Stimulation of chemical reactions by laser radiation[1)]

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Reactions involving molecules excited by laser radiation are considered. It is shown that under certain conditions the reactions proceed with a large difference between the translational and vibrational temperatures of the gas. Thus it seems possible to excite certain bonds in the molecule and keep the excitation localized up to the moment of the reaction. A number of experimental results pertaining to stimulation of chemical reactions are presented.

1. INTRODUCTION

The use of lasers uncovers extensive possibilities of selective stimulation of chemical reactions that require participation of vibrationally-excited molecules[1-3]. It is known that chemical reactions occur only if the energy of the reagents exceeds the activation energy ε^* of the process. From the point of view of the energy effect, chemical transformations are subdivided into two classes: endothermal reactions, which require a definite amount of energy, and exothermal reactions, which are accompanied by the release of heat.

It is obvious that endothermal reactions always require a definite activation energy. But most exothermal transformations likewise do not proceed without activation, for regardless of how favored energywise, a chemical reaction requires close proximity of the reagents. When the particles are close to each other, repulsion forces are usually produced, and to overcome them it is necessary to have a definite energy corresponding to the reaction activation energy. If the reacting molecules have a Maxwellian distribution with temperature T, the number of collisions that lead to a reaction does not exceed the fraction $\exp(-\varepsilon^*/T)$ of the total number of collisions. It is natural to assume that to break a bond or to initiate a reaction it is necessary to expend not only translational energy, but also energy of the internal degrees of freedom of the molecules, vibrational and rotational. Moreover, according to modern concepts[4], the principal role in chemical transformations is played by the vibrational energy of the molecules; for example, the dissociation of an unexcited molecule is exceedingly small, even if the translational energy exceeds the molecule binding energy. The molecules that dissociate are in the main those whose vibrational energy exceeds the binding energy[1,5,6]. Chemical transformations proceed more readily in accordance with the following scheme: when the molecules interact with one another their vibrational levels "rise" to the activation energy ε^*. At an energy $\sim\varepsilon^*$, the molecules enter effectively into the reaction and the characteristic time of the process is thus determined by time necessary for the molecule to acquire the threshold energy ε^*.

The presently available physical methods of acting on chemical processes lead mainly to excitation of all degrees of freedom of the molecule. The translational, vibrational, and rotational degrees of freedom are as a rule in thermodynamic equilibrium. In addition to the nonproductive loss of energy, reactions in which molecules are excited at equilibrium are characterized by a directivity that is already determined potentially by the breaking of the weakest bond.

A fundamentally new approach to the problem of chemical transformations of substances would be to act not on the molecule as a whole, but on its individual bonds. Such a method of selective excitation is provided today by lasers. Molecules initiated by laser radiation and having a vibration-mode temperature reaching tens of thousands of degrees can enter in controlled chemical reactions at rates greatly exceeding the rates of the vibrational-translational relaxation. Laser-chemical reactions are characterized thus not only controllable but also feature abrupt separation of the vibrational and translational temperatures[6-9]. Under definite conditions, the thermodynamic equilibrium is upset also between the internal degrees of freedom; the molecule then enters the chemical process retaining an excited oscillation mode that resonates with the laser radiation.

By way of example we consider the reactivity of a molecule of the type A-B-C. If the A-B bond is the weaker one, the molecule reacts as a rule with dissociation of this bond. When the B-C bond is excited by radiation, the bond that becomes chemically active in the (A-B-C) molecule is not A-B with the reaction center A, but the bond B-C with the reacting fragment C. The chemical properties of the A-B-C molecule differ from those of the selectively-excited (A-B-C) molecule. Laser-chemical reactions are thus distinguished from reactions in which "equilibrium" molecules take part, and constitute a new class, reactions of selectively-excited molecules. It is here that one can indicate ways of controlling chemical processes, namely the ability of exciting the required bonds in the molecule and keeping the excitation local up to the instant of the chemical reaction.

A characteristic feature of laser radiation is the high spectral monochromaticity. This permits selective excitation and subsequent separation of molecules with exceedingly close vibrational frequencies, for example, of molecules with different isotopic compositions. The process reduces to initiation of a chemical reaction (or dissociation) of the molecule of a given isotope by laser radiation with subsequent chemical separation of the mixture products[3].

There is every reason for expecting the laser-initiation method to influence strongly many fundamental chemical production processes, to uncover possibilities of directed decomposition and synthesis of new chemical compounds, to play a role in molecular biology, etc., i.e., it can find application whenever vibrationally-excited molecules participate in the chemical process. In this paper we consider conditions for selective excitations of high vibrational levels of molecules by laser radiation, and present a number of experimental results on stimulated chemical reactions.

2. KINETICS OF LASER HEATING OF MOLECULAR BONDS AND RATES OF CHEMICAL REACTIONS

From the instant when the laser photon is resonantly absorbed to the instant of the chemical reaction, the molecule experiences a number of transformations consisting of population of higher vibrational levels, establishment of equilibrium between the intramolecular degrees of freedom, dissociation, and vibrational-translational relaxation. The set of equations describing these processes is

$$\frac{\partial X_n{}^k}{\partial t} = \left(\frac{\partial X_n{}^k}{\partial t}\right)_{vt} + \sum_j \left(\frac{\partial X_n{}^k}{\partial t}\right)_{vv}^{kj} + \left(\frac{\partial X_n{}^k}{\partial t}\right)_d + \left(\frac{\partial X_n{}^k}{\partial t}\right)_r + \left(\frac{\partial X_n{}^k}{\partial t}\right)_q ;\quad (1)$$

$$\left(\frac{\partial X_n{}^k}{\partial t}\right)_{vt} = Z[{}^kP_{n-1}X_{n-1}^k - {}^kP_{n,n-1}X_n{}^k + {}^kP_{n+1,n}X_{n+1}^k - {}^kP_{n,n+1}X_n{}^k], \quad (2)$$

$$\left(\frac{\partial X_n{}^k}{\partial t}\right)_{vv}^{kj} = Z\Big[\Big(\sum_l {}^{kj}Q_{n-1,n}^{l+1,l} X_{l+1}^j\Big) X_{n-1}^k - \Big(\sum {}^{kj}Q_{n,n-1}^{m,n+1} X_m{}^j\Big) X_n{}^k$$
$$+ \Big(\sum {}^{kj}Q_{n+1,n}^{l,l+1} X_l{}^j\Big) X_{n+1}^k - \Big(\sum_m {}^{kj}Q_{n,n+1}^{m+1,m} X_{m+1}^j\Big) X_n{}^k\Big], \quad (3)$$

$$\left(\frac{\partial X_n{}^k}{\partial t}\right)_d = -{}^kW_{nd}X_n{}^k, \quad \left(\frac{\partial X_n{}^k}{\partial t}\right)_r = -{}^kW_{nr}X_n{}^k, \quad (4)$$

$$\left(\frac{\partial X_n{}^k}{\partial t}\right)_q = [{}^kS_{n-1,n}X_{n-1}^k - {}^kS_{n,n-1}X_n{}^k + {}^kS_{n+1,n}X_{n+1}^k - {}^kS_{n,n+1}X_n{}^k], \quad (5)$$

where $X_n^k(T)$ is the concentration of the molecules at the n-th level of the k-th oscillation mode, ${}^kP_{nm}$ is the probability of vibrational-translational transition of the molecule of the n-th vibrational state of the k-th mode into the m-th state upon collision (the v-t process), Z is the number of molecule collisions per second, ${}^{kj}Q_{n,n+1}^{m+1,m}$ is the probability of transferring a vibrational quantum by the oscillator of the j-th mode in the (m + 1)-st state to the oscillator of the k-th mode in the n-th state (v-v process), ${}^kW_{nd}$ and ${}^kW_{nr}$ are the respective frequencies of dissociation and chemical reaction of the molecule in the (n, k) state, and ${}^kS_{mn}$ is the frequency of the laser-induced transition of the k-th oscillator from the state m into the state n.

The system of kinetic equations (1) is nonlinear, and in the general case it is impossible to indicate the solutions. Nonetheless, the qualitative character of the processes described by Eqs. (1) is clear.

We introduce the characteristic times of the relaxation processes: τ_{vt}^k is the time of vibrational-translational relaxation of the k-th mode, τ_{vv}^{kj} is the time of establishment of equilibrium in vibrational-vibrational exchange of oscillators of the k-th and v-th modes of the molecule, τ_d and τ_r are the molecule decay times in the processes of dissociation and chemical reaction, and τ_q^k is the time of excitation of the k-th mode of the molecule by the laser field.

Under real conditions, the following inequalities are usually satisfied:

$$\tau_{vv}{}^{kk} \ll \tau_{vv}{}^{kj} \ll \tau_{vt}{}^k. \quad (6)$$

According to (6), the first to be established in the molecule system is equilibrium in each vibrational mode, followed by intramolecular equilibrium, and the last is equilibrium between the vibrational and translational degrees of freedom. The situation with respect to times τ_d^k and τ_r^k is more complicated. Dissociation or a chemical reaction proceeds effectively only when the molecule has a sufficient energy reserve; the probability of the indicated processes is $\sim\exp(-\mathcal{E}^*/\Theta)$, where $\mathcal{E}^*$ is the activation energy and Θ is the average energy of the molecule. In thermal heating of the system, the number of active molecules is relatively small and consequently the considered processes are slowest. To the contrary, in selective excitation of molecules by a laser field, Θ can become comparable with $\mathcal{E}^*$, and the processes of dissociation and chemical reaction becomes among the fastest processes in the system.

Thus, the picture of heating of molecules by resonant radiation of a laser, described by the kinetic equations (1), has the following evolution. At low laser-field intensities q (τ_q^k being the longest of all the characteristic times), the system is heated with complete thermodynamic equilibrium preserved. This heating does not differ from thermal heating. With increasing field intensity ($\tau_{vv}^{kj} < \tau_q^k < \tau_{vt}^{kj}$) the vibrational temperature of the molecule begins to differ from the translational one, but the energy distribution within the molecule remains in equilibrium. Finally, in sufficiently strong fields ($\tau_q^k < \tau_{vv}^{kj}$) the equilibrium may become upset and only the molecular bond that resonates with the field becomes selectively heated. The last case is optimal for laser chemistry, and we consider below the conditions for such heating and estimate the necessary laser-radiation parameters.

1. Excitation of harmonic vibrations of a molecule in a laser field. We assume that a chemical reaction proceeds in the system with sufficiently low activation energy $\mathcal{E}^*$, so that molecule vibrations with energy $\mathcal{E} \le \mathcal{E}^*$ can be regarded as harmonic. If the radiation flux is large enough ($\tau_q^k < \tau_{vv}^{kk}$) one can neglect in the kinetic equation all but the field terms. Omitting the index k to simplify the notation, we obtain from (1) the system of equations

$$\frac{\partial X_n}{\partial t} = [S_{n-1}X_{n-1} - S_{n,n-1}X_n + S_{n+1,n}X_{n+1} - S_{n,n+1}X_n] - W_{nr}X_n. \quad (7)$$

For a harmonic oscillator

$$S_{n-1,\,n} = S_{n,\,n-1} = q\sigma_{n-1,\,n}/\hbar\omega, \quad \sigma_{n-1,\,n} = n\sigma_{10}, \quad (8)$$

where q is the laser-radiation flux density, σ_{mn} is the cross section of the resonant transition m → n, and $\hbar\omega$ is the energy of the vibrational quantum, which we assume equal to the emission quantum.

We solve the system (7) under the following assumptions: a) The vibrational quantum energy $\hbar\omega$ is small in comparison with the activation energy $\mathcal{E}^*$. In this case one can change over from discrete level populations X_n to a continuous distribution function $X(t, \mathcal{E})$. This transition is effected formally by letting the quantum $\hbar\omega$ tend to zero. b) The molecules excited to the energy $\mathcal{E} = \mathcal{E}^*$ enter effectively in the reaction. In this case the levels with energy $\mathcal{E} > \mathcal{E}^*$ are not populated in practice.

Under these assumptions, the system (7) reduces to the following diffusion equation:

$$\frac{\partial X}{\partial t} = -\frac{\partial}{\partial \mathscr{E}} J, \quad J = -q\sigma_{10}\mathscr{E}\frac{\partial X}{\partial \mathscr{E}}, \quad (9)$$

where J is the particle flux in energy space, with boundary conditions

$$X(t, \mathscr{E}^*) = 0, \quad J(t, 0) = 0. \quad (10)$$

Representing $X(t, \mathcal{E})$ in the form

$$X(t,\mathscr{E})=\sum_{\mu}T_{\mu}(t)X_{\mu}(\mathscr{E}),$$

we obtain from (9) and (10)

$$X(t,\mathscr{E})=\sum_{\mu}C_{\mu}\exp(-\gamma_{\mu}t)J_0\left(2\left(\frac{\gamma_{\mu}\mathscr{E}}{q\sigma_{10}}\right)^{1/2}\right), \tag{11}$$

$$\gamma_{\mu}=z_{\mu}^2q\sigma_{10}/4\mathscr{E}^*, \tag{12}$$

where z_{μ} are the zeroes of the Bessel function $J_0(z)$.

We neglect next all terms but the first in the expansion (11); in this case, in accordance with (12), the chemical-reaction rate constant is given by

$$\gamma'=z_1^2q\sigma_{10}/4\mathscr{E}^*,\quad z_1\approx 2.4. \tag{13}$$

Expression (13) for γ has a simple physical meaning. Indeed, $1/\gamma$ is the time necessary for the molecule interacting with the field to absorb an energy $\varepsilon \approx \varepsilon^*$. Recognizing that in the mean

$$d\mathscr{E}/dt\sim q\langle\sigma_{mn}\rangle,$$

and assuming that $\langle\sigma_{mn}\rangle \sim \sigma_{10}$, we obtain from

$$\int_0^{1/\gamma}q\langle\sigma_{0m}\rangle\approx\mathscr{E}^*$$

a relation close to (13).

The time $\tau = 1/\gamma$ of the chemical reaction, according to (13), does not depend on the pressure[1)] and is inversely proportional to the laser-radiation flux q. Therefore under conditions when the harmonic approximation is valid we can always indicate sufficiently strong field (or sufficiently low pressures), starting with which only a molecule with an excited absorbing bond takes part in the chemical process. We present numerical estimates: if $q \approx 10^2$ W/cm², $\sigma_{10} \approx 10^{16}$ cm², and $\varepsilon^* \approx 1.5$ eV we have, in accordance with (13), $\gamma = 10^5$ sec⁻¹. Thus, at pressures $\lesssim 100$ Torr, when the time is $\tau_{\mathrm{VV}}^{\mathrm{kj}} \approx 10^{-4}$–$10^{-5}$ sec, there is no time for the intermolecular relaxation to be established and the reaction proceeds only with the excited bond taking part.

2. Excitation of molecule vibrations in a laser field with allowance for vibrational-vibrational relaxation effects. We assume that the excited vibrational bond of the molecule is almost harmonic for vibrational exchange up to the levels from which the chemical reaction proceeds with near-unity probability. At the same time, the anharmonicity is quite appreciable for the absorbed laser radiation, so that absorption is possible only between the ground and first levels of the molecule. This is the most probable situation under real conditions of laser initiation of chemical reactions, in view of the high monochromaticity of laser emission.

We write down the system of equations corresponding to this approximation:

$$\left(\frac{\partial X_n^k}{\partial t}\right)=\left(\frac{\partial X_n^k}{\partial t}\right)_{vv}^{kk}+\left(\frac{\partial X_n^k}{\partial t}\right)_q+\left(\frac{\partial X_n^k}{\partial t}\right)_r. \tag{14}$$

The expression for $(\partial X_n^k/\partial t)_q$ is given in (7)–(9);

$$\begin{aligned}\left(\frac{\partial X_n^k}{\partial t}\right)_{vv}^{kk}=\frac{1}{\tau_{vv}^{kk}}\Big\{&(n+1)\left(1+\frac{\Theta^k}{\hbar\omega}\right)X_{n+1}^k\\&-\left[(n+1)\frac{\Theta^k}{\hbar\omega}+n\left(1+\frac{\Theta^k}{\hbar\omega}\right)\right]+n\frac{\Theta^k}{\hbar\omega}X_{n-1}\Big\},\end{aligned} \tag{15}$$

where $\Theta^k = \sum_n nX_n^k$ is the total number of vibrational quanta at the instant of time t. The collision integral, which describes the v-v relaxation process of the k-th mode of the molecule, can be easily obtained from (3) if it is recognized that for a harmonic oscillator

$${}^{kk}Q_{n+1,n}^{l-1,l}=(n+1)l/Z\tau_{vv}^{kk}. \tag{16}$$

Proceeding to the diffusion approximation, we obtain from (14) and (15) the following kinetic equation for the distribution function $X(t, \varepsilon)$ (we omit the index k):

$$\frac{\partial X}{\partial t}=\frac{1}{\tau_{vv}}\frac{\partial}{\partial\mathscr{E}}\left(X+\Theta\frac{\partial X}{\partial\mathscr{E}}\right)\mathscr{E}+q\sigma_{10}\nu(\mathscr{E}-\mathscr{E}_*)\frac{\partial}{\partial\mathscr{E}}\mathscr{E}\frac{\partial X}{\partial\mathscr{E}}, \tag{17}$$

$\nu(\varepsilon) = 1$ at $\varepsilon < \varepsilon_*$ and $\nu(\varepsilon) = 0$ at $\varepsilon > \varepsilon_*$, where Θ_{V} is the vibrational temperature of the excited bond, and $\varepsilon_* = \hbar\omega$ is the end-point energy, above which the molecules become populated only as a result of resonant excitation transfer.

By representing the solution of equation (17) in the form

$$X(t,\mathscr{E})=e^{-\gamma t}X(\mathscr{E}),$$

where γ is the rate of the chemical reaction, we rewrite it in the form

$$kX=\frac{\partial}{\partial\mathscr{E}}J,\ J=-\mathscr{E}\left\{X+[\Theta_v+\varkappa\nu(\mathscr{E}-\mathscr{E}_*)]\frac{\partial X}{\partial\mathscr{E}}\right\}, \tag{18}$$

where $k = \gamma\tau_{\mathrm{VV}}$ and $\kappa = q\sigma_{10}\tau_{\mathrm{VV}}$. At $\kappa = 0$ (there is no laser field), Eq. (18) has the following solution:

$$X(\mathscr{E})=C_0\exp\left(-\frac{\mathscr{E}}{\Theta_v}\right){}_1F_1\left(-k,1,\frac{\mathscr{E}}{\Theta_v}\right), \tag{19}$$

where C_0 is the integration constant and ${}_1F_1(-k, 1, \varepsilon/\Theta_{\mathrm{V}})$ is a confluent hypergeometric function. At $\kappa \neq 0$, the solution (18) differs from (19), but it is physically clear that if the activation energy ε^* is much higher than the quantum energy $\varepsilon_* = \hbar\omega$, then the difference between the solutions is immaterial. We therefore assume that at $\varepsilon > \varepsilon_*$ the solution of the equation is given by (19). At $\varepsilon < \varepsilon_*$, the solution of (18) is also expressed in terms of a hypergeometric function:

$$X(\mathscr{E})=C_1\exp\left(-\frac{\mathscr{E}}{\Theta_v+\varkappa}\right){}_1F_1\left(-k,1,\frac{\mathscr{E}}{\Theta_v+\varkappa}\right). \tag{20}$$

The chemical reaction constant $\gamma = k/\tau_{\mathrm{VV}}$ is determined from the condition ${}_1F_1(-k, 1, \varepsilon^*/\Theta_{\mathrm{V}}) = 0$. Taking into account the asymptotic ($\varepsilon^*/\Theta \gg 1$) representation of the hypergeometric function

$${}_1F_1\left(-k,1,\frac{\mathscr{E}^*}{\Theta_v}\right)\sim 1-k\frac{\Theta_v}{\mathscr{E}^*}\exp\left(-\frac{\mathscr{E}^*}{\Theta_v}\right), \tag{21}$$

we obtain the following dependence of γ on the vibrational temperature Θ_{V}:

$$\gamma=\frac{1}{\tau_{vv}}\frac{\mathscr{E}^*}{\Theta_v}\exp\left(-\frac{\mathscr{E}^*}{\Theta_v}\right). \tag{22}$$

The vibrational temperature is in turn a function of the reaction constant γ and the flux density q. To find this function we equate the energy absorbed from the field

$$q\sigma_{10}\hbar\omega[X(0)-X(\hbar\omega)]$$

to the energy

$$\mathscr{E}^*\gamma\int_0^{\mathscr{E}^*}X(\mathscr{E})\,d\mathscr{E},$$

carried away by the molecules during the course of the chemical reaction:

$$q\sigma_{10}(\hbar\omega)^2\frac{\partial X(0)}{\partial\mathscr{E}}\approx\mathscr{E}^*\gamma\int_0^{\mathscr{E}^*}X(\mathscr{E})\,d\mathscr{E} \tag{23}$$

(a more rigorous energy-balance condition can be obtained directly from the kinetic equation (18)). Relation (23) contains the constants C_0 and C_1. At $\hbar\omega < \Theta_{\mathrm{V}} < \varepsilon^*$ the constant C_1, which is determined in fact by the normalization condition

$$C_0 \int_0^{\mathscr{E}^*} e^{-\mathscr{E}/\Theta_v}\, {}_1F_1\left(-k, 1, \frac{\mathscr{E}}{\Theta_v}\right) d\mathscr{E} \approx 1,$$

is approximately equal to N/Θ_V. The constant $C_1 \approx C_2$ is obtained from the continuity of the molecule flux $J(\varepsilon)$ at the point $\varepsilon = \varepsilon_*$. Relation (23) then takes the form

$$q\sigma_{10}(\hbar\omega)^2 \frac{1}{\Theta_v(\Theta_v + \varkappa)} \approx \gamma\mathscr{E}^*. \tag{24}$$

Combining (23) with (24) we obtain ultimately

$$\gamma \approx \frac{1}{\tau_{vv}} \frac{\varkappa}{\mathscr{E}^*} \left(\frac{\hbar\omega}{\mathscr{E}^*}\right)^2 \frac{(\mathscr{E}^*/\Theta_v)^2}{1 + \varkappa/\Theta_v},$$
$$\exp\left(-\frac{\mathscr{E}^*}{\Theta_v}\right) \approx \frac{\varkappa}{\mathscr{E}^*} \left(\frac{\hbar\omega}{\mathscr{E}^*}\right)^2 \frac{\mathscr{E}^*/\Theta_v}{1 + \varkappa/\Theta_v}. \tag{25}$$

As follows from (24) and (25), in weak fields ($\kappa \to 0$) the chemical-reaction constant is in fact proportional to the radiation flux density. On the other hand, in strong fields ($\kappa \to \infty$), the vibrational temperature and the reaction constant tend to a finite limit:

$$\Theta_v^\infty = \frac{\mathscr{E}^*}{2\ln(\mathscr{E}^*/\hbar\omega)}, \quad \gamma_\infty = \frac{2}{\tau_{vv}} \left(\frac{\hbar\omega}{\mathscr{E}^*}\right)^2 \ln\left(\frac{\mathscr{E}^*}{\hbar\omega}\right), \tag{26}$$

this being due to the saturation of the transition 0 → 1 in the laser field. At $\bar{\varepsilon}^* = 2$ eV and $\hbar\omega \approx 0.1$ eV we obtain from (26) $\Theta_V^\infty = 0.33$ eV and $\gamma_\infty \approx 1.5 \times 10^{-2}/\tau_{VV}$.

Thus, prior to the onset of the vibrational-translational relaxation processes, but at a noticeable defect (relative to the translational temperature) of the quantum energies of different modes and prior to establishment of the intermolecular equilibrium, the bulk of the molecules enter in the chemical reaction. The laser-radiation fluxes needed for this purpose are relatively low. Indeed, saturation of Θ_V and γ corresponds to the condition $\kappa/\Theta_V \sim 1$. This yields $q \approx 10^2$ W/cm² at $\tau_{VV} \approx 10^{-6}$ sec and $\sigma_{10} \approx 10^{-16}$ cm².

3. Excitation of molecule vibrations in a laser field with allowance for the v-v and v-t processes. We assume that the laser-pulse duration τ is comparable with or exceeds the vibrational-vibrational and vibrational-translational relaxation times. In this case the field-excited k-mode of the vibrations is cooled upon interaction with all the degrees of freedom of the molecule. This situation is nevertheless not the analog of thermal heating, since the mode selected in the field is in general not in thermal equilibrium with the nonresonant degrees of freedom of the molecule and can have a temperature Θ_V greatly exceeding the average temperature of the gas T.

Let us consider the collision integrals of the kinetic equation. Vibrational-translational relaxation corresponds to a collision integral $(\partial X_n^k/\partial t)_{vt}$, the form of which for a harmonic oscillation is

$$\left(\frac{\partial X_n^k}{\partial t}\right)_{vt} = \frac{1}{\tau_{vt}^k}\Big\{(n+1)X_{n+1}^k - \Big[(n+1)\exp\left(-\frac{\hbar\omega^k}{T}\right) + n\Big]X_n^k + nX_n^k \exp\left(-\frac{\hbar\omega^k}{T}\right)\Big\}, \tag{27}$$

where T is the translational temperature. Vibrational-vibrational exchange between the k-th and j-th modes is described by the collision integral

$$\left(\frac{\partial X_n^k}{\partial t}\right)_{vv_j}^{kj} = \frac{1}{\tau_{vv}^{kj}}\Big\{(n+1)\left(1 + \frac{\Theta^j}{\hbar\omega}\right)X_{n+1}^k - \Big[(n+1)\frac{\Theta^j}{\hbar\omega} + n\left(1 + \frac{\Theta^j}{\hbar\omega}\right)\Big]X_n^k + n\Theta_{n-1}^j\Big\}, \tag{28}$$

where Θ^j is the temperature of the j-th mode.

In order for the system to be closed, it is necessary to take into account also the interaction of the nonresonant degrees of freedom of the molecule. At a laser pulse duration τ on the order of or larger than the cross-relaxation time, this effect can be taken into account by simply ascribing a single temperature to the nonresonant degrees of freedom. Assuming this temperature to be T and changing over from the discrete approximation (27) and (28) to the diffusion approximation, we have

$$\left(\frac{\partial X^k}{\partial t}\right)_{vt} = \frac{1}{\tau_{vt}^k} \frac{\partial}{\partial\mathscr{E}} \mathscr{E}\left(X^k + T\frac{\partial X^k}{\partial\mathscr{E}}\right),$$
$$\left(\frac{\partial X^k}{\partial t}\right)_{vv}^{kj} = \frac{1}{\tau_{vv}^{kj}} \frac{\partial}{\partial\mathscr{E}} \mathscr{E}\left(X^k + T\frac{\partial X^k}{\partial\mathscr{E}}\right). \tag{29}$$

When (29) is taken into account, the equation for $X^k(t, \varepsilon) = X(t, \varepsilon)$ takes the form

$$\frac{\partial X}{\partial t} = \frac{1}{\tau_{vv}} \frac{\partial}{\partial\mathscr{E}} \mathscr{E}\left(X + \Theta\frac{\partial X}{\partial\mathscr{E}}\right) + \frac{1}{\tau^0} \frac{\partial}{\partial\mathscr{E}}\left(X + T\frac{\partial X}{\partial\mathscr{E}}\right) + q\sigma_{10}\nu(\mathscr{E} - \mathscr{E}_*)\frac{\partial}{\partial\mathscr{E}}\mathscr{E}\frac{\partial X}{\partial\mathscr{E}}, \tag{30}$$

where we have introduced the cross-relaxation time τ^0 defined by the relation

$$\frac{1}{\tau^0} = \frac{1}{\tau_{vt}} + \sum_{j \neq k} \frac{1}{\tau_{vv}^{kj}}. \tag{31}$$

For $X = X(\varepsilon)e^{-\gamma t}$, the solution of (30) is

$$X(\mathscr{E}) = \begin{cases} C_0 \exp\left(-\dfrac{\mathscr{E}}{\Theta} \dfrac{1+\beta}{1 + \beta T/\Theta_v + \varkappa/\Theta_v}\right) \times {}_1F_1\left[\dfrac{k}{1+\beta}, 1, \dfrac{\mathscr{E}}{\Theta_v}\left(\dfrac{1+\beta}{1 + \beta T/\Theta_v + \varkappa/\Theta_v}\right)\right], & \mathscr{E} < \hbar\omega, \\ C_1 \exp\left(-\dfrac{\mathscr{E}}{\Theta} \dfrac{1+\beta}{1 + \beta T/\Theta_v}\right) {}_1F_1\left[\dfrac{k}{1+\beta}, 1, \dfrac{\mathscr{E}}{\Theta_v}\left(\dfrac{1+\beta}{1 + \beta T/\Theta_v}\right)\right], & \mathscr{E} > \hbar\omega, \end{cases} \tag{32}$$

where $\beta = \tau_{VV}^{kk}/\tau^0$. From this we easily obtain the following relations for the vibrational temperature Θ_V of the resonant mode and for the reaction rate γ:

$$\gamma \approx \frac{1}{\tau_{vv}^{kk}} \frac{\mathscr{E}}{\Theta_v} \frac{(1+\beta)^2}{1 + \beta T/\Theta_v} \exp\left(-\frac{\mathscr{E}^*}{\Theta_v} \frac{1+\beta}{1 + \beta T/\Theta_v}\right), \tag{33}$$

$$\frac{\varkappa}{\Theta_v}\left(\frac{\hbar\omega}{\Theta_v}\right)^2 \frac{(1+\beta)^2}{(1 + \beta T/\Theta_v)(1 + \beta T/\Theta_v + \varkappa/\Theta_v)} \approx \beta\left(\frac{1 + \beta T/\Theta_v}{1+\beta} - \frac{T}{\Theta_v}\right) + \gamma\tau_{vv}\frac{\mathscr{E}^*}{\Theta_v}. \tag{34}$$

We consider particular cases of (33) and (34). At $\kappa = 0$ (no laser field), neglecting in (34) the energy lost to the chemical reaction, we obtain $\Theta_V = T$. Expression (33) then assumes a form typical of the chemical-reaction constant in thermal heating of the system:

$$\gamma = \frac{1}{\tau} \frac{\mathscr{E}^*}{T} \exp\left(-\frac{\mathscr{E}^*}{T}\right), \quad \frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{vv}}. \tag{35}$$

At $\kappa \neq 0$, but in the absence of the jk vibrational exchange and vibrational-translational relaxation ($\beta = 0$), we obtain from (33) and (34) formulas (25) and (24) directly.

Finally, if the v-v and v-t processes are taken into account, when the main energy loss of the resonant mode is due to thermal heating of the gas, it follows from (33) and (34) that

$$\gamma \approx \frac{1}{\tau_{vv}} \frac{\mathscr{E}^*}{\Theta_v} \exp\left(-\frac{\mathscr{E}^*}{\Theta_v}\right), \tag{36}$$

$$\frac{\varkappa}{\Theta_v}\left(\frac{\hbar\omega}{\Theta_v}\right)^2 \frac{\Theta}{\Theta + \varkappa} = \frac{\tau_{vv}}{\tau^0}. \tag{37}$$

According to (37), the vibrational temperature in low laser-radiation fluxes q varies like $q^{1/3}$. At large q, owing to the saturation of the resonant transition, the temperature tends to a finite limit[3)]:

$$\Theta_v^\infty = \hbar\omega(\tau^0/\tau_{vv})^{1/3}, \tag{38}$$

which amounts, for example, to ~10,000° K for $\tau^0/\tau_{VV} \approx 10^2$ and $\hbar\omega \approx 0.1$ eV. To attain the limiting temperatures Θ_V^∞ and velocities γ_∞ of the reaction it is necessary to have relatively low ($\lesssim 10^2$ W/cm²) radiation intensities.

The cross-relaxation processes connected with the transfer of energy to the nonresonant degrees of freedom is obviously harmful. If, however, the radiation pulse duration τ is of the order of the cross-relaxation time τ^0, then the energy loss still remains relatively small, and the energy absorbed from the field is distributed approximately equally among the excited oscillation mode and the remaining degrees of freedom. The change of the average temperature T, especially in the case of a polyatomic molecule, should therefore be negligible in comparison with Θ_V.

4. Excitations of molecule vibrations in generation of stimulated Raman scattering. A number of most important molecules (for example N_2 or O_2) have no proper dipole moment, so that their direct excitation in an optical field may turn out to be ineffective. At the same time, these molecules are active in the generation of Raman scattering. It is known that the probability of Raman scattering is noticeable only if $\Omega = \omega_S + \omega$, where Ω, ω_S, and ω are respectively the frequencies of the absorbed and scattered photons and the frequency of the molecule vibrations. This condition expresses the law of energy conservation in each elementary scattering act, namely, a photon of energy $\hbar\omega$ is absorbed from the external field, a photon $\hbar\omega_S$ of Stokes frequency is simultaneously emitted, and the molecule vibration energy increases by an amount $\hbar\omega$. By the same token, the vibrational mode of the molecule with natural frequency $\omega = \Omega - \omega_S$ is selectively heated in the Raman-scattering process.

The transition frequency $S_{k,k+1}$ of the molecule between levels k and k + 1 in a field

$$E = E_\Omega \cos\Omega t + E_s \cos\omega_s t \tag{39}$$

is given by

$$S_{k,k+1} = kS_{10}, \qquad S_{10} = \frac{6\pi T_2 c^2}{\hbar^2\omega_s^2} q_\Omega q_s Q_0. \tag{40}$$

Here E_Ω, E_S, q_Ω, and q_S are the field intensities and the flux densities of the fundamental and Stokes emissions, c is the speed of light, Q_0 is the total Raman-scattering cross section, and T_2 is the characteristic relaxation time of the excited mode.

When (40) is taken into account, the field term of the kinetic equation takes the form

$$\left(\frac{\partial X}{\partial t}\right)_q = (S_{10}\hbar\omega)\frac{\partial}{\partial\mathscr{E}}\mathscr{E}\frac{\partial X}{\partial\mathscr{E}} \tag{41}$$

and does not differ in form from the field term of the dipole molecule (see (9)). It is therefore possible, by making the substitution $q\sigma_{10} \rightarrow S_{10}\hbar\omega$, to go over directly from the formulas describing the heating of a dipole molecule to formulas describing the heating of a molecule in Stokes scattering of a laser field.

We note that direct generation of the Stokes component in the gas to be excited is apparently not very effective. More interesting, in our opinion, is the case of gas heating in specified fields E_Ω and E_S at relatively low pressure ($p \lesssim 1$ atm), when the relaxation rate $1/T_2$ is small. The fields E_S and E_Ω can be obtained, for example, by passing the fundamental-frequency radiation of molecules of the same sort as the excited molecules through dense gases or liquids.

We present numerical estimates. We consider a case when the field (39) excites transitions only between the ground and first levels of the molecule, and the population of the higher levels is governed by vibrational-vibrational exchange processes. According to (25) and (24), at $\Theta_V/S_{10}\hbar\omega\tau_{VV} \sim 1$ the reaction rate constant γ and the vibrational temperature are close to their limiting values $\gamma = \gamma_\infty$ and $\Theta_V = \Theta_V^\infty$. From this we find in the case $\Theta_V^\infty \approx 10\hbar\omega$ and $\tau_{VV} \approx 10^{-7}$ sec that $S_{10} \approx 10^8$ sec⁻¹. Assuming further that $\hbar\omega \approx 1$ eV, $q_\Omega = q_S = q$, and $T_2 \approx 10^{-9}$ sec we find that the flux needed to saturate γ and Θ is $q \approx 10$ MW/cm². At a laser pulse duration ~ 10^{-6} sec, an appreciable fraction of the molecules can enter into the chemical reaction.

3. EXPERIMENTAL DETERMINATION OF THE PHOTOCHEMICAL ACTION OF LASER RADIATION

We have investigated the reactions listed in the table under the influence of IR emission of a CO_2 laser in different mixtures. We shall discuss in greater detail the reactions of N_2F_4 and SF_6 with NO, in which sulfur tetrafluorohydrazine (with valent vibration frequencies 934 cm⁻¹ and 946–959 cm⁻¹) and sulfur hexafluoride (deformation molecule vibration frequency 943 cm⁻¹) ab-

Laser-chemical reactions in IR radiation, exposure duration 0.5 sec [9]

No.	Reagents	Partial characteristics	Intensity, W	Number of irradiations	Reaction products % by volume	Reaction-product pressure, Torr
1	N_2F_4 NO	100 100	20 ne	$n = 1$	FNO — 34, NF_3 — 21, N_2 — 24, F_2 — 20	212
1a	N_2F_4 NO	100 100	40, e	$n = 1$	FNO — 28, NF_3 — 3, N_2 — 24, F_2 — 46	262
2	N_2F_4 NO N_2	100 200 460	70, e	$n = 1$	NO_2, N_2O, N_2	—
3	N_2F_4 NO_4 CF_4	100 100 200	20, ne	$n = 1$	NF_3, NO, CO_2 — 10, N_2	—
4	N_2F_4 N_2O	300 150	40, se	$n = 3$	NO_2 — 49, NF_3 — 38 N_2O — 5, FNO_3, N_2	512
5	N_2F_4 H_2	50 100	50, e	$n = 1$	N_2, HF	—
6	N_2F_4 CH_4	228 114	50, e	$n = 1$	CF_4 — 22, HF, N_2	534
6a	N_2F_4 CH_4	150 150	40	$n = 1$	CF_4 — 23, C	393
7	N_2F_4 BCl_3	114 114	50, e at $n = 1$	$n = 3$	BF_3, flourides of chlorine	289
8	SiH_4	228	50, e at $n = 1,2$	$n = 3$	H_2 — 34, Si	284
9	SiH_4 BCl_3	112 112	40, e at $n = 1, 2, 3$	$n = 3$	$BHCl_2$, SiH_3Cl	234
9a	SiH_4 BCl_3	300 100	40	$n = 5$	B_2H_6, $BHCl_2$, $SiCl_4$ $SiHCl_3$, $SiCl_3H$, SiH_2Cl_2	431
10	SiH_4 SF_6	300 150	40, e	$n = 1$	SiF_4 — 20, H_2s — 70	698
11	HNF_2	200	40, e	$n = 1$	HF, N_2, F_2	—
12	HNF_2 CH_4	250 100	40, e	$n = 1$	CF_4, C_2F_6, HF, N_2	250
13	HNF_2 SiH_4	250 100	40, e	$n = 1$	SiF_4 — 17, H_2 — 47 N_2, HF	460
14	HNF_2 H_2	100 30	40, e	$n = 1$	N_2, HF	110

Note. The symbols in the "Intensity" column are: ne—no emission, e—emission present, se—stron emission.

sorb resonantly. In the absence of emission, the transformations in the mixture of N_2F_4 and NO begin at temperatures above 600° K (when heated for ~5 minutes); the N_2F_4 does not react in this case with the NO, but decomposes to produce nitrogen trifluoride. No reaction occurs in a mixture of SF_6 with NO heated for a short time to 1000° K.

The behavior of both systems when irradiated depends on the radiation power. Below an intensity of approximately 20 W, at short-duration exposures, no reaction takes place in the system. At an intensity higher than 20 W and exposures shorter than 0.1 sec, instantaneous reactions accompanied by emission of light occur. The reaction products in the system N_2F_4 + NO are FNO, F_2, NF_3 and NO, and their percentages in the mixture depend on the experimental conditions[9]. The conversion of N_2F_4 and NO reaches 100%. In the system SF_6 + NO, thionyl fluoride (SF_2O) is produced.

Calculation shows that if the absorbed laser energy were to be consumed in heating the reacting systems, the temperatures in the SF_6 + NO and SF_4 + NO mixtures would reach 1000° K and 500° K, respectively. At such temperatures and times, which are larger by 2–3 orders of magnitude than the exposures to the light, no thermal reactions are produced in either system.

It has also been shown for the N_2F_4 + NO system[1,9] that the tetrafluorohydrazine does not react in this case if there is no nitrogen oxide in the irradiated system or if its concentration is low. The process begins only at commensurate contents of N_2F_4 and NO. This indicates that no prior dissociation of the tetrafluorohydrazine occurs in the reaction under the given conditions. This does not mean that the tetrafluorohydrazine cannot be dissociated at all by IR radiation. One can expect dissociation to set in when the power is raised above 100 W.

It is important that the products produced in the reactions of N_2F_4 with NO or of N_2F_4 with N_2O or in many other reactions differ from those produced in thermal activation of the process. Thus, decomposition of N_2F_4 in accordance with the reaction $3N_2F_4 = 4NF_3 + N_2$ predominates in both processes, and the nitrogen oxide and nitrous oxide do not react with the N_2F_4. In the laser-chemical reactions, the properties of N_2F_4 are altered. The production of FNO in the reaction $N_2F_4 + 4NO \rightarrow 4FNO + N_2$ points to the acquisition of a fluoriding ability by the N_2F_4, i.e., to activation of the B-F bond, the valent vibration of which is at resonance with the IR frequency and is chemically inactive in the unexcited molecule.

It can be concluded that the IR emission initiates chemical reactions of vibrationally-excited molecules. The reactions are as a rule exothermal and are ultrafast.

Thus, the resonant action of coherent emission makes it possible to heat the vibrational degrees of freedom of a molecule to high temperatures, to control the course of a chemical reaction, to decrease the energy loss, and to obtain products not obtained by thermal heating of the reagents.

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[1] The principal results of the paper were reported at the Ispahan (Iran) symposium on quantum electronics, 1971.

[2] If we disregard the dependence of σ_{10} on p.

[3] A similar formula can be obtained on the basis of the results of [7] for the Q-branch transitions.

[1] N. G. Basov, E. P. Markin, A. N. Oraevskiĭ, and A. V. Pankratov, Dokl. Akad. Nauk SSSR **198**, 1043 (1971) [Sov. Phys.-Dokl. **16**, 445 (1971)].

[2] A. N. Oraevskii and V. A. Savva, Kratkie soobshcheniya po fizike (Brief Communications on Physics), FIAN 7, 50, 1970.

[3] S. W. Mayer, M. A. Kwook, B. W. F. Cross and P. T. Spenser, Appl. Phys. Lett. **17**, 516, 1970.

[4] Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniĭ (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena), Fizmatgiz, 1966.

[5] E. V. Stupochenko and A. I. Osipov, Zh. Fiz. Khim. **32**, 1673 (1958).

[6] N. V. Karlov et al., ZhETF Pis. Red. **11**, 220 (1970) [JETP Lett. **11**, 135 (1970)].

[7] N. D. Artamonov, V. G. Platonenko, and R. V. Khokhlov, Zh. Eksp. Teor. Fiz. **58**, 2195 (1970) [Sov. Phys.-JETP **31**, 1185 (1970).

[8] Yu. V. Afanas'ev, E. M. Belanov, E. P. Markin, and I. A. Poluektov, ZhETF Pis. Red. **13**, 462 (1971) [JETP Lett. **13**, 331 (1971)].

[9] N. G. Basov, E. P. Markin, A. N. Oraevskiĭ, A. V. Pankratov, and A. N. Skachkov, ZhETF Pis. Red. **14**, 251 (1971) [JETP Lett. **14**, 165 (1971)].

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