

Broadband Spectroscopy at the Water/Gas Interface: Temporal Evolution of Bath Gas Dependent Molecular Species

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INTRODUCTION

The difficulties in performing Laser-Induced Breakdown Spectroscopy (LIBS) on the surface or in the bulk of a liquid sample are well-known. Single-pulse "panoramic" (broadband) spectroscopy on the surface of water for a variety of pulse energies, delay times, and experimental configurations has been studied previously.^{1,2}

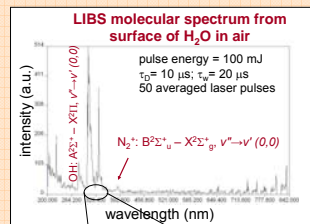
In the absence of intentionally-added calibration elements, the dominant atomic spectral features at short delay times are the hydrogen H-alpha and H-beta emission lines at 656 and 486 nm, respectively. During LIBS in the presence of atmospheric gas, however, the strength of these atomic emissions decreases rapidly with time and by approximately 8 μs after the ablation pulse the emission from molecular species created during and after the ablation process dominates the spectrum.

Dominant spectral features are:

- A²Σ⁺-X²Π OH molecular band system**
O-O band: R and Q branches at 306-308 nm
I-O band: R and Q branches at 281 nm
- A²Π-X²Σ⁺ NH molecular band system**
O-O band: R and Q branches at 330 and 336 nm

These molecular emissions are readily apparent at delay times approaching 40 μs, long after any atomic emission (from hydrogen or atmospheric atomic nitrogen and oxygen) has disappeared.

Using a high-resolution Echelle spectrometer, individual rotational transitions are easily identifiable in the vibration bands, suggesting possible applications for molecular spectroscopy.

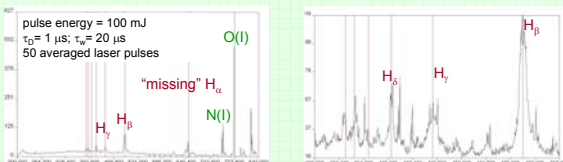


vibrational band: one component of a band system

rotational transitions: each band composed of hundreds of these well-defined peaks

LINES AND BANDS USED IN WATER / AIR ANALYSIS

- H_β (486.134 nm), H_γ (434.047 nm), O (I) triplet (777.194, 417, 539 nm), N (I) line (746.832 nm) NH band, OH band
- H_α emission (656.27 nm) not used due to "gaps" in Echelle spectrometer coverage



ANALYSIS

- Region of empty spectrum near emission line averaged to measure **background**
- Standard deviation of this empty region used to calculate **"noise"**
- Area under the background-subtracted curve = **intensity** (numerical integration performed due to inability to perform fitting on hundreds of rotational peaks in molecular spectra).
- Signal-to-background (**SBR**) and signal-to-noise (**SNR**) calculated.

APPARATUS

LASER

Spectra-Physics LAB 150-10 Series, 650 mJ/pulse max, operating at 1064 nm, pulse repetition frequency = 10 Hz (fixed), pulse duration = 10 ns

SPECTROMETER

LLA ESA3000 Echelle spectrometer with fiber-coupled input. Detection with a 1024 x 1024 pixel Intensified CCD-array (24 μm² pixel size). Spectral range = 200 - 834 nm with 0.005 nm resolution (in the UV).

OPTICS

- f = 39 mm plano-convex lens to focus laser. Beam angled with an AOI=53° on water meniscus.
- 600 μm quartz optical fiber tip ~1 cm away from microplasma.
- Glan-Laser polarizer and λ/2 waveplate to attenuate laser for power-dependence studies.

TARGET HOLDER

8 cm diameter 200 mL Pyrex dish on "z" translation stage. Fiber tip on fully articulated x-y-z stage.

GAS ENVIRONMENT

Positive pressure purge box at atmospheric pressure (~1 ft³) with AR coated window, optical fiber access, and water fill tube.

WATER

Ultra-high-purity distilled water (<1 ppm of all contaminants).

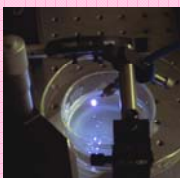
EXPERIMENTAL PARAMETERS

Measurement delay time after laser shot = variable; Gate width = 20 μs

- 1 laser shot for one spectrum. Repetition period 4s (allows surface to calm)
- 2, 50 spectra averaged for one "measurement"
3. Water re-added to Pyrex dish after every measurement until it overflowed



lens / fiber geometry



microplasma on H2O surface

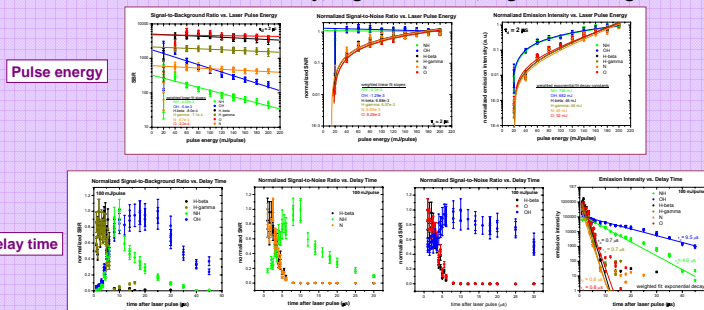


bath gas purge box

This work funded by Wayne State University

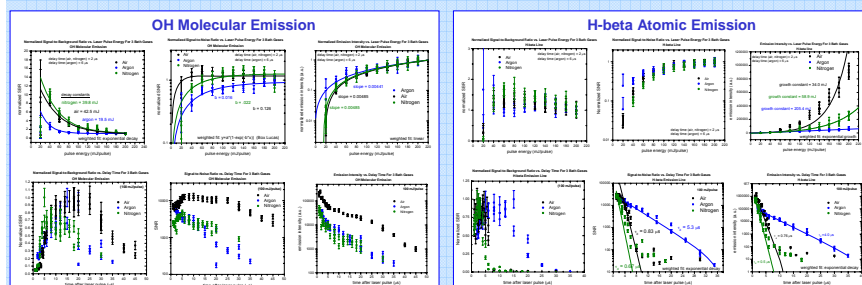
PULSE ENERGY DEPENDENCE AND TEMPORAL EVOLUTION IN AIR

Fluorescence Intensity, Signal-to-Noise, Signal-to-Background

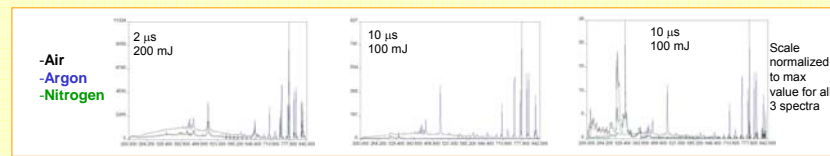


Molecules exhibit significant differences from atomic lines, and in general are more easily observed after atomic emission has ceased. Atoms that recombine to form molecules **originate in BOTH** the ablated sample **and** the bath gas at the interface. To study this dependence, the air above the water was replaced by argon and then nitrogen.

OH / H-beta TEMPORAL AND PULSE ENERGY DEPENDENCE IN 3 BATH GASES



COMPARISON OF SPECTRA IN 3 BATH GASES UNDER IDENTICAL CONDITIONS



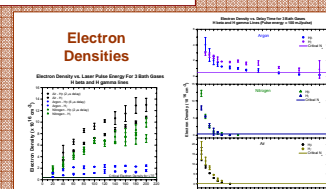
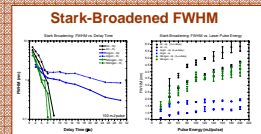
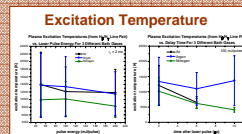
TEMPERATURE / ELECTRON DENSITIES / STARK BROADENING

Temperatures calculated from H_γ / H_β intensity ratio using Boltzmann equation:

$$\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_1}{g_2 A_2 \lambda_2} \exp\left(-\frac{|E_1 - E_2|}{kT_e}\right)$$

FWHM of Stark-broadened H_γ and H_β lines used to calculate electron density, N_e.

$$N_e = C(N_e, T) \Delta \lambda_{FWHM}^{3/2}$$



¹ O. Samek, "Application of laser-induced breakdown spectroscopy to in situ analysis of liquid samples," *Opt. Eng.* **39** (8), pp.2248-2262 (2000)
² B. Charfi, "Panoramic laser-induced breakdown spectrometry of water," *Spect. Acta B* **57**, pp1141-1153 (2002)