Picosecond kinetics of the primary electronic processes in the formation of the latent image in microscopic silver halide crystals

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Picosecond spectroscopy reveals that the fastest primary processes in the formation of the latent-image centers in microscopic AgBr(I) crystals occur in times in the picosecond range and are accompanied by a sensitization of the system to long-wavelength light. This sensitization decays over hundreds of picoseconds. A model is proposed for the kinetics of the effect.

Recent studies with nanosecond light pulses[1,2] have shown that the primary electronic photoprocesses in microscopic silver halide crystals occur over times shorter than 10^{-8} s. In this letter we report a first study of the kinetics of these processes with a picosecond time resolution, determined by the short length ($\Delta t = 3.7$ ps) of the applied light pulses and also by the continuously adjustable delay δt (in picoseconds) between the first pulse, which excites the process, and the second pulse, from whose effect the state of the system is determined. This effect is characterized by a change in the blackening of the developed photographic emulsion containing the microscopic crystals under study.

The experiments were carried out at the PULS complex (the acronym is formed from the Russian words for "picosecond universal laser spectrometer").[3] In the VRP emulsion used, the microscopic AgBr(I) crystals, about 35 nm in diameter, are suspended in a gelatin layer 6 μm thick. The first pulse, which is actinic (at the third or second harmonic of a Nd laser), with $\lambda = 0.35$ μm (3.54 eV) for an emulsion which is not sensitized or $\lambda = 0.53$ μm (2.34 eV) for an emulsion which has been sensitized to green light, is focused on the emulsion in the form of a circle with a diameter $d \approx 0.4$ mm. The second pulse, which is not actinic, is at the fundamental frequency of the same laser, $\lambda = 1.06$ μm (1.17 eV), and is applied in a small circle with $d \approx 0.1$ mm inside the first light pulse. The intensity of each pulse, measured by an optoacoustic detector[4] or an FPM-02 instrument, is adjusted with light filters. When the first (actinic) pulse has an energy density on the order of 10^{-3} J/cm^2, it causes a blackening density $D_a \approx 0.2$–0.4 above the fog. The energy density of the second (nonactinic) pulse was varied from zero to $E_n \approx 1$ J/cm^2, at which this pulse—in the absence of the first pulse—caused no significant blackening D_n of the emulsion. The emulsion was developed by the standard procedure; the blackening densities were measured with a microphotometer.

The results of an experiment for a sensitized emulsion (the first pulse had a wavelength $\lambda = 0.53$ μm) are shown in Fig. 1. Specifically, this is a plot of the blackening density D_{a+n} caused by the application of the two pulses versus E_n for various

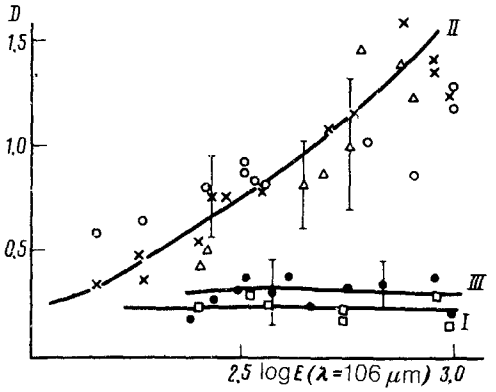

FIG. 1. Blackening density of the photographic material versus the logarithm of the energy of the IR pulse. I: Negative delay of the IR pulse (-30 ps). II: Delays of ($\times$) 0, ($\circ$) 30 ps, and ($\triangle$) 150 ps. III: Delay of 420 ps ($\cdot$).

delays δt: -30 ps ($\square$), 0 ps ($\times$), 30 ps ($\circ$), 150 ps ($\triangle$), and 420 ps ($\cdot$). It follows from these results that when the nonactinic pulse is applied first ($\delta t = -30$ ps) it has no effect on the blackening caused by the actinic pulse (we find $D_{a+n} \approx D_n$ for all values of E_n). When the pulses are coincident in time, the nonactinic light causes a sharp increase in the blackening D_a, ranging up to a factor of four or five [$D_{a+n} \approx (4\text{–}5)D_a$] at an energy density $D_n \sim 1$ J/cm^2. In other words, we observe an effect which is the inverse of the Herschel effect. As the delay of the second pulse is increased, the effect weakens: At $\delta t = 420$ ps the excess blackening D_{a+n} is only slightly greater than D_a.

Similar results were obtained in the case $\lambda = 0.35$ μm and also when we used an unsensitized emulsion, or when we applied a train of pulses ($\approx$20 ps), using the apparatus described in Ref. 5, with $\lambda = 0.53$ μm and $\lambda = 1.06$ μm. It follows that the kinetics of the observed effects is determined by processes which occur in the AgBr(I) microscopic crystals, regardless of whether the exciting light is in the intrinsic absorption band of the microscopic crystals or in the region of spectral sensitization.

These results can be explained by assuming that there are two types of capture centers in these microscopic crystals, lying less than 1.17 eV below the conduction band. The centers of the first type are sensitivity centers, which subsequently form a latent image; the centers of the second type are recombination centers, at which the electron lifetime before recombination is about $\tau \approx 400$ ps, as follows from the dependence of the effect on the delay δt. After the transition from the valence band to the conduction band caused by the actinic light, the electrons quickly become distributed between the different types of centers in a ratio of 1:4 to 1:5, with the recombination centers acquiring most of the electrons. The application of the nonactinic light sends the photoelectrons away from the centers back into the conduction band; the transition from the sensitivity centers is considerably less probable than the transition from the recombination centers. The result is a pumping of electrons to the sensitivity centers. As the population of the recombination centers decreases with increasing δt, the increase in the blackening becomes smaller. At values $\delta t \gg 400$ ps, a "normal" Herschel effect should set in because of a transition of electrons from sensitivity

centers into the conduction band and then to recombination centers which is not canceled by the inverse process.

In summary, we have obtained the first experimental data on the electronic processes which occur in the microscopic crystals of silver halide emulsions, which rise in a time on the order of a few picoseconds and decay over hundreds of picoseconds. These emulsions strongly influence the formation of the latent-image centers. In addition, we have found that there is an exceedingly fast transfer of excitation from molecules of the sensitizer to the crystal lattice of the silver halide (this transfer occurs over a time no longer than a few picoseconds).

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