$$|\varphi_{nn'}(q)|^2=\frac{1}{2\pi\hbar}\frac{d\varepsilon_n}{dn}\frac{d\varepsilon_{n'}}{dn'}\int dx\,dp_1\,dp_2\,\delta(p_1+p_2+\hbar q)$$
$$\times\delta\left(\varepsilon_n-\frac{p_1^2}{2m}-U(x)\right)\delta\left(\varepsilon_{n'}-\frac{p_2^2}{2m}-U(x)\right). \qquad (7)$$

To verify that (5) and (7) are identical, one needs only to perform the integrations in Eq. (7) first over the momenta p_1 and p_2 and then over the coordinate x. The expression (7) is especially convenient in calculating sums over the states n or n', which in the classical limit reduce to integration over an energy, which can be performed easily by means of a δ function.

[1] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, 1974. English translation: Pergamon Press, 1977.

Translated by W. H. Furry

Dependence of the rate of vibrational relaxation of CH_3F on the equilibrium and vibrational temperatures

E. N. Chesnokov, V. N. Shcherbinina, and V. N. Panfilov

Institute of Chemical Kinetics and Combustion, Siberian Branch of the USSR Academy of Sciences

(Submitted 23 June 1978)
Zh. Eksp. Teor. Fiz. 75, 2066–2074 (December 1978)

The double infrared resonance method was used to investigate the rates of vibrational–translational (V–T) relaxation of CH_3F (by interaction with argon) as a function of the equilibrium and vibrational temperatures. It was established that the vibrational temperature increased the V–T relaxation rate more effectively than did the translational temperature because the relaxation from the upper vibrational levels was fast.

PACS numbers: 33.10.Gx, 33.40. – e

The CH_3F molecule is one of the most slowly relaxing polyatomic molecules. Therefore, it is a convenient object for investigating the influence of the vibrational relaxation on its reactivity.[1] In such investigations one requires data on the rate of the vibrational–translational ($V-T$) relaxation of the CH_3F molecules interacting with various gases in a wide temperature range. However, the published rate constants of the relaxation processes are available only for room temperature.[2] Moreover, as shown in Ref. 3, the $V-T$ relaxation rate of CH_3F depends on the populations of the vibrationally excited states even for cw infrared radiation intensities of ~10 W/cm^2. Similar dependences have been observed earlier in the case of pulsed excitation of SF_6 (Ref. 4) by CO_2 laser radiation of $10-10^5$ W/cm^2 intensity, i.e., at high degrees of occupancy of the vibrational levels. The present paper describes an investigation of the temperature dependence of the rate of the $V-T$ relaxation of CH_3F under uniform heating conditions and also in the case of vibrational heating at a fixed translational temperature.

EXPERIMENTAL METHOD AND RESULTS

The double infrared resonance method was used to determine the vibrational relaxation time. The apparatus was basically the same as that described in Refs. 5 and 6. A mixture of gases was admitted to a glass cylindrical cell, which was 80 cm long and had an internal diameter of 2.5 cm; the windows were made of KBr. The cell was placed inside an oven 70 cm long where the temperature was kept constant to within +3°. Two laser beams passed along the cell axis. The probe beam was provided by an He–Ne laser tuned by a magnetic field near the $\lambda = 3.39\ \mu$ wavelength. Molecules were excited either by a Q-switched CO_2 laser (E~1 mJ, $\tau = 1-3\ \mu$sec) or by a cw CO_2 laser with an output power of ~10 W. The cw CO_2 laser beam was interrupted in a time of ~10 μsec at a frequency of 80 Hz by a chopper placed at the focus of the telescope. Before entering the cell the beam was attenuated (if necessary) by a polarizer. Use was made of the $P(20)$ laser line due to the 00^01-02^00 transition, coinciding with the $Q(12,2)$ line of $^{12}CH_3F$ and the $P(32)$ line of the same laser transition coinciding with the $R(4,3)$ line of $^{13}CH_3F$.

The signal was recorded with a Ge:Au photoresistor. The signal/noise ratio was improved by the use of a 64-channel digital store with response up to 1 μsec/channel. The stored signal was used to drive a chart plotter.

The temperature dependences of the relaxation constants of CH_3F interacting with argon and helium were determined with the probe laser beam tuned to an absorption line of $^{12}CH_3F$ in a field of 380 G (the absorption spectra of $^{12}CH_3F$ and $^{13}CH_3F$ in the tuning range of the He–Ne laser were reported in Ref. 6). After a CO_2 pulse there was an increase in the intensity of the probe laser beam and this was followed by exponential relaxation. Figure 1 shows a typical signal and its semilogarithmic anamorphosis. The slope of this anamorphosis can be used to find the vibrational relaxation time. Other figures give the dependences of the reciprocal of the vibrational relaxation time on the argon (Fig. 2) and helium (Fig. 3) pressures obtained at various tempera-

0038-5646/78/1201039-05$02.40

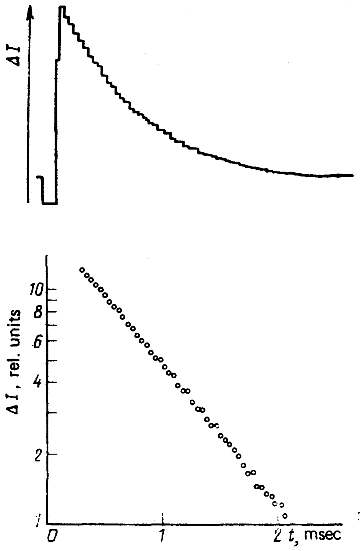

FIG. 1. Double resonance signal and its semilogarithmic anamorphosis for $P(CH_3F)$ 10.6 Torr and $P(Ar) = 11$ Torr at room temperature.

tures and at a fixed pressure of CH_3F. The CH_3F pressures are in the 0.4–2 Torr range. The slopes of the straight lines give the relaxation constants of CH_3F interacting with argon and helium. The results are given in Table I.

The relaxation constant for the interaction with helium at room temperature is close to the value given in the literature, whereas that for the interaction with argon is considerably less (22 instead of 39 $sec^{-1} \cdot Torr^{-1}$ given in Ref. 2).

Measurements under conditions of high concentrations of excited molecules were carried out at absorbing gas pressures of <0.25 Torr. This was necessary to ensure that the heating of the gas, resulting from the absorption of cw laser radiation, was negligible. Calculations based on the absorbed power measurements indicated that the maximum temperature rise on the cell axis could reach 50°K. However, it was always 5–10 times less than the increase in the vibrational temperature. To operate at these pressures, the He–Ne laser was tuned to the strongest absorption lines of $^{12}CH_3F$ and $^{13}CH_3F$.

The duration of a CO_2 laser radiation pulse (~6 msec) formed by the chopper was sufficient to ensure a steady-state concentration of excited molecules corresponding to the incident power. The recording system was switched on 20 μsec before the end of the pulse. A record was made of the kinetic decay of the concentration of the excited molecules from the steady-state value created by the laser radiation to the equilibrium concentration at room temperature.

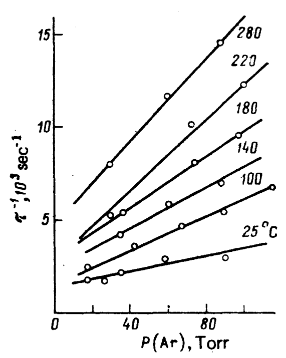

FIG. 2. Dependences of $1/\tau$ on the argon pressure.

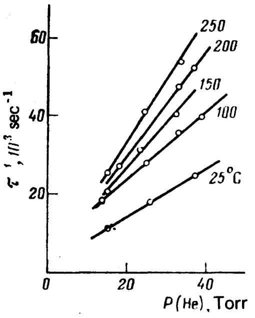

FIG. 3. Dependences of $1/\tau$ on the helium pressure.

The observed signal could be related directly to the concentration of the excited molecules. In fact, since the laser was tuned to an absorption line of the molecules in the ground state and the population of the upper level of the transition was negligible, we readily obtained

$$\Delta I/I = \exp(\sigma n^* l) - 1 \approx \sigma n^* l, \qquad (1)$$

where $\Delta I/I$ is the relative increase in the intensity of the probe beam; σ is the absorption cross section of the probe radiation; l is the path in the gas. Since σ and l were known, the above formula could be used to determine the excited-molecule concentration n^*.

The signal disappeared when the laser radiation was detuned from the absorption line of the molecules in the ground state. Hence, the observed signal did not include a contribution from the absorption by the excited molecules. Otherwise, Eq. (1) would have given an underestimate of the excited-molecule concentration. We could not be absolutely sure that there was no absorption line of the excited molecules coinciding exactly with the line to which the He–Ne laser was tuned but such coincidence was highly unlikely.

Figure 4 gives an example of the kinetic decay curves of the concentration of the exicted $^{13}CH_3F$ molecules starting with various initial values. The initial region is identified by altering the rate of time scanning of the storage channels. The excited-molecule concentrations in Fig. 4 are reduced to the initial value. It is clear from this figure that an increase in the initial concentration of the excited molecules results in faster decay. An analysis of the kinetic curves shows that they are no longer exponential.

The same effect was exhibited also by $^{12}CH_3F$. However, because of the lower absorption coefficient, the concentration of the excited $^{12}CH_3F$ molecules was less.

The kinetic curves of this kind were analyzed as follows. For each curve a relaxation time was introduced and it depended on the initial excited-molecule concen-

TABLE I.

t, °C	K(Ar), sec⁻¹ · Torr⁻¹	K(He), sec⁻¹ · Torr⁻¹	t, °C	K(Ar), sec⁻¹ · Torr⁻¹	K(He), sec⁻¹ · Torr⁻¹
25	22	650	200	–	1420
100	47	900	220	99	–
140	54	–	250	–	1620
150	–	1260	280	115	–
180	66	–			

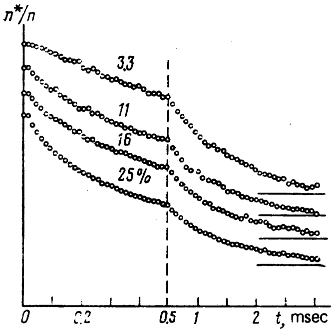

FIG. 4. Kinetic curves of the decay of the excited-molecule concentration after interruption of a cw CO_2 laser beam. The numbers alongside the curves give the concentrations of the excited molecules; $P(^{13}CH_3F) = 0.06$ Torr, $P(Ar) = 28$ Torr.

tration

$$\frac{1}{\tau}=-\frac{1}{n^*}\frac{dn^*}{dt}\bigg|_{t=0}. \tag{2}$$

The relaxation time found in this way had to be corrected for the diffusion of the excited molecules

$$1/\tau=PK(n^*/n)+K_{\text{diff}}, \tag{3}$$

where P is the argon pressure; $K(n^*/n)$ is the relaxation constant depending on the relative concentration of the excited molecule; and K_{diff} is the diffusion constant.

The diffusion constant is independent of the excited-molecule concentration. Therefore, it can be determined using the relaxation constant measured earlier for low values of n^*/n. In this way we can find the dependence of the relaxation constant on the relative concentration of the excited molecules. This dependence is plotted in Fig. 5.

DISCUSSION OF RESULTS

The processes occurring during vibrational relaxation of polyatomic molecules can be divided into several types. The fastest are the processes in which quanta of one vibrational mode are exchanged. If the dipole moment of the transition in this mode is large (as is the case for the ν_3 mode of CH_3F), the exchange of quanta occurs in between one and ten collisions.[7] The next category are the processes of intermode energy exchange. In a CH_3F molecule they occur in times corresponding to several tens of gas-kinetic collisions.[8] Finally, there are the $V-T$ processes in which a vibrational energy quantum is converted into translational energy. In CH_3F, these processes require 10^3–10^5 collisions.[2]

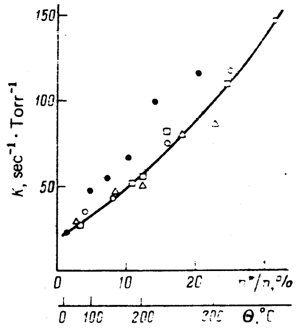

FIG. 5. Dependence of the relaxation constant of CH_3F interacting with argon on the excited-molecule concentration (or on the vibrational temperature) for $P(^{13}CH_3F) = 0.06$ Torr: ○) $P(Ar) = 19.5$ Torr; □) $P(Ar) = 28$ Torr; △) $P(Ar) = 41.5$ Torr. The symbols ● represent the dependence of the relaxation constant on the equilibrium temperature under weak excitation conditions.

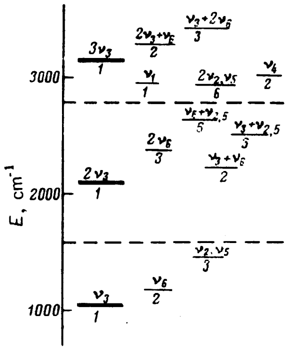

FIG. 6. Vibrational-level scheme of the CH_3F molecule. The number below the bar representing the level gives the degree of its degeneracy. The levels of the ν_3 mode are shown separately: the exchange of quanta in this mode is fastest. The dashed lines represent the separation of the vibrational levels close to a particular level of the ν_3 mode.

A quasisteady distribution of the molecules between the vibrational levels is established rapidly as a result of the intramode and intermode energy exchange processes. This distribution need not be of the Boltzmann type but it is close to the Boltzmann distribution at least at the lowest levels because the fastest processes are those in which quanta of one mode are exchanged.

If the relative concentration of the excited molecules is low, the majority of them are in the first vibrationally excited state ν_3 (Fig. 6). Relaxation of the vibrational energy reduces then to the loss of the ν_3 vibrational quanta. An increase in the relative concentration of the excited molecules transfers an increasing proportion of these molecules to higher vibrational levels. We can see from Fig. 6 that the energy intervals between the vibrational levels decrease rapidly. Therefore, the loss of the vibrational energy by the intermode exchange plays an increasingly important role. Since this process is much faster than the $V-T$ relaxation, the rate of loss of the vibrational energy becomes faster.

In contrast to the results reported in Ref. 4, our experimental data cannot be explained by the anharmonicity of a single molecular mode. A calculation carried out on the basis of a formula given in Ref. 4 shows that the relaxation time in the ν_3 mode should decrease by just 11% on increase of the vibrational temperature from 300 to 600° K. It follows that the observed increase in the rate of relaxation is a specific property of the investigated polyatomic molecule.

We shall give a quantitative description of the results on the basis of the following model of the molecule. We shall consider only the ν_3 mode. The presence of the other vibrational levels will be allowed for by introducing the statistical weight g_i for each of the levels of the

ν_3 mode:

$$g_i=1+\sum_s \exp\left[-\frac{(E_s-i\hbar\omega)}{kT}\right], \tag{4}$$

where E_s is the energy of the s-th state; $\hbar\omega$ is the quantum energy of the ν_3 mode; T is the translational temperature.

Summation is carried out over the nearest vibrational levels allowing for their degeneracy. Splitting of these levels into those close to one or the other level of the ν_3 mode is fairly arbitrary but for the second and third levels this can be done in a natural manner (Fig. 6).

We shall assume that a system of this kind has a quasisteady Boltzmann distribution in the course of the relaxation process. Then, the $V-T$ relaxation constants can no longer be regarded as proportional to the level number. Therefore, we have to introduce a separate relaxation constant for each level.

This model generally reflects the role of the various processes in the population of the vibrational levels of the CH_3F molecule under real conditions. Estimates indicate that even in those strongly dilute CH_3F mixtures with argon which were used in our experiments the time to establish equilibrium in the ν_3 mode is considerably less than the excited-molecule lifetime. Exchange of the quanta of the ν_6, ν_3, and ν_5 deformation vibrations is clearly slower because the dipole moments of the corresponding transitions are an order of magnitude smaller.[9] These states are also fairly rapidly populated by collisions of the molecules in the states $\nu_3, 2\nu_3, \ldots$ with the argon atoms. The distribution within a given group of levels, populated by one level of the ν_3 mode, is governed by the translational temperature.

A calculation of the statistical weights on the basis of Eq. (4) gives the following room-temperature values: $g_1=2.17$, $g_2=3.67$, and $g_3=25.75$.

The rate of loss of the vibrational energy is

$$\frac{dE}{dt}=-\hbar\omega P\sum_{i=1}^{\infty} K_i n_i, \tag{5}$$

where P is the argon pressure; K_i and n_i are the relaxation constant and population of the i-th level. Hence, we obtain the following expression for the relaxation constant, which depends on the excited-molecule concentration:

$$K\left(\frac{n^*}{n}\right)=-\frac{1}{Pn^*}\frac{dn^*}{dt}=\hbar\omega\frac{dn^*}{dE}\sum_{i=1}^{\infty} K_i\frac{n_i}{n^*}. \tag{6}$$

For $n^*/n\to 0$, only the first term remains in the sum. We can easily see that then $K(n^*/n)\to K_1$.

The next terms give corrections linear, quadratic, etc. in n^*/n. The continuous curve in Fig. 5 is calculated on the basis of Eq. (6) including terms up to the second order of smallness in respect of n^*/n, inclusive. The values of the relaxation constants selected in this way are as follows: $K_2=360\ \mathrm{sec}^{-1}\cdot\mathrm{Torr}^{-1}$, $K_3=540\ \mathrm{sec}^{-1}\cdot\mathrm{Torr}^{-1}$. The value of K_3 is only a rough estimate; we can only say that it lies within the interval 300–1000 $\mathrm{sec}^{-1}\cdot\mathrm{Torr}^{-1}$.

It follows that the intermode exchange has the result that the effective relaxation constant of the second level of the ν_3 mode is 17 times greater than the corresponding constant of the first level. The fact that the relaxation constant of the third level is of the same order of magnitude clearly indicates that the conditions of validity of the model employed are not obeyed. Clearly, under our experimental conditions the population in the region of the third level is less than that found from the Boltzmann distribution with the vibrational temperature.

The dependence of the rate of relaxation on the excited-molecule concentration obtained in this way can be regarded as the dependence of the relaxation constant on the vibrational temperature. It is interesting to compare it with the dependence of the relaxation constant on the equilibrium temperature. This comparison should reveal the main cause of the increase in the relaxation constant in the course of equilibrium heating of the gas: it may be due to the increase in the rate of relative motion of the molecules or due to the increase in the role of the processes involving the upper vibrational levels.

However, it is not self-evident that we can compare directly the relaxation constants at some equilibrium temperature with the relaxation constants of a gas which is vibrationally heated to the same temperature by laser radiation because these constants represent different physical processes. Measurements in a vibrationally heated gas are carried out under conditions such that the populations of the excited states are much higher than the equilibrium values, corresponding to room temperature. Under these conditions the relaxation kinetics is governed solely by the processes associated with the loss of the vibrational energy. The reverse processes can be ignored. On the other hand, a pulse from a Q-switched laser increases only slightly the population of the excited states compared with the equilibrium value. In this case the kinetics of the relaxation process is governed by the loss of the vibrational energy and by the reverse processes of the excitation of vibrations by molecular collisions.

We shall now derive an expression for the relaxation constant under conditions such that the reverse processes cannot be ignored. Equation (5) now becomes

$$\frac{dE}{dt}=-\hbar\omega P\sum_{i=1}^{\infty}(K_i n_i-K_i' n_{i-1}), \tag{7}$$

where K_i' is the rate constant for the $(i-1)\to i$ transition in collisions with the argon atoms. The principle of detailed equilibrium states that

$$g_{i-1}K_i'=g_iK_i\exp(-\hbar\omega/kT). \tag{8}$$

Using this principle and the relationship between n_i and i_{i-1}, we obtain

$$\frac{dE}{dt}=-\hbar\omega P\left\{1-\exp\left[-\frac{\hbar\omega}{k}\left(\frac{1}{T}-\frac{1}{\Theta}\right)\right]\right\}\sum_{i=1}^{\infty}K_in_i, \tag{9}$$

where Θ is the vibrational temperature. After a laser pulse, we have

$$\Theta=T+\varepsilon,\quad E=E_0+\varepsilon c, \tag{10}$$

where c is the vibrational specific heat.

Retaining in Eq. (9) the terms of the first order in ε, we obtain

$$\frac{d\varepsilon}{dt}=-\frac{P(\hbar\omega)^2}{kT^2c}\varepsilon\sum_{i=1}^{\infty}K_in_i. \tag{11}$$

Its solution is of the form

$$\varepsilon\sim\exp\left(-\frac{t}{\tau}\right),\quad \frac{1}{\tau}=P\frac{(\hbar\omega)^2}{kT^2c}\sum_{i=1}^{\infty}K_in_i. \tag{12}$$

Clearly, the excited-molecule concentration varies exponentially with the same characteristic time. Therefore, the relaxation constant in the case of a small deviation of the excited-molecule concentration from the equilibrium value is

$$K_0=\frac{(\hbar\omega)^2}{kT^2c}\sum_{i=1}^{\infty}K_in_i. \tag{13}$$

On the other hand, employing the relationships

$$E=\frac{k\Theta^2}{Z}\frac{dZ}{d\Theta} \tag{14}$$

and

$$n^*=1-1/Z, \tag{15}$$

where Z is the vibrational partition function and, in the case of a high concentration of excited molecules, Eq. (6) for the relaxation constant can be rewritten in the form

$$K\left(\frac{n^*}{n}\right)=\frac{\hbar\omega E}{k\Theta^2c(Z-1)}\sum_{i=1}^{\infty}K_in_i. \tag{16}$$

A numerical calculation of $E/\hbar\omega(Z-1)$ for the CH_3F molecule shows that in the investigated temperature range it does not change by more than 15% and is close to unity. Consequently, Eq. (16) becomes analogous to Eq. (13):

$$K\left(\frac{n^*}{n}\right)=\frac{(\hbar\omega)^2}{k\Theta c}\sum_{i=1}^{\infty}K_in_i. \tag{17}$$

This formula differs from Eq. (13) for the relaxation constant in the case of a small deviation from equilibrium only by the fact that the values of K_i in the sum should be taken at room temperature. Thus, a direct comparison of the relaxation constant measured at some high vibrational temperature and the relaxation constant at the same equilibrium temperature can demonstrate the influence of the translational temperature on the rate constants of elementary relaxation processes.

This comparison can be made on the basis of Fig. 5. In this figure the relaxation constant at high concentrations of excited molecules is given also as a function of the vibrational temperature. The vibrational temperature corresponding to the measured excited-molecule concentration was calculated using the CH_3F vibration frequencies given in Ref. 9. We can see from Fig. 5 that at a high equilibrium temperature the relaxation constant exceeds the constant at the same vibrational temperature when the translational temperature has the room value. However, the main reason for the increase in the relaxation constant due to uniform heating is the increase in the vibrational temperature. For example, an increase in this temperature from the room value to 550°K increases the relaxation constant by a factor of 3.7 and a further increase in the translation temperature to 550°K increases it only by a factor of 1.4. In other words, the main reason for the increase in the relaxation rate under equilibrium heating conditions is the relaxation from the higher vibrational levels. This has to be allowed for in, for example, comparing the temperature dependence of the relaxation constants with that calculated theoretically on the basis of some model.

[1] V. P. Strunin, N. K. Serdyuk, and V. N. Panfilov, Dokl. Akad Nauk SSSR **234**, 1395 (1977).
[2] E. Weitz and G. W. Flynn, J. Chem. Phys. **58**, 2679 (1973).
[3] V. P. Strunin, L. V. Kuĭbida, E. N. Chesnokov, and V. N. Panfilov, Kinet. Katal. (in press).
[4] S. A. Akhmanov, V. M. Gordienko, A. V. Mikheenko, and V. Ya. Panchenko, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 603 (1977) [JETP Lett. **26**, 453 (1977)].
[5] E. N. Chesnokov and V. N. Panfilov, Zh. Eksp. Teor. Fiz. **72**, 1694 (1977) [Sov. Phys. JETP **45**, 888 (1977)].
[6] E. N. Chesnokov and V. N. Panfilov, Zh. Eksp. Teor. Fiz. **73**, 2122 (1977) [Sov. Phys. JETP **46**, 1112 (1977)].
[7] B. L. Earl, P. C. Isolani, and A. M. Ronn, Chem. Phys. Lett. **39**, 95 (1976).
[8] F. B. Grabiner, G. W. Flynn, and A. M. Ronn, J. Chem. Phys. **59**, 2330 (1973).
[9] L. M. Sverdlov, M. A. Kovner, and E. P. Kraĭnov, Kolebatel'nye spektry mnogoatomnykh molekul, Nauka, M., 1970 (Vibrational Spectra of Polyatomic Molecules, Wiley, New York, 1974).

Translated by A. Tybulewicz