POSSIBILITY OF LASING IN THE VISIBLE BAND BY MOLECULE PHOTODISSOCIATION

T. L. Andreeva

The lower excited states of certain diatomic radicals and atoms, transitions from which to the ground state lie in the visible and in the near ultraviolet regions of the spectrum, are analyzed. Possible mechanisms of inversion via photodissociation of the molecules by radiation from a source with a continuous spectrum, having a brightness temperature $T \approx 3 \cdot 10^4 {}^\circ K$, are considered.

The advantages of photodissociation as a method of producing an active medium for gas lasers are universally known [1-6]. The basic factor is that the continuous molecule absorption bands responsible for the photodissociation are usually broad (~ 1000 cm^{-1}), and this gives grounds for hoping to make sufficiently effective use of the optical energy of a wide-band source, such as a "black body" with temperature $T \gtrsim 10,000^\circ K$. In fact, the presently well known $\lambda = 1.315$ μm iodine laser, whose action is based on photodissociation of molecules of the type CF_3I [1-6], has a working absorption band ($\lambda_{max} = 270$ nm, $\Delta\lambda \approx 40$ nm $\approx 0.5 \cdot 10^4$ cm^{-1}) which makes it possible to use approximately 10% of the optical energy of a standard flash lamp such as IFP-10,000, whose brightness temperature is close to the black body temperature $T \approx 10,000^\circ K$. One cannot, in principle, exclude simultaneous use of several gases that have displaced absorption bands in different regions of the spectrum, so that the efficiency of the pump optical energy can be additionally increased severalfold.

The number of molecules whose photodissociation leads to lasing on the $\lambda = 1.315$ μm infrared transition of atomic iodine is at present quite large [1-6]. Up to now, however, there was no photodissociation laser emitting in the visible band. Only quite recently, a brief communication reported lasing in the visible band on the electronic transitions of the radical HgBr, produced by photodissociation of $HgBr_2$ molecules. The latter were excited by an excimer laser using the molecules ArF* [7]. Similar lasing was subsequently obtained by prolonged optical pumping with a high-current discharge from an exploding wire [8]. It is important that under conditions of long pumping with $\tau_p \approx 30$ μsec the lasing duration was $\tau_{las} \approx 2$ μsec, which is much longer than the radiative lifetime $\tau_r \approx 23$ nsec of the excited HgBr* molecules. This shows that the lower working level of the HgBr molecule is sufficiently effectively depleted by the recombination reaction HgBr + Br + M$\rightarrow$HgBr$_2$ + M.†

This paper discusses the possibility of obtaining lasing in the visible and in the near ultraviolet using photodissociation of molecules by a continuous light source having a brightness temperature $T \approx 30,000^\circ K$, of the type used in [8]. The proposed lasing media are atoms as well as certain diatomic radicals.

We begin with the radicals, bearing in mind that a diatomic radical is produced when the appropriate molecule is photodissociated.

The main advantage of radicals over atoms is that to obtain lasing on electron-vibrational—rotational transitions of the radical there is no need for inverted population of the ground and excited electronic states. To obtain lasing in this case it suffices that the potential curves of the ground state X and the excited electronic state A of the radical be shifted relative to each other such that $r_{min}X < r_{min}A$.

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† In the last study of this subject known to us [9], lasing was achieved on the forbidden transitions Se($^1S_0$—$^3P_1$, $\lambda = 489$ nm, $^1S_0$—$^1D_2$, $\lambda = 777$ nm) in photodissociation of COSe by the $\lambda = 172$ nm radiation of the excimer Xe$_2^*$.

TABLE 1

Radical	$r^{(0)}_{min}$, Å	$r^{(1)}_{min}$, Å	E_1, eV τ_1, sec	Luminescence region, Å	σ_{amp}, cm^2	ΔN_{thr}, cm^{-3}	Initial molecules	Longwave limit of the photodecay, Å
CO	$X^1\Sigma^+$ 1,128	$a^3\Pi$ 1,206	6 $9,5 \cdot 10^{-3}$	2580—1760	$\sim 10^{-19}$	$\sim 10^{17}$	CO_2 COS	1070 1350
CS	$X^1\Sigma^+$ 1,535	$a^3\Pi$ —	3,4 $41 \cdot 10^{-3}$	3860—3445	$\sim 2 \cdot 10^{-20}$	$\sim 5 \cdot 10^{17}$	CS_2	1500
*CSe	$X^1\Sigma^+$ 1,676	$D^1\Pi^a$ 1,80	4,3 —	3050—2750	$\sim 10^{-14}$	$\sim 10^{12}$	CSe_2	1600
*NO	$X^2\Pi$ 1,15	$B^2\Pi$ 1,45	5,7 $3,16 \cdot 10^{-6}$	6500—2000	$\sim 10^{-16}$	$\sim 10^{14}$	NOCl NOBr	1700 1800
OH	$X^2\Pi$ 1,88	$A^2\Sigma^+$ 2,04	4,4 $8 \cdot 10^{-7}$	3065	$\sim 3 \cdot 10^{-15}$	$\sim 3 \cdot 10^{12}$	H_2O_2 H_2O	2025 1356
SH	$X^2\Pi$ —	$A^2\Sigma^+$ —	~ 4 —	3236	—	—	H_2S H_2Se, H_2Te	2000 —
*PbCl	$X_2\Pi^1/_2$ 2,18	$A^2\Sigma^+$ 2,29	2,7 —	5900—4100	$\sim 10^{-15}$	$\sim 10^{13}$	$PbCl_2$	2000
SnCl	$X^2\Pi^1/_2$ —	$A^2\Sigma^+$ —	2,3	7800—4950	$\sim 10^{-15}$	$\sim 10^{13}$	$SnCl_2$	1850
CaBr	$X^2\Sigma^+$ —	$A^2\Pi i^1/_2$ —	2 $3 \cdot 10^{-8}$	6400—6270	$\sim 10^{-13}$	$\sim 10^{11}$	$CaBr_2$	1800
NH$_2$	—	—	2,4 $3 \cdot 10^{-8}$	5200—5100 α-bands of ammonia	—	—	NH_3 N_2H_4	1800 2460

Naturally, to obtain lasing the absolute values of the populations in the excited electronic state must exceed the threshold values. The lasing spectrum consists in this case of a rather large number of lines, and this may be of interest for various problems in which turning of the lasing radiation is required.

Thus, the main criterion for the selection of the radicals is the location of the curves of the ground state X and the nearest electronic excited state of the radical. Data on the radicals are summarized in Table 1 [10-13]. Only order of magnitude estimates of the gain cross sections are given. The value of ΔN_{thr} was estimated from the condition for obtaining a gain $k = \Delta N \sigma_{amp} \approx 10^{-2}$ cm^{-1}. We note that both the estimates of the amplification cross sections and of the threshold densities are approximate, as needed for a rough search for lasing on the corresponding transitions. The symbols 0 and 1 pertain to the ground and nearest excited electronic state of the radical. E_1 is the energy of the considered excited electronic state of the radical and τ_r is the radiative lifetime of this state.

We discuss briefly the data given in Table 1.

The radical CO can hardly be of practical interest, for the following reasons: 1) the excitation energy of the term $^3\Pi$ closest to the ground term is very large, ~ 6 eV; 2) the known compounds containing the CO radical, such as CO_2 ($E_{dis}(CO_2 = CO + O) \approx 5.5$ eV) or COS ($E_{dis}(COS = CO + S) = 3.1$ eV) have high dissociation energies, so that the total energy needed for the photodissociation of the initial molecule with formation of an excited CO radical is $\geqslant 10$ eV, i.e., $\lambda \leqslant 1000$ Å; 3) the $a^3\Pi$ transition is forbidden, $\tau_r = 9.5$ msec, so that the threshold concentration of the CO radicals needed to obtain lasing should be high, $\sim 10^{16}$-10^{17} cm^{-3} ($\sigma_{amp} \approx 10^{-19}$ cm^2).

We note that the position of the potential curves of the terms $X^1\Sigma$ ($r_{min} = 1.13$ Å) and $a^3\Pi$ ($r_{min} = 1.21$ Å) is perfectly favorable for lasing. In practice, the same situation holds also for the CS radical, and the threshold concentration of the excited CS radicals in the state $a^3\Pi$ is even higher, $\sim 10^{18}$ cm^{-3}, although the energy of the exciting radiation is somewhat lower, ~ 8 eV (see Table 1). For the CSe radical, there is only one published description [10] of the band system $D^1\Pi^a$–$X^1\Sigma^+$. The transition $D^1\Pi^a$–$X^1\Sigma^+$, in contrast to the transitions $a^3\Pi$–$X^1\Sigma^+$ considred above for CO and CS, is allowed. The actual radiative lifetime τ_r for this transition in CSe is unknown, but τ_r for the corresponding transition in CO is 11 nsec. One can, therefore, expect the threshold concentration of the CSe radicals for lasing on the $D^1\Pi^a$–$X^1\Sigma^+$ transition to be relatively low. Assuming $\tau_r = 10$ nsec, we obtain

the estimate $\Delta N_{thr} \approx 10^{12}$ cm^{-3}. In this case it is perfectly feasible to obtain lasing on the band system of the transition $D^1\Pi^a\!-\!X^1\Sigma^+$, $\lambda \approx 3050\text{-}2750$ Å by excitation with light having $\lambda < 1600$ Å, and the radiation intensity I (in photons/cm$^2\cdot$sec) in this spectral region should not be weaker than $I \geqslant 10^{20}$ photons/cm$^2\cdot$sec. Unfortunately, we did not succeed in finding experimental data on the abosrption-band positions and width for compounds containing the CSe radical, such as the CSe_2 molecules, in the far ultraviolet. We recall that the radiation source whose brightness corresponds to absolute black body temperature T = 30,000°K produces an absorption band of molecules of the CF_3I type with λ_{max} = 2700 Å, with half-width $\Delta\lambda_{1/2} \simeq 500$ Å and light flux $I \approx 10^{23}$ photons/cm$^2\cdot$sec [3]. One can, therefore, hope that a radiation source with temperature T = 30,000°K, having a radiation maximum with respect to wavelength in the region $\lambda \approx 1000$ Å, can provide the necessary light flux in the region $\lambda < 1600$ Å, if there exists in this region a sufficiently broad continuous absorption band of the CSe_2 molecule, similar to the absorption band of the CF_3I molecule.

We regard as the most promising in the spectrum of the radical NO to be the β bands, whose radiation in the visible wavelength region was observed, e.g., in a discharge [10]. It is precisely for these bands that the location of the corresponding potential curves is most favorable (see Table 1). The inevitable loss in this case will be the emission of the more intense γ bands of NO, for which the upper state $A^2\Sigma^+$ is located quite close to the upper state $B^2\Pi$ of the β bands, but the corresponding potential curve is hardly displaced relative to the $X^2\Pi$ potential curve of the ground state.

The radicals OH and SH can, in principle, be sources of lasing in the near ultraviolet upon excitation with radiation at $\lambda < 2000$ Å. Unfortunately, there are no data on the position of the potential curves and on the probability of the working transition $A^2\Sigma^+\!-\!X^2\Pi$ for the SH radical.

A shortcoming of the $CaBr_2$ molecule is the need for rather strong heating (T_{boil} = 812°C).

Among the radicals PbCl, SnCl, NH_2, whose radiation lies in the visible part of the spectrum, the most complete and favorable data for lasing are possessed by the radical PbCl. The only missing data are on the probabilities of the working transition $A^2\Sigma\!-\!X^2\Pi$, but the transition is allowed and an estimate of the gain cross section and of the threshold concentration of the excited radicals PbCl was made in analogy with the corresponding transition in OH. To obtain a sufficiently high vapor pressure of the $PbCl_2$ and $SnCl_2$ molecules, it is necessary to have a rather high temperature. Thus, in the case of $PbCl_2$, the vapor pressures needed to obtain 1 and 100 torr are 547 and 784°C, and the respective values for $SnCl_2$ are 316°C and 493°C [14].

Unfortunately, there are very few prospects of obtaining lasing on the α bands of ammonia, owing to the lack of data on the positions of the potential curves. A favorable aspect is the convenience of working with the gaseous molecules NH_3 and $H_2N\!-\!NH_2$ without a high temperature, and the relative ease of obtaining the visible luminescence by excitation with sufficiently longwave radiation (see Table 1).

Thus, the most promising object for lasing in the visible and in the near infrared regions of the spectrum are the radicals NO, CSe, PbCl. As seen from Table 1, the threshold concentrations of the excited radicals CSe, PbCl, and NO vary in the range $\Delta N \approx 10^{12}\text{-}10^{14}$ cm^{-3}. We recall in this connection that the corresponding value for a photodissociation iodine laser with τ_r = 0.2 sec and $\sigma_{amp} \approx 10^{-17}$ cm^2 (for the Doppler line width) is $\Delta N \approx 10^{15}$ cm^{-3} [15]. As can be seen from the foregoing estimates, the threshold concentrations for the radicals are much lower than for the atomic iodine. We must note here, however, the following aggravating circumstances: 1) excitation of these radicals calls for radiation with much shorter wavelengths than the excitation of iodine ($\lambda_{max} \approx 2600$ Å); 2) the short radiative lifetimes of the radicals limit the time of accumulation of the threshold concentrations; thus, for the radicals CSe and PbCl this time is $\tau_r \approx 10^{-8}$ sec; for the NO radicals this time is somewhat longer, $\tau_r \approx 3\cdot10^{-6}$ sec, whereas for atomic iodine, owing to the low radiative probability of the transiton, the time of inversion accumulation is long, amounting under real typical conditions to $\sim 10^{-3}$ sec [16].

We note that when allowed transitions with $\tau_p \approx 10^{-8}$ sec are used, the role of the quenching processes, i.e., of the nonradiative excitation losses, is decreased, inasmuch as only anomalously strong quenching processes can manifest themselves in such short time. Thus, at a quenching-particle concentration $N \approx 10^{18}$ cm^{-3}, the quenching constant k =

$\langle v\sigma_{\tau}\rangle \geqslant 10^{-10}$ cm$^3\cdot$sec^{-1}. We recall that for atomic iodine, whose excitation energy is $\sim$1 eV, much lower than the $E_1 \approx$ 2-5 eV of the considered excitations of the radicals, the largest quenching constants amount to k $\approx 10^{-11}$ cm$^3\cdot$sec^{-1} [17].

Proceeding to a discussion of the atoms, we must note the following circumstance: Bearing in mind the excitation of the atoms in photodissociation of molecules, the most convenient are compounds that produce the atoms in a single photodissociation act. Such compounds are primarily molecules containing monovalent atoms (elements of groups I and VII of the periodic system), a number of molecules containing atoms of group VI, as well as dimers of various elements. It is precisely to these compounds that we shall pay principal attention. The use of atoms with valence larger than unity calls for considerable consumption of optical energy to break the bonds and is therefore of little advantage.

Among the compounds of the elements of the first group, the most convenient objects are halides of metals, such as LiI, LiBr, NaI, NaBr, RbI, CsI, AgI and others, whose photodissociation processes have been well invesstigated [12]. These compounds have not-too-high dissociation energies (1.5-4 eV), but are at the same time stable enough to evaporate without noticeable decomposition. As a result of their investigations, the authors of [12] have reached the conclusions that, depending on the energy of the acting photon, these molecules decay via the following channels:

$$MX + \hbar\omega \rightarrow \begin{cases} \rightarrow M + X, & \text{(I)} \\ \rightarrow M + X', & \text{(II)} \\ \rightarrow M^* + X\,(X'), & \text{(III)} \\ \rightarrow M^+ + X^-, & \text{(IV)} \end{cases}$$

where M is the metal atom; X, halide atom; M* and X', metal and halide atoms in the excited states; and M$^+$ and X$^-$, corresponding ions.

In decay via channel III, the atoms of both the metal and the halide can be in different excited states, depending on the energy of the illuminating photon. These regularities were observed in experiment in the photolysis of the molecules NaI, TlI, and others [12, 18].

Alkali-metal atoms, while having transitions in the visible region of the spectrum, are hardly of any interest at present as active media for high-power gas lasers. The point is that the considered transitions are allowed (s–p) transitions with very high transition probabilities ($\sim$10^7-10^9 sec^{-1}), so that it is impossible to accumulate high concentrations of the excited atom in the nearest state ^2P. We shall pay principal attention hereafter to forbidden atomic transitions, where there is a possibility of accumulating excited atoms for a sufficiently long time. In this case, interest attaches to the secondary processes of recombination of the fragments of the photodissociation of the molecule, as a result of which inverted population of certain atomic states can arise.

Thus, rather excessive material on the investigation of metal halide molecules such as NaI, NaCl, TlI, etc. [12] shows that the most typical in the photodissociation of these molecules is formation of products in all possible excited states that are allowed by the pump-photon energies. In this case, generally speaking, no inverted population of the atomic levels is produced in the very primary photodissociation acts.

The lowest excited states of the atoms of the halides of F, Cl, Br, and I produce transitions in the infrared, the shortest wavelength being for λ = 1.315 μm. It is this atomic-iodine transition $^2P_{1/2}$–$^2P_{3/2}$, λ = 1.315 μm which is used in the already-mentioned and presently well-known photodissociation iodine laser. Photodissociation of molecules of the type CF$_3$I, C$_3$F$_7$I, etc. produces with good accuracy only excited iodine atoms I*($^2P_{1/2}$), and it is this which produces the lasing on the $^2P_{1/2}$–$^2P_{3/2}$.

It is interesting to note that detailed investigation of the kinetics of the reactions that take place in the iodine laser have shown [16, 19] that the unexcited I($^2P_{3/2}$) and excited iodine atoms I*($^2P_{1/2}$)(E($^2P_{1/2}$) $\approx$ 1 eV) recombine entirely differently with the CF$_3$ radicals to form the initial molecule CF$_3$I under conditions when the third body is the CF$_3$I molecule. It was found [16] that the processed I$(^2P_{3/2}) + CF_3 \xrightarrow{k} CF_3I$ is very intense, k = $9\cdot10^{-12}$ cm$^3\cdot$sec^{-1}, whereas the corresponding process with participation of the excited iodine

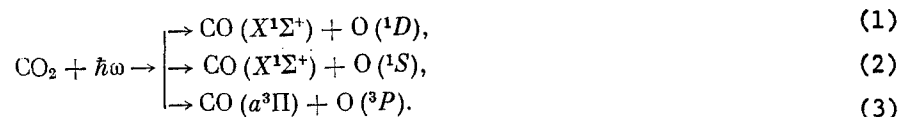$CF_3 + I*(^2P_{1/2}) \xrightarrow{k*} CF_3I$ is not very effective, $k* < 2 \cdot 10^{-13}$ cm$^3 \cdot$sec^{-1}. So large a difference between the rate constants of these recombination reactions gives grounds for hoping to obtain lasing on the transition $^2P_{1/2}-^2P_{3/2}$ of atomic iodine even in the absence of inversion in the very primary photodissociation act of the CF$_3$I molecule.

Thus, even if the inverted population of the atomic levels does not arise in the primary photodissociation act of the molecule, it can appear as a result of recombination of the fragments of the molecule. It seems to us that this mechanism for inversion, both with atomic and with simple molecular fragments of the initial molecule, can be more probable than immediate inversion in the primary act. Unfortunately, there are few data on the shapes of the potential interaction curves (or surfaces for polyatomic molecules) for excited states of atoms contained even in the simplest molecules. For example, for the CF$_3$I molecule, the potential curve corresponding at large distances to the excited state I*($^2P_1/2$) of iodine was heretofore unknown. Measurements [16] of the rate constants have shown that the corresponding potential curve (the fragment CF$_3$ can be regarded with good accuracy as indivisible) I* + CF$_3 \rightarrow$CF$_3$I' either has a very shallow minimum $\Delta E \approx kT \approx 0.02$ eV or has none whatever, i.e., is repulsive. As a rule, the potential curves for excited states have shallower minima located at large distances compared with the corresponding curves for the unexcited states [11]. This means that more typical is a weaker interaction of the neutral particles in electron-excited states than in normal ones. For sufficiently strongly excited states, the potential curves may have no minima at all [20]. Therefore, the situation in the CF$_3$I molecule is apparently not the only exception. Unfortunately, the experimental data on recombination of excited atoms are at present very scanty.

An interesting situation from this point of view pertains to the elements of group VI of the periodic system. For these elements, both possibilities of inversion on atomic transitions can be realized: 1) in the primary photodissociation act of the series of compounds of the type CO$_2$, CS$_2$, CSe$_2$, etc.; 2) as a result of predominant recombination of normal triplet atoms O, S, Se, and Te.

The atoms O, S, Se, and Te of group VI of the periodic system have transitions between terms of the ground electronic configuration, which lie in the visible region of the spectrum and have therefore long attracted attention [21]. Table 2 lists the wavelengths of these transitions and are estimates of the probability. The values of the intermediate-coupling parameters were taken from [20]. The obtained transition probabilities, at $\sim$100% accuracy of our estimates, practically coincide with the published [17, 22] values for oxygen and sulfur for the $^1S_0-^1D_2$ transition. We found no such data for the elements Se and Te in the literature. The values listed in the table for the threshold concentrations of the excited atoms were calculated in the same manner as in Table 1, from the condition that the obtained gain be k = 10^{-2} cm^{-1}. Doppler line widths were assumed. The asterisks mark the transitions that are, in our opinion, most promising. The sources of excited atoms of group VI can be molecules such as CO$_2$, listed in the last column of the table.

Thus, e.g., it is known that the Wigner—Witmer rule is satisfied with good accuracy in photodissociation of the CO$_2$ molecule [11, 13], and that the photodecay proceeds mainly in the following manner [11, 13]:

$$CO_2 + \hbar\omega \rightarrow \begin{cases} \rightarrow CO \, (X^1\Sigma^+) + O \, (^1D), & (1) \\ \rightarrow CO \, (X^1\Sigma^+) + O \, (^1S), & (2) \\ \rightarrow CO \, (a^3\Pi) + O \, (^3P). & (3) \end{cases}$$

Thus, in this case, owing to the spin conservation law, the oxygen atoms are produced predominatly in the singlet excited states ^1D and ^1S. The energetic reaction (1) is possible upon excitation with light of wavelength $\lambda < 1650$ Å, the reaction (2) at $\lambda < 1273$ Å, and the reaction (3) at $\lambda < 1070$ Å [13]. Photodecay in accordance with the reaction (3) does not violate the spin-conservation law, by required excitation of very short wavelength because of the high energy of the state CO($a^3\Pi$), namely $\sim$6 eV (see Table 1). The photolysis of CO$_2$ under the influence of sufficiently intense ultraviolet radiation is, therefore, really the source of the excited oxygen atoms O(^1D) and O(^1S), and can in principle ensure conditions for lasing on the transitions $^1S_0-^3P_1$, $\lambda = 2972$ Å and $^1P_2-^3P_2$, $\lambda = 6300$ Å. As seen from Table 2, the probabilities of these transitions for atomic oxygen are very low and, accordingly, the threshold concentrations of the excited atoms in the states $^1S_0$ and $^1D_2$ are quite high. It is, therefore, quite difficult to obtain lasing on the oxygen atom.

TABLE 2

Element	Transition	λ, A	Transition probability, sec^{-1}	ΔN_{thr}, cm^{-3}	Molecule
O	$^1S_0$—$^1D_2$	5577	1,1	$5 \cdot 10^{16}$ *	CO_2, O_2
	$^1S_0$—$^3P_1$	2972	0,12	$3 \cdot 10^{18}$	
	$^1D_2$—$^3P_2$	6300	10^{-2}	$3 \cdot 10^{18}$	
S	$^1S_0$—$^1D_2$	7725	0,8	$2 \cdot 10^{16}$ *	CS_2, COS, S_2
	$^1S_0$—$^3P_1$	4600	0,6	$1,4 \cdot 10^{17}$	
	$^1D_2$—$^3P_2$	10800	$4 \cdot 10^{-2}$	$1,6 \cdot 10^{17}$	
Se	$^1S_0$—$^1D_2$	7770	1	$2 \cdot 10^{16}$ *	CSe_2
	$^1S_0$—$^3P_1$	4890	7	$\sim 10^{16}$ *	COSe, CSSe, Se_2
	$^1D_2$—$^3P_2$	10400	0,6	10^{16}	
Te	$^1S_0$—$^1D_2$	7900	2	$0,8 \cdot 10^{16}$ *	COTe, CSTe, Te_2
	$^1S_0$—$^3P_1$	5430	10	$\sim 10^{15}$ *	
	$^1D_2$—$^3P_2$	9480	5	$2 \cdot 10^{15}$	

On going to heavier atoms of group VI, however, the transition probabilities increase and the threshold concentrations decrease snd become realistic for the Se and Te atoms (see Table 2). One can expect the photodissociation of the molecules CS_2, CSe_2, COS, COSe, COTe, whose ground state is $X^1\Sigma$, just as of the molecule CO_2, will be similar to the listed photodissociation processes of the CO_2 molecule, i.e., that the processes will have a maximum probability of spin conservation. One can therefore hope to obtain, by photolysis of these molecules, lasing on the transitions $^1S_0$—$^3P_1$, $^1D_2$—$^3P_2$ of the atoms S, Se, and Te. It is not excluded, however, that the spin-conservation rules may be violated for the heavier molecules with Se and Te atoms.

Excited group-VI atoms O, S, Se, and Te can be obtained not only from the CO_2-type molecules listed above, but also from the O_2, S_2, Se_2, and Te_2 dimer molecules. The ground state of such molecules is the term $X^3\Sigma_d^-$, and therefore the principal photodissociation processes, at least for the molecules O_2 and S_2 [11, 13], proceed via triplet excited states. Thus, e.g. [13], the main process of photodissociation of the O_2 molecules in the region of the Schuman—Runge bands $\lambda \approx 2000$ Å is

$$O_2 \,(X^3\Sigma_i^-) + \hbar\omega \to O_2 \,(^3\Sigma_d^-) \to O \,(^3P) + O \,(^1D), \tag{4}$$
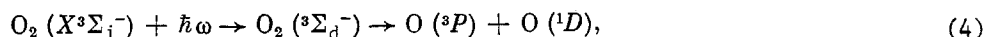
and the following transition is allowed at $\lambda < 1340$ Å:

$$O_2 + \hbar\omega \to O \,(^3P) + O \,(^1S). \tag{5}$$

In contrast to the CO_2 molecule, the photodissociation of O_2 does not lead to inverted population of the levels ^1D and ^1S of atomic oxygen, but can ensure sufficient population of the excited levels ^1D and ^1S. Population inversion of the levels ^1D and ^1S of atomic oxygen can, in principle, be produced by recombination of oxygen atoms in the states ^3P, ^1D, ^1S into the O_2 molecule. It can be expected, however, that the oxygen atoms in singlet states practically do not recombine into molecules because of the fully paired spins, i.e., the processes

$$O \,(^1S) + O \,(^1S) + M \to O_2 + M,$$
$$O \,(^1D) + O \,(^1S, \,^1D) + M \to O_2 + M, \tag{6}$$
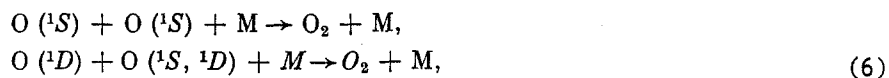
where M is the third body needed for impact stabilization of the molecule, corresponds to almost-repulsive potential curves.

The potential curves having minima correspond to the following recombination reactions:

$$O \,(^3P) + O \,(^3P) + M \to O_2 + M \tag{7}$$

$$O \,(^3P) + O \,(^1D) + M \to O_2 + M, \tag{8}$$

$$O \,(^3P) + O \,(^1S) + M \to O_2 + M. \tag{9}$$

It is easy to verify that in the course of the reactions (7)-(9) inversion can occur on the transitions ^1S—^3P and ^1D—^3P, owing to the additional channel for the departure of the $O(^3P)$ atoms in accord with reaction (7). However, the number of recombination constants of the oxygen atoms in excited states, i.e., of the rate constants of reactions (8) and (9),
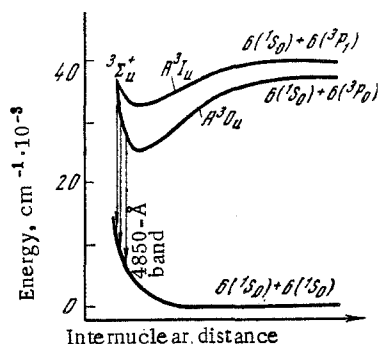
Fig. 1. Potential curves
of lower excited states of
the Hg_2 molecule [13].

is not sufficient for a concrete calculation. The situation may be similar also for the
molecules S_2, Se_2, and Te_2.

An interesting situation that is the direct opposite of the one considered above arises
in the case of recombination of atoms of group II of the periodic system. Since the ground
term of these atoms if $^1S_0$, the atoms in the ground state do not recombine into molecules.
More accurately speaking, the electronic molecular term has a very small minimum connected
with the van der Waals attraction forces [11], but this minimum is locates, as a rule, at
rather large distances and is, therefore, of no significance for our purposes. At the
usual internuclear distances r $\approx$ 1.5-4 Å the potential curve of the ground state of mole-
cules of the second group can be regarded as purely repulsive.

By way of illustration, Fig. 1 shows the potential curves of the molecule Hg_2 [13].
When one of the atoms is excited into the triplet state ^3P, a bound state of the molecule
Hg_2^* can be produced, similar to the excimers Xe_2^*, Kr_2^*, XeF^* and others of noble gases [24].
In principle, the transition of Hg_2^* from the bound A^3O_u state into the ground repulsive
state can be the basis for lasing, in analogy with the presently well-known excimer lasers
using noble gases and their monohalides [24, 25]. It must be noted that the excitation of
the triplet state of atoms of the second group lies much lower than the level of the exci-
tations of the noble gases, and is therefore easier to effect, particularly by using light
or electrons from a discharge. We present below the wavelengths and the probabilities of
the intercombination transitions $^3P_1-^1S_0$ [2]:

Element	Be	Mg	Ca	Sr	Ba	Zn	Cd	Hg
λ, A	4840	4571	6573	6893	7911	3075	3261	2537
A, sec^{-1}	—	260	$5 \cdot 10^3$	10^4	$5 \cdot 10^5$	$4 \cdot 10^4$	$4,6 \cdot 10^5$	10^7

Among the atoms of the second group, the most convenient from the considered point of
view are the atoms Zn, Cd, and Hg. Thus emission of Hg_2^* molecules (4850-Å band) was ob-
served when Hg vapor and nitrogen were eliminated with light at λ = 2537 Å [13]. The con-
sidered intercombination transitions, while forbidden, are characterized for the heavy atoms
Zn, Cd, and particularly Hg, by rather large values of the probabilities and, accordingly,
by low radiative lifetimes. For an effective use of the excited atoms it is, therefore,
necessary that the probability of the recombination process Hg $(^1S_0)$ + Hg (^3P) + M $\xrightarrow{k_p}$ Hg_2^* +
M$\rightarrow W_{rec}$ exceed the probability of the radiative decay of the Hg(^3P) level. For mercury, this
condition (see Table 3) leads to the following limitations on the concentration of the normal
atoms Hg($^1S_0$) and of the buffer gas [M]:

$$W_{rec} = k_r \text{[M] [Hg ($^1S_0$)]} > 10^7 \text{sec}^{-1}.$$

Assuming $k_r \approx 10^{-31}$ cm$^6 \cdot$sec^{-1} (a typical value for a ternary combination of atoms
[26]) we obtain [M][Hg($^1S_0$)] > 10^{38} cm^{-6}. If we assume a buffer-gas concentration [M] =
$3 \cdot 10^{19}$ cm^{-3}, corresponding to atmospheric pressure, the concentration of the Hg atoms in
the ground state $^1S_0$ should be no less than $3 \cdot 10^{18}$ cm^{-3}.

For Zn and Cd atoms, the concentration limits are lower in accordance with the values
of the transition probabilities (see above) [27].

To produce sufficient concentrations of normal and excited (^3P) atoms of Zn, Cd, and Hg, we can use photolysis of organometallic compounds of these elements such as $Zn(CH_3)_2$, $Cd(CH_3)_2$, $Hg(CH_3)_2$, $Zn(C_2H_5)_2$ etc., which have sufficiently high vapor pressures at moderate temperatures. In this case, it is necessary for the light to dissociate two bonds of the atom besides exciting the triplet state. The energy of breaking the second bond is, as a rule, lower than that of the first, therefore, e.g., for dissociation from the molecule $Cd(CH_3)_2$ and dissociation with excitation of the atom $Cd(^3P)$, the photon energy necessary is ~3 eV and, with excitation, $3 + 3.8 = 6.8$ eV, respectively; for $Zn(CH_3)_2$ we have 3.5 and 7.5 eV, and for $Hg(CH_3)_2$ 3 and 8 eV, respectively.

We can, of course, also use in this case the standard device of directly exciting the Zn, Cd, and Hg atoms by electrons or by an electron beam, as is customarily done in excimer lasers.

As for the atoms of the remaining groups of the periodic system, we can note here only the following: Forbidden transitions between terms of the ground electronic configuration in the visible region of the spectrum include, besides the elements of groups II and VI considered above, the atoms of groups IV and V of the periodic system. Since the elements of these groups are polyvalent, to obtain sufficiently high concentrations of the excited atoms the only convenient molecules are dimers of the corresponding elements. As for the atoms of group IV (configuration p^2), on the basis of the complete analogy between the atomic terms and the terms of the atoms of group VI (configuration p^4) one might have expected to obtain inversion for the same reasons discussed above as for the group VI dimers O_2, S_2, Se_2, and Te_2. Thus, in the fourth group the most convenient are dimers of tin Sn_2 ($E_{dis} = 47$ kcal/mole ≈ 2 eV) and lead Pb_2 ($E_{dis} = 24$ kcal/mole ≈ 1 eV). We encounter here, however, an insurmountable contradiction. On the one hand, very high temperatures $T \gtrsim 1000°C$ are needed to obtain sufficient concentrations of the group IV atoms. On the other hand, the binding energies of the dimers are small and at these temperatures practically all the Sn_2 and Pb_2 molecules are thermally dissociated and consist of atoms. It is therefore impossible to speak of production of inversion between the nearest excited and ground states of the atom.

The dimers of group V, namely P_2 ($E_{dis} \simeq 5$ eV), As_2 (≈ 3.9 eV), and Sb_2 ($E_{dis} \approx 3$ eV) have a stronger bond, so that one can hope that even at sufficiently high temperatures $T > 1000°C$ the gas will consist of dimer molecules. However, the photodissociation of these molecules has, at present, hardly been investigated, and information on the inverse recombination reactions of the excited atoms are completely lacking.

In conclusion, we stop to discuss the possibility of simultaneously using both an atomic and a molecular transition in the photodissociation of a molecule. By way of example we consider the possible photodissociation of the CSe_2 molecule under the action of a sufficiently powerful source with a continuous spectrum:

1) $CSe_2 (X^1\Sigma) + \hbar\omega_1 \rightarrow CSe(X^1\Sigma) + Se(^3P)\hbar\omega_1 \gtrsim 3.5$ eV,

2) $CSe_2 + \hbar\omega_2 \rightarrow CSe (X^1\Sigma) + Se (^1D)\hbar\omega_2 \gtrsim 5$ eV,

3) $CSe_2 + \hbar\omega_3 \rightarrow CSe (X^1\Sigma) + Se (^1S) \hbar\omega_3 \gtrsim 6.2$ eV,

4) $CSe_2 + \hbar\omega_4 \rightarrow CSe (^1\Pi) + Se (^3P) \hbar\omega_4 \gtrsim 7.8$ eV,

5) $CSe_2 + \hbar\omega_5 \rightarrow CSe (^1\Pi) + Se (^1D, ^1S) \hbar\omega_5 > 9.3$ eV.

According to the spin conservation law, the channels 1) and 4) may be suppressed, as is the case for the lighter molecule CO_2. But even without this circumstance, inversion can be produced on the atomic levels $Se^1S_0-^3P$ and $^1P-^3P$ as a result of predominant recombination of the unexcited atoms $Se(^3P)$. Thus, the photodecay channels 2) and 3) are useful. Lasing on the allowed molecular transitions $CSe(^1\Pi-X^1\Sigma)$ can, as discussed above, occur also without inversion of the population of the $^1\Pi$ state on account of a shift of the corresponding potential curves (see Table 1). Thus, the only one of the listed photodissociation channels is (1), and the efficiency of the profitable use of energy $\eta = E_{use}/E_{tot}$ in the remaining channels 2)-5) are $\eta_2 \approx 0.3$, $\eta_3 \approx 0.45$, $\eta_4 \approx 0.5$, $\eta_5 \approx 0.4$, respectively. We see, therefore, that an extensive range of emission of a source with photon energy $\hbar\omega > 5$ eV, up to energies $\hbar\omega \gtrsim 9$ eV, can be used in principle by a working medium consisting of CSe_2 molecules to obtain lasing in the visible band, and the efficiency in terms of conversion of the optical pump energy into lasing energy can be quite high, $\sim30-50\%$. We recall that this quantity for an iodine laser on CF_3I molecules is $\sim20\%$.

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