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**COVER SHEET
FOR TRIP REPORTS SUBMITTED TO THE
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**Destination(s) and Dates for
Which Trip Report Being Submitted:** Varese, Italy -- September 15-27, 1990

Name of Traveler: J. P. Young

Joint Trip Report Yes
 No

If so, Name of Other Traveler(s): _____

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ORNL
FOREIGN TRIP REPORT
ORNL/FTR-3774

DATE: October 11, 1990

SUBJECT: Report of Foreign Travel of J. P. Young, Senior Research Staff Member, Analytical Chemistry Division

TO: Alvin W. Trivelpiece

FROM: J. P. Young

PURPOSE: To attend the Fifth International Symposium on Resonance Ionization Spectroscopy and present an invited oral presentation at that meeting. A visit was also made to the University of Camerino to discuss mutual interests in molten salts.

SITES VISITED: 9/16-21/1990 Conference Varese, Italy
9/24/1990 University of Camerino Camerino, Italy

ABSTRACT: J. P. Young attended the Fifth International Symposium on Resonance Ionization Spectroscopy and presented an invited oral presentation on research he and co-workers had carried out in applying diode lasers to resonance ionization mass spectrometry. A summary of the conference is given along with an assessment of some of the presentations that the author found of interest. Young also visited Professor Marassi at the University of Camerino to present a seminar and discuss mutual interests in a new molten salt research project of the author. Some of the studies at Camerino are described. Ideas concerning the author's research that came from private discussions are also presented here.

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The primary purpose of this travel was to attend the Fifth International Symposium on Resonance Ionization Spectroscopy held in Varese, Italy, and to present an invited oral presentation entitled "Application of Diode Lasers to Resonance Ionization Mass Spectrometry". The symposium had a total attendance of approximately 175. It was truly international; some 22 countries were represented with a number of research centers and universities represented from many of these countries. Another interesting point about the 160 pre-registered attendees is that only 49 were from the USA; there are many studies of resonance ionization spectroscopy (RIS) being carried out throughout the world. At meetings concerned with a single research area, the audience and speakers are directed to each other. That was the case in this meeting, and it provided for excellent exchange of ideas and comments both formally and informally. More about this later. The next symposium will be held in about two years in Santa Fe, New Mexico.

The talks were broken up into 13 general sessions dealing with physics treatments of rare atoms, ionization mechanisms, atomic and molecular RIS, environmental and trace analysis, biological and medical applications, short sections on state selected chemistry and sources, ultrahigh resolution studies, and finally an interesting section on surface and bulk analyses. There were generally plenary lectures, invited lectures, and invited oral presentations for most sessions. There were also two lively poster sessions where about 56 contributed research papers were presented. Abstracts for all talks and posters were available at registration, and the proceedings of the symposium are expected to be published by the Institute of Physics, Bristol, England in January or February, 1991. Another continuing change in this symposium was the presence of many more chemists than before. Physicists still dominate, but not as obviously as in some earlier meetings.

The session on physics treatment of rare atoms was very interesting. H. J. Kluge gave the plenary talk. He (and later others) pointed out that hyperfine structure studies were really the only way to determine nuclear spin, I , and the mean square charge radius of isotopes made in small quantities, such as those that are far from stability, synthesized in accelerators, and also short lived. By doing carefully controlled spectroscopic ionization studies leading to a RIS or RIMS detection, the above nuclear information could be obtained. Later I would demonstrate that hyperfine structure could also be obtained from diode laser RIMS. Kluge and others in this area of study can accomplish with an experimental efficiency of $\sim 10^{-4}$ to 10^{-5} (i.e., number of ions detected/number of atoms made). The shortest half life for detection seems to be 9 msec at ISOLDE to perhaps 1 msec by other techniques described. Most all studies of this nature seem to be three photon ionization routes with two or three different colors. The optical routes are complex in this respect, but quite successful. Recent work reported from the USSR deals with RIMS studies of ^3He and $^{81,85}\text{Kr}$. It is an interesting point that Krypton ions neutralized by charge exchange yield Kr metastables that would obviously be amenable to diode laser excitation; a fact I later found out will be used at the University of Bern for their studies of Kr. A number of f-transition element isotopes, and Fr, have been investigated to obtain information about nuclear shape and structure. Many kinds of laser systems have been used, copper vapor lasers (CVL), Ar^+ , Eximer, etc., coupled with dye lasers. A system called radioactive decay RIS, or RADRIS, was described by H. Backe of Mainz. Short-lived product ions are passed through a collision gas to become atoms; the atoms are ionized by RIS; and the photoions are collected on a radioactive detector plate for counting as they decay.

A number of detailed subjects were covered in the laser ionization mechanism sessions. This field still seems open for investigation. One of the interesting presentations was that of P. Lambropoulis. In some cases now he can calculate optical bias effects one might encounter in comparing optical ionization efficiencies for odd and even isotopes of a given element. The good examples have been published. There are, however, other examples where a bias should be seen and isn't, or cases where the bias is much greater than expected. More work is necessary to

understand these cases. As a general comment, it is interesting to note that when precisions were quoted in papers given at this conference, they still generally lie in the 3 to 10% region. In comments after his talk, Kluge asked him to work on Na, and he replied he would like to study U. Included in this session was a discussion of the NIST RIS/RIMS data sheets which are being developed to give details of optical ionization schemes for the elements. They have so far only considered 1 + 1 or 2-photon schemes of one or two colors. Data sheets for 10 elements have been published by E. B. Saloman. Another set is in preparation. The idea of these data is to give known experimental routes along with physical and optical information about the energy levels involved. These data sheets could be very useful.

RIS and RIMS applications to molecules continue to grow. My field is atomic, but the number of studies of molecules is impressive. Both inorganic and organic molecules have been studied. Examples are NO, other simple molecules, C₆₀, halocarbons, transition metal complexes, peptides, proteins, chlorophyll, and biomedical compounds. RIMS is being suggested also for human genome identification possibilities. In one paper it was pointed out that the fragmentation pattern of aromatic compounds is influenced by the wavelength of the exciting laser; this effect is a result of optical saturation fluence variations for different intermediate states of the molecule. Sample matrix will affect organic sample evolution by laser desorption. By varying matrix and sample absorbance or transparency, one can influence the neutral or ion distribution of an adsorbed sample. In another talk it was pointed out that one must use judgment in positioning the second ionizing laser in MS/MS studies. There is a space focus of ions formed from the first MS, so the second ionization can be made highly selective by differences in locating that laser.

The sessions on trace analyses were interesting. For using ⁸¹Kr in dating samples, the RIMS limit is currently 350 atoms and will be going lower if future plans come to fruition. For comparison, the normal mass spectroscopy limit was said to be 10⁵ ⁸¹Kr atoms. Other talks had to do with specific procedures or instrument modifications to do trace analyses better. One speaker noted that the presence of NO₃⁻ enhanced some RIMS signals, notably Al; 20 μl of 2% Mg(NO₃)₂ was always added to their Al samples for thermal vaporization and RIMS analysis. This is a demonstration of how a matrix effect can help; there are probably other examples. An interesting instrument modification was described by F. Ames, using a hot cavity and a laser source. A sample of atoms could be generally confined to the cavity which is interrogated by a 3 color laser ionizing beam. Any ions generated are extracted out of a small hole in the cavity by an electric field. They claim ion counting efficiencies could be as high as 17%. The system is designed to analyze Tc; to keep Tc atoms vaporized, the cavity will be held at 2300K. Many of the environmental applications were planned and not yet operational, but the ideas were interesting.

As had been in the past, there were some presentations that did not really pertain to RIS or RIMS. They did deal with lasers and laser excitation, but used either non-resonant ionization or fluorescent emission as the detection scheme. There were two short sessions on sources and state selected chemistry. Of note was the paper by Bel Bruno that used RIS in solution to promote organic ion-molecule reactions. This could be the beginning of many other similar interesting studies.

There were interesting practical applications of RIMS to surface and bulk analysis. The use of depth profiling RIMS has yielded complimentary and more useful information than SIMS about semiconductor interfaces. There are sometimes some matrix effects, but useful information results from that as well. A comparison was made of non-resonant and resonant ionization schemes for Ag to be determined in Ag-Au layered samples. Non-resonant ionization seems to have higher resolution and provides surface sensitivity to oxides and other surface compounds (it dissociates and ionizes them); resonant techniques provide greater sensitivity. Other locations besides Atom

Sciences and Argonne are getting into developing SIMS-RIMS instruments. In another study of surface desorption and detection of organic molecules for metals, a limit of detection of less than one femtomole of certain organics was demonstrated. The technique utilized soft laser desorption and RIMS detection.

My co-authored talk (with R. W. Shaw and D. H. Smith) described our applications of diode lasers to the optical processes involved in resonance ionization mass spectrometry (RIMS). It was very well received both formally and informally. There were some 15 questions and comments during the presentation and many afterward. We, and others, feel that diode lasers are the "wave of the future," and their use should be exploited. A number of useful comments were directed to our plan to study ionization routes for RIMS that use all diode lasers. We have been concerned that the oscillator strengths for the required transitions to upper Rydberg states would be vanishingly weak; several theorists at the meeting thought that this would not prevent the RIMS process from working. One person with whom I discussed the idea even thought we might be able to ionize some elements by a complete diode laser optical route rather than our planned non-optical ionization route. From the discussions I had, we are the only group using diode lasers for RIMS; I suspect that will change in the intermediate future, however. I found that diode lasers are currently being studied at the University of Bern, University of Swansea, and Ecole Polytechnique Montreal; of course, they have been studied by us at ORNL and for a number of years by Niemax and his group in Germany. At the first three institutions, the studies are related to fluorescence and optogalvanic studies; they all have, or are planning to, double the frequency of the diodes. At Bern they want to apply diode lasers to excite Kr metastables; at Swansea they are interested in Fe and Al but have no data yet; I understand that at Montreal they are interested in the f-transition elements. Several people asked me if we had studied uranium by diode laser RIMS, and I told them we hadn't to date.

I had a long conversation with K. Niemax concerning diode lasers. He has also frequency doubled diode lasers; he wishes to study Ca. He has in press, in Spectrochimica Acta B, an article describing a simple wavemeter design for measuring diode laser linewidths. I had discussed an optical "pedestal" effect that presently seems to limit our ability to achieve high isotopic selectivity with diode laser RIMS studies of La. I attributed this effect either to residual doppler broadening of our atom beam or broad band emission under the diode laser beam. Niemax said it must be the former as they get "perfect isotope separation". I pointed out that La, or Ba, in general have the smallest optical isotope shifts, and in general, selectivity problems would be greatest with these elements. He did admit there was a broad band emission from a diode laser, but he felt it was much too weak to contribute to our problem. Others also told me there is indeed a broad band emission pedestal under the sharp diode laser wavelength.

I had a useful visit with Professor R. Marassi and group at the University of Camerino. I presented a seminar that covered our work with diode lasers and our interest in, and preliminary results obtained for, the molten salt magnesium sensor project. The audience was small, 12 people, but attentive. After the talk I found interest and questions concerning both topics. Marassi has a group of some 6-8 pre- and post-doctoral workers studying various aspects of electrochemistry. One is actively studying the electrochemical behavior of H₂ in palladium. He pointed out the obvious -- that they wish to thoroughly understand this behavior, and then they will go on to D₂ in palladium. I had fruitful discussions with Marassi and some of his workers concerning our molten salt work. One of my reasons for going there was to gather other opinions on what species in our melt, NaCl-KCl-CaCl₂-MgCl₂, will contain ionic oxygen. Will it be, for example, OH⁻, some type of oxychloride, or soluble oxide. Another reason for going was to see if they had any ideas on corrosion of SiO₂ by these melts. Ideas were freely exchanged on both points. I have felt, and it seemed to be confirmed there, that OH⁻ may not exist in the melt; more

likely oxygen will be as some soluble or partially soluble oxide species. We discussed various techniques for identifying the species. They are electrochemists so they pushed that. They also do spectroelectrochemistry. I noticed a very nice spectroelectrochemical electrode design that I think can be modified for our molten salt use. I have had success in identifying O_2^- and other partially oxidized species in molten fluoride salts. The idea came about that perhaps by spectroelectrochemistry we can gain information about the oxide species. Another idea I obtained was the possibility of looking at reflectance spectra of the solid melt in the near IR region for OH^- overtones to see if OH^- did exist in the melt. We had been having trouble trying reflectance spectra of the fundamental infrared OH^- band in solids. We need to protect the sample from the atmosphere as it is hygroscopic. The apparatus available to use for IR studies could not handle a sealed sample. They, of course, wanted us to monitor the Mg electrochemically; I said this may be necessary, but we hope to do it spectrally. I did say we hope to do the F by an electrochemical technique. We all agreed that voltametric studies of our molten salt system should also be carried out to get basic information about possible impurities we will encounter. They were doing some very interesting work on stepwise reduction processes on metal surfaces that could only be observed if the voltamogram was slowly scanned, 10-20 mV/sec. We might want to apply this approach to some of our studies. Concerning corrosion of SiO_2 by the melts of interest; there is confusion in the literature. I have come to believe that perhaps the attack comes from residual HCl and occurs at the high temperature. They had not had direct experience with this problem but agreed that it was certainly possible and that HCl could be complexed to some of the melt species and be available for high temperature reaction. The outcome of this conclusion is that we can prepare a laboratory melt that is corrosion-free in SiO_2 ; the industrial process, however, uses $MgCl_2 \cdot 2H_2O$ to prepare a given Mg concentration. HCl may be present in the industrial melt.

Itinerary

9/15/90	Travel to Varese, Italy
9/16-21/90	Conference
9/22-23/90	Weekend
9/24/90	University of Camerino, Camerino, Italy
9/25-26/90	Personal Leave
9/27/90	Travel to Oak Ridge, Tennessee

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