Report of Foreign Travel of J. M. Ramsey, Group Leader, Analytical Chemistry Division

TO: Alvin W. Trivelpiece

FROM: J. M. Ramsey

PURPOSE: To participate in the Fifth International Symposium on Resonance Ionization Spectroscopy and its Applications and to visit the Joint Research Centre of the European Communities at Ispra, Italy.

SITES VISITED:
- 9/16-21/1990 Conference, Varese, Italy
- 9/24/1990 Joint Research Centre, Ispra, Italy

ABSTRACT:
The Fifth International Symposium in Resonance Ionization Spectroscopy and Its Applications was attended. The Joint Research Centre of the European Communities at Ispra, Italy was also visited. The traveler presented an invited talk, chaired a meeting session and gave an impromptu presentation on how current laser technology limits the development of commercial instrumentation based upon Resonance Ionization Spectroscopy. The conference was truly international with scientists from 19 countries and less than 1/4 from the US. The meeting also provided a health mixture of experimentalists and theoreticians. Technical developments reported included the use of electric field ionization from laser prepared Rydberg states as a way to reduce background signals and commercial development of an optical parametric oscillator for replacing pulsed dye laser. A speaker from the Soviet Union suggested their willingness to market hardware they have developed based upon the resonance ionization technique.

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The primary purpose of this trip was to participate in the Fifth International Symposium on Resonance Ionization Spectroscopy and its Applications held in Varese, Italy. In addition, the Italian site of the Joint Research Centre of the European Communities in Ispra was also visited. The Conference covered all aspects of resonance ionization spectroscopy (RIS) including fundamental physics, instrumentation, and applications to both fundamental and applied problems. It was particularly appropriate for ORNL to have a strong contingent of scientists at this meeting due to the fact that RIS and resonance ionization mass spectrometry (RIMS) were conceived and first demonstrated at ORNL. This meeting had a true international flavor. The conference included scientists from eleven Western European countries, USSR, Hungary, PRC, India, Israel, Japan, Canada, and the USA. There were 160 people pre-registered for the conference, 38 of these from the US, and notably 13 from the Soviet Union. I find it particularly important that US scientists interact with this international community for two reasons: (1) much of the work from the eastern bloc countries is not reported in a timely fashion, and (2) in many cases, the work performed in the European community is reported in European journals that are often considered secondary journals by U.S. workers. The traveler played a significant role in this meeting. An invited presentation was given, a session was chaired, and an impromptu presentation was given assessing how current laser technology limits the development of commercial instrumentation based upon the RIS technique.

Significant experiments reported by foreign workers include the combination of accelerator mass spectrometry with RIS, utilization of electric field ionization techniques to decrease background signals, and developments of new laser technology. The groups of Letokhov, USSR Academy of Sciences, and Kluge, University of Malnix, are performing experiments that allow isotope ratio measurements with very high abundance sensitivity, $10^{5}$. In these experiments ions of the pertinent element are created in an ion source and accelerated to energies of 10-100 keV. The ions are mass analyzed before impinging on a charge exchange cell. The ions are neutralized in the charge exchange cell and in some cases left in metastable states. Most of the neutrals are maintained at the velocity of the accelerated ions and thus there is a velocity difference between the isotopes. The velocity difference enhances the isotopic shifts and thus allows improved spectral selectivity. The neutrals are excited to Rydberg states where they are electric field ionized and detected. The Russian group was able to obtain a spectral selectivity of $10^{-6}$ to $10^{-7}$ between $^{3}\text{He}$ and $^{4}\text{He}$ in a two-color excitation from the 25 metastable state to a Rydberg level. They obtained an abundance sensitivity of approximately $10^{3}$ in these measurements. Some interesting electric field ionization experiments are also being performed in the laboratory of Niemax in Germany. These experiments parallel work underway in our laboratory but utilize a linear quadrupole mass filter rather than a three-dimensional quadrupole ion trap. In these experiments a three-photon CW excitation is performed on atoms emanating from an atomic oven. The atoms are promoted to a Rydberg state from which they are electric field ionized by the extraction lens of the linear quadrupole mass filter. In the particular experiments discussed, lithium was the atom under study and excitation was provided by two diode lasers and a dye laser. Preliminary experiments indicate that this approach will be extremely beneficial for looking at real samples. The lack of a high intensity ionizing photon flux greatly reduces non-resonant background ionization of materials contained in the sample matrix. It is also noteworthy to report on developments in laser technology from the laboratory of Professor Wallenstein from the University of Kaiserslautern. Professor Wallenstein has done a great deal of work in the area of nonlinear frequency conversion of laser radiation. In particular, the generation of harmonic radiation in atomic vapors and optical mixing in non-linear crystals. He reported on recent experiments with an optical parametric oscillator (OPO) using beta barium borate (BBO) with a tuning range from 300 nm to 3 microns. Using 80 mJ of 355 nm pump radiation from a Q-switched Nd:YAG laser, 25% conversion efficiency was obtained at an output wavelength of 545 nm. An efficiency of 45%
was obtained using 200 mJ of 355 nm pump light. This device is very attractive for replacing dye lasers. This single unit provides tunable radiation over a range greater than that obtainable with a dye laser with much greater simplicity and eliminates the need for large numbers of dye solutions which are operationally expensive due to disposal costs. Wallenstein indicated that GWU Laser Technics in Germany is now marketing this OPO for approximately $40,000.

This meeting provides a healthy environment for theoreticians and experimentalists to interact. A noteworthy contribution from the theoretical community is that of Peler. At the last RIS conference in 1988, several experimentalists presented data showing isotopic biases in the photoionization of various elements using single color pulsed excitation. These results were unexpected at the time and an explanation was needed. Lambropoulos in the meantime has undertaken some painstaking theoretical calculations to model these experiments. His results show that an isotopic bias is expected under the conditions that the previous experiments were performed. He has also suggested possible approaches for eliminating or reducing these biases.

D. M. Rayner of the National Research Council of Canada presented an interesting talk on the use of a graphite furnace coupled to a supersonic expansion. They are attempting to use the Doppler tuning provided by the transverse velocity components in the supersonic expansion to measure isotope ratios. A fixed frequency laser is propagated transverse to the nozzle axis. The laser frequency is tuned to the centroid of an isotopically split transition. The different isotopes are then resonant with this laser beam at different spatial positions due to the velocity tuning. In this way they hope to measure isotope ratios simultaneously on very small quantities of material. They suggest that their sensitivity (mass) will be two orders of magnitude better than with ICP-MS.

A final experiment will be described that does not involve RIS but is mentioned because it is rather clever. Work was described by Professor Svanberg of the Lund Institute of Technology in Sweden. They are using lasers to image opaque material in human body tissue. We are all aware of the fact that we can hold our fingers up to a lighbtbulb and see radiation pass through them, but we cannot identify, for example, the bones in the fingers through such an inspection due to the fact that most of the light transmitted undergoes many scattering events. The Swedish workers have been able to overcome this problem by using picosecond pulses of laser radiation for the optical imaging. Their approach to overcoming the scattering problem is to only collect the light that arrives at the detector in the first few picoseconds. The light that arrives at the detector first is from those photons that are transmitted directly without undergoing scattering events. These photons faithfully project or image the opaque features in the human tissue. This technique has many potential applications such as mammography without using ionizing radiation.

I had discussions with Professor Kluge of the University of Mainz about experiments they have performed with quadrupole ion trap devices. They have apparently performed a number of experiments with these devices that have not been reported in the literature. Their primary objective was to detect very low levels of plutonium. They were attempting to do fluorescence excitation spectroscopy on plutonium ions contained within the trap. Trapping of plutonium ions was confirmed by mass measurements but they were never successful in obtaining fluorescence excitation spectra. It is likely that they were not actually trapping plutonium ions but rather, due to the reactivity of plutonium, either a hydride or an oxide of the metal. The communication of this work was quite valuable as it relates to work being done in our laboratory with quadrupole ion trap mass spectrometers. Discussions with Dr. Larry Green of Chalk River Nuclear Laboratory in Canada indicated that they are using three-color photoionization experiments to measure isotope ratios of uranium. They are using copper vapor laser pump dye lasers to perform
these experiments. It is interesting to note that the system they are using for measuring these isotope ratios is very similar to the AVLIS process developed in the US for laser isotope separation.

I also had an opportunity to talk to several of the Russian scientists. Notable discussions were with G. I. Bekov, USSR Academy of Sciences, Institute of Spectroscopy, M. V. Chekalin, USSR Academy of Sciences Institute of Geochemistry and Analytical Chemistry, and O. I. Matveev of Moizaika. The latter two scientists gave their first presentations in the English language as this was their first trip to the western world. The Russians seemed to be much more open in their one-on-one discussions than I have perceived at previous meetings. They indicated that recent political changes have made a big difference in their lives and was indeed giving them much more freedom. George Bekov has been involved in the development of an instrument based upon RIS over the past several years. He indicated in a presentation that they plan to market this device including the Nd:YAG pumped dye laser system. It was quite surprising to see the Russians trying to market their technology. I also had interesting discussions with Ken Ledingham of the University of Glasgow. Our discussions primarily revolved around experiments using a single laser to do laser desorption and RIS. One of his students presented a poster at the meeting on this type of experiment. These experiments have interesting applications to RIMS of solid materials.

On September 24 I visited the Joint Research Centre of the European Communities located in Ispra near Varese. This is one of four laboratories that make up the European Community Joint Research Centre. My host at JRC was Dr. Nicholas Omenetto. He has a laser facility in the Environmental Institute at JRC. His laboratory is involved in a number of practical measurement problems in addition to some fundamental studies. They are involved in studies of nuclear waste containment within glassy host materials. They are studying leaching rates of lanthanide ions from these glassy materials using laser excited luminescence spectroscopy. They are also involved in the development of an airborne laser spectrometer for the detection of oil spills. More recently the same apparatus has been used to study the effects of acid rain on flora. Research indicates that the luminescence of chlorophyll in plant material that is stressed from acid rain gives a different response than that from healthy plants. This stress in the plants is detected long before there is any visual indication. Dr. Omenetto is also involved in fundamental studies of excitation processes in inductively coupled plasmas and the development of atomic vapor sources as resonance detectors.

My impression of the JRC laboratories is that they are very well funded with respect to capital equipment acquisition but they suffer from a lack of manpower to perform their research activities. JRC has programs in place that allow graduate students, postdocs, and visiting scientists to perform collaborative research on site. It appeared that visiting scientists are utilized to a much greater extent than postdoctoral fellows or graduate students.

In summary, this trip was found to be quite useful. The content of the meeting, RIS and its applications, has a very strong overlap with the interests of DOE. This was indicated by the fact that a number of national laboratories had participants at this meeting and also by the fact that DOE/OHER was a major financial supporter. The meeting content strongly overlap with the programs underway in the Analytical Chemistry Division at ORNL as indicated by the fact that both of the Division's representatives were invited speakers. The meeting was successful in bringing together an international group of researchers working in a common area. An additional strength of this meeting is the cross-fertilization between theoreticians and experimentalists. Future support and involvement in this meeting is strongly supported.
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Persons Contacted

Resonance Ionization Spectroscopy Conference

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