**LCLS Department: SXR-TMO**  Select Department

**Title: Spooktroscopy enhanced resonant Auger maps of excited NO2**

**LCLS Lead/Leads** *(department or scientist)*: Ryan Coffee

**LCLS Collaborators:** Averell Gatton, Audrey Therrien, Mike Glownia, Peter Walter, Ryan Coffee

**Non-LCLS/External Collaborators** *(names, affiliations, and* ***description of roles****)*:

Ruaridh Forbes (PULSE): experimental setup, consultation,

Michael Schuurman: external theory support

Thomas Wolf (PULSE): consultation

James Cryan (PULSE): consultation

**Proposal Criteria**

*(select all criteria that are relevant for this proposal)*

|  |  |
| --- | --- |
| ☐ | Proposed activities **are outside** the scope or guidelines for a regular PRP proposal |
| ☐ | **Commissioning & Technical Development** |
| ☐ | **Career Development Opportunity Proposal:**  Developing LCLS staff scientists and expertise to remain at the forefront of their fields. Describe in detail how the proposed activity will advance the scientific career of the proposer. |
| ☐ | **Developing or demonstrating new experimental methods, technical capabilities, or instrumentation** with clear potential to enhance the science impact, and exploit the unique capabilities, of LCLS. (Links to the LCLS strategic development plan, existing programs, initiatives, or development efforts e.g. R&D, L2S-I, XIP, AIP, OIP etc. should be clearly articulated, where appropriate.) |
| ☐ | **Demonstration experiments** to develop a **new user community** and/or **establish a new area of science** where LCLS will have a significant impact. |
| ☐ | **Enhancing the operational effectiveness of LCLS** |
| **Justification for criteria selection**  This proposal involves the commissioning of the Cookiebox R&D prototype along with development and deployment of the data acquisition platforms (FPGA, signal processing, digitizer) and control implementation, all of which will fold directly into implementation of the MRCOFFEE machine.  This work will directly advance the scientific careers of two RA’s (Averell Gatton and Audrey Therrien) by providing an opportunity to publish data from the R&D effort. Otherwise, this effort may not have that opportunity before the installation of MRCOFFEE.  We will advance the development of spooktroscopy as it is applied to Auger spectroscopy at LCLS.  These experiments will establish a new area of ultrafast resonant auger spectroscopy.. | |

**Technical and Experimental Summary [[1]](#footnote-2)**

|  |  |
| --- | --- |
| **Instrument** | CookieBox R&D Prototype (precursor to MRCOFFEE machine)  Time-Tool |
| **Number of Shifts** | 4 |
| **Detailed shifts justification** | 1. CookieBox eToF alignment, tuning, and calibration with Ne 2p line 2. Spatiotemporal overlap with pump laser: 2 color signal 3. Time zero overlap data acquisition at N and O edges 4. Continued time zero data acquisition or possible time resolved scan |
| **Std. configuration** | Y/N : N (if Yes specify : ) |
| **Scheduling constraints** (end of the run, near a user experiment, etc.) | Requires time tool. Will require removal of the C-VMI and Kaesdorf Cube endstation and installation of the CookieBox prototype endstation. |
| **Multiplexing** | Y/N : N (if Yes specify multiplexing scheme : ) |
| **Photon energy** (range) | 399 - 537 eV |
| **Pink/ Mono/CCM** | pink or mono : pink |
| **Operation mode** (SASE, seeded, other ) | SASE |
| **Lasers parameters** | >1e12 W/cm^2 of 400nm pump (2nd harmonic of 800nm) |
| **Resources required** (M&S, equipment, manpower, etc.) | We require technician support for replacing the C-VMI end-station with the CookieBox Prototype. We expect to rely on the proposal collaborators to complete the install. We will require assistance in interfacing with the controls system and data stream. |
| **Additional information** |  |

***Narrative: two-page limit, excluding references***

**What do we intend to do?**

~~Resonant Auger Spectroscopy (RAS) is a highly sensitive probe of the coupling between nuclear and electronic wavefunctions in molecules.~~ We intend to create Resonant Auger Spectroscopy (RAS) maps that time resolve the pumped first excited state in NO2 as it relaxes to the ground state through internal conversion. We expect to be limited by data rate to 2-3 distinct time delays. We have selected NO2 as the target molecule for the fast ~50fs ( citation?) decay of the first excited state that is easily pumped by available 400nm light and because it has recently attracted the attention of our external theory collaborators.

The scheme for RAS in N2O is succinctly summarized in reference [1], and is as follows. In the first step an x-ray photon promotes a k-shell electron to one of several resonant bound orbitals

1st2 1sc2 7sigma2 2pi4 + hw -> 1s-1 (1PI pi\*t, 1SIGMA+ sigma \*t, 1PI pi\*c)

fix equations

where the t and c subscripts denote the terminal and central nitrogen. In the second step, the core shell is filled by either the promoted electron (the participator process) or another electron (the spectator process) and ejects another of the valence electrons. Here we focus exclusively on the participator process, written as:

Add equations here

The participator process leaves the molecule in the exact configurations created by direct photoionization of the valence orbitals and therefore the two paths interfere. The Auger electron’s angular distribution and energy records the character and binding energy of the originating orbital, respectively. Furthermore, the interference encodes phase delays which can be connected to time evolution of the molecular state through theory.

RAS has been widely deployed to study the vibronic and electronic coupling due to the Renner-Teller effect in linear triatomic molecules (N2O, CO2, OCS, CS2) [3, 5], and to elucidate the dissociative pathways with the same final products in e.g. N2O [4] in combined electron ion experiments. In addition, and in contrast to non-resonant KVV auger spectroscopy, RAS spectra exhibit non-isotropic angular distributions induced by the dipole matrix overlap of the resonantly populated molecular orbital with both the x-ray polarization and the site-specific core hole. Only molecules oriented appropriately with respect to the X-ray polarization will have k-shell electrons promoted to the valence orbital, creating an ensemble that is aligned to some degree in the lab frame. Subsequently, the participator Auger decay of this aligned ensemble gives rise to a structured angular emission pattern that reveals the character of the ejected electron’s wave function. This angular information has been used to characterize RAS [1, 10], photoelectron spectroscopy [7], and molecular bond breaking under the axial recoil approximation in total ion yield [6] experiments, all on N2O.

There is far less literature on bent triatomic molecules as they do not exhibit interesting Renner-Teller effects after x-ray photoabsorption. While RAS is sensitive to non-Born Oppenheimer dynamics, synchrotron driven RAS is limited to dynamics on the timescale of the Auger decay immediately after the x-ray probe. We are aware of only one RAS study on NO2 [8]. In [8], spin coupling in the valence orbitals was found to create propensity for the final state to be either singlet or triplet. We propose to take the first steps towards attosecond time resolved RAS using laser pump X-ray probe schemes at the FEL.

We intend to combine the recently developed spooktroscopy method to achieve super resolution of RAS spectra. This is the only available method for achieving attosecond time resolution without obscuring energy features with the inherent broad bandwidth of FEL pulses. The technique requires collecting a detailed energy spectrum of each x-ray pulse with a reference photoelectron spectrum from a well characterized atom such as Helium. The statistical variation in the spectrum can then be used to reconstruct underlying features in the collected Auger electron spectra which are much finer than the bandwidth of the pulse [9].

This experiment is a step in the development of the MRCOFFEE machine that will eventually provide 16 angles for differential angle resolved measurements. RAS measurements that are differential in time, energy, angle, and which apply super resolution via spooktroscopy, will take full advantage of the high rep-rate of LCLS-II.

**Why is this important or urgent? Why now in Run 18?**

It is of vital importance that TMO scientists remain at the forefront of attosecond transient absorption techniques relevant to the high rep rate of LCLS-II. Of these techniques, we believe that RAS in combination with Spooktroscopy will yield a plethora of valuable insights into chemical dynamics of larger biologically relevant molecules. RAS can probe site selective orbital binding energies of molecules like pyridine butadiene, furan, formic acid, acetaldehyde, acetic acid, methyl formate, and methyl oxirane [10]. We believe this experiment will develop the expertise in RAS on excited molecules and pave the way for attosecond transient absorption experiments at LCLS-II.

**Detailed Experimental Description**

**Shift 1:** CookieBox Prototype commissioning. Beam alignment through endstation to time tool: 2hrs. Centering Cookiebox eToF via 2-D scan, 4hrs. Jet positioning: 1hr. Laser alignment onto paddle: 1hr. Equalizing eToF lenses for equal retardation: 2hrs. Maximizing collection efficiency on each eToF: 2hrs.

**Shift 2:** Taking beam: 1hr. Spatiaotemporal overlap with laser on paddle: 2+ hr. Time overlap with Neon 2 color signal: 2+ hr. Data taking, begin program outlined below for shifts 3 & 4: 8- hr.

**Shift 3:** Data collection at the N1s->6a1 transition at 403.73eV and N1s->2b1 transition at ~405eV, scan in x-ray energy of 399-410eV, time overlapped/time delayed: 6hrs/6hrs.

**Shift 4:** Data collection at the O1s->6a1 transition at 530.32 eV and O1s->2b1 transition at 532.36 eV, scan over resonance energy range of ~525 -537eV, time overlapped/time delayed: 6hrs/6hrs. Bonus goal: rotate laser polarization to orient pumped orbitals perpendicular to x-ray polarization and repeat one or more the cases above: x+ hrs.

**Impact***What will be the impact or significance if the proposed activity is successful?  
What will be the impact if the proposed activity is delayed or deferred?*

The continued development of the MRCOFFEE end station is of vital interest to the TMO community. The CookieBox Prototype is the R&D testbed for the final MRCOFFEE end station which is not expected to be substantially different in its construction and operation. Already, the design for MRCOFFEE is largely complete yet requires testing and validation of the prototype in real operating conditions. Lack of an opportunity to test may jeopardize future R&D funding.

From a career development perspective, the CookieBox Prototype will represent the majority effort of two RAs (Averell Gatton, Audrey Therrien) over the course of 2 years. That effort will not be rewarded with publications if the end station cannot be deployed to run an experiment. This will have a negative impact on the carrier development of both.

Furthermore, the strategic goal of building the MRCOFFEE end station may be weakened by a crisis in confidence among the user community that observes no tangible progress. This may lead to a cascading effect where the community does not see the MRCOFFEE project as a viable answer to their spectroscopic needs and demands other solutions in the form of existing spectrometers (Kaesdorf), VMI setups, or a magnetic bottle. Diversion of funds and resources in an already tight schedule and budget environment may delay MRCOFFEE.

MRCOFFEE is a flagship end station intended to enable some of the most exciting science in TMO. MRCOFFEE is the only device capable of attosecond time resolved photoelectron spectroscopy and angular streaking at high rep rate. by providing SASE substructure characterization on a shot to shot basis MRCOFFEE will enable advanced accelerator tuning schemes.

Ultimately, delay of MRCOFFEE will impact the continued development of the LCLS SXR department as a whole.

**References**

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1. IH proposals considered for beamtime must submit the same technical questionnaire required for standard user experiments [↑](#footnote-ref-2)