# Electric field assisted dissociation of charge transfer states as a mechanism of photocarrier production

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# Electric field assisted dissociation of charge transfer states as a mechanism of photocarrier production

Charles L. Braun

*Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755*

The lowest charge-transfer excited state ($CT_1$) of electron donor–acceptor crystals or polymers is demonstrated to be a plausible precursor of free charge carriers when such materials are photoexcited. Rate constants for the dissociation of charge–transfer states are formulated for two approximate descriptions of $CT_1$: classical ion pair and Wannier exciton. The electric field dependence of the dissociation rate constant is postulated to be given by Onsager's 1934 theory (O-34) of ion pair dissociation. This formulation of $CT_1$ dissociation obviates the need to invoke electron–hole "thermalization" lengths of 2 to 3 nm in order to explain free charge carrier formation in donor–acceptor materials.

## I. INTRODUCTION

Many features of the photogeneration of free charge carriers in low-mobility insulators are explained by the 1938 geminate recombination theory[1] of Onsager.[2–4] When, however, that theory is applied to photogeneration in solids containing electron donors $D$ and acceptors $A$, a puzzling result is obtained. Even when optical excitation produces the lowest-lying charge-transfer state ($CT_1$) of such systems, the observed electric field dependence of the free carrier yield implies a large electron-transfer distance (2–3 nm).[5–8] This result, which follows from use of conventional Onsager theory, is inconsistent with spectroscopic evidence that a $CT_1$ exciton involves chiefly nearest-neighbor (0.5 nm) electron transfer.[9–11]

The earliest result of this kind is found in the work of Melz[5] who studied photogeneration of charge carriers in polyvinyl carbazole (PVCz) doped with the strong electron acceptor, 2,4,7-trinitro-9-fluorenone (TNF). By fitting Onsager's theoretical predictions to the electric field dependence of his photogeneration yields, Melz found that the "thermalization lengths" of the geminate charge pairs were 2.5–3.5 nm, depending on sample composition. He did not address the puzzling question of how a charge pair could evolve from an initial nearest-neighbor separation to the much larger thermalized-pair separation. Such an evolution would appear[12] to require an energy expenditure of perhaps 0.5 eV from a source that is not easily identified.

Since Melz's work, a number of other polymeric donor–acceptor systems have been explored. Mikawa and his co-workers (YEMM)[7] have recently addressed the puzzle by postulating that in PVCz doped with various acceptors the initial excitation produces a nonrelaxed exciplex (CT state). The initial state is thought to be the second excited singlet state ($CT_2$). The excess electronic energy of $CT_2$ is then viewed as allowing the formation of a large radius ($\sim 2.5$ nm) species which can either dissociate or collapse into $CT_1$. In this model $CT_1$ plays no role in the formation of free charge carriers. In PVCz doped with TNF, the spectroscopic confusion required by the proposal of YEMM does seem to be present.[13] The $CT_2$ absorption band lies 0.66 eV above the much less intense $CT_1$ band[13]; excitation at most wavelengths would produce both $CT_1$ and $CT_2$ as initial states.

It seems unlikely that the proposal[7] of YEMM has great generality because in many systems, the $CT_1$ and $CT_2$ bands do not overlap.[11] For example, in the 1:1 single crystal comprised of anthracene as donor and pyromelliticdianhydride (PMDA) as acceptor, $CT_2$ lies 0.8 eV above $CT_1$ and each band is spectroscopically distinct.[11] Yet Karl and Ziegler have shown that excitation into the $CT_1$ band produces free carriers, independent of excitation energy.[14]

If, in contrast to the proposal of YEMM, the relaxed, often fluorescent, $CT_1$ state is a significant precursor of free charge pairs, then the conventional interpretation of the results using Onsager's theory of 1938 must be wrong. That theory is the result of solving a diffusion equation for the relative motion of two opposite charges in the net potential provided by their Coulombic attraction and any applied field. Given the initial separation and orientation of a geminate pair, the theory predicts the probability that the pair will separate to infinity. An important boundary condition on the solution is that if the pair separation reaches zero, the pair irrevocably disappears (geminate recombination). We believe that this boundary condition is inappropriate to free charge production from $CT_1$ because $CT_1$ is a metastable state with a lifetime that is typically $10^{-8}$ s. The same point has recently been made in a paper by Samoc and Williams in their discussion[15] of the photo conductivity of anthracene/tetracyanobenzene charge-transfer crystals.

In the present work, the possible role of $CT_1$ as a precursor of free charge carriers is examined. Rate constants for the dissociation of such states are formulated for two approximate descriptions of $CT_1$—classical ion pair and Wannier exciton. For typical organic solids, the predicted rate constants differ only by an order of magnitude. Moreover, the rate constants are large enough to make $CT_1$ a plausible precursor of free charge carriers. The electric field dependence of the dissociation rate constant is postulated to be given by Onsager's 1934 theory of ion pair dissociation. $CT_1$ dissociation as formulated herein appears to provide a consistent description of charge carrier generation in donor–acceptor

$$CT_1 \underset{k_r}{\overset{k_d(E)}{\rightleftharpoons}} D^+ + A^- \text{ (free carriers)}$$
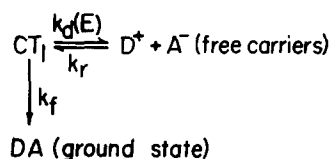
$$\downarrow k_f$$

DA (ground state)

FIG. 1. Kinetics of charge transfer state dissociation.

solids. The paper by Goliber and Pearlstein which follows illustrates that this approach allows a completely plausible interpretation of their data.

## II. RESULTS

### A. The model

We consider the case of free carrier generation from the lowest-lying singlet (or triplet) charge transfer state ($CT_1$), which may be formed by direct optical excitation or indirectly when a neutral donor (acceptor) excited state encounters an acceptor (donor). The possible fates of $CT_1$ are summarized in Fig. 1.

In Fig. 1, $CT_1$ disappears either by dissociation into free carriers with an electric-field dependent rate constant $k_d(E)$ or by decay to the ground state with rate constant $k_f$. One may imagine that during the lifetime

$$\tau(E) = [k_f + k_d(E)]^{-1}$$

of $CT_1$, many partial dissociations take place. The subsequent recombinations regenerate $CT_1$ which might then later dissociate completely. This is in sharp contrast to conventional Onsager theory,[1-4] in which a recombining pair disappears from the system.

In the scheme of Fig. 1, the probability $P(E)$ that $CT_1$ dissociates to free carriers is given by

$$P(E) = k_d(E)/[k_f + k_d(E)] = k_d(E)\tau(E). \quad (1)$$

For simplicity, we take $k_f$ to be field independent. That assumption can be tested at least in the case of fluorescent $CT_1$ states by observing the electric field dependence of the emission lifetime under conditions of high donor and acceptor dilution (to prevent free carrier generation).

The kinetics of Fig. 1 will be important to free carrier generation provided that $k_f$ and $k_d$ have magnitudes which allow zero-field carrier generation quantum yields in the range $10^{-5}$–$10^{-3}$ as observed experimentally. At least for singlet charge–transfer states, the expected value of $\tau(0)$ is $10^{-8}$ s. Thus in order that $P(0)$ be greater than $10^{-5}$, $k_d(0)$ must be of order $10^3$ s$^{-1}$. We will demonstrate that such values are plausible.

### B. Dissociation rate constants

No accurate theory of the dissociation rate constant $k_d$ is available, but useful approximate results exist. Lipnik has shown[16] that the equilibrium constant $K(0)$ for the dissociation of a Wannier exciton in zero applied field is given by

$$K(0) = \left(\frac{\mu kT}{3\pi\hbar^2}\right)^{3/2} e^{-\Delta E/kT}, \quad (2)$$

where $\mu$ is the reduced mass of the exciton and $\Delta E$ is the energy difference between the exciton and the conduction band. In the case of dilute acceptor (donor) surrounded by

donor (acceptor), the Wannier exciton may be an acceptable approximation to the CT exciton.

Morris and Silver[17] argue that the appropriate preexponential quantity in Eq. (2) is simply the density of states in the conduction band which, following Bube,[18] is

$$2(2\pi m_e kT/h^2)^{3/2}.$$

For equal hole and electron effective masses $m_e$, this density of states is essentially equal (20% larger) to that of Eq. (2) and either result will serve.

By detailed balance, $K(0)$ is equal to the ratio of $k_d(0)$ to $k_r$, where $k_r$ is the bimolecular rate constant for hole–electron recombination. In low-mobility solids, $k_r$ is found to have the diffusion-controlled value calculated by Langevin[19]

$$k_r = \frac{\langle u \rangle e}{\langle \epsilon \rangle \epsilon_0}, \quad (3)$$

where $\langle u \rangle$ is the spatially averaged sum of hole and electron mobilities, $e$ the elementary charge, $\langle \epsilon \rangle$ the spatially averaged dielectric constant, and $\epsilon_0$ the permittivity of vacuum. In media of high dielectric constant ($\epsilon > 10$), it might be necessary to use the more complete result for $k_r$ derived by Debye,[20] but we will not be concerned here with such materials.

Thus the dissociation constant at zero applied field is given approximately by

$$k_d(0) = k_r K(0) = \frac{\langle u \rangle e}{\langle \epsilon \rangle \epsilon_0} \left(\frac{\mu kT}{3\pi\hbar^2}\right)^{3/2} e^{-\Delta E/kT}$$
$$= Ae^{-\Delta E/kT}, \quad (4)$$

where the preexponential factor is defined to be $A$. At least in anthracene crystal, hole and electron effective masses are thought to be roughly ten times the free electron mass.[21] The measured value[22] of $k_r$ is $2 \times 10^{-12}$ m$^3$ s$^{-1}$ and thus at 300 K the preexponential (frequency factor) of Eq. (4) may be estimated to be $4.3 \times 10^{14}$ s$^{-1}$. Morris and Silver[17] estimated the frequency factor for the dissociation of $CT_1$ in anthracene crystals to be $5 \times 10^{15}$ s$^{-1}$.

An independent approach to the question of the appropriate form for $K(0)$ is that taken by Fuoss[23] in estimating the equilibrium constant for dissociation of an ion pair

$$K'(0) = \frac{3}{4\pi a^3} e^{-\Delta E/kT}, \quad (5)$$

where $a$ is the ion pair separation and $\Delta E$ the ion pair binding energy [for Coulombic binding,

$$\Delta E \equiv \Delta E_c = e^2/(4\pi \langle \epsilon \rangle \epsilon_0 a)].$$

Taking $a$ equal to $5 \times 10^{-10}$ m and using the measured value of $k_r$ for anthracene[20] yields a value of $4 \times 10^{15}$ s$^{-1}$ for the frequency factor of Eq. (4). Thus, from either of two approaches, $A$ factors of order $10^{14}$–$10^{15}$ s$^{-1}$ appear reasonable.

As discussed above, $k_d(0)$ must be of order $10^3$ s$^{-1}$ or greater in order that $CT_1$ be an important precursor of charge carriers at 300 K. Taking $A = 10^{15}$ s$^{-1}$, $k_d(0) \gtrsim 10^3$ s$^{-1}$ provided that $\Delta E \lesssim 0.71$ eV. Bounds and Siebrand[12] have recently estimated $CT_1$ binding energies of that order. Thus $CT_1$ appears to be a plausible precursor of free carriers.

It should be noted that the expression $k_d(0) = k_r K'(0)$ has been found to be in virtually quantitative agreement with

experiment.[24] The experimental rate constant for the zero-field dissociation of ion pairs consisting of a solvated pyrene cation and solvated $p$-dicyanobenzene anion in dichloromethane ($\epsilon = 8.2$) as solvent is $1.3 \times 10^7$ s$^{-1}$. This can be matched with the reasonable value of $a = 0.7$ nm and

$$\Delta E_c = e^2/(4\pi\epsilon\epsilon_0 a)$$

along with a Stokes Law value of the sum of ion mobilities.[24] Moreover, the barrier to ion pair dissociation has been shown to be inversely proportional to solvent dielectric constant.[25]

## C. Electric field dependence

The dissociation constant $k_d$ is expected to be strongly dependent on applied field. In 1934 Onsager developed an equation for the relative effect of an applied electric field on the dissociation of a weak electrolyte.[26] In fact, his 1938 paper,[1] which has been incorporated in the conventional Onsager theory of geminate pair recombination and escape,[2,27] is an offshoot of the earlier work. It appears that the 1934 paper offers a reasonable approximation to the field dependence to be expected for $k_d$ and $K$. Onsager's 1934 paper has seen relatively little modern use. Geacintov and Pope used the theory in an unsuccessful attempt to fit the field dependence of charge carrier production in anthracene[28] while Pai used the theory to interpret some dark conductivity data.[29] Onsager's 1934 paper (O–34) is a solution to a steady-state diffusion equation which describes the dissociation and recombination kinetics of ion pairs in an applied electric field.[26] The ions are infinitely long lived. The theory gives good fits to experimental data on increases in the conductance of weak electrolyte solutions in strong electric fields (Wien effect).[26] The O-34 result for the *relative* increase with field of the dissociation rate constant and thus of the dissociation equilibrium constant is

$$K(E)/K(0) = J_1[2\sqrt{2}(-b)^{1/2}]/\sqrt{2}(-b)^{1/2}$$
$$= 1 + b + b^2/3 + b^3/18 + \cdots, \quad (6)$$

where $J_1$ is the Bessel function of order one and

$$b = e^3 E /(8\pi\langle\epsilon\rangle\epsilon_0 k^2 T^2).$$

Thus the relative effect of the field is independent of ion pair radius even though $K(0)$ and $k_d(0)$ are expected to depend strongly on radius.

Assuming that Eq. (6) is an adequate approximation to the electric-field dependence of CT exciton dissociation, we write

$$k_d(E) = \nu e^{-\Delta E/kT} J_1[2\sqrt{2}(-b)^{1/2}]/\sqrt{2}(-b)^{1/2}, \quad (7)$$

where from Eq. (4)

$$\nu = A = \frac{\langle u\rangle e}{\langle\epsilon\rangle\epsilon_0}\left(\frac{\mu kT}{3\pi\hbar^2}\right)^{3/2} \quad (8)$$

for Wannier excitations or from Eq. (5)

$$\nu = A' = \frac{3\langle u\rangle e}{4\pi\langle e\rangle\epsilon_0 a^3} \quad (9)$$

in the case of classical ion pairs. When the ion pair description is adequate, the barrier to dissociation $\Delta E$ should equal the Coulomb barrier $e^2/(4\pi\langle\epsilon\rangle\epsilon_0 a)$.
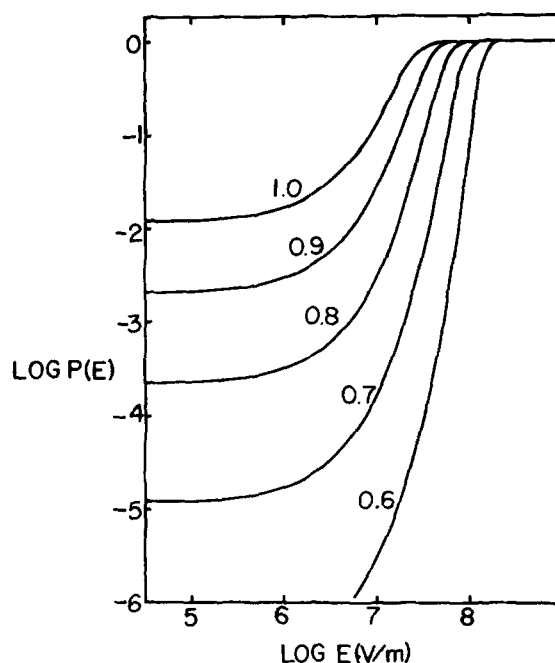


FIG. 2. Electric field dependence of the charge transfer state dissociation probability. The curves were computed using Eqs. (1), (7), and (9), i.e., the ion pair approximation was used. Parameter values used are $\langle u\rangle = 1 \times 10^{-4}$ m$^2$/V·s, $\langle\epsilon\rangle = 3.0$, $T = 300$ K and $\tau = 10^{-8}$ s. The curves are labeled with assumed values of the ion pair radius $a$ in nm. It should be noted that because the O–34 field dependence function [Eq. (6)] contains no adjustable parameters, the entire curve shape is determined once a value of $P(E)$ is specified.

Values of the field dependence of the dissociation probability $P(E)$ which correspond to various values of the zero-field dissociation probability $P(0)$ are given in Fig. 2. A weak initial dependence on field is followed by strong dependence and then saturation as $P(E)\rightarrow 1$. The weak initial field dependence has a slope-to-intercept value $b$ *exactly as in the conventional* 1938 *Onsager theory*.

In the doped-polymer case, for which a distribution of nearest-neighbor donor–acceptor separations presumably exists, $P(E)$ must be averaged over the distribution of charge transfer radii. This topic will be taken up in the paper which follows.

## III. DISCUSSION

### A. Comparison to conventional (1938) Onsager theory

Equation (1) with $k_d(E)$ given by Eqs. (7)–(9) is expected to provide a more realistic interpretation of charge carrier generation via the dissociation of charge transfer states than that provided by conventional Onsager theory. The chief virtue of the new approach is that for reasonable CT state radii of 0.5 to 1 nm, it predicts electric field dependence curves (see Fig. 2) similar to those measured experimentally; there is no need to invoke "thermalization lengths" of 2–3 nm which are difficult to rationalize. The dissociation rate constant [Eq. (7)] is proportional to the sum of free carrier mobilities and for any value of the applied field, the longer the CT lifetime the larger is the dissociation probability [Eq. (1)].

## B. The theory of Noolandi and Hong

The approach taken in this paper turns out to be a special case of the theory worked out by Noolandi and Hong.[30] They solve for the geminate recombination probability of a pair of oppositely charged particles which diffuse subject to the boundary condition of a partly absorbing sphere of finite radius at the origin (radiation boundary condition).[30] As pointed out in the recent review by Mauzerall and Ballard,[31] Noolandi and Hong's result for the quantum yield $\phi(0)$ of charge pair escape at zero applied field is

$$\phi(0) = \frac{e^{-r_c/r_0} + (z-1)e^{-r_c/r_m}}{1 + (z-1)e^{-r_c/r_m}}. \tag{10}$$

In Eq. (10), $z = Dr_c/\kappa r_m^2$,

$$r_c = e^2/(4\pi\langle\epsilon\rangle\epsilon_0 kT),$$

$r_0$ is the radius at which the charge pair is formed (thermalization length), $r_m$ is the radius of the partly absorbing sphere (recombination length), $D$ is the sum of the diffusion constants for cation and anion, $\langle D \rangle = \langle u \rangle kT/e$, and $\kappa$ is the surface recombination rate constant in m/s. For an ion pair of finite lifetime $\tau$, the recombination rate constant may be taken[31] to be $\kappa = r_m/\tau$.

Two limiting cases of Eq. (10) are of interest. As $r_m \to 0$, $\phi(0) \to e^{-r_c/r_0}$, which is Onsager's 1938 result.[1] Even for finite $r_m$, the same result obtains, at least approximately, provided that $r_m < r_0$ and $z$ is of order unity. More interesting, at least for the present application, is the case of large $z$ because it corresponds to an ion pair of finite lifetime and radius $r_m$. Consider the case in which $z \gg 1$ and $r_0 = r_m = a$, i.e., the pair is generated with a separation equal to its recombination radius. Then provided that $\phi(0) \ll 1$, Eq. (10) becomes

$$\phi(0) = ze^{-r_c/a} = \frac{\langle u \rangle e}{\langle\epsilon\rangle\epsilon_0} \cdot \frac{\tau}{4\pi a^3}e^{-r_c/a}$$

$$= k_r K'(0)\tau/3 \tag{11}$$

which is identical to the result of Eqs. (1), (4), and (5) except for a factor of 3. Is the large $z$ limit reasonable for the case of interest? Taking values appropriate to the anthracene/PMDA crystal[9]: $\langle u \rangle = 10^{-6}$ m$^2$/V·s, $\tau = 10^{-8}$ s, $\langle\epsilon\rangle = 3.0$, $T = 300$ K and $a = 1$ nm, one calculates $z = 4.8 \times 10^3 \gg 1$. Thus at least for that material and probably for most other CT crystals and polymers, the large $z$ limit is appropriate and Noolandi and Hong's theory reduces essentially to the approach of this work. Moreover, numerical comparison of the field dependence predicted by the full Noolandi–Hong theory for $\kappa/D = 1.054 \times 10^7$ m$^{-1}$, $r_c = 19$ nm, $r_m = 1$ nm, a set of parameters consistent with $\phi(0) = 10^{-5}$ produces a field dependence curve which is identical to that based on O-34 at least up to $8 \times 10^7$ V/m, the largest value compared.

It is easy to see why the limiting case of Eq. (11) corresponds to the steady-state result of O-34. With $\kappa = r_m/\tau$, $z$ becomes $D\tau r_c/r_m^3$. In cases of interest, $r_c \leqslant 100\, r_m$ and thus for $z \gg 100$, one has $(D\tau)^{1/2} \gg r_m$. However $(D\tau)^{1/2}$ is a diffusion length and thus the large $z$ limit implies that $\tau$ is long enough to establish a quasiequilibrium distribution at least on the distance scale $r_m$. Thus in the large $z$ limit, Noolandi and Hong's theory does appear to reduce to the steady-state theory of O-34. The ion pairs take up a Boltzmann distribu-

tion ranging out just a bit from the origin-centered sphere of radius $r_m$. One expects that at some large value of the applied field $\tau$ will become so short as to invalidate the approach based on O-34. As stated above, such fields are in excess of $8 \times 10^7$ V/m for the one case thus far subjected to numerical test.

## C. The barrier to dissociation

For actual ion pairs in a liquid solvent, the Coulombic expression

$$\Delta E_c = e^2/(4\pi\epsilon\epsilon_0 a)$$

is expected to be fairly accurate. However for CT excited states in a doped polymer or a single crystal, $\Delta E$ may be significantly smaller than the Coulombic value. Bounds and her co-workers have shown that a screened Coulomb potential is remarkably accurate for opposite charges in a medium of low dielectric constant even down to nearest-neighbor separations.[12] However, while attempts have been made to calculate the binding energies of CT excitons in such a potential,[12] they must be regarded as preliminary. A delocalized electron–hole pair in a CT crystal is likely to have a smaller binding energy than $e^2/(4\pi\epsilon\epsilon_0 a)$, where $a$ is the nearest-neighbor spacing both because the exciton radius is larger than nearest-neighbor and because the exciton has internal kinetic energy. In fact the activation energy for free carrier production in anthracene/PMDA is[14] only 0.2 eV compared to $\Delta E_c = 0.9$ eV for $a = 0.5$ nm or 0.45 eV for $a = 1$ nm. Samoc and Williams report an activation energy of 0.4 eV for free carrier generation in anthracene/tetracyanobenzene and Haarer[9] quotes a value of 0.5 eV for phenathrene/PMDA.

## D. Long distance electron transfer

In the doped-polymer case,[5–8] photoexcitation of the donor singlet is an alternative to excitation in the lowest-energy CT absorption band. The singlet excitation may then diffuse around over the donor population until, as one possibility, electron transfer to an acceptor occurs. Because of the inverse exponential distance dependence of electron-transfer rate constants, transfer to nearest-neighbor acceptors will predominate over transfer to more distant acceptors. However, electron transfer to relatively distant (2 nm) acceptors is certainly possible.[32,33] Long-distance transfer is simply improbable in the usual case of high acceptor concentration.

## IV. SUMMARY AND CONCLUSIONS

A kinetic model for field-assisted dissociation of charge transfer states in media of low dielectric constant is presented. The dissociation rate constant is given in both the Wannier exciton and the classical ion pair approximations to the true charge-transfer state. It is suggested that the electric-field dependence of the dissociation rate constant can be realistically approximated by a result of Onsager (O-34).[26] Comparison of the predicted yields of free charge carrier pairs with those measured experimentally makes it clear that relaxed CT states are realistic precursors of free carriers. The expected CT state radii are 1 nm or less; there is no need in this model to invoke "thermalization lengths" for a trans-

ferred electron of 2–3 nm. The model appears to be a special case of the theory of Noolandi and Hong[30] but has the virtue of being much simpler to implement.

## ACKNOWLEDGMENTS

[1]L. Onsager, Phys. Rev. 54, 554 (1938).
[2]R. R. Chance and C. L. Braun, J. Chem. Phys. 59, 2269 (1973); 64, 3573 (1976).
[3]H. T. Choi, D. S. Sethi, and C. L. Braun, J. Chem. Phys. 77, 6027 (1982).
[4]D. M. Pai and R. C. Enck, Phys. Rev. B 11, 5163 (1975).
[5]P. J. Melz, J. Chem. Phys. 57, 1694 (1972).
[6]M. Yokoyama, Y. Endo, and H. Mikawa, Bull. Chem. Soc. Jpn. 49, 1538 (1976).
[7]M. Yokoyama, Y. Endo, A. Matsubara, and H. Mikawa, J. Chem. Phys. 75, 3006 (1981).
[8]M. Yokoyama, S. Shimokihara, A. Matsubara, and H. Mikawa, J. Chem. Phys. 76, 724 (1982).
[9]D. Haarer, Festkoerperprobleme 20, 341 (1980).
[10]D. Haarer, J. Chem. Phys. 67, 4076 (1977).
[11]J. Merski and C. J. Eckhardt, J. Chem. Phys. 75, 3705 (1981); 75, 3731 (1981).
[12]P. J. Bounds, P. Petelenz, and W. Siebrand, Chem. Phys. 63, 303 (1981); P. J. Bounds and W. Siebrand, Chem. Phys. Lett. 75, 414 (1980).
[13]G. Weiser, Phys. Status Solidi A 18, 347 (1973).
[14]N. Karl and J. Ziegler, Chem. Phys. Lett. 32, 438 (1975).
[15]M. Samoc and D. F. Williams, J. Chem. Phys. 78, 1924 (1983).
[16]A. A. Lipnik, Sov. Phys. Solid State 3, 1683 (1962); 6, 823 (1964).
[17]R. Morris and M. Silver, J. Chem. Phys. 50, 2969 (1969).
[18]R. H. Bube, Photoconductivity of Solids (Wiley, New York, 1960), p. 48.
[19]P. Langevin, Ann. Chim. Phys. 28, 289 (1903); 28, 433 (1903).
[20]P. Debye, Trans. Electrochem. Soc. 82, 265 (1942).
[21]D. M. Burland and U. Konzelmann, J. Chem. Phys. 67, 319 (1977).
[22]M. Silver and R. Sharma, J. Chem. Phys. 46, 692 (1967).
[23]M. Fuoss and F. Accascina, Electrolytic Conductance (Interscience, New York, 1959), p. 213; M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, in Progress in Reaction Kinetics, edited by G. Porter (Macmillan, New York, 1964), Vol. 2, p. 294.
[24]T. Hino, H. Masuhara, and N. Mataga, Bull. Chem. Soc. Jpn. 49, 394 (1976).
[25]H. Masuhara, T. Hino, and N. Mataga, J. Phys. Chem. 79, 994 (1975).
[26]L. Onsager, J. Chem. Phys. 2, 599 (1934).
[27]R. H. Batt, C. L. Braun, and J. F. Hornig, J. Chem. Phys. 49, 1967 (1968); Appl. Opt. Suppl. 3, 20 (1969); A. Mozumder, J. Chem. Phys. 60, 4300 (1974).
[28]N. E. Geacintov and M. Pope, Proceedings of the 3rd International Photoconductivity Conference, Stanford, California, 1969, p. 289 (1971).
[29]D. M. Pai, J. Appl. Phys. 46, 5122 (1975).
[30]J. Noolandi and K. M. Hong, J. Chem. Phys. 70, 3230 (1979).
[31]D. Mauzerall and S. G. Ballard, Annu. Rev. Phys. Chem. 33, 377 (1982).
[32]S. G. Ballard and D. C. Mauzerall, J. Chem. Phys. 72, 933 (1980).
[33]J. R. Miller, J. A. Peeples, M. J. Schmitt, and G. L. Closs, J. Am. Chem. Soc. 104, 6488 (1982).