

**G. I. Lashkov.** *Energy transport involving triplet states in phase recording of light.* A radiationless transfer of energy between excited states to the triplet state of donor (D) molecules and unexcited acceptor (A) molecules, with the result that the latter are immediately put in the triplet state, occurs when D and A approach to a distance equal to the sum of the van der Waals radii of the molecules. Under exothermic transfer conditions, with  $E(T_1^D) > E(T_1^A)$  (Fig. 1), the process takes place with unit efficiency.<sup>1</sup>

The filling of  $T_1^A$  in an indirect manner (through the excitation of D), through the use of T-T energy transfer, raises the possibility of a spectral shift of the photosensitivity of A, and this shift may be substantial in several cases. Furthermore, a given D molecule—a spectral sensitizer—can participate many times in events of the absorption of light and the initiation of photoconversions of A. Specifically these properties of processes which are sensitized through T-T energy transfer have been suggested for use in searching for phase photosensitive systems.<sup>2</sup>

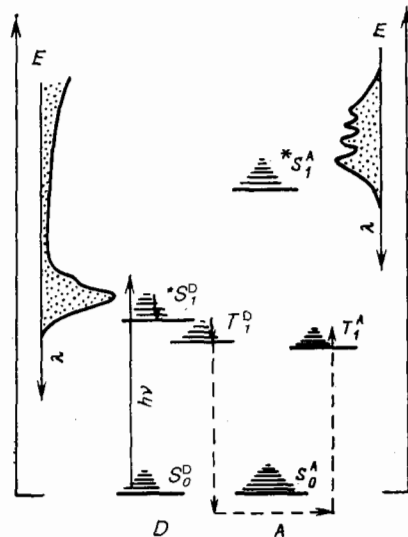


FIG. 1. Spectral sensitization involving triplet-triplet energy transfer.

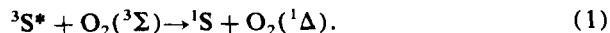
The idea of a phase recording of light which initiates photoprocesses in a system with T-T energy transfer is quite transparent. If the photocovering of A is accompanied by a sharp change in the polarizability of the molecules, the dispersion outside the absorption bands of A will give rise to a change in the refractive index ( $dn$ ). The repeated functioning of a given D molecule leads to a significant value of  $dn$  at a low absorption of the system in the working spectral region.

Actually, even the excitation of A into  $T_1^A$  is accompanied by a dispersive photorefractive effect, since the absorption  $T^A \leftarrow T_1^A$  occurs in a spectral region different from that of  $S_n^A \leftarrow S_0^A$ . We would thus expect that it would be possible to realize phase photosensitive objects based on donor-acceptor systems in vapors, liquids, and doped molecular crystals, where  $dn$  is induced for the lifetime of triplet excited states.

The use of the photooxidation of polyacene compounds<sup>3</sup> as the process responsible for the photorefractive led to the development of a new class of phase recording media, the reoxans.<sup>4</sup>

A reoxan consists of an anthracene compound (An) and a spectral sensitizer (S), both are dissolved in a polymer binder (Fig. 2). The material is sensitized by prolonged exposure to oxygen at an elevated pressure.

Exposure to light may cause the following processes: A transfer of energy as the sensitizer in the T state,  $^3S^*$ , and  $O_2(^3\Sigma)$ , approach each other by diffusion, with the  $O_2$  becoming chemically active:



Oxidation of An by oxygen:

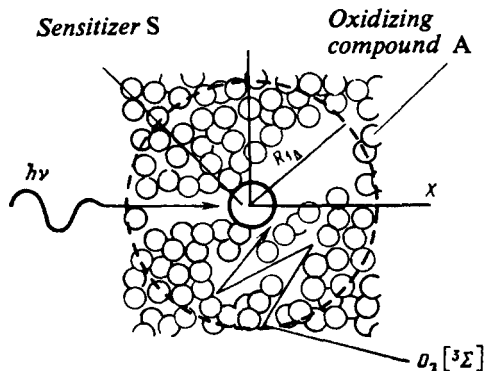


FIG. 2. Model of sensitized photooxidation of a solid matrix.



accompanied by a change in the molecular refraction, which has the magnitude  $(1.0-0.3) \cdot 10^{-22} \text{ cm}^3$  in the spectral interval  $0.44-1.5 \mu\text{m}$ .

Spontaneous decay of  $O_2(^1\Delta)$ :



As a result of process 2, a region with a local change in refractive index forms around S (Fig. 2). The size of this region is determined by the mean square displacement of  $O_2(^1\Delta)$  over the lifetime  $\tau_{1\Delta}$ :

$$R_{1\Delta} = (6D\tau_{1\Delta})^{1/2}.$$

With  $D \sim 10^{-8} \text{ cm}^2/\text{s}$  and  $\tau_{1\Delta} \sim 10^{-4} \text{ s}$ , the value of  $R_{1\Delta}$  in a polymer would be  $10^{-6} \text{ cm}$ . A high spatial resolution of the layer is thus achieved.

The image is fixed as a result of the natural diffusion of oxygen out of the polymer matrix.

Methods have been developed for producing reoxan films with a thickness  $l = 10-3000 \mu\text{m}$ , with values of  $dn$  up to  $2 \cdot 10^{-2}$ , and with a spectral-sensitivity region of  $0.44-0.76 \mu\text{m}$ . The exposure at which the optical shift  $dn \cdot l$  is equal to the wavelength of the light involved,  $\lambda$ , is  $0.5-1.5 \text{ J/cm}^2$ .

Various modifications of reoxan have been proposed: with physical development of the latent image<sup>5</sup> and with photobleaching<sup>6</sup> and with luminescent sensitizers.<sup>6</sup>

The phase-photosensitive systems which have been developed on the basis of this principle will find widespread use in research on holography, adaptive optics, gradient optics, and integrated optics.

<sup>1</sup>V. L. Ermolaev, E. N. Bodunov, E. V. Sveshnikova, and T. A. Shakhverdov, *Bezyzluchatel'nyĭ perenos energii elektronnoĭgo vzbuzhdeniya* (Radiationless Transfer of Electronic-Excitation Energy), Nauka, Leningrad, 1977.

<sup>2</sup>G. I. Lashkov and V. I. Sukhanov, *Opt. Spektrosk.* **44**, 1008 (1978) [*Opt. Spectrosc. (USSR)* **44**, 590 (1978)].

<sup>3</sup>G. I. Lashkov and E. N. Bodunov, *Opt. Spektrosk.* **47**, 1126 (1979) [*Opt. Spectrosc. (USSR)* **47**, 625 (1979)].

<sup>4</sup>G. I. Lashkov, in: *Neserebryanye fotograficheskie protsessy* (Nonsilver Photographic Processes) (ed. A. L. Kartuzhanskiĭ), Khimiya, Leningrad, 1984, p. 130.

<sup>5</sup>G. I. Lashkov, A. P. Popov, and O. B. Ratner, *Opt. Spektrosk.* **52**, 585 (1982) [*Opt. Spectrosc. (USSR)* **52**, 350 (1982)].

<sup>6</sup>A. P. Popov, G. I. Lashkov, A. S. Cherkasov, O. B. Ratner, B. M. Krasovitskiĭ, and V. M. Shershukov, *Opt. Spektrosk.* **58**, 941 (1985) [*Opt. Spectrosc. (USSR)* **58**, 576 (1985)].