Nuclear spin selection rule in the photochemical reaction of CH_3 in solid parahydrogen

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Photolysis of a methyl radical CH_3 in solid parahydrogen produces a methane molecule CH_4 via the reaction between an intermediate singlet methylene $^1CH_2$ and a parahydrogen molecule H_2. Conservation of nuclear spin during the reaction has been investigated by the intensity distribution of the rotation-vibration spectrum of methane produced by the reaction. It was found that the population of each nuclear spin state of methane just after the reaction was different from that of the statistical ratio, which indicates that a nuclear spin selection rule does exist in the reaction. However, the observed population was significantly different from the theoretically predicted ratio. The discrepancy between the experiment and the theory may indicate a breakdown of the nuclear spin conservation during the reaction, if the reaction mechanism in solid parahydrogen is the same as in the gas phase. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1480003]

I. INTRODUCTION

Because of the weak nuclear magnetic interactions, the total nuclear spin angular momentum I is well conserved in most physical processes such as radiative transitions[1] and collisions.[2] One well-known case is the para (p-H_2) and ortho (o-H_2) modifications of hydrogen molecules.[3] The p-$H_2(I=0)$ and o-$H_2(I=1)$ can be treated as different molecules because the conversion between them is almost forbidden in the absence of a paramagnetic catalyst.

It has been observed that the memory of nuclear spin is conserved even in chemical processes, where particle rearrangements occur. Under the assumption of the rigorous conservation, Quack has derived selection rules on the nuclear spin modifications during chemical reactions.[4] The selection rules play an important role in various fields, especially in interstellar chemistry.[5–9] Observation of the abundance of each nuclear spin state of a molecule provides a key to understand the formation of the molecule in the interstellar space.

Despite the importance of the selection rules in various fields, few experimental studies have been reported so far on the quantitative analysis of the nuclear spin modification during chemical reactions. Nuclear spin polarization after a p-H_2 addition reaction has been observed using nuclear magnetic resonance (NMR) spectroscopy.[10–12] Selective generation of o-H_2 by the photodissociation of ortho-H_2CO (Refs. 13, 14) is one evidence of the conservation. Recently, a quantitative experiment on the nuclear spin selection rule in the reactions of $H_2^+ + H_2 \rightarrow H_3^+ + H$ has been performed by Uy, Cordonnier, and Oka.[15,16] They reported that the ortho–para ratio of H_3^+ after the reaction in a plasma can be explained with the theoretically predicted ratio under the assumption of the rigorous conservation.

We have investigated the nuclear spin modification in consecutive reactions of

$$CH_3 + h\nu \rightarrow CH_2 + H \tag{1}$$

and

$$CH_2 + p\text{-}H_2 \rightarrow CH_4 \tag{2}$$

in solid parahydrogen at liquid He temperature. Solid hydrogen is an ideal matrix for the quantitative study of chemical reactions because of (1) weak intermolecular interaction between hydrogen molecules, (2) no "cage effect" for photolysis in the solid,[17–19] (3) fully quantized rotational motion of molecules embedded in the solid,[20–22] and (4) narrow spectral linewidth of optical transitions.[17,21] By virtue of the free rotation of the molecules involved in the above reactions, rotation-vibration transitions of the molecules gave us quantitative information on the nuclear spin modification during the reactions. The observed nuclear spin population after the reactions is compared with the theory to discuss the conservation of the nuclear spin during the reactions.

II. EXPERIMENTS

The methyl radical CH_3 was produced by *in situ* UV photolysis of methyl iodide CH_3I embedded in solid parahydrogen.[18] Method of the sample preparation was the same as described in previous papers.[17,18,23] Briefly, parahydrogen gas containing $<0.01\%$ orthohydrogen was mixed with the methyl iodide ($\sim 0.001\%$) at room temperature and the mixed gas was introduced in a copper optical cell kept at 8.0 K to grow a crystal. A 20 W low pressure mercury lamp with a cutoff filter Toshiba UV-25 was used for the selective photolysis of CH_3I at 253.7 nm to produce CH_3. A half-day irradiation of the 253.7 nm photons led to the photodissociation of most of the iodides into the radical. The methyl radical CH_3 thus produced is completely stable in solid parahydrogen.[23]

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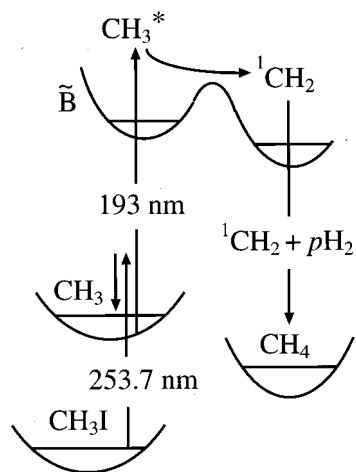
FIG. 1. Schematic diagram of the reactions relevant to the present system. Methane is only produced after the second UV irradiation at 193 nm (Ref. 23).

After the production of the methyl radical, the radical was excited to its $\tilde{B}(^2A_1')$ state[24] by 193 nm UV pulses from an ArF excimer laser (6 mJ/pulse, 30 Hz). A 20 min irradiation of the UV pulses was enough to destroy most of the radical. Along with the destruction of the radical, the formation of methane CH_4 was observed.

Infrared absorption spectra of CH_3I, CH_3, and CH_4 before and after the UV irradiations were observed using a FTIR spectrometer (Bruker IFS120HR) with a resolution of 0.1 cm^{-1}. A KBr beamsplitter and a liquid N_2 cooled MCT detector were used for the spectroscopy. All the measurements were done at 4.6 K.

III. REACTION SCHEME

Figure 1 shows the schematic diagram of the methane formation reaction in solid p-H_2. Detailed analyses of the reaction scheme in the present system have been made in previous papers.[18,23] The UV light at 253.7 nm dissociates the methyl iodide in p-H_2 crystal to produce a methyl radical and an iodine atom. The radical thus produced is stable in solid parahydrogen. Then, the UV light at 193 nm excites the radical to its electronic excited $\tilde{B}$ state, in which the predissociation into a singlet methylene and a hydrogen atom occurs. The methylene thus produced quickly reacts with a nearby hydrogen molecule to produce a methane. Another possibility for the production of CH_4, that is, the abstraction of a hydrogen atom from a hydrogen molecule by the radical in the excited $\tilde{B}$ state could be completely ruled out by a parallel study of the photolysis of CD_3I.[23] If the abstraction reaction took place, the formation of CD_3H should be expected in the system of CD_3I. However, the production of only CD_2H_2, but no trace of CD_3H was observed as a result of the UV irradiation of CD_3. Thus, it is concluded that the methane in the present system is produced only by the reaction of $CH_2 + H_2 \rightarrow CH_4$.

IV. NUCLEAR SPIN POPULATION OF CH₄

Methane CH_4 has three different nuclear spin modifications, that is, $I=2(A)$, $I=1(F)$, and $I=0(E)$ states. Because of the symmetry requirement of the total-wavefunction of CH_4, each nuclear spin state couples with particular rotational states.[25] The $J=0$ rotational state of CH_4 couples with the $I=2$ nuclear spin state, the $J=1$ couples with the $I=1$ state, the $J=2$ couples with both the $I=1$ and $I=0$ states, and so on. Thus, the population of each nuclear spin state can be determined from the intensities of rotationally resolved infrared absorption spectra.

As we discussed in previous papers,[26,27] the conversion among the three nuclear spin states of CH_4 takes place in solid parahydrogen. The temporal change of the infrared absorption of the rovibrational transition revealed that the conversion from the $I=1$ state to the $I=2$ nuclear spin state associated with the rotational relaxation of $J=1 \rightarrow J=0$ occurred in a time scale of a few days, while the conversion from the $I=0$ state to the $I=1$ nuclear spin state was too fast to observe. Temporal changes of the mole fraction $c(t)$ of the $I=2$ nuclear spin state were well fitted with the function,

$$c(t) = [c(0) - c(\infty)]\exp(-kt) + c(\infty), \qquad (3)$$

where $c(0)$ and $c(\infty)$ are the mole fraction at $t=0$ and $t=\infty$, respectively, and k is the conversion rate. The conversion rate depends on the temperature of the crystal. The rate at 4.6 K was found to be $k=2.8\times 10^{-3}$ min^{-1}.[27]

In the present reaction system, the initial nuclear spin population of CH_4 just after the reaction can be obtained from the value of $c(0)$ in Eq. (3). Since the population in the $I=0$ nuclear spin state is negligible, the values of $c(0)$ and $(1-c(0))$ correspond to the population of the $I=2$ state and the $I=1$ state, respectively. Note that the population in the $I=1$ nuclear spin state we observed should be considered as the sum of the population of the $I=1$ and $I=0$ nuclear spin states after the reaction, since all the $J=2$, $I=0$ state had relaxed to the $J=1$, $I=1$ state within our experimental time scale.[27]

Figure 2 shows the ν_3 infrared absorption of CH_4 produced by the 193 nm UV irradiation. Panel (a) in Fig. 2 is the spectrum observed just after the UV irradiation for 20 min, while panel (b) is the spectrum observed 1000 min after the UV irradiation. It is clearly seen that intensities in the transition from the $J=1$ state greatly decreased after 1000 min, while the intensity of the $R(0)$ transition increased. The initial mole fraction $c(0)$ can be determined by the least-squares fitting of the temporal change of the intensities of each rotational branches by the use of Eq. (3).

A plot of the mole fraction $c(t)$ of methane produced by the photolysis is shown in Fig. 3. The time when the second UV irradiation at 193 nm started was taken as the origin of time, that is, $t=0$. From the least-squares fitting, the initial mole fraction of the $I=2$ state was obtained to be $c(0) = 0.19 \pm 0.01$ with the rate constant of $k=3.9 \times 10^{-3}$ min^{-1}. The rate constant was consistent with that observed in pure CH_4/p-H_2 system reported previously.[27] Thus, although the iodine atoms and the methyl radicals were present in the sample,[28] their effect on the nuclear spin conversion process of CH_4 is negligible.
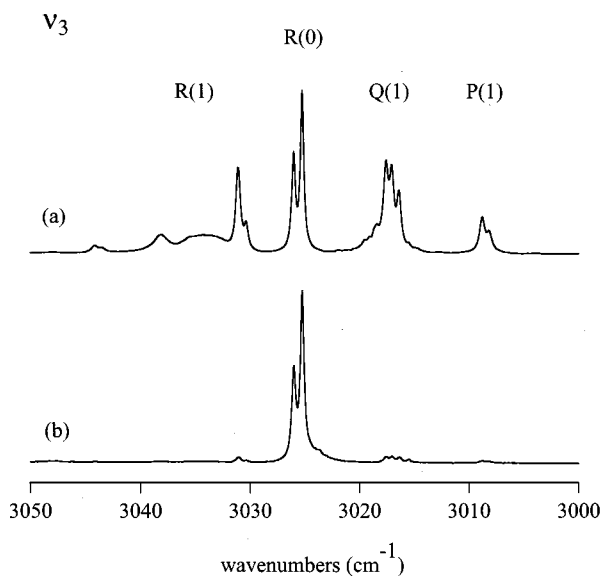
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FIG. 2. Infrared absorption spectra of the ν_3 vibrational transition of CH$_4$ produced by the UV irradiation. Trace (a) is the spectrum observed just after the UV irradiation at 193 nm. Trace (b) is the spectrum observed 1000 min after the UV irradiation.

In Fig. 3, the period of the 193 nm UV irradiation is drawn by a broken curve. Exactly speaking, the temporal change of the mole fraction $c(t)$ during the irradiation does not obey the function in Eq. (3), since methane molecules were produced continuously during the irradiation. However, the irradiation time of 20 min is short enough compared with the nuclear spin conversion rate of 4×10^{-3} min^{-1}. If we take into account the correction, the mole fraction of the $I = 2$ state at the time $t = 0$ must be greater than that determined without the correction, but the difference is estimated to be 5% at most. Therefore, it is safely concluded that the population of each nuclear spin state of CH$_4$ just after the consecutive reactions (1) and (2) was $(I=2):(I=1):(I=0) = 0.2:0.8:0.0$ with the uncertainty of 5%.
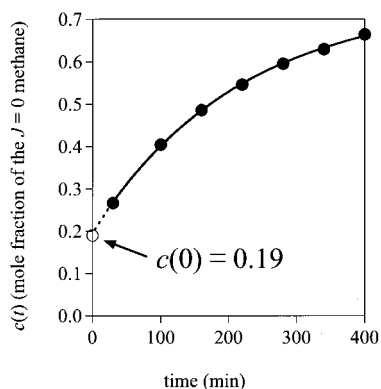

FIG. 3. Temporal behavior of the mole fraction of the $J=0$ methane. Solid circles represent the observed data while the solid line stands for the theoretical curve of Eq. (3). The time when the second UV irradiation started was taken as the origin of time. The mole fraction at the time $t=0$ is shown by an open circle, which was obtained by the extrapolation of the curve to $t=0$.

TABLE I. (a) Ratio of the nuclear spin isomers of ^{1}CH$_2$ produced by the photolysis of CH$_3$. (b) Ratio of the nuclear spin isomers of CH$_4$ after the reaction of ^{1}CH$_2 + H_2 \rightarrow$CH$_4$.

(a)	CH$_3$	$\rightarrow$	^{1}CH$_2$	+H
	I		$(I=0):(I=1)$	
	1/2		1 : 1	
	3/2		0 : 1	
(b)	^{1}CH$_2$ +	H$_2$	$\rightarrow$	CH$_4$
	I	I		$(I=2):(I=1):(I=0)$
	0	0		0 : 0 : 1
	1	0		0 : 1 : 0
	0	1		0 : 1 : 0
	1	1		5 : 3 : 1

V. DISCUSSION

The initial population of the nuclear spin state of $(I=2):(I=1):(I=0) = 0.2:0.8:0.0$ just after the reaction is significantly different from the equilibrium population at the high temperature limit of $(I=2):(I=1):(I=0) = 0.31:0.56:0.13,$[29,30] or the population of $(I=2):(I=1):(I=0) = 0.31:0.69:0.00$ after the fast relaxation from the $J=2$, $I=0$ state to the $J=1$, $I=1$ state. If there is no selection rule on the nuclear spin modification during the chemical reaction, the initial population must be that of the high temperature limit because of the excess energy of the reactions in reactions (1) and (2). The significant difference between the observed population and the population of the high temperature limit indicates that a selection rule on the nuclear spin modification does exist in the present reaction system.

The methyl radical, with the ground electronic state with symmetry $^2A_2''$, has two nuclear spin modifications, that is, $I=3/2$ and $I=1/2$ states. The $J=0$, $K=0$ lowest rotational level couples with the $I=3/2$ nuclear spin state, while the $J=1$, $K=1$ state couples with the $I=1/2$ state.[26] The methyl radical in the present system is rotating almost freely in solid parahydrogen. The infrared absorption of CH$_3$ shows a doublet,[17,18] which indicates that the radical occupies only the $J=0$, $K=0$ state in solid parahydrogen at 4.6 K. We therefore concluded that the radical occupied the nuclear spin state of $I=3/2$ before the 193 nm UV irradiation.

The nuclear spin selection rule in the photodissociation reaction of the radical is shown in Table I(a). The $I=1/2$ CH$_3$ radical produces both the $I=0$ and $I=1$ nuclear spin states of CH$_2$, while the $I=3/2$ radical results in only the $I=1$ state of CH$_2$. Since the methyl radical in the present system occupied the $I=3/2$ state only, the ^{1}CH$_2$ produced by the UV irradiation should occupy only the $I=1$ state, if the nuclear spin selection rule is rigorous.

Table I(b) lists the nuclear spin selection rule in the reaction of ^{1}CH$_2 +$H$_2 \rightarrow$CH$_4$, where we assumed that the reaction is the insertion reaction as in the gas phase.[31] In our system more than 99.99% hydrogen molecules occupied the $I=0$ state, while only the $I=1$ singlet methylene was produced by the photolysis. Thus, the nuclear spin state relevant to the present system is exclusively

TABLE II. (a) Ratio of the nuclear spin isomers of CH_3 produced by the abstraction reaction of $CH_2 + H_2 \rightarrow CH_3 + H$. (b) Ratio of the nuclear spin isomers of CH_4 after the reaction of $CH_3 + H \rightarrow CH_4$.

(a)	CH_2	+	H_2	$\rightarrow$	CH_3	+	H
	I		I		$(I=3/2) : (I=1/2)$		
	0		0		0 : 1		
	1		0		2 : 1		
	0		1		0 : 1		
	1		1		2 : 1		
(b)	CH_3	+	H	$\rightarrow$	CH_4		
	I		I		$(I=2) : (I=1) : (I=0)$		
	3/2		1/2		5 : 3 : 0		
	1/2		1/2		0 : 3 : 1		

$$^1CH_2(I=1) + H_2(I=0) \rightarrow CH_4(I=1). \qquad (4)$$

If the nuclear spin selection rule during the chemical reactions is rigorous, only the $I=1$ nuclear spin state of CH_4 should be produced in the above reaction system, that is, the initial population of CH_4 after the reactions should be $(I=2):(I=1):(I=0)=0.0:1.0:0.0$. However, we observed the significant population in the $I=2$ state of CH_4 just after the reaction. One may think that the production of the $I=2$ state is due to the nuclear spin conversion in the solid after the reactions. However, we can rule out the possibility, because it needs more than 1 h to produce 20% of the $I=2$ methane by the nuclear spin conversion from the $I=1$ methane at 4.6 K. Thus, the $I=2$ nuclear spin state must be produced during the reactions.

The significant population in the $I=2$ nuclear spin state just after the reaction needs to be explained. One possible explanation for this is that the nuclear spin selection rule is partially violated in the present reaction system. Another explanation is that the reaction mechanism in solid parahydrogen is different from that in the gas phase. In the following, we shall discuss the latter possibility in detail.

If the reaction between a methylene and a hydrogen molecule is not the insertion reaction, but an abstraction reaction, the production of the $I=2$ nuclear spin state can be expected as follows:
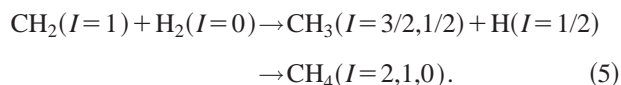
$$CH_2(I=1) + H_2(I=0) \rightarrow CH_3(I=3/2,1/2) + H(I=1/2)$$
$$\rightarrow CH_4(I=2,1,0). \qquad (5)$$

Table II summarizes the nuclear spin selection rule involved in the above stepwise reaction. It is seen that the $I=2$ CH_4 is produced by the reaction between the $I=3/2$ CH_3 radical and $I=1/2$ H atom. The stepwise reaction of the $I=1$ CH_2 and $I=0$ H_2 results in the nuclear spin population of CH_4 as $(I=2):(I=1):(I=0)=0.42:0.50:0.08$, or $(I=2):(I=1):(I=0)=0.42:0.58:0.00$ after the fast relaxation from the $I=0$ state to the $I=1$ state. Thus, a combination of the insertion reaction [reactions (1) and (2)] and the abstraction reaction [reaction (5)] might explain the observed nuclear spin population of CH_4, even if the nuclear spin selection rule is rigorous.

It is known that, in the gas phase, the reaction between a singlet methylene $^1CH_2$ and a hydrogen molecule H_2 is the insertion reaction, while the reaction between a triplet methylene $^3CH_2$ and a hydrogen molecule H_2 is the abstraction reaction.[32,33] Thus, if part of the singlet methylenes $^1CH_2$ relax to the triplet state before the reaction with H_2, the $I=2$ CH_4 is produced by the stepwise reaction in reaction (5). However, since the relaxation rate from the singlet $^1CH_2$ to the triplet $^3CH_2$ is two orders of magnitude slower than the rate of the insertion reaction,[31,34] it seems unlikely that the triplet methylene was formed in solid parahydrogen. Moreover, it is important to note that no infrared absorption corresponding to $^3CH_2$ (Ref. 35) was observed at any stage of the present system.

Nevertheless, because of the proximity between CH_2 and H_2 in the solid, the possibility of the stepwise reaction in reaction (5) cannot be completely ruled out. The experimental result is definitive and it is clear that the nuclear spin selection rule is violated in the present system, if the reaction mechanism is the same as in the gas phase. Further studies are necessary for more quantitative understanding of the nuclear spin selection rule during chemical reactions.

VI. CONCLUSION

The population of the $I=2$ nuclear spin state of CH_4 just after the consecutive reactions of $CH_3 + h\nu \rightarrow CH_2 + H$, $CH_2 + p\text{-}H_2 \rightarrow CH_4$ was found to be 0.2. The population is smaller than that of the high temperature limit of 0.3, which indicates that there exists a selection rule of nuclear spin during the reactions. However, the observed population is significantly different from the theoretically predicted population of 0.0. The discrepancy between the theory and the experiment may be due to a breakdown of the nuclear spin conservation during the chemical reactions. Studies on deuterated system are presently underway in order to understand the reason for the unexpected population of the $I=2$ nuclear spin state of methane after the reactions.

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