

Unified Theory of the Mobilities of Photoinjected Electrons in Naphthalene

V. M. Kenkre

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

John D. Andersen

Department of Physics, Rochester Institute of Technology, Rochester, New York 14623

D. H. Dunlap

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

C. B. Duke

Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352

(Received 21 December 1987)

We present a unified quantitative explanation of the temperature dependence of the drift mobilities of photoinjected electrons in naphthalene for all directions and temperatures. The theory proposed is based on a polaronic description of the charge carriers and the calculational scheme employs site-local states. Excellent agreement of the theory and experiment occurs for known and reasonable parameters.

PACS numbers: 72.10.Di, 72.20.Dp, 72.80.Le

In this Letter we present a resolution of a puzzle¹⁻⁶ in the transport of charges in organic solids that has existed for many years. This puzzle consists of the temperature behavior of the mobility of photoinjected electrons in naphthalene. The mobility is independent of temperature in the c' crystallographic direction over the temperature range $100 < T < 300$ K and decreases rapidly with an increase in temperature for $30 < T < 100$ K. There is also a large anisotropy with respect to crystal orientation in both the magnitude and the temperature behavior of the mobility.

While various specific aspects of these measurements have been interpreted qualitatively, no single theoretical model has succeeded in providing simultaneously a description of all of them. Moreover, several theories have been proposed which initially appeared to provide an explanation of the qualitative features present in the experimental observations, but, on closer scrutiny, have been found to be inapplicable. Indeed, it has been recently remarked⁷ that all theoretical attempts made so far in this direction have essentially failed. In this Letter, we present what we believe to be the first explanation of the behavior of these mobilities, which is internally consistent and compatible with known or estimable parameters.

The various theoretical studies that have appeared in the literature include (i) Sumi's librational phonon theory,⁸ (ii) Reineker, Kenkre, and Kühne's stochastic-Liouville-equation approach,⁹ (iii) Silbey and Munn's formalism,¹⁰ and (iv) a Boltzmann-equation treatment¹¹

of scattering by acoustical phonons presented by Andersen, Duke, and Kenkre. All these theories have provided a qualitative or partial explanation of the measurements. Upon quantitative application to the data, however, they have been found to be inadequate. The analyses of Reineker, Kenkre, and Kühne⁹ and of Sumi⁸ predict the appropriate qualitative behavior but require a phonon frequency which is smaller than the lowest known libration in naphthalene. The Boltzmann-equation treatment,¹¹ while it provides good fits with the data below 100 K in all crystallographic directions, is found to yield mean free paths that are less than a lattice constant for most of the data for the c' direction, and thus fails to be internally consistent. The Silbey-Munn theory¹⁰ is found to result in perturbation parameters which are not consistent with the analysis of the low-temperature mobilities ($T < 100$ K). For the high-temperature mobilities, it is consistent with the data but requires phonon frequencies that are higher than that of the highest librational mode and lower than that of the lowest totally symmetric internal mode in naphthalene.¹² Thus, there exists no satisfactory explanation of the mobility puzzle, in spite of the fact that all models predict qualitatively similar temperature behaviors for the mobility.

Our purpose in this Letter is to present the results of a new analysis of the temperature-dependent electron drift mobilities in naphthalene. This analysis affords an internally consistent quantitative description of the observed mobility tensor. The model Hamiltonian underlying the analysis is given by

$$H = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{m-n} a_m^\dagger a_n + \sum_q \hbar \omega_q (b_q^\dagger b_q + \frac{1}{2}) + N^{-1/2} \sum_{m,q} \hbar \omega_q g_q \exp(i\mathbf{q} \cdot \mathbf{R}_m) (b_q + b_{-q}^\dagger) a_m^\dagger a_m, \quad (1)$$

in which a_m^\dagger creates an electron with energy ϵ_m at a site m in the crystal of N sites, b_q^\dagger creates a phonon with wave vec-

tor q and frequency ω_q , V_{m-n} is the intersite matrix element between sites m and n , and g_q is the dimensionless electron-phonon coupling constant. The quantities \mathbf{q} and \mathbf{R}_m are vectors in the reciprocal and direct lattices, respectively, \mathbf{R}_m being the lattice vector which locates site m . In the usual manner, we transform the Hamiltonian to the polaron picture by using the unitary transformation

$$U = \exp \left[-N^{-1/2} \sum_{m,q} g_q \exp(i\mathbf{q} \cdot \mathbf{R}_m) (b_q - b_{-q}^\dagger) a_m^\dagger a_m \right]. \quad (2)$$

The transformed Hamiltonian is given by

$$H = \sum_m \left\{ \epsilon_m - N^{-1} \sum_q |g_q|^2 \hbar \omega_q \right\} A_m^\dagger A_m + \sum_q \hbar \omega_q (B_q^\dagger B_q + \frac{1}{2}) + \sum_{n,m} V_{n-m} \theta_n^\dagger \theta_m A_n^\dagger A_m + N^{-1} \sum_{n,m,q} |g_q|^2 \hbar \omega_q \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)] A_n^\dagger A_m^\dagger A_n A_m, \quad (3a)$$

$$\theta_m = \exp \left[N^{-1/2} \sum_q g_q \exp(i\mathbf{q} \cdot \mathbf{R}_m) (B_q - B_{-q}^\dagger) \right], \quad (3b)$$

wherein $A_m^\dagger = U a_m^\dagger U^\dagger$ creates a polaron at site m and $B_q^\dagger = U b_q^\dagger U^\dagger$ creates a phonon of wave vector q that is associated with the motion of the ions about their displaced equilibrium positions.

The Hamiltonian and the resulting physical picture are identical to those employed by a large number of workers in the field, most notably Silbey and Munn,¹⁰ but the calculational scheme we employ to obtain the mobility is that given by Kenkre¹³ in the context of excitation transport. We treat ϵ_m to be a fluctuating quantity as a result of one or more of a variety of sources and to be characterized by either a Gaussian or Lorentzian distribution of width $\hbar\alpha$. We adopt the latter distribution here. It is straightforward to use the former in its place. We use the method of Refs. 13 and 14 to deduce from the Hamiltonian in Eqs. (3) the memory functions entering into a generalized-master-equation description of

transport, i.e.,

$$\mathcal{W}_{mn}(t) = \mathcal{W}_{mn}^c(t) \Phi_{mn}^b(t) \exp(-\alpha t), \quad (4)$$

wherein $\mathcal{W}_{mn}^c(t)$ is the memory function for the charge to move from site n to site m under completely coherent conditions, $\Phi_{mn}^b(t)$ is the contribution due to the charge-phonon interaction, as calculated by Kenkre and Rahman,¹⁵ and where the exponential $\exp(-\alpha t)$, which arises from the fluctuations of the site t energy ϵ_m , would be replaced by a Gaussian if we were to use a Gaussian rather than Lorentzian distribution of the site energies. We use the prescription given by Kenkre, Kühne, and Reineker,¹⁶ viz.,

$$\langle v(t) v \rangle_i = -\frac{1}{2} [\partial^2 \mathcal{W}^k(t) / \partial k_i^2]_{k=0}, \quad (5)$$

where \mathcal{W}^k is the discrete Fourier transform of \mathcal{W}_{mn} , to obtain from Eq. (4) the velocity-velocity correlation function $\langle v(t) v \rangle$ for the moving charge:

$$\langle v(t) v \rangle_i = 2 |V_i a_i / \hbar|^2 \exp \left[-\sum_q \{4g_q^2 \sin^2(\frac{1}{2} q_i a_i)\} \{ \coth(\frac{1}{2} \beta \hbar \omega_q) [1 - \cos(\omega_q t)] + i \sin(\omega_q t) \} \right] \exp(-\alpha t). \quad (6)$$

In Eqs. (5) and (6) the index i labels the principal-axis direction, V_i are the effective electronic nearest-neighbor transfer integrals along these directions and are related to the effective electronic bandwidths B_i through $B_i = 4V_i$, and a_i are the lattice constants. It has been shown¹⁶ that there are terms in $\langle v(t) v \rangle$ which are not included in the right-hand side of Eq. (5). We do not display them here because they have a vanishing time integral ($t=0$ to $t=\infty$) and consequently make no contribution to the dc mobility. The final step in our calculation consists of evaluating the sum in Eq. (6) for a band of librational phonons of mean energy $\hbar\omega_0$ and width $\hbar\Delta_i$ in the i th direction and performing the time integral of Eq. (6) to obtain the mobility $\mu_{i,i}$:

$$\mu_{i,i} = 2(ea_i^2)(k_B T)^{-1} |V_i / \hbar|^2 \exp[-2g_i^2 \coth(\frac{1}{2} \beta \hbar \omega_0)] \times \int_0^\infty dt \exp(-\alpha t) I_0 \{ 2g_i^2 \text{csch}(\frac{1}{2} \beta \hbar \omega_0) |J_0(\Delta_1 t) J_0(\Delta_2 t) J_0(\Delta_3 t)| [1 + J_1^2(\Delta_i t) / J_0^2(\Delta_i t)]^{1/2} \}. \quad (7)$$

The g_i are dimensionless electron-libration coupling constants as defined in Eq. (1). The J_m and I_m are, respectively, ordinary and modified Bessel functions of order m . The exact form of the extreme right-hand side of Eq. (7) contains modified Bessel functions of all orders. For narrow phonon bands and small α (with respect to ω_0), however, it is an excellent approximation to retain only I_0 as in Eq. (7).

Equation (7) is the primary result of our theory. Our analysis of the electron drift mobility data in naphthalene¹⁷ based on that result are presented in Figs. 1 and 2. The reported observations of the electron drift mobilities in naphthalene, and consequently the theories constructed to explain their temperature dependence, have referred in the past to the a , b , and c' directions.^{1,2}

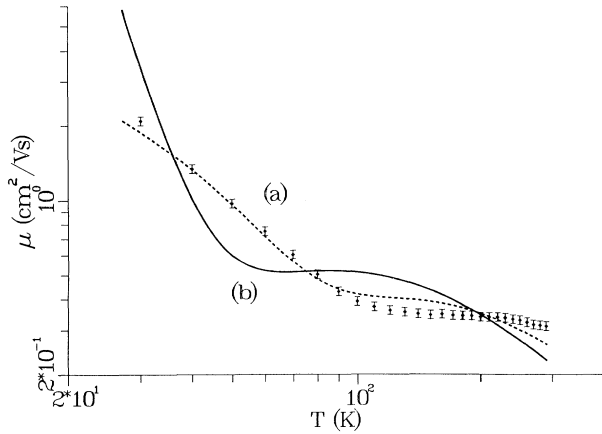


FIG. 1. Explanation of the temperature dependence of the electronic drift mobility along the 3 axis in naphthalene (Ref. 17). Curve *a* represents our theory as given in Eq. (7). Curve *b* represents the theory of Silbey and Munn (Ref. 10).

Recent measurements refer, however, to the 1, *b*, and 3 directions.¹⁷ We have, therefore, chosen to display the results of our analysis in the 1, *b*, and 3 directions. The temperature dependence of the mobilities along the 1 and 3 directions is slightly different from that for *a* and *c'*, respectively. The small difference arises from the temperature-dependent rotation of the mobility tensor,¹⁷ and is apparent only at high temperatures.

The fit provided by our polaron theory to the observations in the 3 direction (which display the apparent transition behavior) is shown as curve *a* of Fig. 1. For comparison, the corresponding best fit provided by the Silbey-Munn theory,¹⁰ which is also a polaron theory but, as has been shown in Ref. 2, is not compatible with the entire mobility data in naphthalene, is presented as curve *b* of Fig. 1. Our description of the mobilities for *all* directions over the entire experimental accessible range of temperature is shown in Fig. 2. We find excellent fits in all directions within the polaron picture.

The parameters appropriate to our application of Eq.

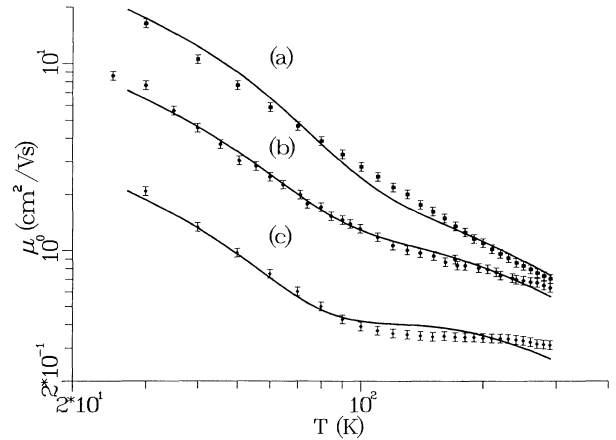


FIG. 2. Explanation of the anisotropy in the temperature dependence of the electronic drift mobility in naphthalene (Ref. 17). The fits correspond to our theory as given in Eq. (7). The principal axes 1, *b*, and 3 are represented by curves *a*, *b*, and *c*, respectively.

(7) to the data are given in Table I. Those of Δ_i and ω_0 are obtained from neutron-diffraction measurements on deuterated naphthalene.¹⁸ Those of V_i , g_i , and α , on the other hand, are extracted from the observed electron drift mobilities through a least-squares-fitting procedure. The resulting values of the ratio of the polaron binding energy $g^2\hbar\omega_0$ to the electronic bandwidth B_i are found to lie between 4.6 and 7.2 and are displayed at the bottom of Table I. This ratio constitutes an important figure of merit. A polaron theory would be inapplicable if $g^2\hbar\omega_0/B_i$ were less than 1. It is thus clear that, unlike earlier attempts discussed above, the analysis presented here does not suffer from problems of internal consistency. It is also of interest to note that, although the observed mobilities obey $\mu_1 > \mu_b > \mu_3$, the deduced B 's (equivalently V 's) in Table I do not follow this sequence. Indeed, a key parameter which decides the magnitude of the mobility is a combination of the "intersite hopping

TABLE I. Parameter values for a least-squares fit of Eq. (7) to the electronic drift mobility data in naphthalene (Ref. 17).

Parameters extracted from fitting procedure	Principal axis direction		
	1	<i>b</i>	3
g	1.615 ± 0.014	1.830 ± 0.013	1.879 ± 0.013
B (meV)	8.41 ± 0.15	10.47 ± 0.14	7.88 ± 0.14
$\hbar\alpha$ (meV)	0.1694 ± 0.0062	0.1694 ± 0.0062	0.1694 ± 0.0062
Phonon parameters			
$\hbar\omega_0$ (meV)	16.0 ± 0.05	16.0 ± 0.05	16.0 ± 0.05
$\hbar\Delta$ (meV)	0.70 ± 0.05	1.40 ± 0.05	0.24 ± 0.05
Figure of merit			
$g^2\hbar\omega_0/B$	5.0 ± 0.1	4.6 ± 0.1	7.2 ± 0.1

integral" V , the electron-phonon coupling constant g , and the inhomogeneity parameter α and may be expressed as $F=2(V^2/\alpha)\exp(-g^2)$. Normalized to its value in the 3 direction, this parameter is found to equal 2.9, 2.2, and 1 for the 1, b , and 3 directions, respectively, and thus to follow the sequence $F_1 > F_b > F_3$ in keeping with the observations.

In summary, we have provided a unified quantitative explanation of the drift mobilities of photoinjected electrons in naphthalene for all directions and temperatures. The physical model is polaronic as suggested by Silbey and Munn,¹⁰ but the calculational scheme includes a perturbation from localized states^{13,14} and treats static disorder simply but explicitly through the parameter α . The important conclusion to be drawn from our results is that a unified quantitative theoretical description of observed electron drift mobilities in naphthalene along all directions and for all temperatures is possible under the assumption that photoinjected charges move as polarons in all directions.

The authors are indebted to L. J. Kennedy for assistance and to N. Karl, L. B. Schein, and W. Warta for many useful discussions. This work was supported in part by the National Science Foundation under Grant No. DMR-8811434. C.B.D. thanks Mark B. Myers and the Xerox Webster Research Center for their support of the initial portion of this work. Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the DOE under Contract No. DE-AC06-76 RLO 1830.

¹L. B. Schein, C. B. Duke, and A. R. McGhie, *Phys. Rev. Lett.* **40**, 197-200 (1978).

²C. B. Duke and L. B. Shein, *Phys. Today* **33**, No. 2, 42 (1980).

³M. Pope and C. E. Swenberg, *Electronic Processes in Or-*

ganic Solids (Clarendon, Oxford, 1982); *Annu. Rev. Phys. Chem.* **35**, 613-655 (1984).

⁴G. G. Roberts, N. Apsley, and R. W. Munn, *Phys. Rep.* **60**, 59-150 (1980).

⁵A. Madhukar and W. Post, *Phys. Rev. Lett.* **39**, 1424-1427 (1977).

⁶S. Efrima and H. Metiu, *J. Chem. Phys.* **69**, 5113-5125 (1978); *Chem. Phys. Lett.* **60**, 226-231 (1979).

⁷W. Warta and N. Karl, *Phys. Rev. B* **32**, 1172-1182 (1985); N. Karl, in *Abstracts of the Ninth Molecular Crystals Symposium*, 1980 (unpublished), p. 149.

⁸H. Sumi, *J. Chem. Phys.* **70**, 3775-3785 (1979); **71**, 3403-3411 (1979).

⁹P. Reineker, V. M. Kenkre, and R. Kühne, *Phys. Lett.* **84A**, 294-296 (1981).

¹⁰R. Silbey and R. W. Munn, *J. Chem. Phys.* **72**, 2763-2773 (1980).

¹¹J. D. Andersen, C. B. Duke, and V. M. Kenkre, *Phys. Rev. Lett.* **51**, 2202-2205 (1983).

¹²J. D. Andersen, C. B. Duke, and V. M. Kenkre, *Chem. Phys. Lett.* **110**, 504-507 (1984).

¹³V. M. Kenkre, *Phys. Rev. B* **12**, 2150-2160 (1975).

¹⁴V. M. Kenkre, *J. Stat. Phys.* **30**, 293-303 (1983); see also V. M. Kenkre, in *Proceedings of the Fourth International Seminar on Energy Transfer in Condensed Matter*, edited by J. Pantoflick and L. Zachoval (Society of Czechoslovak Mathematicians and Physicists, Prague, 1981), p. 54.

¹⁵V. M. Kenkre and T. S. Rahman, *Phys. Lett.* **50A**, 170-172 (1974).

¹⁶V. M. Kenkre, R. Kühne, and P. Reineker, *Z. Phys. B* **41**, 177-180 (1981).

¹⁷N. Karl, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and O. Madelung (Springer-Verlag, Berlin, 1985), Group III, Vol. 17, Pt. i, p. 106.

¹⁸I. Natkaniec, E. L. Bokhenkov, B. Dorner, J. Kalus, G. A. Mackenzie, G. S. Pawley, U. Schmelzer, and E. E. Sheka, *J. Phys. C* **13**, 4265-4283 (1980). See also G. S. Pawley, G. A. Mackenzie, E. L. Bokhenkov, E. E. Sheka, B. Dorner, J. Kalus, U. Schmelzer, and I. Natkaniec, *Mol. Phys.* **39**, 251-260 (1980).