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Abstract

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SPECTRAL DISTRIBUTION OF THE PHOTOCONDUCTIVITY OF CHLOROPHYLL *a* AS A FUNCTION OF LAYER THICKNESS

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When a layer of chlorophyll a + b on a platinum electrode immersed in an electrolyte solution was illuminated, V. B. Evstigneev and A. N. Terenin (ˆ1) first demonstrated the photoelectric sensitivity of chlorophyll. Later, A. N. Terenin and E. K. Putseiko (ˆ2-4), using the method of condenser photo-e.m.f., showed the appearance, in the region of intrinsic absorption by the pigments, of a photopotential both in inorganic semiconductors colored with chlorophyll and in layers of certain chlorophylls deposited from concentrated solutions onto platinum. By the same method they (ˆ5-7) measured the spectral distribution of the photo-e.m.f. in layers and microcrystals of chlorophylls. Recently they (ˆ8) studied the photoelectric sensitivity of crystalline chlorophyll and of green-leaf pigments. The photoconductivity of a layer of chlorophyll a under transverse illumination was investigated by Nelson (ˆ9), and the photoconductivity of dried chloroplasts by Arnold et al. (ˆ10) and Ishimura (ˆ11). The latter carried out measurements in a cell for longitudinal illumination, in which the layer thickness was 0.2 mm.

In all these works a good correlation is noted between the spectra of the photoelectric sensitivity of layers and the optical absorption of pigment solutions. For a number of dyes and pigments we have shown (ˆ12-18) that correlation is observed only for layers whose thickness is hundredths of a micron; for layers whose thickness is tenths of a micron, anticorrelation occurs. To observe correlation in the case of nonlinear photoconductors, it is necessary to take into account the nonlinearity index n (ˆ15-17). But since the latter depends on the illumination level (ˆ13), for a correct determination of the spectral curve of the photocurrent it is also necessary to take into account the spectral dependence of n.

The present work is devoted to the study of the spectral distribution of the photoconductivity of chlorophyll a as a function of layer thickness, taking into account the spectral dependence of n.

Uniform and homogeneous layers of pure chlorophyll a, obtained at the Botanical Institute of the Academy of Sciences of the USSR, were deposited from a

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solution in chloroform into the gap between platinum electrodes applied at a distance of 0.5 mm to the surface of a ground quartz test tube. The thickness of the layers varied from several hundredths to several tenths of a micron. The study was carried out at room temperature both under high-vacuum conditions (10ˆ−5 mm Hg) and in an oxygen atmosphere. The currents were measured with an EMU-3 direct-current amplifier equipped with a set of input resistances. At the highest resistance (68 GΩ) the sensitivity of the measuring circuit was 1.5 · 10ˆ−14 A. The source of the voltage applied to the layer was a battery of dry cells up to 500 V. The spectral distribution of the photocurrent was determined with an ISP-17A mirror monochromator in the range from 0.4 to 0.8 μ, with slit widths of 0.25 mm. The light source was a 100 W incandescent lamp. The relative power distribution of the monochromatic illumination beyond the exit slit was measured with a thermoelement. For measure-

to vary the intensity of the light incident on the layer, blackened metal meshes were used. The absorption spectrum of the layer was measured under vacuum conditions on a quartz photoelectric spectrophotometer SF-4.

Curves 1 and 2 in Fig. 1 belong, respectively, to a solution of the pigment in chloroform and to a layer deposited from this solution onto the surface of a quartz plate. As for many dyes and pigments (19,20), the absorption bands of the chlorophyll *a* layer are shifted relative to the bands of the solution toward longer wavelengths and have a greater width. For the layer, the width of the long-wavelength band (673 mμ) is 850 cm^{-1}, and for the solution of the pigment in chloroform (662 mμ) it is 650 cm^{-1}. The shift of the red maximum is 250 cm^{-1} (0.03 eV). These values are close to those given by Jacobs (21) for a layer and solution of chlorophyll *a* in acetone, and indicate a comparatively weak intermolecular interaction.

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If the layers are thoroughly degassed, then under high-vacuum conditions the resistance of the layers studied at room temperature is so high ($R > 10^{16}$ Ω) that the dark current could not be measured. Admission of dry oxygen (250 mm Hg) leads to an increase in conductivity, as was observed previously (22); however, the dark current at room temperature still remains weak.

Under vacuum conditions, illumination of chlorophyll a layers with monochromatic light in the region of the absorption maximum leads to an increase in conductivity by tens and hundreds of times. The time required to reach the stationary value of the photocurrent under continuous illumination is less than the time constant of the input circuit (< 4 s); the decay time of the photocurrent after the light is switched off is 10–15 s. These times are considerably shorter than those observed by Nelson (~ 5 min.) (9). Oxygen causes an enhancement of the photocurrent, but together with the enhancement the rise and decay times also increase.

photocurrent. Analogous behavior, associated with the photosorption of oxygen, was observed by us for a number of dyes and pigments ([12], [13], [23], [24]).

Since, in the presence of oxygen, the complete decay of the photocurrent lasts no less than several tens of minutes, the spectral dependences of the photocurrent were measured only under vacuum conditions. In Fig. 1, for a thin layer, the spectral dependence of the photocurrent is given (curve 3), calculated from the formula

$$S_\lambda = i_{\phi\lambda}^{1/n_\lambda} / L_\lambda,$$

where L_λ is the intensity of the incident monochromatic light and n_λ is the nonlinearity exponent for the given wavelength. For the layer to which curve 3 pertains, n varied from 0.75 at the maximum to 1 at the edges of the absorption band. Under the given illumination conditions, the spectral course of the variation of n remotely resembles the transmission curve. The variation of n upon variation of the illumination level has also been established for inorganic semiconductors ([25], [26]). In the region 460–760 mμ the photocurrent curve reproduces the absorption curve rather well, the maxima occurring at the same wavelengths as the absorption maxima of the layer. In the region 433 mμ, where absorption is stronger than in the region 673 mμ, a minimum of the photocurrent is observed, which can be explained if recombination at the surface of the photoconductor is taken into account ([27]). For this band the layer is not sufficiently thin for the above-mentioned correlation to be observed. This also explains the small yield of photocurrent as compared with the photocurrent in the region of the red band. The suppression effect also appears in the region of the red band, since the weak absorption bands at 580 and 624 mμ correspond to stronger photocurrent bands.

The correlation under consideration follows from the general formula

$$P = \frac{1 - e^{-Z}}{1 + \xi \operatorname{cth}(\lambda/2)} \left\{ 1 + \frac{\xi\lambda \left[\lambda \operatorname{cth}(\lambda/2) - Z \operatorname{cth}(Z/2)\right]}{\lambda^2 - Z^2} \right\},$$

derived by de Boer ([27]) for the photocurrent arising in a semiconductor specimen of thickness l under transverse (relative to the field) illumination by monochromatic light, for which the absorption coefficient is equal to a. Here P is the photocurrent referred to a unit of incident energy, $Z = al$, $\lambda = l/\sqrt{D\tau}$, where D is the carrier diffusion coefficient, τ is their lifetime in the stationary state, and $\xi = S\sqrt{\tau/D}$ is the ratio of surface recombination to volume recombination; S is the surface recombination velocity.

If the layer is very thin, then $P \approx \lambda(1 - e^{-Z})/2\xi$. If, however, the layer is so thin that even at the absorption maximum $Z = al$ is small, then $P \approx al^2/2\tau S$, whence follows the proportionality between the absorption coefficient and the photocurrent.

As the thickness of the layer increases, the suppression effect extends to weaker bands. The spectral photocurrent curve for a thick layer is shown by curve 4. In the calculation, the spectral dependence of n, varying from 0.68 to 1, was taken into account. Curve 4 is more complex, and its relation to the absorption spectrum is not so obvious. On curve 4, the minimum at 672 mμ corresponds to the maximum on curve 3. Owing to anticorrelation, a long-wavelength band is observed (for this layer at 690 mμ), which may be taken for a shifted band. Although to a lesser extent, the band at 624 mμ also underwent suppression. The band at 433 mμ is suppressed most strongly. On the other hand, the weak absorption bands at 490, 534, and 580 mμ correspond to comparatively strong photocurrent bands. Thus, if anticorrelation is taken into account for strong absorption bands and correlation for weak ones, then the relation between the absorption and photocurrent curves will also become obvious for thick layers. Such a relation serves as an argument in favor of the intrinsic character of the photoconductivity. For direct observation of the correlation it is necessary, if possible, to apply ···

thin layers, which make it possible to determine from their spectral photocurrent curves the optical activation energies of photoconductivity by the Moss method ([28]). It follows from curve 3 that the energy is equal to 1.78 eV. This value is in good agreement with the values obtained by the "photoelectric straight lines" method and by measuring the temperature dependence of the dark conductivity.

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