

Conversion of ortho and para nuclear spin isomers of methanol studied by internal axis method

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ABSTRACT

Quantum statistics of identical nuclei in molecules gives rise to nuclear spin isomers. Except for methanol (CH_3OH) that has internal rotation (*i.e.*, torsion), all the studied molecules so far have overall rotational symmetry. Methanol does not rotate around the overall rotational symmetry axis but the methyl group axis. The identical nuclei in the methyl group produce a specific type of nuclear spin isomers of the *ortho*- CH_3OH and *para*- CH_3OH in methanol. Conversions between these two spin isomers have been observed in the experiment and a theory based on the rho-axis method (RAM) for partially explaining their conversions has been developed by us recently. However, besides RAM the internal axis method (IAM) is a classical method commonly used by many researchers and the coupling of the angular momenta between torsion and overall rotation in methanol can be completely separated from each other in the IAM. In this paper, as a series work we present a general theoretical model about conversion of ortho-para methanol using the IAM based on quantum relaxation theory. The expressions of the ortho-para state-mixing strengths induced by the nuclear spin-spin and nuclear spin-rotation interactions have been analytically deduced and numerically calculated. We found that the ortho-para states-mixings and ortho-para conversion can be induced by all these two intramolecular interactions whereas the nuclear spin-rotation interaction plays a major role. The conversion rate at temperature 300 K and pressure 1 Torr summed over eight ortho-para level pairs with gaps less than 2.7 GHz is calculated to be $1.4 \times 10^{-2} \text{ s}^{-1}$, which is close to the measured value of $2.1 (3) \times 10^{-2} \text{ s}^{-1}$, indicating the quantum relaxation is the leading process in the spin isomers conversions of methanol and suggesting our theory to be valid for other gaseous methanol-like molecules having torsion tunneling of symmetrical group. The most probable gateways in methanol for collision-induced population transfers are found to be levels-pairs in the ground-state $A-E$ species of $(v_t, J, K, p) = (0, 24, 4, 1) - (0, 25, 2, 1)$ by nuclear spin-spin coupling, $(0, 22, 5, p) - (0, 21, 6, -1)$ and $(3, 34, 1, 0) - (3, 35, 0, 1)$ by nuclear spin-rotation coupling.

Introduction

Nuclear spin isomers (NSIs) have fundamental importance in science because their existence is the direct manifestation of the laws of quantum mechanics. The stability of the NSIs is the fundamental concept in quantum mechanics [1] and the NSIs are the basic species of molecular existence. Molecules made of identical nuclei of non-zero spin in symmetrical positions have two or more distinct NSIs with different symmetry of nuclear spin wave functions of identical nuclei in the molecule [1,2]. A well-known example is the NSIs of molecular hydrogen (H_2) [3]: *ortho*- H_2 and *para*- H_2 , with total nuclear spin quantum numbers $I = 1$ and 0, respectively. In accordance with Pauli's principal, only odd

rotational quantum numbers J are allowed for *ortho*- H_2 and only even J for the *para*- H_2 . The intriguing studies on the NSIs of hydrogen and the successful separation of *para*- H_2 from *ortho*- H_2 in 1929 [3,4] have greatly promoted the foundation of quantum mechanics and played a key role in the discovery of the proton spin [5]. The NSIs of pure H_2 are very stable surviving for months at room temperature and atmospheric pressure [3,4]. The storage of liquid hydrogen as a rocket fuel has been extensively used in space exploration. Para hydrogen spin isomers are used to enhance nuclear magnetic resonance (NMR) signals by three to four orders of magnitude [6,7].

Apart from diatomic hydrogen, polyatomic molecules have NSIs too [8,9]. Quantum mechanics predicted that different isomers states of a

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molecule have different nuclear spin statistical weights which results in line intensity alternation of transitions. Accordingly, separation and conversion dynamics have been successfully studied for a few gaseous molecules, including $^{13}\text{CH}_3\text{F}$ (refs. [10,11]), CH_3F (refs. [12,13]), H_2CO (refs. [14,15]), $^{13}\text{CCH}_4$ (ref. [16]), C_2H_4 (ref. [17]), CH_3OH (ref. [18]), and H_2O (refs. [19–21]). With the exception of methanol (CH_3OH), all the NSIs of these molecules are identified by rotational quantum numbers, they have the rotational symmetry axis that interchange the identical nuclei in the molecule. By contrast, methanol belongs to another large class of molecules that have no axis of overall rotational symmetry, instead, it has a symmetric group and a locally rotated axis (i. e., CH_3 axis) of symmetry, it rotates around this methyl group axis with internal rotation or torsion of the CH_3 group relative to the OH group. The identical nuclei in the CH_3 group give rise to the existence of a specific type of nuclear spin isomers in methanol. It is from the three spin-1/2 hydrogen nuclei of the CH_3 group that the *ortho*- CH_3OH ($I = 3/2$) and *para*- CH_3OH ($I = 1/2$) are formed in methanol, which are distinguished respectively by the symmetry quantum numbers $\sigma = 0$ and ± 1 .

In molecular physics, spectral transitions between two distinct species of the *ortho*- CH_3OH and *para*- CH_3OH molecules in the gas phase are not allowed by selection rules of the electric-dipole approximation and the conversion between them is generally considered improbable. Very interestingly, population variations of the *ortho* and *para* isomers and conversions between *ortho*- and *para*- CH_3OH have been observed in the experiment [18]. This is the first observation of nuclear spin conversion processes for a gaseous molecule having torsion tunneling of symmetrical groups. The measured conversion rate between *ortho*- and *para*- CH_3OH is the largest one among those of gaseous molecules studied so far. As a first step to theoretically understand the experimental results, a theory based on the rho-axis method (RAM) for partially explaining conversions between *ortho*- and *para*- CH_3OH has been developed by us recently [22]. Although the symmetric-top-based (STB) wave functions can well be used for the methanol torsion-rotation states, the STB approximation is not appropriate for calculation of the gaps of the close *ortho*-*para* level pairs for methanol, the *ortho*-*para* level intervals have to be calculated by using the precisely measured level energies of methanol studied by the IAM. In addition, just two level pairs in the torsional ground state have been considered for the spin isomers conversion induced by hyperfine spin-spin (SS) and spin-rotation (SR) interactions in Ref. [22].

However, more level pairs follow selection rules required by the SS and SR interactions should be found out and be included in the numerical calculations of the conversion rates of CH_3OH . The strength expression of the SR interaction of *ortho*-*para* mixing in CH_3OH can be separated from the nuclear spin-torsion coupling and be analytically derived. Therefore in this paper, as a series work we present a general theoretical model about conversion of *ortho*-*para* methanol using the IAM based on quantum relaxation theory. Since the IAM is a classical method commonly used by many researchers except the RAM and the coupling of the angular momentum between torsion and overall rotation can be completely separated from each other in the IAM, the expressions of the *ortho*-*para* state-mixing strengths induced by the SS and SR interactions have been analytically derived and numerically calculated here. The mixing level pairs for the conversion rate calculation have been extended to the torsional excited states from the torsional ground state, and the calculated conversion rates are compared with the experimental data. The leading process in governing the conversions of spin-isomers and the most probable gateways for collision-induced population transfers are found. The current application of our general theoretical model to the CH_3OH molecule is also suitable for the analysis of nuclear spin conversions of other methanol-like molecules.

The paper is organized as follows. In Secs. II and III we briefly describe theory of methanol spectroscopy based on the IAM and the developed method for the study on *ortho*-*para* conversion of methanol

in the IAM. The structure, the system of coordinates, and nuclear spin isomers of CH_3OH are summarized in Sec. II. In Sec. III the quantum states, the zeroth-order rotation-torsion Hamiltonian, and wave functions of CH_3OH obtained by the IAM are briefly reviewed. The quantum relaxation model for CH_3OH and the intramolecular nuclear magnetic interactions in CH_3OH are described in details in Secs. IV and V. We present general analytical expressions for the *ortho*-*para* state-mixing strengths F_{SS} and F_{SR} induced by the hyperfine nuclear spin-spin and nuclear spin-rotation interactions, respectively. In Sec. VI we numerically calculate the spin-isomer conversion rates of CH_3OH induced by the mixing of all *ortho*-*para* level pairs having the gaps smaller than 2.7 GHz and discuss the calculation results. Conclusions are given in Sec. VII.

Molecular structure and nuclear spin isomers of CH_3OH

A. Molecular structure and system of coordinates of CH_3OH

The CH_3OH molecule consists of a top of the CH_3 group and a frame of the OH group. The structural parameters of the CH_3OH molecule taken from Refs. 23 and 24 are $r_{\text{CH}} = 1.0936$ (32) Å, $r_{\text{OH}} = 0.9451$ (34) Å, $r_{\text{CO}} = 1.4246$ (24) Å, $\angle_{\text{HCH}} = 108^\circ 38' \pm 42'$, $\angle_{\text{COH}} = 108^\circ 32' \pm 29'$, and methyl tilt $= 3^\circ 16' \pm 29'$. In this study the molecular system of coordinate axes coincides with that used for the descriptions of the nuclear spin isomers of the CH_3F molecule [25].

Figure 1 shows the molecular structure of CH_3OH and the molecular system of coordinate axes. The four hydrogen atoms are numbered from 1 to 4. In this molecule-fixed frame, the z -axis is parallel to the internal rotation axis (assumed to be the symmetry axis of the CH_3 top in this study) with positive direction determined by the clockwise rotation of the numbered hydrogen nuclei H_1 , H_2 , and H_3 , the x -axis is

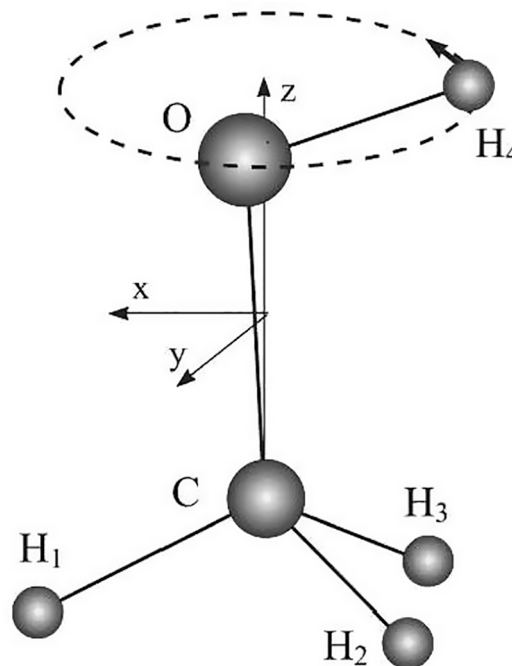


Fig. 1. The CH_3OH molecule with numberings of hydrogen atoms in the coordinate system fixed in the molecule. The three hydrogen atoms of the CH_3 group are numbered 1, 2, and 3, the hydrogen atom of the OH group is numbered 4. The configuration of the CH_3OH molecule is shown in the x - y - z right-handed system of coordinates where the z -axis is along the CH_3 top axis, the x -axis is perpendicular to it, and the x - z plane lies in the H_1 - C - z plane with a torsional angle φ of zero at some points. Internal rotation of the OH_4 group is defined by the torsional angle φ between the x -axis and the projection of the OH_4 bond on the x - y plane.

perpendicular to the z -axis in the H_1 -C- z plane and directed to the H_1 hydrogen nuclei, and the y -axis constitutes the right-handed system of coordinates with both the z and x axes. As an image of this frame, the O atom and H_4 atom are quantum mechanically distributed along the two circles around symmetry axis of CH_3 top, for instance for the H_4 atom as shown in Fig. 1 by the dashed line. In this frame for the IAM, the OH_4 group is rotating (internal rotation), and the CH_3 group is fixed. Internal rotation of the OH_4 group in methanol is defined by the torsional angle φ between the x -axis and the rojection of the OH_4 bond on the x - y plane. The repulsion between the H atoms of the CH_3 top and the H atom of the OH group generates a periodic hindering potential barrier for torsion with a period of $2\pi/3$. The torsional hindering potential $V(\varphi)$ can be denoted as a finite Fourier series of the torsional angle φ as [23,24,26]

$$V(\varphi) = \sum_{n=1}^3 \frac{V_{3n}}{2} (1 - \cos 3n\varphi) \quad (1)$$

where the first term is the dominant one. In the vibrational ground state, the torsional potential height V_3 is about 373.21 cm^{-1} [24]. The expansion coefficients V_6 and V_9 are very small and will be neglected in this study.

The IAM has been often employed by many researchers for better description of the various torsion-rotation-vibration interactions in methanol. In this method, the strong coupling of the angular momentum between the rotation and the torsion can be removed, leading to relatively unimportant matrix elements off-diagonal in torsional state [26]. Because the asymmetric Hamiltonian is small and has no diagonal matrix elements in CH_3OH , we will treat it as perturbation.

B. Nuclear spin isomers of CH_3OH

Usually, the nuclear spin isomers appear if the rotation around molecular axes of inertia cause the interchange of the identical nuclei. One can see from the molecular structure in Fig. 1 that methanol has no such axes of inertia because of its low symmetry. On the other hand, the symmetry of CH_3OH is partially restored by the presence of torsion, although it is an asymmetric rotator because of the OH group.

Due to the different spatial orientations of the nuclear spins in three equivalent hydrogen nuclei of the CH_3 group, the CH_3OH molecule is composed of two basic molecular species of nuclear spin isomers that are combined with the torsional states in accordance with the symmetrization postulate. The *ortho*- CH_3OH isomer is characterized by $I = 3/2$ and corresponds to the symmetry quantum number $\sigma = 0$. Accordingly for the *para*- CH_3OH isomer, $I = 1/2$ and $\sigma = \pm 1$. Here each σ value corresponds to a torsional-symmetry species of A -species ($\sigma = 0$) and E -species ($\sigma = \pm 1$).

Quantum states, Hamiltonian, and wave functions of CH_3OH by the IAM

A. Quantum states of CH_3OH

Methanol is the simplest asymmetric-top molecules with one hindered torsion and eleven normal vibration modes. The rotational and vibration-rotational spectra of methanol are complicated by various interactions among torsion, rotation, and vibrations, which have been extensively studied for many years in microwave, far-infrared, and infrared frequency regions. More than 40 thousands spectral lines in the absorption spectra of CH_3OH have been assigned so far and their transition frequencies have been precisely measured. The upper-state energies of these spectral lines were determined by adding these assigned transition frequencies to the known ground-state energies studied by the IAM. Results for CH_3OH have been reviewed and tabulated by Moruzzi *et al.* [24], and a number of further studies have been reported, for example, by Lees *et al.* [26,27] and Sun *et al.* [28,29] using a high-resolution Fourier transform infrared technique and a precise sub-

Doppler technique of the CO_2 -laser/microwave sidebands for the CO-stretching mode of CH_3OH in the $10\text{-}\mu\text{m}$ region, respectively.

By using the term values of CH_3OH and taking the lowest A -level energy of $127.97549 \text{ cm}^{-1}$ as zero, we have drawn a picture for the rotation-torsion-vibration energy states of *ortho*- CH_3OH and *para*- CH_3OH in the range $0\text{--}1800 \text{ cm}^{-1}$, which is shown in Fig. 2. We see that the *ortho*- CH_3OH and *para*- CH_3OH levels both are very dense and their level energies are very close to each other. Near energy level of 539.5 cm^{-1} , we use a capital letter V to show the intramolecular mixing potential between two close *ortho* (α) and *para* (α') states.

We have also calculated the energy intervals between the mixed level-pairs of the *ortho*- CH_3OH and *para*- CH_3OH . There are 1964 mixed level-pairs with energy intervals less than 50 GHz that follow the selection rules $|\Delta J| \leq 2$ and $|\Delta K| \leq 2$ required in the calculations of the conversion rates (as shown below). Eight level-pairs with energy gaps less than 2.7 GHz and the estimated uncertainties are presented in Table 1. The level labels here and hereafter are the same as those employed in our previous paper using the RAM [22] and have the correspondence to the relevant notations used in Ref. 24. J and K are quantum numbers of the rotational angular momentum (in units of \hbar) and its projection along the molecular symmetry axis of the CH_3 top, respectively; ν_t is the torsional quantum number; $\sigma = 0$ or ± 1 is for the rotation-torsion states of *ortho* isomer ($I = 3/2$) or *para* isomer ($I = 1/2$). For levels of A torsional symmetry for which asymmetry K -doubling is resolved, a $+$ or $-$ superscript is added to K in order to distinguish the A_1 and A_2 doublet components in Ref. [24], which corresponds to $p = 0$ and $p = 1$ in this work, respectively. The correspondence between the relevant level notations used in Ref. [24] and this work are as follows. *Ortho* states with $K = 0$, $(J + p)$ -even are the A , 0^+ states in Ref. [24]; the states with $K = 0$, $(J + p)$ -odd do not exist; *ortho* states with $K \neq 0$, $(J + p)$ -even

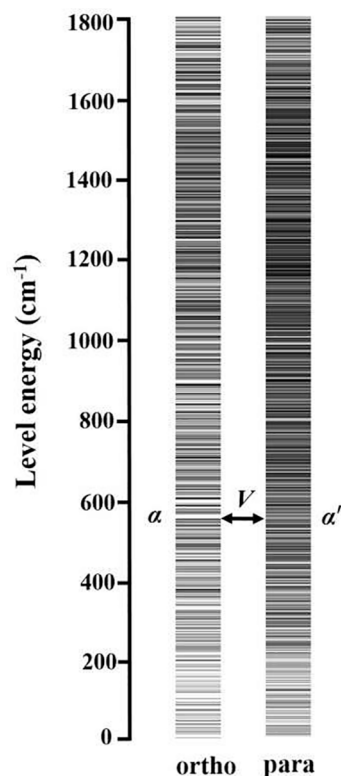


Fig. 2. The *ortho* and *para* state terms of the CH_3OH molecule shown in two columns (subspaces) for level energies from 0 to 1800 cm^{-1} for all the *ortho*- and *para*-state terms referring to the lowest state A -level ($\nu_t = 0$, $J = 0$, $K = 0$, $p = 0$) with $127.97549 \text{ cm}^{-1}$ as zero. The capital letter V refers to the intramolecular mixing potential between two close *ortho* (α) and *para* (α') states near energy level of 539.5 cm^{-1} .

Table 1

Eight mixed pairs of the ortho- and *para*-levels of CH₃OH in the vibrational ground state with energy gaps (in MHz) of $\omega_{aa'}/2\pi$ less than 2.7 GHz and allowed by the selection rules of $|\Delta J| \leq 2$ and $|\Delta K| \leq 2$, their corresponding energy term values in cm⁻¹, and the calculated Boltzmann factors $W_B(\alpha)$ and $W_B(\alpha')$ for all the ortho- and *para*-state terms referring to the lowest state ($v_t = 0, J = 0, K = 0, p = 0$) with an energy of 127.97549 cm⁻¹ as zero. No splittings were observed for K quantum numbers for level pairs #2–#4 in Ref. 24.

| Level | Ortho-level | Term value | W_α | Para level | Term value | $W_{\alpha'}$ | Energy gap |
|--------|-----------------------|-------------|-------------------------|--------------------------|------------|-------------------------|--------------|
| pair # | (v_t, J, K, p) | ortho-level | ortho-level | (v_t, J', K', σ') | para-level | para-level | (MHz) |
| #1 | (0, 13, 1, 1) | 283.55401 | 1.3173×10^{-5} | (0, 13, 0, 1) | 283.53723 | 1.3174×10^{-5} | 503 ± 8 |
| #2 | (0, 13, 4, <i>p</i>) | 330.59627 | 1.0512×10^{-5} | (0, 14, 3, 1) | 330.54753 | 1.0515×10^{-5} | 1461 ± 8 |
| #3 | (0, 17, 5, <i>p</i>) | 470.50837 | 5.3737×10^{-6} | (0, 18, 4, 1) | 470.41877 | 5.3760×10^{-6} | 2686 ± 8 |
| #4 | (0, 22, 5, <i>p</i>) | 631.59051 | 2.4818×10^{-6} | (0, 21, 6, -1) | 631.60126 | 2.4817×10^{-6} | 322 ± 8 |
| #5 | (0, 24, 4, 1) | 667.48812 | 2.0893×10^{-6} | (0, 25, 2, 1) | 667.48968 | 2.0893×10^{-6} | 47 ± 8 |
| #6 | (0, 24, 4, 0) | 667.49848 | 2.0892×10^{-6} | (0, 25, 2, 1) | 667.48968 | 2.0893×10^{-6} | 264 ± 8 |
| #7 | (3, 34, 1, 1) | 1887.74188 | 6.0034×10^{-9} | (3, 35, 0, 1) | 1887.75049 | 6.0032×10^{-9} | 258 ± 8 |
| #8 | (3, 34, 1, 0) | 1887.75088 | 6.0032×10^{-9} | (3, 35, 0, 1) | 1887.75049 | 6.0032×10^{-9} | 12 ± 10 |

or $(J + p)$ -odd are the A, J, K^+ or A, J, K^- states in Ref. [24], respectively. Para states with $K = 0$ are the $E, K = 0$ states in Ref. [24]; para states with K greater than 0, $\sigma = 1$ or K greater than 0, $\sigma = -1$ are the $E, +K$ or $E, -K$ states in Ref. [24], respectively. The label correspondence of state notation between states in this work and those in Ref. [24] are summarized in Table 2.

B. The zeroth-order rotation-torsion Hamiltonian and wave functions of CH₃OH

On the basis of the IAM, the CH₃ top and the OH frame of CH₃OH have equal and opposite torsional angular momenta and the coupling between torsion and overall rotation is removed at zeroth-order by transforming to an internal-axis system [24,30]. For a given small-amplitude vibrational state of CH₃OH, its zeroth-order rotation-torsion Hamiltonian \hat{H}_{RT}^0 can be divided into two parts [23,24,30–33].

$$\hat{H}_{RT}^0 = \hat{H}_{R\text{sym}}^0 + \hat{H}_T^0 \quad (2)$$

where the rotational part $\hat{H}_{R\text{sym}}^0$ is the Hamiltonian of a symmetric rigid rotor, the torsional Hamiltonian \hat{H}_T^0 describes the hindered rotation in CH₃OH. The zeroth-order eigenfunctions of $\hat{H}_{R\text{sym}}^0$ are the usual top wave functions $|r\rangle = |JKM\rangle$, whose explicit forms can be found in Refs. 33 and 34. Here the quantum number M is the projection of the rotational angular momentum (in units of \hbar) along a space-fixed quantization axis.

The IAM torsional Hamiltonian \hat{H}_T^0 can be expressed by Eq. (3) as a function of the torsional angle φ [23,24], which is different from the relevant part in the expression of RAM Hamiltonian where the torsional and rotational angular momentum operators are coupled together by one rotation-torsion Coriolis term [24].

$$\hat{H}_T^0 = F\hat{P}_\varphi^2 + \sum_{n=1}^3 \frac{V_{3n}}{2} (1 - \cos 3n\varphi) \quad (3)$$

where F is a constant and is defined by the moments of inertia of CH₃OH. $\hat{P}_\varphi = -i\partial/\partial\varphi$ is the torsional angular momentum operator. The normalized wave functions of a torsional free rotor has the form of

[23,24]

$$|Km\rangle = \frac{1}{\sqrt{2\pi}} e^{i\rho K\varphi} e^{im\varphi} \quad (4)$$

where integer m is the quantum number of the angular momentum of the methyl top along the symmetry axis (in units of \hbar). The factor $e^{i\rho K\varphi}$ arises from non-periodic boundary conditions in the internal axis system [23], and the scale factor $\tilde{\rho}$ is defined by the moments of inertia of CH₃OH.

The torsional eigenfunctions of \hat{H}_T^0 can be determined from a Mathieu equation, or obtained by using the basis wave functions $|Km\rangle$ and introducing the torsional quantum number v_t to diagonalize the matrix of \hat{H}_T^0 for $-10 \leq N \leq 10$ in $m = 3N + \sigma$ with sufficient accuracy in the energies of the lowest torsional states [23,32]. Here $\sigma = 0, \pm 1$; N is any integer. Hence, the resulting torsional eigenfunctions with eigenvalues of $E_T^0(Kv_t\sigma)$ can approximately be taken as the sum of the basis functions $|Km\rangle$ [23,32,33]

$$|Kv_t\sigma\rangle = \frac{1}{\sqrt{2\pi}} e^{i\rho K\varphi} \sum_{N=-6}^6 a_{3N+\sigma}(Kv_t) e^{i(3N+\sigma)\varphi} \quad (5)$$

The wave functions $|t_\sigma\rangle = |Kv_t\sigma\rangle$ are normalized when the coefficients $a_{3N+\sigma}(Kv_t)$ are chosen to satisfy the condition of

$$\sum_{N=-\infty}^{\infty} a_{3N+\sigma}^2(Kv_t) = 1 \quad (6)$$

By taking $-6 \leq N \leq 6$ and using the methanol parameters [24] in Table 3, Fourier expansion coefficients for ortho- and *para*-states have been calculated, which are shown in Tables 4 and 5, respectively.

The zeroth-order eigenvalues $E_{RT}^0(Kv_t\sigma)$ of \hat{H}_{RT}^0 are

$$\begin{aligned} E_{RT}^0(Kv_t\sigma) &= E_{R\text{sym}}^0(JK) + E_T^0(Kv_t\sigma) \\ &= \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2} \right) K^2 + E_T^0(Kv_t\sigma) \end{aligned} \quad (7)$$

where A, B , and C are the CH₃OH rotational constants. On the basis of the IAM, the zeroth-order rotation-torsion wave functions with eigenvalues $E_{RT}^0(Kv_t\sigma)$ of \hat{H}_{RT}^0 are products of the wave functions of

Table 2

The label correspondence of state notations between this work and those in Ref. [24].

| Spin-isomers state | This work | Ref. [24] |
|--------------------|---|------------------------|
| Ortho state | $ J^{\text{even}}, K, v_t, p = 0\rangle$ | $ J, K^+, n, A\rangle$ |
| | $ J^{\text{odd}}, K, v_t, p = 1\rangle$ | |
| | $ J^{\text{even}}, K \neq 0, v_t, p = 1\rangle$ | $ J, K^-, n, A\rangle$ |
| | $ J^{\text{odd}}, K \neq 0, v_t, p = 0\rangle$ | |
| Para state | $ J, K, v_t, \sigma = 1\rangle$ | $ J, +K, n, E\rangle$ |
| | $ J, K, v_t, \sigma = -1\rangle$ | $ J, -K, n, E\rangle$ |

Table 3

Methanol parameters [24] used in the present work.

| Parameter | Parameter value (cm ⁻¹) |
|----------------|-------------------------------------|
| F | 27.64248 |
| V_3 | 373.21 |
| $\tilde{\rho}$ | 0.81012 |
| A | 4.2523 |
| B | 0.82322776 |
| C | 0.79286785 |
| D_{ab} | -2.612×10^{-3} |

Table 4

The Fourier expansion coefficients $a_{3N+\sigma}(Kv_t)$ in the wave functions of $|Kv_t\sigma\rangle$ by taking $-6 \leq N \leq 6$ calculated for eight *ortho*-levels listed in Table I.

| Level pair # | #1 | #2, #5, and #6 | #3 and #4 | #7 and #8 |
|--------------|-------------------------|-------------------------|-------------------------|-------------------------|
| K, v_t | $K = 1, v_t = 0$ | $K = 4, v_t = 0$ | $K = 5, v_t = 0$ | $K = 1, v_t = 3$ |
| a_{15} | -1.188×10^{-6} | -3.250×10^{-5} | -1.014×10^{-4} | -5.577×10^{-5} |
| a_{12} | -7.150×10^{-5} | -0.001 | -0.004 | -0.003 |
| a_9 | -0.003 | -0.032 | -0.070 | -0.084 |
| a_6 | -0.055 | -0.328 | -0.542 | -0.985 |
| a_3 | -0.466 | -0.910 | -0.823 | 0.152 |
| a_0 | -0.864 | -0.250 | -0.155 | -0.020 |
| a_3 | -0.181 | -0.021 | -0.010 | 0.005 |
| a_6 | -0.013 | -7.960×10^{-4} | -3.343×10^{-4} | 9.005×10^{-4} |
| a_9 | -4.363×10^{-4} | -1.769×10^{-4} | -6.559×10^{-6} | -4.406×10^{-5} |
| a_{12} | -8.875×10^{-6} | -2.548×10^{-7} | -8.536×10^{-8} | -1.086×10^{-6} |

$$\hat{H}_{R_{sym}}^0 \text{ and } \hat{H}_T^0 \text{ as,}$$

$$|r\rangle_{t_\sigma} = |JKM\rangle |Kv_t\sigma\rangle \quad (8)$$

Let us consider now the methanol symmetry of the spatial rotation-torsion states $|r\rangle_{t_\sigma}$. Molecular symmetry for torsion and overall rotation states of methanol based on the IAM in permutation-inversion (PI) group $G_6^{(5)}$ is developed in Ref. [35]. Characters of the PI group- $G_6^{(5)}$ are the same as those of the group G_6 , which are presented in Table 2 in Ref. [22]. Operator (23)* is about the permutation of two hydrogen atoms with particle coordinate inversion. Operation (1 2 3) \equiv (12)(23) is cyclic permutation of three hydrogen nuclei in CH_3 group. By this operation, we have

$$\begin{aligned} (1\ 2\ 3)|JKM\rangle &= e^{i2\pi\rho K/3}|JKM\rangle, \\ (1\ 2\ 3)|Kv_t\sigma\rangle &= e^{i2\pi(\sigma-\rho K)/3}|Kv_t\sigma\rangle, \\ (1\ 2\ 3)|JKM\rangle|Kv_t\sigma\rangle &= e^{i2\pi\sigma/3}|JKM\rangle|Kv_t\sigma\rangle \end{aligned} \quad (9)$$

One can see that the symmetry transformation of the spatial rotation-torsion states $|r\rangle_{t_\sigma}$ here has the same result as that by the RAM in Ref. [22].

C. The total wave functions of CH_3OH

The wave functions that describe the quantum states for the CH_3 top of methanol have a form of a product of the coordinate parts and spin as $|JKM\rangle|Kv_t\sigma\rangle|i\rangle$. Here, the eigenstates $|i\rangle$ are the nuclear spin wave functions of three hydrogen atoms in CH_3 top; I and i ($I = I, I-1, \dots, -I$) are the total spin of three protons and its projection on a space-fixed quantization axis, respectively. Therefore, four nuclear spin wave

functions for ortho isomers are

$$|I = 3/2, i_o = \pm 3/2\rangle, |I = 3/2, i_o = \pm 1/2\rangle; \quad (10)$$

two nuclear spin wave functions for para isomers are

$$|I = 1/2, i_s = \pm 1/2\rangle \quad (11)$$

The spin states are related to both the torsion states and overall rotation states, which is different from other molecules like CH_3F .

Methanol has no principal molecular axes of inertia which leads to the total wave function of each methyl nuclear spin function corresponding to two torsion-rotation states. According to the Pauli principal and the PI group $G_6^{(5)}$, the ortho states are [22]

$$|r, t_o, i_o, p\rangle = f_K[|r, t_o, i_o\rangle + (-1)^{p+J+K}|\bar{r}, \bar{t}_o, \bar{i}_o\rangle] \quad (12)$$

Where $|t_o\rangle = |K, v_t, \sigma = 0\rangle$ and $|\bar{t}_o\rangle = |-K, v_t, \sigma = 0\rangle$ are the torsion wave functions of the ortho states; $f_K = (2 + 2\delta_{K,0})^{-1/2}$; $K \geq 0$; $|\bar{r}\rangle = |J, -K, M\rangle$.

The para states are

$$\begin{aligned} |r, t_s, i_s, p\rangle &= \frac{1}{\sqrt{2}} \left[|r, t_s, i_s\rangle + (-1)^{p+J+K}|\bar{r}, \bar{t}_s, \bar{i}_s\rangle \right], \\ p &= 0, 1. \end{aligned} \quad (13)$$

Where $|t_s\rangle = |K, v_t, s = \pm 1\rangle$ and $|\bar{t}_s\rangle = |K, v_t, -s = \mp 1\rangle$.

In the model on the basis of the IAM in this work, we consider that the internal rotation of the OH group is uncoupled with the CH_3 group, the methanol is in the ground electronic state, and all vibrational modes except torsional mode are assumed to be in the ground state also. Hence, the total wave functions of methanol can be taken as a product of the methyl and the hydroxyl wave functions. For convenience, we use the shorthand notations $|\alpha\rangle$ and $|\alpha'\rangle$ for total ortho and para states as

$$|\alpha\rangle = |r, t_o, I, i_o, p\rangle |I_4 i_4\rangle, \quad (14)$$

$$|\alpha'\rangle = |r', t_s, I', i_s, p'\rangle |I'_4 i'_4\rangle.$$

where I_4 and i_4 are the nuclear spin of the H_4 atom and its projection on the laboratory quantization axis, respectively. Accordingly, the total wave functions of *ortho*- CH_3OH and *para*- CH_3OH allowed by quantum statistics have the forms of

$$|\alpha\rangle = f_K[|\beta_o\rangle + (-1)^{p+J+K}|\bar{\beta}_o\rangle], f_K = (2 + 2\delta_{K,0})^{-1/2}, p = 0, 1,$$

and $K \geq 0$,

$$|\alpha'\rangle = (1/\sqrt{2}) \left[|\beta'_s\rangle + (-1)^{p'+J'+K'}|\bar{\beta}'_s\rangle \right], \quad s = \pm 1. \quad (15)$$

wherein the states notations are

Table 5

The Fourier expansion coefficients $a_{3N+\sigma'}(K'v'_t)$ in the wave functions of $|K'v'_t\sigma'\rangle$ by taking $-6 \leq N \leq 6$ calculated for eight *para*-levels listed in Table I.

| Level pair # | #1 | #2 | #3 | #5 and #6 | #7 and #8 | Level pair # | #4 |
|--------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------|-------------------------|
| K' | $K' = 1$ | $K' = 3$ | $K' = 4$ | $K' = 2$ | $K' = 0$ | K' | $K' = 6$ |
| v'_t | $v'_t = 0$ | $v'_t = 0$ | $v'_t = 0$ | $v'_t = 0$ | $v'_t = 3$ | v'_t | $v'_t = 0$ |
| a_{14} | -1.608×10^{-6} | -4.191×10^{-5} | -1.335×10^{-4} | -1.494×10^{-5} | -5.992×10^{-5} | a_{16} | -7.693×10^{-5} |
| a_{11} | -9.422×10^{-5} | -0.002 | -0.005 | -6.871×10^{-4} | -0.003 | a_{13} | -0.003 |
| a_8 | -0.003 | -0.038 | -0.085 | -0.018 | -0.086 | a_{10} | -0.058 |
| a_5 | -0.067 | -0.367 | -0.608 | -0.231 | -0.983 | a_7 | -0.481 |
| a_2 | -0.525 | -0.902 | -0.777 | -0.904 | 0.160 | a_4 | -0.857 |
| a_1 | -0.833 | -0.225 | -0.135 | -0.356 | -0.023 | a_1 | -0.175 |
| a_4 | -0.160 | -0.018 | -0.008 | -0.036 | 0.008 | a_2 | -0.012 |
| a_7 | -0.011 | -6.515×10^{-4} | -2.671×10^{-4} | -0.002 | 0.001 | a_5 | -4.130×10^{-4} |
| a_{10} | -3.541×10^{-4} | -1.405×10^{-5} | -5.095×10^{-6} | -3.913×10^{-5} | -5.241×10^{-5} | a_8 | -8.338×10^{-6} |
| a_{13} | -6.997×10^{-6} | -1.976×10^{-7} | -6.481×10^{-8} | -6.121×10^{-7} | -1.231×10^{-6} | a_{11} | -1.111×10^{-8} |

$$\begin{aligned}
|\beta_o\rangle &= |r, i_o, I, i_o\rangle |I_4 i_4\rangle, \\
|\bar{\beta}_o\rangle &= |\bar{r}, \bar{i}_o, I, i_o\rangle |I_4 i_4\rangle, \\
|\beta_s\rangle &= |r, i_s, I, i_s\rangle |I_4 i_4\rangle, \\
|\bar{\beta}_s\rangle &= |\bar{r}, \bar{i}_s, I, i_s\rangle |I_4 i_4\rangle
\end{aligned} \quad (16)$$

Quantum relaxation model for CH₃OH

Conversion of NSIs of gaseous molecules can be caused between a pair of mixed quantum states by nonmagnetic collisions in a quantum relaxation process. For methanol, as shown theoretically below, there are many pairs of quantum states that could be efficiently mixed by hyperfine magnetic interactions. During the conversion process, the molecules in, e.g., the ortho subspace reach such mixed states during their rotational relaxations. Then they can be transferred to the subspace of para states through these mixed states by molecular collisions that results in the ortho to para isomer conversion. This conversion phenomenon for methanol has been observed in an experiment recently [18], however, a general theoretical model of ortho-para conversion of gaseous methanol studied by the IAM remains an open issue so far.

The state-mixing theory for the ortho-para conversion of gaseous molecule was proposed in 1967 by Curl *et al.* [36] and developed in 1991 by Chapovsky in the framework of density matrix formalism [25]. Quantum relaxation of ortho-para isomer conversion at low pressures has shown that the relaxation of a non-equilibrium concentration of the ortho or para isomer created at the instant $t = 0$ decays exponentially as $\delta\rho_o(t) = \delta\rho_o(0)e^{-\gamma t}$ with the conversion rate γ given by Chapovsky [25]

$$\gamma = \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma |V_{\alpha\alpha'}|^2}{\Gamma^2 + \omega_{\alpha\alpha'}^2} [W_B(\alpha) + W_B(\alpha')] \quad (17)$$

Where the indexes α and α' run through all ortho and para states of the molecule, respectively; $\omega_{\alpha\alpha'}/2\pi$ is the energy gap of a pair of ortho and para levels in units of frequency.

The Boltzmann factors $W_B(\alpha) = (e^{-E_\alpha/k_B T})/Z_{ortho}$ and $W_B(\alpha') = (e^{-E_{\alpha'}/k_B T})/Z_{para}$ are the relative population of the ro-vibrational α state and α' state calculated by the partition functions Z_{ortho} and Z_{para} , respectively. For methanol, Z_{ortho} can be factored into a product of three separate partition functions of pure vibrations Z_V , overall external rotation Z_r^e , and internal rotation (torsion) Z_r^i as [37]

$$Z_{ortho} = Z_V Z_r^e Z_r^i \quad (18)$$

At temperature $T = 300$ K, the calculated partition functions $Z_V = 1.022$, $Z_r^e = 1.374$, and $Z_r^i = 25635.982$. The calculated partition function of ortho-CH₃OH is $Z_{ortho} = 35998.764$. Partition functions of ortho- and para-CH₃OH are equal because the ortho-levels have twice the nuclear spin statistical weight than the para-levels. In the calculation, the lowest ortho state was assumed to have zero energy. The Boltzmann factors calculated for eight pair-levels between ortho- and para-CH₃OH are listed in Table 1.

In Eq. (19), $V_{\alpha\alpha'}$ is the matrix element of the magnetic interaction that creates a coherence between α and α' states; Γ is the decoherence rate of this coherence that is proportional to the gas pressure with a constant $2\pi \times 20$ MHz/Torr [38]. In this study, Γ is assumed approximately equal for all states. The nuclear magnetic perturbation $\hbar V$ is included in the Hamiltonian \hat{H} of the methanol molecule,

$$\hat{H} = \hat{H}_{RT}^0 + \hat{H}_{R\text{ asym}}^1 + \hat{H}_{RTV}^1 + \hbar \hat{V} \quad (19)$$

The zeroth-order rotation-torsion Hamiltonian \hat{H}_{RT}^0 here is the main part of \hat{H} ; operator \hat{H}_{RTV}^1 represents the first order perturbative term of the

rotation-torsion-vibration interactions other than the asymmetric Hamiltonian $\hat{H}_{R\text{ asym}}^1$.

Recent experimental results have provided evidence of this weak intramolecular hyperfine perturbations for CH₃OH [18], which suggests that the perturbation sources include interactions of nuclear spin-spin and nuclear spin-rotation in CH₃OH. To clarify this experimental phenomenon and to understand the wherein interconversion dynamics of NSIs of the methanol molecule, in the following of this work, the intramolecular nuclear magnetic interactions in CH₃OH are analytically studied on the basis of the IAM, and the evolution time scales of spin isomers induced by the hyperfine interactions are numerically calculated.

Intramolecular nuclear magnetic interactions in CH₃OH

A. Nuclear spin-spin interactions in CH₃OH

There are magnetic interactions among four spin-1/2 hydrogen nuclei of CH₃OH. The nuclear magnetic moment of one hydrogen nucleus produces an averaged magnetic field at the site of another hydrogen nucleus, which causes a coupling potential energy between two magnetic dipole moments. The Hamiltonian of magnetic dipole-dipole interaction between two particles can generally be written in the form [1,25]

$$\hat{V}_{12} = P_{12} \sum_{ij} \hat{I}_i^{(1)} \hat{I}_j^{(2)} T_{ij}^{(1,2)} \quad (20)$$

Where P_{12} is a scaling factor of interaction; operators $\hat{I}_i^{(1)}$ and $\hat{I}_j^{(2)}$ are for the nuclear spins of two particles; the second rank tensor $T_{ij}^{(1,2)}$ represents a spatial part of the nuclear spin-spin interaction between the particle 1 and particle 2. The Cartesian components of this tensor in the laboratory frame has the form of

$$T_{ij}^{(1,2)} = \delta_{ij} - 3n_i^{(1,2)}n_j^{(1,2)}, \quad i, j = x, y, z. \quad (21)$$

Where $\mathbf{n}^{(1,2)}$ is the unit vector directed from the first to the second particle. For hydrogen atoms in CH₃OH, the scaling factor P_{12} for two protons is

$$P_{12} = \frac{\mu_0}{4\pi} \frac{4\mu_p^2}{\hbar r_{12}^3} \quad (22)$$

where r_{12} is the distance between two protons, μ_p is the nuclear magnetic moment of a proton.

By introducing the operator notation $\hat{I}^{(m)}$ for the nuclear spin of the m -th hydrogen, we have operators [25]

$$\hat{V}_{HH} = \sum_{m<n=1}^3 \hat{V}_{H_m H_n} = \sum_{m<n=1}^3 P_{H_m H_n} \sum_{ij} \hat{I}_i^{(m)} \hat{I}_j^{(n)} T_{ij}^{(m,n)} \quad (23)$$

$$\hat{V}_{HH_4} = \sum_{m=1}^3 \hat{V}_{H_m H_4} = \sum_{m=1}^3 P_{H_m H_4} \sum_{ij} \hat{I}_i^{(m)} \hat{I}_j^{(4)} T_{ij}^{(m,4)} \quad (24)$$

where interaction tensors $T_{ij}^{(m,n)}$ and $T_{ij}^{(m,4)}$ are the Cartesian components in the laboratory frame of the tensor for H_m-H_n and H_m-H_4 interactions, respectively; the scaling factors $P_{H_m H_n}$ and $P_{H_m H_4}$ are for two protons of H_m-H_n and H_m-H_4 , respectively. For further calculations of the matrix elements of operators in Eqs. (23) and (24), it is convenient to express these operators in the laboratory coordinate system by the components of spherical tensors. For example, for spin operators $\hat{I}^{(1)}$ and $\hat{I}^{(2)}$ of the protons 1 and 2, by using the well-known formulae in the theory of angular momentum [1], one has

$$\hat{V}_{H_1H_2} = P_{H_1H_2} \sum_q (-1)^q \left(\hat{T}_{2,-q}^{(1)} \hat{T}_{2,q}^{(2)} \right) T_{2q}^{(1,2)} \quad (25)$$

where $(\hat{T}_{2,-q}^{(1)} \hat{T}_{2,q}^{(2)})_{2,-q}$ and $\hat{T}_{2q}^{(1,2)}$ are the spherical tensors of rank 2 ($l=2$). For the interaction operator between nuclei in each of the H atoms in CH₃ top and in H₄ atom in Eq. (24), one can deduce the following formulae by forming a spherical tensor of rank $l=2$ for $\hat{T}_{1q_1}^{(m)} \hat{T}_{1q_4}^{(4)}$

$$\hat{V}_{HH_4} = \sqrt{5} \sum_{q_1 q_4 q} \begin{pmatrix} 1 & 1 & 2 \\ q_1 & q_4 & q \end{pmatrix} \sum_{m=1}^3 P_{H_m H_4} \hat{T}_{1q_1}^{(m)} \hat{T}_{1q_4}^{(4)} T_{2q}^{(m,4)} \quad (26)$$

Here (:::) stands for the 3- j symbol. The interaction tensors $T_{2q}^{(m,4)}$ and $T_{2q}^{(m,n)}$ are in the laboratory frame, they should further be transformed by the matrix of finite rotation to the coordinate system fixed in the molecule. For example for $T_{2q}^{(m,4)}$, we have

$$T_{2q}^{(m,4)} = \sum_{q'} D_{q'q}^2 \tilde{T}_{2q'}^{(m,4)} \quad (27)$$

where the components $D_{q'q}^2$ are Wigner D-matrices and the variable $q' = K' - K$. In the molecular-fixed coordinate, the matrix elements of the spin operator $\hat{T}_{1q_1}^{(m)}$ are connected with each other by

$$\begin{aligned} \langle I' i'_s | \hat{T}_{1q_1}^{(3)} | I i_o \rangle &= \omega_s^{-1} \langle I' i'_s | \hat{T}_{1q_1}^{(2)} | I i_o \rangle \\ &= \omega_s^{-2} \langle I' i'_s | \hat{T}_{1q_1}^{(1)} | I i_o \rangle, \\ \omega_s &= e^{i2\pi s/3} \end{aligned} \quad (28)$$

By applying the Wigner-Eckart theorem, the matrix elements of magnetic interaction operators can now be calculated. For the operator \hat{V}_{HH_4} , it is written in the form of

$$\begin{aligned} \langle \alpha' | \hat{V}_{HH_4} | \alpha \rangle &= \sum_{m=1}^3 \langle \alpha' | \hat{V}_{H_m H_4} | \alpha \rangle \\ &= \delta_{p'p} \sqrt{10} f_K \sum_{q_1 q_4 q} \begin{pmatrix} 1 & 1 & 2 \\ q_1 & q_4 & q \end{pmatrix} \langle I'_4 i'_4 | \hat{T}_{1q_4}^{(4)} | I_4 i_4 \rangle \sum_{m=1}^3 \langle I' i'_s | \hat{T}_{1q_1}^{(m)} | I i_o \rangle \\ &\times \left[\sum_q \langle r' i'_{-s} | P_{H_m H_4} D_{q'q}^2 \tilde{T}_{2q'}^{(m,4)} | r i_o \rangle + (-1)^{p+J+K} \sum_Q \langle r' i'_{-s} | P_{H_m H_4} D_{Q'q}^2 \tilde{T}_{2Q'}^{(m,4)} | \tilde{r} i_o \rangle \right] \\ &= \delta_{p'p} \sqrt{10} f_K i^{j-j'} (-1)^{K'-M'} [J][J'] \sum_{q_1 q_4 q} \begin{pmatrix} 1 & 1 & 2 \\ q_1 & q_4 & q \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ -M' & q & M \end{pmatrix} \langle I'_4 i'_4 | \hat{T}_{1q_4}^{(4)} | I_4 i_4 \rangle \\ &\times \langle I' i' | \hat{T}_{1q_1}^{(1)} | I i \rangle \left[\sum_q T_{HH_4} + (-1)^{p+J+K} \sum_Q T'_{HH_4} \right] \end{aligned} \quad (29)$$

wherein

$$\begin{aligned} T_{HH_4} &= \begin{pmatrix} J' & 2 & J \\ -K' & q & K \end{pmatrix} \langle i'_{-s} | P_{H_1 H_4} \tilde{T}_{2q'}^{(1,4)} + \\ &+ P_{H_2 H_4} \tilde{T}_{2q'}^{(2,4)} \omega_s^{-1} + P_{H_3 H_4} \tilde{T}_{2q'}^{(3,4)} \omega_s^{-2} | i_o \rangle, \\ T'_{HH_4} &= \begin{pmatrix} J' & 2 & J \\ -K' & Q' & -K \end{pmatrix} \langle i'_{-s} | P_{H_1 H_4} \tilde{T}_{2Q'}^{(1,4)} + \\ &+ P_{H_2 H_4} \tilde{T}_{2Q'}^{(2,4)} \omega_s^{-1} + P_{H_3 H_4} \tilde{T}_{2Q'}^{(3,4)} \omega_s^{-2} | \tilde{i}_o \rangle \end{aligned} \quad (30)$$

Where $q' = K' - K$, $Q' = K' - (-K)$; $q_1 = 0, \pm 1$, and $q_4 = 0, \pm 1$. Then, for an ortho-para pair of the states α and α' , by taking the summation over the quantum numbers $M, M', i_o, i'_s, i_4, i'_4$ for the square of modules of \hat{V}_{HH_4} , we have

$$\begin{aligned} \sum |\langle \alpha' | \hat{V}_{HH_4} | \alpha \rangle|^2 &= \frac{2}{9} \delta_{p'p} f_K^2 \times \\ &\times [J']^2 [J]^2 \left| \sum_{q'} T_{HH_4} + (-1)^{p+J+K} \sum_Q T'_{HH_4} \right|^2 \end{aligned} \quad (31)$$

By using the wave functions of $|K v_t \sigma\rangle$ and $\langle K' v'_t \sigma' |$ with Fourier expansion coefficients listed in Tables 4 and 5, we have calculated the square of modules of the matrix element in Eq. (31) by a written program using Mathematics software. In Eq. (31), the symbol $[J]^2 = 2J+1$ and two values of the following square of the reduced matrix element have been used,

$$\left| \left\langle \frac{1}{2} \left\| \hat{T}_1^{(1)} \right\| \frac{3}{2} \right\rangle \right|^2 = \frac{2}{3}, \quad \left| \left\langle \frac{1}{2} \left\| \hat{T}_1^{(4)} \right\| \frac{1}{2} \right\rangle \right|^2 = \frac{3}{2}. \quad (32)$$

For the matrix element of operator \hat{V}_{HH} , it can be written in the form of

$$\begin{aligned} \langle \alpha' | \hat{V}_{HH} | \alpha \rangle &= \sum_{1=m<n}^3 \langle \alpha' | \hat{V}_{H_m H_n} | \alpha \rangle \\ &= \delta_{p'p} \sqrt{2} f_K \times \\ &\times P_{H_1 H_2} \sum_{1=m<n}^3 \sum_q (-1)^q \langle I'_4 i'_4 | I_4 i_4 \rangle \langle I' i'_s | \times \\ &\times \left(\hat{T}^{(m)} \hat{T}^{(n)} \right)_{2,-q} | I i_o \rangle \times \\ &\times \left[\sum_q \langle r' i'_{-s} | D_{q'q}^2 \tilde{T}_{2q'}^{(m,n)} | r i_o \rangle + (-1)^{p+J+K} \sum_Q \langle r' i'_{-s} | D_{Q'q}^2 \tilde{T}_{2Q'}^{(m,n)} | \tilde{r} i_o \rangle \right] \\ &= \delta_{p'p} \sqrt{2} f_K [J][J'] \sum_q (-1)^{q+K'-M'} i^{j-j'} \langle I'_4 i'_4 | I_4 i_4 \rangle \begin{pmatrix} J' & 2 & J \\ -M' & q & M \end{pmatrix} \times \\ &\times \langle I' i' | (\hat{T}^{(1)} \hat{T}^{(2)})_{2,-q} | I i_o \rangle \left[\sum_q T_{HH} + (-1)^{p+J+K} \sum_Q T'_{HH} \right] \end{aligned} \quad (33)$$

wherein

$$\begin{aligned} T_{HH} &= \begin{pmatrix} J' & 2 & J \\ -K' & q & K \end{pmatrix} P_{H_1 H_2} \left(\omega_s^{-1} \tilde{T}_{2q'}^{(1,2)} + \right. \\ &+ \omega_s^{-2} \tilde{T}_{2q'}^{(1,3)} + \omega_s^{-3} \tilde{T}_{2q'}^{(2,3)} \left. \right) \langle i'_{-s} | i_o \rangle \\ T'_{HH} &= \begin{pmatrix} J' & 2 & J \\ -K' & Q' & -K \end{pmatrix} P_{H_1 H_2} \left(\omega_s^{-1} \tilde{T}_{2Q'}^{(1,2)} + \right. \\ &+ \omega_s^{-2} \tilde{T}_{2Q'}^{(1,3)} + \omega_s^{-3} \tilde{T}_{2Q'}^{(2,3)} \left. \right) \langle i'_{-s} | \tilde{i}_o \rangle \end{aligned} \quad (34)$$

The scaling factor $P_{H_1 H_2}$, $P_{H_1 H_3}$, and $P_{H_2 H_3}$ equals to each other, which is calculated to be 21.423 kHz from the bond length of $r_{H_1 H_2} = 1.776 \text{ \AA}$. The reduced matrix element $\langle I' | (\hat{T}^{(1)} \hat{T}^{(2)})_2 | I \rangle = -\sqrt{5/12}$. By taking the square to the modules of the matrix elements of \hat{V}_{HH} , then making the summation of it over the quantum numbers $M, M', i_o, i'_s, i_4, i'_4$, and considering $\sum_{i_4 i'_4} |\langle I'_4 i'_4 | I_4 i_4 \rangle|^2 = 2I_4 + 1 = 2$, we have the form of

$$\sum |\langle \alpha' | \hat{V}_{HH} | \alpha \rangle|^2 = \frac{1}{3} \delta_{p'p} f_K^2 [J']^2 [J]^2 \left| \sum_q T_{HH} + (-1)^{p+J+K} \sum_Q T'_{HH} \right|^2 \quad (35)$$

The mixing strength of one pair of ortho-para states by nuclear spin-spin interactions is given by the expression

$$\begin{aligned}
F_{SS} &= \sum \left| \langle \alpha' | \hat{V}_{HH_4} + \hat{V}_{HH} | \alpha \rangle \right|^2 \\
&= \sum \left| \langle \alpha' | \hat{V}_{HH_4} | \alpha \rangle \right|^2 + \sum \left| \langle \alpha' | \hat{V}_{HH} | \alpha \rangle \right|^2 \\
&= \frac{1}{9} \delta_{p'p} f_K^2 [J']^2 [J]^2 \left\{ 2 \left| \sum_q T_{HH_4} + (-1)^{p+J+K} \sum_{q'} T_{HH_4}' \right|^2 \right. \\
&\quad \left. + 3 \left| \sum_q T_{HH} + (-1)^{p+J+K} \sum_{q'} T_{HH}' \right|^2 \right\}.
\end{aligned} \quad (36)$$

Here, the summation is made over quantum numbers $M, M', i_o, i_s, i_4, i_4'$. Due to summation of the first power matrix elements of the spin operators in the cross terms, the cross terms between matrix elements of operator \hat{V}_{HH_4} and \hat{V}_{HH} vanish [22]. The required numerical values of the nuclear spin-spin tensor components of CH₃OH in Eq. (36) are listed in Table 6.

Then, by using Eq. (37) and considering the selection rules for the nuclear spin-spin mixing in CH₃OH with $|\Delta J| = |J' - J| \leq 2$ and $|\Delta K| = |K' - K| \leq 2$, the ortho-para conversion rate in CH₃OH induced by the nuclear spin-spin interactions can be calculated

$$\gamma_{SS} = \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma F_{SS}}{\Gamma^2 + \omega_{\alpha\alpha'}^2} [W_B(\alpha) + W_B(\alpha')] \quad (37)$$

B. Nuclear spin-rotation interactions in CH₃OH

Besides the intramolecular nuclear spin-spin interactions between molecular nuclei mentioned above, there are also interactions of the nuclear spins of the hydrogen atoms with the magnetic fields generated by the rotations of the nuclear charges and electronic charges of CH₃OH, i.e., the nuclear spin-rotation (SR) couplings. For studying ortho-para conversion of CH₃OH in this work, we are interested in the SR interactions with just three H nuclei in the CH₃ top by neglecting their very weak dependence on the H nucleus in the OH group. Therefore, by using a nuclear spin-rotation tensor $\mathbf{C}^{(n)}$ for the n -th H atom (its nuclear spin operator $\mathbf{I}^{(n)}$) in the CH₃ top, the general form of nuclear spin-rotation interaction operator \hat{V}_{SR} in CH₃OH can be written as a summation of the nuclear spin-rotation coupling Hamiltonian $\hat{V}_{SR}^{(n)}$ as [34,39]

$$\begin{aligned}
\hat{V}_{SR} &= \sum_{n=1}^3 \hat{V}_{SR}^{(n)} = \sum_{n=1}^3 \left(\hat{\mathbf{J}} \cdot \mathbf{C}^{(n)} \cdot \hat{\mathbf{I}}^{(n)} + H.c. \right) / 2 \\
&= \left(\hat{A}_{SR} + \hat{B}_{SR} \right) / 2
\end{aligned} \quad (38)$$

where $\hat{\mathbf{J}}$ is the rotational angular momentum operator of a molecule. The operator \hat{B}_{SR} in Eq. (38) refers to the Hermitian conjugate of the operator \hat{A}_{SR} . Operators \hat{A}_{SR} and \hat{B}_{SR} can be rewritten in Cartesian coordinates or rewritten to be the components in the coordinate system fixed in the CH₃OH molecule that is transformed by the Wigner D-matrices $D_{q'q}^l$ from the spherical components in the laboratory system. For example, for \hat{A}_{SR} ,

Table 6
Nuclear spin-spin tensor components of CH₃OH.

| Level pair # | #1, #2, #3, and #4 | #5 and #6 | #7 and #8 |
|---|--------------------|-----------|-----------|
| $\omega_s^{-1} \tilde{T}_{2,\pm 1}^{(1,2)}$ | 0 | 0 | 0 |
| $\omega_s^{-1} \tilde{T}_{2,\pm 2}^{(1,2)}$ | 0 | -3/2 | 0 |
| $\omega_s^{-2} \tilde{T}_{2,\pm 1}^{(1,3)}$ | 0 | 0 | 0 |
| $\omega_s^{-2} \tilde{T}_{2,\pm 2}^{(1,3)}$ | 0 | -3/2 | 0 |
| $\omega_s^{-3} \tilde{T}_{2,\pm 1}^{(2,3)}$ | 0 | 0 | 0 |
| $\omega_s^{-3} \tilde{T}_{2,\pm 2}^{(2,3)}$ | 0 | -3/2 | 0 |

one has

$$\hat{A}_{SR} = \sum_{n=1}^3 \hat{\mathbf{J}} \cdot \mathbf{C}^{(n)} \cdot \hat{\mathbf{I}}^{(n)} = \sum_{n=1}^3 \sum_{ij} \hat{J}_i \mathbf{C}_{ij}^{(n)} \hat{I}_j^{(n)} \quad (39)$$

$$\hat{A}_{SR} = \sum_{n=1}^3 \sum_{q'q_1q_2} \sum_l (-1)^q \sqrt{2l+1} \begin{pmatrix} 1 & 1 & l \\ q_1 & q_2 & q \end{pmatrix} \left(\hat{\mathbf{J}} \cdot \mathbf{D}_{q'q}^l \cdot \tilde{\mathbf{C}}_{lq'}^{(n)} \right)_{1,q_1} \cdot \hat{\mathbf{I}}_{1,q_2}^{(n)} \quad (40)$$

where $\tilde{\mathbf{C}}_{lq'}^{(n)}$ is the spherical component of the spin-rotation tensor for the n -th nucleus calculated in the molecular frame, which is composed of two tensors $\tilde{N}_{lq'}^{(n)}$ and $\tilde{E}_{lq'}^{(n)}$ due to the nuclear current and electronic current in the molecule [39]

$$\tilde{\mathbf{C}}_{lq'}^{(n)} = \tilde{N}_{lq'}^{(n)} + \tilde{E}_{lq'}^{(n)} \quad (41)$$

The calculation of the electron part is related to electron excited states and is rather difficult to perform. Next, we will neglect the electron part and use the estimation of $\tilde{\mathbf{C}}_{lq'}^{(n)} \approx \tilde{N}_{lq'}^{(n)}$. The explicit form of the components $\tilde{N}_{lq'}^{(n)}$ of the tensor $\tilde{\mathbf{C}}_{lq'}^{(n)}$ for the n -th proton can approximately be written with b_k in Cartesian coordinates as [40]

$$N_{ji}^{(n)} = \sum_{kf} b_k ((\mathbf{r}_k \cdot \mathbf{R}_k) \delta_{jf} - r_{kj} R_{kf}) B_{fi} \quad (42)$$

$$b_k = \mu_0 \mu_p Q_k / h R_k^3 \quad (43)$$

Where h is the Planck constant and μ_0 is the permeability constant; Q_k is the nuclear charge of particle k ; \mathbf{R}_k is the radial vector from the n -th proton to the particle k , and \mathbf{r}_k is the radial vector from the centre of mass to the particle k in CH₃OH. i, j , and f are the Cartesian indices. Index k runs over all nuclei in CH₃OH except the n -th proton. The italic letter B refers to the inverse matrix of inertia moment of CH₃OH, its diagonal matrix elements have the following values (in GHz) [24]: $B_{xx} = 47.54$, $B_{yy} = 49.36$, and $B_{zz} = 254.96$.

The ranks of tensor $\tilde{\mathbf{C}}_{lq'}^{(n)}$ and $\tilde{N}_{lq'}^{(n)}$ are $l = 0, 1, 2$ for $q' = 0, l = 1, 2$ for $q' = \pm 1$, and $l = 2$ for $q' = \pm 2$. The spherical components of $\tilde{N}_{lq'}^{(1)}$ in kHz for one proton in the H atom of the CH₃ group can be determined from their Cartesian components by the definitions of

$$\begin{aligned}
\tilde{N}_{1,\pm 1}^{(1)} &= (1/2) \left[N_{xz}^{(1)} - N_{zx}^{(1)} \pm i \left(N_{yz}^{(1)} - N_{zy}^{(1)} \right) \right], \\
\tilde{N}_{2,\pm 1}^{(1)} &= \pm (1/2) \left[N_{xz}^{(1)} + N_{zx}^{(1)} \pm i \left(N_{yz}^{(1)} + N_{zy}^{(1)} \right) \right], \\
\tilde{N}_{2,\pm 2}^{(1)} &= - (1/2) \left[N_{xx}^{(1)} - N_{yy}^{(1)} \pm i \left(N_{xy}^{(1)} + N_{yx}^{(1)} \right) \right].
\end{aligned} \quad (44)$$

The $\tilde{\mathbf{C}}_{lq'}^{(1)}$ ($\approx \tilde{N}_{lq'}^{(1)}$) is a spherical component of the spin-rotation tensor for one proton in the H₁ atom of the CH₃ group, which will be used in the calculations of the spin conversion rates of CH₃OH induced by the SR interactions next. Unlike the nuclear spin-spin interactions between molecular nuclei discussed above, the magnetic fields at the positions of each individual atom in a molecule interact with the nuclear spins of these atoms to form the nuclear spin-rotation couplings. Hence, as shown below, the SR interactions in CH₃OH can be expressed through the nuclear spin-rotation coupling for one proton in the CH₃ group.

By applying the Wigner-Eckart theorem and angular momentum algebra [1,41], we can now evaluate the matrix element of the operator \hat{A}_{SR} with the tensor $\tilde{\mathbf{C}}_{lq'}^{(1)}$ by using expression (40), we have

$$\langle \alpha' | \hat{A}_{SR} | \alpha \rangle = \delta_{p'p} \sqrt{2} f_K \left[\langle \beta_s' | \hat{A}_{SR} | \beta_o \rangle + (-1)^{p+J+K} \langle \beta_s' | \hat{A}_{SR} | \bar{\beta}_o \rangle \right]$$

$$\tilde{C}_{lq'} = \langle i_{-s}' | \tilde{C}_{lq'}^{(1)} + \omega_s^{-1} \tilde{C}_{lq'}^{(2)} + \omega_s^{-2} \tilde{C}_{lq'}^{(3)} | i_o \rangle$$

$$\begin{aligned} &= \delta_{p'p} \sqrt{2} f_K \sum_{n=1}^3 \sum_{qq_1q_2} \sum_l (-1)^q \sqrt{2l+1} \begin{pmatrix} 1 & 1 & l \\ q_1 & q_2 & q \end{pmatrix} \left[\sum_{q'} \langle \beta_s' | (\hat{\mathbf{J}} \cdot \mathbf{D}_{q'q}^l \tilde{C}_{lq'}^{(n)})_{1,q_1} \cdot \hat{\mathbf{I}}_{1,q_2}^{(n)} | \beta_o \rangle + \right. \\ &\quad \left. + (-1)^{p+J+K} \sum_{Q'} \langle \beta_s' | (\hat{\mathbf{J}} \cdot \mathbf{D}_{Q'q}^l \tilde{C}_{lQ'}^{(n)})_{1,q_1} \cdot \hat{\mathbf{I}}_{1,q_2}^{(n)} | \beta_o \rangle \right] \end{aligned}$$

$$\tilde{C}_{lQ'} = \langle i_{-s}' | \tilde{C}_{lQ'}^{(1)} + \omega_s^{-1} \tilde{C}_{lQ'}^{(2)} + \omega_s^{-2} \tilde{C}_{lQ'}^{(3)} | i_o \rangle \quad (47)$$

By making the summation to the square of matrix elements of the

$$= \delta_{p'p} \sqrt{6} f_K \langle i_4' i_4 | i_4 i_4 \rangle \sum_{qq_1q_2} \sum_l (-1)^q (-1)^{1+J+J'-K'-M'} i^{1-l-J'+J} \sqrt{2l+1} \sqrt{J'(J'+1)(2J'+1)} \sqrt{(2J+1)(2J'+1)} \times$$

$$\begin{aligned} &\times \langle i_s' | \tilde{I}_{1,q_2}^{(1)} | i_o \rangle \begin{pmatrix} 1 & 1 & l \\ q_1 & q_2 & q \end{pmatrix} \\ &\times \begin{pmatrix} J' & 1 & J \\ -M' & q_1 & M \end{pmatrix} \left\{ \begin{matrix} 1 & l & 1 \\ J & J' & J \end{matrix} \right\} \times \\ &\times \left[\sum_{qK'} \begin{pmatrix} J' & l & J \\ -K' & q' & K \end{pmatrix} \tilde{C}_{lq'} + \right. \\ &\quad \left. + (-1)^{p+J+K} \sum_{QK'} \begin{pmatrix} J' & l & J \\ -K' & Q' & -K \end{pmatrix} \tilde{C}_{lQ'} \right] \end{aligned} \quad (45)$$

The matrix element of the operators \hat{B}_{SR} has the form of

$$\begin{aligned} \langle \alpha' | \hat{B}_{SR} | \alpha \rangle &= \sum_{n=1}^3 \sum_{qq_1q_2} \sum_l (-1)^l \sqrt{2l+1} \begin{pmatrix} 1 & 1 & l \\ q_2 & q_1 & -q \end{pmatrix} \times \\ &\times \langle \alpha' | \tilde{I}_{1,q_2}^{(n)} \cdot \left(\mathbf{D}_{q'q}^l \tilde{C}_{lq'}^{(n)} \cdot \hat{\mathbf{J}} \right)_{1,q_1} | \alpha \rangle \end{aligned}$$

operator \hat{V}_{SR} over the quantum numbers $M, M', i_o, i_s, i_4, i_4'$, one can derive the ortho-para state-mixing strength F_{SR} induced by the nuclear spin-rotation interaction and calculate the ortho-para conversion rate γ_{SR} by this F_{SR} using Eq. (50).

$$\begin{aligned} F_{SR} &= \sum |\langle \alpha' | \hat{V}_{SR} | \alpha \rangle|^2 = \frac{1}{4} \sum |\langle \alpha' | \hat{A}_{SR} | \alpha \rangle + \langle \alpha' | \hat{B}_{SR} | \alpha \rangle|^2 \\ &= \frac{3}{5} \delta_{p'p} f_K^2 [J]^2 [J']^2 \times \\ &\times \left| \sum_{qq_1q_2} \sum_l [l] Y(J', J, l, q_1, q_2, q) \left[\sum_{qK'} \begin{pmatrix} J' & l & J \\ -K' & q' & K \end{pmatrix} \tilde{C}_{lq'} + \right. \right. \\ &\quad \left. \left. + (-1)^{p+J+K} \sum_{QK'} \begin{pmatrix} J' & l & J \\ -K' & Q' & -K \end{pmatrix} \tilde{C}_{lQ'} \right] \right|^2 \end{aligned} \quad (48)$$

wherein

$$= \delta_{p'p} \sqrt{6} f_K \langle i_4' i_4 | i_4 i_4 \rangle \sum_{qq_1q_2} \sum_l i^{1-l+J-J'} (-1)^{1+J+J'-K'-M'} (-1)^l \sqrt{2l+1} \sqrt{J(J+1)(2J+1)} \sqrt{(2J+1)(2J'+1)} \times$$

$$\begin{aligned} &\times \langle i_s' | \tilde{I}_{1,q_2}^{(1)} | i_o \rangle \begin{pmatrix} 1 & 1 & l \\ q_2 & q_1 & -q \end{pmatrix} \\ &\times \begin{pmatrix} J' & 1 & J \\ -M' & q_1 & M \end{pmatrix} \left\{ \begin{matrix} l & 1 & 1 \\ J & J' & J \end{matrix} \right\} \times \\ &\times \left[\sum_{qK'} \begin{pmatrix} J' & l & J \\ -K' & q' & K \end{pmatrix} \tilde{C}_{lq'} + \right. \\ &\quad \left. + (-1)^{p+J+K} \sum_{QK'} \begin{pmatrix} J' & l & J \\ -K' & Q' & -K \end{pmatrix} \tilde{C}_{lQ'} \right] \end{aligned} \quad (46)$$

Where $\{\{\cdot\cdot\cdot\}\}$ stands for the 6-j symbol; $\tilde{C}_{lq'}$ and $\tilde{C}_{lQ'}$ have the forms of

$$\begin{aligned} Y(J', J, l, q_1, q_2, q) &= (-1)^q \sqrt{J'(J'+1)(2J'+1)} \times \\ &\times \begin{pmatrix} 1 & 1 & l \\ q_1 & q_2 & q \end{pmatrix} \left\{ \begin{matrix} 1 & l & 1 \\ J & J' & J \end{matrix} \right\} + \\ &+ (-1)^l \sqrt{J(J+1)(2J+1)} \begin{pmatrix} 1 & 1 & l \\ q_2 & q_1 & -q \end{pmatrix} \left\{ \begin{matrix} l & 1 & 1 \\ J & J' & J \end{matrix} \right\} \end{aligned} \quad (49)$$

$$\gamma_{SR} = \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma F_{SR}}{\Gamma^2 + \omega_{\alpha\alpha'}^2} [W_B(\alpha) + W_B(\alpha')] \quad (50)$$

The selection rules for the nuclear spin-rotation mixing in CH_3OH are $|\Delta J| = |J' - J| \leq 1$ and $|\Delta K| = |K' - K| \leq 2, J' + J \geq 1$.

Table 7

The calculated ortho–para state-mixing strength and conversion rate of CH₃OH at a pressure of 1 Torr and a temperature of 300 K. In the table, F_{SS} and F_{SR} are the ortho–para state-mixing strength induced by the nuclear spin–spin and nuclear spin–rotation interaction, respectively, γ_{SS} and γ_{SR} are the calculated nuclear spin conversion rate accordingly. The total nuclear spin conversion rate $\gamma = \gamma_{SS} + \gamma_{SR}$.

| Level | F_{SS} | γ_{SS} | F_{SR} | γ_{SR} | γ |
|------------|-----------------------|-------------------------------------|-----------------------|-------------------------------------|-------------------------------------|
| Pair # | (MHz ²) | (10 ^{−3} s ^{−1}) | (MHz ²) | (10 ^{−3} s ^{−1}) | (10 ^{−3} s ^{−1}) |
| #1 | 2.47×10^{-6} | 6.44×10^{-5} | 8.65×10^{-4} | 2.26×10^{-3} | 2.27×10^{-1} |
| #2 | 4.09×10^{-4} | 1.01×10^{-3} | 1.06×10^{-1} | 2.62×10^{-1} | 2.63×10^{-1} |
| #3 | 5.24×10^{-4} | 1.96×10^{-4} | 2.23×10^{-1} | 8.34×10^{-2} | 8.36×10^{-3} |
| #4 | 6.19×10^{-4} | 7.40×10^{-3} | 4.08×10^{-1} | 4.88 | 4.89 |
| #5 | 2.68×10^{-3} | 1.09 | – | – | 1.09 |
| #6 | 2.68×10^{-3} | 4.02×10^{-2} | – | – | 4.02×10^{-2} |
| #7 | 7.93×10^{-4} | 3.57×10^{-5} | 1.39 | 6.24×10^{-2} | 6.24×10^{-3} |
| #8 | 8.07×10^{-4} | 4.54×10^{-3} | 1.35 | 7.59 | 7.60 |
| Total rate | | 1.14 | | 12.91 | 14.05 |

The calculated nuclear spin conversion rates of CH₃OH and discussions

The derived general expressions described above have been used in calculations of the nuclear spin conversion rates of methanol at room temperature and low pressures below 2 Torr, aiming for making comparisons of the calculated results with experimental results. In Eqs. (37) and (50), as mentioned above, we use the decoherence rate being state-independent quantity $\Gamma = 2\pi \times 20$ MHz/Torr for all the ortho–para pairs of CH₃OH. The 1964 mixed level-pairs of the ortho- and para-CH₃OH allowed by the selection rules of $|\Delta J| \leq 2$ and $|\Delta K| \leq 2$ with energy gaps less than 50 GHz are considered in the calculations of the conversion rates, however, only eight level-pairs have energy gaps less than 2.7 GHz, which are presented in Table 1. For these level pairs, the calculated ortho–para state-mixing strengths and conversion rates of CH₃OH at 1 Torr and 300 K are given in Table 7.

From Table 7, one can find that ortho–para state-mixings which induce spin-isomers conversion differ among eight pairs of state levels. Although states in all eight pairs can be mixed by the nuclear spin–spin and nuclear spin–rotation interactions, the leading process in the spin isomers conversion is the nuclear spin–rotation interaction. The magnetic dipole–dipole interactions between the H₄ proton and each of the protons of H atoms in CH₃ group in a large distance between them are very weak. Above 91% contribution to the total nuclear spin conversion rate is made by nuclear spin–rotation interactions from two ortho–para level pairs of (3, 34, 1, 0)–(3, 35, 0, 1) and (0, 22, 5, p)–(0, 21, 6, −1), and about 8% by nuclear spin–spin interactions from (0, 24, 4, 1)–(0, 25, 2, 1), here the levels pair notation is $(v_t, J, K, p) - (v_t', J', K', \sigma')$. Although the energy gap of the ortho–para level pair of (0, 24, 4, 1)–(0, 25, 2, 1) has a relatively small value of 47 MHz and the levels in the pair of (3, 34, 1, 0)–(3, 35, 0, 1) are the closest states in these eight level pairs, they have high J values and the Boltzmann factors of them are small. Though the K -doublet level pairs (0, 24, 4, 0)–(0, 25, 2, 1) and (3, 34, 1, 1)–(3, 35, 0, 1) have ortho–para state-mixing strengths F_{SS} and F_{SR} almost as large as the pairs of (0, 24, 4, 1)–(0, 25, 2, 1) and (3, 34, 1, 0)–(3, 35, 0, 1), the formers have larger energy gaps than the latters, leading to smaller contributions to conversion rates.

Considering nuclear-spin conversion induced by the nuclear spin–spin and nuclear spin–rotation interactions together, the total nuclear spin conversion rate γ in CH₃OH at a gas pressure 1 Torr and a

temperature 300 K via eight pairs (rather than just two pairs in Ref. 22) of ortho–para levels listed in Table 1 is calculated to be $1.4 \times 10^{-2} \text{ s}^{-1}$, which is close to the measured value of $2.1 (3) \times 10^{-2} \text{ s}^{-1}$ in a recent experiment [18]. This fact indicates that our theoretical model based on the quantum relaxation theory is valid for methanol and suggests that it is also suitable for other gaseous methanol-like molecules having torsion tunneling of symmetrical group. The calculation uncertainty of the nuclear spin–spin interaction between the nuclei is mainly from small errors in the knowledge of the molecular structure and from the assumption about the decoherence rate being state-independent. The calculated conversion rate would be larger than $1.4 \times 10^{-2} \text{ s}^{-1}$ if the following factors are included in the calculations: 1) the electronic contribution of $\tilde{E}^{(n)}$ to the tensor $\tilde{C}^{(n)}$, which could be obtained by *ab initio* calculations in quantum chemistry, 2) the coupling between the methyl group and hydroxyl group, 3) the nuclear spin–torsion coupling. The internal rotation of CH₃OH can also generate a magnetic field and the hyperfine nuclear spin–torsion coupling potential should similarly contribute to the near-degenerate state-mixings and to the spin-isomers conversions. We will address the role of the intramolecular nuclear spin–torsion interaction to the isomer conversion in CH₃OH elsewhere.

The obtained ortho–para conversion rate of CH₃OH is the largest one among three gaseous molecules of ¹³CH₃F, H₂CO, and C₂H₄ studied so far. At a low gas pressure, the decoherence rate of ¹³CH₃F is much smaller than the energy gap of 131 MHz between the closest mixed-states $(J, K) = (11, 1) - (9, 3)$. The CH₃OH has the similar CH₃ top as that in ¹³CH₃F and displays torsion relative to the OH group, which causes more complicated torsion–rotation–vibration interactions and numerous near-degenerate sub-states in CH₃OH. The frequency gap between ortho–para level pairs of (0, 24, 4, 1)–(0, 25, 2, 1) and (3, 34, 1, 0)–(3, 35, 0, 1) are close to the decoherence rate Γ for CH₃OH at low pressures. Therefore, these doorways are more efficient for population exchanges toward equilibration by molecular collisions, causing faster isomers conversion rate in CH₃OH than that in ¹³CH₃F.

Conclusions

A general theoretical model studied by the IAM for the description of spin isomers conversion in CH₃OH has been developed based on the quantum relaxation theory. The ortho–para state-mixing strengths induced by the weak hyperfine intramolecular magnetic interactions have been analyzed. This analysis reveals the important roles of the nuclear spin–spin and nuclear spin–rotation interactions to the states-mixings and spin-isomers conversions in CH₃OH, among which the nuclear spin–rotation interaction plays a major role and the nuclear spin–spin interaction plays a minor role. The calculated spin conversion rate at temperature 300 K and a pressure 1 Torr is $1.4 \times 10^{-2} \text{ s}^{-1}$, which is close to the measured value of $2.1 (3) \times 10^{-2} \text{ s}^{-1}$ in Ref. 18. This result indicates that the nuclear spin isomer conversion of CH₃OH is mainly via quantum relaxation process and suggests our theory to be valid for other gaseous methanol-like molecules having torsion tunneling of symmetrical group. The most probable gateways in methanol for collision-induced population transfers are found to be levels-pairs in the ground-state with A–E species of $(v_t, J, K, p) = (0, 24, 4, 1) - (0, 25, 2, 1)$ by nuclear spin–spin coupling, of (0, 22, 5, p)–(0, 21, 6, −1) and (3, 34, 1, 0)–(3, 35, 0, 1) by nuclear spin–rotation coupling.

CRedit authorship contribution statement

Li-Sha Ma: Conceptualization, Data curation, Formal analysis, Methodology, Software, Writing – original draft. **Zhen-Dong Sun:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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