

Investigation of the nonlinear dependence of the population of inhomogeneously broadened two-level systems on the intensity and width of the spectrum of the exciting radiation

V. A. Khodovoi and V. V. Khromov

(Submitted October 11, 1974)

Zh. Eksp. Teor. Fiz. 68, 1679–1685 (May 1975)

An investigation is made of the nonlinear dependence of the population of the excited state of diatomic molecules of alkali metals with inhomogeneously broadened absorption bands on the power density and the width of the spectral line of the exciting radiation from multimode lasers without mode locking. From the experimental results it follows that in the case when the rate of decay of the excited state is much smaller than the width of the spectral line of the exciting radiation and the rate of transverse relaxation, the average stationary population of the excited state can be calculated sufficiently accurately by summing the contributions to the probability of excitation made by individual harmonics of the exciting radiation.

PACS numbers: 42.65.D, 32.20.L

1. INTRODUCTION

We have earlier reported the observation of nonlinear population of excited states of molecules of K_2 ^[1] and Rb_2 ^[2] by radiation from a ruby laser. The degree of population of excited states was monitored by the change in intensity of molecular fluorescence. As the intensity of the exciting radiation I_0 was increased the intensity of fluorescence was at first proportional to the intensity I_0 and then became proportional to $\sqrt{I_0}$. It was established that, under the conditions realized in these experiments of the absence of quenching of fluorescence and of the duration of the pulse of exciting radiation close to the time constant of the fluorescent decay of the excited states, the observed dependence of the intensity of fluorescence on I_0 coincides with the dependence of the population of the excited states of the molecules regarded as an ensemble of two-level systems with different characteristic frequencies of transition (i.e., of molecules with inhomogeneously broadened absorption bands). From a theoretical analysis it followed that in the absorption spectrum of molecules a dip should be formed whose width at large intensities I_0 is proportional to $\sqrt{I_0}$. The dependence of the width of the dip on I_0 measured by us in^[3] agreed with the predicted one, and this is a direct confirmation of the correctness of the conclusion concerning the possibility of measuring the degree of population of excited states of molecules with inhomogeneously broadened absorption bands in terms of the change in the intensity of molecular fluorescence.

The present paper is devoted to an investigation of the effect of the width of the spectrum of exciting radiation on the nonlinear dependence of the population of such molecular systems on the intensity of exciting radiation^[4,5].

2. EXPERIMENT

For the object of this investigation we have chosen saturated vapor of molecular cesium Cs_2 which has an intense infrared absorption band ${}^1\Sigma_g^- - {}^1\Pi_u$ in the wavelength region of 750–800 nm^[6]. The source of excitation was provided by the radiation of the second Stokes component of stimulated Raman scattering (SRS) of the radiation from a ruby laser in carbon bisulphide at $\lambda = 7693 \text{ \AA}$ (frequency shift $\Delta\nu = 1312 \text{ cm}^{-1}$) and of its first Stokes component of SRS in nitrobenzene at $\lambda = 7705 \text{ \AA}$ (frequency shift $\Delta\nu = 1132 \text{ cm}^{-1}$). These SRS lines fall in the long wavelength edge of the ${}^1\Sigma_g^- - {}^1\Pi_u$

absorption band of Cs_2 .

The experimental arrangement is schematically indicated in Fig. 1. Radiation from a ruby laser with passive Q-factor modulation 1 (KS-19 glass) was focused by a cylindrical lens of focal distance 100 mm into the cell 2 with carbon bisulfide or nitrobenzene placed in a resonator formed by mirrors with reflection coefficients $R_1 = 99\%$ and $R_2 = 50\%$ at a wavelength $\sim 770 \text{ nm}$. The radiation from the ruby laser having passed through cell 2 was focused by a second cylindrical lens of focal distance 30 mm on a cell containing a solution of cryptocyanine in glycerine 3 which served as a power amplifier for the SRS radiation. In this manner it was possible to obtain a power density of the radiation at the indicated wavelengths of the order of 10^7 W/cm^2 with a divergence of the beam of $\sim 5 \times 10^{-3} \text{ rad}$. The resonance fluorescence from the Wood horn 4 containing saturated cesium vapor was observed at right angles to the direction of the exciting radiation. In order to avoid absorption and a change in the spectral composition of the exciting radiation in its passage through the molecular vapor of Cs_2 fluorescence was recorded from a thin layer at a distance of 2 cm from the window of the horn in travelling to which at the utilized pressures of Cs_2 even the greatest possible linear absorption was negligibly small ($< 20\%$). The intensity of the fluorescence was measured by an FÉU-28 photomultiplier, the output of which was fed to an oscillograph with memory C1-42 (7 MHz band). For a stepwise reduction in the intensity of the exciting SRS radiation calibrated light filters Φ were utilized, the power of the SRS pulse was monitored by a photoelectrically calibrated coaxial photocell FÉK-09 recorded by an oscillograph C1-42. To increase the time resolution of the circuit for recording the pulse of the exciting radiation down to 2 nsec the signal from FÉK-09 was applied directly to the deflecting plates of the tube of the oscillograph C1-42. Neutral platinum light filters were utilized for reducing the intensity of light in the channel recording the fluorescence. In observing the fluorescence signal integrated over the whole band $\lambda = 750\text{--}800 \text{ nm}$ it was discovered that over the spectral range of registration indicated above a parasitic signal of the scattering of the SRS radiation is present along with the signal of the fluorescence of the molecular vapor. In order to eliminate it the fluorescence signal was picked out by the monochromator MDR-2 in a narrow spectral region $\sim 100 \text{ \AA}$ situated approximately at the center of the absorption band of molecular cesium. In this region, the ratio of the fluor-

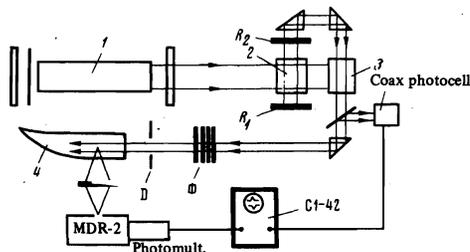


FIG. 1. Diagram of the experimental arrangement.

escence signal to the parasitic signal of the scattered SRS radiation exceeded 50 for all the utilized power levels of the exciting radiation.

In preliminary experiments the shape of the spectrum of the exciting radiation was investigated with the aid of the spectrograph STÉ-1 and of a Fabry-Perot interferometer. In the course of this it was found that in addition to the narrow SRS line there is also present background radiation much weaker per unit interval of the spectrum in the range 20–30 cm⁻¹ on both sides of the center of the SRS line. The intensity of the background radiation integrated over the spectrum amounted in the case of carbon bisulfide to approximately 50% of the total intensity of the radiation. The appearance of background radiation over such a wide spectral region is usually associated with self-focusing and phase modulation of light in the liquid active with respect to SRS^[7-9]. We have established that the angle of divergence of the background radiation exceeds by approximately two orders of magnitude the divergence of the SRS radiation in the narrow spectral line. This enabled us to reduce by approximately three orders of magnitude the intensity of the background radiation by placing a diaphragm D ($\varphi = 1$ cm) in the path of the exciting beam in front of the Wood horn containing cesium vapor. After the introduction of the diaphragm the line of the exciting radiation had a Gaussian shape of width $\Gamma = 0.1$ cm⁻¹ utilizing SRS in carbon bisulfide, and $\Gamma = 1.5$ cm⁻¹ when SRS in nitrobenzene was utilized. The duration of the pulse of the exciting radiation was equal to 5 and 16 nsec respectively for carbon bisulfide and nitrobenzene.

In Fig. 2b,c we have presented on a doubly logarithmic scale the measured dependence of the intensity of resonance fluorescence S and of the population of the excited state F on the intensity I_0 of the exciting radiation. Both dependences were measured at a pressure of the saturated vapor of molecular cesium of 4×10^{-2} mm Hg (pressure of the atomic vapor of cesium was 4 mm Hg). Figure 2a gives the dependence measured by us earlier in^[2] concerned with the excitation of the vapor of molecular rubidium by radiation from a ruby laser with a line width of the radiation $\Gamma = 0.02$ cm⁻¹ at a vapor pressure of molecular rubidium of 5×10^{-2} mm of Hg (the pressure of the atomic vapor of rubidium was 4 mm Hg).

3. DISCUSSION OF RESULTS

In calculating the population of the excited states of the molecules we consider, as in the case of excitation by monochromatic radiation^[1,2], the molecular vapor as an ensemble of two-level systems with different characteristic transition frequencies ω_0 , characterized by their distribution function $\rho(\omega_0)$. In order to calculate the integrated population of the excited state of such a system F one must find the population of the upper level

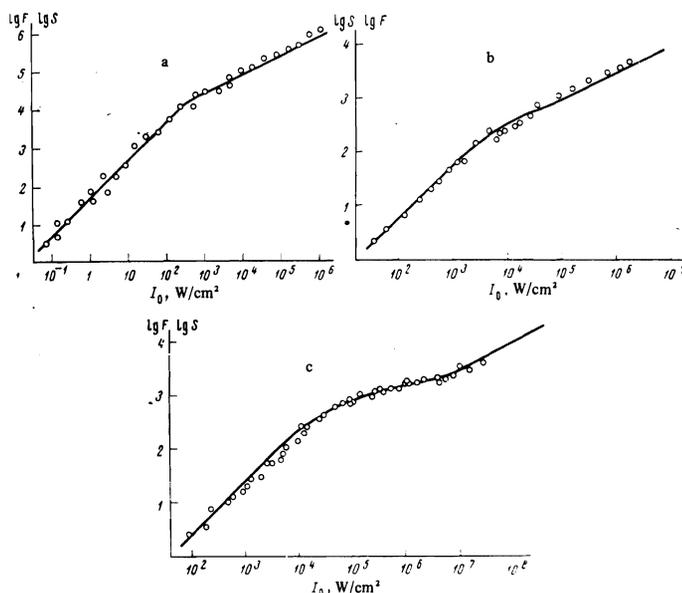


FIG. 2. Dependence of the intensity of molecular fluorescence S and of the population of the excited state F on the power density of the exciting radiation with different widths of the spectral line: a) $\Gamma = 0.02$ cm⁻¹, Rb₂ vapor, excitation at $\lambda = 6943$ Å; b) $\Gamma = 0.1$ cm⁻¹, Cs₂ vapor, excitation at $\lambda = 7693$ Å; c) $\Gamma = 1.5$ cm⁻¹, Cs₂ vapor, excitation at $\lambda = 7705$ Å. Solid lines indicate calculated dependence of $F(I_0)$; experimental values of $S(I_0)$ are shown by dots.

$f(\omega_0)$ for each individual two-level system and then sum it over the frequencies ω_0 :

$$F = \int f(\omega_0) \rho(\omega_0) d\omega_0. \quad (1)$$

The calculation of $f(\omega_0)$ in the field of intense multimode laser radiation represents a complicated theoretical problem. In the paper of Khodovoi and Przhibel'skiĭ^[5] it was shown that for lasers without mode synchronization with a total radiation line width Γ greater than the rate of transverse relaxation γ_2 and the rate of relaxation of the population of excited states γ_1 , the stationary average population $f(\omega_0)$ can be represented in the form

$$f(\omega_0) = W / (\gamma_1 + 2W), \quad (2)$$

where the quantity

$$W = \frac{\gamma_2 d^2}{2\hbar^2} \int \frac{|E(\omega)|^2}{\gamma_2^2 + (\omega_0 - \omega)^2} d\omega \quad (3)$$

has the meaning of the probability of transition per unit time; here d is the matrix element of the component of the dipole moment along the direction of the vector of electric field intensity \mathbf{E} of the exciting radiation. The structure of the expression for W shows that, when the conditions mentioned above are satisfied, the total probability for the transition under the action of the radiation field with random phases of the harmonics is equal to the sum of probabilities of transition under the influence of each of the harmonics¹⁾. In the case of the Gaussian shape of the spectral line of the exciting radiation of central frequency ω_1 realized in our experiments

$$|E(\omega)|^2 = |E(\omega_1)|^2 \exp[-(\omega - \omega_1)^2 / \Gamma^2] \quad (4)$$

the population distribution $f(\omega_0)$ can be represented in the form

$$f(\omega_0) = \left[2 + \frac{2\gamma_1 \hbar^2}{\sqrt{\pi} d^2 |E(\omega_1)|^2 \text{Im} Z(x+iy)} \right]^{-1}, \quad (5)$$

where

$$\text{Im} Z(x+iy) = \pi^{-1/2} \int \frac{\exp(-x^2)}{a^2 + (x-y)^2} dx \quad (6)$$

is the imaginary part of the dispersion function for a plasma^[13], $a = \gamma_2/\Gamma$, $y = (\omega_1 - \omega_0)/\Gamma$.

In order to calculate the dependence of the integrated population of the excited state of the molecular system on the intensity of the exciting radiation using formulas (1) and (2) it is necessary to know the function for the distribution of the molecules over the frequencies $\rho(\omega_0)$, the rates of relaxation γ_2 and γ_1 and also the dipole matrix element for the transition d . Measurement of the rotational-vibrational structure of the spectra of molecular absorption near the wavelength of the exciting radiation has shown that under the conditions of our experiments the distribution function $\rho(\omega_0)$ is practically constant (the variations of the linear coefficient of absorption did not exceed 20%) within the limits of the width of the function $f(\omega_0)$, which in the case of the maximum intensities of the exciting radiations that have been utilized amounted to $\sim 10^{12} \text{ sec}^{-1}$. Therefore in carrying the integration in (1) we have taken the function $\rho(\omega_0)$ to be constant equal to its value of the central frequency ω_1 of the exciting radiation. It is not necessary to know the exact value of $\rho(\omega_1)$, since in the experiment we measured not the absolute value of the population, but only the value proportional to it of the intensity of the fluorescence. The values of the quantities γ_2 , γ_1 and d were taken from the data of reference^[3]: $\gamma_2 = 6 \times 10^8 \text{ sec}^{-1}$, $\gamma_1 = 4 \times 10^7 \text{ sec}^{-1}$ and $d = 10^{-19} \text{ cgs esu}$.

In Figs. 2a,b,c solid lines represent the results of a calculation of the dependence of the integrated population F on the intensity of the exciting radiation I_0 . On the same diagrams the points represent the experimentally measured dependence on I_0 of the magnitude of the intensity of fluorescence which is proportional to the population. The existence of a constant coefficient of proportionality independent of I_0 between the population of the excited state and the intensity of molecular fluorescence leads in the doubly logarithmic scale of Fig. 2 only to a displacement of the whole dependence parallel to the horizontal axis. Superposition of the theoretical and experimental curves (i.e., the choice of the point of "attachment" was achieved by means of a parallel displacement of one of the curves along the vertical axis until best coincidence was attained corresponding to a least mean square deviation of the experimental points from the theoretical curve.

As may be seen from Fig. 2, the general trends of the theoretical and the experimental dependences agree sufficiently well. The most characteristic special features associated with the nonmonochromaticity of the exciting radiation are manifested for a line width of the radiation $\Gamma = 1.5 \text{ cm}^{-1}$. In the case of low intensity of the exciting radiation I_0 , when $d^2|E(\omega_1)|^2/\hbar^2\gamma_1 \ll 1$, the total number of excited molecules is proportional to I_0 . In the range of intensities I_0 for which the relation $\gamma_1 < d^2|E(\omega_1)|^2/\hbar^2 < \Gamma\gamma_1/\gamma_2$ is satisfied the total number of excited molecules depends weakly on I_0 which physically corresponds to the fact that for such values of I_0 saturation occurs of the population of the excited state of the molecules whose absorption frequencies ω_0 fall in the range of frequencies of the spectral line of the exciting radiation, but the intensity I_0 is not yet great enough to excite effectively molecules with transition frequencies outside the line of exciting radiation. For $d^2|E(\omega_1)|^2/\hbar^2 \gg \Gamma\gamma_1/\gamma_2$ effective excitation is observed of molecules characterized by frequencies ω_0 outside the line of the exciting radiation, with the width of the region of effective excitation being proportional to the square root of

I_0 . On a logarithmic scale this corresponds to a reduction in the slope of the dependence $F(I_0)$ by a factor of two compared to the linear dependence (cf., Fig. 2a). Under these conditions the total number of molecules excited by nonmonochromatic radiation with a Gaussian shape of the spectral line is equal to the corresponding value in a monochromatic field of the same power density. In the case of a line width $\Gamma = 1.5 \text{ cm}^{-1}$ the measurement of the dependence $F(I_0)$ at large intensities I_0 is made considerably more difficult by the photodecay of molecules at intensities greater than 10^7 w/cm^2 ^[3]. It has been verified that a significant deviation from the linear dependence of all three curves of Fig. 2 begins at the same spectral density of the exciting radiation $I_0/\Gamma = 5 \times 10^4 \text{ w/cm}$ (the spectral power density per interval of the spectrum of 1 cm^{-1}) in accordance with theory.

At the same time one should still call attention to the small systematic deviation of the experimental dependence from the theoretical one for high intensities of excitation in the case when the width of the spectral line $\Gamma = 0.1 \text{ cm}^{-1}$ (Fig. 2b). These deviations can be explained by an insufficiently complete elimination in the spectrum of the exciting radiation of the background radiation with a broad spectrum the presence of which was mentioned above. We note that in order to explain the observed deviation it is sufficient that the energy of the pulse of background radiation should amount to $10^{-3}-10^{-4}$ of the total energy of the pulse of the exciting radiation. Measurement of the power, of the shape of the pulse and of the spectral composition of such low background radiation presents a very complicated experimental problem.

4. CONCLUSION

Summarizing the results we assume that the average population of the excited state of two-level systems with an inhomogeneous broadening of absorption bands under the action of intense multimode radiation from lasers without mode synchronization in a stationary excitation regime can be sufficiently accurately calculated by summing the contributions of the individual harmonics of the exciting radiation to the probability of excitation. Of considerable interest is the investigation of the dynamics and of the spectrum of the fluctuations in the population of a two-level system in intense radiation fields of multimode lasers. A theoretical analysis of such fluctuations in the case of resonance excitation of a two-level system by noise radiation shows that the relative fluctuations in the difference of populations must increase as the intensity of the exciting radiation is increased^[11].

The authors are grateful to A. M. Bonch-Bruевич, N. N. Kostin and S. G. Przhibel'skiĭ for stimulating conversations and useful discussions of the results of the present work.

¹A similar result has been obtained by Kaplan^[10] and also by D'yakov and Iskanderov^[11] in the special case of excitation of a two-level system by stationary noise radiation of average frequency coincident with the transition frequency for the system. Formula (2) was also obtained by Apanasevich without an indication of the limits on its applicability^[12].

¹V. G. Abramov, O. V. Konstantinov, N. N. Kostin and V. A. Khodovoi, *Zh. Eksp. Teor. Fiz.* **53**, 822 (1967) [*Sov. Phys.-JETP* **26**, 503 (1968)].

²N. N. Kostin, M. P. Sokolova, V. A. Khodovoi and V. V.

- Khromov, Zh. Eksp. Teor. Fiz. **62**, 475 (1972) [Sov. Phys.-JETP **36**, 253 (1972)].
- ³N. N. Kostin, V. A. Khodovoĭ and V. V. Khromov, Izv. Akad. Nauk SSSR, ser. fiz. **37**, 2089 (1973).
- ⁴A. M. Bonch-Bruevich, N. N. Kostin, V. A. Khodovoĭ and V. V. Khromov, Abstracts of papers presented at the 7th All-Union conference on coherent and nonlinear optics, Tashkent, 1972, Moscow State Univ. Press, 1974, p. 206.
- ⁵V. A. Khodovoĭ and S. G. Przhibel'skiĭ, Abstracts of Papers presented at the 7th All-Union conference on coherent and nonlinear optics, Tashkent, Moscow State Univ. Press, 1974, p. 207.
- ⁶N. N. Kostin and V. A. Khodovoĭ, Izv. Akad. Nauk SSSR, ser. fiz. **37**, 2093 (1973).
- ⁷S. A. Akhmanov, A. P. Sukhorukov and R. V. Khokhlov, Usp. Fiz. Nauk **93**, 19 (1967) [Sov. Phys.-Uspekhi **10**, 609 (1968)].
- ⁸A. A. Ostrovskiĭ, in: Nelineĭnye protsessy v optike (Nonlinear Processes in Optics) ed. R. V. Khokhlov, Nauka, Novosibirsk, 1970, p. 12.
- ⁹P. Brewer, Phys. Rev. Lett. **19**, 8 (1967).
- ¹⁰A. E. Kaplan, Abstracts of papers presented at the 6th All-Union conference on nonlinear optics, Minsk, FBAN BSSR, 1972, p. 25.
- ¹¹Yu. E. D'yakov and N. A. Iskanderov, Abstracts of papers presented at the 7th All-Union conference on coherent and nonlinear optics. Tashkent, Moscow State University, 1974, p. 218.
- ¹²P. A. Apanasevich, Zh. Prikl. Spekr. **12**, 231 (1970).
- ¹³W. D. Fried and S. D. Conte, The Plasma Dispersion Function, N.Y.-London, Acad. Press, 1961.

Translated by G. Volkoff
180