

LASER-INDUCED BREAKDOWN SPECTROSCOPY INFRARED EMISSION FROM INORGANIC AND ORGANIC SUBSTANCES

C.S-C. Yang
Battelle Eastern Science and Technology Center
Aberdeen, MD 21001

E. Brown and U. Hommerich
Department of Physics
Hampton University, Hampton, VA 23668

S.B. Trivedi
Brimrose Corporation of America
Baltimore, MD 21152

A.P. Snyder and A.C. Samuels*
Edgewood Chemical Biological Center
Aberdeen Proving Ground, MD 21010

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been established as a powerful method for identifying trace elemental contaminants by analyzing the atomic spectral emission lines that result subsequent to plasmas generated by laser power. The ultraviolet-visible-near infrared (UV-Vis-NIR) spectral region exploited in conventional LIBS largely elucidates the elemental composition of the laser target by profiling these atomic lines; very limited information on molecular species may be derived. To our best knowledge, there is no reference to LIBS measurements on emission processes outside of the UV-Vis-NIR region. In this pioneer work, attempts were made herein to probe the mid-infrared (MIR) emission from a laser-induced breakdown process between 2 to 5.75 μm . Emission features between 4200 to 4800 nm from oxygenated carbon-containing breakdown fragments and between 2000 to 4000 nm from alkali metal-containing breakdown fragments have been successfully identified. These findings could provide additional spectral information to complement the conventional LIBS analysis and launch a new analytical methodology and sensing method for future contamination avoidance applications.

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) has been developed as a versatile and sensitive probe for detection and identification of trace

substances. The atomic emissions from a LIBS event have been widely used to analyze metals (Buckley et al., 2000), glasses (Loebe et al., 2003), graphite (Nemes et al., 2005), soils (Yamamoto et al., 1996), concrete (Pakhmov et al., 1996), aerosols (Hybl et al., 2003), explosives (DeLucia et al., 2003), biological materials (Samuels et al., 2003) and various gaseous (Parrigger et al., 2003) and liquid (Kumar et al., 2003) bulk media. In LIBS, a focused intense laser beam is utilized to atomize and ionize target molecules, thus to create a hot and short-lived (~100 nanoseconds) plasma at the target substance surface.

Valuable information on the identification and concentration of the trace materials can be acquired by monitoring atomic and molecular emissions from the consequent relaxation processes of the excited electron and molecular fragments in the plasma. The major advantages of LIBS have been demonstrated to be: no time-consuming sample preparation needed; the ability to perform real-time on-site analysis because LIBS uses the laser-induced plasma to prepare and excite the sample in one step; and its potential for remote sensing and field applications (Lazic et al., 2001).

However, all the analytical LIBS applications reported in the literature so far have only exploited the simultaneously-monitored emissions in UV-Visible-Near IR region (emission wavelength shorter than 2000 nm) from atoms and very simple molecular fragments (such as OH and C₂). We found no evidence of an attempt to

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 01 NOV 2006	2. REPORT TYPE N/A	3. DATES COVERED -			
4. TITLE AND SUBTITLE Laser-Induced Breakdown Spectroscopy Infrared Emission From Inorganic And Organic Substances		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Battelle Eastern Science and Technology Center Aberdeen, MD 21001		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002075.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

explore the molecular vibrational or rotational emission features known to occur in mid- to far-infrared region in conjunction with LIBS analysis. In LIBS studies of various organic compounds, C₂ UV-Visible emission features are found to be strongly correlated to the presence of aromatic rings in the target compounds (St-Onge et al., 1999), and the aromatic ring arrangements (Protnov et al., 2003) of the target compounds. Moreover, in conventional breakdown emission spectroscopy applications using flames while the molecules are excited, atomized, and ionized by the combustive thermal energy transfer, emission features from atomic and molecular breakdown fragments can be readily observed and monitored in atomic (UV to near-infrared) region (Obertacke et al., 1996), molecular vibrational (mid-infrared) region (Lam, 1990), and molecular rotational (far-infrared) region (Cheville and Grischkowsky, 1995). The discovery of correlations between LIBS atomic emissions to molecular structures and the observation of infrared emission features from flame breakdown molecular fragments suggest the potential of recovering mid-infrared (MIR) molecular emission features from a LIBS event.

By exploring the information content in the MIR region, laser breakdown analysis of molecular vibrations and rotational transitions has the potential to complement conventional LIBS in the characterization and classification of matter. Furthermore, the MIR LIBS analysis is a much better *in-situ* probe than the traditional infrared emission spectroscopies, such as flame spectroscopy and pyrolysis. Another advantage of mid-infrared LIBS analysis over the conventional infrared emission techniques is its capability and simplicity for time-resolved investigation of breakdown reaction products. Being a multi-photon process, it is also more tolerant to pump laser wavelength selection than the laser-induced infrared fluorescence spectroscopy.

The primary goal of this study is to explore the feasibility of LIBS as a mid-infrared emission probe of molecular products that result from reactions initiated by the laser-induced plasma. Attempts are made to exclude molecular vibrational transitions emissions from the hot plasma thermal radiation. Various solid organic and inorganic compounds are examined and their spectra are presented.

2. EXPERIMENTAL SETUP

The MIR emission studies were performed using the 1064 nm output from a Q-switched Nd:YAG laser (pulse width: 5-10 ns, repetition rate 10 Hz) as the excitation source. A schematic of the experimental setup is shown in Fig.1. The pulsed laser beam was focused onto the sample using a convex lens ($f = 20\text{cm}$) resulting in a beam size with diameter less than 0.2 mm. A beamsplitter (~4%) was employed to monitor the laser beam energy during the emission measurements.

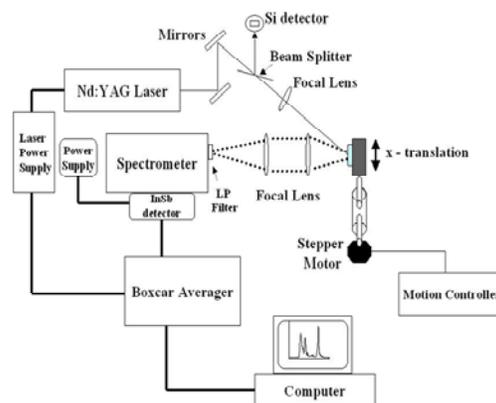


Fig.1 The scheme of the mid-infrared Laser-induced Breakdown Spectroscopy experimental setup

The laser energy throughout the experiment is found to be very stable with less than 1% power fluctuation. The laser energy reaching the sample was approximately 16 mJ per pulse. This laser power is sufficient to induce a plasma on the surfaces of all our solid sample materials: cellulose paper fiber (white index card), polyethylene film, polytetrafluoroethylene (PTFE) sheet, yttrium aluminum garnet (YAG) crystal, quartz window, boron silicate (microscope slide), aluminum foil and salt tablets. The samples, e.g. paper, were vertically mounted onto a linear translation stage attached to a stepping motor with a controller. The sample was translated during the emission scans at speed of ~1.5 mm/min, so the laser pulse would always hit fresh target material during the emission scan. The speed of spectral scan (in wavelength units) is set to be ~ 150 nm per minute from 2000 nm to 6000 nm. The mid-infrared emission from the sample was collimated and focused onto the entrance slit of a 0.15 m grating spectrometer ($\lambda_{\text{blaze}} = 4000 \text{ nm}$, 150 g/mm) using two CaF₂ lenses ($f = 15 \text{ cm}$, $f = 20 \text{ cm}$). The entrance and exit slits of the spectrometer were generally adjusted

to 1 mm during the scans. A 2000 nm long-pass filter was placed in front of the entrance slit to prevent any laser scattering from entering the spectrometer. The mid-infrared emission was monitored using a liquid-nitrogen cooled indium antimonide (InSb) detector and the signal was recorded using a gated electronic circuit (boxcar averager). All emission spectra were corrected for the spectral response of the experimental setup.

3. RESULTS AND DISCUSSION

3.1 MIR LIBS Emission from carbon-containing compounds

The inset of Fig.2 shows the transient spectrum of a paper sample (white index card) with the slits of the spectrometer wide open as measured using a digital oscilloscope in the mid-infrared region between 3000 and 6000 nm. The transient was averaged over ~100 laser pulses. We saw a slowly rising and decaying broad emission following an intense and sharp emission feature. While the sharp and intense MIR emission feature occurs immediately upon laser pulse generation, the broad MIR feature slowly develops and reaches its highest point around 40 μ s after the sharp peak. As we learned in previous UV-Vis LIBS studies (Yueh et al., 2000), the LIBS emission spectrum at the early stage (within 100 nanoseconds of initial plasma formation) is generally dominated by the continuous thermal blackbody emissions due to bremsstrahlung collisions and electron-ion recombination process.

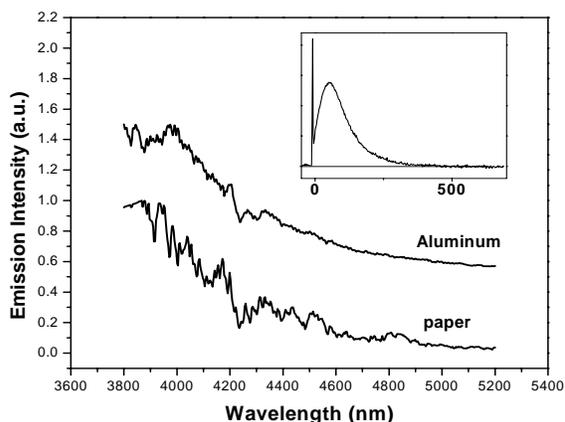


Fig.2 The normalized LIBS emission spectra of paper and aluminum samples that was collected without any delays regarding to the arrival of the laser pulses. The transient spectrum of paper sample recorded up to 600

μ s after the laser pulse arrival measured in the mid-infrared region is shown in the inset.

As the plasma expands and cools down, the blackbody emission decays rapidly and the distinct emission features due to relaxation processes between quantized energy states can be readily detected after hundreds of nanoseconds.

Fig 2 shows the LIBS emission spectrum of paper and aluminum samples that were collected without any delay between the laser pulses and the spectral acquisition. The resulting emission is clearly dominated by the continuous thermal emission of the hot plasma. To eliminate the influence of this hot plasma background, the acquisition of the MIR LIBS emission spectra of the samples was delayed by 40 μ s after the laser pulse, i.e. the initial plasma formation. Fig.3 shows the MIR LIBS emission spectrum of paper between 3000 to 6000 nm with the collection gate width set to be 16 μ s.

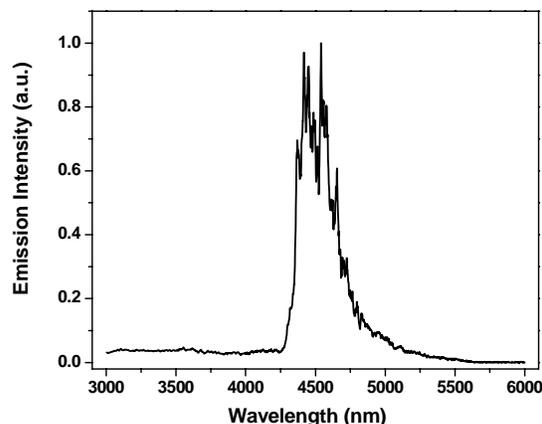


Fig.3 mid-infrared LIBS emission spectrum of paper between 3000 to 6000 nm with the collection gate width set to be 16 μ s and 40 μ s delay after the laser pulse arrival

This spectrum exhibits excellent signal-to-noise ratios, well-defined flat baselines, and is dominated by a strong emission feature between 4200 nm to 4800 nm. Moreover, this feature only shows up in the mid-infrared emission spectra when the laser pulse intensity exceeds the plasma-forming threshold of the sample, i.e. bright white sparks are observed at the sample surface. Fig.4 shows the mid-infrared LIBS emission spectra of a series of organic materials: paper, polyethylene, and PTFE; and inorganic materials: YAG crystal, quartz, glass, and aluminum. As observed with the paper sample, the resulting spectra show no trace of thermal background emission and an

excellent signal to noise ratio. The strong MIR emission between 4200 nm to 4800 nm can be readily observed from cellulose paper fiber, polyethylene, and PTFE. There is no comparable strong emission feature from other three inorganic samples and the aluminum sample holding stage in this spectral region. This strong emission band could be attributed to the CO stretching vibration around 4700nm (Kirby and Hanson, 1999) and CO₂ asymmetric stretching vibration around 4350 nm (Tilotta et al., 1989) resulting from the intense oxidation of the vaporized carbon-containing fragments from the samples, thus explaining the absence of this feature in spectra of carbon-less samples such as metal and silicates. Both CO and CO₂ asymmetric stretching bands appear to be broadened, most likely due to the high temperature and collision rate of the oxygenated carbon fragments. The absence of this band in metal emission spectra also indicates that the contribution from heated CO₂ molecules in the ambient air is negligible.

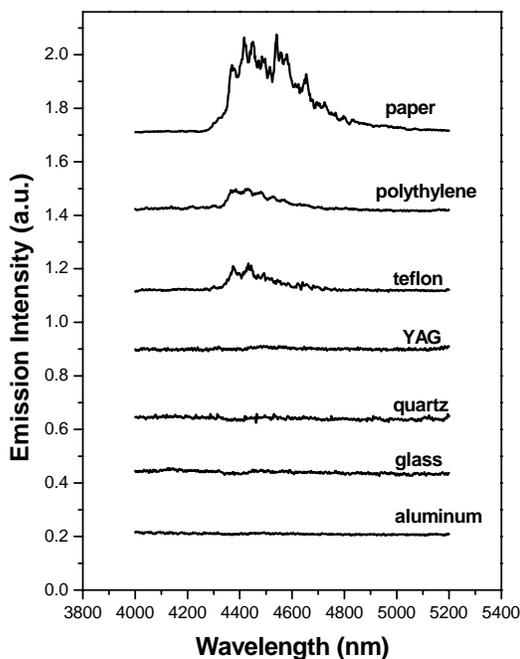


Fig.4 the mid-infrared LIBS emission spectra of a series of organic materials: paper, polyethylene, and PTFE (Teflon); and inorganic materials: YAG crystal, quartz, glass, and aluminum. The paper spectrum shown is 25% of its measurement value.

3.2 MIR LIBS Emission from alkali metal containing compounds

We also examined MIR LIBS emission from a series of alkali metal containing salt tablets (KBr, KCl, NaBr, NaCl), as shown in Fig. 5. There is no emission detected around 4300 nm, which is consistent with our observations in last section. Four distinct MIR emission features were found between 2 to 4 micron from a NaCl tablet: three sharp bands at 2210 nm, 2360 nm, and 3430 nm and a broad band located around 4050 nm. Observation of emission bands at those same wavelengths from NaBr tablets clearly indicates that the emission vibrational bands emanating from the laser breakdown products of the alkali metals are minimally influenced by the halogen counterions. Further investigations of emission from KBr and KCl tablets reveal that the emissions from potassium-containing breakdown products generally shift toward longer wavelengths and have more sub-structures compared with those from sodium-containing breakdown products. The red shift is expected due to the heavier atomic weight of the potassium. The character and nature of these bands are under continuing investigation.

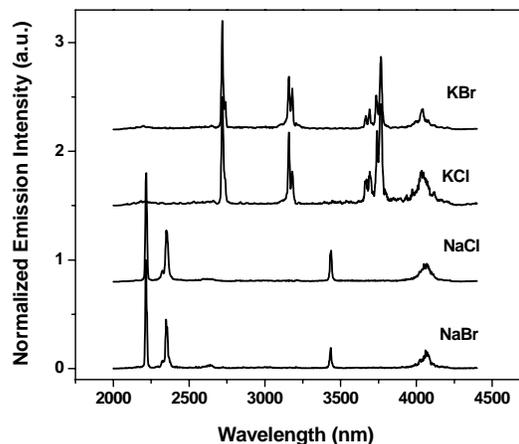


Fig. 5 MIR emission spectra of alkali salt tablets

CONCLUSIONS

This preliminary study has shown the viability of utilizing Laser-induced Breakdown Spectroscopy for molecular mid-infrared emission analysis. Intense thermal blackbody background radiation has been successfully detected and discriminated. Strong mid-infrared emission bands resulting

from vibrational transitions of oxygenated carbon breakdown fragments and of alkali metal breakdown products have been observed. Further efforts on identifying more breakdown reaction products such as hydrogenated fragments and heated molecular fragments are currently being pursued.

REFERENCES

- Buckley, S.G.; Johnson, H.A.; Hencken, K.R.; Hahn, D.W., 2000: Implimentation of laser-induced breakdown spectroscopy as a continuous emissions monitor for toxic metals, *Waste Management*, **20**, 455-462.
- Cheville, R.A.; Grischkowsky, D., 1995: Far-infrared terahertz time-domain spectroscopy of flames, *Opt. Lett.*, **20**, 1646-1648.
- DeLucia, F.C., Jr.; Harmon, R.S.; McNesby, K.L.; Winkel R.J., Jr.; Miziolek, A.W., 2003: Laser-Induced Breakdown Spectroscopy Analysis of Energetic Materials, *Appl. Optics*, **42**, 6148-6152.
- Hybl, J.D.; Lithgow, G.A.; Buckley, S. G., 2003: Laser-Induced Breakdown Spectroscopy. Detection of Biological Material, *Appl. Spectrosc.*, **57**, 1207-1215.
- Kirby, B.J.; Hanson, R.K., 1999: Infrared PLIF Imaging of CO and CO₂, *American Institute of Aeronautics and Astronautics Paper #99-0775*.
- Kumar, A.; Yuen, F.-Y.; Singh, J.P., 2003: Double-Pulse Laser-Induced Breakdown Spectroscopy with Liquid Jets of Different Thicknesses, *Appl. Optics*, **42**, 6047-6051.
- Lam, C.KY.; Tilotta, D.C.; Busch, K.W.; Busch, M.A., 1990: An Investigation of the Signal Obtained from a Flame Infrared Emission (FIRE) Detector, *Appl. Spectrosc.*, **44**, 318-325.
- Lazic, V.; Barbini, R.; Colao, F.; Fantoni, R.; Palucci, A., 2001: Self-absorption model in quantitative laser induced. breakdown spectroscopy measurements on soils and sediments, *Spectrochim. Acta B*, **56**, 807-820.
- Loebe, K.; Uhl, A.; Lucht, H., 2003: Microanalysis of tool steel and glass with laser-induced breakdown spectroscopy, *Appl. Optics*, **42**, 6166-6173
- Nemes, L.; Keszler, A.M.; Hornkohl, J.O.; Parigger, C.G., 2005: Laser-induced carbon plasma emission spectroscopic measurements on solid targets and in gas-phase optical breakdown, *Appl. Optics*, **44**, 3661-3667.
- Obertacke, R.; Wintrich, H.; Wintrich, F.; Leipertz, A., 1996: A new sensor system for industrial combustion monitoring and control using UV emission spectroscopy and tomography, *Comb. Sci. and Technol.*, **121**, 133-151.
- Pakhmov, A. V.; Nichols, W.; Borysow, J., 1996: Laser-Induced Breakdown Spectroscopy for Detection of Lead on Concrete, *Appl. Spectrosc.*, **50**, 880-884.
- Parigger, C.G.; Guan, G.; Hornkohl, J.O., 2003: *App* Measurement and Analysis of OH Emission Spectra Following Laser-Induced Optical Breakdown in Air, *Appl. Optics*, **42**, 5986-5991.
- Protnov, A.; Rosenwaks, S.; Bar, I., 2003: Emission Following Laser-Induced Breakdown Spectroscopy of Organic Compounds in Ambient Air, *Appl. Optics*, **42**, 2835-2842.
- Samuels, A.C.; Delucia, F.C., Jr.; McNesby, K.L.; Miziolek, A.W., 2003: Laser-Induced Breakdown Spectroscopy of Bacterial Spores, Molds, Pollens, and Protein: Initial Studies of Discrimination Potential, *Appl. Optics*, **42**, 6205-6209.
- St-Onge, L.; Sing, R.; Bechard, S.; Sbsabi, M., 1999: *Appl. Phys. A*, **69**, S913-S916.
- Tilotta, C.; Busch, K.W.; Busch, M.A., 1989: Fourier-Transform Flame Infrared Emission Spectroscopy, *Appl. Spectrosc.*, **43**, 704-709.
- Yamamoto, K. Y.; Cremers, D.A.; Ferris, M.J.; Foster, L.E., 1996: Detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument, *Appl. Spectrosc.*, **50**, 222-223.
- Yueh, F.-Y.; Singh, J.P.; Zhang, H., 2000, Elemental Analysis with Laser- Induced Breakdown Spectroscopy , in: Encyclopedia of Analytical Chemistry, RA. Meyers (Ed.), John Wiley & Sons Ltd, Chichester, 2066-2087.