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► To cite this version:

V. Kochelap, V. Datsyuk, I. Izmailov. THEORY OF MOLECULAR LASER EMITTING IN Mid-IR REGION AND UTILIZING SINGLET OXYGEN ENERGY. Journal de Physique IV Proceedings, 1991, 01 (C7), pp.C7-659-C7-662. 10.1051/jp4:19917176 . jpa-00250854

HAL Id: jpa-00250854

<https://hal.science/jpa-00250854>

Submitted on 1 Jan 1991

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THEORY OF MOLECULAR LASER EMITTING IN Mid-IR REGION AND UTILIZING SINGLET OXYGEN ENERGY

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Abstract—A theoretical analysis is made of the kinetics of inverted population of SO_2 levels in a mixture containing vibrationally excited oxygen $O_2(X, v)$, formed as a result of relaxation of the $O_2(^1\Delta)$ electronic energy. It is shown that the gain for the SO_2 transitions at the 12 and 16 μm wavelengths is sufficient to achieve lasing.

1.-Introduction.

At present, chemical singlet oxygen generators have been developed, characterized by the highly efficient formation of electronically excited $O_2(^1\Delta_g)$ molecules [1]. It was established in Refs. 2 and 3 that as a result of the deactivation of a single $O_2(^1\Delta)$ molecule, five vibrational quanta of oxygen are formed in the ground electronic state,

where $n = 0, 1$, and 2 . Therefore, gaseous $O_2(X^3\Sigma_g^-)$ can be obtained at pressures up to 10 Torr with high ($1 + 2$ kK) vibrational and low (300 K) translational temperatures. The high vibrational energy stored in $O_2(X, v)$ may be utilized to obtain lasing in the middle infrared by transfer of vibrational excitation to optically active molecules.

In this paper we give a theoretical background for the development of new mid-IR laser system utilizing the singlet oxygen energy. We propose to use the $O_2(^1\Delta)$ energy by the following two steps. During the first one the $O_2(^1\Delta)$ electronic energy should be converted into the vibrational energy of the $O_2(X^3\Sigma_g^-)$ molecules. During the second step excitation and inverted population of vibrational levels of active molecular acceptor (SO_2) can arise as a result of VV, VV' and VT processes.

2. $O_2(^1\Delta)$ electronic energy conversion into the $O_2(X, v)$ vibrational energy.

The kinetics of the formation of vibrationally excited $O_2(X, v)$ may be investigated taking into account not only process (1) but also the VT relaxation. Numerical calculations show that an appreciable fraction of the $O_2(^1\Delta)$ electronic energy is converted into the $O_2(X, v)$ vibrational energy at temperatures T below 300 K. For example, when $T \leq 250$ K, the efficiency of conversion of the $O_2(^1\Delta)$ electronic energy into the vibrational energy reaches 0.2, and when $T \leq 160$ K, it becomes 0.6. The vibrational temperature of $O_2(X, v)$ may then be $1.5 + 2.5$ kK, depending on the degree of electronic excitation of the oxygen. It is suggested that the vibrationally excited O_2 produced can be used as a vibrational energy reservoir in a laser where $O_2(X, v)$ is mixed with optically active SO_2 molecules.

3. Kinetics of formation of active medium.

The energy levels of O_2 and SO_2 and also the basic vibrational relaxation processes are shown in Fig.1. The kinetics of energy relaxation in an $O_2(^1\Delta)$ - O_2 - SO_2 - O_3 mixture was first studied experimentally in Ref.2. It was established that SO_2 molecules do not interact with $O_2(^1\Delta)$ but have an appreciable influence on the relaxation kinetics of the vibrationally excited $O_2(X)$.

Fig.1. Lowest vibrational levels of SO_2 and O_2 molecules.

The solid arrows indicate the way of the energy transfer and the dashed arrows indicate the laser transitions.

The vibrational relaxation mechanism in an $O_2 - SO_2$ mixture was studied in Refs. 4 and 5. Measurements were made of the times of the main VT and VV' exchange processes. The intramode VV exchange in SO_2 is the fastest process and results in the establishment of a quasi equilibrium distribution of molecules over vibrational levels with a vibrational temperature T_i (i is the mode number). The EV exchange

time in the process (1) is much longer than the times of the VV' exchange between $O_2(\nu_4)$ and $SO_2(\nu_3)$, intermode exchange in SO_2 , and VT relaxation of $SO_2(\nu_2)$. Consequently, in order to obtain lasing on the SO_2 vibrational transitions, SO_2 must be mixed with excited O_2 molecules after completion of process (1).

4. -Population inversion and light gain on SO_2 vibrational transitions.

We have investigated the kinetics of formation of the active medium after mixing of O_2 and SO_2 . The instantaneous mixing approximation has been used. The time dependencies of the T_i have been computed from the rate equations [6] which describe the one- and two- quanta VV' exchange, and VT-relaxation. The change of T has been also taken into account. It was found that the inverted population of the SO_2 vibrational levels arises at a translational temperature of the mixture substantially lower than 300 K. Calculations were made for the case when before mixing the vibrational temperature of $O_2(X, \nu)$ is $T_4 = 1.5$ kK, the oxygen is cooled to $T = 77$ K and its pressure equals 10 Torr. A gas with these parameters can be obtained by cooling a mixture containing 10% $O_2(^1\Delta)$ in a time much shorter than the VT relaxation time of $O_2(X, \nu)$ ($\tau_{VT} = 1 \div 10$ s). The SO_2 parameters before mixing were assumed to be as follows: $T = 200$ K, pressure $1 \div 2$ Torr.

Fig. 2. Time dependences of T_1 (1), T_2 (2), T_g (3), $\Delta N_{32}/5 \cdot 10^{15} \text{ cm}^{-3}$ (4), $\alpha(\lambda = 12 \mu\text{m})/10^{-3} \text{ cm}^{-1}$ (5), $\Delta N_{12}/5 \cdot 10^{15} \text{ cm}^{-3}$ (6), $\alpha(\lambda = 16 \mu\text{m})/10^{-4} \text{ cm}^{-1}$ (7), at SO_2 pressures before mixing of 2 (a) and 1 Torr (b).

The results of the calculations are plotted in Fig.2. It can be seen that after mixing of SO_2 and O_2 , the stretching vibrational modes of SO_2 are populated, and $T_1, T_3 \gg T_2 \approx T$. The population densities ΔN_{i2} of the stretching ($i = 1, 3$) and bending modes have been calculated,

$$\Delta N_{i2} = [\text{SO}_2] Z_v^{-1} [\exp(-g_i/T_1) - \exp(-g_i/T_2)],$$

Here g_i is the characteristic temperature of the i th mode, Z_v is the vibrational statistical sum. The equations from Ref. 6 were used to calculate the optical gains for $001 \rightarrow 010$ ($\lambda = 11.8 \mu\text{m}$) and $100 \rightarrow 010$ ($\lambda = 15.8 \mu\text{m}$) vibrational-rotational transitions:

$$\alpha = \delta_{i2} \Delta N_{i2}$$

where λ is the wavelength; the quantum number of the total rotational moment of the most populated level is five; δ_{32} (in cm^2) = $2 \cdot 10^{-18} \times (200/T)^2 H(\alpha, 0)$; $H(\alpha, 0)$ is the Voigt function /7/; according to the estimates /6/, δ_{12} is 50 times smaller than δ_{32} .

It can be seen from Fig. 2 that the inversion densities $\Delta N_{32} = (2 + 5) \cdot 10^{15} \text{ cm}^{-3}$, and $\Delta N_{12} = 10^{16} \text{ cm}^{-3}$ is maintained for several milliseconds. The gain at $\lambda = 11.8 \mu\text{m}$ is $(1 + 2) \cdot 10^{-3} \text{ cm}^{-1}$. The gain at $15.8 \mu\text{m}$ is higher than 10^{-4} cm^{-1} . The main reason for the loss of the inverted population is heating of the medium that results in filling of the lower laser level. The rate of this heating grows when T increases.

5.-Conclusions.

Singlet oxygen generators make it possible to build a low-temperature continuous-flow molecular laser emitting in the mid-IR spectral region. It is shown that cw lasing at wavelengths of 12 and $16 \mu\text{m}$ can be achieved in $\text{O}_2 - \text{SO}_2$ mixtures by using of the $\text{O}_2(^1\Delta)$ energy.

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