Nuclear spin conversion in formaldehyde

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Abstract

Theoretical model of the nuclear spin conversion in formaldehyde (H$_2$CO) has been developed. The conversion is governed by the intramolecular spin-rotation mixing of molecular ortho and para states. The rate of conversion has been found equal $\gamma/P = 1.4 \cdot 10^{-4}$ s$^{-1}$/Torr. Temperature dependence of the spin conversion has been predicted to be weak in the wide temperature range $T = 200 - 900$ K.

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I. INTRODUCTION

It is well known that many symmetrical molecules exist in nature only in the form of nuclear spin isomers \[1\]. The spin isomers demonstrate anomalous stability. For example, the ortho and para isomers of \( \text{H}_2 \) survive almost 1 year at 1 atm and room temperature \[2\]. Existence of spin isomers is well-understood in the framework of the spin-statistics relation in quantum mechanics. On the other hand, the dynamical part of the problem, viz., the isomer stability, their conversion rates and responsible conversion mechanisms are less clear. This is because experimental data on spin isomers are rare due to substantial difficulties in preparation of enriched spin isomer samples. Thus each new experimental result in this field deserves close attention.

In this paper we perform theoretical analysis of the nuclear spin conversion in formaldehyde (\( \text{H}_2\text{CO} \)). This process was considered theoretically previously \[3\]. But it is worthwhile to perform new analysis in order to account new important information. First, the formaldehyde spin conversion was recently investigated experimentally and the gas phase conversion rate was measured for the first time \[4\]. Second, formaldehyde molecular structure and molecular spectroscopic parameters have been determined very accurately \[5–7\]. Third, simple theoretical model of nuclear spin conversion in asymmetric tops was developed and tested by the spin conversion in ethylene \[8\]. All these circumstances allow to advance significantly theory of the spin conversion in formaldehyde.

II. DIRECT AND INDIRECT CONVERSION MECHANISMS

There are two main mechanisms known for the gas phase spin conversion in molecules. The first one, *direct*, consists in the following. In the course of collision inhomogeneous magnetic field produced by collision partner induces direct transitions in the test molecule between spin states. This mechanism is responsible for the hydrogen isomer conversion by paramagnetic \( \text{O}_2 \) \[9\]. It is important for us that the hydrogen conversion induced by \( \text{O}_2 \) (the rate is equal to \( 8 \cdot 10^{-6} \text{ s}^{-1}/\text{Torr} \) \[2\]) appears to be much slower than the spin conversion in formaldehyde \[4\],

\[
\gamma_{\text{exp}}/P = (1.1 \pm 0.3) \cdot 10^{-3} \text{ s}^{-1}/\text{Torr}. \tag{1}
\]
Note that we refer here to the formaldehyde ortho-para equilibration rate. In notations of [4] this rate is equal to $k_1 + k_2$, where $k_1$ and $k_2$ are the ortho-to-para and para-to-ortho conversion rates, respectively.

Hydrogen is an exceptional molecule due to its anomalously large ortho-para level spacing and high symmetry. It is more appropriate for the present discussion to consider the direct mechanism in polyatomic molecules. The isomer conversion in CH$_3$F induced by O$_2$ was investigated theoretically and experimentally in [10,11]. It was found that this mechanism provides the conversion rate on the order of $10^{-4} - 10^{-5}$ s$^{-1}$/Torr. These rates refer to the collisions with paramagnetic O$_2$ which have magnetic moment close to Bohr magneton, $\mu_B$. An experimental arrangement in [4] corresponds to “nonmagnetic” collision partner having a magnetic moment on the order of nuclear magneton, $\mu_n$, thus by $10^3$ times smaller. The conversion rate by direct mechanism depends on magnetic moment as $\mu^2$ [10]. It implies that the conversion by direct process is too slow to be taken into account for the formaldehyde conversion. In fact, the authors [4] had arrived at the same conclusion.

Second mechanism is applicable to molecules in which different spin states can be quantum mechanically mixed by weak *intramolecular* perturbation. Mixing and interruption of this mixing by collisions with the surrounding particles result in the isomer conversion. We will refer to this mechanism as *quantum relaxation*. Quantum relaxation can provide significantly faster conversion than direct process does for nonmagnetic particles. It can be illustrated by a few examples in which quantum relaxation was established to be a leading process. The most studied case is the spin conversion in $^{13}$CH$_3$F (for the review see [12]). The conversion rate in this molecule was determined as $(12.2 \pm 0.6) \cdot 10^{-3}$ s$^{-1}$/Torr. The conversion rate in ethylene ($^{13}$CCH$_4$) is equal to $(5.2 \pm 0.8) \cdot 10^{-4}$ s$^{-1}$/Torr [13]. In this molecule too the quantum relaxation is the leading process [8]. Thus one can conclude that for the spin conversion in formaldehyde quantum relaxation is an appropriate mechanism.

The formaldehyde molecules have two nuclear spin isomers, ortho (total spin of the two hydrogen nuclei, $I = 1$) and para ($I = 0$). Each rotational state of the molecule can belong only to ortho, or to para isomers. Thus the molecular states are divided into two subspaces as it is shown in Fig. [4]. Simple physical picture of spin conversion by quantum relaxation is given elsewhere, e.g., [12]. Quantitative description of the process can be performed in the framework of the density matrix formalism. The result of this description is as follows [14].
One has to split the molecular Hamiltonian into two parts,

\[ \hat{H} = \hat{H}_0 + \hat{V}, \]  

(2)

where the main part of the Hamiltonian, \( \hat{H}_0 \), has pure ortho and para states as the eigenstates; the perturbation \( \hat{V} \) mixes the ortho and para states. If at initial instant the nonequilibrium concentration of, say, ortho molecules, \( \delta \rho_0(t = 0) \), was created, the system will relax then exponentially, \( \delta \rho_0(t) = \delta \rho_0(0)e^{-\gamma t} \), with the rate

\[ \gamma = \sum_{a \in \text{ortho, } \alpha', \nu' \in \text{para}} \frac{2\Gamma F(a|a')}{\Gamma^2 + \omega_{aa'}^2} (W_o(\alpha) + W_p(\alpha')); \quad F(a|a') \equiv \sum_{\nu \in \text{ortho, } \nu' \in \text{para}} |V_{\alpha \alpha'}|^2. \]  

(3)

where \( \Gamma \) is the decay rate of the off-diagonal density matrix element \( \rho_{\alpha \alpha'} \) (\( \alpha \in \text{ortho} \); \( \alpha' \in \text{para} \)) assumed here to be equal for all ortho-para level pairs; \( \omega_{aa'} \) is the gap between the states \( a \) and \( a' \); \( W_o(\alpha) \) and \( W_p(\alpha') \) are the Boltzmann factors of the corresponding states. The sets of quantum numbers \( \alpha \equiv \{a, \nu\} \) and \( \alpha' \equiv \{a', \nu'\} \) consist of the degenerate quantum numbers \( \nu, \nu' \) and the quantum numbers \( a, a' \) which determine the energy of the states. In Eq. (3) and further the ortho states will be denoted by unprimed characters, but para states by primed characters. For the following it is convenient to introduce the \textit{strength of mixing}, \( F(a|a') \). In the definition of \( F(a|a') \) in Eq. (3) the summation is made over all degenerate states.

The general model (3) was tested comprehensively by conversion in symmetric tops \((^{13}\text{CH}_3\text{F}, ^{12}\text{CH}_3\text{F})\) and asymmetric top, \(^{13}\text{CCH}_4\). It was proven that the ortho-para mixing is performed in these molecules by intramolecular hyperfine interactions. Thus, the spin isomer conversion gives an alternative access to very weak intramolecular forces which was investigated previously by high resolution spectroscopy, e.g., Laser Stark Spectroscopy [15] and Microwave Fourier Transform Spectroscopy [16].

To avoid confusion we stress that \( \gamma \) from Eq. (3) gives the equilibration rate in the system if one would measure the concentration of ortho (or para) molecules. The authors [4] introduced the ortho-to-para \((k_1)\) and para-to-ortho \((k_2)\) rates which are equal, respectively, to the first and second terms in the expression (3) for \( \gamma \). Thus \( \gamma \equiv k_1 + k_2 \). Relation between the formaldehyde ortho and para partition functions (see below) explains the equality \( k_2 = 3k_1 \) [4].
III. ROTATIONAL STATES OF FORMALDEHYDE

The formaldehyde molecule is a prolate, nearly symmetric top having symmetry group $C_{2v}$. The characters of the group operations and its irreducible representations are given in the Table 1. The molecular structure and orientation of the molecular system of coordinates are given in Fig. 2. The formaldehyde is a planar molecule having the following parameters in the ground state $r_{CH} = 1.1003 \pm 0.0005 \text{ Å}$, $r_{CO} = 1.2031 \pm 0.0005 \text{ Å}$, and $\alpha_{HCO} = 121.62 \pm 0.05^\circ$.

Rotational states of formaldehyde in the ground electronic and vibrational state can be determined with high accuracy using the octic order Hamiltonian of Watson [17,5,7],

$$\hat{H}_0 = \frac{1}{2}(B + C)J^2 + (A - \frac{1}{2}(B + C))J_z^2 - \Delta J^4 - \Delta JK J^2 J_z^2 - \Delta K J^4$$
$$+ H_J J^6 + H_{JK} J^4 J_z^2 + H_{KJ} J^2 J_z^4 + H_{KK} J^6$$
$$+ L_{JJK} J^6 J_z^2 + L_{JK} J^4 J_z^4 + L_{KJ} J^2 J_z^6 + L_{KK} J^8$$
$$+ \frac{1}{4}(B - C)F_0 - \delta J^2 F_0 - \delta K F_2 + h_J J^4 F_0 + h_{JK} J^2 F_2 + h_K F_4 + l_{KK} F_4,$$  \hspace{1cm} (4)

where $J$, $J_x$, $J_y$, and $J_z$ are the molecular angular momentum operator and its projections on the molecular axes. The $B$, $C$, and $A$ are the parameters of a rigid top which characterize the rotation around $x$, $y$, and $z$ molecular axes, respectively (see Fig. 2). The rest of parameters account for the centrifugal distortion effects [17]. In Eq. (4) the notation was used

$$F_n \equiv J_z^n (J_x^2 - J_y^2) + (J_x^2 - J_y^2) J_z^n.$$  \hspace{1cm} (5)

We left in the Hamiltonian (4) only those terms for which molecular parameters in [5] were not set to zero.

It is convenient to diagonalise the Hamiltonian (4) in the Wang basis [3],

$$|\alpha, p > = \frac{1}{\sqrt{2}} [ |\alpha > + (-1)^J + K + p |\bar{\alpha} > ]; \hspace{0.5cm} 0 < K \leq J,$$
$$|\alpha_0, p > = \frac{1 + (-1)^{J + p}}{2} |\alpha_0 >; \hspace{0.5cm} K = 0.$$  \hspace{1cm} (6)

Here $p = 0, 1$; $|\alpha >$ are the symmetric-top rotational states; the sets of quantum numbers are $\alpha \equiv \{J, K, M\}$; $|\bar{\alpha} > \equiv \{J, -K, M\}$; $\alpha_0 \equiv \{J, K = 0, M\}$ where $J$, $K$, and $M$ are the quantum numbers of angular momentum and its projection on the molecular symmetry axis and on the laboratory quantization axis, respectively. Depending on the parity of $J$, $K$ and
The states \( |p, p' > \) generate 4 different irreducible representations of the molecular symmetry group \( C_{2v} \), as it is explained in the Table 1. In the following we will need the reduction of the matrix elements of full symmetric operator \( \hat{V} \) in the basis \( |\alpha, p > \) to the matrix elements of symmetric-top states \( |\alpha > \). This reduction reads

\[
< \alpha, p | V | \alpha', p' > = \delta_{p,p'} \left[ < \alpha | V | \alpha' > + (-1)^{J'+p'} < \alpha | V | \alpha' > \right] : K' > 0,
\]

\[
< \alpha, p | V | \alpha'_0, p > = \delta_{p,p'} \frac{1 + (-1)^{J'+p'}}{\sqrt{2}} < \alpha | V | \alpha'_0 > ; K' = 0.
\]

The molecular Hamiltonian, \( \hat{H}_0 \), is full symmetric (symmetry \( A_1 \)). Consequently, the matrix elements between the states of different symmetry disappear. Thus diagonalization of the total Hamiltonian in the basis of (6) is reduced to the diagonalization of four independent submatrices, each for the states of particular symmetry. The rotational states of asymmetric top can be expanded over the basis states (6),

\[
|\beta, p > = \sum_K A_K |\alpha, p >,
\]

where \( A_K \) stands for the expansion coefficients. The summation variable, \( K \), is shown explicitly in (8), although \( A_K \) depends on other quantum numbers as well. All coefficients in the expansion (8) are real numbers because the Hamiltonian (4) is symmetric in the basis \( |\alpha, p > \).

Complete description of the asymmetric-top quantum state needs indication of all expansion coefficients, \( A_K \), from (8) which is not practical. There are a few schemes for abbreviate notations, see, e.g., [12]. We will use here the notations which are somewhat better adopted to the consideration of the spin isomer problem in asymmetric tops [5]. We will designate the rotational states of asymmetric top by indicating \( p, J \) and prescribing the allowed \( K \) values to the eigen states keeping both in ascending order. For example, the eigen state having \( p = 0, J = 20 \), the allowed \( K \) in the expansion (8) equal \( K = 0, 2, 4 \ldots 20 \) and being the third in ascending order will be designated by \( (p = 0, J = 20, K = 4) \). Note the difference between the two characters \( K \) and \( \mathcal{K} \). It gives unambiguous notation of rotational states for each of the four species \( A_1, A_2 (\mathcal{K}-\text{even}) \) and \( B_1, B_2 (\mathcal{K}-\text{odd}) \). This classification becomes exact for a prolate symmetric top for which \( \mathcal{K} = K \).

Calculation of the level energies and wave functions of molecular quantum states were performed in the paper numerically. Accuracy of these calculations can be estimated by
comparing with the experimental rotational spectra in the ground state of formaldehyde \cite{5}. This comparison shows that the accuracy of the calculations for most rotational states is in the range of $10^{-100}$ kHz. This should be sufficient for the investigation of the spin isomer conversion in formaldehyde.

The two equivalent hydrogen nuclei in H$_2$CO have spin 1/2. It implies that the total wave function (product of spin and spatial wave functions) is of symmetry B$_1$. Spin states of the two hydrogen nuclei can be either triplet (ortho, $I = 1$, symmetry A$_1$), or singlet (para, $I = 0$, symmetry B$_1$). In order to have the total wave function of symmetry B$_1$, the ortho molecules should have the spatial wave function of symmetry B$_1$, but the para molecules should have the spatial wave function of symmetry A$_1$. Consequently, in the ground electronic and vibrational state the rotational states A$_1$ and B$_1$ are only positive (even in parity), but the states A$_2$ and B$_2$ are only negative (odd in parity).

The ortho states of the formaldehyde molecule can be presented as

$$|\mu> = |\beta, p> |I = 1, \sigma >; \ K - \text{odd}. \ (9)$$

where $\sigma$ is the projection of the nuclear spin $I$ on the laboratory quantization axis. The para states can be presented as

$$|\mu'> = |\beta', p'> |I' = 0 >; \ K' - \text{even}. \ (10)$$

The Boltzmann factors $W_o(\alpha)$ and $W_p(\alpha')$ in Eq. (3) determine the population of the states $\alpha$ and $\alpha'$ in the ortho and para families,

$$\rho_\alpha = \rho_o W_o(\alpha); \ \rho_{\alpha'} = \rho_p W_p(\alpha'), \ (11)$$

where $\rho_o$ and $\rho_p$ are the total densities of ortho and para molecules, respectively. The partition functions for ortho and para molecules at room temperature (T=300 K) are found to be equal to

$$Z_{ortho} = 2.16 \cdot 10^3; \ Z_{para} = 721. \ (12)$$

In the calculation of these partition functions the energies of the rotational states were determined numerically using the Hamiltonian \cite{4}. The degeneracy over $M$, $\sigma$, as well as the restrictions imposed by the quantum statistics were taken into account.
IV. MIXING OF THE ORTHO AND PARA STATES

There are two known intramolecular perturbations able to mix ortho and para states in polyatomic molecules. The first one is the spin-spin interaction between the molecular nuclei. This interaction has simple form in formaldehyde and can be expressed as

\[
\hat{V}_{SS} = P_{12}\hat{I}^{(1)}\hat{I}^{(2)} \cdot T;
\]

\[
T_{ij} = \delta_{ij} - 3\delta_{i,x}\delta_{j,x}; \quad P_{12} = \mu_p^2/r^3 I^{(1)}I^{(2)}h, \tag{13}
\]

where \(\hat{I}^{(1)}\) and \(\hat{I}^{(2)}\) are the spin operators of the hydrogen nuclei 1 and 2; \(\mu_p\) is magnetic moment of proton; \(i\) and \(j\) are the Cartesian indices. The second rank tensor \(\hat{I}^{(1)}\hat{I}^{(2)}\) acts on spin variables. The second rank tensor \(T\) represents a spatial part of the spin-spin interaction. One can deduce from the angular momentum algebra that all matrix elements of the perturbation \(\hat{V}_{SS}\) between ortho and para states of formaldehyde are vanishing. This is because one cannot draw a triangle having the sides 2, 1, and 0, which are the rank of the tensor \(\hat{I}^{(1)}\hat{I}^{(2)}\), the total spin of ortho, and para states, respectively.

The second intramolecular perturbation which should be considered is the spin-rotation coupling between spins of hydrogen nuclei and molecular rotation. The spin-rotation coupling can be presented in general as

\[
\hat{V}_{SR} = \sum_n \hat{V}_{SR}^{(n)} = \frac{1}{2}\left(\sum_n \hat{I}^{(n)} \cdot C^{(n)} \cdot \hat{J} + h.c.\right); \quad n = 1, 2. \tag{14}
\]

Here \(C\) is the spin-rotation tensor; \(\hat{J}\) is the angular momentum operator. Index \(n\) in (14) refers only to the hydrogen nuclei because we are interested now in the perturbation able to mix ortho and para states.

Calculation of the spin-rotational tensor, \(C\), is a complicated problem. Further, a few simplifications will be made. First, we neglect small contribution to the tensor \(C\) due to the electric fields at the position of protons. The remaining part of the tensor \(C\) originates from the magnetic fields produced by the electrical currents in the molecule. One can split the tensor \(C\) into two terms,

\[
C = eC + nC, \tag{15}
\]

where \(eC\) and \(nC\) are due to the electron and nuclear currents in the molecule, respectively. The electron part, \(eC\), appears as an average over electron state, which has nonzero value.
only in the second order perturbation theory. Its calculation needs the knowledge of electron excited states and thus is rather difficult to perform. On the other hand, the nuclear part, \(^nC\), has nonzero value for the ground electron state and can be easily estimated. In the following we will neglect the electron part, \(^eC\), and will use the estimation \(C \approx \(^nC\). This can be considered as an upper limit for \(C\) because molecular electrons are following the rotation of nuclear frame and thus compensate partially the magnetic field produced by nuclei.

The spin-rotation tensor \(^nC\) can be presented (in Hz) as [21]

\[
C^{(n)} = \sum_{k \neq n} b_k \left[ (r_k \cdot R_k) 1 - r_k R_k \right] \cdot B;
\]

\[
b_k = 2 \mu_p q_k / \sqrt{\hbar R^3_k},
\]

where \(R_k\) is the radial vector from the proton \(H^{(n)}\) to the charge \(k\); \(r_k\) is the radial from the center of mass to the particle \(k\); \(q_k\) are the nuclei’ charges; \(B\) is the inverse matrix of inertia moment. \(B\) is a diagonal matrix having the elements \(B_{xx} = 68.0\) GHz, \(B_{yy} = 77.67\) GHz, and \(B_{zz} = 563.9\) GHz. Index \(k\) runs here over all nuclei in the molecule except the proton \(n\).

Using the symmetry operation \(C_2\) one can prove the equality of the two matrix elements,

\[
< \mu | V_{SR}^{(1)}| \mu' > =< \mu | V_{SR}^{(2)}| \mu' >.
\]

Thus for the evaluation of the spin-rotation coupling in formaldehyde it is sufficient to calculate one matrix element, e.g., \(< \mu | V_{SR}^{(1)}| \mu' >\). We write this matrix element using an expansion over symmetric-top states [8],

\[
< \mu | V_{SR}^{(1)}| \mu' > = < I = 1, \sigma \left| \sum_{K,K'} A_K A_{K'} < \alpha, p| V_{SR}^{(1)}| \alpha', p' > \right| I' = 0 > .
\]

This expression and (17) reduce the calculation of the spin-rotation matrix elements of asymmetric tops to the calculation of symmetric-top matrix elements. Solution for the latter can be found in [22,20,23], which allows to express the strength of mixing in formaldehyde by \(\hat{V}_{SR}\) as

\[
F_{SR}(a'|a) = \frac{1}{4} (2J' + 1)(2J + 1) \left| \sum_{K>0,q} A_K A_{K'} \Phi(J, K' + q|J', K') \right|^2 + \frac{1 + (-1)^{J'+p'}}{\sqrt{2}} A_1 A_0 \Phi(J, 1|J', 0).
\]

Here \(q = \pm 1\); In (18) the notation was used
\[ \Phi(J, K|J', K') = \sum_l \sqrt{2l+1} C_{l,q} \begin{pmatrix} J' & l & J \\ -K' & q & K \end{pmatrix} \times \\
\left[ y(J)(-1)^l \begin{pmatrix} J' & J & l \\ 1 & 1 & J \end{pmatrix} + y(J') \begin{pmatrix} J & J' & l \\ 1 & 1 & J' \end{pmatrix} \right] , \] (19)

where (: : :) stands for the 3j-symbol; { : : } stands for the 6j-symbol; \( y(J) = \sqrt{J(J+1)(2J+1)} \); \( C_{l,q} \) are the spherical components of the spin-rotation tensor of the rank \( l \) \((l = 1, 2)\) for the first proton calculated in the molecular frame. \( C_{l,q} \) can be determined using Eq. (16). For the formaldehyde molecular structure from the Ref. [6] and bare nuclei’ charges these components are

\[ C_{2,1} = 3.39 \text{ kHz}; \quad C_{1,1} = -3.39 \text{ kHz}. \] (20)

We stress that these values give an upper limit to the \( C \)-tensor.

The selection rules for the ortho-para mixing by spin-rotation perturbation in formaldehyde read

\[ \Delta p = 0; \quad |\Delta J| \leq 1. \] (21)

Parity of \( K' \) and \( K \) is opposite.

V. CONVERSION RATES

For the calculations of the isomer conversion rate one needs the value of the ortho-para decoherence rate, \( \Gamma \), see Eq. (3). Experimental determination of this parameter can be based on the level-crossing resonances in spin conversion. Such measurements were performed so far only for the \(^{13}\text{CH}_3\text{F} \) spin conversion and gave \( \Gamma/P \approx 2 \cdot 10^8 \text{ s}^{-1}/\text{Torr} \) (see the discussion in [12]). Estimation of \( \Gamma \) can be done using the pressure line broadening data. For polar molecules the line broadening is on the order of \( \sim 10^8 \text{ s}^{-1}/\text{Torr} \). Further, we will assume the decoherence rate being equal to

\[ \Gamma/P = 1 \cdot 10^8 \text{ s}^{-1}/\text{Torr}. \] (22)

The same value of \( \Gamma \) was used in [4].

It is clear from Eq. (3) that only close ortho-para level pairs can contribute significantly to the spin conversion. Formaldehyde is a light molecule having large level spacing. The
average density of levels in the range 0 – 1000 cm\(^{-1}\) is low, 1 level per each 5 cm\(^{-1}\). As was pointed out already in [3], there are regular and “accidental” ortho-para resonances. An example of regular resonances \((p = 0, J, K = 1) \rightarrow (p' = 0, J, K' = 0)\) is shown in Fig. [3]. The ortho-para gaps in this sequence of states goes rapidly down as \(\sim \exp(-0.23J)\). Analogous phenomenon of collapsing ortho and para states exists also in ethylene where decrease of gaps is even faster [8].

Calculated spin conversion rates are given in the Table 2. The total conversion rate combines contributions from all ortho-para level pair having \(J\) up to 40 and \(|\omega| < 40\) GHz. Thus the spin conversion rate in formaldehyde is

\[
\gamma/P = 1.4 \cdot 10^{-4} \text{ s}^{-1}/\text{Torr}.
\]  

One can conclude from the data presented in Table 2 that the close sequence of states from Fig. 3 does not contribute significantly to the conversion. The same effect was found in the ethylene conversion [3]. Another observation from the Table 2 is that there are no close ortho-para level pairs in formaldehyde which can be mixed by the spin-rotation coupling. The most important ortho-para level pair which contributes more than 50% to the total rate is the pair \((1,18,2)\)–\((1,17,3)\). It has the energy gap \(\simeq 6\) GHz. The expansion coefficients, \(A_K\), for these states are presented in Fig. 4. One can see from these data that the wave functions of these states are rather close to the symmetric-top case which would have just one term in the expansion (8).

VI. DISCUSSION AND CONCLUSIONS

Calculated value of the conversion rate in formaldehyde was found to be almost 10 times smaller than the experimental one [4]. There are two main uncertainties in the present calculations which both can be defined more accurately by future experiments. The first uncertainty comes from the decoherence rate, \(\Gamma\). This parameter can be determined by careful study of the pressure broadening of rotational lines in the formaldehyde ground state. The second uncertainty originates from poor knowledge of the spin-rotation coupling in formaldehyde. The spin-rotation coupling in \(\text{H}_2\text{CO}\) can be investigated using high resolution spectroscopy methods, e.g., Laser Stark Spectroscopy [15] and Microwave Fourier
Transform Spectroscopy \cite{16} which were proven to be efficient for the investigation of hyperfine interactions in molecules.

In general, it is difficult to verify the mechanism of spin conversion in formaldehyde by comparing single values of the theoretical and experimental conversion rates, which depends in theory on a number of parameters and in experiment can be resulted from a few effects, e.g., chemical reactions. It is more appropriate to compare the dependencies predicted by the theory with the experimental dependencies. First, the model predicts rather strong dependence of the conversion rate on the type of buffer gas. By varying the collision partner one can change the decoherence rate, $\Gamma$, by nearly one order of magnitude. In the same proportion the spin conversion rate should be changed if conversion is governed by quantum relaxation. It is alarming that the authors \cite{4} observed very small change of $\gamma$ by adding the argon gas up to the pressure of 760 Torr.

Another experimental verification of the conversion mechanism could be the investigation of temperature dependence. The theoretical temperature dependence of the spin conversion rate in formaldehyde is shown in the Fig. \ref{fig:5}. The calculation were done under an assumption that the decoherence rate, $\Gamma$, is temperature independent. Such assumption is supported by the slow temperature dependence of $\Gamma$ observed in the case of spin conversion in $^{13}$CH$_3$F \cite{12}. The theoretical model predicts rather weak influence of the gas temperature on the formaldehyde conversion rate, $\gamma$, in the wide range of temperatures, $T = 200 - 900$ K.

In conclusion, we have developed theoretical model of the spin conversion in formaldehyde. Although this model has the same basic concepts as the model developed in \cite{3}, the key parameters of the new model are more precise. First of all, it refers to the molecular level energies and the wave functions.

We have analysed the relation between the theoretical model of the formaldehyde spin conversion and the experiment \cite{4}. The theoretical model in its present form gives 10 times smaller conversion rate than the rate measured in \cite{4}. Two types of experiments have been proposed which can help to resolve the puzzle.
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Table 1. The character table for the $C_{2v}$ symmetry group and the classification of the basis states (3).

|     | $E$ | $C_2$ | $\sigma_v$ | $\sigma'_v$ | $K$-even | $K=0$ | $K$-odd | Sign |
|-----|-----|-------|------------|------------|----------|--------|---------|------|
| $A_1$ | 1   | 1     | 1          | 1          | $p=0$    | $p=0$  | $J, p$-even | $+$  |
| $B_2$ | 1   | -1    | -1         | 1          | $p=1$    | $p=1$  | $-$      | $-$  |
| $A_2$ | 1   | 1     | -1         | -1         | $p=1$    | $p=1$  | $J, p$-odd | $-$  |
| $B_1$ | 1   | -1    | 1          | -1         | $p=0$    | $p=0$  | $+$      | $+$  |
Table 2. The most important ortho-para levels and their contributions to the spin conversion in formaldehyde.

| Level pair       | Energy | $\omega/2\pi$ | $F_{SR}$ | $\gamma/P$ |
|------------------|--------|---------------|----------|------------|
| $p', J', K'-p, J, K$ (cm$^{-1}$) (MHz) (10$^{-2}$ MHz$^2$) (10$^{-5}$ s$^{-1}$/Torr) |
| 1,18,2–1,17,3    | 445.87 | -6162         | 6.59     | 7.56       |
| 0,8,2–0,9,1      | 120.93 | 9252          | 0.98     | 2.38       |
| 1,21,4–1,22,3    | 692.52 | -10379        | 12.5     | 1.55       |
| 0,13,2–0,14,1    | 253.82 | 17211         | 2.45     | 0.91       |
| 1,12,2–1,13,1    | 221.18 | -19305        | 2.01     | 0.69       |
| Total rate       | 14.0   |               |          |            |
FIG. 1. Ortho and para states of formaldehyde (H$_2$CO). The levels are calculated using the molecular parameters from Ref. [7]. Bent lines indicate transitions inside the ortho and para subspaces induced by collisions. The level pair most important for the spin conversion in formaldehyde is shown to be mixed by intramolecular perturbation $V$. 
FIG. 2. Formaldehyde molecule, $H_2CO$, and orientation of the molecular system of coordinates.
FIG. 3. Frequency gaps in the regular sequence of close ortho ($p = 0, J, K = 1$) and para $p' = 0, J, K' = 0$ states in formaldehyde.
FIG. 4. The expansion coefficients, $A_K$, for the states most important for the spin conversion in $H_2CO$. (o)–ortho state ($1, J = 17, K = 3$); (●)–para state ($1, J' = 18, K' = 2$).
FIG. 5. Temperature dependence of the total spin conversion rate in formaldehyde.