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# Photonics of Organometallic Semiconductors—Copper Organoacetylides

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Processes associated with the interaction of photons with organometallic photosemiconductors are examined. Attention is concentrated on the nature of the photoelectric and optical properties of copper organoacetylides and also on the elucidation of their structures by methods using electromagnetic radiation. It is shown that the organometallic compounds can be regarded as a new class of semiconducting materials, because they have a number of properties typical for inorganic and organic semiconductors.
The bibliography contains 74 references.

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## I. INTRODUCTION

The history of photoconductivity, which runs to a little more than 100 years[1], has demonstrated convincingly that each significant step forward in the study and applications of this phenomenon was associated with the appearance of new photosensitive materials with specific physicochemical properties. This was initiated by studies of elements such as germanium and silicon and subsequently inorganic compounds of the type $A^3B^5$, $A^2B^6$, and $A^2B^4C_2^5$, and vitreous, organic, and other semiconductors began to be included in the range of photosemiconducting materials. Thus the ways in which the chemical and energetic structures of newly discovered semiconducting compounds have increased in complexity can be clearly traced.

The present review deals with a new type of photosemiconductors—organometallic compounds (OMC). The wide variety of types of bonds ensured by the selection of appropriate organic ligands and metals suggests that such systems have extremely interesting physical and in particular semiconducting properties. The results of studies of the electronic processes in organometallic compounds can be used to determine the structure and energetic parameters of organometallic solids, to elucidate the mechanism of the migration of energy in them in order to find ways of achieving superconductivity in OMC at high temperatures, to model biophysical processes involving microelements in complex macromolecular systems, and to study the mechanisms of catalytic reactions proceeding via intermediate OMC. These studies are of interest also in connection with the likely usefulness of organometallic materials in various kinds of semiconductor devices in optoelectronics, in microelectronics, in the preparation of electrophotographic emulsions, for printing schemes, diapositives, microfilms, etc.

Approximately 100 organometallic compounds are now known in which an internal photoeffect has been observed and investigated. These are copper organoacetylides (COA), silver organoacetylides of the type $(M-C\equiv C-R)_x$[2-45], ferrocene[46,47], and polyconjugated polymers with double and triple bonds in the macromolecule, containing silicon, germanium, tin, and lead atoms in the conjugation chain[48]. The electronic properties and structures of these compounds are usually examined from the standpoint of ligand field theory which is understood as the set of theoretical ideas ranging from the electrostatic crystal field theory to the molecular orbital method[49-54].

Copper organoacetylides whose properties are the subject of the present review are at present the most thoroughly investigated organometallic photoconductors from the standpoint of optical and photoelectric properties. We shall consider initially the structure of copper organoacetylides on the basis of data obtained by methods involving the use of electromagnetic radiation. In considering the optical and photoelectric properties particular attention will be devoted to the relation between these two properties in the structure of copper organoacetylides, the mechanisms of the primary steps in the formation of carriers and their drift, and methods for the chemical and spectral sensitisation of the internal photoeffect in order to increase the integral photosensitivity and expand the spectral photosensitivity of copper organoacetylides. Data are presented concerning the possibility of the practical application of such compounds.

## II. THE STRUCTURE OF THE COMPOUNDS

Copper organoacetylides are complex coordination polymers. The structural formulae of the monomeric units of certain copper organoacetylides, investigated in a number of studies[2-45], are presented in Table 1, which includes also the principal energetic parameters of such organoacetylides determined from the absorption and photoconductivity spectra which will be considered in this review.

The principal information about the synthesis and chemical properties of copper organoacetylides can be found in a series of communications[45,54-56]. These compounds are finely dispersed infusible and insoluble crystalline powders of different colours (from yellow to red) with resistivities

of $10^8$–$10^{11}$ Ω cm.[3,6,41] On the basis of the insolubility of the copper organoacetylides and the fact that the characteristic frequency of the triple bond in infrared spectra is reduced on average by 250 $cm^{-1}$, it has been suggested that copper organoacetylides are coordination polymers[57,58].

The structure of copper phenylacetylide (CPA), based on X-ray diffraction data, has been published in a monograph[49] (Fig. 1). It has the form of an infinite rectangular tube made up of copper atoms separated by specific metal–metal bond lengths and are linked to the phenylethynyl groups arranged outside the tube. Each phenylethynyl group is apparently linked by a σ-bond to one copper atom, by a symmetrical π-bond to a second copper atom, and by an asymmetric π-bond to a third copper atom. For simplicity, Fig. 1 illustrates only half of the rectangular tube. Subsequent study of the infrared spectra of a series of copper organoacetylides showed[8,16,19] that the characteristic frequency of the triple bond has been reduced to 1930–1970 $cm^{-1}$ and depends little on the nature of the substituent in the ethynyl group of the ligand.

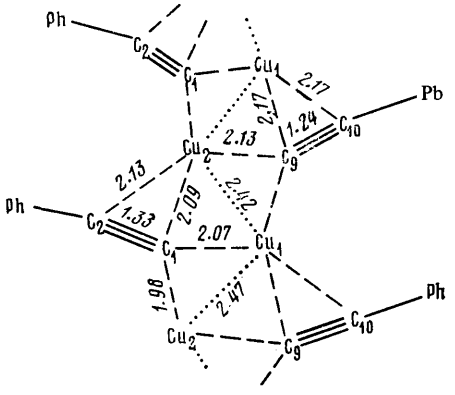



**Figure 1.** The structure of copper phenylacetylide $(CuC{\equiv}CPh)_x$.[49]

It follows from the infrared spectra of the copper derivatives of diacetylenic compounds (Nos. 4 and 6 in Table 1) that the copper atoms in these copper organoacetylides are coordinated to the terminal C≡C bond only. It has been suggested[16,19,20] that, apart from the coordination to the metal atoms, the decrease of the frequency of the triple bond in copper organoacetylides on average by 250 $cm^{-1}$ compared with free organoacetylenes can be explained by the promotion of an electron along the copper–carbon bond $Cu^{\cdots}C{=}C{-}R$, which leads to the vibrations of the Cu=C=C skeleton[59].

A broad asymmetric band at 130–180 $cm^{-1}$, which apparently reflects the presence of the copper–copper bond, has been observed in the far infrared spectra of copper organoacetylides[21]. The infrared and Raman spectra of copper organoacetylides have also been studied in other investigations[60,61].

Thus infrared spectroscopic and X-ray diffraction data make it possible to regard copper organoacetylides as coordination polymers consisting of zigzag chains of copper atoms coordinated to ethynyl groups. This structure and the quasi-allenic nature of the copper–carbon bond is confirmed by X-ray photoelectron spectroscopic data for copper organoacetylides (Table 2)[23]. The considerable shift of the $2p_{3/2}$ level of the copper atom towards higher bond energies compared with the metal indicates an effective charge transfer from the copper atom to carbon atoms of the ligands and the involvement of the *d* orbitals in the hybridisation of the Cu–C bond. The degree of charge transfer from copper atoms increases in the sequence of the compounds in Table 2. On average, the effective charge of the copper atoms in the polymers is only 0.17e when it is calculated using the Pauling electronegativities and assuming that the multiplicity of the copper–carbon bond is two. If it is assumed that the chemical shift due to the change in the effective charge by unity is 5 eV,[62] then the results indicate the transfer of an average charge of 0.4e from the copper atom. The broadening (on average by 0.5 eV) of the electronic lines in the spectra of copper organoacetylides relative to the metal apparently confirms the presence of non-equivalent copper atoms in the molecule (Fig. 1). The chemical shift $\Delta E_b$ suggests that the oxidation state of copper is close to 1.5. The shift of the 1s electronic lines of the carbon atoms in the organic ligands is, as for the level of the copper atom, in the direction of increasing binding energy compared with the free hydrocarbons but is smaller by a factor of 2. This finding indicates the conjugation of the acetylenic bonds with both copper atoms and with substituting organic groups as well as the withdrawal of electrons from these groups towards the acetylenic bond.

**Table 1.** The position of the long-wavelength maximum (λ) and of the optical absorption edge (*E*) and the optical activation energy for photoconduction (Δ*E*) in copper organoacetylides[34].

| No. | Compound | From absorption spectra | | From photoconductivity spectra | |
|---|---|---|---|---|---|
| | | λ, nm | *E*, eV | λ, nm | *E*, eV |
| 1 | CuC≡C—Bu-*p* | 420 | 2.73 | 440 | 2.72 |
| 2 | CuC≡C—CH=$CH_2$ | 435 | 2.5 | 465 | 2.41 |
| 3 | CuC≡C—$CH_2$—Ph | 415 | 2.69 | 445 | 2.65 |
| 4 | CuC≡C—C≡C—Ph | 465 | 2.24 | 500 | 2.22 |
| 5 | CuC≡C—Ph | 465 | 2.45 | 500 | 2.38 |
| 6 | CuC≡C—⟨⟩—C≡C—Ph | 475 | 2.3 | 510 | 2.26 |
| 7 | CuC≡C—⟨⟩—Ph | 468 | 2.37 | — | — |
| 8 | CuC≡C—⟨⟩ | 467 | 2.30 | 507 | 2.22 |
| 9 | CuC≡C—⟨⟩ | 470 | 2.30 | 512 | 2.20 |
| 10 | CuC≡C—⟨⟩ | 530 | 2.14 | 550 | 2.14 |
| 11 | CuC≡C—O—Ph | 485 | 2.13 | 520 | 2.12 |
| 12 | CuC≡C—S—Et | 485 | 2.32 | 530 | 2.2 |
| 13 | CuC≡C—S—Ph | 460 | 2.42 | 530 | 2.08 |
| 14 | CuC≡C—⟨⟩—C≡CCu | 512 | 2.10 | 530 | 2.13 |
| 15 | CuC≡C—⟨⟩—⟨⟩—CCCu | 470 | 2.00 | 540 | 2.14 |
| 16 | CuC≡C—⟨⟩—O—⟨⟩—C≡CCu | 550 | 2.00 | 505 | 2.30 |
| 17 | (HC≡C—CH=$CH_2$+CuC≡CPh)+$Cu^I$ | — | — | 520 | 2.24 |
| 18 | (HC≡CH+HC≡C—Ph)+$Cu^I$ | 540 | 1.88 | 620 | 1.92 |
| 19 | (PhC≡CH+PhSH)+$Cu^I$ | — | — | 465 | 2.42 |
| 20 | CuC≡C$PBu_2$ | 360 | 2.75 | 440 | 2.77 |
| 21 | CuC≡C$PPh_2$ | 370 | 2.74 | 450 | 2.78 |
| 22 | CuC≡C—$AsPh_2$ | 570 | 1.88 | 620 | 1.75 |

In the electron spectra of the 1s level of carbon a fine structure corresponding to different states of the carbon atoms in the ligands was not observed, although the lines are far broader than in the hydrocarbons. The observed lines are apparently due to substituents in the acetylenic groups of the ligands; otherwise one would have to expect the presence of at least two lines of identical intensity in the spectrum of copper vinylacetylide or a significant broadening of the carbon line due to chemical shifts in the different directions. It has been suggested[23] that the electron density is concentrated near the carbon atom nearest to the copper atom and that this atom in fact ensures the coordination polymeric structure of these compounds. An increase of electron density of the carbon atom nearest the metal leads to a decrease of the binding energies for all the levels of the atom, including the valence levels.

**Table 2.** The binding energies $E_b$, the electronic line half-widths $\Delta E_{1/2}$, and the chemical shifts $\Delta E_b$ (all expressed in eV) of copper organoacetylides[31].

| Compound | Cu $2p_{3/2}$ | | | C 1s | | S 2p | |
|---|---|---|---|---|---|---|---|
| | $E_b$ | $\Delta E_{1/2}$ | $\Delta E_b$ | $E_b$ | $\Delta E_{1/2}$ | $\Delta E_b$ | $E_b$ |
| Cu | 932.2 | 1.8 | 0 | — | — | — | — |
| CuS—Ph | 933.9 | 2.2 | 1.7 | 286.5 | 3.2 | 1.5 | 163.9 |
| CuC≡C—Ph | 934.2 | 2.3 | 2.0 | 286.1 | 3.0 | 1.1 | — |
| CuC≡C—$C_4H_9$ | 934.3 | 2.6 | 2.1 | 286.2 | 3.3 | 1.2 | — |
| CuC≡C—CH=$CH_2$ | 934.4 | 2.2 | 2.2 | 286.7 | 3.1 | 1.7 | — |
| CuO | 935.1 | 2.3 | 2.9 | — | — | — | — |
| C in hydrocarbons | — | — | — | 285.0 | 3.0 | 0 | — |
| S | — | — | — | — | — | — | 164.4 |

The valence levels of the carbon atom nearest the copper atom apparently form a sub-band at the top of the valence band. This is also confirmed by the results of the study of the external photoeffect[31]. The photoelectric work functions for compounds with different ligands are very similar and are in the range 5.0–5.4 eV, which shows that the highest occupied state of the copper organoacetylide is determined by the structural unit Cu–C≡C. The weak but regular dependence of the photoelectric work function on the electron-donating properties of the substituent is in good qualitative agreement with the changes in the ionisation potentials of the free molecules containing the ethynyl group[63] due to the positive inductive effect of the substituents.

## III. OPTICAL PROPERTIES

The optical absorption spectra of copper organoacetylides have been studied[6,8,17,20,22,33] by the diffuse reflection method[64]. The data obtained are presented in Table 1. Fig. 2 illustrates the spectra of copper organoacetylides having the general formula $(RC{\equiv}CCu)_x$. The overall characteristics obtained in the analysis of the electronic absorption spectra reduce to the following.

With increase of the conjugation chain length along the monomer unit, a bathochromic shift of the long-wave length maximum is observed. The introduction of aromatic rings leads to the appearance in the spectra of a structure due to the vibrational states. The characteristic frequencies in the absorption, photoconductivity, and photo-e.m.f. spectra can be attributed to the effect of ethynyl bonds (2100–2200 $cm^{-1}$), the out-of-plane deformation vibrations of the benzene ring, and the stretching vibrations of the ≡C–H group (~3200 $cm^{-1}$) (Table 3)[20]. The absence from the electronic absorption spectra of the 1930 $cm^{-1}$ frequency, normally observed in the infrared spectra, suggests that in the excited state there is an alteration of the electronic configuration of the molecule, leading to an increase of the multiplicity of the ethynyl bond linked directly to the copper atom.

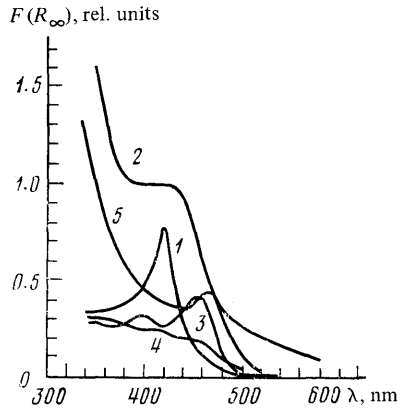
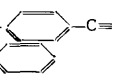



**Figure 2.** Optical absorption spectra of copper organoacetylides $(RC{\equiv}CCu)_x$ with different R: 1) n-Bu; 2) CH=$CH_2$; 3) Ph; 4) PhC≡C; 5) 1,4-$C_6H_4$≡CPh; $F(R_\infty)$ = Kubelka–Munk function taken from Myl'nikov[20].

**Table 3.** The manifestation of the vibrational structure in the absorption and photoconductivity spectra of copper organoacetylides[20].

| Structural formula of monomeric unit | Positions of maxima | | | | Frequency difference in spectra $\Delta\nu$, $cm^{-1}$ | |
|---|---|---|---|---|---|---|
| | absorption spectra | | photoconductivity spectra | | absorption | photoconductivity |
| | λ, nm | $\nu$, $cm^{-1}$ | λ, nm | $\nu$, $cm^{-1}$ | | |
| CuC≡C–  | 455,395 | 22000, 25300 | 500,430 | 20000, 23220 | 3300 | 3220 |
| CuC≡C–C≡C–  | 455,415 | 2200, 24100 | 500,480, 450 | 20000, 20850, 22200 | 2100 | 850,1350 (2200) |
| CuC≡C–  –C≡ ≡C– | 465 | 21500 | 510,490, 440 | 19620, 20450, 22750 | | 830,2300 (3180) |

From the standpoint of the donor–acceptor interaction, one can assume that the bands observed in the visible region are due to the resonance interaction between the *d* electrons of the copper atoms and the π electrons of the corresponding ligands[20]. Indeed acetylenic compounds of the type HC≡CR absorb in the ultraviolet, like copper(I) compounds[65]. The bathochromic shift of the absorption edge observed when the

substituent in the ethynyl group of the ligand is altered and the high absorption coefficient ($>10^4$ $cm^{-1}$) also confirm that the bands are due to charge transfer between the *d* orbitals of copper and the antibonding $\pi$ orbitals of the ligands. Considering copper as a substituent in the main chromophore, it can be assumed that the $d-\pi$ conjugation is manifested in the spectra from the standpoint of the theory of conjugated systems and the theory of colour[20].

Analysis of the edge of the absorption band in the spectra of copper organoacetylides made it possible to determine the energies of the forward transitions[20]. For the compounds considered (the numbering is the same as in Table 1), these energies have the following values (eV): 2.75 (1) 2.53 (2) 2.48 (4), 2.50 (5), and 2.46 (6). It has also been shown that the Urbach rule holds for the edge of the absorption spectrum[20].

By altering the chemical structure, it is possible to achieve a fine control of the energetics and nature of the transitions in the COA.[17,22,33] For example, the introduction of the $CH_2$ group between the benzene ring and the triple bond [see compounds (3) and (5) in Table 1] interrupts the interaction with the $\pi$ electrons of the benzene ring with the $\pi$ electrons of the triple bond, which shifts the absorption maximum from 465 to 415 nm. Introduction of the ethynyl group instead of $CH_2$ [compound (4)] restores this conjugation. An increase in the number of aromatic rings in the ligand [compounds (5) and (7)–(10)] leads to a bathochromic shift of the spectra. Analysis of the spectra indicates a strong non-additive interaction of the electrons of the aromatic substituents with the intrinsic copper acetylide structural unit, which is common to all the molecules. It is known[66] that in the initial series of acenes the frequencies of the singlet–singlet transitions decrease on average by 6000 $cm^{-1}$ following the addition of each benzene ring[66]. In the spectra of the COA with biphenylyl and naphthyl groups the long-wavelength maxima differ by only 200 $cm^{-1}$ from the spectrum of the compound with the phenyl group, while the maximum in the spectrum of the anthracene derivative differs by 2800 $cm^{-1}$. The mode of addition of a further aromatic ring [compounds (7)–(9)] has little influence on the position of the long-wavelength maximum. After the introduction of substituents into the benzene ring, the bathochromic shift in the spectra increases in the following sequence: $Cl < I < OCH_3 < NO_2$.[66] The inclusion of sulphur or oxygen atoms with an unshared electron pair in the molecule increases the delocalisation of electrons along the chain. This is shown particularly strikingly when the spectra of compounds (5) and (11) are compared: evidently the introduction of an oxygen atom gives rise to a bathochromic shift of approximately 20 nm.[33]

For COA having the general formula $(R_2PC{\equiv}CCu)_x$ [compounds (20) and (21)], the nature of the absorption curves is independent of R. This fact as well as comparison of the absorption spectra of copper acetylides containing phosphino-groups with the corresponding absorption spectra of copper organoacetylides shows that the introduction of a phosphorus atom interrupts the conjugation along the monomeric unit. In contrast to phosphorus, the introduction of an arsenic atom does not affect the conjugation. Bearing in mind that the phosphorus and arsenic atoms in the tervalent state have a free electron pair which can be involved in the formation of $p-d$ donor–acceptor bonds, presumably in compounds containing such ligands there is an appreciable weakening of the $\pi-d$ bonds compared with the usual copper acetylides. The polymeric structure of these compounds is apparently due to both types of bonds.

It was noted above that the transitions in the visible region of the spectrum are due to charge transfer between the *d* orbitals of copper and the antibonding $\pi$ orbitals of the ligands. At the same time an increase of absorption on passing to the short-wavelength region is a striking feature of almost all the COA. One should also bear in mind that the power relation between the absorption coefficient and the photon energy above the optical absorption edge has been obtained[20] with a power exponent of 1/2, which is characteristic of forward dipole-allowed transitions; all these features suggest that the charge transfer bands in the long-wavelength region of the absorption spectra are superimposed on transitions of the band–band type. The absorption of light is determined by transitions of the band–band type and by charge transfer between the copper atoms and the ligands.

## IV. PHOTOELECTRIC PROPERTIES

The photoelectric properties of the COA have been studied in fair detail[3–10,12–19,22,24,25,27–34,39–45] by the photoconductimetric and photo-e.m.f. methods. The resistance of the specimens decreases from $10^7$–$10^{11}$ Ω to $10^5$–$10^7$ Ω under the influence of monochromatic light with an intensity of $10^{13}$ photons $cm^{-2}$ $s^{-1}$. The maximum photocurrents reach $10^{-5}$ A.[6]

The dependence of the photocurrent $i_{ph}$ on the degree of illumination *L* is expressed by the formula $i_{ph}=\alpha L^n$, where $0.5<n<1$.[3,6,32,33,41] It has been shown that the COA exhibit a predominantly *p*-type conductivity[3,6,40]. Ohm's law holds for the dark photocurrent only for electric field strengths up to $10^2$ V $cm^{-1}$, after which the current increases faster than the potential, which is apparently associated with space charge. The study of the relaxation of photoconductivity has shown[6,33] that a steady photocurrent is established as a rule after 1–2 min. For the majority of compounds, the descent of the kinetic curves obeys a hyperbolic relation. Specimens with an extremely high degree of inertia, in which the relaxation phenomena take place over a period of several hours, are also encountered [compounds (7) and (22), Table 1].[33]

Prolonged relaxation processes in COA, apparently due to the large number of inhomogeneities and in some cases also photochemical phenomena, are in essence analogues of the memory effects widely investigated in inorganic photosemiconductors[67]. The most reasonable explanation of the prolonged relaxations of photoconductivity in semiconductors is provided by the barrier model[67], which postulates the presence in the specimen of collective (microscopic) potential barriers.

There exist extensive experimental data on the photoconductivity and photo-e.m.f. spectra of copper organoacetylides with various substituents in the ethynyl group of the ligand[3,6,9,14,17,19,22,33,40,41]. The photoconductivity spectra of compounds of the type $(RC{\equiv}CCu)_x$ are presented in Fig. 3[19]. Analysis of the photoconductivity spectra of the COA shows that they exhibit the principal features typical of the absorption spectra of the COA, namely (1) there is a bathochromic shift with increase in the number of electrons in the substituent of the ethynyl group and there is a simultaneous decrease of the optical activation energy for photoconduction (Table 1), (2) the structure of the spectra is determined by the vibrational states, and (3) the bands are due to charge transfer between the Cu atoms and the C≡C bond with manifestation of $d-\pi$ conjugation.

In most compounds photoconductivity is accompanied by a photo-e.m.f.[3,6,8,16,19,22,23,33]. The most common result is a hypsochromic shift of the photo-e.m.f. spectra relative to

the photoconductivity spectra (Fig. 4); the maxima of the photoconductivity spectra then coincide with the minima of the photo-e.m.f. spectra. The optical activation energies for photosensitivity, determined from the photoconductivity and photo-e.m.f. spectra, agree with one another and with the energy of the edge in the optical absorption spectra. Analysis of the photoconductivity and photo-e.m.f. spectra from the standpoint of the influence of the chemical structure of the molecule has been carried out for COA with aliphatic and aromatic substituents[3,6,8,16,17,22,41] and with heteroatoms[15,17,33] in the ligand. Mixed acetylides [compounds (17) and (18) in Table 1] have been investigated together with individual acetylides[16,19].

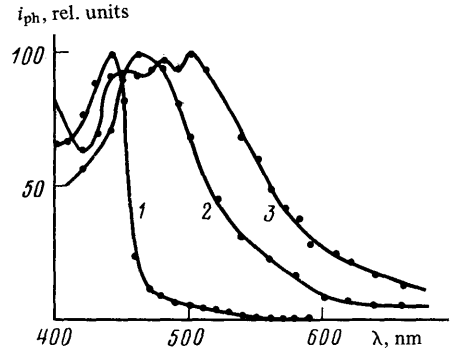



**Figure 3.** Photoconductivity spectra of the compounds $(RC{\equiv}CCu)_x$ with different R: 1) n-Bu; 2) $CH{=}CH_2$; 3) $PhC{\equiv}C$.[19]

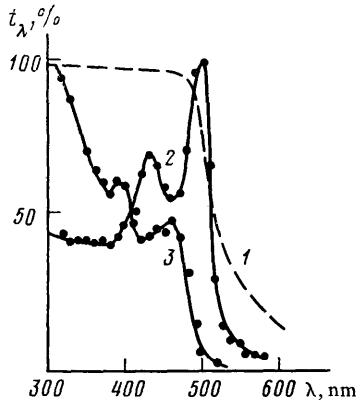



**Figure 4.** Absorption (curve *1*), photoconductivity (curve *2*), and photo-e.m.f. (curve *3*) spectra of copper phenylacetylide[3]; $t_\lambda$ = transmittance.

A study has been made[32] of the photoconductivities of certain COA which occur under the influence of powerful laser radiation. The lux–ampere characteristic of the impurity photoconductivities is close to the characteristic obtained under illumination in the region of the fundamental absorption. This shows that the laser pulse probes the local levels directly. The optical stability of the COA decreases monotonically with decrease of the energy of the optical absorption edge.

## V. RELATION BETWEEN THE OPTICAL AND PHOTOELECTRIC PROPERTIES

In order to understand the nature of the photoelectric processes, it is of interest to compare the photoconductivity and absorption spectra[3,6,17,20,22,33]. Such a comparison has been carried out in Figs. 5, 6, and 7 for COA with different substituents in the ligand. It was shown above (Table 1) that there is a fairly satisfactory correspondence between the optical activation energy for the photoeffect and the energy of the optical absorption edge.

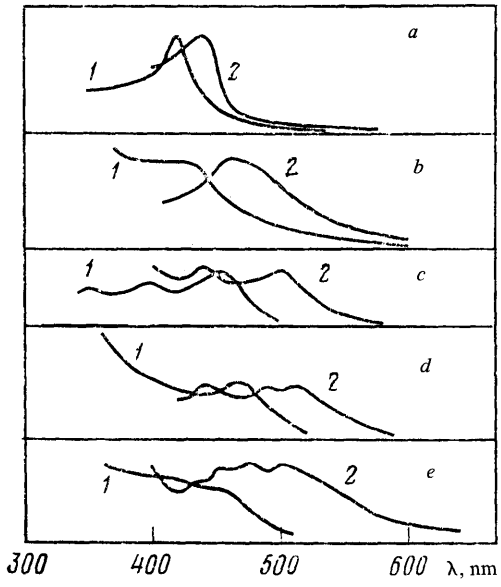



**Figure 5.** Absorption (curves *1*) and photoconductivity (curves *2*) spectra of copper organoacetylides[19,20]: *a*) $(CuC{\equiv}C{-}C_4H_9)_x$; *b*) $(CuC{\equiv}C{-}CH{-}CH_2)_x$; *c*) $(CuC{\equiv}CPh)_x$; *d*) $(CuC{\equiv}C{-}Ph{-}C{\equiv}C{-}Ph)_x$; *e*) $(CuC{\equiv}C{-}C{\equiv}C{-}Ph)_x$.

The principal photoconductivity maximum is as a rule located on the descending branch of the fundamental absorption. This relation between the absorption and photoconductivity spectra is as a rule fairly general in photosemiconductors and can be accounted for by the decrease in the life-time of the photocurrent carriers in the region of strong absorption due to the increased rate of surface recombination[68,69]. It is noteworthy that the low photosensitivity ("tail") in the majority of compounds investigated persists up to 1000 nm. This phenomenon is probably related to the lack of order and different sizes of the coordination blocks.

It was noted above that the absorption and photoeffect spectral bands, due to charge transfer between the ligand and the metal, are apparently superimposed on transitions of the band–band type. Bearing in mind the complex

structure of the spectra, it is difficult to determine unambiguously which types of transition are most effective in the formation of free carriers. The molecular nature (vibronic structure) of the photoconductivity, photo-e.m.f., absorption, and luminescence spectra is one of the indications that, as for organic semiconductors, a molecular excited state of the type of the Frenkel' exciton is involved in the primary step of the internal photoeffect in COA, migrating in the macromolecule until it encounters a defect or another exciton, which results in the formation of free charge carriers. On the other hand, it has been shown[42,43] that the temperature dependence of the photoconductivity of copper phenylacetylide at a frequency of $10^{10}$ Hz is insignificant, which can indicate either that the exciton decomposition energy is low or that band–band transitions are involved in the generation of carriers.

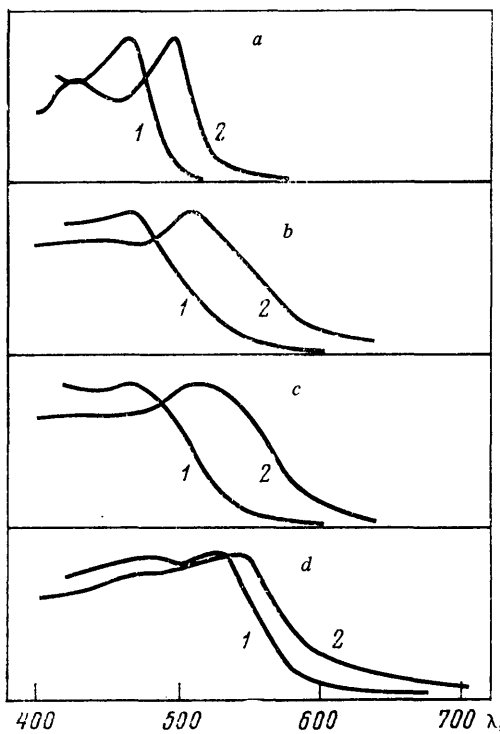



**Figure 6.** Absorption (curves *1*) and photoconductivity (curves *2*) spectra of copper organoacetylides with organic substituents in the ligand[22]: *a*) $(CuC{\equiv}C{-}Ph)_x$; *b*) $\left(CuC{\equiv}C{-}\text{C}_{10}\text{H}_7\right)_x$; *c*) $\left(CuC{\equiv}C{-}\text{C}_{14}\text{H}_9\right)_x$; *d*) $\left(CuC{\equiv}C{-}\text{C}_{14}\text{H}_9\right)_x$.

A direct determination of mobility in copper phenylacetylide yielded 0.10–0.05 $cm^2\ V^{-1}\ s^{-1}$ for holes and 0.18–0.05 $cm^2\ V^{-1}\ s^{-1}$ for electrons. Such mobilities show that the solid state bands in COA are extremely narrow and one must consider a jump mechanism of the movement of carriers in COA. It has been shown[70] that the mobility in copper phenylacetylide depends on temperature with an activation energy of 0.2 eV and that five adhesion levels are located in the valence band in the range of energies 0.07–0.1 eV and are combined into a narrow band with a width of $3 \times 10^{-1}$ eV. The above facts suggest that the mechanism of conduction in COA reduces to a series of consecutive thermally activated jumps involving adhesion levels.

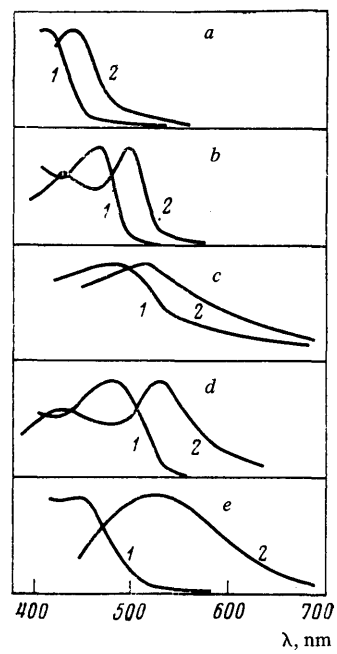



**Figure 7.** Absorption (curves *1*) and photoconductivity (curves *2*) spectra of organoelemental copper acetylides[33]: *a*) $\left(CuC{\equiv}C{-}CH_2{-}\text{C}_6\text{H}_5\right)_x$; *b*) $\left(CuC{\equiv}C{-}\text{C}_6\text{H}_5\right)_x$; *c*) $\left(CuC{\equiv}C{-}O{-}\text{C}_6\text{H}_5\right)_x$; *d*) $(CuC{\equiv}C{-}S{-}C_2H_5)_x$; *e*) $\left(CuC{\equiv}C{-}S{-}\text{C}_6\text{H}_5\right)_x$.

Spectroscopic studies make it possible to discover the influence of molecular structure on optical and photoelectric properties. It has been shown[2,13] that COA exhibit a much greater photoelectric sensitivity than polymers with triple bonds but without metal atoms. This shows that the coordinating copper atoms and the ethynyl groups play an important role in ensuring photosensitivity. Together with these, steric factors, which are determined by the size of the ligands as well as the size of the main chain, are decisive for charge transfer. Thus photosensitivity diminishes in the series of copper phenyl-, naphthyl-, and anthryl-acetylides [compounds (5), (8), (9) and (10) in Table 1][22,41]. The same type of relation has been established for compounds with heterocyclic substituents in the ligand[17,33]. Thus, despite the increase of the number of $\pi$ electrons and of the degree of their delocalisation, the photosensitivity falls. Since the efficiency of light absorption and hence of the

formation of carriers apparently varies little, one must suppose that the decrease of photosensitivity is caused mainly by the fact that drift is difficult owing to the bulky nature of the substituents.

For aromatic substituents, the size of the ligands is fairly large but the latter ensure close packing, probably due to their planar structure, which facilitates charge transfer. In this case one may expect that, in compounds with non-planar bulky substituents, the photosensitivity should be a minimum. This has been confirmed by the finding that no photosensitivity has been observed in $(RC{\equiv}CCu)_x$ with R = t-butyl, ferrocenyl, and *o*-carboranyl[33].

Summarising, one may conclude that the decisive factor for charge transfer in COA is not the length of the conjugation system but intramolecular and intermolecular configuration interactions (short-range order in the terminology of the orthodox semiconductor physics), which lower the potential barriers at the boundaries between the macromolecules.

Apart from copper acetylides, we are aware of only one organometallic compound (ferrocene) whose photoconductivity spectrum has been measured[47]. The photocurrent increased monotonically in the range from 270 to 230 nm and no photoconductivity was observed in the regions with a low oscillator strength (320 and 440 nm). According to Hoestery and Letson[47], the latter can be explained either by the inadequacy of the energies of two excitons for the formation of carriers or by the fact that the life time of excitons is too short and the rate of their migration is too low to ensure a high probability of their annihilation. Bearing in mind the narrowness of the section of the spectrum in which the photocurrent was measured, one should apparently exercise extreme caution in stating that the photoconductivity spectrum is identical with the absorption spectrum in the region of the $\pi-\pi^*$ transitions. We may note that the mobility of holes in a ferrocene single crystal was determined in the same investigation as $2.2\times10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K and a number of considerations concerning the conduction mechanism were put forward.

## VI. THE PHOTOEFFECT AND LUMINESCENCE

The absorption of light leads to the excitation of the macromolecule. Radiationless degradation of energy, luminescence, and the formation of free carriers are the possible ways in which the excited states are deactivated. We shall therefore consider studies[6,8,9] in which the luminescence and photoelectric properties of copper phenylacetylide (CPA) were investigated simultaneously. Fig.8 presents the absorption, photo-e.m.f., and luminescence spectra of CPA. The luminescence yield varies linearly with the excitation intensity in the range 313–436 nm, is insensitive to the presence or absence of air, and has two maxima, at 516 and 583 nm. Preliminary irradiation of CPA with ultraviolet light decreases the integral luminescence yield and simultaneously increases the integral photoeffect[8]. This is manifested spectroscopically (Fig.9) by a redistribution of the maxima in the action spectra, which is most strikingly manifested in the luminescence spectra. Preliminary irradiation *in vacuo* is accompanied by more complex changes in the photo-e.m.f. spectrum[4]. The luminescence is determined by the decay of excitons.

The changes in the spectra on irradiation with ultraviolet light are probably caused by the photolysis of the coordinate bonds in the polymer, which results in a change of the ratio of the polymer-homologues of the substance. When bonds are broken, the decomposition of excitons by defects is facilitated, which increases the photoeffect and diminishes the luminescence yield.

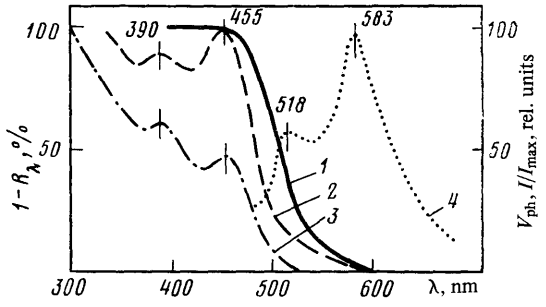



**Figure 8.** Spectroscopic data for copper phenylacetylide; 1) distribution of reflections ($1-R_\lambda$) from CPA in powder form; 2) distribution of reflections ($1-R_\lambda$) from CPA "diluted" with magnesium oxide (1:100); 3) photo-e.m.f.; 4) luminescence at $T = 293$ K.[8]

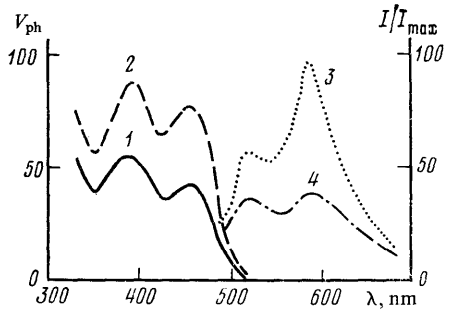



**Figure 9.** Variation of the luminescence intensity and photo-e.m.f. on irradiation of copper phenylacetylide with ultraviolet light: 1) photo-e.m.f. of the initial specimen; 2) ditto after 10 min irradiation with the light from an SVD-120 lamp using a water filter; 3) luminescence of the initial specimen; 4) ditto after 10 min irradiation with the light from an SVD-120 lamp using a water filter according to the data of Lashkov and Myl'nikov[8].

The proposed mechanism has been confirmed by low-temperature luminescence experiments[8] in which it was shown by spectroscopic studies that the degradation of CPA by ultraviolet light takes place as far as the formation of individual diphenylbutadiyne molecules implanted in the polymer structure. It is of interest that the phosphorescence of the diphenylbutadiyne molecules adsorbed on CPA (their absorption band is located at wavelengths below 340 nm) is excited by light at a wavelength of 365 nm. One can therefore postulate energy transfer from the semiconductor support to the diphenylbutadiyne molecules adsorbed on it. The low-temperature experiment showed that the luminescence of CPA is associated with radiative transitions on the surface. It was found that the state of the surface has a significant influence also on the photoelectric properties of organometallic photosemiconductors.

## VII. THE INFLUENCE OF VAPOURS AND GASES ON THE SEMICONDUCTING PROPERTIES OF COA

The influence of oxygen, water vapour, mercury vapour, and electron-accepting molecules on the electrical conductivity, photoconductivity, and photo-e.m.f. of copper phenylacetylide has been studied in a number of investigations[4-9,14,41]. The nature of the change in the electrical conductivity and photoconductivity of CPA under the influence of oxygen is illustrated in Fig.10. The absence of a photochemical interaction of CPA with oxygen was demonstrated, since the spectral characteristics of the photosensitivity hardly changed.

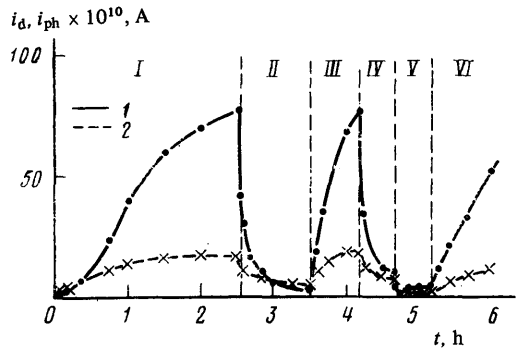



**Figure 10.** The influence of oxygen on the electrical conductivity (curve *1*) and photoconductivity (curve *2*) of CPA: I) evacuation of air to $5 \times 10^{-5}$ mmHg; II) admission of oxygen; III) evacuation; IV) admission of oxygen; V) discharge in oxygen; VI) evacuation[4].

It is known that the adsorption of gases on the surface of the semiconductor can lead to the formation of a double layer due to adsorbed molecules or of new recombination or adhesion centres. For a *p*-type semiconductor, it has come to be assumed that the adsorption of molecules with an electron affinity should increase the photoconductivity owing to the capture of an electron by the adsorbed molecule. CPA, a *p*-type semiconductor, shows the opposite behaviour. Oxygen apparently generates new effective recombination centres, which decrease the lifetime of the majority carriers (holes); this has been demonstrated particularly by the present author[4]. On the basis of the analysis of the effect of oxygen, water vapour, and preliminary ultraviolet irradiation on the photo-e.m.f. and photoconductivity spectra, it was postulated in the same study that *in vacuo* oxygen undergoes effective photodesorption from the CPA surface. The suppression of the electrical conductivity and photoconductivity of eleven copper organoacetylides *in vacuo* compared with dry air has been demonstrated[41].

It has been shown[6,7] that water vapour suppresses reversibly the electrical conductivity and photoconductivity and increases the photo-e.m.f. of CPA, which is caused by the formation of an electrical double layer owing to surface states which capture the majority carriers. The change in the semiconducting properties of polymers under the influence of electron-accepting (quinone, chloranil) molecules is associated with the capture of conductivity electrons by these molecules. The set of results obtained concerning the influence of vapours and gases on the semiconducting properties confirms the significant role of the surface for the understanding of the photoelectric processes in organometallic compounds.

In this connection we may note that CPA proved to be a catalyst[11] of the oxidation of the leuco-form of thionine by atmospheric oxygen. The reaction is of interest, since many catalytic reactions on metals proceed via the formation of intermediate organometallic compounds.

## VIII. THE SENSITISATION OF THE INTERNAL PHOTOEFFECT

The results considered above suggest that COA constitute a new class of substances with photoelectric properties. However, in many instances the photoelectric sensitivity of these materials is low or is observed at shorter wavelengths in the spectrum than are required for practical applications. All these factors give rise to the question of ways of expanding the spectral sensitivity and of increasing the integral photosensitivity of these compounds.

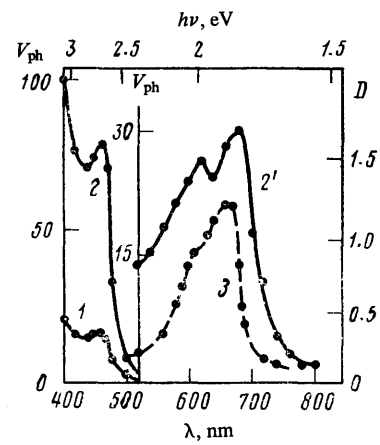



**Figure 11.** Spectral distribution of the photo-e.m.f. of copper phenylacetylide: 1) before dyeing; 2) and 2') after dyeing in solution of Methylene Blue; 3) absorption spectrum of $10^{-3}$ M solution of Methylene Blue in ethanol ($D$ = optical density)[25].

A powerful means of increasing the photoelectric sensitivity of inorganic semiconductors is known to be chemical and spectral sensitisation[71]. Chemical sensitisation can be usefully defined as different kinds of treatment of the semiconductor leading to an increase of the photoelectric sensitivity without an alteration of the spectral characteristics of the material. The effect of spectral sensitisation consists in the manifestation of photoelectric sensitivity in the absorption band of molecules adsorbed on the surface of the semiconductor or injected into the latter. For COA, the spectral sensitisation of the internal photoeffect was first observed in studies[24,25] of the adsorption of dyes on the surface of CPA. Subsequently a number of studies of the principal characteristics of the spectral sensitisation of

copper organoacetylides were carried out[24-30,34]. The sensitisation of the photoconductivity and the photo-e.m.f. has been observed in the visible and near infrared regions of the spectrum using dyes of different classes: cationic (pinacyanol, Methylene Blue, carbocyanines, and pentacyanines), anionic (erythrosine), and non-ionic (chlorophyll, phthalocyanine, and haematin). Typical results for the sensitisation of the photo-e.m.f. and the photoconductivity of CPA are presented in Fig.11 in relation to Methylene Blue.

Analysis of the above studies[24-30,34] has led to the following findings. The sensitised photosensitivity spectrum is close to the absorption spectrum of the dye in solution. The increase in the intensity of the bands in the regions corresponding to dimeric and more highly aggregated forms of the dye in the photosensitivity spectra compared with the absorption spectra of the solutions of the dyes leads to the conclusion that, apart from the molecularly dispersed form of the dye, its more highly aggregated forms are involved in the sensitisation step.

The study of the efficiency of sensitisation as a function of the dye concentration showed that the sensitised photosensitivity reaches 30–40% of the intrinsic sensitivity. A dye concentration in solution of $10^{-3}$ M proved to be the most effective for spectral sensitisation. With increase of the dye concentration from $10^{-6}$ to $10^{-2}$ M, an increase in the intensity of the bands due to the dimeric and more highly aggregated forms has been observed in the sensitisation spectra. The sign of the carriers (positive) in the region of intrinsic photosensitivity of the polymeric photosemiconductor and in the region of sensitisation is as a rule the same. Instances of a change in the polarity of the sensitised photo-e.m.f. relative to the polarity of the intrinsic photo-e.m.f. have also been observed. The nature of such changes in sign as a function of time apparently reflects the kinetics of the adsorption of the dye on the COA surface[25].

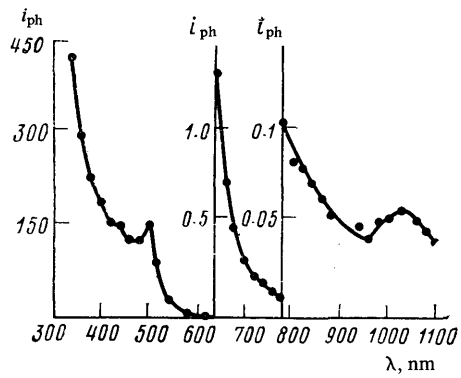



**Figure 12.** The photoconductivity spectrum of copper phenylacetylide dyed with pentacarbocyanine[26].

Systems based on organic semiconductors with photosensitivity in the near infrared are of considerable interest for technical purposes. The sensitisation of the COA photoeffect by pentacarbocyanine (Fig.12), allocyanine, and xenocyanine, which ensure photosensitivity up to 1300 nm, has been observed[26,28,29]. The principal features of the infrared sensitisers are analogous to those observed in sensitisation in the visible region of the spectrum.

It is noteworthy that, apart from the appearance of sensitised photosensitivity, the adsorption of dyes alters the absolute magnitude of the photoeffect in the region of the intrinsic absorption of the COA. For example, the adsorption of erythrosine increases the intrinsic photo-e.m.f. of CPA by a factor of 30.[24] The effect is apparently due to the type of traps generated by the adsorbate. This has been confirmed particularly by the increase of the inertia of the photoconductivity of coloured compounds relative to non-coloured compounds[28,29].

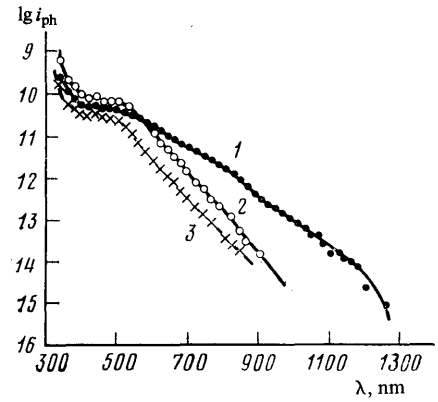



**Figure 13.** The photoconductivity spectrum of copper phenylacetylide dyed with polyoxyphenylene in solutions at different concentrations (g $cm^{-3}$): 1) $10^{-1}$; 2) $10^{-2}$; 3) $10^{-3}$.[30]

As already stated, the use of organic dyes as sensitisers leads to the appearance of photosensitivity, whose spectral characteristics are determined by the absorption spectrum of the dye in solution. The majority of dyes have fairly narrow absorption bands, which makes it impossible to obtain panchromatic sensitivity in wide spectral ranges. In 1968 it was suggested for the first time[72] that organic polymers with conjugated bonds, characterised by diffuse structureless absorption spectra, be used as high-resistance photosemiconductors. Together with panchromatic sensitivity within wide spectral ranges, such polymer sensitisers also exhibit a high thermal stability. In addition, in selecting the appropriate polymer sensitiser, one can in principle do without non-photoactive polymeric binders in preparing electrophotographic layers.

Polyphenylenes and polyoxyphenylenes have been used[27,29,30] as sensitisers of COA. Typical curves for the polyoxyphenylene-sensitised photoconductivity of CPA at different sensitiser concentrations are presented in Fig.13. The principal characteristics of the sensitisation by polymers proved to be the same as those for dyes. In particular, the optimum sensitisation was observed for polymer concentrations in the range $10^{-1}$–$10^{-2}$ g $cm^{-3}$ and the intrinsic photosensitivity of the adsorbent also changed following the adsorption of the polymer sensitisers.

It is noteworthy that a significant difference in the spectral distribution of the sensitiser efficiency has not been observed for polymers with different numbers of monomeric units in the sensitiser macromolecule. This may be associated with the fact that polyconjugation does not extend over the entire length of the polymer chain[30]. There is no doubt that the use of organic polymers as sensitisers will make it possible to increase significantly the integral sensitivity and to expand the spectral sensitivity of photosemiconductor devices (in particular electrophotographic layers) based on high-resistance photosemiconductors. It is to be expected that the use of polymers as sensitisers of photographic emulsions will also prove to be extremely effective.

In considering problems associated with the sensitisation of the photo-effect by organic polymers, one should note that the organometallic compounds themselves can behave as sensitisers when they are introduced into polymer matrices. It has been suggested[18] that CPA introduced into polyvinylcarbazole at the *N*-vinylcarbazole polymerisation stage acts as a sensitiser.

The above study[18] was carried out because the system comprising polyvinylcarbazole and CPA proved to be effective as electrophotographic layers[35,36,48]. In particular, it was shown that such layers exhibit a photosensitivity comparable to the sensitivity of the electrophotographic layers based on zinc oxide and selenium[40]. It was suggested that a complex involving charge transfer between the components is then formed. However, the photoconductivity spectrum of the system virtually coincides with that of CPA, while the sensitivity of the system in the visible region is higher than that of the pure CPA. Thus one can assume that a charge-transfer complex is not formed in such a system or is too weak to be manifested spectroscopically. Apparently, when light is absorbed, the formation of intrinsic carriers in CPA is accompanied by the effective transfer of part of the light energy to polyvinylcarbazole, which generates electron–hole pairs. Presumably the drift of the carriers (holes) in such a system takes place via jump photoconduction[18].

The main problem of the mechanism of spectral sensitisation is known to consist in the fact that, under the influence of a photon whose energy is significantly smaller than the width of the forbidden gap of the semiconductor, the charge carrier appears in the conductivity band. The majority of modern theories deal with alternative mechanisms of the transfer of energy of an electron from an adsorbed sensitiser to a semiconductor[71]. It is noteworthy that the problem of the mechanism of spectral sensitisation has not been finally solved even for inorganic semiconductors.

Analysis of studies[24–30,34] on the sensitisation of the COA photoeffect has shown that its principal features are the same as those observed for inorganic photosemiconductors (zinc oxide, silver halides). This suggests that the sensitisation has identical mechanisms in the two instances.

A critical examination of the existing views suggests that the preferred mechanism of spectral sensitisation involves energy transfer from the adsorbate to the adsorbent. The most significant evidence in support of this is the relative positions of the energy levels of the COA and the sensitiser dyes[34]. It is seen from the example presented in Fig. 14 that the levels of the sensitiser dyes can be located both above (pinacyanol, chlorophyll, and cryptocyanine) and below (erythrosine and Methylene Blue) the ground state of CPA. Furthermore, for the transfer of a hole to a *p*-type semiconductor it is necessary that the singlet ground level of the dye should be located below the top of the filled semiconductor band. For infrared sensitisers, even a correction for the adsorbed state cannot ensure an arrangement of levels necessary for the transfer of a hole. The relative positions of the energy levels of the COA and the sensitiser are thus not decisive for the sensitisation effect.

In previous sections it was stated that water and mercury vapours, the addition of electron-accepting oxygen compounds, as well as the adsorption of dyes and organic polymers on the surfaces of the COA lead to an alteration of the intrinsic photoelectric sensitivity of the latter. All these phenomena can be regarded as the manifestation of the chemical sensitisation of the internal photoeffect in organometallic semiconductors.

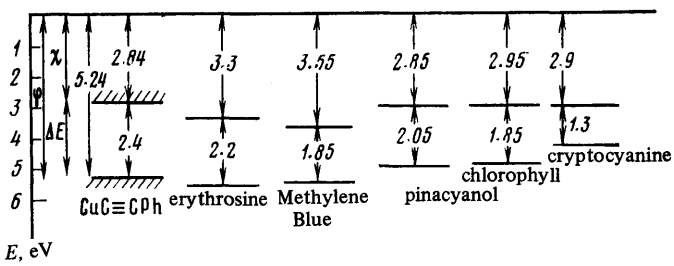



**Figure 14.** Schematic illustration of the energy levels of copper phenylacetylide and sensitiser dyes; $\phi$ = photoelectric work function; $\Delta E$ = energy of the optical absorption edge; $\chi$ = electron affinity[34].

We may also note a study[12] in which it was shown that the photoconductivity, the photo-e.m.f., and the electrical conductivity of CPA increase by 2–3 orders of magnitude when the specimen is treated with deoxyribonucleic (DNA) and ribonucleic (RNA) acids. The nature of the photosensitivity spectra does not then change significantly. The use of pyrimidine (thymine, cytosine, and uracil) and purine (adenine and guanine) bases, which form part of the composition of the acids, shows that the same effects are observed only for adenine and are somewhat smaller in the case of thymine. It is remarkable that these bases are paired in DNA. The observed effects have been explained[12] in terms of a model where the increase of the photosensitivity of the CPA is considered to be a consequence of the introduction into the latter of new recombination centres involving adenine, which increase the lifetime of the majority carriers, this being confirmed particularly by kinetic measurements. Such a model has been considered, for example, in the sensitisation of the photoeffect in cadmium sulphide[73].

We may note that the method of investigating the chemical sensitisation by biologically active molecules in specially sensitised model systems is apparently promising for the understanding of specific properties of such molecules.

## IX. THE APPLICATIONS OF ORGANOMETALLIC PHOTOSEMICONDUCTORS

The discovery and study of the photoelectric sensitivity in organometallic compounds leads to the possibility of using them in many technical devices where the main photosensitive element is made of these materials. In this connection we may point out that COA and polyacetylenes containing germanium, silicon, tin, and lead atoms in the conjugation chain have been suggested as electrophotographic layers[10, 35–40,45,48]. The photosensitivity under electrophotographic conditions, determined from the decrease of the potential by

a factor of two, amounts to 300 lux s for CPA in polyvinylbutyral and 70 lux s in polyvinylcarbazole. Thus layers with COA have an integral sensitivity comparable to those of layers made of amorphous selenium and paper containing zinc oxide[10,39,40].

We may note that studies under electrophotographic conditions[10,40] confirmed the nature of the spectral distribution of the internal photoeffect, the sign of the charge carrier, and the activation of the photosensitivity of COA by preliminary ultraviolet irradiation, which was demonstrated by the photoconductimetric and photo-e.m.f. methods[3-6]. At the same time electrophotographic methods made it possible to obtain a series of new data concerning the mechanism of photoconduction in organometallic compounds.

The procedure for the preparation of transparent electrophotographic layers for diapositives is of great interest[38]. The monomer of the binder (vinylcarbazole) is then polymerised in the presence of finely dispersed COA. This results in the formation of fairly homogeneous systems of the type of "solid solutions", which are suitable for the preparation of electrophotographic layers[37,38]. Copper organoacetylides have proved suitable for printing schemes involving the electrophotographic method, which ensure highly technological and economical set ups[40].

The first steps in the application of organometallic compounds in technology have shown that there are definite prospects and possibilities, the realisation of which depends to a considerable extent on how widely and deeply the electronic phenomena in this new class of semiconducting compounds will be investigated. Apart from the solution of technical problems, the study of the properties of organometallic solids may prove useful in relation to a wide range of problems associated with biocatalysis and carcinogenic activity[74].

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The data considered in this review show that organometallic compounds constitute a large and interesting class of new semiconducting compounds many of which effectively manifest a fundamental property such as the internal photoeffect. The possibility of a wide variation of the types of bonds by selecting the appropriate metals and ligands permits the reliable prediction that in the future the range of organometallic compounds with semiconducting properties will be greatly extended and that the study of the electronic phenomena in them will be vigorously continued.

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