Romanian Reports in Physics, Vol. 64, Supplement, P. 1179–1194, 2012

Dedicated to Professor Ioan-Iovitz Popescu's 80th Anniversary

LASER BEAMS INTERACTION WITH LIQUIDS IN OPTOFLUIDIC EXPERIMENTS

M. BONI, V. NASTASA, ANDRA MILITARU, ADRIANA SMARANDACHE, I.R. ANDREI, ANGELA STAICU, M.L. PASCU*

National Institute for Laser, Plasma and Radiation Physics, P.O.Box MG-6, RO-077125 Bucharest-Magurele, Romania
* Author for correspondence, e-mail: mihai.pascu@inflpr.ro

Received July 23, 2012

Abstract. This paper reports absorption, LIF and Raman spectra of samples of Polydocanol, Vancomycin hidrochloride and ultrapure water, exposed to laser radiation. Conclusions: -medicines molecules exposed to laser radiation are modified and foams may be produced out of them; -Raman measurements on water beads show an important potential for studies of the behaviour of water in the presence of laser radiation.

Key words: microfluidics, optofluidics, laser, unresonant interaction, LIF, Raman spectroscopy.

1. INTRODUCTION

The development of sophisticated new drug delivery routes (transdermal, pulmonary, nasal etc.) may represent methods to improve the efficacy and/or safety of the active pharmaceuticals [1].

Several foam technologies have been developed in recent years with the aim of enhancing and/or facilitating topical drug delivery. They can be categorized into four groups. The first class of topical foams are drug-specific (foaming compositions designed to make more efficient the delivery of particular active agents); the second, includes new methods for foam generation (composition and devices); the foams in the third class enhance cosmetic appeal and the fourth class includes those foams that enhance the skin penetration of active agents [2].

Our study is focused first on the classes 1 and 2 of topical foams and on the study of the behaviour of some drugs at the interaction with laser beams.

An active agent already marketed in the liquid form as a topical foam is Polidocanol (POL), that is the active ingredient in the commercially available drug Aethoxysklerol. This is a drug used in the sclerotherapy of small veins (less than 4 mm in diameter). Clinical observations prove that foam sclerotherapy is preferable

to use instead of liquid sclerosing substances. Detergent-like sclerosing agents can be transformed into fine-bubbled foam by special techniques, named after those who used these methods, first: Monfreux, Tessari, Sadoun, Frullini [3]. After the intravenous injection, the liquid detergent sclerosants become protein bound and are inactivated when mixed with blood. The injected sclerosant foam fills the vein completely, displacing blood from the vein and ensuring that all endothelium is exposed to the sclerosant agent that destroys actually the affected vein [4].

Clinical experimental results prove that the exposure of tissues impregnated with foamed Polidocanol to laser radiation emitted at 1064 nm improves the efficacy of the treatment [5, 6].

Previous absorption studies on Aethoxysklerol solution before and after irradiation with a beam emitted by pulsed Nd:YAG laser at 1064 nm have not shown important spectral modifications of the sclerosant agent [7]. According to our data, the effect of the laser light may be enhanced if the POL is introduced as foam, because the light scattering in the tissue becomes more important and the effective absorption of the laser beam becomes larger.

Concerning the new methods for foam generation, in recent works, pulsed laser submicron foam formation has been demonstrated. Foaming requires a sudden and dense bubble nucleation and growth, which are made possible by the transient acoustic wave induced by the laser pulse [8, 9]. This process has been observed during an irradiation session made both in bulk or on droplets of Vancomycin HCl; the Vancomycin is a glycopeptide used in the treatment of the infections induced by the multiple drug resistant (MDR) gram-positive bacteria.

The second type of study reported in this paper is devoted to the Raman spectra measurements performed on individual microdroplets generated in air in suspended/hanging position. The microdroplets may be used as vectors to transport medicines to targets in systems like lab-on-a chip. The use of individual microdroplets may constitute an alternative to the treatment of some diseases with foams that may contain micrometric and/or nanometric components.

2. MATERIALS AND METHODS

2.1. MATERIALS AND SET-UP

Regarding the foam studies, the Polidocanol (POL) or Lauromacrogol 400, $C_{14}H_{30}O_2$ (CID 24750, molecular weight 230.3868 [g/mol]), is the pharmaceutical active ingredient of commercially available Aethoxysklerol (Kreussler & Co. GmbH, Germany) drug. It is polyethylene glycol ether of Lauryl alcohol, where the average value of polymer is nine [9]. This chemical compound is a viscous liquid at room temperature, having a melting point at 15–21°C. It is miscible with water, has the pH = 6.0–8.0 and a density of 0.97 g/cm^3 at room temperature.

POL should be stored at room temperature (15–25°C). At concentrations of 0.5% to 1%, it is stable during 3 years and it should be stored between 15°C and 30°C. There are no special precautions recommended for the disposal of unused POL (product insert).

The common pharmaceutical presentation form of Aethoxysklerol 2%, which was used in the experimental study is as ampoule of 2 ml injection solution whose composition is a mixture of the following substances: Lauromacrogol 400 (active) – 40 mg, sodium hydrogen phosphate (buffer – inactive)**,** potassium dihydrogen phosphate (buffer – inactive), ethyl alcohol (inactive) – 0.10 ml and pure water (inactive) – 2 ml. For this reason, when the solution is exposed to laser radiation, one should consider actually the interaction of all these compounds that co-exist in the commercial grade substance. The 3D image of POL is shown in Fig. 1, where the carbon atoms are represented in red colour, the hydrogen atoms are dark grey and the oxygen atoms are light blue [10].

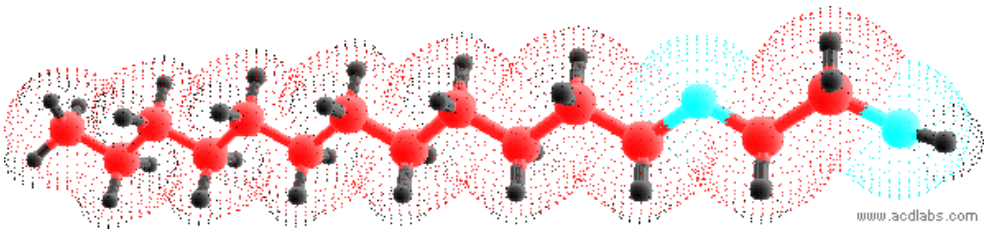

Fig. 1 – 3D image of Polidocanol molecule.

Vancomycin, $C_{66}H_{75}Cl_2N_9O_{24}$, molar weight 1449.3 g/mol (Sigma-Aldrich Co. LLC, U.S.A.) is a tricyclic glycopeptide antibiotic which is originating from *Amycolatopsis orientalis.* Its 3D chemical structure is represented in Fig. 2, where the carbon atoms are shown in red, the hydrogen atoms are dark grey, chloride atoms are pink, nitrogen atoms are yellow, and oxygen atoms are light blue [10].

We investigated the behaviour of 2 mg/ml Vancomycin HCl in ultra-pure water both in bulk and 10 µl volume drops. The used solvent was ultra-pure de-ionized water delivered *via* a sterile filter (TKA Pacific UP/UPW6 and TKA Genpure ultra-pure water system accessory, Thermo Electron LED GmbH, Germany; the flow rate – at 15^0C – 6 L/h and the retention of the bacteria and particles: 99%). Its bacterial content is <1CFU/ml, the particle content <1 at a resistivity of 18.2 MΩxcm and 0.055 µS/cm conductivity, at 25°C.

As for the experiments regarding the Raman spectra measured on single microdroplets, they consisted in the measurement of the Raman scattering signals on pendant/hanging/suspended droplets of ultrapure water and DMSO, generated in air at room temperature and normal conditions of pressure and humidity.

The utilized experimental set-up for laser induced fluorescence (LIF), Raman and absorption spectra measurements is shown in Fig. 3.

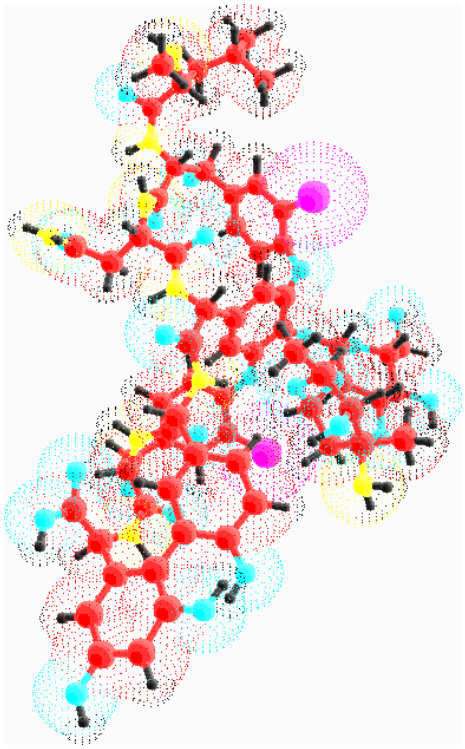

Fig. 2 – 3D chemical structure of Vancomycine.

In the experiments, the Monochromator-CCD-PC2 included a spectrograph SectraPro 2750, Acton Research. At the interaction of an electromagnetic wave with a sample, just one out of 10^6–10^8 photons which are scattered, are Raman scattered [11]. Therefore, the Raman signal has low intensity and needs to be amplified. So, we used a gated ICCD camera, PIMAX1024 (Princenton Instr.). In order to obtain an even more intense Raman signal, the laser beam was focused on the droplet, so that the power density on it reached an allowed maximum value.

The Raman measurements were performed both in droplets and bulk, for comparison and identification of the advantages and disadvantages in one case with respect to the other. In bulk, Raman spectra measurements on foams were also performed. The set-up allowed the collection of the Raman emission at 90°, with respect to the laser excitation beam. The laser source was the second harmonic of the Nd:YAG laser emitted at 532 nm; the pulsed laser radiation had a 10 Hz repetition rate, the pulse duration at half maximum was 5 ns, and the average energy of the emitted beam was 250 mJ.

The set-up described in Fig. 3 was also used to measure the LIF on bulk and droplets samples. For the bulk measurements, it was the case of Vancomycin. The laser beam was emitted as the fourth harmonic generation (266 nm) of the

Nd:YAG laser, with residual emission at 532 nm. Pulse repetition rate was 10 pps and the average beam energy was 20 mJ. The exposure time of the bulk samples was up to 2 h. The laser radiation was collimated with a telescope and focused on the sample with a long focal distance lens. Access of the laser beam to the sample was made *via* a shutter that was either computer (PC 2) or manually controlled, so that the LIF emitted by the sample was collected after a known number of laser pulses by the same PC *via* an Ocean Optics HR4000CG-UV-NIR. LIF was collected and transmitted to the spectrometer *via* an optical fiber (inner core: 1 mm).

The set-up contained also a thermo-camera used to measure the temperatures of the samples and their modifications during the experiments, particularly in the microdroplets case.

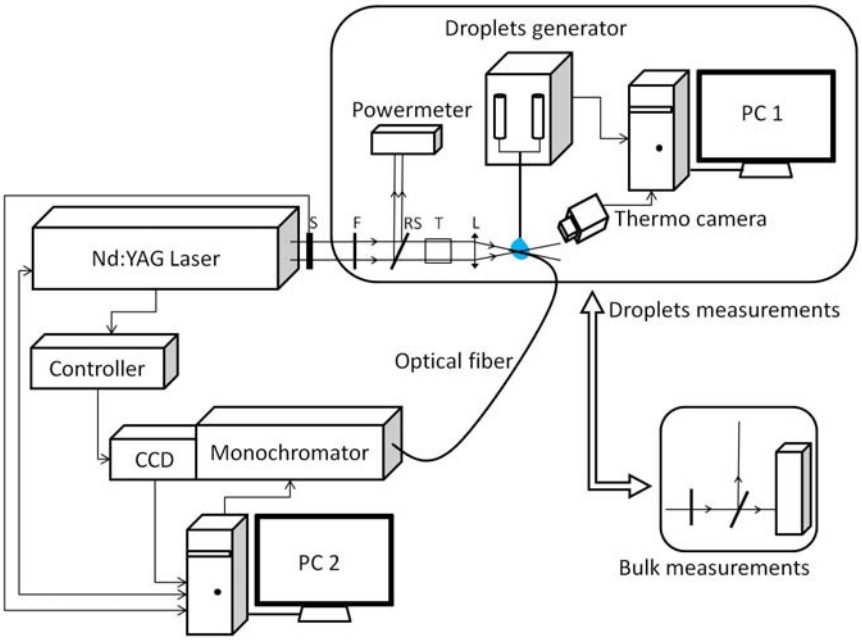

Fig. 3 – The experimental set-up for Raman measurements.
Nd:YAG laser – the optical source used in the experiments, emitting the second/fourth (532/266 nm) harmonic of the 1064 nm fundamental beam; an alternative source deriving from it was the Optical Parametric Oscillator System type Panther OPO SURELITE pumped with it (emitting continuously between 410 nm, and 710 nm); Powermeter – the calibrated unit to measure the average power of the laser beam; Droplets generator – Microlab ML500C Hamilton; Thermo-camera ThermaCAM® E45. Monochromator: a) ocean Optics HR4000CG-UV-NIR monochromator (spectral range 250–1100 nm, optical resolution 0.025 nm, integration time 3.8 ms); b) SectraPro 2750, Acton Research (resolution 0.003 nm and measuring spectral range between 200 nm and 1100 nm). Bulk measurements performed in spectrophotometer quartz cells (2.5 ml). S – Digital Shutter System 845HP Newport (shutter speed: < 1ms); Beam splitter BS reflection less than 1%.

As for investigating the behaviour of laser exposed Vancomycin droplets, we have used the set-up in Fig. 3 which contained the tunable laser source (OPO SURELITE), the droplets generator (Microlab ML500C Hamilton), and the Ocean Optics monochromator HR4000CG-UV-NIR. The sample was exposed to 266 nm wavelength laser radiation, with 3.6 mJ energy.

2.2. METHODS

For the foams measurements, the Tessari method [3] was used to prepare the samples; the foam was produced starting from a mixture of Aethoxysklerol solution and atmospheric air at a mixture ratio of 1:4. The Raman spectra of the foams were measured in different conditions using the set-up described in Fig. 3.

For the droplets measurements, the Vancomycin droplets of 10 µl were generated and exposed to laser radiation. In the experiments any modification of the optical properties of bulk/droplets Vancomycin samples exposed to Nd:YAG laser radiation was evidenced in real time by measuring the LIF spectra emitted by the samples during irradiation. Before and after exposure, the absorption spectra of the samples were also measured using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer in order to detect modifications of the molecular structures.

The Raman spectra of water and DMSO in bulk (2.5 ml liquid volume) were measured and compared with the same spectra measured on beads of 2.5 µl to 10 µl liquid volume.

3. RESULTS AND DISCUSSIONS

3.1. MEASUREMENTS OF LASER INDUCED FLUORESCENCE

The LIF spectra of Vancomycin samples in bulk, at 35 min, 45 min and 55 min exposure to laser beam at 266 nm (Fig. 4) show a broad emission band centred at 358 nm. While exposing at 266 nm, a residual low power green radiation at 532 nm was superposed on the UV radiation, due to the parasite light unfiltered at the output of the SHG/FHG crystal unit. Following 55 min exposure to the laser beam it can be observed a 3 nm shift of the fluorescence emission peak towards higher wavelengths.

The colour of the samples are changing after 15 min of laser exposure to yellow and after a longer exposure time to brown. At 2mg/ml the samples contained only monomers of Vancomycin (data not shown).

The recorded LIF spectra of the laser exposed Vancomycin droplets between 3–7 min show a broad emission band centred on 354 nm (Fig. 5). It is also noticed, both a decrease and a displacement to higher wavelengths of the peak wavelength with the irradiation time. The appearance of small bubbles in the sample was also detected leading finally to foam production.

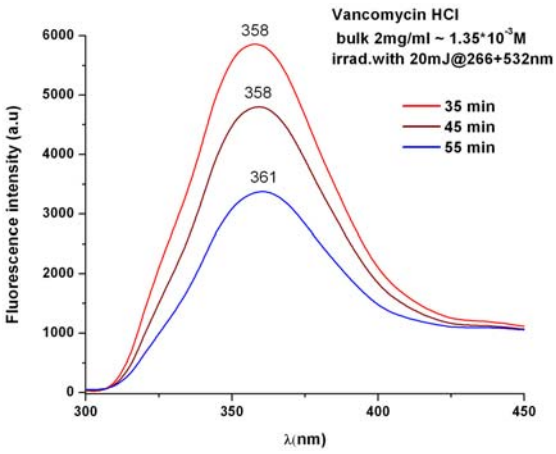

Fig. 4 – LIF spectra of Vancomycin HCl, 2 mg/ml in ultra-pure water in bulk samples.

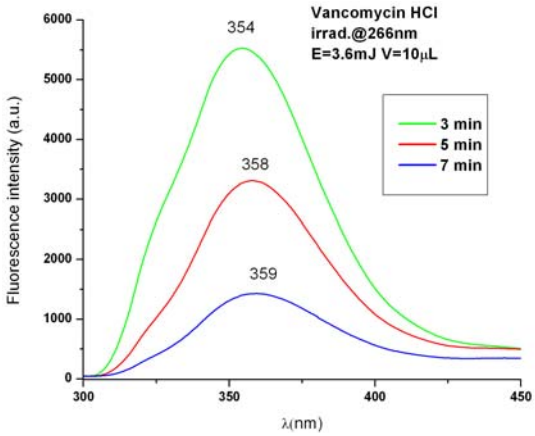

Fig. 5 – Laser Induced Fluorescence spectra of Vancomycin HCl droplets.

These data suggest chemical structure modifications of the compound. The observed changes probably have their origin in the structural modifications induced by foaming and to the local increase of temperature in the irradiated region [8].

It can be pointed out that the observed changes, temperature changes included, are faster in droplet samples compared to bulk presentation of investigated solutions.

3.2. VANCOMYCIN MODIFICATIONS AFTER LASER IRRADIATION

The absorption spectra before and after each irradiation session are measured (Fig. 6).

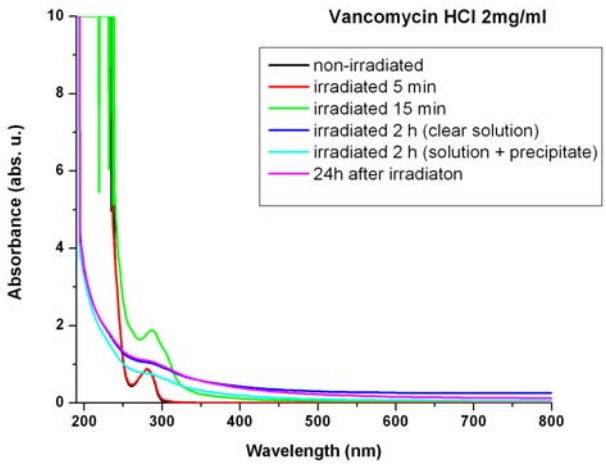

Fig. 6 – The absorption spectra of Vancomycin HCl un-exposed and irradiated bulk samples.

At this high concentration, in the (200–240) nm spectral range the absorption signal is saturated. There are, however at least three specific absorption bands centred at 250 nm, 225 nm and at about 240 nm.

It can be observed that after 15 min of laser beam exposure the characteristic peaks of Vancomycin disappear. The changes can be visualized as colour modification of the irradiated sample, the liquid colour becoming light yellow. Also, after 2 h laser beam irradiation small bubbles at the air-solution interface are observed, and solution precipitates. The Vancomycin sample colour is changing to brown (Fig. 7a).

a) b)

Fig. 7 – Irradiated bulk Vancomycin samples (a) and foamed droplet (b).

As for droplets of Vancomycin solutions in water samples exposed at laser radiation for 7 min one may observe that small bubbles are generated, probably due to the increase in temperature achieved in the small irradiated liquid volume (Fig. 7b). Other explanation is suggested by the absorption spectra shown in Fig. 6 in which the Vancomycin HCl appears to be practically vanished from the sample. It may be that the Cl binding in the molecule is cut-off after the absorption of the 266 nm and the chloride in the gas form remains trapped in the droplet due to the fact that the surface tension of the droplet is high enough and does not allow to the gas to leave the liquid phase.

3.3. RAMAN MEASUREMENTS ON POLIDOCANOL FOAMS

The effect of the laser light on POL may be enhanced if POL is used as foam, because the light scattering in the foam increases the optical path of the laser beam in the sample; the overall effective absorption of the laser beam becomes larger in the foam sample which is introduced in the varicose vein tissues in case of medical application. The laser beam energy absorption in the foam can be amplified by the multiplication of the impacts of the photons at the collisions with the gas bubbles, as well. Moreover, under these circumstances, the number of the POL molecules modified after the absorption of the laser beam is also increased.

In the foam, the Raman signals excited at 532 nm are more intense than for solution samples (Fig. 8), most probably due the same effect: the laser beam optical path is longer in the foam sample. The Raman vibrational lines corresponding to foam sample are more structured and stronger, as well.

The broad band in the 3500–3200 cm^{-1} range in the POL solution Raman spectrum is due to the bonding OH stretch exhibited in water solutions and in alcohols. As for the Raman spectra of the foam sample, the signals < 3000 cm^{-1}, especially those centred on 2850 cm^{-1} and 2935 cm^{-1} are specific to the methyl C-H asymmetric/symmetric stretch proper to the long linear aliphatic chain, which constituted in fact the POL chemical structure.

The characteristic band profiles in the 3600–3200 cm^{-1} range indicate the hydroxyl groups, whose presence linked with the weak Raman signals in the 1650–1450 cm^{-1} interval are typical for the OH stretch signature.

The Raman signals were acquired at different time moments after the preparation of the foam samples (Fig. 9). One may observe that the Raman spectrum is changing relatively fast, so that after 5 min from the foam production, the Raman lines are 10 times less intense than the initial values.

The results indicate that there are some parameters that must be taken into account in understanding the time behaviour of the POL foams, such as the bubble dimensions referred to the foam cohesion. These are important, particularly with reference to the time of exposure of the varicose veins injected with foam POL and exposed in the tissue to laser radiation.

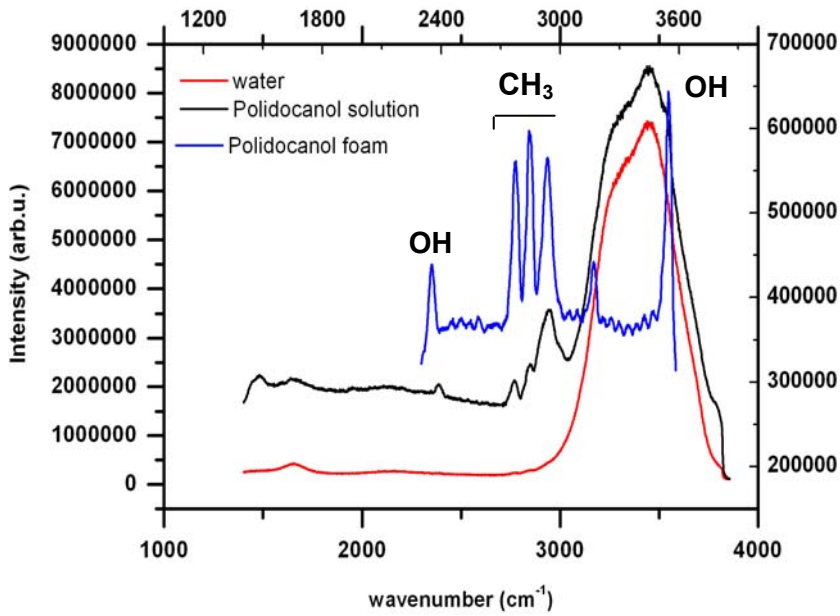

Fig. 8 – The Raman spectra of solution and foam POL samples.

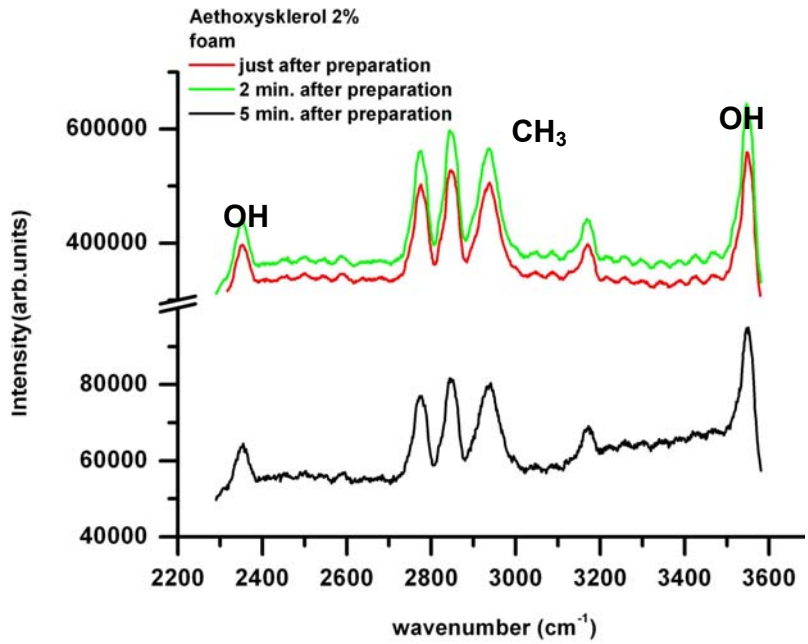

Fig. 9 – The influence of foam separation (in two phases: liquid and remaining foam) on the Raman spectra of a POL foaming sample.

3.4. RAMAN SPECTRA MEASUREMENTS ON DROPLETS AND BULK WATER AND DMSO

In Fig.10 the Raman spectra of DMSO obtained for measurements on bulk samples are shown, when excited at 532 nm. One may observe the characteristic DMSO lines reported in the literature and listed in Table 1 [12, 13].

Table 1

Main vibrations of the Raman spectra of dimethyl sulfoxide in bulk

346 cm^{-1} → CSO in-plane rock	1454 cm^{-1} → HCH deformation
684 cm^{-1} → CS antisymmetric stretch	2945 cm^{-1} → CH symmetric stretching
1068 cm^{-1} → symmetric stretch of monomer	3030 cm^{-1} → CH antisymmetric stretching

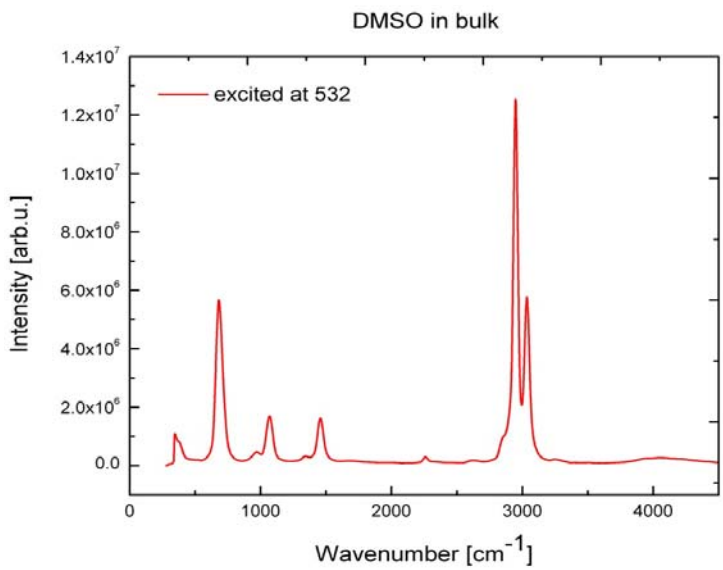

Fig. 10 – Raman spectra of DMSO measured in bulk.

To compare the effects of laser irradiation of micro-droplets, we performed Raman scattering measurements on pendant micro-droplets with 3 mm diameter. This spectrum is shown for DMSO in Fig. 11. There is a decrease in intensity and the loss of several spectral lines by comparison with the spectrum performed on DMSO in bulk. This Raman measurement on beads strengthens the idea that, although it is very weak, the Raman signal can be collected even from small systems such as micro-droplets. This can be explained by the fact that such a spherical system is behaving as a resonant cavity that in specific conditions might work as an amplifier of the Raman emitted radiation.

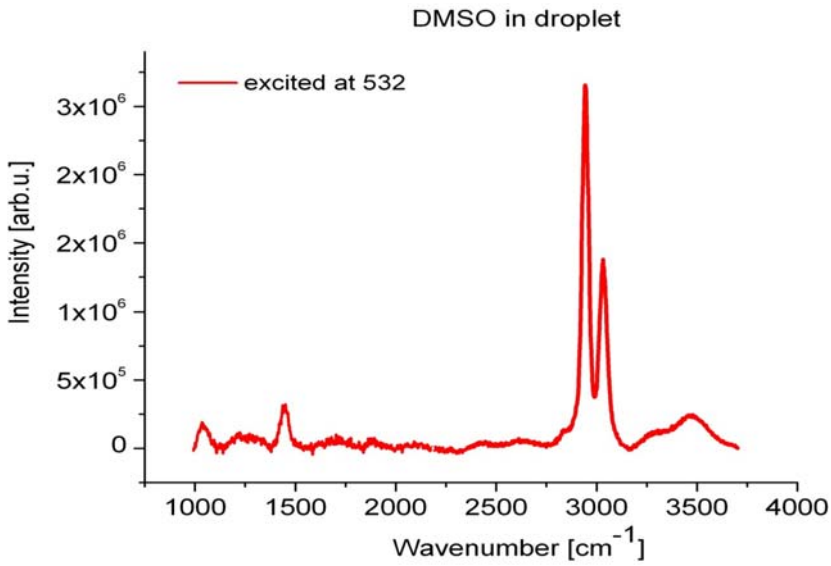

Fig. 11 – Raman spectra of DMSO measured on pendant droplets.

The Raman spectra studies have been completed with Raman measurements on ultra-pure water. In Fig. 12 the Raman spectra obtained for the bulk measurements for two different wavelengths of laser radiation are shown.

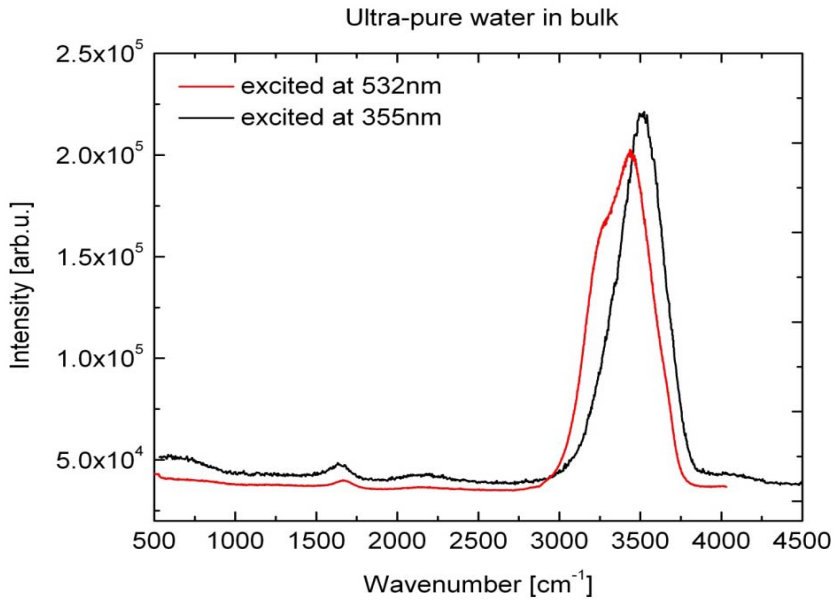

Fig. 12 – The Raman spectra of water in bulk.

Important information about intra- and inter-molecular interactions in water can be obtained from the water Raman scattering spectra. So far, the structure of liquid water is not fully clarified. The processes that describe the vibration patterns in liquid water able to explain the mechanisms of formation of Raman spectral bands have not been set, yet.

There are major contradictions between the theories that describe the resonant interactions in water molecules. The problem of Fermi resonance (resonance between overtone's bending vibration and symmetrical valence vibrations) in the valence band formation of the Raman spectrum is still to be fully clarified.

On the other hand, the Raman spectrum of water is quite complex. It is very difficult to obtain information directly from the spectrum because most of these bands have low intensities and have almost no evidenced internal structure. This is why it is important to study the Raman spectrum changes under the influence of various factors, such as: dissolved compounds, temperature, size and shape of the sample. Under the influence of temperature changes and dissolved substances hydrogen bonds and clusters configurations in water change and may be evidenced by the Raman spectra evolutions.

Experimental data on low-intensity bands of water Raman spectrum are contradictory. These bands can be studied only using very high sensitivity detectors (CCD and photon counting systems). The behaviour of the most intense valence bands have been studied in detail but obviously, the whole set of vibration processes in water may be given only when all the Raman bands are obtained and studied. Intra- and inter-molecular interaction mechanisms are formed in different ways. Literature reports present the following Raman bands of water [14, 15]:

- 50~200 cm^{-1}— bands of intermolecular vibrations;
- 300~900 cm^{-1}— band of intermolecular vibrations;
- 1600~1700 $cm–^{1}$— bending band with maximum at 1645 cm^{-1};
- 2000~2400 cm^{-1}— associative band caused by overtones of intermolecular vibrations;
- 3000~3800 cm^{-1}— valence band with maximum at 3400 cm^{-1};
- 3900~4200 $cm–^{1}$— weak intensity band with maximum at 4000 cm^{-1} caused by overtones of intermolecular vibrations and combination frequencies;
- 6000~7000 $cm–^{1}$— weak intensity band, an overtone of the valence band.

In our case the spectra measured on bulky water samples were compared with the spectra measured on micro-droplets containing only ultrapure water. These results are presented in Fig. 13 from which it results that although the spectra are similar, when measured on beads, new modes of vibration are visualised. These vibration modes are identified in Table 2.

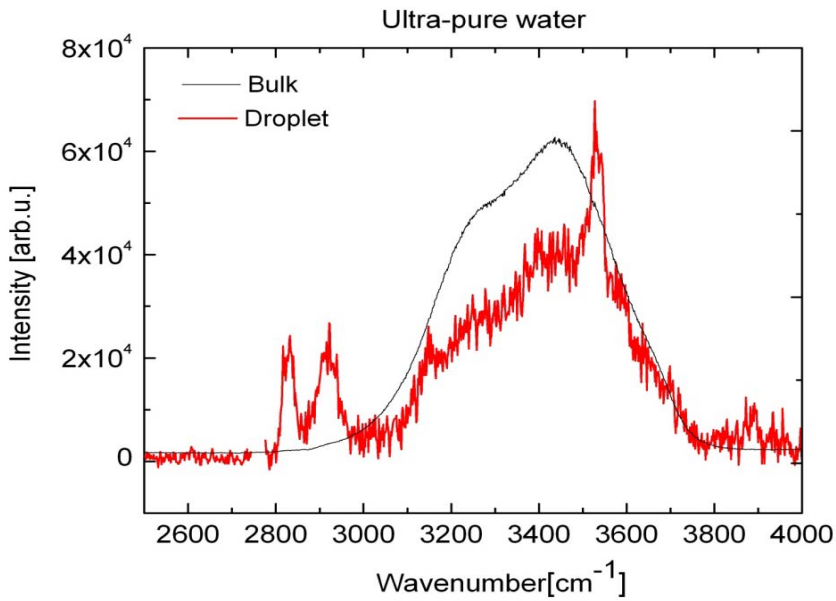

Fig.13 – Raman spectra measured on bulk and pendant droplet.

Table 2

Main vibrations of Raman spectrum of water in volume

Bands	Intermolecular vibrations	Bending	Associative	Valence
Excited at 355 nm (Bulk)	594 cm^{-1}	1641 cm^{-1}	2197 cm^{-1}	3518 cm^{-1}
Excited at 532 nm (Bulk)	610 cm^{-1}	1660 cm^{-1}	2184 cm^{-1}	3436 cm^{-1}
Excited at 532 nm (Droplet)		1500 cm^{-1}	2300 cm^{-1}	3600 cm^{-1}

The evidencing of the vibration modes is, in any case, function of the laser excitation wavelength.

4. CONCLUSIONS

1. The direct clinical application of the Polidocanol assisted by 1064 nm Nd:YAG pulsed laser radiation shows promising possibilities for coagulation of varicose of the lower limbs without the damage of the skin surface [3, 5, 6].

The Raman spectroscopy measurements prove that the Raman signals are more intense for foams than for simple solution/liquid samples. The Raman scattering enhancement is caused by a longer optical path of the laser beam in the foam sample produced by the elastic scattering. The vibrational lines

corresponding to the foam sample are more structured and stronger with respect to the same lines measured on liquid. Comparing the Raman spectra of the same foam sample at different time intervals after preparation, the most intense scattering signal is obtained at 2 min after foaming procedure, due to foam cohesion properties. In case of medical applications, it is consequently recommended to expose the foam to the laser beams in the tissue during the first 2 minutes after foam preparation.

2. The absorption spectra measured after exposure of Vancomycin bulk/droplets samples at laser radiation show the extinction of the spectral fingerprint of the substance. The degradation process is also revealed by the dynamics of the LIF spectra.

The influence of the laser radiation on Vancomycin samples is also producing bubbles both in bulk and droplet samples, as it was observed during the experimental sessions. This behaviour could be influenced by the transient acoustic wave induced by the laser pulses [8, 9] as well as the high temperature achieved in very small volumes, which is the case of droplet samples. The dissociation of Cl from the core structure of the Vancomycin molecules may also lead to the bubbles and foam formation.

3. The excitation of the Raman spectra by laser beams of suitable wavelength, measured on ultrapure water samples both in bulk and droplets show that the use of beads may lead to proper measurements of the Raman scattered radiation. This opens new perspectives if one takes into account the potential of the micro- and nano-droplets to emit laser radiation and even enhanced stimulated Raman scattered beams.

Acknowledgements. This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0922 and by the ANCS (RO) projects LAPLAS 3-PN 09 33, and ANCS-PN2 41-018/2007. A. Militaru, A. Smarandache and M.L. Pascu were supported by the COST Action BM0701-ATENS. A. Militaru and V. Nastasa were supported by projects POSDRU 107/1.5/S/80765 and POSDRU/88/1.5/S/56668, respectively.

REFERENCES

1. I. Pasquali, R. Bettini, International Journal of Pharmaceutics, **364**, 176–187 (2008).
2. Y. Zhao, M. Brown, S. A. Jones, Nanomedicine: Nanotechnology, Biology and Medicine, **6**, 227–236 (2010).
3. A. Smarandache, J. Moreno-Moraga, A. Staicu, M. Trelles, M. L. Pascu, in *Nd YAG Laser*, InTech, Croatia, 2012.
4. P. Coleridge Smith, Semin. Vasc. Surg., **18**, *1*, 19–24 (2005).
5. J. Moreno Moraga, M. J. Isarria Marcos, J. Royo de la Torre, A. Gonzalez Urena, http://www.institutomedicolaser.com/archivos/areacientifica/varices_070306.pdf
6. M. Trelles, J. Moreno Moraga, J. Alcolea, A. Smarandache, M. L. Pascu, In: *Synopsis of Aesthetic Dermatology & Cosmetic Surgery*, M.L. Elsaie (Ed), Nova Science Publishers Inc, NY, USA, 2012.

7. Smarandache A., Trelles M., Pascu M.L., J. Optoelectronics Advanced Materials, **12**, 1942–1945 (2010).
8. S. Gaspard, M. Oujja, C. Abrusci, F. Catalina, S. Lazare, J.P. Desvergne, M. Castillejo, Journal of Photochemistry and Photobiology A: Chemistry, **193,** 187–192 (2008).
9. S. Lazare, V. Tokarev, A. Sionkowska, M. Wisniewski, Appl. Phys. A, **81**, 465–470 (2005).
10. *** PubChem. Polidocanol, In: Compund, August, 2011; http://pubchem.ncbi.nlm.nih.gov/
11. S. Ewen, D. Geoffrey, *Modern Raman Spectroscopy: A Practical Approach*, J. Wiley 2005.
12. A. Selvarajan, *Raman spectrum of dimethyl sulfoxide (DMSO) and the influence of solvents*, Proceedings of the Indian Academy of Sciences – Section A, **64**, *1* 44–50 (1966); DOI: 10.1007/BF03049330
13. W. N. Martens, R. L. Frost, J.Kristof, J. T. Kloprogge, *Raman spectroscopy of dimethyl sulphoxide and deuterated dimethyl sulphoxide at 298 and 77 K*, Journal of Raman Spectroscopy, **33**, *2*, 84–91 (2002); DOI: 10.1002/jrs.827
14. S. A. Burikov, T. A. Dolenko, D. M. Karpov. *Contribution of Fermi resonance to formation of valence band of Raman spectrum of water*, Optics and Spectroscopy, **109**, *2*, 272–278 (2010).
15. S. A. Burikov, S. Dolenko, T. Dolenko, S. Patsaeva, V. Yuzhakov. *Decomposition of water Raman stretching band with a combination of optimization methods*, Molecular Physics, **108**, *6*, 739–747 (2010).