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Molecular emissions in sonoluminescence spectra of water sonicated under Ar-based gas mixtures

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Abstract: Sonoluminescence (SL) spectroscopy is one of the very few ways to study the plasma formed in solutions submitted to ultrasound. Unfortunately, up to now only very limited emission bands were reported in SL spectra of aqueous solutions. It is shown here that by adding some N_2 and/or CO_2 in Ar, new molecular emissions can be observed and that rovibronic temperatures can be derived.

1. Introduction

When a liquid is irradiated with ultrasounds (with a frequency in the range 20 kHz – 1 MHz), a particular chemical activity is observed, called sonochemistry. Its origin is acoustic cavitation: nucleation, growth and violent collapse of microbubbles containing dissolved gases and vapour of the bulk liquid. The formation of a plasma in cavitation bubbles at collapse is now widely admitted[1] even though the underlying mechanism remains unclear. Moreover characterization of this plasma is not straightforward due to its small size (< 1 µm), its short lifespan (< 1 µs) and the stochastic (non-predictable) nature of its apparition. Two main directions can be followed to study it: monitoring of its chemical activity and emission spectroscopy of sonoluminescence (SL, the light emitted by the sonochemical plasma). This work focuses on the different spectroscopic probes that can be observed in SL spectra of water irradiated at 362 kHz under different gas mixtures in Ar.

2. Experimental

Deionized water (Milli-Q 18.2 MΩ cm) was used. Ar and mixtures of N_2 (5%) or CO_2 (0.5%) in Ar were provided by Air Liquide (purity > 99.999%).

For all experiments, 250 mL of deionized water were placed in a thermostated glass reactor equipped with a 362-kHz transducer (ELAC Nautik, 25 cm^2) at its bottom. The absorbed acoustic power was determined calorimetrically (P_{ac} = 43 W). The solution was submitted to a continuous gas flow (82 mL/min) starting half an hour before the experiment and maintained during the ultrasonic treatment. Emission spectra of sonoluminescence were collected through a flat quartz window mounted on the sonoreactor and recorded in the spectral range 250-650 nm by means of SP 2356i Roper Scientific spectrometer (gratings 150blz500, 600blz300 and 1200blz300) coupled with a CCD camera that is equipped with UV coating (SPEC10-100BR Roper Scientific) cooled by liquid nitrogen. Spectral calibration was performed using a Hg(Ar) pen-ray lamp (LSP035, LOT-Oriel). The spectra acquisition was started after reaching a steady-state temperature. For each experiment, at least ten 300-s (150blz500 grating), respectively 600-s (600blz300 and 1200blz300 gratings), spectra were averaged and corrected for the background noise and for the quantum efficiencies of gratings and CCD. Gases formed during the sonolysis were measured online by mass spectrometry (Prima BT, Thermo Fischer Scientific).

3. Results

3.1. Sonoluminescence emission spectra

Figure 1 presents the UV parts of SL spectra of water sonicated at 362 kHz under Ar-5%N_2, Ar-0.5%CO_2 and Ar-0.5%CO_2-5%N_2 gas flows, and Figure 2 their visible parts.

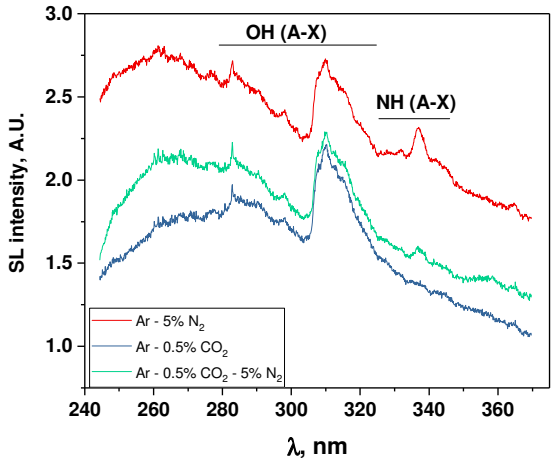

Fig. 1: UV part of SL spectra of water under Ar-5%N_2, Ar-0.5%CO_2 and Ar-0.5%CO_2-5%N_2 (362 kHz, 14°C, 600blz300 grating).

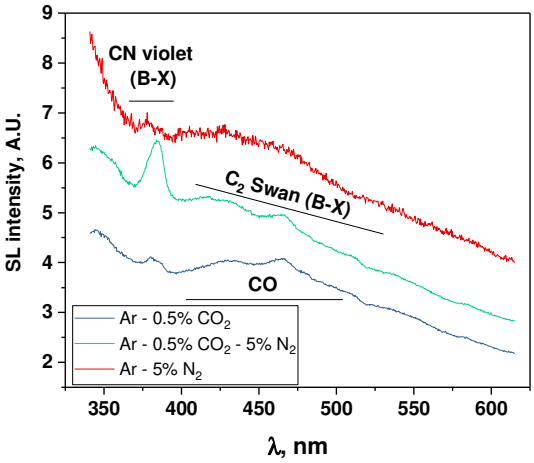

Fig. 2: Visible part of SL spectra of water under Ar-5%N_2, Ar-0.5%CO_2 and Ar-0.5%CO_2-5%N_2 (362 kHz, 14°C, 150blz500 grating).

Like the usually reported SL spectrum of water under Ar, they show an intense continuum spanning from the UV to the near IR and the emission from excited OH radicals (OH (A-X)). The latter arises from the dissociation of water molecules in cavitation bubbles at collapse:

$$H_2O \rightarrow))) \rightarrow H + OH \qquad (1)$$

When the saturating gas is Ar-5%N_2, a molecular emission is present around 337 nm that is assigned to NH (A-X).[2] One mechanism of formation of this excited species is:

$$N_2 \rightarrow))) \rightarrow 2\,N \qquad (2)$$
$$N + H \rightarrow NH \qquad (3)$$

The sonolysis of water in the presence of Ar-0.5%CO_2 gas mixture leads to a complex SL spectrum. A tiny peak appears near 386 nm and is attributed to CN violet[3]; CN can be formed in the presence of air traces:[4]

$$N_2 + CO_2 \rightarrow))) \rightarrow CN + NO_2 \qquad (4)$$

Besides, the maxima of C_2 Swan bands are recognizable but superimpose with a broad not-well-defined emission, likely CO (X-X)[3]:

$$CO_2 \rightarrow))) \rightarrow CO + 1/2\,O_2 \qquad (5)$$
$$CO_2 + H \rightarrow))) \rightarrow CO + OH \qquad (6)$$

The presence of CO was confirmed by mass spectrometry analysis of the outlet gas.

Adding conjointly 0.5% CO_2 and 5% N_2 in Ar leads to the observation of OH (A-X), NH (A-X), CN violet (confirming the nature of the emission at 386 nm) and C_2 Swan bands. The absence of CO emission and the absence of CO in the outlet gas can be traced back to the reaction[4] of CO with N_2:

$$N_2 + CO \rightarrow))) \rightarrow CN + NO \qquad (7)$$

3.2. Derived rovibronic temperatures

Molecular emissions observed in SL spectra were simulated whenever possible using Specair software[5]. Derived rovibronic temperatures are summarized in Table 1 in the form vibrational temperature T_v / rotational temperature T_r.

Table 1. Estimated rovibronic temperatures (± 1000 K unless otherwise specified).

Gas	OH	NH	C_2	CN
Ar – 5% N_2	11500 K / 6500 K	10000 K / 10000 K		
Ar – 0.5% CO_2	11500 K / 6500 K			
Ar – 0.5% CO_2 - 5% N_2	11500 K / 6500 K		22000 K / 5000 K	10000-15000 K / 10000 K

4. Conclusion

Although it was long considered that SL spectra of aqueous solutions were relatively featureless compared to those of exotic liquids (e.g. concentrated sulfuric acid), thus strongly limiting the possibility to study the formed plasma, this study shows that besides usual OH and C_2 emissions and the recently reported NH one, at least two more molecular emissions can be observed in high-frequency SL spectra of aqueous solutions, namely CN and CO. This finding enriches the "toolbox" available to characterize the sonochemical plasma, the conditions reached at collapse of cavitation bubbles and the chemical reactions taking place in bubble cores.

5. References

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