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Photoconductivity and small-polaron effects in tetracyanoquinodimethan*

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Photoconductivity has been observed in high-purity tetracyanoquinodimethan (TCNQ) single crystals and polycrystalline evaporated thin films. The photocurrent was measured as a function of wavelength, light intensity, and temperature. A photoconducting edge is observed at about 1.7 eV. The spectral response of the crystals and films are essentially identical. Comparison with optical-absorption, reflection, and resistivity data imply that the 1.7-eV edge is a measurement of the band gap. The relatively small value is attributed to the high electron affinity of TCNQ and its polaron binding energy. Pulsed photocurrent measurements give a drift mobility for both electrons and holes of about 0.4 cm^2/V sec in single crystals and somewhat lower in thin films. The electron mobility is about 10% higher than the hole mobility, and both are independent of temperature from 204 to 306 °K. The results suggest that conduction occurs by diffusion of small polarons in a conduction band whose width is comparable to the phonon energies. The relevance of this study to other systems is discussed.

I. INTRODUCTION

In the past decade, many workers have investigated photoconductivity in organic molecular crystals.[1] Measurements of photoconductive response have proved valuable in providing information on the conduction mechanisms in a variety of such systems. Recently, there has been considerable interest in the highly conducting organic charge transfer salts based on the strong acceptor molecule tetracyanoquinodimethan (TCNQ).[2] As part of a program to examine these salts, we have investigated TCNQ by a variety of methods to determine some of its own intrinsic properties. Although several papers have recently appeared, for example, on the photoconductivity behavior of TCNQ,[3-6] these studies were plagued with effects from impurities and spurious surface currents. The conduction mechanism in this sytem has not been clarified. In this paper, we report single-crystal and thin-film studies of the photoresponse of ultrapure TCNQ, including the direct measurement of the drift mobility by pulsed photocurrent techniques. The results of these studies allow a mechanism for conduction in TCNQ crystals to be proposed.

These studies are of importance for two reasons. First, by giving information on the properties of TCNQ, they may make it possible to learn more about the charge transfer salts of this molecule. Second, the TCNQ molecular crystal is of interest itself as a likely candidate for observation of small excitonic polaron behavior.[7] Our investigation of the photoconductive response of TCNQ shows that both of these expectations are realized.

II. EXPERIMENTAL

TCNQ was synthesized according to the method of Acker *et al.*[8] under careful experimental conditions. As reported earlier,[9] all syntheses and handling of materials were carried out in a Labcon glove box filled with Matheson 99.999% argon, using freshly washed oven-baked glassware. All solvents and reactant liquids were thoroughly bubbled with argon, vacuum pumped, and back flushed with argon repeatedly before being placed in the glove box. The starting materials, cyclohexane-1, 4-dione (Aldrich) and malononitrile (Aldrich) were twice recrystallized before use. The acetonitrile solvent (MC/B chromatoquality) was refluxed for 24–48 h over BaO and P_2O_5 and then distilled over P_2O_5. As originally reported,[2] the resultant TCNQ is a brilliant yellow-orange crystalline material giving yellow-orange solutions when dissolved in acetonitrile and not a rust-brown powder yielding yellow to yellow-green solutions as previously reported.[8] The TCNQ crystalline material was recrystallized twice from acetonitrile giving large well-formed crystals. These were placed in a gradient sublimator lined either with an inert Kapton or Teflon sleeve, and the sublimator was pumped and back flushed with argon several times. All crystal growth was carried out in the dark. Upon completion of sublimation at 130 °C and pressures as low as 10^{-5} torr, only brilliant yellow-orange TCNQ crystals from the center zone were collected for further use.

Analysis. The calculated values for $C_{12}H_4N_4$ were C = 70.57, H = 1.98, and N = 27.44; the values found were C = 70.55, H = 1.94, and N = 27.40.

The purity of the crystals was checked with respect to metal ion concentration by measuring sodium with atomic absorption spectrometry. Crystals grown by gradient sublimation had <5-ppm sodium, whereas Eastman-supplied TCNQ contained approximately 100 ppm. These results are in agreement with metal content determined independently by ashing and emission spectroscopy.[10] Furthermore, ESR measurements in this laboratory show that the concentration of unpaired spins is <1 ppm in our pure crystals.

Thin-film samples of TCNQ were prepared by sublimation under a vacuum of 10^{-6} to 10^{-7} torr, using a Varian Innovac system. Several different configurations were used. In one method, a silver strip was evaporated onto a quartz substrate. A scratch was made across the film and high-purity TCNQ was sublimed over the scratch, giving a sample approximately 4×10^{-3} by 1.5 cm, and several microns thick. Alternatively, TCNQ was sublimed over a pair of silver cross strips separated by 0.072 cm. Some samples were also made by subliming a layer of TCNQ on a conducting (tin-oxide coated) quartz substrate and depositing a gold counter electrode. It was found, however, that metals evaporated *onto* a TCNQ film showed evidence of reaction with the film, resulting in a sample of uncertain quality and unknown effective thickness.

The spectral response of the steady-state photocurrent was measured using standard techniques. A voltage was applied to the crystal, which was illuminated through a transparent electrode by chopped monochromatic light from either a Perkin-Elmer model 112U monochromator with a quartz prism, or from a Beckman DK-2 spectrophotometer. The current was detected using a lock-in amplifier tuned to the chopping frequency. The incident light intensity was kept constant as the wavelength was varied. Currents smaller than 10^{-13} A could be detected. For pulsed photoconductivity measurements, the sample was illuminated using a General Radio type 1531 Strobotac with a pulse duration of less than 3 μsec. The current was measured using a cathode follower circuit with a time constant of 1 μsec. whose output was monitored on an oscilloscope. In most cases, photocurrents were measured perpendicular to the (001) plane of the crystal. Orientation was determined with a polarizing microscope and by x-ray diffraction.

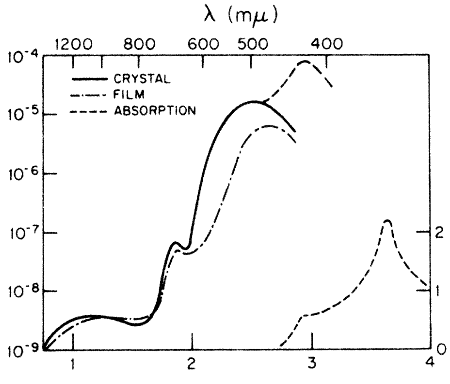

FIG. 1. Spectral response of the quantum efficiency in TCNQ crystals and thin films; optical density of TCNQ crystals. The dashed line shows response observed in some impure crystals.

III. PHOTOCONDUCTIVE RESPONSE

The quantum efficiency for photogeneration of carriers is plotted in Fig. 1 as a function of the incident photon energy for single crystals and thin films. The two curves coincide closely. Since x-ray measurements show the thin films to be polycrystalline with individual crystals randomly oriented, there is apparently little anisotropy in the spectral dependence of the photocurrent. This conclusion is supported by measurements on a single crystal which showed precisely the same spectral response in both the (001) and (110) directions.

The photocurrent and the dark current depended linearly on the applied voltage for field strengths below 5000 V/cm. Thus, space charge limiting effects were not important. At wavelengths shorter than ~0.6 μ, where the optical density is high, the photocurrent for positive polarity was 30–40% less than for negative polarity at the illuminated electrode. The photocurrent was also measured as a function of incident light intensity at fixed wavelengths at each of the peaks in the spectral response. Light intensity was varied by changing the voltage applied to the source, the slit opening being held constant. At the low light intensities used (10^{12} to 10^{13} photons/cm^2 sec) the photocurrent was found to depend linearly on the intensity. Other authors[3-5] have reported a square-root dependence at higher intensities, indicating that recombination was becoming important. No recombination effects were observed at low intensities. The linear intensity dependence is, therefore, evidence that carrier generation does not involve a two-photon process.

The large peak at about 2.9 eV, shown by a dashed line, was observed only on a few crystals known to have large concentrations of impurities, including some crystals grown from solution. This peak coincides with a peak in the optical-absorption spectrum[11] (also shown in Fig. 1), suggesting that this peak is due to intramolecular singlet exciton formation and subsequent interaction with surface impurities to form charge carriers. It should be noted that crystals with this peak present have spectra resembling the "type A" crystals reported by Hiroma *et al.*[3] and that crystals without the 2.9-eV peak resemble their "type B" crystals. All of our type A crystals also showed all structure present in type B crystals. The height of the 2.9-eV peak varied considerably from one crystal to another. Furthermore, when a grounded guard ring was attached to a crystal showing this peak, the 2.9-eV peak disappeared, leaving all other structure unaffected. When the guard ring was disconnected, the 2.9-eV peak reappeared. It is clear, then, that this peak is due to surface currents generated by reaction of singlet excitons with surface impurity states. In the remainder of this paper we will consider only crystals in which this peak did not occur.

Both the photoconductivity and the dark conductivity were measured as a function of temperature. The dark current versus temperature for several crystals is shown in Fig. 2. Above about 230 °K, all crystals showed an activation energy of 0.60 ± 0.04 eV, in agreement with results reported previously.[3,4] At lower temperatures the activation energy decreases to about 0.3 eV. We conclude that conductivity at low temperatures is controlled by traps with an activation energy of 0.3 eV.

The photoconductivity at 500 mμ incident wavelength had an activation energy of 0.28 eV. This value is close to the activation energy measured for the dark current at low temperatures, suggesting that both processes are controlled by traps at a depth of approximately 0.3 eV. Such trap-controlled photoconductivity has been observed in a number of organic materials.[12] The traps reduce the number of free carriers generated, leading to an activated carrier concentration in the steady state.

Returning to the spectral response curve of Fig. 1, we see that the dominant feature of the photocurrent is the large peak which starts at about 1.7 eV and rises nearly three orders of magnitude. It is reasonable to conclude that the edge at 1.7 eV represents the energy gap for electron-hole pair production. The lack of correspondence between the photocurrent and optical density curves is evidence that the carrier generation process does not proceed via the molecular singlet excitation with subsequent scattering to the conduction band. Rather, carriers are generated by lower-energy photons. This lack of correspondence also demonstrates that the measured structure is a true photocurrent and is not simply a modulation of the dark current due to heating. The photoconductivity edge thus provides the best experimental value available for the energy gap in TCNQ.

The spectra in Fig. 1 also show a low peak at about 1.1 eV, which has not been reported previously, although a shoulder at 1.3 eV was observed.[6] This peak was present on all samples measured. In order to eliminate the possibility that this peak is a modulation of the dark current caused by heating due to molecular vibrations, deuterated TCNQ was obtained and its photoresponse was measured. The 1.1-eV peak was unchanged although the vibrational spectrum is changed drastically. It is clear that molecular vibrations have nothing to do with this structure and that it is a genuine photocurrent. Its height depended linearly on both the applied voltage and the incident light intensity. This peak is apparently due to photoexcitation from a donor level approximately 1.1 eV below the conduction band. Such a level would be sufficient also to explain the dark conductivity activation energy of 0.60 ± 0.04 eV.

IV. MOBILITY

Pulsed photoconductivity techniques were used to measure the mobility of TCNQ as a function of temperature. The transient photocurrent is shown for a typical sample in Fig. 3 as a function of time for several applied voltages. The light pulse creates electron-hole pairs in the region close to the illuminated electrode. Those carriers of the same

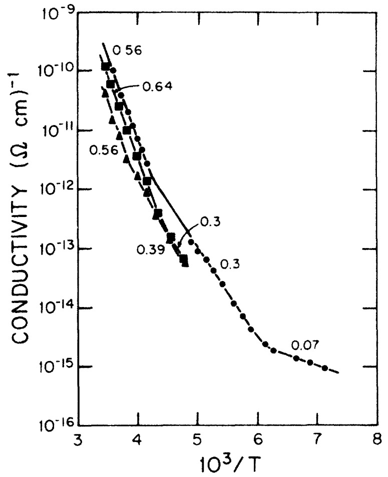

FIG. 2. Dark current vs temperature for TCNQ single crystals. The activation energies (eV) are indicated for each straight section of the curves.

polarity as the illuminated electrode are swept through the crystal and arrive at the opposite face after a transit time t_r given by[13]

$$t_r = 0.8d^2/\mu V, \qquad (1)$$

where d is the thickness of the crystal, μ is the mobility, and V is the applied voltage bias. This equation assumes space-charge limiting of the current. That this is the case is inferred from the shape and voltage dependence of the photocurrent pulses. In fact, the *low* voltage pulses are *not* space-charge limited. The onset of space-charge limiting occurs at approximately 10^4 V/cm. Transit times were measured only on photocurrent pulses which showed space-charge limiting effects, specifically a quadratic dependence of the current on voltage and a cusp (maximum) in the current at a time later than the light pulse. The position of this break in the curve indicates the transit time (arrows). The measured transit times varied inversely with V, as expected, and depended quadratically on the sample thickness. It was found that both the electron and hole mobilities are about 0.4 $\text{cm}^2/\text{V sec}$ with the hole mobility about 10% lower than the electron mobility. Both were found to be independent of temperature, within an experimental error of 10%, from 306 to 204 °K. For the thin films, the room-temperature mobility was somewhat lower, on the order of 0.1 $\text{cm}^2/\text{V sec}$. This value is less accurate than the single-crystal results due to severe trapping effects which made the transit time difficult to resolve.

The crystalline measurements were all performed in the (001) direction. Preliminary results suggest that the mobility in the (110) direction is roughly of the same magnitude.

The magnitude of the transient photocurrent varied exponentially with temperature, with an activation energy of about 0.08 ± 0.01 eV for carriers of both signs. Since the quantum efficiency showed a field dependence consistent qualitatively and quantitatively with geminate recombination effects, we conclude that the activation of the pulsed photocurrent is attributable to geminate recombination.[14]

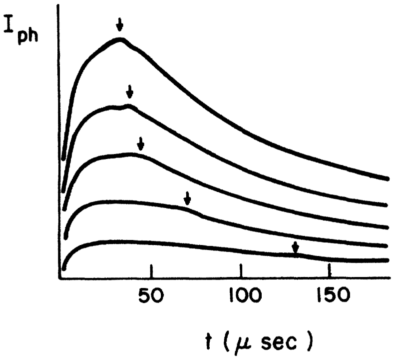

FIG. 3. Transient photocurrent response of electrons in TCNQ single crystal at room temperature. Applied bias is 100–500-V in 100-V steps.

The transient photocurrent traces shown in Fig. 3 have long tails, which are most likely due to surface trapping effects.[15] As the temperature is lowered below 250 °K, the long tails abruptly shorten, as would be expected for traps changing from shallow to deep in character—i.e., below 250 °K, the trapped electrons are unable to thermally excite back to the conduction level. For holes, the transition occurs at a higher temperature, about 260 °K.

V. DISCUSSION

Several conclusions may be drawn from the mobility results regarding the conduction mechanism in TCNQ. Mechanisms to be considered include band, diffusion, and thermally activated hopping mobilities. Of these, activated hopping is most easily ruled out, since no activation energy was observed in the temperature dependence of the mobility. In addition, the value of 0.4 $\text{cm}^2/\text{V sec}$ is larger than is normally found in systems with activated hopping mobilities.[16]

There is a minimum value of the mobility below which it is not possible to apply a band model. Assuming the band width W is greater than kT, the uncertainty principle requires that

$$W\tau > \hbar, \qquad (2)$$

where the scattering time τ is related to the mobility by the relation

$$\mu = e\tau/m^*. \qquad (3)$$

Thus, for the band model to be valid, it must be true that

$$\mu > \hbar e/m^* W. \qquad (4)$$

But in the tight-binding approximation, the effective mass is given by

$$m^* = 6\hbar^2/Wa^2, \qquad (5)$$

where a is the lattice spacing. The minimum band mobility is given, then, by

$$\mu_{\text{min}} = a^2 e/6\hbar = 2.4\times 10^{14} a^2 \ \text{cm}^2/\text{V sec}. \qquad (6)$$

This value is dependent only on the lattice spacing. For TCNQ with $a = 8$ Å, $\mu_{\text{min}} \simeq 2$ $\text{cm}^2/\text{V sec}$.

For the case when the bandwidth $W \lesssim kT$, several authors[16,17] have given modifications of the above argument. The resulting minimum band mobility is given by

$$\mu_{\min} = \frac{ea^2}{\hbar}\,\frac{W}{kT}\,. \tag{7}$$

This condition arises from the requirement that the mean free path must be greater than the lattice constant. Band conduction cannot occur, however, for arbitrarily narrow bands. The electron-phonon coupling causes a modulation of the local one-electron energies at the characteristic phonon frequency (ω_{Debye}). If the bandwidth becomes less than the amplitude of this modulation, electrons can move from one site to the next only when the levels at the two neighboring sites coincide. Thus, the transport becomes diffusive in this limit and is not properly described by the band model.

The mobility for such a diffusion process can be calculated directly by the Einstein relation for diffusive transport

$$\mu = eD/kT\,, \tag{8}$$

where the diffusion constant D is given approximately by

$$D = a^2\nu\,. \tag{9}$$

Here ν is the phonon frequency, taken to be equal to $k\Theta_D/h$, where Θ_D is the Debye temperature, measured as 89.3 °K.[18] At room temperature, the resulting mobility is about 0.47 cm^2/V sec. This is of the same order of magnitude as the measured value.

Thus, we see that the measured mobility in TCNQ is consistent with a diffusion mechanism but is near the borderline between diffusion and band transport mechanisms. The above considerations are somewhat simplified and a rigorous division between the two regimes is not possible. In fact, it is worth noting the relation between the band and diffusion expressions for the mobility [Eqs. (7) and (8)]. The two expressions become identical in the case where $W = h\nu/2\pi$. This effectively defines the minimum bandwidth for which band conduction is possible; i.e., when $W > h\nu/2\pi$, the band description is valid, but when $W \lesssim h\nu/2\pi$, the transport becomes limited by diffusion. The transition from one limit to the other occurs gradually, and no sharp dividing line can be drawn to separate the two regimes.

The above considerations indicate that the room-temperature mobility value is most consistent with a diffusion description of the transport mechanism. The lack of observed temperature dependence of the mobility is not inconsistent with a diffusive process when account is taken of the traps observed to be present at about 0.3 eV. Spear and co-workers[19] observed a nearly temperature-independent ($220\,°\text{K} < T < 330\,°\text{K}$) hole mobility in high-purity crystals of orthorhombic sulfur. They analyzed this result in terms of a gradual transition from a lattice mobility at high temperatures to a trap-controlled mobility at low temperatures. They used the relation

$$\mu = \mu_L\left[1 + (N_t/N)\,e^{\epsilon_t/kT}\right]^{-1} \tag{10}$$

to describe the temperature dependence of the mobility. Here N_t and ϵ_t are the density and energy of the traps, N is the number of sites per unit volume, and μ_L is the "lattice," or trap-free, mobility.

In the present case, μ_L may be replaced by the diffusion mobility given by Eq. (8). Setting $\epsilon_t = 0.3$ eV, Eq. (10) gives a mobility independent of temperature between 200 and 300 °K (within 10%) for $N_t/N \sim 2\times10^{-7}$. In light of the known purity of the crystals studied, this is a very reasonable trap density. Furthermore, the value of N_t/N may be changed by a factor of 2 or more without affecting the temperature dependence appreciably. Variations in N_t/N due to differences in sample purity may, however, account for the observed small variations in the mobility from sample to sample.

The above argument is not intended to be a conclusive derivation of the mechanism of carrier transport in TCNQ. It is a demonstration that a mobility with the observed magnitude and temperature dependence can result from a diffusive process. We will see below that this interpretation is consistent with the observation of small polaron effects which narrow the bandwidth to a value comparable to the phonon energies.

The energy gap for electron-hole pair production as measured by photoconductivity is 1.7 eV. This value is consistent with available literature values of the ionization potential I, the electron affinity A, and the polarization energy P. I has been calculated by Kunii and Kuroda[20] to be 7.8 eV, and A has been measured by Farragher and Page[21] as 2.88 eV. From measurements of the dielectric constant of TCNQ,[22] we have found the mean polarizability to be 27 Å^3. The polarization energy is given semiclassically by $P = \frac{1}{2}\alpha E^2$, where the electric field E is given by $E = e/r_0^2$ and r_0 is the separation between molecules. Due to the uncertainty in the value to be used for r_0, which appears raised to the fourth power, this relation cannot give an accurate value for P. Using a van der Waals separation of 3.5 Å for r_0, a value of 1.3 eV is found for P. A more meaningful estimate can be made[23] by considering the ion to be a spherical cavity of radius a, embedded in a continuous isotropic medium with a dielectric constant ϵ. The polarization energy is given classically by

$$P = e^2(1 - 1/\epsilon)/2a\,. \tag{11}$$

The cavity is taken to have a volume equal to the molecular volume. For TCNQ, $\epsilon = 3.37$[22] and $a = 3.93$ Å, giving $P = 1.3$ eV. Using the relation

$$E_g = I - A - 2P \tag{12}$$

with the experimental value for E_g of 1.7 eV, a value of 1.6 eV is obtained for P, in good agreement with the estimate given above.

In the context of polaron theory, the polarization energy P is considered as the binding energy E_B of the polaron.[7,24-26] In the case of TCNQ, the dominant polarization will be excitonic rather than phononic, although we will see below that molecular vibrations also make a significant contribution to the induced orthogonality band narrowing.

The theory of small excitonic polarons has been presented elsewhere.[7,25] The small polaron limit is relevant when the binding energy E_B is sufficiently larger than the electronic energy bandwidth that the lattice distortion is localized to the immediate vicinity of the electron. Since the electronic bandwidth is expected to be on the order of 0.1 eV or less,[1,27] TCNQ is likely to be in the small polaron limit. We take as a model a molecular crystal consisting of two rigid lattice subsystems: a narrow energy band containing conduction electrons and a separate subsystem of polarizable molecules whose elementary excitations are propagating excitons. The Hamiltonian describing this model can be written[7]

$$\begin{aligned} H = H_{\text{ex}} + H_{\text{el-ex}} + H_{\text{el-el}} + H_{\text{el}} &= \sum_q \hbar\omega_q a_q^\dagger a_q \\ &+ \frac{i\Gamma}{\sqrt{N}} \sum_{q,j,\sigma} (a_q^\dagger e^{-iq\cdot r_j} - a_q e^{iq\cdot r_j}) n_{j\sigma} \\ &+ U \sum_1 n_{i\uparrow} n_{i\downarrow} - t \sum_{ij} C_{i\sigma}^\dagger C_{j\sigma} . \end{aligned} \tag{13}$$

The first term gives the exciton energy and the second term the electron-exciton coupling. The last two terms represent the conduction electrons and are assumed to be of the form of the Hubbard Hamiltonian. Here $a_q^\dagger$ and a_q are, respectively, the creation and annihilation operators for an exciton of wave number q and energy $\hbar\omega_q$; $n_{j\sigma}$ is the occupation number for electrons of spin σ on site r_j; Γ is the electron-exciton coupling constant, assumed to be k independent (i.e., short range); t is the transfer matrix element between sites r_i and r_j; U is the Coulomb repulsion between two electrons on site r_i; and $C_{i\sigma}^\dagger$ and $C_{j\sigma}$ are creation and annihilation operators for electrons on sites i and j, respectively. The coupling constant Γ was shown[7] by a semiclassical argument to be given by

$$\Gamma = \left(\frac{\alpha}{2a_0^3}\right)^{1/2} \left(\frac{e^2\hbar\omega_0}{a_0}\right)^{1/2} , \tag{14}$$

where α is the molecular polarizability and a_0 is the distance between the electron and the nearest-neighbor molecules.

In the case of a single electron in an otherwise empty band, $H_{\text{el-el}} = 0$. The first two terms in Eq. (13) may be diagonalized by a canonical transformation. The electron kinetic energy H_{el} is treated subsequently in tight-binding perturbation theory. The resulting effective tight-binding transfer integral t^* is given by

$$t^* = te^{-S} , \tag{15}$$

where

$$S = \Gamma^2/(\hbar\omega_0)^2 \tag{16}$$

and the polaron binding energy or band shift is

$$E_B = \Gamma^2/\hbar\omega_0 = -\hbar\,\omega_0 S . \tag{17}$$

Here $\hbar\omega_0$ is the average exciton energy. The Coulomb interaction is reduced to $U - 2E_B$ due to the indirect attraction between polarons.

We, therefore, expect two important effects: a band shift by the amount $2E_B$, due to the reduced Coulomb interaction, and an exponential band narrowing due to the induced orthogonality which reduces the electronic site-to-site transfer matrix elements.

For the binding energy E_B, we use the experimentally determined value for P of 1.6 eV. Since the exciton energy is given essentially by the singlet absorption frequency of TCNQ of about 3 eV, the quantity S has a value of about 0.5, so that $t^* \simeq 0.6t$.

An alternate approach to the excitonic polaron problem was taken by Bari,[28] who assumed a single exciton frequency and treated the excitons as fermions rather than bosons. In this theory, the reduction in the Coulomb interaction and the associated band shift remains the same, but the band narrowing is less; the bandwidth remains finite even for infinite electron-exciton coupling. Clearly, neither the fermion nor the boson approximation is exact, and it is not yet established which is more appropriate in a given system. In the case of TCNQ, where the carrier density is low, the boson approximation should not be grossly in error. In any case, for the small value of S determined experimentally for TCNQ, there is little difference between the results of the two theories.

The excitonic polarization, then, reduces the energy gap for pair production significantly and, in addition, causes a band narrowing of nearly a factor of 2. The effective bandwidth is no more than about 0.05 eV.

Molecular vibrations provide an additional source of polarization which should also have significant effects. We now investigate the effect of these modes on small polaron formation. Siebrand[26] has presented a polaron theory based on coupling of the electron to vibrational modes of the molecule. In this theory, each vibrational mode α contributes a binding energy $E_{B_\alpha}=\frac{1}{2}k_\alpha(\overline{q}_\alpha-\overline{q}^{\,0}_\alpha)^2$, where k_α is the force constant and $\overline{q}_\alpha$ and $\overline{q}^{\,0}_\alpha$ are the equilibrium distances in the ion and the neutral molecule, respectively. The quantity $\gamma_\alpha=-E_{B_\alpha}/\hbar\omega_\alpha$ measures the exponential band narrowing contribution from each mode. The total band narrowing and binding energy are obtained by summing over the modes of the molecule. To estimate these quantities, we set

$$\sum_i(\Delta\chi_i)^2=\sum_\alpha(\overline{q}_\alpha-\overline{q}^{\,0}_\alpha)^2, \tag{18}$$

where i runs over the bonds of the molecules and $\Delta\chi_i$ measures the change in bond length between the neutral and the ionized molecule.

Bond-length data exist for both neutral TCNQ[29] and for the negative anion in NMP-TCNQ[30] and in $\mathrm{Cs_2TCNQ_3}$.[31] Since the bond lengths of $\mathrm{TCNQ^-}$ in TCNQ molecular crystals are not known, we assume the two known sets of bond lengths to be representative and to set limits on the values appropriate to the present case. As shown in Table I, the estimated polarization energy is 0.11 eV in NMP-TCNQ and 0.18 eV in $\mathrm{Cs_2TCNQ_3}$, with a total γ of 2.4 and 3.4, respectively. Thus, for TCNQ we estimate $E_B\simeq 0.15$ eV and $\sum_\alpha\gamma_\alpha\equiv\gamma\simeq 3$.

This result is interesting in that it demonstrates how a significant band narrowing can result from the vibrational modes even though the binding energy from this source is small compared to the excitonic contribution. This is possible since it is the ratio of the binding energy to the excitation energy that determines the band narrowing. Even though the excitonic part of the binding energy is very large, on the other hand, the band narrowing is relatively little due to the high energy of the exciton. Thus, in the case of TCNQ, the polaron binding energy comes primarily from one source and the induced orthogonality band narrowing comes mostly from another.

A few comments are in order concerning the validity of these calculations. First, the higher frequency of the excitonic interaction implies that this part should be considered first. Any changes in the bandwidth due to excitonic polaron effects must be taken into account *before* considering the validity of assumptions made in calculating the vibrational contributions. For the same reason, the photoconductive energy gap will be affected by polarization of the excitons but not of the vibrational modes, which are of too-low frequency. The vibrational modes will affect only the transport properties.

The following criteria[24,26] must be true for the small polaron approach to be valid:

$$E_B\gg\tfrac{1}{2}W, \tag{19}$$

$$\tau\gg 2\pi/\omega, \tag{20}$$

where τ is the time the electron stays on one molecule. Siebrand[26] gives a third condition,

$$E_B\gg\hbar\omega, \tag{21}$$

equivalent to the requirement that the distortion to which the electron is bound be relatively immobile.

Applying conditions (19) and (20) to the excitonic

TABLE I. Polaron binding energy and induced orthogonality band narrowing from molecular vibration modes, calculated from the bond length changes between neutral and negatively charged TCNQ molecules.

bond	#	k	ω_α	χ_0	χ_1^-	$\Delta\chi_1$	E_{b_1}	γ_{α_1}	χ_2^-	$\Delta\chi_2$	E_{b_2}	γ_{α_2}
$-\mathrm{C}\equiv\mathrm{N}$	4	17.73	.42	1.140	1.156	0.016	91	0.87	1.152	0.012	51	0.486
$>\mathrm{C}=\mathrm{C}<$	2	9.6	.33	1.346	1.341	0.005	2.4	0.015	1.355	0.009	7.8	0.047
$>\mathrm{C}=\mathrm{C}<$	2	9.6	.33	1.374	1.388	0.014	18.8	0.115	1.411	0.037	132	0.797
$\equiv\mathrm{C}-\mathrm{C}\lesseqgtr$	4	5.18	.18	1.441	1.420	0.021	45.6	1.01	1.419	0.022	50	1.11
$\gtreqless\mathrm{C}-\mathrm{C}\lesseqgtr$	4	4.50	.18	1.448	1.434	0.014	17.7	0.39	1.426	0.022	43.7	0.97
							175.5 =0.11 eV	2.40			284.8 = 0.18 eV	3.41

k in 10^5 dyne/cm
ω in 10^{-12} erg

χ in Å
E_b in 10^{-15} erg

subscript 1: data from NMP-TCNQ(30)
subscript 2: data from $\mathrm{Cs_2TCNQ_3}$(31)

polaron, we see that they are easily satisfied. Condition (21) is weakly violated, however, indicating that TCNQ is at the limit of applicability of small excitonic polaron theory. The bandwidth reduction by $e^{-s} \sim 0.6$ must now be applied to the bandwidth used in considering the vibrational part. Here $E_B \simeq 0.15$ eV and, as noted above, the bandwidth $W \sim 0.05$ eV or less, so inequality (19) is satisfied. If we write $\tau = a/V_{\text{th}}$, where V_{th} is the thermal velocity, inequality (20) is also satisfied if the effective mass is sufficiently large, say $m^* > 10 m_e$. For the extremely narrow bandwidth in question, this should be true. Finally, condition (21) is satisfied for the vibrational part of the interaction. The small polaron approach is justified, then, for both the vibrational and excitonic contributions.

One further point should be made regarding the additivity of the band narrowing exponentials for the two types of interaction. This is simply a consequence of the separability of the total wave function into a vibrational (nuclear) and an excitonic (electronic) part, and of the commutativity of the associated operators.

In summary, we arrive at the following picture. The electron interacts with exciton states of the surrounding molecules to produce a small polaron with a binding energy of 1.6 eV, as deduced from the photocurrent spectral response. The induced orthogonality band narrowing is sufficient to allow interactions with molecular vibrational modes to contribute further to small polaron formation. The additional binding energy is relatively small, but the additional band narrowing effect is significant. The bandwidth is reduced, in all, by a factor of about 30. Thus, if the electronic bandwidth is on the order of 0.1 eV, the resulting polaron bandwidth will be considerably less than kT, and in fact will be comparable to the lattice vibration frequencies. This result is in complete accord with the diffusion conduction mechanism suggested on the basis of the measured mobility. The bandwidth is neither large enough to allow band conduction, nor small enough to result in thermally activated hopping.

We wish to emphasize that the thin films of TCNQ are very easily made and appear to have a stable spectral response over prolonged periods of time. In addition, they have a relatively low photoconductive edge, with appreciable photoresponse throughout much of the visible. These properties, combined with TCNQ's relatively high mobility, would appear to make TCNQ an attractive candidate for application in photoconducting devices.

Finally, we wish to point out the relevance of this study to other systems, in particular, the charge transfer salts of TCNQ. The large polarization contribution to the energy should be present in these crystals as well. Direct experimental verification of this statement comes from the reduced Coulomb interaction measured in NMP-TCNQ.[2] In this case, the polarizability of NMP is particularly important, but the TCNQ polarizability may play a role as well. Another system of great current interest is TTF-TCNQ.[32] The reduced effective interaction makes it possible for this material to remain metallic with Coulomb interactions apparently reduced to playing a minor role. Small polaron formation may similarly be expected in a wide variety of systems involving the TCNQ molecule. In addition, many other organic systems exhibit polarizabilities comparable to that of TCNQ. Significant small polaron effects should be observable in many such systems. Given a sufficient understanding of the nature and origin of polaronic behavior, it should be possible to design organic systems with a wide range of conducting and photoconducting properties.

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