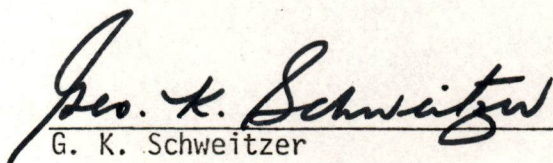
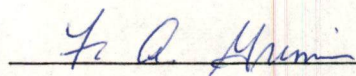


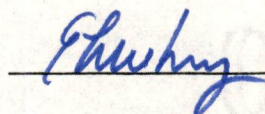
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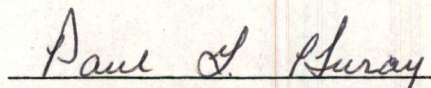
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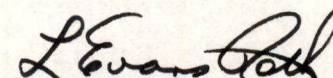
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HIGH-TEMPERATURE PHOTOELECTRON SPECTROSCOPY OF ALKALI
METABORATES, ALKALI TETRACHLOROALUMINATES,
ALKALI TETRAFLUOROALUMINATES, AND
AMMONIUM TETRACHLOROALUMINATE

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Thomas Warren Lassiter

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ABSTRACT

The high temperature HeI photoelectron spectra of the gas phase molecules $K^+BO_2^-$, $Rb^+BO_2^-$, $Cs^+BO_2^-$, $K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, $NH_4^+AlCl_4^-$, $K^+AlF_4^-$, and $Cs^+AlF_4^-$ have been obtained. The vapors were produced by resistance heating a tantalum-strip-wound boron nitride oven ($K^+BO_2^-$, $Rb^+BO_2^-$, and $Cs^+BO_2^-$) or a tantalum-strip-wound platinum-lined quartz sample oven ($K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, $NH_4^+AlCl_4^-$, $K^+AlF_4^-$, and $Cs^+AlF_4^-$) containing the solid compounds. Both ovens were coated with a high temperature ceramic cement. Analysis of the ejected electrons was carried out using a modified truncated cylindrical-mirror-electron spectrometer. The identities of the vapor phase entities above the corresponding solids were correlated with data from the techniques of electron diffraction, mass spectrometry, matrix isolation and vapor infrared spectroscopies. The ionization energies were assigned molecular orbital origins through the use of molecular orbital calculations, and comparisons with X-ray, HeI, and HeII photoelectron data for the solids, and for analogous compounds.

A high temperature structural model called polytopic bonding was thought to be applicable to these high temperature species because all the experimental photoelectron spectra of the same anion were very similar and all the experimental data were correlated with theoretical calculations for the corresponding free anion. However, the observed band breadths were considerably greater than the splits which were expected on the basis of theoretical calculations for various structural parameter changes. Therefore, no judgment could be made concerning the possible polytopicity of these compounds at high temperature.

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CHAPTER I

INTRODUCTION

A. Photoelectron Spectroscopy

Photoelectron spectroscopy is that technique in which molecules, radicals, ions, or atoms are irradiated with monochromatic photons and the electrons ejected by the photoelectric effect are analyzed for their kinetic energies. The photoelectric effect has been recognized for over seventy years¹ but the development of photoelectron spectroscopy did not begin until the early 1960's. The history of photoelectron spectroscopy is well outlined in books and review articles on the subject and will not be described here.²

Photoelectron spectroscopy is carried out in a photoelectron spectrometer which has the following basic components: (a) a monoenergetic photon source, (b) an interaction chamber, (c) an electron kinetic energy analyzer, and (d) an electron detection and recording system. Component (a) is usually a discharge lamp [such as those emitting principally HeI (21.22 ± 0.005 eV) or HeII (40.81 ± 0.005 eV) radiation] or an X-ray tube [such as those emitting principally the AlK α (1486.6 ± 0.5 eV) or the MgK α (1253.6 ± 0.4 eV) line]. Component (b) is an enclosure which allows the introduction of a solid, liquid, or gaseous sample into the monoenergetic photon beam. For gaseous samples a vapor pressure of 0.01 to 0.001 torr must ordinarily be provided in the interaction chamber to give a sufficient count rate. A slit in the wall of the chamber allows the photoejected electrons to enter the analyzer. Component (c) is an electron analyzer which

separates the electrons according to their kinetic energies. These analyzers may be of either an electrostatic or magnetic type. A high vacuum atmosphere (less than 10^{-5} torr) is necessary throughout the interaction chamber and the analyzer in order to provide a collision-free path for the electrons. Annulment of the ambient magnetic field to below 10^{-4} gauss must generally be provided in order to ensure that the trajectory of the electrons is solely determined by the field of the analyzer. The component designated (d) is often an electron channel multiplier (channeltron). The signals produced by the electrons striking this multiplier can be counted digitally or they can be converted to an analog form and read on a rate meter.

The spectrum is usually displayed by recording the count rate (c/s) as a function of kinetic energy (K) of the electron on an xy recorder, or the spectrum is scanned rapidly many times and the number of electrons counted in each of numerous kinetic energy increments is summed in a multichannel analyzer. The contents of the multichannel analyzer can be displayed or recorded. In most spectra, one or more bands can be observed. These bands usually show a single peak, although they may also be split (two or more peaks), and they often display fine structures.

In addition to the irradiation photon energy and the energy required to remove the electron from the irradiated entity, the kinetic energy of the ejected electron is also affected by the recoil energy of the product species and the work function of the electron spectrometer surface. The recoil energy is negligible for all but the simplest species, but the work function of the spectrometer needs to

be taken into consideration. The introduction of a calibrant is ordinarily employed to permit the electron kinetic energies to be corrected for the effect of the spectrometer's work function. Electron ionization energies (I) may be obtained by subtraction of the electron kinetic energies (K) from the energy of the photon source (P). This permits the spectra to be displayed in the form of count rate (c/s) against ionization energy (I).

In most cases, the electron ionization energies obtained by reading the peaks in the count rate against ionization energy spectra can be related to molecular orbital (MO) binding energies which are obtained from theoretical calculations through certain approximations. The simplest and most useful approximation is Koopmans' theorem³ (also known as the frozen orbital approximation). This theorem assumes that for the molecule M the experimental ionization energy (for the process $M + h\nu \rightarrow M^+ + e^-$) is the negative of the theoretically-calculated binding energy (for the neutral M). This means that no reorganization and/or relaxation of the electrons in the ionized species is considered. In reality, relaxation and/or reorganization do/does occur. For inner and outer orbitals errors may vary from a few percent for the former to greater than ten percent for the latter.⁴ In most of the known cases, use of Koopmans' theorem does not involve error in the qualitative ordering of MO's, although the quantitative energy values may be in error.

B. Photoelectron Spectroscopic Studies

Most experimental photoelectron spectroscopic studies to date have concentrated on compounds which exist in the solid, liquid, or

gaseous state at room temperature. Several distinct experimental difficulties have arisen in characterizing solid samples, the major ones being: (a) the relation between the ionization energy, Fermi level, work function, and vacuum level for insulators, (b) charge accumulation by nonconducting samples, (c) differences in the ionization energy of surface and bulk species, (d) increased background noise resulting from secondary electron emission, (e) destruction of the original surface species by extended irradiation, (f) variation of chemical states between the surface and bulk species, and (g) adsorption of contaminants on the solid surface. All of the above effects except (a) lead to broadening and/or shifting of the electron spectral peaks. Those few liquids which have been studied by photoelectron spectroscopy have been ones which give very low vapor pressures (generally less than 10^{-2} torr) at room temperature. If vapor pressures are higher, interference by the vapor spectra makes the liquid photoelectron spectroscopic investigation difficult. Problems similar to those which occur with solids [such as (a), (b), (c), and (d) from above] are also encountered in liquid photoelectron spectroscopic studies.

Room temperature photoelectron spectroscopic vapor studies are beset by problems that are often quite different than those encountered in the photoelectron spectroscopy of solids and liquids. The problems are a weaker signal and a smaller variety of available compounds. However, these problems are far outweighed by the fact that studies at low pressures avoid difficulties encountered in characterizing solid or liquid surfaces [such as (a), (b), (c), (d), (e), (f), and (g) from

above]. The avoidance of these difficulties usually results in better resolution because of the diminishing of spectral broadening and shifting and greater ease in defining the ionization energy with reference to the vacuum. In addition to the above effects, broadening of the photoelectron peaks in solid, liquid, or gaseous samples may result from the following factors: linewidth of the monoenergetic source, instrumental resolution, and the lifetime of the photon induced vacancy.

In order to correlate solid or liquid photoelectron spectroscopic data with theoretical data, theoretical consideration must be given not only to interaction with near neighbors but also the interactions with more remote constituents of the solid lattice or liquid structure [as examples, consider the solid forms of $(\text{Na}^+\text{Cl}^-)_x$, $(\text{SiO}_2)_x$, and $(\text{CO}_2)_x$ and the liquid forms of $(\text{H}_2\text{O})_x$ and $(\text{CCl}_4)_x$ with x ranging from fairly low values to extremely high values]. Theoretical calculations on gaseous species, especially those which are monomers (such as Na^+Cl^- , SiO_2 , H_2O , and CCl_4) are much less complex. When monomer calculations are compared to solid or liquid photoelectron spectroscopic data, corrections are required for the solid state or liquid state structures. A logical extension of photoelectron spectroscopy would be to study heated solids which would yield vapor species having the same atom ratio integrities as the solid state. The development of high temperature capabilities for photoelectron spectroscopic studies of vapors would greatly extend the field, especially for ionic inorganic compounds. The most appropriate substances for such studies would be those which give vapor state

monomers when their solids are heated.

Recently, photoelectron spectroscopy has been explored as a useful technique for the study of vapor species above heated compounds which are solids at room temperature. In order to characterize high temperature vapors by photoelectron spectroscopy, the interaction chamber must be modified with a device which can be heated to temperatures necessary for volatilization of the compounds. The device may be an oven which is placed adjacent to, remote from, or directly within the interaction chamber. Several methods of heating such ovens have included laser beam irradiation, electron bombardment, and wire-wound resistance heating.

Elevated-temperature vapor photoelectron spectroscopy often involves problems which are very distinct from room temperature vapor photoelectron spectroscopy. The major problems are: (a) interference of the magnetic and electrical fields of the heating devices with electron energy analysis, (b) deposition of target molecules on cooler surfaces leading to local and uneven surface charging which may broaden and/or shift spectral bands, (c) sample decomposition and reactions with the oven or the interaction chamber and electron analyzer surfaces, (d) desorption of substances from the spectrometer surfaces, (e) non-equilibrium volatilization which results in non-reproducible mixtures of species, (f) irregular volatilization in which pressure fluctuations may produce band intensity and band position alterations, and (g) vibrational hot banding of the parent molecules.

Several instrumental changes have been made in order to diminish

or eliminate one or more of the above-stated problems. Problem (a) has been handled through the use of shielding, bifilar winding, and phase-sensitive detection. Problem (b) has been addressed by pointing the sample beam toward cooled wells and probes, and away from spectrometer slits. Sample decomposition and reaction which constitutes problem (c) must be treated according to the specific properties of each individual high temperature vapor species. The techniques of baking, employing cooled probes, and introducing a substance which reacts and removes the adsorbed contaminant can often handle the desorption problem (d). The problem denoted (e) has been eased by the use of double ovens, and problem (f) can be dealt with by careful design of the oven and heating equipment. Problem (g) has not been treated as yet; however, the use of molecular beams so designed as to induce vibrational relaxation may provide an answer.

C. High Temperature Anionic Complexes

The use of photoelectron spectroscopy to characterize monomeric vapors over heated solids has reached the stage where several classes of simple species have been studied, most with HeI photons, some with X-ray photons, and a few with both. The monomeric vapor species which are listed in Table I (p 8) are ones containing no more than two atom types which have been previously investigated. Included are examples of the following types: (a) A monatomic vapors, (b) A_2 homonuclear diatomic molecular vapors, (c) MX binary diatomic molecular vapors, (d) MX_2 binary triatomic molecular vapors in both linear and bent molecular configurations, and (e) MX_3 binary tetraatomic molecular vapors including vapors in both the planar triangular and pyramidal structures.

TABLE I
ONE OR TWO ATOM TYPE SPECIES INVESTIGATED BY HIGH TEMPERATURE PES^a

A	(A ₂) _x ^b	MX	MX ₂	MX ₃
Na(5)	P ₂ (27,28,29)	NaCl(40,41)	MgCl ₂ (66)	AlCl ₃ (79)
K(5,6,7,8)	P ₄ (30,31,32,33)	NaBr(40,41)	MgI ₂ (66)	AlBr ₃ (79)
Rb(5,8)	As ₄ (30)	NaI(40,41)	CaCl ₂ (66)	AlI ₃ (79)
Cs(5,8)	Sb ₄ (30)	KCl(40,41,42,43)	CaI ₂ (66)	GaCl ₃ (79,80)
Mg(5,9)	Bi ₂ (22,25)	KBr(40,41,42,43)	SrCl ₂ (66)	GaBr ₃ (79,80)
Ca(10)	S ₂ (8,14,26)	KI(40,41,42,43,44)	SrI ₂ (66)	GaI ₃ (79,80,81)
Sr(9,10)	S ₈ (34,35,36)	RbCl(40,41,43)	BaCl ₂ (66)	InCl ₃ (80)
Ba(10,11,12)	Se ₂ (37,38)	RbBr(40,41,43)	BaI ₂ (66)	InBr ₃ (80)
F(13)	Te ₂ (37,38,39)	RbI(40,41,43)	ZnCl ₂ (67,68,69,70,71)	InI ₃ (80)
Cl(13)		CsF(40,45,46)	ZnBr ₂ (67,68,69,70,71)	SbCl ₃ (82)
Br(13)		CsCl(40,41,43,45,46,47,48)	ZnI ₂ (67,68,69,70,71)	SbBr ₃ (82)
I(13)		CsBr(40,41,43,45,46,48)	CdCl ₂ (67,68,69,70)	SbI ₃ (82)
Zn(9,10,14,15,16,17)		CsI(40,41,43,44,45,46,48)	CdBr ₂ (67,68,69,70)	
Cd(9,10,14,15,16,17,18)		AgCl(49,50)	CdI ₂ (67,68,69,70)	
Hg(15,17,19,20)		AgBr(49,50)	HgCl ₂ (69,70,72,73)	
Pb(20,21,22,23,24)		AgI(49,50)	HgBr ₂ (44,69,70,72)	
Bi(21,22,25)		TlF(51,52,53,54,55)	HgI ₂ (69,70,72)	
Eu(26)		TlCl(44,51,52,55,56)	CrCl ₂ (74)	
Yb(26)		TlBr(51,52,55,56,57)	CrBr ₂ (74)	
		TlI(52,55,56,57)	MnCl ₂ (74)	
		InCl(58)	MnBr ₂ (74)	
		InBr(58)	FeCl ₂ (74)	
		InI(58)	FeBr ₂ (74)	
		SiO(59,60)	CoCl ₂ (74)	
		TeO(61)	CoBr ₂ (74)	
		GeS(62)	NiCl ₂ (74)	
		SnS(62)	NiBr ₂ (74)	
		GeSe(62)	PbCl ₂ (75,76)	
		SnTe(62)	PbBr ₂ (44,56,76)	
		PbTe(62)	PbI ₂ (56,76)	
		PN(63,64,65)	SnCl ₂ (44)	
			SnBr ₂ (44)	
			SiF ₂ (77)	
			SeO ₂ (78)	

^aAll underlined reference numbers indicate the use of X-ray photons.

^b1 ≤ x ≤ 4

In addition to photoelectron spectroscopy, a number of other investigational techniques have been used to characterize high temperature vapor species of the sort mentioned above. The major ones are: thermodynamic vapor measurements, mass spectrometry, electron diffraction, infrared and raman spectroscopy, beam studies, and matrix isolation studies. Valuable information relating to structures, vibrational and rotational characteristics, bond strengths, chemical reactivities, and stabilities of high temperature vapor species have been obtained from these techniques. However, only photoelectron spectroscopy has the potential to provide detailed electronic and bonding information which is expressed in molecular orbital terms. (Another possible technique for this would be X-ray emission and X-ray absorption, but such measurements are difficult to conduct and to interpret for gaseous samples at low pressure.)

Recently, it has been recognized that several ternary molecular species which are inorganic ionic solid compounds at room temperature and which contain a simple cation and a complex anion (or vice versa) may exist chiefly as monomers in the vapor state when heated sufficiently. The monomeric ternary ionic compound vapors which have been studied at elevated temperatures to date are listed in Table II (p 10). All the compounds were investigated using HeI photons.

Several researchers have proposed the idea of polytopic bonding to interpret a number of observations of gaseous high temperature compounds. The idea of polytopicity came from experimental work (mainly electron diffraction, matrix isolated infrared, and microwave

TABLE II
TERNARY COMPOUNDS INVESTIGATED BY HIGH TEMPERATURE PES

Na^+CN^- (83)	Na^+PO_3^- (88)
K^+CN^- (83,84)	K^+PO_3^- (88)
Rb^+CN^- (83)	Rb^+PO_3^- (88)
Cs^+CN^- (83)	Cs^+PO_3^- (88)
$\text{CN}^-\text{Hg}^{++}\text{CN}^-$ (85)	$\text{Na}^+\text{ReO}_4^-$ (89)
Tl^+BO_2^- (86)	K^+ReO_4^- (89)
K^+NO_3^- (87)	$\text{Rb}^+\text{ReO}_4^-$ (89)
Rb^+NO_3^- (87)	$\text{Cs}^+\text{ReO}_4^-$ (89)
Cs^+NO_3^- (87)	$\text{Tl}^+\text{ReO}_4^-$ (86)
Tl^+NO_3^- (87)	$\text{Tl}^+\text{SO}_4^-=\text{Tl}^+$ (86)

studies) and from theoretical calculations on the vapor monomers (ion pairs and triads). The species (such as $M^+BO_2^-$, $M^+NO_3^-$, $M^+SO_4^-M^+$, $Na^+CrO_4^-Na^+$, $Cs^+MoO_4^-Cs^+$, $Cs^+WO_4^-Cs^+$, $Na^+AlF_4^-$, and $K^+AlCl_4^-$) appear to be constituted of a rigid, symmetrical anion with a simple cation (or vice versa). It has been suggested that the cation motions may be represented as large displacements occurring on a surface of high symmetry encompassing the complex anion. The molecule at sufficiently high temperatures can be viewed as having a dynamic configuration in which the cation is seen as belonging to all the anion ligands with equal probability.

D. Proposed Problem

There has been in recent years an increasing interest in studying by ultraviolet photoelectron spectroscopy the vapor species above heated inorganic ionic compounds which are solids at room temperature. The interest originated from an effort to better understand the structure and bonding of high temperature ionic gas phase molecules. The present study is an extension of a continuing effort to investigate vapors of complex-anion containing compounds and complex-cation containing compounds at high temperature.

Specifically, the compounds to be studied are: (a) the alkali metal metaborates ($M^+BO_2^-$), (b) the alkali metal tetrachloroaluminates ($M^+AlCl_4^-$), (c) the alkali metal tetrafluoroaluminates ($M^+AlF_4^-$), and (d) ammonium tetrachloroaluminate ($NH_4^+AlCl_4^-$). Only one other inorganic ionic compound containing metaborate as the complex anion, thallium metaborate, has been characterized by high temperature vapor photoelectron spectroscopy. No compounds containing complex anions

with halogen ligands have been studied by high temperature vapor photoelectron spectroscopy. The vapors above most heated ammonium salts are decomposition products (often in congruent proportions) rather than volatile monomer species representative of the solid (for example, $\text{NH}_4^+\text{Cl}^- + \Delta \rightarrow \text{NH}_3\uparrow + \text{HCl}\uparrow$). Therefore, the vapor photoelectron spectrum of the ammonium ion with an associated anion has not been observed.

The author's hope is that the information gained from the present studies on the gaseous species at high temperatures could be compared to results from other high temperature experimental techniques, and to theoretical molecular orbital calculations. The conclusions drawn from these studies should provide insight into the structure and bonding of these vapors and into future applications of high temperature photoelectron spectroscopy as a chemical problem solving technique.

The instrumental, sample handling, and spectral accumulation techniques employed in the present studies are similar to several previous investigations. These techniques have been described in detail in previous publications and will not be discussed here.^{42,86,89} Specific experimental modifications will be handled in each of the chapters devoted to the particular compounds.

CHAPTER II

ALKALI METABORATES

A. Previous Studies

1. Introduction

A number of experimental approaches have been applied to gaseous, liquid, and solid species which contain metaborate as a complex anion with a simple monovalent cation. Those which are pertinent to this present study include melting and boiling point determinations, vapor pressure studies, mass spectrometric experiments, electron diffraction measurements, infrared spectroscopy of the gaseous species at high temperature and of matrix isolated species prepared by imbedding high temperature molecules in low temperature matrix materials, thermodynamic calculations, HeI and HeII photoelectron spectroscopic investigation of a solid metaborate ($\text{Na}_3\text{B}_3\text{O}_6$), and HeI photoelectron spectroscopic investigation of a gaseous metaborate (Tl^+BO_2^-).

2. Melting and Boiling Points

Several studies^{90,91} have indicated that Li^+BO_2^- melts at 1117°K , and Prophet⁹² has determined the boiling point to be $2050 \pm 100^\circ \text{K}$ under an argon atmosphere. Several investigators^{93,94,95} have reported that Na^+BO_2^- melts at 1239°K and the boiling point has been estimated to be 1750°K .⁹⁶ The melting point of K^+BO_2^- is 1220°K ⁹⁷ and the boiling point has been estimated as 1675°K .⁹⁶ No melting or boiling points are available for Rb^+BO_2^- and Cs^+BO_2^- but extrapolation would place the melting points in the region of 1200°K and the boiling points around 1600°K .

3. Vapor Pressure Studies

The congruent vaporization of Li^+BO_2^- , Na^+BO_2^- , and K^+BO_2^- was demonstrated by Solomin and Potemkina⁹⁸ and by Tamura, Oishi, and Hamano⁹⁹ by free evaporation experiments from melts of $\text{M}_2\text{O} \cdot \text{B}_2\text{O}_3$. Analyses were carried out by weight loss and by chemical methods. Congruent vaporization does not necessarily mean that the compound maintains integrity when vaporized. The terminology simply implies that the vapor has the same net composition as the condensed phase from which it arises. Vapor pressure measurements over liquid Li^+BO_2^- were made by Hildenbrand, Hall, and Potter¹⁰⁰ in the temperature range 1120 to 1280° K using the torsion-effusion method. The total vapor pressure was found to be 2.5×10^{-6} atm. Molecular beams of gaseous Na^+BO_2^- and K^+BO_2^- have been used successfully by Millman, Kusch, and Rabi¹⁰¹ to determine the nuclear magnetic moments of B-10 and B-11. Kröger and Sörström¹⁰² have carried out vapor pressure measurements on Na^+BO_2^- and K^+BO_2^- by the Knudsen method, the weight gain of the target being measured. They obtain a total vapor pressure of 4×10^{-5} atm for Na^+BO_2^- and 1×10^{-3} atm for K^+BO_2^- at 1200° K. Vapor pressure measurements have been carried out by the transpiration method¹⁰³ on the liquid $\text{Rb}_2\text{O} \cdot \text{B}_2\text{O}_3$ system. From the data the vapor pressure of Rb^+BO_2^- has been estimated to be approximately 4×10^{-3} atm at 1200° K. No vapor pressure measurements are available for Cs^+BO_2^- .

4. Mass Spectrometry

The vapors above Li^+BO_2^- and Na^+BO_2^- were investigated mass spectrometrically by Akishin, Gorokhov, and Khodev.¹⁰⁴ They concluded that the principal vapor component is the monomer species

plus a small amount of other undetermined polymeric species. Büchler and Berkowitz-Mattuck¹⁰⁵ carried out a mass spectrometric investigation of the vapors above Li^+BO_2^- and Na^+BO_2^- in an attempt to investigate the polymerization of the species. They concluded that the vapor in the temperature range 1020 to 1220° K for Li^+BO_2^- consists of 90% monomer, 10% dimer, and 0.1% trimer, and that the vapor at 1070° K for Na^+BO_2^- consists of 96% monomer, 4% dimer, and a small amount of trimer. Much more recently, Gorokhov, Gussarow, Makarov, and Nikiten¹⁰⁶ have obtained mass spectrometric data which confirm the high predominance of the monomer with only a few percent dimer in the vapor phase for Na^+BO_2^- , K^+BO_2^- , Rb^+BO_2^- , and Cs^+BO_2^- at 1070° K, 1124° K, 1095° K, and 968° K, respectively.

Usually the high temperature vapor species is allowed to flow from some form of a Knudsen cell into the mass spectrometer. Inside the isothermal Knudsen cell the vapor species is in equilibrium with its evaporating condensed phase. The elevated temperature vapor species is bombarded with an electron beam inside the mass spectrometer and the resultant ions are separated by analysis of their individual mass to charge ratios. The data usually emerge as a plot of ion intensity against mass number. Some difficulties can be encountered in relating the detected ions to their neutral precursors, but several techniques are available for reducing these. Among the techniques are those which relate ion intensity and mass number variations to changes in sample pressure, vaporization temperature, and the ionizing electron beam energy.

Therefore, other high temperature experimental approaches which use nonequilibrium conditions should use data from high temperature mass spectrometric studies with caution because the percentages of monomer, dimer, or higher polymers may differ. Also, the experimental ion intensity against mass number spectrum should give reliable information, but interpretations concerning neutral parents may be subject to error.

5. Electron Diffraction

Electron diffraction studies of Li^+BO_2^- and Na^+BO_2^- vapors were conducted by Akishin and Spiridonov.¹⁰⁷ Also, Ezhov, Tolmachev, and Rambidi¹⁰⁸ have investigated Li^+BO_2^- , Na^+BO_2^- , K^+BO_2^- , and Rb^+BO_2^- vapors by electron diffraction. The results of both studies were interpreted in terms of a linear O-B-O group with unequal O-B distances. However, more recent electron diffraction studies by Ezhov and Komarov^{109,110} of Rb^+BO_2^- , Cs^+BO_2^- , and Tl^+BO_2^- vapor have been interpreted to show that the B-O distances are equal within the error limits of the procedure and that the O-B-O group is linear. A summary of the interatomic distances and angles which have been reported for the alkali metal metaborates from electron diffraction analyses is presented in Table III (p 17). The position of the metal ion could not be fixed rigorously probably because of the large amplitudes of vibration at the temperatures of the experiments. Therefore, M-O-B angles are given as ranges of angles.

In a high temperature electron diffraction experiment, an electron beam of narrow width crosses the high temperature vapor stream of the substance studied and the scattered electrons are

TABLE III
INTERATOMIC DISTANCES AND ANGLES IN GROUP IA METABORATE MONOMERS

Structural Parameter	Li ^a	Na ^a	K ^a	Rb ^b	Cs ^b
M-O distance (Å)	1.82	2.14	2.36	2.57	2.62
O-B distance (Å)	1.29	1.30	1.31	1.26	1.25
B=O distance (Å)	1.19	1.20	1.21	1.26	1.25
O-B=O angle (°)	180	180	180	180	180
M-O-B angle (°)	100±10	106±5	100±5	112±5	129±6

^aRef. 108

^bRef. 110

recorded on a photographic plate. An electron diffraction spectrum is normally presented as intensity plotted against the radial coordinate representing the internuclear distances in the vapor molecule. In practice, a theoretical expression which includes several factors (such as geometric model, internuclear distances, and root mean square amplitudes of the vibrations) is written and used to calculate an expected electron diffraction spectrum. The factors in the theoretical expression are varied until the theoretical and experimental electron diffraction spectra coincide. It may be possible to make a match between theoretical and experimental spectra with one or more geometric models, internuclear distances, or root mean square amplitudes of vibrations.

At high temperatures considerable difficulty is often encountered in the precise determination of internuclear distances by electron diffraction. It is necessary to take into account the excited rotational and vibrational molecular levels which may be appreciably populated and the asymmetry of the potential energy functions of the atomic vibrations. These characteristics of high temperature electron diffraction studies explain why these studies are normally less precise than the best studies at low temperatures. Therefore, other high temperature studies which use data from electron diffraction studies should be aware of both possible sources of error, namely, more than one theoretical model may fit the experimental curve, and corrections may be required for possible excited states at high temperatures.

6. Infrared Spectroscopy

Büchler and Marram¹¹¹ obtained the infrared spectra of gaseous Li^+BO_2^- , Na^+BO_2^- , and Cs^+BO_2^- in the region between 225 cm^{-1} and 2500 cm^{-1} . Bands were observed at 1935 cm^{-1} and 600 cm^{-1} and assigned respectively with the aid of isotopic substitution to the B-O stretch and the O-B-O bending vibrations. They noted that the frequencies remained relatively unchanged on going from one cation to another, indicating that the BO_2^- anion seems to be only minimally perturbed by the metal ion. The spectra corresponded quite well to that obtained for the BO_2^- anion when matrix isolated in alkali halide crystals. Bands are seen at $1959\text{--}1972$ and $587\text{--}590\text{ cm}^{-1}$.

The infrared spectrum has also been determined for Li^+BO_2^- , Na^+BO_2^- , K^+BO_2^- , Rb^+BO_2^- , and Cs^+BO_2^- isolated in Ar or Kr matrices at liquid hydrogen temperatures by Seshadri, Nimon, and White.¹¹² A summary of the infrared bands and their assignments is given in Table IV (p 20). Their assignments were based on a C_s symmetry for the M^+BO_2^- in the matrix. For Li^+BO_2^- , Na^+BO_2^- , and K^+BO_2^- all six of the expected infrared active fundamentals were observed. However, for Rb^+BO_2^- and Cs^+BO_2^- only five were observed. The missing band in each case was found to be the bending frequency involving the metal atom. In order to recognize the value of the information in Table IV (p 20), it should be noted that these molecules are high temperature gaseous molecules which have been frozen into an inert matrix at low temperatures. Therefore, considerations relating to lattice constraint and vibrational state populations should be borne in mind in the interpretation of the spectra.

TABLE IV
INFRARED FREQUENCIES IN MATRIX ISOLATED
GROUP IA METABORATE MONOMERS^a

Frequency	Li	Na	K	Rb	Cs
ν_1 (B=O)(cm ⁻¹)	1976	1960	1952	1951	1945
ν_2 (B-O)(cm ⁻¹)	1094	1087	1081	1080	1077
ν_3 (out-of-plane O-B-O bend)(cm ⁻¹)	578	577	581	582	581
ν_4 (in plane O-B-O bend)(cm ⁻¹)	569	573	577	577	576
ν_5 (M-O stretch)(cm ⁻¹)	471	363	265	225	207
ν_6 (M-O-B bend)(cm ⁻¹)	107	109	99	(70) ^b	(60) ^b

^aRef. 112

^bEstimated values in parentheses

Realizing that $8065\text{ cm}^{-1} \approx 11,600^\circ\text{ K} \approx 1\text{ eV}$ and that the M-O-B (ν_6) bending frequencies from Table IV are less than 120 cm^{-1} (approximately equal to $.015\text{ eV}$ or 170° K) at low temperature, it can be seen that at the temperatures required for vaporization of M^+BO_2^- (over 900° K) the M-O-B (ν_6) bending frequency should be excited to large vibrational amplitudes. Because of this these compounds may possibly be polytopic in nature as is the case proposed for LiNC and the alkali metal cyanides.

7. Thermodynamic Calculations

Table V (p 22) contains a summary of thermodynamic values⁹⁶ for the alkali metal metaborates. Temperature values have been selected for each of the alkali metal metaborates at which the vapor pressure is of the order of 10^{-2} torr. All energy values have been rounded off to the nearest kilocalorie per mole. Experimental thermodynamic values for Rb^+BO_2^- and Cs^+BO_2^- were not available; however, calculated or estimated values are in parentheses.

Rambidi¹¹³ has calculated the root mean square vibrational amplitudes of Li^+BO_2^- , Na^+BO_2^- , and Rb^+BO_2^- at 0° and 1500° K . The amplitude of vibration for B-O changes very little for the above M^+BO_2^- vapors on going from 0° to 1500° K . However, the ratios of the root mean square amplitudes for the M-O stretch (where $\text{M} = \text{Li}^+$, Na^+ , or Rb^+) are 1.81, 2.26, and 2.75 times larger at 1500° K than at 0° K . This trend would seem to indicate that the M-O root mean square amplitude ratio may be even greater for Cs^+BO_2^- .

Ezhov and Komarov¹¹⁰ have calculated the potential energy of the electrostatic interaction between M^+ and BO_2^- ions as a function

TABLE V
THERMODYNAMIC PROPERTIES OF THE GROUP IA METABORATE MONOMERS

	Li ^a	Na ^a	K ^a	Rb	Cs
ΔH (298°) for $MBO_2(s) \rightarrow MBO_2(l)$ (kcal/mole)	5	4	3	(2) ^b	(1)
$MBO_2(l) \rightarrow MBO_2(g)$ (kcal/mole)	84	74	73	(70)	(68)
ΔF (298°) for $MBO_2(s) \rightarrow MBO_2(l)$ (kcal/mole)	4	3	3	(2)	(1)
$MBO_2(l) \rightarrow MBO_2(g)$ (kcal/mole)	70	60	58	(55)	(50)
Temperature for 0.01 torr vapor pressure (°K)	1200	1200	1100	(1000)	(1000)

^aRef. 96

^bEstimated values are in parentheses

of the M-O-B angle and internuclear distance M-O. They say that the map of the potential energy surface for Cs^+BO_2^- shows a minimum which corresponds to the bent (C_s) configuration of the molecule. However, the low value of the potential energy difference (400 cm^{-1}) between linear ($D_{\infty h}$) and bent (C_s) configurations leads one to believe that the M-O-B angle will strongly depend on the temperature. Elevating the temperature should increase the population of excited vibrational levels, thus increasing the effective M-O-B angle. The above calculations would lead one to conclude that the bonding at high temperatures of the alkali metal metaborates may be polytopic in nature.

8. HeI and HeII Photoelectron Spectroscopy

Conner, Considine, and Hiller¹¹⁴ have investigated the surface of solid $\text{Na}^+\text{Na}^+\text{B}_3\text{O}_6^{3-}\text{Na}^+$ using low energy photon sources (HeI and HeII). The HeII experimental bands were interpreted with the aid of ab initio self consistent field molecular-orbital-calculations of the anion ($\text{B}_3\text{O}_6^{3-}$). Four regions of the ionization were reported: (a) 9.7 eV ($2a_2'$, $2a_2''$, $2e''$, $9e'$, and $8e'$), (b) 12.3 eV ($1e''$, $7e'$, and $7a_1'$), (c) 14.5 eV ($1a_2''$ and $6a_1'$), and (d) 16.9 eV ($1a_2'$ and $6e'$). Data from the above calculations indicated that the four bands originate from molecular orbitals which are largely oxygen 2p in character [(a) greater than 90%, (b) 70-80%, (c) 70-80%, and (d) 55-65%]. The HeI ultra-violet photoelectron spectrum of the solid $\text{Na}^+\text{Na}^+\text{B}_3\text{O}_6^{3-}\text{Na}^+$ was not presented because problems of subtracting the steeply rising secondary electron background prevented a usable spectrum from being obtainable.

The HeI ultraviolet photoelectron spectroscopic spectrum of gaseous Tl^+BO_2^- has been recently determined.⁸⁶ In order to interpret the data, the authors carried out semi-empirical theoretical calculations of molecular orbital energies and atomic orbital constituencies for linear ($D_{\infty h}$) and bent (C_s) Tl^+BO_2^- , the dimer (D_{2h}) $\text{Tl}^+\text{B}_2\text{O}_4^-\text{Tl}^+$, and the free BO_2^- ($D_{\infty h}$) ion. The five ionization regions best fit the values determined for the free BO_2^- ion plus a peak associated with the Tl 6s electrons to give the assignments: (a) 10.2 eV (Tl 6s), (b) 11.9 eV ($1\pi_g$), (c) 12.8 eV ($1\pi_u$), (d) 13.0 eV ($3\sigma_u$), and (e) 14.3 eV ($4\sigma_g$).

B. Experimental Procedure

1. Compounds

Anhydrous alkali metal metaborate salts (Li^+BO_2^- , Na^+BO_2^- , K^+BO_2^- , and Cs^+BO_2^-) were obtained from Research Organic/Inorganic Chemical Corporation. All four compounds were stated to be greater than 99.0% pure. The rubidium salt (Rb^+BO_2^-) with a 99.0% stated purity was procured from Pfaltz and Bauer, Inc. A boron nitride rod (hot pressed, 1/4" o.d. and 99.0% stated purity) was purchased from Cerac/Pure, Inc.

2. Equipment

a. Spectrometer. The high temperature photoelectron spectrometer used in these studies was designed by Allen.⁴⁰ A diagram of the spectrometer is shown in Figure 1 (p 25). The basic components of the analyzer are two concentric cylinders, entrance and exit slits, a photon source, and an electron multiplier. The two cylinders and the entrance and exit slits are of marine brass. The outer cylinder

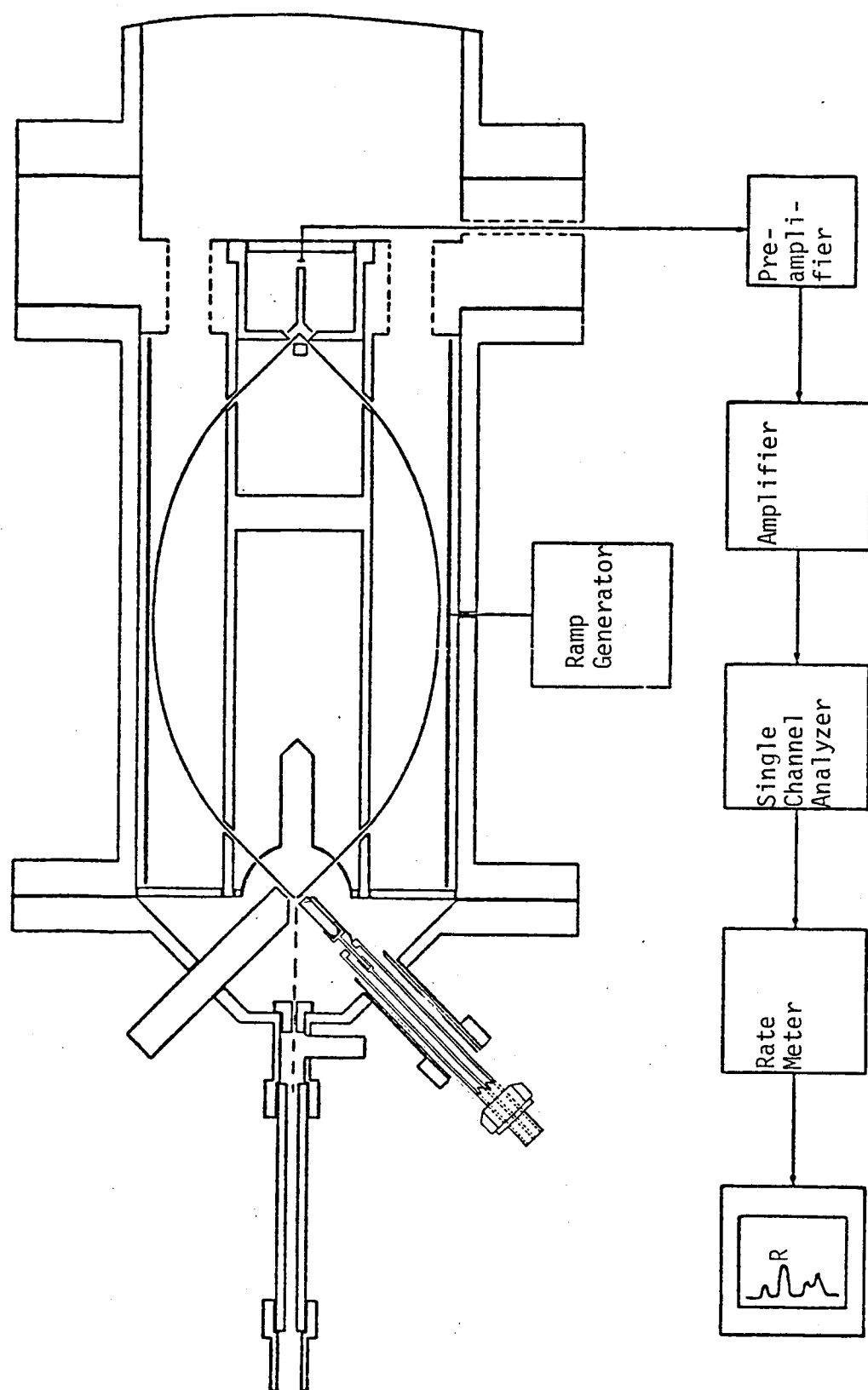


Figure 1. Photoelectron spectrometer with photon source and affiliated components.

is biased negatively while the inner cylinder and slits are grounded. The desired potential differences are achieved by connecting the outer cylinder to a ramp generator which supplies a continuously varying negative voltage. The photon source is a HeI discharge lamp. A direct current discharge at about one torr pressure generates HeI photons ($584 \text{ \AA}$ or 21.22 eV) which pass through a quartz capillary approximately 0.03 inch in diameter. At one end of the cylinder (see Figure 1, p 25) is the sample interaction region and at the other end a Bendix Spiraltron 4219 electron multiplier. Electrons are liberated in the interaction region where the photon beam and the vapor beam come together. The ejected electrons pass through the entrance slits and enter the region between the cylinders where they are separated by the electrostatic field according to their kinetic energies. They then pass through the exit slits and the multiplier slits subsequently being detected as they fall on the electron multiplier.

b. Instrumental Accessories. The photon source which was described previously is powered by a Kilovolt power supply. Welch Model 1405 vacuum pumps are used for differential pumping of the HeI lamp and of the sample interaction region. Pressure inside the spectrometer is maintained at 7×10^{-6} torr by pumping with a Welch Model 3103 turbomolecular pump.

The electron multiplier is powered by a Bendix Model 0301 miniature high voltage supply. Pulses from the Bendix Spiraltron electron multiplier are fed into an Ortec Model 113 preamplifier, then into an Ortec Model 485 amplifier, then into an Ortec Model 406 single

channel analyzer, and finally into an Ortec 441 ratemeter. Data are read out on a Y-Lab servographic strip recorder which takes signals from the ratemeter. A Hewlett Packard 3310A function generator is employed as a ramp generator to place the scan of negative voltages on the outer cylinder.

Three pairs of square Helmholtz coils surround the spectrometer in order to increase resolution and throughput by establishing an environment with a magnetic field of 1 milligauss or less. The instrumental resolution is periodically checked by observing the separation of the argon $^2P_{3/2}$ and $^2P_{1/2}$ ionization lines.

c. The Vapor Oven. The vapor oven used in these studies consists of a tantalum-strip wound boron nitride cell (4 mm i.d. x 2.54 cm) which is heated by the unfiltered output of a half-wave rectifier supplied by a 60 cycle A.C. current. The cell is also coated with Astroceram, a ceramic type cement (chiefly zirconium dioxide) from Chemo-Thermic Industries. In addition to providing insulation, the Astroceram reduces the rate of oxidation of the tantalum strip at high temperatures. A Variac in the power supply is used to control the current to the tantalum strip. A Tennelec TC-303 linear gate is placed between the amplifier and the single channel analyzer so that during the heating cycle (upper half of a 60 cycle sine wave) the detection circuit is gated off. During the counting cycle (lower half of the 60 cycle sine wave) the gate is open, the cell current is off, and electron signals are recorded. The electronic components are active only during the central 160° of the 180° lower half cycle to ensure electrical charge and magnetic field decay of the heated cell.

d. Air Lock. Since the alkali metal metaborates tend to take up water, it was necessary to develop an air lock which could be used for transfer of the loaded vapor cell between the nitrogen filled dry box and the evacuated spectrometer. A schematic diagram of the air lock is shown in Figure 2 (p 29). The vapor oven and air lock were placed in the antechamber of the dry box which was pumped by a vacuum pump for at least 45 minutes. Then the antechamber was backfilled with nitrogen and the air lock and vapor oven were placed in the dry box. The vapor oven was loaded with the metaborate salt and placed inside the air lock (see Figure 2, p. 29) and the vacuum fitting and the gate valve were closed. Finally, the air lock with the loaded vapor oven was placed in the antechamber, then removed and transported to the instrument.

e. Baking System. In order to reduce the amount of adsorbed water on the interior surfaces of the spectrometer, a simple baking system was employed. The system consists of heating tapes which were placed around the spectrometer head, analyzer, and the 7" vacuum line to the turbomolecular pump.

3. Procedures

Several basic steps were incorporated into the experimental technique involved in obtaining spectra for the metaborates. The first step in the general procedure was: (a) cleaning and assembling the spectrometer. After thorough ultrasonic cleaning and drying of the spectrometer, a smooth coating of Aerodag (a colloidal suspension of graphite in 2-propanol supplied by Acheson Colloids Company) was applied to all the inner surfaces, allowed to dry, then baked on with

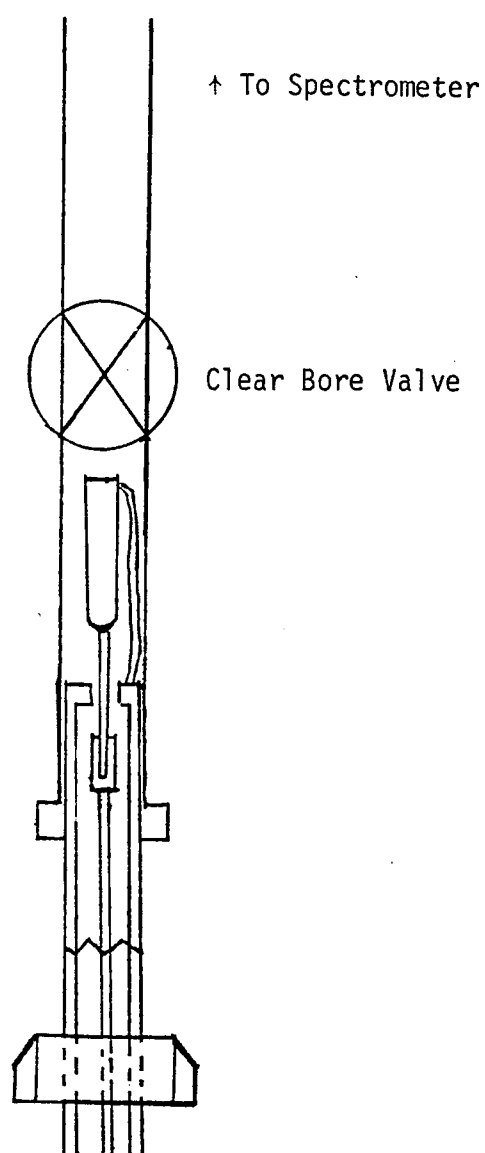


Figure 2. Air lock.

a heat gun. The second step was (b) pumping the instrument down with the baking system in use. During the initial pump down, the spectrometer was pumped and heated for 12-18 hours at a temperature between 100-200° C. The third step was (c) loading the vapor oven with sample and placing the oven in the air lock. The fourth step was (d) closing the instrument down while flushing it with He and Ar. Flushing the system was necessary for proper functioning of the HeI discharge lamp and to remove trace gaseous impurities in the spectrometer system. The fifth step was (e) attaching the air lock with the loaded oven to the instrument. The sixth step was (f) pumping the instrument down. The seventh step consisted of (g) opening the air lock and inserting the oven into the spectrometer. This was followed by the eighth step which consisted of (h) pumping the instrument down, and removing the baking system. Then there followed the ninth step which involved (i) adjusting the Helmholtz coils using a known calibrant, and scanning a range of kinetic energies to determine the spectral background. The tenth step involved (j) stimulating adsorbed water evolution by heating the vapor oven in the spectrometer, and allowing any produced water lines to drop before proceeding, and the eleventh step consisted of (k) controlling the sample vapor concentration by careful adjustment of the Variac so as to produce signals for the predominant bands of 400 to 1000 counts per second. The twelfth step was (l) scanning electron kinetic energies for bands of interest, and finally scanning the entire spectral range repeatedly as the temperature of the emptied oven was slowly decreased.

C. Experimental Results

The HeI photoelectron spectra of the vapors above heated $K^+BO_2^-$, $Rb^+BO_2^-$, and $Cs^+BO_2^-$ are presented in Figures 3 - 5 (pp 32 - 34). Attempts to acquire experimental data for $Li^+BO_2^-$ and $Na^+BO_2^-$ have been unsuccessful because of the extremely high temperature required: on the order of 1200-1400° K. At these temperatures the Astroceram tends to crack allowing the small amount of oxygen in the spectrometer to react with the tantalum heating strip. The tantalum oxide which is formed causes the heating strip to be destroyed. The spectra which are presented in Figures 3, 4, and 5 (pp 32, 33, and 34) are representative of at least 15 spectra obtained for each compound. A nontypical spectrum obtained for $Cs^+BO_2^-$ is presented as Figure 6 (p 35) in order that the reader may view an example of the kind of spectrum that the author chose to reject. The spectral peaks in each figure are labeled with experimental ionization energy values which have been rounded to one decimal. Unnumbered peaks which are designated by the letters Ar or N₂ are due to argon or nitrogen, respectively, used as calibrants. The values assigned to the various band peaks in the spectra for each of the above compounds are listed in Table VI ($K^+BO_2^-$) (p 36), Table VII ($Rb^+BO_2^-$) (p 37), and Table VIII ($Cs^+BO_2^-$) (p 38). The unweighted average ionization energy value ($\bar{x}$), the standard deviation of each individual ionization energy value (σ_i), the 95% confidence limit of the individual ionization energy value ($95\% \sigma_i$), the standard deviation of unweighted average ionization energy value (σ_{av}), and the 95% confidence limit of the unweighted average ionization energy values ($95\% \sigma_{av}$) for each band peak in each

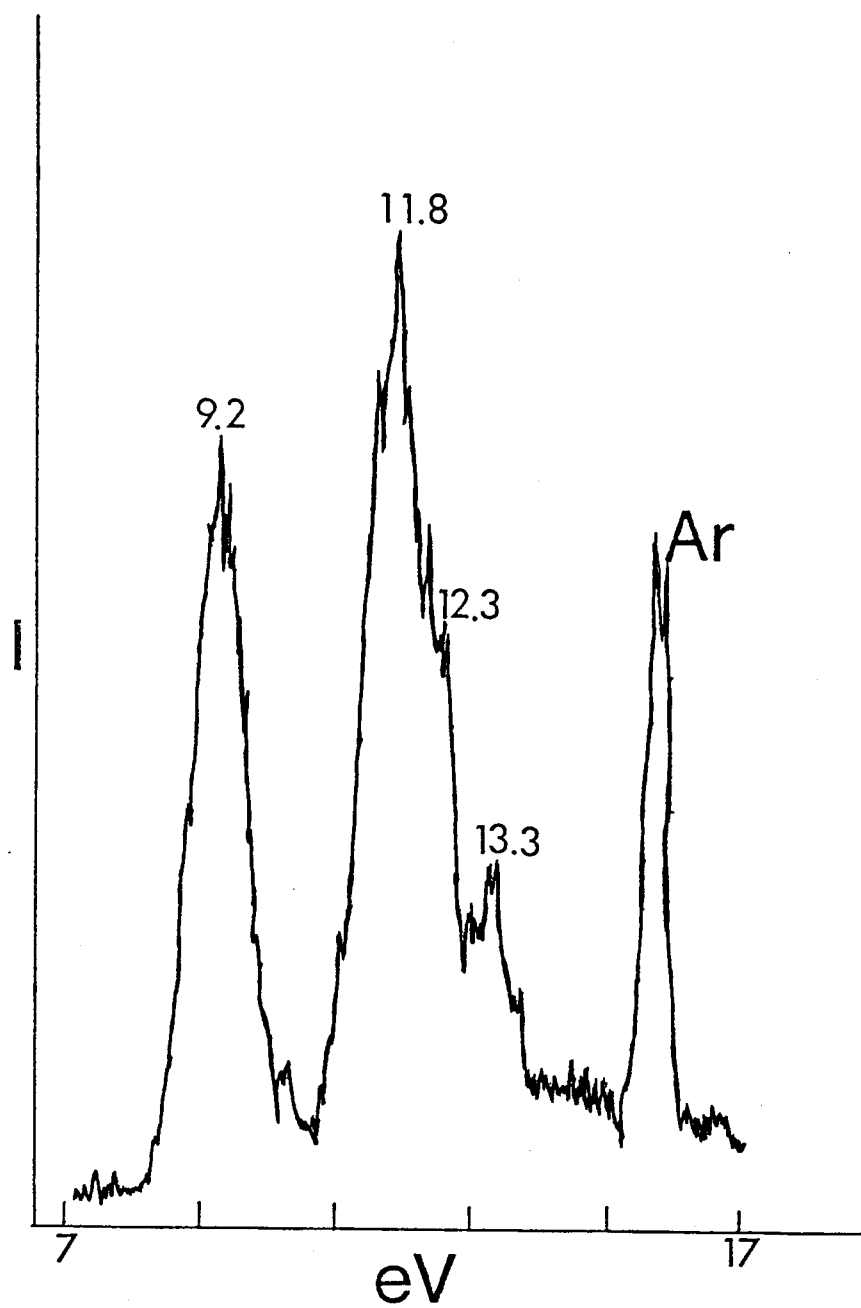


Figure 3. HeI photoelectron spectrum of K^+BO_2^- vapor.

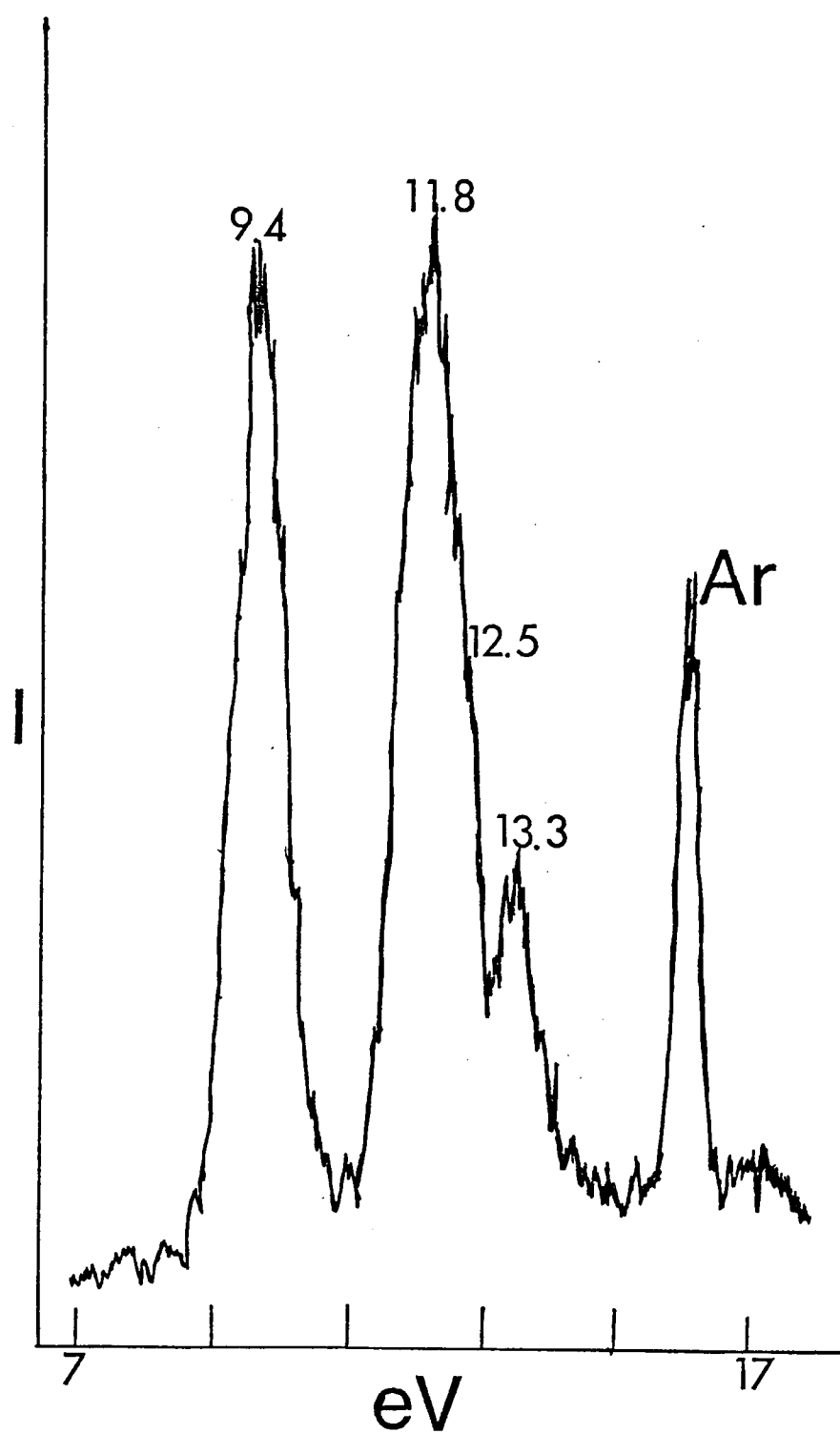


Figure 4. HeI photoelectron spectrum of Rb^+BO_2^- vapor.

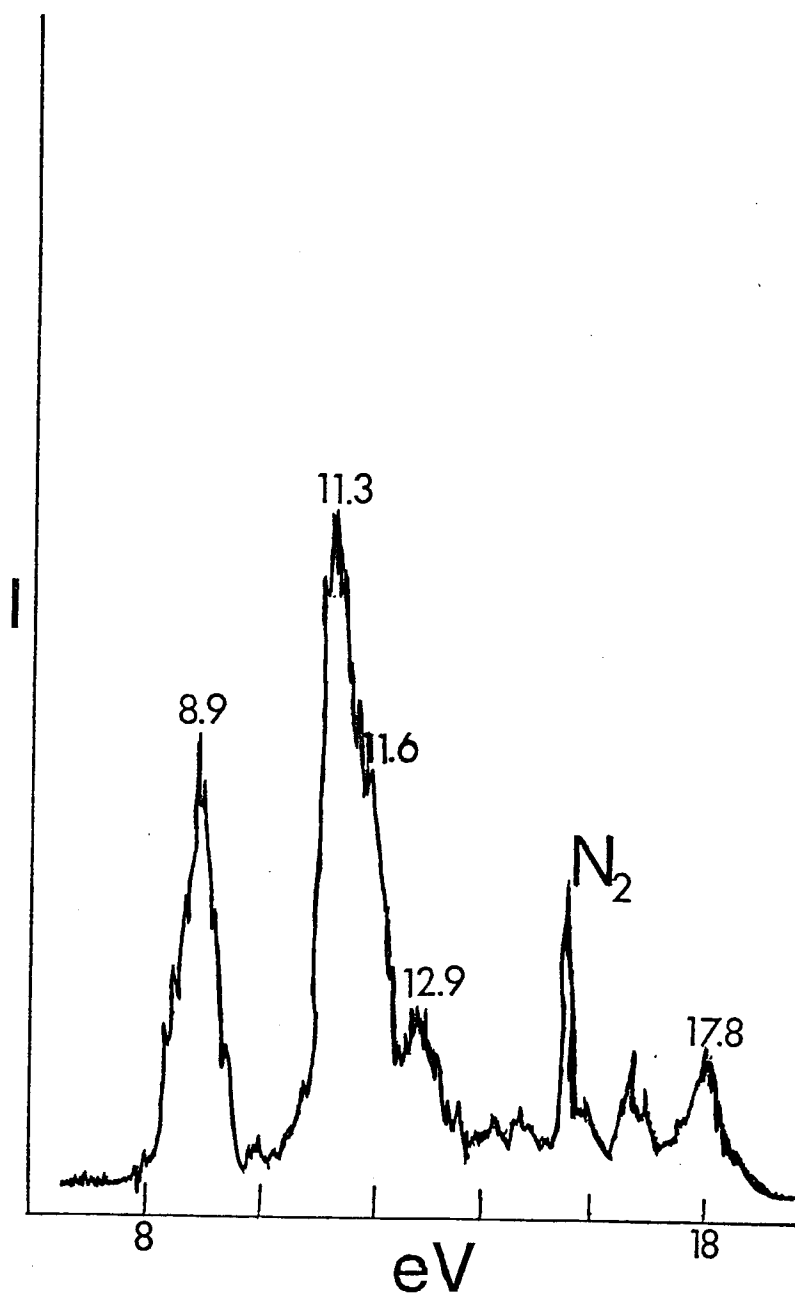


Figure 5. HeI photoelectron spectrum of Cs^+BO_2^- vapor.

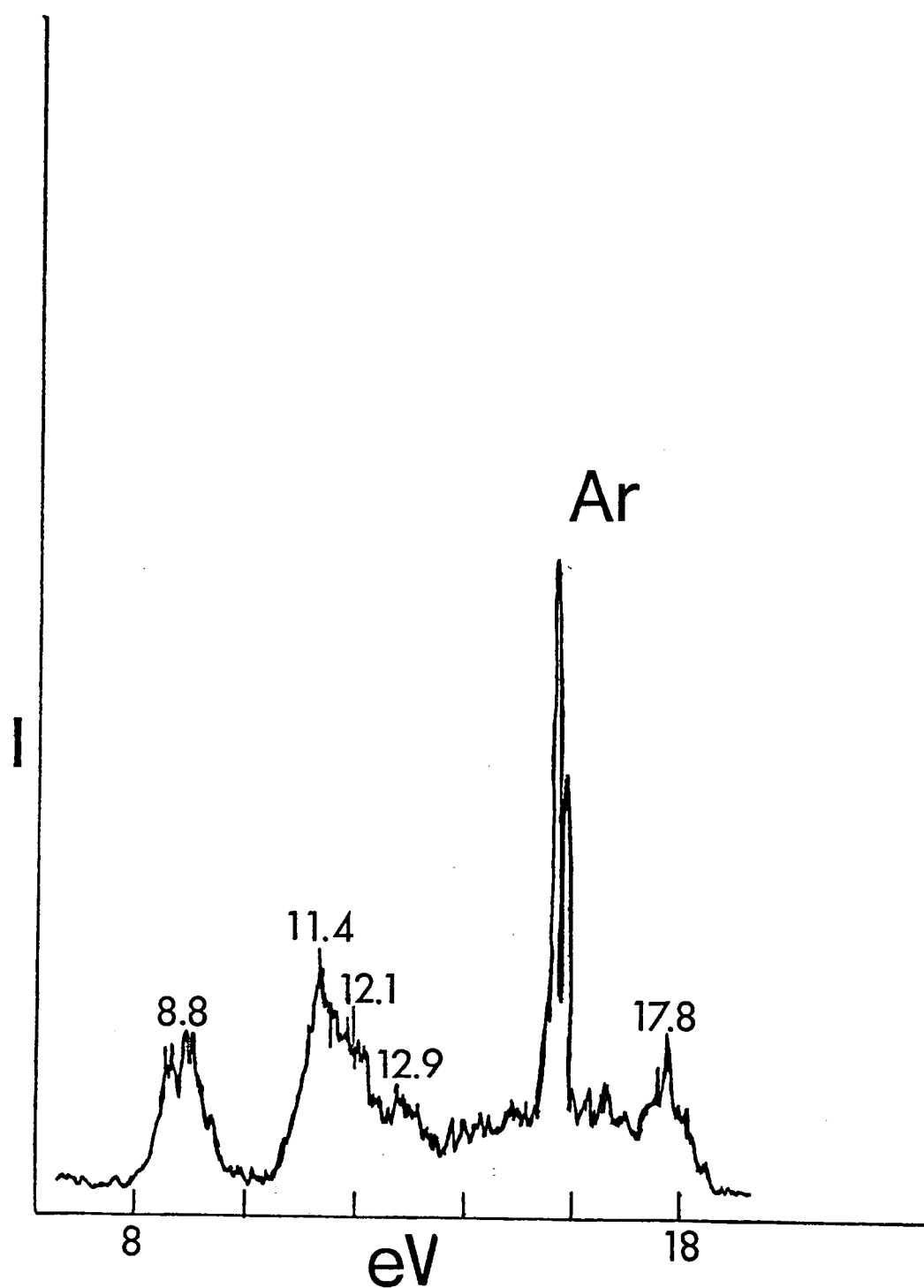


Figure 6. Nontypical HeI photoelectron spectrum of Cs^+BO_2^- vapor.

TABLE VI
BAND PEAK VALUES FOR $K^+BO_2^-$ VAPOR SPECTRA

Item	Peak (-eV)			
	1st	2nd	3rd	4th
Run 1	9.16	11.75	12.55	13.28
Run 2	9.22	11.83	12.46	13.33
Run 3	9.26	11.82	12.48	13.36
Run 4	9.27	11.85	12.59	13.33
Run 5	9.25	11.91	12.44	13.38
Run 6	9.26	11.89	12.61	13.36
Run 7	9.26	11.82	12.55	13.35
Run 8	9.28	11.84	12.50	13.36
Run 9	9.25	11.90	12.58	13.38
Run 10	9.26	11.86	12.54	13.36
Run 11	9.24	11.81	12.62	13.35
Run 12	9.28	11.84	12.59	13.33
Run 13	9.26	11.88	12.56	13.38
Run 14	9.27	11.86	12.54	13.33
Run 15*	9.24	11.83	12.41	13.32
$\bar{X} =$	9.25	11.85	12.54	13.35
$\sigma_i =$	.03	.04	.06	.03
95% $\sigma_i =$	.06	.08	.12	.05
$\sigma_{av} =$	.01	.01	.02	.01
95% $\sigma_{av} =$	.02	.03	.04	.02

TABLE VII
BAND PEAK VALUES FOR Rb^+BO_2^- VAPOR SPECTRA

Item	Peak (-eV)			
	1st	2nd	3rd	4th
Run 1	9.34	11.79	12.34	13.14
Run 2	9.30	11.69	12.49	13.33
Run 3	9.44	11.74	12.31	13.23
Run 4	9.48	11.81	12.51	13.38
Run 5	9.41	11.86	12.29	13.22
Run 6	9.38	11.83	12.44	13.18
Run 7	9.47	11.74	12.38	13.36
Run 8	9.49	11.70	12.46	13.34
Run 9	9.36	11.78	12.30	13.16
Run 10	9.38	11.84	12.35	13.34
Run 11	9.36	11.86	12.37	13.12
Run 12	9.50	11.83	12.47	13.27
Run 13*	9.44	11.80	12.50	13.28
Run 14	9.34	11.77	12.36	13.34
Run 15	9.62	11.92	12.62	13.52
$\bar{X} =$	9.42	11.80	12.41	13.26
$\sigma_i =$	.08	.06	.09	.11
95% $\sigma_i =$	.16	.13	.18	.21
$\sigma_{av} =$	.02	.02	.02	.03
95% $\sigma_{av} =$	.05	.04	.05	.06

TABLE VIII
BAND PEAK VALUES FOR Cs^+BO_2^- VAPOR SPECTRA

Item	1st	2nd	Peak (-eV) 3rd	4th	5th
Run 1	8.97	11.47	11.79	13.13	17.93
Run 2	8.92	11.42	11.97	12.90	17.79
Run 3	9.02	11.42	11.81	12.94	17.79
Run 4	8.85	11.47	11.94	12.96	17.67
Run 5	8.78	11.45	11.77	12.93	17.80
Run 6	8.87	11.45	11.90	13.05	17.89
Run 7	8.87	11.49	11.88	12.96	17.94
Run 8	8.87	11.36	11.98	12.96	17.96
Run 9	8.91	11.36	11.97	12.87	17.80
Run 10	8.96	11.36	11.76	12.84	17.82
Run 11*	8.92	11.32	11.64	12.93	17.84
Run 12	8.94	11.47	11.95	12.95	17.93
Run 13	8.80	11.46	11.89	13.04	17.77
Run 14	8.88	11.44	11.76	12.95	17.70
Run 15	8.96	11.48	11.74	12.88	17.80
$\bar{X} =$	8.90	11.43	11.85	12.95	17.83
$\sigma_i =$	.06	.05	.10	.07	.09
95% $\sigma_i =$	.13	.10	.20	.15	.17
$\sigma_{av} =$	.02	.01	.02	.02	.02
95% $\sigma_{av} =$	.04	.03	.05	.04	.05

compound are given in Tables VI - VII (pp 36 - 38). The starred run in Tables VI, VII and VIII (pp 36, 37 and 38) indicates the spectrum which was chosen for presentation in Figures 3, 4, and 5 (pp 32, 33, and 34) respectively. The spectrum which displayed band peak values similar to the unweighted averaged ionization energy values was chosen. A summary of the unweighted average ionization energy values assigned to the peaks for each compound is listed in Table IX (p 40). These values are followed by their 95% confidence limits.

D. Theoretical Expectations

Dementjev and Kracht¹¹⁵ have performed ab initio self-consistent field calculations on several linear ($D_{\infty h}$ or $C_{\infty v}$) and bent (C_s) geometries for $Li^+BO_2^-$ and have found that the bent configuration with a non-symmetrical linear BO_2^- anion is the most stable. They discovered that their best calculations showed very little energy difference between the linear and bent structures, these results bringing them to the judgment that the bending vibration of the band involving the Li^+ atom has a large amplitude and a small force constant. They have concluded that $Li^+BO_2^-$ is probably polytopic. They obtained bent molecule MO energy values of 557.8 eV (1a'), 557.1 eV (2a'), 205.7 eV (3a'), 67.3 eV (4a'), 33.6 eV (5a'), 33.0 eV (6a'), 15.7 eV (7a'), 14.1 eV (8a'), 13.4 eV (9a'), 13.3 eV (1a''), 10.5 eV (10a'), and 10.4 eV (2a''). In general, MO levels which have values greater than 50 eV may be considered to be largely atomic in character, while those which have values less than 50 eV are ordinarily considered to be characteristic of the overall molecule.

TABLE IX
AVERAGE METABORATE EXPERIMENTAL IONIZATION ENERGIES (-eV)

	Cs^+BO_2^-	Rb^+BO_2^-	K^+BO_2^-
Band 1	8.90±.04	9.42±.05	9.25±.02
Band 2	11.43±.03	11.80±.04	11.85±.03
Band 3	11.85±.05	12.41±.05	12.54±.04
Band 4	12.95±.04	13.26±.06	13.35±.02
Band 5	17.83±.05		

For the present study, UTARC (a semi-empirical, extended Hückel method) calculations have been carried out on Cs^+BO_2^- , Rb^+BO_2^- , K^+BO_2^- , and on the BO_2^- ion. The structural models which were used in the calculations were chosen from electron diffraction studies (Table III, p 17). The purpose of these UTARC calculations was to observe the shifts in the MO envelope and the splittings of the MO levels between the C_s configurations of Cs^+BO_2^- , Rb^+BO_2^- , and K^+BO_2^- and the $D_{\infty h}$ configuration of BO_2^- . The results of the computations are presented in Table X (p 42). The first four rows represent the theoretical ionization values of the MO's from the UTARC program. The fifth row represents the theoretical ionization energies of the MO's for Li^+BO_2^- from an ab initio calculation.¹¹⁵ Rows six through nine show values of the first four rows which have been adjusted to the ab initio values of row five. The values in rows six through nine are adjusted by a Q factor which is proportioned to the breadth of the MO envelope, as well as the absolute magnitude of the first MO ionization energy.

All of the occupied MO levels which are accessible by HeI radiation are predominately oxygen 2p in character. For example, in the $D_{\infty h}$ BO_2^- ion the precent atomic orbital (AO) contributions to the MO's are $1\pi_g$ (100% O 2p), $1\pi_u$ (84% O 2p), $3\sigma_u$ (99% O 2p), and $4\sigma_g$ (90% O 2p) while in the C_s configuration of $M^+\text{BO}_2^-$ ($M = \text{Cs}^+$, Rb^+ , or K^+) the percent AO contributions to the MO's are $2a''$ (99% O 2p), $6a'$ (99% O 2p), $5a'$ (83% O 2p), $1a''$ (85% O 2p), $4a'$ (97% O 2p), and $3a'$ (94% O 2p). The data may be taken to indicate that the presence or absence of a cation near the BO_2^- anion does not strongly affect

TABLE X
 Cs^+BO_2^- , Rb^+BO_2^- , K^+BO_2^- , and BO_2^- SHIFT AND
 SPLIT CALCULATIONS (-eV)

Line		MO's and Energies					
1	$\text{D}_{\infty h} \text{BO}_2^-$ anion ^a	$1\pi_g$ 6.2	$1\pi_g$ 6.2	$1\pi_u$ 7.6	$1\pi_u$ 7.6	$3\sigma_u$ 7.7	$4\sigma_g$ 8.9
2	$\text{C}_s \text{K}^+\text{BO}_2^-$	$2a''$ 10.9	$6a'$ 11.0	$5a'$ 12.3	$1a''$ 12.3	$4a'$ 12.4	$3a'$ 14.2
3	$\text{C}_s \text{Rb}^+\text{BO}_2^-$	$2a''$ 10.5	$6a'$ 10.6	$5a'$ 11.8	$1a''$ 11.9	$4a'$ 11.9	$3a'$ 13.8
4	$\text{C}_s \text{Cs}^+\text{BO}_2^-$	$2a''$ 10.3	$6a'$ 10.3	$5a'$ 11.6	$1a''$ 11.6	$4a'$ 11.7	$3a'$ 13.6
5	$\text{C}_s \text{Li}^+\text{BO}_2^-$ ^b	$2a''$ 10.4	$6a'$ 10.5	$5a'$ 13.3	$1a''$ 13.4	$4a'$ 14.1	$3a'$ 15.7
6	$\text{D}_{\infty h} \text{BO}_2^-$ anion ^c	$1\pi_g$ 10.4	$1\pi_g$ 10.4	$1\pi_u$ 13.2	$1\pi_u$ 13.2	$3\sigma_u$ 13.3	$4\sigma_g$ 15.7
7	$\text{C}_s \text{K}^+\text{BO}_2^-$ ^d	$2a''$ 10.4	$6a'$ 10.5	$5a'$ 12.6	$1a''$ 12.6	$4a'$ 12.8	$3a'$ 15.7
8	$\text{C}_s \text{Rb}^+\text{BO}_2^-$ ^e	$2a''$ 10.4	$6a'$ 10.5	$5a'$ 12.6	$1a''$ 12.6	$4a'$ 12.7	$3a'$ 15.7
9	$\text{C}_s \text{Cs}^+\text{BO}_2^-$ ^f	$2a''$ 10.4	$6a'$ 10.5	$5a'$ 12.5	$1a''$ 12.6	$4a'$ 12.7	$3a'$ 15.7

^aRef. 86

^bRef. 115

^cLine 1 adjusted $Q = 2.0x + 2.2$

^dLine 2 adjusted $Q = 1.7x + 6.9$

^eLine 3 adjusted $Q = 1.6x + 6.5$

^fLine 4 adjusted $Q = 1.6x + 6.1$

the MO energy values or the AO constituencies of the outer MO's. The dissolution of the $D_{\infty h}$ symmetry of the BO_2^- ion (to C_s in the compound) results in only small MO splits, generally no more than a few tenths of an eV.

The BO_2^- ion is isoelectronic with CO_2 and BeF_2 which may provide some help in interpreting the alkali metal metaborate spectra. Theoretical MO values for BO_2^- , CO_2 and BeF_2 and experimental MO values for CO_2 are given in Table XI (p 44). The AO contributions for the outer MO's for CO_2 are largely O 2p in character as in BO_2^- ; however, the entire valence-band-envelope for the metaborate is shifted to smaller binding energies relative to the CO_2 , this being largely due to the negative charge on the metaborate ion. In BeF_2 , the outer MO's are predominately F 2p in character and the whole MO envelope is moved to higher binding energies, this probably resulting from the increased electronegativity of fluorine.

E. Interpretations

Comparisons of the experimental unweighted average ionization energy values from Tables VI - VIII (pp 36 - 38) have been made with the ab initio MO calculations and UTARC calculations of Table X (p 42) and the experimental values pertaining to the isoelectronic molecule CO_2 from Table XI (p 44). The results of these comparisons are presented in Table XII (p 45). It has been concluded that the spectra for the three vapors ($K^+BO_2^-$, $Rb^+BO_2^-$, and $Cs^+BO_2^-$) could be fit by the adjusted $M^+BO_2^-$ ($M = K^+$, Rb^+ , or Cs^+) molecular, the BO_2^- ionic, or the CO_2 molecular theoretical ionization energy values. It is suggested that the anion MO energy order for the three vapors

TABLE XI
MO VALUES FOR BO_2^- ANION, CO_2 , AND BeF_2 MOLECULES (-eV)

	Theo. CO_2^{a}	Expt. CO_2^{b}	Theo. BeF_2^{c}	Theo. $\text{BO}_2^{-\text{d}}$
$1\pi_{\text{g}}$	12.8	13.8	16.9	10.4
$1\pi_{\text{u}}$	17.4	17.6	17.4	13.2
$3\sigma_{\text{u}}$	18.2	18.1	18.5	13.3
$4\sigma_{\text{g}}$	19.7	19.4	18.6	15.7

^aRef. 116

^bRef. 117

^cRef. 118

^dRef. 86

TABLE XII
COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES FOR THE METABORATES (-eV)

Value	$1\pi_g$	$1\pi_u$	$3\sigma_u$	$4\sigma_g$	
Exptl. $K^+BO_2^-$ (from Table IX, p 40)	9.3	11.9	12.5	13.4	
Theor. $K^+BO_2^-$ (from Table X, p 42) ^a	9.3(a'') 9.4(a')	11.0(a') 11.0(a'')	11.2(a')	13.4(a')	
Theor. BO_2^- (from Table X, p 42) ^b	9.3	11.4	11.6	13.4	
Theor. CO_2 (from Table XI, p 44) ^c	9.3	12.0	12.5	13.4	
Exptl. $Rb^+BO_2^-$ (from Table IX, p 40)	9.4	11.8	12.4	13.3	
Theor. $Rb^+BO_2^-$ (from Table X, p 42) ^d	9.4(a'') 9.5(a')	11.0(a') 11.1(a'')	11.1(a')	13.3(a')	
Theor. BO_2^- (from Table X, p 42) ^e	9.4	11.4	11.6	13.3	
Theor. CO_2 (from Table XI, p 44) ^f	9.4	12.0	12.5	13.3	
Exptl. $Cs^+BO_2^-$ (from Table IX, p 40)	8.9	11.4	11.9	13.0	17.8
Theor. $Cs^+BO_2^-$ (from Table X, p 42) ^g	8.9(a'') 9.0(a')	10.5(a') 10.5(a'')	10.6(a')	13.0(a')	
Theor. BO_2^- (from Table X, p 42) ^h	8.9	11.0	11.2	13.0	
Theor. CO_2 (from Table XI, p 44) ⁱ	8.9	11.6	12.1	13.0	

^aAdjusted $Q = 1.3x - 4.2$

^bAdjusted $Q = 1.5x - 0.1$

^cAdjusted $Q = 0.6x + 1.7$

^dAdjusted $Q = 1.2x - 3.0$

^eAdjusted $Q = 1.4x + 0.4$

^fAdjusted $Q = 0.6x + 2.2$

^gAdjusted $Q = 1.3x - 3.9$

^hAdjusted $Q = 1.5x - 0.5$

ⁱAdjusted $Q = 0.6x + 1.3$

($K^+BO_2^-$, $Rb^+BO_2^-$, and $Cs^+BO_2^-$) is $1\pi_g$, $1\pi_u$, $3\sigma_u$, $4\sigma_g$. In the $Cs^+BO_2^-$ vapor spectrum (Figure 5, p 34), the fifth band would be assigned to the ionization from the cesium 5p electrons which lie in that region. The cesium assignment is similar to those made by other investigators for cesium halides, cesium nitrate, cesium metaphosphate, and cesium perrhenate. A summary of the cesium 5p experimental ionization energy values is given in Table XIII (p 47).

The spin orbit split of the Cs 5p levels into the $5p_{3/2}$ and $5p_{1/2}$ was seen for $Cs^+NO_3^-$, $Cs^+ReO_4^-$, Cs^+Cl^- , Cs^+Br^- , and Cs^+I^- , but was not observed for $Cs^+PO_3^-$ or $Cs^+BO_2^-$. Potts and Williams⁴³ have shown that in the diatomic cesium halides the metal p shell environment does not differ markedly from the environment of the free atom. They reported the ionization energies of the free Cs $5p_{3/2}$ and $5p_{1/2}$ levels to be 17.21 eV and 19.1 eV respectively. It does not appear from the above conclusions that the Cs $5p_{3/2}$ and $5p_{1/2}$ ionizations in $Cs^+BO_2^-$ vapor spectrum would be expected to occur under the 17.8 eV band. Two possible explanations for the lack of a peak (Cs $5p_{1/2}$) in the 19.0 eV region in the $Cs^+BO_2^-$ vapor spectrum are presented: (1) the Cs $5p_{1/2}$ ionization band may not be of sufficient intensity to appear above the background, and (2) the ionization energy of the Cs $5p_{1/2}$ level occurs in that region of the spectrum which approaches the sensitivity limit of the spectrometer.

It must be stressed that this MO ordering has been based partly on calculations on ground state entities and therefore relaxation has not been taken into account. Relaxation for delocalized or bonding MO's can be estimated from the relaxations of the parent

TABLE XIII
CESIUM 5p EXPERIMENTAL IONIZATION ENERGY VALUES (-eV)

Compound	Cs 5p	
$\text{Cs}^+\text{NO}_3^{-\text{a}}$	17.7	19.0
$\text{Cs}^+\text{ReO}_4^{-\text{b}}$	17.9	19.3
$\text{Cs}^+\text{Cl}^{-\text{c}}$	17.5	19.3
$\text{Cs}^+\text{Br}^{-\text{c}}$	17.5	19.4
$\text{Cs}^+\text{I}^{-\text{c}}$	17.6	19.3
$\text{Cs}^+\text{PO}_3^{-\text{d}}$	17.9	

^aRef. 89

^bRef. 43

^cRef. 48

^dRef. 88

AO contributions but relaxation for localized MO's are harder to estimate due to electron flow considerations.¹¹⁹ The relaxation of the oxygen 2s and 2p orbitals in atomic oxygen is estimated to be 3.6 eV and 3.2 eV while the relaxation of the boron 2s and 2p orbitals in atomic boron is 1.6 eV and 0.7 eV.¹²⁰ Using this as an approximation, the relaxation for the four outer MO's for the BO_2^- ion would be 3.2 eV ($1\pi_g$), 2.8 eV ($1\pi_u$), 3.2 eV ($3\sigma_u$), and 3.2 eV ($4\sigma_g$). The four outer MO energy values for the BO_2^- ion (Table X, p 42) which have been corrected for relaxation are 9.4 eV ($1\pi_g$), 10.4 eV ($1\pi_u$), 10.8 eV ($3\sigma_u$), and 11.8 eV ($4\sigma_g$). This exercise is only an attempt to modify the theoretical ionization energy values to allow for relaxation. However, the above data would seem to indicate that the four outer MO energy levels would not be reordered.

The MO energy splits which were predicted from UTARC theoretical calculations between C_s M^+BO_2^- molecules and the $\text{D}_{\infty h}$ BO_2^- ion are usually no more than a few tenths of an eV (Table XII, p 45). The instrumental resolution at high temperatures is no better than 0.15 eV, resulting from sample deposition on the cooler walls of the sample interaction chamber and slits. Any possibility of discerning between the MO energy values of the C_s orientation of the vapor M^+BO_2^- and the MO energy values of the $\text{D}_{\infty h}$ BO_2^- ion is very small due to the small splits produced by the metal ion perturbation, to the observed band breadths, and to the observed instrumental resolution. The average experimental ionization energy values would fit either orientation. Therefore, the question of the "polytopicity" of the vapor state M^+BO_2^- molecules cannot be answered by this study.

CHAPTER III

ALKALI METAL AND AMMONIUM TETRACHLOROALUMINATES

A. Previous Studies

1. Introduction

Several experimental approaches have been used to investigate gaseous, liquid, or solid species which contain tetrachloroaluminate as a complex anion with a monovalent cation (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , and NH_4^+). Those which are relevant to this research are melting point and boiling point determinations, X-ray crystallographic experiments on the solid state, Raman spectroscopic studies of the liquid and solid states, vapor pressure experiments, and electron diffraction and mass spectrometric measurements of the vapor species.

2. Melting and Boiling Point

The melting points of equimolar mixtures of M^+Cl^- ($\text{M} = \text{Li}$ or Na) and AlCl_3 have been measured to be 416°K (Li^+) and 304°K (Na^+) by Kendall, Crittenden, and Miller.¹²¹ Korshunov and Lapkina¹²² determined the melting point of an equimolar mixture of Na^+Cl^- and AlCl_3 to be 433°K . The melting point of an equimolar mixture of K^+Cl^- and AlCl_3 has been ascertained to be 529°K by Fischer and Simon.¹²³ Morozov and Simonich¹²⁴ measured the melting point of an equimolar mixture of Cs^+Cl^- and AlCl_3 to be 650°K . Kendall, Crittenden and Miller¹²⁵ have measured the melting point of an equimolar mixture of NH_4^+Cl^- and AlCl_3 to be 304°K and the boiling point was calculated to be $402 \pm 5^\circ \text{K}$ by Morozov and Toptygin.¹²⁶ No melting point for an equimolar mixture of Rb^+Cl^- and AlCl_3 has been reported.

3. X-Ray Crystallography and Raman Spectroscopy

Several investigators^{127,128,129,130} have reported using X-ray crystallography to study the structure of polycrystalline or single crystal samples of salts which result from melting equimolar amounts of M^+Cl^- ($M = Li, Na, K, \text{ and } NH_4$) and $AlCl_3$ together. They reported that the aluminum atom was surrounded by four chlorines in a tetrahedral (T_d) configuration. However, the $AlCl_4^-$ ion was more distorted as the size of the alkali metal cation decreased. Also, studies^{130,131,132} of $M^+AlCl_4^-$ using Raman spectroscopy have shown four bands which are characteristic of the $AlCl_4^-$ (T_d) ion. Further, one investigation¹³³ with molten $Cs^+AlCl_4^-$ using Raman spectroscopy has indicated bands from $AlCl_4^-$ (T_d) in the same regions of the spectrum as with the solid state $Cs^+AlCl_4^-$. The wave numbers of the Raman bands are summarized in Table XIV (p 51).

4. Vapor Pressure Studies

Morozov and Morozov^{134,135} have employed tensimetric analysis to study the vapor pressures of various species over $M^+AlCl_4^-$ ($M = Li, Na, K, Rb, \text{ and } Cs$) in the temperature ranges 773 - 913° K (Li^+); 873 - 1073° K (Na^+), 903 - 1113° K (K^+), 973 - 1153° K (Rb^+), and 1013 - 1173° K (Cs^+). They reported that the partial pressure of $AlCl_3$ was greater than the partial pressure of $Li^+AlCl_4^-$ and $Na^+AlCl_4^-$ at all temperatures, the partial pressure of $K^+AlCl_4^-$ was somewhat higher than that for $AlCl_3$ at all temperatures, the partial pressures of $Rb^+AlCl_4^-$ and $Cs^+AlCl_4^-$ are much greater than the partial pressure of $AlCl_3$ at all temperatures. Vapor pressure studies above solid $Na^+AlCl_4^-$ by Galitskii¹³⁶ and Dewing¹³⁷ agree with the studies of

TABLE XIV
RAMAN SPECTROSCOPIC WAVE NUMBERS OF
TETRACHLOROALUMINATE SALTS (cm^{-1})

$\text{M}^+\text{AlCl}_4^-$	$\nu_1(\text{a}_1)$	$\nu_2(\text{e})$	$\nu_3(\text{t}_2)$	$\nu_4(\text{t}_2)$
K^+ (solid) ^a	354	133	505	181
Rb^+ (solid) ^b	356	127	{486} ^e 505	{180} ^e 185
Cs^+ (solid) ^b	344	128	{485} ^e 503	{180} ^e 187
Cs^+ (molten) ^c	353	120	483	178
NH_4^+ (solid) ^d	356	126	503	184

^aRef. 130

^bRef. 131

^cRef. 132

^dRef. 133

^e ν_3 and ν_4 bands are split due to solid state effects in the slightly distorted AlCl_4^- tetrahedron.

Morozov and Morozov¹³⁴ that the partial pressure of AlCl_3 is larger than the partial pressure of $\text{Na}^+\text{AlCl}_4^-$. Molecular beam studies using $\text{Na}^+\text{AlCl}_4^-$ or $\text{K}^+\text{AlCl}_4^-$ to determine the nuclear magnetic moment of Al-27 have been reported by Millman and Kusch.¹³⁸ Morozov and Toptygin¹²⁶ and Baud¹³⁹ have conducted studies of the vapor pressure of species above solid $\text{NH}_4^+\text{AlCl}_4^-$ by the tensimetric method using a known volume of N_2 passed through the vessel and concluded that $\text{NH}_4^+\text{AlCl}_4^-$ distills without decomposition between 525 - 626° K¹²⁶ and 500 - 625° K.¹³⁹

5. Electron Diffraction and Mass Spectrometry

The structure of the vapor species $\text{K}^+\text{AlCl}_4^-$ has been investigated by Spiridonov, Erokhin and Lutoshkin.¹⁴⁰ They claim that $\text{K}^+\text{AlCl}_4^-$ vaporizes without decomposition, a conclusion in conflict with the vapor pressure studies of Morozov and Morozov.¹³⁵ Their structural conclusion is that the Al is tetrahedrally coordinated by four Cl atoms with the K^+ located above one of the Cl-Cl edges of the tetrahedron in line with the Al atom. The bond angles ($\angle$) and distances (r) for the $\text{K}^+\text{AlCl}_4^-$ vapor species are: $r(\text{Al-Cl}) = 2.16 \pm 0.02 \text{ \AA}$, $r(\text{K-Cl}) = 2.84 \pm 0.02 \text{ \AA}$, $\angle \text{Cl-K-Cl} = 77^\circ$, and $\angle \text{Cl-Al-Cl} = 109.5 \pm 5^\circ$. The Cl-K-Cl angle was reported without any range. They also stated that the mean square amplitude of the vibrations of the K-Cl bonds at high temperatures was $0.13 \text{ \AA}$. More recently, Spiridonov, Ischenko and Zasorin¹⁴¹ stated that it is possible to match the observed electron diffraction pattern for $\text{K}^+\text{AlCl}_4^-$ with a theoretical expression which uses a dynamic stereochemically nonrigid-molecular model (the same model used for some oxyacid salts). They concluded that

the high temperature bonding in potassium tetrachloroaluminate ($K^+AlCl_4^-$) may be "polytopic" in nature. Spiridonov, Erokhin, and Lutoshin¹⁴⁰ refer to a mass spectral study of vapors above $K^+AlCl_4^-$ (done by Erokhin) which indicated that both dimer $K^+Al_2Cl_8^-K^+$ and monomer $K^+AlCl_4^-$ are present with the latter predominating.

B. Experimental Procedure

1. Compounds

Anhydrous chloride compounds (Li^+Cl^- , Na^+Cl^- , K^+Cl^- , Rb^+Cl^- , Cs^+Cl^- , and $AlCl_3$) with a purity of 99.99% were obtained from the Alfa Division of Ventron Corporation. Anhydrous reagent grade ammonium chloride ($NH_4^+Cl^-$) was purchased from the J. T. Baker Chemical Company. Platinum foil (2.5 cm x 2.5 cm) was procured from the Fisher Scientific Company.

2. Procedures and Equipment

Since the $M^+AlCl_4^-$ ($M = Li, Na, K, Rb, Cs$ and NH_4) compounds are very hygroscopic, the samples had to be handled in a dry box. The tetrachloroaluminate salts were prepared by the following procedure. (1) Anhydrous chloride compound M^+Cl^- ($M = Li, Na, K, Rb, Cs$ or NH_4) and $AlCl_3$ were placed in the dry box antechamber which was evacuated for 45 minutes, then (2) the M^+Cl^- and $AlCl_3$ were weighed on a Christian Becker Torbal balance and placed in a clean, dry quartz test tube. The next step (3) was to place a 3" to 4" length of tygon tubing over the end of the test tube and to close off the end of the tygon tubing with a C-type hose clamp. (4) The test tube was removed from the dry box and attached to a vacuum system. (5) After evacuating the tygon tubing for ten minutes, the clamp was opened, and

the dry nitrogen was pumped out. (6) The quartz test tube was closed off with an oxygen-gas torch, was placed in a furnace, and was heated at 800° C for 12 hours. Next, (7) the sealed ampoule containing the melt was removed, allowed to cool for 45 minutes, and placed inside the dry box. Then (8), the sealed ampoule was broken and the melt was removed from the test tube. This was followed by step (9) which was pulverizing the melt with a mortar and pestle and placing the powder in a clean, dry weighing bottle.

The vapor oven used in these studies was a platinum lined resistance-heated tantalum-strip-wound quartz cell. The platinum liner was employed to distribute the heat evenly in the cell. Also, the oven was coated externally with a ceramic type cement (Astroceram). Spectral measurements were made with the equipment and by the procedures which were outlined in Chapter IIB (pp 24-30).

C. Experimental Results

Representative spectra of the vapors above the solids $K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, and $NH_4^+AlCl_4^-$ are presented in Figures 7 - 10 (pp 55 - 58). Each is typical of 12 or more spectra obtained for each compound. The peak which is labeled Ar in each spectrum is due to argon which was employed as a calibrant. A spectrum of the vapors above solid $NH_4^+AlCl_4^-$ without the Ar calibration line is shown in Figure 11 (p 59). The spectra obtained for $Li^+AlCl_4^-$ and $Na^+AlCl_4^-$ included peaks which are characteristic of the $AlCl_3$ monomer and/or the M^+Cl^- ($M = Na$ or Li) monomer. This is reasonable on the basis of vapor studies which have shown that $AlCl_3$ is the predominant vapor species at high temperatures.^{134,136,137} A nontypical spectrum of

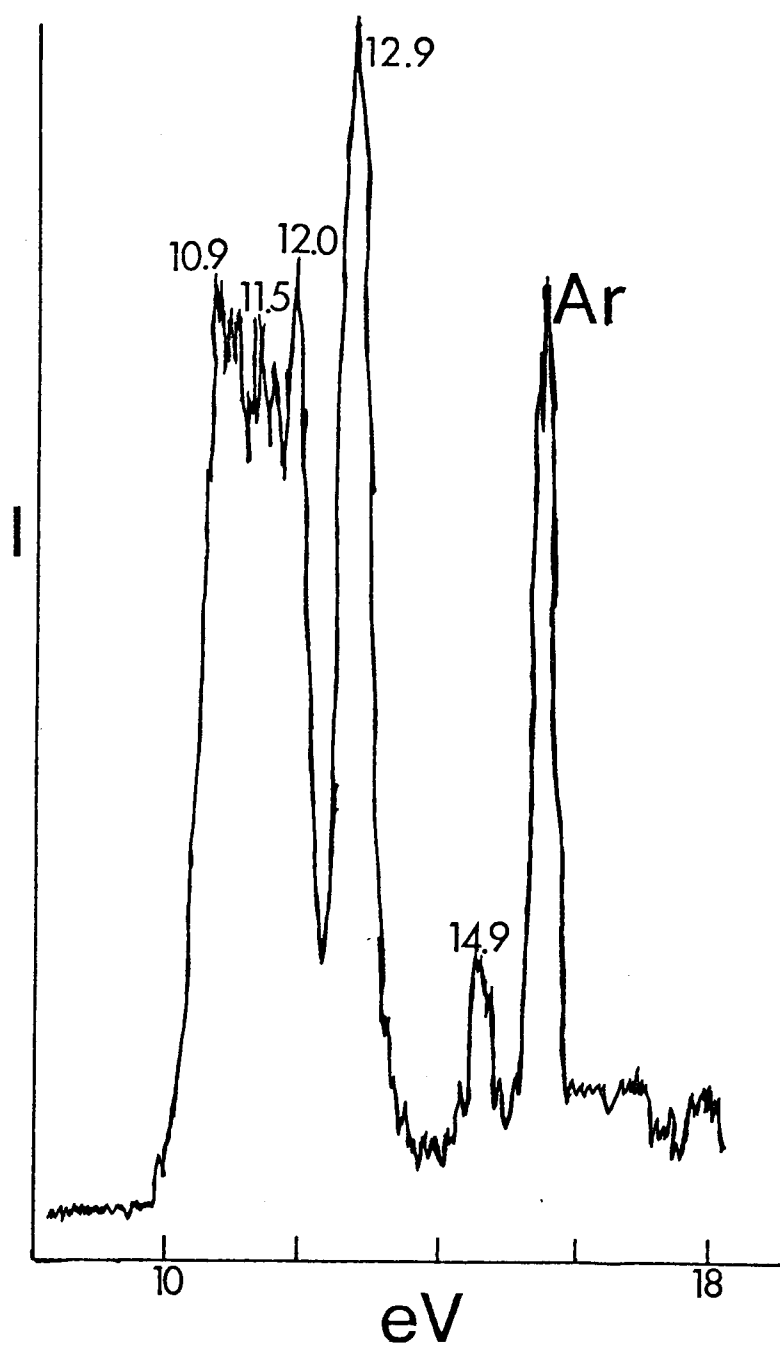


Figure 7. HeI photoelectron spectrum of $\text{K}^+\text{AlCl}_4^-$ vapor.

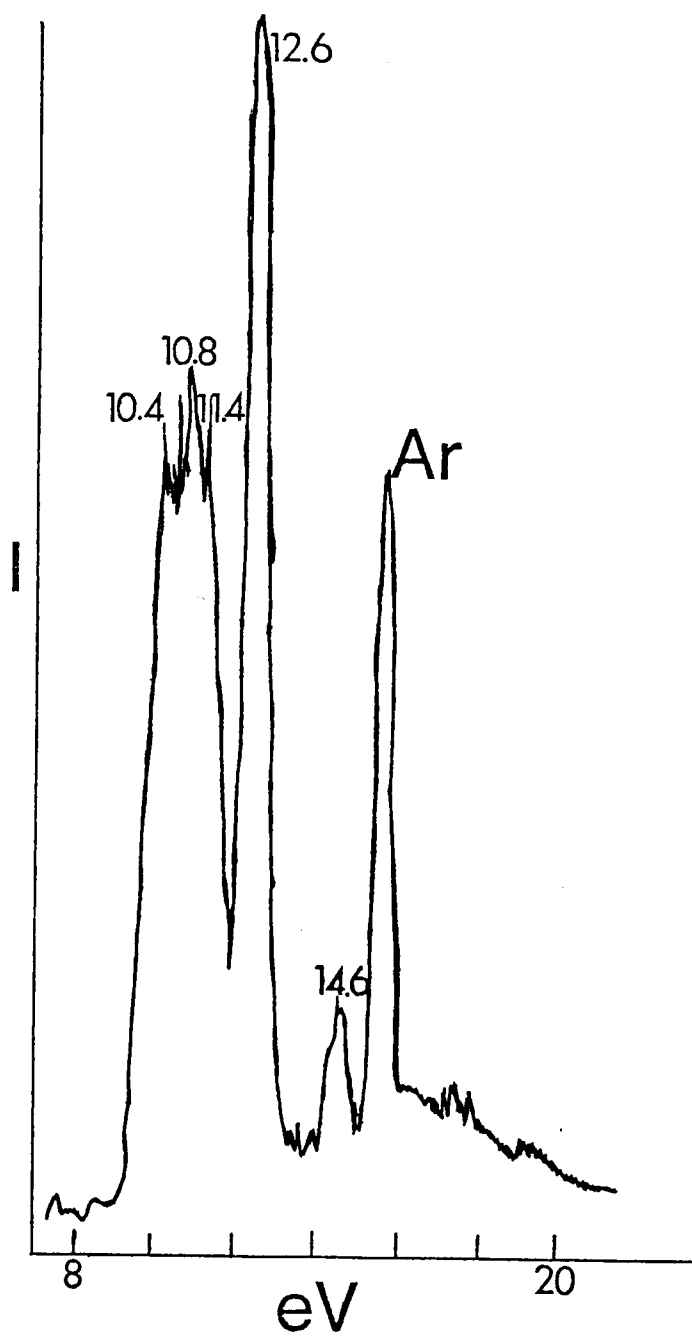


Figure 8. HeI photoelectron spectrum of $\text{Rb}^+\text{AlCl}_4^-$ vapor.

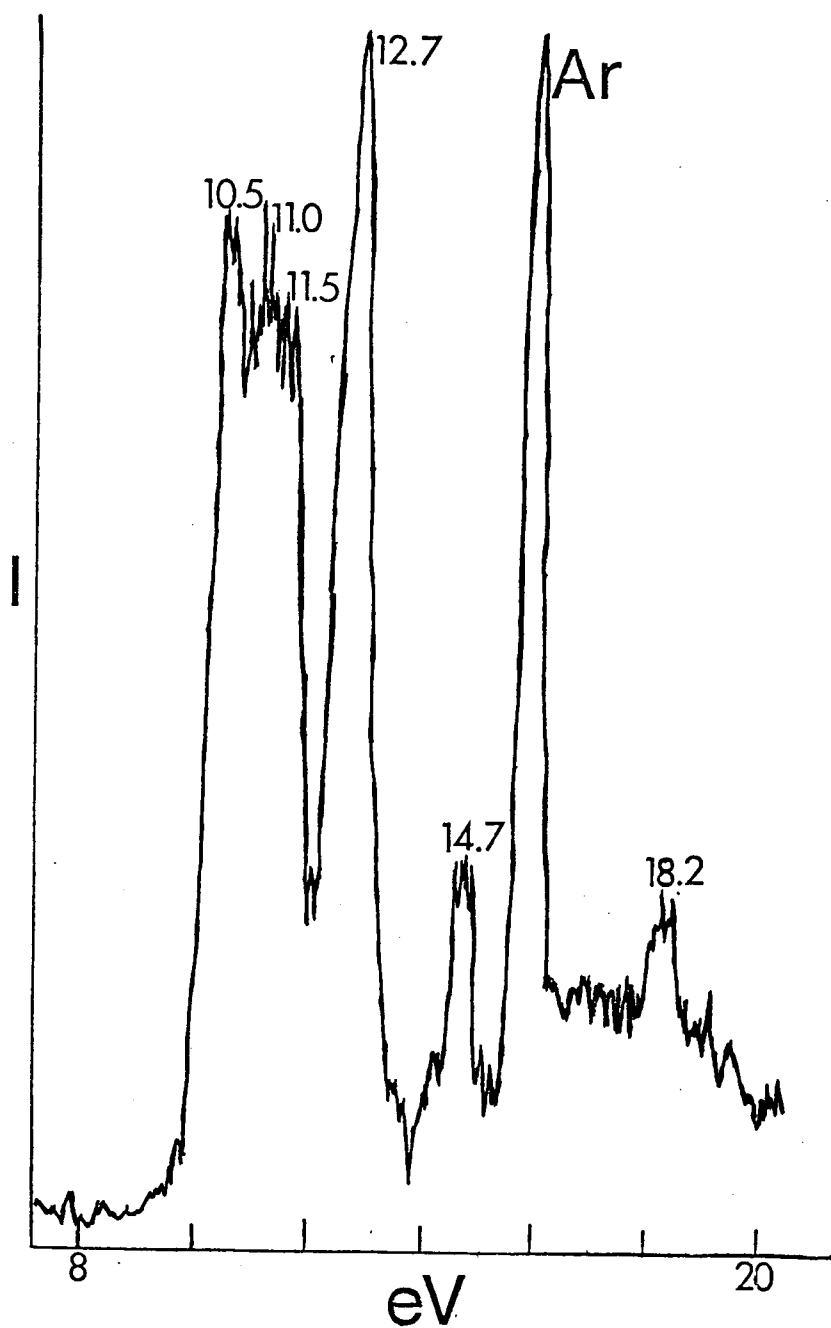


Figure 9. HeI photoelectron spectrum of $\text{Cs}^+\text{AlCl}_4^-$ vapor.

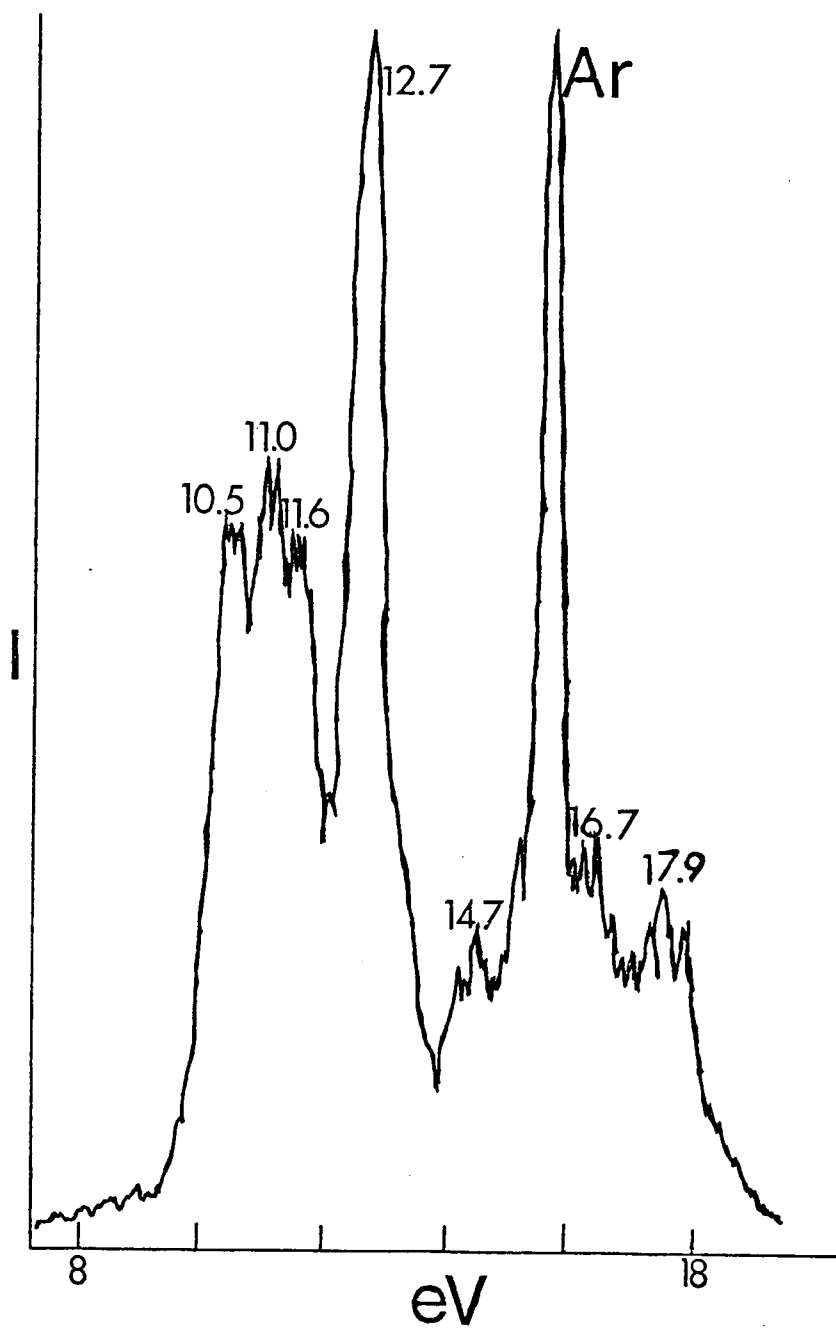


Figure 10. HeI photoelectron spectrum of $\text{NH}_4^+\text{AlCl}_4^-$ vapor.

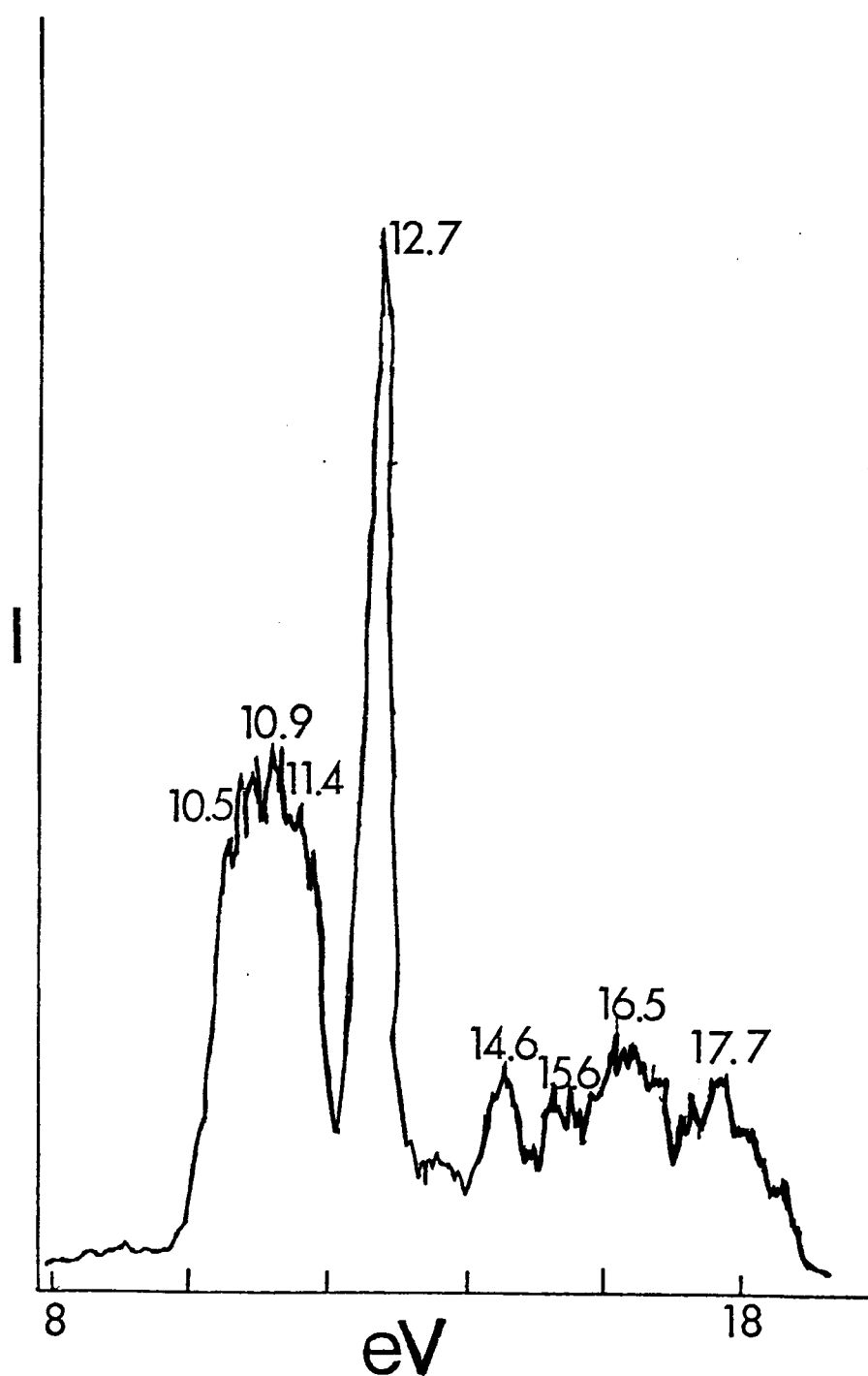


Figure 11. HeI photoelectron spectrum of $\text{NH}_4^+\text{AlCl}_4^-$ without Ar calibration.

$\text{Cs}^+\text{AlCl}_4^-$ vapor which the author chose to reject is presented as Figure 12 (p 61).

The values assigned to the band peaks are listed in Table XV ($\text{K}^+\text{AlCl}_4^-$) (p 62), Table XVI ($\text{Rb}^+\text{AlCl}_4^-$) (p 63), Table XVII ($\text{Cs}^+\text{AlCl}_4^-$) (p 64), and Table XVIII ($\text{NH}_4^+\text{AlCl}_4^-$) (p 65). The unweighted average ionization energy value ($\bar{x}$), the standard deviation of each individual ionization energy value (σ_i), the 95% confidence limit of the individual ionization energy value ($95\% \sigma_i$), the standard deviation of the unweighted average ionization energy value (σ_{av}), and the 95% confidence limit of the unweighted average ionization energy value ($95\% \sigma_{av}$) for each band peak in each vapor are given in Tables XV - XVIII (pp 62 - 65). The starred runs in Tables XV, XVI, XVII, and XVIII (pp 62, 63, 64, and 65) indicate the spectra which were chosen for presentation in Figures 7, 8, 9, and 10 (pp 55, 56, 57, and 58) respectively. The spectra which were selected displayed band peak values similar to the unweighted averaged ionization energy values. A summary of the unweighted average ionization energy values (followed by the $95\% \sigma_{av}$) assigned to the peaks for each mixture is listed in Table XIX (p 66).

D. Theoretical Expectations

For the present compounds, no ab initio calculations have been reported. Therefore, the UTARC program (an extended Hückel method) is the only source of theoretical calculations which have so far been used to study the photoelectron spectroscopy of tetrachloroaluminates. The UTARC program uses some grossly over-simple semi-empirical approximations. In most of the many molecules which have been run with this program, these approximations do not involve error in the qualitative

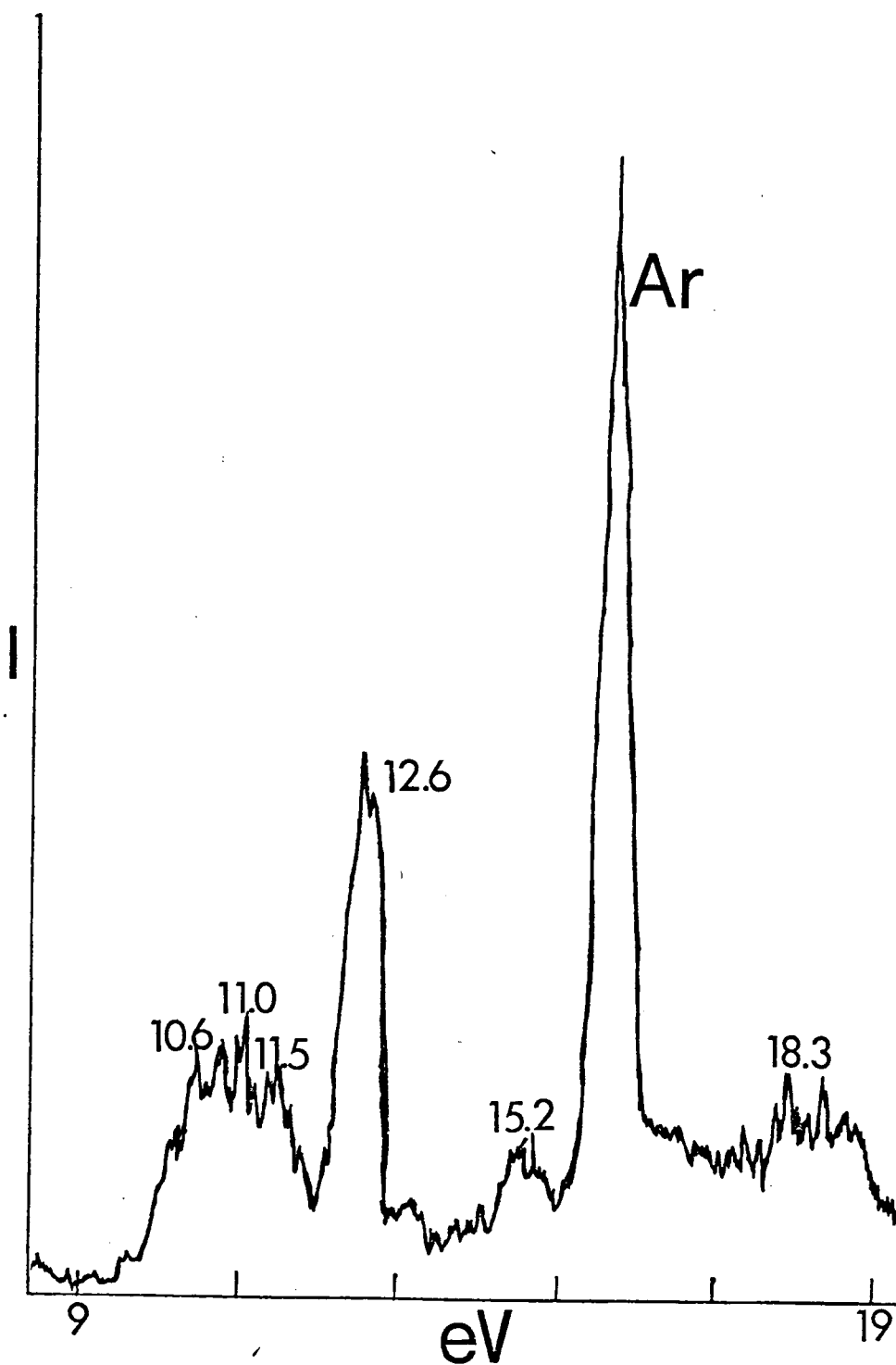


Figure 12. Nontypical HeI photoelectron spectrum of $\text{Cs}^+\text{AlCl}_4^-$ vapor.

TABLE XV
BAND PEAK VALUES FOR $K^+AlCl_4^-$ VAPOR SPECTRA

Item	1st	2nd	Peak (-eV) 3rd	4th	5th
Run 1	11.12	11.51	12.01	12.90	14.87
Run 2	11.02	11.53	11.96	12.85	14.98
Run 3	11.08	11.55	12.05	12.94	14.87
Run 4	10.95	11.42	11.99	12.85	14.83
Run 5	10.99	11.49	11.89	12.82	14.90
Run 6	10.78	11.46	11.88	12.88	14.91
Run 7	11.07	11.61	12.09	13.00	14.85
Run 8	10.99	11.54	11.88	13.01	14.91
Run 9	10.95	11.53	12.09	12.94	14.88
Run 10	10.95	11.48	12.02	12.90	14.86
Run 11*	10.91	11.46	11.96	12.87	14.86
Run 12	10.98	11.38	11.97	12.90	14.87
Run 13	10.89	11.51	11.91	13.01	14.83
Run 14	10.95	11.46	11.86	12.96	14.81
Run 15	10.82	11.49	11.95	12.89	14.97
$\bar{x} =$	10.96	11.49	11.97	12.91	14.87
$\sigma_i =$	.09	.06	.07	.06	.06
95% $\sigma_i =$	.18	.12	.15	.13	.11
$\sigma_{av} =$	.02	.02	.02	.02	.02
95% $\sigma_{av} =$	.05	.03	.04	.04	.03

TABLE XVI
BAND PEAK VALUES FOR $\text{Rb}^+\text{AlCl}_4^-$ VAPOR SPECTRA

Item	1st	2nd	Peak (-eV) 3rd	4th	5th
Run 1	10.49	10.93	11.42	12.84	14.91
Run 2	10.23	10.75	11.28	12.78	14.54
Run 3	10.42	10.91	11.40	12.76	14.47
Run 4	10.51	10.89	11.29	12.57	14.58
Run 5	10.38	10.94	11.33	12.65	14.56
Run 6	10.43	10.94	11.73	12.92	14.92
Run 7*	10.43	10.84	11.43	12.61	14.58
Run 8	10.48	10.92	11.29	12.64	14.57
Run 9	10.37	10.97	11.40	12.61	14.55
Run 10	10.30	10.84	11.49	12.62	14.69
Run 11	10.37	10.74	11.31	12.67	14.62
Run 12	10.42	10.85	11.54	12.43	14.79
Run 13	10.47	10.96	11.40	12.50	14.41
Run 14	10.29	10.66	11.34	12.63	14.72
Run 15	10.23	10.65	11.33	12.62	14.75
Run 16	10.35	10.66	11.52	12.63	14.66
Run 17	10.37	10.97	11.40	12.61	14.55
Run 18	10.23	10.84	11.27	12.50	14.77
$\bar{x} =$	10.39	10.86	11.41	12.65	14.65
$\sigma_i =$	.11	.12	.13	.12	.14
95% $\sigma_i =$	.21	.23	.26	.23	.27
$\sigma_{av} =$	.03	.03	.03	.03	.03
95% $\sigma_{av} =$	.05	.06	.07	.06	.07

TABLE XVII
BAND PEAK VALUES FOR $\text{Cs}^+\text{AlCl}_4^-$ VAPOR SPECTRA

Item	1st	2nd	Peak (-eV)		5th	6th
			3rd	4th		
Run 1	10.35	10.90	11.42	12.58	14.56	17.95
Run 2	10.25	11.02	11.40	12.46	14.74	18.26
Run 3	10.53	11.11	11.86	12.61	14.85	18.26
Run 4	10.65	11.25	11.76	12.87	14.65	18.19
Run 5	10.48	11.12	11.76	12.65	14.65	18.27
Run 6	10.48	10.95	11.65	12.74	14.65	17.97
Run 7	10.53	11.08	11.42	12.78	14.65	18.23
Run 8	10.40	10.91	11.38	12.70	14.57	18.23
Run 9	10.48	11.08	11.50	12.61	14.70	18.14
Run 10	10.57	11.08	11.46	12.70	14.91	18.24
Run 11	10.40	10.91	11.50	12.65	14.65	18.23
Run 12	10.55	11.03	11.50	12.62	14.75	18.26
Run 13	10.69	11.22	11.71	12.85	14.78	18.33
Run 14	10.57	11.12	11.50	12.62	14.65	18.19
Run 15*	10.53	10.99	11.49	12.68	14.67	18.24
Run 16	10.50	10.97	11.38	12.76	14.88	18.22
Run 17	10.49	10.89	11.46	12.64	14.66	18.29
Run 18	10.53	10.96	11.49	12.73	14.54	18.26
Run 19	10.43	10.79	11.29	12.76	14.66	18.26
Run 20	10.59	11.02	11.56	12.69	14.73	18.03
$\bar{x} =$	10.50	11.02	11.52	12.68	14.69	18.21
$\sigma_i =$	.10	.12	.15	.10	.10	.11
95% $\sigma_i =$	.20	.23	.30	.19	.20	.21
$\sigma_{av} =$	.02	.03	.03	.02	.02	.02
95% $\sigma_{av} =$	.05	.06	.07	.05	.05	.05

TABLE XVIII
BAND PEAK VALUES FOR $\text{NH}_4^+\text{AlCl}_4^-$ VAPOR SPECTRA

Item	1st	2nd	3rd	Peak (-eV)	5th	6th	7th
				4th			
Run 1	10.64	11.16	11.60	12.76	14.58	16.70	18.04
Run 2	10.70	11.06	11.47	12.67	14.64	16.60	18.46
Run 3	10.46	11.06	11.46	12.46	14.54	16.89	17.89
Run 4	10.63	11.16	11.63	12.80	14.67	16.85	18.15
Run 5	10.59	11.20	11.63	12.76	14.72	16.79	18.15
Run 6	10.64	11.04	11.48	12.84	14.56	16.64	17.88
Run 7*	10.46	11.05	11.59	12.68	14.67	16.64	17.87
Run 8	10.46	10.94	11.38	12.56	14.62	16.73	18.05
Run 9	10.44	10.88	11.60	12.65	14.60	16.60	17.71
Run 10	10.49	10.94	11.47	12.70	14.70	16.70	18.00
Run 11	10.70	11.17	11.88	12.89	14.97	16.72	17.80
Run 12	10.54	11.12	11.74	12.88	14.98	16.77	17.74
$\bar{x} =$	10.56	11.07	11.58	12.73	14.68	16.71	17.99
$\sigma_i =$	.10	.11	.14	.13	.15	.10	.21
95% $\sigma_i =$	.19	.21	.27	.25	.29	.21	.41
$\sigma_{av} =$	.03	.03	.04	.04	.04	.03	.06
95% $\sigma_{av} =$	.06	.06	.08	.08	.09	.06	.12

TABLE XIX

AVERAGE TETRACHLOROALUMINATE EXPERIMENTAL IONIZATION ENERGIES (-eV)

	$K^+AlCl_4^-$	$Rb^+AlCl_4^-$	$Cs^+AlCl_4^-$	$NH_4^+AlCl_4^-$
Band 1	10.96±.05	10.39±.05	10.50±.05	10.56±.06
Band 2	11.49±.03	10.86±.06	11.02±.06	11.07±.06
Band 3	11.97±.04	11.41±.07	11.52±.07	11.58±.08
Band 4	12.91±.04	12.65±.06	12.68±.05	12.73±.08
Band 5	14.87±.03	14.65±.07	14.69±.05	14.68±.09
Band 6			18.21±.05	16.71±.06
Band 7				17.99±.12

ordering of the MO's but the quantitative values were often somewhat in error, that is, they deviated 1 to 2 eV from ab initio calculations.¹⁴² An ordinarily accepted procedure is to add a Q factor to ab initio data (if available) and to UTARC data on molecules to bring the calculations into line with experimental values. Often UTARC MO values with adjustments both for the outer MO envelope breadth and for the overall energy scale are no more in error than adjusted ab initio MO values. The author thinks that the above tendencies might also adhere to calculations made on $K^+AlCl_4^-$ and $AlCl_4^-$ by UTARC. However, it should be realized that the theoretical MO values and the conclusions which might be drawn from these calculations may be beset with some unknown uncertainties. Nonetheless, because of previous qualitative successes with UTARC, the calculations were done and the results were compared to the experimental photoelectron spectra in the hope that some trends or tendencies might be seen and that their origins might be rationalized, at least qualitatively.

The structural models which were used for the $K^+AlCl_4^-$ calculations were derived by the use of electron diffraction data.¹⁴⁰ The electron diffraction investigators indicated that the experimental radial distribution curve was best fit by a theoretical model in which the bond angles ($\angle$) and distances (r) were $r(Al-Cl) = 2.16 \pm .02 \text{ \AA}$, $r(K-Cl) = 3.47 \pm .02 \text{ \AA}$, $\angle Cl-Al-Cl = 109.5 \pm 5^\circ$, and $\angle Cl-K-Cl = 77^\circ$. However, since the fit was not exact and since some deviation was allowed for the $Cl-Al-Cl$ angles, they did not completely rule out a structure in which the angle between the two chlorine atoms which were closer to the K^+ ion was up to 5° less and/or the angle between

the two chlorine atoms which were farther from the K^+ ion was up to 5° greater than the tetrahedral angle. In light of these two observations, two models were chosen for the calculations. Both have the same bond distances as indicated by the electron diffraction data while one has all $\angle Cl-Al-Cl = 109.5^\circ$ and the second has the bond angles $\angle Cl_2-Al-Cl_3 = 99.5^\circ$ and $\angle Cl_4-Al-Cl_5 = 109.5^\circ$ (although 114.5° could also have been used for this latter value). The first $K^+AlCl_4^-$ model was designated as $K^+AlCl_4^- (T_d)$ and the second as $K^+AlCl_4^- (C_{2v})$.

In addition to the two $K^+AlCl_4^-$ models, computations were made on the free $AlCl_4^-$ anion. It was hoped that this might permit changes in % AO constituencies in the MO's and MO values in the free $AlCl_4^-$ anion as a result of adding a K^+ cation to be more easily observed. The structural models which were chosen for the free $AlCl_4^-$ anion were identical to those chosen for the $AlCl_4^-$ anion in $K^+AlCl_4^- (T_d)$ and $K^+AlCl_4^- (C_{2v})$. The two models for the free $AlCl_4^-$ anions were labeled $AlCl_4^- (T_d)$ and $AlCl_4^- (C_{2v})$. The results of the computations on the four entities [$K^+AlCl_4^- (T_d)$, $K^+AlCl_4^- (C_{2v})$, $AlCl_4^- (T_d)$, and $AlCl_4^- (C_{2v})$] are presented in Table XX (p 69). The first four rows represent the theoretical ionization energy values of the MO's from the UTARC program. Rows five through seven show values of the first three rows adjusted to the values of row four since this represents the configuration which gave the best overall fit to the electron diffraction data. A summary of the shift of the MO values and the splits of the MO values in relation to those from $AlCl_4^- (T_d)$ is shown in Table XXI (p 70). The effect of the K^+ cation on the MO's of the $AlCl_4^-$ anion is largest in the MO's which may be related to the $3t_2$ MO of the $AlCl_4^- (T_d)$ model.

TABLE XX

 AlCl_4^- AND $\text{K}^+\text{AlCl}_4^-$ MO'S AND ENERGIES (-eV)

Row	MO's and Energies									
	$1t_1$	$3t_2$	$1e$	$2t_2$	$2a_1$					
1 $\text{AlCl}_4^- (\text{T}_d)$	9.0	9.4	9.7	10.3	11.9					
2 $\text{AlCl}_4^- (\text{C}_{2v})$	$4b_1$ 8.7 $2a_2$ 9.0 $4b_2$ 9.1	$6a_1$ 9.3 $3b_1$ 9.4 $5a_1$ 9.4	$3b_2$ 9.6 $1a_2$ 9.8	$2b_1$ 10.2 $2b_2$ 10.4 $4a_1$ 10.4	$3a_1$ 11.9					
3 $\text{K}^+\text{AlCl}_4^- (\text{C}_{2v})$	11.3 11.5 11.7	11.9 12.1 12.6	12.9 13.1	13.8 14.1	14.2	15.7				
4 $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$	11.2 11.4 11.6	11.8 11.9 12.7	12.8 13.0	13.6 13.9	13.9	15.5				
5 Line 1 adjusted to 4^a	11.2 11.2 11.2	11.8 11.8 11.8	12.2 12.2 12.2	13.1 13.1 13.1	13.1	15.5				
6 Line 2 adjusted to 4^b	11.2 11.2 11.2	12.0 12.1 12.7	12.4 12.7	13.2 13.5	13.5	15.5				
7 Line 3 adjusted to 4^c	11.2 11.2 11.2	11.8 12.0 12.5	12.8 13.0	13.6 13.9	14.0	15.5				

$$^a Q = 1.5x - 2.1$$

$$^b Q = 1.3x - 0.5$$

$$^c Q = 0.98x + 0.2$$

TABLE XXI

 $K^+AlCl_4^-$ AND $AlCl_4^-$ SHIFT AND SPLIT CALCULATIONS (-eV)

	$AlCl_4^- (T_d)$	$AlCl_4^- (C_{2v})$	$K^+AlCl_4^- (T_d)$	$K^+AlCl_4^- (C_{2v})$
$1t_1$	11.2	11.2-11.7	11.2-11.6	11.2-11.6
$3t_2$	11.8	12.0-12.1	11.8-12.7	11.8-12.5
$1e$	12.2	12.4-12.7	12.8-13.0	12.8-13.0
$2t_2$	13.1	13.2-13.5	13.6-13.9	13.6-14.0
$2a_1$	15.5	15.5	15.5	15.5

All the MO levels which are accessible by HeI radiation are predominately Cl 3p in character regardless of the model chosen [$\text{AlCl}_4^- (\text{T}_d)$, $\text{AlCl}_4^- (\text{C}_{2v})$, $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$ or $\text{K}^+\text{AlCl}_4^- (\text{C}_{2v})$]. The Cl 3p % AO constituencies of each Al atom in $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$, $\text{K}^+\text{AlCl}_4^- (\text{C}_{2v})$, and $\text{AlCl}_4^- (\text{C}_{2v})$ are compared to those of the MO levels in $\text{AlCl}_4^- (\text{T}_d)$ in Table XXII (p 72). The data show the Cl 3p orbitals of all the chlorine atoms to be sharing equally in the MO's of the $\text{AlCl}_4^- (\text{T}_d)$ anion. However, distortion of the AlCl_4^- tetrahedron into a C_{2v} structure [$\text{AlCl}_4^- (\text{C}_{2v})$] strongly affects the % AO constituencies in the MO levels. In the outermost MO's of the $\text{AlCl}_4^- (\text{C}_{2v})$ model which may be related to the $1t_1$ MO of $\text{AlCl}_4^- (\text{T}_d)$, the Cl 3p % AO constituency has shifted markedly (34 to 16) toward Cl 2 and Cl 3 while those which may be associated with the $3t_2$, $1e$, $2t_2$, and $2a_1$ are shifted (24 to 26, 18 to 32, 22 to 28, and 18 to 24) toward the Cl 4 and Cl 5 3p AO's. The data from Table XXII (p 72) indicate that these effects are markedly altered when a K^+ cation is placed between Cl 2 and Cl 3 in the $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$ or the $\text{K}^+\text{AlCl}_4^- (\text{C}_{2v})$ structure. In the two outermost MO's of $\text{K}^+\text{AlCl}_4^-$ which may be related to the $1t_1$ and $3t_2$ MO's of $\text{AlCl}_4^- (\text{T}_d)$, the Cl 3p % AO constituency is strongly shifted (14 to 46 and 11 to 34) to Cl 4 and Cl 5. The MO's in $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$ which may be associated to those from the $1e_1$, $2t_2$, and $2a_1$ MO's of $\text{AlCl}_4^- (\text{T}_d)$ have Cl 3p % AO constituencies which are shifted (48 to 2, 44 to 6, and 33 to 8) significantly toward Cl 2 and Cl 3. When the angle between Cl 2 and Cl 3 is decreased by 10° in $\text{K}^+\text{AlCl}_4^- (\text{C}_{2v})$, the same effect as in $\text{K}^+\text{AlCl}_4^- (\text{T}_d)$ is seen although the magnitude of the change is larger. The Cl 3p % AO

TABLE XXII
Cl 3p % AO'S IN MO'S

	AlCl ₄ ⁻ (T _d)			AlCl ₄ ⁻ (C _{2v})			K ⁺ AlCl ₄ ⁻ (T _d)			K ⁺ AlCl ₄ ⁻ (C _{2v})		
	3p ₂	3p ₃	3p ₄	3p ₅	3p ₂	3p ₃	3p ₄	3p ₅	3p ₂	3p ₃	3p ₄	3p ₅
1t ₁	25	25	25	25	34	34	16	16	4	4	46	46
3t ₂	25	25	25	25	24	24	26	26	11	11	34	34
1e	25	25	25	25	18	18	32	32	48	48	2	2
2t ₂	25	25	25	25	22	22	28	28	44	44	6	6
2a ₁	28	23	23	23	18	18	24	24	33	33	8	8
									35	35	7	7

constituencies in the two outermost MO's which may be regarded as $1t_1$ and $3t_2$ in $AlCl_4^-$ (T_d) are shifted (3 to 47 and 10 to 40) toward Cl 4 and Cl 5, but the Cl 3p % AO constituencies in the MO's which may be associated with the $1e_1$, $2t_2$, and $2a_1$ MO's of $AlCl_4^-$ (T_d) are moved (48 to 2, 45 to 5, and 35 to 7) to Cl 2 and Cl 3. The program would seem to indicate that changes in bond angles do not change the MO energy values appreciably (Table XX, p 69), although the % AO constituencies are changed considerably (Table XXII, p 72).

The general trend for there to be rather small changes in MO energy values with small or even moderate changes in geometry can be experimentally exemplified. To take one example, it has been observed in the HeI photoelectron spectrum of $HgCl_2$ ($D_{\infty h}$) that the outer MO energy envelope is π_g (11.7 eV), π_u (12.3 eV), σ_u (13.0 eV), and σ_g (14.0 eV). In the photoelectron spectrum⁷⁵ of $PbCl_2$ (C_{2v}), a very similar molecule except for an angle of 95° , the MO's which may be related to the π_g and π_u MO's from $HgCl_2$ are split by no more than 0.3 eV making the precise interpretation of the existing experimental MO order quite uncertain. The experimental splits in the MO values are small even though the bond angle in $PbCl_2$ is considerably reduced from the linear bond angle in $HgCl_2$.

E. Interpretations

Comparisons of the unweighted average ionization energy values from Table XIX (p 66) have been made with the UTARC calculations of Table XX (p 69) and the experimental ionization energy values for the isoelectronic molecule $SiCl_4$ which have been reported by Bassett and Lloyd¹⁴³ [11.0 eV (t_1), 11.5 eV (t_2), 12.0 eV (e), 12.6 eV (t_2) and

14.2 eV (a_1)). A summary of these comparisons for the four vapor species ($K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, and $NH_4^+AlCl_4^-$) is given in Table XXIII (pp 75 - 76). It is suggested from all the UTARC calculations using the models that the anion MO energy order for the four entities ($K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, and $NH_4^+AlCl_4^-$) is $1t_1$, $3t_2$, $1e$, $2t_2$, $2a_1$. In the $Cs^+AlCl_4^-$ vapor spectrum (Figure 9, p 57), the sixth band can be assigned to the ionization from the cesium $5p_{3/2}$ electrons. Ionization from the cesium $5p_{1/2}$ level is probably in the background of the region of the spectrum which is near the sensitivity limit of the spectrometer. It should have a value around 19.2 eV, as it does in numerous other ionic compound vapors (Table XIII, p 47).

In the photoelectron spectrum of the vapors over $NH_4^+AlCl_4^-$ (Figure 10, p 58), an intense band which is very broad extends from around 15 to 18 eV. This can be seen more easily in Figure 11 (p 59) which is a $NH_4^+AlCl_4^-$ spectrum without the Ar calibrant. A schematic drawing of the HeI photoelectron spectra of HCl , $^{144}H_2O$, $^{144}CH_4$, $^{144}AlCl_3$, $^{79}Al_2Cl_6$, $^{79}Rb^+AlCl_4^-$, $NH_4^+AlCl_4^-$, Rb^+Cl^- , $^{40}NH_4^+Cl^-$ (which is known to decompose to NH_3 and HCl) is presented in Figure 13 (p 77). The schematic diagram which is designated as the NH_4^+ cation is not a photoelectron spectrum but is the result of subtracting the photoelectron spectral bands of $Rb^+AlCl_4^-$ from those of the $NH_4^+AlCl_4^-$. From the experimental band positions, shapes, and intensities, $AlCl_3$, Al_2Cl_6 , NH_3 , Rb^+Cl^- , and $NH_4^+Cl^-$ may be eliminated as possible vapor species whose photoelectron bands might be contributing to the overall photoelectron spectrum of $Rb^+AlCl_4^-$ or of $NH_4^+AlCl_4^-$.

TABLE XXIII
COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES FOR THE TETRACHLOROALUMINATES

Values	1t ₁	3t ₂	1e	2t ₂	2a ₁
Exptl. K ⁺ AlCl ₄ ⁻ (from Table XIX, p 66)	11.0	11.5	12.0	12.9	14.9
Theor. K ⁺ AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^a	11.0(b ₁) 16.2(a ₂) 11.4(b ₂)	11.5(a ₁) 11.7(b ₁) 12.2(a ₁)	12.4(b ₂) 12.6(a ₂)	13.2(b ₁) 13.5(b ₂) 13.6(a ₁)	14.9(a ₁)
Theor. AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^b	11.0	11.5	11.9	12.7	14.9
Exptl. SiCl ₄ ^c	11.0	11.6	12.2	12.9	14.9
Exptl. Rb ⁺ AlCl ₄ ⁻ (from Table XIX, p 66)	10.4	10.9	11.4	12.7	14.7
Theor. K ⁺ AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^d	10.4(b ₁) 10.6(a ₂) 10.8(b ₂)	11.0(a ₁) 11.2(b ₁) 11.7(a ₁)	11.9(b ₂) 12.2(a ₂)	12.8(b ₁) 12.9(b ₂) 13.2(a ₁)	14.7(a ₁)
Theor. AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^e	10.4	11.0	11.4	12.4	14.7
Exptl. SiCl ₄ ^f	10.4	11.1	11.7	12.6	14.7
Exptl. Cs ⁺ AlCl ₄ ⁻ (from Table XIX, p 66)	10.5	11.0	11.5	12.7	18.2
Theor. K ⁺ AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^g	10.5(b ₁) 10.7(a ₂) 10.9(b ₂)	11.1(a ₁) 11.3(b ₁) 11.7(a ₁)	12.0(b ₂) 12.2(a ₂)	12.9(b ₁) 13.2(b ₂) 13.3(a ₁)	14.7(a ₁)
Theor. AlCl ₄ ⁻ (T _d) (from Table XX, p 69) ^h	10.5	11.1	11.5	12.4	14.7
Exptl. SiCl ₄ ⁱ	10.5	11.2	11.8	12.6	14.7

TABLE XXIII (CONTINUED)

Values	1t ₁	3t ₂	1e	2t ₂	2a ₁	18.0
Exptl. $\text{NH}_4^+ \text{AlCl}_4^-$ (from Table XIX, p 66)	10.6	11.1	11.6	12.7	14.7	16.7
Theor. $\text{K}^+ \text{AlCl}_4^-$ (T _d) (from Table XX, p 69) ^j	10.6(b ₁) 10.8(a ₂) 11.0(b ₂)	11.2(a ₁) 11.3(b ₁) 11.8(a ₁)	12.1(b ₂) 12.3(a ₂)	12.9(b ₁) 13.2(b ₂) 13.3(a ₁)	14.7(a ₁)	
Theor. AlCl_4^- (T _d) (from Table XX, p 69) ^k	10.6	11.2	11.6	12.4	14.7	
Exptl. SiCl_4 ^l	10.6	11.2	11.8	12.7	14.7	

^aAdjusted by $Q = 0.9x + 1.0$ ^bAdjusted by $Q = 1.3x - 1.1$ ^cAdjusted by $Q = 1.2x - 2.4$ ^dAdjusted by $Q = 1.0x - 0.6$ ^eAdjusted by $Q = 1.5x - 2.9$ ^fAdjusted by $Q = 1.3x - 4.4$ ^gAdjusted by $Q = 1.0x - 0.3$ ^hAdjusted by $Q = 1.4x - 2.5$ ⁱAdjusted by $Q = 1.3x - 3.9$ ^jAdjusted by $Q = 0.9x + 0.4$ ^kAdjusted by $Q = 1.4x - 2.1$ ^lAdjusted by $Q = 1.3x - 3.5$

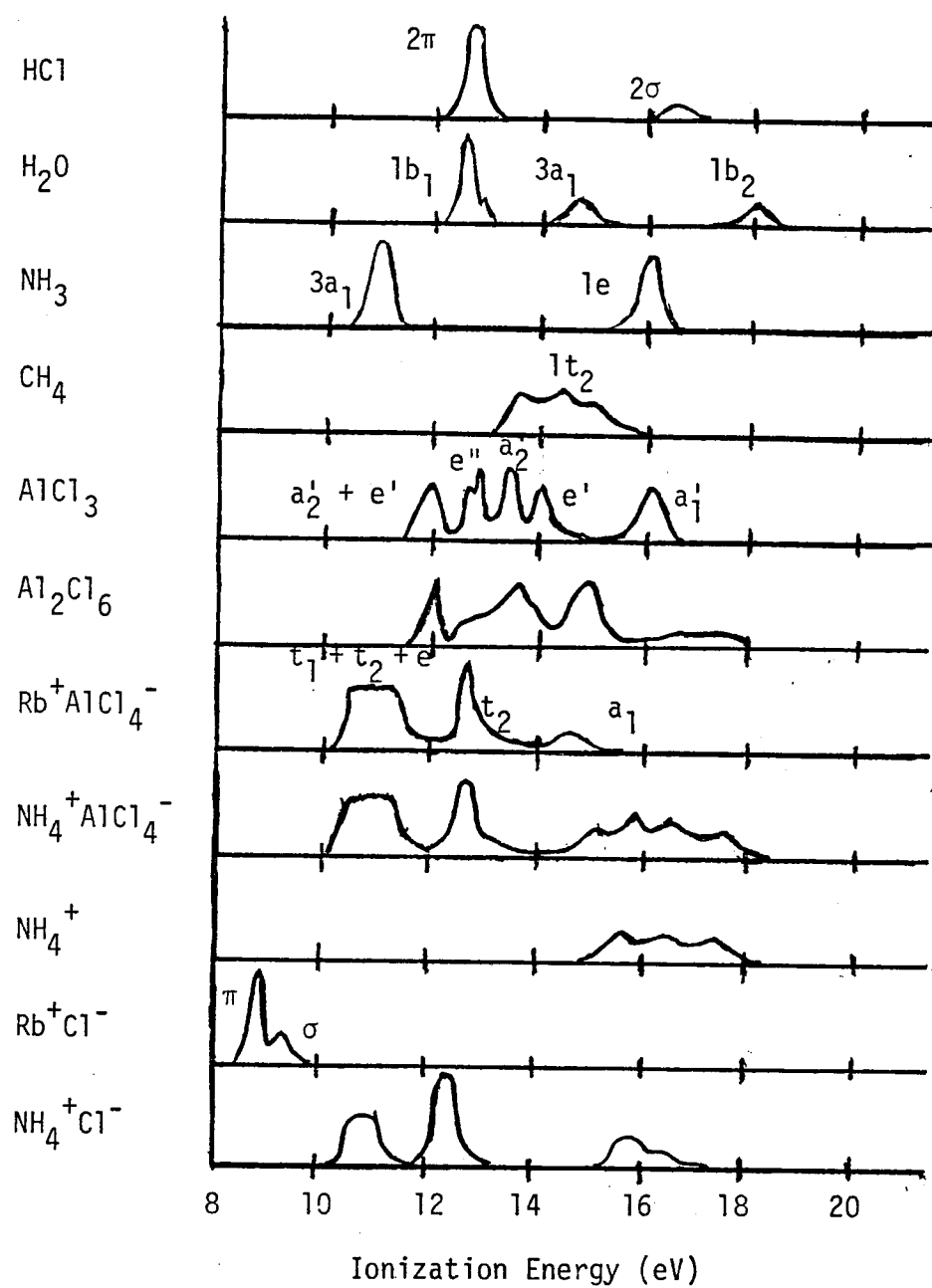


Figure 13. A schematic drawing of HeI photoelectron spectra.

From the schematic diagram it can be seen that the experimental photoelectron bands from H_2O vapor could occur in the same region of the spectrum as bands from $\text{Rb}^+\text{AlCl}_4^-$ or $\text{NH}_4^+\text{AlCl}_4^-$. However, H_2O vapor can be eliminated as a possible interference because the intensity of the H_2O vapor bands was reduced to at least one tenth of the intensities shown in the drawing by proper use of the handling and vaporization procedures which were outlined earlier (Chapter II, p 28, and Chapter 3, p 53). In the $\text{Rb}^+\text{AlCl}_4^-$ and the $\text{NH}_4^+\text{AlCl}_4^-$ vapor spectra, a contribution from HCl is possible because the 2π band in HCl is in the region of the photoelectron spectrum which could overlap with a similar band in the $\text{Rb}^+\text{AlCl}_4^-$ or $\text{NH}_4^+\text{AlCl}_4^-$ spectrum. Because of this observation, the vapors over heated NH_4^+Cl^- solid (known to decompose to NH_3 and HCl) were observed by HeI photoelectron spectroscopy in order to determine the relative intensities of the bands which result from the NH_3 and HCl vapors. The relative intensity of the photoelectron bands from the vapors above heated NH_4^+Cl^- solid which can be related to the 2π and 2σ bands in the photoelectron spectra of HCl was approximately 8 to 1 while the intensity of the photoelectron bands from the vapors above heated NH_4^+Cl^- which can be associated with the $3a_1$ and $1e$ bands in the photoelectron spectra of NH_3 was approximately 5 to 2. Comparison of the experimental intensities in the photoelectron spectra of $\text{Rb}^+\text{AlCl}_4^-$ and $\text{NH}_4^+\text{AlCl}_4^-$ with the experimental intensities of the bands of NH_3 and HCl vapor would seem to eliminate NH_3 and HCl as possible interferences in the $\text{NH}_4^+\text{AlCl}_4^-$ spectrum and HCl as a possible interference in the $\text{Rb}^+\text{AlCl}_4^-$ spectrum.

The photoelectron spectrum of CH_4 is presented because it is isoelectronic with the NH_4^+ cation. It can be seen from the schematic

diagram (Figure 13, p 77) that the broad band ($1t_2$) which extends from 13 to 16 eV in the CH_4 photoelectron spectrum is similar in breadth and intensity to the band which extends from 15 to 18 eV in the $\text{NH}_4^+\text{AlCl}_4^-$ spectrum. Upon closer examination of the photoelectron spectrum of CH_4 , the $1t_2$ band begins at 12.7 eV and terminates at 16.5 eV with the band center at 14.7 eV and the broad band in the photoelectron spectrum of $\text{NH}_4^+\text{AlCl}_4^-$ terminates at 18.5 eV. Assuming that the $1t_2$ band breadth (approximately 3.8 eV) in the photoelectron spectrum of CH_4 applies approximately to the NH_4^+ band, then the NH_4^+ band should begin at about 14.7 eV and end at 18.5 eV with a band center of about 16.5 eV.

UTARC calculations have been carried out on CH_4 and on the free NH_4^+ species. The theoretical ionization energies for the $1t_2$ band in CH_4 and NH_4^+ were 14.5 eV and 20.9 eV. The theoretical ionization energy for the CH_4 molecule agrees with the band center of the experimental spectrum for CH_4 . However, the theoretical ionization energy for the free NH_4^+ cation has been moved to much higher ionization energies than is indicated by the band center of the experimental NH_4^+ band. This is due to the positive charge on the NH_4^+ cation which results in an unusually large shift in the entire NH_4^+ MO envelope. UTARC calculations were carried out on NH_4^+Cl^- to find out if the addition of a Cl^- anion would counter balance some of the positive charge on the NH_4^+ cation. The theoretical ionization energies for the MO's of CH_4 , NH_4^+ , and NH_4^+Cl^- which could be seen by HeI photoelectron spectroscopy are summarized in Table XXIV (p 80). The MO's in the NH_4^+Cl^- which could be related to MO's in the NH_4^+ cation have an average theoretical ionization energy of 15.0 eV which is in

TABLE XXIV
 CH_4 , NH_4^+ , AND NH_4^+Cl^- THEORETICAL MO IONIZATION ENERGIES

MO	T_d CH_4	T_{d+} NH_4^+	MO	C_{2v} NH_4^+Cl^-
--	--	--	a_1	9.3
--	--	--	b_2	10.8
--	--	--	b_1	10.9
t_2	14.5	20.9	a_1	14.8
t_2	14.5	20.9	b_2	14.8
t_2	14.5	20.9	b_1	15.4

the region of the experimental ionization energies shown for the NH_4^+ cation in the $\text{NH}_4^+\text{AlCl}_4^-$ spectrum (Figure 10 and 11, p 58 and 59). Because of the above theoretical and experimental observations, the broad band (15 to 18 eV) in the $\text{NH}_4^+\text{AlCl}_4^-$ spectrum has been assigned to the $1t_2$ band of the NH_4^+ cation.

Band broadening in the first band in the experimental photoelectron spectrum of CH_4 is attributed to the Jahn-Teller effect occurring in relation to the t_2 MO. The Jahn-Teller Theorem predicts that a molecule in a degenerate electronic state is unstable toward distortions that lower the molecular symmetry. Since removal of an electron from the t_2 MO's in CH_4 would form a $^2T_2$ electronic state, the Jahn-Teller Theorem predicts that the CH_4^+ molecule in a $^2T_2$ state would be subject to distortion.

Also, the first band in the photoelectron spectrum of NH_4^+ is predicted to arise from MO's of t_2 symmetry. After photoionization from the t_2 MO's the NH_4^{++} molecule would be in a $^2T_2$ state and should be subject to the Jahn-Teller effect. However, band broadening produced by perturbations of the symmetry of the initial molecule also may influence the NH_4^+ cation but would not affect the CH_4 molecule. In this study the NH_4^+ cation was not free from the influence of the AlCl_4^- anion. A localized AlCl_4^- anion could reduce the symmetry of the initial T_d NH_4^+ cation to C_{3v} or C_{2v} . From an experimental point of view, it is difficult to distinguish between band broadening produced by the Jahn-Teller effect after photoionization of the initial molecule or by a perturbation of the initial anion. If the above observations are correct, high resolution photoelectron spectroscopic experiments

may not be of an assistance in permitting one to select among the various geometric possibilities of the NH_4^+ cation in the $\text{NH}_4^+\text{AlCl}_4^-$ vapor species.

All of the above experimental observations indicate that the AlCl_4^- anion has considerable integrity (the K^+ , Rb^+ , Cs^+ , and NH_4^+ cations affect its MO's only very slightly) and further that all the spectra resemble the SiCl_4 spectrum¹⁴³ with the five outer MO's of $\text{M}^+\text{AlCl}_4^-$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{and } \text{NH}_4$) compressed and moved to lower ionization energies (Table XXIII, pp 75 - 76). No definitive judgment can be made concerning the "polytopicity" of the vapor state $\text{M}^+\text{AlCl}_4^-$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{or } \text{NH}_4$) molecules because the splits produced by the perturbations between $\text{K}^+\text{AlCl}_4^-$ (T_d) or $\text{K}^+\text{AlCl}_4^-$ (C_{2v}) models are very small when compared to the observed band breadths and the instrumental resolution at high temperatures (no better than 0.15 eV). Since the NH_4^+ cation effects the MO's of the AlCl_4^- anion only very slightly, one might think that the AlCl_4^- anion may effect the MO's of the NH_4^+ ion only very slightly.

CHAPTER IV

ALKALI TETRAFLUOROALUMINATES

A. Previous Studies

1. Introduction

A number of experimental methods have been used to study gaseous, liquid, and solid species which contain tetrafluoroaluminate with a simple monovalent cation. Those which are important to these studies are Raman spectroscopic determinations on the liquid state, vapor pressure experiments, mass spectrometric and electron diffraction measurements on the vapor species, infrared spectroscopy on the high temperature gaseous species and on the matrix isolated species prepared by implanting the vapor species in a low temperature solid.

2. Raman Spectroscopy

Gilbert, Mamantov, and Begun¹⁴⁵ have obtained Raman spectra of the AlF_4^- species in a melt of KF-AlF_3 (50-50 mole %) at 725° C. They reported that the vibration frequencies of the AlF_4^- ion were:

$\nu_1 = 622 \text{ cm}^{-1}$ (A_1), $\nu_2 = 210 \text{ cm}^{-1}$ (E), $\nu_3 = 760 \text{ cm}^{-1}$ (T_2), and $\nu_4 = 322 \text{ cm}^{-1}$ (T_2).

3. Vapor Pressure

Vapor pressure measurements over heated $\text{Li}^+\text{AlF}_4^-$ which were made by Hildenbrand¹⁴⁶ using the torsion-effusion technique conclude that the principal vapor species is $\text{Li}^+\text{AlF}_4^-$. The pressure of $\text{Na}^+\text{AlF}_4^-$ as the principal vapor species over heated $\text{Na}^+\text{AlF}_4^-$ was first suggested by Howard¹⁴⁷ on the basis of transpiration experiments. The material showed only slight volatility at about 700° K, but the

volatility becomes considerable up around 1000° K. Further vapor pressure studies by Ginsberg and Böhm,¹⁴⁸ by Vajna and Bacchiega,¹⁴⁹ by Vetyukov, Bluishtein, and Poddymov,¹⁵⁰ by Rolin and Houriez,¹⁵¹ and by Foster¹⁵² all support the idea of a gaseous $\text{Na}^+\text{AlF}_4^-$ species.

4. Mass Spectrometry and Electron Diffraction

Porter and Zeller¹⁵³ and Sidorov *et al.*^{154,155} have made mass spectrometric investigations on vapors over heated $\text{Li}^+\text{AlF}_4^-$ ^{153,154} and $\text{Na}^+\text{AlF}_4^-$ ¹⁵⁵ solids. Both groups state that the data indicate the existence of a stable species M^+AlF_4^- ($\text{M} = \text{Li}$ or Na) which is the major component of the vapor phase. Their cell temperatures were in the region 969 - 1079° K,¹⁵³ 949° K,¹⁵⁴ and 913° K.¹⁵⁵ They also report a second complex molecular species which could be either $\text{Li}^+\text{AlF}_5 = \text{Li}^+$ or $\text{M}^+\text{Al}_2\text{F}_8 = \text{M}^+$ ($\text{M} = \text{Li}$ or Na). Some doubts^{156,157} with regard to the amount of dimer in the vapor above the $\text{Li}^+\text{AlF}_4^-$ and $\text{Na}^+\text{AlF}_4^-$ solids remain. Mass spectrometric studies of vapors over M^+AlF_4^- ($\text{M} = \text{Li}$ and Na) systems by Büchler, Stauffer, and Klemperer¹⁵⁸ (Li^+), by Büchler, Stauffer and Berkowitz-Mattuck¹⁵⁹ (Na^+) confirmed the major vapor species to be $\text{Li}^+\text{AlF}_4^-$ or $\text{Na}^+\text{AlF}_4^-$. The partial pressure of the species found in the vapors over K^+AlF_4^- solid have been measured by Kolosov, Tuvaeva, and Sidorov¹⁶⁰ using mass spectrometry. They obtained data which indicate that the vapor consists of K^+AlF_4^- , $\text{K}^+\text{Al}_2\text{F}_5 = \text{K}^+$, and $\text{K}^+\text{Al}_2\text{F}_8 = \text{K}^+$ with K^+AlF_4^- predominating for melts greater than 25 mole % AlF_3 at 838° K. Kolosov, Tuvaeva, Sidorov, and Akishin¹⁶¹ made a mass spectrometric study of the vapor species over heated $\text{Cs}^+\text{AlF}_4^-$ systems. In the composition range 25 - almost 100 mole % AlF_3 at 752° K, the vapor pressures of the $\text{Cs}^+\text{AlF}_4^-$

and $\text{Cs}^+\text{Al}_2\text{F}_8^-\text{Cs}^+$ species are approximately equal.

Spiridonov, Erokhin, and Lutoshkin¹⁶² have investigated the structure of the vapor species above $\text{Na}^+\text{AlF}_4^-$ using mass spectrometry and electron diffraction. The data from mass spectrometry indicated that the partial pressure of the monomer species ($\text{Na}^+\text{AlF}_4^-$) was approximately ten times higher than the partial pressure of the dimer $\text{Na}^+\text{Al}_2\text{F}_8^-\text{Na}^+$ for a 63 mole % NaF - 37 mole % AlF_3 system at 931° K. However, the electron diffraction study was conducted at temperatures in excess of 1150° K in order to obtain high enough vapor pressure of $\text{Na}^+\text{AlF}_4^-$ to give electron diffraction patterns of sufficient intensity. They concluded that the best overall model involved the Al atom located at the center of a tetrahedron of four F atoms with the Na^+ ion located on a line perpendicular to one of the sides of the tetrahedron and passing through the Al atom. The bond angles ($\angle$) and distances (r) are: $r(\text{Al-F}) = 1.69 \pm 0.02 \text{ \AA}$, $r(\text{Na-F}) = 2.11 \pm 0.02 \text{ \AA}$, $\angle \text{F-Al-F} = 109 \pm 5^\circ$, and $\angle \text{F-Na-F} = 82 \pm 5^\circ$. Recently, Spiridonov, Ischenko, and Zasorin¹⁴¹ stated that it is possible to fit the observed electron diffraction pattern for $\text{Na}^+\text{AlF}_4^-$ with a theoretical expression which uses a dynamic stereochemically non-rigid molecular model (the same model used for some oxyanion salts). They stated that the high temperature bonding in sodium tetrafluoroaluminate ($\text{Na}^+\text{AlF}_4^-$) may be "polytopic."

5. Infrared Spectroscopy

The infrared spectra of gaseous $\text{Li}^+\text{AlF}_4^-$ and $\text{Na}^+\text{AlF}_4^-$ have been studied by McCorry, Paule, and Margrave.¹⁶³ The solid phases they employed were 75 mole % MF (M - Li^+ or Na^+) and 25 mole % AlF_3 .

Infrared bands were centered at 779 and 866 cm^{-1} for both the $\text{Li}^+\text{AlF}_4^-$ and the $\text{Na}^+\text{AlF}_4^-$ vapor species.

Hovdan, Huglen, and Oye¹⁶⁴ and Cyvin et al^{165,166} have isolated the vapors produced by heating M^+AlF_4^- ($\text{M} = \text{Li},^{164,165} \text{Na},^{164,166} \text{K},^{164} \text{Rb},^{164}$ and Cs^{164}) by implanting them in an argon matrix.

An infrared spectral analysis suggested that the data fit either a C_{2v} model with the M^+ ion centered on a line perpendicular to one side of the AlF_4^- tetrahedron and passing through the Al atom, or a C_{3v} model with the M^+ ion located on an Al-F axis just beyond the fluorine. All three studies indicated that the C_{2v} model was preferred. A summary of the wave numbers (cm^{-1}) of the infrared bands for the M^+AlF_4^- ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs) matrix isolated species is given in Table XXV (p 87).

B. Experimental Procedure

1. Compounds

Anhydrous alkali metal fluorides (Li^+F^- , Na^+F^- , K^+F^- , Rb^+F^- , and Cs^+F^-) and anhydrous AlF_3 were purchased from Alfa Division of Ventron Corporation. The six fluoride compounds were stated to be greater than 99.0% (M^+F^-) and 99.99% (AlF_3) purity.

2. Procedures

Since the alkali metal tetrafluoroaluminates tend to take up water, the dry box procedures which were developed for the tetra-chloroaluminates (Chapter IIIB, p 53-54) have been extended to these compounds. Also, the procedures for sample handling and spectral accumulation have been described previously (Chapter IIB, p 24 - 30). The vapor oven was described in Chapter IIIB (p 54). The platinum liner served to distribute the heat evenly.

TABLE XXV
MATRIX ISOLATED INFRARED SPECTROSCOPIC WAVE NUMBERS
OF TETRAFLUOROALUMINATE VAPOR

Band	(Li ⁺)	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
1	891 ^a (901) ^b	877 ^a (811) ^c	859 ^a	858 ^a	854 ^a
2	817 (818)	858 (674)	805	801	798
3	652 (651)	808 (379)	705	707	709
4	517 (577)	684 (323)	343	334	326
5	409 (453)	364 (302)	308	307	304
6	310 (316)	316	301	302	301
7	(269)	300			
8	(222)				

^aRef. 163

^bRef. 164

^cRef. 165

C. Experimental Results

The HeI photoelectron spectra of the vapors above heated K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$ are presented as Figure 14 (p 89) and Figure 15 (p 90). Each is a typical spectrum from at least 15 obtained for each compound. A nontypical spectrum for $\text{Cs}^+\text{AlF}_4^-$ (Figure 16, p 91) is an example of the kind of run that the author chose to reject. Unnumbered peaks which are designated by the letters Ar in each figure are due to the calibrant argon. Many attempts were made to accumulate spectral data on gaseous $\text{Li}^+\text{AlF}_4^-$, $\text{Na}^+\text{AlF}_4^-$, and $\text{Rb}^+\text{AlF}_4^-$, but no success was achieved. Volatilization of $\text{Li}^+\text{AlF}_4^-$ and $\text{Na}^+\text{AlF}_4^-$ was complicated by high temperature oxidation of the tantalum strip and by possible attack of the high temperature tetrafluoroaluminate vapors on the quartz cell. A sample alleged to be anhydrous Rb^+F^- was used to prepare the $\text{Rb}^+\text{AlF}_4^-$ compound. The spectra of the vapors above $\text{Rb}^+\text{AlF}_4^-$ were reproducible but were not consistent with the high temperature spectra of K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$. The spectra contained bands whose shapes and ionization energies matched bands of the photoelectron spectrum of water vapor. The water vapor bands were seen at larger cell currents (15 mA) and intensities (5000 counts/sec) than similar bands from K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$ which were less intense (100 counts/sec) at low cell currents (5 mA) and very weak (< 30 counts/sec) at larger cell currents (10 - 20 mA). These observations led to the conclusion that the Rb^+F^- solid was either hydrated or partially hydrolyzed.

The values assigned to the various band peaks in the spectra for K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$ compounds are listed in Table XXVI (p 92)

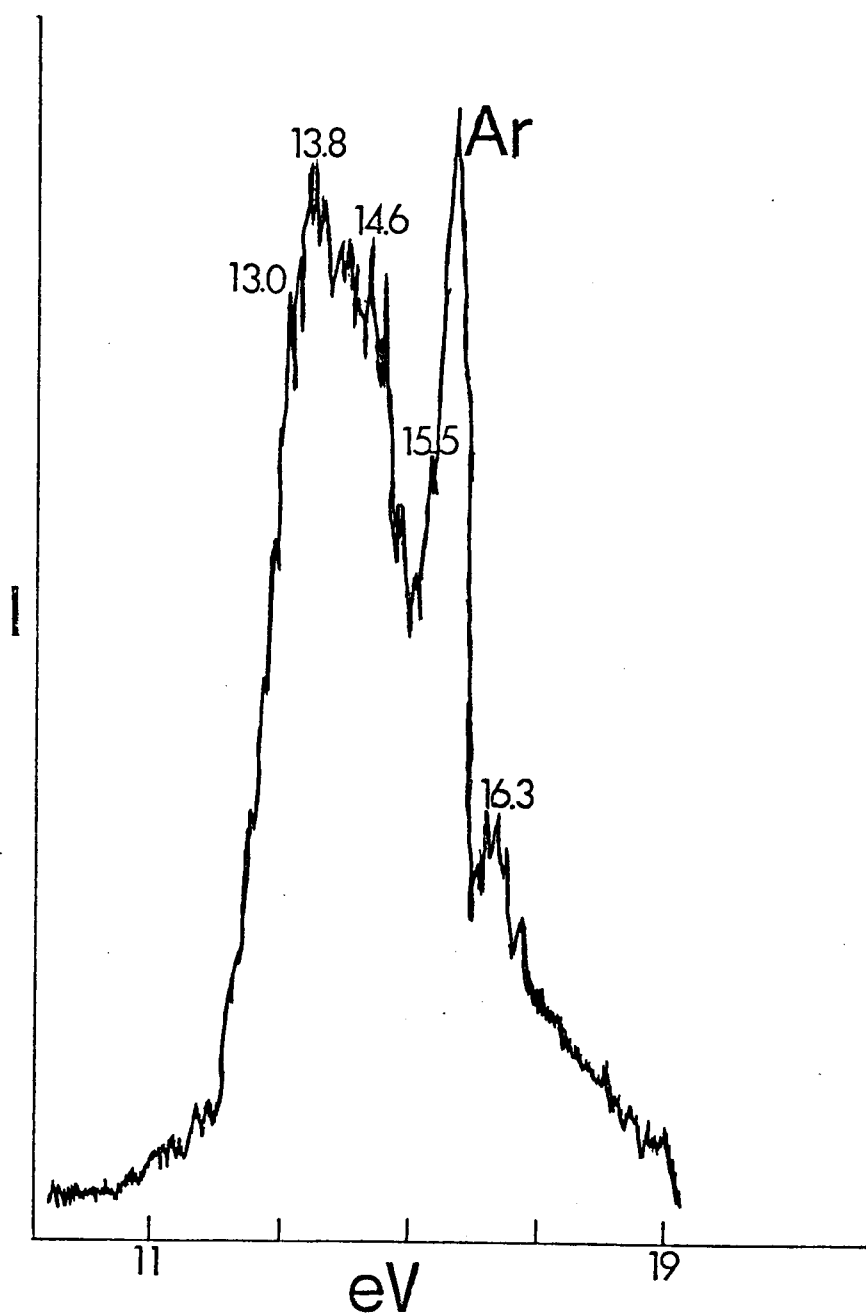


Figure 14. HeI photoelectron spectrum of K^+AlF_4^- vapor.

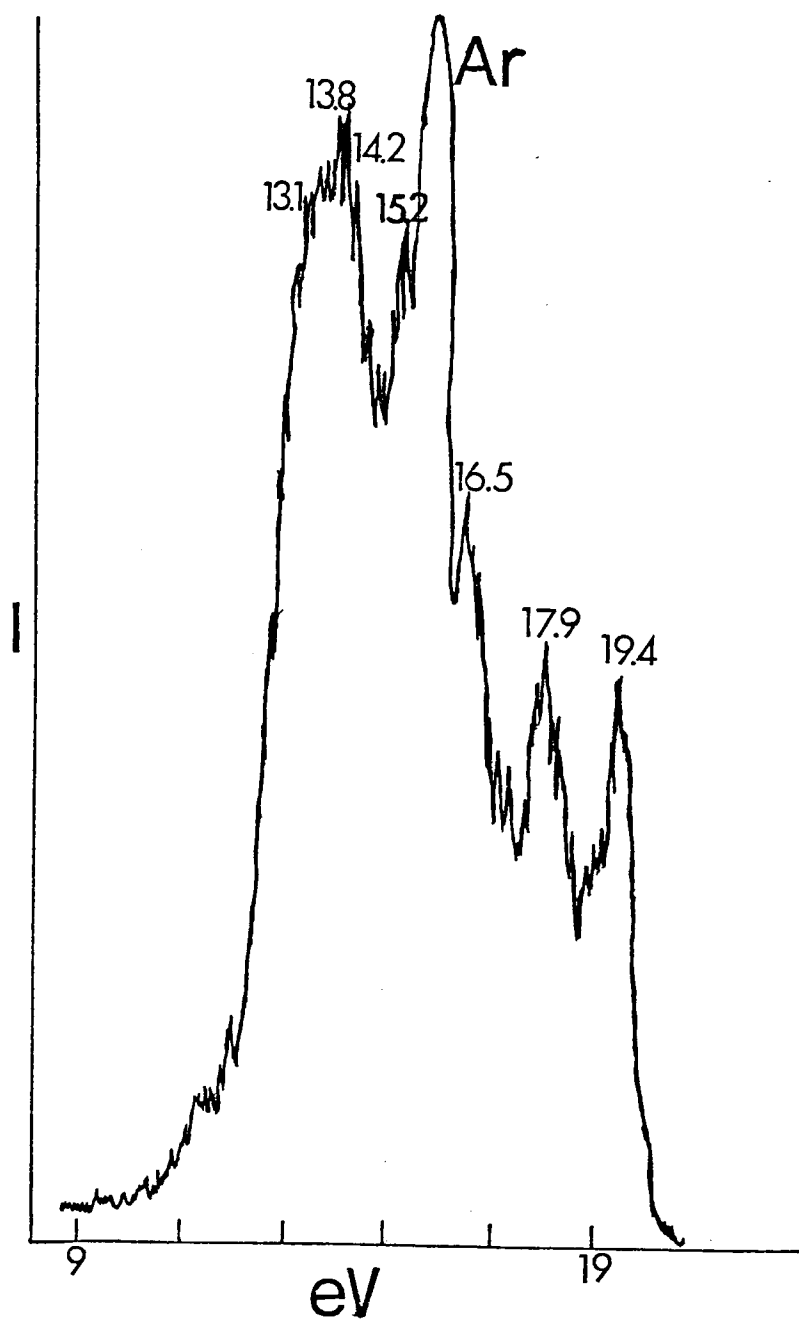


Figure 15. HeI photoelectron spectrum of $\text{Cs}^+\text{AlF}_4^-$ vapor.

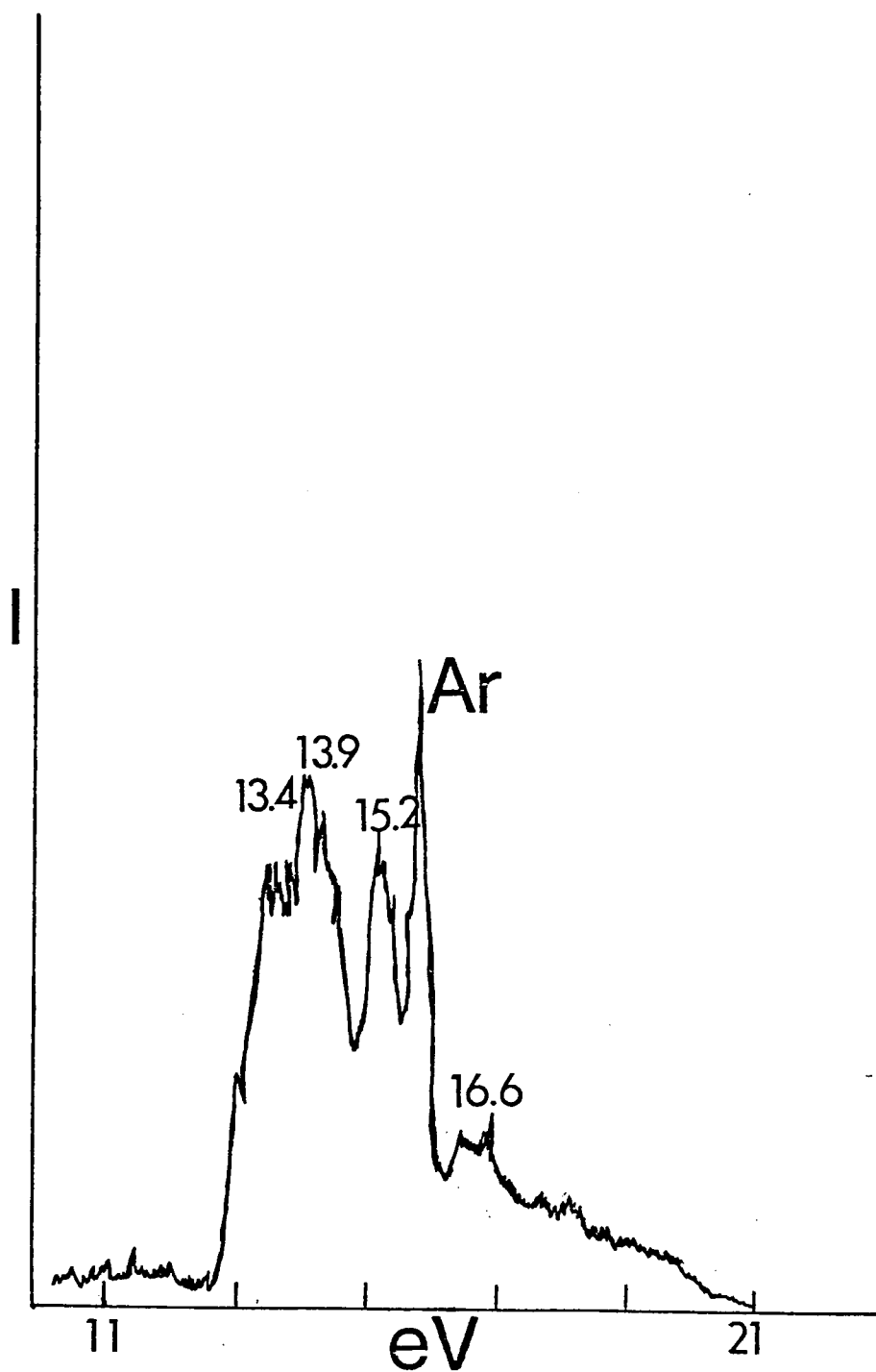


Figure 16. Nontypical HeI photoelectron spectrum of $\text{Cs}^+\text{AlF}_4^-$ vapor.

TABLE XXVI
BAND PEAK VALUES FOR $K^+AlF_4^-$ VAPOR SPECTRA

Item	1st	2nd	Peak (-eV) 3rd	4th	5th
Run 1*	13.04	13.83	14.61	15.52	16.34
Run 2	13.24	13.79	14.37	15.30	16.15
Run 3	13.10	13.67	14.60	15.65	16.24
Run 4	13.05	13.82	14.60	15.53	16.30
Run 5	12.98	13.68	14.54	15.47	16.20
Run 6	13.08	13.86	14.68	15.56	16.35
Run 7	12.90	13.66	14.44	15.38	16.19
Run 8	13.08	13.88	14.70	15.58	16.46
Run 9	12.96	13.76	14.54	15.47	16.26
Run 10	13.08	13.89	14.69	15.60	16.39
Run 11	12.90	13.70	14.49	15.43	16.12
Run 12	12.98	13.78	14.58	15.48	16.28
Run 13	12.94	13.76	14.54	15.45	16.27
Run 14	12.96	13.78	14.59	15.48	16.30
Run 15	13.04	13.88	14.68	15.59	16.40
$\bar{x} =$	13.02	13.78	14.58	15.50	16.28
$\sigma_i =$	.09	.08	.09	.09	.09
95% $\sigma_i =$	.18	.15	.19	.18	.19
$\sigma_{av} =$	.02	.02	.02	.02	.02
95% $\sigma_{av} =$	.05	.04	.05	.05	.05

and Table XXVII (p 94). The unweighted average ionization energy value ($\bar{x}$), the standard deviation of each individual ionization energy value (σ_i), the 95% confidence limit of the individual ionization energy value ($95\% \sigma_i$), the standard deviation of the unweighted average ionization energy value (σ_{av}), and the 95% confidence limit of the unweighted average ionization energy values ($95\% \sigma_{av}$) for each band peak in each run are given in Tables XXVI and XXVII (pp 91 and 93). The starred runs in Tables XXVI and XXVII (pp 92 and 94) indicate the spectra chosen for presentation in Figures 14 and 15 (pp 89 and 90). The spectra which were chosen for the figures had experimental ionization energy values similar to the unweighted averaged ionization energy values. A summary of the unweighted average ionization energy values followed by their $95\% \sigma_{av}$ values is listed in Table XXVIII (p 95).

D. Theoretical Expectations

For the tetrafluoroaluminates, as was the case for the tetrachloroaluminates, no ab initio calculations have been reported. So far, the UTARC program is the only source of theoretical calculations which have been used to study the photoelectron spectroscopy of tetrafluoroaluminates. The approximations and adjustments which were necessary to correct the theoretical MO values from the UTARC program to the experimental photoelectron MO values on the tetrachloroaluminates are thought to apply to calculations on $\text{Na}^+\text{AlF}_4^-$ and AlF_4^- . However, the theoretical MO values and the trends or tendencies which might be concluded from these calculations may be subject to some unknown uncertainties. Nevertheless, the calculations were

TABLE XXVII
BAND PEAK VALUES FOR $\text{Cs}^+\text{AlF}_4^-$ VAPOR SPECTRA

Item	1st	2nd	3rd	Peak (-eV)	5th	6th	7th
				4th			
Run 1*	13.11	13.79	14.21	15.23	16.54	17.92	19.40
Run 2	13.20	13.89	14.24	15.05	16.62	18.06	19.38
Run 3	13.20	13.64	14.12	15.05	16.38	18.10	19.43
Run 4	13.22	13.60	14.03	15.05	16.52	18.03	19.27
Run 5	13.19	13.73	14.13	15.18	16.65	18.07	19.24
Run 6	12.99	13.68	13.93	15.10	16.40	17.78	19.34
Run 7	13.03	13.74	14.16	15.16	16.43	17.86	19.44
Run 8	13.08	13.78	14.38	15.18	16.46	17.81	19.38
Run 9	13.19	13.74	14.34	15.08	16.50	17.84	19.44
Run 10	13.22	13.89	14.10	15.18	16.36	17.92	19.37
Run 11	12.98	13.86	14.14	15.16	16.40	17.94	19.41
Run 12	12.96	13.84	13.98	15.07	16.54	17.98	19.46
Run 13	13.12	13.77	14.18	15.09	16.43	17.90	19.28
Run 14	13.18	13.79	14.34	15.15	16.72	17.86	19.34
Run 15	13.07	13.76	14.28	15.19	16.56	17.91	19.43
$\bar{x} =$	13.12	13.77	14.17	15.13	16.50	17.93	19.37
$\sigma_i =$	.09	.08	.13	.06	.11	.10	.07
95% $\sigma_i =$	.18	.17	.26	.11	.21	.19	.13
$\sigma_{av} =$	.02	.02	.03	.01	.03	.03	.02
95% $\sigma_{av} =$	.05	.05	.07	.03	.06	.05	.04

TABLE XXVIII
AVERAGE TETRAFLUOROALUMINATE EXPERIMENTAL IONIZATION ENERGIES (-eV)

	$K^+AlF_4^-$	$Cs^+AlF_4^-$
Band 1	13.02±.05	13.12±.05
Band 2	13.78±.04	13.77±.05
Band 3	14.58±.05	14.17±.07
Band 4	15.50±.05	15.13±.03
Band 5	16.28±.05	16.50±.06
Band 6		17.93±.05
Band 7		19.37±.04

carried out because of previous successes in predicting the qualitative ordering of MO's in previous molecules.¹⁴² It is hoped that some conclusions might be drawn from the program which could be used for qualitative interpretation of the experimental photoelectron spectra.

The structural models which were used for the $\text{Na}^+\text{AlF}_4^-$ calculations were based on electron diffraction studies of the $\text{Na}^+\text{AlF}_4^-$ vapor species¹⁶² and on infrared studies of the $\text{Na}^+\text{AlF}_4^-$ vapor species¹⁶⁴ trapped in a cool matrix. The electron diffraction data were taken to indicate that the best theoretical model which fits the experimental radial distribution curve has bond angles ($\angle$) and bond distances (r) which were described earlier (p 85). The data from the matrix isolation infrared studies (Table XXV, p 87) could fit a C_{2v} or C_{3v} model but the authors indicated that the C_{2v} model was preferred. Therefore, two $\text{Na}^+\text{AlF}_4^-$ structures were chosen for the UTARC calculations. Both have the same bond distances as shown by electron diffraction while one has all $\angle \text{F-Al-F} = 109.5^\circ$ and the other has bond angles $\angle \text{F}_2\text{-Al-F}_3 = 99.5^\circ$ and $\angle \text{F}_4\text{-Al-F}_5 = 109.5^\circ$. The first $\text{Na}^+\text{AlF}_4^-$ structure was labeled as $\text{Na}^+\text{AlF}_4^- (T_d)$ and the second as $\text{Na}^+\text{AlF}_4^- (C_{2v})$.

Also, calculations were carried out on the free AlF_4^- anion. The AlF_4^- anion was selected because it was thought that any variations in % AO constituencies in the MO's and MO values are a result of adding a Na^+ cation could be more easily seen. The models which were chosen for the free AlF_4^- anion were identical to those chosen for the AlF_4^- anion in $\text{Na}^+\text{AlF}_4^- (T_d)$ and $\text{Na}^+\text{AlF}_4^- (C_{2v})$. The two models for the free AlF_4^- structures were designated $\text{AlF}_4^- (T_d)$ and

$\text{AlF}_4^- (\text{C}_{2v})$. The results of the computations on the four species $[\text{Na}^+\text{AlF}_4^- (\text{T}_d), \text{Na}^+\text{AlF}_4^- (\text{C}_{2v}), \text{AlF}_4^- (\text{C}_{2v}), \text{and } \text{AlF}_4^- (\text{T}_d)]$ are presented in Table XXIX (p 98). The first four lines represent the theoretical ionization energy values of the UTARC program MO's while rows five through seven show the MO values adjusted by a Q factor to row four. The fourth structure was chosen as a result of conclusions drawn from electron diffraction studies. A summary of the shift and splits of MO values in relation to those from $\text{AlF}_4^- (\text{T}_d)$ is shown in Table XXX (p 99). The effect of the Na^+ cation on the AlF_4^- anion MO's seems to be the largest in the MO's which originate from MO's which can be related to the $3t_2$ MO from $\text{AlF}_4^- (\text{T}_d)$. The $3t_2$ MO energy splits from the tetrafluoroaluminates were larger than the $3t_2$ MO energy splits from the tetrachloroaluminate calculations (Table XXI, p 70).

The outer MO levels which can be reached by HeI radiation are largely F 2p in character in $\text{AlF}_4^- (\text{T}_d)$, $\text{AlF}_4^- (\text{C}_{2v})$, $\text{Na}^+\text{AlF}_4^- (\text{T}_d)$, and $\text{Na}^+\text{AlF}_4^- (\text{C}_{2v})$. The F 2p % AO constituency on each F atom in $\text{Na}^+\text{AlF}_4^- (\text{T}_d)$, $\text{Na}^+\text{AlF}_4^- (\text{C}_{2v})$, and $\text{AlF}_4^- (\text{C}_{2v})$ are compared to those in the MO levels in $\text{AlF}_4^- (\text{T}_d)$ in Table XXXI (p 100). The data show that the UTARC program continues the same trends for the $\text{AlF}_4^- (\text{T}_d)$ model as were seen in the $\text{AlCl}_4^- (\text{T}_d)$ calculations. However, the F 2p % AO constituencies in the MO's of $\text{AlF}_4^- (\text{C}_{2v})$ which can be related to the $1t_1$ and $3t_2$ MO's of $\text{AlF}_4^- (\text{T}_d)$ were shifted (38 to 12 and 26 to 24) toward F 2 and F 3. The % AO constituencies in the MO's of $\text{AlF}_4^- (\text{C}_{2v})$ which can be associated to the $1e$, $2t_2$, and $2a_1$ MO's of $\text{AlF}_4^- (\text{T}_d)$ were moved (9 to 41, 23 to 27, and 18 to 30) toward

TABLE XXIX

 AlF_4^- AND $\text{Na}^+\text{AlF}_4^-$ MO'S AND ENERGIES (-eV)

Row	MO's and Energies									
1	AlF_4^- (T_d)	1t ₁	3t ₂	1e	2t ₂	2a ₁				
		10.4	10.8	10.8	11.5	12.5				
2	AlF_4^- (C_{2v})	4b ₁	2a ₂	4b ₂	6a ₁	3b ₁	5a ₁	3b ₂	1a ₂	3a ₁
		10.3	10.5	10.6	10.9	10.9	10.9	11.0	11.1	12.6
3	$\text{Na}^+\text{AlF}_4^-$ (C_{2v})	13.9	14.0	14.2	14.3	14.7	15.3	15.9	16.1	18.0
4	$\text{Na}^+\text{AlF}_4^-$ (T_d)	13.7	13.9	14.0	14.2	14.5	15.1	15.9	15.9	17.8
5	Line 1 adjusted to 4 ^a	13.7	13.7	13.7	14.5	14.5	14.5	14.5	14.5	17.8
6	Line 2 adjusted to 4 ^b	13.7	14.1	14.2	14.8	14.8	14.8	14.9	15.1	17.8
7	Line 3 adjusted to 4 ^c	13.7	13.8	14.0	14.1	14.5	15.1	15.7	15.9	17.8

^aQ = 2.0x - 6.6^bQ = 1.8x - 4.7^cQ = 0.0x - 0.2

TABLE XXX

 AlF_4^- AND $\text{Na}^+\text{AlF}_4^-$ SHIFT AND SPLIT CALCULATIONS (-eV)

	$\text{AlF}_4^- (\text{T}_d)$	$\text{AlF}_4^- (\text{C}_{2v})$	$\text{Na}^+\text{AlF}_4^- (\text{T}_d)$	$\text{Na}^+\text{AlF}_4^- (\text{C}_{2v})$
$1t_1$	13.7	13.7-14.2	13.7-14.0	13.7-14.0
$3t_2$	14.5	14.8	14.2-15.1	14.1-15.1
$1e$	14.5	14.9-15.1	15.9	15.7-15.9
$2t_2$	15.8	15.8-16.2	16.2-16.6	16.3-16.6
$2a_1$	17.8	17.8	17.8	17.8

TABLE XXXI

F 2p % AO'S IN MO'S

	$\text{AlF}_4^- (\text{T}_d)$			$\text{AlF}_4^- (\text{C}_{2v})$			$\text{Na}^+\text{AlF}_4^- (\text{T}_d)$			$\text{Na}^+\text{AlF}_4^- (\text{C}_{2v})$		
	2p ₂	2p ₃	2p ₄	2p ₅	2p ₂	2p ₃	2p ₄	2p ₅	2p ₂	2p ₃	2p ₄	2p ₅
1t ₁	25	25	25	25	38	38	12	12	1	1	49	49
3t ₂	25	25	25	25	26	26	24	24	4	4	46	46
1e	25	25	25	25	9	9	41	41	49	49	1	1
2t ₂	25	25	25	25	23	23	27	27	47	47	2	2
2a ₁	24	24	24	24	18	18	30	30	43	43	4	4

F 4 and F 5. The Cl 3p or F 2p % AO constituencies in the MO's of either AlCl_4^- (C_{2v}) or AlF_4^- (C_{2v}) which can be related to the $1t_1$, $2t_2$, and $2a_1$ MO's of either AlCl_4^- (T_d) or AlF_4^- (T_d) are almost identical. The Cl 3p or F 2p % AO constituencies in the MO's for AlCl_4^- (C_{2v}) or AlF_4^- (C_{2v}) which can be associated to the $3t_2$ and $1e$ MO's of either AlCl_4^- (T_d) or AlF_4^- (T_d) were reversed in the $3t_2$ MO's of AlF_4^- (C_{2v}) in relation to the $3t_2$ MO's of AlCl_4^- (C_{2v}) while the $1e$ MO's of AlF_4^- (C_{2v}) were much larger when compared to the $1e$ MO's of AlCl_4^- (C_{2v}). The same Cl 3p % AO trends which were developed for $\text{K}^+\text{AlCl}_4^-$ (T_d) and $\text{K}^+\text{AlCl}_4^-$ (C_{2v}) in Chapter III (p 71) can be seen in the data for the F 2p % AO constituencies for $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}). However, the changes in the F 2p % AO constituencies for $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}) are larger in all the MO's than the Cl 3p % AO constituencies for $\text{K}^+\text{AlCl}_4^-$ (T_d) and $\text{K}^+\text{AlCl}_4^-$ (C_{2v}). For instance, in $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}) the MO's which can be related to the $1t_1$ and $3t_2$ MO's of AlF_4^- (T_d) show a change (1 to 49 and 4 to 46) toward F 4 and F 5 while those MO's in $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}) which can be associated to the $1e$, $2t_2$, and $2a_1$ MO's of AlF_4^- (T_d) indicate a shift (49 to 1, 47 to 2, and 43 to 4) toward F 2 and F 3. There is little or no difference between the F 2p % AO constituencies in the MO's of $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}).

E. Interpretations

Comparisons of the unweighted average ionization energy values from Table XXVIII (p 95) have been made with UTARC calculations of Table XXIX (p 98) and the experimental ionization energy values for

the isoelectronic molecule SiF_4 which have been reported by Hall et al¹⁶⁷ [16.5 eV ($1t_1$), 17.5 eV ($3t_2$), 18.1 eV ($1e$), 19.5 eV ($2t_2$), and 21.5 eV ($2a_1$)]. The data on the comparisons of the two vapor species (K^+AlF_4^- , and $\text{Cs}^+\text{AlF}_4^-$) are summarized in Table XXXII (p 103). It is suggested from a comparison of band intensities and separations indicated from all the UTARC calculations using all the models that the anion MO energy order for K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$ vapors is $1t_1$, $3t_2$, $1e$, $2t_2$, and $2a_1$. In the $\text{Cs}^+\text{AlF}_4^-$ vapor spectrum (Figure 15, p 90), the sixth and seventh bands (17.9 and 19.4 eV) can be assigned to ionization from the cesium $5p_{3/2}$ and $5p_{1/2}$ electrons. This assignment agrees with the cesium 5p values which have been reported for numerous other ionic compound vapors (Table XIII, p 47).

The first four bands in the photoelectron spectrum of the SiF_4 vapor molecule¹⁶⁷ can be related to the outer four bands of the MO envelope of K^+AlF_4^- and $\text{Cs}^+\text{AlF}_4^-$ with the MO envelope of M^+AlF_4^- ($\text{M} = \text{K}$ or Cs) compressed and moved to lower ionization energies (Table XXXII, p 103). This would seem to indicate that the AlF_4^- tetrahedron MO's are only slightly distorted by the presence of a cation. As a result of the above experimental observations and of the small changes which are expected from MO energy splits of the $\text{Na}^+\text{AlF}_4^-$ (T_d) and $\text{Na}^+\text{AlF}_4^-$ (C_{2v}) models when compared to the observed experimental band breadths, no hope is given to settling the question of possible "polytopicity" of the M^+AlF_4^- vapor species.

TABLE XXXII
COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES FOR THE TETRAFLUOROALUMINATES

Values	$1t_1$	$3t_2$	$1e$	$2t_2$	$2a_1$
Exptl. $K^+AlF_4^-$ (from Table XXVIII, p 95)	13.0	13.8	14.6	15.5	16.3
Theor. $Na^+AlF_4^-$ (T_d) (from Table XXIX, p 98) ^a	13.0(b_1) 13.1(a_2) 13.2(b_2)	13.2(a_1) 13.6(b_1) 14.1(a_1)	14.6(b_2) 14.8(a_2)	15.1(b_1) 15.3(b_2) 15.3(a_1)	16.3(a_1)
Theor. AlF_4^- (T_d) (from Table XXIX, p 98) ^b	13.0	13.6	13.6	14.7	16.3
Exptl. SiF_4^c	13.0	13.7	14.1	15.0	16.3
Exptl. $Cs^+AlF_4^-$ (from Table XXVIII, p 95)	13.1	13.8	14.2	15.1	16.5
Theor. $Na^+AlF_4^-$ (T_d) (from Table XXIX, p 98) ^d	13.1(b_1) 13.2(a_2) 13.3(b_2)	13.4(a_1) 13.8(b_1) 14.3(a_1)	14.8(b_2) 14.9(a_2)	15.0(b_1) 15.3(b_2) 15.3(a_1)	16.5(a_1)
Theor. AlF_4^- (T_d) (from Table XXIX, p 98) ^e	13.1	13.7	13.7	14.9	16.5
Exptl. SiF_4^f	13.1	13.8	14.2	15.1	16.5

^aAdjusted by $Q = 0.8x + 1.8$

^bAdjusted by $Q = 1.6x - 3.3$

^cAdjusted by $Q = 0.7x + 2.1$

^dAdjusted by $Q = 0.8x + 1.6$

^eAdjusted by $Q = 1.6x - 3.7$

^fAdjusted by $Q = 0.7x + 1.9$

CHAPTER V

CONCLUSIONS

A. Review of Conclusions

The experimental photoelectron ionization energies for some alkali metal metaborates, alkali metal tetrachloroaluminates, alkali metal tetrafluoroaluminates, and ammonium tetrachloroaluminate have been determined in this study. In each case, observations from volatilization experiments, electron diffraction studies, mass spectral determinations, and infrared studies were used to make judgments about the composition of the vapor above the heated solids. It was concluded that all the vapors above the heated solids $K^+BO_2^-$, $Rb^+BO_2^-$, $Cs^+BO_2^-$, $K^+AlCl_4^-$, $Rb^+AlCl_4^-$, $Cs^+AlCl_4^-$, $NH_4^+AlCl_4^-$, $K^+AlF_4^-$, and $Cs^+AlF_4^-$ consisted predominately of the corresponding gaseous monomer. The electron diffraction data were also employed to develop structural models which were to be used in theoretical MO calculations.

In the cases of the metaborates, tetrachloroaluminates, and tetrafluoroaluminates for which reproducible spectra could be obtained, the experimental photoelectron spectral bands and ionization energies were assigned MO origins by correlation with theoretical MO calculations for both the neutral monomeric molecular species and the free anionic species. These correlations were made primarily on the basis of calculated electronic structures for the corresponding anions minimally perturbed by the associated cation. Adjustments were carried out by using Q factors to bring the theoretically computed data for free anions and neutral molecules to agreement with the experimental spectra.

Because the experimental photoelectron spectra of all the species containing the same anion with different cations were very similar, it was thought that a newly-proposed high temperature molecular model (principally from electron diffraction, matrix isolation infrared, or microwave studies) called a "polytopic molecule" might be applicable to these vapor molecules. Previous high temperature studies^{83,86-89} on somewhat similar complex anion compounds had considered this possibility but no conclusions could be drawn about the polytopicity of the molecules studied. A similar conclusion has been drawn from the present studies about the possible "polytopicity" of these species.

One approach to interpreting the photoelectron spectra of the tetrahedral tetrachloro- and tetrafluoroaluminates is to compare MO assignments which have been made on other tetrahedral molecules or anions which have been studied by ultraviolet or X-ray photoelectron spectroscopy (UPS and XPS). This approach will be discussed in more detail in the following section.

B. Tetrahedral Molecules and Anions

A summary of the photoelectron bands and the MO assignments for various tetrahedral molecules and tetrahedral or approximately tetrahedral anions is presented in Table XXXIII (pp 106 - 107). It is generally agreed that the most prevalent energy order for tetrahedral molecules and anions is likely to be t_1 , t_2 , e , t_2 , and a_1 . In the many molecules or anion which have halogen ligands, the above energy order is consistently followed. When the energy orders for tetrahedral molecules or anions which have oxygen ligands are

TABLE XXXIII
TETRAHEDRAL MOLECULES AND ANIONS

Entities	t_1	t_2	e	t_2	a_1
CCl_4^a (UPS)	11.6	12.5	13.4	16.7	--
SiCl_4^a (UPS)	12.1	13.0	13.5	15.3	18.1
GeCl_4^a (UPS)	12.2	12.6	13.1	14.9	18.4
SnCl_4^a (UPS)	12.1	12.4	12.7	14.3	17.4
TiCl_4^b (UPS)	11.8	12.8	13.3	13.3	14.0
VCl_4^b (UPS)	11.8	12.8	13.5	13.6	14.3
ZrCl_4^c (UPS)	11.9	12.6	13.2	13.4	13.8
HfCl_4^c (UPS)	12.0	12.8	13.4	13.7	14.2
AlCl_4^- (UPS)	10.4	10.9	11.4	12.9	14.9
AlF_4^- (UPS)	13.0	13.8	14.6	15.5	16.3
CF_4^a (UPS)	16.3	17.5	18.6	--	--
SiF_4^a (UPS)	16.5	17.5	18.1	19.5	--
GeF_4^a (UPS)	16.0	16.6	17.1	18.5	--
OsO_4^d (UPS)	13.2	12.3	13.5	16.3	14.5
RuO_4^d (UPS)	12.9	12.1	13.9	16.0	13.8
CrO_4^{2-e} (XPS)	4.4	5.6	3.0	6.2	24.4
VO_4^{3-e} (XPS)	4.5	5.7	2.7	6.7	23.9
$\text{ReO}_4^{-f,g}$ (XPS)	5.1	7.8	9.3	11.7	6.6
$\text{ReO}_4^{-f,g}$ (UPS)	9.8	10.5	13.2	13.2	11.9
MoO_4^{2-f} (XPS)	5.2	7.1	8.0	9.9	5.4
WO_4^{2-f} (XPS)	2.3	4.7	5.7	7.9	3.5

TABLE XXXIII (CONTINUED)

Entities	t_1	t_2	e	t_2	a_1
OsO_4^{2-f} (XPS)	5.0	5.0	8.0	8.0	5.0
PO_4^{3-h} (XPS)	5.2	6.9	6.9	9.5	12.2
$\text{SO}_4^{2-h,i}$ (XPS)	5.6	7.8	7.8	11.4	14.2
$\text{SO}_4^{2-h,i}$ (UPS)	10.9	11.6	12.4	13.9	17.6
MnO_4^{-h} (XPS)	-----		6.4	-----	
SiO_4^{4-h} (XPS)	5.5	5.5	5.5	9.4	12.0

^aRef. 143^bRef. 168^cRef. 169^dRef. 170^eRef. 171^fRef. 172^gRef. 89^hRef. 173ⁱRef. 86

considered (Table XXXIII, pp 106 - 107), the orders of the MO's are varied, seeming to indicate no preferential pattern. In fact, many of the possible combinations of the outer five MO's have been suggested. The experimental data on the tetrahedral molecules which have halogen ligands would seem to confirm the overall MO assignments on the tetrachloro- and tetrafluoroaluminate anions made in this study.

C. Conclusion

The photoelectron spectroscopic investigation of vapors produced by heating inorganic solids has increased rapidly during the past few years and has been extended to a wide variety of compounds (Tables I, II, and XXXIII, pp 8, 10, and 106 - 107). In this study, the ionization energies of the alkali metal metaborates, alkali metal tetrachloroaluminates, alkali metal tetrafluoroaluminates, and ammonium tetrachloroaluminate have been measured. The bands were assigned MO origins on the basis of MO calculations on the free corresponding anion. No high temperature structural conclusions could be made from the observations of this study. However, it is hoped that this work may provide further insights into other investigations of high temperature vapors and into other possible structural models.

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