

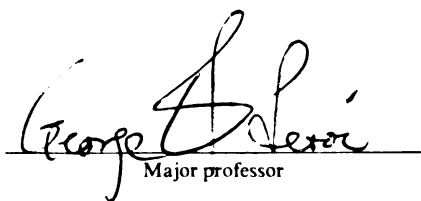
This is to certify that the
dissertation entitled
**PHOTOIONIZATION MASS SPECTROMETRIC
STUDY OF HALOGENATED METHANES**

presented by

Frank Cheng-Yu Wang

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry


Major professor

Date September 12, 1983



RETURNING MATERIALS:
Place in book drop to
remove this checkout from
your record. FINES will
be charged if book is
returned after the date
stamped below.

ROOM USE ONLY

DO NOT CIRCULATE

**PHOTOIONIZATION MASS SPECTROMETRIC
STUDY OF HALOGENATED METHANES**

By

Frank Cheng-Yu Wang

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1983

ABSTRACT

PHOTOIONIZATION MASS SPECTROMETRIC STUDY OF HALOGENATED METHANES

By

Frank Cheng-Yu Wang

Photoionization mass spectrometry(PIMS) is a powerful technique for the investigation of ionization and fragmentation processes of molecules. Accurate ionization potentials(IP) for parent ions and appearance potentials(AP) for fragment ions can be measured directly and the fragmentation mechanism elucidated. In this dissertation, a PIMS investigation of fourteen different halogenated methanes is presented. The energetic and dynamic information obtainable from these results is discussed.

Mass spectra—obtained under full illumination of the helium discharge—of CF_2ClBr , CF_4 , CF_3Cl , CF_3Br , CF_3I , CF_2Cl_2 , CFCl_3 , CCl_4 , CCl_3Br , CF_2Br_2 , CHF_3 , CHF_2Cl , CHFCl_2 , and CHCl_3 , are reported and demonstrate the purity of the samples. Photoionization efficiency(PIE) curves—corrected for detector background counts, stray light, and sample pressure variations—have been obtained for all the parent ions

Frank Cheng-Yu Wang

(except CF_4 , CCl_4 , and CHF_3) and most of the abundant fragment ions.

Appearance potentials extrapolated from fragment PIE curves may be too high due to activation energy of the fragmentation reaction, kinetic shift, competition with other fragment channels, etc. Thus, the heats of formation calculated from experimental APs will always be upper limits to the desired adiabatic value. An improved estimate of the adiabatic value can be extracted by comparing, for a given fragment ion, ΔH_{f0}° obtained from several precursors; the lowest, and thus "best" such values are presented.

Fragment ion appearance potentials are generally consistent with the dissociation mechanism implicit in the quasi-equilibrium theory of mass spectrometry. However, consideration of alternative decomposition pathways for parent halomethane ions produced in excited electronic states suggests that dihalogen cation fragments can be formed in a few vibrational periods, i.e., under kinetic control. A qualitative discussion of the relative stabilities of the trihalomethyl and dihalomethylene cations is also given.

To Tsui-Cheng

To Mom

To Dad

ACKNOWLEDGMENTS

My heartfelt thanks and gratitude are given to two special people; without them this work could not have been accomplished. My wife, Tsui-Cheng has accompanied me throughout my graduate studies and has supported and encouraged me in my research endeavors. My preceptor, Professor George E. Leroi, provided support in many ways. His warmth and his guidance, on matters academic and personal, are particularly appreciated. He helped instill self-confidence and independence, and I feel most fortunate to have had the chance to work with him.

I thank Professor R.H.Schwendeman for his great help in the preparations for my first seminar and second-year oral, and for his careful reading of the dissertation. I am also grateful to Professor J.Allison for his many helpful suggestions and discussions during the course of this research, and for the considerable effort he expended as the second reader of my thesis.

Many members of the MSU Chemistry Department service staff were of particular help in solving problems relating to and in the maintainance of the instrumentation used in this work. I wish to thank especially Tom Atkinson, Marty Rabb, Manfred Langer and Russ Geyer.

Financial assistance from the National Science Foundation and from the Chemistry Department in the form of teaching assistantships and the 1983 Union Carbide Corporation Summer Research Fellowship are also gratefully acknowledged.

TABLE OF CONTENTS

List of Tables.....	ix
List of Figures.....	xii
CHAPTER ONE. INTRODUCTION.....	1
CHAPTER TWO. PHOTOIONIZATION MASS SPECTROMETRY: AN OVERVIEW.....	8
A. Photoionization.....	10
1. Direct Ionization.....	12
2. Autoionization(Preionization).....	19
3. Fragmentation Processes.....	30
B. Experimental Techniques for Measurement of Ionization and Appearance Potentials.....	45
1. Photoionization Mass Spectroscopy.....	46
2. Photoion-Photoelectron Coincidence Spectroscopy.....	51
3. Other Techniques for Measuring Ionization and Appearance Potentials.....	55
(1) Optical Spectroscopy.....	55
(2) Threshold Experiments.....	57
(a) Photoionization.....	57
(b) Electron Impact.....	58
(i) Monoenergetic.....	59
(ii) Quasi-monoenergetic.....	59
(iii) Non-monoenergetic.....	60
(3) Electron Spectroscopy.....	61
(a) Photoelectron Spectroscopy.....	61
(b) Auger Electron Spectroscopy.....	62

(c)	Resonant Photoionization.....	63
(d)	Penning Ionization.....	63
(4)	Other Methods.....	64
(a)	Surface Ionization.....	64
(b)	Charge Transfer Spectra.....	65
CHAPTER THREE.	THRESHOLD BEHAVIOR.....	67
A.	Quantum Theoretical Considerations.....	68
1.	Ionization Threshold Law.....	68
2.	Autoionization Effects.....	70
3.	Franck-Condon Factors.....	71
4.	Degenerate Ionic States.....	78
(a).	Spin-Orbit Coupling.....	79
(b).	Configuration Instability.....	81
B.	Thermal Effects.....	83
1.	Hot Bands.....	83
2.	Thermal Tailing.....	85
C.	Kinetic Effects.....	90
1.	Activation Energy and Heat of Reaction.....	91
2.	Kinetic Shift.....	92
3.	Reaction Path and Reaction Competition.....	93
D.	Instrument Effects.....	93
CHAPTER FOUR.	EXPERIMENTAL APPARATUS AND PROCEDURES.....	96
A.	Introduction.....	96
B.	The Instrument.....	96
1.	Light Source.....	96
2.	Monochromator.....	104

3.	Ionization Region and Sample Inlet System.....	105
4.	Photon Transducer.....	106
5.	Ion Optics and Mass Spectrometer.....	107
6.	Ion Transducer.....	108
7.	Vacuum System.....	108
8.	Interlock System.....	109
9.	Instrument Control and Data Acquisition.....	110
C.	Experimental Procedure.....	112
1.	Samples.....	112
2.	System Pump-Down.....	113
3.	Lamp Spectra.....	114
4.	Mass Spectra.....	115
5.	Experiment Set-Up.....	116
6.	Data Correction.....	117
CHAPTER FIVE. RESULTS AND DISCUSSION.....		119
A.	Results.....	119
1.	CF_2ClBr	122
2.	CF_4	138
3.	CF_3Cl	144
4.	CF_3Br	153
5.	CF_3I	162
6.	CF_2Cl_2	173
7.	CFCI_3	183
8.	CCl_4	193
9.	CCl_3Br	198
10.	CF_2Br_2	208

11. CHF_3	215
12. CHF_2Cl	222
13. CHFC1_3	229
14. CHCl_3	238
B. Discussion.....	245
1. The Heats of Formation of Fragment Ions.....	245
(1) CF_3^+	245
(2) CF_2Cl^+	249
(3) CFC1_2^+	252
(4) CCl_3^+	252
(5) CF_3Br^+	257
(6) CF_2^+	260
(7) CFC1^+	263
(8) CCl_2^+	263
2. Qualitative Consideration of Parent Ion Fragmentation Energetics.....	268
3. Discussion of the Heats of Formation of Trihalomethyl and Dihalomethylene Cations.....	274
4. Mechanism for Formation of Dihalogen Cations.....	278
5. Rationalization of Observed Fragmentation Channels.....	287
CHAPTER SIX. SUMMARY AND SUGGESTIONS FOR FURTHER WORK.....	294
A. Summary.....	294
B. Suggestions for Further Work.....	295
1. Without Change in the Instrument.....	295
(1) Theoretical Investigation.....	295
(2) Heats of Formation.....	295

(3) Parent Ion Stability.....	296
2. With a Small Change to the Instrument.....	296
(1) Temperature Control of the Sample Inlet and Ion Source Systems.....	296
(2) Negative Ion Detection.....	297
(3) Addition of a Second Reaction Chamber.....	297
(4) Laser-Induced Fluorescence of Ions.....	298
BIBLIOGRAPHY.....	299

LIST OF TABLES

table

1-1.	Ratio of photoionization cross section to photoionization efficiency as a function of percent absorption.....	7
2-1.	Some processes following absorption of a vacuum ultraviolet photon by a molecule.....	13
2-2.	Experimental techniques used to measure positive ion energies.....	56
3-1.	Observed and calculated spin-orbit splitting for the halogen acids and halogens.....	80
5-A-1.	Standard enthalpies of formation (0°K. kcal/mole) utilized in thermochemical calculations of ΔH_{f0}° of fragments ions.....	124
5A-1-1.	Photoionization mass spectrum of CF_3ClBr	126
5A-1-2.	Summary of IP, AP, and heats of formation data for all ions from CF_3ClBr	128
5A-2-1.	Photoionization mass spectrum of CF_4	140
5A-2-2.	Summary of IP, AP, and heats of formation data for all ions from CF_4	140
5A-3-1.	Photoionization mass spectrum of CF_3Cl	146
5A-3-2.	Summary of IP, AP, and heats of formation data for all ions from CF_3Cl	146
5A-4-1.	Photoionization mass spectrum of CF_3Br	155
5A-4-2.	Summary of IP, AP, and heats of formation data for all ions from CF_3Br	155
5A-5-1.	Photoionization mass spectrum of CF_3I	164
5A-5-2.	Summary of IP, AP, and heats of formation data for all ions from CF_3I	164
5A-6-1.	Photoionization mass spectrum of CF_2Cl_2	175
5A-6-2.	Summary of IP, AP, and heats of formation data for all ions from CF_2Cl_2	177
5A-7-1.	Photoionization mass spectrum of $CFCI_3$	185

5A-7-2.	Summary of IP, AP, and heats of formation data for all ions from CFCl_3 ,.....	187
5A-8-1.	Photoionization mass spectrum of CCl_4 ,.....	195
5A-8-2.	Summary of IP, AP, and heats of formation data for all ions from CCl_4 ,.....	195
5A-9-1.	Photoionization mass spectrum of CCl_3Br ,.....	200
5A-9-2.	Summary of IP, AP, and heats of formation data for all ions from CCl_3Br ,.....	202
5A-10-1.	Photoionization mass spectrum of CF_3Br ,.....	210
5A-10-2.	Summary of IP, AP, and heats of formation data for all ions from CF_3Br ,.....	212
5A-11-1.	Photoionization mass spectrum of CHF_3 ,.....	218
5A-11-2.	Summary of IP, AP, and heats of formation data for all ions from CHF_3 ,.....	218
5A-12-1.	Photoionization mass spectrum of CHF_2Cl ,.....	223
5A-12-2.	Summary of IP, AP, and heats of formation data for all ions from CHF_2Cl ,.....	223
5A-13-1.	Photoionization mass spectrum of CHFCCl_2 ,.....	231
5A-13-2.	Summary of IP, AP, and heats of formation data for all ions from CHFCCl_2 ,.....	233
5A-14-1.	Photoionization mass spectrum of CHCl_3 ,.....	240
5A-14-2.	Summary of IP, AP, and heats of formation data for all ions from CHCl_3 ,.....	240
5B-1-1.	Estimate of ΔH_{f0}° for CF_3^+ ,.....	247
5B-1-2.	Estimate of ΔH_{f0}° for CF_2Cl^+ ,.....	250
5B-1-3.	Estimate of ΔH_{f0}° for CFCCl_2^+ ,.....	253
5B-1-4.	Estimate of ΔH_{f0}° for CCl_3^+ ,.....	256
5B-1-5.	Estimate of ΔH_{f0}° for CF_2Br^+ ,.....	259
5B-1-6.	Estimate of ΔH_{f0}° for CF_2^+ ,.....	262
5B-1-7.	Estimate of ΔH_{f0}° for CFCCl^+ ,.....	264
5B-1-8.	Estimate of ΔH_{f0}° for CCl_2^+ ,.....	267

5B-2-1.	Relative parent ion stability.....	270
5B-3-1.	Systematic trends in the heats of formation of chloro- fluorocarbon cations and their isoelectronic boron analog.....	275
5B-3-2.	Systematic trends in the heats of formation of bromo- fluorocarbon cations and their isoelectronic boron analog.....	277
5B-3-3.	Heats of formation (kcal/mole) of mixed CF_xBr_y cations.....	280

LIST OF FIGURES

figure

1-1.	Ratio of photoionization cross section to photoionization efficiency as a function of percent absorption.....	7
2-1.	Schematic diagram of potential curves of electronic states and vibronic transitions in a diatomic molecule.....	27
2-2.	The ionization threshold region of NO^+ ; pronounced auto-ionization peaks superposed on the step structure.....	29
2-3.	Potential energy curves illustrating some important dissociation mechanisms.....	34
2-4.	Block diagram of a photoionization mass spectrometer.....	47
2-5.	Spectral distribution of four light sources commonly used in photoionization mass spectrometer.....	48
2-6.	Simplified scheme of a photoelectron-photoion coincidence spectrometer.....	53
3-1.	The effect of Franck-Condon factors and autoionization on a PIE curve and corresponding photoelectron spectra.....	72
3-2.	Effect of Franck-Condon factors on direct ionization thresholds of diatomic molecules.....	74
3-3.	Schematic diatomic molecule potential curves, Franck-Condon factors, and corresponding photoelectron spectrum.....	76
3-4.	HeI photoelectron spectra of halogens and halogen halides....	82
3-5.	Example of the Jahn-Teller effect.....	84
3-6.	The population of the vibrational levels of Br_2 at 300 K.....	86
3-7.	Hot band structure of Br_2^+ at several temperatures.....	87
3-8.	The population of the rotational levels of HCl at 300 K.....	89
3-9.	The effect of a triangular-slit function on a step function..	95
4-1.	The PIMS instrument.....	97
4-2.	The lamp gas delivery system.....	99
4-3.	Helium continuum spectrum.....	100
4-4.	Hydrogen many line spectrum.....	103

5-A-1.	PIE of CF_2Cl^+ from CF_2ClBr	121
5-A-2.	Thermochemical procedure for determining reaction equations appropriate to experimental appearance threshold.....	123
5A-1-1.	Photoionization mass spectrum of CF_2ClBr	125
5A-1-2.	Photoionization efficiency curves for parent and daughter ions from CF_2ClBr	127
5A-1-3.	PIE of CF_2ClBr^+ from CF_2ClBr	129
5A-1-4.	PIE of CF_2ClBr^+ in the threshold region.....	130
5A-1-5.	PIE of CF_2Cl^+ from CF_2ClBr	132
5A-1-6.	PIE of CF_2Br^+ from CF_2ClBr	132
5A-1-7.	PIE of CFC1Br^+ from CF_2ClBr	134
5A-1-8.	PIE of CF_2^+ from CF_2ClBr	134
5A-1-9.	PIE of CFC1^+ from CF_2ClBr	136
5A-1-10.	PIE of CFBr^+ from CF_2ClBr	136
5A-1-11.	PIE of Br^+ from CF_2ClBr	137
5A-2-1.	Photoionization mass spectrum of CF_4	139
5A-2-2.	Photoionization efficiency curves for daughter ions from CF_4	141
5A-2-3.	PIE of CF_3^+ from CF_4	143
5A-2-4.	PIE of CF_2^+ from CF_4	143
5A-3-1.	Photoionization mass spectrum of CF_3Cl	145
5A-3-2.	Photoionization efficiency curves for parent and daughter ions from CF_3Cl	147
5A-3-3.	PIE of CF_3Cl^+ from CF_3Cl	148
5A-3-4.	PIE of CF_3Cl^+ in the threshold region.....	149
5A-3-5.	PIE of CF_2Cl^+ from CF_3Cl	151
5A-3-6.	PIE of CF_2^+ from CF_3Cl	151
5A-3-7.	PIE of CF_2^+ from CF_3Cl	152

5A-4-1.	Photoionization mass spectrum of CF_2Br	154
5A-4-2.	Photoionization efficiency curves for parent and daughter ions from CF_2Br	156
5A-4-3.	PIE of CF_2Br^+ from CF_2Br	157
5A-4-4.	PIE of CF_2Br^+ in the threshold region.....	158
5A-4-5.	PIE of CF_2Br^+ from CF_2Br	159
5A-4-6.	PIE of CF_2^+ from CF_2Br	159
5A-4-7.	PIE of CF_2^+ from CF_2Br	161
5A-4-8.	PIE of Br^+ from CF_2Br	161
5A-5-1.	Photoionization mass spectrum of CF_2I	163
5A-5-2.	Photoionization efficiency curves for parent and daughter ions from CF_2I	165
5A-5-3.	PIE of CF_2I^+ from CF_2I	166
5A-5-4.	PIE of CF_2I^+ in the threshold region.....	167
5A-5-5.	PIE of CF_2^+ from CF_2I	169
5A-5-6.	PIE of CF_2I^+ from CF_2I	169
5A-5-7.	PIE of I^+ from CF_2I	170
5A-5-8.	PIE of IF^+ from CF_2I	170
5A-5-9.	PIE of CF_2^+ from CF_2I	172
5A-6-1.	Photoionization mass spectrum of CF_2Cl_2	174
5A-6-2.	Photoionization efficiency curves for parent and daughter ions from CF_2Cl_2	176
5A-6-3.	PIE of CF_2Cl_2^+ from CF_2Cl_2	178
5A-6-4.	PIE of CF_2Cl_2^+ in the threshold region.....	179
5A-6-5.	PIE of CF_2Cl^+ from CF_2Cl_2	180
5A-6-6.	PIE of CFCI_2^+ from CF_2Cl_2	180
5A-6-7.	PIE of CF_2^+ from CF_2Cl_2	182
5A-6-8.	PIE of CFCI^+ from CF_2Cl_2	182

5A-7-1.	Photoionization mass spectrum of CFCl_3 ,.....	184
5A-7-2.	Photoionization efficiency curves for parent and daughter ions from CFCl_3 ,.....	186
5A-7-3.	PIE of CFCl_3^+ from CFCl_3 ,.....	188
5A-7-4.	PIE of CFCl_3^+ in the threshold region.....	189
5A-7-5.	PIE of CFCl_3^+ from CFCl_3 ,.....	190
5A-7-6.	PIE of CCl_3^+ from CFCl_3 ,.....	190
5A-7-7.	PIE of CFCl_3^+ from CFCl_3 ,.....	192
5A-7-8.	PIE of CCl_3^+ from CFCl_3 ,.....	192
5A-8-1.	Photoionization mass spectrum of CCl_4 ,.....	194
5A-8-2.	Photoionization efficiency curves for parent and daughter ions from CCl_4 ,.....	196
5A-8-3.	PIE of CCl_4^+ from CCl_4 ,.....	197
5A-8-4.	PIE of CCl_4^+ from CCl_4 ,.....	197
5A-9-1.	Photoionization mass spectrum of CCl_3Br ,.....	199
5A-9-2.	Photoionization efficiency curves for parent and daughter ions from CCl_3Br ,.....	201
5A-9-3.	PIE of CCl_3Br^+ from CCl_3Br ,.....	203
5A-9-4.	PIE of CCl_3Br^+ in the threshold region.....	204
5A-9-5.	PIE of CCl_3Br^+ from CCl_3Br ,.....	206
5A-9-6.	PIE of CCl_3^+ from CCl_3Br ,.....	206
5A-9-7.	PIE of CCl_3^+ from CCl_3Br ,.....	207
5A-10-1.	Photoionization mass spectrum of CF_2Br_2 ,.....	209
5A-10-2.	Photoionization efficiency curves for parent and daughter ions from CF_2Br_2 ,.....	211
5A-10-3.	PIE of CF_2Br_2^+ from CF_2Br_2 ,.....	213
5A-10-4.	PIE of CF_2Br_2^+ in the threshold region.....	214
5A-10-5.	PIE of CF_2Br_2^+ from CF_2Br_2 ,.....	215
5A-10-6.	PIE of CFBr_2^+ from CF_2Br_2 ,.....	216

5A-11-1. Photoionization mass spectrum of CHF ₃ ,.....	217
5A-11-2. Photoionization efficiency curves for daughter ions from CHF ₃ ,.....	219
5A-11-3. PIE of CF ₃ ⁺ from CHF ₃ ,.....	221
5A-11-4. PIE of CHF ₂ ⁺ from CHF ₃ ,.....	221
5A-12-1. Photoionization mass spectrum of CHF ₂ Cl.....	222
5A-12-2. Photoionization efficiency curves for parent and daughter ions from CHF ₂ Cl.....	224
5A-12-3. PIE of CHF ₂ Cl ⁺ from CHF ₂ Cl.....	226
5A-12-4. PIE of CHF ₂ Cl ⁺ in the threshold region.....	227
5A-12-5. PIE of CHFCl ⁺ from CHF ₂ Cl.....	228
5A-12-6. PIE of CHF ₂ ⁺ from CHF ₂ Cl.....	229
5A-13-1. Photoionization mass spectrum of CHFCl ₂ ,.....	230
5A-13-2. Photoionization efficiency curves for parent and daughter ions from CHFCl ₂ ,.....	232
5A-13-3. PIE of CHFCl ₂ ⁺ from CHFCl ₂ ,.....	234
5A-13-4. PIE of CHFCl ₂ ⁺ in the threshold region.....	235
5A-13-5. PIE of CHFCl ⁺ from CHFCl ₂ ,.....	237
5A-13-6. PIE of CHCl ₂ ⁺ from CHFCl ₂ ,.....	238
5A-14-1. Photoionization mass spectrum of CHCl ₃ ,.....	239
5A-14-2. Photoionization efficiency curves for parent and daughter ions from CHCl ₃ ,.....	241
5A-14-3. PIE of CHCl ₃ ⁺ from CHCl ₃ ,.....	242
5A-14-4. PIE of CHCl ₃ ⁺ in the threshold region.....	243
5A-14-5. PIE of CHCl ₂ ⁺ from CHCl ₃ ,.....	244
5B-1-1. Photoionization efficiency curves for CF ₃ ⁺ formed by fragmentation of various precursors.....	246
5B-1-2. Photoionization efficiency curves for CF ₂ Cl ⁺ formed by fragmentation of various precursors.....	249

5B-1-3.	Photoionization efficiency curves for CFCl_2^+ formed by fragmentation of various precursors.....	252
5B-1-4.	Photoionization efficiency curves for CCl_2^+ formed by fragmentation of various precursors.....	255
5B-1-5.	Photoionization efficiency curves for CF_2Br^+ formed by fragmentation of various precursors.....	258
5B-1-6.	Photoionization efficiency curves for CF_2^+ formed by fragmentation of various precursors.....	261
5B-1-7.	Photoionization efficiency curves for CFCl^+ formed by fragmentation of various precursors.....	263
5B-1-8.	Photoionization efficiency curves for CCl_2^+ formed by fragmentation of various precursors.....	266
5B-3-1.	Procedure used to estimate the heats of formation of CF_2Br^+ , CFBr_2^+ , CFBr^+ list in the Table 5B-3-2.....	278
5B-4-1.	Thermochemistry of BrCl^+ formation from CF_2ClBr	281
5B-4-2.	Mechanisms of BrCl^+ formation from CF_2ClBr	283
5B-4-3.	Dependence of BrCl^+ ion count rate on CF_2ClBr pressure.....	285
5B-4-4.	Dependence of IF^+ ion count rate on CF_2I pressure.....	286
5B-5-1.	Appearance potential for competitive fragmentations of selected halomethanes.....	288
5B-5-2.	Schematic rerepresentation of vibrational motion leading to BrCl^+ formation on CF_2ClBr^+ excited electronic state potential surface.....	291

CHAPTER ONE

INTRODUCTION

Halogenated methanes are in widespread and daily use. For example, they are regularly employed as refrigerants, foaming agents, aerosol propellants, etc.¹ Because neutral halocarbons are themselves relatively stable and innocuous, their use and disposal was not until recently regulated or even monitored. Many of these compounds (and the halomethanes in particular) are gases or liquids with very high vapor pressure at room temperature, so they are not generally contained, and they spread even into the troposphere and stratosphere. When exposed to light (especially vacuum ultraviolet radiation), these compounds will ionize or dissociate into positive ions, negative ions, free radicals and other neutral fragments, all of which are highly reactive. When these highly reactive species interact with other molecules in the stratosphere, the troposphere or even the atmosphere, what kinds of reactions will occur? What are the mechanisms for these reactions? What are the products? How do these products influence life? All of these questions are important and of interest to scientists. For example, some years ago it was reported² that chlorine and bromine atoms formed by the dissociation of chlorine- and bromine-containing halomethanes by vacuum ultraviolet radiation in the stratosphere and troposphere may be related to the destruction of the earth's protective ozone layer. There are many other effects yet to be determined. In order to initiate such investigations, scientists first need to have

detailed, accurate, complete thermochemical data such as the ionization potentials for parent ions, appearance potentials for fragment ions, and heats of formation for all ions. This information will allow thermodynamic predictions to be made regarding possible reactions and most favorable pathways. A knowledge of the relative stability of ions may provide important clues regarding possible reaction mechanisms. With thermodynamic and kinetic information at hand, better judgments can be drawn about the volatile halocarbons, especially with regard to which reactants need to be carefully controlled to prevent contamination of the environment or destruction of natural resources.

Photoionization mass spectrometry (PIMS) has become an important experimental method in recent years.³ The most successful and important application of this technique has been to determine thermochemical information for ions. Because of its high resolution capability and the energy independence of the photoionization cross section,⁴ photoionization mass spectrometry is recognized as the best technique for such investigations.⁵

Photoionization mass spectrometry is a spectroscopic technique in which the yield of a selected ion from a sample gas is measured as a function of the incident photon energy. Thus, relative photoionization and fragmentation cross sections are measured as a function of energy. They provide a great deal of information, such as ionization and appearance potentials, vibrational and electronic level spacings, and the heats of reaction for different dissociation pathways. From these primary data, coupled with tabulated thermochemical data for neutral species, heats of formation of parent and fragment ions, fragmentation

mechanisms and a variety of other information can be deduced. PIMS, in combination with a few other techniques, can often fully characterize molecular ionization and ionic fragmentation processes.

In this dissertation, fourteen often-used, commercially-available halogenated methanes have been selected for investigation by the photoionization mass spectrometry technique. Ionization potentials of the parent ions and appearance potentials for associated fragment ions have been measured. Heats of formation of the corresponding ions have been calculated and the discussion includes possible decomposition pathways for several reactions and the relative stability of parent and some fragment ions. The thermochemical information derived from the measurements and the discussion of the results should prove helpful in later investigations in this field.

Chapter two of this dissertation presents a general overview of photoionization mass spectrometry. It includes a general discussion of the interaction between light in the 10-20eV energy range and gas phase atoms and molecules. It also includes a brief description of several different techniques to measure ionization and appearance potentials for ions, with emphasis on the advantages of the photoionization mass spectrometry technique. Particular attention is paid to threshold behavior in Chapter three. Effects on the shape of the threshold ranging from the nature of quantum theory through thermodynamics, kinetics and instrumental contributions are considered. In Chapter four, the MSU PIMS instrument is briefly described. All of the experimental work performed in the course of this research was done on this instrument, and this chapter includes a relatively detailed

procedure to introduce future workers to some of its complexities. The data are reported and discussed in detail in Chapter five, which forms the major portion of this dissertation. Chapter six provides a conclusion and suggestions for further investigation.

To complete this introduction, the term "photoionization efficiency", which is widely used in this dissertation, is introduced and clearly defined. Since most of the experimental data are obtained as photoionization efficiencies at selected photon energies, this term is particularly important for the research which will be described.

In the description of absorption or ionization phenomena one typically uses the term "cross section" to describe the "transition probability" or "the probability of interaction with radiation". In photoionization mass spectrometry, one wishes to know the probability of ionization perhaps leading to fragmentation after absorption of a photon or the probability of absorption; these are expressed as the photoionization cross section and absorption cross section, respectively. Because of instrumental restrictions in the energy region of interest, the absorption cross section or photoionization cross section cannot be measured directly. Thus scientists report the photoionization efficiency(PIE), which is defined as:

$$\text{PIE} = \text{ion intensity} / \text{transmitted photon intensity},$$

at a given photon energy for an ion of selected mass. The ion intensity and the transmitted photon intensity are easily and directly measurable. The purpose of the following derivation is to show that under typical

PIMS experimental conditions the PIE is, with negligible error, directly proportional to the desired partial photoionization cross section.

From Beer's law:

$$\log(P_0/P) = A = \epsilon bc, \quad (1-1)$$

where P_0 is the incident light intensity, P is the transmitted light intensity, ϵ is the absorption coefficient, b is the path length of the radiation through the sample, and c is the sample concentration. Alternatively one may write:

$$\ln(P/P_0) = -\sigma bc \quad (1-2)$$

where $\sigma = 2.303\epsilon$ is defined as the absorption cross section. Equation (1-2) can be rewritten in exponential form:

$$P = P_0 \text{EXP}(-\sigma bc). \quad (1-3)$$

The photoionization cross section is defined as:

$$\sigma_i \equiv \sigma N_i / (P_0 - P) = \sigma N_i / P_0 [1 - \text{EXP}(-\sigma bc)] \quad (1-4)$$

where N_i is the ion intensity produced by absorption of incident light.

The photoionization efficiency (PIE) is defined as:

$$\text{PIE} = N_i/P = N_i/P_0 \text{EXP}(-\sigma bc). \quad (1-5)$$

Hence

$$\sigma_i/\text{PIE} = \sigma \text{EXP}(-\sigma bc)/[1 - \text{EXP}(-\sigma bc)] \quad (1-6)$$

or

$$\sigma_i/(\text{PIE}/bc) = [-\ln(P/P_0)](P/P_0)/[1 - (P/P_0)] \quad (1-7)$$

where $[1 - (P/P_0)]$ is the fraction of the light absorbed. Perfect proportionality of the PIE to the photoionization cross section would give a value of one for the ratio in equation (1-7), independent of sample absorption.

Table 1-1 shows how this ratio actually varies as a function of the percent absorption and Figure 1-1 shows the same results graphically. In almost all photoionization mass spectrometry experiments the light absorption is less than one percent, so that the PIE is an accurate representation indeed of the photoionization cross section.

Table 1-1. Ratio of photoionization cross section to photoionization efficiency as a function of percent absorption.

$(1 - \frac{P}{P_0}) \times 100$	0.1	0.5	1	5	10	20	30	40	50
$\sigma_i / (P \cdot I \cdot E) / bc$	0.9995		0.9950		0.9482		0.8322		0.6932
		0.9975		0.9746		0.8926		0.7662	

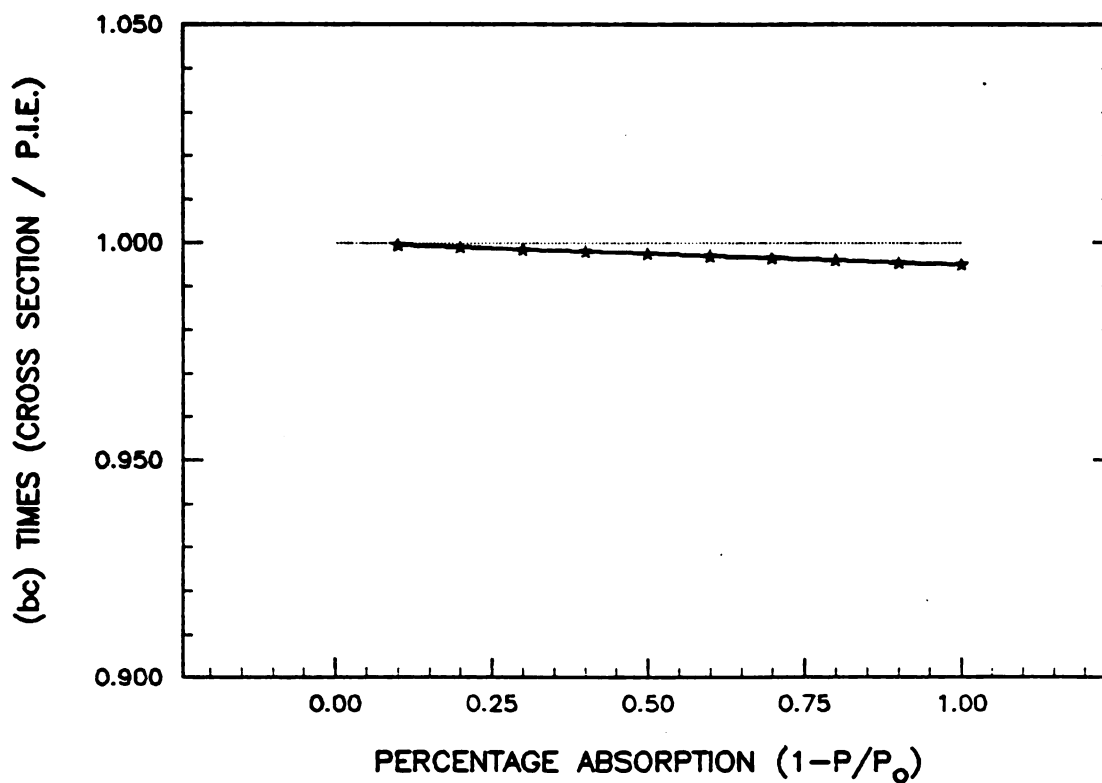


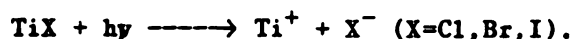
Figure 1-1. Ratio of photoionization cross section to photoionization efficiency as a function of percent absorption, in range 0.0-1.0 percent.

CHAPTER TWO

PHOTOIONIZATION MASS SPECTROMETRY: AN OVERVIEW

The purpose of the photoionization experiment is to measure, as a function of photon energy, the rate of production of specific ions that result from absorption of photons by a neutral molecule. The name photoionization mass spectrometry (PIMS) includes mass spectrometry, but the main aspect of the experiment is the variation of the photon energy. The experiments described in this dissertation are really vacuum ultraviolet absorption experiments, in which the mass spectrometer acts as a powerful ion filter and detector.

The photoionization mass spectrometric method was initiated by Ditchburn and Arnot in 1929⁶ when potassium vapor was irradiated with photons from an iron arc, the light passing through a quartz window into the ion source of a simple magnetic mass analyzer. However, the first valuable results were obtained by Terenin and Popov,⁷ who used the resonance lines emitted by cadmium, zinc or aluminium arcs, in connection with a simple magnetic mass analyzer, to study the ion-pair formation process,



The distinction between direct ionization and ion-pair formation illustrated the advantage of the coupled mass analyzer in comparison with normal optical absorption results. Simple measurement of the total photoion current would not show whether ionization alone or both ionization and fragmentation took place during the experiments.

However, early investigators were restricted by the experimental difficulties associated with photoionization mass spectrometry; in particular, the problems of inadequate light sources and stringent vacuum requirements precluded the realization of the full potential of this new method. In the late 1950's and mid 1960's, Hurzeler et al.^{8,9} introduced the vacuum monochromator to photoionization mass spectrometry systems, and the situation improved somewhat. Still, the wavelengths available were limited to $\geq 1050\text{\AA}$ by the lithium fluoride windows which were employed. The installation of faster pumps to allow windowless operation subsequently overcame this limitation.¹⁰ Thereafter, no major design improvements have been made, although considerable sophistication of the basic design has evolved, particularly as far as the ion detection system is concerned.

Even though photoionization mass spectrometry has been widely used for some time, complete, general and helpful references are few. No comprehensive review of photoionization mass spectrometry has been published since the one by Reid³ in 1971, twelve years ago. Nevertheless that review, plus the work of Rosenstock⁵ and Chupka¹¹ provide a useful introduction to the experimental methodology of PIMS.

Other works discuss photoionization and fragmentation processes,^{5,11-16} applications of the technique,^{5,11,17} and its relationship to other methods.^{5,15,18} Since the introduction to PIMS presented here is just an overview, the reader is urged to consult these references for more detailed information.

In recent years, PIMS has proven to be powerful in investigations in three different areas: the study of the kinetics of unimolecular reactions of polyatomic molecules, the study of the thermodynamics and kinetics of ion-molecule reactions, and the determination of ionization potentials of atoms and molecules and of appearance potentials of fragment ions. All of the work described in this thesis has involved the measurement of ionization potentials and appearance potentials of fourteen halogenated methanes; most of the concepts developed in this chapter relate specifically to such studies.

Section A describes the relevant interaction between photons and chemical species (atoms and molecules), with particular emphasis on the processes of ionization and fragmentation. In section B different experimental techniques for measuring ionization potentials and appearance potentials are discussed: first photoionization mass spectrometry(PIMS), then photoion-photoelectron coincidence spectroscopy(PIPECO), and finally a general description of some other techniques.

A. Photoionization

An atom or molecule can absorb radiation and be transferred from the ground state to an excited state. This process is called

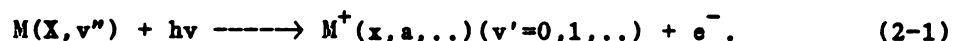
photoexcitation. For an atom, due to the limited degrees of freedom, the transition can only take place between ground and excited electronic states. However, for molecules the absorption spectrum is very much more complex because of the additional degrees of freedom present. The discrete energy states are specified not only by the electronic energy, but also by the vibrational and rotational energies of the entire molecule. Subject to the appropriate selection rules, discrete transitions in free molecules can be observed between rotational levels of the same electronic and vibrational state, giving pure rotational spectral lines in the microwave or far infrared; between rotational levels of the same electronic state but different vibrational states, giving vibration-rotation spectra in the near infrared; or between rotational levels of different electronic and vibrational states, giving band systems in the visible and ultraviolet regions of the spectrum.

If the exciting radiation is of sufficiently high energy, the atom or molecule can also be excited into a region of continuous states lying above the bound states. In this case the absorption spectrum is continuous because the final state can take on continuous energy values over a significant range. This region corresponds to ionization and/or fragmentation processes; the neutral or ionic products can accommodate any energy in excess of the threshold for the reaction as translational and internal energy. In the following pages of this section, those processes which result in an ion, and are consequently important to photoionization mass spectrometry, are discussed. The first part will deal with direct ionization; a description of autoionization and finally a discussion of fragmentation follows. These processes are summarized

in Table 2-1.

1. Direct Ionization

Direct photoionization is the process whereby an electron is ejected from a molecule $M(X, v'')$ in its ground electronic state X and vibrational level v'' to form the corresponding molecular ion $M^+(x, a, b, c, \dots)(v'=0, 1, 2, \dots)$ in its ground or one of its excited electronic states $x, a, b, c, \dots$ and vibrational level v' , according to the expression:



Direct ionization is analogous to an ordinary one-electron transition observed in the visible or ultraviolet region of the spectrum; the one important difference is that the transition terminates in a continuum state instead of a bound state. The probability of such a transition between the molecular ground state characterized by the eigenfunction F'' and the final state (ion + electron) characterized by F' is determined by the absolute square of the transition moment integral:

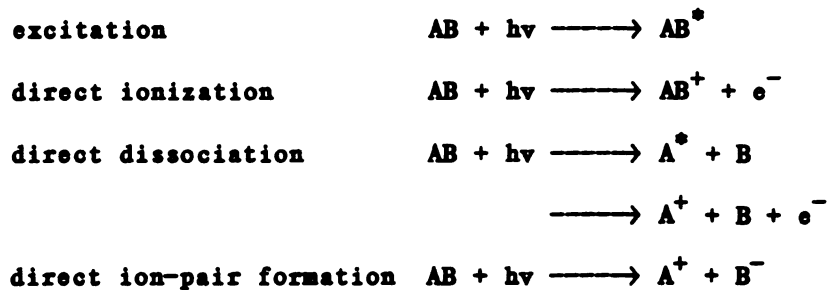
$$T = \langle F'' | \sum \tilde{p} | F' \rangle \quad (2-2)$$

where $\tilde{p}$ is the dipole moment operator and the sum extends over all electrons i and nuclei j .

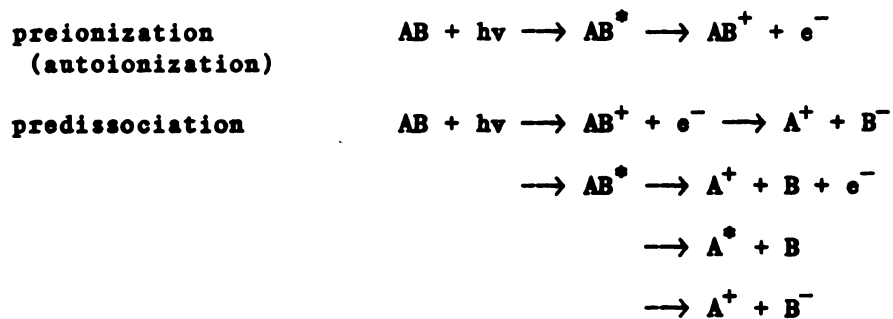
Within the Born-Oppenheimer approximation and neglecting vibration-rotation interaction, the eigenfunctions of the electronic

Table 2-1. Some processes following absorption of a vacuum ultraviolet photon by a molecule.

Direct Processes:



Indirect Processes:



Hamiltonian can be written as:

$$F = F_t(R)F_r(Q)F_v(Q)F_e(Q,q), \quad (2-3)$$

where R are the translational coordinates, Q are the rotational angular coordinates, Q are the so-called "normal coordinates". related to the vibrational coordinates, and q are the electronic coordinates. Under the separation of variables assumption $F_i(i=t,r,v,e)$ denotes the wavefunction for translation, rotation, vibration, or electronic motion, respectively.

Therefore,

$$T = \int F_t'^*(R)F_r'^*(Q)F_v'^*(Q)F_e'^*(q) \left[\sum \tilde{p} \right] F_t''(R)F_r''(Q)F_v''(Q)F_e''(q) d\tau. \quad (2-4)$$

Since the coordinates R and Q are independent of the others, one can rewrite the integral

$$T = \int F_t'^* F_t'' dR \int F_r'^* \cos \Theta F_r'' dQ \int F_v'^* F_e'^* \left[\sum \tilde{p} \right] F_e'' F_v'' dq dQ \quad (2-5)$$

Moreover, since no translational change can be induced by absorption, F_t' and F_t'' must be identical, and the first term is unity. The rotational motion is tacitly neglected since the experimental conditions of PIMS measurements are generally insufficient to resolve rotational structure in direction ionization; thus to a good approximation the second factor in equation (2-5) is also unity. Under

these circumstances, the remaining integral is:

$$T = \int F_e'^* F_v'^* [\sum \tilde{p}] F_e'' F_v'' dq dQ. \quad (2-6)$$

The dipole moment operator can also be separated into an electronic and a nuclear-dependent part:

$$\sum \tilde{p} = \sum_i \tilde{p}_e + \sum_j \tilde{p}_n. \quad (2-7)$$

Then the integral becomes:

$$\begin{aligned} T &= \int F_e'^* F_v'^* (\sum_i \tilde{p}_e + \sum_j \tilde{p}_n) F_e'' F_v'' dq dQ \\ &= \int F_e'^* F_v'^* (\sum_i \tilde{p}_e) F_e'' F_v'' dq dQ + \int F_e'^* F_v'^* (\sum_j \tilde{p}_n) F_e'' F_v'' dq dQ. \end{aligned} \quad (2-8)$$

Now,

$$\int F_e'^* F_v'^* (\sum_j \tilde{p}_n) F_e'' F_v'' dq dQ = \int F_e'^* F_e'' dq \int F_v'^* (\sum_j \tilde{p}_n) F_v'' dQ = 0 \quad (2-9)$$

Because $\tilde{p}_n$ depends only on nuclear coordinates, it may be taken out of the integral over the electronic coordinates. That leaves the integral over electronic coordinates as a simple orthogonality integral which must be equal to zero since one is concerned here with different electronic states. Therefore the vibration-electronic integral reduces

to:

$$\begin{aligned}
 T &= \int F_e'^* F_v'^* (\sum_i \tilde{p}_e) F_e'' F_v'' d\mathbf{q} d\mathbf{Q} = \iint F_e'^* (\sum_i \tilde{p}_e) F_e'' d\mathbf{q} F_v'^* F_v'' d\mathbf{Q} \\
 &= \int \tilde{p}_e F_v'^* F_v'' d\mathbf{Q}
 \end{aligned} \tag{2-10}$$

where

$$\tilde{p}_e = \int F_e'^* (\sum_i \tilde{p}_e) F_e'' d\mathbf{q}$$

and $F_e'^*$ describes both the ion and the free electron and may be represented as a product of a free electron wavefunction and a Slater determinant for the ion.¹⁹

Now, one of the assumptions of the Born-Oppenheimer approximation is that the electronic distribution varies only slightly with $\mathbf{Q}$. Consequently, it is often possible to write the combined vibration-electronic integral as:

$$T = p_e[Q_{ref}] \int F_v'^* F_v'' d\mathbf{Q} \tag{2-11}$$

where Q_{ref} is a nuclear configuration chosen to be of high probability for both states F_v' and F_v'' . On the basis of the above considerations one may write the photoionization transition probability, to a good approximation, as

$$P \propto |p_e[Q_{\text{ref}}]|^2 |\langle F_v' | F_v'' \rangle|^2. \quad (2-12)$$

Whenever the integrals of equation (2-12) are different from zero, direct photoionization transitions are allowed. For direct photoionization transitions the operator in equation (2-10) can be approximated as a one-electron dipole operator whose components transform in the molecular point group as the Cartesian vectors x , y , and z . If the product of the irreducible representations R of the components in equation (2-10), $R(F_e'^*) \times R(\tilde{p}_e) \times R(F_e'')$ is totally symmetric with respect to all symmetry elements of the molecular point group for at least one component of $\tilde{p}_e$ or, in other words, if the product $R(F_e'^*) \times R(F_e'')$ belongs to the same symmetry species as one of the components of $R(\tilde{p}_e)$, then a transition is allowed. In direct photoionization transitions, the final state wavefunction F_e'' consists of antisymmetrized electronic component wavefunctions of the positive ion F_e^+ and the unbound electron f_e . The function f_e is a one-electron continuum wave. The necessary derivation process leads to the result that all one-electron direct photoionization transitions are allowed.¹⁶ After taking into account the spin selection rule, the final conclusion is: the most common direct photoionization transitions are from singlet molecular ground states to doublet states of the positive ion.

The predictions of electronic selection rules are very much simplified compared with those for absorption and emission between two bound states because the case now involves the initial molecular ground state and a final ionic state plus free electron. The transition of the system from molecule plus photon to ion plus electron is governed by the

usual dipole selection rules, but the free electron can leave the ion carrying whatever angular momentum and spin are needed to satisfy these rules. As a result all one-electron direct photoionization dipole transitions are allowed.¹⁵

The vibrational part of equation (2-12), the Franck-Condon factor, places some restrictions on the allowed vibrational transitions within a direct photoionization transition. In order for this integral to be non-zero, the integrand $(F_v' F_v'')$ must be symmetric with respect to all symmetry operations of the point group, i.e. $R(F_v') \times R(F_v'') = R(\text{totally symmetric})$. Therefore, only vibrational levels of the same vibrational symmetry species in the initial and final state can combine. Most molecules exist in the totally symmetric zero-point vibrational level of the ground electronic state at room temperature, thus allowing direct photoionization transitions only to totally symmetric vibrational levels of the ionic state. In polyatomic molecules, where there may be several symmetric vibrational modes, interlocking progressions of these symmetric vibrations are often observed.²⁰

In transitions to degenerate vibrational levels it is necessary to consider the angular quantum number $l_i = v_i, v_i - 2, \dots, 1$ or 0, which characterizes the different possible sublevels that occur.^{21,22} For this quantum number one has the selection rule $\Delta l = 0$. Because l is even or odd when v is even or odd, only $v' = 0, 2, 4, \dots$ are symmetric. This selection rule is rigorous for point groups like D_{2d} , D_{4h} , D_{6h} , and $D_{\infty h}$, but is relaxed in point groups such as D_{3h} , C_{3v} , and T_d , where all overtones of degenerate vibrations contain at least one totally symmetric component. The rule remains rigorous for the $0 \rightarrow 1$ transition

in all point groups because the $v=1$ level of a degenerate vibration is never totally symmetric.

In the event that there is a change of symmetry between the molecule and ion, one must apply the vibrational selection rules using only the common elements of symmetry. Conversely, from the observed structure, conclusions can be drawn about the difference in symmetry between the molecule and ion in the two equilibrium positions. For example, the degenerate bending vibration of π symmetry in a linear molecule is split into two normal modes in the corresponding bent molecule. Since at least one of these split vibrations can be totally symmetric in the point group of the bent species, progressions in every quanta of this mode can be observed.

2. Autoionization(Preionization)

In contrast to direct ionization into the continuum, which is the basis of a photoionization efficiency curve, autoionization is an indirect process. Atoms or molecules are first produced in a neutral excited state with energy above an ionization limit, and then spontaneously emit electrons:



The first step is a resonance process; it can be brought about only by light of the correct energy, and the nature of the accessible excited state is governed by the normal electronic transition selection rules. Autoionization proper is the second step. In other words, if an atom or

molecule is raised to a highly excited state and radiationless transitions take place from the discrete state to the ionization continuum, such a process is called autoionization. In photoionization efficiency curves, autoionization will often appear as sharp, peak-like structure superimposed on the normally featureless direct photoionization continuum, especially for atoms. Autoionization can present a great variety of asymmetrical line shapes, and it may appear as a "window resonance" in which there is a decrease or dip in the photoionization cross section, especially for diatomic and polyatomic molecules.^{12,23,24} The lifetime of autoionizing levels can vary a great deal, ranging from 10^{-14} seconds all the way to about 10^{-6} seconds. For states with short lifetimes, the autoionization structure may be so broadened that it is indistinguishable from the continuum of direct photoionization. If the lifetimes of the autoionizing states are greater than one vibrational period, then the relative intensities of the superimposed structure in the photoionization efficiency curves can be expected to follow the Franck-Condon factors for the radiationless transitions from the autoionizing states of the molecule to the final state of the ion. In contrast with the direct photoionization case, the value of v' in this case is generally not zero. As a result, vibrational structure in autoionized photoionization efficiency curves cannot be used to infer what type of electron (bonding, antibonding, nonbonding) was ejected. Moreover, autoionization features in the photoionization efficiency curves characterize the bound, highly excited states of the neutral, not the final ionic state reached following autoionization. However, from this information resonance photoelectron

spectroscopy experiments can be carried out, which may provide information about the final vibrational states of the ion. This subject will be considered further in chapter three.

In equation (2-13) M^* is the atom or molecule in a highly excited state. Highly excited states with energies in the vacuum ultraviolet region are always Rydberg states that converge to the second, third, or higher ionization potentials. The energy of these discrete Rydberg states can be above the threshold of the ionization continuum. Molecular Rydberg orbitals are analogous to atomic orbitals with large principal quantum numbers. They have a large spatial extent, and in a somewhat simplified but useful approximation Rydberg states can be thought of as one-electron orbitals in which the electron is on the average at so large a distance from the remaining ion core that the core can be approximated as a point charge.²⁵ This approximation is substantiated by the fact that nearly all transitions to Rydberg states (observed in photoionization mass spectrometry experiments as autoionization structure) can be fit into a series described by the Rydberg equation:

$$E_n = IP - R/(n - \delta)^2, \quad (2-14)$$

where E_n is the energy difference of the transition, IP is that ionization potential of the molecule to which the series converges, n refers to the principal quantum number, R is the Rydberg constant (13.605eV), and δ is called the quantum defect, which is essentially an adjustable constant which accounts for penetration of the Rydberg orbital

into the ion core.

The selection rules for autoionization are derived from the radiationless transition probability from the superexcited (quasi-discrete) states, F^a , to the final (continuum) states, F^f . The lifetime of the initial state can be expressed as :

$$\tau^{-1} = 4\pi^2 P^2 \rho(E_f)/h, \quad (2-15)$$

where $\rho(E_f)$ is the density of the final state and P is the matrix element of the perturbation, $P = \langle F^f | \tilde{p} | F^a \rangle$. Based on the treatment given by Berkowitz,²⁶ the nature of the perturbation matrix elements in autoionization will be divided into five cases; the first three cases all concern electronic autoionization, the fourth case is related to vibrational autoionization, and the fifth case involves rotational autoionization.

Case(1):Excitation of an inner-shell electron to a Rydberg level

This mechanism can be understood as the migration of energy from the Rydberg electron to a valence shell electron as the Rydberg electron reoccupies its inner shell hole, or as a valence shell electron dropping into the inner shell hole and releasing its energy to the Rydberg electron. (These are obviously intended as pictorial descriptions, the indistinguishability of electrons must be recognized.) In either event, the interaction is of the form e^2/r_{jk} , where r_{jk} is the distance between the Rydberg electron and some core electron, and the perturbation matrix element which corresponds to the transition probability takes the form

$$\int F_e^f F_v^f (e^2/r_{ij}) F_e^a F_v^a d\mathbf{q} d\mathbf{Q} \quad (2-16)$$

where F_e^f includes the wavefunction of the departing electron. Within the framework of the Born-Oppenheimer approximation, one can rewrite this matrix element in the form

$$\int \bar{F}_e^f (e^2/r_{ij}) \bar{F}_e^a d\mathbf{Q} \int F_v^f F_v^a d\mathbf{Q}. \quad (2-17)$$

where $\bar{F}_e^f$ and $\bar{F}_e^a$ are specified states. The second integral is a vibrational overlap and is like a Franck-Condon factor, but refers to the radiationless transition between the quasi-discrete state and the ionization continuum. If the vibrational distribution predicted by this integral could be observed, it would constitute good evidence for this mechanism. Since the quasi-discrete state is frequently not well characterized, the problem is often inverted to determine the properties of the quasi-discrete state from the observed vibrational distribution.²⁷

Case(2): Valence shell excitation involving a spin flip

This behavior has been observed primarily in the noble gas atoms Ne, Ar, Kr, and Xe, but should also be applicable to such molecules as HCl, HBr, and HI. Since the compounds investigated by this work were much more complicated than those, this phenomenon is less important and unresolvable in the photoionization efficiency curves. This case will therefore not be discussed here. The reader is referred to Berkowitz's book²⁶ for a good description of this case.

Case(3): Simultaneous two-electron excitation

In this case, the excitation energy of each electron, by itself, is sufficient to cause ionization, but the sum of their excitation energies exceeds the ionization threshold. To account for the initial excitation, one must go beyond the independent particle approximation and include either configuration interaction or correlation.

Hence, when the latter effects are important (as in some alkaline earth metal atoms), one may anticipate this type of autoionization to be prominent.

Case(4): Excitation of a valence electron to a Rydberg level and concomitant excitation of vibrational energy

This problem has been treated rather exhaustively by Berry and collaborators,^{28,29} particularly for the case of H_2 . The vibrational energy of the core must somehow be transmitted to the rather distant Rydberg electron. This transfer involves the interaction of vibrational and electron coordinates, and implies a breakdown of the Born-Oppenheimer separation. Two significant conclusions of the analyses for diatomic molecules by Berry, et al.^{28,29} are appropriate for summary here.

(a) As the Rydberg level n increases, the average distance of the Rydberg electron from the nuclear core increases, and hence the interaction should be expected to decrease. Thus, the autoionization transition rate should decrease, and the lines should become narrower with large n .

(b) The major perturbation element is of the form $\int F_V^f(\partial/\partial R) F_V^i dQ$ where R is the internuclear separation of the diatomic nuclei. The operator $(\partial/\partial R)$, when acting on a Hermite polynomial, has the effect of

raising or lowering it by one. The vibrational wavefunctions of both the initial (Rydberg) and final (ionic) states can be well approximated by Hermite polynomials, and each set is orthonormal. Since the vibrational potentials of the two states are quite similar, the primary contribution to the integral is one where v_f and v_i differ by one unit, i.e., $\Delta v = \pm 1$. This is similar to the selection rule for infrared absorption. Higher order terms will affect this conclusion, but the first-order result (the so-called "propensity rule") is seen to differ drastically from the conclusions of case (1), which yields a broad vibrational envelope as a consequence of the autoionization; vibrational autoionization can be expected to yield predominantly one vibrational member.²⁷

Case(5): Rotational autoionization

This mechanism has thus far been identified only in the case of H_2 .^{28,29} so it will not be discussed here.

From the discussion above, it is clear that in molecules autoionization mechanisms can be of at least three varieties: (a) electronically-induced, due to intermediate states with one or more electrons excited; (b) vibrationally induced, involving an intermediate state described by a single highly excited electron outside a vibrationally excited molecule-ion core, with autoionization involving some vibrational relaxation of the core, and (c) rotationally-induced, analogous to the vibrationally-induced case but involving only a rotational transition of the core in the autoionization step. Electronically-induced autoionization is possible only when the total electronic energy of a Rydberg state is greater than the lowest

ionization potential of a molecule. In this case the electron in the Rydberg orbital was excited from a ground state orbital lower in energy than the highest occupied ground state orbital. Autoionization occurs when the ion core of the Rydberg state relaxes to a lower energy configuration. The perturbation causing the relaxation and the subsequent ejection of the Rydberg electron is electron-electron repulsion²⁸. The ion is formed in a different electronic state from that of the core of the autoionizing level. There is no restriction to the ejection of an electron with low kinetic energy, and any final state of the ion with a lower energy than that of the autoionizing state can be produced. In vibrationally-induced autoionization, a Rydberg state in which the molecule-ion core is vibrationally excited may eject the Rydberg electron by vibrational relaxation of the core. This process is caused by a coupling of the oscillating multipoles of the ion core with those of the Rydberg electron. The electron energy of a Rydberg state undergoing vibrational autoionization does not necessarily have to be greater than the lowest ionization potential of the molecule; it is only necessary that the sum of the vibrational and electronic energy be greater than the lowest ionization potential. Figure 2-1 shows vibrationally-induced autoionization. In the figure, the vertical line from M_2 to upper states indicates the excitation process. Curved arrows labeled A, B, and C, indicate, respectively: a $\Delta v = -3$ inter-Rydberg transition from M_2^* to M_2^{**} , which has low probability; a $\Delta v = -1$ transition from M_2^{***} to $M_2^+ + e^-$, a rapid process in general; and a two-step process involving a (presumably slow) $\Delta v = -2$ step from M_2^{**} to M_2^{***} , followed by a transition with $\Delta v = -1$ from M_2^{***} to $M_2^+ + e^-$. It

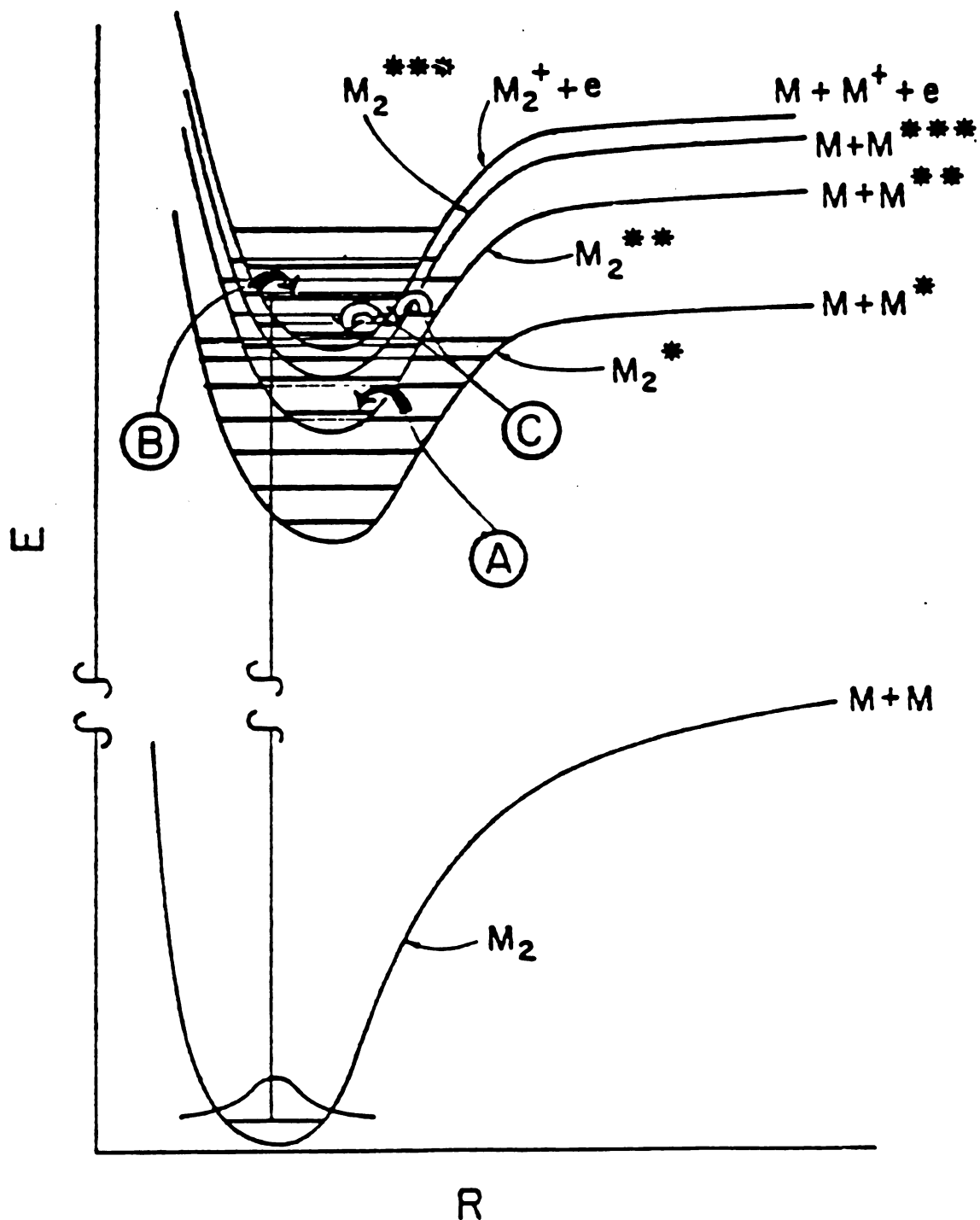


Figure 2-1. Schematic diagram of potential curves of electronic states and vibronic transitions in a diatomic molecule. [From R.S.Berry, J. Chem. Phys. 45, 1228 (1966)].

is interesting to note that vibrational autoionization, which is believed to be the predominant mechanism in small molecules,^{28,30} constitutes a breakdown of the Born-Oppenheimer approximation. Rotationally-induced autoionization, caused by the relaxation of a rotationally excited ion core, arises from the coupling of the rotational angular momentum of the ion core with the orbital angular momentum of the Rydberg electron. The role of rotational contributions to autoionization is not well understood due to the paucity of experimental data where rotational structure can be resolved.

All parent ions produced by photoionization will have contributions from both direct ionization and autoionization. The parent ion photoionization efficiency curves will not only reflect these contributions, but they will also be influenced by decomposition reactions such as: predissociation into neutrals, fragmentation into a fragment ion plus neutral(s), and spontaneous emission of photons. Autoionization may be indistinguishable from the direct photoionization continuum in the photoionization efficiency curve. In fact, it has been recently proposed that direct photoionization be theoretically treated as very fast autoionization.³¹ The photoionization efficiency curves of diatomic molecules, where few channels for predissociation may be open, are often dominated by autoionization.^{24,30,32} For larger polyatomic molecules, where several channels for predissociation may be open and many changes in geometry are possible, photoionization efficiency curves are often featureless, showing only hints of autoionization.^{13,33,34} Figure 2-2 shows a photoionization efficiency curve of NO measured by Paul Killgoar, a former member of this research group, in experiments

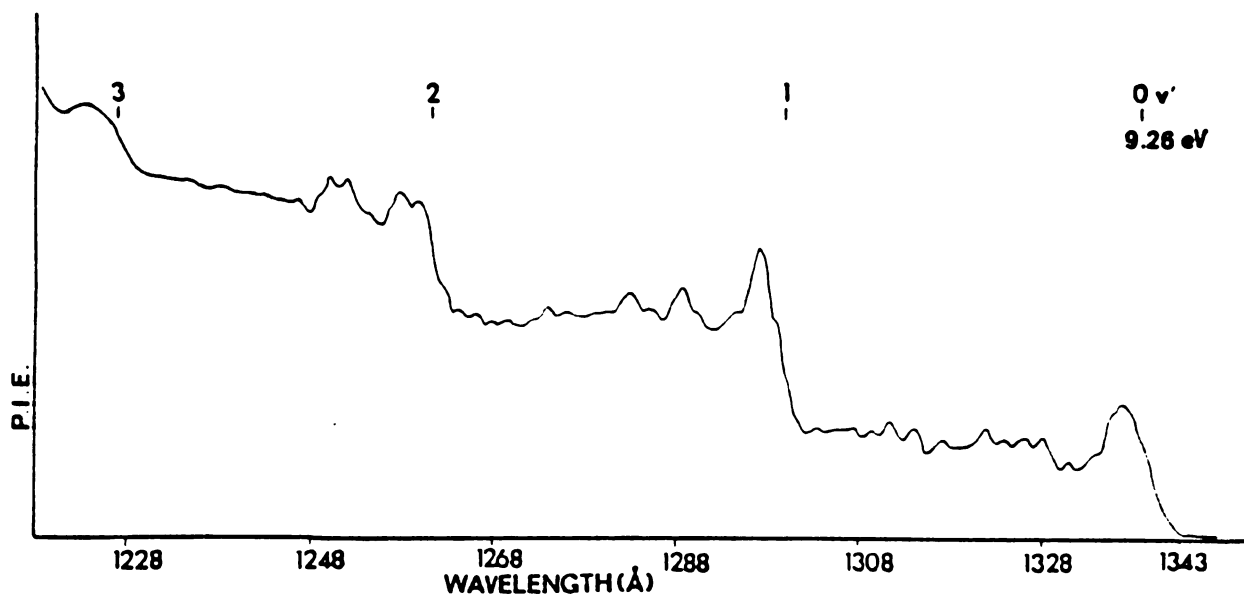
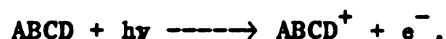


Figure 2-2. The ionization threshold region of NO^+ ; pronounced autoionization peaks superposed on the step structure. [From P.C.Killgoar, Jr., et al., J. Chem. Phys. 58, 803 (1973).]

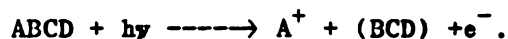
carried out at the Argonne National Laboratory.³⁵ It depicts pronounced autoionization peaks superposed on the staircase structure which arises as new vibrational channels open.

3. Fragmentation Processes

Fragmentation processes are always more complex than direct ionization or autoionization, so they are often more difficult to analyze. For example, consider a tetratomic molecule, ABCD. In direct ionization the overall process is:



The energy of the photon is precisely determined by the monochromator setting, and the internal energy of parent ion is easily calculated by subtracting the electron's kinetic energy and the adiabatic ionization potential from the photon energy. Thus, the energetics and composition of the system are well characterized. When fragmentation occurs, for instance if fragment ion A^+ is detected, then the reaction can be written as:



The photon energy and the kinetic energy of the electron can be measured precisely. But this is only part of the system. The neutral fragment or fragments cannot be detected by the ionic mass analyzer, and their composition is uncertain. (They could be any combination of B, C, and

D.) Moreover, each species leaving the interaction region carries translational energy and perhaps internal energy as well, and these factors are not measurable by photoionization mass spectrometry. The total system is thus not easily characterized compositionally or energetically. Sometimes, thermochemical information can help in reducing the complexity of the processes; on this basis many possible fragmentation pathways can be eliminated, and kinetic energy releases can be estimated. However, accurate estimations require precise thermochemical data, which may not be available for all species of the system.

The following questions are among the objectives of ionic fragmentation investigations. If the parent ion is initially in a particular quantum state and thus has a specific energy, will it dissociate? If it does, which of the energetically possible products will be formed and how fast will they be formed? How will any excess energy be distributed among the products as translational energy, or as electronic, vibrational or rotational energy of the fragments?

In considering dissociation mechanisms, one is concerned with how the parent ion excitation energy is distributed in the course of time until, and indeed after, fragmentation occurs. Fragmentation mechanisms can be classified as direct dissociation or predissociation. According to Herzberg,³⁶ predissociation may be further divided into three cases: (1) electronic predissociation, in which the parent ion makes a radiationless transition into the dissociation continuum of another electronic state; (2) vibrational predissociation, in which the parent ion remains in the same electronic state and only vibrational motion is

involved; (3) rotational predissociation, in which only the higher rotational levels of a particular vibronic state may predissociate. Rotational predissociation processes account for only a very small fraction of observed fragmentation and are not significant to the main thrust of this section. A more general kind of predissociation involves internal conversion followed by vibrational predissociation.

Whether or not an ion can dissociate at all is a question of energy, because for dissociation to be possible the energy of the ion must be higher than the ground-state energy of some set of possible products. If sufficient energy is present, whether dissociation will take place depends on competition from the only other processes that can remove the excess energy of an isolated ion without fragmentation, namely, internal conversion or fluorescence to a stable ionic state. The characteristic lifetime for allowed transitions that emit light in the visible or near ultraviolet spectral region is of the order of 10^{-8} second, so if a particular ionic state has an allowed transition to any stable lower state it must dissociate within 10^{-8} second, if fragmentation is a significant process. If all transitions out of the excited ionic state to stable states are forbidden and internal conversion is relatively slow, or there are no lower-lying stable ionic states, then slower dissociation can occur. Thus, whether a dissociation which does occur will be observed in a particular experiment is also a question of rate. In mass spectrometry, time between formation of ions, and their mass separation is typically about 10^{-5} second and all dissociations that occur within this time will be detected. This includes almost all elementary ion decomposition

processes, and in addition special mass spectrometers (which employ ion trapping techniques) can be built in order to study the few ion reactions with dissociation lifetimes as long as 10^{-4} to 10^{-3} second.

Direct dissociation is the first fragmentation mechanism to be described. If the state of a diatomic ion reached directly in photoionization is repulsive(unbound) or on the repulsive part of a bound surface, the parent ion will dissociate immediately. In the latter case the potential energy surface reached in ionization is effectively unbound even if, according to a normal model of the electronic structure, it is expected to be a bound state. An otherwise bound state may be effectively repulsive because of interaction with a repulsive state involving curve crossing or an avoided crossing. The products will dissociate with most of the excess energy of the parent ion(i.e. energy greater than the the energy of the dissociation limit) released as translational energy, as there is insufficient time available for it to be redistributed among internal modes before the fragmentation occurs. The potential energy curves representing this process in Figure 2-3 are appropriate only for diatomic molecules; for polyatomic molecules, they must be imagined as two-dimensional cuts through a multi-dimensional surface, with the reaction coordinate as the horizontal scale. The diatomic potential curves retain their simple meanings for dissociations and spectra of polyatomic species only if the reaction coordinate and the vibrational motions excited by ionization are the same. It is unlikely that the change in equilibrium molecular geometry produced by ionization of a polyatomic molecule will correspond exactly and exclusively to motion in a reaction coordinate; direct

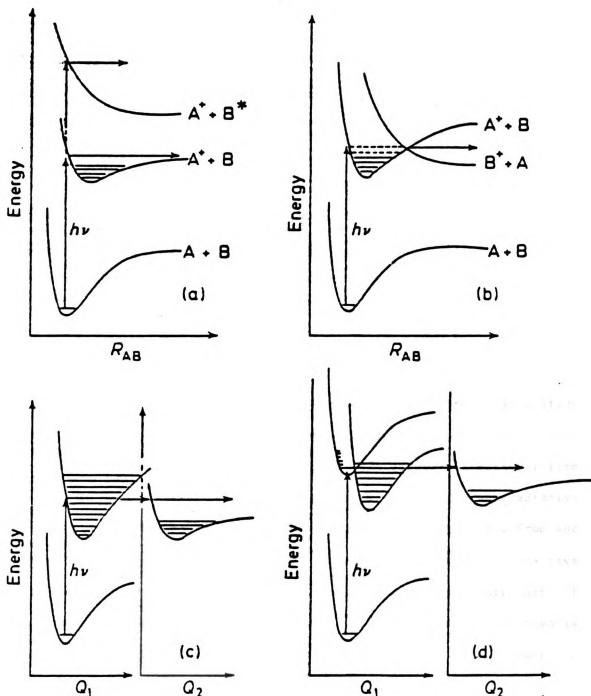


Figure 2-3. Potential energy curves illustrating some important dissociation mechanisms: (a) direct dissociation; (b) electronic predissociation; (c) vibrational predissociation; (d) internal conversion with vibrational predissociation. In (c) and (d) the coordinates Q_1 and Q_2 represent different molecular motions in a polyatomic molecules. [From J.H.D.Eland, Photoelectron Spectroscopy (John Wiley and Sons, New York 1974).]

dissociation in the strict sense can be defined as a process in which it very nearly does so. True direct dissociation as defined above can occur only if the removal of an electron has a strong and specific influence on the bonding in the molecule. A close relationship between the identity of the products and the bonding character of the ionized electron is therefore to be sought in such instances. Unfortunately, there are as yet no clearly-characterized direct dissociations of ions for which this idea can be tested. The detection of a particular product can be considered to be significant only if an alternative decomposition is energetically possible, and this is not so in the few direct dissociations of polyatomic ions that have been recognized up to now.

If a molecular ionic state is definitely bound, when dissociation takes place the process is called predissociation. As noted above, only case(1) and case(2) will be discussed here. In case(1) predissociation occurs by rearrangement of electronic energy; there is a non-radiative transition from the bound state to a continuum state, that is, from one potential energy surface to another. If the two electronic states have the same symmetry, the predissociation is homogeneous; if they are of different symmetry, it is heterogeneous. Electronic predissociation is probably the most common mechanism by which small ions formed in photoionization decompose. The way in which the excess energy is divided among the degrees of freedom of the products, including translation, depends on the details of the potential energy surface, especially at the configuration where the transition takes place. It is possible for a large fraction of the energy to appear as kinetic energy,

but alternatively internal vibrational or rotational energy of the products may be favored. Some correlation between the bonding power of the electron ionized and the identity of the products formed may be sought, as the nature of the electron ionized determines the forms of the initial ionic potential energy surface and of the initial vibrational motion. However, the existence of such correlations will also depend on several other factors, particularly the forms of surfaces that lead to different products and potentially cause the predissociation, and the strengths of their interactions with the bound potential surface. In case(2), predissociation takes place on a single electronic energy surface by rearrangement of the vibrational energy. The excited molecule has sufficient energy to dissociate, but the energy is initially distributed among vibrational modes that do not correspond to the reaction coordinate for dissociation. Most thermally-induced unimolecular reactions are such vibrational pre-dissociations and involve the ground electronic state of the parent ion only. There is very little evidence to show how common this mechanism may be among molecular ion decompositions, but it is probably less important for small ions than electronic predissociation. A more distinct relationship between the identity of the products and that of the electron removed is expected in vibrational predissociation than is possible in Case(1), as the vibrational energy flows from the mode excited upon ionization into other modes, which presumably correspond more closely to different reaction coordinates. According to theories of unimolecular reactions, the excess energy should be distributed among all degrees of freedom of the products, in favorable instances in a

statistical manner.

Under these circumstances the rate constant is given to a first approximation by:¹⁷

$$k = k_0[(E-E_0)/E]^{N-1} = k_0[1-(E_0/E)]^{N-1}, \quad (2-18)$$

where E is the energy available, E_0 the threshold energy, N is the number of vibrational modes in the parent ion and k_0 is of the order of a vibrational frequency, say 10^{13} second⁻¹, and is characteristic of the particular dissociation and the form of the activated complex. Because the factor in parentheses is necessarily less than unity, the larger the molecule the slower is its dissociation for given excess energy above the threshold. Near the threshold there is a minimum reaction rate for parent ions that possess only one quantum of vibrational energy above the threshold. For triatomic molecules, this minimum rate is about 10^9 second⁻¹, for larger molecules, it rapidly become less, being about 10^5 second⁻¹ for a penta-atomic molecule. Equation (2-18), however, is only a first approximation as it is derived not only on the assumption of statistical equilibrium, but also of classical harmonic oscillators, all of which have the same frequency. For details of the more precise forms of equation (2-18) the reader is referred to reference 60.

The next mechanism to be described is internal conversion plus vibrational pre-dissociation. Because of its supposed prevalence, this "mixed" mechanism must be considered separately, although it is a sub-case of predissociation. According to the quasi-equilibrium theory of mass spectra (QET), all excited parent ions relax rapidly by

conversion of their electronic excitation energy into vibrational energy of the parent ion in its electronic ground state, after which fragmentation follows by vibrational predissociation. The first step is an internal conversion from one bound electronic state to another, a process that is strictly controlled by selection rules in small molecules but thought to reach completion in 10^{-11} to 10^{-12} seconds in large molecules.³⁷ In this mechanism, all traces of the identity of the electron originally ionized are lost, and the abundances of different products should depend only on the dissociation limits for their formation and on statistical factors. The excess energy must be distributed statistically among all the internal degrees of freedom of the fragments. Potential energy curves intended to illustrate these three mechanisms are shown in Figure 2-3, but it must be emphasized that the representation is very crude. At least two cuts must be made through the multidimensional potential energy surface in order to indicate vibrational predissociation at all, whereas the molecules themselves have a choice from an infinite number of such cuts. Very many more sub-cases of predissociation can be imagined than are represented in Figure 2-3, and a wider selection has been illustrated by Mulliken.³⁸

Which of the models of ionic dissociation best describes a given decomposition depends first on the nature of the energy surface--particularly whether direct dissociation is possible or not--and then on the rates of the competing elementary processes. Hints to the rates of the elementary processes are provided by the correlation rules, by selection rules, and for vibrational predissociations, by

statistical theories of unimolecular reactions. These last are unfortunately the main clues that are available to the rate of dissociation of most large polyatomic parent ions, because the application of correlation rules or symmetry gives little useful information. Since this dissertation deals only with polyatomic molecules, radiationless transitions, internal conversion and vibrational predissociation are the elementary processes most relevant to the discussion of observed fragmentation reactions.

Both predissociation and internal conversion are examples of radiationless transitions in which the system passes from one electronic state to another at the same energy. The rate of such a process depends on two factors: the strength of the interaction between the electronic states and the agreement between the nuclear positions in the two states at that energy. The rate is proportional to the squared magnitude of a matrix element, which may be separated into an electronic part and a vibrational overlap integral. The two parts cannot always be treated separately because the interaction between the states may be brought about by coupling between nuclear and electronic motion. Deviations from the Born-Oppenheimer approximation must then be taken into account, and potential energy curves are an incomplete model for the dynamic process. Nevertheless, it is helpful to discuss predissociation in terms of deviations from the classical model of distinct potential energy surfaces. If the lifetime of the initial state is τ , there may be many accessible final states that are isoenergetic within the energy uncertainty $\hbar/2\pi\tau$ and the lifetime then depends also on the density of final states, $\rho(E_f)$. These ideas are combined by the "golden rule" of

perturbation theory into an equation for the lifetime:

$$\tau^{-1} = h p^2 \rho(E_f). \quad (2-19)$$

Here p is the matrix element of the perturbation, $p = \langle F_f | \tilde{p} | F_i \rangle$, which may be separable, as an approximation, into an electronic part and a vibrational integral:

$$p \approx \langle F_f | \tilde{p} | F_i \rangle \langle X_f | X_i \rangle \quad (2-20)$$

The main effect of the vibrational term is that radiationless transitions are likely to occur only if the potential energy surfaces cross, or at least come very close to each other. Other factors being equal, the flatter the surfaces are at the crossing point, that is, the less acute the angle at which they cross, the more extended the vibrational wavefunctions are and the greater will be the transition probability. Transitions can occur not only at the crossing point but also above or below it, because of the extension of the wavefunctions past the classical turning points and the breakdown of the Born-Oppenheimer approximation. The rate will be greatest at the crossing point and will fall off on both sides. Above the crossing point, this situation can be related classically to the velocity with which the molecules move through the critical configuration; below the crossing point, the obvious analogy is with quantum mechanical tunneling. The fall-off will be less rapid if the curves cross at an acute angle, as they then remain close together over a greater energy

range. Experimental effects of these vibrational factors have been observed in the electronic spectra of predissociating diatomic molecules.³⁹

In order to calculate the strength of the electronic interaction theoretically, the initial and final wavefunctions would be required, and also a precise description of the perturbation; none of these are normally available, but clues to the strengths of interactions are given by the selection rules for perturbations, originally derived by Kronig.⁴⁰ Although the language of perturbation theory is used, no real perturbation of the molecule exists for predissociation or intersystem crossing as it does, for instance, in a collision process. Instead, the perturbation operator in equation (2-20) represents terms that have been omitted in the original, approximate model of the system. The most important of these terms are interaction between electronic and nuclear motion, and spin-orbit coupling.

As these terms are internal to the molecule, the operator $\tilde{p}$ must be totally symmetric in the point group of the molecule and the general condition for the interaction to be non-zero is simply

$$p_f^{\text{tot}} = p_i^{\text{tot}} \quad (2-21)$$

where p_f^{tot} , p_i^{tot} are the irreducible representations to which the total wavefunctions for the final and initial states belong. The selection rules arise from translation of this condition, together with conservation laws that are valid for an isolated molecule, into the language of spectroscopic quantum numbers. There are three general and

rigorous selection rules, which can be written as:

$$\Delta J = 0, + \leftrightarrow -, s \leftrightarrow a, \quad (2-22)$$

where J is total angular momentum, $+$ and $-$ show symmetry of the total wavefunctions with respect to inversion (parity), and s and a show the symmetry with respect to interchange of identical nuclei. For internal conversion and predissociation of diatomic and linear molecules for which the linear configuration is retained, these rules have important consequences. Conversion between $\sum^+$ and $\sum^-$ is strictly forbidden for singlet states and becomes only weakly allowed for higher multiplets, and if a π state interacts with a $\sum$ state only half of the sub-levels can predissociate. For linear molecules with equivalent identical nuclei, there are further restrictions imposed by the $s \leftrightarrow a$ conditions, which lead to the rule for all centro-symmetric molecules that $g \leftrightarrow u$, the opposite of the rule for optical transitions. For further details of the application of these rules to linear molecules the reader is referred to Herzberg's book.³⁶ For non-linear polyatomic molecules, the strict selection rules still apply, with the necessary modifications according to the appropriate symmetry groups, but they impose no practical restrictions on predissociation; in real cases they can always be fulfilled. In order to apply the selection rules to a predissociation, it is necessary to know or guess the species of the unbound state that causes it. In order to find the possible species, the states of the assumed products are combined according to the correlation rules as before, and the most significant results that can

then emerge are either that for some combination of the products the predissociation is fully allowed, or that it is always spin-forbidden. The symmetries do not indicate the full situation, however, because even if two states have exactly the same symmetry the interaction between them may be weak if they differ in their electron configurations. The ions that are produced by ionization of any closed-shell molecule have an odd number of electrons, and if an ion so formed breaks into two fragments, one has an odd and the other an even number of electrons. Odd electron species have doublet or quartet states, while even electron fragments have singlet or triplet states; higher multiplicities are rarely encountered among molecular species. The only spin-forbidden combination in the decomposition of a doublet parent ion into two fragments is quartet plus singlet. The most important fragments that have quartet ground states are atoms of group V(N,P) and the isoelectronic ions of group VI(O^+ , S^+), and it is only when these species are involved that spin-forbidden predissociations are likely to be encountered. Examples are the predissociation from doublet states to the lowest energy products in CO_2^+ , COS^+ , CS_2^+ and N_2O^+ . In the fragmentation of larger polyatomic molecular ions, where atomic fragments are not involved, spin-forbidden processes are seldom important.

The rate of an internal conversion depends on exactly the same factors as that of a predissociation, that is, the electronic transition probability, the vibrational overlap integral and the density of final states. However, as the transition is between two bound states, the restrictions imposed by selection rules are more severe, particularly

for small molecules.⁴¹ Unfortunately, there is little clear experimental evidence regarding the extent to which internal conversions actually occur, and this is a problem both in photochemistry and in the theory of unimolecular reactions. The quasi-equilibrium theory (QET) of mass spectra assumes that all excited states of molecular ions relax rapidly to the ground state by internal conversion before dissociation. This assumption implies that all primary fragmentations must be in competition with each other and that two fragmentations with different energy requirements cannot proceed at similar rates so as to give ions of comparable intensity in the mass spectrum, whatever the original distribution of excitation energy. Some measurements of the fragmentation of small molecules that contradict this conclusion have been interpreted in terms of isolated electronic states which are not interconverted.⁴² On the other hand, QET has been successfully used in interpreting the mass spectra of large molecules, both qualitatively and quantitatively, and this success may be evidence in favor of its original assumptions. Proponents of the theory claim that it should be valid for molecules with more than five or six atoms, for which the density of the states is high enough, and the restrictions due to selection rules are weak enough, to allow facile internal conversions. Photochemical evidence concerning internal conversions is obtained from a comparison of the absolute quantum yields of fluorescence, phosphorescence, and intersystem crossing for molecules in solution or in rigid glasses. There is, unfortunately, little information available for gases. One would expect that the continual collisions with solvent molecules in a liquid would provide sufficient perturbation to make

radiationless transitions universal despite any selection rules or unfavorable overlap factors, but this is apparently not so. For aromatic molecules in solution at room temperature, the conclusion that internal conversions from the first excited singlet state to the ground state singlet state play a significant role can be drawn only tentatively.³⁹ In some instances there is definitely no such internal conversion as the fluorescence yields are unity; examples are 1,10-dimethylantracene and p-terphenyl in light petroleum. For such large molecules, an advocate of the QET theory would not hesitate to assume that complete internal conversion among all ionic states occurs within 10^{-12} seconds. On the other hand, the higher excited singlet states of aromatic molecules are effectively converted to the lowest excited singlet state by internal conversion in much less than 10^{-8} seconds because, with the exception of azulene and some of its derivatives, all molecules that fluoresce in solution do so from their lowest singlet state, whatever the exciting wavelength. The state of knowledge regarding internal conversions is still unsatisfactory and both experimental and theoretical improvements are needed.

B. Experimental Techniques for Measurement of Ionization and Appearance Potentials

There are many different techniques for measuring ionization and appearance potentials of atoms and molecules. The photoionization mass spectrometric technique will be introduced first, since PIMS is the primary technique used in the investigations described in this dissertation. The experimental chapter (chapter four) contains more

details regarding the instrument and the method. Photoionization mass spectrometry is currently the best technique for measuring precise ionization and appearance potentials, but for related applications, such as studies of the kinetics of unimolecular decay, PIMS has certain disadvantages. In the second part of this section the photoion-photoelectron coincidence spectroscopic technique (PIPECO) is introduced. PIPECO is well suited to kinetic investigations of a wide variety of gas phase reactions. In the final part of this section, a general description of several other methods is provided.

1. Photoionization Mass Spectrometry

Figure (2-4) shows a block diagram of a typical photoionization mass spectrometer. The apparatus consists of four basic components: light source, dispersive element, light detector and ion detector. Selected wavelengths from the dispersed output of the light source pass through the exit slit of the monochromator and interact directly with the sample. The transmitted photon intensity is converted to an electrical signal by the light detector. Ions formed in the interaction region are extracted at a right angle to the light beam and pass through a mass filter to the ion detector, and the ion arrival rate is also converted into an electrical signal. The spectral distributions from four light sources commonly used in photoionization mass spectrometry are shown in Figure (2-5). Generally, different light sources are required for different energy regions. Basically, the synchrotron radiation source is best because it develops relatively high intensities and is stable. Unfortunately, synchrotrons are extremely expensive and

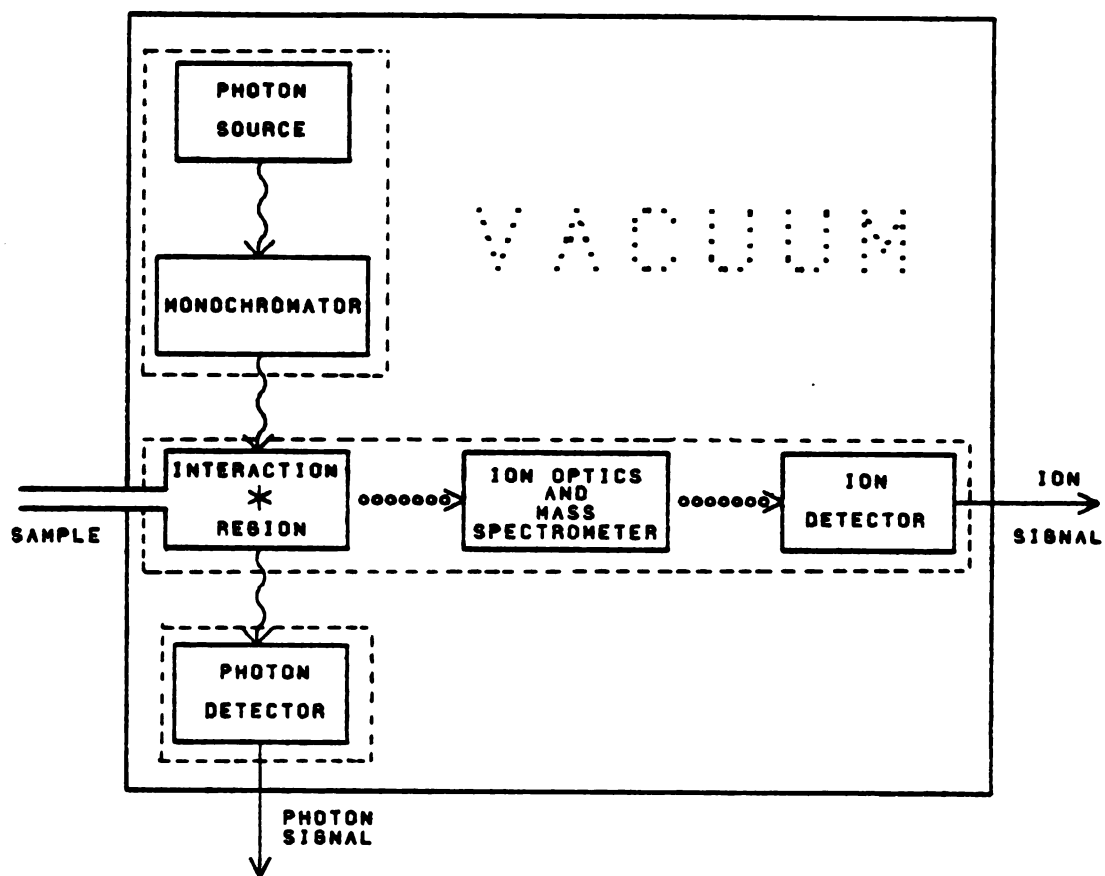


Figure 2-4. Block diagram of a photoionization mass spectrometer.

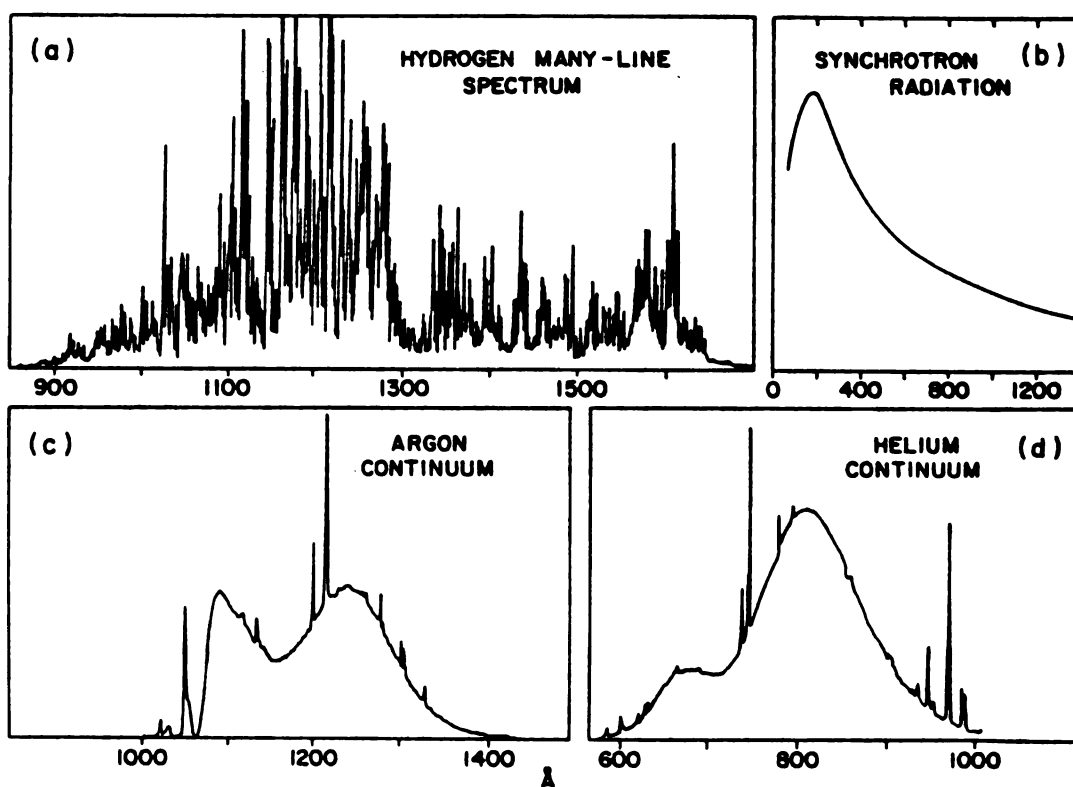


Figure 2-5. Spectral distribution of four light sources commonly used in photoionization mass spectrometer. The hydrogen, argon and helium spectra are measured light intensities at the exit of a normal incidence monochromator, whereas the synchrotron spectrum is that calculated for the 240 MeV storage ring in Wisconsin. [From J. Berkowitz, *Adv. in High Temp. Chem.* 3, 123(1971).]

complicated to operate; only five synchrotron facilities currently exist in the United States.

The photoionization experiment entails very simply the measurement of the intensity of an ion of selected mass as a function of the photon energy incident on the neutral sample. Since the output intensity of the available light sources (shown in Figure (2-5)) is not constant as a function of energy, the photon intensity must be also measured so that the ion intensity can be normalized. It would be most desirable to measure the absolute photoionization cross section, but neither the absolute photon intensity nor the number density of the neutral molecules in the photon beam are readily determined. Instead, a relative quantity, the photoionization efficiency (PIE) is measured. The photoionization efficiency is defined:

$$\text{PIE} = \text{ion intensity} / \text{transmitted photon intensity}.$$

Properly the incident photon intensity should be used to calculate the PIE. However, as noted in chapter one, under normal experimental conditions the attenuation of the incident light by the sample is negligible, and the PIE calculated from the above relationship is directly proportional to the partial photoionization cross section of the ion being observed.⁴³ The plot of the PIE of an ion as a function of incident photon wavelength or energy is referred to as the PIE curve.

There are several fundamental experimental difficulties with PIMS due to limitations imposed by experimental technology and the nature of the fundamental photoionization process. The photon energies needed to

ionize and fragment most molecules correspond to wavelengths in the vacuum ultraviolet(VUV) region.(i.e. $\lambda < 2000\text{\AA}$). Most substances, including nitrogen and oxygen, absorb strongly in the VUV, and consequently the optical path in a photoionization mass spectrometer must be kept evacuated. This is made difficult by the fact that, at wavelengths below the short wavelength cutoff of lithium fluoride at $\approx 1050\text{\AA}$ (i.e. at photon energies above $\approx 11.8\text{eV}$), there are no satisfactory window materials which can be used to isolate the lamp or sample gas from the rest of instrument. The vacuum system must therefore be capable of maintaining an acceptably low pressure($\approx 10^{-5}$ torr) despite the continuous influx of gas. This problem can be solved by modern vacuum technology, although the expense is significant. In addition, no optical materials are available to efficiently transmit and disperse the source radiation. Most substances absorb strongly in the VUV, which also means that reflectivities are low. The best available optical materials have reflectivities on the order of 15%-30% at $1000\text{\AA}$, so that every reflection employed to disperse or to focus the light eliminates a large fraction of the incident light. This problem is exacerbated by the absence of intense light sources. The best available light sources in the VUV region have peak intensities of only about 10^8 - 10^{10} photons $\text{sec}^{-1}\text{\AA}^{-1}$. [The impetus for the development of tunable VUV laser sources is clear.] Thus it is imperative that reflecting surfaces be kept to a minimum; normally a single concave diffraction grating, ruled on a reflecting surface, is the sole optical element employed. Moreover, the ion signal intensities are often very low, even with an excellent ion collection system design and the best available

equipment. Most experiments (with the possible exception of high-pressure ion-molecule reaction studies) must be performed with sample pressures of a few millitorr or less in order to avoid the collisional effects which can distort the PIE curves at higher pressure.⁴⁴ Thus, the ion signal cannot be increased by merely increasing the sample pressure. Any decrease in the photon energy bandwidth to increase resolution also decreases the signal intensity, and further aggravates the problem.

Even when the best available light source is used, when the sample pressure and photon bandwidth have been increased as much as possible consistent with the goal of the experiment, and when ion collection efficiencies approach 100%, many of the processes that might be of interest in a PIMS experiment are still of extremely low intensity—perhaps only a few ions per second, or less. Implementation of ion counting techniques allow sufficiently long integration times that usable data can often be obtained even with such weak signals, but only at the cost of very lengthy experiments.

2. Photoion-Photoelectron Coincidence Spectroscopy

The primary purpose of PIPECO experiments is to select molecular ions with a predetermined internal energy and then to determine the relative probability of decomposition into various fragment channels. Additionally, the kinetic energy of the fragment ions is measured, which aids in the elucidation of the dynamics and in testing theories of unimolecular decay. From the knowledge of the incident photon energy and the energy of the ejected photoelectron, the experimenter knows

exactly which excited state of the molecular ion has been produced. Gating techniques are employed to extract ions formed in coincidence with photoelectrons of a given energy. The mass distribution and kinetic energies of these ions are measured, and the information is used to determine the decomposition pathways of the state-selected precursor ion.

Two types of photoion-photoelectron coincidence experiments are currently being pursued. First, photoelectrons of a single energy are chosen and the mass spectrum of the ions formed in coincidence with electrons of the selected energy is examined. The initial state of the molecular ion formed is known through the conservation condition noted above, and the identities (as in normal mass spectrometry) and the kinetic energies of ions formed within a known period following the photoexcitation event are measured. Second, a particular ion in the mass spectrum can be chosen and the energy spectrum of photoelectrons in coincidence with them can be found. This method provides a spectrum of the excited states of the molecular ion that lead to the production of the particular ion of interest, and it is equivalent to a determination of the breakdown diagram. (This is a plot of the relative abundance of all ions including the parent ion vs. the incident photon energy.)

Figure (2-6) depicts a schematic diagram of a coincidence spectrometer, with nominal signal wave-forms being used in order to illustrate the principles. The photoion-photoelectron coincidence technique involves the use of a photoelectron spectrometer and a mass spectrometer, both of which sample the same ionization events. In order

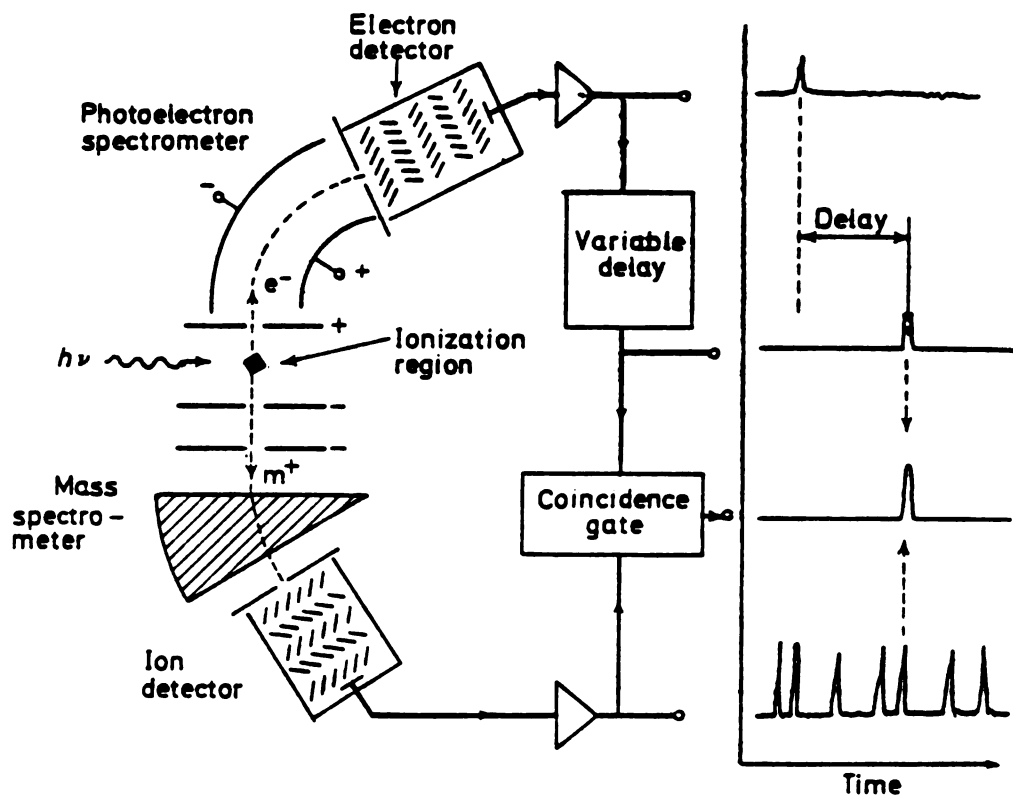


Figure 2-6. Simplified scheme of a photoelectron-photoion coincidence spectrometer. The peaks in the idealized wave-forms on the right indicate detection of single electrons and single ions; there are generally many more ions than electrons because the collection efficiency of mass spectrometer is higher than that of photoelectron spectrometers. [From J.H.D.Eland, Photoelectron Spectroscopy (John Wiley and Sons, New York, 1974).]

to bring the ions into the mass spectrometer, an electric "draw-out" field is needed in the ionization region, and the strength of this field is an important experimental parameter.

Both electrons and ions must be detected as single pulse, and after a delay of the electron signals to compensate for the flight times of the ions through the mass spectrometer the pulses are brought together in a coincidence gate. An output from this gate occurs if its two inputs are simultaneous, and if the delay is correct this should be true only of pulses from the two particles produced in single ionization events. Experimental difficulties arise from the fact that even when the delay does not match the flight time of the ions, some coincidences are still detected because of the random distribution of ion arrival times and the inherent detector background pulses. These are accidental coincidences and their contribution must be calculated or measured and subtracted from the total signal.

All ions of the same mass would not arrive at the ion detector simultaneously, even if they were all produced at the same instant by photoionization. Part of the experimental spread in the flight times of ions is instrumental, but most of it is due to the initial velocities imparted to the ions upon ionization. An ion with an initial trajectory towards the mass spectrometer will clearly arrive there sooner than one which starts in the opposite direction and must be turned around by the electric field. As a result, a curve showing the rate of true coincidences plotted against the delay time (a time-of-flight coincidence spectrum) is characteristic of the initial velocity distribution of the ions. The spread in the flight times of fragment

ions results not only from the initial thermal motion of the molecules prior to photoionization--which is small, but readily observable--but also from the release of kinetic energy in the decompositions that produce them. From the form of the time-of-flight coincidence spectrum, it is possible to deduce how much energy is released as kinetic energy in ionic dissociation, which is most important for the interpretation of dissociation mechanisms.

3. Other Techniques for Measuring Ionization and Appearance Potentials

There are many different kinds of experimental techniques for the measurement of ionization and appearance potentials. They have been conveniently grouped by Rosenstock¹⁰ according to the type of experimental approach and theory, or the rationale employed for interpretation of the data. The ensuing brief descriptions follow this classification scheme; Table (2-2) lists the categories, the techniques, and their accepted abbreviations.

(1) Optical Spectroscopy

In general, spectroscopic techniques give the most accurate data. The instrumentation and calibration have been refined to such a point that in the visible and near UV, for atomic absorption and emission, a measurement can be accurate to 0.001-0.0001 nm (wavelength) or better. A typical modern 21 or 35 foot optical spectrograph will have a resolution of the order of several thousand or more, depending on the grating order used. On the other hand, most molecular spectroscopic studies cited have been done with instrumentation of somewhat lower

Table 2-2. Experimental techniques used to measure positive ion energies

Category	Technique	Abbreviation
Optical spectroscopy	Spectroscopy	S
Threshold Experiments	Photoionization	PI
	(with mass analysis)	PIMS
	Electron impact	EI
Electron Spectroscopy	Photoelectron spectroscopy	PES
	Auger electron spectroscopy	AUG
	Resonant photoionization	RPI
	Penning ionization	PEN
Others	Surface ionization	SI
	Charge transfer spectrum	CTS

resolution. Wavelengths are generally reported to 0.01 nm and occasionally to 0.001 nm. Fairly reliable values of the first (and higher) ionization potentials of atoms and molecules can be obtained by the study of Rydberg series. Rydberg states are observed in UV absorption spectra or in emission, classified as members of a particular series, and the ionic state to which each series converges is determined by fitting the observed data to the Rydberg equation. Details of typical instrumentation and experimental methodology are given in references 64-66.

(2) Threshold Experiments

The second category of experimental techniques may be termed threshold methods, in which the objective is to determine directly the minimum energy necessary to form an ion (parent or fragment) from a neutral species, or sometimes from an ion of lesser charge. Included in this class are photoionization and various electron impact techniques.

(a) Photoionization:

Photoionization measurements can be carried out with (next subsection) or without mass spectrometric analysis. The latter experiments are generally carried out with a near-normal incidence or a Seya-Namioka grazing incidence monochromator. Typical wavelength resolution ranges from 0.04 to between 0.2 and 0.3 nm in first order, and the wavelength scale precision is typically between 0.01 and 0.02 nm from calibration with known emission lines. This represents a best resolution of about 5 meV at 12 eV. The commonly-used light sources are the hydrogen many-line discharge and the helium continuum. From the experimental absorption and ion current measurements, one can calculate

and plot the absorption and ionization coefficients as a function of the incident photon energy. The experimental total ionization cross section curves reveal ionization and appearance potentials, as well as superimposed autoionization from Rydberg states.

(b) Electron Impact:

This technique has been the most widely used over the past half-century in experiments directed towards measurements of ionization and fragmentation energetics. In the electron impact method, ionization or appearance potentials are measured by recording the parent or fragment ion current in a mass spectrometer while increasing the energy of the thermionic electron beam used for ionization. When the electron energy is below the ionization potential, the cross section for electron impact ionization is zero, and it should increase linearly with increasing energy above the threshold. Ionization or appearance potential differences between the sample and a standard are obtained by various methods of extrapolation. There are two main problems with the electron impact method: there is a relatively large spread in the electron beam, and the actual energy maximum of the beam can differ from the nominal energy expected from the applied electron acceleration potential. As a result, it is necessary to calibrate the nominal energy scale by doing experiments with a reference gas or gases, and to employ special conditions to minimize the electron energy spread. Many approaches have been developed to deal with these problems, with varying success. The techniques can be divided into three categories, of progressively decreasing refinement and quality: (i) monoenergetic, (ii) quasi-monoenergetic, and (iii) conventional or non-monoenergetic.

(i) Monoenergetic:

The energy spread of the electron beam is caused by the filament potential drop, filament temperature, field penetration and surface effects. A monoenergetic electron beam technique currently in use limits the electron energy spread by passing the beam through a double hemispherical electron monochromator of known electron optical behavior.⁴⁵ This can improve the electron beam spread from several tenths of an electron volt or more to about 70 meV. Some work has also been done using 127° cylindrical electrostatic analyzers to obtain electron beams of comparably narrow and defined energy spread.⁴⁶

(ii) Quasi-monoenergetic:

A radically different approach to overcoming the energy spread problem is known as the RPD (Retarding Potential Difference)⁴⁷ technique. In this method the electron gun is designed with a potential distribution such that the low energy portion of the electron energy distribution is not transmitted into the ion source. This cut-off potential is rapidly varied between two values differing by a small amount (of the order of 0.1eV). The corresponding difference component of the ion signal is detected and amplified. This component corresponds in principle to the ion current produced by electrons having an energy distribution of that portion of the original distribution lying between the two cut-offs.

A second quasi-monoenergetic method is the EDD (Energy Distribution Difference method).⁴⁸ In this method the ion current measured at a nominal electron energy E is adjusted by subtracting from it a constant fraction, b , of the ion current measured at a nominal

energy $E+\Delta E$. The originators of the method show that this difference current represents the ion current due to a considerably narrower electron distribution. The optimum values of the parameters b and ΔE depend on the form of the electron energy distribution. Before either of these two methods can be used, calibration with a gas of known ionization potential is required, and it is necessary to assume similar threshold behavior for all sample studied.

(iii) Non-monoenergetic:

Most of the remaining electron impact techniques are simply grouped under the category EI. They include the conventional techniques which employ electron beams of broad energy and differ principally in the method of extrapolating to "threshold". Among these methods, described in reference 71, are: linear extrapolation, semi-log plot, extrapolated voltage difference, energy compensation and critical slope. Their accuracy ranges from less than 0.1eV to more than 0.5eV, in an unpredictable manner.

Still another group of extrapolation techniques has been developed and applied to the determination of threshold energies for multiple ionization. There are Square Root Plot (SRP) and Nth Root Extrapolation (NRE) techniques. Their rationale is the assumption that near threshold the cross-section for direct multiple ionization varies with the Nth power of the electron energy in excess of the threshold value, e.g., a quadratic law for double ionization, a cubic law for triple ionization, etc.⁴⁹

Another experimental technique which has been devised to determine threshold energies for multiple ionization is Sequential Mass

Spectrometry (SEQ).⁵⁰ In this technique, the ion source is operated in a potential configuration which employs space charge trapping of the positive ions formed by electron impact. Some of the ions undergo a second ionizing collision with an electron before drifting out of the trapping region. Because of this step-wise ionization, one can determine the ionization potentials of species which have previously been ionized. Trapping times vary from 10^{-4} seconds to almost one second. While this technique offers some advantages in obtaining information on highly charged species, there are considerable difficulties in interpretation because of the large energy spread of the electrons.

(3) Electron Spectroscopy

The third category has as a common principle the energy analysis of electrons ejected from molecules which have been excited by UV photons (photoelectron spectroscopy, PES), X-ray photons (Auger electron spectroscopy, AUG) or electronically metastable atoms and molecules of known energy (Penning ionization, PEN). For a given excitation energy, the energy distribution of accessible energy levels of the target neutral atom or molecule are determined according to the relation:

$$E_{\text{ion}} = h\nu - E_{\text{electron}}.$$

Eland's book¹⁵ is a very good reference to supplement the brief summary which follows.

(a) Photoelectron Spectroscopy

The most widely used photon source in UV photoelectron

spectroscopy is the helium resonance line of wavelength $584.331\text{\AA}$, corresponding to an energy of 21.218eV . Recently other noble gas resonance lines have also been employed as the photon source, and some additional information is obtainable if the source is in resonance with an optical transition of the molecule (RPES). Energy analysis of the ejected photoelectrons has been accomplished with a great variety of analyzers including: cylindrical retarding grid; spherical retarding grid; 180° magnetic sector; 127° electrostatic sector; plane parallel electrostatic analyzer; double-focusing electrostatic prism; and double-focusing hemispherical condenser. The relative merits of these devices and their theoretical basis are discussed in detail in Berkowitz's book.²⁶ At present, the highest resolution attained is of the order $10\text{--}15\text{ meV}$ with a 127° electrostatic analyzer.⁵¹

(b) Auger Electron Spectroscopy

The technique of Auger electron spectroscopy is similar in principle to photoelectron spectroscopy. It, too, is based on energy analysis of ejected electrons. However, in this case the electron is ejected via an Auger cascade following prior inner shell ionization. The inner shell ionization is brought about by a high energy electron beam or a discrete X-ray source. The energy analysis is carried out by means of either a cylindrical mirror analyzer operated at an energy resolution of 0.12% to 0.16% , or a double-focusing electrostatic prism with 0.06% to 0.09% energy resolution. Since the Auger electrons have energies of several hundred volts or more, these percentages imply an energy resolution of several tenths of an electron volt. Calibration of

the energy scale is carried out with known Auger electron energies of neon and argon.

(c) Resonant Photoionization

The resonant photoionization technique, also called threshold photoelectron spectroscopy (TPES), differs from traditional photoelectron spectroscopy in that the photon energy is varied and only those photoelectrons are detected which lie in a narrow energy band essentially corresponding to zero energy of ejection. Thus, in principle, a photon wavelength scan will indicate directly those ion states which are accessible, without interference from autoionization processes involving transitions to lower levels. In practice, due to finite energy resolution, a signal is also obtained from autoionization processes which populate states close to the direct ionization threshold. The zero energy electrons are selected by two different methods. In one, all photoelectrons are accelerated through a known potential drop and only those whose energy corresponds closely to the imposed acceleration potential are selected by a 127° electrostatic analyzer. In the second method the electrons are accelerated through a uniform electrostatic field and non-zero energy photoelectrons are intercepted by passing through channels of small angular aperture oriented parallel to the field (steradiancy analysis). The accuracy of ionization threshold values measured by TPES is reported to be 10-20 meV⁵² and 2-5 meV,⁵³ respectively.

(d) Penning Ionization

The Penning ionization technique is also based on ejected electron energy analysis. In this technique, the ionizing agent is a beam of

metastable neutral rare gas atoms (or sometimes metastable molecules) with known excitation energy or energies. The excited species are generally produced by electron impact. Typically, there are two metastable states (differing in the value of the quantum number J) in a given atom beam, and the Penning spectrum consists of a shifted superposition of two spectra, each formed by one of the metastable species. The relative intensity depends on the relative proportion of the two species and the relative cross-section for the process. Electron energy analysis is performed by a plane parallel retarding grid of 10-20 meV resolution⁵⁴ or a 127° electrostatic sector of better than 60 meV resolution.⁵⁵

(4) Other Methods

(a) Surface Ionization.

The surface ionization method has been applied to the determination of first ionization potentials of some metal atoms, especially of the lanthanide and actinide elements. The principle of the method is based on the assumption that atoms in a beam, after impinging on a hot metal surface, will come to thermodynamic equilibrium, thereby exhibiting a surface concentration of atoms and ions whose composition can be described by the Saha-Langmuir equation:

$$N_+/N_0 = (g_+/g_0) \exp\{[e(\eta - I)]/kT\},$$

where N_+/N_0 is the fraction of the atoms which are ionized, g_+ and g_0 are the statistical weights of the ions and atoms, e is the electronic charge, η is the work function of the metal, I is the ionization

potential of the atom, k is the Boltzmann constant, and T is the absolute temperature. The temperature dependence of the positive ion current will give the ionization potential of the atom, provided that the work function of the surface is known. Complications inherent in the method include the (unknown) effect of surface coverage and/or impurities on the work function, the definition of the effective work function for a polycrystalline surface exhibiting a variety of crystal planes with different work functions, and an occasional lack of reproducibility of experimental results, which is not yet understood. Moreover, the fundamental assumption is open to question. These factors are discussed in detail in references 79 and 80. The difficulties are somewhat reduced by the determination of ionization potential differences accompanying bombardment of the metal surface with a composite beam of atoms of known ionization potential and atoms of unknown ionization potential,⁵⁶ or by comparing the temperature dependence of positive and negative ion emission from the same atomic species.⁵⁷ Where comparisons can be made with more reliable methods, the relative determinations give ionization potentials within several tenths of an electron volt of the more precise value.

(b) Charge Transfer Spectra

The charge transfer spectrum method is a semi-empirical method often used to estimate, or bracket, ionization potentials of large molecules such as polyphenyls, fused ring systems, amines, and certain biochemical compounds. It is based on a semi-empirical theory developed by Mulliken to explain the absorption bands of electron donor-electron acceptor complexes in solution.⁵⁸ These bands

are attributed to transitions from the ground state of the molecular complex to excited states in which an electron is transferred, largely between the donor and acceptor molecules. Hastings et al.⁵⁹ derived from the Mulliken theory a simple algebraic relationship between the frequency of the maximum of the charge transfer band and the ionization potential of the donor, and correlated it with experimental information. The subject has been reviewed extensively by Eriegleb.⁶⁰ A limited comparison of ionization potentials derived by this method and more accurate methods indicates that the estimates are frequently correct to within several tenths of an electron volt.

CHAPTER THREE

THRESHOLD BEHAVIOR

In this chapter, the discussion will focus on the different effects which influence the photoionization efficiency threshold. Theoretically, for an isolated atom or molecule in the absence of experimental influences, the threshold behavior for a one-electron departure from a positively charged core following photoionization should follow a step function-like curve along the energy axis.^{35,61} However, in a real experiment many factors change the threshold shape from a step function to an approximately sigmoidal shape, and sometimes the threshold behavior is even more complicated. Different shapes are diagnostic of different influences on the threshold. Moreover, because not only the shape, but also the apparent energy axis intercept of the photoionization efficiency curve may be altered, the ionization potential or appearance potential obtained from the extrapolation of the observed PIE to a purported threshold may be shifted to a higher or lower value. If an appropriate procedure is used to deconvolute natural and experimental contributions to the threshold region, then reliable ionization or appearance potentials can be extracted. However, an improper deconvolution process will lead to the incorrect assignment of ionization or appearance potentials. To date, no good, unambiguous, consensus method to deconvolute threshold behavior has been established; several different extrapolation methods are employed to find the desired ionization or appearance potential. In the following sections of this

chapter the quantum theoretical basis for the expected step-function threshold law is traced, followed by discussion of several other factors which influence its experimental appearance, in order: the thermal effect, the kinetic effect, and the instrument effects.

It is necessary to emphasize that the main purpose of this discussion is to facilitate interpretation of the experimental observations. It is pointless to try to predict the shape of the threshold or the threshold energy shift via calculations which combine several of these effects together, based on the properties of the compound of interest, without doing a real experiment on that compound. The factors which affect the threshold behavior change dramatically from compound to compound, and good methods to measure or calculate the parameters which determine the magnitude of the real effect are still not available.

A. Quantum Theoretical Considerations

1. Ionization Threshold Law

In chapter two, it was noted that the probability of direct photoionization is proportional to the square of the dipole transition moment integral. Within the Born-Oppenheimer approximation and under the assumption that the electronic part of the wavefunction changes negligibly in the time it takes for a transition to occur, the integral can be separated into an electronic part and a vibrational part. The ionization (or fragmentation) threshold law stems from the electronic part of the dipole moment transition integral.

The determination of the ionization threshold law is based upon

assumptions concerning the energy dependence of the electron impact or photoionization cross section in the neighborhood of the threshold. In a consideration of first ionization and multiple ionization thresholds (the latter will be omitted from the ensuing discussion, since multiple ionization is rarely observed with a source limited to 22eV), Wigner³⁵ and Geltman⁶¹ have calculated the post-threshold cross section behavior of the photoionization process in the limit of zero excess energy above the threshold. In this limit, the details of the absorption probability characteristic of the individual atomic and molecular entities do not enter, and the cross-section is determined by the long range interaction between the departing particles, in this case a positive ion and an electron. The Coulombic attraction then leads to an abrupt onset to a finite cross section, with a post-threshold behavior independent of excess energy (so-called "step-function behavior"). Generally, it was shown that the dependence of the ionization cross section on energy in the threshold region is given by a power law of the form:

$$\sigma(E) = C(E - E_0)^{n-1}, \quad \text{for } E \geq E_0 \quad (3-1)$$

where E is the energy of the ionizing electron or photon, E_0 is the threshold energy, C is a constant, and n is the total number of outgoing electrons for the ionization or fragmentation process. Clearly, this will lead to a step function threshold law for single ionization by photoionization. For electron impact, a linear threshold law for single ionization and a quadratic threshold law for double ionization is predicted, and so on.

The treatments of Wigner and Geltman do not provide information about how far above the threshold the laws are valid. For practical purposes a range of validity of an electron volt or two would be desirable. However, there is no guarantee that the valid range is this large; it may be only several millivolts, or even less, and it may vary from system to system. Thus, there is no theoretical reason to expect that there exist threshold laws of exactly the form, range of validity and universality desired by the experimentist.

It is clear that even in the case of atomic hydrogen the step-function behavior is not fulfilled for any finite energy beyond the threshold. For a molecular systems, the situation is even more complicated. In addition to autoionization phenomena, one must be prepared for variation in ionization probability with vibrational state (Franck-Condon effect), with electron transition moments (which are a function of internuclear distance), with spin-orbit coupling, and with configurational instability of the parent ion. Most photoionization experiments are carried out at room temperature, and it is necessary to take into account the effects of hot bands and the thermal tail. For some fragmentation processes, the kinetic shift and competition with other dissociation channels will affect the threshold, too. Finally, the finite instrumental resolution always contributes some rounding to the sharp edges of the threshold step function.

2. Autoionization Effects

The autoionization effects being considered here involve transitions from the ground electronic state of the parent molecule to bound excited states of the neutral having energy just above the

ionization threshold, followed by radiationless transitions into the ionization continuum. Such an autoionization process leads to a sharp, delta-function shaped peak in the photoionization efficiency curve just above the threshold, which may or may not be distinguishable from it. Autoionization often appears as sharp peak-like structure superimposed on the normally featureless ionization continuum, but when the lifetime of the autoionizing state is short, or when the radiationless transition is also accompanied by emission or predissociation into neutral fragments, the autoionization peak may be broadened and hard to distinguish from the direct ionization continuum. Figure (3-1) shows autoionization structure contributions to the ionization continuum; the same Figure also shows that autoionization exists in every parent ion excited state. In some cases, part of the abrupt rise of the photoionization cross section at threshold is contributed to by autoionization, even in the simplest molecules, such as H_2 , O_2 , and N_2 . The behavior of the underlying continuum is largely obscured by the very strong autoionization feature. Several of the halomethanes studied in this work also exhibit very clear autoionization effects in the threshold region; these will be described in chapter five.

3. Franck-Condon Factors

The second term of equation (2-12), the vibrational integral $|\langle F_v' | F_v'' \rangle|^2$, is in the form of an overlap integral between vibrational eigenfunctions of a neutral parent electronic state and a parent ion electronic state. This integral, called the Franck-Condon factor, is largely responsible for the relative intensities of the vibrational bands in photoionization transitions. This overlap integral does not

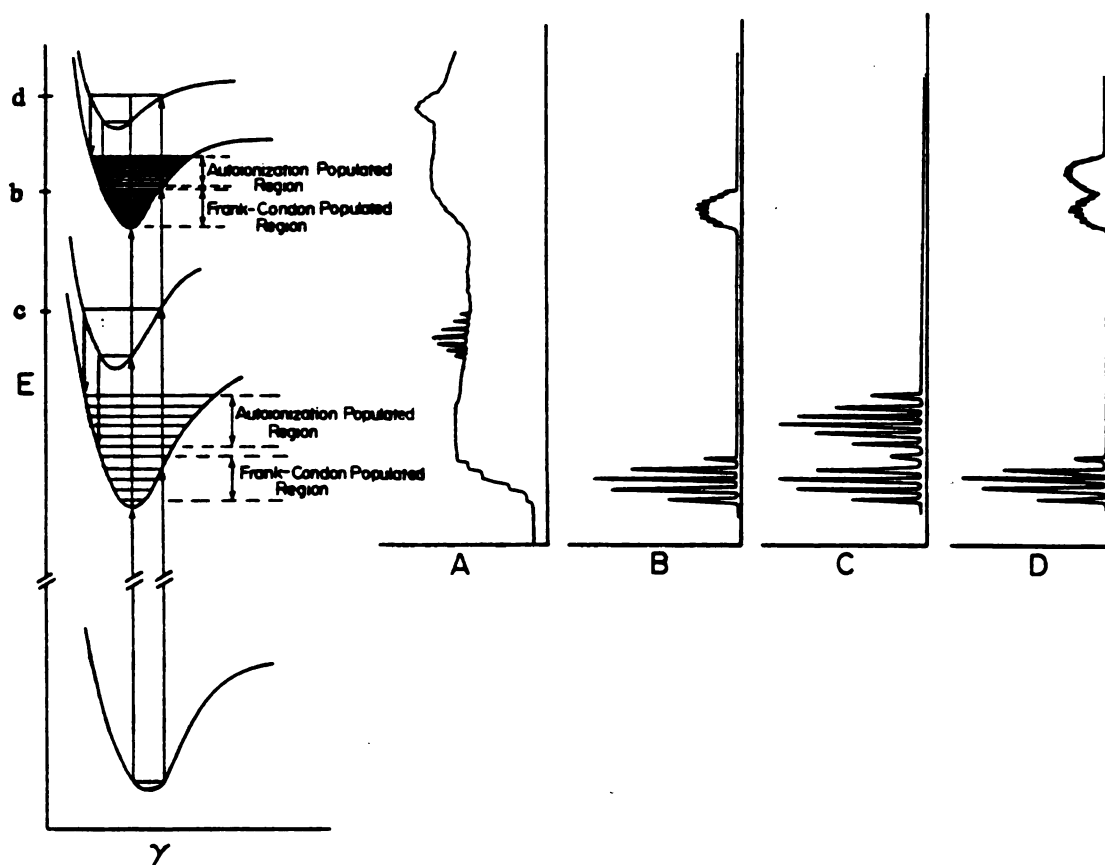


Figure 3-1. The effect of Franck-Condon factors and autoionization on a PIE curve and corresponding photoelectron spectra.

- A. PIE curve.**
- B. PES spectrum with source energy b.**
- C. PES spectrum with source energy c.**
- D. PES spectrum with source energy d.**

vanish by orthogonality because F_v' and F_v'' are vibrational functions belonging to different electronic states. The effect of the Franck-Condon factor on the threshold of a photoionization cross section is to attenuate the electronic step-like threshold by introducing additional step-like structure to the photoionization efficiency curve. The threshold for an electronic state of the parent ion becomes a series of steps, where each step represents a threshold for a vibrational state. The relative heights of successive vibrational steps are proportional to the relative intensities for the corresponding transitions.

The overall shape of the threshold can vary, depending on the difference in equilibrium geometry and bond length between the neutral molecule and the ion. This is illustrated in Figure (3-2) for a diatomic molecule. If the potential energy curve of the ion is very similar in shape and has an equilibrium internuclear separation identical to that of the parent curve (as might be the case following photoionization of non-bonding electron), then essentially only the vibrational ground state of the ion will be accessible from the molecular ground state. The threshold corresponding to this electronic transition will be only a single step. If the ion internuclear distance is a little greater or smaller than that of the neutral molecule (e.g. the electron is removed from a slightly bonding or antibonding orbital), then additional ion vibrational levels become accessible and a vibrational progression will be observed, with a $(0 \leftarrow 0)$ transition and progressively less intense transitions to the higher vibrational levels. The threshold will be characterized by a staircase with a large first

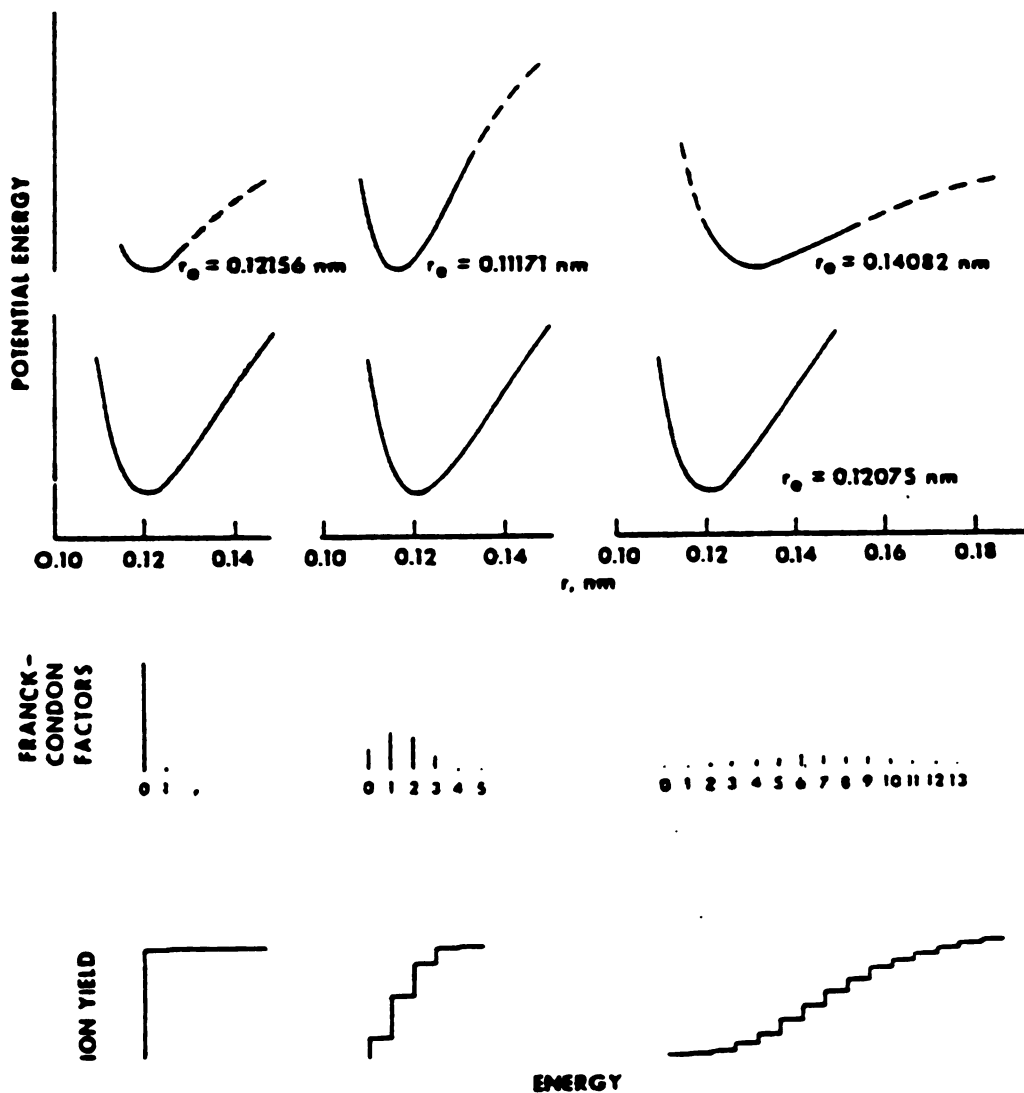
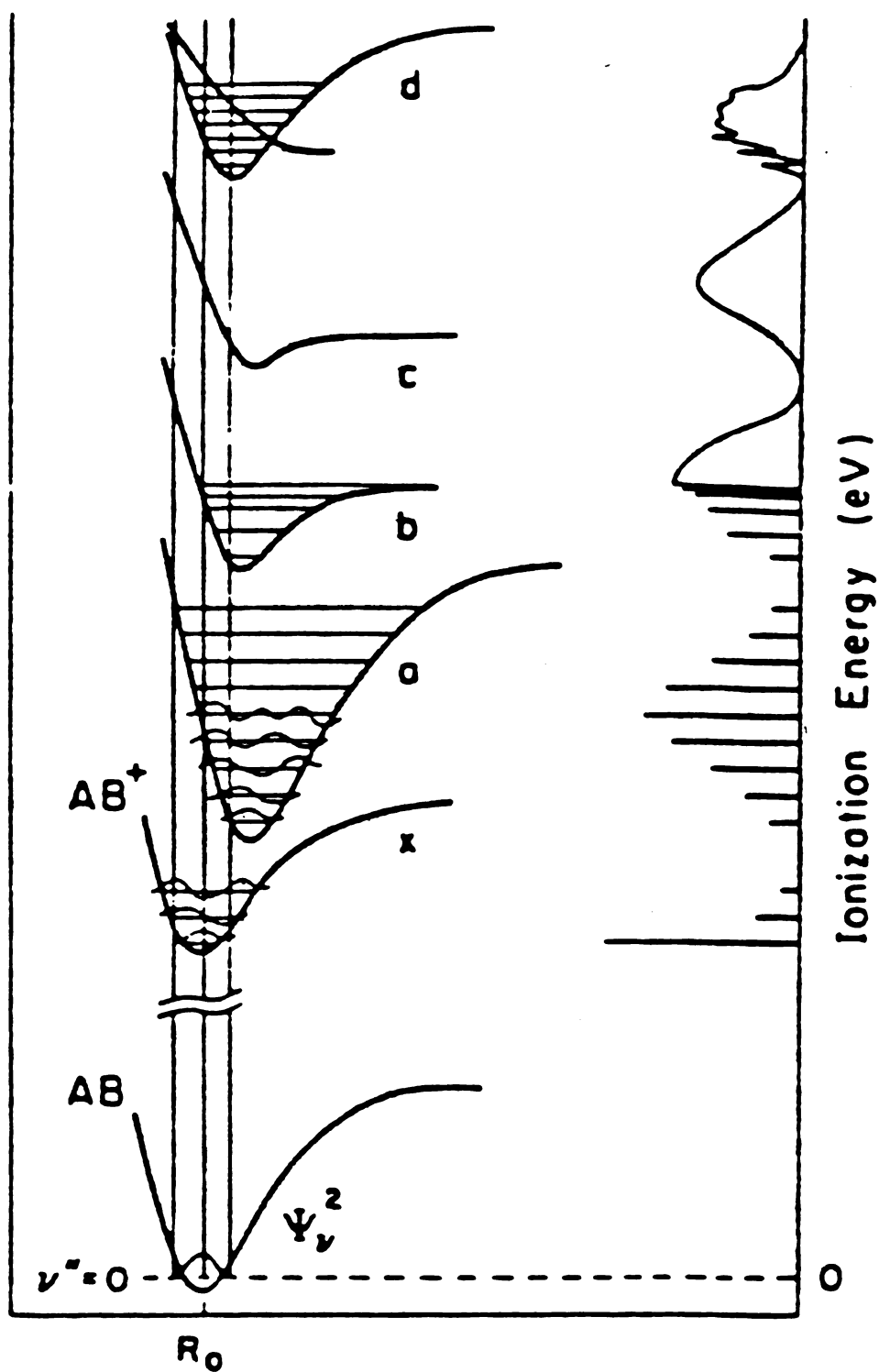


Figure 3-2. Effect of Franck-Condon factors on direct ionization thresholds of diatomic molecules. [From H.M. Rosenstock, *Int. J. Mass Spectrom. Ion Phys.* **20**, 139 (1976).]

step and progressively smaller steps to higher energy. If there is a large difference in internuclear distance, for example when an electron is removed from a bonding or antibonding orbital, the vibrational ground state ($0 \leftarrow 0$) transition is no longer the most intense and the maximum transition probability shifts to a higher vibrational level. Sometimes the ($0 \leftarrow 0$) transition may be so weak as to be unobservable, and the threshold region will exhibit a long progression of vibrational steps.

Figure (3-3) shows schematic potential energy curves for a hypothetical molecule AB in its ground state and the corresponding parent ion AB^+ in several ionic states. The vibrational eigenfunctions drawn into the upper and lower potential wells are intended to approximate those of an anharmonic oscillator. The wavefunctions for the $v=0$ levels are bell-shaped curves whose maxima lie at the equilibrium internuclear separation for the particular electronic configuration. The eigenfunctions of the higher vibrational levels have broad maxima or minima near the classical turning points of the motion. The maxima and minima between these termini are smaller and narrower than those at the terminal positions. The contribution to the overlap integral from these intermediate crests and troughs will roughly cancel one another. For a transition in which $v''=0$, the overlap integral has large values for the upper vibrational levels whose eigenfunctions have their terminal maximum or minimum roughly vertically above the maximum of the eigenfunction of the lowest state. When the minima of the two potential curves lie at the same internuclear distance, the overlap integral for the ($0 \leftarrow 0$) transition is large. But the ($1 \leftarrow 0$) or higher vibrational level bands are obviously small since the positive and



Internuclear Distance (R) —

Figure 3-3. Schematic diatomic molecule potential curves, Franck-Condon factors, and corresponding photoelectron spectrum. [From J.W. Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy (John Wiley and Sons, New York, 1977).]

negative contributions to the integral effectively cancel each other. If the potential curve for the upper state is translated to higher or lower R values, the intensity of the $(1 \leftarrow 0)$ band increases and that of the $(0 \leftarrow 0)$ band decreases. The maximum in the vibrational transition shifts to correspondingly higher v' values as the potential curves are shifted further. The photoelectron spectrum, which also reflects the Franck-Condon factors in the vibronic transition moment, is included at the right of the Figure (3-3). In Figure (3-3), the internuclear separation of the ion in its ground state, X , is the same as that of the molecular ground state. (This implies that the ion was formed by the removal of one nonbonding electron.) The resulting photoionization efficiency curve would exhibit a very sharp jump corresponding to a very intense $(0 \leftarrow 0)$ transition, followed by several small step increases, related to a relatively short vibrational progression. Curve a represents a potential surface in which the internuclear distance R is increased from its ground state value. In the corresponding vibrational transition, the Franck-Condon maximum appears near the middle of a long vibrational progression. In the corresponding photoionization efficiency curve, the highest step will lie near the middle of the threshold area, and two groups of small steps will be found at each side. For schematic curve b the electronic transition consists of a vibrational progression which finally converges into a continuum. This represents ionization into the region both above and below the dissociation limit of the ion in state b. The extrapolated appearance potential from the fragment ion PIE should correlate with the energy onset of the b-state continuum. Curve c shows ionization to a repulsive

potential surface, resulting in broad featureless structure in the photoionization efficiency curve. Curve d corresponds to the crossing or close approach of a repulsive potential surface and a bonding potential. In such a case, the wavefunctions describing the two states are mixed and the ion is subject to the lifetime limitation of the repulsive state. Such a situation is called predissociation. It results in a local sharp decrease in the parent photoionization efficiency curve; but at the same energy a related local sharp increase in the corresponding fragment ion photoionization efficiency curve is observed. The Frank-Condon factor has the same effects for polyatomic molecules, except that many bond lengths may change and the threshold may involve a superposition of several progressions of steps if more than one vibrational mode of the ion is excited. The structure may be complicated. In the absence of competing processes, step-like structure is always observed in the threshold region of the parent ion photoionization efficiency curves.⁶²⁻⁶⁴

4. Degenerate Ionic States

Whenever an electron is ejected from a fully occupied degenerate orbital in a molecule, it will form an orbitally degenerate doublet state of the corresponding ion. The degeneracy of such a state can be lifted either by the coupling between the spin and orbital angular momenta of unpaired electron--spin-orbit coupling, or by a change in molecular shape --configurational instability. For linear molecules the latter is called the Renner effect²¹, for nonlinear molecules it is termed the Jahn-Teller effect.²¹ When both of these effects (spin-orbit coupling and configurational instability) are at work, the threshold of

a photoionization efficiency curve will have steps and these steps will show complex vibrational structure. When the interactions are stronger the threshold may exhibit as many steps as there were electron pairs in the original degenerate orbital, but not more. In some unusual photoionization processes, orbitally degenerate ionic states can be produced that are not also spin degenerate; such states would be susceptible to the configurational instability effect only, and not to splitting by spin-orbit coupling.

(a) Spin-Orbit Coupling

When an electron is ejected from a degenerate orbital of a closed-shell atom or molecule to produce an ion in an electronic state which has orbital angular momentum, the spin angular momentum and orbital angular momentum can combine in different ways to produce new orbitals that are characterized by the total electronic angular momentum. The new states have different energies because the magnetic moments due to electron spin and orbital motion may oppose or reinforce one another. All states with multiplicity greater than one and a non-zero orbital angular momentum are split by this phenomenon called spin-orbit coupling. When this phenomenon is weak, it produces steps in the threshold; when it is strong, under ideal conditions several thresholds will be seen in the overall photoionization efficiency curve. Spin-orbit coupling is generally stronger when heavy atoms are present in the molecule.

Table (3-1) lists the observed and calculated spin-orbit splittings for the hydrogen halides and halogens. The data clearly reveal the heavy atom effect. Since the PIE threshold of most of the

Table 3-1. Observed^a and calculated spin-orbit splitting for the halogen acids and halogens. [From J.W.Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy (John Wiley and Sons, New York, 1977).]

Ionic State	E_i	ΔE_{obsd}	ΔE_{calcd}	E_i	ΔE_{obsd}	ΔE_{calcd}	E_i	ΔE_{obsd}	ΔE_{calcd}	E_i	ΔE_{obsd}	ΔE_{calcd}
	HF			HCl			HBr			HI		
$(2\pi), {}^2\Pi_{1/2}$	16.02	0.04	0.034	12.74	0.08	0.076	11.67	0.33	0.333	10.38	0.67	0.671
$(2\pi), {}^2\Pi_{3/2}$	16.06			12.82			12.00			11.05		
	F_2			Cl_2			Br_2			I_2		
$(1\pi_g), {}^2\Pi_{3/2,g}$	15.70	0.03	0.035	11.51	0.08	0.067	10.51	0.35	0.309	9.22	0.65	0.607
$(1\pi_g), {}^2\Pi_{1/2,g}$	15.73			11.59			10.86			9.87		
$(1\pi_u), {}^2\Pi_{3/2,u}$				13.96			12.41			10.74		
$(1\pi_u), {}^2\Pi_{1/2,u}$	18.39	—	0.038	14.04 ^b	0.08 ^b	0.088	12.75 ^b	0.34 ^b	0.382	11.54	0.80	0.788

^a Experimental data for HF are from Ref. 17; data for HCl, HBr, and HI are from Ref. 19; data for the halogens are from Ref. 23.

^b Uncertain value or values obtained from extrapolation.

halogens and hydrogen halides also show superimposed autoionization structure, it is hard to definitively attribute the steps at threshold to spin-orbit coupling. Experimental verification is clear in the photoelectron spectra reported in Figure (3-4).

(b) Configurational Instability

The electronic transitions which are reflected in a photoionization efficiency curve satisfy the Franck-Condon principle; i.e. they are vertical transitions to points on ionic potential surfaces where the nuclear configuration is identical to that of molecular ground state. If the electronic state of the ion is orbitally degenerate, retention of the ground state nuclear geometry and the orbital degeneracy may not be simultaneously possible, and a nuclear displacement will occur that destroys the orbital degeneracy. Such displacements are called Jahn-Teller or Renner distortions, and can lead to considerable spectral complexity. Only the Jahn-Teller effect will be sketched here, since only non-linear polyatomic molecules are discussed in this dissertation.

There are two kinds of Jahn-Teller effects. When there exist stable distorted configurations, the electronic energy is lowered and there is more than one position of equilibrium with equal energy. In other words, the electronic degeneracy is replaced by vibronic degeneracy. Thus a Jahn-Teller-distorted molecule has a permanent distortion that lowers its symmetry and produces an observable anisotropy. This is called the static Jahn-Teller effect. Alternatively, a change in the electronic energy can be caused by the excitation of one or more degenerate vibrational modes from an

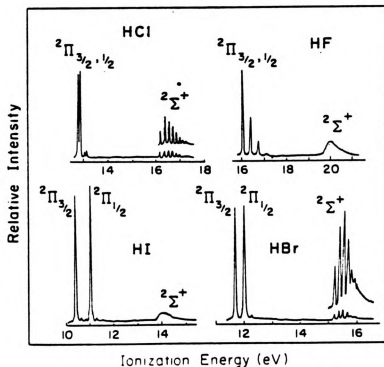
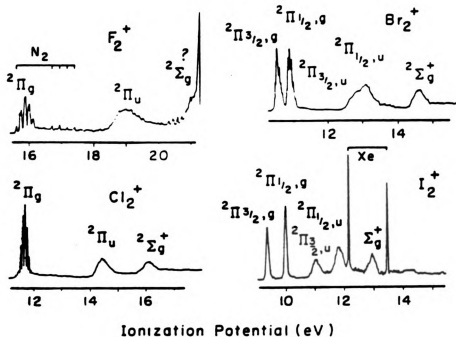


Figure 3-4. HeI photoelectron spectra of halogens and halogen halides. [From J.W.Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy (John Wiley and Sons, New York, 1977).]

originally degenerate electronic state of a molecule which is unstable towards distortions which remove the degeneracy. The total energy can no longer be separated into electronic and vibrational parts; that is, there is strong vibronic coupling. This is called the dynamic Jahn-Teller effect.

Figure (3-5) shows a qualitative picture of the Jahn-Teller effect as it influences the threshold of CH_4^+ , and the experimental photoelectron and photoionization spectra. Steps on the PIE of CH_4^+ due to Jahn-Teller distortion are clearly evident. There are many publications which relate to the Jahn-Teller effect; Derkowitz's²⁶ book contains detailed information of relevance to experimental photoexcitation studies.

B. Thermal Effects

1. Hot Bands

Particularly when molecules have low vibrational frequencies, there may be significant population of excited vibrational states of the ground electronic state at typical experimental temperatures. The threshold of a photoionization efficiency curve may be complicated by this effect, called hot bands. Hot bands are produced by transitions from excited vibrational levels of the ground molecular electronic state, $v'' > 0$, to various vibrational levels of ionic states. When hot bands are observed in the threshold of a PIE, they always contribute intensity to the low energy portion, since transitions $v'' > 0 \rightarrow v' = 0$ will have lower energy than the desired $0 \rightarrow 0$ origin. If a low temperature photoionization mass spectrometric study of the same compound is

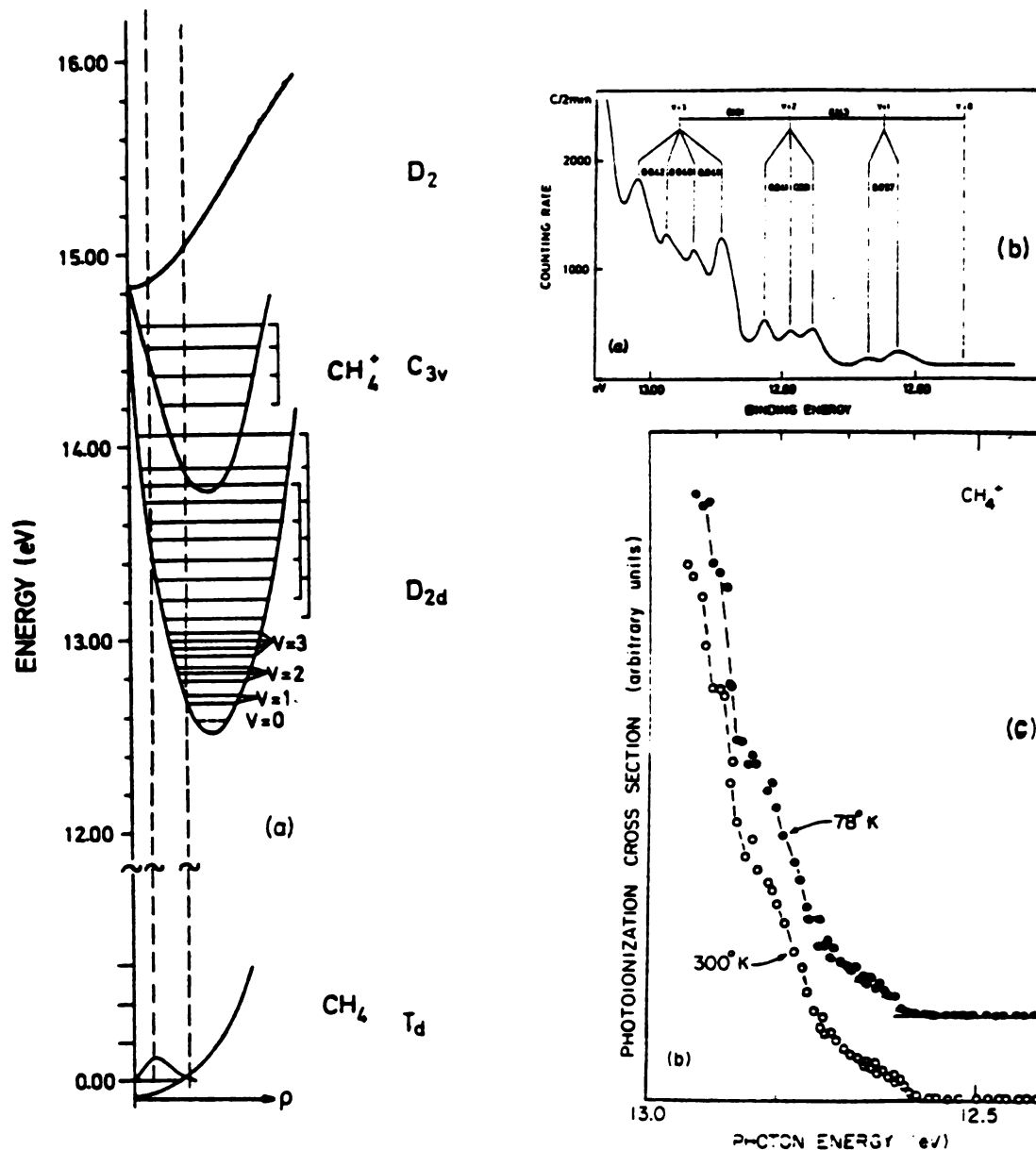


Figure 3-5. Example of the Jahn-Teller effect. (a) Qualitative configuration coordinate diagram of methane along the distortion coordinate ρ . The upper levels are drawn to be consistent with the photoelectron spectrum at the right. (b) PES spectrum of CH_4^+ in the threshold region with 21.2eV incident radiation. [From Rabalias, et al., Phys. Scr. **3**, 13(1971).] (c) Mass-selected photoion yield curve of CH_4^+ in the threshold region with the gas sample at 78 and 300 K. [From W.A.Chupka and J.Berkowitz, J. Chem. Phys. **54**, 4256(1971).] Note: The energy scales of (b) and (c) have been matched so that corresponding structures and thresholds can be directly compared.

possible, the hot band contribution may be discerned by comparing thresholds of the photoionization efficiency curves obtained at different temperatures.

From statistical thermodynamics, it is possible to calculate the relative thermal population of low energy vibrational states in the ground electronic state at room temperature.⁶⁵ Figure (3-6) shows the fractional population of several vibrational states of Br_2 at room temperature. The values were calculated from the equation

$$f(n) = \text{EXP}[-h\nu(n + 1/2)/kT]/q_{\text{vib}}(T), \quad (3-2)$$

$$q_{\text{vib}} = kT/h\nu \quad \text{for} \quad (kT \gg h\nu), \quad (3-3)$$

where $f(n)$ is the fraction of molecules in the vibrational state designated by vibrational quantum number n , q_{vib} is the vibrational partition function, and ν is the vibrational frequency. The result is an exponentially decreasing curve. For polyatomic molecules the threshold vibrational distribution is complicated, but the overall shape is similar.

Dibeler, et al.⁶⁶ show the hot band contribution to the $\text{Br}_2 \rightarrow \text{Br}_2^+ + e^-$ threshold at different temperatures. If the temperature is lowered sufficiently such that only $v''=0$ is significantly populated, the hot band effect disappears.

2. Thermal Tailing

Thermal tail is also an effect arising from the thermal

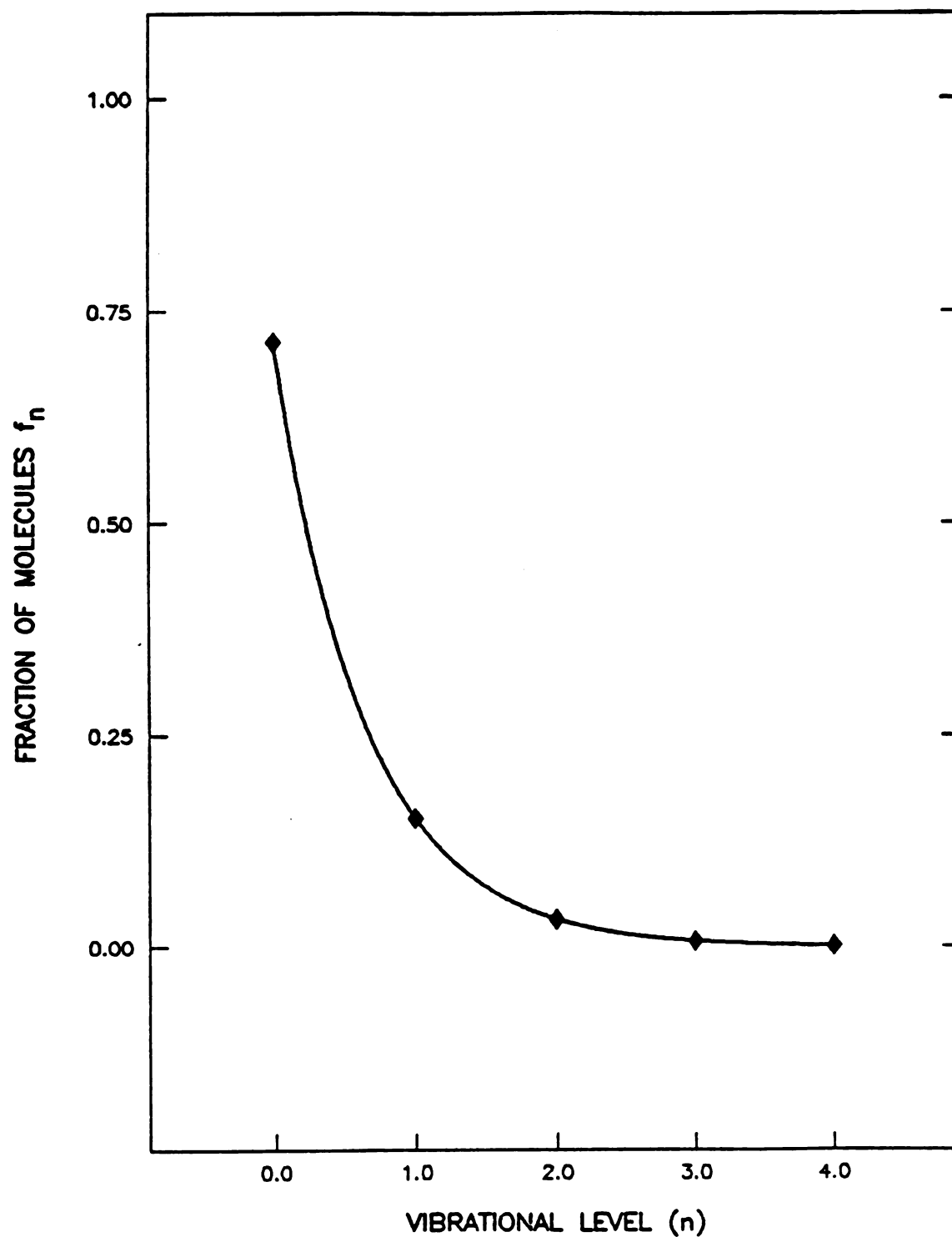


Figure 3-6. The population of the vibrational levels of Br_2 at 300 K. [From D.A. McQuarrie, Statistical Mechanics (Harper and Row Publishers, New York, 1976).]

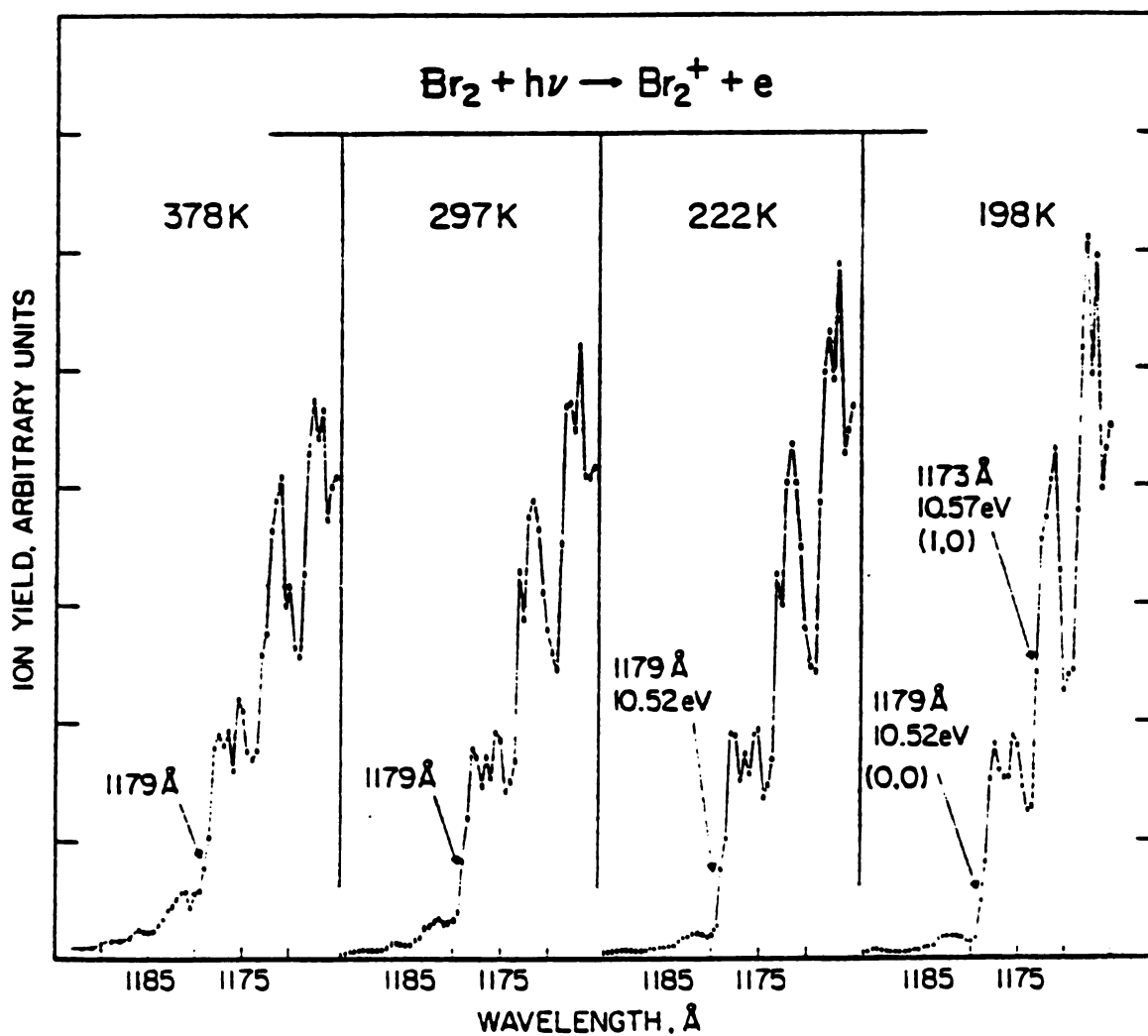


Figure 3-7. Hot band structure of Br_2^+ at several temperatures.
 [From V.H.Dibeler, et al., *Int. J. Mass Spectrom. Ion Phys.* **7**, 209 (1971).]

distribution of populated rotational and vibrational states of the neutral, which are available for fragmentation at lower photon energies than molecules in the ground rovibronic state. Experimentally, the most obvious effect of the thermal energy is to introduce a low intensity, slowly-rising onset--a thermal tail--to the fragment ion photoionization efficiency threshold. If one scans from high to low photon energy, the "thermal tail" approaches the base line asymptotically, and if the data are acquired with a sufficiently sensitive instrument, the tail will continue for several hundred millielectron volts below the thermochemical threshold. Chupka⁶⁷ has studied the effect of thermal energy on photoionization efficiency curves of fragment ions; Guyon and Berkowitz⁶⁸ have shown that the internal thermal energy of the neutral shifts the fragment ion threshold to lower energy by an amount equal to the average thermal energy of the neutral.

Figure (3-8) shows the relative population of the rotational levels of HCl at room temperature (293°K) calculated by statistical thermodynamics.⁶⁵ The equations used in the calculation are:

$$N_j/N = (2J + 1) \text{EXP}[-\theta_r J(J+1)/T] / q_{\text{rot}}(T), \quad (3-4)$$

$$q_{\text{rot}}(T) = (T/\theta_r)(1 + 1/3(\theta_r/T) + \dots), \quad (3-5)$$

where N_j is the number of molecules in j th rotational state, θ_r is the characteristic temperature of rotation, J is the rotational quantum number, and $q_{\text{rot}}(T)$ is the rotational partition function at temperature

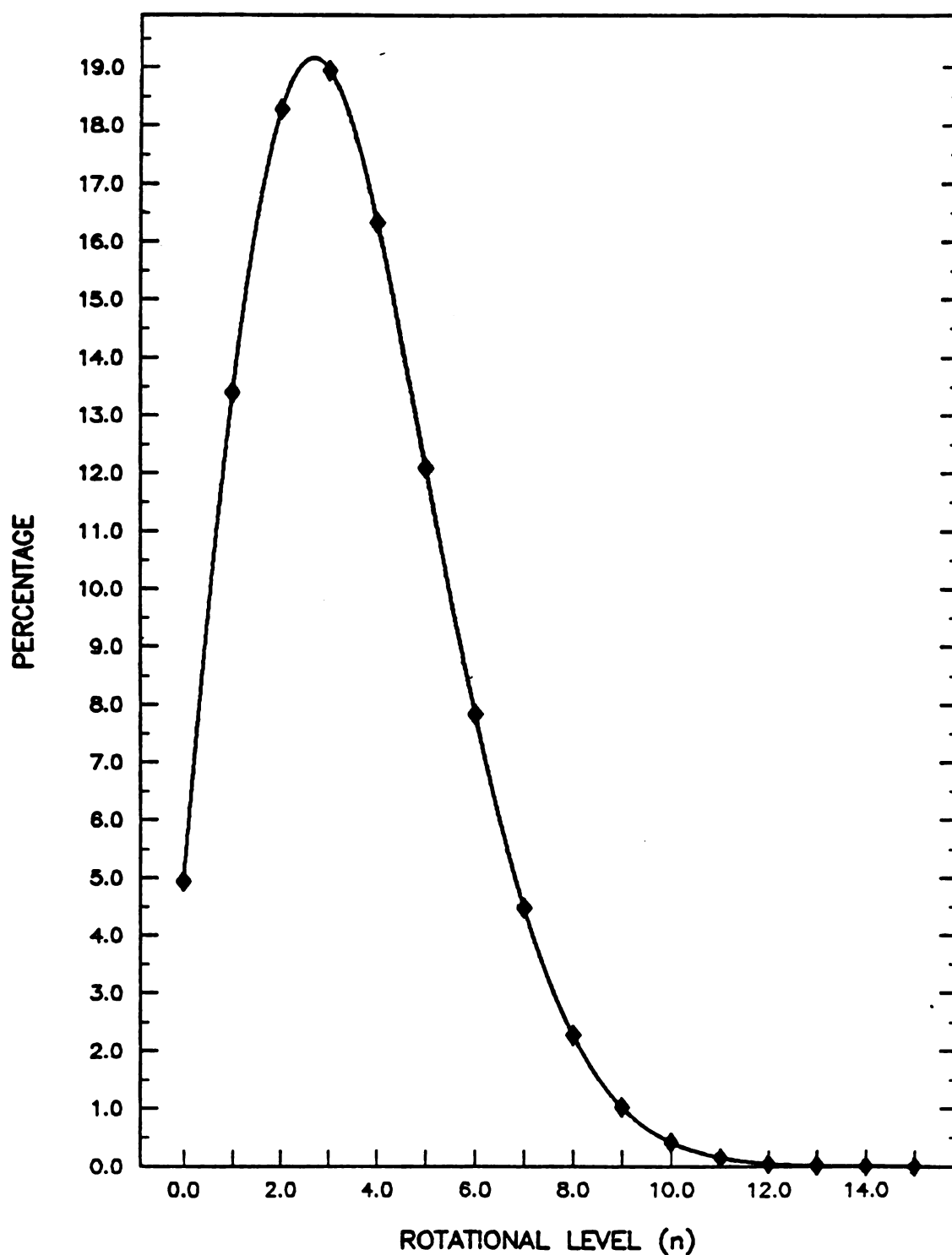


Figure 3-8. The population of the rotational levels of HCl at 300 K. [From D.A. McQuarrie, Statistical Mechanics (Harper and Row Publishers, New York, 1976).]

T. Even in the absence of vibrational hot bands, the thermal rotational energy distribution must be deconvoluted from the experimental PIE.

C. Kinetic Effects

Kinetic effects on the threshold of photoionization efficiency curves are related primarily to fragmentation processes. The generally-accepted, semi-quantitative description of the fragmentation of polyatomic molecules is based on quasi-equilibrium theory (QET).⁶⁹⁻⁷¹ According to this theory: (1) Parent ion fragmentation can be considered in two parts: one is the act producing the ion and the other is internal excitation energy distribution. (2) The fragmentation processes can be described as a series of competing unimolecular reactions. (3) The unimolecular reaction rate constant can be calculated quantitatively by means of activated complex theory.

The term "quasi-equilibrium" refers to the assumption that a parent ion produced directly in an excited electronic state via a transition from the ground electronic state of the neutral molecule will have enough time to undergo internal conversion to form a vibrationally excited ion in its ground electronic state prior to dissociation. Three distinct factors introduced by QET must be taken into account in interpreting thermochemical data from experimental fragmentation thresholds: (1) The relation between activation energy for decomposition and the heat of reaction for the process; (2) the relation between activation energy and the minimum energy to produce observable fragmentation in the mass spectrometer ion source, i.e. the so-called kinetic shift; (3) the effect of competing and consecutive reaction

paths on the shape and extrapolation of fragmentation threshold curves.

1. Activation Energy and Heat of Reaction

Some ionic decomposition processes occur via pathways involving the surmounting of a barrier on the potential surface. Surmounting such a barrier would require an activation energy greater than the heat of reaction of the process. Thus, the determination of thermochemical information from fragmentation threshold energetics is always subject to an uncertainty equal to the activation energy. Thus heats of formation calculated from experimental PIEs will be upper limits. It is sometimes possible, from observations of fragment particle kinetic energies, to deduce the existence of a potential barrier in the reaction coordinate for the decomposition. For example, analysis of the peak shape of an ion formed in metastable transitions, or measurement of delayed kinetic energy release for dissociation processes in the mass spectrometer can be related to the kinetic energy released in the dissociation processes. The translational kinetic energy of the fragmentation partners arises from the excess energy present in the dissociating ion at the excitation energy of the experimental fragmentation threshold.⁷²⁻⁷⁵ The peak shape observed in a time-of-flight spectrometer is related to the travel time distribution of fragment ions of a particular m/z value, which is determined by their initial translational energy distribution.^{76,77}

Investigations to date indicate that fragmentation processes may be accompanied by kinetic energy release ranging from essentially zero to nearly one electron volt. Thus the extrapolated threshold for a fragmentation processes may be shifted to higher energy by an amount in

this range. However, detailed processes for correcting an experimental threshold value for the presence of translational energy distribution remain to be worked out.

2. Kinetic Shift

In order to observe fragment ions in the mass spectrometer, the fragmentation process must occur before the departure of the parent ion from the ion source. (If fragmentation occurs within the quadrupole mass spectrometer, the ionic fragments will still be counted as parents.) The residence time of an ion in the source is roughly several microseconds.⁷⁸ As noted earlier, an ion must contain enough excitation energy to equal or exceed the activation energy for the fragmentation process. However, if the activation energy for the fragmentation is high, or the number of degrees of freedom of the parent ion is large, the rate of ion decomposition at the thermochemical threshold may be too slow to lead to observable fragmentation, i.e., fragmentation while the parent ion is still in the ion source. Additional excitation energy must be supplied to increase the decomposition rate. Thus, under some conditions the measured fragmentation threshold energy will overestimate the activation energy of the process. The term "kinetic shift" has been defined as the excess energy required to produce a measurable current of fragment ions before the parent ion leaves the ion source (i.e., about 10^{-5} sec). The presence of a kinetic shift in the fragmentation threshold can be tested by obtaining fragment PIEs at several different temperatures and can sometimes be inferred from changes in the PIE with acceleration voltage. From the discussion above, it is clear that the fragmentation threshold will vary with temperature.^{79,80} Rosenstock et

al.⁸¹ have emphasized that for large-molecule fragmentation processes the kinetics of decomposition lead to a gradual increase in fragment ion current, so that there is no well-defined threshold. The kinetic shift effect has been studied by many scientists; the subject has been reviewed by Vestal,⁸² Cooks,⁸³ Harrison,⁸⁴ Rosenstock,⁵ Levsen⁸⁵ and Lifshitz.⁸⁶

3. Reaction Path and Reaction Competition

According to quasi-equilibrium theory, the fragmentation processes are a set of competing unimolecular reactions. The parent ion will dissociate through a number of different channels, producing different fragments. The energy dependence of the first-order rate constant may be somewhat different for the various processes, so that some fragment ions will be produced in experimentally detectable amounts only at energies somewhat in excess of the activation energy for the process. The result of reaction competition is therefore a shift, in addition to the kinetic shift, of the minimum observable decomposition rate for the less favored process to high energies. At a given excess internal energy of the parent ion, a dissociation path involving relatively high activation energy will be less favored than all lower energy decomposition channels. As a result, there is no sharp threshold, but instead a very gradual increase in the fragmentation cross section for the higher energy process. For all practical purposes this prevents the determination of precise threshold values for such processes.

D. Instrument Effects

The photoionization threshold is directly influenced by the finite

resolution of the monochromator and the finite widths of the entrance and exit slits. These instrumental effects have been discussed in the literature,³⁷ and the slit-width contribution is presented in Figure (3-9). A step function is assumed for the photoionization cross section for a single, ideal transition from the neutral to the ion. This is combined with a triangular slit function, which has been shown to be a good approximation.³⁸ Convolution of the proper integrated form of the triangle slit function with the theoretical photoionization step function leads to two parabolic curves (one normal and one inverse) connected at the inflection point, which is the true threshold position. A line drawn tangent to the inflection point in the PIE intercepts the energy axis at $\delta/2$ below the threshold (δ is the slit width in energy units). Application of this result to the threshold region of photoionization efficiency curves shows that the slit widths account for about half the breadth in the rise of the step.

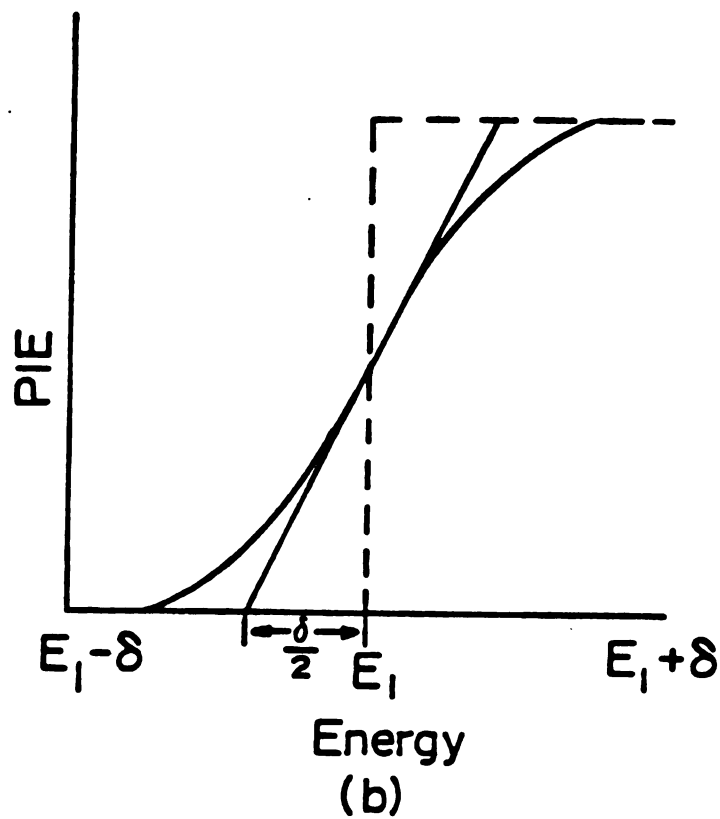
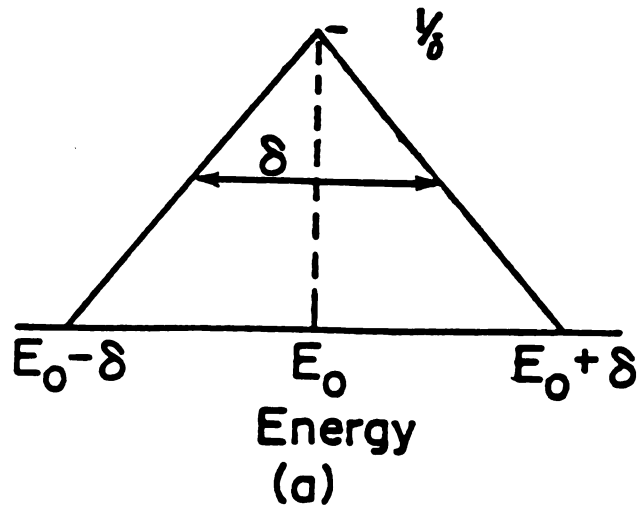


Figure 3-9. The effect of a triangular-slit function on a step function. (a) Triangular-slit function; (b) Triangular-slit function convoluted with a step function. [From D.M.Rider, Ph.D. Thesis, MSU, 1980.]

CHAPTER FOUR

EXPERIMENTAL APPARATUS AND PROCEDURES

A. Introduction

The purpose of this chapter is: (1) to present a brief description of the MSU instrument in its current operating mode; (2) to document the experimental conditions under which the data presented in next chapter were recorded; (3) to discuss experimental problems which might be encountered in the use of this complex instrument; and (4) to serve as a reference guide for future operators. The instrument has been described in detail in the experimental chapters of the Ph.D. dissertations of two previous workers--Ed Darland¹³ and David Rider⁸⁹--and a brief overview is included here to facilitate the discussion in this chapter. A diagram of the apparatus is shown in Figure 4-1. Many instrumental problems were encountered during the course of this investigation. To solve these problems one needs experience and patience. All these problems were overcome; however, some of them are likely to occur again due to the age of the instrument. It is hoped that the following description will be of help to future users of the instrument.

B. The Instrument

1. Light Source

The light source is a Hinterregger-type windowless discharge lamp with a water-cooled anode and cathode. The discharge tube is a

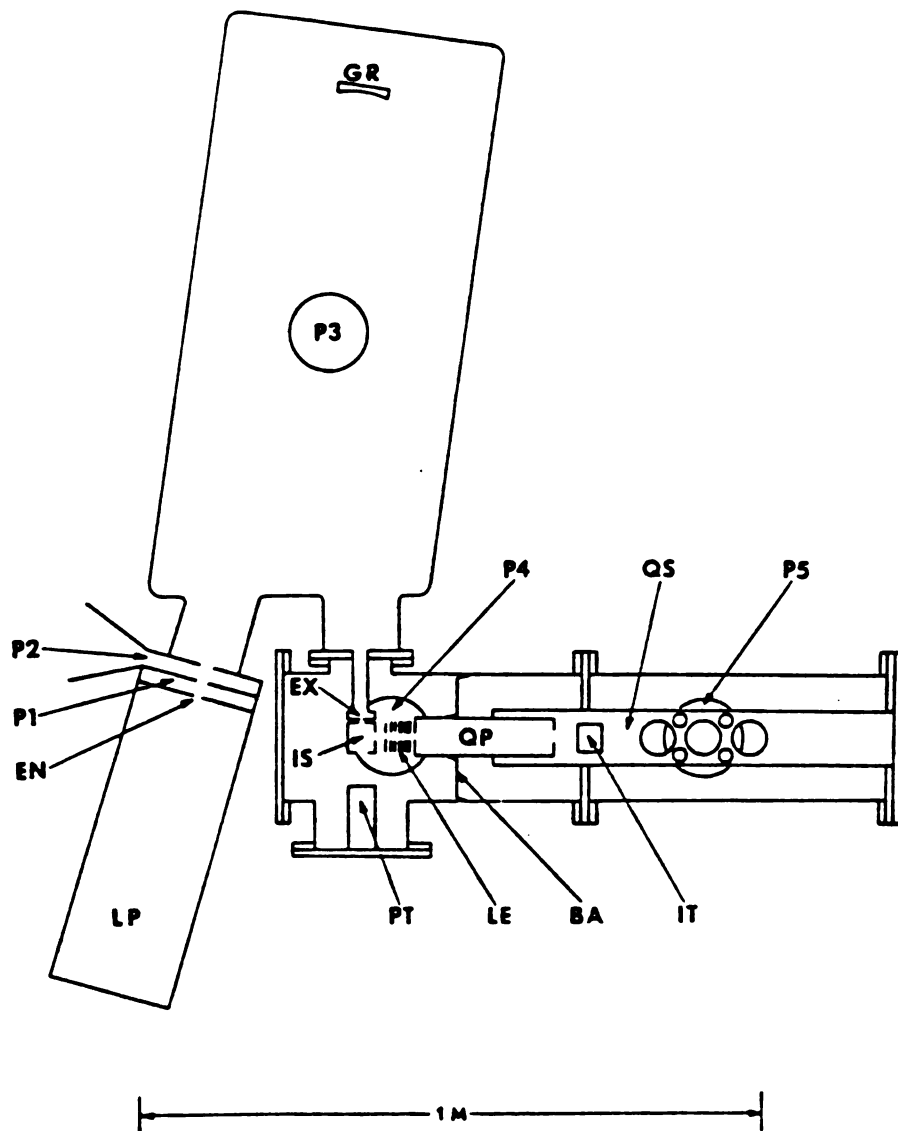


Figure 4-1. The PIMS Instrument.

- BA: baffle
- EN: entrance slit
- EX: exit slit
- GR: grating
- IS: ion source
- IT: ion transducer
- LE: ion lens
- LP: lamp
- P1: first differential pumping port
- P2: second differential pumping port
- P3: monochromator pumping port
- P4: sample chamber pumping port
- P5: quadrupole chamber pumping port
- PT: photon transducer
- QP: quadrupole rods
- QS: quadrupole support

water-jacketed quartz capillary (25 cm long x 4 mm ID) to which the discharge gas is admitted at the anode and back-pumped at the cathode. Two kinds of gas served as light sources: helium and hydrogen. The all-glass lamp gas inlet system has been designed for easy maintenance and testing, and is mounted on a metal frame located so as to minimize the chance of breakage. The purpose of the lamp gas delivery system shown schematically in Figure 4-2, is: (1) to adjust and control the lamp gas pressure; (2) to purify the commercial-grade cylinder helium, which passes through a molecular sieve trap which is immersed in liquid nitrogen, thus condensing argon, oxygen and most other impurities; (3) to adjust and maintain a small differential back-pumping pressure at the cathodic end of the lamp, which stabilizes the discharge and minimizes sputtering of the cathode onto the monochromator entrance slits.

Emission from rare gas continua is generally produced by a high-power pulsed discharge through the pure gas; in the work to be described, the Hopfield continuum of helium was employed. The lamp gas operating pressure is about 70 torr, and the discharge electronics include a home-built, single vacuum tube and high-power switching circuit to pulse the output of a high voltage d.c. power supply. The switching circuit is in turn driven by a Cober A model 605P high-power pulse generator. (For details, see references 16 and 88.) The emission from this source under the conditions listed in the caption is shown in Figure 4-3.

The intensity of the helium continuum is controlled by several variables: helium pressure and purity, pulse width and frequency, d.c. discharge voltage, Cober pulse generator peak output voltage, and the

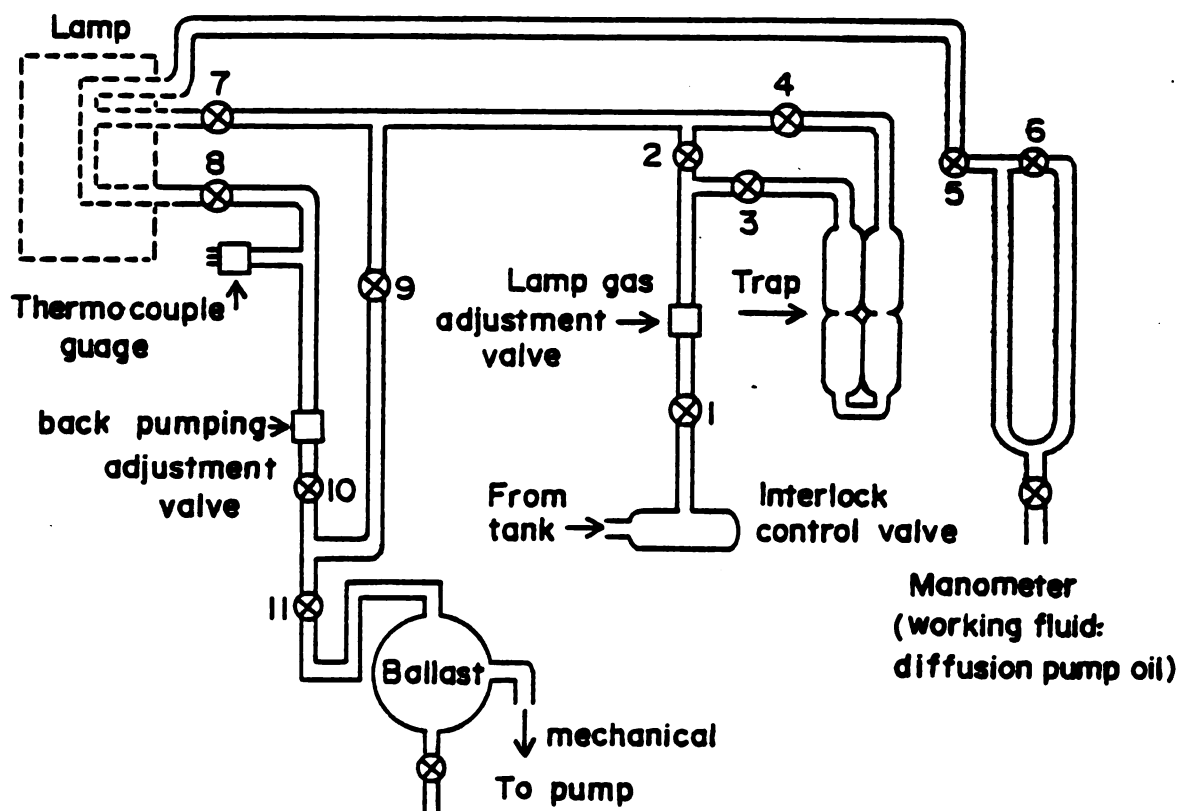


Figure 4-2.

The lamp gas delivery system.

In order to run the lamp, valves 1,5,7,8,10 and 11 must be open;

additionally:

for hydrogen, valve 2 is opened,

for helium, valves 3 and 4 are opened.

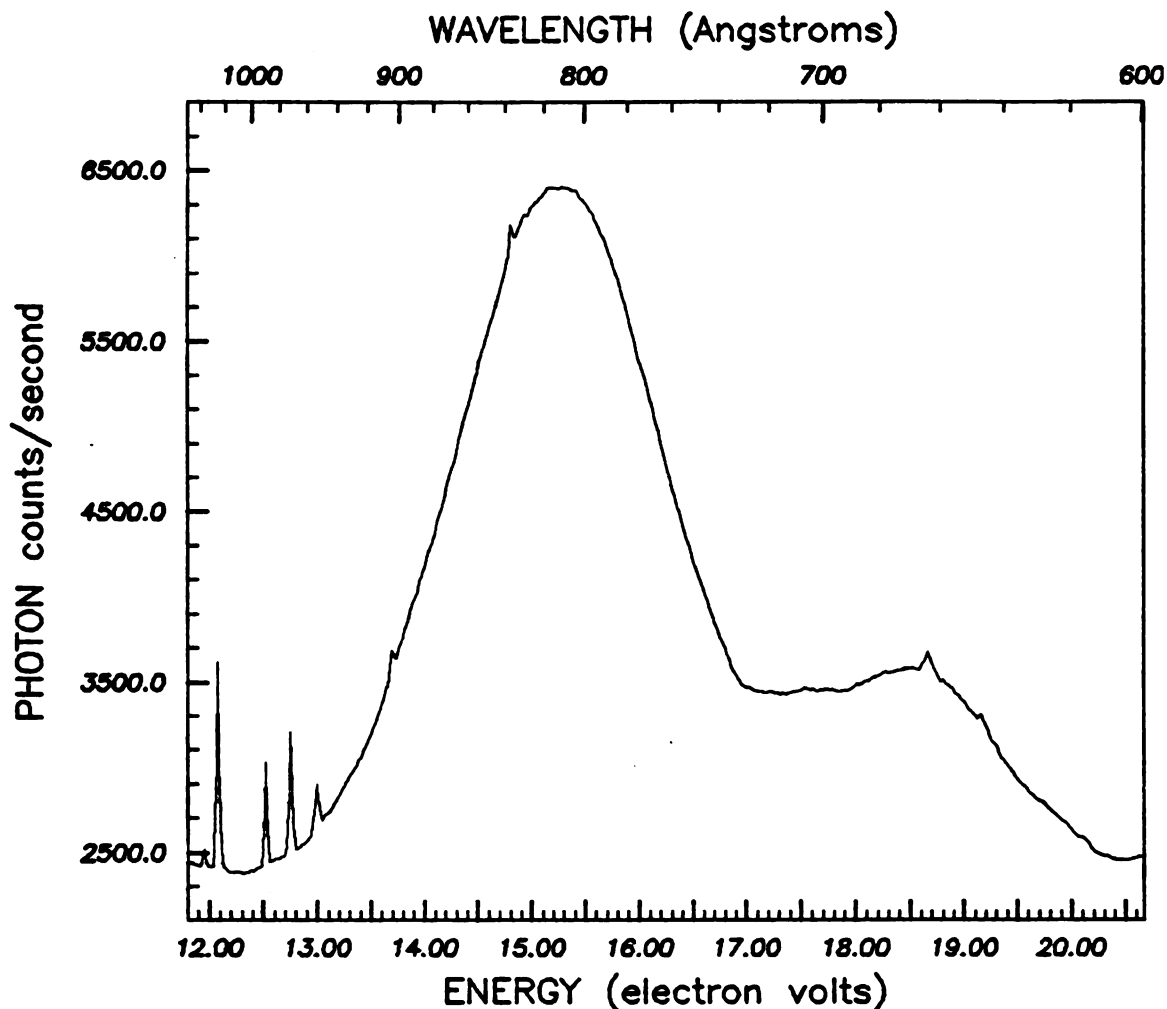


Figure 4-3. Helium continuum spectrum.

DATE: 15-SEP-82

LAMP GAS: Helium

PRESSURE: 70.0 torr

MEGAVOLT SUPPLY: 10.0kV, 100mA

PULSE VOLTAGE: 1.40kV

PULSE WIDTH: 0.50 microseconds

PULSE PERIOD: 50.0 microseconds

**MONOCHROMATOR: 600L/mm grating
100/100 micron slits**

PHOTOMULTIPLIER: 1200V

CURRENT AMPLIFIER: 1.0E-05

V-F CONVERTER: 20kHz

condition of the lamp electrodes. Higher helium pressure generally produces higher lamp output intensity. For the MSU instrument, maximum pressure is limited by the differential pumping between the lamp and monochromator and by the pumping speed of the monochromator pump. Typically, 70 torr of helium in the lamp and 100 μm entrance slits are used. The pulse frequency, pulse width and pulse voltage are adjusted by the Cober pulse generator. The capabilities of the Cober and the limitations and requirements of the switching circuit constrain these parameters. The optimal set of parameters are: a pulse width of 0.5 μs , a pulse period of 50 μs (translating to a one percent duty cycle), and a Cober high voltage setting of 1400 volts. (The Cober meter read 1400 volts, but the voltage measured was 1050 volts.) A narrower pulse width would allow a higher frequency repetition rate, which would increase the lamp intensity. However, the pulse width is limited to 0.42 μs by the turn-on time of the switching circuit. With the above settings on the Cober and 70 torr of helium, the maximum intensity is attained with the Megavolt high voltage d.c. power supply set at 10 kilovolts. Under these conditions a current of 100 to 110 mA is drawn from the Megavolt power supply when the lamp gas is pure and the lamp electrodes are clean. Increasing the voltage above 10 kilovolts increases the current drawn from the Megavolt power supply, but hardly improves the lamp intensity.

The hydrogen many-line pseudo continuum is produced by a d.c. discharge through a pressure of 2 to 4 torr. The switching circuit is disconnected in this application, and the hydrogen discharge is powered directly from the Megavolt high voltage d.c. power supply. A 1500 Ω ,

1500 W resistor limits the current drawn from the supply. The output from this light source is shown in Figure 4-4; the experimental conditions are listed in the caption.

Many of the potential problems with the lamp have been discussed in detail by David Rider,⁸⁹ and will not be repeated here. Under typical operating conditions, the molecular sieve trap will function well for about five days, or three tanks of helium; thereafter, the molecular sieve will be full and inadequate purification will result. This is revealed by checking the color of the lamp; if the original light-pink color changes to purple, the helium gas contains significant impurities. These impurities add sharp atomic lines to the helium continuum output. The aluminum cathode of the quartz high voltage discharge tube is quickly contaminated when helium is used. After continuous operation for about three months(maximum time), the intensity of the light drops if the lamp is not cleaned. The entire discharge system should be disassembled and cleaned as a part of routine maintenance. The detailed procedures (including alignment of discharge tube) can be found in the PIMS operations manual. At the same time, the Delrin insulators in the lamp housing should be carefully checked, since the high voltage discharge will corrode them quite quickly. Be sure that each insulator in this part is still usable.

The high voltage power supply, the switching circuit, the Cober pulse generator and the cathode discharge tube have been working very well for more than a year, and caused no problems during the course of this research. If a problem should arise, turn off all the power in the order specified in the operations manual (inverse of turn-on procedure).

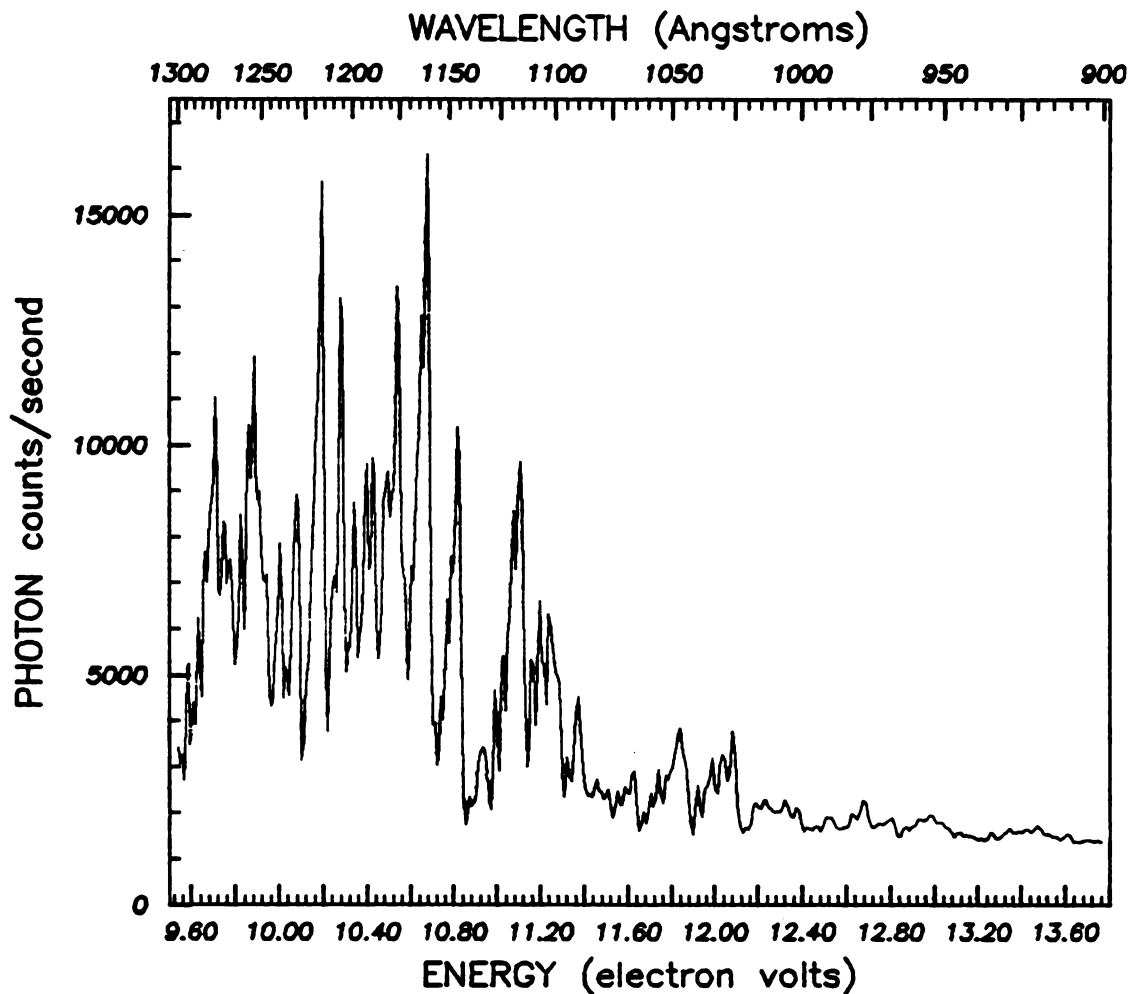


Figure 4-4. Hydrogen many line spectrum.

DATE: 25-MAY-82

LAMP GAS: Hydrogen

PRESSURE: 3.0 torr

MEGAVOLT SUPPLY: 2.75kV, 700mA

**MONOCHROMATOR: 600L/mm grating
100/100 micron slits**

PHOTOMULTIPLIER: 1200V

CURRENT AMPLIFIER: 1.0E-05

V-F CONVERTER: 20kHz

Never try to make repairs in the lamp power supply circuits by oneself, especially if one lacks experience with high voltage devices. Indeed, one should never work on the high voltage circuits alone, and it would be best if someone who is familiar with electrical hazards is present. The lamp system is not only dangerous, but also very expensive and it is not easy to obtain replacement parts. If the vital parts are damaged by improper treatment, it may take more than three months for replacements to arrive.

2. Monochromator

The monochromator is a McPherson model 225, 1-meter, near-normal-incidence instrument. The dispersing element used for this research is a concave osmium-overcoated aluminum grating, ruled with 600 lines/mm and blazed at $900\text{\AA}$. (Another grating, magnesium fluoride overcoated, ruled with 1200 lines/mm and blazed at $1200\text{\AA}$ is also available in the laboratory.) The grating has a reciprocal dispersion of $16.8\text{\AA}$ per mm.

Two interchangeable entrance slit plates are available. Each plate has a blank port plus three fixed slit widths: $10\mu\text{m}$, $50\mu\text{m}$ and $100\mu\text{m}$, or $100\mu\text{m}$, $300\mu\text{m}$, and $500\mu\text{m}$. For a given plate, the entrance slit can be changed without breaking vacuum via a knob located outside of the vacuum chamber. Interchangeable exit slit tracks are also available, each of which has four fixed slit widths: $10\mu\text{m}$, $50\mu\text{m}$, $100\mu\text{m}$ and $300\mu\text{m}$, or $100\mu\text{m}$, $300\mu\text{m}$, $500\mu\text{m}$ and $1000\mu\text{m}$. Any one of the four slits on a given track can be selected from outside the vacuum via a knob-chain-gear system.⁸⁹ The procedure for interchanging entrance and exit slit mounts

is given in the PIMS operations manual. The grating is driven by a stepping motor which can be operated manually or with a computer.

The grating should be cleaned when the helium lamp spectrum shows significant scattered light below $500\text{\AA}$. To clean the grating, first rinse with Freon 11 (CFCl_3), followed by high purity methanol. The methanol rinse is best done by simultaneously applying the methanol from a squeeze bottle and drying the grating with low pressure, clean, compressed air, working from top to bottom. The removal, cleaning, replacement, realignment and focusing procedures are listed in the McPherson monochromator manual. Because realignment of the grating requires adjustment of many parameters, a great deal of time can be saved if the grating is cleaned in situ. In this case, care should be taken to direct the cleaning solvents only on the grating (some absorbing material--such as Kimwipes--can be placed around the bottom of the grating mount), and sufficient time thereafter (about one day) should be allotted to allow vaporization of the solvents from the loosely-covered monochromator under moderate nitrogen gas flow.

3. Interaction Region and Sample Inlet System

The ion source is a cubical stainless steel box, one inch per side, located one centimeter beyond the exit slit of the monochromator. It has two rectangular apertures on opposite sides to enable transmission of the photon beam. The widths of the rectangular apertures are adjustable to allow uninhibited passage of the photon beam with any chosen exit slit. On the horizontal perpendicular to the optic axis is a one-quarter inch diameter ion exit hole. The ion aperture is

covered with a high-transmission fine wire grid to minimize penetration into the source of electric fields from the ion focusing lenses located just outside. The repeller, an electrically-insulated stainless steel plate, is positioned inside the ion source across from the ion exit aperture. An adjustable voltage is applied to the repeller to accelerate the ions from the source into an ion lens system.

The sample is admitted through a tube located behind the repeller and the sample pressure is measured through a tube in the top of the ion source. The sample pressure is controlled with a Granville-Phillips model 203 adjustable leak valve and measured with a Datametrics model 1014-A Barocell capacitance manometer. The leak valve and manometer are outside of the high vacuum.

4. Photon Transducer

The photon transducer is a sodium salicylate phosphor whose emission intensity is measured with an RCA 8850 photomultiplier tube. Because sodium salicylate possesses a nearly constant quantum yield throughout the helium continuum, and that portion of the hydrogen many line output of interest in this work, it is superior to ordinary(bare) photomultiplier dynode chains. The sodium salicylate emission intensity can be accurately measured with a standard photomultiplier and the emission band does not shift with the exciting wavelength. The output current of the photomultiplier is amplified with a Keithley 1800 current amplifier and converted to a voltage. Then it is digitized with a voltage-to-frequency converter and a computer-interfaced counter.¹³

When used with the Hopfield helium continuum, the sodium

salicylate transducer detects a great deal of scattered light. This effect is corrected by making automatically repeated measurements of the scattered light during the course of an experiment, then subtracting this contribution from the observed intensities. The scattered light problem is much less bothersome when the hydrogen lamp is used, since this source emits less visible and near ultraviolet radiation and since the many-lined spectrum does not begin until wavelengths greater than $800\text{\AA}$, which is a region where the scattered light distribution has fallen off considerably.

5. Ion Optics and Mass Spectrometer

The ions are guided from the ion source and focused onto the quadrupole mass filter with four electrostatic aperture lenses. The electrostatic lens system was supplied with the commercial mass filter, and has been modified by removal of the electron impact source. The mass filter is an Extranuclear 324-9 quadrupole mass filter, with rods 1.9 cm in diameter times 22.0 cm long. It is powered by a model 311 power supply, equipped with a model E (mass range 0-200amu) or a model 13 (mass range 0-400amu) high Q head. The quadrupole (as well as the lenses and ion transducer which are connected to it) is mounted on a support which is easily moved several inches in a direction parallel to the quadrupole axis. This permits placement of the quadrupole at an appropriate distance from the photon beam for use with single or dual chamber ion sources of various depths. The mass of the ions transmitted by the mass filter is controlled by a dial on the front panel of the quadrupole power supply or by a voltage applied to a connector on the

back side of power supply. To obtain a mass spectrum, the transmitted mass is scanned by a mass scanner which applies a voltage ramp to the connector on the back panel of quadrupole power supply; the mass scanner was designed and constructed by David Rider.⁸⁹

When the high Q head is changed or after about six months of continuous use of a given head, the mass filter needs to be "tuned up" to rematch the RF frequency of the quadrupole power supply and the high Q head. The detailed procedures are listed in the Extranuclear quadrupole filter manual.

6. Ion Transducer

The ion transducer, located on-axis at the exit hole of the quadrupole, is a Channeltron continuous-dynode electron multiplier, model CEM 4816, supplied by Galileo Electro-optics. The channeltron output is measured either in a direct-current or a pulse-counting mode. In the former mode the output is amplified with a Keithley model 417 electrometer. However, since the direct-current method has several disadvantages compared to pulse counting when the output current is small, it was used only for setting up an experiment. All data were collected with the pulse-counting technique, where the output pulses are amplified and discriminated with a circuit developed here.

7. Vacuum System

In order to maintain the required pressure differential between the lamp ($\approx 10^2$ torr) and the monochromator ($\approx 10^{-5}$ torr), two stages of differential pumping are used. The monochromator is equipped with a

McPherson model 820 differential pumping assembly, the first stage of which is pumped with a 300 liter/sec Roots blower pump. The second stage is pumped by a 300 liter/sec, four-inch diffusion ejector pump, and the monochromator with a 2400 liter/sec, six-inch diffusion pump. The sample and quadrupole chambers are also pumped with six-inch diffusion pumps, rated at 2400 liter/sec and 1800 liter/sec respectively. A baffle around the quadrupole also provides some measure of differential pumping of the sample gas in these chambers.

The pumping speeds quoted above are for untrapped pumps. All four diffusion pumps are trapped with Freon-cooled baffles to reduce the amount of oil back-streaming into the chambers; thus the actual pumping speed in the various chambers will be significantly lower. When the system was pumped down, the best pressure obtained was 2.0×10^{-7} torr. Nevertheless, these pumps are sufficient to maintain a pressure on the order of 10^{-5} torr in the monochromator with 70 torr of helium in the lamp (100 μ m entrance slits). The pressure in the quadrupole region can be maintained below 2×10^{-5} torr for a sample pressure below 2×10^{-3} torr, even with the relatively open ion source currently in use.

8. Interlock System

The vacuum and utility service systems in the PIMS instrument are quite complex. Even though each component in the system may be rather dependable, there are so many components involved that the possibility that something will fail in any given time period is quite high. Moreover, even if the individual vacuum components were completely reliable, the necessary electrical and water utilities supplied by the

university are not. Thus occasional failures of the vacuum system are inevitable. If proper procedures are not taken, the expensive components inside the vacuum chambers (the grating, channeltron, and quadrupole rods) may be irreparably damaged. All of these components are extremely sensitive to the presence of even very thin contaminating films of pump oil. Thus a security interlock system which monitors the foreline pressure of all diffusion pumps, water pressure of the diffusion pump cooling system, baffles, lamp gas pressure, electric part of the lamp and all mechanical pumps has been implemented¹³ to reduce the chance of catastrophic damage to the PIMS apparatus.

The interlock system for this instrument was designed as a "stand-alone" system which is not computer operated; it can thus be used to protect the instrument between experiments as well as during them, allowing the instrument to remain safely under full vacuum conditions at all times. Even so, the interlock system is not sufficiently sophisticated to totally automate the pump down procedure. However, it does mandate the correct sequence of operations during start-up, which greatly reduces operator's errors--although it cannot eliminate them. When used to protect the unattended instrument, the action taken by the safety interlock system when an error condition is detected is very simple: any device which, if left on, could conceivably be harmed or cause harm to another device is deactivated. The vacuum system then remains shut down until an operator decides that it is safe to start again.

9. Instrument Control and Data Acquisition

The computer used to control the PIMS instrument during the course of this research was an antiquated PDP 8/I minicomputer, which uses a 12-bit word length and has 12K of memory. After this investigation was completed, 8K of the memory was inexplicably damaged and required repair. The PDP 8/I was then scrapped, and the PIMS instrument is now controlled by a surplus PDP 8/F minicomputer (still 12-bit word length), which has 16K of memory. A PDP 8/M (12-bit word length, 12K memory) is also available for PIMS experiments. Data and program storage peripherals include a dual floppy disc drive (Sykes 7200 series) and an interchangeable hard disc (WANGCO F-1221). Interaction between the user and the computer takes place via a Heath Z-19 terminal or a Tektronix 4010 graphics display terminal.

The data are collected by using a variable integration time technique which permits recording data of the desired quality in an optimum amount of time. The monochromator wavelength is stepped in preset intervals, and, after each step, ion and photon counts are accumulated until the datum has the desired signal-to-noise ratio. Photon and ion count rates, wavelengths and integration times are stored on a floppy or hard disc. The course of the experiment is continuously monitored via a computer-interfaced, stepped, stripchart recorder on which the real time PIE is plotted. Periodic measurements of "light" and "dark" photon and ion count rates are made at a reference wavelength so that the data can be corrected for sample pressure and instrument drift. Approximate corrections for stray light are made by measuring the light intensity at two wavelengths where the helium continuum does not emit. Final corrections of the data for sample pressure variations,

instrument drift and stray light, as well as the final plot, are discussed in the procedure section of this chapter.

C. Experimental Procedure

This section presents a flow chart to show how to run a photoionization mass spectrometry experiment. The difference between this section and the operations manual is that this discussion indicates when and why to do each procedure, whereas the operations manual describes how to do it.

The experimental procedure introduced will follow the order of an experiment. Sometimes several steps may be started at the same time; higher priority steps will be listed first. To continue an aborted run, or to start a new experiment upon termination of another, the entire sequence may not have to be repeated. Under these circumstances, just skip unnecessary steps and continue to the next one. Finally, the procedure described here contains just the main concepts; for the detailed step-by-step procedures one must consult the operations manual.

1. Samples

The gas samples: CF_4 , CF_3Cl , CF_3Br , CF_3I , CF_2Cl_2 , CHF_3 , CHF_2Cl , CHFCl_2 , CF_2Br_2 , and CF_2ClBr were all purchased from PCR Research Inc. They were used without further purification; a pressure regulator and gauge was attached to the commercial cylinder, and then directly connected to the ion source leak valve via a Cajon O-ring fitting through 1/4-inch O.D. polyflow tubing.

The liquid samples: CHCl_3 and CCl_4 , were obtained from Fisher

Scientific, CFCI_3 , from PCR Research, and CCl_3Br from Eastman Kodak. All liquid sample purities were reported by the manufacturer to be better than 99.9%. Each liquid sample was placed in a pyrex bulb, degassed through several freeze-pump-thaw cycles, stored under liquid nitrogen, and later used without further purification. The samples in the pyrex bulbs (at room temperature) were connected to the leak valve via a Cajon O-ring fitting through 1/4-inch outside diameter glass tubing. The temperature of the room in which the instrument is located varies by as much as 2.5°C during the course of an experiment. The data were collected with sample pressures between 6.0 to 10.0×10^{-4} torr; for a given sample, the pressure varied by less than 10% throughout an experiment.

2. System Pump-Down

If the PIMS instrument is completely shut down, the following procedure is required. Two parts of the overall system must be initially pumped down, the main part of the system (monochromator, sample and quadrupole chambers) and the lamp gas system. In the main part of the system, after all the diffusion pumps have been turned on and all the gate valves have been opened, the system pressure should be lower than 1.0×10^{-5} torr. Normally it is easy to reach 2.0×10^{-6} torr with a proper degas; sometimes the pressure can be as low as 2.0×10^{-7} torr. After the main chambers have been pumped down, the sample gas line should be evacuated. The purposes of doing this are: (1) to pump out the air in the sample gas line, (2) to remove any residue of previous gas samples, and thus avoid contamination of the sample; and

(3) to check for leaks in the sample gas line connection. Any leak in the sample gas line will allow air to enter the system, which will change the sample gas purity and lead to extra peaks in the mass spectrum. The lamp gas system is pumped by a mechanical pump only. This part of the system must be absolutely leakproof; this is tested by closing the valve between the line and the mechanical pump, and monitoring the pressure change via a thermocouple gauge. If the rate of pressure increase is less than 1.0×10^{-2} torr/min, the lamp gas system is considered sufficiently leakproof. Any leaks in the lamp gas system will contaminate the lamp gas, and produce dirty lamp spectra, including many sharp atomic lines. A dirty lamp gas system (especially when the helium discharge is used) will make data correction harder. The molecular sieve trap in the lamp gas system has to be cleaned periodically when helium gas is used. To clean the sieve, heat the heating tape around it up to 200–210°C and continue pumping until the pressure of whole system returns to normal.

3. Lamp Spectra

The main purpose of running a lamp spectrum is to check the lamp system quality. Are the emission intensities as expected, and do the wavelength settings in the computer coincide exactly with several calibration lines? From a lamp spectrum, one can determine the condition of the lamp, the calibration of the monochromator and the purity of the lamp gas. Different observed phenomena infer different kinds of problems. A lamp spectrum provides not only the information mentioned above, but also information about the optimum voltage setting

of photomultiplier, the scale of the amplifier, the photon signal, etc., which are parameters to be set before an experiment is initiated. The lamp spectrum can be generated with the grating rotation either under manual or computer control.

4. Mass Spectra

Before photoionization efficiency curves from a given precursor can be obtained, the mass spectrum of the sample gas must be acquired on the PIMS instrument. Photoionization of the sample is accomplished under full illumination of the helium light source. To obtain the mass spectrum, set the monochromator to the "central image", i.e. zero Ångstroms, which is offset by $\approx 100\text{Å}$ on the wavelength counter, whereby all of the light from source is reflected from the grating into the reaction region. If the entrance and exit slits are opened to their widest position, maximum photon intensity from the light source impinges on the sample gas. The mass spectrum serves several purposes: (1) It provides a test of the sample gas purity. Because most standard mass spectra are obtained under bombardment of 70eV electrons, one must be careful when comparing PI and EI mass spectra. Although there was generally good agreement between the mass spectra obtained in this work and those tabulated in the literature, the expected variation in the relative intensities of the peaks (both parent and fragment ion) was observed, and highly fragmented daughter ions produced at high ionization energies were sometimes missing from the PI mass spectra. If the photoionization mass spectrum shows several extra peaks compared to the standard mass spectrum, it is probable that the sample gas may be

contaminated by some impurity, or that the sample gas inlet line has a leak. (2) One can easily determine how many ions can be produced from this sample gas by the light source. In principle, a PIE curve is obtainable for every ion revealed by a peak in the mass spectrum; the intensity of each peak gives a good idea about how difficult it will be to do that experiment. (3) It is convenient to change the conditions to start the next procedure. Simply change the entrance and exit slits to the desired positions. For a given photon energy range, the lamp gas (helium or hydrogen) can be maintained while PIEs are measured for several different ions from a single sample gas.

5. Experimental Set-Up

After the mass spectrum has been obtained, the next step is the choice of an ion for which the photoionization efficiency curve is to be measured. After a particular ion is chosen, the mass filter is set to the corresponding mass region, and the ion optics are adjusted to maximize the ion intensity. Scan the mass in the appropriate region to confirm that the transmitted ion is indeed the one selected; this is facilitated if the ion of interest contains atoms which have characteristic relative isotopic abundance patterns. Sometimes improper adjustment of the ion optics will still allow ions to pass through the mass filter, but the isotopic ratios will not be correct. Once the desired ion is properly identified, reduce the resolution to broaden the peak and thus increase the ion signal. (However the resolution must not be lowered so far that ions of different m/z are transmitted.) Find a relatively smooth portion of the broadened mass spectrum and lock the

mass filter at this m/e value. Then small drifts in the quadrupole tuning during the course of long experiments will not affect the photoionization efficiency. All these procedures above can be done either by the computer or manually. Hereafter, all the procedures will be done under computer control.

Many parameters must be considered when setting up a photoionization mass spectrometry experiment; these parameters have a great influence on the resulting photoionization efficiency curve. It is necessary to do a quick experiment (or perhaps several) to help decide how to choose these parameters. From the quick run, one can draw conclusions about the following aspects of the final experimental photoionization efficiency curve: (1) the desired signal-to-noise ratio (consistent with time constraints); (2) the duration of the experiment; (3) the energy region which is to be scanned; (4) the wavelength to be chosen for the reference measurement; (5) the desired wavelength resolution; (6) the wavelength interval between successive data points, and (7) the sample pressure. For the actual experiment one also needs to decide: (1) how frequently and for how long to measure the background and reference signals, and (2) where and for how long to measure the stray light. After all these parameters are determined, one can start an experiment.

6. Data Correction

Once an experiment is set up, data collection and storage are controlled with a PDP 8/M or PDP 8/F minicomputer. The periodic reference measurement is made to correct for sample pressure variation

and instrument drift. A shutter is closed in front of the monochromator exit slit under computer control so that periodic background measurements can be made. Dark counts generated in the detectors are also stored and will be subtracted from the ion and photon signals, which are obtained when the shutter is open, in the later procedures. The stray light measurement is made to correct for the stray light contribution to the photon data. After these three corrections, which are made at the department computer facility (PDP 11/34), a comparison of the ion signal with the photon signal is made to ascertain whether corrections are necessary for artifacts caused by the finite slit width, scattered light, or detector misalignment. (For more detailed information on these points, see reference.¹³) After all of these corrections are made, the final photoionization efficiency curve is plotted out and the experiment is complete.

CHAPTER FIVE

RESULTS AND DISCUSSION

A. Results

In this section, all of the data obtained in this investigation of fourteen halomethanes will be presented. For each compound, a figure showing the mass spectrum and a table listing the relative intensity assignments will be given first. This is followed by a figure depicting all of the PIE curves measured from the neutral precursor, plotted together, and then a summary table of all IP, AP and heat of formation values corresponding to each ion. A brief summary is provided for each ion, including a plot of the individual PIE and a description of any unusual features, plus a statement of the reaction equation upon which the heat of formation calculation was based.

The ionization potential of a parent ion is obtained by fitting (the fit program is called KINFIT4, which is developed by the MSU Chemistry Department) the threshold region of the PIE curve with an error function,⁸⁹ which represents the Gaussian distribution of instrumental and equilibrium rotational contributions to the ion signal. A precise value for the adiabatic ionization energy is obtained from the inflection point of the error function, which corresponds to the peak of the Gaussian distribution.

Since many factors influence the threshold region of fragment PIE curves, there is no single suitable fitting function. Each fragment ion PIE curve is first smoothed for easier and more accurate extrapolation.

and then a straight line is drawn from the higher energy part of the threshold down to the base line. The smooth program, written by P.Hoffman and P.Aiello of the MSU Chemistry Department, employs a modified Savitsky-Golay algorithm where the data points in a selected sliding window are fit to a linear equation. The energy at which the extrapolated line intersects the base line, plus the equipartition value of the rotational energy, is chosen as the appearance potential. An example is shown in Figure 5-A-1. In the remainder of this thesis, energy in eV are converted to kcal/mole, the conversion factor $23.06 \text{ kcalmole}^{-1}/\text{eV}$ was used.

The origin of a particular ion at threshold must be carefully considered. It might be from an impurity, a sequential series of reactions, or one of several alternative decomposition channels from the parent ion which involve different neutral fragments. As noted in chapter four, it is unlikely that impurities contribute. Mass spectra obtained under both photoionization and electron impact conditions revealed no detectable impurity in any of the samples. Moreover, except for the parent ion and the dihalogen cations, none of the neutral precursors are stable molecules. Impurities having the same mass as the parent ion are hard to imagine, and there are no geometrical isomers for the halomethanes. The threshold region of each parent ion PIE is sharp and shows no step structure; thus there is no evidence of contribution from impurities. PIE curves of BrCl^+ and IF^+ were measured; the precursors are clearly not neutral dihalogen impurities, since the experimental appearance potentials are much higher than the reported ionization potentials. For a given threshold, the assignment of the

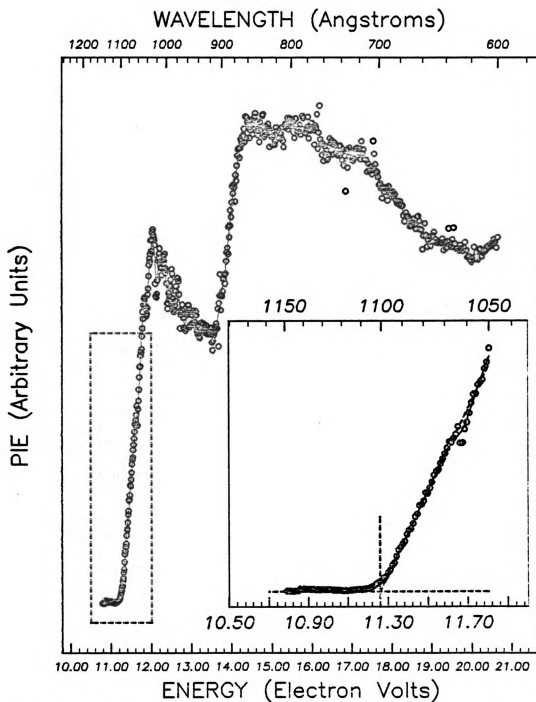


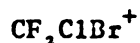
Figure 5-A-1. PIE of CF_2Cl^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points. The inset shows the extrapolation method used to obtain the appearance potential.

appropriate decomposition reaction was made by considering all likely fragmentation pathways, and calculating the fragment ion heat of formation from each reaction equation. The possible contribution of sequential reactions involving first fragmentation into neutral species followed by ionization of one fragment is rather unlikely under PIMS experimental conditions, and was similarly evaluated. Comparison of the calculated heat of formation values for the fragment ion to those given in thermochemical compendia or the chemical literature helped determine the best choice for the dissociation mechanism. The procedure is illustrated in Figure 5-A-2 for the photofragmentation of CF_4 to give $\text{CF}_3^+ + \text{F} + \text{e}^-$ and for its decomposition to give CF_2^+ and alternative neutrals.

For each PIE curve measured, the corresponding reaction equation, and the fragment ion heat of formation calculated from the experimental appearance potential and tabulated heats of formation of the neutrals involved, is given in subsection 1-14 below. The heat of formation values of the neutrals which were employed in the ion heat of formation calculations are listed in Table 5-A-1.

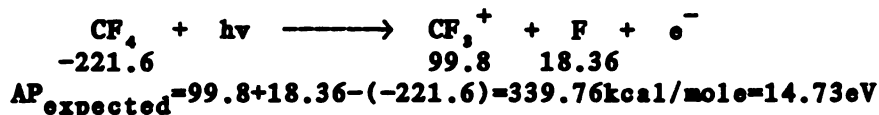
1. CF_2ClBr

The photoionization mass spectrum of CF_2ClBr , obtained under full illumination of the helium continuum, is shown in Figure 5A-1-1. Relative intensities of the peaks and their assignments are presented in Table 5A-1-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-1-2, and the summary of thermochemical information for these ions is given in Table 5A-1-2.

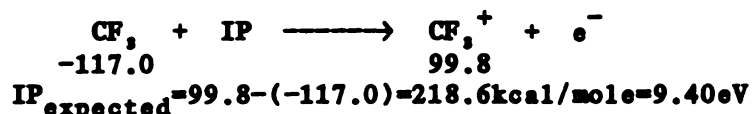
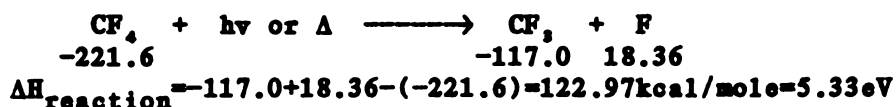


I. Possible pathways by which CF_3^+ can be formed from CF_4 .

A. C-F bond breakage:



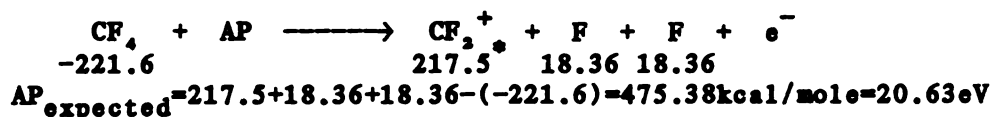
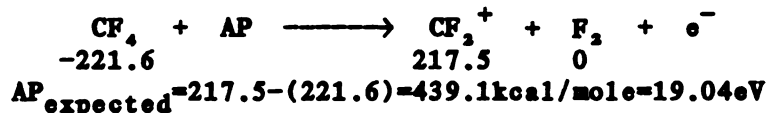
B. Consider a two-step process:



No CF_3^+ is detected in the 9.40eV range. Direct ionization/fragmentation is the correct reaction.

II. Different pathways for producing CF_3^+ .

A. Fragmentation to form two F atoms:

B. Fragmentation to form one F_2 molecule:

* "Best" previous literature value: H.W. Jochims, W. Lohr and H. Baumgärtel, Ber. Bunsenges. Phys. Chem. 80, 130 (1976).

The excess energy of 1.4 eV accompanying F_2 formation is unlikely and unprecedented;; with the "best" $\Delta H_{f0}^\circ(\text{CF}_3^+) = 204.36 \text{ kcal/mole}$ from this work that value would be about 2 eV. The decomposition reaction which yields two fluorine atoms is correct; it involves kinetic energy release of about 0.4 eV.

Figure 5-A-2. Thermochemical procedure for determining reaction equations appropriate to experimental appearance thresholds. Example: CF_3^+
(Heats of formation in kcal/mole from Table 5-A-1.)

Table 5-A-1. Standard enthalpies of formation (0°K , kcal/mole) utilized in thermochemical calculations of ΔH_{f0}° of fragment ions [From JANAF thermochemical tables, unless otherwise noted.]

CF_3ClBr	-107.66^a	CF_3	-117.00 ± 1.0
CF_4	-221.61 ± 0.3	CF_3^+	99.80 ± 2.8
CF_3Cl	-168.00 ± 0.8	CF_2	-43.60 ± 1.5
CF_3Br	-152.20 ± 0.7	CF_2^+	223.50
CF_3I	-139.40 ± 0.8	CCl_3	19.15 ± 2.0
CF_3Cl_2	-116.50 ± 2.0	CCl_3^+	56.70 ± 5.0
CFCI_3	-68.24 ± 1.5	F	18.36 ± 0.4
CCl_4	-22.42 ± 0.5	Cl	28.52 ± 0.0
CCl_3Br	-11.00^b	Br	28.19 ± 0.1
CF_3Br_2	-96.89^a	I	25.63 ± 0.1
CHF_3	-164.90 ± 0.8	BrCl	5.28 ± 0.3
CHF_2Cl	-113.60 ± 3.0	IF	-22.19 ± 0.9
CHFCI_2	-66.36 ± 3.0		
CHCl_3	-23.49 ± 0.3		

^a value from G.Kauschka and L.Kolditz, Z. Chem. 10, 377 (1976)

^b value from J.L.Franklin, J.G.Dillard, H.M.Rosenstock, J.T.Herron and K.Draxl, Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS 26 (1979).

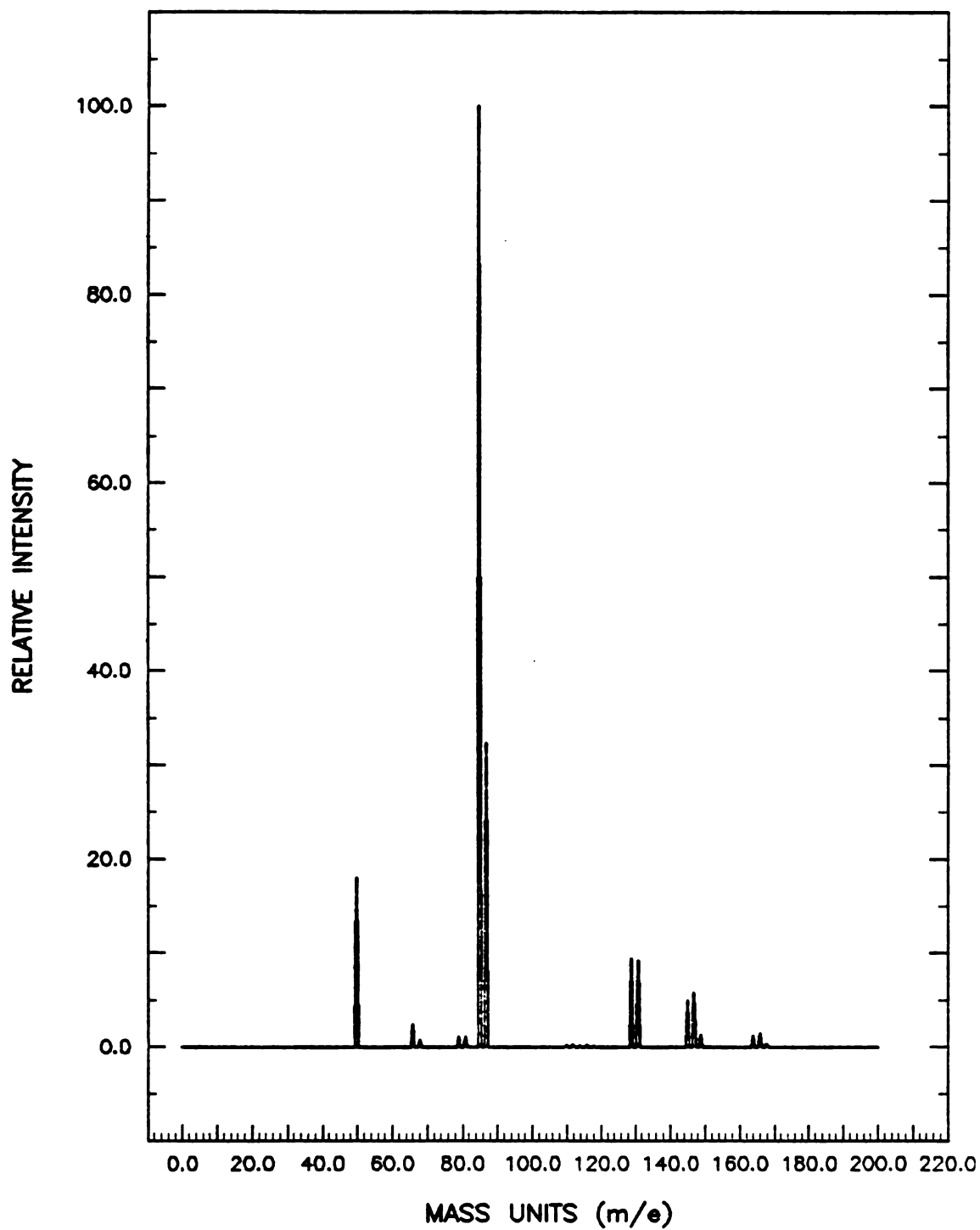


Figure 5A-1-1. Photoionization Mass Spectrum of CF_2ClBr (obtained under full illumination of the helium discharge).

Table 5A-1-1. Photoionization Mass Spectrum of CF_2ClBr^a

m/e	Intensity Relative to CF_2Cl^+	Percent of Total Ion Production	Probable Formula
50	18.0	9.47	CF_2^+
66	2.4	1.28	$\text{CF}^{35}\text{Cl}^+$
68	0.7	0.38	$\text{CF}^{37}\text{Cl}^+$
79	1.2	0.60	$^{79}\text{Br}^+$
81	1.1	0.56	$^{81}\text{Br}^+$
85	100.0	52.60	$\text{CF}_2^{35}\text{Cl}^+$
87	32.3	16.98	$\text{CF}_2^{37}\text{Cl}^+$
110	0.2	0.12	$\text{CF}^{79}\text{Br}^+$
112	0.2	0.11	$\text{CF}^{81}\text{Br}^+$
114	0.2	0.09	$^{35}\text{Cl}^{79}\text{Br}^+$
116	0.2	0.12	$^{35}\text{Cl}^{81}\text{Br}^+, ^{37}\text{Cl}^{79}\text{Br}^+$
118	0.1	0.03	$^{37}\text{Cl}^{81}\text{Br}^+$
129	9.5	4.97	$\text{CF}_2^{79}\text{Br}^+$
131	9.2	4.81	$\text{CF}_2^{81}\text{Br}^+$
145	5.0	2.63	$\text{CF}^{35}\text{Cl}^{79}\text{Br}^+$
147	5.7	3.00	$\text{CF}^{35}\text{Cl}^{81}\text{Br}^+, \text{CF}^{37}\text{Cl}^{79}\text{Br}^+$
149	1.3	0.68	$\text{CF}^{37}\text{Cl}^{81}\text{Br}^+$
164	1.2	0.62	$\text{CF}_2^{35}\text{Cl}^{79}\text{Br}^+$
166	1.5	0.76	$\text{CF}_2^{35}\text{Cl}^{81}\text{Br}^+, \text{CF}_2^{37}\text{Cl}^{79}\text{Br}^+$
168	0.4	0.19	$\text{CF}_2^{37}\text{Cl}^{81}\text{Br}^+$

^aObtained under full illumination of the helium discharge.

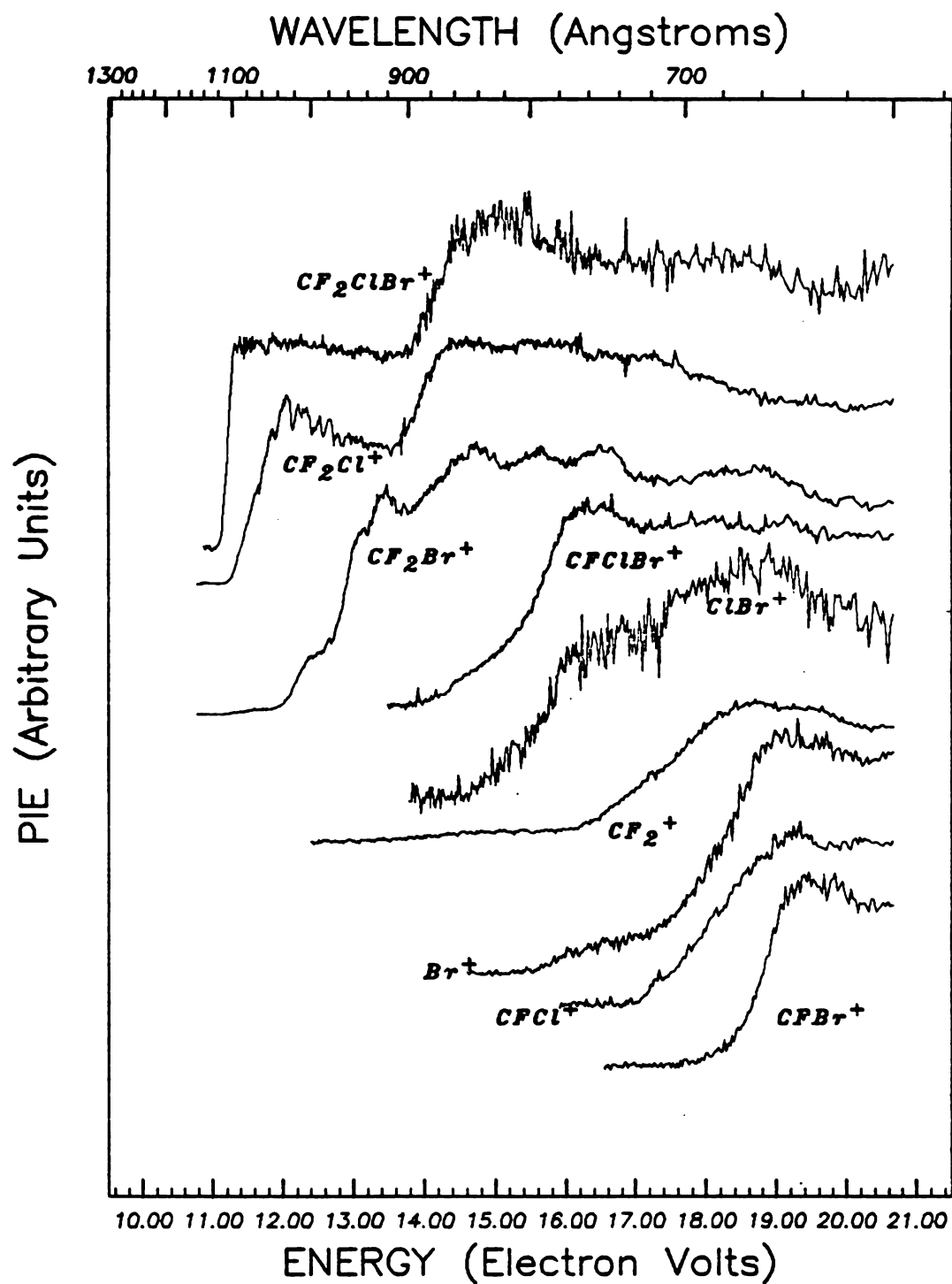


Figure 5A-1-2. Photoionization efficiency curves for parent and daughter ions from CF_2ClBr .

Table 5A-1-2. Summary of IP, AP and Heat of formation data for all ions from CF_2ClBr .

ION	IP or AP (eV) ^a	Products of $\text{CF}_2\text{ClBr} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_2ClBr^+	11.21	$\text{CF}_2\text{ClBr}^+ + e^-$	150.84
CF_2Cl^+	11.30	$\text{CF}_2\text{Cl}^+ + \text{Br} + e^-$	124.73
CF_2Br^+	12.00	$\text{CF}_2\text{Br}^+ + \text{Cl} + e^-$	140.54
CFCIBr^+	14.15	$\text{CFCIBr}^+ + \text{F} + e^-$	200.28
CF_2^+	15.99	$\text{CF}_2^+ + \text{Cl} + \text{Br} + e^-$	204.36
CFCl^+	17.02	$\text{CFCl}^+ + \text{F} + \text{Br} + e^-$	237.93
CFBr^+	17.80	$\text{CFBr}^+ + \text{F} + \text{Cl} + e^-$	255.93
BrCl^+	14.63	$\text{ClBr}^+ + \text{CF}_2 + e^-$	273.31
Br^+	15.45	$\text{Br}^+ + \text{CF}_2\text{Cl} + e^-$	321.80

^asee text for uncertainties.

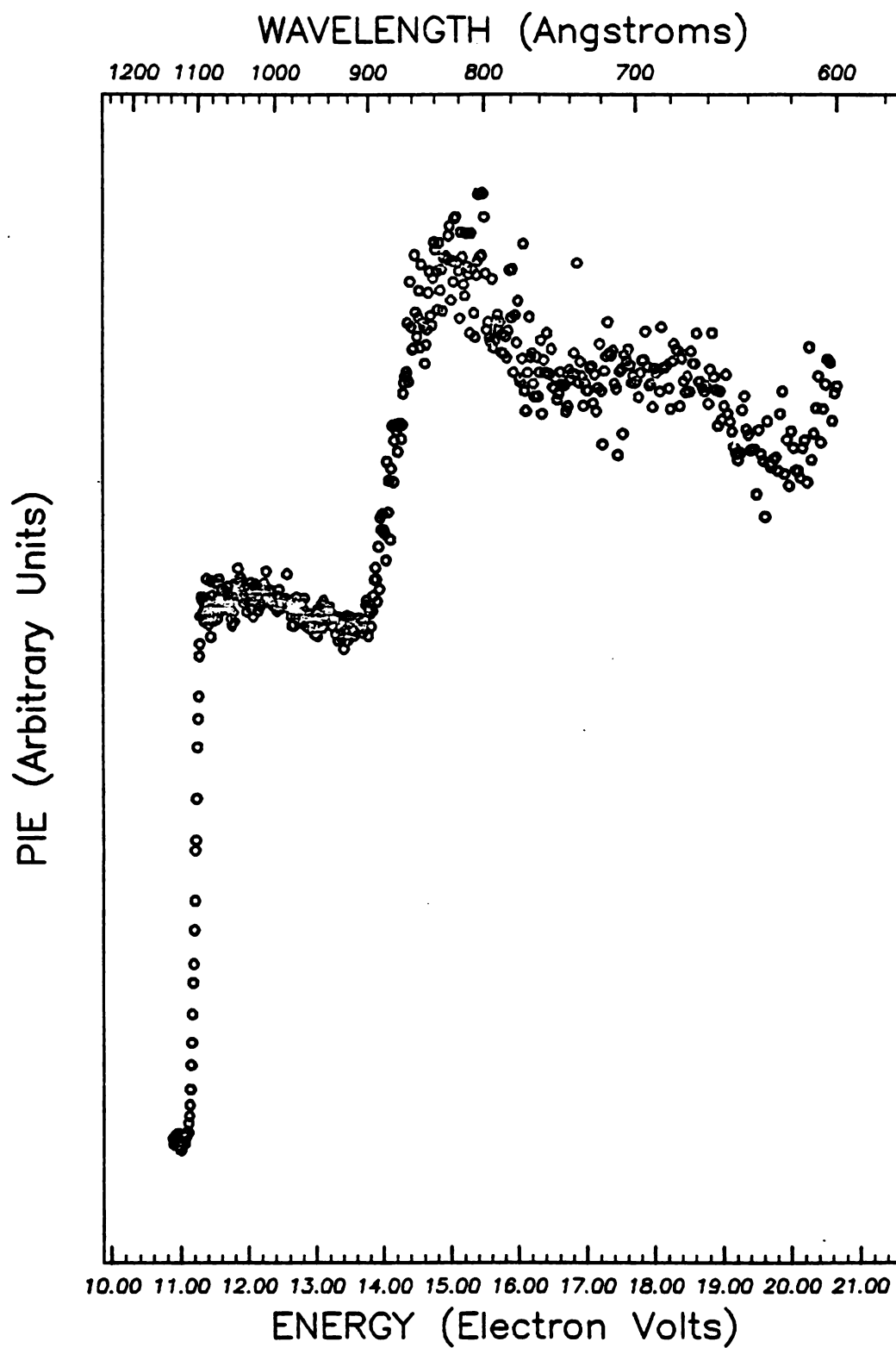


Figure 5A-1-3. PIE of CF_2ClBr^+ from CF_2ClBr .

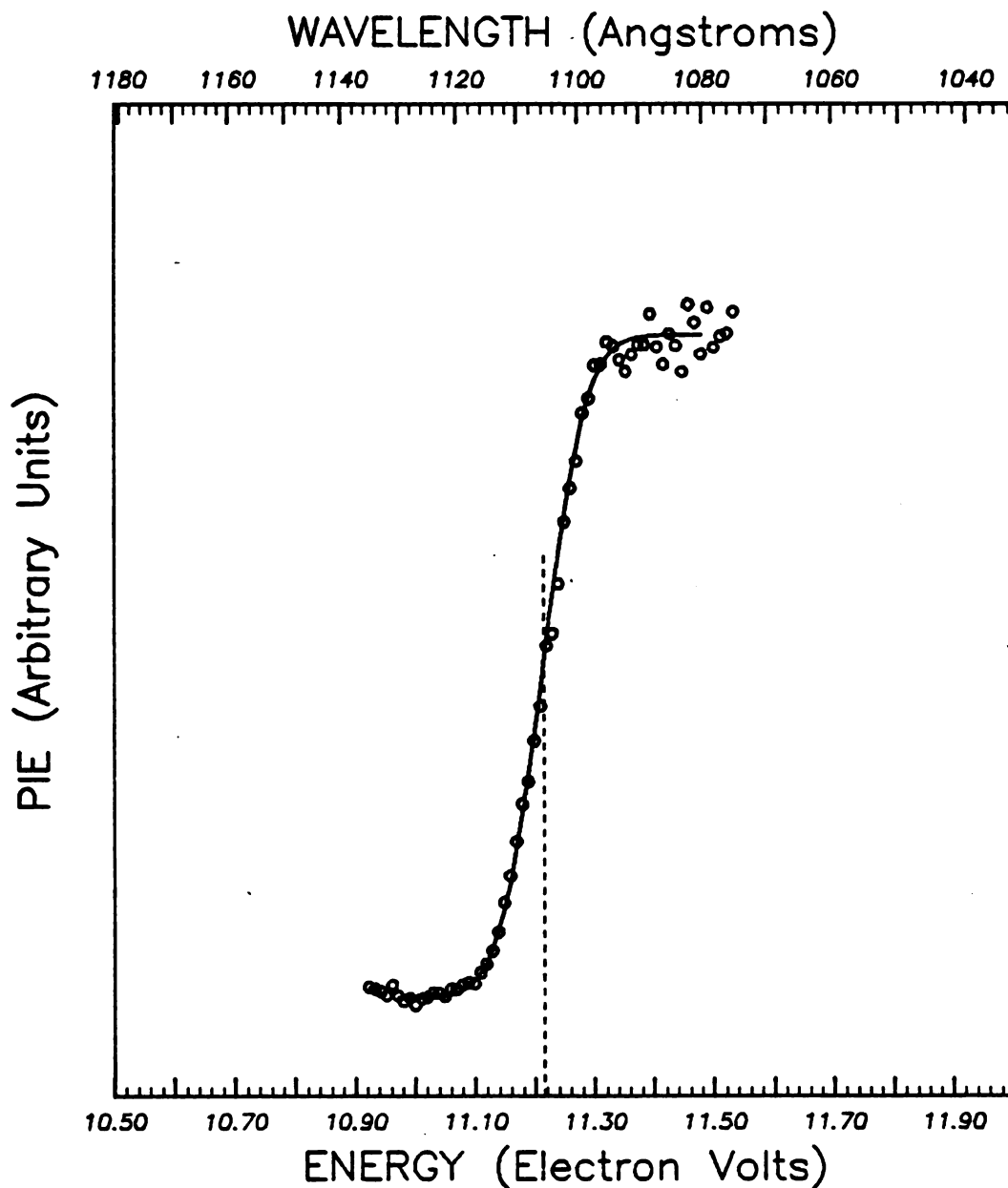
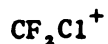


Figure 5A-1-4. PIE of CF_2ClBr^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

The parent ion PIE is shown in Figure 5A-1-3, where it may be seen that the threshold starts to rise at about 11.10eV. Figure 5A-1-4 shows the fit of the error function to the threshold region. In the post-threshold region, the PIE curve shows a relatively flat region, about 3eV wide; presumably other fragmentation channels compete with direct ionization in this energy range. After this region, the PIE curve rises up again, showing a second threshold. Based on the photoelectron spectrum,⁹⁰ this threshold corresponds to a transition in which the parent ion is raised to an excited electronic state. The adiabatic IP of the parent ion is 11.21 ± 0.02 eV, which is slightly lower than and in reasonable agreement with previous literature values: 11.33 eV³⁴ and 11.51 eV.⁹⁰ From the reaction equation:



the value of $\Delta E_{f0}^0(\text{CF}_2\text{ClBr}^+)$ is calculated to be 150.84 ± 1.5 kcal/mole.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-1-5. The PIE starts to rise sharply at threshold (near 11.20eV), and in the post-threshold region it shows a series of peak-like features, which are suspected to be autoionization structure. As for the parent ion, at an energy of about 14.0eV the CF_2Cl^+ PIE shows a second threshold, corresponding to fragmentation of the parent ion in an excited electronic state. The AP value of this fragment ion is 11.30 ± 0.04 eV; no previous literature value is available for comparison. From the reaction equation:

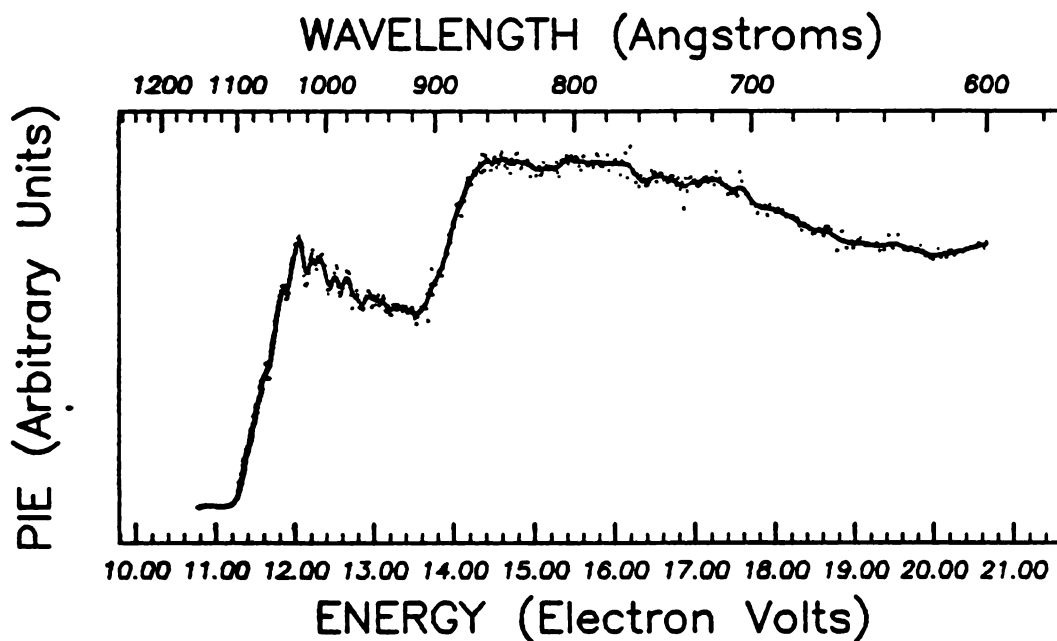


Figure 5A-1-5. PIE of CF_2Cl^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

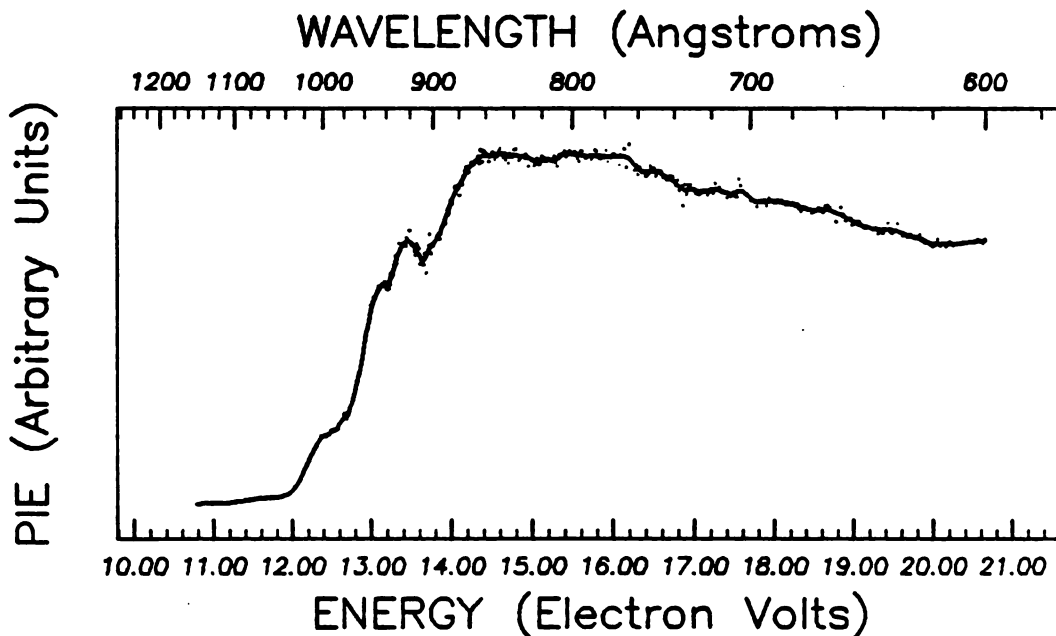
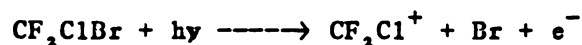


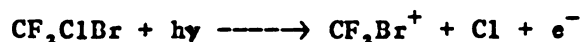
Figure 5A-1-6. PIE of CF_2Br^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Cl}^+)$ is calculated to be $124.73 \pm 2.0 \text{ kcal/mole}$.



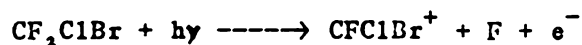
The second fragment ion is CF_2Br^+ , for which the PIE is shown in Figure 5A-1-6. The PIE shows a relatively sharp threshold at around 12eV, and again another threshold is observed near 14eV. The AP value of this fragment ion is $12.00 \pm 0.04 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+)$ is calculated to be $140.54 \pm 2.0 \text{ kcal/mole}$.



This fragment corresponds to breaking the C-F bond in the parent ion. The PIE curve is shown in Figure 5A-1-7. Since the C-F bond is strong, a great deal of energy must be deposited in the parent ion, and the fragment ion PIE exhibits a slow increase above threshold. The AP value is $14.15 \pm 0.07 \text{ eV}$. By using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFC1Br}^+)$ is calculated to be $200.28 \pm 3.0 \text{ kcal/mole}$.



The PIE curve for CF_2^+ is shown in Figure 5A-1-8. Now two bonds are broken, and the onset of the threshold is not so sharp as those for

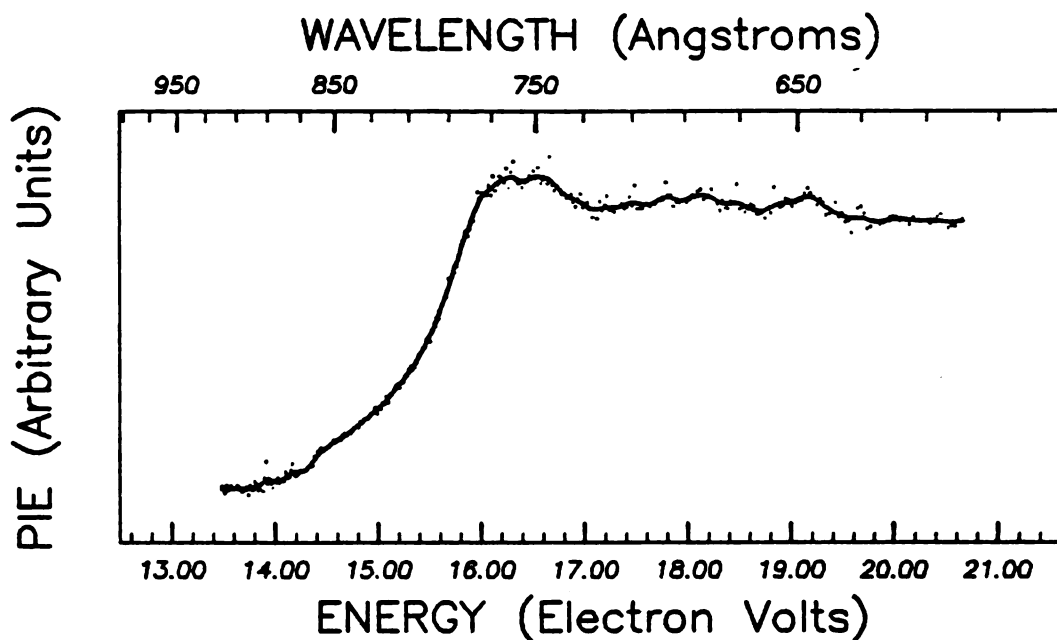


Figure 5A-1-7. PIE of CFC1Br^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

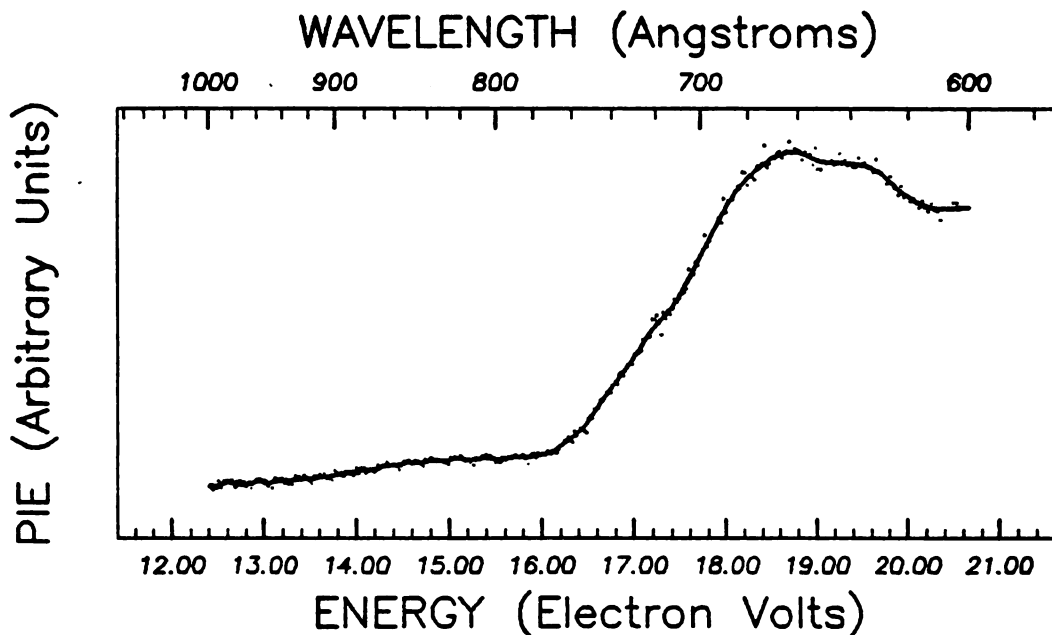
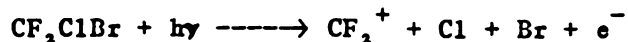


Figure 5A-1-8. PIE of CF_2^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

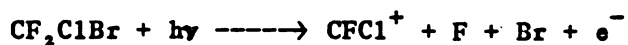
fragment ions where only one bond is broken. The AP value is $15.99 \pm 0.07 \text{ eV}$, and according to the equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2^+)$ is calculated to be $204.36 \pm 2.7 \text{ kcal/mole}$.



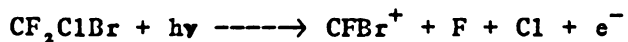
This fragment results when the C-Br and one C-F bond in the parent ion are broken. The PIE curve, reproduced in Figure 5A-1-9, shows a smoothly-rising threshold which leads to an AP value of $17.02 \pm 0.1 \text{ eV}$. According to the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFCl}^+)$ is calculated to be $237.93 \pm 3.9 \text{ kcal/mole}$.



Rupture of the C-Cl bond and one C-F bond in the parent ion requires slightly higher energy than the previous fragmentation reaction. The PIE curve of CFBr^+ is shown in Figure 5A-1-10; the AP value is $17.80 \pm 0.1 \text{ eV}$. From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFBr}^+)$ is calculated to be $255.93 \pm 3.8 \text{ kcal/mole}$.



This fragment results not from simple bond cleavage, but via a

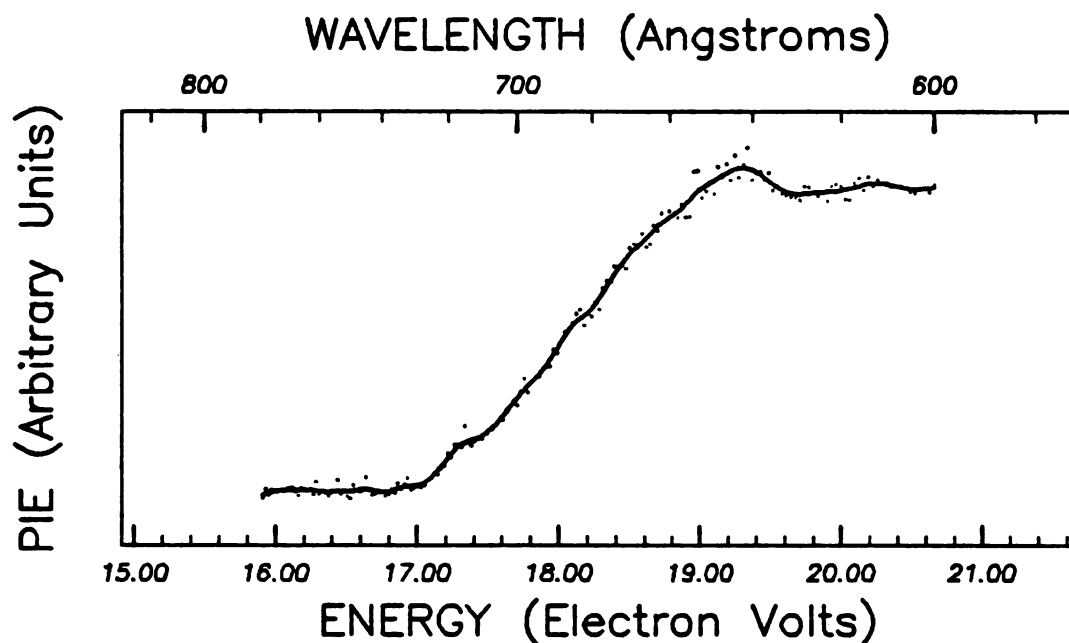


Figure 5A-1-9. PIE of CFC1^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

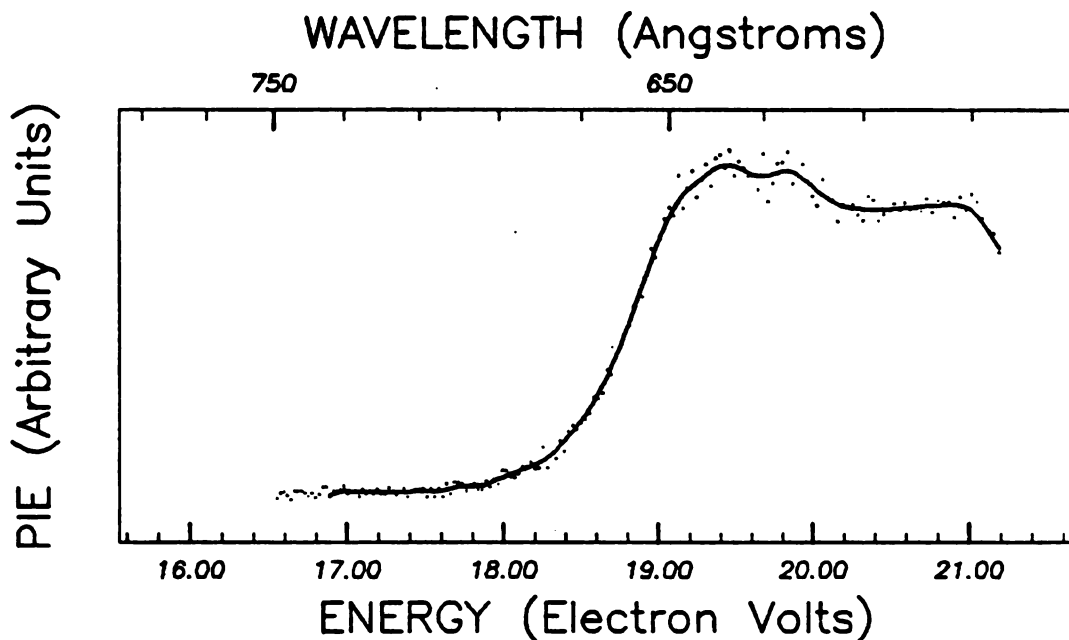


Figure 5A-1-10. PIE of CFCBr^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

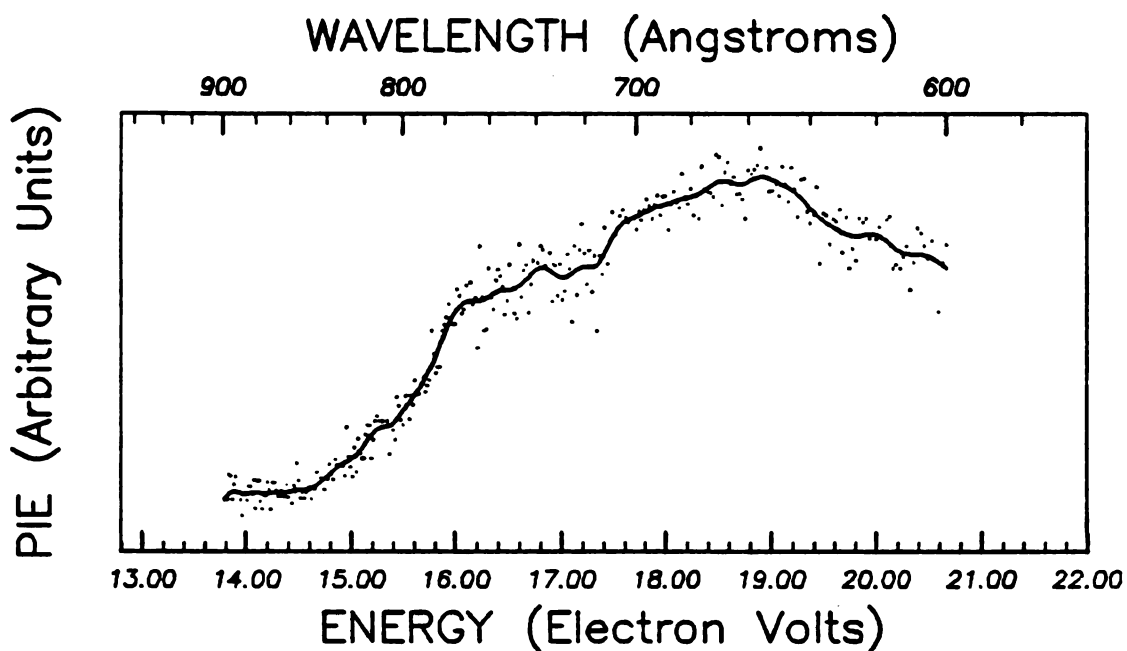


Figure 5A-1-11. PIE of ClBr^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

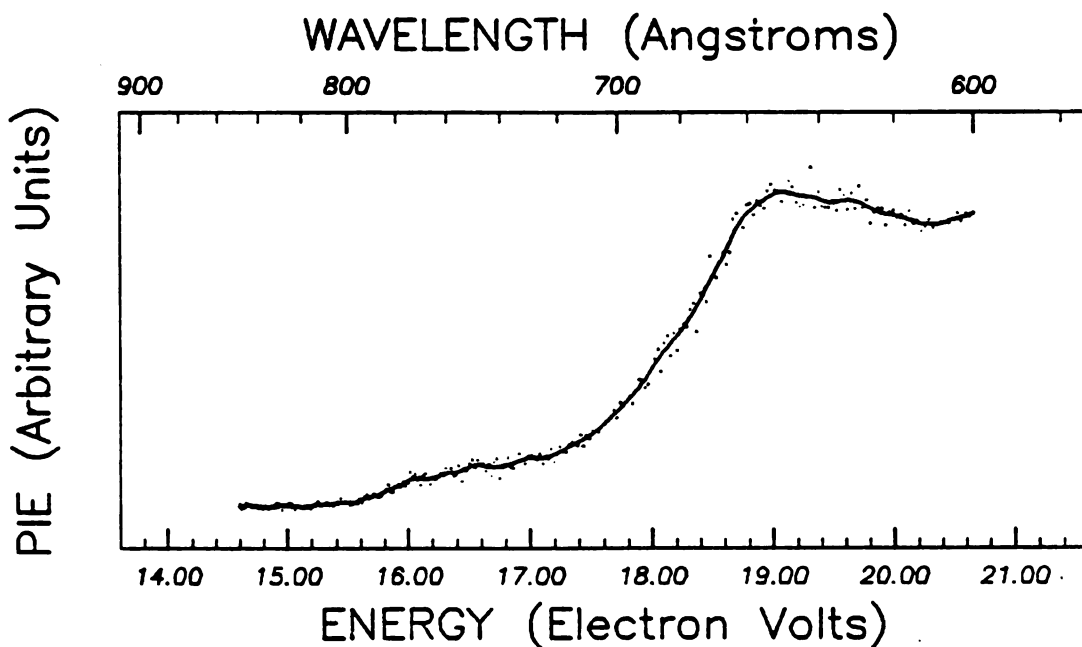
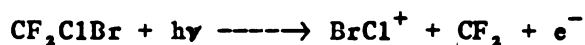


Figure 5A-1-12. PIE of Br^+ from CF_2ClBr . The solid line represents a smooth fit to the experimental data points.

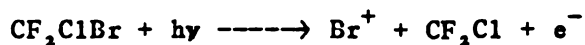
special mechanism which will be discussed later in this chapter. The AP of BrCl^+ obtained from the PIE curve shown in Figure 5A-1-11 is $14.63 \pm 0.3 \text{ eV}$. The reaction equation is most probably:



the value of $\Delta H_{f0}^0(\text{BrCl}^+)$ is calculated to be $273.00 \pm 8.4 \text{ kcal/mole}$.



Production of Br^+ in the fragmentation process is similar to the production of the first fragment, CF_2Cl^+ ; however, in this case the positive charge resides on the bromine. The PIE curve is shown in Figure 5A-1-12. After careful consideration of alternative photodissociation processes, the AP of Br^+ is $15.45 \pm 0.1 \text{ eV}$ and the most likely reaction equation is:



the value of $\Delta H_{f0}^0(\text{Br}^+)$ is calculated to be $312.80 \pm 3.8 \text{ kcal/mole}$.

2. CF_4

The photoionization mass spectrum of CF_4 , obtained under full illumination of the helium continuum, is shown in Figure 5A-2-1. Relative intensities of the peaks and their assignments are presented in Table 5A-2-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-2-2, and the summary of thermochemical information for these ions is given in Table 5A-2-2.

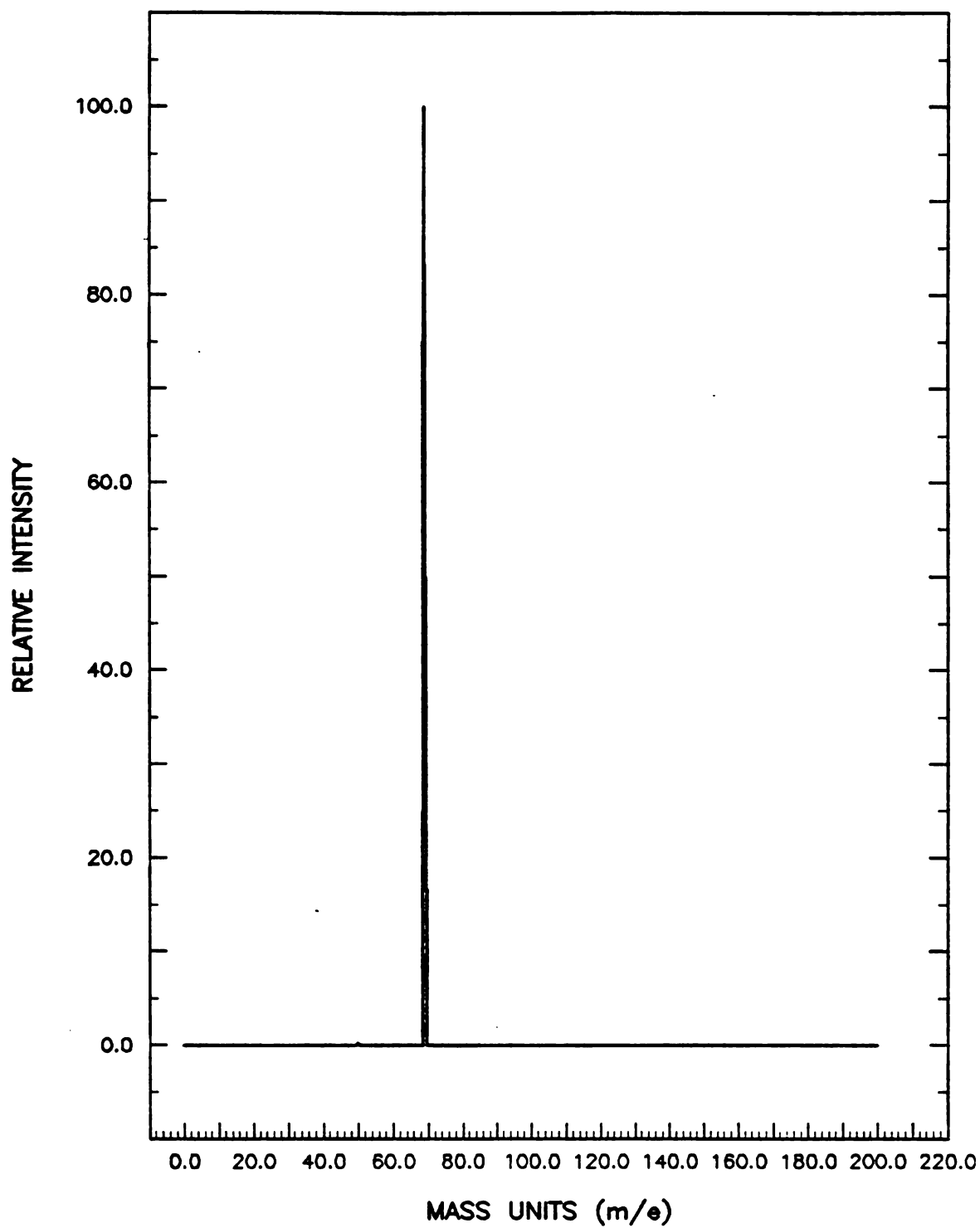


Figure 5A-2-1. Photoionization Mass Spectrum of CF₄
(obtained under full illumination of the
helium discharge).

Table 5A-2-1. Photoionization Mass Spectrum of CF₄^a

m/e	Intensity Relative to CF₃⁺	Percent of Total Ion Production	Probable Formula
50	0.3	0.25	CF₂⁺
69	100.0	99.75	CF₃⁺

^aObtained under full illumination of the helium discharge.**Table 5A-2-2. Summary of IP, AP and Heat of formation data for all ions from CF₄.**

ION	IP or AP (eV)^a	Products of CF₄ + hν	Heats of formation(0°K) (Kcal/mole)^a
CF₃⁺	15.44	CF₃⁺ + F + e⁻	116.08
CF₂⁺	20.44	CF₂⁺ + F + F + e⁻	213.02

^asee text for uncertainties.

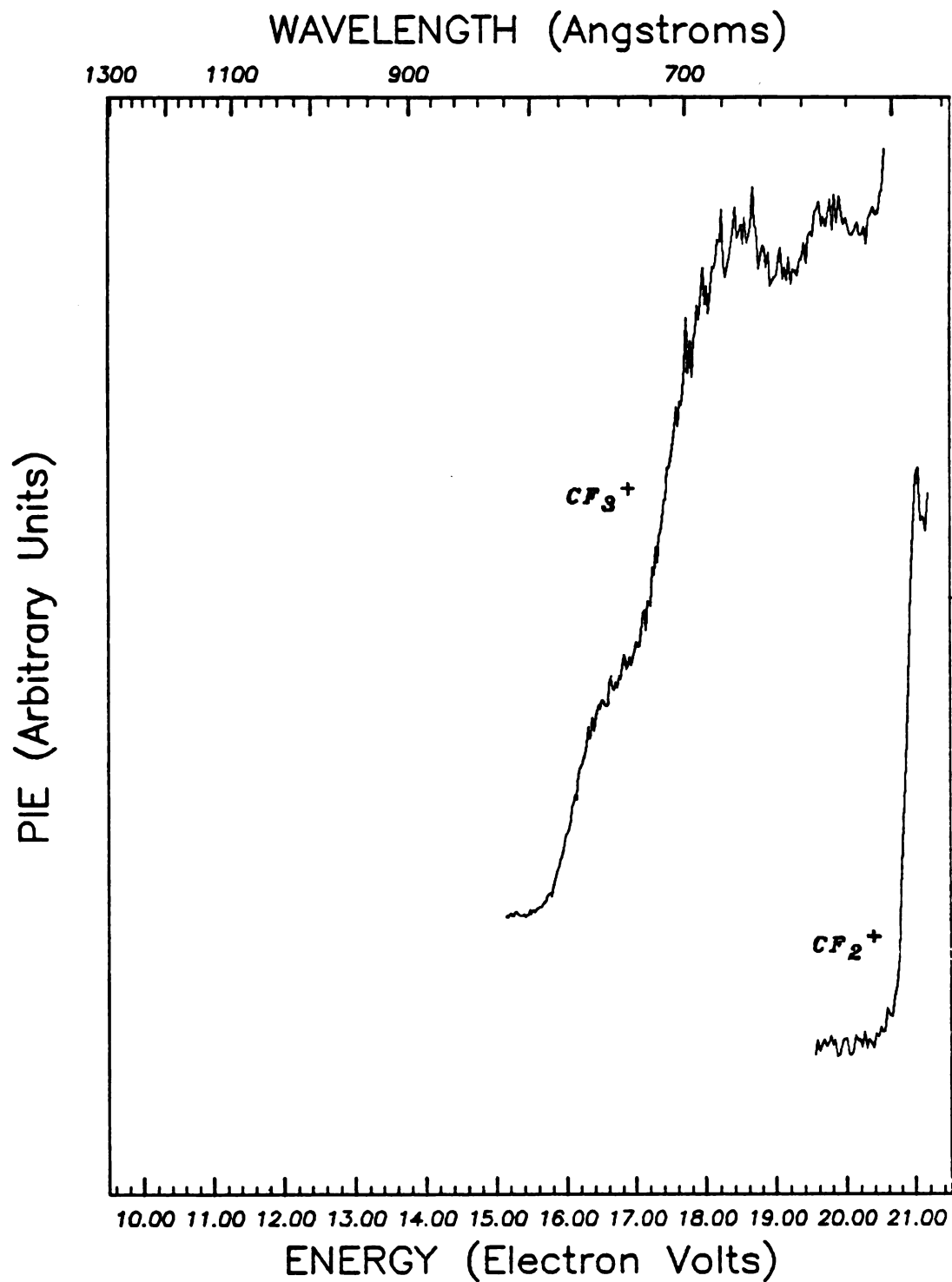


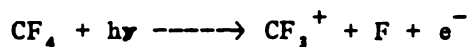
Figure 5A-2-2. Photoionization efficiency curves for daughter ions from CF_4 (no parent ion is detectable).



The parent ion of CF_4 was not observed in this work, nor has any previous study successfully detected CF_4^+ . It may be assumed that the parent ion lifetime is too short for mass spectrometric detection. Among factors which influence the lifetime of parent ion are: the symmetries of the neutral and the ion, Franck-Condon factors, breakdown of the Born-Oppenheimer approximation, Jahn-Teller distortions, spin-orbit effects, and accessible decomposition channels. A rather large geometry difference is expected between CF_4 and CF_4^+ ,¹⁵ and this most likely contributes strongly to the parent ion instability. (Similar considerations apply to CCl_4 , for which the parent ion has not been observed, also.)



The lowest photon energy fragment PIE curve, shown in Figure 5A-2-3, is that of the CF_3^+ fragment. The PIE starts to rise sharply at threshold (near 15.80 eV), and the PIE curve shows two steps. The AP value of this fragment ion is 15.44 ± 0.07 eV, which is slightly lower than and in a very good agreement with the previous literature value 15.52 ± 0.02 eV.⁹¹ From the reaction equation:



the value of $\Delta H_{f0}^0(\text{CF}_3^+)$ is calculated to be 116.08 ± 2.3 kcal/mole.



The second fragment ion is CF_2^+ , for which the PIE is shown in Figure 5A-2-4. The PIE shows a relatively sharp threshold at around

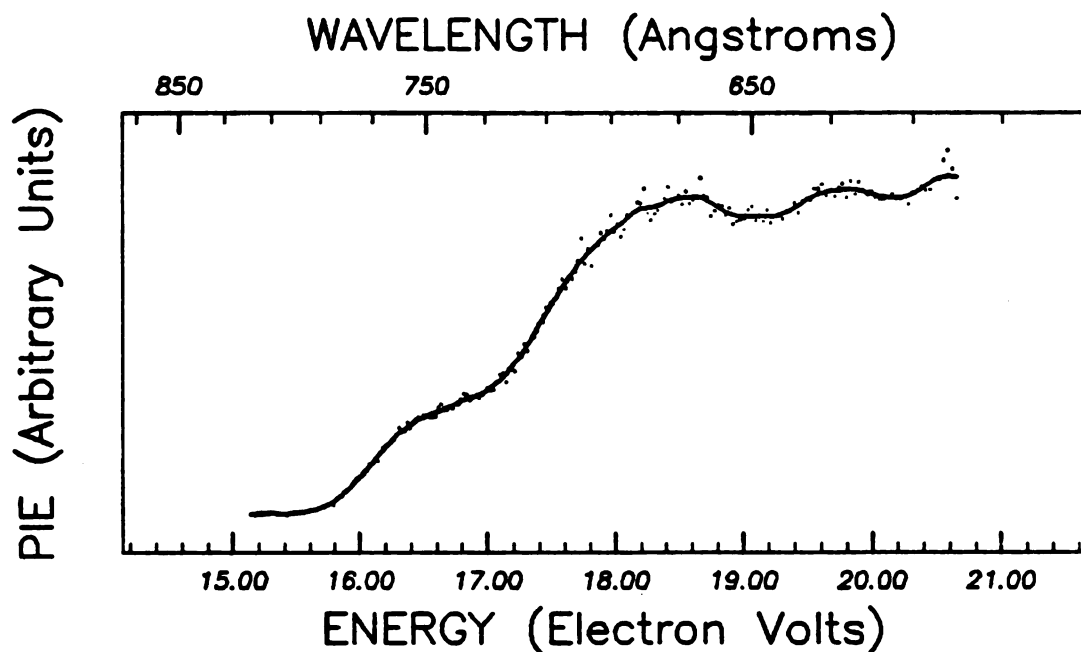


Figure 5A-2-3. PIE of CF_3^+ from CF_4 . The solid line represents a smooth fit to the experimental data points.

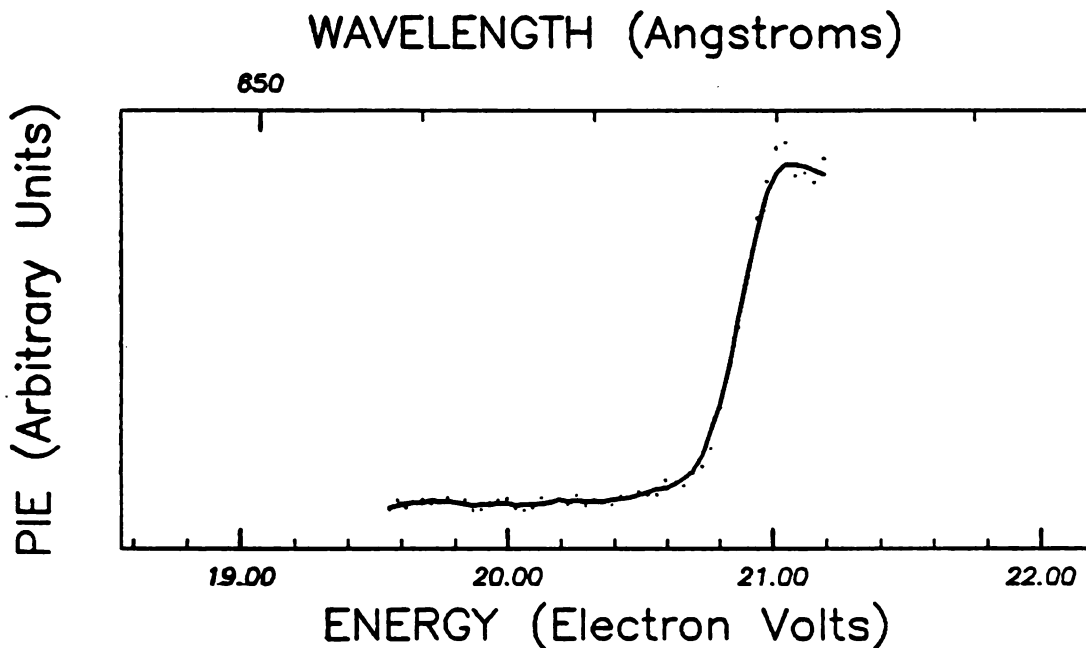
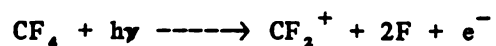


Figure 5A-2-4. PIE of CF_2^+ from CF_4 . The solid line represents a smooth fit to the experimental data points.

20.7eV. The AP value of this fragment ion is $20.44 \pm 0.1 \text{eV}$, which is slightly higher than and in a good agreement with previous literature value: $20.3 \pm 0.5 \text{eV}$.¹²⁴ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2^+)$ is calculated to be $213.02 \pm 3.4 \text{kcal/mole}$.

3. CF_3Cl

The photoionization mass spectrum of CF_3Cl , obtained under full illumination of the helium continuum, is shown in Figure 5A-3-1. Relative intensities of the peaks and their assignments are presented in Table 5A-3-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-3-2, and the summary of thermochemical information for these ions is given in Table 5A-3-2.



The parent ion PIE is shown in Figure 5A-3-3, where it may be seen that the threshold starts to rise at about 12.50eV. Figure 5A-3-4 shows the fit of the error function to the threshold region. The adiabatic IP of the parent ion is $12.60 \pm 0.02 \text{eV}$, which is slightly higher than and in a good agreement with previous literature value: 12.45eV.⁹² From the reaction equation:

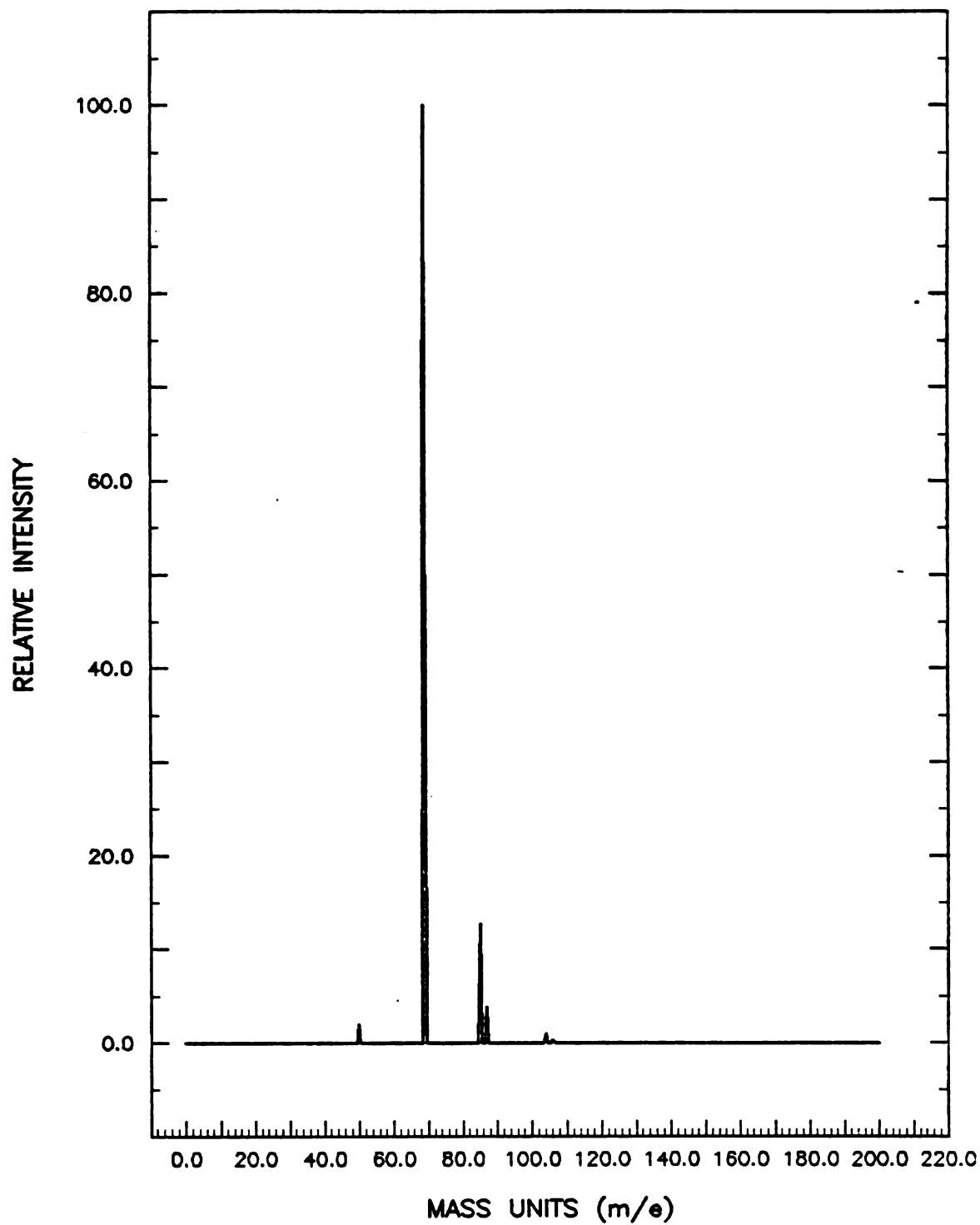


Figure 5A-3-1. Photoionization Mass Spectrum of CF₃Cl (obtained under full illumination of the helium discharge).

Table 5A-3-1. Photoionization Mass Spectrum of $\text{CF}_3\text{Cl}^{\text{a}}$

m/e	Intensity Relative to CF_3^+	Percent of Total Ion Production	Probable Formula
50	1.9	1.62	CF_2^+
69	100.0	83.87	CF_3^+
85	12.1	10.21	$\text{CF}_2^{35}\text{Cl}^+$
87	3.8	3.19	$\text{CF}_2^{37}\text{Cl}^+$
104	1.0	0.84	$\text{CF}_3^{35}\text{Cl}^+$
106	0.3	0.27	$\text{CF}_3^{37}\text{Cl}^+$

^aObtained under full illumination of the helium discharge.Table 5A-3-2. Summary of IP, AP and Heat of formation data for all ions from CF_3Cl .

ION	IP or AP (eV) ^a	Products of $\text{CF}_3\text{Cl} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_3Cl^+	12.60	$\text{CF}_3\text{Cl}^+ + e^-$	290.56
CF_3^+	12.70	$\text{CF}_3^+ + \text{Cl} + e^-$	96.34
CF_2Cl^+	14.44	$\text{CF}_2\text{Cl}^+ + \text{F} + e^-$	146.63
CF_2^+	18.49	$\text{CF}_2^+ + \text{F} + \text{Cl} + e^-$	211.50

^asee text for uncertainties.

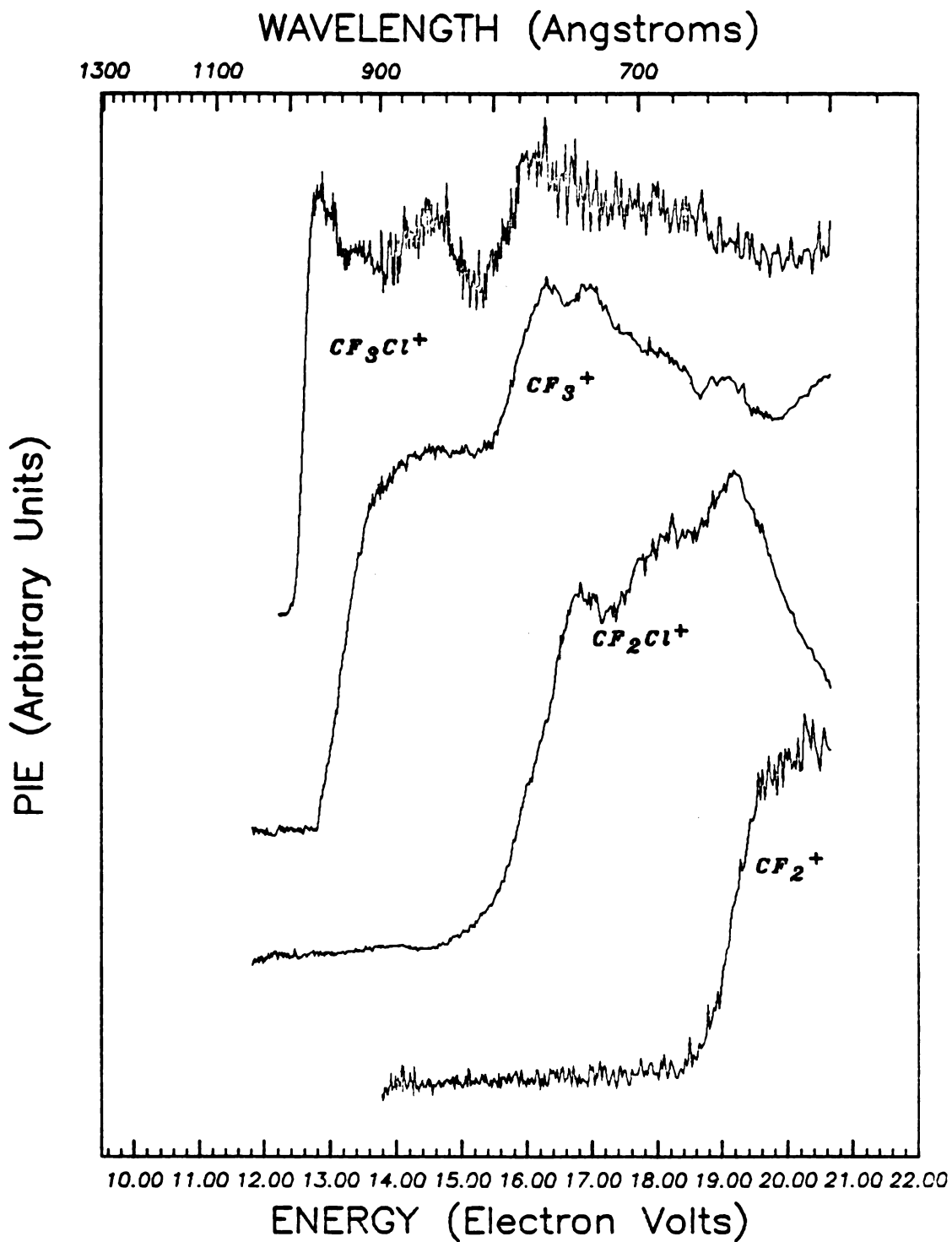


Figure 5A-3-2. Photoionization efficiency curves for parent and daughter ions from CF_3Cl .

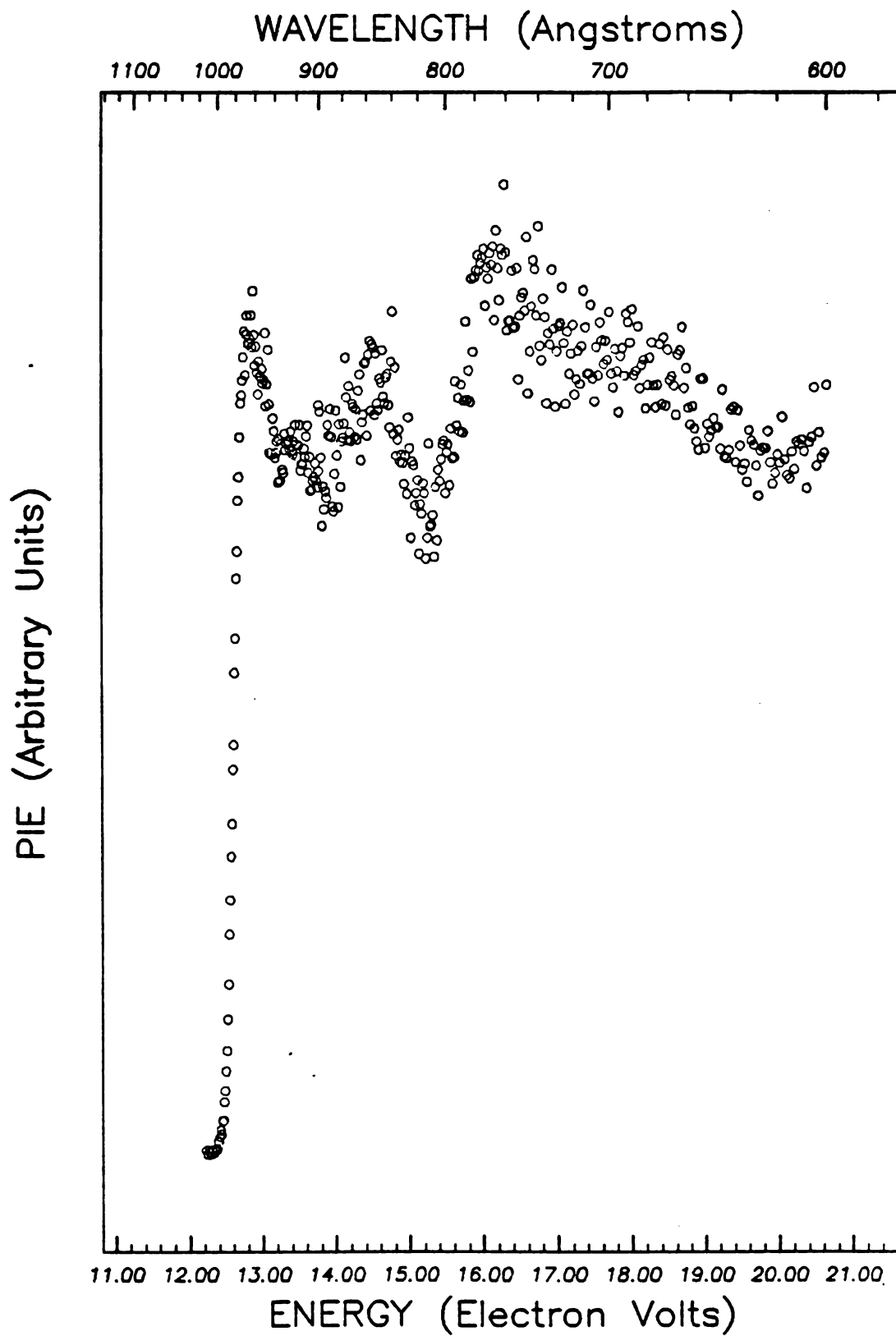


Figure 5A-3-3. PIE of CF_3Cl^+ from CF_3Cl .

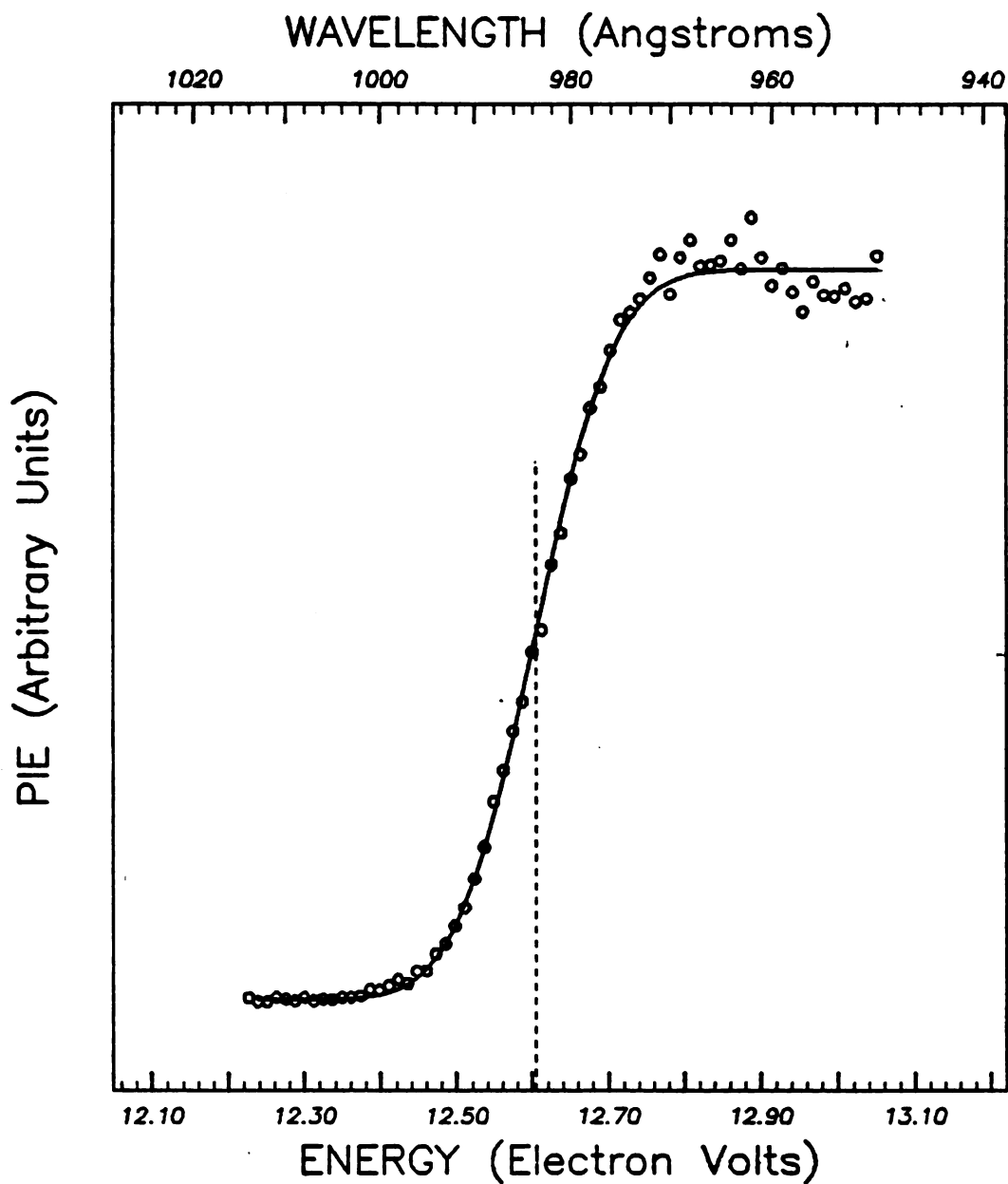
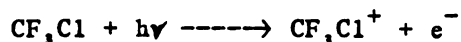
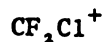


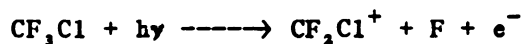
Figure 5A-3-4. PIE of CF_3Cl^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Cl}^+)$ is calculated to be $290.50 \pm 1.3 \text{ kcal/mole}$.



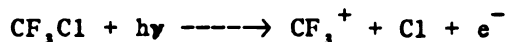
The PIE of the CF_2Cl^+ fragment ion is shown in Figure 5A-3-5; it shows a relatively sharp threshold at approximately 15.5eV. The AP value of this fragment ion is $14.44 \pm 0.07 \text{ eV}$, which is slightly higher than and in a good agreement with the previous literature value: 14.25eV.⁹¹ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Cl}^+)$ is calculated to be $146.63 \pm 2.8 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve from CF_3Cl is shown in Figure 5A-3-6. The PIE starts to rise sharply at threshold (near 12.70eV). The AP value of this fragment ion is $12.70 \pm 0.07 \text{ eV}$, which is slightly higher than and in a very good agreement with previous literature values: 12.63eV⁹¹ and 12.55eV.⁹² From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is calculated to be $96.34 \pm 2.4 \text{ kcal/mole}$.



The last fragment ion is CF_2^+ , for which the PIE is shown in

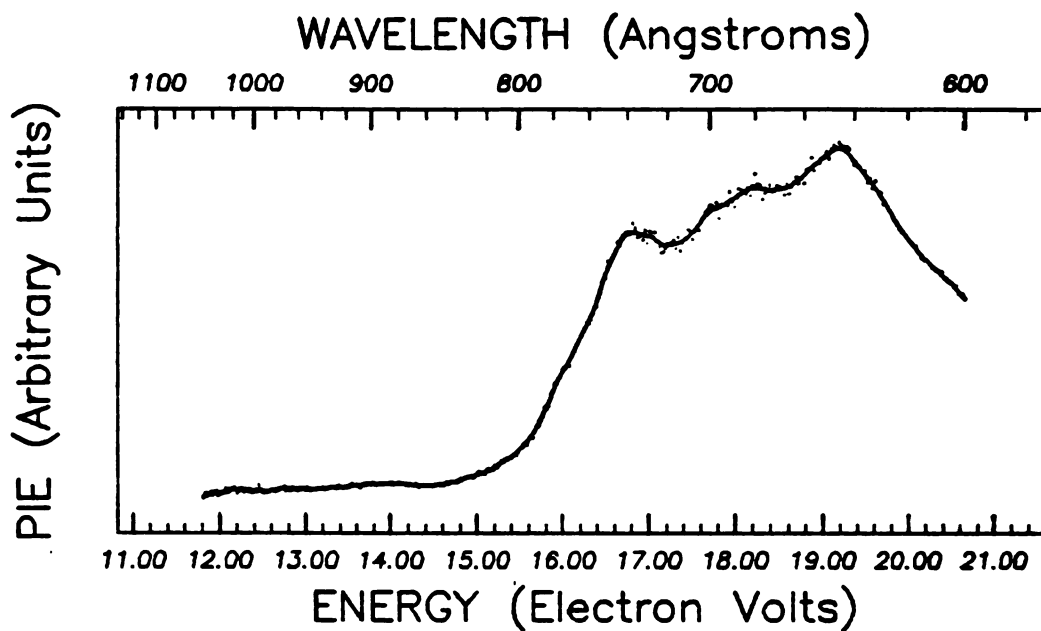


Figure 5A-3-5. PIE of CF_2Cl^+ from CF_3Cl . The solid line represents a smooth fit to the experimental data points.

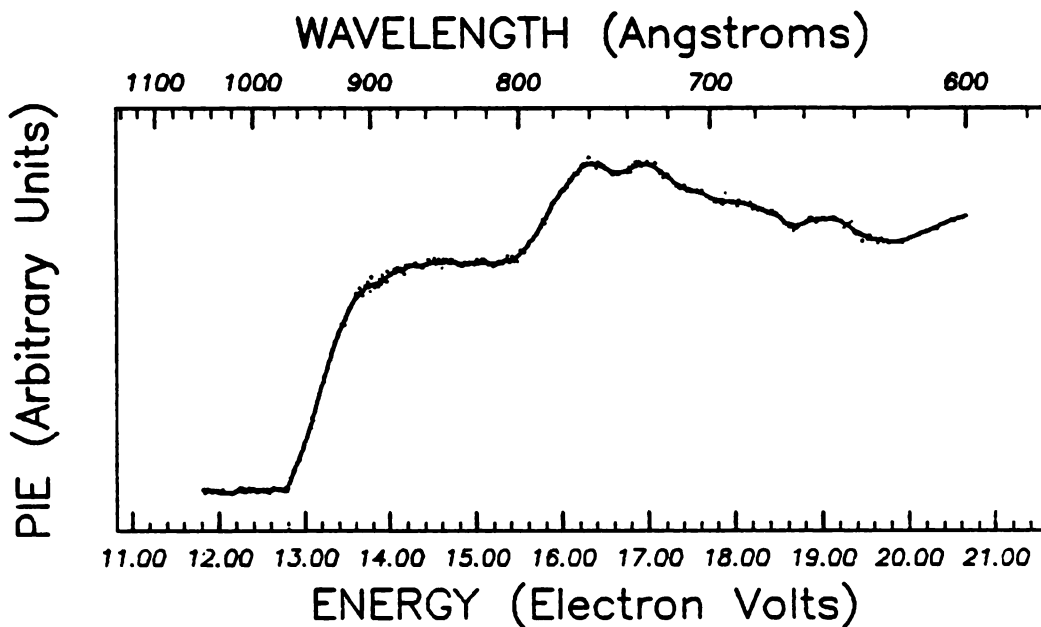


Figure 5A-3-6. PIE of CF_3^+ from CF_3Cl . The solid line represents a smooth fit to the experimental data points.

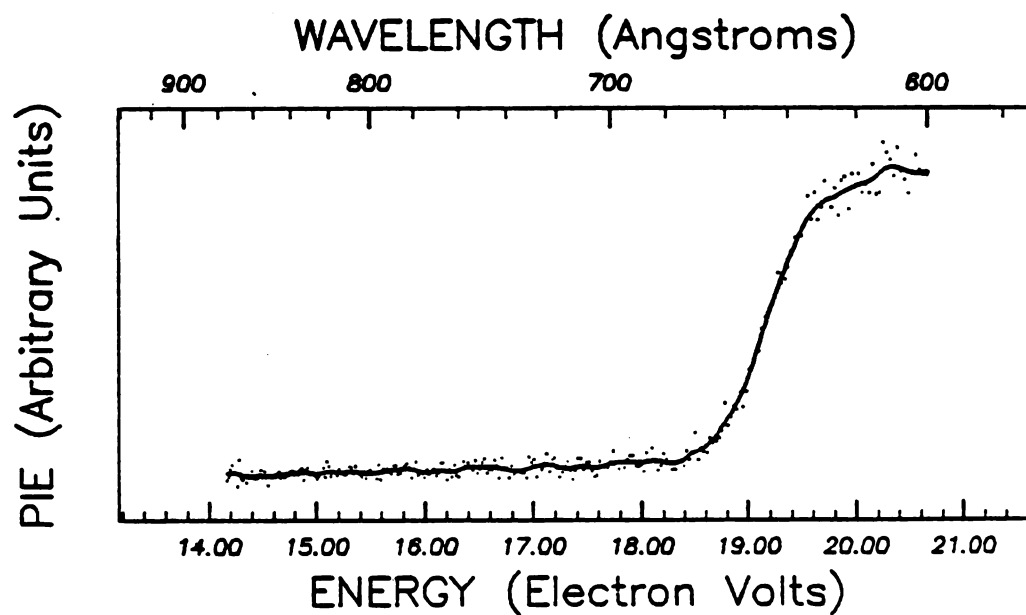
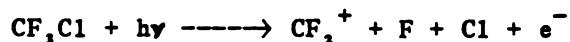


Figure 5A-3-7. PIE of CF_2^+ from CF_3Cl . The solid line represents a smooth fit to the experimental data points.

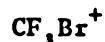
Figure 5A-3-7. The PIE shows a relative sharp threshold at around 18.5eV. The AP value of this fragment ion is $18.49 \pm 0.1 \text{ eV}$, which is slightly lower than and in a satisfactory agreement with the previous literature value: 18.85eV.⁹² By using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2^+)$ is calculated to be $211.50 \pm 3.5 \text{ kcal/mole}$.

4. CF_3Br

The photoionization mass spectrum of CF_3Br , obtained under full illumination of the helium continuum, is shown in Figure 5A-4-1. Relative intensities of the peaks and their assignments are presented in Table 5A-4-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-4-2, and the summary of thermochemical information for these ions is given in Table 5A-4-2.



The parent ion PIE is shown in Figure 5A-4-3, where it may be seen that the threshold starts to rise at about 11.70eV. Figure 5A-4-4 shows the fit of the error function to the threshold region. The adiabatic IP of the parent ion is $11.76 \pm 0.02 \text{ eV}$, which is slightly lower than and in a good agreement with the previous literature value: 12.0eV.⁹³ From the reaction equation:

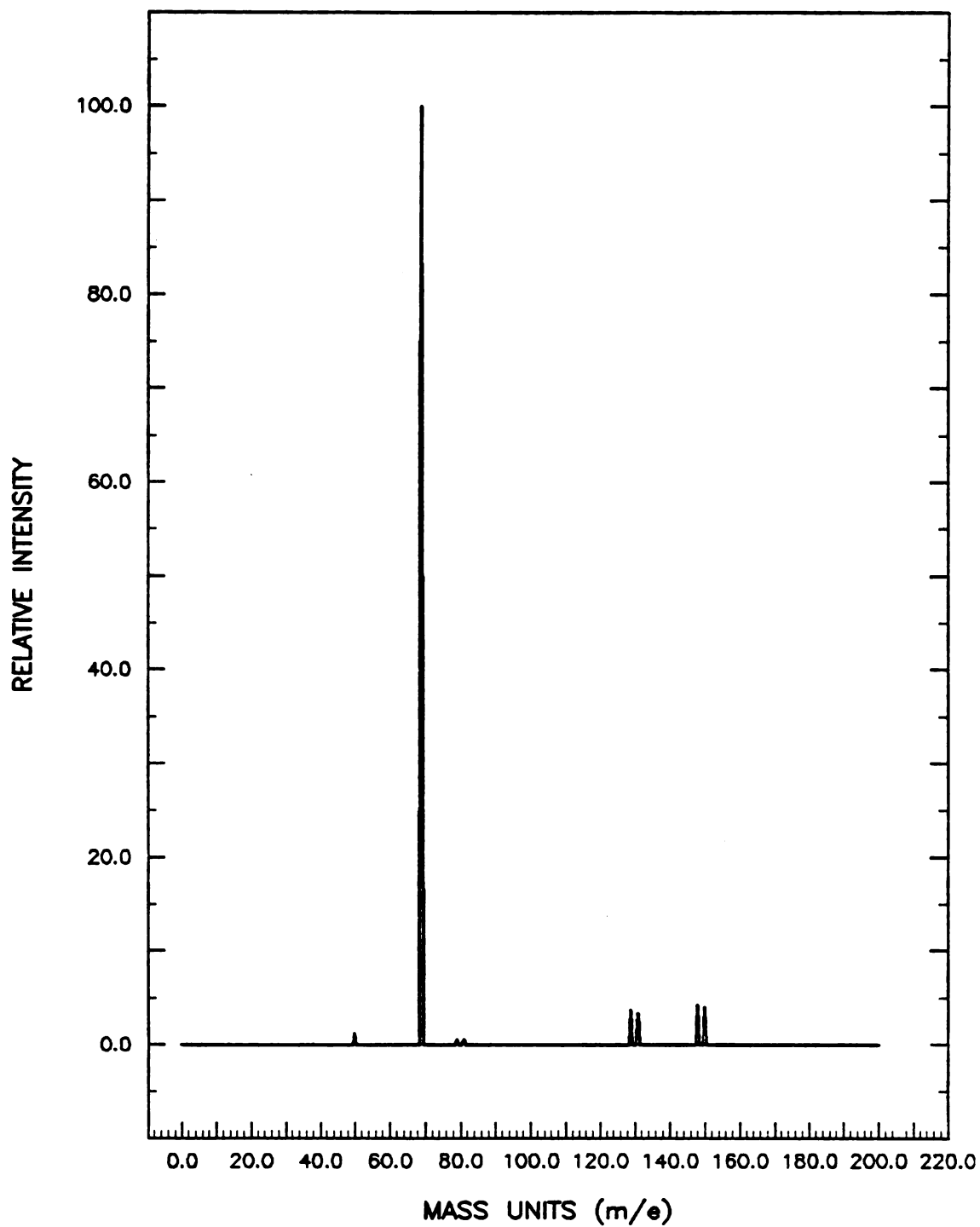


Figure 5A-4-1. Photoionization Mass Spectrum of CF₃Br (obtained under full illumination of the helium discharge).

Table 5A-4-1. Photoionization Mass Spectrum of $\text{CF}_3\text{Br}^{\text{a}}$

m/e	Intensity Relative to CF_3^+	Percent of Total Ion Production	Probable Formula
50	1.2	0.99	CF_2^+
69	100.0	85.09	CF_3^+
79	0.6	0.51	$^{79}\text{Br}^+$
81	0.6	0.47	$^{81}\text{Br}^+$
129	3.7	3.14	$\text{CF}_2^{79}\text{Br}^+$
131	3.3	2.78	$\text{CF}_2^{81}\text{Br}^+$
148	4.2	3.58	$\text{CF}_3^{79}\text{Br}^+$
150	4.0	3.40	$\text{CF}_3^{81}\text{Br}^+$

^aObtained under full illumination of the helium discharge.Table 5A-4-2. Summary of IP, AP and Heat of formation data for all ions from CF_3Br .

ION	IP or AP (eV) ^a	Products of $\text{CF}_3\text{Br} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_3Br^+	11.76	$\text{CF}_3\text{Br}^+ + \text{e}^-$	118.99
CF_3^+	11.88	$\text{CF}_3^+ + \text{Br} + \text{e}^-$	93.56
CF_2Br^+	14.54	$\text{CF}_2\text{Br}^+ + \text{F} + \text{e}^-$	164.73
CF_2^+	17.66	$\text{CF}_2^+ + \text{F} + \text{Br} + \text{e}^-$	208.49
Br^+	14.94	$\text{Br}^+ + \text{CF}_3 + \text{e}^-$	304.01

^asee text for uncertainties.

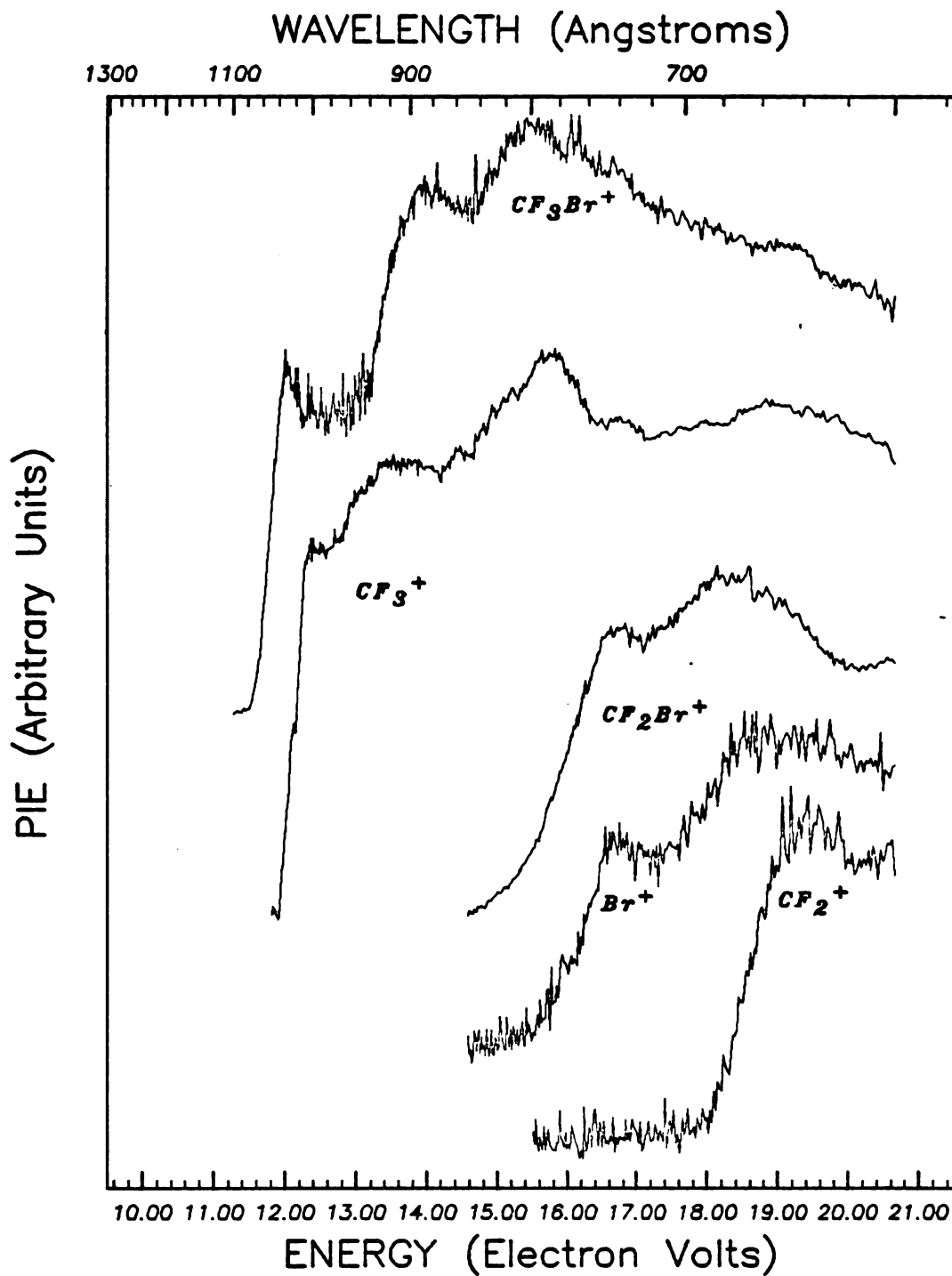


Figure 5A-4-2. Photoionization efficiency curves for parent and daughter ions from CF_3Br .

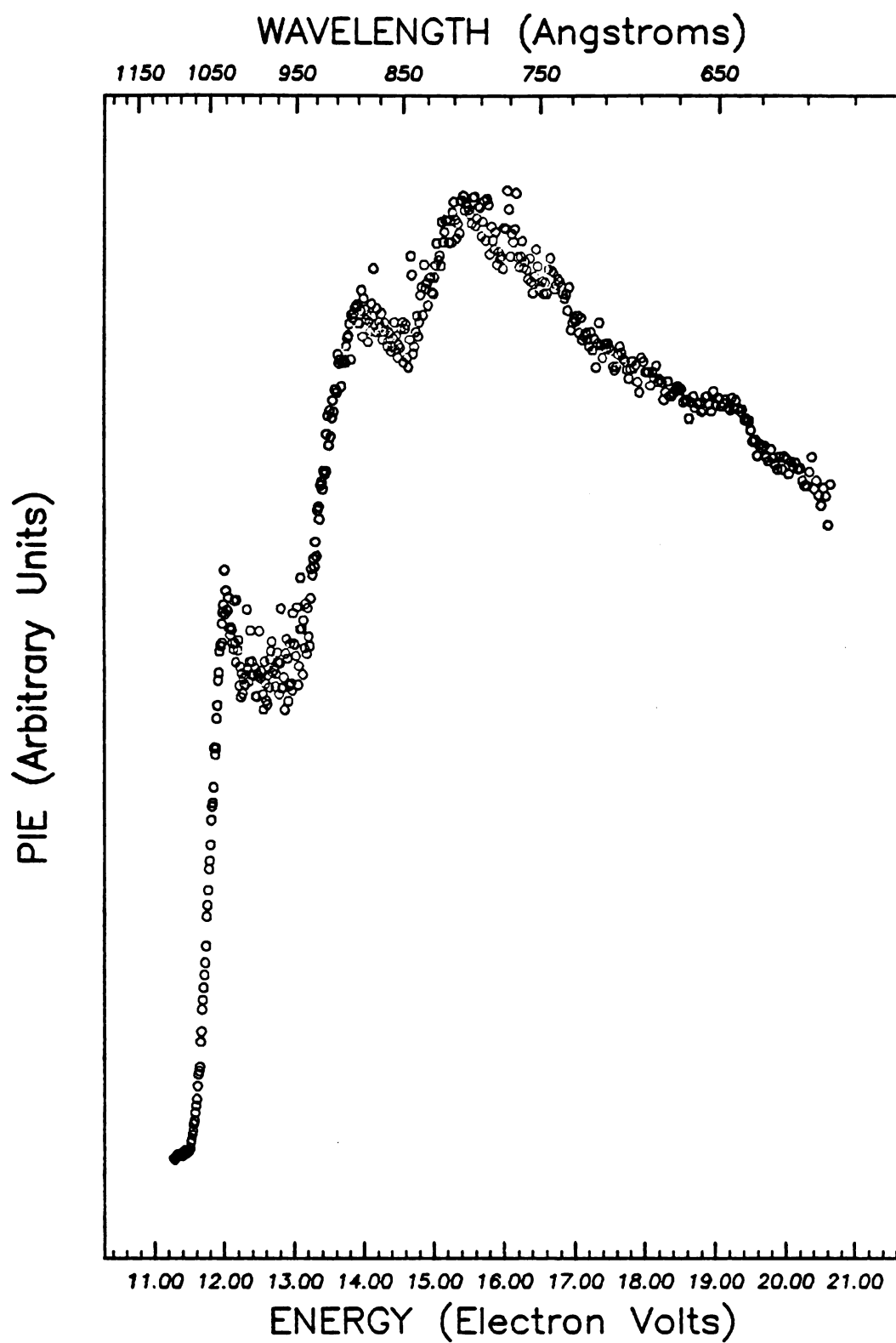


Figure 5A-4-3. PIE of CF_3Br^+ from CF_3Br .

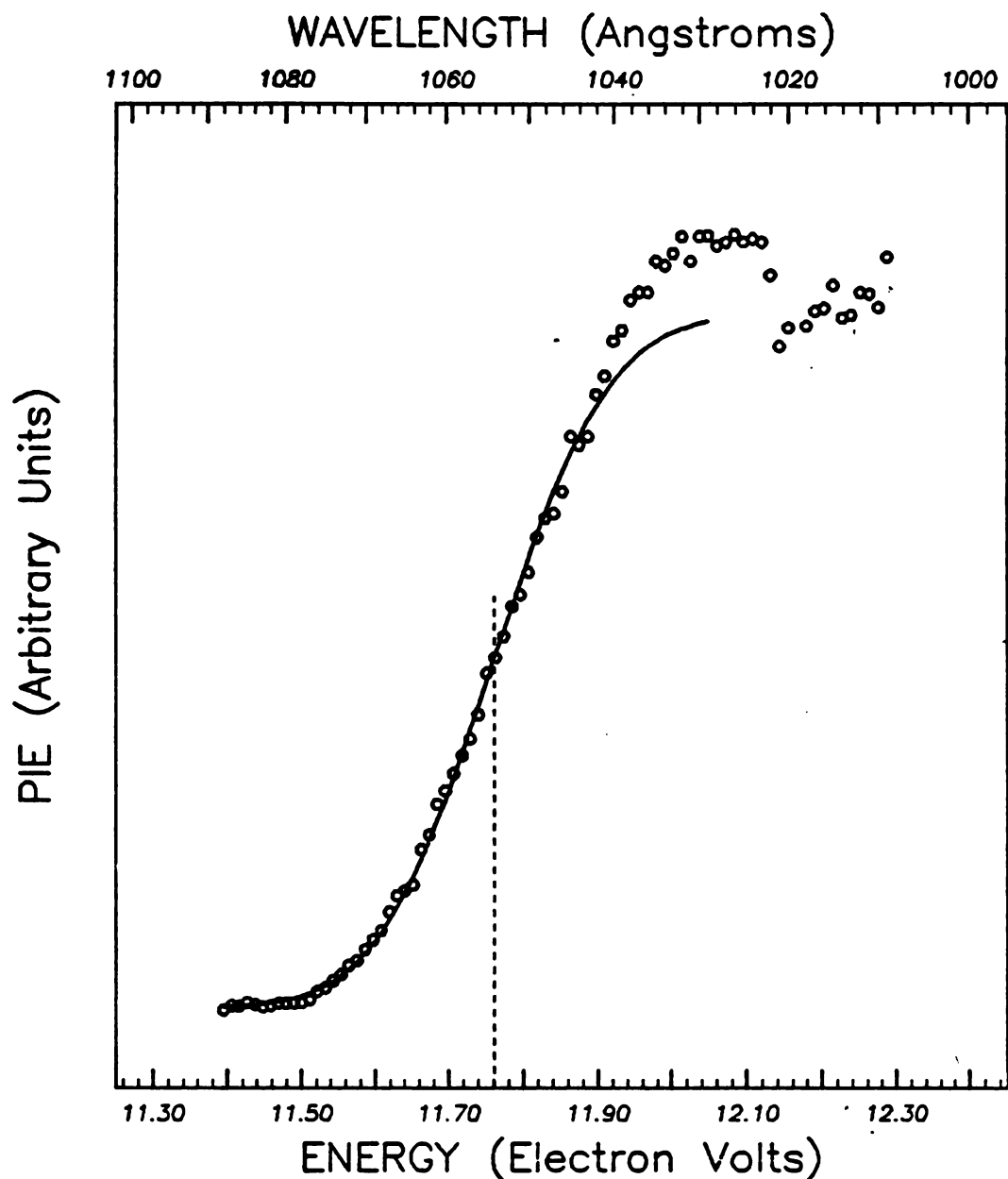


Figure 5A-4-4. PIE of CF_3Br^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

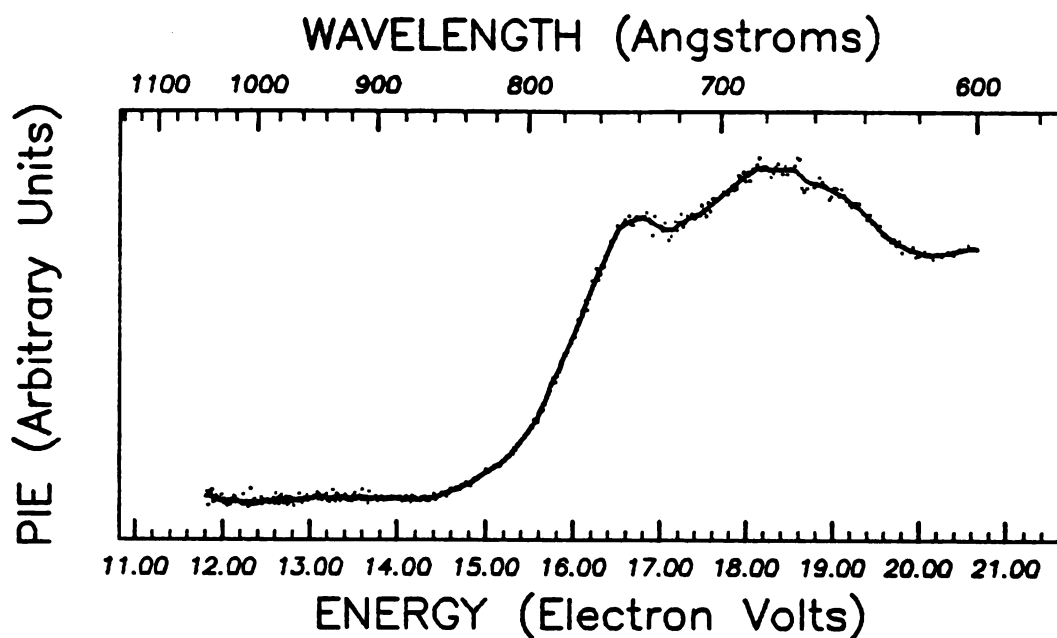


Figure 5A-4-5. PIE of CF_2Br^+ from CF_3Br . The solid line represents a smooth fit to the experimental data points.

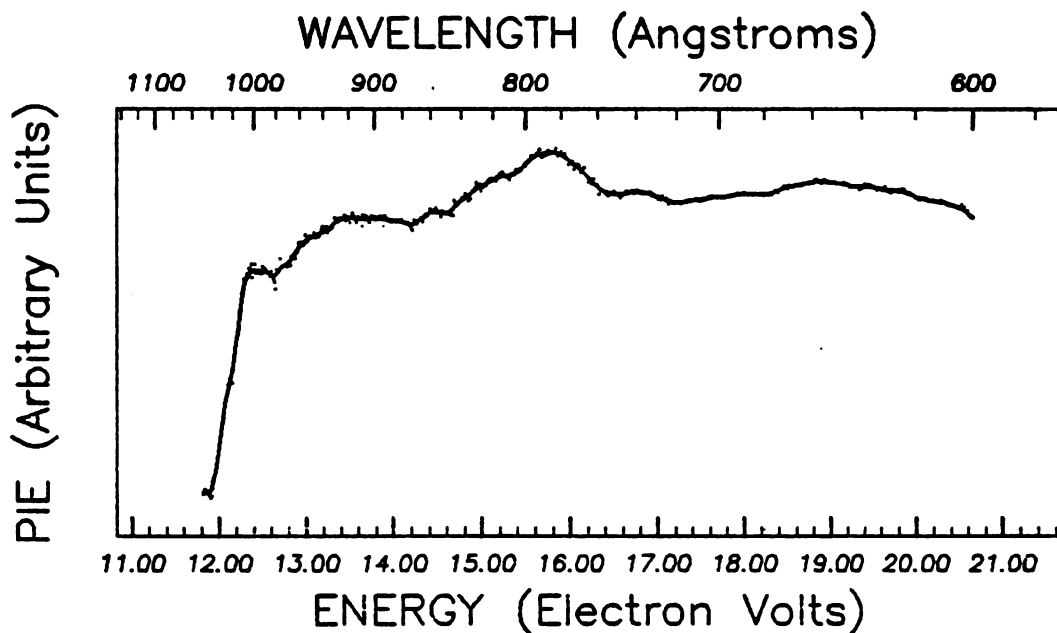
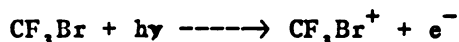


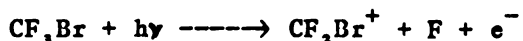
Figure 5A-4-6. PIE of CF_3^+ from CF_3Br . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CF}_3\text{Br}^+)$ is calculated to be $118.99 \pm 1.2 \text{ kcal/mole}$.



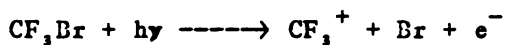
The PIE of CF_3Br^+ is shown in Figure 5A-4-5. The PIE shows a relative smooth threshold at around 14.5eV. The AP value of this fragment ion is $14.54 \pm 0.07 \text{ eV}$; no previous literature value is available for comparison. By using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3\text{Br}^+)$ is calculated to be $164.73 \pm 2.7 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve from CF_3Br is shown in Figure 5A-4-6. The PIE starts to rise sharply at threshold (near 12.0eV). The AP value of this fragment ion is $11.88 \pm 0.04 \text{ eV}$, which is slightly higher than and in a good agreement with the previous literature value $11.71 \pm 0.02 \text{ eV}$.⁹¹ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is calculated to be $93.56 \pm 1.7 \text{ kcal/mole}$.



The next fragment ion is CF_2^+ , for which the PIE is shown in Figure 5A-4-7. The AP value of this fragment ion is $17.66 \pm 0.1 \text{ eV}$, which

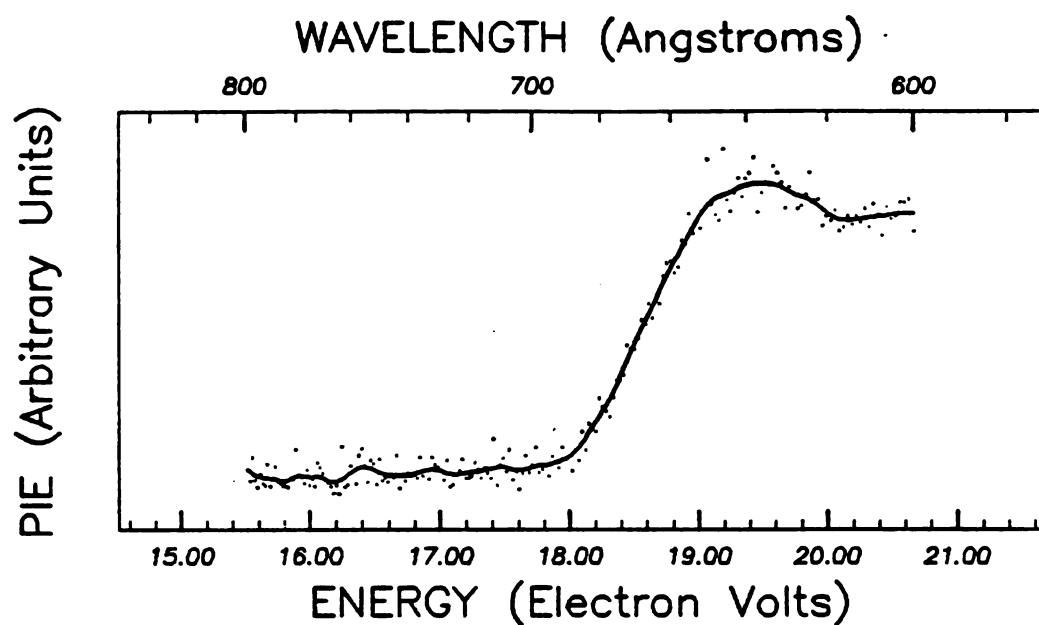


Figure 5A-4-7. PIE of CF_2^+ from CF_3Br . The solid line represents a smooth fit to the experimental data points.

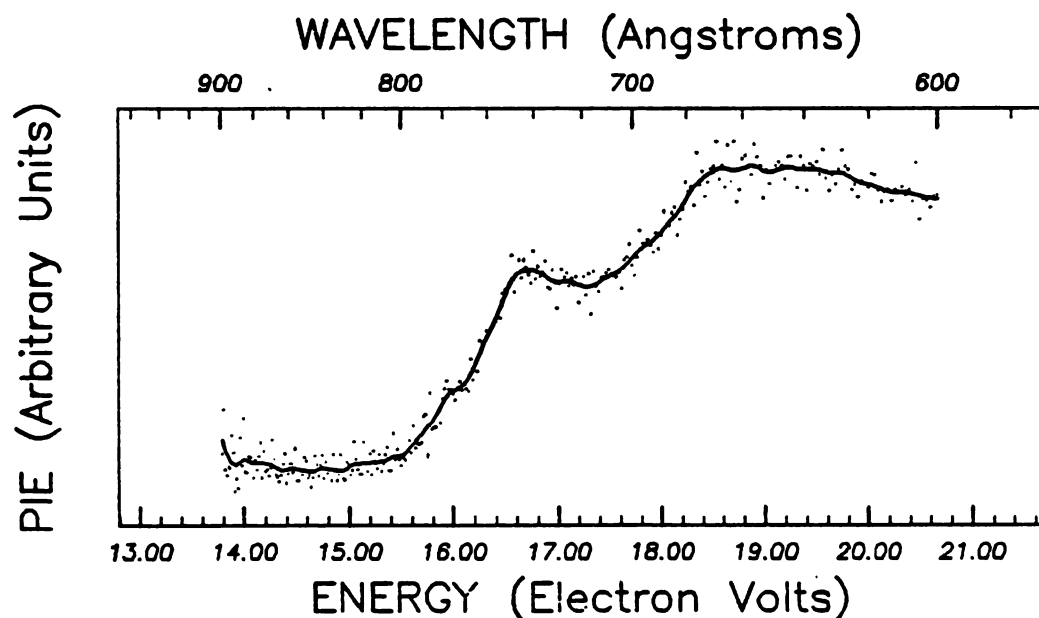


Figure 5A-4-8. PIE of Br^+ from CF_3Br . The solid line represents a smooth fit to the experimental data points.

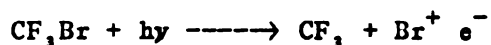
is in excellent agreement with the previous literature value: 17.66eV⁹³. From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2^+)$ is calculated to be 208.47±3.5kcal/mole.



The last fragment ion is Br^+ , for which the PIE is shown in Figure 5A-4-8. The AP value of this fragment ion is 14.90±0.3eV; using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{Br}^+)$ is calculated to be 303.09±8.6kcal/mole.

5. CF_3I

The photoionization mass spectrum of CF_3I , obtained under full illumination of the helium continuum, is shown in Figure 5A-5-1. Relative intensities of the peaks and their assignments are presented in Table 5A-5-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-5-2, and the summary of thermochemical information for these ions is given in Table 5A-5-2.



The parent ion PIE is shown in Figure 5A-5-3. The threshold starts to rise at about 10.3eV. Figure 5A-4-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is

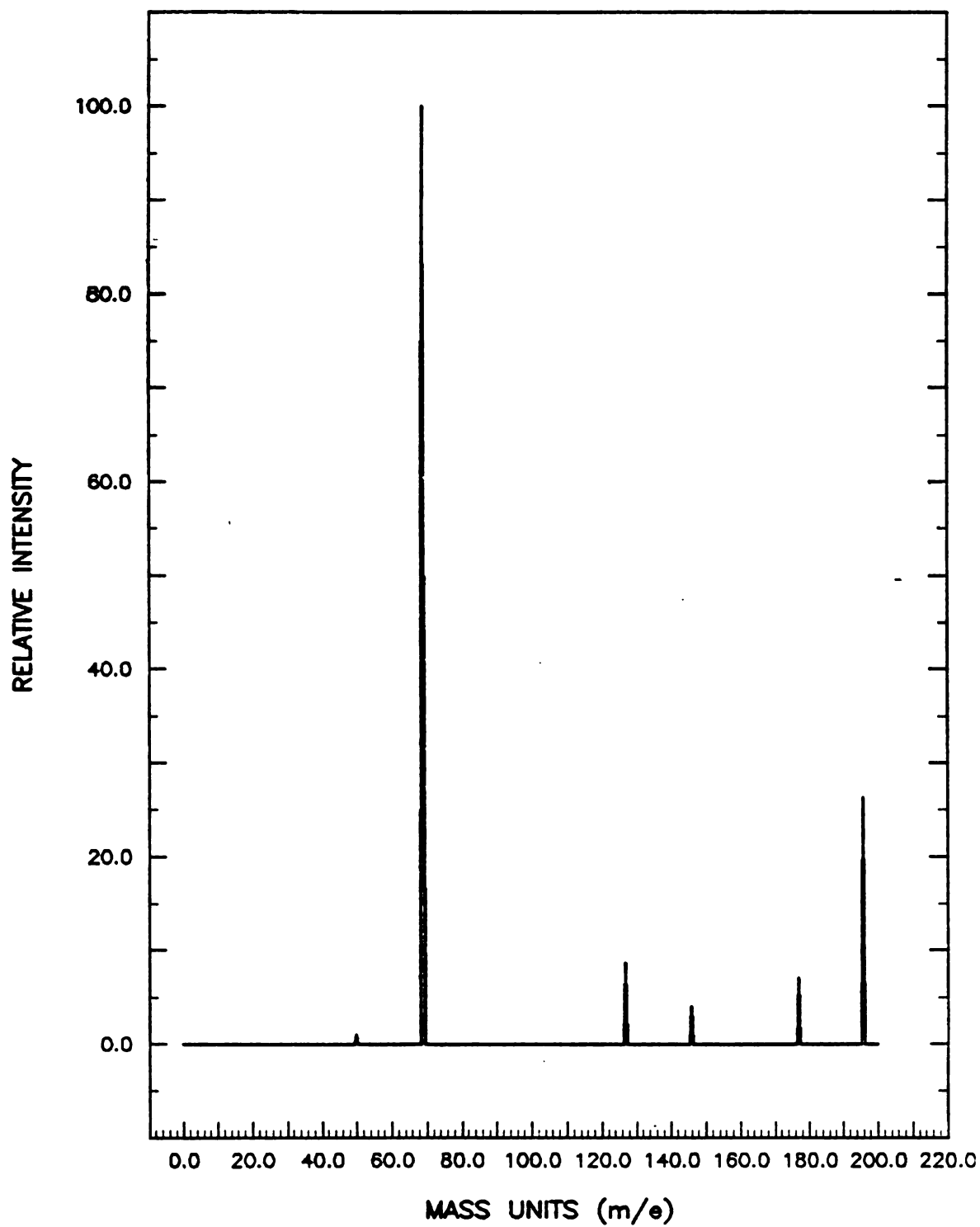


Figure 5A-5-1. Photoionization Mass Spectrum of CF_3I
(obtained under full illumination of the
helium discharge).

Table 5A-5-1. Photoionization Mass Spectrum of $\text{CF}_3\text{I}^{\text{a}}$

m/e	Intensity Relative to CF_3^+	Percent of Total Ion Production	Probable Formula
50	1.0	0.68	CF_2^+
69	100.0	68.03	CF_3^+
127	8.7	5.90	I^+
146	4.0	2.72	IF^+
177	7.0	4.76	CF_2I^+
196	26.3	17.91	CF_3I^+

^aObtained under full illumination of the helium discharge.Table 5A-5-2. Summary of IP, AP and Heat of formation data for all ions from CF_3I .

ION	IP or AP (eV) ^a	Products of $\text{CF}_3\text{I} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_3I^+	10.38	$\text{CF}_3\text{I}^+ + e^-$	99.96
CF_3^+	11.11	$\text{CF}_3^+ + \text{I} + e^-$	91.15
CF_2I^+	14.64	$\text{CF}_2\text{I}^+ + \text{F} + e^-$	180.07
CF_2^+	16.94	$\text{CF}_2^+ + \text{F} + \text{I} + e^-$	207.94
IF^+	14.12	$\text{IF}^+ + \text{CF}_2 + e^-$	229.81
I^+	12.93	$\text{I}^+ + \text{CF}_3 + e^-$	270.47

^asee text for uncertainties.

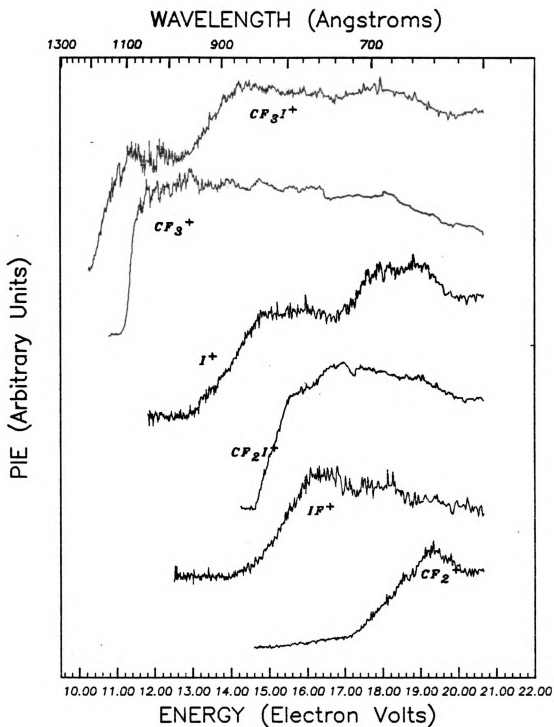


Figure 5A-5-2. Photoionization efficiency curves for parent and daughter ions from CF₃I.

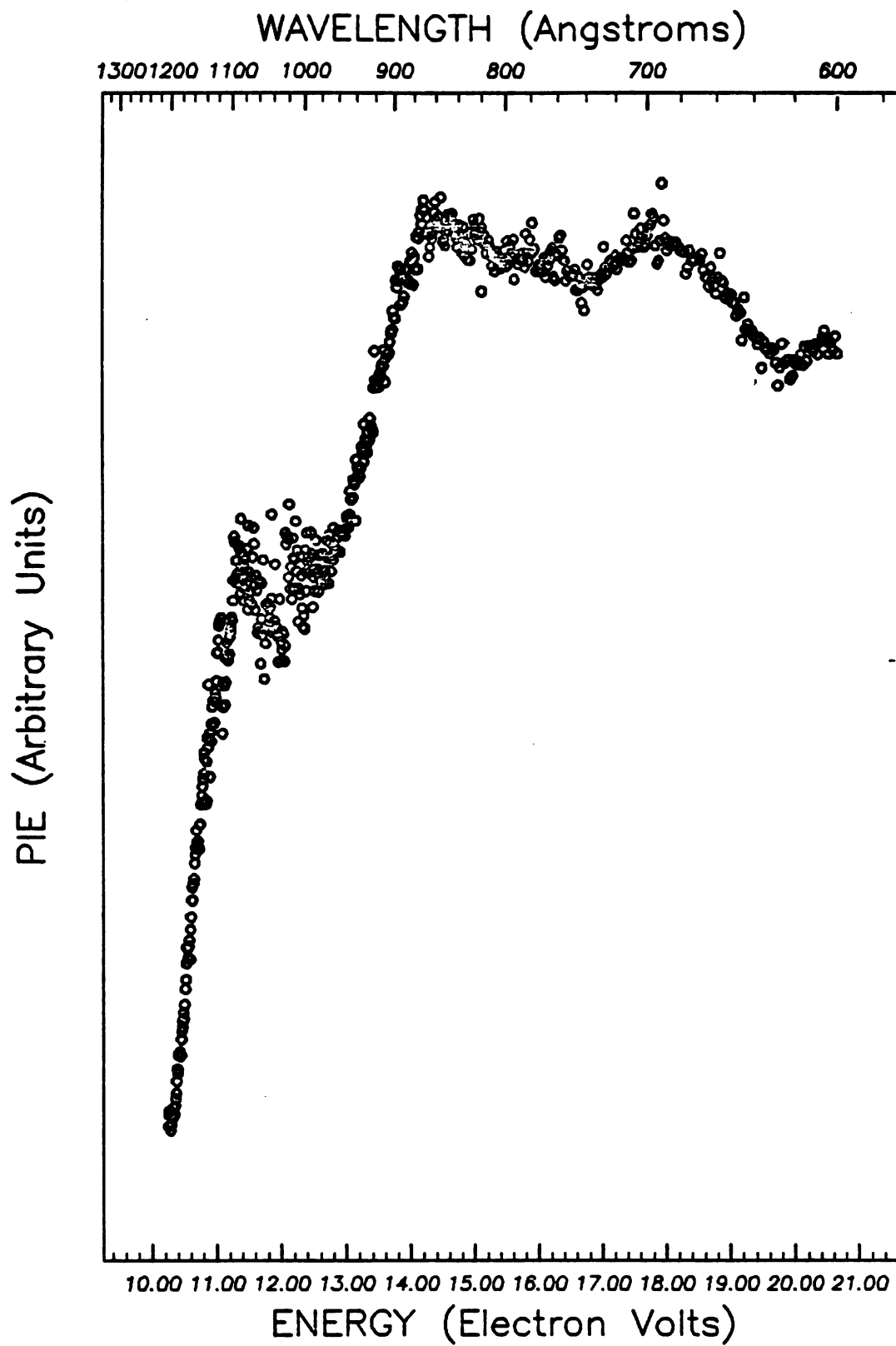


Figure 5A-5-3. PIE of CF_3I^+ from CF_3I .

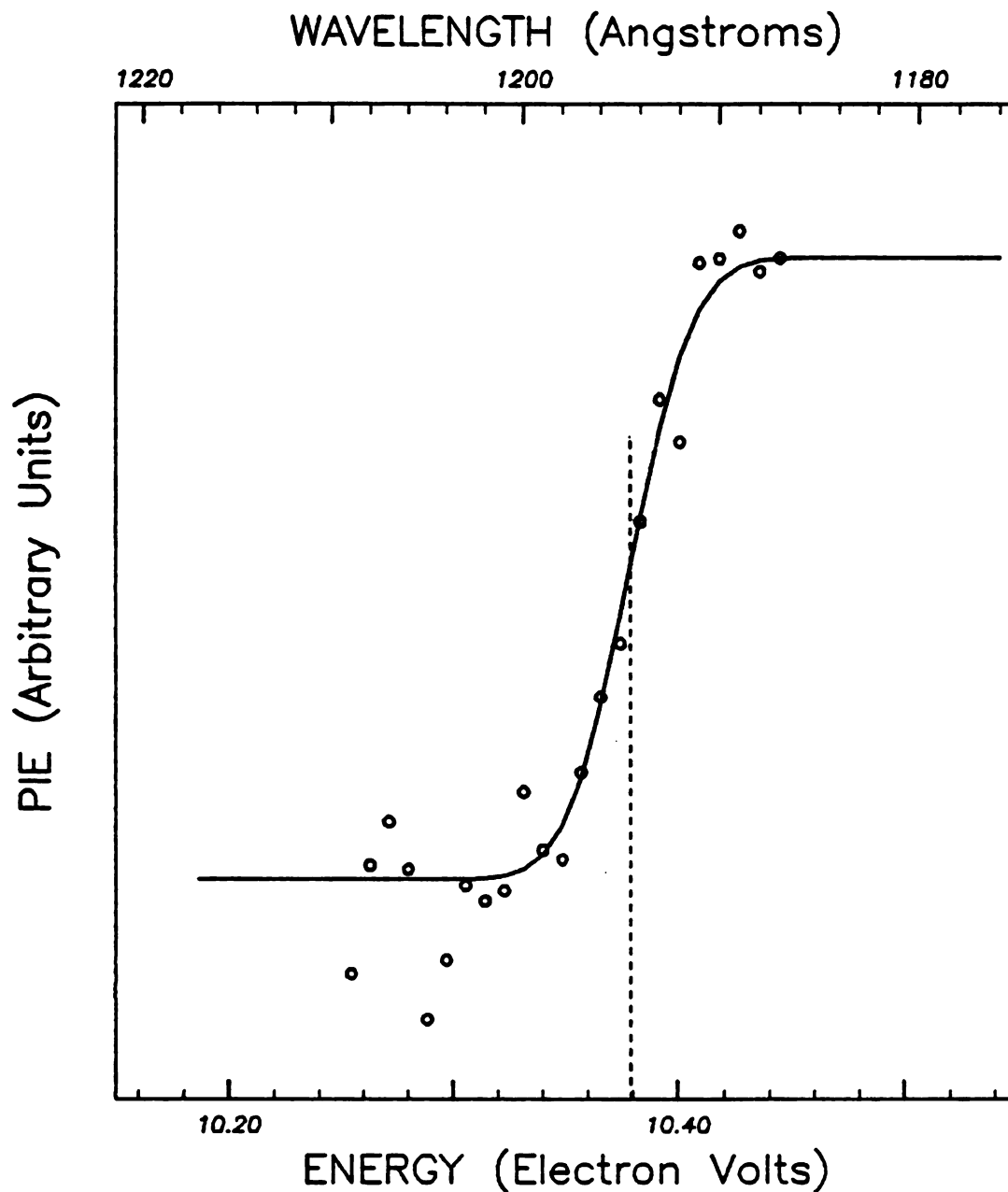
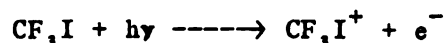


Figure 5A-5-4. PIE of CF_3I^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

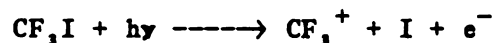
10.38±0.02eV, which is slightly lower than previous literature value: 11.11eV.⁹⁴ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3\text{I}^+)$ is calculated to be 99.96±1.3kcal/mole.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-5-5. The PIE starts to rise sharply at threshold(near 11.2eV). The AP value of this fragment ion is 11.11±0.04eV, which is slightly higher than the lowest previous literature value 10.89eV.⁹¹ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is calculated to be 91.15±1.7kcal/mole.



The PIE of CF_2I^+ from CF_3I is shown in Figure 5A-5-6. The PIE shows a relatively sharp threshold at around 14.6eV. The AP value of this fragment ion is 14.64±0.1eV, which is slightly lower than previous literature value: 15.3eV,⁹⁵ and by using the reaction equation:

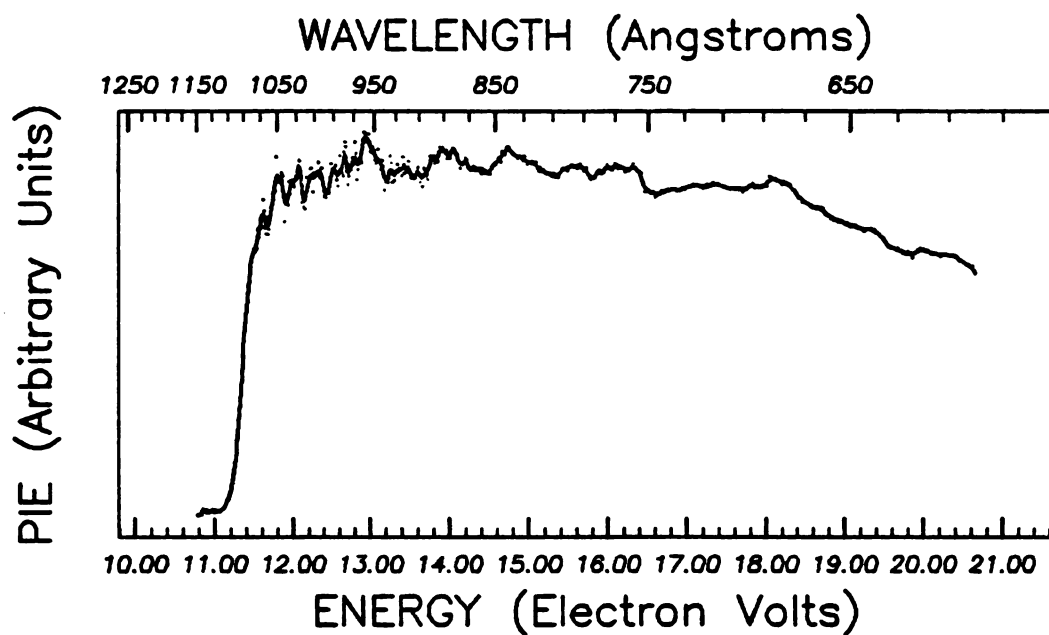


Figure 5A-5-5. PIE of CF_3^+ from CF_3I . The solid line represents a smooth fit to the experimental data points.

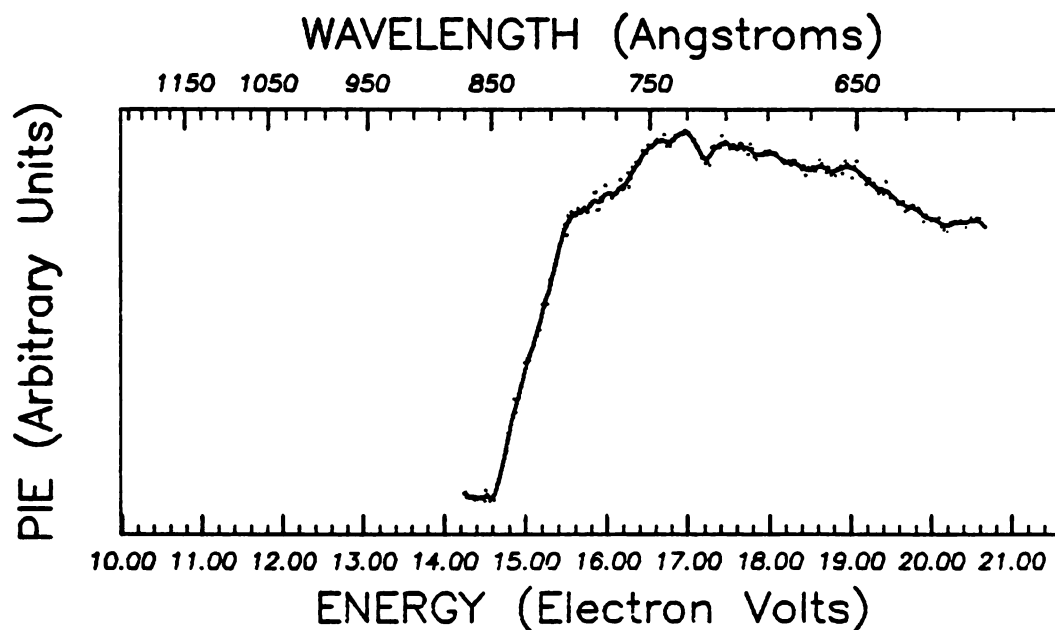


Figure 5A-5-6. PIE of CF_2I^+ from CF_3I . The solid line represents a smooth fit to the experimental data points.

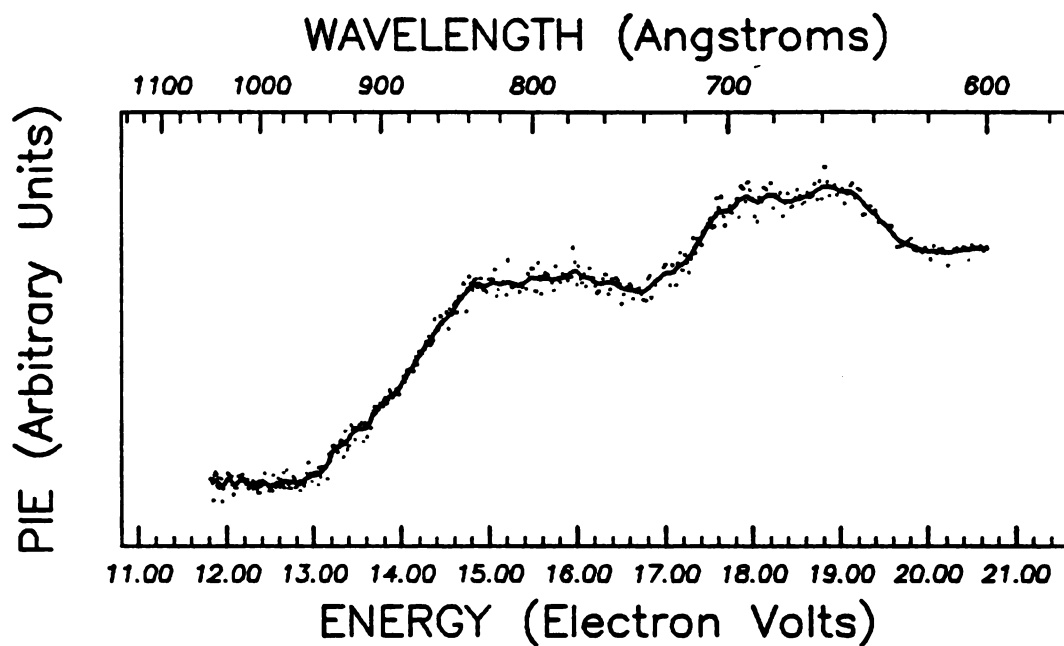


Figure 5A-5-7. PIE of I^+ from CF_3I . The solid line represents a smooth fit to the experimental data points.

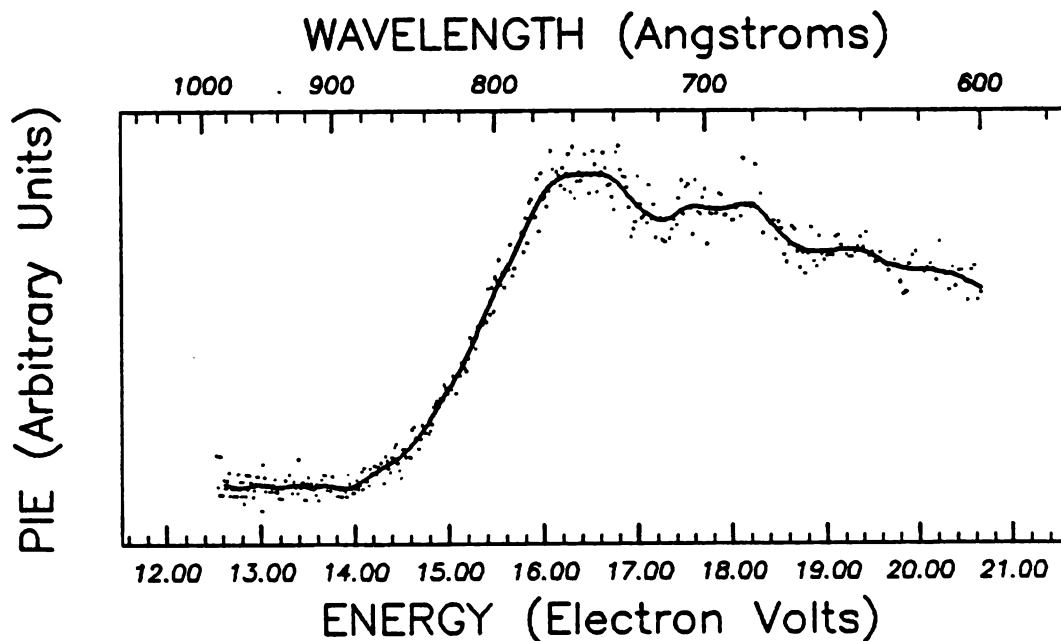
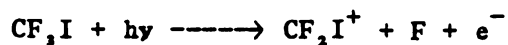


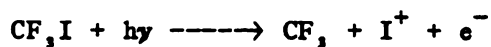
Figure 5A-5-8. PIE of FI^+ from CF_3I . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{I}^+)$ is calculated to be $180.07 \pm 2.8 \text{ kcal/mole}$.



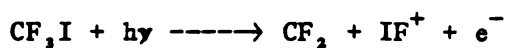
The PIE of the iodine cation is shown in Figure 5A-5-7. The AP value of this fragment ion is $12.93 \pm 0.3 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{I}^+)$ is calculated to be $270.47 \pm 8.7 \text{ kcal/mole}$.



The PIE of the dihalogen cation IF^+ is shown in Figure 5A-5-8. The AP value for this fragment ion is $14.12 \pm 0.3 \text{ eV}$; by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{IF}^+)$ is calculated to be $229.81 \pm 9.2 \text{ kcal/mole}$.



The last fragment ion is CF_2^+ , for which the PIE is shown in Figure 5A-5-9. The PIE shows a relatively smooth threshold at around 17 eV . The AP value of this fragment ion is $16.94 \pm 0.1 \text{ eV}$. From the reaction equation:

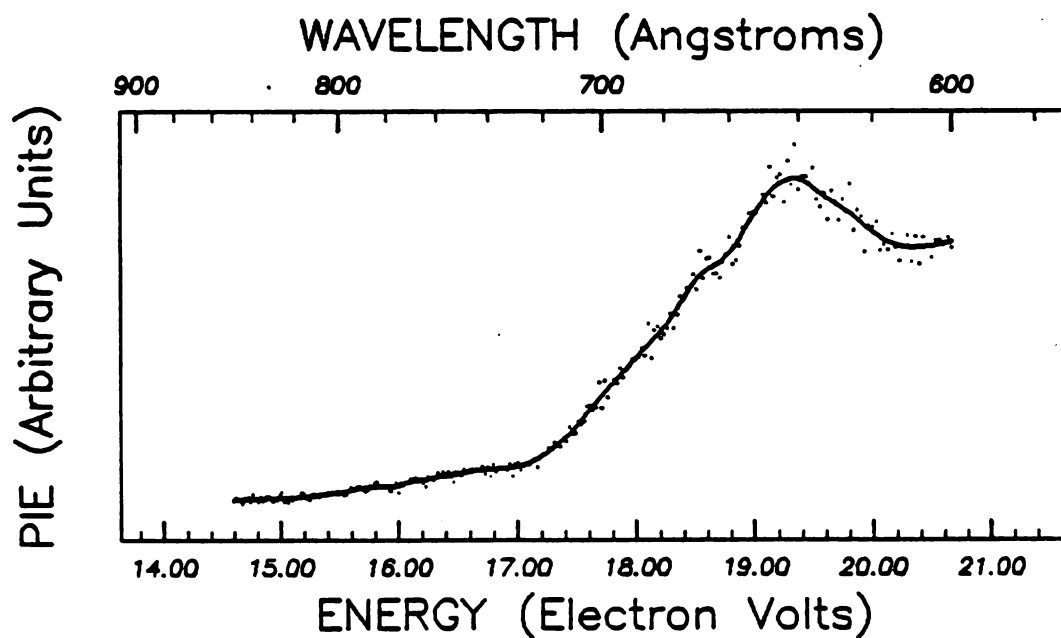
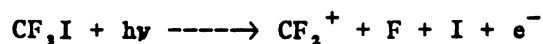


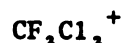
Figure 5A-5-9. PIE of CF_2^+ from CF_3I . The solid line represents a smooth fit to the experimental data points.



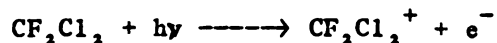
the value of $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is calculated to be $207.94 \pm 3.5 \text{ kcal/mole}$.

6. CF_2Cl_2

The photoionization mass spectrum of CF_2Cl_2 , obtained under full illumination of the helium continuum, is shown in Figure 5A-6-1. Relative intensities of the peaks and their assignments are presented in Table 5A-6-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-6-2, and the summary of thermochemical information for these ions is given in Table 5A-6-2.



The parent ion PIE is shown in Figure 5A-6-3, where it may be seen that the threshold starts to rise at about 11.80eV. Figure 5A-6-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $11.87 \pm 0.02 \text{ eV}$, which is slightly higher than and in a very good agreement with the previous literature value: 11.75eV.⁹² From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Cl}_2^+)$ is calculated to be $157.22 \pm 2.5 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-6-5. The PIE starts to rise sharply at threshold (near 11.80eV). The AP value of this fragment ion is $11.88 \pm 0.04 \text{ eV}$, which is

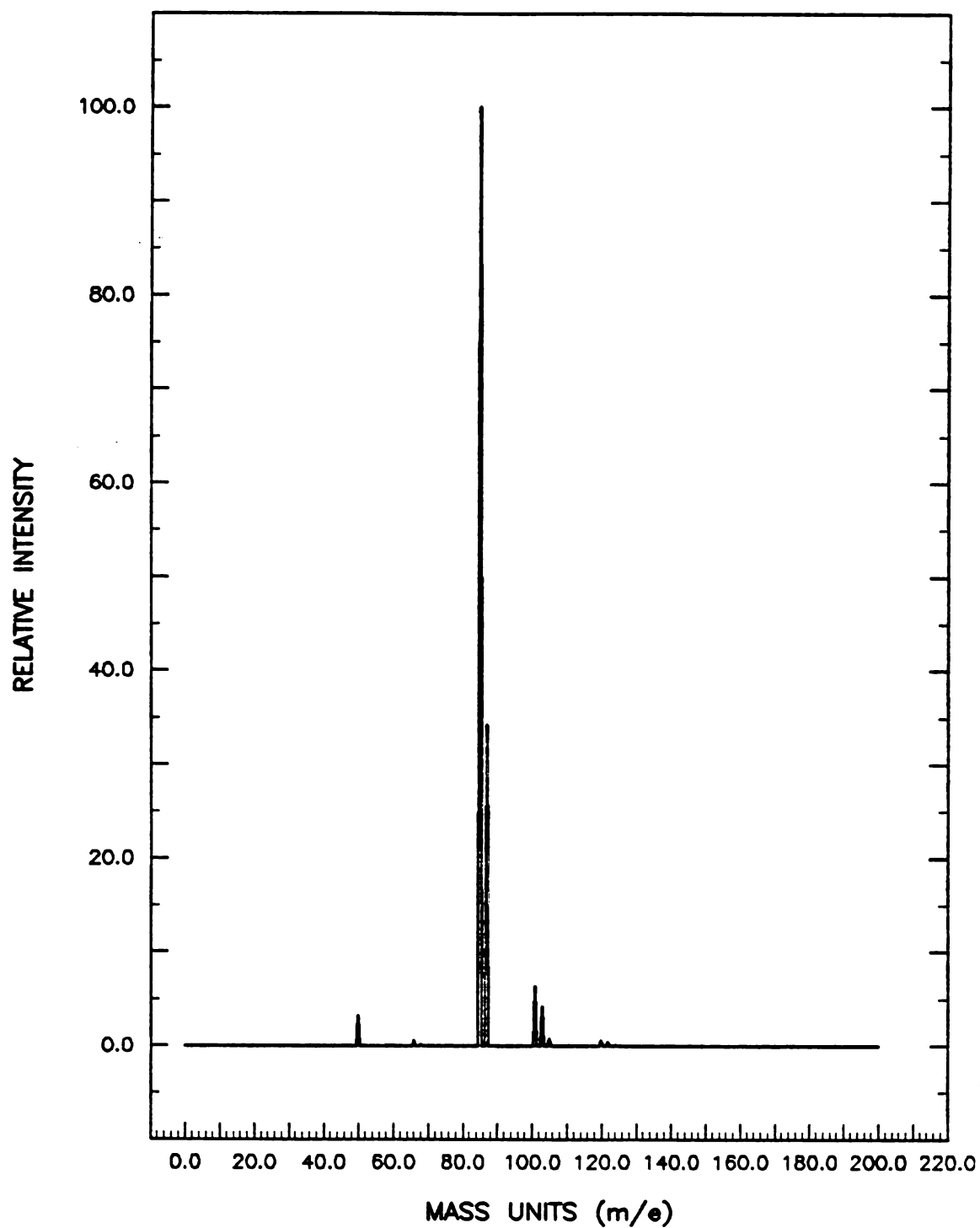


Figure 5A-6-1. Photoionization Mass Spectrum of CF₂Cl₂
(obtained under full illumination of the
helium discharge).

Table 5A-6-1. Photoionization Mass Spectrum of CF₂Cl₂^a

m/e	Intensity Relative to CF₂Cl⁺	Percent of Total Ion Production	Probable Formula
50	3.2	2.10	CF₂⁺
66	0.6	0.35	CF³⁵Cl⁺
68	0.2	0.11	CF³⁷Cl⁺
85	100.0	66.53	CF₂³⁵Cl⁺
87	34.2	22.78	CF₂³⁷Cl⁺
101	6.3	4.19	CF³⁵Cl₂⁺
103	4.2	2.78	CF³⁵Cl³⁷Cl⁺
105	0.8	0.53	CF³⁷Cl₂⁺
120	0.6	0.36	CF₂³⁵Cl₂⁺
122	0.4	0.23	CF₂³⁵Cl³⁷Cl⁺
124	0.1	0.04	CF₂³⁷Cl₂⁺

^aObtained under full illumination of the helium discharge.

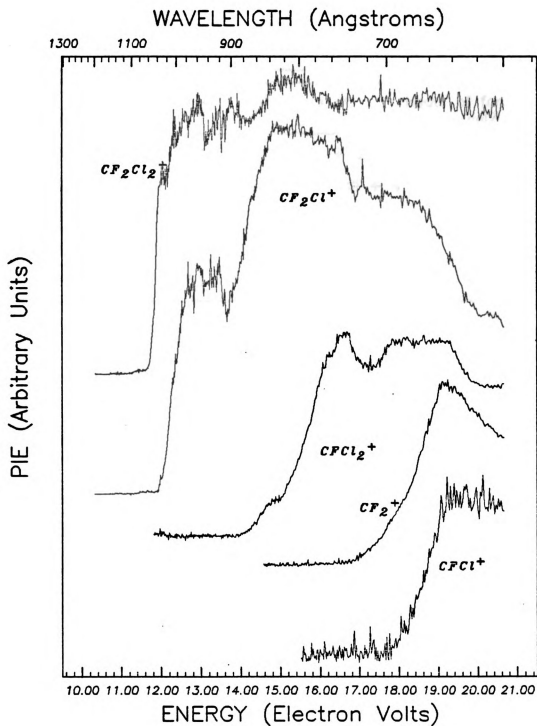


Figure 5A-6-2. Photoionization efficiency curves for parent and daughter ions from CF_2Cl_2 .

Table 5A-6-2. Summary of IP, AP and Heat of formation data for all ions from CF_2Cl_2 .

ION	IP or AP (eV) ^a	Products of $\text{CF}_2\text{Cl}_2 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_2Cl_2^+	11.87	$\text{CF}_2\text{Cl}_2^+ + e^-$	157.22
CF_2Cl^+	11.88	$\text{CF}_2\text{Cl}^+ + \text{Cl} + e^-$	128.93
CFCl_2^+	14.02	$\text{CFCl}_2^+ + \text{F} + e^-$	188.44
CFCl^+	17.76	$\text{CFCl}^+ + \text{F} + \text{Cl} + e^-$	246.17
CF_2^+	16.51	$\text{CF}_2^+ + \text{Cl} + \text{Cl} + e^-$	207.18

^asee text for uncertainties.

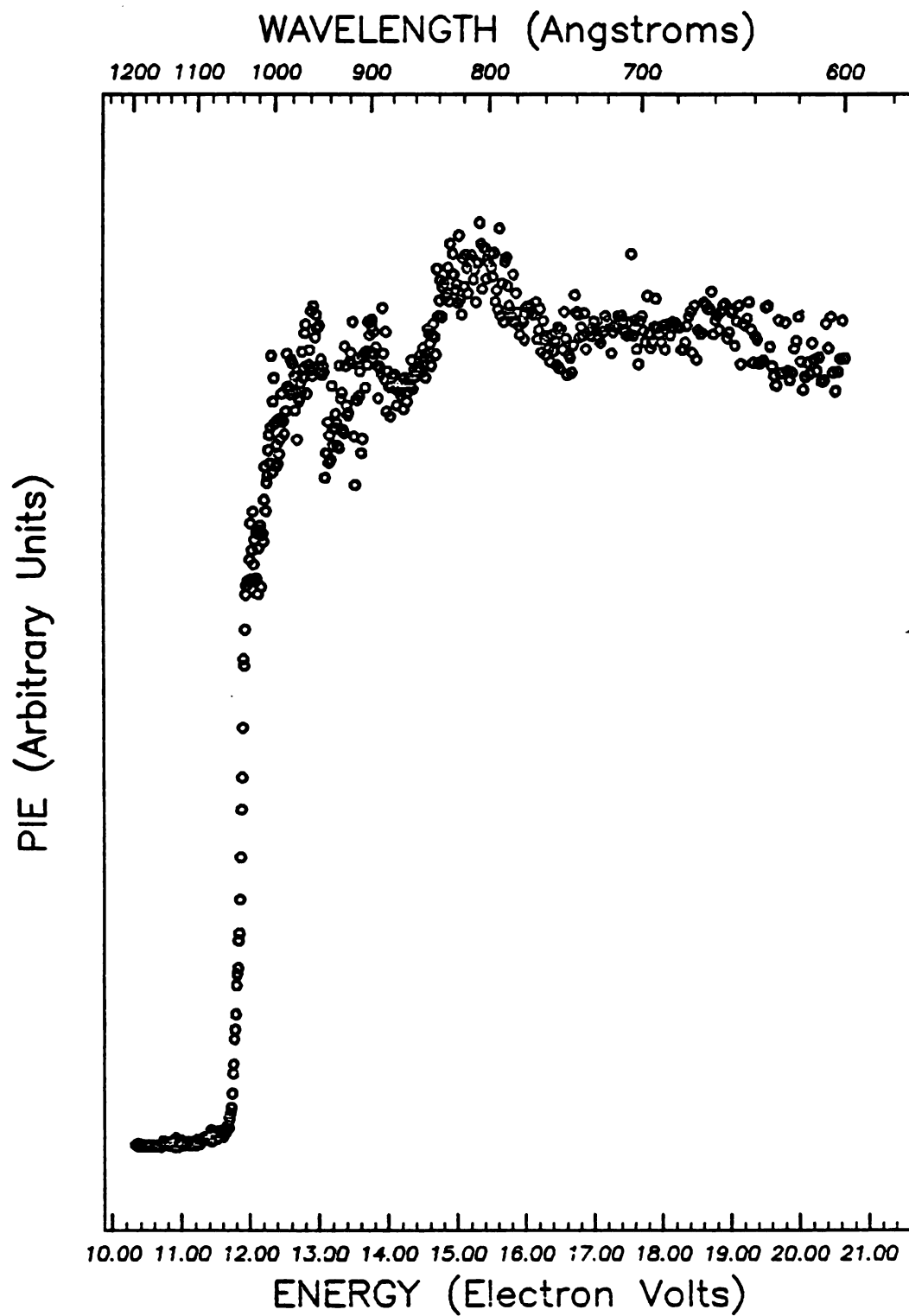


Figure 5A-6-3. PIE of CF_2Cl_2^+ from CF_2Cl_2 .

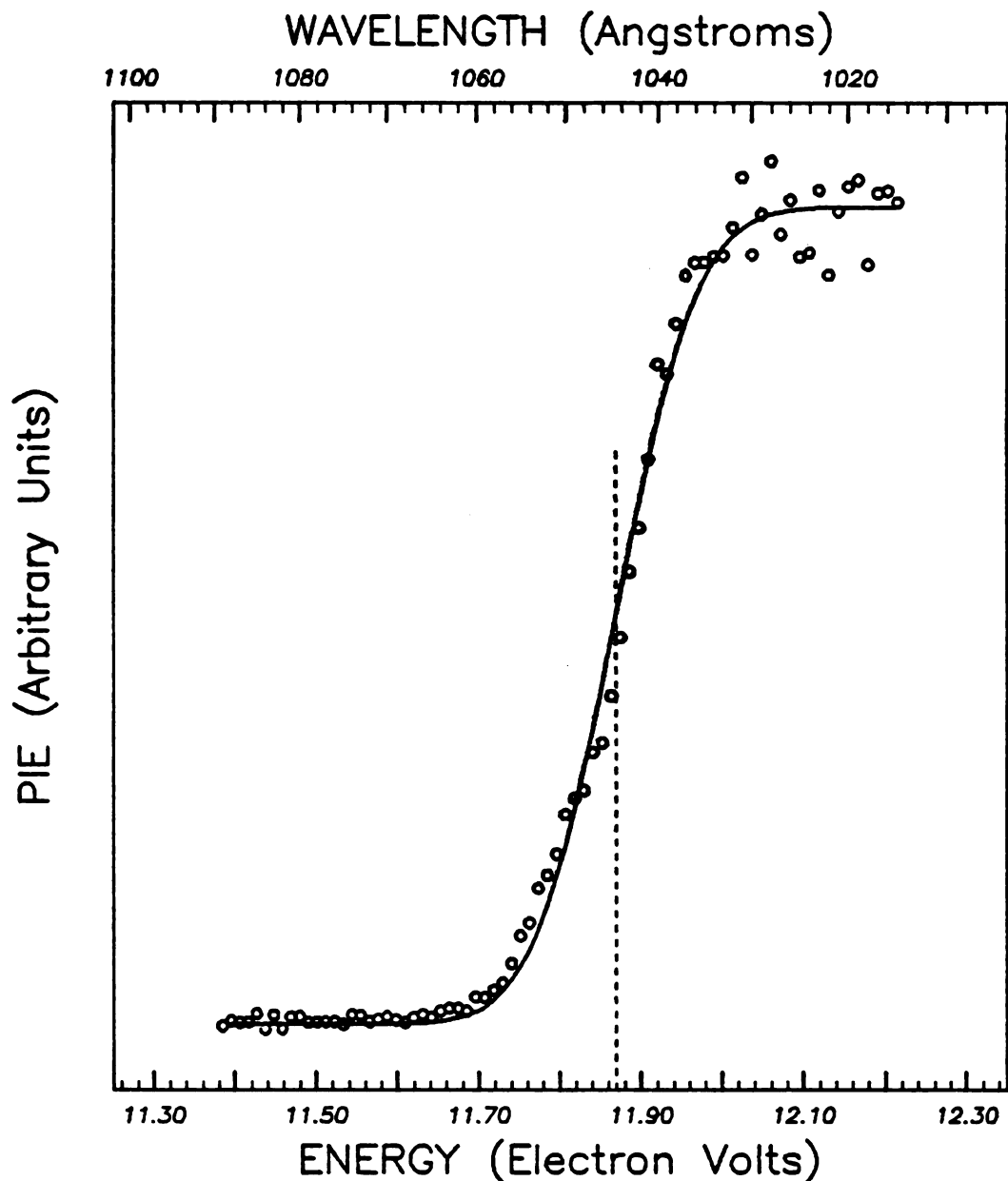


Figure 5A-6-4. PIE of CF_2Cl_2^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

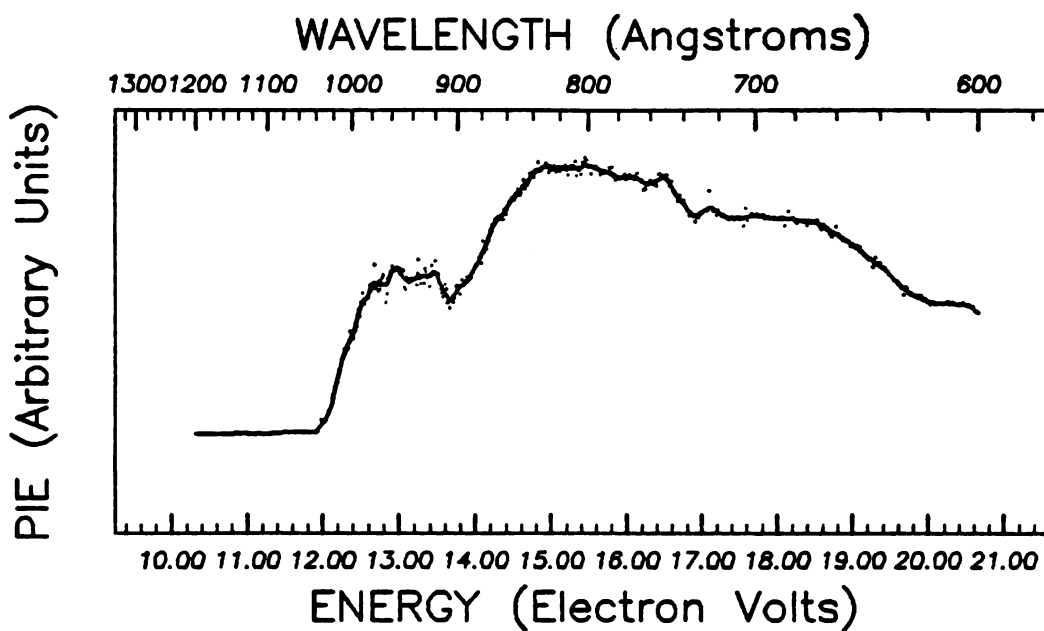


Figure 5A-6-5. PIE of CF_2Cl^+ from CF_2Cl_2 . The solid line represents a smooth fit to the experimental data points.

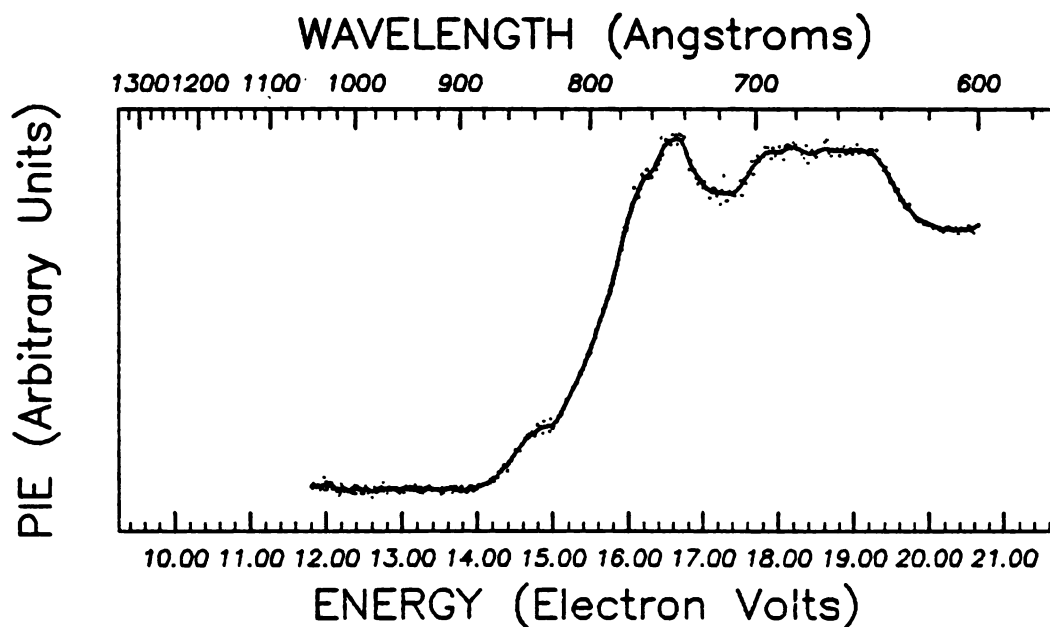
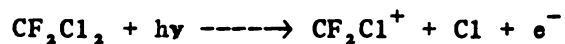


Figure 5A-6-6. PIE of CFCl_2^+ from CF_2Cl_2 . The solid line represents a smooth fit to the experimental data points.

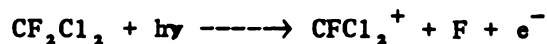
slightly lower than the previous literature value: $12.10 \pm 0.02 \text{ eV}$.⁹² From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Cl}^+)$ is calculated to be $128.93 \pm 2.9 \text{ kcal/mole}$.



The second fragment ion is CFCI_2^+ , for which the PIE is shown in Figure 5A-6-6. The PIE shows a threshold at around 14.0 eV . The AP value of this fragment ion is $14.02 \pm 0.07 \text{ eV}$, which is slightly lower than and in a good agreement with the previous literature value: 14.15 eV .⁹² By using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFCI}_2^+)$ is calculated to be $188.44 \pm 4.0 \text{ kcal/mole}$.



The fragment ion is CF_2^+ , for which the PIE is shown in Figure 5A-6-7. The PIE shows a relatively smooth threshold at around 16.5 eV . The AP value of this fragment ion is $16.51 \pm 0.07 \text{ eV}$, which is slightly lower than and in a satisfactory agreement with the previous literature value: 16.98 eV .⁹¹ From the reaction equation:

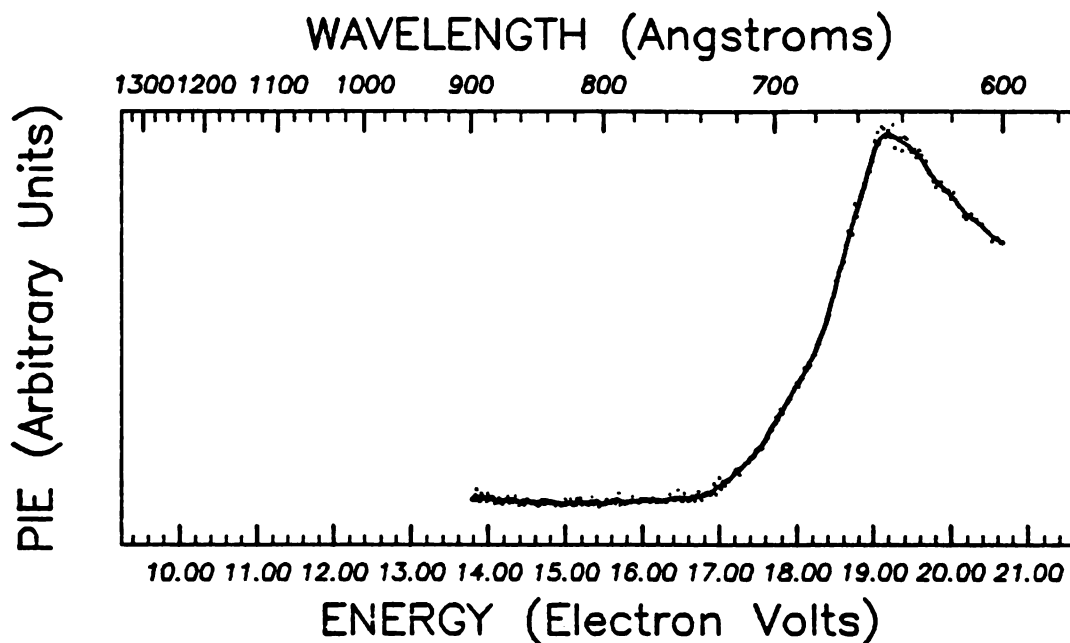


Figure 5A-6-7. PIE of CF_2^+ from CF_2Cl_2 . The solid line represents a smooth fit to the experimental data points.

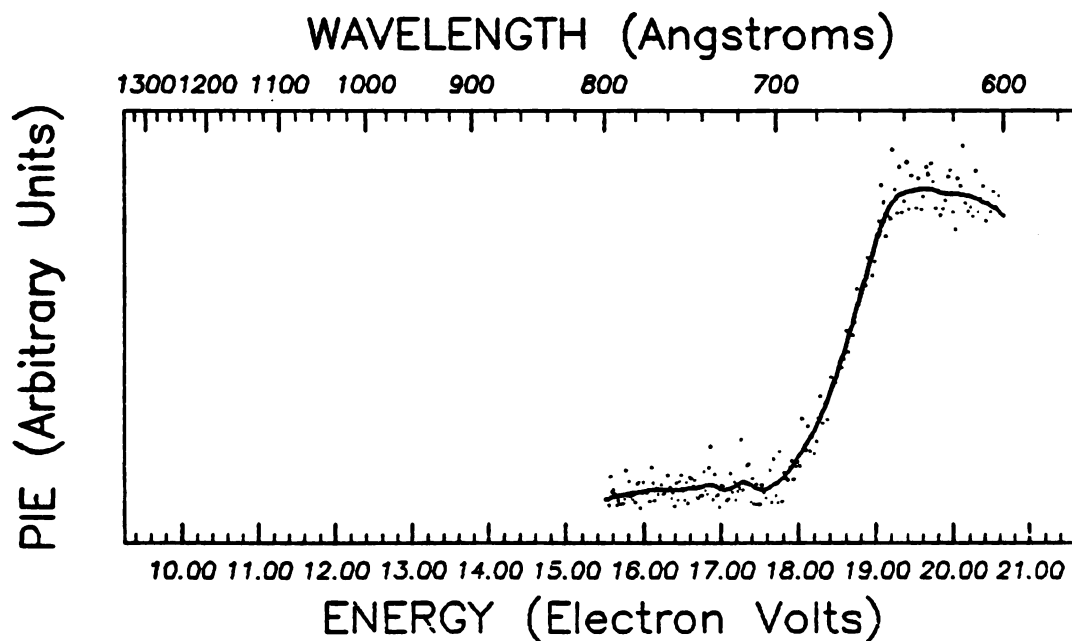
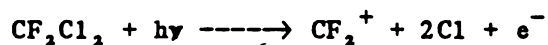


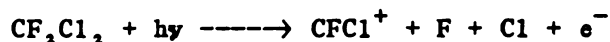
Figure 5A-6-8. PIE of CFC1^+ from CF_2Cl_2 . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^0(\text{CF}_2^+)$ is calculated to be $207.18 \pm 3.7 \text{ kcal/mole}$.



The last fragment ion is CFC1^+ , for which the PIE is shown in Figure 5A-6-8. The PIE shows a relatively smooth threshold at around 17.7eV. The AP value of this fragment ion is $17.76 \pm 0.3 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^0(\text{CFC1}^+)$ is calculated to be $246.17 \pm 8.4 \text{ kcal/mole}$.

7. CFC1_2

The photoionization mass spectrum of CFC1_2 , obtained under full illumination of the helium continuum, is shown in Figure 5A-7-1. Relative intensities of the peaks and their assignments are presented in Table 5A-7-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-7-2, and the summary of thermochemical information for these ions is given in Table 5A-7-2.



The parent ion PIE is shown in Figure 5A-7-3, where it may be seen that the threshold starts to rise at about 11.4eV. Figure 5A-4-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $11.46 \pm 0.02 \text{ eV}$, which is slightly lower than and in a satisfactory agreement with the previous literature value: 11.85 eV .⁹²

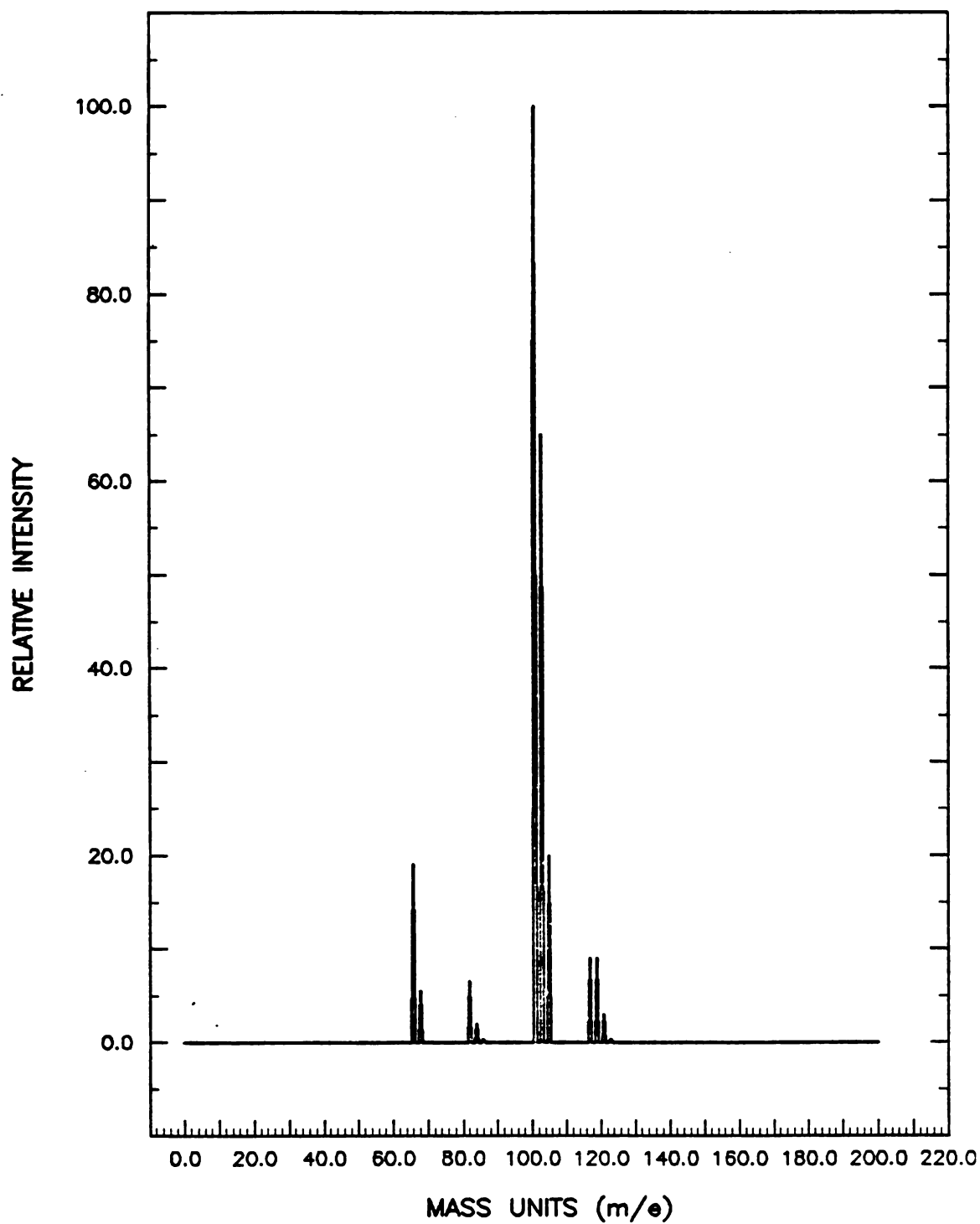


Figure 5A-7-1. Photoionization Mass Spectrum of CFCl_3 (obtained under full illumination of the helium discharge).

Table 5A-7-1. Photoionization Mass Spectrum of CFCl_3 ^a

m/e	Intensity Relative to CFCl_2^+	Percent of Total Ion Production	Probable Formula
66	19.0	7.92	$\text{CF}^{35}\text{Cl}^+$
68	5.5	2.29	$\text{CF}^{37}\text{Cl}^+$
82	6.5	2.71	$\text{C}^{35}\text{Cl}_2^+$
84	2.0	0.83	$\text{C}^{35}\text{Cl}^{37}\text{Cl}^+$
86	0.3	0.13	$\text{C}^{37}\text{Cl}_2^+$
101	100.0	41.72	$\text{CF}^{35}\text{Cl}_2^+$
103	65.0	27.12	$\text{CF}^{35}\text{Cl}^{37}\text{Cl}^+$
105	20.0	8.34	$\text{CF}^{37}\text{Cl}_2^+$
117	9.0	3.75	$\text{C}^{35}\text{Cl}_3^+$
119	9.0	3.75	$\text{C}^{35}\text{Cl}_2^{37}\text{Cl}^+$
121	3.0	1.25	$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2^+$
123	0.4	0.17	$\text{C}^{37}\text{Cl}_3^+$
136	trace		$\text{CF}^{35}\text{Cl}_3^+$
138	trace		$\text{CF}^{35}\text{Cl}_2^{37}\text{Cl}^+$
140	trace		$\text{CF}^{35}\text{Cl}^{37}\text{Cl}_2^+$
142	trace		$\text{CF}^{37}\text{Cl}_3^+$

^aObtained under full illumination of the helium discharge.

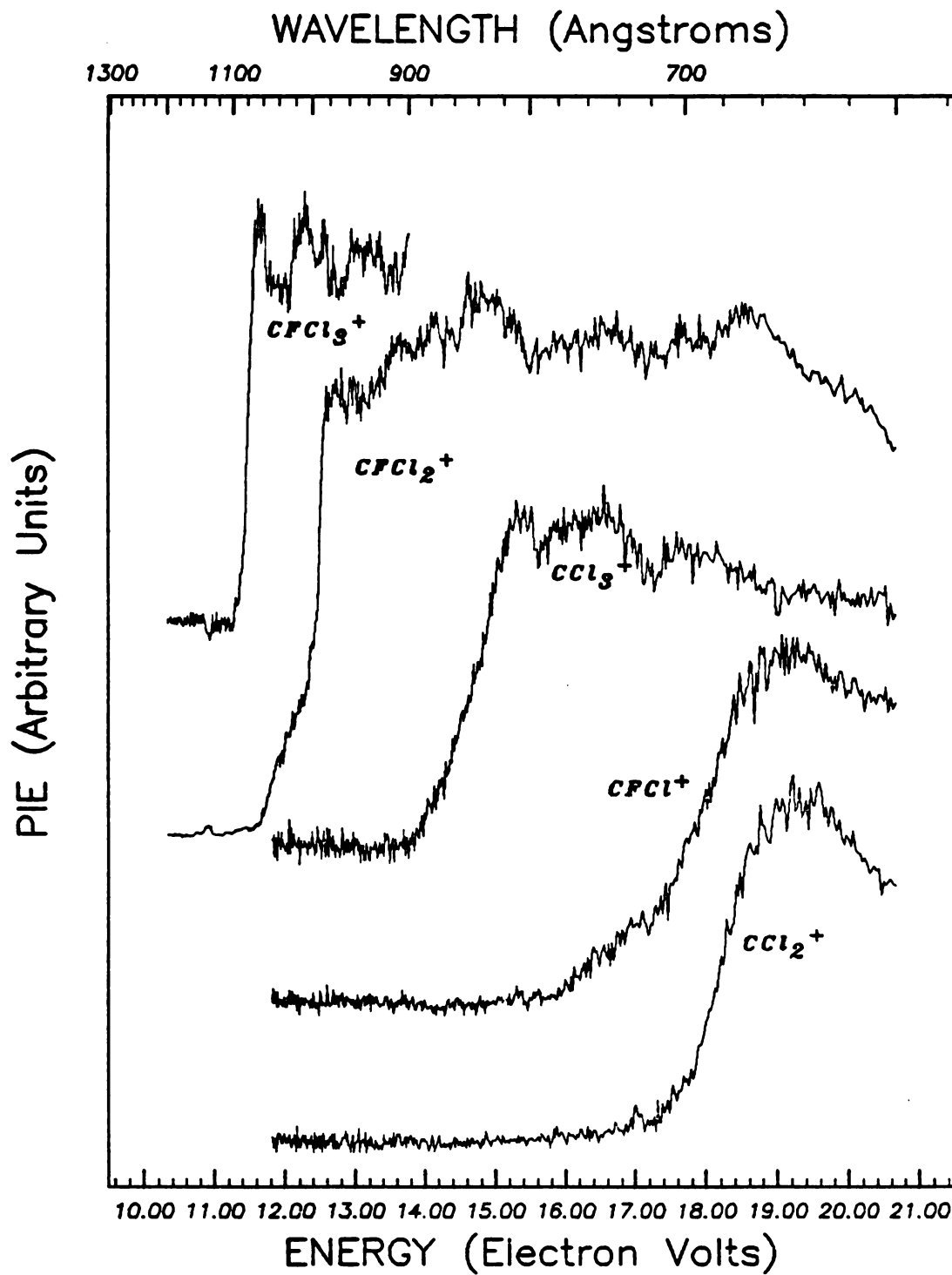


Figure 5A-7-2. Photoionization efficiency curves for parent and daughter ions from CFCl_3 .

Table 5A-7-2. Summary of IP, AP and Heat of formation data for all ions from CFCl_3 .

ION	IP or AP (eV) ^a	Products of $\text{CFCl}_3 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CFCl_3^+	11.46	$\text{CFCl}_3^+ + e^-$	196.03
CFCl_2^+	11.52	$\text{CFCl}_2^+ + \text{Cl} + e^-$	168.89
CCl_3^+	13.59	$\text{CCl}_3^+ + \text{F} + e^-$	226.79
CCl_2^+	16.40	$\text{CCl}_2^+ + \text{F} + \text{Cl} + e^-$	263.06
CFCl^+	15.50	$\text{CFCl}^+ + \text{Cl} + \text{Cl} + e^-$	231.35

^asee text for uncertainties.

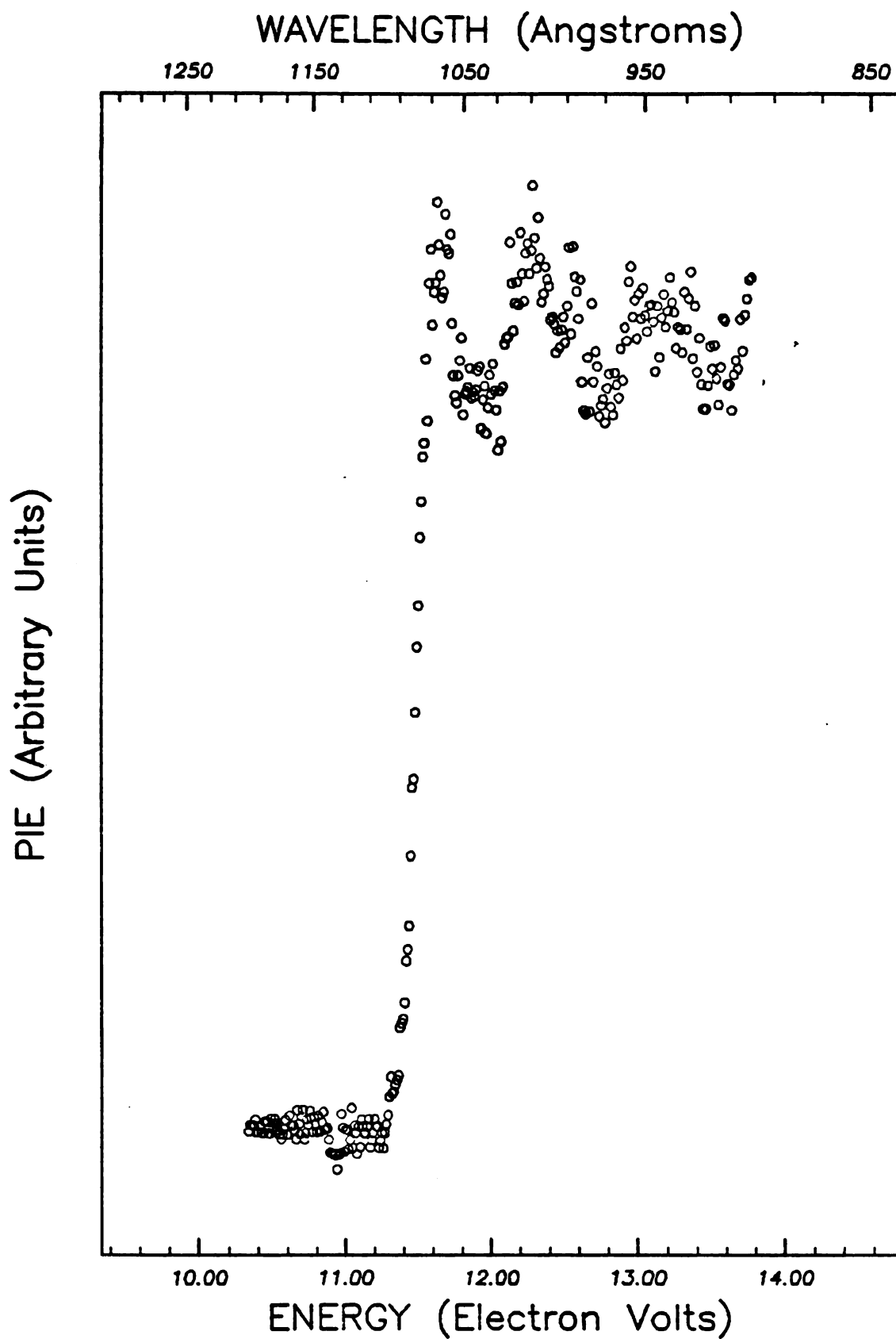


Figure 5A-7-3. PIE of CFCl_3^+ from CFCl_3 .

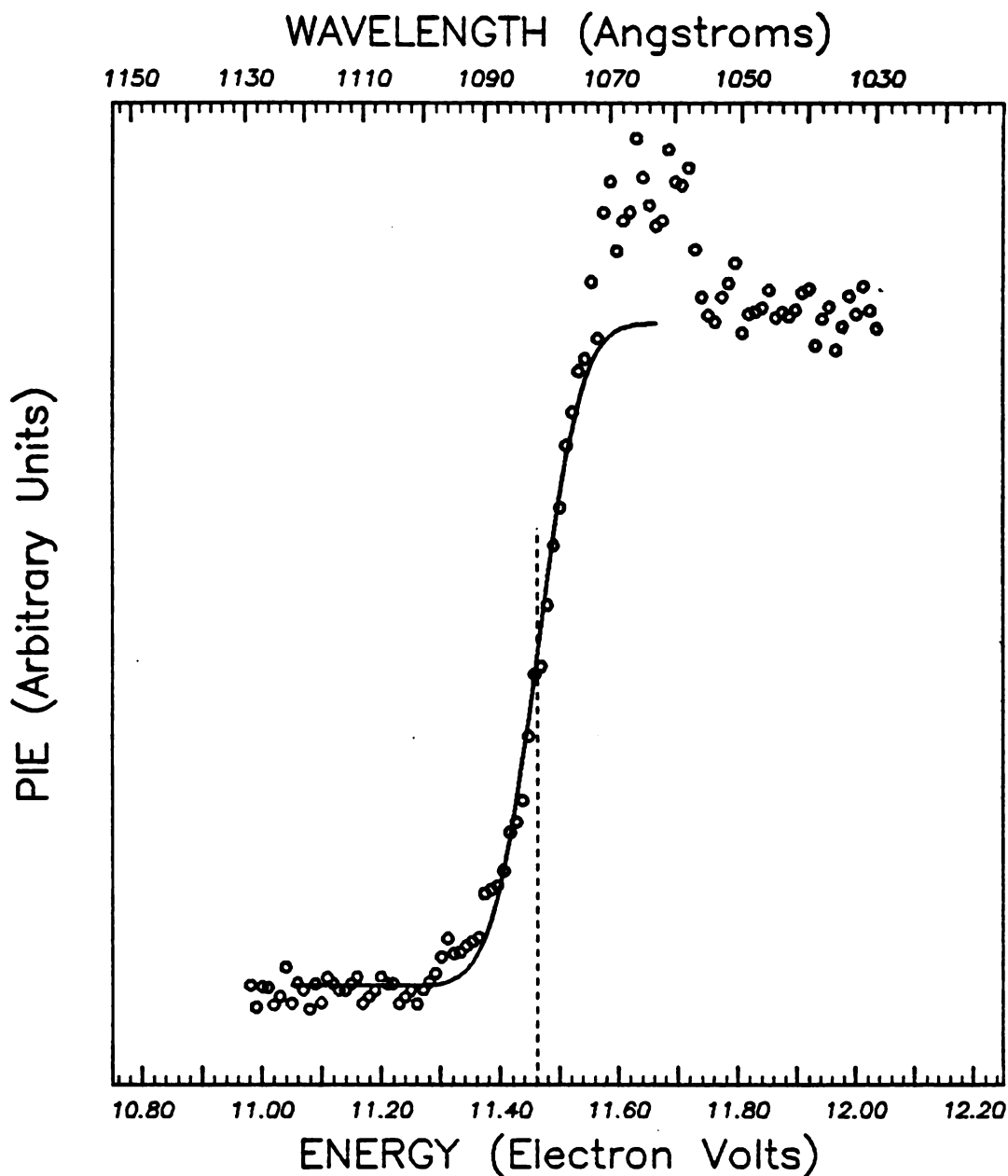


Figure 5A-7-4. PIE of CFCl_3^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

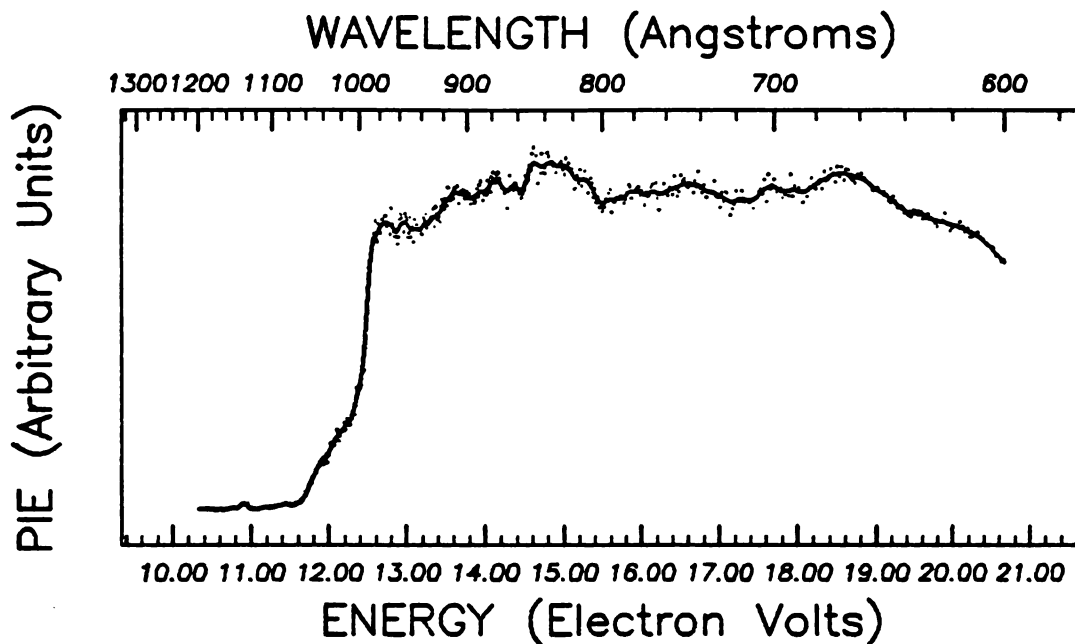


Figure 5A-7-5. PIE of CFCl_2^+ from CFCl_3 . The solid line represents a smooth fit to the experimental data points.

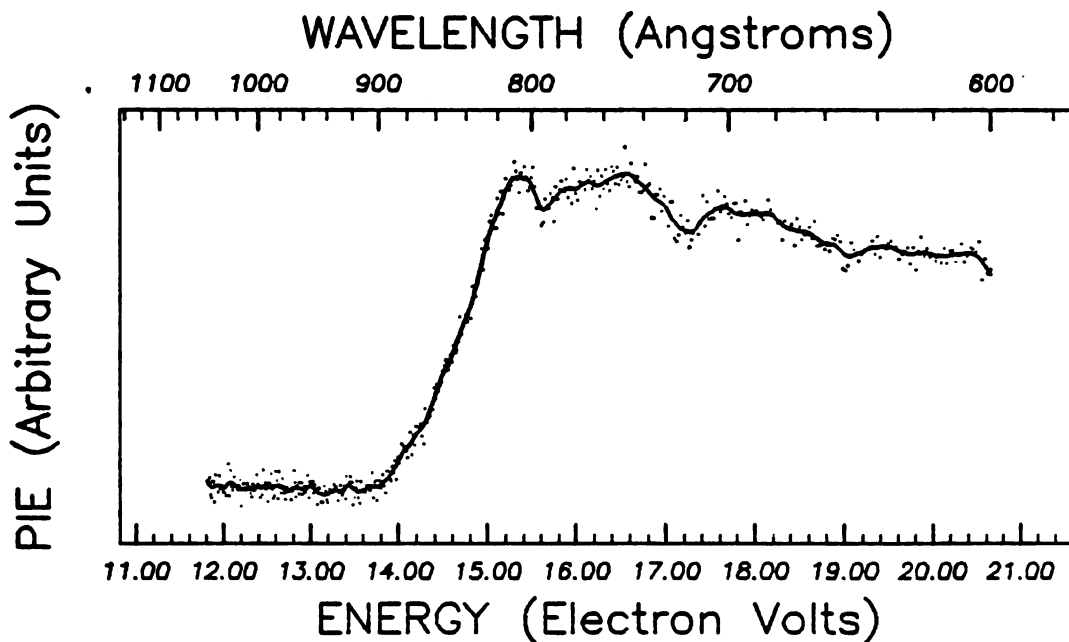
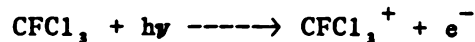


Figure 5A-7-6. PIE of CCl_3^+ from CFCl_3 . The solid line represents a smooth fit to the experimental data points.

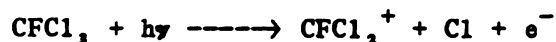
From the reaction equation:



the value of $\Delta H_{f0}^0(\text{CFCl}_2^+)$ is calculated to be $196.03 \pm 2.0 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-7-5. The PIE starts to rise sharply at threshold (near 11.5eV), and the PIE curve shows two steps. The AP value of this fragment ion is $11.52 \pm 0.02 \text{ eV}$, which is slightly lower than and in a good agreement with the previous literature: value 11.65eV.⁹² From the reaction equation:



the value of $\Delta H_{f0}^0(\text{CFCl}_2^+)$ is calculated to be $168.89 \pm 3.1 \text{ kcal/mole}$.



The second fragment ion is CCl_2^+ , for which the PIE is shown in Figure 5A-7-6. The PIE shows a relatively smooth threshold at around 13.5eV. The AP value of this fragment ion is $13.59 \pm 0.1 \text{ eV}$, which is slightly higher than and in a very good agreement with the previous literature value: 13.5eV.⁹⁵ From the reaction equation:

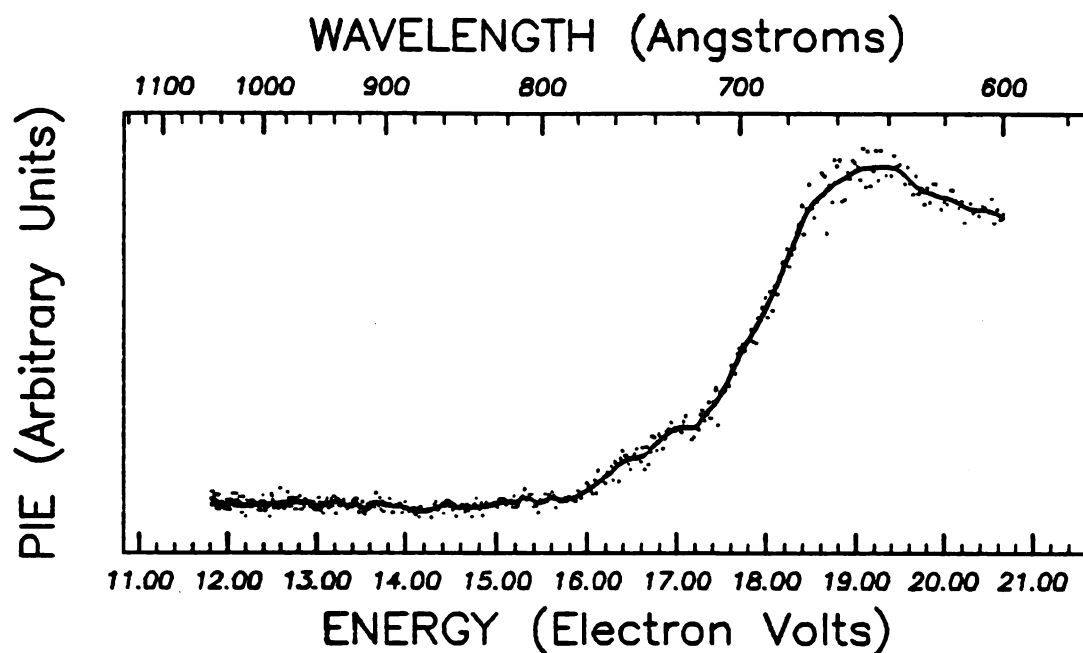


Figure 5A-7-7. PIE of CFCl^+ from CFCl_3 . The solid line represents a smooth fit to the experimental data points.

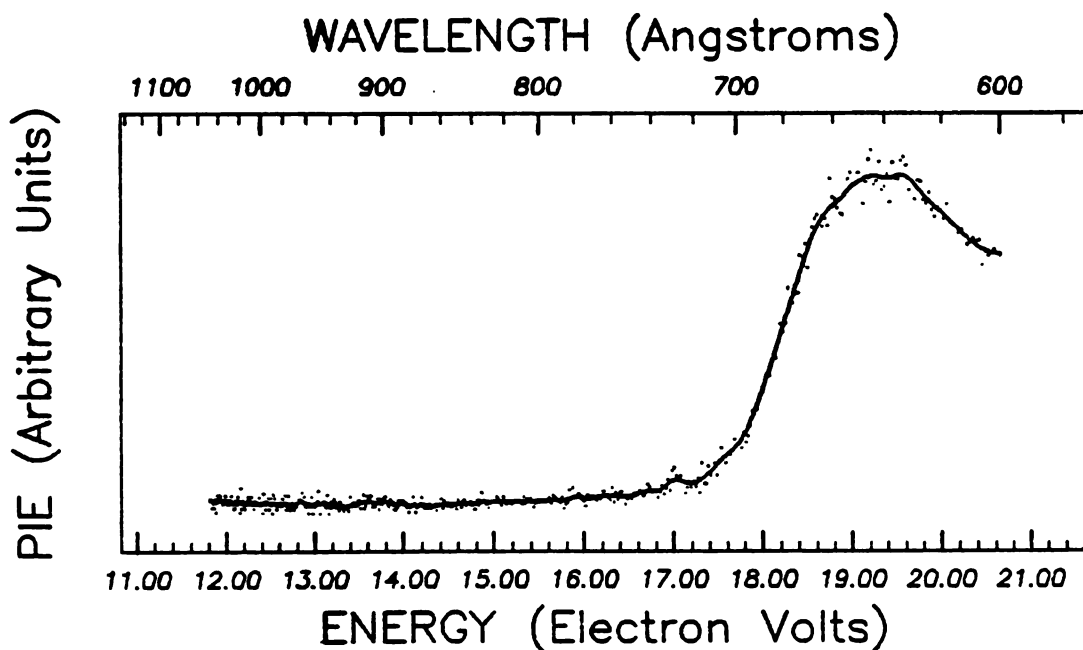
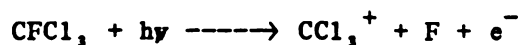


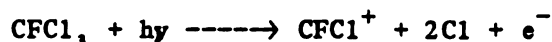
Figure 5A-7-8. PIE of CCl_2^+ from CFCl_3 . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CCl}_3^+)$ is calculated to be $226.79 \pm 4.2 \text{ kcal/mole}$.



The next fragment ion is CFCI^+ , for which the PIE is shown in Figure 5A-7-7. The AP value of this fragment ion is $15.50 \pm 0.3 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFCI}^+)$ is calculated to be $231.35 \pm 8.5 \text{ kcal/mole}$.



The last fragment ion is CCl_2^+ , for which the PIE is shown in Figure 5A-7-8. The PIE shows a relatively smooth threshold at around 16.4 eV . The AP value of this fragment ion is $16.40 \pm 0.1 \text{ eV}$, which is slightly lower than and in a reasonable agreement with previous literature value: 17.0 eV .⁹² By using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CCl}_2^+)$ is calculated to be $263.06 \pm 4.2 \text{ kcal/mole}$.

8. CCl_4

The photoionization mass spectrum of CCl_4 , obtained under full illumination of the helium continuum, is shown in Figure 5A-8-1. No parent ion is detectable. Relative intensities of the peaks and their

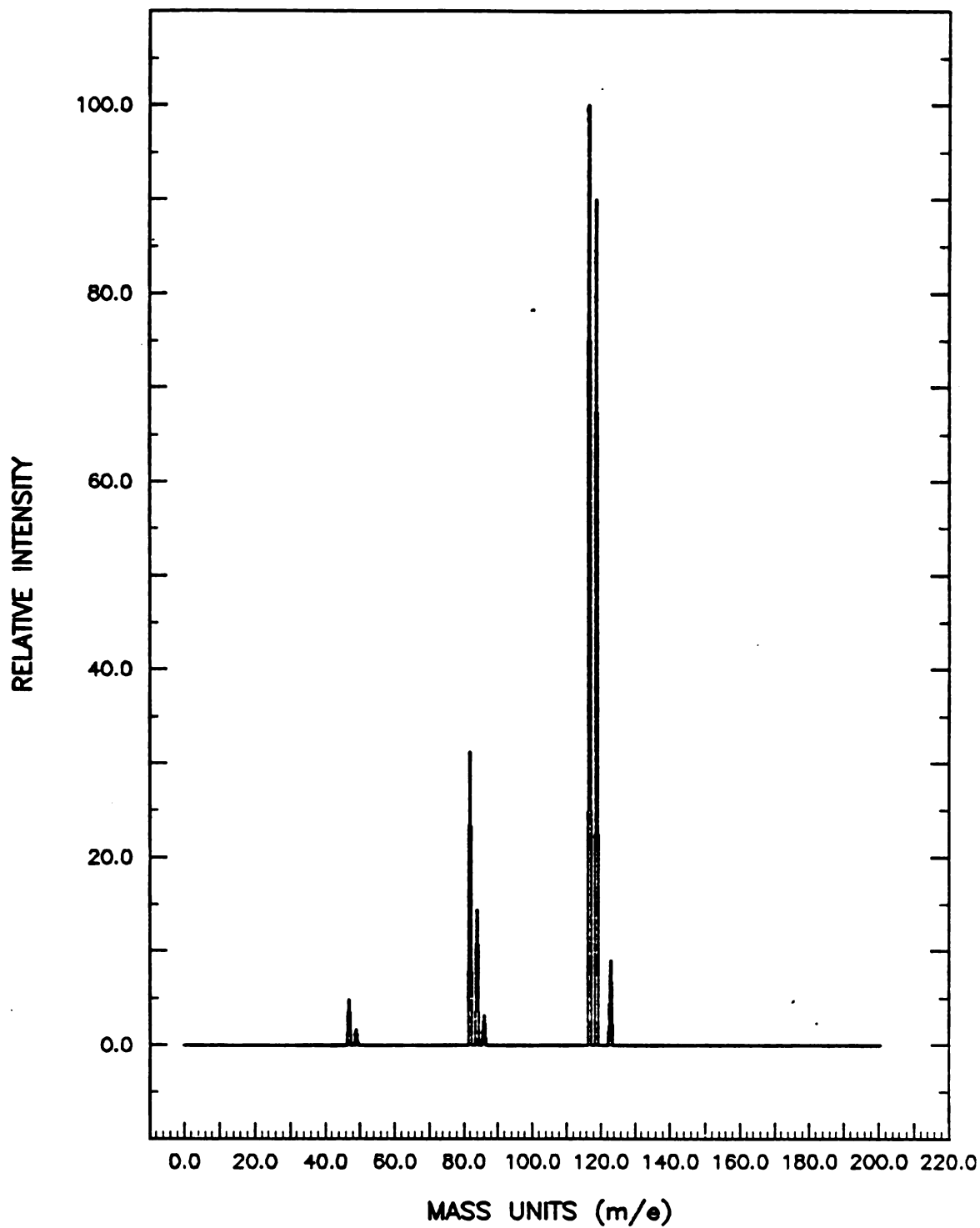


Figure 5A-8-1. Photoionization Mass Spectrum of CCl₄
(obtained under full illumination of the
helium discharge).

Table 5A-8-1. Photoionization Mass Spectrum of CCl_4^a

m/e	Intensity Relative to CCl_3^+	Percent of Total Ion Production	Probable Formula
47	4.8	1.59	C^{35}Cl^+
49	1.6	0.53	C^{37}Cl^+
82	31.2	10.36	$\text{C}^{35}\text{Cl}_2^+$
84	14.4	4.78	$\text{C}^{35}\text{Cl}^{37}\text{Cl}^+$
86	3.2	1.06	$\text{C}^{37}\text{Cl}_2^+$
117	100.0	33.20	$\text{C}^{35}\text{Cl}_3^+$
119	90.0	29.88	$\text{C}^{35}\text{Cl}_2^{37}\text{Cl}^+$
121	47.0	15.60	$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2^+$
123	9.0	2.98	$\text{C}^{37}\text{Cl}_3^+$

^aObtained under full illumination of the helium discharge.Table 5A-8-2. Summary of IP, AP and Heat of formation data for all ions from CCl_4 .

ION	IP or AP (eV) ^a	Products of $\text{CCl}_4 + \text{h}\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CCl_3^+	11.46	$\text{CCl}_3^+ + \text{Cl} + \text{e}^-$	213.42
CCl_2^+	14.74	$\text{CCl}_2^+ + \text{Cl} + \text{Cl} + \text{e}^-$	260.46

^asee text for uncertainties.

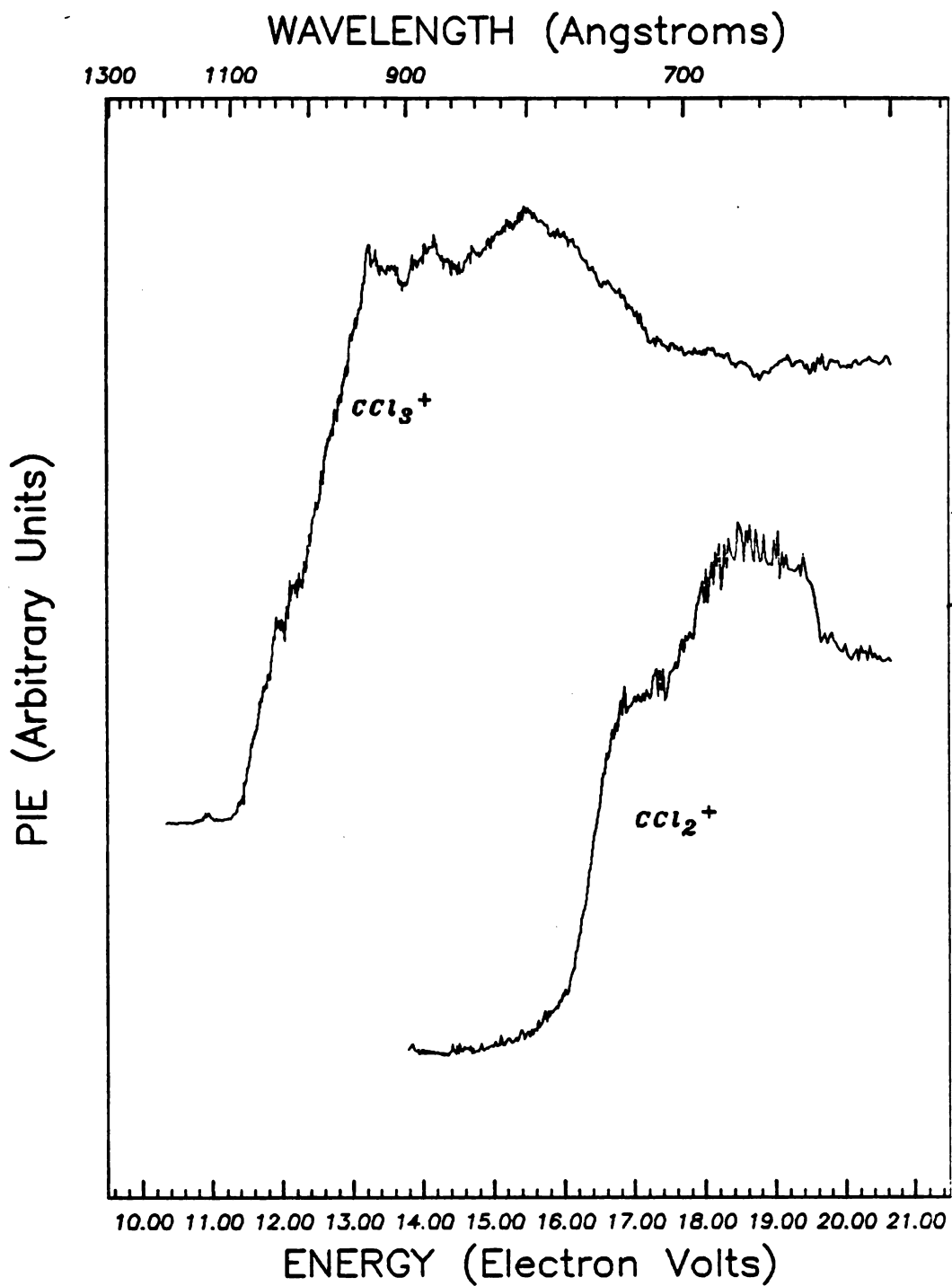


Figure 5A-8-2. Photoionization efficiency curves for daughter ions from CCl_4 (no parent ion is detectable).

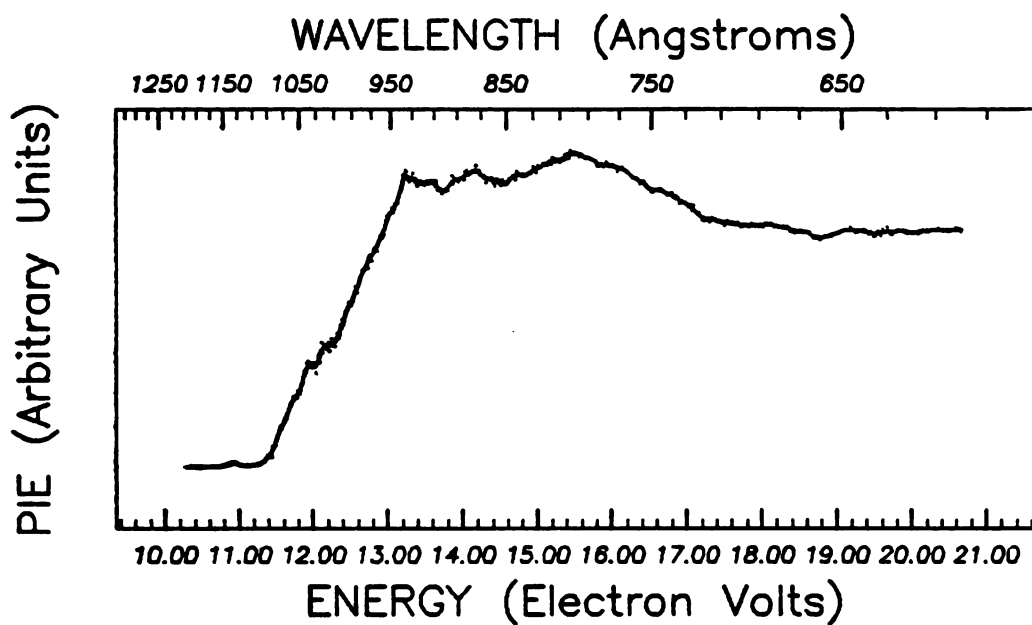


Figure 5A-8-3. PIE of CCl_3^+ from CCl_4 . The solid line represents a smooth fit to the experimental data points.

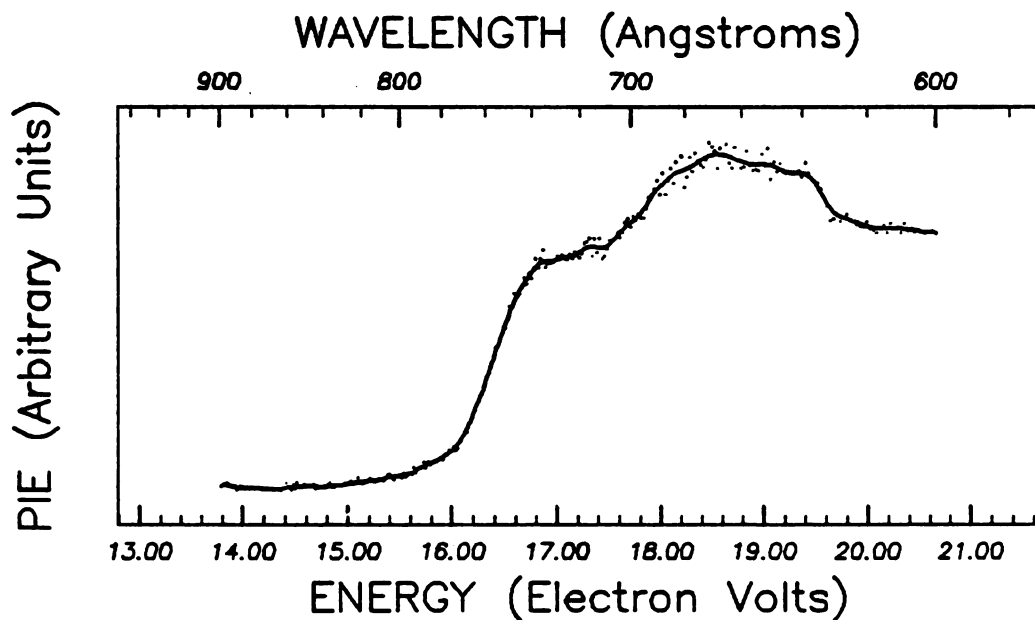
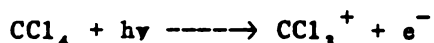


Figure 5A-8-4. PIE of CCl_2^+ from CCl_4 . The solid line represents a smooth fit to the experimental data points.

assignments are presented in Table 5A-8-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-8-2, and the summary of thermochemical information for these ions is given in Table 5A-8-2.



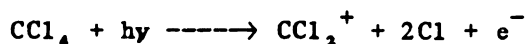
The first, lowest photon energy fragment PIE curve is shown in Figure 5A-8-3. The PIE starts to rise sharply at threshold (near 11.46 eV), and the PIE curve shows two steps. The AP value of this fragment ion is 11.46 ± 0.04 eV, which is slightly higher than and in a good agreement with the previous literature value 11.28 ± 0.03 eV.⁹⁶ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CCl}_3^+)$ is calculated to be 213.43 ± 1.5 kcal/mole.



The second fragment ion is CCl_2^+ , for which the PIE is shown in Figure 5A-8-4. The PIE shows a relatively smooth threshold at around 14.7 eV. The AP value of this fragment ion is 14.74 ± 0.07 eV, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CCl}_2^+)$ is calculated to be 260.46 ± 2.2 kcal/mole.

9. CCl_3Br

The photoionization mass spectrum of CCl_3Br , obtained under full

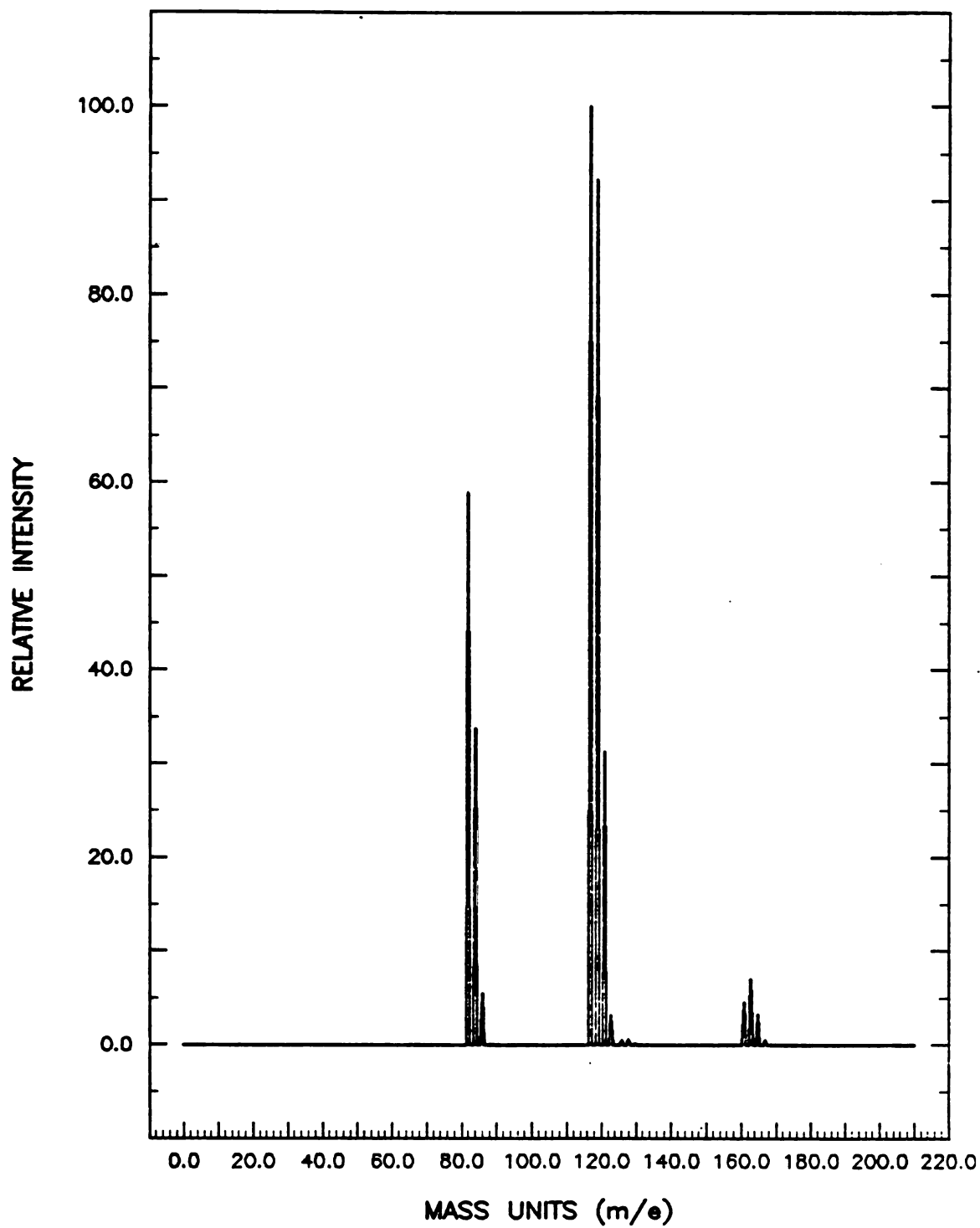


Figure 5A-9-1. Photoionization Mass Spectrum of CCl_3Br (obtained under full illumination of the helium discharge).

Table 5A-9-1. Photoionization Mass Spectrum of CCl_3Br^a

m/e	Intensity Relative to CCl_3^+	Percent of Total Ion Production	Probable Formula
82	58.9	17.26	$\text{C}^{35}\text{Cl}_2^+$
84	33.8	9.89	$\text{C}^{35}\text{Cl}^{37}\text{Cl}^+$
86	5.5	1.60	$\text{C}^{37}\text{Cl}_2^+$
117	100.0	29.30	$\text{C}^{35}\text{Cl}_3^+$
119	92.2	27.02	$\text{C}^{35}\text{Cl}_2^{37}\text{Cl}^+$
121	31.2	9.16	$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2^+$
123	3.1	0.92	$\text{C}^{37}\text{Cl}_3^+$
126	0.5	0.14	$\text{C}^{35}\text{Cl}^{79}\text{Br}^+$
128	0.6	0.18	$\text{C}^{35}\text{Cl}^{81}\text{Br}^+, \text{C}^{37}\text{Cl}^{79}\text{Br}^+$
130	0.2	0.05	$\text{C}^{37}\text{Cl}^{81}\text{Br}^+$
161	4.5	1.32	$\text{C}^{35}\text{Cl}_2^{79}\text{Br}^+$
163	7.0	2.06	$\text{C}^{35}\text{Cl}_2^{81}\text{Br}^+, \text{C}^{35}\text{Cl}^{37}\text{Cl}^{79}\text{Br}^+$
165	3.3	0.96	$\text{C}^{37}\text{Cl}_2^{79}\text{Br}^+, \text{C}^{35}\text{Cl}^{37}\text{Cl}^{81}\text{Br}^+$
167	0.5	0.14	$\text{C}^{37}\text{Cl}_2^{81}\text{Br}^+$
196	trace		$\text{C}^{35}\text{Cl}_3^{79}\text{Br}^+$
198	trace		$\text{C}^{35}\text{Cl}_3^{81}\text{Br}^+, \text{C}^{35}\text{Cl}_2^{37}\text{Cl}^{79}\text{Br}^+$
200	trace		$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2^{79}\text{Br}^+, \text{C}^{35}\text{Cl}_2^{37}\text{Cl}^{81}\text{Br}^+$
202	trace		$\text{C}^{37}\text{Cl}_3^{79}\text{Br}^+, \text{C}^{35}\text{Cl}^{37}\text{Cl}_2^{81}\text{Br}^+$
204	trace		$\text{C}^{37}\text{Cl}_3^{81}\text{Br}^+$

^aObtained under full illumination of the helium discharge.

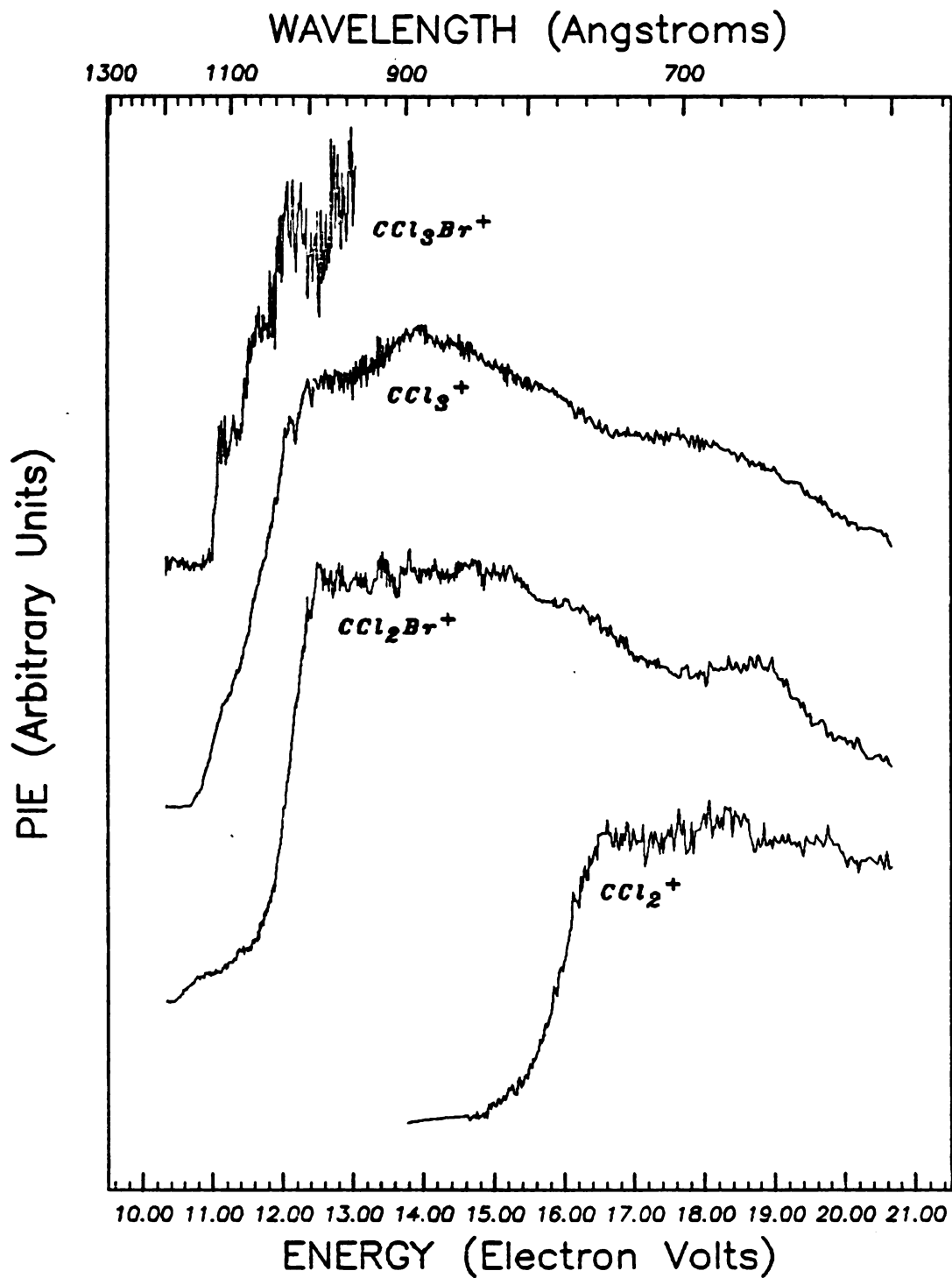


Figure 5A-9-2. Photoionization efficiency curves for parent and daughter ions from CCl_3Br .

Table 5A-9-2. Summary of IP, AP and Heat of formation data for all ions from CCl_3Br .

ION	IP or AP (eV) ^a	Products of $\text{CCl}_3\text{Br} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CCl_3Br^+	11.05	$\text{CCl}_3\text{Br}^+ + e^-$	243.81
CCl_3^+	10.71	$\text{CCl}_3^+ + \text{Br} + e^-$	207.78
CCl_2Br^+	11.39	$\text{CCl}_2\text{Br}^+ + \text{Cl} + e^-$	223.13
CCl_2^+	13.95	$\text{CCl}_2^+ + \text{Cl} + \text{Br} + e^-$	253.98

^asee text for uncertainties.

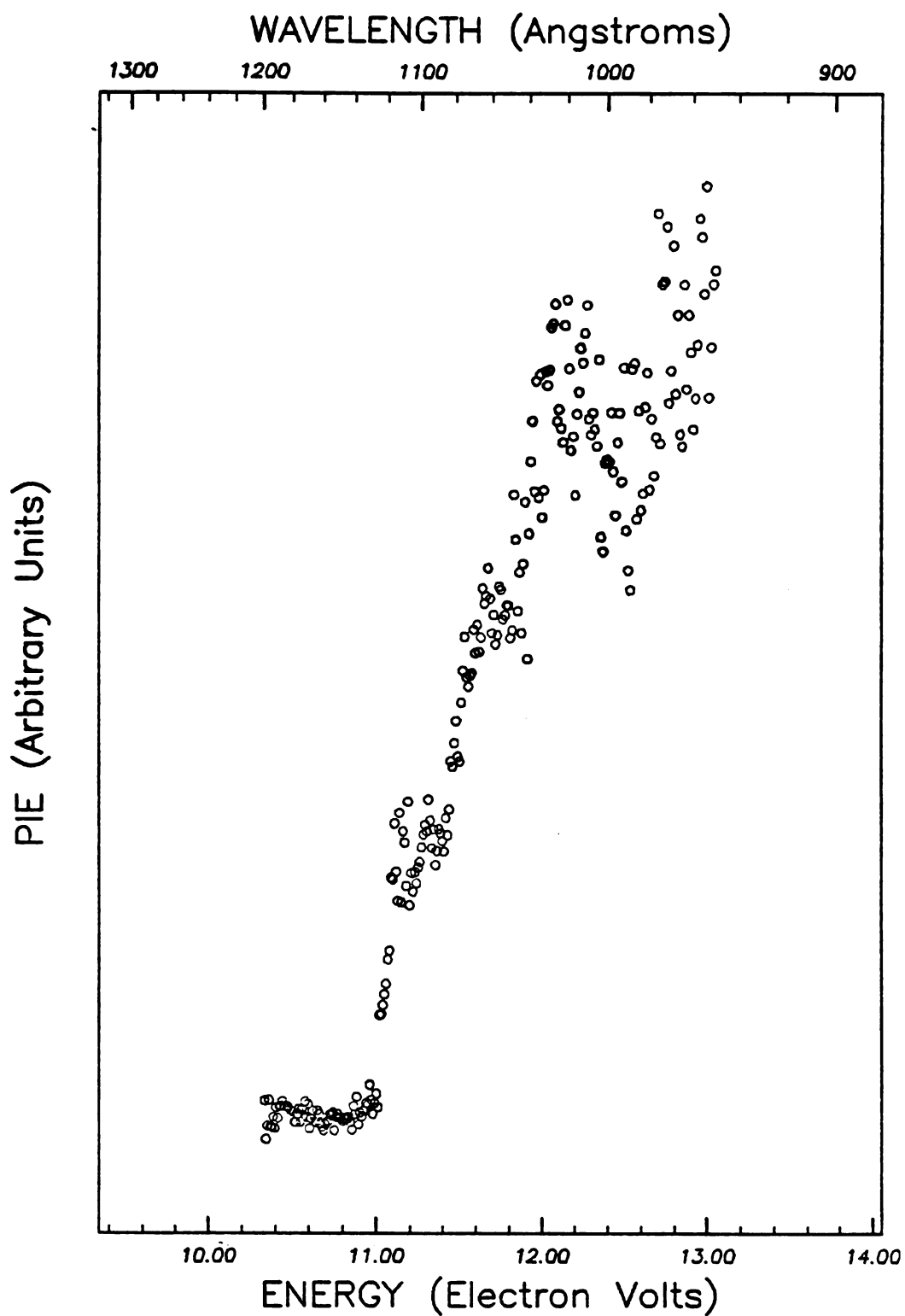


Figure 5A-9-3. PIE of CCl_3Br^+ from CCl_3Br .

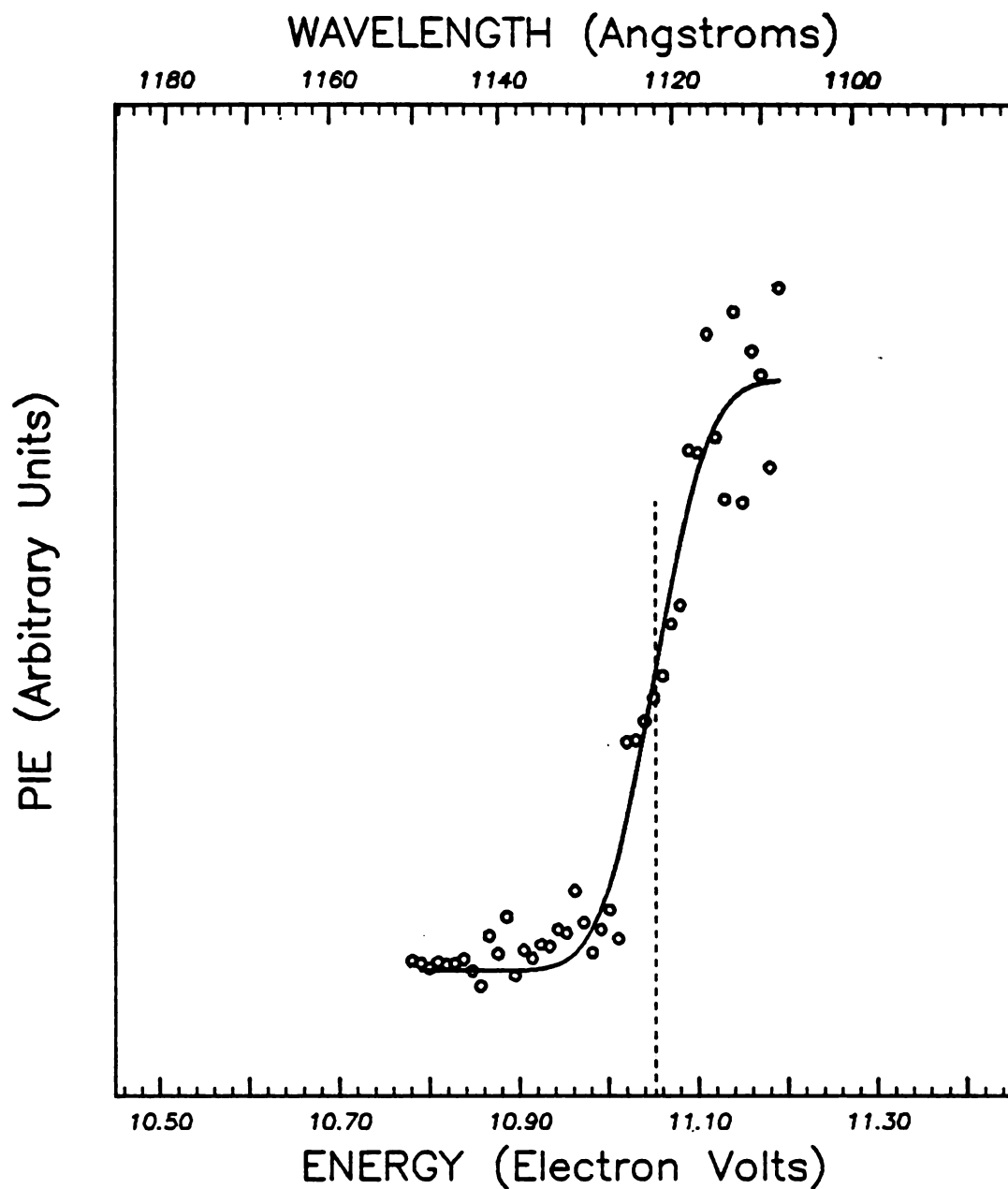
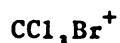


Figure 5A-9-4. PIE of CCl_3Br^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

illumination of the helium continuum, is shown in Figure 5A-9-1. Relative intensities of the peaks and their assignments are presented in Table 5A-9-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-9-2, and the summary of thermochemical information for these ions is given in Table 5A-9-2.



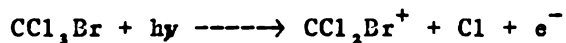
The parent ion PIE is shown in Figure 5A-9-3, where it may be seen that the threshold starts to rise at about 11.00eV. Figure 5A-9-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $11.05 \pm 0.02 \text{ eV}$. From the reaction equation:



the value of $\Delta H_{f0}^0(\text{CCl}_2\text{Br}^+)$ is calculated to be $243.81 \pm 1.5 \text{ kcal/mole}$.



The PIE of the CCl_2Br^+ fragment is shown in Figure 5A-9-5. The AP value of this fragment ion is $11.39 \pm 0.04 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^0(\text{CCl}_2\text{Br}^+)$ is calculated to be $223.13 \pm 2.0 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-9-6. The PIE starts to rise sharply at threshold (near 10.7eV); the AP value ion is $10.71 \pm 0.07 \text{ eV}$. From the reaction equation:

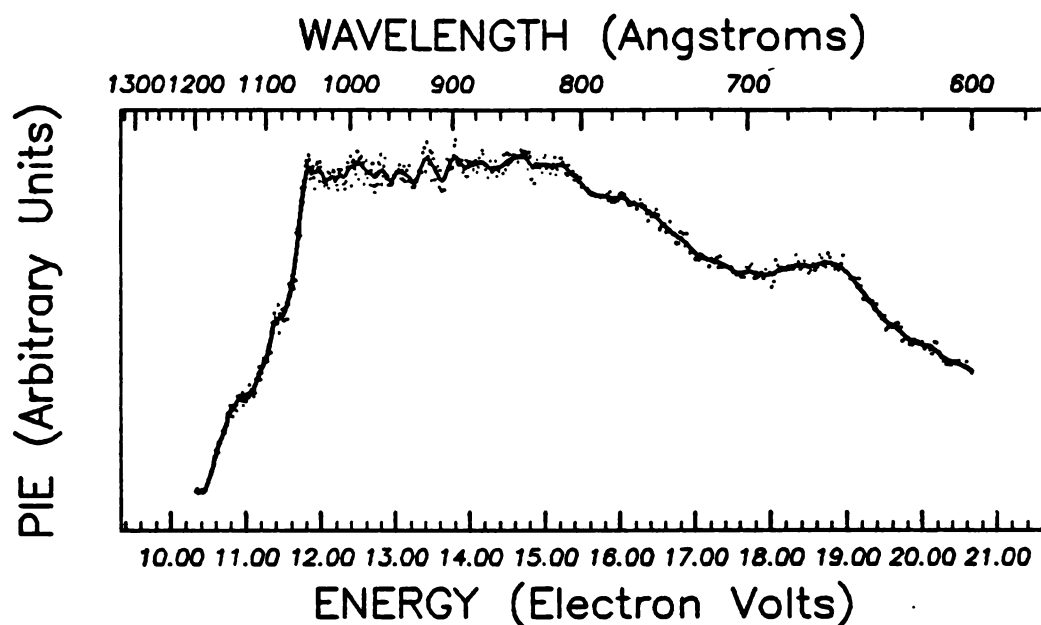


Figure 5A-9-5. PIE of CCl_2Br^+ from CCl_3Br . The solid line represents a smooth fit to the experimental data points.

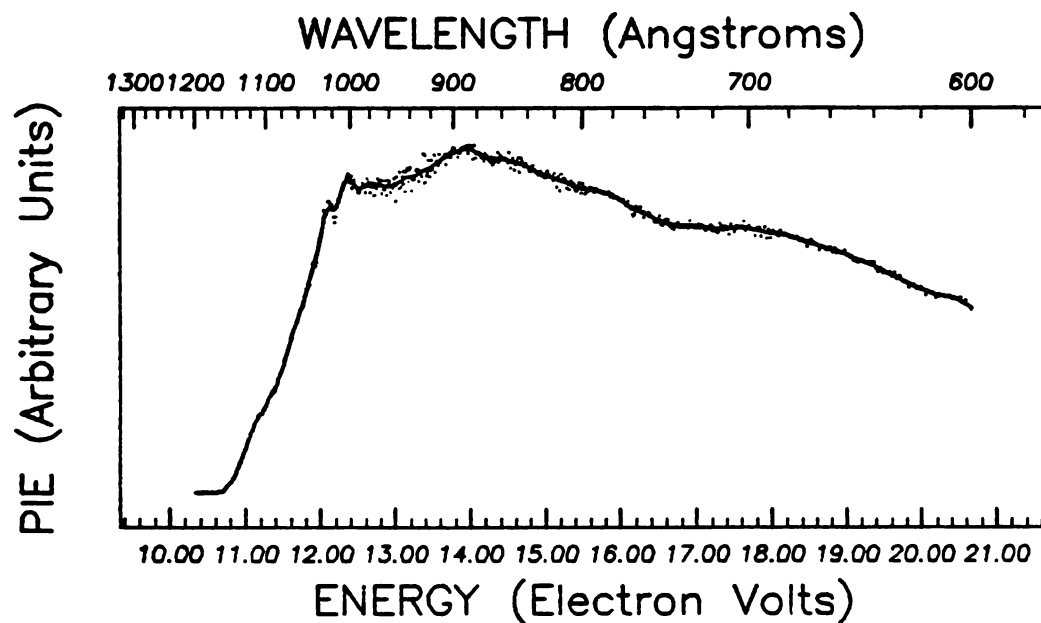


Figure 5A-9-6. PIE of CCl_3^+ from CCl_3Br . The solid line represents a smooth fit to the experimental data points.

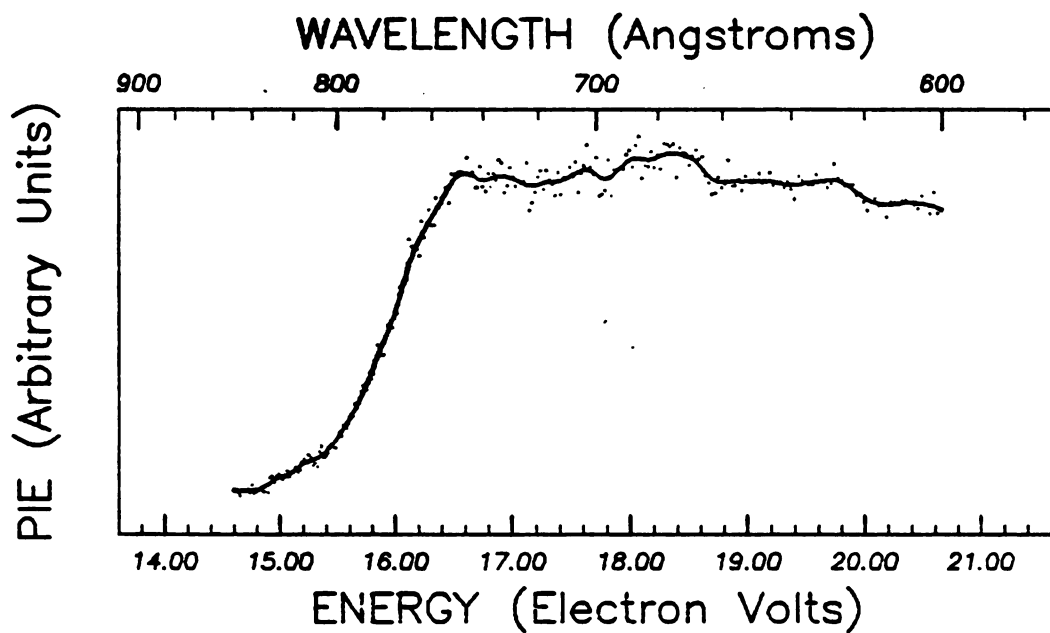
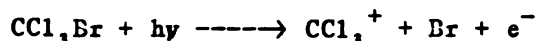


Figure 5A-9-7. PIE of CCl_2^+ from CCl_3Br . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CCl}_3^+)$ is calculated to be $207.78 \pm 2.7 \text{ kcal/mole}$.



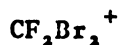
The second fragment ion is CCl_2^+ , for which the PIE is shown in Figure 5A-9-7. The PIE shows a relatively smooth threshold at around 13.9eV. The AP value of this fragment ion is $13.95 \pm 0.07 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CCl}_2^+)$ is calculated to be $253.98 \pm 2.7 \text{ kcal/mole}$.

10. CF_2Br_2

The photoionization mass spectrum of CF_2Br_2 , obtained under full illumination of the helium continuum, is shown in Figure 5A-10-1. Relative intensities of the peaks and their assignments are presented in Table 5A-10-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-10-2, and the summary of thermochemical information for these ions is given in Table 5A-10-2.



The parent ion PIE is shown in Figure 5A-10-3, where it may be seen that the threshold starts to rise at about 10.90eV. Figure 5A-10-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $10.98 \pm 0.02 \text{ eV}$, which is slightly lower than and in a good agreement with previous literature value: 11.18eV.³⁴ From

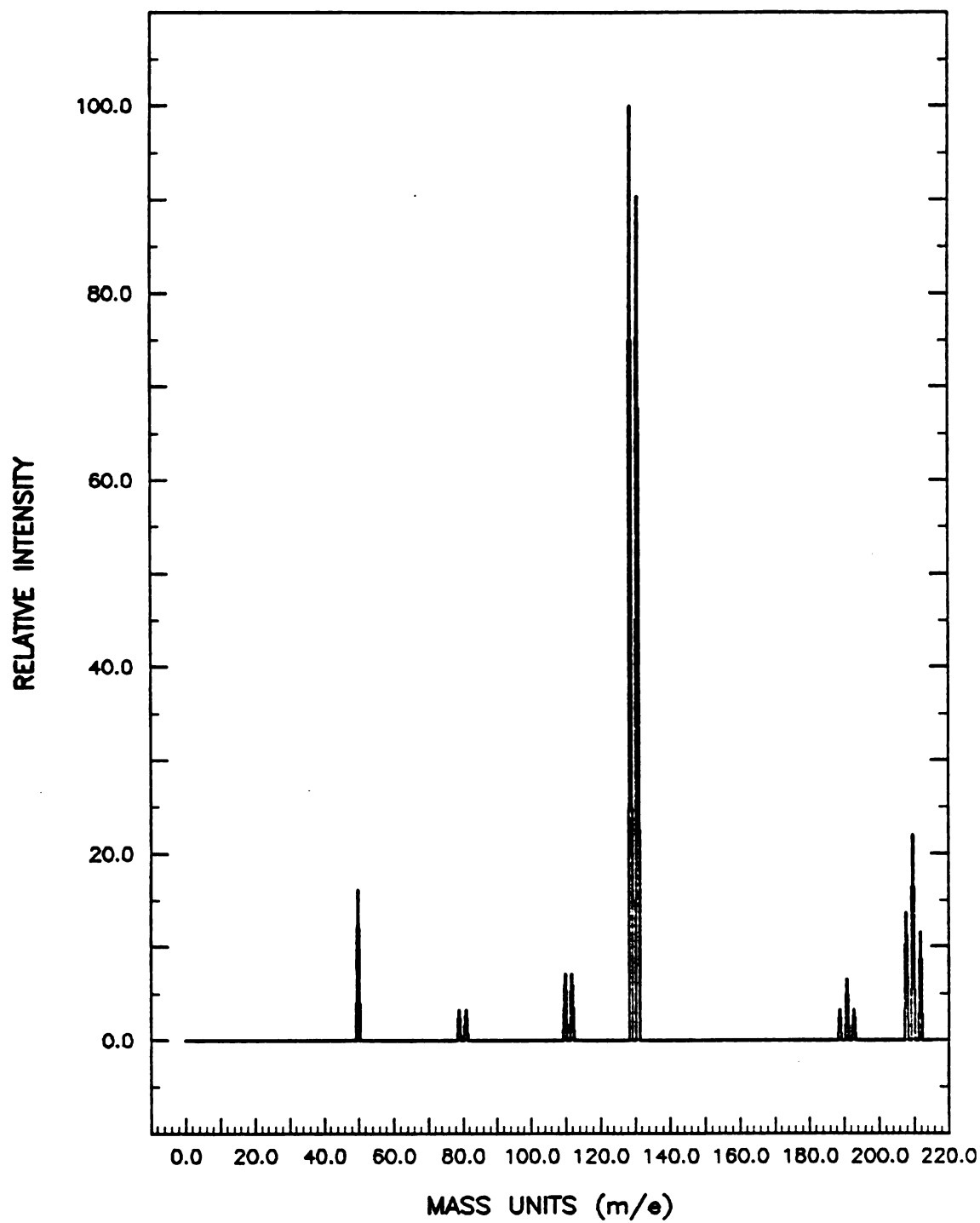


Figure 5A-10-1. Photoionization Mass Spectrum of CF₂Br₂ (obtained under full illumination of the helium discharge).

Table 5A-10-1. Photoionization Mass Spectrum of CF₂Br₂^a

m/e	Intensity Relative to CF ₂ Br ⁺	Percent of Total Ion Production	Probable Formula
50	16.1	5.62	CF ₂ ⁺
79	3.2	1.12	⁷⁹ Br ⁺
81	3.2	1.12	⁸¹ Br ⁺
110	7.1	2.47	CF ⁷⁹ Br ⁺
112	7.1	2.47	CF ⁸¹ Br ⁺
129	100.0	34.83	CF ₂ ⁷⁹ Br ⁺
131	90.3	31.46	CF ₂ ⁸¹ Br ⁺
189	3.2	1.12	CF ⁷⁹ Br ₂ ⁺
191	6.5	2.25	CF ⁷⁹ Br ⁸¹ Br ⁺
193	3.2	1.12	CF ⁸¹ Br ₂ ⁺
208	13.6	4.72	CF ₂ ⁷⁹ Br ₂ ⁺
210	21.9	7.64	CF ₂ ⁷⁹ Br ⁸¹ Br ⁺
212	11.6	4.04	CF ₂ ⁸¹ Br ₂ ⁺

^aObtained under full illumination of the helium discharge.

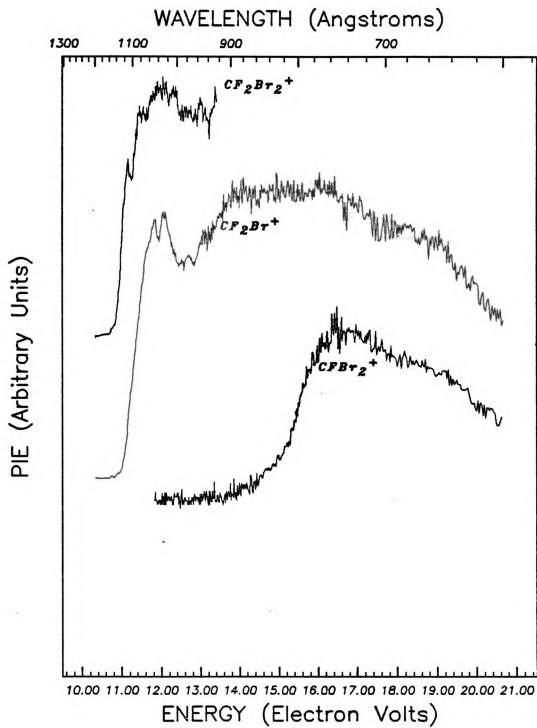


Figure 5A-10-2. Photoionization efficiency curves for parent and daughter ions from CF_2Br_2 .

Table 5A-10-2. Summary of IP, AP and Heat of formation data for all ions from CF_2Br_2 .

ION	IP or AP (eV) ^a	Products of $\text{CF}_2\text{Br}_2 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_2Br_2^+	10.98	$\text{CF}_2\text{Br}_2^+ + e^-$	156.31
CF_2Br^+	11.00	$\text{CF}_2\text{Br}^+ + \text{Br} + e^-$	128.58
CFBr_2^+	14.24	$\text{CFBr}_2^+ + \text{F} + e^-$	213.12

^asee text for uncertainties.

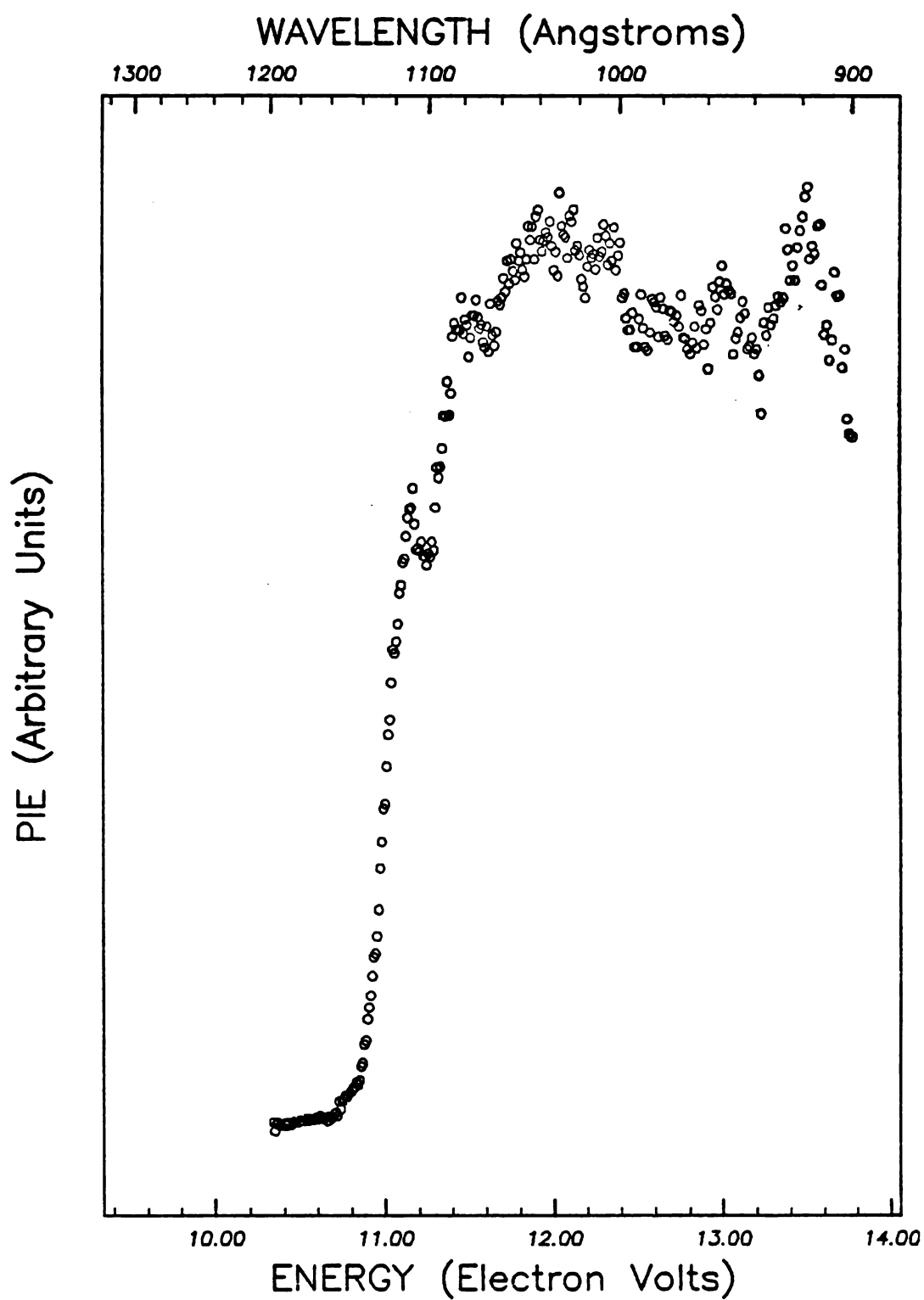


Figure 5A-10-3. PIE of CF_2Br_2^+ from CF_2Br_2 .

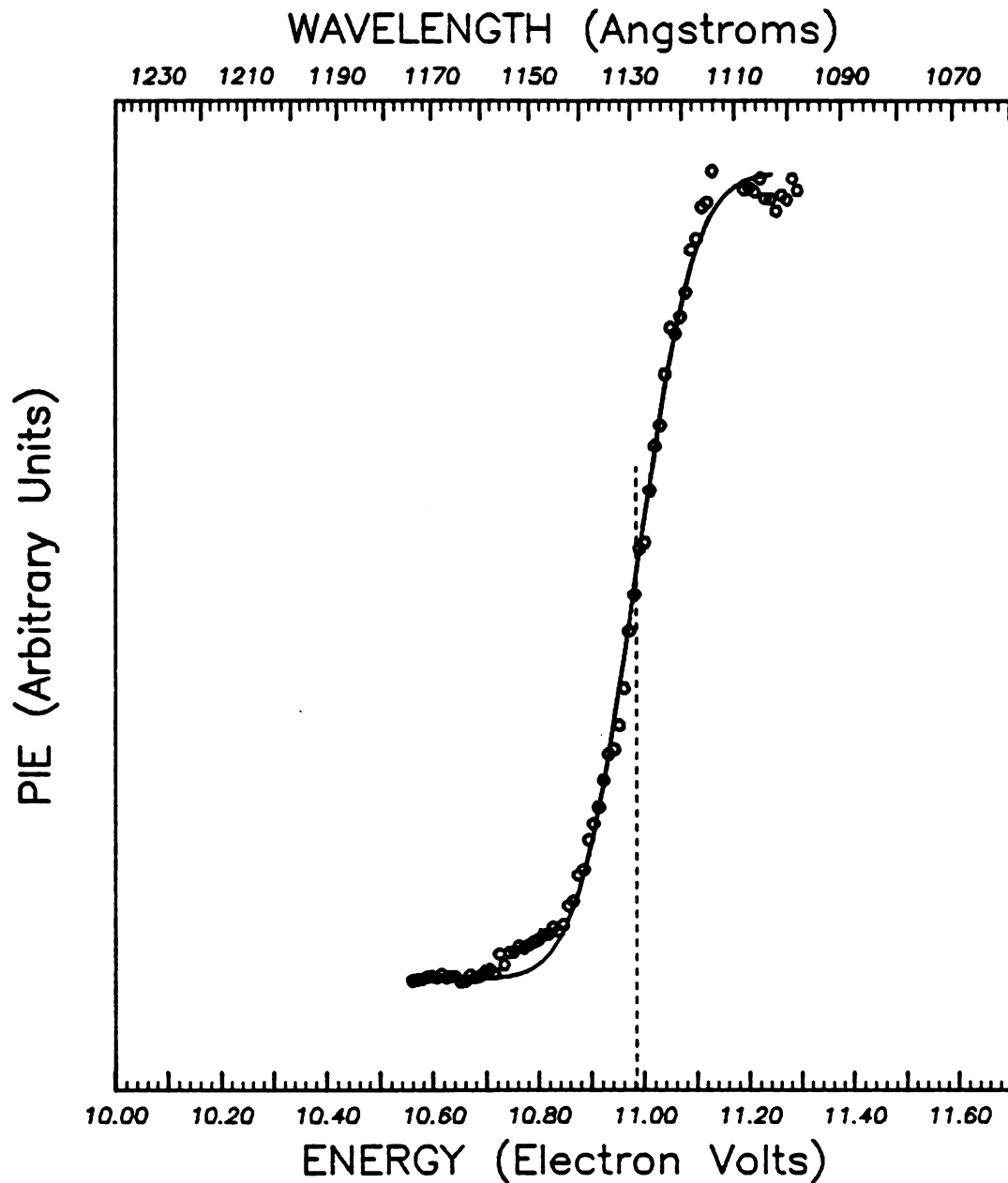
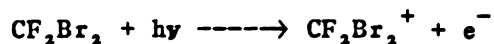
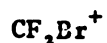


Figure 5A-10-4. PIE of CF_2Br_2^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

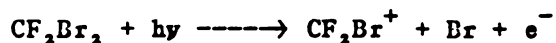
the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}_2^+)$ is calculated to be $156.31 \pm 1.5 \text{ kcal/mole}$.



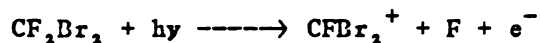
The first, lowest photon energy fragment PIE curve is shown in Figure 5A-10-5. The PIE starts to rise sharply at threshold (near 11.0 eV). The AP value of this fragment ion is $11.00 \pm 0.04 \text{ eV}$, and from the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+)$ is calculated to be $128.58 \pm 2.0 \text{ kcal/mole}$.



The second fragment ion is CFBr_2^+ , for which the PIE is shown in Figure 5A-10-6. The AP value of this fragment ion is $20.44 \pm 0.3 \text{ eV}$, and by using the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CFBr}_2^+)$ is calculated to be $213.12 \pm 8.5 \text{ kcal/mole}$.

11. CHF_3

The photoionization mass spectrum of CHF_3 , obtained under full illumination of the helium continuum, is shown in Figure 5A-11-1.

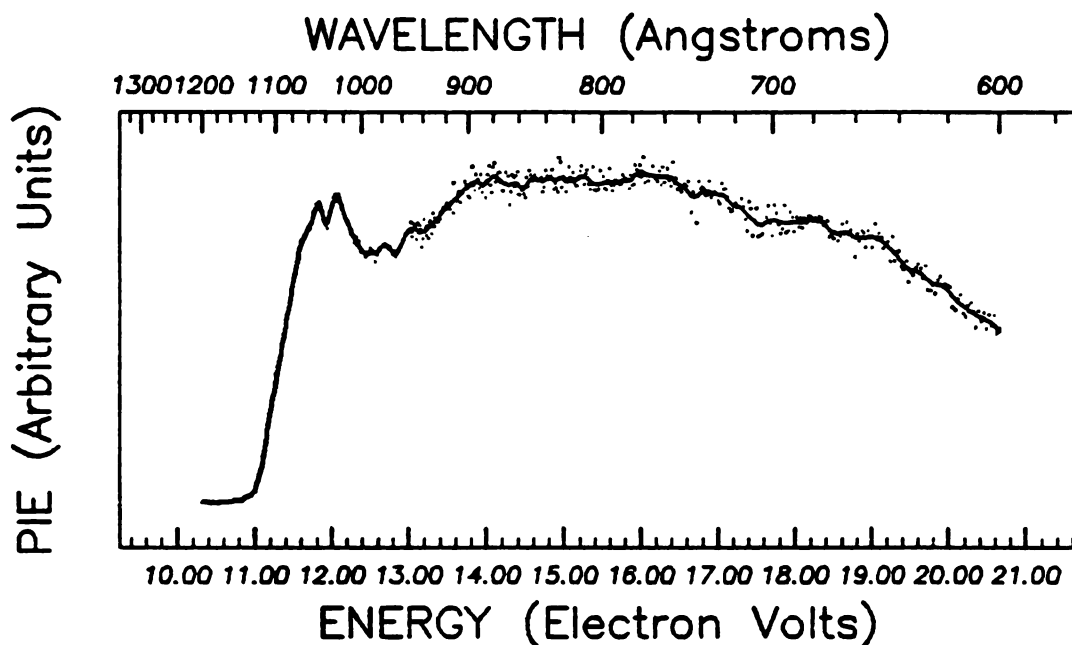


Figure 5A-10-5. PIE of CF_2Br^+ from CF_2Br_2 . The solid line represents a smooth fit to the experimental data points.

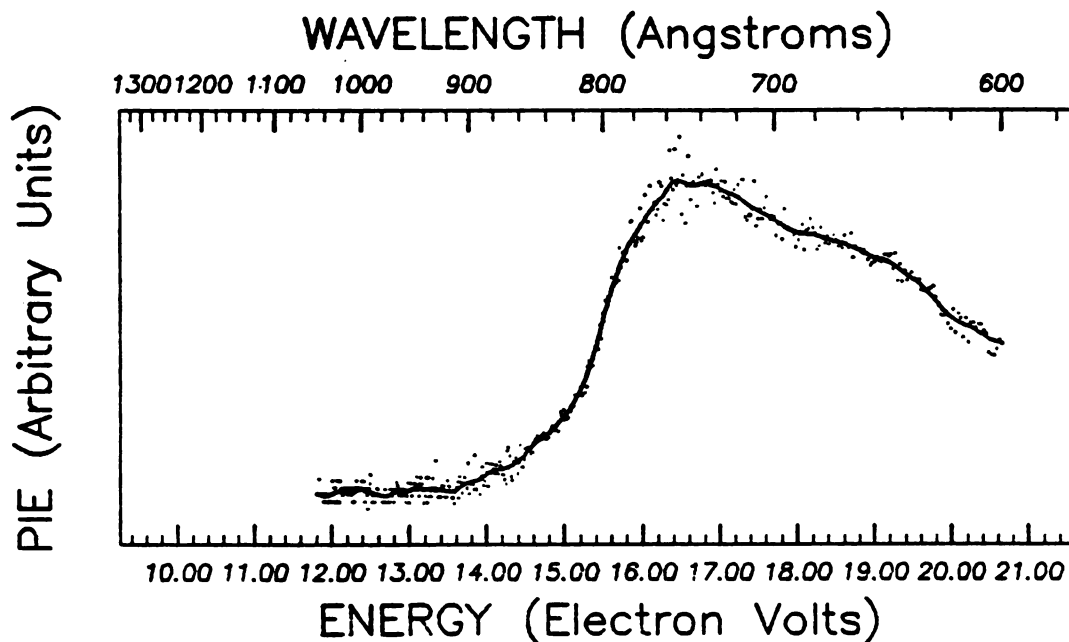


Figure 5A-10-6. PIE of CFBr_2^+ from CF_2Br_2 . The solid line represents a smooth fit to the experimental data points.

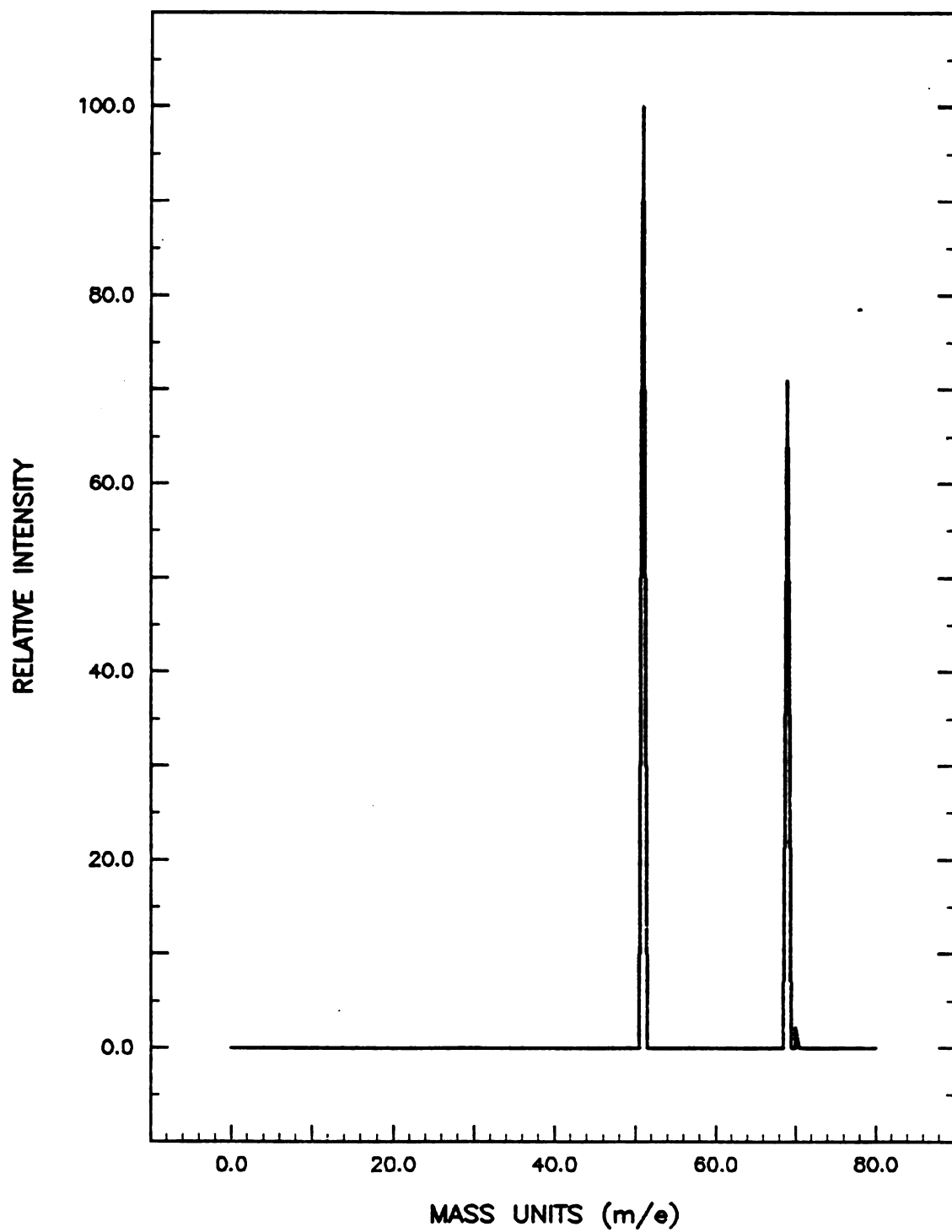


Figure 5A-11-1.

Photoionization Mass Spectrum of CHF₃
(obtained under full illumination of the
helium discharge).

Table 5A-11-1. Photoionization Mass Spectrum of CHF_3^{a}

m/e	Intensity Relative to CHF_2^+	Percent of Total Ion Production	Probable Formula
51	100.0	57.77	CHF_2^+
69	71.0	41.02	CF_3^+
70	2.1	1.21	CHF_3^+

^aObtained under full illumination of the helium discharge.Table 5A-11-2. Summary of IP, AP and Heat of formation data for all ions from CHF_3 .

ION	IP or AP (eV) ^a	Products of $\text{CHF}_3 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CF_3^+	14.14	$\text{CF}_3^+ + \text{H} + \text{e}^-$	109.54
CHF_2^+	14.94	$\text{CHF}_2^+ + \text{F} + \text{e}^-$	161.26

^asee text for uncertainties.

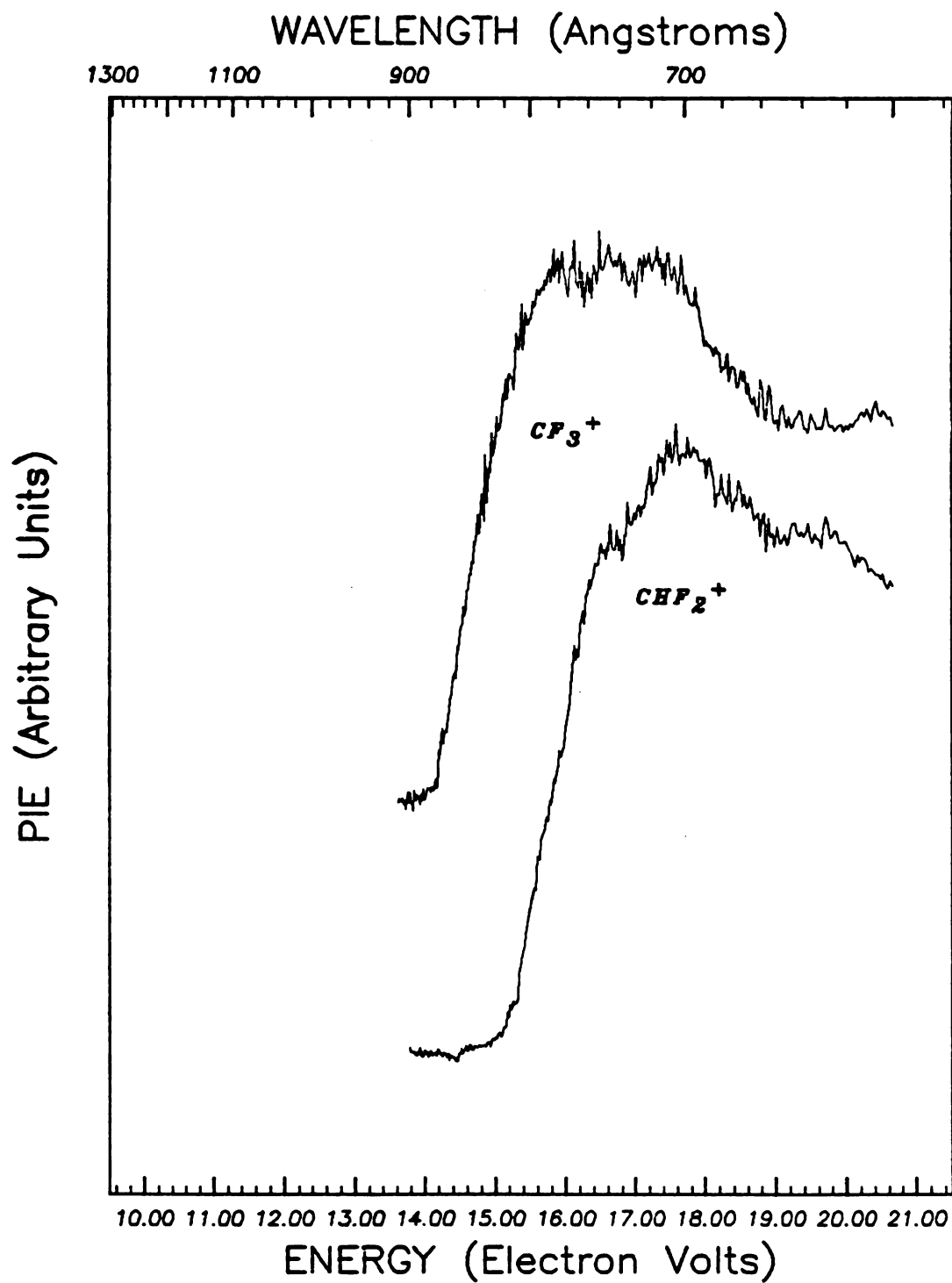
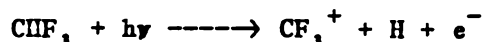


Figure 5A-11-2. Photoionization efficiency curves for daughter ions from CHF_3 .

Relative intensities of the peaks and their assignments are presented in Table 5A-11-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-11-2, and the summary of thermochemical information for these ions is given in Table 5A-11-2.



Under high mass resolution conditions, the CHF_3^+ parent ion appears weakly in the photoionization mass spectrum obtained with undispersed helium radiation. However, its intensity is not sufficient to allow a PIE curve to be measured. Therefore, the first PIE recorded from CHF_3 is that of CF_3^+ , which is shown in Figure 5A-11-3. The PIE starts to rise at threshold (near 14.1eV). The AP value of this fragment ion is $14.14 \pm 0.04 \text{ eV}$, which is in excellent agreement with the previous literature value $14.14 \pm 0.02 \text{ eV}$.⁹¹ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is calculated to be $109.54 \pm 1.7 \text{ kcal/mole}$.



The second fragment ion is CHF_2^+ , for which the PIE is shown in Figure 5A-11-4. The AP value of this fragment ion is $14.94 \pm 0.04 \text{ eV}$, and by using the reaction equation:

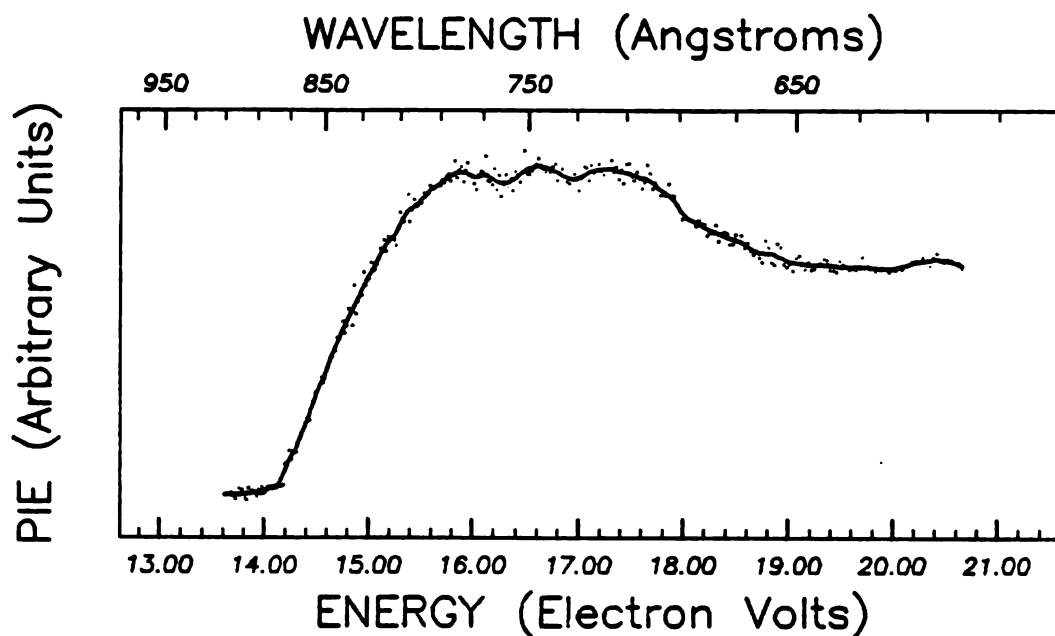


Figure 5A-11-3. PIE of CF_3^+ from CHF_3 . The solid line represents a smooth fit to the experimental data points.

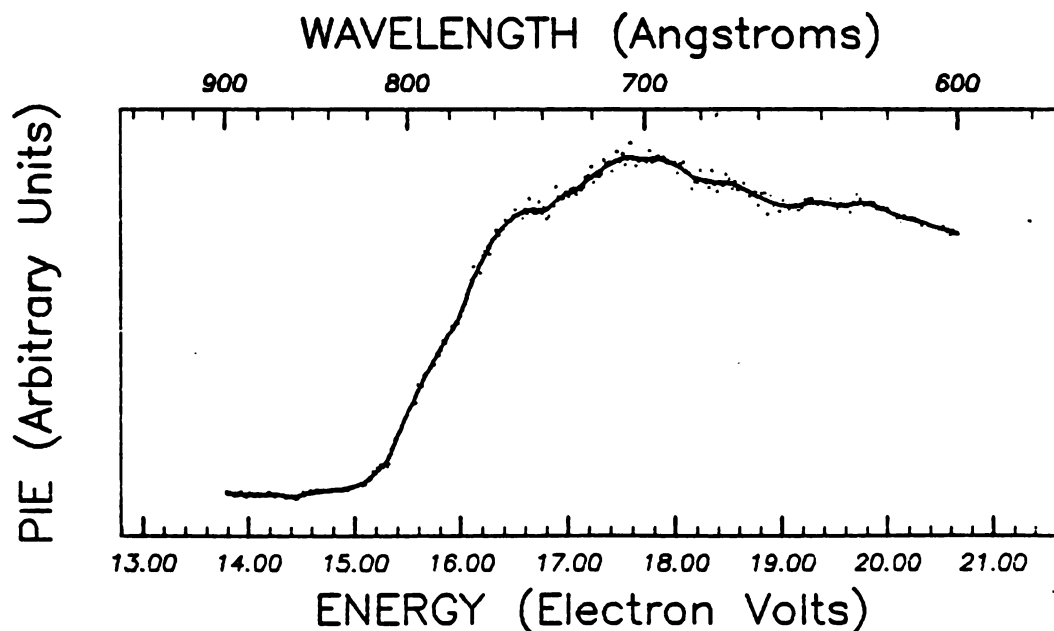
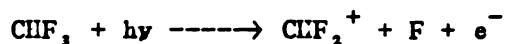


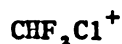
Figure 5A-11-4. PIE of CHF_2^+ from CHF_3 . The solid line represents a smooth fit to the experimental data points.



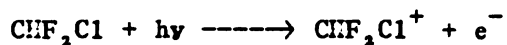
the value of $\Delta H_{f0}^\circ(\text{CHF}_2^+)$ is calculated to be $161.26 \pm 2.1 \text{ kcal/mole}$.

12. CHF_2Cl

The photoionization mass spectrum of CHF_2Cl , obtained under full illumination of the helium continuum, is shown in Figure 5A-12-1. Relative intensities of the peaks and their assignments are presented in Table 5A-12-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-12-2, and the summary of thermochemical information for these ions is given in Table 5A-12-2.



The parent ion PIE is shown in Figure 5A-12-3, where it may be seen that the threshold starts to rise at about 12.2eV. Figure 5A-12-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $12.28 \pm 0.02 \text{ eV}$, which is slightly higher than and in a good agreement with the previous literature value: 12.60eV.⁹³ From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CHF}_2\text{Cl}^+)$ is calculated to be $169.58 \pm 3.5 \text{ kcal/mole}$.



The PIE of CHFCl^+ from CHF_2Cl is shown in Figure 5A-12-5. The PIE shows a relatively smooth threshold at around 12.0eV. The AP value of this fragment ion is $14.44 \pm 0.3 \text{ eV}$, and by using the reaction equation:

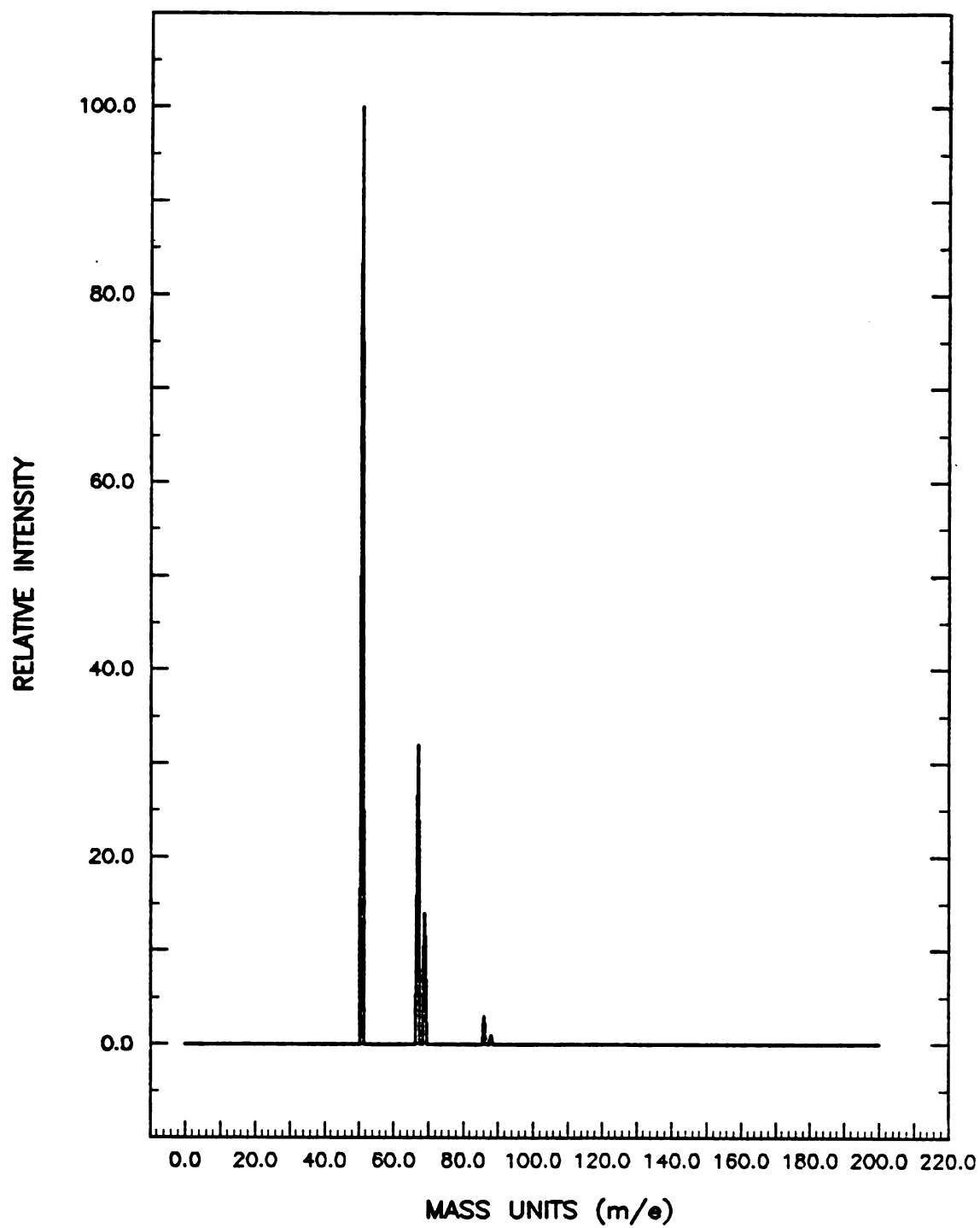


Figure 5A-12-1. Photoionization Mass Spectrum of CHF_2Cl (obtained under full illumination of the helium discharge).

Table 5A-12-1. Photoionization Mass Spectrum of $\text{CHF}_2\text{Cl}^{\text{a}}$

m/e	Intensity Relative to CHF_2^+	Percent of Total Ion Production	Probable Formula
51	100.0	66.67	CHF_2^+
67	32.0	21.33	$\text{CHF}^{35}\text{Cl}^+$
69	14.0	9.33	$\text{CHF}^{37}\text{Cl}^+$
86	3.0	2.00	$\text{CHF}_2^{35}\text{Cl}^+$
88	1.0	0.67	$\text{CHF}_2^{37}\text{Cl}^+$

^aObtained under full illumination of the helium discharge.Table 5A-12-2. Summary of IP, AP and Heat of formation data for all ions from CHF_2Cl .

ION	IP or AP (eV) ^a	Products of $\text{CHF}_2\text{Cl} + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CHF_2Cl^+	12.28	$\text{CHF}_2\text{Cl}^+ + e^-$	169.58
CHF_2^+	11.98	$\text{CHF}_2^+ + \text{Cl} + e^-$	134.14
CHFCl^+	14.44	$\text{CHFCl}^+ + \text{F} + e^-$	201.13

^asee text for uncertainties.

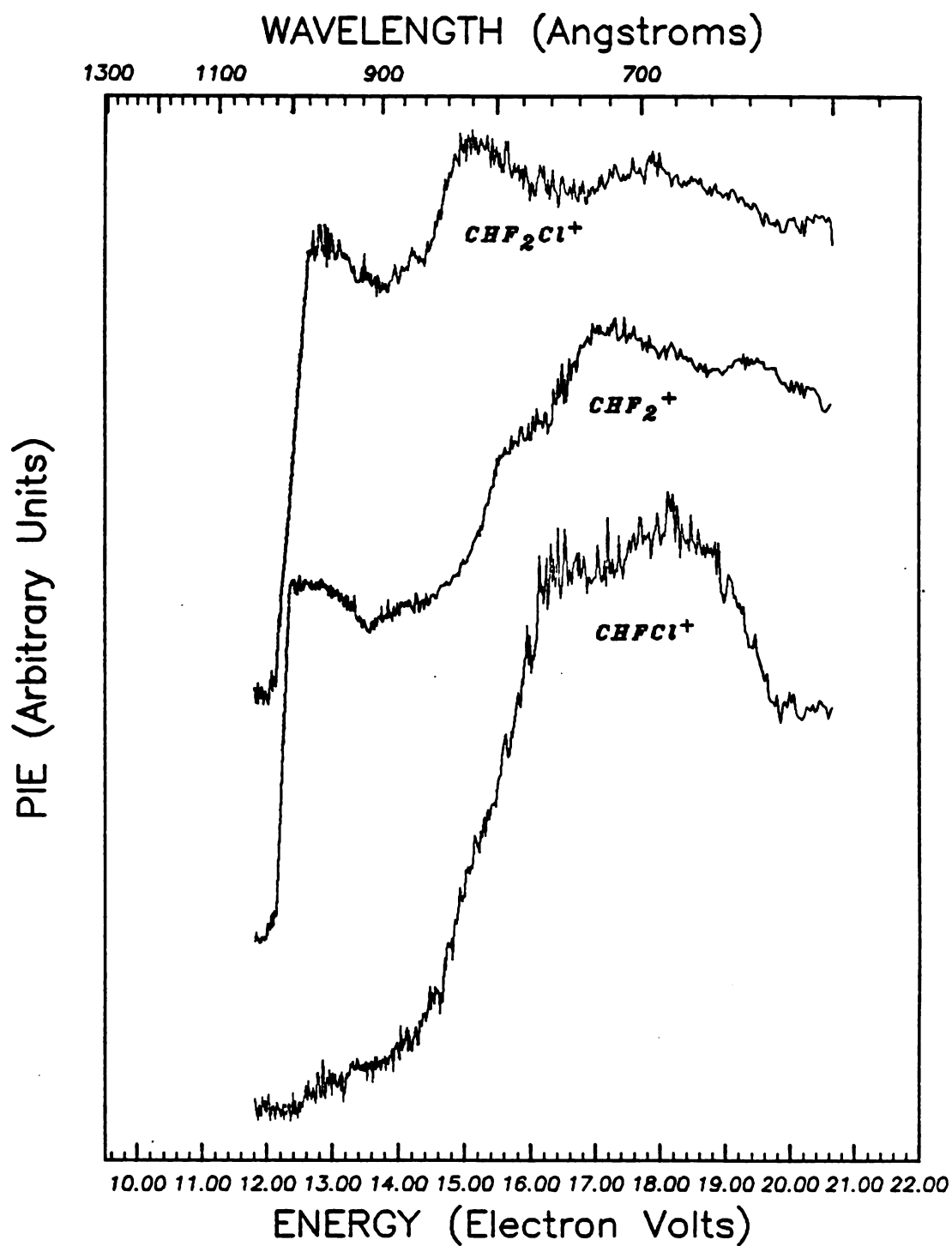


Figure 5A-12-2. Photoionization efficiency curves for parent and daughter ions from CHF_2Cl .

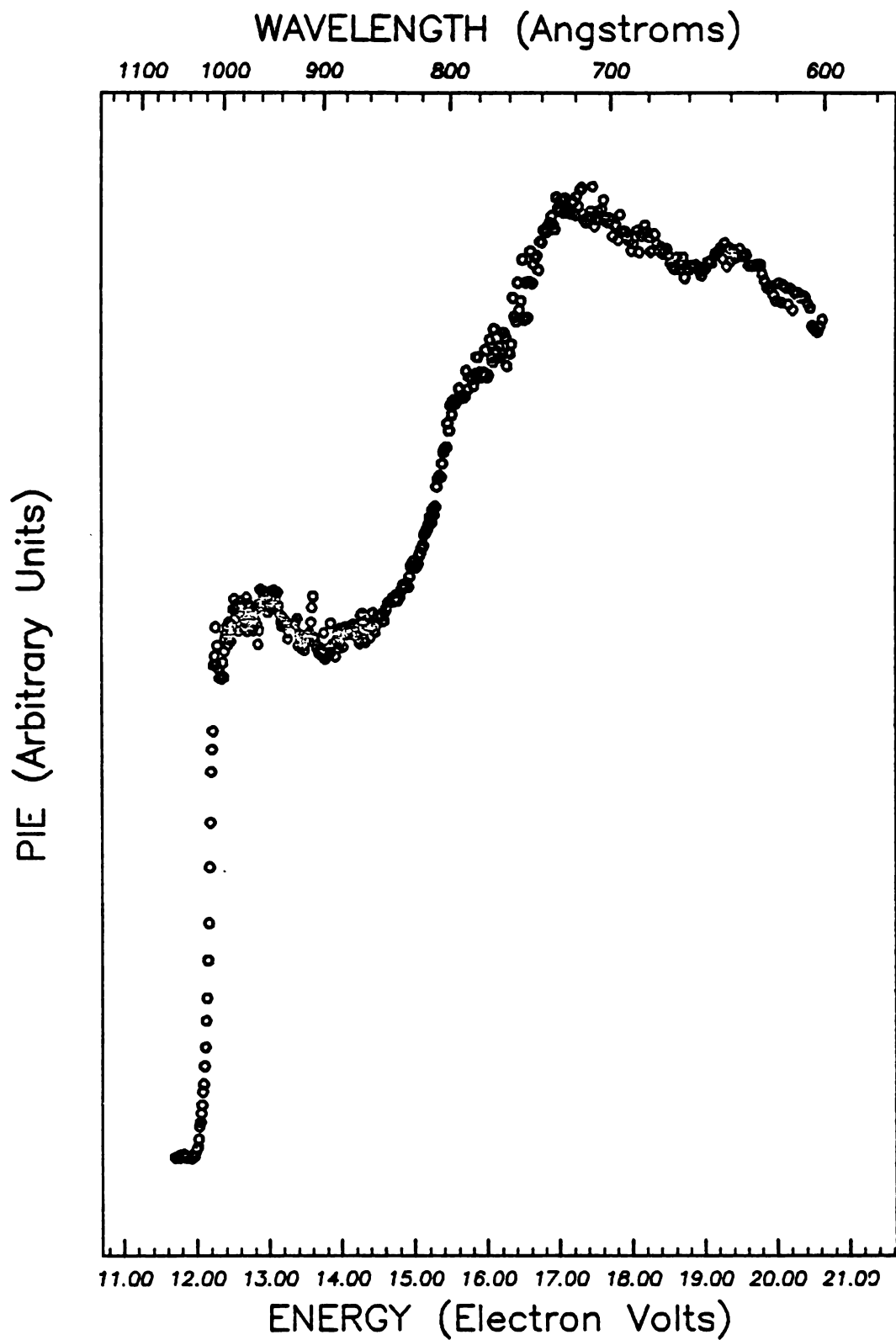


Figure 5A-12-3. PIE of CHF_2Cl^+ from CHF_2Cl . The solid line represents a smooth fit to the experimental data points.

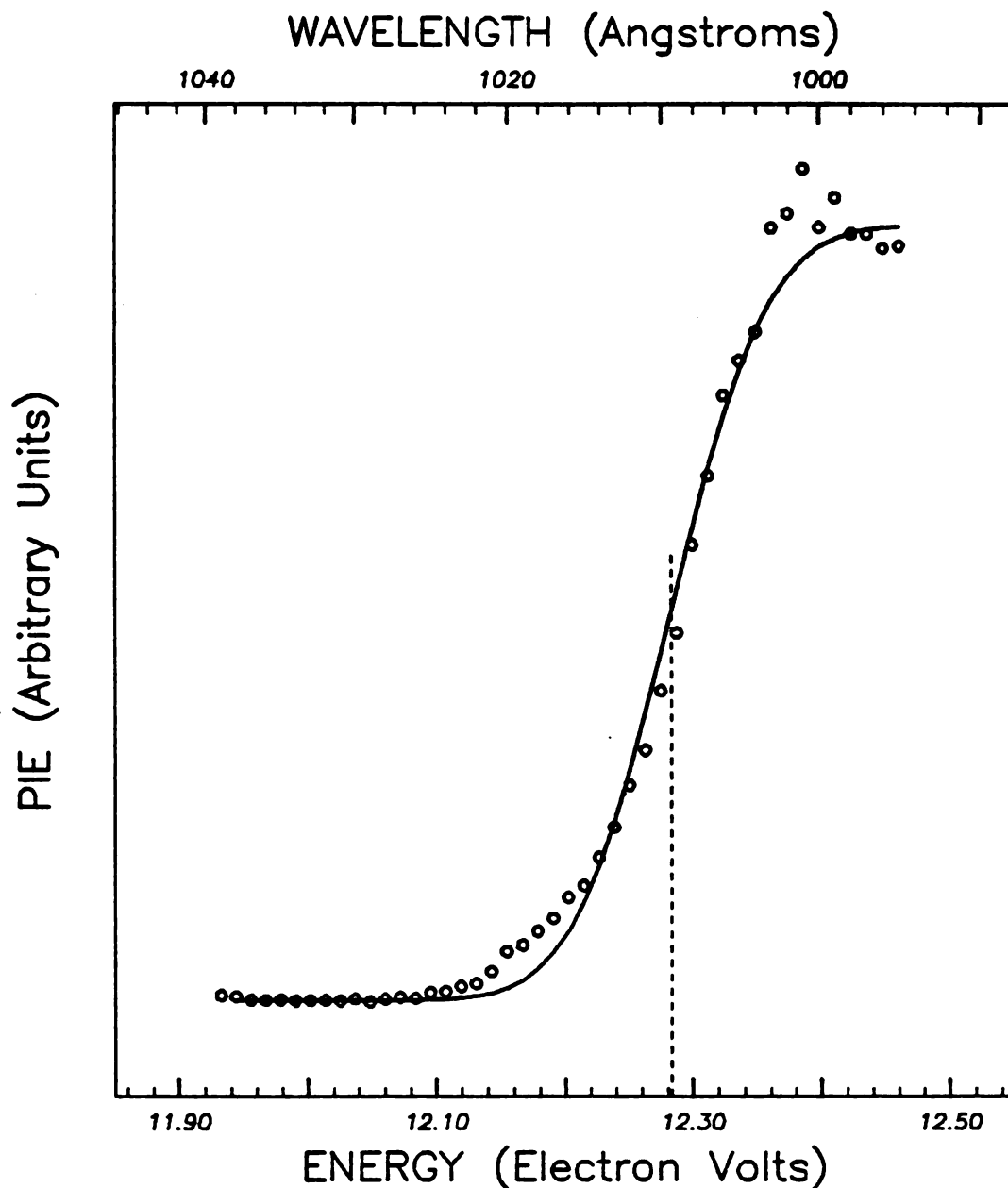


Figure 5A-12-4. PIE of CHF_2Cl^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

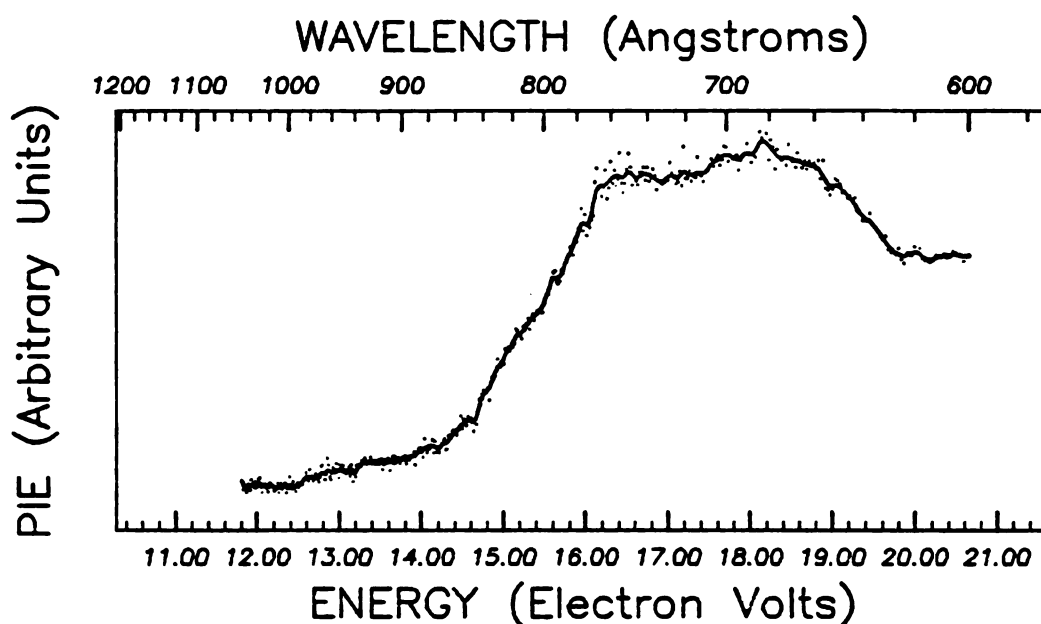


Figure 5A-12-5. PIE of CHFCl^+ from CHF_2Cl . The solid line represents a smooth fit to the experimental data points.

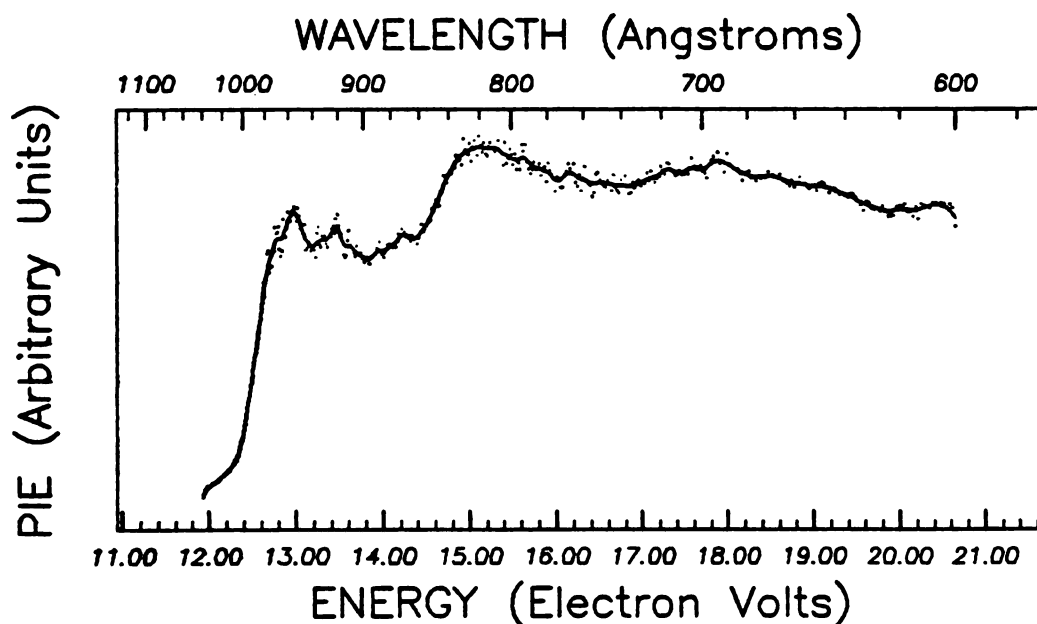
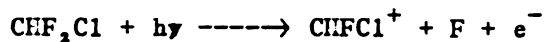


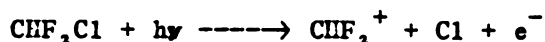
Figure 5A-12-6. PIE of CHF_2^+ from CHF_2Cl . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CHFCl}^+)$ is calculated to be $201.03 \pm 10.4 \text{ kcal/mole}$.



The first, lowest photon energy fragment PIE curve is shown in Figure 5A-12-6. The PIE starts to rise at threshold (near 12.0 eV). The AP value of this fragment ion is $11.98 \pm 0.04 \text{ eV}$. From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CHF}_2^+)$ is calculated to be $134.14 \pm 4.0 \text{ kcal/mole}$.

13. CHFCl_2

The photoionization mass spectrum of CHFCl_2 , obtained under full illumination of the helium continuum, is shown in Figure 5A-13-1. Relative intensities of the peaks and their assignments are presented in Table 5A-13-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-13-2, and the summary of thermochemical information for these ions is given in Table 5A-13-2.



The parent ion PIE curve is shown in Figure 5A-13-3. The PIE starts to rise sharply at threshold near 11.50 eV. Figure 5A-13-4 shows the fit of the error function to the threshold region. The small disagreement between the fit curve and experimental PIE curve is attributed to the charge exchange reaction between the neutral parent

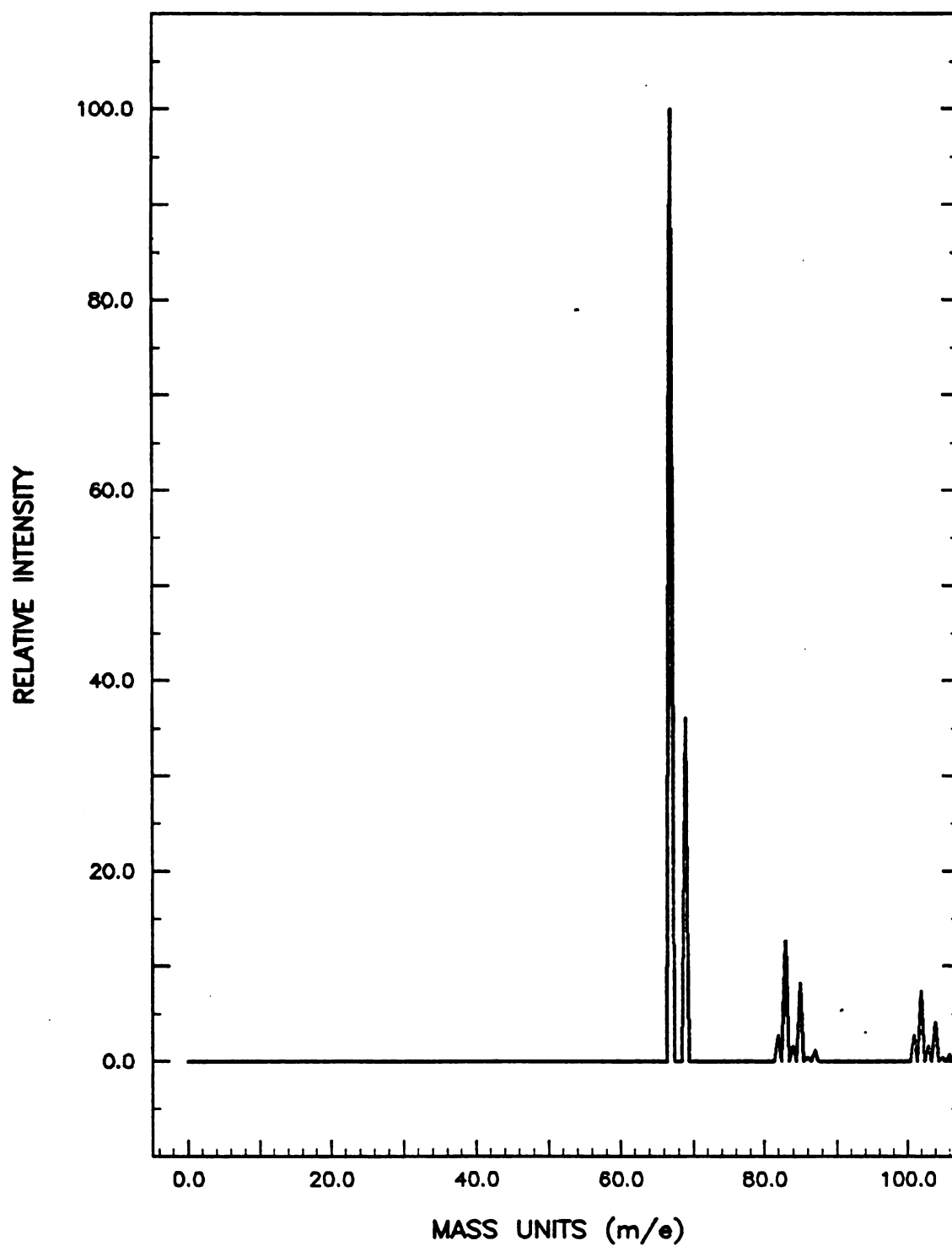


Figure 5A-13-1. Photoionization Mass Spectrum of CH_2Cl_2 (obtained under full illumination of the helium discharge).

Table 5A-13-1. Photoionization Mass Spectrum of CHFCl_2^a

m/e	Intensity Relative to CHFCl^+	Percent of Total Ion Production	Probable Formula
67	100.0	55.71	$\text{CHF}^{36}\text{Cl}^+$
69	36.1	20.09	$\text{CHF}^{37}\text{Cl}^+$
82	2.7	1.37	$\text{C}^{35}\text{Cl}_2^+$
83	12.7	7.08	$\text{CH}^{35}\text{Cl}_2^+$
84	1.6	0.91	$\text{C}^{35}\text{Cl}^{37}\text{Cl}^+$
85	8.2	4.57	$\text{CH}^{35}\text{Cl}^{37}\text{Cl}^+$
86	0.4	0.23	$\text{C}^{37}\text{Cl}_2^+$
87	1.2	0.68	$\text{CH}^{37}\text{Cl}_2^+$
101	2.7	1.37	$\text{CF}^{35}\text{Cl}_2^+$
102	7.4	4.11	$\text{CHF}^{35}\text{Cl}_2^+$
103	1.6	0.91	$\text{CF}^{35}\text{Cl}^{37}\text{Cl}^+$
104	4.1	2.28	$\text{CHF}^{35}\text{Cl}^{37}\text{Cl}^+$
105	0.4	0.23	$\text{CF}^{37}\text{Cl}_2^+$
106	0.8	0.46	$\text{CHF}^{37}\text{Cl}_2^+$

^aObtained under full illumination of the helium discharge.

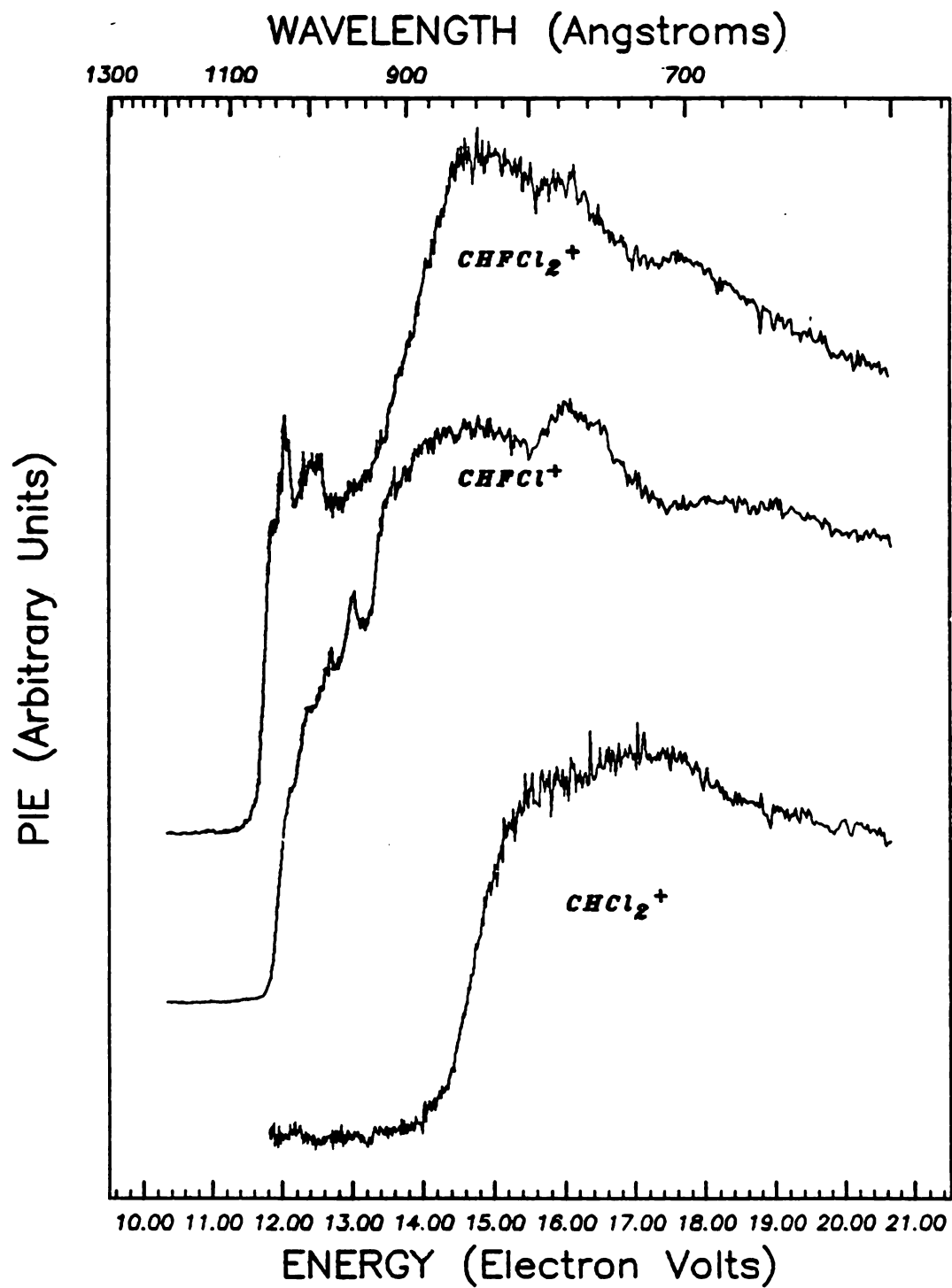


Figure 5A-13-2. Photoionization efficiency curves for parent and daughter ions from CHFCl_2 .

Table 5A-13-2. Summary of IP, AP and Heat of formation data for all ions from CHFCl_2 .

ION	IP or AP (eV) ^a	Products of $\text{CHFCl}_2 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CHFCl_2^+	11.75	$\text{CHFCl}_2^+ + e^-$	204.49
CHFCI^+	11.67	$\text{CHFCI}^+ + \text{Cl} + e^-$	174.23
CHCl_2^+	13.84	$\text{CHCl}_2^+ + \text{F} + e^-$	234.83

^asee text for uncertainties.

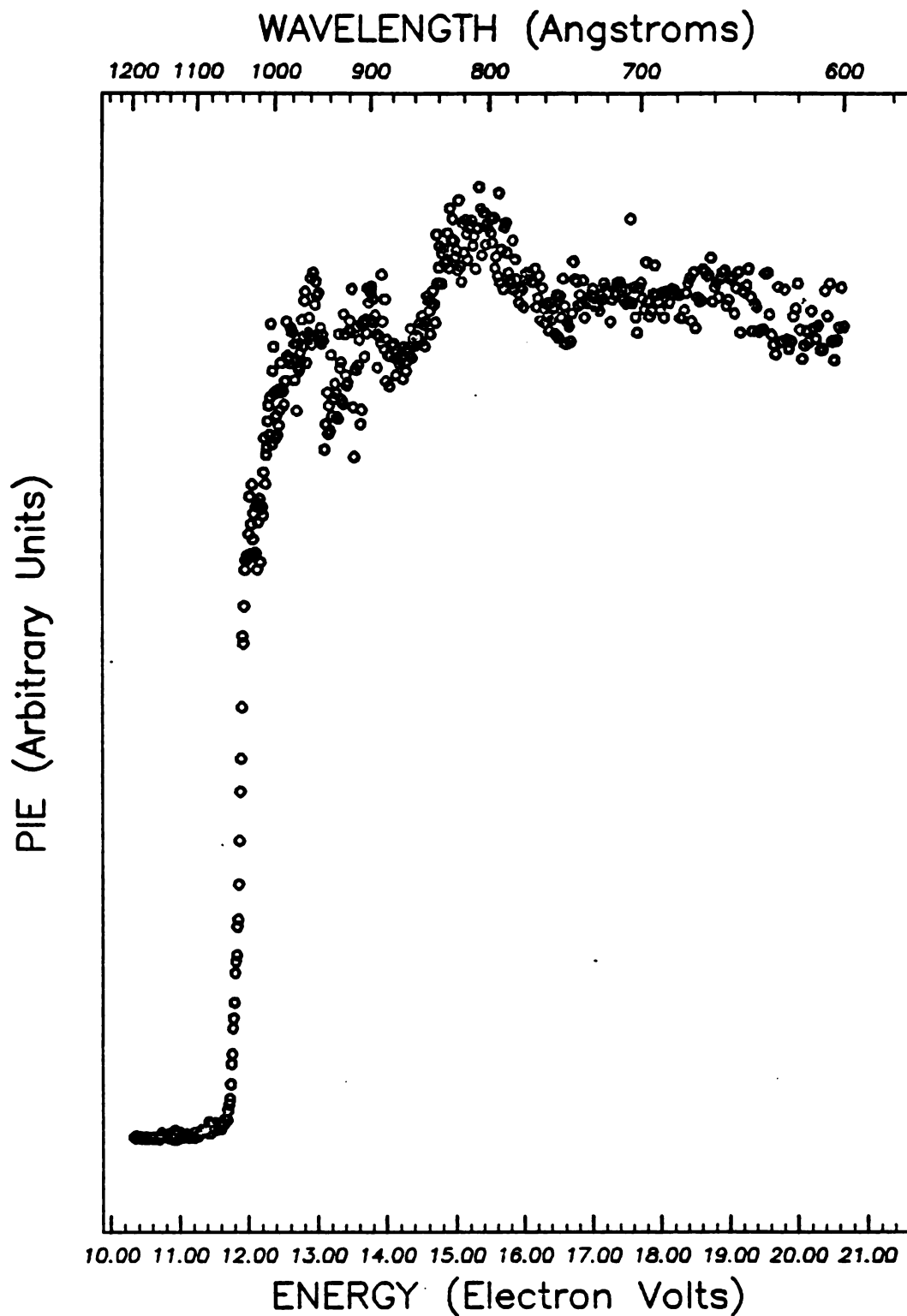


Figure 5A-13-3. PIE of CHFCl_2^+ from CHFCl_2 .

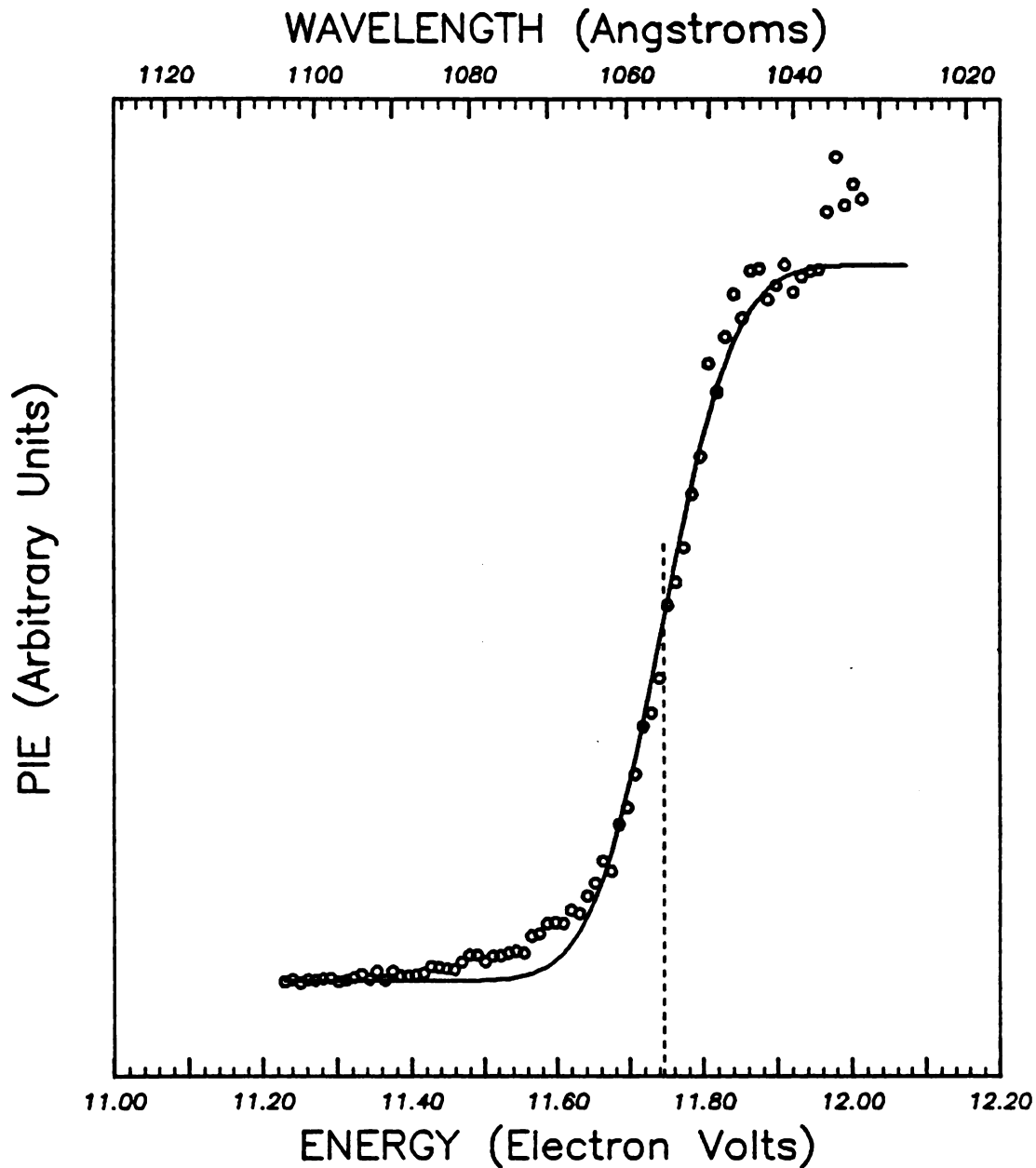
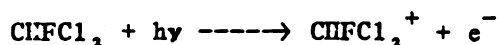


Figure 5A-13-4. PIE of CHFCl_2^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

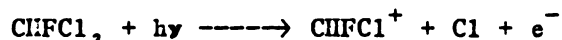
and first fragment ion, which has a lower AP than the IP. The adiabatic IP value of parent ion is $11.74 \pm 0.02 \text{ eV}$, which is lower than and in a good agreement with the previous literature value: 12.0 eV .⁹³ From the reaction equation:



the value of $\Delta H_{f0}^0(\text{CHFCl}_2^+)$ is calculated to be $204.49 \pm 3.5 \text{ kcal/mole}$.



The first fragment PIE curve is shown in Figure 5A-13-5. The PIE shows a sharp threshold at around 11.6 eV . In the post-threshold of this fragment ion PIE curve, autoionization structures are observed. The AP value is $11.67 \pm 0.04 \text{ eV}$, which is 0.07 eV lower than the IP of the parent molecule. It is interesting to compare this with the previous literature value: $12.69 \text{ eV} \pm 0.15 \text{ eV}$,⁹³ one electron volt higher. Loss of a chlorine atom is easily distinguished in the mass spectrum, and there is no chance that the parent ion interfered with the measurement of the CHFCl^+ PIE curve. Because it is lower than the previous determination, the current value for the AP should be accepted as more reliable. From the reaction equation



the value of $\Delta H_{f0}^0(\text{CHFCl}^+)$ is calculated to be $174.23 \pm 4.0 \text{ kcal/mole}$.



The PIE curve for CHCl_2^+ is shown in Figure 5A-13-6. The PIE

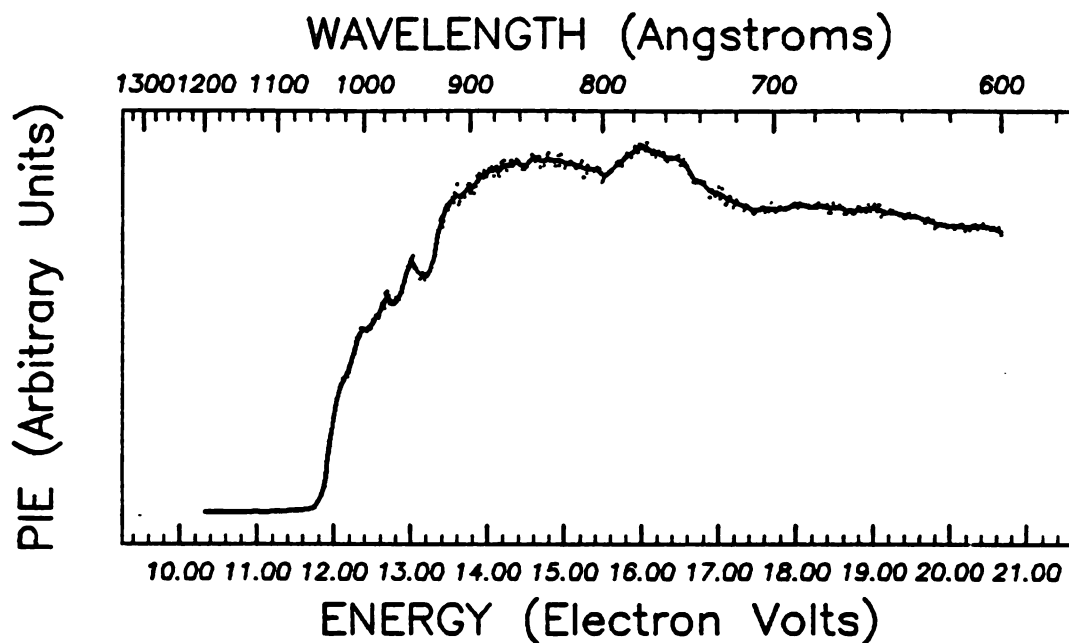


Figure 5A-13-5. PIE of CHFC1^+ from CHFC1_2 . The solid line represents a smooth fit to the experimental data points.

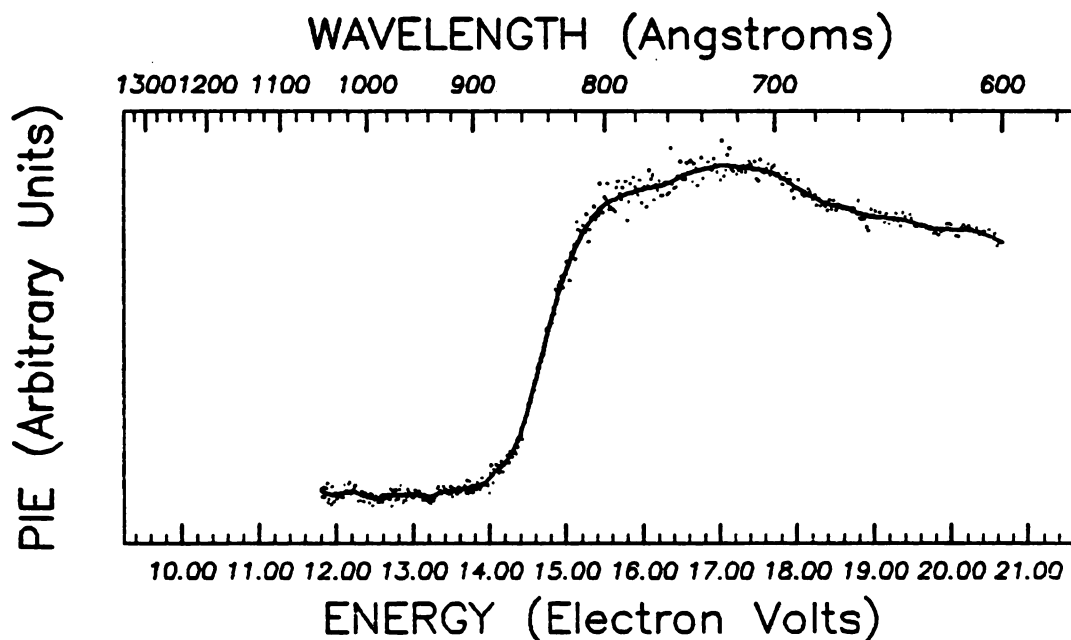
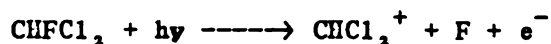


Figure 5A-13-6. PIE of CHCl_2^+ from CHFC1_2 . The solid line represents a smooth fit to the experimental data points.

shown a smooth threshold around 13.5eV. The AP value of this fragment ion is $13.84 \pm 0.1 \text{ eV}$. No previous literature value is available for comparison. From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CHCl}_2^+)$ is calculated to be $234.83 \pm 5.7 \text{ kcal/mole}$.

14. CHCl_2

The photoionization mass spectrum of CHCl_2 , obtained under full illumination of the helium continuum, is shown in Figure 5A-14-1. Relative intensities of the peaks and their assignments are presented in Table 5A-14-1. All PIE curves of ions emanating from this compound are shown in Figure 5A-14-2, and the summary of thermochemical information for these ions is given in Table 5A-14-2.



The parent ion PIE curve is shown in Figure 5A-14-3, where it may be seen that the threshold includes two steps. Figure 5A-14-4 shows the fit of the error function to the threshold region. The adiabatic IP of parent ion is $11.41 \pm 0.02 \text{ eV}$, which is slightly higher than and in a very good agreement with previous literature values: $11.39 \pm 0.12 \text{ eV}$ ⁹⁶ and $11.37 \pm 0.02 \text{ eV}$.⁹⁷ From the reaction equation:

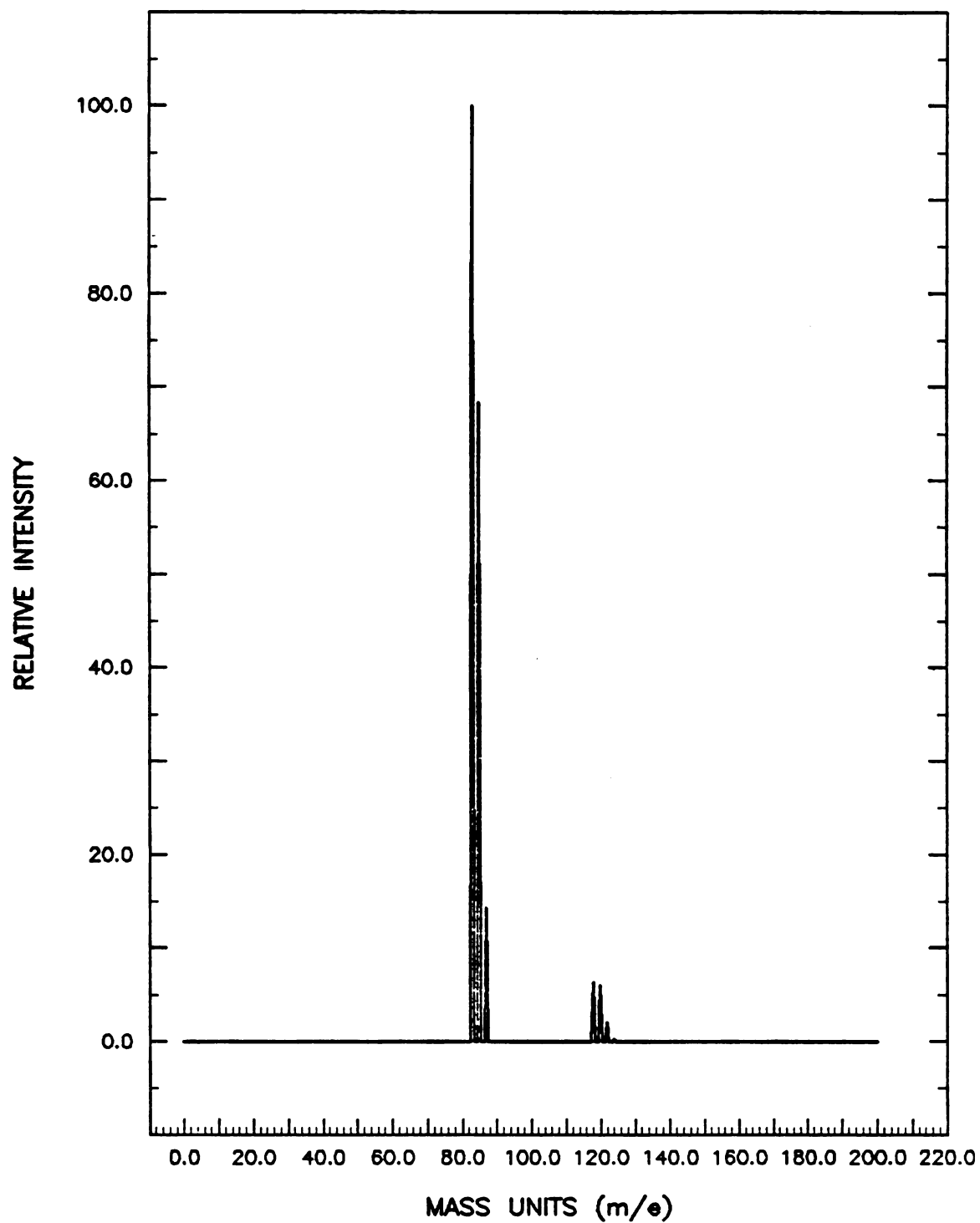


**Figure 5A-14-1. Photoionization Mass Spectrum of CHCl_3
(obtained under full illumination of the
helium discharge).**

Table 5A-14-1. Photoionization Mass Spectrum of CHCl_3^{a}

m/e	Intensity Relative to CHCl_2^+	Percent of Total Ion Production	Probable Formula
83	100.0	50.70	$\text{CH}^{35}\text{Cl}_2^+$
85	68.3	34.61	$\text{CH}^{35}\text{Cl}^{37}\text{Cl}^+$
87	14.3	7.24	$\text{CH}^{37}\text{Cl}_2^+$
118	6.3	3.22	$\text{CH}^{35}\text{Cl}_3^+$
120	6.0	3.06	$\text{CH}^{35}\text{Cl}_2^{37}\text{Cl}^+$
122	2.1	1.05	$\text{CH}^{35}\text{Cl}^{37}\text{Cl}_2^+$
124	0.3	0.12	$\text{CH}^{37}\text{Cl}_3^+$

^aObtained under full illumination of the helium discharge.Table 5A-14-2. Summary of IP, AP and Heat of formation data for all ions from CHCl_3 .

ION	IP or AP (eV) ^a	Products of $\text{CHCl}_3 + h\nu$	Heats of formation(0°K) (Kcal/mole) ^a
CHCl_3^+	11.41	$\text{CHCl}_3^+ + e^-$	239.71
CHCl_2^+	11.42	$\text{CHCl}_2^+ + \text{Cl} + e^-$	211.34

^asee text for uncertainties.

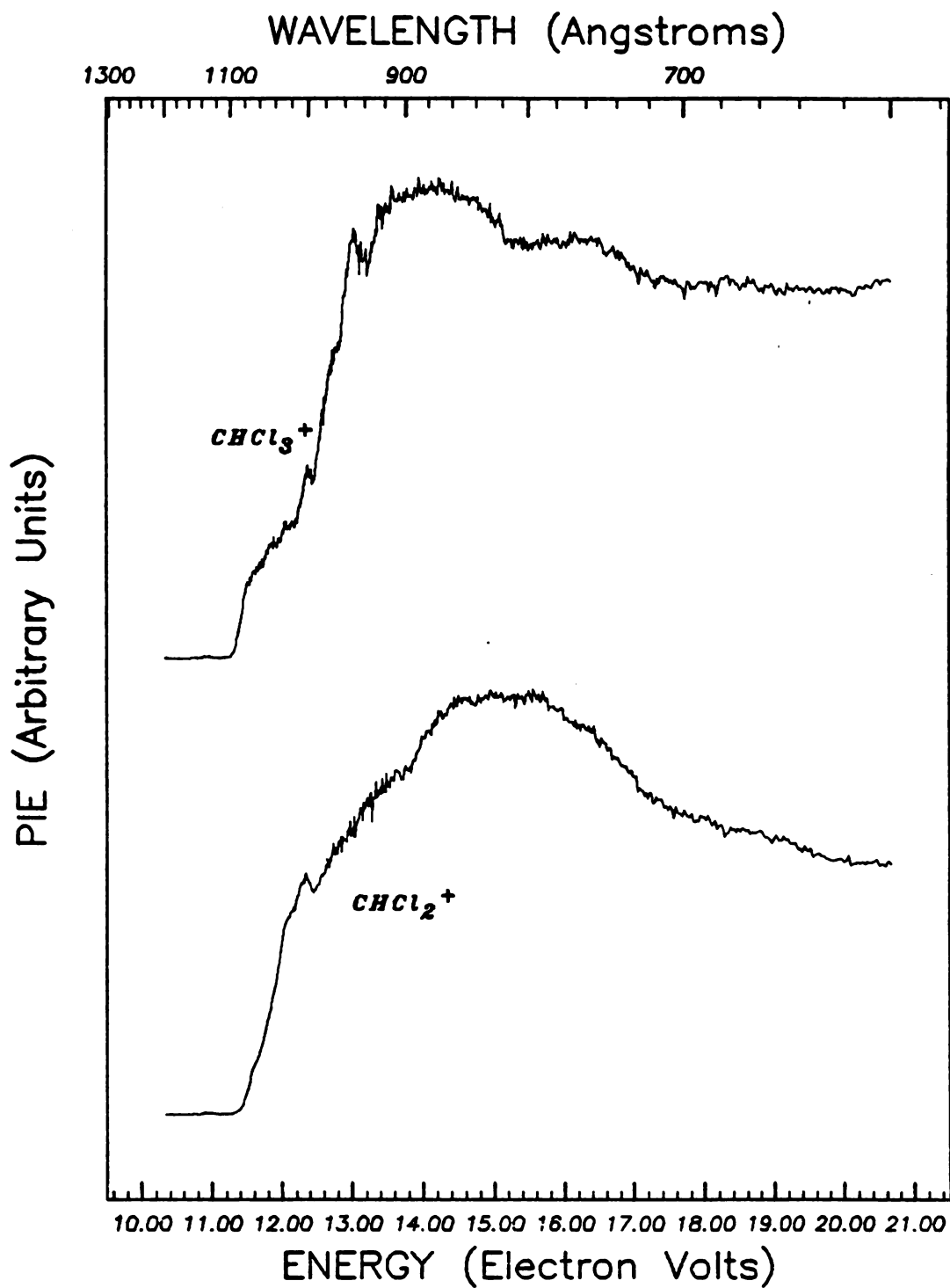


Figure 5A-14-2. Photoionization efficiency curves for parent and daughter ions from CHCl_3 .

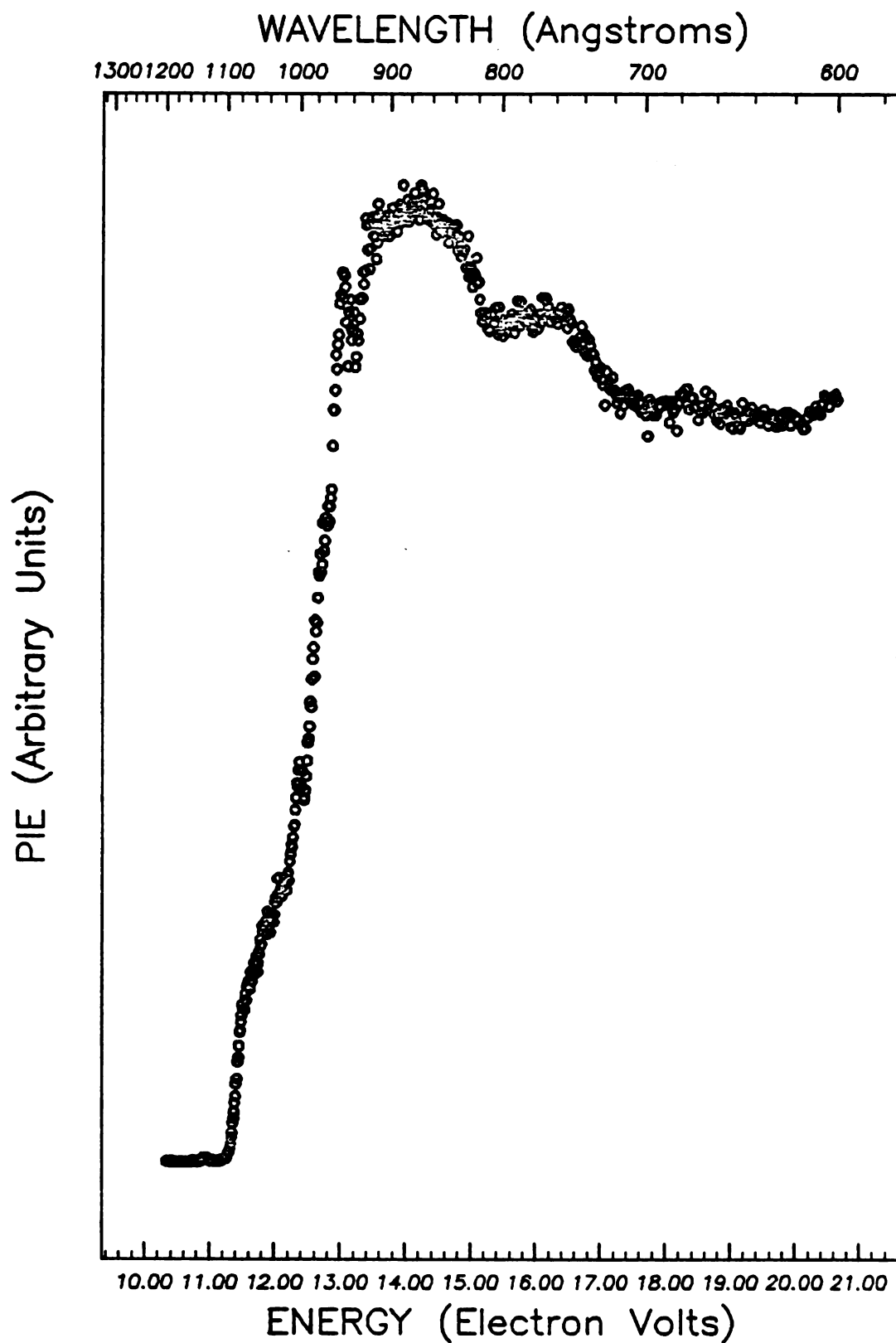


Figure 5A-14-3. PIE of CHCl_3^+ from CHCl_3 .

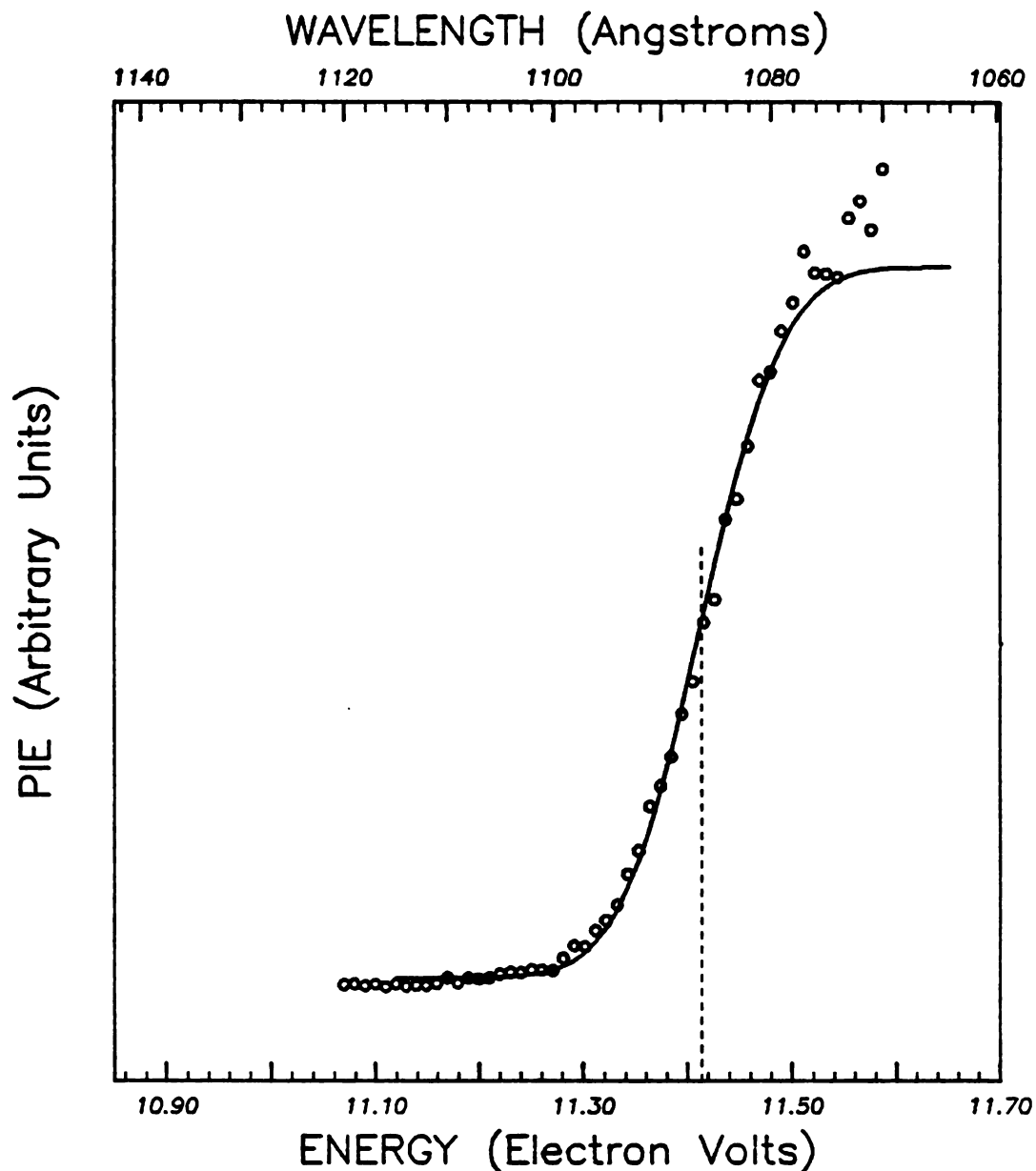


Figure 5A-14-4. PIE of CHCl_3^+ in the threshold region. Circles denote experimental points. The solid line is the best fit of a Gaussian representation of rotational and instrumental contributions. The dashed line indicates the position of the corrected ionization potential.

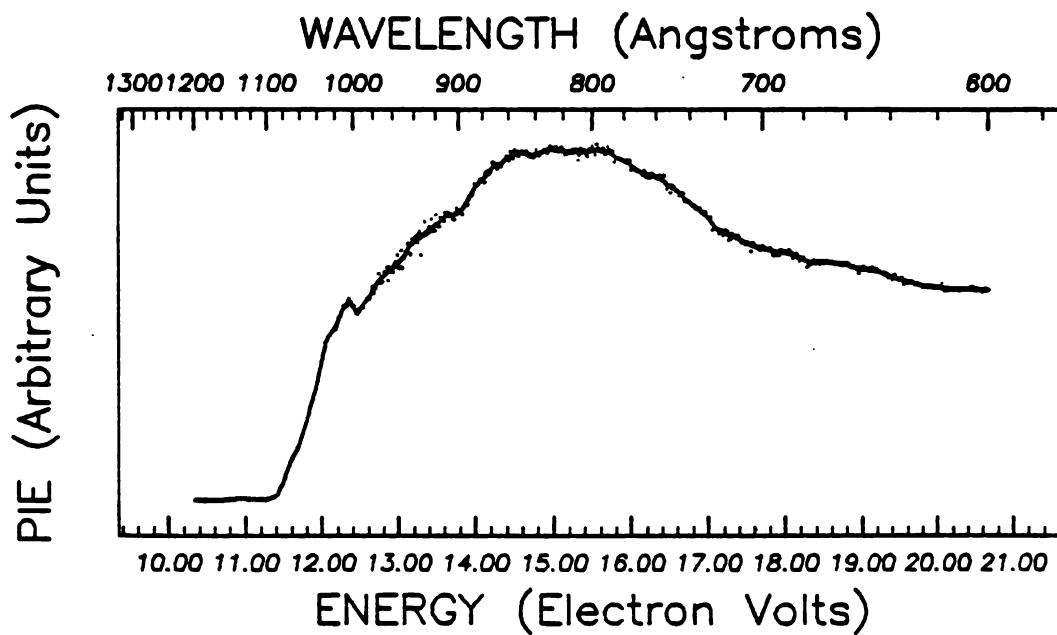
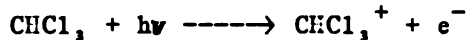
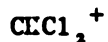


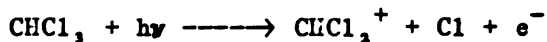
Figure 5A-14-5. PIE of CHCl_2^+ from CHCl_3 . The solid line represents a smooth fit to the experimental data points.



the value of $\Delta H_{f0}^\circ(\text{CHCl}_2^+)$ is calculated to be $239.71 \pm 0.8 \text{ kcal/mole}$.



The only fragment PIE curve measured from CHCl_2 is shown in Figure 5A-14-5. The PIE shows steps at threshold and autoionization structure in the post-threshold region. The experimental AP obtained from the PIE curve is $11.42 \pm 0.04 \text{ eV}$, which is slightly lower than and in a good agreement with previous literature values: $11.64 \pm 0.02 \text{ eV}^{97}$ and $11.49 \pm 0.02 \text{ eV}^{96}$. From the reaction equation:



the value of $\Delta H_{f0}^\circ(\text{CHCl}_2^+)$ is calculated to be $211.34 \pm 1.3 \text{ kcal/mole}$.

B. Discussion

1. The Heats of Formation of Fragment Ions

Because of the factors described in chapter four, experimental appearance potentials are upper limits to the desired thermochemical threshold values. Thus the heat of formation of a given fragment ion calculated from an experimental AP is also an upper limit. The lowest value obtained for a given ion is thus considered "best".

(1) CF_3^+

Figure 5B-1-1 shows the photoionization efficiency curves of CF_3^+ from all the precursors studied in this work. Table 5B-1-1 lists the heats of formation (0°K) of CF_3^+ derived from the measured appearance

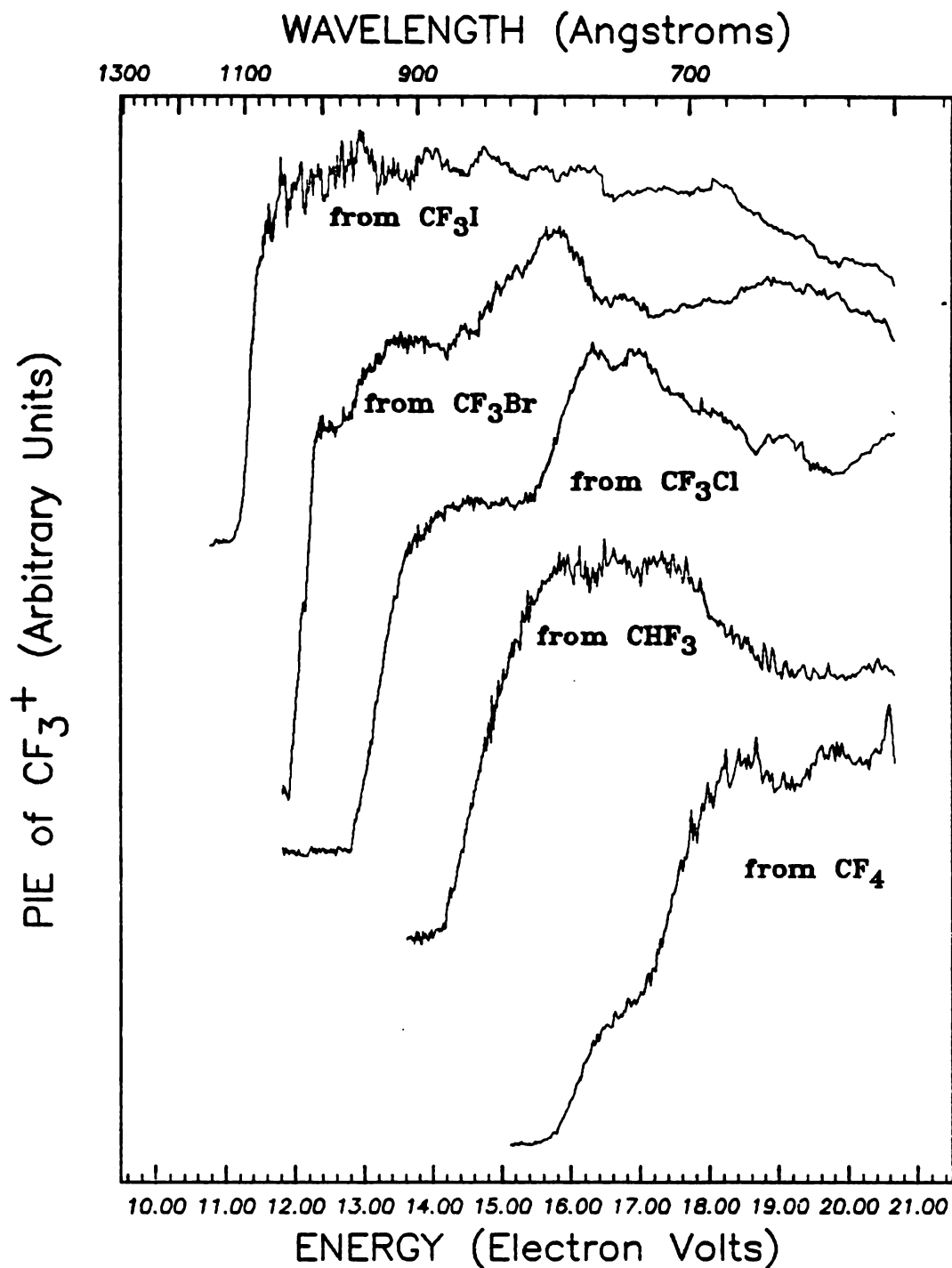


Figure 5B-1-1. Photoionization efficiency curves for CF_3^+ formed by fragmentation of various molecular precursors.

Table 5B-1-1. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CF_3^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CF_4	F	116.08 ± 2.3	PI*
CHF_3	H	109.54 ± 1.7	PI*
CF_3Cl	Cl	96.34 ± 2.4	PI*
CF_3Br	Br	93.56 ± 1.7	PI*
CF_3I	I	91.15 ± 1.7	PI*
CF_3I	I	87.3	PI
CF_3Cl	Cl	$93.5(300^{\circ}\text{K})$	PI
CF_3Cl		93.8 ± 2.0	ICR
CF_3I	I	96.17 ± 1.2	PIPECO
C_2F_4	CF	99.2 ± 3.2	PI
$\text{CF}_3\text{I}, \text{CF}_3$	I, -	99.8 ± 2.8	PI
CF_3		107.37 ± 1.0	EI
CF_3OF	OF	185.39 ± 17.6	EI

*this work.

potentials. It is clear from the Table that the stronger the bond which is broken, the greater is the apparent excess energy deposited into the CF_3^+ ion. The lowest $\Delta H_{f0}^\circ(\text{CF}_3^+)$ obtained in this investigation is calculated from the fragmentation of CF_3I ; the value is $91.15 \pm 1.7 \text{ kcal/mole}$. Table 5B-1-1 also lists previous literature values, and the techniques used to obtain the primary data. Ajello et al.⁹⁸ used the PIMS technique, and found $\Delta H_f^\circ(300^\circ\text{K}) = 93.5 \text{ kcal/mole}$. Lias and Ausloos⁹⁹ used the results of an ICR investigation of $\text{CD}_5^+ + \text{CF}_3\text{Cl} \rightarrow \text{CF}_3^+ + \text{DCl} + \text{CD}_4$ to get the $\Delta H_{f0}^\circ(\text{CF}_3^+)$ value $93.8 \pm 2.0 \text{ kcal/mole}$. Bombach et al.,⁹⁴ from a PIPECO study of CF_3I , found $\Delta H_{f0}^\circ(\text{CF}_3^+) = 96.2 \pm 1.2 \text{ kcal/mole}$. Walter et al.¹⁰⁰ studied photoionization and fragmentation of C_2F_4 . Their value for the heat of formation of CF_3^+ ($99.2 \pm 3.2 \text{ kcal/mole}$) is higher than those obtained from direct bond rupture processes, probably because rearrangement of the parent ion prior to fragmentation into $\text{CF}_3^+ + \text{CF}$ is required. Most likely this requires promotion to an excited state of C_2F_4^+ , with the excess energy being deposited in the fragments. The JANAF¹⁰¹ thermochemical tables list $\Delta H_{f0}^\circ(\text{CF}_3^+) = 99.8 \pm 2.8 \text{ kcal/mole}$; that value was chosen from the average of photoionization determinations from the CF_3I and CF_3 radical. Syrvatka et al.¹⁰² studied the IP of CF_3 , and obtained $\Delta H_{f0}^\circ(\text{CF}_3^+)$ equal to $107.37 \pm 1.0 \text{ kcal/mole}$. Thyme and Macneil¹⁰³ investigated CF_3OF by the EI technique; their value for $\Delta H_{f0}^\circ(\text{CF}_3^+)$ is almost double all the others reported in the Table.

From an early photoionization study of halomethanes, Noutary¹²³ derived $\Delta H_{f0}^\circ(\text{CF}_3^+) = 87.3 \text{ kcal/mole}$. Inspection of the original paper reveals that the extrapolation method employed to determine appearance

potentials is suspect, and the compilers of the JANAF Table¹⁰¹ ignored Noutary's result in their critical evaluation. From the data at hand, it seems safe to say that the heat of formation of CF_3^+ lies in the range 90-95kcal/mole. It is probably close to the lowest upper limit calculated from the PIMS experiments in this work; i.e. $\Delta H_{f0}^0(\text{CF}_3^+) \leq 91.15 \pm 1.7 \text{ kcal/mole}$.

(2) CF_2Cl^+

Figure 5B-1-2 shows the photoionization efficiency curves of CF_2Cl^+ from all the precursors studied in this work. Table 5B-1-2 lists the heats of formation (0°K) of CF_2Cl^+ derived from the measured appearance potentials. It is clear from the Table that the stronger the bond which is broken, the greater is the apparent excess energy deposited into the CF_2Cl^+ ion. The lowest $\Delta H_{f0}^0(\text{CF}_2\text{Cl}^+)$ obtained in this investigation is calculated from the fragmentation of CF_2ClBr ; the value is $124.73 \pm 2.0 \text{ kcal/mole}$. Table 5B-1-2 also lists previous literature values, and the technique used to obtain the primary data. Ajello⁹⁸ studied CF_2Cl_2 , gave $\Delta H_f^0(300^\circ\text{K})(\text{CF}_2\text{Cl}^+) = 130.0 \text{ kcal/mole}$. Lias and Ausloos⁹⁹ and found the results of an ICR investigation of the reaction $\text{C}_2\text{H}_5^+ + \text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}^+ + \text{C}_2\text{H}_5\text{Cl}$ to get the $\Delta H_{f0}^0(\text{CF}_2\text{Cl}^+)$ value $130.0 \pm 4.0 \text{ kcal/mole}$. Jochims et al.⁹² studied CF_2Cl_2 , and obtained $\Delta H_{f0}^0(\text{CF}_2\text{Cl}^+) = 132.45 \text{ kcal/mole}$. Leyand et al.¹⁰⁴ studied $\text{CF}_2\text{ClCF}_2\text{Cl}$ by electron impact and provided the $\Delta H_{f0}^0(\text{CF}_2\text{Cl}^+)$ value $133.7 \pm 2.0 \text{ kcal/mole}$. Syrvatka et al.¹⁰² studied $\text{CF}_2=\text{CClF}$, by EI; they give $\Delta H_f^0(298^\circ\text{K})(\text{CF}_2\text{Cl}^+) = 130.05 \text{ kcal/mole}$. Jochims et al.⁹² also studied CF_3Cl , and obtained $\Delta H_{f0}^0(\text{CF}_2\text{Cl}^+) = 140.6 \text{ kcal/mole}$. From the data at hand, it appears that the heat of formation of CF_2Cl^+ is probably close to the

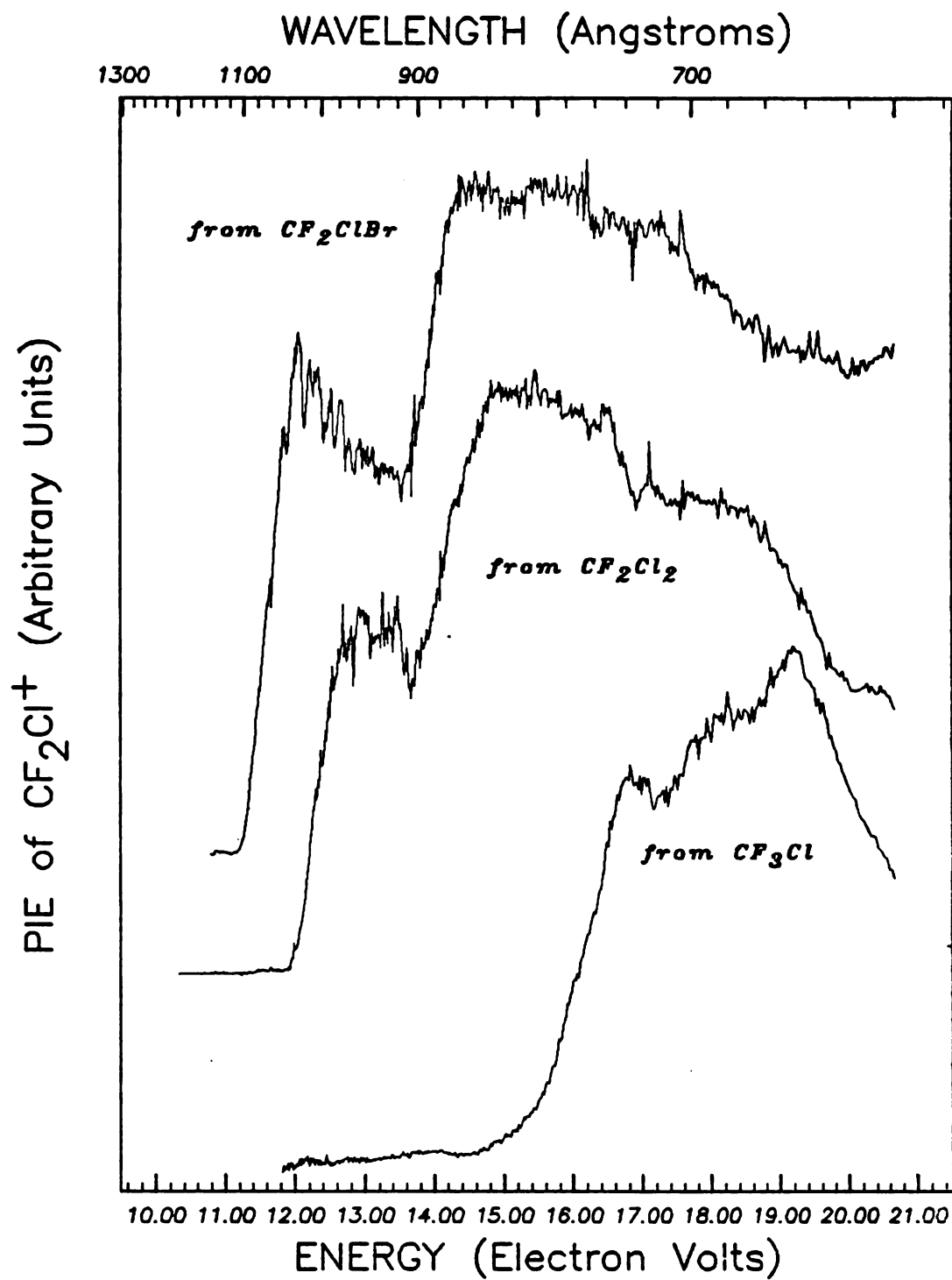


Figure 5B-1-2. Photoionization efficiency curves for CF_2Cl^+ formed by fragmentation of various molecular precursors.

Table 5B-1-2. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CF_2Cl^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CF_3Cl	F	146.63 ± 2.8	PI*
CF_2Cl_2	Cl	128.93 ± 2.9	PI*
CF_2ClBr	Br	124.73 ± 2.0	PI*
CF_2Cl_2	Cl	$130.0(300^{\circ}\text{K})$	PI
CF_2Cl_2		130.0 ± 4.0	ICR
CF_2Cl_2	Cl	132.45	PI
$\text{CF}_2\text{ClCF}_2\text{Cl}$	CF_2Cl	133.7 ± 2.0	EI
$\text{CF}_2=\text{CFCl}$	CF	$136.05(298^{\circ}\text{K})$	EI
CF_3Cl	F	140.8	PI

*this work.

lowest upper limit calculated from the PIMS experiments in this work; i.e. $\Delta H_{f0}^{\circ}(\text{CF}_2\text{Cl}^+) \leq 124.73 \pm 2.0 \text{ kcal/mole}$.

(3) CFCl_2^+

Figure 5B-1-3 shows the photoionization efficiency curves of CFCl_2^+ from all the precursors studied in this work. Table 5B-1-3 lists the heats of formation (0°K) of CFCl_2^+ derived from the measured appearance potentials. It is clear from the Table that the stronger the bond which is broken, the greater is the apparent excess energy deposited into the CFCl_2^+ ion. The lowest $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+)$ obtained in this investigation is calculated from the fragmentation of CFCl_3 ; the value is $168.89 \pm 3.1 \text{ kcal/mole}$. Table 5B-1-3 also lists previous literature values, and the technique used to obtain the primary data. Lias and Ausloos⁹⁹ note that no reaction was observed in an ICR investigation of the system $\text{sec-C}_4\text{H}_7^+ + \text{CFCl}_3$, which lead them to determine $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+) = 155.0 \pm 5.0 \text{ kcal/mole}$. Ajello et al.⁹⁸ used the PIMS technique to obtain $\Delta H_f^{\circ}(300^\circ\text{K})(\text{CFCl}_2^+) = 168.6 \text{ kcal/mole}$. Jochims et al.⁹² used the same technique, and gave $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+) = 170.6 \text{ kcal/mole}$. Syrvatka et al.¹⁰² used the EI technique, to provide a heat of formation value 170.6 kcal/mole at 298°K . From CF_2Cl_2 , Ajello et al. obtained $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+) = 181.9 \text{ kcal/mole}$. Jochims et al. also investigated CF_2Cl_2 , which gave $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+) = 189.9 \text{ kcal/mole}$. From the data at hand, it seems safe to say that the heat of formation of CFCl_2^+ lies in the range $167\text{--}170 \text{ kcal/mole}$. It is probably close to the lowest upper limit calculated from the PIMS experiments in this work; i.e. $\Delta H_{f0}^{\circ}(\text{CFCl}_2^+) \leq 168.89 \pm 3.1 \text{ kcal/mole}$.

(4) CCl_3^+

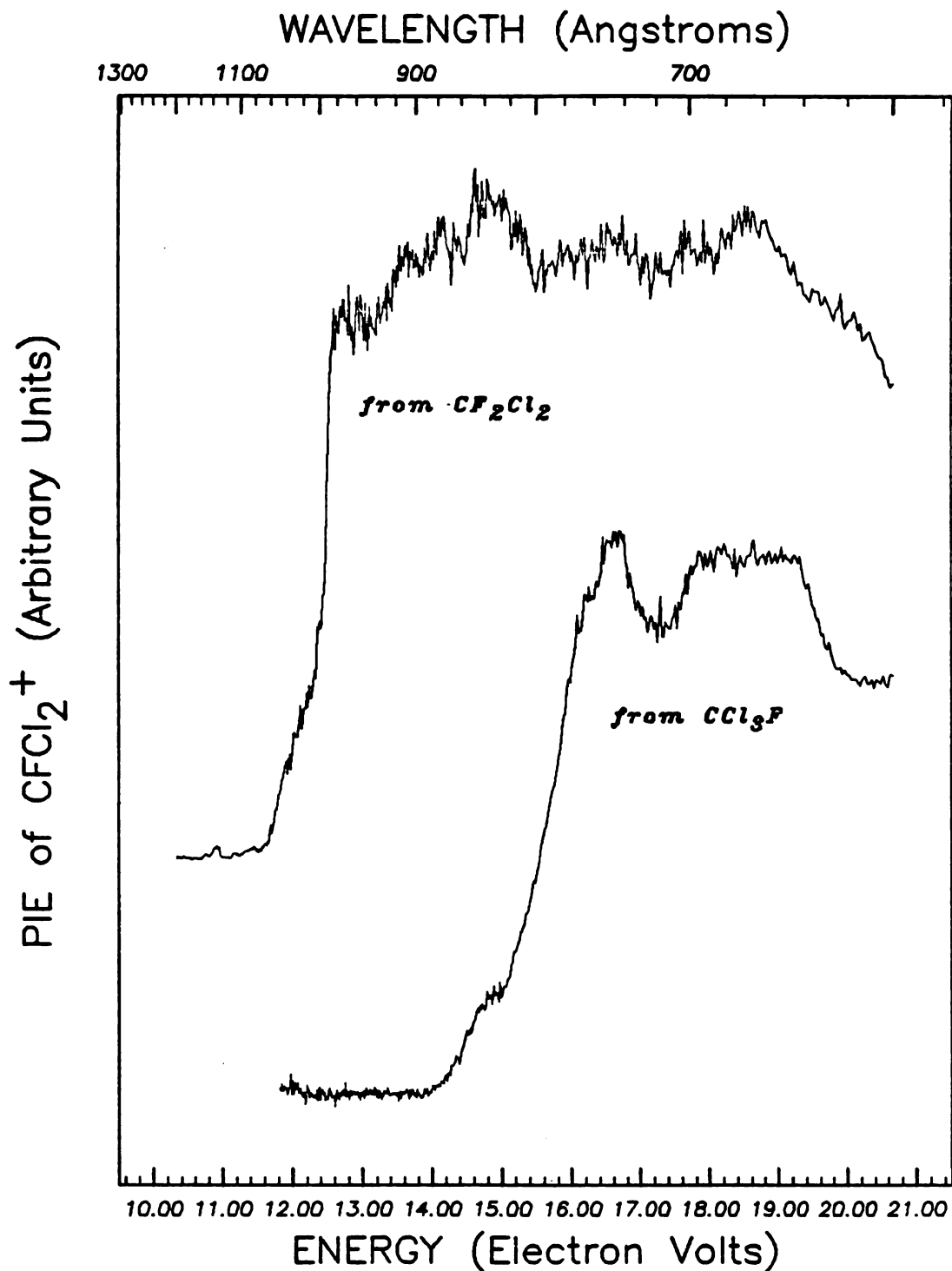


Figure 5B-1-3. Photoionization efficiency curves for CFCl_2^+ formed by fragmentation of various molecular precursors.

Table 5B-1-3. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CFCl_2^+

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CF_2Cl_2	F	186.44 ± 4.0	PI*
CFCl_3	Cl	168.89 ± 3.1	PI*
CFCl_2^+		155.0 ± 5.0	ICR
CFCl_3	Cl	$163.6(300^{\circ}\text{K})$	PI
CFCl_3	Cl	170.6	PI
$\text{CFCl}=\text{CFCl}$	CF	$170.64(298^{\circ}\text{K})$	EI
CF_2Cl_2	F	181.9	PI
CF_2Cl_2	F	189.9	PI

*this work.

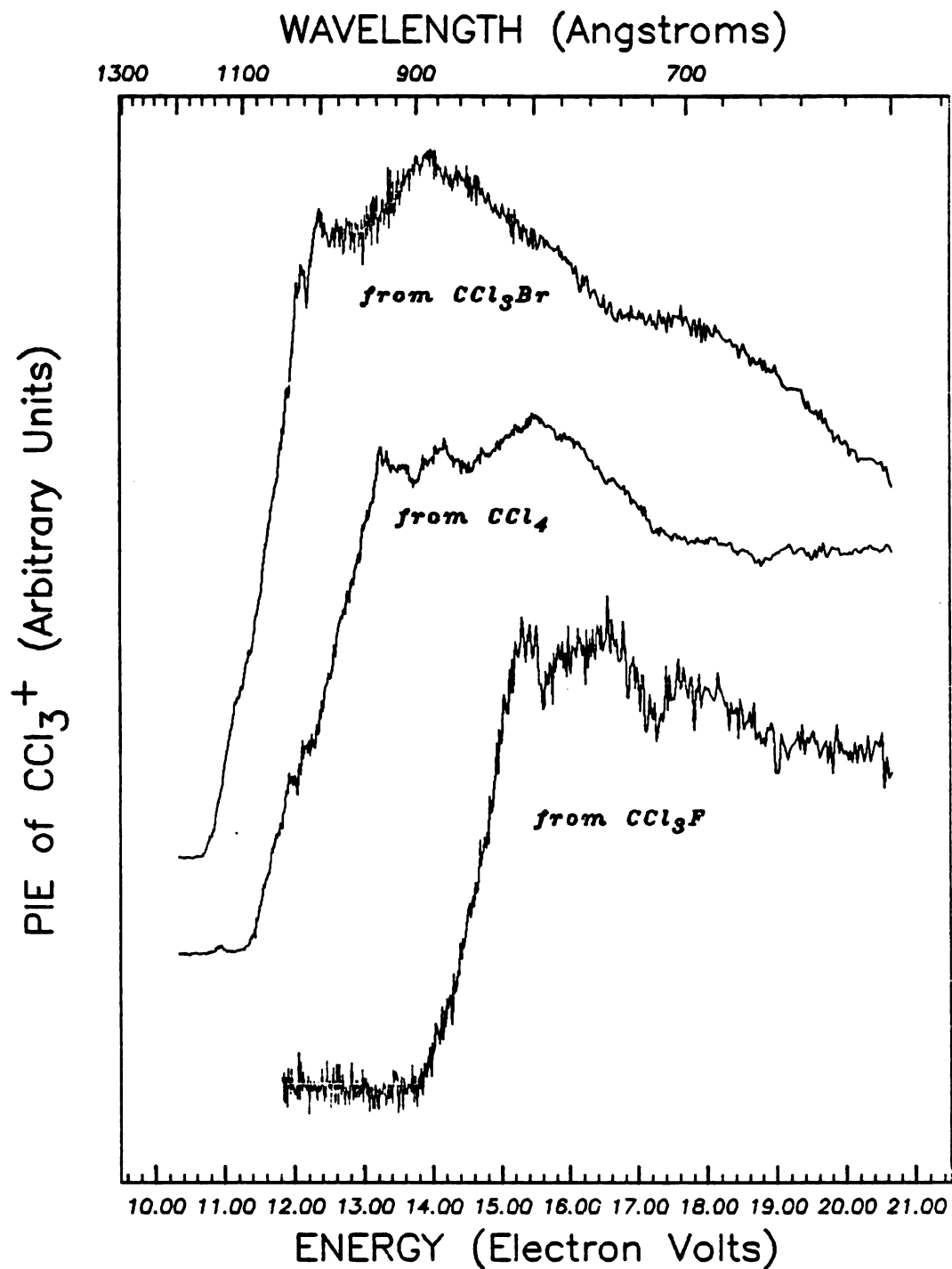


Figure 5B-1-4. Photoionization efficiency curves for CCl_3^+ formed by fragmentation of various molecular precursors.

Table 5B-1-4. Estimates of $\Delta H_{f0}^0(0^\circ\text{K})$ for CCl_3^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^0(0^\circ\text{K})$ (kcal/mole)	TECHNIQUE
CFCl_3	F	226.79 ± 4.2	PI*
CCl_4	Cl	213.43 ± 1.5	PI*
CCl_3Br	Br	207.78 ± 2.7	PI*
		198.0 ± 7.0	ICR
CCl_4	Cl	$208.8(298^\circ\text{K})$	PI
CFCl_3	F	$217.5(300^\circ\text{K})$	PI
CFCl_3	F	223.54	PI

*this work.

Figure 5B-1-4 shows the photoionization efficiency curves of CCl_3^+ from all the precursors studied in this work. Table 5B-1-4 lists the heats of formation (0°K) of CCl_3^+ derived from the measured appearance potentials. It is clear from the Table that the stronger the bond which is broken, the greater is the apparent excess energy deposited into the CCl_3^+ ion. The lowest $\Delta H_{f0}^\circ(\text{CCl}_3^+)$ obtained in this investigation is calculated from the fragmentation of CCl_3Br ; the value is $207.78 \pm 2.7 \text{ kcal/mole}$. Table 5B-1-4 also lists previous literature values, and the technique used to obtain the primary data. Lias and Ausloos used the results from an ICR study to provide $\Delta H_{f0}^\circ(\text{CCl}_3^+) = 198.0 \pm 7.0 \text{ kcal/mole}$. Werner et al.⁹⁶ used the PIMS technique to investigate CCl_4 , and gave $\Delta H_f^\circ(298^\circ\text{K})(\text{CCl}_3^+)$ equal to 208.8 kcal/mole . Ajello et al.⁹⁸ used the same technique, and found CFCl_3 , obtained $\Delta H_f^\circ(300^\circ\text{K})(\text{CCl}_3^+) = 217.5 \text{ kcal/mole}$. Jochims et al.⁹² also studied CFCl_3 , and found $\Delta H_{f0}^\circ(\text{CFCl}_3^+) = 223.54 \text{ kcal/mole}$. From the data at hand, it seems safe to say that the heat of formation of CCl_3^+ lies in the range $206\text{--}210 \text{ kcal/mole}$. It is probably close to the lowest upper limit calculated from the PIMS experiments in this work; i.e. $\Delta H_{f0}^\circ(\text{CCl}_3^+) \leq 207.78 \pm 2.7 \text{ kcal/mole}$.

(5) CF_2Br^+

Figure 5B-1-5 shows the photoionization efficiency curves of CF_2Br^+ from all the precursors studied in this work. Table 5B-1-5 lists the heats of formation (0°K) of CF_2Br^+ derived from the measured appearance potentials. It is clear from the Table that the stronger the bond which is broken, the greater is the apparent excess energy deposited into the CF_2Br^+ ion. The lowest $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+)$ obtained in this

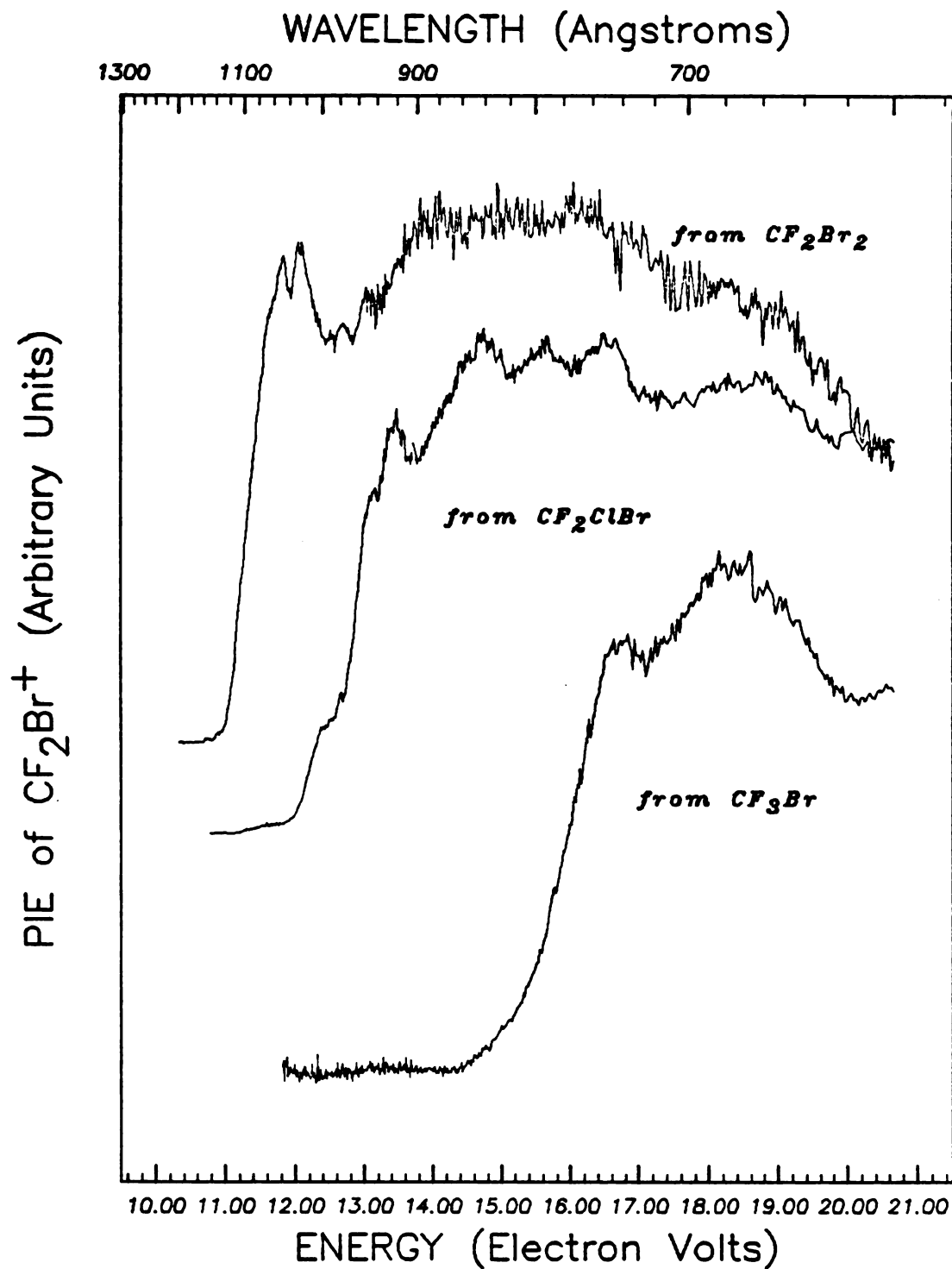


Figure 5B-1-5. Photoionization efficiency curves for CF_2Br^+ formed by fragmentation of various molecular precursors.

Table 5B-1-5. Estimates of $\Delta H_{f0}^0(0^\circ\text{K})$ for CF_2Br^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^0(0^\circ\text{K})$ (kcal/mole)	TECHNIQUE
CF_3Br	F	164.73 ± 2.7	PI*
CF_2ClBr	Cl	140.54 ± 2.0	PI*
CF_2Br_2	Br	128.58 ± 2.0	PI*
CF_3Br	F	175.8 ± 2.9	EI

*this work.

investigation is calculated from the fragmentation of CF_2Br_2 ; the value is $128.58 \pm 2.0 \text{ kcal/mole}$. Table 5B-1-5 also lists previous literature values, and the technique used to obtain the primary data. Marriott and Craggs¹⁰⁵ used EI technique on CF_2Br and obtained $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+) = 175.8 \pm 2.9 \text{ kcal/mole}$. From the data at hand, it seems safe to say that the heat of formation of CF_2Br^+ lies in the range 125-140 kcal/mole. It is probably close to the lowest upper limit calculated from the PIMS experiments in this work; i.e. $\Delta H_{f0}^\circ(\text{CFCl}_2^+) \leq 128.58 \pm 2.0 \text{ kcal/mole}$.

(6) CF_2^+

Figure 5B-1-6 shows the photoionization efficiency curves of CF_2^+ from all the precursors studied in this work. Table 5B-1-6 lists the heats of formation (0°K) of CF_2^+ derived from the measured appearance potentials. The lowest $\Delta H_{f0}^\circ(\text{CF}_2^+)$ obtained in this investigation is calculated from the fragmentation of CF_2ClBr ; the value is $204.38 \pm 2.7 \text{ kcal/mole}$. Table 5B-1-6 also lists previous literature values, and the technique used to obtain the primary data. Ajello et al.⁹⁸ used the PIMS technique to investigate both CF_2Cl_2 and CF_2Cl ; he obtained the heat of formation values 216.2 kcal/mole and 217.4 kcal/mole at 300°K . Jochims⁹² used the same technique, and from CF_2Cl and CF_2Cl_2 obtained $\Delta H_{f0}^\circ(\text{CF}_2^+) = 217.5 \text{ kcal/mole}$ and $\Delta H_{f0}^\circ(\text{CF}_2^+) = 221.4 \text{ kcal/mole}$. Hildenbrand¹⁰⁶ investigated the IP of CF_2 , and gave the heat of formation as $219.28 \pm 1.5 \text{ kcal/mole}$. Steele¹⁰⁷ studied CF_2F_2 by EI and obtained $\Delta H_{f0}^\circ(\text{CF}_2^+) = 235.39 \pm 9.6 \text{ kcal/mole}$. From the data at hand, it seems safe to say that the heat of formation of CF_2^+ lies in the range 200-210 kcal/mole. It is probably close to the lowest upper limit

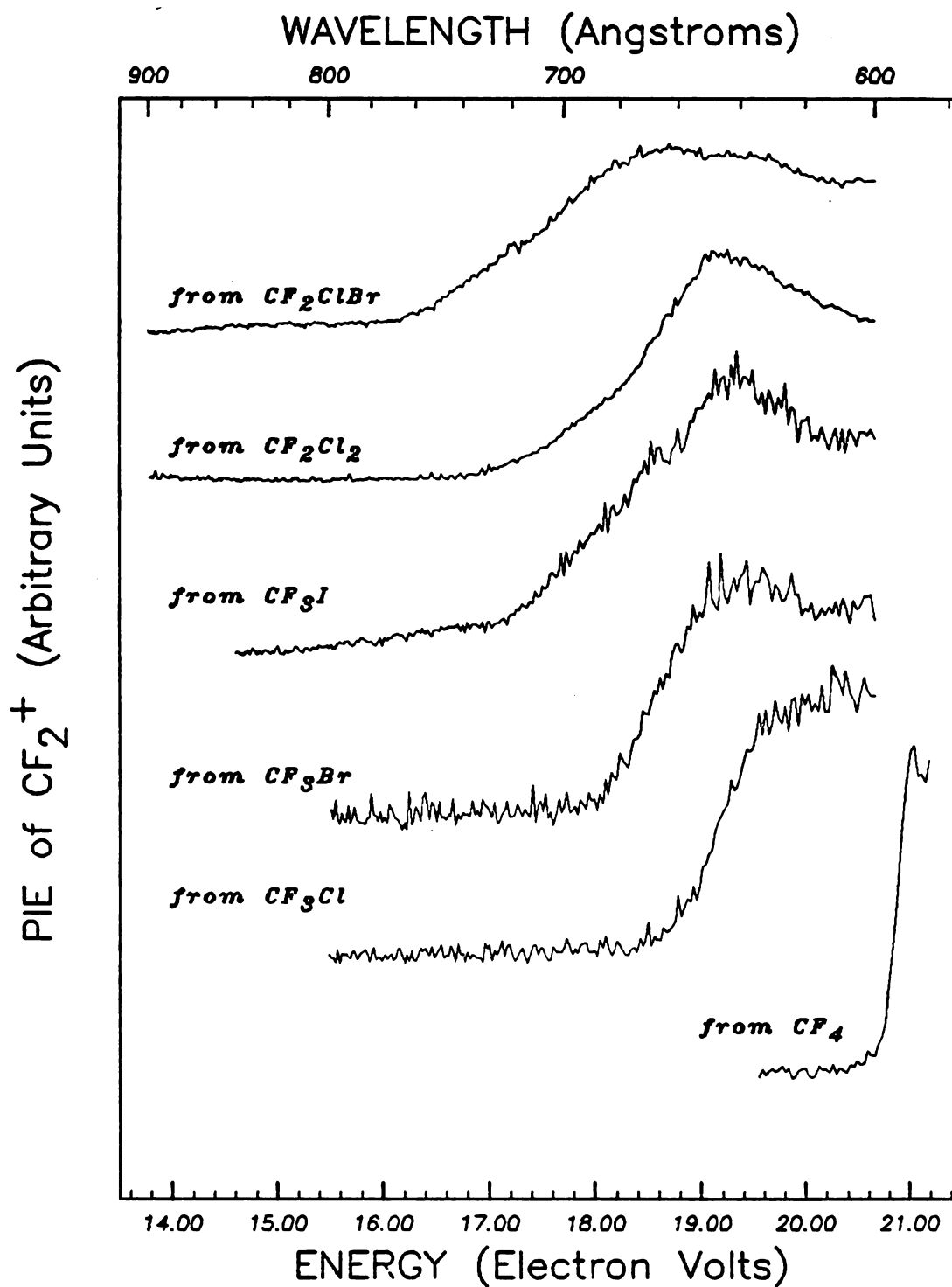


Figure 5B-1-6. Photoionization efficiency curves for CF_2^+ formed by fragmentation of various molecular precursors.

Table 5B-1-6. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CF_2^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CF_4	F,F	213.02±3.4	PI*
CF_3Cl	F,Cl	211.5±3.5	PI*
CF_3Br	F,Br	208.49±3.5	PI*
CF_3I	F,I	207.94±3.5	PI*
CF_2Cl_2	Cl,Cl	207.18±3.7	PI*
CF_2ClBr	Cl,Br	204.36±2.7	PI*
CF_2Cl_2	Cl,Cl	216.2(300°K)	PI
CF_3Cl	F,Cl	217.4(300°K)	PI
CF_3Cl	F,Cl	217.5	PI
CF_2		219.28±1.5	EI
CF_2Cl_2	Cl,Cl	221.4	PI
CH_2F_2	H_2	235.39±9.6	EI

*this work.

calculated from the PIMS experiments in this work; i.e.

$$\Delta H_{f0}^{\circ}(\text{CF}_2^+) \leq 204.36 \pm 2.7 \text{ kcal/mole.}$$

(7) CFCl^+

Figure 5B-1-7 shows the photoionization efficiency curves of CFCl^+ from all the precursors studied in this work. Table 5B-1-7 lists the heats of formation (0°K) of CFCl^+ derived from the measured appearance potentials. The lowest $\Delta H_{f0}^{\circ}(\text{CFCl}^+)$ obtained in this investigation is calculated from the fragmentation of CFCl_2 ; the value is $231.35 \pm 8.5 \text{ kcal/mole}$. Table 5B-1-7 also lists previous literature values, and the technique used to obtain the primary data. Ajello et al.⁹⁸ used the PIMS technique to investigate both CFCl_2 and CF_2Cl_2 and obtained the heat of formation values 242.5 kcal/mole and 242.2 kcal/mole at 300°K . Syrvatka et al.¹⁰² studied $\text{CF}_2=\text{CFCl}$ and $\text{CFCl}=\text{CFCl}$; they calculated heat of formation values $256.0 \pm 7.0 \text{ kcal/mole}$ and $262.0 \pm 6.0 \text{ kcal/mole}$. Horbock and Kisen,⁹⁷ from EI on CHF_2Cl , supplied the heat of formation value 264.0 kcal/mole . From the data at hand, it seems safe to say that the heat of formation of CFCl^+ lies in the range $230\text{--}240 \text{ kcal/mole}$. It is probably close to the lowest upper limit calculated from the PIMS experiments reported in this work; i.e. $\Delta H_{f0}^{\circ}(\text{CFCl}^+) \leq 231.35 \pm 8.5 \text{ kcal/mole}$.

(8) CCl_2^+

Figure 5B-1-8 shows the photoionization efficiency curves of CCl_2^+ from all the precursors studied in this work. Table 5B-1-8 lists the heats of formation (0°K) of CCl_2^+ derived from the measured appearance potentials. The lowest $\Delta H_{f0}^{\circ}(\text{CCl}_2^+)$ obtained in this investigation is calculated from the fragmentation of CCl_2Br ; the value is

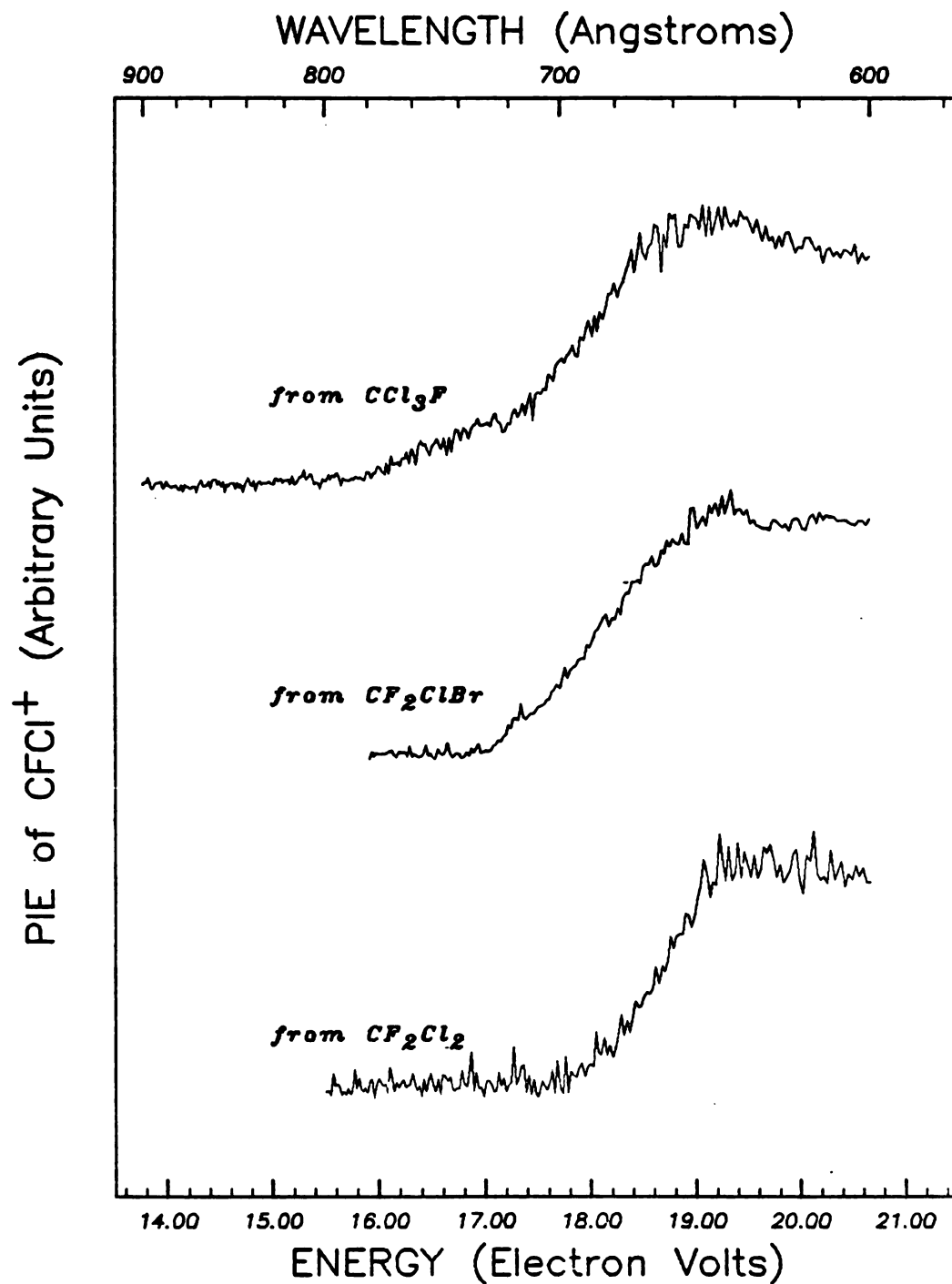


Figure 5B-1-7. Photoionization efficiency curves for CFCI^+ formed by fragmentation of various molecular precursors.

Table 5B-1-7. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CFCI^+

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CF_2Cl_2	F, Cl	246.19 ± 8.4	PI*
CF_2ClBr	F, Br	237.93 ± 3.9	PI*
CFCI_3	Cl, Cl	231.35 ± 8.5	PI*
CFCI_3	Cl, Cl	$242.5(300^{\circ}\text{K})$	PI
CF_2Cl_2	F, Cl	$244.2(300^{\circ}\text{K})$	PI
$\text{CF}_2=\text{CFCI}$	CF_2	256.0 ± 7.0	EI
$\text{CFCI}=\text{CFCI}$	CFCI	262.0 ± 6.0	EI
CHF_2Cl	H, F	264.0	EI

*this work.

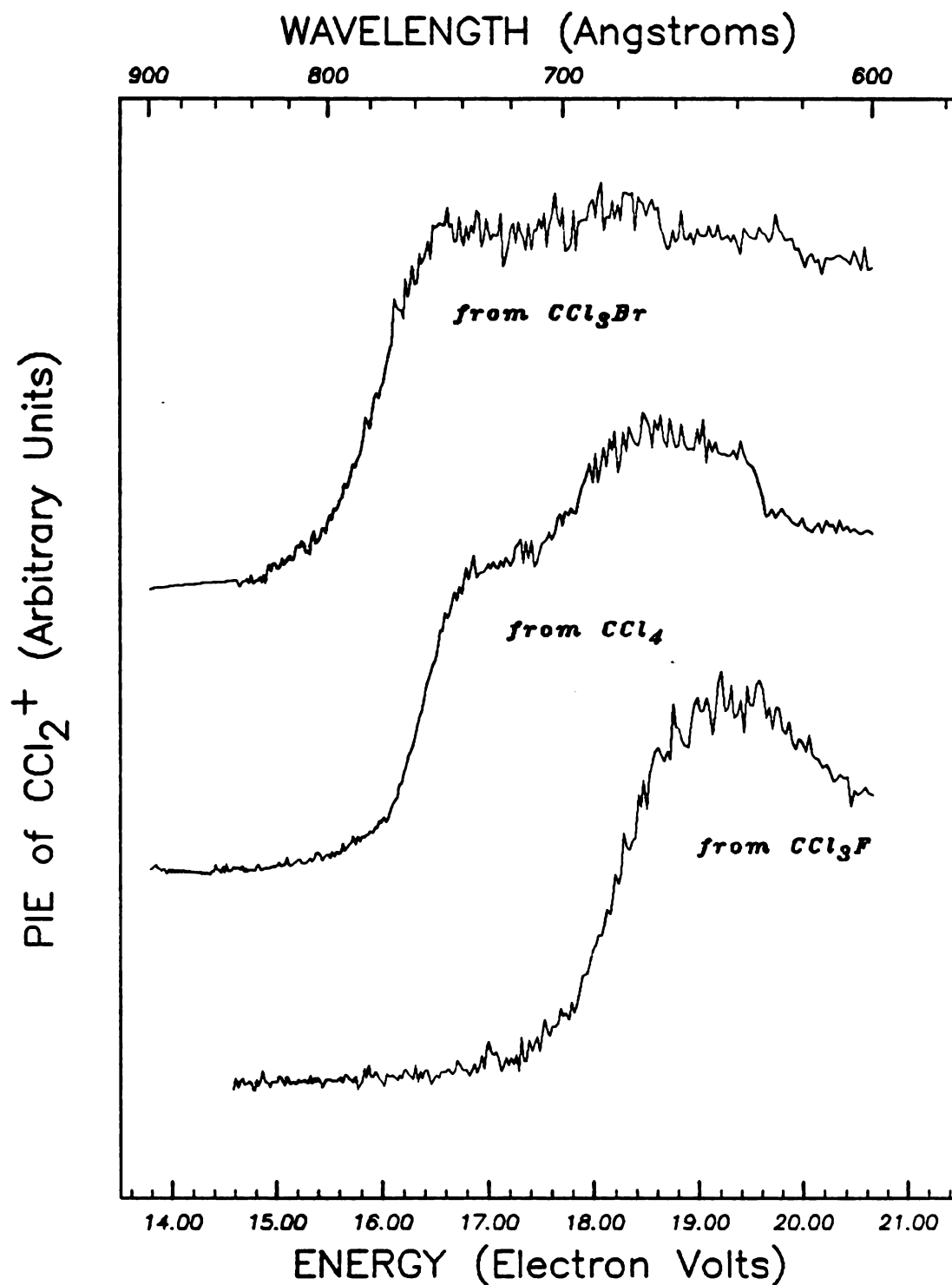


Figure 5B-1-8. Photoionization efficiency curves for CCl_2^+ formed by fragmentation of various molecular precursors.

Table 5B-1-8. Estimates of $\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ for CCl_2^+ .

PARENT NEUTRAL	OTHER PRODUCT	$\Delta H_{f0}^{\circ}(0^{\circ}\text{K})$ (kcal/mole)	TECHNIQUE
CCl_3F	F, Cl	263.06 ± 4.2	PI*
CCl_4	Cl, Cl	280.46 ± 2.2	PI*
CCl_3Br	Cl, Br	253.98 ± 2.7	PI*
CCl_4	Cl, Cl	275.66 ± 0.6	EI
CFCl_3	F, Cl	$278.0(300^{\circ}\text{K})$	PI
$\text{CCl}_2=\text{CCl}_2$	CCl_2	279.44 ± 5.7	EI
CHCl_3	HCl	279.86 ± 0.4	EI
CCl_2		281.77 ± 5.0	EI
$\text{CFCl}=\text{CFCl}$	CF_2	$283.83(298^{\circ}\text{K})$	EI

*this work.

253.98±2.7kcal/mole. Table 5B-1-8 also lists previous literature values, and the technique used to obtain the primary data. Ajello et al.⁹⁸ studied CFCl₃ by PIMS and obtained $\Delta H_f^\circ(300^\circ\text{K})(\text{CCl}_3^+) = 278\text{kcal/mole}$. Syrvatka¹⁰² investigated CFCl=CFCl by the EI technique and provided the heat of formation value 283.83±6.8kcal/mole at 298°K. Shapiro and Lossing¹⁰⁸ studied CCl₂, CCl₄, CEC₃, and C₂Cl₄ by EI. They obtained the heat of formation values: 281.77±5.0kcal/mole, 275.66±0.56kcal/mole, 279.86±0.35kcal/mole and 279.44±5.7kcal/mole, respectively. From the data at hand, it seems safe to say that the heats of formation of CCl₃⁺ lies in the range 250-260kcal/mole. It is probably close to the lowest upper limit calculated from the PIMS experiments reported in this work; i.e. $\Delta H_{f0}^\circ(\text{CCl}_3^+) \leq 253.98 \pm 2.7\text{kcal/mole}$.

2. Qualitative Consideration of Parent Ion Fragmentation

Energetics

In chapter three it was noted that three factors which influence the fragment threshold are: (1) the activation energy and heat of reaction, (2) the kinetic shift and (3) competitive reactions. The fragmentation processes of all halomethanes investigated in this work are all highly endothermic. Under these circumstances the activation energy for the dissociation reaction and the heat of the reaction are expected to be similar. In other words, the activation energy for the reverse, highly exothermic recombination reaction is likely to be small. This generalization almost certainly pertains to the ion-radical reactions of interest here.¹⁰⁹ The difference between the activation energy and the heat of the forward reaction is distributed to the

fragments as translational and internal energy; that difference is probably negligible or small, and thus contributions to the fragmentation threshold energy from factor (1) above will be ignored in the remaining discussion.

From the experimental results, it is clear that the excess energy deposited in the decomposition products when only one bond of the parent ion breaks depends strongly on the nature of the bond which is broken. For example, C-F bond scission is accompanied by about 20-30kcal/mole excess energy deposited as either translational or internal energy of the fragments, according to the experimental heats of formation of a given ion from various precursors. For the C-Cl bond, a somewhat smaller comparison indicates an excess energy of about 10-15kcal/mole, while for a C-Br bond rupture the corresponding value is only about 5 kcal/mole. Since the rupture of one bond is generally the lowest or second-lowest energy fragmentation process, there will be few or no competitive reactions. Thus the kinetic shift must be the factor of primary influence in these one-bond fragmentations.

The kinetic shift is itself an imprecise term which encompasses many contributions, including the geometry and the lifetime of the parent ion, its complexity and the coupling among its normal modes of vibration, and the nature of the bond(s) broken in the decomposition reaction. The parent ions of the halogenated methanes investigated in this work show highly variable stabilities under uniform experimental conditions (see Table 5B-2-1). One can view photoionization as a two-step process involving (vertical) absorption to quasi-discrete states of the neutral, followed by radiationless transfer into the

Table 5B-2-1. Relative parent ion stability.

Ion	<u>Ionization potential</u>		Relative stability [CF ₃ ⁺ =100]
	This work [eV±0.02eV]	Literature value ^a [eV]	
CF ₃ ClBr	11.21	11.83	5.13
CF ₃ Cl	12.60	12.39	11.54
CF ₃ Br	11.76	12.00	51.28
CF ₃ I	10.38	10.45±0.05	100.00
CF ₃ Cl ₂	11.87	11.75±0.04	5.13
CFC1 ₃	11.46	11.77±0.01	0.04
CCl ₃ Br	11.05	10.91 ^b	0.03
CF ₃ Br ₂	10.98	11.18	6.41
CHF ₃ Cl	12.28	12.60	8.33
CHFCl ₃	11.75	12.00	23.08
CHCl ₃	11.41	11.37±0.02	69.23

^a R.D.Levin and S.G.Lias, Ionization and Appearance Potential Measurement, 1971-1981, NSRDS-NBS 71 (1981).

^b I.Vovak, T.Cvitas and L.Klasinc, J. Chem. Soc. Faraday Trans. 2, 77, 2049 (1981).

ionization continuum via preionization or predissociation.²⁶ The ionization rate will depend on the symmetries of the states involved (including possible Jahn-Teller distortion), spin-orbit coupling, the applicability of the Born-Oppenheimer approximation, and the stability of the parent ion with respect to fragmentation.

If a vertical transition from the ground electronic state of the neutral intersects the repulsive portion of a potential surface describing the reaction coordinate in the (ground or excited state) parent ion, then direct photoionization with dissociation may occur before quasi-equilibrium can be established. This is almost certain the case for CF_4 , where parent ions are not detected and $\text{CF}_4^+ + \text{F} + \text{e}^-$ is the lowest-energy ionization process observed. This mechanism has also been involved to account for the kinetic energy releases measured upon fragmentation of CF_3Cl^+ and CF_3Br^+ ions prepared in excited electronic states.¹¹⁰

However, most of the halomethane cation ground states are sufficiently stable that complete PIE curves could be measured. Because fragmentation generally involves significant distortion of the most stable ionic configuration, at threshold it is likely to be a rather slow process. Thus the closer is the geometry of the parent ion to that of the activated complex for the decomposition, the more likely will the products be formed with little excess energy.⁸⁶ Alternatively, a more stable parent ion is more likely to live long enough to obtain the proper, near-threshold fragmentation geometry which releases little kinetic energy to the products. The CF_3^+ heats of formation obtained from photoionization of CF_3X ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) follow this trend; the more

stable is the parent ion, the lower is the ΔH_{f0}^0 upper limit calculated from the measured CF_3^+ appearance potential.

For parent ions with similar lifetimes, the kinetic shift from the desired fragment threshold appearance energy will depend on the nature of the bond which is broken. According to quasi-equilibrium theory, excess vibrational energy in the parent ground ionic state is randomly distributed among the vibrational normal modes, among which it flows in the usual(RRKM) unimolecular decay formulism. For a given number of normal modes, the probability that sufficient vibrational energy flows into a given stretching mode to rupture the bond clearly depends on the bond energy; for a given total internal energy, strong bonds are much less likely to break than are weak bonds. In other words, in order to produce a detectable ion signal in the mass spectrometer, the stronger bond fragmentation process will require more excess energy deposited into original parent ion. This leads to a larger kinetic shift in the threshold for the corresponding fragment ion, and part of this excess energy remains in the dissociation products. Thus CF_2Cl_2 and CF_2ClBr have similar stabilities, but Br loss shows smaller kinetic energy release.

The various contributions to the kinetic shift cannot be considered independently. For example, CF_2Cl^+ is more stable than CF_2Cl_2 (Table 5B-2-1), yet the heat of formation of CF_2Cl^+ calculated from the appearance potential from the dichloro precursor is lower. The larger kinetic shift in the CF_2Cl^+ threshold from the more stable CF_2Cl^+ parent ion arises from (a) the larger excess energy required to break the more stable C-F bond, and (b) competition from the lower-energy

Cl-loss fragmentation process.

For fragmentation processes involving breakage of two bonds, for example the production of CF_2^+ from several different precursors, the calculated values of the heat of formation are rather independent of the composition of the parent ion. That is, unlike one-bond rupture, the excess energy does not depend significantly on which bonds are broken in the fragmentation process. In this case the kinetic shift in its usual sense is not the predominant factor controlling the experimental appearance potential; rather, the shape of the fragment PIE threshold region is governed by the effects of competitive reactions. Since the energy required to produce fragments with two bonds broken is much higher than that needed for any one-bond cleavage, when the former process occurs, the majority of parent ions still dissociate through the lower-energy pathways in which only one bond breaks. To produce a detectable amount of two-bond-broken fragment ions enough excess energy has to be deposited into the parent ion to overcome the low rate of production, and the photofragmentation cross section increases only slowly with increasing photon energy above the threshold. This is also a kind of kinetic shift, caused here primarily by the competitive reactions, rather than by vibrational energy redistribution effects. Now the excess energy contained in the excited parent ion is so high that the small differences in the traditional kinetic shift involved in breaking single C-X (X=halogens) bonds are insignificant.

In all cases where dihalomethylene cations are formed upon photoionization of the halomethane precursors studied in this work, thermochemical calculations indicate that the neutral products are two

halogen atoms, rather than the dihalogen molecules which would require less energy (lower AP). The same, rather striking behavior has been observed by the Baumgärtel group when two halogen bonds are broken in the halogenated ethylenes.¹¹¹ It is possible that these fragmentation occur directly on an excited electronic state surface of the parent ion under kinetic control, rather than by the QET mechanism described in the preceeding paragraph. Or perhaps the two-bond fragmentation is sequential, with a short-lived trihalomethyl cation being formed first, followed by dissociation of a second C-X bond. One might expect to see evidence of these mechanisms in the PIE curves of the parent or primary fragmentation ions: a step corresponding to a new electronic state or a dip in the photoionization cross-section concomitant with the rise of the dihalomethylene fragment. No obvious correlation of this type is observed (see composite PIE curves for each parent), although the intensity of the dihalomethylene cation is so much lower than that of the trihalomethyl fragments that the effect might not be discernible. Also, the energetics of these fragmentation pathways are likely to be parent-specific, and this is not observed. Thus there is no direct evidence of non-statistical behavior in the observed multi-bond fragmentations.

3. Discussion of the Heats of Formation of Trihalomethyl and Dihalomethylene Cations.

The values obtained in this work for the lowest upper limit of the heats of formation of the trihalomethyl and dihalomethylene cations form a coherent pattern. One can tabulate these data together and compare

them with corresponding values for the analogous, neutral trihaloboron and dihaloboron compounds, which are assumed to have the same geometric configuration. Table 5B-3-1 lists the heats of formation of all the fluoro-chloro methyl and methylene cations calculated from the photoionization measurements and the values for the corresponding boron halocompounds, obtained from the thermochemical literature. It is clear that the heat of formation values of these cations depend mainly on which kinds and how many halogens are attached to the central carbon atom. For example, a change of one fluorine atom to a chlorine atom in the trihalomethyl cations will increase the heat of formation by about 20-30 kcal/mole; in the dihalomethylene cations this substitution will increase the value of the heat of formation by about 38 kcal/mole. Since other factors such as symmetry, steric effects, local charge density, etc., also influence the heats of formation, the difference accompanying substitution of chlorine for fluorine is not exactly the same between series. An examination of the haloboron compounds in Table 5B-3-1 reveals that they also follow the same trend, although the numerical differences are not the same. The different magnitude is attributed to the different central atom; it is interesting to note (middle column of Table 5B-3-1) that the ratio of the difference in the heat of formation of successive members of a given series upon substitution of chlorine for fluorine is approximately constant within each series.

Table 5B-3-2 gives the heats of formation of the fluoro-bromo methyl cations, methylene cations, and corresponding haloboron compounds. Based on the trends shown by the fluoro-chloro series, one

Table 5B-3-1. Systematic trends in the heats of formation of chloro-fluorocarbon cations and their isoelectronic boron analogs.

ION	CF_3^+	CF_2Cl^+	CFCl_2^+	CCl_3^+
ΔH_{f0}° (a,b)	91.15±1.7	124.73±2.0	168.89±3.1	207.78±2.7
DIFFERENCE (a)	33.58±3.7	44.16±5.1	38.89±5.8	
RATIO OF DIFFERENCE	1.48	1.52	1.48	
DIFFERENCE (a)	49.70±5.4	67.0±10.0	58.00±5.5	
ΔH_{f0}° (a,c)	-270.7±0.4	-221.0±5.0	-154.0±5.0	-96.08±0.5
COMPOUND	BF_3	BF_2Cl	BFCl_2	BCl_3
ION	CF_3^+	CFCl^+	CCl_2^+	
ΔH_{f0}° (a,b)	204.36±2.7	231.35±8.5	253.98±2.7	
DIFFERENCE (a)	33.58±3.7	44.16±5.1		
RATIO OF DIFFERENCE	2.42	2.47		
DIFFERENCE (a)	65.4±10.0	55.9±10.0		
ΔH_{f0}° (a,c)	-141.1±3.0	-75.7±7.0	-91.3±3.0	
COMPOUND	BF_3	BFCl	BCl_2	

^a kcal/mole

^b Lowest upper limit, this work

^c From JANAF Thermochemical Tables

Table 5B-3-2. Systematic trends in the heats of formation of bromo-fluorocarbon cations and their isoelectronic boron analogs.

ION	CF_3^+	CF_2Br^+	CFBr_2^+	CBr_3^+
ΔH_{f0}° (a)	91.15 ± 1.7^d	[139.5]	[186.2]	207.78 ± 2.7^f
DIFFERENCE (a,b)		[48.3 $\pm$ 6.5]	[46.7 $\pm$ 12.]	[47.5 $\pm$ 6.4]
RATIO OF DIFFERENCE		1.59 ^g		
DIFFERENCE (a)		77.0 $\pm$ 10.4	74.5 $\pm$ 20.0	75.7 $\pm$ 10.2
ΔH_{f0}° (a,c)	-270.7 $\pm$ 0.4	-193.7 $\pm$ 10.	-119.2 $\pm$ 10.	-43.5 $\pm$ 0.22
COMPOUND	BF_3	BF_2Br	BFBBr_2	BBBr_3
ION	CF_3^+	CFBr_2^+	CBr_3^+	
ΔH_{f0}° (a)	204.36 ± 2.7	[257.9]	(311.5 $\pm$ 10) ⁱ	
DIFFERENCE (a,b)		53.60 $\pm$ 8.1	53.60 $\pm$ 16.	
RATIO OF DIFFERENCE		1.49		
DIFFERENCE (a)		79.5 $\pm$ 12.0	79.5 $\pm$ 24.0	
ΔH_{f0}° (a,c)	-141.1 $\pm$ 3.0	-61.55 $\pm$ 9. ^h	18.2 $\pm$ 15.	
COMPOUND	BF_3	BFBBr	BBBr_3	

^a kcal/mole

^b Estimate value, from different ratio (middle row)

^c From JANAF Thermochemical Tables

^d This work

^e Obtained from $(\text{BBBr}_3 - \text{BF}_3) / (\text{CBr}_3^+ - \text{CF}_3^+)$

^f A.S.Werner, B.P.Tasi and T.Baer, J. Chem. Phys. 60, 3650 (1974).

^g Obtained from $(\text{BBBr}_3 - \text{BF}_3) / (\text{CBr}_3^+ - \text{CF}_3^+)$

^h Calculated under the assumption that $\text{BF}_3 + \text{BBBr}_3$ is thermoneutral.

ⁱ Average of two values reported by R.I.Reed and W.Sneeden, Trans. Faraday Soc. 54, 301 (1958).

can roughly predict the heats of formation of CF_2Br^+ , CFBr_2^+ and CFBr^+ ; these values are not available in the previous literature or thermochemical tables. The procedure by which these three values are estimated is shown in Figure 5B-3-1. The predicted values of ΔH_{f0}° for CF_2Br^+ , CFBr_2^+ and CFBr^+ are: 139.45 kcal/mole, 186.2 kcal/mole and 257.93 kcal/mole, respectively. Not surprisingly, the heat of formation change upon substitution of bromine for fluorine is rather different than that observed upon chlorine substitution. There are many differences between chlorine and bromine atoms, such as size, reactivity, electronegativity, etc, which can account for the different ratios observed.

The heat of formation values of CF_2Br^+ , CFBr_2^+ and CFBr^+ predicted by the constant-ratio procedure are compared with the values obtained in this work in Table 5B-3-3; the agreement is quite good. This implies that the assumptions upon which the predictions were made are sound. The boron/carbon ratioing procedure proposed here has been satisfactorily tested, and it might be expected to yield good qualitative results when applied to other isoelectronic series for which thermochemical data are incomplete.

4. Mechanism for the Formation of Dihalogen Cations

Several dihalogen cations were detected in the photoionization mass spectra of the fourteen halomethanes investigated in this work, two of them in sufficient intensity that photoionization efficiency curves could be obtained. Appearance potentials for BrCl^+ from CF_2ClBr and IF^+ from CF_3I were extracted from the corresponding PIE curves. Neither

From the $\text{CF}_n\text{Cl}_{3-n}^+$ and $\text{CF}_n\text{Cl}_{2-n}^+$ thermochemical data one may expect:

$$\begin{aligned} \frac{\Delta H_{f0}^\circ(\text{BF}_2\text{Br}) - \Delta H_{f0}^\circ(\text{BF}_3)}{\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+) - \Delta H_{f0}^\circ(\text{CF}_3^+)} &\cong \frac{\Delta H_{f0}^\circ(\text{BFBr}_2) - \Delta H_{f0}^\circ(\text{BF}_2\text{Br})}{\Delta H_{f0}^\circ(\text{CFBr}_2^+) - \Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+)} \cong \frac{\Delta H_{f0}^\circ(\text{BBr}_3) - \Delta H_{f0}^\circ(\text{BFBr}_2)}{\Delta H_{f0}^\circ(\text{CBr}_3^+) - \Delta H_{f0}^\circ(\text{CFBr}_2^+)} \\ &\cong \frac{\Delta H_{f0}^\circ(\text{BBr}_3) - \Delta H_{f0}^\circ(\text{BF}_3)}{\Delta H_{f0}^\circ(\text{CBr}_3^+) - \Delta H_{f0}^\circ(\text{CF}_3^+)} \\ \frac{77.0}{\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+) - 91.15} &\cong \frac{74.5}{\Delta H_{f0}^\circ(\text{CFBr}_2^+) - \Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+)} \cong \frac{75.7}{233.7 - \Delta H_{f0}^\circ(\text{CFBr}_2^+)} \\ &\cong \frac{227.2}{142.55} = 1.59 \end{aligned}$$

Then $\Delta H_{f0}^\circ(\text{CF}_2\text{Br}^+) \cong 139.5 \text{ kcal/mole}$

$\Delta H_{f0}^\circ(\text{CFBr}_2^+) \cong 186.2 \text{ kcal/mole}$

By the same procedure for $\text{CF}_n\text{Br}_{2-n}^+$ one would find:

$\Delta H_{f0}^\circ(\text{CFBr}^+) \cong 257.9 \text{ kcal/mole}$

Figure 5B-3-1. Procedure used to estimate the heats of formation of CF_2Br^+ , CFBr_2^+ , CFBr^+ list in the Table 5B-3-2.

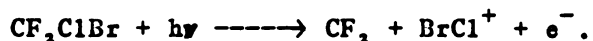
Table 5B-3-3. Heats of formation (kcal/mole) of mixed CF_xBr_y cations.

ION	ESTIMATED FROM PREVIOUS TABLE	THIS WORK
CFBr^+	257.9	255.93 (from CF_2ClBr)
CF_2Br^+	139.5	128.58 (from CF_2Br_2) 140.54 (from CF_2ClBr)
CFBr_2^+	186.2	213.12* (from CF_2Br_2)

*An activation energy of 20-30 kcal/mole is typical in cases involving C-F bond breakage.

BrCl^+ nor IF^+ include the central carbon atom, and the neutral parents have no direct bonding between halogen atoms; thus the mechanism which produces such fragments seems particularly interesting. BrCl^+ will be used as an example in the following discussion; a similar reaction mechanism and reaction equation apply to IF^+ , although the energetic details are of course different.

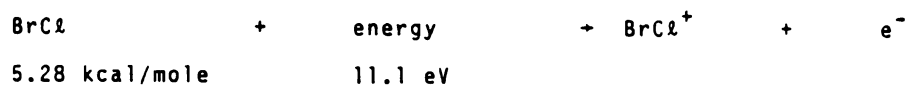
Figure 5B-4-1 shows calculations of the heat of formation of BrCl^+ according to all possible reaction equations. Comparison with literature values of the heat of formation of BrCl^+ from other reliable sources clearly reveals which pathway is correct. The overall reaction equation is:



Possible reaction mechanisms are illustrated in Figure 5B-4-2. Mechanism (1) involves rearrangement prior to decomposition. Since the rearrangement requires considerable nuclear motion, parent ions must be produced with significant excess energy. It is postulated (and supported by the step near 14eV in the experimental PIE curves for CF_2ClBr) that the parent ion is first placed in an excited electronic state which facilitates formation of an incipient three-membered ring, which upon appropriate distribution of vibrational energy can decompose to form BrCl^+ and CF_2 directly. (Whether the three membered ring ion is a true reaction intermediate or an activated complex is not important in this discussion.) This mechanism takes place entirely on the surface of the excited electronic state, in competition with the expected QET

$$\Delta H_f^0(\text{BrCl}) = 5.28 \text{ kcal/mole}$$

$$\text{IP}(\text{BrCl}) = 11.1 \text{ eV}$$



$$\Delta H_f^0(\text{BrCl}^+) = 11.1 \times 23.06 + 5.28 = 261.25 \text{ (kcal/mole)}$$



$$\Delta H_f^0(\text{BrCl}^+) = 14.63 \times 23.06 + (-107.66) - (-43.6) = 273.31 \text{ (kcal/mole)}$$

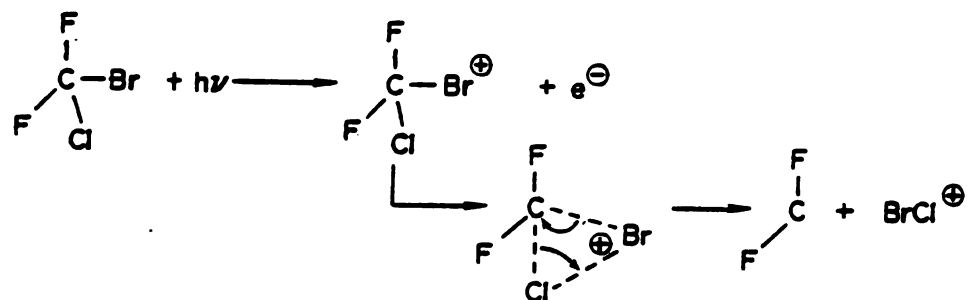
$$[] = \text{CF} + \text{F} \quad \Delta H_f^0(\text{BrCl}^+) = 151.25 \text{ (kcal/mole)}$$

$$[] = \text{C} + \text{F}_2 \quad \Delta H_f^0(\text{BrCl}^+) = 58.82 \text{ (kcal/mole)}$$

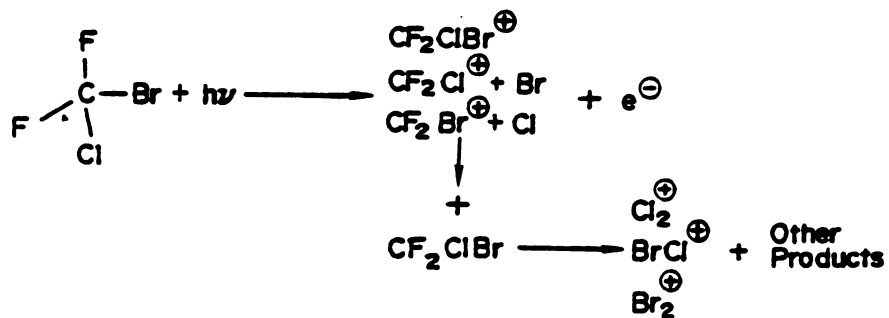
$$[] = \text{C} + \text{F} + \text{F} \quad \Delta H_f^0(\text{BrCl}^+) = 22.10 \text{ (kcal/mole)}$$

Figure 5B-4-1. Thermochemistry of BrCl^+ formation from CF_2ClBr . Heats of formation of neutral species from Table 5-A-1. $\text{IP}(\text{BrCl})$ from J.L. Franklin, J. G. Dillard H.M. Rosenstock, J.T. Herron and K. Draxl, Ionization Potential, Appearance Potential, and Heats of Formation of Gaseous Positive Ions. NSRDS-NBS 26, (1969).

I. Rearrangement-Decomposition



II. Ion-Molecule Reaction

Figure 5B-4-2. Mechanisms of $\text{BrCl}^{\oplus}$ formation from CF_2ClBr .

behavior. A necessary condition for any postulated unimolecular step is that it be linearly dependent on the reactant pressure. Thus, mechanism (1) requires that the BrCl^+ production rate be directly proportional to the parent neutral pressure.

Mechanism (2) involves an ion-molecule reaction. From this mechanism, unlike the first one, other dihalogen positive ions (Br_2^+ , Cl_2^+) also should be produced. The probability of their formation depends on the probability of producing primary (one broken bond) fragment ions and the relative rate of ion-molecule reaction between those ions and neutral parents. This in turn is governed primarily by thermodynamic factors. Moreover, the rate of production of BrCl^+ or other dihalogen cations will not be linearly dependent on the parent neutral pressure.

The results of parent pressure dependence measurements are shown in Figure 5D-4-3 for BrCl^+ and 5D-4-4 for IF^+ . An excellent linear relationship between the parent neutral pressure and the dihalogen cation count rate is observed in each case. These results provide direct and strong evidence that this ion not the product of an ion-molecule reaction.

Although only a few dihalogen cations were detected in the PIMS studies reported here, examination of the normal (generally 70eV) electron impact mass spectra of the halomethanes reveals that many of them contain dihalogen positive ions.¹¹² The photon energy (<21eV) of the PIMS excitation is not high enough to produce several of the dihalogen cations, and the intensities of others are too low to obtain PIE curves. Nevertheless, the general observation of products similar

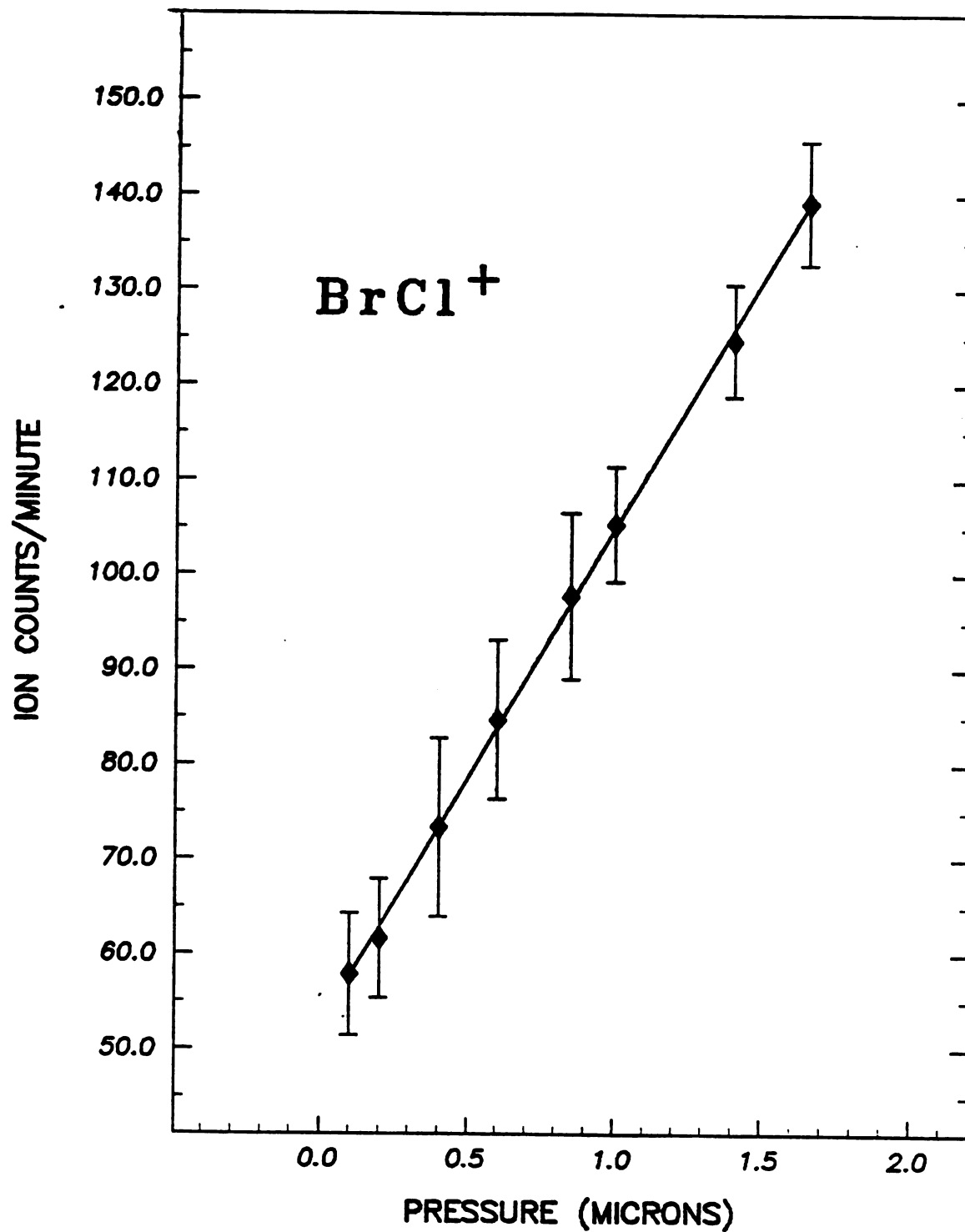


Figure 5B-4-3. Dependence of BrCl^+ ion count rate on CF_2ClBr pressure.

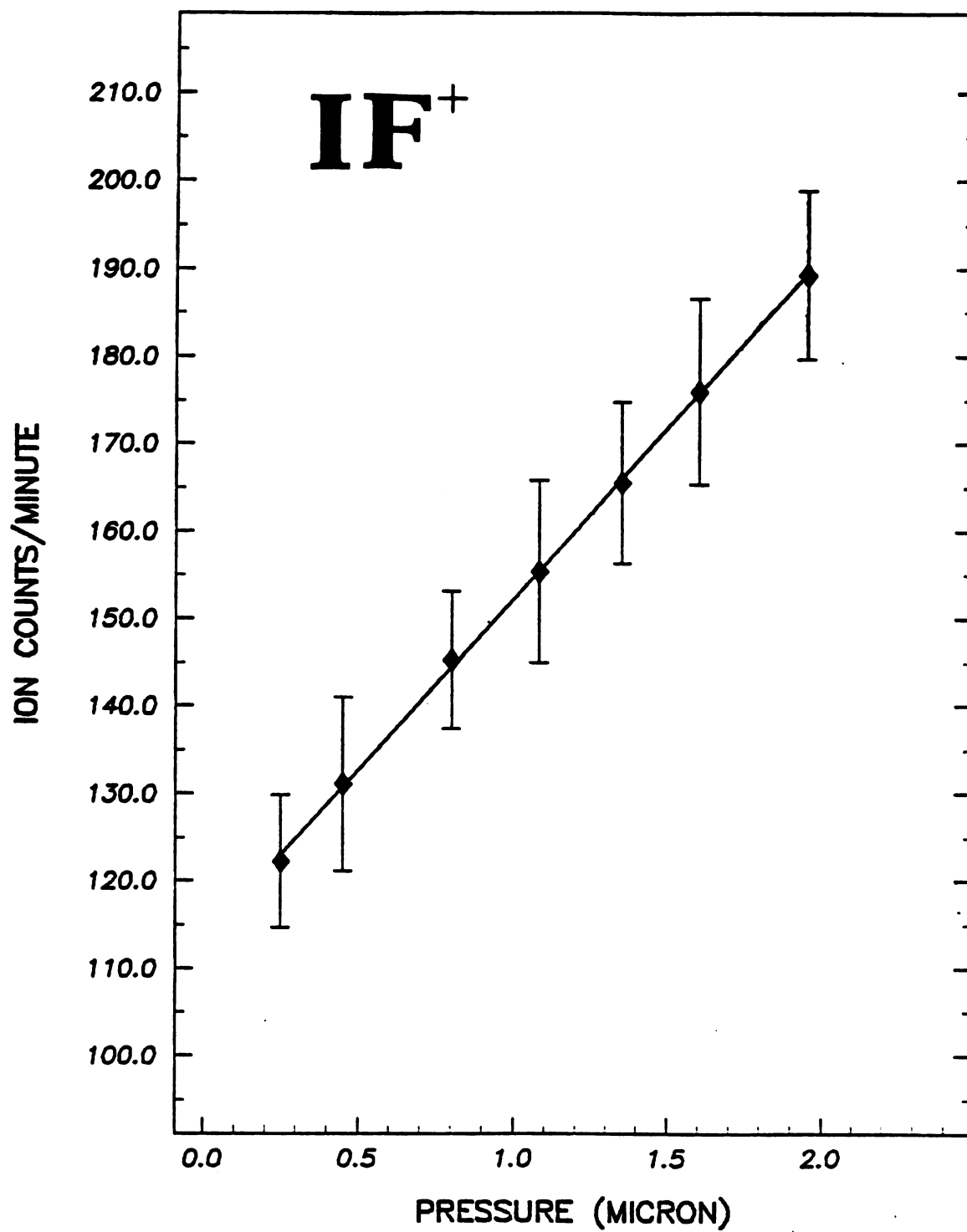


Figure 5B-4-4. Dependence of IF⁺ ion count rate on CF₃I pressure.

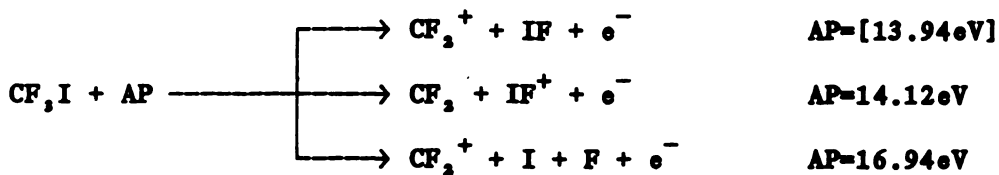
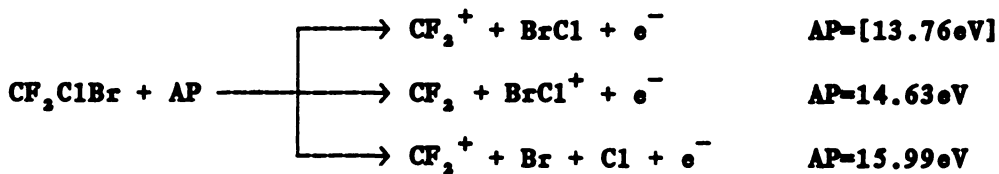
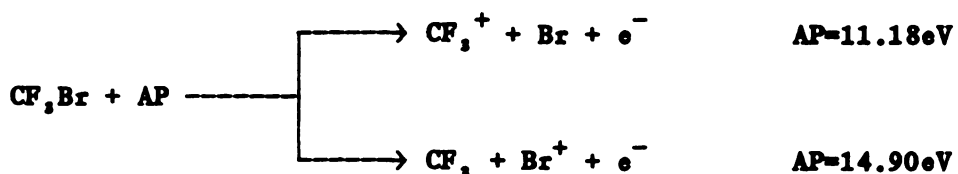
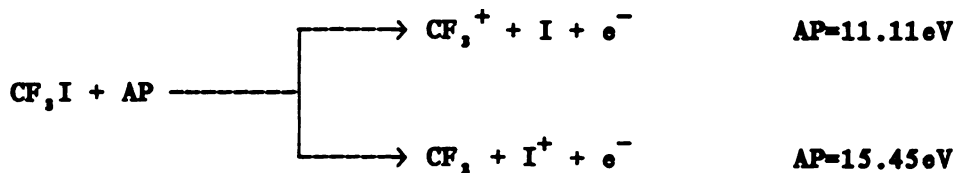
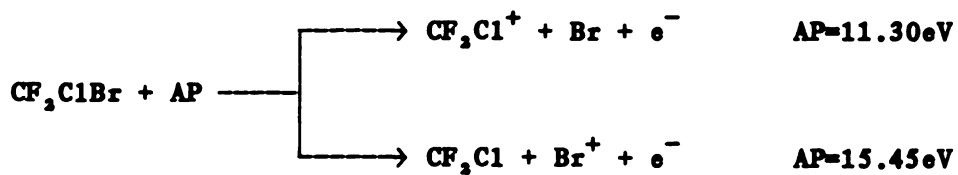
to those predicted by mechanism (1), even for simple molecules such as methane, suggest that (providing sufficient energy is available) reaction pathways involving rearrangement and dissociation are common. Rearrangement-dissociation mechanisms involving small-ring intermediate are often invoked in organic mass spectrometry interpretations.

There are at least two research groups^{113,114} using multiphoton dissociation techniques to investigate halogen molecules and their direct elimination from halomethanes. Although these studies concentrate only on the neutral species, it is interesting to note that the proposed elimination mechanism for the analogous dissociations also involve a three-membered ring intermediate.

5. Rationalization of Observed Fragmentation Channels

The absence of some possible fragment ions from the halomethane photoionization mass spectra, and the observation of experimental appearance potential values for some other fragment ions which are higher than might be expected deserve comment. Also worth consideration is the identity of which partner in a given dissociation may be expected to carry the positive charge. Both thermodynamic and kinetic effects are important in the interpretation of the experimental results.

The top portion of Figure 5B-5-1 gives the appearance potentials observed for alternate charge disposition upon single bond fragmentation of CF_2ClBr , CF_2I and CF_2Br . The relative values for Br^+ production from CF_2Br and CF_2ClBr indicate that the C-Br bond is about half an electron volt stronger in the latter molecule. The trend is consistent with the electronegativity difference between Cl and F, which leads to a lower



Note: numbers in [] are calculated values.

Figure 5B-5-1. Appearance potentials for competitive fragmentations of selected halomethanes.

Top: Alternative charge disposition upon single bond breakage.

Bottom: Possible reactions involving two broken bonds.

electron density at carbon in CF_3Br , and therefore a weaker C-Br bond. As noted earlier, the experimental results for decomposition reactions which involve breaking one bond of the parent ion are consistent with the expectations of quasi-equilibrium theory. That is, a photoexcited parent ion in an excited electronic state will, by internal conversion, become a (highly) vibrationally excited ion on the ground electronic state surface and then follow fragmentation channels which are determined by the thermodynamic stability of the products. Under thermodynamic control, the lowest energy dissociation path should predominate. Both theoretically and experimentally it is expected that the halocarbonium ion should be more stable than the halogen cation, and the experimental results for the three molecules cited substantiate this prediction. It is interesting to note that Br^+ was not detected in an earlier photoionization study of CF_3Br .¹¹⁵

The situation is more complicated when two bonds of the parent ion are broken upon fragmentation. As illustrated for CF_2ClBr and CF_2I in the lower portion of Figure 5B-5-1, three possible fragmentation reactions merit consideration in each case. (Rupture of two C-F bonds in CF_2I , or one C-F bond plus a C-Br or C-Cl bond in CF_2ClBr is unlikely on energetic grounds. For example, about 76 kcal/mole more energy is required to break two C-F bonds in CF_2I than is needed to break one C-F bond and one C-I bond.¹¹⁶ A similar energy difference would apply to CF_2ClBr .) The approximate appearance potential for each of these competitive processes can be calculated from tabulated thermochemical data; the expected values fall in the 14-17eV range, with fragmentation to form of CF_2^+ plus a neutral dihalogen molecule being the lowest

energy path in both cases. Yet CF_2^+ formed by this mechanism was not detected from either CF_2ClBr or CF_2I . Rather, formation of the dihalogen cation is the lowest energy fragmentation involving the rupture of two bonds. CF_2^+ is observed only at higher photon excitation energies, under conditions where two halogen atoms are the likely neutral fragments. These results can be rationalized by the model that follows.

It is assumed that all reactions leading to scission of two bonds require photon energy at least equal to the excitation energy of an excited electronic state of the ion, an electronic state (above 14eV) which facilitates formation of the three-membered ring described in the previous subsection. According to QET, parent ions in this electronic state should form vibrationally-excited ground state ions, which dissociate under thermodynamic control as noted in the previous paragraph. However, if a competing fragmentation process can occur prior to the establishment of the "quasi-equilibrium", i.e. within a very few vibrational periods, then the products of the alternate mechanism might be observed. This is an example of kinetic control, and the ion count rates from such fragmentation processes are expected to be very much lower than those of products of the thermodynamically favored competitive pathways.

Consider CF_2ClBr as an example. The positive charge on the electronically-excited parent ion most probably resides on the bromine site. If the C-Cl and C-Br bonds are broken during the first few vibrational periods following photoexcitation to the excited electronic state of the ion near 14eV, then neither QET nor charge redistribution

will be established, and fragmentation to form BrCl^+ may occur. A schematic sequence depicting this mechanism is shown in Figure 5B-5-2. (The lower energy path by which CF_2^+ plus a neutral dihalogen are formed is temporally not competitive with the QET fragmentations, which involve breaking only one bond, with the excess energy being deposited in the fragments.)

Why then is CF_2^+ observed at high appearance potentials? Possibly a new excited state of the ion is reached which involves nuclear rearrangement conducive to formation of CF_2^+ and two halogen atoms under kinetic control. Or perhaps QET is operative, and the fragmentation to form CF_2^+ occurs on the ground electronic state surface. At these photon energies (16-17eV), so much excess energy (on the order of 6eV) is deposited in the fragments that sufficient internal energy resides in the putative dihalogen neutral to cause dissociation into neutral atomic partners, or perhaps the two-step fragmentation mentioned in section 5.B.2. takes place.

In summary, a reaction can occur on the potential surface of an excited electronic state of an ion, provided that the products form before internal conversion is established. The details of the nuclear dynamics are very important under these kinetic control conditions. On the other hand, most decompositions occur on the ground electronic state surface of the parent ion. Then the predictions of QET are valid, and the competition among alternative fragmentation channels will be determined by energetic considerations, i.e. thermodynamic control. Thus CF_2^+ is not observed from the lower-energy neutral dihalogen pathway because the dynamic requirements on the excited-state surface

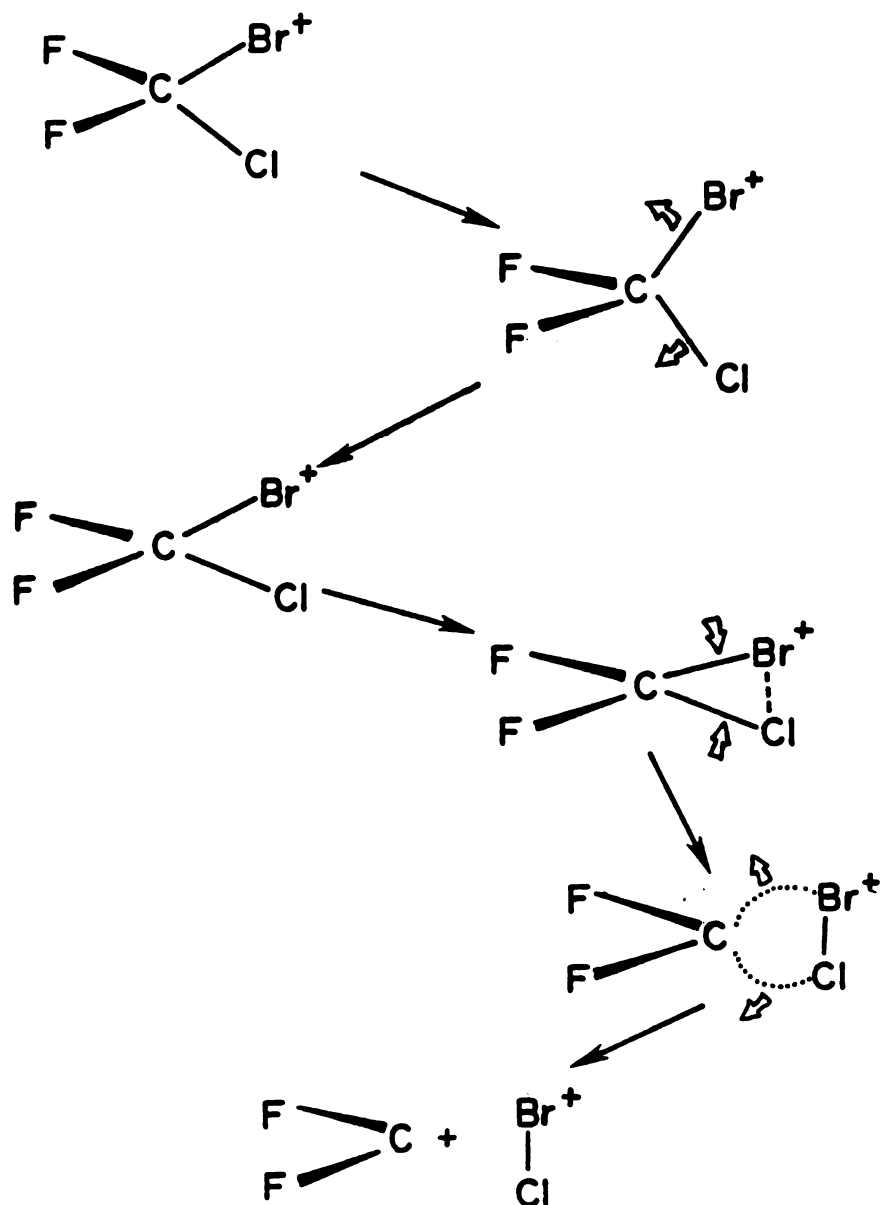


Figure 5B-5-2. Schematic representation of vibrational motion leading to BrCl^+ formation on CF_2ClBr^+ excited electronic state potential surface.

cannot compete efficiently with internal conversion, whereas lower energy fragmentations will dominate the decomposition reactions in the ionic ground state.

CHAPTER SIX

SUMMARY AND SUGGESTIONS FOR FURTHER WORK

A. Summary

Fourteen halogenated methanes have been investigated by photoionization mass spectrometry. Ionization potentials for eleven parent ions and appearance potentials for all abundant fragment cations were obtained. These data, combined with other necessary thermochemical information, were used to calculate the heats of formation of the ions. These are direct, short-range applications. The experimental data are good; they are reliable and fairly precise. Undoubtedly other scientists will use these results in broader contexts.

From comparison of heats of formation of a given ion from a series of precursors, the "best" value (i.e. lowest upper limit) has been determined for several fragment ions. These heat of formation values are sensibly related to those of the isoelectronic neutral boron compounds.

The threshold behavior of fragment PIE curves has been described in terms of quasi-equilibrium theory. Where one bond is broken the kinetic shift governs the value of the extrapolated appearance potential. Competitive reactions involving lower-energy channels dominate the thresholds for fragment ions involving cleavage of two bonds in the parent ion. A special fragmentation pathway has been proposed for the formation of dihalogen cations, and a discussion of alternative decomposition pathways for a given pair of dissociation

partners, in which the location of the positive charge is controlled by either thermodynamic or kinetic considerations, has been presented.

B. Suggestions for Further Work

1. Without Change in the Instrument

(1) Theoretical Investigation

An almost complete experimental investigation of the ionization and fragmentation of fourteen different halomethanes has been carried out; the results have been presented and discussed in chapter five. The spectroscopic study most likely provides more accurate transition energies and thermodynamic information for these ions than one could currently calculate theoretically. However, the understanding of the relative stabilities of the ions is less well founded, and a theoretical study would prove most useful. Theoretical predictions similar to those advanced on experimental grounds would enhance the reliability of the interpretations postulated here, and would provide more detailed understanding of the factors which influence the experimental results. A possible theoretical project would: (1) find the lowest energy of the neutral and ionic compounds; (2) determine the corresponding molecular electronic structure and nuclear geometry; and (3) evaluate possible excited state potential surfaces, in order to substantiate or negate the conclusions drawn here on the basis of the experimental observations.

(2) Heats of formation

The primary advantage of PIMS is the precise determination it provides of IPs and APs. If thermochemical information for a class of

compounds of interest is incomplete or imprecise, PIMS remains a useful tool, although for a given fragment ion only an upper limit to the desired heat of formation can be established. Among the compounds of choice in new studies are those of aeronomical interest, since VUV radiation is particularly important in atmospheric chemistry.

(3) Parent Ion Stability

Only a qualitative discussion of parent ion stability is possible at this time because all fourteen molecules studied in this work contain a central carbon atom. A natural extension would involve molecules containing Si, Ge, and/or Ti as the central atom. Stability trends could then be followed as a function of the central atom, and as the halogen atom distribution is altered. More complete experimental results would be quite useful, and if they were combined with theoretical predictions of parent and fragment ion stabilities, more quantitative conclusions regarding halomethane ion chemistry could be drawn.

2. With a Small Change to the Instrument

(1) Temperature Control of the Sample Inlet and Ion Source Systems

The PIMS instrument currently can accept only samples in the gas phase or those of liquids with moderate vapor pressure at room temperature. If the sample handling system and the ion source were modified to have temperature flexibility, then the capability would be extended to include the study of almost all compounds. In addition, with the availability of a temperature control system, the temperature dependence of ionization and fragmentation processes could be followed.

The most obvious application is the determination of the hot band contribution to the threshold region of experimental PIEs. In the investigation of some reaction mechanisms to determine the thermodynamic or kinetic control of the reaction rate, a temperature dependence study could also play an important role.

(2) Negative Ion Detection

With only slight changes in the electronics which bias the ion detector, the MSU PIMS apparatus would have the capability to detect negative ions.⁸⁹ Ion-pair formation following photoexcitation of the halomethanes is an interesting possibility,¹¹⁷ especially since the relative values of the pertinent electron affinities and bond energies are such that this reaction might occur at an energy below the molecular ionization potential. Compared with direct ionization, the intensity of ion-pair formation reactions is rather low, and contributions from this mechanism are difficult to discern in a normal (cation) PIE curve. However, if negative ions are monitored directly, the contribution from ion-pair formation will be readily apparent, since other sources of negative ions (e.g. electron attachment) are not important in photoionization experiments. A study of ion-pair formation in the halomethanes would make this investigation complete.

(3) Addition of a Second Reaction Chamber.

One advantage of PIMS is that precise control of the source energy is provided; thus for simple atoms or molecules, PIMS can produce predictable ions with relatively well-defined internal energy. Addition of a second chamber to the interaction region would allow ion-molecule reactions to be studied in which the products of the reaction of

"state-selected" ions from the first chamber of the ion source with neutral molecules in the second chamber could be monitored mass spectrometrically. An important application is to reactions which might occur in the troposphere or stratosphere. This kind of study would be of great help to the understanding of ion-molecule reaction theory.

(4) Laser-Induced Fluorescence of Ions

Laser induced fluorescence measurements, which provide information about excited electronic states, could be carried out on the ions produced by photoionization--provided that the ion production rate is sufficiently high. If only the parent ion is of interest, the PIMS photon energy could be set below the first fragmentation threshold and the laser beam could intercept the ion beam immediately after it leaves the source; otherwise the laser could be placed after the quadrupole, where interaction with mass-selected ions would be effected. In either case the fluorescence would be collected and detected perpendicular to the ion and laser beams. It is recommended that a careful evaluation of ion densities, absorption cross-sections and fluorescence quantum yields be made before laser-induced fluorescence projects are undertaken.

Bibliography

- [1] D.M.Giloland, G.B.Fazekas, W.D.Taylor and G.A.Takacs, J. photochem. 14 335, (1980).
- [2] L.T.Molina and M.J.Molina, U.S. Environ. Prot. Agency, Off. Res. Dev., [Rep.], EPA 1980. EPA-600/9-80-003, Proc. Conf.
- [3] N.W.Reid, Int. J. Mass Spectrom. Ion Phys. 6, 1 (1971).
- [4] S.Geltman, Phys. Rev. 102, 171 (1956).
- [5] H.M.Rosenstock, Int. J. Mass Spectrom. Ion Phys. 20, 139 (1976).
- [6] R.W.Ditchburn and F.L.Arnot, Proc. Roy. Soc. A123 516, (1969).
- [7] A.Terenin and E.Popov, Phys. Z. Sowjetunion, 2 299, (1932).
- [8] H.Hurzeler, M.G.Inghram and J.D.Morrison, J. Chem. Phys. 27 313, (1957).
- [9] H.Hurzeler, M.G.Inghram and J.D.Morrison, J. Chem. Phys. 28 76, (1958).
- [10] F.A.Elder, D.Villarejo and M.G.Inghram, J. Chem. Phys. 43 758, (1966).
- [11] W.A.Chupka, in Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet, C. Sandorfy, P.J. Ausloos and H.B.Robin, eds., (D.Reidel, Boston, 1974) pp.431-463.
- [12] G.Harr, Photoionization Processes in Gases (Academic Press, New York, 1967)
- [13] E.J.Darland, Ph.D. Thesis, Michigan State University, 1977.
- [14] J.Berkowitz, "Photoionization Mass Spectrometry and Photoelectron Spectroscopy in High Temperature Vapors", in Advances in High Temperature Chemistry, vol.3, ed. by L.Eyring (Academic Press, New York, 1971) pp123-177.
- [15] J.H.D.Eland, Photoelectron Spectroscopy (John Wiley and Sons, New York, 1974).
- [16] J.W.Rabalais, Principles of Ultraviolet Photoelectron Spectroscopy (John Wiley and Sons, New York, 1977).
- [17] W.A.Chupka, "Ion-Molecule Reactions by Photoionization Techniques", in Ion-Molecule Reactions, Vol 1, ed. by J.L.Franklin (Plenum Press, New York, 1972) pp 33-77.
- [18] J.A.R. Samson, Phys. Rept. 28, 303 (1976).

- [19] F.O.Ellison, J. Chem. Phys. 61, 507 (1974).
- [20] J.W.Rabalais, T.Bergmark, L.O.Werme, L.Karlsson and K.Seigbahn, in Electron Spectroscopy, D.A.Shirley, ed. (North-Holland, Amsterdam, 1972.) p.425
- [21] G.Herzberg, Molecular Spectra and Molecular Structure III, Electronic Spectra and Electronic Structure of Polyatomic Molecules, (Van Nostrand, Princeton, New Jersey, 1967.)
- [22] H.C.Longuet-Higgins, M.H.L. Pryce and R.A.Sack, Proc. Roy. Soc. Ser. A244, 1 (1958).
- [23] P.C.Killgoar, Jr., G.E.Leroi, W.A.Chupka, and J.Berkowitz, J. Chem. Phys. 59, 1370 (1973).
- [24] U.Fano and J.W.Cooper, Rev. Mod. Phys. 40, 441 (1968); Phys. Rev. A137, 1364 (1965).
- [25] U.Fano, Phys. Rev. 124, 1866 (1961).
- [26] J. Berkowitz, Photoabsorption Photoionization and Photoelectron Spectroscopy, (Academic Press, New York 1979).
- [27] J.Berkowitz and W.A.Chupka, J. Chem. Phys. 51, 2341 (1969).
- [28] R.S.Berry, J. Chem. Phys. 45, 1228 (1966).
- [29] R.S.Derry and S.E.Nielsen, Phys. Rev. A383, 395 (1970).
- [30] P.M.Dehmer and W.A.Chupka, J. Chem. Phys. 66, 1972 (1977).
- [31] S.Nardholm, J. Chem. Phys. 71, 2313 (1979).
- [32] J.A.R.Samson and R.B.Cairns, Phys. Rev., 173, 80 (1968).
- [33] R.Botler, J.M.Dechine and H.M.Rosenstock, Int. J. Mass Spectrom. Ion Phys. 25, 7 (1977).
- [34] H.W.Jochems, W.Lohr and H.Daumgärtel, Ber Bunsenges, Physik. Chem. 80, 130 (1976).
- [35] S.Geltman, Phys. Rev. 102, 171 (1956).
- [36] G.Herzberg, Spectra of Diatomic Molecules, 2nd ed, (Van Nostrand, New York, 1950.) p. 413.
- [37] D.W.Setser, MITP International Review of Science, Physical Chemistry, Series one, Volume 9, "Chemical Kinetics", (Butterworths, London 1972).
- [38] R.S.Mulliken, J. Chem. Phys. 33, 247 (1960).

- [39] J.G.Calvert and J.N.Pitts, Photochemistry, (John Wiley, New York, 1966) p. 186.
- [40] R.D.Kronig, Z. Physik 50, 347 (1928).
- [41] R.P.Forsch, in Excited State Chemistry, J.N.Pitts, ed. (Gorden and Breach, New York 1970).
- [42] H.M.Rosenstock, in Advanced in Mass Spectrometry, Vol.4 E.Kendrick, ed. (Institute of Petrolaun, London, 1968). p. 523.
- [43] A.J.C.Nicholson, J. Chem. Phys. 39, 954 (1963).
- [44] W.A.Chupka and J.Berkowitz, J. Chem. Phys. 48, 5726 (1968)
- [45] J.A.Simpson and C.E.Kuyatt, Rev. Sci. Instrum. 34, 265 (1963).
- [46] E.M.Clarke, Can. J. Phys. 32, 764 (1954).
- [47] R.E.Fox, W.M.Hickam, D.J.Grove and T.Kjeldasas,Jr., Rev. Sci. Instrum. 26, 1101 (1955).
- [48] R.E.Winters, J.H.Collins and W.L.Courchene, J. Chem. Phys. 45, 1931 (1966).
- [49] F.H.Porman, J.D.Morrison and A.J.C.Nicholson, J. Chem. Phys. 31, 1335 (1959).
- [50] F.A.Baker and J.B.Hasted, Phil. Trans. Roy. Soc. London, A261, 33 (1966).
- [51] D.W.Turner, Proc. Roy. Soc. A307, 15 (1968).
- [52] D.Villarejo, J. Chem. Phys. 48, 4014 (1968).
- [53] R.Spohr, P.H.Guyon, W.A.Chupka and J.Berkowitz, Rev. Sci. Instrum. 42, 1872 (1971).
- [54] H.Hotop and A.Niehaus, Z. Phys. 222, 68 (1969).
- [55] C.E.Erion, C.A.McDowell and W.D.Stewart, Chem. Phys. Lett. 13, 79 (1972).
- [56] G.R.Kertel, J. Chem. Phys. 48, 2053 (1968).
- [57] M.D.Scheer and J.Fine, J. Chem. Phys. 50, 4343 (1969).
- [58] R.S.Mulliken, J. Amer. Chem. Soc. 74, 311 (1952).
- [59] S.H.Hastings, J.L.Franklin, J.C.Schiller and F.A. Masten, J. Amer. Chem. Soc. 75, 2900 (1953).

- [60] G.Eriegleb, Electron-Donator-Acceptor-Komplex, (Springer-Verlag, Berlin, 1964).
- [61] E.P.Wigner, Phys. Rev. 73, 1002 (1948).
- [62] P.C.Killgoar, Jr., G.E.Leroi, J.Derkowitz and W.A.Chupka, J. Chem. Phys., 58, 803 (1973).
- [63] V.H.Dibeler and J.A.Walker, Int. J. Mass Spectrom. Ion. Phys. 11, 49 (1973).
- [64] V.H.Dibeler, J.A.Walker and H.M.Rosenstock, J.Res. Natl. Bur. Stds. 70A, 459 (1966).
- [65] D.A.McQuarrie, Statistical Mechanics (Happer and Row Publishers, New York, 1976)
- [66] V.H.Dibeler, J.A.Walker, K.E.McCulloh, and H.M.Rosenstock, Int. J. Mass Spectrom. Ion Phys. 7, 209 (1971).
- [67] W.A.Chupka, J. Chem. Phys. 54, 1936 (1971).
- [68] P.A.Guyon and J.Derkowitz, J. Chem. Phys. 54, 1814 (1971).
- [69] H.M.Rosenstock, M.B.Wallenstein, A.L.Wahrhaftig and H.Eyring Proc. Nat. Acad. Sci. 38 667, (1952).
- [70] H.M.Rosenstock, Advan. Mass Spectrom. 4, 523 (1968).
- [71] A.L.Wahrhaftig in ITP Int. Rev. of Sci. Vol 5. Mass Spectrometry, A.Maccoll, ed.(University Park Press, Baltimore, 1972) Chapter one.
- [72] J.H.Beynon and A.E.Fontaine, Z. Naturforsch. A22, 334 (1967).
- [73] J.H.Beynon, R.A.Saunders and A.E.Williams, Z. Naturforsch. A23, 358 (1968).
- [74] R.G.Cooks, J.H.Beynon, R.M.Caprioli and G.R.Lester, Metastable Ions, (Elsevier, Amsterdam, 1973).
- [75] C. Ottinger, Phys. Lett. 17, 269 (1965).
- [76] R.E.Ferguson, K.E.McCulloh and H.M.Rosenstock, J. Chem. Phys. 42, 100 (1965).
- [77] J.L.Franklin, P.M.Hierl and D.A.Whan, J. Chem. Phys. 47, 3148 (1967).
- [78] K.Meier and J.Seibl, Int. J. Mass Spectrom. Ion Phys. 14, 99 (1974).
- [79] B.Steiner, C.F.Giese and M.G.Ingbram, J. Chem. Phys. 34, 139

(1961).

- [80] W.A.Chupka, J. Chem. Phys., 54, 1936 (1971).
- [81] H.M.Rosenstock, J.T.Larkins and J.A.Walker, Int. J. Mass Spectrom. Ion Phys. 11, 309 (1973).
- [82] M.L.Vestal, in Fundamental Processes in Radiation Chemistry P.Ausloos, ed, (Interscience Publishers, New York, 1968). pp. 92-98.
- [83] R.G.Cooks, I.Howe and D.H.Williams, Org.Mass Spectrom. 2, 137 (1968).
- [84] A.G.Harrison, in "Topics in Organic Mass Spectrometry" Advances in analytical Chemistry and Instrumentation Vol.8 A.L.Burlingame, ed. (Wiely-Interscience Publishers, New York 1970). pp.128-132.
- [85] K.Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Progress in Mass Spectrometry, Vol.4 H.Budzikiewicz, ed. (Verley Chime Wein-heim, New York, 1978). pp.108-113.
- [86] C.Lifshitz, Adv. Mass Spectrom. 7A, 31 (1978).
- [87] P.M.Guyon and J.Berkowitz, J. Chem. Phys. 54, 1814 (1974).
- [88] R.D.Hudson and V.L.Carter, J. Opt. Soc. Am. 53, 227 (1968).
- [89] D.H.Rider, Ph.D. Thesis, Michigan State University, 1980.
- [90] T. Cvitas, E.Gusten, L.Klasine, I. Novadj and H.vaneik Z. Naturforsch. 33a, 1528 (1978).
- [91] C.J.Noutary. J. Res. Natl. Bur. Stds. 72A, 479 (1969).
- [92] H.W.Jochims, W.Lohr, and H.Baumgärtel, Ber, Dunsenges. Phys. Chem. 30, 130 (1976).
- [93] J.Doucet, P.Sauvageou and C.Sandfory, J. Chem. Phys. 53, 3708, (1973).
- [94] R.Bombach, J.Dannacher, J-P. Stadelmann, J. Vogt, L.E.Thorne and J.L.Deauchamp, Chem. Phys. 66, 403 (1982).
- [95] V.H.Dibeler, R.M.Reese and F.L.Mohler, J. Res. Natl. Bur. Stds 57, 113 (1956)
- [96] A.S.Werner, D.P.Tsai and T.Bear, J. Chem. Phys. 60, 3650 (1974).
- [97] D.L.Hobrock and E.W.Kiser, J. Phys. Chem. 68, 575 (1964).
- [98] J.M.Ajello, W.T.Huntress, Jr. and P.Rayermann. J. Chem. Phys. 64, 4746 (1976).

- [99] S.G.Lias and P.Ausloos. *Int. J. Mass Spectrom. Ion Phys.* 23, 273 (1977).
- [100] T.A.Walter, C.Lifshitz, W.A.Chupka and J.Berkowitz, *J. Chem. Phys.* 51, 3531 (1970).
- [101] D.R.Stull, H.Prophet, et al., *NSRDS-NBS* 37 (1971); M.W.Chase, Jr., J.L.Curnutt, A.Y.Hu, H.Prophet, A.N.Syverud and L.C.Walker, *J. Chem. Phys. Ref. Data*, 3, 311 (1974); M.W.Chase, Jr., J.L.Curnutt, H.Prophet, R.A.McDonald and A.N.Syverud, *ibid* 4, 1 (1975); *ibid* 7, 793 (1978); M.W.Chase, Jr., J.L.Curnutt, J.R.Downey, Jr., R.A.McDonald, A.N.Syverud and E.A.Valenzuela, *ibid* 11, 695 (1982).
- [102] E.G.Syrvaika, M.M. Gil'burd and A.L.Bel'ferman, *Zh. Org. Khim.* 8, 1553 (1972). [Engl. transl.: *J. Org. Chem. USSR* 8, 1587 (1972).
- [103] J.C.T.Thynne and K.A.G.Macneil, *Int. J. Mass Spectrom. Ion Phys.* 5, 95 (1970).
- [104] L.M.Leyland, J.R.Majer and J.C.Robb, *Trans. Faraday Soc.* 66, 898 (1970).
- [105] J.Marriott and J.D.Craggs, *J. Elec. Spec.* 1, 405 (1956).
- [106] D.L.Hildenbrand, *Chem. Phys. Lett.* 32, 523 (1975).
- [107] W.C.Steele, *J. Chem. Phys.* 68, 2359 (1964).
- [108] J.S.Shapiro and F.P.Lossing, *J. Phys. Chem.* 72, 1552 (1968).
- [109] J.Nicholas, Chemical Kinetics (Harper and Row Publishers, London, 1976)
- [110] I.Powis, *Mol. Phys.* 39, 311 (1980).
- [111] H.Baumgärtel, private communication.
- [112] E.Stenhagen, S.Abrahamsson and F.W.McLatterty, Registy of Mass Spectral Data Vol 1-4, (John Wiley and Sons. New York, 1974)
- [113] R.J.Morrison, R.F.Loring, R.L.Farley and E.R.Grant. *J. Chem. Phys.* 75, 148 (1981).
- [114] D.Krajnovich, F.Huisken, Z.Zhang, Y.R.Shen and Y.T.Lee. *J. Chem. Phys.* 77, 5977 (1982).
- [115] I.Powis and C.J.Danby, *Chem. Phys. Lett.* 65, 390 (1979).
- [116] R.C.Weast, et al. CRC Handbook of Chemistry and Physics (CRC press, 52nd 1972)

- [117] H.Schenk, H.Oertel and H.Daumgärtel, Ber Bunsenges. Phys. Chem.
83, 683 (1979).