SOVIET PHYSICS JETP VOLUME 34, NUMBER 6 JUNE, 1972

Possibility of Designing Optical Pumping Gas Lasers with Allowed Electron Transitions in Molecules

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Submitted June, 16, 1971

Zh. Eksp. Teor. Fiz. **61**, 2293–2297. (December, 1972)

The gain for allowed electron transitions in molecules of gases at high pressures (tens or hundreds of atmospheres) is estimated. It is suggested that electron-excited molecules be obtained by optical pumping in which use is made of either transitions between the ground and excited states of the working molecules themselves or of resonant absorption lines of noble gas atoms; the excited atoms thus formed should then transfer their energy by collisions to the working molecules. In both cases a sufficiently broad pumping band can be produced at the expense of strong shock broadening of the absorption lines. A small lifetime of particles on the lower laser level may be attained as a result of vibrational-vibrational relaxation of the molecules, provided that the lower laser level is a vibrational excited state of the molecules. As the pumping source in such lasers it seems reasonable to employ powerful electric discharges.

1. The magnitude of the threshold inverted level population in lasers is proportional to the time τ of the radiative transition between these levels, so that the problem of producing lasers based on allowed transitions for which τ is small, $\sim 10^{-8}-10^{-9}$ sec, is therefore attractive. At sufficiently high pressures, an important role can be played in gas lasers by nonradiative deactivation processes of the upper laser level (quenching, chemical reactions, etc.)[1,2], but they become substantial only when the rate of nonradiative deactivation exceeds τ^{-1}, i.e., from this point of view it is also convenient to use transitions with small τ.

In order to obtain a sufficiently large duration and high generation energy at allowed transitions, it is necessary that the lifetime of the particles at the lower level be smaller than τ. For molecular systems, there is a sufficiently universal mechanism, which can ensure a rapid withdrawal of the particles from the lower laser level, namely vibrational relaxation, if the lower laser level is an excited vibrational state of the molecule. It should be noted that relaxation through the vibrational levels is already used in liquid dye lasers[3], where by virtue of the complexity of the molecules themselves this relaxation proceeds very rapidly without participation of other particles. For simpler molecules, the decisive role is played by the collisions between the vibrationally-excited molecule and other particles, to which it transfers its energy. The fastest process in this case is vibrational-vibrational relaxation, at which almost resonant transfer of a molecular quantum from the excited molecule to the unexcited one takes place[4]. The rate of vibrational-vibrational relaxation depends exponentially on the magnitude of the resonance defect. In particular, at a vibrational-quantum difference between the colliding particles of approximately 100 cm^{-1}, approximately 100 collisions are necessary in order to transfer the excitation[5]. At high pressures, when an important role is assumed by multiparticle collisions, the probability of deexcitation of a vibrationally-excited molecule increases.

If we assume as an estimate that the probability of the deexcitation of the vibrationally-excited molecule is $\gamma = 1/100$, then the lifetime of the molecules at the upper vibrational levels will be smaller than 10^{-8} sec if the pressure of the buffer gas, whose vibrational quantum is close to the vibrational quantum of the working molecule, is larger than 10 atm ($N > (\gamma\sigma v\tau)^{-1}$, where $\sigma \sim 10^{-15}$ cm^2 is the collision cross section and $v \sim 4 \times 10^4$ cm/sec is the average velocity). The role of the buffer-gas molecules can also be played by the unexcited working molecules themselves. The choice of a suitable buffer gas is determined by the fact that the constant of the nonradiative deactivation of the upper laser level by this gas should be smaller than the rate of vibrational-vibrational relaxation:

$$k < \gamma\sigma v. \tag{1}$$

In view of the sufficiently large rate of vibrational-vibrational relaxation, one can hope that condition (1) will be satisfied for a large number of molecular systems.

2. The most direct method of obtaining electron-excited molecules is direct optical pumping using the transitions between the ground (X) and excited (A) electronic states of the molecule. At room temperature, the predominantly populated molecular levels are the rotational ones with energy not exceeding (2–3) kT = 400–600 cm^{-1}. If the pressure of the working mixture is so large that the rotational-structure lines superimpose on each other as a result of impact broadening, then each electron-vibrational band has the form of a continuous absorption band with width on the order of (2–3) kT. As a rule, the Franck-Condon factors do not differ strongly for neighboring electron-vibrational bands, and therefore several such bands will take part in the pumping, with a summary effective width 1000–2000 cm^{-1}, i.e., of the same order as in solid-state lasers. The magnitude of the impact broadening can be regulated by introducing noble gases into the working mixture, and the necessary pressure scale amounts to several times 10 atm.

Let us estimate the gain k_g for the $Av' \rightarrow Xv$ transition in the case of direct optical pumping ($X \rightarrow A$), assuming that during the lifetime of the molecules in the state A they do not have time to relax through the vibrational levels of this state. In this case there will exist several independent pump channels ($X0 \rightarrow Av'$) and generation channels ($Av' \rightarrow Xv$). If we disregard the distribution of the molecules over the rotational levels and the concrete arrangement of the rotational-structure lines, and assume that there is one radiation band with width $\Delta\omega \sim kT$, then (according to[6])

$$k_{\mathrm{g}} = \frac{\lambda^2}{4} \frac{q_{v'v} N}{\tau \Delta\omega}$$

where λ is the radiation wavelength, $q_{v'v}$ is the Franck-Condon factor, and N is the total number of molecules at the level Av'. Since

$$N = \tau \int k_{\mathrm{p}}(\omega) I(\omega) d\omega \approx \tau k_{\mathrm{p}} I(\omega) \Delta\omega_{\mathrm{p}}$$

(where $I(\omega)$ is the spectral density of the pumping light flux in photon/cm^2 sec-sec^{-1}, $\Delta\omega_p$ is the pump bandwidth over one electron-vibrational band, and $\Delta\omega_p \approx \Delta\omega \sim kT$, and k_p is the absorption coefficient of the pump light), then

$$k_{\mathrm{g}} = \frac{1}{4} k_{\mathrm{p}} \lambda^2 q_{v'v} I(\omega). \tag{2}$$

If we use a pumping light source with brightness temperature 30 000°K, then $I(\omega) = 2 \times 10^8$ photons/cm^2 in the 1500 Å region. We then find for $\lambda = 2000$ Å, $k_p = 5$ cm^{-1}, and $q_{v'v} = 0.2$ that $k_g = 0.02$ cm^{-1}, which at an excited-layer length ~ 10—100 cm is perfectly sufficient to obtain lasing.

Expression (2) underestimates the gain, which may turn out to be much higher under favorable location of the rotational-structure lines and when account is taken of the vibrational relaxation of the state A.

Direct optical pumping can be used to excite a great variety of molecules. The most interesting is the possibility of exciting hydrogen and deuterium in order to obtain lasing in the vacuum ultraviolet on the transitions $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $C^1\Pi_u \rightarrow X^1\Sigma_g^+$. Owing to the large anharmonicity of the oscillations in the ground state, unexcited hydrogen itself cannot ensure rapid relaxation through the upper vibrational levels. As the buffer gases for H_2 we can use D_2 and N_2. The anharmonicity of the oscillations of D_2 is much smaller than that of H_2, so that the D_2 vibrational levels with v = 2 can become depleted at a high rate without introducing additional buffer gases. In addition, the buffer gas for D_2 can be N_2.

3. At sufficiently high pressures, a very strong broadening of the resonant absorption lines of noble-gas atoms takes place[7]. These strongly broadened lines can be used for optical pumping so that the excited atoms produced will transfer their energy by collision to the molecules of the working gases. An analysis of the experimental data of[8,9] shows that to transfer the excitation from the Xe and Ar atoms to the molecules N_2, H_2, CH_4, CO_2, and O_2 it is necessary to have on the order of 10—100 collisions. Such rates are apparently also characteristic of other analogous processes. Therefore the necessary molecular-gas pressures at which the time of energy transfer is smaller than the time of radiative damping of the excited atoms (10^{-7}—10^{-9} sec) range from 0.1 to 10 atm.

There are two main causes of strong impact broadening of resonance lines of noble-gas atoms.

1) By virtue of the van der Waals interaction, noble gases contain a small number of diatomic molecules, which upon absorption of photons go over into an electronically-excited state[10-13]. Electronically-excited molecules are also produced when a photon is absorbed at the instant of collision of two atoms[14]. The molecular-absorption bands lie on the long-wave side of the resonance line and cover a wave band of ~ 1000 cm^{-1}. The possibility of using molecular absorption bands of xenon for optical pumping and for producing a vacuum-ultraviolet laser operating on xenon molecules was already pointed out in[15].

2) At high pressures, strong impact broadening of resonance absorption lines of noble-gas atoms takes place[16,17]. The statistical line wing[6] lies in this case on the short-wave side[18]. Estimates show that the statistical-wing pump band, for which the absorption coefficient lies in the specified range (1—10 cm^{-1}), can reach several thousand cm^{-1}.

In estimating the gain, expression (2) must be multiplied by the ratio $\Delta\omega_p/\Delta\omega \approx \hbar\omega_e/kT$, where $\hbar\omega_e$ is the energy of the vibrational quantum of the molecule in the upper electronic state. As a rule, $\hbar\omega_e > kT$, and therefore pumping via noble gases should lead to larger gains than direct optical pumping. In addition, a possibility appears of obtaining generation at allowed transitions which are not coupled to the ground electronic state of the molecule. Then the lower level of the laser transition can become depleted by rapid quenching.

On the basis of this principle it is possible to obtain lasing on the 2^+ nitrogen band system ($C^3\Pi_u \rightarrow B^3\Pi_g$), the level $C^3\Pi_u$ of which is effectively excited by collisions with metastable Ar[19,20]. In accordance with the results of[21], in which the quenching constants of the $C^3\Pi_u$ and $B^3\Pi_g$ levels by the nitrogen itself were measured, the lifetime of the molecules at a concentration $N_2 > 2.5 \times 10^{18}$ cm^{-3} will be smaller at the $B^3\Pi_g$ level (v = 3) than at the level $C^3\Pi_u$ (v = 0), and quasistationary inversion can be obtained between these levels.

4. It is expedient to use as laser pump sources flash lamps with bulbs of lithium fluoride, in which the gas pressure should compensate for the working-mixture pressure. Powerful electrical discharges in gases at atmospheric pressure were investigated both experimentally and theoretically[22-25]. Their characteristic feature is the formation of a cylindrical plasma column with brightness temperature of several times 10 000°, which expanded at a rate (1—2) km/sec, thus generating a shock wave.

The discharge parameters at high pressures can be estimated by starting from the self-similar relations derived in[24,25]. It follows from them that the plasma radius is $R \sim \rho_0^{-1/4}$ and the temperature $T \sim \rho_0^{1/8}$, where ρ_0 is the initial gas density. At sufficiently high pressures, the plasma will apparently expand at a rate close to the speed of sound in the cold gas, and have a brightness temperature approximately equal to that at atmospheric pressure. At high pressures, the optical thickness of the plasma also increases, which gives grounds for hoping to obtain large pump fluxes in the vacuum ultraviolet region (up to 1000 Å). Discharges at high pressures and relatively slow current growth rates were investigated in[26-28], and the results of these investigations agree with the considerations advanced above.

In conclusion, the author is deeply grateful to V. S. Zuev for useful discussions and for support of the work.

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Translated by J. G. Adashko
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