Study of vibrational relaxation of SF_4 at low temperatures by the method of double infrared resonance

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V—T relaxation of SF_6 in mixtures with Ar, Xe, and CH_3F is investigated by the method of double infrared resonance in the temperature interval 320–150 K. A decrease in the vibrational relaxation time is observed at $T < 270$ K. It is shown that the experimentally observed temperature dependence of the V—T exchange interaction can be attributed to an increasing influence of the attraction potential. The influence of strong excitation at low temperatures on the vibrational deactivation is discussed.

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1. INTRODUCTION

The important role of the vibrational-translational energy exchange in reactions of selective dissociation of SF_6 molecules in an IR radiation field, and the possibility of decreasing the effectiveness of these processes with decreasing temperature, were discussed in a number of papers.[1,2] It should be noted that the mechanism of vibrational relaxation of polyatomic molecules was investigated in sufficient detail only at relatively high temperatures. In particular, all the hitherto-performed measurements of the rate of vibrational relaxation of SF_6 were made in the temperature region $T \gtrsim 300°$ K.[3-5] The character of the temperature dependence of these results corresponds to the Landau-Teller relation $\ln(p\tau) \sim T^{-1/3}$. This suggests that at low temperatures the process slows down substantially.

However, the data obtained even in the very first studies of relaxation at $T < 300°$ K point in many cases to a noticeable deviation of the kinetic characteristics from those predicted by the simple theory.[6] The reason for this deviation is apparently the fact that at low temperatures the influence of the long-range part of the intermolecular interactions increases, and for molecules with large depth of the potential well ε it can reach appreciable values.[7]

In the present study we investigated in the temperature interval 150–320° K the vibrational-translational relaxation in the systems SF_6 + Ar, SF_6 + Xe and SF_6 + CH_3F with sufficiently large and at the same time different values of ε/k which are equal, for a Lennard-Jones potential to 157, 211, and 258° K, respectively.[8] The temperature experiments were performed with the aid of a double IR resonance method, which, first, differs in having a sufficiently high sensitivity, and, second, makes it possible to use optical cryostats of relatively simple construction for the kinetic measurements.

2. RESULTS OF TEMPERATURE MEASUREMENTS

A block diagram of the setup is shown in Fig. 1. The temperature experiments were carried out in the optical cryostat 7. The investigated gas mixture was admitted into a monel cell 6 of length 70 mm, with windows of BaF_2, sealed with indium gaskets. The necessary temperature was set with the aid of a heater 9 and a coolant 8 and was monitored by thermocouple 10. The SF_6 molecules were excited with a TEA tunable pulsed CO_2 laser 2, described in Ref. 9, radiation from which was directed with the aid of a flat mirror 3 into the optical cryostat and at a beam divergence ~ 0.4° filled practically uniformly the cross section area ~ 1.5 cm² of the cell located at a distance 2 m from the laser 1. A small fraction of this radiation was diverted by NaCl beam-splitting plate 13 to a photoresistor 12 and was used to start the oscilloscope 16.

The probing radiation of cw tunable CO_2 laser tuned to the generation line $P(26)$ of the 10.6-μm transition (938.688 cm^{-1}) passed through the volume of the excited gas at an angle ~ 4° relative to the exciting beam and, before striking the receiving area of photoresistor 14, it was separated by a monochromator with a fraction grating 11 from the scattered radiation of the pulsed laser. It should be noted that the use of the monochromator made it possible to carry out the measurements while working on neighboring lasing lines. The amplified signal was registered on the screen of an oscilloscope. The gain of the amplifier 15 was of the order of 200, and the time constant of the receiving-amplifying system was not worse than 1 μsec.

The absorption of the probing radiation at the indicated frequency is small even at the maximum temperature of the experiment, and is determined mainly by the population of the upper vibrational levels. This is confirmed by the appreciable decrease of the absorption coefficient, from 0.08 to 0.04 cm^{-1} Torr^{-1} when the temperature is lowered from 310 to 200° K. In the course of the experiments, the cw laser power did not exceed 50mW, so that no change in the translational temperature of the mixture was observed as a result of the absorption of probing radiation. After the excitation, the absorption of the probing radiation increases sharply, this being due to the population of the upper vibrational-rotational levels on account of fast $V-V$ and

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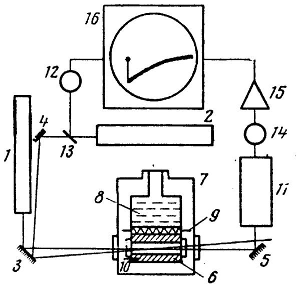

FIG. 1. Block diagram of setup: 1—cw CL_2 laser with diffraction grating of 100 lines/mm, 2—TEA pulsed CO_2 laser with diffraction grating 150 lines/mm, 3,4,5—flat mirrors, 6—cell, 7—optical cryostat, 8—coolant, 9—heater, 10—thermocouple, 11—spectrometer, 13-14—Ge:Au photoresistors, 13—beam-splitting plate, 15—amplifier, 16—oscilloscope S-1-33.

R–T processes. The slow change of the signal observed in the course of time is determined mainly by *V–T* relaxation of the SF_6 from the level $\nu_6 = 363\ cm^{-1}$ (Ref. 3).

The pulsed TEA laser operating in the TEM_{00q} regime was retuned in the course of the temperature measurements from the line *P*(20) (944.194 cm^{-1}) to *P*(16) (947.782 cm^{-1}), in accordance with the experimentally established high-frequency shift of the maximum of the absorption coefficient with decreasing temperature. The pulse duration was ≤ 200 sec, and its energy, measured with IMO-2 instrument, did not exceed 2mJ.

Figures 2a and 2b show typical oscillograms of probing signal for the SF_6 + Ar system. The relative change of the signal in all the experiments did not exceed 15%. In the experiment the gases Ar and Xe were spectrally pure, while SF_6 and CH_3F contained ≤ 0.2% of impurities after low-temperature distillation. The experiments were performed in dilute gas mixtures with pressures 0.3–0.7, 10–50, 100–400, and 0.5–1.0 Torr for SF_6, Ar, Xe, and CH_3F, respectively. The translational temperature of the system therefore remained likewise unchanged by the pulsed excitation, and the constant level of the signal after completion of *V–T* relaxation did not differ from the initial one. The characteristic *V–T* relaxation time were determined from the slope of the lines used to approximate the time dependences in I (Fig. 3a,b), where ΔI is the deviation of the signal from the equilibrium value (Fig. 2). At temperatures below 213° K and at Ar pressures up to 20 Torr and Xe pressures up to 80 Torr, the signal deviated from an exponential dependence in the initial Δt sections of the kinetic curves (Fig. 3a). In these cases, the straight lines were drawn with the experimental values of ln ΔI for $t > \Delta t$.

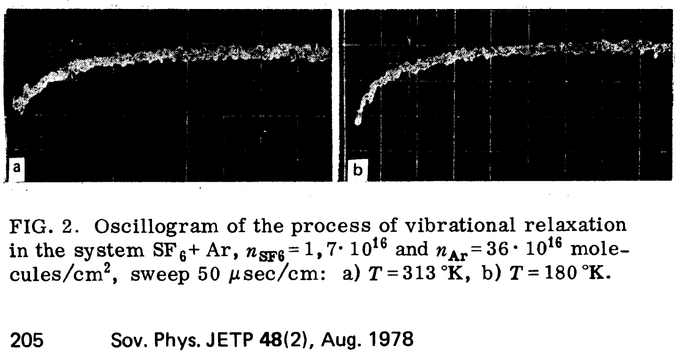

FIG. 2. Oscillogram of the process of vibrational relaxation in the system SF_6+ Ar, $n_{SF_6} = 1,7 \cdot 10^{16}$ and $n_{Ar} = 36 \cdot 10^{16}$ molecules/cm^2, sweep 50 μsec/cm: a) $T = 313$ °K, b) $T = 180$ °K.

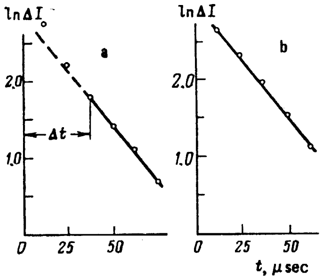

FIG. 3. Semilogarithmic plots of the relative change of the signal ln ΔI with time, $n_{SF_6} = 1,7 \cdot 10^{16}$ molecules/cm^2, $n_{Ar} = 36 \cdot 10^{16}$ molecules/cm^2: a) $T = 180$ °K, b) $T = 213$ °K.

From the linear dependences of τ^{-1} on the pressure of the inert gas at the corresponding temperature, we determined the values of $p\tau$ (Figs. 4a,b). At 290° K, these values for SF_6+Ar and SF_6+Xe are respectively $(0,56 \pm 0.07) \cdot 10^3$ and $(3.9 \pm 0.5) \cdot 10^3$ μsec-Torr, the first of these quantities being in good agreement with the value given in Refs. 3 and 4. The vibrational deactivation of SF_6 by CH_3F molecules was investigated in the mixture $SF_6 + CH_3F$ +Xe with Xe pressure ≈ 10 Torr. The presence of Xe included in this case the change of the vibrational temperature of the system and the influence of very slow deactivation processes SF_6 and CH_3F by xenon under these conditions could be neglected. The time of the vibrational relaxation in this mixture $p\tau = 28 \pm 4$ μsec-Torr at 293° K was determined by the most effective collisions, and correspond in practice to the process of vibrational deactivation of SF_6 by CH_3F molecules.

Figures 5a–5c show the temperature dependences of *V–T* relaxation time of SF_6 in collisions with Ar, Xe,

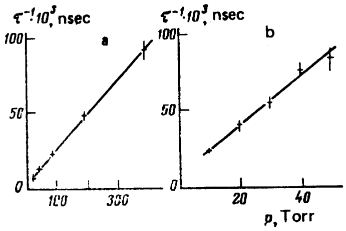

FIG. 4. Dependence of the rate of vibrational relaxation τ^{-1} on the pressure of the inert gas, $T = 293$ °K $p_{SF_6} = 0,3$ Torr, a) SF_6 +Xe, b) SF_6+ Ar.

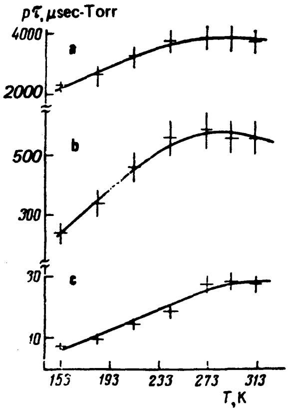

FIG. 5. Temperature dependence of $p\tau$ for the systems: a) SF_6+Xe, b) SF_6+Ar, c) SF_6+CH_3F.

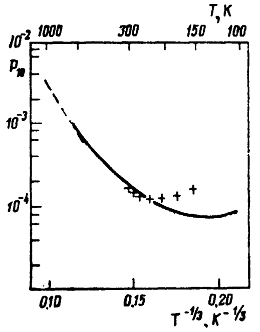

FIG. 6. Temperature dependence of P_k for the system SF_6+Ar: Crosses—present work, dashed—results of Ref. 8, solid line—from formula (4): $\sigma_1=0.25$ Å.

and CH_3F, respectively. Attention is called to the fact that their form differs substantially from the Landau-Teller dependence usually observed at high temperatures. In the temperature interval 313–153° K, in all cases, the value of $p\tau$ first increases slightly, reaches a certain maximum, and then decreases. The probability P_{10} of the $V-T$ relaxation, calculated on the assumption that the transfer of the vibrational energy to the translational degrees of freedom takes place from the lowest vibrational level $\nu_6=363$ cm^{-1} of the SF_6 molecules is seen in similar fashion:

$$P_{10}=\frac{1}{zp\tau[1-\exp(-h\nu_6/kT)]}, \tag{1}$$

$$z=2n_x\left(\frac{\sigma+\sigma_x}{2}\right)^2\Omega^{2,2*}\left[\frac{2\pi kT(m+m_x)}{mm_x}\right]^{1/2} \tag{2}$$

is the gaskinetic number of collisions of the SF_6 molecules with particles of x (Ar, Xe, CH_3F) at a pressure of 1 Torr, n_x is the number of particles in the unit volume at a pressure of 1 Torr, m_x is the mass of the x particles, $m=242.5\times10^{-24}$ g, and σ and ε are the parameters of the Lennard-Jones Potential:

$$V(r)=4\varepsilon[-(\sigma/r)^6+(\sigma/r)^{12}]. \tag{3}$$

The values $\Omega^{2,2*}=f(Tk/(\varepsilon\varepsilon_x)^{1/2})$ were taken from Ref. 8. It is important that there exist a certain temperature region where the rate of the process of the vibrational-translational energy transfer is minimal.

The temperature dependences of the probability of $V-T$ relaxation, observed in the present experiment, cannot be attributed to the presence of specific intermolecular interactions, as in the case of hydrogen-halide,[10] by virtue of the high symmetry and inertness of the SF_6 molecule.[3] The possibility of the deviation of the temperature dependence of P_{10} from the Landau-Teller curve for nonpolar molecules was noted in a treatment of the problem of the $V-T$ relaxation with allowance for the attraction mode of the potential of the intermolecular interactions.[7,11] Such a problem was solved in Ref. 11 with the potential (3), and the expression obtained for the temperature dependence of the $V-T$ relaxation is

$$P_{10}\approx A\exp\left[-3\chi+1.48\left(\chi\frac{\varepsilon}{kT}\right)^{1/2}+0.51\frac{\varepsilon}{kT}+\frac{h\nu_6}{2kT}\right], \tag{4}$$

where A is a coefficient that does not depend on the temperature,

$$\chi=\left[\frac{2\pi^4c^2\nu_6{}^2mm_x\sigma_1{}^2}{(m+m_x)kT}\right]^{1/3}$$

is the adiabatic parameter ($2\chi\gg1$),

$$\sigma_1=\frac{\Gamma(7/12)}{\pi^{1/2}\Gamma(1/12)}\left(\frac{4\varepsilon}{E^*}\right)^{1/2}\sigma$$

is the radius of the exchange forces, and E^* is the collision energy corresponding to the maximum value of P_{10}.

In the case of gas mixtures containing χ, when the temperature decreases from 313 to 93° K, the value of the parameter χ changes in the range 5–10, and at values $\varepsilon/k>100$°K the second and third factors can make a noticeable contribution that leads to an increase of the $V-T$ relaxation probability. Figure 6 shows for the SF_6+Ar system the values of P_{10} obtained in the present paper at low temperature, and those calculated from the results of measurements in shock waves.[5] It is possible to draw through the aggregate of the experimental data in the temperature interval 1000–90° K a curve described by expression (4) which, being in good agreement with the results of the high-temperature measurements, describes qualitatively correctly the experimentally observed low-temperature dependence.

In this case ε/k is equal to 300° K and differs from the usually observed geometric mean value $\varepsilon=(\varepsilon_{SF_6}\varepsilon_{Ar})^{1/2}=157$ K. A discrepancy of this order is not unexpected, inasmusch as the values $\varepsilon_{SF_6}=200$ K and $\varepsilon_{Ar}=124$ K, used for the calculation, were obtained from results of viscosity measurements.[8] In addition, it should be noted that the intermolecular interactions with participation of so large a molecule as SF_6 are in general poorly described by a Lennard-Jones potential, and it would be useful to consider the vibrational-relaxation problem with, say, a Kihara potential, which takes more correct account of the finite dimensions of the molecule.

Extrapolation of the values of the probability P_{10} into the region of liquid agron temperature shows that the rate of the $V-T$ relaxation under these conditions is in any case not lower than at room temperature. If it is assumed that the same relaxation mechanism operates in the liquid and gas phases, the time of deactivation of SF_6 in liquid argon does not exceed 0.5 nsec. The first attempt to measure the rate of vibrational deactivation of SF_6 dissolved in liquid Ar, performed by the method of double IR resonance (excitation by the pulsed laser emission line $P(26)$ of the 10.6 - μm transition) has shown that the relaxation time in such a system is much shorter than the resolution $\tau \sim 1$ μsec of the appartus.

3. MODEL OF VIBRATIONAL DEACTIVATION OF SF_6 AT LOW TEMPERATURES

It was noted above that at low temperatures the process of vibrational deactivation proceeds with high speed for a time Δt (Fig. 3a). The possible reason is that the rate of $V-T$ relaxation of polyatomic molecules, defined as $R_i = d\ \ln|E_i - E_{i0}|/dt$, depends on the degree of excitation of a system, i.e., on the deviation of the vibrational temperature T_{vi} from the translational.[5] For a system described by a single vibrational temperature $T_{vi} = T_v$, the value of R_i is determined not only by the change of T_v, but also by the energy $\Theta_i = h\nu_i/k$ of the given vibrational:

$$R_i = \frac{\Theta_i T_v^{-2}[1-\exp(-\Theta_i/T)]}{\{1-\exp[-\Theta_i(1/T-1/T_v)]\}[1-\exp(-\Theta_i/T_v)]}\frac{dT_v}{dt}\ . \tag{5}$$

The dependence of the velocity on Θ_i vanishes at a small deviation of T_v from T, when

$$\Theta_i(1/T-1/T_v) \ll 1. \tag{6}$$

The system relaxation process proceeds in this case with a single time τ:

$$\tau^{-1} = R = R_i = \frac{1/T_v^2}{1/T-1/T_v}\frac{dT_v}{dt}. \tag{7}$$

We note that the degree of excitation $\Theta_i(1/T - 1/T_v)$ increases not only with increasing excitation power, but also, to a larger degree, when the gas temperature is decreased. An estimate of the influence of both factors was carried out within the framework of a simple harmonic model with intramolecular $V-V$ exchange, where SF_6 was represented in the form of a system with three normal modes (Fig. 7). The calculated relative change of the rate R_I/R_{III} for typical values of the absorbed energy ΔE at temperatures 313 and 153° K, obtained from formula (5), is listed in the table. It is seen from the table that with decreasing temperature, during the initial stage of the vibrational deactivation, a significant role is assumed by the rapid energy-exchange processes with participation of high-frequency oscillations, particularly the processes of $V-T$ relaxation from the overtone levels with probability $P_{i,i-1} = iP_{10}$. In a polyatomic molecule their contribution increases on account of the increase of the population of the overtone levels in resonant $V-V$ exchange. A similar increase of the rate of the vibrational relaxation in SF_6 was observed[12] when the intensity of the selective laser excitation was increased.

Thus, it must be emphasized that when the temperature is lowered the probability of the vibrational-translational energy transfer from the level ν_6 does not change radically, but the deactivation process itself becomes on the whole more complicated and the initial section Δt of the kinetic curve carries some information on the $V-T$ relaxation from upper vibrational levels.

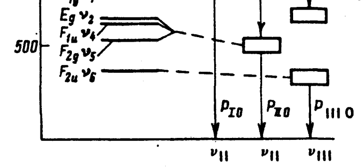

FIG. 7. Three-mode model of fundamental oscillations of SF_6: $\nu_I = 1000$, $\nu_{II} = 500$ and $\nu_{III} = 333$ cm^{-1}, $P_{I0} \ll P_{II0} \ll P_{III0}$.

TABLE I.

ΔE, mJ	Δe*, K	T, K	T_{v0}**, K	$\frac{\Theta_I(T_{v0}-T)}{TT_{v0}}$ ($\Theta_I = 1440$ K)	$\frac{\Theta_{III}(T_{v0}-T)}{TT_{v0}}$ ($\Theta_{III} = 480$ K)	$\left.\frac{R_I}{R_{III}}\right\vert_{t=0}$ $T = 300$ K	$\left.\frac{R_I}{R_{III}}\right\vert_{t=0}$ $T = 150$ K
4	906	300 150	397 303	1.2 4.9	0.4 1.6	1.4	2.4
1	227	300 150	327 205	0.4 2.6	0.1 0.9	1.1	2.0

*Δe—mean value of energy absorbed by one molecule.
**T_{v0}—initial vibrational temperature.

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