

## Influence of Resonant rf Radiation on Gas/Liquid Interface: Can It Be a Quantum Vacuum Radiation?

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Sonoluminescence, a resonant cavitation of the gas/liquid interface with the kHz ultrasound, produces visible light and splitting of water. According to the quantum vacuum radiation model of sonoluminescence, high- $Q$  resonant radio frequency (rf) or microwave cavity with movable walls should produce similar effects. The similarity of the effects of highly resonant nonthermal rf described in this Letter and sonoluminescence suggests that quantum vacuum radiation might indeed be the most feasible model to explain both phenomena. [S0031-9007(98)05506-9]

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The concept of treating the gas/water interface with different stimuli to produce unusual effects has received considerable attention in recent years due to significant interest in the sonoluminescence phenomenon. Sonoluminescence [1–3] is an emission of light resulting from resonant ultrasonic treatment of water containing bubbles. The generation of visible light from 24 kHz ultrasound is an amazing amplification in frequency of 11 orders of magnitude. Interestingly, while the duration of ultrasound pulses is in microseconds, the emitted visible light pulses burst in picoseconds [1]. The mechanisms of the sonoluminescence phenomenon are still largely unknown. Eberlein recently proposed a quantum vacuum radiation theory of sonoluminescence [4] which predicts that an oscillating electromagnetic field (EMF) strongly influences the hydrophobic gas/water interface. In this model, the two interfaces with different polarizabilities (water and bubbles) are treated as a possible two-photon state source during excitation by electromagnetic fields. The virtual two-photon state becomes real when the dielectric moves due to an EMF. An oscillating EMF can influence the bubble/liquid interface simply by producing coherent oscillations of hydrogen bonded dielectric water molecules. Sonoluminescence results in the breakup of water molecules and the production of hydrogen and hydroxyl free radicals, which yield hydrogen peroxide upon disproportionation. It was recently suggested that highly resonant microwave or radio frequency (rf) cavities with movable walls could produce effects similar to sonoluminescence, if quantum vacuum radiation is the mechanism of both phenomena [2].

We showed that the effects of high- $Q$  resonant EMF's modify the gas/liquid interface [5]. It takes a long time to reequilibrate such systems after they are perturbed. We and others [5,6] also identified the reactive oxygen and hydrogen species present in EMF treated water for hours or days after treatment. Most remarkably, Shirata and co-workers [6] recently discovered that atomic hydrogen, present after the electrolysis of water, was stable for years

and survived freezing, thawing cycles or boiling in a closed container. It was also realized that careful outgassing of the water solutions resulted in the lack of any measurable EMF effects. Atomic hydrogen seems to be stabilized in a hydrophobic hydration cage of argon or carbon dioxide. Sonoluminescence phenomena also cease to exist in the absence of noble gases or carbon dioxide [3]. Outgassed water has to be sparged with gases containing either a small amount of noble gases or carbon dioxide to produce sonoluminescence or EMF effects on the gas/liquid interface. Our preliminary experiments even identified delayed rf emissions upon cessation of primary rf treatment (unpublished data). The association of two hydrogen atoms into a hydrogen molecule radiates 20 cm wavelength rf's. This is the frequency that radio telescopes are programmed to identify. Others have noticed that the presence of water clusters and hydrophobic argon gas influences the splitting of molecular hydrogen and the stability of the produced atomic hydrogen. Kikuchi and co-workers [3] realized that the addition of argon and water vapor to hydrogen enhanced the yield of atomic hydrogen after plasma treatment by up to 80 times.

To further reinforce our hypothesis that it is the gas/liquid interface, and consequently the structure of bulk and interfacial water which is modified in both phenomena, we performed a series of molecular (spectroscopic) and other bulk physicochemical experiments. Surface tension decreased from 72 to 68 dyn/cm after EMF treatment with the high- $Q$  resonant helical resonator rf generator (see Fig. 1) described in [6]. Water was placed in a Teflon container and placed 10 cm away from the rf source. Both the rf source and the Teflon bottle were inserted into a water container, since we realized that this enhanced the effects. The experimental setup is shown in Fig. 2. Oscillations in surface tension between 68 and 70 dyn/cm were observed for hours until the whole system returned to the initial value of 72 dyn/cm after 8 h. Oscillations could also be followed in the amount of dissolved argon or carbon dioxide.

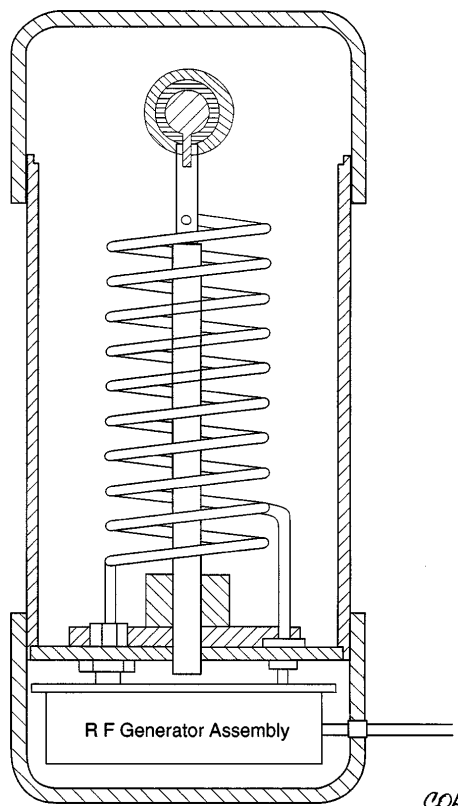


FIG. 1. A schematic presentation of the high- $Q$  helical resonator rf delivery source. A helical coil terminates with a gold plated sphere placed in a Teflon box. A very thin film of water (ca. 0.5 mm) is filled in between the golden sphere and the Teflon walls. A helical resonator is operated at 27.2 MHz. Voltages used range from 1000–20000 V [6].

Further, we attempted to identify the changes of the air/water interface at the molecular level. Sum-frequency generation (SFG) is a nonlinear spectroscopic technique which is sensitive only to the noncentrosymmetric water molecules which are strongly oriented at the interfaces. No signal is observed from the bulk water [7]. The details of the technique, experimental setup, and its use to study air-water interfaces can be found in [8]. As with the Raman and Fourier-transform infrared (FTIR) spectroscopies, three water absorption bands are located in the infrared region of the spectrum. The band near  $3200\text{ cm}^{-1}$  is characteristic for the strongly hydrogen bonded water, the band at  $3400\text{ cm}^{-1}$  is assigned to the somewhat distorted hydrogen bond, and the bands at  $3600$  or  $3750\text{ cm}^{-1}$  are assigned to the more free nonhydrogen bonded water molecules. Usually, when the influence of temperature on water structure is followed, the intensity of bands at  $3600$  and  $3200\text{ cm}^{-1}$  change in the opposite direction (more hydrogen bonded water means fewer free water molecules are available). Surprisingly, the rf treatment increased the intensity of all three bands from ca. 1.5 to 2.1 (arbitrary SFG scale). Some dramatic change occurred at the air/water interface. Unfortunately, we cannot explain what the change actually means, since no similar behavior was

## PRIMARY RF WATER TREATMENT

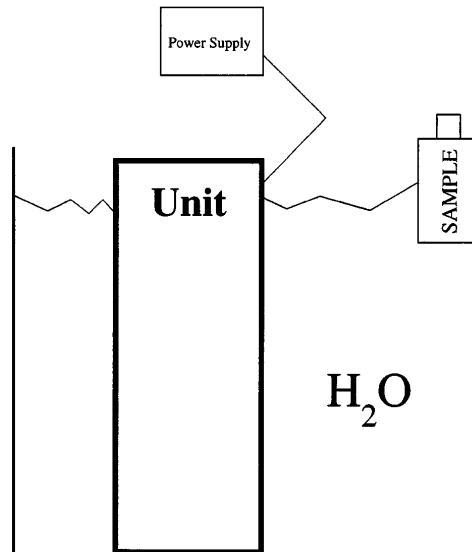


FIG. 2. A schematic presentation of the experimental setup. A Teflon bottle with a water/gas interface to be treated is placed in a water bath approximately 10 cm away from the nonthermal rf source. Samples were treated for 15 min. A helical resonator was tuned inside the water bath to maximum resonance.

ever observed when changing temperature or adding ions. Since the intensity of all three lines increased proportionally, it seems as if the concentration of water increased at the air/water interface. Maybe the conformation of the interfacial water changed in such a way as to cause better packing at the interface. Eventually, stabilized atomic hydrogen might accumulate near the hydrophobic air/water interface. More work will be performed to understand this behavior. The SFG spectra at the air/water interface before and after rf treatment are presented in Figs. 3(a) and 3(b). As in the case of surface tension measurements, oscillations in the SFG signal with time after rf treatment could be followed.

The SFG spectra of water before and after rf treatment were also measured at the hydrophobized fused quartz/water interface as explained in more detail in [9]. Octadecyltrichlorosilane (OTS) was used to coat the silica surface and make it hydrophobic [10]. As expected, a large peak at  $3750\text{ cm}^{-1}$  was observed. This is a characteristic of the broken hydrogen bonds near the hydrophobic alkyl chains. The intensity of the signal at  $3750\text{ cm}^{-1}$  decreased significantly after rf water treatment from 2.45 to 1.6 arbitrary SFG units. On the other hand, the intensity of the signal at  $3400\text{ cm}^{-1}$  characteristic of the distorted hydrogen bonds increased after rf treatment from 1.6 to 1.95 arbitrary units. These results suggest the appearance of more distorted hydrogen bonds and fewer free water molecules after rf treatment. If a similar increase in ordering is happening

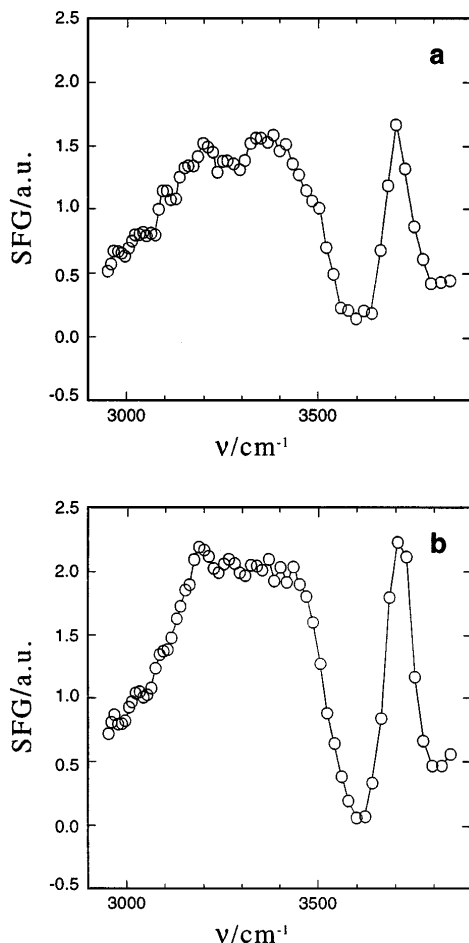


FIG. 3. (a) SFG spectra of air/water interface before rf treatment; (b) SFG spectra of air/water interface after rf treatment. The experimental setup is described in [7,8]. The sum-frequency output, visible input, and IR input were  $s$ -,  $s$ -, and  $p$ -polarized, respectively.

at the air/water interface but is not showing as directly in the SFG spectra, this increased ordering might be responsible for the higher packing density of the interfacial water. Much more work remains to be done to resolve these issues. SFG spectra of the hydrophobic quartz/water interface before and after rf treatment are shown in Figs. 4(a) and 4(b). Both hydrogen and argon are hydrophobic and would be expected to accumulate near hydrophobic OTS chains and modify hydrophobic hydration.

The difference between sonoluminescence and EMF treatment of the gas/water interface is in the fact that bubbling is not needed for the effects of EMF to be measured (even though it amplifies the effects observed). By means of a multitude of techniques, Ninham, Bunkin, and co-workers recently identified the presence of nanosized bubbles in nonoutgassed samples [11–14]. That could explain why gas bubbling was not needed for EMF effects on the gas/water interface. Pugh and co-workers [15] correlated the effects of numerous salts on the water structure with the oxygen solubility and bubble stability (coales-

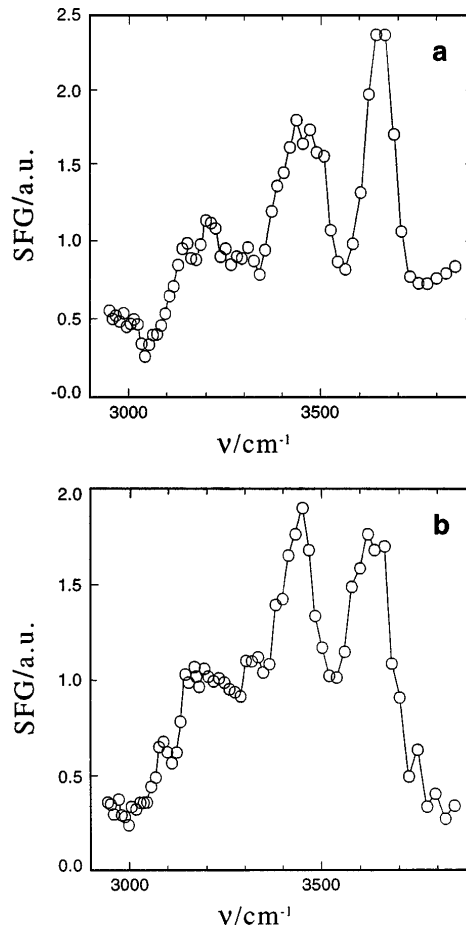


FIG. 4. (a) SFG spectra of hydrophobic OTS/water interface before rf treatment and (b) after rf treatment; the experimental setup is described in [7,9]. The sum-frequency output, visible input, and IR input were  $s$ -,  $s$ -, and  $p$ -polarized, respectively.

cence). As Ninham teaches us [16], the role of dissolved gas and effects of electromagnetic radiation on gas/liquid interfaces in water chemistry might be much more important than expected. Ninham even suggested that, in the related phenomena of dispersion forces and their dependence on different parameters, current models starting with Casimir-Polder theory and involving Lifshitz modifications do not hold [17]. Finally, Ninham suggested that hydrophobic surfaces might be separated from water through vacuum [18]. In that case, even single atoms/molecules of hydrophobic gas could represent a “surface” with different polarizability needed for the quantum vacuum radiation phenomenon. It is a well known fact that noble gases and carbon dioxide promote a clathratelike water structure even around single atoms and/or molecules. Maybe there is a vacuum between single entities of hydrophobic matter and hydrophobic hydration water. This hypothesis is currently being tested through measurement of the effects of resonant nonthermal rf on hydrophobic hydration of hydrophobic ions such as tetramethylammonium chloride.

To conclude, it seems that the main “receptor” of the high- $Q$  resonant electromagnetic radiation is a hydrophobic gas/water interface. Gas might be present in water in the form of the recently discovered intrinsic nanobubbles [11], hydrophobic single atoms or molecules, or be freshly produced through the action of electric or electromagnetic fields. The reactive oxygen or hydrogen species are often produced during EMF treatment and might have a more important consequence (oxidation, reduction, dissolution, luminescence) on the system behavior than does the change in water structure. The fact that nonthermal highly resonant rf produced the same effects on the gas/liquid interface, as in the case of sonoluminescence, might suggest that quantum vacuum radiation is indeed the feasible explanation of both phenomena. Yet the quantum vacuum radiation model of sonoluminescence as well as the presence of nanobubbles of gases in water or vacuum between hydrophobic entities and water are still speculative hypotheses and more work should be done to prove or disprove them.

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