

RADIO SPECTROSCOPY OF ORGANIC SEMICONDUCTORS

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I. INTRODUCTION

THE intensive development of solid-state physics in the last decade has involved not only the fact that the results of the studies could be readily applied in practice, but also new experimental possibilities that have only recently arisen. Semiconductor physics, which is of great practical significance, is growing very intensively. Along with study of the classical inorganic semiconductors (Cu₂O, Si, Ge, InSb, InAs, etc.) many studies are being published now on photoconductivity of various organic compounds and their electrical conductivity. Organic semiconductors are currently attracting more and more attention.^[1] Above all, this is due to the extensive possibilities of varying the resistivities and types of conduction afforded by organic compounds. Organic compounds can be semiconductors, as the first studies of Vartanyan^[2,3] on the photoconductivity of these compounds have shown.

The studies of Soviet scientists have made a decisive contribution to the development of semiconductor theory. As early as 1931, Ya. I. Frenkel' introduced the concept of the exciton^[4] to explain the strong absorption of light in a region of decreased photoconductivity. According to this idea, light quanta can transfer electrons from the filled valence band to exciton levels in the forbidden band. Thus light absorption occurs without the appearance of conduction. However, if an electron enters the conduction band, an electric current can be detected. Dissociation of excitons gives rise to current carriers in the form of holes and electrons. Often the edge of the exciton band coincides in position with the bottom of the conduction band,^[5] so that entry of an electron into the

conduction band is equivalent to dissociation of excitons.

Spectroscopic studies of light absorption have made it possible to prove the existence of excitons, and have lent clarity to our understanding of the photoeffect.

E. F. Gross^[5] has observed narrow exciton absorption lines in a Cu₂O crystal at low temperatures. Their arrangement in the spectrum corresponds to the Rydberg formula with $n > 2$. The Stark and Zeeman effects on the exciton absorption lines were studied. The exciton state in a crystal is mobile. In moving through a crystal, an exciton can lose its energy in recombination processes. However, owing to its electrical neutrality, it does not contribute to the electrical conductivity.

A. S. Davydov^[6] has developed a detailed theory of molecular excitons. The further development of the exciton concept has proved very fruitful also in explaining the properties of organic semiconductors.

The modern theory of organic semiconductors is based on the band theory of solids.^[7] The band theory is also related to the studies of Soviet authors on the theory of "polarons." The polaron theory was developed by S. I. Pekar.^[8] When an electron in the conduction band moves, a polarization state created by it accompanies it. These formations are called polarons.

All organic semiconductors can be divided into three classes: charge-transfer complexes, which are produced by donor-acceptor reaction of organic donors and often of inorganic acceptors, organic semiconductors of low molecular weight containing molecules having conjugated π -bonds (anthracene,

naphthalene, etc.), and semiconducting polymers. The width of the conduction band in organic semiconductors increases with increasing overlap of the electron clouds of the molecules. Since the overlap integrals in organic crystals of low molecular weight are small, their resistivities are large.

Electrons can jump to exciton levels of a crystal under the action of heat or light. The electron migrates from molecule to molecule, owing to the tunnel effect, so that hole and electron conduction become possible. The electrical conductivity of organic semiconductors can be altered greatly by introducing various impurities into the sample. Study of the semiconductor properties of organic compounds is important not only in designing semiconductor devices, but also in connection with their great role in biochemistry.^[9] The first rectifier elements based on organic molecules^[10] have been recently built, as well as infrared detectors,^[11] and organic semiconductors have been applied in television.^[12] This new field of semiconductor physics is being intensively developed. In the last ten years, tens of new organic materials having enhanced electrical conductivity (resistivities from 10^{-2} to 10^6 ohm-cm) have been discovered. These studies are of great significance for biology in connection with energy-transfer processes, biocatalysis, photosynthesis, the mechanism of color vision, etc.

The radiospectroscopic methods, especially nuclear quadrupole and electron paramagnetic resonance, have opened up completely new possibilities in studying either the nature of chemical bonds or the mechanism of electrical conduction. In essence, NQR is now the only method permitting study of the nature of chemical bonds in a solid, while EPR opens up vast possibilities of studying mobility of carriers, determining activation energies, and establishing the nature of carriers, etc.

The advances in radiospectroscopy have opened up a broad avenue for using resonance methods to study matter. The various radiospectroscopic methods, which are based on studying the resonance absorption of radio waves, are used to detect free radicals, for quantitative and qualitative analysis, for studying the structure and dynamics of crystal lattices and the structure of molecules, to study the kinetics of chemical reactions, defects in solids, etc. Even a simple listing of the varied applications of radiospectroscopy takes several pages of text. This review is concerned with a narrower theme: the study of organic semiconductors by radiospectroscopic methods.

We shall not aim in this review to present all the extensive material on organic semiconductors, especially since there are already several monographs on this subject.^[1,13] Nevertheless, some fundamental results have been recently obtained in radiospectroscopy of organic semiconductors that demonstrate the promise of these methods in this type of studies. Insofar as we know, no generalization of these studies has been

made. Part of this review will be devoted to the results obtained in the radiospectroscopy laboratory of the Perm' State University. Above all, this pertains to the EPR study of biologically-important organic semiconductors, the determination of their activation energies, and also the study of the nature of chemical bonds and spin-lattice relaxation processes in a series of charge-transfer complexes.

We discuss in detail also the results of studying the triplet states of charge-transfer complexes and the triplet states of molecules in organic semiconductors. The concept of "triplet excitons" has proved very fruitful in explaining a number of features of the EPR spectra of organic semiconductors.

EPR was first discovered by E. K. Zavoiskii in Kazan'.^[14] This discovery has stimulated a vast number of radiospectroscopic studies.

Considering that the experimental methodology, especially in EPR, has been rather well described in a number of monographs in our country^[15,16] and abroad,^[17] we shall spend no time on it. This also holds for NQR^[18,19] and NMR.^[20] The essence of these phenomena has also been rather well outlined in the above-cited monographs and review articles.

Hence, we shall hardly discuss purely spectroscopic problems, but shall concentrate our attention on the results of studying organic semiconductors, trying to demonstrate the new possibilities that have arisen in this new promising field.

II. ELECTRON PARAMAGNETIC RESONANCE IN ORGANIC SEMICONDUCTORS

1. EPR Observation of Triplet States in Organic Crystals

a) The spin Hamiltonian of local triplet states.

Study of local or molecular triplet states in organic crystals makes it possible to understand many properties of organic semiconductors. In particular, these studies have involved the introduction of the concept of the triplet exciton. Local triplet states have been found to show fine structure of the EPR lines. It is due to the direct magnetic interaction between the electron spins.

Molecules in the triplet state are characterized by splitting of the spin states in the absence of an external magnetic field. The threefold spin degeneracy can be completely or partially removed, depending on the symmetry of the molecule and the nature of the triplet state of the molecular wave function. In aromatic molecules, the interaction responsible for this behavior is primarily the electronic spin-spin interaction:

$$\mathcal{H}_D = g^2 \beta^2 \sum_{i < j} \left(\frac{\mathbf{S}_i \mathbf{S}_j}{r_{ij}^3} - \frac{3 (\mathbf{S}_i \mathbf{r}_{ij}) (\mathbf{S}_j \mathbf{r}_{ij})}{r_{ij}^5} \right), \quad (2.1)$$

where g is the electronic g factor, β is the Bohr magneton, \mathbf{S}_i is the spin operator of the i -th electron in units of \hbar , and \mathbf{r}_{ij} is the radius vector between the i -th and j -th electrons. This expression is equivalent

to the following effective spin Hamiltonian:^[21,22]

$$\mathcal{H}_s = D \left(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E \left(\hat{S}_x^2 - \hat{S}_y^2 \right), \quad (2.2)$$

where D and E are the spin-spin interaction constants in the absence of an external magnetic field.

A Zeeman-interaction term is added to \mathcal{H}_s , as usual, upon application of an external magnetic field:

$$\mathcal{H}_z = g\beta SH. \quad (2.3)$$

Electrons occurring in a local triplet state can be described by the model that has been used in nuclear magnetic resonance to calculate the spectrum of a pair of close magnetic particles. This situation is equivalent^[20] to that discussed by Pake in NMR for molecules of water of crystallization in crystalline hydrates.

The experiments are usually conducted at low temperatures, using solid solutions in a suitable indifferent solvent of molecules whose triplet states are easily excited.

One often uses the complete spin Hamiltonian in a somewhat different form^[23] in order to calculate the resonance field, i.e., the magnetic field causing the splitting of the two energy levels, which is equal to the quantum of radio-frequency energy:

$$\begin{aligned} \mathcal{H} &= g\beta SH + D \left(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E \left(\hat{S}_x^2 - \hat{S}_y^2 \right) \\ &= g\beta SH - (X\hat{S}_x^2 + Y\hat{S}_y^2 + Z\hat{S}_z^2). \end{aligned} \quad (2.4)$$

The two sets of constants are related as follows:

$$X = \frac{1}{3} D - E, \quad Y = \frac{1}{3} D + E, \quad Z = -\frac{2}{3} D. \quad (2.5)$$

X, Y, and Z are precisely the quantities that one tries to get from the observed EPR spectrum.^[24]

Evidently, the spin Hamiltonian of (2.4) coincides in structure of the spin operators occurring in it with the Hamiltonian used in nuclear spin resonance.^[25,26]

Detailed solutions have been obtained in the latter case, in particular, for a spin of unity.^[27-29] In the absence of an external magnetic field, the electronic spin Hamiltonian of (2.2) is equivalent to the Hamiltonian used in nuclear quadrupole resonance.

The splitting of the EPR lines of the triplet states becomes averaged in polycrystalline specimens. However, just as in NMR, a pair of "close spins" alters the shapes of the lines, so that the constants in the spin Hamiltonian of (2.1) can be estimated.

b) Experimental study of EPR spectra of aromatic molecules. Hutchison and Mangum^[30,31] were the first to observe the electron resonance of triplet levels of naphthalene molecules. They performed the experiment on a single crystal of a solution of naphthalene in durene at 77° K. The triplet levels of naphthalene were filled by intense ultraviolet irradiation. The constants D and E were found to be $\pm 0.1006 \text{ cm}^{-1}$ and $\mp 0.0136 \text{ cm}^{-1}$, respectively. That is, the splitting in the absence of an external magnetic field should

actually be comparable with the Zeeman splitting. The measurements at liquid-helium temperature made in^[32] showed that D and E are positive in sign.

In a series of studies,^[23,24,33,34] van der Waals and de Groot were able to show that the EPR of photo-excited molecules in the triplet state can be observed also in solid glassy solutions. As the theory implies,^[24,27] one observes here transitions having $\Delta m = \pm 2$, in addition to those having $\Delta m = \pm 1$.^[35]

A large number of aromatic molecules have been studied recently^[36-49] and are continuing to be studied by paramagnetic resonance. Triplet excited states of molecules have been studied in the polycyclic aromatic hydrocarbons (benzene, naphthalene, anthracene, phenanthrene, etc.), in organic molecules containing nitrogen (nitrenes, etc.), and in compounds of high molecular weight (plastics,^[46] etc.).

Further, we note that the data obtained in these studies (splitting of triplet levels, lifetime of triplet states, energy of singlet-triplet transitions, etc.) is of great practical significance in designing laser devices based on organic compounds.^[50]

c) Splitting of triplet states in the absence of an external magnetic field. The EPR method permits one to study local triplet states of organic molecules in the absence of an external magnetic field at relatively low frequencies (50–200 MHz). However, the search for EPR signals is more complicated in this case than in strong magnetic fields, since the splittings of the triplet levels are not known a priori. It has become necessary to calculate these splittings by various quantum-mechanical methods.^[51-54]

In a series of studies, Gouterman and his associates have calculated the constants D and E for a number of polycyclic aromatic molecules, on the basis of the following relations:

$$\begin{aligned} \begin{pmatrix} D \\ E \end{pmatrix}_{a, b, c, d} &= \frac{g^2 \beta^2}{4hc a_0^3} \int \int \varphi(r_{1a}) \varphi(r_{1b}) \\ &\times \begin{bmatrix} 3(r_{12}^2 - 3z_{12}^2) \\ 3(y_{12}^2 - x_{12}^2) \end{bmatrix} r_{12}^{-5} \varphi(r_{2c}) \varphi(r_{2d}) d\tau_1 d\tau_2. \end{aligned} \quad (2.6)$$

Here the $\varphi(r)$ are normalized $2p_z$ Slater functions, the Z axis is taken perpendicular to the plane of the molecule, a_0 is the atomic radius, and the subscripts a, b, c, and d specify the spin states of electrons 1 and 2.

We shall not discuss here the various approximations (from the two-electron density-matrix method of McWeeny^[55] to the simple LCAO MO method of Hückel^[56]) that have been applied by different authors to calculate splittings in the absence of an external magnetic field, since they have been rather well discussed in recent papers.^[57,58]

Study of local triplet states of molecules by the EPR method has shown that semiconductor-type conduction of many organic compounds directly results from delocalization of π electrons. The activation energy for electrical conduction proves to be of the

order of magnitude of the ordinary energy values for exciting π electrons, and in particular, the energies of singlet-triplet transitions.

2. Triplet Excitons in Charge-transfer Complexes and Other Organic Semiconductors

a) Triplet excitons in molecular crystals and the mechanism of electrical conduction. Molecular organic crystals differ from inorganic crystals in a number of peculiarities that give rise to qualitatively new properties. First, the molecules interact through molecular or van der Waals bonding, which is the weakest of all the fundamental types of bonding in condensed systems (ionic, covalent, and metallic). Furthermore, this intermolecular bonding is considerably weaker than the intramolecular chemical bonding. Second, the building blocks of these crystals are large, and contain relatively asymmetric molecules. Hence, each individual molecule in most known crystal structures interacts mainly with one or two neighboring molecules. This is the basis of the classification of molecular crystals made by McConnell and Lynden-Bell.^[59,60]

Class I crystals contains those in which the interaction occurs essentially between two neighboring molecules, while Class II contains those in which each molecule interacts essentially with two or more neighbors. As will be evident from the discussion below, paramagnetic triplet excitons can arise in Class I crystals (to which the charge-transfer complexes mainly belong). This makes it possible to observe EPR signals.

As was mentioned above, the exciton concept first introduced by Frenkel^[4] has subsequently been developed in many Soviet and foreign studies. In particular, Wannier^[61] has supplemented Frenkel's exciton concept in the strong electron-hole binding approximation with the idea of excitons showing weak binding. In distinction from Frenkel excitons, the electron and hole belong to different structural units in Wannier excitons.

The concept of neutral excitons propagated throughout the crystal has been successfully used to explain many characteristic features of absorption spectra of crystals, such as their relation to the spectra of the isolated molecules, Davydov splitting, etc. However, the ordinary exciton theory has proved inadequate in treating the electric and magnetic properties of molecular crystals. It has been necessary to introduce the concept of multiplet excitons, i.e., excitons in excited electronic states.

The excited electronic states of molecular crystals can be described in various ways.

Lyons^[62] has introduced the concept of an ionized electronic state, the essence of which is as follows. Since aromatic molecules (like anthracene) simultaneously possess a low ionization potential and a positive electron affinity, they can donate and capture

electrons. The pair of molecular ions M^+ and M^- thus obtained forms a dipole ($\sim 4-6 \text{ \AA}$). The energy of formation of such an ionized state in aromatic crystals is about 1-3 eV.^[63] We note that the width of the energy gap for conduction in these crystals is also of the order of 1-3 eV.^[63] However, a current does not appear when an external electric field is applied, since the positive and negative charges are bound in hydrogen-like orbitals and must migrate as pairs. The ion pair must be dissociated for a current to appear. This is the fundamental process for generating current carriers.

Thus, the states of the crystal can be described both as neutral exciton waves

$$X(\mathbf{k}, 0) = N^{-1/2} \sum_{n=1}^N |\exp(i\mathbf{k}\mathbf{r}_n) | P_n, \quad (2.7)$$

where

$$P_n = \varphi_1 \varphi_2 \varphi_3 \dots \varphi_{n-1} \varphi'_n \varphi_{n+1} \dots \varphi_N,$$

and as ionized exciton waves

$$X(\mathbf{k}, \mathbf{R}) = N^{-1/2} \sum_{n=1}^N |\exp(i\mathbf{k}\mathbf{r}_n) | Q_{m, m+r}, \quad (2.8)$$

where

$$Q_{m, m+r} = \varphi_1 \varphi_2 \dots \varphi_{m-1} \varphi_m^+ \varphi_{m+1} \dots \varphi_{m+r}^- \varphi_{m+r+1} \dots \varphi_N;$$

$$\mathbf{R} = \mathbf{r}_{m+r} - \mathbf{r}_m;$$

Here N is the number of molecules in the crystal, \mathbf{r}_n and \mathbf{r}_m are the position vectors of the molecules, and \mathbf{k} is the wave vector. The wave functions of the unexcited and excited molecules are denoted by φ_n and φ'_n . The symbols φ_m^+ and φ_{m+r}^- denote the wave functions of molecules having position vectors \mathbf{r}_m and \mathbf{r}_{m+r} , one of which has lost an electron, while the other has captured it.

In recent studies^[64,45] these excited states of molecular crystals have been called transfer excitons. Owing to the weakness of the intermolecular interactions, transfer excitons can have low-lying states with non-zero magnetic moments. Such excitons can be called triplet excitons, since their spins are unity, just like the spin of an ordinary local triplet state.

Let us examine in more detail the mechanism of formation of triplet excitons in molecular crystals.^[66] Molecular crystals of aromatic compounds are unique in the sense that the electron overlap between adjacent molecules is very small, both in the ground and in the lowest excited states. In this case, the crystalline zero-order wave functions can be taken in the form of products of the φ functions in both the ground state (the case treated by Davydov^[6]) and in the lowest excited triplet state, to which direct optical transitions from the ground state are practically forbidden by the spin selection rules.

Triplet exciton states can be derived by a simple extension of the ordinary exciton theory.^[66]

The Hamiltonian of a rigid crystal structure can be written in the form

$$\mathcal{H} = \sum_{m\alpha} \mathcal{H}_{m\alpha} + \sum_{m\alpha < n\beta} V_{m\alpha, n\beta}, \quad (2.9)$$

where $\mathcal{H}_{m\alpha}$ is the Hamiltonian of the m -th isolated molecule in the α -th unit cell, and $V_{m\alpha, n\beta}$ is the potential of the pair interaction between the molecules. The zero-order wave functions of the ground and excited states are the following:

$$\Phi_0 = A \prod_{n\beta} \varphi_{n\beta}^0, \quad (2.10)$$

$$\Phi_{m\alpha}^f = A \varphi_{m\alpha}^f \prod_{m\alpha \neq n\beta} \varphi_{n\beta}^0. \quad (2.11)$$

Here A is the antisymmetrization operator

$$A = [(a!)^{2N} / (hNa!)^{1/2}] \sum_p (-1)^p P, \quad (2.12)$$

where a is the number of electrons per molecule, N is the number of unit cells in the crystal, h is the number of molecules in the unit cell, $\varphi_{n\beta}^0$ is the wave function of the isolated molecule, and the superscript f specifies the three spin states, which are the eigenfunctions of the operators \hat{S}^2 and \hat{S}_z^2 (i.e., $S = 1$ and $M = 0, \pm 1$).

Let us treat the special case of a crystal of monoclinic symmetry with space group C_{2h} (e.g., naphthalene). The unit cell of such a crystal contains two molecules. The result of taking account of the interaction of one molecule with all the molecules not translationally equivalent to it in the crystal is that two excitation energies correspond to each value of the wave vector \mathbf{k} . Here the excitation energy of the crystal on going from the ground state to an excited state is written in the form^[66]

$$E^f(\mathbf{k}) = \Delta\epsilon_f + D_f + E_f^\pm(\mathbf{k}), \quad (2.13)$$

where $\Delta\epsilon_f$ is the excitation energy of the free molecule, D_f is the change in the interaction energy of a given molecule with all its neighbors when it enters the f -th excited state, and $E_f^\pm(\mathbf{k})$ is the increment in the excitation energy. In crystals having two molecules per unit cell, one non-degenerate excited state of the free molecule corresponds to two bands of excited states, rather than one. For triplet states, this Davydov splitting is

$$\Delta E^f = E_f^+(k) - E_f^-(k) = 2 \sum_{m_2} (I_{m_2, n_1}^f + K_{m_2, n_1}^f), \quad (2.14)$$

where \mathbf{k} is the wave vector. One can estimate this splitting by calculating the corresponding exchange integrals I_{m_2, n_1}^f and K_{m_2, n_1}^f . Although no one has reported a direct observation of splitting of a triplet exciton state of a crystal, attempts of this type already have been made^[67, 68] in studying singlet-triplet transitions. A possibility of studying singlet-triplet transitions in organic semiconductors has arisen, involving application of laser technique. The Davydov splitting for triplet states of molecules is small. For example,

it is calculated to be about 35 cm^{-1} for anthracene at 300°K .^[66]

McConnell and his associates^[21, 59, 60] have given the first and most complete treatment of the application of the theory of triplet excitons to EPR spectra. They showed in the first study^[21] that, in contrast to local triplet states of isolated aromatic molecules incorporated in an indifferent matrix, pure molecular crystals of the same compounds should show triplet excitons observable by EPR. Here the exciton spectra should differ qualitatively from those of local triplet states in several respects. These will be manifested most characteristically if: a) there are two or more molecules in the unit cell not related by a center of symmetry; b) the Davydov splitting of the triplet exciton states is large in comparison with the constants $|D|$ and $|E|$, as is usually always true.

McConnell et al. have shown that the EPR spectrum of triplet excitons in pure aromatic single crystals should consist of only two lines,* since the non-equivalence of the positions in the unit cell should have no effect. Furthermore, the nuclear hyperfine structure of the EPR spectra that has been observed for triplet states should be absent, owing to the movement of the triplet excitons through the crystal.

The next step in the studies of McConnell et al.^[59, 60] was made in applying theory to the EPR spectra of complex compounds (or, as they are sometimes called, solid free-radical compounds). They proposed^[59] that the term "triplet exciton" should be taken to mean any excited state with $S = 1$ that can be propagated through the crystal, regardless of whether the motion is a pure wave motion having no activation energy, or a diffusional motion with an activation energy.

The first experimental observation of EPR spectra of triplet excitons was made specifically on charge-transfer complex crystals, which can be assigned as Class I crystals.

b) EPR of triplet excitons. An entire series of interesting physical properties has been discovered in the new class of ion-radical compounds (charge-transfer complexes) based on the strong electron acceptor tetracyanoquinodimethane (TCNQ)^[69-71] (Fig. 1):

- 1) an unusual behavior of the static magnetic susceptibility with varying temperature;
- 2) triplet-exciton EPR spectra;
- 3) semiconductor-type electrical conduction, with a relation to the EPR spectra;
- 4) exchange narrowing of the paramagnetic resonance lines;
- 5) phase transitions at high pressure.

Kepler^[72] has measured the magnetic susceptibility of TCNQ complexes at different temperatures. It turned

*According to the observations of Hutchison and Mungum^[31] in monocystals of durene containing naphthalene molecules, there are four EPR lines from local triplet states, owing to the two non-equivalent positions in the unit cell.

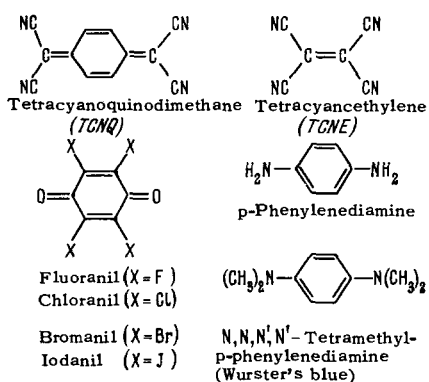


FIG. 1. Some of the most widely-used acceptors and donors for preparing semiconductive charge-transfer complexes.

out that the magnetic susceptibility does not obey the Curie law. He showed that the paramagnetic contribution to the susceptibility obeys the relation

$$\chi = \frac{2Ng^2\beta^2}{3kT} \left[1 + \frac{1}{3} e^{I/hT} \right]^{-1}, \quad (2.15)$$

where I is the activation energy for the singlet-triplet transitions. He measured the electrical conductivity of the same samples. The latter proved to be of semiconductor type. The deviations observed in certain samples could be explained by the presence of a paramagnetic impurity (0.1–4%) having $S = \frac{1}{2}$, whose paramagnetic susceptibility follows the Curie law:

$$\chi = \frac{C}{T}. \quad (2.15a)$$

The authors of [69,70] have suggested in their initial studies that the nature of the triplet states results from formation of some doubly-degenerate supermolecule of TCNQ. However, in subsequent studies [71] influenced by McConnell's [21] ideas, they have concluded that triplet excitons are observed in these systems classifiable as charge-transfer complexes, rather than "isolated" or localized triplet states.

Because of the movement of the triplet excitons through the crystal, the EPR spectrum should lack a nuclear hyperfine splitting. Since no hyperfine splitting was observed, the authors concluded that the frequency of exciton jumps is much greater than the value of the hyperfine splitting, i.e., 10^7 Hz.

However, the fine structure of the EPR spectrum became blurred as well with increasing temperature. This is the fundamental criterion for observing triplet-exciton spectra.

We should note that an exciton state corresponds to simultaneous excitation of many molecules in a certain rather large region of the crystal. This excitation region can move through the crystal. In other words, the concept of an exciton refers to the system of molecules, rather than to a single molecule.

Figure 2 gives a typical EPR spectrum at different temperatures for a randomly oriented crystal of $(\Phi_3XCH_3)^+ \cdot (TCNQ)_2^-$ (where X is a phosphorus or

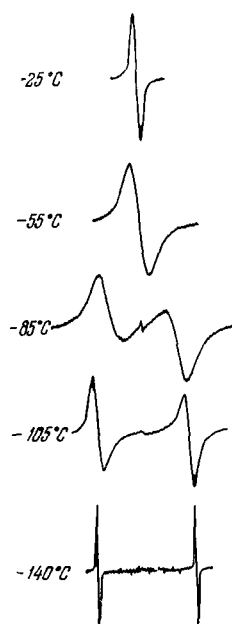


FIG. 2. The triplet-exciton EPR spectrum of the complex $(\Phi_3XCH_3)^+ \cdot (TCNQ)_2^-$ at different temperatures.

arsenic atom). Two narrow doublet components are observed at low temperatures (about -150°C).

With increasing temperature, the EPR lines broaden and approach one another, and then merge into a single signal. The EPR line narrows with further increase in temperature, and attains a width of one gauss at room temperature. This behavior of the EPR lines involves exchange interactions of the triplet excitons. This interaction becomes appreciable only at high enough temperatures.

One can measure the fine-structure constants of the triplet-exciton EPR spectrum at low temperatures. For the complex cited above, $|D| = 6.17 \times 10^{-3} \text{ cm}^{-1}$, and $|E| = 9.82 \times 10^{-4} \text{ cm}^{-1}$.

Chesnut and Phillips [69] have also observed a transition having $\Delta m = \pm 2$. The observation of a "forbidden" transition also permits one to determine the constants $|D|$ and $|E|$ at low temperatures. The results of measuring the activation energies for singlet-triplet transitions will be discussed in Sec. 3 of this chapter. [73,74]

The EPR of a single crystal of Wurster's blue was studied in the temperature range $20\text{--}77^\circ\text{K}$ in [75]. The authors concluded that the elementary excited states in this crystal are triplet excitons of activation energy $I = 246 \text{ cm}^{-1}$. This conclusion is based on the absence of hyperfine structure and the behavior of the lines of the EPR spectrum with increasing temperature. Unfortunately, the discussion in [75] does not make clear the mechanism of formation of the triplet excitons, which are treated as the pairing of spins of two close positive ions, nor the meaning of the spin Hamiltonian, in which $D = 0$, while $E \neq 0$.

We shall now proceed to take up some of the features of triplet-exciton EPR spectra in organic semi-

conductors. In particular, the problem of exchange narrowing of EPR lines is very important.

To a considerable degree, the exchange narrowing of exciton EPR lines is equivalent to the case previously treated in NMR for high-resolution spectra of ethanol. Jones and Chesnut^[71] as well as Chesnut and Phillips^[69] have determined the exchange frequency at different temperatures. When the fine-structure splitting is greater than the exchange frequency ν ,

$$(\Delta\nu_{1,2})^2 = (\nu_1 - \nu_2)^2 - 8\nu^2, \quad (\nu_1 - \nu_2)^2 > 8\nu^2. \quad (2.16)$$

Analogously, for rapid exchange:

$$(\Delta\nu_{1,2})^2 = 0, \quad (\nu_1 - \nu_2)^2 < 8\nu^2. \quad (2.17)$$

The exchange frequency for triplet excitons is a function of the temperature:

$$\nu = \nu_0 \exp\left(-\frac{\Delta E}{kT}\right) = n\sigma v, \quad (2.18)$$

where ΔE is the activation energy for exchange, n is the concentration of triplet excitons, v is the velocity of propagation of the excitons in the crystal, and σ is the effective collision cross-section of the excitons.

The concentration of triplet excitons increases with rising temperature:

$$n \sim 3 \exp\left(-\frac{\delta}{kT}\right), \quad (2.19)$$

where δ is the activation energy for singlet-triplet transitions.

Since it has been found experimentally from EPR spectra that $\Delta E > \delta$, we can assume that $\nu \sim \exp(-\Delta E_V/kT)$, and then neglect the temperature-dependence of σ . Hence we find that $\Delta E = \delta + \Delta E_V$. Thus, triplet-triplet collisions are the main influence on EPR spectrum. Collisions of triplet excitons with paramagnetic impurities can also exert some influence; these impurities are often produced in the synthesis of organic semiconductors. Current carriers can be produced by the collision of excitons: (triplet) + (triplet) \rightarrow (singlet) + (hole)⁺ + (electron)⁻. Choi and Rice^[76] have proposed such a mechanism.

Thus, the triplet-exciton concentration in organic semiconductors can be related to their conductivity.

First-order phase transitions have been found^[73] from the EPR spectra of triplet excitons in $(\Phi_3\text{PCH}_3)^+(\text{TCNQ})_2^-$. The phase transition occurs at 42°C at atmospheric pressure. The transition temperature T_c decreases with increasing hydrostatic pressure, the pressure coefficient being

$$(\partial T_c / \partial P) H_0 = -0.02^\circ \text{C/atm.}$$

McConnell and his associates^[74,75] have recently discovered an interesting behavior of the EPR signals in the complexes $(\Phi_3\text{PCH}_3)^+(\text{TCNQ})_2^-$ and $(\Phi_3\text{AsCH}_3)^+(\text{TCNQ})_2^-$. Triplet-exciton magnetic resonance was observed at 170 MHz over the temperature range 220–362°K and pressure range 1–9 kilobars. First-order phase transitions were observed in both these

compounds at different temperatures and pressures. At a given temperature, the phase transition occurring upon pressure increase was easily detected by the great change in the width of the magnetic resonance line. A mild hysteresis was observed near the phase transition.

The pressure-temperature phase diagram was experimentally determined. This diagram was approximated by the following relation:

$$p = C_1 + C_2 T \ln \frac{1 - \rho_I}{1 - \rho_{II}},$$

where ρ_I and ρ_{II} are the minimum and maximum triplet-exciton densities before and after the phase transition, respectively. The C constants for the complex $(\Phi_3\text{AsCH}_3)^+(\text{TCNQ})_2^-$ were found to be:

$$C_1 = 3.26 \text{ kbar/}^\circ \text{K}, \quad C_2 = 11.8 \text{ kbar/}^\circ \text{K.}$$

The comparison of theoretical and experimental data was quite satisfactory.

While the radio-frequency spectra of organic semiconductors have begun to be studied relatively recently, there are already a considerable number of studies^[76–80] in which EPR was observed and the resistivity measured. However, these studies have not established the unequivocal nature of the EPR signals, the type of current carriers, nor have the activation energies for the spin concentration and the electrical conductivity been compared. Establishment of the nature of the current carriers and paramagnetic centers in these crystals will advance our understanding of the mechanism of electrical conduction. We note that the triplet-exciton problem is very important in biology. A calculation was made in^[82] of the velocity of propagation of triplet excitons in proteins.

EPR makes it possible not only to detect easily the formation of triplet excitons, but also to determine an entire series of characteristics: the exchange frequency, the thermal activation energy, and the fine-structure constant.

Exciton magnetic resonance in the absence of an external magnetic field (zero field) is of great interest. This phenomenon is analogous to a considerable degree to NQR. The method has been termed the "zero magnetic field method."

c) Exciton magnetic resonance in the absence of an external magnetic field. Studying triplet-exciton magnetic resonance in the absence of an external magnetic field has the advantage that it does not require monocrystalline specimens, which are notoriously difficult to grow (especially among the complexes). The zero-field technique, just as in the case of strong magnetic fields, permits one easily to determine the zero-field splitting constants, and furthermore, to determine more easily their temperature-dependence.

In the absence of a magnetic field, the spin Hamiltonian of a triplet exciton of wave vector \mathbf{k} has the form^[75,83]

$$\mathcal{H}_k = D_k \hat{S}_z^2 + E_k (\hat{S}_x^2 - \hat{S}_y^2), \quad (2.20)$$

where D_k and E_k depend on $\cos k$. If the energy of motion of the exciton^[75] is small in comparison with kT and its mean free path is small, then the spin Hamiltonian will no longer depend on k . That is, it will coincide in form with the expressions (2,2) and (2,4) given above:

$$\mathcal{H} = X\hat{S}_x^2 + Y\hat{S}_y^2 + Z\hat{S}_z^2. \quad (2.21)$$

The eigenvalues of this spin Hamiltonian are given in Fig. 3. The x, y, and z axes are taken so that

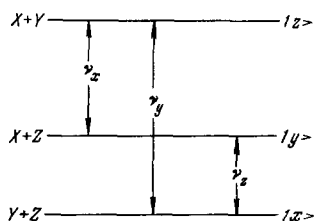


FIG. 3. Triplet-exciton levels at "zero magnetic field."

$X > Y > Z$. The triplet-exciton energy levels are analogous to the NQR levels for spin 1.^[26] In this case one can observe three transitions. The frequencies of these transitions are $X - Y$, $X - Z$, and $Y - Z$, and they are linearly polarized along the z, y, and x axes. However, in a polycrystalline specimen the radio-frequency field excites all three transitions simultaneously. As we know, when $S = 1$, a zero-field experiment permits us easily to determine the constants D and E . When $E = 0$, there are only two energy levels, the splitting between which is D . However, when $E \neq 0$, the splitting between the upper and middle levels is $2E$; then D is determined as the splitting between the lower level and the mean between the upper and middle levels (cf. Eq. (2.5)). McConnell and his associates^[83] have observed exciton magnetic resonance at "zero magnetic field" in the polycrystalline complex $(\Phi_3\text{AsCH}_3)^+(\text{TCNQ})_2^-$ over the temperature range 75–140°K. The frequencies of the three transitions at 111°K were $\nu_z = 64.4$ MHz, $\nu_x = 163.8$ MHz, and $\nu_y = 225.4$ MHz. The absorption frequencies were found to be strongly temperature-dependent. Figure 4 shows the temperature dependences of the frequencies ν_y and ν_x . We note that exciton magnetic resonance at "zero magnetic field" can be observed only at low temperatures, since at high temperatures the motion of the excitons leads to fading of the signal, just as in NQR. The temperature coefficient of the frequency was $(1/\nu_0)(d\nu/dT) = -3 \times 10^{-4} \text{ deg}^{-1}$. The authors of^[83] proposed several mechanisms to explain the temperature-dependency of the frequencies. If we take into account the exchange interactions, then

$$\frac{1}{\nu} \frac{d\nu}{dT} \sim \frac{2I_{\text{eff}}}{\nu^2} \frac{dI_{\text{eff}}}{dT}, \quad (2.22)$$

where I_{eff} is the mean "effective" exchange interaction of two excitons of spin $S = 1$. Upon obtaining the

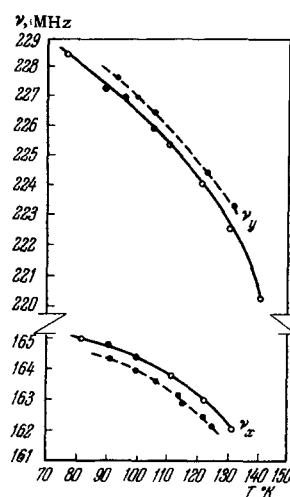


FIG. 4. Temperature-dependence of the triplet-exciton EPR frequencies at "zero field" for the complex $(\Phi_3\text{AsCH}_3)^+(\text{TCNQ})_2^-$.

values $I_{\text{eff}} \sim 1.5$ MHz and $dI_{\text{eff}}/dT \sim 2 \times 10^{-2}$ MHz/°K from the temperature-dependence of the line width, the authors concluded that the exchange contribution to the frequency shift must be smaller than 1.5×10^{-6} MHz/°K, i.e., much smaller than and opposite in sign to the experimental value. Thus, exchange interactions do not contribute to the observed temperature-dependence of the transition frequencies in the temperature range 80–100°K.

A small shift in the resonance frequency in a "contaminated" specimen with respect to that in a pure specimen can be ascribed to exchange interaction between the excitons and an admixture of free radicals of spin $S = 1/2$.

By treating a simple libration model in which two benzene ions (with parallel planes) librate at frequency ω_1 with the small libration angle θ , McConnell derived the following expression:

$$\frac{1}{D} \frac{dD}{dT} = -3 \frac{d\langle \theta^2 \rangle}{dT}, \quad (2.23)$$

where $\langle \theta^2 \rangle$ is the mean deviation of the z axis from its equilibrium position during the libration process. If $kT \gg \hbar\omega_1$, then $\langle \theta^2 \rangle$ is proportional to the temperature, i.e., $\langle \theta^2 \rangle = \lambda T$. Furthermore, we can estimate $\langle \theta^2 \rangle$ by comparing the energy of librational motion with the mean energy of a harmonic oscillator. In^[83], $\langle \theta^2 \rangle$ was estimated from x-ray structural data to follow, $\lambda \sim 2.7 \times 10^{-4}$, which gives an estimate $(1/D)(dD/dT) = -8 \times 10^{-4} \text{ deg}^{-1}$. Thus, good agreement with experiment was found. This shows a strong analogy with NQR, for which the temperature-dependence of the frequencies also arises from libration of the molecules within the crystal structure.

Undoubtedly, exciton magnetic resonance in organic semiconductors will have a great future. A remarkable fact is that one can use nuclear quadrupole resonance apparatus to study this new phenomenon.

3. Activation Energy of Singlet-triplet Transitions and Width of the Forbidden Band

Much attention has been paid recently to problems of formation of molecular charge-transfer complexes. Mulliken^[84] has developed a quantum-mechanical theory based on transfer of an electron from the donor (D) to the acceptor (A). According to Mulliken, the wave function of the ground state of the molecular complex is given in the form

$$\Psi = a\psi_0(D, A) + b\psi_1(D^+A^-), \quad (2.24)$$

where ψ_0 is the wave function of the complex when its components are bound only by van der Waals forces, and ψ_1 is the wave function of the ionic state, in which an electron has been transferred from the donor to the free levels of the acceptor molecule. In order that the Mulliken theory hold, the wave functions of the two states must overlap, i.e., $S = \int \psi_0\psi_1 d\tau \neq 0$. If the acceptor level lies low enough and the donor level high enough, a spontaneous charge transfer can occur.

A fundamental difficulty of the Mulliken theory is the smallness of the overlap integrals for Slater orbitals at distances of 3–3.5 Å, as are typical of molecular crystals ($S \sim 0.005$). In the Mulliken theory the ionic state is assumed to be endothermic, and one cannot understand how it contributes to the energy of the ground state, since the coefficient b is usually small.

The structures of certain complexes of iodine and bromine with aromatic compounds also contradict Mulliken's principle of maximum overlap. According to Mulliken's theory, the oscillator strength of the charge-transfer bands should decrease with increasing ionization potential of the donor. Actually, the opposite situation is observed. All these difficulties of the theory force us to seek other more suitable models.

Transfer excitons can be produced in a solid when an electron is transferred from filled levels of the donor to exciton levels. The bound electron and positive hole can occur either in the same or different unit cells of the crystal. Since the electron and hole have opposite spins and charges, the ground state of the ionic complex (D^+ , A^-) must be a singlet. On the other hand, an excited state of the complex can be a triplet and show paramagnetism.

Such a situation as applied to organic semiconductors was first discussed in^[85]. When the A^- and D^+ ions strongly interact in the complex, a state can be a singlet (antiparallel spins) or a triplet (parallel spins). In the case of strong donors and acceptors, the triplet paramagnetic state is densely occupied, and the complex shows paramagnetic properties (biradical compounds).

Usually the triplet state of the complex lies higher than the singlet state by the amount of the activation energy δ . In some cases the ionic state can lie considerably above the ground state (~ 10 eV). Such a compound will be diamagnetic.

Whereas normal paramagnetic substances obey Curie's law (the intensity of the EPR signal $U \sim 1/T$), for singlet-triplet transitions^[85]

$$U \sim \frac{1}{T \left[\exp\left(\frac{\delta}{kT}\right) + 3 \right]}. \quad (2.25)$$

Equation (2.25) makes it possible to determine the activation energy δ for singlet-triplet transitions in complexes.

In principle, the triplet state can lie even lower than the singlet for very strong donors and acceptors. Such a case cannot be treated at all within the framework of Mulliken's theory. Here the triplet state is densely occupied, and the complex will show considerable paramagnetism. Finally, we should note another possibility: two doublet states lying above the ground state by the amount of the activation energy δ . Powder experiments do not permit one to distinguish this latter case from singlet-triplet transitions. However, the latter alternatives are less probable, and hence study of polycrystals of organic semiconductors permits one to determine their activation energies.

The value of δ was determined in^[86-88] for a number of biologically important complexes. The complexes were prepared by reaction of the components in alcohol solution with mild heating. Chemically pure substances were used as acceptors (including riboflavin); all the sulfanilamide preparations, tryptophan, indole, cysteine, and penicillin were chemically pure. All the samples were studied as powders sealed in ampules. In all the studied complexes $g = 2.003$. The standard sample was the complex $p\text{-C}_6\text{Cl}_4\text{O}_2 \cdot p\text{-C}_6\text{H}_4(\text{NH}_2)_2$. This complex shows a weak anisotropy of the g factor at room temperature ($g_{\parallel} = 2.003$; $g_{\perp} = 2.006$). Comparison with a standard sample of diphenylpicrylhydrazyl (DPPH) shows that this complex contains 2.5×10^{17} uncompensated spins per cm^3 at 300°K .

Equation (2.25) describes satisfactorily the temperature-dependence of the signals in the complex. At 77°K , one can easily observe two EPR signals from the A^- and D^+ radicals. As the sample is heated, the EPR signal becomes a singlet at 250°K because of exchange effects, and then it splits because of the anisotropic g factor. However, if the complex is prepared by melting the powders together, the line becomes isotropic. Now the temperature dependence of the signal is described by the normal Curie law, indicating the formation of free radicals (Fig. 5).

The fine structure of the EPR spectrum at 77°K makes it possible to estimate the constant D in the chloranil- p -phenylenediamine complex. It turned out to be $1.1 \times 10^{-3} \text{ cm}^{-1}$. This fine structure involves the interaction of the spins of A^- and D^+ . Thus, "zero-field exciton resonance" in this specimen will be observed at the frequency $\nu \sim |D| = 33 \text{ MHz}$ at 77°C . The temperature "blurring" of the fine structure gives an estimate for the potential barrier $\Delta E = 37 \cdot T_{\text{cr}}$

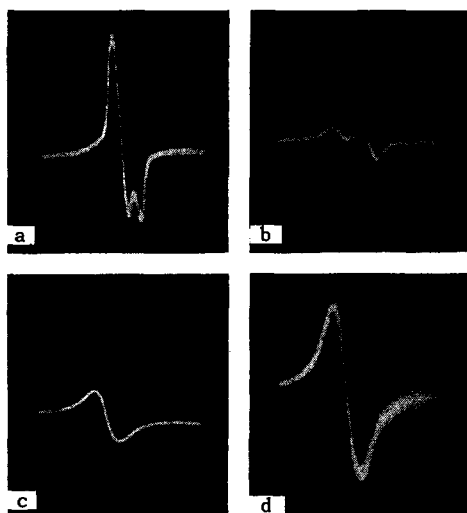


FIG. 5. EPR signals of the semiconductive complex chloranil-p-phenylenediamine (1:1). a—room temperature; $g_{\parallel} = 2.003$; $g_{\perp} = 2.006$; doublet structure is not observed; the complex was prepared by mixing the components. b—77°K, same complex as in a. c—room temperature; the complex was prepared by melting the components together. d—77°K, same complex as in c.

= 8.1 kcal/mole = 0.35 eV. From measurements of the electrical conductivity of this crystal, $\delta = 0.28$ eV.^[72]

Figure 6 shows the temperature dependence of the integral intensity of the EPR signal of the vitamin B₂-penicillin complex. We can reconcile theory and experiment if we assume that the paramagnetism of this complex is due to "triplet excitons" having an activation energy $\delta = 0.3$ eV. In order to explain the temperature-dependence of the EPR signal at low temperatures, we also have to take into account a free-radical impurity to the extent of 0.005%.

The free radicals can be formed in the process of synthesizing the complex. The intensity of the EPR

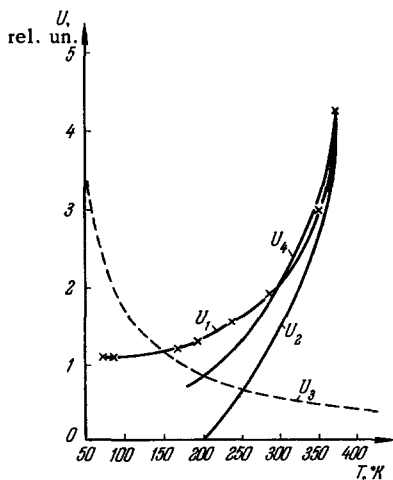


FIG. 6. Temperature dependence of the EPR signal intensity of the B₂-penicillin complex. U₁—experimental curve. U₂—calculated for triplet excitons having $\delta = 0.3$ eV. U₃—calculated for free radicals (C = 0.005%). U₄—calculated total curve.

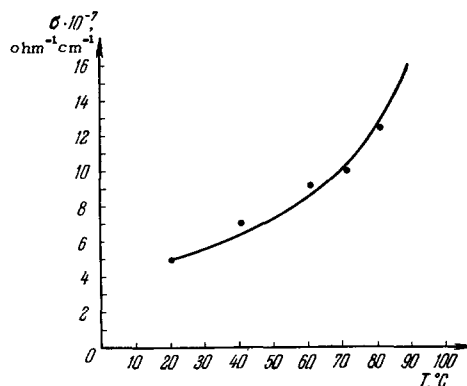


FIG. 7. Temperature-dependence of the conductivity of the B₂-penicillin complex.

signal of various paramagnetic impurities satisfies the Curie law. This is the reason for the considerable contribution of the paramagnetic impurities at low temperatures where the triplet state is poorly populated.

Analogous studies have been performed on the chloranil-adenine complex. As we know, adenine takes part in the triplet code of genetic information of DNA. For the chloranil-adenine complex, $\delta = 0.42$ eV. At the same time, the resistivity of these complexes was measured in cylindrical pressed tablets ($l = 1.5$ mm, $d = 3.4$ mm). The conductivity of the complexes proved to be considerably higher than that of the original components. The temperature-dependence of the conductivity of the B₂-penicillin complex is shown in Fig. 7. Experiment showed that the conductivity of the biologically important complexes varies according to the law

$$\sigma = \sigma_0 e^{-\frac{E_g}{2kT}}, \tag{2.26}$$

where E_g is the width of the energy gap between the valence band and the conduction band. For the B₂-penicillin complex, $E_g = 0.4$ eV, while for the chloranil-adenine complex $E_g = 0.41$ eV. Thus, the law of variation of the conductivity unequivocally proves the semiconductor properties of the complexes.

The lack of a Hall effect in the complexes can be ascribed to low mobility of the carriers ($\mu \leq 0.04$ cm² V⁻¹ sec⁻¹) or to a chain mechanism of conduction. In any case, it would be hard to expect an exponential temperature-dependence of the mobility of the carriers. An exponential temperature dependence of the carrier concentration is more probable. The closeness of the values of the activation energies for electrical conduction and for the spin concentration permits us to assume that the very same electrons act as current carriers and as paramagnetic centers. However, a free-radical impurity makes an additional contribution to the paramagnetism of the specimens at low temperatures. Hence, the intensity of the EPR signals remains almost constant while the

conductivity continues to decline. Irreversible changes occur in the biologically-important semiconductors when they are strongly heated. They involve formation of free radicals, and then the intensity of the EPR signals begins to follow the normal Curie law.

Precise measurements were made in [89] of the spin concentrations in semiconducting molecular complexes of perylene and pyrene with iodine. They also found the spin concentration to be temperature-dependent. The activation energies for the spin concentration and the electrical conductivity almost coincided. A discrepancy was noted only at low temperatures, but the authors did not correct for paramagnetic impurities, and hence their results at low temperatures are not satisfactory. The complexes of iodine with pyrene and perylene had very low resistivities at 300°K: 75 and 8 ohm-cm, respectively. [90] The activation energies E_g for these complexes proved to be 0.14 and 0.019 eV. Since no Hall effect was detected, they could only state an upper limit of the carrier mobility $\mu \leq 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

More detailed experiments can be performed by using single crystals. [69] The activation energy for singlet-triplet transitions was found to be 0.034 eV in the complex $[(\text{C}_2\text{H}_5)_3\text{NH}]^+ \cdot (\text{TCNQ})_2^-$; and 0.062 eV in the complex $(\Phi_3\text{PCH}_3)^+ \cdot (\text{TCNQ})_2^-$. We should bear in mind that such determinations are possible if the effect of paramagnetic impurities is taken into account. This is also indicated by the results of magnetic susceptibility measurements. [72] This often complicates the establishment of a sharp correlation between the electric and magnetic properties of complexes.

It was found in [91] that the conductivity and spin concentration are exponential functions of the temperature for the chloranil-p-phenylenediamine complex. However, there was no unequivocal correlation between these quantities, owing to the presence of oxygen.

Of course, the effect of saturation at low temperatures must also be taken into account.

If the concentration of paramagnetic centers is small, then line broadening can occur in a strong radio-frequency field owing to the saturation effect, especially at low temperatures. The saturation effect can be eliminated by decreasing the radio-frequency power in the resonator.

Dependence of the spin concentration on the method of preparing certain iodine complexes was studied in [92]. However, the temperature-dependence of the integral intensity of the EPR signals in the studied complexes followed the Curie law.

There are as yet no studies at all on the effect of donor and acceptor impurities on the conductivity and spin concentration in organic semiconductors.

The EPR method makes it possible to observe the kinetics of movement of carriers when an electric current is passed through an organic semiconductor.

Compounds have now been found among the organic complexes having very low activation energies for con-

duction. Apparently such organic semiconductors can be used as thermoresistors, since their resistance is often very stable and unvarying in time.

III. NUCLEAR QUADRUPOLE AND NUCLEAR MAGNETIC RESONANCE OF ORGANIC SEMICONDUCTORS

An explanation of the different mechanisms of conduction in organic semiconductors presupposes a knowledge of the nature of the chemical bonds in them, as well as their crystal structures. These data can be found by using the nuclear quadrupole resonance (NQR) method, and in part by using the nuclear magnetic resonance method.

As a rule, a suitable elemental composition of the crystal structure is necessary for observation of NQR. [93] The NQR method opens up a number of new possibilities for studying the distribution of the inhomogeneous electric field in organic semiconductors. If, for example, the complex contains several resonating nuclei, it becomes possible to measure the electric field gradient at different points. This permits one to draw conclusions on the nature of the intermolecular interaction.

1. Study of the Nature of Chemical Bonds in Charge-transfer Complexes

The interest in searching for new organic semiconductors has recently stimulated study of the nature of the chemical bonds in them. A series of studies [94-98] has reported on charge-transfer complexes based on SbCl_3 and SbBr_3 . These complexes are very convenient for applying the NQR method, since they contain a large number of different resonating nuclei. They show heightened conductivity.

The NQR method permits one to measure the quadrupole coupling constant eQq_{ZZ} and the asymmetry parameter η . The electronic structure of the molecules exerts a substantial influence on these constants.

The constants eQq_{ZZ} and η are usually measured directly from the NQR frequencies, provided that the nuclear spin is not $\frac{3}{2}$. For example, for $I = \frac{5}{2}$, two NQR frequencies are observed:

$$\left. \begin{aligned} \nu_1 &= \frac{3}{20} eQq_{zz} (1 + 1.09259\eta^2 - 0.63403\eta^4), \\ \nu_2 &= \frac{3}{10} eQq_{zz} (1 - 0.20370\eta^2 + 0.1621\eta^4). \end{aligned} \right\} \quad (3.1)$$

Since the NQR frequencies extend over a broad range (from 1 to 1000 MHz), to detect them has required the development of special wide-range radiospectrometers. These spectrometers use a set of radiofrequency generators. Various NQR apparatus are described in [18].

Now we shall discuss the results of [94-98].

The NQR signals of Sb^{121} , Sb^{123} , Cl^{35} , Br^{79} , and Br^{81} have been observed in the wide-range NQR radiospectrometer. If the experiment is performed at a low enough temperature, the effect of the dynamic proper-

ties of the crystal structure can then be neglected. The difference in the absorption frequencies then is determined by the difference in the electronic structure of the complexes. A change in the electric field gradient q_{zz} at the antimony nuclei upon complex formation can involve the following factors:

- 1) distortion of the shapes of the molecules in the complexes;
- 2) contribution to q_{zz} from the electrons in the vacant orbitals;
- 3) change in the electron distribution in the molecule (e.g., a change in the hybridization of the antimony orbitals).

We might expect that the effect will differ considerably in complexes with aromatic ethers and oxygen-containing bases, since different acceptor orbitals are used to accept the π electrons of the aromatic ring and the free electron pair of oxygen.

Symmetric filled electron shells do not contribute to the electric field gradient q_{zz} . If a p shell is not completely filled, then the electric field gradient is basically determined by the number of uncompensated p electrons, since the s electrons do not give rise to an inhomogeneous field at the nucleus, while the d electrons are rather far from the nucleus, and their contribution is small. The number of uncompensated p electrons is

$$U_p = \frac{1}{2}(N_x + N_y) - N_z, \quad (3.2)$$

where N_x , N_y , and N_z are the numbers of electrons in each of the three orbitals. In SbCl_3 , $N_z > \frac{1}{2}(N_x + N_y)$. Hence, when the p_z orbital of antimony is overlapped, $eQq_{zz} = U_p eQq_{at}$ must increase, whereas it must decline when p_x and p_y are overlapped. The p_z orbital is directed along the pyramid axis of SbCl_3 , and hence this orbital can happen to overlap with the orbitals of the unshared pair of oxygen atoms. On the other hand, the p_x and p_y orbitals of the antimony atom most probably undergo overlap when the π electrons of an aromatic ring are accepted. Such measurements permit one to estimate the degree of s-hybridization of the bonds within the framework of the Dailey-Townes theory (see, e.g., [99]):

$$U_p = -3\alpha_1(1+2\beta) \text{— for the antimony atom,}$$

$$U_p = (1-\alpha_2)(1-\beta) \text{— for the chlorine atom,} \quad (3.3)$$

where α_1 and α_2 are the degrees of s-hybridization of the bonds for the respective atoms, and β is the amount of ionic character of the bond.

A number of complexes have shown a strong variation in the asymmetry parameter η .

The asymmetry parameter is defined in terms of the components of the electric field gradient tensor q_{xx} , q_{yy} , and q_{zz} :

$$\eta = \left| \frac{q_{xx} - q_{yy}}{q_{zz}} \right|, \quad q_{xx} < q_{yy} < q_{zz}.$$

The condition $q_{xx} \neq q_{yy}$ must hold for the asymmetry parameter to differ from zero. When the molecules contain double bonds, asymmetry of a chemical bond can result from a "deficiency" of π electrons. If the fact that $\eta \neq 0$ involves a distortion of the shape of the pyramid of SbCl_3 and SbBr_3 in the complex, we should naturally expect splitting of the chlorine or bromine signals. This has been observed experimentally.

The effect of the shape of the structural pyramid on the asymmetry parameter has been treated in [100]. Let us consider a molecule of type AC_3 , where the resonating nucleus is A. Let all three A-C bonds be non-equivalent, and inclined at angles θ_1 , θ_2 , and θ_3 to the axis. We shall assume that the distribution of the electron cloud in each A-C bond is cylindrically symmetric. That is, the contribution to the electric field gradient at the A nucleus from one A-C bond will be

$$q_{z'z'}^{(0)} \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (3.4)$$

where the z' direction coincides with that of the A-C bond. The A nucleus precesses in the mean electric field gradient produced by the three non-equivalent A-C bonds. Let us transform the electric field gradient tensor to the system of axes x , y , and z , which are the principal axes of the electric field tensor at the A nucleus. Using the law of transformation of a second-order tensor, we get:

$$q_{zz} = \frac{3}{2} q_{z'z'}^{(0)} (\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 - 1),$$

$$q_{xx} = q_{z'z'}^{(0)} \left[\left(1 - \frac{3}{2} \cos^2 \theta_1 \right) + \cos^2 \psi_2 \left(1 - \frac{3}{2} \cos^2 \theta_2 \right) + \cos^2 \psi_3 \left(1 - \frac{3}{2} \cos^2 \theta_3 \right) - \frac{1}{2} (\sin^2 \psi_2 + \sin^2 \psi_3) \right],$$

$$q_{yy} = q_{z'z'}^{(0)} \left[\sin^2 \psi_2 \left(1 - \frac{3}{2} \cos^2 \theta_2 \right) + \sin^2 \psi_3 \left(1 - \frac{3}{2} \cos^2 \theta_3 \right) - \frac{1}{2} (1 + \cos^2 \psi_2 + \cos^2 \psi_3) \right], \quad (3.5)$$

where ψ_2 and ψ_3 are the azimuthal angles of two of the A-C bonds, one of the A-C bonds lying in the zx plane. Hence, if we assume that small changes in the angles of the SbCl_3 pyramid do not greatly change $q_{z'z'}^{(0)}$, we have

$$\eta = \frac{\sin^2 \theta_1 + \sin^2 \theta_2 \cos 2\psi_2 + \sin^2 \theta_3 \cos 2\psi_3}{\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 - 1}. \quad (3.6)$$

If the pyramid is regular, then $\theta_1 = \theta_2 = \theta_3$; $\psi_2 = 120^\circ$; $\psi_3 = 240^\circ$; and $\eta = 0$. Equation (3.6) has made it possible to estimate the most probable distortions of molecules in complexes.

Most 2:1 complexes have shown a multiplet structure of the NQR lines of Sb^{121} and Sb^{123} . For example, the complex $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{OH}$ has four non-equivalent antimony positions in the crystal structure. Two groups of lines are observed for the isotope Sb^{121} : low-frequency and high-frequency. The asymmetry parameters differ by a factor of more than two in these two

positions. Apparently the two SbCl_3 molecules in the complex are non-equivalent. Furthermore, an additional splitting involves the influence of the crystal structure. Twelve lines are observed from the Cl^{35} nuclei in this complex.

The observed frequency shifts amounted to as much as 12%. For example, the increase in eQq_{ZZ}^{121} in the complex $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{OCH}_3$ was +28.831 MHz with respect to SbCl_3 . On the other hand, $\Delta eQq_{ZZ}^{121} = -20.238$ MHz in the complex $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{C}_6\text{H}_5$.

The existence of several non-equivalent positions of the SbCl_3 and SbBr_3 molecules in the complexes makes it possible to explain the complicated character of the Raman spectrum in the region of the stretching vibrations of SbCl_3 .

The observation of EPR signals in certain complexes (e.g., in $2\text{SbCl}_3 \cdot \text{anthracene}$) makes it possible to relate the spin concentrations with the semiconduction.

NQR in other classes of intermolecular complexes has been treated in a number of studies.^[101-104]

Relatively large NQR frequency shifts have been found only in CHCl_3 complexes.^[103] Here also the multiplicity of the NQR spectrum changed upon complex formation, and the Cl^{35} frequencies were shifted by as much as 1 MHz. It was concluded from the NQR data that a chlorine atom directly participates in forming a chemical bond in complexes with benzene derivatives, various ethers, acetone, etc.

It has not yet been possible to establish an unambiguous correlation between the NQR frequency shift, the spin concentration, and the semiconduction of complexes.

For example, EPR signals are often observed in complexes of chloranil with certain aromatic donors. However, the NQR frequency shifts of Cl^{35} in these complexes are insignificant.

NQR permits one to obtain the following data on the electronic structure of organic semiconductors:

1. The very fact that NQR signals are observed indicates that the crystal structure of the organic semiconductor is sufficiently perfect. Partial decomposition of the sample or incorporation of impurities will broaden the absorption lines.

2. Measurement of eQq_{ZZ} and η at low temperatures permits one to draw conclusions on distortions of the shape of the molecules in the crystal structure, on the number of non-equivalent positions, and on the nature of the chemical bonding.

3. It has been possible in a number of cases to draw conclusions on strength of the donor-acceptor interaction in charge-transfer complexes, or on the mutual arrangement of the donors and acceptors, which is of importance in explaining the chain mechanism of conduction.

Additional information can be obtained by studying the temperature-dependence of the NQR frequencies and the relaxation times.

2. Temperature Dependence of Frequencies

The quadrupole coupling constant eQq_{ZZ} and the asymmetry parameter η are functions of the temperature. Detailed data on the temperature-dependence of NQR frequencies can be found in a catalog containing information on more than 750 compounds for which quadrupole resonance has been studied at different temperatures.^[105]

Ordinarily the temperature coefficients of the NQR frequencies in organic semiconductors are rather large.^[95,96] For example, the variation of the Sb^{121} frequency ($1/2 \leftrightarrow 3/2$ transition) is as much as -18 kHz/deg in the complex $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{C}_2\text{H}_5$. Such large temperature coefficients of the frequencies, together with the considerable intensity of the NQR signals (signal-to-noise ratio ~ 20 on the oscillograph screen), make it possible to use these compounds as working substances in secondary temperature standards.^[106]

In the complexes of SbCl_3 and SbBr_3 , the temperature coefficient for the chlorine and bromine nuclei is always 1.5-2 times smaller than for the antimony nuclei.

Since a large asymmetry of the electric field gradient is observed at the antimony nuclei, the variation of the NQR frequency involves both the temperature dependence of the electric field gradient q_{ZZ} and that of the asymmetry parameter. However, if we know the temperature-dependence of the quadrupole interaction constant eQq_{ZZ} , then it becomes possible to study the lattice-vibration spectrum.

Among all the form of lattice vibrations, the ones that most influence the NQR frequencies prove to be the librations of the molecules about their fixed centers of gravity. Since the libration frequencies are considerably greater than the NQR frequencies, the components of the electric field gradient tensor becomes averaged by the librations. If $\xi_i^0 \cos \omega_i t$ is the i -th normal coordinate of the lattice, then the NQR frequency can be written in the form^[93]

$$\nu = \nu_0 \left[1 - \frac{3}{4} \sum_i (\xi_i^0)^2 A_i \right], \quad (3.7)$$

where ν_0 is the NQR frequency in the absence of lattice vibrations; A_i is a coefficient having no simple description in the general case; $A_i = \alpha_i - \frac{2}{3} \delta_{ij}$; $\theta = \sum_i \alpha_i \xi_i$; $q_{ZZ} = q_0 (1 + \sum_i \beta_i \xi_i + \sum_{ij} \delta_{ij} \xi_i \xi_j)$; θ is the deviation angle of the axis of the electric field gradient from the equilibrium position; and q_0 is the electric field gradient in the absence of lattice vibrations.

Since the binding between the components of the complex is weak, the SbCl_3 and SbBr_3 molecules in the complex can perform independent librations about the fixed center of gravity. The moments of inertia of these molecules can be easily calculated from their known crystal structures. We note that distortions of

the shape of the SbCl_3 and SbBr_3 molecules in the complexes do not affect appreciably the principal moments of inertia. For the antimony nuclei, which lie at the vertex of the structural pyramids, only the librations about the X and Y axes passing through the center of inertia of the molecule have an effect on the temperature-dependence of the NQR frequencies. If we neglect the contribution of the zero-point vibrations, we can derive the relation

$$\frac{eQq_{zz} - eQq_{zz}^{(0)}}{eQq_{zz}^{(0)}} = -\frac{3h}{3\pi^2 I_t \nu_t} \frac{1}{\left(\frac{h\nu_t}{kT} - 1\right)} = -\frac{167,4 \cdot 10^{-40}}{I_t \nu_t} \frac{1}{\left(\frac{\nu_t}{e^{0,696T}} - 1\right)}, \quad (3.8)$$

where $eQq_{ZZ}^{(0)}$ are the quadrupole coupling constants at $T = 0^\circ \text{K}$, T is the absolute temperature, I_t is the average moment of inertia of the molecule about the X and Y axes, ν_t is the mean frequency of the librations of the molecule in cm^{-1} , and eQq_{ZZ} is the quadrupole coupling constant at the given temperature T . This relation permits one not only to determine ν_t from the known moments of inertia, but also to find the temperature-dependence of the libration frequencies. While for SbCl_3 at 170°K , $\nu_t = 67.8 \text{ cm}^{-1}$, at 290°K , $\nu_t = 57.8 \text{ cm}^{-1}$, and $I_t = 504 \times 10^{-40} \text{ g}\cdot\text{cm}^2$. For the organic semiconductor 2SbCl_3 anthracene at 170°K , $\nu_t = 61.6 \text{ cm}^{-1}$, and at 290°K , $\nu_t = 51.53 \text{ cm}^{-1}$. In all cases, complex formation lowers the libration frequencies.

A knowledge of the frequencies ν_t permits one to calculate the temperature-dependence of the NQR frequencies of Sb^{121} and of the triplet excitons at zero field. Thus the determination of the libration frequencies is of great theoretical importance.

One should make use of the temperature-dependence of the halogen frequencies in the SbCl_3 and SbBr_3 complexes to determine the frequency ν_z . In this case, the libration axes will lie at certain angles to the principal axes of the electric field gradient tensor. Hence we must introduce an additional parameter:^[107]

$$\langle \theta_i^2 \rangle = \alpha_i^2 \langle \varphi_i^2 \rangle, \quad (3.9)$$

where θ is the angular displacement of an Sb-X bond from its equilibrium position due to the librations about an axis perpendicular to the Sb-X bond; φ is the angular displacement of an Sb-X bond during the librations about the principal axes of the inertia tensor of the molecule; and α_i is the sine of the angle between the direction of Sb-X and a principal axis of libration.

Thus we obtain:

$$\frac{eQq_{zz} - eQq_{zz}^{(0)}}{eQq_{zz}^{(0)}} = -\frac{3h^2}{8\pi^2} \sum_i \frac{\alpha_i}{I_i \nu_i} \frac{1}{\left(\frac{h\nu_i}{kT} - 1\right)}. \quad (3.10)$$

As applied to SbCl_3 and SbBr_3 complexes, this form can be rewritten as

$$\frac{eQq_{zz} - eQq_{zz}^{(0)}}{eQq_{zz}^{(0)}} = -\frac{3h}{8\pi^2} \left[\frac{(\alpha_x^2 + \alpha_y^2)}{I_t \nu_t} \frac{1}{\left(\frac{h\nu_t}{kT} - 1\right)} + \frac{\alpha_z^2}{I_z \nu_z} \frac{1}{\left(\frac{h\nu_z}{kT} - 1\right)} \right]. \quad (3.11)$$

The latter relation permits one to determine the frequency ν_z , since ν_t is already known from the temperature-dependence of the NQR frequencies of Sb^{121} or Sb^{123} .

One can check the determined frequencies by using the relation

$$\nu_i = \frac{n}{2\pi} \sqrt{\frac{V_0}{2I_i}}, \quad (3.12)$$

where V_0 is the height of the potential barrier for librations of the molecule, and n is the order of the symmetry axis of the librations. Usually $\nu_z < \nu_t$.

For example, for SbCl_3 $\nu_z = 49.5 \text{ cm}^{-1}$ at 290°K , while for SbBr_3 $\nu_z = 27.8 \text{ cm}^{-1}$ at the same temperature.

Calculations show that in most molecular semiconductors the temperature-dependence of the NQR frequencies can be explained by taking into account only the librations about the three principal axes of the inertia tensor, without bringing in translational lattice vibrations or volume effects.^[108]

NQR also permits one to determine the temperature-dependence of the libration frequencies. Calculations show that the lattice-vibration frequencies are related to the temperature as follows^[109]:

$$\nu_i = \nu_i^0 (1 - g_i \Delta T), \quad (3.13)$$

where ν_i^0 is the libration frequency at the temperature T_0 ; and $\Delta T = T - T_0$. For the SbCl_3 and SbBr_3 complexes, $g_i \approx 0.0015$ over the temperature range 170 – 290°K .

The potentials V_0 decrease upon complex formation, and this decreases the libration frequencies.

Although low-frequency Raman spectra also permit one to determine all the vibration frequencies^[110,111] including the vibration frequencies of both components of the complex, as well as the translational vibration frequencies in the complex, however, it is often hard to assign these frequencies to definite forms of vibrations. For example, this might be because the spectra of the individual components overlap. Hence, data from Raman spectra cannot be used to explain the temperature-dependence of triplet-exciton frequencies at "zero field," whereas NQR directly enables one to get the required frequencies. The value of the NQR data further consists in the fact that this method gives the values of the effective libration frequencies, which appear in the corresponding formulas for the temperature-dependence of the "zero-field" EPR frequencies of the triplet excitons.

The asymmetry parameter η is also a function of the temperature^[112]:

$$\eta = \frac{eQq_{zz}^{(0)}}{eQq_{zz}} \left\{ \left[\eta_0 - \frac{\eta_0}{2} (\langle \theta_x^2 \rangle + \langle \theta_y^2 \rangle) - 2\eta_0 \langle \theta_z^2 \rangle \dots \right] \right\}, \quad (3.14)$$

where θ_x , θ_y , and θ_z are the angular deviations of the electric field gradient tensor from its equilibrium position during the librations of the molecule about the principal axes of the inertia tensor. In contrast to the

quadrupole interaction constant, whose temperature-dependence can often be explained by the variation in the amplitudes and frequencies of the librations alone, volume effects (i.e., variation in the interatomic distances with temperature) greatly affect the asymmetry parameter. For example, certain SbCl_3 complexes have shown a positive temperature coefficient of η , while the temperature-dependence of the NQR frequencies and eQq_{ZZ} is well explained by taking into account the Bayer^[113] mechanism alone. In the complex $2\text{SbCl}_3 \cdot p\text{-C}_6\text{H}_4(\text{CH}_3)_2$, $(1/\eta_0)(d\eta/dT) = +1.4 \times 10^{-4} \text{ deg}^{-1}$ at 290° K for Sb^{121} , while in the complex $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{C}_2\text{H}_5$, $(1/\eta_0)(d\eta/dT) = -13.6 \times 10^{-4} \text{ deg}^{-1}$ at the same temperature.

The temperature-dependence of the triplet-exciton EPR frequencies in molecular semiconductors recalls in form the temperature-dependence of the NQR frequencies. However, the mechanisms can sometimes differ somewhat. In the first case volume interactions also take part, while in the second case only the librations of the molecules do so, although the shape of the temperature-dependence curves and the order of magnitude of the temperature coefficients are the same.

One can easily take the influence of volume effects into account, since they result in a positive temperature coefficient.

3. Temperature Dependence of Relaxation Times

Study of quadrupole and magnetic relaxation in organic semiconductors makes it possible to gain a variety of information on the lattice vibrations and the concentration of triplet excitons. In principle, one can also establish here a correlation with the conductivity. Thus far very few studies have been concerned with this problem.

Bayer^[113] was the first to develop a theory of quadrupole relaxation for nuclear spin $\frac{3}{2}$. In this case, relaxation of the extent of occupation occurs between quadrupole energy levels. If the nuclear spin is half-integral and greater than $\frac{3}{2}$ (e.g., $\frac{5}{2}$, $\frac{7}{2}$, or $\frac{9}{2}$), then the number of quadrupole energy levels is greater than two (3, 4, or 5, respectively), and the relaxation process will be more complex in nature.

In addition to treating the concrete mechanism of relaxation in these cases, we must take into account the relation between the one-quantum and two-quantum relaxation mechanisms by solving the kinetic equations. A multilevel quadrupole system can be applied to construct a "zero-field" quadrupole maser. Thus, study of the relaxation process that occurs when a radio-frequency field acts simultaneously on several transitions is of great practical significance. A number of studies^[114-118] have been concerned with quadrupole relaxation in a system having several levels. A method of deriving the kinetic equations with account taken of one-quantum and two-quantum relaxation mechanisms is described in^[119]. In general

form, the kinetic equation for the degree of occupation N_m is written in the form

$$\frac{dN_m}{dt} = \sum_n (W_{nm}N_n - W_{mn}N_m), \quad (3.15)$$

where W_{nm} and W_{mn} are the probabilities of the direct and reverse transitions between the levels n and m . For pure quadrupole resonance, we must consider two transition probabilities:^[120,121]

$$W(m \pm 1, m) = \frac{(2m \pm 1)^2 (I \mp m) (I \pm m + 1)}{2I^2 (2I - 1)^2} W_1,$$

$$W(m \pm 2, m) = \frac{(I \mp m) (I \mp m - 1) (I \pm m + 1) (I \pm m + 2)}{2I^2 (2I - 1)^2} W_2, \quad (3.16)$$

where I is the nuclear spin, m is the magnetic quantum number, W_1 is the probability of the one-quantum relaxation mechanism, and W_2 is the probability of the two-quantum relaxation mechanism. For $I = \frac{7}{2}$, we obtain:^[117]

$$\begin{aligned} \dot{n}_3 + (6 + \gamma)n_3 - 16(2 + \gamma)n_2 - 30\gamma n_1 &= 4(47 - 5\gamma)n_0, \\ \dot{n}_2 - 14(3 - \gamma)n_3 + 4(16 + 11\gamma)n_2 - 10(1 + \gamma)n_1 \\ &= 8(-1 + 15\gamma)n_0, \\ \dot{n}_1 - 14\gamma n_3 - 16(2 - \gamma)n_2 + 10(2 + 11\gamma)n_1 \\ &= 4(-11 + 25\gamma)n_0, \end{aligned} \quad (3.17)$$

where

$$n_{\pm i} = N_{\pm i \mp 1/2} - N_{\pm i \pm 1/2}; \quad \gamma = \frac{W_2}{W_1}; \quad \frac{W_1 t}{147} = \tau; \quad n_0 = \frac{\Delta N}{4};$$

$N_i = N/4$, $\Delta = h\nu_Q/kT$; ν_Q is the NQR frequency for the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition; N is the total number of resonating nuclei; $n_3 = N_{5/2} - N_{7/2}$; $n_2 = N_{3/2} - N_{5/2}$; and $n_1 = N_{1/2} - N_{3/2}$.

The determinant of this system can be written in the form

$$\Delta = \begin{vmatrix} p + 14(6 + \gamma) & -16(2 + \gamma) & -30\gamma \\ -14(3 - \gamma) & p + 4(16 + 11\gamma) & -10(1 + \gamma) \\ -14\gamma & -16(2 - \gamma) & p + 10(2 + \gamma) \end{vmatrix} \quad (3.18)$$

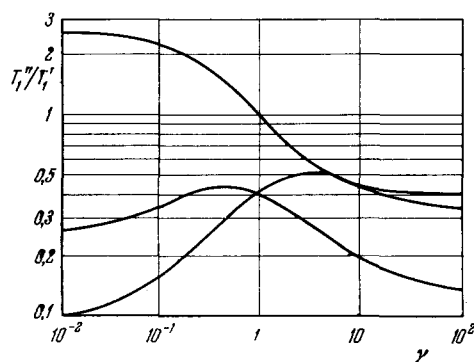
We can derive the relation between the relaxation constants (in this case, $T_{ii} = 147/p_i W_i$) by solving (3.18). The ratio of roots of this equation for various values of γ is shown in Fig. 8. We see from the diagram that the relaxation process is complex in nature, and is usually described in terms of three relaxation constants. Thus, experimental measurement of the ratio T_{ii}'/T_{ii} permits one to estimate $\gamma = W_2/W_1$.

The probabilities W_1 and W_2 are functions of the temperature:^[113]

$$W_1 = \frac{3}{4} (h\nu_Q)^2 \frac{\tau_a}{h\nu_I \nu_I} \left[\frac{2(\text{ch } x - 1)}{1 + 4\pi^2 \nu_I^2 (e^x - 1)^2 \tau_a^2} + \frac{3 - e^{-x}}{e^x - 1} \frac{1}{1 + 4\pi^2 \nu_I^2 \tau_a^2} \right];$$

$$W_2 = \frac{3}{32} (h\nu_Q)^2 \frac{\tau_a}{(\pi I_t \nu_I)^2} \frac{2(\text{ch } x - 1)}{1 + 4\pi^2 \nu_I^2 \tau_a^2 (e^x - 1)^2} + \frac{2 \text{ch } x - 1}{1 + 4\pi^2 \nu_I^2 \tau_a^2}, \quad (3.19)$$

where τ_a is the mean lifetime of librational quanta; $x = h\nu/kT$; and ν is the NQR frequency at the given

FIG. 8. Ratio of the quadrupole relaxation times for $I = 7/2$.

temperature. Since ν_t and I_t are determined from the temperature-dependence of the NQR frequencies, one can determine τ_a from relaxation measurements. It is also of great interest to study the temperature-dependence of the mean lifetimes of librational quanta.

The initial conditions (application of a saturating radiofrequency field to the different transitions) also influences the relaxation process.

Usually the relaxation times are measured with a spin echo apparatus. The transverse relaxation time T_2 is conveniently measured by Hahn's^[122] method, while it is better to use the stimulated echo method (Fig. 9) to measure T_1 . Stimulated quadrupole echo is observed after the third 90° pulse (the sequence 90° ; 180° ; 90° is used). The relaxation time T_1 is determined from the decline in the amplitude of the stimulated echo.

Let us consider relaxation in the complex $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{OCH}_3$. From the ratio of the relaxation constants for Sb^{123} at 77°K we obtain $\gamma \sim 2$. Thus, γ is found to be considerably smaller here than Bayer's theory implies.^[113]

We note that in certain organic semiconductors (e.g., $2\text{SbCl}_3 \cdot \text{C}_{10}\text{H}_8$) the relaxation process is described by a single exponential law ($T_1 = 18 \mu\text{sec}$ at 77°K for the $\frac{1}{2} \leftrightarrow \frac{3}{2}$ transition, and $T_2 = 250 \mu\text{sec}$; while for the $\frac{3}{2} \leftrightarrow \frac{5}{2}$ transition (Sb^{123}) $T_2 = 2200 \mu\text{sec}$, and $T_1 = 4.6 \mu\text{sec}$).

Usually the value of T_2 for the antimony nuclei for $\frac{1}{2} \leftrightarrow \frac{3}{2}$ transitions is greatly shortened by complex formation, owing to the increase in the local magnetic fields. On the other hand, T_2 for $\frac{3}{2} \leftrightarrow \frac{5}{2}$ transitions does not decrease as greatly. This indicates that the magnetic interactions have less influence on these transitions.

Paramagnetic "triplet excitons" can contribute considerably to the relaxation, especially at high temperatures, since their concentration increases with rising temperature. As a rule, organic semiconductors show a very strong temperature-dependence of the spin-lattice relaxation times. Quadrupole relaxation makes a considerable contribution to the quadrupole resonance.

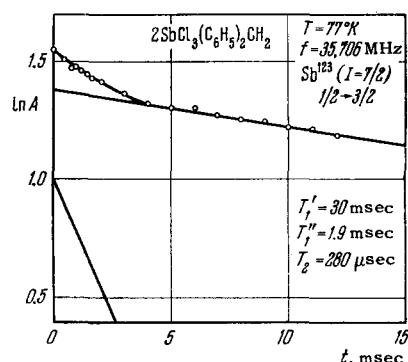


FIG. 9. Measurement of quadrupole relaxation times by the stimulated-echo method.

While in NQR one can determine the effect of triplet excitons on the relaxation from the temperature-dependence of T_1 , in nuclear magnetic resonance the value of T_1 itself often permits one to determine whether a specimen is paramagnetic.^[123]

The temperature-dependence of T_1 for protons in $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ was studied in^[124]. The spin-lattice relaxation time declines by almost two orders of magnitude over the range from 100° to 300°K . Here the times T_1 were unusually small for a dipole-dipole mechanism of nuclear spin-lattice relaxation. The author relates the decline of the times T_1 in NMR with the degree of occupation of the triplet state.

Analogous measurements in various organic semiconductors can not only give information on the concentration of triplet excitons, but also on their propagation in crystals by diffusion, and on triplet-triplet collisions generating current carriers in the form of electrons and holes.

Studies along this line are just beginning. It is of interest to establish various correlations between the physical characteristics of organic semiconductors.

IV. CONCLUSION

We have tried to show in this review that radio-spectroscopic methods make it possible to obtain much valuable information on current carriers, triplet excitons, activation energies, and widths of forbidden bands in organic semiconductors. Bearing in mind the great future of organic semiconductive materials, we may hope that interest in using EPR, NQR, and NMR methods to study them will increase.

All the methods applicable to study organic semiconductors are interrelated. Study of electrical conductivity and photoconductivity can be related to that of paramagnetic resonance of triplet excitons and paramagnetic centers. Results obtained by the NQR method are also essential in explaining the temperature-dependence of "zero-field" triplet-exciton EPR frequencies.

Data from radiospectroscopic studies lend clarity

to our understanding of the mechanism of conduction in organic semiconductors. It is currently thought that conduction in organic compounds of low molecular weight involves transition of an electron from the normal singlet level to excitation levels. Such an excited electron can subsequently move from molecule to molecule by the tunnel effect. Thus a vacancy ("hole") is produced in the ground state of the molecule, and this makes possible a relay mechanism of conduction. It is hard to overestimate the importance of radiospectroscopic methods in studying mobile excited states in organic semiconductors. Exciton magnetic resonance at "zero magnetic field" is of especial interest, and is a complete analogue of nuclear quadrupole resonance. Such studies are completely analogous even in their experimental methodology; they are performed in the same wide-range NQR radiospectrometers and spin-echo apparatus.

Undoubtedly, further studies of exciton magnetic resonance at "zero field" are very interesting and promising, especially those of spin-lattice relaxation processes of triplet excitons in spin-echo apparatus. The point is that "zero-field" experiments can be made on polycrystalline specimens, and this is especially valuable for studying biologically important organic semiconductors. On the other hand, it is practically impossible to grow single crystals of biologically-important charge-transfer complexes. Unfortunately, no empirical ways of estimating the order of magnitude of the expected absorption frequencies are possible, owing to the lack of enough experimental material.

Individual biologically-important macromolecules can also show solid-state properties. Energy can migrate via conduction bands in living systems. The discovery of semiconductive properties in certain proteins and the possibility of constructing rectifiers from biologically-important complexes are of great significance in biology, since capture or release of electrons can set a biological system into action.

Radiospectroscopy of biologically-important semiconductors is just beginning to develop. However, this field seems most important and fundamental to us, since it involves the problem of life.

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