Ultrasonics Sonochemistry 19 (2012) 668–681

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Spectroscopic and thermodynamic features of conical bubble luminescence

F.A. Godínez [a], M. Navarrete [a,*], C. Sánchez-Ake [b], E.V. Mejía-Uriarte [b], M. Villagrán-Muniz [b]

[a] Instituto de Ingeniería, Universidad Nacional Autónoma de México, Av. Universidad 3000, Universidad Nacional Autónoma de México, C. U. Distrito Federal, 04510 México, Mexico
[b] Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Av. Universidad 3000, Universidad Nacional Autónoma de México, C. U. Distrito Federal, 04510 México, Mexico

ARTICLE INFO

Article history:
Received 15 May 2010
Received in revised form 28 May 2011
Accepted 29 August 2011
Available online 10 September 2011

Keywords:
Sonoluminescence
Transient cavitation
Sulphuric acid
Bubble dynamics

ABSTRACT

The influence on luminescence from conical bubble collapse (CBL) with varying Ar gas content while perturbing the liquid 1,2-Propanediol (PD) has been investigated. The temporal, spatial, and spectral features were analysed with regards to the dynamics of collapse and liquid degradation. Sulphuric acid and sodium chloride were added to disturb the liquid. The following three cases were studied: PD/Ar, (**I**), (PD + H_2SO_4)/Ar, (**II**), and (PD + H_2SO_4 + NaCl)/Ar, (**III**). The intensities of those cases decrease as **III** > **II** > **I**. Temporally, single and multiple light emissions were found to occur. The pulse shape exhibited a large variety of profiles with a main maximum and up to two local maxima around the main maximum. These local maxima resembled those generated by laser cavitation. Spatially, no radial symmetry was detected in the light emissions. Spectrally, the Swan, CH and CN lines were observed at low volumes of gas and driving pressure. The ·OH radical and OH–Ar bands, as well as the Na and K lines, consistently appeared superimposed on an underlying continuum that almost disappeared in (**III**). The Na line was observed with two satellite diffuse bands representing Na–Ar complexes in (**I**) and (**II**), whereas in (**III**), only the line of sodium could be seen. Weak and diffuse emission lines from the Ar atom in the near-IR region were observed in (**I**) and (**II**).

The proposed mechanism of bright CBL was based on the energy transfer from electron-excited homolytic cleavage products to the chromophore molecules generated during the collapse-rebound time line (~8200 K and ~1 ms of collapse time from model), which had accumulated inside the liquid and remained on the walls of cavity during the repetition of the collapse. A general mechanism for the bright CBL is broached.

1. Introduction

Cavitation can be defined as a homogeneous or non-homogeneous formation, with a subsequent growth and collapse of cavities (or bubbles) in addition to associate activities in a fluid, resulting in very high energy densities on the order of $1–10^{18}$ kW/m^3 [1]. A large "local" force is the consequence of the collapse which causes damage to metals, emulsification, degasification, sonoluminescence, sonochemistry, triboluminescence, destruction of microbes, and other powerful phenomena. The luminescence caused by acoustic cavitation corresponds to a weak glow, and the energy released through this pathway is very small, albeit highly concentrated [2].

A large part of the available energy during the collapse is transferred and stored in a compression wave well before the inward motion is finally arrested [3]. The fundamental dynamics of this phenomenon were demonstrated very clearly by Rayleigh in his 1917 analysis [4]. He also recognised that a more realistic physical model of the cavitation phenomenon would include a small quantity of insoluble gas, whose compression at minimum volume arrests the inward motion and causes the cavity to "rebound".

Refinements of this theory, including the compressibility of the liquid, have been achieved by Gilmore [5], Hickling and Plesset [6], Ivany [7], and Keller [8], among others. Numerical simulations have been performed taking into account the nonequilibrium evaporation and condensation of water vapour at the bubble wall, nonequilibrium chemical reactions, and the ionisation of gas and vapour inside the bubble, as well as thermal conduction on both the inside and outside of the bubble [9–11]. Varying physical effects have been added to the original Rayleigh theory such as those mentioned above, significantly damping the radial motion and thus reducing the predicted temperature of a typical sonoluminescing bubble.

In the past, several procedures have been used to experimentally monitor and study the collapse. Some procedures involve the application of tension to the liquids by means of acoustic

* Corresponding author. Address: Instituto de Ingeniería, Coordinación de Mecánica y Energía, Universidad Nacional Autónoma de México, Circuito Exterior, Edificio 12, Ciudad Universitaria, Coyoacán, 04510 México, D. F., Mexico. Tel.: +52 55 5623 3600x8841; fax: +52 55 5623 3600x8051.
E-mail address: mnm@pumas.iingen.unam.mx (M. Navarrete).
URL: http://www.iingen.unam.mx (M. Navarrete).

1350-4177/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2011.08.011

waves or by changing the pipeline geometry, e.g., single bubble sonoluminescence (SBSL) [12,13], multibubble (MBSL) [14,15], Venturi tube [16], the tube arrest [17], the hammer method [18], and conical bubble collapse (CBL) [19–29]. Other procedures deposit energy locally by light burst [30,31], spark discharge [32] or elementary particles [33] through the liquid. These studies have permitted calculations of the extraordinary conditions inside the bubble (temperatures up to 15,000 K, pressures of 100–1000 bar, and heating/cooling rates $>10^{12}$ K s^{-1}) surrounded by a cold liquid. Earlier calculations have indicated values of $\sim 10^8$ K, while recent estimates converge to temperature values between 10,000 and 20,000 K [34,35].

Based on spectroscopic studies in SBSL and MBSL, it is believed that the atomic, molecular and continuum emissions arise from several chemical pathways occurring during discrete time intervals. This is the result of the emergence of different local temperatures that are spatially and temporally distributed along the collapse-rebound time line. The continuum emission is attributed to transitions of electrons produced by high temperature ionisation confined to voids in the dense fluid formed in the latter stages of the cavitational collapse [34,35].

The space parameter of SL that had been initially developed for the water–Ar system has been expanded with the discovery of very bright luminescence using concentrated sulphuric acid solutions containing noble gases in both SBSL and MBSL [36–43]. The emission spectra from these experiments contain molecular (SO, SO_2), atomic (Ar, Xe, Ne), and ionic (O_2^+, Xe^+, Ar^+) bands and lines which have been explained by the formation of an opaque plasma core generated in submicron collapse bubbles. Moreover, the simultaneous observation of Ar and Na line emissions, and Na**.**Ar complex bands, in MBSL and SBSL suggest the injection of liquid nanodroplets into the interior of the bubble evaporating and complex redox processes generating the excited states of the Na atom. The mechanism is known as the injected droplet model [42] and provides an explanation of the origin of emission from nonvolatile species during MBSL.

Under appropriate conditions, regardless of the method by which rapid bubble compression is achieved, a light flash is emitted during the final stages of collapse only if a small amount of noble gas is contained in the bubble [40]. One or more light emission mechanisms can be activated depending on the details of collapse. The intensity and shape of the emitted light depend not only on the initial gas pressure and the driving pressure but also on the physicochemical properties of the host liquid and substances dissolved in it. These are capable of penetrating into the cavity and either enhancing or quenching the luminescence.

Conical bubble collapse (CBL) implies the emission of UV–VIS light generated by the violent collapse of a conical bubble driven by a liquid piston [19–29]. The advantages of the CBL procedure include that solid boundaries tend to stabilise the gas–liquid interface, that the heat may be transferred between the system and its surroundings through the interface and/or solid boundaries, and that the centre of the collapse is well defined [20,21]. Furthermore, CBL renders it possible to control the initial volume of the bubble, the inert gas volume in the bubble, the host liquid impurities and the driving force.

According to radial dynamical models, the collapse time in SBSL and MBSL ($\sim$0.5 μs) is shorter than in CBL ($\sim$1 ms). This produces a large difference in both the pressure and temperature that are reached. However, a longer collapse time implies a greater interaction among the inert gas and atomic and molecular components. Hundreds of chemical reactions can occur within the conical cavity during the timeline of the slow collapse, and the study of these reactions is more feasible in CBL. Most reactions could be chemiluminescent, which would explain the large and bright pulses from CBL compared with the flashes from SBSL and MBSL.

The present work describes the influence on the luminescence from CBL when perturbing the host liquid. Temporal, spatial and spectral features of the luminescence have been studied for three cases. The organic host liquid (PD) has been perturbed with small quantities of sulphuric acid and sodium chloride using Ar gas at different initial pressures to promote collisions. The second objective was to identify the mechanisms of atomic and molecular excitation/de-excitation guided by the obtained results and the model predictions.

2. Apparatus, instrumentation and operating procedure

A U-tube apparatus was assembled based on the conical device originally employed by other authors, e.g., Kosky [20,21] and Hawtin [21], for studying the collapse of water vapour cavities, Leighton et al. [22,23] for analysing the dynamics of the collapse, Chen et al. [24,25] for obtaining the spectroscopic features and other authors [26–29] that studied similar topics.

Fig. 1 shows a schematic of the U-tube device with its measurement equipment. The conical end was milled from PMMA with a hexagonal external shape, and on the inside, it contained a right circular cone of 30° that terminated in a hole that was 1.5 mm in diameter. The VIS-transmittance by the material thickness in the hexagonal faces was about 45%. The cone apex was sealed by a quartz window and was then used to record the spectra. Three photomultipliers (Hamamatsu, R5783-04 module, PMTs) were fixed around the apex cone to capture the luminescence. The signal from a dynamic force sensor (PCB Piezotronics, ICP 200B05, 75 MHz) on the top-plate provided data about the dynamic oscillating forces from a pressure pulse that was caused by the bubble collapse. All signals were captured with a Tektronix DPO7054 digital oscilloscope (500 MHz, 5GS/s). Optical emissions from the bubble were collected on the vertical axis through a quartz window with quartz optical fibre directed towards the entrance slit of a 50 cm focal length spectrometer (Princeton Instruments, SpectraPro 500i) equipped with a 150 lines/mm grating. The dispersed light was analysed by a gated intensified charge-coupled device (ICCD) camera (Princeton Instruments, PI-MAX2 1020 × 1024) equipped with a pulse/delay generator. The wavelength was calibrated using an Hg lamp.

Two data acquisition systems were implemented: one to capture the spectrum and another to acquire the initial state (with pressure gauges and thermocouples) and the transient response (PMTs, force transducers, and laser velocimetre). A signal from a pulse/delay generator (A) (Stanford, DG535) controlled the opening of valve B and provided a trigger for the two data acquisition systems.

The procedure to compress the gas pocket in the conical end was as follows. First, the U-tube was partially filled with a degasified liquid (270 ± 10 mL) at ambient conditions. Subsequently, the free and dissolved air was removed from the system, until a vacuum pressure around 1500 Pa was reached. Next, a small volume of inert gas was injected into arm 1, filling the free pipe volume and displacing the liquid in arm 2. This pressure was measured as a differential height, Δh. At some arbitrary zero time, valve B was opened, thereby allowing air pressure into arm 2, P_{ext}, after which the liquid started to move until the gas collapsed on the conical end. The displacement air–liquid interface blocked two laser lines that were separated by 50 mm. These signals were used to calculate the velocity of the liquid in the cylindrical part, V_0. The procedure of applying pressure on the liquid interface was not instantaneous and took approximately 50 ms. The compression, collapse, rebounds and re-expansion until the equilibrium was reached approximately in 100 ms, during which the remaining gas pocket and liquid were balanced by the external pressure.