Spectroscopic investigations on Laser Induced Breakdown in Water.

A Nath and A Khare
Department of Physics
Indian Institute of Technology Guwahati, Guwahati-781039, India
E-mail: alika@iitg.ernet.in

Abstract. The band spectrum of molecular and radical species generated via laser induced breakdown in water is reported. The dependence of band spectra of various species on to the different regions of plasma is analyzed.

1. Introduction
Laser Induced Breakdown Spectroscopy (LIBS) has been used as a detector for trace elements in water, monitor for corrosion extent in nuclear power plants, analysis of chemical composition of sediments, rocks under ocean etc [1]. The technique is simple and doesn’t require any sample preparation. It is non-invasive technique and in situ measurements can be done which makes it ideal for working in extreme physical conditions [2]. When a high power laser is focused inside a liquid media, breakdown of the liquid medium leads to plasma formation. The excited molecular and atomic species within plasma emits the characteristic optical radiation. The collection, detection and characterisation of these optical emission forms the basis of LIBS technique. In the present paper, band spectra of water vapour, molecular oxygen, hydroxyl peroxide $\text{HO}_2^*$ and $\text{OH}$ radical in the laser induced breakdown of distilled water is reported. $\text{OH}$ radicals are the most important species in oxidation processes from technological point of view as it is a primary chain carrier in flame chemistry [3].

2. Experimental Set-up
The schematic of the experimental set-up, used for LIBS technique is shown in figure 1.

![Figure 1. Schematic of experimental set-up.](image)
A pulsed high power laser was focused by a lens L1 (10 cm focal length) inside a liquid cell filled with distilled de-ionized water. Focusing of high power laser leads to plasma formation. The plasma emits the characteristic line, band spectra of its constituent species. The plasma radiation was imaged by lens L2, onto the entrance slit of the monochromator and detected by the PMT at the exit slit of the monochromator interfaced with the computer.

3. Results and Discussion
The laser induced breakdown (LIB) and resulting plasma formation leads to excitation, ionisation and dissociation of water molecules. The reaction dynamics within plasma can be given by the following reactions [4].

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^* \\
\text{H}_2\text{O} & \rightarrow \frac{1}{2} \text{H}_2\text{O}_2 + \frac{1}{2} \text{H}_2
\end{align*}
\]

\[
\begin{align*}
\text{OH}^* + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
\text{OH}^* + \text{OH}^* & \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2
\end{align*}
\]

\[
\begin{align*}
2\text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}_2^* + \text{OH}^* & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

The emission band spectrum (figure 2 (a)) in the spectral region 230-250 nm in laser induced breakdown in water is due to hydrogen bonded OH radical. The dissociated molecular and radical species results in further propagation of reaction (reaction (3)) followed by termination reaction which produces neutrals (reaction (4), (5) and (6)). B band of molecular oxygen $\text{b}^3\Sigma_u^+ (\nu' = 1)$ due to electronic transition (686-688 nm) and vibrational overtones of 4\nu polyads of water vapour (695-705 nm) is also observed as shown in figure 2(b) [5]-[7]. When the laser intensity is high and above the threshold energy for water breakdown, optical breakdown takes place at the focus and extends to the Rayleigh length of the incident beam on either side of the focus. The formation of plasma is observed visually in the form of an elongated spark.

![Figure 2](image)

**(a)** Band spectra of (a) hydrogen bonded OH radical at 240 nm, (b) Molecular oxygen (686-688) nm and water vapour (695-705 nm)

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Figure 3. Band spectra of water vapour, molecular oxygen and hydroxyl peroxide radical at (a) forward front of plasma (b) focal region (c) backward front of plasma.
Figure 3 shows the band spectra of molecular oxygen, water vapour and hydroxyl peroxyde radical for different region of plasma; forward front, focal region and backward front as in figure 3(a), 3(b) and 3(c) respectively. The recorded band spectra of figure 3(a) in the forward front indicates presence of vibrational overtones of excited HO$_2^*$ species. Its emission band is centred at 670 nm [8].

The initial plasma formed due to laser induced breakdown, absorbs the incoming laser energy and achieves high pressure and temperature thereby ionizing the surrounding liquid layer. This is mainly dominated in the forward front of plasma. The new layer of plasma further absorbs the incoming laser energy and obstructs it from reaching regions beyond the focal volume. The rapid expansion of plasma leaves a rarefied region in the focal volume, which results in plasma cooling and favours recombination processes leading to formation of molecular oxygen at and beyond focal volume. Traces of molecular oxygen (686-688 nm) and water vapours (695-705 nm) are observed in figure 3(b) and figure 3(c). Excited hydroxyl radical, HO$_2^*$ are formed in a three step process (reaction (1), (2) and (3)) and requires higher energy so HO$_2^*$ species are confined to focal and the forward front of plasma whereas oxygen and water vapour bands are prominent in the backward front, figure 3(c).

4. Conclusion
Band emission spectrum for various molecular and radical species is recorded. B band of molecular oxygen, hydrogen bonded OH radical, vibrational overtones of excited HO$_2^*$ radicals and water vapour are detected. The dependence of molecular band spectra in different plasma regions is analyzed.

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