Ortho-Para Conversion in CH$_3$F.
Self–Consistent Theoretical Model*

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Abstract

A complete theoretical model of the nuclear spin conversion in $^{13}$CH$_3$F induced by intramolecular ortho-para state mixing is proposed. The model contains parameters determined from the level-crossing spectra of the $^{13}$CH$_3$F spin conversion. This set of parameters includes the ortho-para decoherence rate, the magnitude of the hyperfine spin-spin interaction between the molecular nuclei and the energy gap between the mixed ortho and para states. These parameters are found to be in a good agreement with their theoretical estimates.

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I. INTRODUCTION

The study of nuclear spin isomers of molecules was started by the discovery of the ortho and para hydrogen in the late 1920’s [1]. It became clear already in that time that many other symmetrical molecules should have nuclear spin isomers too. Nevertheless, their investigation has been postponed by almost 60 years. The reason for this delay was severe difficulties in the enrichment of spin isomers. The situation is improving now (see the review in Ref. [2]) but yet we are at the very early stage of this research: in addition to the well-known spin isomers of H₂ only a few molecules have been investigated so far. Among them, the CH₃F nuclear spin isomers occupy a special place being the most studied and understood.

The conversion of CH₃F nuclear spin isomers has been explained [3,4] in the framework of quantum relaxation [5], which is based on the intramolecular ortho-para state mixing and on the interruption of this mixing by collisions. This mechanism of spin conversion has a few striking features. The nuclear spin states of CH₃F appeared to be extremely stable surviving $10^9 - 10^{10}$ collisions. Each of the collision changes the energy of the molecule by $10 - 100 \text{ cm}^{-1}$ and shuffles the molecular rotational state substantially. Nevertheless, the model predicts that the spin conversion is governed by tiny intramolecular interactions having the energy $\sim 10^{-6} \text{ cm}^{-1}$.

Under these circumstances, the validity of the proposed theoretical model should be checked with great care. This is especially important because the CH₃F case gives us the first evidence of the new mechanism behind the nuclear spin conversion in molecules. Hydrogen spin conversion, which is the only other comprehensively studied case, is due to the completely different process based on direct collisional transitions between ortho and para states of H₂.

Presently there is substantial amount of the experimental data on CH₃F isomer conversion (see [2] and references therein). Theory and experiment on the CH₃F isomer conversion were compared in a number of papers but these comparisons were never aimed to determine a complete set of parameters necessary for a quantitative description of the process. The purpose of the present paper is to construct such self-consistent theoretical model of the CH₃F isomer conversion.
II. QUANTUM RELAXATION

The CH$_3$F molecule is a symmetric top having the C$_{3v}$ symmetry. The total spin of the three hydrogen nuclei in the molecule can be equal to $I = 3/2$ (ortho isomers), or $I = 1/2$ (para isomers). The values of the molecular angular momentum projection on the molecular symmetry axis ($K$) are specific for these spin isomers. Only $K$ divisible by 3 are allowed for the ortho isomers. All other $K$ are allowed for the para isomers. Consequently, the rotational states of CH$_3$F form two subspaces which are shown in Fig. 1 for the particular case of the $^{13}$CH$_3$F molecules.

Let us briefly recall the physical picture of the CH$_3$F spin conversion by quantum relaxation. Suppose that a test molecule was placed initially in the ortho subspace of the molecular states (Fig. 1). Due to collisions in the bulk the test molecule will undergo fast rotational relaxation inside the ortho subspace. This running up and down along the ortho ladder proceeds until the molecule reaches the ortho state $m$ which is mixed with the para state $n$ by the intramolecular perturbation $\hat{V}$. Then, during the free flight just after this collision, the perturbation $\hat{V}$ mixes the para state $n$ with the ortho state $m$. Consequently, the next collision is able to move the molecule to other para states and thus to localize it inside the para subspace. Such mechanism of spin isomer conversion was proposed in the theoretical paper [6].

The quantum relaxation of spin isomers can be quantitatively described in the framework of the kinetic equation for density matrix [3]. Let us consider first a free molecule which is not subjected to an external field. One needs to split the molecular Hamiltonian into two parts

$$\hat{H} = \hat{H}_0 + h\hat{V},$$

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. In the first order perturbation theory the nuclear spin conversion rate, $\gamma$, is given by

$$\gamma = \sum_{\alpha' \in p, \alpha \in o} \frac{2\Gamma_{\alpha'\alpha}|V_{\alpha'\alpha}|^2}{\Gamma^2_{\alpha'\alpha} + \omega^2_{\alpha'\alpha}} (W_p(\alpha') + W_o(\alpha)),$$
where $\Gamma_{\alpha'\alpha}$ is the decay rate of the off-diagonal density matrix element $\rho_{\alpha'\alpha}$ ($\alpha' \in \text{para}; \ \alpha \in \text{ortho}$); $\hbar \omega_{\alpha'\alpha}$ is the energy gap between the states $\alpha'$ and $\alpha$; $W_p(\alpha')$ and $W_o(\alpha)$ are the Boltzmann factors of the corresponding states. The parameters $\Gamma_{\alpha'\alpha}$, $V_{\alpha'\alpha}$, and $\omega_{\alpha'\alpha}$ are crucial for the quantitative theoretical description of the $^{13}$CH$_3$F spin isomer conversion.

All previous comparisons between the experiment on the CH$_3$F spin conversion and the theory were performed using “total” rates of conversion which summarize all contributions to the rate from many ortho-para level pairs. The “total” rate is just a single number and obviously cannot provide unambiguous determination of all parameters which are present in the expression (2). One may combine the experimental data on “total” rates with theoretical calculations of some parameters but it is not easy. In this case one has to perform extensive calculations of the intramolecular ortho-para state mixing. Even more difficult is to calculate the decoherence rates $\Gamma_{\alpha'\alpha}$. Consequently, development of the self-consistent model of the nuclear spin conversion in which all parameters are unambiguously determined should be based on a different approach.

### III. LEVEL–CROSSING RESONANCES

Theoretical model of spin conversion predicts strong dependence of the conversion rate, $\gamma$, on the level spacing $\omega_{\alpha'\alpha}$ (see Eq. (2)). This can be used to single out the contribution to the conversion from each level pair which should substantially simplify the quantitative comparison between theory and experiment. It was proposed in [7] and performed in [8] to use the Stark effect for crossing the ortho and para states of CH$_3$F. These crossings result in sharp increase of the conversion rate $\gamma$ giving the conversion spectra if electric field is varied.

The experimental data [8] are presented in Fig. 2. It is evident that such spectrum contains much more information than the ”total” conversion rate which is just a single number.

Comparison of the conversion spectrum in Fig. 2 with the theory needs a modification of the model in order to incorporate the Stark effect. Homogeneous electric field lifts partially the degeneracy of the $\alpha$-states of CH$_3$F (see Appendix). The new states, $\mu$-basis, can be found in a standard way [9]:

$$|\mu > \equiv |\beta, \xi > |\sigma_F > |\sigma_C >; \ \xi = 0, 1.$$  \hspace{1cm} (3)
Because electric field in the experiment is relatively small, it is sufficient to consider only diagonal matrix elements of the Stark perturbation over angular momentum $J$ when calculating the $\mu$-states. Energy of the $\mu$-states are given by the expression

$$E(\mu) = E_{\text{free}}(J, K) + (-1)^\xi \frac{K|\mathbf{M}|}{J(J+1)}|d|E|,$$

where $E_{\text{free}}(J, K)$ is the energy of free molecule; $d$ is the molecular permanent electric dipole moment; $E$ is the electric field strength. The new states are still degenerate with respect to the spin projections $\sigma$, $\sigma_F$, and $\sigma_C$, and to the sign of $M$. An account of the Stark effect in the spin conversion model is straightforward. Eq. (2) should be rewritten in the $\mu$-basis with the level energies determined by the Eq. (4).

## IV. FITTING OF THE EXPERIMENTAL DATA

Nuclear spin conversion in $^{13}$CH$_3$F at zero electric field is governed almost completely by mixing of only two level pairs $(J'=11, K'=1)$–$(J=9, K=3)$ and $(21,1)$–$(20,3)$ [4,10]. The spectrum presented in Fig. 2 is produced by crossings of the $M$-sublevels of the para $(11,1)$ and ortho $(9,3)$ states. This pair of states is mixed by the spin-spin interaction between the molecular nuclei [4]. There is no contribution to the mixing of this level pair from the spin-rotation interaction because of the selection rule for spin-rotation interaction $|\Delta J| \leq 1$ [11]. This is fortunate because the spin-spin interaction can be calculated rather accurately. Contrary to that, the spin-rotation interaction in CH$_3$F is known only approximately. For more details on spin-rotation contribution to the CH$_3$F spin conversion see Refs. [11–15]

The second pair of ortho-para states $(21,1)$–$(20,3)$, which is also important for the spin conversion in $^{13}$CH$_3$F at zero electric field, is mixed by both the spin-spin and spin-rotation interactions. The magnitude of the latter is presently unknown. Nevertheless, it does not complicate the fitting procedure because in the vicinity of the $(11,1)$–$(9,3)$ resonances presented in Fig. 2 the $(21,1)$–$(20,3)$ pair gives very small and almost constant contribution.

Let us find out now an analytical expression for modelling the experimental data. We start by analyzing the contribution to the conversion rate produced by the level pair $(11,1)$–$(9,3)$ which will be denoted as $\gamma_a(E)$. This contribution can be obtained using the results of Refs. [4,7]:
\[
\gamma_a(\mathcal{E}) = \sum_{M' \in \mathcal{P}; M \in \mathcal{O}} \frac{2\Gamma|V_{M'M}|^2}{\Gamma^2 + \omega_{M'M}^2(\mathcal{E})} (W_p(\mu') + W_o(\mu));
\]

\[
|V_{M'M}|^2 = (2J + 1)(2J' + 1) \begin{pmatrix} J' & J & 2 \\ -K' & K & K' - K \end{pmatrix} \begin{pmatrix} J' & J & 2 \\ -M' & M & M' - M \end{pmatrix}^2 \mathcal{T}^2.
\]

Here \(V_{M'M} \equiv <\mu'|V|\mu>\) are the matrix elements of the perturbation \(\hat{V}\) in which only \(M\)-indexes were shown explicitly; (\(:::\)) stands for the 3j-symbol; \(\mathcal{T}\) is the magnitude of the spin-spin interaction. Note, that the selection rules for the ortho-para state mixing by the spin-spin interaction result from Eq. (5): \(|\Delta K|; |\Delta J|; |\Delta M| \leq 2\). In the fitting procedure \(\mathcal{T}\) will be considered as an adjustable parameter. In Eq. (5) we have assumed all \(\Gamma_{M'M}\) being equal: \(\Gamma_{M'M} \equiv \Gamma\). This property of \(\Gamma\) is the consequence of the spherical symmetry of the media. The decoherence decay rate \(\Gamma\) is another unknown parameter which needs to be determined.

The spacing between the \(M'\) and \(M\) states in an electric field follows directly from the Eq. (4)

\[
\omega_{M'M}(\mathcal{E}) = \omega_0 + \left( \frac{K'|M'|}{J'(J' + 1)} - \frac{K|M|}{J(J + 1)} \right) |d\mathcal{E}|,
\]

where \(\omega_0\) is the gap between the states \((J',K')\) and \((J,K)\) at zero electric field. We have considered in Eq. (5) only pairs of states which have \(\xi' = \xi\). They are the only pairs which contribute to the spectrum in the electric field range of Fig. 2. The level spacing \(\omega_0\) will be considered as an adjustable parameter in the fitting. The dipole moment of \(^{13}\text{CH}_3\text{F}\) in the ground state, which is necessary for the calculation of \(\omega_{M'M}(\mathcal{E})\), was determined very accurately from the laser Stark spectroscopy of \(^{13}\text{CH}_3\text{F}\) and was found equal \(d = 1.8579 \pm 0.0006\) D [16].

At zero electric field the level pair (21,1)–(20,3) contributes nearly 30% to the total conversion rate [10]. At electric fields, where \(\gamma_a(\mathcal{E})\) has peaks, this contribution is on the order of \(10^{-2}\) in comparison with \(\gamma_a(\mathcal{E})\). The first crossing of the pair (21,1)-(20,3) occurs at \(\simeq 4000\) V/cm thus having its peaks far away from the electric field range of Fig. [3]. In the electric field range of Fig. 4 (1–1200 V/cm) the contribution from the pair (21,1)-(20,3) is changing by 10% only. Consequently, in the fitting procedure the (21,1)-(20,3) contribution is assumed to be constant. This quantity will be denoted as \(\gamma_b\).
To summarize, the function which will be used to model the experimental data is

\[ \gamma(E) = \gamma_a(E) + \gamma_b. \]  

(7)

This function contains adjustable parameters \( T, \Gamma, \omega_0, \) and \( \gamma_b. \)

The result of the least-square fit is shown in Fig. 2 by solid line. The error of the individual experimental points in Fig. 2 was estimated as 7%. The values of the parameters are given in the Table 1, where one standard deviation of statistical error is indicated.

Electric field in the Stark cell was determined in experiment [8] by measuring the voltage applied to the electrodes and assuming the distance between them equal to 4.18 mm, which is the spacer thickness. It was found out after the experiment [8] was performed that the thickness of the glue used to attach the Stark electrodes was not negligible. The updated spacing between the electrodes in the Stark cell is \( l = 4.22 \pm 0.02 \) mm. Such correction of the spacing gives 1% systematic decrease of the experimental electric field values given in [8]. This shift is taken into account in Fig. 2.

V. THEORETICAL ESTIMATION OF THE PARAMETERS

Let us compare the parameters obtained in the previous section with their theoretical estimates. We start from the analysis of the level spacing \( \omega_0. \) The best sets of the ground state molecular parameters of \(^{13}\text{CH}_3\text{F}\) are given in Ref. [17]. The spacing between the levels (11,1) and (9,3) is presented in the Table 1 where the set having most accurate molecular parameter \( A_0 \) was used. The theoretical value appears to be close to the experimental one obtained from the spin conversion spectra. The difference between them is

\[ \omega_0(\text{exp}) - \omega_0(\text{theor}) = 1.0 \pm 0.3 \text{ MHz}, \]  

(8)

which is less than 1% in comparison with \( \omega_0 \) itself.

Next, we calculate the parameter \( T \) which characterizes the spin-spin mixing of the level pair (11,1)–(9,3) in \(^{13}\text{CH}_3\text{F}\). The spin-spin interaction between the two magnetic dipoles \( \mathbf{m}_1 \) and \( \mathbf{m}_2 \) separated by the distance \( r \) has the form [9]:

\[ \hbar \hat{V}_{12} = P_{12} \hat{I}^{(1)} \cdot \hat{I}^{(2)} \cdot \mathbf{T}^{(12)}, \]

\[ T_{ij}^{(12)} = \delta_{ij} - 3n_in_j; \quad P_{12} = m_1m_2/r^3I^{(1)}I^{(2)}, \]  

(9)
where $\hat{I}^{(1)}$ and $\hat{I}^{(2)}$ are the spin operators of the particles 1 and 2, respectively; $\mathbf{n}$ is the unit vector directed along $\mathbf{r}$; $i$ and $j$ are the Cartesian indexes.

For the spin-spin mixing of the ortho and para states in $^{13}$CH$_3$F one has to take into account the interaction between the three hydrogen nuclei ($\hat{V}_{HH}$), between the three hydrogen and fluorine nuclei ($\hat{V}_{HF}$), and between the three hydrogen and carbon nuclei ($\hat{H}_{HC}$). Thus the total spin-spin interaction responsible for the mixing in $^{13}$CH$_3$F is

$$\hat{V}_{SS} = \hat{V}_{HH} + \hat{V}_{HF} + \hat{V}_{HC}. \quad (10)$$

The complete expressions for all components of $\hat{V}_{SS}$ can be written by using Eq. (9) for the spin-spin interaction between two particles. For example, for $\hat{V}_{HF}$ one has

$$\hat{V}_{HF} = P_{HF} \sum_n \hat{I}^{(n)} \hat{I}^F \cdot T_{nF}; \quad n = 1, 2, 3. \quad (11)$$

Here $P_{HF}$ is the scaling factor analogous to $P_{12}$ in Eq. (9); $n$ refers to the hydrogen nuclei in the molecule.

$\mathbf{T}$ can be calculated in a way similar to that used previously [4]. It gives

$$|\mathbf{T}|^2 = 3|P_{HH} T^{(12)}_{2,2}|^2 + 2|P_{HF} T^{1F}_{2,2}|^2 + 2|P_{HC} T^{1C}_{2,2}|^2. \quad (12)$$

Here $T^{1q}_{2,2}$ is the spherical component of the second rank tensor $\mathbf{T}^{1q}$ calculated in the molecular system of coordinates. The superscripts $1q$ indicate the interacting particles: 1 refers to the hydrogen nucleus H$^{(1)}$ and $q$ refers to the nucleus of H$^{(2)}$, or F, or C.

The calculation of $\mathbf{T}$ needs the knowledge of the molecular structure. We used the ground state structure of $^{13}$CH$_3$F determined in [18,19]: $r_{CF} = 1.390(1)$ Å, $r_{CH} = 1.098(1)$ Å, and $\beta(\mathbf{F} - \mathbf{C} - \mathbf{H}) = 108.7^o(2)$. The numbers in parentheses represent the error bars in units of the last digit. By using these parameters one can obtain the value of $\mathbf{T}$ which is given in the Table 1. The difference between the experimental and theoretical values of $\mathbf{T}$ is equal to

$$T_{exp} - T_{theor} = -5.1 \pm 0.5 \text{ kHz}. \quad (13)$$
VI. DISCUSSION

Small difference between the experimental and theoretical values of $\omega_0$ unambiguously confirms that the mixed ortho-para level pair (9,3)–(11,1) was determined correctly. From the spectroscopical data [17] one can conclude that there are no other ortho-para level pairs which can mimic the level spacing $\omega_0 = 130.99$ MHz. It is also true if one takes into account even all ortho-para level pairs ignoring the restrictions imposed by the selection rules for the ortho-para state mixing.

The difference between experimental and theoretical values of the level spacing at zero electric field, $\omega_0$, is only $1.0 \pm 0.3$ MHz. The main error in theoretical value of $\omega_0$ is caused by the error in the molecular parameter $A_0$. It gives nearly half of the error indicated in the Table 1. On the other hand, the $J$ and $K$ dependences of the molecular electric dipole moment are too small [16] to affect our determination of the theoretical value of $\omega_0$. It is possible that the experimental value of $\omega_0$ is affected by the pressure shift, which magnitude we presently do not know. Further investigations can precise the frequency gap between the states (9,3) and (11,1).

The difference between the experimental and theoretical values of $T$ is rather small ($\approx 7\%$) but well outside the statistical error. This difference may originate from our method of calculating $T_{\parallel\parallel}$ in which we used the molecular structure (bond lengths and angles) averaged over ground state molecular vibration. More correct procedure would be to average an exact expression for $T$ over molecular vibration. This requires rather extensive calculations.

There are a few contributions to the systematic error of value of $T_{\parallel\perp}$. The response time of the setup used to measure the concentration of ortho molecules ($\approx 1$ sec) was not taken into account in the processing of the experimental data. This gives $\approx 2\%$ systematic decrease in the value of $T_{\parallel\perp}$. Another few percent of the systematic error may appear due to the procedure employed in [8] to find out the conversion rate inside the Stark cell. This procedure relies on the ratio of the Stark cell volume to the volume outside the electric field. Taking these circumstances into account we can estimate that up to $\approx 10\%$ difference between the experimental and theoretical values of $T$ can be explained by the systematic errors. Despite this difference, it is rather safe to conclude that our analysis has proven
that the levels (9,3) and (11,1) are indeed mixed by the spin-spin interaction between the molecular nuclei. It is impressive that the level-crossing spectrum in the $^{13}$CH$_3$F isomer conversion has allowed to measure the hyperfine spin-spin coupling with the statistical error of 0.5 kHz only.

Comparison between the measured spectrum and the model supports our choice for the $\Gamma_{M'M}$ being independent on $M$ and $M'$. Independence of this parameter on $M$ is the direct consequence of the spatial isotropy of the media. The independence on $M' - M$ is more intricate. This will be discussed in more detail elsewhere.

The value of $\Gamma$ obtained from the fitting procedure, $\Gamma = (1.9 \pm 0.1) \cdot 10^8 \text{ s}^{-1}/\text{Torr}$, appeared to be close to the level population decay rate $1.0 \cdot 10^8 \text{ s}^{-1}/\text{Torr}$ measured in Ref. [20] for the state $(J=5, K=3)$ of $^{13}$CH$_3$F. The factor 2 difference is not surprising. $\Gamma$ refers to the decay rate of the off-diagonal density matrix element $\rho_{\mu'\mu}$ between the states (11,1) and (9,3) which should be different from the population decay rate. In addition, the rotational quantum numbers in these two cases are different too.

Column designated as $\gamma(0)$ in the Table 1 gives the rates at zero electric filed. The “theoretical value” is the magnitude of $\gamma(0)$ given by the solid line in Fig. 2. The theoretical value coincides well with the experimental one from Ref. [21]. Finally we would like to mention that our analysis of the spin conversion spectrum has allowed to disentangle for the first time the contributions to the conversion rate which arise from the mixing of the two level pairs: (9,3)–(11,1) and (20,3)–(21,1).

VII. CONCLUSIONS

We have performed the first quantitative comparison of the level-crossing spectrum of the nuclear spin conversion in $^{13}$CH$_3$F with the theoretical model. This approach has allowed to single out the contribution to the spin conversion caused by the mixing of one particular pair of the ortho-para rotational states of the molecule and confirmed unambiguously that the mechanism of the intramolecular state mixing is the spin-spin interaction between the molecular nuclei.

All important parameters of the theoretical model which describe the nuclear spin conversion in $^{13}$CH$_3$F due to the spin-spin mixing of the ortho-para level pair (9,3)–(11,1) are
determined quantitatively. These parameters are the decoherence rate, $\Gamma$, the spin-spin mixing strength, $\mathcal{T}$, the level spacing, $\omega_0$, and the contributions to the conversion rate from the two level pairs separately (9,3)-(11,1) and (20,3)-(21,1). While the decoherence rate $\Gamma$ is difficult to estimate on the basis of independent information, the experimental values for the spin-spin mixing, $\mathcal{T}$, and the level spacing, $\omega_0$, are found to be close to their theoretical values. These results prove that the nuclear spin conversion in the $^{13}$CH$_3$F molecules is indeed governed by the quantum relaxation.

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VIII. APPENDIX

The CH$_3$F quantum states in the ground electronic and vibration state can be classified as follows [22–24]. CH$_3$F is a rigid symmetric top but it is more transparent to take molecular inversion into account and classify the states in $D_{3h}$ symmetry group. First, one has to introduce an additional (molecular) system of coordinates which has the orientation defined by the numbered hydrogen nuclei and $z$–axis directed along the molecular symmetry axis.

Next, one introduces the states

$$|\beta > \equiv |J, K, M > |I, \sigma, K >; \; K \geq 0 ,$$

(14)

which are invariant under cyclic permutation of the three hydrogen nuclei: $P_{123}|\beta >= |\beta >$. In Eq. (14), $|J, K, M >$ are the familiar rotational states of symmetric top, which are characterized by the angular momentum ($J$), its projection ($K$) on the $z$-axis of the molecular system of coordinates and the projection ($M$) on the laboratory quantization axis $Z$. $I$ and $\sigma$ are the total spin of the three hydrogen nuclei and its projection on the $Z$-axis, respectively. The explicit expression for the spin states $|I, \sigma, K >$ is given in [22].
Permutation of any two hydrogen nuclei in CH$_3$F inverts $z$-axis of the molecular system of coordinates. Consequently, the action of such operation ($P_{23}$, for instance) on the molecular states reads: $P_{23}|\beta\rangle = |\overline{\beta}\rangle$, where $\overline{\beta} \equiv \{J, -K, M, I, \sigma\}$. Note that the complete set of the molecular states comprises both $\beta$ and $\overline{\beta}$ sets.

Using the states $|\beta\rangle$ and $|\overline{\beta}\rangle$ one can construct the states which have the proper symmetry with respect to the permutation of any two hydrogen nuclei:

$$|\beta, \kappa\rangle = \frac{1}{\sqrt{2}} [1 + (-1)^\kappa P_{23}] |\beta\rangle; \quad \kappa = 0, 1.$$  \hspace{1cm} (15)

The action of the permutation of two hydrogen nuclei on the state $|\beta, \kappa\rangle$ is defined by the rule: $P_{23}|\beta, \kappa\rangle = (-1)^\kappa |\beta, \kappa\rangle$ and by similar relations for the permutations of the other two pairs of hydrogen nuclei.

In the next step, one has to take into account the symmetric ($|s = 1\rangle$) and antisymmetric ($|s = 0\rangle$) inversion states. The action of the permutation of the two hydrogen nuclei on these states, for example $P_{23}$, reads

$$P_{23}|s = 0\rangle = -|s = 0\rangle; \quad P_{23}|s = 1\rangle = |s = 1\rangle.$$  \hspace{1cm} (16)

Evidently, the cyclic permutation of the three hydrogen nuclei of the molecule does not change the inversion states.

The total spin-rotation states of CH$_3$F should be antisymmetric under permutation of any two hydrogen nuclei, because protons are fermions. Consequently, the only allowed states of CH$_3$F are $|\beta, \kappa = s\rangle |s\rangle$.

Finally, the description of the CH$_3$F states should be completed by adding the spin states of fluorine and carbon ($^{13}$C) nuclei, both having spin equal 1/2:

$$|\alpha\rangle = |\beta, \kappa = s\rangle |s\rangle |\sigma_F\rangle |\sigma_C\rangle,$$  \hspace{1cm} (17)

where $\sigma_F$ and $\sigma_C$ are the Z-projections of the F and $^{13}$C nuclei’ spins, respectively. In the following, we will denote the states [17] of a free molecule as $\alpha$-basis. For the rigid symmetric tops, as CH$_3$F is, the states $|\alpha\rangle$ are degenerate over the quantum numbers $s$, $M$, $\sigma$, $\sigma_F$, $\sigma_C$. 

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Table 1. Experimental and theoretical parameters of the nuclear spin conversion in $^{13}$CH$_3$F by quantum relaxation.

|       | $\omega_0/2\pi$ (MHz) | $\mathcal{T}$ (kHz) | $\Gamma$ (10$^8$ s$^{-1}$/Torr) | $\gamma(0)$ (10$^{-3}$ s$^{-1}$/Torr) | $\gamma_b$ (10$^{-3}$ s$^{-1}$/Torr) |
|-------|------------------------|---------------------|---------------------------------|--------------------------------------|----------------------------------|
| **Experiment** | 132.06 ± 0.27 | 64.1 ± 0.5 | 1.9 ± 0.1 | 12.2 ± 0.6$^{(4)}$ | 4.6 ± 0.7 |
| **Theory** | 130.99 ± 0.15$^{(1)}$ | 69.2 ± 0.2$^{(2)}$ | 1.0$^{(3)}$ | 12.04 ± 0.5$^{(5)}$ | – |
| **Difference** | 1.0 ± 0.3 | -5.1 ± 0.5 | – | 0.15 ± 0.8 | – |

$^{(1)}$Calculated using the molecular parameters from Ref. [17], (Table 1, column 2).

$^{(2)}$Calculated using the molecular structure determined in Ref. [18,19].

$^{(3)}$The level population decay rate from Ref. [20].

$^{(4)}$Experimental value from Ref. [21].

$^{(5)}$Zero-field value predicted by the theoretical curve in Fig. 4.
FIG. 1. Ortho and para states of $^{13}$CH$_3$F in the ground vibrational state. The level energies were calculated using the molecular parameters from [17]. The (11,1)–(9,3) pair of states is shown to be mixed by the intramolecular perturbation. The bent lines indicate the rotational relaxation induced by gas collisions. These collisions do not provide direct ortho-para transitions.
FIG. 2. Experimental [8] and theoretical ortho–para conversion spectrum in $^{13}$CH$_3$F.