# Short Note

# The sonoluminescence spectrum of seawater

Luann Becker[a], Jeffrey L. Bada[a], Kathleen Kemper[b] and Kenneth S. Suslick[b]

[a]*Scripps Institution of Oceanography, University of California at San Diego, La Jolla,
CA 92093-0212, USA*
[b]*School of Chemical Sciences, University of Illinois at Urbana–Champaign, Urbana, IL 61801, USA*

ABSTRACT

Becker, L., Bada, J.L., Kemper, K. and Suslick, K.S., 1992. The sonoluminescence spectrum of seawater. *Mar. Chem.*, 40: 315–320.

The sonoluminescence spectra of seawater and of a sodium chloride solution were determined by irradiation with ultrasound at 20 kHz. Ultrasound creates sonoluminescence through the process of acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid. The sonoluminescence spectra of both seawater and NaCl in water are characterized by an emission line at 589 nm from excited-state sodium. Excited-state Na atoms are produced from the reaction of $Na^+$ with high-energy hydroxyl radicals formed directly during the cavitation event. Emission at 589 nm could be useful in determining whether sonochemical processes associated with cavitation occur in breaking waves or other turbulent flows.

INTRODUCTION

Cavitation and sonochemical processes have been suggested as a widespread natural phenomena that could occur during the breaking of waves in the oceans (Anbar, 1968). The compression of gas bubbles during cavitation gives rise to intense localized heating, generating temperatures of approximately 5000 K (Flint and Suslick, 1991a). Sonolysis of water leads to the formation of highly reactive species such as hydrogen peroxide, hydroxyl radical, and hydrated electrons (Suslick, 1990), components which are generally associated with photochemical processes in the oceans (Zika, 1987).

The experiments carried out by Anbar (1968) over 20 years ago used a Teflon-lined rotary pump to focus a jet stream of 0.8 M NaCl onto a water surface. Light emission at 589 nm, apparently resulting from the excitation of sodium atoms, was used as a criterion for cavitation in the region of impact. Anbar inferred that cavitation takes place when water impinges on water at

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*Correspondence to*: L. Becker, Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093-0212, USA.

relatively low linear velocities. Although acoustic techniques and in situ 3-D holographic imaging have been used successfully to observe cavitation nuclei produced during the breaking of waves, the formation of whitecaps and during biological activity (O'Hern, 1987), whether the cavitational collapse of bubbles and sonolysis take place in the oceans is unknown. The actual temperatures and pressures created as the result of the collapse of the bubbles associated with these oceanic processes have yet to be determined.

Ultrasound provides a means for creating acoustic cavitation in the laboratory (Suslick, 1990). During the violent collapse of the bubbles produced by ultrasound, the incapsuled gases and solvent vapor are rapidly heated, causing them to react. Sonoluminescence associated with acoustic cavitation provides a spectroscopic probe of the species and conditions produced during cavitation (Flint and Suslick, 1989, 1991a,b). The emission from sonoluminescence in aqueous solutions is extremely fast and is estimated to occur on time-scales of less than 100 ps (Barber and Putterman, 1991). We have used ultrasound to create acoustic cavitation in seawater, and measured its sonoluminescence spectrum. We conclude that light emission associated with excited-state sodium produced during cavitation provides a potential method for detecting sonochemical processes directly in the oceans.

EXPERIMENTAL

The sonoluminescence spectra were collected with the instrumentation described elsewhere in detail (Flint and Suslick, 1989). High-intensity ultrasound was generated by a titanium immersion horn (Heat Systems Model W373 (Farmingdale, NY)) operating at 20 kHz and approximately $110\,W\,cm^{-2}$. Forty milliliters of each sample were purged with argon for 1 h before and during ultrasonic irradiation. The sonoluminescence spectra were collected at a cell temperature of approximately 35°C using a Princeton Instruments (Princeton, NJ) IRY 512N diode array detector with a Thermo Jarrell-Ash (Franklin, MD) MonoSpec-18 0.25 m spectrograph. Surface and deep seawater samples from the North Atlantic (24°31′N, 64°01′W) and from the Eastern Central Pacific off Point Sur (36°08′N, 122°38′W) were analyzed. The North Atlantic samples were unfiltered whereas the Point Sur samples were filtered (0.7 $\mu$m glass filters), to assess the contributions of particulates in seawater to the overall intensity of the spectra. Ten 30 s spectra were collected for each seawater sample, and these spectra were averaged. The sonoluminescence spectrum of a sodium chloride control containing $Na^+$ at the same concentration as seawater ($10.56\,g\,l^{-1}$) was obtained under conditions identical to those for the seawater samples. In addition, tap-water was run as a blank.
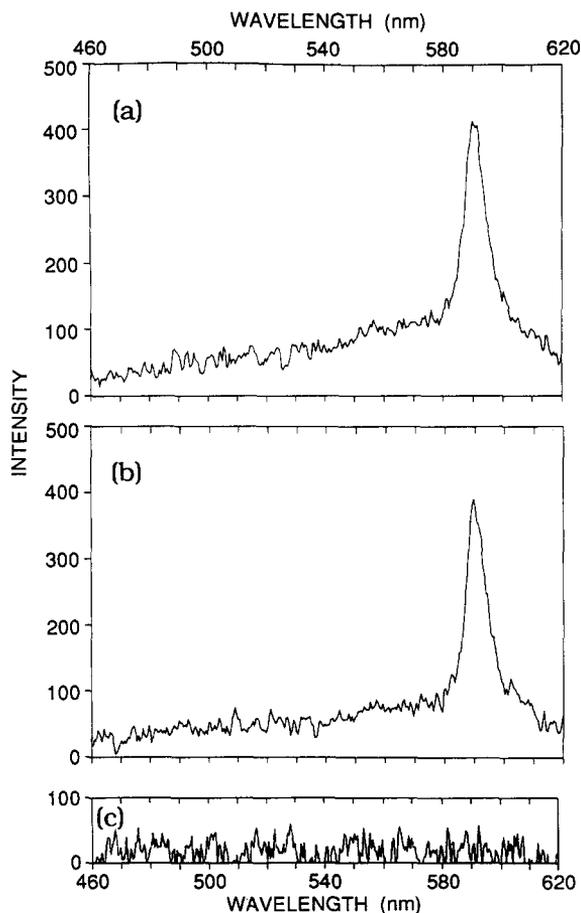
Fig. 1. Sonoluminescence spectra of (a) deep water from the North Atlantic, (b) $10.65\,gl^{-1}$ NaCl control and (c) tap-water. The spectral measurements were carried to longer wavelengths, but no emission features were observed. There are no distinguishable differences between seawater samples of surface and deep-oceanic waters.

## RESULTS AND DISCUSSION

The sonoluminescence spectra of seawater (a), the sodium chloride control (b) and tap-water (c) are shown in Fig. 1. The spectra for both the seawater sample and the sodium chloride control show a single line at around 589 nm, with similar intensity and bandwidth. The emission at 589 nm has been observed previously in the sonoluminescence spectrum of sodium salts in water (Anbar, 1968; Taylor and Jarman, 1970; Sehgal et al., 1979; Flint and Suslick, 1991b), and corresponds to the emission line of excited-state sodium. Although seawater contains other alkali-metal ions, their concentrations are

much less than that of sodium, and thus the intensities of emission lines associated with the excited states of these ions are too weak to be observed.

We found that the sonoluminescence spectra for all of the seawater samples were identical. No distinguishable differences were observed between surface and deep waters and filtered and unfiltered samples. These results imply that dissolved organic carbon and other minor components such as nutrients and particles, which have different concentrations in surface and deep oceanic waters, do not play a significant role in the cavitational processes involved in the formation of excited-state sodium. The sonoluminescence spectrum for tap-water has a peak at 310 nm (not shown), arising from the return to the ground state of the excited hydroxyl radical (Taylor and Jarman, 1970). The spectrum for tap-water shows no emission lines in the region 460–620 nm, as there are no excited-state ions present to combine with high-energy hydroxyl radical.

Flint and Suslick (1991b) recently investigated the sonoluminescence spectrum of alkali-metal solutions and found that the line width and peak position of the alkali-metal emission are independent of cavitation temperature and are unaffected by solvent vapor pressure or gas composition. The intensity of sonoluminescence decreased with decreasing cavitational temperature. Based on these observations, Flint and Suslick (1991b) suggested that secondary chemical reactions which took place outside the collapsing bubble cavity were responsible for the excited-state alkali-metal emission. Thus, the line width and peak position of the resonance lines do not change as cavitation conditions change because the environment around the emitting atom is not in the cavitation hotspot, but rather in the surrounding solution.

From the Flint and Suslick (1991b) alkali-metal ion sonoluminescence studies, the following reactions can be used to explain the seawater observations:

$$H_2O \xrightarrow{\text{}} H^{\cdot} + HO^{\cdot} \tag{1}$$

$$H^{\cdot} + Na^+ \rightarrow Na + H^+ \tag{2}$$

$$H^{\cdot} + OH^{\cdot} + Na \rightarrow Na^* + H_2O \tag{3}$$

$$H^{\cdot} + NaOH \rightarrow Na^* + H_2O \tag{4}$$

$$Na^* \rightarrow Na + h\nu \tag{5}$$

$$Na^* + S \rightarrow Na + S + heat \tag{6}$$
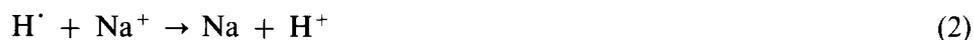
The symbol $\xrightarrow{\text{}}$ denotes ultrasonic-induced cavitation. Radicals produced from the ultrasonic irradiation of water are shown in eqn. (1). The radicals $H^{\cdot}$ and $OH^{\cdot}$ are formed in the hotspot of the cavitation event. High-energy radicals produced from solvent vapor in the cavitation event diffuse out of the hotspot where they react to produce excited-state atoms. These $H^{\cdot}$ and $OH^{\cdot}$

radicals are capable of both reducing $Na^+$ to atoms and promoting atoms to the excited state via chemiluminescence (eqns. (2) and (3)). The reaction in eqn. (2) was proposed by Taylor and Jarman (1970) for the sonoluminescence from NaCl solutions. A third possibility is that the cation is excited and reduced in one step (eqn. (4)). The excited atom can either emit a photon (eqn. (5)) or can be totally quenched by a solvent molecule (eqn. (6)) (Riesz, Kondo and Krisna, 1990). The rapid quenching by solvent leads to resonance line broadening in the sonoluminescence spectra of seawater, and of NaCl and other alkali-metal ion solutions.

These reactions explain the sonoluminescence from nonvolatile species such as $Na^+$ ion which would not be expected to be present inside the cavitating bubble. The effective concentration of the solvent in the secondary reaction zone, and thus the rate of quenching and the lifetime of the excited state, is essentially independent of the solvent, solvent vapor pressure, or gas thermal conductivity.

CONCLUSIONS

The question of whether cavitation occurs under natural conditions in seawater is still under dispute. According to Furduev (1966), whitecaps create turbulent pressure fluctuations that are sufficiently strong to cause non-linear bubble oscillations. This could give rise to cavitation. However, in the ocean, pressure fluctuations from turbulence may not occur at a sufficient magnitude to cause the compression of a bubble to the degree needed to support cavitation (Prosperetti and Lu, 1988). Other problems that remain unanswered are the effects of ocean chemistry on bubble densities. Organic skins encasing bubbles would change the surface tension and could inhibit the diffusion between water and a gaseous cavity (Kerman, 1984). There is the possibility that cavitation and sonochemistry may also take place in the deep ocean in the regions associated with hydrothermal vent discharges. The strange observation of diffuse light emission from deep-ocean hydrothermal vent discharges (Van Dover, 1988–1989) could, in fact, be due to the sonochemical formation of excited-state sodium (or other vent metal ions) produced from collapsing bubbles present in vent waters. Finally, sonoluminescence may also be associated with other natural processes. It has been proposed that light emissions during earthquakes is the result of molecular reactions in water that has been strongly shaken by compressional (P) waves produced during earthquakes (Johnston, 1991).

An effective way to measure directly the occurrence of cavitation in the oceans and in natural waters is needed to resolve these issues. Sonoluminescence may provide such a probe. The in situ measurement of the 589 nm sodium emission line, or perhaps the 310 nm hydroxyl emission line, would provide strong support that sonochemical processes occur naturally in a liquid

medium such as the oceans or are associated with other processes such as seismic activities.

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