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Akos Vertes & Annemie Bogaerts

Modelling of particle formation during/after laser ablation (LA) of solids.

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Annemie Bogaerts, °1971, Belgium. PhD in Science, Universiteit Antwerpen. Docent, Department of Chemistry, Universiteit Antwerpen.

Professor Akos Vertes conducted his research at the VLAC for three months, calculating, thinking and writing in the quiet of the premises in the heart of Brussels. Besides the group PLASMANT (Plasma Laser Ablation and Surface Modelling Antwerpen) headed by Prof. Bogaerts, guest researcher Akos Vertes also interacted with the Department of Analytical Chemistry, run by prof. Frank Vanhaecke and prof. Luc Moens at the Universiteit Gent and the research unit 'Clusters, Hybrid Nanosystems and Laser Spectroscopy' of the KULeuven where he met the senior researchers prof. Roger E. Silverans, prof. Peter Lievens and dr. Erno Vandeweert. He participated in discussions and seminars and he also gave lectures at the three universities.

Studying laser-initiated processes/plasmas is an activity in which prof. Bogaerts and prof. Vertes have had a previous informal collaboration. Earlier laser ablation calculations were mostly carried out for vacuum conditions. In the present research project, the model has been extended to allow the presence of a background gas. The presence of a background gas up to atmospheric pressure releases a plethora of processes, which cannot be described with current models. This introduces significant complications in the mathematical model. Background gas provokes new effects, such as the splitting of the laser plume, the formation of a contact layer and more efficient condensation of clusters. Under atmospheric pressure the expanding plume shows additional characteristics such as shock waves in the expansion, spatial confinement, prolonged lifespan and formation of molecular species, turbulence and Rayleigh-Taylor instabilities. These new phenomena result in severe complications in modelling the expanding laser plume. The project at the VLAC is designed to explore how the present model can be extended to describe the most significant properties of laser ablation in the presence of a background gas.

What exactly is your speciality? Is it chemistry or bio-chemistry?

Vertes: "My primary position is professor of Chemistry. But lately, I have been involved in the applications of biochemical methods and I have an affiliation with the Department of Biochemistry. At the George Washington University, I head a research group of seven graduate students and one postdoc. And another postdoc is being hired. This is a relatively small group but in this particular field, the field of mass spectrometry and lasers, it is a good size. I am also affiliated with the Institute for Proteomics Technology and Applications. We started this institute with a colleague from the biochemistry department two years ago and here the focus is to develop new methods, new technologies to analyse proteins and also to implement these methods in unique applications like cancer or AIDS research."

Could you explain the broad outlines of your fields of research?

Vertes: "To be honest, the term laser ablation is not broad enough. If I want to classify the work in my group we have to distinguish three major directions.

The first one is the interaction of lasers and materials for analytical applications. This is where I can classify my current trip to Belgium. This work is funded by the United States Department of Energy. We have had six years of funding already in this field and historically this is where my strength has been. When I came to Antwerpen as a guest researcher – I worked there between 1987 and 1991 with prof. Renaat Gijbels – the primary focus was on laser ablation and its theoretical modelling. So this is one direction.

Then there is a second one, which deals with a new phenomenon – the phenomenon itself is not so new but it has a very exciting new application – called electrospray ionization where we apply high voltage to a liquid and disperse it into very fine droplets. These droplets can in turn be the source of protein ions. Electrospray in combination with mass spectrometry is very useful for biomedical analysis. So this is the second direction in my lab, carried out by a second team and this is funded by the National Science Foundation.

The third one, an emerging new direction, related to the first one but clearly different, is the development of an entirely new instrument for protein microscopy. We would like to observe the distribution of proteins in living cells and tissues. In order to do this, we need very high spatial resolution and also very high specificity. It is therefore essential that we be able to distinguish the different proteins we are dealing with. We plan to combine scanning near-field optical microscopy with mass spectrometry. This is our newest project, funded by the W.M. Keck Foundation. These are the three directions we distinguish in the group. As I have mentioned, my current stay in Belgium is related to the first direction, which is laser-solid interactions."

"The collaboration has already resulted in some nice recognition. The 2003 Elsevier/Spectrochimica Acta Award for the best paper of the year was granted to the PLASMANT-group."

The project focuses on solids. But do other substances come in the picture? And how would you define the process of ablation?

Vertes: "The main interest of my collaborator Annemie Bogaerts at the Universiteit Antwerpen is metals (e.g. copper) and other inorganic solids but as you can tell I am also very interested in the biomedical field. I suggested bringing the laser ablation of water and ice targets into the picture as well as tissues. Biological tissues contain 60 to 80 percent water. Thus, the ablation of water is very relevant, because that's the primary driving factor in tissue ablation. The word ablation is used in this context to describe the creation of a material plume that is a mixture of vapour as well as tiny droplets leaving a crater in the target. Of course, if a liquid target is used there is no crater. This entire process, i.e., the removal of a certain amount of material and the transfer of that material into the gas phase is called ablation. The practical applications of solid ablation, which was the initial driving force behind this collaboration, had to do with the trace analysis of metals, ceramics and other insulating materials. It turns out that the best and most widely used method for elemental trace analysis, analysis of components present in very low concentration, is ICPMS (Inductively Coupled Plasma Mass Spectrometry). This method is based on creating an argon plasma using an

induction coil. A prerequisite for the analysis is the transfer of the liquid or solid sample into this plasma. This sounds simple, but it is not at all trivial, especially with solid samples. And here comes the role of the laser. With the laser ablation process you create a collection of nanoparticles which then can be streamed into the plasma using an argon gas flow. So the primary application targeted by this collaboration is the laser ablation of metals and insulators (solids) for ICPMS. But, as I have mentioned, there are other very interesting practical applications including laser surgery and the analysis of biological tissue."

How did the sabbatical at the VLAC take shape. Have you known prof. Bogaerts for a long time? And how did you get acquainted with her work?

Vertes: "Between 1987 and 1991, I was in Antwerpen as a guest researcher working with prof. Gijbels in his PLASMANT-group (Plasma, Laser Ablation and Surface Modelling Antwerpen). When I moved to the United States in 1991, we kept this collaboration going. In the meantime, prof. Bogaerts was still a student at the Universiteit Antwerpen. I got to know her when I came back in 1995 for a short period and she was already finishing her doctorate. Last year, when prof. Gijbels retired, prof. Bogaerts took over the project. She developed a keen interest in laser ablation. Our research project came as a natural idea, as I had had a long history in this field and she developed an interest. So, why shouldn't we come together and see where this would take us? And so I embarked on the sabbatical at the VLAC. Actually the collaboration has already resulted in some nice recognition: the 2003 Elsevier/Spectrochimica Acta Award (joint award of the publisher and the journal) for the best paper of the year was granted to us for one of our papers. It proves that our work together is indeed a well-recognized collaboration."

You divided your stay at the VLAC into two periods: one month in 2004 and two months in 2005. Had the splitting practical reasons or was there a strategy behind it?

Vertes: "This was primarily a practical arrangement. My sabbatical leave from GW started last September and I had had a position of visiting professor at the ETH (Eidgenössische Technische Hochschule, Swiss Federal Institute of Technology) at Zürich lined up to start in October. So in that fall semester, I combined one month at the VLAC with three months at the ETH. During the winter I continued working with prof. Bogaerts and her postdoc, Zhaoyang Chen, developing the co-operation on laser ablation. By the time the second period came around in April 2005 we already had had some very promising preliminary results. So I think it was originally a practical arrangement but the division in two periods turned out to be very useful also."

What results do you hope to achieve with the project?

Vertes: "The focus of the project is to describe the formation of nanoparticles in the laser ablation plume. This has major implications for metal ablation and analytical laser ablation. It also has some very important consequences in biomedical applications for laser surgery and laser ablation for biomedical analysis. Now, I have to say that my stay here has proven to be very useful because we have come to realize that several new phenomena have to be included in the description of laser ablation. These phenomena were not included in the traditional ablation models.

One of them, called 'phase explosion' is of particular interest. You can contrast this process with surface evaporation. When you heat a piece of metal or liquid very fast, the surface evaporation is

not sufficiently rapid to remove all the energy. This results in superheating of the material. When that happens, the surface layers can quickly and violently turn into vapour, just as in an explosion. That process has very important implications for our project.

Another effect that surfaced during our research is related to the specifics of laser light absorption in the material. Light absorption is usually considered to be linear. In other words, light is absorbed by the material with a certain constant efficiency. With lasers however we can achieve very high light intensity, that's one of the reasons people use lasers, and it has a very profound effect on the material. The light absorption becomes intensity dependent. You can reach an energy density in the material where the target becomes temporarily transparent to the laser light. That's a very significant effect so it has to be taken into account.

Finally, there is another interesting little story about an aspect of the plume expansion into the atmosphere. When the plume developed by the laser moves out and expands into the atmosphere, it creates a shock wave at its front. So the plume pushes the air in front of it and there, at the interface, creates a shock wave. It turns out from our calculations that this shock wave follows the same kinetics, the same movement in time, as a nuclear explosion. If you take the time dependence of the position of the shock front in a nuclear explosion the relationship shows a dependence on time to the two-fifths power and on the energy of explosion to the one-fifth power. If you determine the position of the shock front in the laser plume it follows exactly the same kinetics: two-fifths power of time, and one-fifth power of energy. It's remarkably the same. That information turns out to be very useful and enables us to verify our model. And that's what's going on right now. We are in the finishing phase of verifying the model and then we expect to be able to describe the plume expansion and the formation of nano particles."



How do you look back at your stay in the VLAC. Wasn't the absence of a laboratory on the premises a handicap to a researcher of an exact science? And did you meet other colleagues for discussions? Did you get involved in other activities at the VLAC?

Vertes: "I really enjoyed the environment here. It was very peaceful and quiet. And that's exactly what a researcher needs to come up with new ideas. On the other hand, with the current means of communication and computer networks especially on a project like this, it is easy to access the necessary scientific data and resources. Remember, this is purely a modelling project. So experiments and data came from the literature which we could access through the computer network. The calculations were done on a computer in Antwerpen, and I could easily consult them by logging in from here or even run them from here. The communication with the colleagues there mainly happened by phone and I also visited them five times during these two months. So the interaction was really optimal. I also gave three lectures – one in Antwerpen on 'Fundamental Processes in Soft Ionization Methods for Biomedical Analysis,' and one in Leuven ('Laser Desorption/Ionization from Nanostructured Surfaces: DIOS - Silicon Nanowires - Black Silicon') where the host was prof. Peter Lievens. It was a very nice visit and I thoroughly enjoyed touring their lab, as well. They have really world class state-of-the-art research going on there. The third lecture entitled 'Laser-solid interactions below and above the plasma ignition threshold' was in Gent. It was a tutorial talk on the fundamentals of laser ablation. These were the interactions. And no, I didn't feel lonely at the VLAC. I met another fellow, prof. Gabor Boros, who was a compatriot from my native Hungary. He is a philosopher. We often had lunch together and when he organized a contact forum called 'Leibniz on Love' I went and listened to it."

The collaboration won't end with the project here, I suppose?

Vertes: "The postdoc, dr. Chen, is finishing up in the lab of prof. Bogaerts. He is interested in joining my group. So we are certainly keeping in contact. And obviously we are going to publish the results of our VLAC-project together. And there is a fair chance that the discussions, meetings and seminars at the three campuses will lead to common publications as well. This 'Flemish connection' could mark the beginning of an international interdisciplinary collaboration in which I can play the role of a catalyst."