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Conjectures on random-walk models of electron migration and spectral relaxation in molecular glasses

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A recent suggestion by Funabashi and Hamill that trapped electrons in molecular glasses may display a continuous-time random walk is critically analyzed.

In recent articles, Funabashi and Hamill[1] made an interesting suggestion that the behavior of excess electrons (e_t^-) trapped in aqueous glasses doped with ionic salts and alcoholic and alkane glasses, might be related to the photocurrent phenomenology of certain amorphous semiconductors. In the latter systems, measurements of carrier drift mobility by time-of-flight techniques showed unusual current-vs-time behavior. At short times the current j can be represented by the power law $j \propto t^{-1+\alpha}$, while at long times by $j \propto t^{-1-\alpha}$.[2] The change in time dependence occurs when a significant fraction of the fastest carriers are collected at one or other of the electrodes, and $0 \leq \alpha \leq 1$. These observations precipitated the development of a continuous-time random-walk (CTRW) model by Scher and Montroll.[2] Noolandi[3] has shown how, in the continuum limit, such a model of carrier transport is essentially transfer from the injection site via intermediate traps (dispersed in both relative energy and mutual separation distance) to the collection electrode. The translation probability of site-to-site transfer appears to be of an exchange type, and so exponentially dependent on the distance of separation of trapping sites. Funabashi and Hamill[1] remarked on a dispersion in the reported mobility of excess electrons in glassy systems,[4] and used this hallmark of CTRW to justify their suggestion that excess electrons in glasses move by CTRW.

It is the purpose of this article to remark that there is a large body of evidence which argues strongly against such a view of excess electron transport in glassy-molecular solids and to consider some of these points.[5]

Recent work has shown unequivocally that the reported excess-electron-drift-mobility measurements[4] were artifactual.[6] Whether using light from a quartz halogen lamp, a xenon flash lamp, or a Q-switched ruby laser, the photostimulated current due to trapped electrons has a time dependence similar to the intensity of the light source; and so the lifetime of the trapped electron in a conducting state is short ($\lesssim$10 ns).[6] Following the peak light intensity, the photostimulated current delays monotonically and at some time t (in seconds) the current signal-to-noise ratio is approximately unity. The electrical current density at this time is $\lesssim 10^{-9}/t$ A m^{-2} (which reflects the greater sensitivity of measuring currents at longer times, since larger RC smoothing time constants can be used). During such experiments the light fluence (photons m^{-2}) is comparable to or greater than the number density of trapped electrons times the sample thickness. Providing the sample's optical density is at least of the order unity,[6] and the quantum efficiency of promotion to an excited state in which the electron is mobile is also of the order unity (~0.1–0.3, according to Nguyen and Walker[7]), then most trapped electrons will be photoexcited to the conduction state at least once during photostimulation. Consequently the flux of electrons after photoexcitation and on returning to a nonconducting state is $\lesssim 10^{10}/t$ m^{-2} s^{-1}; using the Nernst-Einstein relation, this corresponds to a diffusion coefficient of ~$10^{-21}/t$ m^2 s^{-1} for a trapped-electron concentration of 3×10^{-5} mol dm^{-3}. Can such a flux of trapped electrons account for the trapped electron decays observed in irradiated glasses containing electron scavenger? The particle current of electrons towards scavengers is $k_T(t)[e_t^-]$, where $k_T(t)$ is the macroscopic (time-dependent) tunneling rate constant defined by Rice and Pilling[8] and ~ $10^{-28}/t$ m^3 s^{-1} from Miller's studies.[9] With $[e_t^-] \sim 3 \times 10^{-5}$ mol dm^{-3}, the particle current of electrons towards scavengers is ~$2 \times 10^{-6}/t$ s^{-1}. If the reaction radius of an electron-scavenger pair is 1 nm (the largest likely if e_t^- is still to be observable in the presence of 0.1 mol dm^{-3} electron scavenger), the flux of trapped electrons towards scavenger molecules is $\gtrsim 10^{11}/t$ m^{-2} s^{-1}. Using the Smoluchowski expression for a diffusion-limited rate constant, this corresponds to a time-dependent diffusion coefficient $\gtrsim 10^{-20}/t$ m^2 s^{-1}, and is at least one order of magnitude greater than that estimated from the current after a pulse of visible light had stimulated trapped electrons to a mobile state (followed by their rapid relaxation to a nonconducting state). Hence the transport processes in these experiments must be different.

As no drift currents are measurable and the mobilities are small, there is no evidence for any conductivity of e_t^- in glasses 10^{-9} s to 10^3 s after photoexcitation. Yet that implies any motion of excess electrons in glasses over that time interval is not of the continuous-time random-walk type.

Funabashi and Hamill[1] have suggested that such a trap-to-trap electron migration (cf. the similar suggestion by Buxton and Kemsley[10]) could explain the dependence of the observed decay of the electron concentration and the concomitant changes that occur to the optical-absorption spectra of excess electrons in glasses. They draw a quantitative agreement to CTRW theory. However, the only experimentally observable characteristic of this theory is a current-vs-time relation, whose dependence is of the form $j \propto t^{-m}$, where $1 < m < 2$ for external absorption, and even m cannot be predicted from our limited knowledge of amorphous semiconductors, as yet. Rice and Pilling[8] have discussed the behavior of excess electrons in both glassy and liquid systems and have shown that the decay of the electron concentration is in semiquantitative agreement with the prediction of direct-tunneling models[9-12]; often the agreement is quantitative. It is worthwhile to reconsider some of the more salient points. In a series of elegant experiments, Miller[9] has followed the decay of the excess electron in glassy 6 M NaOH(aq) alcohols, ethers, and alkanes due to the presence of an added electron scavenger (electron decay in the absence of an electron scavenger is small[9]). In all cases the observed decays are well described by a simple model of direct electron tunneling (long-range electron transfer) from the localized trap to a scavenger molecule. At a particular time (e_s^-) is exponentially dependent on scavenger concentration (i.e., it decays by a pseudo-first-order reaction). In addition, to a good approximation, $\ln(e_s^-)$ is linear in $\ln t$, which is predicted because the transfer probability is dependent exponentially on distance. The exponential factor monitors the attenuation of the eigenfunction of e_s^-, and it correlates well with independent estimates of the solvated electron binding energy. The pre-exponential factor (Franck-Condon weighted state densities) is quite well correlated with the exothermicity of the overall electron-transfer process.[13,14] From 77 to 140 K these two quantities are constant to within experimental error. At and above the glass transition temperature (hydrodynamic) diffusion begins, and the predicted change in time-dependent rate constants has been seen by Miller[8] and Buxton and Kemsley.[10] In these studies, electron migration to neutral scavengers is not driven by a Coulomb interaction, nor at these low temperatures (4–100 K) is thermal promotion likely.[10,15] Funabashi and Hamill[1] derived some justification for their usage of CTRW ideas from the recent suggestion of Baxendale and Sharpe[16] that the electron migrates by trap-to-trap or thermally activated hopping (Buxton and Kemsley[10] had made similar suggestions in 1975). However, Miller[9] has shown that these suggestions are open to considerable doubt, and indeed may be reconciled with the ideas of direct tunneling.[8]

Many reports have been made of the luminescence emitted by the excited state(s) formed subsequent to the recombination of ions produced by radiolysis or photolysis,[17] in a wide range of solvents at temperatures from 4 to 150 K. Almost without exception the recombination luminescence decays at t^{-m} where $0.8 < m < 1.8$. Such delays are consistent with the direct-tunneling model, providing the distribution of electron-cation pairs is correlated,[12] for which there is considerable independent evidence.[18] Furthermore, the enhancement of the recombination luminescence by application of an external electric field is in excellent agreement with the direct-tunneling model.[11] Finally, in other experiments, Miller[9] and Zamaraev and Khairutdinov[19] showed that electrons (or even holes) formed by radiolysis of glasses could be temporarily localized (and observed) on an ionic or molecular solute which is a moderately strong electron acceptor, and subsequently transfer to a second solute of greater electron affinity. (The latter process occurs with similar kinetics to e_s^- transfer to scavengers in glasses.) However, in this case e_s^- transfer to the solute of greater electron affinity is mediated by an intermediate site. As this intermediate is a molecular state, the quantum-mechanical aspects of electron-transfer processes[13,14] prohibit more than one intermediate site being invoked in the transfer of any one electron. Such studies are hard to reconcile with the CTRW model.

Funabashi and Hamill[1] concur with other workers[20] that the reactions of solvated electron in liquids display hydrodynamiclike motion. The time constant for a long-time-absorption spectrum of e_s^- to develop in liquids is generally in good agreement with the monomer dielectric relaxation time of that solvent.[21] It is widely accepted that the electron solvation occurs by local solvent reorientation and the quantitative details of this clustering process are emerging.[22] In glasses spectral changes occur over many decades of time, showing a blue shift in the absorbance maximum, from 1000 to 2000 nm at 1 ns to about 500–800 nm at 1 s after formation.[8,16,23] To relate such gross changes of spectrum to the changes in distribution of electrons in traps of different depths, as the electrons transfer progressively to stronger binding sites (rather than deepening their initial traps), is an interesting idea. Yet it should be remarked that at present there is no unequivocal evidence of such a process. To our knowledge, no significant optical-absorption changes have been reported for those systems which do display CTRW current-vs-time behavior. Indeed perhaps such optical effects should be sought. Furthermore, as Funabashi and Hamill have conceded, some solvent reorientation around e_s^- probably occurs in glasses too.[24] The latter are expected to exhibit more extensive local order than a liquid since much of the fluctuating dynamical structure of the fluid has been literally frozen in. At subpicosecond times electrons will scatter through what appears to be a quasicrystalline matrix until becoming initially localized at the nearest site with a favorable configuration.[22] At longer times, the glass does display soft local modes of motion which may contribute to the observed reorientation effects about the electron. However, the relative times scales of molecular motion and nonradiative relaxation rates, tunneling, and reactive encounters differ by orders of magnitude on moving from liquid to glass, so one is not justified *a priori* in extrapolating from one phase to the other. Johari[25] has observed considerable dispersion in dielectric relaxation times for glassy systems, and this is also probably important in interpreting spectral relaxation effects of e_s^- in glasses.

In conclusion, there is no experimental or theoretical evidence at the present time to argue that any form of CTRW of e_s^- occurs in glasses. Indeed, we have endeavored to emphasize that all available evidence supports the notion that, once localized in a glass, electrons are essentially immobile unless they tunnel directly to an electron acceptor.

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