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a. REPORT	b. ABSTRACT	c. THIS PAGE			Christine Isborn
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as of 03-Dec-2019

Agency Code:

Proposal Number: 67310CHREP **Agreement Number: W911NF-15-1-0519**
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Report Date: 20-Nov-2019 Date Received: 20-Nov-2019
Final Report for Period Beginning 21-Aug-2015 and Ending 20-Aug-2019
Title: Improved Prediction of the Optical Properties of Coupled Chromophores for Electro-optics
Begin Performance Period: 21-Aug-2015 **End Performance Period:** 20-Aug-2019
Report Term: 0-Other
Submitted By: Christine Isborn Email: cisborn@ucmerced.edu
Phone: (209) 228-4693
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 4

Major Goals: RESEARCH GOALS

Much time and energy has been spent optimizing organic electro-optic (OEO) chromophores at the single molecule level for use in optoelectronics, optical data processing, and telecommunications. This optimization has led to the design of new donor and acceptor groups and a resulting substantial increase in molecular second-order polarizability, or hyperpolarizability ?. Desire for increasing the molecular second hyperpolarizability, ?, responsible for third order optical nonlinearities, is also of interest for maximizing the intensity dependent refractive index (optical Kerr effect).

However, these nonlinear optical (NLO) molecular improvements do not necessarily translate into the same significant progress at the macroscopic level. This disappointing progress is due to our lack of understanding of how the electro-optical properties that are so carefully engineered at the single molecule level change as the chromophores are packed closely together. Dipole coupling between chromophores may be so strong that, even with techniques such as electric field poling, they pack in an anti-parallel fashion that washes out most of the electro-optic effects.

The next generation of OEO chromophores should be optimized not at the single molecule level but instead for their properties upon inclusion in a practical material. This feat requires understanding the structure of chromophores when packed together and the electro-optical properties of these coupled chromophores. Modeling of these chromophores and their properties will provide molecular level understanding of how structure and electronics determine bulk behavior. This new knowledge can transform understanding of chromophore design for improved performance in EO devices.

The objectives of the proposed research are:

(1) to determine the density functional theory (DFT) method that provides the simultaneous best description of absorption maximum and hyperpolarizabilities for a test set of chromophores. Because the intramolecular charge transfer electronic transitions pose a challenge for standard density functional techniques, long-range corrected (range-separated) hybrid functionals will be used in conjunction with optimally tuning the range-separation parameter.

(2) to relate structure (molecular shape) and electronic properties (molecular charges, dipole, and polarizability) to how OEO chromophores pack together. With knowledge from these relationships, chromophores will be altered for improved bulk performance, for example by adding spacer groups or changing the total dipole moment with added functional moieties outside of the conjugated carbon chain.

(3) to calculate electronic, optical, and electro-optical properties of coupled chromophores in order to correlate their relative distance and orientation to the overall material properties. This objective requires developing new theoretical methods for treating many tens to hundreds of coupled chromophores. Our goal here will be to simulate absorption spectra in different environments, as well as to compute a 'bulk' hyperpolarizability of many chromophores using a modified two-state model. When combined with the knowledge of chromophore packing from Objective 2, this new understanding of coupled chromophore properties will provide guidance for optimizing bulk electro-optic effects.

EDUCATION GOALS

As a minority-serving institution in which 46% of the undergraduate population are Hispanic, 52% of the population belong to a racial minority and 65% are first generation college attendees, UC Merced brings educational and research opportunities to many students in California's Central Valley. My goal to help UC Merced's students be successful in science careers will undoubtedly lead to an increased number of graduates in scientific fields and a more diverse scientific workforce. Unfortunately, often because of cultural differences or because they are facing more substantial challenges on the path to a science degree, these underrepresented minority students do not choose to pursue a career in science or find themselves struggling to succeed upon reaching the upper division course level. In particular, even though students have already completed their first two years of course work, we have found significant attrition within the Chemistry major at the upper division level when the rigorous physical chemistry courses require students to use more sophisticated mathematics skills. I plan to address this problem by achieving the following objectives through my proposed educational outreach:

(1) help struggling UC Merced upper division undergraduate students succeed in their Chemistry major by developing a workshop program that reviews the mathematical and chemical prerequisites necessary for their upper division coursework.

(2) support women and minorities to pursue careers in the sciences by expanding the Women in STEM mentoring program to also include fellowship and grant writing sessions.

Accomplishments: In terms of the research goals for this project, over the duration of this project, we list the following accomplishments:

1) We have determined which density functional approximations are best suited to modeling the linear and nonlinear optical properties of organic electro-optic chromophores, both individually and in aggregate. In particular, we have shown in our published work (JCTC, 10, 3821, 2014 and JCTC, 13, 3787, 2017) that a large amount of exact exchange and long-range correction is required for accurately capturing intramolecular charge transfer character, although the popular procedure of 'optimally tuning' the exchange may not be the most accurate for larger extended conjugated systems.

2) We have developed a method for computing the linear absorption spectra of disordered chromophore aggregates that accounts for inter-chromophore polarization and excitonic interactions. (JCTC, 13, 3787, 2017)

3) We have extended this method to computing the hyperpolarizabilities of disordered chromophore aggregates (JPC C, 123, 13818, 2019) and studied the role of excitonic interactions in increasing or decreasing electro-optic effects in chromophore aggregates. This work was featured on the cover of the Journal of Physical Chemistry C.

4) We have put together a video tutorial of how to perform these calculations, to hopefully disseminate these results to a broad group of researchers. This work is currently accepted for publication and in production for the Journal of Visualized Experiments (JoVE).

In terms of the education goals for this project, we have focused mostly on helping struggling UC Merced undergraduate students succeed in their Chemistry major.

After using the funding from this grant to develop material for and support the teaching of supplementary problem-

solving sessions for upper division quantum chemistry, the positive feedback from the students has led the administration to approving an official discussion session for the upper division classes. The materials developed as part of this grant are now being used in these discussion sessions. The weekly sessions that were offered the fall 2016 semester gave students a review of the requisite mathematical concepts and then provided them with guidance in setting up and thinking through how to solve problems so that they would be better prepared to succeed in the class, and these sessions were made required by students in fall 2017. The problem-solving skills developed will help them beyond the subject of quantum chemistry, and should help them be better prepared to enter the STEM fields after graduation.

We have also begun assessing weaknesses in our students at the lower-division level, identifying areas of content weakness as well as areas to help increase students' sense of belonging within Chemistry and in STEM fields. We plan to start developing active learning content that will promote more peer interactions as well as a sense of community among first generation college students.

Training Opportunities: Post-doc Dr. Aleksey Kocherzhenko started a Tenure-track Assistant Professor position at California State University East Bay.

Post-docs on this project Drs. Sapani Soni and Brad Barker have been learning our recently developed methodologies by working closely with faculty and Prof. Kocherzhenko. Dr. Barker is currently on the faculty job market.

Dr. Sapana Soni attended an active learning workshop intended to prepare her for a position in academia and is currently applying for post-doctoral fellowships.

Dr. Sapana Soni presented a tutorial on using Jupyter notebooks at the retreat for the Center for Chemical Computation and Theory at UC Merced.

Graduate student Jacob Wilmer gained experience working with undergraduates as an instructor for computational chemistry tutorials. He also attended at summer school at Stanford on coding for QM/MM and AIMD methods.

Undergraduate student, Jessica Maat, began graduate school at UC Irvine and attended a Theoretical Chemistry Summer School at Stanford University.

The PI organized a summer school on Time-Dependent Density Functional Theory in summers of 2017 and 2019.

Many UC Merced undergraduate students benefited from this grant support because of the problem-solving materials developed to help them succeed in their upper division quantum chemistry course. Lessons learned from working with students will be taken into account for developing new problem-solving materials for lower division courses.

The PI was on panel aimed at answering questions pertaining transitioning from post-doc to academia and participated in a webinar supporting women in high-performance computing.

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Results Dissemination: One experiment-theory collaborative manuscript was published in the Journal of Lightwave Technology.

Collaborator Dr. Lewis Johnson presented some of our results at his talk at the SPIE Organic Photonics and Electronics meeting, with a follow up paper, on “Poling induced birefringence in OEO materials under nanoscale confinement.”

One recent manuscript was published in J. Phys. Chem. C, outlining our theoretical method for simulating the hyperpolarizability of chromophore aggregates and analyzing the role of excitonic interactions, which was featured on the cover of the journal.

Our method development will be featured in the Journal of Visualized Experiments, allowing more researchers to implement these methods and study similar systems.

Regular virtual meetings were held with the Robinson group at the University of Washington to discuss our research and future directions.

The PI presented this project to UC Merced undergraduate Chemistry majors as part of her computational chemistry class.

Honors and Awards: The PI received the UC Merced Senate Award for Distinguished Early Career Research. The PI also was awarded tenure at UC Merced.

Protocol Activity Status:

Technology Transfer: Nothing to report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Sapana Soni
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Brad Barker
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

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Date Submitted: 11/20/19 12:00AM Date Published:
Publication Location:
Article Title: Unraveling Excitonic Effects for the First Hyperpolarizabilities of Chromophore Aggregates
Authors: Aleksey A. Kocherzhenko, Sapana V. Shedge, Xochitl Sosa Vazquez, Jessica Maat, Jacob Wilmer, And
Keywords: exciton, organic electro-optic materials, two-state model, first hyperpolarizability
Abstract: Excitonic interactions often signifcantly affect the optoelectronic properties of molecular materials. However, their role in determining the nonlinear optical response of organic electro-optic materials remains poorly understood. In this paper we explore the effects of excitonic interactions on the frst hyperpolarizability for aggregates of donor-acceptor chromophores. We then use both time-dependent density functional theory calculations and the molecular exciton approximation to parametrize the two-state model. Using the molecular exciton approximation to the two-state model (i) is appropriate for disordered aggregates (unlike band theory), (ii) is computationally effcient enough for calculating the first hyperpolarizability of materials that consist of thousands of interacting chromophores, and (iii) allows the unraveling of the effects of both excitonic interactions and electrostatic polarization.
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Volume: Issue: First Page #:
Date Submitted: Date Published:
Publication Location:
Article Title: Excitonic Hamiltonians for Calculating Optical Absorption Spectra and Optoelectronic Properties of Molecular Aggregates and Solids
Authors: Aleksey A. Kocherzhenko, Sapana V. Shedge, Pauline F. Germaux, Mohammad Heidarian, and Christir
Keywords: Exciton model, multiscale modeling, numerical simulations, absorption spectra, molecular materials, optoelectronics
Abstract: Rational design of disordered molecular aggregates and solids for optoelectronic applications relies on our ability to predict the properties of such materials using theoretical and computational methods. However, large molecular systems where disorder is too significant to be considered in the perturbative limit cannot be described using either first principles quantum chemistry or band theory. Multiscale modeling is a promising approach to understanding and optimizing the optoelectronic properties of such systems. It uses first-principles quantum chemical methods to calculate the properties of individual molecules, then constructs model Hamiltonians of molecular aggregates or bulk materials based on these calculations. In this paper, we present a protocol for constructing a tight-binding Hamiltonian that represents the excited states of a molecular material in the basis of Frenckel excitons: electron-hole pairs that are localized on individual molecules that make up the material. The
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Acknowledged Federal Support: **Y**

CONFERENCE PAPERS:

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Conference Name: Organic and Hybrid Sensors and Bioelectronics XI
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Conference Location: San Diego, United States
Paper Title: Poling-induced birefringence in OEO materials under nanoscale confinement
Authors: ewis E. Johnson, Delwin L. Elder, Aleksey A. Kocherzhenko, Andreas F. Tillack, Christine M. Isborn, Lar
Acknowledged Federal Support: **Y**

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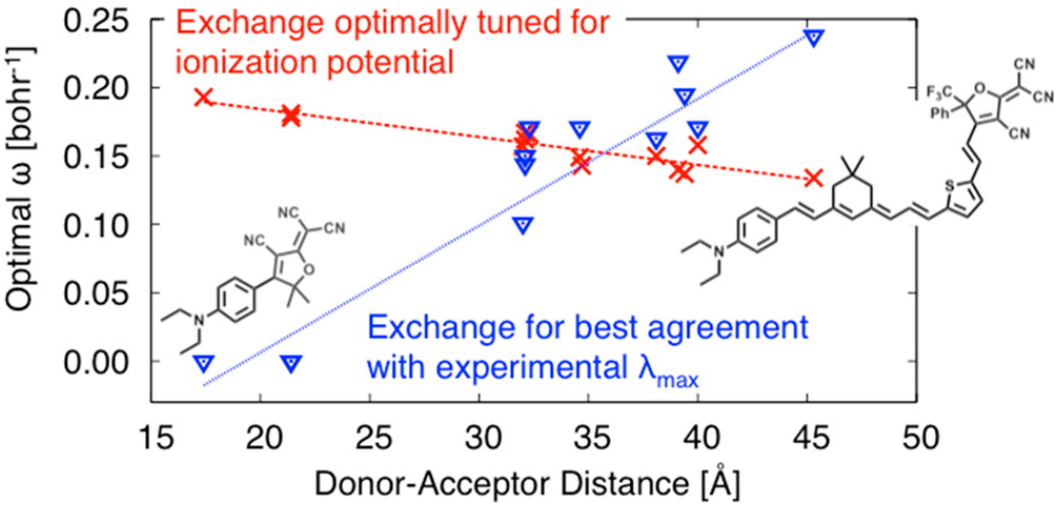
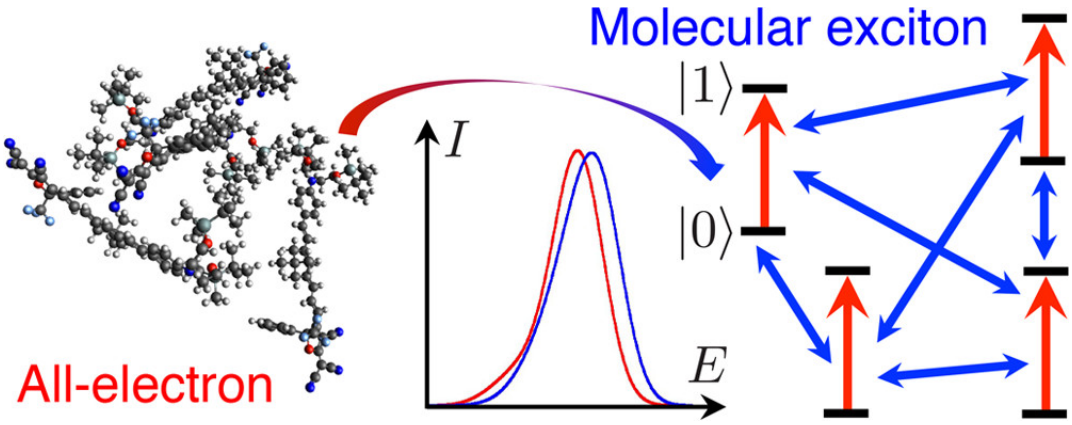
In terms of the **research goals** for this project, over the duration of this project, we list the following accomplishments with figures that highlight these results.

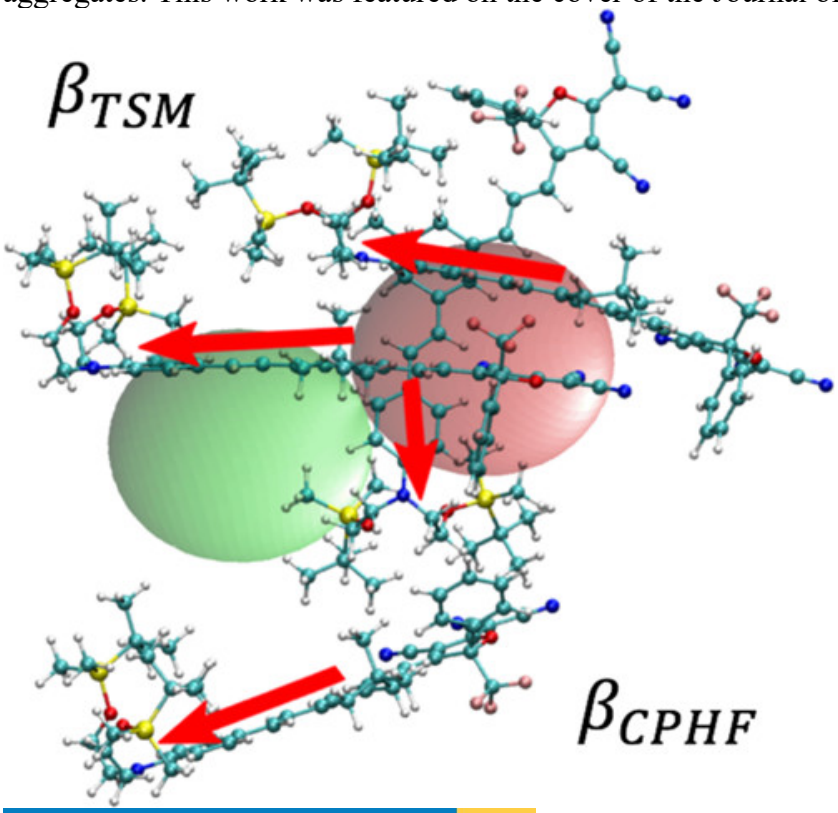
1) We have determined which density functional approximations are best suited to modeling the linear and nonlinear optical properties of organic electro-optic chromophores, both individually and in aggregate. In particular, we have shown in our published work (JCTC, 10, 3821, 2014 and JCTC, 13, 3787, 2017) that a large amount of exact exchange and long-range correction is required for accurately capturing intramolecular charge transfer character, although the popular procedure of 'optimally tuning' the exchange may not be the most accurate for larger extended conjugated systems.



2) We have developed a method for computing the linear absorption spectra of disordered chromophore aggregates that accounts for inter-chromophore polarization and excitonic interactions. (JCTC, 13, 3787, 2017)



3) We have extended this method to computing the hyperpolarizabilities of disordered chromophore aggregates (JPC C, 123, 13818, 2019) using a two-state model (TSM), compared these results to more rigorous coupled perturbed Hartree-Fock studied the role of excitonic interactions in increasing or decreasing electro-optic effects in chromophore aggregates. This work was featured on the cover of the Journal of Physical Chemistry C.



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