

## Molecular emission from single-bubble sonoluminescence

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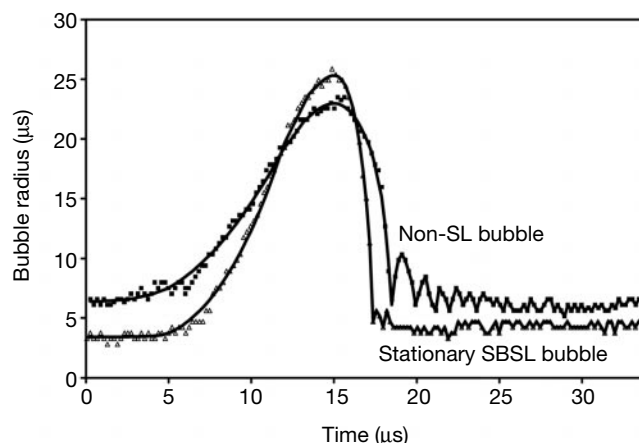
Ultrasound can drive a single gas bubble in water into violent oscillation; as the bubble is compressed periodically, extremely short flashes of light (about 100 ps) are generated with clock-like regularity<sup>1–4</sup>. This process, known as single-bubble sonoluminescence, gives rise to featureless continuum emission<sup>4,5</sup> in water (from 200 to 800 nm, with increasing intensity into the ultraviolet). In contrast, the emission of light from clouds of cavitating bubbles at higher acoustic pressures (multi-bubble sonoluminescence<sup>1</sup>) is dominated by atomic and molecular excited-state emission<sup>6–11</sup> at much lower temperatures<sup>6</sup>. These observations have spurred intense effort to uncover the origin of sonoluminescence and to generalize the conditions necessary for its creation. Here we report a series of polar aprotic liquids that generate very strong single-bubble sonoluminescence, during which emission from molecular excited states is observed. Previously, single-bubble sonoluminescence from liquids other than water has proved extremely elusive<sup>12,13</sup>. Our results give direct proof of the existence of chemical reactions and the formation of molecular excited states during single-bubble cavitation, and provide a spectroscopic link between single- and multi-bubble sonoluminescence.

The origin of the featureless emission of single-bubble sonoluminescence (SBSL) in water has become the subject of many theoretical speculations, and several mechanisms have been proposed, including black-body radiation<sup>5</sup>, bremsstrahlung<sup>14,15</sup>, ion–electron recombination<sup>15</sup>, and confined electrons<sup>16</sup>. Regardless of the detailed mechanism, a consensus has emerged that SBSL involves extraordinary temperatures inside the bubble<sup>14–16</sup>.

Whereas SBSL from water has been extensively studied, SBSL from other liquids in air has not<sup>12</sup>. For a single cavitating bubble in water, Lohse and co-workers have argued convincingly that N<sub>2</sub> and O<sub>2</sub> are removed from the bubble's interior by reaction to form NO<sub>x</sub> (which dissolves in and reacts with the bulk water), leaving primarily monatomic argon inside the bubble<sup>17,18</sup>. In addition, sonolysis of water (to H atoms and OH radicals) is highly reversible. These properties make water a nearly perfect liquid for SBSL under air: cavitation-induced reactions do not yield gaseous polyatomic products that would hinder compressional heating of the bubble.

The only previous report<sup>13</sup> of SBSL from liquids other than water found a weak emission from organic liquids (mostly alcohols), but only for unstable, moving xenon bubbles (*n*-butanol in air apparently also gives a very weak emission about 200 times less intense than water<sup>13</sup>). The spectra of these liquids under Xe again are featureless continua (we note, however, that emission from an excited state of C<sub>2</sub> was observed from a xenon bubble pulsating asymmetrically on a thermocouple wire in dodecane<sup>19</sup>). In contrast to water, sonolysis of other liquids produces small polyatomic gases<sup>8</sup> during the entropy-driven, high-energy chemistry that occurs within the bubble. We believe that build-up of such gases inside a single cavitating bubble precludes the heating necessary to generate SBSL.

From this hypothesis, we predict that a liquid will support SBSL under air if it has (1) a low vapour pressure (necessary to minimize the amount of gas formed during sonolysis) and (2) a high content of heteroatoms such as O or N (to form species that dissolve in or react with the surrounding liquid, and thus are removed from the

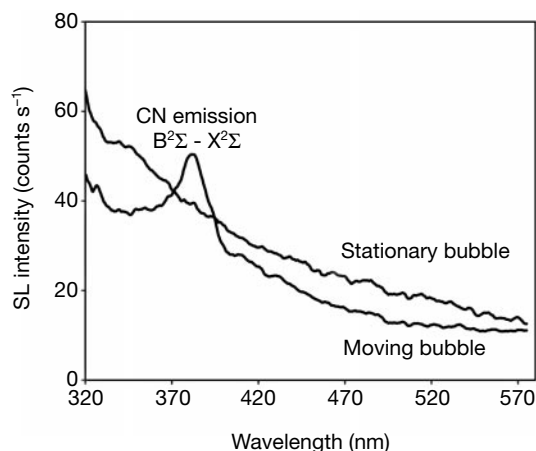


**Figure 1** Radius versus time curves for single-bubble cavitation in methylformamide. Data are shown slightly below and slightly above the sonoluminescence (SL) threshold (acoustic pressure,  $\sim 1.1$  bar). The radius data (shown as data points) were generated from stroboscopic imaging, so the time axis is relative and does not represent the phase of the bubble with respect to the acoustic field. The SBSL apparatus consisted of a spherical, quartz, 100-ml cell with a cylindrical piezoceramic transducer cemented to the bottom. The transducer was driven by a function generator and amplifier at a resonant frequency of about 30 kHz. A calibrated needle hydrophone (DAPCO) was used to measure the approximate pressure amplitude at the bubble location. The stroboscopic imaging system was similar to that used in ref. 21. The image of the bubble was recorded through a microscope by a Pulnix 9701 CCD camera. The bubble was illuminated by a light-emitting diode, which was driven by a pulse generator (HP 8116A). One of the outputs from HP 8904A signal synthesizer was used to trigger the pulse generator and the other sent to the power amplifier that drove the SBSL cell.

bubble). The kinetics of the reactions that form emissive excited states (of, for example, C<sub>2</sub> or CN) may also be important, given the short period of emission during SBSL. Using these criteria, we have discovered intense SBSL in air from numerous polar, aprotic liquids, including formamide (H<sub>2</sub>NCHO), *N*-methylformamide ((H<sub>3</sub>C)HNCHO), *N,N*-dimethylformamide ((H<sub>3</sub>C)<sub>2</sub>NCHO), *N*-methylacetamide ((H<sub>3</sub>C)HNC(CH<sub>3</sub>)O), 1,2-diaminoethane (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), dimethylsulphoxide ((H<sub>3</sub>C)<sub>2</sub>SO) and adiponitrile (NC(CH<sub>2</sub>)<sub>4</sub>CN). In keeping with our prediction, the intensity of sonoluminescence in these liquids can be comparable to, or even higher than, that of water. We note that both constraints—that is, (1) and (2) above—on the liquid properties must be met: SBSL is not observed from silicone oil or long-chain aliphatic alcohols (which have very low volatility, but low heteroatom content) in air, nor from formic acid (which has a high heteroatom content, but high volatility).

Both the dynamics of bubble motion in these organic liquids and their SBSL spectra differ significantly from that seen in water. We will discuss the bubble behaviour of *N*-methylformamide in detail. A bubble can be trapped at low acoustic pressure ( $P_A \approx 0.9$  bar for *N*-methylformamide) in the centre of the flask (see Fig. 1 legend for details), where it is spatially stationary and pulsates without emitting light. As  $P_A$  is increased, the bubble starts to move around the flask's centre and sonoluminescence is first observed (at  $P_A \approx 1.3$  bar for *N*-methylformamide). The velocity of the bubble motion at this point is about 3 mm s<sup>-1</sup>, and its trajectory is often circular or elliptical. The light intensity and the bubble movement both increase with increasing  $P_A$ . Microbubble shedding<sup>20</sup> or bubble-induced detuning may be responsible for such bubble motion, but additional work is required to explain this phenomenon.

We will refer to light emission from a non-stationary bubble as moving single-bubble sonoluminescence, M-SBSL. These M-SBSL bubbles can be maintained at maximum emission intensities for several minutes. The maximum emission intensities (relative to water at 1.0) are adiponitrile, 2.0; formamide, 1.2; methylforma-



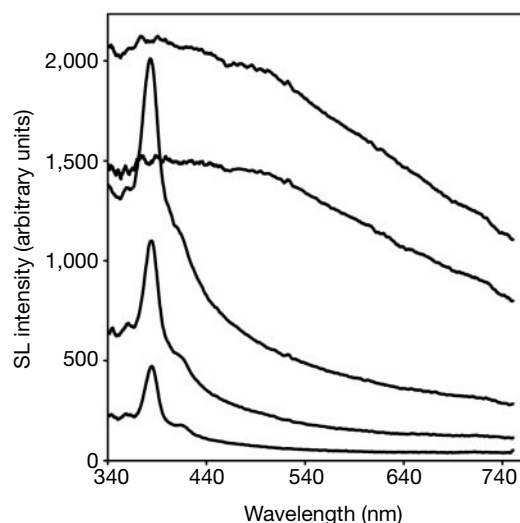
**Figure 2** S-BSSL spectra of methylformamide at an acoustic pressure of  $\sim 1.1$  bar for both a stationary and a moving single bubble. The excited-state CN comes from the liquid vapour rather than from the nitrogen gas initially present inside the bubble, because (1) M-SBSL spectra under a partial pressure of Ar (in the absence of  $N_2$  or  $O_2$ ) show greater CN emission; and (2) M-SBSL spectra from dimethylsulphoxide (which contains no nitrogen) in air do not exhibit CN emission. S-BSSL spectra of methylformamide were collected at 295 K under 10 torr of air, using a Jobin-Yvon Triax 320 monochromator with a Spectrum One CCD detector (Instrument SA,  $1,024 \times 256$  array). Spectra were corrected for both the light absorption by the solutions and the response of the optical system against standard lamps (which could be traced back to NIST standards).

amide, 0.14; dimethylsulphoxide, 0.14; dimethylformamide,  $< 0.05$ ; and 1,2-diaminoethane,  $< 0.05$ ; intensities were measured in the same cell with the spectrograph in zeroth order. These liquids all absorb light much more strongly in the ultraviolet region than water does, so the relative intensities of emission can only be taken as an approximate measure of the efficiency of SBSL. Above about 1.5–1.6 bar in *N*-methylformamide, the bubble cannot be held at the centre of the flask and disappears; such behaviour is typical for all liquids reported here.

Hysteresis is observed for SBSL in these liquids. By decreasing the amplitude of ultrasound reaching a moving emitting bubble, it was possible to get light emission at lower  $P_A$  than the initial threshold of sonoluminescence inception for all of our non-aqueous liquids. In the cases of formamide and methylformamide, upon decreasing the acoustic amplitude to about 1.1 bar, the bubble becomes stationary and still emits; we will refer to this as stationary single-bubble sonoluminescence, S-SBSL. The intensity of sonoluminescence under the conditions of S-SBSL was approximately the same as, or a little higher than, the emission intensity during M-SBSL at the same acoustic pressure. S-SBSL can be obtained only by first establishing a bubble showing M-SBSL and then reducing  $P_A$ .

Stroboscopic imaging<sup>21</sup> revealed that the stationary emitting bubble pulsates regularly with only a few, weak after-bounces. In contrast, a non-emitting stationary bubble is much larger in size and shows strong, multiple afterbounces (Fig. 1). This difference in dynamics between sonoluminescent and non-sonoluminescent bubbles has also been observed in water, and is consistent with gas removal from the bubble by chemical reactions during SBSL<sup>18,21</sup>.

The emission spectra from these liquids are especially revealing. In contrast to the featureless spectrum of water SBSL, M-SBSL from adiponitrile, formamide and methylformamide all show relatively strong emission from excited-state CN ( $B^2\Sigma^- - X^2\Sigma^+$ ). At or near the minimum  $P_A$  necessary for M-SBSL, this molecular emission is superimposed on an underlying continuum (Figs 2, 3). As the  $P_A$  increases, the continuum increases in intensity until the CN emission is no longer discernible (Figs 3, 4). The bubble hysteresis made it possible to collect spectra from *N*-methylformamide for both S-SBSL (which is featureless) and M-SBSL (which



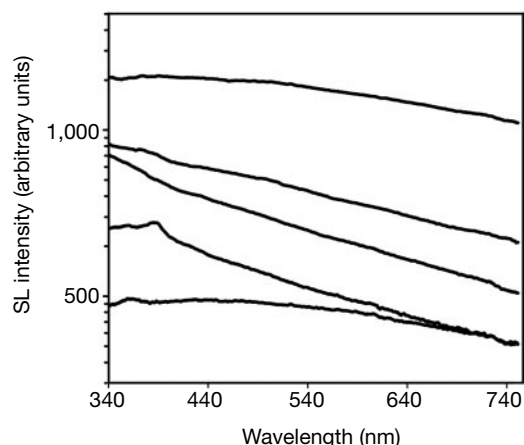
**Figure 3** M-SBSL spectra of adiponitrile. Acoustic pressure increases from bottom to top, from 1.7 to 1.9 bar.

shows CN emission) under essentially identical acoustic conditions (Fig. 2).

We propose that the difference between S-SBSL and M-SBSL spectra at similar acoustic pressure lies in the sphericity and severity of the bubble collapse and the effect this has on the bubble contents. A moving bubble cannot collapse as symmetrically as a stationary bubble; it is therefore likely that the effective temperatures reached during S-SBSL are much higher than during M-SBSL. The observation of emission from CN excited states during M-SBSL shows that the temperature is below about 15,000 K under these conditions, for at least part of the emitting bubble; above this temperature the CN (whose dissociation energy is 7.8 eV) would not be stable long enough to emit<sup>22</sup>. In the case of S-SBSL (which is presumably at higher temperatures than M-SBSL), CN is either thermally dissociated or no longer is formed within the collapsing bubble, and CN emission is not observed.

Several experimental parameters are found to affect the intensity and stability of SBSL in these liquids. Vapour pressure (which plays an essential role in the intensity and temperature of MBSL<sup>6</sup>) appears to be important for SBSL: all of our successful non-aqueous liquids have very low volatilities. For example, adiponitrile (vapour pressure  $< 0.1$  torr at 22 °C; ref. 23) gives intense SBSL, whereas acetonitrile ( $CH_3CN$ , vapour pressure 90 torr), a liquid very similar in chemical properties to adiponitrile, fails to give any SBSL. Similarly, the intensity of SBSL decreases more than 20 times from formamide (vapour pressure 0.05 torr at 22 °C) to methylformamide (0.2 torr at 22 °C), to dimethylformamide (3.2 torr at 22 °C). M-SBSL occurs in *N*-methylformamide equilibrated with air pressures from 10 to 150 torr; as the gas pressure increases, M-SBSL occurs at higher acoustic pressures and the bubble's spatial stability decreases.

The acoustic pressure during M-SBSL significantly affects the emission spectra (Fig. 3). As  $P_A$  is increased during M-SBSL, the intensity of bubble collapse will also increase, leading to higher temperatures and an initial increase in CN emission as more CN excited states are formed. As the  $P_A$  is further increased, however, CN is either thermally dissociated or no longer formed within the collapsing bubble, and a sharp decrease in the intensity of CN emission is observed. Subsequent experiments have shown that the transition between the absence and presence of CN emission occurs on a timescale of about 0.1 s. This is further evidence that CN emission comes from sonolysis of vapour of the liquid, rather than dissolved  $N_2$ , because  $N_2$  diffusion into the bubble requires several



**Figure 4** M-SBSL spectra of adiponitrile, formamide, water, methylformamide and dimethylsulphoxide (from the top to the bottom of the figure). The acoustic pressure was 1.4 bar for all liquids except adiponitrile, where it was  $\sim 1.9$  bar. High-purity non-aqueous liquids ( $> 99\%$  purity) were used as purchased. Water was purified by ion exchange (to  $18\text{ M}\Omega\text{ cm}$ ) and filtration through  $0.2\ \mu\text{m}$  pore filters.

seconds to replenish<sup>17</sup>. The observation of CN emission during SBSL also proves that chemical reactions are taking place during SBSL, as has been suggested from hydrodynamic modelling of single-bubble cavitation<sup>17,18</sup>.

The M-SBSL spectra of dimethylsulphoxide and adiponitrile at high acoustic intensities are significantly different from those of other liquids (Fig. 4): their intensity is essentially flat above 380 nm and cannot be fitted to black-body emission at a single temperature. Because there is no nitrogen in dimethylsulphoxide, there is no CN emission observed. One might have hoped to see band emission from  $\text{S}_2$ , SO,  $\text{SO}_2$  or other species that should be produced from sonolysis of dimethylsulphoxide. None of these species, however, is as stable as CN at high temperatures. For reference, the dissociation energies for SO and CN are 5.4 and 7.8 eV, respectively<sup>23</sup>.

The origin of the continuum in SBSL remains an open question. There are two likely contributors: (1) the sum of broadened emission from multiple molecular and atomic sources, and (2) bremsstrahlung emission from partial ionization of the heated gas within the bubble. The continuum in flames is generally assigned to the former mechanism<sup>24</sup>. For example, broadened CO emission could be a significant ultraviolet component of SBSL spectra as it has a dissociation energy considerably higher than that of CN (11.1 eV; refs 24, 25). Emission from  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , NO and  $\text{NO}_2$  (refs 24–26) may also be contributors to the continuum. Recent experiments on the timing of the SBSL flash from water<sup>27</sup> showed that the emission at long wavelengths can last slightly longer than that at short wavelengths; this difference could originate from the varying emissivities and lifetimes of multiple emitting species as a function of wavelength and internal temperature.

The other likely component of the continuum emission is bremsstrahlung radiation from electron–neutral and electron–ion interactions due to partial ionization of the heated gas within the bubble. Calculations show that lower-temperature bremsstrahlung (approximately 12,000 K) could give wavelength-independent intensities similar to those we observe in dimethylsulphoxide (Fig. 4; P.L. Hagelstein, personal communication). Under conditions of maximum collapse efficiency (that is, stationary single-bubble cavitation, minimum solvent vapour pressure, Xe gas within the bubble, and so on), the temperature within the cavity increases, and bremsstrahlung emission is expected to increase. From comparison of our experimental data to Hagelstein's calculations, the

wavelength dependence of S-SBSL from *N*-methylformamide is consistent with an effective bremsstrahlung emission temperature of approximately 30,000 K.

We believe that M-SBSL represents less extreme conditions ( $< 15,000\text{ K}$ ) than those present during S-SBSL, due to the less-effective collapse of moving bubbles. M-SBSL therefore provides a long-sought spectroscopic link between the phenomena of single-bubble cavitation (which occurs at low acoustic pressures) and bubble-cloud cavitation (which occurs at high acoustic pressures). As the sphericity of bubble collapse increases (from MBSL to M-SBSL to S-SBSL), the efficacy of compression increases, the effective temperatures within the bubble increase, and the emission changes from spectra dominated by excited-state molecular emission to featureless (bremsstrahlung-like) spectra. □

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