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Sonoluminescence in Liquid Metals

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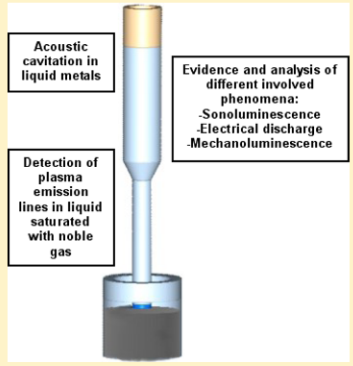
ABSTRACT: Multibubble sonoluminescence experiments have been performed in two liquid metals: mercury and the eutectic alloy of Ga, In, and Sn, commonly known as galinstan. The experiments were executed at ambient temperature, using a quartz horn to serve the two-fold purpose of inducing ultrasonic cavitation and providing an optically transparent window to detect the sonoluminescence (SL) radiated from bubbles generated in proximity of the quartz/metal interface. The typical emission lines of the metal under test could be detected, and their intensity was found to be correlated with the level of applied acoustic pressure. Their origin could be associated with two concurrent physical mechanisms: electrical microdischarges and true SL emissions. The contribution of these different processes was singled out by the deposition of an electrically conductive optically transparent film on the end face of the quartz horn. Typical SL broad-band emission could be detected in both types of liquid metals, while the emission lines corresponding to Sn and In excited states appeared only when testing galinstan in special experimental conditions. This point requires further investigations, and observation suggests the possible contribution of mechanoluminescence phenomena. Finally, in a preliminary experiment performed while maintaining mercury under a steady argon flow, we observed emission lines associated with the noble gas excited states, even in the presence of the conductive transparent film: this result excludes a significant contribution of the microdischarge mechanism and represents a strong evidence in favor of the formation of a warm and dense plasma.



INTRODUCTION

Sonoluminescence (SL) is the name given to the light emitted during acoustic cavitation of liquids. When the light emission originates randomly from cavity clusters generated by ultrasonic transducers, the phenomenon is known as multibubble sonoluminescence (MBSL). The light intensity, its spectrum, and the duration of the single flashes that form the detectable radiation are determined by the chemical nature of the liquid and the physical conditions of the experiment (acoustic pressure, frequency, static pressure, temperature, and composition of the gas content). In recent papers, Suslick and coworkers[1,2] evidenced the extreme conditions produced in the gas bubbles during acoustic cavitation of sulphuric acid, assessing peak temperatures of about 16 000 K and pressures of thousands of atmospheres (recent reports on high density plasma states support the possibility for even higher temperature conditions, according to a detailed analysis of emission lines from argon gas inside a collapsing bubble[3]). It is commonly accepted that the ideal fluid for inertial cavitation should have both a very low vapor pressure and a great dissolution power against a wide range of possible sonochemical products, in order to avoid the interior of the bubble being rapidly "poisoned" by small molecules and reactive species. Since early works on SL, in particular, single bubble sonoluminescence (SBSL),[4] it was supposed that liquid metals, such as mercury or other fused alloys, should give very intense SL, because of their low vapor pressure and chemical stability. The mechanisms of cavity formation in the bulk of liquid metal samples are similar to those observed in water, even if the surface tension of mercury is 6 times greater than that of water. When mercury is not degassed, the cavitation threshold seems to be dominated by the gas saturation effect.[5] In the experiments reported here, adhesion properties of liquid metals to glassy surfaces become the issue of main concern, since only the effects of cavities strongly interacting with a solid and transparent wall are liable to an optical inspection. Sonoluminescence is directly related to the collapse phase of inertial cavitation events, and this phase of the bubble dynamics is dominated by the density of the liquid phase; mercury and galinstan are from 7 to 13 times heavier than water, making these fluids an interesting subject for cavitation luminescence investigations. However, despite the renewed interest in high intensity cavitation in "exotic" liquids, such as molten salts, eutectic alloys, and liquid metals,[6] after the pioneering work by Kuttruff in 1962[7] and Smith in 1967,[8] to our knowledge, no updated observations of SL in liquid metals have been reported, except for the recent work of Futakawa[9] in which the cavitation phenomena of mercury, used in pulsed spallation neutron source, were investigated.

Here, we report the results obtained from multibubble sonoluminescence (MBSL) in mercury and in an eutectic alloy of Ga, In, and Sn, commercially known as galinstan, at ambient temperature and without the addition of gas to the samples. In both liquids, it was possible to observe very intense broad-band luminescence, with the concurrent formation of emission lines that involve different activation mechanisms: a discharge-like

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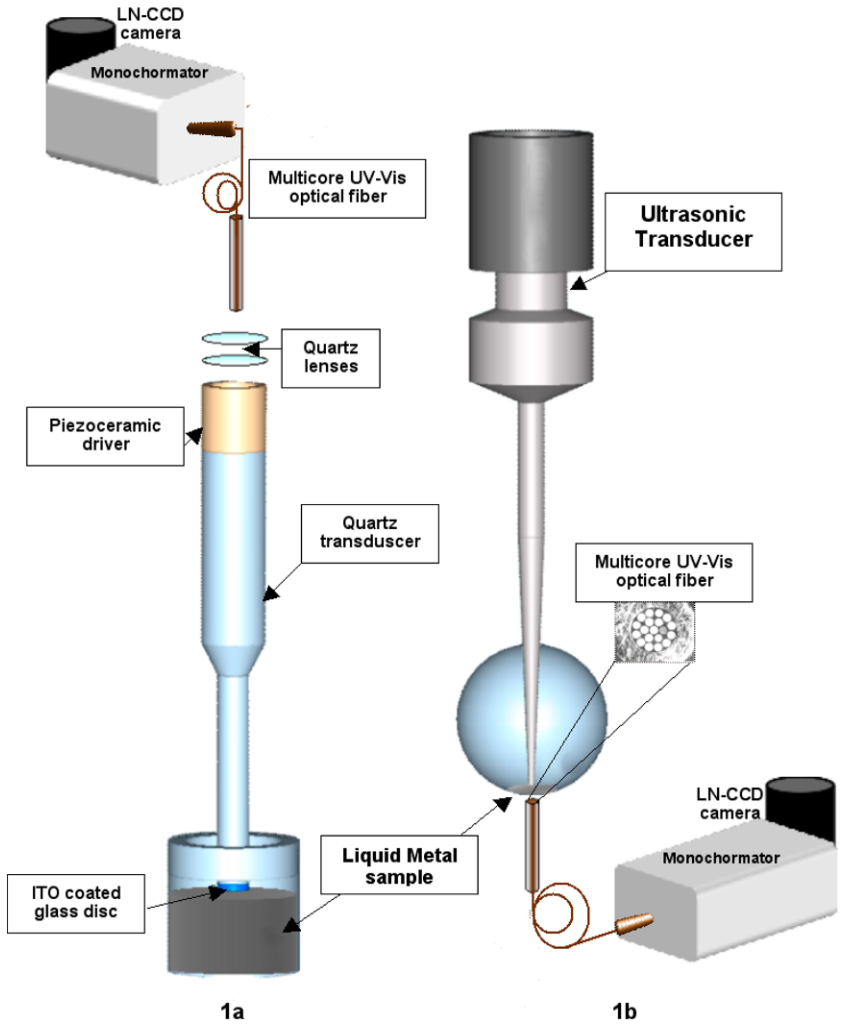

Figure 1. (a) Schematic representation of the quartz sonotrode type (1) setup. The blue part at the end of the quartz horn represents the glass disc coated with ITO thin film. (b) Type (2) setup. The titanium probe is immersed in a shallow liquid metal pool, at 2 mm from the flask bottom.

emission in Hg and a possible mechanoluminescence contribution in galinstan. Although these emission lines arise from activation mechanisms different from the typical ionization processes occurring in the interior of adiabatically collapsing bubbles, it was possible to assess the production of high-energy concentration phenomena in cavitating liquid metals.

In a further experiment performed under an Ar atmosphere, it was possible to detect noble gas emission lines from an ultrasonically irradiated liquid metal, implying the formation of a plasma hot spot. These last results represent an intriguing starting point for the investigation of extreme energy focalization processes during bubble implosion.

■ EXPERIMENTAL SETUP

Because of the opaque nature of liquid metals, a direct observation of the light radiated by collapsing bubbles near the tip of an ultrasonic horn is quite difficult to realize. Two different configurations are possible: (1) a transparent glass ultrasonic horn immersed in the bulk liquid metal or (2) a metallic horn operated in proximity of a transparent glass window. Both configurations were tried during the experiments described here, but it is worth noting that no visible radiation can be gathered from bubbles collapsing in the liquid bulk. Any spectral information comes from cavities that are strongly interacting with a solid interface (a stationary surface in case 2 and a moving one in case 1), so the bubble wall dynamics and the light-producing phenomena can be very different from what is experienced with MBSL and SBSL in standard transparent liquids.

In the type (1) setup, cavitation was generated by a custom-made quartz horn with two optically transparent, plane and parallel end surfaces. These surfaces had unequal cross sections due to the stepped-cylindrical geometry of the horn. A piezoceramic tube, attached by epoxy to the wider end face of the horn, excited ultrasonic waves at about 22 kHz and allowed a free optical access to the immersed face of the horn.[8] The acoustic pressure level was determined by the technique described in ref 10 and reached 0.8 MPa at the maximum output power of the amplifier. SL radiation was collected by two quartz lenses and a multicore UV−vis optical fiber connected through a micrometric slit with a monochromator (Acton SP 2300). The spectra were recorded by a LN/CCD camera (Princeton Instruments LN) coupled with the Acton SP 2300, during 60 s of horn operation; the total spectra resolution was about ±1 nm.

To discriminate possible contributions from electrical discharge emissions, produced by the fast detachment of the liquid metal from the insulating surface of the horn tip during

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cavitation,[11] some experiments were conducted with the addition of a thin pyrex disk to the sound-emitting horn tip. The disk was externally coated with an electrically conductive transparent ITO (indium tin oxide) film and fixed by transparent epoxy; a comparison of spectra from a standard deuterium lamp measured before and after this modification confirmed a negligible contribution of the epoxy−pyrex−ITO composite material in the spectral region of interest. The complete type (1) setup is outlined in Figure 1a.

Since the quartz ultrasonic probe had a limited output power, a type (2) setup was implemented, allowing the investigation of a wider range of acoustic pressure levels. A commercial ultrasonic head (Bandelin HD2200) was provided with an exponential titanium probe. The probe tip was positioned near the bottom of a spherical quartz flask, containing a small amount of the liquid metal under test. Ultrasonic irradiation was performed at 20% of the maximum output power, corresponding to 1 MPa acoustic pressure (for details about the calibration procedure, see ref 10). The SL signal was acquired by an optical fiber, held outside the flask, and geometrically aligned with the titanium tip (the complete type (2) setup is shown in Figure 1b).

The addition of gases was avoided during these experiments, except for the tests illustrated in Figures 6 and 7, in which case a continuous flow of argon through a capillary immersed in the liquid was maintained during sonication.

RESULTS AND DISCUSSION

MBSL in Mercury. Figure 2 shows two spectra obtained in Hg from our type (1) and type (2) setups (black and gray lines, respectively); the quartz transducer was not modified by the conductive ITO film at the end face and was operated at its maximum amplitude. Two points have to be emphasized: the presence of typical Hg emission lines and the brightness of the signal. The integrated light intensity from water, using the quartz transducer in the same working conditions, is about 10 times lower than that from Hg. Previous works about SL in mercury, in particular,[8] did not report the presence of any emission lines in the spectrum, even if the limitations in terms of resolution and sensibility of those dated experimental equipments should be considered; however, Kuttruff's pioneering work confirmed the expected enhancement in light intensity with respect to water or other organic liquids, such as glycerine and silicone oil.

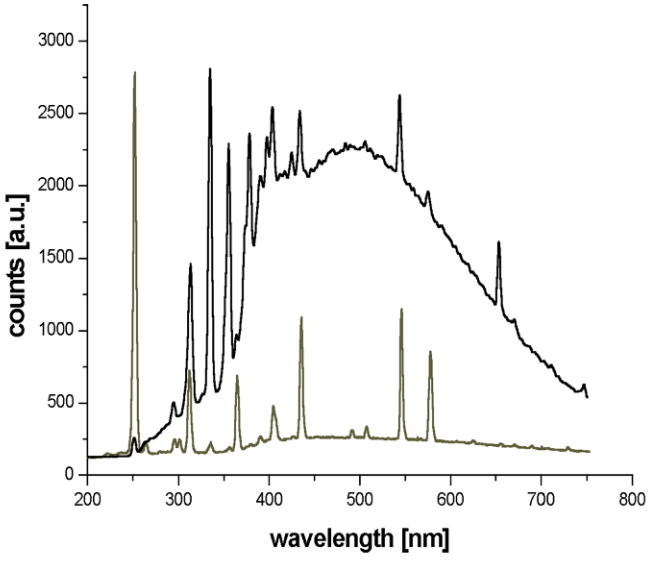

Figure 2. MBSL spectra in Hg: the gray line refers to the titanium probe setup; the black curve refers to the quartz sonotrode setup. Note the typical Hg emission lines (252, 313, 334, 355, 365, 380, 403, 435, 546, and 652 nm).

The spectra referenced in Figure 2 showed the typical discharge emission lines from mercury with most prominent lines located at 253, 313, 365, 403, 435, and 546 nm. When the quartz transducer was used, a second set of lines (334, 355, 380, 652 nm) acquired a greater intensity, the superimposed broad-band emission being anyway the dominating feature of the spectrum. This pattern is less pronounced in the case of the titanium probe sonicating a shallow Hg sample (type (2) setup, Figure 1b), although higher acoustic pressure levels can be generated. These observations seemingly indicate that at least two processes are going on: an adiabatic heating of the bubble gaseous content, accounting for the broad-band features of the spectrum, and electrical surface microdischarges, mainly responsible for the emission lines. It is well-known from the literature[11](and references therein) that a characteristic light emission can be produced from liquid mercury moving over glass surfaces under vacuum, due to charge accumulation and successive discharge relaxation, not all details of the process being yet completely understood. Since the presence of an insulating surface seems to be essential for the primary charge separation, an investigation using the conductive transparent film was mandatory in order to point out the role of electrical discharge in the production of emission lines. Upon fixture of the ITO coated glass disk to the quartz transducer, the spectrum in Figure 3 was obtained. The broad-band

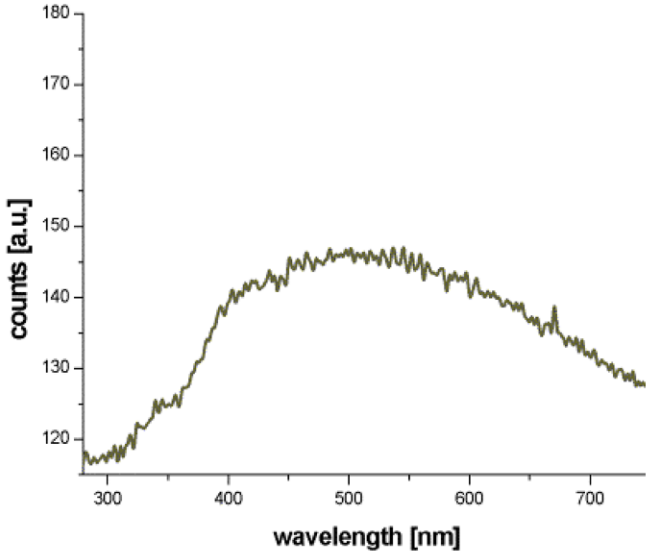

Figure 3. MBSL in Hg using conductive ITO thin film.

contribution, associated with genuine SL emission, was still present, but the emission lines were almost completely suppressed. These data enforce the hypothesis of their electrical origin.

In a subsequent series of experiments, we tried to assess the role of acoustic pressure in the manifestation of the emission lines. Figure 4 shows a sequence of MBSL spectra acquired in similar experimental conditions, increasing the acoustic

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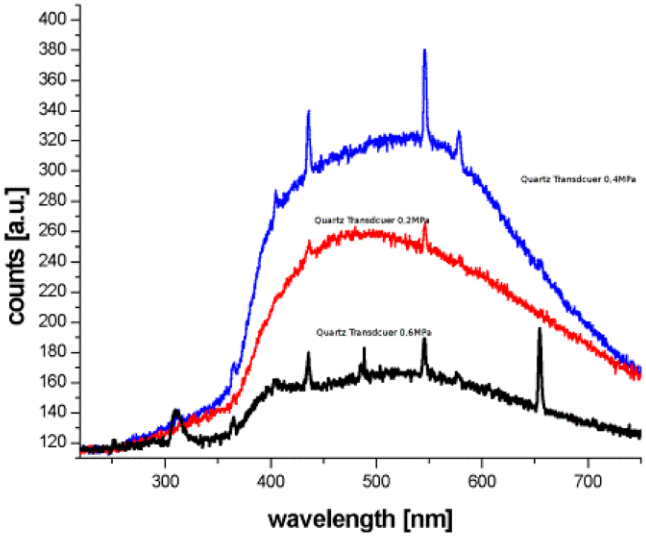

Figure 4. MBSL spectra in Hg at different acoustic pressures: red curve, 0.2 MPa; blue curve, 0.4 MPa; black curve, 0.6 MPa. The total light intensity of the black curve is lower due to a lower acquisition time.

pressure in a step of 200 kPa from 0.2 to 0.6 MPa. At 0.2 MPa, only the 435 and 546 nm lines were present. When the 0.6 MPa level was reached, an entire series of lines could be detected (576, 652, 365, 309 nm), with a concomitant decreasing in the broad-band emission power, indicating that a greater bubble activity at the transducer surface favors the electrical discharge mechanism. A weakness of this experimental setup was the rapid erosion of the transducer end surface, with the consequent degradation of the transducer efficiency in releasing acoustic power to the liquid. Figure 5 shows two microphotographs of the quartz tip after 120 s of operation at its maximum power. It is possible to see small mercury droplets set in the fractured quartz surface. To amend the consequences of this erosion process, periodical cleaning of the tip of the transducer with concentrated HNO_3 and subsequent polishing of its end surface were required. This procedure caused gradual acoustic detuning of the piezoceramics driver-quartz horn system, setting a practical limit to the possible duration of single experimental runs and the total number of consistent tests available for statistics.

Finally, we address the problem of noble gas saturation as an enhancing factor for MBSL emission. Some preliminary experiments were conducted cavitating the mercury sample in the presence of a bubbling argon flux. As it is possible to see in Figure 6, the SL spectrum shows clearly the presence of

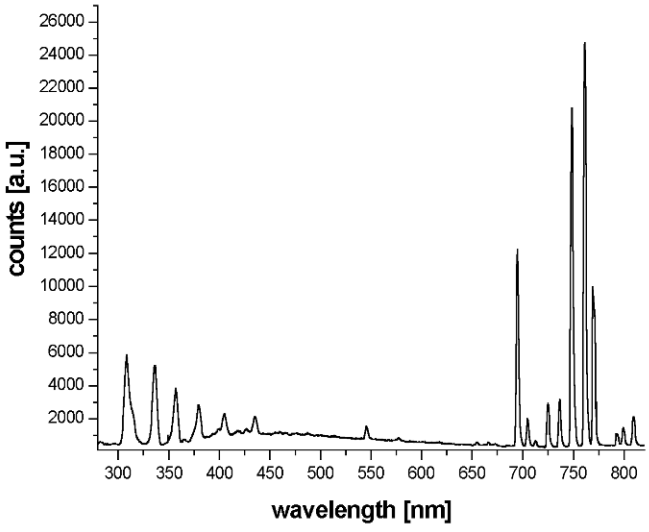

Figure 6. MBSL spectrum in Hg under argon bubbling flux. Acoustic pressure: 0.3 MPa. Note the presence of argon emission lines in the 700−900 nm region, corresponding to the 4p−4s manifold, and the asymmetric shape of the emission lines from mercury at 313, 334, 355, 380, 403, and 435 nm.

mercury (253, 313, 365, 403, 435, 546, 345, 456, 546, 457 nm) and argon (700−900 nm range) lines, superimposed to the broad-band continuum. The argon lines derive from the 4p−4s manifold as reported in ref 12. The asymmetry of the lines' shape suggests a pressure broadening effect taking place in the hot and compressed bubble interior at the end of collapse, although electrical discharge phenomena could not, at this stage, be ruled out. To assess this point, we repeated the experiment adding the conducting ITO-coated disk to the quartz transducer: the results are shown in Figure 7. Contrary to what was observed in the absence of argon flux, the emission lines were not suppressed, weakening the electrical discharge hypothesis.[13] It worth noting that erosion of the conductive film cannot be an explanation for this effect, because the ITO film showed a complete electrical continuity after this cavitation test. These data strongly support the hot-spot model for SL under argon saturation, implying the formation of a high-

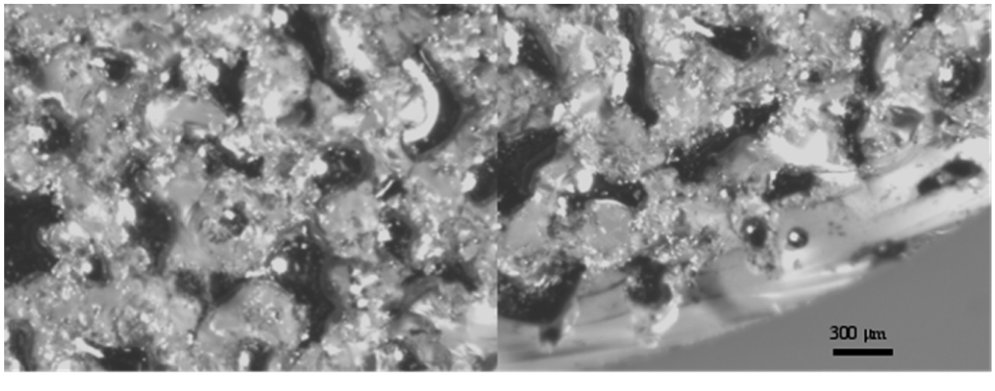

Figure 5. Microphotograph of the quartz horn tip after a 120 s operation cycle at maximum power. The mercury droplets fill up the erosion cracks generated by the intense acoustic cavitation.

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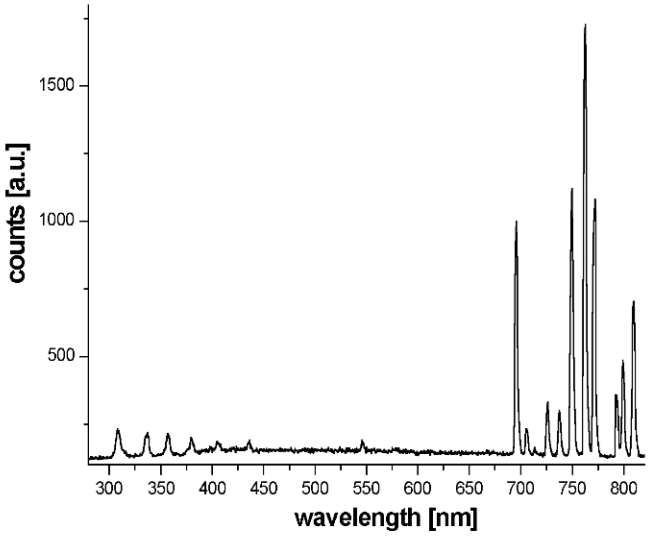

Figure 7. Same conditions of Figure 6, but after the addition of ITO film to the quartz horn transducer. The presence of emission lines from noble gas and metal vapor strongly supports the hypothesis of dense plasma formation.

temperature plasma with subsequent ionization of the liquid metal vapor.

MBSL in Galinstan. Searching for different liquid metals or metallic alloys at ambient temperature, our attention was drawn by an eutectic alloy, made of 68.5% Ga, 21.5% In, and 10% Sn, commercially known as Galinstan. This metal alloy has several attractive physical properties for MBSL experimenters:

- A very low vapor pressure: about 9 Torr at 500 °C, 10 times lower than the corresponding vapor pressure of mercury.
- A low surface tension.
- A strong wetting power; it adheres to many insulating materials, forming a thin film.
- It is nontoxic.

An example of MBSL spectra in galinstan is reported in Figure 8; they are obtained using type (1) and type (2) setups, delivering the maximum power available for each apparatus in continuous wave mode. No emission lines were detectable. We then performed additional tests, positioning the titanium probe very close to the wall of the flask. Emission lines, associated with Sn, In, and Ga excited states, appeared in addition to the ordinary broadband SL continuum (Figure 9, black curve). To assess the possible role of electrical discharges, as in the case of mercury, the quartz horn transducer was equipped again with the conductive ITO-coated glass disc and operated in pulse mode to maximize the output acoustic power. Weak, but clearly discernible, lines appeared in the spectrum (Figure 9, gray curve). It is worth noting that, after the ultrasonic pulse, the glass disc was no longer electrically conductive, even if not eroded by cavitation and optically transparent. The detachment of "ITO film" was probably the origin of line emission formation; since the elements that form the thin film were two of the three that compose the liquid (indium and tin), the lines can be assigned to the emission from metallic elements (In, Sn, and Ga, when using the titanium probe). These preliminary results lead us to suppose that a different mechanism is in action when the galinstan/glass interface is strongly stressed by cavitation bubbles, due to the uncommon wetting properties of this alloy. A suggestion could be derived from the fact that the

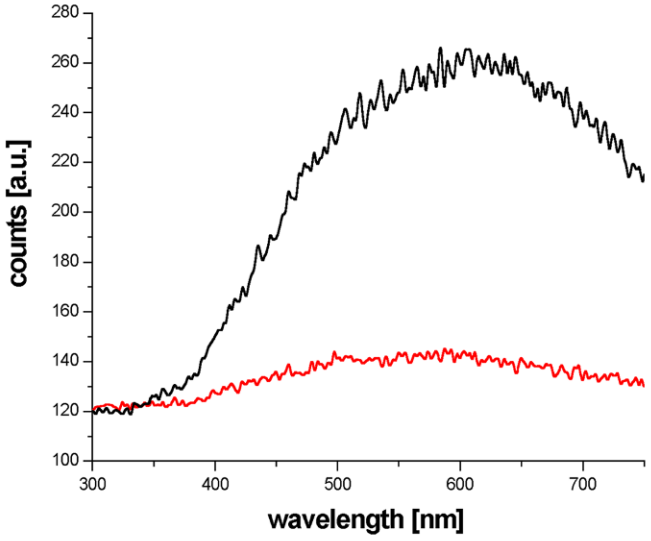

Figure 8. MBSL spectra from galinstan. Red curve: SL produced by the quartz horn transducer. Black curve: SL from the titanium probe, at maximum available power.

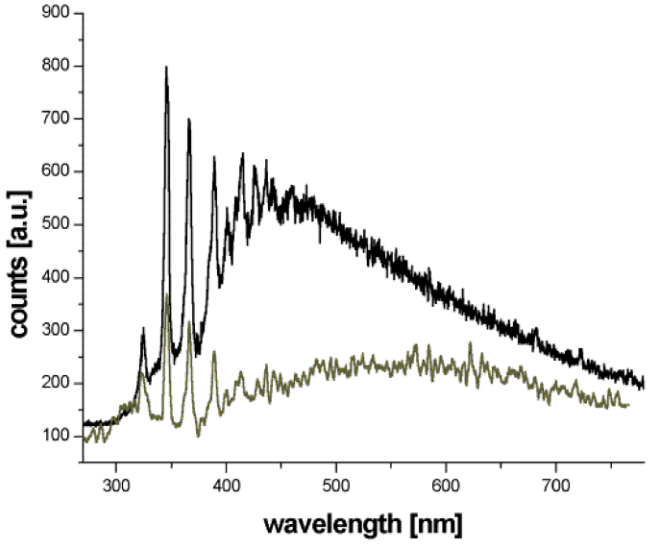

Figure 9. MBSL spectra from galinstan. Black curve: using the titanium probe in the proximity of the flask wall. Gray curve: using the quartz transducer equipped with the ITO thin film. The emission lines from Sn, In, and Ga at 315, 345, 366, 389, 401, and 414 nm are clearly visible.

energy levels associated with the emission lines of Ga, In, and Sn correspond to the temperatures deduced in ref 14 for mechanoluminescence phenomena.

Finally, we investigated galinstan cavitation under argon flux with type (1) and type (2) experimental configurations. No emission lines were detected, neither from metals nor from noble gas excited states.

■ CONCLUSION

In 1982, Flynn[15] deposited what is considered the first patent related to sonofusion reactors: in his hypothetical, but suggestive, device, high intensity cavitation in liquid metals would have produced the nuclear fusion of deuterium atoms. To date, there is no evidence that sonofusion is a real and attainable effect, but it is remarkable that, 30 years ago, liquid

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metals were already considered the best choice for an extreme energy concentrator based on cavitation phenomena. Our spectroscopic results are a first step toward a complete definition of a complex problem, using luminescence as a probe for the collapsing bubbles inner conditions. Different emission mechanisms seem to be at work: the adiabatic compression of the gas and vapor fraction (accounting for the broad-band continuum in the spectra) and low-pressure electrical discharges (emission lines). Discharges are produced only when a very high acoustic pressure is applied to mercury. Although emission lines seem to be associated, in standard condition, with electrical processes at the solid/liquid interface, the experiments with conductive ITO films under argon flux confirm the possibility of thermal ionization of metal atoms in the vapor phase, due to the presence of a high-temperature plasma. Further evidence of high density plasma conditions could be found by higher-resolution spectroscopic techniques and improved experimental setups, possibly overcoming the limitations of the present apparatus.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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