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14. ABSTRACT
We seek to advance our fundamental understanding of the liquid state and the phase diagram of carbon by performing detailed nonlinear optical electronic and vibrational spectroscopy studies of both the bulk and the surface of liquid carbon, and to exploit our novel laser technology to explore the nature of the newly-discovered Q-carbon form. The liquid will be prepared by non-thermal melting of graphite targets with both femtosecond and nanosecond lasers. The vibrational and electronic structures of the bulk liquid will be probed as a function of delay time from the melting pulse (and thus as a function of temperature and pressure) with our recently developed

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Richard Saykally
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Report Title

Final Report: Liquid Carbon, Glassy Carbon, and Their Surfaces

ABSTRACT

We seek to advance our fundamental understanding of the liquid state and the phase diagram of carbon by performing detailed nonlinear optical electronic and vibrational spectroscopy studies of both the bulk and the surface of liquid carbon, and to exploit our novel laser technology to explore the nature of the newly-discovered Q-carbon form. The liquid will be prepared by non-thermal melting of graphite targets with both femtosecond and nanosecond lasers. The vibrational and electronic structures of the bulk liquid will be probed as a function of delay time from 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 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. This collection of experiments, interpreted with state of the art theoretical calculations performed in collaboration with Berkeley-area theorists, 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 all known phases and properties of carbon.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2016 E. Roger Washburn Memorial Lectureship in Physical Chemistry
(University of Nebraska)

2014 CaSTL (Chemistry at the Space-Time Limit) Lecturer
(University of California-Irvine)

2013 W. A. Noyes Distinguished Lecture in Physical Chemistry
(University of Austin, Texas)

Graduate Students

NAME	PERCENT_SUPPORTED
Christopher Hull	100
Sumana Raj	100
FTE Equivalent:	**2.00**
Total Number:	**2**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
Richard Saykally	0.20
FTE Equivalent:	**0.20**
Total Number:	**1**

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Femtosecond Chirped CARS Spectroscopy of Liquid Carbon: Characterizing the Bulk Liquid
NSF Fellow Sumana Raj joined the project in October of 2013, completed her required coursework, and passed her preliminary doctoral exam. She designed built, and tested a femtosecond chirped CARS experiment to probe laser melted highly ordered pyrolytic graphite(HOPG). She first obtained CARS vibrational spectra of the pristine HOPG surface. Initially, the laser pulses were damaging the sample, producing excessively broad linewidths; the experiment was adjusted to improve the spectral resolution. However, the resulting spectral linewidths still did not agree with literature values. She then investigated polystyrene for use as a possible calibration standard, and is in the process of adjusting the experiment to obtain the correct spectral characteristics.

Once we fully understand the HOPG spectrum, we will study the spectrum of melted HOPG and how it deviates from that of the pristine solid. Sumana has begun preliminary trials to look at the liquid ~100 fs after melting. She will study the liquid at various times after melting to observe how it evolves over time and eventually ablates.

In addition to this work, we also plan to use the new FERMI free electron laser at Trieste to further characterize liquid carbon using x-ray scattering techniques. A proposal for time on the FERMI facility has been submitted and approved for funding. We expect to perform the experiments this fall. This work will provide complementary insight into the poorly understood liquid state of carbon.

Femtosecond Second Harmonic Generation Spectroscopy of Liquid Carbon: Electronic Structure of the Liquid Surface

Wei-Li Research Fellow Chris Hull joined this project in October, 2013, completed his required coursework, and passed his preliminary doctoral exam. The experimental configuration for carrying out the second harmonic generation (SHG) study of liquid carbon has been designed and constructed. Testing of the system with a gallium arsenide sample has demonstrated the ability to produce, guide and detect second harmonic radiation from the irradiated sample.

Current experimental efforts focus on switching over to the HOPG samples, seeking to establish both the SHG signal level and the necessary incident flux for melting of the carbon. We have indeed observed signal from the HOPG targets which appear to be the second harmonic, although further experimental verification is required, as there is a very large background due to blackbody remission from the laser heated sample. To remedy this, the detection wavelength is being moved farther into the UV, where the black body background will be smaller. Additionally attempts are being made to characterize the white light spectrum in order to confirm it is thermal radiation. Once these goals are accomplished, SHG data will be collected as a function of wavelength, temperature and pressure, via variation of melting pulse fluence and time delay, characterizing the evolution of electronic structure of the liquid carbon surface.

Surface-specific soft X-ray second harmonic generation: A New Probe for Liquid Carbon
Graduate students Sumana Raj, Royce Lam, and former group members Craig
Schwartz and Walter Drisdell headed an experimental team that travelled to Treste, Italy to use the new high power, high coherence free electron laser to explore second harmonic generation on carbon targets, anticipating the use of this new technique to study the liquid state of carbon in the next set of experiments.
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 at the carbon K-edge (~284 eV) from graphite thin films, generated by high intensity, coherent soft X-ray pulses at the FERMI free electron laser in Trieste. Our experimental results and accompanying first principles theoretical analysis highlight the effect of resonant enhancement and show the technique to be surface specific in a centrosymmetric sample, with second harmonic intensity arising only from the first two atomic layers. This technique, coupled with the developed theoretical framework, offers the ability to probe interfaces with elemental specificity, providing a new tool for a range of scientific problems.

Progress Report Details:
See Attachment.

Technology Transfer

ARO Proposal Number: 63229MS
Proposal Title: Liquid Carbon, Glassy Carbon, and Their Surfaces
Final Report for Period From October 01, 2013 To September 30, 2016
Title: Liquid Carbon, Glassy Carbon, and Their Surfaces

PROPOSED RESEARCH

We propose to advance our understanding of the liquid state and the phase diagram of carbon by performing detailed time- and frequency-resolved electronic and vibrational spectroscopy studies of the bulk and the surfaces of liquid carbon, as well as the amorphous glassy state. The liquid will be prepared by nonthermal melting with a femtosecond laser. The vibrational and electronic structures of bulk samples will be probed as a function of delay time from the melting pulse (and thus as a function of temperature) with our recently developed chirped femtosecond CARS technique, exploiting both electronic and vibrational resonances; the surfaces of the liquid and glass will be probed with similar surface-sensitive femtosecond broadband sum frequency generation methods. The core-level absorption spectrum, which reveals the nature of the vacant orbitals (LUMO, etc), which are, in turn, very sensitive to the local chemical environment, will be measured for both bulk samples and surfaces with a newly designed Auger electron spectrometer. This collection of experiments, interpreted with state of the art theoretical calculations performed in collaboration with Berkeley theorists, will seek to thoroughly characterize the structure, bonding, and dynamics of liquid carbon/glassy carbon and their surfaces. The combined theoretical and experimental information obtained will ultimately be used to construct improved potential models which can describe all known phases of carbon. Second generation studies could address the process of nucleation of nanowires and the glassy state.

CHIRPED CARS VIBRATIONAL SPECTRA OF LASER MELTED CARBON

Sumana Raj, a graduate student and NSF graduate research fellow, is pursuing the use of chirped Coherent Anti-Stokes Raman Vibrational Spectroscopy (c-CARS) to study non-thermally melted liquid carbon. Liquid carbon is prepared by non-thermally melting a graphite source using an 800 nm, 100 fs laser pulse. The liquid is formed within a few femtoseconds, and will be inertially confined for ca. 10 picoseconds before expansion and ablation occurs. Thus, the liquid can be probed at various times in its formation and expansion using c-CARS. In c-CARS, a transform limited femtosecond laser pulse is stretched to a few picoseconds using a grating pair. This c-CARS pump pulse is combined with a femtosecond Stokes pulse and the coherent, anti-Stokes output is detected. With this technique high resolution, broadband CARS vibrational spectra can be obtained with single laser pulses.

After designing and building the laser apparatus, the CARS spectrum of highly ordered pyrolitic graphite (HOPG) and glassy carbon substrates were obtained using an 800 nm, 10 ps CARS pump pulse (Figure 1). Attempts at studying melted carbon were then made. To ensure

that an undamaged spot is probed with each laser shot, the sample is rastered during the experiment. However, a large background from the melting pulse, likely a combination of black body radiation and other effects, obscured the CARS signal from the sample (Figure 2). When probing a single spot on the sample and using irises and filters to minimize the background, some changes in the CARS signal with time after melting can be seen (Figure 3). However, as the sample is being damaged in this case (inset on figure 3) and the signal to background is fairly low, this technique is less than ideal. The background from the melting pulse is weaker around 400 nm and can be subtracted from the CARS spectrum when a 400 nm CARS pump is used. Low resolution c-CARS spectra of melted graphite have been obtained (Figure 4) and currently work is being done to obtain high resolution spectra with a 400 nm CARS pump.

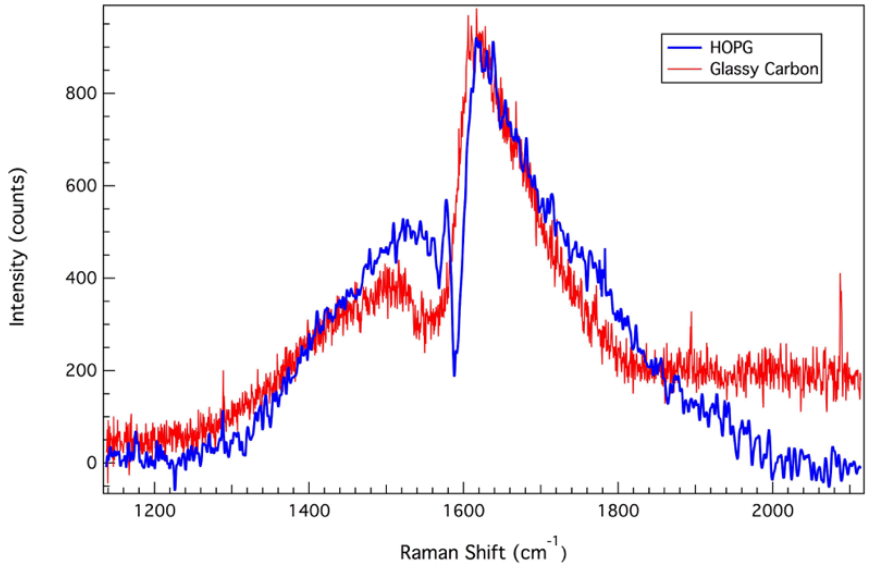

Figure 1: c-CARS of HOPG and glassy carbon. c-CARS spectra were obtained while rastering the sample, using an 800 nm, 10 ps c-CARS pump pulse. The pump pulse was p-polarized and Stokes pulse was s-polarized. The graphite G peak resonance at 1580 cm^{-1} can be clearly seen. The non-resonant CARS background has not been subtracted.

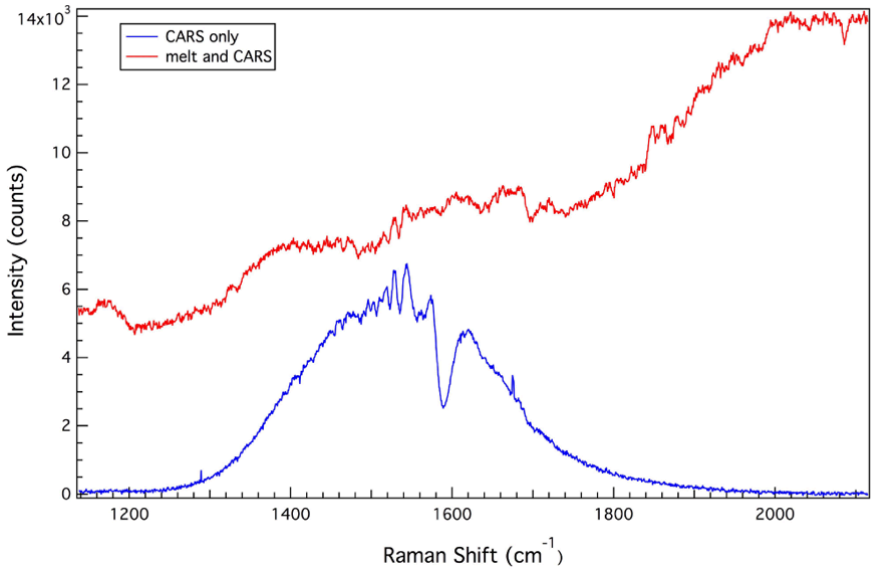

Figure 2: c-CARS of HOPG with and without melting pulse. c-CARS spectra were obtained while rastering the sample, using an 800 nm, 10 ps c-CARS pump pulse. Both CARS pulses are s-polarized. When the sample is probed after the melting pulse, the large background from the melting pulse overwhelms the CARS signal and cannot be subtracted.

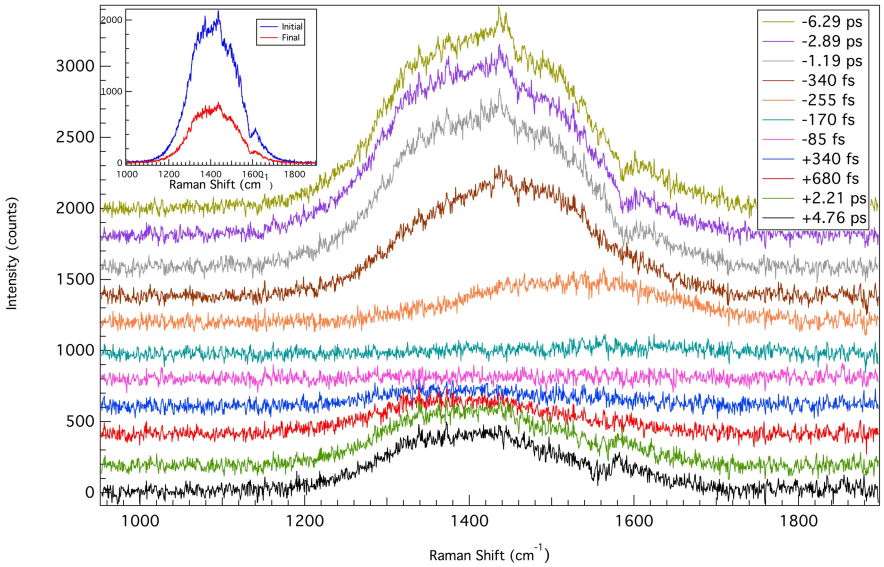

Figure 3: c-CARS of HOPG at various delay times after melting. c-CARS spectra were obtained using an 800 nm, 10 ps c-CARS pump pulse with both CARS pulses s-polarized. The sample was not rastered between laser shots so a single spot was probed. The listed times are the times between the melting and CARS pulses, with negative times indicating that the CARS pulses probed the sample before melting. The CARS signal is clearly dependent on the relative timing of the two pulses. The inset shows the CARS signal of the sample before and after the various melting experiments. *The CARS signal has decreased due to damage but not completely, suggesting that the changes seen with the melting are due to transient effects.*

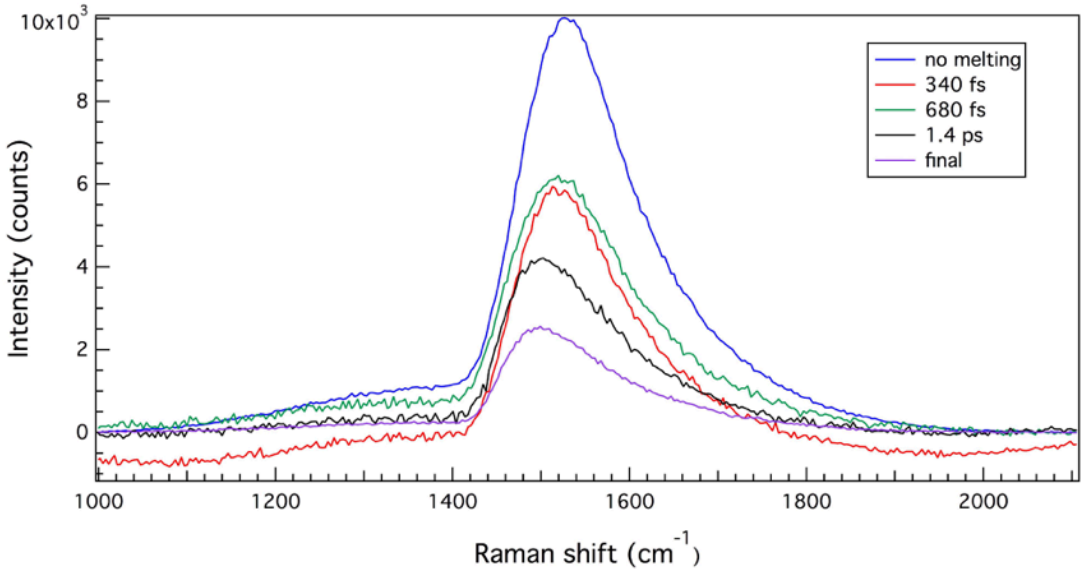

Figure 4: **c-CARS of HOPG with and without melting while rastering the sample**. c-CARS spectra were obtained using an 400 nm, 3 ps c-CARS pump pulse with both CARS pulses p-polarized. The blue trace is the c-CARS spectrum of HOPG without any melting and the purple trace is the c-CARS spectrum of the sample minutes after melting occurred. Times listed are the delays between the melting pulse and the CARS probes. The background from the melting pulse has been subtracted. The peak is due to the G-peak resonance, however, the low resolution makes it unclear if significant shifts and broadening is occurring.

CHARACTERIZATION OF LIQUID CARBON/Q CARBON BY LASER REFLECTIVITY

ARO-funded student Chris Hull is pursuing the development of second harmonic generation (SHG) experiments to probe the electronic and vibrational states of the surfaces of liquid and glassy carbon, using the laser melting approach. Laser reflectivity is measured along with the SHG spectra. We are currently grappling with the obfuscation of SHG spectra by the laser melting pulse.

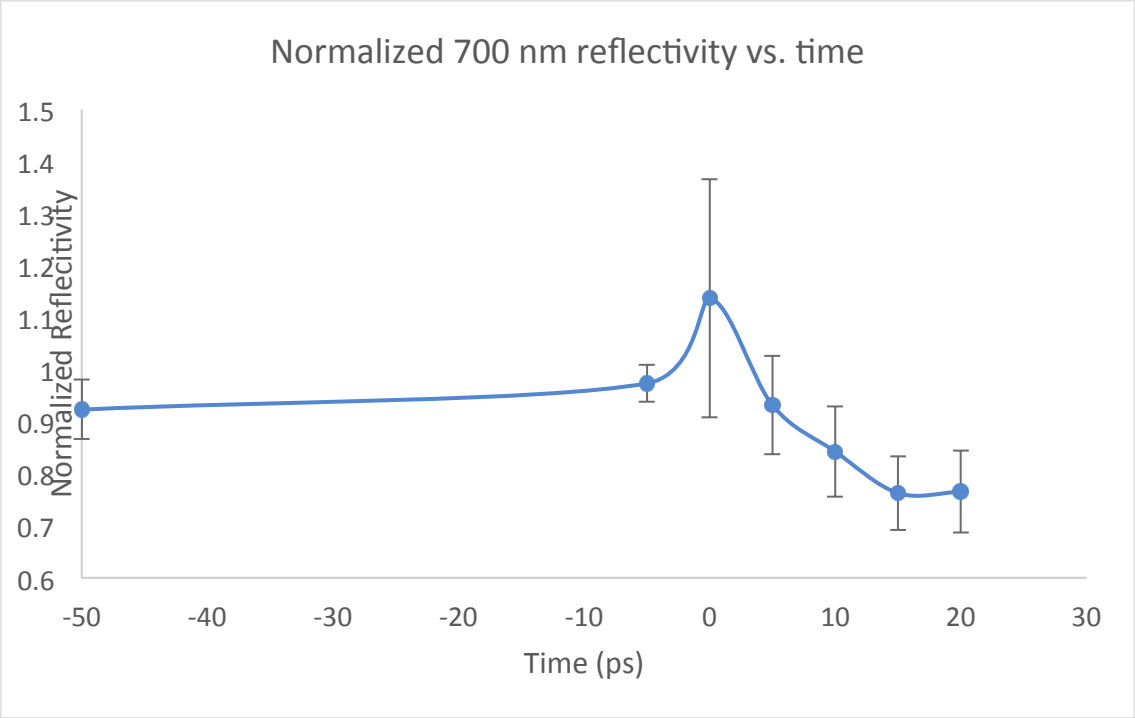

Fig. 5 LIQUID CARBON REFLECTIVITY Plot of normalized reflectivity vs time for laser melted graphite. Melting power employed is 180 mW, corresponding to a fluence of 1 J/cm^2. Time steps for the experiment were 5 ps. Data is normalized to the reflectivity of unmelted graphite. Reflectivity shows a large, highly variable increase near time zero, attributed to the formation of the liquid and a slow long term decrease which results from the ablation of the material from the surface.

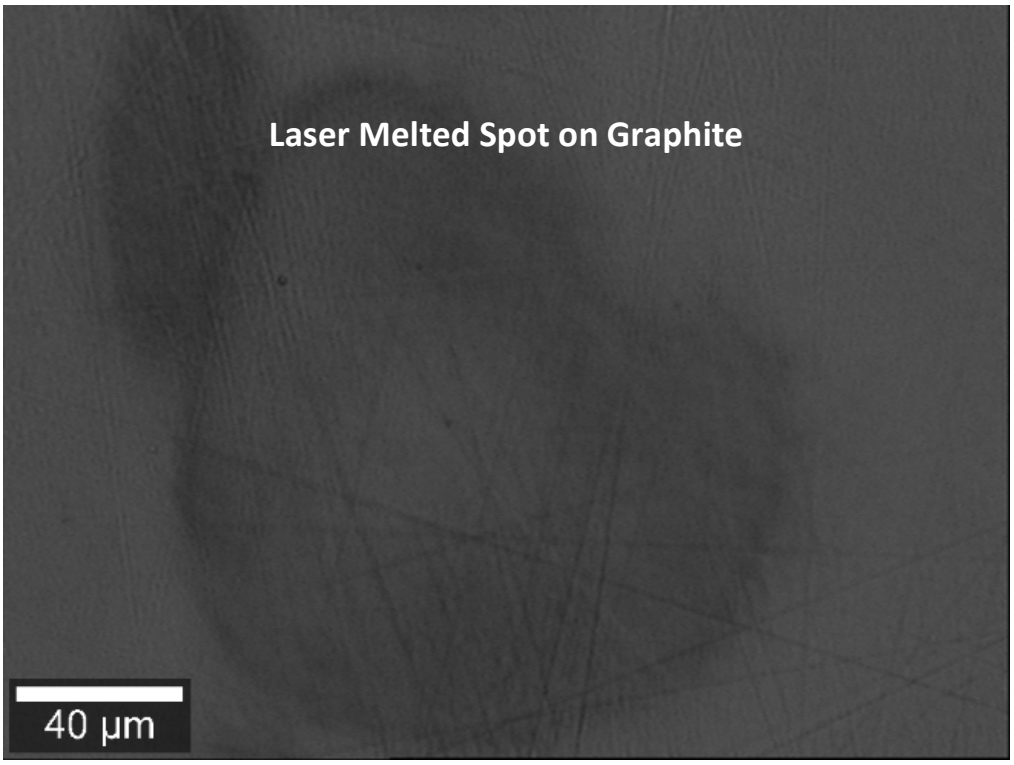

Fig. 6 LASER MELTED GRAPHITE Confocal microscope image of melt and probe spot on amorphous carbon target. Image clearly shows impact crater resultant from melting and additionally confirms that a new spot is melted for each shot in the experiment, which is critical for accurately measuring the impact of melting. In this experiment the melt (larger crater) and probe (small oblong crater) were deliberate misaligned so that both could be observed.