

Chamber Investigation of Radical Budget and Oxidant Photochemistry for Improved Air Pollution Inventories in the South Coast Air Basin

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August 23, 2002

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Abstract

The chemistry of free radical species plays a central role in air pollution photochemistry for both ozone (O_3) and fine particulates ($PM_{2.5}$). The radical species of interest include the hydroxyl (OH), the hydroperoxyl (HO_2), and organic peroxy (RO_2); the family of radical species is defined as $HO_x = OH + HO_2 + RO_2$. For urban conditions, the concentrations of O_3 and $PM_{2.5}$ and their responsiveness to precursor control strategies are determined by the sources, lifetime and sinks of free radicals. Production of O_3 and $PM_{2.5}$ is initiated when the OH radical attacks volatile organic compounds (VOC) to initiate a sequence of chemical reactions that produce secondary air pollutants including O_3 , nitric acid (HNO_3), and sulfuric acid (H_2SO_4). Subsequently, several of these gas-phase species are converted to $PM_{2.5}$ in the form of aerosol nitrates, sulfates and secondary organic aerosols.

Because the radical species initiate the production of secondary air pollutants, it is essential to represent accurately the chemistry of these species in the photochemical mechanisms and air quality models that are used to design control strategies for O_3 and fine PM. Moreover, several observation-based methods (OBMs) have been proposed in which ambient data are used to determine whether O_3 and $PM_{2.5}$ are primarily sensitive to VOC or NO_x . The theoretical basis for these OBMs is based on a theoretical analysis of the radical species, and an accurate characterization of the radical budgets is required to confidently use the ambient data to identify VOC sensitive or NO_x sensitive conditions for pollutant control.

Radical species are highly reactive and exist at low concentrations in ambient air. Mixing ratios are typically less than 50 ppt for HO_2 and less than 0.5 ppt for OH, making them very difficult to measure. As a result, the budgets of OH and HO_2 are poorly understood, and there is a critical need for laboratory studies of HO_x photochemistry. This proposed project will address uncertainty in oxidant photochemistry and radical budgets through construction and operation of a laser-induced fluorescence (LIF) instrument for measuring concentrations of OH and HO_2 and a chemical amplifier (CA) instrument for measuring RO_2 during VOC- NO_x irradiation experiments in a new, state-of-the-art chamber facility at the University of California at Riverside. The LIF and CA instruments will be used in experiments designed to elucidate the photochemistry of HO_x radicals for a range of VOC, NO_x , and O_3 conditions representative of ambient air in southern CA. The project will also support subsequent analysis of experimental results and development of improved photochemical mechanisms both for modeling the chamber experiments and for use in urban to regional scale photochemical air quality models. This will provide more accurate predictions of formation of O_3 and fine particulates and will assist in the development of optimal emissions reductions strategies to meet O_3 and fine particulate air quality goals.

The total amount requested in this proposal is \$470,624. Approximately \$300,000 will cover the costs of constructing, evaluating, and utilizing the LIF for measuring OH and HO_2 . Funding of approximately \$171,000 will support construction and testing of the CA instrument. Significant co-funding is coming from our EPA project to develop and characterize the new state-of-the-art chamber facility at UCR, and from the California Air Resources Board to conduct experiments for low NO_x mechanism evaluation and characterizing ozone formation potentials of architectural coatings. These programs will cover most of the costs of conducting the experiments in which these radical measurements will be made.

1. Technical Proposal

A. Objectives

The goal of this project is to build a laser-induced fluorescence (LIF) instrument and a chemical amplifier (CA) instrument for measuring OH, HO₂, and RO₂ and to operate these instrument in VOC-NO_x irradiation experiments in a new environmental chamber facility at UC Riverside. The instruments will be operated in a set of chamber experiments designed to characterize the budgets of OH, HO₂ and RO₂ for a range of VOC and NO_x concentrations that are representative of conditions ranging from rural to urban, and for conditions ranging from the relatively low VOC/NO_x ratios in Los Angeles to the somewhat higher VOC/NO_x ratios typical of other polluted urban areas such as Atlanta and Houston. The results of these experiments will be used to test and improve photochemical mechanisms as follows:

First, measurements of OH and HO₂ will provide a much more complete description of the photochemistry in the chamber experiment, and this provides a much more rigorous test of the photochemical mechanisms that are developed using these chamber experiments. Results of the chamber experiments will be used in this project to compare the measured versus modeled ratios of species such as HO₂/OH, NO₂/OH and HO₂/NO, and this will provide an extremely rigorous test for assessing whether current photochemical mechanisms accurately represent the photochemistry.

Second, several O₃ sensitivity indicators have been proposed that would distinguish air masses in which O₃ production is primarily sensitive to reductions in either VOC or NO_x. These indicators have been developed based on analyses of steady-state radical budgets (Sillman, 1995; Kleinman et al., 1997) or on an analysis of radical propagation efficiency (Tonnesen and Dennis, 2000a,b). To date, O₃ sensitivity indicators have only been evaluated in model simulations; there has been no empirical evaluation of the indicator concept. In analyzing radical propagation efficiency, Tonnesen and Dennis (2000a) found that the concentration of HO₂ was a robust indicator of O_x production sensitivity, and that this formed the basis for the usefulness of several of the other proposed indicators. The chamber experiments employed here will be used to test the robustness of HO₂ as an indicator, thereby testing the theory on which the indicators are based. If the indicator concept is shown to be valid, indicators of O₃ sensitivity would be of great use both for evaluating the ability of chemical mechanisms to correctly simulate O₃ sensitivity to changes in precursor emissions, and for directly assessing the O₃ sensitivity to changes in precursors using ambient data.

Third, a major source of uncertainty in chamber experiments is the production of radicals or radical precursors from heterogeneous chemistry on chamber walls. Chamber radical sources can be quantified in chamber characterization experiments, and wall effects can be minimized by chamber design and treatment. Nevertheless, wall effects continue to be an area of concern, and direct measurements of OH and HO₂ in chamber characterization experiments would significantly help quantify chamber radicals sources and would increase the usefulness of subsequent chamber experiments for mechanism development and evaluation.

Finally, measurements of radicals in chambers provides an opportunity to attempt to balance the radical budget in carefully controlled, reproducible laboratory conditions, and it provides an

opportunity to systematically study the factors that affect radical budgets, for example, studying the possible effect of aerosols concentration on HO₂ termination (e.g., see Cantrell et al., 1997). This research will lead to better understanding of urban photochemistry and is also of great importance for understanding regional and global budgets of radicals and their effects on important greenhouse gasses such as methane and sulfate aerosols.

This proposed project is relevant to the SCAQMD's air quality management programs for both O₃ and PM_{2.5}. The improved photochemical reaction mechanisms and measurement technologies developed in this project will be used to develop more accurate photochemical mechanisms and air quality models. This will provide more reliable models for evaluating the reactivity of precursor species. It also will provide more accurate assessments of O₃ and PM_{2.5} attainment strategies in modeling studies. It will provide information on OBMs and indicator species that can be used to assess pollutant sensitivity to precursors and to track progress in air quality management. Ultimately this research will lead to the development of more effective precursor reduction strategies to promote more rapid attainment of air quality standards while minimizing the economic cost of precursor controls.

B. Approach

B.1 Description of LIF Method for OH and HO₂

Sensitive, reliable and real-time methods for *in situ* measurements of hydroxyl (OH) and hydroperoxyl (HO₂) radicals are the key for the success of the smog chamber experiments proposed in this project. For OH, three established methods are currently in use for ambient OH measurements (for a review, see O'Brien and Hard, 1993; Eisele and Bradshaw, 1993; Crosley, 1995):

1. Chemical methods (Eisele and Tanner, 1991; Felton et al., 1990).
2. Long-path absorption (Dorn et al., 1988; Armerding et al., 1991; Hofzumahaus et al., 1991; Mount, 1992)
3. Laser-induced fluorescence (LIF) (Stevens et al., 1994; Wennberg, et al., 1994; Holland, et al., 1995; Hard, et al., 1995; Creasey, et al., 1997).

LIF can provide local, *in situ*, sensitive and specific measurements of OH, and it can be used for HO₂ (with chemical conversion) as well. This technique couples better with the smog chamber experiments than the long-path absorption apparatus, and can provide higher sensitivity under these conditions. Furthermore, sensitive detection of NO₂ (15 ppt, Thornton, et al., 2000) can also be achieved by using the same apparatus (with little modification on optics).

In this proposed project, OH and HO₂ radicals will be detected by using a specific version of LIF technique, FAGE (fluorescence assay by gas expansion). The FAGE technique, pioneered by Hard and O'Brien, is an established method for atmospheric measurements of ambient OH and HO₂ radicals. The demonstrated detection sensitivity are 1 x 10⁵ molecules/cm³ for OH radical and ~ 10⁶ molecules/cm³ for HO₂ radical in tens of seconds of sampling time, respectively (for example, Stevens et al., 1994). The FAGE technique is based on detection of OH by LIF in a low-pressure chamber. The air sample is expanded through a small nozzle into a low-pressure

cell and is irradiated by laser pulses at a repetition rate of several kHz. OH radicals in this air sample beam are excited via single rotational transitions in the $A^2\Sigma^+ (v' = 0) - X^2\Pi_i (v'' = 0)$ band by the tunable laser radiation at *ca.* 308 nm. The resultant fluorescence emitted on resonance via the same band (at *ca.* 308 nm) is detected by gated photon counting. Fluorescence detection at low pressure minimizes quenching of electronically excited OH radicals, and thus dramatically increases the fluorescence quantum yield, offsetting the reduction of OH number density in the sample. Furthermore, the fluorescence lifetime of OH is extended to several hundred nanoseconds at the low pressure, which allows gated photon counting to greatly reduce the laser-induced scattered background from Mie, Rayleigh and wall scattered light that follows closely with the laser temporal profiles (<30 ns). Detection of OH by excitation and fluorescence near 308 nm is advantageous compared to early approaches using 282 nm excitation [$A^2\Sigma^+ (v' = 1) - X^2\Pi_i (v'' = 0)$], which minimizes interfering OH signals from photolysis of O_3 ($O(^1D)$ is produced from O_3 photolysis at 282 nm and reacts with H_2O to generate OH radical). High repetition rate probe laser radiation at much lower peak power also significantly reduces the interfering OH signals from O_3 photolysis, and avoids saturation in OH LIF signals. Finally, HO_2 can be measured by using the same apparatus. This is based on chemical conversion of HO_2 to OH by upstream injection of NO and by the fast reaction $HO_2 + NO \rightarrow OH + NO_2$, and subsequently detection by using LIF.

The details of our utilization of the FAGE technique to detect OH and HO_2 in the smog chamber experiments are described in the following. The schematic diagrams of the proposed low-pressure LIF detection system are shown in Figures 1-1 and 1-2.

The laser system will consist of a Q-switched, high-repetition-rate Nd:YAG laser (Spectra Physics, T40-X30S-532Q) and a pumped dye laser (Lambda Physik Scanmate I). The Nd:YAG pump laser produces 532 nm radiation pulses at 8-10 kHz repetition rate with an average power of 3 W. The output light from the dye laser (at ~616 nm) is frequency doubled to generate UV radiation at ~308 nm, with an estimated power of 5 mW (Wennberg, 2000). The spectral linewidth of the UV output is $\sim 0.2 \text{ cm}^{-1}$.

The air sample is expanded into the fluorescence cell through a small nozzle of 0.4 mm diameter. The flow rate is estimated to be $\sim 0.02 \text{ L/s}$ (standard condition, at the ambient pressure and temperature). This flow rate is small enough to ensure minimal effect on the gas volume and pressure in the smog chamber during the course of the experiments. The air sample forms a supersonic molecular beam in the cell held at a low pressure of $\sim 0.5 \text{ Torr}$. To couple to the smog chamber, the fluorescence cell will be mounted directly underneath the Teflon bag of the smog chamber, and the air will be directly sampled from the nozzle that is installed on the bottom wall of the smog chamber (see Figure 1-2).

The excitation laser light at *ca.* 308 nm is baffled (to minimize scattered light) and excites the OH radicals in the sampling beam. The OH fluorescence is imaged to the photomultiplier (PMT) by a lens system with a back reflector for high collection efficiency. The fluorescence signals are collected by the PMT, and the photon signals are amplified and recorded by a gated photon counter (SRS 400, 200 Mhz).

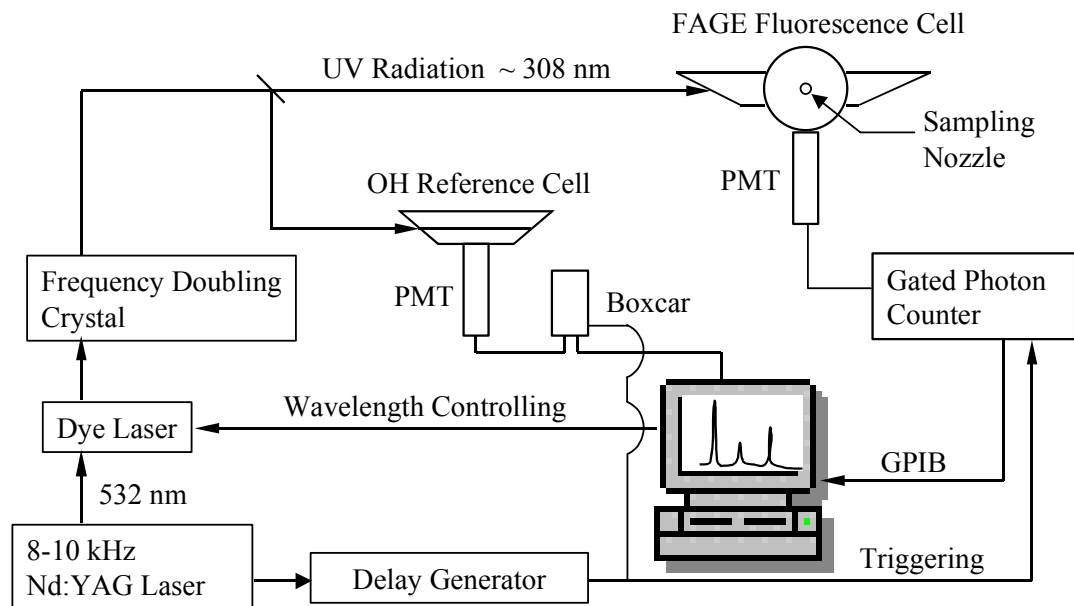


Figure 1-1. Schematic diagram of the FAGE instrument for low-pressure LIF detection of OH and HO₂.

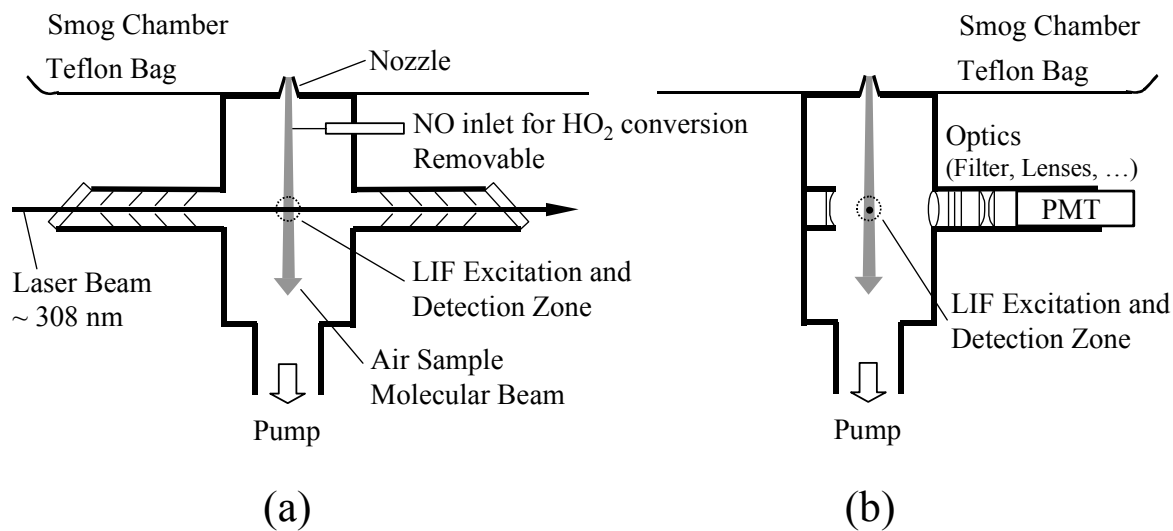


Figure 1-2. Diagram of the side views of the fluorescence cell. (a) The excitation UV laser beam enters and exits the cell in the horizontal plane through the two long baffled arms; (b) the fluorescence light is collected at right angles with respect to the excitation laser beam and the sample molecular beam.

A low-pressure reference cell that contains a small amount of OH is to be constructed for laser wavelength calibration (Figure 1-1, based on LIF detection of OH, see Stevens et al., 1994; Wennberg, et al., 1994; Holland, et al., 1995; Hard, et al., 1995; Creasey, et al., 1997). Calibration of the absolute OH number density in the OH LIF measurements will be carried out by using chemical actinometry (Aschmutat, et al., 1994; Schultz, et al., 1995; also see Stevens et al., 1994; Creasey, et al., 1997) or by using titration of NO₂ with excess amount of H atoms (for example, Stevens et al., 1994; Wennberg, et al., 1994).

HO₂ in the air sample can be converted to OH by injection of excess amount of NO upstream of supersonic beam. The converted OH will then be detected by the LIF downstream.

The FAGE technique can be readily adapted for the smog chamber experiments. This combination provides a unique opportunity to examine the budget of OH and HO₂, as well as that of NO₂ in the controlled smog chamber experiments. The anticipated concentrations of OH and HO₂ radicals in the smog chamber are estimated to be $1-7 \times 10^6$ molecules/cm³ and $10^7 - 10^8$ molecules/cm³, respectively. The well-established detection sensitivity and selectivity of the FAGE technique for OH and HO₂ radicals will ensure the success of the proposed experiments. The first stage of this proposed research project will be construction and characterization of the FAGE instrument. This includes installation of the laser and optics systems, fabrication of the low-pressure fluorescence cell and the reference cell, and optimization of the detection sensitivity (with nozzle size, probe laser location, and background reduction). The second stage involves installation of the FAGE instrument to couple with the smog chamber and to carry out the proposed OH and HO₂ measurements. The project team has extensive experience with laser, laser spectroscopy, LIF, electronics, molecular beam, and vacuum system, and the construction and incorporation of the well-established FAGE instrument in the smog chamber experiments can be readily carried out.

It is also important to point out that the proposed FAGE instrument can be utilized for LIF measurement of NO₂ with little modification of optics. The air sample that contains NO₂ will be expanded in the low-pressure fluorescence cell, and the NO₂ molecules will be excited on resonance near 585 nm. The resultant fluorescence around 750 nm, which is red-shifted from the excitation laser radiation and whose lifetime is extended to several hundred nanoseconds at the low pressure, will be detected by gated photon counting (Thornton et al., 2000). Detection sensitivity has been demonstrated to be 15 ppt in 10 seconds of sampling time (Thornton, et al., 2000). NO₂ detection based on this FAGE instrument will provide a direct and sensitive spectroscopic measurements of NO₂ concentration, in addition to those from the NO_x analyzer in the proposed smog chamber studies.

B.2 Description of LIF Method for HO₂ and RO₂

The chemical amplifier (CA) method is used to measure the concentrations of HO₂ and RO₂ radicals. This method has been widely employed in field studies (Cantrell et al., 1996a,b; 1993; 1984). As in the case of the LIF instrument, operation of the instrument will be greatly facilitated in the laboratory setting, which will removes problems associated with calibrating and operating instruments in the field.

The approach used in the CA instrument is based on a chemical reaction chamber that amplifies the number of NO to NO conversions induced by each HO₂ or RO₂ radical. The method relies on a numerical model of the radical chemistry to determine radical chain length in the reaction chamber and hence the concentration of radicals in the sample gas. Because of uncertainties in the modeling of the radical chain length, the CA method cannot be used reliably to provide an absolute measure of HO₂ and RO₂ radicals. However, if an accurate measurement of HO₂ is available it can be used to calibrate the CA instrument. The, the LIF instrument will be used as the reference method for HO₂ and will be used to calibrate the CA instrument. This will provide an measurement of RO₂ which cannot be obtained from the LIF method.

The inlet system for the CA instrument will be comprised of a double-wall, stainless-steel tube. Ambient air enters the system through a 2 mm ID glass orifice to prevent rejection of reagents due to air turbulence. Although the Pyrex-glass orifice eliminates distortion of the flow pattern due to turbulence, laboratory tests revealed that the orifice also reduced the chain length by approximately 10%, so its appropriateness for use with environmental chamber systems will be investigated.. The inner, 8 mm ID tube is the reagent tube. The reagent gases CO and NO are delivered ring-shaped to the inlet through the slit between the two tubes, this serves to cover the wall of the reagent tube with CO and NO, which minimizes wall losses. A Scintrex LMA-3 instrument will be used to measure NO₂ by detection of the chemiluminescence produced during the reaction of NO₂ with proprietary Luminol II solution (Scintrex).

The CA instrument will be constructed by CE-CERT staff who are familiar with the construction and use of such instrumentation.

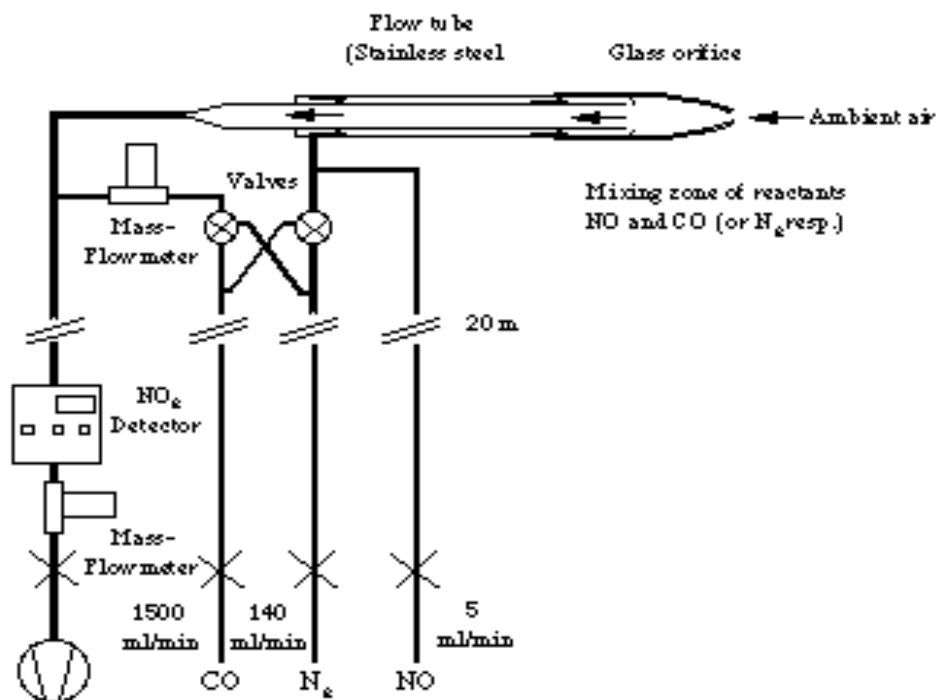


Figure 1-3. Schematic illustrating the design of the chemical amplifier instrument.

B.3 Chamber Experiments for Characterizing Radical Budgets

UC Riverside has developed a “next-generation” chamber at CE-CERT under funding from the U.S. EPA (Cooperative Agreement 827331-01-0; see Carter et al., 1999; Carter, 2002). The new chamber facility is located in a building specifically designed for this purpose. This project will provide significant co-funding for this proposal and cover the costs for many of the characterization experiments that need to be carried out. A description of the current status of this project, and the first progress report, is available at <http://www.cert.ucr.edu/~carter/epacham>.

The chamber’s design is intended to maximize the accuracy of simulations of nearly clean air, measurements of particle formation under more polluted conditions, and assessments of VOC reactivity under more urban-like conditions using the facility’s advanced analytical instrumentation. The chambers are of large volume (~20,000 - 50,000 liters) to minimize surface effects, and also to permit analyses using instruments with high sample flow requirements.

The chamber includes a high-capacity air purification system that is capable of removing CO as well as NO_x and organics and other pollutants to the lowest practical level. Utilizing highly purified air and avoiding outside contamination is also critical. Exploratory experiments in our laboratory using procedures to improve air purification have shown that this reduces some effects that were attributed to chamber walls. To avoid introduction of contaminants from laboratory air into the chamber (through leaks or diffusion through the Teflon walls), the reactors are located in a “clean room” which itself is flushed with purified air.

The chamber includes a temperature control system constructed with the design goal of holding the chamber enclosure at a constant and controlled temperature between ~5 C and ~50 C to within ±1°C. The chamber will be constructed indoors with artificial lights to allow for complete temperature and lighting control and adequate characterization of chamber conditions. Argon arc lights are employed because they provide the most realistic spectrum (Carter et al., 1995b; Carter, 2002). The instrumentation that will be available in the new chamber facility are described in more detail elsewhere (Carter, 2002).

Radical budgets will be investigated in several types of chamber experiments. Pure air, NO_x-air and other types of background characterization experiments will be conducted to assess background effects. A series of experiments will be performed using a simple mixture in which the photochemical reactions are believed to be well understood (e.g., a methane-CO-NO_x mixture). The simple mixture will be used to establish whether the radical budget can be balanced under well understood conditions. Subsequently, experiments will be performed using progressively more complex systems, ranging from single VOC - NO_x irradiations using VOCs with differing types of mechanisms to NO_x - air irradiations employing representations of the complex VOC mixtures observed in ambient air. Exploratory experiments with varying particle loadings to assess whether particles affects radical budgets in unexpected ways (e.g., Cantrell et al., 1997), and if so further experiments of this type will be conducted. Temperature and humidity will also be varied in selected experimental systems, with additional experiments being conducted if unexpected results are obtained.

For both the simple and the complex mixture systems, chamber experiments will be performed to characterize HO_x budgets for a range of VOC and NO_x concentrations and VOC/NO_x ratios. In

terms of an O₃ isopleth diagram, shown in Figure 1-4, experiments will be designed to “map out” the O₃ response surface as illustrated by the crosses in Figure 1-4.

In addition, the LIF and CA instruments will be used in other chamber experiments designed to characterize chamber wall effects and in experimental studies designed to elucidate the chemical reaction mechanisms and the reactivity of various organic compounds including aromatic compounds and biogenic VOC.

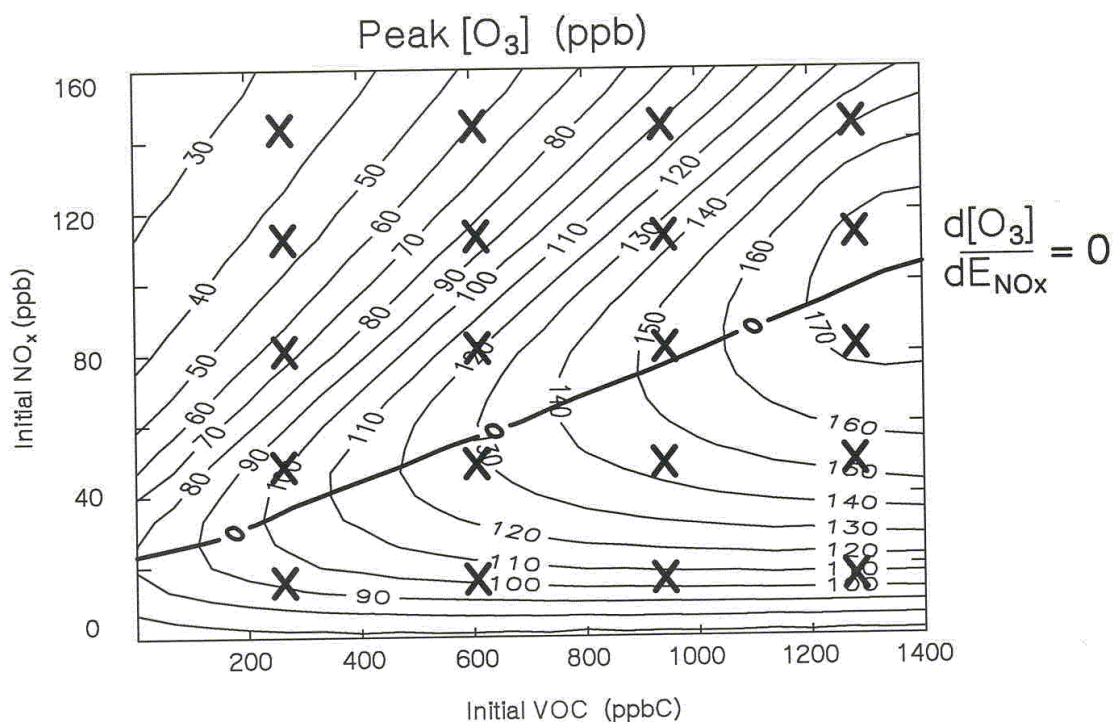


Figure 1-4. O₃ isopleth diagram showing isolines of model simulated peak O₃ concentration as a function of initial VOC and NO_x concentrations. The bold line shows the ridgeline of maximum O₃ concentration defined by $\partial[O_3]/\partial E_{NO_x} = 0$, and the crosses illustrate the range of VOC and NO_x concentrations to be performed in chamber experiments.

B.4 Modeling and Analysis of Experimental Results

Modeling of the photochemical reactions in the chamber experiments will constitute an important component of this project. A standard box model (Gery and Crouse, 1991) using a Gear solver will be used to simulate the chamber experiments. The model is capable of representing dilution of chamber and has a flexible mechanism reader to allow for changes in the photochemical mechanism. An extensive set of model simulations will be run prior to the experimental stage to select the concentrations levels of VOC and NO_x to be used in the chamber experiments. The model simulations will be used to setup a suite of experiments that will cover a

range of conditions from NO_x limited (with high HO_2/OH ratios) to low VOC/NO_x , radical limited conditions (with low HO_2/OH ratios). After completing the experiments, times-series of species measured in the chamber experiments will be compared with the model predicted results, and additional model simulations will then be performed to attempt to obtain better fits to the experimental data by modifying the chemical mechanism as appropriate. This comparison of model results and chamber results will constitute an important test of the accuracy of current photochemical mechanisms and will likely lead to improvements in the photochemical mechanisms.

In addition to evaluating the species concentration time-series, two kinds of model simulations will be used to provide a more detailed evaluation of radical budgets.

First, radical concentrations will be calculated using a constrained, steady-state calculation (e.g., Kleinman et al., 1994). This approach has been used in previous field studies (Stevens et al., 1997), and most recently in the 1999 Nashville field study (Frost, 2000), and it is useful for assessing whether the model correctly represents radical sink and source terms. The results from previous field studies have shown that there sometimes exist large inconsistencies in the radical budgets (Cantrell et al., 1997, Stevens et al., 1997; Carpenter et al., 1998). Preliminary results for the Nashville 1999 field study presented at a data analysis workshop (Frost, 2000; Cohen, 2000) indicated that the high NO_2 concentrations did not significantly inhibit O_x production. This result would contradict our current understanding of radical and oxidant photochemistry, and hence it raises concern over the accuracy with which current photochemical mechanisms characterize radical budgets.

Second, model simulations will also be used to balance the radical budgets in terms of the production and sinks of HO_x radicals. Rates of new radical initiation must be balanced by radical termination, and the primary sinks for radical species are believed to be the production of radical termination products: HNO_3 , PAN, organic nitrates, hydrogen peroxide (H_2O_2), and organic peroxides. This budget analysis will be performed by calculating the integrated rates of the radical initiation reactions in the model simulations, and then comparing integrated radical initiation with the concentrations of radical termination products. Because species such as HNO_3 and H_2O_2 may also be deposited on surfaces or consumed in subsequent reactions, it will be necessary to use model simulations that include wall deposition to provide a full accounting for the budget of each of these species, and then to compare the budgets for radical initiation and termination. The ability to compare radical initiation rates with accumulation of radical termination products represents an important advantage of studying radical budgets in a chamber – in ambient field studies the radical termination products are dispersed by advective or turbulent transport processes and hence cannot be easily compared with the radical initiation rates.

Finally, the concentration of HO_2 is believed to be a useful indicator of O_x production sensitivity to changes in VOC and NO_x , where an HO_2 concentration of 20 ppt is strongly associated with conditions of equal O_x production sensitivity to VOC and NO_x (Tonnesen and Dennis, 2000a). The suite of chamber experiments to be performed in this study will bracket the conditions in which O_x production transitions from being VOC sensitive to NO_x sensitive for a range of O_3 levels and VOC/NO_x ratios, and this will provide an opportunity to test whether the HO_2 concentration is a robust indicator of O_x production sensitivity. Because this indicator also represents a component in the theoretical basis for other photochemical indicators of O_x

production and O₃ concentration sensitivity (Tonnesen and Dennis, 2000a,b) this analysis will be useful in evaluating the potential usefulness of photochemical indicators more generally.

C. Relationship to Current State of Knowledge

C.1 Atmospheric Chemistry and Measurement

Oxidant photochemistry in the troposphere is controlled by the availability of reactive nitrogen oxides (NO_x=NO+NO₂) and the sources and sinks of odd hydrogen radical species (HO_x=OH+HO₂+RO₂) (Levy, 1971; Logan et al., 1981). The budgets of the hydroxyl radical (OH) and hydroperoxyl radical (HO₂) are particularly important because HO₂ is rapidly converted to OH in the presence of NO_x, and OH attack on volatile organic compounds (VOC) and carbon monoxide (CO) is the primary source of tropospheric O₃ (NRC, 1991). Reactions of OH with VOC also contribute to production of potentially toxic compounds including carbonyls and secondary organic aerosols. Reactions of OH with NO₂ and SO₂ produce nitric acid (HNO₃) and sulfuric acid (H₂SO₄), which are important constituents of fine particulate matter and contribute to acid deposition (Finlayson-Pitts and Pitts, 1997). Reactions of HO_x also contribute indirectly to other aerosol production pathways. For example, reactions of HO₂ form hydrogen peroxide (H₂O₂), which converts SO₂ to H₂SO₄, and OH produces NO₂ and O₃, which subsequently can form N₂O₅ and HNO₃ in heterogeneous night time reactions (Dentener and Crutzen, 1993). Finally, the OH radical also plays a vital role as the primary cleansing agent in the troposphere by removing several important trace species, including the following: nitrogen oxides, organic compounds, carbon monoxide, methane (CH₄) which is an important greenhouse gas, and hydrogenated fluorocarbons which can affect stratospheric O₃ if transported to the stratosphere (Finlayson-Pitts and Pitts, 1997).

Radical species are extremely reactive and hence short-lived. As a result they exist at low concentrations in ambient air, typically less than 50 ppt for HO₂ and less than 0.5 ppt for OH, making them very difficult to measure (Mather, 1997; Cantrell, 1997). Because of the difficulty in obtaining ambient measurements for all relevant ambient conditions, and because of the complexity of the processes that affect trace gas photochemistry, the budgets of OH and HO₂ are poorly understood for both urban and rural conditions (Crosley, 1997).

Because of its central role in the photochemical reactions that produce oxidants and aerosols, HO_x plays a critical role in several topics of concern to the SCAQMD. Efforts to attain ambient air quality standards for oxidants and particulates will affect choices of transportation systems and fuel types. The role of radicals in VOC chemistry will also determine the VOC reactivity and will affect the selection of reactivity based VOC substitution strategies. An accurate understanding of the chemical reactions that control the budget of OH is essential for developing chemical mechanisms and atmospheric models that can be used to predict the effects of energy use on these diverse air quality problems and to suggest possible energy use and energy development strategies that will minimize harmful effects in the future.

Photochemical mechanisms of tropospheric chemistry are developed through a combination of laboratory kinetics experiments and irradiations of complex mixtures of trace species in environmental chambers including both outdoor chambers (Jeffries et al., 1985a,b; Hess et al.,

1992; Simonaitis and Bailey, 1995; Becker, 1999) and indoor chambers (Carter et al., 1995a, 1999, Carter, 2000, 2002, and references therein). The resulting mechanisms are then tested and further evaluated using data from ambient monitoring and intensive field studies that attempt to measure many of the species of interest. Although such studies have been carried for over 30 years, there remain important uncertainties in our understanding of the HO_x budget. This is true in part because analytical methods to measure OH and other radical species have only recently been developed. For example, measurements of OH, HO₂ and other important species are lacking in the existing data base of environmental chamber experiments that was used to develop current gas-phase and aerosol photochemical mechanism. The trace species that are routinely measured in chamber experiments typically include O₃, NO_x by chemiluminescence, speciated VOC by gas chromatography, and peroxyacylnitrates (PAN). In some cases, data for HCHO and total NO_y are also available, and more rarely, HONO, H₂O₂, HNO₃. While measurements of O₃, NO_x, VOC and PAN are essential for studying oxidant photochemistry, this set of species measurements does not provide a non-ambiguous analysis of the system because each of these species has a complex, non-monotonic dependence on precursor concentration levels. The limited set of species data available in the historical chamber database raises concern that there may be significant errors in mechanisms developed from this data.

2. Schedule, Milestones, and Deliverables

A. Project Schedule and Milestones

Figure 2-1 presents the schedule of tasks and major milestones for the proposed project.

	10/02	11/02	12/02	1/03	2/03	3/03	4/03	5/03	6/03	7/03	8/03	9/03
Develop LIF instrument	■	■	■	■	■	■						
Develop chemical amplifier instrument	■	■	■	■	■	■						
Integrate new instruments into chamber					■	■	■	■	■			
Chamber experiments					■	■	■	■	■			
Reporting	■	■	■	■	■	■	■	■	■	■	■	■

Figure 2-1. Project schedule and milestones.

B. Deliverables

Deliverables for this project will include:

- Period progress reports and financial reports.
- A final report describing the project and its results.
- Manuscripts of any journal articles or presentations prepared during the course of the project that describe the research activities and their results. The District will be provided with the opportunity to review and comment on the manuscripts before they are submitted.

3. Facilities, Equipment, and Other Resources

A. Atmospheric Processes Laboratory

The Atmospheric Processes Laboratory is fully equipped for two major areas of study: measurement of pollutants in the ambient air and evaluations of the chemical reactivity of chemical species for formation of ozone and fine particulate matter. Thus, the laboratory maintains a full array of monitors for SO₂, NO/NO_x, NO_y, O₃, CO, CO₂, HC, PM₁₀, PM_{2.5}, denuder systems, and meteorological equipment. This includes a Luminol-based NO₂/PAN GC developed at CE-CERT and selected research grade instruments. CE-CERT performs extensive reactivity research utilizing the environmental smog chamber described below.

In 1999, the University entered into an agreement with the U.S. Environmental Protection Agency to develop a “next-generation” chamber at CE-CERT (Cooperative Agreement 827331-01-0) (Figure 3-1). This chamber began operation in late 2001, and is the world’s largest indoor atmospheric reactivity chamber. Based on the experience gained from the operation of the earlier chambers and evaluations of prototype systems, the design of this system was enhanced by consultation with atmospheric chemistry experts from academic institutions, government agencies, and specialized industries around the world.

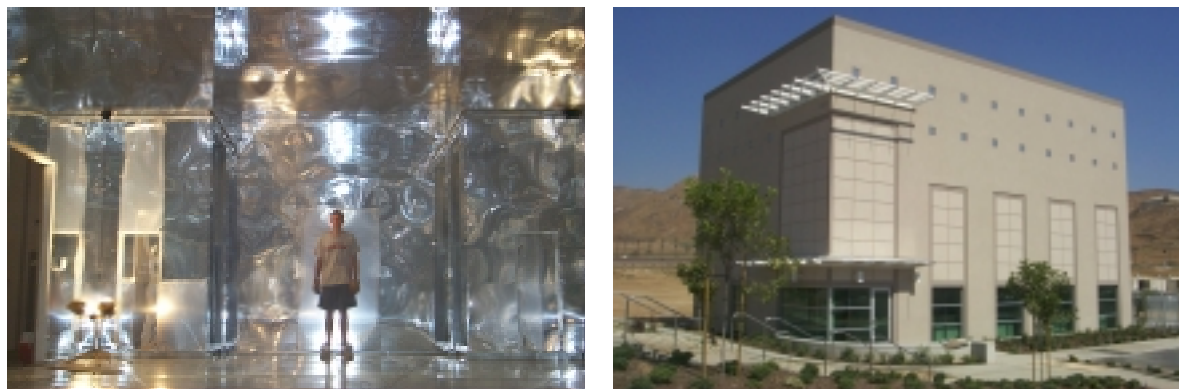


Figure 3-1. (a) Interior of CE-CERT atmospheric processes chamber and (b) exterior of purpose-built structure housing it.

A single, water-cooled 200 kW Xenon arc light provides the simulated sunlight for reactivity experiments. This source provides the most realistic spectrum achievable in an indoor chamber. In addition, blacklights are employed for lighting the reaction bags for cleaning and flushing. The chamber is capable of handling two 74 m³ reaction bags simultaneously. This approach enables precision tests, minimizes surface effects, and permits analyses using instruments with high sample flow requirements, enabling testing of instruments designed for field use. The chamber is contained within a “clean room,” flushed with purified air, to prevent polluted background air from interfering with experiments. The system is capable of multi-day experiments without significant dilution or loss of volume and without buildup of wall effects, enabling simulations of

rural or long-range transport scenarios. The chamber is capable of holding a constant and controlled temperature between $\sim 5^{\circ}\text{C}$ and $\sim 50^{\circ}\text{C}$, to within $\pm 0.5^{\circ}\text{C}$.

Analytical Instrumentation

An essential component of any environmental chamber facility is the quality of the measurements of the pollutants. The requirements for this advanced facility also include the need to measure these pollutants accurately at low levels. Automated measurements of air pollutants in the reaction bags are performed with a full array of standard O_3 , NO_2 , CO , and HC analyzers. In addition, the chamber facility also contains a set of experimental and specialized instruments, including the following:

Research Instrumentation for Gas-Phase Analyses:

High-sensitivity NO Analyzer. This is a research grade, low-range, NO-only analyzer with a detection limit of 40 ppt. It is sufficiently sensitive to detect steady-state NO levels in the presence of NO_x and O_3 in light, a capability beyond that of a commercial NO/ NO_x analyzer.

High-sensitivity total carbon, NMHC, and CO analyzers. These analyzers are used for evaluating the air purification system.

NO_2 /PAN GC. This analyzer was designed and developed by CE-CERT. It uses Luminol detection combined with a GC column to separate NO_2 from PAN and other species that are then detected by Luminol to provide a specific analysis for NO_2 . The sample air is drawn through the instrument by a micro pump and flows across a fabric wick wetted with Luminol solution. The central portion of the wick is viewed by a photomultiplier, the signal of which is proportional to the NO_2 concentration. Its detection limit for NO_2 is 200 ppt. It will also provide data for PAN, though its reliability and accuracy for this purpose has not yet been fully established.

NO_2 / HNO_3 and $\text{HCHO}/\text{H}_2\text{O}_2$ Tunable Diode Laser Absorption Spectroscopy Systems (TDLAS). These research grade analyzers (2) are based on measuring single rotational-vibrational lines of the target compounds in the near to mid-infrared using laser diodes with very narrow line widths and tunability. Monitoring “true” NO_2 is particularly important, and because of interferences commercial NO/ NO_x analyzers are not suitable for this purpose. The sample for analysis is flushed through closed absorption cells with multi-pass optics held at low pressure (~ 25 Torr) to minimize spectral broadening. Because of the narrow bandwidth of the diode lasers required to obtain the highly species-specific measurement, separate diode lasers are usually required for each compound monitored. However, both TDLAS systems acquired for this project have two lasers and detection systems, permitting analysis of up to four different species.

Formaldehyde Analyzer. This continuous HCHO analyzer is based on the wet chemical method of Dasgupta and others. This analyzer is in the development and testing phase, and will be used as a backup and/or a replacement for the TDLAS if proved sufficiently reliable.

Gas Chromatographs. Three separate GC systems are utilized in this laboratory. The first two are standard laboratory GC-FID systems. They are used to monitor at least some of the oxidation products, such as simple aldehydes, ketones, and organic nitrates, provided that their identities

are established by other means. The loop sampling method is currently used for the more volatile and less sticky compounds, and is sufficient for monitoring reactant VOCs, but it may not be sensitive enough for monitoring trace VOCs for pure air experiments or to verify the performance of air purification experiments. The trap sampling method (Carter et al., 1996) is employed when more sensitive analysis is required. The Tenax cartridge sampling method used for the lower volatility or more “sticky” VOCs (Carter et al., 1996) has been adapted for more sensitive analysis by sampling larger volumes of air through the trap. The GCs as currently configured allow use of three different columns for loop or trap sampling, and a fourth column for Tenax cartridge sampling. This permits a variety of types of compounds to be separated. The third GC is fitted with ECD detection for more sensitive monitoring of organic nitrates and certain other types of compounds for which ECD detection is sensitive.

Aerosol Instrumentation

The following instruments have been incorporated into the laboratory system for studying fine PM:

Ion Chromatograph. This instrument is used to analyze particulate matter for anions following extraction with an aqueous solvent.

Elemental Carbon/Organic Carbon Analyzer. This analyzer is used to determine the elemental and organic carbon content of particulate matter collected from the chamber using high purity quartz filters.

Standard Aerodynamic Particle Sizer. This instrument is used to determine the particle size-number distribution for particles greater than 0.3 μm aerodynamic diameter.

Scanning Electrical Mobility Analyzers (SEMS). Two of these instruments have been designed and built by CE-CERT to simultaneously measure size and number distributions of aerosols formed in each reactor. Separate instruments have been provided for each reactor because aerosol materials will not pass through solenoid valves without undergoing modification that is difficult to characterize. The aerosol sizes and number distributions are the primary physical measurements needed to determine amounts of aerosol formed and how they grow or are removed during an experiment. The instrument measures in the range of 0.03 μm to 0.8 μm electrical mobility diameter, and consists of three major components: a Thermo Systems Inc. (TSI) model 3077 ^{85}Kr neutralizer which generates a Fuch’s charge distribution, a TSI model 3081 differential mobility analyzer long column which selects for particle sizes based on the voltage applied and the particles electrical mobility, and a TSI model 3760A condensation particle counter (CPC) used to detect particles.

Tandem Differential Mobility Analyzer (TDMA). This analyzer consists of a reconfiguration of the SEMS to measure the size and number distribution of particles within a single size range, then passing the sample through a chamber exposing the particles to humidity, heat, or other conditions of interest. The principle of operation and further information about this instrument, which is based on the design of Rader and McMurry (1986), is given by Cocker et al. (2001). The instrument can therefore be used to determine the effects of humidity, temperature, or other

changes to the environment to aerosol size and number distributions. This information is useful to investigate important aerosol properties such as hygroscopicity and volatility, and thus gives an indication of their major chemical characteristics.

Constant Output Atomizer, Diffusion Dryer, Aerosol Neutralizer. This combination of equipment is used to add a synthetic seed aerosol to allow secondary organic aerosol (SOA) to condense on existing aerosol rather than self-nucleate.

It is important to recognize that organic photooxidation products that are expected to be formed under low-NO_x conditions will be different from those formed under higher-NO_x conditions, and among these low-NO_x products there will be unstable and difficult to monitor species such as hydroperoxides. One high-priority focus of the analytical development for this program will be to develop and evaluate methods suitable for monitoring hydroperoxides and other low-NO_x organic product species. Where necessary, the participation of synthetic organic chemists will be utilized to prepare authentic samples for analytical development and calibration.

B. Environmental Modeling

The Environmental Modeling group is equipped with high-end Unix and DOS/Windows computers capable of storing and manipulating large data sets. CE-CERT's computer laboratory is designed to process large data sets for modeling and analysis. The computer laboratory consists of an SGI 4-CPU Origin 2000 workstation as well as 13 Unix (Sun, SGI) and PC (Pentium) workstations. These workstations are served by a large file system (over 100 gigabytes shared and 30 gigabytes local). Several of these workstations have advanced graphics capability (SGI Onyx system with extreme graphics) allowing for real-time model animation and data visualization. The computer workstations and various devices are integrated through a 10baseT ethernet network, with a T1 gateway to the Internet. The data backup/archiving system includes 8mm tape drives and a DLT autoloading cartridge system capable of performing unattended archive/backups of 245 GB (uncompressed). Also available through the Internet are the University of California's supercomputer facilities, located in San Diego.

CE-CERT has developed an expertise in creating new models and utilizing existing models in air pollution research. These models can be divided into emission models (EPA's MOBILE and PART, CARB's MVEI, CALINE, etc.), transportation models (CE-CERT's ITEM, TRANPLAN, SCAG's CTP, FRESIM, TRAF-NETSIM, PATH's SmartPath, SmartAHS, and SmartCAP, etc.) and atmospheric models (UAW, RADM, CMAQ, EKMA, Models3). In addition, CE-CERT uses state-of-the-art analysis tools in their research, including MATLAB, Mathematica, Vis5D and PAVE.

4. Key Personnel

The key personnel for this project are Bill Carter and Gail Tonnesen at CE-CERT, and Jingsong Zhang, Assistant Professor of Chemistry and a researcher at the Air Pollution Research Center. Summary biographical sketches are provided on the following pages.

William P.L. Carter
Research Chemist

CE-CERT 022, University of California, Riverside, CA 92521-0434 carter@cert.ucr.edu

Professional Preparation

University of California, Riverside
University of Iowa, Iowa City

Chemistry
Physical Chemistry

B.A., 1967
Ph.D., 1973

Professional and Academic

1973-present. University of California, Riverside, Air Pollution Research Center (APRC) and College of Engineering-Center for Environmental Research and Technology (CE-CERT) (since 1992). Develops chemical mechanisms for atmospheric models and methods for evaluating atmospheric impacts of organic compounds. Directs environmental chamber research program to evaluate atmospheric chemical mechanisms and VOC reactivities. Research Chemist (1987-present), Associate Research Chemist (1981-87), Assistant Research Chemist (1976-81), and Postgraduate Research Chemist (1973-76).

1970-73. University of Iowa, Graduate Research Assistant. Studied chemical activation systems of free radical reactions. Graduate Teaching Assistant (1970-72).

1967-69. California Institute of Technology, Pasadena, CA, Graduate Research Assistant. Studied the mechanism of unimolecular pyrolysis reactions.

Relevant Professional Activities

Principal Investigator for the development of the "Next Generation" environmental chamber facility for the EPA (1999-2003). Developed ozone reactivity scale that is used in the California Vehicle regulations and is proposed for California consumer products regulations (1994-2000). Research has been used as a basis for VOC exemptions adopted by the U.S. Environmental Protection Agency (1993-2000). Chairman of the Science Team responsible for preparing the Reactivity Research Working Group (RRWG) VOC reactivity science assessment document and RRWG draft work plan (1998-99). Selected as peer reviewer of California Air Resources Board Modeling Protocol Document (2001).

Selected Relevant Publications and Reports Since 1990

Carter, W. P. L. (2002). Development of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Research. Report to the United States Environmental Protection Agency, January 3, 2002. Available at <http://www.cert.ucr.edu/~carter.epacham>.

Wang, L, J. B. Milford, and W. P. L. Carter (2002). Analysis of Chamber-Derived Incremental Reactivity Estimates for N-Butyl Acetate and 2 Butoxy Ethanol. *Atmospheric Environment*, 36, 115-135 (2002)

Carter, W. P. L. (2001). Peer Review of ARB Ozone Modeling for Southern California. Report to the California Air Resources Board, July 2, 2001

Carter, W.P.L. (2000). Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment. Final Report to California Air Resources Board Contract No. 92-329, and 95-308, May. Available at <http://www.cert.ucr.edu/~carter/absts.htm#SAPRC99>

Carter, W.P.L. (2000). Investigation of Atmospheric Reactivities of Selected Consumer Product VOCs. Final Report to California Air Resources Board Contract No. 95-308, May 30. Available at <http://www.cert.ucr.edu/~carter/absts.htm#cpreport>.

Wang, L.; Milford, J.B, and Carter, W.P.L. (2000). Reactivity Estimates for Aromatic Compounds 1. Uncertainty in Chamber-Derived Parameters. *Atmos. Environ.*, **34**, 4337-4348.

Tuazon, E.C., Aschmann, S.M. Atkinson, R. and W.P.L. Carter (1998). The reactions of Selected Acetates with the OH radical in the Presence of NO: Novel Rearrangement of Alkoxy Radicals of Structure RC(O)OCH(O.)R'. *J. Phys. Chem A* **102**, 2316-2321.

Carter, W.P.L., (1996). Atmospheric Photooxidation Mechanisms for Isoprene. *Atmos. Environ.* **24**, 4275-4290.

Carter, W.P.L. and Atkinson, R. (1996). Development and Evaluation of a Detailed Mechanism for the Atmospheric Reactions of Isoprene and NO_x. *Int. J. Chem. Kinet.* **28**, 497-530.

Carter, W.P.L., (1995). Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmos. Environ.* **29**:2513-2527.

Carter, W.P.L., Pierce, J.A., Luo, D. and Malkina, I.L. (1995): Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmos. Environ.* **29**, 2499-2511.

Carter, W.P.L. (1994). Development of Ozone Reactivity Scales for Volatile Organic Compounds. *J. Air & Waste Manage. Assoc.* **44**:881-899.

Atkinson, R. and W.P.L. Carter (1992). Reactions of Alkoxy Radicals under Atmospheric Conditions: The Relative Importance of Decomposition versus Reaction with O₂. *J. Atm. Chem.*, **13**, 195-210.

Carter, W.P.L., and Lurmann, F.W. (1991). Evaluation of a Detailed Gas Phase Atmospheric Reaction Mechanism Using Environmental Chamber Data. *Atmos. Environ.* **25A**:2771-2806.

Carter, W.P.L. (1990). A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds. *Atmos. Environ.*, **24A**, 481-518.

Gail S. Tonnesen***Manager, Environmental Modeling, Assistant Research Engineer***

CE-CERT 022, University of California, Riverside, CA 92521-0434 tonnesen@cert.ucr.edu

Education

Ph.D., Environmental Engineering, University of North Carolina, Chapel Hill, 1995.

M.S., Environmental Engineering, University of North Carolina, Chapel Hill, 1990.

B.S., Chemical Engineering, Michigan State University, 1983.

Professional and Academic

1999-present. Manager of Environmental Modeling, College of Engineering-Center for Environmental Research and Technology, University of California, Riverside. Responsibilities include managing a research program in environmental modeling, in particular a multi-scale Eulerian photochemical air quality modeling program.

1995-98. National Research Council Research Associate, U.S. Environmental Protection Agency, Research Triangle Park, NC. Developed a conceptual model and methodology for the use of process diagnostics to evaluate numerical models of atmospheric chemistry and applied this model to develop diagnostics useful for the comparison of model predictions to field measurements.

1989-93. Consultant on several projects in numerical modeling of urban air pollution and in the evaluation of control strategies for urban ozone.

1987-88. Environmental Engineer, Air Management Division, U.S. Environmental Protection Agency, Region 9. Worked with state and local air pollution control agencies in development and evaluation of regulations for volatile organic compounds.

1983-87. Field Coordinator/Volunteer Leader/Peace Corps Volunteer, Republic of Zaire. Worked with a Zairian counterpart to plan and supervise the activities of a regional office of the Zairian National Family Fish-farming Project. Organized intensive seminars to provide advanced training for groups of farmers. Provided technical, logistical and counseling support for 13 Peace Corps volunteers.

1980-82. Student-intern at Shell Oil. Worked in the maintenance crew at a natural gas processing plant and in a facilities engineering group developing criteria for replacement of leaking oil-field pipelines.

Professional Memberships

American Geophysical Union

Selected Publications

Tonnesen, G.S., and Dennis, R.L. (1999) Analysis of Radical Propagation Efficiency to Assess Ozone Sensitivity to Hydrocarbons and NO_x. Part 1: Local Indicators of Odd Oxygen Production Sensitivity, *J. Geophys. Res.* (*in press*).

Tonnesen, G.S., and Dennis, R.L. (1999) Analysis of Radical Propagation Efficiency to Assess Ozone Sensitivity to Hydrocarbons and NO_x. Part 2: Long-lived Species as Indicators of Ozone Concentration Sensitivity, *J. Geophys. Res.* (*in press*).

Tonnesen, G.S. (1999) Effects of Uncertainty in the Reaction of the Hydroxyl Radical with Nitrogen Dioxide on Model Simulated Ozone Control Strategies. *Atmos. Environ.* **33**:1587-1598.

Dennis, R.L.; Arnold, J.R.; Tonnesen, G.S.; and Li, Y. (1999) A New Response Surface Approach for Interpreting Eulerian Air Quality Models Sensitivities. *Computer Physics Communication*, (*in press*).

Arnold, J.R.; Dennis, R.L.; and Tonnesen, G.S. (1998). Advanced Techniques for Evaluating Eulerian Air Quality Models: Background and Methodology. In: *Preprints of the 10th Joint Conference on the Applications of Air Pollution Meteorology with the Air & Waste Management Association*, January 11-16, 1998, Phoenix, Arizona, pp. 1-5.

Graduate and Postgraduate Advisors

Harvey Jeffries, University of North Carolina, Chapel Hill
Robin Dennis, Atmospheric Modeling Division, National Oceanic and Atmospheric Administration, Research Triangle Park, NC

Jingsong Zhang***Department of Chemistry and Air Pollution Research Center***

University of California, Riverside, CA 92521

Tel: (909) 787-4197; Fax: (909) 787-4713; E-mail: jszhang@ucr.ac1.ucr.edu

Education

Ph.D., Physical Chemistry, University of California at Berkeley, 1993. Thesis: "Crossed Molecular Beam Studies of Atmospheric Chemical Reaction Dynamics."

B.S., Chemistry (Highest Honors), University of Science and Technology of China, 1987. Thesis: "Effects of Aggregation of Silver Halide Colloids on Surface-Enhanced Raman Scattering (SERS) of Pyridine Adsorbed on Silver Halide Colloids."

Research Experience

University of California, Riverside (1996-present). Assistant Professor of Chemistry, and Assistant Research Chemist, Air Pollution Research Center. Research includes photochemistry and reaction dynamics of small molecules and free radicals using laser spectroscopy, mass spectrometry, and molecular beam techniques.

University of Southern California, 1993-96. Postdoctoral Research Associate. Research included photodissociation dynamics of small molecules (including state-selected) and van der Waals clusters; utilized excimer, dye, and various solid-state (Nd:YAG, Ti:sapphire, OPO) lasers.

University of California, Berkeley, 1987-93. Graduate Research Assistant. Research focused on reaction dynamics via crossed molecular beams: atmospheric ($\text{Cl} + \text{O}_3$, $\text{Br} + \text{O}_3$, $\text{Cl} + \text{NO}_2$) and combustion ($\text{D} + \text{C}_2\text{H}_2$, $\text{D} + \text{C}_2\text{H}_4$) reactions; photochemistry of small molecules. Graduate Research Assistant (1987-89) in photoelectron spectroscopy using synchrotron radiation.

University of Science and Technology of China (USTC), 1986-87. Undergraduate Research Assistant.

Honors and Awards

UC Regents' Faculty Fellowships and Faculty Development Award, UC Riverside	1996/1998
The Camille and Henry Dreyfus New Faculty Award	1996
Guo Muo-Ruo Award (Highest Honors of a graduate of USTC)	1987
Yilida Award in Experimental Chemistry, Hong Kong	1986

Professional Memberships

American Chemical Society
American Physical Society
American Association for the Advancement of Science

Selected Publications

J. Zhang and Y.T. Lee, Crossed Molecular Beam Study of the Reaction $\text{Cl} + \text{O}_3$. *J. Phys. Chem.* **101**, 6485 (1997).

J. Zhang, T.T Miao and Y.T. Lee, Crossed Molecular Beam Study of the Reaction $\text{Br} + \text{O}_3$. *J. Phys. Chem.* **101**, 6922 (1997).

K. Xu and J. Zhang, Photodissociation of Vinyl Radical (C_2H_3) via the First Excited State: the $\text{C}_2\text{H}_2(\tilde{\text{X}}^1\Sigma_g^+) + \text{H}$ Channel. *J. Chem. Phys.* **111**, 3783 (1999).

K. Xu, G. Amaral and J. Zhang, Photodissociation Dynamics of Ethanol at 193.3 nm: The H-atom Channel and Ethoxy Vibrational Distribution. *J. Chem. Phys.* **111**, 6271 (1999).

S.D. Chambreau, J.C. Traeger, J. Zhang and T.H. Morton, Photoionization of Methyl *tert*-butyl Ether (MTBE) and *tert*-octyl Methyl Ether (TOME) and Analysis of Their Pyrolyses by Supersonic Jet/Photoionization Mass Spectrometry. *Int. J. Mass Spec.* (in press).

L. Wang and J. Zhang, Detection of Nitrous Acid (HONO) by Cavity Ring-down Spectroscopy, *Environ. Sci. & Tech.* (submitted).

Other Significant Publications

B.A. Balko, J. Zhang and Y.T. Lee, 193 nm Photodissociation of 1,1 and 1,2 Difluoroethylene. *J. Phys. Chem.*, **101**, 6611 (1997).

M.J. Dulligan, M.F. Tuchler, J. Zhang, A. Kolessov and C. Wittig, HCO Rotational Excitation in the Photoinitiated Unimolecular Decomposition of H_2CO . *Chem. Phys. Lett.* **276**, 84 (1997).

J. Zhang, K. Xu and G. Amaral, Photodissociation of HN_3 at 248 nm, in *Laser Techniques in Chemical Physics, SPIE Proceedings*, Vol. **3271**, 271 (1998).

J. Zhang, K. Xu and G. Amaral, Ultraviolet Photodissociation Dynamics of HN_3 : the $\text{H}+\text{N}_3$ Channel. *Chem. Phys. Lett.* **299**, 285 (1999).

Collaborators in the past 48 months: None

Current Graduate Students: Gabriel Amaral, Kesheng Xu, Steve Chambreau, Liming Wang, and Peter Wong

Total number of Graduate Students: 5

PI's Graduate Advisor: Prof. Yuan T. Lee, University of California at Berkeley

PI's Postdoctoral Advisor: Prof. Curt Wittig, University of Southern California

John T. Pisano
Senior Development Engineer

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Education

B.App.Sc., Applied Physics, McMaster University, 1983.

M.Sc., Atmospheric Physics, York University, 1997.

Professional and Academic

2000-present. University of California, Riverside. Senior Development Engineer, specializing in measurements of emissions and ambient pollutants using advanced spectroscopic techniques.

1996-2000. Unisearch Associates Inc., Concord, Ontario, Canada. Technical Sales Manager.

1985-96. Scintex Ltd./Unisearch Associates Inc., Concord, Ontario, Canada. Research Engineer.

1983-95. Chromollay Photographic Corporation Inc., Malton, Ontario, Canada. Engineering Supervisor.

Selected Publications

Fitz, D.R.; Pisano, J.T.; and Tuazon, E.C. (2001) Comparison of Methods for Measuring Nitric Acid in Southern California. Submitted to Atmospheric Environment in July, awaiting review.

Fitz, D.R.; Pisano, J.T.; Goorahoo, D.; Krauter, C.F.; and Malkina, I.L. (2001) A Passive Flux Denuder for Evaluating Emissions of Ammonia at a Dairy Farm. Submitted to Science World, September 2001, awaiting review of revisions.

Pisano, J.T.; Drummond, J.W.; and Hastie, D. (1996) A Lightweight NO₂ Instrument for Vertical Height Profiles. Atmospheric and Oceanic Technology 13(2):400-405.

Pisano, J.T.; McKendry, I.; Steyn, D.G.; and Hastie, D.R. (1996) Vertical Nitrogen Dioxide and Ozone Concentrations Measured from a Tethered Balloon in the Lower Fraser Valley. Atmospheric Environment 30(12):2125-2132.

Abbe, A.; Pisano, J.T.; and Franz, M. (1999) Gegenuberstellung von drei Verfahren zur Messung der HF Emission. Erzmetall 52(9):465-471.

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Pisano, J.T.; Mackay, G.; Kimmerle, F.M.; and Noel, L. (1997) COS, CS₂ and SO₂ Emissions from Prebaked Hall Heroult Cells. Light Metals, 153-157.

Schiff, H.I.; Nadler, S.D.; Pisano, J.T.; Mackay, G.I.; and Tsiboulia, A. (1997) Measurements of HF in Stacks and Pot Rooms Using a Remote Sensing Laser. *Light Metals*, 361-365.

Schiff, H.I.; Bechara, J.; Pisano, J.T.; and Mackay, G.I. (1994) Measurements of CF₄ and C₂F₆ in the Emissions from Aluminum Smelters. *Air and Waste Management Paper A243*, Cincinnati, OH, June.

Awards and Honors

- Best Paper Award, The Light Metals Section of the Metallurgical Society of CIM, 2001
- McMaster University Merit Scholastic Award 1980

Claudia G. Sauer**Postdoctoral Researcher**

CE-CERT 022, University of California, Riverside, CA 92521-0434 sauer@cert.ucr.edu

Education

Ph.D., Atmospheric Chemistry/Spectroscopy, University Wuppertal, Germany

Diplom-Chemikerin (M.S.), Chemistry, University Wuppertal, Germany

Vordiplom Chemie (B.S.), Chemistry, University Wuppertal, Germany

Professional and Academic

2000-present. University of California, Riverside, Postdoctoral Researcher. Projects have included development and operation of measurement systems for the “next-generation” atmospheric chamber and other air quality measurement projects.

1996-2000. Bergische Universität-Gesamthochschule Wuppertal, Germany, FB 9 – Physikalische Chemie, Scientific Employee.

1994-96. Bergische Universität-Gesamthochschule Wuppertal, Germany, FB 9 – Physikalische Chemie. Scientific Assistant

Selected Publications

Sauer, C.G.; Pisano, J.T.; and Fitz, D.R. (2002) TDLAS Measurements of Ambient Nitrogen Dioxide, Nitric Acid, Formaldehyde, and Hydrogen Peroxide During CCOS 2000. In preparation.

Sauer, C.G.; Barnes, I.; and Becker, K.H. (2002) Atmospheric Degradation of Dimethoxymethane in the Absence of Nitrogen Oxides. *Journal of Atmospheric Chemistry*, to be submitted.

Thüner, L.P.; Barnes, I.; Maurer, T.; Sauer, C.G.; and Becker, K.H. (1999) Kinetic Study of the Reaction of OH with a Series of Acetals at 298 ± 4 K *International Journal of Chemical Kinetics* **31/11**:797-803.

Sauer, C.G.; Barnes, I.; Becker, K.H.; Geiger, H.; Wallington, T.J.; Christensen, L.K.; Platz, J.; and Nielsen, O.J. (1999) Atmospheric Chemistry of 1,3-Dioxolane: Kinetic, Mechanistic, and Modeling Study of OH Radical Initiated Oxidation. *Journal of Physical Chemistry A* **103/30**:5959-5966.

Sauer, C.G.; Barnes, I.; and Becker, K.H. (1999) FT-IR Kinetic and Product Study of the Br-radical Initiated Oxidation of α , β -unsaturated Organic Carbonyl Compounds. *Atmospheric Environment* **33**:2969-2979.

Platz, J.; Christensen, L.K.; Sehested, J.; Nielsen, O.J.; Wallington, T.J.; Sauer, C.; Barnes, I.; Becker, K.H.; and Vogt, R. (1998) Atmospheric Chemistry of 1,3,5-Trioxane: UV Spectra of $c\text{-C}_3\text{H}_5\text{O}_3(\cdot)$ and $(c\text{-C}_3\text{H}_5\text{O}_3)\text{O}_2(\cdot)$ Radicals, Kinetics of the Reactions of $(c\text{-C}_3\text{H}_5\text{O}_3)\text{O}_2(\cdot)$ Radicals

with NO and NO₂, and Atmospheric Fate of the Alkoxy Radical (c-C₃H₅O₃)O(·). *Journal of Physical Chemistry A* **102**:4829-4838.

5. Budget

A. Funding Request

The total cost of the proposed project, which includes development of the LIF and the CA systems, is \$470,624. The cost of the LIF approach alone is \$299,918. Detailed summary budgets are provided on the following pages.

Note that the project period spans October 2002 to December 2003. We estimate that the proposed research will require 12 months. To avoid the potential need for a no-cost extension, however, we have proposed an extra three months in the period of performance.

Approximately \$300,000 of the proposed funding will be used to develop and integrate the laser-induced fluorescence (LIF) instrumentation in the chamber. The remaining funds are proposed for the chemical amplifier (CA) system development and instrumentation.

B. Co-Funding

The U.S. Environmental Protection Agency has allocated \$2.9 million for 1999-2003 for development and initial operation of the new CE-CERT atmospheric chamber. This project will be fundamentally complete in January 2003. Therefore, a portion of EPA funding (~\$80,000) can be counted as concurrent co-funding for AQMD funds.

Follow-on funding from the EPA has been proposed, and a decision is pending. The follow-on funding also can be counted toward co-funding, although the amounts and precise timing will not be known for a few more months.

The California Air Resources Board (CARB) has committed \$300,086 to a project titled "Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions" (contract 00-333) over a project period of June 2001 to May 2005. Additional funding for a limited number of chamber experiments is also provided by the CARB project titled "Development and Evaluation of a Gas-Phase Reaction Mechanism for low NO_x Conditions" (Contract 01-305). The concurrent portion of this funding also can be applied as co-funding. The experiments to be conducted in the ARB-sponsored project will be used for application of the instrumentation proposed here.

The related projects that will be providing this significant co-funding are described in Section 7, below.

LIF ONLY

Project: Chamber Investigation of Radical Budget and Oxidant Photochemistry at Ambient Condition
Agency: South Coast AQMD
Institution: UC Riverside CE-CERT and Dept. of Chemistry (off-campus proposal)
Project Period: 10/1/02-12/31/03

Base Budget**LIF APPROACH ONLY**

<u>PERSONNEL</u>	<u># MO</u>	<u># People</u>	<u>% TIME</u>	<u>MONTHLY RATE</u>	<u>SALARY</u>	<u>BENEFIT RATE</u>	<u>FRINGE</u>	<u>TOTAL</u>
Gail S. Tonnesen Co-Principal Investigator (CE-CERT)								
10/1/02-12/31/03	12	1	10%	6,838	8,206	17.00%	1,395	9,601
William Carter Co-Principal Investigator (CE-CERT)								
10/1/02-12/31/03	12	1	10%	8,580	10,296	17.00%	1,750	12,046
Jingsong Zhang Co-Principal Investigator (Chemistry)								
10/1/02-12/31/03	2	1	100%	6,838	13,676	17.00%	2,325	16,001
John Pisano Senior Development Engineer (CE-CERT)								
10/1/02-12/31/03	12	1	40%	5,401	25,925	22.00%	5,703	31,628
Claudia Sauer Postdoctoral Researcher								
10/1/02-12/31/03	12	1	15%	3,350	6,030	17.00%	1,025	7,055
TBD Graduate Students								
10/1/02-6/30/03	0	2	50%	3,000	0	1.30%	0	0
7/1/03-9/30/03	0	2	100%	3,000	0	3.00%	0	0
Mitch Boretz Technical Planning Manager								
10/1/02-12/31/03	12	1	5%	6,073	3,644	22.00%	802	4,445
TBD Undergraduate Student Assistant								
10/1/02-12/31/03	0	1	20%	1,800	0	1.30%	0	0
TOTAL PERSONNEL					67,776		13,000	80,777

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SUPPLIES & EXPENSES					6,000
BC44 Misc. printing, copying, mailing, publishing				500	
BC44 Misc. chamber materials and supplies				5,500	
COMMUNICATIONS/CONNECTIVITY					199
	FTEs	Rate	Total		
Computing fee, faculty/staff, yr 1	9.6	20.750	199		
Computing fee, undergraduate	0	10.375	-		
SUBTOTAL 1					86,976
EQUIPMENT					171,650
Components for construction of LIF					
YAG Laser (Spectra Physics, T40-X30S-532Q)				58,850	
Tunable dye laser (Lambda Physik Scanmate I)				63,800	
Frequency doubling system				15,000	
Optics and photon detection system				12,000	
Data acquisition system				10,000	
Fluorescence cell and pumping system				7,000	
Calibration cell				5,000	
SUBTOTAL 2					258,626
OTHER					19,200
Facilities Rental (Prorated on a full time equivalent basis)					
Office Space: 1000 sq. ft.	x 2.00	12	0.80	19,200	
TOTAL DIRECT COSTS					277,826
INDIRECT COSTS					
	25.40%	of Modified Total Direct Costs		86,976	22,092
TOTAL PROJECT COST					299,918

LIF + CA

Project: Chamber Investigation of Radical Budget and Oxidant Photochemistry at Ambient Conditions
Agency: South Coast AQMD
Institution: UC Riverside CE-CERT and Dept. of Chemistry (off-campus proposal)
Project Period: 10/1/02-12/31/03
Base Budget

<u>PERSONNEL</u>	<u># MO</u>	<u># People</u>	<u>% TIME</u>	<u>MONTHLY RATE</u>	<u>SALARY</u>	<u>BENEFIT RATE</u>	<u>FRINGE</u>	<u>TOTAL</u>
Gail S. Tonnesen Co-Principal Investigator (CE-CERT) 10/1/02-12/31/03	12	1	10%	6,838	8,206	17.00%	1,395	9,601
William Carter Co-Principal Investigator (CE-CERT) 10/1/02-12/31/03	12	1	10%	8,580	10,296	17.00%	1,750	12,046
Jingsong Zhang Co-Principal Investigator (Chemistry) 10/1/02-12/31/03	2	1	100%	6,838	13,676	17.00%	2,325	16,001
John Pisano Senior Development Engineer (CE-CERT) 10/1/02-12/31/03	12	1	40%	5,401	25,925	22.00%	5,703	31,628
Claudia Sauer Postdoctoral Researcher 10/1/02-12/31/03	12	1	67%	3,350	26,934	17.00%	4,579	31,513
TBD Graduate Students 10/1/02-6/30/03 7/1/03-9/30/03	9 3	2 2	50% 100%	3,000 3,000	27,000 18,000	1.30% 3.00%	351 540	27,351 18,540
Mitch Boretz Technical Planning Manager 10/1/02-12/31/03	12	1	5%	6,073	3,644	22.00%	802	4,445
TBD Undergraduate Student Assistant 10/1/02-12/31/03	12	1	20%	1,800	4,320	1.30%	56	4,376
TOTAL PERSONNEL					138,000		17,501	155,501

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SUPPLIES & EXPENSES					25,000
BC44 Misc. printing, copying, mailing, publishing				1,000	
BC44 Misc. chamber materials and supplies				24,000	
COMMUNICATIONS/CONNECTIVITY	FTEs	Rate	Total		665
Computing fee, faculty/staff, yr 1	30.84	20.750	640		
Computing fee, undergraduate	2.4	10.375	25		
SUBTOTAL 1					181,166
EQUIPMENT					201,650
Components for construction of LIF					
YAG Laser (Spectra Physics, T40-X30S-532Q)			58,850		
Tunable dye laser (Lambda Physik Scanmate I)			63,800		
Frequency doubling system			15,000		
Optics and photon detection system			12,000		
Data acquisition system			10,000		
Fluorescence cell and pumping system			7,000		
Calibration cell			5,000		
Components for construction of Chemical Amplifier					
NO2 detector			15,000		
Valves, pumps, and reaction chamber			15,000		
SUBTOTAL 2					382,816
OTHER					41,792
Facilities Rental (Prorated on a full time equivalent basis)					
Office Space: 1000 sq. ft.	x 2.00	12	1.32	31,680	
Graduate student partial fee remission and health insurance (2 studer				10,112	
TOTAL DIRECT COSTS					424,608
INDIRECT COSTS	25.40%	of Modified Total Direct Costs		181,166	46,016
TOTAL PROJECT COST					470,624

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7. Related Programs

This proposal has a significant level of co-funding from an EPA and two California Air Resources Board projects that are summarized in this section. The EPA project is covering the cost of constructing the facility that will be used for the proposed instrumentation, and will cover a significant portion of the costs of the characterization experiments and measurements needed to use the data for model evaluation. The CARB projects cover the costs for experiments for which measurements with the proposed instrumentation would serve the objectives of this proposal. Given below is a summary of period of performance, amounts, objectives and status of these projects.

Title: **DEVELOPMENT OF A NEXT-GENERATION ENVIRONMENTAL CHAMBER FACILITY FOR CHEMICAL MECHANISM AND VOC REACTIVITY EVALUATION**

Agency: United States Environmental Protection Agency

Period: 6/1/99 - 6/30/03

Amount: \$2,925,000

Status: Funded. EPA Cooperative Agreement No. CR 827331-01-0

Objectives and progress: The objectives are to develop the next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining secondary aerosol yields, and for measuring VOC reaction products indicator species under more realistic and varied environmental conditions than previously has been possible. The facility will then be employed to provide data that are most relevant to today's pollution problems and control strategy issues.

Information about the status and project is available at <http://www.cert.ucr.edu/~carter/epacham>. The new chamber facility has been designed and constructed and housed in a new building designed for this purpose, and the major analytical equipment was acquired. These are currently being evaluated. A successful international workshop on chamber research was held and a draft research plan was developed and submitted to the EPA and the Reactivity Research Working Group. A number of experiments were carried out to evaluate chamber effects that need to be minimized, and methods to conduct experiments at very low NO_x levels were developed. Experiments with the reactor and light source in near-final configuration were carried out beginning in February, 2002, and construction of the final configuration and a second reactor should be completed by September.

As with most complex development projects, the level of effort required to construct and evaluate the new facility was somewhat greater than initially hoped,

and additional funding will be needed to complete the research plan. However, the remaining funding should be sufficient to complete chamber characterization, so experiments from the CARB projects can be used for model evaluation.

Title: **EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS.**

Agency: California Air Resources Board

Period: 6/30/01 – 6/29/04

Amount: \$300,113, of which about \$205 K is available for ~50 chamber runs

Status: Funded. CARB Agreement No. 00-333

Objectives: The purpose of this three-year project is to carry out priority research needed to reduce uncertainties in ozone reactivity estimates for selected major types of Coatings VOCs. The project will be carried out in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee. The specific tasks include the following:

- Further develop and evaluate the direct reactivity method developed under the current ARB and ACC projects so they can be applied to low volatility materials.
- Utilize the new environmental chamber facility being developed for the EPA to investigate the ozone and other atmospheric impacts of 2,2,4-trimethyl-1,3-pentanediol isobutyrate (trade name Texanol®), which is widely used in water-based coatings. This will require developing procedures for conducting environmental chamber experiments for low volatility materials such as this.
- Develop improved procedures for estimating ozone impacts of various types of petroleum distillates and quantifying uncertainties of reactivity estimates for these materials in cases where limited data are available.

Conduct environmental chamber experiments to determine the effects of at least five selected types of coatings constituents on ozone and PM formation under a range of reactant concentrations. At least four of these would be selected types of petroleum distillates representing different reactivity ranges, but an additional water-based coatings constituent may also be studied. The results will then be used to evaluate the predictions of existing and updated atmospheric reaction mechanisms or reactivity estimation methods for this compound or mixture.

- Apply the direct reactivity screening method to the full range of compounds and petroleum distillates being used or considered for use in architectural coatings in California.

The priorities for specific compounds or mixtures to be studied will be determined as part of the overall project, in conjunction with discussions with the CARB staff and the CARB Reactivity Research Advisory Committee. The procedures to be developed under CARB contract 00-333 to assess reactivities and uncertainties in petroleum distillates, along with results of market surveys and input from industry groups, will be used to guide the selection of specific types of petroleum distillates chosen for study.

Title: **DEVELOPMENT AND EVALUATION OF A GAS-PHASE
ATMOSPHERIC REACTION MECHANISM FOR LOW NO_x
CONDITIONS**

Period: 12/1/01 - 11/30/04

Amount: \$79,884, of which about \$35 K is available for 7-9 chamber runs

Status: Funded. CARB Agreement No. 01-305

Objectives: The purpose of this project is to evaluate and improve the performance of the SAPRC chemical mechanism for simulating atmospheric transformations under low and very low NO_x conditions. The specific objectives will include the following:

- Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism that is designed to more accurately predict organic product formation under very low NO_x conditions.
- Evaluate the performance of both the standard and the low NO_x versions of the SAPRC-99 mechanism in simulating available environmental chamber simulating low NO_x conditions, including TVA and CSIRO chamber experiments not used previously in SAPRC mechanism evaluation.
- Utilize the new environmental chamber facility being developed under EPA funding to carry out selected low NO_x mechanism evaluation experiments deemed to be the most useful for mechanism evaluation in the near term.
- Update or modify the mechanisms as appropriate based on the results of the evaluation against chamber data and other data that may become available.

The results of this study will then be used to develop recommendations concerning mechanisms to use when modeling low NO_x conditions in regional model simulations, and priorities for future research aimed at reducing uncertainties in chemical mechanisms used in regulatory and research applications.