Time Scales for Quenching Single-Bubble Sonoluminescence in the Presence of Alcohols

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The rate at which single-bubble sonoluminescence is quenched in the presence of alcohol is examined. Single-bubble sonoluminescence bubbles are generated in a partially degassed argon−water/alcohol mixture. Quenching rates are measured by recording the instantaneous bubble response and corresponding light emission during a sudden increase in driving pressure. The light emission intensity initially grows as the bubble settles into a steady-state. The intensity then decreases as endothermic processes begin to dominate. Quenching rates increase with the carbon chain length (C_1−C_4). Complete quenching in the presence of methanol requires over 8000 acoustic cycles, while quenching with butanol occurs in about 50 acoustic cycles (driving frequency = 22.5 kHz). These observations are consistent with the view that quenching requires the repetitive injection of alcohol molecules leading to the accumulation of (hydrocarbon) gaseous products within the bubbles.

Introduction

Single-bubble sonoluminescence (SBSL) refers to the light emission from a single bubble, trapped by an acoustic standing wave.[1,2] It is perhaps the hotter cousin of multi-bubble sonoluminescence (MBSL), in which some bubbles within a cavitation field emit light.[3] Although MBSL has the potential for industrial applications such as monitoring cavitation activity and enhancing chemical activity (sonoluminescence bubbles are tiny microreactors), the complex nature of MBSL makes it difficult to understand and optimize for many systems. There is thus interest in learning of associations between SBSL and MBSL in order to facilitate a better understanding of MBSL systems.

One particular area of study has been on the quenching of light emissions by the addition of surfactants.[4−8] Such studies were initially used in an attempt to establish the mechanism of light emission (thermal vs electrical). Because a very small amount of surfactant can dramatically alter the light emission properties of sonoluminescence, there is also the potential for MBSL to identify small contaminants in process streams.

In this paper, we limit our discussion to the effects of alcohol. Alcohol-induced suppression of light emission from MBSL requires about an order of magnitude greater alcohol concentration than with SBSL.[5,6] Even so, quenching studies for both MBSL and SBSL have shown similar trends. For each system, as the carbon chain length increases, one needs a smaller bulk concentration to effect a complete quenching of the light. Although the bulk concentration of each species may be different, the calculated minimum 2-dimensional surface excess concentration (molecules/cm^2) needed for complete quenching is similar for all these short chain alcohols.[5,6] Presumably, due to the hydrophobicity of the alcohols within the bulk liquid, they accumulate in excess at the bubble surface. From there, they can evaporate into the bubble interior. Once inside, the alcohol molecules reduce the effective adiabatic exponent of the gas, resulting in a decreased bubble temperature and less light output,[7] without affecting the global bubble dynamics (at least for SBSL).[6,9]

The quenching process is similar to that for un-doped air bubbles, for which chemical consumption of nitrogen and oxygen limit the light emission. With air bubbles, the light emission increases only after the diatomic species are consumed (via dissociation and subsequent expulsion from the bubble), leaving only un-reactive argon in the bubble interior. With alcohol-doped systems, their consumption produces products that are not miscible in water, and thus accumulate within the bubble interior.

Although it appears clear that alcohol molecules evaporate into the bubble and remove energy through chemical reactions, there are questions as to *how* this process takes place. The issue revolves around the time scales for alcohol evaporation into the bubble interior. Ashokkumar et al.[6] argue that alcohol-doped SBSL bubbles are still almost entirely covered with water molecules. Alcohol molecules account for only about 0.2% of the bubble surface. They argue that quenching must therefore depend on repetitive evaporation over many acoustic cycles so that enough species can be evaporated into the bubble to produce complete quenching.

Tögel et al.[7] have also shown that alcohol-doped SBSL bubbles are quenched; however, they argue that the temperature within the bubble is too hot to accumulate reaction products over many acoustic cycles. They favor the notion that most, if not all, of the alcohol adsorbed onto the bubble surface near its maximum size, is injected into the bubble interior during collapse, and that the numbers must be sufficient to produce the observed quenching. A supportive argument for the view of Tögel et al. can be made by noting that the (diatomic) dissociation energy of these low-chain aliphatic alcohols is on the order of 10^{-12} J/molecule, and that an argon SBSL flash also has about the same energy (based on estimates from the optical spectrum of argon SBSL). Thus, the number of alcohol molecules needed to completely quench SBSL should not be large.

To resolve the issue, we have utilized a pressure-jumping technique that was originally developed to determine the validity of the dissociation hypothesis, and in fact was suggested by Tögel et al.[7] to resolve the issue. It will be helpful to review

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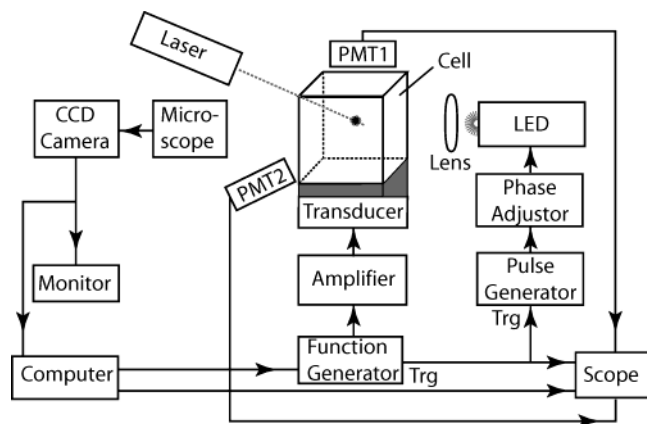* Corresponding author. E-mail: matula@apl.washington.edu.

Figure 1. Experimental setup. The computer controls the pressure jump by changing the voltage of the function generator. One PMT is used to measure the instantaneous bubble dynamics; the other PMT records the light emission from the bubble. An LED is sometimes used for bubble imaging to verify bubble stability.

Figure 2. Hydrophone measurements of a pressure jump (in an open cell) showing the transient behavior of the peak pressure before it settles into a steady-state. The voltage was converted into a pressure using an experimentally determined calibration factor.

the hypothesis and technique used to test the hypothesis. The dissociation hypothesis stated that an SBSL bubble filled with air would undergo chemical activity resulting in the dissociation of the diatomic gases N_2 and O_2, leading to the formation of NO_x compounds and H_2O_2, and that these solutes would then condense into the surrounding water because of their high miscibility in water. The resulting bubble would thus be filled only with the nonreacting species argon. In other words, an SBSL air bubble would turn into an argon bubble.[10−12]

In that experiment we sought to measure the time scales over which N_2 and O_2 were dissociated within an air-filled SBSL bubble. To do so we measured the instantaneous light intensity, each acoustic cycle. As the diatomic gases were consumed and the products ejected, the light intensity increased, until an equilibrium intensity was reached. The time to reach this equilibrium intensity was equal to the time for an air bubble to become an argon bubble.[13]

We used the same technique for this work. By monitoring the bubble's instantaneous light intensity as a function of time, we were able to measure the time scales for alcohol quenching. Our results will show that quenching occurs rapidly (although on scales larger than a single acoustic cycle). Furthermore, the quenching rate increases with the chain length of the alcohol.

Experiment

Our experimental setup is diagrammed in Figure 1. The driving system includes a function generator (Hewlett-Packard 33120A) to drive the cell's resonant frequency (22.5 kHz) and a power amplifier (Krohn-Hite 7500) to amplify the signal and drive the transducer attached to the bottom of a sealed rectangular cell. The detection system includes a 30-mW HeNe laser light-scattering system to measure the radial motion of the bubble. A photomultiplier tube (PMT) light detector (with an attached laser line filter, not shown) is used to monitor the scattered light intensity. Also, a second PMT, with a short-pass filter (not shown) to remove the scattered red HeNe light, is used to monitor the light emission from the bubble. Both signals are collected with a fast oscilloscope (LeCroy LT342L).

The dissolved gas used in the experiments was argon, degassed to 1 Torr above the vapor pressure of water (approximately 20 °C). Air was also used for comparison purposes (degassed to approximately 83 Torr above the vapor pressure), but because of the dissociation time scales of the diatomic gases nitrogen and oxygen (on the order of seconds), air bubbles are
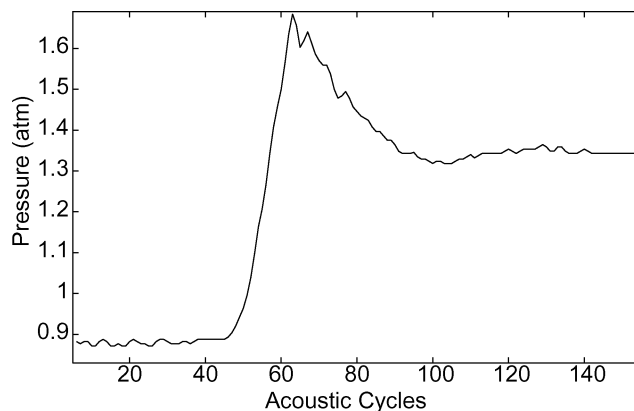
not appropriate for measuring quenching time scales for alcohols. The argon studies were complicated because of the necessity to seal the water-filled container from its surroundings. We were unable to introduce the alcohol into the cell after filling it with degassed water. By necessity, we instead introduced the alcohol into a water vessel prior to degassing and back-filling with argon. Because of the volatility of the alcohol (and subsequent removal during degassing), a much greater concentration of alcohol was initially mixed into the solution than would otherwise have been necessary. Experimenting with different initial concentrations resulted in finding a concentration that after degassing would produce a stable argon bubble, yet at the same time, result in complete quenching of the light when in the steady-state. The initial alcohol concentration depended on the particular alcohol used and the degassing time. Once the initial concentration was determined, subsequent experiments with that particular alcohol employed the same procedure. A short current pulse through a wire in the cell caused bubbles to form, and they coalesced at the pressure antinode (the center of the cell), forming a single bubble.

Pressure jump experiments were conducted in the following way. Low and high pressure levels were found by experimentation with an un-doped argon bubble. The low pressure was below the luminescence threshold, but not so low that the bubble dissolved quickly. The high pressure was near the middle of the light-emitting range for a stable argon bubble. The lower and upper pressure levels were approximately 0.9 and 1.3 atm.

Unless otherwise stated, each experiment was initiated from the low pressure. After the bubble stabilized at this low pressure for approximately 10 s, the pressure amplitude was suddenly increased to the high pressure setting. Steady-state for the cell pressure was reached after approximately 50 acoustic cycles, as measured with a hydrophone (see Figure 2).

An example of a control experiment, using only un-doped argon−water mixtures, is shown in Figure 3. The light scattering signal (Figure 3a) records the timing of the pressure jump, as felt by the bubble. Thus, delays inherent in the system are accounted for. After the jump is initiated, the bubble begins to grow to a new equilibrium size. Data are collected in a sequence mode, capturing one complete acoustic period every fourth acoustic cycle. The maximum data point from the cycle (corresponding to the maximum radius of the bubble) is then saved.

Sonoluminescence measurements are made at the same time. The peak signal is collected and used as a measure of the light emission intensity (Figure 3b). The emission intensity is low
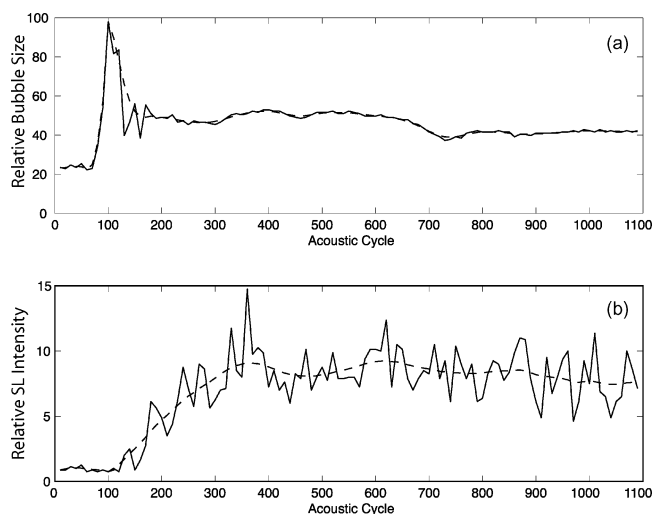
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Figure 3. Pressure jump with an un-doped argon bubble. (a) Scattered laser light shows when the pressure jump was initiated (near the 80th acoustic cycle). A transient bubble response is followed by a steady-state increase in the maximum bubble size. (b) The corresponding light emission intensity from the bubble. A maximum is reached at approximately cycle number 350. The dashed lines are running averages.

Figure 4. Pressure jump with a propanol-doped argon bubble. (a) Scattered laser light shows when the pressure jump was initiated (near the 120th acoustic cycle). (b) The corresponding light emission intensity from the bubble. The light intensity increases until approximately cycle number 180 before quenching begins to dominate. Complete quenching is achieved approximately 100 cycles later. The dashed lines are running averages (because of the transient nature of the experiment, the quenching spikes in the plot are not reproducible, although they may be real).

Figure 5. Pressure jump with methanol-doped argon bubble. (a) Scattered laser light shows when pressure jump was initiated (near acoustic cycle number 950). (b) The corresponding light emission intensity from the bubble. The light intensity increases until approximately cycle number 1500 before quenching begins to dominate. Complete quenching is achieved after cycle number 9000.

due to the short-pass filter that is used to block out the laser wavelengths. Because of the transient nature of the pressure jump experiment, there will be some variability to the data. A running average is also shown (dashed line).

We arbitrarily call the initiation of the pressure jump, as recorded by the light-scattering system, time $t = 0$ (for this figure, the pressure jump was initiated at about cycle number 80). The change in light intensity is related to the growth of the bubble. For the control experiment, one can see that after an initial delay, the bubble reaches a quasi-steady state at about cycle number 350. The time to reach this steady-state condition is therefore equivalent to about 270 acoustic cycles. This duration is longer than previous studies using a spherical quartz resonator. It is possible that there was some air in the system that was not removed, which would then lead to an increase in the time necessary to achieve steady-state. The geometry of the resonator may also contribute to the differences observed between previous and current experiments.

The experiment was then repeated with the alcohols methanol, ethanol, 1-propanol, and 1-butanol. These alcohols were chosen because they form a simple relationship, in that the carbon chain increases in unit steps with each alcohol. In addition, there is preexisting sonoluminescence data for these alcohols in the literature, as described above.

Figures 4 and 5 illustrate the effect of alcohol doping with 1-propanol and methanol. By comparing with Figure 3, one notices that soon after the bubble begins to emit light, it is quenched, and quenched relatively rapidly. Furthermore, the bubble never emits much light compared to the control data. In Figure 4, for example, the maximum light intensity is near 5 mV, compared to over 10 mV in the control system. This feature is observed in all the data sets, and suggests that some quenching is always present.

Two more important pieces of information can be obtained. Consider Figure 4. First, the rise-time of the signal (which we call T1), measured with respect to $t = 0$, is approximately 70 acoustic cycles. T1 is thus the time (in number of acoustic cycles) to reach the maximum light emission intensity before quenching processes dominate. As stated above, T1 for the control experiment shown in Figure 3 is approximately 270
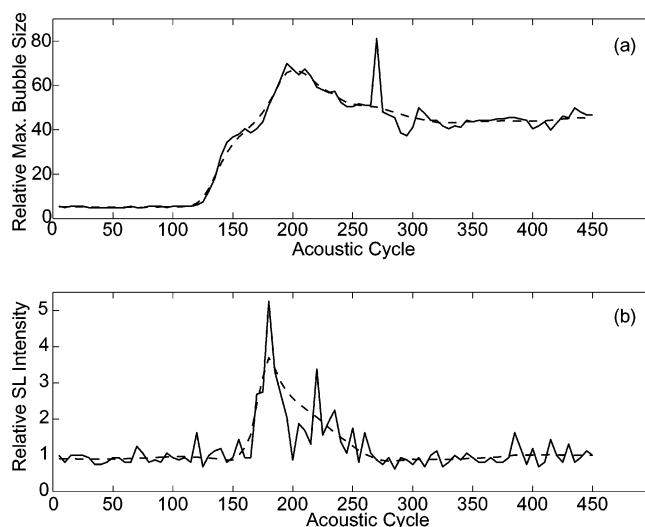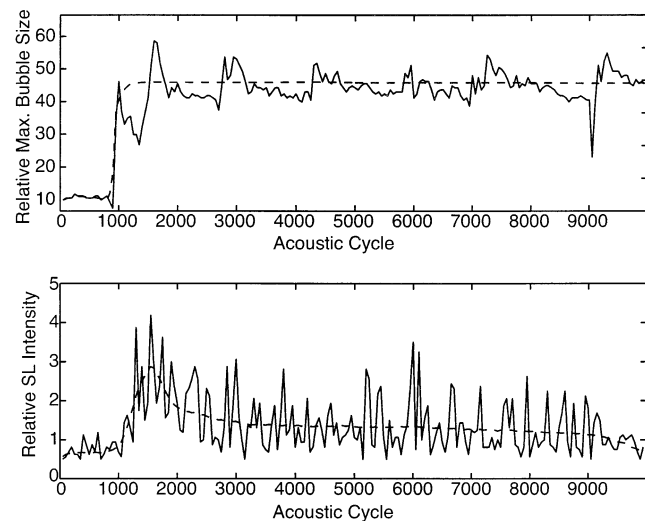
acoustic cycles. Another piece of information is the lifetime of the signal (which we call T2). The lifetime is a measure of the duration of light emission before complete quenching occurs. For the propanol data shown in Figure 4: T2 is approximately 150 cycles. That is, the pressure jump occurs around cycle number 120 (Figure 4a), and complete quenching occurs around cycle number 270 (Figure 4b).

Another feature observed in all the data sets is that there is a time lag between the beginning of bubble growth ($t = 0$) and beginning of the light emission. The delay is mostly due to the number of acoustic cycles necessary for a bubble to reach the luminescence threshold (minimum R_{max}/R_0), but chemical consumption and nonspherical perturbations in the bubble (not resolvable in our experiment) may also contribute to the delay.
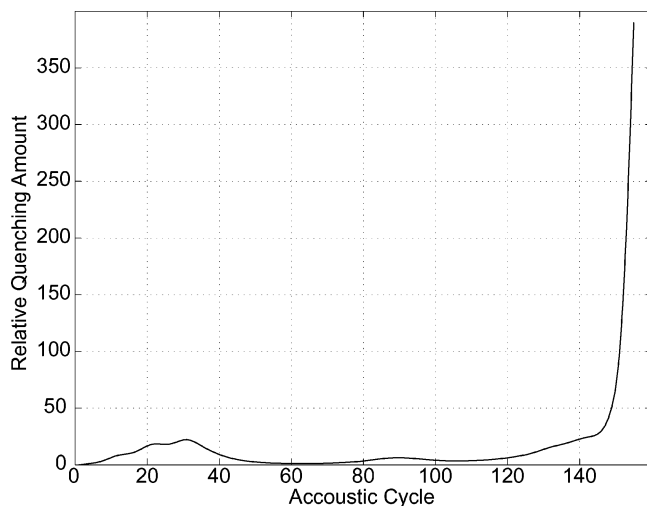
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Figure 6. A ratio of the smoothed control data with the smoothed data of Figure 4. We offset the acoustic cycle number to correspond to time $t = 0$, which is set from the initial increase in the maximum radius of the scattered light intensity. As the propanol-doped bubble begins to be quenched, the ratio increases. We define the acoustic cycle number that first exceeds the value of 100 as the lifetime T2. For the data set of Figure 4, the value exceeds 100 near cycle 150, thus, T2 = 150 acoustic cycles.

TABLE 1: Sonoluminescence Rise-times and Lifetimes of Alcohol-Doped Argon Bubbles

alcohol	T1 (acoustic cycles)	SD	T2 (acoustic cycles)	SD
methanol	520	180	8650	500
ethanol	150	50	380	125
propanol	70	60	150	70
butanol	30	20	50	20

We chose to measure T1 and T2 with respect to $t = 0$, because estimating the start of light emission is difficult, and introduces subjective bias. Furthermore, energy consumption (quenching) begins when R_{max} begins to grow, making $t = 0$ a more appropriate reference point. Nevertheless, we have noticed that the delay between bubble growth and light emission appears to be approximately 50 acoustic cycles for most data sets. In the following tables, if one wishes, one can subtract 50 acoustic cycles from the given T1 and T2 to account for this delay.

Because of the variability in the data from experiment to experiment, we chose to measure T2 by taking the ratio of the control data to the alcohol data, point by point. An example of this is shown in Figure 6, where we take the ratio of the control data to the alcohol data of Figure 4b. We arbitrarily define the lifetime where the control intensity increases to 100 times the alcohol-doped intensity. This technique is simply a consistent way of measuring T2 for all data sets. Note that this ratio exceeds 100 near acoustic cycle 150, which is what we have already determined.

Values of T1 and T2 (mean and standard deviation) for various systems are shown in Table 1. Between 7 and 12 experiments were performed to generate the mean and SD, except for methanol, where it was difficult to generate a stable bubble with the amount of alcohol necessary to produce complete quenching. Thus, for methanol only 3 experiments were performed.

For completeness, we also performed a sample pressure-jump experiment using air instead of argon. In Table 2 we show that the rise-time and lifetime of a propanol-doped air bubble, labeled Air(Low-High), is dramatically longer than any of the alcohol-doped argon bubbles. These time scales are consistent with the time scales for dissociation of N_2 and O_2. Furthermore, if we

TABLE 2: Sonoluminescence Rise-times and Lifetimes of Propanol-Doped Bubbles

	T1	SD	T2	SD
Argon (Low-High)	90	60	150	70
Argon (High-Low-High)	50	15	80	15
Air (Low-High)	124 000	72 000	283 000	100 000
Air (High-Low-High)	50	20	2400	300

initialize an air bubble in the sonoluminescing regime, and then perform the pressure jump experiment by first dropping to a low pressure and then jumping back up, we find that the time scales are considerably reduced (see Table 2, labeled Air(High-Low-High)). Again, this is evidence that the air bubble has turned into an argon bubble while in the sonoluminescing state. The time scales, at least for T1, are consistent with a propanol-doped argon bubble. The lifetime T2 is not as well-defined, and is probably contaminated by the presence of N_2 and O_2 still within the bubble.

Discussion

The experiments we have described were undertaken to resolve the issue as to how quickly alcohol enters the bubble in order to quench sonoluminescence. We emphasize here that some quenching is always present in our experiments. The light intensity never approaches levels corresponding to un-doped argon bubbles. In some cases, the light intensity is an order of magnitude lower than the un-doped argon bubbles. Nevertheless, we do observe that even in the cases where light emission is very dim, there are time scales over which the emission decreases further, until no emission is observed. We have attempted to determine the time for *complete* quenching.

Our data supports the notion that although *complete* quenching occurs rapidly, it is not instantaneous. Apparently, alcohol molecules are repeatedly injected into the bubble over many acoustic cycles leading to the accumulation of (hydrocarbon) gaseous products within the bubbles. Sonoluminescence can be completely quenched in as little as 50 acoustic cycles for butanol, to over 8000 cycles for methanol!

An interesting case is seen with air bubbles in the low-high experiment. Although the time scales are very long, the light emission for these bubbles remains very dim at all times. There is an apparent complex competition between the consumption of nitrogen and oxygen, leading to an argon bubble (which would normally result in a brighter bubble), and the consumption and accumulation of alcohol products (which keeps the emission dim).

Ashokkumar et al.[6] argue that because alcohol molecules account for only 0.2% of the bubble surface, quenching must result from repetitive evaporation over many acoustic cycles. Tögel et al.[7] argue that the temperature within the bubble is too hot to accumulate reaction products over many acoustic cycles, so that quenching must occur much faster.

Ashokkumar et al. also argue that the minimum surface excess concentration needed for complete quenching is approximately 0.02×10^{14} molecules/cm^2. The decreased lifetimes for the larger molecules is consistent with this view. Even if equal numbers of alcohol molecules are injected into the bubble interior, the larger molecules will remove energy faster.

Although our data supports in part the arguments of Ashokkumar et al., we must be cautious with quantifying the effect. The doped bubbles are always much dimmer than the un-doped bubble, implying that there is some quenching that occurs even at the beginning of the experiment. Because of statistical variations in the intensity, our experiments were not able to

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quantify this effect. However, complete quenching does take some time.

In an ideal experiment, there would be no alcohol in the bubble at the start of the pressure jump. We hypothesized that a preexisting concentration of alcohol vapor within the bubble would skew the data to decreased rise-times and lifetimes. We thus attempted to simulate a different initial condition by beginning the experiment while the bubble was in a sonoluminescing state. We then performed the same experiment that we had previously done with air. We first dropped the pressure level to the Low state for a few milliseconds. Then we jumped the pressure back up. Our results for the rise-time and lifetime are shown in Table 2, in the row labeled "Argon (High-Low-High)". This row should be compared to the row labeled "Argon (Low-High)", in which the experiment was simply from low to high pressure.

Apparently, if one starts at a low pressure, the lifetime of the light emission is on the order of 150 acoustic cycles, but under different initial conditions within the bubble, the lifetime drops to 80 cycles. These results suggest that there is an increase in rectified diffusion of alcohol molecules when in a sonoluminescing state, and that the dissociation products can remain within the bubble for extended periods. These product species contribute to decreasing the lifetime of sonoluminescence when the pressure jump experiment is conducted.

Another issue that we were unable to resolve: Because alcohol was necessarily added to the solution prior to degassing, we were unable to provide absolute bulk concentration values for the alcohols (although within a specific series of experiments for each alcohol, the concentration was not varied). As a consequence, we were unable to relate the quenching rates to the surface excess concentration, specific molecular size, or other physical properties of the molecules. To serve as an upper bound, the initial concentrations prior to degassing were 1.3 mM 1-butanol and 1-propanol, 6 mM ethanol, and 35 mM methanol. We attempted to compare these values with steady-state data from Figure 1 of Ashokkumar et al.[6] Although complete quenching data is not available in that paper, the *extrapolated* (lower bound) quenching concentration appears to occur with 1 mM 1-butanol, 2 mM 1-propanol, 5 mM ethanol,

and 15 mM methanol. We point out that it is difficult to compare the steady-state extrapolated data from the reference and the current rate-dependent experiments; nevertheless, the differences are not substantial.

Conclusion

In conclusion, we report here the time scales over which short chain aliphatic alcohols quench sonoluminescence. The data suggest that alcohol quenching occurs over time scales ranging from 50 acoustic cycles for the larger butanol molecules to over 8000 cycles for the smaller methanol molecules. Repeated injection of alcohol is necessary for the observed effect. Furthermore, the larger the molecule, the faster the energy is removed.

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