CONFERENCE REPORT

*PDMS '93, Hirschegg, Kleinwalsertal, Austria,
June 19–26, 1993*

This year marks the 20th anniversary of the discovery of ^{252}Cf -plasma desorption mass spectrometry (^{252}Cf -PDMS) and the 60th birthday of one of its founders. Hartmut Jungclas (Marburg) used this occasion to organize an informal workshop on particle-induced desorption mass spectrometry (June 19–26, 1993). The setting was truly ideal, a country inn nestled in an alpine valley surrounded by snow-capped mountains in the Hirschegg, Kleinwalsertal region of Austria just across the German border. The inn is owned by supporters of Marburg University and is efficiently operated by a family in their employ. It is used for seminars and vacations for faculty and staff of the University, a most civilized and enlightened venture for a modern university.

The arrangement was similar to a New England Gordon conference, with some quaint differences. All the participants (36) stayed together in the inn and had meals in a diningroom that was well designed to take advantage of the beauty of the surroundings. Breakfasts were typically continental with fresh hard rolls, local cheeses and meats, and a variety of quarks, yogurts, whole grains, and berries that seem to be part of alpine fare. We bussed our own dishes and made our own lunches from the breakfast leftovers. In the evening, we had home-cooked meals featuring some of the local cuisine.

The seminar room, a recent addition, was ringed with picture windows so that it was possible to hear the latest news on electrospray mechanisms while watching a cable car nervously inch its way from one mountain peak to another. And if the speaker was particularly soft spoken, the gentle sounds of the bovine bell choir could be heard in the distance.

The workshop began promptly at 9:00 AM Sunday morning with a paper by Karl Wien, Professor at the Institute of Nuclear Physics, TH, Darmstadt. In recent years Karl has been studying the ^{252}Cf -PDMS of frozen hydrocarbon gases to learn more about the mechanisms of ion formation by studying simple matrices. He showed evidence for chemical synthesis in fission tracks, a topic that is gaining interest in the PDMS world.

Igor Baranov from the Khlopin Radium Institute in St. Petersburg, Russia, presented some startling evidence that massive Au cluster ions with molecular masses up to 10^6 Da are desorbed in PDMS from matrices consisting of 20 nm dia. Au clusters. Detection and mass spectrometric analysis were carried out using a clever pulsed acceleration field coupled with an electrostatic deflector to disperse the ions according to mass-to-charge ratio. This paper was one of the

most startling of the meeting, taking experimentalists and theoreticians by surprise. Many private discussions took place on this subject throughout the meeting, with translations provided by Professor Baranov's talented and charming daughter, Olga Baranova, who is a professional linguist.

The concluding talk in the Sunday morning session was the fulfillment of a dream that the PDMS veterans had hoped would someday become reality: to be able to image an individual ion track in a solid. Much speculation and theory have focused on the dynamics of the interaction of PDMS-energy ions with solids and predictions of transient pressure pulses, shock waves and for the first time, these phenomena have been captured and visualized by scanning force microscopy (SFM). Christina Trautmann (GSI, Darmstadt) showed that 220 MeV Pb ions burrow into the smooth surface of mica or graphite, transforming the surface into an alpine-like terrain of 0.5 nm high mountains with diameters of 1–2.5 nm. That these structures were formed with conducting graphite was an unexpected observation because the standard PDMS lore is that the material must be an insulator to observe electronic sputtering. Several papers on imaging fast ion tracks were presented throughout the workshop and it was clear that this activity will be an important and welcome new feature of PDMS-type research. Gunther Dollinger (Munich) showed SFM images of single crystal MgO bombarded with 120 MeV Au ions which sputtered material at the surface leaving grooves 5 nm wide, 1 nm deep, and 150 nm long. Curt Reimann and Judit Kopniczky (Uppsala) showed latent tracks generated by 78 MeV I ions in single crystals of valine using a novel SFM where the probe taps the surface to produce clearer images. One spectacular track knocked the corner off a step location defect and burrowed into the next crystal plane, forming a permanent elongated ripple on the surface, a clear visual confirmation of the collective motion that emanates from the heavy ion track. Curt Reimann showed the first SFM images of impact sites of an 800 keV 50 kD protein molecular ion (formed by electrospray ionization) incident on single crystal graphite consisting of huge (on a molecular scale) oblong hillocks 44 nm wide, 75 nm long, and 2 nm high. The shape of these hillocks seemed to be dependent on the conformational state of the protein. Linking the nanoscale imaging technology with desorption of molecules and ions from surfaces is one of the most exciting new developments in the field.

On Sunday afternoon, Ron Macfarlane (Texas A & M) gave a report on current research in his laboratory that included the use of pulse amplitude analysis of the signals from an MCP secondary ion detector to distinguish ions according to velocity and composition. He also reported on a new investigation of the use of involatile, liquid matrices for PDMS and concluded with another example of in-situ chemical reactions to study the interactions of transition metal ions with

peptides. This paper was followed by a contribution from R. M. Papaleo, a student from one of the Brazilian PDMS groups who is spending a year in the Sundqvist group at Uppsala. He reported on some very nice studies of the radial distribution of carbon cluster ions from the PDMS of polyvinylidene fluoride (PVF) and polystyrene (PS) using a Standing reflectron to achieve high mass resolution. They found that for PVF, C_n^+ clusters tend to be ejected along the axis of the fission track while $C_nH_x^+$ clusters from the same matrix were ejected tangentially, indicating ejection from a lower temperature part of the track. Surprisingly, these effects were not observed for cluster ions ejected from a PS matrix. This paper elicited considerable discussion on the evidence for elaborate chemical synthesis in the fission track versus pyrolysis of the polymeric structure. No conclusions could be drawn on this question.

Monday morning featured a talk by Ken Standing, a distinguished contributor to TOF-MS from the University of Manitoba. He raised considerable excitement with a description of his ESI-TOF system which uses the orthogonal extraction technique but coupled with fast single ion electronics which makes it compatible for a PDMS laboratory. This paper was followed by an excellent presentation from Hans-Walter Fritsch, a talented and versatile graduate student in Hartmut Jungclas' group at Marburg and one of the efficient local organizers. He studied the effect of fluoride treatment on the chemical composition of the tooth. The unique feature of this study was that an Ar^+ ion etching unit was coupled to the PDMS system. The depth of incorporation of fluoride into the tooth was studied by recording PD mass spectra, etching away a controlled depth of the surface, and repeating the PD mass measurement. The paper which closed the Monday session was contributed by a relative newcomer to the PDMS community, J-P. Thomas from the University of Lyon, who also introduced a new application of PDMS to the study of the nanostructure of electronic devices. Using PDMS, he was able to demonstrate that for metal oxide films, the depth of emission was on the order of 0.5 nm, on the order of a monolayer. A side issue of this study is that these findings add to the present state of confusion regarding surface versus multilayer ionic desorption, an issue not yet settled.

Tuesday was elected as the day for excursion into the mountains because of a break in the weather that was a typical alpine mix of sun, rain, mist, with variability on an hourly scale. The group was divided into two sets depending on desired level of exertion and set off by foot in different directions. The majority was the most heroic group which climbed for 3 hours through a steep and treacherous rock and ice field to a cozy Bierstube for an afternoon respite. But this was just the starting point for the Erlangen group (plus a few others), notorious for their adventures in the Himalayans and accelerator-based PDMS. Peter Duck (Erlangen/ABB Informatik) led a group to the summit

of the rugged needlelike "Hammerspitze" complete with all of the terror and intrigue that sea-level lovers prefer to read about, while another group, headed by Helmut Voit (Erlangen), could be seen through binoculars tightropeing a narrow, towering ridge in the face of a sudden, violent thunderstorm. At the other end of the scale, another group picked wild flowers, watched a 3-year-old child participant wade in an icy mountain stream, and drank beer in a mountain top terrace at the end of a chair lift. Incredibly, everyone was present intact for dinner that evening, evidence that this PDMS crowd, like the technique, is at the same time gentle and durable.

The Wednesday morning session included the report of a new approach to surface-induced dissociation by Lothar Schmidt (Marburg), where the ions make a grazing encounter with a surface without hitting it and in the process dissociate due to interaction with the surface potential. In the afternoon session, Ebs Hilf (Oldenburg), the eminent nuclear-theorist-turned-PDMS-theorist, dazzled us in typical fashion with complex quantum-mechanical analyses, soliton waves, and touched on the C_{60} fullerene formation in fission tracks as well as interpretation of the results presented by Wien on frozen gases. He provided theoretical support for the possibility of chemical synthesis in the fission track but indicated that carbon cluster formation in PVC is the result of a combination of unique chemistry and breakdown of the PVC structure. A question left dangling was how do we know that a true fullerene molecular ion is formed in a fission track and not a geometric isomer. Dieter Brandl gave a report on his work at Erlangen with Helmut Voit on the PDMS of Langmuir-Blodgett films, which confirms earlier work from the Orsay and Uppsala laboratories. For these matrices, ion emission from depths up to several monolayers deep is observed, an observation that is part of the confusing situation on understanding the factors that determine depth of ion emission in PDMS.

The Thursday morning session brought the meeting to the applications arena. The purists were obliged to remain because they could not escape from the valley. It started off in spectacular fashion with a report by Michael Glocker from Przybylski's group at Konstanz. This group has demonstrated the highest level of creativity in applying PDMS to problems in molecular biology, and this presentation was one more in an impressive string of achievements. Antigen-antibody interactions were studied where the epitope site was identified by antibody shielding to enzymatic degradation followed by peptide mapping after removal of the antibody. Some experiments were reported where ESI and PDMS were used in a complementary fashion to study tertiary structure. These studies are probably the harbinger of how the modern techniques of mass spectrometry (PDMS, MALDI, ESI) will be used in a biological laboratory. The laboratory of Erwin Schmid

with Gunter Allmaier and E. Pittenauer at the University of Vienna is rapidly becoming a major applications contributor to PDMS.

The Thursday afternoon session was chaired by an old friend of PDMS and frequent PDMS symposium organizer, Catherine McNeal. She made use of a week-long respite in her medical studies to participate in this meeting along with her 3-year-old daughter, Caitlin, who was already immortalized as an in-vivo participant at a previous PDMS workshop 3.5 years ago in Spiegelroog, Germany. The first paper in this session was given by Wilfred Tuszynski, a molecular spectroscopist at Oldenburg who in the past few years has applied his considerable talents in molecular spectroscopy to learn more about energy and charge transport in PDMS. There were several important results presented by him and by a student, Christoph Krafft, relating to the role of the matrix in PDMS. One of the conclusions: adsorption of analyte on nitrocellulose occurs as single isolated molecules while adsorption on other substrates involves clusters of molecules. Desorption of the analyte as ions is much higher when single molecules are desorbed. Some redox chemistry is occurring in the ionization process. This effect was clearly demonstrated in the PDMS of chlorophyll a and b mixtures. Matrix isolation PDMS was again demonstrated, a technique first introduced by Jungclas prior to MALDI in his work on quantitating drug levels by PDMS. In this latest work, the Oldenburg group introduced various basic aromatic matrices in 1:100 molar ratios to enhance the yield of high molecular weight oligosaccharides in PDMS and showed that laser desorption from the same matrix gave essentially the same spectrum. The first link between PDMS and MALDI was clearly established by this study. However, matrix-assisted PDMS of proteins does not track what is observed by MALDI, so the issue is not yet clearly defined.

Two additional papers in the applications part of

the program deserve special mention. The first is a contribution from Josefin-Beate Holz, an M.D. internist in Hartmut Jungclas's group at Marburg. "Josi" was also one of the local organizers of the meeting and played an important role in establishing the warm, friendly atmosphere of the meeting. She is currently involved in treating cancer patients with the antitumor drug, etoposide, and has developed a rapid method for plasma level analysis using TLC separation combined with PDMS to quantitate and control the proper level. The participants were introduced to some of the real-world protocols in the field of drug therapy and how mathematical models are used to control and predict blood levels.

The final paper to be mentioned in this report comes from the laboratory of Yannik Hoppilliard at the Ecole Polytechnique, Palaiseau, an established "card-carrying" mass spectroscopist who has adopted the PDMS community. There is a consensus that if she had been involved in the early stages of the development of PDMS, the method would have been more easily and universally accepted. With virtuosa competence, she showed the participants how much information is contained in the PD mass spectrum of a simple peptide, how aromatic amine isomers give vastly different fragmentation patterns. Her message: the primary PD mass spectrum is as rich in structurally relevant information as any of the other techniques. It is a method that has both hard and soft ionization components.

The conference was supposed to conclude with a panel discussion on "The future of PDMS?" But when it came to that time, we preferred to enjoy the local beer, taste some very acceptable German red wine, and not worry about the future.

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