Chronological characteristics of laser spark emission spectra in water

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Prelude experimental results are reported on the chronological characteristics of laser spark emission spectra. Sparks were engendered in HBr mixed water by the focused beam of a Q-switched Nd:YAG laser. The pH changes, hydrogen concentration and breakdown current near by plasma ball have been focused. Potential of the laser plasma spectroscopy for in-situ breakdown extent and monitoring in HBr mixed water is briefly discussed. The acquired results imply that this approach has significant potential to develop as an effective method not only for underwater cation and anion detection but in the field of medical for cancer tumor management

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1. Introduction

Laser Induced Breakdown is a somewhat straightforward spark spectro-chemical technique that uses a short-pulsed laser focused on the sample to be looked over to create microplasma [1-2]. The microplasma is a fleeting event where the temperature arrives at 10,000 – 20,000 K. In this setting the sample is converted into plasma and the chemical bonds are broken to create electronically excited atoms and ions [3]. Direct decomposition of water is very complicated in normal stipulation. The pyrolysis reaction crops up at high temperatures above 3700C^{o} [4]. Water in the liquid state has the exceptionally high absorption coefficient at a wavelength of 2.9 μm [5]. The production of an electric signal, when IR-laser radiation having the power density below the plasma formation threshold interacts with a water surface, has been ascertained [6]. The electrical signals induced by lasers were already reported by [7-8].

Most of the research works on water splitting has carried out by flash lamps. A very little work was done by lasers [9-10]. Since laser light is monochromatic, coherent, intense and polarize, so it was of great significance to use the laser beams as an excitation source in water. Laser beam analytical methods are widely used in all the material sciences and have extended literature [11]. There is a large variety of these methods; however, most of them are based on selective excitation of the atoms, ions or molecules of interest, utilizing spectrally tunable laser sources. These equipments are relatively intricate and less unfailing, consequently not well suited for off laboratory measurements. In contrast, laser spark in gases, liquids or on solid targets can be generated simply by focusing the beam of a medium laser power. Relatively inexpensive, reliable Q-switched Nd:YAG lasers are well suited for this purpose. The power density needed to produce laser spark is in the range of 10-100 MW/cm^2 [12].

The laser spark is absorbed mainly via multi-photon ionization and inverse Bremsstrahlung. The unshackled initial electrons of high initial kinetic energy are multiplicated by avalanche course of action as they collide with the neighboring atoms and positive ions. Accordingly and within few nanoseconds, a very dense plasma ball is created with a diameter of few micrometers [13]. While this laser spark is escalating very fast, its temperature is decreasing and consequently the initial radiation of incessant spectra radiation is followed by the emission of ionic and after 50-100 ns of atomic spectral line. As in the first stage of the plasma configuration, complete ionization crop up, the spectrum emitted in the decaying interval is attributed for the elemental composition of the targeted material. Heating of water adjoining the hot plasma by its bremsstrahlung radiation, points out substantial breakdown of water molecules in the plasma [14]. Applications of the laser spark for chemical analysis of gases and solids is appraised extensively in literature [15]. Spectro-analytical facets of laser sparks in liquid have been much less studied. Related to optical breakdown most of previous measurements were concentration over the plasma plume, in water splitting research intentions are focus more on bond stretching.

Our work on lasers has revealed the important parameters which played a critical role in-situ measurement of under water treatment using water breakdown by laser. Since laser light has special properties; so it is of great interest to use the laser beams as an excitation source in water. HBr was mixed in water because of its frequent use in chemical dying, textile finishing and especially the pharmaceutical industry. It can also be used to help dissolve minerals during the processing of ores to extract metals. The study was focused on pH changes, breakdown current (electron density) and hydrogen concentration, not only the nearby plasma focus but away from the plasma ball.

2. Methodology and setup

The experimental set-up is shown in Figure 1. The source used for the plasma production was a Q-switched Nd:YAG laser emitting radiation at 1064 nm (10 Hz repetition rate with maximum output energy of 200 mJ for 10 ns pulse length). A camera lens (28 mm of focal length) focused the laser beam into the cuvette with dimension of 30 x 30 x 30 mm^3. The emitted light of the spark was occurred at 15 mm depth under the water surface and observed through one of the glass walls of the cuvette. The image of this plasma was projected onto the entrance slit of a CCD camera linked with a PC. In order to evaluate the pH changes of the solution nearby plasma ball, the pH meter was inserted inside the cuvette. A digital multimeter (DMM model METEX M-4650CR) was connected with electrodes (Steel and Zinc) which introduced inside the solution. The breakdown current was recorded by multimeter. Different liquid samples were studied in a preliminary experimental series, in order to learn the proper conditions and the limitations of the laser plasma productions. Finally plasma was generated in HBr (Hydrogen bromide) aqueous solutions.

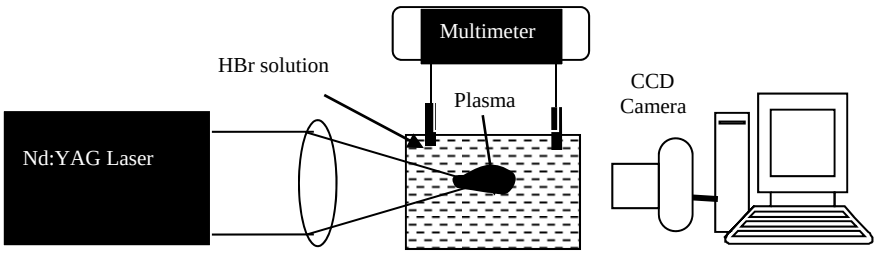

Figure 1: Experimental set up of laser Spark emission spectra

3. Results

In order to investigate hydrogen production induced by the laser spark emission in HBr mixed water, various experiments were carried out. On the basis of these experiments some important factors were determined avowed under this section.

3.1 Reaction dynamics

The laser induced breakdown (LIB) and resulting plasma formation leads to excitation, ionization and dissociation of water molecules. The reaction dynamics within plasma [16] can be expressed as

$$H_2O \rightarrow H^+ + OH^* \quad (1)$$

$$H_2O \rightarrow \frac{1}{2}H_2O_2 + \frac{1}{2}H_2 \quad (2)$$

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2^* \quad (3)$$

$$OH^* + OH^* \rightarrow H_2O + \frac{1}{2}O_2 \quad (4)$$

$$2HO_2^* \rightarrow H_2O_2 + O_2 \quad (5)$$

$$HO_2^* + OH^* \rightarrow H_2O + O_2 \quad (6)$$

When the laser intensity was high and above the threshold energy for water breakdown, optical breakdown taken place at the focus and extends to the Rayeligh length of the incident beam on either side of the focus. The formation of plasma was observed visually in the form of an elongated spark. The initial plasma formed due to laser induced breakdown, absorbs the incoming laser energy and pull offs high pressure and temperature thereby ionizing the surrounding liquid layer. This was mainly taking over in the forward frontage of plasma. The new layer of plasma further absorbed the incoming laser energy and impeded it from reaching regions beyond the focal volume. The hasty expansion of plasma left a rarefied region in the focal volume, which results in plasma cooling and favors recombination processes leading to formation of molecular oxygen at and beyond focal volume.

3.1 Plasma formation in air

Prior to produce plasma in water, an optical breakdown was produced by focusing a high-power laser pulse in air. The experiment was performed in a dark room. When plasma initiated, its formation can be observed by a bright luminous spark at the focal region. It occurred once every time the laser was triggered. Once the plasma is formed, the CCD video camera was synchronized to grab the plasma formation. Since the plasma is formed as a bright luminous spark in a dark room, so the CCD video camera can only detect the bright plasma as an object in a black background. When the image is displayed on the monitor, the plasma can be noted by a bright image with a dark background. As the CCD camera can only operate in grayscale mode, so the plasma image was seen as a white image surrounded by a blurred area with a black background. The image of plasma formation in air was grabbed by using a CCD video camera. The data obtained was recorded by personal

computer. Matrox Inspector software was employed in order to analyze the image. When the laser beam is focused, the temperature at the focal point was in excess of 1000^{o} C. Electric field strength was of the value 10^{7} V/cm. In the case of plasma formed in air originally at atmospheric pressure and room temperature, is heated to about 10^{5} C°. Most of the energy emitted was in ultraviolet region. The emitted energy has an absorption length of several millimeters in the hot plasma, but only a fraction of a millimeter in the surrounding air. These radiations are emitted in all directions from the plasma. The formation of plasma has a structure of bead-like ellipsoidal shape as shown in Figure 2. The bead size increased with increase in laser power.

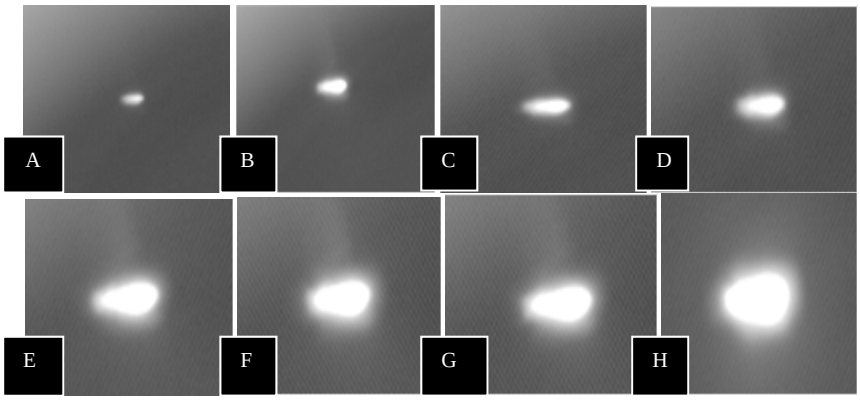

Fig. 2: Plasma Plumes using single lens with 28 mm focal length in air. The peak power in the series are A:16MW, B:18.3MW, C:19.8MW, D:21.1MW, E:22.1. F:25MW, G:26.9MW, H:28.

3.2 Laser water interaction

To facilitate and investigate the laser spark emission in HBr mixed water, an assortment of experiments were carried out after each other. The pulse energy of laser was varied and corresponding results were documented.

3.3.1 Effect on pH of water

The effect of laser pulse on the pH of the solution is shown in Figures 3. The results envisaged that when laser pulse evened on water the pH value chop down rapidly. That brings about the dissociation and ionization processes as shown in reactions (6.1), (6.2) and (6.3). Initially, when number of pulses was less, the pH value was found to be large. As soon as number of pulses increased pH value found to be decreased. The bends of the curvature show the neutralization response as described in reactions (6.4), (6.5) and (6.6). It was also examined that as long as the pulse energy increased the pH value decreased. For pulse energy 60 mJ, pH value changed form 0.8 to 0.69, where as for 64 mJ pulse energy these value varied from 0.19 to 0.16.for the pulse energy 70 mJ the pH value ranged form 0.16 to 0.12. The minimum pH value at pulse energy 60 mJ was at 0.69 where as at 64 mJ it was 0.16, while at 70 mJ it was 0.12. This phenomenon predicts that at higher pulse energy the bond infringement process is more dominant than lower pulse energy. Thus the more H_2 production was observed. For high pulse energy, pH value decreased more. At this time dissociation and ionization reactions (1), (2) and (3) were frequent, which caused the recurrent changes in the pH value of HBr mixed water.

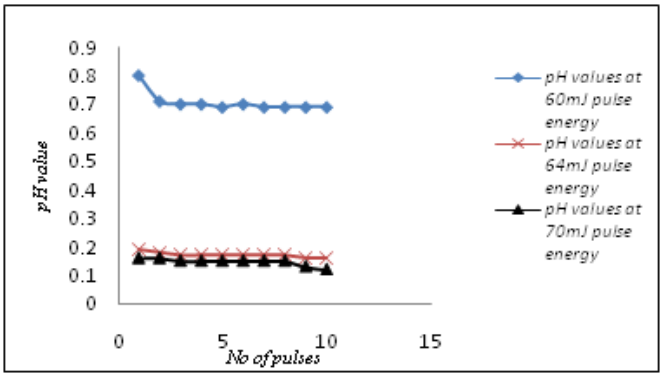

Fig. 3: A graph of laser pulses versus pH value at different pulse energies

3.3.2 Breakdown current

The current exist after breakdown is referred as breakdown current. The measurement of breakdown current with respect to the number of pulses is shown in Figure 4. It is evident from the results that as long as number of pulses increased the breakdown current also increased. At the same time pH values of the solution decreasing. The increasing value of the breakdown current was due to the induction of dissociation and ionization reactions (3), (4) and (5). The maximum breakdown current at pulse energy 70 mJ was 34.4 µA whereas at 64 mJ it was 23.3 µA while at 60 mJ it was 19.4 µA. This trend predicts that at higher laser pulse energy the breakdown process was more dominant than lower pulse energy. For the laser pulse energies 60 mJ and 64 mJ the

breakdown current initially increased then almost remained constant, while for pulse energy 70 mJ, breakdown current initially increased slowly until 4 pulses but after that it increased abruptly. Beyond 8 pulses all of a sudden, breakdown current raised from 24.5 µA to 34.5 µA. At this energy ionization reactions were maximum. So this energy was enough to split the water in to hydrogen. For 64 mJ pulse energy current slightly decreased from 22 µA to 20 µA after two pulses then again it increased. The decrement of current was may be due to neutralization response as described in reactions (4), (5) and (6).

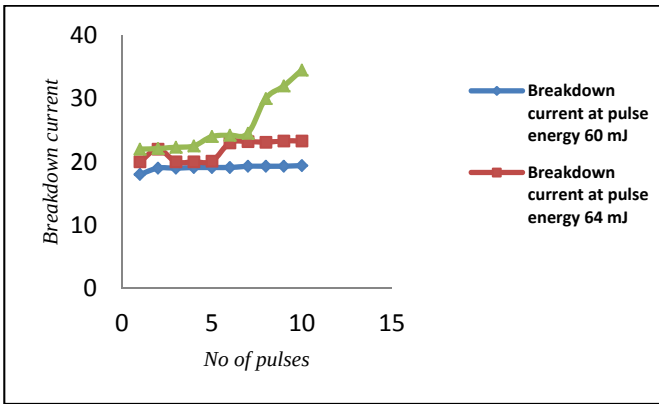

Fig. 4: A graph of laser pulses versus breakdown current at different pulse energies

3.3.3 Effect on the hydrogen concentration

The relationship between pulse energy and hydrogen yields are shown in Figure 5.The results demonstrated that hydrogen yield swelled up with increase in the number of laser pulses. At the same time the hydrogen yield was found to be reliant on the laser energy. The higher the laser energy the greater will be the hydrogen yield. At the outset when pulse energy was 60 mJ the hydrogen yield increased from 0.15 moles to 0.20 moles at the span of 3 pluses to 5 pulses, after that for each number of pulses the hydrogen yield remained approximately the same at 0.20 moles. Whereas at pulse energy 64 mJ; it increased slowly from 0.66 to 0.69 moles. The hydrogen yield remained about the same at 0.67 moles from 2 to 8 pulses. Similarly when pulse energy was set to be 70 mJ the hydrogen yield was initially at 0.69 moles at the span of 1 to 3 pulses then after 3 pulses, it steeped up to a value of 0.70 moles at 4 pulses. Then from 4 to 8 pulses it maintained this value and again it rose up after 9 pulses and reached at the value of 0.75 moles. For high pulse energy pH value was found to be decreased while break down current was found to be increased due to dissociation and ionization reactions (3), (4) and (5). These reactions intern made possible excess hydrogen production.

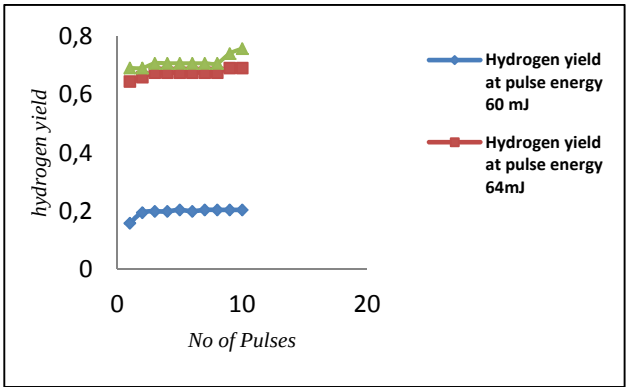

Fig. 5. A graph of laser pulses versus Hydrogen yield at different pulse energies

4. Conclusions

Chronological characteristics of laser spark emission were successfully engendered in HBr mixed water by the focused beam of a Q-switched Nd:YAG laser. The breakdown current, pH changes and hydrogen concentration in HBr aqueous solution were determined with reference to laser pulses at different energy. The pH value found to be decreased with increased in the laser pulse energy. This implies the higher the laser pulse the level of acidity is higher, consequently the more the proton of H+. This is confirmed by the increased of breakdown current and hydrogen yield when the laser energy increased. Such outcome has important information in chemical and textile industry, photodynamic therapy (PDT), laser induced thermotherapy (LIIT) and electrochemical therapy (ECT) of cancer tumor [17].

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