Conversion of nuclear spin modifications of CH_3F molecules in the gaseous phase

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(Submitted 14 November 1989)
Zh. Eksp. Teor. Fiz. **97**, 1585–1596 (May 1990)

An experimental study showed that conversion of nuclear spin modifications of CH_3F molecules took place in the gaseous phase. The spin conversion rate was proportional to the gas pressure and the coefficients of proportionality were $1.1 \pm 0.1\ \mathrm{h^{-1}\cdot Torr^{-1}}$ for the $^{12}CH_3F$ molecules and $0.85 \pm 0.06\ \mathrm{min^{-1}\cdot torr^{-1}}$ for $^{13}CH_3F$. The conversion was clearly due to "nonmagnetic" collisions of molecules under conditions of mixing of energetically similar ortho- and para-levels in the ground state of a molecule.

Investigations of nuclear spin modifications of molecules have a long history. In the late twenties the existence of ortho- and para-modifications of molecular hydrogen was first predicted[1] and then confirmed.[2] Since then for over sixty years the unusual properties of the spin modifications of hydrogen have attracted the interest of researchers. The stability of these specific states of hydrogen is very striking: the very low binding energy of the spin in a molecule (associated with a weak hyperfine interaction) means that the conversion time of the spin modifications of H_2 may exceed a year at atmospheric pressure.[3]

The existence of nuclear spin modifications of molecules is a consequence of very general principles of quantum mechanics and is due to the symmetry of the molecule and the statistics of equivalent nuclei in the molecule.[4] Therefore, nuclear spin modifications should be exhibited in general by all the molecules with equivalent nuclei with a nonzero spin. This has been confirmed convincingly by the line intensity alternation effect which is familiar in molecular spectroscopy (see, for example, Ref. 5). Therefore, the existence of nuclear spin modifications of molecules with equivalent nuclei follows from theoretical predictions, has been confirmed experimentally, and is now accepted as a matter of course.

By analogy with hydrogen, it is equally generally assumed that the spin states of all molecules have long lifetimes. However, it has been very difficult to obtain any experimental configuration of this view because over a period of several decades the attempts to separate1) spin modifications of all the molecules with the exception of H_2, D_2, and T_2 have been unsuccessful. The situation had seemed to be so hopeless that the interest in the study of spin modifications of complex molecules completely disappeared. The situation has changed recently. New methods have appeared for the separation of spin modifications. Selective photoionization has been used to separate the spin modifications of I_2 (Ref. 6), H_2 (Ref. 7), and formaldehyde (Ref. 8), the light-induced drift effect has been used to separate the spin modifications of CH_3F (Ref. 9), whereas the condensation in a molecular beam has been used to do the same for H_2O molecules.[10]

Naturally, these are only the first steps in a new and extensive topic of the properties of spin modification of complex molecules. There are still many unsolved problems. In particular, some of the published papers report measurements and estimates of the conversion time of spin modifications, but not the conditions under which conversion has been induced by collisions in the gaseous phase. However, in studies of the physics of spin modifications of complex molecules it is the type of conversion occurring in the gaseous phase which is important, because the most completely developed theory is available for the conversion process in this phase.

The present paper reports an investigation of the conversion of the nuclear spin modifications of CH_3F. Preliminary results of the first separation of the nuclear spin modifications of complex molecules (specifically CH_3F molecules) and of the first measurements of the conversion times were reported in Refs. 9, 11, and 12.

1. NUCLEAR SPIN MODIFICATIONS OF CH_3F

The molecule of CH_3F is a symmetric top. The relationship between the nuclear spin and the rotation of such molecules is well known.[4] The total spin of the three equivalent hydrogen nuclei in this molecule can have the values $S = 3/2$ and $S = 1/2$, forming the ortho- and para-states of the molecule (in accordance with the terminology adopted in Ref. 3). In the case of the ortho-modification (o-CH_3F) the allowed rotational states of the molecule are those with the quantum numbers K (representing projections of the angular momentum along the axis of the molecule), which are multiples of 3 or $K = 0$. In the case of the para-modification (p-CH_3F) the allowed states are those with K, which are not multiples of 3. The nuclear statistical weights of the ortho- and paramodifications are in the ratio 2:1, but because the o-CH_3F molecules have half their rotational levels in p-CH_3F, the total concentrations of the two modifications are approximately equal.

The reported experiments[9,11,12] provide important information on the properties of the spin modifications of the CH_3F molecules. It has been found that the spin modifications of CH_3F are long-lived: 2–3 h for $^{12}CH_3F$. In the case of $^{13}CH_3F$ the lifetime of the two modifications is found to be approximately an order of magnitude less. No significant acceleration of the para–orthoconversion has been found on the surfaces of iron, copper or Duralumin. However, fast and complete conversion has been observed on a powdered $Fe(OH)_3$. This powder is known as a catalyst of the ortho–paraconversion of molecular hydrogen.

2. SEPARATION OF NUCLEAR SPIN CONFIGURATIONS BY THE LIGHT-INDUCED DRIFT EFFECT

The physical picture of this light-induced drift (LID) effect[13] is simplest in the case of two-level absorbing parti-

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cles. A monochromatic traveling wave, which excites particles selectively in respect of their velocities, creates Bennett structures in the velocity distributions of the particles, which gives rise to counterpropagating fluxes of excited and unexcited particles. In a buffer gas medium these fluxes experience friction, and the magnitude of the friction is generally different for the excited and unexcited particles. This gives rise to a force acting between the absorbing and buffer particles, i.e., it gives rise to the LID. The LID results in the repulsion of the absorbing and buffer particles from one another, which can be used—if suitable apparatus is available—to separate spatially these particles. This is exactly the approach used in the separation of the spin modifications of molecules by the LID effect reported in Ref. 9.

As in the case of two-level particles, the LID of molecules appears because of the difference between the frictional forces experienced by the fluxes of excited and unexcited molecules interacting with buffer molecules. However, a microscopic picture of the LID of these molecules and a detailed description of the influence is very complex, because through migration of the Bennett structures the particle fluxes reach many rotational levels and the drag experienced by these fluxes is due to a variety (elastic and inelastic) collisions.

The situation is thus complicated and it is not possible to develop a detailed microscopic theory of the effect. However, it has been shown experimentally[14] that a fully satisfactory description of the LID of molecules can be based on a relatively simple theoretical model of the effect[15] postulating constant transport frequencies of the collisions.

Consider the LID effect due to the interaction of light with a vibrational–rotational transition in a molecule. The force acting between the absorbing particles in a state α ($\alpha = m$ and n for the absorbing particles in the excited and unexcited vibrational states, respectively) and the buffer particles can be represented in the form

$$\mathbf{F}_\alpha{}^b = -M\nu_\alpha{}^b\rho_\alpha(\mathbf{u}_\alpha - \mathbf{u}_b), \tag{1}$$

where M is the mass of the absorbing molecules and ν_α^b is the transport collision frequency of particles in the state α with the buffer particles; ρ_α, $\mathbf{u}_\alpha$, and $\mathbf{u}_b$ represent the concentrations and the velocities of the fluxes of the components of the mixture. The relationship (1) corresponds to the case when the incident light is absorbed by one component of the mixture. There are no special difficulties in generalizing this to a complex situation.

The collision frequencies ν_α^b defined by Eq. (1) depend in a complicated manner on the distributions of the molecular velocities and rotational levels. High-intensity light distorts these distributions, which are no longer identical with the equilibrium ones. Introduction of the transport collision frequencies ν_α^b makes it easier to analyze the transport (kinetic) equations, but does not generally simplify the process of finding their exact solution, because the complexity of the original transport equation is simply transferred to calculation of the frequencies ν_α^b, which at present cannot be carried out fully in the case of molecules. The central feature of the proposed approximate theory is the assumption that the transport collision frequencies are independent of the characteristics of the incident light, which corresponds to a negligible influence of the distortions of the distributions of the velocities and rotational levels on the values of the frequencies ν_α^b.

The force $\mathbf{F}_\alpha^b$ given by Eq. (1) acts between the absorbing and buffer particles and creates a concentration grating of the absorbing particles in a cell with closed ends. The steady-state drop of the concentration of the absorbing particles between the ends of a cell ($\Delta\rho$) may be related to the optical power absorbed in the length of the cell (ΔS):

$$\Delta\rho = -\frac{\Delta\nu}{\nu}\frac{1}{1+R}\frac{2\Delta S}{\hbar\omega v_0}\varphi \equiv \frac{1}{1+R}f, \qquad \frac{\Delta\nu}{\nu} = \frac{\nu_m{}^b - \nu_n{}^b}{\nu_m{}^b},$$
$$\varphi = \sum_J \int p_J(\mathbf{v})v_x\,d\mathbf{v} \Big/ \sum_J \int p_J(\mathbf{v})\,d\mathbf{v}, \qquad R = \rho/\rho_b, \tag{2}$$

where ω is the frequency of the incident laser light, $p_J(\mathbf{v})$ is the probability of excitation to a level mJ of the molecules traveling at a velocity $\mathbf{v}$ (all the rotational levels are labeled arbitrarily with one variable J), ρ_b is the concentration of the buffer particles, and the coordinate x is selected along the wave vector of the incident laser light.

The system of equations (2) for the concentration drop $\Delta\rho$ is valid in the case of a mixture of gases with similar collisional characteristics when the relationship $\rho_b\nu_m^n = \rho_n\nu_m^b$ is obeyed. These may be mixtures of nuclear spin and isotopic modifications of molecules. A calculation of the function φ is easiest for strong collisions, which ensures an accuracy sufficient for the LID problems. If the spectroscopic data are insufficient to calculate the function φ, it can be found experimentally from measurements of $\partial\Delta S/\partial\omega$ (Ref. 16).

Most of the LID experiments carried out so far on molecules dealt with the separation of the isotopic modifications. The separation of these modifications in the LID effect can as a rule be accompanied by separation also of the spin modifications, since the spectral selectivity of the LID is sufficient to separate gases with allowed absorption lines. These are exactly the spectra which are exhibited by different spin modifications.

We now obtain the relationships between the isotopic and spin effects. Let us assume that light excites only the ortho-molecules (present in a concentration ρ_o) of one isotopic modification. The para-molecules (concentration ρ_p) and the second isotopic modification (concentration n) act as the buffer particles. We assume that the spin modifications are long-lived and that the transport characteristics of all three types of particle are identical. The steady-state drops of the concentrations of the components of the mixture are related by

$$\Delta\rho_o + \Delta\rho_p + \Delta n = 0, \qquad \Delta\rho_p/\rho_p = \Delta n/n. \tag{3}$$

The first expression follows from the constancy of the total concentration of the particles participating in the LID effect, the second follows from the fact that two types of buffer particles are here equivalent. We now use Eq. (2) to obtain the spin effect ($\Delta\rho_o$) and the isotopic effect ($\Delta\rho_o + \Delta\rho_p$). Using the relationships in Eq. (3), we readily find from Eq. (2) that

$$\Delta\rho_o = \frac{1}{1+\rho_o/(\rho_p+n)}f, \qquad \Delta\rho_o + \Delta\rho_p = \frac{1}{1+(\rho_o+\rho_p)/n}f. \tag{4}$$

These expressions give the values of the spin and isotopic effects when gases are separated with the aid of the LID. In particular, for $\rho_o, \rho_p \ll n$, the spin and isotopic effects (concentration drops) are equal.

3. EXPERIMENTS: DETERMINATION OF THE CONVERSION TIMES

We separated the spin modifications and measured the conversion times using an improved method[9,11,12] based on the Stark effect. The apparatus employed is shown schematically in Fig. 1.

The spin modifications of the CH_3F molecules were separated using radiation from a cw CO_2 laser (radiation power $\lesssim 10$ W), which had a diffraction grating inside the resonator (for the purpose of selection of the rotational lines) and an electronic frequency stabilization system tuned to the center of the CO_2 line using the maximum lasing power. The LID effect was induced by focusing this CO_2 laser radiation in a glass separation cell (with an internal diameter of 1.3 mm and 1.5 m long), where the radiation traveled in a waveguide regime.

A gas of the CH_3F molecules enriched with respect to the spin modification was collected in a glass measurement cell (with an internal diameter 4 mm and 25 cm long) connected to the end of the separation cell, as shown in Fig. 1. The absorption coefficient of the gas in the measurement cell was modulated using external electrodes (and a field of ≈ 100 V/cm intensity). The measurement cell was probed with part of the CO_2 laser radiation used in the separation procedure.

The signal/noise ratio was increased by using a null measurement method. This was done employing a reference cell which was similar to the measurement cell and coaxial with the latter. The Stark modulation of the absorption coefficient in the reference cell was in antiphase to the modulation in the measurement cell (because the modulating voltages were shifted in phase by $\pi/4$). The reference cell was connected to a ballast chamber so that the concentrations of the spin modifications in the reference cell were in equilibrium.

Before the process of separation was started, the pressures in the measurement and reference cells were equalized, and the amplitudes of the modulating voltages and their relative phase were selected so that the component of the radiation transmitted by both cells alternating at the frequency 2Ω (Ω is the Stark modulation frequency, which in our experiments was $\Omega \approx 16$ kHz) was minimal.

The separation of the spin modifications altered the concentration of the absorbing component in the measurement cell (at a constant total pressure), so that a signal of frequency 2Ω appeared in the radiation transmitted by the two cells. The amplitude of this signal $I_{2\Omega}$ depended on the intensity I and frequency ω of the laser radiation:

$$I_{2\Omega} \propto I d^2(\alpha_{\text{meas}} - \alpha_{\text{ref}})/d\omega^2, \qquad (5)$$

where α_{meas} and α_{ref} are the absorption coefficients of the gas in the measurement and reference cells. The noise at the $I_{2\Omega}$ signal frequency was mainly due to fluctuations of the intensity and frequency of the laser radiation. This noise was reduced significantly by the following procedure. A small part of the reference cell was used to generate one more Stark signal of frequency 2ν ($\nu \approx 1$ kHz) in the transmitted radiation. The amplitude of this signal was proportional to the radiation intensity and to the absorption coefficient of the gas in the reference signal:

$$I_{2\nu} \propto I d^2 \alpha_{\text{ref}}/d\omega^2. \qquad (6)$$

Recording apparatus (Fig. 1) was used to measure the signals $I_{2\Omega}$ and $I_{2\nu}$ in the digital form; the signals were averaged over a given interval of time; they were then divided in accordance with $I_{2\Omega}/I_{2\nu} = Y$ and the ratio Y was stored to be used in subsequent processing. The value of Y was proportional to the relative change in the concentration of the absorbing spin modification created by the separation procedure and was independent (if the system operated ideally) of the intensity and frequency of the laser radiation used in these experiments.

The compensation and division of the signals made it possible to reduce the noise of Y to less than 10^{-2} of the total signal (no balancing was used; the absorption coefficient was modulated only in the reference cell). The residual noise Y was clearly due to variation of the electric field in the Stark modulators, as well as due to the divergence of the laser radiation and the optical saturation effect, i.e., due to the factors responsible for the difference between the Stark modulation conditions in the measurement and reference signals.

Experiments on $^{12}CH_3F$ molecules

The CO_2 laser radiation emitting the P20 line of the 9.6 μm vibrational band was absorbed as a result of the Q(12,1) and Q(12,2) transitions (in the para-modification of the molecule) within the ν_3 vibrational band of the $^{12}CH_3F$ molecule. When the laser radiation was tuned to the center of the absorption line, the LID effect occurred because the absorbing molecules drifted in the direction of propagation of the laser radiation (for details of the LID effect experienced by the CH_3F molecules see Refs. 14 and 17).

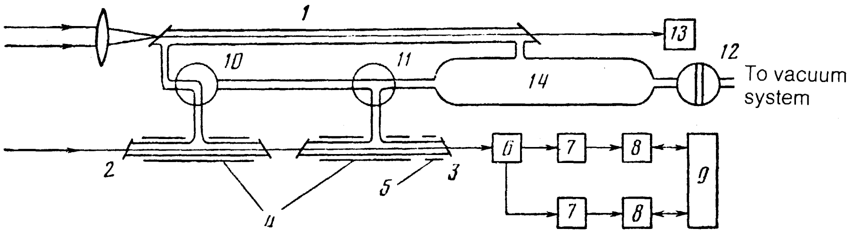

FIG. 1. Schematic diagram of the apparatus: 1), 2), 3) separation, measurement, and reference cells, respectively; 4), 5) electrodes used in the Stark modulation processes at frequencies Ω and ν; 6) detector and frequency filters; 7) narrow-band amplifiers; 8) voltage–frequency transducers, pulse counters, buffer registers; 9) computer; 10, 11), 12) vacuum valves; 13) radiation power meter; 14) ballast chamber.

The conversion time of the spin modifications of $^{12}CH_3F$ was determined as follows. The high-power laser radiation was directed to a cell 1 (Fig. 1). The gas pressures in cells 2 and 3 were equalized by connecting them temporarily to a ballast chamber by means of valves 10 and 11. The voltage applied to electrodes 4 was selected so that the Stark modulation effects in the cells 2 and 3 largely cancelled one another. Under these conditions we determined the value of the ratio $Y_1(0)$. Then, the valve 10 was opened to connect the measurement cell to the separation cell. When sufficient separation was reached after 5–10 min (we usually limited ourselves to an enrichment amounting to $\sim 10\%$), the ratio $Y_2(0)$ was determined and the total signal $V(0)$ (with the modulation of the measurement cells switched off) was recorded. The ratio[2)]

$$\tilde{Y}(0)=[Y_2(0)-Y_1(0)]/V(0)$$

was then compared with the corresponding ratio

$$\tilde{Y}(t)=[Y_2(t)-Y_1(t)]/V(t),$$

measured after a time t. The value of $Y_1(t)$ was found by "interrupting" the conversion process and equalizing the pressures in the measurement and reference cells. The quantity $\tilde{Y}(t)$ obtained in this way was proportional to the nonequilibrium correction and to the concentration of the absorbing spin modification. The time dependence $\tilde{Y}(t)$ was approximated by an exponential relationship

$$\tilde{Y}(t)=\tilde{Y}(0)\exp(-\gamma t)$$

(see below), which gave the values of the conversion rate γ for each pair of the measured quantities $\tilde{Y}(t)$ and $\tilde{Y}(0)$. These measurements were carried out repeatedly for different delay times t and at different pressures. The resultant dependence of the conversion rate had the form shown in Fig. 2. The considerable error in these measurements was due to the need to employ long delay times, amounting to many hours. The results obtained indicated that the rate of conversion of the spin modifications of the $^{12}CH_3F$ molecules increased approximately linearly with pressure:

$$\gamma_{12}=(1.1\pm0.1)(\text{h}^{-1}\cdot\text{Torr}^{-1})P.$$

Experiments on $^{13}CH_3F$ molecules

The CO_2 laser radiation representing the $P\,32$ line in the 9.6 μm band was absorbed due to the $R(4,3)$ transition (in the ortho-modification of the molecule) of the ν_3 vibration of $^{13}CH_3$.F The molecules absorbing in the field of this radiation drifted toward the laser. The conversion time of the spin modifications of $^{13}CH_3F$ could be determined more readily than for $^{12}CH_3F$ because of the much higher conversion rate.[12] In the latter case it was sufficient to record only the kinetics of the $Y(t)$ signal. The procedure for determining the conversion rate is explained in Fig. 3a. After connecting the cells 1 and 2 (Fig. 1) we found that the signal Y increased because of enrichment of the mixture with the absorbing modification (section I of the curve in Fig. 3a). When the cell 2 was disconnected from the separation cell, the signal began to decrease because of the conversion process. Section II of the same curve was approximated numerically by a function $A\exp(-\gamma t)+B$ using the least-squares method, which gave the value of the conversion rate γ of interest to us (Fig. 3b). In these experiments we used gaseous CH_3F with a natural isotopic abundance and a small proportion of the $^{13}CH_3F$ molecules ($^{13}CH_3F$:$^{12}CH_3F$ = 1:89).

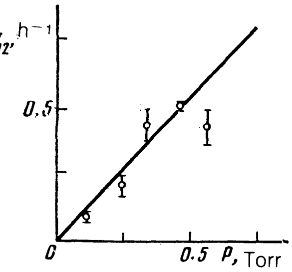

FIG. 2. Pressure dependence of the rate of conversion of the nuclear spin modifications of the $^{12}CH_3F$ molecules.

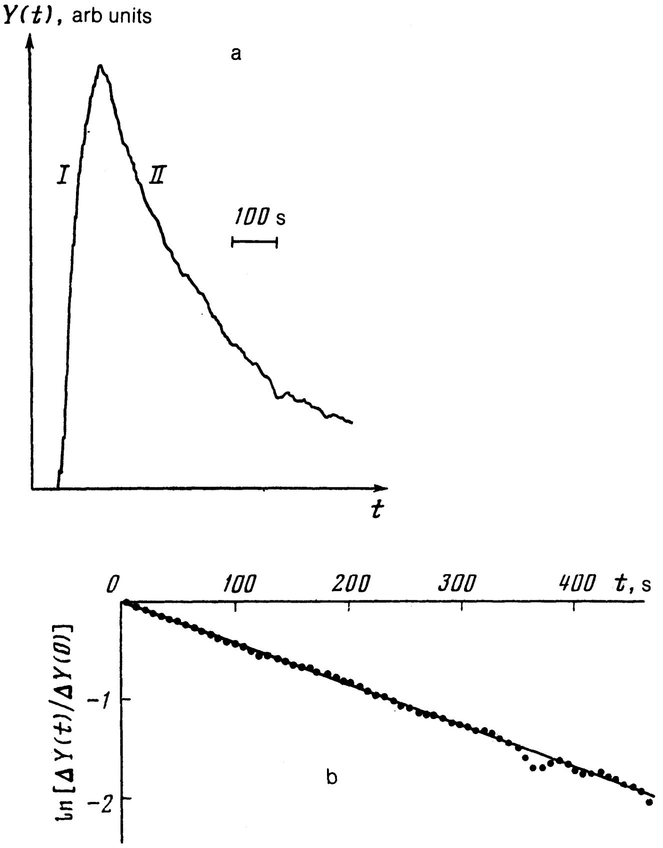

FIG. 3. Separation of the spin modifications of $^{13}CH_3F$: a) $Y(t)$ signal, representing separation (I) and conversion (II); b) conversion [alternating part of the signal $\Delta Y(t)=Y(t)-Y(\infty)$].

The pressure dependence of the spin modification conversion rate is plotted in Fig. 4. With a high degree of accuracy, the results could be approximated by the linear dependence

$$\gamma_{13}=(0.85\pm0.06)\,(\text{min}^{-1}\cdot\text{Torr}^{-1})\,P.$$

The results of our measurements gave the following value of the ratio of the rates of conversion of the spin modifications of the $^{13}CH_3F$ and $^{12}CH_3F$ molecules:

$$\gamma_{13}/\gamma_{12}=46\pm5. \qquad (7)$$

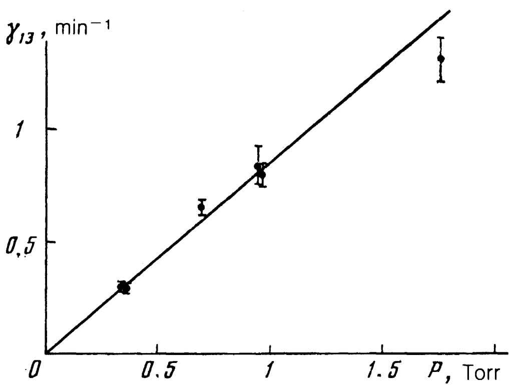

FIG. 4. Pressure dependence of the rate of conversion of the nuclear spin modifications of the $^{13}CH_3F$ molecules.

4. CONVERSION DUE TO MIXING OF SPIN STATES

The mechanism of spin conversion of the CH_3F molecules is understood only in general terms. The CH_3F molecules have zero spin and zero angular momentum of electrons. Therefore, the collisions of these molecules with one another are "nonmagnetic" and they can hardly induce nuclear spin reversals of hydrogen in a molecule. In the case of molecular hydrogen, the conversion due to such collisions should of course be very slow. It is most likely that the CH_3F molecules are characterized by a conversion mechanism due to mixing of spin states because of internal interactions in the molecules. This mechanism for the conversion of the spin modifications of the H_2O, H_2CO, and CH_4 molecules was proposed theoretically in Ref. 18, but had not yet been observed experimentally.

We shall obtain an expression for the conversion rate using the transport equation for the density matrix. We represent the Hamiltonian H of a molecule in the form of a sum of two terms $H_0 + V$, where H_0 is the part not subject to mixing of the spin states and V is the term mixing the spin states, regarded as a small perturbation. We use the variable α to denote the wave functions of the unperturbed states: $|\alpha\rangle = |JKMS\sigma I\mu\chi\rangle$, where J, K, and M are respectively the angular momentum, its projection along the axis of the molecule, and the projection along an axis fixed in space, S and σ represent the total spin of the hydrogen nuclei and the projection of this spin, I and μ represent the spin of the remaining nuclei and its projection, and χ are the other quantum numbers of the investigated state (see Ref. 19). The transport equation for the density matrix obtained in the H_0 representation has its usual form:

$$\frac{\partial \rho_{\alpha\alpha'}}{\partial t} = S_{\alpha\alpha'} - i\sum_{\alpha_1}[V_{\alpha\alpha_1}\rho_{\alpha_1\alpha'} - \rho_{\alpha\alpha_1}V_{\alpha_1\alpha'}], \qquad (8)$$

where $S_{\alpha\alpha'}$ is the collision integral and the summation with respect to α_1 extends to all the ortho- and para-states of the molecule.

The spin conversion processes recorded for the CH_3F molecules are many orders of magnitude slower than the rotational relaxation processes. Therefore, in the case of each spin configuration the rotational levels follow a Boltzmann distribution. The population of a specific rotational level, needed in the calculation of the absorption coefficient, is then related simply to the total concentration of the molecules with a given spin modification. Let us calculate the evolution of the total concentration ρ_o of the ortho-molecules. We do this by summing Eq. (8) for the diagonal elements of the density matrix ρ_o over all the ortho-states. We then obtain

$$\frac{\partial \rho_o}{\partial t} = 2\,\mathrm{Re}\sum_{\substack{\alpha\in o\\ \alpha_1\in p}} i\rho_{\alpha\alpha_1}V_{\alpha_1\alpha}, \qquad \rho_o = \sum_{\alpha\in o}\rho_{\alpha\alpha}. \qquad (9)$$

It is pointed out here that the summation over the variable α should be carried out over the ortho-states, whereas the corresponding summation over α_1 should apply to the para-states. Equation (9) is derived using the relationship

$$\sum_{\alpha\in o} S_{\alpha\alpha} = 0,$$

which follows from the condition of conservation of the number of particles with the ortho-modification in the course of the collisions.

It follows from Eq. (9) that the kinetics can be calculated if we know the off-diagonal elements of the density matrix $\rho_{\alpha\alpha}$ (here, $\alpha\in o$, $\alpha_1\in p$). In finding $\rho_{\alpha\alpha}$ we have to turn back to Eq. (8) subject to the condition $\alpha\in o$, $\alpha_1\in p$. In this case $S_{\alpha\alpha_1}$ contains only the outgoing term: $S_{\alpha\alpha_1} = -\Gamma\rho_{\alpha\alpha_1}$, where Γ is the frequency of quenching of the rotational levels. In the case of a steady-state perturbation V, which is considered here, we can represent $\rho_{\alpha\alpha_1}$ as a product of slow and fast functions of time:

$$\rho_{\alpha\alpha_1} = \tilde{\rho}_{\alpha\alpha_1}(t)\exp(-i\omega_{\alpha\alpha_1}t).$$

This makes it possible to replace the left-hand side of Eq. (8) approximately with $-i\omega_{\alpha\alpha_1}\rho_{\alpha\alpha_1}$. Using the above relationship, it follows from Eq. (8) that

$$(\Gamma - i\omega_{\alpha\alpha_1})\rho_{\alpha\alpha_1} = -i\sum_{\alpha'}[V_{\alpha\alpha'}\rho_{\alpha'\alpha_1} - \rho_{\alpha\alpha'}V_{\alpha'\alpha_1}]. \qquad (10)$$

In the first approximation with respect to V we need to retain only the terms with the diagonal elements of the density matrix on the right-hand side of Eq. (10). In this approximation we find that

$$(\Gamma - i\omega_{\alpha\alpha_1})\rho_{\alpha\alpha_1} = -iV_{\alpha\alpha_1}(\rho_{\alpha_1\alpha_1} - \rho_{\alpha\alpha}). \qquad (11)$$

Substituting $\rho_{\alpha\alpha_1}$ from Eq. (11) into Eq. (9), we obtain

$$\frac{\partial \rho_o}{\partial t} = \sum_{\substack{\alpha\in o\\ \alpha_1\in p}} \frac{2\Gamma|V_{\alpha\alpha_1}|^2}{\Gamma^2 + \omega^2_{\alpha\alpha_1}}(\rho_{\alpha_1\alpha_1} - \rho_{\alpha\alpha}). \qquad (12)$$

Since the particles follow a Boltzman distribution in the rotational levels of each spin configuration, we can write down

$$\rho_{\alpha_1\alpha_1} = \rho_p W_B(\alpha_1), \quad \rho_{\alpha\alpha} = \rho_o W_B(\alpha), \quad \rho_o + \rho_p = N, \qquad (13)$$

where $W_B(\alpha)$ and $W_B(\alpha_1)$ are the Boltzmann factors, ρ_o and ρ_p are the total concentrations of the ortho- and para-molecules, and N is the total concentration of both modifications. Combining Eqs. (12) and (13), we obtain

$$\frac{\partial \rho_o}{\partial t} = -\sum_{\substack{\alpha\in o\\ \alpha_1\in p}} \frac{2\Gamma|V_{\alpha\alpha_1}|^2}{\Gamma^2 + \omega^2_{\alpha\alpha_1}}[W_B(\alpha)\rho_o - W_B(\alpha_1)\rho_p]. \qquad (14)$$

We now introduce a quantity $\delta_{\rho o}(t)$, which is equal to the deviation of the concentration of the ortho-molecules from its equilibrium value such that

$$\rho_o = \rho_{o,\mathrm{st}} + \delta\rho_o(t), \tag{15}$$

where $\rho_{o,\mathrm{st}}$ is the steady-state value of ρ_o which follows from Eq. (14) if we substitute $\partial_{\rho o}/\partial t = 0$. In the case of $\delta_{\rho o}(t)$ we find from Eq. (14) that

$$\delta\rho_o(t) = \delta\rho_o(0)\, e^{-\gamma t},$$

where

$$\gamma = \sum_{\substack{\alpha\in o\\ \alpha_1\in p}} \frac{2\Gamma |V_{\alpha\alpha_1}|^2}{\Gamma^2 + \omega^2_{\alpha\alpha_1}} [W_B(\alpha) + W_B(\alpha_1)]. \tag{16}$$

The above expression for the spin conversion rate γ is identical with that obtained in Ref. 18 by a different method using the probability amplitudes.

The pressure dependence of the rate of conversion, predicted by Eq. (16) differs considerably in the two limiting cases: for $\Gamma \ll \omega_{\alpha\alpha_1}$, the conversion rate is proportional to the gas pressure P, because $\Gamma \propto P$; in the opposite limiting case when $\Gamma \gg \omega_{\alpha\alpha_1}$, the pressure dependence is opposite: $\gamma \propto P^{-1}$.

It follows from the experimental results that $\gamma \propto P$. We can confirm that this dependence is in agreement with the actual situation in the CH_3F molecules by finding the frequencies of the transitions between the nearest levels of the ortho- and para-modifications which can be mixed by the familiar interactions. The nearest pairs of levels belong to the ground state of the molecule and the interactions which can mix them are the magnetic dipole–dipole interaction between the nuclei and the interaction between the hydrogen spins and the rotation of the molecule.[18]

A complete set of the molecular constants of the ground state was published[20] for the $^{12}CH_3F$ molecule, so that there should not be any problem in calculating the frequencies $\omega_{\alpha\alpha_1}$. The nearest pair of the rotational levels is characterized by $J' = 28$, $K' = 5$ and $J = 27$, $K = 6$. The difference between their energies is 1.2 GHz in terms of the frequency. This is the only pair of such a closely spaced ortho- and para-levels of the $^{12}CH_3F$ molecule in the range $J, K \leqslant 40$. The other pairs are characterized by larger separations.

All the necessary molecular constants of the $^{13}CH_3F$ molecule had also been published,[21] with the exception of A_0 and D_0^K. Since in the case of $^{13}CH_3F$, compared with $^{12}CH_3F$, the atom located on the axis of the molecule is replaced by its isotope, we can assume approximately that A_0 and D_0^K are not affected. A calculation of the energy levels in the ground state of $^{13}CH_3F$ gives the closest pair with $J' = 11$, $K' = 1$ and $J = 9$, $K = 3$. The difference between the energies of these levels is 0.23 GHz.

The isotopic correction to the constant A_0 is small, but important for the resonance in question.[3)] The correction appears because of the isotopic dependence of the anharmonic shift of the equilibrium position and also because of the isotopic dependence of the amplitude of vibrations of the hydrogen atom. In the case of the $^{12}CH_3F$ molecules the constant A_0 is $5.182\,009 \pm 12\times10^{-6}$ cm^{-1} (Ref. 20), whereas in the case of $^{13}CH_3F$ an estimate gives $A_0 = 5.182\,40 \pm 6\times10^{-5}$ cm^{-1}. When this correction is allowed for, the difference between the energies of the levels with $J' = 11$, $K' = 1$ and $J = 9$, KK $= 3$ amounts to 135 ± 15 MHz. The other resonances of the ground state of the $^{13}CH_3F$ molecule have higher frequencies for the levels in the range $J, K \leqslant 40$.

We shall now compare the frequencies of these resonances with the value Γ. The rate of deexcitation of the rotational levels of the CH_3F molecule can be determined by direct measurements[22] and it amounts to $\Gamma/P = (1.05 \pm 0.06)\cdot 10^8$ s$^{-1}\cdot$torr^{-1}.

Hence, in these experiments the value of Γ is less than ≈ 30 MHz. If we compare this value with the separation between the nearest levels of the two spin configurations, which can be mixed by the familiar interactions, we find that the condition $\Gamma \ll \omega_{\alpha\alpha_1}$ is obeyed. Mixing of the ortho- and para-states belonging to different vibrational or electronic levels is known to satisfy the inequality $\Gamma \ll \omega_{\alpha\alpha_1}$. Therefore, the pressure dependence of the rate of conversion of the spin modifications of $^{12}CH_3F$ and $^{13}CH_3F$ should be of the form $\gamma \propto P$ in the range of pressures investigated by us. This was in fact observed.

5. ISOTOPIC EFFECT IN SPIN CONVERSION OF CH_3F

In accordance with the above model the process of spin conversion is due to mixing of the ortho- and para-states in a molecule. The mixed states may belong to one or several electronic or vibrational levels. The expression (16) for the conversion rate naturally retains its form. In the case of the CH_3F molecules we find that, out of the many types of mixing, we have to select only those which account for the experimentally observed strong isotopic dependence γ. The dependence in question can be explained in a natural manner if the conversion occurs because of mixing of the pairs of the closest levels of the ground state.

In the expression (16) the conversion rate assumes the following form when only two levels are mixed:.

$$\gamma = \frac{2\Gamma [W_B(\alpha) + W_B(\alpha_1)]}{\Gamma^2 + \omega^2_{\alpha\alpha_1}} \sum |V_{\alpha\alpha_1}|^2. \tag{17}$$

The summation is carried out over all the degenerate levels of the states α and α_1. The nucleus of the ^{13}C atom has a magnetic moment. The magnetic moment of the nucleus ^{12}C is zero. In both molecules ($^{13}CH_3F$ and $^{12}CH_3F$) the magnetic moment of the nucleus of the F atom exerts approximately the same "mixing" effect as the nucleus of the carbon atom. Therefore, there are no grounds for assuming that the sum $\Sigma |V_{\alpha\alpha_1}|^2$ in Eq. (17) for the $^{13}CH_3F$ and $^{12}CH_3F$ molecules is very different. The ratio of the conversion rates γ_{13}/γ_{12} can then be readily estimated. For the pairs of the levels given above we find that this ratio is $\gamma_{13}/\gamma_{12} \sim 10^3$. Therefore, even these rough estimates demonstrate the existence of a strong isotopic effect in the process of conversion of the spin modifications of the $^{13}CH_3F$ and $^{12}CH_2F$ molecules.

6. CONCLUSIONS

The rate of conversion of the spin modifications of the CH_3F molecules was determined as a function of the gas containing these molecules. In the case of $^{12}CH_3F$ the conversion rate was characterized by $\gamma_{12}/P = 1.1 \pm 0.1$ h$^{-1}\cdot$torr^{-1}, whereas in the case of the $^{13}CH_3F$ molecules the corresponding coefficient was $\gamma_{13}/P = 0.85 \pm 0.06$ min^{-1} $\cdot$torr^{-1}. The pressure dependence of the conversion rate agreed with the theoretical dependence predicted for the conversion in the gaseous phase due to "nonmagnetic" collisions when the nuclear spin states are mixed.[18] The strong isotropic effect in the spin conversion of the CH_3F molecules can be explained by assuming that the conversion is due to mixing of the energetically close ortho- and para-levels of the ground state of the molecule.

The author is deeply grateful to T. Egawa and K. Kuchitsu for kindly calculating the constant A_0 of the $^{13}CH_3F$ molecule. It is a pleasant duty to thank S. G. Rautian, F. Kh. Gel'mukhanov, L. N. Krasnoperov, V. P. Strunin, and A. M. Shalagin for numerous helpful discussions of the topics considered above and for their encouragement.

[1)] When we shall speak of the separation of the spin modifications, we shall mean creation of a nonequilibrium ratio of these concentrations.

[2)] This additional normalization is necessary to avoid the errors associated with a change in the amplitude of the voltage applied to the Stark electrodes.

[3)] The isotopic correction to the constant A_0 for $^{13}CH_3F$ was calculated by T. Egawa and K. Kuchitsu.

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Translated by A. Tybulewicz