Relaxation of the vibrational energy of the (00^01) level of the CO_2 molecule

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A phase method was used to measure the temperature dependence of the vibrational relaxation time τ_{00^01} of CO_2 molecules situated at the $(00^0 1)$ level, in the temperature interval 300–1000°K. The relaxation is determined by the collisions of CO_2 with CO_2 and N_2 molecules and with ^{4}He atoms. The broadest energy-variation channel is separated on the basis of an analysis of the kinetic equations. A regularization method is used to calculate the cross section of deactivation via the selected channel and to plot the temperature dependence of τ_{00^01} in an expanded temperature range 250–2500°K. The results are compared with experiment.

1. INTRODUCTION

The use of laser methods to investigate vibrational relaxation and gases makes it possible, for the first time, to determine reliably the relaxation time of molecules situated at a definite vibrational level. Earlier research methods, based on the dispersion of the velocity and absorption of ultrasound in the gas[1,2], on relaxation of the gas behind the front of a shock wave[3], and on the spectral-background method[4], determine the characteristic relaxation time of the energy of the vibrational motion of molecules on a group of low-lying levels.

Research methods using lasers have much higher measurement accuracy than the earlier methods. It is shown in the present paper that the phase method of measurements[5,6] makes it possible to determine the deactivation cross section as a function of the kinetic energy of the colliding particles. This new characteristic of the relaxation process makes it possible to consider the problem of vibrational relaxation of molecules in a gas with arbitrary particle velocity distribution, and not only a Maxwellian distribution.

The last 6–8 years have seen rapid development of the physics and technology of high-power CO_2 lasers, both cw and pulsed. The most important parameter that determines the inverted population is the time of the vibrational relaxation of the CO_2 molecules on the upper laser level (00^01). The absence of exact data on the temperature dependence of the rate constant of the deactivation of this level, on the influence of the impurities of different gases, and on its value, hinders to a certain degree the progress in these promising laser systems.

2. ANALYSIS OF KINETIC EQUATIONS. DEACTIVATION CROSS SECTION

Let us show what type of information can be obtained from measurements of the vibrational-relaxation times. By way of example we consider relaxation in the CO_2 molecule. The analysis will be based on the kinetic equations describing the change in the energy of a harmonic oscillator situated in an environment of other oscillators whose quanta are not equal in the general case. Such equations were obtained for an arbitrary number of interacting oscillators in[7]. It is assumed in the derivation of these equations that in one elementary act it is possible to have a multiquantum transition in which some of the oscillators participating in the transition lose several quanta each, while the others acquire one number of quanta or another. The population of the vibrational levels is determined by the Boltzmann distribution with its vibrational temperature for each oscillator.

We use the results obtained in[7] for the case of three oscillators, which takes place in the CO_2 molecule. We take into account the fact that one of these oscillators (deformational vibration) is doubly degenerate. We designate by $i = 1, 2, 3$ the symmetrical, deformational, and asymmetrical modes of CO_2. Then the equation for the change of the vibrational energy of the asymmetrical oscillator takes the form[8]

$$\frac{d\varepsilon_3}{dt}=\sum_{\{l_1,l_2,l_3\}} ZP\begin{pmatrix} l_3\to 0\\ 0\to l_2\\ 0\to l_1\end{pmatrix} l_3[(1+\varepsilon_{30})^{l_3}(2\varepsilon_{20})^{l_2}\varepsilon_{10}{}^{l_1}]^{-1} \times\{[\varepsilon_{30}(1+\varepsilon_3)]^{l_3}[\varepsilon_2(2+\varepsilon_{20})]^{l_2}[\varepsilon_1(1+\varepsilon_{10})]^{l_1} -[\varepsilon_3(1+\varepsilon_{30})]^{l_3}[\varepsilon_{20}(2+\varepsilon_2)]^{l_2}[\varepsilon_{10}(1+\varepsilon_1)]^{l_1}\}. \tag{1}$$

Here $\epsilon_i = r_i x_i/(1 - x_i)$ is the average number of vibrational quanta of the i-th oscillator per particle; r_i is the multiplicity of the degeneracy of the oscillator; $x_i = \exp(-\Theta_i/T_i)$; Θ_i is the value of the vibrational quantum of the i-th oscillator in °K; T_i is the vibrational temperature; $\epsilon_{i0} = r_i x_{i0}/(1 - x_{i0})$; $x_{i0} = \exp(-\Theta_i/T)$, where T is the gas temperature; Z is the total number of collisions of the CO_2 molecule per unit time; P is the probability of the vibrational transition per collision; l_1, l_2, and l_3 are the corresponding quantum jumps that occur on the oscillators in one collision.

At temperatures $T < 2000$°K one can assume with good accuracy that the decisive mechanism producing the time variation of ϵ_3 is relaxation of the 00^01 level. From the point of view of the proximity of a high-probability transition to resonance, one can distinguish between five principal channels corresponding to five sets of (l_1, l_2, l_3):

l_1:	1	0	1	0	0
l_2:	1	3	0	2	4
l_3:	1	1	1	1	1

Other sets are also present in the sum (1), but their contribution is negligible in view of the large energy defect of these transitions. On the other hand, the theory[9] and calculations[10] of the probabilities of the indicated five processes show that the predominant transitions are those with the sets $(l_1, l_2, l_3) = (1, 1, 1)$ and $(0. 3, 1)$. The probabilities of the indicated transi-

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tions are higher by more than one order of magnitude than the remaining ones. Then, retaining in (1) only two terms corresponding to these transitions, and assuming for simplicity $T_1 = T_2 = T$ and $h\nu_1 = 2h\nu_Z$, we obtain an equation of the type

$$d\varepsilon_3/dt = -\tau^{-1}(\varepsilon_3 - \varepsilon_{30}), \tag{2}$$

where

$$\tau^{-1} = (1-x_{20})^{-3}(1-x_{30})ZP(00^01 \to 11^10,\ 03^10),$$
$$P = (1+\varepsilon_{20})^{-1}P(00^01 \to 11^10) + P(00^01 \to 03^10).$$

It should be noted that this formula differs from

$$\tau^{-1} = ZP(1 \to 0)(1-x_0)$$

which is customarily assumed for the relaxation of a two-level system (see, e.g.,[3]) in the presence of the factor $(1 - x_{20})^{-3}$. The physical reason for this factor in the expression for τ is that, unlike the case of vibrational-translational (V-T) relaxation of a two-level system, the departure of a quantum from an asymmetrical vibration is accompanied by excitation of three deformation-oscillation (or one deformation and one symmetrical) quanta, which subsequently relax to translational degrees of freedom.

On the other hand, if the vibrational temperatures T_1 and T_2 are not equal to the gas temperature, then to find the connection between the experimentally measured relaxation time τ and the probabilities of the elementary processes it is necessary to solve the complete system of equations for all three oscillations. Thus, for the phase method of measuring τ[5,6,8] the equations describing the energy relaxation take the form

$$\frac{d\varepsilon_3}{dt} = ZP\left[\left(\frac{\varepsilon_2}{2}\right)^3(1+\varepsilon_3)e^{-500/T} - \varepsilon_3\left(1+\frac{\varepsilon_2}{2}\right)^3\right] + C[1-e^{-i\omega t}],$$
$$\frac{d(\varepsilon_2+2\varepsilon_1)}{dt} = -3ZP\left[\left(\frac{\varepsilon_2}{2}\right)^3(1+\varepsilon_3)e^{-500/T} - \varepsilon_3\left(1+\frac{\varepsilon_2}{2}\right)^3\right] \tag{3}$$
$$-ZP_{20}(1-x_{20})(\varepsilon_2-\varepsilon_{20}) - 2C[1-e^{-i\omega t}].$$

Here $P = P(00^01 \to 11^10,\ 03^10)$, P_{20} is the probability of the (V-T) relaxation of the lower level of the deformation mode (see, e.g.,[11]), and C is the amplitude of the pump intensity in units of quanta per second per particle. We note that the second equation of (3) describes the summary process of relaxation of the average number of vibrational quanta $h\nu_2$ in modes 1 and 2 with a common vibrational temperature $T_1 = T_2$ under the condition $h\nu_1 = 2h\nu_2$, $\epsilon_2 + 2\epsilon_1 \approx \epsilon_2$.

Assume that the system is thermostatically controlled so that the gas temperature does not change in time as a result of the pumping. Then the steady-state solution (3) can be obtained in the form of a sum of harmonics having a frequency ω and decreasing in amplitude:

$$\varepsilon_j(t) = \sum_{k=0}^{\infty} \varepsilon_j^k e^{-i\omega k t}, \quad j=2;3.$$

In this case, when determining ϵ_j^N we can neglect both the contribution of the terms nonlinear in ϵ_j^n and the contribution of the harmonics with $k > n$. We separate the first harmonics from the sum and determine the phase shift φ_3^1, due to the delay in the form of the relaxation processes, between the first harmonic ϵ_3 and the modulated radiation of intensity C;

$$\operatorname{tg}\varphi_3^1 = \frac{\omega}{A}\frac{(\omega^2+B^2)+A\beta[4B+(3\beta+\alpha)A]}{\alpha(\omega^2+B^2)+\beta(A\alpha B+2\omega^2)}. \tag{4}$$

Here $A = ZP$, $B = ZP_{20}(1 - x_{20})$, and the quantities

$$\alpha = \left(1+\frac{\varepsilon_2^0}{2}\right)^3 - \left(\frac{\varepsilon_2^0}{2}\right)^3 e^{-500/T},$$
$$\beta = \frac{3}{2}\left[\left(\frac{\varepsilon_2^0}{2}\right)^2(1+\varepsilon_3^0)e^{-500/T} - \varepsilon_3^0\left(1+\frac{\varepsilon_2^0}{2}\right)^2\right]$$

are expressed in terms of the zeroth harmonics:

$$\varepsilon_2^0 = \varepsilon_{20} + C/B,$$
$$\varepsilon_3^0 = \left[\left(\frac{\varepsilon_2^0}{2}\right)^3 e^{-500/T} + \frac{C}{A}\right] \Big/ \left[\left(1+\frac{\varepsilon_2^0}{2}\right)^3 - \left(\frac{\varepsilon_2^0}{2}\right)^3 e^{-500/T}\right]. \tag{5}$$

Thus, measuring the phase shift φ_3^1 between the radiation of the asymmetrical oscillation and the pump, we can calculate the value of A from the solution of the quadratic equation (4). We note that the relation (5) is valid when the amplitude of the modulated radiation is low enough. The corresponding condition at $A \sim B > \omega$, $\alpha \approx 1$, and $\beta \ll 1$ can be expressed in the form

$$C \ll \min\left\{\frac{2x_{20}B}{1-x_{20}}, \frac{x_{30}A}{(1-x_{20})^3}\right\}. \tag{6}$$

The influence of the intensity of the exciting radiation on the phase shift at low temperatures comes into play at $C \gtrsim 2Bx_{20}/(1 - x_{20})$ and leads in first approximation to an effective decrease of A. In this case, to calculate A it is necessary to solve numerically a system of nonlinear equations (3) with concrete values of C and B.

At low absorbed radiation intensity (in comparison with the equilibrium fluxes of the excited particles), the results of (4) and (5) turn out, in accordance with (6), to be independent of the values of B, and for temperatures $T \lesssim 1000°K$ we have

$$A \approx \frac{\omega}{\operatorname{tg}\varphi_3^1}\frac{(1-x_{20})^3}{1-x_{30}} \tag{7}$$

in full agreement with (2).

The phase shift φ_2^1 between the first harmonic ϵ_2 and the modulated radiation with amplitude C is expressed by the formula

$$\operatorname{tg}\varphi_2^1 = \omega\frac{3\alpha AB+\alpha^2A^2+3\alpha\beta A^2-2\omega^2}{\alpha^2A^2B-\omega^2(2B+3\alpha A+6\beta A)}, \tag{8}$$

which, under the assumptions indicated above and at $A \sim B \gg \omega$, reduces to the form

$$B = \left(\frac{\operatorname{tg}\varphi_2^1}{\omega} - \frac{3}{\alpha A}\right)^{-1}. \tag{9}$$

Relations (7) and (9) connect in quite simple fashion the measured quantities with the probabilities of the elementary deactivation processes. A similar analysis can apparently be carried out also for other methods of measuring the time of vibrational relaxation.

The relations obtained lead to new possibilities of a phase method of interpreting the experimental results[5,6,12] and make it possible to go over from the vibrational relaxation time to a dynamic characteristic of the collision act, namely the effective deactivation cross section.

It is known that the rate constant of the process k and the effective cross section σ are connected by

$$k = \int_0^\infty v\sigma(v)f(v)\,dv, \tag{10}$$

where $f(v)dv$ is the fraction of particles whose relative velocity v lies between v and $v + dv$. In the particular case when σ is independent of the velocity we have $k = \sigma\bar{v}$, where $\bar{v}$ is the average relative velocity. It is precisely in this manner that the deactivation cross section was determined in[13-15], but this is wrong, since the cross section depends strongly on the relative kinetic energy of the colliding particles. Therefore dependences of $\sigma = k/\overline{v}$ [13-15] on the gas temperature do not have a profound physical meaning. Greatest interest attaches to σ as a function of the relative-motion energy. In this case, assuming that the investigated gas is a mixture of neutral atoms and molecules in the ground or in the excited states, that the particle velocity distribution is Maxwellian, and that the total number of particles is conserved, we reduce (10) to the form

$$\left(\frac{1}{T}\right)^{3/2}\int_0^\infty \sigma'(\varepsilon)e^{-\varepsilon/T}\varepsilon\,d\varepsilon=\frac{4{,}7\cdot10^{-24}\,T}{\tau'}\left(\frac{2m_X}{m_{CO_2}+m_X}\right)^{1/2}, \tag{11}$$

where T is the gas temperature in eV, ϵ is the energy of the relative motion of the particles in eV, m is the particle mass, $\tau' = \tau_{3\text{-}2}^{CO_2\text{-}X}$ is the experimental relaxation time in atm-sec and corresponds to the transition $(00^01) \rightarrow (11^10), (03^10)$; X denotes the gas with which CO_2 relaxes, and $\sigma' = \sigma_{3\text{-}2}^{CO_2\text{-}X}$ is the deactivation cross section in cm^2.

The problem of solving (11) belongs to the class of the so-called incorrectly posed problems. It was solved numerically by a regularization method that led to minimization of the smoothing functional M_0[16-18]. The solution program was practically identical with that described in[18], i.e., (11) was reduced to an Euler integro-differential equation with boundary conditions $\sigma'(0) = 0$ and $d\sigma'(\epsilon)/d\epsilon|_{\epsilon=\infty} = 0$ and was solved with a computer by a finite-difference method. The initial data were the values of $\tau'(T)$ chosen from the experimental results of present paper with equal energy steps Δ. From the aggregate of the solutions corresponding to the different parameters for regularization of δ[16] and to different integration intervals, we chose the solutions satisfying the conditions

$$\sigma'_{\delta_i,\Delta}(\varepsilon)\geqslant 0, \tag{12a}$$

$$\|\sigma'_{\delta_i,\Delta}(\varepsilon)-\sigma_{\delta_{i+1},\Delta}(\varepsilon)\|=\min, \tag{12b}$$

$$\left\|\int_0^\infty \sigma'_{\delta_i\,\Delta}(\varepsilon)\varepsilon e^{-\varepsilon/T}\,d\varepsilon-\psi(T)\right\|=\min. \tag{12c}$$

Here $\|\ldots\|$ denotes the quadratic norm of the deviation, and $\psi(T)$ is the right-hand side of (11).

It should be noted that whereas conditions (12b) and (12c) reflect the mathematical aspect of the problem, relation (12a) is connected with the physical meaning of the definition of the deactivation cross section. Satisfaction of this condition offers indirect evidence of the reliability of the experimental data used in the calculations.

3. RESULTS OF MEASUREMENTS AND CALCULATIONS

An experimental investigation of $k(T)$ $(k = k_{00^01}^{CO_2\text{-}X})$ was carried out by a phase-shift method using the setup described in[6,18]. Modulated CO_2 radiation in the $(00^01) \rightarrow (10^00)$ band was absorbed in a cell with the investigated gas and excited the 00^01 vibrational level of CO_2. The radiation intensity of wavelength $\lambda \approx 4.3\ \mu$ of this level was varied periodically at the same modulation frequency but with a phase shift relative to the pump. It is this phase shift which determines, according to (7) the relaxation rate constant $k'(T)$ connected with the $(00^01) \rightarrow (11^10), (0.3^10)$ channel.

Three initial parameters are specified in the experiment: the modulation frequency $\omega/2\pi$, the gas pressure p, and the gas temperature T and the phase shift is determined. Table I lists the corresponding experimental conditions. The moisture content of the investigated gases was less than 60 ppm. The laser emission power ranged from 5 to 20 W, so that condition (6) was satisfied. The indicated operating conditions corresponded to the linear relation $\log\tau \sim \log p^{-1}$ and agreed with the model concepts considered in Sec. 2.

The experimental values of $\tau'(T)$ were approximated with a computer by a relation of the type

$$\tau'(T)=\exp\sum_{j=0}^{m}D_jT^{-j/3}, \tag{13}$$

where D_j are the polynomial coefficients calculated by least squares, T is the gas temperature in °K, and τ' is the vibrational relaxation time in μsec-atm. The accuracy with which z_n was approximated was defined as the mean-squared deviation of the n experimental and approximated values of τ'. The degree of the polynomial (13) was chosen to satisfy the condition that z_n vary little with increasing degree of the polynomial. Table II lists the coefficients of the polynomials for the experimental $\tau'(T)$ relations in the intervals 300—1000°K. The errors at the boundaries of the investigated temperature range amounted to 5—8 and 15—20° of the measured quantity, respectively. The relaxation rate constant of the 00^01 level for pure CO_2 is compared with the results obtained by other methods[14,19-22] in Fig. 1. In the temperature interval 300—700°K, all the data agree within the limits of the experimental errors. At T > 700°K there is a noticeable discrepancy between our data and the results of the pulsed excitation method[14,19,20]). In our opinion this discrepancy is due to the low accuracy of the oscillographic method of recording the intensity of the time variation of the signal in this method at just the high temperatures, when the level of the thermal background can be appreciable. Synchronous detection of the signal in the phase method[5,6] makes it possible to increase appreciably the ratio of the useful signal to the noise and results in more reliable measurements.

The procedure considered in Sec. 2 was used to determine from the data of Table II the effective cross sections for three types of collisions. Figure 2 shows plots of the deactivation cross sections σ' against the energy of the relative motion of the interacting particles. They were plotted using ~40 values of $\sigma'(\epsilon)$ obtained from the solution of (11). The optimal values of δ and Δ for each of the σ' were varied in the ranges $\delta = (1-5) \times 10^{-5}$ and $\Delta = (1-2) \times 10^{-2}$ eV.

The data obtained on $\sigma'(\epsilon)$ indicate that the most effective collisions occur at energies $\epsilon > 0.1-0.3$ V, i.e., several times larger than the average translational-

TABLE I. Pressure, gas temperature, and radiation-modulation frequency ranges

	Composition of gas		
	CO_2	$CO_2 : N_2 = 1 : 3$	$CO_2 : {}^4He = 1 : 3$
ΔP, Torr	30—150	90—300	90—200
ΔT, °K	250—1100	300—1000	300—1000
$\Delta(\omega/2\pi)$, kHz	3—6	1—3	1—3

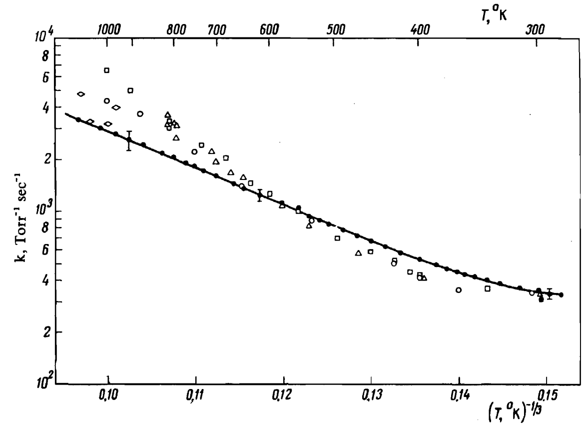

FIG. 1. Temperature dependence of the rate constant k = $k_{00^01}^{CO_2-CO_2}$: ●—present results (phase-shift method), ○—[19], □—[20], △—[14], pulsed excitation method; ◇—[24], shock tube; ■—[22], spectrophone method.

TABLE II. Coefficients D_j of the polynomial (13) that approximates the experimental values of τ' in the temperature interval 300–1000°K, z_n—approximation accuracy, n—number of experimental points

X	D_0	D_1	D_2	D_3	z_n	n
CO_2	$+2.447\cdot10^1$	$-5,9272\cdot10^2$	$+4.7641\cdot10^3$	$-1.2226\cdot10^4$	0,16	220
N_2	$+1.8666\cdot10^1$	$-5.0783\cdot10^2$	$+4,5749\cdot10^3$	$-1.2724\cdot10^4$	0,41	140
^4He	$-1,7356\cdot10^1$	$+2.6548\cdot10^2$	$-7.6332\cdot10^2$	$-7,1283\cdot10^2$	1.06	160

motion energy[23]. The cross section is determined essentially by the type of the colliding particles. There are still no published experimental or theoretical data on the cross sections for deactivation via a selected channel. We can therefore only qualitatively compare the results with the data of[24], which show calculations of the cross section $\sigma_{03}(\epsilon)$ for the excitation of 00^01 from the ground state as a result of CO_2—CO_2 collisions. From the quantum-mechanical analog of the detailed-balancing principle it follows that the deactivation cross section $\sigma_{30}(\epsilon)$ obtained from the $\sigma_{03}(\epsilon)$ data[24] should increase monotonically up to energies of several eV. This relation is qualitatively confirmed by the results presented in our paper.

The regularization method[25] has enabled us not only to calculate $\sigma'(\epsilon)$, but also to determine $\tau(T)$ in a much larger temperature interval than is known from experiment. Thus, the data of Table II were extrapolated with the aid of $\sigma'(\epsilon)$ of Fig. 2 into the temperature region 250—2500°K, The calculation sequence is schematically represented as follows:

$$\varphi_{\text{obs}} \to \tau_{\text{obs}}^{CO_2-X}(300\text{--}1000^\circ K) \to$$
$$\to \tau(300\text{--}1000^\circ K) \to \tau'(300\text{--}1000^\circ K) \to$$
$$\to \sigma'(\varepsilon) \to \tau'(250\text{--}2500^\circ K) \to$$
$$\to \tau(250\text{--}2500^\circ K).$$

An important element of this scheme is that it considers the concrete elementary deactivation process.

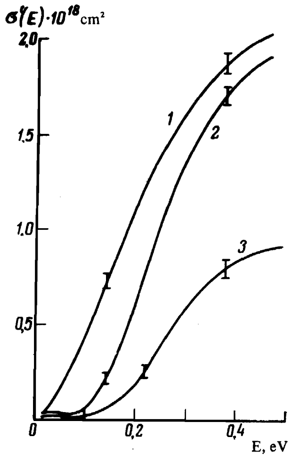

FIG. 2. Dependence of the deactivation cross section σ' on the relative kinetic energy of the colliding particles: 1—CO_2: CO_2, 2—CO_2 : N_2, 3—CO_2 : ^4He.

TABLE III. Coefficients D_j of the polynomial (13) for the numerical continuation of τ into the temperature region 250—2500°K

X	D_0	D_1	D_2	D_3
CO_2	-4.138	-7.495	$6.3124\cdot10^2$	$-2.239\cdot10^3$
N_2	1.863	$-2.133\cdot10^2$	$2.7962\cdot10^3$	$-9,0019\cdot10^3$
^4He	3.276	$-2.914\cdot10^2$	$3.8318\cdot10^3$	$-1.2688\cdot10^4$

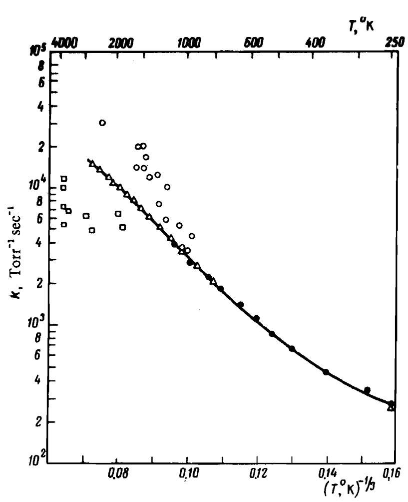

FIG. 3. Temperature dependence of the rate constant k = $k_{00^01}^{CO_2-CO_2}$: ●—experimental data, △—calculation from the cross section $\sigma'(\epsilon)$ of the present paper; □—[26], ○—[21], shock tube.

Table III shows, in accord with (13), the approximations of the calculated data on $\tau(T)$ in the temperature region 250—2500°K. Estimates show[25] that the error of the numerical continuation of the function $\tau(T)$ at T < 2500°K is not more than 5–7%. If it is recognized that the uncertainty in the experimental values of $\tau(T)$ reaches 15—20% at T = 1000°K, then the error in the data at 2500°K is 20—30%. Figure 3 illustrates the efficiency of the procedure for the numerical continuation of the deactivation rate constant into the region of high and low temperature. It is seen from the figure that at T > 1000°K d(T) agrees satisfactorily with the results obtained in shock-tube experiments[20,26], recognizing, of course, that the error of these data is $\gtrsim 50\%$.

Thus, an exact measurement of the rate constant of the process makes it possible to obtain, by the regularization method, the characteristic of the elementary interaction act which, in turn, makes it possible, without resorting again to experiment, to calculate the rate constant in the gas-temperature region, where a precision experiment is almost impossible to perform.

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[1] I. G. Mikhaĭlov, V. A. Solov'ev, and Yu. P. Syrnikov, Osnovy molekulyarnoĭ akustiki (Principles of Molecular Acoustics), Nauka (1964).

[2] Physical Acoustics, Vol. 2A (W. Mason, ed.), Academic, 1965.

[3] E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka (1965).

[4] T. L. Cottrell and J. C. McCoubrey, Molecular Energy Transfer in Gases, London, Butterworth (1961).

[5] V. K. Konyukhov, V. V. Korogod, and V. I. Tikhonov, Zh. Prik. Spektr. 10, 252 (1969).

[6] A. S. Biryukov, R. I. Serikov, and E. S. Trekhov, Zh. Eksp. Teor. Fiz. 59, 1513 (1970) [Sov. Phys.-JETP 32, 825 (1971)].

[7] A. S. Biryukov and B. F. Gordeits, Prik. Mat. Teor. Fiz. 6, 29 (1972).

[8] A. S. Biryukov, V. K. Konyukhov, A. I. Lukovnikov, and R. I. Serikov, FIAN Preprint No. 9 (1973).

[9] E. E. Nikitin, Teoriya elementarnykh atomno-molekulyarnykh protsessov v gazakh (Theory of Elementary Atomic and Molecular Processes in Gases), Khimiya (1970).

[10] K. F. Herzfeld, J. Chem. Phys. 47, 743 (1967).

[11] R. L. Taylor and S. Bitterman, Rev. Mod. Phys. 41, 26 (1969).

[12] A. S. Biryukov, V. K. Konyukhov, A. I. Lukovnikov, V. A. Myslin, R. I. Serikov, and E. S. Trekhov, Zh. Prik. Spectr. 2, 249 (1972).

[13] J. C. Stephenson and C. B. Moore, J. Chem. Phys. 52, 2333 (1970).

[14] J. C. Stephenson, R. E. Wood, and C. B. Moore, J. Chem. Phys. 54, 3097 (1971).

[15] J. C. Stephenson and C. B. Moore, J. Chem. Phys. 56, 1295 (1972).

[16] A. N. Tikhonov, Dokl. Akad. Nauk SSSR 151, 501 (1963).

[17] A. N. Tikhonov, Dokl. Akad. Nauk SSSR 153, 49 (1963).

[18] A. M. Gubanov, E. K. Eroshchenkov, O. A. Malkin, and L. S. Polak, Kinetika i kataliz 13, 33 (1972).

[19] W. A. Rosser, A. D. Wood, and E. T. Gerry, J. Chem. Phys. 50, 4996 (1969).

[20] W. A. Rosser and E. T. Gerry, J. Chem. Phys. 54, 4131 (1971).

[21] D. J. Seery, J. Chem. Phys. 56, 4714 (1972).

[22] P. V. Slobodskaya, Opt. Spektrosk. 34, 678 (1973

[23] V. V. Volenko, R. I. Serikov, and E. S. Trekhov, Fifth All-Union Conf. on the Physics of Electronic and Atomic Collisions, Abstracts of Papers (in Russian), Uzhgorod, 1972.

[24] R. Mariott, Proc. Phys. Soc. 84, 877 (1964).

[25] A. N. Tikhonov and B. V. Glasko, Zh. vychisl. matem. i matem. fiz. 4, 564 (1964).

[26] M. Camac, Avco Everett Research Laboratory, Research Report, No. 194 (1964).

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