

**ABSTRACT:** Here we propose a mechanism by which spin-polarization can be generated dynamically in chiral molecular systems undergoing photoinduced electron transfer. The proposed mechanism explains how spin-polarization emerges in systems where charge transport is dominated by incoherent hopping, mediated by spin–orbit and electronic exchange couplings through an intermediate charge transfer state. We derive a simple expression for the spin-polarization that predicts a nonmonotonic temperature dependence, consistent with recent experiments, and a maximum spin-polarization that is independent of the magnitude of the spin–orbit coupling. We validate this theory using approximate quantum master equations and the numerically exact hierarchical equations of motion. The proposed mechanism of chirality induced spin selectivity should apply to many chiral systems, and the ideas presented here have implications for the study of spin transport at temperatures relevant to biology and provide simple principles for the molecular control of spins in fluctuating environments.

**KEYWORDS:** Chirality, electron transfer, spin, spintronics, biological electron transport, spin transport

Chirality induced spin selectivity (CISS), in which molecular chirality controls the spin-polarization of electrons, has been observed in a wide variety of systems, including in photoinduced electron transfer in artificial systems, such as quantum dots, and biological molecules, such as photosystem I and DNA. On this basis, it has been suggested that CISS may serve some biological functions and that it could be exploited in nanoscale and molecular-scale spintronics technologies. Here we focus on the CISS effect in photoinduced molecular electron transfer. This effect is particularly puzzling, as it goes against the conventional notion that the initial singlet spin state of the system is preserved in this process.

Theoretical descriptions of CISS have primarily been confined to either the coherent regime, where electron transport is treated as a coherent tunneling process through a chiral molecular junction between leads, or static spin-polarizations produced by spin–orbit coupling in the ground state of chiral molecules. However, photoinduced electron transfer in molecules like photosystem I, where electrons incoherently hop between a discrete set of donor and acceptor sites, cannot be described by either of these theories. In such systems, coupling of the electron transfers to molecular vibrations is strong, and electronic exchange interactions can also be significant. This necessitates the development of a theory of CISS that is appropriate for this incoherent regime of electron transport. Fortunately, such theories have been developed, primarily for understanding rates and dynamics of electron transfer reactions, and through the tools of quantum master equations these theories can be adapted to describe spin transport. These techniques have recently been used to show that spin coherence, but no spin-polarization, arises in a single electron transfer step in a chiral environment mediated by spin–orbit coupling. Here, we expand on this theory and show how the interplay of chirality induced spin coherence, electron hopping, and electronic exchange coupling can dynamically produce large spin-polarizations in electron transfer reactions. The theory presented here will be shown to explain the observed temperature dependence of CISS in photosystem I, and it also provides a framework for engineering molecules to maximize the CISS effect.

Let us start by reviewing how photoinitiated charge transfer, between a donor D and acceptor A, in chiral molecules generates spin coherence in charge transfer states, as described in ref 26. This process generally proceeds via an electron transfer reaction from a bright locally excited singlet state, $S_1 = D^*-A$, to a charge transfer state, $CT = D^{**}-A^-$, which can exist in either a singlet or triplet spin state

$$S_1 \rightarrow CT$$

**Received:** June 17, 2021
**Revised:** July 19, 2021
**Published:** July 22, 2021
As discussed in ref 26, direct diabatic coupling generates the CT state in a singlet (S) = \( |1_D \downarrow 1_A \rangle - |1_D \uparrow 1_A \rangle / \sqrt{2} \) spin state, whereas spin–orbit coupling (SOC) generates the CT state in A\( T_0 \) = \( |1_D \downarrow 1_A \rangle + |1_D \uparrow 1_A \rangle / \sqrt{2} \) (taking the z axis to be defined by the spin–orbit coupling vector).\(^{27}\) So, overall, this electron transfer, mediated by spin–orbit coupling in a chiral molecule, generates the CT state in a coherent superposition of singlet and A\( T_0 \) triplet spin states, and its initial spin density operator, \( \hat{\delta}_{CT}(t) \), is given by

\[
\hat{\delta}_{CT}(0) = |\psi_o \rangle \langle \psi_o |
\]

where \( |\psi_o \rangle = \cos \theta |S \rangle + i \sin \theta |T_0 \rangle \). The mixing angle, \( \theta \), is determined by the relative strength of the spin-preserving diabatic coupling \( V_{DA} \) and the spin–orbit coupling \( \Lambda_{DA} \) as \( \theta = \arctan(\Lambda_{DA}/2V_{DA}) \), and because the sign of \( \Lambda_{DA} \) depends on the chirality of the molecule, the sign of \( \theta \) also depends on chirality. The spin-polarization of the CT state is defined as the difference in the z component of the spins between D and A. This is given by the expectation value of \( \Delta \hat{P}_z = \hat{S}_D - \hat{S}_A = |S \rangle \langle T_1 | + |T_1 \rangle \langle S | \), so the spin-polarization is proportional to the real part of the singlet–triplet coherence, \( \langle \hat{S}_A \hat{S}_T | T_0 \rangle \). However, the CT state is generated with purely imaginary singlet–triplet coherence, so no spin-polarization is formed directly by the electron transfer.\(^{26}\)

Now let us consider how the spin state \( \hat{\delta}_{CT} \) evolves when there exists an exchange coupling between the donor and acceptor electrons in the CT state. In this case, the spin Hamiltonian for the CT state can be taken to be \( \hat{H}_{CT} = -2i\hat{P}_z \) (\( \hat{P}_z \) is a triplet spin projection operator),\(^{28}\) and the time evolution of the spin state is given by

\[
e^{-i\hat{H}_{CT}/\hbar} |\psi_o \rangle = \cos \theta |S \rangle + i \sin \theta e^{2i\theta/\hbar} |T_0 \rangle
\]

We see that exchange coupling generates a complex-valued oscillating singlet–triplet coherence in the CT spin density operator, and thus, the CT state now has an oscillating real part of its singlet–triplet coherence. This means that the exchange coupling produces an oscillating spin-polarization in the CT state which is given by

\[
\langle \Delta \hat{P}_z(t) \rangle = -\sin(2\theta)\sin(2\pi t/\hbar)
\]

Overall, the presence of exchange coupling effects a chirality-dependent transient oscillating spin-polarization in the CT state. However, this spin-polarization clearly averages over time to zero. This naturally raises the question of how a static spin-polarization can be generated in a photoinduced charge transfer reaction. The answer lies in the fact that many photogenerated CT states are not formed by a simple direct electron transfer, but rather the final CT state is often formed via a sequence of downhill electron transfers via intermediate CT states.\(^{11,20,22}\) The final CT state is often a well-separated radical ion pair state. In this state, the exchange coupling between donor and acceptor spins is very weak, but the intermediate CT states often have a significantly larger exchange coupling, due to the closer proximity of the unpaired electrons.\(^{11}\) In this way, imaginary-valued singlet–triplet coherence created through spin–orbit coupled charge transfer can be transiently converted into a net spin-polarization between the donor and acceptor electrons in an intermediate CT state with a large exchange coupling. This spin-polarization can be transferred to the final CT state via a subsequent incoherent electron transfer, which would preserve the electron spin state. The spin-polarization transferred to the final CT state no longer oscillate due to the weak exchange coupling in this state; thus, a net static spin-polarization is generated. This is the basic mechanism by which static spin-polarization can be generated in multistep electron transfer reactions in chiral molecules.

We will now explore this further, by considering the simplest multistate model including only one intermediate CT state in the chiral system (i.e., a three state model)

\[
S_i k_{ET1} S_j k_{ET2} S_k
\]

We take the precursor state to be an excited donor state, \( S_i = D^a-A_1^-A_2 \), the intermediate charge transfer state corresponds to an electron transfer from D to a primary acceptor \( A_1 \), so \( CT_j = D^a-A_1^-A_2 \), and the final charge transfer state \( CT_k \) is taken as the state formed by electron transfer from the primary acceptor \( A_1 \) to the secondary acceptor \( A_2 \), so \( CT_k = D^a-A_1^-A_2^a \). The CT states can exist in either singlet or triplet spin states, but the \( S_i \) state only exists in the singlet spin state. A schematic of this system is shown in Figure 1. To start with, for simplicity we will assume these downhill electron transfers occur irreversibly, and we will also assume that only the first electron transfer is spin-dependent, and occurs via chiral spin–orbit coupled charge transfer.

In this model, the spin density operators for each state obey the following set of equations:\(^{25,26}\)

\[
\frac{d}{dt} \hat{\delta}_{S_i}(t) = -k_{ET1} \hat{\delta}_{S_i}(t)
\]

\[
\frac{d}{dt} \hat{\delta}_{CT_j}(t) = -i \left[ \hat{H}_{CT_j} + \delta_{CT_j} |\psi_o \rangle \langle \psi_o |, \hat{\delta}_{CT_j}(t) \right]
\]

\[
+ k_{ET1} |\psi_o \rangle \langle \psi_o | \hat{\delta}_{S_i}(t) |\psi_o \rangle \langle \psi_o | - k_{ET1} \hat{\delta}_{CT_j}(t)
\]

\[
\frac{d}{dt} \hat{\delta}_{CT_k}(t) = -i \left[ \hat{H}_{CT_k}, \hat{\delta}_{CT_k}(t) \right] + k_{ET2} \hat{\delta}_{CT_k}(t)
\]

Here \( \hat{H}_{CT_j} \) and \( \hat{H}_{CT_k} \) are the spin Hamiltonians for the CT\(_j\) and CT\(_k\) states, describing all the spin interactions in these states. Here the spin Hamiltonians are simplified to just include the exchange couplings, so \( \hat{H}_{CT_j} = -2i\hat{P}_z \) and
$\hat{H}_{\text{CT}} = 0$ (the energy differences between different CT states enter into the master equations via the rate constants). This set of coupled equations can be obtained straightforwardly using perturbative Nakajima–Zwanzig theory,\textsuperscript{25,26} as has been described previously (a summary of the approximations in ref 25 and 26 will be discussed shortly). The shift term $\delta \epsilon$ naturally emerges from the master equation theory, and its value will depend on the details of the electron transfer process. For a large downhill driving force, $\Delta G_{\text{ET1}}$, it can be estimated as $\delta \epsilon \approx -(V_{\text{DA}}^2 + (\Lambda_{\text{DA}}/2V_{\text{DA}}^2))/\langle \lambda_{\text{ET1}}^2 - \Delta G_{\text{ET1}} \rangle$, where $\lambda_{\text{ET1}}$ is the reorganization energy for the first electron transfer. We can also understand the $\delta \epsilon$ term as a net chiral superexchange spin–orbit coupling term, which couples $S$ and $T_0$ states via the $S_1$ state.

One can then solve these (eq 4) analytically for an initial state where only $S_1$ is populated, with $\sigma_0(z) = |S\rangle\langle S|$, from which the final spin-polarization in CT$_2$ given by $\langle \Delta P_z \rangle = \lim_{\tau \rightarrow \infty} \text{tr} \left\{ (\hat{S}_{Dz} - \hat{S}_{A} \sigma_{\text{CT}n}) \sigma_{\text{CT}n}(t) \right\}$ is found to be

$$\langle \Delta P_z \rangle = -\frac{k_{\text{ET2}}^2(2/\hbar)\sin(2\theta)}{k_{\text{ET2}}^2 + \Omega^2}$$

where $\hbar\Omega = \sqrt{4J^2 + \delta \epsilon^2 + 4J\delta \epsilon \cos(2\theta)}$. Simultaneously, a zero quantum coherence (which depends on the imaginary part of the $S_{-T_0}$ coherence) is produced:

$$\langle S_{Dz}S_{A} - S_{Dz}S_{A} \rangle = \sin(2\theta) \left( 1 - \frac{2J/\hbar^2}{k_{\text{ET2}}^2 + \Omega^2} - \frac{\delta \epsilon \cos(2\theta)}{(\hbar\Omega)^2} \right)$$

This zero quantum coherence is produced directly by the initial SOC mediated electron transfer from $S_1$, and modified by the spin dynamics in CT$_1$.\textsuperscript{26} Last, we find the final singlet population is given by

$$\langle \rho_{\text{S}} \rangle = \cos^2 \theta \left( 1 + \frac{2J\delta \epsilon/\hbar^2}{k_{\text{ET2}}^2 + \Omega^2} - \frac{2\delta \epsilon \cos(2\theta)}{(\hbar\Omega)^2} \right)$$

and the $T_0$ population is given by $\langle \rho_{\text{T}} \rangle = 1 - \langle \rho_{\text{S}} \rangle$. We see the final spin density operator for the CT$_2$ is a combination of the phenomenological theory in ref 31 and the theory obtained from the one-step transfer model in ref 26.

Let us now discuss a few points of interest in the expression for the spin-polarization in eq S. First, this expression is an odd function of $\theta = \arctan(\Lambda_{\text{DA}}/2V_{\text{DA}})$; so, when changing the chirality of the system, the sign of this polarization is reversed, because the sign of $\Lambda_{\text{DA}}$ changes, which confirms that this corresponds to a CISS effect. Second, in the absence of the shift term $\delta \epsilon$, the spin-polarization is bounded by $|\langle \Delta P_z \rangle| \leq \sin(2\theta)$ as $k_{\text{ET2}}^2/(2J)$ is varied. In the limit of weak spin–orbit coupling, this bound is simply $|\Lambda_{\text{DA}}/2V_{\text{DA}}|$, which is the ratio of the spin–orbit coupling to the diabolic coupling for the first electron transfer. However, when the shift term is included, it is possible for $\Omega^2 < (2J)^2$, and therefore $\langle \Delta P_z \rangle$ can exceed $\sin(2\theta)$. Using eq S, we find $\langle \Delta P_z \rangle$ is extremized at $\langle \Delta P_z \rangle = 1/2$ when $k_{\text{ET2}}^2 = (2J/\hbar^2 - (\delta \epsilon/\hbar)^2$ and $\delta \epsilon/(2J) = -\cos(2\theta))$. Remarkably for any nonzero SOC contribution to the electron transfer, i.e., any value of $\theta$, a spin-polarization of up to $\pm 50\%$ can be observed in this mechanism if $\delta \epsilon$, $2J$, and $k_{\text{ET2}}$ satisfy the two equations above. The feasibility of this maximum being attained in a real system depends on the relative magnitudes of $2J$ and $\delta \epsilon$. The values of these parameters will depend on the electronic structure of the specific system in question, but we can argue that $\delta \epsilon/(2J) = -\cos(2\theta)$ could feasibly be satisfied in a real molecule. In CT states, indirect superexchange type couplings are often the dominant contributions to $2J$,\textsuperscript{11} so

$$2J \approx \frac{\sum_{T} V_{\text{CT}n}^2}{\Delta E_{\text{CT}n}} - \frac{\sum_{S} V_{\text{CTS}}^2}{\Delta E_{\text{CTS}}}$$

where $V_{\text{CT}n}$ is the electronic coupling between the CT$_1$ state and singlet/triplet state $S_n/T_m$ and $\Delta E_{\text{CT}n}$ is the vertical energy gap. Analogously

$$\delta \epsilon \approx \frac{V_{\text{CTS}}^2 + \Lambda_{\text{CTS}}^2/4}{\Delta E_{\text{CTS}}}$$

(noting $V_{\text{CT}n} = V_{\text{DA}n} = \Lambda_{\text{CT}S_n} = \Lambda_{\text{DA}n}$). So, because both $2J$ and $\delta \epsilon$ have similar dependences on the electronic state couplings and energy gaps, $\delta \epsilon/(2J) = -\cos(2\theta)$ could possibly be satisfied to extremize $\langle \Delta P_z \rangle$ in a real system.

As a final point, we note that the magnitude of the spin-polarization $\langle \rho_{\text{S}} \rangle$ goes through a maximum (at fixed $\theta$) when $k_{\text{ET2}} = \Omega$. This can be understood simply as follows. When $k_{\text{ET2}}$ is very high compared to the frequency at which polarization in CT$_1$ oscillates, $\Omega$, then there is no time for spin-polarization to build up in CT$_1$ before this state decays to CT$_2$. Conversely, when $k_{\text{ET2}}$ is very low compared to $\Omega$, the spin-polarization is averaged to zero by the oscillations as it is transferred, so no net spin-polarization in CT$_2$ is observed. This observation has important implications for the temperature dependence of $\langle \Delta P_z \rangle$, as we will discuss shortly.

In order to further explore this theory, and to demonstrate the validity of the perturbative quantum master equations (QMEs) and additional approximations used to obtain the expressions above, we performed simulations of the three state condensed phase electron transfer processes illustrated in Figure 1. We employ both numerically exact quantum dynamics and the approximate QMEs, with the nuclear degrees of freedom treated as a harmonic bath. The total Hamiltonian in this model is a sum of nuclear (bath) kinetic energy, potential energy terms for the different states, and a diabatic/SOC term (further details are given in the SI, eq S.1). Using the hierarchical equations of motion (HEOM), we can compute the exact dynamics when the potentials are harmonic.\textsuperscript{32}

For comparison, we also perform simulations of this model with the full perturbative QMEs, eq 4, modified to include back reaction terms.\textsuperscript{26} To briefly summarize the approximations used in refs 25 and 26 to obtain these, in these QMEs we assume that the coherences between different electron transfer states, e.g., $\langle S_1 \rangle$ (CT$_1$, S) are short-lived and small (due to the large differences between potential energy surfaces), so these coherences are projected out using Nakajima–Zwanzig theory (but spin coherences are retained). The Nakajima–Zwanzig kernel is then expanded at the lowest order in the diabatic couplings, with spin Hamiltonian terms in the kernel ignored (due to the large separation in energy scale between the nuclear motion and spin dynamics), and the population transfer dynamics are treated as Markovian. For the harmonic bath model given above, the second-order QME parameters (rate constants and $\delta \epsilon$) can be computed exactly from the
These parameters are chosen to be representative of electron which follows straightforwardly from Fermi mated with Marcus theory the high-temperature limit, these rates can be well-approximation dependence on the nuclear con diabatic and spin exchange coupling in the CT (approximately 1.16 meV), in line with superexchange couplings observed in CT states.\textsuperscript{11}

Figure 2 shows the results of these simulations for a range of values of the $J$ coupling (decreasing from top to bottom) in the intermediate state for populations (left) and spin-polarizations (right). The population dynamics clearly show that hopping dominates the ET process in these examples, with a significant transient population of the CT$_1$ appearing on a time-scale of $\sim 0.25$ ns and decaying on a time-scale of $\sim 1$ ns. We see that the final spin-polarization in CT$_2$ increases and then decreases with decreasing $J$ (note the different $\Delta P_{fi}(t)$ scales from top to bottom), as predicted by the simple theory in eq 5. Large spin-polarizations, on the order of 40%, can be observed even with a small fraction of triplet states formed in ET1. The second-order QMEs in this example are very accurate for both population and spin-polarization dynamics, which validates the approximations of Markovian dynamics and spin-independent rate constants invoked to derive these. The prediction from eq 5 for the final spin-polarization (shown as a black dashed line in the left panels of Figure 2) provides an accurate estimate in these examples, with small deviations due to back reactions.

In the above examples, we have only considered a regime where second-order perturbation theory is valid for the rate constants and $\delta \epsilon$. The general form of the master equation presented above is only slightly altered by including higher-order effects in the electronic coupling; specifically, we should add a decoherence term of the form $-i(\delta \epsilon / 2)[\langle \eta_A \rangle [\eta_A^*], [\eta_B^*] \langle \eta_A \rangle, \delta_{CT}(t)]$ to the equation for $\delta_{CT}(t)$. This causes the spin-polarization in the intermediate state to decay, but for sufficiently large $2J$ significant spin-polarization can still emerge and subsequently be transferred to the final CT state. This is demonstrated in Figure 3 where we show the population dynamics (top panel), spin-polarization (bottom panel, solid lines), and zero quantum coherence (bottom panel, dashed lines) for the three state model with $\Gamma_{DA} = 10$ meV, $V_{AA} = 5$ meV, and $J/g_\mu B = 2$ T. In this limit, spectral density,\textsuperscript{25} the details of which are given in the SI. In the high-temperature limit, these rates can be well-approximated with Marcus theory

$$k_{ET} = (1/h)G_{DA}(\pi/\lambda_{ET}k_B T)^{-1/2} e^{-\Delta G_{ET} / k_B T}$$

where $G_{DA} = (V_{DA}^2 + \lambda_{DA}^2 / 4)^{1/2}$ is the combined diabatic/SOC coupling for the electron transfer. This assumes the diabatic and spin–orbit coupling terms have only a weak dependence on the nuclear configuration (i.e., applying the Condon approximation\textsuperscript{25}). In this case, the inclusion of spin–orbit coupled electron transfer simply modifies the coupling term in the Marcus expression from $V_{DA} \rightarrow V_{DA}^2 + \lambda_{DA}^2 / 4$, which follows straightforwardly from Fermi’s golden rule. Although we only consider harmonic potential energy surfaces here, the QMEs apply to general potential energy surfaces for the electron transfer states.

We set the free energy changes of the electron transfers to be $\Delta G_{ET1} = -0.1$ eV and $\Delta G_{ET2} = -0.25$ eV, with reorganization energies of $\lambda_{ET1} = 0.1$ eV and $\lambda_{ET2} = 0.2$ eV. Diabatic state couplings are taken as $\Gamma_{DA} = (V_{DA}^2 + \lambda_{DA}^2 / 4)^{1/2} = 0.5$ meV ($S_i$–CT$_1$ coupling) and $\Gamma_{AA} = V_{AA} = 0.25$ meV (CT$_1$–CT$_2$ coupling), and $\theta = \pi/16$, which corresponds to $\sim 4\%$ of CT$_1$ molecules being formed in the triplet state.\textsuperscript{33–35} In these models, we treat the intramolecular vibrational modes and solvent bath as a single harmonic bath with a Debye spectral density,\textsuperscript{32} $\mathcal{J}(\omega) = 2\delta D_{\beta} \omega^2 / (\omega^2 + \omega^2)$, with a cutoff frequency of $h\omega_D = 0.05k_BT$, at $T = 300$ K, and with $\delta D = \lambda_{ET1}$. These parameters are chosen to be representative of electron transfers in typical organic donor–acceptor systems,\textsuperscript{25,36} while being computationally tractable with the HEOM method. The $J$ couplings are taken to be in the range 1–100 $g_\mu B$ mT (approximately $1.16 \times 10^{-3}$ to 0.116 meV), in line with superexchange couplings observed in CT states.\textsuperscript{11}
the second-order rate constants for the first electron transfers are approximately a factor of 5 too large compared to those obtained by fitting the population dynamics, so this example is clearly outside of the limits of second-order perturbation theory. However, we still clearly see the emergence of a large static spin-polarization (~30%) in the CT2 state, as well as significant zero quantum coherence. This demonstrates that this mechanism can produce significant spin-polarizations even outside the second-order limit.

Having validated the general theory on a model of condensed phase electron transfer, let us consider how this hopping mechanism predicts a temperature-dependent spin-polarization in chiral systems. Returning to eq 5 for \( \langle \Delta P_f \rangle \), we can see how this temperature dependence emerges. Typically, the exchange coupling and energy shift terms are, to a good approximation, independent of temperature,\(^\text{25}\) whereas if the electron transfer is activated, \( k_{ET} \) will have an exponential dependence on inverse temperature.\(^\text{22}\) Therefore, increasing \( T \) will generally increase the ratio \( k_{ET}/\Omega \), so the spin-polarization will go through a maximum at a particular temperature, where \( k_{CT}/\Omega = 1 \). Interestingly, this temperature dependence of the spin-polarization has been observed in the experiments of Carmeli et al. on CISS in electron transfer in photosystem I,\(^\text{6}\) which is known to proceed via several electron hopping steps.\(^\text{20}\) We have fitted the experimental temperature-dependent spin-polarization, relative to its maximum value, for photosystem I to a model based on eq 5 assuming that Marcus theory\(^\text{7}\) can be applied to describe the temperature dependence of the rate constants. The experimental data and model are shown in Figure 4, where we see that this model is consistent with the available experimental data, and the fitted activation energy of \( E_a = 0.32 \text{ eV} \) is in line with the activation energies of the electron transfers in photosystem I.\(^\text{35}\) It should be noted that the spin-polarization reported in these experiments exceeds the theoretical maximum predicted by eq 5 of 50%. We believe this is due to the error in the correction procedure employed in ref 6 for obtaining the spin-polarizations, which, as discussed by the authors, introduces a large error in the corrected spin-polarization. The “uncorrected” experimental spin-polarizations, which have a maximum value of <10%, still have a nonmonotonic dependence on temperature,\(^\text{6}\) which is still consistent with our proposed mechanism of CISS.

As a final point of note, the mechanism of CISS described here is closely related to the mechanism by which chemically induced dynamic electron-polarization (CIDEP) can be generated in singlet born radical pairs at large applied magnetic fields.\(^\text{38}\) CIDEP can be generated by the combination of the \( \Delta g \) mechanism, in which a radical pair is generated in a coherent but nonpolarized superposition of IS) and IT) states by different precession frequencies of the radical electron spins in a large applied magnetic field. The resulting state can then become transiently spin-polarized if the radical pair has a strong exchange coupling, and this can be frozen out if the radical pair diffuses apart into a configuration with a very weak exchange coupling.\(^\text{37,38}\) In this CIDEP mechanism, the \( \Delta g \) mechanism plays a role similar to that of the spin–orbit coupling mediated electron transfer, effectively rotating one electron spin relative to the other.

To conclude, in this work we have shown how photoinduced spin–orbit coupled charge transport in chiral systems, together with multistep charge transport via CT states with significant exchange couplings, generates the CISS spin-polarization effect. We also see that a zero quantum coherence in the final CT state emerges. The CISS effect described here depends strongly on electron transfer parameters, in particular the rate constant for downhill electron transfer for intermediate CT states. This predicts a specific form for the temperature dependence of the spin-polarization, which is consistent with the experiments of Carmeli et al. in ref 6. Furthermore, this theory predicts a maximum spin-polarization of 50% which is independent of the magnitude of the spin–orbit coupling (provided it is nonzero). This observation could help explain how such large spin-polarizations can be observed in various systems, even when the spin–orbit coupling is extremely weak.

This theory of the CISS effect in molecular systems opens the door to many potential avenues of research. With a theory for the ZQCs and spin-polarizations generated in chiral molecules, well-established principles for synthetically tuning electronic properties of donor–acceptor systems\(^\text{1,4,40}\) could be applied to engineer systems displaying large CISS effects, which can be probed using a variety of possible experiments.\(^\text{3,4,26,31,41}\) In fact, the first examples of such molecules have already been synthesized.\(^\text{35}\) These systems could find an array of uses in single-molecule-scale quantum computing and quantum information applications.\(^\text{1,40}\) It is also known that electron hopping occurs in many important biological electron
transfer systems, such as in photosynthesis in photosystem I and in cryptochromes, which are involved in signaling and potentially in magnetoreception. What role could molecular CISS play in these systems? For example, could biological systems have evolved to inhibit singlet-selective electron recombination reactions using CISS? Equipped with a microscopic theory of chirality induced spin effects in electron transfer reactions, it may be possible to answer such questions.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c02370.

Further details of the HEOM and QME calculations, and a brief analysis of the effects of competing back reactions and singlet—triplet dephasing on spin-polarization (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Thomas P. Fay — Department of Chemistry, University of California, Berkeley, California 94720, United States; orcid.org/0000-0003-0625-731X; Email: tom.patrick.fay@gmail.com

**Author**

David T. Limmer — Department of Chemistry, University of California, Berkeley, California 94720, United States; Kavli Energy Nanoscience Institute at Berkeley, Berkeley, California 94720, United States; Chemical Sciences Division and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0002-2766-0688

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.nanolett.1c02370

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We would like to thank Anthony Poggioli for useful comments on this manuscript. We are also thankful to Peter Hore for pointing out the connection between this work and the CIIDEP effect in the EPR literature. T.P.F and D.T.L. were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, CPIMS Program Early Career Research Program under Award DE-FOA0002019.

### REFERENCES


Supporting Information to “The origin of chirality induced spin selectivity in photo-induced electron transfer”

Thomas P. Fay\textsuperscript{1,a)} and David T. Limmer\textsuperscript{1,2,3,4}

\textsuperscript{1)} Department of Chemistry, University of California, Berkeley, CA 94720, USA
\textsuperscript{2)} Kavli Energy Nanoscience Institute at Berkeley, Berkeley, CA 94720, USA
\textsuperscript{3)} Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
\textsuperscript{4)} Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

I. SIMULATION METHODS

The HEOM method is used to perform simulations on a three state model, where the diabatic potential energy surfaces are treated as a set of harmonic oscillators. This model is given by the following Hamiltonian, which can be split into bath kinetic energy $\hat{h}_b$, diabatic potential terms $\hat{v}_A$, with $A = S_1$, CT$_1$ and CT$_2$, and the diabatic+spin-orbit coupling term $\hat{v}_{ET}$,

\begin{equation}
\hat{H} = \hat{h}_b + \hat{v}_{S_1} + \hat{v}_{CT_1} + \hat{v}_{CT_2} + \hat{v}_{ET} \tag{S.1a}
\end{equation}

\begin{equation}
\hat{v}_{S_1} = |S_1\rangle\langle S_1| \hat{v}_b \tag{S.1b}
\end{equation}

\begin{equation}
\hat{v}_{CT_1} = |CT_1, S\rangle\langle CT_1, S| (\hat{v}_b + E_{CT_1} + J + \hat{B}_{CT_1}) + |CT_1, T_0\rangle\langle CT_1, T_0| (\hat{v}_b + E_{CT_1} - J + \hat{B}_{CT_1}) \tag{S.1c}
\end{equation}

\begin{equation}
\hat{v}_{CT_2} = (|CT_2, S\rangle\langle CT_2, S| + |CT_2, T_0\rangle\langle CT_2, T_0|) (\hat{v}_b + E_{CT_2} + J + \hat{B}_{CT_2}) \tag{S.1d}
\end{equation}

\begin{equation}
\hat{v}_{ET} = \Gamma_{DA_1} (\cos \theta |CT_1, S\rangle\langle S_1| + i \sin \theta |CT_1, T_0\rangle\langle S_1|) \tag{S.1e}
\end{equation}

where $\hat{h}_b = \sum_k \hat{p}_k^2 / (2m_k)$ is the bath kinetic energy, $\hat{v}_b = \sum_k (m_k \omega_k^2 / 2) \hat{q}_k^2$ is the unshifted harmonic potentials, $\hat{B}_{CT_1} = \sum_k c_k \hat{q}_k$ is the bath coupling operator for CT$_1$, $\hat{B}_{CT_2} = [((\sqrt{E_{ET_1}} + \sqrt{E_{ET_2}}) / \sqrt{E_{ET_1}}) \hat{B}_{CT_1}$ is the bath coupling operator for CT$_2$, and the state energies are related to the reorganization energies and free energy changes by $E_{CT_1} = \Delta G_{ET_1} + \lambda_{ET_1}$, and $E_{CT_2} = \Delta G_{ET_1} + \Delta G_{ET_2} + (\sqrt{E_{ET_1}} + \sqrt{E_{ET_2}})^2$. The spectral density, $J(\omega) = (\pi / 2) \sum_k (c_k^2 / (m_k \omega_k)) \delta(\omega - \omega_k)$, which fully defines the harmonic bath, is taken to be of Debye form $J(\omega) = 2 \lambda_D \gamma D \omega / (\gamma_D^2 + \omega^2)$.

\textsuperscript{a)} Electronic mail: tom.patrick.fay@gmail.com
with $\lambda_D = \lambda_{ET}$. The $T_\pm$ states of the CT states are uncoupled from this set of ET states in this model, so we do not need to include them.

HEOM calculations are performed using the frequency based cut-off scheme for the hierarchy of auxiliary density operators (ADOs) described in Ref. 1, along with with ADO rescaling scheme in Ref. 2. A cut-off of $\Gamma = 250\gamma_D$ is used, generating a hierarchy of 375 ADOs with contributions from the first two the Matsubara modes, and the remaining ADOs are treated with the Markovian approximation.\(^3\) The equations of motion are integrated using the short iterative Arnoldi method\(^4\) with a Krylov subspace dimension of 16 and an adaptive time step, in which the Krylov subspace is updated when the coefficient of the last Krylov vector is greater than $\epsilon = 10^{-11}$ times the norm of the HEOM state vector.

The second order master equation rate constants are given by
\[
k_{A \rightarrow B} = \frac{2\Gamma_{AB}^2}{\hbar^2} \text{Re} \int_0^\infty dt \frac{\text{Tr}_b[e^{-\beta H_b^A} e^{\lambda e^{i\int H_b^A}} e^{-i\int H_b^B}]}{\text{Tr}_b[e^{-\beta H_b^A}]}, \tag{S.2}
\]
where $H_b^A$ is the nuclear bath Hamiltonian for state $A$, $H_b^B = H_b + E_A + B_A$, and $\Gamma_{AB}$ is the coupling between states $A$ and $B$. Similarly the shift term is given by,
\[
\delta \epsilon = \frac{\Gamma_{DA}^2}{\hbar} \text{Im} \int_0^\infty dt \frac{\text{Tr}_b[e^{-\beta H_{CT1}^B} e^{\lambda e^{i\int H_{CT1}^B}} e^{-i\int H_{CT2}^B}]}{\text{Tr}_b[e^{-\beta H_{CT1}^B}]}. \tag{S.3}
\]
For the harmonic bath model these depend only on the spectral density $\mathcal{J}(\omega)$, second order master equation parameters are calculated using the expressions in Ref. 5, with the spectral density discretized into 2000 modes using the standard procedure.\(^6\) The full expression for the integrand in the above expressions is,
\[
\frac{\text{Tr}_b[e^{-\beta H_b^A} e^{\lambda e^{i\int H_b^A}} e^{-i\int H_b^B}]}{\text{Tr}_b[e^{-\beta H_b^A}]}
\]
\[
= \exp \left( \frac{i}{\hbar} \int_0^\infty \frac{\mathcal{J}_{AB}(\omega)}{\omega^2} \left[ \coth \left( \frac{\hbar \omega}{2k_B T} \right) (1 - \cos(\omega t)) + i \sin(\omega t) \right] d\omega \right), \tag{S.4}
\]
where $\Delta E_{AB} = -\Delta G_{A \rightarrow B}$, and $\mathcal{J}_{AB}(\omega)$ is the spectral density with the reorganization energy, set to that for the A $\rightarrow$ B electron transfer. This expression straightforwardly reduces to the Marcus theory rate expression by taking the high temperature, $T \rightarrow \infty$, limit of this expression.\(^6\)

The master equations themselves form a linear system of equations are numerically integrated by directly exponentiating the generator for this system of equations.
II. DEPHASING AND RECOMBINATION PROCESSES

Let us briefly consider two processes which could affect the spin polarization observed in this mechanism: competing electron recombination reactions such as $\text{CT}_1 \xrightarrow{k_{ET0}} S_0$, and singlet-triplet dephasing in intermediate CT states. Competing back reactions will both lead to singlet-triplet decoherence in the intermediate $\text{CT}_1$ state at a rate of $k_{ET0}/2$, but they will also reduce the yield of the final $\text{CT}_2$ state but removing, so the spin polarization, relative to the final yield can increase or decrease. Singlet-triplet dephasing will lead to additional decay of singlet-triplet coherences at a rate $k_{STD}$, which will reduce the final spin polarization. In the limit where $|2J| \gg |\delta\epsilon|$, by solving a modified version of Eq. (4) the spin polarization relative to the $\text{CT}_2$ yield is found to be,

$$
\frac{\langle \Delta P_z \rangle}{\phi_{\text{CT}_2}} = -\frac{\sin(2\theta)k_{ET2}\left(\frac{2J}{\hbar}\right)\left(1 + \frac{k_{ET0}}{k_{ET2}}\right)}{\left(\frac{\sin^2 \theta k_{ET0}}{k_{ET2}} + 1\right)\left(\frac{2J}{\hbar}\right)^2 + \left(\frac{k_{ET0}}{2} + k_{ET2} + k_{STD}\right)^2}.
$$

(S.5)

so we see that the back electron transfer rate $k_{ET0}$ can either increase or decrease the spin polarization, but the singlet triplet-dephasing rate will always decrease the spin polarization.