A recombination laser based on electron transitions in diatomic molecules

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An analysis is made of the conditions for stimulated emission of visible radiation due to electron transitions in diatomic molecules formed as a result of recombination of atoms. The population inversion mechanism is considered for the O_2 molecule and an estimate of the gain is obtained for the $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$ transition ($\lambda = 4881$ Å). The possibility of stimulated emission of other wavelengths is considered briefly.

Molecular gases are used widely as the active media of lasers. Infrared lasers utilizing vibration-rotational transitions in diatomic (CO, HF, HCl, . . .) and polyatomic (CO_2, N_2O, . . .) molecules are of considerable practical importance. We shall show that efficient laser action should be obtained in the visible and ultraviolet range by utilizing transitions between the electronic states of diatomic molecules formed as a result of recombination in a dissociated gas.

We shall consider the characteristic features of the proposed lasers by analyzing the specific case of the O_2 molecule. Figure 1 shows the potential curves of the oxygen molecule. The energy ~5.1 eV of the dissociation producing $O(^3P) + O(^3P)$ corresponds to six bound electronic states $c\,^1\Sigma_u^-$, $A\,^3\Sigma_u^+$, $C\,^3\Delta_u$, $b\,^1\Sigma_g^+$, $a\,^1\Delta_g$, $X\,^3\Sigma_g^-$; the other nine terms which converge to the same energy are repulsive. Radiative transitions between any of these six electronic states are forbidden and the corresponding lifetimes are $\gtrsim 0.1$ sec. A transition from a higher term $B\,^3\Sigma_u^-$ ($B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-$), corresponding to the dissociation products $O(^3P) + O(^1D)$, is allowed and the lifetime in this case is $\sim 10^{-5}$ sec.[1]

We shall consider the recombination kinetics. Under full thermodynamic equilibrium conditions corresponding to a temperature T_0 and pressure P_0, the degree of dissociation is

$$\varkappa = [(K^2+4KP_0)^{1/2} - K]/2P_0, \qquad (1)$$

where $K = 8.46 \cdot 10^4\, T_0^{0,5} \exp(-59\,380/T_0)$ [atm] is the equilibrium constant of the reaction $O_2 \rightleftarrows 2O$. At $T_0 \lesssim 4000$°K, the bulk of the atomic oxygen is in the ^3P ground state and the oxygen molecules are in the states $X\,^3\Sigma_g^-$ ($v \approx 0$–3). Rapid cooling (such as that during expansion) results in the recombination of atomic oxygen which can occur along two channels:

$$O+O \rightarrow O_2 + h\nu, \qquad (2a)$$

$$O+O+M \rightarrow O_2 + M. \qquad (2b)$$

The first of these channels represents the bimolecular reaction between the $O(^3P)$ atoms along one of the dissociating terms (most probably $^3\Pi_u$), which produces the excited electronic state $B\,^3\Sigma_u^-$ ($v \sim 4$) and results in the emission of a photon due to the allowed transition $B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-$.[2] Although the rate of this process is relatively low, because it involves only the atoms which have translational relative-motion energies of $\gtrsim 3kT$, it plays an important role at low pressures (below 1 atm). Estimates of the rates of the reactions (2a) and (2b) obtained using the rate constant found in[2] for (2a) indicate that at temperatures $T_0 = 4000$°K and pressures $P_0 \gtrsim 10$ atm the reaction (2b) predominates.

The three-particle process (2b) produces molecules in the highest vibrational levels of any one of the electronic states and these levels lie within the interval ~kT. Since the three highest terms are shallow, only a few collisions are needed to fill them. Relaxation to lower electronic states is difficult and requires $\gtrsim 10^5$ collisions (according to Izod and Wayne,[3] the number of collisions needed to empty the state $^1\Sigma_g^+$ is $\sim 10^5$, whereas, in the case of the state $^1\Delta_g$, the number of collisions found by Clark and Wayne[4] is $\sim 5 \times 10^7$). Therefore, during rapid cooling, the upper electron states, which are unstable, will be overpopulated. The filling of the terms $b\,^1\Sigma_g^+$, $a\,^1\Delta_g$, $X\,^3\Sigma_g^-$ by multistage transitions between vibrational levels is governed, because of their considerable depth, by the "bottleneck" v^*, where the rates of the vibration-translational (V-T) relaxation and of the vibration-vibrational (V-V) exchange become equal; in the case of diatomic molecules, we have $v^* \sim 10$–20.[5] There is a considerable probability of the escape back to the continuous spectrum in the case of molecules with $v > v^*$.

Thus, recombination processes should result in a population inversion between the lowest vibrational levels of the states $c\,^1\Sigma_u^-$, $A\,^3\Sigma_u^+$, $C\,^3\Delta_u$ and the high ($v \gtrsim 6$) levels of the upper electronic states.

We shall consider in greater detail the probability of a population inversion due to transitions in the first Herzberg band system $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$. Measurements of the absolute intensities $S_{v'v''}$ of this system were made in[6] for $v' = 0$–11 and $v'' = 0$–12. These intensities can be substituted in the formula

$$A_{v'v''} = 64\pi^4 S_{v'v''}/3hg\lambda^3_{v'v''} \qquad (3)$$

in order to calculate the Einstein coefficients $A_{v'v''}$ of spontaneous transitions ($g = 3$ is the degree of degener-

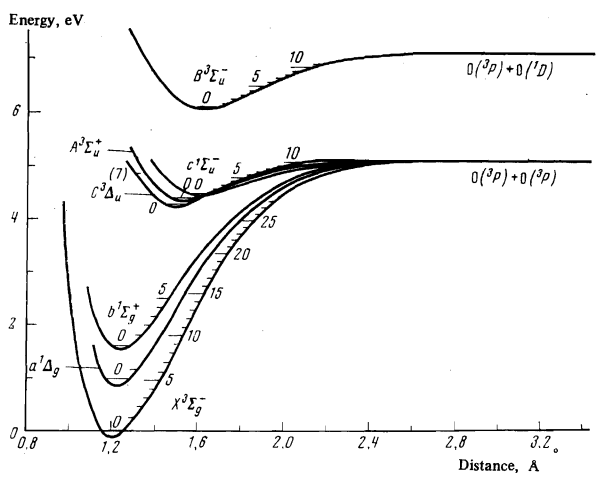

FIG. 1. Potential curves of the O_2 molecule.

TABLE I

	v′	v″								
		4	5	6	7	8	9	10	11	12
$\lambda_{v'v''}$, Å	0	3457	3641	3843	4064	4308	4579	4881	5219	5600
$A_{v'v''}$, sec^{-1}		—	—	0.4	0,572	0.67	0.636	0.505	0.332	0.197
$\lambda_{v'v''}$, Å	1	3367	3541	3732	3940	4169	4422	4703	5016	5367
$A_{v'v''}$, sec^{-1}		0.436	0.763	0.94	0.88	0,533	0.171	—	—	—

acy of the upper level). Table I gives the results for v′ = 0 and 1 and v″ = 4–12. The higher values of v′ are excluded because of their low populations and the higher values of v″ are excluded because of their relatively high populations.

It is clear from Table I that, in the wavelength range 3500–4900 Å there are several transitions with comparable probabilities $A_{v'v''}$.[7] The laser action is more likely as a result of the transitions v′ = 0 → v″ = 8–10. This conclusion is based on the following considerations: v′ = 0 has a higher population than v′ = 1; transitions to $v'' \lesssim 6$ are less likely; for a Lorentzian line width the gain falls as the square of the wavelength and at λ ~ 3500 Å it is, other conditions being equal, half the gain at λ ~ 4900 Å; in the case of the transitions corresponding to the shortest wavelengths, there is a significant reabsorption of the radiation because of the allowed $X\,^3\Sigma_g^- \rightarrow B\,^3\Sigma_u^-$ transitions in the Schumann-Runge bands. The transition v′ = 0 → v″ = 10 (λ = 4881 Å) satisfies most fully the Franck-Condon principle.

In addition to the $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$ transitions, a population inversion is also possible at other wavelengths, for example,

$$
\begin{aligned}
&c\,^1\Sigma_u^-(v'=0) \rightarrow X\,^3\Sigma_g^-(v''=12), \quad \lambda\sim 5300\ \text{Å},\\
&c\,^1\Sigma_u^-(v'=0) \rightarrow a\,^1\Delta_g(v''\sim 11), \quad \lambda\sim 7600\ \text{Å},\\
&c\,^1\Sigma_u^-(v'=0) \rightarrow b\,^1\Sigma_g^+(v''\sim 9), \quad \lambda\sim 9200\ \text{Å},\\
&A\,^3\Sigma_u^+(v'=0) \rightarrow a\,^1\Delta_g(v''\sim 8), \quad \lambda\sim 6400\ \text{Å},\\
&A\,^3\Sigma_u^+(v'=0) \rightarrow b\,^1\Sigma_g^+(v''\sim 7), \quad \lambda\sim 8100\ \text{Å},\\
&C\,^3\Delta_u(v'=0) \rightarrow X\,^3\Sigma_g^-(v''\sim 8), \quad \lambda\sim 4400\ \text{Å},\\
&C\,^3\Delta_u(v'=0) \rightarrow a\,^1\Delta_g(v''\sim 7), \quad \lambda\sim 6300\ \text{Å},\\
&C\,^3\Delta_u(v'=0) \rightarrow b\,^1\Sigma_g^+(v''\sim 6), \quad \lambda\sim 7550\ \text{Å}.
\end{aligned}
\tag{4}
$$

However, in contrast to the $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$ transition, no information is available on the Einstein coefficients of the forbidden transitions of Eq. (4). Even in the case of inversion, if $A_{v'v''}$ is too small, the gain may be insufficient for laser action.

A qualitative estimate of the capabilities of a laser utilizing the $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$ transition can be obtained by assuming that a gas at an initial temperature T_0 = 4000° K and initial pressure P_0 = 10 atm [$\kappa \approx 35\%$, see Eq. (1)] expands through a Laval nozzle into vacuum. This results in an intensive recombination of atomic oxygen into molecules and the rate of this process falls rapidly with decreasing density. We can assume that chemical reactions are "frozen" when the pressure ~1 atm is reached and the temperature falls to ~2000°K. These conditions can be achieved after a very short expansion time ~10^{-5} sec. During this time interval, the particles experience not more than 10^4-10^5 collisions. This makes it possible to establish a quasiequilibrium distribution over the vibrational levels of the electronic states and bring into equilibrium the states $c\,^1\Sigma_u^-$, $A\,^3\Sigma_u^+$, $C\,^3\Delta_u$ as a result of nonadiabatic transitions.

We shall assume, for the sake of simplicity, that the recombination of atoms is equally likely to terminate at any one of the six lower electronic states. This means that the particle flux Q(t) to the higher vibrational levels of each of these states can be written in the form

$$Q(t) \approx {}^1/_6 [K^{O}\varkappa + K^{O_2}(1-\varkappa)]\varkappa^2 N^3, \tag{5}$$

where K^O and K^{O_2} are the recombination rate constants in the reaction (2b) for M = O and M = O_2; N is the total number of particles per unit volume. Equation (5) ignores the reverse dissociation process because, during rapid cooling, the equilibrium of the reaction (2b) is shifted strongly to the right. Stimulated transitions from one of the higher terms may enhance the recombination flux to all three upper states because they are emptied rapidly in the resonator. Initially, Q(0) exceeds ~3×10^{23} $cm^{-3} \cdot sec^{-1}$. Subsequently, the ratio Q(t)/Q(0) tends to zero with decreasing κ and N but, during the flow time, about 10^{16}-10^{17} molecules per 1 cm^3 may appear in the upper laser level as a result of recombination. Since the lower levels of the transitions under discussion (for example, v″ = 10 in the $A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-$ case) are practically empty, the quoted values of the population of the upper level may be regarded as a rough estimate of the population inversion.

A population inversion of 10^{16}-10^{17} cm^{-3} for the $A\,^3\Sigma_u^+(v'=0) \rightarrow X\,^3\Sigma_g^-(v''=10)$ transition gives rise to a gain of ~10^{-4} cm^{-1}. An increase in the initial pressure to 30–50 atm increases the gain by an order of magnitude.

An analysis of the recombination processes producing the N_2, CO, and NO molecules shows that population inversion should be obtained for several electron transitions.

It follows from the above discussion that the laser action due to electron transitions in diatomic molecules formed as a result of recombination in an atomic gas may be efficient if the initial temperatures and pressures are high. The collisional mechanism (fast V-V exchange) of clearing the lower levels should make it possible to excite large volumes and the gas-dynamic cooling method should help in achieving continuous or quasi-continuous emission.

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