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# Tunneling chemical reactions in solid parahydrogen: A case of $CD_3+H_2\rightarrow CD_3H+H$ at 5 K

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Ultraviolet photolysis of CD<sub>3</sub>I in solid parahydrogen at 5 K gives CD<sub>3</sub> radical, which decreases in a single exponential manner with a rate constant of  $(4.7\pm0.5)\times10^{-6}$  s<sup>-1</sup>. Concomitantly, CD<sub>3</sub>H is formed, which is accounted for by the quantum tunneling reaction CD<sub>3</sub>+H<sub>2</sub> $\rightarrow$ CD<sub>3</sub>H+H. Under the same conditions, CH<sub>3</sub>I yields CH<sub>3</sub> radical, but the corresponding reaction between CH<sub>3</sub> and H<sub>2</sub>, expected to give CH<sub>4</sub>+H, does not proceed measurably at 5 K. The difference between the two systems is attributed to the difference in the zero point energy change. © *1998 American Institute of Physics*. [S0021-9606(98)00417-6]

#### I. INTRODUCTION

Gas-phase chemical reactions at subambient temperatures are current topics in connection with the modeling of chemical and photochemical processes in the stratosphere as well as in interstellar clouds.<sup>1,2</sup> In particular, chemical reactions of the type  $X+H_2 \rightarrow XH+H$  are regarded as constituting major links in molecular processes in outer space because of the overwhelming abundance of hydrogen in the universe. Until recently, X was considered to be a positive ion as in the example  $CH^++H_2 \rightarrow CH_2^++H$ . This is because ion-molecule reactions proceed with temperatureindependent Langevin rate coefficients<sup>3</sup> so that they can be candidates for molecular evolution compatible with the environment in the outer space. However, as reviewed by Herbst,<sup>1</sup> reactions between neutral radicals and molecules also appear surprisingly rapid at low temperatures. As one such reaction, Herbst studied theoretically the reaction  $C_2H+H_2 \rightarrow C_2H_2+H$ , which has an activation energy as large as  $\approx 1000 \text{ cm}^{-1}$ , and showed that the rate constant increases at temperatures below 50 K, reaching a value of 2.2  $\times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 10 K when the tunneling contribution is included.<sup>4</sup> Under the circumstances, an experimental investigation on the tunneling contribution to chemical reactions between neutral molecules is desirable. Numerous studies on the tunneling effect have been carried out for reactions where the tunneling agent is an electron, a proton, and a hydrogen atom, as is reviewed in textbooks.<sup>5-7</sup> As for reactions at cryogenic temperatures, a typical example hydrogen atom transfer of is of the type  $RH + \cdot CH_3 \rightarrow \cdot R + CH_4$ , which is studied ESR by spectroscopy.<sup>8</sup> In the present work, we are concerned with reactions of the type  $X+H_2 \rightarrow XH+H$ , with X being a neutral species, as in the reaction studied by Herbst.

We have been using solid parahydrogen  $(p-H_2)$  as a matrix for matrix-isolation spectroscopy.<sup>9–15</sup> By virtue of the softness of the matrix, solid  $p-H_2$  is free from the cage effect, and unstable molecules such as free radicals can easily be produced by photolysis in the matrix. The radicals thus produced in the solid  $p-H_2$  are subjected to reactions with

surrounding hydrogen molecules, if the reaction is thermodynamically allowed. In this paper, we have studied chemical reactions (I) and (II) between a methyl radical and a hydrogen molecule:

$$CH_3+H_2 \rightarrow CH_4+H,$$
 (I)

$$\cdot CD_3 + H_2 \rightarrow CD_3H + H \tag{II}$$

The radicals were produced by the UV photolysis of methyl iodide and its deuterated species as in (III):

$$CH_3I/CD_3I + h\nu \rightarrow CH_3/CD_3 + I \text{ in } p-H_2.$$
 (III)

As a result, we have found that reaction (II) takes place at 5 K in solid p-H<sub>2</sub>, while reaction (I) does not measurably under the same conditions. Since the activation energy of these reactions is  $\approx 3700 \text{ cm}^{-1}$  (see below), thermal activation for the reactions at 5 K is prohibitive. Therefore, the occurrence of reaction (II) must be ascribed exclusively to quantum tunneling. To our knowledge, the present work provides the first direct spectral evidence for an exclusive tunneling reaction between neutral molecules.

#### **II. EXPERIMENT**

Normal hydrogen gas was converted to p-H<sub>2</sub> which contained about less than 0.01% residual orthohydrogen. The converted gas was mixed with either CH<sub>3</sub>I or CD<sub>3</sub>I at room temperatures. The concentration ratio of the iodides to  $p-H_2$ was typically 0.005%. The mixed gas was introduced into a cylindrical copper cell of dimensions 5 to 10 cm long and 2 cm in diameter attached with BaF2 windows at both ends of the cylinder. The temperature of the cell was kept at about 9.0 K during the introduction of the sample gas for some 1.5 h. Then, the temperature was slowly lowered to  $5.1\pm0.2$  K and kept at the same temperature throughout the experiment. A low pressure 20 W mercury lamp was used without filters for the photolysis of the methyl iodides. The optical measurement was performed using a Nicolet Magna 750 FTIR spectrometer with a resolution of  $0.25 \text{ cm}^{-1}$  in combination with a KBr beam splitter and a liquid N2 cooled MCT-

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FIG. 1. Infrared absorption spectra of perdeuterated methyl iodide (CD<sub>3</sub>I) in solid p-H<sub>2</sub> at about 5 K in the spectral region of  $2388-2407 \,\mathrm{cm}^{-1}$ . The spectra are for the sample as deposited and recorded before UV irradiation (top), after a 4 h UV irradiation (middle), and after about 1.5 days in the dark at about 5 K (bottom). The bottom spectrum has ~60% of the intensity of the spectrum in the middle.

(HgCdTe) detector. For reference, the infrared spectra of methane and methane- $d_3$  dispersed in solid p-H<sub>2</sub> were measured under the same conditions as those for the iodide systems. Further details of the experiment are given in our previous papers.<sup>9–15</sup>

#### **III. RESULTS**

The experiment consists of a series of infrared absorption measurements of the  $CH_3I/p-H_2$  and the  $CD_3I/p-H_2$ systems before and after UV irradiation and after subsequent standing in the dark at  $5.1\pm0.2$  K. Figures 1 and 2 show representative portions of the spectra of the  $CD_3I/p-H_2$  system before UV irradiation (top), after a 4 h irradiation (middle), and after subsequent standing for about 1.5 days (bottom). A total of four runs of the experiment were carried out to ascertain the reproducibility of the experimental results. The arrowed peaks at 2398.7, 2395.6, 2394.3, 2390.5, and 2388.7 cm<sup>-1</sup> in the middle spectrum are attributed to the



FIG. 2. Infrared absorption spectra of perdeuterated methyl iodide (CD<sub>3</sub>I) in solid p-H<sub>2</sub> at about 5 K in the spectral region of 2978–3004 cm<sup>-1</sup>. The spectra are for the sample as deposited and recorded before UV irradiation (top), after a 4 h UV irradiation (middle), and after about 1.5 days in the dark at about 5 K (bottom).



FIG. 3. The  $\nu_{3a}$  band of CD<sub>3</sub>H in solid p-H<sub>2</sub> at about 5 K.

doubly degenerate C–D stretching mode ( $\nu_3$ ) of the CD<sub>3</sub> radical by comparison with the reported band origin of the radical at 2381 cm<sup>-1</sup> in a Ne matrix<sup>16</sup> and at 2381.088 cm<sup>-1</sup> in the gas.<sup>17</sup> The  $\nu_3$  band extends over  $\approx 2400-2330$  cm<sup>-1</sup> according to the gas phase study.<sup>17</sup> The spectral structure of CD<sub>3</sub> in Figs. 2 and 3 is attributed to rotational structure subjected to crystal field splitting.<sup>12-14</sup> A detailed analysis of the spectrum of the CD<sub>3</sub> radical will be published separately.<sup>18</sup> Due to the strong absorption of carbon dioxide, the peaks of  $CD_3$  below 2388 cm<sup>-1</sup> are not shown in Fig. 1. The peaks attributed to CD<sub>3</sub> diminish to about 60% after standing 1.5 days as shown in the bottom spectrum of Fig. 1. Figure 2 demonstrates that the absorption of  $CD_3H(\nu_{3a}^{19})$  appears during the 1.5 days standing (the bottom spectrum). This spectrum should be compared with Fig. 3, showing the  $v_{3a}$ band of  $CD_3H$  isolated in solid  $p-H_2$ .<sup>20</sup> One may notice a slight difference in the intensity distribution between the reference spectrum in Fig. 3 and the bottom spectrum of Fig. 2. This can be accounted for in terms of the slow relaxation of the nuclear spin state of CD<sub>3</sub>H, in the same way as the prototypical system  $CH_4/p-H_2$ .<sup>12,14</sup> Although not shown, other absorptions of CD<sub>3</sub>H assigned to  $\nu_{3b}$ ,  $\nu_2$ , and  $\nu_{4a}^{19,20}$  also appeared in parallel with the absorption of  $\nu_{3a}$ .

As for the CH<sub>3</sub>I/*p*-H<sub>2</sub> system, the absorption of CH<sub>3</sub> radical appeared upon the UV irradiation as a doublet at 3171.4/3170.6 cm<sup>-1</sup> (strong), 1402.7/1401.6 cm<sup>-1</sup> (strong), and 2780.1/2779.3 cm<sup>-1</sup> (weak), reproducing our previous work.<sup>9</sup> These absorptions are assigned to the crystal field split doublet R(0) line of the doubly degenerate C–H stretching ( $\nu_3$ ), the doubly degenerate C–H bending ( $\nu_4$ ), and the overtone of  $\nu_4$  of CH<sub>3</sub>, respectively.<sup>12</sup> As in our previous work, these absorptions of the methyl radical were found not to diminish measurably at 5 K in the dark over a period of a few days. The absence of the decrease of the CH<sub>3</sub> radical in the dark is in remarkable contrast to the case of CD<sub>3</sub> radical shown in Fig. 1.

Figure 4 demonstrates the time dependence of the logarithmic absorbance of  $CD_3$  at 2388.7 cm<sup>-1</sup> during the standing in the dark. The t=0 point in Fig. 4 corresponds to the sample after a 4 h UV irradiation (corresponding to the middle spectrum of Fig. 1). Similarly, Fig. 5 demonstrates the time dependence of the absorbance of  $CD_3H$  at

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FIG. 4. The logarithmic intensity of CD<sub>3</sub> as a function of time while standing at 5 K in the dark. The solid line is the theoretical curve of Eq. (1) with  $k = (4.7 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$ .

2995 cm<sup>-1</sup> in arbitrary units. In both figures the observed peak height *I* was normalized relative to the intrinsic absorption of p-H<sub>2</sub> at 2410.5384 cm<sup>-1</sup> which is known to correspond to the  $J=6 \leftarrow 0$  transition.<sup>21</sup> If we assume that reaction (II) occurred during the dark period, the temporal change of the infrared absorption intensity of CD<sub>3</sub>, designated as  $I_{CD_3}(t)$ , and that of CD<sub>3</sub>H, designated as  $I_{CD_3H}(t)$ , should be described by the following equations:

$$I_{\rm CD_2}(t) = Ce^{-kt},\tag{1}$$

$$I_{\rm CD_2H}(t) = C'(1 - C''e^{-k't}), \qquad (2)$$

where *C*, *C'*, and *C''* are arbitrary constants. Equation (1) is based on the consideration that the bimolecular reaction (II) is a statistical process to conform to an exponential decay. The parameters *k* and *k'* represent the rate constants. The decay of CD<sub>3</sub> in Fig. 4 is fitted to Eq. (1) by the least squares method to obtain  $k = (4.7 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$  while the fitting of the increase of CD<sub>3</sub>H in Fig. 5 to Eq. (2) gives the value of  $k' = (4.1 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$ . The best fitted curves are drawn in Figs. 4 and 5. Due to the noise and the uncertainty



FIG. 5. The intensity of  $CD_3H$  in arbitrary units as a function of time while standing at 5 K in the dark. The solid line is the theoretical curve of Eq. (2) with  $k' = (4.1 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$ .

of the background absorption the accuracy of k and k' is only moderate, but k and k' may be regarded as being equal within the error, which is consistent with reaction (II) during the dark period.

One might consider that the formation of  $CD_3H$  in the  $CD_3I/p-H_2$  system is due to a reaction between  $CD_3$  and H atoms, the latter being produced by some unknown reaction in our system. Reactions of such migratory H atoms have been discussed by Miyazaki *et al.*<sup>22</sup> However, there seems no mechanism to have migratory H atoms in our system, which makes us consider the direct reaction between  $CD_3$  and  $H_2$ . Moreover, if H atoms were produced by some overlooked reaction, they would be produced plausibly in the  $CH_3I/p-H_2$  system also, and one would obtain  $CH_4$  by the corresponding reaction of  $CH_3+H\rightarrow CH_4$ , which is not substantiated in our experiment.

#### **IV. DISCUSSION**

Gas-phase reactions of the type  $X+H_2\rightarrow XH+H$  with X being the isoelectronic series of F, OH, NH<sub>2</sub>, and CH<sub>3</sub> have been studied both experimentally and theoretically.<sup>23</sup> In particular, the reaction  $CH_3+H_2\rightarrow CH_4+H$  and its deuterium analogues have been intensively studied by Truhlar and his co-workers because of their fundamental importance in hydrocarbon chemistry and because of the availability of experimental kinetic data over a wide range of temperature.<sup>24–27</sup> Deuterium isotope effects in the reaction have also been investigated by Schatz *et al.*<sup>28</sup> In these previous studies, focus was placed on normal (high temperature) chemistry and the contribution of the tunneling effect to the reaction was treated rather secondarily because the major part of the reaction is due to thermal processes.

In the present experiment carried out at about 5 K, the occurrence of reaction (II) must be ascribed exclusively to tunneling because the experimentally determined activation energy for reactions (I) and (II) amounts to 10.9  $\pm$  0.5 kcal/mol( $\cong$ 3700 cm<sup>-1</sup>).<sup>23</sup>

Quantum tunneling in chemical reactions has long attracted chemists' interest.<sup>5–7</sup> The nonlinearity of the Arrhenius plot of reaction rate constant versus the inverse of temperature is taken customarily as an indication of the involvement of tunneling. However, the nonlinearity itself should not necessarily be attributed to tunneling because of other possible causes such as the temperature dependent effect of solvent in the case of reactions in liquids and frozen solvents. Therefore, convincing evidence for tunneling based on the temperature dependence of reaction rate constants is scarce<sup>29</sup> and Siebrand stated that "it is difficult to prove that a given reaction proceeds via tunneling." <sup>30</sup>

The present result demonstrated in Figs. 1–4 provides spectral evidence for the occurrence of reaction (II), which must proceed via tunneling at the low temperature of  $\approx 5$  K. It is noted that the amplitude of the zero point vibration of p-H<sub>2</sub> molecule amounts to as much as  $\approx 18\%$  of the lattice constant<sup>31</sup> so that the overlap of the wave function of the reacting p-H<sub>2</sub> molecule with that of the radical is considered to be essential for inducing the tunneling.

One may think that the iodine atom produced by the photodissociation of the methyl iodides [reaction (III)] plays

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TABLE I. Zero point vibrational energies (ZPE) of reactions (I) and (II) in units of kcal  $mol^{-1}$ .

$(I) \\ CH_3 + H_2 \rightarrow CH_4 + H$		(II) $CD_3+H_2\rightarrow CD_3H+H$	
ZPE(CH <sub>3</sub> )	18.90	ZPE(CD <sub>3</sub> )	13.80
$ZPE(H_2)$	6.29	$ZPE(H_2)$	6.29
$ZPE(CH_4)$	28.34	ZPE(CD <sub>3</sub> H)	22.71
$\Delta ZPE^{a}$	3.15	$\Delta ZPE^{a}$	2.62

<sup>a</sup> $\Delta$ ZPE=ZPE(CH<sub>4</sub>/CD<sub>3</sub>H)-ZPE(CH<sub>3</sub>/CD<sub>3</sub>)-ZPE(H<sub>2</sub>).

some role in reactions (I) and (II). However, we can deny the possibility as follows. The analysis of the rotation-vibration spectra of CH<sub>3</sub> and CD<sub>3</sub> reveals that these radicals are rotating almost freely in a crystal field of  $D_{3h}$  symmetry.<sup>12,18</sup> The conservation of the symmetry of the crystal surrounding the radicals indicates that the iodine atom is separated enough from the radicals not to disturb the energy levels of the radicals. Since most of the excess energy of reaction (III) is transferred to the radicals as translational energy, 32,33 the radical and the iodine atom are plausibly well separated in the soft medium.

The crux of the present work is the finding that reaction (II) takes place while reaction (I) does not under the same experimental conditions. With such a clear-cut difference between the two systems, one may be inclined to call on such a physical cause as the symmetry selection rules for reactants and products consisting of several identical H (fermions) and D (bosons).<sup>34</sup> However, it is found that symmetry considerations on the product of the rotational and the nuclear spin states of the reactants and products do not lead to any restrictive selection rule. Since the usual isotope effect is kinetic rather than thermodynamic and generally predicts slower rate constants for deuterated systems, we seek a thermodynamical cause as responsible for the apparently inverted isotope effect in the present study.

The zero point vibrational energies (ZPE) pertaining to reactions (I) and (II) and the difference defined as  $\Delta ZPE = \Sigma ZPE(products) - \Sigma ZPE(reactants)$  are given in Table I.<sup>35</sup> The difference of the potential minima of reactants and products is called here the reaction energy<sup>23</sup> and is denoted as  $\Delta E_R$ , while the sum of  $\Delta E_R$  and  $\Delta$  ZPE is called the reaction enthalpy  $\Delta H_R$ .<sup>23</sup> Then, in so far as  $\Delta E_R$  is assumed to be common to reactions (I) and (II), reactions (I) and (II) are slightly endo  $[\Delta H_R(I) < 0]$  and exothermic  $[\Delta H_R(II) > 0]$ , respectively, if  $\Delta E_R$  is in the range of  $2.62 \text{ kcal mol}^{-1} - 3.15 \text{ kcal mol}^{-1}$  (see Fig. 6).

According to an ab initio MO calculation, the reaction energy in free space is predicted to be 2.79, 3.46, and 4.01 kcal/mol<sup>23</sup> and 2.76 kcal/mol<sup>36</sup> depending upon the quality of the basis set for calculation. These values are compatible with the above range of 2.62-3.15 kcal/mol. In view of the subtlety of the situation drawn in Fig. 6 and in view of the fundamental importance of the reaction, quantum chemical calculations to the accuracy of less than 1 kcal/mol should be valuable.



FIG. 6. An energy diagram for reactions (I) and (II). The horizontal lines at the bottom and at the top correspond, respectively, to the energy levels without and with the zero-point energies of the reactants and the products.

amplitude zero-point vibration of  $p-H_2$  favoring the overlap of wave functions of the reacting hydrogen molecule and the radical.

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In conclusion, we have demonstrated spectral evidence for tunneling in the reaction  $CD_3+H_2\rightarrow CD_3H+H$ , which is attributed to the very subtle exothermicity and to the large

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