Rovibrational transitions and nuclear spin conversion of methane in parahydrogen crystals

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Solid parahydrogen is an excellent matrix for matrix-isolation spectroscopy because of its high spectral resolution. Here we describe the rovibrational structure and nuclear spin conversion of CH$_4$ embedded in parahydrogen crystals studied by infrared absorption spectroscopy. The vibration–rotation absorptions of CH$_4$ exhibit time-dependent intensity changes at 4.8 K. These changes are interpreted to be a result of the $I = 1 \rightarrow I = 2$ nuclear spin conversion that accompanies the $J = 1 \rightarrow J = 0$ rotational relaxation. The half-lifetime of the upper $J = 1$ rotational state is unchanged by the addition of up to 2% orthohydrogen molecules but decreases with more than 10% orthohydrogen molecules. The increase of the decay rate at higher orthohydrogen concentration indicates that the magnetic field gradient across CH$_4$ due to the orthohydrogen molecules mixes the nuclear spin states, which accelerates the conversion. © 2000 American Institute of Physics. [S1063-777X(00)00609-5]

1. INTRODUCTION

Matrix isolation spectroscopy at cryogenic temperatures has grown to be a methodology for a variety of applications in the field of molecular spectroscopy. Its application to the study of unstable molecules has piloted gas-phase spectroscopy.1 Not only unstable but also stable molecules in cryogenic matrices have been the subject of studies for understanding physics and chemistry in the condensed phase.2

In the early works by Lewis in the 1940s, organic molecular solids were used as the isolation matrices.3 Rare gas matrices, which were introduced by Pimentel and his co-workers,4 have been widely used in recent studies because of their chemically inert property and weak perturbations. The interaction from the environment, however, is not small due to the proximity of surrounding atoms and molecules, which makes the spectral linewidths of matrix-isolated species broader than those in the gas phase. The typical linewidth of vibrational transitions in rare gas matrices is on the order of 0.1–1 cm$^{-1}$. The spectra in the condensed phase must contain much important information, such as intermolecular interactions and hindered motion of molecules under perturbation of the surrounding electrostatic potentials. Unfortunately, the broadening of the spectra wipes out most of the fine spectral structures containing such information.

Recently, it was found that the spectra of molecules in parahydrogen crystals are surprisingly sharp, as was initially noted by Oka and his co-workers.5–7 They studied parahydrogen crystals using high-resolution infrared and Raman spectroscopy and showed that not only the parahydrogen itself but also isotopic impurities such as orthohydrogen and deuterated hydrogen in parahydrogen crystals exhibit sharp absorption features.8,9 The sharpest transition so far observed is the absorption of deuterated hydrogen, whose width is only 4 MHz (full width at half maximum, FWHM).8 The width is almost two orders of magnitude narrower than that of Doppler-limited gas phase spectra.

The sharp linewidth indicates that parahydrogen crystals are a promising medium for high-resolution matrix isolation spectroscopy.7,10 Following the work of the group in Chicago, the authors’ group in Kyoto11 and Fajardo’s group at Edwards Air Force Base12,13 have independently initiated high-resolution spectroscopic studies of atoms and molecules embedded in parahydrogen crystals. We showed that most of the spectral widths of molecules in parahydrogen crystals are sharper than 0.01 cm$^{-1}$ at low temperatures.14 The spectral resolution of 0.01 cm$^{-1}$ is high enough to discuss intermolecular interactions and molecular motions in the condensed phase in great detail.11

In a series of papers we have extensively studied rotation–vibration transitions of methane molecules embedded in parahydrogen crystals by high-resolution infrared absorption spectroscopy.14–19 The analysis of observed spectra reveals that the rotational energy levels of the methane is fully quantized, having the rotational quantum number $J$ as a good quantum number. Here, we again discuss methane molecules in parahydrogen crystals, but we focus on the nuclear spin conversion of methane.

In the case of CH$_4$, the four equivalent protons can be coupled into three nuclear spin states, $I = 0$, 1, and 2. The Pauli principle requires that only certain nuclear spin wave functions couple with any particular electron–vibration–rotation wave-functions.20,21 As a result, the $J = 0$ rotational state is associated with the $I = 2$ nuclear spin quintet state and the $J = 1$ state is the $I = 1$ triplet state, while the $J = 2$ state is coupled with both the $I = 1$ triplet state and the $I = 0$ singlet state. Even if the temperature is lowered sufficiently, the equilibrium distribution cannot be achieved because conversion among the different nuclear spin states is forbidden.22 Only weak nuclear spin–nuclear spin magnetic interaction and spin–rotation interaction may cause the conversion among different nuclear spin states in the gas phase.23–25 In condensed phases, evidence for the triplet ($I$
The importance of parahydrogen as the matrix for infrared spectroscopy was first proposed by Oka et al. and has been proved by the authors’ group and Fajardo’s group. Independently, Miyazaki et al. found that the parahydrogen matrix is useful for ESR spectroscopy because parahydrogen does not have any magnetic moments which cause a broadening of ESR linewidths. Visible and UV spectroscopy of atoms in solid hydrogen has been conducted by Fajardo et al. They have studied the reactive dynamics of dopants in solid hydrogen with the ultimate aim of finding high-performance rocket propellants.

Infrared studies of rovibrational transitions of molecules isolated in parahydrogen crystals have been developed by the authors’ group and Fajardo’s group, independently. Techniques for making parahydrogen crystals in two groups are different. In Kyoto, we made the crystals in an enclosed cell, as is described in the next section. In the Edwards Air Force Base research, Fajardo developed a technique to grow transparent crystals on a cold surface in an open vacuum. Due to the relatively high vapor pressure of H2 even at liquid He temperatures, the standard deposition technique which is usually employed for isolation spectroscopy of rare gas matrices can not be applied straightforwardly. Fajardo found a condition for growing completely transparent crystals of millimeter thickness by controlling the deposition rate and the temperature of the substrate. On the other hand, our enclosed cell technique allows us to grow crystals at a higher temperature, which maintains the equilibrium between gas and solid phases without encountering the problem of vaporization of samples.

The two methods have their own advantages and disadvantages. The advantage of growing the crystal in an enclosed cell is that the crystal structure surrounding the guest molecules becomes completely hcp. Therefore the fine structure of the observed spectra in an enclosed cell can be treated by a quantitative analysis of the molecular interaction and molecular motions in the condensed phase based on first principles. Crystals grown by Fajardo’s deposition technique are found to be a mixture of hcp and fcc structures. The different environment surrounding embedded molecules causes extra transitions, which makes the quantitative analysis of the spectra more difficult. On the other hand, one can dope any molecules in solid hydrogen by the deposition technique, while a very limited number of molecules can be isolated by our enclosed cell technique.

3. EXPERIMENTS

Parahydrogen crystals were grown in a cylindrical copper cell with both ends enclosed by BaF2 windows with indium gaskets. Pure parahydrogen gas containing less than 0.05% orthohydrogen was obtained by passing high purity (>99.9995%) normal hydrogen gas through an ortho–para converter at 14 K. A detail of the converter is given in a previous review article. About 10 ppm of methane was
mixed with the converted hydrogen gas at room temperature. Concentrations of orthohydrogen higher than 0.05% were controlled by adding normal hydrogen to the converted parahydrogen gas. Then, the mixed gas was continuously introduced into the copper cell installed under the cold surface of a standard Dewar-type liquid He cryostat. The temperature of the cell was kept at 8 K during the crystal growth, which takes about 2 hours. The typical flow rate of the gas was 100 cm$^3$/min. The crystal, which was completely transparent, was grown from the copper wall toward the inside. The crystal thus grown is a completely hexagonal close-packed structure, as is proved by the stimulated Raman gain spectroscopy of the $Q_1(0)$ transition and infrared absorption of methane in the crystal.\textsuperscript{16,19} The $c$ axis of the crystal is along the direction of crystal growth.

Infrared absorption spectra were observed by a Fourier transform infrared (FTIR) spectrometer (Nicolet Magna 750) with a resolution of 0.25 cm$^{-1}$. A globar source, KBr beam splitter, and a liquid-N$_2$-cooled HgCdTe (MCT) detector were used for recordings. All the measurements were done at 4.8 K.

In an experiment to determine the concentration dependence of orthohydrogen impurity on the conversion rate, orthohydrogen molecules were added to the premixed gas in concentrations of 0.05, 0.2, 2, 10, 20, 30, and 75% while maintaining the concentration of CH$_4$. The conversion rate was followed by observing the relative intensities of the FTIR absorption of the lines arising from different nuclear spin states. Several spectra were recorded for each sample intermittently at reasonably separated times. One recording took about 10 minutes. During the interval of the recordings, the globar source was turned off in order to avoid conversion due to photoexcitation by the globar light.

\section*{4. Observed Spectra and Rotational Energy Levels of Methane}

Since the intermolecular distance of solid hydrogen of 3.78 Å is significantly larger than the van der Waals diameter of methane at about 3.24 Å, methane molecules can rotate almost freely in para-hydrogen crystals.\textsuperscript{42} In previous papers, we have shown that the rotational quantum number $J$ of the methane is still a good quantum number in parahydrogen crystals and that the effective rotational constant is only 10% smaller than that in free space.\textsuperscript{15,16,18}

Figure 1 shows an FTIR spectrum of the $v_3$ band of methane in a parahydrogen crystal. The orthohydrogen concentration is 0.05%. The large splitting, of about 30 cm$^{-1}$, is assigned to the rotational branches of methane; the transitions at around 3008 cm$^{-1}$ are assigned to $P(1)$, those at around 3017 cm$^{-1}$ to $Q(1)$, those at around 3025 cm$^{-1}$ to $R(0)$, and those at higher than 3031 cm$^{-1}$ to $R(1)$. The small splittings of 0.5 cm$^{-1}$ appearing in each rotational branch are due to the $M$ quantum number of methane, which is the projection of the rotational quantum number $J$ along the crystal axis. The splitting of the $M$-sublevels is caused by the crystal field of solid parahydrogen.

All the transitions appearing in Fig. 1 can be quantitatively interpreted by assuming that methane occupies a substitutional site of the hcp crystal structure of solid hydrogen, and the methane, having $T_d$ symmetry, rotates freely under the crystal field of $D_{3h}$ symmetry. In this case, the first anisotropic crystal field potential is found to be

$$V(\Omega) = \varepsilon_{3c} \frac{1}{2} \left[ D_{2s,3}^{(2)}(\Omega) - D_{2s,3}^{(3)}(\Omega) \right]$$

$$+ D_{2s,3}^{(1)}(\Omega) - D_{2s,3}^{(3)}(\Omega) \right]$$

$$= \varepsilon_{3c} \sqrt{\frac{6}{4}} \left[ -2 \cos 2 \chi \cos \theta \cos 3 \varphi \right.$$

$$+ \sin 2 \chi (1 + \cos^2 \theta) \sin 3 \varphi \left. \right] \sin \theta$$

where $\Omega = (\chi, \theta, \varphi)$ is the Euler angle of methane relative to the crystal axis, and $D_{m,n}^{(l)}(\Omega)$ is Wigner’s rotation matrix.\textsuperscript{43} The definition of the Euler angles and of Wigner’s rotation matrix is the same as employed by Hougen.\textsuperscript{24} The symbol $\varepsilon_{3c}$ is a crystal-field parameter to be determined by analysis of the observed spectra. Equation (1) can be easily derived with the use of the extended group theory.\textsuperscript{15,43}

The interaction potential $V(\Omega)$ in Eq. (1) causes the splittings of degenerate $M$-sublevels of the spherical rotor in the free space. The rotational energy levels in the ground vibrational state can be calculated as the eigenvalues of the matrix of Hamiltonian $H = B''J^2 + V(\Omega)$ where $J$ is the rotational angular momentum operator, and $B''$ is the rotational constant of the ground state. The rotational levels in the triply degenerate excited vibrational states can be obtained by taking into account the Coriolis interaction in addition to the rotational Hamiltonian. In a previous paper, we have determined molecular constants of methane and the crystal field parameter, $\varepsilon_{3c}$, by the least-squares fitting of the observed transition wave numbers with the use of the crystal-field potential given in Eq. (1).\textsuperscript{16} Refer to our previous papers for a complete analysis.\textsuperscript{15,16}

It should be noted that all the observed absorption lines can be assigned to the rotational branches, and thus the so-called rotationless transition\textsuperscript{46,47} is absent in our spectrum. Rotationless transition have been observed in the case of water isolated in rare gas matrices.\textsuperscript{46,47} Recently, it was observed that H$_2$O in solid parahydrogen also exhibits a rotationless transition.\textsuperscript{48} The presence of rotationless transitions were interpreted as indicating that the molecules are firmly trapped in interstitial sites of the lattice. The absence of the rotationless transition in the case of methane in parahydro-
Methane crystals confirms that methane occupies a substitutional site of the crystal, but not any interstitial sites.

Figure 2 represents a time-dependent change of spectral structure for the $\nu_3$ transition of CH$_4$ in para-hydrogen crystals with orthohydrogen concentrations of 0.05% (a) and 10% (b). The solid line is the spectrum observed just after crystal growth. The dotted line is the spectrum observed 2 hours after crystal growth. The sharp spikes are due to the absorption of moisture in the air.

In Table I the observed integrated intensities of the $R(0)$ and $Q(1)$ transitions at various times are given for the crystals with orthohydrogen concentrations of 0.05, 0.2, 2.0, 10, 20, 30, and 75%, respectively. Note that the time when we finished making the crystal was taken as the origin of time ($t=0$) given in the second column. It is observed that the integrated intensity of the $R(0)$ transition increases with time, while that of the $Q(1)$ transition decreases. The time-dependent absorption changes are due to the nuclear spin conversion of methane. In the next section we discuss the conversion in detail.

5. NUCLEAR SPIN CONVERSION

It is convenient to review the salient features of the nuclear spin modification of the methane molecule. The Pauli principle requires the total wave-function of molecules to be antisymmetric with respect to the permutation of any identical nuclei. It follows the fact that only certain nuclear spin wave function couples with any particular electron-vibration-rotation wave functions. The symmetry of the rotational wave function of a CH$_4$ molecule is connected to the symmetry of the nuclear spin wave function by the requirement that the total wave function be antisymmetric with re-

TABLE I. Time-dependent absorption intensities of CH$_4$ in parahydrogen crystals.

<table>
<thead>
<tr>
<th>ortho concentration, %</th>
<th>Time, min$^a$</th>
<th>$I[R(0)]^b$</th>
<th>$I[Q(1)]^b$</th>
<th>Sum$^c$</th>
<th>$c(t)^d$</th>
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<td>0.041</td>
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$^a$ The time when we finished making the crystals was taken as the origin of time ($t=0$).

$^b$ Integrated intensity of all $M$-sublevels of each transition.

$^c$ The value of $I[R(0)] + 2.9I[Q(1)]$, which is supposed to be a constant irrespective of time after the crystal growth (see text). The absolute value of the sum varies depending on the concentration of CH$_4$ in crystals.

$^d$ The mole fraction of $J=0$ methane, defined in Eq. (2).
spect to the interchange of any two protons. It was fully discussed by Wilson\(^7\) that the requirement is met if both rotation and spin wave functions belong to the same representation in the pure rotational tetrahedral (\(T\)) point group. The two \(I = 0\) states

\[
12^{-1/2}[2|a\alpha b\beta \alpha \beta \alpha \beta \alpha - a\alpha b\beta \alpha \beta \alpha \beta \alpha - a|a\alpha b\beta \alpha \beta \alpha \beta \alpha - a|a\alpha b\beta \alpha \beta \alpha \beta \alpha ]],
\]

\[
4^{-1/2}[\beta \beta \alpha \beta \alpha - \beta \beta \alpha \beta \alpha + \beta \alpha \beta \alpha - \beta \alpha \beta \alpha ]
\]

belong to the irreducible representation \(E\), the nine \(I = 1\) states

\[
4^{-1/2}[|a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha a\alpha 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of the temperature of CH$_4$, as is seen in Table II, but we have never observed transitions from the $J = 2$ levels. The absence of the $J = 2$ population may be explained by fast relaxation from the $J = 2$ levels to $J = 1$. The $J = 2$ rotational state is coupled not only with the $I = 0$ nuclear spin state but also with the $I = 1$ nuclear spin states. Due to the proximity between the $I = 0$ and $I = 1$ in the $J = 2$ level, the nuclear spin–rotation interaction could yield mixing between the $I = 0$ and $I = 1$ nuclear spin states, which results in the fast relaxation from the $J = 2$ to $J = 1$ rotational states. The relaxation might be too fast to observe on our experimental time scale. In the following, we consider only the conversion from the $J = 1$ levels to $J = 0$.

In order to discuss the nuclear spin conversion process quantitatively, we define the mole fraction of the $J = 0$ state as

$$c(t) = [J = 0]/([J = 0] + [J = 1])$$

where $[J = 0]$, represents the concentration of $J = 0$ molecules at time $t$. The mole fraction is related to the integrated absorption intensities as

$$c(t) = I[R(0)]/I[R(0)] + AI[Q(1)]$$

where $I[R(0)]$ and $I[Q(1)]$ are the integrated intensities of the $R(0)$ and $Q(1)$ transitions, respectively, and $A$ is a constant which is equal to the ratio of the transition probabilities of $R(0)$ and $Q(1)$. Although we do not know the transition probability exactly, we can estimate it by the fact that the sum of $[J = 0] + [J = 1]$, which is proportional to $I[R(0)] + AI[Q(1)]$, should be constant at all times. We found that the value of $A = 2.9$ gives approximately constant values of $I[R(0)] + AI[Q(1)]$, as is seen in the fifth column of Table I. We therefore assume here that the $R(0)$ transition is 2.9 times stronger than the $Q(1)$ transition for the $\nu_5$ mode of CH$_4$ in parahydrogen crystals. With the assumption of $A = 2.9$, the mole fraction at any given time is obtained as shown in the last column of Table I.

The change of the mole fraction with time is plotted in Fig. 3 for different orthohydrogen concentrations. If we treat the time-dependent change of the methane absorption spectra with first-order kinetics, the time dependence of the mole fraction $c(t)$ may be written as

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

where $k$ is the sum of the $J = 1 \rightarrow J = 0$ rate and the $J = 1 \leftarrow J = 0$ rate. In Fig. 3 the best-fit functions of the form of Eq. (4) are also drawn for each concentration. Here the value of $c(\infty) = 0.89$, given in Table II as the equilibrium distribution, was assumed for the samples with low orthohydrogen concentration ($\leq 10\%$). For higher orthohydrogen concentration ($\geq 10\%$), we treated the $c(\infty)$ as a parameter of the fitting. The conversion rate $k$ defined in Eq. (4) obtained from the least-squares fitting method are plotted in Fig. 4 as a function of the orthohydrogen concentration.

The first-order kinetics in Eq. (4) gives acceptable agreement with all the experimental time dependence, as is seen in Fig. 3. This indicates that the simple first-order kinetics is appropriate for the nuclear spin conversion of methane in parahydrogen crystals.
tal is a hexagonal close-packed structure whose nearest-neighbor distance is 3.783 Å, it is roughly obtained that the average distances between methane and orthohydrogen molecules are 9.8 Å, 7.2 Å, and 6.2 Å for concentrations of 1, 2, and 5%, respectively. On the other hand, one orthohydrogen molecule always exists next to methane in the case of 8%, and two or more orthohydrogen molecules exist next to methane for more than 16%.

The fact that the conversion rate is unchanged below 2% indicates that the magnetic field of orthohydrogen is only effective when the orthohydrogen is next to methane. The basic interaction which causes nuclear spin conversion is the intermolecular magnetic dipole–dipole interaction between protons, which has been discussed by Wigner for the case of gas phase H₂ spin conversion,⁵⁰ by Motzukie and Nagamiya for H₂ spin conversion in solid hydrogen¹¹, and by Nijman and Berlinsky for CH₄ conversion in solid methane.⁵² The distance dependence of the conversion rate in the condensed phase caused by the intermolecular magnetic dipole–dipole interaction has been found to be R⁻⁸ or higher.¹¹,⁵² Therefore, it is reasonable to consider that the conversion by orthohydrogen is applicable only for nearest neighbors in our case. Consequently, we can conclude that the increase of the conversion rate of above 10% orthohydrogen is caused by the magnetic dipole–dipole interaction between methane and the nearest-neighbor orthohydrogen molecule(s), while the conversion at lower concentrations is caused by other mechanisms.

The mechanisms of the conversion at lower orthohydrogen concentrations are not yet clear. One possibility is the conversion caused by a strong paramagnetic impurity of O₂ molecules. Evidently, trace O₂ could not be eliminated in our sample. We guess that the concentration of O₂ molecules in our crystal is 10⁻⁸ or less. In order to clarify the role of O₂ impurity, the oxygen concentration dependence of the conversion rate has to be observed. However, we would like to note that the observed conversion rate of 3×10⁻³ min⁻¹ at low orthohydrogen concentration is one-half of the conversion rate of CH₄ in solid Ar matrix which is 6×10⁻³ min⁻¹ (Ref. 36). The observed 6×10⁻³ min⁻¹ rate has been interpreted as due to the spin–spin interaction within the molecule.⁶ Therefore, we believe that the conversion rate of 3×10⁻³ min⁻¹ in solid parahydrogen is likely to be caused by mechanisms other than an impurity of O₂ molecules.

The data presented in this article are still preliminary. Further experiments are indispensable for a quantitative discussion on the mechanisms of the nuclear spin conversion of CH₄. Since the rotational energy levels of methane in parahydrogen crystals are completely determined, we will be able to discuss not only the basic mechanisms of the conversion, but also more finery details such as rotational M-sublevel dependence of the conversion. Since the parahydrogen crystal has been characterized much better than any other crystal, the observed nuclear spin conversion may play a priming role for a deeper understanding of the nuclear spin conversion processes in the condensed phase.

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Since the interaction between orthohydrogen and methane is much stronger than that between parahydrogen and methane, molecular parameters of methane with orthohydrogen next to it could be different from those of methane surrounded by only parahydrogen molecules. Therefore, the equilibrium value $c(\infty)$ is not necessarily equal to 0.89 for higher orthohydrogen concentration. The $c(\infty)$ values determined by the least-squares fitting were 0.85 (10%), 0.82 (20%), 0.81 (30%), and 0.80 (75%).


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