[14] P. D. Drummond and H. J. Carmichael, Opt. Commun. 27, 160 (1978).
[15] L. M. Narducci, D. H. Feng, R. Gilmore, and G. S. Agarwal, Phys. Rev. A 18, 1571 (1979).
[16] R. Bonifacio and L. A. Lugiato, Opt. Commun. 19, 122 (1976).
[17] H. J. Carmichael and D. F. Walls, J. Phys. B 10, L 685 (1977).
[18] G. S. Agarwal, L. M. Narducci, D. H. Feng, and R. Gilmore, Phys. Rev. Lett. 42, 1260 (1979).
[19] P. Lancaster, Theory of Matrices, Academic, 1969 (Russian translation, Nauka, Moscow, 1978, p. 173).
[20] R. Z. Khas'minskiĭ, Teor. veroyatn. i ee prim. 8, 3 (1963).
[21] B. Ya. Zel'dovich, A. M. Perelomov, and V. S. Popov, Zh. Eksp. Teor. Fiz. 55, 589 (1968) [Sov. Phys. JETP 28, 308 (1969)]; Preprint ITÉF No. 622.
[22] P. A. Apanasevich, Osnovy teorii vzaimodeĭstviya sveta s veshchestvom (Principles of the Theory of Interaction of Light with Matter), Nauka i tekhnika, Minsk, 1977, p. 216.

Translated by J. G. Adashko

---

# Nonlinear processes in vibrational–translational relaxation of a gas of strongly excited molecules

S. A. Akhmanov, V. M. Gordienko, V. V. Lazarev, A. V. Mikheenko, and V. Ya. Panchenko

*M. V. Lomonosov State University, Moscow*

(Submitted 15 October 1979)
Zh. Eksp. Teor. Fiz. 78, 2171–2189 (June 1980)

An analysis is made of the characteristics of vibrational relaxation processes in strongly excited molecules. An important class of new phenomena occurring under these conditions are the nonlinear (depending on the rate of excitation) vibrational relaxation processes. Under strong excitation conditions we can expect the appearance of new relaxation channels (including stimulated processes); another manifestation of nonlinearity is the dependence of the relaxation kinetics on the rate of excitation. The results are reported of experimental and theoretical investigations of nonlinear processes in a vibrational–translational (VT) relaxation in molecular gases $CD_4$ and $SF_6$ excited resonantly by laser radiation. Nonexponential VT relaxation processes in strongly excited molecules are characterized by an "instantaneous" relaxation time $\tau_{VT}$ dependent on the initial vibrational temperature $T_v(0)$ and on the time $t$ from the moment of excitation: $\tau_{VT} = \tau_{VT}[T_v(0), t]$. The experimental results on the behavior of $\tau_{VT}$ of pure gases and mixtures have made it possible to determine the nonlinear mechanisms. It is shown that the contribution to the observed effects is due to the anharmonicity of the vibrations and also due to an increase in the average translational energy of the gas. In the case of the $CD_4$ molecule these qualitative considerations are supported by a detailed quantitative calculation. In the case of a two-mode model of the vibrations in $CD_4$ the results of a calculation of "weakly nonlinear" relaxation kinetics agree to within at least 20% with the experimental data. A simple one-mode model may be used for relatively rough estimates in the case of polyatomic molecules. The nonlinear effects can be very strong also in the case of other intermolecular and intramolecular relaxation processes.

PACS numbers: 33.80.Kn, 33.10.Gx

## INTRODUCTION

1. Investigation of the mechanisms of transformation of the optical excitation energy by molecules and molecular complexes is undoubtedly one of the central problems in the physics of resonant interaction of laser radiation with matter. Many important results have been obtained in the last decade. Various new experimental methods have been proposed, ways of dissipation of the vibrational excitation energy in gases and liquids have been studied, rates of energy conversion have been determined, and laws governing the distribution of energy between vibrational modes in polyatomic molecules have been investigated (see, for example, the reviews in Refs. 1–5).

One of the interesting aspects of this new stage of research on vibrational relaxation is related to the feasibility of investigating the decay of strongly excited states. Many-photon dissociation, including isotopically selective dissociation of many polyatomic molecules has been achieved using lasers emitting far and near infrared radiation.[6,7] It is natural to expect that in the case of such strong excitation there should be nonlinear vibrational relaxation effects, i.e., the nature of relaxation processes may depend on the rate of excitation. In the case of highly excited systems we can expect new relaxation processes and this is true of intermolecular as well as intramolecular relaxation. On the other hand, the energy transfer rates (characteristic relaxation times) for channels already known may depend on the degree of excitation.

2. These problems are now attracting increasing at-

0038-5646/80/061087-10$02.40

tention. Our investigation[8] of the molecular gas $SF_6$ excited by a pulsed $CO_2$ laser at a rate of $I \sim 10^5$ W/cm$^2$ revealed a considerable (by a factor of 2–3) increase in the rate of excitation of the vibrational–translational (VT) relaxation compared with that observed at low intensities.[1)] In recent investigations[10,11] similar effects were observed in $CH_3F$ and diacetyl molecules. The influence of strong excitation on the VT relaxation in $SF_6$ at low temperatures was discussed in Ref. 12. In Ref. 13 we reported the results indicating an increase in the rate of vibrational-vibrational (VV′) exchange in the $CH_4+SF_6$ and $CD_4+CH_4$ mixtures excited by $CO_2$ laser radiation. There is also a considerable interest in the possibility of observing stimulated processes as a result of *intramolecular* vibrational relaxation in polyatomic molecules; we are speaking here clearly of a strongly nonlinear process which may have a threshold (see, for example, Refs. 14 and 15).

Attempts to observe experimentally processes of this kind in the case of optical phonons in crystals have been unsuccessful[16] (see also the review in Ref. 5). Moreover, the rapid progress in the technology of nanosecond and particularly picosecond tunable lasers emitting infrared radiation has made it possible to carry out new experiments on molecular kinetics, at least in the case of polyatomic molecules. One should also note that strong nonlinearities (considerable changes in the rates of relaxation processes depending on the excitation intensity) have been observed recently in the relaxation of molecular complexes of photoreaction centers excited by high-power picosecond laser pulses of visible and near infrared radiation (see, for example, Refs. 17 and 18).

3. The dependence of the rate of vibrational relaxation on the excitation intensity may have a considerable influence on many photophysical and photochemical processes. By way of example we may mention the situations in which such effects are particularly important including many-photon photodissociation of molecules in the presence of collisions (see Ref. 19). Moreover, it is possible to use nonlinear processes in vibrational relaxation to increase the selectivity of optical excitation (see Refs. 13 and 14). Finally, the relaxation nonlinearity may become an important source of new information on the physics of conversion of optical radiation energy, particularly on the VT relaxation from higher vibrational levels. Therefore, it would be desirable to investigate in detail the various nonlinear relaxation mechanisms. As in the case of nonlinear processes of other kinds, it would be interesting to give also a phenomenological description of nonlinear relaxation. Such nonlinear processes can be described by parameters known as the relaxation times and defined as follows:

1) in the case of relaxation of the population $N$

$$\tau_N = -\frac{N-N_\infty}{dN/dt}, \tag{1a}$$

2) in the case of relaxation of the energy $\mathscr{E}$ stored in some internal degree of freedom

$$\tau_{\mathscr{E}} = -\frac{\mathscr{E}-\mathscr{E}_\infty}{d\mathscr{E}/dt}, \tag{1b}$$

3) in the case of relaxation of the temperature $T$,

$$\tau_T = -\frac{T-T_\infty}{dT/dt}. \tag{1c}$$

The last constant is called the thermalization time. The equilibrium values of the various quantities are denoted by the index $\infty$ in the expressions (1a)–(1c).

The relaxation times are known to depend on the translational temperature. We have pointed out above that in some experiments it has been established that at high rates of excitation the parameters $\tau$ depend on the degree of excitation of molecules and are consequently functions of time (i.e., the relaxation processes are not exponential). Nonlinear effects have thus been found in relaxation processes. In classifying these phenomena in accordance with the "degree of nonlinearity" it is most natural to expand the relaxation time as a series in terms of the degree of excitation:

$$\begin{aligned} \tau_N &= \tau_N(T)\{1+\beta_1 N+\beta_2 N^2+\ldots\}, \\ \tau_{\mathscr{E}} &= \tau_{\mathscr{E}}(T)\{1+\gamma_1\mathscr{E}+\gamma_2\mathscr{E}^2+\ldots\}. \end{aligned} \tag{2}$$

In the expressions (2) we have distinguished in the functions $\tau(T)$ only the dependence of $\tau$ on the vibrational temperature (for example, in the case of the VT relaxation process this is the Landau–Teller dependence). The coefficients $\beta_i$ and $\gamma_i$ can be regarded as nonlinear susceptibilities of a given molecule in the processes of energy redistribution. The use of these coefficients provides a unified approach to the analysis of various relaxation processes and makes it possible to compare relaxation nonlinearities in different processes and for different molecules.

4. The present paper reports the results of experimental and theoretical investigations of nonlinear VT relaxation processes in molecular gases $SF_6$ and $CD_4$. The $SF_6$ molecule was selected because of its very extensive use in modern laser photochemistry; however, the complexity of the vibrational level system of this molecule makes it difficult to provide a quantitative interpretation of the experimental results. Therefore, special attention was given to the $CD_4$ molecule; in the theoretical description of the VT relaxation in a gas of this and similar molecules one can use effectively a model of a binary mixture of anharmonic oscillators allowing for the VV′ and VT exchange processes.

We shall develop a theory for pure $CD_4$ gas and for $CD_4$ in a rare-earth gas "thermostat" and we shall show that the theory agrees with the experimental data to within at least 20%. This agreement allows us to conclude that at pressures of $p\sim 1$ Torr and for laser excitation intensities in the range $I \lesssim 10^6$ W/cm$^2$ the nonlinear reduction in the relaxation time $\tau_{VT}$ on increase in the intensity may be attributed to the anharmonicity of the individual modes and to the heating of the gas (Landau–Teller effect).

5. An experimental investigation of the VT processes under strong excitation conditions (more correctly, they should be described as thermalization processes) imposed specific requirements on the method. In particular, the widely used technique of double infrared resonance, in which a probe infrared laser beam is used to

find the population of some vibrational level (difficult to identify under strong excitation conditions), can be used to study the relaxation of the population of just this level [see Eq. (1a)] and not of the energy stored in the whole molecule [Eqs. (1b) or (1c)]. However, it follows from a comparison of Eqs. (1a) and (1b) that in the case of strong excitation these processes may evolve differently with time ($\tau_N \neq \tau_{\mathscr{E}}$). Therefore, all the main experiments were carried out using an interference method which made it possible to study directly the process of thermalization of vibrational excitation.

## §1. METHOD FOR EXPERIMENTAL DETERMINATION OF THE KINETICS OF VIBRATIONAL–TRANSLATIONAL RELAXATION

### Apparatus

An experimental study of the establishment of a gas temperature in resonantly excited molecular gases $SF_6$, $SF_6 + Ar$, $CD_4$, and $CD_4 + Ar$ was carried out using apparatus shown schematically in Fig. 1. The source of molecular excitation was a $CO_2$ laser capable of "instantaneous" (on the VT process scale) application of excitation.

An important apsect was the selection of the experimental method. About four methods are used widely in investigation thermalization kinetics: interferometric,[20] optoacoustic,[21] infared luminescence,[1] and probe beam.[1] At low rates of excitation of molecular vibrations these methods are approximately equivalent. However, in the case of strongly excited molecular gases, it is preferable to use interferometric and optoacoustic methods. When the other two methods are used, interpetation of the results on thermalization kinetics requires development of a detailed theoretical model which is not always a feasible process.

We employed the interferometric method which seemed to be the most accessible and universal. Selective excitation was provded by tuning the emission frequency of the $CO_2$ laser by a diffraction grating. The zeroth-order diffracted radiation was shaped by a lens and a stop into a beam which was homogeneous along the length of a gas cell. The dynamics of thermal changes in the gas were studied with a Michelson interferometer. It consisted of one semitransparent, two non-transmitting, and one germanium mirrors (the last was used also as the entry window for the gas cell). The interferometer was illuminated with He–Ne laser radiation ($\lambda = 0.63$ $\mu$). An interference pattern was formed on the entry slit of an FÉU-79 photomultiplier. The output signal from the output multiplier was fed to an S8-11 storage oscilloscope.

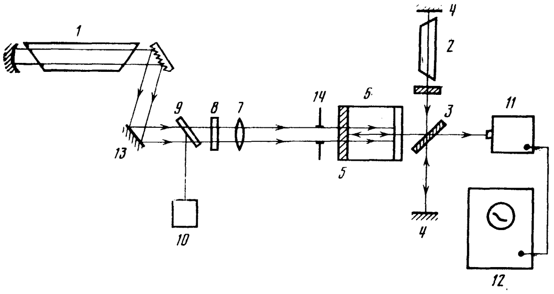

FIG. 1. Block diagram of the apparatus: 1)$CO_2$ laser; 2) He–Ne laser; 3) semitransparent mirror; 4), 13) nontransmitting mirrors; 5) germanium mirror; 6) cell; 7) lens; 8) filters; 9) NaCl plate; 10) calorimeter; 11) photomultiplier; 12) oscilloscope; 14) stop.

The laser radiation intensity was varied by means of attenuating filters. The energy in a pulse was measured by deflecting part of the radiation to a calorimeter by an NaCl plate. In experiments on different gases use was made of cells with geometric dimensions designed to ensure the maximum sensitivity of the interferometer and minimum distortions due to an acoustic wave reflected from the cell walls.

### Interferometric method

In the interferometric method the measured quantity is the phase difference $\Delta\varphi(t)$ between two beams in a Michelson interferometer and this difference is related to the change in the refractive index $\Delta n$ of the investigated gas:

$$\Delta\varphi(t)=2\pi l\lambda^{-1}\Delta n(t), \tag{3}$$

where $l$ is the effective length of the gas cell and $\lambda$ is the wavelength of the He–Ne laser radiation. The change $\Delta n$ is related to the gas density change $\Delta\rho$

$$\Delta n(t)=K\Delta\rho(t),$$

where $K$ is the Gladstone–Dale coefficient. The gas density is related to the temperature $T$ and the pressure $p$ by the equation of state. Therefore, $\Delta\varphi(t)$ can be described by

$$\Delta\varphi(t)=\frac{2\pi lpmK}{\lambda k_B}\left(\frac{1}{T(t)}-\frac{1}{T_0}\right), \tag{4}$$

where $m$ is the mass of a molecule and $T_0$ is the initial temperature of the gas. We can thus see that the phase changes in the interferometer are proportional to the changes in the temperature of the gaseous medium.

The main shortcoming of the interferometric and optoacoustic methods is the time lag between the establishment of a given density or pressure in a gas after the establishment of its temperature. This point will be discussed in detail later.

In the process of relaxation the vibrational energy $\mathscr{E}$ is converted to the translational and rotational degrees of freedom, altering the gas temperature $T$:

$$\frac{d\mathscr{E}}{dt}=C_p^{RT}\frac{dT}{dt}, \tag{5}$$

where $C_p^{RT}$ is the specific heat of the rotational and translational degrees of freedom at a constant pressure. The VT relaxation time is understood to be the thermalization (i.e., gas heating) time in the process of relaxation of the vibrational energy defined in accordance with Eq. (1c), where $\tau_T = \tau_T(t)$ is not in general a constant quantity.[2]

### Analysis of results. "Instantaneous" VT relaxation time

In an analysis of the experimental results it is convenient to use normalized values of $\Delta\tilde{\varphi}(t)$ which are obtained by subtracting from $\Delta\varphi(t)$ the steady-state experimental value of $\Delta\varphi$ (corresponding to $t \gg \tau$) and then dividing by this value. We thus find from Eq. (3) that

$$\Delta\tilde{\varphi}(t)=\frac{T_0[T(t)-T_\infty]}{T(t)[T_\infty-T_0]}. \tag{6}$$

Using Eqs. (5) and (6), we readily obtain the following expression for the vibrational energy of a gas:

$$\frac{\mathscr{E}_0-\mathscr{E}(t)}{\mathscr{E}_0-\mathscr{E}_\infty}=1-\frac{|\Delta\tilde{\varphi}(t)|(1+\Delta T/T_0)}{1+|\Delta\tilde{\varphi}(t)|\Delta T/T_0}, \tag{7}$$

where $\mathscr{E}_0$ is the initial store of the vibrational energy $t=0$; $\mathscr{E}_\infty$ is the equilibrium value; $\Delta T = T_\infty - T_0$. The values of $\Delta T/T_0$ are found from Eq. (4) using the known value of $K$ and the experimentally determined $\Delta\varphi$ at time $t \gg \tau$.

The expression relating the required $\tau(t)$ with the experimentally determined $\Delta\tilde{\varphi}(t)$ is easily obtained from Eqs. (1c) and (7):

$$\frac{1}{\tau}=-\frac{dT/dt}{T(t)-T_\infty}=-\frac{d\mathscr{E}/dt}{\mathscr{E}(t)-\mathscr{E}_\infty}=\frac{d[\ln\psi(t)]}{dt}, \tag{8}$$

where

$$\psi(t)=\frac{|\Delta\tilde{\varphi}(t)|(1+\Delta T/T_0)}{1+|\Delta\tilde{\varphi}(t)|\Delta T/T_0}. \tag{9}$$

It thus follows from Eqs. (8) and (9) that in the case of low values of $\Delta T/T_0$ at each moment $t$ the relaxation time $\tau$ can be found from the slope of $\ln\Delta\tilde{\varphi}(t)$ relative to the time axis; in the opposite case, the value of $\tau$ is found from the slope $\ln\psi(t)$.

In our experiments the cell length was selected so that measurements of the phase difference $\Delta\varphi$ due to the heating of the gas during relaxation time satisfied the condition $-45° \lesssim \Delta\varphi \lesssim 45°$. In this case the working point was located on the linear part of the interferometer characteristic and the determination of the intensity in the field of an interference pattern was proportional to the change in the phase difference $\Delta\varphi$. Moreover, the experimental conditions were selected so that the diffusion of heat could be ignored in the analysis of the experimental data.

Figure 2 shows an oscillogram of $\Delta\varphi(t)$ and the dependences $\Delta\tilde{\varphi}(t)$, $\psi(t)$, and $\tau(t)$ deduced from it as described above. In this procedure the realization length is divided into time intervals $\Delta t$ and at each moment the values of $\Delta\varphi$, $\Delta\tilde{\varphi}(t)$, $\psi(t)$, and $\ln\psi(t)$ are determined. The relaxation time $\tau(t)$ is found from Eq. (8) using the slope of $\ln\psi(t)$ relative to the axis in each time interval, i.e.,

$$\frac{1}{\tau}=\frac{\ln\psi(t+\Delta t)-\ln\psi(t)}{\Delta t}.$$

The time interval is selected so that $\Delta t > \Delta t_{\text{corr}}$, where $\Delta t_{\text{corr}}$ is the correlation interval. A detailed description of a procedure used in treating transient processes of this kind can be found, for example, in Ref. 22.

As mentioned already, the main source of error in the interferometric method for the determination of the relaxation time $\tau$ is the delay between the establishment of the density (pressure) in a gas and the establishment of its temperature. The delay is governed by the acoustic transit time $\tau_{\text{ac}}$ across the enclosure in which the gas temperature is measured.

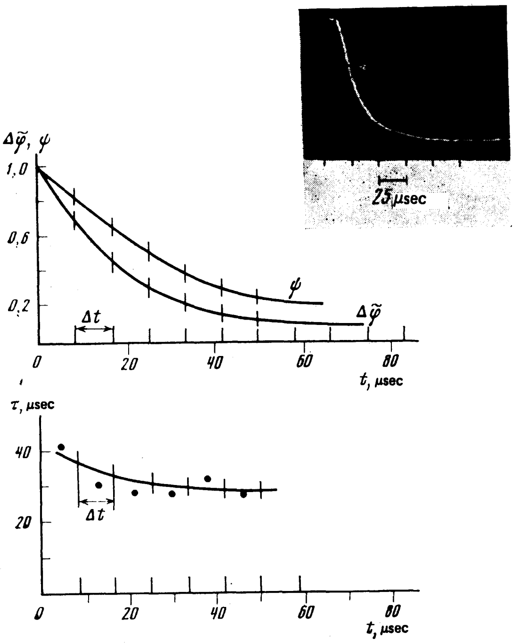

FIG. 2. Oscillogram of $\Delta\varphi(t)$ (at the top) and dependences of $\Delta\tilde{\varphi}$, $\psi$, and $\tau$ on time $t$.

## Acoustic delay

The influence of the acoustic delay on the errors in the determination of the thermalization time can be estimated *a priori* by preliminary calculations.

Let us assume that the heating of a gas follows the law

$$T(t)=T_\infty[1-\exp(-t/\tau_{\text{eq}})],$$

where $\tau_{\text{eq}}=\text{const}$ is the time taken to establish an equilibrium temperature. The change in the density is in its turn found by solving the wave equation

$$\partial^2\rho'/\partial t^2-v_{\text{ac}}^2\Delta_\perp\rho'=\rho_\infty v_{\text{ac}}^2\beta\Delta_\perp T, \tag{10}$$

where $\beta$ is the volume expansion coefficient of the gas and $\rho'=\rho(t)/\rho_\infty$.

Figure 3a shows the time dependence of $\rho'$ found by numerical solution of Eq. (10) for $\tau_{\text{eq}}=4\tau_{\text{eq}}$ and $\tau_{\text{eq}}=10\tau_{\text{eq}}$. For comparison, curve 1 gives the dependence $\rho'=1-\exp(-t/\tau_{\text{eq}})$, obtained using (9) from the equation of state for a gas on the assumption that $[T(t)-T_\infty]/T_\infty \ll 1$ and that the acoustic delay is negligible. It is clear from these graphs that there is a considerable divergence between the dependences in the time interval $t<3\tau_{\text{ac}}$ The delay is establishment of the density in the illuminated volume gives rise to different values of $\tau(t)$ deduced from changes in the temperature and density. This has to be allowed for in the experimental determination of $\tau(t)$. For comparison, Fig. 3b shows the dependences $\tau(t)$ calculated from the change in the density in accordance with

$$\frac{1}{\tau}=-\frac{d\rho/dt}{\rho-\rho_\infty}$$

substituting $\tau_{\text{eq}}=\text{const}$ in Eq. (9) ($\tau_{\text{eq}}=4\tau_{\text{ac}}$, $\tau_{\text{eq}}=6\tau_{ac}$, $\tau_{\text{eq}}=10\tau_{\text{ac}}$). It is clear from the graphs that at times

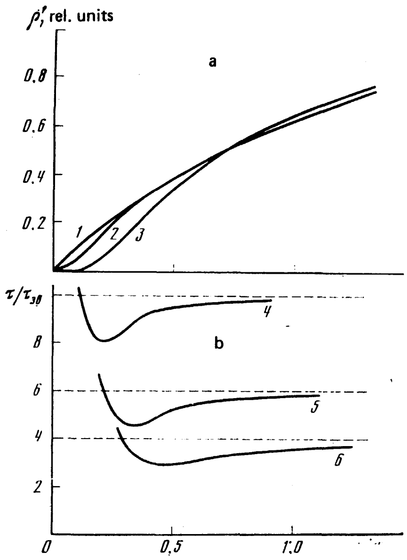

FIG. 3. a) Time dependences of the gas density on the beam axis: 1) without allowance for the acoustic delay; 2) $\tau_{eq}=4\tau_{ac}$; 3) $\tau_{eq}=10\tau_{ac}$. b) Dependences of the relaxation time $\tau$ on time $t$: 4) $\tau_{eq}=10\tau_{ac}$; 5) $\tau_{eq}=6\tau_{ac}$; 6) $\tau_{eq}=4\tau_{ac}$ (the values of $t/\tau_{eq}$ are plotted along the abscissa).

$t \gtrsim \tau$ the discrepancy between $\tau(t)$ and $\tau_{eq}$ is slight. Detailed information on the changes in the density during thermalization of a vibrationally excited gas is obtained by simultaneous solution of the wave equation (10), the kinetic equation, and the equation for temperature [see Eq. (13) below] which describe—in terms of the model proposed below—the thermalization process itself. In our measurements the condition for the correct experimental results $\tau_{ac} \ll \tau$ was satisfied.

### Determination of the vibrational temperature

The initial vibrational temperature of the excited gas $T_v(0)$ was determined by measuring the absorbed energy $\mathscr{E}_{abs}=N\mathscr{E}^*$ ($N$ is the number of molecules within the laser beam). The known value of $\mathscr{E}^*$ was used to find $T_v(0)$ from the dependence of the vibrational energy $\mathscr{E}$ on the vibrational temperature $T_v$ (Ref. 23):

$$\mathscr{E}=\sum_i E_i[\exp(E_i/T_v)-1]^{-1}, \tag{11}$$

where the summation is carried out over all the vibrational modes allowing for degeneracy. Introducing $\mathscr{E}(0)=\mathscr{E}_0+\mathscr{E}^*$ ($\mathscr{E}_0$ is the value at $T=300\,^\circ$K and $\mathscr{E}^*$ is the energy absorbed by one gas molecule), the vibrational temperature corresponding to $\mathscr{E}(0)$ could be found.

The vibrational temperature $T_v(0)$ was also deduced from the change in the gas temperature $T$ known from interference measurements. This was done using a relationship deduced from Eq. (3):

$$\mathscr{E}(T_v(0))-\mathscr{E}(T_0+\Delta T)=C_p^{RT}\Delta T. \tag{12}$$

The values of $T_v(0)$ determined by these two methods were in good agreement.

The vibrational temperatures found by the above methods were average or effective, because the true values decreased along the length of the sample due to attenuation of the "pump" radiation by absorption. In our experiments the true temperatures differed from the average values by 10%.

## §2. EXPERIMENTAL RESULTS

The results of determination of the VT relaxation (thermalization) time are plotted for pure $SF_6$ and for an $SF_6+Ar$ mixture in Figs. 4 and 5.[3)] Figure 4 gives the effective times $\bar{\tau}$ (i.e., the times in which the initial deviation of the gas temperature from the equilibrium value changes by a factor of $e$) as a function of the vibrational temperature $T_v(0)=f(I)$, where $I$ is the optical excitation intensity. It is clear from the graphs in Fig. 4 that the time $\bar{\tau}$ decreases strongly on increase in $T_v(0)$ and for pure $SF_6$ it decreases more.

Figure 5 shows the results of measurements of the VT relaxation time $\tau$ as a function of the time $t$ from the moment of excitation, plotted for various values of $T_v(0)=f(I)$. The results represent sampling of 4–6 values and statistical analysis using the Student distribution.26 The reliability of the confidence interval given there is 70%. It follows from the results obtained that in the case of the $SF_6$ gas the value of $\tau$ decreases with time (at high rates of excitations) and at the beginning of the relaxation process when the gas temperature rises slowly the value of $\tau$ is less than at low excitation rates. In the case of $SF_6$ which is in a rare-gas (Ar) thermostat the relaxation time increases with time but again at the beginning of the relaxation process it is considerably less than $\tau$ corresponding to low rates of excitation.

The values of $\tau$ obtained at relatively low intensities are in satisfactory agreement with the results reported by several other authors.11,24,25

Figure 6 shows the results of similar measurements made on the $CD_4$ gas and on the $CD_4+Ar$ mixture. It is clear from these data that in the case of pure $CD_4$ the relaxation time $\tau$ decreases with time $t$ in the case of sufficiently high values of $T_v(0)$ and decreases on increase in $T_v(0)$. For the $CD_4+Ar$ mixture the value of $\tau$ varies slowly with $t$ but again it depends on $T_v(0)$.

We can thus see that the relaxation time of the investigated $SF_6$, $SF_6+Ar$, $CD_4$, and $CD_4+Ar$ gases is not a constant but a function of the optical excitation intensity

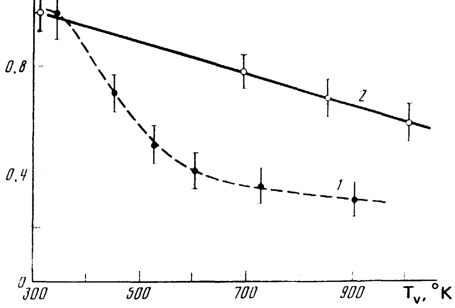

FIG. 4. Dependences of the relaxation time $\bar{\tau}$ on the vibrational temperature $T_v(0)$: 1) $SF_6$ gas at 1 Torr, $\langle\tau\rangle=110$ μsec; 2) $SF_6+Ar$ mixture at 0.1+4 Torr, $\langle\tau\rangle=90$ μsec.

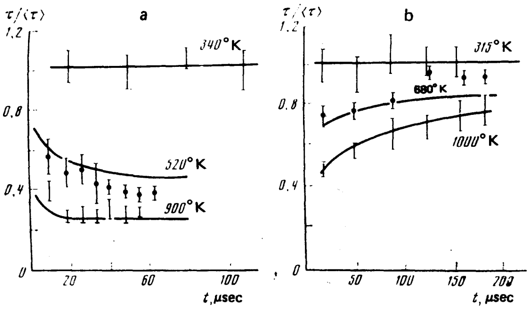

FIG. 5. Time dependences of the relaxation time: a) $SF_6$ gas at 1 Torr, $\langle\tau\rangle=110$ μsec; b) $SF_6+Ar$ at $0.1+4$ Torr, $\langle\tau\rangle=90$ μsec. The values of $T_v(0)$ are given alongside the curves. The continuous curves are calculated.

or of the corresponding initial vibrational temperature of the molecules $T_v(0)$ and of the time from the moment of excitation.

## §3. THEORETICAL CALCULATIONS

### Phenomenological description

The following factors are known at present to result in nonlinearity of the thermalization of excited molecular gases: the anharmoncity of individual modes, intramode and intermode (VV and VV′) exchange, and gas heating. The anharmonicity of molecular vibrations has the effect that even in the case of diatomic molecules the thermalization of a gas as a result of the VT relaxation is nonexponential; the characteristic thermalization time depends strongly on the energy absorbed by the gas. The resultant heating of the gas accelerates the VT relaxation process in accordance with the Landau-Teller mechanism. The occurrence of nonresonant VV and VV′ relaxation processes may distort the nature of thermalization because of the heating of the gas and because of the appearance of additional channels for the redistribution of the vibrational energy.

Under our experimental conditions the VT relaxation process can be described quite accurately (as shown below) by the approximation of weakly anharmonic oscillators[9] whose relaxation time can be represented in the form

$$\tau=\tau^{\text{harm}}\left[1-\frac{\mathscr{E}}{gE}(e^{\delta}-1)\right]^{2}, \tag{13}$$

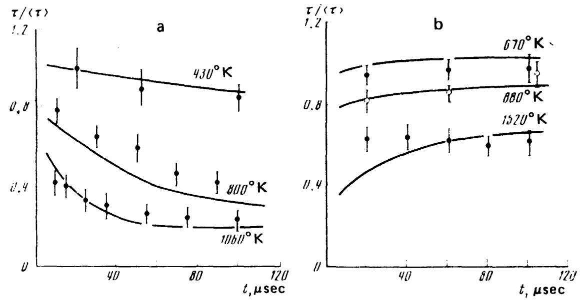

FIG. 6. Time dependences of the relaxation time: a) $CD_4$ at 15 Torr, $\langle\tau\rangle=150$ μsec; b) $CD_4+Ar$ at $3+60$ Torr, $\langle\tau\rangle=115$ μsec. The value of $T_v(0)$ is given alongside the curves. The continuous curves are calculated.

where $\tau^{\text{harm}}$ can be described by the Landau-Teller formula and determines the main dependence of $\tau$ on the translational temperature; $g$ is the multiplicity of the degeneracy of a relaxing mode with a quantum energy $E$; $\mathscr{E}$ is the vibrational energy stored in this mode per one molecule; $\delta$ is the parameter representing the molecular anharmonicity[3] and depending weakly on the gas temperature. We can see that Eq. (13) describes acceleration of the VT relaxation process on increase in the energy absorbed by the gas.

Using Eq. (13), we can determine the values of the nonlinear susceptibilities $\gamma_1$ and $\gamma_2$ introduced in Eq. (2):

$$\gamma_1=-2(e^{\delta}-1)/gE,\quad \gamma_2=(\gamma_1/2)^2. \tag{14}$$

In the expansion (2) the quantity $\mathscr{E}$ is (under our conditions) a function of time like $T$, i.e.,

$$\tau(t)=\tau(T(t))\{1+\gamma_1\mathscr{E}(t)+\gamma_2\mathscr{E}^2(t)\}. \tag{15}$$

It follows from the law of conservation of energy that

$$C^{RT}dT=-d\mathscr{E}, \tag{16}$$

where $C^{RT}$ is the specific heat of the translation-rotational degrees of freedom of the molecule. Hence, we find that

$$\mathscr{E}(t)=\mathscr{E}(0)-C^{RT}[T(t)-T_0].$$

Here, $\mathscr{E}(0)$ can be represented as the sum of the vibrational energy of the system before excitation and of the absorbed energy $\mathscr{E}(0)=\mathscr{E}_0+\mathscr{E}^*$.

Thus, if we know the nonlinear susceptibilities $\gamma_1$ and $\gamma_2$ defined by Eq. (14) and if we have experimental data on the change in the temperature $T(t)$ and also on the parameters $\mathscr{E}_0$, $\mathscr{E}^*$, and $\tau^{\text{harm}}$, we can find the relaxation time for different degrees of excitation at any moment. The calculations carried out in this way are in satisfactory agreement with the experimental data (see Figs. 5 and 6).

In addition to this phenomenological description of nonlinear VT relaxation processes, we shall carry out a detailed theoretical calculation using the gaskinetic equations.

### Model for $CD_4$

It is difficult to describe vibrational relaxation in a gas of polyatomic molecules because of the absence of detailed information on elementary processes. Therefore, some simplifications have to be made. In particular, in the case of $CD_4$ we can use the fact that the structure of the lower vibrational levels of this molecule allows us to approximate this structure sufficiently accurately (under our conditions) by a two-mode scheme. In fact, the energies of the principal transitions are as follows: 300°K for the symmetric mode $\nu_1$, 158°K for the degenerate mode $\nu_2$, 3250°K and 1434°K for the triplet degenerate modes $\nu_3$ and $\nu_4$; the frequencies $2\nu_2$ and $\nu_1$ are linked by a Fermi resonance.[27] The values of $\nu_1$ and $\nu_3$ are quite close to the overtones $\nu_2$ and $\nu_4$, and the population of the lower levels of these modes is (under experimental conditions) considerably less than the population of $\nu_2$ or $\nu_4$. Moreover, the $CD_4$ molecule (like $SF_6$) has spherical symmetry so we need consider only the VT processes and ignore the dissipation of the vibrational energy by rotation, which can occur in the case of strongly excited polyatomic molecules of the asymmetric top type.[28] All this makes it possible to describe the vibrational relaxation processes in $CD_4$ by a model of two-mode anharmonic oscillators, with modes 1 and 2 corresponding to the real modes $\nu_2$ and $\nu_4$, and just two relaxation channels: vibrational-translational (VT) and intermode vibrational-vibrational (VV′).

The processes of the intramode VV exchange are much faster than those being considered and, therefore, we shall assume that they represent the initial conditions in our problem. For times $t \gg \tau_{VV}, \tau_{1p}$ ($\tau_{VV}$ is the characteristic VV exchange time and $\tau$ is the duration of a laser pulse) the influence of laser radiation can be allowed for by introducing nonequilibrium initial conditions for the storage of vibrational quanta in the pumped mode, corresponding to a specific vibrational temperature established by this time. Lack of allowance for the VV processes can give rise to a small error in the determination of the initial conditions and this error will be estimated later.

The kinetic equations for the stored quanta $\alpha_i$ and the equation for the gas temperature $T$ are

$$\begin{aligned} \frac{d\alpha_1}{dt} &= -\frac{\alpha_1-\alpha_{1\infty}}{\tau^{(1)}_{VT}} + \frac{\alpha_2(g_1+\alpha_1)e^{\Delta}-\alpha_1(g_2+\alpha_2)}{g_1 g_2 \tau_{VV'}}, \\ \frac{d\alpha_2}{dt} &= -\frac{\alpha_2-\alpha_{2\infty}}{\tau^{(2)}_{VT}} - \frac{\alpha_2(g_1+\alpha_1)e^{\Delta}-\alpha_1(g_2+\alpha_2)}{g_1 g_2 \tau_{VV'}}, \\ \frac{dT}{dt} &= -\frac{1}{C^{RT}}\left[E_1\frac{d\alpha_1}{dt}+E_2\frac{d\alpha_2}{dt}\right]. \end{aligned} \tag{17}$$

Here, $\alpha_i$ is the store of quanta of energy $E_1 = 1434\,^\circ\mathrm{K}$ corresponding to the pumped mode; $\alpha_2$ is the store of quanta in the "cold" mode of energy $E_2 = 1518\,^\circ\mathrm{K}$; $\alpha_{i\infty}$ is the equilibrium store of quanta corresponding to the gas temperature at a given moment; $g_{1,2}$ are the multiplicities of the degeneracy of the modes; $\Delta = (E_1 - E_2)/T$; $C^{RT}$ is the specific heat of the translational-rotational degrees of freedom per one molecule. For time intervals $t \lesssim \tau_{ac}$ ($\tau_{ac}$ = 3–7 μsec under our conditions: it represents the time taken by sound to travel across the laser beam) the value of $C^{RT}$ is equal to the specific heat of an isochoric process: $C^{RT} = C_v^{RT}$; for time intervals $t \gtrsim \tau_{ac}$ the specific heat $C^{RT}$ is equal to $C_p^{RT}$ representing the specific heat of the process at constant pressure.

In using the expressions for $\alpha_i$, $\tau_{VT}^{(i)}$, and $\tau_{VV'}$ we must bear in mind that under our experimental conditions the relaxation process includes conflicting contributions from the level populations lying below the minimum of the Treanor distribution function ($n_{\min}$) established in the modes in a characteristic time $\tau_{VV}$. This corresponds to reality since in the case of the radiation-absorbing mode $\nu_4$ we have

$$n_{min} = \frac{E_1}{2\Delta E}\frac{T}{T_1} + \frac{1}{2} \leqslant 8$$

(the vibrational temperature is $T_i \leqslant 1400\,^\circ\mathrm{K}$, the anharmonicity is $\Delta E = 20\,^\circ\mathrm{K}$, $T \geqslant 300\,^\circ\mathrm{K}$, $E_1 = 1434\,^\circ\mathrm{K}$) and the average number of the absorbed $CO_2$ laser photons per molecule does not exceed unity. In this case it is sufficient to allow for the anharmonicity of the molecular vibrations only in the expressions for the relaxation times[29] describing $\tau_{VT}$ by Eq. (13) with the substitution $\mathscr{E}/E = \alpha$ describing $\tau_{VV'}$ by the expression[13]

$$\tau_{VV'} = \tau_{VV'}^{\text{harm}}\left\{\left[1+\frac{\alpha_1}{g_1}(1+e^{-\delta_1})\right]\left[1-\frac{\alpha_2}{g_2}(e^{\delta_2}-1)\right]\right\}. \tag{18}$$

Here[3]

$$\delta_i = \Delta E_i\left[4\left(\frac{0.32}{\varkappa}\right)^{2/3}\left(\frac{\mu}{TF_i}\right)^{1/3} - \frac{1}{T}\right]$$

are the parameters proportional to the anharmonicities $\Delta E_i$ depending weakly on $T, E_i$, reduced mass of the colliding oscillators (molecules) $\mu$, and argument $\varkappa$ of the exponential function in the intermolecular interaction potential ($\sim e^{-\varkappa r}$). The values of $\alpha_i$ can be calculated sufficiently accurately in the harmonic approximation:

$$\alpha_i = \alpha_i(T_V^{(i)}) = \frac{g_i}{\exp\{E_i/T_V^{(i)}\} - 1}. \tag{19}$$

As found in the experiments on $CD_4$ (Ref. 31), the time $\tau^{\text{harm}}$ in Eq. (13) obeys the usual Landau-Teller dependence:

$$\tau^{\text{harm}} = \frac{\exp(AT^{-1/3})}{Z[1-\exp(-E_i/T)]}. \tag{20}$$

Here, $A$ is the Landau-Teller parameter and $Z$ is the number of collisions between molecules per unit time. In numerical calculations use is made of the parameter $A$ found from $\tau_{VT}^{\text{harm}}$ calculated using the experimental data obtained at a low laser radiation intensity. The number of collisions $Z$ between molecules per unit time is found from the self-diffusion coefficient of methane on the assumption that the effective cross sections of the molecules $CD_4$ and $CH_4$ are identical.

The quantity $\tau_{VV'}^{\text{harm}}$ in Eq. (18) has the usual meaning $\tau_{VV'}^{\text{harm}} = (ZQ'_{10})^{-1}$, where $Q'_{10}$ is the probability of a one-quantum VV′ exchange in a collision. The nonequilibrium initial store of quanta in the pumped mode is introduced into the model on the basis of the experimental data using either the directly determined absorbed radiation energy or the gas temperature at the end of the relaxation process $T_\infty$ found from

$$\begin{aligned} \alpha_{10} &= \alpha_1(T_\infty) + \frac{C_p^{RT}}{E_1}(T_\infty - T_0) + \frac{E_2}{E_1}(\alpha_{2\infty}-\alpha_{20}), \\ \alpha_{20} &= \alpha_2(T_0). \end{aligned} \tag{21}$$

Here $T_0 = 300\,^\circ\mathrm{K}$ is the initial gas temperature.

In general, this definition of the initial conditions is somewhat inaccurate because due to slightly nonresonant intramode VV relaxation processes (assumed to be completed before the processes under consideration) the gas temperature differs from $T_0$ by an amount $\Delta T$ (Ref. 32). We shall estimate this difference in the three-level approximation assuming that the populations $x_0$, $x_1$, and $x_2$ of all the levels are the same (this corresponds to the absorption of one photon per molecule). Then, the gas heating in a time $\tau_{VV}$ can be found from

$$\Delta T = \int_0^{\tau_{VV}} \frac{2ZQ_{10}}{C_v^{RT}}\left(\frac{x_1}{x_0+x_1+x_2}\right)^2 \Delta E\, dt.$$

Setting an upper limit by postulating that the populations $x_0$, $x_1$, and $x_2$ remain equal during the VV relaxation process and bearing in mind that $\tau_{VV}=(ZQ_{10})^{-1}$, we obtain

$$\Delta T=2\Delta E/9C_v^{RT}. \tag{22}$$

Substituting in Eq. (22) the values $\Delta E=20\,^\circ\mathrm{K}$ and $C_V^{RT}=3$ corresponding to $CD_4$, we find that $\Delta T=1.5\,^\circ\mathrm{K}$ showing that $\Delta T$ is a small correction to $T_0$.

## Comparison with experiment and discussion of results on $CD_4$

A comparison of the calculated values of $\tau_{VT}^{(i)}$ with the experimental thermalization time $\tau$ deduced from the change in the gas temperature during the process under discussion will be made as follows. Integrating the equation for $T$ in the system (17), we obtain

$$T(t)-T_\infty=-\frac{E_1(\alpha_1-\alpha_{1\infty})+E_2(\alpha_2-\alpha_{2\infty})}{C_p^{RT}},$$

from which it follows that

$$\frac{1}{\tau}=-\frac{dT/dt}{T(t)-T_\infty}=\frac{E_1 d\alpha_1/dt+E_2 d\alpha_2/dt}{E_1(\alpha_1-\alpha_{1\infty})+E_2(\alpha_2-\alpha_{2\infty})}.$$

Considering the "slow" part of the relaxation process with the time scale $\tau_{VT}$, we find from the system (17) that

$$\frac{1}{\tau}=\frac{E_1(\alpha_1-\alpha_{1\infty})/\tau_{VT}^{(1)}+E_2(\alpha_2-\alpha_{2\infty})/\tau_{VT}^{(2)}}{E_1(\alpha_1-\alpha_{1\infty})+E_2(\alpha_2-\alpha_{2\infty})}.$$

At time intervals $t\gg\tau_{VV'}$ the changes in $\alpha_1$ and $\alpha_2$ become "synchronized" in accordance with the Osipov relationship[33]:

$$\frac{\alpha_1(t)}{g_1+\alpha_1(t)}=\frac{\alpha_2(t)}{g_2+\alpha_2(t)}e^{\Delta(t)},$$

from which it follows that if $\Delta\ll 1$ the values of $\alpha_1$ and $\alpha_2$ are close to one another. Using this circumstance, we can obtain the relationship between the measured relaxation time $\tau$ and that found by calculation $\tau_{VV}^{(i)}$:

$$\tau=2\frac{g_1+g_2}{g_1}\frac{\tau_{VT}^{(1)}\tau_{VT}^{(2)}}{\tau_{VT}^{(1)}+\tau_{VT}^{(2)}}(1-\xi), \tag{23}$$

where

$$\xi=\frac{1}{2}\left[\Delta\left(\frac{\alpha_1-\alpha_{1\infty}}{g_1}+1\right)-\frac{E_2-E_1}{E_1}\right]$$

is in our case a small quantity.

Since there are no data on the rate of the VT relaxation of the modes $\nu_2$ and $\nu_4$ of the $CD_4$ molecule and since our experimental results give only the thermalization time [see Eq. (10)], the calculations are carried out using the relationships between $\tau_{VT}^{(1)}$ and $\tau_{VT}^{(2)}$ in the two limiting cases: $\tau_{VT}^{(1)\,\mathrm{harm}}=\tau_{VT}^{(2)\,\mathrm{harm}}$ and $\tau_{VT}^{(1)\,\mathrm{harm}}\ll\tau_{VT}^{(2)\,\mathrm{harm}}$. In both cases the values of $\tau$ at low radiation intensities and Eq. (20) are used to find the Landau–Teller parameter $A$. The results of calculations of $\tau(t)$ obtained from Eq. (20) using the values of $\tau_{VT}^{(i)}(t)$ are practically indistinguishable from one another in these two limiting cases. Hence, we can conclude that the values of $\tau(t)$ calculated in this way should not be affected for an arbitrary relationship between $\tau_{VT}^{(i)}$. These results are presented in Fig. 6, which shows that they are in satisfactory agreement with the experimental data.

One should also mention that the establishment of the gas temperature $T$ is a nonmonotonic process. During the initial stage the gas temperature decreases because of nonresonant VV′ processes[4] and because of the RT relaxation processes in the course of absorption of laser radiation in the $P$ branch of a vibrational transition.[34] A study of the mechanisms of cooling of the molecular gas $CD_4$ by the stimulated $CO_2$ laser radiation is reported in Ref. 35.

In the calculation of the nonlinear susceptibilities $\gamma$ of Eq. (14) practically no allowance is made for the mode structure of the investigated molecules. Therefore, it is desirable to carry out kinetic calculations similar to those described above using the one-mode model which allows effectively for the real energy level scheme of the $CD_4$ molecules. Such a description is valid only for times $t\gg\tau_{VV'}$.

In introducing the one-mode approximation for the $CD_4$ molecule we can use the similarity of the lower vibrational levels of the $\nu_2$ and $\nu_4$ modes and replace the system (17) with the following:

$$\frac{d\alpha}{dt}=-\frac{\alpha-\alpha_\infty}{\tau_{VT}},\quad \frac{dT}{dt}=-\frac{E_1}{C_p^{RT}}\frac{d\alpha}{dt}. \tag{24}$$

All these quantities are defined in the same way as in Eq. (17). In the case when the initial store $\alpha$ is found from the final gas temperature $T_\infty$, use can be made of

$$\alpha_0=\alpha(T_\infty)+\frac{C_p^{RT}}{E_1}(T_\infty-T_0).$$

In contrast to the two-mode model we now have $\tau_{VT}=\tau$ [compare with Eq. (23)], which alters the Landau–Teller parameter deduced from the experimental value of $\tau$. The degree of degeneracy (multiplicity) $g$ is taken to be equal to $g_1+g_2$.

The results of a numerical solution of the system (24) are practically indistinguishable from the curves shown in Fig. (6) and representing the solution of the system (17).

## Model for $SF_6$

The $SF_6$ molecule is a spherical top, like $CD_4$. However, its vibrational structure is much more complex. It is not possible to use a many-mode model. A description of the process of thermalization in $SF_6$ by a one-mode scheme can be justified as follows. It is known from the experimental results that the energy of laser radiation absorbed in $SF_6$ is distributed between all the modes in a time ~1 μsec Torr (Ref. 36) and subsequently the VT relaxation process is characterized by a single time of the mode $\nu_6$ which has the lowest quantum energy $E=523\,^\circ\mathrm{K}$. Therefore, the calculations for $SF_6$ can be made using the system (24), where $E$ and $\alpha$ refer to the real mode $\nu_6$ of $SF_6$ but the expression for $\alpha$ given by Eq. (19) includes the effective mode degeneracy parameter $g_{\mathrm{eff}}$ allowing for the vibrational energy of the other modes. The quantity $g_{\mathrm{eff}}$ is introduced in such a way that at the end of the VT relaxation process the change in the initially stored vibrational energy of one mode corresponds to the experimentally observed heating of the gas. This is ensured by using the equation

$$g_{\text{eff}}\{[\exp(E/T_v(0))-1]^{-1}-[\exp(E/T_\infty)-1]^{-1}\}=C_p^{RT}(T_\infty-T_0). \quad (25)$$

Here, $T_v(0)$ is the initial vibrational temperature which is found from Eqs. (11) and (12) using again the gas heating but allowing for all the $SF_6$ modes. The values of $g_{\text{eff}}$ found in this way are similar for all the temperatures $T_v(0)$ and their averages used in the calculations are 13.4 for $SF_6$ and 12.8 for $SF_6$ + Ar. As before, the temperature $T_0$ can be assumed to correspond to the initial temperature of the gas since the VV and VV′ exchange processes can result in a difference of no more than 2–4 °K between these temperatures, as estimated from Eq. (22).

The above reasoning justifying a model of the VT relaxation in $SF_6$ are valid if the mode structure concept is valid. In the case of the $SF_6$ molecule this approach is meaningful when more than two photons are absorbed per molecule. Otherwise, the density of the levels becomes very high, mode mixing takes place (quantization of the vibrational energies are important), and the vibrational relaxation process must clearly be regarded as the diffusion in the vibrational energy space, exactly as it is done for diatomic molecules at high temperatures.[4]

The results of our calculations shown in Figs. 5 and 6 describe qualitatively the time dependence of $\tau$ and ensure quantitative agreement to within 20%.

### Value of $\gamma$

A satisfactory agreement between the above calculations carried out in the effective one-mode approximation with the experimental data makes it possible to determine the numerical values of the parameters $E$ and $g$ in the formula for the nonlinear relaxation susceptibility (14): $E$ is the energy of the first level of the relaxing (lower) mode and $g$ is the effective degree of degeneracy introduced above for $CD_4$ and $SF_6$. If $E$ and $\mathscr{E}$ are measured in reciprocal centimeters, we find that for $SF_6$

$$\gamma_1=-1.35\times10^{-4}\ \text{cm}, \quad \gamma_2=0.46\times10^{-8}\ \text{cm}^2,$$

for $SF_6$ + Ar

$$\gamma_1=-1.05\times10^{-4}\ \text{cm}, \quad \gamma_2=0.28\times10^{-8}\ \text{cm}^2,$$

for $CD_4$

$$\gamma_1=-6.52\times10^{-4}\ \text{cm}, \quad \gamma_2=10.63\times10^{-8}\ \text{cm}^2,$$

and for $CD_4$ + Ar

$$\gamma_1=-5.67\times10^{-4}\ \text{cm}, \quad \gamma_2=8.06\times10^{-8}\ \text{cm}^2.$$

It is clear from the above values of $\gamma_i$ that the $CD_4$ molecule is most strongly nonlinear in the thermalization process. The above values of $\gamma$ are calculated for the translational temperature of $T=300$ °K. As pointed out earlier, their dependence on $T$ is very weak; for example, when $T$ is doubled, the values of $\gamma_1$ decrease by just 25–30%. This is why there is a good agreement between the experimental results and the phenomenological description in which the parameters $\gamma_1$ and $\gamma_2$ are assumed to be constant during the process and also with the results of a direct theoretical calculation in which an allowance is made for the dependence of the parameter $\delta$ [see Eqs. (14) and (18)] on the temperature $T$ which increases with time.

### CONCLUSIONS

The above theoretical and experimental data thus show that a description of the vibrational–translational energy exchange in the excitation of lower levels of polyatomic spherical-top molecules can be provided using simple models of a gas of anharmonic oscillators with a limited number of modes. The initial vibrational energy store is governed by the energy absorbed by the whole molecule. The simultaneous effects of the anharmonicity of the vibrations and of the temperature dependence of the rate of vibrational relaxation accelerate the thermalization process whose characteristic rate is a function of time. Good qualitative and quantitative agreement between the theoretical and experimental results confirms this conclusion.

The satisfactory agreement between the results of a phenomenological description, direct kinetic calculations, and experimental data allows us to recommend the phenomenological expansion of the (2) type for the description of the experimental results. The nonlinear susceptibilities $\gamma_1, \gamma_2$, etc. can easily be found by approximating the experimental dependence $\tau=\tau(\mathscr{E})$ with a polynomial in powers of $\mathscr{E}$. Then, in each case the value of $\mathscr{E}$ can be determined quite simply by measuring the energy absorbed in a gas. This approach makes it possible to unify the description of nonlinear properties of the excited molecules without invoking any model considerations.

The nonlinear effects described above may manifest themselves also in other relaxation processes. For example, this may be true of the VV′ vibrational–vibrational intermode energy exchange,[13] which can be used to excite selectively a given mode.

---

[1)] The nonlinearity of the V-T relaxation in a gas of diatomic molecules was first investigated in shock tubes.[9]

[2)] Here and later we have only the V-T relaxation time so that we shall omit the indices in subsequent descriptions.

[3)] In these and later figures the data are normalized to $\langle\tau\rangle$ corresponding in each case to the maximum V-T relaxation time (at the minimum optical excitation intensity).

[1] C. B. Moore, Ann. Rev. Phys. Chem. 22, 387 (1971).

[2] E. Weitz and G. Flynn, Ann. Rev. Phys. Chem. 25, 275 (1974).

[3] B. F. Gordiets, A. I. Osipov, E. V. Stupochecko, and L. A. Shelepin, Usp. Fiz. Nauk 108, 655 (1972) [Sov. Phys. Usp. 15, 759 (1973)].

[4] E. E. Nikitin and A. I. Osipov, Kolebatel'naya relaksatsiya v gazakh (Vibrational Relaxation in Gases), VINITI, M., 1977.

[5] A. Laubereau and W. Kaiser, Rev. Mod. Phys. 50, 607 (1978).

[6] R. V. Ambartsumyan (Ambartzumian) and V. S. Letokhov, in Chemical and Biochemical Applications of Lasers (ed. by C. B. Moore), Vol. 3, Academic Press, New York, 1977, p. 167.

[7] H. L. Dai, A. H. Kung, and C. B. Moore, Phys. Rev. Lett. **43**, 761 (1979).

[8] 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)].

[9] S. A. Losev, O. P. Shatalov, and M. S. Yalovik, Dokl. Akad. Nauk SSSR **195**, 585 (1970) [Sov. Phys. Dokl. **15**, 1037 (1971)].

[10] E. N. Chesnokov, V. N. Shcherbinina, and V. N. Panfilov, Zh. Eksp. Teor. Fiz. **75**, 2066 (1978) [Sov. Phys. JETP **48**, 1039 (1978)].

[11] K. S. Rutkovskiĭ and K. G. Tokhadze, Zh. Eksp. Teor. Fiz. **75**, 408 (1978) [Sov. Phys. JETP **48**, 204 (1978)].

[12] N. A. Borisevich, S. I. Blinov, A. V. Dorokhin, G. A. Zalesskaya, and A. A. Kotov, Dokl. Akad. Nauk SSSR **241**, 801 (1978) [Sov. Phys. Dokl. **23**, 575 (1978)].

[13] S. A. Akhmanov, V. M. Gordienko, V. V. Lazarev, A. V. Mikheenko, B. Ya. Panchenko, Izv. Akad. Nauk SSSR Ser. Fiz. **42**, 379 (1979).

[14] S. A. Akhmanov, A. A. Vigasin, and V. N. Seminogov, Dokl. Akad. Nauk SSSR **237**. 1066 (1977) [Sov. Phys. Dokl. **22**, 751 (1977)].

[15] C. D. Cantrell, S. M. Freund, and J. L. Lyman, "Laser-induced chemical reactions and isotope separation," in: Laser Handbook, Vol. 3, North-Holland, Amsterdam, 1979, p. 485.

[16] G. P. Quigley, "Collisional effects in multiple photon IR absorption," in: Advances in Laser Chemistry (ed. by A. H. Zewail), Springer-Verlag, Berlin, 1978, p. 374.

[17] A. Campillo and S. L. Shapiro, in: Ultrashort Light Pulses (ed. by S. L. Shapiro), Springer-Verlag, Berlin, 1977, p. 317.

[18] S. A. Akhmanov, A. Yu. Borisov, R. V. Danielius, V. S. Kozlovskii (Kozlovskij), A. S. Piskarskas, and A. P. Razzhivin (Razjivin), in: Pico-second Phenomena (ed. by C. V. Shank, E. P. Ippen, and S. L. Shapiro), Springer-Verlag, Berlin, 1978, p. 134.

[19] P. Avouris, M. M. T. Loy, and I. Y. Chan, Chem. Phys. Lett. **63**, 624 (1979).

[20] S. A. Akhmanov, V. M. Gordienko, and V. Ya. Panchenko, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 10, 11, 14 (1977).

[21] T. Aoki and M. Katayama, Jpn. J. Appl. Phys. **10**, 1303 (1971).

[22] S. A. Losev, Tr. Inst. Mekh. Mosk. Gos. Univ. **21**, 3 (1978).

[23] I. M. Godnev, Vychislenie Termodinamicheskikh funktsiĭ po molekulyarnym dannym (Calculation of Thermodynamic Functions from Molecular Data), M., 1956.

[24] J. I. Steinfeld, I. Burak, D. G. Sutton, and A. V. Nowak, J. Chem. Phys. **52**, 5421 (1970).

[25] W. D. Breshears and L. S. Blair, J. Chem. Phys. **59**, 5824 (1973).

[26] D. J. Hudson, Lectures on Elementary Statistics and Probability, CERN Report CERN 63-29 (Aug. 1963), 101 pp., continued as: Statistics Lectures II: Maximum Likelihood and Least Squares Theory, CERN Report CERN 64-18 (April 1964), 211 pp.

[27] G. Herzberg, Molecular Spectra and Molecular Structures, Vol. 2, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York (1945).

[28] E. E. Nikitin, Dokl. Akad. Nauk SSSR **239**, 380 (1978).

[29] B. F. Gordiets, A. I. Osipov, and V. Ya. Panchenko, Zh. Prikl. Mekh. Tekh. Fiz. No. 4, 3 (1974).

[30] B. F. Gordiets, M. S. Mamedov, and L. A. Shelepin, Preprint No. 28, Lebedev Physics Institute, Academy of Sciences of the USSR, M., 1974.

[31] P. F. Zittel and C. B. Moore, J. Chem. Phys. **58**, 2004 (1973).

[32] S. A. Zhdanok, A. P. Napartovich, and A. N. Starostin, Zh. Eksp. Teor. Fiz. **76**, 130 (1979) [Sov. Phys. JETP **49**, 66 (1979)].

[33] A. I. Osipov, Zh. Prikl. Mekh. Tekh. Fiz. No. 1, 41 (1964).

[34] B. F. Gordiets and V. Ya. Panchenko, Pis'ma Zh. Tekh. Fiz. **4**, 1396 (1978) [Sov. Tech. Phys. Lett. **4**, 564 (1978)].

[35] V. M. Gordienko, A. V. Mikheenko, and V. Ya. Panchenko, Pis'ma Zh. Tekh. Fiz. **5**, 457 (1979) [Sov. Tech. Phys. Lett. **5**, 186 (1979)].

[36] R. D. Bates Jr., G. W. Flynn, J. T. Knudtson, and A. M. Ronn, J. Chem. Phys. **53**, 3621 (1970).

Translated by A. Tybulewicz