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# Tunneling chemical reactions in solid parahydrogen: Direct measurement of the rate constants of $R+H_2\rightarrow RH+H$ ( $R=CD_3, CD_2H, CDH_2, CH_3$ ) at 5 K

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Tunneling chemical reactions between deuterated methyl radicals and the hydrogen molecule in a parahydrogen crystal have been studied by Fourier transform infrared spectroscopy. The tunneling rates of the reactions  $R+H_2\rightarrow RH+H$  ( $R=CD_3, CD_2H, CDH_2$ ) in the vibrational ground state were determined directly from the temporal change in the intensity of the rovibrational absorption bands of the reactants and products in each reaction in solid parahydrogen observed at 5 K. The tunneling rate of each reaction was found to differ definitely depending upon the degree of deuteration in the methyl radicals. The tunneling rates were determined to be  $3.3\times 10^{-6} s^{-1}$ ,  $2.0\times 10^{-6} s^{-1}$ , and  $1.0\times 10^{-6} s^{-1}$  for the systems of  $CD_3$ ,  $CD_2H$ , and  $CDH_2$ , respectively. Conversely, the tunneling reaction between a  $CH_3$  radical and the hydrogen molecule did not proceed within a week's time. The upper limit of the tunneling rate of the reaction of the  $CH_3$  radical was estimated to be  $8\times 10^{-8} s^{-1}$ . © 2004 American Institute of Physics. [DOI: 10.1063/1.1642582]

## I. INTRODUCTION

The tunneling effect becomes important in chemical reactions at low temperature because of the suppression of thermally activated reaction processes. Such a situation is expected to be realized in interstellar clouds, for example.<sup>1</sup> However, the determination of bimolecular rate constants for cryogenic reactions is not easy because most systems are immobilized by condensation at low temperatures.

Compared with this difficulty inherent in bimolecular reactions, unimolecular reactions involving intramolecular tunneling processes are relatively easy to study in cryogenic crystals. For example, a long-range hydrogen transfer by tunneling in a radiation damaged dimethylglyoxime crystal was studied by electron spin resonance (ESR) spectroscopy.<sup>2</sup> Hydrogen atom exchange by tunneling in a malonaldehyde crystal was also studied using microwave spectroscopy.<sup>3</sup> More recently, a *cis-trans* isomerization of formic acid in rare gas matrices was studied in connection with the matrix effect on the tunneling process in the isomerization.<sup>4</sup>

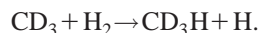
As for bimolecular reactions, the reaction  $CH_3+CH_3OH\rightarrow CH_4+CH_2OH$  was studied extensively using ESR spectroscopy.<sup>5,6</sup> Another example of the bimolecular reaction by tunneling was reported between hydrogen atoms and molecules.<sup>7,8</sup> We ourselves have been studying the reaction between methyl radicals and the parahydrogen molecule in a parahydrogen crystal (*p*-H<sub>2</sub>) at cryogenic temperatures.<sup>9,10</sup>

In the present work we extend our previous studies by

covering all isotomeric radicals  $CD_3$ ,  $CD_2H$ ,  $CDH_2$ , and  $CH_3$ . The aim of the present study is to shed more light on the intrinsic nature of the reactions promoted by tunneling. In order to provide a general background to our study, we will first recapitulate our previous work.

During the past decade we have been studying rovibrational spectra of molecules embedded in solid *p*-H<sub>2</sub> which has several salient features in both high resolution spectroscopic and *in-situ* photolytic studies.<sup>9-23</sup> The *p*-H<sub>2</sub> matrix is capable of providing not only high resolution spectroscopic information regarding embedded molecules but also subtle intermolecular interaction between trapped molecules and the matrix hydrogen molecule.<sup>12,13,15-18,21,22</sup> The feasibility of the study of *in-situ* photolysis stems from the fact that molecules in solid *p*-H<sub>2</sub> happen to be free from the cage effect, which allows us to study photolytically produced fragments such as radicals originating from the parent molecule.<sup>9,14,23-26</sup>

In a previous paper we have observed Fourier transform infrared (FTIR) spectra of the  $CD_3$  radical trapped in solid *p*-H<sub>2</sub> crystal.<sup>9</sup> The decrease in the absorption intensity of  $CD_3$  and the increase in the intensity of  $CD_3H$  were observed over a span of about one week at 5 K. As a result of that study, it was found that  $CD_3$  reacts with surrounding hydrogen molecules through tunneling as follows:



Since the activation energy of the above reaction has been estimated to be 11–14 kcal/mol ( $\approx 5500$ – $7000$  K),<sup>27,28</sup> the occurrence of the above reaction at 5 K must be ascribed exclusively to pure tunneling. Assuming that the reaction can

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be expressed by a pseudo first-order rate law, the tunneling rate constant was determined to be  $(4.7 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$ .<sup>9</sup> In the same experiment no appreciable spectral change was observed for the  $\text{CH}_3/p\text{-H}_2$  system under the same conditions. This difference between the two systems was explained in terms of the enthalpic difference including the zero-point energies of the reactants and products. The reaction between the methyl radical and hydrogen molecule is nearly thermoneutral since the zero-point dissociation energies of  $\text{H}_2$  ( $D_0 = 4.4781 \text{ eV}$ )<sup>29</sup> and  $\text{CH}_4$  ( $D_0 = 4.406 \text{ eV}$ )<sup>30</sup> are very close. Consequently, the small difference in zero-point vibrational energies between the  $\text{CD}_3/p\text{-H}_2$  and  $\text{CH}_3/p\text{-H}_2$  reaction systems would cause the drastic change in the tunneling rate.

In the present work we have improved the spectroscopic resolution from  $0.25 \text{ cm}^{-1}$  for the previous work to  $0.1\text{--}0.01 \text{ cm}^{-1}$  and compared all the four isotopomeric systems. As a result, a systematic difference in the rate constant of the tunneling reaction was revealed. In order to find further clues for the quantum level dependence of the tunneling reaction, a preliminary test on the effect of the monitoring IR beam on the reaction rate was also attempted.

## II. EXPERIMENT

Solid parahydrogen used as the matrix was prepared by the same technique described in our previous papers.<sup>9,25</sup> The methyl radicals,  $\text{CH}_3$ ,  $\text{CDH}_2$ ,  $\text{CD}_2\text{H}$ , and  $\text{CD}_3$ , were produced through *in-situ* photolysis of the corresponding methyl iodides  $\text{CH}_3\text{I}$ ,  $\text{CDH}_2\text{I}$  (>98 atom % D),  $\text{CD}_2\text{HI}$  (>98 atom % D), and  $\text{CD}_3\text{I}$  (>99 atom % D), which were premixed with the  $p\text{-H}_2$  gas containing less than 0.05% of orthohydrogen.<sup>10</sup> The admixture was introduced into a copper optical cell kept at about 8.2 K to grow a transparent mixed crystal. The size of the optical cell was 3.0 cm in length and 1.7 cm in diameter.  $\text{BaF}_2$  was used for the windows of the optical cell and the cryostat. A low pressure 20 W Hg lamp emitting both 253.7 nm and 184.9 nm photons was employed for photolysis of the iodides. A 4-hour long UV irradiation gave sufficient concentrations of the methyl radicals.

A Bruker IFS 120HR FTIR spectrometer was used throughout the experiment. To cover both the mid-IR and near-IR spectral regions two types of the light sources were employed: for the mid-IR region ( $10\text{--}2 \mu\text{m}$ ) a glowbar source was used, while for the near-IR region ( $2\text{--}1 \mu\text{m}$ ) a tungsten lamp was used. A KBr beam splitter and a liquid nitrogen cooled HgCdTe (MCT) detector were used in common to the measurements of the two spectral regions.

After the UV irradiation, the following three different measurements were performed in order to examine any possible effect of the light source on the samples:

(1) The IR spectra were measured with no optical filter between the light sources and the sample. Since the sample was exposed for a long period to the monitoring IR beam covering a range of  $700 \text{ cm}^{-1}$ , which was a limit of transmission of the  $\text{BaF}_2$  windows, through  $7500 \text{ cm}^{-1}$ , a limit of the KBr beam splitter, it was suspected that the light sources might have some effect on the sample in

this mode of measurement. The results of the measurement are listed in the second row of Tables II and III.

- (2) To test the suspicion mentioned in the measurement (1) above, spectral recording was carried out with several IR filters inserted between the light sources and the sample. Depending upon the spectral bands of our interest, several filters were selected as summarized in the third, fourth, and fifth rows of Tables II and III. To be more specific, IR filters passing either ranges of  $785\text{--}1390 \text{ cm}^{-1}$  or  $2170\text{--}3905 \text{ cm}^{-1}$  were used for  $\text{CD}_3\text{I}$ , a filter of  $2170\text{--}3905 \text{ cm}^{-1}$  for  $\text{CD}_2\text{HI}$ , and a filter of  $1330\text{--}2240 \text{ cm}^{-1}$  for  $\text{CDH}_2\text{I}$ , respectively.
- (3) To further test the possible effect of exposing the sample to the monitoring beam, the measurement 3 was also made, where the light sources were turned off except for the period of spectral scanning which took about 1 or 2 hours for both the mid-IR (with a glowbar source) and the near-IR (with a tungsten lamp). During the remaining 22 to 23 hours of the day, the sample was kept in complete darkness. This measurement regime was repeated every day for about one week. Since the effect of this turning off the light sources turned out to be negligible, the measurement (3) was made only for the  $\text{CD}_3\text{I}/p\text{-H}_2$  system as shown in the last row of Tables II and III.

The temperature of the crystal was maintained at  $5 \pm 0.1 \text{ K}$  throughout the duration of the experiment.

## III. RESULTS AND DISCUSSION

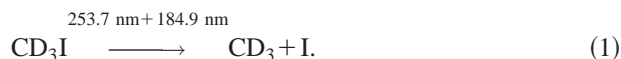
### A. Observed spectra

Figures 1–4 show the results of the systems of  $\text{CD}_3\text{I}/p\text{-H}_2$ ,  $\text{CD}_2\text{HI}/p\text{-H}_2$ ,  $\text{CDH}_2\text{I}/p\text{-H}_2$ , and  $\text{CH}_3\text{I}/p\text{-H}_2$  recorded using the measurement (1) stated in Sec. II.

In these figures trace (I) shows spectra as deposited at 5 K, trace (II) after a four-hour UV irradiation, and trace (III) the same as trace (II) after one week. In each figure spectra due to methane ( $\text{CD}_3\text{H}$ ,  $\text{CD}_2\text{H}_2$ ,  $\text{CDH}_3$ ,  $\text{CH}_4$ ) are shown at the bottom for the convenience of comparison with the spectra of products seen in (II) and (III). The symbols I, R, and M stand for methyl iodide, methyl radical, and methane, respectively. The observed frequencies of the vibrational fundamental bands of the iodides, the radicals, and the methanes are summarized in Table I along with the values observed in the gas phase<sup>31,32</sup> or the values obtained by an *ab-initio* calculation.<sup>33</sup> In the table, frequencies at the center of the band are adopted as the frequency of the band origin in solid  $p\text{-H}_2$ . The details of the results of each system is discussed below.

### 1. $\text{CD}_3\text{I}$

Trace (I) of Fig. 1 shows the  $\nu_2$  and  $\nu_4$  fundamental bands of  $\text{CD}_3\text{I}$  peaking at  $947$  and  $2298 \text{ cm}^{-1}$ . These are close to the reference values in the gas phase.<sup>31</sup> Trace (II) shows the spectra due to the perdeuterated methyl radical (R) and the residual iodide,



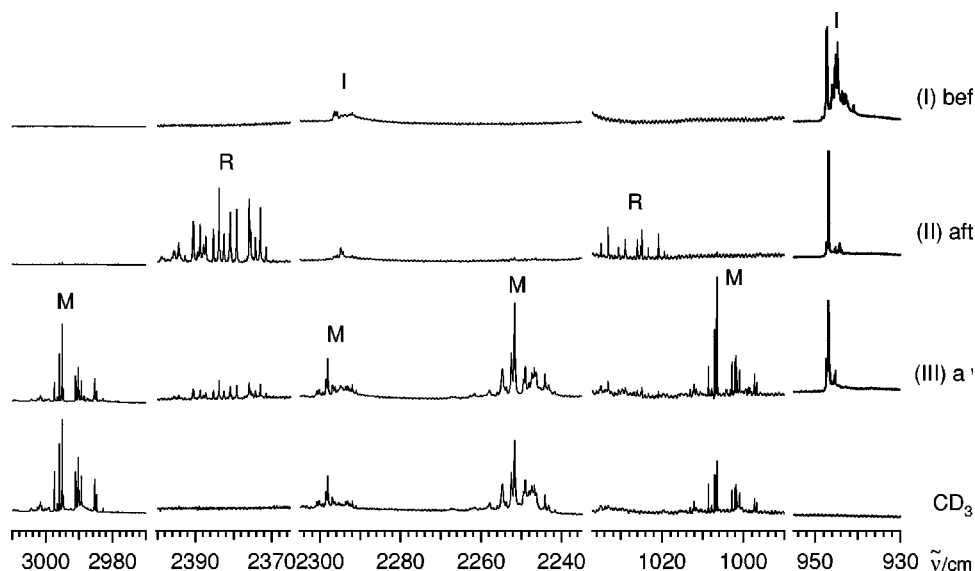


FIG. 1. Infrared absorption spectra of  $\text{CD}_3\text{I}$  in solid  $p\text{-H}_2$ . (I) As deposited at 5 K. (II) Same as (I) after a 240 min UV irradiation. (III) Same as (II) after one week. The spectra at the bottom is  $\text{CD}_3\text{H}$  in solid  $p\text{-H}_2$  at 4.8 K. The symbols, I, R, and M stand for the methyl iodide ( $\text{CD}_3\text{I}$ ), methyl radical ( $\text{CD}_3$ ), and methane ( $\text{CD}_3\text{H}$ ), respectively. Spectra (I)–(III) are displayed in the same scale.

The  $\nu_3$  and  $\nu_4$  bands of  $\text{CD}_3$  were observed at  $2379\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$  respectively. Contrary to the previous paper where the  $\nu_3$  band of  $\text{CD}_3$  was heavily overlapped with the absorption band of  $\text{CO}_2$ , the spectrum in trace (II) of Fig. 1 shows an uncontaminated  $\nu_3$  band of  $\text{CD}_3$  because the residual air in the spectrometer was evacuated in the present experiment. Structures of the  $\nu_3$  and  $\nu_4$  bands are attributed to the molecular rotation and to the crystal field splitting as in the case of the previous work.<sup>12,34</sup>

Although almost unrecognizable in trace (II) of Fig. 1, a very weak absorption due to  $\text{CD}_2\text{H}_2$  was observed at  $2973\text{ cm}^{-1}$ . This methane was produced via the following

reactions<sup>25</sup> (cf. bottom of Fig. 2):



Trace (III) of Fig. 1 recorded after one week demonstrates sharp peaks at  $2990$ ,  $2248$ ,  $1035$ , and  $1002\text{ cm}^{-1}$ , all of them being attributable to  $\text{CD}_3\text{H}$  as is supported by the nice matching with the authentic spectrum shown at the bottom of Fig. 1.

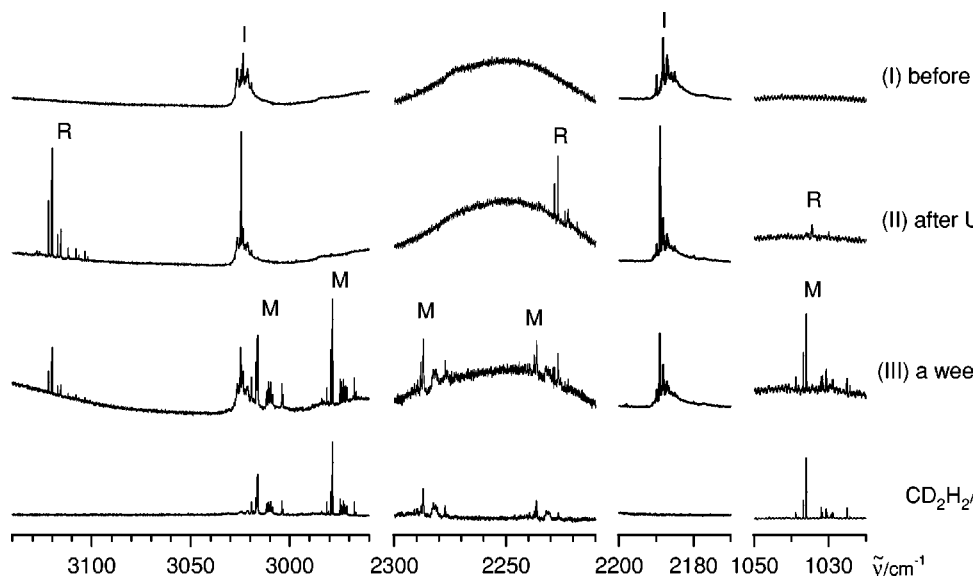


FIG. 2. Infrared absorption spectra of  $\text{CD}_2\text{HI}$  in solid  $p\text{-H}_2$ . (I) As deposited at 5 K. (II) Same as (I) after a 240 min UV irradiation. (III) Same as (II) after one week. The spectra at the bottom is  $\text{CD}_2\text{H}_2$  in solid  $p\text{-H}_2$  at 4.8 K. The symbols, I, R, and M stand for the methyl iodide ( $\text{CD}_2\text{HI}$ ), methyl radical ( $\text{CD}_2\text{H}$ ), and methane ( $\text{CD}_2\text{H}_2$ ), respectively. Spectra (I)–(III) are displayed in the same scale.

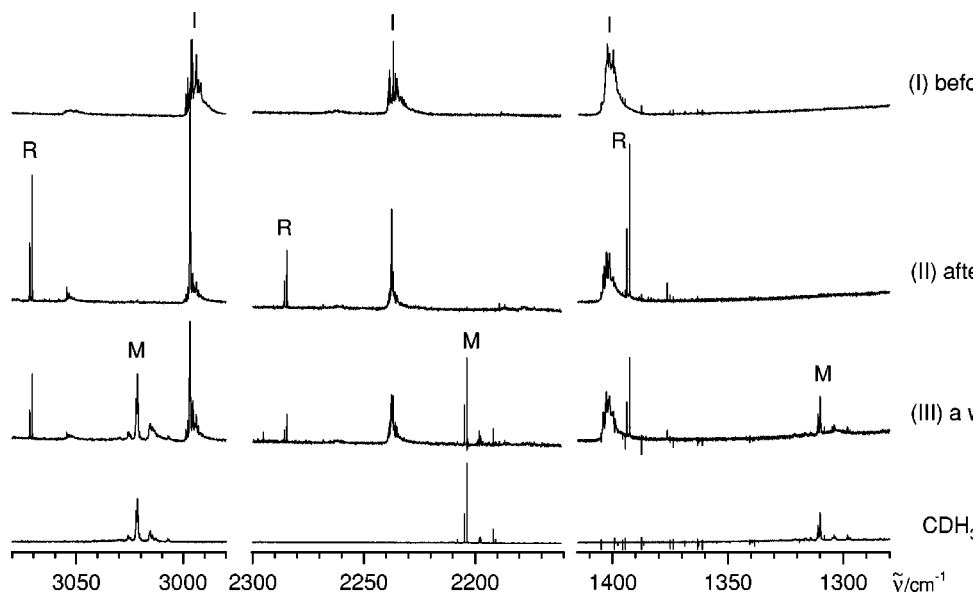


FIG. 3. Infrared absorption spectra of  $\text{CD}_2\text{I}$  in solid  $p\text{-H}_2$ . (I) As deposited at 5 K. (II) Same as (I) after a 240 min UV irradiation. (III) Same as (II) after one week. The spectra at the bottom is  $\text{CDH}_3$  in solid  $p\text{-H}_2$  at 4.8 K. The symbols, I, R, and M stand for the methyl iodide ( $\text{CD}_2\text{I}$ ), methyl radical ( $\text{CDH}_2$ ), and methane ( $\text{CDH}_3$ ), respectively. Spectra (I)–(III) are displayed in the same scale.

## 2. $\text{CD}_2\text{HI}$

The  $3027\text{ cm}^{-1}$  band in trace (I) of Fig. 2 assigned to the  $\nu_4$  absorption of  $\text{CD}_2\text{HI}/p\text{-H}_2$  is in good agreement with the gas phase spectrum.<sup>32</sup> The absorption bands around 3121, 2228, and  $1035\text{ cm}^{-1}$  in trace (II) are close to those of the  $\text{CD}_2\text{H}$  radical observed in the gas phase. They also compare favorably with the results of the *ab initio* calculation for the radical<sup>33</sup> and can be assigned to the  $\nu_1$ ,  $\nu_5$ , and  $\nu_3$  bands of  $\text{CD}_2\text{H}$ , respectively. Comparison of trace (III) with the spectrum at the bottom of Fig. 2 clearly indicates that the peaks at

about 3010, 2973, 2265, 2231, and  $1031\text{ cm}^{-1}$  are associated with  $\nu_6$ ,  $\nu_1$ ,  $\nu_4 + \nu_9$ ,  $\nu_8$ , and  $\nu_4$  of  $\text{CD}_2\text{H}_2$ , respectively.

## 3. $\text{CDH}_2\text{I}$

In trace (I) of Fig. 3 the  $\nu_4$ ,  $\nu_1$ , and  $\nu_5$  bands of  $\text{CDH}_2\text{I}$  are observed at 2997, 2237, and  $1402\text{ cm}^{-1}$  which are close to those in the gas phase.<sup>32</sup> The bands at around 3071, 2285, and  $1393\text{ cm}^{-1}$  in trace (II) can be assigned to the  $\nu_5$ ,  $\nu_2$ ,

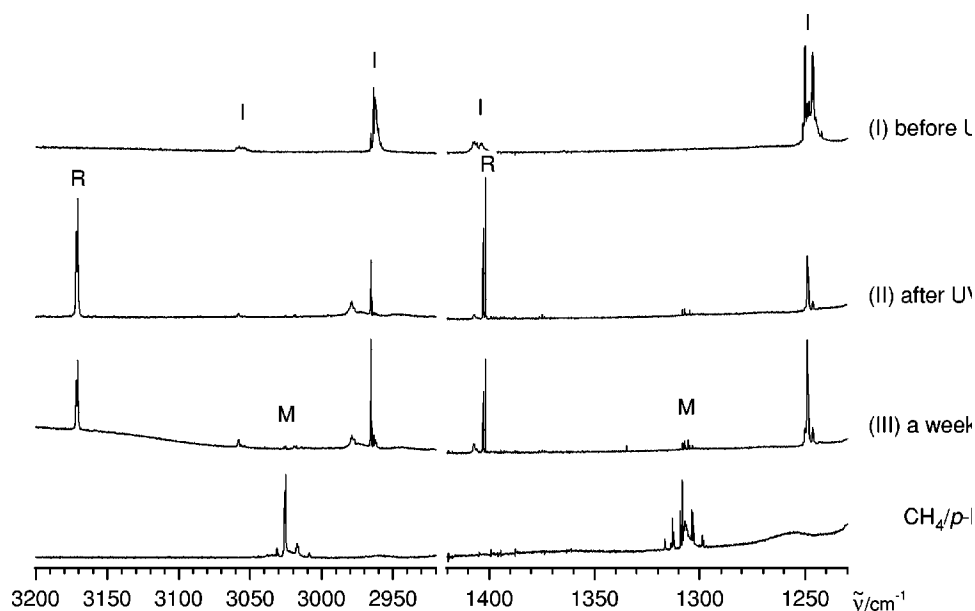


FIG. 4. Infrared absorption spectra of  $\text{CH}_3\text{I}$  in solid  $p\text{-H}_2$ . (I) As deposited at 5 K. (II) Same as (I) after 240 min UV irradiation. (III) Same as (II) after one week. The spectra at the bottom is  $\text{CH}_4$  in solid  $p\text{-H}_2$  at 4.8 K. The symbols, I, R, and M stand for the methyl iodide ( $\text{CH}_3\text{I}$ ), methyl radical ( $\text{CH}_3$ ), and methane ( $\text{CH}_4$ ), respectively. Spectra (I)–(III) are displayed in the same scale.

TABLE I. The observed and calculated wave numbers of the vibrational absorption bands of deuterated methyl iodides, methyl radicals, and methanes in solid  $p$ -H<sub>2</sub>. The units are in cm<sup>-1</sup>. Labels in the parentheses represent the character of the vibrational modes.

CH <sub>3</sub> I		CD <sub>3</sub> I		CDH <sub>2</sub> I		CD <sub>2</sub> HI			
(C <sub>3v</sub> )	$p$ -H <sub>2</sub>	gas <sup>a</sup>	$p$ -H <sub>2</sub>	gas <sup>a</sup>	(C <sub>s</sub> )	$p$ -H <sub>2</sub>	gas <sup>b</sup>	$p$ -H <sub>2</sub>	gas <sup>b</sup>
$\nu_1$ (a <sub>1</sub> )	2979	2970	2151	2155	$\nu_1$ (a')	2237	2241	2189	2194
$\nu_2$ (a <sub>1</sub> )	1249	1252	947	951	$\nu_2$ (a')	1171	1172	1016	1018
$\nu_3$ (a <sub>1</sub> )		533		501	$\nu_3$ (a')		518		508
$\nu_4$ (e)	3059	3060	2298	2298	$\nu_4$ (a')	2997	3002	3027	3030
$\nu_5$ (e)	1433	1436	1047	1049	$\nu_5$ (a')	1402	1415	1170	1170
$\nu_6$ (e)	886	882		656	$\nu_6$ (a')		710		754
					$\nu_7$ (a'')	3055	3057	2341	2336
					$\nu_8$ (a'')	1234	1240	1280	1287
					$\nu_9$ (a'')	866	862		659

CH <sub>3</sub>			CD <sub>3</sub>			CDH <sub>2</sub>			CD <sub>2</sub> H		
(D <sub>3h</sub> )	$p$ -H <sub>2</sub>	gas <sup>a</sup>	calc. <sup>c</sup>	$p$ -H <sub>2</sub>	gas <sup>a</sup>	calc. <sup>c</sup>	(C <sub>2v</sub> )	$p$ -H <sub>2</sub>	calc. <sup>c</sup>	$p$ -H <sub>2</sub>	calc. <sup>c</sup>
$\nu_1$ (a' <sub>1</sub> )		3004	2925		2158	2070	$\nu_1$ (a <sub>1</sub> )		2985	3121	3035
$\nu_2$ (a'' <sub>2</sub> )		606	620		458	460	$\nu_2$ (a <sub>1</sub> )	2285	2210		2135
$\nu_3$ (e')	3171	3161	3080	2379	2381	2300	$\nu_3$ (a <sub>1</sub> )	1393	1365	1035	1015
$\nu_4$ (e')	1402	(1396) <sup>d</sup>	1370	1034	(1029) <sup>d</sup>	1015	$\nu_4$ (b <sub>1</sub> )		570		520
							$\nu_5$ (b <sub>2</sub> )	3071	3080	2228	2295
							$\nu_6$ (b <sub>2</sub> )	1179	1145	1281	1255

CH <sub>4</sub>			CD <sub>3</sub> H			CDH <sub>3</sub>			CD <sub>2</sub> H <sub>2</sub>	
(T <sub>d</sub> )	$p$ -H <sub>2</sub>	gas <sup>a</sup>	(C <sub>3v</sub> )	$p$ -H <sub>2</sub>	gas <sup>a</sup>	$p$ -H <sub>2</sub>	gas <sup>a</sup>	(C <sub>2v</sub> )	$p$ -H <sub>2</sub>	gas <sup>a</sup>
$\nu_1$ (a <sub>1</sub> )		2917	$\nu_1$ (a <sub>1</sub> )	2990	2993	2972	2973	$\nu_1$ (a <sub>1</sub> )	2973	2976
$\nu_2$ (e)		1534	$\nu_2$ (a <sub>1</sub> )	2140	2142	2198	2200	$\nu_2$ (a <sub>1</sub> )		2202
$\nu_3$ (f <sub>2</sub> )	3017.3	3019	$\nu_3$ (a <sub>1</sub> )	1002	1003	1304	1300	$\nu_3$ (a <sub>1</sub> )		1436
$\nu_4$ (f <sub>2</sub> )	1303.6	1306	$\nu_4$ (e)	2248	2263	3015	3017	$\nu_4$ (a <sub>1</sub> )	1031	1033
			$\nu_5$ (e)	1290	1291	1472	1471	$\nu_5$ (a <sub>2</sub> )		1329
			$\nu_6$ (e)	1035	1036	1155	1155	$\nu_6$ (b <sub>1</sub> )	3010	3013
								$\nu_7$ (b <sub>1</sub> )	1090	1090
								$\nu_8$ (b <sub>2</sub> )	2231	2234
								$\nu_9$ (b <sub>2</sub> )	1234	1234

<sup>a</sup>Reference 31.<sup>b</sup>Reference 32.<sup>c</sup>Reference 33.<sup>d</sup>Ne matrix measurement.

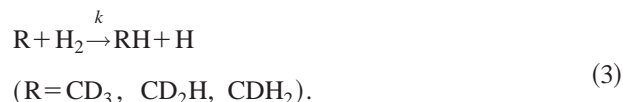
and  $\nu_3$  bands of the CDH<sub>2</sub> radical, respectively, from the comparison with the calculation.<sup>33</sup> Reference to the spectrum at the bottom of Fig. 3 supports the assignment of the bands at about 3015, 2198, and 1304 cm<sup>-1</sup> in trace (III) to the  $\nu_4$ ,  $\nu_2$ , and  $\nu_3$  bands of CDH<sub>3</sub>, respectively.

#### 4. CH<sub>3</sub>

Figure 4 for the prototypical system is shown for the sake of the completeness of all the isotopomeric systems. The result in Fig. 4 is in complete agreement with the result of our previous work.<sup>9,25</sup> In brief, the conversion from the CH<sub>3</sub> radical (R) to methane (M) was almost negligible during the one week standing [cf. (II) and (III) in Fig. 4]. The decrease in the intensity of R was counterbalanced by the increase in the intensity of the methyl iodide (I). This result suggests that only some of the radicals recombined with the geminately produced iodine atom. Details of the recombination are also discussed below.

#### B. Spectral change

A common feature throughout Figs. 1–3 is that the absorption of the radicals observed in trace (II) diminished, to be replaced by the absorption of the appropriate methane, shown in trace (III). From this result the following reaction scheme is immediately derived in accordance with our previous study:<sup>9</sup>



In sharp contrast to Figs. 1–3, the pure isotope system shown in Fig. 4 showed almost no measurable change in one week. This result indicates that the tunneling reaction between CH<sub>3</sub> radical and parahydrogen does not occur or is too slow to detect by our experiment,



Figures 5 and 6 demonstrate the temporal change in the intensity of the absorption band of various methyl radicals

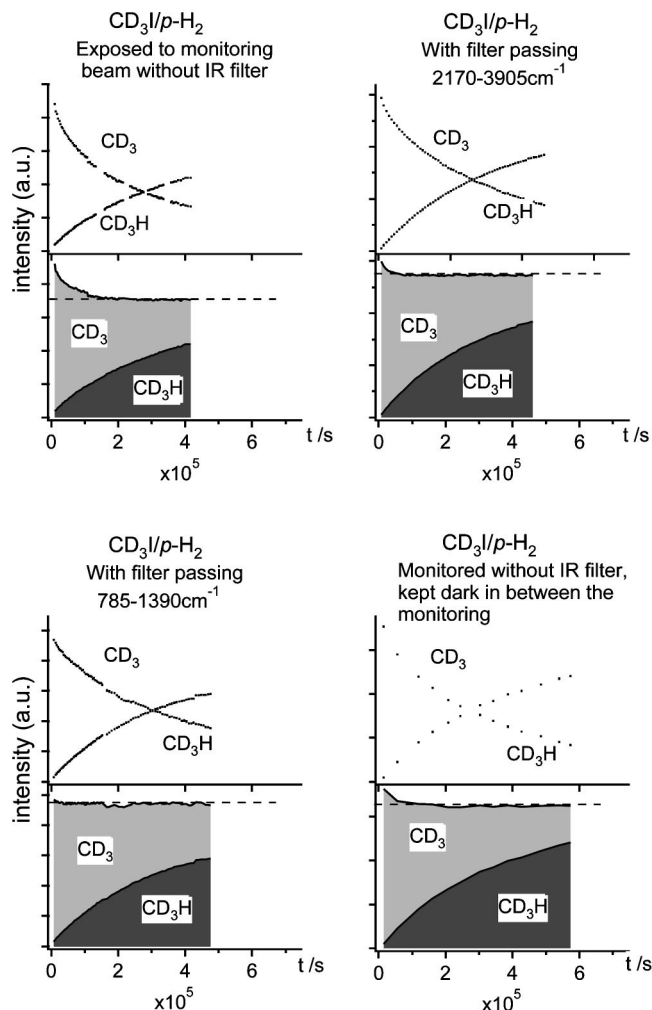


FIG. 5. The temporal change of  $\text{CD}_3$  and  $\text{CD}_3\text{H}$  in solid  $p\text{-H}_2$  at 5 K after UV irradiation. Upper left, the sample was exposed to the monitoring IR beam throughout the experiment with no IR filter being inserted. Lower left, same as above with a filter passing  $785\text{--}1390\text{ cm}^{-1}$ . Upper right, same as the lower left except that a filter passing  $2170\text{--}3905\text{ cm}^{-1}$  was used. Lower right, same as the upper left, but during the idle period of the optical measurement the light source was turned off.

and the corresponding methanes produced by the irradiation of  $\text{CD}_3\text{I}$ ,  $\text{CD}_2\text{HI}$ , and  $\text{CDH}_2\text{I}$  systems. The changes obtained using different filters or the measurement (3) stated in Sec. II are compared in Figs. 5 and 6 for later discussion. Probably because the baseline determination was not very reliable owing to the long-term fluctuation of the background signal, the absorption intensities obtained by the direct integration of the observed band turned out to deviate quite significantly. In order to reduce the deviation, the absorption intensity was obtained by assuming a Lorentzian line shape to which the recorded spectral bands were least-squares fitted. In each panel the upper half shows the temporal changes of the methyl radicals and the counterpart methanes in arbitrary units, the latter change being multiplied by an arbitrary constant so as to make the decay of the radicals and the increase of the methanes look as if they were mirror images.

In order to interpret the results shown in the upper part of each panel of Figs. 5 and 6 we have attempted the following two analyses. Eventually, the second method of analysis

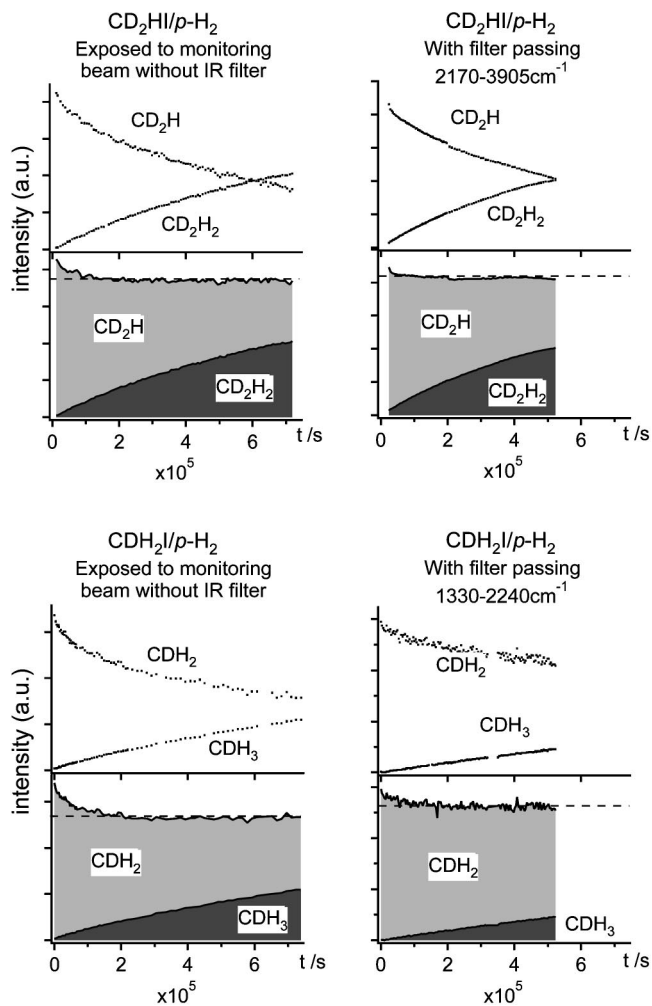


FIG. 6. The temporal changes of  $\text{CD}_2\text{H}$  and  $\text{CD}_2\text{H}_2$  (the upper two panels) and the changes of  $\text{CDH}_2$  and  $\text{CDH}_3$  (the lower two panels). Upper left, the sample was exposed to the monitoring IR beam throughout the experiment with no filters being inserted. Upper right, same as the left except that a filter passing  $2170\text{--}3905\text{ cm}^{-1}$  was used. Lower left, the sample was exposed to the monitoring IR beam throughout the experiment with no IR filters being inserted. Lower right, same as the left except that a filter passing  $1330\text{--}2240\text{ cm}^{-1}$  was used.

was adopted for later discussion. However, the result of both methods is explained herein. In the first analysis it was assumed that the temporal changes of the radicals and the methanes were entirely due to the reactions in Eq. (3). In this case the sum of the numbers of disappearing radicals and appearing methanes should remain constant as expressed in Eq. (5), where  $I_R$  and  $I_M$  represent the integrated intensities and  $A_R$  and  $A_M$  stand for the absorption coefficients of the radicals and methanes, respectively,

$$\frac{I_R}{A_R} + \frac{I_M}{A_M} = \text{const.} \quad (5)$$

The unknown parameters  $A_R$  and  $A_M$  were determined by least-squares fitting. The result of the fittings, however, totally disproved the constancy of the above equation over the entire time of all observations.

As a succeeding trial, it was presumed that some of the radicals were formed and decayed independently of the counterbalancing reaction (3). This presumption is based on

TABLE II. First-order rate constants for the rapidly decaying component of the  $\text{CD}_3$ ,  $\text{CD}_2\text{H}$ , and  $\text{CDH}_2$  radicals. The numbers in the table represent the first-order rate constant ( $k$ ) in units of  $10^{-6} \text{ s}^{-1}$ . The decay corresponds to the area shown in gray exceeding the broken horizontal lines in Fig. 5. Because the temporal change of this component was rapid and weak the precision of the rate constants in Table II is inferior to that in Table III. The second through sixth rows correspond to the three sets of conditions used in the experiments (see text in Sec. II).

	$\text{CD}_3$	$\text{CD}_2\text{H}$	$\text{CDH}_2$
No IR filter	$18 \pm 11$	$16 \pm 20$	$15 \pm 12$
Filter (2170–3905 $\text{cm}^{-1}$ )	$49 \pm 26$	$21 \pm 41$	
Filter (1330–2240 $\text{cm}^{-1}$ )			$17 \pm 57$
Filter (785–1390 $\text{cm}^{-1}$ )	$66 \pm 25$		
Dark	$30 \pm 21$		

the graphical features seen in the lower part of each panel which show the summation of the intensities of the methanes in black area and the radicals in gray. It is seen that the level of the summation becomes quickly horizontal (within less than  $2 \times 10^5 \text{ s}$ ) as shown in broken lines and that in the early stage a rapidly decaying component of the radical exists. It was found that the rapidly decaying component roughly fits an exponential curve, for which the exponents are summarized in Table II. The variance of the exponents is admittedly large. All we can say is that a small fraction of the methyl radicals is subjected to a fast decay process, perhaps a recombination with the counterpart iodine atom produced from the parent iodide through photolysis.

The fact that a horizontal line is attained by subtracting the above rapidly decaying component suggests that the major component of the radical is associated with the reaction (3), which requires that the sum of the radical and the methane produced therefrom remains constant over the entire time of all observations. In the next section this major reaction (3) will be discussed after the examination of the geminate recombination between the radical and the iodine atom.

### C. Reaction rate

#### 1. Recombination between methyl radical and iodine atom

In order to substantiate the assumption of the additional reaction of the radical with the counterpart iodine atom we have surveyed the near infrared region of the photolyzed sample. In that region the magnetic dipole allowed transition of the iodine atom,  $^2P_{1/2} \leftarrow ^2P_{3/2}$ , is known to exhibit a characteristic peak at  $7638 \text{ cm}^{-1}$ .<sup>26</sup> The peak was detected easily and showed a temporal change, as illustrated for the  $\text{CD}_3\text{I}$  system in the upper panel of Fig. 7. Concomitantly, one of the absorption lines of  $\text{CD}_3\text{I}$  observed at  $947.3 \text{ cm}^{-1}$  increased as shown in the lower panel of Fig. 7. The rates of the decay and the increase was found to be in agreement with each other within their standard deviations. Similar comparative measurements were done for all the iodide systems with no IR filter being set in between the sample and the monitoring IR beam. The observed decay rate of the iodine atom  $1.0\text{--}1.1 \times 10^{-5} \text{ s}^{-1}$  was found to be comparable with the rate of the rapid decay of the radicals as listed in Table II. These results suggest that some of the photolyzed iodides left

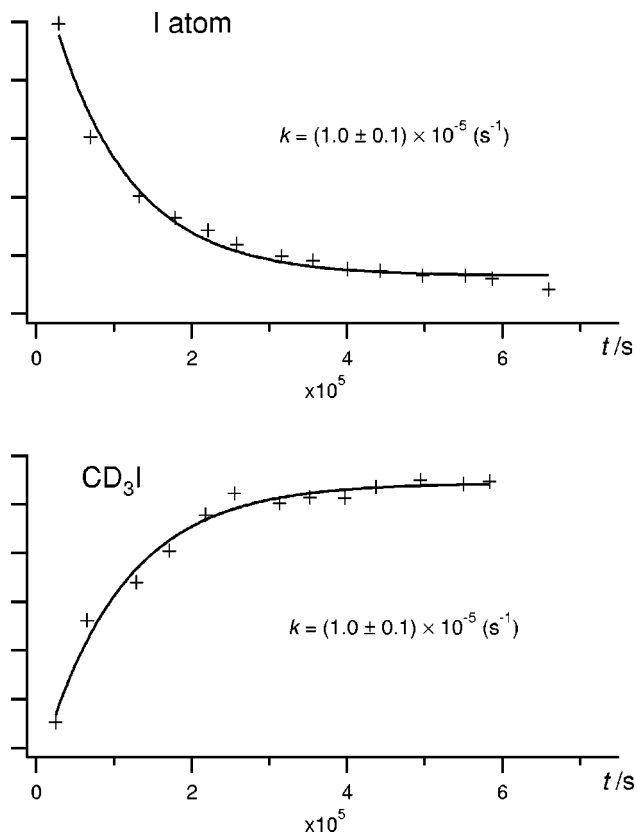
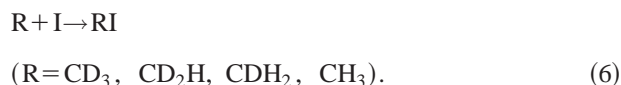


FIG. 7. The temporal changes of the absorption of I atom ( $7638 \text{ cm}^{-1}$ ) and  $\text{CD}_3\text{I}$  ( $947.3 \text{ cm}^{-1}$ ) in solid  $p\text{-H}_2$ . The solid lines represent least-squares fitting of the observed relative intensities to a single exponential function. The determined rate  $k$  is shown in each panel.

the geminately produced radicals and iodine atoms close to each other and were subjected to the following recombination:



While there is no information on the distance between the reacting partners in the reaction (6), they may well be close enough to recombine at the low temperature of 5 K. The radicals far apart from the iodine atom are considered to be subjected to the tunneling reaction with the surrounding hydrogen molecules, which will be discussed in the next section.

#### 2. Reaction between methyl radical and surrounding hydrogen

As repeatedly stated, one of the salient features of the  $p\text{-H}_2$  matrix is that it allows *in-situ* photolysis because of the negligibly small cage effect.<sup>35,36</sup> In the present systems too the major process must be the photolytic separation of the pair of the radicals and the counterpart iodine atom. The subsequent major process is obviously the tunneling reaction between the radicals and the surrounding hydrogen molecules in the reaction (3).

Although the reaction (3) is a bimolecular reaction, the reaction in the present system should be treated as those of a unimolecular reaction, because the reaction rate in the



TABLE III. First-order rate constants for the increase in the intensity of the three methanes shown graphically in Figs. 5 and 6. The numbers in the table represent the first-order rate constant ( $k$ ) in units of  $10^{-6} \text{ s}^{-1}$ . The second through sixth rows correspond to the three sets of conditions used in the experiments (see text in Sec. II).

	CD <sub>3</sub>	CD <sub>2</sub> H	CDH <sub>2</sub>
No IR filter	3.24(5)	1.34(3)	0.97(4)
Filter (2170–3905 cm <sup>-1</sup> )	3.47(3)	2.00(2)	
Filter (1330–2240 cm <sup>-1</sup> )			0.95(4)
Filter (785–1390 cm <sup>-1</sup> )	3.46(4)		
Dark	3.0(1)		

present system does not depend on the concentration of H<sub>2</sub>; all the radicals were surrounded by 12 H<sub>2</sub> molecules with the equal distance of  $\sim 3.8 \text{ \AA}$  at all times. Therefore, the number of methanes at time  $t$ , that is  $N_{\text{methane}}(t)$ , must be described by the following equation, where  $N_{\text{methane}}(\infty)$  stands for the number at an infinitely long period:

$$N_{\text{methane}}(t) = N_{\text{methane}}(\infty)[1 - \exp(-kt)]. \quad (7)$$

It could be said that the concentration dependence of H<sub>2</sub> molecules on the rate of the standard bimolecular reaction (3) is renormalized in the “pseudo”-first-order rate constant  $k$  in Eq. (7). However, the crucial difference between standard “gas phase” bimolecular reactions and the reaction in the present system is that the interaction time between the radical and H<sub>2</sub> for the reaction is infinitely long in the present system, while it is very short in standard (high-temperature) gas phase reactions. The longer interaction time is characteristic of reactions at very low temperatures.<sup>37</sup> The first-order rate constants  $k$  determined by the least-squares fitting of the increase of the intensity of methane to Eq. (7) for each system are listed in Table III.

The rate constant  $k$  can be determined independently from the slowly decaying components of the radical. The decay of the number of the radical at time  $t$ , that is  $N_{\text{radical}}(t)$ , should be described by the following equation:

$$N_{\text{radical}}(t) = N_{\text{radical}}(0)\exp(-kt), \quad (8)$$

where  $N_{\text{radical}}(0)$  stands for the number of radicals at  $t=0$ . Note that  $N_{\text{radical}}(0) = N_{\text{methane}}(\infty)$ , if the reverse of the reaction (3) is negligible. The rates  $k$  determined from the fitting of the slowly decaying components of the radical to Eq. (8) were comparable with those determined from the increase of the intensity of methane within the standard deviations. Since the intensity of the radicals consists of both rapidly and slowly decaying components, the uncertainty of the rate of the decay of the radical is larger than that of the increase of methane. Thus, we adopted the values determined by Eq. (7) for the following analysis of the reaction (3).

As the second row of Table III shows, the rate constant obtained by monitoring the absorption spectra without using any IR filter diminished as the degree of the deuteration in the radicals decreases. This tendency of the decrease in the rate constant with the decrease of the degree of the deuteration was also noticed in the experiments using the IR filters as is seen in the third through fifth rows of Table III.

As for the CD<sub>3</sub>I system, we also tried to see any possible effect of the week-long IR beam which might affect the reaction through the excitation of the reactions to their vibrational excited states by using different filters or the measurement (3) stated in Sec. II. Temporal changes of the intensity of CD<sub>3</sub> and CD<sub>3</sub>H are drawn in Fig. 5 for different conditions used in the experiments. It turned out that the effects of the IR light source on the rate constant of CD<sub>3</sub> were roughly within 10% as is seen in Table III.

## D. Discussion

First, we discuss the effect of the monitoring IR beam of the spectrometer on the reaction rate. A disadvantage of using an FTIR spectrometer for the observation of the tunneling reaction is that the sample is exposed to the light source of the spectrometer during scans. Since the tunneling rate must depend on the quantum number of the vibration-rotation states of reactants, excitation by the light source, although very weak, may change the overall reaction rate. Fortunately, as shown in Table III, the effect of the light source on the rate of the CD<sub>3</sub> and CDH<sub>2</sub> systems was found to be negligibly small. Thus, the average of the rates shown in Table III can be considered to be the tunneling rate constant of the ground vibrational state of CD<sub>3</sub> and CDH<sub>2</sub>, namely,  $(3.3 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$  for the system of CD<sub>3</sub> and  $(0.96 \pm 0.05) \times 10^{-6} \text{ s}^{-1}$  for the system of CDH<sub>2</sub>. Note that the tunneling rate of CD<sub>3</sub> determined here ( $3.3 \times 10^{-6} \text{ s}^{-1}$ ) is slightly smaller than that we determined in the previous paper ( $4.7 \times 10^{-6} \text{ s}^{-1}$ ).<sup>9</sup> The reason for the difference was that the rate we determined in the previous paper was actually the convolution of the tunneling process and the fast decay process due to the geminate recombination in the reaction (6) that we could not resolve in the previous work.

On the other hand, a significant increase in the tunneling rate of CD<sub>2</sub>H was observed when the IR beam was filtered out except for the region of 2170–3905 cm<sup>-1</sup> as shown in Table III. The increase of the tunneling rate of CD<sub>2</sub>H with the IR filter may indicate that the tunneling rate of the backward reaction,



is accelerated by the excitation of the IR light of 3900–7500 cm<sup>-1</sup>. However, it remains totally unexplained at the moment. The problem awaits further studies. In any case, it is safe to assume that the tunneling rate constant of the ground vibrational state of CD<sub>2</sub>H is  $2.0 \times 10^{-6} \text{ s}^{-1}$ .

As for CH<sub>3</sub>, we did not observe any appreciable change of the spectrum of CH<sub>3</sub> nor CH<sub>4</sub> even one week after the radical was produced except for the fast decay component of the radical attributable to the geminate recombination reaction in the reaction (6). Since the sensitivity of our measurements was better than a few percent in absorption, we concluded that the change of the signal was at most 5% after one week. The reaction rate that yields a 5% signal change is calculated to be  $8 \times 10^{-8} \text{ s}^{-1}$ . This must be the upper limit of the tunneling rate constant of the system of CH<sub>3</sub>.

One of the important findings of the present study is that the tunneling rate depends drastically on the degree of deuteration of the radicals. In our previous paper the difference

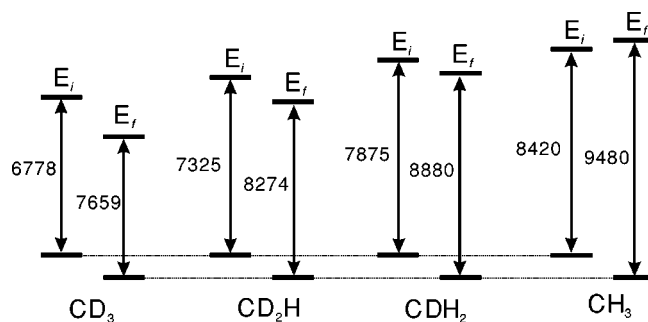


FIG. 8. The thermicity of  $R + H_2 \rightarrow RH + H$  for  $R = CD_3$  through  $CH_3$ . In each system, the left bars show energies of the reactant with (top) and without (bottom) the zero-point vibrational energies, and the right bars show those of the product. The numbers for the vertical lines represent the sum of the zero-point vibrational energies of the reactants (initial) and products (final). The units are in  $\text{cm}^{-1}$ . In order to make the values consistent, calculated vibrational frequencies were used for all the methyl radicals (Ref. 33), while vibrational frequencies observed in the gas phase were used for all the methane molecules (Ref. 31) and the hydrogen molecule (Ref. 29). The differences  $\delta E = E_f - E_i$  are 881, 949, 1005, and  $1060 \text{ cm}^{-1}$  for the  $CD_3$ ,  $CD_2H$ ,  $CDH_2$ , and  $CH_3$  systems, respectively. The horizontal bars at the bottom common to the four systems represent the energy levels of the potential minima for the initial (reactants) and the final (products) states. The upper horizontal bars show the levels with the zero-point energies included. The figure is drawn such that the final state with the zero-point energies (upper horizontal bar) is higher than the initial state for the  $CH_3$  system, while the final states are lower than the initial states for all other systems.

in the reactivity between  $CD_3$  and  $CH_3$  in the reaction (3) was ascribed to the difference in the enthalpy including the zero-point energies of the reactants and products.<sup>9</sup> A similar discussion may be applied to all the deuterated systems. Figure 8 demonstrates the thermicity including the zero-point vibration energies for all the four isotopomeric systems. It is seen that as methyl radicals become heavier, the value of  $\delta E = E_f - E_i$  decreases. Thus, if the criterion of the occurrence of the reaction depends upon *exo*- or *endo*-thermicity of the reaction as tentatively suggested in the previous paper, the demarcation line to divide the occurrence and nonoccurrence of the reaction seems to be between  $CDH_2$  and  $CH_3$  (see the upper horizontal bars in Fig. 8). However, such a discussion could be too crude as we only determined the upper limit of the reaction rate of the system of  $CH_3$ .

The tunneling reaction rate should be analyzed on the basis of the transition probability between the initial and final states of the reaction. An accidental degeneracy of the energies of the initial and final rovibrational states may drastically change the tunneling rate, which is known as the resonance effect.<sup>37</sup> Since the energy levels of the final (product) state are more dense for heavier systems due to the smaller rotational constant, the chance that the initial and final states resonantly overlap becomes larger for heavier systems, which may have relevance to the difference in the rate constants summarized in Table III.

Meanwhile, the difference in the potential energy surface of the whole reaction path should not be disregarded. The potential energy surface of the whole reaction path is slightly different for different degrees of deuteration due to the difference in zero-point vibrations.<sup>28</sup> The tunneling rate must be sensitive to such small differences in the potential energy

surfaces. Precise calculation of the potential energy surface is necessary for further discussion.

#### IV. CONCLUSION

The significant conclusions of the present work can be summarized as follows:

- (1) All the deuterated methyl radicals reacted with  $p\text{-H}_2$  molecules at 5 K by tunneling to produce methanes. The first order rate constants of the tunneling reaction were determined to be  $3.3 \times 10^{-6} \text{ s}^{-1}$ ,  $2.0 \times 10^{-6} \text{ s}^{-1}$ , and  $1.0 \times 10^{-6} \text{ s}^{-1}$  for the  $CD_3$ ,  $CD_2H$ ,  $CDH_2$  radicals, respectively. Conversely, the tunneling reaction between a  $CH_3$  radical and the hydrogen molecule did not proceed within a week's time. The upper limit of the rate constant of the tunneling reaction  $CH_3 + H_2$  was estimated to be  $8 \times 10^{-8} \text{ s}^{-1}$ .
- (2) The effect of the monitoring IR beam upon the above reaction was not significant except for  $CD_2H$ .
- (3) Most of the radical and its companion iodine atom were far separated upon the UV photolysis in solid  $p\text{-H}_2$ . However, some of the geminate pairs lie close enough to be subject to a rapid recombination to the parent iodide. The first order rate constant of  $5 \times 10^{-5} \text{ s}^{-1}$  was about one order of magnitude larger than the other reaction involving the surrounding hydrogen molecule.

For deeper understanding of the tunneling effect on chemical reactions, further experimental studies are indispensable. Detailed experiments on the frequency dependence of excitation light on the tunneling rate will be necessary to clarify the quantum level dependence of the tunneling reaction. On the other hand, temperature dependence on the tunneling rate has not yet been studied yet, but it should be. This dependence will give us important information on the effect of the fluctuation of environments on the tunneling process. Solid parahydrogen will provide a useful matrix for such studies.

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