SAND2011-4438P

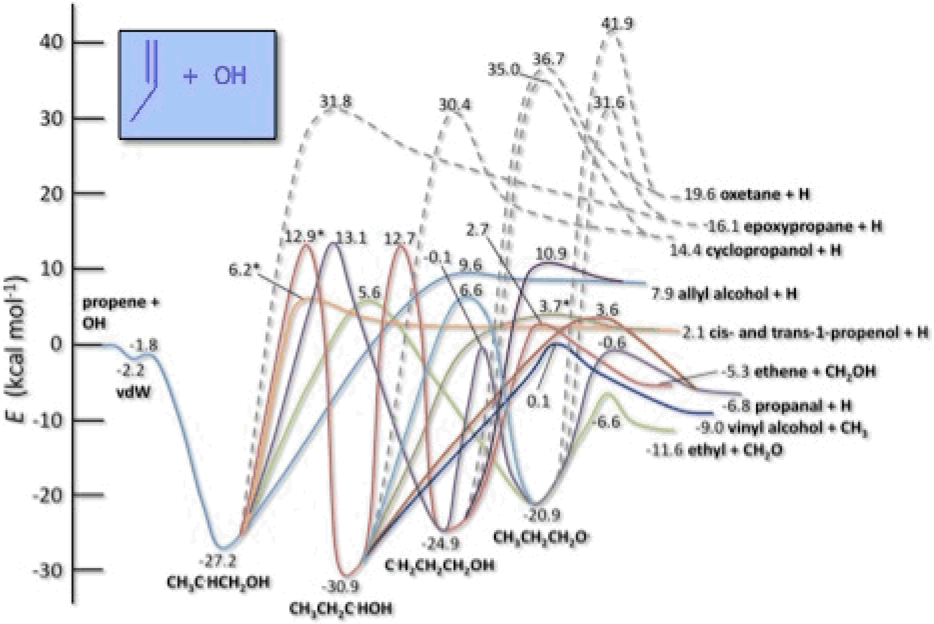
COMBUSTION CHEMISTRY

The Combustion Chemistry Program, under the principal sponsorship of the Department of Energy's Office of Basic Energy Sciences, seeks to reveal the key chemical processes that underlie the complex mechanisms of combustion. The program emphasizes determination of the rates and mechanisms of chemical reactions, characterization of molecular structure and energetics, and development of full descriptions of chemical composition and evolution of combustion systems.

[Graphics: TBD]

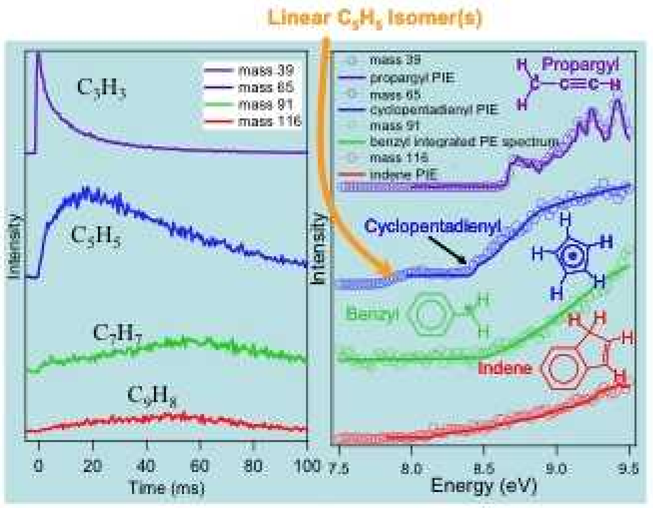
THEORY AND MODELING

In the Combustion Chemistry Program at the CRF, the fundamental chemistry of combustion is studied using a wide variety of theoretical methods including high-level quantum chemistry, transition state theory, master equation, and trajectory calculations. One goal of this work is the development and validation of theoretical strategies for obtaining quantitative rate coefficients for elementary reactions and for elucidating reaction mechanisms. An accurate and complete first principles theoretical description is the goal for small to moderate sized systems, and more approximate methods are being developed for larger and more complex systems. This program benefits considerably from interactions with experimentalists at the CRF and elsewhere who provide data with which to test the theoretical methods. In turn, theoretical insights gained using the validated methods are useful for interpreting data obtained under less straightforward experimental conditions. The resulting combined theoretical/experimental rate coefficients are more accurate and obtained over a broader range of environmental conditions that would be obtained via theory or experiment alone.



COMBUSTION KINETICS

The chemistry that drives combustion is a highly complicated web of reactions. To describe the combustion of a single fuel compound, say iso-octane, in full chemical detail requires hundreds of species that participate in thousands of individual chemical reactions. Each of these reactions in turn has a detailed description in terms of fundamental physical principles. The combustion kinetics research at the CRF is aimed at discovering and characterizing important elementary reactions at this most fundamental level.



[at this point, you could put a "read more" link to expand to the following]

Which elementary reactions are important for understanding and controlling combustion? When nineteenth-century inventors were creating the first internal combustion engines, chemists didn't even have the fundamental knowledge that combustion is governed by chain reactions of radicals. Diesel and Otto didn't need to know any chemistry beyond fuel + air = heat! However, in the intervening years the operation of engines has become far more sophisticated, and the demands on engine performance have vastly increased. Important modern engine design considerations such as minimizing pollutant formation or controlling autoignition, require models that can reliably predict chemical species that occur at sub-part-per-million levels in the combusting mixture. The two subjects of pollutant formation and autoignition chemistry are areas where the details of the chemistry make a difference in predicting the performance of real devices, and much of the recent chemical kinetics research at the CRF has focused on reactions that are relevant to one of these topics.

Even within these two areas the challenges for detailed combustion chemistry are vast. Rate coefficients and branching fractions for individual reactions must be known over wide ranges of temperature and pressure – far wider than is practical to experimentally investigate. Moreover, when one considers that petroleum distillates like gasoline may already include thousands of chemically distinct fuel compounds one clearly sees that we can't simply measure every individual reaction in detail, or even every important reaction! Fundamental chemistry research can make a timely contribution to combustion modeling, and hence to the design of future clean and efficient combustion technologies, by defining the underlying physical principles that will allow confident prediction of chemical reactions under unexplored conditions.

- **Chemistry of particulate formation**
    - Controlling the production of soot and particulates is one of the most stubborn problems in current combustion science. The molecular weight growth process that culminates in formation of soot from aliphatic fuels hinges critically on the details of reactions of small unsaturated hydrocarbon radicals – especially resonance-stabilized radicals. The formation of the first and second aromatic rings are particularly important steps in determining the production of soot. The iconic example is the reaction of two propargyl radicals, C3H3, to form isomers of C6H6. This reaction is one of the most important means for introducing the first aromatic ring, for the most stable C6H6 isomer is benzene. However, other C6H6 isomers are also formed in the reaction, and are more readily oxidized and more benign for particulate formation. Understanding the isomeric product formation in this and similar

reactions as a function of pressure and temperature is crucially important for modeling the initial steps of molecular weight growth.

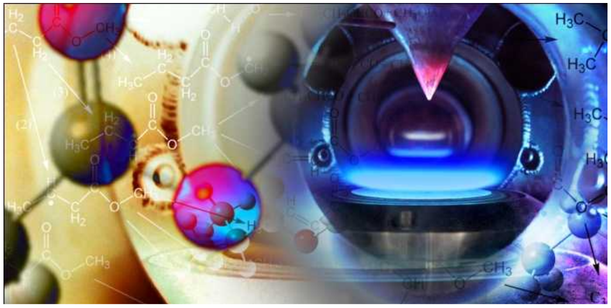
- **Chemistry of autoignition**
    - [text under development]
- **Chemistry at high pressures**
    - [text under development]

FLAME CHEMISTRY

Research in the Flame Chemistry and Diagnostics Laboratory focuses on developing a detailed understanding of the chemistry of combustion through a coordinated program of diagnostic development, experimental study of simple flames, and flame chemistry modeling. The goal is to provide a rigorous basis for the elucidation of chemical mechanisms of combustion. The experimental program concentrates on the development and application of state-of-the-art diagnostics based on both laser and mass spectrometer techniques for measuring the concentrations of key combustion chemical species. These diagnostics are used to study simple, laboratory-based model flames.

Recent work has focused on a newly developed mass spectrometer, which allows isomer-specific detection of combustion intermediates. VUV photoionization ionization molecular beam mass spectrometry has been demonstrated to be an exceptional method for determining the chemical compositions of complex flames. We apply this tool to study a variety of different flames using hydrocarbon fuels representing the major classes of chemicals appearing in modern fuel blends: alkanes, alkenes, alkynes, cyclic hydrocarbons, and aromatics. Our latest efforts include investigations of the combustion chemistry of oxygenated compounds likely to be found in the next generation of biomass-derived alternative fuels, e.g. alcohols, ethers, and esters.

[Graphics: "LowPFlameArt.jpg"]’



CHEMICAL DYNAMICS

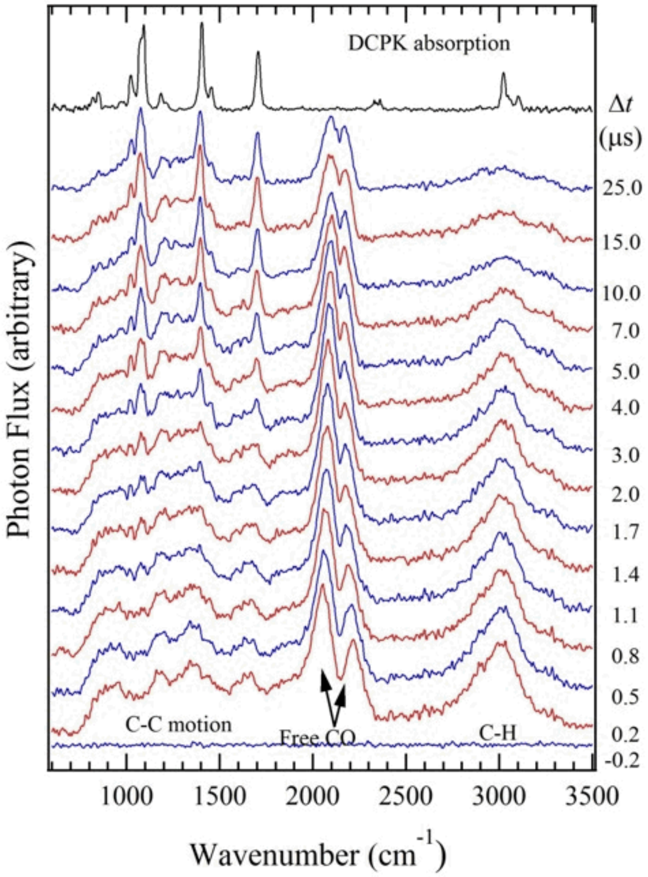
Scattering Dynamics
[text under development]

Photodissociation Dynamics

Photodissociation may occur when a molecule absorbs a photon whose energy is greater than the bond strength of one or more bonds in the molecule. The energy deposited by the photon can cause the molecule to fragment, and in so doing, reveal many details about the forces that bind the atoms of the molecule together. Photodissociation dynamics experiments provide a direct means of studying the forces that act on a molecule during bond breaking. These experiments are a well-defined method for studying the fundamental nature of chemical reactions, in which we try to determine:

- What are the nascent products?
- Is there more than one product channel participating?
- What is the bond strength, or heat of reaction, for each product channel?
- How quickly does the bond break?
- How is the excess energy distributed among the products?
- Can we determine the photodissociation mechanism from this information?

At the Combustion Research Facility we use a variety of techniques to study the dynamics of photodissociation. One technique, ion imaging, was invented at the CRF, and has since become a ubiquitous technique for understanding not only photodissociation, but also bimolecular reactions and the characteristics of ultrafast lasers. We also use time-resolved Fourier transform spectroscopy to study the rotational and vibration state distributions of photodissociation products in real time as they are created and subsequently cooled via collisions.



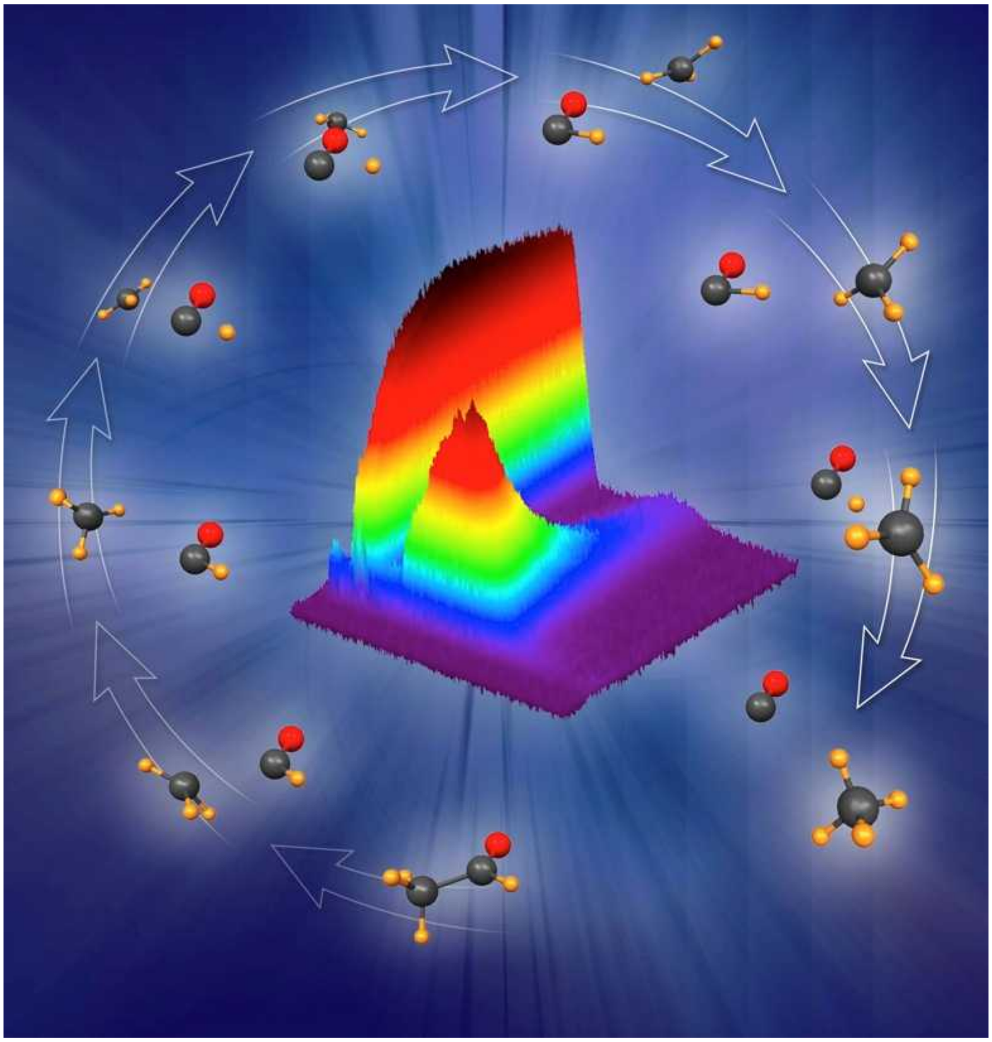
Time-resolved FTIR emission spectrum of dicyclopropyl ketone after photodissociation with a 193 nm photon. Analysis of the spectra show that free CO is formed, which the C3H5 radical fragments isomerizes from the cyclic cyclopropyl radical to the resonance stabilized allyl radical.]

Roaming Molecule Dynamics

The recent discovery of roaming atom dynamics in the photodissociation of formaldehyde (Arthur Suits, Joel Bowman, and co-workers) led to a study at the CRF to determine whether roaming molecule reactions of neutrals might exist. In the photodissociation of acetaldehyde (CH3-CHO), the main process following UV excitation is cleavage of the CC bond:

CH3CHO → CH3 + HCO

The experimental study at the CRF, together with molecular dynamics simulations from Emory University, uncovered another process, in which the CH3 and HCO fragments have insufficient energy to separate completely. In this case the two radicals "roam" around each other until the reach an appropriate configuration in which the CH3 radical can abstract the H atom from HCO, forming CH4 + CO. The spectra and calculations provide evidence that the newly formed CH4 molecule has an exceptional amount of vibrational energy, up to 95% of the C-H bond strength in methane.



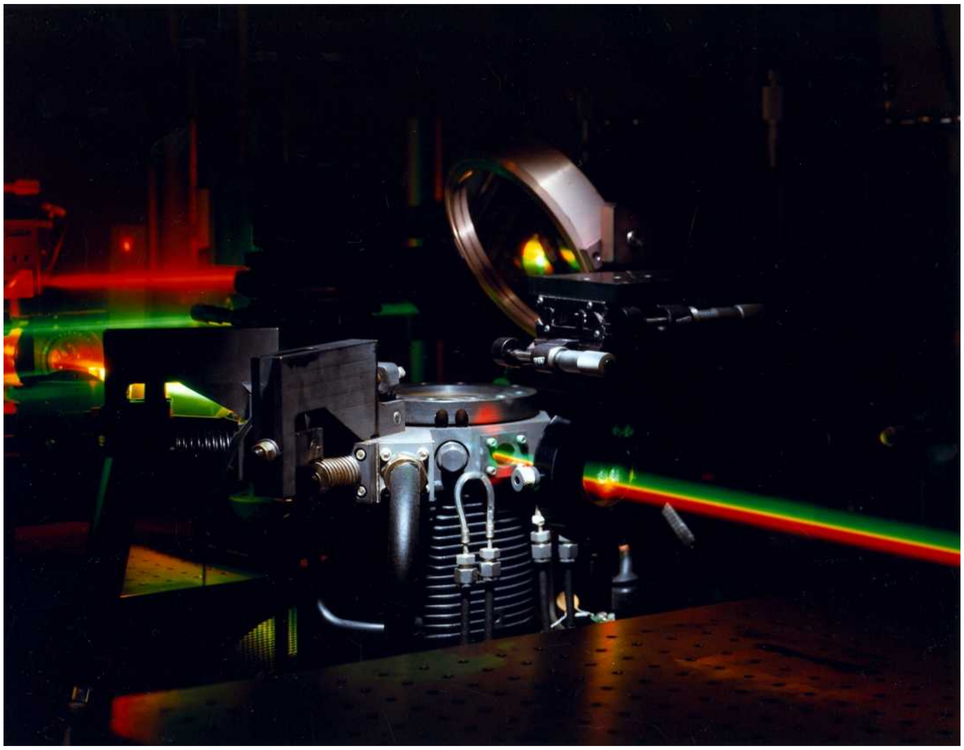
Time-resolved Fourier transform infrared spectra of acetaldehyde photodissociation at 308 nm are surrounded by snapshots from a quasi-classical trajectory calculation of the dissociation that demonstrations the roaming molecule mechanism.]

DIAGNOSTICS

The development and use of laser-based diagnostics is the hallmark of the CRF. Laser-based technologies are the cornerstone upon which the CRF was founded approximately 30 years ago, and to this day, it maintains an enduring commitment to nurturing staff expertise in this area. In addition, the CRF has one of the most comprehensive collections of state-of-the-art and custom-built lasers used for combustionstudies in the world.

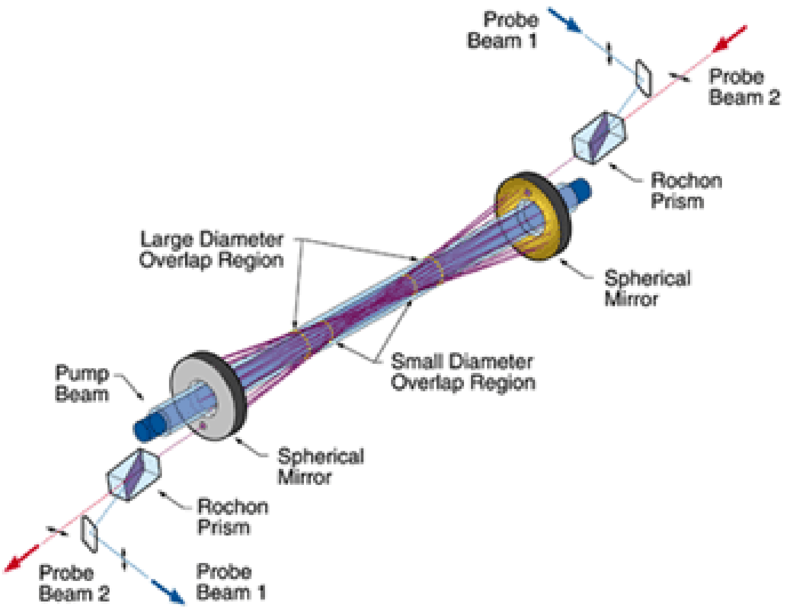
Laser-based diagnostics are a necessary tool for the study of combustion. They allow researchers to nonintrusively study and measure combustion events in a wide variety of environments, such as inside engines and burners.

The CRF's strengths in laser-based diagnostics have extended beyond the realm of combustion studies. This expertise is fundamental to ongoing efforts in remote sensing, explosives and chemical- and biological-warfare-agent detection, and single-molecule studies of biological systems.



LONG-PATH ABSORPTION

Sensitive spectroscopic methods are required to probe chemical kinetics, as in general the reactive radical species of interest are present only at low concentration. Fluorescence methods are exquisitely sensitive; however many important radicals, for example HO_2, do not fluoresce. Moreover, determination of absolute concentrations from fluorescence measurements normally requires extensive calibration. For these reasons sensitive absorption techniques have been used in the Laser Chemistry Laboratory (PI: Craig A. Taatjes). As shown in the figure, a Herriott-type multi-pass cell is used to send a probe beam many times through a long flow reactor. The multipass cell is combined with either simple differential absorption or two-tone frequency modulation (FM) absorption spectroscopy to further enhance the sensitivity. The overlap between the probe laser beams and the large diameter photolysis beam, which triggers the chemical reactions, is confined to the middle region of the reactor. This probe region is specifically designed to be precisely temperature controllable from room temperature to over 800 Kelvin. Multiple probe laser beams at different wavelengths are coupled into the cell to monitor several species simultaneously. For example, this setup has recently been applied to measure absolute concentrations of both HO_2 (in the near infrared) and OH (in the mid infrared) formed in laser-initiated biofuel oxidation reactions. These two radicals are the most important radical products in the initial steps leading to autoignition, and knowing their production rates is key to understanding these important chemical steps.



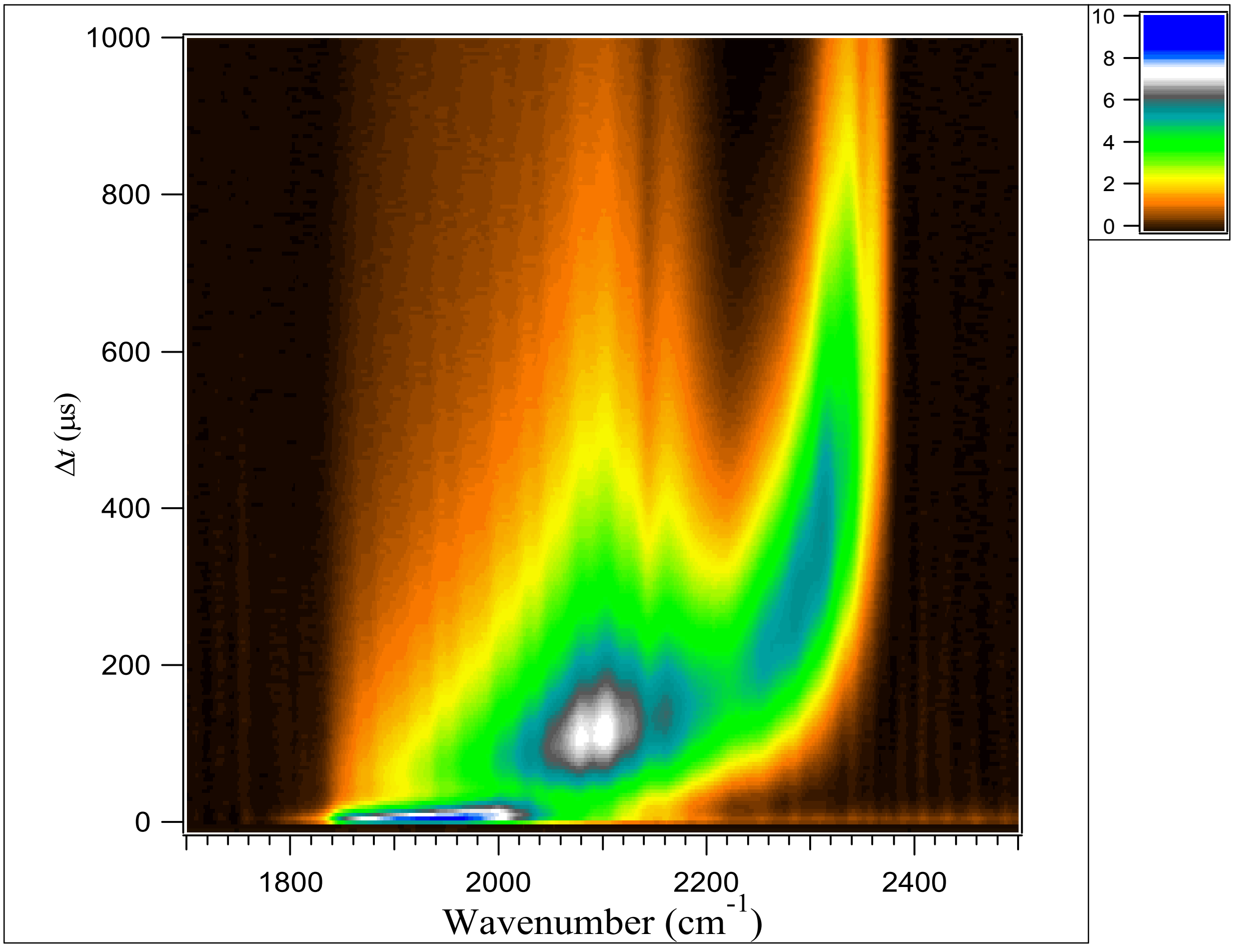
GAS-PHASE DIAGNOSTICS

The goal of the Laser Diagnostics Research Program at the CRF is to develop and characterize optical laser techniques that enable the detection and quantification of important gas-phase species, temperature, and particulate matter in temporally and spatially resolved measurements. A major component of the program is the investigation of the fundamental physical and chemical processes that directly affect quantitative application of these techniques to complex combustion systems. Ultimately this knowledge enables development of new approaches and comprehensive models for the diagnostic techniques. These models, then, serve as the interface between diagnostic research and experimental combustion research. The diagnostic models enable experimentalists to optimally configure their experiment and to extract meaningful data from their measurements, which facilitates the fruitful interaction between experimental and theoretical combustion research.

Time-resolved FTIR:

Combustion chemistry involves many exothermic reactions, which produce hot molecules. For these vibrationally or electronically excited molecules, emission-based time-resolved Fourier transform spectroscopy (TR-FTS) can be a fruitful way to study the reaction rate, product state distribution, and branching ratios of elementary combustion reactions. Time-resolved Fourier transform spectroscopy (TR-FTS) yields measurements of thermal rate coefficients as a function of temperature and pressure, and its inherently multiplexed nature makes it possible to simultaneously measure product branching ratios, internal energy distributions, energy transfer, and spectroscopy of radical intermediates. Together with total rate coefficients, this additional information provides further constraints upon and insights into the potential energy surfaces that control chemical reactivity.

While there has been great progress in gas phase emission-based TR-FTS, David Osborn is also developing absorption techniques because they are more general than emission methods and are not complicated by fluorescence lifetime effects or predissociation. Another thrust of this program is toward kinetic measurements of larger molecules. The development of absorption-based TR-FTS in the mid-infrared "fingerprint" region will enable reactivity studies of larger hydrocarbons (C_3—C_6) found in practical fuels.



Time-resolved infrared emission of the HCCO + O2 reaction. The sharp fin of emission near time zero is from the reactant HCCO. Emission of the products CO and CO2 grows (due to chemical production of these molecules) and then decays (due to vibrational energy transfer) as a function of time. The much faster rate of vibrational cooling of CO2 vs. CO is graphically demonstrated by the time-resolved blue-shifting emission leading to the band origins of the CO emission (2,143 cm-1) and CO2 emission (2,349 cm-1).

LASER-INDUCED FLUORESCENCE

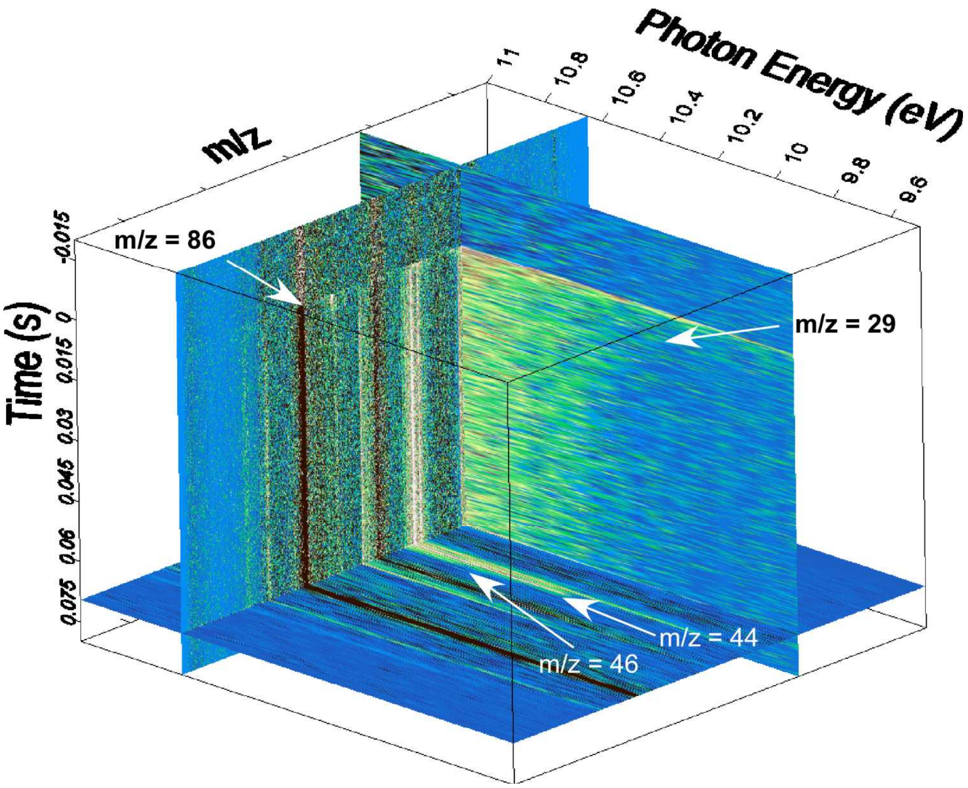
Laser-induced fluorescence (LIF) is a powerful technique that is routinely used in combustion research laboratories for sensitive, spatially resolved detection of minor species. The quantitative application of the technique in flames, however, can be precluded by a lack of a predictive understanding of the signal generation process in these complex environments. For example, changes in collisional conditions in the flame affect the laser-molecule interaction by modifying spectral line shapes and population distributions during the laser pulse. Laser-induced fluorescence measurements are also particularly sensitive to collisional electronic energy transfer (quenching) rates, which can dramatically vary with changes in the collisional conditions, resulting in a strong dependence of the fluorescence yield on local conditions. Consequently, quantitative measurements require accounting for dependence of the laser diagnostic signal on changes in collisional conditions in the flame. Furthermore, the intense laser pulses used to generate measurable fluorescence signals can cause photochemical interferences. Scientists at the CRF study these collisional and photochemical processes that are relevant to fluorescence-based detection of important radical species.

NONLINEAR LASER SPECTROCSCOPY

Nonlinear laser spectroscopy research at the CRF focuses on the development of innovative laser-based optical wave-mixing strategies for the detection and quantification of important combustion radicals, major species concentrations, and temperature. Emphasis is placed on techniques which exhibit high spatial and temporal resolution. The fundamental physical and chemical processes that directly affect quantitative application of these techniques are explored. These investigations include the study of fundamental spectroscopy, energy transfer, and photochemical processes. This aspect of the research is essential to the correct interpretation of diagnostic signals, enabling reliable comparisons of experimental data and detailed combustion models. These investigations use custom-built tunable picosecond (ps) lasers, which enable efficient nonlinear excitation, provide high temporal resolution for pump/probe studies of collisional processes, and are amenable to detailed physical models of laser-molecule interactions. Nonlinear optical techniques investigated in this program include time-resolved coherent anti-Stokes Raman spectroscopy (CARS), degenerate four-wave mixing (DFWM), coherent 1D and 2D imaging techniques, two-color four-wave mixing (TC-FWM) and polarization spectroscopy (PS).

PHOTOIONIZATION MASS SPECTROSCOPY

CRF researchers have pioneered the use of multiplexed mass spectrometry – detection of many masses simultaneously – in combination with photoionization by tunable synchrotron radiation – which provides isomeric specificity through the photoionization spectroscopy – as a powerful tool for investigating elementary reaction kinetics and the chemistry of low-pressure flames. This method provides multidimensional sets of data as a function of mass, photon energy, and the physical dimension of the system, e.g., distance from the burner or time after reaction initiation, as depicted in Figure #!.



The data can be quantitatively correlated and integrated along any of the dimensions to compare to traditional measurements such as time or distance profiles of individual chemical species or photoionization spectra for isomeric analysis.

The technique has two substantial advantages for analysis of complex chemical systems such as flames or multiple-channel chemical reactions. First, the simultaneous detection of multiple species gives a time advantage and also “automatically” detects even unexpected chemical intermediates. Second, and perhaps more valuably, the easily tunable photon energy allows determination of isomeric composition through the photoionization spectrum. This can be made quantitative through comparison to reference spectra, as shown in the figure #*^below, where the isomers at mass @%@% are determined in two low pressure flames.

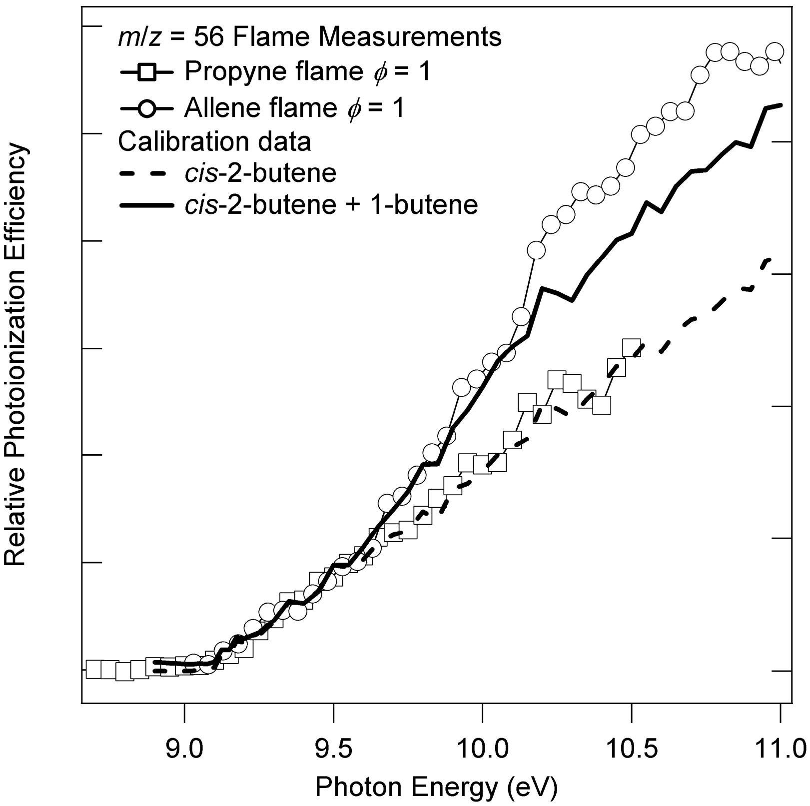
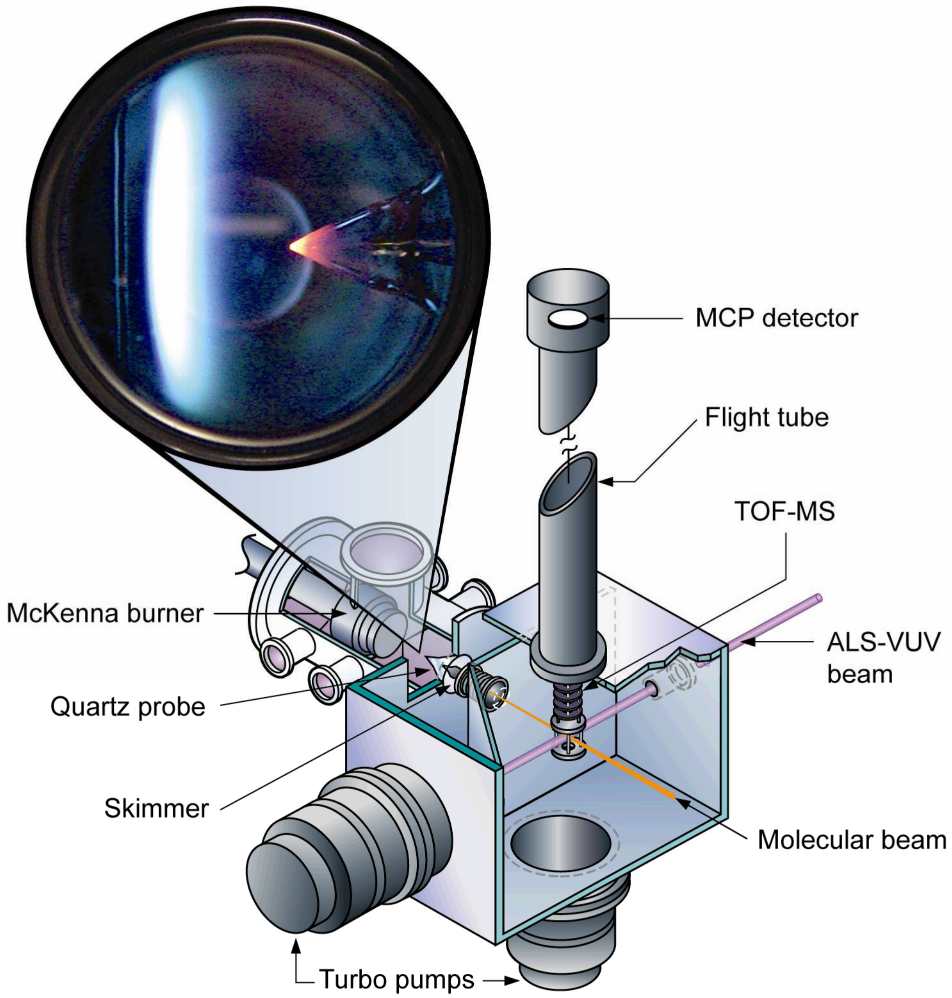


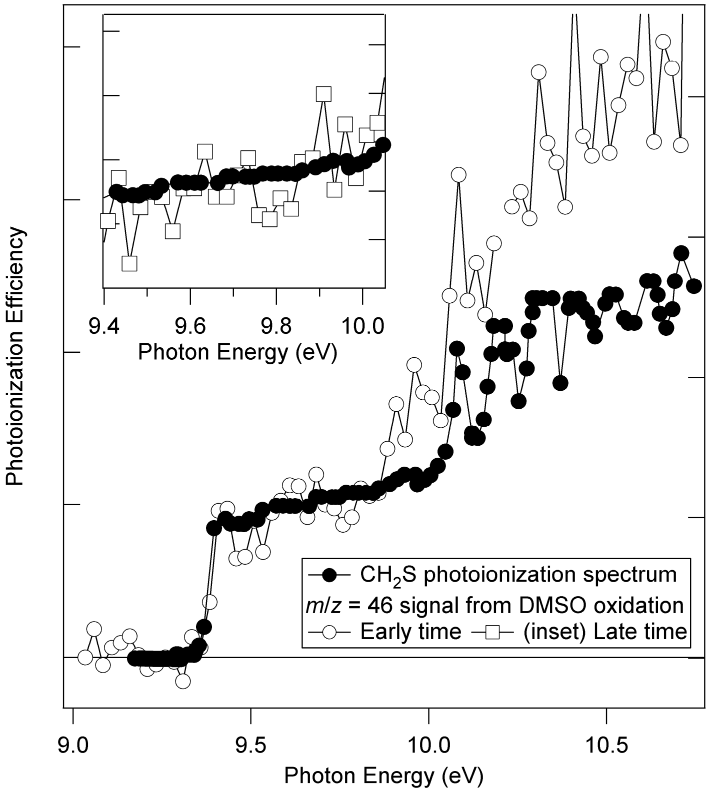
Figure #*^

Flame examples (not described in other sections)—enols? isomeric fuels?

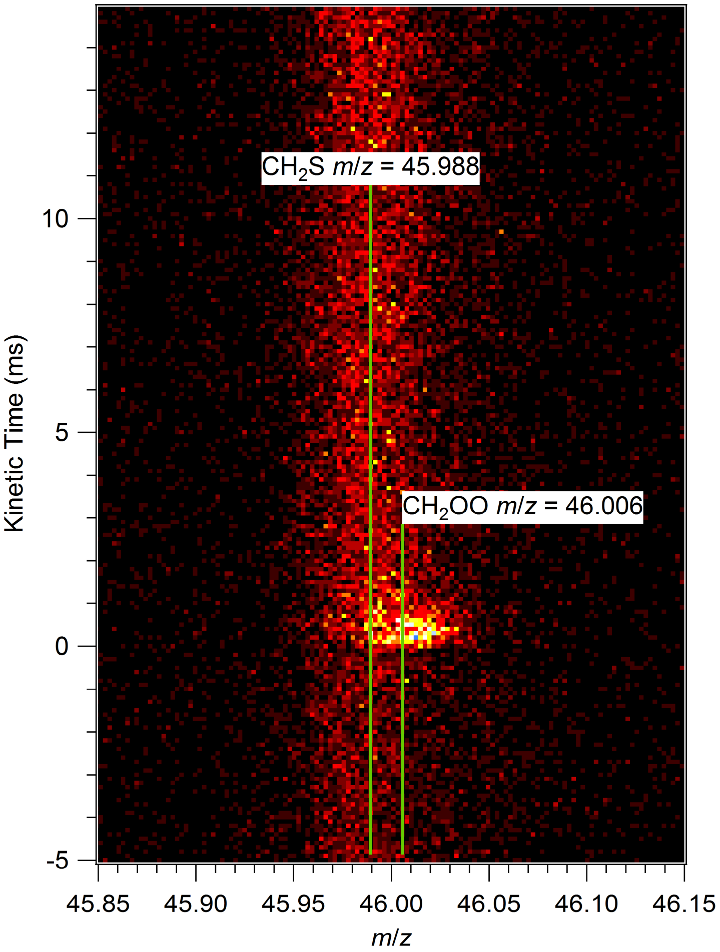

MCP detector
Flight tube
TOF-MS
McKenna burner
ALS-VUV beam
Quartz probe
Skimmer
Molecular beam
Turbo pumps

Kinetics The CRF multiplexed chemical kinetics reactor extends the laser-photolysis / photoionization mass spectrometry method pioneered by Gutman to incorporate multiple-mass detection and synchrotron photoionization. In these experiments, as schematically depicted below, a chemical reaction is initiated by laser photolysis in a quartz slow-flow reactor. Molecules are continuously sampled from an orifice in the side of the reactor and are ionized by the synchrotron radiation. The ions are subsequently mass analyzed. In the first configuration of this apparatus, shown in the figure, this analysis was accomplished by a dual-focusing (Mattauch-Herzog) sector instrument. Recently the detection has been upgraded with an orthogonal acceleration time-of-flight spectrometer, which has superior mass resolution.

Isomeric resolution enables discrimination of different isomers in reactants or determination of isomer profiled in reaction products. In some cases novel isomeric species can be detected by photoionization that are difficult to measure by other means. One prominent example is formaldehyde oxide, the simplest example of a Criegee intermediate, critical steps in the ozonolysis of alkenes that had never been directly seen in the gas phase before its detection in dimethyl sulfoxide (DMSO) oxidation by CRF researchers in collaboration with atmospheric chemists from University of Bristol and University of Manchester. In these experiments, measured with the sector instrument, the CH_2OO isomer was separated spectroscopically from the substantial CH_2S side product, which has very nearly the same mass.



With the implementation of the orthogonal acceleration mass spectrometer, however, the mass resolution is just sufficient to resolve these species in mass:



Multiplexed detection has substantial advantages in the measurement of kinetics, not only because of the time advantages in looking at all of the expected species simultaneously, but because the detection of unexpected species can provide new insights into reaction mechanisms. One example is given by the self-reaction of vinyl radicals. Literature values for the rate coefficient of this reaction were surprisingly high; reinvestigation by both laser and mass spectrometric probing showed a substantially lower rate coefficient (see Figure @#$).

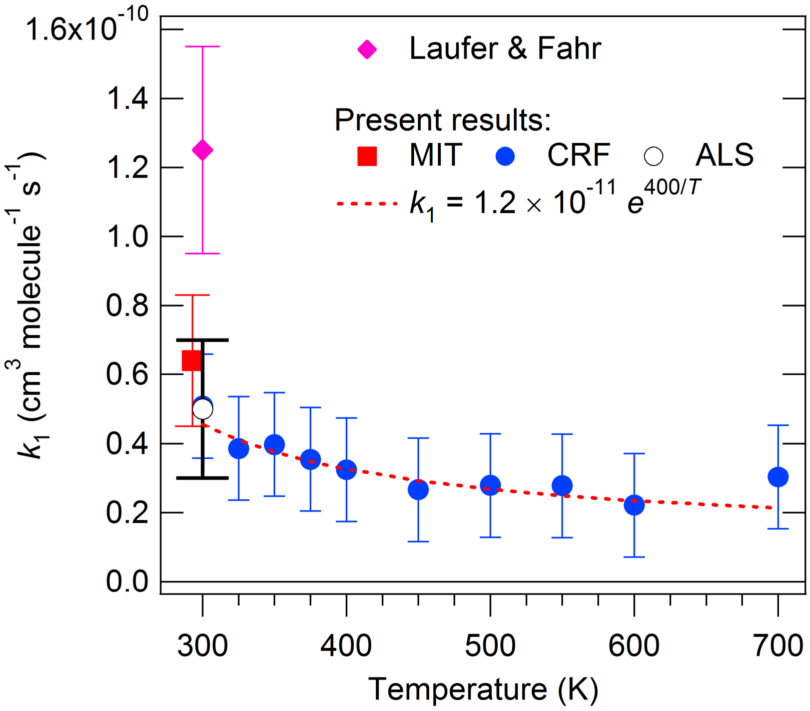


Figure @#$

The source of this discrepancy is made clear by the resolution of all of the products of the reaction. Determination of the second order rate coefficient requires knowledge of the absolute radical concentration. In the literature reports the vinyl concentration was derived from measured concentrations of butadiene product, in conjunction with a branching fraction for butadiene production that assumed that recombination (to form butadiene) and disproportionation (to form ethene and acetylene) were the sole product channels. However, measurement using multiplexed photoionization mass spectrometry shows that the unexpected radical products methyl (visible at *m*/*z* = 15 in the figure @$^ below) and propargyl (*m*/*z* = 39) are in fact substantial.

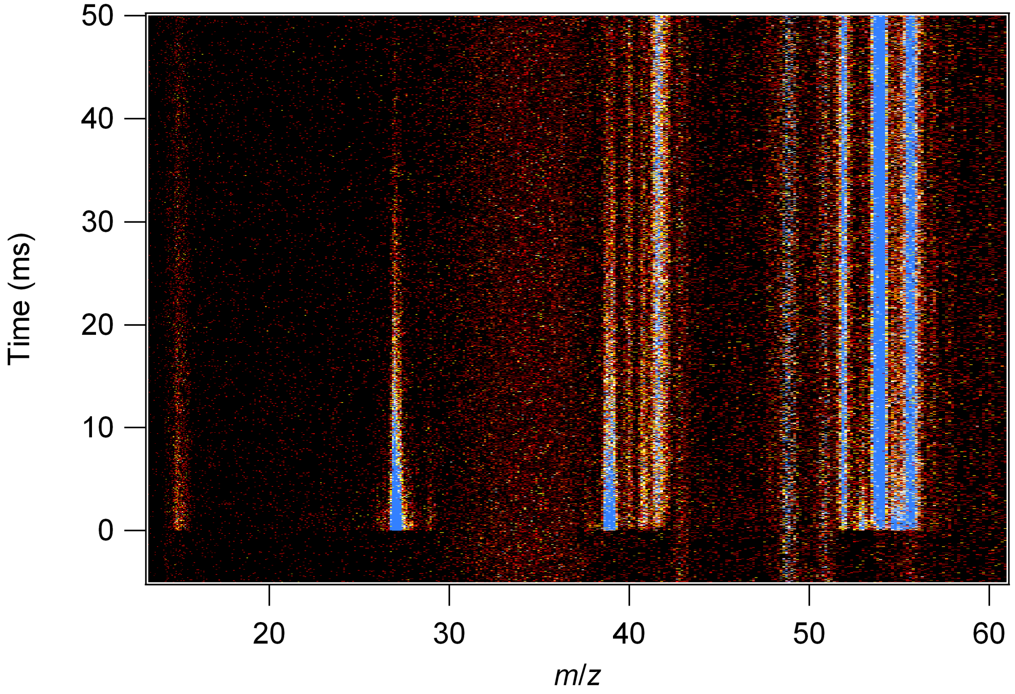


Figure @$^

In fact the data show that the branching to methyl + propargyl is ~ 50% at 300 K. Including this channel in the interpretation of the literature experiments would therefore increase the derived vinyl radical concentration , and hence reduce the rate coefficient, by approximately a factor of two, bringing them into agreement with the new absolute measurements.

DIAGNOSTICS FOR GREENHOUSE GAS SOURCE ATTRIBUTION AND CARBON-CYCLE SCIENCE

Anthropogenic greenhouse gas (GHG) emissions are predominantly attributable to combustion. Fossil-fuel combustion is responsible for 80% of anthropogenic GHG emissions and 98% of anthropogenic CO_2 emissions. Approximately 60% of anthropogenic CO_2 emissions are from the use of transportation fuels. In order to address the need for methods to identify and characterize GHG emission sources, we have developed and deployed a mobile laboratory facility for measuring GHGs and co-emitted tracers of their anthropogenic and biogenic sources. Our mobile facility includes two 30-ft trucks, a temperature-controlled trailer, and a suite of in situ and remote sensing instruments. The payload is designed for developing methodologies for climate treaty verification, municipal GHG emissions mitigation policy support, and carbon-cycle science and includes the following:

- a high-precision, fast CO_2 isotope analyzer for measuring abundances and fluxes of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, and H_2O via multi-pass absorption of emission from a quantum-cascade laser near 4.32 µm (Aerodyne Research),
- a gas analyzer for measuring CO_2, CH_4, and H_2O using cavity-ringdown spectrometry (Picarro)
- a high-sensitivity proton-transfer reaction mass spectrometer for measuring volatile organic compounds (VOCs) (Ionicon Analytik Gesellschaft)
- a drum sampler for elemental particle composition (Streetman Precision Engineering)
- a condensation particle counter (TSI)

- an AirCore system for sampling aloft (Restek)
- a UV-absorption instrument for measuring O_3 (Ecotech)
- an filter-based IR absorption instrument for measuring CO (Ecotech)
- a chemiluminescence instrument for measuring NOx (Ecotech)
- a UV –fluorescence instrument for measuring SO_2 (Ecotech)
- a non-dispersive infrared absorption CO_2 analyzer (LI-COR)
- a three-D sonic anemometer for wind speed and direction (Gill)
- a thermal sensor for soil fluxes (Hukseflux)
- soil temperature probes and temperature and relative humidity sensors (Campbell Scientific)
- a solar-viewing Fourier transform infrared (1-15 µm) spectrometer for multiple species (ABB-Bomem)
- a multi-wavelength robotic sun-photometer for aerosols (AERONET/CIMEL)
- a total sky imager for clouds (Yankee Environmental Systems)
- a Lidar ceilometer for boundary layer height (Vaisala)

Additional instruments owned by collaborating labs include

- an automated flask-sampling system to collect air samples for ^{14}C analysis (NOAA)[1]
- a gas analyzer for measuring CO_2, CH_4, and H_2O using cavity-ringdown spectrometry (Picarro)[1]
- a gas analyzer for measuring CO_2, H_2O, and δ^{13}C-CO_2 using cavity-ringdown spectrometry (Picarro)[1]
- a photoacoustic aerosol spectrometer (Droplet Measurement Technology)[2]
- a water (vapor and liquid) stable O, H isotope analyzer using cavity-ringdown spectrometery (Piacarro)[2]

[1] Lawrence Livermore National Laboratory; [2] Los Alamos National Laboratory

Measurements from these instruments are coupled with inverse modeling and uncertainty quantification techniques to identify and characterize anthropogenic and biogenic GHG sources and sinks. We are also developing new instruments and augmenting existing equipment to expand technology for tracer measurements.

PARTICLE DIAGNOSTICS

Combustion processes often produce solid carbon particles, i.e., soot. These particles may be oxidized to form gas-phase species or released into the exhaust stream, where they can be coated with liquid coatings. These coatings can be comprised of any of a number of components, including unburned fuel, lube oil, sulfuric acid, water, and other combustion by-products. The Particle Diagnostics research program focuses on the development of optical diagnostics for soot particles in combustion environments and combustion exhaust plumes. The goal of this work is in situ measurements of volume fraction, size, composition, and morphology of combustion-generated particles with fast time response and high sensitivity. Measurement techniques are targeted for studies of soot formation and evolution and must be versatile enough to probe particles throughout their entire life cycle. Techniques are developed for detection and characterization of particles in combustion environments from incipient particles that are 2-20 nm in diameter and composed of condensed large organic species to mature soot particles composed of aggregates of carbonaceous primary particles resembling polycrystalline graphite. Diagnostics are also developed for characterization of inhomogeneous exhaust particles.

- Interfacial Diagnostics