Nuclear spin conversion in CH₃F at elevated temperatures

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Experimental data on the temperature dependence of the ortho-para nuclear spin conversion rate of gaseous CH_3F are presented. In the range 300–750 K, the $^{12}CH_3F$ conversion rate increases by one order of magnitude. By contrast, the conversion rate for $^{13}CH_3F$ *decreases* with increasing temperature (for $T < 600$ K). These results are in qualitative agreement with a theoretical model based on mixing of states due to *intramolecular* spin-spin interactions between the molecular nuclei. Above 600 K, the rate in $^{13}CH_3F$ starts to increase again, indicating a possible additional mechanism for the conversion. [S1050-2947(98)07505-2]

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I. INTRODUCTION

All symmetrical molecules having two or more identical nuclei with nonzero spin appear in nature as different nuclear spin isomers. A well known example is molecular hydrogen, which has two nuclear spin isomers: ortho- and para-H_2 [1]. The former has total nuclear spin $I = 1$, while the latter has $I = 0$. Many other symmetrical molecules have nuclear spin isomers as well [2].

Until recently, only the spin isomers of H_2 and D_2 were separated and studied. Since the development of convenient methods to separate the nuclear spin isomers also of polyatomic molecules, data about the conversion times have been published for CH_3F [3], D_2O [4], and H_2CO [5]. However, the mechanism behind the nuclear spin conversion remained largely unexplained.

In recent years extensive studies have been devoted to the nuclear spin conversion (ortho-para conversion) of CH_3F; see, e.g., Refs. [6–9] and references therein. CH_3F is so far the only molecule shown to have spin conversion in the gaseous phase without the aid of magnetic catalysts. The first experiments gave the following conversion rates for gaseous $^{12}CH_3F$ and $^{13}CH_3F$ (in units of 10^{-3} s^{-1}/Torr): 0.31 ± 0.03 and 14 ± 1 [6], respectively. More recent measurements yielded for $^{13}CH_3F$ a conversion rate of 12.2 ± 0.6 [7,10].

These data show that the nuclear spin conversion rates in CH_3F exhibit an anomalously large isotope dependence. For $^{13}CH_3F$ and $^{12}CH_3F$, the difference in conversion rates is a factor 46 ± 5 [6]. Big isotope effects are very unusual for gas phase collisional processes; see, for example, [11]. Presently, the anomalous isotope effect in the nuclear spin conversion of CH_3F is qualitatively understood [12,13]. Yet there are various unresolved problems, such as the lack of a quantitative explanation of the spin conversion process in $^{12}CH_3F$ molecules.

The present picture of the CH_3F nuclear spin conversion

for both C isotopes looks as follows. For $^{13}CH_3F$ the spin conversion is caused by intramolecular ortho-para state mixing due to spin-spin interaction between the molecular nuclei [6,8,12]. On the other hand, this mechanism gives too slow rates for $^{12}CH_3F$. Additional mixing by spin-rotation perturbation would bring the theoretical value closer to the experimental values in $^{12}CH_3F$ [14–17], but the parameters of the spin-rotation coupling in CH_3F remain largely unknown.

So far, no other processes that can contribute significantly to the spin conversion in CH_3F have been found. For example, the contribution to the spin conversion in CH_3F from the magnetic moment of the collision partner was shown to be very small [10,18]. Moreover, this contribution exhibits almost no isotope dependence [18].

In view of these uncertainties, additional experimental information is highly desirable. So far, all experiments on the nuclear spin isomers of CH_3F were performed at room temperature. A study of the spin conversion at elevated temperatures can elucidate the role of the excited molecular states in the conversion process. It can also help to learn more about possible mechanisms for intramolecular state mixing, and about the contribution to the conversion rate from other unknown processes.

The purpose of this paper is to present experimental results on the temperature dependence of the nuclear spin conversion in CH_3F. This temperature dependence, in turn, is compared with the mixing-of-states model.

II. EXPERIMENT

The CH_3F molecules have two nuclear spin isomers: ortho-CH_3F (the total spin of the three protons $I = 3/2$) and para-CH_3F ($I = 1/2$) [2]. The quantum states of ortho- and para-CH_3F should be antisymmetric under exchange of any two hydrogen nuclei. This implies a selection rule for the rotational quantum number K with respect to the total proton spin I. Here, K refers to the projection of the angular momentum **J** upon the molecular axis of symmetry. For the ortho-CH_3F isomer, K has to be zero or a multiple of 3, i.e., $K = 3n$ (with $n = 0,1,2,...$). For para molecules, $K \neq 3n$.

In the present experiments, the separation of the CH_3F
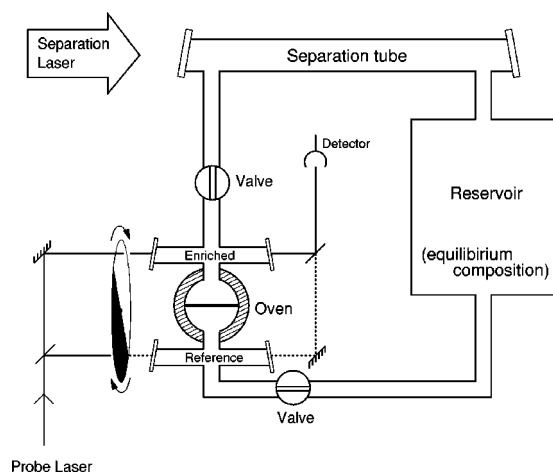
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FIG. 1. Principle of the setup used for separating and monitoring the nuclear spin isomers of CH$_3$F. The separation laser is tuned into the blue Doppler wing of a rovibrational absorption line, producing an ortho-enriched sample in the upper probe cell by light-induced drift. After closing the valves, the decay of the enrichment to the natural abundance ratio is monitored by a differential absorption measurement.

FIG. 2. An example of the enrichment and subsequent decay curve for the ^{12}CH$_3$F spin conversion at room temperature. The gas pressure is 0.79 Torr. The spin conversion rate in this example is 0.42×10^{-3} s^{-1}

nuclear spin isomers was achieved by using the light-induced drift (LID) effect, as was done in all our previous studies of the spin conversion in CH$_3$F (see, for example, [7]). This method is based on velocity selective excitation of one of the spin isomers in the Doppler wing of an absorption line by laser radiation. In our experiments we use rovibrational excitation at a wavelength of 9.6 μm. Since the gas-kinetic cross section of CH$_3$F is changed upon this excitation, drift of the resonant isomer (e.g., ortho) occurs relative to the nonresonant isomer (e.g., para). In a closed tube, this drift gives rise to a spatial separation of the isomers. For more details about the LID effect of CH$_3$F, the reader is referred to Refs. [19, 20].

The experimental setup is presented in Fig. 1. It was essentially similar for the experiments on both C isotopes of CH$_3$F. The separation of the ^{13}CH$_3$F nuclear spin isomers was achieved in a glass tube having an inner diameter of 3 mm and a length of 30 cm. The power of the CO$_2$ laser used for the isomer separation was 20 W.

For the separation of ^{13}CH$_3$F, we used the $9P(32)$ line of a CO$_2$ laser, which has a coincidence with the $R(4,3)$ transition in the ν_3 fundamental vibrational band. For separation of spin isomers of ^{12}CH$_3$F, we used the $9P(20)$ line of the CO$_2$ laser, which is close to the $Q(12,2)$ transition in the same ν_3 fundamental vibrational band. The LID effect for ^{12}CH$_3$F molecules is much smaller than for ^{13}CH$_3$F, mainly due to the smaller absorption coefficient. In order to obtain sufficient separation efficiency in the case of ^{12}CH$_3$F, we used a separation cell having a length of 1 m and an inner diameter of 1.1 mm.

For the detection of the conversion process, we monitored the time evolution of the absorption of an enriched sample. To this end an additional, low-power, waveguide CO$_2$ laser was used. The intensity and polarization of this laser were stabilized using an acousto-optic modulator (AOM) in a feedback loop. The frequency of the detection laser was locked to the line center of the $R(4,3)$ and the $Q(12,3)$ tran-
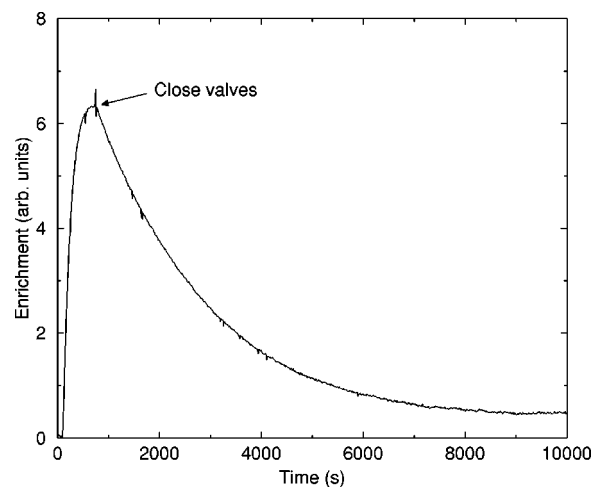
sition of ^{13}CH$_3$F and ^{12}CH$_3$F, respectively, to guarantee long term stability of the detection system. In case of ^{12}CH$_3$F molecules, the laser frequency was shifted by 180 MHz to bring the radiation frequency closer to the $Q(12,3)$ absorption line. This was achieved by using a double pass of the laser beam through the AOM.

In order to perform experiments at elevated temperatures, two extra volumes inside a temperature-controlled oven were connected to the detection cells (cf. Fig. 1), one of which served as a reference cell containing the equilibrium composition of the spin isomers. The choice of having two high-temperature volumes was made to keep the setup symmetrical, thus reducing drift and other instabilities of the detection signal. The setup was able to cover a temperature range of 300–900 K. The drift of the temperature inside the oven was less than 1 K in 30 min.

A measurement typically consisted of two stages: First, an enrichment of one nuclear spin isomer was produced with the two valves open (see Fig. 1). The enrichment was usually on the order of 5–10 %. The separation time was dependent on the length of the separation tube and the gas pressure and was in the range of 20–200 sec.

After the necessary amount of the enriched gas was collected in the test cell, the valves were closed and the decay of the enrichment to the natural abundance ratio of the two CH$_3$F spin isomers was monitored by the detection system. Modeling of this dependence by an exponential decay gives the conversion rate.

To be able to obtain reliable data about the conversion rate, we measured this decay during a few ''time of life'' periods. A typical decay curve for the ^{12}CH$_3$F molecules is shown in Fig. 2. In the case of ^{12}CH$_3$F molecules, the duration of each measurement was up to a few hours. This made the measurements rather difficult because of the long-term stability requirements involved. In the case of ^{13}CH$_3$F molecules, the measurements were much easier to perform, because of the faster conversion (almost two orders of magnitude).

III. RESULTS

We have measured the conversion rate of CH_3F as a function of the gas temperature at pressures ranging from 0.2 to 2 Torr at room temperature and from 0.25 to 0.65 Torr at the higher temperatures. Given the geometry of the setup and the pressures employed, diffusion was always fast compared to the time scale of the conversion process. Consequently, the enriched sample can be considered to a good approximation to be homogeneous throughout the cell. Since the molecules do not spend all of their time inside the heated volume, the measured conversion rate has to be corrected to yield the high-temperature value. To this end we assume that the probe cell consists of two volumes having elevated (''hot'') and room temperature (''cold''). Ignoring the temperature gradients between those two parts, we write the experimentally measured conversion rate γ_{meas} as

$$\gamma_{\mathrm{meas}} = \gamma_{\mathrm{cold}} P_{\mathrm{cold}} + \gamma_{\mathrm{hot}} P_{\mathrm{hot}}, \qquad (1)$$

where γ_{cold} and γ_{hot} are the conversion rates in volume V_{cold} and V_{hot}, respectively. P_i (i = hot, cold) is the probability for a molecule to be in volume V_i. From Eq. (1) we find

$$\gamma_{\mathrm{hot}} = \gamma_{\mathrm{meas}} + \frac{P_{\mathrm{cold}}}{P_{\mathrm{hot}}} (\gamma_{\mathrm{meas}} - \gamma_{\mathrm{cold}}). \qquad (2)$$

It is evident that in the case of fast diffusion, the probabilities P_i are equal to the ratio of the number of molecules in V_i to the total number of molecules in the cell. Since we operate in the hydrodynamic limit ($\bar{l}/R \ll 1$, where $\bar{l}$ is the mean-free path and R the relevant dimension of the cell), thermomolecular pressure difference can be neglected. This allows us to directly write $P_{\mathrm{cold}}/P_{\mathrm{hot}} = V_{\mathrm{cold}} T_{\mathrm{hot}}/(V_{\mathrm{hot}} T_{\mathrm{cold}})$, since the pressure is uniform. The ratio of the volumes in the setup of Fig. 1 was $V_{\mathrm{cold}}/V_{\mathrm{hot}} = 0.16$ for the experiments with $^{13}CH_3F$ and 0.17 for $^{12}CH_3F$. The difference arises from the longer detection tube used for $^{12}CH_3F$ to compensate for the smaller absorption coefficient.

In order to find the conversion rate γ in the gas phase, the contribution caused by molecule-surface interactions must be subtracted. Therefore, the conversion rate at each temperature was measured as a function of the gas pressure p. The slope of the conversion rate versus the gas pressure p yields the desired conversion rate γ in the bulk (see also Ref. [7]).

The observed temperature dependence of the conversion rate γ for $^{13}CH_3F$ is depicted in Fig. 3. It is seen that the conversion rate first *decreases* with increasing temperature and subsequently increases again at gas temperatures above $T \approx 600$ K. The experimental results for $^{12}CH_3F$ are depicted in Fig. 4. It is found that the conversion rate *increases* by more than one order of magnitude when the temperature is increased from room temperature to 750 K.

The immediate conclusion from these data is that there is indeed a big isotope effect in the CH_3F nuclear spin conversion at room temperature, consistent with the result obtained in [6]. The updated ratio between the spin conversion rates in $^{13}CH_3F$ and $^{12}CH_3F$ molecules at room temperature is
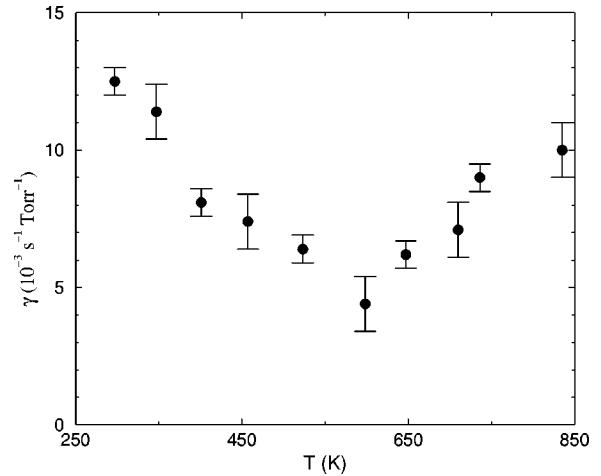
$$\gamma_{13}/\gamma_{12} = 55 \pm 4. \qquad (3)$$

FIG. 3. The conversion rate in $^{13}CH_3F$ as a function of the gas temperature.

The present measurements show that at elevated temperatures the difference in conversion rates gradually decreases and becomes very small above 600 K.

IV. DISCUSSION

So far the conversion process for CH_3F molecules could be understood in the framework of the mixing-of-states model (see, e.g., [12]). In this model, the conversion is caused by the ortho-para state mixing due to the *intramolecular* interactions, such as spin-spin interactions between the molecular nuclei. From a general treatment of spin conversion due to intramolecular state mixing, one finds for the conversion rate

$$\gamma = \sum_{\alpha' \alpha} \frac{2\Gamma}{\Gamma^2 + \omega_{\alpha' \alpha}^2} |V_{\alpha' \alpha}|^2 (W_\alpha + W_{\alpha'}). \qquad (4)$$

Here, Γ is the relaxation rate, which can be associated with the rotational level population decay rate, $\hbar \omega_{\alpha' \alpha}$ is the en-
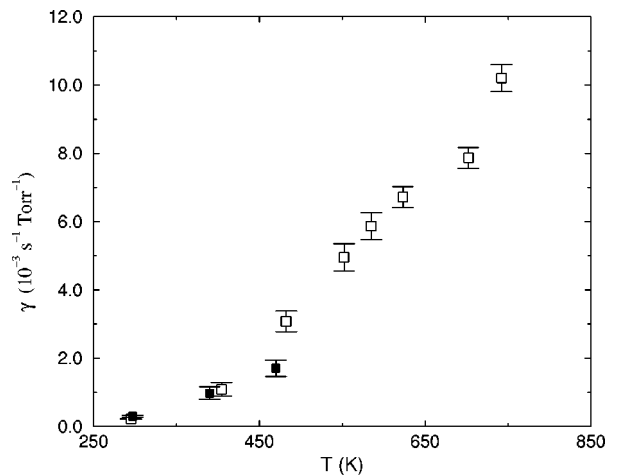

FIG. 4. The conversion rate in $^{12}CH_3F$ as a function of temperature. The open squares were measured in a setup as described in Sec. II. The solid squares were measured in a setup as described in [6] with two extra heaters attached to the detection cells to be able to operate at elevated temperatures.

TABLE I. Energy differences of the level pairs that are most strongly mixed by nuclear spin dipole-dipole interactions in CH$_3$F and their calculated contributions to the conversion rate at 1 Torr and 295 K. The energy difference $\omega_{\alpha'\alpha}$ is calculated using spectroscopic data from [21] and [22] for ^{12}CH$_3$F and ^{13}CH$_3$F, respectively. The rotational relaxation rate is taken as $\Gamma = 10^8$ s^{-1} in these calculations.

Molecule	Level pair	$\omega_{\alpha'\alpha}$ (GHz)	$\gamma(10^{-3}$ s$^{-1})$
^{12}CH$_3$F	(9,2)-(10,0)	8.5917	5.191×10^{-3}
	(15,7)-(17,6)	1.7457	3.785×10^{-3}
	(28,5)-(27,6)	1.1892	8.753×10^{-3}
	(51,4)-(50,6)	-0.0413	1.998×10^{-2}
^{13}CH$_3$F	(11,1)-(9,3)	0.1310	4.432
	(21,1)-(20,3)	-0.3510	2.521

ergy gap between para (α') and ortho (α) rotational levels, $V_{\alpha'\alpha}$ is the matrix element of the intramolecular interaction, which mixes $|\alpha\rangle$ and $|\alpha'\rangle$ states, W_α is the Boltzmann occupation of the rotational state $|\alpha\rangle$, and the summation has been taken over all ortho-para level pairs.

If we apply this mixing-of-states model to CH$_3$F, we find that only a few pairs of levels can be efficiently mixed (see Table I) [12]. This has as a consequence that the molecules ''funnel'' through those levels from the ortho to the para subspaces and vice versa. For the ^{12}CH$_3$F molecule, there are only four level pairs efficiently mixed by nuclear spin-spin interaction. For ^{13}CH$_3$F there are only two important pairs.

The strongly mixed level pairs are situated at very different energies for the two C isotopes (see Fig. 5). For ^{12}CH$_3$F, the most important (J,K)-(J',K') level pair (50,6)-(51,4) is at $E/hc \approx 2313$ cm^{-1} (10 times higher than the thermal energy at room temperature), whereas for ^{13}CH$_3$F the most strongly mixed level pair (9,3)-(11,1) is situated near thermal energy: $E/hc \approx 114$ cm^{-1} ($kT = 205$ cm^{-1} at room temperature).

From Eq. (4) we see that the dependence of the conversion rate on the temperature is caused, first of all, by the level occupations W_α and $W_{\alpha'}$. Since the efficiently mixed levels
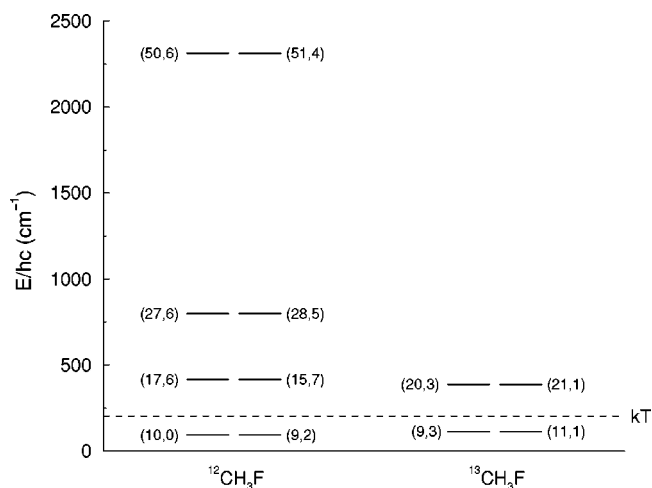

FIG. 5. Energy diagram of the strongly mixed levels by the spin-spin interaction between the molecular nuclei for both C isotopes of CH$_3$F.
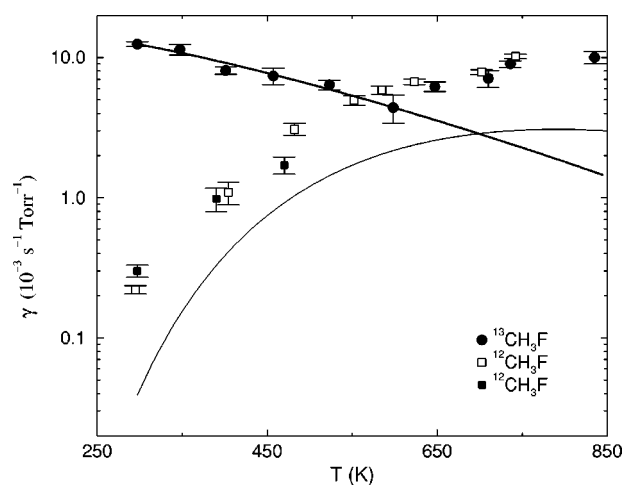

FIG. 6. The measured conversion rate as a function of temperature for ^{12}CH$_3$F (filled and open squares) and ^{13}CH$_3$F (●) on a logarithmic scale. The solid lines are the calculated conversion rates in the mixing-of-states model for ^{12}CH$_3$F (—) and ^{13}CH$_3$F (——). In the calculation, the same temperature dependent values for Γ were taken for both C isotopes of CH$_3$F [see Eq. (5)].

are situated at very different energies in ^{12}CH$_3$F and ^{13}CH$_3$F molecules, we expect different temperature dependences for the two C isotopes.

An additional temperature dependence may appear due to the possible temperature dependence of the relaxation rate Γ [see Eq. (4)]. Since it is very difficult to measure or to calculate Γ, we took Γ to be slightly temperature dependent in order to fit the measured conversion rates of ^{13}CH$_3$F in the temperature range of 300–600 K. This yields the following temperature dependence of Γ (in units of 10^8 s^{-1}/Torr):

$$\Gamma(T) = 1.8 - (T - T_{\text{cold}}) \times 1.5 \times 10^{-3}, \qquad (5)$$

where the temperature T should be taken in K, and T_{cold} is room temperature (295 K). The temperature dependence (5) was subsequently used to calculate the conversion rate in ^{12}CH$_3$F.

The modeling (5) of Γ gives only 25% correction to Γ in the temperature range 300–600 K. On the other hand, the decrease of the ^{13}CH$_3$F conversion rate in the same temperature range is almost threefold. Thus the main reason for the decrease of the spin conversion rate in ^{13}CH$_3$F is the decrease of the occupation of the mixed levels at elevated temperatures.

We have calculated the temperature dependence of the conversion rate for ^{12}CH$_3$F and ^{13}CH$_3$F assuming that the mixing of the ortho and para states is caused by the nuclear spin-spin interaction between the molecular nuclei. The results of these calculations are shown as solid lines together with the experimental data in Fig. 6. Here we took into account that at high temperatures part of the molecules are in excited vibrational states, which are assumed not to contribute to the conversion (i.e., the energy levels are assumed to be no longer near-degenerate in the excited vibrational states). It should be stressed, however, that this is a mere conjecture since the details of the rotational level structure in the vibrationally excited state are not known to a sufficiently high accuracy.

As seen from Fig. 6, one finds qualitative agreement between the calculated and the measured conversion rates in CH_3F. The measurements and the calculations both exhibit similar trends: *decrease* of the conversion rate in $^{13}CH_3F$ and fast *increase* of the conversion rate in $^{12}CH_3F$. Yet there is a difference between the numerical values of the calculated rates in $^{12}CH_3F$ and the measured rates. This can be partially attributed to our simplified modeling of the relaxation rates Γ, which were taken to be the same for all rotational levels involved. Additional room for improvement would be taking into account spin-rotation mixing in $^{12}CH_3F$ molecules [14–17].

For $^{13}CH_3F$ we see that the conversion rate above 600 K rises, in contrast to what one expects on the basis of the mixing-of-states model. It is possible to give a qualitative explanation for this behavior if we assume that part of the conversion takes place in the excited vibrational states. This may be experimentally verified in the future.

V. CONCLUSIONS

The temperature dependence of the conversion rate has been measured for both carbon isotopes of CH_3F. For $^{13}CH_3F$, the conversion rate *decreases* with increasing temperature (in the temperature range 300–600 K), whereas for $^{12}CH_3F$ the conversion rate rapidly increases with temperature. These opposite temperature dependences can be explained qualitatively in the framework of a model based on ortho-para state mixing by intramolecular spin-spin interactions between the molecular nuclei. This model predicts that the most strongly mixed level pairs are situated at very different energies for the two molecules studied. The most strongly mixed level pairs for $^{12}CH_3F$ are situated at energies that are one order of magnitude higher than kT at room temperature, but for $^{13}CH_3F$ the most strongly mixed levels are situated near thermal energy at room temperature. Consequently, a change in temperature affects the occupation of these levels quite differently, which results in an opposite temperature dependence of the spin conversion rates in $^{12}CH_3F$ as compared to $^{13}CH_3F$.

The measurements of the conversion rates at temperatures above 600 K for $^{13}CH_3F$ suggest that there is a possible additional process effective in the excited vibrational states. Since the occupation of these levels at temperatures below 600 K is very small, this effect was not seen before. Further investigation to clarify this point is required.

ACKNOWLEDGMENTS

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