Graduate Research Plan Statement

I propose to develop and implement a new approach to quantum-light spectroscopy. I will benchmark the new approach against established classical-light techniques, namely nonlinear coherent spectroscopy, and use classical- and quantum-light spectroscopies to investigate the mechanism of circularly polarized photoluminescence from chiral perovskite thin films.

Introduction: Quantum light has been the subject of research in many physics subdisciplines, but until recently has not been considered as a tool for molecular spectroscopy by physical chemists. Much of the current research on spectroscopy using quantum light has focused on using entangled photon pairs (EPPs) for nonlinear spectroscopies involving two-photon absorption[1], effectively using quantum light as an analog for classical light in nonlinear applications. I propose to use an established technique in the field of quantum photonics – quantum-state tomography – in **a spectroscopic application that treats both the quantum light and the light-matter interaction fully quantum mechanically**.

The advantage of the proposed quantum-light spectroscopy over known nonlinear ultrafast spectroscopy techniques is the ability to directly investigate the quantum mechanical nature of a material system and its dynamics. By measuring changes in the state of quantum light due to light-matter interactions, we can learn about phenomena such as entanglement of correlated species in matter and spin-orbit coupling. Chiral perovskite thin films are an exciting and important material system to investigate with this spectroscopy. Recent studies have shown that **chiral perovskites act as sources for circularly polarized photoluminescence (CPL)**, a highly sought-after feature applicable to bioresponse imaging, 3D-LED displays, quantum computing, spintronics, and more.[2] An investigation of chiral perovskite thin films by Di Nuzzo, *et al*. has shown that the unknown mechanism of CPL in Ruddlesden-Popper perovskite thin films does not agree with the model of Rashba spin-orbit coupling,[3] the primary model used to describe spin-orbit coupling in 2D-semiconductors. I propose to use quantum-light spectroscopy, as well as two-dimensional photoluminescence (2DPL) and photo-induced absorption (2DPIA) spectroscopies, to **explore the claim that the CPL of chiral perovskite thin films is due to the charge of photoexcited Wannier excitons and study the chiral symmetry transfer from optically inactive cations to excitons.**

Background: Quantum-state tomography is a technique used to completely characterize a quantum state by measuring its density matrix. Photonic-state tomography involves the measurement of an ensemble of polarization-entangled photon pairs to determine the full two-photon density matrix[4]. I propose to use the spectroscopic setup in Figure 1, in which EPPs are generated in a polarization basis via spontaneous parametric down conversion (SPDC) using a pair of BiBO crystals. The two photons, the signal and the idler, are spatially separated along the edges of the SPDC emission cone and sent down distinct optical paths. The idler photon is sent directly to a polarimeter composed of a quarter wave plate (QWP), a half wave plate (HWP), and a polarizing beam splitter. The signal photon interacts with a sample before being sent to an identical polarimeter. The polarimeters project both photons onto a polarization basis defined by horizontal (H), vertical (V), diagonal (D), and right (R) polarizations. Finally, the photons are detected by single photon detectors that drive a coincidence counter. By determining the change in the full density matrix of the biphoton state, we can identify the transformation matrix associated with the light-matter interaction in the polarization basis.

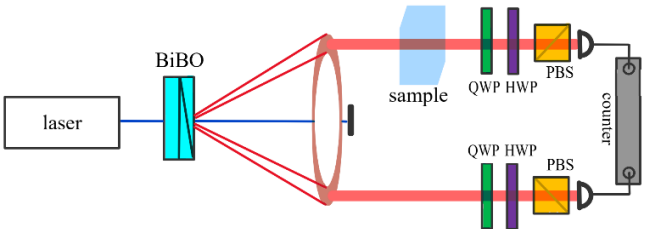

Figure 1. Proposed quantum-light spectroscopy setup

Previous Work: The experimental set-up in Figure 1 has been realized in the Silva lab and validated by taking tomographic measurements of several prepared biphoton states of the form $c_{HH}|HH\rangle+c_{VV}|VV\rangle$ and

with a quarter waveplate (QWP) in the place of a sample. In the defined polarization basis, a QWP performs a unitary transformation defined by a 90° rotation of the Poincaré sphere about an axis dependent on the waveplate angle. Measurements taken with our experimental setup of a QWP at 0°, 22.5°, and 45° indicate such a transformation, corresponding to a rotation without loss of purity in the biphoton state.

The proposed experimental set up is also easily combined with other spectroscopic techniques familiar to the Silva lab, such as pump-probe spectroscopy. Preliminary data taken with a similar experimental set up in which the sample is excited by a pump laser has shown that the quantum state of the probe biphoton pair is altered by scattering off of a triplet-triplet intermediate state involved in singlet fission. Through experimental measurements of bis(triisopropylsilylethynyl)tetracene (TIPS-tetracene) samples obtained through collaboration with Prof. John Anthony at the University of Kentucky and theoretical development done in collaboration with Prof. Eric Bittner at the University of Houston, we have studied the nature of the long-lived correlated triplet pair of TIPS-tetracene, which has been assumed to be entangled in the spin basis without experimental evidence.[5] The experimental data, along with simulations of the TIPS-tetracene system and the many-body scattering theory of the biexciton probe have all contributed to a manuscript to be submitted to the *Journal of Physical Chemistry C.*

Aim I – Theoretical comparison of quantum-light and 2D spectroscopies: The implementation of quantum-light spectroscopy is nontrivial; working in the photon counting regime and with ensemble measurements requires precise environmental control and careful error analysis. It is necessary to show the proposed quantum-light spectroscopy will yield information that is inaccessible with known spectroscopic techniques and worth the challenge. I intend to do this theoretically using Lindbladian models to predict the data that can (and cannot) be obtained for chiral perovskite systems comparatively with 2D and quantum-light spectroscopies as shown in our paper published on ArXiv[6] for TIPS-tetracene.

Aim II – Experimental investigation of CPL of chiral perovskite thin films: In concert with the proposed theoretical development, I intend to interrogate the mechanism by which chiral Ruddlesden-Popper perovskite thin films impart circular polarization on unpolarized incident light using 2DPL, 2DPIA, as well as the proposed quantum-light spectroscopy. I plan to synthesize the thin films with the help of Esteban Rojas-Gatjens, a groupmate co-advised by Prof. Seth Marder. To my knowledge, these thin films have not been characterized with any 2D-spectroscopy which could probe their exciton dynamics.

Intellectual Merit: I am ideally positioned to do this research. As part of the Silva group, I have access to a full toolbox of 2D- and ultrafast spectroscopic techniques which are regularly used by our group to investigate perovskites. Moreover, the project will benefit from continued collaboration with Prof. Eric Bittner and future collaboration with Andrei Piryatinski at the Center for Nonlinear Studies at Los Alamos National Laboratory. The proposed research has potential to establish the experimental and theoretical basis for a new form of quantum-light spectroscopy while also learning about the fundamental mechanism of CPL from chiral perovskites, which could improve understanding of spin-orbit coupling in chiral materials.

Broader Impacts: Understanding the chiroptical properties of chiral perovskite thin films would contribute to many possible applications, as cited above. However, chiral perovskite thin films are just one of many interesting material systems that the proposed quantum-light spectroscopy can be used to study. Development of a new quantum-light spectroscopy would expand the capacity of spectroscopists to study fundamental quantum mechanical phenomena. It could be used to characterize gates used in quantum computation, singlet fission materials, spin-based memory devices, and so on.

[1] S. Mukamel, et al. *J. Phys. B.,* **53**, 072002 (2020). [2] G. Long, et al. *Nat. Rev. Mat.*, **5**, 423-439 (2020). [3] D. Di Nuzzo, et al. *ACS Nano*, **14**, 7610-7616, (2020). [4] J. Altepeter, et al. *Adv. Atom. Mol. Opt. Phys*, **52**, 105-159 (2005). [5] C. Yong, et al. *Nat. Comm.*, **8**, 15953 (2017). [6] arXiv:1909.12869