DISTRIBUTION OF ELECTRONS BY KINETIC ENERGIES IN THE EXTERNAL PHOTOEFFECT FROM DYE LAYERS

Table 1

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Abstract

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DISTRIBUTION OF ELECTRONS BY KINETIC ENERGIES IN THE EXTERNAL PHOTOEFFECT FROM DYE LAYERS

(Presented by Academician A. N. Terenin, 12 VI 1961)

The present work is a continuation of studies (^1, ^2) being carried out in our laboratory on the investigation of the external photoeffect from organic semiconductors, and was performed on an apparatus described earlier (^1, ^3). Layers of dyes were deposited on the inner electrode of a spherical capacitor from an alcoholic solution or by sublimation in vacuum, when there was assurance that the dye did not decompose upon heating to 250–300°. The curves of the distribution of electrons by kinetic energies for layers of the same dye, obtained by the two indicated methods, coincide with one another within the limits of experimental error. The thickness of the dye layers was not measured; instead, measurements of the distribution of electrons by energy were carried out for several layers of the same dye of different thickness. For thick layers the voltage drop across the layer has an effect; however, the shape of the curve changes only slightly. For layers of smaller thickness, the distribution curves coincide within the limits of experimental error.

Table 1

Values of the photoelectric work function φ, the position of the Fermi level relative to the bottom of the filled band F, the width of the forbidden band E, and the electron affinity χ for dye layers
(all values are given in electron volts)

Dye	φ	F	E	$\chi = \varphi - E$
Crystal violet	5.0	0.5		
Malachite green	5.2	0.6		
Rhodamine B	5.1	0.5	2.0	3.1
Alizarin blue	5.4	0.5	1.8	3.6
Quinoline blue	4.5	0	2.0	2.5
Methylene blue	5.4	0.2	1.8	3.6
Merocyanine	5.6	0.3	2.3	3.3
Indigo blue	5.4	0.2		
Indigo red	5.0	0.2		
Phenosafranine	5.4	0.4	2.1	3.3

Fig. 1. Electron distribution over kinetic energies in the external photoelectric effect from a photographic sensitizer for different energies of light quanta.

Figure 1: Fig. 1. Electron distribution over kinetic energies in the external photoelectric effect from a photographic sensitizer for different energies of light quanta.

Dye	φ	F	E	$\chi = \varphi - E$
Photographic sensitizer*	4.8	0.2	1.7	3.1

* 3-allyl-3′-ethyl-5, 6′-dimethyl-4-keto-5-(1-dihydroquinoliden-4-ethylidene)-thiazalinooxacyanine bromide.

Table 1 gives the values of the photoelectric work function φ and the position of the Fermi level F, obtained from the current-voltage curves of the external photoeffect of the dyes studied, as well as the values of the width of the forbidden ...

forbidden band E (according to literature data (^{4})) and the magnitude of the electron affinity $\chi = \varphi - E$.

In using these data it should be remembered that in solid dye layers, as in the case of alkali-halide crystals (^{5}), upon irradiation with far-ultraviolet radiation various metastable defects may arise, which can substantially disturb the thermodynamic and electrical equilibrium in the crystal. The magnitudes of the electric

Fig. 1. Electron distribution over kinetic energies in the external photoelectric effect from a photographic sensitizer for different energies of light quanta. Energy of the incident radiation: 1 –6.85 eV, 2 –7.13 eV, 3 –7.60 eV, 4 –10.10 eV. The curves are reduced to unit intensity of the incident radiation.

fields arising because of the absence of such equilibrium cannot be estimated, and the position of the Fermi level, determined as $h\nu - (V_{\text{stop}} - \varphi_{\text{coll}})$, where V_{stop} is the stopping potential and φ_{coll} is the work function of the collector, may have a large error. The different contact potential obtained from current-voltage curves at different energies of light quanta clearly testifies to this. The total experimental error is estimated by us as 0.2–0.3 eV. Such a large error arises because the current-voltage curves in the region of zero photocurrent and in the saturation region approach the horizontal axis of the graphs very smoothly, which is evidently connected both with the large scattering of photon energies in the dyes and with the different work functions of individual portions of the surface of the dye layers.

Figure 1 shows the curves of electron distribution over kinetic energies in the external photoelectric effect from a layer of photographic sensitizer.* The distribution curves for malachite green, crystalline violet, indigo red, and indigo blue

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

are similar to the curves in Fig. 1. For the external photoelectric effect from the indicated group of dyes, the following phenomenon is characteristic: when the energy of the quanta exceeds the work function by 2.2-3 eV, the maximum in the distribution of electrons over energies shifts into the region of low electron energies. This indicates that, at the given photon energy, it becomes possible to tear out more strongly bound electrons, or else to tear out weakly bound electrons with simultaneous excitation of the resulting positive ion to one of the electronic levels, or, as was found in the case of inorganic semiconductors (^{9}), a discrete loss of electron energy occurs during their motion toward the surface, transferring electrons from the filled band into the conduction band.

Figure 2 gives the curves of the distribution of electrons by kinetic energies for the external photoeffect from alizarin blue. An analogous distribution of electrons by energies is obtained for the external photoeffect from dye films: quinoline blue, phenosafranine, rhodamine B, and pinacryptol yellow.

Fig. 2. Distribution of electrons by kinetic energies in the external photoeffect from the dye alizarin blue for different energies of the incident radiation: 1 – 7.45 eV, 2 –8.55 eV, 3 –9.70 eV, 4 –10.60 eV. The curves are reduced to one value of the saturation current.

In the study of the external photoeffect from the indicated dyes, the appearance of a group of slow electrons was not observed, but at high energies the maximum in the distribution is strongly broadened. Probably in this case there is a more intense exchange of energy into vibrational degrees of freedom than in the case of the first group of dyes indicated by us.

A characteristic feature of the external photoeffect from films of the dyes studied by us is that the maximum in the distribution of electrons by kinetic energies shifts only very slightly (by 0.3-0.5 eV) when the energy of the light quanta is increased by 4-5 eV. In the work of one of the authors (^{1,5}), this effect was explained by exchange of part of the quantum energy within the absorbing molecule into excitation of electronic and vibrational levels. To test this hypothesis, we measured the distribution of electrons by kinetic energies upon photoionization of the vapors of the dye rhodamine 6Zh.

Fig. 3. Distribution of electrons by kinetic energies in the photoionization

* 3-allyl-3′-ethyl-5′,6′-dimethyl-4-keto-5-(1-dihydroquinoliden-4-ethylidene)-thiazalinooxacyanine bromide.

of rhodamine 6Zh vapors at a temperature of 205–300° and an energy of the ionizing-radiation quanta equal to 10.1 eV.

The cylindrical condenser used by us in measurements of the electron distribution in the photoionization of benzene derivatives (7) was placed in a metal cuvette, which could be heated to 250–300°. Because of the difficulty of the experiment, we succeeded in making a reliable measurement for only one dye and one energy of the ionizing quanta.

of the exciting radiation. The curve of the electron energy distribution upon photoionization of rhodamine 6Zh vapor is shown in Fig. 3. The photon energy is 10.1 eV and exceeds the previously determined ionization potential of the dye (8) by 2.8 eV. The maximum in the electron energy distribution lies at an energy of 0.1 eV. It follows from this that, even in the photoionization of free dye molecules, a considerable part of the photon energy is exchanged within the molecule for the excitation of electronic and vibrational levels.

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[1] F. I. Vilesov, A. N. Terenin, DAN, **133**, No. 5 (1960).
[2] F. I. Vilesov, A. N. Terenin, DAN, **134**, 71 (1960).
[3] F. I. Vilesov, Instruments and Experimental Techniques, No. 4, 89 (1958).
[4] I. A. Akimov, A. N. Terenin, Journal of Scientific and Applied Photography and Cinematography, **6**, 108 (1961).
[5] N. Phillipp, E. A. Taft, L. Apker, Phys. Rev., **120**, 49 (1961).
[6] F. I. Vilesov, DAN, **141**, No. 5 (1961).
[7] F. I. Vilesov, B. L. Kurbatov, A. N. Terenin, DAN, **138**, No. 6 (1961).
[8] F. I. Vilesov, DAN, **132**, 632 (1960).
[9] L. Apker, E. Taft, J. Dickey, J. Opt. Soc. Am., **43**, 78 (1953); E. Taft, L. Apker, J. Opt. Soc. Am., **43**, 81 (1953).

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