

In situ Raman spectroscopy at plasma-water interfaces

David Pai^{1,2}

1) LPP (CNRS, École Polytechnique, Sorbonne Université, Université Paris-Saclay, IP-Paris), 91128 Palaiseau, France

E-mail : contact@your.institute.es

2) Institut Pprime (CNRS–Université de Poitiers–ENSMA), F-86962 Futuroscope Chasseneuil, France

The plasma-water interfacial region is believed to play an important role in applications involving plasma-activated water (PAW), such as graphene quantum dot synthesis in aqueous solution using a DC microplasma electrochemical reactor [1,2]. As a simplified test case, we experimentally investigated the interfacial region using in-situ Raman microspectroscopy with a spatial resolution of several microns. The plasma reactor of choice is a DC glow generated in ambient air using a pin electrode placed above an optical cell filled with deionized water. First, we examined the solvent itself, tracking the –OH stretch band of water. This band experiences increasing intensity of the fundamental frequency distribution around $3400 - 3500 \text{ cm}^{-1}$, which is weakly coupled to other hydrogen bonds. The peak around $3200 - 3300 \text{ cm}^{-1}$, resulting from intermolecular coupling and strong hydrogen bonding, experiences decreasing intensity. We will discuss both rapid and gradual changes to the Raman spectra over the course of plasma treatment, as well as the reversibility of these changes once the plasma is switched off. The effect of depth below the plasma-water interface will also be discussed: the changes to the Raman spectra become more pronounced as the detection volume approaches the interface. Second, we track the concentration of PAW species via their calibrated Raman spectra. The Raman modes of the –OO stretch of H_2O_2 , symmetric stretch of NO_3^- , and –OH bend of water were measured simultaneously. In the bulk liquid, the molar concentration of aqueous NO_3^- increased at a linear rate of $48 \mu\text{M}/\text{minute}$, whereas aqueous H_2O_2 growth stopped at about 5 mM . The concentrations of H_2O_2 and NO_3^- both increased when measuring at depths less than about $20 \mu\text{m}$ from the interface. Previous models of plasma-water interfaces have predicted interfacial layers of similar depth for short-lived aqueous species such as OH but not for long-lived species such as NO_3^- .

References

- [1] Orrière, T., Kurniawan, D., Chang, Y. C., Pai, D. Z., & Chiang, W. H. (2020). *Nanotechnology* 31 (485001).
- [2] Yang, J. S., Pai, D. Z., & Chiang, W. H. (2019). *Carbon*, 153, 315-319.