Feasibility of lasing in collision-induced dipole transitions of singlet molecular oxygen

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It is proposed to use molecular oxygen as a source of radiation of powerful ultrashort light pulses by exciting it in the singlet state with a neodymium laser operating in the free-running regime.

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Singlet molecular oxygen $O_2\ ^1\Delta_g$, $O_2\ ^1\Sigma_g^+$, is presently under diligent investigation.[1] Interest in singlet oxygen is due primarily to the fact that owing to its high chemical activity and long lifetime it can play an important role in many physical, chemical, and biological processes. The analysis undertaken in this study shows that singlet oxygen can serve as a high-capacity energy storage device with the possibility of coherent emission of the stored energy in a short pulse. The ground state of O_2 molecule is $^3\Sigma_g^-$, and therefore electric dipole transitions from $^1\Delta_g$ and $^1\Sigma_g^+$ are forbidden. Accordingly, the radiation lifetimes of these states are 45 minutes and 7.1 seconds. The intermolecular interaction lifts the hindrance on the emission for the oxygen, and the so-called cooperative optical transitions are observed[1] with an intensity much higher, determined by the number of collisions per unit time. The transition in the dimer O_2O_2

$$[(^1\Delta_g,\ v=1)(^3\Sigma_g^-)] \leftarrow [(^3\Sigma_g^-)(^3\Sigma_g^-)], \quad \lambda = 1.06\ \mu \tag{1}$$

is at resonance with the emission of Nd^{3+}-glass lasers ($\lambda = 1.06\ \mu$). This makes possible the formation of con-

siderable concentrations of $O_2{}^1\Delta_g$ in the gas phase as well as in the liquid and solid phases. When oxygen is excited into the singlet state, population inversions become possible in various electron-vibrational transitions. Consider, for example, the transitions

$$^1[(^1\Delta_g)(^1\Delta_g)] \to {}^1[(^3\Sigma_g^-, v=1)(^3\Sigma_g^-)], \quad \lambda = 0.703\ \mu, \qquad (2)$$

$$^3[(^1\Delta_g)(^3\Sigma_g^-)] \to {}^3[(^3\Sigma_g^-, v=1)(^3\Sigma_g^-)], \quad \lambda = 1.58\ \mu, \qquad (3)$$

for which the onset of inversion is facilitated by the low population of the final state of the transition at ordinary temperatures. Nor can we exclude the possibility of inverse excitation of the short-wave transitions

$$^1[(^1\Delta_g)(^1\Delta_g)] \to {}^1[(^3\Sigma_g^-)(^3\Sigma_g^-)], \qquad \lambda = 0.634\ \mu,$$

$$^3[(^1\Delta_g)(^3\Sigma_g^-)] \to {}^3[(^3\Sigma_g^-)(^3\Sigma_g^-)], \qquad \lambda = 1.27\ \mu,$$

if the final-state energy of these transitions differs by more than kT from the energy of the removed molecules.

Let us estimate the energy level and pump power necessary for the realization of specially high gains in transitions (2) and (3). The gain of the light wave is equal to

$$\alpha = \frac{c^2}{8\pi^2\nu^2\Delta\nu} \begin{cases} k_2 N_{O_2^*}^2 & \text{for transition (2),} \\ k_3 N_{O_2^*} N_{O_2} & \text{for transition (3),} \end{cases} \qquad (4)$$

where k_2 and k_3 are the emission rate constants for the transitions (2) and (3) respectively, and N_{O*_2} and N_{O_2} are the concentrations of $O_2\ ^1\Delta_g$ and $O_2\ ^3\Sigma_g^-$. The energy of the neodymium-laser flash is effectively absorbed of oxygen in a length $1/\kappa$, where κ is the absorption coeffcient at the given frequency, and the concentration of the $O_2\ ^1\Delta_g$ in the absorption region is

$$N_{O_2^*} = E\kappa/\epsilon S, \qquad (5)$$

where E is the flash energy, ϵ is the quantum energy, and S is the beam cross-section area. We neglect the collision relaxation, since it can be easily estimated from the rate constant of the $O_2\ ^1\Delta_g$ relaxation, namely 2×10^{-18} cm^3 sec^{-1},[2] that the flash duration, several dozen microseconds, is much shorter than the relaxation time up to 200 atm. Substituting (5) in (4) and recognizing that $\kappa = 10^{-6}\,p^2$,[3] where p is the pressure, we obtain for the transition (2)

$$\alpha = \frac{c^2 k_2}{8\pi^2\nu^2\Delta\nu}\left(\frac{E\,10^{-6}p^2}{\epsilon S}\right)^2. \qquad (6)$$

According to the measurements[4-6] we have $k_2 = 2.7\times10^{-23}$ cm^3 sec^{-1} and $\Delta\nu = 10^{-2}\nu$,[1] and for a neodymium laser $\epsilon = 3.3\times10^{-19}$ J. Thus, in accordance with (6), if a laser with an energy flux 1.3×10^4 J/cm^2 per pulse is used for the pumping, then it is possible to obtain in oxygen at a pressure of 200 atm a gain of 10^{-3} cm^{-1} for the transition (2). Since the dissipative processes are not effective, we can expect a high conversion coefficient. The effective absorption length is in this case ~25 cm.

Let us turn to the analysis of the transition (3). Since the emission rate constant in transition (3) is not known exactly, we use the absorption data. The absorption coefficient κ can be expressed in terms of the emission cross section σ_{ul} in the following manner:

$$\kappa = \sigma_{ul}\frac{g_u}{g_l} N_l = \sigma_{ul}\frac{g_u}{g_l} V N_{O_2}^2,$$

where the subscripts u and l pertain to the upper and lower levels respectively, g_u and g_l are the statistical weights of the levels, N_l is the concentration of the absorbing dimers, and V is a factor on the order of the molecule volume. At the same time, the gain α is equal to

$$\alpha = \sigma_{ul} N_u = \sigma_{ul} V N_{O_2^*} N_{O_2},$$

where N_u is the concentration of the emitting dimers. We assume by way of estimates that the factor V is the same for the absorption and emission processes, and that the absorption cross sections for the transitions (1) and (3) are approximately equal.[1] Then

$$\alpha = \kappa\frac{g_l}{g_u}\frac{N_{O_2^*}}{N - N_{O_2^*}}, \qquad (7)$$

where N is the summary concentration of the molecules. It follows from (5) and (7) that to attain a specified gain it is necessary to have a pulse energy flux

$$W = \frac{E}{S} = N\epsilon/[\kappa(\kappa g_l/\alpha g_u + 1)]. \qquad (8)$$

Using the data given above we find that to realize a gain of $\sim10^{-3}$ cm^{-1} in transition (3) in O_2 compressed to 200 atm the necessary value of W amounts to 700 J/cm^2, i.e., less by approximately one order of magnitude than for transition (2). The width of the luminescence spectrum of the considered transitions is ~100 Å, so that picosecond light pulses can be produced.

The neodymium-glass laser is one of the most widely used systems for experiments on laser thermonuclear fusion.[7] The efficiency of such lasers when producing nanosecond pulses is relatively low. In the free-running regime (pulse duration 10^{-4} and larger) the efficiency of the neodymium laser is higher by one order of magnitude. Therefore by storing energy in the molecular oxygen by pumping it with lasers operating in the free-running regime, and then emitting this energy in short pulses, we can increase the total efficiency of the system and obtain the necessary energy levels by simpler means.

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[1] M. Kasha and A.U., Khan, Ann. N.Y. Acad. Sci. 171, 5 (1970).
[2] F.D. Findlay and D.R. Snelling, J. Chem. Phys. 55, 545 (1971).
[3] J. Parker and D. Ritke, J. Chem. Phys. 59, 3713 (1973).
[4] A.M. Falick and V.N. Mahan, J. Chem. Phys. 47, 4778 (1967).
[5] E.W. Gray and E.A. Ogruzlo, Chem. Phys. Lett. 3, 658 (1969).
[6] R.G. Derwent and B.A. Thrush, Trans. Faraday Soc. 67, 2036 (1971).
[7] N.G. Basov, O.N. Krokhin, G.V. Sklizkov, and S.I. Fedotov, Trudy FIAN 76, 146 (1974).