

Laser-Ionization Time-of-Flight Mass Spectrometry of High Molecular Mass Inorganic Complexes



TABLE OF FIGURES

CHAPTER I. INTRODUCTION

Figure I. 1- (a) Linear metric configuration Time-of-Flight mass spectrometer	
(b) Single-stage reflectron Time-of-Flight mass spectrometer	5
Figure I. 2: Primary space focus principles as illustrated for	
(a) single-stage extraction/acceleration	19
(b) Wiley-McLaren dual-stage extraction and acceleration.....	19
Figure I. 3: Principles of energy-focusing as illustrated in a single-stage reflectron .	24
Figure I. 4: Dual-stage reflectron.....	26

CHAPTER II. EXPERIMENTAL SETUP

Figure II. 1: Our complete reflectron-design TOF-MS.	32
Figure II. 2: Dual-stage ionization chamber of our LI-TOF-MS.....	34
Figure II. 3: Two-stage reflectron design for second-order space focusing in our LI-TOF-MS.	36
Figure II. 4: Electronics configuration and triggering for the LI-TOF-MS.	40
Figure II. 5: Timing of ion generation and extraction events.	41

CHAPTER III. INSTRUMENT CHARACTERIZATION

Figure III. 1: Linear mode instrument operation--Poor resolution for the W^+ ion....	45
Figure III. 2: Reflectron mode of instrument operation-- Distinct resolution of all W^+ isotopes.....	45
Figure III. 3: Primary space focus investigation-- dependence of spectral characteristics on the extraction (repeller) and acceleration (flight tube) potentials of the Al^+ peak from the aluminum sample.....	50
Figure III. 4: Primary space focus investigation-- dependence of spectral characteristics on the extraction (repeller) and acceleration (flight tube) potentials of the CaO^+ peak from the 0.033% Eu:CaO sample.	55
Figure III. 5 : Second-order space focus investigation-- Optimization of the reflectron-- Constant front lens potential.	58
Figure III. 6 : Second-order space focus investigation-- Optimization of the reflectron-- Constant rear lens potential.	58
Figure III. 7 : Single-shot spectrum of pure C_{60}	60
Figure III. 8 : Spectrum of pure C_{60} compiled as the average of 100 laser shots.....	60
Figure III. 9 : Calibration example and mass accuracies.....	65

TABLE OF FIGURES (cont.)

Figure III. 10: Plot of the optimum repeller pulse delay time as a function of the mass of the ablated ion.....	74
Figure III. 11: Velocities of the ablated ions as a function of mass.....	75
Figure III. 12: Signal saturation and loss of resolution as repeller delay is optimized for the Ca ⁺ peak.....	83
Figure III. 13: Increased resolution as the repeller delay is shifted away from the optimal for the saturated peak.....	83
CHAPTER IV. DOPED METAL OXIDE SYSTEMS	
Figure IV. 1: Typical mass spectrum of the 5% Eu:Y ₂ O ₃ sample.....	87
Figure IV. 2: Typical mass spectrum of the 0.033% Eu:CaO sample (TOF-MS conditions optimized for 100-200 amu mass range).	89
Figure IV. 3: Mass spectral resolution and quantitation of tungsten isotopes.	94
CHAPTER V. FULLERENES ANALYSIS	
Figure V. 1: Low laser energy ablation of the pure C ₆₀ sample.....	105
Figure V. 2: Moderate laser energy ablation of the pure C ₆₀ sample.....	105
Figure V. 3: High laser energy ablation of the pure C ₆₀ sample.....	106
Figure V. 4: "Magic number" ion peaks for low laser energy ablation of the C ₇₀ soot.....	108
Figure V. 5: Moderate laser energy ablation of the C ₇₀ soot.	108
Figure V. 6: High laser energy ablation of the C ₇₀ soot.	109
Figure V. 7: Odd-numbered low-mass fullerenes.	111
Figure V. 8: Isotope resolution for low-mass fullerenes.	111
CHAPTER VI. ANALYSIS OF HIGH MOLECULAR MASS INORGANIC COMPLEXES USING MATRIX-ASSISTED-LASER DESORPTION/IONIZATION (MALDI)	
Figure VI. 1: Schematic of the heteronuclear trimetallic complex $\{[(bpy)_2Ru(dpp)]_2IrCl_2\}(PF_6)_5$ ("JSB").....	121
Figure VI. 2: Schematic of the monometallic complex $[Ir(dpp)_2Cl_2](PF_6)$ ("Dbl-Ir").	122
Figure VI. 3: Schematic of the homonuclear, trimetallic complex $\{[(bpy)_2Ru(dpp)]_2RuCl_2\}(PF_6)_4$ ("Tri-Ru").	123
Figure VI. 4: $[Ir(dpp)_2Cl_2](PF_6)$ ("Dbl-Ir"); Spectrum obtained for 4 μ J ablation energy of a straight ablation sample.	128
Figure VI. 5: $[Ir(dpp)_2Cl_2](PF_6)$ ("Dbl-Ir"); Spectrum obtained with 7 μ J ablation energy of a straight ablation sample.	128
Figure VI. 6: $[Ir(dpp)_2Cl_2](PF_6)$ ("Dbl-Ir"); Spectrum obtained with	

TABLE OF FIGURES (cont.)

20 μJ ablation energy of a straight ablation sample.....	129
Figure VI. 7: $[\text{Ir}(\text{dpp})_2\text{Cl}_2](\text{PF}_6)$ (“Dbl-Ir”); MALDI spectrum of a sample prepared in DHB matrix (TOF-MS optimized for $\sim 400\text{-}1000$ amu region)..	131
Figure VI. 8: $[\text{Ir}(\text{dpp})_2\text{Cl}_2](\text{PF}_6)$ (“Dbl-Ir”); MALDI spectrum of a sample prepared in DHC matrix (TOF-MS optimized for $\sim 400\text{-}1000$ amu region)..	132
Figure VI. 9: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2\}(\text{PF}_6)_4$ (“Tri-Ru”); Typical spectrum of a directly ablated sample TOF-MS optimized for $\sim 200\text{-}700$ region.).....	137
Figure VI. 10: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2\}(\text{PF}_6)_4$ (“Tri-Ru”); MALDI spectrum of a sample prepared in DHB with acetone solvent (TOF-MS optimized for $\sim 300\text{-}800$ region)	139
Figure VI. 11: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2\}(\text{PF}_6)_4$ (“Tri-Ru”); MALDI spectrum of a sample prepared in DHB with acetonitrile solvent (TOF-MS optimized for $\sim 300\text{-}800$ amu region).....	140
Figure VI. 12: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{RuCl}_2\}(\text{PF}_6)_4$ (“Tri-Ru”); MALDI spectrum of a sample prepared in DHC matrix (TOF-MS optimized for $\sim 200\text{-}700$ amu region).....	140
Figure VI. 13: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); Typical spectrum of a straight ablation sample (TOF-MS conditions optimized for the $50\text{-}300$ amu region).....	145
Figure VI. 14: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); Typical spectrum of a straight ablation sample (TOF-MS optimized for $\sim 300\text{-}900$ amu region).	145
Figure VI. 15: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); MALDI spectrum of a sample prepared in DHB matrix.....	148
Figure VI. 16: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); MALDI spectrum of a sample prepared in DHB with ethanol solvent.	148
Figure VI. 17: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); MALDI spectrum of a sample prepared in 9-nitroanthracene matrix (TOF-MS optimized for $\sim 200\text{-}700$ amu region).....	149
Figure VI. 18: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); MALDI spectrum of a sample prepared in sinapinic acid matrix with ethanol solvent (TOF-MS optimized for $\sim 200\text{-}700$ amu region).....	149
Figure VI. 19: $\{[(\text{bpy})_2\text{Ru}(\text{dpp})]_2\text{IrCl}_2\}(\text{PF}_6)_5$ (“JSB”); MALDI spectrum of a sample prepared with DHC matrix (TOF-MS optimized for $\sim 300\text{-}900$ region).....	150