DEVELOPMENT OF LASER-ION BEAM PHOTODISSOCIATION METHODS

Progress Report

December 1, 1991- November 30, 1992

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PROGRESS REPORT FOR THE PERIOD DECEMBER 1991 THROUGH NOVEMBER 30, 1992.

During this report period our research efforts have concentrated on the continued development of the tandem magnetic sector (EB)/reflectron-time-of-flight (TOF) instrument, preliminary experiments with the tandem TOF/TOF (E/R-TOF) instrument, developing the methodology for performing photodissociation with pulsed lasers on the EB/R-TOF instrument, preliminary experiments with laser ionization on the aerosol-particle beam apparatus, development of a vacuum ultra-violet laser for photoionization/photoexcitation of gas phase ions, and fundamental studies on matrix-assisted laser desorption ionization (MALDI)

Development of tandem EB/R-TOF instrumentation This project is a major focal point of our current instrument development efforts. The EB/R-TOF instrument provides a marked improvement in instrumentation for tandem mass spectrometry and an improvement in our abilities for developing laser-ion beam photodissociation. The basic EB/R-TOF instrument is now operational. We are continuing development of the instrument hardware, in an effort to facilitate data acquisition, but parallel with this work we are using the instrument for performing photodissociation and tandem mass spectrometry experiments. The operation of the instrument is described in a recent paper (paper #1), and in a sequel paper (paper #2) we describe a data acquisition mode that improves the instrument performance by approximately a factor of 5 and decreases the data acquisition time by a factor of 6.

The EB/R-TOF concept is also having considerable impact on the current thinking about tandem mass spectrometry. Although we have not yet demonstrated the EB/R-TOF instrument as a routine method, its simply too early in the development, the interest in the method is considerable. We have had over 300 request for reprints of paper #1 and I am receiving a large number of invitations to speak at national and international meetings and at academic and industrial laboratories.

PAPERS

1) "Neutral-Ion Correlation Measurements: A Novel Tandem Mass Spectrometry Data Acquisition Mode for Tandem Magnetic Sector/Reflectron-Time-of-Flight Instruments," F. H. Strobel; L. M. Preston; K. S. Washburn; D. H. Russell *Anal. Chem.* 1992, 64, 754-762.

2) "Signal-to-Noise Enhancement of Neutral-Ion Correlation Measurements for Tandem Time-of-Flight Mass Spectrometry," F. H. Strobel; D. H. Russell *Anal. Chem.* 1992, 64, in press.

PRESENTATIONS

"Time-array Detectors for High Sensitivity/High Resolution Tandem Mass Spectrometry," F. H. Strobel; D. H. Russell Pittcon 92, New Orleans, LA, March 9-13, 1992, paper #768.

"Merging Tandem Mass Spectrometry with Lasers and Time-Array Detectors," D. H. Russell, Plenary Lecture, 2nd European Conference on Tandem Mass Spectrometry, University of Warwick, July 19-22, 1992.

"New Concepts in Tandem Mass Spectrometry," D. H. Russell, 204th ACS National Conference, Washington, DC., Symposium on "Time-of-Flight Mass Spectrometers as Tandem Instruments," paper 102.

Development of Tandem Time-of-Flight (TOF/TOF) Methods for MS/MS We have modified an old MS-902 magnetic sector instrument to perform TOF/TOF experiments. The magnet was removed and replaced by a reflectron-TOF. The electrostatic energy analyzer (ESA) is used as a direction and energy focussing element to direct an energy selected ion beam into the R-TOF. Ionization is performed by matrix-assisted laser desorption ionization (MALDI) and neutral-ion correlation is used to obtain the MS-II (R-TOF) spectrum. The R-TOF is operated in the same manner as the R-TOF on the EB/R-TOF. At present the instrument is functioning and is being used for a variety of fundamental studies of the MALDI (see abstracts listed below). In particular, this instrument design is very well suited for measuring the kinetic energy of laser desorbed ions. We will continue these studies with particular emphasis on the mechanism of ionization and the temporal profile of ion formation. During the month of September, 1992 we will begin the preliminary tandem TOF/TOF experiments.

PAPERS

Two papers are in preparation; (i) a descriptive paper on the operation of the instrument, this paper will address the issues of TOF tandem mass spectrometry, esp. the question of m/z resolution of MS-I; (ii) High resolution m/z measurements with an E/R-TOF configuration of MALDI formed ions.

PRESENTATIONS

"Investigations of the Kinetic Energy and Temporal Profiles of Ion Generation during MALDI using an E/R-TOF Mass Spectrometer," G. R. Kinsel; D. H. Russell 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, DC, May 31-June 5, 1992, paper FOA 12:45.

Pulsed laser photodissociation experiments with the EB/R-TOF A significant portion (ca. 50% of 1 man year) of our efforts over the past 6-8 months has been spent on designing the pulsed laser-EB/R-TOF photodissociation experiments. The greatest obstacle for this experiment is designing methods for subtracting background signal, *e.g.*, correcting for metastable ion and collision-induced dissociation (CID) signals. The initial studies have focussed on photodissociation of H⁺-bound species (esp. dimers, trimers, etc.). The interest in photodissociation of H⁺-bound species relates to our proposed "cluster emission model" for MALDI. Studies on 4-nitroaniline/glycerol species have been used to develop the experiment and preliminary results on these studies were presented at the most recent ASMS conference (Washington, DC May 1992). Later in this calendar year we will begin studies on the photodissociation of model organic compounds.

PAPERS

Two invited papers on tandem TOF mass spectrometry are in preparation; these are not duplicates of the ones cited for the E/R-TOF. Both of these papers contain descriptions of the EB/R-TOF pulsed laser photodissociation experiments and results (not duplicated) from the experiment. One paper, in particular, presents our logic for probing the mechanism of MALDI by using tandem mass spectrometry type experiments.

PRESENTATIONS

"Photodissociation of Proton Bound Clusters on a Magnetic Sector/Reflectron TOF Instrument," F. H. Strobel; D. H. Russell 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, DC, May 31-June 5, 1992, paper TOC 12:15.

Preliminary Experiments with an Aerosol-Particle Beam Apparatus The objectives of building the aerosol-beam apparatus are to test the "cluster emission model" for MALDI and develop laser ionization/laser induced fluorescence of aerosol particles. Nozzles provide unique approach to mass spectrometry of liquid/solid materials. Also it is important to understand the role of aerosols in environmental chemistry, but the problem, of course, is developing methods for studying aerosols. Thus our studies provide the basis for development of a novel analytical method and potentially a new approach to aerosol chemistry. In addition, this apparatus could (a long-term objective of the research) provide a new method for combining liquid chromatography and capillary zone electrophoresis (CZE) with mass spectrometry. We have the apparatus working in the laser multiphoton ionization (MPI at 266 nm) mode. Currently we are focussing on demonstrating the aerosol experiment on a variety of systems, specifically "cranking" out a few demonstration papers to validate the method. Results for two papers are now in hand and a third paper is in the data collection stage. The results of these experiments are interesting, in that we observed chemistry uncharacteristic of gas-phase ionization, that both demonstrate

we are indeed dealing with "particles" and that novel information is obtained for particles that are not observed for gas-phase molecules. See spectra A-C that are attached.

PRESENTATIONS

"Liquid Aerosol Nozzles for Analytical Applications," L. R. Beeler; K. K. Murray; D. H. Russell 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, DC, May 31-June 5, 1992, TOC 10:15

"Studies of Proton Transfer Reactions within Aerosol Particles," K. K. Murray; L. R. Beeler; D. H. Russell 40th ASMS Conference on Mass Spectrometry and Allied Topics Washington, DC, May 31-June 5, 1992, paper FOA 1:15.

Development of a Vacuum Ultra-Violet Laser System Development of a VUV systems was not part of the originally proposed studies. Dr. Gary Kinsel joined by group as a post-doc about the time that our new Nd:YAG laser arrived. He had experience with VUV systems and I have always wanted to look at post-ionization of laser desorbed neutrals as a structural mass spectrometry method. We decided to build the light-pipe necessary to perform VUV (118 nm) experiments. This system is now operational and we are beginning to perform post-ionization of MALDI formed neutrals. This experiment will be used as another test of our "cluster emission model" for MALDI. This experiment provides a unique approach to structural mass spectrometry, e.g., a means to produce fragment ions of laser desorbed species. The results obtained in this experiment will be complimentary to laser-ion beam photodissociation.

Fundamental Studies of Matrix-Assisted Laser Desorption Ionization (MALDI) In case it is not obvious from the renewal application and our work over the past two years, I'm extremely excited about the possibilities of MALDI, both as a molecular weight and structural mass spectrometry method. In addition, MALDI, because the reactive precursor is formed by photon absorption, provides an excellent opportunity to probe the fundamentals of desorption ionization, esp. the chemical reactions leading to ion production. We have made excellent progress in this area over the last year. We have published a paper on excited state proton transfer reactions, we have demonstrated that MALDI combined with FTICR has enormous potential for characterization of large peptides and proteins, and that a number of our current experiments (esp. laser-ion beam photodissociation (LIBP), because both LIBP and MALDI are the results of electronic excitation) help to shed light on the MALDI process. All aspects of the work described in the previous sections impact our MALDI program.

PAPERS

"Are Proton Transfer Reactions of Excited States Involved in UV Laser Desorption Ionization," M. E. Gimón; L. M. Preston; T. Solouki; M. A. White; D. H.

Russell C., *Mass Spectrom.* 1992, 27, 827-830.

"Laser Desorption Studies of High Mass Biomolecules in Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry," T. Solouki; D. H. Russell *Proc. Natl. Acad. Sci. USA* 1992, 89, 5701-5702.

PRESENTATIONS

"Photochemistry/Photophysics in Matrix-Assisted Laser Desorption Ionization of Polar Molecules," M. A. White; D. H. Russell PITTCON 92, New Orleans, LA, March 9-13, 1992, paper 763.

"Gas-Phase Ion Molecule Reactions of Biomolecules in MALDI with FTICR," T. Solouki; J. V. B. Oriedo; D. H. Russell 40th ASMS, paper MOD 1:15.

Tandem Mass Spectrometry of MALDI formed Ions using a Magnetic Sector(EB)/R-TOF," F. H. Strobel; D. H. Russell 40th ASMS, paper MOC 12:00

"Studies of Peptide Negative Ions by Using MALDI: Matrix Selection and Correlation with Positive Ion Data," L. M. Preston; D. H. Russell 40th ASMS paper FOA 1:00

"Comparison of Arrival-Time Distributions of Mass Selected Ions Produced using MALDI," M. A. White; D. H. Russell 40th ASMS, paper MP 141.

Calibrate &
Mass Spec
for Instrument
Paper

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Figure A

Figure B

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Figure C

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