The measurement of gas temperature in nanosecond pulsed discharge in liquids via optical emission spectroscopy

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Abstract: We present the results of optical emission spectroscopy studies performed on nanosecond pulsed discharges in liquids. This regime of microplasmas has been shown previously to be formed directly in the liquid phase (no bubbles). The measurement of temperature is an important plasma parameter needed to qualify the applicability of these plasmas for applications purposes. We argue the non-thermal nature of the discharge and present results of Boltzmann analysis of OH(\(A^2\Sigma \rightarrow X^2\Pi\)) rotational lines, its applicability to the current regime, and challenges to the interpretation of these measurements accurately.

Keywords: spectroscopy, liquids, diagnostics, microplasmas, non-equilibrium

1. Introduction

The possibility of forming plasma directly in the liquid phase without an initial bubble nucleation phase has been reported in previous works [1-4]. This unique plasma regime has the potential to be utilized in applications where very high densities of plasma and chemical species are desirable without liquid vaporization associated with pre-initiation bubbles, for instance as reported in [5-7]. Perhaps the most important parameter needed when considering these micro-discharges for sensitive applications are the associated temperatures – electron temperature which will influence chemical activity, and gas temperature which will determine the extent to which the bulk liquid heats up. Certainly, in the context of recent developments of plasmas in liquids employed in biology, medicine, and material synthesis [8], a non-thermal plasma would attract much attention.

The electron temperature of this regime of plasma in liquids was previously estimated from optical emission spectroscopy reported in [1] and found to be \(~3\text{eV}\). These results were obtained through deconvolution of the Van der Waal’s and Stark contributions of the measured H\(_\text{\alpha}\) and O I lines, based on integrated emission spectra. Time resolved spectroscopy would later reveal that the emission due to a single nanosecond pulse (direct liquid ignition) is dominated by strong broadband emission with no measureable atomic transitions. The integrated spectra reported in [1] contained emission from phases associated with voltage ringing (multiple reflections) on the HV line.

The measurement of gas temperature is even more elusive, as the traditional low-budget techniques typically rely on the assumption of thermal equilibrium between the rotational temperature of ground-state molecules and the gas molecules [9]. This is a problem for plasma in liquids, especially water, where collisional quenching significantly hinders equilibration of rotational states, and, multiple distributions exist due to several mechanisms of formation of the rotationally excited molecule OH [10].

In this work, we present the results of optical emission spectroscopy performed on nanosecond pulsed discharges in water. Both time integrated and time resolved spectra were analysed, and a high-resolution analysis of the OH(A-X) band was performed. Typical analytical techniques were applied based on gross assumptions.

2. Experimental Setup

The plasma reactor setup is identical to that reported in [3], except the anode (pin electrode) was an Iridium probe with \(~5\text{nm}\) radius of curvature tip. Discharge was ignited in distilled, deionized water between submerged electrodes in a 3mm gap and the pulse frequency was limited to 10Hz to allow the liquid to recover between subsequent pulses. The problem of voltage ringing (reflections) due impedance mismatch of the load and the HV cable still existed and contributed to re-illuminations and liquid vaporization. High voltage pulses with \(+24\text{kV}\) amplitude was delivered to the plasma reactor via 100ft coaxial cable, with a return current shunt used for signal triggering and pulse monitoring. We will refer to the ‘first pulse’ as the leading voltage pulse associated with a single trigger of the power supply. Thus, in 1 second there will be 10 ‘first pulses’, each with a series of reflection transients lasting < \(4\mu\text{s}\).

Spectra were collected using a fibre-optic cable with 200\(\mu\text{m}\) core, coupled to a Princeton Instruments SP-500i monochromator system with two gratings: 750/l/mm and 1800/l/mm. A PI: Max 1K Gen II detector was used, with a spectral response from 250-900nm and a detector pixel width of 13\(\mu\text{m}\). The instrument function of the entire system was measured to be \(~0.05\text{nm}\) FWHM for high-resolution spectral measurements, with an entrance slit to the monochromator set to \(40\mu\text{m}\).
3. Results

The measured integrated spectrum is shown in Fig. 1. The exposure time was 2s and emission is an accumulation of light from multiple re-illuminations per applied voltage pulse (due to reflections), while, the spectrum corresponding to emission from only the first incident pulse is shown in Fig. 2. This emission profile was also corrected for wavelength sensitivity of the CCD detector in Fig. 2. Comparing the two spectra, one observes that in the first 50ns there is no emission from atomic hydrogen ($H_\alpha$) or oxygen (OI), or from ro-vibrationally excited OH. Time resolved studies of the development of the spectrum show that these distinct spectral features develop in the emission from reflected pulses. In these experiments, these correspond to re-strikes occurring in gas channels remnant of the plasma from the first pulse, consequently associated with different initiation and propagation mechanisms.

The emission from the OH band near 308 nm is shown in Fig. 3. Much of the structure associated with rotational temperatures greater than 600K is absent, though a few band heads could be discerned. In contrast, the OH emission activity is clearly present after the initial phase as shown in Fig. 4 with the R₂ band well developed. Boltzmann analysis of the distribution is in progress for the $R_2, P_1, Q_1, Q_2$ lines as performed in [11]. Conclusions based on this analysis however will only be valid for plasma formed in gas phases channels are described above.

Analysis of the FWHM of the measured $H_\alpha$ line was performed previously in [1], and in this work, a time-resolved study of the development of this emission line was performed. The results match those reported by Marinov et al. at a previous meeting. Analysis of the evolution of electron temperature and density as related to the FWHM of this line is also in progress.
4. Discussion

The wideband spectrum recorded for this regime of plasma in liquids is typical of what is observed with laser induced breakdown plasma [12-14]. Careful analysis shows that the emission does not fit Planck’s equation and cannot be attributed to blackbody radiation. As discussed in [15], this intense continuum radiation is most likely due to radiative recombination and Bremsstrahlung of high energy electrons. Both of these mechanisms are plausible given the high density (n0~10^22cm^-3) of molecules in water, assuming initiation directly in the liquid phase. This result indicates the existence of a large population of high energy electrons in the initial stages of the plasma development, a theory supported by the electrostriction based initiation hypotheses discussed in [2, 16, 17]. The absence of atomic hydrogen lines in the early stages could be due to several reasons, including the emission lines being dominated by the continuum background and the plasma being optically thick. Non-dissociative recombination of H_2O+ (or H_3O+) ions could lead to the formation of non-Boltzmann distributed OH radicals, as well as atomic hydrogen and oxygen according to [10], though perhaps the rotational-translational equilibrium might be true for low rotational quantum numbers. Boltzmann analysis of the OH rotational structure is currently underway to determine the deviation from equilibrium and the various temperatures associated with each rotational distribution.

The measurement of gas temperature from the optical emission spectroscopy of these types of discharges requires many assumptions, the validity of which needs to be properly assessed. Firstly, the optical thickness of the plasma in the early stages needs to checked. Furthermore, typical methods which are based on the measurement of rotationally excited OH requires equilibrium with the gas molecules, as well as thermalization of the OH states. The significant effect of collisional quenching by water vapour on the rotational energy transfer for discharges in gases will be amplified for discharges directly in the liquid phase. The increased density however, might allow efficient rotational energy transfer and establishment of equilibrium with the gas molecules. These factors are currently being scrutinized.

The existence of the dark phase throughout the emission lifetime from a single pulse supports that the plasma itself is non-thermal. One can draw this conclusion from comparison to laser induced breakdown where the plasma development and ablation is sustained by gas temperature[18]. Shadowgraphic studies performed previously showed post-plasma gas channels develop only along the filament channels and so is probably due to dissociative recombination of water ions and electrons into hydrogen gas.

5. Conclusions

Nanosecond pulsed discharges in liquids have been shown to develop directly in the liquid phase without bubbles. The temperature associated with these discharges is difficult to measure, but can be argued as non-thermal. Boltzmann analysis of OH emission spectrum will reveal some information about how far the rotational distribution is from equilibrium, however the bigger challenge is in determining whether the rotational-translational equilibrium can be attained in this environment. Electron temperatures are likely to be very high, and have been estimated to be ~3eV previously, but these results cannot be interpreted as the electron temperature associated with the direct liquid mode.

We remark finally that the interesting aspect to be investigated in this work lies in the study of the plasma formed due to a single nanosecond pulse (without reflections). From what was observed so far, continuum emission dominates this initial stage and temperature characterization from traditional OES techniques require many assumptions that may not be valid. Active diagnostics such as LIF might offer a better chance at quantifying the gas temperature in this regime.

6. References


