Small-polaron hopping via defect centres: anomalous temperature and voltage dependence of current through fatty-acid monolayers

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Abstract

We study electron hopping in thin metal–insulator–metal structures which involves two defect centres with a strong electron–phonon coupling. We calculate the dependences of the current, J, on voltage, V, and temperature, T, and show that they are consistent with those observed in molecular monolayers of fatty acids. We analyse in detail an unusual, near-exponential temperature dependence of the current: $J(T) \propto \exp(T/T_0)$ observed at $T \gtrsim 50$ K in eicosanoic acid (C20) organic monolayers sandwiched between Pt electrodes, where the parameter T_0 increases with the bias voltage. We show that at relatively high voltages the two-defect small-polaron hopping results in N-shape current–voltage characteristics which were observed in some organic molecular monolayers.

The technological drive to produce low-cost active and passive devices for electronic circuitry has attracted much interest to molecular monolayers [1–3]. It is natural to expect that the current through an organic monolayer sandwiched between two metal electrodes is dominated by temperature-independent direct electron tunnelling [4]. In particular, this behaviour was reported for fatty-acid monolayers long ago (see, e.g. [5]), as well as in recent publications [6]. Meanwhile, certain samples of the same fatty-acid monolayers reveal a pronounced temperature dependence of the current [7, 8], which is inconsistent with the direct tunnelling mechanism. Moreover, a large body of research has addressed complex conductivity phenomena, such as rectification [9], negative-differential resistance [10], and switching [11] in various organic dielectric monolayers. This diverse and sometimes controversial behaviour of organic monolayers has been the subject of recent discussions [2]. The monolayers are known to contain a certain density of defects, both those intrinsic to the monolayer formation [12] and those induced by subsequent deposition of a top metal electrode [2, 13, 14].

We present here a theoretical model in which deviations from simple tunnelling are attributed to conduction via such defects, by way of two-impurity hopping. We will demonstrate that, in particular, the model is consistent with the anomalous near-exponential temperature dependence observed in recent experiments [8]. Several previous descriptions of impurity conduction in thin dielectric layers have addressed resonant tunnelling via one impurity state [15–17] and electron hopping via two and more impurity states [18]. However, none of these models predict a strong temperature dependence. In each case, the current J through the monolayers of thickness d is proportional to $\exp(-2d/a)$ for direct tunnelling [4–6], and to $\exp(-d/a)$ and to $\exp(-2d/3a)$ for resonant tunnelling via one [15–17] or two impurities [18], respectively. (Here a is a typical decay of the electron wavefunction determined by the height of the metal–dielectric interface barrier, $a \simeq 1$ Å.) Thus, even a small number of molecular chains with two impurities can dominate the conductivity of monolayers when $d \gg a$. The chains with three and more impurities can play a significant role only at extremely high concentrations of defects.

In this paper, we study electron transport through a thin dielectric layer which involves two-defect hopping. Contrary to [18], we consider small-polaron hopping via defects with a strong electron–phonon coupling. We show that the anomalous dependences of current on temperature and voltage, observed in different fatty-acid monolayers [7, 8], are consistent with this mechanism. We systematically compare the results of our calculations with our experimental data on electron transport through organic molecular monolayers of eicosanoic acid (C20 with $d = 2.8$ nm) with Pt contacts. The experiment is reported in detail in [8].

Let us consider a pair of defect centres 1 and 2 with strong electron–phonon coupling separated by a distance r greater than the localization length a. We will assume that only one electron is localized at this pair. In the representation of the creation and annihilation operators a_i^+ and a_i of an electron at the sites $i = 1$ or 2, the Hamiltonian of such a system can be written in the form [19–21]

$$H = \sum_{i=1,2} \left(n_i \epsilon_i + \frac{P_i^2}{2M} + \frac{1}{2} M \omega^2 q_i^2 - n_i \lambda q_i \right) + H_e, \tag{1}$$

where $n_i = a_i^+ a_i$ is the electron occupation number of a site i such that $n_i = 0$ or 1 and $n_1 + n_2 = 1$. In equation (1), the first term represents the 'bare' energy of an electron localized at a site i, which incorporates its possible shift under the applied voltage V; ω is the frequency of a local phonon corresponding to the soft mode q_i interacting with the localized electron; $P_i = -i\hbar \partial/\partial q_i$ is the momentum that is conjugate to the configuration coordinate q_i so that the second term is the operator of the kinetic energy of the centre while the third term represents its elastic energy; M is the mass of the centre. The last term under the summation sign describes the electron–phonon interaction which is proportional to the local lattice distortion with λ being the electron–phonon coupling constant. Electron capture leads to a local reconstruction of the centre, resulting in the shift of the equilibrium value of the configuration coordinate from 0 to $2q_c$ and in lowering the electron energy from E^0 to $E_0 = E^0 - I_p$ by a quantity $I_p = \lambda^2/2M\omega^2$, called the polaron shift. (Here $q_c = \lambda/2M\omega^2$.) The last term in equation (1) is the electron transfer Hamiltonian which is responsible for electron hopping between two sites:

$$H_e = -t(r) \left(a_1^+ a_2 + a_2^+ a_1 \right), \tag{2}$$

where $t(r) = t_0 \exp(-r/a)$ is the hopping (tunnelling) integral.

The electron transport through the thin insulator, which involves two impurity localized states, consists of three steps:

  (i) the jump of a free electron from the left metal contact to a first impurity,

(ii) the jump of the electron from the first impurity to a second one, and

(iii) the jump of the electron to the right contact.

The rate of (ii) is $\nu_{1,2} \propto |t(r_{12})|^2 \propto \exp(-2r_{12}/a)$ and the rates of (i) and (iii) are $\nu_e \propto \exp(-2x_i/a)$, where r_{12} is the distance between the impurities and x_i is the distance between a centre and the nearest contact [16, 18]. From here it follows that when $d \gg a$, the current is determined by the optimum impurity configuration in a chain with $x_i \simeq r_{12} = x_{1,2} \simeq d/3$ [18], where x is the direction along the chain (perpendicular to the contacts). The fact that both $\nu_{1,2}$ and ν_e are exponentially small allows us to employ the non-adiabatic approximation to describe small-polaron hopping [21]. We assume that the concentration of the impurities is high, $N \gtrsim 10^{18}$ cm^{-3}, and that the Fermi level F is actually pinned by the impurity band [19]. The potential barrier height Δ at the metal–dielectric (semiconductor) interface, as a rule, fluctuates strongly [22] from one molecular chain to another and so does the localized electron energy level E_0 which follows Δ. (Within one chain, the fluctuations of E_0 are considered small.) As a result, in the vicinity of F the density of the electron states can be treated as constant, $g(E = F) \simeq g_0$, in a wide energy interval $\delta \gtrsim I_p \simeq 0.1 eV$. This assumption explains the absence of a threshold in the current–voltage characteristics. It also means that the concentration of the impurities involved in the electron transport increases with voltage as $p \simeq g_0 eV_0 |V/V_0|^\alpha$, $V_0 = 1$ V and $\alpha \simeq 1$. Then the current can be written as

$$J \propto p[f_1(1 - f_2)\nu_{1,2} - f_2(1 - f_1)\nu_{2,1}], \tag{3}$$

where f_1 and f_2 are the populations of the first and second impurity centres, respectively. In the case under consideration, $f_1 \simeq 1$ and $f_2 \simeq 0$ (see [18] and further discussion), i.e. the current $J \propto p\nu_{1,2}$ is determined by inter-impurity hopping.

In the two-site polaron model described by the Hamiltonian (1), non-adiabatic inter-impurity hopping is a transition between the initial (with the electron at the left site: $n_1 = 1$, $n_2 = 0$) and the final (with the electron at the right site: $n_1 = 0$, $n_2 = 1$) states of the system. The potential energies of these states (terms), $U_1(q_1, q_2)$ and $U_2(q_1, q_2)$, are different for they correspond to different electronic configurations of the pair. (This is similar, for instance, to two different potential-energy curves corresponding to the bonding and anti-bonding configurations of H_2^+-molecule [23].) The potential energies $U_1(q_1, q_2)$ and $U_2(q_1, q_2)$ are paraboloids of revolutions that have their minima $U_{10} = E_0$ and $U_{20} = E_0 - eV_{12} + \varepsilon$ located at points $q_1 = q_c$, $q_2 = 0$ and $q_1 = 0$, $q_2 = q_c$, respectively, where $V_{12} = Vx_{12}/d$ is the voltage bias between the centres and ε is the difference in their 'bare' ground state energies. The minima are separated by a distance $2\sqrt{2}q_c$. If $V_{12} = \varepsilon = 0$, the minimum potential barrier that separates the paraboloids, $E_a = I_p/2$, is located at a point $q_1 = q_2 = q_c/2$. (This point and the paraboloids' minima belong to the same plane $q_1 + q_2 = q_c$.) This minimum barrier determines high-temperature small-polaron activation hopping between identical centres when $V_{1,2} \to 0$ [21]. Notice that the height of the activation barrier for the contact-to-impurity (i) or impurity-to-contact (iii) hopping is equal to $I_p/4$, i.e. it is half that required for the inter-impurity transition, $E_a = I_p/2$. Therefore, the rates of (i) and (iii) are much higher than that of (ii) and they depend on T and V more weakly then $\nu_{1,2}$ [16, 17]. As a result, the populations $f_1 \simeq 1$ and $f_2 \simeq 0$ as previously suggested. In the plane $q_1 + q_2 = q_c$, the expressions for potential energies of the initial and final terms can be rewritten as

$$U_1(q) = \tfrac{1}{2}M\omega^2(q + q_c')^2 + E_0 = E_a(z + 1) + E_0, \tag{4}$$

$$U_2(q) = \tfrac{1}{2}M\omega^2(q - q_c')^2 + E_0 + \varepsilon - eV_{1,2}$$
$$= E_a(z - 1) + E_0 + \varepsilon - eV_{1,2}, \tag{5}$$

where $q_c' = \sqrt{2}q_c$, $q = q_1 - q_2$ and $z = q/q_c'$. As a result, both the small-polaron hopping [21] and capture of the electrons by the impurity centres with strong electron–phonon coupling [24]
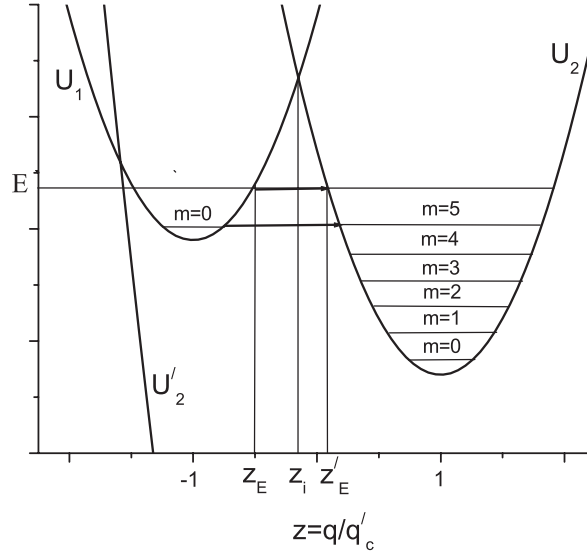
Figure 1. Potential energies $U_1(q)$ and $U_2(q)$ of the impurity centres as functions of a generalized coordinate q ($z = q/q'_c$) describing the distortion of their local environment for a voltage $eV_{1,2} = m\hbar\omega + \varepsilon$ ($m = 5$). The $U'_2(q)$ curve corresponds to $V_{12} > V_m = 2I_p/e$.

can be treated as essentially one-dimension problems. Since $x_{1,2} \gg a$, the hopping rate $\nu_{1,2} \ll \omega$ so that after the hopping event the left centre that accepts the electron has enough time to relax before hopping to the right centre occurs. At low temperatures, the electron that is localized at the ground state of the left impurity can jump to the mth excited state of the right impurity at a voltage difference such that $eV_{1,2} = m\hbar\omega + \varepsilon$ (figure 1).

If $H_e = 0$, the wavefunctions of the centres $|i, m\rangle$ can be written as products of the wavefunctions of light electrons, $\psi_i(r, q)$, and those of heavy impurity centres, $\phi_m(q \pm q'_c)$, in the ground ($m = 0$) or in an excited state ($m \geqslant 1$). The equilibrium states of the centres correspond to $q = \pm q'_c = \pm\lambda/\sqrt{2}M\omega^2$, respectively. The wavefunctions $\phi_m(q)$ are those of the harmonic oscillator [23]:

$$\phi_0(q) \propto \exp\left(-\frac{q^2}{2a_1^2}\right), \qquad \phi_m(q) = \frac{1}{\sqrt{2^m m!}}\phi_0(q)H_m\left(\frac{q}{a_1}\right), \tag{6}$$

where $a_1 = (\hbar/M\omega)^{1/2}$ and $H_m(\xi)$ are the Hermite polynomials. By treating the electron transfer Hamiltonian H_e in equation (1) as a perturbation, the hopping rate can be calculated by means of the 'golden rule' [21, 23]

$$\nu_{12}(r) = \frac{2\pi}{\hbar} \sum_{m,m'} |\langle 2, m |H_e| 1, m'\rangle|^2 \delta\left(eV_{12} - \varepsilon - (m - m')\hbar\omega\right), \tag{7}$$

where $H_e(r)$ is given by equation (2). Assuming that the scatter, ε, in the ground state energies of nearby centres has the dispersion $\gamma \lesssim \hbar\omega \simeq 0.01eV$, one can derive from equation (7) that the low-temperature current

$$J \propto p\nu_{12} \propto p\left[\exp\left(-\frac{2x_{1,2}}{a}\right)\right] D_{1,2} \exp\left[-\frac{(eV_{1,2} - m\hbar\omega)^2}{2\gamma^2}\right], \tag{8}$$

$$D_{1,2} = |\langle\phi_0(q + q'_c)|\phi_m(q - q'_c)\rangle|^2 = \left[\frac{1}{m!}\left(\frac{2I_p}{\hbar\omega}\right)^m - 1\right]\exp\left(-\frac{2I_p}{\hbar\omega}\right). \tag{9}$$
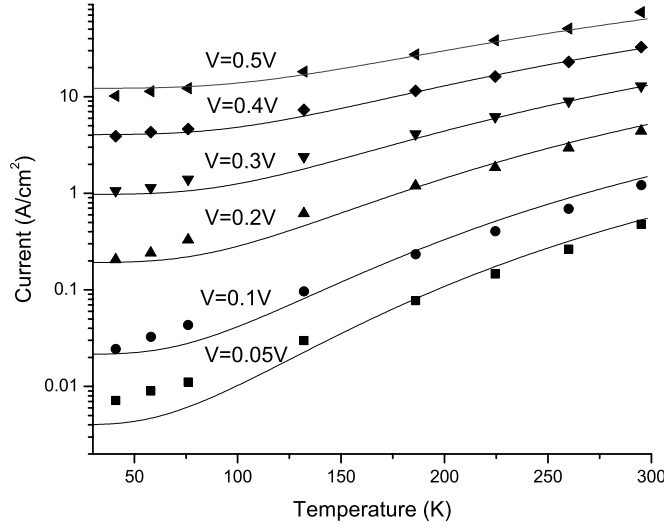
Figure 2. Temperature dependences of current through an organic molecular monolayer of eicosanoic acid (C20) for different voltage biases. The experimental data are shown by the points and theoretical results, calculated by means of equations (13)–(16) for $I_p = 0.33$ eV and $\hbar\omega = 0.052$ eV, are presented by the continuous curves. For all these curves, $J_0 = 2100$ A and $\alpha = 1$ with the exception of the upper curve ($V = 0.5$ V) for which $\alpha = 1.15$.

Here the first exponential factor in equation (8) originates from the electron transfer integral $t(x_{12})$, while the matrix element $D_{1,2}$ describes tunnelling in the heavy-impurity subsystem [21, 23], which is accompanied by a radical reconstruction of both the impurity centres. $D_{1,2}$ is exponentially small for the centres with strong electron–phonon coupling when $I_p \gg \hbar\omega$. Therefore, at low temperatures and biases hopping via two centres is suppressed, so that current will be determined either by direct tunnelling or by hopping via one impurity which requires tunnelling through half as small barrier. However, the tunnel transparency of the inter-impurity hopping barrier increases with bias, $V_{1,2} = V/3$, and the two-impurity channel becomes dominant at relatively large biases. When V is large, $m = eV/3\hbar\omega$ can be treated as a continuous function of V. Then, from equation (8), by using the Stirling formula we find that for low temperatures

$$J(V) = J_0 \left|\frac{V}{V_0}\right|^{\alpha} \left[\exp\left(-\frac{2d}{3a} - \frac{2I_p}{\hbar\omega}\right)\right] \left(\exp\left\{\frac{eV}{3\hbar\omega}\left[1 + \ln\left(\frac{6I_p}{eV}\right)\right]\right\} - 1\right). \tag{10}$$

The two-impurity channel also dominates the conductivity at elevated temperatures because it involves tunnelling via excited impurity states with $m \gg 1$. To analyse the high-temperature current we employ the quasiclassical method [23] developed for the description of electron capture and ionization of deep impurities [24] and for small-polaron hopping [21]. In this case,

$$D_{1,2} \propto \int_0^\infty dE \exp\left[-\frac{E}{kT} - 2S(E)\right], \tag{11}$$

where $\exp(-E/kT)$ is the Boltzmann factor and $S(q, E)$ is the imaginary part of the dimensionless action of a 'classical particle' moving with the energy E in the inverted potentials $U_1(q)$ and $U_2(q)$ [23], given by equations (4) and (5), respectively. The 'particle' moves in the inverted potential $U_1(q)$ from the left turning point $z_E = q_E/q_c' = -1 + \sqrt{2E/I_p}$ to the point of the intersection of the potentials, $z_i = eV_{1,2}/2I_p$ (figure 2). Then it moves in the

inverted potential $U_2(q)$ from point z_i to the right turning point $z'_E = +1 - \sqrt{2(E + eV_{1,2})/I_p}$. Therefore,

$$S(E) = \frac{q'_c\sqrt{M}}{\hbar}\left[\int_{z_E}^{z_i}dz\sqrt{I_p(z+1)^2 - 2E} + \int_{z_i}^{z'_E}dz\sqrt{I_p(z-1)^2 - 2(E+eV_{1,2})}\right], \quad (12)$$

given $eV_{12} \gtrsim \varepsilon \simeq 0.01eV$. Calculating the integrals in equation (12) yields

$$S(E) = \frac{I_p}{2\hbar\omega}\left\{2H(y,v) - y\ln\left(\frac{[H(y,v)+(1-v)]}{\sqrt{y}}\right)\right.$$
$$\left. - (y+4v)\ln\left(\frac{[H(y,v)+(1+v)]}{\sqrt{(y+4v)}}\right)\right\}, \quad (13)$$

where $H(y,v) = \sqrt{(1-v)^2 - y}$, $y = 2E/I_p$ and $v = eV_{1,2}/2I_p$. The function $f(E) = E/kT + 2S(E)$ in (11) has a sharp maximum at the saddle-point with the energy

$$E_s = \frac{I_p}{\sinh^2 b}\left[\cosh b\sqrt{1 + v^2\sinh^2 b} - 1 - v\sinh^2 b\right], \quad (14)$$

where $b = \hbar\omega/2kT$. Calculating the integral over E in equation (11) by means of the saddle-point technique gives

$$D_{1,2}(V,T) \propto \exp\left[-\frac{E_s}{kT} - 2S(E_s)\right]. \quad (15)$$

Thus, according to equation (8)

$$J(V,T) = J_0|V/V_0|^\alpha[\exp(-2d/3a)]D_{1,2}(V,T). \quad (16)$$

At low temperatures, $kT \ll \hbar\omega$, the value $E_s \simeq 0$ and equations (16), (15), and (13) are reduced to equation (10). In the other limiting case of $V \to 0$, but at relatively high temperatures, from equations (13) to (16) it follows that

$$J(V,T) \propto V|V|^\alpha\exp\left[-\frac{2I_p}{\hbar\omega}\tanh\left(\frac{\hbar\omega}{4kT}\right)\right]. \quad (17)$$

Since $I_p = 2E_a$, equation (17) coincides with the formula obtained by Holstein for small-polaron band hopping [21]. One can use the following interpolation for equation (17):

$$\ln J(V \to 0, T) \propto \left(\frac{T}{T_0^0}\right) - 2.3\left(\frac{I_p}{\hbar\omega}\right), \qquad T_0^0 = \frac{(\hbar\omega)^2}{3I_p} \quad (18)$$

valid for a negligibly small bias with an accuracy of 5% in the temperature interval $0.2\hbar\omega \lesssim kT \lesssim \hbar\omega/2$. From figure 2 it can be seen that equations (13)–(16) describe the experimental $J(T,V)$ data fairly well. At low temperatures ($T \lesssim 50$ K), the measured current through the structure depends very weakly on temperature T, while for $T > 50$ K the current grows exponentially with T, $J \propto \exp(T/T_0)$, where parameter T_0 increases from $T_0 \simeq 35$ K to $T_0 \simeq 100$ K when V increases from 20 to 500 mV. Theoretically, for finite biases V, parameter T_0^0 in equation (18) should be substituted with $T_0(V)$ which increases with voltage as $T_0(V) \simeq T_0^0(1 + 4eV/3I_p)$, contrary to the Holstein results [21] where it is constant. Discrepancies between theory and experiment are observed only for low temperatures and voltages, when, as noted above, the two-impurity channel is not dominant. Note that at $V_{12} = V_m = 2I_p/e$ the parabolic terms $U_1(q)$ and $U_2(q)$ intersect at a point $q = -q'_c$ where $U_1(q)$ has a minimum, i.e. the activation barrier between the terms vanishes. However, the barrier appears again when V_{12} exceeds V_m (the curve $U'_2(q)$ in figure 1). Therefore the current can actually decrease with the increase of voltage $V_{12} = V/3 > V_m$, i.e. the current–voltage characteristics are N-shaped. Such N-shaped behaviour has been observed in alkyl

monolayers [10]. For the C20 samples reported here, the threshold voltage, $V_t \simeq 2$ V, exceeds the breakdown voltage so that the negative resistance, if present, could not be observed.

We have shown that

(i) hopping via two impurity centres with strong electron–phonon coupling can dominate the current through thin insulators at relatively high voltages and/or temperatures, and results in unique dependences of the current on temperature and voltage;

(ii) this mechanism is consistent with the near-exponential temperature dependence of the current observed experimentally in some samples of fatty-acid monolayers. This may be due to the presence of metallic atoms or structural defects within the organic film.

Acknowledgments

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