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Nuclear spin conversion in CH_3F induced by an alternating electric field

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Abstract. The nuclear spin conversion in CH_3F molecules subjected to an alternating electric field was investigated experimentally. The conversion rate was found to be almost unaffected by low electric fields ($\leq$ 200 V/cm) but sharply increased tenfold when the electric field amplitude exceeds the values ($\simeq$ 800 V/cm) sufficiently high to produce crossings of the ortho and para states of the molecule. A theoretical model for the molecular conversion in alternating electric field was developed. The results of the experiment were found to be in a good agreement with the theory.

PACS. 31.30.Gs Hyperfine interactions and isotope effects, Jahn-Teller effect – 32.80.Bx Level crossing and optical pumping – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules

1 Introduction

Conversion of CH_3F nuclear spin isomers (relaxation between molecular ortho and para forms) is governed by the specific mechanism based on the intramolecular hyperfine mixing of ortho and para states and collisional interruption of this mixing. This mechanism of conversion (*quantum relaxation*) was recently confirmed by a few experimental and theoretical results which are reviewed in [1]. This made the role which CH_3F plays in the spin isomer conversion rather unique. CH_3F is the first and so far the only polyatomic molecule in which spin conversion mechanism was identified. Good knowledge of the isomer conversion by quantum relaxation is important because it is likely that similar processes will be found in other molecules when an investigation of their nuclear spin isomers will be carried on.

One of the important experimental test of the CH_3F conversion mechanism was recently performed by observing the level-crossing resonances in the conversion of CH_3F molecules subjected to a permanent electric field [2]. In the present paper we investigate, both experimentally and theoretically, the spin conversion in $^{13}CH_3F$ molecules subjected to an alternating electric field.

There are a few reasons for such a study. First, the level-crossing resonances in spin conversion is a new phenomenon and it is important to study it in a wide range of experimental conditions. Using an alternative electric field instead of a permanent field substantially changes the experimental arrangement. Second, nuclear spin conversion in alternating fields, as soon as it will be well understood, gives the method to influence the spin conversion in time. Another reason is that in some circumstances it is easier or even necessary, to apply an alternating electric field instead of a permanent field, when, for example, internal metal electrodes should be excluded in the system. It is known that metal surfaces can affect the conversion of hydrogen spin isomers [3].

2 Theory of the CH_3F isomer conversion

Let us recall that the CH_3F molecules exist in the form of two nuclear spin isomers [4]. The total spin of the three hydrogen nuclei in the molecule can have the magnitude either $I = 3/2$ (ortho isomers), or $I = 1/2$ (para isomers). Angular momentum projections (K) on the molecular symmetry axis divisible by 3 are allowed only for ortho isomers. For para isomers all other values of K are allowed.

It is useful to start with the essence of the CH_3F isomer conversion. Quantum states of CH_3F are divided into two subspaces, which are the ortho and para states (Fig. 1). Suppose that at the instant $t = 0$ a test molecule is placed into the ortho subspace. Due to collisions with surrounding gas particles, the test molecule starts to perform fast migration along rotational states inside the ortho subspace. This is the familiar rotational relaxation. This running up and down along the ladder of the ortho states continues until the molecule jumps in the state m

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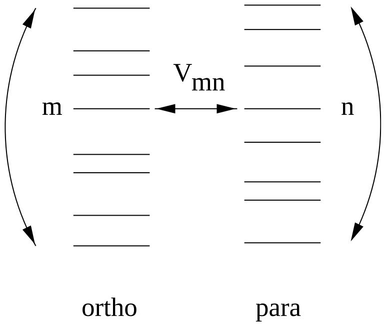

Fig. 1. Schematic of the ortho and para states of CH_3F. Only one pair of ortho and para states is shown to be mixed by intramolecular perturbation V. Bent lines indicate the transitions inside the ortho and para subspaces induced by the collisions with the surrounding particles.

which is mixed by an *intramolecular* perturbation with the energetically close para state n. During the free flight after this collision, para state n will be admixed to the ortho state m. Consequently, the next collision can transfer the molecule in other para states and thus localizes it inside the para subspace. Such a mechanism of spin isomers conversion was proposed in the theoretical work by Curl *et al.* [5] (see also [6]).

The picture given above is for the spin conversion of free molecule. Isomer conversion induced by a permanent electric field is essentially the same. One has to take into account the splitting of the molecular states due to the Stark perturbation. The isomer conversion induced by a time dependent perturbation is more complicated. In this case level energies and spin conversion itself are both time dependent.

2.1 Stark splitting of molecular states

When an external alternating electric field $\mathcal{E}_0 \cos \varOmega t$ is applied to the molecule, the following Stark perturbation term arises,

$$\hat{V}_{\mathrm{St}} = -\hat{\mathbf{d}}\mathcal{E}_0 \cos \varOmega t, \tag{1}$$

where $\hat{\mathbf{d}}$ is the molecular electric dipole moment operator; $\mathcal{E}_0$ is the amplitude of the electric field and $\varOmega$ is the frequency of the Stark modulation. Perturbation (1) introduces to the spin conversion an additional time dependence which has not been analysed so far.

Let us divide the molecular Hamiltonian into three parts

$$\hat{H} = \hat{H}_0 + \hat{V}_{\mathrm{St}} + \hat{V}. \tag{2}$$

Here $\hat{H}_0$ is the main part of the Hamiltonian of the free molecule which has ortho and para molecular states as the eigenstates; $\hat{V}$ is the small part of the molecular Hamiltonian which mixes the ortho and para states of the molecule.

We start by considering the eigen states of the molecule subjected to an electric field and ignoring the small perturbation $\hat{V}$ in (2). The Stark perturbation $\hat{V}_{\mathrm{St}}$ lifts partially the degeneracy of CH_3F states by mixing the states having $|\varDelta s| = 1$; $|\varDelta J| \leq 1$ (see notations of the molecular quantum states in the Appendix). In the following, we will consider relatively weak electric fields which produce the Stark shift on the order of ~ 1 GHz being much smaller than the J-splitting (~ 500 GHz). Consequently, the Stark mixing of states having $|\varDelta J| = 1$ can be neglected.

In a standard way [4], by solving the Schrödinger equation for double degenerate states $|\alpha_0\rangle$ and $|\alpha_1\rangle$, one can find the new eigen states of the Hamiltonian $\hat{H}_0 + \hat{V}_{\mathrm{St}}$ which accounts now for the Stark perturbation. The new states (μ-basis) are

$$|\mu\rangle \equiv |\alpha, \xi\rangle = \frac{1}{\sqrt{2}}[|\alpha_0\rangle - (-1)^{\xi}|\alpha_1\rangle] \times \mathrm{e}^{-\mathrm{i}(R_\mu \varOmega^{-1} \sin \varOmega t + E_\alpha t)}; \quad \xi = 0, 1. \tag{3}$$

Here $\hbar E_\alpha$ is the energy of free molecule in the degenerate α-state; ξ is the quantum number of the new molecular states; $\hbar R_\mu = (-1)^{\xi}\mathcal{E}_0|\langle\alpha_0|\hat{d}|\alpha_1\rangle|$ gives the Stark shift of the molecular energy.

2.2 Kinetic equation and the first order solution

Let us turn now to the problem of isomer conversion itself. Conversion is described by the kinetic equation for the density matrix, which has the following form in the μ-basis

$$\frac{\partial \rho_{\mu\mu_1}}{\partial t} = S_{\mu\mu_1} - \mathrm{i}\,[\hat{V}, \rho]_{\mu\mu_1}. \tag{4}$$

Here $S_{\mu\mu_1}$ is the collision integral.

In the experiment we are interested in the dynamics of the total concentration of one isomer species, *e.g.*, ortho, $\rho_{\mathrm{o}} = \sum_{\mu \in \mathrm{ortho}} \rho_{\mu\mu}$. Equation of motion for this quantity can be obtained directly from the equation (4)

$$\frac{\partial \rho_{\mathrm{o}}}{\partial t} = 2\,\mathrm{Re} \sum_{\mu \in \mathrm{o}, \mu' \in \mathrm{p}} \mathrm{i}\rho_{\mu\mu'} V_{\mu'\mu}. \tag{5}$$

This equation was obtained assuming that the collisions cannot provide the ortho-para transitions in the molecule directly (for more details see [6]).

To proceed further with equation (5), we need to know the off-diagonal density matrix elements. These elements are affected, in general, by the time dependence of the external perturbation. On the other hand this dependence is insignificant if the time scale of the perturbation evolution, which is given by $\varOmega$ in our case, is relatively slow: $\varOmega \ll \varGamma$, where $\varGamma$ is the decay rate of the off-diagonal matrix element. In the present experiment this condition for the quasi-stationary description is fulfilled (see next section). Thus, the calculation of the off-diagonal matrix element $\rho_{\mu\mu'}$ can be done in the first order perturbation theory similar to [6]. This brings us to the equation which describes the isomer conversion

$$\frac{\partial \rho_{\mathrm{o}}}{\partial t} = -\sum_{\mu\in \mathrm{o},\mu'\in \mathrm{p}} \gamma_{\mu\mu'}[\rho_{\mathrm{o}} - N W_{\mu'}(W_\mu+W_{\mu'})^{-1}];$$

$$\gamma_{\mu\mu'} = \frac{2\Gamma|V_{\mu\mu'}|^2(W_\mu+W_{\mu'})}{\Gamma^2+(\omega_{\alpha\alpha'}+(R_\mu-R_{\mu'})\cos\Omega t)^2}\,. \qquad (6)$$

Here N is the total concentration of $^{13}CH_3F$ molecules; $\hbar\omega_{\alpha\alpha'}$ is the energy gap between the states α and α' of free molecule. W_μ is the Boltzmann factor of the molecular state $|\mu\rangle$.

In the equation (6) only the ortho-para level pairs having very small energy gaps of the order of $\hbar\Gamma$ are important for the spin conversion. For such level pairs the ratio of Boltzmann factors $W_{\mu'}(W_\mu+W_{\mu'})^{-1} \simeq 1/2$. Using this approximation one can solve equation (6) by representing the concentration of ortho molecules as $\rho_{\mathrm{o}} = N/2+\delta\rho_{\mathrm{o}}(t)$. Consequently, the nonequilibrium part of the concentration of ortho molecules, $\delta\rho_{\mathrm{o}}(0)$, created at the instant $t=0$, will relax as

$$\delta\rho_{\mathrm{o}}(t) = \delta\rho_{\mathrm{o}}(0)\exp\left[-\int_0^t \sum_{\mu\in \mathrm{o},\mu'\in \mathrm{p}} \gamma_{\mu\mu'}\mathrm{d}t\right]. \qquad (7)$$

This dynamics of the spin conversion appears to be rather complicated. On the other hand, it is simpler in the time range $t \gg \Omega^{-1}$. For these large t the integral in equation (7) grows linearly in time [7] and can be approximated as $\gamma_{\mathrm{St}}t$, where

$$\gamma_{\mathrm{St}} = \frac{1}{T}\int_0^T \sum_{\mu\in \mathrm{o},\mu'\in \mathrm{p}} \gamma_{\mu\mu'}\mathrm{d}t, \qquad (8)$$

and T being the period of the Stark modulation. Consequently, in this limit one has the exponential decay

$$\delta\rho_{\mathrm{o}}(t) = \delta\rho_{\mathrm{o}}(0)\exp(-\gamma_{\mathrm{St}}t); \quad t \gg \Omega^{-1}, \qquad (9)$$

where γ_{St} plays the role of the isomer decay rate induced by the alternating electric field.

2.3 Numerical calculation of the conversion rates

To calculate the conversion rate γ_{St} one needs to know the molecular level spacing $\omega_{\alpha\alpha'}$, the matrix elements of the perturbation $\hat{V}$, the decoherence rate Γ and the Stark splitting of the molecular states. All these data are available from the publications. Below we review the information.

The $^{13}CH_3F$ level energies are analyzed in a few papers. Most precise molecular parameters for the ground state of this molecule are given in [8]. It is shown [6,9] that the mixing of only two ortho-para level pairs is important for the nuclear spin conversion in $^{13}CH_3F$. These level pairs are ($J=9$, $K=3$)–(11, 1), the gap is 131 MHz, and (20, 3)–(21, 1), the gap is 351 MHz. At the electric fields used in our experiment, only crossings arising from the first level pair are essential. The second level pair gives small and almost field independent contribution to the rate.

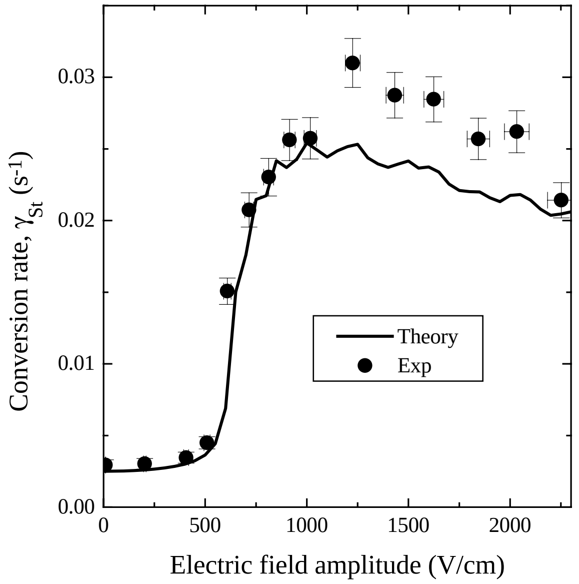

Fig. 2. Experimental and theoretical dependences of the ortho-para conversion in $^{13}CH_3F$ as a function of the electric field amplitude. Gas pressure equals to 0.20 torr. The Stark modulation frequency is 950 Hz.

The pair (9, 3)–(11, 1) is mixed by the spin-spin interaction between the molecular nuclei [6]. Matrix elements $V_{\mu\mu'}$ in μ-basis can be expressed through the matrix elements $V_{\alpha\alpha'}$ in α-basis [6] using the relation between these two bases given by equation (3).

Stark effect in $^{13}CH_3F$ was comprehensively investigated in [10]. This allows to calculate the splitting of the $^{13}CH_3F$ levels with high accuracy. The last parameter needed is the decoherence rate Γ. It was determined in the reference [2] by fitting the $^{13}CH_3F$ conversion rate at zero electric field. In the present numerical calculation we use the value $\Gamma = 1.75\times10^8$ s^{-1}/torr [2].

Numerical calculations of the conversion rate as a function of electric field amplitude are presented in Figure 2. Calculations were done for the gas pressure of 0.20 torr.

3 Experimental setup and results

Like in all previous studies of the CH_3F spin conversion, the light-induced drift effect [11] was used to enrich the spin isomers. The experimental setup is shown in Figure 3 [12]. The enrichment were produced in the separation tube (glass cylinder of 1 mm inner diameter and 1 m long) by a CW radiation of a CO_2-laser (model PL5, Edinburgh Instruments). Power of the laser was 10−15 W. To enrich the spin isomers of $^{13}CH_3F$ molecules the laser was tuned to the P32 line in 9.6 μ band of CO_2. Its frequency was stabilized to the CO_2 line center. The laser radiation is absorbed by R(4, 3) transition from the ν_3 fundamental

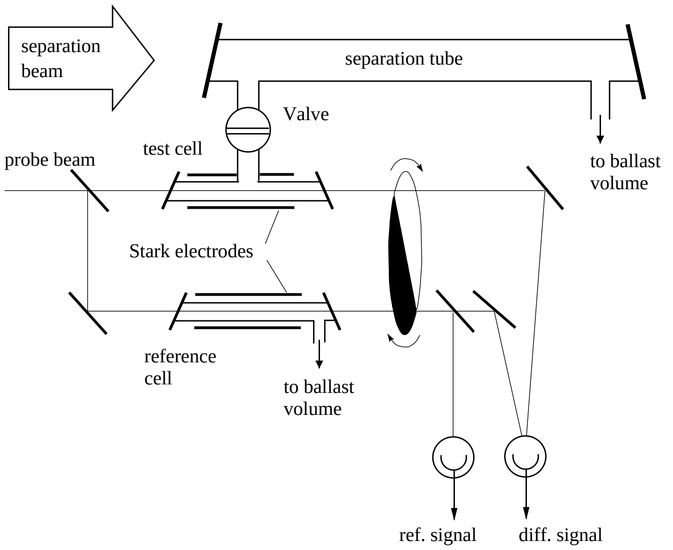

Fig. 3. Schematic of the experimental setup. Rear sides of the separation and reference cells are connected to the same ballast volume.

band of $^{13}CH_3F$. The absorbing molecules are the ortho species.

Electric field was created by Stark electrodes attached outside both the test and the reference cells. These cells were glass cylinders having 3 mm inner diameter and 8 mm outside diameter. The Stark electrodes were driven by a sinusoidal voltage source at the frequency 950 Hz.

Detection of spin isomer concentration was performed with the help of an additional waveguide CO_2-laser tuned to the same 9P32 line as was the separation laser. Its radiation frequency was stabilized to the center of the absorption line of $^{13}CH_3F$. To increase the sensitivity of the detection we used the differential measurements which were performed by comparing the intensities of the two probe beams after the test and reference cells. The two beams were modulated by a chopper in antiphase at the frequency 320 Hz and then directed to the same detector as it is shown in the Figure 3. The differential signal from this detector was measured by a lock-in amplifier. To compensate the instability of the probe beam intensity, the intensity after the reference cell was monitored by additional detector and lock-in amplifier. This reference signal was used to normalize the differential signal.

In our experiment the same volume in both cells was used to measure the concentration of spin isomers and to apply the Stark modulation. It helped us to increase the "ratio of volumes" (see below) and consequently made the measurements more accurate. There were no negative influence of the Stark modulation on differential signal. On the other hand, Stark modulation at high voltages decreases the absorption coefficient up to threefold. This change of the absorption coefficient caused the necessity to apply the Stark modulation to both, test and reference, cells in order to keep the balance of the two channels unchanged.

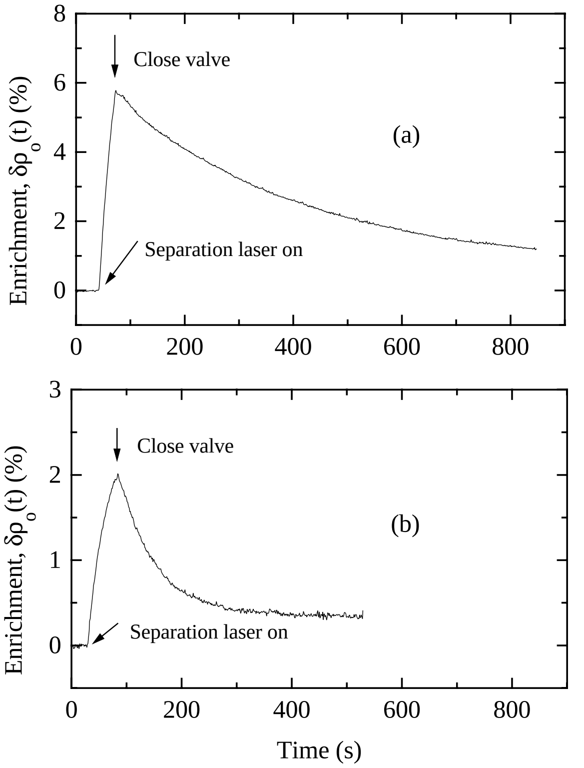

Fig. 4. Examples of the spin conversion in $^{13}CH_3F$. The pressure is 0.20 torr. (a) No electric field applied; (b) electric field amplitude is equal to 1017 V/cm.

Differential and reference signals were digitized by ADCs and stored as data files for further processing. As an example, we show in Figure 4 two records of the enrichment and decay curves for zero and $\mathcal{E}_0 = 1017$ V/cm electric field amplitudes. One can see the large difference between the conversion rates in these two cases.

Decay curves at various Stark modulation amplitudes were fit by the expression $a\exp(-\gamma_{\rm exp}t) + b$ in order to determine the experimental value of the ortho-para conversion rate $\gamma_{\rm exp}$ in the test cell. Constant part in this expression accounts for possible offset in the decay signal. This offset can be caused, for example, by small pressure rise in the test cell due to the light-induced viscous flow effect [13,14].

Conversion rate measured in this way ($\gamma_{\rm exp}$) is not directly the rate induced by the alternating electric field, because the electric field does not fill the volume of the test cell completely. The rate inside the Stark cell ($\gamma_{\rm St}$) was found by the equation [2]

$$\gamma_{\rm St} = \gamma_{\rm exp} + \frac{V_0}{V_{\rm St}}(\gamma_{\rm exp} - \gamma_0), \qquad (10)$$

where V_0 and $V_{\rm St}$ are the volumes outside and inside the Stark field, respectively; γ_0 is the conversion rate at zero Stark field. In our setup the volume ratio was $V_0/V_{\rm St} = 0.98 \pm 0.05$.

Results of the measurements of the spin isomer conversion rate in $^{13}CH_3F$ molecules in alternating electric field at the gas pressure 0.20 torr are presented in Figure 2. As the error bar, we indicate one standard deviation. This includes also the systematic errors which are mainly due to the uncertainty in the ratio $V_0/V_{\rm St}$. The conversion rate at zero electric field was found to be equal $(12.0 \pm 0.6) \times 10^{-3}$ s^{-1}/torr, which is consistent with the rates found in the previous studies [1].

4 Discussion

As it is seen from the Figure 2 the experimental data are rather close to the prediction made by the theory. They both give rates almost constant at low electric field, then a very sharp rise at the same electric field amplitude and a plateau of approximately the same height. We stress that the theoretical curve is not a fit of the present experimental data, but a calculations based on independent parameters.

The dependence of the conversion rate on the electric field amplitude in Figure 3 resembles the dependence measured for a permanent field [2]. This similarity is counterintuitive to some extend because crossings of the ortho-para level pairs take place only during very short time intervals. One may expect a more complicated picture of the spin conversion in this case.

The position of the sharp rise in the curve of the Figure 2 corresponds to the first crossings of the magnetic sublevels of the ortho (9, 3) and para (11, 1) states. The rise of the conversion in the case of alternating field is smaller than in the case of permanent electric field. This can be understood because in alternating field crossing of states takes place during only a fraction of each period of Stark modulation.

Experimental rates at the plateau are $\simeq$ 10% higher than predicted by the theory. This difference can be attributed to the uncertainty of the theoretical curve. Accuracy of the estimation [2] of the decoherence rate Γ is about 10%. Accuracy of the matrix elements of the spin-spin interaction is about 5%. These two factors introduce the main uncertainty to the plateau height of the theoretical curve. Consequently, the difference between experimental and theoretical data at the plateau is too small to be considered significant at the present stage of the theory and experiment. We are going to address this matter in a later study.

Our measurements have shown that Stark effect in alternating electric field can be used to influence the CH_3F conversion in time. It indicates also that care should be taken if a detection method is based on the Stark modulation of the absorption coefficient. Thus an electric field having amplitude below $\sim$ 200 V/cm can be used rather safely, whereas higher fields can substantially affect the CH_3F spin conversion.

5 Conclusion

The measurements of the nuclear spin conversion induced by an alternating electric field have been performed. Similar to the CH_3F spin conversion in permanent field [2], it was found that the conversion rate is significantly increased when the electric field amplitude reaches the value sufficient to cross the ortho and para states of the molecule.

Theoretical model of the CH_3F spin conversion induced by an alternating electric field has been developed. The experimental data were found to be in a good agreement with the calculations in the first order perturbation theory.

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A Appendix

A.1 Stationary molecular states

CH_3F is a rigid symmetric-top molecule which has C_{3v} symmetry. Nevertheless, its quantum states are most transparent to classify by D_{3h} symmetry group taking into account the molecular inversion also. Spin-rotation states in the ground electronic state of CH_3F can be constructed as follows [15,16]. Let us introduce the states which are invariant under cyclic permutation of the three hydrogen nuclei

$$\begin{aligned} |\beta\rangle &\equiv |J,K,M\rangle|I,\sigma,K\rangle, \\ |\overline{\beta}\rangle &\equiv |J,-K,M\rangle|I,\sigma,-K\rangle; \quad K \geq 0. \end{aligned} \tag{A.1}$$

Here $|J,K,M\rangle$ are the usual rotational states of symmetric-top characterized by the angular momentum (J), its projection (K) on the z-axis of the molecular system of coordinates and the angular momentum projection (M) on the quantization Z-axis of laboratory system of coordinates. I and σ are the total spin of the three hydrogen nuclei and its projection on the Z-axis, respectively. The explicit expressions for the spin states $|I,\sigma,K\rangle$ are given in [15]. They specify the allowed K-quantum numbers for the ortho and para spin isomers as explained in Section 2.

Permutation of any two hydrogen nuclei in CH_3F inverts the z-axis of the molecular system of coordinates. Such permutations, *e.g.*, the permutation P_{23}, acts on the state $|\beta\rangle$ as $P_{23}|\beta\rangle = (-1)^J|\overline{\beta}\rangle$. Because the states $|\beta\rangle$ are invariant under cyclic permutation of the three hydrogen nuclei, similar result is valid for the other two permutations of hydrogen pairs: P_{12} and P_{31}.

States $|\beta\rangle$ and $|\overline{\beta}\rangle$ generate two-dimensional representation of the molecular symmetry group. Spin-rotation states, which generate one-dimensional representations are

$$|\beta,\kappa\rangle \;\equiv\; \frac{1}{\sqrt{2}}\left[(-1)^{\kappa}+P_{23}\right]|\beta\rangle;\quad \kappa=0,1. \tag{A.2}$$

The symmetry of states $|\beta,\kappa\rangle$ is determined 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 protons.

Furthermore, one has to take into account the molecular inversion states. Let us designate the antisymmetric and symmetric inversion states of the molecule as $|s=0\rangle$ and $|s=1\rangle$, respectively. Permutation of two protons, *e.g.*, P_{23}, acts on the inversion states as [16]

$$P_{23}|s=0\rangle \;=\; -|s=0\rangle;\quad P_{23}|s=1\rangle \;=\; |s=1\rangle. \tag{A.3}$$

Cyclic permutations of the three hydrogen nuclei in the molecule do not change the inversion states.

The total quantum states of CH_3F have to be antisymmetric under the permutation of any two hydrogen nuclei because protons are fermions. Consequently, the only allowed molecular states are $|\beta,\kappa=s\rangle|s\rangle$.

In the last step one has to take into account the spin states of the fluorine and carbon (^{13}C) nuclei, both having spin 1/2. Finally, the molecular states are

$$|\alpha_s\rangle \;\equiv\; |\beta,\kappa=s\rangle|s\rangle|\sigma^{\mathrm{F}}\rangle|\sigma^{\mathrm{C}}\rangle;\quad s=0,1, \tag{A.4}$$

where σ^{F} and σ^{C} denote, respectively, the projections of the fluorine and carbon nuclear spins on the laboratory quantization Z-axis. The states (A.4) of free molecule will be denoted as α-basis. For rigid symmetric-tops, like CH_3F is, the states $|\alpha_s\rangle$ are degenerate in the quantum numbers M, σ, σ^{F}, σ^{C} and s.

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