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CRF NEWS

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Using kinetics to characterize photoionization of key combustion intermediates

The reactions of alkyl radicals, denoted by R, with molecular oxygen (O_2) are key components in the chemistry of autoignition, and in the atmospheric oxidation of hydrocarbons. These reactions proceed via formation, isomerization, and dissociation of alkylperoxy radicals, RO_2 (*CRF News* 23, No. 1). Recently, CRF researchers Giovanni Meloni, Peng Zou, Craig Taatjes, and David Osborn, in collaboration with Lawrence Berkeley National Laboratory (LBNL) scientists Musahid Ahmed and Stephen Leone, undertook experiments to characterize the photoionization of these important intermediate species. Calculations to analyze the experimental data were carried out in collaboration with Stephen Klippenstein, a former CRF researcher, now at Argonne National Laboratory.

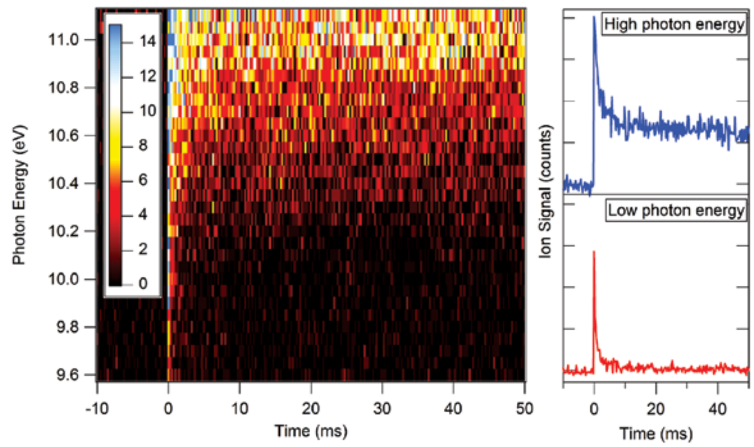

Figure 1. Measurements of m/z = 29 ions formed from photoionization following photolysis of diethyl ketone (to produce ethyl radicals) in the presence of O_2. The traces on the right show the time behavior of the signal at low photon energy, which contains only direct ionization of ethyl radicals, and at high photon energy, which has contributions from direct ionization of ethyl radicals (that rapidly decay by reaction with oxygen) and from dissociative ionization of ethylperoxy radicals, which persist for longer times.

Photoionization is an important analytical tool for combustion and kinetics studies that can yield isomer-specific data about flame chemistry (*CRF News* 27, No. 4) and elementary reaction kinetics. However, photoionization of alkylperoxy radicals had

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Estimating bioterror attacks from patient data: A Bayesian approach

In recent years, CRF researchers have developed stochastic methods for uncertainty quantification in chemically reacting flows. These techniques allow accurate propagation of uncertainty, from input parameters to model predictions, enabling models to be validated against experimental measurements. Stochastic methods have applications well beyond combustion, including determining gene regulatory networks and solving inverse problems. CRF reseseachers recently used these tools for detecting the source of a terrorist release of a chemical or biological agent.

Covert releases of pathogenic aerosols pose a particularly difficult detection problem, especially if a sustainable response strategy is desired. Small releases, for instance in an urban warfare context, will probably go unnoticed by environmental sensors, while larger ones, especially on facilities embedded in large civilian populations, will probably record a "confirmed" hit approximately when the first symptomatic people are diagnosed (e.g. 2-3 days for a high-dose inhalational anthrax

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Sandia researchers develop mercury emissions monitor

Coal, an important domestic energy resource, also can contain trace heavy metals such as mercury which can be dispersed via power plant emissions. Sandia researchers are developing a portable, real-time, mercury (Hg) emissions monitor designed to measure the two primary gas-phase, Hg-containing species emitted from coal-fired power plants, mercuric chloride ($HgCl_2$) and elemental mercury (Hg^0). This work will enable coal-fired power plant operators and regulators to evaluate and optimize Hg emissions control technologies in their efforts to meet the more stringent requirements for Hg emissions set forth in the Environmental Protection Agency's Clean Air Mercury Rule.

Coal typically contains ~100 parts per billion (ppb) Hg. Without appropriate environmental controls on the exhausted flue gas, coal combustion releases this Hg into the atmosphere. Moreover, the effectiveness of these controls depends strongly on the distribution of Hg compounds in the flue gas, which in turn depends on the fuel stock and combustion conditions. The most abundant form of oxidized Hg emitted by most coal-fired boilers, $HgCl_2$, and other forms of oxidized Hg, can be efficiently removed by filtration or particle injection. However, Hg^0 is much more difficult and costly to collect. Furthermore, $HgCl_2$ and Hg^0 undergo different environmental and biological processes upon release into the atmosphere. Accurate measurements of $HgCl_2$ and Hg^0 are therefore

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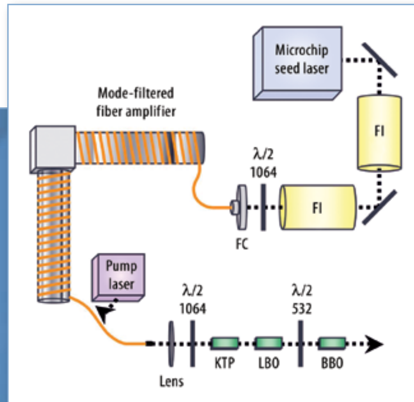

Figure 1. Diagram of the fiber amplifier and frequency conversion apparatus. FI: Faraday isolator, FC: fiber coupler, λ/2: half-wave plate (at the designated wavelength in nm). Dashed lines denote free-space beams.

Sandia National Laboratories

Estimating bioterror attacks

infection in a large population). Characterizing the incident from incomplete data necessitates the concurrent calculation of confidence intervals, if these are to be used meaningfully to plan responses. Current approaches are typically based on curve-fitting; these fail to provide the necessary confidence intervals and consequently have been of modest utility in logistical planning. Thus, while most response plans err on the side of caution by being broad and rapid, sustainability has not been considered a viable issue.

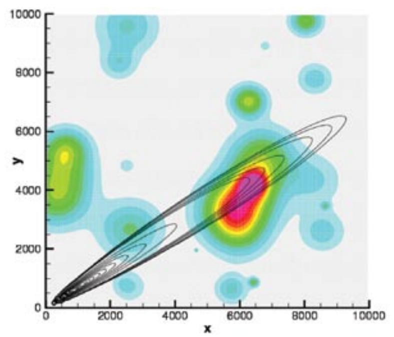

Figure 1. *1 Dosage contours over a hypothetical population distribution in a 10 km square domain.*

Researchers Jaideep Ray, Habib Najm, and Youssef Marzouk formulated a Bayesian problem to quantitatively infer an incident's characteristics, given sparse and incomplete data. They defined an incident as the release of aerosolized anthrax or smallpox over a spatially distributed population (Figure 1). Individuals received variable dosages and exhibited symptoms after an incubation period, which is drawn from a dose-dependent distribution. The number of people showing symptoms over successive 24-hour intervals formed the input (the "observations") to the inverse problem. They analytically derived a likelihood function for observing a time-series n_0, $n_1 \ldots n_M$ of symptomatic patients over M days, given an attack characterized by (N, τ, D), where N is the number of infected individuals, τ is the time delay between the release and the first presentation of symptoms and D is the average dose received by the N infected people. Bayes' rule, along with prior beliefs regarding the distribution of N, τ, and D, is used to develop an expression $\pi(N,\tau,D \mid \text{ni}, i=0 \ldots M)$ for the probability of an (N, τ, D) attack. Individual PDFs (probability density functions) for N, τ, and D are obtained by marginalizing the joint probability distribution $\pi(N, \tau, D \mid n_i, i = 0 \ldots M)$.

This capability [1, 2], developed in collaboration with NORAD-NORTHCOM, requires 3-5 days of observations to develop PDFs specific enough to be used for decision making. Inferences are more accurate if data are collected at a finer time resolution, e.g. on 6-hour intervals. Both N and τ are easily inferred, but the dosage poses a harder challenge. Given the poor characterization of the incubation periods of most select agents, competing models exist. Tests where one model was used to simulate the outbreak while the other was used to infer the characteristics (a means of estimating the sensitivity of the inference with respect to model error) showed that one could still infer the size of the outbreak within a factor of two. The Bayesian approach was applied to the anthrax outbreak in Sverdlovsk (modern day Yekaterinburg in Russia) in April, 1979, which is believed to have been caused by an accidental release of anthrax spores from a military facility [3]. The time of release is estimated to be April 2nd, 1979, with the first symptomatic patient appearing on April 4th. Medical countermeasures, which suppressed/prolonged the incubation period, were instituted on April 12th and the outbreak lasted well into May. Seventy deaths and 80 patients were recorded. Figure 2 (left) details the PDFs for τ indicating the time of release to be -2, *i.e.* two days before the first symptomatic patient recorded on April 4th. This agrees with [3]. In Figure 2 (right), PDF for N is plotted. Thus by Day 9 (April 13th), it was clear that the number of infected people was probably less than 200. However, the medical response (antibiotics and vaccination), designed without access to such characterizations, was put into place on April 15th and affected 59,000 residents of Chkalovskiy *rayon* – 80% were vaccinated at least once.

Thus, the ability to quantitatively characterize a bioterror attack has obvious utility in calibrating an effective response. This was explicitly identified during the "Dark Winter" exercise [4]. Apart from its use in the logistics of mounting a response, such quantitative characterizations can also be used develop measured response plans, where the probabilistic nature of the characterization allows the use of risk-based strategies. These, along with risk-mitigation via hedging of resources, can form the basis of a sustainable strategy for dealing with such threats.

Bayesian methods provide a conceptually straightforward means of "fusing" disparate data together via prior beliefs, and are often favored in data-starved environments. This approach may admit significant acceleration via priors for N and τ, drawn from syndromic surveillance nets. Furthermore, it can be extended to contagious diseases by posing a non-stationary Bayesian inverse problem of disease spread over a social network to infer the size and rate of propagation, predicated on incomplete observations of symptomatic people. Such a capability, coupled to a transportation network, can be used as a quantitative early-warning system for diseases with an asymptomatic contagious period (*e.g.* influenza).

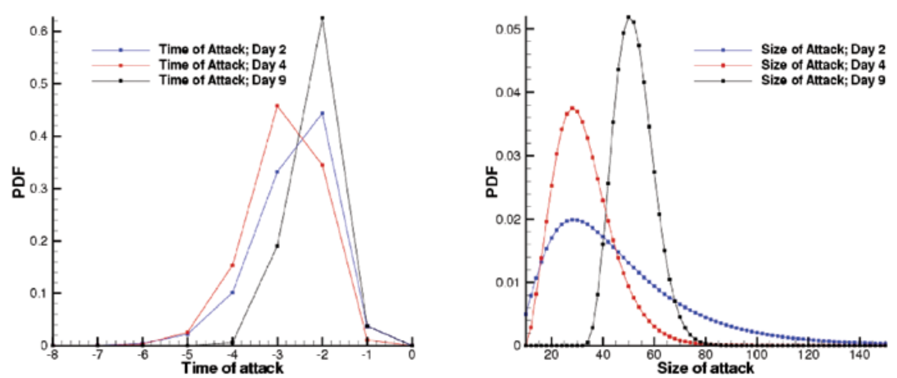

Figure 2. *PDFs for the time of release (left) and number of infected people (right) for the Sverdlovsk incident, developed from 9 days of data. The most probable values are seen to be two days before first symptoms, which were presented on April 4th, 1979, lasted 42 days and infected 70 people.*

References

1. *J. Ray, Y.M. Marzouk, H.N. Najm, M. Kraus and P. Fast, "A Bayesian method for characterizing distributed microreleases: I. The single-source case for non-contagious diseases", Sandia Technical Report SAND2006-1491. Printed March 2006. Sandia National Laboratories, Livermore, CA*

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3. *M. Meselson, J. Guillemin, M. Hugh-Jones, A. Langmuir, I. Popova, A. Shelokov, and O. Yampolskaya, "The Sverdlovsk anthrax outbreak of 1979", Science, 266:1202-1208. 1994.*

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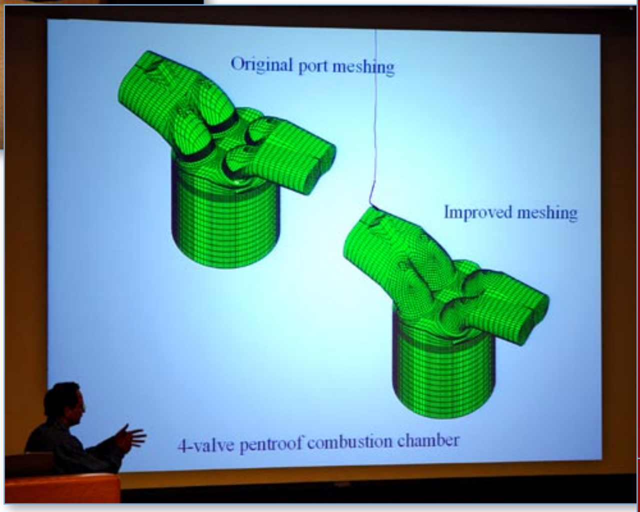
HCCI Working Meeting

The semi-annual Advanced Engine Combustion (AEC) and Homogeneous Charge Compression Ignition (HCCI) university working groups met at Sandia Feb 6th-8th, 2007. Their research is funded by the U.S. Department of Energy through the Office of FreedomCAR and Vehicle Technologies.

Meeting presenters discussed the latest in industry and academic research.



Presenters from universities, DOE and auto companies were joined this year by fuels companies interested in developing new fuel mixtures for advanced engines.

This year five energy companies, (ConocoPhillips, BP, ExxonMobil, Chevron, and Shell) joined existing AEC Memorandum of Understanding (MOU) participants, comprised of ten automotive and engine companies (Caterpillar Corporation, Cummins Corporation, DaimlerChrysler Corporation, Detroit Diesel Corporation, Ford Motor Company, General Electric Global Research Center, General Motors Corporation, International Truck, John Deere, and Mack Trucks, Inc.) and five national laboratories (Lawrence Livermore, Los Alamos, Oak Ridge, Argonne, and Sandia).

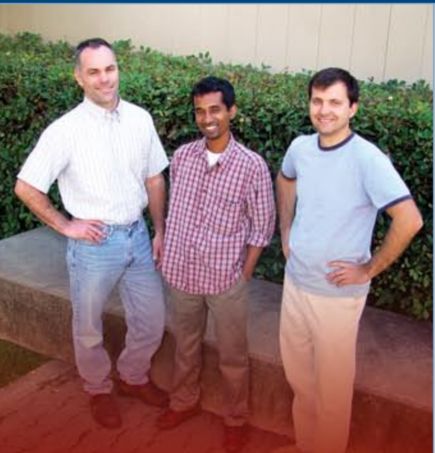
Discussions ranged from low-temperature combustion strategies to fuel effects on low-temperature combustion. This program is meant to develop both the knowledge base encompassing in-cylinder mixing, combustion, and emission processes relevant to advanced engine combustion as well as predictive models--essential for developing the next generation of efficient, clean engines.

Duk Sang Kim

Duk Sang Kim, visiting scientist from the Automotive Technology Research Institute at Kookmin University in Korea, will be working with Paul Miles over the next year on the in-cylinder imaging of pollutants.

Jonathan Baker

Jonathan Baker, a visiting chemist from the Atomic Weapons Establishment, a U.K. quasi-governmental institute, is working with Rich Behrens for a month on a joint energetic materials application.

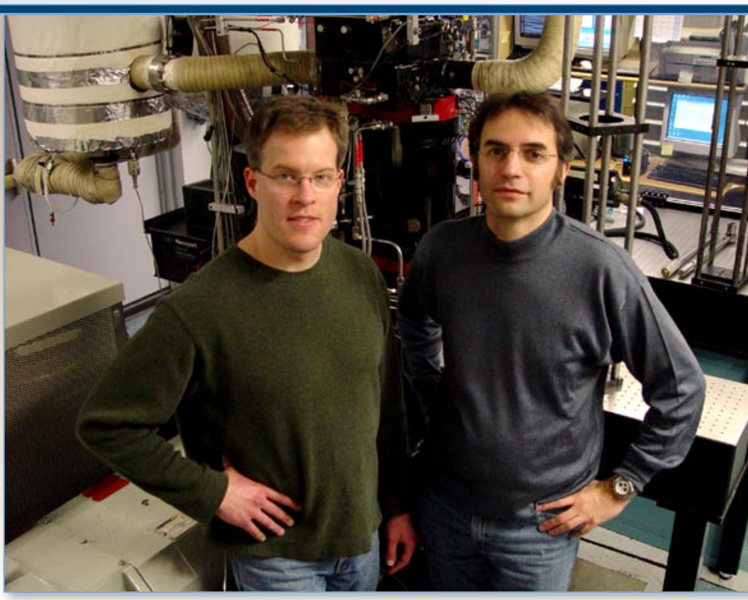


Joe Oefelein, Vaidyanathan Sankaran, and Tomasz Drozda

Trio of CRF researchers win best paper award at 31st Combustion Symposium

CRF researchers Joe Oefelein, Vaidyanathan Sankaran and Tomasz Drozda received a Distinguished Paper Award for their paper "Large eddy simulation of swirling particle laden flow in a model axisymmetric combustor" at the 31st Annual Combustion Symposium in August 2006 at Universität Heidelberg in Germany. Their paper focused on the application of the Large Eddy Simulation (LES) technique to a swirling particle-laden flow in a model combustion chamber. A series of calculations were performed and compared directly with detailed experimental measurements. Results highlighted the accuracy of the subgrid-scale model used for spray dispersion and the predictive capabilities of LES when implemented with the appropriate numerics, grid resolution and well defined boundary conditions.

Thierry Lachaux joins turbine company in Switzerland



Marc Musculus and Thierry Lachaux in the engines laboratory

Thierry Lachaux completed his post doc working with Mark Musculus, has taken up a position conducting gas turbine combustion research at ABB, a subsidiary of French multinational company Alstrom, at a branch near Zurich. At the CRF, Lachaux worked in the Heavy-Duty Low-Temperature Combustion/Diesel Combustion optical engine laboratory. Lachaux mainly focused on using multiple optical diagnostics such as planar laser-induced fluorescence (PLIF) of formaldehyde, PLIF of the hydroxyl radical (OH), and PLIF of toluene as a fuel tracer to identify the in-cylinder processes that lead to unburned fuel emissions from advanced low-temperature combustion diesel engine operating modes. Lachaux's research showed that in-cylinder mixtures after the end of fuel injection are stagnant, and when they rapidly mix with air, the fuel concentration becomes too low to support complete combustion. In this way, some of the fuel escapes combustion and is exhausted from the engine.

Evatt Hawks returns to Australia for university post

Evatt Hawkes, a post doc working with Jackie Chen, is taking up a faculty position as lecturer in the School of Photovoltaic & Renewable Energy Engineering, Faculty of Engineering, University of New South Wales in Sydney, Australia. Hawkes spent the past five years at the CRF simulating aspects of turbulent flows.

Seungmook Oh finishes year at CRF

Seungmook Oh, a visiting scientist working with Paul Miles for the past year, returned to the Korea Institute of Machinery and Materials. During his stint at the CRF, Oh developed Laser Induced Fluorescence techniques to measure in-cylinder CO.

Using kinetics

(Continued from page 1)

been reported only for the simplest RO_2 species, methylperoxy (CH_3OO), and its ionization energy had never been measured. Detection of larger alkylperoxy radicals was difficult and was thought to be limited by low ionization cross sections. The work of the CRF researchers shows that it is rather the instability of the ROO^+ cations that prevented detection of the larger alkylperoxy radicals by photoionization.

The experiments that allowed characterization of alkylperoxy ionization utilized the Multiplexed Chemical Kinetics Photoionization Mass Spectrometer (*CRF News* 28, No. 1), operating at LBNL's Advanced Light Source. In this apparatus, chemical reactions are initiated by laser photolysis of a suitable precursor in a quartz reactor. The reactor contents are then continuously sampled and analyzed by synchrotron photoionization mass spectrometry using a double-focusing mass spectrometer, yielding mass spectra of the reacting mixture as a function of time after the initiating laser pulse. This machine combines the power of photoionization by easily and widely tunable vacuum ultraviolet synchrotron radiation with simultaneous time-resolved detection of multiple masses.

The CRF scientists photolyzed symmetric ketones (e.g., acetone, diethyl ketone) in the presence of oxygen to create alkyl peroxy radicals. Because the mass spectrometer simultaneously probes all species in the reactor, the disappearance of the initially formed alkyl radicals through reaction with oxygen and the corresponding appearance of alkylperoxy radicals can both be monitored. Reacting methyl radicals, created from acetone photolysis with oxygen, created an easily discernable signal of methylperoxy CH_3OO at the parent mass, m/z = 47. The team monitored this signal as a function of the ionizing photon energy, and combined it with computation of Franck-Condon factors that model the shape of the ionization threshold, to make the first measurement of the adiabatic ionization energy of the methylperoxy radical.

However, similar experiments to follow the reaction of ethyl and propyl radicals with oxygen showed no signals at the masses of the corresponding alkylperoxy radicals. Nevertheless, because the full mass spectrum was measured as a function of time and ionizing photon energy, the signature of alkylperoxy ionization could still be discerned. Figure 1 shows the signal observed at m/z = 29, the mass of the ethyl radical, as a function of time and photon energy, in the reaction of ethyl radicals with oxygen. The spectrum shows two sources of $C_2H_5^+$. The $C_2H_5^+$ formed by direct ionization of ethyl radicals can be seen as the peak near t = 0, present at all photon energies in the figure. This signal rapidly decays to the baseline level for photon energies below about 10 eV, reflecting the removal of ethyl radicals by reaction with oxygen. At higher photon energies, however, m/z = 29 signal persists for long periods. This signal can be attributed to dissociative ionization of ethylperoxy radical, C_2H_5OO, to form $C_2H_5^+$ and O_2. The instability of the ethylperoxy cation is related to the stability of the ethyl cation, which arises from its unusual three-center, two-electron bonding. Calculations carried out by the CRF researchers and their collaborators suggest that other linear alkyl cations that exhibit similar bonding will also not have stable alkylperoxy cations. Even so, time-resolved, tunable photoionization permits the contributions of direct ionization and dissociative ionization to be separated, as seen in Figure 1, enabling the concentration of the alkylperoxy radical to be monitored by photoionization detected at the alkyl cation mass.

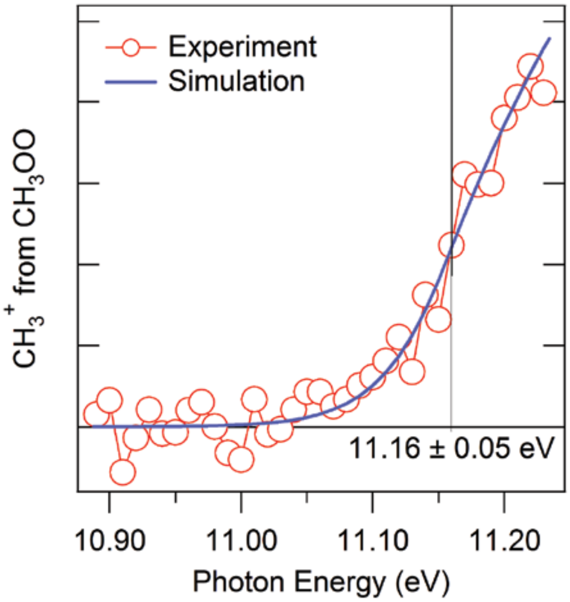


Figure 2. *Photon energy dependence of the dissociative ionization of methylperoxy radicals to give methyl cations and oxygen molecules. The fit yields the appearance energy of methyl cations from methylperoxy radicals.*

Finally, measurement of similar dissociative ionization processes in the CH_3OO radical allowed the researchers to measure the CH_3– O_2 bond energy, an important thermodynamic quantity for combustion modeling. Figure 2 shows the photon energy dependence of the dissociative ionization of CH_3OO to form CH_3^+ and O_2. The photon energy dependence is fit to account for the thermal energy (298 K) in the ion, yielding the appearance energy of CH_3^+ from CH_3OO, which is related to the CH_3– O_2 bond energy via the very well-known ionization energy of CH_3. The derived bond energy of (127.6 $\pm$5) kJ/Mol supports previous kinetic determinations of the CH_3 – O_2 bond energy and is slightly larger than more recent negative-ion measurements.

Future studies of peroxy radical photoionization will include measurements of peroxy radicals formed from unsaturated, resonance-stabilized, and aromatic hydrocarbon species to investigate the fundamental physics that governs the stability of alkylperoxy cations. The Multiplexed Chemical Kinetics Photoionization Mass Spectrometer is currently being employed by a team from multiple institutions including researchers from Howard University, Texas A&M University, and the Catholic University of America, in addition to the CRF and LBNL scientists, to investigate the chemistry of hydrocarbon oxidation (including alkylperoxy radical reactions), molecular weight growth and soot formation and hydrocarbon chemistry in the Earth's and extraterrestrial atmospheres.

Sandia researchers *(Continued from page 1)*

essential for modeling Hg transport and for evaluating and optimizing the effectiveness of possible Hg control technologies.

With funding from the National Energy Technology Laboratory, CRF researchers Alex Hoops and Tom Reichardt demonstrated photofragment emission (PFE) detection of $HgCl_2$ using a fiber-based, ultraviolet (UV) laser source. In PFE detection of $HgCl_2$, emission is detected from excited Hg^0 daughter fragments produced by the photodissociation of $HgCl_2$. Hoops and Reichardt previously characterized and quantified the $HgCl_2$ PFE method by evaluating the potential impact of interference gases, determining the dependence of the PFE signal strength on laser irradiance, and examining the effects of collisional quenching by major flue-gas constituents N_2, O_2, and CO_2 (*CRF News*, Vol. 27, No. 3). These studies were performed with a Nd:YAG-pumped dye laser frequency converted into the UV; although useful for proof-of-concept and optimization experiments, the physical characteristics of this laser preclude its use in real-world field environments. For a field-worthy instrument, the laser source must be compact, rugged, and light-weight, while maintaining high average and peak powers with the requisite spatial beam quality for a stand-off approach. Frequency conversion of pulsed, rare-earth-doped, fiber-based lasers has the potential to meet these requirements for a practical laser source.

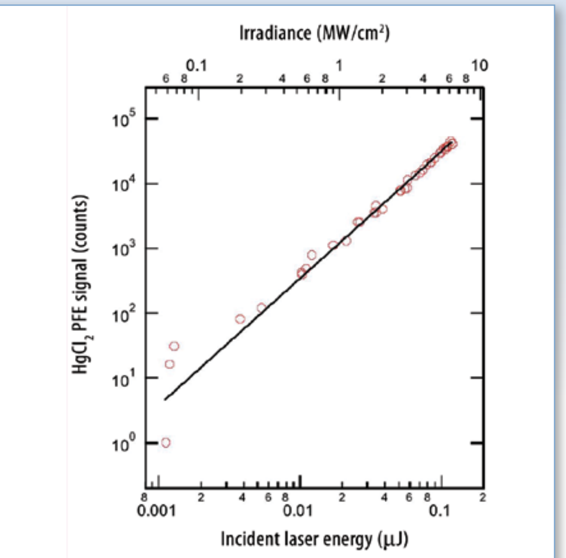


Figure 3. *$HgCl_2$ PFE signal strength versus laser pulse energy (bottom axis) and laser irradiance (top axis) obtained with 7 x 10^{-5} Torr of $HgCl_2$ in 0.4 Torr of N_2. Each data point (open circle) comprises 10^5 laser shots. The fit of the experimental data (solid line) yields a power dependence of 1.96 ± 0.01.*

Hoops and Reichardt recently used the 213-nm output of a Sandia-built, frequency-quintupled fiber laser (Figures 1 and 2), developed by Dahv Kliner, Jeffrey Koplow, and Sean Moore, to detect $HgCl_2$ by PFE. The laser system employed a ytterbium-doped fiber amplifier based on the patented "mode-filtering" technique developed by Sandia researchers (*CRF News*, Vol. 23, No. 2). This technique allows dramatic power scaling of fiber lasers by more than two orders of magnitude, while maintaining high efficiency and diffraction-limited beam quality (critical for both efficient nonlinear frequency conversion and stand-off detection). The fiber amplifier was seeded by a compact microchip laser operating at a wavelength of 1064 nm and repetition rate of ~6 kHz, and the amplifier output was frequency quintupled to 213 nm using standard nonlinear crystals operating at ambient temperature. A photon-counting approach was incorporated for this low-light measurement involving the acquisition of less than one photon per count cycle, which greatly reduced the measurement uncertainty by eliminating electronic noise sources. The high repetition rate of the pulsed fiber amplifier made possible the acquisition of sufficient count levels within measurement times that are reasonable for a real-time device. Hoops and Reichardt measured a quadratic dependence of the $HgCl_2$ PFE on laser irradiance (Figure 3) in a low-pressure nitrogen atmosphere, indicating that the photodissociation mechanism involves the absorption of two photons. In addition, they demonstrated the ability to detect 90 ppb of $HgCl_2$ using the compact, all-solid-state, fiber laser source in a gas mixture typifying the flue-gas composition and they extrapolated these results to a detection limit of 0.1 ppb for a signal acquisition time of 5 minutes.

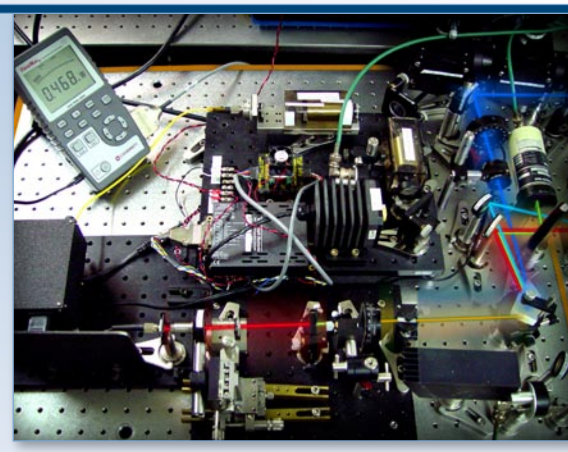


Figure 2. *Photograph of the fiber amplifier and frequency conversion apparatus. Laser beams are color-enhanced for visibility. Red=1064 nm, green= 532 nm, aqua =355 nm, dark blue =213 nm, yellow is a combination of all.*

These experiments show that the physical and optical characteristics of the frequency-converted fiber amplifier, combined with photon counting make this $HgCl_2$ PFE suitable for a sensitive, real-time, fieldable instrument. In the near future, Hoops and Reichardt will team with CRF researchers Jude Kelley and Dennis Morrison to develop a portable breadboard instrument for $HgCl_2$ PFE measurements and initial tests of the instrument will be performed in the CRF's Multifuel Combustion Laboratory.

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