Effect of Dissolved Gases on Sonoluminescence Signal from Aqueous Solutions Irradiated with Megasonic Energy

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Megasonic Cleaning Process

- **Sound waves with frequency of ~ 1 MHz or greater used in combination with different cleaning chemistries for particle removal**

- Advantage: High particle removal efficiency
- Disadvantage: Damage to fragile features

Particles removal mechanism:

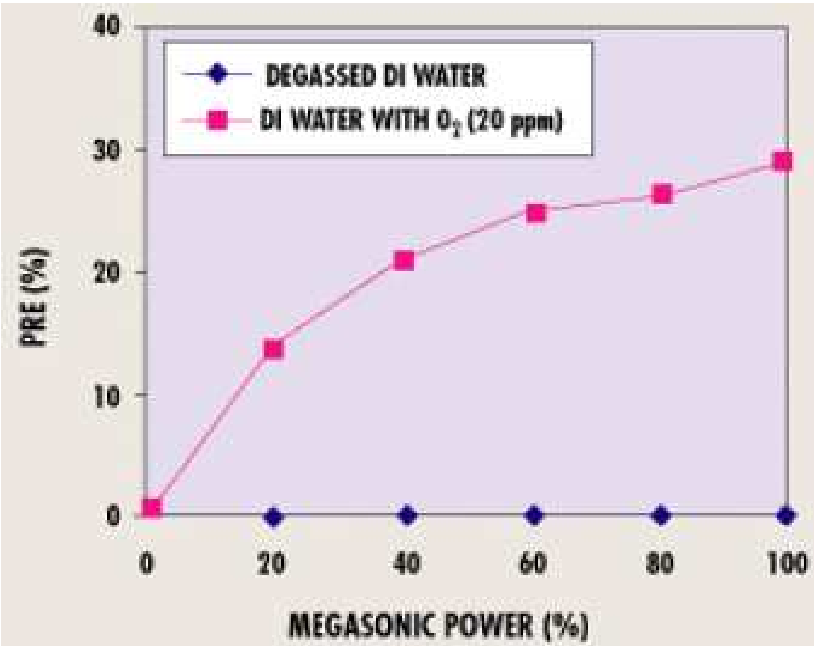
- **Reduction in Boundary Layer Thickness:**
  1) At 1 MHz of sound frequency, acoustic boundary layer thickness in water is ~ 0.5 µm and decreases to 0.3 µm at 3 MHz sound frequency
  2) Hydrodynamic boundary layer thickness in water varies from 2000 to 400 µm for flow velocity of 2 to 10 m/s
- **Acoustic Streaming**: Eckart, Schlichting and Microstreaming
- **Acoustic Cavitation**: **Stable and Transient**

Physical Effect of Cavitation

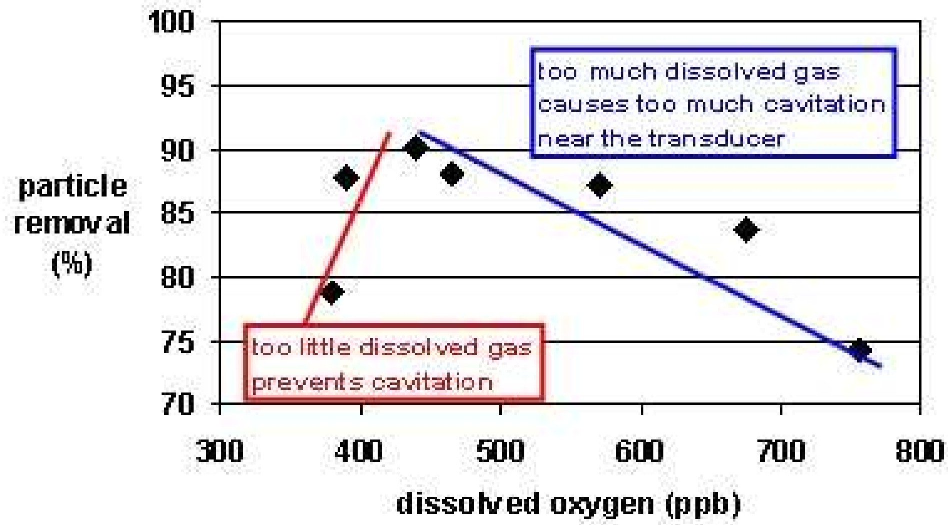
Sonoluminescence (Photon emission)

- **At collapse, the gas inside the cavity reaches extremely high temperatures (4000 °C) and pressures (a few hundred bars).**
- **Results in production of free radical species**
- **Recombination of free radicals gives rise to photon emission.**

Particle Removal Studies in Oxygenated Water



Vereecke et al. (IMEC), Micro Magazine , vol 22, pp. 57-63 (2004).: 34 nm silica particles on SiO_2 surface as a function of megasonic power and at 720 kHz.



Courtesy: Dr. Jeff Butterbaugh (FSI)

- **Effect of dissolved gases shows cavitation to be important for particle removal**
- **It is not clearly known how different gases affect cavitation**

SL from Water Saturated with different Dissolved Gases

Relative SL intensities from water saturated with various dissolved gases.

Gas	Relative intensity *(Young 1976)	Thermal conductivity ($10^{-2}\,W\,m^{-1}\,K^{-1}$)
Air	1	2·52
Nitrogen	0·51	2·52
Oxygen	1·00	1·64
Carbon dioxide	0·36	1·56
Hydrogen	0·36	18·4
Helium	0·48	14·3
Neon	1·33	4·72
Argon	12·5	1·73
Krypton	21	0·94
Xenon	52	0·55

* F. Young, J. Acoust. Soc. Am., vol 60, pp. 100-104 (1976)

- **Aqueous solution containing saturated level of gas was subjected to 20 KHz sound frequency at 10 W/cm^2 and SL was measured by a photomultiplier tube (165 to 650 nm)**
- **Gases with Higher thermal conductivity showed lower SL**

Objectives of this Work

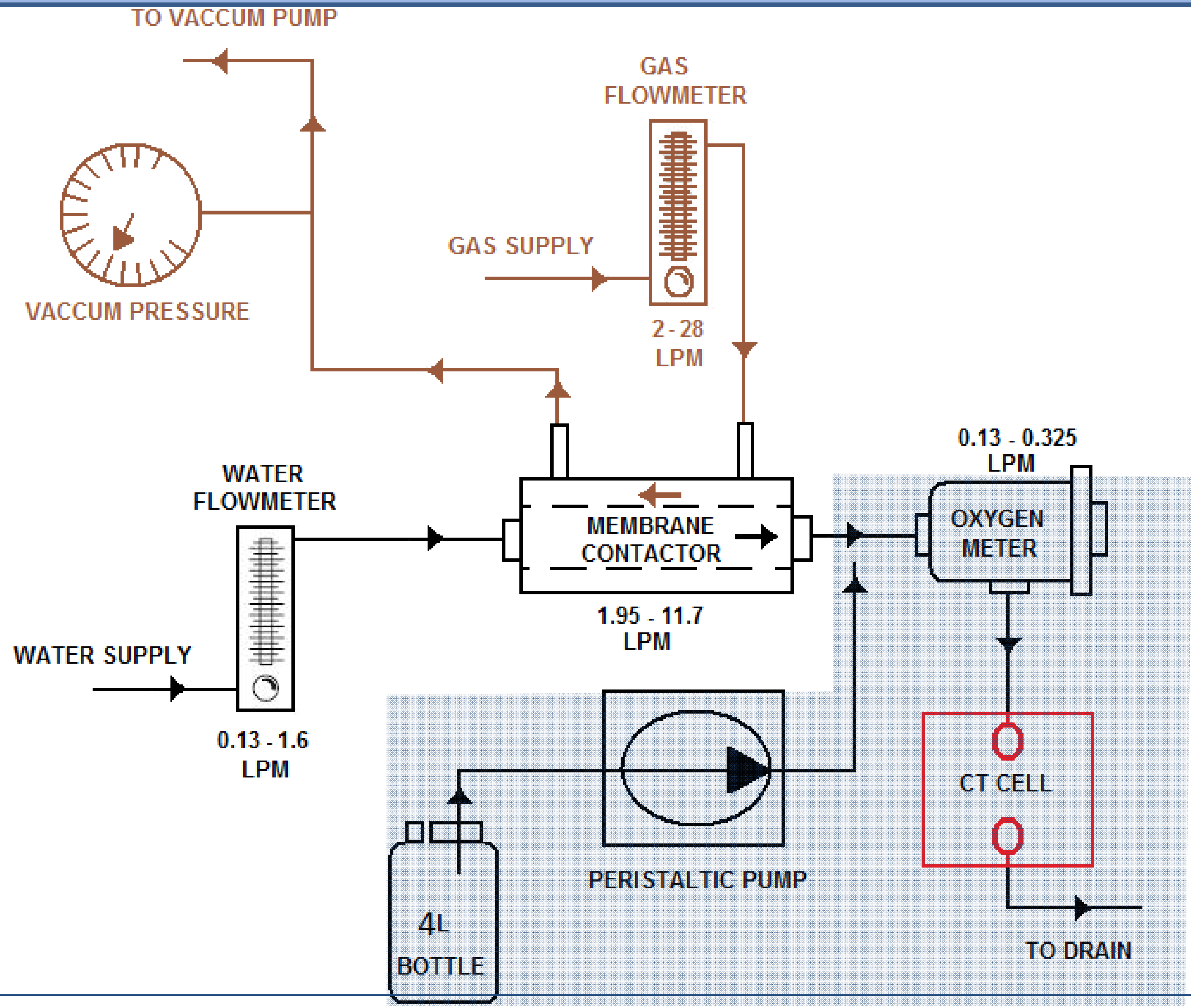
- To study the SL-behavior of major dissolved gases (N_2, O_2, Ar and CO_2) in a controlled manner in Aqueous Solutions

Component	Symbol	Volume	
Nitrogen	N_2	78.084%	99.998%
Oxygen	O_2	20.947%	
Argon	Ar	0.934%	
Carbon Dioxide	CO_2	0.033%	

- To Control SL by consumption/release of some of these gases using chemical means

- ***THE MAJOR OBJECTIVE OF THIS RESEARCH IS TO CARRY OUT SYSTEMATIC INVESTIGATIONS TO DETERMINE IF AND HOW OXYGEN AND CARBON DIOXIDE ALTERS SL SIGNAL.***

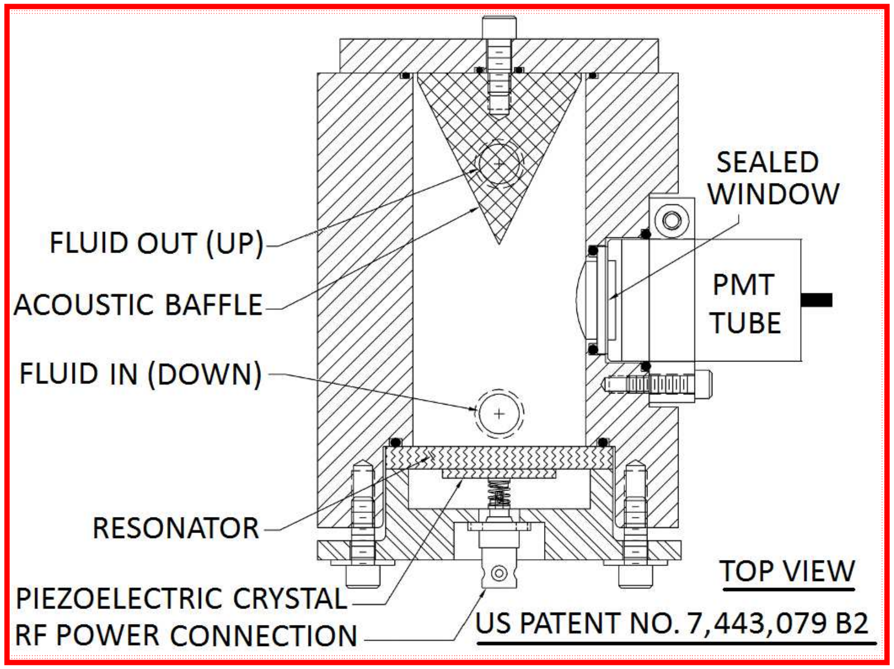
ProSys CT Cell and the Experimental Setup

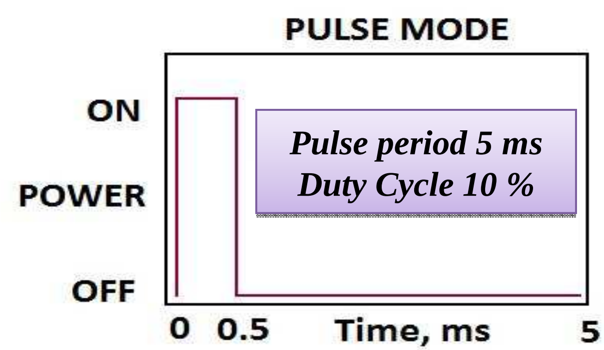


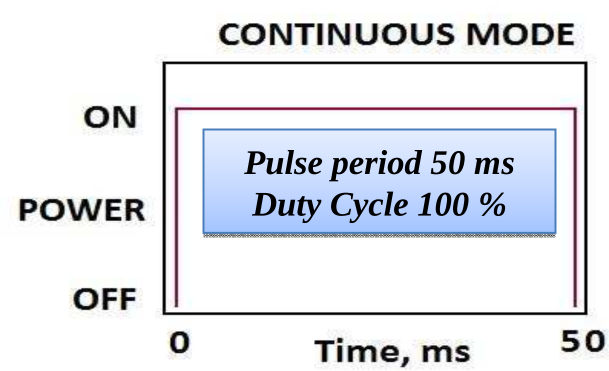
ProSys CT Cell and the Experimental Setup…Continued

CT Cell Details

- *Volume = 163 cc, Length = 10.4 cm*
- *Internal Diameter = 4.8 cm*
- ***Frequency = 0.93 MHz***
- ***Wavelength Range = 270 to 650 nm***







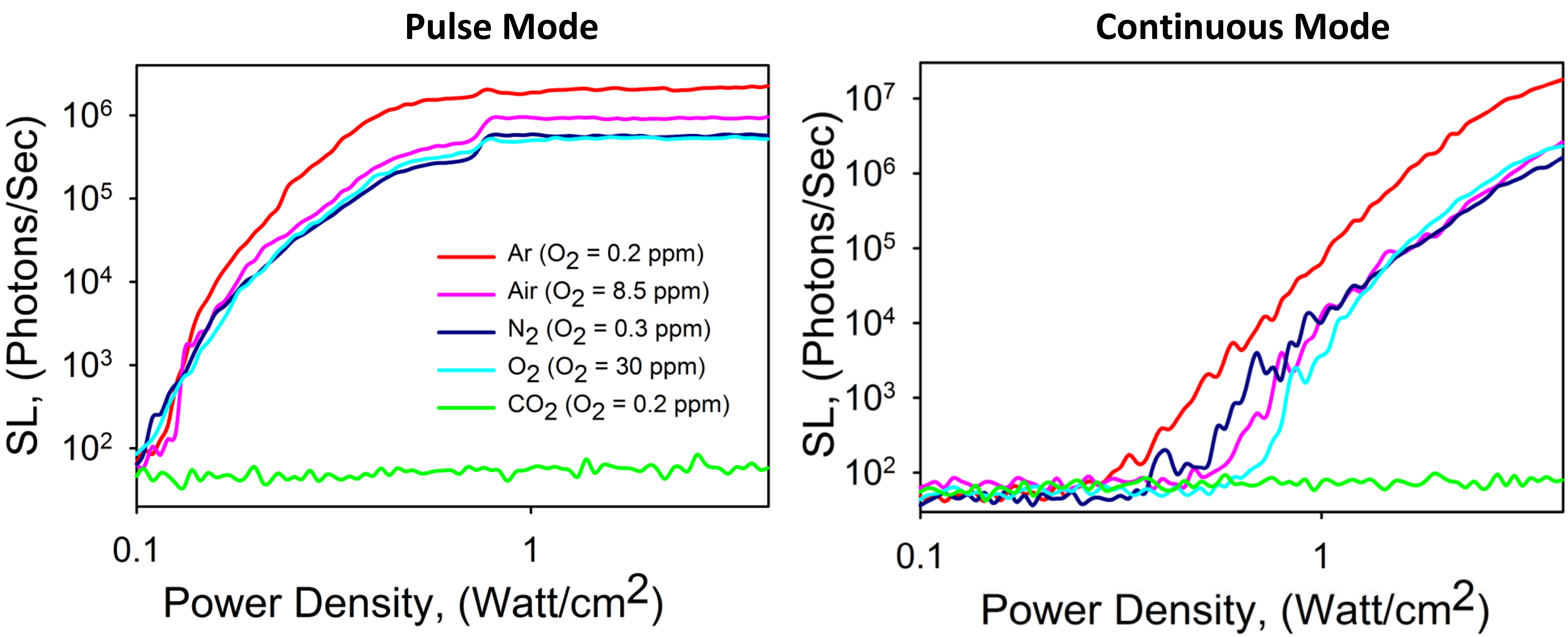
Gas Solubilities in DI Water

Saturating Gas Levels at 25 °C, 1 atm pressure

[Gas]	DIW Saturated With				
PPM	Air	N_2	O_2	CO_2	Ar
N_2	13.6	17.5	-	-	-
O_2	8.4	-	44	-	-
CO_2	0.5	-	-	1500	-
Ar	0.5	-	-	-	55

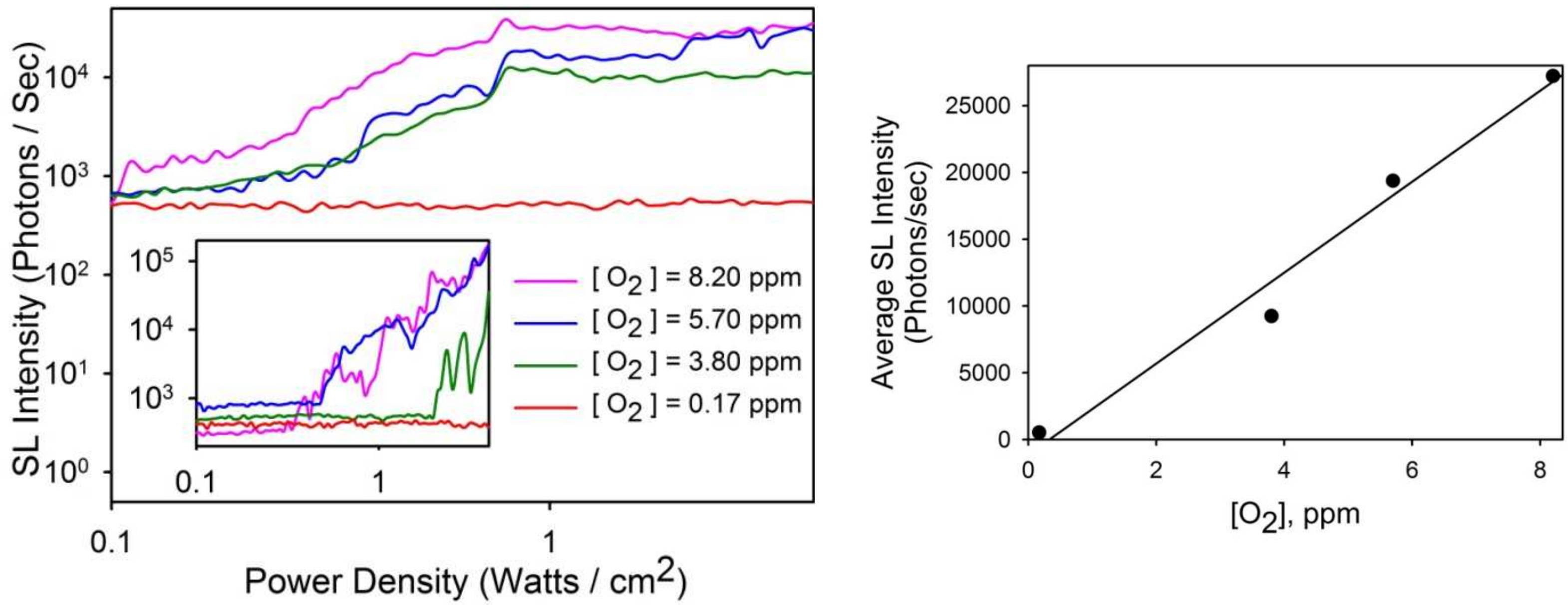
- **Ar, N_2, CO_2** were bubbled in DI Water until **[O_2] < 0.3 ppm**
- **Air Saturated Water** obtained by overnight exposure of DI water to clean room air and confirmed by ensuring **[O_2] > 8.2 ppm**

SL in DI Water Saturated With Different Gases



- **All gases except CO_2 (pH ~ 4, dissolved CO_2 ~ 1500 ppm) are capable of generating SL. CO_2 is completely incapable**
- **N_2 and O_2 saturated DI Water generates SL efficiently even though Ar, a gas believed to be essential for SL, is presumably absent**

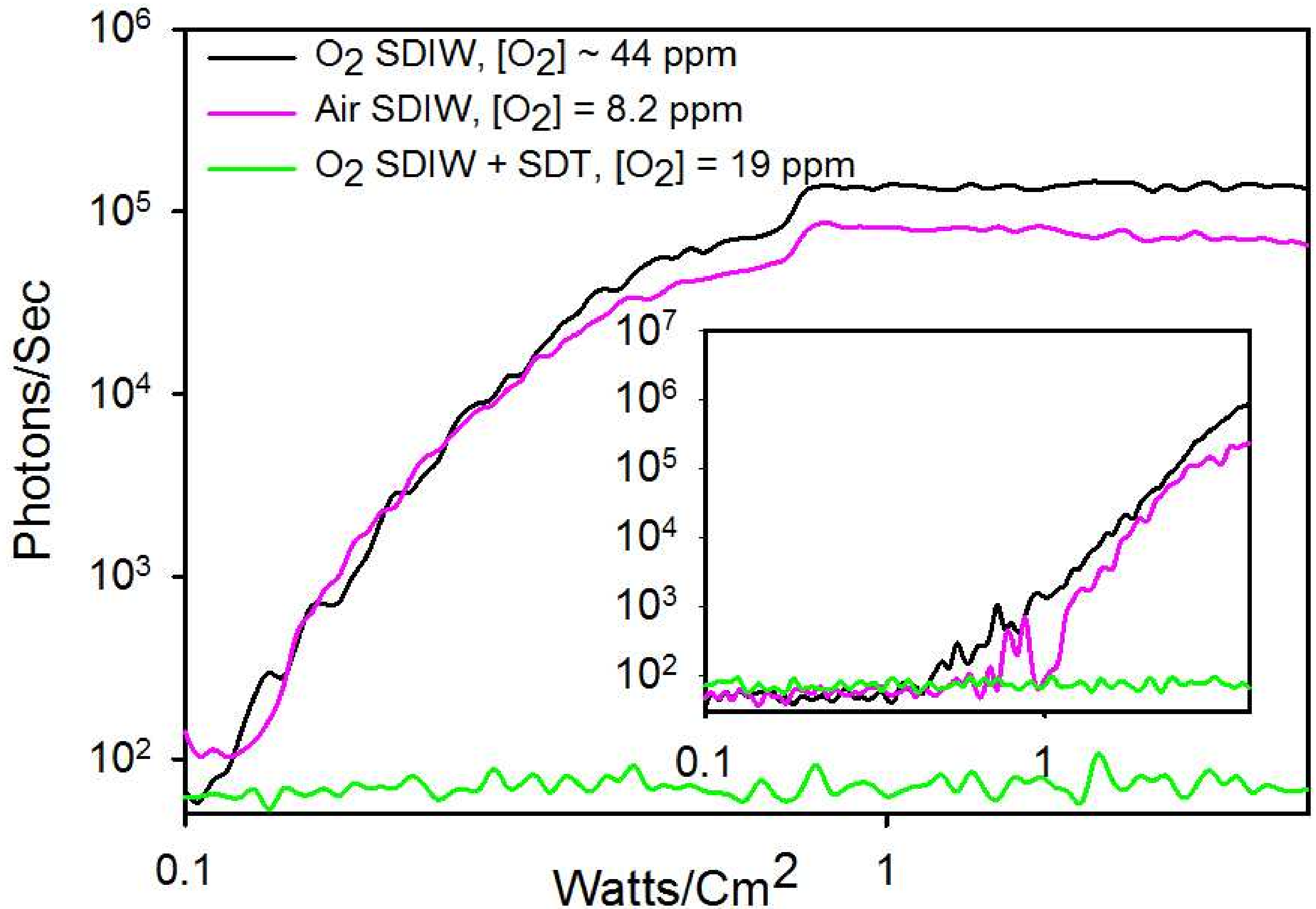
O_2 Removal From Air-Saturated DI Water by an Inorganic O_2 - Scavenger Kills SL Completely



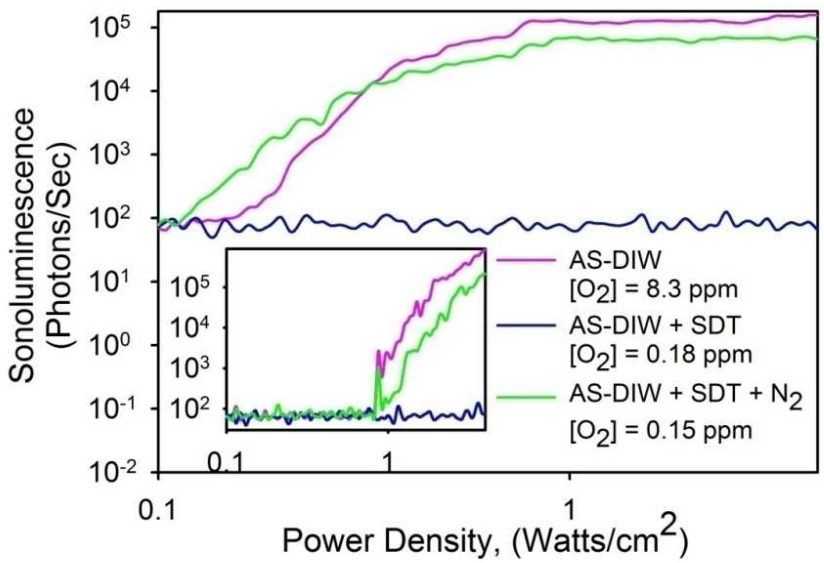
- Oxygen decreases from 8.2 to 0.17 ppm upon addition of *Scavenger (dithionite salt)*

- Total gas decreases from 23 ppm to 14.5 ppm

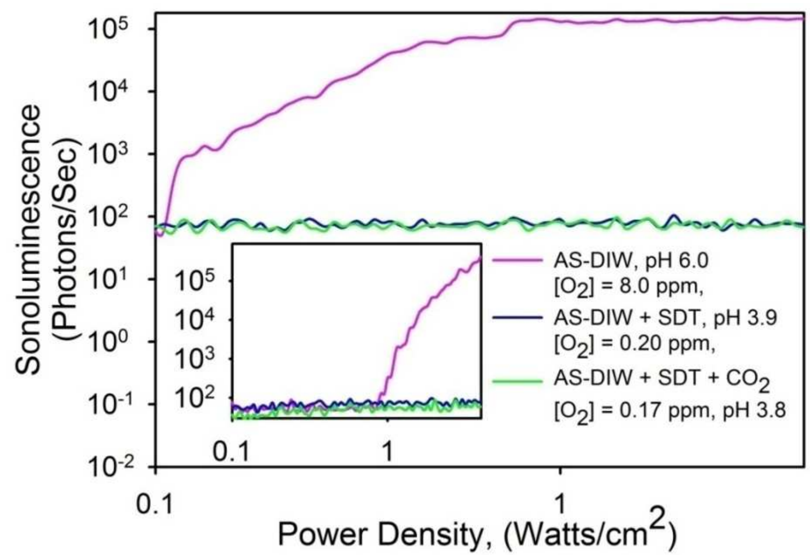
Scavenging of O_2 in O_2-Saturated DIW From 44 to 19 ppm Kills SL Completely



SL-Capable N_2 Can "Replace" O_2 For SL But SL-Incapable CO_2 Cannot

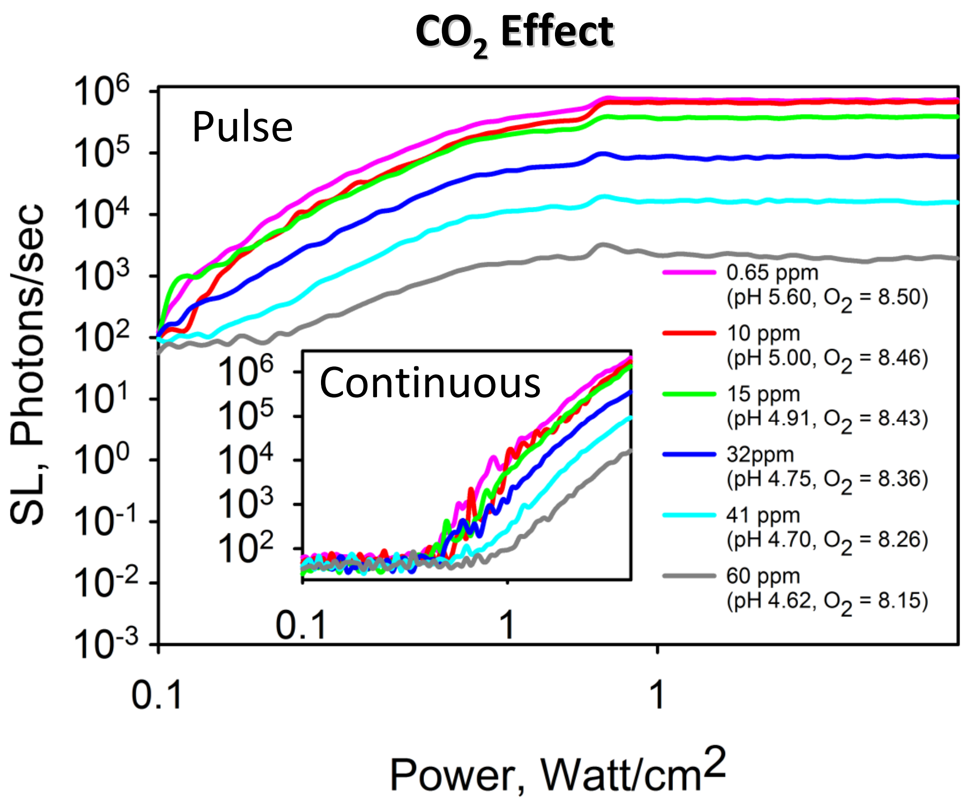


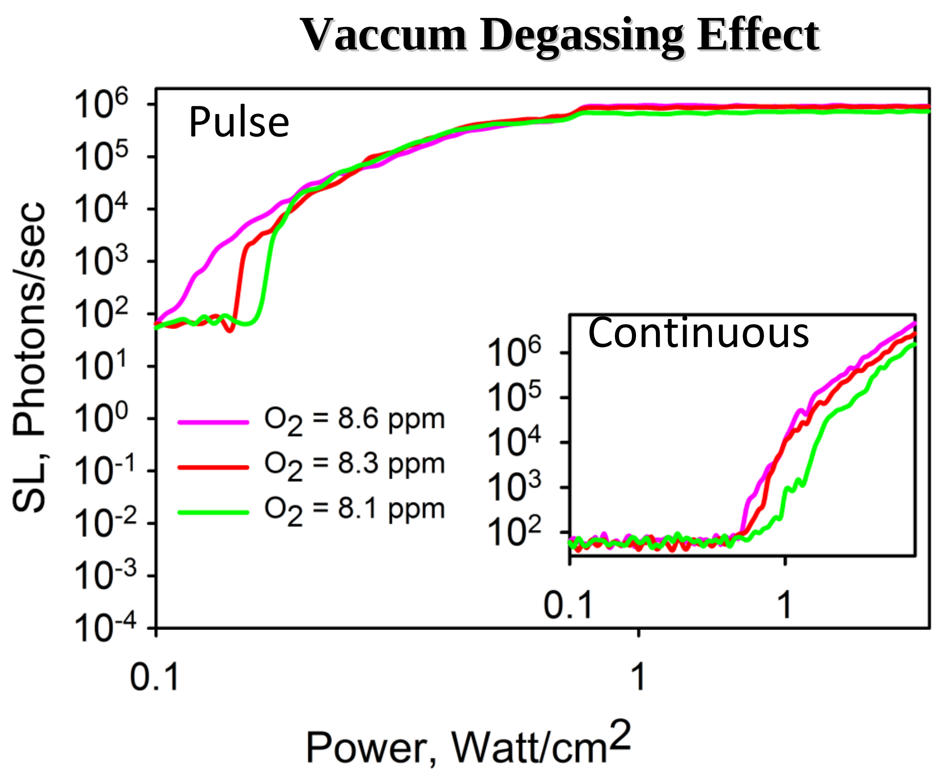
N_2 Restores SL of Air Saturated DI Water From Which O_2 Has Been Removed Using O_2 Scavenger



CO_2 Does NOT Restore SL of Air Saturated DI Water From Which O_2 Has Been Removed Using O_2 Scavenger

SL Suppression by Bubbling of CO_2

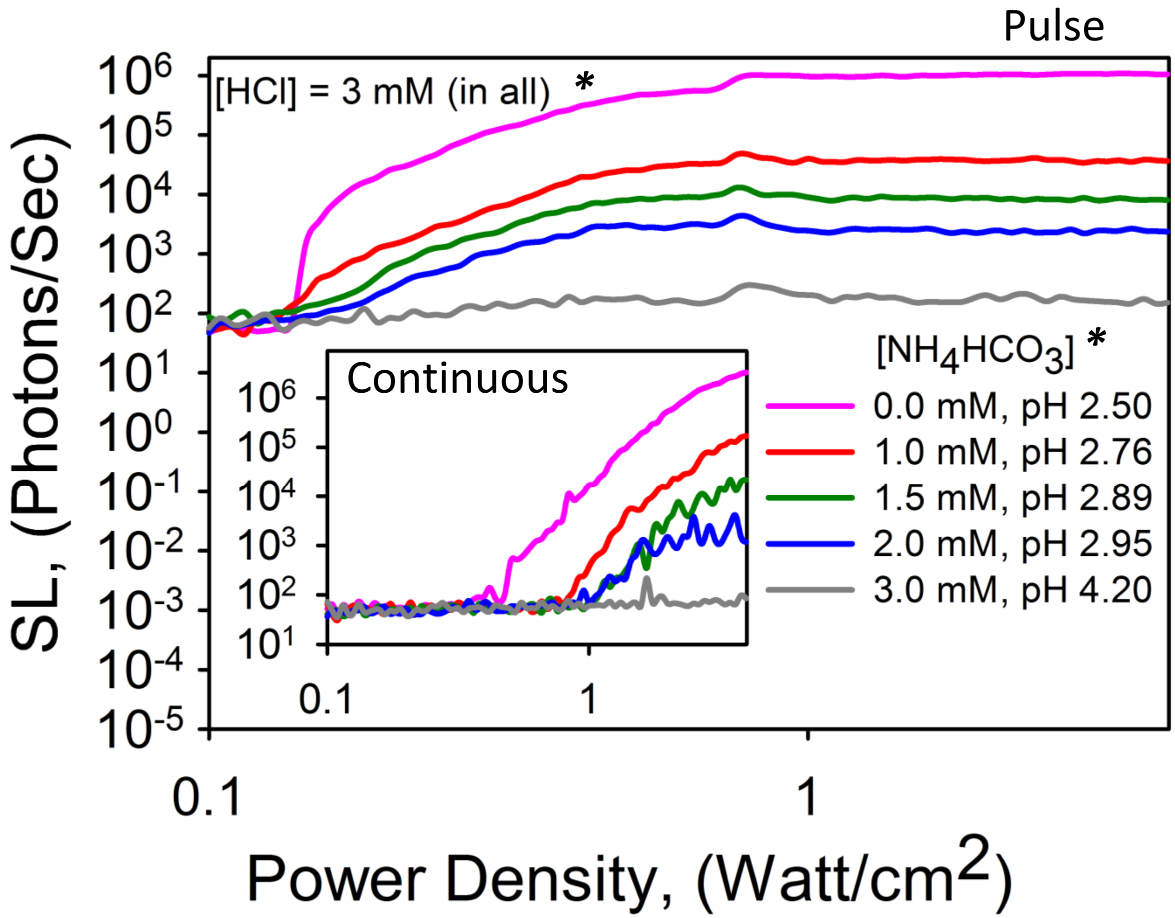




CO_2 > 60 ppm suppresses SL almost completely. Addition of CO_2 decreases levels of other dissolved gases slightly.

When Air-saturated DI Water is vaccum degassed to a comparable level, SL remains unaffected. Thus, SL suppression is due to added CO_2 and not due to removal of other gases upon addition of CO_2.

SL Suppression by CO_2 Released From NH_4HCO_3

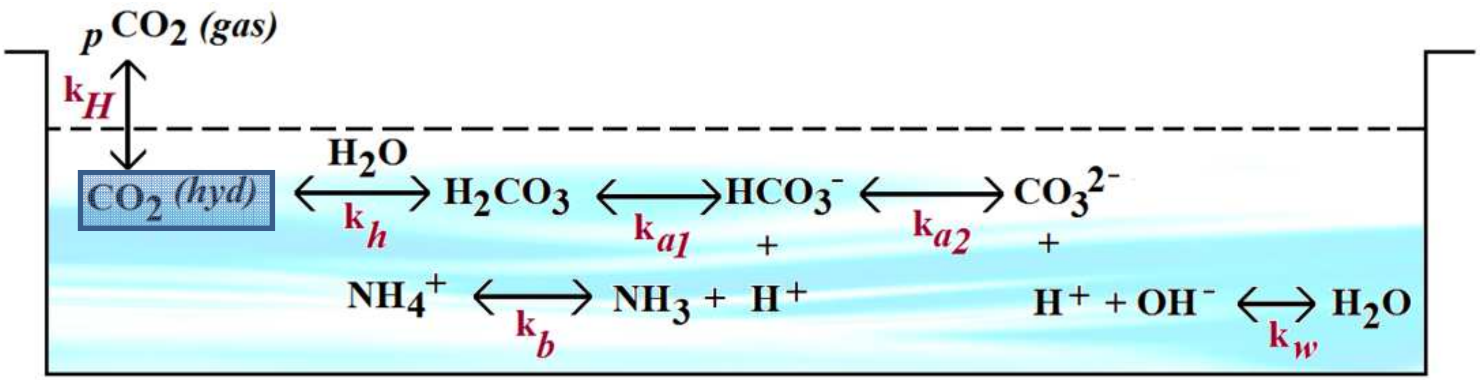


These results show CO_2 to be not only incapable but also a strong inhibitor of SL generation.

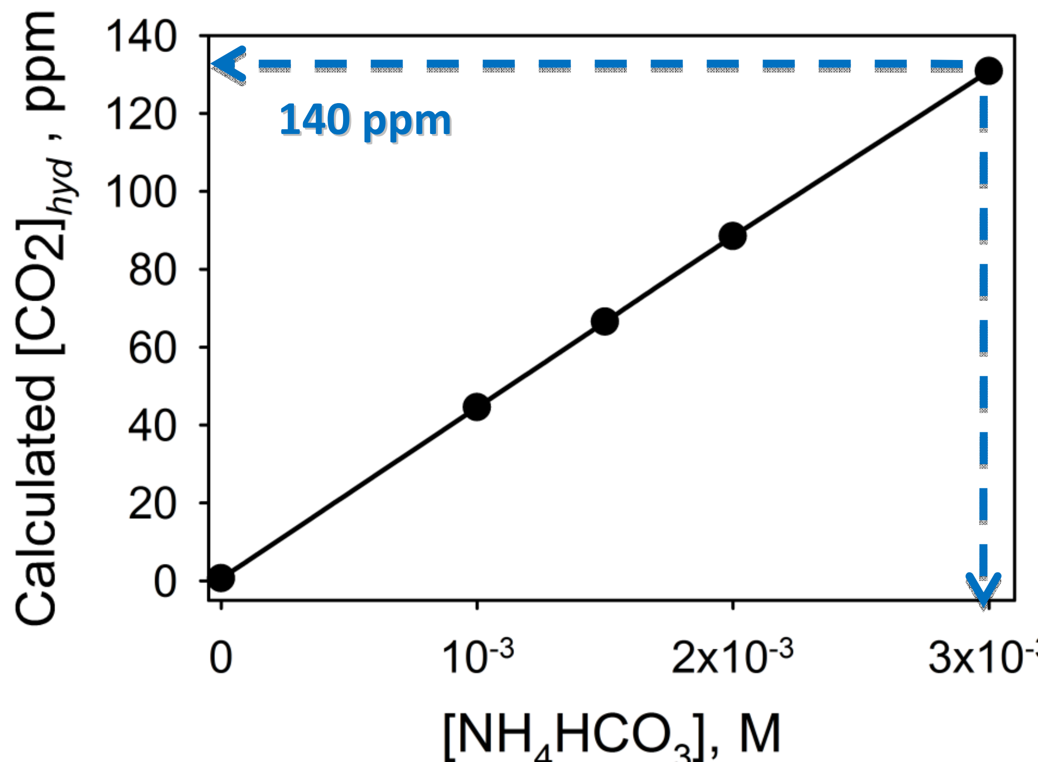
** Neither HCl alone nor NH_4HCO_3 alone had any effect on SL, ruling out any role of HCO_3^- or H^+ (pH)*

- **3 mM HCl is added to induce release of CO_2 from NH_4HCO_3**
- **NH_4HCO_3 = 3 mM suppresses SL almost completely**
- **Initial dissolved gases is unchanged in this experiment as indicated by $[O_2]$ = 8.5 ppm, thus SL suppression is due to CO_2 release**

Calculation of CO_2 Evolved From NH_4HCO_3



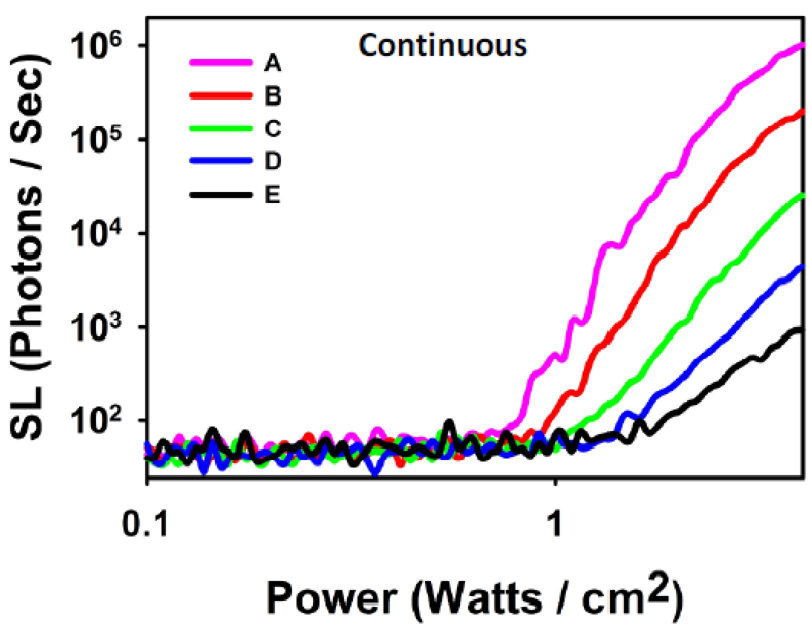
- Upon acidification of NH_4HCO_3 the linked equilibria in water is shifted towards formation of hydrated CO_2 i.e. CO_2 (*hyd*).
- The Equations for equilibrium, mass and charge conservation can be solved numerically and [CO_2(*hyd*)] and [H^+] concentrations determined as a function of added [NH_4HCO_3].
- Minimum [CO_2 (*hyd*)] concentration necessary for Complete SL suppression using CO_2 release compounds is 140 ppm, which compares well with >60 ppm value obtained with direct CO_2 bubbling experiments

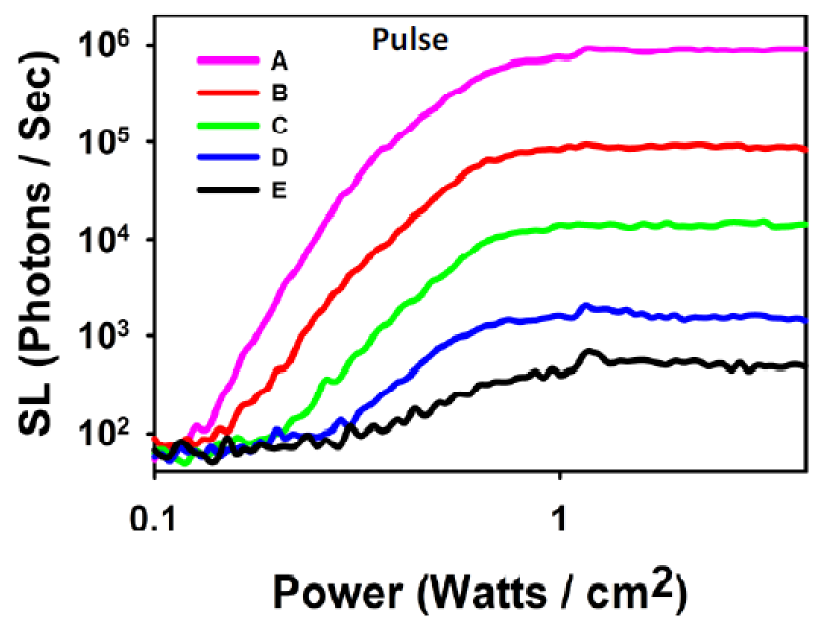


SL Suppression by CO_2 can also occur at higher pH (~ 6) Value

Profile	Initially Added CO_2 (mM)	Initially Added NH_4OH (mM)	Measured pH	Theoretically Calculated CO_2 (ppm)	Theoretically Calculated pH
A	0.0	0.00	5.65	0.6 *	5.65
B	1.0	0.16	5.7	37	5.65
C	2.0	0.32	5.7	74	5.65
D	3.0	0.48	5.7	111	5.65
E	4.0	0.64	5.7	148	5.65

* (from CO_2 in air)





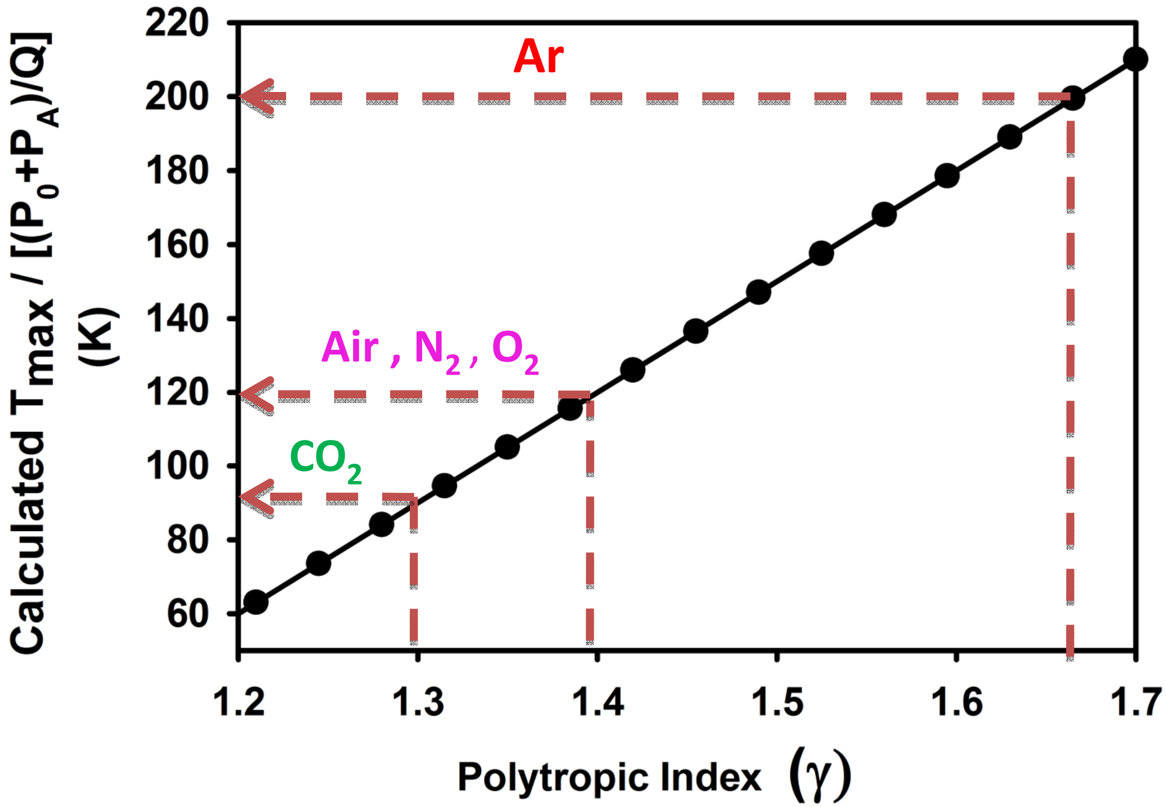
SL Generation Correlates With γ = Cp/Cv

- ***SL*** **is generated when the maximum temperature inside a bubble reaches a certain threshold value**

- ***T_{max}*** **, the Maximum temperature reached in an acoustic cavity depends on γ and is given by**

$$T_{\max} = T_0 \left[\frac{(P_0 + P_A)(\gamma - 1)}{Q} \right]$$

$$\frac{T_{\max}}{(P_0 + P_A)/Q} = T_0(\gamma - 1)$$



$T_{\max}$ = Max Temperature, Q = Initial Pressure in the Bubble,
T_0 = Initial Temperature, γ = Polytropic Index
P_A = Acoustic Pressure Amplitude,
P_0 = Pressure in Bulk Solution in Absence of Sound Waves

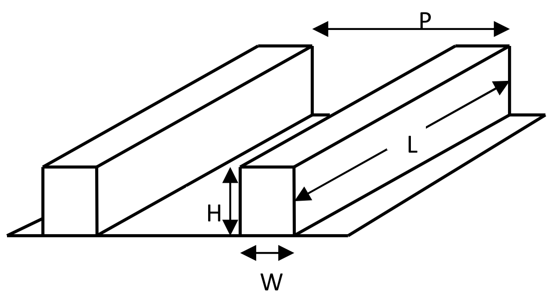
Suslick and Co-workers (*J. Phys. Chem. A 1999*) have reported T_{max} = 4000 deg C for Argon saturated water-benzene mixtures, which can be reproduced from the plot above using (P_0+P_A)/Q = 21.4 and γ = 1.67 for Argon.

Plausible Mechanisms For Reduction Of SL Signal By Carbon Dioxide

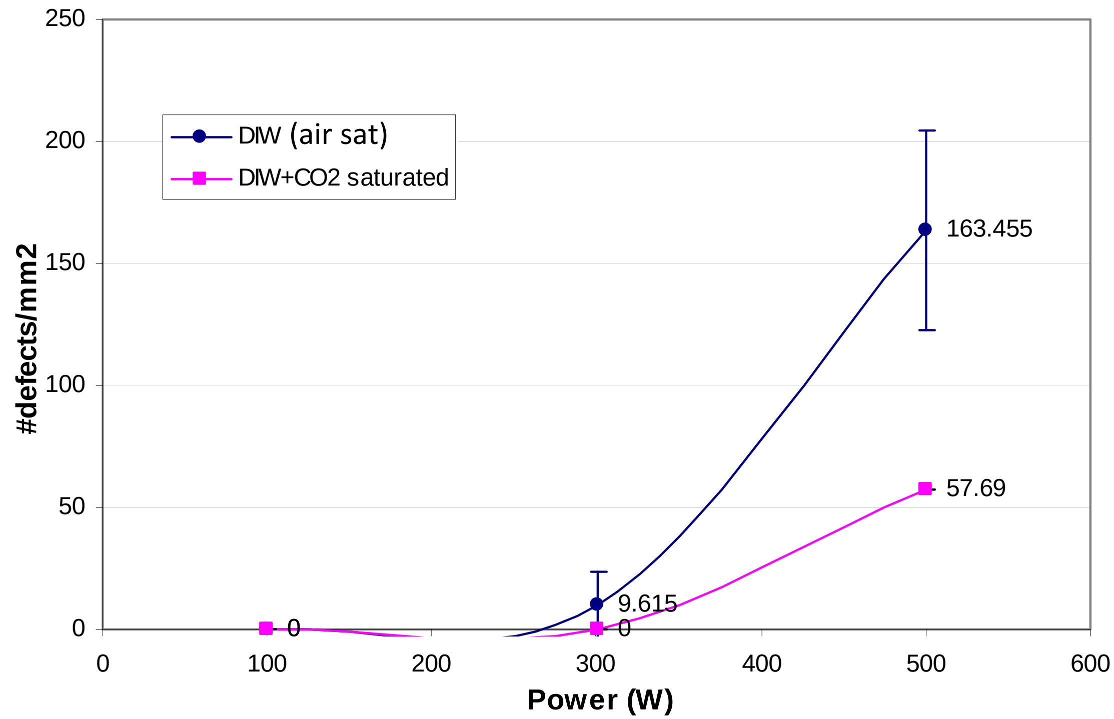
1. **The maximum temperature reached in a carbon dioxide bubble is lowest because of its low γ value.**

2. ***CO_2*** **may scavenge free radicals that may contribute in the generation of SL signal (It is a common practice to bubble CO_2 in ozonated DI water to kill free radicals and extend ozone half life)**

Effect of dissolved CO_2 on Damage to Features



Silicon on Insulator (SOI)
H = 70 nm, W = 30 nm



Courtesy of Mr. Hrishi Shende (Completed M.S degree under supervision of Prof. Srini Raghavan from Univ. of Arizona)

➢DI water saturated with CO_2 gas (1500 ppm) was used.

- Lower pattern damage was observed for CO_2 + DI water system.

Conclusions

- SL-Capability order of dissolved gases: Ar > Air ≈ N_2 ≈ O_2
- SL can be decreased gradually using O_2 Scavenger
- CO_2 has a strong inhibitory role in SL generation and suppresses SL even in presence of sufficient amounts of other SL-capable gases.
- 60 to 150 ppm CO_2 is sufficient for complete suppression of SL in Air Saturated DI Water
- NH_4HCO_3 can be acidified to release CO_2 in-situ and reduce SL (Cavitation)
- SL suppression by CO_2 can also occur at higher pH (~ 6) value

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and

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