Continuous emission of radiation under ion bombardment of some transition metals

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The spectrum of the radiation produced by bombarding polycrystalline nickel, molybdenum, and tungsten with 1–30 keV potassium and inert-gas ions was investigated in the range 200–830 nm in a high vacuum. For the molybdenum and tungsten targets, the spectrum contains both line and continuous components, and the origin of the latter is still not clear. It was found that the continuous emission in the case of molybdenum and tungsten was not the same and was very dependent on the vacuum conditions. It is suggested that the observed continuous emission is connected with the evaporation of excited polyatomic particles, containing atoms of the target metal and gases adsorbed by its surface (mainly metal-oxygen complexes), as well as purely metallic complexes (dimers, trimers, and so on).

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1. INTRODUCTION

The emission spectra recorded during the bombardment of certain transition metals by ions have been found[1–12] to contain both line and continuous components. The line spectrum is known to be due to dispersed and evaporated excited particles of the material of the target and the bombarding beam. The nature of the continuous radiation is more difficult to establish because of the relatively small amount and, to some extent, contradictory nature of existing experimental data. For exchange, Kiyan *et al.*[4,5] have suggested that the observed continuous component is emitted by oscillating electron clouds in ejected target atoms. Kerkdijk *et al.*[7] consider that the radiation is produced by neutral molecules of the metal, and White *et al.*[8] associate it with the evaporation of excited dimers, trimers, or polyatomic target particles. Parilis and Ferleger[13] report a possible connection between the continuous radiation and quantum transitions in clusters retaining the band structure of the metal.

In this paper, we report the results of an investigation of the emission spectra between 200 and 830 nm, produced by bombarding the surfaces of nickel, molybdenum, and tungsten with 1–30 keV potassium and inert-gas ions. Some mechanisms of continuous spectrum emission are discussed.

2. EXPERIMENTAL PROCEDURES

Our experiments with inert-gas ions were carried out on the "Karpaty" mass-spectrometer installation.[14] The ion beam was passed through a 180° magnetic mass analyzer and was then allowed to enter the collision chamber through a 2×5 mm diaphragm. The gas-discharge ion source produced maximum current density of up to 1 mA/cm^2. The ion energy was varied between 0.5 and 30 keV. The pressure in the collision chamber was held below 10^{-7} Torr with the aid of an ion pump.

The experiments with the potassium ions were carried out with the ultrahigh-vacuum "Ion-mishen" (Ion-Target) system, incorporating diffusion and ion pumps. A pressure of 5×10^{-8} Torr could be maintained under working conditions. The surface-ionization source was filled with chemically pure potassium vapor and produced a current density of 1 mA/cm^2 at 10 keV on the surface of the bombarded target. The ion energy could be varied between 0.5 and 20 keV.

In both installations, the target was bombarded along the normal to its surface. The radiation generated near the surface was collected by a quartz lens at right-angles to the direction of bombardment and was analyzed with a high-luminosity diffraction monochromator with a reciprocal linear dispersion of 2 and 4 nm/mm in the ranges 200–630 and 630–830 nm, respectively. The radiation was detected photographically by counting the number of photoelectrons in selected FÉU-106 photomultipliers cooled down to −60 °C. The detection system was highly sensitive and had a large linear dynamic range. The noise level was of the order of a few pulses per second and the maximum signal under optimum experimental conditions was about 10^5 sec^{-1}. The spectra were recorded on the KSP-4 electronic potentiometer with monochromator slits of 0.05–0.2 nm and scanning rates of 2.5 and 5 Å/sec in the 200–630 and 630–830 nm ranges, respectively. The spectral sensitivity of the detection system was calibrated between 200 and 830 nm against standard tungsten and helium lamps.

The specimens were fixed in a holder which was used to introduce them into the bombardment region without releasing the vacuum in the collision chamber. The measured ion current was corrected for secondary electron emission only in the experiments with the potassium ions. While the spectrum was recorded, the ion current could be held constant to better than ± 2%.

Polycrystalline targets were prepared from high-purity metal in the form of 6×12 mm plates. After mechanical polishing and washing, the target surface was cleaned by ion bombardment for 0.5 h. During the initial period of bombardment, the intensity of the emission from the target was found to fall exponentially with time, but remained practically constant after 10–20 min bombardment.

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3. RESULTS

The radiation produced near the surface of nickel, molybdenum, and tungsten under potassium and inert-gas ion bombardment was carefully investigated in the wavelength band between 200 and 830 nm for different ion energies (1–30 keV) and pressures in the region of the bombarded target in the range 10^{-6}–10^{-8} Torr. Figures 1 and 2 show some typical spectra.

In the case of molybdenum and tungsten targets exposed to He^+, Ne^+, Ar^+, Kr^+, and K^+ ions, the emission spectra contained broad continuous emission bands in addition to the line spectra. In the case of the nickel target, the continuous spectrum was also observed in the region of about 570 nm during the initial bombardment of a new specimen. However, after surface clean-up, the intensity of this radiation was found to reduce rapidly down to the background level and, as can be seen in Fig. 1a, the spectrum eventually contained only lines due to the evaporated and dispersed particles of the material of the target and the bombarding beam.

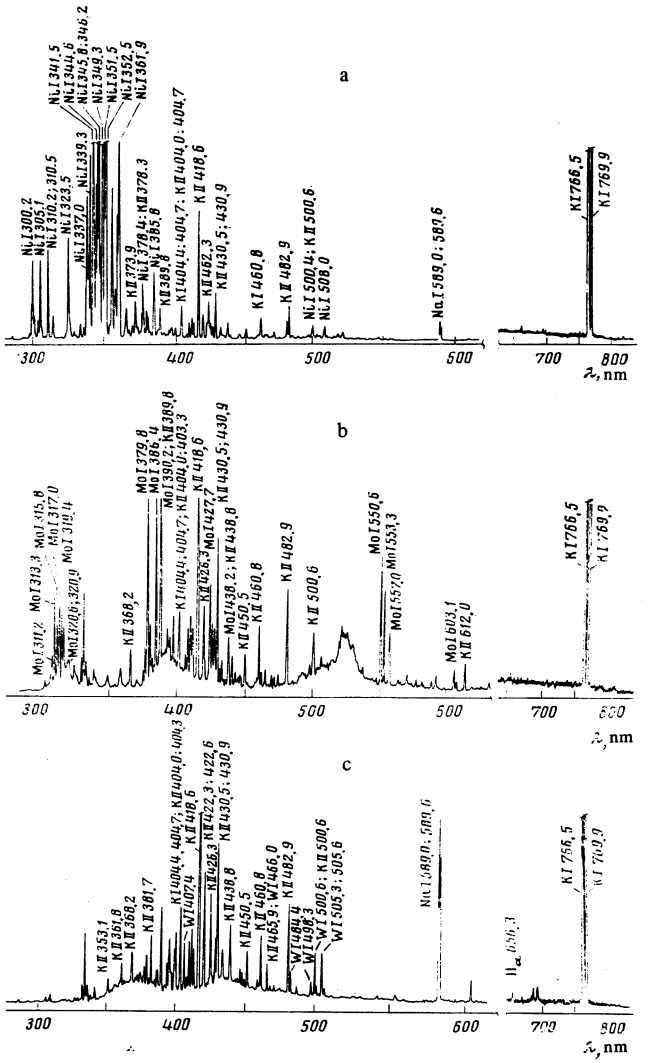

FIG. 1. Emission spectra recorded for nickel (a), molybdenum (b), and tungsten (c) bombarded by 12-keV potassium ions. Beam current 10^{-3} A/cm^2; residual-gas pressure ~5 $\times 10^{-8}$ Torr.

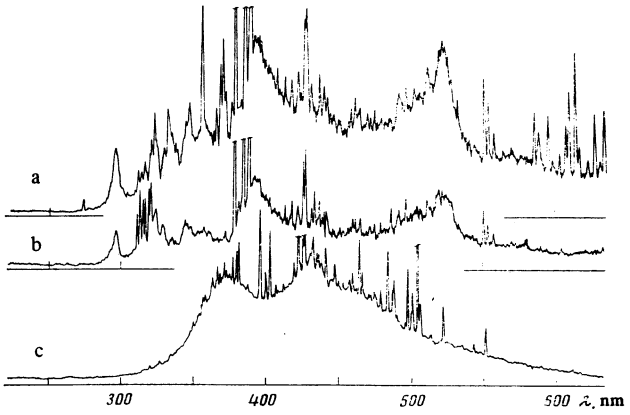

FIG. 2. Segments of the emission spectra recorded for molybdenum bombarded by neon (a) and argon (b) ions, and for tungsten bombarded by argon ions (c). Ion energy 12 keV; beam current density 2×10^{-4} A/cm^2; residual-gas pressure 10^{-7} Torr.

A large number of lines was identified in the recorded spectra. We now report the main results obtained as a result of the examination of the continuous radiation.

3.1. Dependence of the continuous spectrum on the target material

The continuous spectra emitted under bombardment of tungsten and molybdenum surfaces by the above ions at sufficiently low pressures ($\lesssim 10^7$ Torr) are substantially different. It is easily seen by comparing the typical spectra given in Figs. 1b, c and 2b, c for K^+ and Ar^+ ions, respectively. In the infrared, which is not shown in Fig. 2, the intensity of the continuous radiation is found to fall monotonically with increasing wavelength in a way similar to that shown in Fig. 1.

The spectrum recorded for the molybdenum target at a pressure of about 10^{-8} Torr contain (Fig. 1b) three well-defined broad continuous emission bands at 325, 395, and 520 nm. The spectrum obtained for tungsten under similar conditions is found to contain only two bands, one at 380 and the other at 430 nm (Fig. 1c). We note that the compared spectra were recorded under identical experimental conditions, i.e., for the same residual gas pressure, ion energy, ion beam current, radiation collection geometry, and so on. It will be shown that this is an important point in the present context. In particular, differences between experimental conditions appear to be responsible for the discrepancies between the results reported by different authors. Thus, Kiyan *et al.*[4,5] have found the same intensity distribution in the visible part of the continuum in the case of molybdenum and tungsten bombarded by He^+, Ne^+, and Ar^+, but this is in disagreement with our results. On the other hand, the experiments of White *et al.*,[8] performed in a better vacuum than those described by Liyan *et l.*,[4,5] are in good agreement with our data. The results obtained by Kerkdijk *et al.*[7] for molybdenum are similar to our results.

In several experiments[15–17] concerned with the investigation of the emission by molybdenum and tungsten under ion bombardment continuous emission was not observed at all, and this may have been due to insuffi-

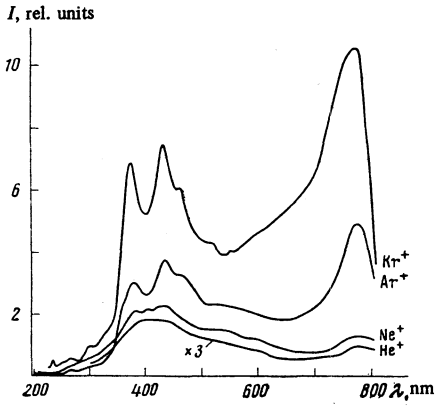

FIG. 3. Intensity distribution in the continuous spectrum recorded for tungsten bombarded by helium, neon, argon, and krypton ions (ion energy 12 keV; beam current density 0.6×10^{-4}–2×10^{-4} A/cm^2). Data corrected for the spectral sensitivity of the radiation-detecting system.

cient sensitivity of the recording equipment. It is therefore important to call attention to the fact that it is essential to use high-luminosity spectrometers and high-sensitivity low-noise detection systems that are linear in a broad range of values of the measured quantity.

3.2. Dependence of the spectrum on the type, energy, and current density of bombarding particles

Figure 3, which is corrected for the spectral sensitivity of the optical system, shows the intensity distribution in the continuous spectrum of a tungsten target bombarded with 12-keV He^+, Ne^+, Ar^+, and Kr^+ ions with beam density of 0.6×10^{-4}–2×10^{-4} A/cm^2 at a residual gas pressure of about 10^{-7} Torr. It is clear from the figure that the character of the intensity distribution does not depend on the type of bombarding ion. The same conclusion is reached by analyzing all the molybdenum spectra illustrated in Figs. 2a and b for the Ne^+ and Ar^+ ions. It is also important to note that when a chosen target is bombarded under comparable vacuum conditions with K^+ and inert-gas ions of the same energy and same beam current density, the continuous spectra are found to be similar. Hence, it follows that the beam particles implanted in the target surface are not responsible for the observed features of the continuous spectrum.

An increase in the ion energy to 10–30 keV results in an increase in the intensity of the radiation but not in an appreciable change in its spectral distribution. At low ion energies ($E\lesssim4$ keV), the spectrum is found to contain features similar to those observed when the vacuum conditions are poorer (see Sec. 3.3). It would appear that, at low energies, the rate of adsorption of the residual gas particles on the target surface exceeds the rate at which they are removed as a result of evaporation under ion bombardment, and the observed changes in the spectrum are due to changes in the state of the target surface.

It is clear from Fig. 3 that, given the ion energy, the intensity of the continuum increases with increasing mass of the bombarding ion.

At low pressures ($\lesssim10^{-7}$ Torr), the intensity of the continuous radiation increases linearly with increasing current density in the ion beam. This is also observed for the spectral lines due to the dispersed and evaporated particles. This effect was examined only at ion energies of 10–15 keV although it will be important to perform such measurements at low ion energies and at a constant energy but different residual-gas pressures.

3.3. Dependence on vacuum conditions

Figure 4 shows some of the many recorded spectra illustrating the dependence of the spectral distribution and the intensity of the continuous radiation on the residual-gas pressure, which we have found[9–11] in the region in which the beam interacts with the target. As can be seen from the figure, the continuous spectrum of molybdenum bombarded by K^+ at a pressure of 5×10^{-8} Torr (Fig. 4c) is appreciably different from the spectra obtained at higher pressures, i.e., at $\sim5\times10^{-7}$ Torr (Fig. 4b) and $\sim2\times10^{-6}$ Torr (Fig. 4a). The well-defined maxima at 325, 395, and 520 nm can no longer be seen, as the vacuum deteriorates, against the much higher intensity of the continuous spectrum throughout the wavelength range under investigation. Strong narrow bands are found to appear at 296 and 346 nm (half-width 3–5 nm). It is important to note that the variation of the intensity of different parts of the continuum with pressure is not the same. Whilst the narrow bands at 296 and 346 nm are found to increase almost in proportion to the improvement in the residual-gas pressure, and totally disappear at pressures of about 10 Torr, the broad bands at 325, 395, and 520 nm are less dependent on the residual-gas pressure. When a pressure of about 10^{-7} Torr is reached, the intensity is only slightly dependent on further improvement in the vacuum conditions. The spectral-line intensity is also only slightly

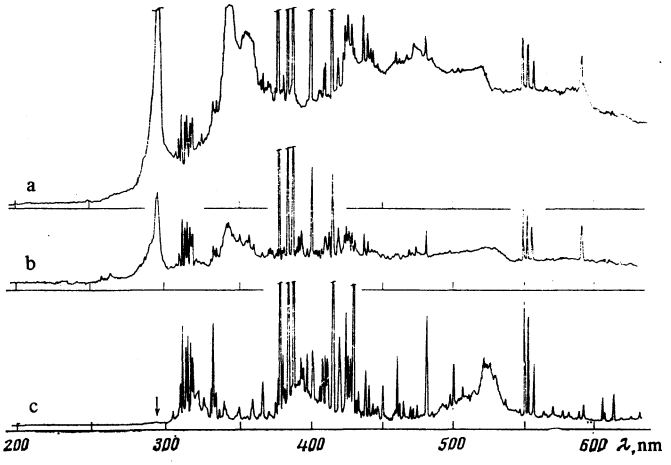

FIG. 4. Emission spectra obtained for molybdenum bombarded by potassium ions (ion energy 12 keV; beam current density 0.2×10^{-3} A/cm^2) at the following residual-gas pressures: a) $\sim2\times10^{-6}$ Torr; b) $\sim5\times10^{-7}$ Torr; c) $\sim5\times10^{-8}$ Torr.

affected (by less than a factor of two) when the pressure is reduced from 10^{-5} to 10^{-7} Torr.

The continuous spectrum emitted by tungsten is found to vary with the residual-gas pressure mainly in intensity, but retains most of the features of the spectral distribution shown in Figs. 1c and 2c. At a pressure of about 10^{-6} Torr, the difference between the continuous spectra of molybdenum and tungsten is appreciable only in the ultraviolet. In the visible, on the other hand, the spectra of molybdenum and tungsten have no well-defined distinguishing features under these conditions, and this is in agreement with the observations of Kiyan *et al.*[4,5] under roughly similar vacuum conditions.

3.4. The effect of radiation collection and spectral resolution of the equipment

In order to identify the source of the continuous radiation, the spectra were recorded under different collection conditions. In some experiments, the radiation was collected by a system whose optical axis was placed, with the aid of a laser, at an angle of 2° to the plane of the target, i.e., so that the area bombarded by the ions was in the field of view. In other experiments, the optical axis of the system was at a small negative angle, so that the radiation was collected only from the aureole in front of the target. In all experiments, the collecting lens produced a magnification of $s = 1$, so that the size of the region from which the radiation was collected was determined by the width of the entrance slit of the monochromator. Comparison of the spectra recorded in these experiments shows that the overall character of the distribution of the continuous radiation was the same in all cases. On the other hand, the intensity of the radiation falls with increasing distance from the surface, and this is faster for the line spectra than for the continuous spectra. For example, the aureole of the continuous spectrum in the case of molybdenum is still observed at a distance of about 1 cm. Most of the spectrograms, including those in Figs. 1–4, were recorded with a resolution of 0.3–0.4 nm in the spectral band 200–630 nm and a resolution of 0.6–0.8 nm in the band 630–830 nm. An improvement in the spectral resolution to 0.1 nm did not reveal any structure in the observed continuous spectrum.

4. DISCUSSION OF RESULTS

Analysis of the data obtained for the continuous radiation generated under ion bombardment on the surface of polycrystalline molybdenum and tungsten specimens leads to the following conclusions.

1. The radiation is observed in the aureole, i.e., it is emitted by particles leaving the bombarded target surface.

2. The continuous emission has different spectral distributions for different targets.

3. The intensity of a given segment of the continuous spectrum of molybdenum is very dependent on the gas pressure near the target but, for other metals, it is practically independent of this pressure.

4. The type of bombarding ion has no effect on the overall character of the spectral distribution of the continuous radiation from a given target.

5. The intensity of the continuous spectrum for a given target depends on the energy and mass of the bombarding ion.

6. The intensity of the continuous spectrum observed under good vacuum conditions ($\lesssim 10^{-7}$ Torr) is a linear function of the current density in the ion beam, as is the intensity of the line spectrum.

The above results lead us to the suggestion that the two groups of bands observed in the continuous spectrum, which exhibit different behavior depending on the vacuum conditions under which bombardment takes place, are connected with the radiative deexcitation of different diatomic and polyatomic particles leaving the surface of the target in excited states. Some of these particles may emit continuous radiation as a result of free-bound transitions.[18] The first group of bands is very dependent on the vacuum conditions and is probably emitted by evaporated complexes containing atoms of the bombarded metal and residual gas-atoms adsorbed on the target surface. As they leave the target surface in the excited state, they emit, in the case of molybdenum, the relatively narrow bands at 296 and 346 nm. They are, most likely, oxygen-molybdenum complexes whose spectra are not, unfortunately, well known. There is a striking correlation found, by White *et al.*,[8] between the observed bands and the absorption spectra of molybdenum isolated in an inert-gas host.[19] However, if we adopt the suggestion[8] that the observed radiation is associated with metal dimers, it is not clear how one can explain the total disappearance of these bands which we have found when molybdenum was bombarded at very low pressures (10^{-8} Torr). The second group of bands, whose intensity is not very pressure-dependent between 10^{-6} and 10^{-8} Torr, may be connected with the evaporation of excited dimers, trimers, etc. The observed linear dependence of their intensity on the ion current in the beam supports this suggestion. It is, therefore, important to investigate the role of bulk contamination (especially gases dissolved in the metal) which may also be responsible for the observed radiation.

To obtain a deeper understanding of the nature of the continuous radiation, it will be necessary to carry out composite studies of the emission of photons under ion bombardment, using mass-spectrometric and spectroscopic methods simultaneously, and to investigate the emission spectra of metal molecules excited in the gaseous phase by electron or ion impact.

[1] N. H. Tolk, C. W. White, and P. Sigmund, Bull. Am. Phys. Soc. **18**, 686 (1973).

[2] V. V. Gritsyna, T. S. Kiyan, Yu. E. Logachev, and Ya. M. Fogel', V sb. Vzaimodeĭstvie atomnykh chastits s tverdym telom (in: Interaction Between Atomic Particles and Solids), Part 2, Kiev, 1974, p. 7.

[3] W. F. Van der Weg and E. Lugujjo, Atomic Collisions in Solids, Plenum Press, New York, 1975, p. 511.

[4]T. S. Kiyan, V. V. Gritsyna, Yu.E. Logachev, and Ya.M. Fogel', Pis'ma Zh. Eksp. Teor. Fiz. **21**, 77 (1975) [JETP Lett. **21**, 35 (1975)].
[5]T. S. Kivan, V. V. Gritsyna, and Ya.M. Fogel', Nucl. Instrum. Methods **132**, 415 (1976).
[6]S. F. Belykh, V. I. Veksler, R. N. Evtukhov, and I. F. Lifshits, Fiz. Tverd. Tela (Leningrad) **17**, 1852 (1975) [Sov. Phys. Solid State **17**, 1217 (1975)].
[7]C. B. W. Kerkdijk, K. H. Shartner, R. Kelly, and F. W. Saris, Nucl. Instrum. Methods **132**, 427 (1976).
[8]C. W. White, N. H. Tolk, J. Kraus, and W. F. Van der Weg, Nucl. Instrum. Methods **132**, 419 (1976).
[9]S. S. Pop, A. I. Imre, I. P. Zapesochnyĭ, A. I. Dashchenko, and S. A. Evdokimov, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 421 (1976) [JETP Lett. **23**, 381 (1976)].
[10]S. A. Evdokimov, S. S. Pop, V. G. Drobnich, and S. F. Gara, in: Vzaimodeĭstvie atomnykh chastits s tverdym telom (Interaction Between Atomic Particles and Solids), Part 2, Kharkov, 1976, p. 181.
[11]S. S. Pop, A. I. Imre, A. I. Dashchenko, V. S. Vukstich, S. A. Evdokimov, and I. P. Zapesochnyĭ, in: Vzaimodeĭstvie atomnykh chastits s tverdym telom (Interaction Between Atomic Particles and Solids), Part 2, Kharkov, 1976, p. 184.
[12]T. U. Arifov, K. K. Vasil'eva, D. D. Gruich, V. P. Peshekhonov, S. V. Pichko, and Z. S. Settarova, in: Vzaimodeĭstvie atomnykh chastits s tverdym telom (Interaction Between Atomic Particles and Solids), Part 2, Kharkov, 1976, p. 210.
[13]E. S. Parilis and V. Kh. Ferleger, in: Vzaimodeĭstvie atomnykh chastits s tverdym telom (Interaction Between Atomic Particles and Solids), Part 2, Kharkov, 1976, p. 202.
[14]I. P. Zapesochnyi, A. I. Imre, A. I. Dashchenko, V. S. Vukstich, F. F. Danch, and V. A. Kel'man, Zh. Eksp. Teor. Fiz. **63**, 2000 (1972) [Sov. Phys. JETP **36**, 1056 (1973)].
[15]I. Terzič and B. Perović, Surf. Sci. **21**, 86 (1970).
[16]H. Kerkow, Phys. Status Solidi A **10**, 501 (1972).
[17]I. S. T. Tsong, Phys. Status Solidi A **7**, 451 (1971).
[18]M. A. El'yashevich, Atomnaya i molekulyarnaya spektroskopiya (Atomic and Molecular Spectroscopy), Fizmatgiz, 1962.
[19]D. W. Green and D. M. Gruen, J. Chem. Phys. **60**, 1797 (1974).

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Determination of the relaxation characteristics by a polarization method in nonlinear spectroscopy

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Various aspects are considered of a new spectral method, free of Doppler broadening and proposed by Wieman, Hansch, *et al.* (Phys. Rev. Lett. **36**, 1170, 1976; Opt. Comm. **18**, 227, 1976). The method is based on registration of the signal of a test field passing through a crossed polaroid, with a definite choice of the polarization of the strong laser field that produces the nonlinear phenomena. It is noted in the cited papers that this "polarization" method is much more sensitive than earlier nonlinear spectroscopy methods. In the present paper it is shown theoretically that, in addition to sensitivity, the polarization method affords unique possibilities for the investigation of relaxation processes. It can be used to investigate the relaxation of the "polarization moment" of a quantum system (the total population of the levels, the orientation, the alignment) separately, something impossible with the earlier methods. An optimal experimental sequence is recommended for the investigation of the relaxation characteristics. In the analysis of concrete cases it is noted that in practice the homogeneous saturation characteristic of longlived systems (molecules, atomic metastable formations) should not appear in experiments with crossed polaroids. This conclusion is most important for the problem of developing lasers with very high frequency stability.

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1. INTRODUCTION

A new method of nonlinear spectroscopy has been recently proposed,[1,2] based on the following known phenomenon. Polarizing laser radiation produces anisotropy when it interacts nonlinearly with the medium: a gas medium becomes uniaxial (if the radiation is linearly polarized) or gyrotropic (in the case of circular polarization), and is characterized by phenomena typical of anisotropic media, such as dichroism and birefringence. In particular, a linearly polarized trial wave passing through a medium becomes elliptically polarized and at the same time the axes of the ellipse rotate. The gist of the method of[1,2] consists of recording the signal of the trial wave passing first through the medium and then through a polaroid crossed relative to the initial polarization of the wave. The resultant signal is due only to the anisotropy induced by the strong field, and it is therefore patently of nonlinear origin. It was proposed in[1,2] to use this "polarization" method for high-resolution spectroscopy in systems with Doppler-broadened lines. By registering only the nonlinear part of the signal, the influence of the Doppler broadening is eliminated. It was shown at the same time[1,2] that the polarization method is much more sensitive than the

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