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Precise measurement of hyperfine coupling in ^{13}CH$_3$F based on nuclear spin conversion

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Abstract. A new method is proposed for the experimental determination of the hyperfine coupling in molecules. The method is based on the level-crossing effect in the spin isomer conversion in alternating electric fields. An experiment performed with the ^{13}CH$_3$F molecules has revealed the strength of the off-diagonal in K ($\Delta K = 2$) nuclear spin-spin coupling 69.6 ± 1 kHz, which is only by 0.4 ± 1 kHz larger than the theoretical value calculated on the basis of the molecular structure.

PACS. 31.30.Gs Hyperfine interactions and isotope effects, Jahn-Teller effect – 32.80.Bx Level crossing and optical pumping – 33.15.Dj Interatomic distances and angles

1 Introduction

There is a significant amount of experimental and theoretical data which proves that ortho-para conversion in CH$_3$F is governed by quantum relaxation (for the review see [1]). This specific type of relaxation has two main ingredients: *intramolecular* mixing of ortho and para states and interruption of this mixing by *collisions*. One can expect similar mechanism of conversion in other polyatomic molecules. A possible application of this phenomenon is to study an intramolecular hyperfine coupling making use of the fact that it is responsible for the ortho-para mixing. Such a method would be complementary to those developed in high-resolution spectroscopy because it would supply information hardly accessible in another way. As an example we refer to the proposal [2] to use the CH$_3$F isomer conversion to measure a transverse anisotropy of the spin-rotation hyperfine interaction in this molecule.

Mixing of many ortho-para level pairs usually contributes to the isomer conversion which complicates the analysis of the process. An efficient way to disentangle these contributions is to use the level-crossing effect [3] and to measure the conversion spectra. It allows, in principle, to reveal the intramolecular hyperfine coupling for each individual ortho-para level pair. This approach was proven to be feasible in references [3,4] where nuclear spin-spin coupling was determined with the accuracy ≈ 10%. Naturally, the question arises whether this accuracy can be improved further.

One way to solve the problem would be to improve the measurements of the conversion spectra. Unfortunately, it appeared to be not easy. There are two experimental arrangements proposed so far. The first one [3] consists in measuring the conversion spectrum point by point. The main drawback is that one has to take many points at well-defined experimental conditions in order to be able to fit the complicated spectrum of the isomer conversion.

Measurement of the conversion spectra using continuous scanning of electric field was demonstrated in references [5,6]. The spectrum resembles both the theoretical curve and the spectrum taken point by point in [3]. Unfortunately, an exact meaning of "y-axis" of the spectrum obtained by continuous scanning remains uncertain at the moment. The signal is resulting from a complicated interplay between an enrichment process and isomer conversion which is difficult to calibrate experimentally or describe theoretically.

Recently it was demonstrated [7] that the CH$_3$F spin conversion can be controlled in time by using an alternating electric field to produce ortho-para level crossings. An adequate theoretical model of the conversion in an alternating electric field was also proposed in [7]. This work opens up a variety of new possible applications of the spin conversion in molecules. The goal of the present paper is to demonstrate that the spin conversion in alternating electric field having a specific form and high homogeneity (both different from that used in [7]) can serve as a new approach to the problem of precise measurement of the hyperfine coupling in molecules. As will be shown below, the method appeared to be rather accurate, relatively simple and free from many disadvantages of the previous

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approaches. The theory and experiment in the present paper are done for the ^{13}CH$_3$F molecules.

2 Theory

The CH$_3$F molecules exist in the form of two nuclear spin isomers [8]. 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. Consequently, the rotational quantum states of CH$_3$F are divided into two, ortho and para, subspaces.

The essence of the CH$_3$F isomer conversion can be briefly described as follows. Suppose that at the instant $t = 0$ a test molecule is placed into the ortho subspace. Due to collisions with surrounding gas particles, which cannot change molecular spin state, the test molecule starts to perform rotational relaxation *inside* the ortho subspace. This running up and down along the ladder of the ortho states continues until the molecule jumps in the state m 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.* [9] (see also [10]).

Quantitative description of the process can be performed in the framework of density matrix formalism. It was shown [10] that relaxation of a nonequilibrium concentration of, *e.g.*, ortho molecules, $\delta\rho_{\rm o}(0)$, created at the instant $t = 0$ will decay exponentially: $\delta\rho_{\rm o}(t) = \delta\rho_{\rm o}(0)\exp(-\gamma t)$, with the rate

$$\gamma = \sum_{\alpha\in {\rm o},\alpha'\in {\rm p}} \frac{2\Gamma_{\alpha\alpha'}|V_{\alpha\alpha'}|^2}{\Gamma^2_{\alpha\alpha'} + \omega^2_{\alpha\alpha'}} \left(W_\alpha + W_{\alpha'}\right) . \qquad (1)$$

Here the summation was made over all ortho-para level pairs. $\Gamma_{\alpha\alpha'}$ is the collisional decay rate of the off-diagonal density matrix element $\rho_{\alpha\alpha'}$ ($\alpha \in$ ortho, $\alpha' \in$ para); $\hat{V}$ is the intramolecular perturbation which mixes the ortho and para states; $\omega_{\alpha\alpha'}$ is the gap between the states $|\alpha\rangle$ and $|\alpha'\rangle$; W_α and $W_{\alpha'}$ are the Boltzmann factors.

The level-crossing effect in isomer conversion [3] appears if one crosses the ortho and para states, by using, *e.g.*, an external electric field. In the low pressure limit, $\Gamma \ll \omega$, such crossings produce sharp rise of the conversion rate, as it is evident from equation (1). Scanning of the electric field gives the *conversion spectra*. Analysis of the conversion spectra allows, in principle, to find out all parameters of the model. Nevertheless, the difficulties remain because each peak in the conversion spectrum is characterized by its position, width and height. Consequently, one should perform complicated measurements of the line profile of each peak. There is also the problem of the overlapping of different peaks in the conversion spectra. The situation is quite similar to classical spectroscopy with one important difference that measurements of the conversion spectra are more complicated at present than in spectroscopy.

Let us turn now to the essence of the method proposed in this paper. First we note that an integral over all frequencies of any individual peak in equation (1) does not contain Γ any more. Indeed, one has

$$2|V|^2\left(W + W'\right)\int_{-\infty}^{\infty} \frac{\Gamma}{\Gamma^2 + \omega^2}{\rm d}\omega = 2\pi|V|^2\left(W + W'\right) . \qquad (2)$$

Here we dropped for simplicity the indexes which specify the molecular states. This result constitutes the well-known fact that the area under a Lorentzian curve does not depend on the line width [11]. The relation (2) is in the heart of our method. In short, one should mimic the integration over frequency by measuring the conversion spectra in an alternating electric field adjusted such that molecule pass many times through the profile of each level-crossing resonance during the conversion process. Such experimental arrangement should make the contribution to the conversion arising from each level pair being independent on Γ and position of the peak. Let us consider this process in more detail for a single ortho-para level pair. Similar to the reference [7] one can show that if the frequency of an alternating electric field responsible for the level crossings is much larger than the conversion rate, the isomer conversion is exponential with the decay rate, $\gamma_{\rm St}$, given by the expression

$$\gamma_{\rm St} = \frac{1}{T}\int_0^T \frac{2\Gamma|V|^2}{\Gamma^2 + \omega^2(t)}\left(W + W'\right){\rm d}t, \qquad (3)$$

where $\omega(t)$ is the frequency gap between the ortho and para states which is now time dependent due to the time dependent Stark effect. T is the period of Stark modulation.

In case of triangular type Stark modulation, the frequency gap is given, at first order of the Stark effect, by

$$\omega(t) = \omega_0 + Rf(t), \qquad (4)$$

where ω_0 is the gap between the states without electric field; R is the amplitude of the Stark modulation; $f(t)$ is a periodic function shown in Figure 1.

It is easy to calculate integral (3) with $\omega(t)$ from (4). Note that the two halves of the period gives equal integrals. Thus one has

$$\gamma_{\rm St} = \frac{|V|^2\left(W + W'\right)}{R} \times \left[\arctan\left(\frac{\omega_0 + R}{\Gamma}\right) - \arctan\left(\frac{\omega_0 - R}{\Gamma}\right)\right] . \qquad (5)$$

If the electric field is large, $R \gg \{\omega_0, \Gamma\}$, the conversion rate becomes equal

$$\gamma_{\rm St} = \pi\frac{|V|^2}{R}\left(W + W'\right) , \qquad (6)$$

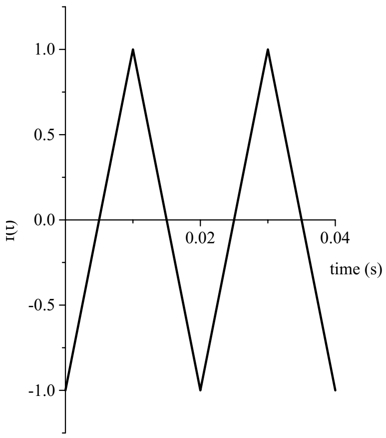

Fig. 1. Modulation function used in the experiment. Frequency of modulation equals to 50 Hz.

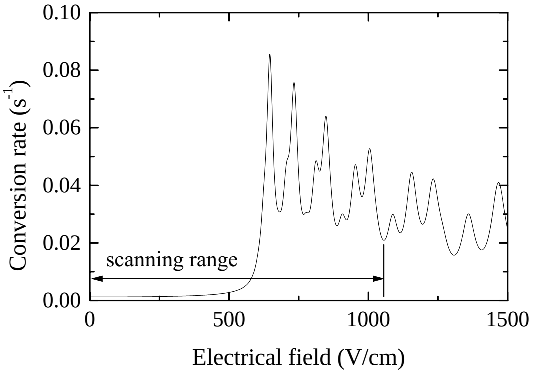

Fig. 2. "Conversion" spectrum for the isomer conversion in ^{13}CH$_3$F. Gas pressure is equal to 0.1 torr.

and does not depend on Γ and ω_0. However, it is not practical to make the Stark modulation amplitude R extremely large. Consequently, one cannot eliminate the pressure dependence completely. The expression for $\gamma_{\rm St}$ up to the first order correction is

$$\gamma_{\rm St} = \frac{|V|^2\,(W+W')}{R}\left(\pi - 2\frac{\Gamma}{R}\right); \quad R^2 \gg (\omega_0^2+\Gamma^2). \tag{7}$$

This pressure dependence is weak because usually $\Gamma \ll R$. Equation (7) gives simple intuitive picture of the difference between the conversion spectra in DC electric field and in AC electric field proposed here. The height of each peak in conversion spectra is proportional to $1/\Gamma$ (see Eq. (1)). Thus the knowledge of the decoherence rate, Γ, is essential for determination of the strength of the ortho-para mixing from the conversion spectra in a DC electric field. Contrary to that, by using the alternating electric field, one has a conversion rate in which the Γ-dependent term is a small correction. Even more, this pressure dependence can be eliminated if one extrapolates $\gamma_{\rm St}$ to zero pressure ($\Gamma = 0$).

Let us consider now the ^{13}CH$_3$F isomer conversion in more detail. There are only two ortho-para level pairs which almost completely determine the isomer conversion in this molecule. The most important level pair ($J = 9, K = 3$)-$(11,1)$ has the gap 131 MHz. The level-crossing spectrum of the isomer conversion in a DC electric field [3, 12] produced by the crossings of magnetic M-sublevels of this level pair is shown in Figure 2. The second important level pair $(20,3)$-$(21,1)$ has a larger gap (350 MHz) and consequently has its peaks well outside the electric field range shown in Figure 2. The amplitude of each peak of the spectra in Figure 2 is given by

$$\frac{2}{\Gamma_{\alpha\alpha'}}\langle J',K',2,q'|J,K\rangle^2\langle J',M',2,M{-}M'|J,M\rangle^2|\mathcal{T}_{2,q'}|^2 \times (W_\alpha + W_{\alpha'})\,. \tag{8}$$

Here $\langle\cdots|\cdots\rangle$ stands for the Clebsch-Gordan coefficient; $\mathcal{T}_{2,q'}$ is the strength of the off-diagonal ($q' = K - K'$) spin-spin coupling in ^{13}CH$_3$F: for more detail about ortho-para spin-spin mixing in ^{13}CH$_3$F and on the conversion spectra in a DC electric field see [10,12]. The value of $\mathcal{T}$ calculated on the basis of the ^{13}CH$_3$F vibrational ground state averaged structure: $r_{\rm CF} = 1.390(1)$ Å, $r_{\rm CH} = 1.098(1)$ Å, and β(F−C−H) $= 108.7(2)°$ [13,14] reads

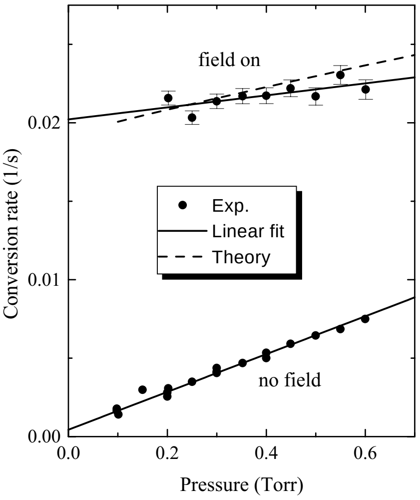

Fig. 3. Conversion rate in ^{13}CH$_3$F as a function of the gas pressure.

$$\mathcal{T}_{2,2} = 69.2 \pm 0.2 \text{ kHz}. \tag{9}$$

In our experiment the available amplitude of Stark modulation was limited by electric breakdown of the CH$_3$F gas. The right choice of the Stark amplitude R should be such that scanning of an electric field ends up in the middle between two peaks in the conversion spectra [15]. We have chosen the electric field amplitude equal to the amplitude of 1070±10 V/cm. This scanning range is indicated in Figure 2.

The numerical calculation of the conversion rate $\gamma_{\rm St}$ in an alternating electric field was done on the basis of equation (5) which was applied to all magnetic sublevels of the ortho-para level pair ($J = 9, K = 3$)-$(11,1)$. The contribution to the rate arising from the level pair ($J = 20, K = 3$)-$(21,1)$ appeared to be small (10% at 0.5 torr) and proportional to pressure. Furthermore, the contribution to the conversion from this level pair disappears if one extrapolates the conversion rate to zero gas pressure. The results of the calculation are given by the dashed line in Figure 3.

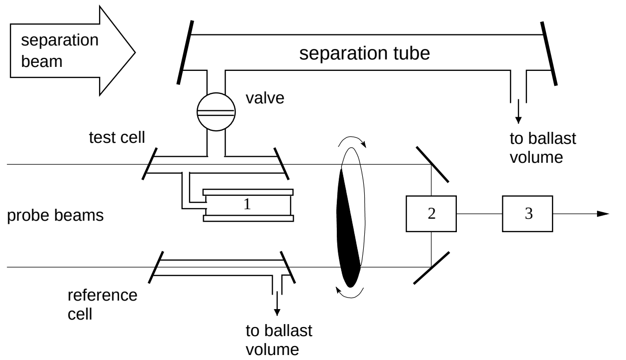

Fig. 4. Schematic of the experimental setup. The two weak (probe) beams are modulated in antiphase by a chopper and are sent to the same detector (2). The reference cell and the rear side of the separation cell are connected to the same ballast volume to ensure an equilibrium isomer composition; (1)-Stark cell; (3)-lock-in amplifier

3 Experiment

Schematic of the experimental setup in shown in Figure 4. In contrast to the previous experiment with an alternating electric field [7] the level crossings are now produced in a separate Stark cell (the same cell was used in [3]). This change was made in order to avoid an uncertainty in the electric field strength which is present if one uses external Stark electrodes. The Stark cell was made from a glass cylinder of 4.22 mm high and 19 mm of inner diameter sealed off by two flat gold coated glass plates which served as Stark electrodes. Triangular shape electric voltage was applied to the Stark cell from a high voltage amplifier which was driven by a Philips PM5193 programmable synthesizer.

As in the previous experiments on CH_3F spin isomers, we used the Light-Induced Drift effect [16] for the spin isomer enrichment. It was done in a glass capillary (1 mm inner diameter, 1 m long) by a ≈10 W beam from a CO_2-laser (PL5, Edinburgh Instruments) tuned to the 9P32 line. This radiation is absorbed by the $R(4,3)$ line from the ν_3 vibrational band of $^{13}CH_3F$. Relative positions of the CO_2-laser lines and absorption lines of $^{13}CH_3F$ see, *e.g.*, in [17]. The detection of the spin isomer concentration was performed with the help of an additional, frequency stabilized, waveguide CO_2-laser tuned also to the 9P32 line. Example of the enrichment and decay is given in the Figure 5. Such curves were recorded for various pressures with and without Stark field. The isomer decay rate ($\gamma_{\rm exp}$) was found by fitting the decay part by the expression $a\ \exp(-\gamma_{\rm exp}t) + b$, where the term b accounts for the possible offset in the signal. Similar processing was performed in [7].

4 Results and discussion

As was concluded above, one should extrapolate the conversion rate $\gamma_{\rm St}$ to zero gas pressure. It is clear that this value of $\gamma_{\rm St}$ will contain also a “wall contribution” in addition to the bulk contribution, which we only need. The wall contribution can be determined from the pressure dependence of the conversion rate without electric field. Results of these measurements are given in Figure 3. These data are well fit by a linear pressure dependence of the form

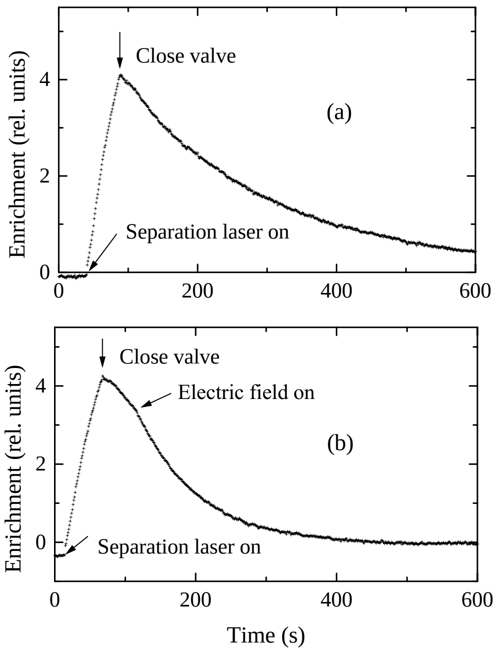

Fig. 5. The isomer enrichment and decay curves. The gas pressure equals to 0.5 torr; (a)-without electric field; (b)-electric field was switched on in the course of the decay.

$$\gamma = (0.44 \pm 0.11) \times 10^{-3} + (12.1 \pm 0.6) \times 10^{-3} P. \quad (10)$$

Here the rate is in s^{-1} and P is a pressure in torr. In (10) and below we indicate one standard deviation of statistical error. The y intercept of the pressure dependence (10) gives the wall contribution to the rate in our setup: $(0.44 \pm 0.11) \times 10^{-3}\ s^{-1}$.

Stark electric field fills only part of the test cell volume. Consequently, the measured “field-on rates”, $\gamma_{\rm exp}$, should be processed in order to find the conversion rate inside the Stark cell, $\gamma_{\rm St}$. This point needs careful consideration. If the diffusion equilibration inside the test cell would be much faster than the conversion rate (the steady-state case) the conversion rate would be [3]

$$\gamma'_{\rm St} = \gamma_{\rm exp} + \frac{V_0}{V_{\rm St}}(\gamma_{\rm exp} - \gamma_0), \quad (11)$$

where $V_{\rm St}$ and V_0 are the Stark cell volume and the rest of the test cell volume, respectively; $\gamma_{\rm exp}$ and γ_0 are the measured rates with and without electric field, respectively.

In fact, diffusional equilibration in the test cell is not infinitely fast. One can model the diffusion process by assuming the test cell in the form of two volumes: $V_{\rm St}$ and V_0 connected by a small volume canal which has in our setup the cross-section $s = 0.8\ {\rm mm}^2$ and the length $l = 4$ cm.

An account of the diffusion in such a system leads to the following expression for the conversion rate

$$\gamma_{\rm St} = \frac{\gamma'_{\rm St} + \gamma_{\rm exp}\gamma_0\tau_{\rm d}}{1 + (\gamma_0 - \gamma_{\rm exp})\tau_{\rm d}}, \tag{12}$$

where $\tau_{\rm d} = V_0 l/Ds$ is the diffusion time in the system; D is the diffusion coefficient. Equation (12) gives $\approx 4\%$ bigger values at the gas pressure 0.5 torr in comparison with equation (11). One may note that this correction disappears if the gas pressure is extrapolated to zero because $\tau_{\rm d} \rightarrow 0$. This is one extra reason to perform an extrapolation of the conversion rates to zero gas pressure.

The conversion rates, $\gamma_{\rm St}$, are given in Figure 3. They are well approximated by a linear pressure dependence. The y intercept of the fit after subtracting the wall contribution is $(19.7 \pm 0.6) \times 10^{-4}$ s^{-1}, which corresponds to the hyperfine coupling equals to 69.6 ± 1 kHz. This result being compared with (9) gives the difference between experimental and theoretical values of the spin-spin interaction in ^{13}CH$_3$F

$$\mathcal{T}_{\rm exp} - \mathcal{T}_{\rm theor} = 0.4 \pm 1 \text{ kHz}. \tag{13}$$

Thus we can see that these values are identical within the experimental error. It gives the quantitative test of the isomer conversion in ^{13}CH$_3$F by quantum relaxation.

The interesting point is to which extend the isomer conversion can be useful for the verification of the molecular structure. This goal can be reached only if the accuracy of the measurements would be considerably improved to be able to compete with the present very accurate methods [18]. On the other hand, present accuracy of the isomer conversion experiment is already sufficient to distinguish between the molecular equilibrium ($r_{\rm e}$) and ground state averaged ($r_{\rm z}$) structures, which correspond, respectively, to

$$\mathcal{T}_{2,2}(r_{\rm e}) = 71.6 \pm 0.4 \text{ kHz};\quad \mathcal{T}_{2,2}(r_{\rm z}) = 69.2 \pm 0.2 \text{ kHz}. \tag{14}$$

These theoretical values should be compared with the experimental one, 69.6 ± 1 kHz. It is clear that the molecular ground state averaged structure is relevant to the isomer conversion because of very fast molecular vibration in comparison with the conversion.

5 Conclusions

We have proposed a new method for the measurements of the intramolecular hyperfine coupling based on the conversion of nuclear spin isomers. It consists in the use of the level-crossing effect in isomer conversion induced by an alternating electric field. We performed measurements for the ^{13}CH$_3$F molecules which results in accurate determination of the nuclear spin-spin coupling off-diagonal in K ($\varDelta K = 2$). The experimentally determined hyperfine coupling term differs from the theoretical value calculated on the basis of the molecular structure by 0.4 ± 1 kHz only. (One standard deviation of statistical error is indicated here.) This result provides the most stringent present test of the theory of the isomer conversion in ^{13}CH$_3$F.

In this paper we concentrated mainly on testing the feasibility of the proposed method and did not spent too much efforts on polishing the measurements themselves. Even in this first trial, the method has allowed to determine the hyperfine coupling with the accuracy of 1 kHz. Further improvement of the experimental accuracy by factor of 10 is possible at relatively low cost.

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