

## Dominant spin relaxation mechanism in compound organic semiconductors

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Despite the recent interest in “organic spintronics,” the dominant spin relaxation mechanism of electrons or holes in an organic compound semiconductor has not been conclusively identified. There have been sporadic suggestions that it might be hyperfine interaction caused by background nuclear spins, but no confirmatory evidence to support this has ever been presented. Here, we report the electric-field dependence of the spin-diffusion length in an organic spin-valve structure consisting of an Alq<sub>3</sub> spacer layer, and argue that these data, as well as the available data on the temperature dependence of this length, contradict the notion that hyperfine interactions relax spin. Instead, they suggest that the Elliott-Yafet mechanism, arising from spin-orbit interaction, is more likely the dominant spin relaxing mechanism.

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Spin relaxation in most solids is caused primarily by mechanisms associated with spin-orbit and contact hyperfine interactions. Since compound organic semiconductors are typically made of light elements (hydrogen, oxygen, and carbon), the spin-orbit interaction in them should be very weak since it is proportional to the fourth power of the atomic number of the constituent elements. At the same time, contact hyperfine interaction (between electron and nuclear spins) should also be very weak—at least in  $\pi$ -conjugated organic molecules—because the  $\pi$ -electrons’ wave functions are mainly  $p_z$  orbitals that have nodes in the molecular plane.<sup>1</sup> As a result, organics tend to exhibit long spin relaxation times that could exceed those in inorganic semiconductors by several orders of magnitude at temperatures well above that of liquid nitrogen. This has generated significant interest in organic spintronics<sup>2–5</sup> owing to the realization that organic semiconductors could very well emerge as the material of choice in many spintronic applications.

Despite all this interest and research, a question of fundamental importance has remained unanswered: which of the two mechanisms—spin-orbit interaction or hyperfine interaction—is the dominant causative agent for spin relaxation in organics. Because spin-orbit interaction is so much weaker in organics than in inorganics, the trend has been to conjecture (tacitly) that contact hyperfine interaction must be the dominant spin relaxation mechanism.<sup>5–7</sup> However, to our knowledge, no conclusive evidence has ever been presented to substantiate this belief. This remains an open question.

In this Brief Report, we show that a large body of experimental evidence does not support the notion that hyperfine interaction is the dominant spin relaxation mechanism in the most widely studied organics. Instead, it points to the Elliott-Yafet mechanism,<sup>8</sup> arising from spin-orbit interaction, as being the more likely culprit. We reach this conclusion based on the reported temperature and electric-field dependences of the spin-diffusion length—the latter reported here—which are not consistent with hyperfine interaction, but are consistent with the Elliott-Yafet mechanism being dominant. In the rest of this Brief Report, we elucidate the arguments leading to this conclusion.

At a temperature  $T$  and in an electric field  $E$ , the spin-diffusion length  $L_s(E, T)$  of a spin carrier in any solid is related to the spin relaxation time  $\tau_s(E, T)$  and the carrier mobility  $\mu(E, T)$  according to the relation<sup>9,10</sup>

$$L_s(E, T) = \frac{1}{-\frac{e|E|}{2kT} + \sqrt{\left(\frac{e|E|}{2kT}\right)^2 + \frac{e}{kT\mu(E, T)\tau_s(E, T)}}, \quad (1)$$

where  $k$  is the Boltzmann constant and  $e$  is the electronic charge.

Since carriers in organics travel by hopping from site to site assisted by thermal excitation in an electric field (similar to Poole-Frenkel conduction)<sup>11</sup> the mobility is usually expressed as<sup>12</sup>

$$\mu(E, T) = \frac{ed^2(E, T)}{\tau_0(E, T)\beta(T)\sqrt{E}} \tanh\left(\frac{\beta(T)\sqrt{E}}{kT}\right) \times \exp\left(\frac{\beta(T)\sqrt{E} - \Delta(T)}{kT}\right), \quad (2)$$

where  $d(E, T)$  is the mean hopping distance,  $\tau_0(E, T)$  is the mean hopping time,  $\Delta(T)$  is the activation energy for hopping, and  $\beta(T)$  is the field emission constant. In low electric fields [ $|E| \ll \sqrt{kT/\{e\mu(E, T)\tau_s(E, T)\}}$ ], Eq. (1) simplifies to

$$[L_s(E, T)]_{low\ E} \approx \sqrt{\frac{kT}{e}} \mu(0, T) \tau_s(0, T), \quad (3)$$

where [see Eq. (2)]

$$\mu(0, T) = \frac{ed^2(0, T)}{\tau_0(0, T)kT} \exp\left(\frac{-\Delta(T)}{kT}\right). \quad (4)$$

Substituting Eq. (4) in Eq. (3), we get

$$[L_s(E, T)]_{low\ E} = d(0, T) \sqrt{\frac{\tau_s(0, T)}{\tau_0(0, T)}} \exp\left(\frac{-\Delta(T)}{2kT}\right). \quad (5)$$

The last equation is very instructive. The quantities  $d(0, T)$ ,  $\tau_0(0, T)$ , and  $\Delta(T)$  should not have strong temperature dependence at cryogenic temperatures. Therefore, Eq. (5) tells us that the low-field and low-temperature spin-diffusion length  $[L_s(E, T)]_{low\ E}$  must increase with increasing temperature, *unless*  $\tau_s(0, T)$  decreases with increasing temperature. This makes sense intuitively, and we could have predicted it from Eq. (3) directly. Since carriers travel by Brownian motion, an increased temperature should result in an increased spin-diffusion length unless the spin relaxation

time decreases with increasing temperature. Thus, if we ever observe  $[L_s(E, T)]_{low E}$  decreasing with increasing temperature (at cryogenic temperatures), then we must conclude that  $\tau_s(0, T)$  also decreases with rising temperature. Consequently, the temperature dependence of the spin-diffusion length at low temperatures is very revealing; it tells us how the spin relaxation time varies with temperature. In turn, it allows us to decipher the major spin relaxing mechanism.

So far, every experiment reported in the literature has found that in organics,  $[L_s(E, T)]_{low E}$  decreases with increasing temperature in the cryogenic range, slowly,<sup>13</sup> moderately,<sup>14</sup> or rapidly.<sup>15</sup> That then tells us that  $\tau_s(0, T)$  must also decrease with rising temperature, slowly, moderately, or rapidly. The rapid decrease *cannot* be consistent with hyperfine interaction because in that mechanism, spin relaxation is caused by the magnetic field of the nuclear spins, which—at best—can have weak temperature dependence. Indeed, theories based on spin diffusion in a disordered organic in the presence of the hyperfine magnetic field predict a weak temperature dependence of the spin-diffusion length.<sup>6</sup> Therefore, the observation in Ref. 15, which showed a *rapid* decrease in  $[L_s(E, T)]_{low E}$  with increasing temperature, is clearly inconsistent with the notion that hyperfine interaction could have been the dominant spin relaxing mechanism in that organic.

To probe this matter further and correctly identify the dominant spin relaxation mechanism, we can investigate the electric-field dependence of the spin relaxation length and spin relaxation time in an organic, which—to our knowledge—has never been attempted. Here, we report some data on the electric-field dependence of the spin-diffusion length in an organic and infer the electric-field dependence of the spin relaxation time from that data. This sheds further light on the dominant spin relaxation mechanism.

In Ref. 16, we carried out experiments in organic spin valves to extract the spin-diffusion length under varying electric fields, where the organic was tris(8-hydroxyquinolinolato aluminum) or  $Alq_3$  with a chemical formula of  $C_{27}H_{18}N_3O_3Al$ . The spin valves were nanowires of  $Alq_3$  with cobalt and nickel contacts. We will assume that  $P_1$  and  $P_2$  are the spin polarizations at the Fermi energy in the injecting (cobalt) and detecting (nickel) contacts,  $\alpha_1$  and  $\alpha_2$  are the effective spin injection and detection efficiencies at the two contacts, and  $L$  is the organic layer thickness. Schottky barriers form at both contacts because of the energy-level alignment.<sup>17</sup> The picture of carrier transport in these spin valves presented in Refs. 13 and 14 is that carriers first tunnel through the Schottky barrier at the injecting contact with a spin polarization  $P_1\alpha_1$ , then drift and diffuse through the bulk of the organic with exponentially decaying spin polarization  $e^{-L/L_s(E, T)}$ , and finally tunnel through the second Schottky barrier to reach the detecting contact. Therefore, the spin-valve magnetoresistance ratio  $\Delta R/R$  will be given by the modified Jullieré formula (adapted from Refs. 13 and 14)

$$\frac{\Delta R}{R} = \frac{2P_1\alpha_1P_2\alpha_2e^{-L/L_s(E, T)}}{1 - P_1\alpha_1P_2\alpha_2e^{-L/L_s(E, T)}}. \quad (6)$$

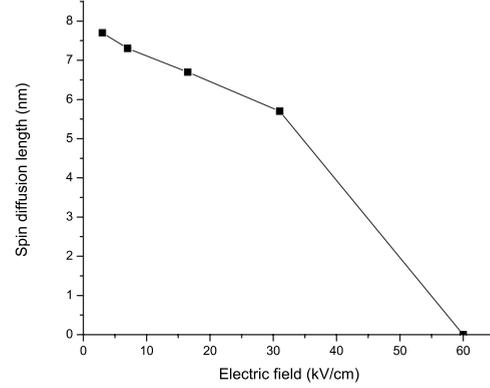


FIG. 1. Spin-diffusion length as a function of electric field. The measured spin-diffusion length in 50 nm diameter  $Alq_3$  nanowires as a function of electric field at a temperature of 1.9 K.

In order to verify this transport picture, we had measured the current-voltage ( $I$ - $V$ ) characteristics of the spin valves at varying temperatures.<sup>13</sup> They were nearly temperature independent and almost piecewise linear. The current increased quasilinearly with a small slope up to a threshold voltage of  $\sim 2$  V, and then increased rapidly with a much larger slope. This behavior is inconsistent with tunneling through pinholes in the organic—which has been proposed as an alternate transport model<sup>18</sup>—since that would have produced two features which are absent. First, tunneling causes the  $I$ - $V$  characteristic to be superlinear but smooth (not abrupt like a piecewise linear characteristic)<sup>19</sup> and, second, tunneling makes the junction resistance temperature dependent.<sup>19</sup> Since neither feature is observed, we can rule out tunneling through pinholes. References<sup>20,21</sup> carried out high-resolution transmission electron microscopy studies of ferromagnet/organic junctions and found them to be abrupt with no evidence of interdiffusion. This further eliminates the existence of pinholes in the organic since they would have caused interdiffusion.

The observed  $I$ - $V$  behavior is however very consistent with the transport picture presented in Refs. 13 and 14. At low bias voltages, the Schottky barrier at the injecting contact is thick enough to suppress tunneling, so that the current is mostly due to thermionic emission. With increasing bias, the interface Schottky barrier becomes progressively thinner owing to band bending and the tunneling increases. At some threshold bias, the tunneling current exceeds that due to thermionic emission. Thereafter, the tunneling injection dominates and with increasing bias (decreasing barrier thickness) it increases rapidly. Thus, the current remains small up to a threshold bias ( $\sim 2$  V), at which point crossover from thermionic emission to tunneling takes place, and then the current takes off. Since the tunneling probability is independent of temperature, the  $I$ - $V$  characteristic is virtually temperature independent. Therefore, the observed  $I$ - $V$  characteristic is in qualitative agreement with the transport picture presented in Refs. 13 and 14.

In Ref. 16, we measured the ratio  $\Delta R/R$  (in Eq. (6)) as a function of electric current through the organic at a temperature of 1.9 K.<sup>16</sup> In our samples,  $L \approx 30$  nm. We assume  $P_1 = 0.4$  (cobalt contact),<sup>22</sup>  $P_2 = 0.3$  (nickel contact),<sup>22</sup> and  $\alpha_1$

$=\alpha_2=1$ , which is the same assumption as in Refs. 13 and 14. In reality, the spin injection and detection efficiencies are never quite 100%, but they can be very high at organic/ferromagnet interfaces—as high as 85–90% in some cases.<sup>23</sup> Since  $L_s(E, T)$  is not very sensitive to  $\alpha_1$  or  $\alpha_2$ , our assumptions regarding these parameters are not critical in any case.

Equation (6) relates  $L_s(E, T)$  to  $\Delta R/R$ . Hence, measurement of  $\Delta R/R$  at various current levels allows us to determine the spin-diffusion length as a function of current through the organic. Knowing the current, we can find the electric field across the organic as follows: we apply Ohm's law to find the voltage  $V$  across the organic from the relation  $V=IR$ , where  $I$  is the current and  $R$  is the measured resistance of the organic. The average electric field in the organic

is then found from the relation  $E=V/L$ . This allows us to determine  $L_s(E, T)$  as a function of  $E$ . The electric field in the organic is of course not spatially uniform, but the arguments presented here do not require the field to be uniform.

In Fig. 1, we plot  $L_s(E, T)$  versus  $E$  extracted from the  $\Delta R/R$  versus  $I$  data in Ref. 16. The plot shows that the spin-diffusion length  $L_s(E, T)$  monotonically decreases with increasing electric field. That implies that the spin relaxation time decreases *very rapidly* with increasing electric field. To understand this, note first that we are operating in the high-field regime where  $|E| \gg kT/[eL_s(E, T)]$ . In our experiment, the average electric-field strength  $|E|$  varied between 3.16 and 60 kV/cm, whereas  $kT/[eL_s(E, T)]$  varied between 220 and 303 V/cm. This puts us in the high-field regime. In this regime, Eqs. (1) and (2) yield

$$\begin{aligned} [L_s(E, T)]_{high\ E} &\approx \mu(E, T)E[\tau_s(E, T)]_{high\ E} = \left\{ \frac{ed^2(E, T)\sqrt{E}}{\tau_0(E, T)\beta(T)} \tanh\left(\frac{\beta(T)\sqrt{E}}{kT}\right) \exp\left(\frac{\beta(T)\sqrt{E} - \Delta(T)}{kT}\right) \right\} [\tau_s(E, T)]_{high\ E} \\ &= \frac{kT}{\beta} \sqrt{E} \mu(0, T) \tanh\left(\frac{\beta(T)\sqrt{E}}{kT}\right) \exp\left(\frac{\beta(T)\sqrt{E} - \Delta(T)}{kT}\right) [\tau_s(E, T)]_{high\ E}, \end{aligned} \quad (7)$$

which tells us that the spin relaxation time  $[\tau_s(E, T)]_{high\ E}$  will have to drop off superexponentially with the square root of the average electric field in the organic if  $[L_s(E, T)]_{high\ E}$  decreases with increasing field. Since that is the behavior of  $[L_s(E, T)]_{high\ E}$  we observe experimentally, we conclude that the spin relaxation time must have decreased very rapidly with increasing average field in the organic.

The rapid decrease in the spin relaxation time with increasing electric field is once again *not* consistent with hyperfine interactions. To first order, the strength of hyperfine interaction is independent of the electric field. This strength is proportional to the sum of the carrier probability densities (squared modulus of the wave function) at the nuclear sites.<sup>24</sup> An external electric field can skew the carrier wave functions in space (as in quantum confined Stark effect<sup>25</sup>) and change the interaction strength, but it requires a very high electric field to skew the wave function appreciably since carriers in organics are quite strongly localized. Even in quantum confined Stark effect, where the carriers are relatively delocalized, it takes field strengths of several hundreds of kV/cm to change the overlap between electron and hole wave functions by a few percent. Therefore, we do not expect the hyperfine interaction strength to be particularly sensitive to electric field.

There is a second effect to be considered. Even though the hyperfine interaction strength may not be sensitive to electric field, the spin relaxation rate due to this interaction may become sensitive because the ensemble averaged spin relaxation rate  $\langle 1/\tau_s \rangle$  is equal to  $\int_0^\infty d\epsilon f(\epsilon)[1/\tau_s(\epsilon)]/\int_0^\infty d\epsilon f(\epsilon)$ , where  $f(\epsilon)$  is the carrier distribution function in energy space  $\epsilon$ . Since an electric field can change  $f(\epsilon)$ , it could influence  $\langle 1/\tau_s \rangle$ , but such an influence would be small because, ac-

cording to the variational principle of transport, a first-order change in the distribution function induces only a second-order change in ensemble averaged transport parameters such as  $\langle 1/\tau_s \rangle$ .<sup>26</sup> Therefore,  $[\tau_s(E, T)]_{high\ E}$  could not be a strong function of electric field if hyperfine interactions were dominant.

If  $[\tau_s(E, T)]_{high\ E}$  did not depend strongly on electric field—as would be the case with hyperfine interactions—then that would make the spin-diffusion length  $[L_s(E, T)]_{high\ E}$  increase superexponentially with the square root of the electric field according to Eq. (7). This rapid increase in  $[L_s(E, T)]_{high\ E}$  with electric field is what Ref. 6 also predicted if hyperfine interaction is the primary spin relaxation mechanism. However, what we find experimentally is not a rapid increase but rather a *decrease* in  $[L_s(E, T)]_{high\ E}$  with increasing field. This trend alone indicates that hyperfine interaction is most likely not the dominant spin relaxation mechanism in  $Alq_3$ . Of course, hyperfine interaction is suppressed in a magnetic field,<sup>6,27</sup> and therefore it is possible that the magnetic fields used in the experiments of Ref. 16 quenched the hyperfine interaction. Nonetheless, we can say that at magnetic field strengths *commonly encountered in spintronic applications*, hyperfine interaction is not likely to be the major spin relaxing mechanism.

Finally, there are theoretical objections against hyperfine interaction as well. Most organics of interest are  $\pi$ -conjugated molecules where the delocalized electron states are  $p_z$  orbitals whose nodal planes coincide with the molecular plane. Therefore, contact hyperfine interaction should be vanishingly small in them.<sup>1</sup> In some organic semiconductors like  $Alq_3$ , the electron wave functions may tend to localize over carbon atoms,<sup>28</sup> whose natural isotope  $^{12}C$

has no net nuclear spin. Hence, contact hyperfine interaction should typically be weak in organics.

Before we conclude, we point out that the data in Fig. 1 may actually suggest that the Elliott-Yafet mechanism<sup>8</sup> is the major spin relaxer. This mechanism has its origin in the fact that any spin-orbit interaction makes the eigenspinors of a carrier in the lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO) states of a  $\pi$ -conjugated molecule like  $\text{Alq}_3$  momentum dependent, so that whenever an electron or hole scatters and loses (or gains) momentum, its spin relaxes. Although spin-orbit interaction in organics is weak, it may not be so weak as to preclude the Elliott-Yafet mechanism altogether. This is the conclusion we reached in Ref. 13 as well.

In order to understand why spin relaxation via the Elliott-Yafet mode could make  $[\tau_s(E, T)]_{\text{high } E}$  decrease rapidly with increasing electric field (and therefore make  $[L_s(E, T)]_{\text{high } E}$  decrease with increasing electric field—consistent with the data in Fig. 1), consider the fact that, in this mechanism, the spin relaxation rate  $1/\tau_s(E, T)$  is roughly proportional to the momentum relaxation rate  $1/\tau_m(E, T)$  and is given by<sup>29</sup>

$$\frac{1}{\tau_s(E, T)} \approx \frac{\Lambda(E)}{E_g} \frac{1}{\tau_m(E, T)}, \quad (8)$$

where  $\Lambda(E)$  is the (electric-field-dependent) spin-orbit interaction strength in the LUMO levels for electrons or HOMO levels for holes, and  $E_g$  is the HOMO-LUMO gap. The momentum relaxation rate  $1/\tau_m(E, T)$  will increase with electric field  $E$  because of enhanced scattering, but more importantly the spin-orbit interaction strength  $\Lambda(E)$  will also increase with electric field. The spin-orbit interaction Hamiltonian is given by the expression<sup>29</sup>

$$H_{so} \propto (\vec{E} \times \vec{p}) \cdot \vec{\sigma}, \quad (9)$$

where  $\vec{p}$  is the momentum operator,  $\vec{E}$  is the total electric field that the carrier sees (which includes the externally applied field), and  $\vec{\sigma}$  is the Pauli spin matrix. Therefore,  $\Lambda(E)$  should increase with  $E$ . This is a well-known fact in *inorganic* semiconductors and one of its manifestations is the celebrated Rashba effect.<sup>30</sup> We can expect a similar effect in a disordered organic as well. That, taken together with the fact that the momentum relaxation rate also increases with  $E$ , should make the spin relaxation time  $\tau_s(E, T)$  decrease rapidly with increasing  $E$ . This then should make  $L_s(E, T)$  decrease with increasing electric field, consistent with our experimental observation and the data in Fig. 1.

The Elliott-Yafet mechanism is also consistent with the observed temperature dependence of the spin relaxation time in Ref. 13. According to Eq. (8), the spin and momentum relaxation rates should have the same temperature dependence since  $\Lambda(E)$  and  $E_g$  are nearly temperature independent. Hence,  $\tau_s(E, T)$  should exhibit weak temperature dependence if Coulomb scattering is the dominant momentum relaxing mechanism, since this scattering mechanism is elastic and makes the momentum relaxation rate nearly temperature independent. In Ref. 13, the major momentum relaxing mode was Coulomb scattering and  $\tau_s(E, T)$  expectedly exhibited weak temperature dependence. Therefore, in the end, both the temperature and the electric-field dependences of spin relaxation time are consistent with the Elliott-Yafet mechanism, but not with hyperfine interactions.

In conclusion, we have shown that the experimental evidence gathered so far tends to favor the Elliott-Yafet mechanism more than hyperfine interactions as the dominant spin relaxation mechanism of carriers in the most widely studied organics. Nonetheless, further experiments are required to resolve this issue conclusively.

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