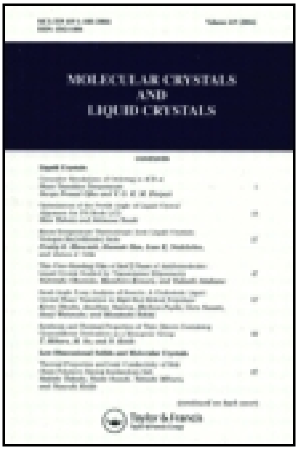

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Migration of Triplet Excitons in Molten Naphthalene

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Abstract—Upon illumination of pure molten aromatic compounds like naphthalene a photocurrent is observed which is due to the generation of the lowest excited triplet state by light. A model is proposed basing on the assumption that triplet excitons can migrate over large distances from the excitation region to the anode where they can produce charge carriers. Numerical calculations support the model.

1. Introduction

It has been well established by a number of papers that in aromatic crystals like anthracene triplet excitons can move over large distances because of their long life-time and the large exchange interaction between an excited and an unexited molecule.[1, 2, 3] For liquid aromatic systems no such data are available. Nevertheless radiolytic experiments about cis-trans-isomerization of butene or stilbene in benzene solution[1] have provided some evidence that triplet energy transfer is important in liquid systems too. The present paper will support this view by a discussion of photoconductivity measurements in liquid aromatics.

2. Experimental results

Extensive measurements were carried out with pure molten naphthalene. The material used was fifty times zone-refined. Informative measurements were performed with purified α- and β-methylnaphthalene, biphenyl, anthracene, and pyrene. Figure 1 shows the Pyrex-vacuum conductivity cell. The electrodes were made of gilded brass, their spacing varied from 0,05 to 2,5 cm. Leakage currents outside the cell were prevented by a silver-paste guard ring. The direction of the incident light was parallel to the electrodes. The size of the irradiated volume $q \times x$(q = area of the electrodes) between the electrodes could be varied by a moveable screen outside the cell. Direct illumination of the electrodes was excluded. A XBO 1600 W Xenon arc lamp served as a light source. The wavelength of the excitation light was varied by filters. The conductivity cell was mounted in an air thermostate with a silica window. The applied voltage could be varied up to 5000 volts.

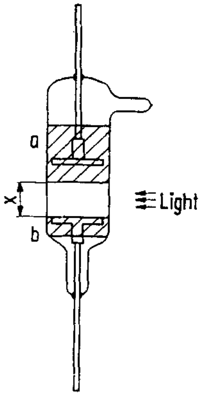

Figure 1. Vacuum-conductivity cell. a) moveable screen, b) grounded silver paste ring preventing direct illumination of the anode, too.

Irradiation of the hydrocarbons mentioned above in their liquid state with the full spectrum of the beam produces a photocurrent similar to that discribed by Kallmann, Krasnansky and Orenstein,[5] who have irradiated α-methylnaphthalene through a transparent electrode with UV. After a rise time varying between 0.02 and 0.3 sec it reaches an equilibrium value and decreases within the same order of time after switching off illumination. (Irreversible increase of the conductivity is observed only if impurities are persent enabling radical formation with illumination.) The rise time depends on material (the lower bounds hold for anthracene and pyrene) and on the size of the irradiated volume. The saturation value i_{ph} of the photocurrent generally increases linearily with photon-intensity[6] and slightly superlinearily with applied field (about $i_{ph} \sim F^{1,3}$).

The spectral response curves of the photocurrent in naphthalene and pyrene are shown in Figs. 2 and 3. The same type of curve with two main peaks is obtained with all compounds investigated. The long-wave-peak coincides with the wavelength of maximum absorption attributed to the

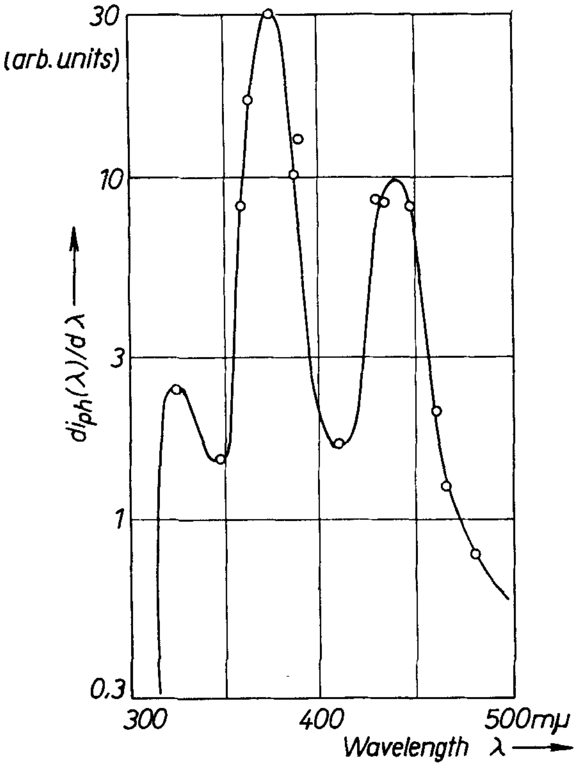

Figure 2. Spectral response curve of the photocurrent in molten naphthalene

forbidden singlet-triplet transition. The short-wave-peak lies at the singlet absorption edge. (In melts this edge is shifted to the red compared with the spectrum of the isolated molecule because of Franck-Condon broadening.) Light of shorter wavelengths which is strongly absorbed in a thin surface layer of the liquid near the glass wall does not produce any photocurrent.

The photocurrent depends on the size of the irradiated volume. Figure 4 gives a plot of i_{ph} versus x, where x indicates the distance of the screen from the anode. For small values of x i_{ph} rises about linearily with x and approaches a constant value for $x > 1$ cm. A logarithmic plot of the first derivative of $i_{ph}(x)$ versus x^2 shows a straight line (Fig. 5). An important fact is that illumination is ineffective in creating a photo-

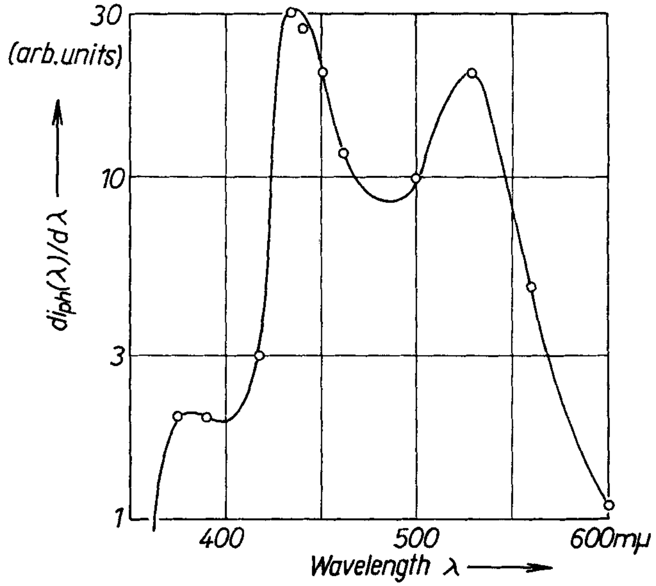

Figure 3. Spectral response curve of the photocurrent in molten pyrene (160°C).

current if transient currents with blocking silica electrodes are measured.

3. Discussion

Energy condition for charge-carrier production

Ionization by optical excitation within the bulk of the dielectric liquid requires fulfilment of the energy relation $E_x \geqq I - A - (P^+ + P^-)$. ($E_x$ = excitation energy, I = ionization energy of the isolated molecule, A = electron affinity, P = polarisation energy). For molten naphthalene one obtaines $E_x \geqq 5.5$ eV with $I = 8.14$ eV,[7] $A = 0.2$ eV[8] $P^+ = P^- = 1.25$ eV.† The energies of the first excited singlet and the lowest triplet state of naphthalene are 3,75 resp. 2.65 eV. That means that in a medium of low dielectric constant optical ionization is neither possible by a single

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† This value can be calculated applying the Born formula cited in [9] (Ref. 20). It is slightly smaller than for crystalline naphthalene ($P = 1{,}39$ eV)[7]) because of the drop of the dielectric constant from 2,87 to 2,54 at the melting point.[10]

photon process nor by bimolecular triplet annihilation. This agrees with recent results obtained by Kawada and Jarnagin[9] showing that triplet-triplet interactions os excited phenanthrene molecules leads to charge-carrier formation only if tetrahydrfuran ($\varepsilon = 7.5$) is used as solvent, but not with hexane ($\varepsilon = 1.9$), because P is proportional to $\frac{\varepsilon - 1}{\varepsilon}$.

Therefore reaction at the electrodes have to be considered. If an excited molecule gets ionized at the anode the electron is received by the metal anode, i.e. the energy condition for hole injection[11] holds: $E_x \geqq I - \Phi - P^+ = 2.2$ eV (work function of gold: 4,75 eV). It follows that a triplet exciton can produce a cation at the anode which can move to the cathode. In comparison anion production at the cathode would require the energy $E_x \geqq \Phi - A - P^- = 3.3$ eV.

The prediction that from energetic reasons charge carrier production should take place at the anode is confirmed by our experiments:

i) Only illumination of the anodic region between the electrodes produces a photocurrent. (See Fig. 4; Current saturation can be excluded because the relation $i_{ph} \sim$ Intensity holds for the whole curve $i_{ph}(x)$.)

ii) Conducting electrodes are necessary. (Triplet dissociation at a quartz surface should be possible, too, but with respect to the low conductivity of quartz, a surface charge-layer is build up which prevents further dissociation.)

iii) The field dependence of i_{ph} seems reasonable because the recombination probability of the cation at the anode is expected to be a function of the time during which the cation remains within a certain recombination sphere. This time decrease with increasing drift velocity towards the cathode.

iv) Charge carrier production should follow monomolecular kinetics in agreement with the observed linear dependence of i_{ph} on photon intensity (bimolecular annihilation neglected.)

The spectral response curves provide evidence that the charge carrier production occurs via triplet states. These are generated directly by $S_0 - T_1$ transition and by intersystem crossing from the first excited singlet state.

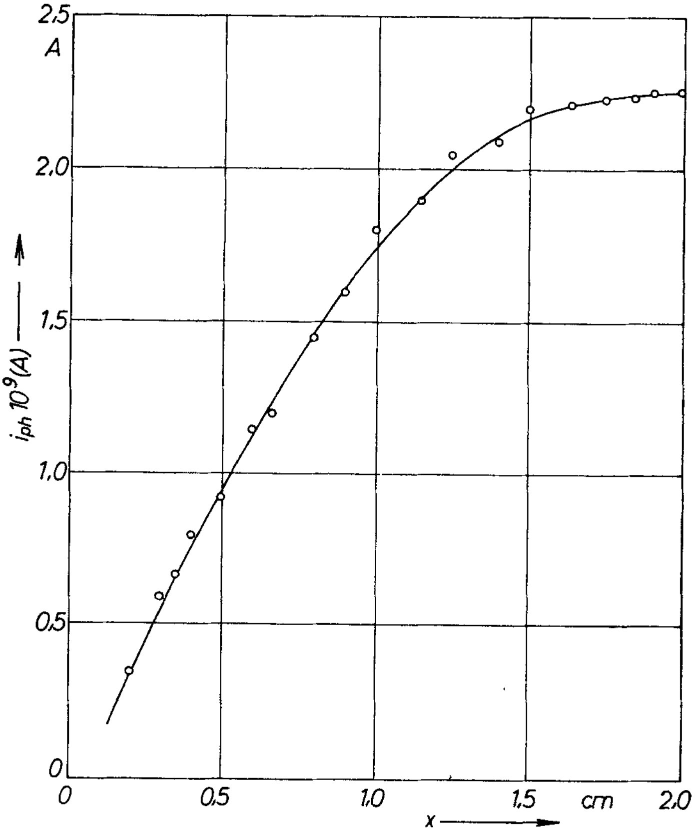

Figure 4. Variation of the photocurrent $i_{ph}(x)$ with the size of the irradiated volume. x indicates the distance of the limiting screen from the anode.

Model

The essential problem for the discussion of our experimental results is how to explain the way by which triplet energy is transported from the excited volume to the anode. We have tried to assume long range triplet exciton migration and will show that this assumption is consistent with all our experiments.

Numerical calculations

We have irradiated pure molten naphthalene in the $S_0 - T_1$ absorption region. The parameters have been: electrodes' spacing 0.5 cm, diameter of the electrodes 2 cm, applied voltage 3 kV, incident photon flux in the effective spectral region 5×10^{16} photons per second (determined by a bolometer). Assuming a molar extinction coefficient $\varepsilon_m \cong 3 \times 10^{-5}$ (calculated from the oscillator strength of the $S_0 - T_1$ transition in crystals, published by Hanson and Robinson[3]) there are generated $n_t \approx 10^{13}$ triplets per second. We assume that half of these will reach the anode. The observed current is $5 \times 10^{-9}\,A$, that are 3×10^{10} mobile charges per second. There is an indication that the $i_{ph}(F)$-curve approaches a saturation value of about $10^{-7}\,A$ at the field $F_s \approx 10^5$ V/cm, i.e. the saturation limit for charge carrier production is about $n_s \approx 5 \times 10^{11}\,\text{sec}^{-1}$. From these values we can estimate a maximum yield for charge carrier production: $\eta = \dfrac{n_s}{n_t/2} \approx 0.1$ (error: 1 order of magnitude). For $F < F_s$ part of these carriers will recombine with the electrode. This means that charge carrier production by triplet excitons hitting a metallic electrode is quite an effective process. Several conclusions concerning the contribution of spurious effects can be drawn from this calculation.

i) One might suppose that the diffusion length of the triplet excitons is in the range of 10–100 microns just as in anthracene crystals[1, 2] and that in our experiments only absorption of scattering light near the electrode is effective. Assuming $\eta = 1$ the intensity of the scattering light had to be greater by one order of magnitude than the total photon flux.†

ii) Radical reactions have to be taken into account, too. For example the rise time, of the photocurrent might correlate with the lifetime of radicals. But because the binding energy of a C–H bound is in the range of 4 eV radical formation by action of triplet excitons should be effective only if impurity molecules are involved. Furthermore only those radicals might contribute to the photocurrent which are generated within a distance from the electrodes which is in the order of the diffusion length for molecules (about 100 microns, assuming $D \approx 10^{-4}\ \text{cm}^2\,\text{sec}^{-1}$ and $\tau = 1$ sec). Therefore the explanation of a quantum yield $\eta = 0.1$ requires the assumption of a very effective radical formation (enhanced by

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† Furthermore scattering light should cause quite a different dependence of i_{ph} on the size of the irradiated volume. This is confirmed by an experiment: The anode was replacet by a ZnS screen and the intensity of fluorescence caused by scattering light was measured as a function of the irradiated volume.

triplet energy transfer) and a charge injection probability per radical which is greater than unity, i.e. each radical must inject several charge carriers during its lifetime. In order to gain some information about this mechanism we have tried to induce radical formation by addition of oxygen (it reacts with hydrocarbons upon illumination) and bromonaphthalene (the C-Br binding energy is approximately equal to the energy of the T_1 state of naphthalene). In both cases a photocurrent was obtained but its time dependence was quite a different one. The current was rising during illumination (about 10 sec) and reached its dark value after switching off illumination not before several minutes (in the case of O_2) and not at all in the case of bromonaphthalene as an additive. A similar result is obtained with illumination of pure p-dichlorobenzene in the triplet absorption region.†

This can be explained assuming that certain radicals (probably containing electronegative atoms) can form very stable lavers at the electrodes which can catalyse charge injection. Thus it is stated that certain radicals are able to inject charges with a formal probability greater than unity. But a calculation shows that in very pure samples the possible radical-concentrations are too small to account for the observed "reversible" photocurrent.

Furthermore if radicals were dominant in charge carrier production the current ought to increase with stimulated convection within the liquid because the number of radicals reaching the electrodes should increase. This was not observed indicating that energy transfer occurred faster than molecular transport by convection.

Calculation of the curve $i_{ph}(x)$

The dependence of the photocurrent i_{ph} on the screen-distance x from the anode (see Fig. 4) may easily be explained assuming the triplet diffusion model: In a volume layer $q\,dx$ in the distance x from the anode there may be generated n_0 excitons per second. After the time t there will be still

$$n(t) = n_0 \exp(-\alpha t)$$

alive. (Bimolecular annihilation being neglected.) Within the time t the

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† If we use samples which were purified less carefully we observe superposition of both photocurrents, the formerly described one and the radical-induced one: the resulting current does not approach a constant value but is slightly increasing during illuminaton.

excitons will diffuse over the mean distance $x = \sqrt{2Dt}$. Therefore the number of excitons which are able to migrate over the distance x is given by

$$n(x) = n_0 \exp\left(-\frac{\alpha}{2D}x^2\right).$$

If a concentration gradient exists in both directions perpendicular to the generation layer, $1/2n(x)$ excitons will hit the anode. Therefore illumination of the volume αx will yield the photocurrent

$$i_{ph}(x) \sim \int_0^x n_0 \exp\left(-\frac{\alpha}{2D}x^2\right)dx \tag{1}$$

respectively

$$\ln\frac{\partial i}{\partial x} = -\frac{\alpha}{2D}x^2 + \text{const}. \tag{2}$$

This is confirmed by experiments. From the slope of the curve in Fig. 5 the diffusion length of triplet excitons in liquid naphthalene can be obtained: $L = \sqrt{\frac{2D}{\alpha}} = 1.1 \pm 0.1$ cm. Table 1 summarizes the values for the diffusion lengths of triplet excitons for several hydrocarbons together with the maximum rise time of the corresponding photocurrent. The diffusion coefficient D is calculated by $D = \frac{L^2}{2\tau}$ assuming that the current rise time τ is identical with the lifetime of the triplets.† This might not be exactly true because the current rise time could be affected by space charge phenomena.

TABLE 1

	diffusion length L (cm)	rise time (sec)	diffusion coeff. D (cm^2 sec^{-1})
Naphthalene	1.1	0.3	2
β-methylnaphthalene	0.25	0.3	0.1
α-methylnaphthalene	0.1	0.3	0.02
pyrene	0.13	0.04	0.2
diphenyl	0.4	0.3	0.3

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† According to Kallmann[5] it must be presumed that the transittime of the charge-carriers between the electrodes is shorter than the diffusion time of the excited states. This condition was fulfilled in our experiments assuming that the mobility of the cations is in the order of 10^{-3} cm^{2}V^{-1} sec^{-1}.

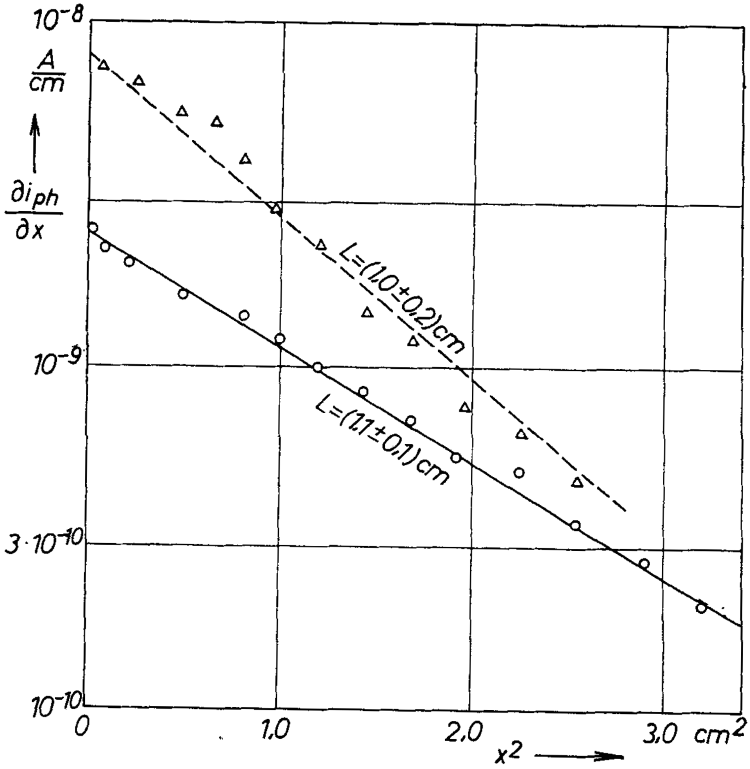

Figure 5. Dependence of lg $\frac{\partial i}{\partial x}$ on x^2. The solid curve is obtained by graphical differentiation of the plot $i(x)$, the dashed curve has been achieved by illumination through a slit in the distance from the anode. (From experimental reasons only the slopes of both curves can be compared).

Problems

One serious problem for the discussion of the present measurements is the lifetime of the triplet states. We must assume that it is in the same order as in crystals.† (For anthracene crystals observation of the delayed fluorescence yields[16] 10–20 msec.) According to Hilpern, Porter and Stief[17] desactivation of triplet states in liquid solution is mainly due to quenching by oxygen not fully removed by the outgassing procedure.

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† For a direct measurement of the triplet lifetime in pure liquid naphthalene by flash spectroscopy the triplet-concentration is to low: Because of energy transfer bimolecular annihilation is expected to be very effective so that the stationary concentration will be lower than 10^{12} cm^{-3}.

It may be expected that in molten aromatic hydrocarbons a lower oxygen content can be achieved than in aliphatic hydrocarbons at room-temperature because oxygen reacts with aromatic molecules upon illumination at elevated temperatures so that kind of a self-cleaning process can occur at the beginning of the measurements. This means that oxygen quenching might be reduced in melts. Information concerning the contribution of radiationsless transitions to monomolecular triplet decay and their temperature dependence is not yet available.

The second problem is how to explain the fact that the diffusion coefficient for triplet excitons in liquids is higher than in crystals. From the Davydov splitting of 40 cm^{-1} of the lowest triplet state in naphthalene crystals measured by Hanson and Robinson[3] a diffusion coefficient D 10^{-2} cm^2 sec^{-1} can be estimated with trapping effects neglected (Calculated by $D = \frac{1}{2} a^2 Z$, with $a = 5$ Å, hopping frequency $Z = 10^{13}$ sec^{-1}). In order to explain a higher D-value it is necessary to assume the existence of microcrystalline regions in the melt within which the arrangement of the molecules is more favourable for triplet transfer than in crystals. There are hints that such domains really exist: From X-ray scattering it has been concluded that liquid naphthalene contains domains of about 100 molecules[18] and that probably in liquid benzene there are regions with plane-on-plane arrangement of the molecules[19,20] Electron diffraction studies by Roth[21] have shown that in 1-bromonaphthalene the molecules are oriented mainly with parallel molecular planes (plane distance 3,74 Å) and finally Burton *et al.*[22] have presented evidence for domain formation in liquid benzene-cyclohexane systems by energy-transfer-experiments, too. It can be expected that steric hindrance of the molecules is reducing the probability for domain formation with enhanced plane-on-plane arrangement of the molecules. From thispoi nt of view the fact that the diffusion coefficients of the series naphthalene, β-and α-methyl-naphthalene decreases according to $D_N : D_{\beta MN} : D_{\alpha MN} = 1 : 0.05 : 0.01$ provides further argument for the model proposed.

Acknowledgement

I am geatly indebted to Professor N. Riehl for many helpful and stimulating discussions.

Note added in proof. (September 1967): A series of experiments has been performed since this paper was written. Thereby it has been shown that in lignit naphthalene, pyrene, and anthracene bimolecular reaction of two triplet states can produce charge carriers, too. In the case of naphthalene this effect probably has influenced the dependence of the photocurrent on the size of the irradiated volume between the electrodes thus giving a too large value for the diffusion length. From independent measurements the diffusion coefficient $D = (6 \pm 2) \cdot 10^{-2}$ cm^2 sec^{-1} was obtained yielding $L = 0.2 \pm 0.05$ cm (assuming the life time $\tau \sim 250$ msec). These more recent results are published in Electrochimica Acta (in press) and J. Chem. Phys. (in press).

Furthermore in these papers more accurate spectral response curves for the photocurrent are reported revealing the similarity with the $S_0 - T_1$ absorption curve more obviously.

REFERENCES

1. Williams, D. F., Adolph, J. and Schneider, W. G., *J. Chem. Phys.* **45**, 575 (1966).
2. Ern, V., Avakian, P., Merrifield, R. E., to be published in *Phys. Rev.*
3. Hanson, D. M. and Robinson, G. W., *J. Chem. Phys.* **43**, 4174 (1965).
4. Cundall, R. B., and Griffith, P. A., *Disc. Farad. Soc.* **36**, 111 (1963).
5. Kallmann, H., Krasnansky, V. J. and Orenstein, A., *J. Chem. Phys.* **40**, 3740 (1964), **43**, 1631 (1965).
6. Baessler, H. and Dries, B., *Z. Naturforschg.* **21a**, 441 (1966).
7. Lyons, L. E., in *Physics and Chemisrty of Organic Solid State* Vol. I, Fox, Labes and Weissberger (ed.), John Wiley 1963.
8. Choi, S. I., Jortner, J., Rice, S. A. and Silkey, R., *J. Chem. Phys.* **41**, 3294 (1964).
9. Kawada, A. and Jarnagin, R. C., *J. Chem. Phys.* **44**, 1919 (1966).
10. Landolt-Börnstein, *Zahlenwerte und Funktionen*, Vol II, 6, Berlin 1959.
11. Pope, M. and Kallmann, H., in *Symp. on Electrical Conductivity in Organic Solids*' ed. by Kallmann, H. and Silver, M., Interscience-Publ. N.Y. 1961.
12. Hirota, N. and Hutchison, C. A., jr., *J. Chem. Phys.* **42**, 2869 (1965).
13. Kinoshita, M. and McGlynn, S. P., this Symposium.
14. Kearugs, D. R., *J. Chem. Phys.* **36**, 1608 (1962).
15. Baessler, H., *Z. Naturforschg.* **21a**, 454 (1966).
16. Helfrich, W., *Phys. Rev. Letters*, **16**, 401 (1966).
17. Hilpern, J. W., Porter, G., Stief, L. J., *Proc. Roy. Soc.* (*London*) A **277**, 437 (1964).
18. Cennamo, F., *Nuovo Cimento* **12**, 165 (1954).
19. Kruh, R. F., *Chem. Rev.* **62**, 319 (1962).
20. Bell, P. H. and Davey, W. P., *J. Chem. Phys.* **9**, 441 (1941).
21. Roth, G., *Z. Naturforschg.* **18a**, 516 (1963).
22. Nosworthy, J. M., Magee, J. L. and Burton, M., *J. Chem. Phys.* **34**, 83 (1961).