Combustion Research Facility News

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Multiscalar measurements yield instantaneous NO production rates

Rob Barlow, Greg Fiechtner, and Tom Prast have demonstrated an experimental method for determining oxygen atom concentrations and instantaneous thermal production rates of NO (nitric oxide) in turbulent flames. Thermal production of NO, which involves the reaction of N_2 with oxygen atoms at high temperature, is an important mechanism for pollutant formation, particularly in combustion devices that rely on diffusion flames. The new method provides data for validating predictive models, and it yields valuable information about the effects of turbulence/chemistry interactions on oxygen atom concentrations and on the pollutant formation process.

The instantaneous concentration of oxygen atoms is determined from simultaneous measurements of temperature, the major species concentrations, and the OH radical concentration, based upon partial equilibrium (equal forward and backward rates) of the rapid reaction $OH+OH=O+H_2O$. The thermal NO production rate is then calculated from this derived O-atom concentration, the measured nitrogen concentration, the measured temperature, and well-established kinetics.

Figure 1 shows results for instantaneous and conditionally averaged O-atom mole fractions in a jet flame of nitrogen-diluted hydrogen. Results are plotted versus the mixture fraction, which is zero in air, unity in the pure jet fluid, and has a stoichiometric value of 0.116 in this flame. The peak of the conditionally averaged O-atom curve is 7.5 times the maximum value for full equilibrium. This result quantifies the frequently postulated contribution of super-equilibrium O-atom concentrations to NO formation.

In Figure 2 experimental results for NO production rate and NO mole fraction are compared with predictions by a Monte Carlo pdf simulation carried out by J.-Y. Chen (University of California, Berkeley). This simulation included detailed chemistry (14 species, 48 steps) and was conducted as a blind prediction, based only on the experimental flow rates. Agreement between measured and predicted NO mole fractions is remarkably close. The peaks of the experimental and predicted NO production rates are 70% and 90% higher than the maximum rate based on adiabatic equilibrium conditions.

This experimental approach may be applied in any flame where partial equilibrium is satisfied. Work is in progress to determine how effective it will be in turbulent jet flames of $CO/H_2/N_2$ and in lean methane flames.

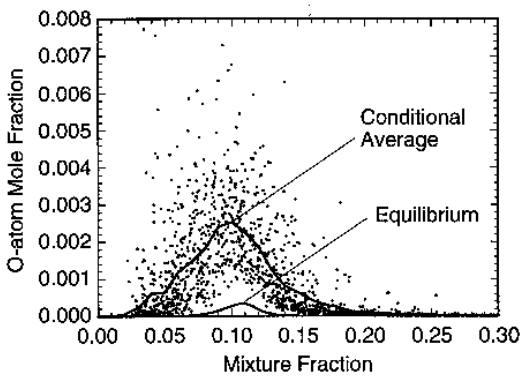


Figure 1. Instantaneous and conditionally averaged results show that O-atom mole fractions are at super-equilibrium levels in a turbulent jet flame of nitrogen-diluted hydrogen at a streamwise location 30 nozzle diameters from the base. The conditional average is calculated after sorting the data by mixture fraction.

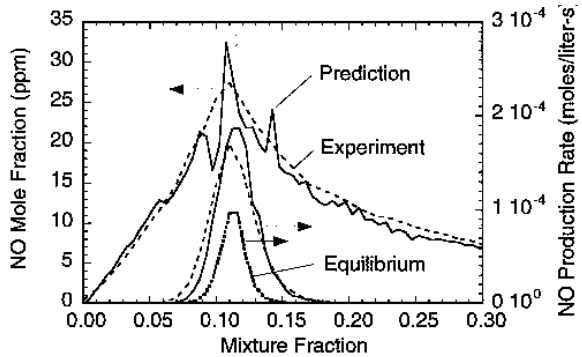


Figure 2. There is close agreement between experimental results (– – – –) and Monte Carlo pdf model predictions (———) for the conditionally averaged thermal NO production rate and NO mole fraction versus mixture fraction. NO production rates in the turbulent flame are significantly higher than those calculated for adiabatic equilibrium conditions(• • • • •). Jaggedness in the prediction is due to statistical noise in the Monte Carlo simulation.

Diamond films grown in stagnation-flow reactor

A team composed of David Hahn, Chris Edwards (Stanford University), John Wirdzek, and Kevin McCarty has been successful in growing two-inch diameter diamond films using a scaled-up, stagnation-flow reactor developed at Sandia. This work was part of a project supported by Department of Energy / Lab-Directed Research and Development and Advanced Research Projects Agency that focused on combustion driven, large-area diamond growth via chemical vapor deposition.

Since the late 1980s when diamond was first grown in a standard oxy-acetylene torch, researchers have tried to exploit the high growth rates of combustion synthesis methods as compared to the more established microwave-plasma and DC plasma-torch technologies. A stagnation-flow flame configuration showed promise for uniform diamond deposition, but several issues remained before scaling to large growth areas was feasible.

The Sandia stagnation-flow reactor uses a 90 kW, premixed acetylene / oxygen / hydrogen flame that impinges against the deposition surface, a pure molybdenum substrate, as shown in Figure 1. Uniform nucleation and growth of diamond are contingent upon achieving a true flat flame, while high growth rates are realized by pressing the flame close to the substrate. The relevant issues include conditioning of the reactant flow, flame stabilization, and extracting the high heat fluxes in a controlled way that provides for real-time substrate temperature control.

The scaled-up reactor utilizes a unique nozzle design that optimizes reagent usage by approximating the outer streamline of an ideal stagnation-flow. Mary Bui-Pham, Ellen Meeks, and Bob Kee provided comprehensive modeling of the flame that was used for nozzle design, as well as for optimization of flame parameters during diamond growth. A flame-anchoring stabilizer was designed forthe highly strained flame conditions, and a novel spray cooling strategy was implemented that allows real time substrate temperature control.

Diamond films have been deposited over the entire two-inch diameter substrate. The detachable diamond films are of good quality as characterized by Raman spectroscopy. The spectrum in Figure 2 exhibits a peak near 1332 cm^{-1} that is characteristic of diamond, with no graphitic carbon features present.

Work is continuing to optimize diamond deposition rates, currently about 25 µm / hr, and to correlate growth rates and film quality with the combustion process parameters.

Pulse combustor design code ready for industry

Pamela Barr and Jay Keller have completed development of a computational tool to assist industry with the pulse combustor design process (Barr and Keller, *CRF News* **17**:3). The Sandia Pulse Combustor Design Code, or SPCDC, runs on personal computers running on a Microsoft Windows platform and has a graphical user interface. Users will benefit from the insight gained from over ten years of pulse combustion research and development funded by the DOE, GRI, and others.

SPCDC simulates an entire pulse combustion system, from the intake line to the exhaust decoupler. Although SPCDC will never replace the time-proven method of actually building and testing a unit, it can significantly reduce the number of units that must be tested. And it can help produce a superior pulse combustion system tailored to a specific application. When used by heating system designers, it will help bring the inherent advantages of pulse combustion systems – high efficiency, lower emissions without external controls, improved venting, and lower manufacturing costs – to a wider range of residential, commercial, and industrial heating systems.

Contact Pamela Barr for additional information on SPCDC.

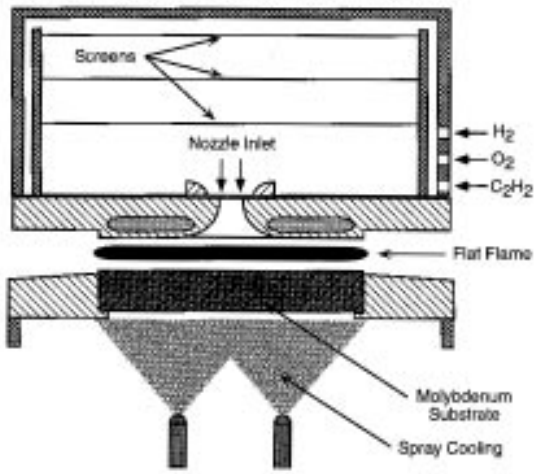


Figure 1. Stagnation-flow reactor for chemical vapor deposition of 2" diameter diamond films.

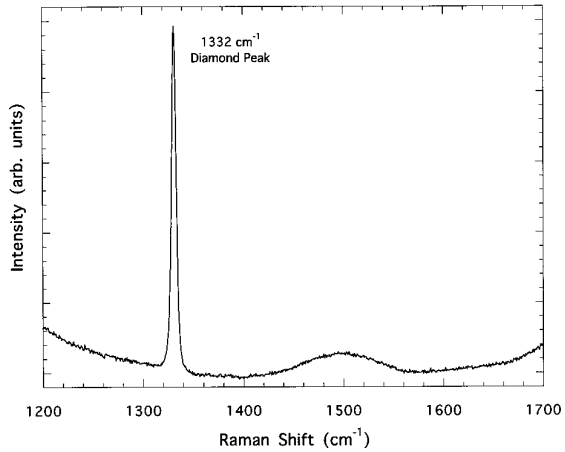
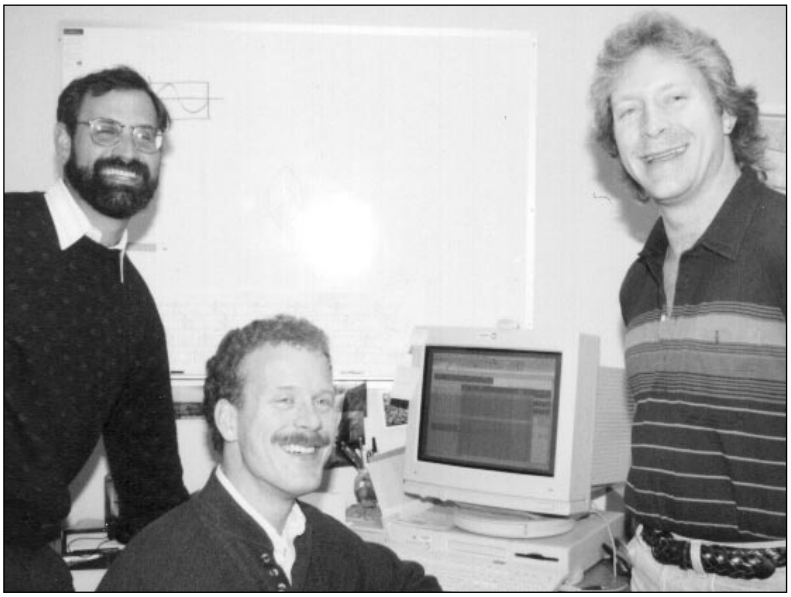


Figure 2. Raman spectrum of a 36-µm thick, flame grown diamond film.

Peter Loftus of Arthur D. Little visited the Burner Engineering Research Laboratory during the test of a Gas Research Institute-sponsored ultra-low NO_x (<5 ppm) refinery process heater burner being developed by Arthur D. Little and Callidus Technologies. Shown (from left): Neal Fornaciari (seated), Jason Yee, Peter Loftus, Lloyd Claytor (EER), and Peter Walsh (EER).

Rahn named OSA Fellow

Larry Rahn was recently awarded the status of Fellow of the Optical Society of America. This honor is reserved for no more than 10% of the membership who have served with distinction in the advancement of optics. Larry was cited for fundamental and applied contributions of high-resolution nonlinear optical spectroscopy to combustion diagnostics.



Tom Hunter completed his postdocotoral stay with Steve Rice and the supercritical water oxidation project in December. He has taken a permanent position at 3M Corporation in Minnesota. Pictured from left are Steve Rice, Tom Hunter, and Russ Hanush.

John Card (right) worked with Ken Marx (left) and Bill Ashurst (center) on postdoc research. John recently joined the research staff in the Department of Mechanical Engineering at Yale University. During his stay at the CRF, John first collaborated with Bill on curved diffusion flames, then worked with Ken to develop a diesel engine model using the KIVA computer code.

Mary Bui-Pham spent two years as a postdoctoral associate with Jim Miller, working on flammability limits and extinction limits in premixed flames, and one year with Bob Kee modeling diamond deposition in flames (see article, p. 3). She recently joined Lawrence Berkeley Laboratory.

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Isotope effects clarify reaction mechanisms

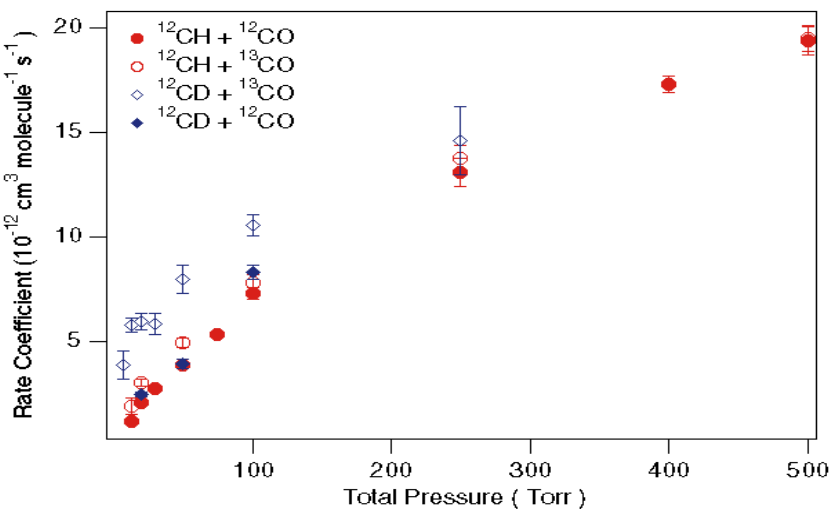
Craig Taatjes is using a flash photolysis/cw laser induced fluorescence (LIF) technique to measure the kinetics of the reaction between CH and CO. The CH radical is an important combustion species, and the reaction of CH with CO forms the HCCO radical, which is also a product in the reaction of $O[^3P]$ with C_2H_2. By comparing the rates of different isotopically substituted species, new information is acquired about the mechanism of the CH + CO reaction.

Measurements of rate coefficients for the various isotopic variants of the CH + CO reaction are shown in the figure. The reaction proceeds via a highly excited (~60 kcal/mol) $HCCO^*$ adduct:

$$\begin{array}{ccccc} {}^{12}CH + {}^{13}CO & \Leftrightarrow & H^{12}C^{13}CO^* & \Leftrightarrow & H^{13}C^{12}CO^* \Leftrightarrow {}^{13}CH + {}^{12}CO \\ & & \Downarrow M & & \Downarrow M \\ & & H^{12}C^{13}CO & & H^{13}C^{12}CO \end{array} \qquad (1)$$

The disappearance of ^{12}CH is monitored, so the difference between the measured rates for ^{12}CH with ^{13}CO and with ^{12}CO (where the two CH + CO pathways in (1) are indistinguishable) gives the rate for carbon atom exchange. The data show that the exchange is relatively facile, and that deuterium substitution significantly enhances the exchange rate, especially at low pressure.

The structure of the ground state of the HCCO radical is known. The reaction kinetics studies give information about the vibrationally excited $HCCO^*$ adduct. One question of interest is whether the oxiryl configuration of HCCO, where the two carbon atoms and the oxygen atom are linked in a three-membered ring, is accessible at these energies. Exchange of the two carbon atoms in HCCO could involve an oxiryl-like intermediate state.



Pressure dependence of the reaction-rate constant for isotopic variants of $^{12}CH + CO \rightarrow$ products at 298 K. The error bars are two standard deviations and include both systematic and random contributions.

The change in the exchange rate for ^{12}CD versus ^{12}CH is an important clue in uncovering the reaction pathway. The large inverse kinetic isotope effect reflects the competition between exchange and stabilization. The faster rate for the heavier species shows that the transition state for exchange is thermally accessible and that hydrogen transfer is not the reaction coordinate. This is consistent with an oxiryl intermediate where the C-C-O bending is the critical motion for exchange.

In future work, the isotope effects and the pressure and temperature dependencies for the CH + CO reaction will be used to evaluate theoretical estimates of possible transition-state geometries.

Pre-Symposium workshop

In collaboration with several researchers in the international combustion community, Rob Barlow is organizing an International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames to be held in Naples, Italy on July 26-27, preceding the Combustion Symposium. The objectives of the workshop will be to identify a set of well documented experimental flames and to define guidelines for collaborative comparisons of model predictions of these flames. Workshop information is available on the Web (http//www.ca.sandia.gov/tdf/Workshop) or by phone at 510/294-2688.

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