Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Carrier Yield in Molecular Systems due to Photo and High Energy β Particle Ionization

M. Silver [a] & R. C. Jarnagin [b]

[a] Physics Department, University of North Carolina, Chapel Hill, North Carolina

[b] Chemistry Department, University of North Carolina, Chapel Hill, North Carolina

Version of record first published: 21 Mar 2007.

To cite this article: M. Silver & R. C. Jarnagin (1968): Carrier Yield in Molecular Systems due to Photo and High Energy β Particle Ionization, Molecular Crystals, 3:4, 461-469

To link to this article: http://dx.doi.org/10.1080/15421406808082891

Molecular Crystals. 1968. Vol. 3, pp. 461–469

Printed in Great Britain

Carrier Yield in Molecular Systems due to Photo and High Energy β Particle Ionization†

M. SILVER
Physics Department
and
R. C. JARNAGIN
Chemistry Department
University of North Carolina, Chapel Hill, North Carolina

Received November 11, 1967
Revised received December 12, 1967

Abstract—The problem of recombination in molecular crystals and liquids is considered from the point of view of continuity of current. The probability for escape of an electron from its parent molecule depends exponentially upon how far it travels before thermalization. When account is taken of the temperature dependence of this distance, good agreement with experiment is obtained. Comparison between β particle and photo excitation suggests that initial back recombination between the emitted electron and the parent molecule may not be important in photoconductivity.

Introduction

It has been suggested by Coppage and Kepler[1] and by Pope and Burgos[2] that the observed small quantum yield and the temperature dependence of photoconductivity in anthracene crystals can be attributed to the dominance of initial back recombination between the emitted electron and the parent molecule. Recently this

† Supported in part by Army Research Office, Durham, National Science Foundation, and Advanced Research Projects Agency through Contract SD-100.

monomolecular process has been termed "geminate recombination". Kepler and Coppage[3] also extended the argument to account for the low yield of carriers from X-ray excitation of anthracene crystals. The principal feature of these considerations rests on the assumption that only those electrons which have a range greater than the Coulomb radius may escape from the parent molecule. Thus, under X or β irradiation the high energy recoil electrons produce secondaries, tertiaries, etc., and of these electrons only those which initially come into thermal equilibrium with the lattice at a distance from a positive center in excess of $e^2/\epsilon kT$ may escape.

Hummel *et al.*[4] have clearly shown that such a sharp cut-off model causes a serious under estimation of the observed number of carriers generated by β particles in liquid hexane. They find that the range of low energy secondary electrons must contribute significantly to the resulting currents. It is difficult to understand why the range of low energy electrons in anthracene crystals should be much lower than those in liquid hexane, therefore it seems worth while to re-examine these processes in the crystal.

Proposed Model

The following model is proposed to account for the efficiency and temperature dependence of charge separation for a group of very dilute carriers in thermal equilibrium with a lattice. It will be assumed that initially the distance just after thermalization between the positive ion and the electron (negative ion) of the same pair is r_0. The probabilities for recombination and dissociation are obtained from boundary conditions expressed in terms of carrier concentrations at $r=0$ and $r=\infty$. There is little experimental or theoretical information upon which to base a prediction of the magnitude of r_0 under various modes of excitation; however, we can infer certain properties of r_0, its temperature dependence, and to some extent its dependence upon medium. Although these inferences are speculative they nonetheless give some insight into the relaxation processes involved in establishing a given r_0.

In spherical coordinates, the radial particle current is

$$\frac{I}{4\pi r^2} = -D\frac{\partial}{\partial r}n(r)+n(r)\,\mu E(r). \tag{1}$$

For a Coulomb interaction, $E(r)=-e/\epsilon r^2$, the solution of (1) is

$$n(r) = \left\{\frac{I}{4\pi D}\int_r^{r'}\frac{1}{x^2}\exp[-e^2/\epsilon kTx]\,dx+C\right\}\exp[e^2/\epsilon kTr]. \tag{2}$$

Equation (2) is exact for only one mobile carrier. If both carriers are mobile then the arithmetic average of their respective μ's and D's should be used. The form of the results is of main concern. The upper bound of the integral represents the distance of closest approach without recombination for a pair of opposite charges.

Equation (2) is general for a Coulomb interaction and can be used to solve problems of recombination, dissociation, and escape over a barrier. Distinction between the three cases lies in the boundary conditions employed.

Suitable boundary conditions for recombination are $n(r')=0$ and $n(\infty)=n_0$, the average bulk carrier density. Then with use of the Einstein relation, $D=\mu kT/e$, (2) reduces to

$$I = n_0\,4\pi\mu e/\epsilon\{1-\exp[-e^2/\epsilon kTr']\}^{-1}. \tag{3}$$

Since the recombination coefficient, R, is the current per unit density, I/n_0, then

$$R = 4\pi\mu e/\epsilon\{1-\exp[-e^2/\epsilon kTr']^{-1}, \tag{4}$$

which for $e^2/\epsilon kTr \gg 1$ becomes the well-known Langevin[5] formula for recombination. Putting μ in terms of D yields the Debye[6] result for ions of equal diffusivity.

For dissociation, the boundary conditions become $n(\infty)=0$ and $n(r')=n_0$ where n_0 is the effective density of one charge in the volume of closest approach. In this case $C=n_0\exp(-e^2/\epsilon kTr')$ and the solution for I is

$$I = \frac{4\pi\mu e n_0}{\epsilon}\exp[-e^2/\epsilon kTr']\{1-\exp(-e^2/\epsilon kTr')\}^{-1}. \tag{5}$$

Since I is the flow away from one center, it is the specific decay rate of a pair. Once again the term in parentheses is negligible for $e^2/\epsilon kTr' \gg 1$.

Escape of a particle over a Coulomb barrier when the particle has initially come into thermal equilibrium with the lattice at r_0 is handled through equation (2) with boundary conditions $n(r') = 0$, $n(\infty) = 0$, and $n(r_0) = n_0$. In this situation n_0 is the effective density of one particle in a thin spherical shell of radius r_0.

Integration from r' to r_0 gives the recombination current, I_{recomb}, while integration from r_0 to ∞ gives the dissociation current, I_{dis}. Thus the probability for escape, P_{esc}, is

$$P_{\text{esc}} = \frac{I_{\text{dis}}}{I_{\text{dis}} + I_{\text{recomb}}} = \exp(-e^2/\epsilon kTr_0). \tag{6}$$

The probability that an electron escapes from an oppositely charged center following an ionizing event is found to be an exponential function of the product $1/Tr_0$, and thus the temperature dependence of the escape probability depends on $1/Tr_0$. At room temperature an r_0 of about 20 Å corresponds to a yield (P_{esc}) of about 10^{-4}.

Photoionization or impact ionization in the presence of an applied field requires a correction to equation (6) for the field perturbation. Onsager[7] has calculated the necessary correction and obtained

$$P_{\text{esc}} = \exp\{(-e^2/\epsilon kTr_0)\}(1 + \tfrac{1}{2}e^3 E_a/k^2T^2). \tag{7}$$

Thus, one should extrapolate to zero field to get information on r_0.

A one-dimensional case which resembles photoionization is the emission of an energetic electron from a metallic electrode into an insulating lattice. In this case it is desired to find the current in the presence of an applied field and the image field. To do this a modified form of equation (1) was used, the principle feature of which is the inclusion of an emission current, $j_0 \exp(-x/x_0)$. This term arises by statement of the n_0 boundary condition in terms of the initial emission current density of high energy electrons, j_0, including the effects of relaxation to near thermal equilibrium with

the lattice through the factor $\exp(-x/x_0)$ and making the density of thermal electrons equal to zero at the electrodes.

To arrive at the relaxation term we imagine a flux of energetic electrons initiating from $x=0$ in a lattice in which the field driven drift velocity is small relative to an average emission diffussion velocity. It is assumed that the distribution in energy, W, of the effective diffusion constant $D(W)$ can be adequately represented by an average, D_e, and that the energy loss of the energetic particles can be treated with a relaxation time, $1/k$. Thus the representative diffussion velocity may be taken constant and combination of the continuity equation $\nabla \cdot j_e + kn_e = 0$ with the diffusion equation $j_e = -D(\partial n_e/\partial x)$ shows $j_e = j_0 \exp(-x/x_0)$; $x_0 = (D_e/k)^{1/2}$. The current from a planar electrode is now given by the sum of the emission current, and field driven current,

$$j(x) = j_0 \exp(-x/x_0) - D\frac{\partial n(x)}{\partial x} + n(x)\mu E(x). \tag{8}$$

The field includes both applied field, E_a, and image field, $-e/4x^2$, for unit dielectric constant.

Carriers successfully surmounting the potential maximum caused by the image barrier can escape, thus the probability of escape is $P_{\text{esc}} \simeq j(x_m)/j_0$ where $x_m = (e/4E_a)^{1/2}$ is the position of potential maximum. At this point the field driven term vanishes and if the diffusion current is small relative to the emission current then

$$P_{\text{esc}} \simeq \exp(-x_m/x_0), \tag{9}$$

a form analogous to (6) for ionization in the bulk and similar to a result derived by Chandrasekhar[8] for one-dimensional diffusion over a barrier.

One can calculate the form for the temperature dependence of yield in either the radial case or the planar case through the $1/Tr_0$ factor in the exponent of equation (6) or (9). Either r_0 or x_0 is proportional to $(D_e)^{1/2}$. If it is assumed that D_e is proportional to T^{-1}, as follows if the scattering length is determined by

fluctuations in the lattice density and independent of particle kinetic energy in excess of kT; then

$$P_{esc} = \exp(-\gamma T^{-1/2}) \tag{10}$$

rather than the usual $\exp(-\gamma' T^{-1})$ form.

Discussion

The above ideas are consistent with several bits of evidence. First among these is the recent observation of "hot electron" emission into liquid helium.[9] When liquid helium is prepared in pure form then because of its low polarizability it makes an almost ideal insulator and serves as suitable test for equation (9). Silver *et al.*[9] injected energetic electrons into liquid helium from a metallic electrode and found the current to follow equation (9).

Hummel and Allen[10] have made careful measurements of carrier yield and its temperature dependence in liquid hexane irradiated with 1 MeV β particles. They extrapolated all their data to zero applied field to avoid uncertainties in field correction. They found the number of ions to be given by

$$N = \int_0^{10^6} P(W) \exp(-e^2/\epsilon k T r_0)\, dW. \tag{11}$$

The function $P(W)$ used by Hummel and Allen is shown in Fig. 1. They assumed $r_0 = aW_0^2$ where W_0 was the initial energy of the particle. Such a treatment seriously underestimated the yield or carriers for lower energies. A second possibility was tried in which

$$r_0 = 75\ \text{Å} + aW^2. \tag{12}$$

This attempt correlated with experiment very well for all particle energies at 300°K, but failed to correlate with the observed temperature dependence. Their experimental results and their calculations using (11) and (12) are shown in Fig. 2. Taking into account the temperature dependence for r_0 given by equation (10) results in much better correlation with experiment as is shown in Fig. 2.

There is little data concerning photocurrents in liquids which can be compared with solids except that obtained by Chaiken and Kearns.[11] They measured the quantum yield of photocurrent in

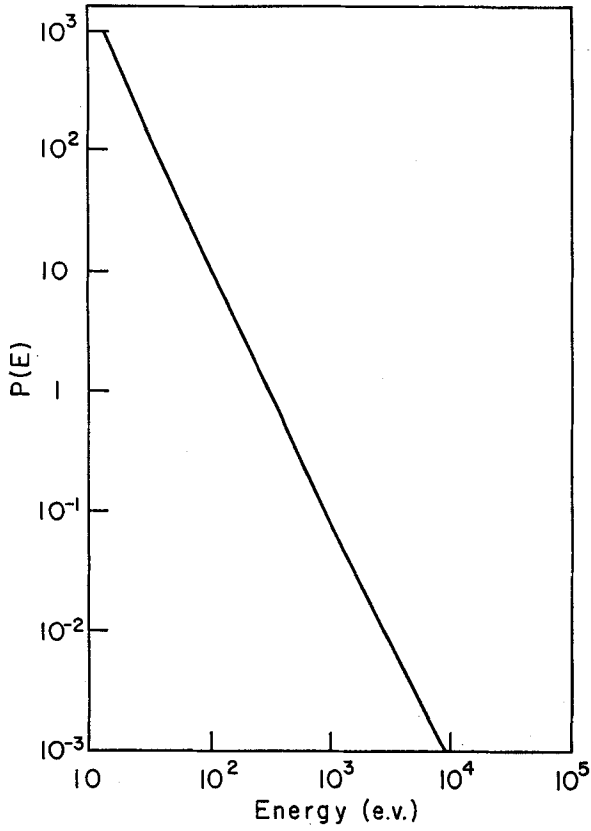

Figure 1. Number of secondaries ejected with energy E from a 1 MeV β particle excitation as a function of E. Taken from A. Hummel and A. O. Allen, *J. Chem. Phys.* **46**, 1602 (1967).

anthracene melt (227°C) and also in anthracene crystal (200°C) below the melting point (217°C). They found that the yield in the melt was about ten to twenty times smaller than in the crystal. This result and the present model can be used to estimate the

importance of "geminate recombination" in anthracene crystals at room temperature. Assuming that the relaxation of low energy electrons in anthracene melt is similar to that in liquid hexane then the approximate 75 Å value of r_0 found by Hummel and Allen[10] at 300°K can be scaled to 500°K for anthracene melt. Then $r_0 = 58$ Å and $\exp(-e^2/\epsilon kTr_0) = 0.115$ in the melt. The yield in crystals is

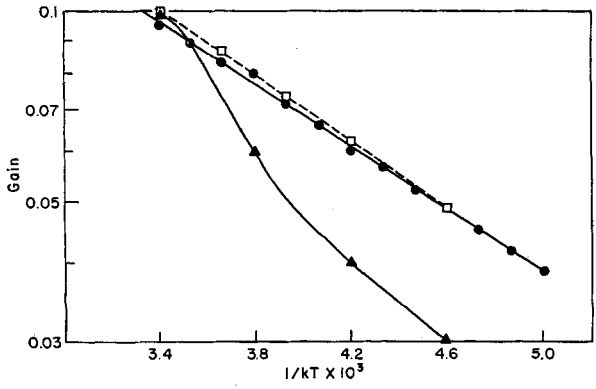

Figure 2. Temperature dependence of the yield of carriers per 100 eV of incident energy due to β particle excitation in hexane; solid circles experimental results; and triangles calculations taken from A. Hummel and A. O. Allen, *J. Chem. Phys.* **46**, 1602 (1967); squares calculated yields including temperature dependence of r_0.

about ten times larger and therefore at 200°C the exponential term is about unity and r_0 is about 125 Å. Scaling this factor back to room temperature results in a yield of about 0.2. Thus "geminate recombination" can account for at most a reduction of the yield to 1/10. The observed 10^{-4}–10^{-5} yield must in large part be due to other inherent factors.

Coppage and Kepler[1] have observed a temperature dependence of ruby laser induced bulk photoconductivity and have claimed a correlation between these results and the temperature dependence of photoconductivity excited with strongly absorbed light. The apparent correlation was attributed to operation of a similar sharp cut-off model in both instances with no temperature dependence

of r_0. Using the temperature dependence for r_0 as proposed here, then the apparent correlation can only be viewed as accidental.

In summary a model concerning escape of an electron from a potential well is discussed. The initial separation, r_0, of the charged pair is determined by the relaxation of an ejected energetic electron to lattice temperature. The model was shown to be consistent with experiment in two cases and to permit useful estimations and comparisons in others.

REFERENCES

1. Coppage, F. N. and Kepler, R. C., *Mol. Cryst.* **2**, 231 (1967).
2. Pope, M. and Burgos, J., *Mol. Cryst.* **1**, 395 (1966).
3. Kepler, R. G. and Coppage, F. N., *Phys. Rev.* **151**, 610 (1966).
4. Hummel, A., Allen, A. O. and Watson, F. H., *J. Chem. Phys.* **44**, 3431 (1966).
5. Langevin, P., *Ann. Chem. Phys.* **28**, 287, 433 (1903).
6. Debye, P., *Trans. Electrochemical Soc.* **83**, 265 (1942).
7. Onsager, L., *Phys. Rev.* **54**, 554 (1939).
8. Chandrasekhar, S., *Rev. Mod. Phys.* **15**, 63 (1943).
9. Silver, M., Onn, D., Smejtek, P., and Masuda, K., *Phys. Rev. Lettrs.* **19**, 626 (1967).
10. Hummel, A. and Allen, A. O., *J. Chem. Phys.* **46**, 1602 (1967).
11. Chaiken, R. F. and Kearns, D. R., *J. Chem. Phys.* **45**, 3966 (1966).