SOVIET PHYSICS JETP VOLUME 26, NUMBER 3 MARCH, 1968

NONLINEAR ABSORPTION OF RUBY LASER LIGHT BY MOLECULAR POTASSIUM VAPOR

V. G. ABRAMOV, O. V. KONSTANTINOV, N. N. KOSTIN, and V. A. KHODOVOĬ

A. F. Ioffe Physico-technical Institute, Academy of Sciences, U.S.S.R.; S. I. Vavilov Optics Institute, Academy of Sciences, U.S.S.R.

Submitted April 8, 1967

Zh. Eksp. Teor. Fiz. 53, 822—830 (September, 1967)

Nonlinear absorption of light from a ruby laser by molecular potassium vapor was observed. The dependence of the intensity of resonance fluorescence of potassium on the laser radiation flux was measured. For an excitation intensity of 10^3—10^6 W/cm^2 the fluorescence intensity is proportional to the square root of the excitation intensity. A theoretical interpretation of this dependence is presented, which shows that with increasing intensity of the light beam the effect of the latter on the system of molecules changes from that of an incoherent set of harmonics to that of a monochromatic wave.

1. INTRODUCTION

IN the investigation of the Stark effect in atomic-potassium vapor under the influence of the electric field of ruby-laser radiation, we observed that the laser emission pulse was accompanied by scattered radiation with spectral components near the resonant doublet of atomic potassium (λ = 7665, 7669 Å)[1,2] In this communication we report the results of an experimental investigation of this phenomenon and its theoretical interpretation. The appearance of scattered radiation with mixed spectral components is related by us to the excitation of the red fluorescence band as a result of absorption of the ruby-laser light (λ = 6942 Å) by vapor of molecular potassium K_2. A feature of the observed effect is that the fluorescence intensity turns out to be proportional not to the intensity of exciting radiation, as is usually the case, but to the square root of the intensity, that is, to the electric field intensity of the exciting radiation. It will be shown below that such a dependence of the fluorescence intensity on the excitation intensity is quite common if the fluorescence is excited in a sufficiently broad inhomogeneously broadened absorption band of the medium, provided the intensity of the exciting light exceeds a certain critical value necessary to overcome the relaxation and the saturation of the excitation probability by the individual absorbing molecules of the medium[1].

2. EXPERIMENT

A molybdenum-glass vessel (Wood's horn) with saturated potassium vapor was exposed to giant monopulses of ruby laser emission ($\Delta t \approx 60$ nsec), produced with the aid of a passive shutter of KS-19 glass (Fig. 1). The temperature of the vessel could be varied in the range 20—400°C by air heating. The possibilities of increasing the vessel temperature above 400°C were limited by the softening of the glass and by the rapid drift of the potassium to the glass. The scattered radiation was observed in a direction perpendicular to the laser beam. The intensity of the scattered radiation was measured with the aid of an FÉU-28 photomultiplier feeding an S1-11 pulsed oscilloscope. To measure the intensity of the laser radiation incident on the vessel with the potassium vapor, part of the laser beam was diverted by a light-splitting plate to a photocell (F-5) feeding a pulsed oscilloscope (S1-7). The system for monitoring the ruby-laser power was graduated with the aid of a vacuum calorimeter.

Under the described conditions, we observed a distinct scattering signal with displaced spectral components; the magnitude of the signal increased with increasing vessel temperature or with increasing ruby-laser emission power. At a ruby-laser emission power close to 2 MW, the magnitude of the signal scattering corresponded to a scattering power, integrated over all directions, on the order of 10^{-2} W. To verify that the observed scattering is connected with the potassium vapor, we checked that the scattering signal vanished when the metallic potassium was removed from the vessel (all other conditions were the same). A preliminary investigation of the spectrum of the scattered radiation with the aid of a DFS-12 spectrometer has shown that it consists of a band in the 620—900 nm region. The form of the observed scattering signal duplicated approximately the form of the laser pulse. At the same time, we observed in the spectrum two narrow intense lines with λ = 7665 and 7699 Å. When the signal was observed in these lines the pulse duration exceeded by 4—5 times the duration of the ruby-laser pulse, and reached 200—300 nsec. The appearance in the scattering spectrum of discrete lines with the indicated wavelengths can be uniquely related with the excitation of the states $4P_{1/2}$ and $4P_{3/2}$ of atomic potassium and their subsequent radiative decay. The relatively large duration of these pulses, exceeding the fluorescence time constant

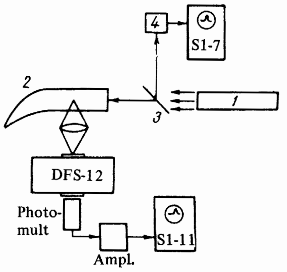

FIG. 1. Diagram of experimental setup for the observation of fluorescence of molecular potassium: 1 – Ruby laser, 2 – vessel with potassium vapor, 3 – light-splitting plate, 4 – F-5 photocell.

---

[1] In the discussion of the results of this work, A. M. Prokhorov and A. A. Manenkov have pointed out to us that similar phenomena were observed in the radio band in investigations by EPR methods [3].

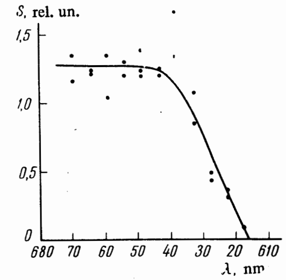

FIG. 2. Spectrum of anti Stokes wing of resonant fluorescence of molecular potassium, S – fluorescence intensity.

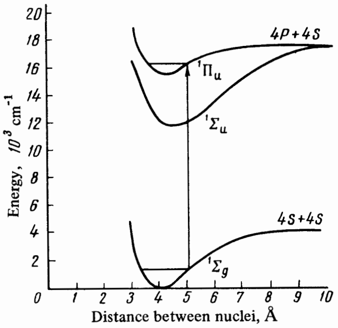

FIG. 3. Potential curves of the ground and lower excited states of molecular potassium

$\tau = 2.7 \times 10^{-8}$ sec[4], is apparently due to the fluorescence diffusion[5], which is possible at the atomic-potassium pressures used in the experiment (0.01–1 mm Hg). The atomic-potassium fluorescence lines could be distinguished clearly against the background of the continuous band of the scattering spectrum at a spectrometer (DFS-12) spectral gap width smaller than 20 Å. The signal observed under these conditions was too weak for a detailed investigation of the fluorescence of the atomic potassium.

Measurement of the scattering spectrum entailed considerable difficulties, in view of the presence in the investigated spectral region (620–900 nm), besides the scattering pulse produced by the potassium vapor, of a parasitic scattering signal, the magnitude of which, at a ruby-laser emission power of 10 MW, was comparable with the signal due to the scattering by the potassium vapor. In the experiments in which the vessel did not contain potassium, we found out that this signal appeared as a result of the action of the ruby-laser emission on the glass of the vessel, its duration was equal to the duration of the ruby-laser pulse, and its magnitude was constant over the spectrum, independent of the vessel temperature, and increased linearly with increasing ruby-laser emission. Owing to the square-root dependence of the potassium-vapor scattering signal, the ratio of the useful signal to the parasitic signal decreased with increasing ruby-laser emission power. This circumstance limited the maximum power of the laser emission used to observe the spectrum of the scattering radiation. The range of variation of the scattering spectrum was limited in this case by the sensitivity of the registration channel of the scattered radiation.

Figure 2 shows the spectrum of the anti-Stokes scattering wing. For minimal signals, the ratio of the potassium-vapor scattering signal to the parasitic signal is equal to 4. The maximum variation of the scattering signal is by a factor of 20. To increase this range in further experiments, we measured the potassium-vapor scattering signal integrated over the spectrum (720–900 nm).

The observed scattering spectrum can be interpreted as a result of absorption of the ruby-laser light by the vapor of molecular potassium K_2 with subsequent resonant fluorescence of the K_2 molecules and the decay of the K_2 molecules into two potassium atoms, one of which turns out to be in the excited states $4P_{1/2}$ and $4P_{3/2}$ and decays spontaneously, giving the discrete spectrum lines λ = 7665 Å (transition $4P_{3/2}$–$4S_{1/2}$) and λ = 7699 Å (transition $4P_{1/2}$–$4S_{1/2}$). An estimate of the saturated-vapor pressure of the molecular potassium[6] has shown that in the investigated temperature interval the concentration of the molecular-potassium vapor is high enough to ensure the observed scattering power. An analysis of work on the spectra of molecular potassium[7-9] has shown that the absorption of the ruby-laser light is most probably connected with the $^1\Sigma_g$–$^1\Pi_u$ transition of the K_2 molecule from the ground state $^1\Sigma_g$ to the excited state $^1\Pi_u$. The K_2 molecule in the excited $^1\Pi_u$ state can break up into two K atoms, one of which turns out to be excited in the states $4P_{1/2}$ and $4P_{3/2}$. The ruby-laser emission frequency $\omega = 14405 \pm 0.5$ cm^{-1} coincides, according to[8], with the frequencies of the transitions from the vibrational levels $v'' = 20$–25 of the ground state to the vibrational levels $v' = 11$–16 of the excited $^1\Pi_u$ state (Fig. 3).

The identification of the ground state vibrational level, responsible for the absorption of the ruby-laser light can be based on the data on the position of the anti-Stokes edge of the fluorescence band of K_2, if no relaxation of the molecules to lower vibrational states of the excited term occurs during the time of the spontaneous decay of the excited $^1\Pi_u$ state. The time τ of the spontaneous decay of the state $^1\Pi_u$, according to measurements of the integral absorption cross section of the $^1\Sigma_g$–$^1\Pi_u$ band[9] and of the duration of the resonance fluorescence[10], amounts to $(5$–$10) \times 10^{-9}$ sec, which is shorter by several orders of magnitude than the time of the vibrational relaxation of the diatomic molecules at the potassium pressure used in the experiment ($\gtrsim 10^{-3}$ sec). The position of the anti-Stokes edge of the fluorescence band of K_2 (Fig. 2) gives the value of the energy of the vibrational level of the ground state, from which absorption of the ruby laser light, corresponding to $v'' \sim 20$, takes place.

To confirm the connection between the observed scattering and the absorption of the ruby-laser light by the molecular-potassium vapor, we measured the dependence of the resonant-fluorescence signal on the mole-

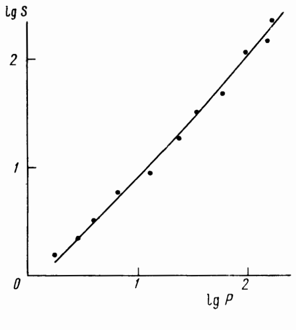

FIG. 4. Dependence of the intensity S of resonance fluorescence under pressure P of the molecular-potassium vapor.

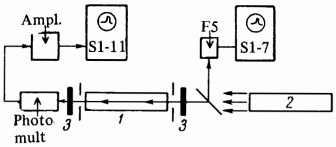

FIG. 5. Diagram of experimental setup for the measurement of nonlinear absorption of ruby laser emission by molecular potassium vapor: 1 – cell with potassium vapor, 2 – ruby laser, 3 – filters attenuating the laser beam by a factor 10^5.

cular-potassium vapor pressure in the temperature range 260–370°C (Fig. 4) at a ruby laser emission power ~1 kW. The vapor pressure was calculated from data on the saturated-vapor pressure of the molecular potassium[6]. Within the limits of the measurement accuracy (±30%), the intensity of the resonance fluorescence is proportional to the saturated-vapor pressure of the molecular potassium.

In the direct measurement of the absorption cross section of the laser ruby light by the K_2 vapor, we observed a nonlinear absorption effect. The scheme of this experiment is shown in Fig. 5. Cell 1 of length 60 cm, of molybdenum glass with sapphire windows, was exposed to radiation from ruby laser 2 under the same giant monopulse regime (duration ~60 nsec, power density $\sim 10^4$ W/cm^2). The system for monitoring the ruby-laser pulse power was the same as in the observation of the scattered radiation (Fig. 1). The ruby laser emission power passing through the cell 1 with potassium vapor saturated at 400°C was measured by a photomultiplier (FÉU-28) feeding an S1-11 pulsed oscilloscope. Calibrated light filters attenuated the intensity of the laser beam by a factor 10^5. The intensity of the light passing through the cell was measured at two positions of the filters: behind the cell 1 and in front of it. In the former case, the intensity of the transmitted beam equaled its intensity when the potassium vapor was frozen out, that is, no absorption of the beam was observed. In the latter case (filters in front of the cell 1), we registered attenuation of the laser beam by a factor 20–300 in the individual monopulses. The relatively large scatter in the value of the attenuation of the laser beam (corresponding to a change in the absorption cross section of the molecular potassium by a factor of 2) is apparently connected with the rotational structure of the absorption spectrum of the molecular potassium and with the variation of the ruby-laser generation frequency from pulse to pulse.

The maximum scatter of the ruby laser frequency from pulse to pulse, measured with the aid of a Fabry-Perot interferometer, was 1 cm^{-1}, whereas the width of the emission spectrum of one pulse was 0.02 cm^{-1}. The absorption of the molecular-potassium vapor over the wavelength of the ruby laser $\lambda = 6942$ Å was measured also in a standard setup (band lamp, the cell described above with potassium vapor saturated at 400°C, DFS-12 spectrometer, and FÉU-28 photomultiplier feeding a microammeter), and coincided with the mean value of the cross section for the absorption of low-intensity ruby-laser emission at the same vapor temperature. The measured absorption cross section $\sigma = 0.2 \pm 0.1) \times 10^{-16}$ cm^2 is in satisfactory agreement with the value expected from the literature data[9]. The spectral width of the DFS-12 spectrometer slit in the last experiment was 6 Å, that is, the measured value of the absorption cross section is averaged in the spectral region 6942 ± 3 Å.

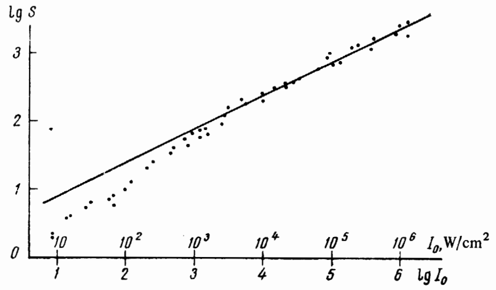

FIG. 6. Intensity of resonance fluorescence S of molecular potassium vs. ruby-laser emission intensity I_0.

As already noted, the dependence of the intensity of the resonant fluorescence of K_2 on the ruby-laser emission intensity I_0 turn out to be unexpected (Fig. 6): instead of being linear, the fluorescence intensity turned out to be proportional to $\sqrt{I_0}$ at $I_0 > 10^3$ W/cm^2, that is, proportional to the intensity of the electric field of the laser emission (the temperature of the vessel with the potassium vapor was in this case approximately 400°C). It is seen from Fig. 6 that at $I_0 \approx 10^3$–10^6 W/cm^2 the intensity of the fluorescence signal is proportional to $\sqrt{I_0}$ within the limits of the measurement accuracy (±30%), whereas at $I_0 \approx 10$–10^3 W/cm^2 a deviation from the square root dependence is observed, exceeding the limits of the fluctuations. The range of variation of the intensity I_0 was limited from below by the sensitivity of the scattered-light registration channel (Fig. 1), and from above by the parasitic signal of the scattering of the ruby-laser light by the walls of the vessel and by the potassium vapor. The presence of a square-root dependence of the fluorescence signal of molecular potassium on the excitation intensity I_0 is attributed by us to the nonlinear character of the absorption of the high-intensity light in the case of the inhomogeneously broadened band of the molecular potassium.

3. INTERPRETATION OF THE SQUARE-ROOT DEPENDENCE OF THE FLUORESCENCE INTENSITY ON THE INCIDENT-LIGHT INTENSITY

1. In the interpretation of this dependence, we start from the simplified model of a two-level system. In the K_2 molecule there is a band of vibrational and rotational levels, pertaining to the electronic ground state ${}^1\Sigma_g$, and a band of vibrational and rotational levels pertaining to the excited electronic state ${}^1\Pi_u$. From each of the rotational-vibrational terms of the ground state, a transition is possible only to three rotational levels with the same vibrational number, pertaining to the excited electronic state. We emphasize that owing to the small spectral width of the incident light and the large distance between the vibrational terms, each vibrational term of the ground state corresponds to a single vibrational term of the excited state. Thus, under our conditions, owing to the small spectral width of the incident light and the selection rules with respect to the rotational number, a four-level scheme is realized when light is absorbed.

each term of the ground state there corresponds a single "partner" from the excited electronic configuration. We thus assume that the absorbing pairs constitute a set of two-level systems with different natural transition frequencies, that is, we deal with a two-level system subject to the influence of inhomogeneous broadening. In our case the inhomogeneous broadening is the result of the Doppler effect and of the rotational structure in the spectrum of the K_2 molecules.

2. The mechanism whereby the light acts on the two-level system depends essentially on its spectral width ν, the intensity, and the lifetime $1/\gamma$ of the excited state. The intensity of the light is best characterized by the quantity $dE/\hbar$, where d is the matrix element of the dipole moment of the transition and E is the average intensity of the electric field (the intensity integrated over the spectrum is proportional to E^2). If the spectral width of the light is large and its intensity is small, so that $\nu \gg \gamma \gg dE/\hbar$ then the transition probability W per second is determined by the usual formulas of perturbation theory[10]

$$W \sim (dE/\hbar)^2/\nu.$$

The population of the excited level f is described by the usual balance equations, and the stationary population

$$f_{\text{stat}} \approx \frac{W}{\gamma} \sim \left(\frac{dE}{\hbar}\right)^2 \frac{1}{\gamma\nu} \ll 1$$

turns out to be a small quantity. Obviously, the intensity of the stationary fluorescence will in this case be proportional to the intensity of the incidental light.

3. If the other limiting case is realized—the case of a monochromatic field, when $\nu \ll \gamma$—then the character of the interaction depends here on the relation between $dE/\hbar$, the width of the level γ, and the deviation from resonance $\Delta\omega = \omega_1 - \omega_0$, where ω_1 is the frequency of the center of the line of the incident light, and ω_0 is the transition frequency. The action of a monochromatic field on a two-level system is analyzed by means of the equation for the density matrix of this system, which includes the Hamiltonian of its interaction with the alternating field of the light wave, and the width of the excited level is taken into account by the relaxation term in the equation. Such an analysis, without account of relaxation, is universally known[1], and the allowance for the relaxation is very simple within the framework of this equation.

It turns out here that for low intensities, when $dE/\hbar \ll \gamma$, the dynamic equation for the density matrix reduces to the balance equation, in which the transition probability per second takes the form

$$W \sim \left(\frac{dE}{\hbar}\right)^2 \frac{\gamma}{\gamma^2 + \Delta\omega^2}.$$

The population f_{stat} will in this case be small:

$$f_{\text{stat}} \sim \left(\frac{dE}{\hbar}\right)^2 \frac{1}{\gamma^2 + \Delta\omega^2} \ll 1.$$

The fluorescence intensity will here also be proportional to the light intensity.

For large intensities, when $dE/\hbar \gg \gamma$, the dynamic equation does not reduce to the balance equation. If we find the population of the upper level f as a function of the time, when the field of the wave is turned on at t = 0, then it approaches the stationary value, experiencing with respect to it damped oscillations with a period $[(dE/\hbar)^2 + \Delta\omega^2]^{-1/2}$, and with a damping time $1/\gamma$. The stationary value of the population takes the form

$$f_{\text{stat}} = \frac{1}{2}\frac{(dE/\hbar)^2}{(dE/\hbar)^2 + \Delta\omega^2 + \gamma^2}. \tag{1}$$

4. If the two-level system is subject to the action of nonmonochromatic radiation of large intensity, then an investigation of its behavior is complicated. In a recently paper Burshteĭn[12] analyzed the case when the radiation, whose spectrum has a Lorentz form and a width ν, acts on a system in which the level width is $\gamma = 0$. It turned out that the behavior of the system is determined by the relation between $dE/\hbar$ and ν. If $dE/\hbar \ll \nu$, then the balance equations hold, as already mentioned above. On the other hand, if $dE/\hbar \gg \nu$, then the behavior of the system in a nonmonochromatic field is similar to its behavior in a monochromatic field. When the field is turned on at the instant t = 0, the population f reaches the stationary vaulu, experiencing damped oscillations with a frequency equal to $[(dE/\hbar)^2 + \Delta\omega^2]^{1/2}$, and with a damping time $1/\gamma$. The stationary value, determined as before by formula (1), where $\gamma = 0$.

5. Summarizing the results given in Secs. 3 and 4, we can state that in the case of a strong field $dE/\hbar \gg \gamma$, ν the population arrives at a stationary value within a time determined by the larger of the quantities, γ or ν, with f_{stat} determined by formula (1). Under experimental conditions the duration of the pulse greatly exceeds the reciprocal width of the spectra $1/\nu$, so that it can be stated that the population of the excited state follows in practice the intensity of the excited light.

6. Formula (1) gives the degree of filling of the excited state of one molecule with a transition frequency ω_0. For a qualitative explanation we assume a simple two-level model with inhomogeneous broadening, that is, we assume that there exists an ensemble of such two-level molecules with a distribution function $\rho(\omega_0)$ over the natural frequencies. In such a schematization, to obtain the degree of occupation of the excited state f_{stat} over the entire ensemble of molecules it is necessary to integrate formula (1) with respect to ω_0:

$$F_{\text{stat}} = \int d\omega_0 f_{\text{stat}}(\omega_0)\rho(\omega_0). \tag{2}$$

The distribution function $\rho(\omega_0)$ is very smooth, its effective width is of the order of the width of the absorption band ($\sim 10^{14}$ sec^{-1}). The width of the function (1) at the maximum employed intensities does not exceed 10^{11} sec^{-1}. Therefore

$$F_{\text{stat}} = \rho(\omega_1)\frac{1}{2}\frac{dE}{\hbar}\int_{-\infty}^{\infty} d(\Delta\omega)\frac{dE/\hbar}{(dE/\hbar)^2 + \Delta\omega^2}. \tag{3}$$

we recall that ω_1 is the frequency of the center of the incident-light line. Expression (3) has been presented for the case of large intensity, when $dE/\hbar \gg \gamma$. The integral (3) can be calculated in elementary fashion:

$$F_{\text{stat}} = \rho(\omega_1)\frac{\pi}{2}\frac{dE}{\hbar}. \tag{4}$$

Formula (4) gives a square-root dependence of F_{stat}, and consequently also of the fluorescence intensity, on the intensity of the exciting light, since $F_{\text{stat}} \sim E$. The transition from the square-root dependence to the linear dependence will occur at intensities such that $dE/\hbar$ is of the order of the larger of the two quantities, ν or γ.

4. CONCLUSION

It is seen from the theoretical interpretation of the phenomenon that a light ray, with respect to its action on a system of molecules, is transformed with increasing intensity from an incoherent set of harmonics into a monochromatic wave. Therefore further investigation of the interaction between high-intensity radiation and atomic and molecular system is of interest from the point of view of the study of the coherent properties of light. Inasmuch as the intensity of the light corresponding to the transition from the linear dependence of the fluorescence intensity to the square-root dependence depends on the relaxation width γ (homogeneous broadening), the investigation of the nonlinear absorption is a new method of measuring the magnitude of the homogeneous broadening under conditions of an inhomogeneously broadened absorption band of the material. The square-root dependence of the population of the excited state at high excitation intensities must be taken into account when considering the mechanism of stimulated fluorescence in dye solutions[13], the kinetics of bleaching of passive shutters used for laser Q-switching, and also in the analysis of the phenomena of self-focusing as a result of absorption saturation[14].

The authors are deeply grateful to E. B. Aleksandrov and V. I. Perel' for help with the work, and also to A. M. Bonch-Bruevich for support and interest in the investigations.

[1] E. B. Aleksandrov, A. M. Bonch-Bruevich, N. N. Kostin, and V. A. Khodovoĭ, ZhETF Pis. Red. **3**, 85 (1966) [JETP Lett. **3**, 53 (1966)].

[2] A. M. Bonch-Bruevich, N. N. Kostin, and V. A. Khodovoĭ, ZhETF Pis. Red. **3**, 425 (1966) [JETP Lett. **3**, 279 (1966)].

[3] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[4] A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Macmillan, 1934.

[5] M. I. D'yakonov and V. I. Perel', Zh. Eksp. Teor. Fiz. **47**, 1483 (1964) [Soviet Phys.-JETP **20**, 997 (1965)].

[6] A. N. Nesmeyanov, Davlenie para khimicheskikh elementov (Vapor Pressure of Chemical Elements), AN SSSR, 1961.

[7] F. W. Loomis, Phys. Rev. **38**, 2153 (1931).

[8] F. W. Loomis and R. E. Nusbaum, Phys. Rev. **39**, 89 (1932).

[9] M. Lapp and L. P. Harris, J. Quant. Spectr. and Radiat. Transfer **6**, 169 (1966).

[10] L. Schiff, Quantum Mechanics, McGraw Hill, 1955.

[11] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Fizmatgiz, 1963 [Quantum Mechanics, Addison-Wesley, 1958].

[12] A. I. Burshteĭn, Zh. Eksp. Teor. Fiz. **48**, 850 (1965) [Soviet Phys.-JETP **21**, 567 (1965)].

[13] F. P. Schafer, W. Schmidt, and K. Marth, Phys. Lett. **24A**, 280 (1967).

[14] A. Javan and P. L. Kelley, IEEE J. Quant. Electr. **QE-2**, 470 (1960).

Translated by J. G. Adashko
93