

The Gurevich-Kubelka-Munk function was used to investigate absorption spectra of polymeric compounds consisting of monomers of the type  $\text{Cu}-\text{C}\equiv\text{C}-\text{R}_1$  and  $\text{Cu}-\text{C}\equiv\text{C}-\text{R}_2-\text{C}\equiv\text{C}-\text{Cu}$ . The absorption is due to transfer of charge between copper d-electrons and ligand  $\pi$ -electrons with the appearance of ligand vibrational structure. Forbidden band widths and direct transition energies lie between 2.0 and 2.7 eV and agree with similar values obtained from photoconductivity spectra. Structural details of copper acetylides are discussed.

The goal of the present investigation is to study absorption spectra of representatives of a new class of organo-metallic semiconductors—copper acetylides—which promise to solve a whole series of scientific and technological problems [1-5]. Since the compounds are insoluble finely dispersed coordination polymers, their spectra were studied by the diffuse reflection method [6, 7]. The ordinate of the graphs was used to plot the function  $F(R_\infty) = (1-R_\infty)^2 / (2R_\infty)$ , where  $R_\infty$  is the relative diffuse reflection layer relative to a nonabsorbing standard (magnesium oxide). The concentration of the investigated compound was  $5 \cdot 10^{-4}$  of that of magnesium oxide. Measurements were carried out with an SP-700 spectrometer over the 340-800 nm region. The samples were prepared as in [5].

#### RESULTS AND DISCUSSION

Absorption spectra of copper n-butyl (I), copper vinyl (II), copper phenyl (III), copper ethynylphenyl (IV), and copper diphenylethynyl (V) acetylide are shown in Fig. 1. Spectra of copper acetylides derived from n-diethynylbenzene (VI), 4,4'-diethynyldiphenyl (VII), and 4,4'-diethynyldiphenyl oxide (VIII) are shown in Fig. 2. It should be noted that the copper content of compounds VI-VIII does not exactly correspond to the indicated formula, since, due to steric problems, not all of the acetylenic hydrogens were replaced by copper. A mixture (~1 : 1) of mono- and diacetylides of the bisacetylenes was apparently obtained.

Analysis of the spectra shows that they appear very similar to the photoconductivity spectra obtained in [4]. All of the compounds are characterized by a maximum in the longwave region between 400 and 500 nm (Table 1). It is evident that the maximum undergoes a marked bathochromic shift as the length of the conjugated chain of the ligand increases, indicating localization of excitation in the conjugated chain of the monomeric unit. A comparison of the spectra shows that bathochromic shifts of the maxima with increasing conjugated chain length are accompanied by the appearance of certain kinds of structure in the absorption spectra. Thus, only one band is observed for the butyl and vinyl groups, and the maxima are in the 420 nm region, whereas compounds with the phenyl group show maxima at 455 and 395 nm, compounds with the phenylethynyl group at 460 and 420 nm, and those with the diphenylethynyl group at 465 nm. Spectra of the bisacetylenes (VI-VIII) also contain structure. It should be noted that this structure was much more clearly resolved in the photoconductivity spectra [4]. The appearance of the bands is due to the appearance of vibrational energy and is related to the introduction of aromatic groups, which impart coplanarity to the molecules, thus ensuring a longer lifetime for the excited state. To confirm the vibrational nature of the spectra we calculated the frequency difference between absorption maxima obtained in this study and between the photoconductivity maxima obtained in [4] for compounds III-V. The results are shown in Table 2. Characteristic frequencies can be assigned to the ethynyl bond ( $\sim 2100-2200 \text{ cm}^{-1}$ ), out-of plane bends of benzene ring CH group ( $830-850 \text{ cm}^{-1}$ ), and the  $\equiv\text{CH}$  stretching vibration ( $\sim 3200 \text{ cm}^{-1}$ ). The latter frequency may also be a complete vibration. Actually, a triple bond in the second ethynyl group is observed in IR spectra of compounds IV

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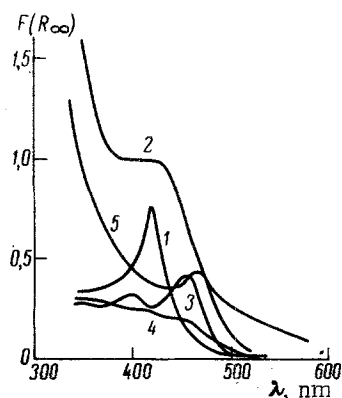


Fig. 1

Fig. 1. Absorption spectra of copper acetylides of the type  $\text{CuC}\equiv\text{C}-\text{R}$ , where R is: 1) n-butyl (I); 2) vinyl (II); 3) phenyl (III); 4) ethynylphenyl (IV); 5) diphenylethynyl (V) group.

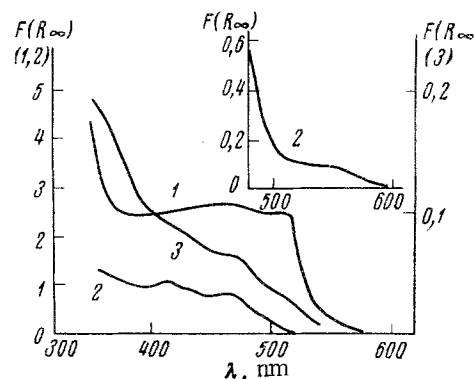


Fig. 2

Fig. 2. Absorption spectra of copper acetylides: 1) n-diethynylbenzene; 2) 4,4'-diethynyldiphenyl oxide; 3) 4,4'-diethynyldiphenyl.

TABLE 1. Longwave Maxima, Forbidden Band Widths ( $\Delta E$ ), and Direct Transition Energies ( $\Delta E_{\text{dir}}$ ) for Copper Acetylides

No.	Structural formula of monomeric unit	From absorption spectra			From photoconductivity spectra [4]	
		position of long-wave maximum, nm	E, eV	$E_{\text{dir}}$ , eV	position of long-wave maximum, nm	E, eV
I	$\text{CuC}\equiv\text{C}-\text{C}_4\text{H}_9$	420	$2,73\pm 0,05$	$2,75\pm 0,03$	440	$2,72\pm 0,02$
II	$\text{CuC}\equiv\text{C}-\text{CH}=\text{CH}_2$	435	$2,5\pm 0,05$	$2,53\pm 0,03$	465	$2,41\pm 0,02$
III	$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_5$	455	$2,4\pm 0,05$	$2,50\pm 0,03$	500	$2,38\pm 0,02$
IV	$\text{CuC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	455	$2,24\pm 0,05$	$2,48\pm 0,03$	500	$2,22\pm 0,02$
V	$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	465	$2,3\pm 0,05$	$2,46\pm 0,03$	510	$2,26\pm 0,02$
VI	$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Cu}$	512	$2,10\pm 0,1$		530	$2,13\pm 0,04$
VII	$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{CCu}$	470	$2,00\pm 0,1$		540	$2,14\pm 0,04$
VIII	$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CCu}$	550	$2,00\pm 0,1$		505	$2,30\pm 0,04$

and V [4]. It is interesting that the most characteristic frequency for these compounds (in the  $1930\text{ cm}^{-1}$  region) [2, 4, 8] (see below) does not appear. We used published luminescence and photo-emf spectra of copper phenyl acetylide [1, 2] to carry out an analysis of the vibrational structure. The results are shown in Table 3 where characteristic frequencies again appear. The presence of the  $2240\text{ cm}^{-1}$  frequency and the  $3300\text{ cm}^{-1}$  band together with the characteristic IR frequency of  $1930\text{ cm}^{-1}$  [2, 4, 8] suggests that when excitation occurs in compounds of this type there is a change in the electron configuration leading to a strengthening of the ethynyl bond.

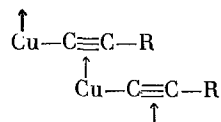
On the basis of insolubility and IR spectral data (a decrease in the characteristic triple bond frequency by  $350\text{ cm}^{-1}$  on the average) it would customarily be assumed that copper acetylides interact mainly through coordination of the copper atom with an ethynyl group of a neighboring unit [8]:

TABLE 2. Vibrational Structure in Absorption Spectra and Photoconductivity Spectra of Copper Acetylides

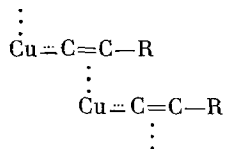
Structural formula of monomeric unit	Position of maxima in spectra				Difference in spectral frequencies $\Delta\nu, \text{cm}^{-1}$	
	absorption		photoconductivity		absorption	photoconductivity
	$\lambda, \text{nm}$	$\nu, \text{cm}^{-1}$	$\lambda, \text{nm}$	$\nu, \text{cm}^{-1}$		
$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_5$	455 395	22 000 25 300	500 430	20 000 23 220	3300	3220
$\text{CuC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	455 415	2 200 24 100	500 480 450	20 000 20 850 22 200	2100	850 1350 } 2200
$\text{CuC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	465	21 500	510 490 440	19 620 20 450 22 750		830 2300 } 3180

TABLE 3. Vibrational Structure in Spectra of Copper Phenyl Acetylide

Type of spectrum	$\lambda, \text{nm}$	$\nu, \text{cm}^{-1}$	$\Delta\nu, \text{cm}^{-1}$
Absorption	395	25 300	3300
Luminescence	455	22 000	
In air at 296°K	516	19 420	2240
In air at 77°K	583	17 180	
Under vacuum at 77°K	568	17 700	1800
	630	15 900	
	680	17 250	850
Photoconductivity	610	16 400	3220
	430	23 200	
Photo-emf	500	20 000	3300
	395	25 300	
	455	22 000	



Interactions between Cu and the ethynyl group within the monomeric unit with promotion of an electron along the copper-ethynyl bond are apparently of equal importance:



The medium intensity IR band observed in the  $1930 \text{ cm}^{-1}$  region may again be due to a  $\text{X}=\text{C}=\text{X}$  ground state skeletal vibration [9]. In the excited state, as noted above, the ethynyl bond is strengthened.

We note that for complex compounds, where the bond is formed by participation of the metal d-shell, the distribution of electrons around the heavy atom is very complex. In this case, even the idea of a chemical bond as some sort of preferred direction along which electrons are localized is rather vague. Actually, in the case of copper phenyl acetylide, for example, the confirmed x-ray structure for  $(\text{CuC}\equiv\text{CPh})_x$  shown in Fig. 3 is cited in Green's book [10] with reference to a communication by Scherrer and Corfield. The polymer is an infinite rectangular tube of copper atoms bonded to each other. The  $\text{PhC}\equiv\text{C}$  groups are situated on the outside of this tube. Each of these groups is apparently sigma-bonded to one Cu atom, symmetrically bonded to another, and asymmetrically bonded

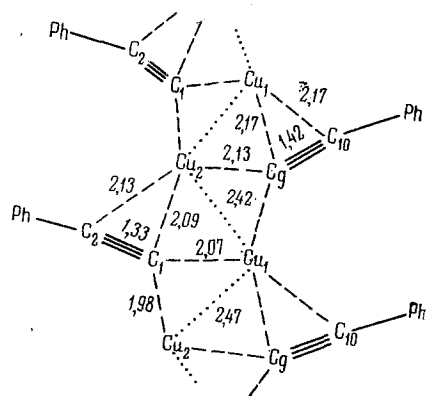


Fig. 3. Structure of copper phenyl acetylide.

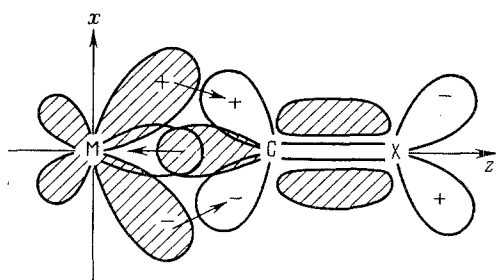


Fig. 4. Interactions of d- and  $\pi$ -electrons in a  $M-C \equiv C-R$  type system.

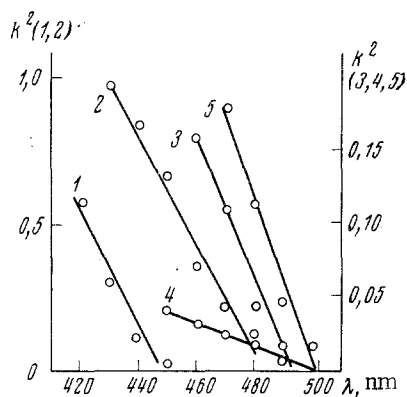


Fig. 5. Direct transitions for: 1) copper butyl; 2) copper vinyl; 3) copper phenyl; 4) copper ethynylphenyl; 5) copper diphenylethynyl acetylide.

unshared electron pairs on the oxygen either to antibonding  $\pi$ -orbitals ( $n-\pi$  transition) or to d-orbitals of the copper atoms.

The analysis of copper acetylide absorption spectra is of considerable interest from the standpoint of solid state physics, which regards these compounds as new photoconducting materials [1-5]. It is known that the analysis of edge absorption makes it possible to determine the width of the forbidden zones and the nature of transitions between zones. For direct and indirect transitions, the absorption coefficient  $k$  depends on frequency in the following manner:

$$k_{\text{dir}} = A (h\nu - \Delta E_{\text{dir}})^{1/2}, \quad k_{\text{indir}} = B (h\nu - \Delta E_{\text{indir}})^2,$$

to a third. For simplicity, Fig. 3 shows only one half of such a tube. In essence copper acetylides belong to a new, quite interesting type of substance - clusters. It is clear that the electron configurations of such compounds are extremely complicated and interpretation of their spectra is difficult. It should be noted that the theory of spectra of compounds formed from elements with d-shells is practically undeveloped.

It is interesting to approach spectra interpretation from the point of view of the chromaticity theory of organic compounds and from the position of donor-acceptor reactions regarding copper as a constituent of a basic chromophore. It is known that liquid acetylenic compounds of the type  $HC \equiv C-R$ , where R is  $n-C_4H_9$ ,  $-CH=CH_2$ ,  $C_6H_5$ , or  $n-C_6H_4C \equiv C-C_6H_5$ , absorb in the region below 370 nm [11]. On the other hand, the monovalent copper ion also absorbs in the UV region of the spectrum. It should be noted, of course, that the color is determined by the coordination number as well as by the valence. It is clear that the absorption observed in the visible region of the copper acetylide spectrum is due to resonance interactions between d-electrons on the copper atoms and  $\pi$ -electrons of the appropriate ligands. An idea of such interactions can be obtained from Fig. 4, which shows the electron density distribution of the  $M-C \equiv C-R$  system in the yz plane. The absorption bands are determined by the transfer of charge between copper d-orbitals and antibonding  $\pi$ -orbitals on the ligands.

It should be noted that the lack of information about the scattering coefficient and the dimensions of the particles makes it impossible to determine the exact value of the absorption coefficient. Calculation shows, however, that its value is in no case smaller than  $10^4 \text{ cm}^{-1}$ . This confirms that the spectra are due to charge transfer. The observed bathochromic shift when substituents on the ligand ethynyl groups are changed also supports this hypothesis.

Using the theory of conjugated systems it can be assumed that d- $\pi$  conjugation arises in our absorption spectra. It should be noted that the stronger the metallic character of an element the more it lowers the excitation energy of a basic chromophore. Actually, acetylenic derivatives of silicon, germanium, and mercury absorb light in the UV region of the spectrum [12]. It is interesting that a comparison of the spectra of compounds III and VI reveals that both copper atoms in VI participate in d- $\pi$  conjugation. It should also be noted that the introduction of an oxygen atom between the phenyl groups of VIII leads to the appearance of a maximum with a small extinction coefficient in the 550 nm region. This maximum is apparently caused by the transfer of

where A and B are constants;  $\Delta E_{\text{dir}}$  is the energy of a direct transition;  $\Delta E_{\text{indir}}$  is the energy of an indirect transition (a transition with phonon participation). Since the function  $F(R_{\infty})$  determines the form of the absorption coefficient, we tried to use it to analyze edge absorption of copper acetylides. In this case

$$k_{\text{dir}}(F) = C (h\omega - \Delta E_{\text{dir}})^{1/2}, \quad k_{\text{indir}}(F) = D (h\omega - \Delta E_{\text{indir}})^2.$$

Then plots of  $k_{\text{dir}}^2(F)$  or  $k_{\text{indir}}^{1/2}(F)$  versus frequency intersect the x axis at energies corresponding to the direct and indirect transitions. Plots of  $k^2(F)$  for compounds I-V are shown in Fig. 5, and the direct transition energies are shown in Table 1. Because of the ambiguous nature of compounds VI-VIII, analysis of direct energies was not carried out for these compounds. We did not analyze indirect transitions since their energies cannot be uniquely determined from absorption spectra measured at room temperature. Table 1 also gives values of forbidden band widths for compounds I-VIII obtained by extrapolating the descending portions of the longwave edge absorption to the x axis and values obtained from photoconductivity data [4]. It should also be noted that edge absorption of compounds I-V completely satisfied the Urbach rule.

The agreement of zone widths as obtained from absorption spectra and from photoconductivity spectra shows that copper acetylides are natural semiconductors. With regard to this it should be noted that both direct and indirect transitions contribute to photoconductivity. This follows from the fact that the photoconductivity activation energy (especially for compounds III-V) exceeds the direct transition energy by approximately 0.2 eV. It should be kept in mind that absorption at the direct transition boundary may also be due to disorder or to the different sizes of coordination units. This absorption is responsible for the longwave photoconductivity "tail" observed in [4]. We note that the absorption maxima for all compounds coincide with minima in the photoconductivity spectra, which indicates a rather rapid surface recombination of charge carriers.

In conclusion, we note that the diffuse reflection method in conjunction with other data provides valuable information about the structures of insoluble, finely dispersed heteroorganic compounds.

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