

I joined the Stoll Lab after meeting Dr. Stoll through his Physical Chemistry class in autumn 2012. I found the material fascinating and enjoyed discussing it with him. Upon being offered a research opportunity later, I eagerly accepted.

My research concerns the dynamics of charge generation in organic solar cells, also known as organic photovoltaics (OPVs). OPVs consist of an electron donor-acceptor mixture connected to an electrode, where the donor is typically a highly conjugated polymer and the acceptor is a fullerene derivative. Under illumination, one of the polymer's electrons absorbs energy, moving to an excited state. Next, they are transferred from donor to acceptor, forming a polarized ion pair. If this pair separates, the charge will move towards the electrode, creating a potential difference—that is, voltage. However, there are many causes of inefficiency, such as electron pair recombination to a triplet state (which annihilates the charge) or electron trapping in potential wells. My work is a synthesis of experiment, theory, and computation, with each aspect supplementing the other.

Although the general scheme of the reaction is known, many specifics are not. My goal is to use electron paramagnetic resonance (EPR) spectroscopy, where a magnetic field splits the energy levels of spin centers to generate a spectroscopic signal, to further clarify the kinetics of charge generation and recombination, avenues for charge loss, etc. By doing so, I can determine methods to improve charge generation efficiency in OPVs and thereby increase the efficiency of organic solar cells. As such, this research potentially has great environmental ramifications.

I began by improving our method of sample creation. The protocol a previous group member used involved dissolving a donor-acceptor mixture in solvent and spincoating it onto mylar, which was then cut up and put into EPR tubes. However, this method was tedious, inconsistent, and yielded a weak signal. I designed a protocol for the creation of wallcoated samples, which give a significant improvement in signal strength. With a lower number of scans, I obtained a much stronger signal for a PIDT-PhanQ/PCBM blend (Fig. 1), which gives notoriously weak spectroscopic signals.

Using this new method, scans of a P3HT/PCBM sample at different temperatures and microwave powers revealed that the relative intensity of the PCBM vs. P3HT signal (calculated by fitting spectra to a simulation and taking the ratio of the weights) was temperature-dependent. Also, EasySpin<sup>1</sup> simulations failed

to replicate the full range of spectral features. This suggests a temperature-dependent feature that renders PCBM radicals undetectable—perhaps rapid PCBM-PCBM electron transfer or a shortening of radical lifetime past the detection limits of EPR. Since OPVs will have to function in sunlight, determination of temperature-related charge inefficiencies is of great significance.

The inadequacy of our simulations suggested the necessity of a more sophisticated theoretical approach that directly incorporates donor-acceptor coupling as well as other sources of recombination loss. By adjusting the parameters of such a model to fit experimental data, we can determine the kinetics of these recombination models.

At the suggestion of Dr. Stoll, I began with the Bloch equations<sup>ii</sup>

$$\frac{d}{dt}\vec{M} = \gamma\vec{M} \times B$$

a set of equations which govern the time evolution of electrons' spin magnetization. I wanted to obtain a generalized steady-state solution for all periodic excitations, so I represented both the excitation and the magnetization  $M(t)$  as Fourier series. Eventually, I derived

$$\begin{aligned} a_k M_{ky} = & -f_k b^2 M_{ky} - \sum_{j=1}^{\infty} d_j b M_{(k-j)y} - \sum_{j=1}^{\infty} d_j^* b M_{(k+j)y} - \frac{1}{T_2} M_{ky} - e_k c^2 M_{ky} + \frac{e_k c M_0 \delta k_0}{T_1} \\ & - \sum_{j=1}^{\infty} d_j f_{k-j} b M_{(k-j)y} - \sum_{j=1}^{\infty} \sum_{l=1}^{\infty} d_j d_l f_{k-j} M_{(k-j-l)y} - \sum_{j=1}^{\infty} \sum_{l=1}^{\infty} d_j d_l^* f_{k-j} M_{(k-j+l)y} \\ & - \sum_{j=1}^{\infty} d_j^* f_{k+j} b M_{(k+j)y} - \sum_{j=1}^{\infty} \sum_{l=1}^{\infty} d_j^* d_l f_{k+j} M_{(k-j+l)y} - \sum_{j=1}^{\infty} \sum_{l=1}^{\infty} d_j^* d_l^* f_{k+j} M_{(k+j+l)y} \end{aligned}$$

which describes a system of linear equations relating all of the different Fourier coefficients of  $M(t)$  in the y-direction,  $M_{ky}$ . By solving this system numerically, we obtain all of those coefficients simultaneously and can trivially calculate the  $n$ th harmonic absorption spectrum for  $n = 0, 1, \dots$  up to any arbitrarily chosen limit. With  $M_{ky}$  we can calculate  $M_{kx}$ , which is the set of Fourier coefficients for  $M(t)$  in the x-direction, giving us the  $n$ th harmonic dispersion spectrum. An example is shown in Fig. 3 for one modulation period.

Previously, Nielsen<sup>iii</sup> and Robinson<sup>iv</sup> have described methods for solving the Bloch equations for a steady-state system using a Fourier expansion, and Harbridge<sup>v</sup> has done the same through direct time-

integration. However, the former method can only calculate one harmonic at a time, and the latter method is slow. My computational method is thus an improvement in both respects. Moreover, previous methods assume that the excitation is a cosine or sine function; my generalized model can account for any type of periodic excitation, such as a triangular or square function.

We can use the magnetization to directly simulate EPR spectra. For instance, we can simulate a “powder” spectrum, where molecules are assumed to be oriented in a uniformly random manner. An example of such a simulation is shown in Fig. 2 alongside a simulation generated using EasySpin (the match is not exact because relaxation times and broadening parameters were arbitrarily chosen). Although my method is slower, EasySpin is again only capable of simulating one harmonic at a time, whereas I obtain them all simultaneously. A major advantage of my simulation is that I supply the microwave power, the longitudinal relaxation time ( $T_1$ ), and the transverse relaxation time ( $T_2$ ) as inputs. The power input allows me to account for saturation effects; also, by fitting simulation parameters to experimental data, I can obtain  $T_1$  and  $T_2$  for any EPR sample, which tells me about the lifetime of radical species.

Since the magnetization can be obtained by solving a system of linear equations, we can calculate the magnetization for multiple independent chemical species by putting those systems into block-diagonal form. However, when those species are coupled (as in OPVs), the off-block-diagonal elements become nonzero. My current work is focused on the determination of those elements, which will allow for a steady-state simulation of any coupled chemical system in EPR.

As an initial “proof-of-concept” attempt, I modeled the concentrations of a precursor, donor, and acceptor with differential equations:

$$\begin{aligned}\frac{dn_P}{dt} &= k_{RC}n_Dn_A - k_G \\ \frac{dn_A}{dt} &= \frac{dn_D}{dt} = k_G - k_{RC}n_Dn_A\end{aligned}$$

Assuming the system is at equilibrium allows for the determination of a “reliability function”  $R(t)$  and a “failure density function”  $f(t)$ :

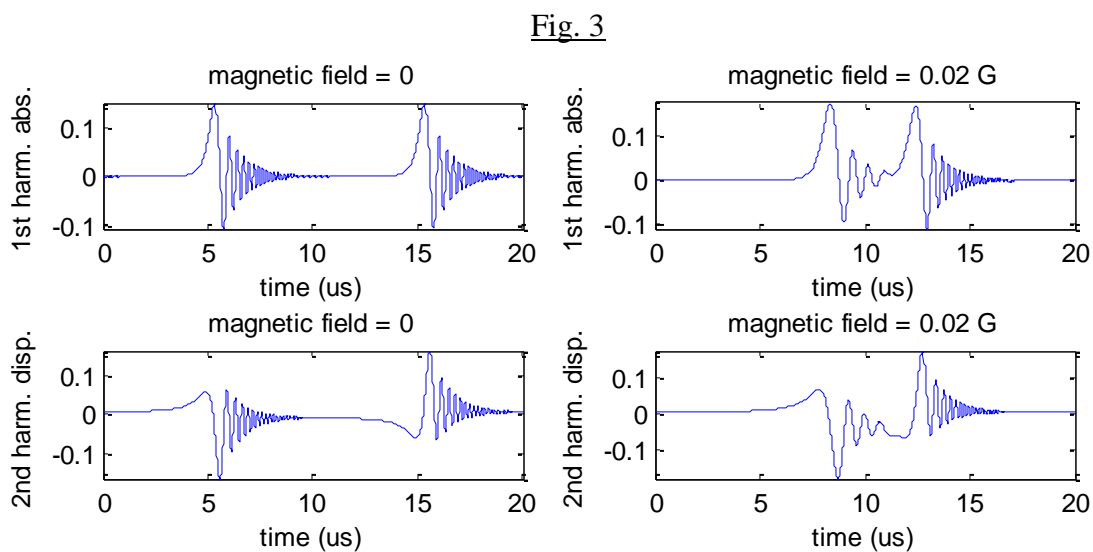
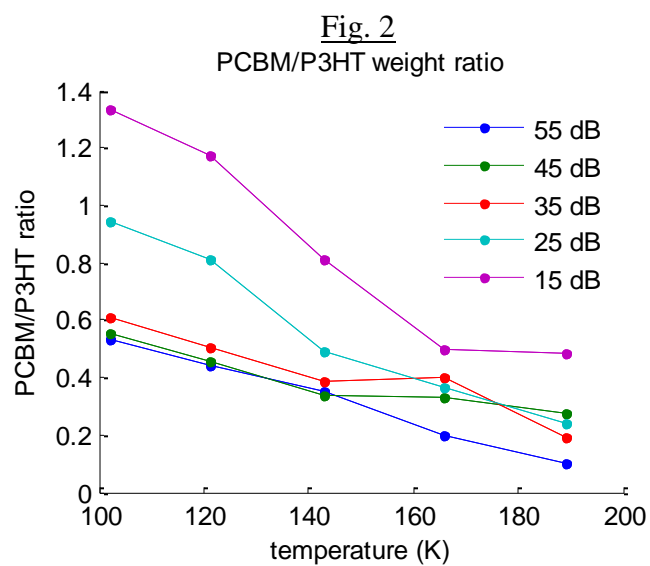
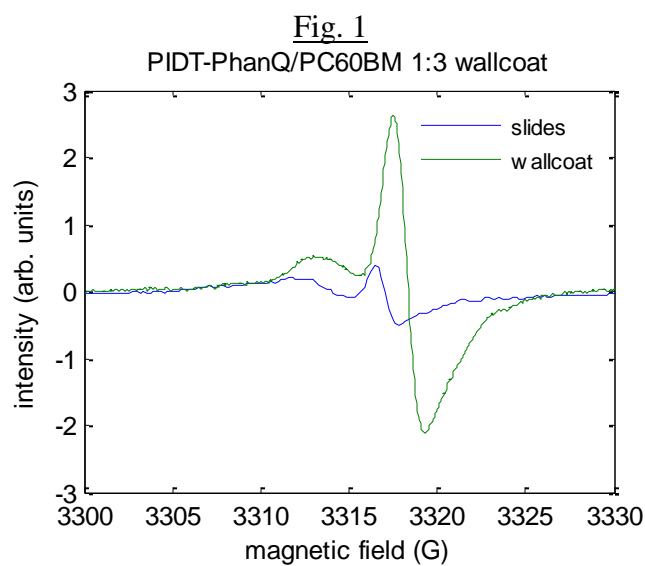
$$R(t) = 1 - \frac{k_G t}{\sqrt{\frac{k_G}{k_{RC}}} + k_G t}$$

$$f(t) = -\frac{dR}{dt} = \frac{k_G \sqrt{\frac{k_G}{k_{RC}}}}{\left(\sqrt{\frac{k_G}{k_{RC}}} + k_G t\right)^2}$$

where the former expresses the probability that a molecule does not undergo recombination after a time  $t$  and the latter gives the distribution of the time each molecule “survives” until recombination. In the future, I hope to apply an analogous process to more complex systems of differential equations that represent a more complex set of chemical interactions.

This research has allowed me to apply my knowledge from classes such as Dr. Stoll’s Physical Chemistry and graduate-level Quantum Chemistry. Furthermore, my immense enjoyment of this research has cemented my decision to pursue a Ph.D. in Chemistry after my undergraduate studies.

## Figures



<sup>i</sup> S. Stoll et al, *J. Magn. Reson.*, 178, 42-55 (2006)

<sup>ii</sup> F. Bloch, *Nuclear Induction*, Physical Review 70, 460-473 (1946)

<sup>iii</sup> Nielsen et al, *J. Magn. Reson.* 170 345-371 (2004), Appendix A

<sup>iv</sup> Robinson et al, *J. Magn. Reson.* 138 199-209 (1999), Appendix

<sup>v</sup> Harbridge et al, *J Magn. Reson.* 156 41 (2002)