Kinetics of excitation of a polyatomic molecular gas by a strong laser field in the presence of collisions

V. M. Akulin, S. S. Alimpiev, N. V. Karlov, B. G. Sartakov, and L. A. Shelepin

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted January 19, 1976)
Zh. Eksp. Teor. Fiz. **71**, 454–463 (August 1976)

The behavior of a polyatomic molecular gas in a strong laser field is considered. The effect of collisions on the excitation and dissociation of the molecules is taken into account. Some qualitative features of the processes (such as absorption of large amounts of energy in short periods of time, threshold effects, time dependences) are investigated. Problems connected with separation of isotopes and activation of chemical reactions are discussed.

PACS numbers: 34.50.Hc, 31.70.Hq

In a preceding paper[1] we have proposed and analyzed a radiative mechanism of exciting high vibrational levels of polyatomic molecules in a high-intensity IR laser pulse field. The possibility of such excitation is brought about by the fact that a multilevel resonant system, or even a single quasicontinuous background of levels, can be produced at a sufficient level density and a corresponding laser power. Allowance for this mechanism has explained a number of phenomena occurring when laser radiation interacts with matter (such as instantaneous dissociation[2,3]) and has made it possible to predict the "instantaneous appearance" of charged particles.[4] The radiation mechanism makes it possible to explain the singularities of the excitation of a molecule when it absorbs electromagnetic-field energy. For a more complete description of the behavior of a molecular gas it is necessary to take into account the collisions between molecules excited by a strong laser field. An analysis of the influence of the collisions greatly alters the prevailing ideas concerning the interaction between laser radiation and a gas in the case of strong fields and makes it possible to consider such qualitative features of the process as the high efficiency of the action of the radiation—absorption of a large amount of energy within short time intervals, the appreciable degree of dissociation of the molecules, and the preservation of the selectivity of the excitation in the collision stage of the process.

The analysis will be carried out within the framework of the following simple model. We divide the time evolution of the process into two stages.

The first and earlier stage is bounded by the time $\tau_{\rm rad}$ of action of the laser radiation and includes the pure radiative coherent population of a sequence M of equidistant levels of a molecule that absorbs resonantly the laser radiation. As will be shown in Sec. 1 (Fig. 1), the molecules acquire in this case a quasi-uniform vibrational-level distribution up to the dissociation limit. Each molecule interacting with the field stores on the average an energy $M\hbar\omega/2$. A fraction of the molecules that have reached the upper energy states dissociates. However, the fraction of the molecules that have dissociated during the radiative stage of the process is small (less than 1% of the number of molecules interacting with the field). This fraction can be roughly estimated by the ratio of the time of action of the radiation to the characteristic time in which the highly excited molecules go over to dissociation.

During the second stage of the process, in the absence of a laser field, a quasi-equilibrium distribution of the molecules is produced under the influence of the collisions. Inasmuch as a large amount of energy is stored in the system, an appreciable fraction of the particles dissociates during the course of the V–V relaxation. According to estimates given in Sec. 2, this fraction is ~20% of the total number of molecules that have interacted with the field. An interesting feature of this stage of the process is discussed in Sec. 3, namely, the isotopic selectivity is conserved in the case of isotopically selective excitation of the molecules during the first stage of the process (Figs. 2, 3, 4).

In the analysis of rotational-collisional processes it is necessary to consider the ratio of the characteristic times. These times are: the radiative characteristic time $\tau' = \hbar/d\mathscr{E}$ (d is the smallest dipole moment of the sequence of resonantly absorbing transitions while $\mathscr{E}$ is the intensity of the light field[1]), the times τ_{VV} and $\tau_{VV'}$ of vibrational exchange between different types of vibrations in the collisions, and the characteristic time τ_D that it takes the molecule to dissociate.

In all cases when $\tau' \ll \tau_{\rm pul}, \tau_{VV}, \tau_{VV'}, \tau_D$, the above-described division of the process into two stages is valid. This condition means in effect a weak influence of the collisions on the dynamics of the radiative population of the successive levels. At the same time, even if this condition is satisfied, the collisions, by broadening the levels, lead to a pressure dependence of the

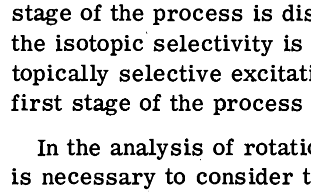

FIG. 1. Dependence of the population of the first vibrational level on the time in the radiative state. Zero time coincides with the start of the laser pulse.

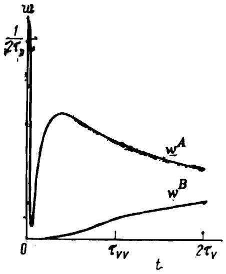

FIG. 2. Time dependences of the dissociation rates of molecules of sort A excited by a laser field and of the unexcited molecules of sort B. Zero time coincides with the end of the laser pulse.

threshold intensity of the radiative stage of the process. It is easy to show that the character of this dependence is described by

$$I_{\text{thr}}(p)=I_{\text{thr}}(0)[1-(p/p_0)^2],$$

where p_0 is the pressure at which overlap of the rotational sublevels of the vibrational state takes place. For polyatomic gases such as BCl_3, this overlap occurs already at a pressure on the order of 100 Torr. We confine ourselves to this brief remark concerning the possible influence of the collisions on the first phase of the process, assuming henceforth that

$$\tau'\ll\tau_{\text{pul}}<\tau_{VV}<\tau_{VV'},\ \tau_D.$$

1. The radiative stage of excitation of the molecule was theoretically investigated by us earlier.[1] Let us recall briefly the results. The radiative population of a sequence of almost equidistant levels is characterized by the presence of a threshold laser-radiation intensity, which is determined by the relation

$$I_{\text{thr}}=\frac{c}{4\pi}\left(\frac{\hbar\Delta\omega}{d}\right)^2,$$

where $\Delta\omega$ is the frequency detuning that results from the non-equidistance of the levels. Our estimates[1] yield a value $I_{\text{thr}}\approx10^8$ W/cm^2, which coincides with the known experimental data of[2,3], in which instantaneous dissociation of SiF_4 and BCl_3 was investigated. In addition, there have been a number of studies[9,8] of the instantaneous dissociation at intensities below threshold. The results of these investigations can be explained within the framework of our model[1] by recognizing that at intensities below threshold the population of the lower n-th level still increases at the initial instant of time like $(I/I_{\text{thr}})^n$, i.e., the threshold is quite soft. In addition, we have established[1] the existence of a threshold for the area under the laser pulse:

$$\int\frac{\mathscr{E}d}{\hbar}dt>1$$

and have estimated the characteristic radiative kinetic time $\tau'\approx10^{-9}-10^{-8}$ sec for polyatomic molecules of the BCl_3 type. However, as shown by further investigations, this condition is not sufficient for an effective population of the upper vibrational levels. A sufficient condition is in this case the more rigorous inequality

$$\int\frac{\mathscr{E}d}{\hbar}dt>M,$$

and the characteristic time of population of the upper vibrational levels, as will be shown below (Fig. 1) is the time $\tau_M=M\tau'$. To investigate further the radiative-collision excitation of a molecular gas it is necessary to know the average reserve of the vibrational energy of the molecule that has interacted with the field, and also the distribution function of the populations formed during the radiative stage of the process.

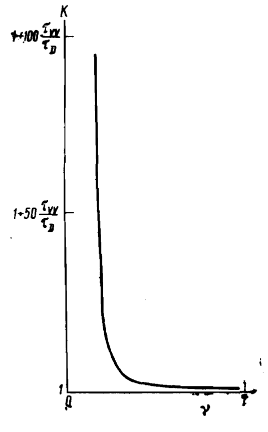

FIG. 3. Enrichment coefficient K of the dissociation products of a single irradiation of the gas volume vs the initial concentration of the molecules of isotopic composition A resonantly excited during the radiative stage of the process ($M=100$).

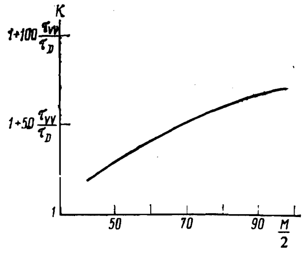

FIG. 4. Dependence of the enrichment coefficient of the dissociation products on the average reserve of vibrational energy of the molecule interacting with the field.

Assume that the number of equidistant levels taking part in the absorption of the laser pulse is limited, for example, by the low probability of the transition from the last M-th level (the energy levels are numbered in order of increasing energy) to a higher state by absorbing a radiation quantum. Physically this may be connected with the fact that the upper dissociation limit sets a bound on the capability of the system to accumulate energy.

To find the population distribution function over the levels, we write down the kinetic equation for a system of M equidistant levels in an external resonant field

$$i\hbar\dot{\psi}_n=\mathscr{E}(d_n\psi_{n+1}+d_{n-1}\psi_{n-1}). \tag{1}$$

We confine ourselves to the case $d_n=\text{const}=d$. We introduce a new variable

$$\tau=\int_{-\infty}^{t}\frac{\mathscr{E}d}{\hbar}dt.$$

The equations for the ψ functions then take the form

$$\frac{\partial\psi_n}{\partial\tau}=\psi_{n+1}+\psi_{n-1}. \tag{2}$$

We solve Eqs. (2) with the initial condition

$$\psi_n|_{\tau=0}=\delta_{n,0}.$$

The solution of the equation for ψ_M is then

$$\psi_M=\sum_{K=0}^{M}\exp(iz_K\tau)\operatorname{res}_{z_K}\frac{1}{U_M(z/2)}, \tag{3}$$

where $U_M(z/2)$ is a Chebyshev polynomial of the second kind and z_K are its roots. For the M-level harmonic oscillator $d_n=n^{1/2}d$ the solution of (1) is

$$\psi_M=\sum_{K=0}^{M}\exp(iz_K\tau)\operatorname{res}_{z_K}\frac{1}{D_M(z)}, \tag{4}$$

where $D_M(z)$ are parabolic-cylinder functions.

The population of the M-th level, determined from (3), was analyzed with a computer. It was found that

$$\rho_{M,M}(\tau)\equiv\psi_M(\tau)\psi_M^*(\tau).$$

It is a certain function of the parameter τ, localized in the vicinity of the mean value of $\rho_{M,M}\sim 1/M$ with rare sharp spikes, exceeding by several times the average value—"flickering" populations (Fig. 1). The transition of a multilevel system into a state of flickering populations certainly occurs within a time on the order of $\tau_M\sim M\tau'$.

From the quasi-uniformity of the distribution functions it follows that the average energy reserve of a molecule interacting with the field is approximately $M\hbar\omega/2$. Even if it is assumed that the excited molecule remains within the limits of the electronic ground state, the average value of the absorbed energy per molecule interacting with the field is 50–60 laser quanta. Thus, the molecules store as a result of the considered radiative process an energy much larger than in resonant absorption with thermalization over the vibrational modes (the latter process was considered, for example, by Stupochenko *et al.*[7]).

2. The radiative-excitation stage is followed by a collision stage. The initial quasi-uniform distribution produced by the radiative excitation is transformed as a result of the collisions into quasi-equilibrium collisional distributions that subsequently relax to equilibrium distributions. The collision stage causes dissociation of a large number of molecules, as determined by the energy stored in the system. To estimate this number we shall assume that the process of establishment of the quasi-equilibrium distributions in the vibrational mode is faster than the molecule dissociation (τ_{VV}, $\tau_{VV'}\ll\tau_D$), i.e., the quasi-equilibrium distribution functions are established almost instantaneously. In addition, we assume that the equilibrium is established only as a result of molecule dissociation, neglecting $(V-T)$ relaxation ($\tau_D<\tau_{VT}$) and recombination.

As the initial distribution we take a quasi-equilibrium Boltzmann distribution expressed in terms of the continuous variable E (the molecule energy in units of $\hbar\omega$),

$$n(E)=\frac{Ne^{-mE/\theta}E^{m-1}}{(\theta/m)^m(m-1)!}.$$

Here $n(E)$ is the distribution function for m vibrational modes, θ is the average energy stored in all the modes, and N is the concentration of the molecules. Both N and θ vary in time as a result of dissociation of the excited molecules:

$$\begin{aligned}\frac{dN}{dt}&=\frac{1}{\tau_D}N\int_{k_0}^{\infty}\frac{e^{-Em/\theta}E^{m-1}}{(\theta/m)^m(m-1)!}dE,\\ N\frac{d\theta}{dt}&=-\frac{m}{\tau_D}N\int_{k_0}^{\infty}\frac{e^{-Em/\theta}E^{m}}{(\theta/m)^m(m-1)!}dE-\theta\frac{dN}{dt}.\end{aligned} \tag{5}$$

We assume that the molecule can dissociate with a characteristic time τ_D only when it lies higher than a certain level k_0, the meaning of which is the lower dissociation threshold of the polyatomic molecule. It follows from (5) that

$$\frac{dN}{d\theta}=\frac{N}{mk_0}\sum_{k=0}^{m-2}\frac{1}{k!}\left(\frac{k_0m}{\theta}\right)^k\Big/\sum_{k=0}^{m-1}\frac{1}{k!}\left(\frac{k_0m}{\theta}\right)^k.$$

For $m>1$ and $k_0m\gg\theta$ we easily obtain the approximate solution

$$N=N_0\exp\left[(\theta^2-\theta_0^2)\frac{m-1}{2m^2k_0^2}\right].$$

Recognizing that θ decreases in time and that the final value $\theta(\infty)$ is much smaller than $\theta_0=\theta|_{t=0}$, we obtain an estimate of the fraction of the number of dissociated molecules

$$\frac{\Delta N}{N_0}=\frac{N_0-N(t=\infty)}{N_0}$$

in terms of the average stored energy $\theta_0=M/2$, the number of vibrational degrees of freedom m, and the lower dissociation limit k_0:

$$\frac{\Delta N}{N_0}=\frac{m-1}{2}\left(\frac{\theta_0}{mk_0}\right)^2. \tag{6}$$

As follows from (6), the dissociation is quite effective in the collision stage. At $m=6$, $\theta_0=60$, and $k_0=40$ approximately 20% of the molecules interacting with the field dissociate in the collision stage. This value greatly exceeds the fraction of the molecules dissociating in the instantaneous stage, which can be estimated at $\tau_D\gg\tau_{\text{pul}}$ at

$$\frac{\Delta N}{N_0}\sim\frac{\tau_{\text{pul}}}{\tau_D}\frac{M-k_0}{M}$$

At $\tau_{\text{pul}}=10^{-7}$ sec and $\tau_D\approx 10^{-5}$ sec[6] we have $\Delta N/N_0\lesssim 1\%$. Thus, the $(V-V)$ relaxation that follows the stage of collisionless radiative accumulation of energy by the molecules leads to dissociation of a relatively large number of molecules.

3. When the dissociation of molecules in the field of a high-power laser pulse is investigated, greatest interest attaches to the possibility of realizing isotopically selective dissociation. In the instantaneous state, i.e., during the time of action of the laser pulse, the selectivity is ensured by the resonant character of the action of the laser radiation on the molecules and the isotopic

shift of the vibrational frequencies. In the instantaneous stage, however, many more molecules dissociate than in the succeeding collision stage, therefore, if the dissociation is not selective in the collision stage, then the selectivity of the dissociation is small as a result.

As the measure of the selectivity of the dissociation we choose the coefficient of enrichment of the dissociation products in the irradiated volume by a single action of a laser pulse on the gas

$$K=\frac{\Delta N_A}{N_A}\Big/\frac{\Delta N_B}{N_B},$$

where N_A is the concentration of molecules of isotopic composition A; N_B is the concentration of molecules of isotopic composition B; ΔN_A is the number of dissociated molecules A; ΔN_B is the number of dissociated molecules B. The radiation interacts resonantly with the molecules of type A. The enrichment coefficient is easily expressed in terms of the statistical mean values $w^A(t)$ and $w^B(t)$ of the rates of dissociation of the molecules of type A and B, respectively

$$K=1+\int_0^\infty (w^A-w^B)\,dt\Big/\int_0^\infty w^B\,dt, \tag{7}$$

where $w^A(t)$ and $w^B(t)$ are calculated per molecule. The integral in the numerator of (7) determines the fraction of the selectively dissociated molecules, while the integral in the denominator of (7) determines the total number of the dissociated particles (obtained in the preceding section).

To obtain the quantity

$$S=\int_0^\infty (w^A-w^B)\,dt,$$

it is necessary to consider equalization of the average dissociation rates by the vibrational relaxation. Usually the fastest vibrational-relaxation process is $(V-V)$ exchange ($\tau_{VV}\ll\tau_{VV'},\tau_{VT}$). To calculate S we therefore confine ourselves to consideration of the process of $(V-V)$ relaxation over the mode excited by the laser.

The kinetic equations of the $(V-V)$ exchange for the populations of the energy levels of the vibrational mode of the molecule take, in the harmonic-oscillator approximation, the form[7]

$$\frac{dn_k^{A,B}}{d\tau}=(k+1)[(1+\theta_0)n_{k+1}^{A,B}-\theta_0 n_k^{A,B}]-k[(1-\theta_0)n_k^{A,B}-\theta_0 n_{k-1}^{A,B}], \tag{8}$$

where $\tau=t/\tau_{VV}$; n_k^A and n_k^B are respectively the populations of the k-th level of the vibrational mode of the molecules A and B; $\theta_0=\nu M/2$; $\nu=N_A/(N_A+N_B)$ are the relative concentrations of the molecules A. We shall solve the system (8) with the initial conditions

$$n_k{}^A=\begin{cases}0, & k\geqslant M;\\ 1/M, & k<M;\end{cases}$$
$$n_k{}^B=\begin{cases}0, & k\geqslant 1;\\ 1, & k=0.\end{cases}$$

It is assumed here that the molecules not excited by the field are in the vibrational ground state, while the excited molecules (molecules A) are uniformly distributed over the vibrational levels up to the level M (see Sec. 2).

With the aid of the generating functions

$$\Phi^{A,B}(x,\tau)=\sum_{k=0}^\infty n_k^{A,B}(\tau)x^k$$

we reduce the system (8) to the form

$$\begin{aligned}\frac{\partial\Phi^A}{\partial\tau}&=(x-1)\theta_0\Phi^A+(x-1)[x\theta_0-(\theta_0+1)]\frac{\partial\Phi^A}{\partial x},\\ \frac{\partial\Phi^B}{d\tau}&=(x-1)\theta_0\Phi^B+(x-1)[x\theta_0-(\theta_0+1)]\frac{\partial\Phi^B}{\partial x},\end{aligned} \tag{9}$$

with initial conditions

$$\Phi^A(x,0)=\frac{1-x^M}{M(1-x)},\quad \Phi^B(x,0)=1.$$

The solution of (9) is

$$\begin{gathered}\Phi^A(x,\tau)=\left\{1-\left[1+\frac{(1-x)e^{-\tau}}{\theta_0(e^{-\tau}-1)(1-x)-1}\right]^M\right\}\frac{e^\tau}{M(1-x)},\\ \Phi^B(x,\tau)=1/[1+\theta_0(1-e^{-\tau})(1-x)].\end{gathered} \tag{10}$$

Recognizing that the dissociation of the molecule proceeds with a certain characteristic time τ_D only if the molecule is in a vibrational state with a number larger than or equal to k_0, the statistically averaged dissociation rate satisfies the equation

$$w^{A,B}(\tau)=\frac{1}{\tau_D}\sum_{k=k_0}^\infty n_k^{A,B}(\tau).$$

Here, as above, we neglect recombination, assuming the dissociation process to be irreversible.

Using the relation

$$n_k^{A,}(\tau)=\frac{1}{k!}\frac{\partial^h}{\partial x^k}\Phi^{A,B}(x,\tau)\,|_{x=0}, \tag{11}$$

we obtain

$$w^{A,B}(\tau)=\frac{1}{\tau_D}\left\{1-\frac{1}{(k_0-1)!}\frac{\partial^{k_0-1}}{\partial x^{k_0-1}}\left[\frac{\Phi^{A,B}}{1-x}\right]\Big|_{x=0}\right\}. \tag{12}$$

After substituting (10) in (12) we obtain the final expression

$$\begin{gathered}w^A(\tau)=\frac{1}{\tau_D}\frac{\theta_0}{M}\frac{e^\tau-1}{\theta_0(e^\tau-1)-1}\frac{[1-1/\theta_0(e^\tau-1)]^M}{[1+1/\theta_0(1-e^{-\tau})]^{k_0}}\sum_{i=1}^M C_M{}'\left[\frac{1}{\theta_0(e^\tau-1)-1}\right]^{i-1}\\ \times\sum_{j=0}^{i-1}(i-j)C^j_{k_0-1+j}\left[\frac{1}{1+\theta_0(1-e^{-\tau})}\right]^j,\end{gathered} \tag{13}$$

$$w^B(\tau)=\frac{1}{\tau_D}\left[1+\frac{1}{\theta_0(1-e^{-\tau})}\right]^{-k_0}. \tag{14}$$

Analogously, the expression for S is

$$S=\frac{\tau_{VV}}{\tau_D}\sum_{i=2}^M\frac{C_M{}^i}{M(i-1)}\left(\frac{1}{\theta_0}\right)^{i-1}\left(\frac{\theta_0}{\theta_0+1}\right)^{k_0}. \tag{15}$$

Expressions (13) and (14) were calculated with a

Wang-2200 computer. The results of the calculation of the time dependence of the dissociation rates of molecules A and B are shown in Fig. 2. It is seen from an analysis of Fig. 2 that immediately after the end of the excited pulse the rate of dissociation of the molecules A decreases. This decrease is in fact the decay of the instantaneous dissociation phase as a result of the rapid $(V-V)$ exchange on the upper vibrational levels that lie near the dissociation limit of the gas. The dissociation rate of the molecules A then begins to increase as a result of excitation of molecules located at the lower vibrational levels, and reaches an extremum within a time $\sim 0.4\tau_{VV}$, after which it already tends to an equilibrium value. The rate of dissociation of the molecules B increases monotonically to an equilibrium value with a characteristic time τ_{VV}. After a time on the order of several τ_{VV}, the dissociation rates of the molecules A and B become equalized, meaning in effect violation of the selectivity of the excitation. The equilibrium dissociation rate tends slowly (in comparison with τ_{VV}; not indicated in Fig. 2) to a zero value with a characteristic time τ_D.

For the enrichment coefficient K we obtain from (7)

$$K=1+S\Big/\int_0^\infty w^B\,dt,$$

where S is calculated from (15), and the exception for the integral $\int_0^\infty w^B\,dt$ was obtained in the preceding section:

$$\int_0^\infty w^B\,dt=\frac{m-1}{2}\left(\frac{\theta_0}{mk_0}\right)^2,$$

here $\theta_0=\nu M/2$.

The calculated dependences of the enrichment coefficient K on ν and M are shown in Figs. 3 and 4. It is seen from an analysis of Fig. 3 that the enrichment coefficient K decreases with increasing relative concentration of the isotope excited by the field, from which it follows that when a depleted isotope is excited the selectivity of the collisional stage is not higher than when an enriched isotope is excited. An analysis of Fig. 4 shows a plastically linear increase of the enrichment coefficient with increasing field-pumped energy M.

Thus, using the singularities of the equalization of the dissociation rates of molecules of varying isotopic compositions under selective excitation, it is possible to separate isotopes effectively during the collisional stage of the process.

We note in conclusion that the mechanism discussed here offers also certain prospects of stimulating chemical reactions. It must be emphasized above all that the energy can be pumped into the medium with high efficiency. In contrast to resonant absorption in one transition, a smaller fraction of energy goes over into heat. It should also be noted that electric reactions are possible. In the case of pure radiative population of levels belonging to different composite vibrations, the breaking of certain bonds is no longer selective. In the collisional stage, the selectivity can be restored by introducing an admixture of diatomic molecules that resonantly deactivate the molecules in certain vibrational modes.

[1] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, and L. A. Shelepin, Zh. Eksp. Teor. Fiz. **69**, 836 (1975) [Sov. Phys. JETP **42**, 427 (1975)].
[2] N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, Can. J. Phys. **51**, 1281 (1973).
[3] R. V. Ambartsumyan, V. S. Dolzhikov, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Zh. Eksp. Teor. Fiz. **69**, 72 (1975) [Sov. Phys. JETP **42**, 36 (1975)].
[4] V. M. Akulin, S. S. Alimpiev, N. V. Karlov, N. A. Karpov, Yu. N. Petrov, A. M. Prokhorov, and L. A. Shelepin, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 100 (1975) [JETP Lett. **22**, 45 (1975)].
[5] B. V. Gnedenko, Kurs teorii veroyatnosti (Course of Probability Theory), GITTL, M. 1954.
[6] G. Herzberg, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand Reinhold, 1966. (Russ. transl., Mir, 1969, p. 484).
[7] E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, 1965.
[8] R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 96 (1975) [JETP Lett. **22**, 44 (1975)].
[9] R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and A. A. Puretskiĭ, *ibid.*, 389 [177].

Translated by J. G. Adashko