PHYSICAL REVIEW A VOLUME 43, NUMBER 7 1 APRIL 1991

CH_3F spin-modification conversion induced by nuclear magnetic dipole-dipole interactions

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(Received 7 May 1990)

A theory has been constructed for the CH_3F molecule's nuclear-spin conversion induced by the intramolecular magnetic dipole-dipole nuclei interaction. It is shown that for $^{13}CH_3F$ molecules this mechanism leads to the rate of spin conversion $(0.71\pm0.2)\times10^{-2}$ s^{-1}/Torr, which is approximately one-half of the experimentally registered value.

I. INTRODUCTION

It was experimentally shown in a previous paper[1] that the conversion of nuclear-spin modifications of the CH_3F molecules (ortho-para conversion) takes place in the gas phase. The CH_3F molecules have in the ground electronic state neither orbital angular nor spin electron momentum, so it is possible to consider the collisions between the CH_3F molecules as nonmagnetic. In accordance with the theoretical model suggested by Curl, Kasper, and Pitzer[2] the conversion of the spin modifications under nonmagnetic collisions can take place if there are intramolecular interactions which provide the mixing of ortho- and paramolecular wave functions. The suggested conversion process, however, has not been experimentally observed yet.

In the CH_3F case we have most probably for the first time an example of the molecular spin conversion in a gas phase. It gives us the possibility of verifying both the theory of conversion induced by mixing of ortho- and paramolecular states[2] and finding new intramolecular interactions. The problem now is to understand whether the intramolecular interactions in the CH_3F provide an efficient mixing of ortho- and paramolecular wave functions or not. In this paper the calculation of the CH_3F nuclear spin conversion induced by magnetic dipole-dipole interaction of the nuclei has been made.

II. CONVERSION UNDER MIXING THE ORTHO- AND PARAMOLECULAR WAVE FUNCTIONS

Different nuclear spin modifications of the CH_3F molecules have different resultant spins of the hydrogen nuclei. The resultant hydrogen spin of the ortho modifications equals $\frac{3}{2}$, while the resultant spin of the para modifications equals $\frac{1}{2}$. The ortho modifications have the quantum number K (projection of the angular momentum on the molecular axis) either divisible by 3 or equal to 0. The para modifications have K nondivisible by 3.

First of all, let us consider the general theory of the ortho-para conversion under wave-function mixing of different molecular spin states. The Hamiltonian of the molecule is taken as a sum of two terms: $H=H_0+\hbar V$, where H_0 is the molecular Hamiltonian, which does not mix the ortho- and paramolecular states, and $\hbar\hat{V}$, which is assumed to be a small perturbation, can mix ortho and para states. The wave functions of the nonperturbed states are characterized by the label α, including both the rotational and spin quantum numbers. The density matrix kinetic equation in the basis of the eigenfunctions of the operator H_0 has the usual form

$$\frac{\partial\rho_{\alpha\alpha_1}}{\partial t}=S_{\alpha\alpha_1}-i\sum_{\alpha'}(V_{\alpha\alpha'}\rho_{\alpha'\alpha_1}-\rho_{\alpha\alpha'}V_{\alpha'\alpha_1})\ , \tag{1}$$

where $S_{\alpha\alpha_1}$ is the collision integral, and the summation over α' is extended to all states of the molecule.

Now, let us calculate the evolution of the total molecular concentration for one of the spin modifications, e.g., orthomolecules ρ_o. For this we sum up Eq. (1) for diagonal elements of the density matrix $\rho_{\alpha\alpha}$ over every ortho state. As a result we have

$$\frac{\partial\rho_o}{\partial t}=2\,\mathrm{Re}\sum_{\substack{\alpha\in o\\ \alpha'\in p}} i\rho_{\alpha\alpha'}V_{\alpha'\alpha},\quad \rho_o=\sum_{\alpha\in o}\rho_{\alpha\alpha}\ . \tag{2}$$

It is indicated here that the summation for the variable α should be done over orthomolecular states, while that for the variable α' over paramolecular states. The relation $\sum_{\alpha\in o}S_{\alpha\alpha}=0$ has been taken into account when deriving Eq. (2). This equality follows from the condition of conservation the number of orthomolecules under nonmagnetic collisions. These collisions themselves do not change the nuclear spin of the molecules, they provide only the transitions between different rotational levels belonging to the same spin modifications.

Equation (2) contains the nondiagonal elements of the density matrix $\rho_{\alpha\alpha'}$. To find $\rho_{\alpha\alpha'}$ one should again use Eq. (1) with $\alpha\in o$, $\alpha'\in p$. In this case $S_{\alpha\alpha'}$ contains only the relaxation term of decay:

$$S_{\alpha\alpha'}=-\Gamma_{\alpha\alpha'}\rho_{\alpha\alpha'},\quad \Gamma_{\alpha\alpha'}=(\Gamma_\alpha+\Gamma_{\alpha'})/2\ , \tag{3}$$

where Γ_α, $\Gamma_{\alpha'}$ are the relaxation rates of the population density of rotational levels α and α'.

For the perturbation $\hat{V}$ under consideration, which does not contain the time explicitly, $\rho_{\alpha\alpha'}$ can be represented as a product of slow and fast functions of time: $\rho_{\alpha\alpha'}=\tilde{\rho}_{\alpha\alpha'}(t)\exp(-i\omega_{\alpha\alpha'}t)$, where $\omega_{\alpha\alpha'}$ is Bohr frequency

$(E_\alpha - E_{\alpha'})/\hbar$. This enables one to approximately substitute the left-hand side of Eq. (1) by $-i\omega_{\alpha\alpha'}\rho_{\alpha\alpha'}$. Taking into account the above relations we obtain from (1)

$$(\Gamma_{\alpha\alpha'} - i\omega_{\alpha\alpha'})\rho_{\alpha\alpha'} = -i\sum_{\alpha''}(V_{\alpha\alpha''}\rho_{\alpha''\alpha'} - \rho_{\alpha\alpha''}V_{\alpha''\alpha'}) . \qquad (4)$$

To first order in V only the summand with diagonal elements of the density matrix in the right-hand side of Eq. (4) should be retained. In this approximation one has

$$(\Gamma_{\alpha\alpha'} - i\omega_{\alpha\alpha'})\rho_{\alpha\alpha'} = -iV_{\alpha\alpha'}(\rho_{\alpha'\alpha'} - \rho_{\alpha\alpha}) . \qquad (5)$$

This equation gives the nondiagonal matrix element $\rho_{\alpha\alpha'}$. Substituting $\rho_{\alpha\alpha'}$ from Eq. (5) into (2) we obtain

$$\frac{\partial \rho_o}{\partial t} = \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma_{\alpha\alpha'}|V_{\alpha\alpha'}|^2}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2}(\rho_{\alpha'\alpha'} - \rho_{\alpha\alpha}) . \qquad (6)$$

The particle distribution over rotational levels for every spin modification is of the Boltzmann type. Hence we can write

$$\rho_{\alpha\alpha} = \rho_o W_B(\alpha), \quad \rho_{\alpha'\alpha'} = \rho_p W_B(\alpha'), \quad \rho_o + \rho_p = N \qquad (7)$$

where $W_B(\alpha), W_B(\alpha')$ are Boltzmann factors, ρ_o, ρ_p are total concentrations of ortho- and paramolecules, and N is their resultant concentration. Combining Eqs. (6) and (7) we have

$$\frac{\partial \rho_o}{\partial t} = -\sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma_{\alpha\alpha'}|V_{\alpha\alpha'}|^2}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2}[\rho_o W_B(\alpha) - \rho_p W_B(\alpha')] . \qquad (8)$$

We now introduce the value $\delta\rho_o(t)$ equal to the deviation of the orthomolecules concentration from the equilibrium value:

$$\rho_o = \langle \rho_o \rangle + \delta\rho_o(t) , \qquad (9)$$

where $\langle \rho_o \rangle$, the equilibrium value of ρ_o, comes out from Eq. (8) at $\partial\rho_o/\partial t = 0$. For $\delta\rho_o(t)$ from Eq. (8) we obtain

$$\begin{gathered} \delta\rho_o(t) = \delta\rho_o(0)e^{-\gamma t}, \\ \gamma = \sum_{\substack{\alpha \in o \\ \alpha' \in p}} \frac{2\Gamma_{\alpha\alpha'}|V_{\alpha\alpha'}|^2}{\Gamma_{\alpha\alpha'}^2 + \omega_{\alpha\alpha'}^2}[W_B(\alpha) + W_B(\alpha')] . \end{gathered} \qquad (10)$$

This expression for the spin conversion rate γ coincides with that obtained in Ref. 2 in another way, i.e., by the probability amplitude's formalism.

The dependence of conversion rate γ on pressure, predicted by Eq. (10), essentially differs in two limiting cases. In the limit $\Gamma_{\alpha\alpha'} \ll \omega_{\alpha\alpha'}$, the conversion rate is $\gamma \propto \mathcal{P}$ ($\mathcal{P}$ is the gas pressure) because the relaxation frequency is $\Gamma_{\alpha\alpha'} \propto \mathcal{P}$. In the opposite limiting case ($\Gamma_{\alpha\alpha'} \gg \omega_{\alpha\alpha'}$) we have an inverse dependence on pressure, $\gamma \propto \mathcal{P}^{-1}$.

III. MAGNETIC DIPOLE-DIPOLE INTERACTION IN CH_3F

The operator of the particle's magnetic moment ($\hat{\mu}$) is expressed through the operator of the particle's spin ($\hat{\mathbf{S}}$): $\hat{\mu} = \mu\hat{\mathbf{S}}/S$, where μ is the magnetic moment and S is the particle's spin. Then the magnetic dipole-dipole interaction (MDDI) between two particles ($\hat{V}_{12}$) can be written in the following way (see, for example, Landau and Lifshitz[3]):

$$\begin{gathered} \hat{V}_{12} = \sum_{i,j} P_{12}\hat{S}_i^{(1)}\hat{S}_j^{(2)}T_{ij}^{(1,2)} , \\ P_{12} = \mu_1\mu_2/r_{12}^3 S^{(1)}S^{(2)}, \quad T_{ij}^{(1,2)} = \delta_{ij} - 3n_i n_j . \end{gathered} \qquad (11)$$

Here r_{12} is the distance between the particles, $\mathbf{n}$ is the unit vector directed from the first to the second particle.

Figure 1 shows the numbering of hydrogen atoms in the CH_3F molecule and orientation of the coordinate system fixed in the molecule. The molecular structural parameters are tabulated in Table I. One can see in the same table the values of scale factors P_{HH}, P_{FH}, and P_{CH} which describe the nuclei MDDI in a CH_3F molecule. The MDDI between carbon and hydrogen implies interaction between a ^{13}C nucleus and a hydrogen nucleus. The magnetic moment of a ^{12}C nucleus equals zero. The expressions for these scale factors are analogous to those for P_{12} in Eq. (11). The magnitudes of magnetic moments for hydrogen, fluorine, and carbon nuclei are from Ref. 6, the CH_3F bond lengths are from Ref. 4.

Let us introduce the notation $\hat{\mathbf{S}}^{(m)}$, $\hat{\mathbf{I}}$, and $\hat{\mathbf{R}}$ for the spin operators of mth hydrogen, fluorine, and carbon nuclei, respectively. The coordinate tensors for interactions $H_m - H_n$, $F - H_m$, and $C - H_m$ we denote as $T_{ij}^{(m,n)}$, $Q_{ij}^{(m)}$, and $\theta_{ij}^{(m)}$, respectively. The MDDI operators between the CH_3F nuclei in Cartesian coordinates in the laboratory system have the form

$$\begin{aligned} \hat{V}_{HH} &= P_{HH}\sum_{m<n}\sum_{i,j}\hat{S}_i^{(m)}\hat{S}_j^{(n)}T_{ij}^{(m,n)}, \quad m,n = 1,2,3 \\ \hat{V}_{FH} &= P_{FH}\sum_{m}\sum_{i,j}\hat{S}_i^{(m)}\hat{I}_j Q_{ij}^{(m)} , \\ \hat{V}_{CH} &= P_{CH}\sum_{m}\sum_{i,j}\hat{S}_i^{(m)}\hat{R}_j\theta_{ij}^{(m)} . \end{aligned} \qquad (12)$$

For convenience in further calculations let us express the operators (12) through the components of spherical tensors. Using the well-known formulas from the theory of angular momentum[3] the operators (12) in the laborato-

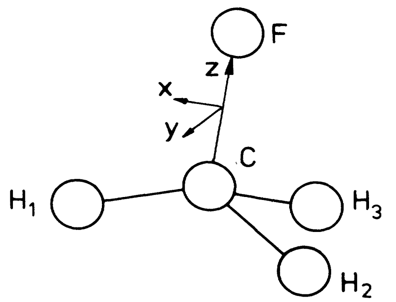

FIG. 1. Numbering of the atoms in the CH_3F molecule and orientation of the Cartesian coordinate system fixed in the molecule.

TABLE I. Molecular-structure parameters.

Bond lengths[a] (Å)	Scale factors (kHz)	Spherical tensors[b]
$r_{\mathrm{HH}}=1.819$	$P_{\mathrm{HH}}=20$	$\tilde{T}^{(1,2)}_{2,\pm 2}=-\frac{3}{2}e^{\pm 2\pi i/3}$
$r_{\mathrm{FH}}=2.037$	$P_{\mathrm{FH}}=13.4$	$\tilde{Q}^{(1)}_{2,1}=1.325$ $\tilde{Q}^{(1)}_{2,2}=0.4$
$r_{\mathrm{CH}}=1.108$	$P_{\mathrm{CH}}{}^{c}=22.2$	$\tilde{\theta}^{(1)}_{2,1}=0.911$ $\tilde{\theta}^{(1)}_{2,2}=1.346$

[a] Average values for ground vibrational state (Ref. 4) are tabulated.

[b] Spherical tensor components in the system of coordinates fixed in the molecule.

[c] Given for ^{13}C.

ry coordinate system are given as follows:

$$\hat{V}_{\mathrm{HH}}=P_{\mathrm{HH}}\sum_{m<n}\sum_{q}(-1)^{q}(\hat{S}^{(m)}\hat{S}^{(n)})_{2,-q}T^{(m,n)}_{2,q}\ , \tag{13a}$$

$$\hat{V}_{\mathrm{FH}}=P_{\mathrm{FH}}\sum_{m}\sum_{q,q_1,q_2}\sqrt{5}\begin{bmatrix}1 & 1 & 2\\ q_1 & q_2 & q\end{bmatrix}\hat{S}^{(m)}_{1,q_1}\hat{I}_{1,q_2}Q^{(m)}_{2,q}\ , \tag{13b}$$

$$\hat{V}_{\mathrm{CH}}=P_{\mathrm{CH}}\sum_{m}\sum_{q,q_1,q_2}\sqrt{5}\begin{bmatrix}1 & 1 & 2\\ q_1 & q_2 & q\end{bmatrix}\hat{S}^{(m)}_{1,q_1}\hat{R}_{1,q_2}\theta^{(m)}_{2,q}\ . \tag{13c}$$

Here $(\hat{S}^{(m)}\hat{S}^{(n)})_{2,-q}$ is the spherical tensor of rank 2 constructed with the components of the vectors $\hat{\mathbf{S}}^{(m)}$ and $\hat{\mathbf{S}}^{(n)}$. The rest of the notations in Eq. (13) are standard.[3]

IV. WAVE FUNCTIONS

This paper describes the nuclear-spin conversion induced by mixing the wave functions of the ground electronic-vibrational state of CH_3F molecules. The wave functions can be classified in the group of molecular symmetry (MS) of CH_3F-C_{3V}.[5] Besides the unity operator, the group contains two operators of cyclic permutation of three hydrogen atoms, e.g., $(123)\equiv(12)(23)$ and also the permutation of two hydrogen atoms with particle coordinate inversion, e.g., operator $(23)^*$. Each symmetry operator of the MS group can be put into conformity with an equivalent molecular rotation.

The wave functions, possessing adequate symmetry properties, have the form

$$|J,K,M,S,\sigma,\kappa\rangle=\frac{1}{\sqrt{2}}[\,|J,K,M,S,\sigma\rangle+(-1)^{J+K+\kappa}|J,-K,M,S,\sigma\rangle\,]\ ,\quad \kappa=0,1,\ K\geq 0\ . \tag{14}$$

Here J,K,M are the angular momentum, its projection on the molecular axis, and on the axis fixed in space, respectively; S,σ is the resultant spin of three hydrogen nuclei and its projection on the axis fixed in space. An explicit form of the functions $|J,K,M,S,\sigma\rangle$ is given by Townes and Schawlow.[6]

The action of the MS group operators on the functions $|J,K,M,S,\sigma\rangle$ results in the following:

$$(123)|J,K,M,S,\sigma\rangle=|J,K,M,S,\sigma\rangle\ , \tag{15a}$$

$$(23)^*|J,K,M,S,\sigma\rangle=(-1)^{J+K}|J,-K,M,S,\sigma\rangle\ . \tag{15b}$$

From these relationships it directly follows that the wave functions (14) at $\kappa=0$ realize a full-symmetrical representation A_1 of the group C_{3V}, and at $\kappa=1$, a representation A_2. In order that the total wave functions satisfy the Pauli principle one has to appropriately combine the functions $|J,K,M,S,\sigma,\kappa\rangle$ with vibronic wave functions.[6]

V. MATRIX ELEMENTS

The calculation of matrix elements of the operators (13) for the transitions between ortho- and paramolecular states can be simplified. Let us consider, for example, the operator $\hat{V}_{\mathrm{HH}}$. To reduce the expression we denote the set of the quantum numbers for orthomolecular states as $\alpha=\{J,K,M,S,\sigma\}$ and for paramolecular states as $\alpha'=\{J',K',M',S',\sigma'\}$. We first consider the calculation of the matrix elements for the transitions from the orthomolecular states with $K\neq 0$ (K' is always nonzero, because it belongs, by the agreement, to paramolecular states). The matrix element of the operator $\hat{V}_{\mathrm{HH}}$ is equal to

$$\begin{aligned}\langle\alpha',\kappa'|\hat{V}_{\mathrm{HH}}|\alpha,\kappa\rangle=0.5[M_{+,+}&+(-1)^{J'+K'+\kappa'}M_{-,+}\\&+(-1)^{J+K+\kappa}M_{+,-}\\&+(-1)^{J',K'+\kappa'+J+K+\kappa}M_{-,-}]\ ,\end{aligned} \tag{16}$$

where the notations

$$M_{\pm,\pm}=\langle J',\pm K',M',S',\sigma'|\hat{V}_{\mathrm{HH}}|J,\pm K,M,S,\sigma\rangle$$

are introduced. There are relationships between the matrix elements $M_{\pm,\pm}$, which can be found using the symmetry transformation (15b):

$$M_{+,+}=(-1)^{J'+K'+J+K}M_{-,-}\ ,$$

$$M_{+,-}=(-1)^{J'+K'+J+K}M_{-,+}\ .$$

With the help of these relations we give expression (16) in the form

$$\langle\alpha',\kappa'|\hat{V}_{\mathrm{HH}}|\alpha,\kappa\rangle=[M_{+,+}+(-1)^{J+K+\kappa}M_{+,-}]\delta_{\kappa'\kappa}\ . \tag{17}$$

This type of dependence of the matrix elements on κ',κ enables one to easily perform a summation over κ',κ in expression (10) for the conversion rate. The degeneracy over κ gives in the magnitude of Boltzmann factors the coefficient 0.5. The sum of the matrix elements required for the calculation of the conversion rate has the form

$$\sum_{\kappa',\kappa}|\langle\alpha',\kappa'|\hat{V}_{\mathrm{HH}}|\alpha,\kappa\rangle|^2=2|M_{+,+}|^2,\quad K\neq 0\ . \tag{18}$$

When deriving the above relation we took into account that $|\Delta K| \leq 2$, according to the rotational selection rules for the matrix elements $M_{\pm,\pm}$ (see below). So, the only term $M_{+,+}$ remains in the right-hand side of (17).

Now we calculate matrix elements for transitions from the states with $K=0$. From a consideration similar to those above, one can obtain an expression for the matrix elements

$$\langle \alpha',\kappa'|\hat{V}_{\mathrm{HH}}|J,K=0,M,S,\sigma,\kappa\rangle = M_{+,0}[1+(-1)^{J+\kappa}][1+(-1)^{J+\kappa'}]/2\sqrt{2} \ , \quad (19)$$

where the matrix element $M_{+,0} = \langle \alpha'|\hat{V}_{\mathrm{HH}}|J,K=0,M,S,\sigma\rangle$. Using equality (19) one can illustrate that the degeneracy over κ can be taken into account also for the states with $K=0$, if the sum of matrix elements, which is analogous to (18), is written in the form

$$\sum_{\kappa',\kappa} |\langle \alpha',\kappa'|\hat{V}_{\mathrm{HH}}|J,K=0,M,S,\sigma,\kappa\rangle|^2 = 2|M_{+,0}|^2 \ . \quad (20)$$

The operators $\hat{V}_{\mathrm{FH}}$ and $\hat{V}_{\mathrm{CH}}$ depend on the spins of fluorine and carbon nuclei. The wave functions containing these variables are given in the form

$$|\alpha,\sigma_{\mathrm{F}},\sigma_{\mathrm{C}}\rangle = |\alpha\rangle|\sigma_{\mathrm{F}}\rangle|\sigma_{\mathrm{C}}\rangle \ , \quad (21)$$

where $\sigma_{\mathrm{F}},\sigma_{\mathrm{C}}$ are the projections of fluorine and carbon nuclei spins on the axis fixed in space.

To explain the procedure of calculations we calculate, for example, the matrix elements of the operator $\hat{V}_{\mathrm{FH}}$. First we note that the wave functions $|\alpha\rangle$ have the form of a product of the spin and coordinates parts: $|\alpha\rangle = |J,K,M\rangle|S,\sigma\rangle$.[6] The relations between the matrix elements of the operators $\hat{S}^{(1)}_{1q_1}$, $\hat{S}^{(2)}_{1q_1}$, and $\hat{S}^{(3)}_{1q_1}$,

$$\langle S',\sigma'|\hat{S}^{(2)}_{1q_1}|S,\sigma\rangle = \epsilon_{K'}^{-1}\langle S',\sigma'|\hat{S}^{(1)}_{1q_1}|S,\sigma\rangle, \quad \epsilon_{K'} = e^{2\pi i K'/3}$$

$$\langle S',\sigma'|\hat{S}^{(3)}_{1q_1}|S,\sigma\rangle = \epsilon_{K'}^{-2}\langle S',\sigma'|\hat{S}^{(1)}_{1q_1}|S,\sigma\rangle \ , \quad (22)$$

follow directly from an explicit form of the functions $|S',\sigma'\rangle$ and $|S,\sigma\rangle$. Let us express now the $Q^{(m)}_{2q}$ tensor components in a laboratory system via the tensor components $\tilde{Q}^{(m)}_{2q'}$ in the coordinate system fixed in the molecule:

$$Q^{(m)}_{2q} = \sum_{q'} D^{(2)}_{q'q}\tilde{Q}^{(m)}_{2q'} \ . \quad (23)$$

Here $D^{(2)}_{q'q}$ are Wigner functions. Different components $\tilde{Q}^{(m)}_{2q'}$ $(m=1,2,3)$ are connected by obvious relationships:

$$\tilde{Q}^{(2)}_{2q'} = \omega_{q'}\tilde{Q}^{(1)}_{2q'}, \quad \tilde{Q}^{(3)}_{2q'} = \omega^2_{q'}\tilde{Q}^{(1)}_{2q'}, \quad \omega_{q'} = e^{2\pi i q'/3} \ . \quad (24)$$

The numerical values of the $\tilde{Q}^{(1)}_{2q'}$ components are tabulated in Table I.

Using expressions (22) and (24) the matrix element of the operator $\hat{V}_{\mathrm{FH}}$ can be written as

$$\langle \alpha',\sigma'_{\mathrm{F}}|\hat{V}_{\mathrm{FH}}|\alpha,\sigma_{\mathrm{F}}\rangle = P_{\mathrm{FH}}\sqrt{5}\sum_{q,q_1,q_2,q'}\langle S',\sigma'|\hat{S}^{(1)}_{1q_1}|S,\sigma\rangle\langle\sigma'_{\mathrm{F}}|I_{1q_2}|\sigma_F\rangle\begin{bmatrix}1 & 1 & 2\\ q_1 & q_2 & q\end{bmatrix}\langle J',K',M'|D^{(2)}_{q'q}\tilde{Q}^{(1)}_{2q'}|J,K,M\rangle \times[1+\epsilon_{K'}^{-1}\omega_{q'}+\epsilon_{K'}^{-2}\omega^2_{q'}] \ . \quad (25)$$

In accordance with the theory of the matrix elements for the symmetrical top[3] the q' variable value is fixed in (25): $q' = K'-K$. Since $q'-K' = -K$ is divisible by 3, one can easily see that for the last term in (25) the following expression is valid:

$$1+\epsilon_{K'}^{-1}\omega_{q'}+\epsilon_{K'}^{-2}\omega^2_{q'} = 3 \ .$$

To calculate the matrix elements of the spin operators $\hat{S}^{(1)}_{1q_1}$ and $\hat{I}_{1q_2}$ one should use the Wigner-Eckart theorem. The reduced matrix elements are equal to

$$\langle S'\|\hat{S}^{(1)}_{1}\|S\rangle = -\sqrt{\tfrac{2}{3}}, \quad \langle \tfrac{1}{2}\|\hat{I}_1\|\tfrac{1}{2}\rangle = \sqrt{\tfrac{3}{2}} \ . \quad (26)$$

The matrix elements of the Wigner functions in Eq. (25) are well known.[3] If then we make the summation over all degenerate sublevels of the states α and α', we obtain the quantity needed for the calculation of the conversion rate according to expression (10):

$$\sum|\langle \alpha',\sigma'_{\mathrm{F}}|\hat{V}_{\mathrm{FH}}|\alpha,\sigma_{\mathrm{F}}\rangle|^2 = P^2_{\mathrm{FH}}(2J'+1)(2J+1)\begin{bmatrix}J' & 2 & J\\ -K' & q' & K\end{bmatrix}^2 |\tilde{Q}^{(1)}_{2q'}|^2 \ . \quad (27)$$

Here the summation was made over the quantum numbers $M',M,\sigma',\sigma,\sigma'_{\mathrm{F}},\sigma_{\mathrm{F}}$. The summation over κ',κ is then made in accordance with formulas (18) and (20).

Now let us consider the MDDI in ^{12}CH$_3$F molecules as a whole. In this case the mixing of ortho- and paramolecular states is contributed by the MDDI between the fluorine nucleus and hydrogen nuclei and also that of hydrogen nuclei:

$$\hat{V} = \hat{V}_{\mathrm{HH}} + \hat{V}_{\mathrm{FH}} \ . \quad (28)$$

To calculate the matrix elements of the operator $\hat{V}_{\mathrm{HH}}$ it is convenient to use the following expression for matrix element of the spin operator $(S^{(1)}\hat{S}^{(2)})_{2,-q}$:

$$\langle S',\sigma'|(\hat{S}^{(1)}\hat{S}^{(2)})_{2,-q}|S,\sigma\rangle=\sqrt{\tfrac{5}{12}}\epsilon_{K'}^{-2}\begin{bmatrix} S' & 2 & S \\ -\sigma' & -q & \sigma \end{bmatrix}, \tag{29}$$

which one can obtain by expansion of the spin wave functions $|S',\sigma'\rangle$ in states with definite values of the resultant spin of the first and second hydrogen nuclei and using the Wigner-Eckart theorem. The resultant spin of the first and second hydrogen nuclei in every state $|S,\sigma\rangle$ (ortho states) always equals 1.

The calculation of a sum of the matrix elements for one pair of levels which enters the expression for the conversion rate (10) leads to the expression

$$\sum|\alpha',\sigma'_{\rm F}|\hat{V}_{\rm HH}+\hat{V}_{\rm FH}|\alpha,\sigma_{\rm F}\rangle|^2$$
$$=(2J'+1)(2J+1)\begin{bmatrix} J' & 2 & J \\ -K' & q' & K \end{bmatrix}^2 \times(1.5|P_{\rm HH}\tilde{T}_{2q'}^{(1,2)}|^2+|P_{\rm FH}\tilde{Q}_{2q'}^{(1)}|^2)\ . \tag{30}$$

Here $\tilde{T}_{2q'}^{(1,2)}$ are the components of the spherical tensor of rank 2, $T_2^{(1,2)}$ in the system of coordinates fixed in the molecule (see Table I). The summation in (30) is made over the variables $M',M,\sigma',\sigma',\sigma'_{\rm F},\sigma_{\rm F}$. The summation over κ',κ should be then made according to formulas (18) and (20).

For ^{13}CH$_3$F molecules, the mixing of ortho- and paramolecular states is induced by all three MDDI's of the molecule:

$$\hat{V}=\hat{V}_{\rm HH}+\hat{V}_{\rm FH}+\hat{V}_{\rm CH}\ . \tag{31}$$

The sum which is analogous to (30) has the form

$$\sum|\alpha',\sigma'_F,\sigma'_C|\hat{V}_{\rm HH}+\hat{V}_{\rm FH}+\hat{V}_{\rm CH}|\alpha,\sigma_F,\sigma_C\rangle|^2$$
$$=(2J'+1)(2J+1)\begin{bmatrix} J' & 2 & J \\ -K' & q' & K \end{bmatrix}^2(3|P_{\rm HH}\tilde{T}_{2q'}^{(1,2)}|^2+2|P_{\rm FH}\tilde{Q}_{2q'}^{(1)}|^2+2|P_{\rm CH}\tilde{\theta}_{2q'}^{(1)}|^2)\ . \tag{32}$$

In this expression the summation is made over the variables $M',M,\sigma',\sigma,\sigma'_{\rm F},\sigma_{\rm F},\sigma'_{\rm C},\sigma_{\rm C}$; $\tilde{\theta}_{2q'}^{(1)}$ are the components of a spherical tensor of rank 2, $\theta_2^{(1)}$ in the system of coordinates fixed in the molecule (see Table I). The two times difference of the coefficients in front of $|\tilde{T}_{2q'}^{(1,2)}|^2$ and $|\tilde{Q}_{2q'}^{(1)}|^2$ in expression (32) compared to (30) appears as a result of additional summation over the variables $\sigma'_{\rm C},\sigma_{\rm C}$. It can be seen that in general formula (10) in the case of ^{13}CH$_3$F molecules the Boltzmann factors must contain additional coefficients equal to $\frac{1}{2}$.

The rotational selection rules for matrix elements of the MDDI operators follow directly from expressions (30) and (32). The change in J and K may be equal:

$$|J'-J|\le 2,\quad |K'-K|\le 2\ . \tag{33}$$

VI. RESONANCES IN ^{12}CH$_3$F AND ^{13}CH$_3$F MOLECULES

According to expression (10) for the spin conversion rate the nuclei MDDI mixes most efficiently the levels which are energetically close. Let us find such pairs in the ground electronic-vibrational state of CH$_3$F molecules. The energy of a rotational level with the quantum numbers J and K is given by the expression

$$\begin{aligned}E(J,K)=&B_0J(J+1)+(A_0-B_0)K^2-D_0^JJ^2(J+1)^2\\&-D_0^{JK}J(J+1)K^2-D_0^KK^4+H_0^JJ^3(J+1)^3\\&+H_0^{JK}J^2(J+1)^2K^2+H_0^{KJ}J(J+1)K^4\ .\end{aligned} \tag{34}$$

The rotational constants in (34) were measured for the CH$_3$F ground electronic-vibrational state in a number of papers. A complete set of rotational constants, however, was measured only for ^{12}CH$_3$F molecules by Graner.[7] Using relationship (34) one can find pairs of energetically close levels. The pairs of the levels tabulated in Table II appeared to be closest among all rotational levels with $J,K\le 80$.

Naturally, only those pairs of levels are tabulated, whose mixing is allowed by the selection rules for matrix elements of the MDDI operators (33).

For ^{13}CH$_3$F molecules the situation connected with rotational constants is less definite: two parameters (A_0 and D_0^K) for this molecule have not been measured yet. Of most importance is the absence of any data on A_0, i.e., the rotational constant connected with rotation of a molecule around the symmetry axis. It can be easily seen, however, that the correction to A_0, resulting from the substitution of ^{12}C by ^{13}C has to be small because the carbon atom is on the molecular symmetry axis. As is pointed out by Egawa and Kuchitsu,[8] the correction still appears due to the isotopic dependence of the harmonic oscillation amplitude of the C—H bond and the isotopic dependence of the unharmonic shift of hydrogen's equilibrium position. For ^{12}CH$_3$F molecules $A_0=5.182\,009\pm 12\times 10^{-6}$ cm^{-1}.[7] For ^{13}CH$_3$F molecules the calculation[8] gives $A_0=5.18240\pm 6\times 10^{-5}$ cm^{-1}.

The pairs of closest rotational levels of ^{13}CH$_3$F with $J,K\le 80$ are tabulated in Table II. For A_0 a corrected

TABLE II. Pairs of energetically close rotational levels in the CH$_3$F ground vibrational state. Spin conversion rates.

Molecule	(J',K')-(J,K)	Energy differences δE (GHz)	$\gamma/\mathcal{P}$[a] (s^{-1}/Torr)	Refs. for rotational constants
^{13}CH$_3$F	(11,1)-(9,3)	0.135+ −0.02	$(4.36\pm1.3)\times10^{-3}$	7–9
	(21,1)-(20,3)	−0.345±0.03	$(2.7\pm0.5)\times10^{-3}$	
			$(7.1\pm2)\times10^{-3}$	
^{12}CH$_3$F	(9,2)-(10,0)	8.59	5.27×10^{-6}	7
	(15,7)-(17,6)	1.75	3.84×10^{-6}	
	(28,5)-(27,6)	1.19	8.92×10^{-6}	
	(51,4)-(50,6)	0.067	8.8×10^{-6}	
			3.02×10^{-5}	
^{12}CH$_3$F	(9,2)-(10,0)	8.59	5.27×10^{-6}	7,10
	(15,7)-(17,6)	1.75	3.84×10^{-6}	
	(28,5)-(27,6)	1.19	8.92×10^{-6}	
	(51,4)-(50,6)	−0.025	6.23×10^{-5}	
			8.4×10^{-5}	

[a] Partial conversion rates induced by mixing the given pairs of rotational levels. Overall spin conversion rates are given under the lines.

value is taken,[8] D_0^K is taken from Ref. 7 with no correction, the rest of the parameters, from Ref. 9. The calculation accuracy of energy of the levels under such "combining" of the rotational constants needs additional investigation which, however, is beyond the scope of the given paper.

VII. CONVERSION RATES

Now let us apply the results obtained above to the calculation of spin conversion rates in ^{12}CH$_3$F and ^{13}CH$_3$F molecules. For this we restrict ourselves to the calculation of γ within the low-pressure range, where the condition $\Gamma_{\alpha\alpha'} \ll \omega_{\alpha\alpha'}$ is true. According to the experimental data[1] this pressure range really exists. It was found in Ref. 1, that for ^{12}CH$_3$F molecules an approximately linear growth of the conversion rate is observed up to $\mathcal{P}\simeq 0.5$ Torr:

$$\gamma_{12}/\mathcal{P}=1.1\pm0.1\ \mathrm{h}^{-1}/\mathrm{Torr}\ , \tag{35}$$

while for ^{13}CH$_3$F molecules a linear growth of the spin conversion rate was observed in the gas pressure range from 0.3 to 1.7 Torr:

$$\gamma_{13}/\mathcal{P}=0.85\pm0.06\ \mathrm{min}^{-1}/\mathrm{Torr}\ . \tag{36}$$

The above data demonstrate that the spin conversion rates in ^{13}CH$_3$F and ^{12}CH$_3$F molecules differ substantially:

$$\gamma_{13}/\gamma_{12}=46\pm5\ . \tag{37}$$

Let us make calculations for the spin conversion rates on the bases of relationships (10), (18), (20), (30), and (32), with the following assumption. The population decay rates of all rotational levels we assume to be equal to 1×10^8 s^{-1}/Torr. This is an experimental value found by Jetter *et al.*[11] for the population decay rate of ^{13}CH$_3$F rotational levels in the ground vibrational state in the CH$_3$F gas. In the calculation of the total spin conversion rates we will take into account all pairs of rotational levels with the splitting ≤ 50 GHz. More than 60 such pairs appeared to be among the levels of the ground vibrational state with $J,K \leq 80$. The calculation results are tabulated in Table II. Conversion rates induced by individual pairs of levels and also by all pairs with splitting ≤ 50 GHz are shown in this table.

First we discuss the calculation of the spin conversion rate for ^{13}CH$_3$F molecules (γ_{13}). The main contribution to the quantity γ_{13} is made by mixing only two pairs of levels. Other pairs of levels contribute less than 1% to the total conversion rate. Because these levels are low-lying rotational levels, the calculation accuracy of the energy differences is probably sufficiently high even in spite of the "combining" of the rotational constants given by different authors and the evaluations (but not measurements) of the rotational constant A_0. The approximate values for the errors of the calculated energy differences are given in Table II.

A relatively high accuracy of calculation of the levels splitting enables one to make a reliable calculation of the spin conversion rate. The resultant value γ_{13} is

$$\begin{aligned}\gamma_{13}/\mathcal{P}&=(7.1\pm2)\times10^{-3}\ \mathrm{s}^{-1}/\mathrm{Torr}\\ &=0.43\pm0.12\ \mathrm{min}^{-1}/\mathrm{Torr}\ .\end{aligned} \tag{38}$$

This value of the conversion rate is approximately two times less than the experimentally measured value for ^{13}CH$_3$F molecules (36).

Note that at present not all molecular parameters needed for numerical calculation of the conversion rate of ^{13}CH$_3$F molecules are available. Thus, we have no relaxation frequencies for particular ^{13}CH$_3$F rotational levels mixed by MDDI. Also, the whole set of $^{13}CH_3F$ molecular parameters is not yet measured. This introduced additional uncertainties in the calculated value (38), but the order of magnitude of the results will be correct.

The situation representing the calculation of the spin conversion rate in $^{12}CH_3F$ molecules appears to be much less definite in spite of the more detailed information on the rotational constants. The reason is the following. The $^{12}CH_3F$ molecule spin conversion is mainly induced by the mixing of four pairs of levels. One of those pairs of levels, (51,4)-(50,6), which makes a considerable contribution to the conversion, is situated at a very high energy with high J numbers. For such high values of J the error in the magnitude of the energy splitting essentially exceeds the splitting itself because of the relatively low accuracy of the rotational constants. This is illustrated by the calculations of the energy splitting with two sets of rotational constants (Table II). It can be seen that when going from one set of the rotational constants to another even the sign of splitting of a pair of rotational levels $\delta E = E(51,4) - E(50,6)$ changes.

Thus, the data from Table II on the $^{12}CH_3F$ spin conversion rate induced by mixing the states (51,4)-(50,6) should be treated as an estimation only. As a whole, there is a qualitative agreement with the measured value (35).

VIII. CONCLUSION

The theory has been constructed for the CH_3F molecular spin (ortho-para) conversion, induced by mixing the ortho- and paramolecular states by magnetic dipole-dipole nuclear interaction. The numerical calculations of the spin conversion demonstrated that this mechanism explains approximately one-half of the measured[1] conversion rate for $^{13}CH_3F$ molecules. For $^{12}CH_3F$ molecules only approximate calculations have been carried out because of the absence of high-accuracy rotational constants. The calculations show a qualitative agreement between the measured and calculated rates of a spin conversion for $^{12}CH_3F$ molecules.

Because of the uncertainties of the calculated conversion rate of $^{12}CH_3F$ molecules, the ratio γ_{13}/γ_{12} of conversion rates can only be estimated. The result is $\gamma_{13}/\gamma_{12} \sim 10^2$, which is in good qualitative agreement with ratio (37) measured experimentally. We conclude that the main reason for the large isotopic effect in the nuclear conversion rate of CH_3F molecules is the strong dependence of the energy differences between closest rotational levels of CH_3F molecules on isotopic substitution.

Thus, this analysis of nuclear-spin conversion in CH_3F molecules reveals the important role of the magnetic dipole-dipole interaction between molecular nuclei. The construction of a more reliable and detailed picture of the spin conversion in CH_3F molecules requires a high-accuracy measurement of rotational constants both for $^{12}CH_3F$ and $^{13}CH_3F$ molecules. It is also necessary to analyze the role of other intramolecular interactions for nuclear-spin conversion in CH_3F.

ACKNOWLEDGMENTS

I would like to express my deep gratitude to T. Egawa and K. Kuchitsu for their kind help in the calculation of the A_0 constant for $^{13}CH_3F$ molecules; to S. G. Rautian and A. M. Shalagin for the stimulating discussions and their support of this work; and also to V. G. Zelevinsky, L. V. Il'ichev, O. P. Sushkov, and V. V. Flambaum for the fruitful discussions of the problems described in the paper. This work was financially supported by the U.S.S.R. Academy of Sciences.

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