On spin-rotation contribution to nuclear spin conversion in $C_{3v}$-symmetry molecules. Application to CH$_3$F

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(October 12, 2018)

Abstract

The symmetrized contribution of $E$-type spin-rotation interaction to conversion between spin modifications of $E$- and $A_1$-types in molecules with $C_{3v}$-symmetry is considered. Using the high-$J$ descending of collisional broadening for accidental rotational resonances between these spin modifications, it was possible to coordinate the theoretical description of the conversion with (updated) experimental data for two carbon-substituted isotopes of fluoromethane. As a result, both $E$-type spin-rotation constants are obtained. They are roughly one and a half times more than the corresponding constants for (deutero)methane.

PACS numbers: 31.30.Gs, 33.50.-j

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I. INTRODUCTION

The purpose of the present work is to compare the theoretical description of spin-modification (or, differently, spin-isomer) conversion \[1,2\] with updated experimental data for two carbon-substituted isotopes of fluoromethane \[3,4\]. The main difficulties on this way are conditioned, firstly, by the lack of data about E-type spin-rotation constants of this molecule and, secondly, by the insufficiently reliable data about values and collisional broadenings of conversional accidental resonances of rotational levels of its spin modifications. Resigning oneself to the latter, we attempt to extract at least preliminary information on this constants by reversing the problem on the conversional contribution of spin-rotation interaction. It is useful to compare the obtained constants for fluoromethane with the known ones for methane presenting them in the similarly orientated molecule-fixed frames.

In the beginning, it is necessary to make two corrections. The consideration of spin-modification conversion for \(C_{3v}\)-symmetry molecules in \[2\] explores the spin-rotation Hamiltonian form of limited applicability. Being widely encountered in papers and books (see, e.g., \[7,8\]), this form is non-Hermitian for nonspherical tops of nonlinear molecules. It is necessary to use the standard symmetrizing procedure \[9\] in order to come to Hermitian form of the Hamiltonian. The second correction deals with the contribution of Thomas precession to the spin-rotation constants \[10\]. As the most important consequence, the components of these tensorial constants even in \(R\)-forms \[3\] may have asymmetry, i.e., transposed matrices \(R^\dagger \neq R^T\) for off-axial nuclei. The number of independent components of \(R\)-form \[4\] may grow up to five, i.e., two of \(A_1\)-type and three (but not two as in \[2\]) of \(E\)-type.

The two carbon-substituted isotopes of fluoromethane \(^{12,13}\text{CH}_3\text{F}\) in the room-temperature gaseous phase have essentially different rates of mutual conversion of para- and ortho-modification. According to \[3\,3\,11\], the updated pressure-normalized rates of spin-modification conversions, i.e. \(\gamma^{(P)} = \gamma/P\), are

\[12\gamma^{(P)} = 35.3(31) \ \mu\text{Hz/Torr} \tag{1}\]

and

\[13\gamma^{(P)} = 1942(95) \ \mu\text{Hz/Torr}. \tag{2}\]

It may be compared with the \(P\)-normalized collisional broadening (halfwidth) of rotational lines

\[\Gamma^{(P)}_{J\prime K'/J K} = \Gamma_{J\prime K'/J K}/P\]

where

\[1\]See Eq. (6) below.

\[2\]My attention to them was turned by P. L. Chapovsky. For comparison, see also \[3\].

\[3\]In this paper all the rates (or frequencies) are angular but measured in Hz = \(2\pi \text{ s}^{-1}\).
\[ \Gamma_{J'K'/JK} = (\Gamma_{J'K'} + \Gamma_{JK})/2. \tag{3} \]

According to [12], we have
\[ \Gamma^{(P)}_{5,3/4,3} = 15.2(8) \text{ MHz/Torr}. \]

The theoretical estimates of nuclear spin-spin contribution to \( \gamma^{(P)} \) were obtained in [1] assuming the same broadening for all the conversional transitions. These estimates make up 7\% of (1) for \(^{12}\)CH\(_3\)F and 43\% of (2) for \(^{13}\)CH\(_3\)F. But this simple assumption leads to an incompatibility between (1) and (2), if, following [2], one attempts to add the spin-rotation contribution to the spin-spin one. The rejection of the last high-\(J\) para-ortho resonance standing out against the rest for \(^{12}\)CH\(_3\)F might be a possible way out of this situation. The reason for that has been found in [13]. It turned out that the collisional broadening of rotational lines is decreased with increasing \(J\). As a result, the contribution of the high-\(J\) resonance is effectively suppressed and the indicated incompatibility is eliminated.

It makes sense to collect together all spin-rotation constants of fluoromethane and (deutero)methane. Further, comparing them, we can make the definite conclusion on signs of the \(E\)-type constants for fluoromethane.

**II. SYMMETRIZED FORM OF SPIN-ROTATION HAMILTONIAN**

The spin-rotation interaction appears as a consequence of action of a local magnetic field \( \hat{B}^\varsigma \) on the magnetic moment \( \hat{\mu}^\varsigma = \mu^\varsigma \hat{I}^\varsigma \) of nucleus labelled by \( \varsigma \). Here \( \mu^\varsigma = g^\varsigma \mu_N \), \( g^\varsigma \) is the nuclear \( g \)-factor, \( \mu_N \) is the nuclear magneton, and \( \hat{I}^\varsigma \) is the nuclear spin undimensioned by Planck’s constant \( \hbar \). The intramolecular field \( \hat{B}^\varsigma \) is conditioned by rotation of nuclear framework and internal motions of electrons. The non-symmetrized Hamiltonian of this interaction is

\[ \hat{V}_{sr} = -\sum \hat{B}^\varsigma \cdot \hat{\mu}^\varsigma \tag{4} \]

where \( \hat{B}^\varsigma = \hat{J} \cdot \mathbf{C}^\varsigma / \mu_N^\varsigma \), \( \hat{J} \) is rotational angular momentum (also undimensioned by \( \hbar \)), and \( \mathbf{C}^\varsigma \) is spin-rotation tensor. The energy (as well as \( \mathbf{C}^\varsigma \)) is measured in frequency units. The convenient unit of measurement for \( \mathbf{C}^\varsigma \) usually is kHz. In molecule-fix frame the components of \( \mathbf{C}^\varsigma \) are constant but \([\hat{J}_z, \hat{I}_z] = -i\varepsilon_{ijk}\hat{J}_k\) unlike \([\hat{J}_i, \hat{I}_j] = 0 \) in space-fix frame. Hence, by Hermitian conjugation, we have operator \( \hat{V}_{sr}^\dagger \neq \hat{V}_{sr} \). To convert \( \hat{V}_{sr} \) into Hermitian one, we must use the standard symmetrization procedure [3] (see also, as an example, [14]), i.e.,

\[ \hat{J}_z \hat{I}_z \to (\hat{J}_z \hat{I}_z + \hat{I}_z \hat{J}_z)/2. \]

As a result, we come to symmetrized spin-rotation Hamiltonian

\[ \hat{V}_{sr}^{(+)} = (\hat{V}_{sr} + \hat{V}_{sr}^\dagger)/2 = -\frac{1}{2} \sum \hat{J} \cdot \mathbf{C}^\varsigma \cdot \hat{\mu}^\varsigma + \hat{\mu}^\varsigma \cdot \mathbf{C}^\varsigma^\top \cdot \hat{J}. \tag{5} \]

\(^4\)Projections onto this frame are underscored. E.g., Cartesian ones \( \hat{J}_z = \mathbf{u}_z \cdot \hat{J} = \hat{J} \cdot \mathbf{u}_z \).
The initial components $C_{ij}^\kappa$ have reducible lower and upper indices respectively for the group of arbitrary molecular rotations and inversions, $O_3 = SO_3 \otimes C_1$, and the group of permutations of spatial and spin coordinates for identical nuclei, $S_3 \cong C_{3v} \subset O_3$. Transforming this components into double irreducible ones $C_{(11)\kappa\ell}^\lambda$ defined in [2], we can also obtain

$$\hat{V}_{sr}^{(+)} = -\frac{1}{2} \sum_{\kappa\lambda} \sqrt{|\kappa|} \left\{ (-1)^\kappa \left[ \hat{J}_1 A_1 \otimes C_{(11)\kappa\ell}^\lambda \otimes \hat{I}_{10}^\lambda \right]_{0+} + \left[ \hat{I}_1 \otimes C_{(11)\kappa\ell}^\lambda \otimes \hat{J}_1 A_1 \right]_{0+} \right\}$$

where $\kappa = 0, 1, 2$ and $\lambda = A_1, E$ (the last type exists only for off-axial nuclei). The single symbols in square brackets designate dimension of their respective representations. E.g., in the case of the $SO_3$ group, we have $[\kappa] = 2\kappa + 1$. Just this form of spin-rotation Hamiltonian is used in analytical calculations (cp. with [2]). It is necessary to note directly now, that the non-commutation of $\hat{J}_i$ and $\hat{I}_\kappa$ has a little significance at high $J$. We shall see this situation does take place for fluoromethane.

III. ISOTOPICALLY INDEPENDENT SPIN-ROTATION CONSTANTS

In order that the spin-rotation constants do not change with isotopic substitutions, it is convenient to use their modified $R$-form, i.e., let

$$C^c = g^c \hat{B} \cdot R^c.$$

Here $\hat{B} = 2\mathbf{B} = \hbar \mathbf{l}^{-1}$, i.e. proportional to the inverse tensor of inertia moment localized (as well as $\hat{J}$) in inertia center. The factor $\hbar$ is chosen for $\hat{B}$ to have frequency dimensions as well as $C^c$. The tensor $\mathbf{B}$ is defined by rotational spectrum of molecule (16). Choosing the molecule-fix frame with its $z$-axis along the axis of molecular symmetry ($C \rightarrow F$) we obtain the diagonal

$$\hat{B} = \begin{pmatrix} \perp \hat{B}_{z} & 0 \\ \perp \hat{B}_{z} & \hat{B}_{z} \end{pmatrix} .$$

For isotopes $^{12,13}\text{CH}_3\text{F}$ we have transverse components $^{12}\hat{B}_{\perp} = 51.1(1)$ GHz and $^{13}\hat{B}_{\perp} = 49.7(1)$ GHz, both longitudinal ones $^{12,13}\hat{B}_{z} = 310.7(1)$ GHz. The non-dimensional tensor $R^c$ is only defined by electric charge distribution. It is one and the same for all the isotopes of molecule in their invariable geometry. Another attractive property of $R^c$ is much greater symmetry in comparison with $C^c$, i.e., we may have $R^c_{(-)} = 0$ but $C^c_{(-)} \neq 0$ where $R^c_{(\pm)} \equiv (R^c \pm R^{cT})/2$. At last, it is known [15] that

$$R^c \simeq m_n \sigma_{ma}^c / m_p$$

where tensor $\sigma_{ma}^c = \sigma_{\text{molecule}}^c - \sigma_{\text{atom}}^c$, i.e. the difference of nuclear magnetic shielding for nucleus $\varsigma$ by forming the molecule from free atoms. Thus, it is convenient to measure $R$-constants in ppb $= 10^{-9}$, i.e. parts per billion, as well as $\sigma$-constants in ppm $= 10^{-6}$.

Some (most likely small) asymmetry of tensor $R^c$ may be for off-axial spins by taking into account the Thomas correction dependent on motion of spinning nuclei [16]. We are
going to neglect this asymmetry for fluoromethane, having in view of the zero asymmetric part and small contribution of the Thomas correction in the symmetric one \[10\] for methane used here as a sample.

Now let us divide, as in \[3\], all the nuclei \(\varsigma\) into axial (vertical) \(v = F, C\) and off-axial (horizontal) \(h = H^1, H^2, H^3\). The use of the \(C_{3v}\)-symmetry group for off-axial nucleus \(H^1\) leads to the following form of tensor

\[
R^{H^1} = \begin{bmatrix}
\frac{R^{HA_1}}{z} + \frac{R^{HE}}{z} & \frac{R^{HE}}{z} & \frac{R^{HE}}{z}
0 & 0
0 & \frac{R^{HE}}{z}
\frac{R_{(+)z}^{HE}}{z} - \frac{R_{(-)z}^{HE}}{z}
\end{bmatrix}
\]

In other cases \(\hat{\delta}^{H^1}_v \rightarrow \hat{\delta}^{h}_v\) and \(\mathbf{n}^{H^1} \rightarrow \mathbf{n}^h\) as describing in \[3\]. The same symmetry of spin-rotation interaction for axial nuclei \(v\) retains only \(A_1\)-type components, i.e.,

\[
R^v = \begin{bmatrix}
\frac{R^{HA_1}v}{z} & 0
\frac{R^{HA_1}v}{z}
\end{bmatrix}
\]

If we designate the components of \(C^{H^1}\) and \(C^v\) by analogy with \[10\] and \[11\] then

\[
C^{\varsigma A_1} = g^\varsigma \hat{B} \frac{R^{\varsigma A_1}}{z}, \quad C^{\varsigma A_1} = g^\varsigma \hat{B} \frac{R^{\varsigma A_1}}{z}
C^{HE} = g^H \hat{B} \frac{R^{HE}}{z}, \quad C^{HE}_{(\pm)z} = g^H \left( \hat{B}_{(\pm)} \frac{R^{HE}}{z} + \hat{B}_{(\mp)} \frac{R^{HE}}{z} \right)
\]

where \(\hat{B}_{(\pm)} = (\hat{B}_{(\pm)} \pm \hat{B}_{(\mp)})/2\). Here \(\hat{B}_{(-)}\) and \(C^{HE}_{(-)z}\) are defined with the reverse signs to \[2\].

**IV. THE COMPLETE HYPERFINE CONTRIBUTION TO SPIN-MODIFICATION CONVERSION IN \(C_{3v}\)-SYMMETRY MOLECULES**

The states of \(E\)- and \(A_1\)-types for three hydrogen spins of fluoromethane differ in total spin \(I^H = \sum_h \hat{I}^h\), i.e., \(I^H = 1/2\) (para) and 3/2 (ortho) respectively. Under equilibrium conditions, according to detailed balancing principle, the increment and decrement of the populations of this states (in- and out-terms) compensate each other, i.e., \(\gamma_{\frac{1}{2}}/\gamma_{\frac{3}{2}}(\infty) = \gamma_{\frac{1}{2}}/\gamma_{\frac{3}{2}}(\infty)\). As a result, the equilibrium ratio of the partial population to the total one is \(\rho_{1H}(\infty)/\rho = (\gamma - \gamma_{1H})/\gamma \approx 1/2\) for fluoromethane. Using light-induced drift method \[17\], we can breakdown the equilibrium. Owing to the mutual conversion, the non-equilibrium populations decay. This decay is described with one exponent, i.e., \(\delta \rho_{1H}(t) = \delta \rho_{1H}(0)e^{-\gamma t}\) and \(\sum_{1H} \delta \rho_{1H}(t) = 0\). Let us consider now the expression for the conversional rate \[1\]

\[
\gamma = \gamma_{\frac{1}{2}} + \gamma_{\frac{3}{2}}
\]
\[
\begin{align*}
&= \sum_{J'K'/JK} \sum_{p} \frac{2\Gamma_{J'K'/JK} [\mathcal{W}_B^{(1)} (J'_p K'_p) + \mathcal{W}_B^{(2)} (J_p K_0)]}{\Gamma_{J'K'/JK}^2 + \omega_{J'pK'/Jp0}^2} \\
& \times \sum_{(a')(a)} |\langle (a') J'_p K' | (\hat{V}_{sr} + \hat{V}_{ss}) | (a) J_p K_0 \rangle|^2.
\end{align*}
\]

We have described the symmetrized spin-rotation interaction \( \hat{V}_{sr}^{(+)} \) in \( [3] \) and \( [8] \), the spin-spin one \( \hat{V}_{ss} \) in \( [2] \). The halfwidth \( \Gamma_{J'K'/JK} \) was defined in \( [3] \). The frequency difference

\[
\omega_{J'pK'/Jp0} \equiv \omega_{J'pK'} - \omega_{JpK_0}.
\]

Here \( J \geq K_r \geq 0 \) and \( K \) is congruous with \( r \) modulo 3, i.e., \( K \equiv r \mod 3 \) where \( r \in \{0, 1, 2\} \). The level parity

\[
p = (-1)^{J+1} \delta_{K,0} \pm (1 - \delta_{K,0}).
\]

The rotational spectrum \( \omega_{JpK} \) may be expressed by the formula

\[
\omega_{JpK} = B_K J^2 + B_J J^2 - D_K J^2 - D_{KJ} J^2 J + D_{J}\bar{J} J + F_K J^6 + F_{JK} J^2 J^6 + F_{J}\bar{J} J^6 + \delta_{K,3} F_{J}^{(3)} p(-1)^J \bar{J} J + 2 (-2) [ \bar{J} J - 6].
\]

Here, for short, \( J \equiv J(J + 1) \). \( B_K = B_{\bar{J}} - B_J \) and \( B_J = B_{\bar{J}} \). We take into account quartic and sextic centrifugal distortions in the ground electronic and vibrational states \( [18] \). Here the alphabetical choice for designation of the coefficients is connected with the powers of perturbations. Almost all the \( BDF \)-coefficients of isotopes \( ^{12,13}\text{CH}_3\text{F} \) may be found in \( [19,20] \). We assume the unknown \( ^{12}F_K \) is just a little less then the known \( ^{13}F_K \), i.e., \( ^{13}F_K - ^{12}F_K \approx 3 \text{ Hz} \). \( F_{J}^{(3)} \) defines \( K \)-doubling in the parity of rotational levels with \( K = 3 \). Its estimate can be found in \( [21] \).

The wave functions of every spin-rotation subsystem are \( \left| (K_r)^{(G_{JpH})} (A_{Jp} H)_{M_J M_H} \right| \prod_v |I^v M^v_I \rangle \) where the first factor is \( \left| (K_r)^{(G_{JpH})} (A_{Jp} A_{Jp} H)_{M_J M_H} \right| \) or \( \left| (K_r)^{(A_{Jp} A_{Jp} H) A_{Jp} H}_{M_J M_H} \right| \) (see \( [2] \)). The populations of levels are characterized by their Boltzmann factors

\[
\mathcal{W}_B^{(1)} (J_p K_r) = e^{-\hbar \omega_{JpK_r} / k_B T} / Q_{sr}^{(1)}.
\]

The spin-rotation statistical sum

\[
Q_{sr}^{(1)} = \prod_v |I^v \rangle [I^v] \sum_J \sum_{K_r p} e^{-\hbar \omega_{JpK_r} / k_B T}.
\]

The square brackets, as defined after Eq. \( (8) \), designate the degree of space-degeneracy (or statistical weight) for rotational angular momentum or nuclear spins. By room temperature \( (20 \degree C) \) we have \( B_{\bar{J}} \ll k_B T / \hbar \approx 6108.2 \text{ GHz} \) and

\[5\]Cp. with the less justified assumption \( ^{12}F_K = 0 \) in \( [11] \).
\[ Q_{\text{st}}^{(1/3)} \simeq Q_{\text{st}}^{(2/3)} \simeq \prod_v[I_v] \frac{4k_B T}{3hB_\perp} \sqrt{\frac{\pi k_B T}{hB_\perp}}. \]

Hence, for isotopes of fluoromethane, it follows

\[ 1^2 Q_{\text{st}}^{(H)} \simeq \prod_v[I_v] 3554, \quad 1^3 Q_{\text{st}}^{(H)} \simeq \prod_v[I_v] 3625. \]

Here it is convenient to represent already symmetrized form of expression (92) from [2]:

\[ \sum_{(a')} |\langle (a') J'_p K'_p |(\hat{V}_{\text{st}}^{(\perp)} + \hat{V}_{\text{st}}^{(\parallel)})|a)J_p K_0 \rangle|^2 = \prod_v[I_v'](1 + \delta_{K',0})(1 + \delta_{K,0})[J] \]

\[ \times \left\{ \frac{\delta_{|\Delta K|,1}}{4} \left[ C_{(-)}^{HE} \langle J' K' |2D K JK \rangle \sqrt{(J' + J + 3)(J' + J - 1)} + C_{(-)}^{HE} \langle J' K' |1D K JK \rangle \Delta K \Delta J (J' + J + 1) \right]^2 \right\} + \langle J' K' |2D K JK \rangle^2 \]

\[ \times \left[ \frac{\delta_{|\Delta K|,2} \sum_v I_v^2}{16} \sum_v I_v^2 \left( \frac{\delta_{|\Delta K|,2} \sum_v I_v^2}{4} \right) (J' + J + 1) \right]. \quad (17) \]

Here, also for short, \( \hat{I}^2 \equiv I^2(I^2 + 1) \). The dimensional \( C \)-constants are expressed \textit{via} non-dimensional \( R \)-constants according to Eq. (1). \( hS_\perp = \mu J \mu J / \gamma_\perp^2 \) and \( \mu J \) is defined before (1). The subscript \( O \) designates the intersection point of molecular symmetry axis with the base resting on three hydrogen nuclei. \( \Delta J = J' - J \) and \( \Delta K = K'_p - K_0 = |\Delta K|(-1)^r+\Delta K \) by \( |\Delta K| = 1, 2 \). It is useful to have in mind that, in the resonance conditions \( \omega_{J',K'/JK} \simeq 0 \),

\[ \Delta J/\Delta K \simeq -B_K(K' + K)/B_J(J' + J + 1). \quad (18) \]

In particular, one can see that \( \Delta J \) and \( \Delta K \) have always different signs for fluoromethane (as prolate top). Formally, the symmetrization changes only one factor to \( C_{(+)}^{HE} \) in expression (92) from [4], i.e.,

\[ \left\{ \begin{array}{c} J' \\ 1 \\ J \\ J \\ J \\ 1 \end{array} \right\} \sqrt{\hat{J}^2[J]} \]

is replaced by

\[ \frac{1}{2} \left\{ \left\{ \begin{array}{c} J' \\ 1 \\ J \\ J \\ 1 \end{array} \right\} \sqrt{\hat{J}^2[J]} - \left\{ \begin{array}{c} J \\ 1 \\ J \\ J' \\ 1 \end{array} \right\} \sqrt{\hat{J}^2[J]} \right\} = \frac{\delta_{|\Delta J|,1}}{2} \Delta J (J' + J + 1) \sqrt{6}. \quad (19) \]

The analogue factor to \( C_{(+)}^{HE} \) and \( C_{(+)}^{HE} \), in explicit form, is

\[ \left\{ \begin{array}{c} J' \\ 1 \\ J \\ J \\ 1 \\ J \end{array} \right\} \sqrt{\hat{J}^2[J]} = -\frac{\delta_{|\Delta J|,1}}{2} \sqrt{(J' + J + 3)(J' + J - 1) / 10}. \quad (20) \]
and not changed. Now, taking into account also the definite symmetry of Wigner coefficients, i.e.,
\[ \langle J'K'|\varepsilon \Delta K JK \rangle \sqrt{|J|} (-1)^{J+K} = \langle JK|\varepsilon \Delta K J'K' \rangle \sqrt{|J'|} (-1)^{J'+K'}, \]
one can see the expression (17) is invariant under the transposition \((J', K' \leftrightarrow J, K)\).

V. CONVERSIONAL SPIN-ROTATION CONSTANTS OF FLUOROMETHANE

It is convenient to collect the quantitative characteristics of the most important accidental resonances for conversional transitions of fluoromethane in Table I. The contribution of the individual resonance reaches maximum for pressure
\[ P^{(\text{max})}_{J'K'/JK} = \omega_{J'K'/JK}/\Gamma_{J'K'/JK}. \] (21)
All the resonances have \( \Gamma_{J'K'/JK} \ll |\omega_{J'K'/JK}| \) for pressure \( P \ll \min_{J'K'/JK} P^{(\text{max})}_{J'K'/JK} \), i.e., much less than 17 Torr for \(^{12}\text{CH}_3\text{F}\) and 7 Torr for \(^{13}\text{CH}_3\text{F}\). \( K \)-doubling in the parity for mentioned resonances with \( K = 3 \) does not matter practically, i.e., \( \omega_{JpK} \simeq \omega_{JK} \) for all \( K \). Thus, using (15), one can sum over \( p \) in (13), i.e.,
\[ \sum_p (1 + \delta_{K,0}) \{ \ldots \} = 2 \{ \ldots \}. \] (22)
Let us write out the explicit dependence of the \( P \)-normalized conversional rate on spin-rotation \( R \)-constants:
\[ \gamma^{(P)} = \sum_{J'K'/JK} \left( \gamma^{(P)}_{ss(J'K'/JK)} + \gamma^{(P)}_{ss(J'K'/JK)} \right), \]
with
\[ \gamma^{(P)}_{ss(J'K'/JK)} = a^{HR}_{(J'K'/JK)} (R_{\text{HE}})^2 + \sum_{\sigma'\sigma} a^{HR(\sigma'\sigma)}_{(J'K'/JK)} R_{(\sigma'\sigma)z} R_{(\sigma'\sigma)z}. \] (23)
Here the quadratic form are positive semi-definite, i.e. \( \geq 0 \). By \( \Gamma_{J'K'/JK} \ll |\omega_{J'K'/JK}| \), the coefficients \( a^{HR}_{(J'K'/JK)} \) and \( a^{HR(\sigma'\sigma)}_{(J'K'/JK)} \), as well as the conversional rate terms \( \gamma^{(P)}_{ss(J'K'/JK)} \) and \( \gamma^{(P)}_{ss(J'K'/JK)} \), are constant and given in Table II for every resonance separately.

For \(^{12}\text{CH}_3\text{F}\) one can calculate
\[ S_{\text{HF}} = 13.4 \text{ kHz}, \quad S_{\text{HC}} = 22.2 \text{ kHz}, \quad S_{\text{HH}} = 19.9 \text{ kHz}. \] (24)
Hence, for isotope \(^{13}\text{CH}_3\text{F}\), it follows
\[ ^{13}S^{(P)}_{\text{ss}} = 1210 \mu \text{Hz/Torr}, \] (25)

\(^6\)It is sometimes convenient for the negative sign to be denoted as overbar.
i.e. 62% of (2). For the rest, we obtain an equation

\[ 13_\text{ss}^{(P)} = 12.5(R_{\perp}^{HE})^2 \times 10^{18} \text{ Hz/Torr} = 732 \text{ Hz/Torr}. \] 

(26)

Its solution is

\[ |R_{\perp}^{HE}| \approx 7.65 \text{ ppb}. \] 

(27)

Similarly, for isotope \(^{12}\)CH\(_3\)F, we have

\[ 12_\text{ss}^{(P)} = 2.85 \text{ Hz/Torr}, \] 

(28)

i.e. 8% of (1). For the rest, we obtain another equation

\[ 12_\text{ss}^{(P)} = \left[ 0.151(R_{\perp}^{HE})^2 + 0.92(R_{(+)}^{HE})^2 ight. \\
-1.87 \times 10^{-3}R_{(+)}^{HE}R_{(-)}^{HE} + 10^{-6}(R_{(-)}^{HE})^2 \right] \times 10^{18} \text{ Hz/Torr} = 32.45 \text{ Hz/Torr}. \] 

(29)

Using (27) and setting \(R_{(-)}^{HE} = 0\), we come to the solution

\[ |R_{(+)}^{HE}| \approx 5.07 \text{ ppb}. \] 

(30)

VI. COMPARISON OF SPIN-ROTATION CONSTANTS OF FLUOROMETHANE

AND (DEUTERO)METHANE

Here the conversional spin-rotation constants of fluoromethane are found for the first time. To compare them with known respective constants of methane (or deuteromethane), we must equally orientate both molecules so that F of CH\(_3\)F corresponds to H\(^4\) of CH\(_3\)H (or D of CH\(_3\)D). The spin-rotation constants of CH\(_4\) are usually cited in the following form [22]:

\[ C^{HA_1} = g^H_1 \tilde{B}(2R_{\perp}^H + R_{\parallel}^H)/3 = 10.4(1) \text{ kHz}, \quad C^{HF} = g^H_1 \tilde{B}(R_{\perp}^H - R_{\parallel}^H) = 18.5(5) \text{ kHz}. \]

From here, using \(\tilde{B} = 314.2(1) \text{ GHz}\) (see, e.g., [23]), one can obtain

\[ R_{\perp}^{H_4}(\tilde{H}_4) = \begin{bmatrix} R_{\perp}^{H_4} & 0 \\ 0^\top & R_{\parallel}^H \end{bmatrix} = \begin{bmatrix} 9.46(11) & 0 \\ 0^\top & -1.1(2) \end{bmatrix} \text{ ppb} \] 

(31)

and

\[ R_{\perp}^{H_4}(\tilde{H}_4) = \frac{1}{9} \left[ (5R_{\perp}^H + 4R_{\parallel}^H)\mathbf{i}_2 - 4(R_{\perp}^H - R_{\parallel}^H)\hat{\sigma}^H_\nu \sqrt{8(R_{\perp}^H - R_{\parallel}^H)n^H_1} \right] \right. \\
\left. \left. \sqrt{8(R_{\perp}^H + R_{\parallel}^H)n_{1\parallel}} \right] \right. \\
= \begin{bmatrix} 4.76(11) & 4.69(13)\hat{\sigma}^H_\nu & 3.31(9)n^H_1 \\ 3.31(9)n^{H_1\parallel} & 8.27(10) \end{bmatrix} \text{ ppb} \] 

(32)

where \(\hat{\sigma}^H_\nu\) and \(n^{H_1}\) are defined in [11]. One may see \(R_{\perp}^{H_4} \ll R_{\parallel}^{H_4}\). Take notice \(R_{\perp}^{HE} = (n)R_{\perp}^{HE} + (c)R_{\perp}^{HE} < 0\) as well as nuclear term \(n^{(a)}R_{\perp}^{HE}\) easily calculated from [10]. To make complete the set of methane constants, we cite from [24].
\[ \mathbf{R}^C(\tilde{z}_H) = -28(7)\mathbf{i}_3 \text{ ppb.} \]  

(33)

The diagonal components of tensor $\mathbf{C}$ for CH$_3$F can be found in [25]. Using the components of $\mathbf{B}$ from (8), we obtain

\[ \mathbf{R}^F(\tilde{z}_F) = \begin{bmatrix} 15(7)\mathbf{i}_2 & 0 \\ 0^\top & -31.4(8) \end{bmatrix} \text{ ppb}, \]  

(34)

\[ \mathbf{R}^H(\tilde{z}_F) \simeq \begin{bmatrix} 2.9(54)\mathbf{i}_2 - 7.65\mathbf{\tilde{\sigma}}_{i}^{H^i} \\ 5.07\mathbf{n}^{H^i}^\top \end{bmatrix} \text{ ppb.} \]  

(35)

Here we have added the above obtained off-diagonal components. Their signs are supposed to be just like the ones of (deutero)methane constants in (32). To make complete also the set of fluoromethane constants, we can use (9) and data from [26,8]. As a result, one may estimate

\[ \mathbf{R}^C(\tilde{z}_F) \simeq \begin{bmatrix} -80 \times \mathbf{i}_2 & 0 \\ 0^\top & -35 \end{bmatrix} \text{ ppb.} \]  

(36)

VII. CONCLUSION

Summing up, we notice the following. Unlike [2], the symmetrized spin-rotation contribution to nuclear spin-modification conversion in C$_3$v-symmetry molecules has been produced. But the symmetrization is important only for low $J$.

Both conversional spin-rotation constants $R^{HE}_{\pm}$ and $R^{HE}_{(\pm)}$ obtained here for fluoromethane are roughly one and half times more than the respective constants of (deutero)methane. This difference in reality is slightly less even because to estimate the conversional rate we have taken into account only the most sharp accidental resonances, i.e. the most coupled rotational levels of nuclear spin modifications. There is a more complete set of these resonances with $J \leq 80$ in [11].

The degree of asymmetry for spin-rotation tensor $\mathbf{R}$ still remains unclear. The asymmetry of $\mathbf{R}$ is absent for methane because of sufficiently high $T_d$-symmetry. But we have only supposed the antisymmetric term $\mathbf{R}^{(\pm)}_{\mp}$ to be zero for fluoromethane.

The constant $R^{HE}_{\pm}$ in contrast to both $R^{HE}_{(\pm)}$ manifests itself in spectra as hyperfine doubling of rotational levels with $K = 1$ [27,4]. One can find it, e.g., using the magnetofield spectrum of nonlinear-optical resonance [2]. More promising alternative way of finding all the three conversional spin-rotation constants was described by authors of [28]. They had suggested to measure the nuclear spin conversion of fluoromethane in the presence of electric field. The Stark-induced crossings of rotational levels would allow to disentangle the conversional spin-rotation and spin-spin contributions. The spin-spin contribution can be used as a scale to measure the spin-rotation one in this method. The last circumstance is especially attractive since it allows to remove the problems connected with the broadening of accidental resonances.

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7See also the footnote on p. 6.
ACKNOWLEDGMENTS

The author is indebted to P. L. Chapovsky and L. V. Il’ichov for the useful remarks and assistance. This work was financially supported by the Russian Fund for Basic Researches (Grant No. 98-03-33124a).
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TABLES

TABLE I. The most weighty conversional resonances for $^{12,13}$CH$_3$F isotopes.

| Isotope | $J', K'/J, K$ | $\Delta J/\Delta K$ | $\omega_{J'K'/JK}$ | $\omega_{J'K'/JK}$ | $\Gamma_{J'K'/JK}$ | $P_{J'K'/JK}$ |
|---------|----------------|---------------------|-------------------|-------------------|-----------------|-------------|
| $^{12}$CH$_3$F | 9, 2/10, 0 | 1/2 | 2816.8/2808.2 | 8.592 | 17.4 | 494 |
| — | 15, 7/17, 6 | 2/1 | 12476/12474 | 1.756 | 18.8 | 93 |
| — | 28, 5/27, 6 | 1/1 | 23931/23930 | 1.185 | 8.8 | 135 |
| — | 51, 4/50, 6 | 1/2 | 69356/69356 | -0.048 | 2.8 | 17 |
| $^{13}$CH$_3$F | 11, 1/9, 3 | 2/2 | 3411.3/3411.2 | 0.130 | 17.4 | 7 |
| — | 21, 1/20, 3 | 1/2 | 11605/11605 | -0.352 | 16 | 22 |

$^a$In accordance with [1].
$^b$(GHz).
$^c$(MHz/Torr). See [13].
$^d$(Torr).

TABLE II. The coefficients $a_{\perp(J'K'/JK)}^{HR}$ and $a_{\perp(J'K'/JK)}^{HR(\sigma'\sigma)}$ of quadratic $R$-forms in (23). The conversional spin-rotation and spin-spin contributions.$^a$

| $a_{\perp(J'K'/JK)}^{HR}$ | $a_{\perp(J'K'/JK)}^{HR(++)}$ | $2a_{\perp(J'K'/JK)}^{HR(+-)}$ | $a_{\perp(J'K'/JK)}^{HR(-+)}$ | $\gamma_{ss(J'K'/JK)}^{(P)}$ | $\gamma_{ss(J'K'/JK)}^{(P)}$ |
|------------------------|--------------------------|--------------------------|--------------------------|-------------------|-------------------|
| 0.011 | 0 | 0 | 0 | 0.64 | 0.91 |
| 0 | 0 | 0 | 0 | 0 | 0.71 |
| 0 | 0.92 | -1.87 $\times$ 10$^{-3}$ | 10$^{-6}$ | 23.65 | 0.78 |
| 0.14 | 0 | 0 | 0 | 8.19 | 0.45 |
| 0 | 0 | 0 | 0 | 0 | 800 |
| 12.5 | 0 | 0 | 0 | 732 | 410 |

$^a$The rows of Table I are continued here.
$^b$(10$^{18}$)$\mu$Hz/Torr.
$^c$($\mu$Hz/Torr).