

# Sonochemistry and Sonoluminescence in Aqueous Systems

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## ABSTRACT

The sonochemistry of water based systems is of interest in a large number of areas including pollution remediation, chemical synthesis and safety implications for medical systems. In an attempt to clarify the precise mechanism of aqueous sonochemistry, measurements of radical production as well as monitoring sonoluminescence emission and recording acoustic emission spectra have indicated how additives affect the cavitation field and also demonstrated large differences in the nature of both cavitation products and the cavitation field when using ultrasound with two different ultrasound set-ups; a 20 kHz horn and a 515 kHz emitting transducer. A possible model to explain some of these results has been proposed suggesting that the type of cavitation is different in the two situations in terms of the proportion of stable and transient bubbles that exist. Applications of the methods to characterising ultrasonic dental instruments has shown a detailed dependence of cavitation on the design and properties of the tip.

## INTRODUCTION

Cavitation is one of the most studied but perhaps least thoroughly understood phenomena in physical acoustics. It occurs when a sufficiently negative pressure is generated in a liquid [1] and can arise for example due to large pressure drops in pumps or around propeller blades (hydrodynamic cavitation) or by a propagating sound - usually ultrasound - wave (acoustic cavitation). During the rarefaction phase of the wave, a microscopic bubble (cavity) can be produced [2] which grows before finally collapsing with the release of large amounts of energy.

Cavitation bubbles may grow rapidly and collapse after only a few acoustic cycles ('transient' cavitation) or may oscillate about a mean size for many thousands of oscillations ('stable' cavitation). Changes in the ultrasound intensity and other experimental conditions may cause a switch between the different types of cavitation. Cavitation may occur in all types of fluid but, given their importance in a wide range of industrial, medical and chemical processes, only aqueous, water-based systems will be considered here. The maximum diameter of a cavitation bubble in water is typically 50 – 100  $\mu\text{m}$  although this depends on the sound intensity and frequency as well as properties of the liquid such as density, vapour pressure and surface tension. However the overall effect in any cavitating system is the result of a field or 'cloud' of many bubbles so that of equal importance is the way that bubbles interact with each other.

In some cases, cavitation is undesirable or even potentially damaging; an example is in fetal imaging. In other medically related applications of ultrasound [3] such as lithotripsy, generation of cavitation is advantageous. Cavitation has a number of applications in cleaning [4] and industrial processing [5] and has also been applied to a variety of chemical reactions and purification procedures [6]. A range of chemi-

cal reactions used in synthesis are promoted by ultrasonically generated cavitation [7]. One consequence of cavitation bubble collapse is the generation, on a microsecond timescale, of extremely high temperatures and pressures, of the order of  $\sim 5000\text{ K}$  and  $> 500\text{ atm}$  [8] and these lead to breakdown of the liquid to form reactive species such as free radicals. For example in water, hydroxyl ( $\text{OH}\bullet$ ) and hydrogen ( $\text{H}\bullet$ ) radicals are formed. Small amounts of additives or contaminants in water can react with these species and this has formed the basis of a method of water purification and treatment [9]. It is apparent from this range of uses that reliable methods to detect and quantify and control cavitation are needed and this paper will illustrate some of the methods we have applied to sonochemical systems in an attempt to gain an understanding of the effects of various experimental parameters and how and our work in this area by comparing cavitation measurement from a number of ultrasound sources.

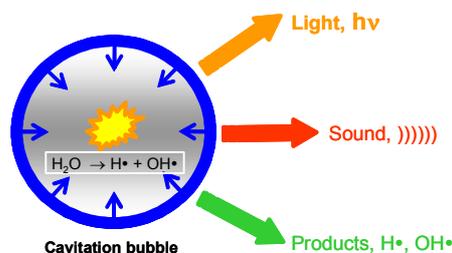


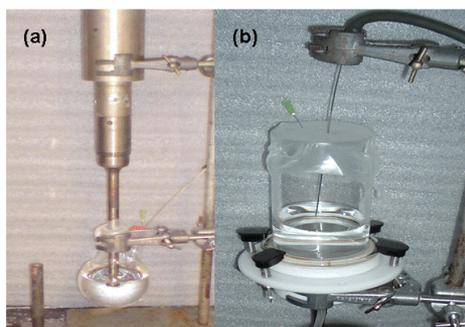
Figure 1: Potential methods for studying cavitation

Potential ways of measuring the effects of cavitation are suggested by Figure 1. The products arising from the breakdown of solvent during cavitation ('solvolysis') and further chemical reactions can be quantified. In aqueous systems, hydroxyl radicals can be trapped with terephthalic

acid and quantified by fluorescence spectroscopy [10]. Further analysis of reaction products gives information on reaction mechanisms in and around cavitation bubbles. Collapsing bubbles act as secondary sound sources and so the acoustic emission can be detected [11]. This has proved to be a sensitive monitor of the types of cavitation occurring. Finally, cavitation collapse also results in the emission of a brief flash of light, so-called sonoluminescence (SL) [12]. The spectral characteristics and changes in the emission intensity gives further information on cavitation. Each of these methods has yielded valuable information on the conditions that are needed to generate cavitation and the effect that changing the experimental conditions has on the number and distribution of cavitation bubbles in a sound field.

## EXPERIMENTAL

The sonochemistry apparatus used is shown in Figure 2. Sonication at 23 kHz was carried out with a Sonics & Materials VC 600 fitted with a 1 cm diameter titanium horn (Figure 2(a)). 150 cm<sup>3</sup> of the solution under investigation was measured into a beaker or flask fitted with a water jacket to allow for temperature regulation. Care was taken to ensure that the horn, camera, acoustic sensor, sampling ports etc. were placed in the same position for all experiments. A fresh sample of solution was used for each experiment when changing intensity. For higher frequency, 515 kHz, sonication, an Undatim UL03/1 reactor employing a 5 cm diameter plate transducer was used (Figure 2(b)). 150 cm<sup>3</sup> of solution was contained in a jacketed cylinder over the transducer. The intensity of ultrasound used was measured by calibrated calorimetry in the usual manner [13]. The ultrasonic dental scaler was a Piezon miniMaster provided by Electro Medical Systems, Nyon, Switzerland. The scaler operates at a nominal frequency of 30 kHz, and can be set to any of ten incremental power settings from a control panel. These were also calibrated calorimetrically to determine the ultrasound intensities used.



**Figure 2.** Sonication apparatus (a) 23 kHz, (b) 515 kHz. Thermostatting jackets have been removed for clarity

In order to record sonoluminescence images, the apparatus was contained in a light-proof box. After saturation of the solution with Argon gas, images were recorded on an Artemis CCD camera with a 35 mm focal length lens capable of an f2.8 aperture and incorporating a Sony ICX285AL low-light CCD sensor with an imaging resolution of 1392 x 1040 pixels (1.4 megapixels). The total intensity of the emission was calculated after subtraction of background levels using ImageJ software [14] which was also used for further image manipulation.

For some experiments, enhanced images were obtained by sonicating a solution of chemiluminescent luminol. This was

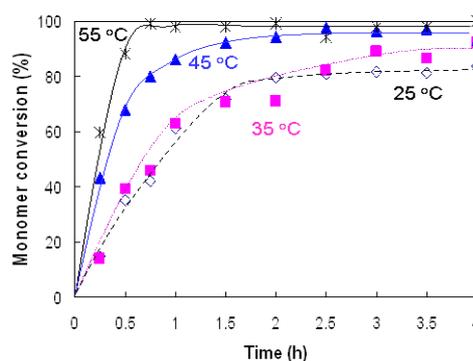
prepared by dissolving 1 mmol of luminol (3-aminophthalhydrazide, 97%), 0.1 mol hydrogen peroxide and 0.1 mol EDTA (ethylenediaminetetraacetic acid) in 1 dm<sup>3</sup> of 0.1 M sodium carbonate. The solution was adjusted to pH 12 by adding sodium hydroxide. High resolution video images were obtained using a Sony DCR106 video camera.

Acoustic emission from cavitating solutions was monitored using a 'Cavimeter', developed by the National Physical Laboratory in the UK [15]. It consists of a strip of piezoelectric material embedded in a sound absorbing plastic cylinder. The design of the sensor is such that the response arises solely from activity inside this cylinder. The signal produced is integrated over a 2 s period and analysed for 'subharmonics', recorded at frequencies of one-half and one-quarter of the fundamental which is indicative of the onset of transient cavitation. This type of cavitation is also quantified by measuring the 'cavitation' signal from emission at high frequencies between 1.5 and 5 MHz which arise from shock waves emitted by the collapse of transient bubbles.

All chemicals were obtained from Aldrich (UK). Aqueous solutions were prepared in deionised water from a MilliQ system and had a resistance > 10 MΩ.

## RESULTS AND DISCUSSION

A reaction typical of those to be investigated is an emulsion polymerization to form a latex. Here, an organic compound such as styrene or methyl methacrylate is dispersed in water with the aid of a surfactant emulsifier such as sodium dodecylsulfate, SDS. The polymerization reaction is conventionally started by heating to decompose an added initiator. This is an example of a reaction initiated by radicals and is common in the polymer, surface coatings, cosmetics and food industries. A number of workers [16 – 18] have reported the application of ultrasound to enhance the reaction. Potential advantages include the mixing effects in multi-phase systems due to streaming and microjetting near a boundary (reducing or eliminating the need for added emulsifiers) and radical production at rates comparable with those from a thermal initiator (obviating the need for addition such chemical initiators). Ultrasonically initiated emulsion polymerizations of styrene were conducted, as shown in Figure 3, using the 23 kHz 'horn' apparatus shown in Figure 2(a).



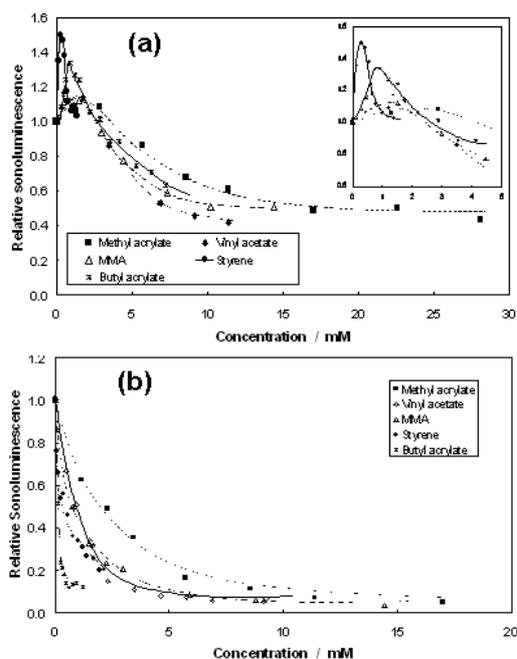
**Figure 3.** Emulsion polymerization of styrene at the indicated temperature using 23 kHz ultrasound. (From [19])

The results [19] show that the reaction is rapid with essentially complete conversion of the styrene to polymer occurring in ~ 40 min at 55 °C. In the absence of ultrasound, longer reaction times (~ 3–4 h) or higher temperatures (~ 75 °C) are required. There is a high reaction rate even at 25 °C

where, in the absence of ultrasound, less than 15% conversion was achieved after 4 h. When the reaction is conducted at the higher frequency of 515 kHz, it is noteworthy that very little reaction takes place. Related measurements indicate that radical formation does take place but the mixing and perturbation of the liquids is very much reduced so that little latex is formed.

### Sonoluminescence quenching

In order to investigate the detailed properties of this reaction, the sonoluminescence (SL) from dilute solutions of styrene and other monomers was measured [20]. The intensity of SL emission from water was measured and that from solutions related to this value as shown in Figure 4.



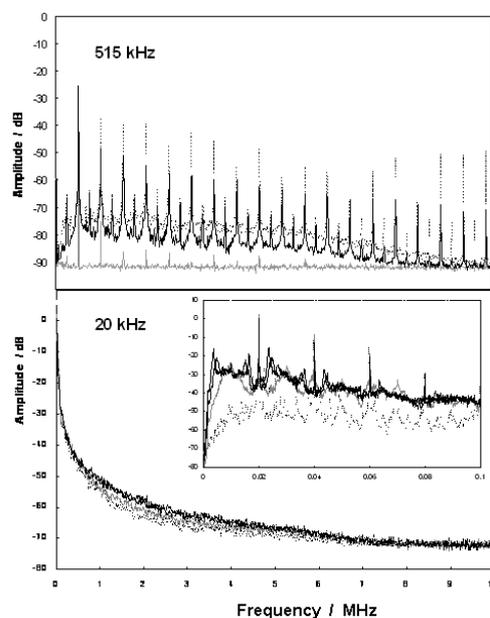
**Figure 4.** Sonoluminescence emission (relative to pure water) for air-saturated aqueous solutions of vinyl monomers sonicated at (a) 23 kHz, (b) 515 kHz. (from [20])

At 515 kHz, the five monomers each caused effective quenching of SL. Even for the least efficient quencher – methyl acrylate – a concentration of 10 mM ( $10 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) was sufficient to quench 90% of the luminescence observed from pure water. In contrast, at 20 kHz, the quenching efficiency followed a different order from that at the higher frequency and the minimum emission was  $\sim 40\%$  of that from water. The major difference is that at very low concentrations, the emission was *enhanced* by up to 50%, as clearly shown in the inset to Figure 4(b). This enhancement was not seen at 515 kHz. In contrast to the results from the higher frequency, concentrations of 10 mM caused reductions of only around half of the SL even with the most efficient quencher. The quenching is due to the evaporation of the monomer into the bubble where it is subject to pyrolysis as well as the build up of pyrolysis products such as lower hydrocarbons [20]. This reduces the temperature produced on collapse and hence the intensity of SL. Since these products have very low solubility in water, they diffuse into and accumulate in the cavitation bubbles. The order of quenching followed the hydrophobicity of the monomers indicating that the accumulation at the solution / bubble interface is important.

At 20 kHz, the extent of quenching is lower, suggesting that pyrolysis products build up to a lower extent; there was no correlation with monomer hydrophobicity. Our contention here was that 20 kHz bubbles, while growing to a larger size and producing more radicals on collapse, have a relatively short lifetime and so the opportunity to build up gases in the bubble is limited. The cavitation field at 20 kHz is more chaotic than at the higher frequency and our explanation for the SL enhancement is that the hydrophobic compounds migrate to some extent to the bubble surface and prevent them from coalescing. This means that there are more bubbles emitting SL than would be the case in water alone.

### Acoustic emission spectra

To further investigate this difference in sonochemical reactions at different frequencies, acoustic emission spectra were recorded at both frequencies for water and a number of solutions using the NPL ‘Cavimeter’ as shown in Figure 4. The spectrum recorded from sonication at 23 kHz is relatively featureless over the 0 – 10 MHz scale. The inset shows a small section of the emission at lower frequencies up to 100 kHz. The peak at  $\sim 20$  kHz is due predominantly to the direct field as well as bubble oscillation at the driving frequency. However, it is apparent that there are a series of overtones at multiples of the fundamental and also at several other frequencies. By the fifth overtone (i.e. 100 kHz) there is very little intensity in the peaks and the spectrum consists largely of broadband emission. This relatively unstructured spectra is characteristic of transient cavitation, as is the presence of sub-harmonics. In contrast, the spectrum recorded when using 515 kHz ultrasound has much more structure and more prominent overtones, even up to the 20<sup>th</sup> harmonic. These harmonics arise from non-linear bubble motion, usually associated with stable cavitation. However, there is some broadband emission suggesting that some transient cavitation does take place to some degree.



**Figure 5.** Acoustic emission from water sonicated at 515 or 23 kHz at various acoustic intensities. Inset shows emission between 0 – 100 kHz. (from [22])

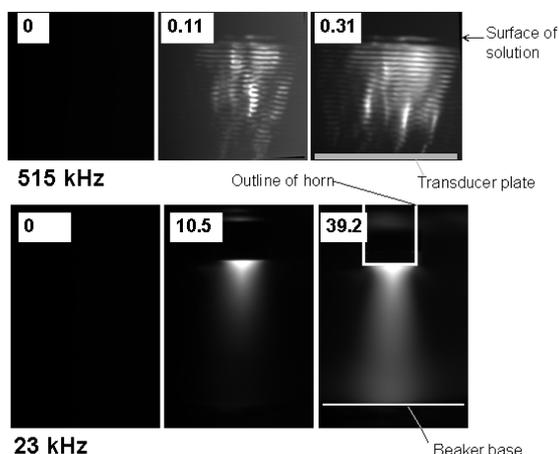
From further analysis of the spectra [21, 22] we were able to conclude that only 1 – 2 % of the total emission energy is contained in the peaks at 23 kHz while the corresponding value at 515 kHz is 85 – 90% depending on the power used. Thus, the horn primarily gives rise to transient cavitation

while stable cavitation predominates in the 515 kHz plate transducer system. We also showed that the total emitted energy correlated reasonably well with the sonoluminescence emission and with the production of  $\text{OH}\bullet$  radicals under identical conditions.

### Luminol mapping

As well as the difference in the type of cavitation detected, the differing geometry of the transducers and generators give rise to different cavitation fields. In order to investigate this, luminol photography was used to 'map' the cavitationally active zones in the two types of apparatus.

Figure 6 shows the light emission from luminol solutions sonicated with each type of apparatus [23]. Similar results were obtained for sonoluminescence from pure water (i.e. with no added luminol) although much longer exposures were needed reducing the detail in the images. Bright areas in the images indicate light emission from areas where  $\text{OH}\bullet$  radicals arising from sonolysis of water are generated to react with luminol. Hence bright areas are indicative of where cavitation takes place. It is apparent that the volume of solution that is cavitationally active is different for sonication in the two systems. For the 23 kHz horn, there is a small cone-shaped volume with very concentrated emission; at the higher frequency, emission is much more even throughout the solution volume. The 'layers' of emission correspond to a standing wave field with spacing corresponding to the wavelength ( $\sim 3$  mm) of sound in water at this frequency. As might be expected, in both cases the amount of light emission – and hence cavitation – increased with rising ultrasound intensity. Note that the intensities are very different, partly as a result of the larger emitting area of the 515 kHz plate. The sound energy emitted corresponded to 1.2 – 6.0 W compared with 12 – 60 W into the same volume of solution with the 23 kHz horn.



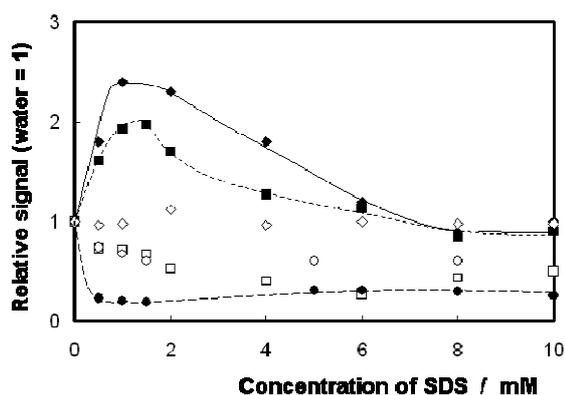
**Figure 6.** Luminol emission from cavitating solutions (1 min exposure). Values indicate the ultrasound intensity in  $\text{W cm}^{-2}$  (from [23])

### Effect of additives

The foregoing work, both acoustic and SL emission, indicates that both the cavitation field and the nature of cavitation is different when using a 23 kHz horn or a 515 kHz emitting plate. In applications of sonochemistry, there will always be dissolved solutes so that it is important to understand how these influence cavitation – and conversely, how cavitation affects the solutes. As a model system, solutions of SDS were investigated. SDS is a highly surface active, anionic surfac-

tant which preferentially migrates to the solution – air interface; in a cavitating system, SDS will migrate to the solution – bubble interface and hence coat the bubble, giving it a negative charge.

Figure 7 shows the relative changes of acoustic emission (i.e. the emitted sound energy) and SL emission when SDS is added to water when sonicated at 515 kHz. As small amounts are added, both emission energies increase but recover to the water value as more SDS is added. Significantly, if the experiment is repeated in the presence of an electrolyte, sodium perchlorate, the variation is not observed (the open points in Figure 7). Also shown are independent measurements [24, 25] of the extent of bubble coalescence. In addition, if the experiments are performed using 23 kHz ultrasound, no significant change in emission is observed.



**Figure 7.** Comparison of acoustic energy emission (■, □), SL emission (◆, ◇) and bubble coalescence (●, ○) from solutions of SDS (filled points) and SDS + 0.1 M  $\text{NaClO}_4$  (open points) sonicated at 515 kHz. (From [22])

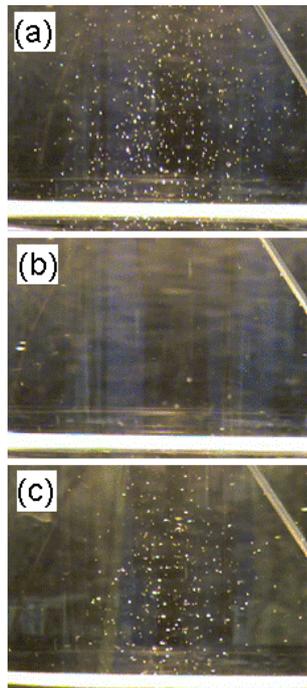
Our interpretation is that the surfactant coats the bubbles and keeps them separated in an acoustic field by electrostatic repulsion. Hence coalescence is prevented so that there are more active bubbles which emit. In the presence of an electrolyte, the electrostatic repulsion is screened by the perchlorate. The standing wave nature of the field at 515 kHz which does not generate large bubble motion and streaming ensures that these effects are observable. Conversely, at 23 kHz, the motion due to acoustic streaming pushes bubbles together with sufficient force to overcome the repulsion and no variation in emission intensity was observed, attributed to the short lifetime of the bubble not allowing sizable partitioning of the surfactant to take place.

Further evidence to support these assertions is given by Figure 8 which shows still photographs taken from video recordings of 515 kHz sonications. In Figure 8(a), some large, coalesced bubbles can be seen which arise from degassing of the solution when using water. These are too large to be stable cavitation bubbles and so are not sonochemically active and do not emit SL. They are gradually lost to the surface of the solution by buoyancy. Repeating the experiment in the presence of  $1 \text{ mmol dm}^{-3}$  SDS (Figure 8(b)) shows that these bubbles do not form; coalescence is reduced and more smaller, sonochemically active bubbles exist in solution. The SL and acoustic emission therefore are higher than with water. As Figure 8(c) shows, addition of background electrolyte screens the bubble-bubble repulsion and so the solution acts in a similar fashion to water.

### Ultrasonic dental instruments

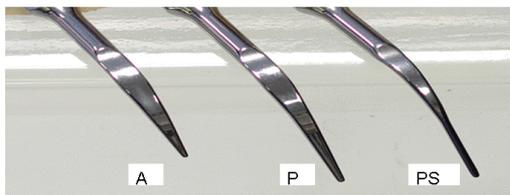
As an illustration of how these methods can be applied to

other applications of ultrasound, we have been investigating the behaviour and characteristics of ultrasonic dental instruments such as the scalers used to remove deposits from the surfaces of teeth as well as between the tooth and the gum.



**Figure 8.** Photographs of 515 kHz sonication at  $0.31 \text{ W cm}^{-2}$ . (a) pure water (b) aqueous 1 mM SDS solution (c) aqueous 1 mM SDS + 0.1 M sodium perchlorate (from [23])

The scaler consists of a piezoelectric transducer in a handpiece attached to a metal 'tip' which contacts the tooth. The tip design of scalers varies between manufacturers, but as shown in Figure 9 is generally a J-shaped metal (often titanium) tip, approximately 15 mm in length, attached to a handpiece that is manipulated by the clinician. During use, a transducer in the handpiece induces vibration as shown in Figure 10 at ultrasonic frequencies (in this case  $\sim 30 \text{ kHz}$ ) and the free end of the tip is placed against the tooth, mechanically removing deposits on the surface. An irrigant solution is passed over the tip both to prevent heating and to assist in washing debris from the surface. It has been suggested that cavitation might occur in the cooling water and that this might aid the cleaning process so that we set out to characterise dental scalers using the methods that we had previously applied to sonochemical systems.

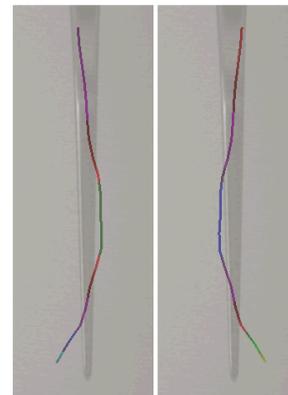


**Figure 9.** Design of the A, P and PS descaler tips. Each is ca. 15 mm in length. The free end of the tip is placed side-on to the tooth during treatment. (from [26])

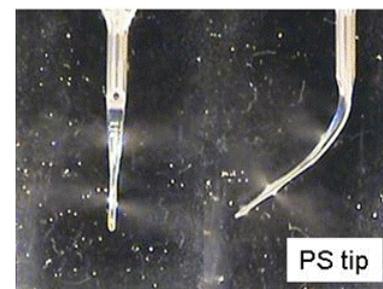
Three different tip designs, shown in Figure 9, were used. The vibration characteristics were measured [26] using scanning laser vibrometry as reported by Walmsley et al. [27]. This technique measures the displacement of 15 points along the tip during the vibration which allows reconstruction of the motion as shown in Figure 10. The maximum motion

occurs at the end of the tip but also at antinode points along the length. This motion is sufficient to generate cavitation which has been measured in several ways.

Firstly, the cavitation bubble field can be observed visually. Figure 11 shows an example of one of the tips and the cavitation field can be seen emanating from the side of the tip. To confirm that these were cavitation bubbles, emission from luminol solutions for each of the tips was recorded, the results being shown in Figure 12(a) (only photographs from the highest power setting experiments are shown). As above, light regions indicate areas of high cavitation activity, with dark regions indicating little or no activity. The data shows intense regions of activity surrounding the bend for each tip and at some other areas along their lengths although little to no activity was observed at the free end of the tip. This confirms that cavitation is indeed generated in water around scalers and that the regions of highest activity correspond, with the exception of the ends of the tips, to the regions of maximum motion. The data also show that, even though the tip designs are superficially quite similar, the cavitation patterns are very different, demonstrating the influence of tip design on performance.

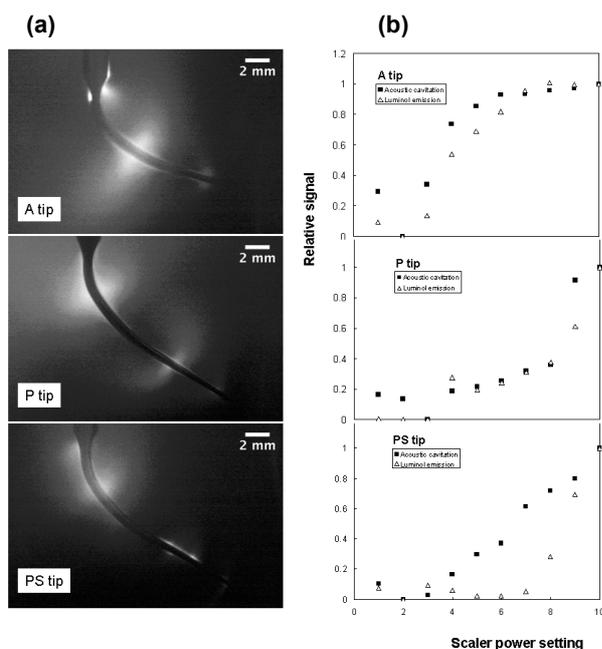


**Figure 10.** Computer generated, exaggerated images of a P tip at maximum displacement as measured by scanning laser vibrometry. (from [26])



**Figure 11.** Photograph of PS scaler tips in operation at maximum power

The acoustic emission from the cavitating scaler tips was also analysed and is compared with the luminol emission intensity in Figure 12(b) which shows the energy in the sub-harmonic region of the spectrum as well as the total luminol emission intensity. Analysis of the acoustic emission characteristics suggests that the type of cavitation occurring is mainly transient. As expected, higher power settings produced greater intensities, but the variation in both acoustic and luminol emission was similar for each tip. Again though, there were sizable variations in behaviour between the tips. Further work is currently underway to assess the role that cavitation might play in the cleaning performance of the tips and the design parameters that maximise its efficiency.



**Figure 12.** (a) Luminol photography of A, P and PS tips at power 10/10. (b) Comparison of the results obtained via the 'Cavimeter' device and by luminol photography (from [26])

## CONCLUSIONS

The objective of this paper was to demonstrate some methods to detect and quantify cavitation. Use of a luminol solution can reveal the spatial and temporal dependence of cavitation through the chemiluminescent emission from reaction with radical species generated during cavitation collapse. Measurement of the intensity can quantify the cavitation as can analysis of the acoustic emission arising from cavitating systems. The latter method can also be used to characterize the type of cavitation that occurs in particular situations and the effect of varying the experimental conditions. These methods have been applied to chemical reactions as well as to the characterization of ultrasonic dental instruments.

## ACKNOWLEDGMENTS

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