

## OC-43: Non-Equilibrium Vibrational Excitation of OH Radicals Generated During Multibubble Cavitation in Water

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The OH<sup>•</sup> radicals are important reaction intermediates in a large variety of advanced oxidation processes initiated by acoustic cavitation in aqueous solutions (Mason and Morimer, 1998; Adewuyi, 2005). These species are produced during the violent implosion of gas filled microbubbles in liquids submitted to power ultrasound. In water saturated with noble gases, acoustic cavitation is accompanied not only by the generation of chemically reactive species but also by light emission, named sonoluminescence (SL) (Young, 2004). Spectroscopic analysis of the SL spectra allows to better understand the origin of the extreme conditions inside the cavitation bubbles, conditions that are still under debate. The multibubble SL spectra in water saturated with argon are composed of the emission of excited OH<sup>•</sup> radicals and a broad continuum ranging from UV to NIR spectral ranges which probably results from the superposition of several emissions: H+OH<sup>•</sup> recombination, water molecule de-excitation, and OH(B<sup>2</sup>Σ<sup>+</sup>-A<sup>2</sup>Σ<sup>+</sup>) emission (Sehgal et al., 1980). Recently, SL from OH(A<sup>2</sup>Σ<sup>+</sup>) and OH(C<sup>2</sup>Σ<sup>+</sup>) excited states has been observed in sonicated water saturated with noble gases at various ultrasonic frequencies (Pflieger et al., 2010). These results clearly showed a strong effect of gas nature and frequency of ultrasound on the population ratios between (0-0) and (1-1) vibrational transitions of the OH(A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π<sub>i</sub>). Moreover, the observation of OH(C<sup>2</sup>Σ<sup>+</sup>-A<sup>2</sup>Σ<sup>+</sup>) emission in the presence of Kr and Xe revealed non-thermal plasma formation during multibubble cavitation in water. The OH(A-X) system could be a very useful tool to study the non-Boltzmann behaviour of plasmas generated within the cavitation bubbles. However, the vibrational transitions in SL spectra are still poorly investigated and mostly only used to identify excited species. The major difficulty in the quantification of SL spectral data is that OH(A-X) emission yields dense overlapping vibrational structures. Rotational structures of these emission lines are not observed most probably due to strong collisional or van der Waals broadening. This paper focuses on the development of an original approach allowing to deconvolute OH(A-X) emission in multibubble SL spectra and to probe the intra-bubble conditions via the vibrational population distribution of OH(A<sup>2</sup>Σ<sup>+</sup>) state as a function of ultrasonic frequency.

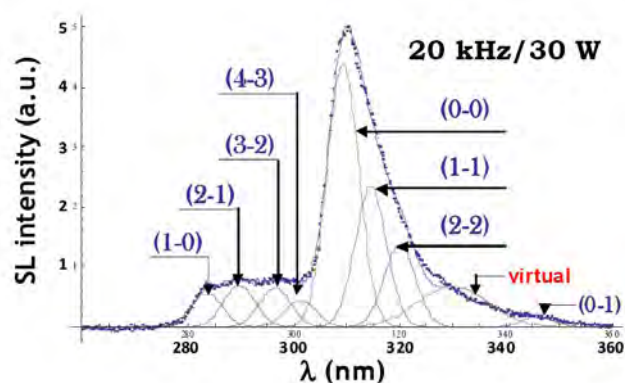


Figure 1: Deconvoluted SL spectra of the OH(A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π<sub>i</sub>) system, H<sub>2</sub>O, Ar, 20 kHz. Dotted line—experimental spectrum, solid line – fit.

The SL spectra of OH (A<sup>2</sup>Σ<sup>+</sup>) excited state produced during the sonolysis of water saturated with argon at various ultrasonic frequencies (20, 204, 362, 609 and 1057 kHz) were measured. To analyze them, the first step was to deconvolute the dense overlapping emission bands. While thermal equilibrium would lead to a spectrum dominated by (0-0), (1-0) and (1-1) transitions, the SL spectrum measured at 20 kHz exhibits also strong emission from higher vibrational excited states, such as (2-1) and (3-2) (Fig.1). The vibrational over-population is even stronger at high ultrasonic frequency.

From the deconvoluted spectra it is possible to obtain the relative populations of  $\text{OH}(A^2\Sigma^+)$  vibrational states from  $v \in 1$  up to  $v \in 4$ . The calculated values of  $N_v^r$  are plotted in Fig. 2 as a function of the vibrational energy for each studied ultrasonic frequency. For comparison, data computed with Lifbase ab-initio code for an equilibrium distribution ( $P=200$  bars and  $T=5000$  K) are also included. Fig. 2 shows unequivocally that, in contrast to a thermalized system, the relative population distribution obtained from the SL spectra deviates strongly from the equilibrium Boltzmann distribution. At 20 kHz, the vibrational population distribution of  $\text{OH}(A^2\Sigma^+)$  appears to follow an hyperbolic distribution function known as Brau's distribution typical for weak vibrational excitation (Fridman, 2008). At higher ultrasonic frequencies it follows the Treanor exponentially parabolic distribution function which describes strong vibrational excitation (Fridman, 2008).

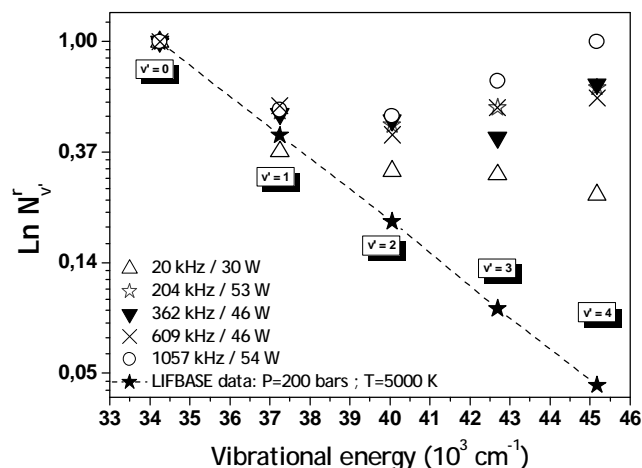


Figure 2: Relative vibrational population distribution of  $\text{OH}(A^2\Sigma^+)$  as a function of vibrational energy for different ultrasonic frequencies.

To make a more detailed diagnostics, vibronic temperatures ( $T_v$ ,  $T_e$ ) of the  $\text{OH}(A-X)$  system have been estimated for all studied ultrasonic frequencies by comparison of the deconvoluted experimental spectra with simulated ones having electronic and vibrational temperatures as input parameters. This analysis shows that non-equilibrium plasmas generated during the sonolysis of argon-saturated water obey the classical inequality  $T_e > T_v$ . The  $T_e$  and  $T_v$  values increase with the ultrasonic frequency reaching  $T_e \sim 1$  eV and  $T_v \sim 9800$  K at 1057 kHz. This trend clearly indicates that acoustic collapse creates more drastic conditions at higher ultrasonic frequencies.

#### Acknowledgments

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