

**SPECTROSCOPY AND KINETICS OF INTERMEDIATES
IMPORTANT IN NITRAMINE DECOMPOSITION**

FINAL REPORT

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TABLE OF CONTENTS

	Page
I. Statement of Work and Description of Work Accomplished	1
A. Spectroscopy and Kinetics of the Methylene Amidogen Radical	1
B. The Electronic Spectrum of the Methyleneimine Molecule	5
C. Implementation of Cavity Ring-Down Spectroscopy in the IR	7
D. Kinetic and CFD Modeling of the LIBS Plume	9
II. Literature Citations	11
III. List of Publications Prepared under ARO Grant DAAD19-02-1-0323	14
IV. List of Participating Scientific Personnel	14
V. List of Inventions	14

I. STATEMENT OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

This project has mainly involved investigation of the spectroscopy and kinetics of several important polyatomic intermediates in the decomposition of nitramines. These studies were carried out through the use of the recently developed technique of cavity ring-down spectroscopy (CRDS),^{1,2} which is very sensitive means of performing absorption spectroscopy with a very long effective path length in a table-top apparatus. CRDS experiments were initially carried on electronic transitions in the UV and, more recently, on vibrational transitions in the IR.

In addition, the Principal Investigator has been working with Drs. Andrzej W. Miziolek, Frank DeLucia Jr., and Michael J. Nusca at the Army Research Laboratory, Aberdeen Proving Ground, MD, as well as Dr. Valeri I. Babushok (NIST) in the kinetic modeling of the process of laser-induced breakdown spectroscopy (LIBS). LIBS provides an analytical capability for the non-destructive, rapid and sensitive testing of a variety of materials.^{3,4} The goal of this collaborative project is the development of kinetic and computational fluid dynamics (CFD) models for modeling of the processes that are responsible for the generation of LIBS signal.

The following sections describe the specific projects carried out and brief discussions of the results obtained.

A. Spectroscopy and Kinetics of the Methylene Amidogen Radical

The methylene amidogen radical (H_2CN) is an important species in the dark zone and was observed many years ago in the vapors above decomposing HMX by ESR spectroscopy.⁵ Marston and Steif⁶ reviewed the spectroscopic and kinetic data available on H_2CN as of 1989. Electron-impact ionization through a sampling port in a flow tube was employed by Stief and co-workers for the measurement of rate constants of some elementary bimolecular reactions of H_2CN .

Sensitive spectroscopic detection of H_2CN has proven to be problematic. The vibrational spectrum has been observed for matrix-isolated H_2CN by Jacox.⁷ Flash photolysis studies utilizing formaldoxime (H_2CNOH) and formaldazine ($\text{H}_2\text{CN-NCH}_2$) as precursors identified electronic absorptions in the spectral region around 280 nm.^{8,9} However, the excited states of these transitions predissociate,¹⁰ and the excited molecule falls apart to yield $\text{H} + \text{HCN}$ fragments.¹¹ This precludes the use of fluorescence excitation as a diagnostic for H_2CN .

There have been several recent quantum chemical studies of the ground and low-lying excited electronic states of H_2CN .^{12,13} The ground \tilde{X}^2B_2 electronic state has planar C_{2v} geometry, and the low lying excited states have 2B_1 , 2A_1 , and 2B_1 symmetry.

The ${}^2A_1 \leftarrow \tilde{X}{}^2B_2$ transition is electric-dipole allowed and was recently assigned by Eisfeld to the 280 nm transition through high-quality quantum chemistry calculations,¹³ in contrast to previous assignments as the vibronically allowed, but electric-dipole forbidden ${}^2B_1 \leftarrow \tilde{X}{}^2B_2$ transition to the lowest excited state. In our laboratory, we have employed CRDS on the 280 nm electronic transition for spectroscopic and kinetic studies on H_2CN .¹⁴ The radical was prepared by 193 nm photolysis of formaldoxime (H_2CNOH). This precursor is convenient because both photolytic fragments, H_2CN and OH , can be spectroscopically observed near 280 nm [the latter through its $A - X(1,0)$ band]. We had previously observed the OH fragment by laser fluorescence detection.¹⁰

Since H_2CN does not fluoresce, we applied the technique of CRDS to observe this species through absorption, so that we could use this spectroscopic diagnostic for concentration measurements in kinetics studies. In CRDS experiments, the photon decay lifetime in an optical cavity is monitored, and absorption is detected by observing a reduction in this lifetime. As in the early flash photolysis experiments,^{8,9} the room-temperature CRDS spectrum of H_2CN displays two broad features centered at 285 and 281 nm, with additional structure on each.¹⁴ We defer discussion of our spectroscopic analysis and first describe our kinetic studies.

In order to be able to make quantitative measurements of the H_2CN concentration, we have determined the absorption cross section at 285 nm.¹⁴ Two different techniques were employed. The first involved estimating the H_2CN concentration from the 193 nm absorption cross section of the precursor and the estimated photolysis laser photon flux, in combination with the observed H_2CN absorbance. The second method involved comparing the observed absorbances of the H_2CN and OH fragments, and using the known¹⁵ absorption cross section for the $OH A - X(1,0)$ band. We make the assumption that the quantum yields for formation of H_2CN and OH are both unity. Since the OH fragment reacts with the residual formaldoxime,¹⁴ we also took into account the reduction of the OH concentration in the time between the photolysis and probe laser pulses through this reaction. The derived absorption cross section from both methods were in good agreement.

With mass spectrometric detection, Stief and co-workers¹⁶ reported room-temperature rate constants for the $H + H_2CN$ and $N + H_2CN$ reactions. We have employed CRDS to investigate further the room-temperature kinetics of H_2CN reactions. In our initial work, we have measured the room-temperature H_2CN self-recombination rate constant in 5 Torr argon.¹⁴ With the derived absorption cross section, we determine a value of $(7.7 \pm 2.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this rate constant.¹⁴ We have also attempted to observe reactions of H_2CN with a number of stable molecules (O_2 , C_2H_4 ,

CO, CH₄, H₂) at room temperature. The reagents were added to H₂CN/Ar mixtures, and we looked for alteration of the H₂CN time-dependent concentration from self-recombination. We were not able to observe any reaction over and above the self-recombination and set an upper limit of $< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the bimolecular rate constants of H₂CN with these reagents. We were precluded from studying the important H₂CN + NO₂ reaction since NO₂ absorbs strongly in the visible and UV.

By photolyzing a large fraction of the H₂CNOH precursor, we have also been able to derive an estimate of the rate constant for the OH + H₂CN reaction.¹⁴ In this case, the size of the photolysis zone was reduced while keeping the photolysis laser energy the same. We compared the time dependence of the decay of the OH concentration (measured by laser fluorescence detection) with a low and high fractional dissociation of the precursor, while also measuring the time-dependent H₂CN concentration. From these data, we estimate the OH + H₂CN room-temperature rate constant to be $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In order to investigate the reaction kinetics of H₂CN at elevated temperatures, we have constructed a new CRDS apparatus suitable for such studies. This apparatus, in which the reaction zone can be heated to ~500 °C, is illustrated in Fig. 1. Within this heated region, an excimer laser crosses at a small angle with the CRDS beam path to prepare H₂CN photolytically over a several cm path length. This apparatus employs higher reflectivity mirrors than in our initial study,¹⁴ which provides a higher CRDS detection sensitivity.

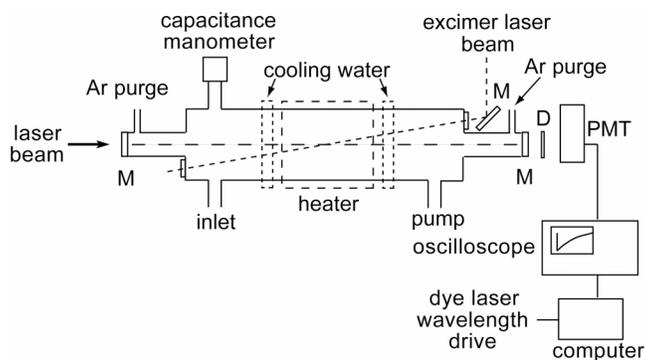


Fig 1. Schematic diagram of our high-temperature cavity ring-down apparatus. M denotes high-reflectivity mirrors, D diffuser.

We would like to employ this apparatus for the investigation of the unimolecular thermal decomposition of H₂CN, as well as bimolecular reactions of H₂CN, at elevated temperatures. These high-temperature studies have been limited by the low total pressures we can achieve with formaldoxime as the photolytic precursor and still detect

H₂CN by CRDS. Formaldoxime exists as a polymeric solid, which must be heated to 50°C in order to generate the monomer in the gas phase. We found it difficult to mix the monomeric vapor with a buffer gas to achieve sufficiently high partial pressures of formaldoxime for CRDS detection of H₂CN in ≥ 100 Torr of buffer gas, as we would like for the kinetics experiments. The measured decays in H₂CN concentration appear to be dominated by diffusion out of the probe laser beam at our current operating pressures.

We will be investigating an alternative source of monomeric formaldoxime. The pyrolysis of *t*-butyl nitrite, (CH₃)₃CONO, is known to yield nitrosomethane, CH₃NO.¹⁷ Nitrosomethane, in turn, is found to isomerize to formaldoxime.¹⁸ Pyrolysis of TBN should be convenient for our kinetic studies since TBN is a volatile liquid and can be mixed with a buffer gas at arbitrary total pressures. We should be able to monitor the decomposition of TBN, and the CRDS detection of the formaldoxime precursor and photolytically generated H₂CN, in our high-temperature apparatus (Fig. 3) by CRDS in the IR (see Sec. I.C).

We have been collaborating with W. Eisfeld, a quantum chemist at Tech. U. Munich, Germany, and author of the most recent theoretical study on H₂CN,¹³ to resolve the uncertainties about the electronic spectrum of H₂CN. Eisfeld interprets the two features in the electronic spectrum of H₂CN as vibronic transitions associated with excitation of the ground vibrational level and $v=2$ of the ν_4 (b_1) umbrella mode in the second excited (2A_1) state. It is well known that the rotational structure of a polyatomic band can be analyzed to determine the inertial axis along which the transition moment lies,²⁰ and hence the symmetry relation between the upper and lower electronic states. We compared the experimentally observed rotational contours of the two observed bands with simulations based on computed rotational constants. Since the excited-state potential energy surface is floppy in the umbrella coordinate, Eisfeld has computed rotational constants by appropriate averaging over this motion in the upper and lower states.

Figure 2 presents a comparison of experimental and simulated spectra for the two observed bands of H₂CN. From the symmetry of the upper and lower electronic states, the transition moment for the $^2A_1 \leftarrow \tilde{X}^2B_2$ transition lies along the b inertial axis. It can be seen that the simulated spectra reproduce our observations very well and provide definitive proof to this electronic assignment. Simulations with the transition moment assumed to lie along the a or c axes disagree greatly with the experimental spectrum. The differences in the rotational contours of the origin and $2b_1$ bands results from the dependence of the excited-state rotational constants upon the umbrella coordinate. Evidence for excited-state dissociation comes from the Lorentzian width (FWHM

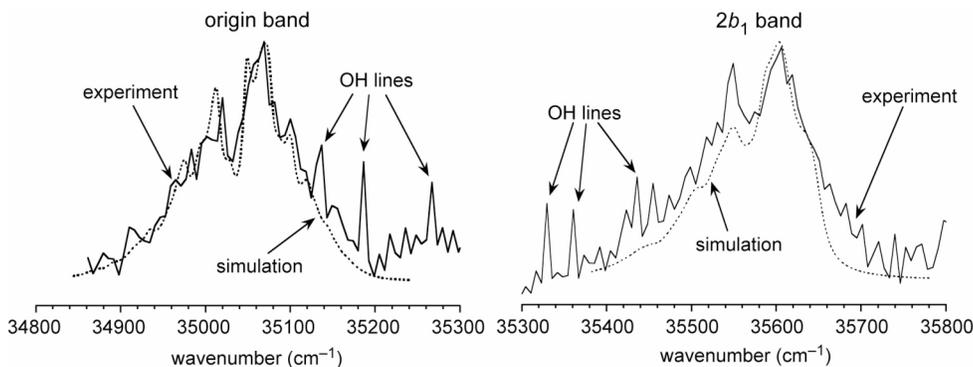


Fig 2. Comparison of experimental and simulated bands in the room-temperature electronic spectrum of H_2CN . To account for excited-state predissociation, a Lorentzian width of 10 cm^{-1} was assumed. Lines due to the OH co-fragment from the photolysis of formaldoxime are also observed in the spectrum.

10 cm^{-1}) needed in the simulations to fit the experimental spectrum. This spectral width corresponds to a lifetime of 0.5 psec. We will be writing a joint paper with Eisfeld to describe this proof of the electronic assignment, with calculations and comparison with experimental spectra.

Two points remain to be unraveled in the electronic spectrum of H_2CN . The first is that only two bands are observed, while Franck-Condon considerations suggest that there should be more bands at higher excitation energy. At the energies of the origin and $2b_1$ bands, there appears to be a barrier to direct excited-state dissociation, and internal conversion to the ground electronic state must occur before dissociation. The absence of higher-energy bands could be due to direct excited-state dissociation; this would lead to a broadening of the bands, and perhaps washing them out into the background.

The other point to be clarified is that the origin band appears to have a slightly different contour at higher pressures. For example, the spectrum in Fig. 2 differs slightly with our published¹⁴ spectrum, which was recorded at significantly higher concentrations. Similar differences are seen in the molecular beam H atom photofragment action spectrum of Davis and co-workers¹¹ and the original flash photolysis spectrum.⁹ We plan to carry out further study in order to sort out the possible pressure dependence of the spectrum.

B. The Electronic Spectrum of the Methyleneimine Molecule

This transient intermediate (H_2CNH) was identified in the CO_2 laser assisted decomposition of RDX.²¹ This species has also been included in theoretical modeling of the network of reactions describing the decomposition of RDX.²² It is the simplest imine.

This class of organic compounds is very reactive and normally decomposes in condensed phases by polymerization, oxidation, or hydrolysis.

The microwave spectrum of H_2CNH has been reported, and a molecular structure for the ground electronic state derived.²³ Its infrared absorption spectrum has been investigated by both matrix isolation spectroscopy²⁴ and in the gas phase. All nine vibrational transitions have been observed,²⁵ and high-resolution gas-phase spectra have been analyzed.²⁶⁻²⁸ In all these gas-phase studies, H_2CNH was prepared by pyrolysis of methyl amine.

Surprisingly, the electronic spectrum of methyleneimine had not been reported prior to our CRDS study.²⁹ There has been some theoretical work to characterize the excited states. The ground electronic state has a planar equilibrium geometry. As in the isoelectronic ethylene molecule,³⁰ the S_1 and T_1 states are computed to have nonplanar geometries, with a dihedral angle of 90° between the planes containing the CH_2 and NCH moieties.^{31,32} The vertical excitation energies are thus greater than the excitation energies to the zero-point levels of the excited states, and it is expected that the lowest electronic transition would be spread over a broad wavelength range.

The dependence of the electronic energies of the ground S_0 and excited S_1 and T_1 states of H_2CNH upon the dihedral angle between the two halves of the molecule has been investigated computationally.³¹ An intersection of the potential energy surfaces of the S_1 and S_0 states was found near the geometry of the minimum energy of the S_1 state. This crossing will lead to internal conversion in the molecule, and there is enough energy in the S_0 state to allow dissociation to yield H or H_2 fragments.

We have employed CRDS to observe the electronic spectrum of methyleneimine.²⁹ Methyl amine was not considered to be a suitable precursor since it absorbs in the same spectral region where H_2CNH is expected to absorb. Photoelectron studies have shown that pyrolysis of methyl azide is a very convenient method to generate H_2CNH .³³ This process occurs by loss of N_2 and a 1,2-hydrogen shift. Methyl azide is a convenient precursor here since its electronic absorption spectrum³⁴ possesses a weak maximum at 286 nm and a strong peak at 215 nm and should hence cause less spectral interference than methyl amine. Moreover, methyl azide should be suitable as a photolytic precursor in kinetic studies.³⁵ We have employed this pyrolytic generation technique with CRDS to observe the $S_1 \leftarrow S_0$ transition in methyleneimine.

We have taken CRDS spectra over the 235 – 260 nm wavelength range of flows of methyl azide diluted in argon as a function of the temperature of a short heated section of tubing upstream of the CRDS cell. We find quantitative conversion of methyl azide to methyleneimine by $\sim 800^\circ\text{C}$. Heating to higher temperatures causes methyleneimine to

decompose to HCN.³³ The absorption spectrum of H₂CNH is very broad and structureless and peaks near 250 nm. The large spectral width of the transition is consistent with the computed³¹ large geometry change upon electronic excitation according to the Franck-Condon principle, and the lack of structure provides indirect evidence for dissociation after excitation.

We have obtained more direct evidence for fragmentation of H₂CNH excited to the S₁ state, through exploratory multiphoton UV laser ionization experiments.²⁹ In contrast to the 118 nm (tripled 355 nm) one-photon ionization, no parent ions were observed with UV irradiation. Rather, the ion representing the loss of one hydrogen atom (or deuterium atom in the case of perdeuterated methyleneimine) was observed strongly and can be assigned to H₂CN⁺ or HCNH⁺. From quantum chemistry calculations³⁶ on the dissociation pathways for H₂CNH, the former is more likely since no feasible pathway to form HCNH from the dissociation of H₂CNH was found. The appearance of the H₂CN⁺ ion can be explained by dissociation of electronically excited methyleneimine and subsequent ionization of the H₂CN fragment.

Further spectroscopic studies of methyleneimine, involving IR CRDS, are described in the next section.

C. Implementation of Cavity Ring-Down Spectroscopy in the IR

With the support of a DURIP grant (ARO grant no. W911NF-04-1-0133) for the acquisition of a tunable IR laser system (optical parametric oscillator (OPO) pumped by a Nd:YAG laser), we are turning to the IR spectral region for spectroscopic studies of the larger transient intermediates. We have constructed an IR CRDS apparatus suitable for spectroscopic and kinetic studies of transient polyatomic intermediates. Currently, we have high-reflectivity mirrors for the range 2700 – 3600 cm⁻¹, which covers the hydride stretching region. The spectral resolution of the system is governed by the bandwidth of the OPO, which is 0.08 cm⁻¹, as verified by scans of the well documented spectrum of methane. Our motivation for moving to the IR spectral region is to allow more selective detection of the larger intermediates. The use of electronic transitions as a probe of larger polyatomic intermediates becomes more problematic because of the broad and unstructured nature of electronic transitions of these species.

In our initial experiment with this apparatus, we have studied the hydride stretch fundamentals of methyleneimine, which we previously investigated by UV CRDS of its electronic transition,²⁹ as discussed in the previous section. As in this earlier experiment, methyleneimine is prepared by pyrolysis of methyl azide.³⁷ We found that the absorption cross section of methyleneimine at the peak of its electronic transition at 250 nm was an

order of magnitude larger than that of the methyl azide precursor. This difference in cross sections is not large enough to allow the use of methyl azide as a photolytic precursor of methyleneimine in kinetics studies with UV CRDS detection. By contrast, spectroscopic detection in the IR allows the selective detection of methyleneimine since not all its hydride stretch vibrational transitions are overlapped by those of methyl azide. All nine fundamental vibrational transitions of methyleneimine have been observed in high-resolution gas-phase experiment using Fourier transform and laser Stark spectroscopy.^{26-28, 38} The gas-phase vibrational spectrum of methyl azide has previously been reported.^{39, 40} Table 1 gives the frequencies of the fundamental hydride stretch transitions of methyl azide and methyleneimine.

Figure 4 presents a CRDS spectrum of a portion of the hydride stretch region of methyl azide. Prominent in the spectrum are the sharp Q branches of the ν_{11} band; also visible in the spectrum is the weaker ν_2 band. The rotational constants of methyl azide

Table 1. Hydride stretch fundamental transitions

Methyl azide			Methyleneimine		
Transition	Frequency (cm ⁻¹)	Band type	Transition	Frequency (cm ⁻¹)	Band type
ν_1 (A)	3023	A	ν_1	3262.62	A
ν_2 (A')	2946	A	ν_2	3024.45	B
ν_{11} (A'')	2962	C	ν_3	2914.18	A

are small, so that the spectrum is not rotationally resolved. The ν_2 and ν_{11} bands are overlapped, while the ν_1 band (not shown in Fig. 4) appears as a separate feature in the spectrum.

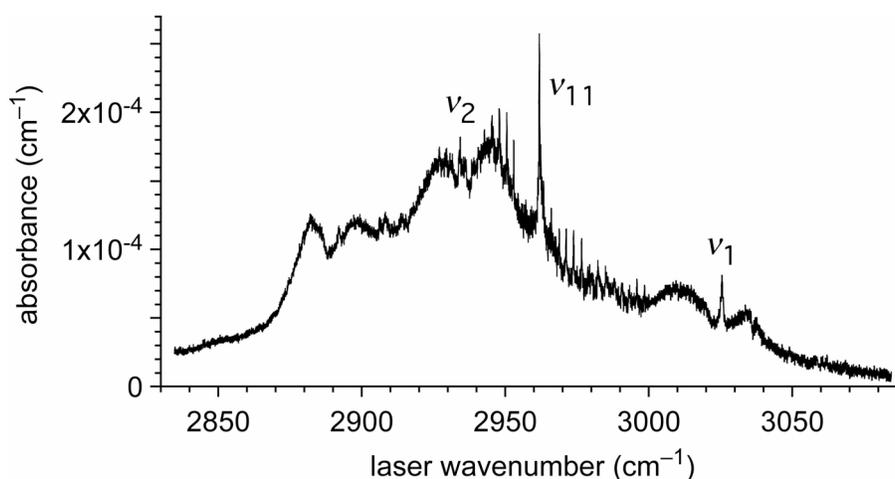


Figure 4. CRDS spectrum of a portion of the hydride stretch Region of methyl azide (partial pressure 0.01 Torr in 0.9 Torr argon).

We have also examined the evolution of the IR CRDS spectrum as the temperature of the heated section upstream of the CRD cell is raised. Figure 5 compares

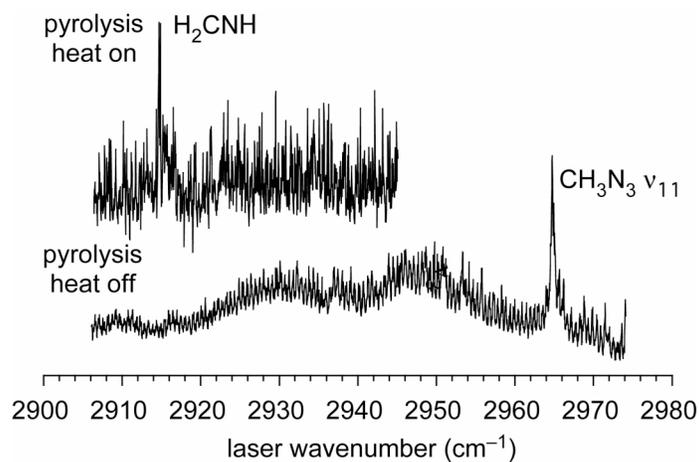


Figure 5. CRDS spectrum of a portion of the hydride stretch region of methyl azide (partial pressure ~ 0.01 Torr in argon).

spectra with the heater off and on. The intensity of the Q branch peak in the ν_{11} band at 2962 cm^{-1} drops as the temperature is raised, as a result of the pyrolysis of methyl azide to form methyleneimine. In the spectrum of pyrolyzed methyl azide, we observe the ν_3 band of methyleneimine, reflecting its presence as a product of methyl azide decomposition. The ν_1 band of methyleneimine is an even cleaner means of detecting this molecule since this band is not overlapped by bands of the methyl azide precursor.

With our previous results on the UV detection of methyleneimine,²⁹ we have also compared the detection sensitivity of methyleneimine with UV and IR CRDS. With our narrowband IR laser source, the sensitivity of IR detection actually appears to be greater than for UV detection. The strong Q branches of the ν_1 and ν_3 bands of methyleneimine are a convenient, sensitive, and selective means of detection for this transient intermediate. Similar advantages of IR CRDS with a narrow-band laser source should apply to the detection of other intermediates of importance in the decomposition of energetic materials.

D. Kinetic and CFD Modeling of the LIBS Plume

We have been collaborating with Drs. Andrzej W. Mizolek, Frank DeLucia Jr., and Michael J. Nusca of ARL (Aberdeen Proving Ground, MD) and Dr. Valeri I. Babushok (NIST) on fundamental studies of laser-induced breakdown spectroscopy (LIBS). LIBS is a relatively new laser sensor technology which can detect all elements in a sample with ppm sensitivity on a single-shot basis. LIBS shows great promise as a

real-time sensor with chemical sensitivity and is applicable in a variety of important applications,^{4, 41, 42} such as detection of energetic materials.⁴³

We are interested in developing a full chemical model of the LIBS plume of metallic lead in various atmospheres and to incorporate this model into a two-dimensional computational fluid dynamics (CFD) model of the plume. We have chosen to study metallic lead because of the relative simplicity of its air chemistry and the importance of the detection of lead in the environment. Our overall goal is to acquire a detailed understanding of the physical and chemical factors that control the LIBS signature (atomic emission lines). In our initial study,⁴⁴ we considered LIBS of lead in an air atmosphere. The kinetic model developed included a set of air reactions and ion chemistry, as well as the oxidation, excitation, and ionization of lead atoms. A total of 38 chemical species (including 9 electronic states of atomic Pb, to allow formation of emitting excited Pb states) and 220 reactions were included in the kinetic model. Initial CFD calculations on the LIBS plume were also carried out. These computational results were compared with experimental measurements of the spatial and temporal dependence of a number of Pb emission lines. The kinetic calculations show that the presence of O₂ in the atmosphere decreases the concentration of excited Pb atoms, and hence the intensity of the LIBS signals. This results from an increase in the concentrations of atmospheric ions and the loss of neutral Pb atoms by charge transfer processes, as well as excited-state oxidation. The calculations also showed that water vapor reduced the concentration of excited Pb atoms.

We have extended our initial work to the study of LIBS of lead in inert gas atmospheres, specifically argon.⁴⁵ Because of the simplified chemistry, this system had a total of 15 chemical species and 90 reactions in the kinetic model. Results from a comprehensive kinetic modeling have been compared with laboratory measurements. In both the experimental observations and the modeling results, the formation of excited, emitting Pb states was greater with an Ar than air atmosphere. The principal difference between air and argon atmosphere found in the modeling is the high electron concentration and the greater importance of direct electron excitation of Pb atoms in the latter. In addition, excited Pb atoms are not lost in Ar by oxidation processes, as they are in air.

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III. LIST OF PUBLICATIONS PREPARED UNDER ARO GRANT DAAD19-02-1-0323

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5. Paul J. Dagdigian, Alexey Teslja, and Wolfgang Eisfeld, "Experimental and Theoretical Study of the Electronic Spectrum of the Methylene Amidogen Radical (H_2CN): Verification of the $^2A_1 \leftarrow ^2B_2$ Assignment," manuscript in preparation.

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V. LIST OF INVENTIONS

None