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14. ABSTRACT Infrared (IR) laser spectroscopy has been employed for both the spectroscopic and kinetic study of transient intermediates of importance in the decomposition of energetic materials using cavity ring-down spectroscopy (CRDS) and for the detection of organic residues, including energetic materials, by laser-induced breakdown spectroscopy (LIBS) with infrared laser irradiation. CRDS in the hydride stretching region of the IR was employed to study the thermal decomposition of methyl azide to form methyleneimine (H <sub>2</sub> CNH). Direct CRDS detection of					
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**FINAL REPORT**  
**PAUL J. DAGDIGIAN**  
**GRANT NO. W911NF-06-1-0206**

**1. Statement of the Problem Studied**

Spectroscopy with mid-infrared (IR) lasers was employed in two related problems. In the first, cavity ring-down spectroscopy (CRDS) was employed with mid-infrared lasers to investigate the spectroscopy and kinetics of transient intermediates of importance in the decomposition of energetic materials, with specific interest in the nitramines. In previous work, electronic spectroscopy was employed to probe the smaller intermediates in the later stages of decomposition.<sup>1</sup> Study of larger intermediates is better carried out with IR vibrational spectroscopy, because of the diffuseness of the electronic spectra of these species. We constructed a CRDS apparatus for the spectroscopic investigation in the hydride stretch fundamental spectral region of polyatomic intermediates.

There has been considerable interest in the development of laser-based methods for the detection of energetic materials. One technique which has emerged as a powerful method for the detection and characterization of residues of organic compounds, including energetic materials, is laser-induced breakdown spectroscopy (LIBS).<sup>2</sup> Most modern LIBS experiments employ either the Nd:YAG fundamental wavelength (1064 nm) or one of its harmonics. However, other wavelengths may have advantages. We have investigated two other irradiation wavelength regions. One of these was at the near-IR wavelength of 1500 nm, which lies in an atmospheric "window" and has an eye damage threshold energy ~8000 times higher than 1064 nm. In the detection of a residue on a substrate, it would be desirable to ablate the residue with as little ablation of the substrate as possible. We report promising results on LIBS of several polymers for which the irradiation wavelength was tuned to vibrational fundamental wavelengths near 3000 nm. The LIBS signals were found to be significantly enhanced when the laser wavelength coincided with a vibrational transition.

**2. Summary of the Most Important Results**

**(a) Spectroscopic investigations of transient intermediates**

We are particularly interested in small polyatomic reactive intermediates, such as H<sub>2</sub>CN, H<sub>2</sub>CNH, and H<sub>2</sub>CNO, which are important intermediates in the decomposition of energetic materials but for which there is little spectroscopic or kinetic information available. For most of these species, photolytic methods must be used for their generation since they are chemically labile.

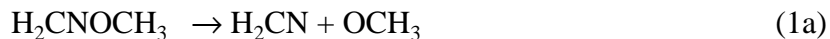
With help of funding from a DURIP grant, we constructed an apparatus for CRDS experiments in the mid-IR, in the hydride stretching region. The source of the mid-IR

laser radiation is an optical parametric oscillator/amplifier (OPO/OPA) built by Laser Vision (Bellevue, WA), which is pumped by a Nd:YAG laser. The mid-IR output has a pulse energy of several mJ and a spectral bandwidth of  $0.08\text{ cm}^{-1}$ . This radiation was injected into a resonant optical cavity bounded by two mirrors with high reflectivity ( $R \approx 99.93\%$ ) in the mid-IR. The time-dependent circulating light intensity in the cavity was monitored with a fast InSb detector/preamplifier viewing the light leaking out the rear mirror. The detector signal was read by a 12-bit digital oscilloscope card in a PC, and the photon decay time constant is computed on each laser shot. Absorbance was detected by a reduction in the decay constant, which is due mainly to the finite reflectivity of the mirrors in an empty cavity.

In our initial IR CRDS study,<sup>3</sup> we investigated the thermal decomposition of methylene azide to form methyleneimine ( $\text{H}_2\text{CNH}$ ). The pyrolysis of methyl azide was studied over  $2835\text{-}3280\text{ cm}^{-1}$ . We were able to observe vibrational transitions of  $\text{H}_2\text{CNH}$  without interference from the methyl azide precursor, in particular the  $\nu_1$  band (N–H stretch) of the intermediate. We also observed HCN from incipient pyrolysis of methyleneimine.

We then turned to the study of intermediates which must be generated by photolysis,<sup>4</sup> in particular the important  $\text{H}_2\text{CN}$  radical. In our earlier UV CRDS study of this species,<sup>5</sup> we employed formaldoxime ( $\text{H}_2\text{CNOH}$ ) as the precursor. This is not a very convenient compound since it must be depolymerized to prepare the monomer in the gas phase. As a result, this precursor is not suitable for studies at higher total pressures ( $> 10$  Torr). We investigated the use of several volatile, monomeric precursors. The most promising precursor was formaldehyde O-methyl oxime ( $\text{H}_2\text{CNOCH}_3$ ). It should be mentioned that all the precursors investigated needed to be synthesized in our laboratory. The identity and purity of the synthesized compounds were checked by GC-MS and FTIR spectra.

With 193 nm (ArF excimer laser) pyrolysis of the O-methyl oxime, we observed the stable products  $\text{CH}_4$  and HCN along with the parent molecule, but not the  $\text{H}_2\text{CN}$  intermediate. The production of these stable compounds can be rationalized in the following way. The photolysis of the O-methyl oxime can proceed in two ways:



Observation of  $\text{CH}_4$  and HCN provides indirect confirmation that both photolytic pathways are occurring. Methane can be produced by H-atom abstraction from the O-methyl oxime by the  $\text{CH}_3$  radical formed in reaction (1b), while HCN can be formed by dissociation of the second weak C–H bond in the initially formed [reaction (1a)], energized  $\text{H}_2\text{CN}$  radical.

We also searched for formation of  $\text{H}_2\text{CN}$  in the photolysis of formaldehyde O-ethyl oxime [ $\text{H}_2\text{CNOCH}_2\text{CH}_3$ ] and formaldehyde dimethylhydrazone [ $\text{H}_2\text{CN}-\text{N}(\text{CH}_3)_2$ ] and of  $\text{CH}_3\text{CHN}$  in the photolysis of acetaldazine [ $\text{CH}_3\text{CHN}-\text{NCHCH}_3$ ]. In no case, were we

able to detect the reactive intermediates over absorptions due to the precursor in the mid-IR spectral region.

We then collaborated with Don Thompson's group (U. MO Rolla), who computed band strengths for fundamental vibrational transitions of H<sub>2</sub>CN, H<sub>2</sub>CNO, H<sub>2</sub>CNOH, and H<sub>2</sub>CNOCH<sub>3</sub>. Their calculations show that the symmetric C–H stretch of H<sub>2</sub>CN, at 2920 cm<sup>-1</sup>, is quite weak. The asymmetric stretch, at 3103 cm<sup>-1</sup>, is much stronger, but we found that it is overlapped with combination bands of the H<sub>2</sub>CNOCH<sub>3</sub> precursor. Below we present the computed band strengths for H<sub>2</sub>CN and for transitions of H<sub>2</sub>CNOCH<sub>3</sub> close in frequency.

H <sub>2</sub> CN			H <sub>2</sub> CNOCH <sub>3</sub>		
Mode	Freq (cm <sup>-1</sup> )	<i>S</i> (km/mol)	Mode	Freq (cm <sup>-1</sup> )	<i>S</i> (km/mol)
<i>v</i> <sub>1</sub>	912	7.3	<i>v</i> <sub>6</sub>	823	46
<i>v</i> <sub>2</sub>	954	32.3	<i>v</i> <sub>7</sub>	950	34
<i>v</i> <sub>3</sub>	1337	15.9	<i>v</i> <sub>12</sub>	1373	5
<i>v</i> <sub>4</sub>	1725	0.8	<i>v</i> <sub>16</sub>	1641	12
<i>v</i> <sub>5</sub>	2820	0.2	<i>v</i> <sub>17</sub>	2908	53
<i>v</i> <sub>6</sub>	3103	12.0	<i>v</i> <sub>20</sub>	3005	14

The best prospect for detecting H<sub>2</sub>CN lies in the fingerprint region, namely the *v*<sub>3</sub> band at 1337 cm<sup>-1</sup>. Unfortunately, our OPO/OPA laser system can scan to wavenumbers only as low as ~2500 cm<sup>-1</sup>. The IR fingerprint region appears to be a promising spectral region for the study of transient intermediates such as H<sub>2</sub>CN and H<sub>2</sub>CNO.

#### (b) LIBS at near-IR and mid-IR irradiation wavelengths

We have carried out a comprehensive comparison of LIBS of organic residues on Al substrates with laser irradiation at the Nd:YAG fundamental wavelength (1064 nm) and an "eyesafe" wavelength of 1500 nm.<sup>6</sup> To our knowledge, such a comparison had not been previously carried out, although there has been much interest in exploring LIBS with near-IR laser irradiation.

In order to have similar beam profiles at the two wavelengths, an optical parametric oscillator (Panther, Continuum Lasers, Santa Clara, CA) tuned to the two wavelengths was employed as the laser source. The pulse energy available was 7 mJ, which was focused onto the substrate with a 75 mm focal length lens. The compounds studied were anthracene, caffeine, glucose, 1,3-dinitrobenzene, 2,4-dinitrophenol, and 2,4-dinitrotoluene, which were laid down on Al foil substrate with surface coverages of 20-140 μg/cm<sup>2</sup>. For all compounds, the overall emission intensity was found to be much smaller at 1500 nm than at 1064 nm. Molecular emission (C<sub>2</sub> and CN bands) was found to be strong for the aromatic compounds, but much weaker at 1500 nm than at 1064 nm in comparison with the H atomic emission intensity. The ratios of the C, N, and O

emission intensities relative to that for H were approximately the same at the two wavelengths.

In an effort to understand the differing emission intensities at the two wavelengths, we determined the plasma temperature and electron density, averaged over the several  $\mu$ s observation window. The temperature was determined from the ratio of the intensities of the Al 308 and 394 nm lines, while the electron temperature was obtained from the observed Stark broadening of the H 656 nm line. The plasma temperature and electron density were both found to be slightly higher at 1500 nm than at 1064 nm. One possible reason for the differences in LIBS at 1500 nm vs. LIBS at 1064 nm is that the plasma shielding is greater than the former wavelength.

We have extended our study of LIBS at near-IR laser irradiation wavelengths to the mid-IR. In this case, we are interested to investigate irradiation at wavelengths coincident with wavelengths of vibrational transitions of the compound of interest can enhance the LIBS signals. This could be a way to enhance the ablation of a residue over that of the underlying substrate. In our initial study,<sup>7</sup> we investigated LIBS of bulk polystyrene over the 2700-3500  $\text{cm}^{-1}$  spectral region. The laser pulse energy was maintained at 7 mJ, which was focused onto the sample with a 50 mm f.l.  $\text{CaF}_2$  lens.

We observed a significant enhancement in the LIBS signals when the irradiation laser is tuned through the C–H stretch fundamental bands. Moreover, we found that the LIBS enhancements do not track the one-photon absorption cross sections. The enhancement was greater with irradiation on an aromatic C–H stretch fundamental than on an aliphatic C–H stretch fundamental. Mode specific effects were also observed in resonant pulse laser ablation and deposition of polystyrene.<sup>8</sup> The differing enhancement of the LIBS signals must be related to the lifetimes of the excited vibrational levels in the solid material.

We also compared LIBS signals with mid-IR and 1500 nm laser irradiation, with beams of similar transverse intensity profiles. The absolute emission intensities were much greater at 1500 nm than for mid-IR irradiation. This behavior is similar to what we observed in our comparison of LIBS at 1064 nm and at 1500 nm, namely that the intensities are greater for irradiation at the shorter wavelength.

We also considered the use of resonant mid-IR LIBS for the detection of residues on surfaces. From knowledge of the polystyrene absorption cross sections and its density, we estimate a laser beam  $1/e$  penetration depth of  $\sim 10 \mu\text{m}$  at 2930  $\text{cm}^{-1}$ , considering only one-photon absorption. Assuming surface coverage of 100  $\mu\text{g}/\text{cm}^2$  would absorb only  $\sim 10\%$  of the incident radiation. This suggests that resonance enhanced LIBS may be most appropriate for bulk materials.

In order to test this hypothesis and to investigate other materials, we have recorded LIBS spectra as a function of the mid-IR irradiation laser wavelength for two polymers, a poly(vinyl alcohol-ethylene) co-polymer and Nylon 12, both spin coated to a thickness of 3  $\mu\text{m}$  on Si wafers. These polymers were chosen for study because they

contain O–H or N–H bands, as well as C–H bonds, and we can compare enhancements on different kinds of hydride stretches. In the case of poly(vinyl alcohol-ethylene), the strongest enhancements are observed in the O–H stretch region, but the spectral profile of the enhancement does not match that of the O–H transition. Moreover, there is an enhanced signal peaking at  $\sim 3200\text{ cm}^{-1}$ , which is not coincident with any vibrational transition. An enhanced signal is observed for Nylon 12 in the region of the N–H stretch fundamental near  $3300\text{ cm}^{-1}$ , but again significant enhancements are also observed at wavelengths not coincident with vibrational transitions. To provide a comparison, we are currently recording LIBS spectra of bulk Nylon 12. The LIBS signals are significantly smaller than with the spin-coated samples. It appears that the Si substrate is participating in the absorption of the incident laser radiation, as also suggested by the presence of strong Si atomic emission in the LIBS spectra. It is unlikely that the Si plasmon resonances are playing a role, as do the corresponding Ag resonances in surface-enhanced Raman spectroscopy, since the Si resonances occur deep in the UV.

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