Kinetics of electron trapping reactions in amorphous solids; a non-Gaussian diffusion model

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Decay patterns of trapped electrons in aqueous glasses have been analyzed over the time span of more than eight decades in terms of a time-dependent "rate constant" of the form $t^{\alpha-1}$, $0 < \alpha < 1$, which can be derived from the long-tail hopping-time distribution of Scher and Montroll. The curve fitting of experiments in our model is quite satisfactory with $\alpha \sim 0.1$ and with another adjustable parameter which depends on the trapping species and varies within one order of magnitude from one system to another. The time-dependent spectral shift for the absorption spectrum of trapped electrons can also be fitted by $\alpha \sim 0.1$, providing fairly direct evidence that non-Gaussian diffusion of electrons from shallow to deep traps underlies the $t^{\alpha-1}$ dependence.

INTRODUCTION

When excess charges are introduced in a solid with a constant external field, it is well known that a transient current flows for a certain period until a steady state is established. For disordered materials of low mobilities, this transient period can be quite extensive. Scher and Montroll[1] made the first quantitative analysis of transient photocurrents in terms of the continuous-time-random-walk (CTRW) model of Montroll and Weiss.[2] The crux of the Scher-Montroll formalism is the specific nonexponential form of the hopping-time distribution[3] $\psi(t)$ which characterizes the electron dynamics in amorphous media.

The purpose of this paper is to apply the CTRW model for the decay dynamics of trapped electrons in the presence of electron-accepting impurities in amorphous media. Specifically we are interested in testing the applicability of the Scher-Montroll form of $\psi(t)$ for our problem.

Excess electrons trapped in rigid glassy matrices have often been observed to react slowly with electron-accepting impurities.[4,5] Typically, no simple conventional rate law is obeyed, successive half-lives increasing greatly. Related phenomena include spontaneous recombination[5,7] and marked changes in optical-absorption spectra of trapped electrons.[8] The rates may be independent of temperature over a wide range.[7,9]

The peculiar modes of electron decay and the apparent absence of temperature dependence have been described by a tunneling mechanism[9,10] which invokes direct electron-transfer processes between acceptors and the *initial* solvent traps over a typical distance of ~50 Å. Although the barrier-penetration model for electron tunneling gives the same exponential dependence of the transfer rate on the two-site separation distance as more rigorous theories[11,12] of electron-transfer processes, the

applicability of the tunneling theory and its implication, such as the absence of temperature dependence of the transfer rate even for highly nonresonant transfers, are questionable. Moreover, the absence of electron transport in the tunneling mechanism is an assumption which is difficult to justify and is not consistent with experiments.[8]

We will show that a certain class of decay patterns for trapped electrons in aqueous glasses can be described by the time-dependent scavenging "rate constant" of the form $t^{\alpha-1}$, with $0 < \alpha < 1$. Furthermore, this particular time-dependent form is shown to be consistent with the long-tail jump time distribution function for a random walk in disordered materials.

KINETIC SCHEME

The system under consideration consists of trapped electrons in the matrix and impurity molecules (acceptors) whose concentration is far in excess of that of the electrons. In this section we are interested in the survival fraction of the electrons as a function of time. Our model is based upon the following assumptions: (i) The electron concentration is so low that the electron-electron interaction and correlation are negligible; (ii) the reactions of electrons with acceptors are "diffusion-controlled," although the electron diffusion itself can not be described by a simple classical scheme with a constant diffusion coefficient throughout the system; (iii) in comparison with experiments, the optical absorbance for the trapped electrons is assumed to be proportional to the number of electrons which have survived the scavenging reactions.

Under these assumptions, the number of electrons at time t, $N(t)$, obeys the equation

$$\frac{dN(t)}{dt} = -C_s k(t) N(t) , \qquad (1)$$

where C_s is the acceptor concentration and $k(t)$ is the number of electrons reacting with acceptors of unit concentration at time t (i.e., the rate constant). Integration of (1) gives

$$\frac{N(t)}{N_0} = \exp\left[-C_s \int_0^t k(t)\,dt\right],\qquad (2)$$

where N_0 is the initial number of electrons, which is not directly observable. Similarly the initial time is also not well defined in many experiments. As we shall explain later, the very short-time behavior of $k(t)$ is not sensitive to the long-time result for $N(t)/N_0$ and N_0 takes the role of an adjustable parameter. We also note that by experimental as well as theoretical reasons, $k(t)$ is a more desirable observable, as recombination luminescence[7] intensity, for example, than the survival fraction, although we shall be concerned mainly with the latter in this paper.

The usual diffusion treatment[13] gives

$$k(t) = 4\pi DR\left[1 + R/(\pi Dt)^{1/2}\right],\qquad (3)$$

where D is the diffusion coefficient and R is the reaction radius. For long-time behavior the Smoluchowski transient becomes negligible so that Eqs. (2) and (3) predict essentially an exponential decay of trapped electrons. As long as the jump time is constant or has an exponential distribution, the random-walk treatment[14] of this problem gives basically the same result for a long time decay pattern.

For the time being let us assume that the rate constant $k(t)$ behaves as

$$k(t) = B t^{\alpha-1},\qquad (4)$$

where B and α are time-independent constants. Substitution of (4) into (2) gives

$$\log_{10}\log_{10}[N_0/N(t)] = \log_{10}(B'C_s/2.3)$$
$$+ \alpha\log_{10}t;\quad B' = B/\alpha.\qquad (5)$$

Using assumption (iii), the ratio $N_0/N(t)$ can be equated to the ratio of optical absorbances A^0/A, leading to

$$\log_{10}\log_{10}(A^0/A) = \log_{10}(B'C_s/2.3) + \alpha\log_{10}t.\qquad (6)$$

We shall call the parameter B' as the efficiency factor

EXPERIMENTAL EVIDENCE

Measurements by Miller[9] in the range 10^{-6}–10^3 sec for $6M$ aqueous NaOH at $\geqslant 77$ K are most valuable for considering the effects of time, temperature, acceptor efficiency, and concentration. The outstanding facts requiring explanation are (1) the approximately linear decrease in the optical absorbance of trapped electrons e_t^-, with the loga-
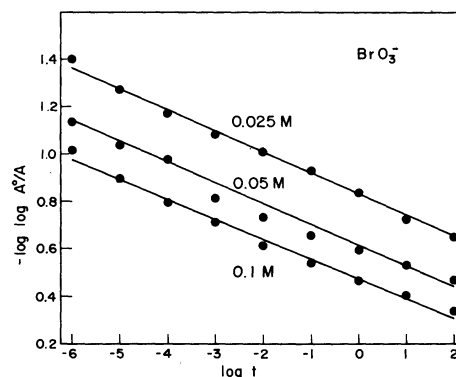

FIG. 1. Decay of the normalized optical absorbance at 550 nm of the trapped electron in aqueous $6M$ NaOH at 77 K. The data points are taken from Fig. 5 of Ref. 6. Values of A^0 are 0.86, 0.70, and 0.46 for 0.025 M, 0.05M, and 0.1M BrO_3^-.

rithm of time, (2) the lifetime of e_t^- decreasing 10^6-fold for a tenfold increase in acceptor concentration and (3) diffusion[8] of e_t^- in rigid glassy solids, even at low temperature.

In terms of the tunneling model, BrO_3^- was considered to be abnormal and an arbitrary "inefficiency factor" of 10^{-11} was assigned. The data appear in Fig. 1 (as points) plotted according to Eq. (6). The slopes are nearly equal, 0.087. The large change in lifetime with acceptor concentration arises from the very small slope.

Values of A in Fig. 1 are the same as A/A^0 reported by Miller,[9] i.e., the absorbance at 550 nm in the doped glass relative to that for the undoped glass at the same time. Equation (6) requires further normalization to A^0, the absorbance at time zero, which is not directly measurable. The parameter A^0 must be established by trial, in part because e_t^- decays rapidly at $\leqslant 10^{-6}$ sec, and in part because of spectral change.
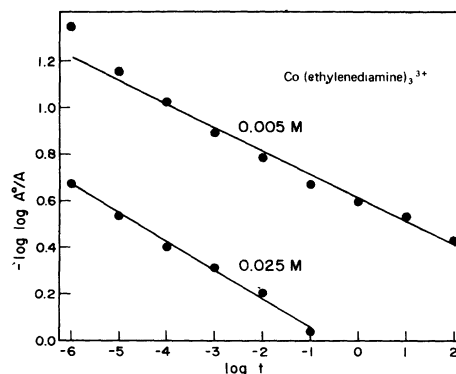

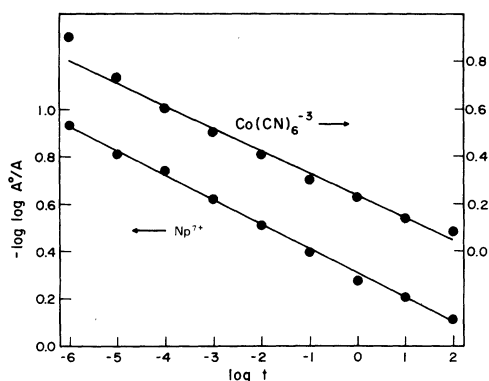FIG. 2. Similar to Fig. 1. Values of A^0 are 1.00 and 0.80 in 0.005M and 0.025M Co(ethylenediamine)$_3^{3+}$.

FIG. 3. Similar to Fig. 1. Values of A^0 are 1.00 for 0.025M Co(CN)$_6^{3-}$ and 0.76 for 7.7×10^{-3}M Np^{7+}

In terms of tunneling Co(ethylenediamine)$_3^{3+}$ was normal with an efficiency factor of unity. The slopes of the lines in Fig. 2 are 0.100 and 0.080. The efficiency factor for Co(CN)$_6^{3-}$ was also taken as unity, but that for Np^{7+} was 10^4.[9] The data in Fig. 3 give slopes 0.096 and 0.103, respectively.

The relative efficiencies (i.e., B') of these electron acceptors in terms of Eq. (6), from Figs. 1–3 and in the order of presentation, are 0.1, 0.5, 0.4, and 1.

The ordinates for 0.05 and 0.1M BrO$_3^-$ should be shifted by log 2 and log 4 relative to the data for 0.025M BrO$_3^-$. The actual shifts are 0.22 and 0.58. From Fig. 2 the shift is 0.60 rather than log 5.

The decay of absorbance at 875 nm in undoped 6M NaOH at 77 K is also fitted by Eq. (6). The slope is 0.100, providing evidence that spectral relaxation of e_t^- involves diffusion of the electron.

In 1-propanol at 108 K the decay of e_t^- absorbance at 1300 nm and growth at 550 nm (Ref. 8) are both fitted by Eq. (6). The slopes are ~0.5 and ~0.6, respectively. Again, diffusion of e_t^- is indicated and also supported by the effect of scavenger to suppress the increase of absorbance at 550 nm.[8]

RANDOM WALK MODEL

We now turn to the theoretical basis for Eq. (4). In order to calculate $k(t)$ by the theory of random walk, we need to calculate the flux of walkers arriving at the sink, which is chosen to be the origin of the lattice, as a function of time. Each lattice site is initially occupied by the walker with equal probability.

The flux at the origin, $I(t)$ is then given by

$$I(t) = \sum_{s \neq 0} F(s, t), \qquad (7)$$

where $F(s, t)$ is the probability density of reaching the origin for the first time at time t starting from site s. Following Montroll and Weiss,[2] the Laplace

transform of (7) is given by

$$I(u) = \sum_{s \neq 0} \sum_{n=0}^{\infty} F_n(s)[\psi^*(u)]^n, \qquad (8)$$

where $F_n(s)$ is the probability that a random walker reaches the origin for the first time at step n starting from s, and $\psi^*(u)$ is the Laplace transform of the hopping-time distribution function $\psi(t)$:

$$\psi^*(u) = \int_0^{\infty} \psi(t)e^{-ut} dt. \qquad (9)$$

Equation (8) can be written

$$I(u) = \sum_{s \neq 0} F(s, \psi^*(u)), \qquad (10)$$

where $F(s, z)$ is the generating function for $F_n(s)$:

$$F(s, z) = \sum_{n=1}^{\infty} F_n(s)z^n. \qquad (11)$$

Using the random-walk generating function, which is defined by

$$P(s, z) = \sum_{n=0}^{\infty} P_n(s)z^n, \qquad (12)$$

where $P_n(s)$ is the probability that the random walker is at the origin after n steps starting from s, and the equalities[2]

$$F(s, z) = [P(s, z) - \delta_{s,0}]/P(0, z), \qquad (13)$$

and

$$\sum_s P(s, z) = (1 - z)^{-1}, \qquad (14)$$

Eq. (10) becomes

$$I(u) = \frac{1}{[1 - \psi^*(u)]P(0, \psi^*(u))} - 1. \qquad (15)$$

Scher and Montroll[1] and Shlesinger[3] have shown that certain transient photocurrents in amorphous materials can be described by the hopping time distribution of the following asymptotic form:

$$\psi(t) \sim [At^{1+\alpha}\Gamma(1-\alpha)]^{-1}, \quad 0 < \alpha < 1, \qquad (16)$$

where A is a constant and Γ is the gamma function. The Laplace transform of (16) is given by[3]

$$\psi^*(u) = \exp(-u^\alpha/A) \sim 1 - u^\alpha/A, \quad u \to 0. \qquad (17)$$

The asymptotic form of $P(0, z)$ is also known for a simple cubic lattice[2]

$$P(0, z) \sim 1.516\,386 - (3/\pi)(\tfrac{3}{2})^{1/2}(1 - z)^{1/2} + \cdots. \qquad (18)$$

Using (17) and (18), the asymptotic form $(u \to 0)$ of (15) can be written

$$I(u) \sim \beta A u^{-\alpha}, \quad u \to 0 \qquad (19)$$

where $\beta = 0.659\,46$. The Laplace inverse of (19) gives the long-time asymptotic form for $I(t)$:

$$I(t) \sim \frac{\beta A t^{\alpha-1}}{\Gamma(\alpha)} \equiv \frac{\beta A'(wt)^{\alpha-1}}{\Gamma(\alpha)}, \qquad (20)$$

where w is the characteristic rate constant of the system. Equation (20) is valid when the dimensionless wt is much greater than unity. Since $I(t)$ and $k(t)$ are related only by a scaling factor, Eq. (20) provides a *qualitative* justification for the empirical expression (4).

Use of the asymptotic expression (4) in (2), which involves integration from time zero to t, requires an explanation. The situation is quite analogous to the usual practice of using a time-independent rate constant k, which is only the asymptotic value, $4\pi DR$, of (3) in the Smoluchowski treatment, and of integrating from time zero to t, to obtain an exponential decay of the survival fraction. Such an approximation, however, turns out to be quite accurate for a long-time survival fraction, $N(t)/N_0$, compared to those which can be obtained using an accurate $k(t)$ by the continuous-time-random-walk model[14] or even using (3) itself. A special case of the hopping-time distribution function, which prescribes the entire region of time scale and gives the asymptotic form (16) with $\alpha = 0.5$ (i.e., the second repeated integral of the error function),[1] has also been considered[14] in detail, in which $\ln(N/N_0)$ is shown to be a linear function of $t^{1/2}$ except for a very small dimensionless time wt. This result could have been obtained directly by substituting the asymptotic form (20) with $\alpha = 0.5$ into (2).

DISCUSSION

The key point of this paper is to demonstrate that the concept of transient electron transport is consistent with the logarithmic decay of trapped electrons, and the absence of diffusion assumed in the tunneling scheme is not necessary. The transient transport arises from the highly dispersive hopping-time distribution of the disordered material in the Scher-Montroll[1] model. A recent work by Noolandi[15] showed that the multiple-trapping theory is basically equivalent to the theory of

Scher and Montroll. In addition to the mathematical simplicity, Noolandi's work shows that at higher temperature the electron transport becomes nondispersive. This is in agreement with experiment for electron reactions in glasses.[9]

The choice between the random-walk model and the multiple-trapping theory may depend upon the details of electronic structure of the system.

Our scheme of arranging the experimental points in $\log\log(A^0/A)$ versus $\log t$ plots has the advantage of a much smaller efficiency factor ($\sim \times 10$) than those required in the curve-fitting process for tunneling ($\sim 10^{18}$). The effect of varying the acceptor concentration is to shift the curve without changing the slope and, for a given observation time, $N(t)$ is an exponential function of the acceptor concentration.

According to our scheme, temperature dependence of the decay pattern is contained in those of w and α in (20), which is related to the structure of the amorphous material and to the detail of the electron-phonon interaction.

For the hopping transport in amorphous materials, Mott[16] has shown that the activation energy is independent of temperature in the high-temperature range, while the jump frequency takes the form of $\nu \exp(-B/T^{1/4})$ in the low-temperature range; the temperature dependence is effectively reduced because of the increased participation of distant neighboring sites for the hopping motion.

It should also be noted that most of the electron traps in low-temperature glasses are not in a fully relaxed state. Increase in temperature for an electron in such metastable traps may result in two opposite effects as far as the rate of release of this electron is concerned. The first is simply to increase the jump rate because of the increased phonon population in the vibrationally excited states. The other is to increase the trap depth due to an enhanced relaxation rate at the higher temperature, resulting in a net decrease in the jump rate. For a certain range of temperature, these two effects may cancel each other to make the decay pattern apparently temperature independent. A more detailed explanation of the temperature effect is certainly desirable.

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