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CRF NEWS

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Fluorescence-based bioaerosol sensing project advances to third phase

A flurry of recent activity to make fast-response bioaerosol detectors has been spawned by the need to protect against bioterrorism threats; however, available devices often false alarm on non-biological particles. Sandia researchers (Tom Kulp, Scott Bisson, Tom Reichards, Bob Crocker, and Scott Ferko) have been involved in a program to characterize one such class of sensors—those based on single-particle laser-induced fluorescence (LIF)—and to augment their operation to reduce false alarms. This program, called the Enhanced Bioaerosol Detection System (EBADS), is funded by the Department of Homeland Security (DHS). It is a multilab collaboration between Sandia, Oak Ridge, Lawrence Livermore, Pacific Northwest, and Los Alamos National Laboratories (SNL, ORNL, LLNL, PNNL, and LANL). Within this group,

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Important source of unburned hydrocarbons for low-temperature diesel combustion identified

Diesel engine developers are exploring many novel alternative combustion strategies to ensure that diesel engines will comply with impending emissions regulations. The ignition dwell, which is the time from the end of injection to autoignition of the fuel, is generally much longer for these new strategies than for conventional diesel engines. Although long ignition dwells help to achieve low-temperature combustion (LTC) and reduce formation of particulate matter and nitrogen oxides, some fuel is often incompletely combusted, which decreases fuel efficiency and increases unburned hydrocarbon (UHC) emissions.

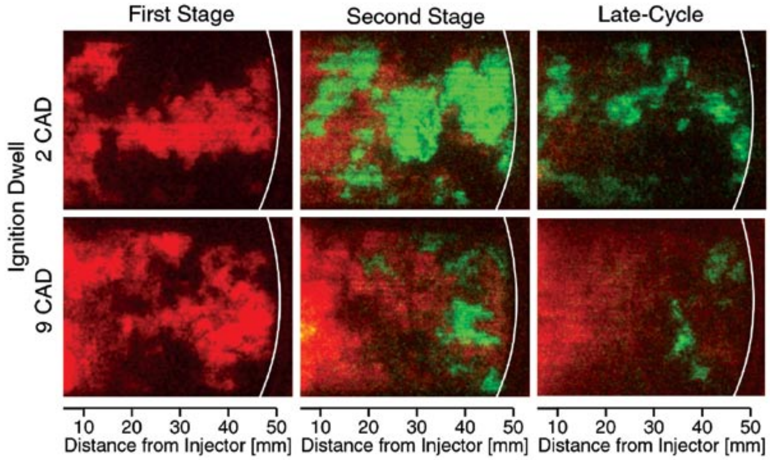

Figure 1. *Simultaneous images of formaldehyde (red) and OH (green) fluorescence with 2 CAD (crank angle degree) (top row) and 9 CAD (bottom row) ignition dwells. The curved white line represents the piston bowl, and the scale indicates the distance from the fuel injector.*

Recently CRF researchers Mark Musculus and Thierry Lachaux have been using simultaneous formaldehyde (H_2CO) and hydroxyl (OH) planar laser-induced fluorescence imaging to study the in-cylinder sources of UHCs for LTC diesel engines. Shown in Figure 1 are two sets of three images acquired at two different ignition dwell conditions during (i) first stage ignition, (ii) second state ignition, and (iii) very late in the engine cycle when combustion

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JANNAF workshop on new energetic materials in munitions identifies new needs in chemical sciences

A JANNAF (Joint Army, Navy, NASA, Air Force) workshop on “R&D Required to Implement New Energetic Ingredients in Munitions” was organized by Rich Behrens (CRF), Bill Anderson (ARL), Brad Forch (ARL) and Bob Shaw (ARO) and held on Aug. 29-31, 2006, in Aberdeen, MD. Over 50 program managers, engineers and scientists from industry, DoD and DOE laboratories, as well as academia participated in the workshop.

The workshop objective was to create a plan for R&D investment strategies that will enable the rapid utilization of new energetic ingredients (e.g., high nitrogen compounds, energetic binders, and ionic liquids) needed to reach new munition goals, address insensitive munition (IM), aging, quality assessment and cost requirements. Historically, it has taken decades to introduce a new energetic ingredient into a munition.

The participants discussed: (1) conventional methods for evaluating ingredients, (2) system requirements for new energetic materials, (3) what technically limits the implementation of new ingredients in munitions, (4) new experimental concepts for evaluating performance and deleterious features of new ingredients, and (5) new modeling/simulation methods for evaluating and predicting performance and deleterious features of new compounds and materials. These discussions revealed that using the current empirical synthesize-scaleup-and-test paradigm is costly and its likelihood of success is low. A more scientific approach to new energetic materials development is necessary. A new strategy to improve the likelihood of success requires focusing programmatic efforts on controlled chemical propulsion, interaction at targets, and meeting IM requirements; and implementing new experimental and theoretical methods that furnish more insight into reactive processes to provide meaningful data 100 times faster with 100 times less material.

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Sandia National Laboratories

Fluorescence-based

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SNL and ORNL scientists have been collaborating to develop an improvement on LIF-based detection that uses fluorogenic reactions (those producing a fluorescent product upon reaction). Recently, the SNL-ORNL team passed a blind-sample testing exercise conducted by DHS and the Edgewood Chemical and Biological Center (ECBC), which qualifies their approach to proceed to a third phase of development. In the first phase of EBADS, false alarms generated by two commercial LIF-based sensors were correlated with the readings of single-particle analytical measurements to find out which classes of materials produce "biological-like" LIF spectra. That work occurred at the San Francisco International Airport (SFO), where the ambient particles in the air-handling system were monitored using single particle mass spectrometry and selective collection and analysis of particles causing alarms in the LIF systems. The results showed that most of the SFO particles that triggered LIF sensors were not innocuous bacteria or spores but were non-biological in composition.

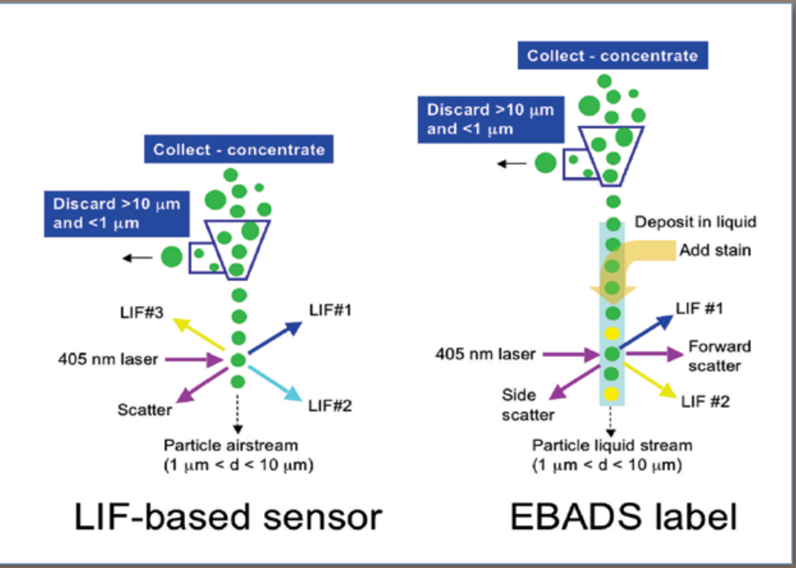


Figure 1. *Comparison of the EBADS hydrosol measurement (right) with that of a typical LIF-based aerosol sensor. The EBADS measurement is made in a liquid, rather than an air stream, and it adds a fluorimetric stain to the particles to label protein molecules within them.*

After the tests, the SNL-ORNL team proposed and demonstrated an improved method to better select between biological and non-biological particles. To maintain low operating costs, they turned to fluorimetric chemical reactions to allow better recognition of biomolecules within aerosols. Specifically, the protein-sensitive dye fluorescamine was used because it creates a fluorescent product when it reacts with primary amine groups on proteins. They found it is best to measure the response of individual aerosols to this dye when the aerosols are entrained in the fluidic stream of a flow cytometer (see Figure 1), because this allows simultaneous measurement of the laser scattering by each particle, in addition to its LIF; and this method provides the needed solvent requirement for the dye to react. Scattering measurement occurs in two directions, forward (sensitive to particle size) and sideways (sensitive to particle shape or structure). When in the fluid, the particles are referred to as hydrosols.

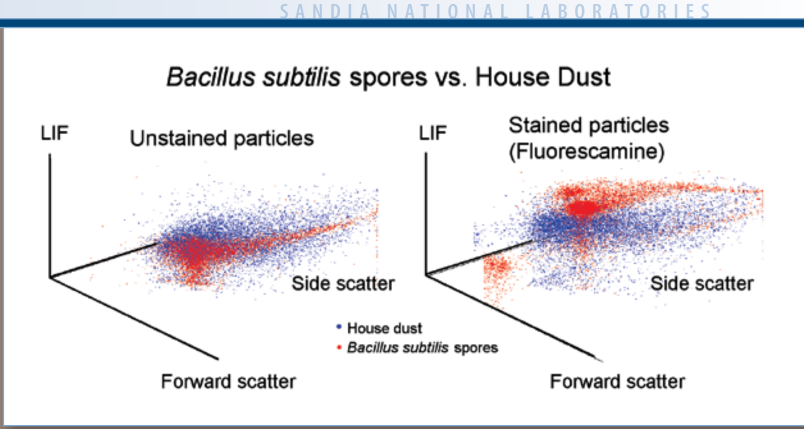


Figure 2. *Plots of the pre-stained (left) and stained (right) data collected from bacillus subtilis spores (red) and house dust background (blue). Each dot represents the meaurement from a single particle. Note that the spores are affected greatly (the LIF scale is logarithmic) by staining, whereas the house dust is not.*

LIF/scattering data from each hydrosol contributes to a three dimensional distribution (see Figure 2) depicting the response of the particle population to each of these three measurements. Populations of similar particles (e.g., spores) produce characteristic patterns in these plots that allow their discrimination from background mixtures. Because they are composed of a broad range of particle sizes and composition, the latter produce broad distributions of points. The response of samples to fluorescamine further distinguishes them from backgrounds because their uniform "stainability" causes their LIF to increase dramatically on staining, relative to the generally non-biological background materials (see Figure 2).

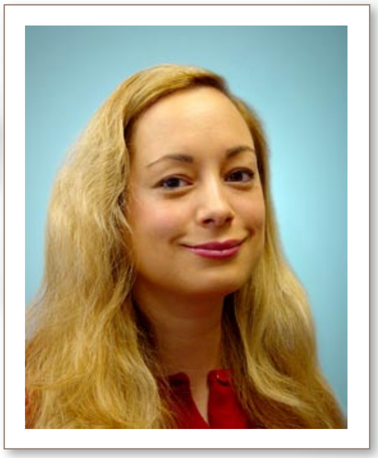
A challenge to this process is the fact that some threat agents (i.e., viruses and toxic proteins) are too small to trigger the described particle measurement. Although they may have been imbedded in respirable-sized salt (or other co-precipitate) aerosols when collected, they likely will dissolve in their native form in the hydrosol state.

This problem has been addressed by measuring the stainability of the fluid as a measure of the presence of viruses and protein toxin surrogates. In this case, it is important to ensure that a triggerable sample particle is not in the fluid volume being probed, because that would bias the measurement. To ensure this, the sample was seeded with non-fluorescent, uniformly-sized silica beads. The fluorescence of those beads was measured by the cytometer in the stained and unstained state. Because they are both non-fluorescent and non-stainable, any LIF in those measurements is assumed to arise from the fluid around the beads. The concentration of large particles in the fluid is low enough to ensure none is in the volume with the seeded bead.

These methods were applied to the measurement of twenty unknown mixtures of cells, spores, viruses, and/or proteins in various background particles. Analysis of the particle "clouds" was enabled by decomposing observed data distributions into linear combinations of pre-measured distributions for various threat and background materials using three dimensional linear analysis. In all cases, the staining approach correctly identified the presence or absence of the threat agent simulants. The project is now proceeding to a phase in which it will address "real-world" samples collected at a remote site, such as SFO. This study will be accomplished by bringing samples from SFO to SNL and, ultimately, by deploying an instrument on site at SFO.

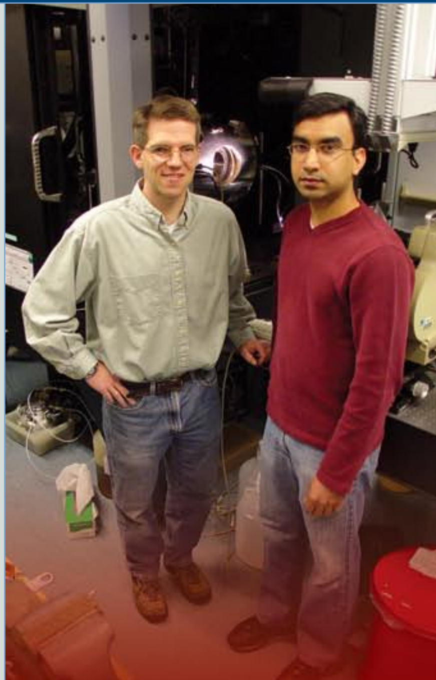
Truman Fellow Whitney Colella joins the CRF

Whitney Colella has joined the CRF as a Sandia Truman Fellow. She is working with Jay Keller and Andy Lutz on computer simulations of alternative energy systems. The models she is developing will be used to examine alternative designs for stationary tri-generative fuel cell power plants tuned to the electricity, heating, and cooling demand curves for the buildings they could serve. These analyses will enable evaluation of the energy supply by fuel cell systems and distributed energy devices relative to the energy demand in surrounding buildings.



This fellowship in National Security Science and Engineering, established in memory of President Harry S. Truman, is a three-year appointment at Sandia that allows scholars to perform postdoctoral research related to national security and address a major scientific or engineering problem, or provide a new approach or insight into a major problem. Truman Fellows are selected from U. S. citizen applicants from universities across the nation.

Colella has a B.S. in mechanical engineering and a minor in public policy from Princeton, an M.S. in science and public policy from University of Sussex, an M.S. in mechanical engineering from Stanford, an MBA from Oxford, and a D.Phil. in engineering science from Oxford. She has received scholarships and fellowships from British Marshall, Fulbright, National Science Foundation, T.J. Watson, Gilbreath, and Overseas Research.



Cherian Idicheria goes to General Motors

Cherian Idicheria has accepted a position as Research Engineer at General Motors Powertrain Systems research laboratory in Warren, MI. Idicheria has been a post-doc in the Engine Combustion group at the CRF for the past two and a half years working with Lyle Pickett on advanced low-temperature diesel combustion.

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Jude Kelley taking up position at College of Holy Cross

Jude Kelley, post doc in remote sensing, will be leaving for the College of the Holy Cross in Worcester, MA, where he will be taking up the position of assistant professor of chemistry. While at the CRF, Kelley worked with Tom Reichardt developing a laser ionization ion mobility spectrometer (IMS) for trace detection of explosives.

Brianna Haezlewood, visiting researcher in Osborn laboratorty

Brianna Haezlewood, a student from the University of Sydney, Australia, is a visiting researcher in the laboratory of Dave Osborn. She is working on a project with Osborn on the photodissociation of acetaldehyde, in hopes of finding evidence for a roaming methyl group mechanism in this photodissociation.

Chuck Mueller receives an Excellence in Oral Presentation Award

Chuck Mueller received an SAE Excellence in Oral Presentation Award in January for his talk, “Investigation of the Impact of Biodiesel Fueling on NO_x Emissions Using an Optical Direct Injection Diesel Engine,” at the Powertrain & Fluid Systems (P&FS) Conference and Exhibition in Toronto, October 16-19, 2006.

SAE

In Recognition of

Charles J. Mueller

for Excellence in Oral Presentation

“Investigation of the Impact of Biodiesel Fueling on NOx Emissions Using an Optical Direct Injection Diesel Engine”

Powertrain & Fluid Systems Conference and Exhibition
October 16-19, 2006

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CRF researchers receive awards at SAE Congress

Magnus Sjöberg (left) was honored with the SAE Russell S. Springer Award for SAE paper 2005-01-2125, which explains how he used a multi-zone chemical-kinetics model (developed by Andy Lutz) in combination with experiments to show how the in-cylinder thermal stratification needs to be adjusted across the engine-operating map in order to achieve smooth HCCI operation with acceptable pressure-rise rates.

John Dec (right) received the SAE Lloyd L. Withrow Distinguished Speaker Award. This award recognizes his accomplishment of sustained excellence in oral presentations at SAE’s technical sessions for papers on diesel- and HCCI-engine combustion.

Source of unburned hydrocarbons

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has essentially ceased. The images were acquired in a heavy-duty optical diesel engine fueled with n-heptane, a non-fluorescing diesel-type fuel.

For the shorter, 2-crank angle degree (CAD) ignition-dwell condition (top row), formaldehyde (red) is formed throughout much of the jet during the first stage of autoignition. Later, during the second-stage autoignition, OH (green) appears in pockets throughout the jet as the formaldehyde and remaining fuel are consumed. Late in the cycle, OH continues to appear in pockets throughout the jet, but only a tiny amount of formaldehyde fluorescence remains. Similar to diesel fuel, n-heptane displays 2-state autoignition chemistry, with formaldehyde formed during the first state, and OH formed during the second stage when formaldehyde and UHCs are consumed. Being a product of incomplete combustion (first state only), formaldehyde is a marker of UHCs. The absence of late-cycle formaldehyde, combined with appearance of OH throughout the jet, indicates that few UHCs remain late in the cycle for the short ignition-dwell condition in the top row of Figure 1.

In contrast, for the longer 9-CAD ignition-dwell condition (bottom row of Figure 1), formaldehyde remains late in the cycle, and OH appears only in the downstream region of the jet during the second-stage autoignition (right side of the images). The persistence of formaldehyde late in the cycle, combined with the absence of OH in the upstream region of the jet (left side of images), indicates that UHCs arise from the region on the left side of the images, which is near the fuel injector.

The in-cylinder mechanism for the rapid increase in UHC emissions for LTC conditions with long ignition dwells is of great interest to LTC engine developers. In addition to showing the near-injector regions from which in-cylinder UHC arises, the late-cycle formaldehyde persistence also suggests the phenomenon causing incomplete combustion. Using chemical kinetics mechanisms developed at Lawrence Livermore National Laboratory, computer simulations predict that the most likely cause for late-cycle formaldehyde (and UHCs) that do not achieve second-stage combustion is over-mixing due to fuel-lean conditions. This prediction is surprising because the near-injector region where formaldehyde persists is normally very fuel rich during the diesel injection event, so the fuel-lean mixtures must be formed quickly after the end of injection.

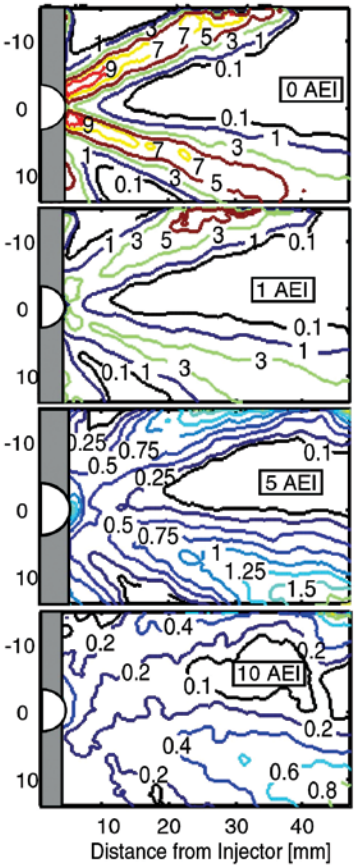

Figure 2. *Equivalence ratio contours acquired at four times after the end of injection (AEI). In each image, the fuel injector is on the left side, and portions of two fuel jets are within the field of view, at the 2 o'clock and 4 o'clock positions.*

To confirm the UHC mechanism of rapid fuel-lean mixture formation, and to quantify the amount of in-cylinder UHC from the near-injector region, Musculus and Lachaux used a second optical imaging diagnostic, planar laser-induced fluorescence of toluene, to measure local in-cylinder fuel concentrations. The fuel was doped with 0.5% toluene, and to allow quantitative measurements, fuel fluorescence images were acquired under non-combusting conditions. Equivalence ratio contours of the fuel jets at various times after the end of injection are shown in Figure 2. In the plots, two jets are partially visible, at the 2 o'clock and 4 o'clock positions, propagating outward from the injector located on the left side of each plot.

In the top image of Figure 2, which was acquired at the end of injection, the fuel distribution is typical of quasi-steady diesel jets, with fuel-rich regions (large equivalence ratios) near the injector and leaner mixtures farther downstream in the jets. After the end of injection, however, the regions near the injector quickly become much leaner. Peak equivalence ratios near the injector drop from 9 to only 3 within one crank angle degree after the end of injection (AEI), so that upstream regions are already more fuel-lean than downstream regions. This fuel-leaning trend continues, with peak equivalence ratios near the injector decreasing to 0.5 and later to 0.2 at times of 5 and 10 CAD AEI, respectively. These direct measurements of fuel-lean mixtures are consistent with the model predictions of lean mixtures responsible for the persistence of formaldehyde (late cycle) near the injector for the long ignition dwell condition (Figure 1).

Finally, volume integration of fuel concentration measurement shows that the total fuel in the lean regions that do not achieve complete combustion is significant, and is comparable to exhaust UHC emissions measured in production LTC diesel engines. Together, these measurements show that rapid leaning of fuel-air mixtures near the injector after the end of injection leads to combustion inefficiencies and significant UHC emissions. This work is a continuation of the project to extend Sandia's conceptual model of diesel combustion to LTC conditions, which was described in the September/October 2005 issue of CRF News.

JANNAF Workshop

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While reactions of energetic materials used in rocket motors are typically viewed in terms of gas-phase combustion, the reactions that often limit the use of new energetic compounds occur in the condensed phase at lower temperatures, where long-term stability and safety are of concern. Careful consideration of the reaction processes that may occur in CHNO-type organic compounds (e.g., cyclic nitramines such as HMX and RDX) in the condensed phase suggests that the concepts typically used to characterize chemical reactivity in the gas-phase or dilute solutions are not directly applicable to these materials. Many attempts to use older techniques to address these condensed-phase issues have had limited success. New approaches with greater information content, such as Sandia's STMBMS methods (simultaneous thermogravimetric modulated beam mass spectrometry), are needed.

A rocket or gun propellant is a composite of several different ingredients, typically including energetic compounds, such as RDX or ammonium perchlorate, and fuels, such as aluminum, as well as binders and bonding agents to form a material with the required energetic and mechanical properties. The resulting material is inhomogeneous and has local reaction environments (LRE) that span a wide range of spatial scales as illustrated in Figure 1. To accurately characterize the condensed-phase reactivity of energetic materials requires identifying the LREs within the material and then characterizing the elementary reaction manifolds (ERM) associated with each different type of LRE. Characterizing an ERM may start with determining its global behavior over a range of conditions and then trying to unravel the various elements of the ERM. This concept of an LRE and its associated ERM provides the basis for defining the need for new experimental and theoretical approaches aimed at understanding and characterizing the complex reaction processes that underlie the behavior of new energetic ingredients.

New diagnostic tools are required to facilitate the rapid development of new energetic materials for future munitions. These tools must identify LREs and characterize the associated ERMs induced by thermal, mechanical (impact and shock), and electrical energy. These tools must also show how the response of a material is associated with its molecular properties. This association will enable us to develop new compounds and material configurations that satisfy new munition requirements.

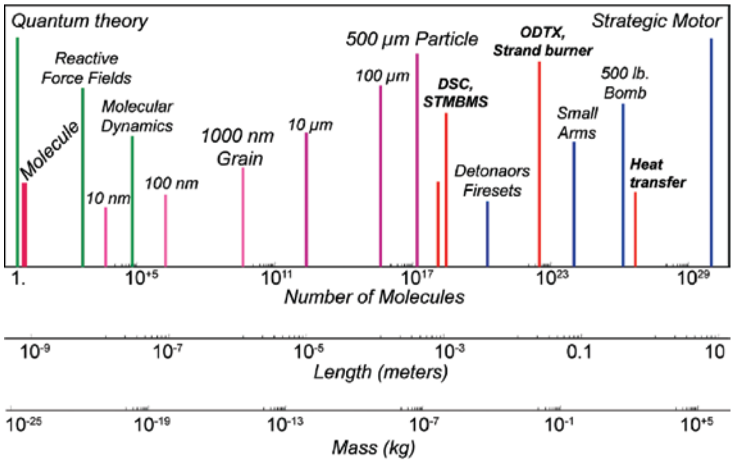

Figure 1. *Spatial scales of interest in reactions of energetic materials. (1) Dimensions of assets (blue). (2) Dimensions of samples used in various experiments (red). (3) Dimensions of various types of local reaction environments that are present in propellants (purple). (4) Molecular dimensions that may be addressed by different types of theory (green).*

Participants in the workshop are currently working to identify methods for new diagnostic tools for formulation development. They are also working to define requirements for further research. They will focus on the connections between material response and processes at the molecular level. One example is the response of energetic materials to electrical energy. Another is how mechanical energy initiates chemical reactions, which leads to ignition of energetic materials. The participants also identified the issues that are limiting our nation's ability to design new energetic materials for future defense needs. To chart a new future course requires us to shift the development paradigm from empiricism to science. While the empirical approach was the best available when it was developed in WWII, recent advances in techniques enable us to unravel complex physico-chemical reaction mechanisms. This information can then be used, in a scientific approach, to develop more effective and less vulnerable energetic materials for our nation.

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