Non-equilibrium Plasma in Multibubble Sonoluminescence

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01/2008: I was appointed at CEA / ICSM to work on sonoluminescence combined to sonochemistry

   But: building under construction, no lab

   Collaboration with MPI-KG Potsdam: there, SBSL, at ICSM, MBSL

Looking at the literature: specialists in SBSL nearby, in Göttingen

03/2008: Visit on a snowy day

T. Kurz explained me everything you should know to get started

Prof. Lauterborn was not there but I could admire some of his paintings

Akustische Blasenfallen
für die
Sonolumineszenz

Diplomarbeit
vorgelegt von
Reinhard Geisler
aus
Göttingen

angefertigt im
Dritten Physikalischen Institut
der Georg–August–Universität zu Göttingen

1998

06/2008: my first ESS (ESS-16)

Robert Mettin going from a poster to the next one and giving advice to every student

Sharing knowledge as common trait in their group?
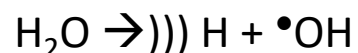
10/2011: Workshop Kavitation Drübeck

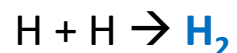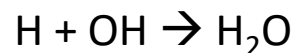Finally I met Prof. Lauterborn!

12/2013: Göttingen, experiments & visit of the labs

Acoustic cavitation & Sonochemistry

The very violent collapse of cavitation bubbles leads to the formation of a plasma
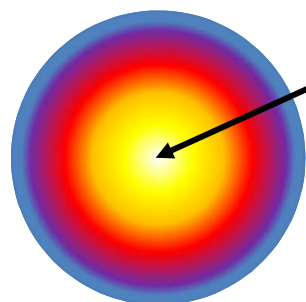**Radical generation** in the sonochemical plasma:

$$H_2O \rightarrow))) \; H + {}^{\bullet}OH$$

Subsequent recombination :

$$H + OH \rightarrow H_2O$$
$$H + H \rightarrow \mathbf{H_2}$$
$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow \mathbf{H_2O_2}$$
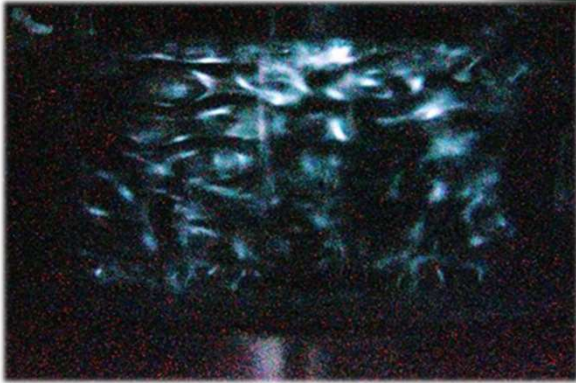
Basis of sonochemical activity in aqueous solutions

3 zones of sonochemical activity:

Hot bubble core, plasma (thousands of degrees, hundreds of bars) (< 1 µm, 100 ps)

Overheated bubble-solution interface (hundreds of degrees)

Volume of the solution

Suslick, *Science* (1990)
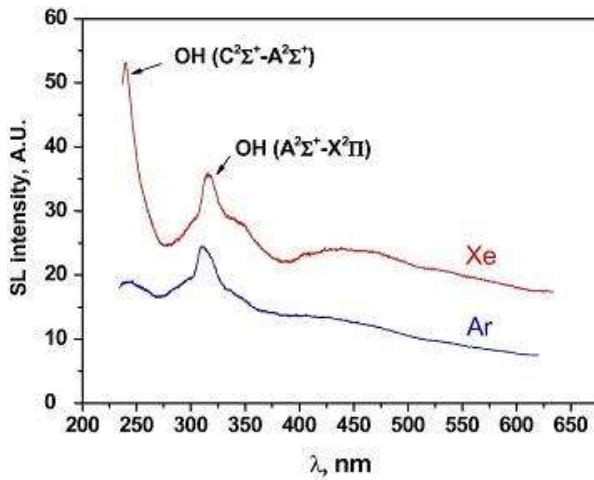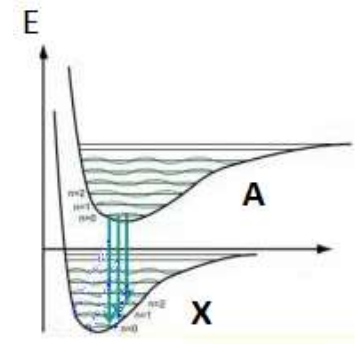
Sonoluminescence

Light emitted by the sonochemical plasma
probe of the conditions reached inside bubbles

Intense continuum + emissions from
electronically excited species

- Hints on formed species, on mechanisms
  of reactions
- Emissions are characteristic of the species
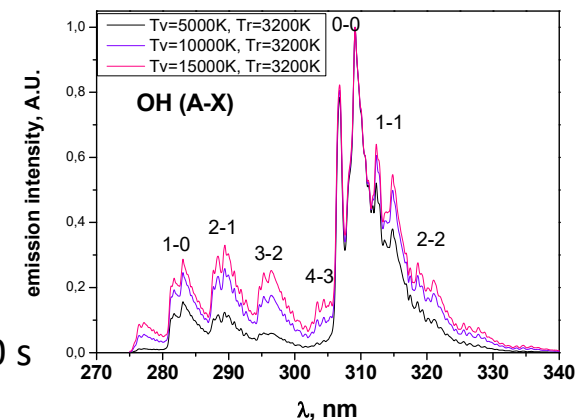 and its excitation state
  Estimation of temperatures

⚠️ Average on time and space

Wavelength in water: 4.1 mm
at 362 kHz

Typical acquisition time of a spectrum: 10-600 s
Plasma lifetime < 1 µs
US period: 50 µs at 20 kHz, 2.8 µs at 362 kHz

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Sonoluminescence

- 1933: Marinesco and Trillat observed that a photographic plate submitted to US went blurred

- 1934: Frenzel and Schultes noticed a faint luminescence, responsible for the blurring

- Many measurements (PMT…) : cyclic flashes of light, frequency-dependent etc. But averages

- Revolution in 1962 (Yosioka and Omura) - 1970 (Temple) – 1990 (Gaitan and Crum) : discovery of **single-bubble sonoluminescence (SBSL)**
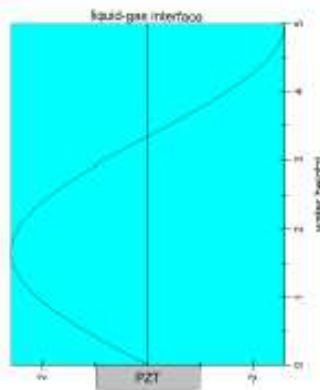

Crum, 1994

SBSL made it possible to measure bubble dynamics, light emission etc.

t(exp) 15 sec
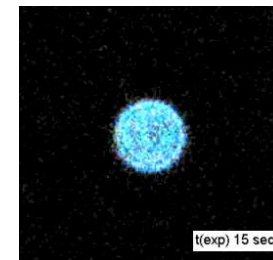
- Avoid 'natural' cavitation:
  - → degas solution to be **under the cavitation threshold**

- Introduce and stabilise a bubble
  - → bubble trap: **standing wave**

$$h = \frac{(2n+1)}{4}\lambda$$

$$\lambda = \frac{c}{f}$$

c sound speed, in water at 20°C c=1480 m.s^{-1}
f US frequency
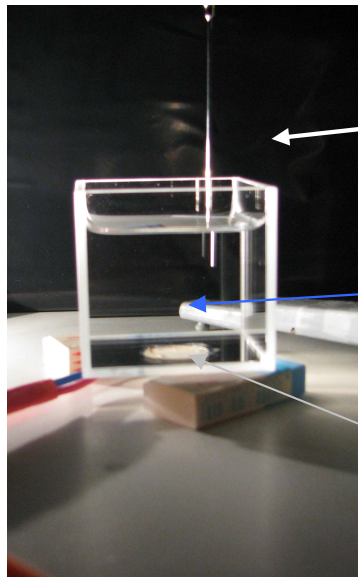At 20 kHz : λ=7.4 cm
At 300 kHz : λ=4.9 mm

By controlling the amount of dissolved gas and the acoustic pressure, it is possible to stabilise a single bubble for hours.

PhD Julia Schneider (2008-2012)

First SBSL reactor:
inspired by Göttingen

SBSL in controlled conditions:
temperature, gas nature et partial
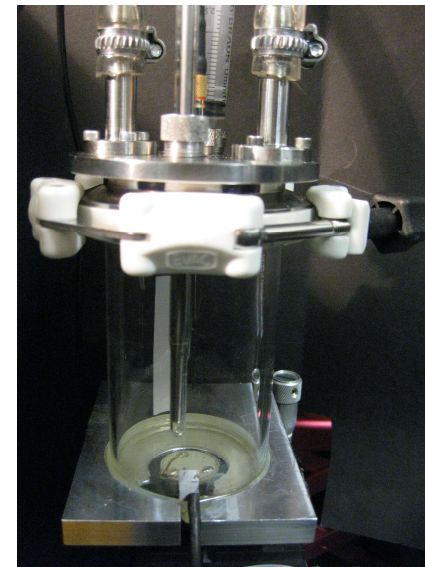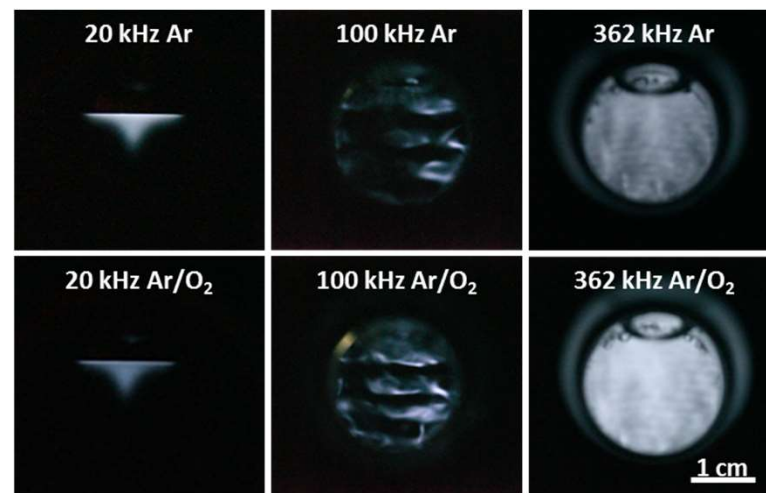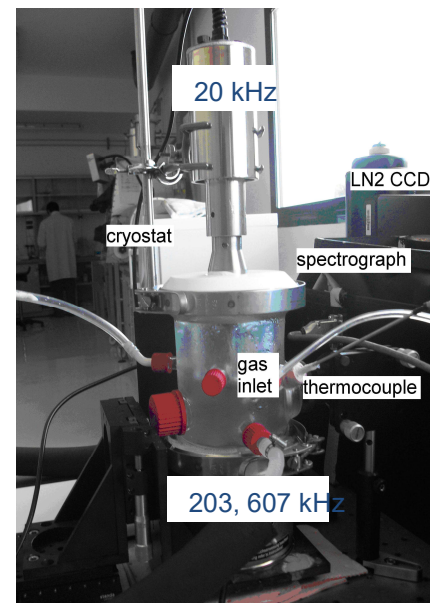pressure, acoustic pressure
106 mL; 27.6 kHz

Hydrophone

Single bubble
trapped in the
stationary wave

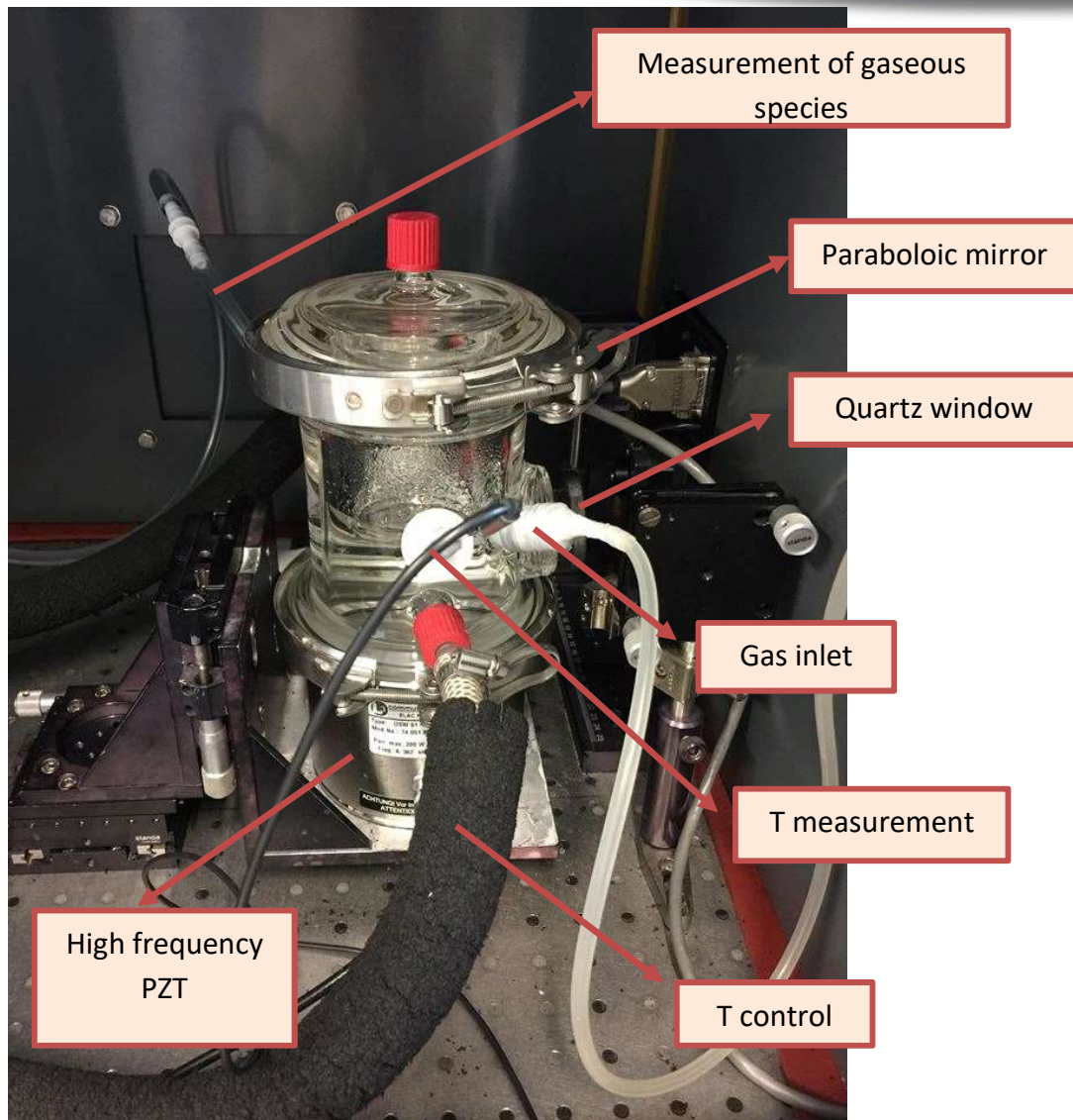Piezo-element

SBSL in water (air)
(10 s exposure time)

Measurement of gaseous species

Paraboloic mirror

Quartz window

Gas inlet

T measurement

High frequency PZT

T control

20 kHz

LN2 CCD

cryostat

spectrograph

gas inlet

thermocouple

203, 607 kHz

| 20 kHz Ar | 100 kHz Ar | 362 kHz Ar |
| 20 kHz Ar/O_2 | 100 kHz Ar/O_2 | 362 kHz Ar/O_2 |

1 cm

250 mL, continuous gas flow, 10 °C
Frequency: 20 / 100 / 200 / 362 / 600 / 1057 kHz

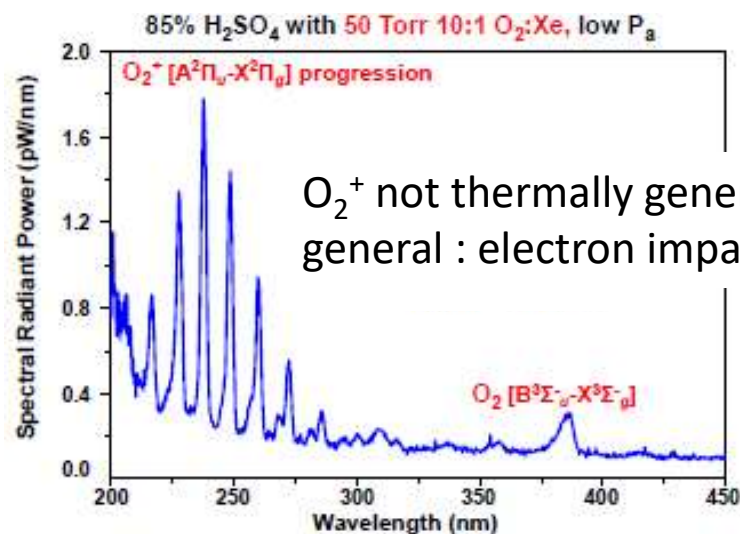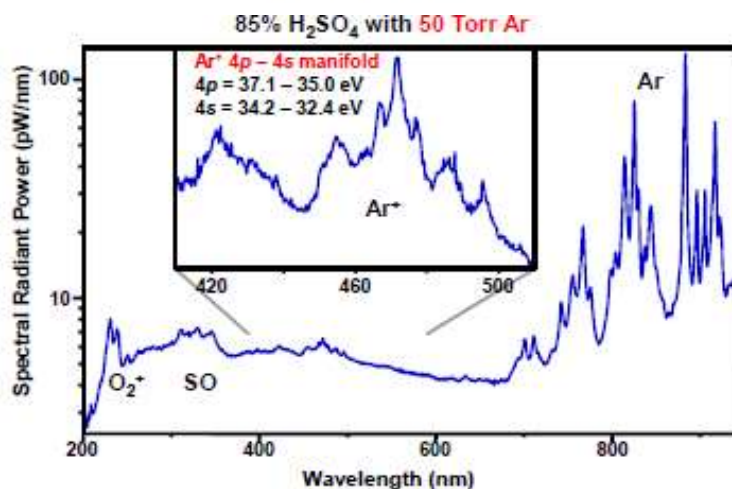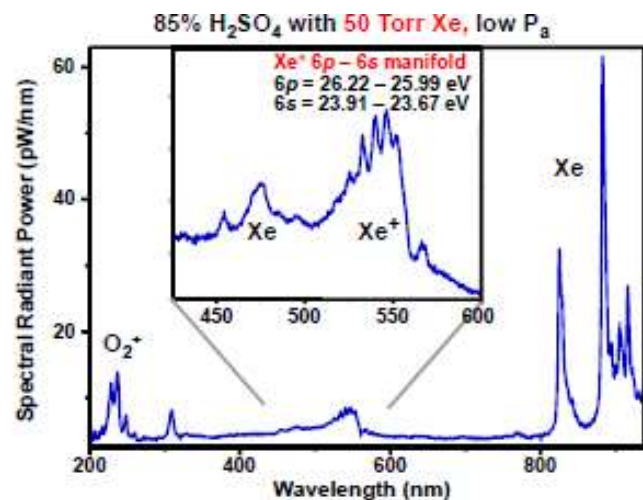Camera Lucida, common work of artists and scientists,
Göttingen (H_2SO_4, Xe)

Concentrated H$_2$SO$_4$:

exotic system far from applications
but generating beautiful spectra

Very low vapour pressure (from water)

H$_2$SO$_4$ 95 wt % : 2.10^{-3} mbar (10,000 times less than water)

$\Rightarrow$ Bubble content = dissolved (rare) gas

$\Rightarrow$ More efficient energy concentration

$\Rightarrow$ Less quenching

SBSL, 85% H$_2$SO$_4$, 67 mbar gas

Very high energy levels of emitting species

85% H$_2$SO$_4$ with 50 Torr Xe, low P$_a$

Xe* 6p – 6s manifold
6p = 26.22 – 25.99 eV
6s = 23.91 – 23.67 eV

85% H$_2$SO$_4$ with 50 Torr Ar

Ar* 4p – 4s manifold
4p = 37.1 – 35.0 eV
4s = 34.2 – 32.4 eV

85% H$_2$SO$_4$ with 50 Torr 10:1 O$_2$:Xe, low P$_a$

O$_2^+$ [A$^2\Pi_u$-X$^2\Pi_g$] progression

O$_2$ [B$^3\Sigma_u^-$-X$^3\Sigma_g^-$]
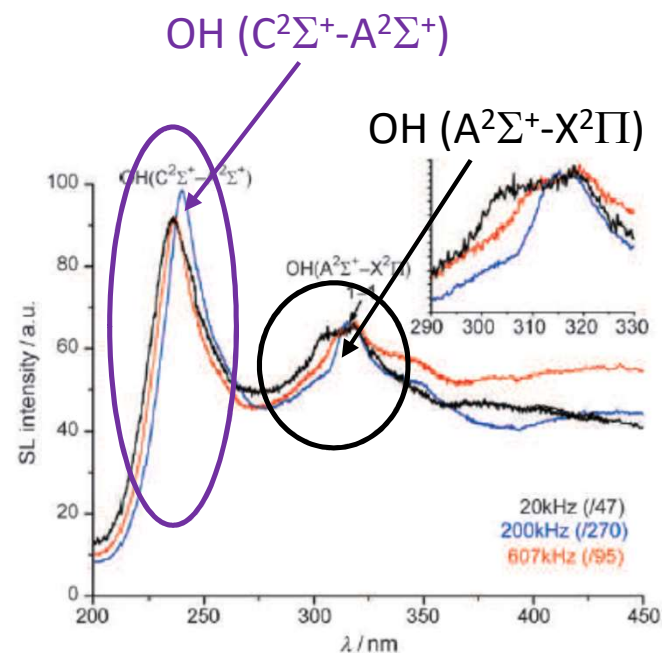
O$_2^+$ not thermally generated (in general : electron impact 50-100 eV)

Ion emission extremely rare in SL

In aqueous solutions: no ions
                          but OH (C-A) transition

OH ($C^2\Sigma^+$-$A^2\Sigma^+$)

OH ($A^2\Sigma^+$-$X^2\Pi$)

OH ($C^2\Sigma^+$-$A^2\Sigma^+$)

OH ($A^2\Sigma^+$-$X^2\Pi$)
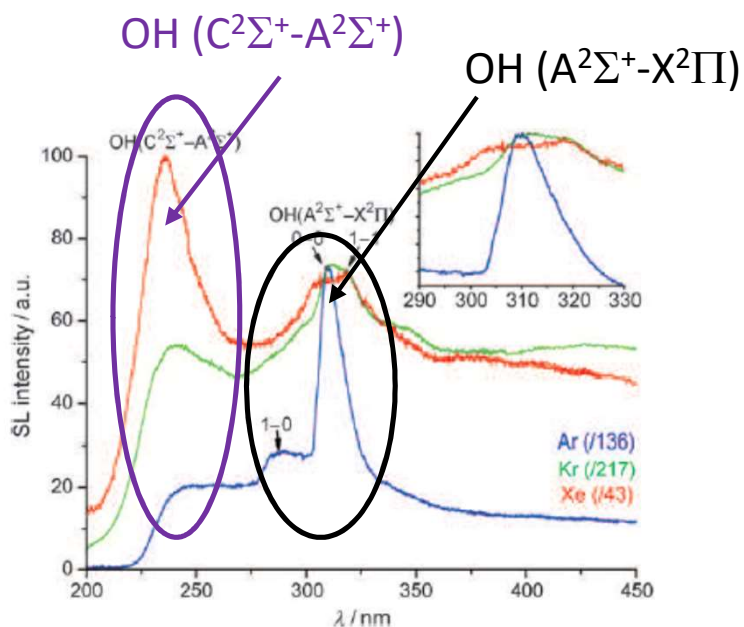
MBSL spectra H_2O, Ar/Kr/Xe, 20 kHz

MBSL spectra H_2O, Xe, 20/200/607 kHz

Intensity of OH ($C^2\Sigma^+$ - $A^2\Sigma^+$): Ar < Kr < Xe and increases with the US frequency

Emission never observed in flames,

  only in **discharges** through water vapor *(Shuaibov, Technical Phys. 2009)*,

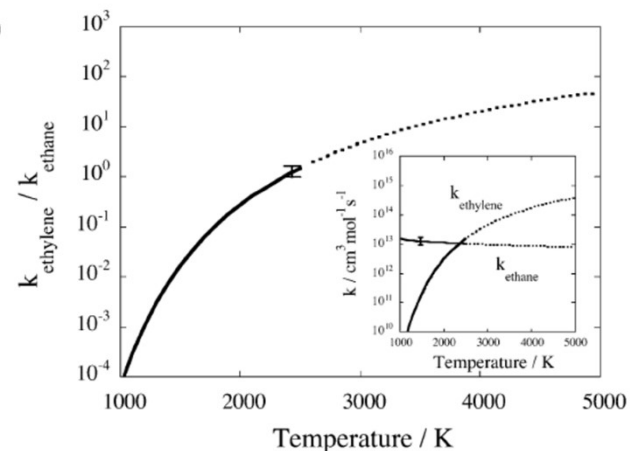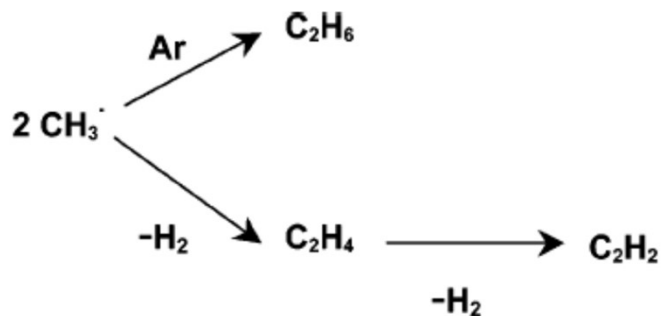 and in γ-**irradiated water** *(Sitharamarao, j. Phys. Chem. 1963)*

Sonoluminescence spectroscopy in aqueous solutions:
what temperatures are estimated?

Mean bubble temperature

Ciawi et al.: Aqueous solutions of *tert*-butanol, Ar

Methyl radical recombination method: temperature estimated from the kinetics of recombination reactions (thermal equilibrium assumed)

Extrapolation of the temperature to zero concentration:

US frequency, kHz	Chemical temperature, K
20	3400 ± 200
355	4300 ± 200
1056	3700 ± 200

Measurement but:
- "*mean chemical temperature*": spatial and temporal resolutions not well defined
- parallel reaction pathways neglected

Sonoluminescence is emitted at the last stage of collapse
It reflects the most extreme conditions reached

First approach = **temperature derivation from the SL continuum shape**
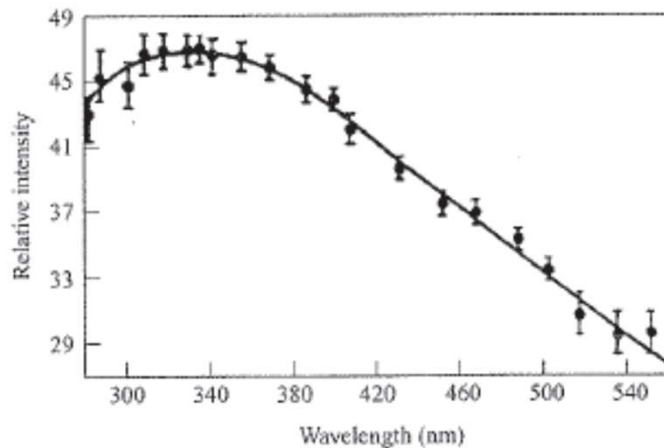Approach particularly used in SBSL measurements

Figure 4.1   Spectral distribution for oxygen-saturated water. Solid line is the theoretical curve for black-body temperature of 8800 K. (Srinivasan and Holroyd (1961).)
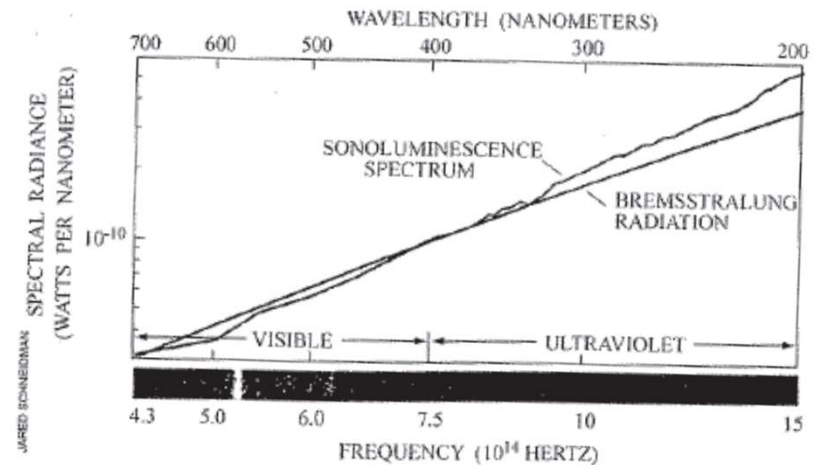

Figure 4.4a   Spectrum of sonoluminescence shows that most of the emitted light is ultraviolet. As pointed out by Paul H. Roberts and Cheng-Chin Wu of the University of California at Los Angeles, the signal compares closely with bremsstrahlung radiation – that is, light emitted by a plasma at 100,000 K. (Putterman (1995).)
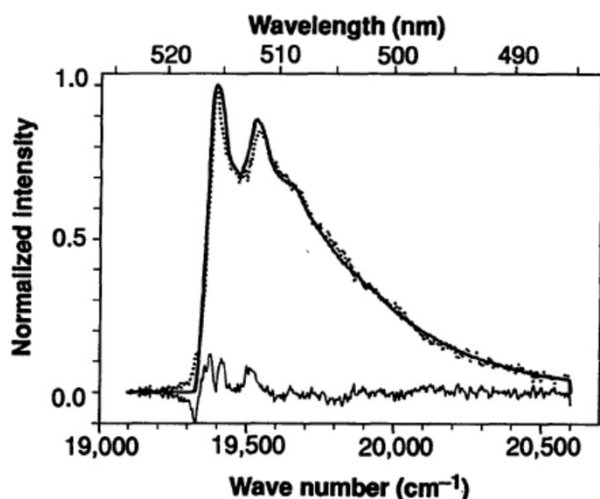
Black-body: 8800 K   Bremsstrahlung: 100,000 K

Highly model dependent!
And: why should there be only one contribution to the continuum?

Molecular emissions provide a more direct approach since their shape reflects their excitation level (i.e. the relative populations of excited levels).

The temperature of cavitation,
Flint & Suslick (1991)
= the first one
Silicon oil, Ar, 20 kHz
C_2 Swan bands

Hot spot conditions during cavitation in water, Didenko et al (1999)
Rare example in aqueous solutions
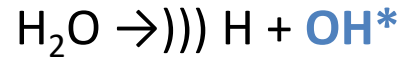Benzene aq. solution, 20 kHz, Ar
C_2 Swan bands

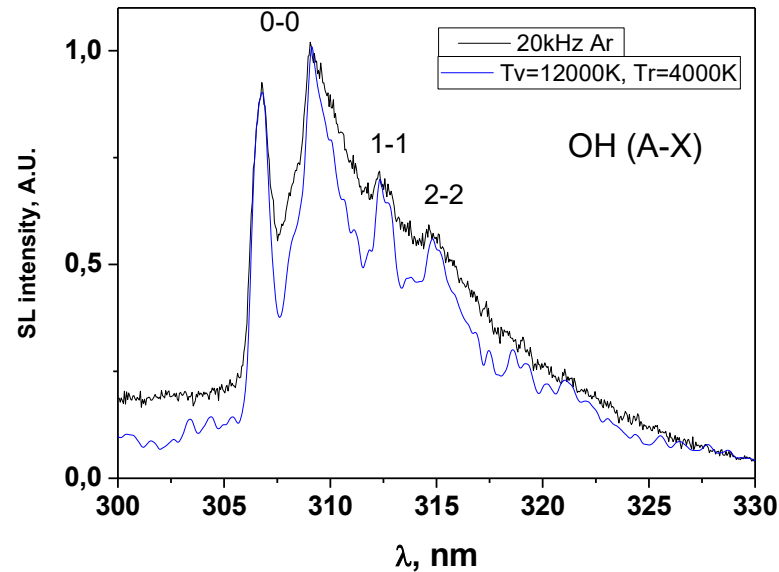Unicity of temperature was assumed
5075 ± 156 K
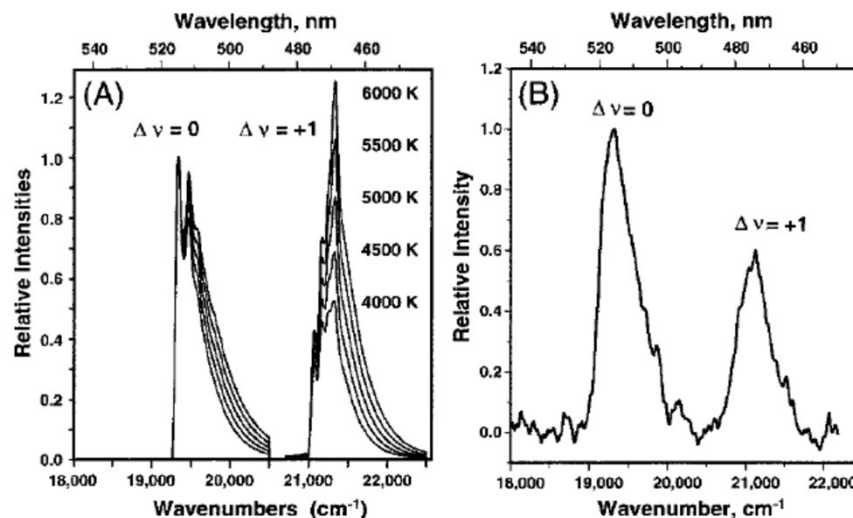
Unicity of temperature was assumed
4300 ± 200 K

SL spectroscopy of water, Ar, 20 kHz

$$H_2O \rightarrow))) H + OH*$$

OH (A-X) emission
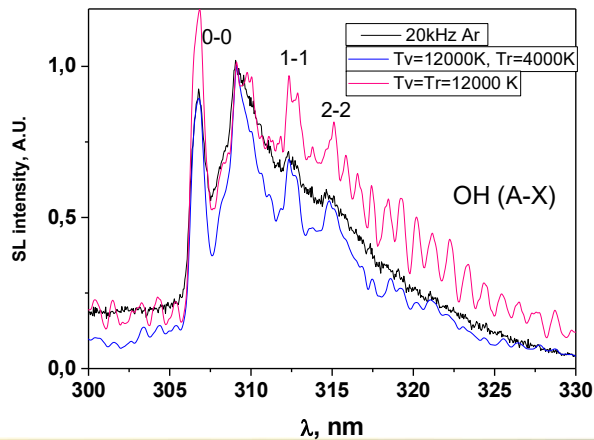
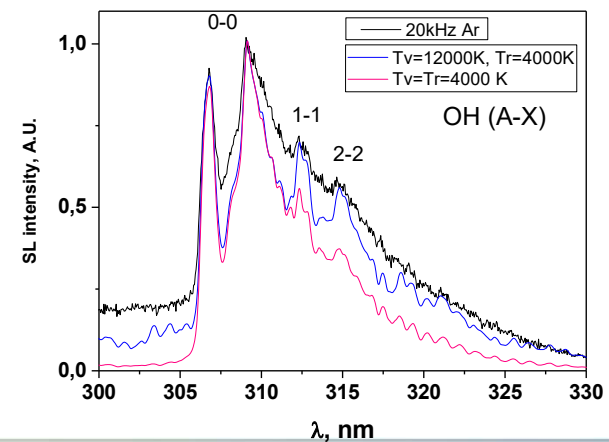Simulations realized with Specair software

Assuming p = 500 bar

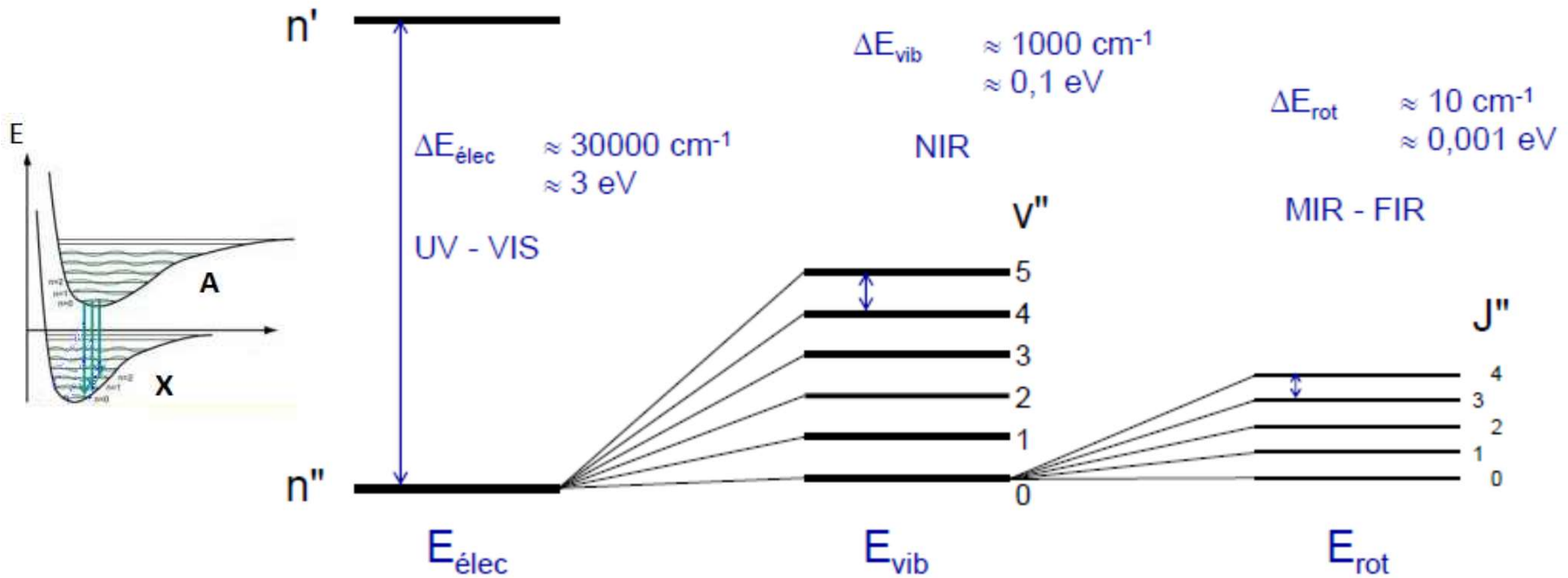**Need to introduce different temperatures!**

$T_v = 12000$ K, $T_r = 4000$ K

For $T_v = T_r = 12000$ K

For $T_v = T_r = 4000$ K

Electronic levels
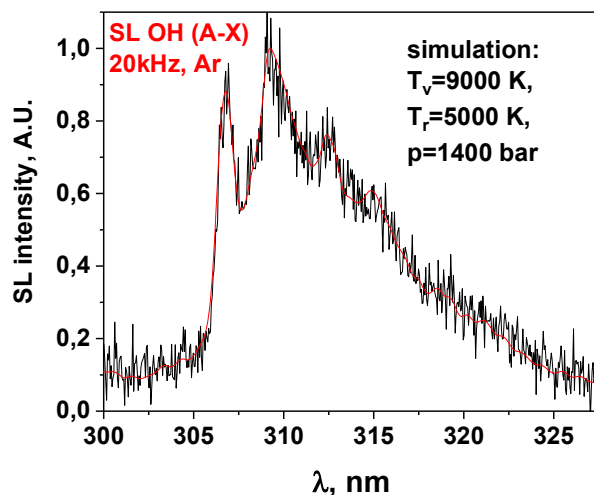Relative population of each determined by the electronic temperature T_e

Vibrational levels
Relative population of each determined by the vibrational temperature T_v
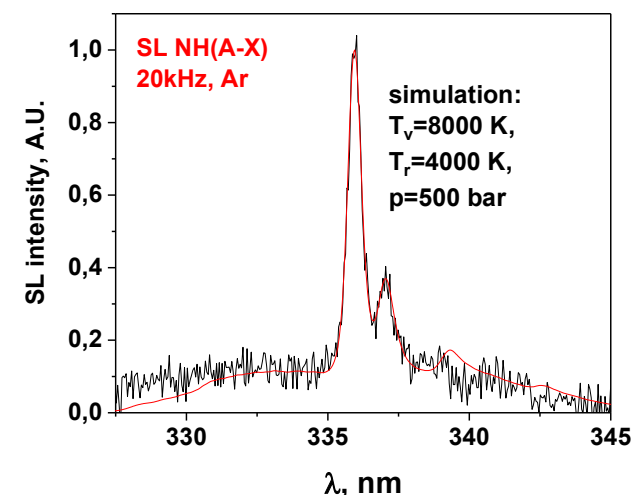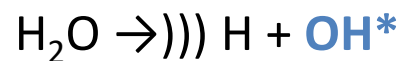
Rotational levels
Relative population of each determined by the rotational temperature T_r

If time scales are too short, thermal equilibrium is not reached
**General case in a non-equilibrium plasma: $T_e > T_v > T_r \sim T_{gas}$**

SL OH (A-X) 20kHz, Ar

simulation: T$_v$=9000 K, T$_r$=5000 K, p=1400 bar

0.1 M NH$_3$·H$_2$O, Ar

2 molecular emissions:

OH (A-X) & NH (A-X)

$$H_2O \rightarrow))) H + OH^*$$

$$NH_3 \rightarrow))) NH^* + 2 H$$

SL NH(A-X) 20kHz, Ar

simulation: T$_v$=8000 K, T$_r$=4000 K, p=500 bar

transition	US frequency	$T_v \pm 1000$	$T_r \pm 500$	p, bar
NH (A$^3\Pi$-X$^3\Sigma^-$)	20 kHz	7000 K	4000 K	500 ± 50
OH (A$^2\Sigma^+$-X$^2\Pi$)	20 kHz	9000 K	5000 K	1400 ± 200
OH (A$^2\Sigma^+$-X$^2\Pi$) in water	20 kHz	12000 K	4000 K	1400 ± 200

$T_v > T_r$: non-equilibrium plasma, as in H$_2$O, Ar

Good agreement between OH & NH temperatures
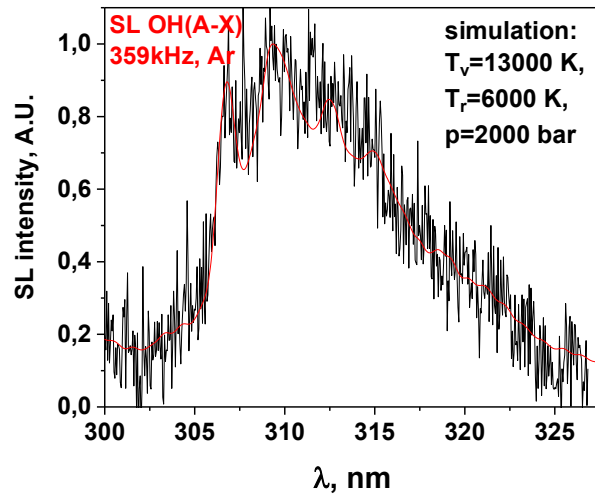
Lower T_v in ammonia solution compared to water

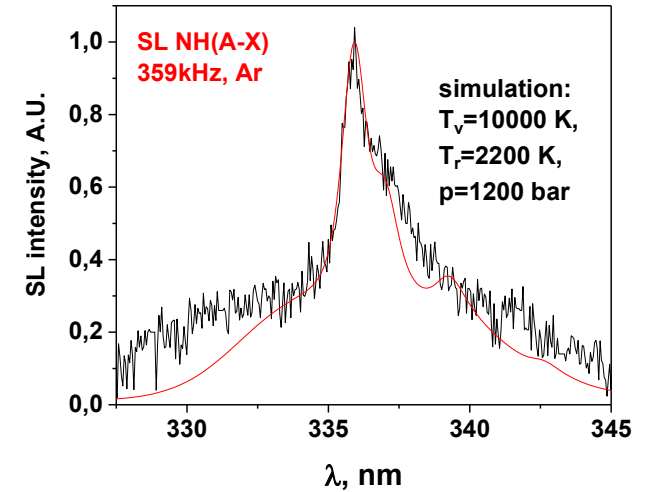0.1 M t-BuOH, Ar, 20 kHz, 11°C
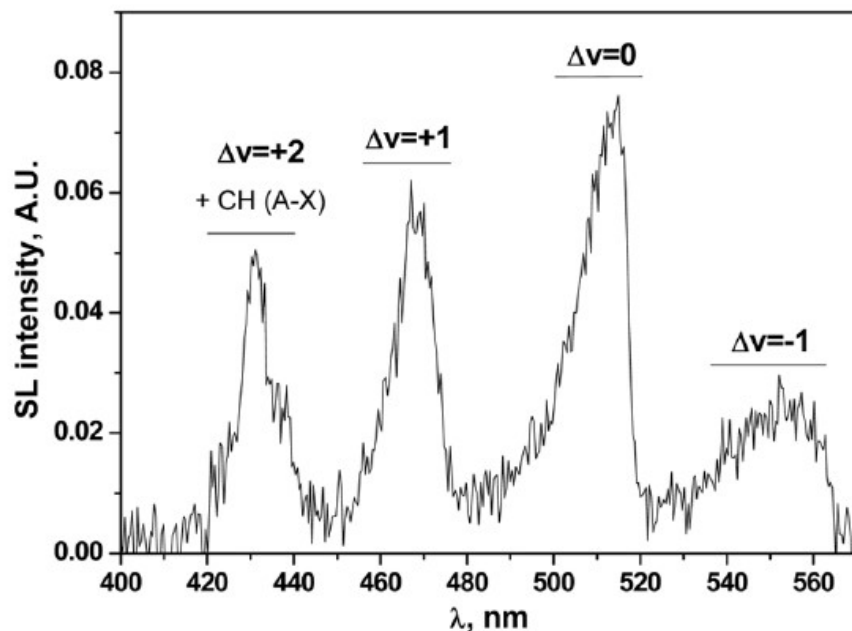
[t-BuOH] = 0.05 – 0.4 M

SL spectra present **C$_2$ Swan bands**
C$_2$ (d$^3\Pi_g$ – a$^3\Pi_u$)

Solution	transition	US frequency	T$_v$ ± 1000	T$_r$ ± 500
water	OH (A$^2\Sigma^+$-X$^2\Pi$)	20 kHz	12000 K	4000 K
NH$_3$.H$_2$O	NH (A$^3\Pi$-X$^3\Sigma^-$)	20 kHz	7000 K	4000 K
	OH (A$^2\Sigma^+$-X$^2\Pi$)	20 kHz	9000 K	5000 K
Tert-butanol	C$_2$ (d$^3\Pi_g$ – a$^3\Pi_u$)	20 kHz	6300 K	4800 K

0.1 M NH$_3$·H$_2$O, Ar
359 kHz

OH (A-X) & NH (A-X)
emissions

transition	US frequency	T$_v$, K	T$_r$, K	p, bar
NH (A$^3\Pi$-X$^3\Sigma^-$)	359 kHz	10000 ± 1000	2200 ± 500	1200 ± 100
OH (A$^2\Sigma^+$-X$^2\Pi$)	359 kHz	13000 ± 2000	6000 ± 1000	2000 ± 500

$T_v > T_r$
Good agreement between OH & NH temperatures

8.5 10^{-4} M t-BuOH, Ar, 362 kHz, 5°C
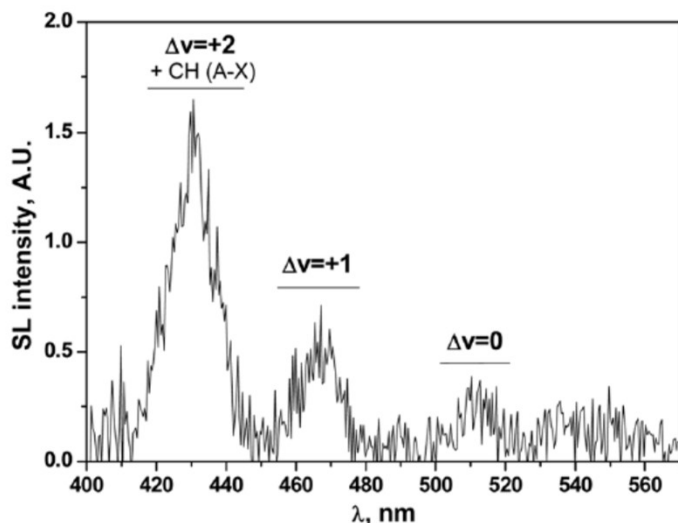
[t-BuOH] = 1.10^{-3} – 5.10^{-3} M; 362 kHz

SL spectra present C$_2$ Swan bands
C$_2$ (d$^3\Pi_g$ – a$^3\Pi_u$)

Solution	transition	US frequency	T$_v$ ± 1000	T$_r$ ± 1000
NH$_3$.H$_2$O	NH (A$^3\Pi$-X$^3\Sigma^-$)	359 kHz	10000 K	2200 K
	OH (A$^2\Sigma^+$-X$^2\Pi$)	359 kHz	13000 K	6000 K
Tert-butanol	C$_2$ (d$^3\Pi_g$ – a$^3\Pi_u$)	359 kHz	6300 K	4800 K
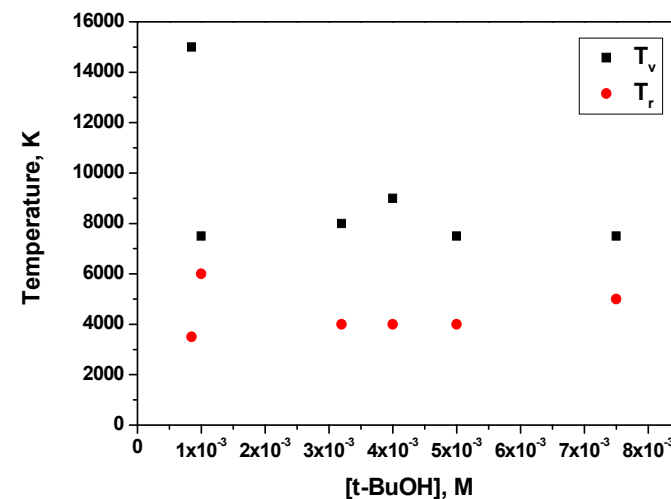
The presence of volatile solutes induces a decrease in T$_v$, in agreement with observations made on ammonia solutions.

What about the pressure estimation?

Two experimental techniques to determine pressure / intrabubble density:

➢ **Shift in wavelength**

- Lepoint-Mullie (*Ultrason Sonochem* 2001) (Rb*, 20 kHz, Ar) : $d_{rel} = 18 \pm 2$
- McNamara (*Nature* 1999) (Cr*, 20 kHz, Ar, silicone oil) : $d_{rel} = 19 \pm 2$

(corresponding to 300 bar at 4700 K)
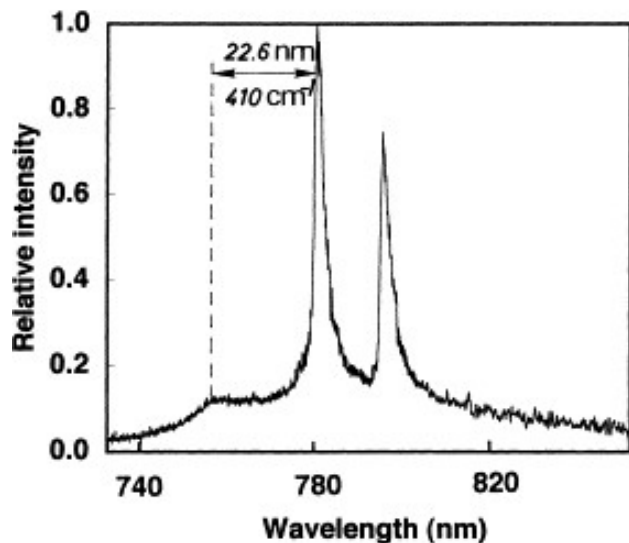
|		Transitions in Ar gas			
		$^2P_{3/2}-^2S_{1/2}$		$^2P_{1/2}-^2S_{1/2}$	
		(nm)	(cm^{-1})	(nm)	(cm^{-1})
Shift					
	H_2O	0.41	6.7	0.56	8.9
	1-octanol	0.58	9.5	0.67	10.6
		$\times 10^{-26}$ (m^{-3}) (amagats)		$\times 10^{-26}$ (m^{-3}) (amagats)	
Density					
	H_2O	4.2	15.7	5.0	18.7
	1-octanol	5.4	20.2	5.6	20.9

Lepoint-Mullie (*Ultrason Sonochem* 2001)

➤ **Peak broadening** (present approach also)

- Hypothesis: pressure = main source of peak broadening

- Sehgal (*J Chem Phys* 1979) (Na*, 460 kHz, Ar): d_{rel} = 36-50

- Choi (*J Phys Chem B* 2008) (Na*, 138 kHz, Ar): d_{rel} = 59,5 (i.e. 880 bar for 4300 K)

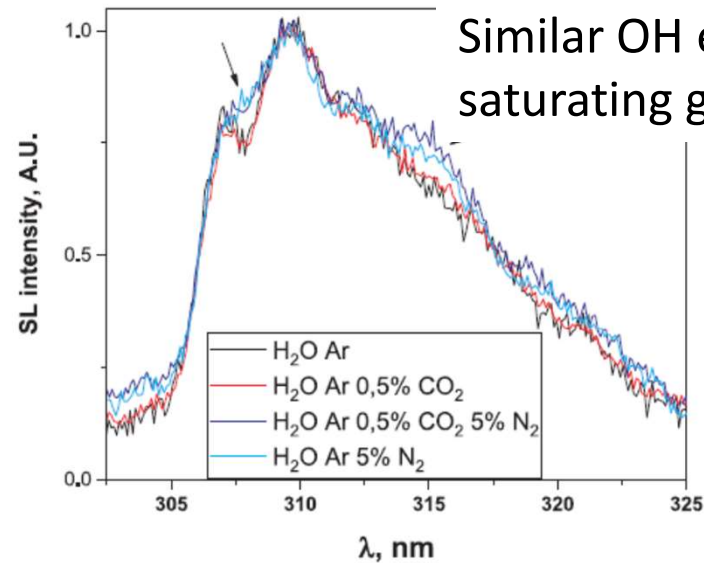- Kazachek (*Techn Phys Lett* 2009) (Na*, 22/44 kHz, Ar): 800-1200 bar

Obtained values are much higher! >> d_{rel} = 18 ± 2 given by Lepoint-Mullie

Other source of peak broadening?
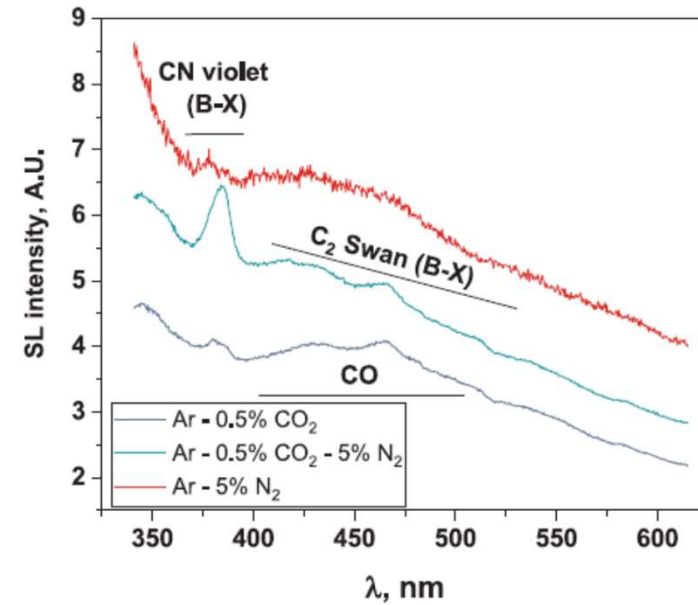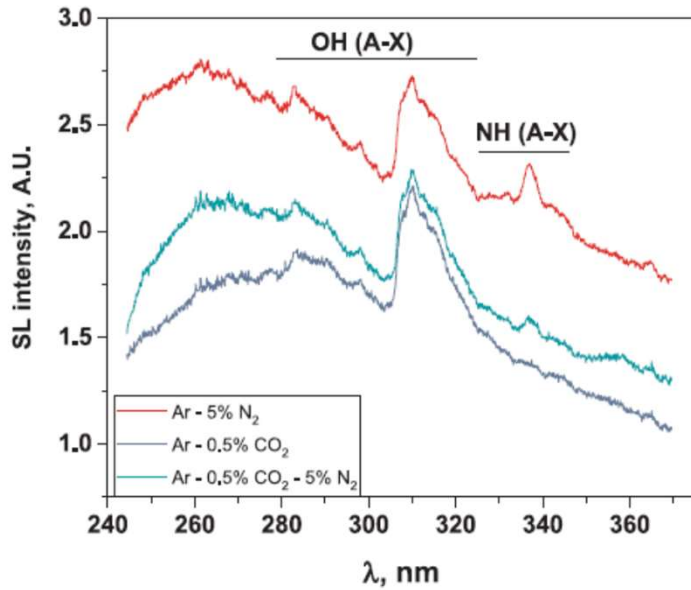
Observed emissions:
Ar: OH
Ar – 5% N_2: OH, NH
Ar – 0.5% CO_2: OH, CO, (CN)
Ar – 0.5% CO_2 – 5% N_2: OH, C_2, CN

Similar OH emission for all saturating gases

→ Emissions attributed to NH (c-a) and N_2 (C-B) prevent fitting of OH in some cases

Specair software; T_v, T_r ± 1000 K; P_{eff} ± 300 bar

gas	OH	NH	C_2	CN
Ar	9,000 K / 6,500 K / **1,000 bar**			
Ar – 5% N_2		10,000 K / 10,000 K / **4,000 bar**		
Ar – 0.5% CO_2 – 5% N_2			22,000 K / 5,000 K / **6,000 bar**	10,000-15,000 K / 10,000 K / **10,000 bar**

Large discrepancy in the obtained p_{eff} value depending on the considered species

This value of **effective pressure quantifies the broadening** of the emissions.
It is **not a real pressure.**

Another source of peak broadening, the **perturbation by the charged species present in the plasma (Stark effect) must be taken into account**

Neutral species → pressure broadening

Charged species → Stark broadening
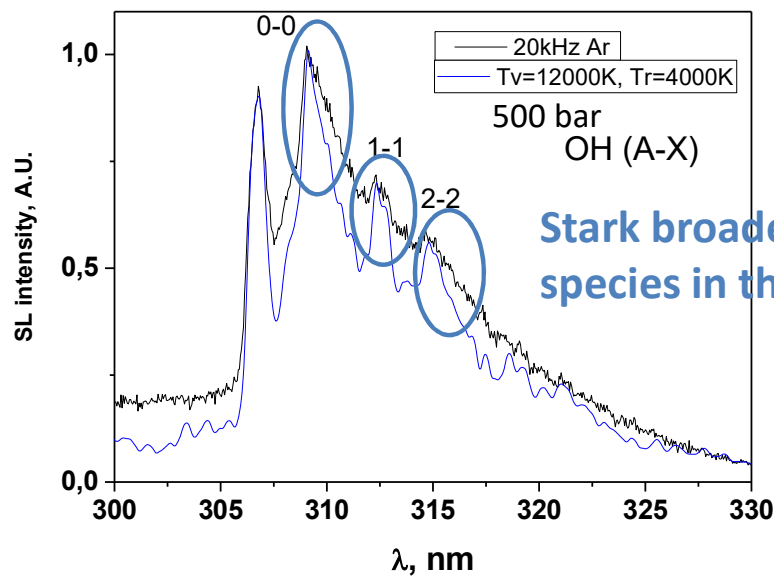
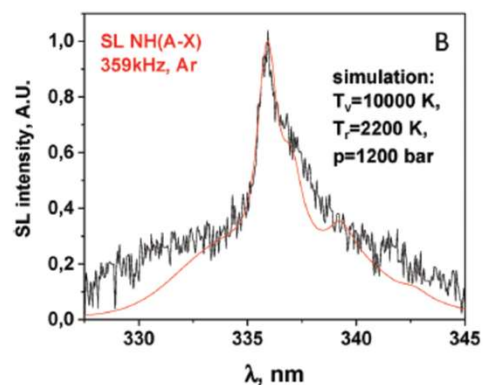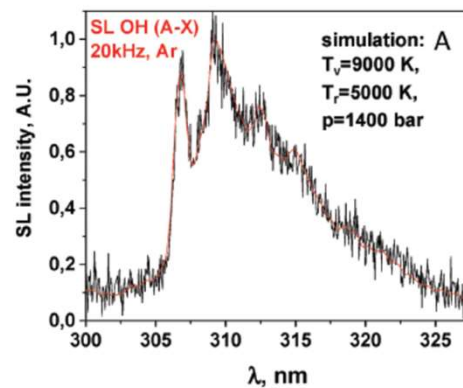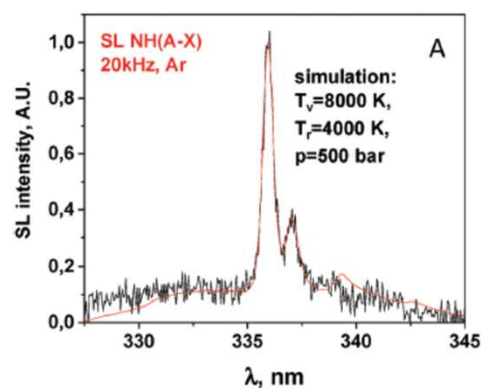**Stark broadening: mark of the charged species in the plasma**

Approach previously adopted in SBSL by Flannigan (*Phys Rev Lett* 2006) (Ar*, H_2SO_4)

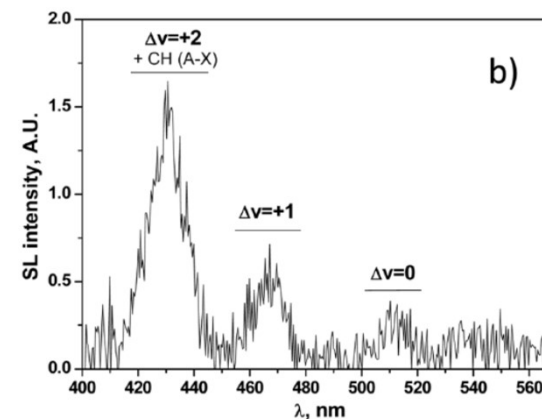Molecular emissions (MBSL, H_2O) much more complex to model (lack on tabulated data on Stark parameters)

Strong broadening of emissions at HF

Estimated T_v (Specair) HF > BF

More ionized plasma at HF

Fig. 5: Molecular emission of OH ($A^2\Sigma^+$-$X^2\Pi$) and NH ($A^3\Pi$-$X^3\Sigma^-$) in SL spectra of 0.1 M ammonia solutions sonicated under Ar at 20 kHz and 359 kHz, and their simulations with Specair
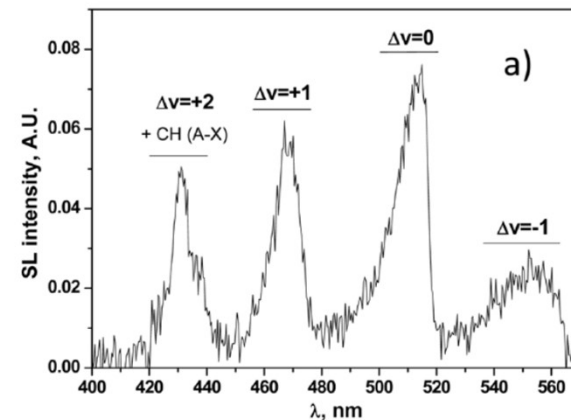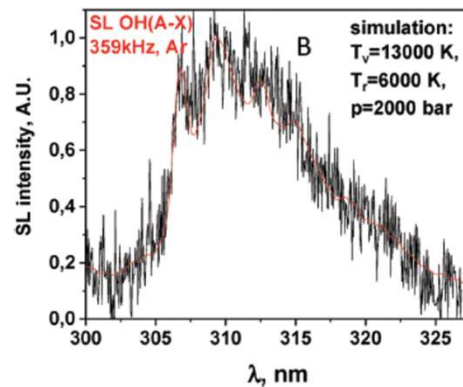
20 kHz :
6300 /
4800 K

362 kHz :
8000 /
4000 K

t-BuOH aq, 20 kHz 0,1M Ar (a) &
362 kHz 8,5 10^{-4}M Ar (b)

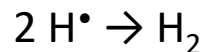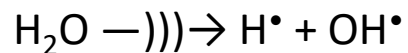Pflieger et al, PCCP 2017
Pflieger et al, J Phys Chem B, 2015

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Link SL spectra – sonochemical activity

Luminol sonochemiluminescence

	20 kHz	100 kHz	362 kHz
Ar			
Ar-20%O$_2$			

Under Ar:

$H_2O \, —))) \rightarrow H^\bullet + OH^\bullet$

$2 \, H^\bullet \rightarrow H_2$

$2 \, OH^\bullet \rightarrow H_2O_2$

In the presence of O$_2$:

$O_2 + H^\bullet \rightarrow HO_2^\bullet$

$2 \, HO_2^\bullet \rightarrow H_2O_2 + O_2$

$O_2 \, —))) \rightarrow 2 \, O$ \quad (5.15 eV/bond)

$O + H_2O \rightarrow 2OH^\bullet$

$O + H^\bullet \rightarrow OH^\bullet$
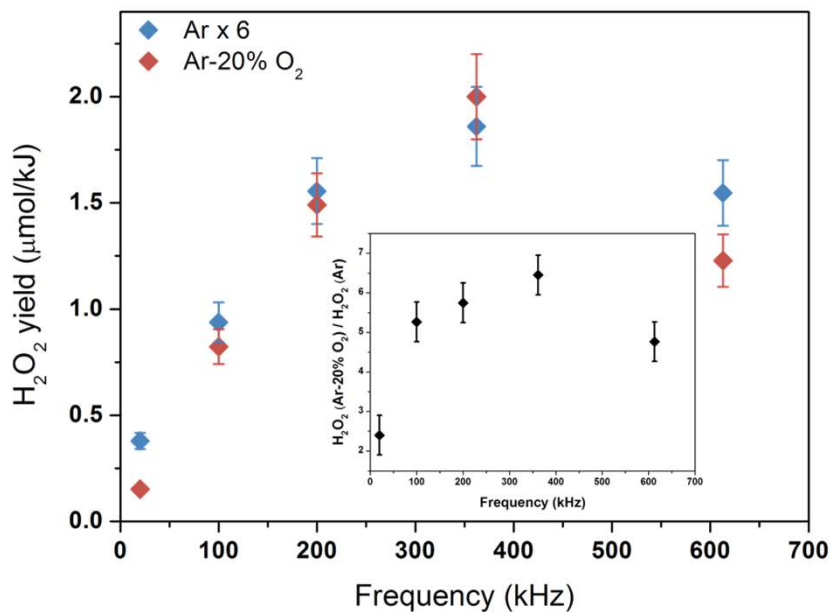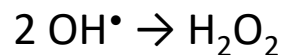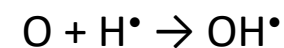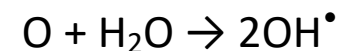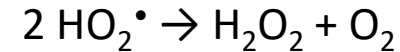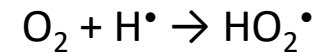
Higher increase in H$_2$O$_2$ yield at à HF

Pflieger et al., Ultrason Sonochem 2015
Ji et al., *J Phys Chem C* 2018

Adding 20%O$_2$ in Ar: LF: H$_2$O$_2$ ↑, SL ↓

HF: H$_2$O$_2$ ↑, SL ↑

$O_2 + H^\bullet \rightarrow HO_2^\bullet$

$2\ HO_2^\bullet \rightarrow H_2O_2 + O_2$

$O_2 \ -)))\rightarrow 2\ O$ (5.15 eV/bond)
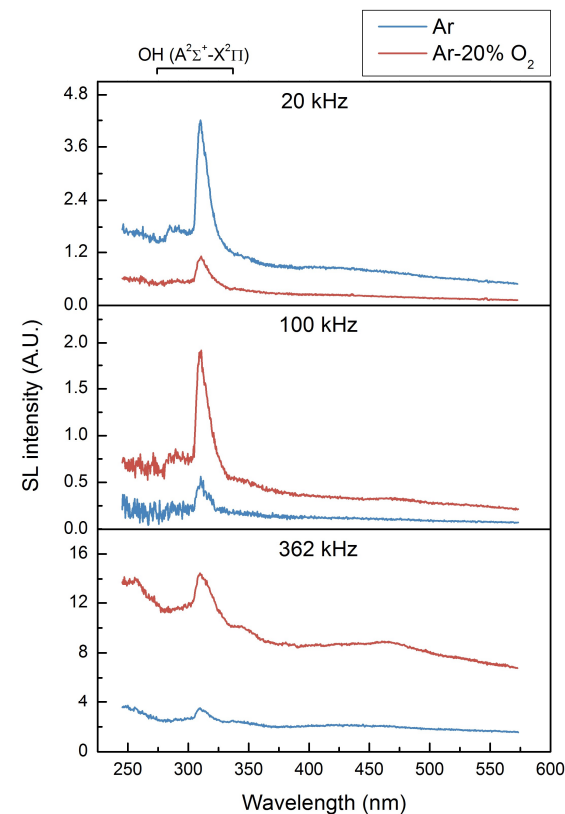
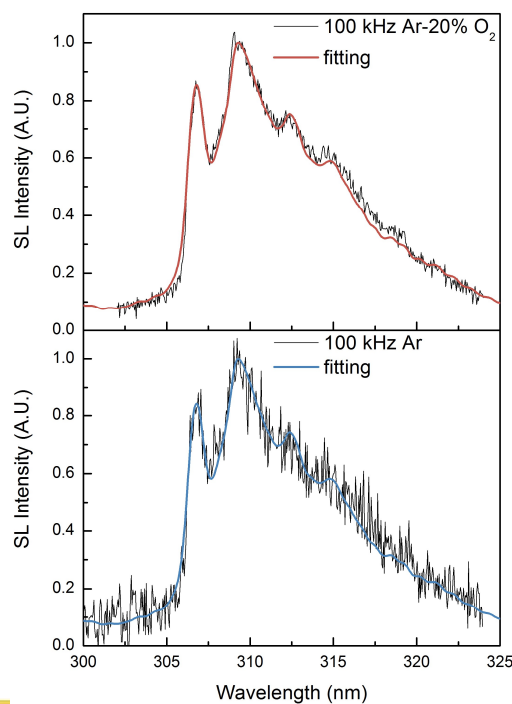$O + H_2O \rightarrow 2OH^\bullet$
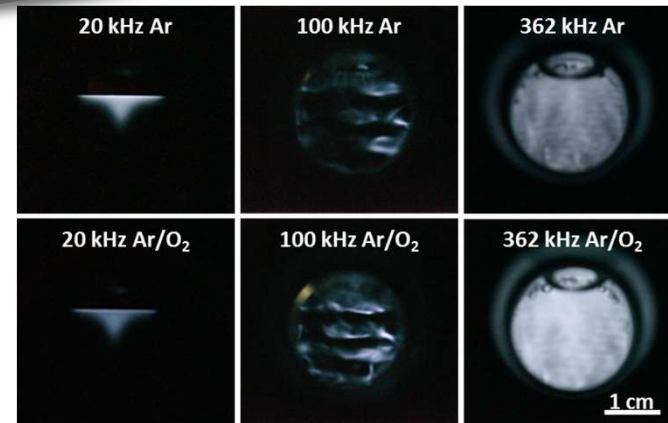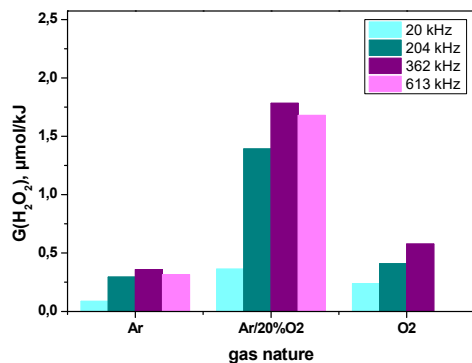
$O + H^\bullet \rightarrow OH^\bullet$
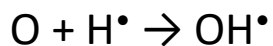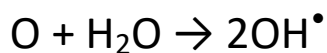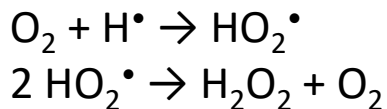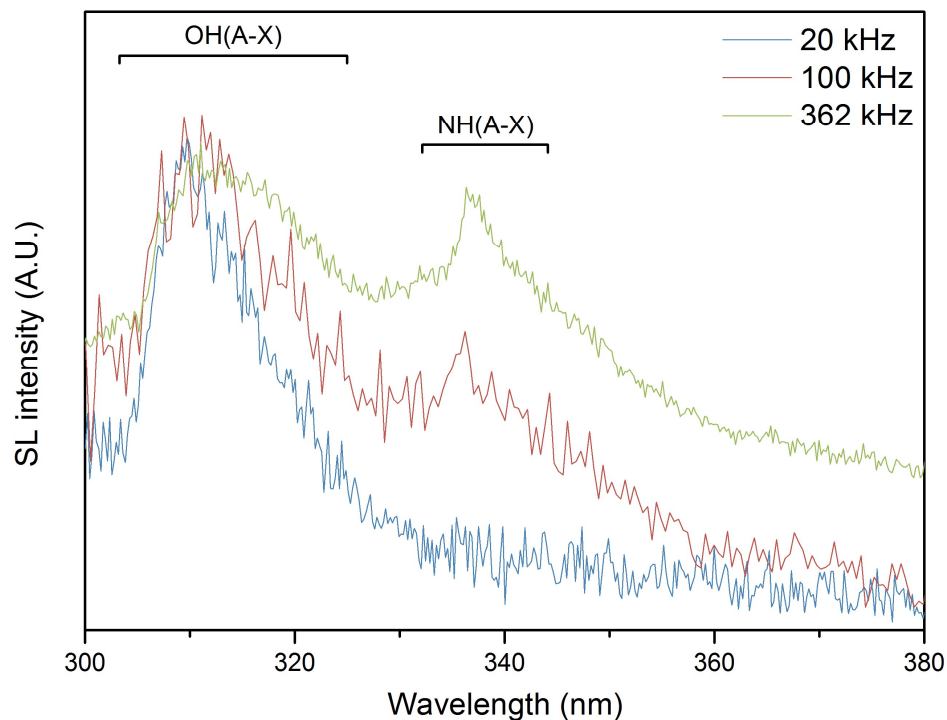
At HF: O$_2$ dissociation gets important

➢ Different degradation mechanisms can be observed at HF and LF

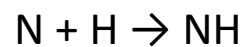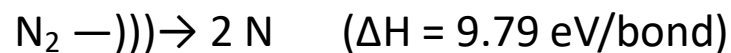Different formation pathways for OH result in different T$_v$

	Ar	Ar/O$_2$
100 kHz T$_v$, K	6500 ± 500	7250 ± 250
T$_r$, K	4750 ± 250	5200 ± 200

Pflieger et al., *Ultrason. Sonochem.* (2015)
Ji et al., *J Phys Chem C* 2018

Water Ar-20%N_2
MBSL spectra

20 kHz (P_{ac} = 33 W)
100 kHz (P_{ac} = 40 W)
362 kHz (P_{ac} = 43 W)
18° C, 100 mL.min^{-1} Ar/(20 vol.%)N_2

$$N_2 \,—)))\rightarrow 2\,N \qquad (\Delta H = 9.79 \text{ eV/bond})$$

$$N + H \rightarrow NH$$

$$N + H_2 \rightarrow NH + H$$

Dissociation of N_2 at high and intermediate frequencies (≥ 100 kHz)

Non-equilibrium sonochemistry?

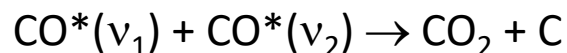20 kHz sonication of **water saturated with Ar - 20% CO**:

$$CO + OH \rightarrow CO_2 + H$$
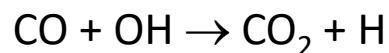
But also formation of a solid similar to $(C_3O_2)_n$ polymer

$$CO^*(\nu_1) + CO^*(\nu_2) \rightarrow CO_2 + C$$

$$C + CO(\nu_0) + Ar \rightarrow CCO + Ar$$

$$CCO + CO(\nu_0) + Ar \rightarrow C_3O_2 + Ar$$

$$n\ C_3O_2 \rightarrow (C_3O_2)_n$$
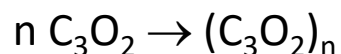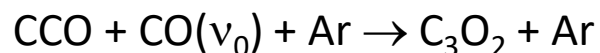
**A sound reaction**: The ultrasonically driven disproportionation of CO in water causes formation of hydrated polymer of carbon suboxide $(C_3O_2)_n$ (see picture) enriched with a heavy ^{13}C isotope. This finding indicates the presence of vibrationally excited CO molecules with a non-equilibrium Treanor distribution inside the cavitating bubble.

20 nm
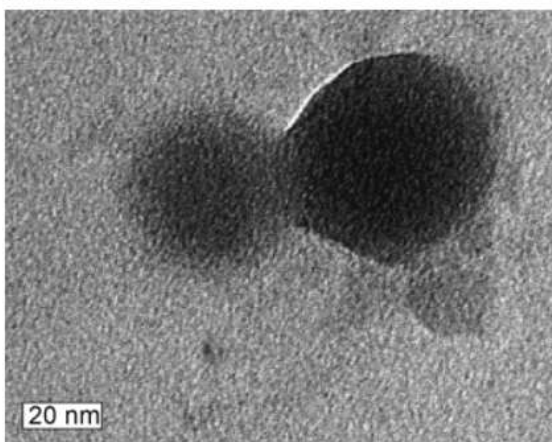
$(C_3O_2)_n$ **solid enriched in ^{13}C isotope**
Non equilibrium

At **equilibrium, enrichment with light isotope** expected: it reacts faster due to its higher zero vibrational level energy.

Here the reaction occurs via **vibrational excitation**: heavier isotopes have higher T_v.
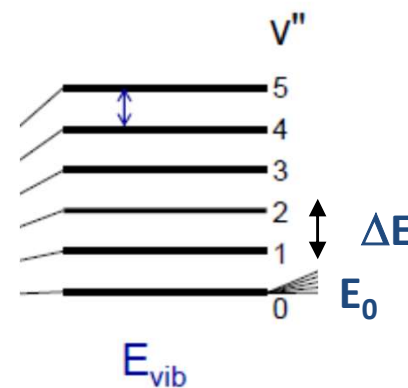
20 kHz sonolysis of **H_2O/D_2O mixtures saturated with Ar / Xe**

Measurement of H_2, D_2, HD in the gas phase (MS)

$$\boxed{\text{H/D isotope separation factor } \alpha}$$

$$\alpha = \frac{\left(\frac{H}{D}\right)_{product}}{\left(\frac{H}{D}\right)_{initial}} = \frac{\left(\dfrac{I(H_2) + \frac{1}{2}I(HD)}{I(D_2) + \frac{1}{2}I(HD)}\right)}{\left(\dfrac{H_2O}{D_2O}\right)}$$
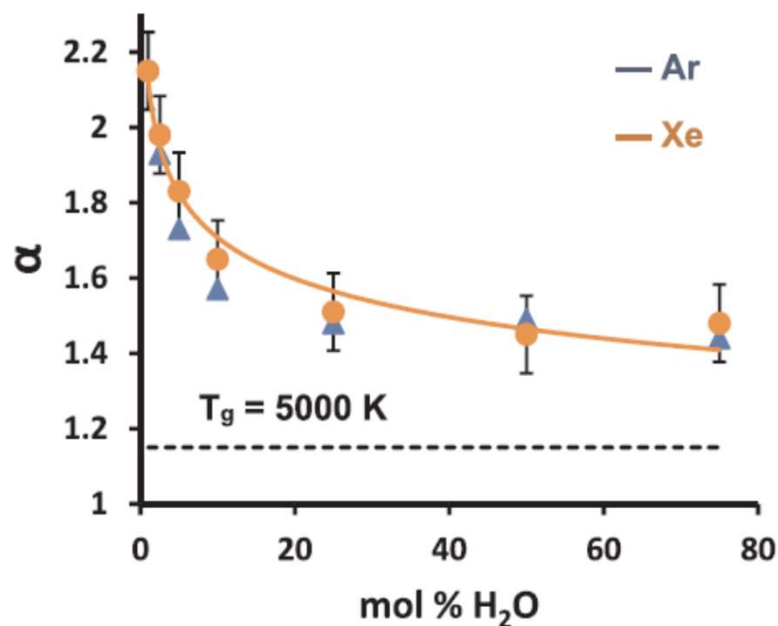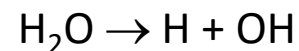

Fig. 3. Dependence of H/D KIE (α) on H_2O concentration in H_2O/D_2O mixtures sparged with Ar (▲) and Xe (●). The dotted line shows calculated α value at T_g = 5000 K presuming classical behavior.

Equilibrium case (T_g=5000 K) α < 1.2

98% D_2O $\alpha \approx 2$

Enrichment in light isotope

Not only water molecule splitting as usually reported

$$H_2O \rightarrow H + OH$$

But more complex plasma mechanism involving e^-_h, D_2O^+, HD_2O^+...

Indoubtedly the **hot spot** formed in cavitation bubbles **is a non-equilibrium plasma**, even in MBSL in aqueous solutions

➢ **plasma**: presence of **electrons & charged species**

in aqueous solutions, no emission of ions in SL
indirect indication of their presence = strong broadening of emissions (Stark effects)

➢ **non-equilibrium**: no unique temperature characterizes excited species

Implications of this non-equilibrium in sonochemistry have been illustrated by few experimental studies but would deserve more interest.

Thank you

For your kind attention!