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RPPR Final Report
as of 29-Nov-2022

Agency Code: 21XD

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Agreement Number: W911NF-17-1-0163

INVESTIGATOR(S):

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Report Date: 30-Apr-2022

Date Received: 29-Nov-2022

Final Report for Period Beginning 01-May-2017 and Ending 31-Jan-2022

Title: Laser Spectoscopy of Liquid Carbon, Q-Carbon, and Their Surfaces; Application to Material Science

Begin Performance Period: 01-May-2017

End Performance Period: 31-Jan-2022

Report Term: 0-Other

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees:

STEM Participants:

Major Goals: We propose to advance our fundamental understanding of novel forms of carbon by performing detailed spectroscopy studies of their bulk and surfaces, using novel and state-of-the-art techniques.. Liquid and Q-carbon will be prepared by non-thermal melting of both diamond and graphite targets. With femtosecond and nanosecond lasers. The vibrational and electronic structures of the bulk forms will be probed as a function of the delay time of the melting pulse (and thus as a function of temperature and pressure) with our recently developed chirped femtosecond coherent anti-Stokes Raman spectroscopy (c-CARS) technique. Our new broadband deep-UV, electronic sum frequency generation(DUV-ESFG) spectroscopy technique will be used to probe the corresponding surfaces. Our Single Photon InfraRed Emission Spectroscopy (SPIRES) spectrometer will be used to monitor the evolution of the "super-undercooled" liquid carbon into the Q-carbon stages. Results from this collection of experiments will characterize the structure, bonding, and dynamics of liquid carbon, Q-carbon, and the various diamond structures(needles, nano/microdiamonds, ...) nucleated from Q-carbon. Time-resolved experiments will address the nucleation mechanisms of carbon nanotubes and diamond structures from the liquid and Q-carbon forms. Addition of dopants (e.g. N, B) to the diamond nano/micro-structures will be explored. The combined theoretical and experimental information obtained will ultimately be used to construct improved potential models that can describe properties of all known forms of carbon, and to predict additional, yet undiscovered forms that may be of much technical interest.

Accomplishments: Problems engendered by the COVID pandemic forced a significant refocusing of our efforts to study liquid carbon and the proposed new forms of carbon, as outlined in our original proposal. We encountered serious laboratory shutdowns due to COVID restrictions, and most seriously, due to supply chain issues when one of our major laser systems failed. Accordingly, we refocused our efforts on the use of international free electron laser (FEL) facilities and the development of new tools for investigating carbon and its interfaces.

In addition to the results presented in the publications listed below, during the last three years, we have managed to accumulate unprecedented new data for laser-melted carbon using several international FEL facilities. The measurements comprise Resonant Inelastic X-ray Scattering (RIXS) and X-ray Emission Spectroscopy (XES) data, which will provide a new level of detail regarding the geometric and electronic structure of the liquid state of carbon when the requisite accompanying theoretical modeling of the data is completed by our theory collaborators in Stockholm and LLNL. Unfortunately, these ongoing calculations are exceedingly complex and time-consuming and are essential to extract meaningful structural and chemical information from the measurements, and progress has been very slow-exacerbated by the COVID lockdown scenarios. Finally, we have very recently made STM measurements on laser-melted carbon samples, in collaboration with Miquel Salmeron group at LBNL. Analysis of these data is also underway.

Building on the technical advances attending our recent (2018) development of soft X-ray second harmonic generation spectroscopy, intended for the study of laser-melted carbon, we have developed the capability to study buried interfaces at Angstrom-level spatial resolution and with atom selectivity, as described in the publication below. We expect this new technology to be useful for a wide range of technically important interfaces.

We have also addressed the phenomenon of saturable absorption (SA) and two-photon absorption (TPA) of soft X-ray synchrotron radiation by graphite samples. We systematically studied both phenomena in one experiment by exposing graphite films to soft X-ray-free electron laser pulses of varying intensity. By applying real-time electronic structure
calculations, we find that for lower intensities, the nonlinear contribution to the absorption is dominated by SA, attributed to ground-state depletion; our model suggests that TPA becomes dominant for higher intensities (>1014 W/cm2). Our results demonstrate an approach of general utility for interpreting free electron laser spectroscopies.

Training Opportunities: The Graduate Students are trained in International X-Ray Laser Facilities as well in laboratory laser
experiments.

Results Dissemination: Nothing to report.

Honors and Awards: 2021 - Paul C. Cross Lecture in Physical Chemistry (University of Washington)
2019 - The Claude and Janice Trottier Lectures (University of Rhode Island)
2019 - Helmholtz International Fellowship Award (Helmholtz Society, Berlin)
2019 - Swiss Chemical Society Lectureship (Swiss Chemical Society)

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

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Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Project Contribution:
National Academy Member: N

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Project Contribution:
National Academy Member: N

Participant Type: Other (specify)
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Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Participant Type: PD/PI
Participant: Richard Saykally
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

International Collaboration:

USA

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Article Title: Two-photon absorption of soft X-ray free electron laser radiation by graphite near the carbon K-absorption edge
Authors: Royce K. Lam, Sumana L. Raj, Tod A. Pascal, C.D. Pemmaraju, Laura Foglia, Alberto Simoncig, Nicola
Keywords: X-ray second harmonic generation, surface sensitivity, resonance enchantment
Abstract: We have examined the transmission of soft X-ray pulses from the FERMI free electron laser through carbon films of varying thickness, quantifying nonlinear effects of pulses above and below the carbon K-edge. At typical of soft X-ray free electron laser intensities, pulses exhibit linear absorption at photon energies above and below the K-edge, ?308 and ?260?eV, respectively; whereas two-photon absorption becomes significant slightly below the K-edge, ?284.2?eV. The measured two-photon absorption cross section at 284.18?eV (?6?×?10?48?cm4?s) is 7 orders of magnitude above what is expected from a simple theory based on hydrogen-like atoms – a result of resonance effects.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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as of 29-Nov-2022

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Article Title: Soft X-Ray Second Harmonic Generation as an Interfacial Probe

Authors: R.K. Lam, S.?L. Raj, T.?A. Pascal, C.?D. Pemmaraju, L. Foglia, A. Simoncig, N. Fabris, P. Miotti, C.?J.

Keywords: Soft X-Ray, Second Harmonic Generation, Interfacial Probe

Abstract: Nonlinear optical processes at soft x-ray wavelengths have remained largely unexplored due to the lack of available light sources with the requisite intensity and coherence. Here we report the observation of soft x-ray second harmonic generation near the carbon K edge (?284 eV) in graphite thin films generated by high intensity, coherent soft x-ray pulses at the FERMI free electron laser. Our experimental results and accompanying first-principles theoretical analysis highlight the effect of resonant enhancement above the carbon K edge and show the technique to be interfacially sensitive in a centrosymmetric sample with second harmonic intensity arising primarily from the first atomic layer at the open surface. This technique and the associated theoretical framework demonstrate the ability to selectively probe interfaces, including those that are buried, with elemental specificity, providing a new tool for a range of scientific problems.

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Partners

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I certify that the information in the report is complete and accurate:
Signature: Richard J. Saykally
Signature Date: 11/29/22 2:26PM

ARO FINAL REPORT

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1. Summary of key scientific accomplishments

In addition to the results presented in the publications listed below, during the last three years, we have managed to accumulate unprecedented new data for laser-melted carbon using several international free electron laser facilities. The measurements comprise Resonant Inelastic X-ray Scattering (RIXS) and X-ray Emission Spectroscopy (XES) data, which will provide a new level of detail regarding the geometric and electronic structure of the liquid state of carbon, when the accompanying theoretical modeling of the data is completed by our theory collaborators in Stockholm and LLNL. Unfortunately, these ongoing calculations are exceedingly complex and time consuming, and are essential to extract structural and chemical information from the measurements, and progress has been very slow-exacerbated by the pandemic lockdown scenarios. The data taken are shown in the attached slides. Finally, we have very recently made STM measurements on laser melted carbon samples, in collaboration with Miquel Salmeron group at LBNL. Analysis of these data is also underway.

Building on the technical advances attending our recent (2018) development of soft X-ray second harmonic generation spectroscopy, intended for the study of laser-melted carbon, we have developed the capability to study buried interfaces at Angstrom-level spatial resolution and with atom selectivity, as described in the publication below. We expect this new technology to be useful for a wide range of technically important interfaces.

We have also addressed the phenomenon of saturable absorption (SA) and two photon absorption (TPA) of synchrotron radiation by graphite samples. We systematically studied both phenomena in one experiment by exposing graphite films to soft X-ray free electron laser pulses of varying intensity. By applying real-time electronic structure calculations, we find that for lower intensities the nonlinear contribution to the absorption is dominated by SA, attributed to ground-state depletion; our model suggests that TPA becomes dominant for higher intensities (>1014 W/cm2). Our results demonstrate an approach of general utility for interpreting free electron laser spectroscopies.

2. Recent Honors and Awards.

2021 - Paul C. Cross Lecture in Physical Chemistry *(University of Washington)*
2019 - The Claude and Janice Trottier Lectures *(University of Rhode Island)*
2019 - Helmholtz International Fellowship Award *(Helmholtz Society, Berlin)*
2019 - Swiss Chemical Society Lectureship *(Swiss Chemical Society)*

3. Publications, patents, journal cover features that acknowledge ARO support.

Hull, C. J., Raj, S. L., Lam, R. K., Katayama, T., Pascal, T., Drisdell, W. S., Saykally, R. J., Schwartz, C. P. "Early Time Dynamics of Laser-Ablated Silicon Using Ultrafast Grazing Incidence X-ray Scattering" *Chem. Phys. Lett.*, **736 (136811)**, (2019).

Hull, C. J., Raj, S. L., Saykally, R. J. "The Liquid State of Carbon" *Chem. Phys. Lett.,* **749 (137341)**, (2020) *Cover Article.

Raj, S. L., Devlin, S. W., Mincigrucci, R., Schwartz, C. P., Principi, E., Bencivenga, F., Foglia, L., Gessini, A., Simoncig, A., Kurdi, G., Masciovecchio, C., Saykally, R. J. "Free Electron Laser Measurement of Liquid Carbon Reflectivity in the Extreme Ultraviolet". *Photonics* **7(2)**, 35 (2020).

Schwartz, C. P., Raj, S. L., Jamnuch, S., Hull, C. J., Miotti, P., Lam, R. K., Nordlund, D., Uzundal, C. B., Pemmaraju, C. D., Mincigrucci, R., Foglia, L., Simoncig, A., Coreno, M., Masciovecchio, C., Gianessi, L., Poletto, L., Principi, E., Zuerch, M., Pascal, T. A., Drisdell, W. S., Saykally, R. J. "Angstom-resolved Interfacial Structure in Organic-Inorganic Junctions". *Phys. Rev. Lett* **127**, 096801 (2021).

Hoffmann, L., Jamnuch, S., Schwartz, C.P., Helk, T., Raj, S.L., Mizuno, H., Mincigrucci, R., Foglia, L., Principi, E., Saykally, R.J., Drisdell, W.S., Fatehi, S., Pascal, T.A., Zuerch, M. "Saturable absorption of free-electron laser radiation by graphite near the carbon K-edge" *J. Phys. Chem. Lett.*, **13**, 8963-8970 (2022) - **ACS Editor's Choice**. *Cover Article

4. Brief description of scientific or technology transition that have occurred between your group and government/industrial labs under the program over the past 2 years. Note: we consider a "transition" to occur when someone else invests resources (time, money, etc.) based on your research.

N/A

5. Brief description of interactions with Army scientists & engineers during the past 2 years.

N/A