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KINETICS OF A PULSED CHEMICAL CARBON MONOXIDE LASER WITH PHOTOINITIATED OXIDATION OF CARBON DISULFIDE

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An experimental investigation was made of a pulsed chemical CO laser with photoinitiated oxidation of a CS_2–O_2 mixture. Laser oscillations were observed due to vibrational-rotational transitions of the CO molecule ($\lambda = 4.7–5.7\ \mu$) in a wide range of pressures (from 0.5 to 100 torr), compositions of the working mixture ($[O_2]/[CS_2]$ was varied from 3 to 58), and initiation energies (from 0.5 to 4.0 kJ). The maximum energy yield in the form of laser radiation was about 2×10^{-5} J/cm^3 and the chemical efficiency of the laser was 0.5%. An investigation was made of the amplitude and the time characteristics of the laser signal in the presence of the following gases in the working mixture: He, CO_2, N_2, CO, OCS, NO_2. It was found that the stimulated emission was due to the following sequence of chemical processes:

$$CS_2 + h\nu \xrightarrow{\tau_0} CS + S\ (0),\quad S + O_2 \xrightarrow{k_1} SO + O\ (I),\quad O + CS_2 \xrightarrow{k_2} CS + SO\ (II),$$
$$O + CS \xrightarrow{k_3} CO^* + S\ (III),\quad S + CS_2 + M \xrightarrow{k_4} CS_3 + M\ (IV),$$

The vibrational relaxation of the CO molecules was not the rate-limiting process. An analysis showed that the maximum value of the peak emission intensity $J_{\text{peak}}^{\max}$ was attained when the CS_2 pressure was given by the expression $(k_4\tau_0[O_2]/[CS_2])^{-1/2}$. This intensity was equal to $\bar{v}k_1k_3\delta^2/\tau_0k_2k_4$, where $\bar{v}$ is the average number of the quanta emitted per CO molecule and δ is the degree of photodissociation. The formulas derived were found to be in good agreement with the experimental results.

ONE of the most interesting chemical reactions which can be utilized for stimulated emission in the infrared region is the oxidation of carbon disulfide. This process includes several very rapid elementary stages and a considerable fraction of the energy evolved in this process is transferred to the vibrations of the CO molecule whose relaxation characteristics are very convenient for its use as the laser-active molecule.[1]

The published descriptions of the lasers utilizing the CS_2–O_2 mixture include cw systems (using freely burning flames[2,3] and electrical discharges[4-11]) and pulsed systems (using photoinitiation[12,13] and electrical discharges[14-16]). The emission spectra have been investigated and studies have been made of the dependences of the output power on the composition of the mixture, the relative flow of the components, and the presence of admixtures of various gases. Studies have also been made of the time characteristics of the laser pulses. It is now established that the elementary event responsible for the laser action is the process $CS + O \rightarrow CO^* + S$ (III). This is supported by the spectroscopic investigations of the populations of the vibrational levels of the CO molecules that are formed in this reaction. These investigations have shown that a considerable fraction of the thermal energy released in this elementary event is transferred to the vibrations of the CO molecule and that population inversion is attained for many vibrational levels ($v \leq 13$).[17] The same conclusion follows also from the studies of the laser emission spectra.

However, there is no information (even of hypothetical nature) on the kinetics of the laser action, on the processes governing the output power, the efficiency, and the duration of the laser pulses, and on the dependence of the laser characteristics on the composition of the mixture. The situation is complex because the action of chemical lasers is governed not only by the relaxation and optical emission processes but also by the kinetics of chemical reactions and the oxidation of carbon disulfide is very complex from the kinetic point of view: there are many possible elementary events and the relative contributions of these events to the overall process are not known. For example, in spite of the fact that the branched-chain nature of this reaction has been proved a long time ago,[18] the processes responsible for the branching and continuation of the chain have not yet been identified reliably.[19]

In this respect the simplest situation is that which obtains in a pulsed laser in which the reaction is initiated by optical excitation. In this case we can always identify the active particles that initiate the reaction.

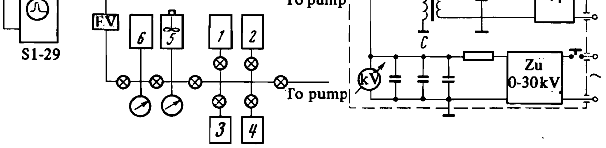

FIG. 1. Schematic diagram of the apparatus: RD is a radiation detector (Ge:Au photoresistor kept at 77°K); S1-29 is an oscillograph; EV is an electromagnetic valve; 1-4—cylinders for storing various gases; 5—cylinder for forced mixing; 6—cylinder for storing prepared mixture; D is a multielectrode discharger; kV is a kilovoltmeter; C is a capacitor bank; ZU is a high-voltage unit.

Moreover, since the emission times are extremely short, only the fastest elementary events need be considered in the kinetics of the process. In view of this it was decided to investigate the characteristics of a carbon monoxide chemical laser with photoinitiated $CS_2 + O_2$ reaction and to study how these characteristics depend on the value of $\alpha = [O_2]/[CS_2]$, the presence of different gases, the total pressure, and the photoinitiation energy. The purpose of this investigation was to obtain general information on the kinetic and relaxational features of the process, which could be used later to determine the detailed mechanism.

EXPERIMENTAL METHOD

The schematic diagram of the apparatus is shown in Fig. 1. A laser tube was made of optical quartz (which transmitted up to 200 nm). Its internal diameter was 2 cm and it was 50 cm long. The tube was closed at both ends by calcium fluoride (or barium fluoride) windows. An optical resonator was formed by aluminized quartz mirrors of 100 cm radius of curvature, separated by a distance of 130 cm. An aperture of 2 mm diameter was made at the center of one of the mirrors for extraction of the radiation.

The absorption of ultraviolet light by carbon disulfide, resulting in its dissociation into CS and S, was known to occur in 180–220 nm range.[20] The photoinitiation was provided by two xenon-filled (20 Torr) quartz lamps connected in series. The dimensions of the lamps and the materials used in their construction were the same as for the laser tube. The transfer of the ultraviolet radiation from the lamps to the laser tube was maximized by placing the lamps and the tube inside a cylindrical reflector lined with aluminum foil.

A capacitor bank C (Fig. 1) of 3–9 μF capacitance, charged to 15–32 kV, was the source of the electrical energy of the pulse-discharge lamps. The breakdown in the lamps occurred on application of the voltage via a pulsed multielectrode discharger. The half-period of the current pulses through the lamps was about 20 μsec.

A gas mixture of the required composition was prepared in a special cylinder 5 in which forced mixing could be applied. This mixture was admitted, in the required concentration, to the laser tube, which was first evacuated by a backing pump to 10^{-2} torr. The storage of the mixture for several days did not alter significantly the nature of the subsequent laser action. Carbon disulfide of the TG-12142 brand (of East German origin) was purified in order to remove the products of the decomposition of this compound. This was done by distillation over lime, followed by treatment with potassium permanganate, mercury, mercury sulfate, and second distillation over $CaCl_2$.[21] Carbonyl sulfide used as an admixture was synthesized by the standard method.[22] The remaining gases were taken directly from suppliers' cylinders and were not subjected to any additional purification.

The laser radiation was detected with a Ge : Au photoresistor cooled to 77°K and its energy was measured with an IÉK-1 laser calorimeter. No investigation was made of the separate oscillation lines.

The windows and walls of the laser tube were cleaned periodically from the deposited film (probably a polymer of —CS— and sulfur), which absorbed strongly in the region of 200 nm.

EXPERIMENTAL RESULTS

The laser action in the 4.7–5.7 μ spectral range was observed in a wide range of compositions of the working mixture, initiation energies (from 0.5 to 4 kJ), and pressures (from 0.5 to 100 torr). The light pulses emitted by the flashlamps and typical laser signals are shown in Fig. 2.

The experiments showed that the dependence of the output energy on the photoinitiation energy W (more precisely on the energy stored in the capacitors) was strongly nonlinear near the laser threshold. This behavior was evidently due to a large number of simultaneous rotational-vibrational transitions in the CO molecule (Gregg and Thomas[12] observed about 300 lines) whose laser thresholds could differ significantly.

The total duration of an emission pulse was about 50 μsec, which decreased slightly at high initiation energies and increased right up to 120 μsec at very low pressures. At low initiation energies the emission pulse had a "toothed" structure (each "tooth" lasted several microseconds) but this structure disappeared when the initiation energy was raised.

The dependence of the peak emission intensity on the pressure in the working mixture is plotted in Fig. 3 for $\alpha = 15$ and different photoexcitation energies W. The pressure at which the maximum value of the peak intensity was achieved increased with the initiation energy approximately as $W^{1/2}$ and the maximum value of the peak intensity J_{peak}^{max} first increased very rapidly with increasing W (threshold behavior) and then became proportional to $W^{1.5-2}$. Similar dependences were observed for all the investigated compositions of the working mixture and it was found that for a given initiation energy W the maximum value of the peak emission intensity J_{peak}^{max} was always reached at practically the same partial pressure of CS_2.

The dependence of the peak emission intensity on the ratio of the oxygen and carbon disulfide concentrations $\alpha = [O_2]/[CS_2]$ is plotted in Fig. 4. In the $\alpha = 15–20$ range the output energy measured with the IÉK-1 calorimeter was $(1.8–2.0) \times 10^{-3}$ J for the optimal pressure in the mixture and W = 4 kJ, which corresponded to a peak output power of about 100 W and a specific energy output $w_L \approx 2 \times 10^{-5}$ J/cm³. The chemical efficiency of the laser, κ^{chem} (i.e., the ratio of the laser output energy to the total energy evolved in the chemical reaction), reached 0.5%.1)

Suart et al.[11] found that the addition of various gases had quite a strong and specific influence on the emission intensity of a cw laser. For example, the action of CO increased the emission intensity in the range $\beta \equiv [CO]/[CS_2] = 0–4$; very small amounts of OCS also increased the emission intensity; CO_2, N_2, Ar, and NO_2 gave rise to a monotonic increase in the output power. However, our experiments (carried out on a mixture with $\alpha = 15$) showed that He, CO_2, and N_2 had practically no effect on the laser characteristics up to

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1)The heat evolved in the reaction $CS_2 + (5/2)O_2 = CO + 2SO_2$ was 196 kcal per mole of CS_2.

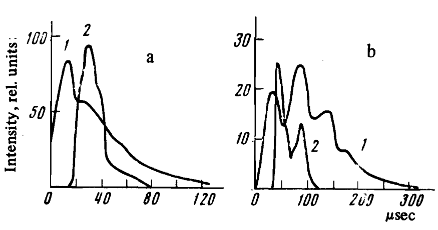

FIG. 2. Initiating radiation (1) (C = 9.0 μF, W = 2.7 kJ) and laser output (2) ($CS_2:O_2:CO$ = 1:10:1, $P_{CS_2} \approx 1.0$ Torr) pulses: a—"inductance-free" discharge circuit; b—circuit with an additional 50 μH inductance. Time constant of the infrared radiation detector 3 μsec.

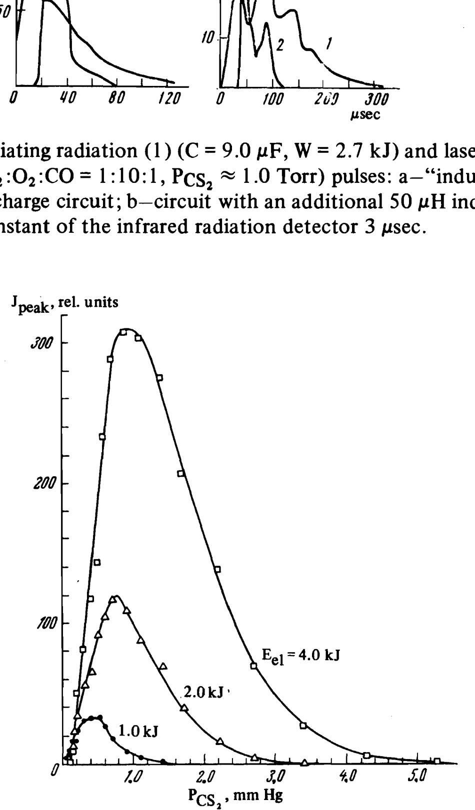

FIG. 3. Dependence of the peak emission intensity on the partial pressure of CS_2 in a $CS:O_2$ = 1:15 mixture for different initiation energies.

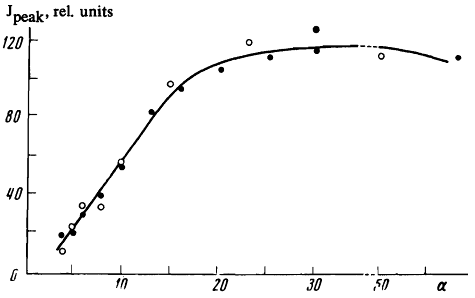

FIG. 4. Dependence of the peak emission intensity on the ratio α = $[O_2]/[CS_2]$ at a constant pressure (O—W ≈ 2.8 kJ, ●—W ≈ 1.0 kJ). $P_{CS_2} \approx 0.5$ mm Hg.

$\beta \equiv [X]/[CS_2] \sim 20$ ([X] is the concentration of a gas X); addition of small amounts of CO ($\beta < 1$) simply doubled the pulse duration; addition of CO in larger amounts had no effect on the laser signal. Only OCS and NO_2 reduced the emission intensity (J_{peak}^{max} was halved for mixtures with $\beta_{OCS} = 0.1$ and $\beta_{NO_2} \approx 0.5$).

This difference between the behavior of cw and pulsed lasers was due to the following reasons. In cw lasers the concentrations of the excited CO molecules and the rates of their relaxation are governed by all the elementary events contributing to the overall chemical process. Moreover, the addition of various gases has a difficult-to-predict influence on the macroscopic features of the combustion process. In pulsed lasers the stimulated emission ends 50—100 μsec from the beginning of the initiation process and, consequently, only the chemical events or the rotational relaxation characterized by the time constants τ not exceeding 10^{-4} sec can have any significant influence on the laser action. We can write these time constants in the form

$$\tau = 1/kn, \qquad (1)$$

where n is the concentration of the gas which is added and k represents a variety of physical effects. If the influence of an admixture on the laser action is of chemical origin, k represents the rate constant of the relevant bimolecular elementary process or the product of the rate constant of the trimolecular process and the concentration of the particles participating in triple collisions with the particles of the added gas. In both cases estimates show that the active particle (an atom of O or S or, possibly, a free SO radical) should participate in the chemical process. However, if the influence of the added gas on the laser action is due to its participation in the vibrational relaxation of the excited CO* molecules, k represents the rate constant of the relaxation process involved.

The He atoms are chemically neutral and the rate constants of the elementary events involving the N_2 and CO_2 molecules with the active particles are very small. Therefore, the experimental data and Eq. (1) yield the following estimates of the vibrational-translational relaxation constants (cm^3/sec) at T ≈ 300°K:

$$k_{He,CO} \lesssim 10^{-14}, \; k_{N_2,CO} < 6 \cdot 10^{-15}, \; k_{CO_2,CO} \lesssim 2 \cdot 10^{-14},$$

which are in qualitative agreement with the published data.

The quenching action of the NO_2 molecules is due to the influence of the known[23] fast elementary chemical process $NO_2 + O \rightarrow NO + O_2$ characterized by the rate constant $k \approx 10^{-11}$ cm^3/sec at 300°K, which uses up the oxygen atoms. On the other hand, the carbonyl sulfide molecule is known to destroy the vibrational excitation of the CO molecule[24] (for example, $k_{OCS,CO} \approx 4.5 \times 10^{-11}$ and 7×10^{-12} cm^3/sec, respectively, for v = 4 and 9). Therefore, naturally, the addition of carbonyl sulfide in amounts in excess of 10^{-2} torr must reduce the laser emission intensity.

Experiments on the influence of the CO molecules on the laser emission are of special importance. The observed effects cannot be explained by chemical reactions involving CO, for example the recombination $O + CO + M \rightarrow CO_2 + M$ or the process $S + CO + M \rightarrow OCS + M$ followed by the relaxation of the CO molecule because of the interaction with OCS; the effect is not explained either by the vibrational relaxation of the inverse-populated "hot" CO molecules because of their interaction with the "cold" molecules. The observed influence of the CO molecules on the laser action is probably due to the appearance of an additional (to process III) channel of inversion of the vibrational states of the CO molecules because of the transfer of the electronic excitation of the SO_2^* molecules to CO (this mechanism is suggested by Gregg and Thomas[12]) or because of the relaxation of the "hot" (but not populationinverted) CO due to its interaction with the "cold" CO molecules (the probability of the vibrational exchange with the ground state decreases rapidly with increasing level number of the vibrational CO quanta: a similar mechanism applies also to electric-discharge CO lasers).

Apart from the nature of the observed lengthening of the laser output pulses, the results obtained in the present investigation suggest that the stimulated emission does not stop and does not become shorter with increasing pressure of the working mixture because of the production of the "cold" CO in the course of the reaction (the vibrational exchange between this gas and the "hot" molecules destroys the inversion in the same way as in HF and HCl chemical lasers[25,26]). Hence, it follows that the emission is quenched either because of the vibrational relaxation of the CO molecules interacting with intermediate or final products of the reaction (for example, OCS) or because of the chemical exhaustion of the O or S atoms in various reactions. The observed dependence of the emission intensity solely on the partial pressure of carbon disulfide shows that CS_2 is itself the chemical cause of the exhaustion of the O and S atoms. The vibrational relaxation of CO because of interaction with CS_2 can be ignored because of the large resonance defect of the vibrations of these molecules.

The predominant quenching process was determined in additional experiments. We started by checking that the emission stopped because of the accumulation of intermediate reaction products, which could destroy effectively the inversion of the CO molecules. With this aim in mind we trebled the duration of the photoinitiation pulses by including an inductance of about 50 μH into the discharge circuit. This resulted in a proportional lengthening of the laser output pulses (Fig. 2b) but the dependence of the amplitude of the output pulses on the intensity of the initiating light remained unaffected. Thus, the reaction products did not affect the stimulated emission process, at least during the first 120 μsec from the beginning of the light pulse. The influence of the final reaction products was studied by repeatedly illuminating the working mixture with ultraviolet light produced by the flashlamps (Fig. 5). When the initial pressure of the mixture was raised above certain value, no laser action was observed after the first flash. However, such action appeared during one of the subsequent flashes, reached its maximum amplitude during some particular flash, and then decayed from flash to flash until it disappeared completely. The highest amplitude of the laser pulses was close to the amplitude obtained using a mixture at its optimal pressure (for a given value of the initiation energy). In the experiments involving repeated illumination the duration of the laser output pulses was approximately twice the duration of the pulses obtained after single illumination. As mentioned earlier, such lengthening of the laser output pulses occurred also when carbon monoxide was added to the working mixture. Evidently, in both cases the effect was due to the CO molecules generated in preceding flashes. This meant that the increase in the duration of the laser pulses occurred even in the presence of very small amounts of CO.

The following conclusions can be drawn from the results obtained.

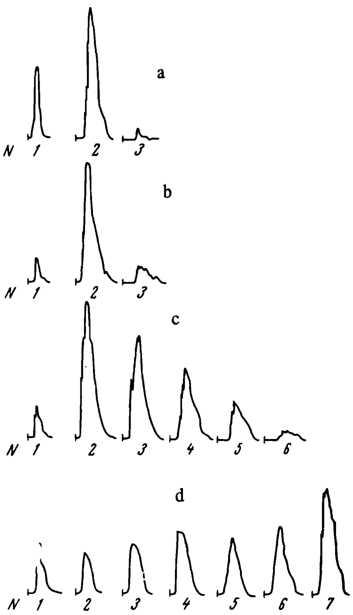

FIG. 5. Laser emission pulses obtained by repeated initiation ($W \approx$ 2 kJ): a–CS_2:O_2 = 1:15, P_{CS_2} = 1.1 Torr; b–CS_2:O_2:He = 1:15:5, P_{CS_2} = 1.13 Torr; c–CS_2:O_2: He = 1:15:15, P_{CS_2} = 0.95 Torr; d–CS_2: O_2:He = 1:15:25, P_{CS_2} = 0.72 Torr.

1. The laser parameters are not affected by the final products of the oxidation reaction with the exception of the CO molecule which increases the duration of the laser pulses without altering their amplitude.

2. The variation of the amplitude of the pulses obtained in a series of repeated flashes is explained by the gradual decrease of the concentration of CS_2 in the working mixture.

If we compare the dependences of the amplitude of the laser pulses on the number of successive flashes and on the concentration of CS_2 in a mixture under single-flash conditions, we can estimate the degree of dissociation of carbon disulfide under the influence of light flashes. This was done using a mixture with a high value of α ($\alpha = [O_2]/[CS_2] = 15$). Then, an increase in α because of exhaustion of carbon disulfide should not alter the amplitude of the laser pulses. The mixture was diluted with helium in order to eliminate the possibility of exhaustion of CS_2 because of the high temperature of the gas after the end of a flash. The calculations were performed by extrapolating to infinitely low dilutions. We used the dependences plotted in Fig. 5 and assumed that the maximum output power corresponding W = 2 kJ was attained for P_{CS_2} = 0.80 Torr. This yielded the estimate

$$\delta\nu(W = 2\ \text{kJ},\ P_{CS_2} = 0.80\,\text{Torr}) \approx 0.03,$$

where $\delta = [CS]/[CS_2]$ is the degree of dissociation and ν is the length of the reaction chain (the number of the CS_2 molecules oxidized as a result of dissociation of one carbon disulfide molecule). We thus found that $\delta \leq 0.03$.

The dependence of the degree of photodissociation of CS_2 on the intensity of the ultraviolet radiation emitted by the lamp was governed by the absorption line profile, the spectral composition of the ultraviolet radiation, the geometry of the system, and the concentration of carbon disulfide. In our experiments the medium was optically dense, at least for $P_{CS_2} > 0.2$–0.4 torr in the presence of a reflecting screen. Therefore, the estimate of δ could be extrapolated to all the initiation energies and all the CS_2 pressures in the following manner:[2)]

$$\delta = \xi W P_{CS_2}^{-1/2}, \quad \xi \approx 1.35 \cdot 10^{-2} \text{ kJ}^{-1} \text{ Torr}^{1/2} \tag{2}$$

The experiments carried out showed that the laser action can be described completely by the following processes: the photodissociation of CS_2, the chemical reactions between oxygen atoms and carbon disulfide and between oxygen molecules and sulfur, and the laser reaction $CS + O \rightarrow CO^* + S$. The vibrational-vibrational and the vibrational-translational relaxation in the laser-active molecules, which play the dominant role in the infrared-emitting lasers, are not the rate-limiting processes. This means that the principal laser parameters of the system considered can be deduced directly from the chemical kinetics equations.

We shall do this by considering all possible chemical processes in a mixture of carbon disulfide and oxygen produced by the action of ultraviolet light pulses. We shall take into account only the fast processes which, at the investigated concentrations of the reagents, can make a significant contribution during a laser pulse lasting 20–100 μsec. The ultraviolet pulses emitted by the flashlamps in the 180–220 nm range are responsible for the photodissociation of carbon disulfide

$$(0)\, CS_2 + h\nu \xrightarrow{\tau_0} CS + S,$$

in which S atoms and free CS radicals are formed at the rate

$$\frac{\partial[S]}{\partial t} = \frac{\partial[CS]}{\partial t} = q(t), \tag{3}$$

where q(t) is the product of the intensity of the absorbed light and the quantum yield of the reaction (0).

The laser action is due to the process[27]

$$(III)\, O + CS \xrightarrow{k_3} CO^* + S, \quad k_3 \approx 1{,}6 \cdot 10^{-10} \text{cm}^3/\text{sec at } T = 300° \text{ K}.$$

The fastest reaction which can produce the O atoms necessary for the laser reaction (III) is[27][3)]

$$(I)\ S + O_2 \xrightarrow{k_1} O + SO, \quad k_1 \approx 1.6 \cdot 10^{-15} \text{ cm}^3/\text{sec at } T = 300° \text{ K}.$$

We must also consider the fast processes resulting in the exhaustion of the chemically active particles which are the O and S atoms (the CS and SO radicals do not undergo any fast reactions). Only two processes have characteristic times of the order of the stimulated emission time[28,29][4)]

$$(II)\, O + CS_2 \xrightarrow{k_2} CS + SO, \quad k_2 \approx 3{,}5 \cdot 10^{-12} \text{cm}^3/\text{sec at } T = 300° \text{ K},$$

$$(IV)\, S + CS_2 + M \xrightarrow{k_4} CS_3 + M, \quad k_4 \approx 1 \cdot 10^{-30} \text{cm}^6/\text{sec at } T = 300° \text{ K}.$$

The system (0)—(IV) is complete for times of the order of the duration of the laser pulses. In the case of large values of α the system might have to be supplemented by the trimolecular process $S + O_2 + O_2 \rightarrow SO_2 + O_2$ whose rate constant is unknown.

The S atoms are used up in the processes (I) and (IV). The ratio of the rates of these processes is

$$\frac{k_1[O_2][S]}{k_4[M][CS_2][S]} \approx \frac{10^{-15}[O_2]}{10^{-30}[M][CS_2]} < \frac{10^{15}}{[CS_2]}. \tag{4}$$

In other words, at pressures $P_{CS_2} > 3 \times 10^{-2}$ Torr the process (IV) predominates over the process (I). For this reason we can ignore the formation of the S atoms in the process (III) because the rate of this process, which is one of the reactions that exhaust the O atoms, cannot be greater than the rate of the process (I), which is the only one in which the O atoms are formed.

Since the S atoms are used up mainly in the reaction (IV), only a small fraction of these atoms is transformed into the CS radicals as a result of the processes (I) and (II). On the other hand, we can ignore the loss of CS by the reaction (III) because the ratio of the rates of the reaction (III) and the CS-producing process (II) is

$$\frac{k_3[O][CS]}{k_2[O][CS_2]} = \frac{k_3}{k_2}\frac{[CS]}{[CS_2]} \approx 30\delta, \tag{5}$$

i.e., for $\delta \leq 0.03$ the rate of the reaction (III) is less than or comparable with the rate of the reaction (II). Thus, the concentration of the free CS radicals can be regarded as governed by the external initiation source:

$$[CS(t)] = \int_0^t q(\tau)\, d\tau. \tag{6}$$

If these assumptions are made, the kinetics of the process is found to be governed by the following system of equations:

$$\frac{\partial[S]}{\partial t} = q - \frac{[S]}{\tau_4}, \quad \frac{\partial[O]}{\partial t} = \frac{[S]}{\tau_1} - [O]\left[\frac{1}{\tau_2} + \frac{1}{\tau_3(t)}\right]; \tag{7}$$

$$\tau_1^{-1} = k_1[O_2], \quad \tau_2^{-1} = k_2[CS_2],$$

$$\tau_3^{-1}(t) = k_3[CS(t)], \quad \tau_4^{-1} = k_4(\alpha + \beta)[CS_2]^2. \tag{8}$$

The quasisteady-state laser emission intensity J is

$$J(\text{cm}^{-3} \cdot \text{sec}^{-1}) = \bar{v}\frac{d[CO^*]}{dt} = \bar{v} k_3[O][CS], \tag{9}$$

where $\bar{v}$ is the average number of quanta emitted per one CO molecule. A complete numerical solution of the system (7) yields results that do not have clear physical meaning. However, even a simple analysis reveals the principal features of the process.

Figure 6 shows the dependences of the characteristic times of the chemical reaction and photoinitiation processes on the CS_2 pressure, plotted on the assumption that $\tau_3 \gtrsim \tau_2$, which follows from Eq. (5). The results in Fig. 6 are applicable to mixtures with $\alpha < 10^2$. It follows from the curves in this figure that at low carbon disulfide concentrations, $[CS_2] \ll [CS_2]^0$, we can ignore the trimolecular reaction involving the "capture" of sulfur atoms (IV) whereas at high values of $[CS_2]$ this reaction predominates. We shall now consider the solution of our system of kinetic equations in these two ex-

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[2)] The dependence (2) was obtained by approximating the long-wavelength "wing" of the absorption band of CS_2 by a Lorentzian curve. It was also assumed that the spectral density of the ultraviolet radiation produced by the lamps varied weakly with the wavelength in the region where the absorption was significant.

[3)] The possible electronic or kinetic excitation of the sulfur atoms is ignored.

[4)] The rate constant of the trimolecular process (IV) was measured by Basco and Pearson [29] in the case when the third particle was an atom of Ar. The present estimates are based on the assumption that the effectiveness of an O_2 molecule as the third body in a triple collision is approximately the same as that of an Ar atom and that CS_2 is β times more effective than oxygen in the de-excitation of CS_3^*.

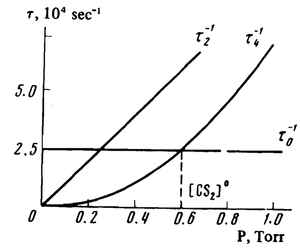

FIG. 6

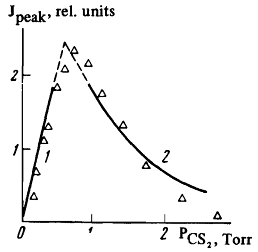

FIG. 7

FIG. 6. Dependences of the characteristic time constants on the pressure of CS_2 ($\alpha + \beta \approx 25$).

FIG. 7. Dependence of the peak emission intensity J_{peak} on the CS_2 pressure: 1—curve calculated using Eq. (19) for low CS_2 pressures; 2—curve calculated using Eq. (19) for high CS_2 pressures ($\alpha + \beta \approx 25$); Δ—experimental points for a discharge energy $W \approx 2$ kJ and $\alpha = 15$.

treme cases of low and high concentrations of carbon disulfide.

A. Low Values of $[CS_2]$ ($[CS_2] \ll [CS_2]^0$).

In this case $\tau_4 \gg \tau_0$ and $\tau_4 \gg \tau_2$, so that the concentration of the sulfur atoms is

$$[S] = \int_0^t \exp\left(-\frac{t-\theta}{\tau_4}\right) q(\theta)\,d\theta \approx [CS(t)]\exp\left(-\frac{t}{\tau_4}\right), \tag{10}$$

and the concentration of the oxygen atoms begins to "follow" the concentration of the S atoms after a time τ_2:

$$[O] = \frac{\tau_1^{-1}}{\tau_2^{-1} + \tau_3(t)^{-1}}[S(t)] \approx \frac{\tau_1^{-1}}{\tau_2^{-1} + \tau_3(t)^{-1}}[CS(t)]\exp\left(-\frac{t}{\tau_4}\right). \tag{11}$$

An expression for the intensity of the laser signal can be obtained from Eqs. (6), (9), and (11):

$$J(t) = \bar{v}\frac{k_3}{\tau_1(\tau_2^{-1} + \tau_3(t)^{-1})}[CS(t)]^2 \exp\left(-\frac{t}{\tau_4}\right) \qquad (t \gg \tau_2). \tag{12}$$

The laser pulse amplitude reaches its peak value at the end of the initiation pulse:

$$J_{peak} = \bar{v}\frac{k_3}{\tau_1(\tau_2^{-1} + \tau_3^{-1})}[CS]_0^2,$$

$$[CS]_0 = \int_0^\infty q(\theta)\,d\theta, \qquad \tau_3^{-1} = k_3[CS]_0, \tag{13}$$

and after $t > \tau_0$ this amplitude decays exponentially with a characteristic time τ_4.

B. High Values of $[CS_2]$ ($[CS_2] \gg [CS_2]^0$)

In this case $\tau_0 \gg \tau_2$ and $\tau_0 \gg \tau_4$ and it follows from the first equation of the system (7) that after a time of the order of τ_0 from the beginning of the initiation process the concentration of the sulfur atoms attains its quasisteady-state value:

$$[S] = q(t)\tau_4, \tag{14}$$

and after a time $t \gtrsim \tau_2$ the concentration of the oxygen atoms again "follows" [S]. Consequently, after a time $t \gtrsim \tau_2, \tau_4$, we have

$$[O] = q(t)\frac{\tau_4}{\tau_1(\tau_2^{-1} + \tau_3(t)^{-1})}. \tag{15}$$

The laser signal is now described by the formula

$$J(t) = \bar{v}\frac{k_3\tau_4}{\tau_1(\tau_2^{-1} + \tau_3(t)^{-1})} q(t)\int_0^t q(\theta)\,d\theta. \tag{16}$$

In this case the laser emission ends approximately at the same time as the initiation pulse and the peak value of the laser emission intensity (for low degrees of dissociation of CS_2 amounting to $\delta \leq 3\%$) corresponds to the maximum of the function

$$\Phi = q(t)\int_0^t q(\theta)\,d\theta.$$

We can show that

$$J_{peak} = \bar{v}\frac{k_3\gamma_1}{\tau_0\tau_1(\tau_2^{-1} + \gamma_2\tau_3^{-1})}[CS]_0^2, \tag{17}$$

where γ_1 and γ_2 are numerical factors which depend on the shape of the initiation pulse; for example, in the case of a pulse which decays in accordance with law $q = q_0\exp(-t/\tau_0)$, we have $\gamma_1 = 1/4$ and $\gamma_2 = 1/2$.

This, in the two extreme cases of high and low concentrations (pressures), we obtain the following expressions for the laser emission intensity:

$$J_{peak} = \bar{v}\frac{k_1k_3}{k_2}\alpha\delta^2 \begin{cases} \dfrac{[CS_2]^2}{1 + k_3\delta/k_2}, & [CS_2] \ll [CS_2]^0, \\ \dfrac{\gamma_1}{k_4\tau_0}\dfrac{1}{\alpha + \beta}\dfrac{1}{1 + k_3\gamma_2\delta/k_2}, & [CS_2] \gg [CS_2]^0. \end{cases} \tag{18}$$

The formulas obtained can be compared conveniently with the experimental results by expressing the degree of dissociation δ in terms of the initiation energy (ignoring the value of τ_2/τ_3 compared with unity). Then

$$J_{peak} = \xi^2\bar{v}\frac{k_1k_3}{k_2}\alpha W^2 \begin{cases} [CS_2], & [CS_2] \ll [CS_2]^0, \\ \dfrac{\gamma_1}{k_4\tau_0[CS_2]}\dfrac{1}{\alpha + \beta}, & [CS_2] \gg [CS_2]^0. \end{cases} \tag{19}$$

The dependence (19) is plotted in Fig. 7. Extrapolation to intermediate values gives an estimate of the intensity of the laser emission corresponding to the optimal pressure of CS_2. It is found that the emission intensity reaches its maximum value

$$J_{peak}^{max} \approx \xi^2\bar{v}\frac{k_1k_3}{k_2}\frac{\alpha}{(\alpha + \beta)^{1/2}}W^2\left[\frac{\gamma_1}{k_4\tau_0}\right]^{1/2} \tag{20}$$

at the following optimal value of the partial pressure of carbon disulfide:

$$[CS_2]_{W\to 0}^{opt} = \left[\frac{\gamma_1}{k_4\tau_0(\alpha + \beta)}\right]^{1/2}. \tag{21}$$

One can easily obtain an expression for $[CS_2]^{opt}$ in the limiting case of high initiation energies (when $\delta \gg 0.03$ and $\tau_3 \ll \tau_2$):

$$[CS_2]_{W\to\infty}^{opt} = \gamma_1^{-1/2}[CS_2]_{W\to 0}^{\text{опт}}. \tag{21'}$$

The above analysis makes it possible to compare the theoretical dependences obtained on the assumption of "purely chemical" nature of the laser with the results of a study of the laser characteristics obtained in flash photolysis of the $CS_2 + \alpha O_2$ mixture.

1. The dependence of the laser emission intensity on the pressure of the mixture (19) describes correctly the experimental results (Fig. 7). Equations (21) and (21′) can be used to estimate the absolute value of the optimal partial pressure of CS_2 and of the pressure of the working mixture. If we substitute $\tau_0 = 40$ μsec, $\gamma_1 = 1/4$, $\alpha + \beta = 15\text{–}25$,[5] $k_4^{O_2} \approx k_4^{Ar} = 1 \times 10^{-30}$ cm⁶/sec, we obtain

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[5] The value of β does not exceed 5-10 because otherwise the rate constant of the trimolecular reaction $S + CS_2 + CS_2 \rightarrow CS_3 + CS_2$ should be greater than the highest value known for such reactions (10^{-29} cm⁶/sec).

$$(P_{CS_2}^{opt})_{W\to 0}=(0.5\div 0.6)\text{ Torr} \qquad (P_{CS_2}^{opt})_{W\to\infty}=(1.0\div 1.2)\text{ Torr}$$

These estimates are in good agreement with the experimental values of $P_{CS_2}^{opt}$ obtained for mixtures with $\alpha = 15$: these values are 0.45 torr for W = 1 kJ and 1.0 torr for W = 4 kJ.

2. The experimental results indicate that $J_{peak}^{max} \sim W^n$, where $1.5 < n < 2$. The maximum value of the peak laser emission intensity, given by Eq. (20), should increase with the initiation energy as W^2. However, it should be pointed out that the practical way of increasing the initiation energy is to increase the capacitance of the discharging unit. This results in an increase of τ_0 which is approximately proportional to $W^{1/2}$. When this point is taken into account, it follows from Eq. (20) that n = 1.75.

3. Our study of the laser emission from mixtures with different values of α shows that in the $\alpha \lesssim 10-15$ range the value of J_{peak}^{max} increases approximately proportionally to α but at higher values of α it is practically independent of this parameter. Moreover, the dependences $J_{peak}^{max}(\alpha)$ are symbatic for different initiation energies. A comparison with Eq. (20) shows that when $\beta \approx 5$ the theory agrees satisfactorily with the experimental data up to $\alpha \approx 15$. The discrepancy observed in the behavior of the emission intensity at very high dilutions with oxygen is due to the competition of the process $S + O_2 + O_2 \rightarrow SO_2 + O_2$, ignored in the calculations, with the process (IV).

4. The total laser output energy can be found from Eqs. (2), (20), and (21), to within a numerical factor of the order of unity (it is assumed that $\alpha \sim 10$ and the pressure of the mixture has its optimal value):

$$W_{\mathrm{L}}^{max}=\bar{v}\,\frac{k_1k_3}{k_2k_4}\,\delta^2 V\bar{\varepsilon}_{\mathrm{vib}}, \tag{22}$$

where V is the working volume of the laser and $\bar{\epsilon}_{vib}$ is the average energy of the vibrational quanta emitted by CO ($\bar{\epsilon}_{vib} \approx 0.2$ eV).

An estimate of the degree of dissociation obtained from our repeated illumination experiments gives a value $\delta \lesssim 3 \times 10^{-2}$ for W = 3 kJ. If the working volume of the laser is V = 100 cm^3, Eq. (22) yields $W_L \sim 0.5 \times 10^{-3}$ J (this estimate is obtained on the assumption that one CO molecule emits five quanta, i.e., that $\bar{v} = 5$). The experimental value obtained under the same conditions is $(0.8-1) \times 10^{-3}$ J.

This discussion shows that the proposed model of a chemical laser describes correctly the experimental results and, moreover, it predicts correctly the absolute values of the laser output energy, the optimal pressure of the working mixture, and the duration of the laser pulses.

Thus, a pulsed chemical CO laser utilizing oxidation of carbon disulfide is a unique chemical-laser system whose output parameters can be calculated almost completely using just the chemical kinetics equations and the published value of the rate constants of elementary chemical processes.

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