Vibrational energy transfer between the ortho- and para-modifications of $^{12}CH_3F$ and $^{13}CH_3F$ molecules

E. N. Chesnokov and V. N. Panfilov

Institute of Chemical Kinetics and Mining, Siberian Branch, USSR Academy of Sciences
(Submitted July 6, 1977)
Zh. Eksp. Teor. Fiz. 73, 2122–2130 (December 1977)

The double resonance method was used to measure the rate constant for the vibrational energy transfer between the ortho- and para-modifications of $^{12}CH_3F$ and $^{13}CH_3F$ molecules. It was found to be $(9.5 \pm 1.5) \times 10^5$ Torr^{-1} sec^{-1}. The rate constant for vibrational energy transfer between isotropic molecules, measured under the same conditions, is lower by a factor of two: $(5 \pm 1) \times 10^5$ Torr^{-1} sec^{-1}.

The method of laser-induced infrared luminescence has been used to examine such fast processes as resonance transfer of vibrational energy between isotopic molecules, for example, $^{12}CO_2$ and $^{13}CO_2$,[1] and $H^{35}Cl$ and $H^{37}Cl$.[2] It is essential to know the rate constants in order to understand the mechanism responsible for the excitation of vibrational degrees of freedom of molecules by laser radiation, and this assumes particular importance in connection with the development of infrared laser photochemistry and laser methods of isotope separation.[3]

However, there is a class of vibrational energy transfer processes that is no less important for the excitation of molecules by laser radiation than energy transfer processes between isotopes. Thus, it is well known[4] that a gas consisting of molecules having equivalent nuclei with nonzero spins is a mixture of different gases corresponding to different total spin of these nuclei. The transformation of the different modifications into each other occurs very slowly, and these modifications have different rotational structure of vibrational absorption bands. It therefore frequently turns out that laser radiation will excite one of the modifications without affecting any of the others. In fact, the other modifications can be excited only as a result of energy transfer from the molecules interacting directly with the laser radiation. Such energy transfer processes have not yet been observed.

We have investigated vibrational energy transfer processes between $^{12}CH_3F$ and $^{13}CH_3F$ molecules with resultant total spins of 3/2 (ortho-CH_3F) and 1/2 (para-CH_3F). The CH_3F molecule is a symmetric top and its vibrational state is characterized by angular momentum J and its component K along the axis of the molecule. The electronic and vibrational ground state of the molecule is nondegenerate. According to[4], the relationship between the spin of the protons and the allowed rotational quantum numbers is as follows: $I = 3/2$, $K = 0, 3, 6, 9, \ldots$ and J arbitrary; $I = 1/2$, $K = 1, 2, 4, 5, 7, 8, \ldots$ and J arbitrary. Since the statistical weight of the $I = 3/2$ state is greater by a factor of two than each of the two $I = 1/2$ states, the total number of molecules of the ortho- and paramodification at room temperature is the same.

Vibrational energy transfer processes between different modifications of the CH_3F molecule are interesting not only in connection with isotope-selective chemical reactions occurring when CH_3F is illuminated by infrared laser radiation,[5] but also in connection with the possible use of CH_3F in laser generation in the far infrared.[6]

EXPERIMENTAL METHOD

We have used the double resonance method to measure the rate constant for vibrational energy transfer. The molecules were excited by a Q-switched CO_2 laser (energy per pulse ~0.001 J, pulse length 1–3 μsec). The energy transfer process was investigated by examining the variation in the transmitted He–Ne laser-beam intensity. The experimental setup employed was largely as described in our previous paper.[7] The only difference is that, in the present work, we used a magnetic-field tuned He–Ne laser similar to that described by Gerritsen and Ahmed.[8] The magnetic field was parallel to the axis of the He–Ne laser tube and was produced by a water-cooled solenoid of length 1 m and internal diameter 8 cm. The field could be varied in the range 0–1600 G, which corresponded to a radiation frequency change by ± 0.1 cm^{-1}. For fields in excess of 1000 G, the solenoid was capable of operation without overheating for periods of 10–30 sec. This was quite sufficient to enable us to carry out the measurements. A laser placed in a longitudinal magnetic field generates the Zeeman components σ_+ and σ_- with right-handed and left-handed circular polarization and frequencies above and below the laser frequency in zero field. The σ_+ and σ_- components were transformed into linearly polarized components with mutually perpendicular planes of polarization by passing them through a quartz quarter-wave plate. The component with the higher or lower frequency was then isolated with the aid of a polarizer, as required. We used composite supplies for the discharge tube, consisting of direct and high-frequency alternating current sources, because high laser noise levels were observed when the discharge tube was supplied in the magnetic field with direct current only.

We used $^{12}CH_3F$ of 99% purity, $^{13}CH_3F$ enriched with carbon to more than 90%, and argon of 99.9% purity.

Figure 1 shows segments of the absorption spectra of $^{12}CH_3F$ and $^{13}CH_3F$, obtained by varying the He–Ne laser frequency. The absorption-line frequencies of $^{12}CH_3F$ shown in the figure were taken from the litera-

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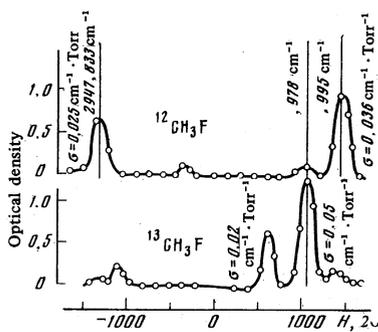
FIG. 1. Segments of the absorption spectra of $^{12}CH_3F$ and $^{13}CH_3F$ obtained with the aid of a tunable He–Ne laser.

ture.[9] The absorption coefficient for He–Ne laser radiation is shown above each line.

Unfortunately, the rotational quantum numbers for these vibrational-rotational absorption lines are not known because the high-resolution spectra of the CH_3F molecule are not available in the literature for the region near 3μ. There are reasons to suppose[10] that, in the case of the $^{12}CH_3F$ molecule, the tuning range of the He–Ne laser contains the $P_Q(10, K)$ line of the symmetric C–H valence vibration (lines with different K were not resolved by Freund et al.[10]). For the $^{13}CH_3F$ molecule, there is a lack of even low-resolution spectral data in this region. The absence of spectroscopic information prevents us from predicting which of the absorption lines in the laser tuning range belong to the ortho-modification and which to the para-modification.

ENERGY TRANSFER BETWEEN ORTHO- AND PARA-CH$_3$F

Figure 2 shows the double-resonance oscillograms for a mixture of $^{13}CH_3F$ and argon. The helium-neon laser was tuned to the absorption line in a field of 1070 G. After the CO_2 laser pulse, the intensity of the He–Ne laser beam transmitted by the cell is found to increase because of the reduction in the number of molecules in the vibrational ground state which are responsible for the absorption of the He–Ne laser radiation. When the
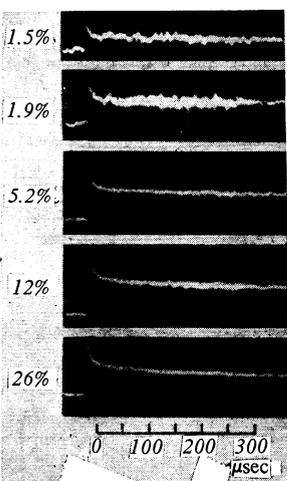
FIG. 2. Oscillograms of the double resonance signal from $^{13}CH_3F$ for different excitation levels. $^{13}CH_3F$ pressure 0.13 Torr, argon pressure 4.6 Torr.

argon pressure amounts to a few Torr, rotational relaxation occurs in a time much less than 1 μsec, i.e., the vibrational-level equilibrium is established practically immediately after the pulse. The size of the signal is therefore directly related to the amount of excited molecules of the gas to whose absorption line the He–Ne laser has been tuned.

The signal decays in two stages, one with a characteristic time of about 10 μsec and a slower component with a characteristic time of about 1 msec. The slow stage describes the reduction in the concentration of excited molecules due to $V-T$ relaxation and diffusion out of the region in which the molecules were originally formed. The fast stage can naturally be explained by assuming that the vibrational rotational line of $^{13}CH_3F$, which absorbs the CO_2 laser radiation, and the line to which the He–Ne laser is tuned both belong to the same modification of the molecules. If this is so, this decay stage corresponds to energy transfer to the other modification.

Another explanation of the fast decay stage is also possible. Since the CO_2 laser radiation excites the lowest vibrational level of the CH_3F molecule, some of the molecules will return to the ground state during the establishment of vibrational equilibrium. However, estimates show that the fraction of initially excited molecules which return to the ground state in this way is insufficient to explain the depth of the fast stage. Moreover, this fraction should decrease with decreasing amount of initially excited molecules, and it is clear from Fig. 2 that this is not, in fact, observed. The amount of initially excited molecules varies from 26 to 1.5%, whereas the fast decay stage is always roughly half the maximum signal size. This is in good agreement with the former of the above two explanations because the concentrations of the ortho- and para-modifications are equal.

When the He–Ne laser is tuned to the $^{13}CH_3F$ absorptione line in a field of 610 G, the signal is found to have a similar shape but is smaller in magnitude because the absorption coefficient corresponding to this line is smaller.

Figure 3 shows the double-resonance signals due to $^{12}CH_3F$, corresponding to the He–Ne laser tuned to the different absorption lines of this material. It is clear from the figure that one observes both signals with the fast decay stage (absorption line in the field of -1340 G) and signals with a growth stage (at the line corresponding to 1450 G). If the signal decay stage corresponds to energy transfer from the modification to which the He–Ne laser is tuned, the growth stage corresponds to the excitation of the other modification. It is clear from the figure that, for the double-resonance signals due to $^{12}CH_3F$, the magnitude of the fast decay stage is less than half the maximum size of the signal. Moreover, when the argon pressure is increased to 35 Torr, the fast stage is absent altogether. This also applies to the growth stage observed for the line in a field of 1450 G. To explain all this, we must consider the absorption spectrum of $^{12}CH_3F$ near the CO_2-laser line.

FIG. 4. Absorption spectra of $^{12}CH_3F$ near the $P(20)$ line of CO_2 laser and $^{13}CH_3F$ near the $P(32)$ line of CO_2 laser calculated from the data of Freund et al.[10]
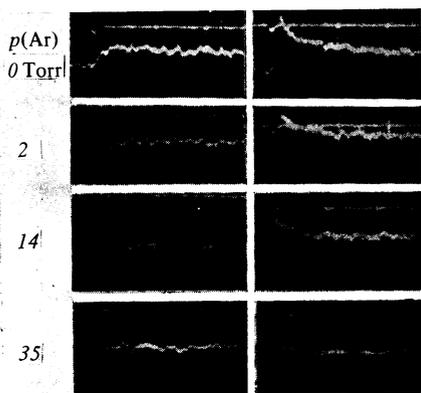
FIG. 3. Oscillograms of the double resonance signal from $^{12}CH_3F$ and from mixtures with argon. The $^{12}CH_3F$ pressure is 0.15 Torr. Right—laser tuned to the absorption line corresponding to $H = -1340$ G; left—$H = 1450$ G. Upper trace—CO_2 laser pulse. Time scale—10 μsec per division.

In contrast to the absorption spectrum near 3 μ, the spectrum in the region of 9.6 μ has been adequately investigated for the two isotopic molecules of CH_3F. There is, in fact, a paper on the Stark spectroscopy of these molecules using CO_2 laser radiation[11] in which the molecular constants, the knowledge of which enables us to calculate the absorption line frequencies in this region, have been determined with high precision. The $^{12}CH_3F$ spectrum calculated on the basis of these data in the neighborhood of the $P(20)$ line of the CO_2 laser and the $^{13}CH_3F$ spectrum near the $P(32)$ line are shown in Fig. 4. The figure indicates the Doppler widths of the lines at room temperature. The relative line intensities were calculated on the basis of the transition probability as a function of the quantum numbers J and K and the equilibrium populations of rotational levels.

It is clear from this figure that, at low pressures, when collisional broadening is unimportant, the $P(20)$ line of the CO_2 laser can be absorbed by the $Q_Q(12.1)$ and $Q_Q(12.2)$ lines. These two lines belong to the para-modification of $^{12}CH_3F$. At a distance of about 160 MHz from the $P(20)$ line, there is the stronger $Q_Q(12.3)$ line which belongs to the ortho-modification. When the argon pressure is increased, this line becomes broadened and the CO_2 laser excites both the para- and ortho-modifications. Under these conditions, less than half the initial energy should be transferred from the para- to the ortho-modification in order to establish vibrational equilibrium. This, in fact, ensures that the fast signal-decay stage becomes less than half the maximum signal and then vanishes altogether as the argon pressure is increased.

The $P(32)$ line of the CO_2 laser is absorbed by the $R_Q(4.3)$ line of $^{13}CH_3F$, which belongs to the ortho-modification. In contrast to the last case, the successive absorption lines of the para-modification, $R_Q(4.1)$, $R_Q(4.2)$, and $R_Q(4.4)$, do not exceed the main line which coincides with the laser frequency. One would therefore expect that the fast stage of the double-resonance signal due to $^{13}CH_3F$, which is connected with the ortho-para energy transfer, will persist at higher argon pres-

sures than in the case of $^{12}CH_3F$. In fact, it vanishes only at argon pressures of about 100 Torr. The shape of the double-resonance curve obtained when the He—Ne laser is tuned to different absorption lines, and the spectroscopic data indicating that the CO_2 laser excites the para-modification in $^{12}CH_3F$, suggest that the absorption line corresponding to -1340 G belongs to the para-modification of $^{12}CH_3F$, whereas that corresponding to the field of 1450 G belongs to the ortho-modification. The difference between their absorption coefficients is a consequence of the intensity alternation in the spectrum of the molecule with three equivalent protons: the absorption lines of the ortho-modification are roughly twice as strong because of the greater nuclear statistical weight.
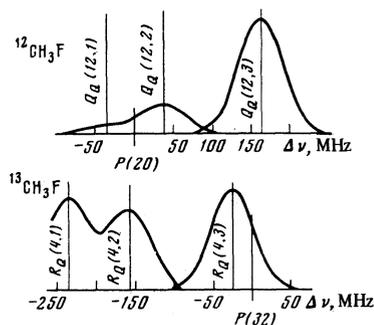
In precisely the same way, we may conclude that the two observed $^{13}CH_3F$ lines belong to the ortho-modification. The fact that the two lines of the ortho-modification (lines with the same K) were observed side by side appears to indicate that they are related to the perpendicular absorption band. The $^{12}CH_3F$ lines, on the other hand, are related to the parallel absorption band. The fact that the He—Ne laser tuning range contains the absorption lines of $^{12}CH_3F$ and $^{13}CH_3F$ corresponding to different bands is not in conflict with existing data on the C_3F absorption spectrum near 3 μ. It has been reported[11] that the absorption spectrum in this region is a superposition of a number of parallel and perpendicular bands.

Thus, the assumption that the fast stage of the double resonance signal decay in CH_3F corresponds to energy transfer between the ortho- and para-modifications is capable of explaining all the experimental results. By measuring the duration of this stage at different pressures, we can determine the rate constants for energy transfer between the ortho- and para-modifications. It is easily shown that the concentration of excited molecules of ortho- or para-modifications will approach the equilibrium values in accordance with the law

$$n - n_e = \text{const} \cdot \exp\left(-k_1 [CH_3F] t\right),$$

where n is the concentration of excited ortho- or para-molecules, n_e is the concentration after the ortho-para-equilibrium has been established, $CH_3F = [\text{ortho-}CH_3F] + [\text{para-}CH_3F]$ is the concentration of CH_3F, and k_1 is
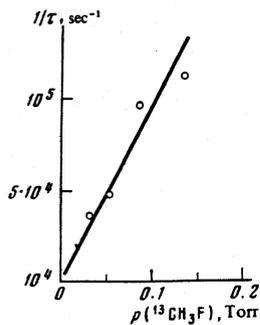
FIG. 5. Reciprocal of the time constant of the fast stage of the $^{13}CH_3F$ signal decay as a function of the pressure $p(^{13}CH_3F)$. Argon pressure 4.6 Torr.

the rate constant for the process ortho-CH_3F + para-$CH_3F^* \rightleftharpoons$ para-CH_3F + ortho-CH_3F^* (the rate constants in the two directions are equal).

Figure 5 shows the reciprocal of the time of the fast decay stage of the $^{13}CH_3F$ signal as a function of pressure. The time of this stage was determined by plotting the corresponding signals on a semilogarithmic scale. The slope of the straight line drawn through the experimental points gives the following value for the ortho-para vibrational energy transfer in $^{13}CH_3F$: $(9.5 \pm 1.5) \times 10^5$ Torr$^{-1} \cdot$ sec^{-1}.

Similar measurements could not be performed for $^{12}CH_3F$ because of the smaller size of the signal and the short duration of the fast stage in mixtures with argon. However, estimates based on the oscillograms shown in Fig. 3 indicate that the rate constant for the ortho-para vibrational energy transfer in $^{12}CH_3F$ has the same value.

ENERGY TRANSFER BETWEEN $^{12}CH_3F$ AND $^{13}CH_3F$

Since the absorption lines of $^{12}CH_3F$ and $^{13}CH_3F$ for the He–Ne laser radiation do not overlap, we have the possibility of measuring the rate constant for the vibrational energy transfer between the isotopic molecules. There are a number of ways in which this can be done. They differ by the absorption lines to which the He–Ne laser and CO_2 laser are tuned. We have carried out the following measurements for $^{12}CH_3F : {}^{13}CH_3F \approx 1 : 1$ mixtures in argon:

1) CO_2 laser excites ortho-$^{13}CH_3F$ molecules, He–Ne laser tuned to the absorption line of ortho-$^{12}CH_3F$ ($H = 1450$ G). The intensity of the transmitted beam is found to increase after the pulse due to the energy transfer between the molecules of ortho-$^{12}CH_3F$. This increase can be described by an exponential. Figure 6 shows the reciprocal of the growth time as a function of the total pressure of $^{12}CH_3F$ and $^{13}CH_3F$. As can be seen, this relationship is linear and the slope of the corresponding straight line (1) is 5×10^5 Torr$^{-1} \cdot$ sec^{-1}.

2) CO_2 laser excites, as before, the molecules of ortho-$^{13}CH_3F$, but the He–Ne laser is tuned to the absorption line of para-$^{12}CH_3F$. These measurements were carried out only for one mixture of the gases. The growth time was found to be the same as in the last case.

3) CO_2 laser excites the molecules of para-$^{12}CH_3F$ and the He–Ne laser is tuned to the absorption line of ortho-$^{13}CH_3F$ ($H = 1070$ G). Figure 6 shows the reciprocal of

the signal growth time as a function of the total pressure of $^{12}CH_3F$ and $^{13}CH_3F$. The result is a straight line (2) whose slope is 4.5×10^5 Torr$^{-1} \cdot$ sec^{-1}.

The vibrational energy transfer process in the $^{12}CH_3F - {}^{13}CH_3F$ mixture involves four gases, The possible transfer channels are as follows:
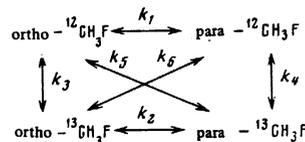
The experiments on ortho-para energy transfers in $^{12}CH_3F$ and $^{13}CH_3F$ thus enable us to conclude that $k_2 = 9.5 \times 10^5$ Torr$^{-1} \cdot$ sec^{-1} and $k_1 \approx k_2$. The rate constants for four of the energy transfer channels between the isotopic molecules are therefore unknown. The direct way of determining these constants would involve experiments in a two-component mixture, i.e., for example, to determine k_3, we would need a mixture of ortho-$^{12}CH_3F$ and ortho-$^{13}CH_3F$. In principle, the rate constants for these processes can also be determined from experimental data on four-component mixtures, but this would require high precision in the determination of the kinetic curves for the process, so that the resultant curve could be resolved into component exponentials. The precision of our experiments was not high enough to enable us to do this and we are therefore forced to confine ourselves to noting some general features of the rate constants $k_3 - k_6$.

Thus, firstly, the energy transfer between isotopic molecules is, "on the average," slower by a factor of two than between ortho- and para-modifications. In fact, if the rate constants for all the transfer channels between the isotopes are equal to the ortho-para transfer constants, i.e., $k_3 = k_4 = k_5 = k_6 = 9.5 \times 10^5$ Torr$^{-1} \cdot$ sec^{-1}, the concentration of the excited molecules of any of the components after the pulse is given by

$$n = \text{const}_1 \cdot \exp(-9.5 \cdot 10^5 pt) + \text{const}_2,$$

where p is the total pressure of $^{12}CH_3F$ and $^{13}CH_3F$ in Torr. In point of fact, it follows from Fig. 6 that the
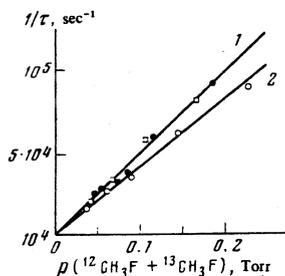
FIG. 6. Reciprocal of the signal growth time for the mixture of $^{12}CH_3F$ and $^{13}CH_3F$ as a function of the total pressure $p(^{13}CH_3F + {}^{12}CH_3F)$. ●—$^{13}CH_3F$ excited. Helium-neon laser tuned to the $^{12}CH_3F$ absorption line at $H = 1450$ G. Argon pressure 10 Torr. □—Ditto at argon pressure of 2.75 Torr. ○—$^{12}CH_3F$ excited. Helium-neon laser tuned to the $^{13}CH_3F$ line at $H = 1070$ G. Argon pressure 10 Torr.

E. N. Chesnokov and V. N. Panfilov   1115
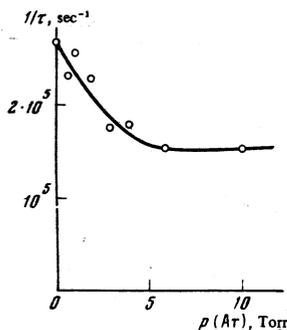
FIG. 7. Increase in the rate of energy transfer between $^{13}CH_3F$ and $^{12}CH_3F$ at low argon pressures. $^{13}CH_3F$ excited. Helium-neon laser tuned to the $^{12}CH_3F$ absorption line at $H = 1450$ G. Pressure $p(^{13}CH_3F) = p(^{12}CH_3F) = 0.16$ Torr.

increase in the concentration of excited molecules of the isotope that is not directly excited by the laser is described by an exponential with a characteristic time greater by a factor of two.

Secondly, it appears that k_3, k_4, k_5, k_6 are not very different. This follows from the fact that the experimental kinetic curves can be described by a single exponential with satisfactory precision. This would not be possible if, among the constants k_3-k_6, there were a constant much smaller than all the others. For example, if k_3 were to be small, the excitation of the molecules of ortho-$^{13}CH_3F$ would be followed by an increase in the concentration of excited ortho-$^{12}CH_3F$ molecules, which would initially rise as the square of the time.

The most natural description of all the experimental data is achieved if it considered that $k_3 = k_4 = k_5 = k_6 = 5 \times 10^5$ Torr$^{-1} \cdot$sec^{-1}, i.e., if the energy transfer between different isotopic molecules is slower by a factor of roughly two as compared with the ortho-para energy transfer, independently of which particular modification these constants belong to.

The rate constants for vibrational energy transfer between the ortho- and para-modifications of CH_3F (9.5×10^5 Torr$^{-1} \cdot$sec^{-1}) and between the isotopic molecules of $^{12}CH_3F$ and $^{13}CH_3F$ (5×10^5 Torr$^{-1} \cdot$sec^{-1}) correspond to about ~10 and ~12 gas-kinetic collisions. However, the rate constant must not be ascribed to transfers from the state ν_3 of CH_3F, excited by the laser radiation. It has been shown[7] that, when the argon pressure amounts to a few tens of Torr, the equilibrium between the excited state ν_3 and the doubly degenerate state ν_6

$= 1197.7$ cm^{-1} is rapidly established, and, when this is so, the ν_3 and ν_6 populations are equal. The vibrational energy transfer processes which we have investigated are resonant processes and are due to the dipole-dipole interaction. Since the dipole moment of the $0-\nu_6$ transition is greater by an order of magnitude than that of the $0-\nu_3$ transition,[12] the probability of transfer from the state ν_6 should be much smaller than the probability of transfer from the state ν_3. A reduction in the argon pressure should then lead to an increase in the vibrational energy transfer rate (by a factor of more than two). This is, in fact, observed in the experiment (Fig. 7). Analogous results are also obtained for the vibrational energy transfer rate between the ortho- and para-modifications of CH_3F.

In conclusion, the authors would like to express their gratitude to V. N. Shcherbinina for assistance in the experiments and to L. N. Krasnoperov for participation in the interpretation of the results.

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Translated by S. Chomet