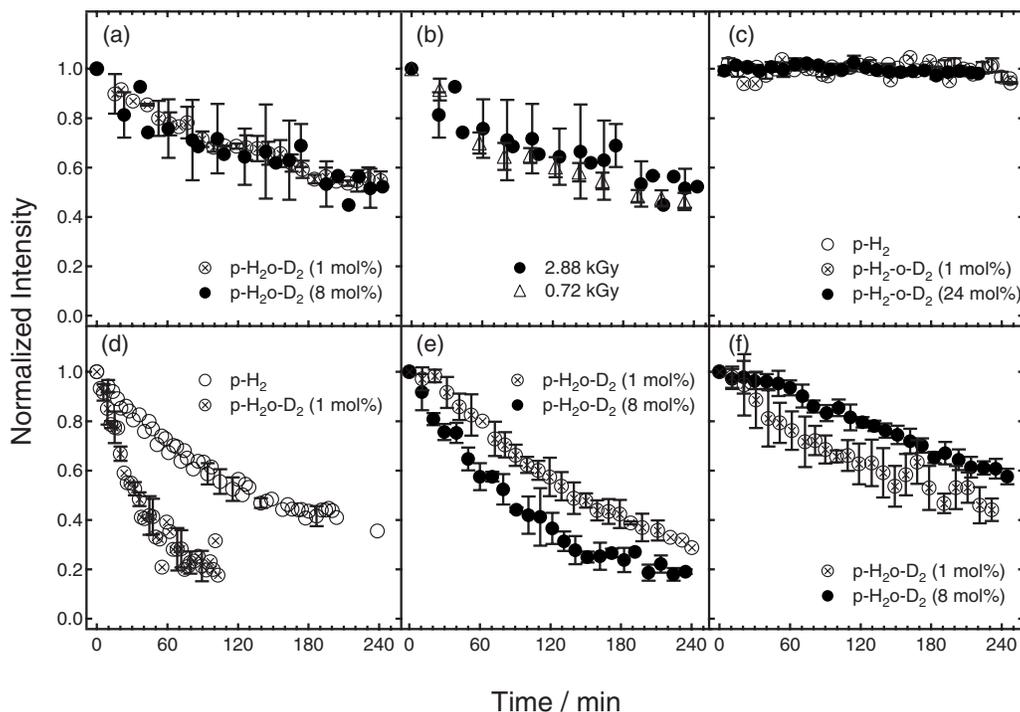


FIG. 4. Decay behaviors of (a) e_t^- , (b) e_t^- at different γ -ray irradiation doses, (c) H atom radicals, (d) H_6^+ , (e) $H_4D_2^+$, and (f) $H_2D_4^+$ in p- H_2 and p- H_2 -o- D_2 mixtures. Decay of e_t^- in (b) were measured in a p- H_2 -o- D_2 (8 mol %) mixture.

quadrupole interactions between e_t^- with H_2 or with D_2 were calculated by assuming a point-charge model.²⁴ 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 . θ denotes the orientation of the hydrogen molecule with respect to R and $P_2(\cos \theta)$ is the Legendre polynomial. α and γ 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, Ψ_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.*²⁵ 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.*²⁶

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

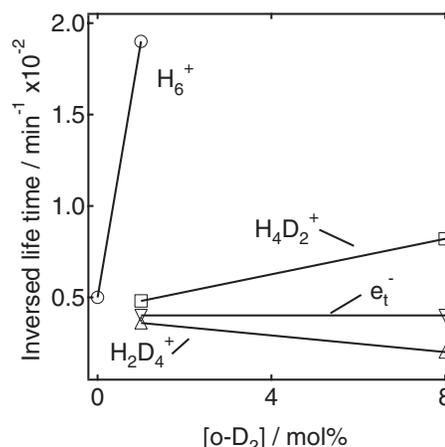


FIG. 5. Decay rates of e_t^- , H_6^+ , $H_4D_2^+$, and $H_2D_4^+$ as a function of o- D_2 concentration. Decay rates are shown as inverse life times.

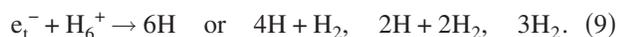
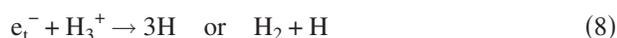
the 1 and 8 mol % samples, respectively. For the 1 mol % samples, it is expected that one e_t^- mostly interacts with one HD or o- D_2 molecule if one e_t^- occupies a substitutional site of an hcp structure in solid p- H_2 . Yields of e_t^- for the 8 mol % samples including HD or o- D_2 molecules increased 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,¹³ 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 .⁹ 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.²³ 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 ~ 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-

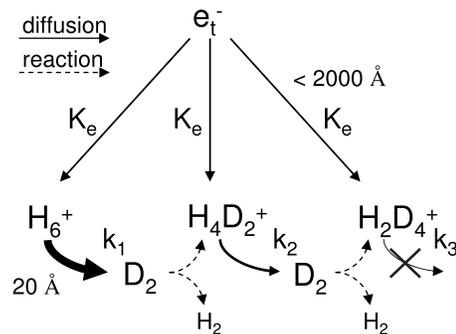


FIG. 6. Schematic representing the reactions of e_t^- , H_6^+ , $H_4D_2^+$, and $H_2D_4^+$ in solid p- H_2 -o- D_2 mixtures. Rate constants K_e , k_1 , k_2 , and k_3 correspond to reactions (9) and (11)–(13), respectively.

tions of the tunneling reaction ($H+H_2 \rightarrow H_2+H$).^{19,27} 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.²⁸ 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.²³ Theoretical studies proposed that H_6^+ is produced by rearrangement reaction between H, H_3^+ , and H_2 .^{29,30} 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,

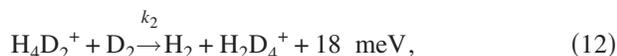
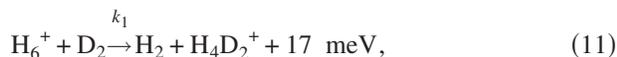
$$-\frac{d[e_t^-]}{dt} = K_e[e_t^-], \quad (10)$$

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,³¹ but our method almost satisfies the fit.

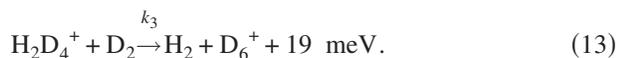
C. Isotope condensation reactions of H_6^+

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 min^{-1} for p- H_2 -o- D_2 (1 mol %) and 0.0039 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

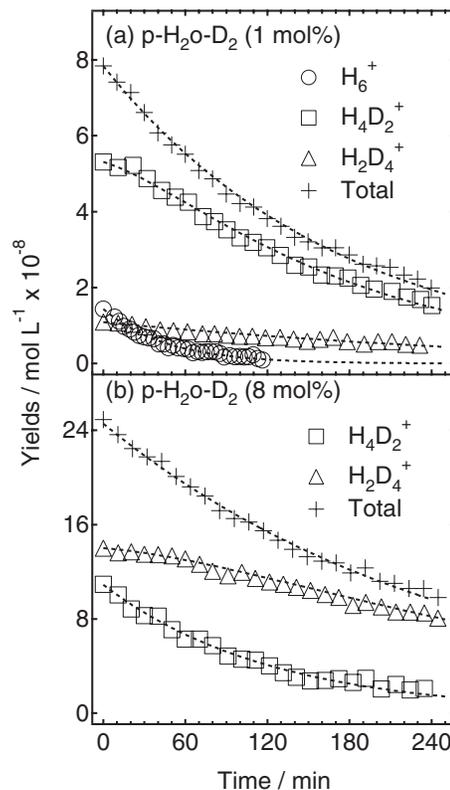
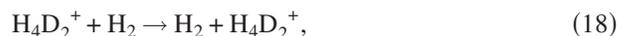
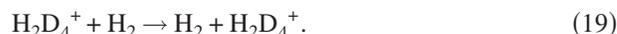


FIG. 7. Time course of the yields of H_6^+ (open circles), $H_4D_2^+$ (open squares), and $H_2D_4^+$ (open triangles) and the total yield (crosses) in p- H_2 -o- D_2 : (a) 1 mol % and (b) 8 mol %. Broken lines are simulated decays obtained using K_e' , k_1 , k_2 , and k_3 in Eqs. (14)–(16).



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.²²

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^{13,16–18} 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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