Activation Energy for Photoconduction in Molecular Crystals

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Abstract

The carrier dynamics of photoconduction (PC) are complicated because the systems contain optically and thermally excited carriers with different relaxation mechanisms. In addition, molecular crystals generally have highly anisotropic and correlated electronic systems. Accordingly, the photoconduction mechanism of molecular crystals is full of unanswered basic problems such as how to distinguish PC from a coexistent thermal carrier’s contribution originating from heating effects involved with irradiation. In this work, the activation energy ($E_a$) for PC of molecular crystals was found to decrease monotonically with an increase in the intensity ($I$) of light. The values of $E_a$ upon irradiation were not related to band gaps, unlike those for dark conductions. Based on the observed $I$-dependence of the photocurrent ($I_{ph}$), the $I$-dependence of the $E_a$ is explained quantitatively. This $E_a$ analysis makes it possible to clearly distinguish PC from the coexistent conduction originating from thermal carriers.

Keywords: Organic charge-transfer salt; Carrier dynamics; Heating effect; Metal-dithiolene complex; π-conductor.

1. Introduction

Photoconduction (PC) is a well-known phenomenon observed in a variety of compounds [1-5]. In addition to unique experimental tools for studying carrier dynamics in unusual conductors [1-3], PC is applied in various imaging and sensor devices such as copy machines, charge-coupled devices (CCD), complementary metal-oxide-semiconductors (CMOS), and photovoltaic cells [4,5]. Since such devices play an indispensable role in daily life, clarifying the mechanism of PC is important in order to develop more efficient photoconductors. The carrier dynamics of PC are complicated, because the systems contain both thermally and optically activated carriers at the same time. As a result, in addition to the relaxation of electrical conduction, that of optical and thermal excitations takes places simultaneously in photocarrier systems. Recently organic photoconductors have attracted more and more attention because of their possibility of light, flexible, and inexpensive products with low power consumption. PC in organic compounds can simultaneously involve different but nearly degenerate energy bands. They generally exhibit marked anisotropy in electrical conduction. Additionally, they are characterized by strong electron-electron and electron-phonon interactions, which often produce various kinds of relaxation processes and meta-stable states. All of these characteristics make the PC behavior more complicated than other groups of materials. Thus, there remain a number of basic problems and open questions about the PC mechanism of organic compounds, which includes how to distinguish PC from a coexistent thermal carrier’s contribution originating from inevitable heating effects. In order to solve these unanswered problems, study on PC in single crystals is more advantageous than that in thin films, because the former samples are structurally well-defined, serving as a simplest model. Therefore understanding and findings on single crystalline samples can provide an important clue for general and basic understanding of PC mechanism in organic materials. In this perspective, the samples selected in this study exhibit unusually large photoresponse, i.e. photocurrent $I_{ph}$, and marked dependence on light-intensity $I$. Such samples have been recently found among [Ni(dmit)$_2$] salts, where dmit = 1,3-dithiole-2-thione-4,5-dithiolate (Figure 1). The [Ni(dmit)$_2$] radical anion salts have been paid particular attention for long time as building blocks for molecular optical materials, magnets, metals and superconductors [6-18]. NMQ[Ni(dmit)$_2$] (1) (NMQ = N-methyl quinolinium; Figure 1) is a highly insulating molecular salt when in the dark, but exhibits unusually high PC. At 200 K, it demonstrates ~880 times higher conductivity when exposed to UV radiation (375 nm, 15.7 mWcm$^{-2}$) than when in the dark [19].
Figure 1. Molecular structures.

The salt is a band insulator [Figure 2(a)] having a two-dimensional network of Ni(dmit)$_2$ moieties [Figure 2(b)] which is used as the PC conduction pathway. In addition, there exists a non-linear dependence of $I_{ph}$ on $I$. In conventional photoconductors, whether they are organic or not, $I_{ph}$ is proportional to $I$. Because the detailed $I$-dependence of $I_{ph}$ including linearity can be controlled by irradiation conditions in salt 1, it is the sample of choice for covering different patterns of $I_{ph}(I)$ of different photoconductive materials. Herein are reported the $I$-dependence of effective $E_a$ for PC of molecular crystals, and a quantitative interpretation of the $E_a$ behavior based on the observed $I$-dependence of $I_{ph}$. In the discussion below, only the total number of carriers in the PC is considered; the photoexcited states are not considered in detail. This is advantageous for application of the analysis presented below to as wide a variety of photoconductive materials as possible.

2. Materials and Methods

The single crystals of salts 1 and 2 (MV[Ni(dmit)$_2$]). MV = methyl viologen, Figure 1) were prepared according to previous reports [19, 23]. Electrical resistivity measurements were carried out on single crystals via a two-probe method in air using a homemade cryostat and a UV laser (375 nm, max 20 mW) with adjustable focus and intensity. Many samples were studied in order to examine sample-dependence and reproducibility, as well as durability to irradiation in air. The electrical resistivity was measured along the longitudinal direction of the single crystal ($h//b$-axis for both salts 1 and 2), which coincides with most conductive directions. At a given temperature the current-voltage curves were measured from -10 V to +10 V with an interval of 2 V, and $I_{ph}$ was the observed current under an applied voltage of 10 V. Gold wires (25 µm in diameter) and gold paste (No.8560, Tokuriki Chemical Research Co., Ltd.) were used as electrical contacts. In order to change the value of $d$ (mm), the distance $L$ between the two electrical leads were decreased stepwise by adding the Au paste after each measurement (Figure 3). Full experimental details are provided in the Supporting Information.

![Figure 1](http://ccaasmag.org/CHEM)

![Figure 2](http://ccaasmag.org/CHEM)

![Figure 3](http://ccaasmag.org/CHEM)
3. Results and Discussion

3.1 Dependence of photocurrent on light-intensity, and on distance between electrical leads. In contrast with dark conductivity, even under a constant applied voltage, \( I_{ph} \) generally depends on experimental conditions such as radiation wavelength/power [Figure 4(a)]/etc. and the net distance \( d \) between electrical leads [Figure 4(b)]. This is because the number \( N_{ph} \) of photocarriers depend on light intensity, wavelength and so on. For instance, \( d \) becomes, the fewer photocarriers arrive at the opposite lead before they optically relax and disappear.

In Fig. 4(b) the best-fit curve uses the following equation,

\[
\frac{I_{ph}}{I_{dark}} = y_0 + A \exp \left( -\frac{d}{\tau} \right)
\]

, where \( y_0, A, \) and \( \tau = 1.08, 3.65, 0.56 \) (mm), respectively.

With regard to the non-linear dependence of \( I_{ph} \) on \( I \), \( I_{ph} \) is well described by a polynomial of \( I \) for salt 1 [Figure 4(a)]

\[
I_{ph} = \sum_{i=0}^{N} K_i I^i
\]  

(1),

where \( K_i \) (i = 0,1,2,...) are experimentally-determined constants (fitting parameters dependent on temperature \( T \)) and \( K_0 \) is equal to the observed current under dark conditions \( I_{dark} \).

\[
K_0 = I_{dark}
\]  

(2)

Depending on the irradiation conditions, some of the coefficients \( K_i \) can be zero.

3.2 Dependence of activation energy on light-intensity. The activation energy \( E_a \) of salt 1 decreases under 375 nm UV light with increasing \( I \) (Figure 5).

\[
E_a(I) = E_{a,0} \frac{N_{th}(I)}{N_{th}(I) + N_{ph}(I)}
\]  

(3)

where \( N_{th}(I), N_{ph}(I) \) and \( E_{a,0} \) indicate the number of thermally activated carriers, the number of optically excited carriers, and the activation energy under dark conditions, respectively.
conditions [~ (0.24 ± 0.02) eV], respectively. First, it should be noted that dark- and photo-conductivity (σ_{dark} and σ_{ph}, respectively) are proportional to the dark- and photo-current (I_{dark} and I_{ph}, respectively) under a constant applied voltage, and that the currents are proportional to the respective number of carriers: 
\[ \sigma \propto I \]
\[ I \propto N \]
where \( \sigma, I, \) and \( N \) can designate \( \sigma_{dark} \) and \( \sigma_{ph} \), \( I_{dark} \) and \( I_{ph} \), and \( N_{th}(I) \) and \{\( N_{th}(I) + N_{ph}(I) \)\}, respectively.

\[ \{N_{th}(I) + N_{ph}(I)\} \propto I_{ph} \]

Then, as the observed \( I_{ph} \) obeys Eq. (1),
\[ N_{th}(I) + N_{ph}(I) = A \sum_{i=0} K_i I^i \]
where \( A \) is a proportionality constant, and
\[ A = \frac{L^2}{e \mu \epsilon} \]
where \( L, V, \mu, e \) indicate distance between the two electrical leads, applied voltage, mobility of the carriers, and elementary charge, respectively, as shown in Supporting Information.

Substitution of Eqs. (5) and (7) in Eq. (3) gives
\[ E_a(I) = \frac{a + bI}{A \sum K_i I^i} E_{a,0} \]

Eq. (10a) may be transformed into a linear relationship in order to unambiguously fit the observed behavior as follows:
\[ E_a(I) \sum_{i=0} K_i I^i = \frac{1}{A} (a + bI) E_{a,0} = a' + b'I \]

where \( a' = \frac{E_{a,0}}{A} a \), and \( b' = \frac{E_{a,0}}{A} b \).

3.3 Comparison of observed behavior with theory. The validity of the discussion thus far can be evaluated by comparing Eq. (10b) and the observed behavior. All of the parameters \( K_i \) in Eq. (10b) can be determined directly from the observation of \( I_{ph} \) vs. \( I \), i.e. the relationship in Eq. (1), as shown in Figure 4. (The parameters obtained from the curve-fitting (\( K_i, a', \) and \( b' \) are in Table S2 in the Supporting Information.) Similarly, the I-dependence of \( E_a \) can be directly observed, as shown in Figure 5.

Thus, using Eq. (10b) and the values of \( K_i \), a curve-fitting analysis was carried out on the I-dependence of \( E_a(I) \sum K_i I^i \) (Figure 6). All of the relationships were found to be linear, which means that Eq. (10b) is consistent with the observed behavior.

3.4 Separation of thermally activated carriers from optically activated carriers. Here if \( \mu \) is known, this analysis enables \( N_{th}(I) \) [Eq. (5)] and \( N_{ph}(I) \) [Eq. (11)] to be found unambiguously using the values of \( AK_i, a', \) and \( E_{a,0} \) as shown below. Otherwise, it is always difficult to distinguish unavoidable thermal effects from purely optical effects in these kinds of experiments.

\[ N_{ph}(I) = \{N_{th}(I) + N_{ph}(I)\} - N_{th}(I) \]
\[ = A(K_0 + K_1 I + K_2 I^2 + K_3 I^3 + \cdots - (a + bI)) \]
\[ = (AK_1 - b)I + AK_2 I^2 + AK_3 I^3 + \cdots \] (\( \because AK_0 - a = 0 \) )

If Eq. (1) is replaced with other types of equations, the discussion thus far remains essentially unaltered, except
for the details of Eqs. (7), (10a), and (10b). In fact, salt 1 gave different $I$-dependences of $I_{ph}$ [Eq. (1)] under different measurement conditions. However, the analysis here still can be applied to give similarly consistent results (See Figures S2 and S3 in Supporting Information).

![Figure 6](image_url)

**Figure 6.** $I$-dependence of $E_a(I)(\Sigma K_i I^1)$ for the same sample with that in Figure 5. Data observed in air (for corresponding data for other samples, see Figure S3 in Supporting Information). Best fit lines generated using Eq. (10b). Fitting parameters are in Table S2 in the Supporting Information.

### 3.5 Similar analysis of a different salt.

In order to examine the validity of the discussion thus far, the same analysis is applied to salt 2, which belongs to “photomagnetic conductors” [22,23]. Salt 2 is a non-magnetic insulator under dark conditions, yet it produces paramagnetic metallic state under UV (375 nm) irradiation. There is an interaction between the localized spins on the MV cations and the carriers on the [Ni(dmit)$_2$] anions, which is corroborated by ESR and temperature-dependent electrical resistivity measurements (for the crystal structure and the physical properties, see Figures S4-S6 in Supporting Information). Thus the carrier dynamics in PC in salt 2 is different from those in salt 1, as experimental results for such an interaction or localized spins in PC have not been observed in salt 1. The results corresponding to Figures 4-6 are shown in Figures 7(a)-7(d), respectively. Irrespective of $d$, $E_a(I)$ is also well described by Eq. (10a) [Figure 7(c)], and $E_a(I) \times I_{ph}(I)$ is linearly dependent on $I$ [Figure 7(d)]. For the obtained fitting parameters, see Tables S4 and S5 in Supporting Information. These results mean that the analysis of $E_a$ and separation of thermal and photocarriers’ contributions can be valid in different PC mechanism as long as $I_{ph}(I)$ is known like Eq. (1). How this analysis can be generalized is now under study by examination of further different kinds of PCs.

![Figure 7](image_url)

**Figure 7.** (a) $I_{ph}/I_{dark}$ vs. $I$ curve at 298 K with different distances between the electrical leads (gold wires) for the same single crystal of salt 2. Circles and squares: observed; curves: best-fit curves using Eq. (S1) (for details, see Table S4 in Supporting Information). (b) $I_{ph}$ vs. $I$ curve for salt 2. The same data as in Figure 7(a). Circles and squares: observed; curves: best-fit curves
using Eq. (1) (for details, see Table S5 in Supporting Information). (c) $E_s(I)$ vs. $I$ curve for salt 2. Data observed in air. Best fit curves generated using Eq. (10a) with fitting parameters in Table S5 in the Supporting Information. (d) $I$-dependence of $E_s(I/2K, I')$ for the same sample with that in Figures 7(a) - 7(c). Data observed in air. Best fit lines generated using Eq. (10b). (Fitting parameters are in Table S5 in the Supporting Information.)

4. Conclusion

In the temperature-dependence of PC of some molecular crystals, finite values of $E_a$ were observed to be dependent on $I$ and could be explained on the assumption that thermally activated and optically activated carriers equally serve as carriers. Examination of the $I$-dependences of $E_a$ and $I_{th}$ makes it possible to experimentally distinguish PC from the coexistent conduction originating from thermal carriers. This analysis considered to be applied to other photoconductive materials as long as the $I$-dependences of $I_{th}$ and values of $\mu$ are known.

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References


[20] If the possibility that there are different bands for thermally-excited carriers is considered, $N_{th}$ requires their summation. However, in any case, $N_{th}$ is constant at a given temperature and $I$. Thus, this
correction does not alter the succeeding discussion.

[21] Here, details concerning the electronic structure of the photoexcited state are not required, nor are details concerning optical excitations. This is because only the total number of carriers is required in the following discussion [Eq. (6)], and the total number is obtained from experimentation [Eq. (7)]. Similarly, the discussion here is independent of the PC mechanism.
