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Biological Effects of Ultrasonic Cavitation

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Abstract

Cavitation energy in a nearly evacuated bubble is shown to *not likely* reside in the thermal state of the water molecule. In a spherical bubble compression and until the bubble assumes a pancake collapse shape, a temperature increase does not occur in the bubble gas because the mean free path likely exceeds the bubble diameter. The subsequent collapse of the pancake shape to liquid density occurs with only a negligible volume change so that the temperature increase for compression heating of bubble gases is insignificant. Even near liquid density, a temperature increase does not occur as the energy transfer by molecular collisions is in the adiabatic limit for both vibrational and rotational modes. Instead, the IR radiation energy density present within the bubble is increased as required to satisfy standing wave boundary conditions with the bubble walls in the direction of collapse. For biological tissue in an opaque environment, bubble collapse is found to increase the 5-10 μm IR thermal radiation at ambient temperature to about 3-5 eV that is capable of dissociating the water molecule and forming the chemically reactive hydroxyl radical. Hence, the biological effects of ultrasonic cavitation are proposed to be caused by the chemical reaction of the organisms with the excited electronic states of dissolved oxygen and water molecules.

1. Introduction

Currently, the biological effects of ultrasonic cavitation[1-2] observed in water based systems are thought to be caused by high bubble gas temperatures postulated during cavitation that form reactive hydrogen and hydroxyl radicals. Subsequent disintegration of biological molecules occurs by chemical reaction or simply by the mechanical stresses of cavitation.

In this paper, the biological effect of ultrasonic cavitation is proposed to be of a quantum mechanical origin and is quite different from the current interpretation in that the bubble collapse occurs without a significant change in bubble gas temperature.

2. Theoretical Background

The biological effects of ultrasonic cavitation are presented for the nearly evacuated bubble prior to collapse that is filled solely with the vapor pressure of the water surroundings at ambient temperature, but may include trace amounts of dissolved gases. The cavitation of bubbles filled with external gases at atmospheric pressure bubbled through water in excess of saturation is similar in that bubble expansion tends to evacuate the bubble by cryogenic condensation prior to collapse.

Pancake Collapse Geometry

Bubble collapse is an unstable process following a minimum energy path. Since the collapse of a spherical bubble follows a path of maximum energy, a spherical collapse shape is an unlikely event during ultrasonic cavitation. Instead, a pancake-like shape of characteristic dimension δ following a minimum energy path is likely as illustrated in Figure 1.

If the initial bubble pressure is near atmospheric pressure, say by bubbling gases through the water, bubble expansion cools the gas molecules to cryogenic temperatures and tends to evacuate the bubble by condensation before collapse. The bubble *may be* initially spherical , but eventually is required to assume a pancake shape. Since the change in volume of a pancake collapse is negligible, a temperature increase by compression heating of the bubble gases is insignificant. A temperature increase, if any, may only occur over the time the volume changes and the bubble remains in an almost *exactly* spherical unstable state. In contrast, if the bubble initially is nearly evacuated before expansion, say filled with water vapor and only trace amounts of external gases, the bubble shape is unstable and likely pancake-like even prior to collapse so a temperature change during collapse is very unlikely.

Collision Induced Energy Change in a Nearly Evacuated Bubble

A bubble nucleated in water based biological tissue at temperature may be considered nearly evacuated as the vapor pressure is much less than atmospheric pressure. During bubble compression, changes in the thermal energy state of the water molecule depend on intermolecular collisions and may be quantified by the mean free path mfp in relation to the bubble radius $D_o / 2$ prior to collapse ,

$$mfp = \frac{\sqrt{2}K_b T_{vapor}}{2P_{vapor}d^2} \tag{1}$$

where, P_{vapor} , T_{vapor} are the water vapor pressure and temperature and K_b is Boltzmann's constant.

The condition for a change in the thermal state is the likelihood of intermolecular collisions within the bubble where $mfp < D_o / 2$. Conversely, if $mfp > D_o / 2$, a change in the thermal state of gas molecules within the bubble is unlikely as the molecules are likely to be found in the walls of the bubble. Since photon emission is only known to occur from excited electronic states of the water molecule, photon emission is favored if a thermal state does not change, $mfp > D_o / 2$. Based on the vapor properties of water[3], the mfp of the water molecule from 0 to 40 C for $d = 0.3$ nm is shown in relation to bubble radius in Figure 2. At 20 C, the $mfp = 13.5$ μm. The mfp is observed to decrease and increase above and below 20 C. This means photon emission is favored at low temperatures.

In sonoluminescence, the observed[4] increase in photons at low ambient temperatures is also consistent with the dependence of photon emission on the mfp and the bubble radius $D_o / 2$. Schwinger commented[5] that the temperature independent Casimer model found difficulty in explaining the remarkable increase in photons as the temperature of liquid water nears the freezing point. However, an abrupt increase in photon emission is expected as the temperature is lowered. From Figure 2, in a nearly evacuated bubble the mfp ~ 50 and 13.5 μm at 0 and 20 C. Since the bubble radius cited in Schwinger's comment was 40 μm, and since $mfp >$ 40 μm, photon emission is favored at 0 C. In contrast, $mfp <$ 40 μm and a temperature change is favored at 20 C.

Collision Induced Energy Change Near liquid Density

As the liquid water walls of the bubble collide, the water molecule temperatures may increase by molecular collisions. The likelihood of temperature changes in the water molecule may be estimated[6] from the vibrational and rotational adiabaticity parameters ξ_v , ξ_r that provides a measure of the efficiency of the kinetic energy transfer in the collision,

$$\xi_v = \frac{t_c}{t_v} \quad \text{and} \quad \xi_r = \frac{t_c}{t_r} \tag{2}$$

where, t_c is the duration of the collision and t_v, t_r is the vibrational and rotational period of the water molecule. The collision time $t_c \sim a / V_{rel}$ where a is the range of intermolecular forces and V_{rel} is the relative velocity in the collision. At liquid water density, the range of intermolecular forces is of the order of the molecular spacing, $a \sim 0.3$ nm . For a pancake collapse at sonic velocity from both sides, $V_{rel} = 2\, V_{sonic}$, $t_c \sim a / 2\, V_{sonic}$. For water, $V_{sonic} \sim 1460$ m/s and $t_c \sim 0.1$ ps.

The vibrational period may be estimated from Planck's relation, $t_v \sim h / \Delta E_v$ where ΔE_v is energy level spacing and h is Planck's constant. For the observed[4] VIS energetics of the water molecule, $\Delta E_v > \sim 1$ eV and $t_v \sim 0.004$ ps. Hence, $\xi_v \sim 250 \gg 1$ and the molecular collision for the vibrational mode is in the adiabatic limit with very inefficient energy transfer. Usually, rotational energy transfer is efficient at ambient temperature because the energy level spacings ΔE_r are about 3 orders of magnitude smaller than ΔE_v for vibration, so $t_r \sim 1000\, t_v$ and $\xi_r \sim 0.25 < 1$. However, at liquid density in the close packed spacing of neighbor molecules, the water molecule is restrained from rotation, so that t_c is large and $\xi_r \gg 1$, or the rotational mode is also in the adiabatic limit. Hence, temperature changes are not expected as the bubble walls collide at liquid density .

Electronic Excitation Mechanism

The Doppler effect that increases the radiation energy density within the bubble from the IR to the UV as the bubble dimension δ vanishes during collapse is proposed as the mechanism to excite the electronic state of the water molecule to explain the biological effects in ultrasonic cavitation. Wien in formulating the displacement law[7] derived the relation between radiation wavelength and cavity size based on the Doppler shift from the collapse of a perfectly reflecting sphere. In the limit $\delta \rightarrow 0$, bubble collapse may increase IR radiation to soft X-rays.

The IR energy of the liquid surrounding the bubble of dimension δ_o is given by $E_o = hc/2\delta_o$, where $\delta_o = \lambda_o/2$ as required to satisfy the half wave boundary conditions with the bubble walls. At any instant of bubble collapse, the dimension $\delta < \delta_o$ requires an increase in the Planck energy $E > E_o$. Hence, bubble collapse serves as means of increasing the IR energy density. The unavailability of the thermal state is important. If the thermal state is available, energy is converted to a temperature increase instead of Planck energy.

A continuum of Doppler excitation frequencies from the IR to the X-ray limit may are generated as the bubble collapses. The dissociation of the water molecule to hydroxyl radicals requires the breaking of chemical bonds at about 5 eV and the oxygen singlet state may be excited from water molecule or dissolved oxygen at about 10 eV. The photon emission for noble gases is greater than for diatomic oxygen and triatomic water molecules because bonds are not present to quench the increase in the electronic state of the photo electrons. If the Doppler frequency does not match one of the excited states of the water molecule, the radiation is Rayleigh scattered elastically back throughout the bubble cavity. The energy required to excite the entrained bubble gas molecules follows Planck's law, $E = h\upsilon$, where, υ = excitation frequency of the respective electronic state.

Doppler Effect on Radiation Wavelength and Pulse Measurement

The Doppler effect for the relation of the bubble dimension δ to the wavelength λ of the radiation within the bubble cavity follows the Richtmyer[8] analogy for the adiabatic expansion and compression of blackbody radiation trapped between a piston and cylinder. For a pancake bubble of dimension δ collapsing at a velocity V, the average of the rate of change of the wavelength in the bubble cavity,

$$\left\langle \frac{d\lambda}{dt} \right\rangle = \frac{\lambda}{3\delta}\frac{d\delta}{dt} \tag{3}$$

Integrating from the nucleated bubble dimension δ_o and wavelength λ_o, the Doppler shifted wavelength λ is,

$$\lambda = \lambda_o \sqrt[3]{\frac{\delta}{\delta_o}} \tag{4}$$

Generally, the radiation may fill the bubble cavity with m modes of half wavelength $\lambda_o / 2$ where $m \geq 1$. Now, a wavelength change is negligible for large m where $\delta_o >> \lambda_o$. Only for $m = 1$ and specifically for $\delta_o > \delta > \delta_c$ is the wavelength change significant. Hence, the bubble gas molecules are excited by a blue shifted wavelength λ relative the IR bubble wavelength λ_o as the dimension $\delta \rightarrow \delta_c$.

The pancake collapse time $t_{collapse}$ provides an estimate of the pulse duration over which the Planck energy is concentrated and depends on how rapidly the wavelength changes as the bubble walls collapse, $t_{collapse} > \delta / 2\ V_{sonic}$. For a photon detector with a range between 230 and 600 nm, the dimension $\delta \sim 370/2 \sim 185$ nm gives $t_{collapse} \sim 60$ ps and is consistent with the 50 ps observed[4].

Planck Energy and Work in Compressing Radiation Pressure

During cavitation, the radiation energy density ψ in the bubble during collapse is increased from the energy density ψ_o in the bubble before collapse. The Planck energies before and during collapse, E_o, E are,

$$E_o = A_o\, \delta_o \psi_o \text{ and } E = A\, \delta\, \psi \tag{5}$$

where, A_o, A are the areas orthogonal to the collapse direction and δ_o, δ are the bubble dimensions. Since the radiation pressure $p = \psi / 3$, the work done by the liquid walls to compress the radiation wavelength is $pdV_{vol} = -\ 1/3\ A\psi\ d\delta$. For a pancake collapse, $A \sim A_o$ and $A\ d(\delta \psi) = A\ (\psi d\delta + \delta\ d\psi)$. Hence, $d\psi / \psi = -4/3\ d\delta / \delta$ and $\psi / \psi_o = (\delta_o / \delta)^{4/3}$. Substituting in (5) gives $E = A\psi_o\, (\delta_o / \delta)^{4/3} = E_o A/A_o\, (\delta_o / \delta)^{1/3}$. For $A \sim A_o$, $E = E_o (\delta_o / \delta)^{1/3}$ and since $E_o = hc / \lambda_o$,

$$E = \frac{hc}{\lambda_o \sqrt[3]{\dfrac{\delta}{\delta_o}}} = \frac{hc}{\sqrt[3]{2\delta\lambda_o^{\ 2}}} \tag{6}$$

The Planck energy E as a function of the collapse dimension δ_c for various wavelengths λ_o of energy in the bubble cavity are shown in Figure 3.

Biological Surroundings Opaque to UV-VIS

For biological tissue in an environment opaque to UV-VIS, the bubble energy available for collapse depends solely on the IR thermal radiation of the water surroundings. At a blackbody temperature of 293 K, the maximum IR energy occurs at $\lambda_o \cong 9.86\ \mu$m with a half wavelength corresponding to a nucleated bubble dimension $\delta_o \cong 5\ \mu$m. For a liquid density collapse $\delta_c \sim 0.31$ nm, the Planck energy is about 3.15 eV corresponding to a blue photon at about 390 nm. Although the IR energy at 5 μm is only 20% of that at 9.86 μm, the Planck energy is higher at about 5 eV corresponding to bactericidal UV at 250 nm.

Biological Surroundings Transparent to UV-VIS

If the organisms are isolated and placed in liquid water transparent to UV-VIS radiation, the Planck energy may be enhanced if the bubbles in the water are filled with UV-VIS photons. The bubbles are assumed to be filled with UV-VIS radiation at wavelength $\lambda_o = 2\delta_o$, say from external light sources. For UV irradiation at 200 nm, the Planck energy for a liquid density collapse is about 42 eV corresponding to XUV at about 30 nm.

3. Summary and Conclusions

The bubble collapse during the ultrasonic cavitation of water based systems most likely takes the shape of a pancake without a temperature change. A spherical bubble collapse produces high gas temperatures, but is an unlikely event.

The IR thermal energy at ambient temperature is increased to UV-VIS levels because the energy density trapped within the bubble is increased as the dimension in the pancake direction vanishes. The VIS blue light at about 390 nm observed in sonoluminescence is explained by the liquid density collapse of IR energy at 9.86 μm. However, 20 % of the IR energy is converted to bactericidal UV at about 250 nm. The VIS-UV energy pulse duration for a photon detector sensitive to from 600 nm VIS to 230 nm UV is on the order of 60 ps and may be longer if the IR above 600 nm is detected as well .

It is possible, at least in principle, to envision ultrasonic cavitation as a means of converting externally supplied UV radiation energy at 200 nm to XUV.

The energy amplification in ultrasonic cavitation from the IR at 9.86 μm to a blue photon in the VIS at 390 nm is about 25:1.

A dramatic increase in photons is predicted as the ambient temperature approaches the freezing point of water if the mean free path of the bubble gases exceeds the bubble radius after bubble expansion and prior to collapse.

There is no need to postulate high temperatures during bubble collapse to explain the biological effects of ultrasonic cavitation. For water in opaque biological tissue, near UV radiation is predicted at about 3-5 eV and is sufficient to form hydroxyl radicals. If the biological organisms are placed in a water solution irradiated with 200 nm UV, XUV capable of significant biological effects state are predicted.

An experimental program is underway to test the effects of UV enhanced ultrasound on E-coli and cholera. The latter are of significance for cleansing of water tanks holding live fish for human consumption in Hong Kong restaurants.

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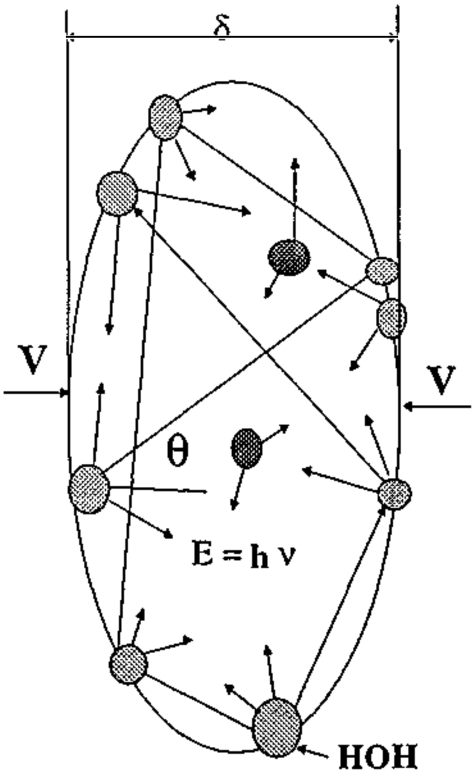

FIGURE 1 BUBBLE COLLAPSE IN ULTRASONIC CAVITATION

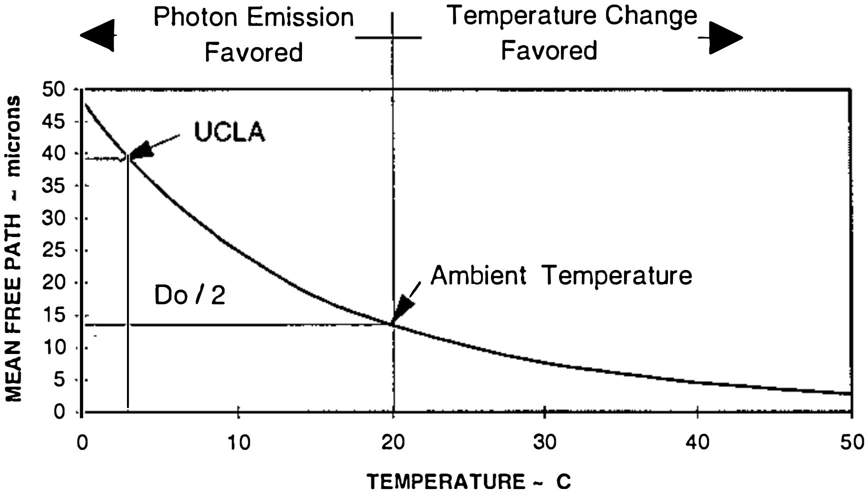

FIGURE 2 WATER MOLECULE ~ MEAN FREE PATH

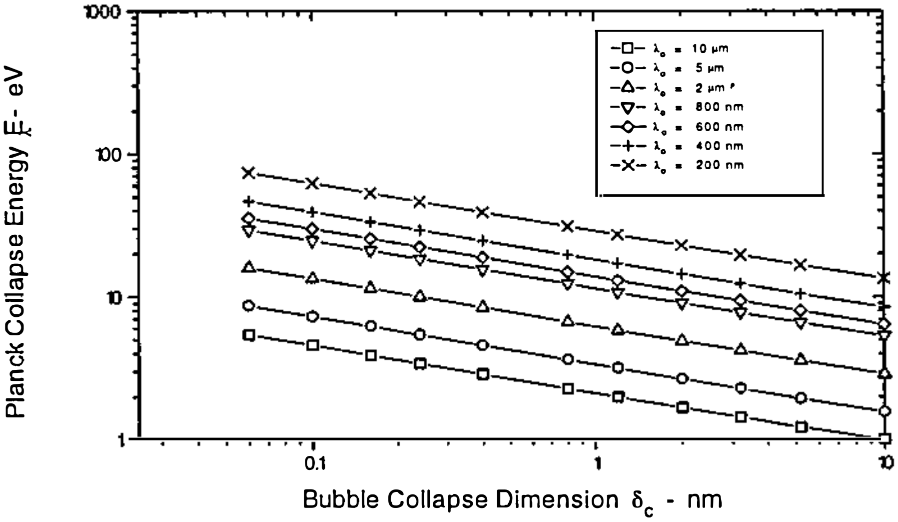

FIGURE 3 PLANCK ENERGY AND WAVELENGTH