Vibrational relaxation and lasers based on intramolecular vibrational transitions in liquids and in molecular crystals

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(Submitted January 3, 1975)
Zh. Eksp. Teor. Fiz. 69, 467–476 (August 1975)

We consider the singularities of vibrational relaxation in liquids and molecular crystals. We discuss the role of collective interactions. We estimate the characteristic times of the vibrational processes. On this basis, we analyze the possibility of obtaining inverted population and amplification of radiation via interamolecular vibrational transitions in liquids and in molecular crystals. It is shown that intense electron beams can be used to develop effective lasers. The possibilities are considered of using a liquid medium in laser chemistry, when the chemical reactions at low translational temperature are initiated by high-power infrared radiation.

PACS numbers: 82.40.Tc, 42.60.Eb, 32.20.Pc

Much attention has been paid recently to the development of high-power gas lasers on vibration-rotation transitions of molecules with large (~1–20 atm) pressure of the working gas.[1,2] An important advantage of such systems is the feasibility, in principle, of obtaining large concentrations of active molecules by simultaneously increasing the gas pressure and the pump intensity. It is clear that from this point of view liquids and molecular crystals offer promise as active laser media.

Compared with gases of moderate density (~20 atm at 300°K), liquids and molecular gases of a number of obvious advantages: they have much higher (by approximately two orders of magnitude) density and at the same time require no special containment means. In addition, the widths of their vibrational bands remain essentially the same as in gases of moderate density ($\Delta\nu \sim$ 5 to 20 cm^{-1}, which is of no little importance when it comes to considering the question of amplifying the radiation. For molecular crystals, compared with ultradense gases and liquids, an important advantage is also (as will be shown by the subsequent exposition) the slowing down of the rate of vibration-translation relaxation, which greatly facilitates the attainment of the necessary population inversion and gain.

Besides the problem of developing liquid lasers, there is undisputed interest in the stimulation of chemical reactions that occur in liquids via selective buildup of the oscillations by infrared laser radiation. This type of research was restricted heretofore to the gas phase.[3-7]

It is clear, however, that to consider the possibilities of using liquids in laser chemistry, and also liquids and molecular crystals for the development of IR lasers operating on vibrational transitions of molecules, it is necessary to analyze the vibrational kinetics in these media and primarily to estimate the characteristic times for the vibration-translation and vibration-vibration energy exchange (VT and VV processes). The difficulties of the investigation are connected here with the need for taking into account the collective interactions. Owing to the important role of these interactions, the vibrational relaxation in liquids, and particularly in molecular crystals, can differ substantially from relaxation in a gas.

To describe the collective effects, following[8,9], we consider the interaction of a molecule with $\tilde{N}$ partner molecules, located on the surface of a spherical cell of radius a, and will describe the action on a molecule situated at the center of the cell by a sum of Lennard-Jones potentials. If the molecule is deflected by a distance $R \ll a$, then after expanding the summary interaction potential V in powers of R/a we have

$$V=\sum_{i=0} A_i (R/a)^i, \quad i=0, 2, 4, \ldots, \tag{1}$$

where the expansion coefficients A_i are

$$A_i=\varepsilon\tilde{N}\frac{1}{\beta^2}\frac{2}{5}\frac{(i+10)!}{9!(i+1)!}\left[1-\frac{5\cdot 9!(i+4)!}{2\cdot 3!(i+10)!}\beta\right], \tag{2}$$
$$a^3=M\tilde{N}/4\pi\rho, \quad \beta=(a/r_0)^6.$$

Here ϵ and r_0 are the constants in the Lennard-Jones potential for a substance with an individual-molecule mass M and density ρ. Following[8], we shall henceforth put $\tilde{N}$ = 12.

In expression (1), the term with i = 0 determines the binding energy. In first-order approximation (i = 2) the molecule executes harmonic oscillations about the center of the cell, with frequency $\nu = \nu_D/\sqrt{2}$, where ν_D is the Debye frequency:

$$\nu_D[\mathrm{sec}^{-1}]=\frac{10.4}{a\beta}\sqrt{\frac{\varepsilon}{M}\left(1-\frac{5}{22}\beta\right)}. \tag{3}$$

The next anharmonic terms ($i \geq 4$) in (1) describe the interaction of the intermolecular vibrations with the intramolecular ones. We calculated for this interaction, in general form, the probabilities of the intramolecular vibrational transitions in a polyatomic molecule. We consider the transition of one quantum of a vibrational mode with frequency ν_1 into m quanta of another mode of frequency ν_2 with participation of n phonons. Recognizing that $R = R_c + b_1x_1 + b_2x_2$, where R_c is the coordinate of the mass center of the molecule while x_1, x_2 and b_1, b_2 are the intramolecular coordinates and direction cosines, we represent (1) in the form of a series in powers of R_c, x_1, and x_2. For simplicity in the calculation of the matrix elements we shall use the wave functions of harmonic oscillators (for both the intramolecular and intermolecular vibrations). In this case, from among the anharmonic terms in (1), the term responsible for the transition in question is

$$\frac{(m+n+1)!}{m!n!}\frac{A_{m+n+1}}{a^{m+n+1}}R_c{}^n b_1x_1(b_2x_2)^m.$$

Then, using ordinary perturbation theory, we get

$$q_{10}^{0m}(v_1\to v_1\pm1;\ v_2\to v_2\pm1;\ldots v_n\to v_n\pm1)$$

$$=\frac{4\pi^2}{h^2}\left[\frac{(m+n+1)!\,b_1b_2{}^mA_{m+n+1}}{m!\,n!\,a^{m+n+1}}\right]^2|\langle1|x_1|0\rangle|^2|\langle0|x_2{}^m|1\rangle|^2 \tag{4}$$

$$\times|\langle v_1|R_{c1}|v\pm1\rangle|^2\cdot\ldots\cdot|\langle v_n|R_{cn}|v_n\pm1\rangle|^2\delta\left[m\nu_2-\nu_1+\sum_{j=1}^{n}\nu_i{}^{\Phi}(v_j\pm1-v_j)\right].$$

Expression (4) is the probability that the transition 1 → 0 and 0 → m will take place in the molecule in the intramolecular modes ν_1 and ν_2, and that the transitions $v_j \to v_j \pm 1$ will take place among n phonons. To obtain the total probability Q_{10}^{0m} of the intramolecular transition with participation of n phonons it is necessary to sum (4) over all the possible transitions $v_j \to v_j \pm 1$ with allowance for the Boltzmann distribution of the phonons over the vibrational levels v (with a temperature equal to the temperature T of the medium) and to integrate over the entire spectrum of the phonon frequencies from 0 to ν_D. These operations can be carried out for the case of high temperatures ($kT > h\nu_D$) and for a Debye frequency distribution function $D(\nu) = 3\nu^2/\nu_D^3$. Using the explicit form of the matrix elements, we obtain ultimately for the probability Q_{10}^{0m} of the process occurring in the exothermal direction ($\nu_1 - m\nu_2 > 0$)

$$Q_{10}{}^{0m}[\mathrm{sec}^{-1}]=\left[\frac{(m+n+1)!\,A_{m+n+1}}{m!\,n!\,h\nu_D}\right]^2\frac{hb_1{}^2}{2M_1\nu_1a^2}$$

$$\times\left[\frac{3kT}{8\pi^2M\nu_D{}^2a^2}\right]^n\left[\frac{hb_2{}^2}{8\pi^2M_2\nu_2a^2}\right]^m\left[n-\frac{\nu_1-m\nu_2}{\nu_D}\right]^{n-1}\frac{\nu_D}{(n-1)!\,m!}. \tag{5}$$

Here M_1 and M_2 are the masses of the oscillators for the normal modes ν_1 and ν_2. The number n of the phonons participating in the vibrational transition is an integer in the interval

$$(\nu_1-m\nu_2)/\nu_2<n\leqslant(\nu_1-m\nu_2)/\nu_2+2 \tag{6}$$

which satisfies the condition that $n + m + 1 = i$ be an even number. The probability Q_{01}^{m0} of the inverse process is determined from the detailed balancing principle: $Q_{01}^{m0} = Q_{10}^{0m}\exp\{-(h\nu_1 - mh\nu_2)/kT\}$.

Expression (5) is quite general and can describe, besides the VV′ process, also other relaxation channels. Thus, at $m = 1$, $\nu_1 = \nu_2$, $M_1 = M_2$, and $b_1^2 = b_2^2 = 1/3$ we obtain from (5), taking (2) and (6) into account, an expression for the probability of the resonant VV process

$$Q_{10}{}^{01}[\mathrm{sec}^{-1}]=2.1\cdot10^{-4}\left(\frac{M\nu_D}{M_1\nu_1}\right)^2\left(\frac{kT}{\varepsilon}\right)^2\frac{(1-\beta/14{,}3)^2}{(1-\beta/4{,}4)^4}\beta^4\nu_D. \tag{7}$$

In analogy with (7), we can easily write down expressions also for the probabilities of single-quantum exchange (both resonant and nonresonant) between highly-excited states. Such probabilities for an anharmonic oscillator were calculated by a somewhat different method by Ovchinnikov.[10] At m = 0, expression (5) represents the probability P_{10} of the VT transition 1 → 0 with participation of n phonons:

$$P_{10}[\mathrm{sec}^{-1}]=\frac{(n+1)^2}{(n-1)!}\left(\frac{A_{n+1}}{h\nu_D}\right)^2\frac{h}{6M_1\nu_1a^2}\left(\frac{3kT}{8\pi^2M\nu_D{}^2a^2}\right)^n\left(n-\frac{\nu_1}{\nu_D}\right)^{n-1}\nu_D. \tag{8}$$

In the particular case n = 3, the quantity P_{10} was calculated in[8], where, however, an inaccurate integration was carried out over the phonon spectrum, so that the result was an incorrect dependence of P_{10} on ν_1 and ν_D.

Since in a liquid there is also disordered motion of the particles besides the collective motion, the vibrational relaxation can be strongly influenced also by ordinary binary collisions that cause this random motion. To assess the contribution of the binary collisions to the probability of the vibrational transitions, one can use in the estimate of these probabilities the usual Herzfeld-Schwartz-Slavsky procedure. Table I lists for several liquids the probabilities P_{10} and Q_{10} calculated from expressions (7) and (8) (P_{10}^{coll} and Q_{10}^{coll}), and from the Herzfeld-Schwartz-Slavsky formulas P_{10}^{bin} and Q_{10}^{bin} (see, e.g.,[9,11]). The calculation was carried out for a normal vibration with the lowest frequency for the given molecule, inasmuch as usually it is precisely this normal vibration which determines on the whole the character of the VT processes.

Table I lists also the experimental values P_{10}^{exp} taken from[9,12]. It is seen that at room temperatures the experimental probabilities P_{10}^{exp} agree better with the theoretical ones calculated under the assumption of binary collisions. The conclusion that the dominant role is played by binary collisions for VT processes in weakly-associated liquids was drawn earlier.[9,12]. It is clear, however, that owing to the different dependences of P_{10}^{coll} and P_{10}^{bin} on the frequency ν_1 of the intramolecular vibrations and on the temperature T, this conclusion cannot be generalized to include a wide range of temperatures and all the liquids. With decreasing T and at low frequencies $\nu_1 < 3\nu_D$ the principal role for VT process can be played by collective effects, when the decay of the intramolecular vibration is only into three phonons.

An important conclusion of the calculations of the times of the vibrational relaxation is also the fact that in liquids, just as in single-component molecular gases, the VT and VV processes occur with different times, and $\tau_{VV} \sim 1/Q_{10} \ll \tau_{VT} \sim 1/P_{10}$. This makes it possible to apply certain results of vibrational kinetics in a gas to a liquid, and in particular, to characterize the degree of excitation of various types of intramolecular vibrations in a liquid by vibrational temperatures, for owing to the smallness τ_{VV} there will be established within each vibrational mode a quasistationary distribution (a Boltzmann distribution for the harmonic model).

Besides the VT and VV processes, an important role can be played for vibrational modes of a polyatomic molecule also by VV′ processes, i.e., exchange of energy between different modes. In many cases (this is confirmed by calculation with even only binary collisions taken into account, as well as by experiments[13]), the times of these processes are shorter for liquids than the vibration-translation relaxation times of the mode

TABLE I

Liquid	T, K	$\nu\cdot10^{-12}$, sec^{-1}	$\nu_D\cdot10^{-12}$ sec^{-1}	n	P_{10}^{coll}, sec^{-1}	P_{10}^{bin}, sec^{-1}	$P_{10}^{\mathrm{exp}}\cdot10^{-9}$, sec^{-1}	$Q_{10}^{\mathrm{bin}}\cdot10^{-10}$, sec^{-1}	$Q_{10}^{\mathrm{coll}}\cdot10^{-9}$, sec^{-1}	$Z^{\mathrm{bin}}\cdot10^{-11}$, sec^{-1}
C_6H_6	303	12	4.10	3	$1.8\cdot10^6$	$6\cdot10^8$	3.7	4	1.6	60
CS_2	298	11.9	3.71	5	$1.3\cdot10^4$	10^9	0.4	6	2.8	10
CCl_4	293	6.51	2.90	3	$2.2\cdot10^8$	$2\cdot10^9$	8.4	4	1.3	4
C_4H_4O	276	16.5	4.94	5	494	$3.4\cdot10^7$	0.7	2.3	0.8	7
$CHCl_3$	300	3.3	3.15	3	$5.3\cdot10^9$	$2\cdot10^{11}$	6.6	30	11	5
CH_2Cl_2	300	8.55	5.60	3	$5.2\cdot10^8$	$6\cdot10^9$	1.5	9	2.3	8

Notes: 1) n is the number of phonons participating in the VT process; 2) in the calculation of P_{10}^{bin} and Q_{10}^{bin} we assumed the value $\alpha = 5$ Å^{-1} for the parameter of the potential of the intermolecular interaction $\sim\exp(-\alpha r)$; 3) the frequencies of the binary collisions Z^{bin} were calculated by linear interpolation into the region of large particle densities (corresponding to liquids) of the values of these frequencies for gases.

with the lowest frequency, and the relaxation of the vibrational energy of the molecules is characterized by only one time of the VT process, which is usually measured in experiment for liquids by an acoustic method.[12] To use liquids as active media for lasers operating on vibrational transitions, however, a more favorable (although not obligatory) situation is one in which the relaxation of the energy from some vibrational mode (or group of modes) is slower than from other modes, and consequently the relaxation of the vibrational energy on the whole is characterized not by one but by several times. The presence of several times of vibrational relaxation in a number of liquids is evidenced by experiments performed by acoustic methods.[12,14]

All the foregoing results, and in particular formulas (1)—(18), concerning the influence of collective interactions on the vibrational relaxation in liquids, pertain equally well to molecular crystals. The decisive role for the latter is played in the vibrational relaxation by the collective interactions, while the binary interactions are inessential. By way of illustration, Table II gives the probabilities of certain vibrational processes, calculated from formulas (2)—(8) at $T = 170^\circ K$ for the molecular crystal CO_2. An important conclusion of the analysis of (5) and (8) and of the concrete calculations is the fact that the VT processes in molecular crystals can be much slower than in liquids and in compressed gases, especially if the crystal temperature is low and the lowest of the frequencies of the intramolecular vibrations greatly exceeds the Debye frequency ν_D, so that the VT relaxation takes place with participation of a large number of phonons.

We turn now to consideration of the possibility of using a liquid as an active medium for a laser operating on vibrational transitions. Of great importance here is the choice of a pumping method that would make it possible to excite oscillations in a relatively large volume of matter to obtain the gains needed for lasing. We shall show that these conditions can be realized by using contemporary high-power electron beams.

The depth of penetration δ (cm) of an electron beam into a substance can be estimated from Feather's well known formula[15]

$$\delta=(0.546E_e-0.16)/\rho,$$

where E_e is the energy of the electron in the beam (in MeV), and ρ is the density of the liquid in g/cm^3. At $E_e \approx 2$ MeV and $\rho \approx 0.9\ g/cm^3$ the value of δ is ~ 1 cm, and consequently when beams with transverse dimensions $\sim 1 \times 10$ cm are used, their energy can be pumped into an appreciable volume of liquid.

It is known that the beam energy is lost mainly to ionization. One act of ionization usually consumes an energy $E_i \approx 30$ eV. Nonetheless, it is possible also to excite effectively molecule vibrations. Indeed, there are at least two channels through which the energy can be converted into vibrational degrees of freedom: 1) direct excitation of the vibrations by secondary ionization electrons having an initial energy $E_i/2 \approx 15$ eV; 2) pumping via recombination processes. The efficiency of the first pumping channel is determined by the ratio of the cross sections for the excitation of the oscillations by the electrons to the cross sections of the remaining processes in the secondary-electron energy region from 15 eV down.

TABLE II

	T (K)	$Q_{10}(1)$, sec^{-1}	$Q_{10}(2)$, sec^{-1}	$Q_{10}(3)$, sec^{-1}	$P_{10}(2)$, sec^{-1}	$Q'(3 \longrightarrow 1,2)$, sec^{-1}	$Q'(1 \longrightarrow 2)$, sec^{-1}
Molecular crystal	170	$2.8 \cdot 10^8$	$1.1 \cdot 10^9$	$9.6 \cdot 10^7$	12	$1.1 \cdot 10^8$	$2.0 \cdot 10^7$
Gas (p = 1 atm)	300				$8.5 \cdot 10^4$	$2.9 \cdot 10^5$	

Note. $Q_{10}(1)$, $Q_{10}(2)$, $Q_{10}(3)$, and $P_{10}(2)$ are the probabilities of the VV and VT processes respectively in the symmetrical, deformation, and asymmetrical modes; $Q'(3 \rightarrow 1, 2)$ is the probability of the VV' transition of a lower quantum of an asymmetric mode into lower quanta of a symmetric and deformation mode. $Q'(1 \rightarrow 2)$ is the probability of a VV' transition of a lower quantum of a symmetric mode into two lower quanta of a deformation mode.

The second pumping mechanism is effected in the following manner. After a certain cooling of the secondary electrons, electron-ion dissociative recombination sets in. The neutral particles produced as a result of this reaction then recombine and form molecules at high vibrational levels, thereby ensuring pumping of energy into the vibrational degrees of freedom. The use of the chemical reaction of atom recombination to produce lasers operating on vibrational transitions in molecular gases was discussed in[16,17].

Let us examine the possibility of using high-power electron beams to pump a liquid laser on vibrational transitions, using as a concrete example a beam with the following parameters: current density $j \approx 500$ A/cm^2, electron energy in the beam $E_e \approx 2$ MeV, beam pulse duration $\tau_{beam} \approx 5 \times 10^{-8}$ sec. These are perfectly feasible parameters[18] and correspond to a beam power $19^9\ W/cm^2$ and to an energy $\sim 55\ J/cm^2$. The chosen liquid is carbonyl sulfide COS at a temperature 150°K (density $\rho = 1.24\ g/cm^3$, molecular weight $M = 60$ at. un., molecule concentration $N_{liq} = 1.24 \times 10^{22}\ cm^{-3}$). A calculation based on binary collisions yields for this liquid a relaxation time $\tau \approx 2 \times 10^{-8}$ sec of two modes with frequencies $\nu_1 = 862\ cm^{-1}$ and $\nu_2 = 516\ cm^{-1}$, while the mode with frequency $\nu_3 = 2050\ cm^{-1}$ has $\tau \approx 2 \times 10^{-7}$ sec.[10]

Let us estimate now the vibrational-level inverted population that can be expected by pumping the oscillations with an electron beam. We consider first the recombination pumping mechanism. The cooling time τ_{cool} of the secondary electrons from an energy $\sim E_i/2 \approx 15$ eV to thermal energies is short and at the typical cross section $\sigma_i \approx 10^{-17}\ cm^2$ of inelastic scattering by molecules it amounts to $\tau_{cool} \approx 1/\langle \sigma v \rangle N_{liq} \ll \tau_{beam}$. The time dependence of the volume concentration N_e of these cooled electrons is approximately described by the equation $dN_c/dt = J - k_r N_e^2$ and is equal to

$$N_e(t)=\left(\frac{J}{k_r}\right)^{1/2}\frac{1-\exp\{-2(k_rJ)^{1/2}t\}}{1+\exp\{-2(k_rJ)^{1/2}t\}}, \tag{9}$$

where k_r is the dissociative recombination rate constant, J is the volume rate of ionization by the electron beam:

$$J \approx \frac{E_e}{E_i}\frac{j}{e\delta}, \tag{10}$$

and e is the electron charge. For the electron-beam and liquid parameters indicated above we have $\delta \approx 0.75$ cm, $J \approx 2.6 \times 10^{26}\ cm^{-3}\ sec^{-1}$. At these ionization rates and at the typical value $k_r \approx 10^{-7}\ cm^3/sec$, the quasistationary value is $N_e = \sqrt{J/k_r} = 5 \times 10^{16}\ cm^{-3}$, and the time of establishment of the quasistationary regime is $\tau_{est} \sim 1/2\sqrt{k_r J} \approx 10^{-10}$ sec. Since $\tau_{est} \ll \tau_{beam}$ in our example, it can be assumed that during the entire time of bombardment of the liquid by the fast beam electrons the recombination flux $k_rN_e^2$, which ensures in final analysis the energy pumping into the vibrational degrees of freedom, is equal to the volume ionization rate J. The total recombination energy flux is consequently $E_iJ/2$, but it is clear that only a fraction η of this flux enters in the vibrational degrees of freedom. If the molecules are produced upon recombination on vibrational levels close to the dissociation limit with energy D_e, then $\eta_{max} \approx 2D_e/E_i$ can be of the order of unity. In the estimates that follow we shall use the value $\eta \approx 0.2$, assuming thus that only 20% of the recombination energy flux (or 10% of the total flux E_iJ) goes to the vibrational degrees of freedom.

Upon direct excitation of the vibrations by the secondary electrons in the quasistationary regime, it can also be assumed that the rate of energy pumping into the oscillations is $\eta E_iJ/2$, where η is determined by the ratio of the cross section for the excitation of the oscillations by the electrons to the total cross section of their inelastic scattering and by the average value of the energy converted into the oscillations in one act of excitation.

To determine the populations of the individual vibrational levels it is also necessary to know, besides the total energy flux that goes into oscillations of the polyatomic molecules, also how the various oscillation modes are excited. The most favorable for the population inversion is the situation wherein the modes with large relaxation times are predominantly excited. (This is precisely the case realized in the CO_2 gas laser with electric pumping.) Since, however, the relative rates of energy pumping into various modes are unknown, we shall henceforth take them to be equal. Assuming now that in a liquid of polyatomic molecules with m normal intramolecular oscillations there are two groups of modes n and k (n + k = m), we obtain for the nonequilibrium energy reserve $E_{vib}(n)$ and $E_{vib}(k)$ in each of the groups of modes towards the end of the action of the pulse[1]

$$E_{vib}(n)=\frac{n}{m}\eta\frac{E_i}{2}J\tau(n)+E^0_{vib}(n), \quad E_{vib}(k)=\frac{k}{m}\eta\frac{E_i}{2}J\tau_{beam}+E^0_{vib}(k), \tag{11}$$

where E^0_{vib} are the equilibrium (at temperature T) reserves of vibrational energy. Estimating E_{vib} and recognizing that in each of the groups of modes n and k, owing to the fast exchange of energies between the modes, there is established a Treanor quasi-equilibrium ratio,[11] we can easily determine the populations of the different levels. Thus, for the considered example in COS we have n = 2 and k = 1, and the populations of the lower levels $N_1(n)$ and $N_1(k)$ of the modes with the smallest quanta, $\nu_2 = 516\ cm^{-1}$ and $\nu_3 = 2050\ cm^{-1}$ from the groups n and k will be respectively equal to 2×10^{20} and $5 \times 10^{19}\ cm^{-3}$. The population inversion sets in then between the 001 level and the 100 level from the group n = 2 of the rapidly relaxing modes ν_1 and ν_2, and amounts to $\sim 4 \times 10^{19}\ cm^{-3}$. We note that it is precisely with this transition (wavelength $\lambda = 8.4\ \mu$) that inverted population and lasing were obtained for gaseous COS with electric pumping.[20]

Assuming for the line width and for the probability of the spontaneous radiative transition the typical values $\sim 10\ cm^{-1}$ and $1\ sec^{-1}$, we find that for the indicated transition the gain is $\alpha \approx 5 \times 10^{-2}\ cm^{-1}$, i.e., it is fully sufficient for lasing. We note also that at these values of α the time required for lasing to develop, $\tau_{gen} \sim 40(\alpha c)^{-1}$ (c is the speed of light),[21] amounts to 3.3×10^{-8} sec and is shorter than the pulse duration.

An important factor influencing the operation of the liquid laser (as well, incidentally, of an electro-ionization gas laser), is the heating of the medium. In liquids, however, owing to the much larger specific heat per unit volume, this heating can be small even at relatively large energy inputs. Thus, in the case considered here, the maximum heating of the liquid following absorption of the energy of one electron-beam pulse ($\sim 75\ J/cm^3$) does not exceed $\sim 50°$.

From the particle flux to the upper vibrational laser level with energy $n\nu_3$ we can also estimate roughly the expected power W_{rad} and energy E_{rad} in one radiation pulse:

$$W_{rad} \leq \frac{\nu_{rad}}{\nu_3}\frac{k}{m}\eta\frac{E_i}{2}J, \quad E_{rad} \leq W_{rad}\tau_{beam}.$$

For the example considered we have $W_{rad} \lesssim 2 \times 10^7\ W/cm^3$ and $E_{rad} \lesssim 0.9\ J/cm^3$. These estimates show that in the case when liquid lasers are produced on vibrational transitions, they can compete successfully with respect to their energy characteristics with modern electro-ionization lasers.[1,2] To be sure, when pumping with an electron beam, owing to the predominant beam energy loss to ionization, the efficiency of such liquid lasers is low in comparison with electro-ionization gas lasers. However this efficiency can apparently be increased, and by the same token one can improve additionally the energy characteristics of the laser, by using a combined excitation method that employs both an electron beam and an external electric field that heats the secondary electrons. Thus, simple estimates show that if the cross section for the excitation of the oscillations by electrons is $\sim 10^{-18}\ cm^3$, in the region of epithermal energies ~1–3 eV the concentration N_e of the secondary electrons (in our example $5 \times 10^{16}\ cm^{-3}$) is sufficient to obtain a concentration $5 \times 10^{21}\ cm^{-3}$ of vibrationally-excited molecules. Analogous calculations yield for liquid CS_2 at T = 195°K an inverted population on the order of $6 \times 10^{20}\ cm^{-3}$, and the value for furane (C_4H_4O) is of the order of $10^{19}\ cm^{-3}$ following excitation with epithermal electrons of energy 2 eV.

With decreasing temperature, owing to the increase of the vibration-relaxation times the efficiency of liquid laser increases. It is of interest from this point of view to use molecular crystals as active laser media. In molecular crystals, unlike in liquids, only the collective interactions play an important role. As seen from the estimates given above for the probabilities, the rates of the VT processes in collective interactions are usually lower than in binary interactions. Particularly small values P_1^{coll} are obtained for molecular crystals with $\nu_{min}/\nu_D > 3$, where consequently the intramolecular vibrational excitations decay into five or more Debye quanta. For these cases the resonant or close to resonant collective VV process, which calls for participation of only two Debye quanta (see (7)), is much faster, i.e., the relation $\tau_{VV} \ll \tau_{VT}$ between the characteristic times of the VV and VT processes remains satisfied. Therefore in such molecular crystals, just as in single-component gases and crystals, a quasistationary distribution is established among the modes. This circumstance was used in[22] to obtain a Treanor distribution in a system of anharmonic oscillators.

Energy exchange between different modes (the VV′ process) in molecular crystals can proceed at various rates, but it is clear that for multiquantum exchange with an appreciable energy defect, which calls for participation of several Debye modes in the process, these rates can be relatively small, so that on the whole the vibrational relaxation will be characterized by several relaxation times. Thus, the use of molecular crystals as an active medium for lasers employing vibrational transitions between levels of various intramolecular modes offers some promise and makes it possible, in principle, to obtain large inverted populations and gains. It is quite interesting to use for this purpose solid carbon dioxide, since the spectroscopic parameters and the cross sections for excitation by electron impact are well known for CO_2. The pumping, as for liquids, can be by means of high-power electron beams. Estimates carried out for a beam with the parameters cited above and based on the probabilities of Table II have shown that at the end of the action of the pumping pulse the inversion on the vibrational transition $00^01 \rightarrow 10^00$ amounts to 2×10^{19} cm^{-3}, corresponding to a stored energy 0.4 J/cm^3.

We now discuss briefly the question of stimulation of chemical reactions in the liquid phase by heating individual intramolecular modes with IR laser radiation. It is known[3,5,7] that when energy is dissipated from a mode as a consequence of a VT or VV′ process, with probability P_{10}, to obtain a vibrational mode temperature equal to the characteristic temperature of this vibration, the laser radiation must ensure an optical-pumping probability $W_{10} \approx P_{10}$. In this case, taking into account the connection between the pumping intensity I and the probability W_{10}, we have for I

$$I \approx 1.5 \cdot 10^{-11} \frac{\nu_{\text{rad}}^3 \Delta\nu}{q A_{10}} P_{10},$$

where I is given in W/cm^2; ν_{rad} and $\Delta\nu$ are the frequency of the absorbed radiation and the width of the absorption line (in cm^{-1}); q is the fraction of the molecules participating in the absorption, while the radiative and collision probabilities A_{10} and P_{10} are expressed in sec^{-1}. At typical values $P_{10} = 10^9$ sec^{-1}, $A_{10} \approx 10$ sec^{-1}, $q \approx 0.15$, $\Delta\nu \approx 10$ cm^{-1}, and $\nu_{\text{rad}} \approx 10^3$ cm^{-1} (the CO_2-laser emission frequency) we have $I \sim 10^8$ W/cm^2 and the vibrational temperature of the mode is ~1400°K. To obtain a vibrational temperature 2.3 times smaller (~610°K), the power required is ~10^7 W/cm^2. These powers, although much larger than in the case of stimulation of laser-chemical reactions in gases at low pressures (~1—100 Torr), are nonetheless attainable with modern pulsed IR lasers.

An important feature of laser-chemical reactions in the liquid phase is also their local character, due to the high concentration of the radiation-absorbing molecules. Thus, in the indicated example, the radiation absorption cross section is $\sim 2 \times 10^{-19}$ cm^2, which corresponds, at a liquid-molecule density $\sim 10^{22}$ cm^{-3}, to a radiation penetration depth $\delta \sim 5 \times 10^{-4}$ cm. Using radiation of a frequency that is a multiple of the oscillation frequency, for which the absorption cross section is appreciably smaller (by an approximate factor 10^2 and more) than for the resonant frequency, it is possible to increase considerably the volume in which the reaction takes place.

We note that an interesting communication was recently published concerning[23] first experiments on the realization of biochemical reactions in the liquid phase under the influence of IR laser radiation. To be sure, the employed radiation powers were not high, which seems to indicate either anomalously low probabilities of the deactivation of the excitation energy, or a thermal character of the course of the biochemical processes in this experiment. We note also that the estimates given above pertained to ordinary chemical reactions. They can be used for biochemical reactions only with great caution, since the rates of these reactions can be extremely sensitive to the translational temperature, the change of which is inevitable when a laser acts on a substance.

On the whole, the results obtained in this study point to the feasibility of effecting laser-chemical reactions in liquids, and to the favorable prospects of using liquids and molecular crystals as active media for lasers operating on intramolecular vibrational transitions.

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1) In the considered example, for the group of mode n we have $\tau(n) < \tau_{\text{beam}}$, i.e., a quasistationary relaxation regime is established. On the other hand for the group of modes k we have $\tau(k) > \tau_{\text{beam}}$. Therefore in (11) the expressions for $E_{\text{vib}}(n)$ and $E_{\text{vib}}(k)$ contain respectively the times $\tau(n)$ and τ_{beam}.

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Translated by J. G. Adashko
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