DRIFT MOBILITY OF PHOTO-ELECTRONS IN ORGANIC MOLECULAR CRYSTALS: QUANTITATIVE COMPARISON BETWEEN THEORY AND EXPERIMENT

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A quantitative comparison of a simple theoretical prediction for the drift mobility of photo-electrons in organic molecular crystals, calculated within the model of the coupled band-like and hopping motion, with experiments in napthalene of Schein et al. and Karl et al. is given.

Considerable experimental and theoretical activity has recently centered around the problem of the temperature dependence of the mobility of photogenerated charge carriers in molecular crystals. Anthracene and napthalene are the most thoroughly studied systems. A nearly temperature-independent mobility between about 300 K and 100 K, and a steep increase below 100 K, observed particularly in napthalene, constitute the intriguing observations [1–3]. Although alternative explanations, which focus on the anisotropy of the mobility tensor, have not been completely ruled out [3], it is generally believed that we have here the band-hopping transition long awaited from the small-polaron model [4]. However, the temperature dependence of the mobility cannot be explained within that model [1,2].

For that reason, recently several theoretical attempts [5–8] have been made to address the description of the observed transition in the temperature behaviour of the mobility. Madhukar and Post [5] have shown how Kubo's linear response theory [9] and a simple assumption in a stochastic Liouville equation (SLE) first derived by Haken, Reineker and Strobl [10–12] can reproduce the constant mobility at high temperatures. Sumi [6] has offered an explanation based on a band motion in the a, b plane of napthalene and a hopping motion in the c' direction. Efrima and Metiu [7] have concentrated on the effect of anharmonicities, and Silbey and Munn [8] have given a very general treatment of the problem. Brief descriptions of at least some of these theories, along with critical comments, appear in the recent reviews by Duke and Schein [13] and by Roberts et al. [14].

The purpose of this letter is not to add another competing theory to the above mentioned ones but to show that the basic transition behaviour of the mobility is compatible with, and a direct consequence of an extremely simple and natural description of the combined phonon-assisted (incoherent) and phonon-hindered (coherent) motion of the charge carriers inherent in those theories. This description is essentially that given by a number of authors [10–12, 15] in the context of exciton transport and uses as its basic equation of motion the stochastic Liouville equation (SLE):

$$\frac{\partial \rho_{mn}}{\partial t} = -\mathrm{i} \sum_r (H_{mr}\rho_{rn} - H_{rn}\rho_{mr}) + 2\delta_{m,n} \sum_r (\gamma_{mr}\rho_{rr} - \gamma_{rn}\rho_{mm}) - (1-\delta_{m,n})\, 2\Gamma\rho_{mn} + (1-\delta_{m,n})\, 2\bar{\gamma}_{m\,-n}\rho_{nm} \qquad (1)$$

for the density matrix elements ρ_{mn} of the charge carriers. Here m, n denote the sites of the crystal,

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γ_{mn} and $\bar{\gamma}_{m-n}$ are transfer rates arising usually from the phonon-assisted part of the hamiltonian, H_{mn}'s are interaction matrix elements not so assisted, and $\Gamma = \Sigma_m \gamma_{n,n+m}$ is the rate of destruction of off-diagonal elements of ρ. It is well known [5,8,16,17] that eq. (1) results in the following expression for the drift mobility when only interactions with nearest neighbours are taken into account (the drift mobility and the dc conductivity are identical up to a constant factor ne, with n denoting the density and e the charge of the electrons):

$$\sigma(0) = \beta[2\gamma_1 + H_1^2/(\Gamma + \bar{\gamma}_1)] ,$$

$$\Gamma = \sum_i \gamma_i , \quad \beta = 1/k_B T . \tag{2}$$

This expression for $\sigma(0)$ contains essentially the diffusion constant known from exciton motion and consists of two terms, where the first one, $\beta\, 2\gamma_1$, describes the purely hopping part of the motion and stems from the non-local fluctuations of the hamiltonian. The second term has its origin in the combined actions of coherent and incoherent parts of the hamiltonian and is able to describe band-like motion.

The parameters γ_0, γ_1 and $\bar{\gamma}_1$ describe the strength of the fluctuations and therefore depend on the phonon occupation numbers

$$n = [\exp(\hbar\omega/kT) - 1]^{-1} ,$$

where $\hbar\omega$ is a characteristic phonon frequency. Treating the phonons as a heat bath, it can be shown [8,15, 18,19] that in the simplest approximation and for not too low temperatures there is a linear relation between the γ's and n. Writing $\gamma_i(T) = \bar{\gamma}_i n(T)$ and introducing $T' = kT/\hbar\omega$, i.e. T' is the temperature measured in units of the characteristic phonon frequency, one obtains from (2)

$$\sigma(0) = \sigma_\infty \left(\frac{n(T')}{T'} + c\, \frac{1}{n(T')T'} \right) ,$$

$$\sigma_\infty = 2\bar{\gamma}_1/\hbar\omega , \quad c = H_1^2/2\tilde{\gamma}_1(\Gamma + \tilde{\bar{\gamma}}_1) , \tag{3}$$

which in the high-temperature limit gives

$$\sigma(0) \approx \sigma_\infty \left(1 + c\, \frac{1}{T'^2} \right) , \tag{4}$$

which is, of course, the result obtained by Madhukar and Post [5]. Eq. (3) shows that the high-temperature dc mobility is given by $2\tilde{\gamma}_1/\hbar\omega$. Assuming that the temperature dependence of the γ's also holds for low temperatures, we have $n(T') \approx e^{-1/T'}$ and thus

$$\sigma(0) \approx \sigma_\infty \left(\frac{1}{T'} e^{-1/T'} + c\, \frac{1}{T'} e^{1/T'} \right) , \tag{5}$$

which shows that for very low temperatures the mobility increases exponentially.

Fig. 1 represents the dc mobility according to eq. (3) normalized to the mobility at $T = 300$ K for a phonon frequency of $\hbar\omega = 5.6$ meV corresponding to 65 K in temperature units. The points marked by circles and crosses are experimental values of Schein and McGhie for the dc mobility of naphthalene in the c' direction (see fig. 1 of ref. [2]). The squares are measurements of Karl and Warta [3]. For $c = 0.3$ in the regions of constant and exponentially increasing mobility we have a rather good coincidence between experimental values and the theoretical curve. In the transition region the coincidence is only qualitative.

The application of the stochastic Liouville equation to this problem has been criticized by Sumi [6] on the grounds that the phonon band widths in naphthalene are not large enough to justify the usual δ-function form of the relevant correlation functions. The following comments are therefore in order. Firstly, the phonon band width is not the only parameter that enters into such a justification. Even when the phonon band width is small, a coupling to the bath (i.e. the remaining degrees of freedom in the system), if strong enough, will provide such a justification. Furthermore, the dc mobility is determined by the diffusion constant, i.e. by the derivative of the mean square displacement, of the charge carrier in the limit of *long times*. In this limit the details of the decay of the correlation functions are unimportant (markoffian limit). Thus, if one uses [16,17] a generalization [20] of the SLE, which has correlations more general than δ-function ones, the mobility in the limit $\omega = 0$ is identical to expression (2). It should be remembered that the theories of Sumi and others can be formally expressed as a generalized stochastic Liouville equation of the above-mentioned form [20], as is evident from the work of many authors (e.g. ref. [15]).

We have by no means presented a new theory here. The basic idea is only a slight generalization of those in refs. [5–8]. The purpose of this letter is to point out the fact that a rather close quantitative fit can be obtained to experimental observations with natural values for the parameters.

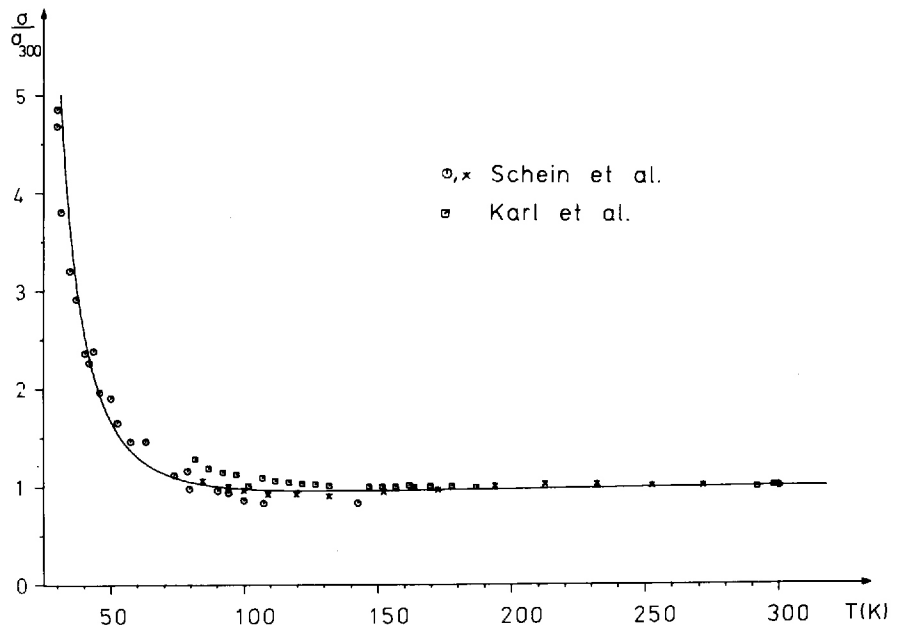

Fig. 1. Mobility as a function of temperature for $c = 0.3$ and a phonon frequency corresponding to 65 K normalized to the mobility at $T = 300$ K. The dots and crosses represent experimental values for the mobility in the c' direction of naphthalene according to Schein and McGhie (fig. 1 of ref. [2]). The squares are measurements of Karl and Warta [3].

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References

[1] L.B. Schein, C.B. Duke and A.R. McGhie, Phys. Rev. Lett. 40 (1978) 197.
[2] L.B. Schein and A.R. McGhie, Phys. Rev. B20 (1979) 1631.
[3] N. Karl and W. Warta, unpublished; see also W. Warta, Diplomarbeit, Univ. Stuttgart (1978); N. Karl, Abstracts 9th Molecular crystal Symp. (1980) p. 149.
[4] T. Holstein, Ann. Phys. (NY) 8 (1959) 325, 343.
[5] A. Madhukar and W. Post, Phys. Rev. Lett. 39 (1977) 1424; 40 (1978) 70 (E).
[6] H. Sumi, Solid State Commun. 28 (1978) 309; J. Chem. Phys. 70 (1979) 3775.
[7] S. Efrima and H. Metiu, J. Chem. Phys. 69 (1978) 5113.
[8] R. Silbey and R.W. Munn, J. Chem. Phys. 72 (1980) 2763.
[9] R. Kubo, J. Phys. Soc. Japan 12 (1957) 570.
[10] H. Haken and G. Strobl, The triplet state, ed. A.B. Zahlan (Cambridge U.P., 1967); Z. Phys. 249 (1972) 253.
[11] P. Reineker, Phys. Lett. 42A (1973) 389; Z. Phys. 261 (1973) 187.
[12] E. Schwarzer and H. Haken, Phys. Lett. 42A (1972) 317.
[13] C.B. Duke and L.B. Schein, Phys. Today 33 (2) (1980) 42.
[14] G.T. Roberts, R. Apsley and R.W. Munn, Phys. Rep. 60 (1980) 59.
[15] M.K. Grover and R. Silbey, J. Chem. Phys. 54 (1971) 4843.
[16] V.M. Kenkre, R. Kühne and P. Reineker, Z. Phys. B41 (1981) 177.
[17] R. Kühne, P. Reineker and V.M. Kenkre, Z. Phys. B41 (1981) 181.
[18] H. Haken and P. Reineker, Excitons, magnons and phonons, ed. A.B. Zahlan (Cambridge U.P., 1968).
[19] P. Reineker and S. Scheuing, unpublished; see also A. Scheuing, Diplomarbeit, Univ. Ulm (1979).
[20] V.M. Kenkre, Phys. Rev. B11 (1975) 1741; B12 (1975) 2150.