Sonoluminescence at Ambient Temperature?

Thomas V. Prevenslik
14B, Brilliance Court, Discovery Bay, Hong Kong

Abstract Sonoluminescence (SL) is the light produced from the collapse of bubbles in water under ultrasound. Generally, SL is thought caused by the high temperatures that accompany the compression heating of air in bubble collapse. But the bubbles are filled with water vapor – not air, the water vapor during collapse condensing to liquid without any increase in temperature, and therefore the SL light is produced at ambient temperature. This is a significant finding in that some yet unknown mechanism exists by which SL light is produced at ambient temperature, thereby offering the economic potential of artificial lighting powered by a limitless source of clean renewable energy from the ambient thermal environment. SL at ambient temperature is proposed explained by a mechanism that treats the bubble as a quantum electrodynamics (QED) cavity having an electromagnetic (EM) resonant frequency that continually increases during collapse. This means EM radiation that resided in the QED cavity from the prior instant is continuously suppressed. But suppressed EM radiation in a QED cavity is energy loss that may only be conserved by an equivalent gain at its current resonant frequency, and therefore bubble collapse continually produces higher frequency EM radiation - the process called cavity QED induced EM radiation. Initially, the far infrared (IR) radiation from the ambient thermal kT energy of the water molecules in the bubble wall is suppressed to produce, say near IR radiation when the QED cavity collapses to near IR resonance. As the QED cavity resonance reaches visible frequencies, the near IR radiation is suppressed to produce visible radiation, and so forth. At ultraviolet (UV) resonance the visible radiation is suppressed to produce UV radiation while vacuum UV (VUV) radiation is produced from suppressed UV radiation at VUV resonances. Leakage of EM radiation from the bubble wall surface through the surrounding water appears as SL light having a broad featureless background spectrum from the near IR to the VUV. The VUV radiation produces OH* radicals that upon dissociation produce OH* emissions that superpose on the broad SL background spectrum. The generality of cavity QED induced EM radiation is shown applicable to SL from metal salt solutions, organics, and cryogenic liquids – including diverse applications in the solid state. Finally, a solid state device that produces light at ambient temperature is shown to satisfy limitations imposed by the 2nd law of thermodynamics.

Keywords: cavity QED, sonoluminescence.

1. Introduction

SL is the phenomenon of light emission [1] from a cavitation bubble generated within liquids irradiated with ultrasound, the light extended over a wide spectrum [2] from the near IR to the far VUV while having an extremely short duration [3] from 60 to 250 ps. SL is generally thought caused by high temperatures by the compression heating [4] of air during an adiabatic bubble collapse. Currently, the SL light is explained [5, 6] by the conversion of the air bubble into an Ar bubble as N_2 and O_2 are removed by chemical reaction at the high temperatures caused by adiabatic heating. But how air or Ar, and not water vapor fill a bubble nucleated in water under ultrasound has never been fully explained. Nevertheless, a consensus has emerged [7] that SL involves extraordinary temperatures in the bubble.

But there is a fundamental problem [8, 9] with high SL temperatures in bubbles nucleating and collapsing in water under ultrasound. Contrarily, the bubbles are not filled with air or Ar, but rather condensable water vapor as there is insufficient time at ultrasonic frequencies for air or Ar dissolved in the water to diffuse into the bubble. Vapor bubbles are required by Le Chatelier's principle[1] to maintain 2-phase equilibrium with the liquid bubble walls, and therefore the vapor tends to remain at ambient temperature and pressure as the

---

[1] Le Chatelier's principle states: "A system in equilibrium subjected to an external stress responds to reduce the effect of the stress." (1888). In a liquid-vapor system, an increase in pressure caused by a decrease in volume will cause the system to retreat from the increased pressure by the conversion of some vapor into liquid.

volume vanishes during bubble collapse – in sharp contrast to non-condensable gases like air or Ar where the gas temperature and pressure do indeed significantly increase as the volume vanishes [4].

Le Chatelier's principle is a statement of equilibrium between the water vapor and the liquid bubble wall. But the volume decrease in bubble collapse momentarily creates a non-equilibrium state of increased vapor temperature and pressure, and therefore some vapor condenses to liquid to lower the vapor temperature and pressure and restore thermal equilibrium with ambient conditions along a path governed by the Hertz-Knudsen [10] relation. Since the liquid bubble wall is a massive ambient temperature sink to the small quantity of vapor, the vapor remains at ambient temperature. Indeed, the Hertz-Knudsen relation was included [8,9] in computer solutions of bubble dynamics by the Rayleigh – Plesset (RP) equation [11] to show the temperature increase in a typical SL bubble is sufficiently small that the bubbles may be considered to collapse almost isothermally.

Yet, most of the early SL computer simulations [12] excluded water vapor in bubble collapse by making the assumption the bubbles are filled with air, and by treating the collapse as adiabatic instead of isothermal, air temperatures from 2000 to 10 million degrees were computed. More recently, RP simulations [13] including vapor condensation have been performed, but notably differ from [8,9] with regard to the condensation coefficient α_c, and limits on the validity of the RP equation.

The condensation coefficient α_c in the Hertz-Knudsen relation is defined as the probability of a vapor molecule sticking to the liquid water wall. If $\alpha_c = 0$, there is no sticking and the water vapor behaves as a non-condensable gas, such as air, giving bubble temperatures from 2000 to 10 million degrees. For $\alpha_c > 0$, the bubble temperature is reduced. But this is an academic exercise because the probability α_c the vapor molecule sticks to the wall can only be unity, i.e., even if sticking does not occur on the first collision, the molecule eventually sticks on subsequent collisions, as it cannot escape the bubble. Recent simulations [13] use $\alpha_c = 0.4$, and therefore predict far higher temperatures than actually [8, 9] occur.

The RP equation is only valid if the bubble remains spherical during collapse, i.e., the water vapor pressure in the bubble is required to be greater than the pressure in the liquid wall. If not, the bubble wall fragments injecting microscopic liquid particles into the bubble cavity, and therefore the RP equation requires modification. One such modification [8, 9] replaces the RP equation with 1-D flow simulating the injection of particles into the bubble. Bubble wall break-up precludes spherical focussing of fluid flow to sonic velocities while limiting the bubble collapse velocity to 150 –200 ms^{-1}. Thus, the vapor molecules at ambient temperature having a RMS velocity of about 500 ms^{-1} are always colliding to stick on the slower moving bubble wall as if the bubble wall is stationary.

It is therefore concluded based on Le Chatelier's principle and supported by computer simulations [8, 9] that the SL bubbles collapse almost isothermally at ambient temperature rather than by an adiabatic collapse at temperatures from 2000 to 10 million degrees.

2. Purpose

The SL light is most likely produced at ambient temperature – not at high temperature. The purpose of this paper is to present one such explanation of how SL light might be produced at ambient temperature – cavity QED induced EM radiation.

3. Objectives

Since SL is likely produced in an isothermal bubble collapse, a review of SL objectives is proper at this time to establish whether it is more promising to direct future SL research toward high or ambient temperature. The objective of SL at high bubble temperatures was to produce electricity by nuclear fusion in a bubble, the process called bubble fusion was first disclosed [14] in 1976. Recently, bubble fusion was even claimed [15] to be the discovery of the century in offering a source of limitless energy.

But the irony of science is that sometimes the converse of a premise proves more significant than the premise itself. Stated another way, SL at ambient temperature might instead truly embody the discovery of the century by providing a limitless source of artificial lighting from ambient temperature.

Because of Le Chatelier's principle, if the comparison of SL objectives were made over a decade ago, SL at ambient temperature might have been the more attractive choice. Indeed, the objective of SL at ambient temperature producing artificial light may be of far greater economic potential than by the electricity produced in miniature fusion reactors with inherent safety and radioactivity issues. Although not a direct producer of electricity, SL at ambient temperature may significantly reduce the burden of conventional power plants that otherwise supply the electricity for artificial lighting.

SL from liquids is not conducive to artificial lighting. In single bubble SL (SBSL), a single bubble is positioned at the center of a spherical pressure field by an arrangement of ultrasonic transducers. Since the intensity of light from a single SBSL bubble is faint even in a darkened room, the very large number of SBSL systems required to produce artificial light of commercial intensity renders SBSL impractical. In contrast, multi-bubble SL (MBSL) produces a swarm of SL bubbles from ultrasonic transducers spread over a wide region of liquid. But the spacing between the bubbles is still relatively large, and therefore a compact arrangement of MBSL bubbles is not possible. Both SBSL and MBSL require electrical energy to power the ultrasonic transducers, and therefore artificial light sources in liquids are not attractive economically.

Absent ultrasound, stationary nanoscale bubbles observed on solid surfaces under water that stabilize by nucleating on solid nanometer particles cannot be a source of commercial light because the particles quench the QED induced VUV radiation. Since the bubbles do not collapse, even if Ar.OH* excimers do form under VUV radiation there is no mechanism by which the Ar.OH* excimers may decompose to produce the SL light.

However, passive solid state materials fabricated into hollow nano shells might convert the steady heat flow from the ambient into VUV radiation that by photoluminescence is transformed into a commercial source of artificial light. See Appendix A.

4. Theoretical Background

Generally, the laws of thermodynamics preclude the spontaneous transformation of thermal kT energy from IR to VUV levels. But this is not true for IR radiation from the surface of a VUV resonant QED cavity. Indeed, the frequency up-conversion associated with transforming IR to VUV is the consequence of conserving EM energy in a QED cavity.

Cavity QED induced EM radiation follows from the most basic laws of physics – that low frequency EM radiation is suppressed in a high frequency QED cavity - the generality of the law applicable to QED cavities in both the solid and liquid state. Typically, IR radiation from QED cavity surfaces at ambient temperature is suppressed from atoms within the penetration depth of the resonant VUV radiation standing across the QED cavities. But in a QED cavity the EM energy loss from the suppression of IR radiation can only be conserved

by an equivalent gain at its resonant frequency, and therefore the atoms in the QED cavity surface are spontaneously excited by VUV radiation, the significance of which is that VUV radiation is produced at ambient temperature.

Generally, consider a spherical void of radius R in a solid or liquid as a QED cavity having an EM resonance emitting a VUV photon $h\upsilon$ shown in Fig. 1.
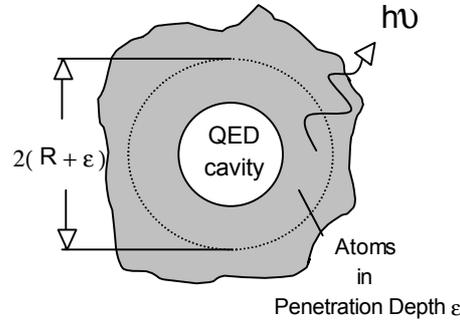

Fig. 1 – Spherical Void in the Solid or Liquid State

The QED cavity extends beyond the surface of the void to include the penetration depth ε of the resonant standing EM wave. Initially for $\varepsilon = 0$, there are no atoms in the penetration depth of the standing EM wave for the respective IR radiation to be suppressed, and therefore the standing EM wave having an EM resonant wavelength $\lambda = 4R$ is absent EM energy. But for $\varepsilon > 0$, the EM wave gains energy by conserving the loss from the IR radiation suppressed from the atoms. The EM wave has resonant wavelength λ and includes the depth ε necessary to assure absorptive (or reflective) boundary condition:

$$\lambda = 4(R + \varepsilon) \tag{1}$$

The Beer-Lambert law gives the depth ε by the absorption coefficient α of the cavity wall at the EM resonant wavelength $\lambda = 4R$ of the QED cavity. The EM radiation intensity I at depth ε is related to the intensity I_o at the QED cavity surface by,

$$I/I_o = \exp(-\alpha\varepsilon) \tag{2}$$

For $\alpha\varepsilon = 5.15$, over 99 % of the surface intensity is absorbed.

At ambient temperature, the thermal kT energy of atoms in depth ε is emitted as EM radiation at IR frequencies given [16] by the harmonic oscillator in Fig. 2.
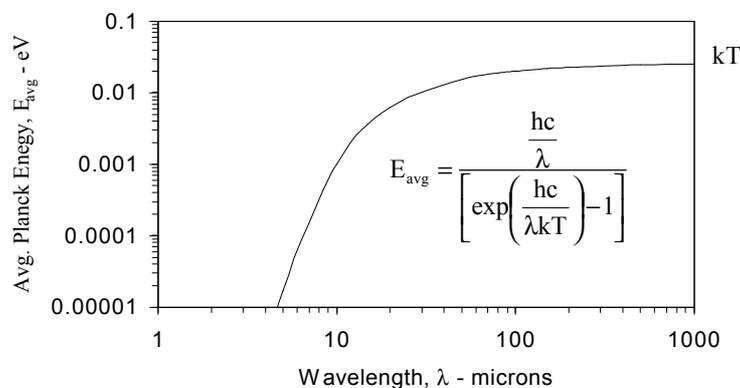

Fig. 2 – Harmonic Oscillator at 300 K. In the inset, k is Boltzmann's constant, T is absolute temperature, h is Planck's constant, and c is the speed of light.

The suppression of IR radiation by cavity QED depends on the dimension [17] of the voids in the liquid and solid state. For IR radiation having wavelength λ_{IR}, the IR radiation is suppressed during bubble collapse at the instant $\lambda_{IR} > \lambda = 4(R + \varepsilon)$.

Rather than conserving the suppressed IR radiation by emitting a VUV photon, the temperature of the atoms in the penetration depth might approach absolute zero, but this takes time. Eventually, the loss of thermal kT energy does indeed lower the atom temperatures to absolute zero. However, the preferred path for prompt EM energy conservation is by the spontaneous frequency up-conversion of the suppressed IR radiation to the VUV resonant frequency of the QED cavity. Indeed, frequency up-conversion is the consequence of promptly conserving EM energy in a QED cavity.

Since the EM resonance of the QED cavity here is considered from the near IR to the VUV, the low frequency IR radiation of the atoms in the depth ε is suppressed. The total IR energy U_{IR} suppressed,

$$U_{IR} = \frac{4\pi}{3} \Psi \left[(R + \varepsilon)^3 - R^3 \right] \tag{3}$$

where, Ψ is the EM energy density, $\Psi \sim N_{dof} \times \frac{1}{2} kT / \Delta^3$, and Δ is the cubical spacing between atoms at solid or liquid density. N_{dof} is the number of degrees of freedom of the atoms and molecules. Typically, for solids and liquids, $N_{dof} = 3$ and 6, respectively.

Suppressed IR is a loss of EM energy that in a QED cavity may only be conserved by an equivalent gain in Planck energy at its resonant frequency. For QED cavities having EM resonance from the near IR to VUV, the conservation of EM energy may be expressed by,

$$NE = U_{IR} \tag{4}$$

where, N is the number of photons having average Planck energy E over the depth ε,

$$E = \frac{hc}{4(R + 0.5\varepsilon)} \tag{5}$$

and if the leakage through the bubble walls during bubble collapse is neglected, then $NE = N_{near\ IR} E_{near\ IR} = N_{visible} E_{visible} = N_{VUV} E_{VUV}$. But the leakage of QED induced EM radiation is the well-known featureless SL background continuum, the simulation of which is presented later in this paper. Combining, the number N of photons having Planck energy E produced in the penetration depth ε,

$$N = \frac{8}{3} \pi \frac{kT}{hc} N_{dof} (R + 0.5\varepsilon) \left[\frac{(R + \varepsilon)^3 - R^3}{\Delta^3} \right] \tag{6}$$

Generally, cavity QED induced EM radiation is produced at VUV frequencies *anytime* voids at the nanoscale are formed in solids and liquids thereby explaining why electrons by the photoelectric effect and photons by photoluminescence are observed at ambient temperature.

Although the IR radiation from the atoms in the penetration depth is incoherent, the VUV radiation becomes coherent [18] by the selective feedback of the QED cavity as an optical resonator. After emission of the VUV photon, the recovery of ambient temperature for the subsequent VUV emission depends on the liquid or solid state.

In the liquid state, the voids are nanobubbles. Under ultrasound, the thermal kT energy of the molecules in the penetration depth is recovered every cycle by the flow of liquid at ambient temperature. Work is required to flow the liquid, and therefore the 2nd law of thermodynamics is not violated. Although the number of SL photons produced by cavity QED induced EM radiation is discrete every cycle, the SL at ultrasonic frequencies appears as steady light.

The voids are nanogaps in the solid state. Solids absent fluid flow recover thermal kT energy in the penetration depth by conductive heat flow at ambient temperature across the boundary of the penetration depth. In the steady state, the suppression of IR radiation eventually causes the temperature of the atoms in the penetration depth to approach absolute zero. This enables heat to flow into the penetration depth from the ambient while cavity QED precludes any increase in temperature of the atoms in the penetration depth. Thus, EM energy is conserved by the spontaneous conversion of heat into VUV radiation.

In both liquid and solid states, the source of cavity QED induced EM radiation is *always* the thermal kT energy of the atoms at ambient temperature.

5. Applications

Cavity QED induced EM radiation is applied to SL at ambient temperature from liquid water, organics, metal-salt solutions in water and primary alcohols, and cryogens.

5.1 SL in Water

Historically, SL in water was first observed after saturation with Ar or air. But SL in water is also observed after saturation by other gases including N_2, O_2, He, Ne, and Xe. Similarity to Ar suggests the formation of OH* radicals by cavity QED induced EM radiation is common to all gases, the specifics depending on chemistry.

5.1.1 Ar and Air Saturated Gases

Discoveries in the evolution of cavity QED induced EM radiation as a source of SL in water saturated with Ar or air are too numerous to cite, the more important beginning in 1939 with the finding [19] that SL in water was chemiluminescence. In 1983, radicals were identified [20, 21] in the ultrasonic irradiation of water and alkanes thereby supporting the notion that SL is caused by chemical reactions. In 1991, theoretical support [22] for SL by chemical reaction by radicals was established. The OH* emission in the dissociation of the OH* radical was first described [23] in 1996. In 1997, Ar gas doping was found [24] to be crucial to SL in water, the source of Ar in typical SL experiments being the ~ 1 % Ar in the atmospheric air naturally dissolved in water. In 2001, SL spectral lines were confirmed [25] to be the emission from dissociation of the OH* radical.

But how the OH* radical is produced at ambient temperature consistent with Le Chatelier's principle remains to be discovered. In this paper, the OH* radicals are proposed formed in the bubble wall by cavity QED induced EM radiation.

Water Absorption, Planck Energy, and Number of VUV Photons and OH Radicals*

The QED cavity walls are required to have absorptive (or reflective) boundary conditions to support momentary VUV standing waves. The absorption coefficient α of water [26] at ambient temperature is shown in Fig. 3.
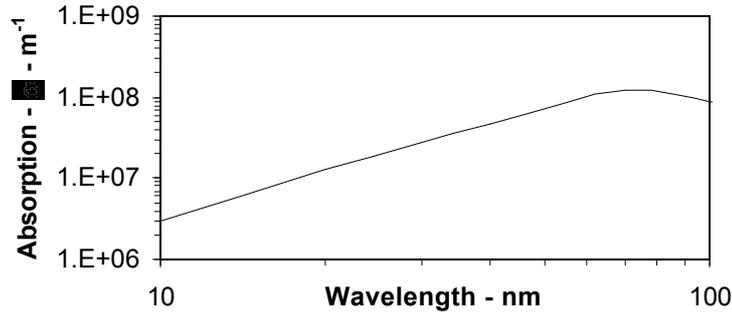
Fig. 3 – Absorption coefficient α of Water

For αε = 5.15, the mean Planck energy E and number N of photons at fractions n of the penetration depth ε from the QED cavity surface are shown in Figs. 4 and 5. The maximum Planck energy E at n = 0.35, 0.1, and 0.05 is about 10, 16, and 20 eV, respectively. The corresponding number N of VUV photons are ~ 1×10^5, 9×10^3, and 3×10^3. The VUV photons from 10 to 20 eV are consistent with the SL spectra [27] showing the spectral lines of the Ar atom and the O_2^+ ion are excited in sulfuric acid.
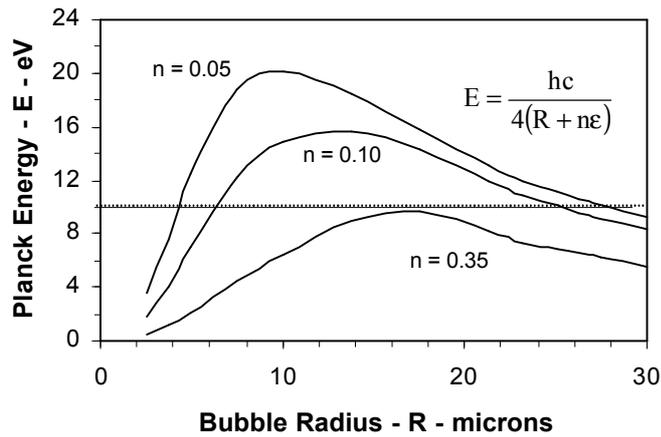

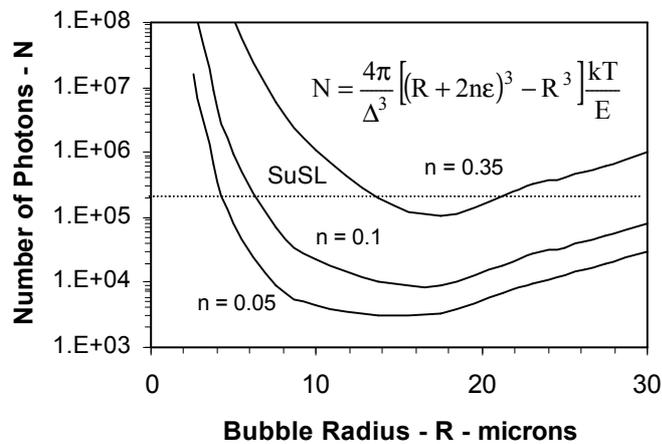**Fig. 4** – Planck energy and Bubble Radius R

Fig. 5 – Number of VUV photons and Bubble Radius

In water, the penetration depth ε as a function of bubble radius is depicted in Fig. 6. The minimum ε is about 30 nm and occurs at about R ~ 18 nm.
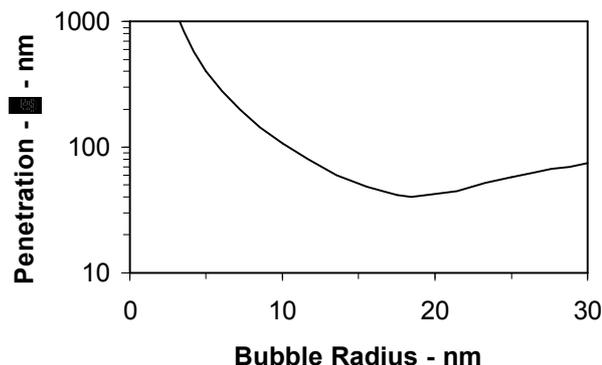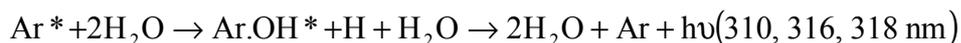

Fig. 6 – Penetration Depth ε and Bubble Radius R

Link between Ar Atoms and OH* Emissions

In both SBSL and MBSL, water absent Ar [24] does not produce SL. Given the OH* emissions can only be caused by OH* radicals, it follows [28,29] the Ar atoms somehow initiate the formation of Ar.OH* excimers. Thus, cavity QED induced EM radiation forms Ar.OH* excimers either from excited (1) Ar* atoms, or (2) H_2O* molecules.

(1) *Argon Excited Excimers.* The VUV photons from cavity QED induced EM radiation at 9.85 eV at 126 nm [30] excite the Ar atom to produce the excited state Ar*. The excited Ar* atom efficiently combines with a pair of water neighbors by a three body reaction to form the Ar.OH* excimer,

$$Ar + h\upsilon(126\ nm) \rightarrow Ar* \tag{7}$$

$$Ar*+2H_2O \rightarrow Ar.OH*+H+H_2O \rightarrow 2H_2O+Ar+h\upsilon(310,\ 316,\ 318\ nm)$$
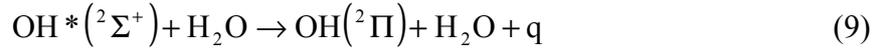
The excited Ar* can combine with a pair of Ar atoms in a three body reaction to form the excimer (Ar.Ar)*. However, the concentration of Ar in water is dilute, and therefore the three-body reaction is highly unlikely.

(2) *Water Excited Excimers.* Cavity QED induced EM radiation produces VUV photons that monotonically increase in Planck energy as the bubble collapses. The first singlet state $H_2O*(\widetilde{A})$ of the water molecule [29] is excited at ~ 7.5 eV and dissociates into H atoms and OH* radicals without producing SL light. Next, the $H_2O*(\widetilde{B})$ state at ~ 8.3 eV is reached but the yield is < 10% although excited radicals $OH*(^2\Sigma^+)$ are produced that emit SL light upon dissociation to H atoms OH radicals. The only significant SL light production of OH* radicals occurs upon the formation of the stable second singlet $H_2O*(\widetilde{C})$ state of water at 9.9 eV. Without Ar* or Ar.OH*, SL light from both $H_2O*(\widetilde{C})$ and $H_2O*(\widetilde{B})$ is possible.

$$H_2O(\widetilde{C}) \rightarrow H_2O(\widetilde{A}) \rightarrow OH*(^2\Sigma^+) \rightarrow OH(^2\Pi)+h\upsilon(280,\ 310,\ 340\ nm) \tag{8}$$

However, the $OH*(^2\Sigma^+)$ radical [29] is quenched q by the water molecules.

$$OH*\left(^2\Sigma^+\right)+H_2O \rightarrow OH\left(^2\Pi\right)+H_2O+q \qquad (9)$$

Although the $OH*(^2\Sigma^+)$ radical is formed by the VUV radiation, SL is not produced because the $OH*(^2\Sigma^+)$ radical is quenched.

Decomposition of Ar.OH* Excimers and Dissociation of OH* Radicals

The Ar.OH* excimers decompose in the high pressures of bubble collapse. This is a likely event in that the energy of forming the Ar.OH* excimer is not high given the Ar.OH* dissociation [29] energy is ~ 0.02 eV. Indeed, the decomposition of the Ar.OH* excimer is the path for SL light production.

For SBSL, the 3-D stagnation pressure P_S as the bubble walls collide, $P_S \sim 3 \times \frac{1}{2}\rho\, V_C^2$. From [8, 9], the bubble collapse velocity $V_C \sim 150 - 200$ ms^{-1} and $P_S \sim 340$ to 600 atm. Since the dissociation pressure [29] of Ar hydrates is about 105 atmospheres, the Ar.OH* decomposition is likely. Lower collapse pressures are expected in MBSL.

The Standard Unit of SL

The standard unit of SL (SuSL) is the experimental [24] number of SL photons emitted from a SBSL bubble in air saturated water, i.e., SuSL ~ 2×10^5. Figs. 4 and 5 show the excited Ar* state comprises N ~ 1×10^5 photons at E ~ 10 eV, and therefore cavity QED induced EM radiation is consistent with the SuSL, i.e., N ~ SuSL is reasonable.

RP Response at the Nanoscale

RP simulations of bubble collapse give wall velocities V_C and vapor pressure ratios P_{vap}/P_{vapo} that depend on the minimum radius R_{min}. Early RP simulations [8, 9] at the microscale for $R_{min} \sim 0.5$ μm gave $V_C \sim 150 - 200$ ms^{-1} and $P_{vap}/P_{vapo} \sim 5 - 10$. But cavity QED induced EM radiation having Planck energy E > 5 eV is produced at bubble radii R < 50 nm, and therefore requires the RP response at the nanoscale.

However, the microscale RP response [8, 9] is valid at the nanoscale if the mean free path MFP of the water vapor molecule is greater than the bubble diameter 2R, i.e., MFP > $2R_{min}$. If so, the vapor has condensed on the bubble wall. The condensation criterion,

$$2R_{min} < MFP = \frac{kT}{\sqrt{2}\pi P_{vapo}d^2} \qquad (10)$$

where, d is the diameter of the water molecule, d ~ 0.2 nm. For $P_{vapo} \sim 2340$ Pa and T ~ 300 K, MFP ~ 10 μm and $R_{min} \sim 5$ μm. Following [8,9] under the constraints of the Hertz-Knudsen relation and unity condensation coefficient, the microscale RP response for a typical bubble dissolving under atmospheric pressure to radius R_{min} is shown in Fig. 7.
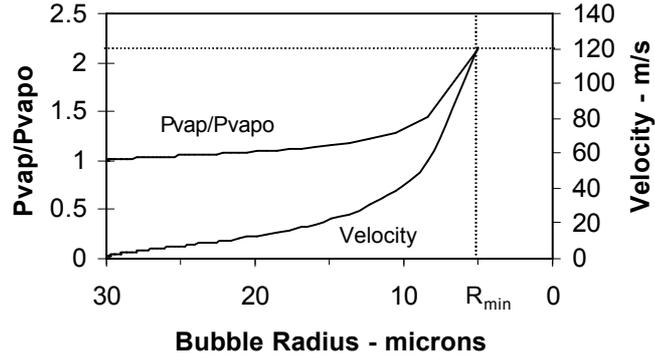
Fig. 7 – Bubble Dissolving under Atmospheric Pressure - Microscale RP Response

The microscale RP response at radius $R_{min} \sim 5$ µm gives $V_C \sim 120$ ms^{-1} and $P_{vap} / P_{vapo} \sim$ 2.2. Thus, $P_{vap} \sim 5150$ Pa giving an equilibrium temperature $T \sim 33$ C for the water vapor that does not increase further as the bubble collapses to the nanoscale, i.e., the bubble collapses almost isothermally. Moreover, the velocity V_C does not change significantly over the time it takes for the bubble walls to collide, and therefore the microscale RP response [8,9] for the velocity $V_C \sim 150 - 200$ ms^{-1} is a reasonable estimate of V_C at the nanoscale.

Featureless SL Spectra

In bubble collapse, SL light is continually produced in the bubble wall by cavity QED induced EM radiation. SL begins in the far IR, although recorded SL spectra begin in the near IR. Regardless, the EM radiation continues through the VIS and VUV until the bubble walls collide. Thus, the spectrum of SL light appears to have a continuous and featureless background consistent with [2] observation. If the EM radiation coincides with atomic lines or molecular bands of a species dissolved in the liquid or the liquid itself, the SL spectrum shows peaks above the background, e.g., the SL light from the decomposition of Ar.OH* excimers superposed on the featureless SL spectra from cavity QED induced EM radiation.

The featureless SL spectra may be understood by considering a spherical bubble of radius R described above dissolving under atmospheric pressure. Photons stand across the diameter in the penetration depth e at the EM resonance of the bubble. From Eqns. 5-6, the EM energy at any instant in the bubble collapse may be written,

$$U = \frac{1}{2} NE \qquad (11)$$

where, N is the number of water molecules in the penetration depth e, ½ N is the number of QED photon pairs standing across the bubble, and E is the average Planck energy in the depth ε. Combining,

$$U = \frac{1}{6} \pi \left[\frac{(R + \varepsilon)^3 - R^3}{\Delta^3} \right] \left(\frac{hc}{R + 0.5\varepsilon} \right)$$

For e << R,

$$U \cong \frac{\pi}{2\Delta^3} hc\varepsilon R \qquad (12)$$

During bubble collapse, the SL power P emitted is the rate of change of the Planck energy in the penetration depth e and depends on the absorption coefficient α. Fig. 6 shows ε for water is lower bound at ~ 30 nm, and therefore is taken to lower bound the power P.

10

$$P = \frac{dU}{dt} = \left(\frac{\partial U}{\partial R}\right)\frac{dR}{dt} \cong \frac{\pi}{2\Delta^3}hc\varepsilon V_C \qquad (13)$$

where, $dR/dt = V_C$ is the velocity of the bubble collapse. The absorption of the QED induced EM radiation between the bubble and the photomultiplier is assumed negligible, at least until VUV radiation is produced just before the bubble walls collide.

IR radiation is suppressed as the bubble collapses to radius $R_o \sim 25$ microns. Why this is so may be understood from Fig. 2. The kT energy at ambient temperature is observed to saturate at 0.0258 eV for $\lambda > 100$ microns. Since $\lambda = 4R$, the minimum R necessary to reach the full kT energy is 25 microns. During collapse, the suppressed IR is conserved by successively higher frequency photons by the increasing EM resonance of the bubble. The EM radiation that leaks out of the penetration depth produces the featureless broadband SL spectrum. If the EM radiation coincides with a quantum state of a chemical species in the bubble wall the emission appears as a spike on the broadband background.

Clearly, the IR radiation suppressed at the beginning of collapse leaks out apidly, thereby depleting the available kT energy to produce higher energy VIS and VUV photons. But the thermal kT energy of water molecules in the penetration depth ε is constantly being replaced by water molecules from the underlying bulk. The total amount of thermal kT energy U_o available to supply the SL power P is that necessary to fill the bubble of radius R_o at the beginning of collapse,

$$U_o = \frac{1}{2}N_o N_{dof}\frac{kT}{2} = \frac{2\pi}{3}\left(\frac{R_o}{\Delta}\right)^3 3kT = 2\pi kT\left(\frac{R_o}{\Delta}\right)^3 \qquad (14)$$

where, N_o is the number of water molecules in sphere of radius R_o. The thermal energy U_o as the source of broadband EM emission is assumed far greater than that necessary to produce the broadband SL power spectrum. The RP equation is solved numerically by assuming the water molecules in the penetration depth are always maintained at ambient temperature T as the bubble collapses. The thermal kT energy U accumulates every time step,

$$U = U_{old} + Pdt \qquad (15)$$

where, $U_{old} = 0$ at $t = 0$, and dt is the time step in the RP solution..

The SL power P emitted from the bubble and the fraction U/U_o as a function of time t are shown in Fig.8. The maximum power P is found to be about 34 mW. This agrees with the SL power [47] of 30 mW measured in 1992. The fraction $U/U_o \sim 4 \times 10^{-4}$ shows the available thermal kT energy in filling the bubble is hardly diminished by that necessary to produce the broadband EM radiation, and therefore the assumption that the penetration depth e is generally populated by water molecules at ambient temperature is justified.

The broadband SL spectrum produced as the bubble dissolves under atmospheric pressure is shown in Fig. 9. The SL spectrum does not begin in the near IR, but rather in the far IR at about 100 microns. In effect, cavity QED induced EM radiation is a continuous variable frequency excitation source that produces the spectral lines and broadband featureless of the liquid and impurities observed in SL spectra. The continuous nature of cavity QED induced EM radiation is important as otherwise the precise lines of Ar at 9.85 eV, bond breakage of O_2 and O_2^+ at 5.1 and 6.5 eV, and ionization of O_2 at 12.1 eV cannot be excited. Indeed, absent cavity QED induced EM radiation, the Ar.OH* excimers do not form and OH* spectral lines are not observed.
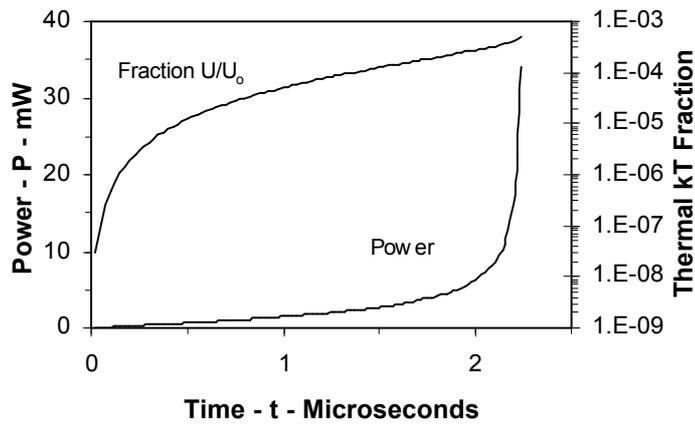
Fig. 8 Bubble dissolving under Atmospheric Pressure – Power and Fraction of Available kT Energy Depleted during Bubble Collapse
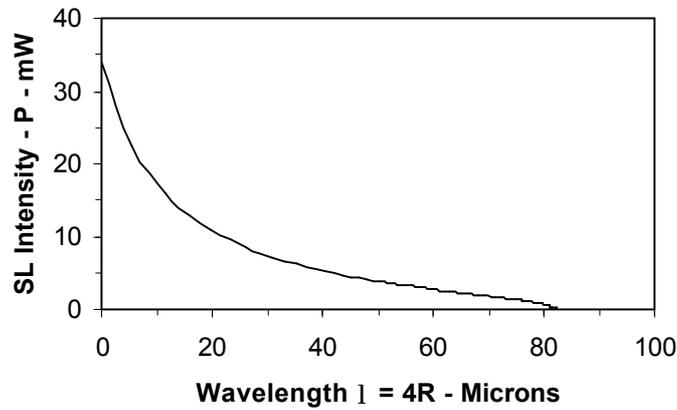

Fig. 9 Bubble dissolving under Atmospheric Pressure - Broadband SL Emission Spectrum

The SL spectrum [27] for sulfuric acid and water is nearly flat over the range of wavelengths from 800 to 200 nm because of the uniform SL excitation produced in cavity QED induced EM radiation. The ~ 2×10^5 VUV photons at ~ 20 eV having wavelength ~ 62 nm have always been present in SL but not previously observed because of the cut-off of water at about 200 nm. But ~20 eV photons are observed in SL from sulfuric acid because sulfuric acid is transparent down to and below 200 nm.

SL Broadband Spectrum and Bremsstrahlung

The broadband SL spectrum is the response of the liquid surrounding the bubble to cavity QED induced radiation from the near IR to the VUV as depicted above in Fig 10. Similar to sulfuric acid, the SL spectrum from water is a complex relation of transmission coefficients with wavelength. The correctness of cavity QED induced EM radiation may be assessed by comparing SL emission [31] to bremsstrahlung radiation from plasma at 100,000 K in water or from plasma at 200,000 K in sulfuric acid. This is not to say plasma exists in bubble interior in water or sulfuric acid during collapse, as the bubble remains at ambient temperature. But if the Planck energy E given by cavity QED induced EM radiation, say in water is equivalent to bremsstrahlung temperatures of 100,000 K, it is also consistent with the measured SL spectrum.

Taking the wavelength λ of the Planck energy E produced in the QED cavity as the minimum cutoff wavelength λ_{min} associated with the bremsstrahlung radiation,

$$E = \frac{hc}{\lambda_{min}} = \frac{hc}{4(R + 0.5\varepsilon)} = kT_B \qquad (16)$$

where, T_B is the plasma temperature, or $T_B \sim 11,600$ K/ eV. Fig. 11 shows Planck energy E from cavity QED induced EM radiation is inversely proportional to λ_{min} consistent with bremsstrahlung radiation. For E ~ 8.3 eV, $T_B \sim 100,000$ K, and therefore cavity QED induced EM radiation also closely follows the measured SL spectrum.
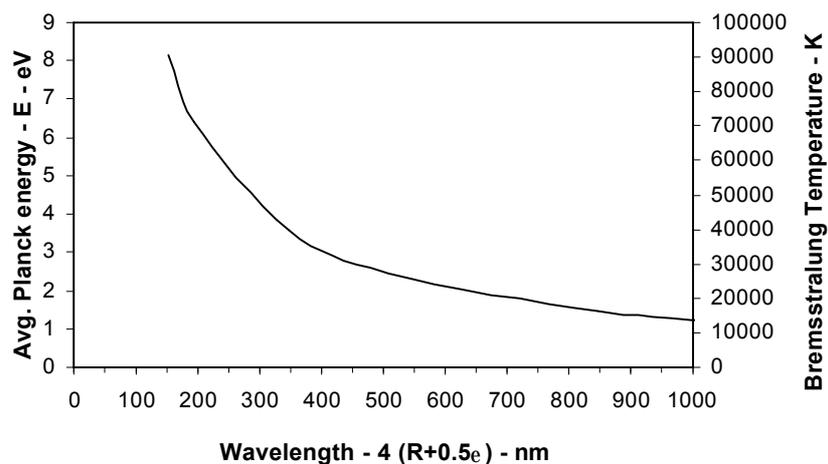

Fig. 11 – Cavity QED induced EM radiation and equivalent bremsstrahlung temperatures

5.1.2 Saturated Gases other than Ar and Air

Although SL is commonly observed in water saturated with air containing Ar at atmospheric concentration, SL in water is also observed after saturation by other gases including N_2, O_2, He, Ne, and Xe that otherwise are absent Ar or air. In cavity QED induced EM radiation, SL in water saturated with *any* gas X follows that described above for Ar.

Source of SL and the IR to VUV Continuum

The source of SL for any gas X including Ar and air is cavity QED induced EM radiation from the IR to the VUV that in a photochemical process has the Planck energy at ambient temperature to produce the second singlet $H_2O*(\widetilde{C})$ state of water. Stated another way, the excited states of water are produced from the broadband excitation by cavity QED induced EM radiation in the manner of a variable frequency IR to VUV laser.

In contrast, the source of the IR to VUV continuum is thought [28] to be the OH* emissions caused by high temperatures (~ 15000-30000 K) in adiabatic bubble collapse. That high temperature alone is insufficient to explain SL follows from the fact that drastically different SL spectra are found for additives, i.e., small amounts of *n*-butanol suppress SL while carbon disulfide in small quantities does not change SL. Both CS_2 and *n*-butanol are dissociated at high temperatures, and therefore both additives would have similar – not drastically different effects on SL. On this basis, it was concluded [28] that the additives chemically react with the H atoms and OH radicals to yield the observed SL effects.

But the statement alone that chemical reactions explain the SL spectra of additives dissociated at high bubble temperatures is insufficient. Chemical reactions require highly specific time and temperature ranges both of which for diverse additives such as *n*-butanol and CS_2 are difficult to independently control in a typical adiabatic SL bubble collapse.

MBSL

In MBSL, chemiluminescence in water saturated by gas X comprising He, Ar, Kr, and Xe including N_2 and O_2 reacting with OH* radicals was formulated [29] over a decade ago because only OH* emission from X.OH* excimers provided a reasonable explanation for the observed SL spectra.

Recent MBSL spectra (Fig. 2 of [28]) for saturated Ar, Kr, and Xe in water show there is virtually no difference in the broadband IR to VUV continuum while the OH* emission at 310 nm decreases from Ar to Xe which for Xe becomes indistinguishable from the broadband continuum. The peak in the OH* emission at 310 nm is found to decrease in the order Ar > Kr > Xe as 4.2:3.2:2.2 as illustrated in Fig. 12.
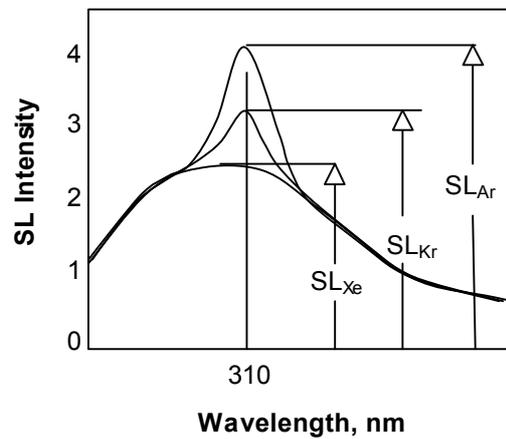

Fig. 12 – SL Spectra of Water Saturated With Ar, Kr, and Xe

The SL intensity ratio SL_X/SL_{Xe} of gas X to Xe may be approximated by assuming the number $N \sim 1 \times 10^5$ VUV photons of cavity QED photons at ~ 10 eV only excite the same number of X or Xe gas atoms, even though the number of X and Xe atoms in solution given by their solubility Φ in water may differ from each other, i.e., the ratio SL_X/SL_{Xe} is independent of solubility. But the SL is quenched [29] by collisions of the excited X* or Xe* atoms with water molecules. Here the SL_X/SL_{Xe} ratio is taken to be inversely proportional to the collision cross-sections σ_X and σ_{Xe} of X and Xe atoms,

$$\frac{SL_X}{SL_{Xe}} = \frac{\sigma_{Xe}}{\sigma_X} = \left(\frac{R_{Xe}}{R_X} \right)^2 \qquad (17)$$

where, $\sigma_X \sim \pi R_X^2$ and $\sigma_{Xe} \sim \pi R_{Xe}^2$, and R_X and R_{Xe} are the radii of X and Xe atoms. The atomic radius R_X of Ar < Kr < Xe increase in the order 0.88:1.03:1.24 angstroms. For $SL_{Xe} \sim$ 2.2, SL_{Ar} and $SL_{Kr} \sim 4.37$ and 3.18 reasonably approximate SL in Ar and Kr at 4.2 and 3.2.

SBSL is usually characterized by a featureless IR to VUV broadband spectrum absent the OH* emission bands that only appear in MBSL. However, the OH* emission at 310 nm was recently observed (Fig. 1 of [32]) in SBSL at low acoustic drive pressures.

In cavity QED induced EM radiation, SBSL is absent OH* emission bands because the high acoustic drive pressure compacts the excited X*states by water neighbors in the final collapse configuration and tends to quench the formation of the excited X.OH* excimers. In contrast, MBSL having lower acoustic drive pressures displays OH* emissions because fewer water neighbors are available to quench X.OH* formation. Indeed, the compact SBSL configuration likely consists of a single nanovoid; whereas, multiple nanovoids characterize MBSL. The compactness in the final SBSL and MBSL collapse configurations is illustrated in Figs. 13(a) and (b).
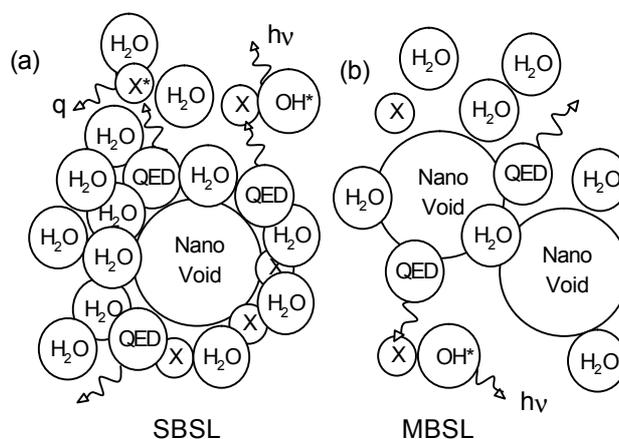

Fig. 13 –SBSL and MBSL – Molecular Emission and Quench

In SBSL, the cavity QED photons travel through the water by the 3 paths depicted in Fig. 13(a). Most QED photons do not encounter an X atom and pass through the water to the spectrophotometer to be detected as the featureless IR to VUV broadband spectrum. Other QED photons form the X* state and by three body reaction with pairs of water neighbors form the X.OH* excimer that upon dissociation produces OH* emissions [29] detected by the spectrophotometer,

$$X*+2H_2O \rightarrow X.OH*+H+H_2O \rightarrow 2H_2O+X+h\upsilon(310\,nm) \qquad (18)$$

Still other X* states are quenched [29] by water molecules, and therefore fewer Ar.OH* excimers form. The quench q of the excited X* state may be described by,

$$X*+H_2O \rightarrow X+H_2O+q \qquad (19)$$

MBSL having a low acoustic pressure produces a less compact configuration of X atoms and water molecules than SBSL as illustrated in Fig. 13(b). Similar to SBSL, some QED photons do not encounter the X atoms and are detected by the spectrophotometer as the featureless IR to VUV broadband spectrum. The remaining QED photons excite the X atoms produce the X.OH* excimer. By Eqn. 18, the decomposition of the X.OH* excimer produces hυ photons that are detected by the spectrophotometer as OH* emission.

Thus, MBSL spectra or SBSL spectra at low acoustic pressures show OH* emission bands superposed on the broad IR to VUV background that are not observed in SBSL at high acoustic pressures.

5.2 SL in Organics

Cavity QED induced EM radiation is not only applicable to SL from water, but also to SL from organic liquids absent OH* radicals. It is emphasized that the QED induced broadband IR to VUV radiation is applicable to *any* liquid and is a *real* source of EM radiation from the atoms in the penetration depth of the bubble surface. Molecular emissions in the broadband IR to VUV background depend on the chemistry of the organic radicals R* and represent the optical response of the chemical species to the EM radiation induced by cavity QED.

In cavity QED induced EM radiation, the SL intensity from the organic liquid is proportional to the number of atoms in the penetration depth of the bubble surface at VUV frequencies, and therefore a comparison to that of another liquid may be made based on penetration depths. In this regard, water having the greatest penetration depth at VUV frequencies is the optimum SL liquid. Even so, small amounts of additives can reduce the penetration depth in water and significantly reduce the amount of IR suppressed in the surface, and therefore the depth estimate must include concentrations of additives intensity of SL. But absorption coefficients of water with additives are not readily known.

SL from Non-Aqueous Solutions

SL from non-aqueous solutions as a chemiluminescence process is summarized in [33]. Over a wide range of organic liquids comprising hydrocarbons under Ar, and systems containing nitrogen, oxygen, and chlorine, the SL spectra show the molecular emission of the chemical species superposed on the IR to VUV background.

For hydrocarbon dodecane under Ar, the SL spectrum shows the Swan transition bands of C_2 and CH superposed on a broadband continuum from 340 – 700 nm. Similar to OH* emission in water, the IR to VUV background is thought to caused by C_2* and CH* radicals. In SL from dodecane under15%N_2/85%Ar the C_2 and CN peaks are observed and attributed to C_2* and CN* radicals. SL from dodecane under 10%O_2/90%Ar show the CO_2, OH, CH, and C_2 peaks from the C_2* and CO_2* radicals. SL from tetrachloroethylene under Ar show the C_2 and Cl_2 emissions attributed to C_2* and Cl_2* radicals.

All of the SL chemistry from this diverse range of organic liquids was attributed [33] to chemiluminescence from radicals R* formed by high temperatures, but can be produced at ambient temperature by photochemical processes from cavity QED induced EM radiation.

SL Quencher Experiments

For some time, SL research has been guided by the emission of light taking place in the gaseous cavities - not in the bubble walls. In 1939, volatile organic compounds were found [19] to quench SL, and interpreted in [14] to mean that the emission of SL light takes place in the gas cavities. More recent experiments show:

(1) The most efficient quenchers of excited OH* states in a liquid – nonvolatile KI and α-naphthol – do not affect the total SL flux [34], and

(2) Benzene and aliphatic alcohols that quench OH* radicals in liquids lower the level of total SL flux more when the molecular weight and boiling point are higher [35].

On this basis, the conclusion was reached in [14,34] that absent the effect of SL quenching by non-volatile KI and α-naphthol in the liquid state while SL was quenched when alcohols were added indicate the SL light emission occur in the gaseous – not the liquid state. However, cavity QED induced EM radiation suggests the SL light emission occurs in the liquid state. Specifically,

> (1) Since the excited OH* states only produce feeble lines in the SL continuum, the total SL flux [34] is essentially the same as the SL continuum. By cavity QED induced EM radiation, the SL continuum does not depend on excited OH* states, and therefore the lack of reduction in total SL intensity observed is expected. Similar to a laser, cavity QED induced EM radiation can produce OH* radicals, but its intensity is unaffected by the presence of excited OH* state quenchers, and

> (2) Benzene and aliphatic alcohols are known [35] to be effective OH* scavengers in aqueous solution. In the gaseous state, similar scavenging is expected at high temperature, but bubble temperatures are near isothermal during collapse, and therefore it is unlikely the reduction in the SL continuum was caused by OH* quenching in the gaseous or liquid states. Given the OH* flux is a small fraction of the SL continuum, it is more likely the organic compounds act as impurities on the bubble surface that increase the absorption coefficient α of water, thereby decreasing the penetration depth. Since the suppressed IR radiation is reduced because of the reduced penetration depth, the SL continuum is reduced. But absorption coefficients α for water with organic impurities are not available to support this conclusion.

The SL quencher experiments not only affirm cavity QED induced EM radiation, but also give SL a luminescent nature [14, 34] occurring in cold cavitation bubble - not at high bubble temperatures as predicted by the hot spot [4] theory. Indeed, SL in a cold cavitation bubble is consistent with SL at ambient temperature by cavity QED induced EM radiation.

5.3 SL from Metal Salt Solutions in Water and Primary Alcohols

The application of cavity QED induced EM radiation to SL from metal salt solutions in water and alcohols like SL from other liquids is only qualitatively assessed. Beyond the large volume of literature, a quantitative evaluation similar to that described above for SL in water is not possible for lack of data, in particular the absorption coefficient α for the diverse liquids. The seminal paper [22] on SL from alkali-metal salt solutions in water and primary alcohols guides the following discussion.

Mechanism of Chemical Excitation

SL in water under Ar is described by the chemistry of OH* radicals formed by cavity QED induced EM radiation. Similarly, carbon P* and oxygen Q* based radicals are formed in the ultrasonic irradiation of primary alcohols under Ar. The generality of cavity QED induced EM radiation as a source of photochemical excitation is applicable to SL from *any* liquid under Ar, although the SL spectra of the liquids is likely to require highly specific and complex chemical analysis.

In the hot spot theory, the chemical excitation process is assumed to form in the high temperatures [22] within the bubble interior, the radicals diffusing rapidly out into the bubble wall where the reaction with alkali-metal atoms takes place. But this is unlikely because OH* radicals in water or P* and Q* radicals in alcohols cannot diffuse in the bubble wall and react with Ar atoms faster than their lifetimes. However, cavity QED induced EM radiation travels through the bubble wall to be absorbed by Ar impurities, the transfer of which to water neighbors forms the OH* radicals, or to alcohol neighbors forms the P* and Q* radicals.

Thus, cavity QED induced EM radiation promptly forms radicals in the bubble wall that readily explains SL from non-volatiles present in the liquid and not in the bubble.

Effect of Vapor Pressure

The SL intensity of K in 1-alcohols decreases exponentially with increasing vapor pressure (Fig. 3 of [22]). For optimum cavity QED induced EM radiation, the suppressed IR radiation is conserved by the gain in VUV radiation in the wall of an otherwise evacuated QED cavity. If vapor is present in a SL bubble, the VUV radiation in the wall as the source of chemical excitation is reduced because of that absorbed by the vapor, and therefore the SL intensity is reduced as the vapor pressure increases.
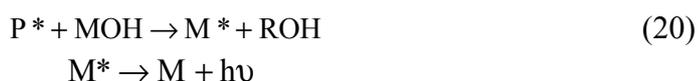
Spectral Line Width and Position

In the hot spot theory, the SL intensity is reduced with increased vapor pressure. Since SL is thought caused by high temperatures in the bubble, the hot spot theory expects the spectral line width and position to also change as a function of the vapor pressure. But this is contrary to the data (Fig. 4 of [22]). In fact, the observed line width and peak position are independent of cavitation conditions. The conclusion, therefore, is that the excited state atoms are not in the hot spot of the cavitation event when the emission occurs.

In contrast, SL by cavity QED induced EM radiation occurs by chemical excitation in the bubble wall, and therefore is consistent with the data (Fig. 4 of [22]) that shows the spectral line width and position are only dependent on the liquid state and do not depend on the vapor pressure within the bubble. Indeed, the spectral lines are naturally broadened by the quenching of photon emission by the solute in the liquid state, as shown for K in (Fig. 2 of [22]) from a hollow cathode lamp in a vacuum compared to the SL spectra in liquid water and 1- octanol.

Atomic and Ionic emission

The chemical reactions [22] by which radicals P* reduce alkali-metal cations M^+ to atoms M and photons $h\upsilon$ are,

$$P * + MOH \rightarrow M * + ROH \qquad (20)$$
$$M* \rightarrow M + h\upsilon$$

Recently, SL from metal salt solutions [36] in Ar saturated ethylene glycol showed the D-line of atomic Na, although only the Na^+ ion is present in the liquid state absent ultrasonic radiation. However, the P* radical produced in ultrasonic irradiation reduces the Na^+ ion to the Na atom before emitting the $h\upsilon$ photon. By extending the study to $CaCl_2$, it was thought emission from Ca^{++} or Ca^+ might occur, and if only Ca lines were found would show the emission occurred in the gas phase rather than the liquid state. Indeed, only the Ca line near 422 nm was found. But this does not mean the Ca emission occurred in the gas phase because in the liquid state the P* radical can not only reduce Ca^{++} to Ca^+, but also reduce Ca^+ to the Ca atom before emitting the $h\upsilon$ photon.

Whether the Ca emission is occurring in the liquid state may be deduced by the broadening of the spectral lines, not by the position of peak lines itself. In the hot spot theory, the high pressures that accommodate the high bubble temperatures in non-condensable gases are required to explain the broadened spectral lines. But in cavity QED induced EM radiation, the bubble is filled only liquid vapor at ambient temperature, and therefore pressure

broadening is insignificant. Instead, the SL spectra in ethylene glycol are naturally broadened because the SL emission is quenched by the liquid state.

Nature of the Continuum

In the hot spot theory, the discrete atomic lines and molecular bands in the SL spectra are well understood, but the nature of the underlying continuum in both SBSL and MBSL remains a mystery. The SL continuum has been thought [37] caused by confined electrons, blackbody radiation, electrical discharge, and emission from small molecules formed during the cavitation event. Current thought excludes plasma emission while claiming the continuum is produced by molecular excitations.

But a molecular continuum finds difficulty in explaining the almost continuous SL spectra found in the liquids. The molecular bands in the liquid would have to be continuously distributed from the IR through the visible to the VUV – a non-physical constraint on any molecular liquid. In cavity QED induced EM radiation, the SL light is produced from the near IR to the far VUV without any need to invoke the molecular continuum.

5.4 SL in Cryogenic Liquids

SL under Ultrasound

SL in cryogens by bubble nucleation and collapse under ultrasonic irradiation was first studied [38] in liquid helium at 1.8 K. Although the upper limit to the size of the bubbles was about 30 μm, the SL light intensity was found to be less than 10^{-4} of that from a comparable size SBSL bubble in water at 300 K. Cavity QED induced EM radiation explains the lower SL response in liquid helium to be primarily due the fact that liquid helium at 1.8 K has only 1.8/300 ~ 0.006 of the thermal kT energy available for suppression.

Laser SL

In 1979, SL was initiated [39] in liquid nitrogen (LN) by lasers. The process called laser SL focuses a laser in a container of pressurized LN. Upon absorption by impurities, the laser pulse vaporizes the LN to produce a vapor bubble that expands against the surrounding LN. After the bubble expands to the maximum radius R, the vapor promptly condenses with SL observed in the bubble collapse. It was found the LN required pressurization of a few atmospheres for SL to be observed. Estimates of the temperature in the cavity by adiabatic compression of the vapor were less than 1000 K, and therefore the high bubble temperature by the hot spot theory [4] was considered an unlikely explanation of laser SL.

Later in 1998, laser SL observed [40] in LN was found characterized by pulse widths of order 100-1000 ns. This is significant, as the pulse width for SBSL bubbles in water is of order 300 ps. In 2001, laser SL experiments in LN confirmed [41] the long pulse widths. Surprisingly, the OH* molecular band at 310 nm was observed for bubbles having a radius greater than 1000 μm, most likely because of impurities. Moreover, the SL intensity in laser SL was characterized by an integrated SL intensity more than 3 orders of magnitude greater than the single source of SBSL in water suggesting multiple sources in the LN bubble region.

In cavity QED induced EM radiation, laser SL in [38-41] is explained by the compression of microscopic voids formed during the condensation of LN. Prior to collapse, the pressure in the bubble balances the LN pressure. The bubble vapor temperature although initially hot, promptly cools to LN temperature thereby lowering the bubble vapor pressure causing the bubble wall to collapse. Because of the heterogeneity in condensation, the

condensed LN may be characterized by a bubble region of spherical shape containing voids distinct from the surrounding bulk LN.

For the purposes here, the spherical LN bubble region is considered to have a condensation radius Rc that corresponds to the mass of LN vapor in the bubble at maximum radius R. But the inertia of the collapsing bubble wall compresses the bubble region of radius Rc and reduces the size of the microscopic voids. Once the void size reaches nanoscale dimensions, say less than 20 nm, SL light is emitted spontaneously as cavity QED induced EM radiation. Depending on the homogeneity of the LN in the condensation process, voids may exist anywhere in the bubble region, and therefore SL light may be emitted at multiple locations. Since the bubble region is mostly LN, the SL pulse width may be estimated by the time τ it takes for a sound wave in LN to travel at velocity Vs from the surface of the bubble region at radius Rc to the center, and then back to the surface,

$$\tau \sim \frac{2Rc}{Vs} \qquad (21)$$

where,

$$Rc = R\left(\frac{PM}{\rho R_G T}\right)^{\frac{1}{3}}$$

where, Vs is the sound velocity in LN, R is the maximum bubble radius, P is pressure of the LN and bubble vapor, M is the molecular weight of nitrogen vapor, ρ is the density of LN, R_G is the gas constant, and T is the absolute temperature of the vapor.

Numerically, $\rho = 807$ kg/m^3 and Vs = 869 ms^{-1} at T = 66 K. Fig. 14 shows the pulse width τ versus the bubble radius R for pressures P = 6 and 12 bar in relation to the best fit of the experimental (Fig. 7 of [41]) data. Thus, cavity QED induced EM radiation is consistent with the pulse width in LN that is linear with the maximum bubble radius R.
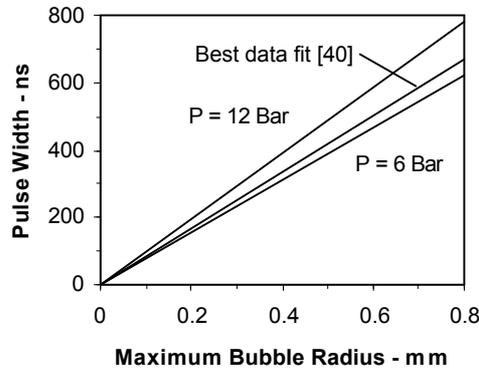

Fig. 14. Laser induced SL in LN – Pulse Width and Bubble Radius

In SBSL bubbles, only the water vapor at ambient temperature is present in the bubbles. At 20 C, the vapor pressure is about 2440 Pa in bubbles of radius about 30 μm having a condensation radius R ~ 0.78 μm. By cavity QED induced EM radiation, SBSL in water is produced with voids having radii < 20 nm, and therefore a single source of SL light is expected for SBSL. But the bubbles in LN by laser SL have a radius of about 1000 μm and a vapor pressure in excess of a few bars have respective condensation radii Rc ~ 200 to 300 μm, and as such are likely to have multiple sources. But the SL emission spot is likely to be concentrated over a smaller area. Indeed, observations in laser SL shows a near spherical emission spots of 70 μm, or radius of ~ 35 μm.

6. SL Criterion

In cavity QED induced EM radiation, the crucial SL parameter in *any* liquid is the minimum bubble radius R_{min}. For SL to be observed, $R < R_{min}$, where $R_{min} \sim 20$ nm. Indeed, R_{min} is more than one order of magnitude smaller than the hard core radius $R_C \sim 0.8$ μm of non-condensable bubble gases usually assumed in SL. But the collapsed bubble need not have a radius $R > R_C$ because vapor bubbles only have traces of non-condensable gases. Although R_{min} may be difficult to verify, it is unequivocal that all vapor bubbles collapse to the spacing Δ between molecules at liquid density. Since $R_{min} > \Delta$, the criterion that $R < R_{min}$ for SL to be observed is reasonable even though experimental proof of R_{min} from 20 kHz to 1 MHz is lacking. Conversely if $R > R_{min}$, SL by cavity QED induced EM radiation is not observed.

7. Summary and Discussion

➤ The chemical excitation of atoms and molecules in the bubble walls at ambient temperature by cavity QED induced EM radiation explains both SBSL and MBSL as the consequence of the underlying cavity QED physics – suppressed IR radiation from atoms in the bubble surface is frequency up-converted to coherent VUV radiation, the VUV forming radicals that by chemical reaction with dissolved species produce the observed SL.

➤ In water, cavity QED induced EM radiation is a continuous IR to VUV excitation source that produces both the SL spectrum of a broadband continuum from the near IR to the VUV and superposed atomic lines and molecular bands of dissolved gases, or the liquid itself. The OH* spectral lines are produced by VUV excitation of Ar atoms that by three body reaction with water neighbors form Ar.OH* excimers. Indeed, OH* spectral lines are not produced absent Ar atoms.

➤ The broadband SL continuum is not produced by excited states of the atoms and molecules, but rather directly from cavity QED induced EM radiation. This is substantiated by the experimental fact that non-volatile SL quenchers only present in the liquid state do not affect the SL continuum. Additives that increase the absorption of water reduce the number of atoms in the penetration depth of the EM waves standing across the bubble, and therefore the SL continuum is reduced because the suppressed IR radiation is similarly reduced.

➤ The recent 'Nature' article [27] reported the finding of excited atomic argon and oxygen ion states in the SL spectra from argon saturated sulfuric acid. The finding is significant in that the excited states have not been previously observed. But the interpretation of this finding is that the SL light is caused by high temperature plasma from the compression heating of bubble vapor. Extensions to the 18 eV necessary to excite the oxygen ion suggests plasma temperatures of ~ 200,000 degrees. However, the high temperature plasma relied upon to explain the SL light is precluded by Le Chatelier's principle that requires the vapor to condense to liquid without an increase in temperature. Thus, the bubble collapses near ambient temperature – not at 200,000 degrees!!!

➤ Cavity QED induced EM radiation featuring variable frequency lasing produces high energy VUV photons to 20 eV and finds utility by producing photons, electrons, and ions at ambient temperature, the embodiments of which are protected by US patent pending.

➤ In the solid state, cavity QED induced EM radiation has explained static electricity [42], the Casimir effect [43], and thermophotovoltaics [44]. The QED cavities are not 3-D

spherical or near spherical bubbles as in liquids, but rather evacuated 1-D gaps between solid surfaces. But the QED physics remains the same – the EM energy loss from the suppression of IR radiation from atoms in the surfaces is conserved by the gain in VUV radiation at the resonant frequency of the gap - the VUV radiation producing: electrons by the photoelectric effect in static electricity, the electrostatic attractive force in the Casimir effect, and the electrical photocell current in the thermophotovoltaic effect.

➤ In SL from the liquid state, ultrasound is commonly used to repetitively nucleate and collapse bubbles. But what is called SL from liquids need not be initiated by ultrasound. SL light can be produced from any pressure fluctuation that induces hydrostatic tension in a liquid, even in a single nucleation and collapse event. Provided the bubbles collapse to, or nucleate from a radius $R < R_{min}$ the effects of acoustic energy and ultrasound frequency in SL bubbles are not of primary importance in producing the observed light.

➤ Unlike collapse, bubble nucleation requires hydrostatic tension to overcome surface tension. Typically, the smallest bubble that nucleates in water is about 3 microns in diameter, thereby precluding the formation of nanobubbles less than 100 nm. Recent observations [45] of nanobubbles in equilibrium on hydrophobic surfaces do not mean that nanobubbles are formed in the bulk because the bubbles may nucleate on solid nanoparticles. If so, the solid particle would quench the SL. Momentary nanobubbles absent nanoparticles that form in the non-equilibrium process of nucleating the 3 micron-sized bubbles are likely to produce VUV radiation that can electrify the liquid. In flow electrification, nanobubbles are proposed [46] as a likely source of VUV radiation, the VUV radiation producing electrons by the photoelectric effect or photons by photoluminescence.

➤ In thunderstorms, the electrification of the atmosphere is proposed to occur from the charge produced in the nucleation of nanobubbles in the volume expansion of supercooled particles in combination with the charge produced by collisions of upward moving supercooled particles and downward moving all-ice particles. Both sources of charge may be explained by the Planck energy formed by cavity QED induced EM radiation that dissociates water molecules into hydronium and hydroxyl ions that electrify the atmosphere.

➤ SL is produced from thermal kT energy extracted from the atoms in the penetration depth by the suppression of IR radiation. Effectively, the atom temperatures are lowered to absolute zero, and therefore the atoms are required to recover ambient temperature prior to the suppression of IR in the next cycle. To do this, water at ambient temperature is pumped to replace the water in the penetration depth. In effect, pump work raises the atom temperatures from absolute zero to ambient, and therefore the 2nd law of thermodynamics is not violated in SL by cavity QED induced EM radiation.

➤ Artificial light from solid state devices differs from SL under ultrasound in that the steady flow of heat replaces the cyclic flow of water. Since work is not provided, it might be thought the 2nd law of thermodynamics is violated. But this is not true. The time for the atoms in the penetration depth to recover ambient temperature is long in relation to the time for IR radiation to be suppressed, and therefore the atom temperatures tend to absolute zero. Heat from the ambient continues to flow into the penetration depth, but the temperature cannot increase because of cavity QED. Thus, EM energy can only be conserved by the spontaneous conversion of heat to VUV radiation that produces visible light by photoluminescence. Thus, the artificial light does not violate the 2nd law.

References

[1]   R. E. Verral and C. M. Segdal, "Sonoluminescence in *Ultrasound: Its Chemical, Physical and Biological Effects* (ed. K. S. Suslick), New York, 227, 1988.

[2]   R. A. Hiller, S. J. Putterman, and K. R. Wenninger, "Time-resolved spectra of sonoluminescence," *Phys. Rev. Lett.*, 80, 1182, 1998.

[3]   B. Gompf, R. Gunther, G. Nick, R. Pecha, and W. Eisenmenger, "Resolving sonoluminescence pulse widths with single photon counting," *Phys. Rev. Lett.*, 79,105, 1997.

[4]   B. E. Noltingk and E. A. Neppiras, "Cavitation produced by ultrasonics," *Proc. Phys. Soc. B,* 63, 674-685, 1950.

[5]   S. Hilgenfeldt, S. Grossman, and D. Lohse, "A simple explanation of light emission in a sonoluminescencing bubble," *Nature*, 398, 402, 1999.

[6]   D. Lohse and S. Hilgenfeldt, "Inert gas accumulation in sonoluminescing bubbles," *J. Chem. Phys.*,107, 6986, 1997.

[7]   Y. T. Didenko, W.R. McNamara III, and K.S. Suslick, "Molecular emission from single-bubble sonoluminescence," *Nature*, 407, 877, 19 October 2000.

[8]   T. V. Prevenslik, "The paradigm of high temperatures in a collapsing bubble and sonoluminescence, sonochemistry, and D-D fusion," presented at Fifth biennial SSE European meeting, University of Amsterdam, October 2000. Unpublished.

[9]   T. V. Prevenslik, "The cavitation induced Becquerel effect and the hot spot theory of sonoluminescence," *Ultrasonics*, 41, 312, 2003.

[10]   P. Gajewski, A. Kulicki, A. Wisnewski, and A. Zgorzelski, "Kinetic theory approach to the vapor-phase phenomena in a nonequilibrim condensation process," *Phys. Fluids* 17, 321-27, 1974.

[11]   C. E. Brennen, *Cavitation and Bubble Dynamics*, Oxford University Press, 1995.

[12]   L. A. Crum, "Bubbles hotter than the sun," *New Scientist*, 36-40, 1995.

[13]   M. P. Brenner, S. Hilgenfeldt, and D.Lohse, "Single-bubble sonoluminescence," *Reviews of Modern Physics*, 74, 425-452, 2002.

[14]   M. A. Margulis, *Sonochemistry and Cavitation*, Gordon & Breach, 1995.

[15]   L. A. Crum, "Sonoluminescence and Acoustic Inertial Confinement Fusion," Fifth International Symposium on Cavitation, Osaka, Japan, 1-4 November 2003.

[16]   R. W. Christy and A. Pytte, *The Structure of Matter*: *Introduction to Modern Physics*, Benjamin, New York, 1965.

[17]   S. Harouche and J-M Raimond, "Cavity Quantum Electrodynamics," *Scientific American*, 54, April 1993.

[18]   R. van Zee, *Cavity-Enhanced Spectroscopies – Spontaneous Emission in a Microsphere: Cavity QED*, Vol. 40 in *Experimental Methods in the Physical Sciences* – Edited by: R. Celotta and T. Lucatorto, Academic Press, 2002.

[19]   E. N. Harvey, "Sonoluminescence and Sonic Chemiluminescence," *J. Am. Chem. Soc.*, 61, 2392, 1939.

[20]   M. Makino, M. M. Mossoba, and P. Riesz, "Formation of .OH and .H in aqueous solutions by ultrasound using clinical equipment," *J. Phys. Chem.*, 91, 3654, 1983.

[21]   K. S. Suslick, J. J. Gawienowski, P. F. Schubert, and H. H. Wang, "Alkane Sonochemistry," *J. Phys. Chem.*, 87, 2299, 1983.

[22]   E. B. Flint and K.S. Suslick, "Sonoluminescence from Alkali-Metal Salt Solutions," *J. Phys. Chem.*, 95, 1484-88, 1991.

[23]   Y. T. Didenko, S. P. Pugach, and T. V. Gordychuk, "Sonoluminescence Spectra of Water: Effect of Ultrasonic Irradiation Power," *Optics and Spectroscopy*, 80, 821-826, 1996.

[24]   R. T. Hiller, K. Wenninger, S. J. Putterman, and B.P. Barber, "Effect of noble gas doping on single bubble sonoluminescence," *Science*, 266, 248-250, 1997.

[25]   T. Le Pointe, et al., "Observation of 'Ar-HO' van der Waals molecules in multibubble sonoluminescence," Ultrasonics International 2001, T. U. of Delft, 2-5 July 2001.

[26] D. J. Segelstein, "The complex refractive index of water," MS Thesis, University of Missouri, Kansas City, 1981.

[27] D. J. Flannigan and K. S. Suslick, "Plasma formation and temperature measurement during single-bubble cavitation," *Nature*, Vol. 434, 52-55, 2005.

[28] Y. T. Didenko and T. V. Gordychuk, "Multibubble Sonoluminescence Spectra of Water which Resemble Single-Bubble Sonoluminescence," *Phys. Rev. Lett.*, 84, 5640, 2000.

[29] Y. T. Didenko and S. P. Pugach, "Spectra of Sonoluminescence," *J. Phys. Chem.*, 98, 9742-49, 1994.

[30] M. Link, R. Mehnert, and L. Prager, "Design and Performance Characteristics of Windowless Argon Source," 5th Inter. Symposium on Ionizing Radiation and Polymers, 21- 26, September, 2002.

[31] Putterman, "Sonoluminescence: Sound into light," *Scientific American*, Feb.1995.

[32] J. B. Young, J. A. Nelson, and W. Kang, "Line Emission in Single-Bubble Sonoluminescence," *Phys. Rev. Lett.*, 86, 2673-2676, 2001.

[33] E. B. Flint and K. S. Suslick, "Sonoluminescence from Nonaqueous Liquids: Emission from Small Molecules," *J. Am. Chem. Soc.*, 111, 6987-92, 1989.

[34] M. A. Margulis and A. F. Dmitrieva, "Processes of sonoluminescence quenching by various additives," *Russ. J. Phys. Chem.*, 66, 751, 1992.

[35] C. Sehgal, R. P. Steer, R. G. Sutherland, and R. E. Verrall, "Sonoluminescence of Aqueous Solutions," *J. Phys. Chem.*, 81, 2618, 1977.

[36] V. H. Arakeri, "Sonoluminescence from Metal Salt Solutions," Fifth International Symposium on Cavitation, Osaka, Japan, 1-4 November 2003.

[37] W. B. McNamara III, Y. T. Didenko, and K. S. Suslick, "The Nature of the Continuum in Multibubble Sonoluminescence," *J. Am. Chem. Soc.*, 122, 8563, 2000.

[38] P. Jarman and K. Taylor, "The sonically induced cavitation of liquid helium,", *J. Low Temp. Phys.* 2, 389, 1970.

[39] P. I. Golubnichi, P. I. Dyadyushkin, G. S. Kaluzhnyi, and S. D. Korchikov, "Laser sonoluminescence in liquid nitrogen", *Sov. Tech. Tech. Phys.*, 24 (8) August 1979.

[40] O. Baghdassarian, B. Tabbert, and G. A. Williams, "Luminescence from laser-created bubble in cryogenic liquids," *Physica B*, 284-288, 392-394, 2000.

[41] O. Baghdassarian, H. C. Chu, B. Tabbert,and G. A. Williams, "Spectrum of Luminescence from Laser-Induced Bubbles in Water, and Cryogenic Liquids," CAV2001: Fourth International Symposium on Cavitation, California Institute of Technology, 20-31 June 2001.

[42] T. V. Prevenslik, "Cavity QED Induced Photoelectric Effect," *Proceedings ESA-IEJ Meeting*, Northwestern University, 230-40, 25-28 June 2002.

[43] T. V. Prevenslik, "The Casimir force – neutral or electrostatic?", 4th French Electrostatics Society Congress, Poitiers, 2-3 September 2004.

[44] T. V. Prevenslik, "The cavity QED induced thermophotovoltaic effect", 14th Inter. Photovoltaic Sci. & Eng. Conf., PVSEC-14, Bangkok, 27 Jan.-1 Feb.,2004.

[45] J. W. G. Tyrrell and P. Attard, "Images of Nanobubbles on Hydrophobic Surfaces and their Interaction," *Phys. Rev. Lett.*, 87, 176104, 2001.

[46] T. V. Prevenslik, "Flow electrification in micro porous filters," 5th International EHD Workshop, Poitiers, 30-31 August 2004.

[47] R. Hiller, S. J. Putterman, and B. P. Barber, "Spectrum of Picosecond Sonoluminescence," *Phys. Rev. Lett.*, 69, 1182-84, 1992.

Appendix A
Ambient Temperature Energy Source

Beyond SL, passive solid state devices that simulate cavity QED induced EM radiation might find utility by providing artificial lighting powered by IR radiation at ambient temperature. Typically, processed silica structures[2] having a large number of irregular voids are proposed as sources of visible light that might prove competitive with lighting powered by conventional sources of electricity. A hollow spherical structure representing one of a plurality of irregular shaped voids in the structure is depicted in Fig. A-1.
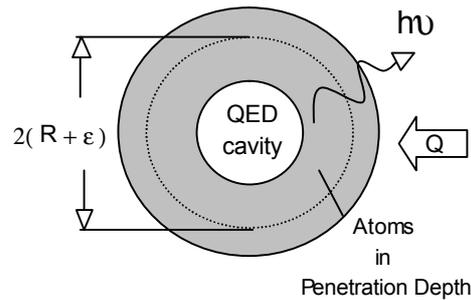

Fig. A-1
Artificial Light Source

Only IR radiation from thermal kT energy at ambient temperature is proposed to power the light source. For ($R + 0.5\varepsilon$) ~ 63.5 nm, the average wavelength λ ~ 4($R + 0.5\varepsilon$) ~ 254 nm. Thus, in the penetration depth ε, the average EM radiation is in the VUV. The VUV radiation then excites the silica[3] to produce red light. Processed structures having QED cavities with a random distribution of wavelengths $\lambda < 254$ nm produces white light. By extracting heat Q continuously from the environment, the ambient light source claims to produce a never ending supply of light !!

What about the 2nd law of thermodynamics?

SL in water under ultrasound

SL is produced from the VUV radiation induced by cavity QED by the suppression of IR radiation at ambient temperature from atoms in the penetration depth of the VUV radiation standing across the QED cavity every ultrasonic cycle. The thermodynamic diagram is illustrated in Fig. A-2(a). VUV radiation is produced by the suppression of IR radiation from the thermal kT energy of the atoms in the penetration depth. But suppression of IR radiation tends to reduce the atom temperatures to absolute zero, and therefore the atoms must be returned to ambient temperature prior to production of VUV radiation in the next ultrasonic cycle. In SL, the water in the penetration depth is recycled by the flow of water at ambient temperature. Since work W is expended to pump the water, SL by cavity QED induced EM radiation does not violate the 2nd law.

$$VUV = kT - W$$

---

[2] A. Colder, et al., "Strong visible photoluminescence from hollow silica nanoparticles," *Nanotechnology* 15, L1-L4, 2004.
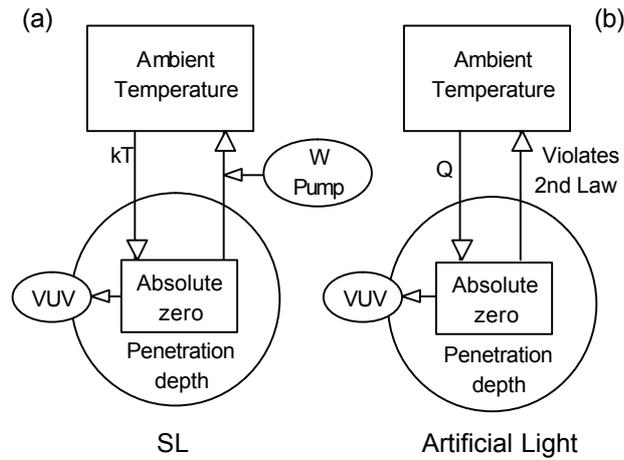[3] *Ibid.*

Fig. A-2
Cavity QED induced EM radiation
Thermodynamic Diagrams – (a) SL and (b) Artificial Light Source

Artificial light source

The thermodynamic diagram of the artificial light source is shown in Fig. A-2(b). In the solid state, the temperature of the atoms in the penetration depth is recovered by conductive heat Q through the thin walled hollow structure because of the temperature difference between the outer and inner surfaces at ambient T_{amb} and near absolute T_o temperatures,

$$Q = \frac{KA}{t^*}\left(T_{amb} - T_o\right)$$

where, K is thermal conductivity, A is area, and t* is a fraction of the wall thickness. But the thermal response of the atoms in the penetration depth takes time; whereas, the IR radiation is instantaneously suppressed by cavity QED. Thus, the heat Q is removed as soon as it flows into the penetration depth, and therefore the atom temperatures tend to absolute zero. Without expending work W to raise the temperature of the atoms to ambient, it might be thought the ambient light source violates the 2nd law.

But this is not true. Heat Q continues to flow into the penetration depth, but cavity QED precludes any increase in temperature. Moreover, the heat Q cannot escape from the penetration depth to the ambient because this would violate the 2nd law by a flow of heat from cold to hot temperatures. Thus, the only path available to conserve the 1st law is for the heat Q to undergo spontaneous conversion to VUV radiation,

$$VUV = Q$$

By making the wall thickness t of the hollow structures small, the heat flow Q converted to VUV radiation can be significant compared to SL which is limited to the thermal kT energy available to the atoms in the penetration depth.

26