Lasing on the electronic *B–X* transition of the I_2 molecule optically pumped by a copper-vapor laser

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(Submitted 16 August 1979)
Zh. Eksp. Teor. Fiz. **78**, 1349–1364 (April 1980)

It is proposed to use pulsed metal-vapor lasers for optical pumping of gas lasers based on electronic transitions of molecules. This uncovers prospects for the development of effective lasers with high average and peak power, which are tunable in the visible and in the infrared. The first step in this direction are experiments on optical pumping of molecular iodine by a copper-vapor laser ($\lambda = 5106$ and 5782 Å). Results of spectroscopic investigations are reported. It was found that the pumping is by five absorption lines of the $X^1\Sigma_g^+ - B^3\Pi_{0u}^+$ system of the I_2 molecule, three of which give rise to lasing. The principal pumping was by the 5782 Å line. Lasing was obtained on 14 vibrational transitions of the $B^3\Pi_{0u}^+ X^1\Sigma_g^+$ system in the region 1.016–1.342 μm region. The average generation power in the multifrequency regime was 7 mW at an optical-energy conversion efficiency 4%. It was observed that a noticeable competition takes place between the pump channels of the 5106 and 5782 Å lines, and leads to a decrease in the total lasing power. Prospects are discussed of using gas lasers on electronic transitions of molecules optically pumped by metal-vapor vapors, particularly for the development of frequency-tunable optical systems with intensity amplifiers.

PACS numbers: 33.80.Be, 42.55.Hq

INTRODUCTION

Much attention is being paid of late to lasers operating on electronic transitions of diatomic homonuclear molecules, optically excited by pulsed and cw lasers. The possibility of obtaining lasing of this type has been obvious for a long time.[1,2] The experimental research, however, expanded extensively only in recent years. By now, this mechanism was realized on a large number of transitions of the molecules I_2,[3-8] Na_2,[9-13] Li_2,[11,14] Br_2,[15] S_2,[6,16] Bi_2,[17,18] Te_2,[18,19]. Continuous lasing was realized in practically all the systems with the exception of Br_2. A distinguishing feature of lasers of this class is the possibility of almost continuous tuning over the narrow lines in a wide range of the spectrum, from ultraviolet to the near infrared. The lasers are stable in operation, and under favorable conditions they can deliver an appreciable average power at rather high efficiency. Thus, for example, in the cw regime an energy conversion efficiency of 10% was obtained with the molecules Na_2 (Ref. 13) and Bi_2 (Ref. 18), and 15% with the I_2 molecule.[8]

Optically pumped lasers based on electronic transitions are of interest for the solution of many physical and practical problems. They can be extensively used for spectroscopy of simple and complex molecules, including precision determination of various molecular constants, for the study of the kinetics of chemical reactions and of physical processes, for isotope separation, to improve of the spatial structure of modes, to develop optical-frequency standards, as well as to develop stable lasers with tunable frequency in many spectral ranges. They can serve also as diagnostic tools in the search for effective laser systems, for example with gas-discharge excitation. In addition, great interest, from our point of view, attaches also to the possibility of using optical pumping of molecules to develop line-tunable intensity amplifiers for optical systems operating in various regions of the spectrum and tunable over the lines.

Up to now, the cited molecules were excited either by pulsed lasers operating at low repetition frequency (second harmonic of a neodymium laser,[3,9,15] pulsed dye lasers[4,10,17,19]), or else cw argon lasers.[5-7,11-13,18] In our opinion, good prospects for optical pumping of molecules are uncovered by the use of pulsed metal-vapor lasers. The high peak power of the latter makes it possible to exceed relatively easily the molecular lasing threshold, and the short lasing duration (usually 5–30 nsec) permits pumping of the levels of most molecules within less than their decay times. These features can ensure high populations on the upper molecular levels, and by the same token uncover ways of producing broadband lasers with simultaneous generation, for example, in the entire visible region of the spectrum.

Many metal-vapor lasers at a pulse repetition frequency 5–20 kHz, and at efficiency higher than of other lasers used for optical molecule pumping, have an average lasing power exceeding 1 W, and the copper-vapor laser has even 40 W. Further improvement in the characteristics of these lasers is expected. The relatively rapid decay of the lower working levels of the employed molecules, which is proved by the presence of continuous lasing, makes it possible to use a pump with high repetition frequency and thus obtain appreciable average molecular-generation powers. The presence of a large number of metal-vapor lasers in the visible, near infrared, and ultraviolet regions makes for a large choice of molecules with the desirable characteristics. All these circumstances make metal-vapor pulsed lasers quite promising for optical pumping of molecules.

As the first step in this direction we have investigated experimentally lasing on transitions of the iodine molecule pumped by a copper-vapor laser. This combination was chosen because the copper-vapor laser has presently the best characteristics from among this class of lasers (average power 43.5 W and efficiency

1% at a pulse repetition frequency 16.7 kHz, Ref. 20), and is naturally the most leading candidate for the role of a donor laser, while the iodine molecule is one of the most investigated molecules suitable for optical pumping by this laser.

EXPERIMENTAL SETUP

The iodine vapor was kept in a quartz tube (cell) 26.5 cm long and with inside diameter 16 mm. The end faces of the cell, inclined at the Brewster angle, were covered with quartz windows welded to them. In the middle of the tube there was a sidearm in which thoroughly purified iodine crystals were kept. The crystal temperature determined in fact by the iodine vapor density in the cell. The temperatures of the cell and of the stub could be varied independently, but the cell temperature was always somewhat higher than that of the sidearm.

The iodine vapors were optically pumped along the cell axis by a copper-vapor laser. The latter was focused with a quartz lens of focal length 0.5 m (or 1 m) into the center of the cell. The copper-vapor laser (Cu-laser) operated at repetition frequencies from 3 to 12 kHz. In most cases the frequency was 7 kHz. The laser generated on two lines: green (5106 Å, 19581 cm^{-1}) and yellow (5782 Å, 17290 cm^{-1}), whose intensity ratio varied with the laser operating conditions. Usually the ratio of the average powers in these lines was 3 : 1–2 : 1. The total average lasing power varied up to a maximum value 10 W. The cell with the iodine vapor was placed in a resonator made up of two flat mirrors with multilayer dielectric coatings and with reflection coefficient of approximately 97% in the molecular-lasing region.

The transmission of the input mirror was 57% for the yellow line of the Cu laser and 78% for the green line. The distance between mirrors was 50 cm. The resonator was not optimized in this study.

The spectral composition of the iodine lasing was investigated with a DFS-13 spectrograph with inverse linear dispersion 4 Å/mm. The fluorescence spectrum was recorded with "izpankhrom" film type 15, and the lasing spectrum with photographic plates of type I-1070. For reliable registration of the spectra in the 1.0–1.34 μm range the plates had to be hypersensitized in vapor of aqueous solution of ammonia. The reference was the emission spectrum of a neon gas discharge. The hyperfine structure and the pump and lasing line contours were investigated with a system consisting of a scanning Fabry–Perot interferometer, an MDR-3 monochromator, a type ÉLU photomultiplier, an S7-8 stroboscopic oscilloscope, and an S1-18 oscilloscope. This system ensured a time resolution of 3 nsec and a spectral resolution 0.015 cm^{-1}. To measure the shape and duration of the light pulses we used an FÉK-15 photocell (for the copper-vapor laser) and FÉU-62 and ÉLU photomultipliers (for molecular registration) in conjunction with an S7-8 two-beam oscilloscope.

EXPERIMENTAL RESULTS

The lasing on the I_2 transition took place in the range 1.016–1.342 μm on 26 lines belonging to the 14 vibrational-rotational bands of the $B^3\Pi_{0^+u} - X^1\Sigma_g^+$ system. As will be shown below, the overwhelming majority of the molecular-lasing lines were due to pumping by the 5782 Å yellow line. At an average pump power 0.7 W entering the cell with the iodine vapor, and at a pulse repetition frequency 7 kHz, the average molecular lasing power in the broadband regime reached 7 mW. The efficiency of conversion of the light energy, i.e., the ratio of the lasing energy to the energy absorbed by the iodine molecules was 4%. These parameters were obtained at sidearm and cell temperatures 50 and 97°C. The lasing power depended noticeably on the stub temperature, this being due primarily to the change in the pressure of the working gas in the cell. An example of such a dependence is shown in Fig. 1. It is seen that the optimal temperatures reached in the region 50°C, which corresponds according to Ref. 21 to an approximate iodine pressure 1.5 Torr. Recognizing that the iodine vapor consists practically entirely of I_2 molecules, it can be assumed that the total density of the working molecules at these optimal conditions was 3.9×10^{16} cm^{-3}. It should be noted, however, that the optimal pressure, is not constant and increases within definite limits with increasing pump power.

The iodine lasing was delayed in time relative to the pump pulse. With increasing pump power, the delay decreased and reached 50 nsec at room temperature and at 0.5 W pump. The lasing pulse, which was somewhat asymmetrical (with a steeper leading front), had a duration of the order of 30 nsec at half-height. This is approximately 1.5–2 times longer than the duration of the pumping pulse. The lasing power in each pulse turned out to be 30 W.

The effectiveness of using one laser or another for optical pumping depends in many respects on the extent to which the pump line and the absorption lines of the pump molecules can successfully coincide in position and in width, as well as on which precisely levels of the lower state absorb the pump radiation, on the size of their propagation, and on the processes in which they take part. If a mercury-vapor laser is used, this question is particularly important, since the copper lasing line has a complicated hyperfine structure that varies with time, and a width that changes during the

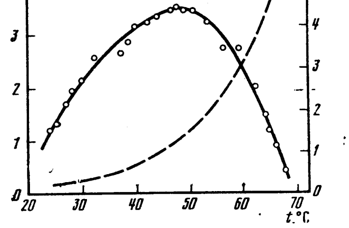

FIG. 1. Dependence of the average power W of an I_2 laser on the temperature t of the sidearm with the iodine crystals. Dashed curve—saturated iodine vapor pressure p. Cell temperature 97°C.

course of the pulse. Knowledge of the spectral and temporal characteristics is very important also for the understanding of the physical processes that occur in the laser. In most cases, including the present one, the foregoing problems can be solved only experimentally, inasmuch as the extensive superposition of bands and the large number of closely spaced transitions do not permit, at the accuracy of the existing spectroscopic constants, to solve sufficiently reliably this problem by calculation, even when dealing with so thoroughly investigated a molecule as I_2.

The experiments performed with a scanning interferometer with a resolution 0.015 cm^{-1} and a time registration system with a resolution 3 nsec made it possible to determine the following: the spectral regions in which absorption of the pump by strong molecular transitions takes place, the efficiency of the absorption as a function of the iodine pressure, the change in the pumping density in the region of the absorption by iodine during the course of the pulse, and the contour and the spectral width of the I_2 laser lines. The results of these experiments will be described in greater detail elsewhere. We point out only that all the lasing lines have similar contours and are slightly asymmetrical with a steeper edge on the low-frequency side. The spectral half-width of the iodine lasing is approximately 0.1 cm^{-1} and greatly exceeds the Doppler-contour width, this being due to the rich hyperfine structure of the iodine transitions. Figure 2 shows oscillograms of the contours of the 5106 and 5782 Å copper lines in the regime of practically spontaneous emission without absorption, and with absorption by iodine vapor at room temperature. Two dips are clearly seen in the contour of the yellow line and one in the contour of the green line, both due to the iodine absorption. The sweep of the spectra on the oscillograms is linear in frequency (scale 0.063 cm^{-1}/diversion). Making use of the data on the energy levels[22] and on the hyperfine splitting constants[23] in the copper atom, we estimate the frequencies of the absorption line centers to be 19581.183 cm^{-1} for the 5106 Å line, and 17289.786 and 17290.037 cm^{-1} for the 5782 Å line. Unfortunately, for the principal line 5106 Å of the Cu laser the agreement between the pump and absorption line is not very good. It is more satisfactory for the other line, 5782 Å. It was also observed that all the bands of the iodine lasing due to the 5782 Å line increase in power (some of them by several times) when the pumping by the 5106 Å line stops, and vice versa. It was found that in the absence of the 5106 Å line the threshold energy of pumping by the 5782 Å line is less than 1 μJ.

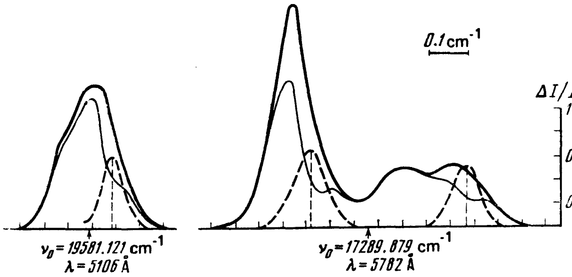

FIG. 2. Contours of the lines $4p\,^2P_{3/2}{}^0-4s\,^2D_{5/2}$ (5106 Å) and $4p\,^2P_{1/2}{}^0-4s\,^2D_{3/2}$ (5782 Å) of the spontaneous emission of copper. The thin lines indicate the contours of the copper lines when they are absorbed by iodine vapors at room temperature, the thick lines—without absorption, dashed—contour of the absorption lines $\Delta I/I_0=(I_0-I)/I_0$; I_0 is the intensity of the incident light, I—intensity of light passing through the cell.

To determine the physical processes that govern the operation of a given laser, it was necessary primarily to identify reliably the molecule energy levels that participate in the absorption in the lasing. Therefore principal attention was paid in the present study to spectroscopic investigations. To determine the vibrational and rotational levels from which the pumping takes place, and the transitions corresponding to the obtained absorption frequencies, we investigated the spectrum of the resonant fluorescence of iodine vapor. The vibrational-rotational transitions of the fluorescence lines were identified by comparing the experimentally obtained combination frequencies $\Delta_2F(J'')$ and $\Delta G(V'')$ with their theoretical values obtained on the basis of the molecular constants from Refs. 24–26.

The combination difference $\Delta_2F(J'')$ is the difference between the rotational turns of the lower vibrational levels with rotational quantum numbers that differ by two. Its value, generally speaking, depends on the vibrational number v and can be obtained theoretically from the formula

$$\Delta_2F_v(J'')=F_v(J+2)-F_v(J''), \qquad (1)$$

where the rotational term with quantum numbers J and v is given by

$$F_v(J)=B_vJ(J+1)-D_v[J(J+1)]^2. \qquad (2)$$

The rotational constants B_v and D_v were calculated with the aid of the formulas

$$B_v=\sum_{i=0}^{n}C_{bi}(v+{}^1/_2)^i=B_e+\alpha_e(v+{}^1/_2)+C_{b2}(v+{}^1/_2)^2 +C_{b3}(v+{}^1/_2)^3+C_{b4}(v+{}^1/_2)^4+\ldots, \qquad (3)$$

$$D_v=\sum_{i=0}^{n}C_{bi}'(v+{}^1/_2)^i=D_e+\beta_e(v+{}^1/_2)+C_{b2}'(v+{}^1/_2)^2+\ldots. \qquad (4)$$

The numerical value of the coefficients in (3) and (4) for the ground state $X^1\Sigma_g^+$ of the I_2 molecule were taken from Ref. 24 and are equal to

$$C_{b0}(B_e)=0{,}037395\ \mathrm{cm}^{-1},\ C_{b1}(\alpha_e)=-1{,}2435\cdot10^{-4}\ \mathrm{cm}^{-1},C_{b2}=4{,}498\cdot10^{-7}\mathrm{cm}^{-1},$$
$$C_{b3}=-1.482\cdot10^{-8}\ \mathrm{cm}^{-1},\quad C_{b4}=-3.64\cdot10^{-11}\ \mathrm{cm}^{-1},$$
$$C_{b0}'(D_e)=4.54\cdot10^{-9}\ \mathrm{cm}^{-1},\ C_{b1}'(\beta_e)=1.7\cdot10^{-11}\ \mathrm{cm}^{-1},C_{b2}'=7.0\cdot10^{-12}\ \mathrm{cm}^{-1},$$

The value of $\Delta_2F(J'')$ can be obtained from experiment as the difference between the frequencies of the P and R lines emitted from one upper level, i. e., from the splitting of the rotational doublet.

The other combination difference $\Delta G(V)$ is the difference between neighboring vibrational terms of the same lower electronic state. Its theoretical vlaue can be obtained from the expression

$$\Delta G(v)=G(v+1)-G(v), \qquad (5)$$

where the vibrational term is determined from the formula

$$G(v)=\sum_{j=1}^{m} C_{kj}(v+{}^1/_2)^j=\omega_e(v+{}^1/_2)+\omega_e x_e(v+{}^1/_2)^2+\omega_e y_e(v+{}^1/_2)^3$$
$$+\omega_e z_e(v+{}^1/_2)^4+\omega_e a_e(v+{}^1/_2)^5+\omega_e b_e(v+{}^1/_2)^6+\omega_e c_e(v+{}^1/_2)^7+\omega_e d_e(v+{}^1/_2)^8$$
$$+\omega_e f_e(v+{}^1/_2)^9+\omega_e g_e(v+{}^1/_2)^{10}+\dots\,. \qquad (6)$$

The numerical values of the vibrational constants in for the ground electronic state $X^1\Sigma_g^+$ were taken from Ref. 24 and are equal to:

$$C_{k1}(\omega_e)=214.5481\ \mathrm{cm}^{-1},\quad C_{k2}(\omega_e x_e)=-0.616259\ \mathrm{cm}^{-1},$$
$$C_{k3}(\omega_e y_e)=7.5707\cdot10^{-5}\ \mathrm{cm}^{-1},\quad C_{k4}(\omega_e z_e)=-1.263643\cdot10^{-4}\ \mathrm{cm}^{-1},$$
$$C_{k5}(\omega_e a_e)=6.198129\cdot10^{-6}\ \mathrm{cm}^{-1},$$
$$C_{k6}(\omega_e b_e)=-2.0255975\cdot10^{-7}\ \mathrm{cm}^{-1},\quad C_{k7}(\omega_e c_e)=3.9662824\cdot10^{-9}\ \mathrm{cm}^{-1},$$
$$C_{k8}(\omega_e d_e)=-4.6346554\cdot10^{-11}\ \mathrm{cm}^{-1},\quad C_{k9}(\omega_e f_e)=2.9330755\cdot10^{-13}\ \mathrm{cm}^{-1},$$
$$C_{k10}(\omega_e g_e)=7.61\cdot10^{-16}\ \mathrm{cm}^{-1}.$$

The value of $\Delta G(v)$ can be obtained from experiment as the difference between the frequencies of the P (or R) lines of neighboring vibrational bands that start from the same upper vibrational level. When comparing the experimental and theoretical values of $\Delta G(v)$, however, it must be borne in mind that Eq. (6) pertains to the case when there is no rotation ($J=0$), whereas lines with $J\neq 0$ are observed in experiment. Therefore the theoretical value that agrees with experiment should be obtained from the expression

$$\Delta G(v)=G(v+1)-G(v)+F_{v+1}(J)-F_v(J). \qquad (7)$$

The last two terms of the right-hand side of (7) are obtained from Eq. (2).

For the analysis of the fluorescence spectra we chose transitions that terminate at the lowest vibrational levels of the ground state of the iodine molecule. The reason for this choice was that for the lower levels the calculation of the terms is the most accurate one. In addition, the corresponding transitions lie in the visible region of the spectrum, where the accuracy of the measurement of the wavelengths is high enough. Helpful for the solutions of our problem is also the fact that the study of the fluorescence spectra in the pump-line wavelength region uncovers a possibility of establishing the presence or absence of anti-Stokes components, and by the same token limits the region in which a search is made for the vibrational levels from which the pumping stems. The form of the spectrum in the immediate vicinity of the pump line, in turn, makes it possible to identify unambiguously the type (P or R) of the rotational transition of the pump channel, depending on whether the pump line coincides with the "right" or "left" component of the rotational doublet.

The analysis performed in the indicated manner has shown that the copper-vapor laser emission is absorbed by the intercombination electronic transition $X^1\Sigma_g^+ - B^3\Pi_{0^+u}$ of the I_2 molecule. The pumping is on five absorption lines. Three of them coincide with the yellow (5783 Å) line of the Cu-laser, and two with the green one (5106 Å). The results of the analysis are given in Table I. The first column of the table lists the rounded-off values of the wavelengths (in air) and of the frequencies (in vacuum) of the pumping lines. The second and third colums give the identification of the absorbing vibrational-rotational transitions. The fourth column gives the theoretical values of their frequencies, while the fifth column gives the frequencies obtained from experiments on the hyperfine structure of the line. Figure 3 illustrates the level scheme of the I_2 molecule, and shows the potential curves of the combining electronic states and some of their vibrational levels. Besides the pump channels marked by upward arrows, the diagram shows some of the laser transitions observed in the present study, as well as the scheme (from the top down) of formation of the rotational doublet in the I_2 radiation.

TABLE I. Channels of optical pumping of I_2 molecule on the electronic transition $B^3\Pi_{0+u} - X^1\Sigma_g^+$ by Cu-vapor laser lines.

Pump line	Absorbing transitions			
	Vibrational band $v'' \to v'$	Rotational transition $J'' \to J'$	ν_{calc}, cm^{-1}	ν_{exp}, cm^{-1}
5106 Å, 19581 cm^{-1}	0–47	23–24 R	19581.200	19581.183
	0–51	80–81 R	19581.014	–
5782 Å, 17290 cm^{-1}	0–14	51–52 R	17289.967	17290.037
	1–16	31–30 P	17289.758	17289.786
	2–20	124–125 R	17289.615	–

By way of example of identification of the transitions indicated in Table I, Fig. 4a shows the comparison of the theoretical and experimental dependences of the combination frequency $\Delta_2F(J'')$ on the vibrational quantum number v'' of the lower state, in the case of pumping by the 5782 Å of a copper laser. Each experimental point is marked by the maximum scatter of the results of the measurements of this difference. The theoretical relation, with which the experimental data agree, is shown by the thick line. It is seen that reliable identification of the rotational transition of I_2 is possible only if the transition frequencies are determined with sufficiently high accuracy. In absolute value it should not be worse than 0.07 cm^{-1}, which corresponds to a relative accuracy $(3-4)\times10^{-6}$ in the visible region of the spectrum. In our experiments the average scatter in the frequencies of sufficiently intense fluorescence

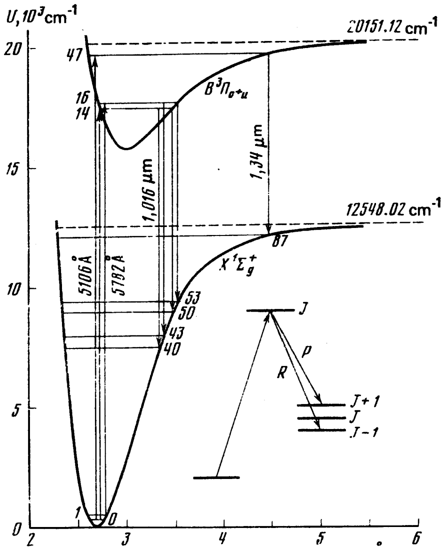

FIG. 3. Diagram of the levels of the I_2 molecule and scheme of formation of rotational doublet.

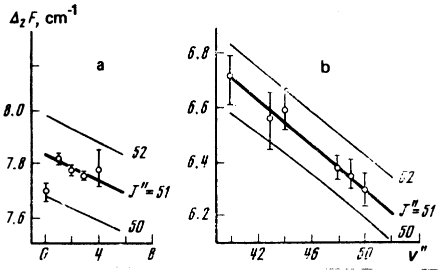

FIG. 4. Doublet splitting $\Delta_2 F(J'') = R(J'') - P(J'+2) = F_v(J'+2) - F_v(J'')$ for the fluorescence lines (a) and the lasing lines (b) of I_2 when pumped by the 5782 Å line. Solid lines—theoretical plots, points—experimental data (with indication of the measurement scatter).

lines in the visible was ±0.01 cm^{-1}, i. e., a relative accuracy 5×10^{-7} was attained.

Each of the pump channels produces in the fluorescence a characteristic series of rotational doublets. This series consists of a sequence of vibrational bands corresponding to transitions from one upper vibrational level (v' = 14, 16, 20, 47, 51) to various vibrational levels of the lower electronic states. Each band is represented in their ideal case by a single doublet, the mechanism of formation of which is clear from Fig. 3 (see the lower right). By virtue of the selection rules, only P and R radiative transitions are allowed for a given electronic transition, i. e., the initial quantum number J can change only by +1 and −1, respectively.

The schematic form of the fluorescence spectra in the immediate vicinity of the pump lines is shown in Fig. 5. The thick bars distinguish those lines whose wavelengths coincide with the pump-line wavelengths. On both sides of the spectrogram (top and bottom) is shown the identification of the iodine emission lines: the rotational transition (with indication of the lower quantum number J'') and the vibrational transition. It should be noted, however, that actually the form of the fluorescence spectrum is more complicated than in the idealized case of Fig. 5. Besides the indicated strong lines, which form the principal doublets, a large number of closely lying weak lines were observed, with an intensity estimated to be two orders of magnitude lower than that of the principal lines. An interpretation has shown that these lines corresponded to transitions from rotational levels that are neighbors of the pumped level. This fact is evidence of the presence of a noticeable rotational relaxation in the upper electronic state.

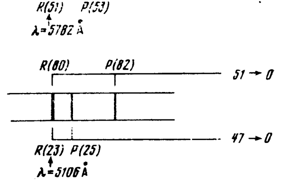

FIG. 5. Schematic form of the spectra of the resonant fluorescence of the molecule I_2 in the case of optical pumping by copper-vapor laser lines (pumping lines 5106 and 5782 Å).

Identification of the pump channels, the use of the procedure described above for the determination of the rotational and vibrational numbers of the lower levels of the generating transitions (see, e.g., Fig. 4b), as well as direct calculation of the frequencies of the expected lasing lines, have made it possible to establish with sufficient reliability the transitions that take part in the lasing. The results of the spectroscopic analysis of the transitions are given in Table II and in Fig. 6. The first and second columns list the experimentally determined wavelengths and frequencies (with indication of the average scatter) of the observed lasing lines; the third column gives the theoretical frequencies calculated on the basis of the molecular constants from Ref. 24 for the X state and from Refs. 25 and 26 for the B state. The fourth column gives the vibrational and rotational numbers of the combining levels. We see that out of the five levels pumped by the Cu-laser (see Table I) lasing is produced under our conditions by only three $v'=14(J'=52)$, $v'=16(J'=30)$ and $v'=47(J'=24)$. By coincidence, all three levels belong to one nuclear symmetry. In this case they are asymmetrical and furthermore ortholevels, i. e., they have a larger nuclear statistical weight than levels of another nuclear symmetry (symmetrical rotational levels).

All the transitions observed in the lasing were identified, with the exception of two doublets in the region of

TABLE II. Lasing lines on the transition $B^3\Pi_{0+u} - X^1\Sigma_g^+$» of the I_2 molecule optically pumped by a Cu-vapor laser.

λ_{exp}, Å (in air)	ν_{exp} cm^{-1} (in vacuum)	ν_{calc}, cm-1 (in vacuum)	Vibrational band*	Vibrational transition
10163.57	9836.37±0.045	9836.162	14–40	R (51)
10170.50	9829.67±0.045	9829.459		P (53)
–	–	9586.436	16–43	R (29)
10432.62	9582.70±0.075	9582.599		P (31)
10658.63	9379.50±0.058	9379.468	14–43	R (51)
10666.08	9372.95±0.048	9372.877		P (53)
10829.57	9231.45±0.047	9231.076	14–44	R (51)
10837.31	9224.86±0.033	9224.525		P (53)
11103.50	9003.70±0.050	9003.468	16–47	R (29)
11108.13	8999.95±0.047	8999.724		P (31)
		8797.865	14–47	R (51)
11370	8793	8791.436		P (53)
11547.73	8657.34±0.018	8657.567	14–48	R (51)
11556.24	8651.00±0.029	8651.181		P (53)
11735.03	8519.16±0.028	8519.382	14–49	R (51)
11743.78	8512.82±0.025	8513.040		P (53)
11826.46	8453.30±0.025	8453.618	16–51	R (29)
11831.54	8449.68±0.025	8449.975		P (31)
11925.47	8383.12±0.027	8383.348	14–50	R (51)
11934.42	8376.83±0.030	8377.051		P (53)
12014.01	8321.34±0.030	8321.612	16–52	R (29)
12019.22	8317.73±0.027	8317.996		P (31)
12204.50	8191.46±0.039	8191.867	16–53	R (29)
–	–	8188.279		P (31)
13340	7494	7525.087	47–85 **	R (23)
		7523.247		P (25)
13416.55	7451.44±0.019	7449.778	47–87	R (23)
13419.59	7449.76±0.011	7448.031		P (25)

*The levels $v'=14$ and 16 are excited by the 5782 Å copper line, the level $v'=47$ by the 5106 Å line.

**The identification of this doublet is preliminary.

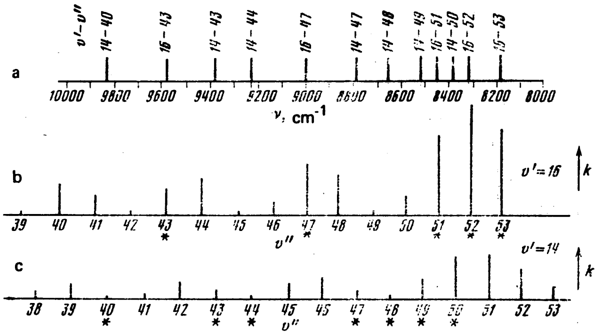

FIG. 6. a) Diagram of I_2 lasing spectrum (without the 1.334 and 1.342 μm doublets) on the transition $B^3\Pi_{0+u}-X^1\Sigma_g^+$ following optical pumping by a Cu-vapor laser. b), c) Distribution of the calculated gain k over the bands of the sequences $(14\rightarrow v'')$ and $(16\rightarrow v'')$ of the $B^3\Pi_{0+u}-X^1\Sigma_g^+$ transition of iodine.

1.137 and 1.334 μm. They turned out to be too weak to be photographed even with highly hypersensitized plates. These lines were recorded only photoelectrically with an FÉU-62 photomultiplier. The accuracy of the measurement of the wavelengths was insufficient for a reliable identification of these transitions. Taking various consideration into account, however, the lines near 1.37 μm can be identified with a certain degree of reliability as the doublet $R(51)$–$P(53)$ of the 14–17 band. As to the lines near 1.334 μm, they are close in accord with their position to the 47–85 band, but their doublet splitting is noticeably less than should be the case for lines of this band that start out from the rotational level $J'=24$. The accuracies of the wavelength measurements and of the calculation of the terms for such high rotation levels do not make it possible to identify definitely the working transition.

An analysis of the molecular-iodine lasing spectrum has shown that in addition to the expected properties it has a number of singularities that are not yet clear. As expected, each of the optically excited levels of the B state gave a series of doublets with variable intensity. Since all the doublets of one series begin from the same level, the distribution of the intensity from doublet to doublet should be determined by the Franck–Condon factors. The correspondence should be exact for spontaneous emission and approximate for stimulated emission. When comparing the distribution of the intensity over the band sequences it was observed that a certain "shift" is observed in the lasing spectra of the bands $v'=14\rightarrow v''$ (i.e., for high v''). Figures 6b and c show the relative distribution of the gain, calculated for two sequences of the bands that start from $v'=14$ and $v'=16$. The data on the intensity factors of the vibrational bands were taken from Ref. 27, with account taken of the correction proposed in Ref. 28 in accord with the numbering of v'. The asterisks on the figure mark the bands observed in lasing. In the sequence $14\rightarrow v''$, the most powerful are the bands 14–49 and 14–48, followed by 14–44. In the sequence $16\rightarrow v''$, the most powerful are the bands 16–52 and 16–51, followed by the band 16–47. It is clearly seen that whereas for the sequence $16\rightarrow v'$ there is good qualitative agreement between calculation and experiment, this agreement can be "reached" for the $14\rightarrow v''$ bands if all the asterisks are shifted two positions to the right. We note that a similar situation (which has remained, to be sure, unnoticed) occurred also in Ref. 4. The authors of that paper pumped optically the same vibration level $v'=14$, but in this case with a dye laser excited by an argon laser. It is not excluded that to eliminate the indicated disparity it is necessary to introduce a correction to the form of the potential curves of the B and X states in the region of high vibrational levels.

The next singularity is connected with the distribution of the intensity between the components of the doublet. Even though for a single electronic transition one of the components,[29] for example the P line, will always predominate in the doublet of any vibrational band, there are cases when different components generate in doublets that start from a single rotational level. This is the situation, for example, with the bands 16–53 and 16–43. Whereas in the 16–43 band the P line is readily recorded on the photographic plate, the R line is so weak that it can be detected only with a photomultiplier. On the other hand, only the R line generates in the 16–53 doublet.

When comparing the experimental values of the lasing line frequencies within the experimental ones, some discrepancy is observed and varies systematically with changing v''. This is clearly seen in Fig. 7, which shows data on the energies of the upper laser levels, obtained by adding the measured frequency and the vibrational-rotational term of the lower laser levels, calculated from formulas (2) and (5). For comparison, the figure shows also the theoretical values of the terms of the upper laser levels (dashed horizontal lines). They were calculated from the formula

$$E(v'J')=T_e+G(v')+F_v(J'), \tag{8}$$

where the vibrational and rotational terms were obtained with the aid of (2) and (6), and the electronic term $T_e=15768.32$ cm^{-1} and the vibrational and rotational constants of the B state were taken from Ref. 25, the data of which are apparently the most reliable ones. The corresponding values of the constants for the vi-

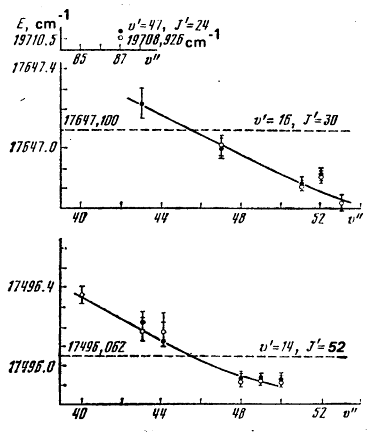

FIG. 7. Energy of the upper laser levels, obtained from the formulas $E(v',J')=\nu_{las}+G(v'')+F_{v''}(J')$; ×—from measurements of the P-line frequencies, ○—from measurement of the R-line frequencies.

brational term $G(v')$ are

$$C_{k1}(\omega_e)=126.1650\ \mathrm{cm}^{-1},\ C_{k2}(\omega_e x_e)=-0.86733\ \mathrm{cm}^{-1},$$
$$C_{k3}(\omega_e y_e)=1.07448\cdot10^{-2}\ \mathrm{cm}^{-1},$$
$$C_{k4}(\omega_e z_e)=-1.012324\cdot10^{-3}\ \mathrm{cm}^{-1},\ C_{k5}(\omega_e a_e)=4.55014\cdot10^{-5}\ \mathrm{cm}^{-1},$$
$$C_{k6}(\omega_e b_e)=-1.334168\cdot10^{-6}\ \mathrm{cm}^{-1},$$
$$C_{k7}(\omega_e c_e)=2.499684\cdot10^{-8}\ \mathrm{cm}^{-1},\ C_{k8}=(\omega_e d_e)=-2.809711\cdot10^{-10}\ \mathrm{cm}^{-1},$$
$$C_{k9}(\omega_e f_e)=1.722584\cdot10^{-12}\ \mathrm{cm}^{-1}\quad C_{k10}(\omega_e g_e)=-4.431776\cdot10^{-15}\ \mathrm{cm}^{-1},$$

for the rotational constant $b_{v'}$ we have

$$C_{b0}(B_e)=0.028939\ \mathrm{cm}^{-1},\ C_{b1}(\alpha_e)=-1.204\cdot10^{-4}\ \mathrm{cm}^{-1},$$
$$C_{b2}=-5.608\cdot10^{-6}\ \mathrm{cm}^{-1},$$
$$C_{b3}=2.988\cdot10^{-7}\ \mathrm{cm}^{-1},\ C_{b4}=-1.159\cdot10^{-8}\ \mathrm{cm}^{-1},\ C_{b5}=2.195\cdot10^{-10}\ \mathrm{cm}^{-1},$$
$$C_{b6}=-2.047\cdot10^{-12}\ \mathrm{cm}^{-1},\ C_{b7}=7.579\cdot10^{-15}\ \mathrm{cm}^{-1};$$

and for the rotational constant $D_{v'}$ (centrifugal distortion):

$$C_{b0}'=1.797\ \mathrm{cm}^{-1},\ C_{b1}'=2.48\cdot10^{-2}\ \mathrm{cm}^{-1},\ C_{b2}'=-4.06\cdot10^{-4}\ \mathrm{cm}^{-1},$$
$$C_{b3}'=3.45\cdot10^{-5}\ \mathrm{cm}^{-1},\ C_{b4}'=-6.41\cdot10^{-7}\ \mathrm{cm}^{-1},\ C_{b5}'=4.17\cdot10^{-9}\ \mathrm{cm}^{-1}.$$

It must be noted, however, that in the calculation of the centrifugal-distortion constant $D_{v'}$ for the B state we used not formula (4), but the expression

$$\ln(D_{v'}\cdot10^9)=\sum_{i=0}C_{bi}'(v+{}^1/_2)^i. \qquad (9)$$

that it is preferable to use high vibrational levels of the B state, which are close to the dissociation limit, a logarithmic representation of the centrifugal-distortion constant is pointed out in Refs. 25 and 26. The calculations performed under these assumptions show that for transitions with $v'=14$ and $v'=16$, in the range 0.3–0.4 cm^{-1}, the agreement is good and confirms by the same token the validity of formula (9). On the other hand, the presence of a systematic discrepancy in the range 0.3–0.4 cm^{-1} points to the need of correcting the molecular constants of the X state only in the terms of higher order. A somewhat more serious correction should be introduced into the constants of the high vibrational levels. We see that for the 47–87 band this deviation amounts already to ~1.6 cm^{-1}. To be sure, it is difficult to determine in which state (B or X) this should be done, since the experimental data are available only for one band. We note that the level $v'=87$ is at present the highest of the levels observed in the X state. Another interesting fact is also that it is located only 290 cm^{-1} below the X-state dissociation limit (for a temperature optimal for the operation of the I_2 laser, $kT=224\ \mathrm{cm}^{-1}$).

DISCUSSION OF RESULTS

Our study has shown that optical pumping of molecules of I_2 by a pulsed copper-vapor laser leads to sufficiently effective generation on the electronic transition $B^3\Pi_{0^+u}-X^1\Sigma_g^+$. The pumping was effected by both lasing lines of the Cu-laser (5106 and 5782 Å) on five absorbing transitions, three of which (0–14, 1–16, 0–47) lead to the onset of molecular generation on 14 vibrational bands: 14–40, 14–43, 14–44, 14–47, 14–48, 14–49, 14–50, 16–43, 16–47, 16–51, 16–52, 16–53, 47–87, and one unidentified. The most effective turned out to be the weak line, 5782 Å, which ensured generation on 12 out of 14 bands. The advantage of the 5782 Å line over 5106 Å is due to its better agreement with the frequencies of the absorbing transitions and to the larger number of the latter. Each lasing band is represented by a characteristic doublet of P and R lines. The region of the spectrum covered by the lasing lines extends from 1.016 to 1.342 μm. The measurements of the lasing wavelengths point to the need for refining the molecular constant for the high vibrational levels of the B and X states. The I_2 molecules take part in the lasing only in the ortho modification, a fact that can be used for chemical separation[3] of ortho-iodine from para-iodine. Optimization of the operating conditions of the I_2 laser, including the resonator, should improve noticeably its energy characteristics, and the use of a tunable selective resonator should lead to new laser lines, including some in the visible spectrum.

When molecules are optically pumped by a pulsed copper-vapor laser, a number of pecularities of the latter must be taken into account. The first is connected with the presence of a hyperfine structure in its lasing lines. Most important in this case is the fact that the composition of the hyperfine structure and the ratio of the intensities of its components depend noticeably on the operating conditions of the laser and, in particular, change basically during the time of the lasing pulse. It is important to take this into account if an attempt is made to develop molecular lasers with high average power.

The second singularity is connected with the presence, in the Cu-laser radiation of two emission lines of comparable intensity. Simultaneous pumping by these lines can lead to a competition between the absorbing transitions, even if the pumping of the molecules by both lines takes place from different rotational levels. This competition can be the result of rapid rotational relaxation, as well as a result of 2-photon processes. Thus, for example, in the case of iodine, a photon with frequency equal to double the frequency of the 5106 Å line should be absorbed by an electronic transition $X^1\Sigma_g^+-D^1\Sigma_u^+$. It is not excluded that such a process decreased in a definite manner the effectiveness of the green line of copper. Experience with the use of the 5782 Å copper line, with its rather large width and low pump threshold (<1 μJ), indicates that it is possible to use effectively for optical pumping of molecules the emission from sources with broad lines. The abundance of absorbing transitions over the entire width of the pump line uncovers prospects of developing lasers operating simultaneously over a considerable part of the optical band. The sources of this pump can also be pulsed and continuous lamps emitting on the resonant transitions of atoms, or else molecular lasers with many lasing lines (e.g., using the molecules N_2 and CO). However, as shown by experience with the Cu laser, and the latter case one should be ready for the interaction of many lines of molecular generation of the donor laser in the course of the pumping.

Finally we wish to dwell also on one important question in connection with the use of metal-vapor lasers for optical pumping of molecules. We have in mind the use of such systems to develop frequency-tunable optical devices with intensity amplifiers. To accomplish this it is necessary above all to ensure a high gain, comparable with the gains of metal-vapor pulsed lasers, which are themselves presently used as intensity amplifiers in optical systems. The gain for the line center, as is well known, is given by

$$k(\lambda_0)=\frac{\lambda_0^2}{8\pi}\frac{A}{\Delta\nu}\Delta N, \tag{10}$$

where λ_0 is the wavelength, $\Delta\nu$ is the width of the gain line, A is the probability of the working transition, and ΔN is the inverted population. The wavelength of the optically pumped laser is larger, and its line width can be also smaller than for the pump laser. The duration of the pumping metal-vapor pulsed laser is usually much shorter than the reciprocal of the probability of the working transition. It is therefore possible without loss of inversion, to excite levels with decay probabilities much larger than the probability of the transition of the pumping level. Thus, even if the optically pumped level decays via many transitions, as is typical of molecules, the probability of each transition can be comparable with the probability of the transition of the pumping laser. If we assume that 1) the pumping laser operates in the saturation regime and uses all the stored energy, 2) all the pump photons are lost to excitation of the upper working level of the molecule, 3) the lower level of the molecule is not saturated, and 4) the values of the active medium of the pumped and pumping lasers are close, then inversion on the molecular transition will be comparable in magnitude with the inversion in the pump laser. In this case the gains can also be comparable under favorable experimental conditions and if the working transitions are properly chosen. Concentrating the pump with the aid of a suitable optical system into smaller volumes one can obtain an even higher gain, and transform in a side range the shape and dimensions of the amplifying medium. Once a molecular laser that generates in the entire visible region of the spectrum is developed, one can hope to develop, for example, a laser projection microscope, which produces images of microscopic objects magnified by thousands of times with their natural color retained.

Thus, the use of metal-vapor pulsed lasers for optical pumping of molecules can uncover really good prospects in the fields of laser physics, molecular spectroscopy, and also in the field of development of optical systems with brightness amplifiers, operating on many lines simultaneously and tunable in frequency in various regions of the spectrum.

In conclusion the authors thank professor V. I. Malyshev and A. A. Isaev for many helpful suggestions on the experimental technique and for taking a part in the discussion of the results.

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Translated by J. G. Adashko