Combustion Research Facility News

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New thermochemical data predicted using the BAC-MP4 method

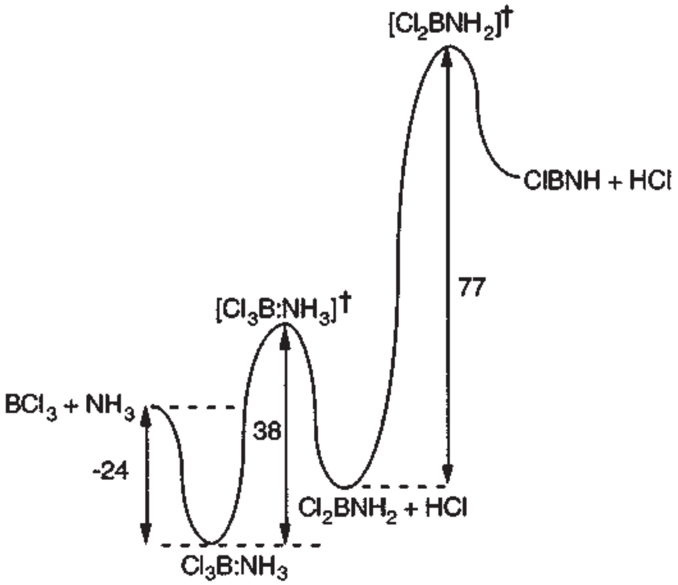
Using theoretical techniques originally developed to treat problems related to combustion and energetic materials, Carl Melius and Mark Allendorf have predicted thermochemical data for compounds containing the elements boron, nitrogen, chlorine, and hydrogen.

The BAC-MP4 (bond additivity correction–fourth-order Møller-Plesset perturbation theory) method was developed by Melius to predict thermochemistry – which includes heats of formation, entropies, and heat capacities – for molecules found in flames and explosions. These data are essential to the development of numerical models of these high-temperature processes. However, data for many molecules are unavailable, since the compounds of interest are often reactive and short-lived. Theoretical methods such as BAC-MP4 allow the necessary quantities to be predicted for these species, some of which have not been detected.

Boron chemistry interested combustion scientists in the 1960s because of its potential application to rocket propulsion. The current investigation was motivated by the development of chemical vapor deposition (CVD) processes for making boron nitride (BN). CVD of BN is used in the manufacturing of ceramic composites, where thin coatings on reinforcing fibers creates a weak interface between the fiber and the surrounding matrix material. This allows the fibers to slip relative to the matrix when the composite is under stress, transferring the load to the strong axial dimension of the fibers. The BN thickness must be tightly controlled, however, to obtain a high-strength, tough composite.

The objective of the current research is to develop models incorporating detailed gas-phase chemistry that can be used to identify processing conditions yielding uniform boron nitride coatings. The work is sponsored by the Department of Energy, Office of Industrial Technologies, Advanced Industrial Materials Program.

BAC-MP4 predicts thermochemical data by calculating molecular energies using high-level *ab initio* quantum-chemistry methods, then correcting these values using empirically derived corrections (bond-additivity corrections, or BACs). The method can predict heats of formation for stable species with an accuracy of ± 2 kcal mol^{-1}, often as good as values arrived at experimentally. It can also be used to predict activation energies for chemical reactions, as shown in the figure.



Potential-energy surface (energies in kcal mol^{-1}) for the reaction between boron trichloride and ammonia, as predicted by the BAC-MP4 method. The results are consistent with the products and rate constant observed experimentally.

In collaboration with Allendorf and Pauline Ho, Melius extended BAC-MP4 to a wide range of problems related to high-temperature materials processing. In addition to boron and other compounds containing first-row elements, molecules containing silicon have been investigated in great detail, due to their importance in the fabrication of materials ranging from integrated circuits to ceramic compounds.

The new data are available as polynomial fits that are compatible with the Chemkin Thermodynamic Database. They may be obtained in electronic form from the Web at http://herzberg.ca.sandia.gov/~melius.

Photos of summer visitors to the CRF, usually included in the September/October issue, can be found on the CRF News Website at http://www.ca.sandia.gov/CRF/Visitors/ or in the “What’s HOT at the CRF” section for August.

Raman lidar receives ARM citation

A team of Sandians received one of only two awards presented at the 1997 Atmospheric Radiation Measurement (ARM) Program Science Team meeting held during March, 1997. The citation on the plaque reads, “Presented to John Goldsmith, Scott Bisson, and Forest Blair for their singular achievement in the successful development and implementation of the water vapor Raman lidar for the Department of Energy’s Atmospheric Radiation Measurement Program.”

For decades lidar has held the promise of filling a variety of chemical remote sensing needs. Many complex, manpower-intensive instruments have been developed, but use of these systems has not gone beyond the demonstration phase. This Raman lidar system is the first chemical sensing lidar that is sufficiently automated, simple to start up, and reliable enough for routine, unattended operation in the field (literally a farmer’s field in Oklahoma). The need for this instrument was important enough that the ARM program funded the development and construction. The quality and quantity of data being provided by the Raman lidar has already made significant contributions to the program, as recognized by the ARM citation.

Professor Brian Haynes, University of Sydney, Australia, paid a short visit to the CRF recently to continue planning activities for the 27th International Symposium on Combustion. Brian (right) and Don Hardesty (left) are Program Co-Chairs for the Symposium. Brian and Don also visited the Symposium site at University of Colorado, Boulder, to meet with Professor Mel Branch and his organizing committee. During his visit to Sandia, Brian presented a seminar on his recent research on surface heterogeneity effects during carbon oxidation.

Ken Aniolek (left), a mechanical engineering Ph.D. student from Drexel University, has spent the past year working in the low-pressure flame laboratory. Ken worked with Jim Scherer and Dave Rakestraw (right) applying cavity ringdown laser absorption spectroscopy to measure HCO and CH_3 radicals in flames.

Recent meetings

The Spring Meeting of the Western States Section of the Combustion Institute was held on April 14-15 at the CRF. The meeting was attended by over 150 people, including 50 students. Twenty-five awards of $150 each were presented to student speakers.

Following the WSSCI meeting, Sandia co-hosted (with the Federal Energy Technology Center) the IEA Workshop on Emerging Issues in Coal Combustion and the IEA’s 17th Executive Committee Meeting on Coal Combustion Sciences. Invited papers were presented at the IEA Workshop by Sandians Larry Baxter, on coal / biomass cofiring, and by Melissa Lunden, on the influence of mineral matter on coal reactivity.

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Sandia National Laboratories,
Livermore, California, 94551-0969.
Director: William J. McLean
Mail Stop 9054, (510) 294-2687
Editor: Lizbette Cox
Mail Stop 9056, (510) 294-2322
lrcox@Sandia.gov

If you haven’t already done so, you may want to look at the Sandia Combustion Research 1997 Technical Review at http://www.ca.sandia.gov/CRF/Publications/SCRTR.

Understanding NO_x formation in diesel engines using PLIF imaging

Using an optically accessible diesel engine and a unique laser system, John Dec, Eldon Porter, and Robert Canaan have obtained single-shot PLIF (planar laser-induced fluorescence) images of the NO-radical distribution in the combustion chamber of an operating diesel engine. These images show where and when NO (the source of NOx emissions) forms during diesel combustion, and they provide important insight into how NO formation is related to the overall diesel combustion process. These experiments are part of an ongoing diesel combustion CRADA (Cooperative Research and Development Agreement) with the heavy-duty diesel engine manufacturers (Cummins, Caterpillar, and Detroit Diesel).

The researchers conducted these NO-PLIF measurements in an optically accessible direct-injection diesel engine of the heavy-duty size-class, which was described in *CRF News* **15**:3. The experiments were conducted at a medium speed (1200 rpm) operating condition with a motored TDC (top dead center) temperature and pressure of 992 K and 5.0 MPa, which are representative diesel-engine conditions.

A unique laser system was used to create the high-energy sheet of 226 nm light required to excite the NO fluorescence for this investigation. This laser system utilized a tripled Nd:YAG laser to pump a narrow-line OPO (optical parametric oscillator) whose output was doubled to obtain 226 nm. Although somewhat more complicated than a classic dye-laser system, this OPO system provided 12-15 mJ / pulse at 226 nm, which is approximately 4 times the energy of a typical dye-laser system.

Due to low laser energies, previous studies had to rely on oxygen-enriched air to boost NO levels and / or averaging the NO signal over multiple engine cycles. These techniques compromised the integrity and resolution of the measurements. In contrast, the high laser energies in the current investigation allowed single-shot NO images to be obtained under realistic diesel-engine operating conditions.

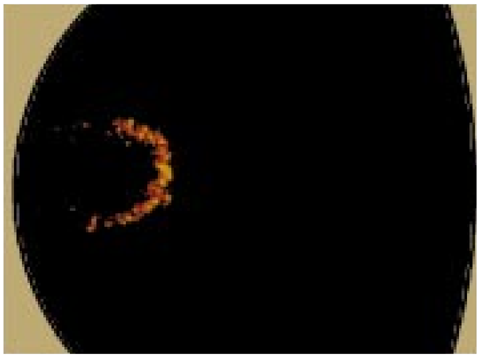

Figure 1. A typical PLIF image of the early NO distribution in the cylinder of an operating diesel engine. The image was taken just after the onset of the diffusion flame, 6° BTDC (before TDC). Note that this image was obtained through the cylinder-head window, so only the leading portion of the fuel jet is visible. The curves at the left and right show the edges of the window.

The figures show typical NO PLIF images at two different crank angles. As shown in Fig. 1, NO is first detected around the periphery of the fuel jet just after the diffusion flame has formed. NO formation occurs at this location (on the lean side of the diffusion flame which forms around the jet periphery) where oxygen is available and temperatures are high.

It is important to note that these images showed no NO being produced by the initial premixed-portion of the diesel combustion event. This is in agreement with recent measurements from our laboratory that showed that the initial premixed burn is too fuel-rich to produce significant NO; however, it contrasts with a long-held speculation by the diesel community that the premixed burn contributed preferentially to NO production.

Once NO formation begins, the data show that NO production continues around the jet periphery through the remainder of the combustion event. By the time combustion is over, NO exists throughout that portion of the combustion chamber where a reacting fuel jet has traveled, as shown in Fig. 2.

A comparison of Figs. 1 and 2 shows that in addition to occurring over a wider region, NO concentrations are higher by the end of combustion as indicated by the increased image intensity in Fig. 2. Intensities can be compared because changes in pressure broadening and quenching have only a small effect between these two images.

The results of this investigation are providing guidance for numerical modelers and are important to diesel engine manufacturers who must meet increasingly stringent standards for NO_x emissions but until now have only been able to speculate on where and when NO formation occurred.

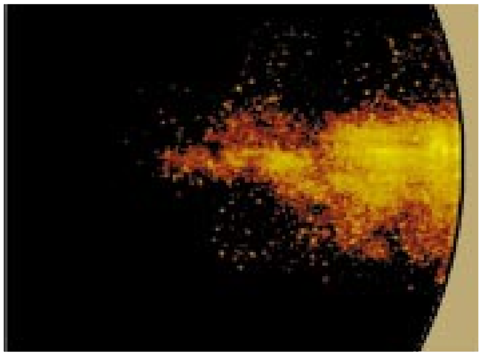

Figure 2. A typical diesel-combustion NO PLIF image taken near the end of the apparent heat release, 18° ATDC (after TDC). This image was obtained through the piston-crown window and shows the trajectory of one of the eight fuel jets. The injector is located near the left edge of the image, and the curve at the right shows the location of the combustion-chamber wall.

Flame acceleration simulated

A distorted flame propagating into a large volume of premixed fuel and air has the ability to enhance its speed, that is, accelerate by comparison with a smooth flame moving into the same mixture. This enhanced burning may have serious consequences with regard to surrounding structures in an accidental flame-ignition event. Bill Ashurst has constructed a potential flow model of an expanding circular flame that suggests the formation of a particular flame shape is the cause of the acceleration; this shape resembles the cycloid curve.

The burning velocity of a premixed flame, S_L – the rate at which the flame surface advances into the unburnt gas in front of the surface – depends upon the fuel-air composition. Expanding from a point source, the flame speed is given by σS_L where σ is the density ratio across the flame (unburnt over burnt). This speed does not depend upon the flame size but does require a smooth flame surface (spherical or circular). When the flame is distorted, and thereby acquires more surface area, the speed will be larger than σS_L. Darrieus and Landau showed long ago that the flame surface will acquire distortions due to a hydrodynamic instability; this instability occurs when S_L is constant.

Our numerical model of flame propagation has this Darrieus-Landau instability at long wavelengths, but we have also included a short wavelength stability that occurs when S_L has some dependence upon the local flame curvature (caused by changes within the flame structure but not included in these simulations).

Figure 1 shows the evolution of one calculated flame: the flame is actually growing within a wedge shape but the spatial scaling has been doubled between each image in order to display both the large- and small-width flames. From the calculated radial growth of the average flame location we can determine the flame speed. We find that a transition occurs from the constant σS_L value to a speed with a square root dependence upon time, see Figure 2.

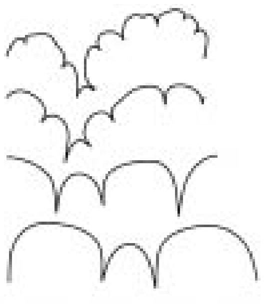

Figure 1. From bottom to top, the computed evolution of a flame expanding in two dimensions reveals the flame shape to be bulges connected by cusps (the cusps point towards the burnt gas side of the flame). The cusp-bulge-cusp shape resembles a cycloid curve.

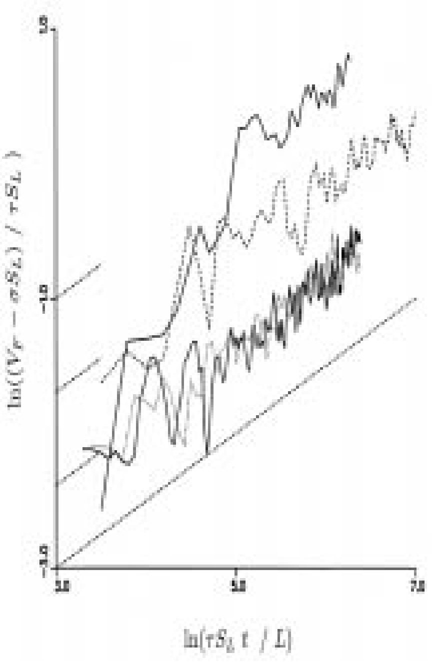

Figure 2. The computed flame speed V_F, minus the smooth flame speed of σS_L, grows like the square root of time (shown by the straight dashed lines). The flame density ratio values σ are 7 (bottom, two cases), 13, and 25 (top); the parameter τ (= σ -1) is the volume production ratio.

Thus, in the large flame limit, the radius will grow like the 3/2 power of time. This is the same behavior that has been experimentally observed when the flame size is larger than a meter. The flame radial dependence may be expressed $R = R_1 + 0.002\,\sigma^2 S_L^2 t^{\{3/2\}} / \sqrt{\kappa}$ where R_1 is the transition radius and κ is the thermal diffusivity of the unburnt gas mixture. The numerical coefficient from the simulations agrees with the experimental value given above.

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Sandia National Laboratories
Mail Stop 9056
P.O. Box 969
Livermore, California 94551-0969

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