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MERLIN, AN RT-LTE SOFTWARE SUPPORTING THE DIAGNOSTIC APPLICATION OF LIBS TO H-ISOTOPE MEASUREMENTS

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Boubert

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December 1-2, 2020 - Szeged, Hungary

INTERNATIONAL WORKSHOP ON LASER- INDUCED BREAKDOWN SPECTROSCOPY

BOOK OF ABSTRACTS

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Organizers:

Department of Inorganic and Analytical Chemistry,
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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 extended abstracts 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 CO₂ 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

István Rigó (Wigner Research Centre for Physics, Hungary): *Effect of surface roughness on SERS enhancement of patterned gold substrates*

Aurélien Favre (Normandy University, France):
MERLIN, an RT-LTE software supporting the diagnostic application of LIBS to H-isotope measurements

12:00-14:00 Lunch break

14:00 - 16:00 **Poster session II.**
Analytical methodology

Patrick Janovszky (University of Szeged, Hungary):
Identification and Be, Li content assessment of mineral in granitoid rock samples by LIBS

Sára Strítežská (Brno University of Technology, Czech Republic):
Toxicity assessment of photon-upconversion nanoparticles and their bioimaging by using laser-induced breakdown spectroscopy in Brassica oleracea L. plant

Anna Šindelářová (Brno University of Technology, Czech Republic):
Implementation of laser-induced breakdown spectroscopy elemental imaging into the histopathological analysis of soft tissues

Patrick Janovszky (University of Szeged, Hungary):
Investigation of size and exposure time dependent bioaccumulation of silver nanoparticles in plants by LIBS

Nikolai Sushkov (Lomonosov Moscow State University, Russia):
Exploratory analysis of zooplankton spectra using matrix decomposition techniques

Dávid J. Palásti (University of Szeged, Hungary):
LIBS-based approaches for the classification of glass microfragment samples

Daniel Holub (Brno University of Technology, Czech Republic):
Classification of plastics using LIBS and Raman spectroscopy data fusion

Lukas Brunnbauer (Vienna University of Technology, Austria): *Matrix effects in quantitative polymer analysis: a comparison of ns and fs laser systems*

Patrick Janovszky (University of Szeged, Hungary):
Analysis of uranium-bearing materials by laser-induced breakdown spectroscopy

Ádám Bélteki (University of Szeged, Hungary):
On-line and off-line LIBS detection of nanoaerosols generated by electrical discharges

**ORAL
PRESENTATIONS**

MERLIN, AN RT-LTE SOFTWARE SUPPORTING THE DIAGNOSTIC APPLICATION OF LIBS TO H-ISOTOPE MEASUREMENTS

**Aurélien Favre^{1*}, Morgan Lesage¹, Vincent Morel¹,
Arnaud Bultel¹, Pascal Boubert¹**

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1. INTRODUCTION

Laser-induced plasmas can be used to determine the multi-elemental composition of solid, liquid or gaseous samples. Using a pulsed laser beam focused on the sample, the resulting absorption leads to a temperature increase of several 10,000 K [Morel 2016], therefore to a neutral phase to plasma transition. During the relaxation phase over which the recombination takes place, a continuum then lines radiation is emitted. Its analysis based on Optical Emission Spectroscopy (OES) may lead to the composition of the plasma if fundamental assumptions are fulfilled [Morel 2015]. The most restrictive one is the achievement of the Local Thermodynamic Equilibrium (LTE). The characterization of LTE is therefore one of the key points of this analysis method, also known as Laser-Induced Breakdown Spectroscopy (LIBS) [Mizolek 2006].

A high electron density n_e in the plasma ensures an important collision frequency which permits a satisfactory coupling between electrons and heavy particles. LTE is then achieved which allows a synthetic spectrum computation. The composition is then derived from the comparison between the computed and experimental spectra by an iterative procedure. The reliability of such a determination is directly linked to the quality of experimental data but also to the computational process itself (broadening effect and/or homogeneity).

MERLIN (MultiElemental Radiative equilibrium emission) has been developed to support OES interpretation and more particularly laser-induced experiments. This software computes equilibrium composition to generate the corresponding emission spectrum of any input mixture through a radiative transfer (RT) calculation. The user has a large set of input possibilities such as choosing input species, enabling different physical broadening effects or even choosing the spectral database used for computation. For this communication, a specific application of MERLIN devoted to LIBS H-isotopes measurements in gaseous, porous and metallic media is presented.

2. DESCRIPTION OF MERLIN

The computation of equilibrium composition is based on a fictitious chemical kinetics (for which the detailed balance principle is assumed). The final result is derived from

solving a coupled system of differential equations obtained from equilibrium laws (mass action, Saha for ionization and Guldberg & Waage for dissociation). The system is bounded by user inputs: ionization degree and species length have to be given. The software automatically requests necessary data (ionization, dissociation potentials and partition function) online. A temperature looped computation enables the obtention of the mixture composition at fixed pressure.

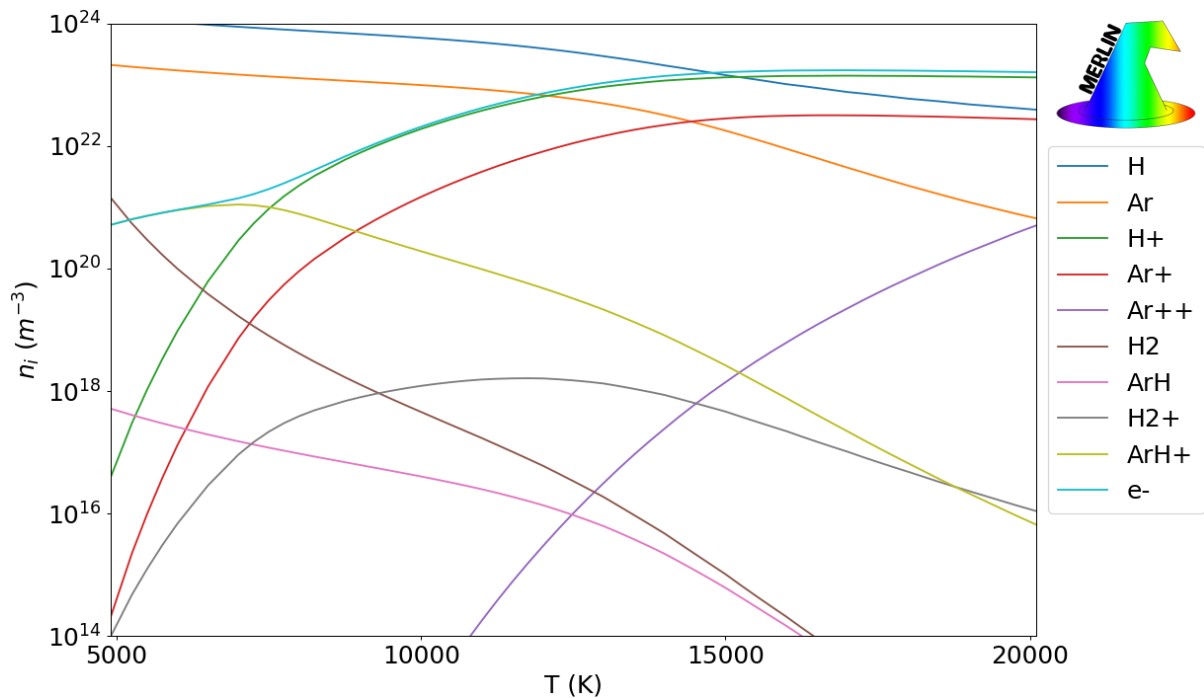


Figure 1. Composition of 0.25Ar - 0.75H₂ (expressed in mole fractions) mixture at equilibrium versus temperature at atmospheric pressure.

An example of this procedure is given for a 0.25Ar - 0.75H₂ mixture in **Figure 1**. [Liu 2009, Stancil 1994, Maltsev 2019, Capitelli 2012]. MERLIN shows a satisfactory agreement with similar published compositions computed by Fauchais *et al.* [Fauchais 1994]. This explains why neutral species remain dominant for $T < 12\ 000$ K. Also, for higher temperature the ionization degree increases, which leads to H⁺, Ar⁺ and Ar²⁺ formation. A competition between ionization and dissociation for H₂⁺ is observed through a non-monotonic evolution with temperature.

3. RESULTS AND DISCUSSION

Nowadays research and environmental politics agree to say that hydrogen is an element of interest for the future of humankind for many reasons. First, hydrogen isotopes are nuclear fusion reaction fuels which can be considered as tomorrow's energy. Second, it allows a carbon and NO_x free combustion. In addition to this, hydrogen is often used for instance in industrial processes such as plasma vapor deposition, ceramic treatment or

even fundamental research studies. We propose here to describe its emission into plasmas obtained from gas, porous substrates or even metallic samples.

Every spectrum presented below have been computed considering no Van Der Waals or Doppler broadenings. Also, the apparatus function has been fixed to a nominal lorentzian distribution with 0.0145 nm as FWHM (Full Width at Half Maximum), which corresponds to our experimental conditions. Concerning the Stark broadening, the FWHM are fixed as follows (respectively Mijatovic *et al.* [Mijatovic 2020], Fantoni *et al.* [Fantoni 2017]):

$$\Delta_{H-Stark}^{Lorentz} = 1.098 \left(\frac{n_e \text{ (m}^{-3}\text{)}}{10^{23}} \right)^{0.67965} \text{ nm}$$

$$\Delta_{other-Stark}^{Lorentz} = 2 \omega_S(T) \frac{n_e \text{ (m}^{-3}\text{)}}{n_{e,ref}} \text{ nm}$$

$$\omega_S(T) = 4.8767 \times 10^{-4} + 1.6385 \times 10^{-8}T - 1.8473 \times 10^{-13}T^2$$

Of course, this default correlation can reveal unsubstantial compared to published electron impact parameters and it can be mandatory to inject measured values to obtain realistic Stark broadenings. But this communication only aims to claim the purpose of numerical tools to support experimental LIBS measurements.

3.1. Gas mixture: H mole fraction influence in Ar-H₂ mixture

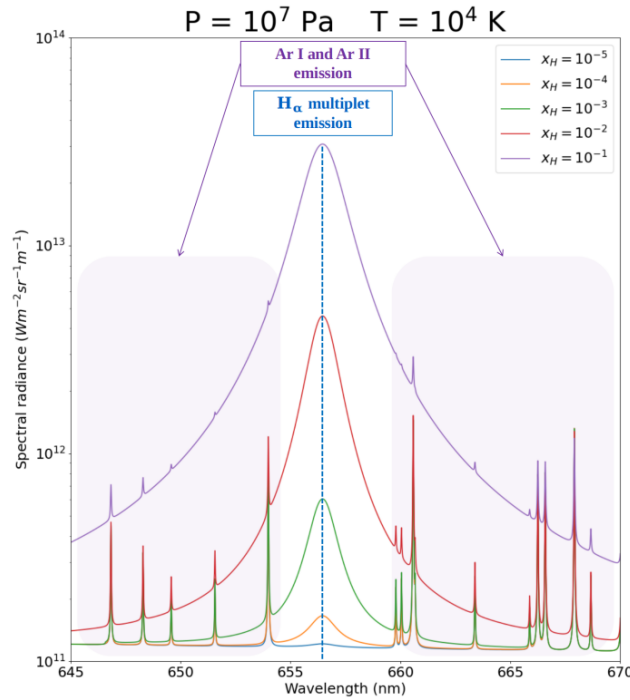


Figure 2. Equilibrium emission spectrum of an Ar - H₂ mixture diluted at X_H mole fraction of hydrogen.

Experimentally, argon is often used as surrounding gas for LIBS experiments because of its spectral data in addition to its high confinement capacity resulting from its atomic mass. As gaseous H-retention, we have chosen to present the emission of an Ar-H₂ mixture with variable H dilution (see **Figure 2**).

These results are obtained by fixing the plasma pressure at $P = 10^7$ Pa and the temperature at $T = 10^4$ K. Namely, H dilution leads to a stronger H_α emission. Diluting also appears to lead to greater n_e values characterized by a strong Stark broadening.

3.2. Porous substrate: temperature influence in zeolite-like structure

Zeolites are crystal lattices which are mainly composed of gaps. This results to a porous material able to capture light species like hydrogen. Several studies are linked to hydrogen retention in those materials which appear to be a reliable solution to hydrogen storage. The LIBS hydrogen probing in such matrices can be used to estimate the capture efficiency. Different computations for a special zeolitic structure have been made at atmospheric pressure (see **Figure 3**).

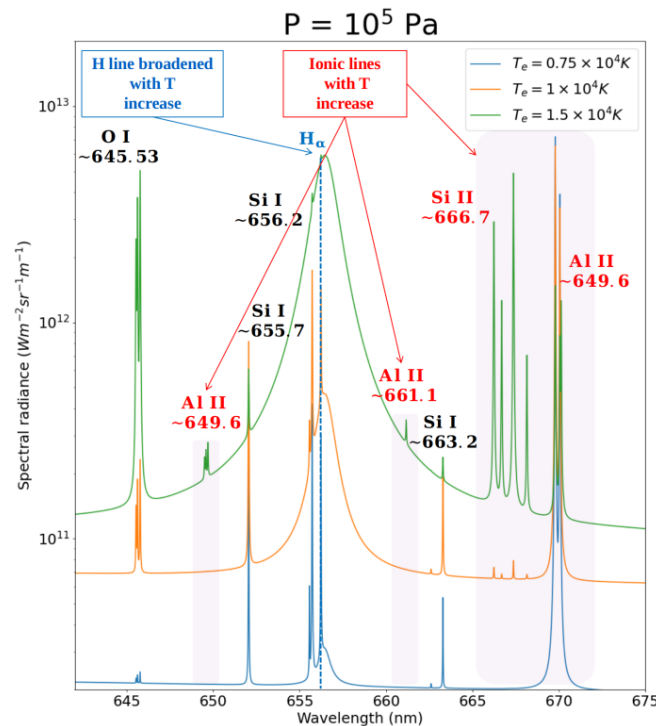


Figure 3. Equilibrium emission spectrum of zeolite-like (0.087H / 0.087Al / 0.217Si / 0.609O) structure versus plasma temperature.

The studied zeolite composition is 0.087H / 0.087Al / 0.217Si / 0.609O without any retention. A temperature increase leads to a higher ionization degree: this is directly observable through the appearance of Al II (around 649.6 nm, 661.1 nm and 649.6 nm) and Si II (around 666.7 nm) lines. In terms of composition, a significative n_H decrease is noticed. In addition, at low temperature, the hydrogen LIBS diagnostic is perturbed by

SI lines around 656.2 nm: probing another Balmer line is therefore requested if the diagnostic is performed in the visible spectral range.

3.3. Metallic samples: H/D mole fraction ratio influence in bulk tungsten

Hydrogen isotopes are used as fuels in nuclear fusion reaction. In a tokamak, a strong magnetic field is used to avoid a contact between the fusion plasma and machine walls (the term «magnetic confinement» is commonly used). The lower part of the tokamak, also named divertor, is more exposed to radiation and high flux density. Divertors are made in tungsten due to its high fusion temperature and its mechanical properties. The LIBS detection of hydrogen and/or deuterium retention in metallic heavy matrix such as tungsten is challenging: since low permeation factor and screening effect due to mass difference increase the limit of detection. We have performed calculations of the resulting emission of a 0.99 W / 0.01(H-D) plasma with variable light elemental mole ratio (see **Figure 4**).

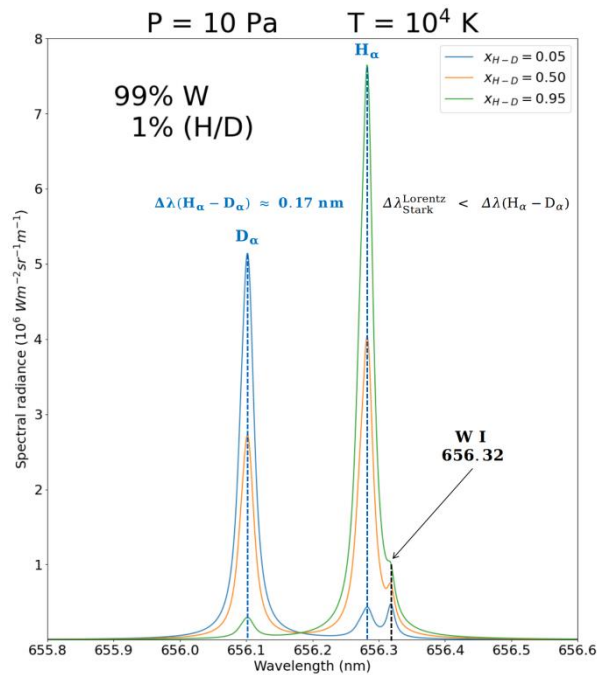


Figure 4. Equilibrium emission spectrum of H/D retention in bulk W (0.99 W / 0.01(H-D)).

A particular attention has to be paid to the spectral scale. In fact, the isotopic shifting of H and D Balmer- α lines is about 0.17 nm. Experimentally, it does not appear to be a limitation as long focal or high gratings spectrometers allow such a resolution with no particular problem. The main issue is residing in broadening which can hardly be as weak as shown on **Figure 4**. Indeed, inner plasma pressure cannot be as low as 10 Pa. Another limitation is due to the perturbation of a W I line emitting at 656.32 nm. In addition to this, a major probing issue is linked to light element concentration profile which is particularly low (the per cent is the order of magnitude) in surface and becomes tinier in a volumic point of view. All of those make the H_α and D_α tricky to

detect in a bulk W matrix. Fortunately, many alternatives can be explored to probe light element in a heavy matrix (VUV H-isotopes Lyman series, stronger H/D concentrations or even implantation in another matrix such as Al with no line around 656.3 nm).

4. CONCLUSIONS

MERLIN has been presented as a relevant tool in support of experimental laser-induced spectral emission data. The software is able to compute a synthetic equilibrium emission spectrum of any kind of mixture from a known spectroscopic setup (apparatus broadening) in known thermodynamic conditions like (P,T) or (n_i , T), with i a user chosen mixture species. This is a valuable indicator concerning the power of resolution or even the observability of a probed species in known plasma conditions.

Different applications of H and its isotopes retention have been developed to show the predictive capabilities of the software. Stark broadening for non-H species has been generalized for the simplicity of presentation but must be precised for a fine spectroscopic analysis or a crossed n_e determination. Such a numerical approach allows to observe a competition between apparatus and Stark broadenings when probing near range lines. It is also indicating the necessary conditions to observe ionic emission of a given species.

The upgrade of MERLIN is planned and includes many incoming features to enhance its prediction quality by implementing potential lowerings, resonant and Zeeman broadenings, non-homogeneous emitting media, better molecular emission support or even multi-temperature support.

5. REFERENCES

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