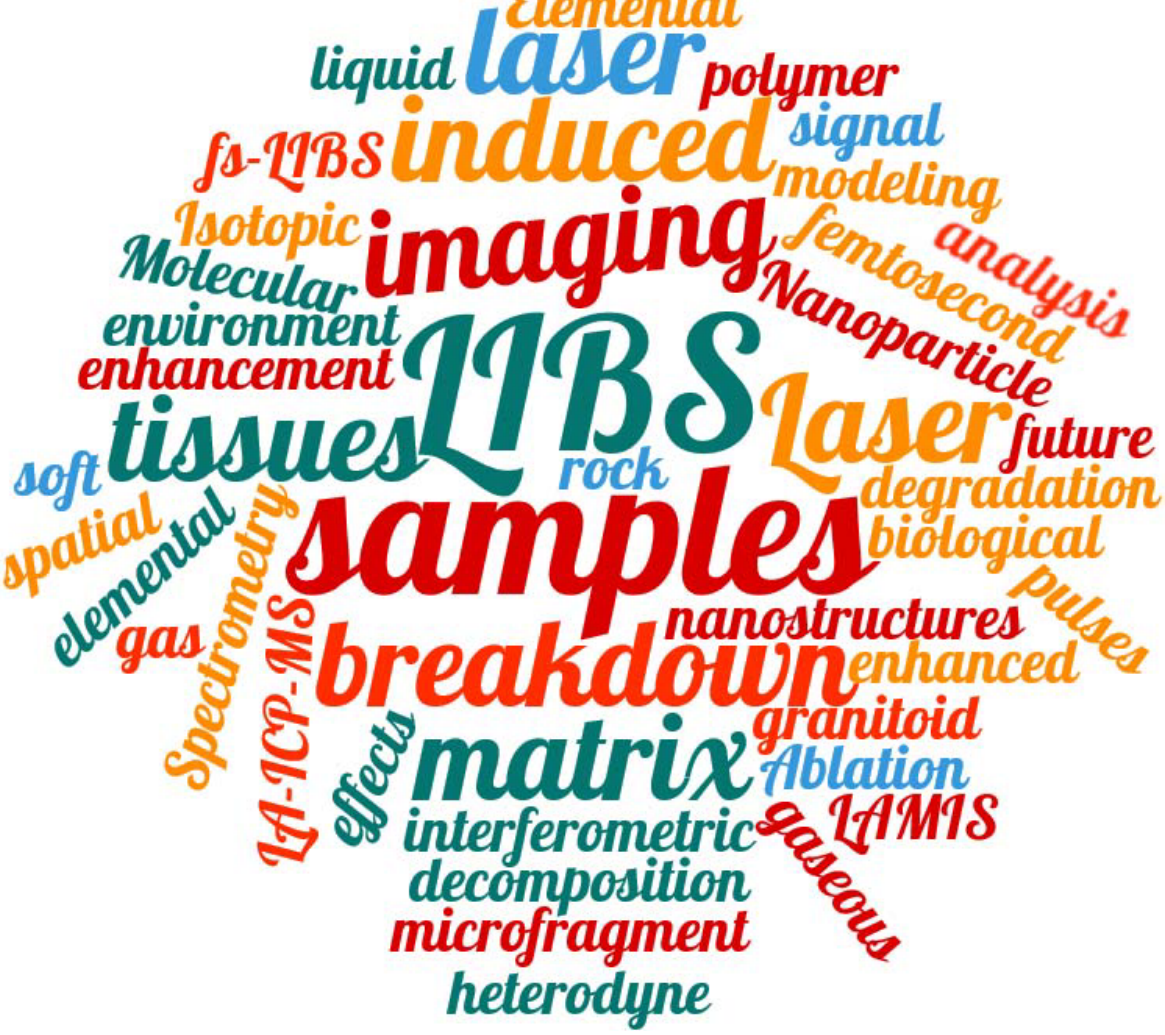

INTERNATIONAL WORKSHOP ON LIBS

December 1-2, 2020 – Szeged, Hungary

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INTERNATIONAL WORKSHOP ON LASER-INDUCED BREAKDOWN SPECTROSCOPY

PROCEEDINGS

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Organizers:

Department of Inorganic and Analytical Chemistry,
University of Szeged, Hungary

Spectrochemical Working Committee
of the Hungarian Academy of Sciences

ELI-ALPS Research Institute, Szeged, Hungary

Ultrafast physical processes in atoms, molecules, nanostructures
and biological systems, EFOP 3.6.2-16-2017-00005 project

Editors:

Gábor Galbács

Albert Kéri

2020

PREFACE

This workshop was originally conceptualized as a one-day meeting, with the support of several scientific organizations, but especially from a consortial research project being conducted at the University of Szeged (Ultrafast physical processes in atoms, molecules, nanostructures and biological systems, EFOP 3.6.2-16-2017-00005). The intention behind the meeting was that it would facilitate the sharing of new scientific results in the LIBS field and could boost the building of new cooperative projects between laser ablation/spectroscopy research groups operating in Hungary and worldwide. We also have a shiny, new, large laser facility (Extreme Light Infrastructure Attosecond Light Pulse Source, ELI-ALPS), which has much to offer for the field of LIBS research in terms of ultra-short, tunable, high repetition rate and high intensity laser pulses. We originally intended to organize a classic workshop, with meeting in person, laboratory visits, fine dining, etc. Unfortunately, due to the covid-19 pandemic, we can now only have an online event (http://www2.sci.u-szeged.hu/libsconf/), which format imposes some limitations.

We are thankful for the support of the international participants, illustrious invited scientists – chemists, physicists and engineers – and we are sure that all participants will have a great time listening to the exciting, altogether 29 presentations from ten countries around the world. We wish everyone excellent health and we hope that this online event, now expanded to two days, will be able to come close to reaching our original, ambitious goals.

This volume contains the papers of all presentations, oral or poster, as well as associated vendor materials.

Prof. Gábor Galbács (University of Szeged), conference-chair
Prof. Sándor Szatmári (University of Szeged), conference co-chair
Prof. Katalin Varjú (ELI-ALPS), conference co-chair
Dr. Albert Kéri (University of Szeged), conference secretary

November 30, 2020.
Szeged, Hungary

SCIENTIFIC PROGRAM

December 1, 2020

(Budapest time, GMT +1)

9:00 - 9:10	Opening address by **Gábor Galbács** (University of Szeged)
9:10 - 9:15	Opening address by **Sándor Szatmári** (University of Szeged)
9:15 - 9:30	Opening address by **Katalin Varjú** (ELI-ALPS, Szeged)
9:30 - 10:10	**Igor B. Gornushkin** (Federal Institute for Materials Research and Testing, Germany): *Laser induced gas breakdown in reactive mixtures containing halides of boron and silicon: diagnostics and modeling*
10:10 - 10:50	**Alessandro De Giacomo** (University of Bari, Italy): *Nanoparticle enhanced laser induced breakdown spectroscopy: fundamentals and perspectives*
10:50 - 11:30	**Pavel Veis** (Comenius University, Slovak Republic): *Why is LIBS the future online analytical technique for plasma-facing materials of thermonuclear reactors?*
11:30 - 13:00	Lunch break
13:00 - 13:40	**Andreas Limbeck** (Vienna University of Technology, Austria): *Assessment of polymer degradation by the combined use of LIBS and LA-ICP-MS*
13:40 - 14:20	**Timur A. Labutin** (Lomonosov Moscow State University, Russia): *Non-analytical applications of laser-induced breakdown spectrometry*
14:20 - 15:00	**Tamás Smausz** (University of Szeged, Hungary): *Study of the fragmentation of solid drug particles during ablation with different pulse length lasers*
15:00 - 15:40	**Pavel Pořízka** (Brno University of Technology, Czech Republic): *Recent advances in the imaging of biological tissues at the Brno University of Technology*
15:40 - 16:00	Coffee break

16:00 - 16:40 **Vincent Motto-Ros** (University of Lyon, France), **Benoit Busser** (Grenoble Alpes University Hospital, France): *Elemental imaging with laser spectroscopy is entering the clinic as a new diagnostic tool*

16:40 - 17:20 **Viktor Chikán** (Kansas State University, USA/ELI-ALPS Research Institute, Hungary): *Characterization of the CN(B) and CH(A) radical formation in plasma generated by femtosecond laser pulses via step-scan FT-UV-VIS spectroscopy*

17:20 - 18:00 **Jhanis Gonzalez** (Lawrence Berkeley National Laboratory/ Applied Spectra Inc., USA): *Laser Ablation Molecular Isotopic Spectrometry (LAMIS) - overview*

18:00 - 18:40 **Vincenzo Palleschi** (University of Pisa, Italy): *About the use of laser-induced breakdown spectroscopy for the determination of fundamental spectroscopic parameters*

18:40 - 18:50 Closing of the oral session

December 2, 2020

(Budapest time, GMT +1)

10:00 - 12:00 **Poster session I.**
Instrumental, theoretical and numerical approaches

Dávid J. Palásti (University of Szeged, Hungary):
Optical and numerical modeling of a spatial heterodyne laser-induced breakdown spectrometer

Lajos P. Villy (University of Szeged, Hungary):
Signal enhancement of gaseous samples in the presence of nanoaerosols generated by a spark discharge

Jelena Petrović (University of Belgrade, Serbia):
Enhancement of the TEA CO_2 LIBS emission using Ag and Ag/Zn nanostructures

Eszter Nagy (University of Szeged, Hungary):
Laser ablation of meloxicam in liquid environment

Jakub Buday (Brno University of Technology, Czech Republic):
Computation of blast wave energy in LIBS using shadowgraphy

Roman Holomb (Uzhhorod National University, Ukraine/Wigner Research Centre for Physics, Hungary):
Reversible laser-assisted structural modification and laser-driven mass transport at the surface of chalcogenide nanolayers

CHARACTERIZATION OF THE CN(B) AND CH(A) RADICAL FORMATION IN PLASMA GENERATED BY FEMTOSECOND LASER PULSES VIA STEP-SCAN FT-UV-VIS SPECTROSCOPY

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1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) is mostly used for simultaneous analysis of multiple elements measuring the atomic emission lines or the emitted light from diatomic radicals in excited states [Rao 2015, Moros 2019]. Typical LIBS measurements apply nanosecond laser pulses [Dong 2011] however, recent publications suggest potential benefits of using femtosecond lasers [Moros 2019, Kotzagianni 2013]. Seven explosive nitropyrazoles were studied by fs-LIBS technique (~40 fs, 800 nm, 1 kHz, ~2.5 mJ pulse energy) [Rao 2015]. Rao et al. studied the atomic emission lines from C, H, O, and N, the molecular emissions of cyanide (CN, violet bands) and diatomic carbon (C_2, Swan bands). Authors collected time-resolved spectral data for the characterization of the plasma dynamics in different atmospheres, such as air, argon and nitrogen. They found a clear decreasing trend in the CN and C_2 decay times with the increasing number of nitro groups. Moros et al. concluded in their review work about the LIBS of organic compounds that the molecular emission from CN and C_2 radicals is stronger with fs-LIBS technique compared with those obtained using nanosecond laser pulses [Moros 2019].

We report a novel approach producing CN(B) and CH(A) radicals from different small organic molecules in gas phase with a high repetition rate femtosecond laser (100 kHz, 1030 nm, ~43 fs, 250 μJ/pulse). The emission spectra can be collected with high temporal and spectral resolution (5 ns and 1 cm^{-1}) with a Fourier transform UV-Vis spectrometer in step-scan measurement mode [Mogyorosi 2020].

2. EXPERIMENTAL

The experiments were performed in a vacuum chamber typically at 5-100 mbar total pressures in argon or nitrogen gas in the presence of organic vapors (bromoform, methanol or acetonitrile) introduced through a bubbler. The HR-1 laser beam at ELI-ALPS with 1030 nm central wavelength, 100 kHz repetition rate, ~43 fs pulse length and 25 W average power was focused into the vacuum chamber with an achromatic lens (f = 10 cm). The intensity in the focal point was estimated to be 1.1×10^{16} W/cm^2. Overview spectra were monitored with a QEPro spectrometer. The emitted light was also collected with a collimating lens and measured with a Bruker Vertex80 FT-UV-Vis spectrometer with high resolution in step-scan mode (5 ns and 1 cm^{-1}).

3. Results and discussion

3.1. CN(B) radical formation

The overview emission spectra from acetonitrile in nitrogen and argon are shown in **Figure 1**. The CN violet system ($B^2\Sigma$-$X^2\Sigma$, $\Delta\nu$ = 0, -1 and +1; 370-395 nm, 350-365 nm and 410-425 nm, respectively) and the C_2 Swan system ($d^3\Pi_g$-$a^3\Pi_u$, $\Delta\nu$ = 0, -1 and +1; 450-480 nm, 500-520 nm and 540-570 nm, respectively) can be observed.

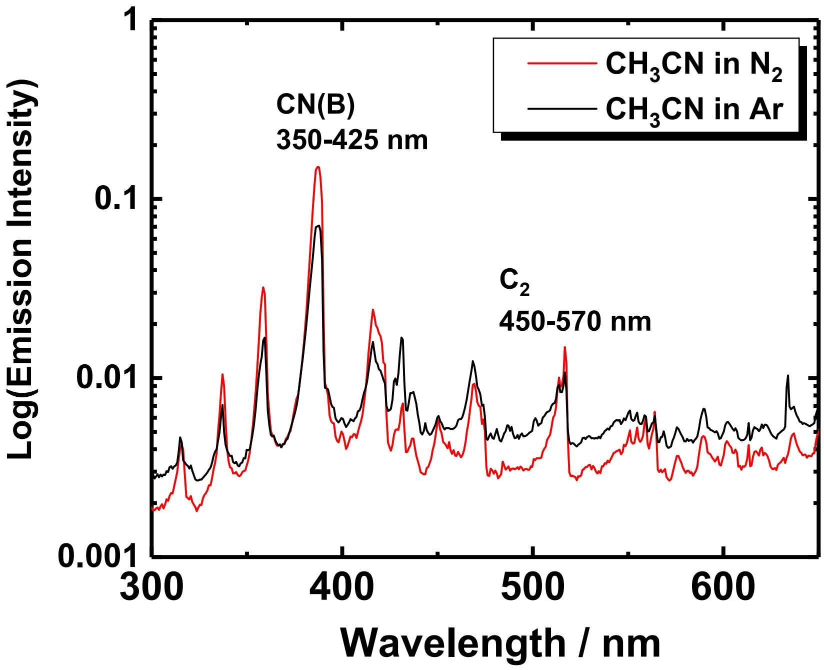

Figure 1. Overview spectra of CN(B) and C_2 radicals generated from acetonitrile.

The highest intensity of CN(B) radicals was observed from bromoform in nitrogen plasma due to the production of reactive carbon atoms and CH radicals. The experimental data obtained with time-resolved Fourier transform spectroscopy were used for the determination of the rotational and vibrational temperatures via fitting (**Figure 2.**) [Western 2017].

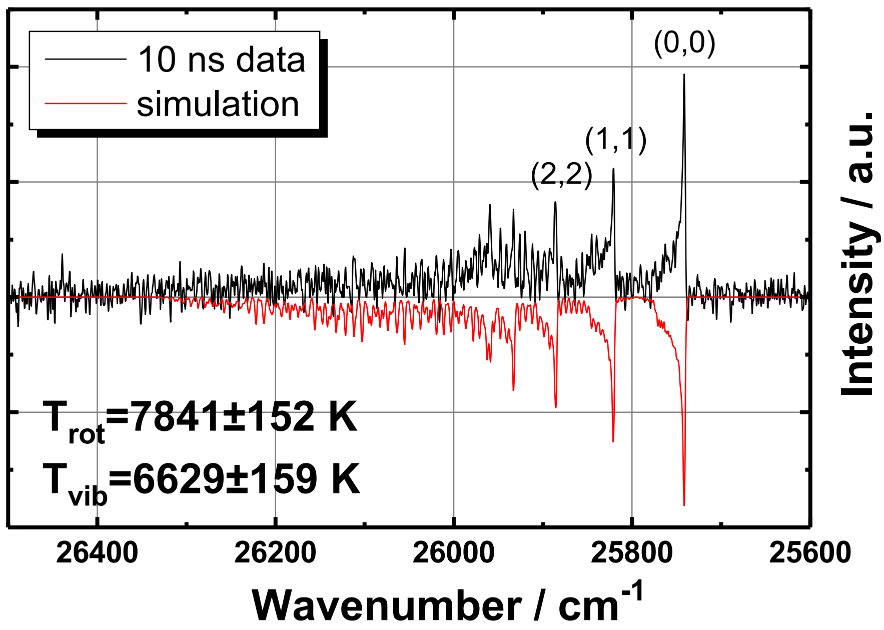

Figure 2. Measured and simulated ro-vibrational spectra of CN from acetonitrile 5 mbar - N_2 95 mbar mixture at 10 ns time point.

The rotational and vibrational temperatures were very high (T_{rot}~6000-8500 K and T_{vib}~4500-8000 K) at about 10 ns for the CN(B) radicals generated from all organic molecules. T_{rot} determined for bromoform and acetonitrile rapidly decreased in all instances within 40 ns. The time-dependent integrated fluorescence signal of the (0,0) band of acetonitrile/Ar (5 mbar/95 mbar) sample is fitted with a mono-exponential curve with a time constant of 87 ns. The CN(B) emission in nitrogen follows a bi-exponential decay. The shorter time constant of this decay (35-40 ns) is close to the natural lifetime of CN(B) emission (~30-90 ns). The longer time constant (130-160 ns) probably belongs to slower chemical reactions involving carbon atoms, C_2 radicals and nitrogen containing species.

3.2. CH(A) radical formation

Based on the overview spectrum of bromoform/Ar (5 mbar/5 mbar) plasma, the formation of CH(A) radicals was confirmed by the observation of a peak at 431 nm. The atomic lines of hydrogen (H-alpha, 656.8 nm) and bromine (827.8 nm) were also noticed. In the case of methanol/Ar (5 mbar/5 mbar), the P-, Q- and R-branches are also recognizable in the high-resolution static spectra. The CH(A) formation kinetic curves are shown in **Figure 3**.

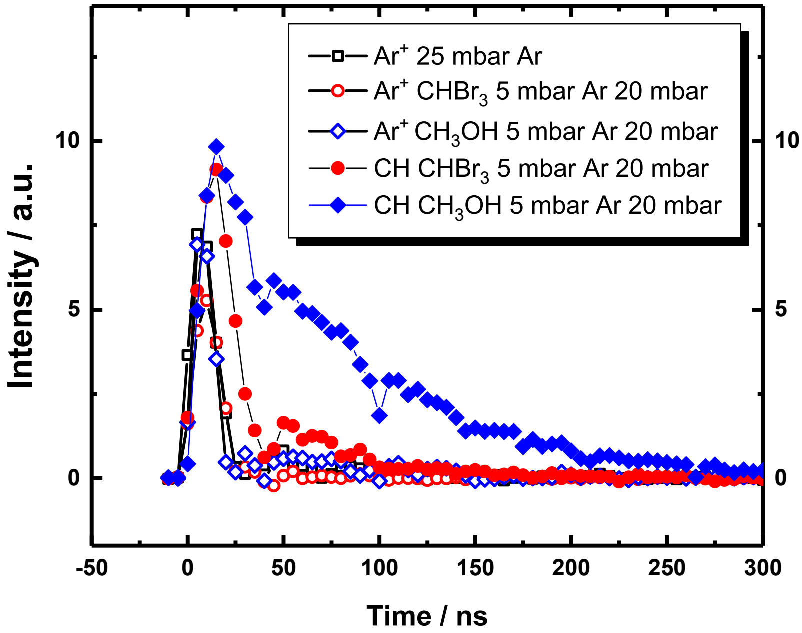

Figure 3. CH(A) formation kinetics in bromoform/argon and methanol/argon mixtures (5 mbar organics/20 mbar argon).

The appearance of the Ar^+ signal occurs in the 5-10 ns time range (that is about the instrument response time). The CH(A) signal formation is similarly fast but the emission decay is different for the bromoform/argon mixture (t = 10.4 (2.2) ns) compared to that of methanol/argon mixture (t_1 = 7.8 (2.2) ns and t_2 = 81.5 (1.7) ns). In the case of methanol, it is likely that the stepwise loss of hydrogen atoms from the CH_3 group results in slower decay of the CH(A) emission.

4. Conclusions

The step-scan Fourier transform UV-Vis spectroscopy combined with the high repetition rate femtosecond laser (100 kHz, ~43 fs) is an excellent tool for the determination of atomic and molecular composition of samples. The method can be applied for gas, liquid and solid phase samples as well. Due to the localization of the pulse energy of the femtosecond pulse, small quantities can be analyzed with high rate. The main advantage of using femtosecond laser pulses is due to the high starting temperatures (4500-8000 K). This allows the detection of multiple elements and radicals simultaneously, including those which are hardly measurable with the traditional ns-LIBS techniques. It has been demonstrated on model samples that the kinetics of the formation and decomposition of light emitting species can be monitored with high temporal resolution.

5. Acknowledgements

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6. References

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