Spectra of Stable Non-Noble Gas Single Bubble Sonoluminescence

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A commonly accepted view is that stable Single Bubble Sonoluminescence (SBSL) can only be achieved in the presence of a noble gas or hydrogen. In air-seeded bubbles, the content of diatomic gasses is burned off to leave the small amount of argon needed to sustain stable operation. Here we report that long term stable SBSL can be sustained with only nitrogen, oxygen, or nitrogen/oxygen mixtures being present. Compared to that of a stable argon bubble, the emission is much weaker and the spectrum looks much colder. Oscillating states as well as recycling states are also observed. An intriguing saturation effect seems connected with the presence of water vapor in the bubble.

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Recently we reported a second type of recycling mode in Single Bubble Sonoluminescence (SBSL) [1]. This occurs for air-seeded bubbles with dissolved gas content higher than approximately 20% of the saturation level, when driven past their shape instability limit. In contrast to the usual recycling mode denoted type 1, which reaches the same maximum intensity level as that of the stable bubble, the intensity in the new type 2 mode is down by approximately a factor of 20. Furthermore, spectra of the emission from a single bubble in the type 2 mode look like the bubble is much colder than an argon dominated bubble, thus providing a link to multi bubble sonoluminescence (MBSL).

The dissociation hypothesis [2] was invented to explain the stability of SBSL air-seeded bubbles at dissolution levels, where the bubble growth elsewise would not be limited. This hypothesis, since verified in many experiments, suggests that the bubbles burn off their content of diatomic gasses leaving behind the small amount of argon needed to sustain stable operation. The chemical reaction products, readily dissolvable, diffuse out of the bubble during the expansion and following contraction. Our interpretation of the type 2 mode follows this picture. The bubble is driven so hard that after the splitting off of a microbubble as is the usual explanation for the type 1 event, it sucks in air too fast to burn off the diatomic molecules. Thus it grows to the instability limit while still being predominantly an air bubble. The role of the water vapor could not be established.

In order to check this hypothesis we prepared a cell with gas mixtures involving no noble gasses (nor hydrogen). Gasses used are either pure nitrogen, oxygen, or a 4:1 nitrogen-oxygen mixture to simulate air without argon. The noble gas content in all cases are below 1ppm.

As we had expected, SBSL in the type 2 recycling state is possible and at the same level of emission. The spectrum also looks very similar to that obtained from air-seeded bubbles. Thus our hypothesis regarding the type 2 recycling seems verified.

However, to our surprise, stable SBSL was also possible. This has to the best of our knowledge not been reported before. The stable radiation was obtained for extended periods of up to 45 minutes for nitrogen bubbles. The fluctuations and long term drift of the relative phase of the flashes were 100 ns or less with short term fluctuations within 40 ns and no preferred direction of drift. At higher levels of gas pressure an oscillating state is encountered at the low end of the emission range. Such an oscillating state has previously been reported for nitrogen bubbles [3]. These authors also reported on irregular peaking emission. This phenomenon we find to be associated with small amounts of argon being allowed to diffuse into the cell.

The spectrum of the stable phase very much coincides with that of the type 2 case for air seeded bubbles with total output being similar in the case of nitrogen and the nitrogen/oxygen mixture but an order of magnitude lower for pure oxygen which also seems to be colder. Thus this experiment is further verification of the dissociation theory and fits the picture of the strong and hotter emission from an air-seeded bubble being connected with argon accumulation. To obtain stable emission from non-noble gasses, however, must call for a delicate balance between the diffusion into the bubble and the burning of diatomic gasses. Presumably this leaves the bubble much more susceptible to environmental factors like microstreaming, nearby particles, and chemical balance. All factors, that are expected to affect the long term stability. In view of this, while the levels of fluctuations and long term drift are higher than would be expected for e.g. air or argon seeded bubbles at high levels of emission which can be stable at ns levels, the changes are still surprisingly small.

The cell used is described in more detail in ref. 4, but is essentially a 5 or 6 cm high and 6 cm diameter cylindrical quartz cell with metal caps at both ends so it can be sealed using a pressure relief bag. Piezoelectric transducers are mounted on one or both caps for the drive, which for most experiments reported (6 cm cell), is at a frequency of 22140 Hz. A notable difference is the use of a heater to avoid contamination with hydrogen.

The procedure finally adopted to prepare the water
FIG. 1: Timeseries showing a progression for stepwise increase of sound pressure through stable states into type 2 behavior. Gas content 880 mbar nitrogen/oxygen 4:1 mixture as prepared at room temperature. Measurement performed at 9°C. Upper trace emission at 486 nm ± 5nm. Lower trace the relative phase. Average over 1000 flashes.

is as follows. The water is subjected to alternating degassing at water vapor pressure and flushing with the final gas to be used for several hours in 15 minutes intervals. Under this whole process the water is violently stirred by a magnetic stirrer. After a final 15 min. flushing with the final gas composition and concentration, the water is transferred in a closed system to the cell and cooled to the operating temperature (9°C) for several hours before commencing measurements.

As described in ref. [1] a crude spectrum is obtained by placing 7 photomultiplier tubes (PMT’s) around the cell with narrow band (10 nm) optical filters in front. The signals are amplified and collected by a computer with an extra PMT giving the timing signal for the sampling. This method was chosen primarily because it allows us to get spectra of weak and shortlived states but also since it allows us to get flash by flash control of the averaging time of the spectra. Thus we have precise knowledge of the time of collection so the radiative state of the bubble can be established. The timing of the flash is also recorded with a resolution of 50 ns with averaging providing a better resolution for slower fluctuations. For extremely weak signals (oxygen bubbles), however, a different procedure, to be described later, was used.

The stable states were in the case of the nitrogen/oxygen mixture found in the whole interval investigated from dissolved gas levels of 180 to 900 mbar. For nitrogen the range of degassing where a stable state was observed is 100 to 320 mbar, with the intensity level falling below our limit of detection at the low end. However, type 2 emission was observed up to 900 mbar. At low levels of dissolved gas, the interval of stability is quite narrow with the range of stability seemingly being wider for pure nitrogen than for the nitrogen/oxygen mixture. Near ambient pressure the intervals open up and we are able to measure the change in spectrum versus amplitude of the drive. Apart from type 2 (only recycling state present), we also see the oscillating state observed by Hiller et al. [2]. These states look very much like those recently observed for air-seeded bubble at very low drives by Thomas et al. [3]. This suggests that these low intensity states from air-seeded bubbles have the same origin of being mainly nitrogen/oxygen bubbles.

With gas levels of more than approximately 200 mbar, we encounter the type 2 recycling. This has essentially the same time scale of recycling as the air-seeded bubbles, which strongly supports our explanation of type 2 recycling having its origin in incomplete burn-off. Also it indicates the size $R_0$ of the bubbles at breaking point to be of the same scale of approximately 6 µm. This is corroborated by observation of an anisotropic 10% period doubling in the measurements of the 280 mbar nitrogen bubble just before and at the level of type 2 recycling.

In Fig. 1 we display a 100 s long timeseries obtained for a single bubble in water prepared at a dissolved gas level of 880 mbar (nitrogen/oxygen (4:1) mixture) at room temperature and cooled to 9°C. The amplitude of the drive is stepped up rapidly at 4 distinct short time intervals with stable regions of emission in between, before finally type 2 recycling sets in. Note the overlap in regimes, as the bubble several times relapses into the quiet state, although the sound pressure is kept constant in this last part of the sequence. Since the emission is weak and narrow band optical filters are employed, the average number of photons recorded per flash is of the order of 1. Our claim of stability is therefore based on the absence of oscillations or peaking and the stability of the relative phase.

FIG. 2: Spectra of constant emission ($\times$) dissolved gas level 220 nitrogen, (+) 220 mbar oxygen normalized with emission from stable air bubble. The curves are fitted black body radiation normalized within a constant with black body radiation at 14000 K. Upper curve $T = 8000$ K, lower curve 6580 K. Drive frequency 23200 Hz
In Fig. 2 we show spectra taken for stably emitting nitrogen bubbles (dissolved gas level of 220 mbar) and oxygen bubbles (220 mbar). Especially the oxygen bubble is so weak that it can hardly be discerned by the unaided eye even after long time adjustment to complete darkness. These spectra are therefore obtained by freerunning the data acquisition cards set at 5 MHz alternatingly for a prolonged period. Using the information from the phaselocked sawtooth signal fed to both cards one can then obtain averaged flash intensities from the remaining 6 channels with a highly improved signal/noise ratio. The spectra have been normalized by the spectrum of an air bubble driven at a sufficiently low level to ensure that the spectrometer is not overloaded. The latter spectrum has in a separate experiment been shown to fit well to 14000 K blackbody radiation in the regime of 300 nm - 700 nm but dropping below this in the extreme ultraviolet range (VUV) (see e.g. [6]). The spectra can be well fitted to black body radiation with temperatures 8000 K and 6580 for nitrogen respectively oxygen with the slight overshoot in the VUV range caused by the corresponding drop in the normalizing spectrum. By comparison a stable weakly radiating air-seeded bubble still displays a spectrum like that of the reference bubble apart from a scaling factor. The temperatures obtained are remarkable close to the expected dissociation temperatures for the gasses involved.

The change in the spectrum when increasing the amplitude in the type 2 case displayed in Fig. 1 is shown in Fig. 3. The spectrum starts out looking very much like those obtained for the stable case but gradually change to look like a blackbody spectrum. For comparison we have included the spectrum of a type 2 state measured for a air-seeded bubble at the same level of dissolution [7]. The curve is black body radiation at 8000 K normalized with black body radiation at 14000 K for comparison.

FIG. 2: Spectrum of a type 2 recycling state at the end of Fig. 1. From bottom to top the drive amplitude is (□) 130.0 mV, (▲) 130.5 mV, (×) 132.0 mV, (+) 133.4 mV. As seen by comparison to Fig. 2 there is an overlap with the constant emission state. For comparison we have included the spectrum of a type 2 state measured for a air-seeded bubble at the same level of dissolution (■). The curve is black body radiation at 8000 K normalized with black body radiation at 14000 K for comparison.

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into the cell, the behavior changes dramatically. In what follows we show the result of a simple analysis on some examples of states observed for a nitrogen seeded bubble at 28 % saturation contaminated with argon.

Since we are not able to follow the bubble movements simultaneously with obtaining the spectrum, we resort to using the relative phase for calculating the bubble size [8]. The model is based on the Rayleigh-Plesset equations taking into account water vapor but disregarding the chemical processes. A problem is that for obvious reasons we are not able to use the dissociation theory to calculate the actual composition of the gas inside the bubble as we clearly deal with incomplete burn-off.

The calibration can thus only be based on two fixpoints, the occurrence of period doubling, and the onset of shape instability leading to type 2 recycling. This fixes the bubble size to approximately 6-7 µm at the onset of type 2 behavior. The absolute pressure $P_0$ is more difficult to assess. However, a knowledge of the cell gained from measurements on air seeded bubbles leads us to adopt the value 1.5 bar for the corresponding pressure. Assuming a constant average concentration of nitrogen in the bubble, a model calculation leads to $c \approx 0.001$ compared to the degassing level of $c \approx 0.3$. From the diffusion equation we find that the bubble must burn approximately $10^5$ molecules of nitrogen per flash which is the same order of magnitude as found for an air-seeded bubble [9].

The spectral temperature is determined by fits to the blackbody spectrum which for the nitrogen spectrum fits quite well. For the oscillating state at drive levels below that of the stable state and a transient state into the
stable state, the apparent temperature also oscillates or peaks. For the transient state (results shown in Fig. 4), for most of the time the light emission is quite low compared to the stable emission. In the peaks, however, the emission goes up at all wavelengths but most in the ultraviolet and actually overshoots the stable emission. At the same time the bubble is decreasing in size, the inference being that the bubble is trying to burn off nitrogen and turn into an argon dominated bubble. Due to the normalization with the known spectrum of an argon bubble, the prefactor is proportional to a product of emitting surface area and duration of flash. Exact knowledge of these factors would be necessary for a complete analysis. Unfortunately, both parameters would be very hard to measure due to the short timescale involved. It is clear though, that the lower the drive and the smaller the bubble, the higher the apparent temperature. This trend, also found for air-seeded bubbles, could be connected with the presence of water vapor.

Although it is difficult to get quantitative information from this analysis, some interesting information arise from assuming the bubble radius at the time of emission to be proportional to $R_0$, with a proportionality factor that is relatively independent of drive amplitude, and plotting the prefactor as function of the radius $R_0$ squared. In Fig. 4 we present this kind of plot for an oscillating state and a peaking state below the stable state, the transient state, and a peaking state above the stable state, together with an analysis for a type 1 state (air-seeded) at a similar level of degassing for comparison. As seen, in the case of pure nitrogen, the prefactors at small ambient radii are proportional to $R_0^2$, but at higher values of the ambient radius saturation sets in. Naively one could therefore interpret the slopes to be proportional to the flash duration. A tentative explanation for the saturation could be that the actual volume of emission is smaller than the actual bubble size. As the apparent temperatures do not show much variation, this interpretation is in fact relatively robust independent of whether volume or surface emission is assumed. In fact assuming volume emission would aggravate the problem of reconciliating the changes in emission with the changes in bubble size. We wish to stress that while the absolute values of $R_0$ and $P_a$ are naturally questionable, the functional dependences displayed in Figs. 4 & 5 are robust.

The result for the recycling state of an air-seeded bubble is quite different. The recycling is of type 1 but having the hump that eventually results in type 2 recycling at higher levels of applied sound pressure. For small bubble radius, where the bubble according to our analysis of recycling states is mostly an air bubble we find the same linear behavior as for the nitrogen bubble ending with a trend towards saturation before the shrinking associated with the burn-off takes over. Finally we observe a new linear increase associated with the continued argon intake. Stable states are all located to the right of the transient curves.

To conclude we have shown the possibility of obtaining stable SBSL using non-noble gasses with total removal of noble gasses as a critical condition for stability. The experiments confirm the interpretation of the newly found type 2 recycling mode as originating in incomplete burn-off of diatomic gasses. The presence of stable emission is only permitted if the different gasses are prohibited from accumulating in the bubble. In the case of nitrogen, the only chemical processes possible involve water vapor. This raises the intriguing question of whether the stability could be caused by hydrogen actually accumu-
ating in the bubble. Such an accumulation is, however, not possible for the stable oxygen seeded bubble where the only possible reaction products are \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \). It is worth noting that the black body fits give \( \approx 8000 \) K for nitrogen, and \( \approx 6600 \) K for oxygen which could be related to the known dissociation temperatures for these diatomic molecules. Finally, gas depletion in a boundary layer around the bubble might very well be an important factor. Furthermore, both the apparent higher temperatures for smaller bubbles and the saturation points to the amount of water vapor being an important factor. Obviously an extension of the dissociation hypothesis also for air-seeded bubbles at low drive and/or low content argon is needed.

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