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<b>14. ABSTRACT</b> This project investigates the explosive combustion of aerosol fuels using a single particle mass spectrometer. Initiating explosive reactions of small samples (~10 <sup>-12</sup> grams) in vacuum allows the intermediate products of the reaction to escape into a collisionless region where we detect them using laser spectroscopy. Recent results from our laboratory explore the mechanism of amine sensitization in nitromethane. We initiate the decomposition of nitromethane/diethylamine aerosols using a CO <sub>2</sub> laser and observe the intermediates of the reaction using laser ionization coupled with time-of-flight mass spectroscopy. The laser ionization source is a vacuum-ultraviolet laser developed using funds from this grant, and it enables near threshold ionization of most radical reaction intermediates. We find that reactions of the aci-anion of nitromethane, formed in an acid-base equilibrium with the amine, are critical in the sensitization mechanism.					
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# The Mechanism and Dynamics of Explosive Combustion in Aerosol Fuels

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## FINAL REPORT

### 2. Objectives:

This research investigates the explosive combustion of aerosol particles (diameter of 1-10  $\mu\text{m}$ ) in the high vacuum environment of a laser time-of-flight mass spectrometer as well as in the medium pressure (1-2 atmospheres) environment of a flow tube. Pulsed infrared radiation from a  $\text{CO}_2$  laser initiates the reaction in both cases. The use of small samples in the form of aerosols permits reaction intermediates to escape the reaction volume and we detect them using laser spectroscopic methods traditionally used in the study of unimolecular and bimolecular reaction dynamics. In the low-pressure studies, we follow the time evolution of the reaction intermediates and/or products using time delayed ionization with a vacuum ultraviolet (VUV) laser and time-of-flight (TOF) mass analysis, or by laser-induced fluorescence of specific products such as OH, HONO, and NO. In the medium pressure environment, a step-scan FTIR spectrometer with a time resolution of 0.01  $\mu\text{s}$  monitors the reaction products. Although the different pressures result in different reaction environments, the data from the two experiments are complimentary. In addition, we can control the extent of the explosive reaction by varying the particle size. The smaller the aerosol, the more readily will intermediates escape, and by varying the particle size ( $10^{-11}$  to  $10^{-14}$  grams) we can investigate the reaction mechanisms over a range of reaction steps. Our experiments will also probe the effect of aerosol composition on the reaction mechanism and rate.

### 3. Status of effort:

Since the inception of this grant from AFOSR, we have added a vacuum ultraviolet laser system to our aerosol mass spectrometer facility, greatly enhancing the flexibility and power of the instrument. The system comprises an aerodynamic lens inlet, two stages of differential pumping, a light scattering station, and a laser-based time-of-flight mass spectrometer. An aerosol particle ( $\sim 1 \mu\text{m}$ ) from an external stream enters the aerodynamic lens through a 100  $\mu\text{m}$ , flow-limiting orifice. The aerodynamic lens inlet consists of a series of orifices of successively decreasing diameter, and it focuses aerosol particles onto a well-defined axis, greatly increasing the efficiency with which we detect them. The focused particles accelerate through two stages of differential pumping to speeds on the order of 100 m/s before entering the main chamber. The particles then pass

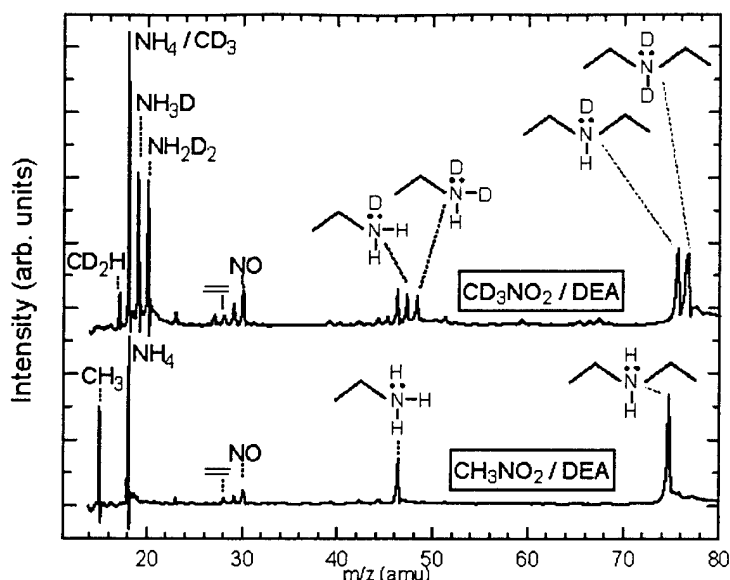
through two 532 nm diode laser beams placed 10 cm apart. Separate photomultiplier tubes detect the scattered light from each diode laser, and a digital timing circuit calculates the velocity of the particle based on the time delay between the two scattered light signals. The circuit then triggers the pulsed lasers to fire when the particle arrives in the spectrometer.

A pulsed TEA - CO<sub>2</sub> laser, which produces 0.2 - 0.8 Joules/pulse of light near 10.6 μm, at once initiates chemistry in the aerosol particle and vaporizes it. After a delay of about 1 μs, a 118.5 nm VUV laser beam, produced by frequency tripling about 20 mJ of the 355 nm output of a Nd:YAG laser in a Xe gas cell, ionizes the vapor cloud for time-of-flight mass analysis. In general, the chemistry we observe produces both neutral and ionic species. *The rapid vaporization induced by the CO<sub>2</sub> laser directly promotes the ionic species into the gas phase, while the VUV laser is needed to ionize the neutral products.* Because the CO<sub>2</sub> and VUV lasers are not coincident in time, we pulse the ion extraction field about 1 ms after the VUV laser pulse so that all the products have the same start time in the time-of-flight spectra.

#### 4. Accomplishments and new findings:

Our initial experiments explored the mechanism of vaporization/ionization in liquid and nitrobenzene aerosols using CO<sub>2</sub> laser evaporation and 193 nm excimer laser ionization. Those experiments were critical in characterizing the capabilities of our apparatus and in laying the framework for the behavior of *non-reactive* species in our two-laser design. The use of multi-photon ionization schemes with the excimer laser resulted in highly fragmented mass spectra, making the identification of reaction products difficult. Therefore, in preparation for studies of more reactive, high-energy materials, we developed a vacuum-ultraviolet (VUV) laser, which ionizes molecules with very little fragmentation. We developed the VUV laser using funds from this grant. The VUV ionization technique makes our approach quite flexible and powerful in the elucidation of reaction mechanisms.

One of the systems we are currently investigating is amine-sensitized nitromethane. Although, the effect of amines on the failure diameter of nitromethane samples was first observed in the 1940's, there is still no consensus on the chemical mechanism of the sensitization. In our work, we can directly observe the intermediate chemical species that form in the early stages of reaction. For example, the bottom trace of Figure 1 shows time-of-flight mass spectra obtained from a mixture of nitromethane with diethylamine (DEA). Some of the species in the spectrum, such as the protonated form of the amine and its decomposition products, NH<sub>4</sub><sup>+</sup> and CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, are ionic species and appear in the spectrum without the VUV laser. Neutral reaction products, like CH<sub>3</sub> and NO, appear only when the VUV laser is present. By comparing this spectrum to one recorded using deuterated nitromethane, we can test proposed mechanisms and extend them. Our results for nitromethane indicate that the acid/base equilibrium of the amine and nitromethane plays a role in the sensitization mechanism. For example, the observation of CD<sub>2</sub>H in the top spectrum strongly suggests that the de-protonated anion of nitromethane *first* abstracts a hydrogen atom from a nearby amine



molecule making  $\text{CD}_2\text{HNO}_2^-$  and then dissociates to form the  $\text{CD}_2\text{H}$  radical. The radical formation is critical in initiating the chain reaction and energy release in the detonation.

**Figure 1.** Time-of-flight mass spectra obtained by initiating the decomposition of nitromethane/diethylamine mixtures using a  $\text{CO}_2$  laser and ionizing the neutral reaction products using VUV.

### 5. Personnel Supported:

The people supported by the grant are:

Dr. Jerry Cabalo (recently graduated Ph.D.)	Research Assistant	100% effort
Dr. Ephraim Woods III (post-doctoral student)	Research Associate	100% effort
Mr. Yury Dessiaterik (graduate student)	Research Associate	100% effort
Mr. Jay Raval (senior undergraduate)		
Prof. Roger Miller (co-PI)		10% effort
Prof. Tomas Baer (co-PI)		10% effort

### 6. Publications:

*Mass Spectrometry of Liquid Aniline Aerosol Particles by IR/UV Laser Irradiation*,  
A.Zelenyuk, J. Cabalo, T. Baer, and R.E. Miller, *Anal. Chem.* **1999**, *71*, 1802-1808.

*Two-Color Laser Time of Flight Mass Spectrometry of Single Aerosol Particles*  
J. Cabalo, A. Zelenyuk, T. Baer, and R.E. Miller, *Aerosol Science and Technology* (to be submitted)

*\*\*Direct Observation of Reaction Intermediates in the Decomposition of Liquid Nitromethane/Diethylamine Mixtures, (manuscript in preparation).\*\**

*\*\*Quantitative Characterization of Organic Aerosols using CO<sub>2</sub> Laser Evaporation and VUV Laser Ionization Coupled with Time-of-flight Mass Spectroscopy, (manuscript in preparation).\*\**

## **7. Interactions:**

### **Seminars:**

Jerry Cabalo, *Two-Color Desorption-Ionization Laser Time of Flight Mass Analysis of Aerosol Particles* 17th Annual American Association for Aerosol Research meeting, Cincinnati, Ohio, June 22-26, 1998

Roger Miller, *Combustion and Atmospheric Aerosols: Laboratory Studies using Laser - Mass Spectrometry* invited talk at University of Bonn, Germany, July 7, 1998

Tomas Baer, *Blasting Single Aerosol Particles with Laser Light* invited talk at Wake Forest University, Winston Salem, September 23, 1998

### **Poster Presentations:**

Jerry Cabalo, *Two-Color Desorption-Ionization Laser Time of Flight Mass Analysis of Aerosol Particles*, NATO Advanced Study Institute on Energetics of Stable Molecules and Reactive Intermediates at Castelo Branco, Portugal, July 14-24, 1998

Alla Zelenyuk, *Mass Spectrometry of Liquid Aniline Aerosol Particles by IR/UV Laser Irradiation*, International Aerosol Conference, in Edinburgh, Scotland

Ephraim Woods III, *Exploring the Mechanisms and Dynamics of Explosive Combustion Through Single Particle Analysis*, AAAR Annual Conference, Tacoma, WA, November 1999.